Brownian Motion and Glassy Dynamics with Disparately Separated Time Scales

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Contents

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Chapter 1

Introduction

This thesis is concerned with several problems related with the concept of time scale separation. On the first part of the thesis we work on Brownian motion with constraint conditions. Particularly we focus on the overdamp limit, where the momentum of the Brownian particle has been relaxed to the Maxwell distribution and the dynamics is described by position variable only, as the result of time scale separation between momentum and position. Studies on these issues are motivated by a mean field scenario of the glass transition, based on the analogy between a certain class of spin glasses and molecular glasses. On the second part we consider theories of slow dynamics near the glass transition point of a p-spin spherical model and binary mixtures with disparate size ratio between large and small species. Below we describe briefly what is the glass transition, why interest on the glass transition leads to the problems concerned in the present thesis, and why these topics are tied with the concept of "disparately separated time scales".

When a liquid is cooled below its freezing temperature, it forms a crystalline solid. The crystallization , however, can be avoided by cooling the liquid sufficiently fast (i.e. quench) or by introducing frustrations. A liquid below its freezing temperature realized in this way is called a supercooled liquid. Microscopic dynamics of molecules of supercooled liquids slows down dramatically upon further cooling. It leads to abrupt elevation of the viscosity, ranging from order of several Poise to about 10^{13} Poise which is the measurement limit of viscosity. To measure the viscosity of a fluid it must flow within a measurement time. But if fluid is too viscous it cannot flow. This is what happens in supercooled liquid around 10^{13} Poise. This is the phenomenon what is called the glass transition. While the supercooled liquids experience such a drastic slowing down, its static structure remains indistinguishable from ordinary liquids. Thus in short the glass transition can be viewed as a solidification without crystallization. Understanding the

origin of this slowing down is the ultimate goal of investigation on the glass transition. What makes understanding of the glass transition difficult is reduced to its randomness and the strong many body effect. Since the structure of the glass is as random as liquid one can hardly find the appropriate order parameter to characterize the slow dynamics. Furthermore since the glass transition occurs in high density liquids the dynamics of the constituent molecules becomes strongly correlated. Not only just the glass transition is a challenging problem to solve but it is also a universal phenomena. Molecular liquids are the most popular glass forming systems for experimentalists. SiO_2 and GeO_2 are typical network-forming glass materials. Glasses made of metallic alloys are much stronger than usual alloys. Soft matters are consist of mesoscopic(sub-micron order) units like polymers and colloids. Among of them, some foods like yogurt, which is a colloidal dispersion, can sustain their shape against gravity. They also achieve solidity without crystallization. Recently colloidal glasses are actively investigated since the interaction between them is isotropic and thus can be handled theoretically. Rubber made of polymers also becomes glass at low temperature. In industrial purpose it is very important to control the temperature dependence of elastic properties of rubber tire since it is used from daytime to midnight, from summer to winter. The universality of the glass transition is not restricted in real materials. Recently the analogy between the spin glass and molecular glass has been pointed out, as we will discuss later. Spin glass was originally introduced to model a dilute ferromagnet but it turned out that its concepts can be applied to optimization problems, computational physics, and molecular glasses.

The Mode-Coupling Theory(MCT) is the one and only microscopic first-principles theory that partly succeeded to describe the slow dynamics of supercooled liquids [1]. MCT was proposed and have been examined by Götze and co-workers about 3 decades ago. Now it has established a strong presence as an important milestone of the kinetic theory of supercooled liquids. But at the same time it has some flaws. For example, MCT for binary mixtures has a serious defect, although it can be obtained as a straightforward extension from one-component MCT. The binary MCT predicts that the large and small components form glasses at the same temperature, irrespective of size ratio between large and small particles. But as intuitively expected when small species is much smaller than larger one, the larger particles undergo the glass transition while the smaller ones remain in fluid phase [2]. We investigate this conflict in detail in Chapter 5. There is an another example. MCT predicts a power law divergence of relaxation time of density correlation function of liquid at finite temperature $T_{\rm d}$, called the dynamic transition temperature. While in real liquids the relaxation time diverges exponentially,

at much lower temperature than $T_{\rm d}$. In other words, MCT captures the slow dynamics of supercooled liquids qualitatively but not quantitatively. This is one reason why MCT is called "a mean field theory of glass transition". The another reason comes from the similarity of the MCT with the exact solution for a mean field spin glass model.

A certain class of spin glass models can help lifting above two difficulties while keeping the phenomenology of the glass transition. Spin glasses are models with spins arranged on a prescribed lattice interacting randomly. Thus randomness is controlled more easily than molecular liquids. Among of them the p-spin spherical model(PSM) is a mean field spin glass model belonging to the 1-step Replica Symmetry Breaking(1RSB) universality class. The mean field character of the PSM suppresses the many body effects and allows one to handle it theoretically. Since the analogy between structural glasses and PSM was pointed out in [3], many efforts have been made to understand the glass transition with the help of knowledge on the spin glasses. The slow dynamics of PSM is the only link between glasses and spin glasses. But the analysis of the dynamics of the PSM was carried out in an instrict way. The model is imposed a holonomic constraint condition called spherical constraint. This constraint condition must be satisfied time by time and in each ensembles. But in the previous derivation [4,5] the spherical constraint condition is satisfied only in average, i.e., not in time by time and not in each ensemble. Our study on the dynamics of PSM presented in Chapter 4 is intended to give a strict treatment of the spherical constraint condition and see whether the link between glass and spin glass remains intact or not.

The dynamics of PSM is modeled by a stochastic differential equation originally used to describe the dynamic critical phenomena [6]. We found that the stochastic dynamics with constraint conditions is poorly understood and even controversial results are reported. It motivated us to study on formulation of the stochastic dynamics with constraint conditions. This is developed in Chapter 3. It turned out that the constrained Brownian motion appears not only in the dynamics of PSM but in many other situations, e.g., dynamics of polymers, membranes where monomers are interconnected by almost inextensible bondings. In these examples, idealizing the vibrating bondings as rigid inextensible rods amounts to the situation that one is interested in the long time dynamics of polymers, compared with the characteristic time of the bond vibration. In such a long time scale the momentum of monomers have been relaxed to the Maxwell distribution and one can describe the dynamics of polymers and membranes only using the position of monomers. Thus we concentrate on such situation, which is called the overdamp limit. In PSM, since spins do not have momentum, its dynamics is characterized only by the values of spins from the beginning.

Constrained Brownian motion is inevitably described by the Langevin equation with a multiplicative noise. A multiplicative noise appears for e.g., in the following Langevin equation in the overdamp limit,

$$\dot{x} = f(x) + g(x)\xi(t) \tag{1.1}$$

where ξ is a Gaussian white noise and $f(x), g(x)$ are given functions of x. A multiplicative noise in (1.1) is the term $g(x)\xi(t)$. In general it is defined by the white noise multiplied with function of stochastic variables(in the present case x). It is known that the first order Langevin equation driven by the multiplicative white noise cannot be defined uniquely unless its rule for integration is given. Unfortunately in many case one cannot intuitively infer the rule of integration. This is the famous Ito-Stratonovich dilemma [7], named after two major integration rules, first pointed out explicitly by van Kampen more than 30 years ago. We find that some of the controversy on constrained Brownian motion has been caused by this mathematical subtlety. In order to carry out the correct calculation and terminate the controversy we revisited this old problem in Chapter 2. The multiplicative noises are ubiquitous in physics. It appears not only in constrained Brownian motion but also in dynamics of nonlinear chemical reactions, systems with temperature gradient and with hydrodynamic interactions.

We find that all issues treated throughout the thesis are loosely related by the concept of "time scale separation", with hindsight. The concept of scale separation (not only in time but also in space) represents a paradigm of modern physics. For example it appears in a hierarchy in fundamental laws of physics. A motion of macroscopic object is governed by Newton's equation. But in nanometer scale it breaks down and quantum mechanics starts to play a central role. In high energy region the theory of relativity must be applied, rather than the Newtonian mechanics. Nevertheless the Newton's equation remains correct at macroscopic scale , thanks to separation of the scales between microscopic quantum world and macroscopic one, and the separation of the scales between velocity of the systems and light speed. Such structures are present inside the each class of the classic, quantum, and the relativistic world. For example, since nuclei is more than 10^3 times heavier than electron it can be assumed that the wave function of electron is not affected by motion of nuclei, which is known as celebrated Born-Oppenheimer approximation. In the binary mixtures with disparate size ratio, whether the binary MCT can describe the time scale separation between the large and small components is tested. Modelling the Brownian motion with Langevin equation includes an idealization of motion of solvent particle as random stochastic processes. It is justified by the scale separation between colloidal and solvent particle. Within the Brownian motion, the

overdamp limit is nothing but the situation realized as a result of time scale separation between fast relaxing momentum and slowly evolving position of the Brownian particle. Modelling the vibrating chemical bonds by inextensible rigid rods in polymer needs time scale separation between fast vibration of the bonds and slow dynamics of a polymer chain.

As seen above the both overdamp limit in multiplicative Langevin equation and constrained Brownian motion themselves have enough motivations to study. Thus we think they worth devoting separated chapters. This thesis is organized as follows. In the first part of the thesis we formulate the Brownian motion with constraint. We start from revisiting the problem on overdamp limit in Chapter 2. Then by using the result obtained in Chapter 2 we construct a theory of constrained Brownian motion in Chapter 3. The latter part of the thesis is devoted to studies directly related with glass transition. We apply the formalism for Brownian motion with rigid constraint condition to p-spin spherical model in Chapter 4. We report the numerical result on MCT for binary mixtures with disparate size ratio in Chapter 5. Some mathematical and formal methodology used in the main text are reviewed in Appendices.

Part I

Overdamp limit for constrained Brownian motion

Chapter 2

Overdamp Limit for Brownian Motion with Multiplicative Noises

2.1 Introduction

The concept of adiabatic elimination of the fast degrees of freedom to obtain the equation for slow variables is ubiquitous in physical problems [8]: mechanical systems [9], stochastic processes [10] and in quantum mechanics [11]. Among of them, the adiabatic elimination in Brownian motion is a highly non-trivial problem. In Brownian motion the momentum of the Brownian particle normally damps instantly, while its position varies much more slowly. In other words, the time scales between the momentum and position are well separated. Then it is possible to describe the dynamics of the system within the position variables by adiabatically eliminating the fast relaxing momentum. This situation is called 'overdamp limit'. On the other hand, in shorter time scales than momentum relaxation time the system is called 'underdamped' [12].

Brownian particle is agitated by the thermal fluctuations of surrounding solvent particles and, at the same time, it loses its inertia by the Stokes' drag force. In literature the coefficient of the Stokes' force is often assumed to be a constant. But it may vary with position of Brownian particles. In other words, the transport coefficient can be position-dependent. Such problem is not only interesting from the viewpoint of generalization of theory of Brownian motion but indeed can be realized in experimental systems. Below we give some examples. When the concentration of the Brownian particles becomes dense the effect of interactions between the particles starts to play a

central role. Among of these interactions, the hydrodynamics interactions enter in the Langevin equation as a state-dependent friction coefficient [13–15]. The friction coefficient of Brownian particles near the wall also varies with distance from the wall due to the hydrodynamic interactions [16]. Recent developments on experimental techniques enable us to observe this effect directly [17,18]. As an yet another important example, let us take the Brownian motion with rigid constraint. In general the motion of the particles becomes limited on the curved manifolds, called the constrained surface, as the result of the constraint condition. Even if the transport coefficient in Cartesian coordinate is constant one inevitably faces the position-dependent transport coefficient in curved constrained surface. Formulation of the constrained Brownian motion is interested not only as theoretical extension of Brownian motion into the one on a manifold [19,20], but it also has practical demand in soft matter physics [15, 21], high energy physics [22], chemical physics [23, 24] and even spin systems [5, 25]. We leave the details to Chapter 3. In most cases one is interested in the morphology or configuration of molecules or spins, rather than momentum, which always relaxes much more quickly to the Maxwell-Boltzmann distribution.

Overdamp limit for Brownian motion with the state-dependent friction is thus ubiquitous and is in great demand both conceptually and practically. Nevertheless, very little is known or even controversial results are reported. We deduce the reason as follows. Brownian particle is agitated randomly by surrounding solvent particles. Resulting random force is often modeled by a white noise since its correlation decays in short time scales relevant with dynamics of solvent molecules, which can be negligible compared with the characteristic time of Brownian particles. This idealization makes the stochastic process Markovian and allows us to handle relatively easily, but at the same time one has to be careful of the mathematical subtlety caused by its delta correlated nature. Indeed, the subtlety causes a grave problem in the Brownian motion with state-dependent transport coefficient. In such situation, by the fluctuation-dissipation theorem (FDT), noise becomes multiplied by a function of position of Brownian particle. More concretely let us consider the following Langevin equation:

$$\dot{x} = f(x) + g\xi(t). \tag{2.1}$$

Here overdot represents the time derivative, $f(x)$ is the deterministic term and $\xi(t)$ is the white Gaussian noise. When g is constant (2.1) is defined uniquely. But when g depends on x, the noise term becomes multiplicative with respect to the stochastic variable x. It is known that the multiplicative noises cannot be defined uniquely without giving a rule to integrate them. This feature affects the solution of the first order Langevin equation like

(2.1). Integration rule for multiplicative noise is often called 'interpretation of the multiplicative noise'. The interpretation can be explicitly prescribed in discretized form of (2.1),

$$\Delta x \equiv x(t+\Delta t) - x(t) = f(x)\Delta t + g(x^*)\Delta W. \tag{2.2}$$

Here Δt is the increment of time, ΔW is the discretized Wiener process defined by

$$\Delta W \equiv \int_t^{t+\Delta t} ds\xi(s). \tag{2.3}$$

This ΔW satisfies a formula

$$\Delta W^2 = \Delta t, \tag{2.4}$$

as shown in Appendix A.1. This somewhat peculiar property of the discretized Wiener process comes from the white nature of the noise, which is merely an idealization of the random collision by surrounding solvent particles. The formula (2.4) implies that ΔW is orders of $\Delta t^{1/2}$ which is much larger than Δt. Thus the right hand side (RHS) of (2.2) starts from not Δt but $\Delta t^{1/2}$. In other words $\Delta x \sim \Delta t^{1/2}$. This feature of the overdamp Langevin equation with the white Gaussian noise is the root of the subtlety. For example, the multiplicative noise in the RHS of (2.2) varies with value of x^*, evaluated at the time before, or after the particle is kicked by the noise. To see this more concretely, let us define a parameter α varies from 0 to 1 and define x^* in general form as

$$x^* \equiv \alpha x(t+\Delta t) + (1-\alpha)x(t). \tag{2.5}$$

Thus, the value of x^* is the sum of the value before a kick, $x(t)$ and the value after the kick, $x(t+\Delta t)$ with the mixing ratio of $(1-\alpha) : \alpha$. $\alpha = 0$ is called the Ito discretization or the Ito interpretation of the multiplicative noise [26], $\alpha = 1/2$ is called the Stratonovich [27], $\alpha = 1$ is called the Hänggi-Klimontvich [28, 29] or Isothermal [17]. In this thesis we call $\alpha = 1$ the anti-Ito since it corresponds to opposite definition with the Ito interpretation. We demonstrate that a multiplicative noise $g(x^*)\Delta W$ explicitly affects the stochastic process depending on the choice of α. The difference between general α convention and the Ito is calculated as

$$\begin{aligned} g(x^*)\Delta W &= g(x(t)+\alpha\Delta x)\Delta W \\ &= g(x(t))\Delta W + \alpha g\frac{\partial g}{\partial x(t)}\Delta W^2 \\ &= g(x(t))\Delta W + \alpha g\frac{\partial g}{\partial x(t)}\Delta t. \end{aligned} \tag{2.6}$$

From the second to the third line of (2.6), we have made use of the formula (2.4). The second term in the RHS of (2.6) represents the difference between α convention and the Ito. It is clear that the difference was caused from the fact that $\Delta x \sim \Delta t^{1/2}$.

The solution of the overdamp Langevin equation like (2.2) or in general the first order stochastic differential equation driven by the multiplicative noise depends on the interpretation of the multiplicative noise. Unfortunately it is often difficult to infer which interpretation should be applied to (2.2). This difficulty is called the Ito-Stratonovich dilemma [7, 30–32], named after the two major interpretations of multiplicative noises. Such problems appear not only in Brownian motion in equilibrium but also in non-equilibrium states like systems under the temperature gradient [33–36] and in noise induced phase transitions [37, 38], where origin of stochastic noise is external and non-thermal nature. On the other hand, the underdamped Langevin equation, which describes the short time dynamics, is not suffered from the Ito-Stratonovich dilemma. In short, this feature follows from the fact that in underdamped regime $\Delta x = v\Delta t$ is order of Δt, not $\Delta t^{1/2}$, where v is the velocity of the Brownian particle. We give a detailed proof in Appendix A.4.

If the noise is not multiplicative, or additive, the overdamp limit becomes identical with ignoring the inertial term in the underdamped Langevin equation. This fact is better known than that of multiplicative case and reviewed in literature [12, 39]. We also show the derivation in Appendix B.1. Let us consider the following underdamped Langevin equation.

$$m\ddot{x}(t) = -\zeta\dot{x}(t) - \frac{\partial U}{\partial x} + \sqrt{2k_BT\zeta}\xi(t) \tag{2.7}$$

Here m is the mass of the Brownian particle, ζ is a constant friction coefficient, U is the potential, k_B is the Boltzmann constant and T is the temperature of the system. Magnitude of the noise, $\sqrt{2k_BT\zeta}$, is prescribed by the condition of the thermal equilibrium, called the FDT. The overdamp limit for (2.7) is given by

$$\dot{x}(t) = \zeta^{-1}\left(-\frac{\partial U}{\partial x} + \sqrt{2k_BT\zeta}\xi(t)\right), \tag{2.8}$$

which is identical with ignoring the inertia in (2.7): $m\ddot{x} = 0$. This result is often interpreted as follows. The solvent is so viscous that inertia of the Brownian particle damps very quickly. But in the case of the multiplicative noises this interpretation is no longer applicable. Actually, one cannot determine their interpretation by simply ignoring the inertia. As will be shown in this chapter, in general, ignoring the inertia never gives the correct result.

In the presence of the multiplicative noise one has to go back to the original definition of the overdamp limit. It is defined by a limiting situation that the time scale one is interested in is much longer than the relaxation time of momentum, given by $\tau_p = m/\zeta$. Indeed, the overdamp limit for additive noise system is derived in the spirit of this definition and the neglect of the inertia is merely the result. Thus on considering the overdamp limit for the Langevin equation driven by multiplicative noises, we follow the same strategy with that presented in Appendix B.1.

Taking the correct overdamp limit from the underdamped Langevin equation with the multiplicative noise is a longstanding problem and there are many preceding studies. Ermak and Maccamon [13], Hess and Klein [40] and Sancho et al. [41] followed the strategy presented above for models with the state-dependent transport coefficient. Hasegawa et al. [42], Sancho et al. [41] and Peters [43] proposed a rather heuristic argument that the overdamp limit is identical with ignoring inertia and interpreting the multiplicative noise as Ito and interpreting the state-dependent transport coefficient as Stratonovich. We summarize the heuristic argument in Appendix B.3. Preceding studies listed above intended to calculate overdamp limit directly from the underdamped Langevin equation. On the other hand, the overdamp limit can be also computed through the Fokker-Planck equation for the probability distribution function, rather than the Langevin equation for stochastic variables. Such problem is called Kramers problem [10] and its general solution has already been established by several authors [44–47], see also literature [48, 49]. In this method one make use of the projection operator formalism of Mori and Zwanzig to project the probability distribution in the position and momentum onto the one in the position only. In other words, the method provides the way to adiabatically eliminate the fast relaxing momentum from the Kramers equation (the Fokker-Planck equation for the position and momentum) and obtain the Smoluchowski equation (the Fokker-Planck equation for position only). Working on the Fokker-Planck equation, instead of Langevin equation, has two merits. One is that the procedure is directly applicable to the systems with the position-dependent transport coefficient. The second is that it is free from the Ito-Stratonovich dilemma, since one does not treat the stochastic differential equation. We demonstrate the details of this method in Appendix B.2.

Even when the transport coefficient is constant and does not depend on the position of the Brownian particle, the multiplicative noise appears in the system with temperature gradient since the magnitude of noise is proportional to $\sqrt{2k_BT\zeta}$ by FDT. The computations of the overdamp limit in such situation are carried out by Sekimoto [33] by using the Langevin equation and by several authors [34, 35, 50] by using the Fokker-Planck equation.

For the system with state-dependent transport coefficient and temperature gradient see [36, 51–54].

Because of accumulating studies on the overdamp limit for multiplicative Langevin equations, the correct expression is already known, see for the example, [55]. Our purpose for revisiting this old problem nonetheless is twofold. One is to show that no preferred interpretation exists for the overdamp multiplicative Langevin equation, by performing the calculation of the overdamp limit within the Langevin equation with arbitrary interpretation of the multiplicative noise. The second is to extend the method to arbitrary non-equilibrium situation, including the systems under the temperature gradient.

The organization of present chapter is as follows. We demonstrate our method to compute the overdamp limit within the Langevin equation for the most simple 1 dimensional system in Section 2.2. In Section 2.3 we extend it to multi-dimensional systems. Our method is capable of deriving the Ito, the Stratonovich and the anti-Ito multiplicative noise. We perform these extensions in Section 2.4 and 2.5. We further show the extension to arbitrary noise interpretation in Section 2.6. In Section 2.7 we loosen the FDT and extend the whole derivation to non-equilibrium cases. In the constrained Brownian motion treated in the next chapter we inevitably face the Langevin equation in curved space. To this end we present the way to take the overdamp limit in such situation in Section 2.8. In Section 2.9 we show a derivation of the overdamp limit proposed by Hess and Klein [40], and by Sancho et al. [41] more than 30 years ago, to explicitly point out what was wrong in their calculations. Section 2.10 is devoted to summary, discussion and perspectives.

2.2 One dimensional case

Consider a Brownian motion with a state-dependent transport coefficient. We represent the position of the Brownian particle at time t by $x(t)$. In the underdamped case, the dynamics of the Brownian particle is described by following Langevin equation

$$\ddot{x}(t) = -\zeta(x(t))\dot{x}(t) + b(x(t))\xi(t). \tag{2.9}$$

$\xi(t)$ is white Gaussian noise defined by

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t_1)\xi(t_2) \rangle = \delta(t_1 - t_2). \tag{2.10}$$

For simplicity we set the mass of the Brownian particle unity and ignored the external force. The extension to the case where an external force is

present is straightforward since the stochastic nature is not affected by the external force. $\zeta(x(t))$ is the state-dependent friction coefficient. $b(x(t))$ is also state-dependent and satisfies the FDT:

$$b^2(x(t)) = 2k_B T\zeta(x(t)), \tag{2.11}$$

here k_B is the Boltzmann constant and T is the temperature of the system. We compute the overdamp limit for the underdamped Langevin equation (2.9) based on the strategy of Sekimoto [33], but use slightly different method so that it can be directly applicable to the multi-dimensional systems. The formal solution of (2.9) is given by

$$\dot{x}(t_1) = \int_{-\infty}^{t_1} dt_2 G(t_1, t_2) b(x(t_2))\xi(t_2). \tag{2.12}$$

Here $G(t_1, t_2)$ is a propagator defined as

$$G(t_1, t_2) \equiv \exp\left[-\int_{t_2}^{t_1} dt_3 \zeta(x(t_3))\right]. \tag{2.13}$$

The overdamp limit is expressed as the time scale separation between relaxation time of the momentum: $\tau_p \sim \zeta^{-1}$ and other time scales which appear in the formal solution (2.12) such as t_1 and t_2. Thus one can perform a perturbation expansion with respect to a small parameter τ_p. From the formal solution (2.12) one can show that $\dot{x}$ is order of τ_p^0 and $x(t_2) - x(t)$ is $\mathcal{O}(\tau_p^1)$, by using the following rule to compute the order of small parameter τ_p.

1. Roughly speaking the propagator is $G \sim \mathrm{e}^{-\zeta t}$. Thus a time integral applied to the propagator produces $\zeta^{-1} \sim \tau_p^1$. Note that this rule is not always applicable in general. When a time integral passes through the propagator G it does not cause τ_p.

2. $b(x) = \sqrt{2k_B T\zeta(x)}$ is order of $\tau_p^{-1/2}$ since $\zeta \sim \tau_p^{-1}$.

3. The white noise $\xi(t)$ is $\mathcal{O}(\tau_p^{-1/2})$. The two ξs can be replaced by its average value $\delta(t - t')$ thanks to the Gaussian nature of ξ. It prevents one to get τ_p according to the rule 1 above. Thus effectively ξ acts as $\tau_p^{-1/2}$.

By using these facts, one can show that $x(t_2) - x(t) \sim \mathcal{O}(\tau_p)$. Thus one can expand the friction coefficient $\zeta(x(t_2))$ around $x(t)$ with $t_2 > t$,

$$\zeta(x(t_2)) = \zeta(x(t)) + \frac{\partial\zeta(x)}{\partial x(t)}\left[x(t_2) - x(t)\right] + \mathcal{O}(\tau_p) \tag{2.14}$$

Substituting this expansion (2.14) into the underdamped Langevin equation (2.9) yields

$$\begin{aligned}\ddot{x}(t_2) &= -\zeta(x(t))\dot{x}(t_2) - \frac{\partial\zeta(x)}{\partial x(t)}\left[x(t_2)-x(t)\right]\dot{x}(t_2) \\ &\quad +b(x(t_2))\xi(t_2)+\mathcal{O}(\tau_p). \end{aligned} \tag{2.15}$$

We again solve (2.15) formally by regarding the second and third terms as inhomogeneous terms and obtain

$$\dot{x}(t_1) = \int_{-\infty}^{t_1} dt_2 \mathrm{e}^{-\zeta(x(t))(t_1-t_2)} \left\{ -\frac{\partial\zeta(x)}{\partial x(t)}\left[x(t_2)-x(t)\right]\dot{x}(t_2) + b(x(t_2))\xi(t_2)\right\} \tag{2.16}$$

This expression is slightly different from the formal solution (2.12), directly obtained from the underdamped Langevin equation (2.9). In fact these expression is completely identical but only the method using the formal solution (2.16) can be generalized into the multidimensional case. This method may correspond to switching to the 'interaction picture' in time t in the quantum mechanics. In order to determine the interpretation of the multiplicative noise appears in the RHS of (2.16) one has to discretize it by further integrating (2.16) from time t to $t+\Delta t$.

$$\begin{aligned}\Delta x \equiv& x(t+\Delta t)-x(t) = \int_t^{t+\Delta t} dt_1 \dot{x}(t_1) \\ =& \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 \mathrm{e}^{-\zeta(t_1-t_2)} b(x(t_2))\xi(t_2) \\ &- \frac{\partial\zeta(x)}{\partial x(t)} \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 \mathrm{e}^{-\zeta(t_1-t_2)}\left[x(t_2)-x(t)\right]\dot{x}(t_2) + \mathcal{O}(\tau_p^2). \end{aligned} \tag{2.17}$$

The first term on the right hand side of (2.17) appeared from the multiplicative noise in the Langevin equation. The second term is correction caused by the position dependence of the friction coefficient. Hereafter in this section we denote $\zeta(x(t))$ just as ζ. It is shown in [33] that the integral from $-\infty$ to t in t_2 in (2.16) can be negligible since it is smaller than other part of the integral by the order of $\sqrt{\tau_p}$. Thus one can replace $\int_{-\infty}^{t_1} dt_2 \cong \int_t^{t_1} dt_2$. Below we evaluate the RHS of (2.17) in the leading order in τ_p to obtain the overdamped Langevin equation.

We expand $b(x(t_2))$ along the same line with that of $\zeta(x(t_2))$ performed in (2.14).

$$b(x(t_2)) = b(x(t)) + \frac{\partial b(x)}{\partial x(t)}\left[x(t_2)-x(t)\right] + \mathcal{O}(\tau_p^{1/2}). \tag{2.18}$$

Note that $x(t_2) - x(t)$ is order of $\sim \Delta x$ since $t \leq t_2 \leq t_1 \leq t + \Delta t$. Thus the expansions (2.14) and (2.18) can be also interpreted as expansion in Δx. As we have already pointed out, in the overdamp limit, Δx starts from $\Delta t^{1/2}$ (see equation (2.2) and discussion around it). Thus the above expansions (2.14) and (2.18) can also be viewed as power series expansion in $\Delta t^{1/2}$. This interpretation is in fact more convenient than interpreting (2.14) and (2.18) as power series expansion with respect to τ_p^1, since one do not need to worry about the exception of the rule 1 above. By substituting the expansion (2.18) into $b(x(t_2))$ in the first term of the right hand side of the formal solution (2.17), we have

$$\begin{aligned}\int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(t_1-t_2)} b(x(t_2))\xi(t_2) = b(x(t)) \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(t_1-t_2)}\xi(t_2) \\ + \frac{\partial b(x)}{\partial x(t)} \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(t_1-t_2)} \left[x(t_2) - x(t)\right] \xi(t_2).\end{aligned} \tag{2.19}$$

The second term in the right hand side of (2.19), which appears from the x-dependence of the multiplicative noise term, vanishes as Sekimoto has shown in [33]. Here we check this. Set

$$I^{b,\mathrm{Ito}} \equiv \frac{\partial b(x)}{\partial x(t)} \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(t_1-t_2)} \left[x(t_2) - x(t)\right] \xi(t_2). \tag{2.20}$$

One can evaluate $[x(t_2) - x(t)]$ in the right hand side of (2.20) by integrating the formal solution (2.16) from t to t_2;

$$\begin{aligned}x(t_2) - x(t) = \int_t^{t_2} dt_3 \int_t^{t_3} dt_4 \mathrm{e}^{-\zeta(t_3-t_4)} \\ \times \left\{ -\frac{\partial \zeta(x)}{\partial x(t)} \left[x(t_4) - x(t)\right] \dot{x}(t_4) + b(x(t_4))\xi(t_4) \right\}.\end{aligned} \tag{2.21}$$

In $\{\cdots\}$, the first term is $\mathcal{O}(\tau_p^2)$ (or $\mathcal{O}(\Delta t)$), while the second term is $\mathcal{O}(\tau_p)$ (or $\mathcal{O}(\Delta t^{1/2})$). Thus in (2.21) the leading contribution comes from the second term. In computation of $I^{b,\mathrm{Ito}}$ one is interested in the lowest order in τ_p or Δt. Thus, one can neglect the first term in the RHS of (2.21).

$$\begin{aligned}x(t_2) - x(t) &= \int_t^{t_2} dt_3 \int_t^{t_3} dt_4 \mathrm{e}^{-\zeta(t_3-t_4)} b(x(t_4))\xi(t_4) + \mathcal{O}(\tau_p^2) \\ &= b(x(t)) \int_t^{t_2} dt_3 \int_t^{t_3} dt_4 \mathrm{e}^{-\zeta(t_3-t_4)} \xi(t_4) + \mathcal{O}(\tau_p^2).\end{aligned} \tag{2.22}$$

From the first to the second line we expand $b(x(t_4))$ around $x(t)$ like (2.18) and take the lowest order in τ_p. By substituting (2.22) into the definition of $I^{b,\mathrm{Ito}}$ in (2.20) one has

$$\begin{aligned} I^{b,\mathrm{Ito}} &= \frac{\partial b(x)}{\partial x(t)} \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(t_1-t_2)} b(x(t)) \int_t^{t_2} dt_3 \int_t^{t_3} dt_4 \\ &\quad \times \mathrm{e}^{-\zeta(x(t))(t_3-t_4)} \xi(t_4)\xi(t_2). \end{aligned} \tag{2.23}$$

We can replace the quadratic term of the noise ξ by its average according to (2.10). The solution of the Langevin equation is not affected by this replacement. In other words, the corresponding Fokker-Planck equation does not change with this replacement [56]. This feature is guaranteed by the Gaussian nature of the noise ξ. Then,

$$\begin{aligned} I^{b,\mathrm{Ito}} &= \frac{\partial b(x)}{\partial x(t)} \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(t_1-t_2)} b(x(t)) \int_t^{t_2} dt_3 \int_t^{t_3} dt_4 \\ &\quad \times \mathrm{e}^{-\zeta(t_3-t_4)} \delta(t_2-t_4). \end{aligned} \tag{2.24}$$

This integral vanishes since the integral ranges satisfy $t < t_4 < t_3 < t_2 < t_1 < t + \Delta t$ and no choice of t_2 and t_4 can make argument of delta function $t_2 - t_4 = 0$. Then

$$I^{b,\mathrm{Ito}} = 0. \tag{2.25}$$

This fact has been already pointed out by Sekimoto [33].

We next calculate the first term in the RHS of (2.19). One can change the order of $dt_1 dt_2$ integral as

$$\int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 = \int_t^{t+\Delta t} dt_2 \int_{t_2}^{t+\Delta t} dt_1. \tag{2.26}$$

This enables us to carry out the integral over t_1 in (2.19) as

$$\begin{aligned} b \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(t_1-t_2)} \xi(t_2) &= b \int_t^{t+\Delta t} dt_2 \int_{t_2}^{t+\Delta t} dt_1 \mathrm{e}^{-\zeta(t_1-t_2)} \xi(t_2) \\ &= \zeta^{-1} b \int_t^{t+\Delta t} dt_2 \left[1 - \mathrm{e}^{-\zeta(t+\Delta t-t_2)}\right] \xi(t_2) \\ &. \end{aligned} \tag{2.27}$$

Here since ζ is very large, $\mathrm{e}^{-\zeta(t+\Delta t-t_2)}$ is equal to unity only in the vicinity of $t_2 = t + \Delta t$ and can be neglected otherwise. Thus one can approximate

$$1 - \mathrm{e}^{-\zeta(t+\Delta t-t_2)} = \begin{cases} 1 & t_2 \neq t + \Delta t \\ 0 & t_2 = t + \Delta t \end{cases}. \tag{2.28}$$

Then (2.27) becomes

$$\begin{aligned}\zeta^{-1}b\int_t^{t+\Delta t} dt_2\left[1-\mathrm{e}^{-\zeta(t+\Delta t-t_2)}\right]\xi(t_2) &= \zeta^{-1}b\int_t^{t+\Delta t-0} dt_2\xi(t_2)\\ &= g(x(t))\Delta W, \end{aligned} \tag{2.29}$$

where we have defined $g(x)\equiv\zeta^{-1}(x)b(x)$ and

$$\Delta W = W_{t+\Delta t}-W_t = \int_t^{t+\Delta t} dt_1\xi(t_1), \tag{2.30}$$

is the discretized Wiener process [49]. (2.29) is the multiplicative noise in the overdamped Langevin equation. It is clear that the interpretation of the multiplicative noise becomes the Ito one since $g(x)$ is evaluated with x at the time before the particle is kicked by the noise: $x(t)$. It has its origin in the choice of reference point around which the expansion of $\zeta(x)$ and $b(x)$ in (2.14) and (2.18) are performed. There is freedom in choosing this reference point. For example one can choose $x(t+\Delta t)$ instead of $x(t)$. The resulting multiplicative noise becomes anti-Ito, as will be demonstrated in Section 2.4. The choice $[x(t)+x(t+\Delta t)]/2$ leads the Stratonovich, demonstrated in Section 2.5.

Next, we compute the second term in the RHS of (2.17). We shall denote it as $I^{\zeta,\mathrm{Ito}}$. It can be evaluated to the lowest order in τ_p or Δt by substituting (2.16) and (2.22) for $\dot{x}(t_2)$ and $[x(t_2)-x(t)]$. As we have already shown the second term in the RHS of (2.16) is the leading contribution. Then

$$\begin{aligned} I^{\zeta,\mathrm{Ito}} &= -\frac{\partial\zeta}{\partial x}\int_t^{t+\Delta t} dt_1\int_t^{t_1} dt_2\mathrm{e}^{-\zeta(t_1-t_2)}\int_t^{t_2} dt_3\int_{-\infty}^{t_3} dt_4\mathrm{e}^{-\zeta(t_3-t_4)}b\xi(t_4)\\ &\quad\times\int_t^{t_2} dt_5\mathrm{e}^{-\zeta(t_2-t_5)}b\xi(t_5). \end{aligned} \tag{2.31}$$

Replacing the quadratic term in ξ by its average, carrying out the time integrals, and dropping $\mathrm{e}^{-\zeta\Delta t}\ll 1$ by the scale separation $\tau_p\ll\Delta t$ one obtain to the lowest order in τ_p,

$$I^{\zeta,\mathrm{Ito}} = k_BT\frac{\partial L(x)}{\partial x}\Delta t+\mathcal{O}(\tau_p^2). \tag{2.32}$$

Here we defined $L(x)=\zeta^{-1}(x)$ and made use of the FDT. Note that the RHS of (2.31) looks $\mathcal{O}(\tau_p^2)$, within the rule of power counting described above. While the result of integration (2.32) is $\mathcal{O}(\tau_p)$. This discrepancy has been caused from the exception of the rule 1; the time integration does not give

rise to the term of the order of τ_p when it pass through $\mathrm{e}^{-\zeta t}$. Indeed the integral over t_1 in (2.31) does not act on $\mathrm{e}^{-\zeta t}$ but it just produces Δt.

Now that we have computed all the corrections appeared in the RHS of the formal solution (2.17) to the linear order in τ_p or Δt. Plugging (2.25), (2.29) and (2.32) with (2.17) one reaches the final expression,

$$\Delta x(t) = g(x(t))\Delta W + k_B T \frac{\partial L(x)}{\partial x(t)} \Delta t. \tag{2.33}$$

One finds that the overdamped Langevin equation with multiplicative white noise, whose origin is the state-dependent transport coefficient, is not just an equation obtained by ignoring the inertia in underdamped Langevin equation (2.9), but there appears so called Ito drift term $k_B T \frac{\partial L}{\partial x} \Delta t$. Such terms are also 'derived' in [55], by assuming that the RHS of (2.33) as the sum of interpretation-dependent unknown deterministic term and multiplicative noise term, and determined it by requiring the corresponding Fokker-Planck equation to have the Boltzmann distribution as the stationary solution. While derivation by [55] is based on an inductive reasoning, ours is deductive. We will discuss this point more thoroughly at the end of this chapter. We notice that overdamped version of the FDT between g and L holds: $g^2 = 2k_B T L$.

Extension of the above argument to the situation where an external force is present is straightforward, since such a term is deterministic and its contribution to the overdamped Langevin equation is $\mathcal{O}(\Delta t)$ from the beginning. Therefore we can add the external force to the underdamped Langevin equation (2.9).

$$\ddot{x}(t) = -\zeta(x(t))\dot{x}(t) - \frac{\partial U}{\partial x} + b(x(t))\xi(t). \tag{2.34}$$

The overdamp limit is simply given by

$$\Delta x(t) = -L(x)\frac{\partial U}{\partial x}\Delta t + g(x(t))\Delta W + k_B T \frac{\partial L(x)}{\partial x} \Delta t. \tag{2.35}$$

Let us summarize our strategy to take the overdamp limit within the Langevin equation.

1. Expand the friction coefficient $\zeta(x)$ and the coefficient of the multiplicative noise $b(x)$ around some reference point

2. Write down the formal solution of the underdamped Langevin equation in the form of $\Delta x = x(t + \Delta t) - x(t) = \cdots$.

3. Estimate it in the linear order of Δt and τ_p with $\Delta t \gg \tau_p$.

In our method one can realize any interpretation of the multiplicative noise, by choosing the reference point where the expansion of ζ and b are performed. Note also that the FDT is not necessary to carry out the calculation. Thus the procedure demonstrated above can be applied for far more general situations.

Ermak and MacCammon [13] have performed for the first time the correct calculation of overdamp limit in the same strategy as ours, more than 30 years ago. They implicitly used the Ito type expansion for the state-dependent transport coefficient $\zeta(x)$. But they did not carry out the expansion for $b(x)$. As shown by Sekimoto [33] and us the correction due to the x-dependence of multiplicative noise term vanishes, i.e., $I^{b,\mathrm{Ito}} = 0$. Thus even if one missed this correction one can obtain the correct result. In this sense Ermak et al. have obtained the correct result accidentally.

2.3 Extension to multi-dimensional case

Our method works also for multi-dimensional case. Let $i, j, k, \cdots = 1, \ldots, N$ be indices of the degree of freedom and consider the following underdamped Langevin equation for the position variables x_i.

$$\ddot{x}_i(t) = -\zeta_{ij}(x(t))\dot{x}_j(x(t)) + b_{ij}(x(t))\xi_j(t), \tag{2.36}$$

which is a straightforward extension of (2.9). Hereafter we assume that repeated indices are summed from 1 to N. $\zeta_{ij}(x)$ is the state-dependent friction matrix. $b_{ij}(x)$ is also state-dependent matrix which satisfies the FDT: $b_{ik}(x)b^{\dagger}_{kj}(x) = 2k_BT\zeta_{ij}(x)$. ξ_i is the white Gaussian noise and satisfies,

$$\langle \xi_i(t) \rangle = 0, \quad \langle \xi_i(t_1)\xi_j(t_2) \rangle = \delta_{ij}\delta(t_1 - t_2). \tag{2.37}$$

We perform the expansion of $\zeta_{ij}(x(t_2))$ with t_2 being $t < t_2 < t + \Delta t$.

$$\zeta_{ij}(x(t_2)) = \zeta_{ij}(x(t)) + \frac{\partial \zeta_{ij}(x)}{\partial x_k(t)} \left[x_k(t_2) - x_k(t) \right] + \mathcal{O}(\Delta t). \tag{2.38}$$

This expansion amounts to the power series expansion with small parameter τ_p or $\Delta t^{1/2}$. See Section 2.2 for detail. By substituting (2.38) into (2.36) , we have

$$\begin{aligned} \ddot{x}_i(t_2) &= -\left\{ \zeta_{ij}(x(t)) + \frac{\partial \zeta_{ij}(x)}{\partial x_k(t)} \left[x_k(t_2) - x_k(t) \right] \right\} \dot{x}_j(t_2) + b_{ij}(x(t_2))\xi_j(t_2) \\ &= -\zeta_{ij}(x(t))\dot{x}_j(t_2) - \frac{\partial \zeta_{ij}(x)}{\partial x_k(t)} \left[x_k(t_2) - x_k(t) \right] \dot{x}_j(t_2) + b_{ij}(x(t_2))\xi_j(t_2). \end{aligned} \tag{2.39}$$

The formal solution of (2.39) is given by

$$\begin{aligned}\dot{x}_i(t_1) &= \int_t^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(x(t))(t_1-t_2)}\right]_{ij} \\ &\quad \times \left\{-\frac{\partial \zeta_{jk}(x)}{\partial x_l(t)}\left[x_l(t_2)-x_l(t)\right]\dot{x}_k(t_2) + b_{jk}(x(t_2))\xi_k(t_2)\right\}.\end{aligned} \tag{2.40}$$

Here the leading contribution comes from the multiplicative noise term, namely the second term in $\{\cdots\}$ in the RHS of (2.40). Thus in the lowest order in τ_p or Δt, (2.40) is written as

$$\dot{x}_i(t_1) = \int_t^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(x(t))(t_1-t_2)}\right]_{ij} b_{jk}(x(t))\xi_k(t_2) + \mathcal{O}(\tau_p). \tag{2.41}$$

We discretize the formal solution (2.40) by integrating both side from t to $t+\Delta t$.

$$\begin{aligned}\Delta x_i(t) = &\int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(x(t))(t_1-t_2)}\right]_{ij} \\ &\times \left\{-\frac{\partial \zeta_{jk}(x)}{\partial x_l(t)}\left[x_l(t_2)-x_l(t)\right]\dot{x}_k(t_2) + b_{jk}(x(t_2))\xi_k(t_2)\right\} + \mathcal{O}(\Delta t^{3/2}).\end{aligned} \tag{2.42}$$

Again the leading contribution comes from the second term in $\{\cdots\}$ in the RHS of (2.42). Thus by integrating both side of (2.40) from t to t_2 and taking the lowest order we obtain

$$x_l(t_2) - x_l(t) = \int_t^{t_2} dt_3 \int_t^{t_3} dt_4 \left[\mathrm{e}^{-\zeta(t_3-t_4)}\right]_{ln} b_{no}(x(t))\xi_o(t_4) + \mathcal{O}(\Delta t), \tag{2.43}$$

where the argument of ζ_{ij}, which is $x(t)$, is omitted hereafter in this section. Next we expand $b_{jk}(x(t_2))$ appearing in the second term in $\{\cdots\}$ in the RHS of (2.42).

$$b_{jk}(x(t_2)) = b_{jk}(x(t)) + \frac{\partial b_{jk}(x)}{\partial x_l(t)}\left[x_l(t_2)-x_l(t)\right] + \mathcal{O}(\Delta t). \tag{2.44}$$

Plugging (2.41), (2.43) and (2.44) into $\dot{x}_k(t_2)$, $x_l(t_2)-x_l(t)$ and $b_{jk}(x(t_2))$ in the RHS of (2.42) we have

$$\Delta x_i(t) = \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(t_1-t_2)}\right]_{ij} b_{jk}(x(t))\xi_k(t_2) + I_i^{\zeta,\mathrm{Ito}} + I_i^{b,\mathrm{Ito}} + \mathcal{O}(\Delta t^{3/2}), \tag{2.45}$$

where,

$$I_i^{\zeta,\mathrm{Ito}} \equiv -\int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(t_1-t_2)}\right]_{ij} \frac{\partial \zeta_{jk}(x)}{\partial x_l(t)} \tag{2.46}$$
$$\times \int_t^{t_2} dt_3 \int_t^{t_3} dt_4 \left[\mathrm{e}^{-\zeta(t_3-t_4)}\right]_{ln} b_{no}(x(t))\xi_o(t_4)$$
$$\times \int_t^{t_2} dt_5 \left[\mathrm{e}^{-\zeta(t_2-t_5)}\right]_{kp} b_{pq}(x(t))\xi_q(t_5),$$
$$I_i^{b,\mathrm{Ito}} \equiv \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(t_1-t_2)}\right]_{ij} \frac{\partial b_{jk}(x)}{\partial x_l(t)} \tag{2.47}$$
$$\times \int_t^{t_2} dt_3 \int_t^{t_3} dt_4 \left[\mathrm{e}^{-\zeta(t_3-t_4)}\right]_{ln} b_{no}(x(t))\xi_o(t_4)\xi_k(t_2).$$

By repeating the same discussion as (2.26)–(2.29), the first term in the RHS of (2.45) becomes the multiplicative noise interpreted in the Ito sense.

$$\int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(t_1-t_2)}\right]_{ij} b_{jk}(x(t))\xi_k(t_2) = g_{ij}(x(t))\Delta W_j, \tag{2.48}$$

where we defined

$$\boldsymbol{g} \equiv \boldsymbol{\zeta}^{-1}\boldsymbol{b}. \tag{2.49}$$

One of the the correction terms $I_i^{b,\mathrm{Ito}}$ vanishes in the same manner as 1-dimensional case:

$$I_i^{b,\mathrm{Ito}} = 0. \tag{2.50}$$

The correction term $I_i^{\zeta,\mathrm{Ito}}$ remains finite as in 1-dimensional case. By replacing the order of integral over t_1 and t_2 as well as t_3 and t_4 respectively by using (2.26) one can carry out the integral over t_1 and t_3. As a result we have

$$\begin{aligned} I_i^{\zeta,\mathrm{Ito}} &= -\frac{\partial \zeta_{jk}}{\partial x_l} b_{no} b_{pq} \int_t^{t+\Delta t} dt_2 \zeta_{ir}^{-1} \left\{\delta_{rj} - \left[\mathrm{e}^{-\zeta(t+\Delta t-t_2)}\right]_{rj}\right\} \\ &\quad \times \int_t^{t_2} dt_4 \zeta_{ls}^{-1} \left\{\delta_{sn} - \left[\mathrm{e}^{-\zeta(t_2-t_4)}\right]_{sn}\right\} \xi_o(t_4) \\ &\quad \times \int_t^{t_2} dt_5 \left[\mathrm{e}^{-\zeta(t_2-t_5)}\right]_{kp} \xi_q(t_5). \end{aligned} \tag{2.51}$$

Here we denote $\zeta_{ij}(x(t))$ and $b_{ij}(x(t))$ simply by ζ_{ij} and b_{ij} respectively. Since the friction coefficient is very large one can replace $\delta_{rj} - \left[\mathrm{e}^{-\zeta(t+\Delta t-t_2)}\right]_{rj}$ in dt_2 integral by

$$\delta_{rj} - \left[\mathrm{e}^{-\zeta(t+\Delta t-t_2)}\right]_{rj} = \begin{cases} 0 & t_2 = t+\Delta t, \\ \delta_{rj} & t_2 \neq t+\Delta t. \end{cases} \tag{2.52}$$

Thus one can approximate (2.51) as

$$\begin{aligned} I_i^{\zeta,\mathrm{Ito}} &= -\zeta_{ij}^{-1}\frac{\partial\zeta_{jk}}{\partial x_l}b_{no}b_{pq}\int_t^{t+\Delta t-0}dt_2 \\ &\quad\times\int_t^{t_2}dt_4\zeta_{ls}^{-1}\left\{\delta_{sn}-\left[\mathrm{e}^{-\zeta(t_2-t_4)}\right]_{sn}\right\}\xi_o(t_4) \\ &\quad\times\int_t^{t_2}dt_5\left[\mathrm{e}^{-\zeta(t_2-t_5)}\right]_{kp}\xi_q(t_5). \end{aligned} \tag{2.53}$$

Note that in the integral over t_4 one cannot use this approximation (2.52). Next we replace the quadratic term in ξ by the delta function, which is justified by the Gaussian nature of the noise, $\xi_o(t_4)\xi_q(t_5)=\delta_{oq}\delta(t_4-t_5)$. It enables us to carry out the integral over t_5.

$$I_i^{\zeta,\mathrm{Ito}} = -2k_BT\zeta_{ij}^{-1}\frac{\partial\zeta_{jk}}{\partial x_l}\int_t^{t+\Delta t}dt_2\int_t^{t_2}dt_4\left\{\delta_{ln}-\left[\mathrm{e}^{-\zeta(t_2-t_4)}\right]_{ln}\right\}\left[\mathrm{e}^{-\zeta(t_2-t_4)}\right]_{nk}. \tag{2.54}$$

We used the FDT and ignored "-0" in the upper endpoint of the integral over t_2 since it only causes the difference in higher order. Remaining integrals over t_2 and t_4 can be analytically carried out and one has

$$I_i^{\zeta,\mathrm{Ito}} = -k_BT\left(\zeta^{-1}\right)_{ij}\frac{\partial\zeta_{jk}}{\partial x_l}\left(\zeta^{-1}\right)_{lk}\Delta t = k_BT\frac{\partial\left(\zeta^{-1}\right)_{ij}}{\partial x_j}\Delta t = k_BT\frac{\partial L_{ij}}{\partial x_j}\Delta t, \tag{2.55}$$

to the lowest order in τ_p and Δt. $\boldsymbol{L}$ is the Onsager coefficient matrix defined by

$$\boldsymbol{L}=\boldsymbol{\zeta}^{-1}. \tag{2.56}$$

Using (2.48), (2.50), and (2.55), the overdamped Langevin equation (2.45) becomes

$$\Delta x_i(t) = g_{ij}(x(t))\Delta W_j + T\frac{\partial L_{ij}}{\partial x_j}\Delta t. \tag{2.57}$$

Here g_{ij} satisfies the overdamped version of the FDT.

$$\boldsymbol{g}\boldsymbol{g}^\dagger = 2T\boldsymbol{L}. \tag{2.58}$$

In the presence of the external force, the underdamped Langevin equation is given by

$$\ddot{x}_i(t) = -\zeta_{ij}(x(t))\dot{x}_j(x(t)) - \frac{\partial U}{\partial x_i} + b_{ij}(x(t))\xi_j(t). \tag{2.59}$$

The overdamp limit is not affected by the external force and given by

$$\Delta x_i(t) = -L_{ij}(x)\frac{\partial U}{\partial x_j}\Delta t + g_{ij}(x(t))\Delta W_j + T\frac{\partial L_{ij}}{\partial x_j}\Delta t. \tag{2.60}$$

2.4 Anti-Ito expansion

In Section 2.2 and 2.3 one can determine the interpretation of the multiplicative noise in the overdamped Langevin equation as the Ito one since we have expanded ζ and b around $x(t)$, which is the value of stochastic variable evaluated at time before kicked by the noise. One expects that, by changing the reference point at which the expansion is performed, resulting multiplicative noise in the overdamp limit will be interpreted in another fashion. In this section we choose the reference point as $x(t+\Delta t)$. The resulting multiplicative noise is expected to be the anti-Ito type. The anti-Ito interpretation itself is less familiar than the Ito or Stratonovich. The reason we perform this calculation nonetheless it is unfamiliar is twofold. First, Hess et al. [40] and Sancho et al. [41] has tried to compute the overdamp limit by writing down the formal solution and implicitly performed the anti-Ito like expansion of multiplicative noise term. We make a comparison of our result obtained in this section with theirs in Section 2.9. Second, it is argued that the anti-Ito is the most natural interpretation of multiplicative noises [17, 18], since in one dimension the correct overdamp Langevin equation is identical with that obtained by ignoring inertia and interpreting the multiplicative noise in anti-Ito manner. We show that it is just an accident and in multi-dimensional systems ignoring the inertial term never gives the correct overdamped Langevin equation.

One dimensional case

We expand the state-dependent transport coefficient $\zeta(x(t_2))$ and the factor of the multiplicative noise $b(x(t_2))$ around $x(t+\Delta t)$. We assume that $t_2 < t+\Delta t$.

$$\begin{aligned}\zeta(x(t_2)) =&\zeta(x(t+\Delta t) - [x(t+\Delta t) - x(t_2)]) \qquad (2.61)\\ =&\zeta(x(t+\Delta t)) - \frac{\partial \zeta(x)}{\partial x(t+\Delta t)}\left[x(t+\Delta t) - x(t_2)\right] + \mathcal{O}(\tau_p),\\ b(x(t_2)) =&b(x(t+\Delta t) - [x(t+\Delta t) - x(t_2)]) \qquad (2.62)\\ =&b(x(t+\Delta t)) - \frac{\partial b(x)}{\partial x(t+\Delta t)}\left[x(t+\Delta t) - x(t_2)\right] + \mathcal{O}(\tau_p^{3/2}).\end{aligned}$$

Note that this expansion is slightly different from the Ito expansion ((2.14) and (2.18)) demonstrated in Section 2.2. Substituting these expansions into

the underdamped Langevin equation (2.9) one has

$$\begin{aligned}\ddot{x}(t_2) &= -\zeta(x(t+\Delta t))\dot{x}(t_2) + \frac{\partial\zeta(x)}{\partial x(t+\Delta t)}\left[x(t+\Delta t)-x(t_2)\right]\dot{x}(t_2) \\ &\quad +b(x(t+\Delta t))\xi(t_2) - \frac{\partial b(x)}{\partial x(t+\Delta t)}\left[x(t+\Delta t)-x(t_2)\right]\xi(t_2) \\ &\quad +\mathcal{O}(\tau_p^2). \end{aligned} \tag{2.63}$$

By regarding the second term and after as inhomogeneous terms one sees that the formal solution of (2.63) is given by

$$\begin{aligned}\dot{x}(t_1) = \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(x(t+\Delta t))(t_1-t_2)} \Bigg\{ &\frac{\partial\zeta(x)}{\partial x(t+\Delta t)}\left[x(t+\Delta t)-x(t_2)\right]\dot{x}(t_2) \\ &+b(x(t+\Delta t))\xi(t_2) - \frac{\partial b(x)}{\partial x(t+\Delta t)}\left[x(t+\Delta t)-x(t_2)\right]\xi(t_2)\Bigg\} \end{aligned} \tag{2.64}$$

Here we have ignored the contribution from the time integral $\int_{-\infty}^{t} dt_2$ since it is $\tau_p^{1/2}$ times smaller than other contributions, as in previous sections. $x(t+\Delta t)-x(t_2)$ in the RHS of (2.64) can be estimated in the lowest order by integrating (2.64) from t_2 to $t+\Delta t$ as

$$x(t+\Delta t)-x(t_2) \cong b(x(t+\Delta t))\int_{t_2}^{t+\Delta t} dt_3 \int_t^{t_2} dt_4 \mathrm{e}^{-\zeta(x(t+\Delta t))(t_3-t_4)}\xi(t_4), \tag{2.65}$$

Here we only take the leading order in τ_p in the RHS of (2.65). Next we integrate the formal solution (2.64) from time t to $t+\Delta t$.

$$\begin{aligned}\Delta x &= \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(x(t+\Delta t))(t_1-t_2)} \\ &\quad \times\Bigg\{\frac{\partial\zeta(x)}{\partial x(t+\Delta t)}\left[x(t+\Delta t)-x(t_2)\right]\dot{x}(t_2) \\ &\quad +b(x(t+\Delta t))\xi(t_2) - \frac{\partial b(x)}{\partial x(t+\Delta t)}\left[x(t+\Delta t)-x(t_2)\right]\xi(t_2)\Bigg\}, \end{aligned} \tag{2.66}$$

We denote the corrections come from the first and third term in $\{\cdots\}$ in the RHS of (2.66) as $I^{\zeta,\mathrm{aI}}$ and $I^{b,\mathrm{aI}}$, respectively, i.e.,

$$I^{\zeta,\mathrm{aI}} \equiv \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(x(t+\Delta t))(t_1-t_2)} \frac{\partial\zeta(x)}{\partial x(t+\Delta t)}\left[x(t+\Delta t)-x(t_2)\right]\dot{x}(t_2), \tag{2.67}$$

$$I^{b,\mathrm{aI}} \equiv -\int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(x(t+\Delta t))(t_1-t_2)} \frac{\partial b(x)}{\partial x(t+\Delta t)}\left[x(t+\Delta t)-x(t_2)\right]\xi(t_2). \tag{2.68}$$

Then the formal solution (2.66) becomes

$$\Delta x = \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 e^{-\zeta(x(t+\Delta t))} b(x(t+\Delta t))\xi(t_2) + I^{\zeta,\mathrm{aI}} + I^{b,\mathrm{aI}}. \quad (2.69)$$

The first term in the RHS of (2.69) is the multiplicative noise interpreted in anti-Ito.

$$b\int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(x(t+\Delta t))(t_1-t_2)}\xi(t_2) = g(x(t+\Delta t))\Delta W. \quad (2.70)$$

We omit the proof since the derivation is almost the same as that have performed in (2.26) in Section 2.2. The correction terms, $I^{\zeta,\mathrm{aI}}$ and $I^{b,\mathrm{aI}}$, in the RHS of (2.69) can be evaluated by the same manner as in Section 2.2. By substituting the formal solution for $\dot{x}$ with (2.64) and $x(t+\Delta t) - x(t_2)$ with (2.65) in their lowest order one has

$$I^{\zeta,\mathrm{aI}} = 2k_BT\zeta'\zeta\frac{\Delta t}{2\zeta^3} + \mathcal{O}(\tau_p^2) = -k_BT\frac{\partial\zeta^{-1}(x)}{\partial x(t+\Delta t)}\Delta t + \mathcal{O}(\tau_p^2), \quad (2.71)$$

$$I^{b,\mathrm{aI}} = -b'b\frac{\Delta t}{\zeta^2} + \mathcal{O}(\tau_p^2) = k_BT\frac{\partial\zeta^{-1}(x)}{\partial x(t+\Delta t)}\Delta t + \mathcal{O}(\tau_p^2). \quad (2.72)$$

$I^{\zeta,\mathrm{aI}}$ and $I^{b,\mathrm{aI}}$ are identical aside from their signs and cancel each other. Thus the correction terms arisen from the state-dependence of the transport coefficient and the multiplicative noise vanish. The resulting overdamp Langevin equation becomes

$$\Delta x(t) = g(x(t+\Delta t))\Delta W. \quad (2.73)$$

Needless to say, the obtained Langevin equation (2.73) represents the identical stochastic process with the Ito result (2.33). The correction terms vanish in the anti-Ito case, in contrast with the Ito case. But this is merely an accidental result and in multi-dimensional system the corrections do not cancel each other, as shown below. In the presence of the external force the result is, in continuum expression,

$$\text{(aI)} \quad \dot{x} = -L(x)\frac{\partial U}{\partial x} + g(x)\xi(t). \quad (2.74)$$

Here (aI) stands for the anti-Ito interpretation of the multiplicative noise. This result is identical with the underdamped Langevin equation (2.34) without inertia. This is the reason why Lançon et al. [17] and Volpe et al. [18] have misguidedly concluded that the anti-Ito is the correct interpretation of multiplicative noise.

multi-dimensional case

The extension into the multi-dimensional systems is straightforward. As before, we first expand $b_{ij}(x(t_2))$ and $\zeta_{ij}(x(t_2))$ around $x(t+\Delta t)$. Since we assumed that $t_2 < t+\Delta t$,

$$\begin{aligned} b_{ij}(x(t_2)) &= b_{ij}(x(t+\Delta t)) - \frac{\partial b_{ij}(x)}{\partial x_k(t+\Delta t)}\left[x_k(t+\Delta t) - x_k(t_2)\right] \\ &\quad +\mathcal{O}(\tau_p^{3/2}), \end{aligned} \tag{2.75}$$

$$\begin{aligned} \zeta_{ij}(x(t_2)) &= \zeta_{ij}(x(t+\Delta t)) - \frac{\partial \zeta_{ij}(x)}{\partial x_k(t+\Delta t)}\left[x_k(t+\Delta t) - x_k(t_2)\right] \\ &\quad +\mathcal{O}(\tau_p). \end{aligned} \tag{2.76}$$

By substituting (2.75) and (2.76) into the underdamped Langevin equation (2.36) we have

$$\begin{aligned} \ddot{x}_i(t_2) &= -\zeta_{ij}(x(t+\Delta t))\dot{x}_j(t_2) + \frac{\partial \zeta_{ij}(x)}{\partial x_k(t+\Delta t)}\left[x_k(t+\Delta t) - x_k(t_2)\right]\dot{x}_j(t_2) \\ &\quad +b_{ij}(x(t+\Delta t))\xi_j(t_2) - \frac{\partial b_{ij}}{\partial x_k(t+\Delta t)}\left[x_k(t+\Delta t) - x_k(t_2)\right]\xi_j(t_2) \\ &\quad +\mathcal{O}(\tau_p). \end{aligned} \tag{2.77}$$

Formal solution to (2.77) is then

$$\begin{aligned} \dot{x}_i(t_1) &= \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(x(t+\Delta t))(t_1-t_2)}\right]_{ij} \\ &\quad \times \left\{ \frac{\partial \zeta_{jk}(x)}{\partial x_l(t)}\left[x_l(t+\Delta t) - x_l(t_2)\right]\dot{x}_k(t_2) + b_{jk}(x(t+\Delta t))\xi_k(t_2) \right. \\ &\quad \left. -\frac{\partial b_{jk}}{\partial x_l(t+\Delta t)}\left[x_l(t+\Delta t) - x_l(t_2)\right]\xi_k(t_2) \right\}. \end{aligned} \tag{2.78}$$

Discretizing (2.78) in time yields

$$\begin{aligned} \Delta x &= \int_{t}^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(x(t+\Delta t))(t_1-t_2)}\right]_{ij} \\ &\quad \times \left\{ \frac{\partial \zeta_{jk}(x)}{\partial x_l(t)}\left[x_l(t+\Delta t) - x_l(t_2)\right]\dot{x}_k(t_2) + b_{jk}(x(t+\Delta t))\xi_k(t_2) \right. \\ &\quad \left. -\frac{\partial b_{jk}}{\partial x_l(t+\Delta t)}\left[x_l(t+\Delta t) - x_l(t_2)\right]\xi_k(t_2) \right\}. \end{aligned} \tag{2.79}$$

$x_l(t+\Delta t) - x_l(t_2)$ in the RHS of (2.78) is estimated in leading order in τ_p as

$$x_l(t+\Delta t) - x_l(t_2) = \int_s^{t+\Delta t} dt_3 \int_{-\infty}^{t_3} dt_4 \left[\mathrm{e}^{-\zeta(x(t+\Delta t))(t_3-t_4)}\right]_{ln} b_{no}(x(t+\Delta t))\xi_o(t_4) + \mathcal{O}(\tau_p^2). \tag{2.80}$$

Applying (2.78) and (2.80) to (2.79) one has

$$\begin{aligned}\Delta x_i &= \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(x(t+\Delta t))(t_1-t_2)}\right]_{ij} b_{jk}(x(t+\Delta t))\xi_k(t_2) \\ &\quad + I_i^{b,\mathrm{aI}} + I_i^{\zeta,\mathrm{aI}}.\end{aligned} \tag{2.81}$$

where

$$\begin{aligned}I_i^{b,\mathrm{aI}} &\equiv -\frac{\partial b_{jk}}{\partial x_l} b_{nm} \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(x(t+\Delta t))(t_1-t_2)}\right]_{ij} \\ &\quad \times \int_{t_2}^{t+\Delta t} dt_3 \int_{-\infty}^{t_3} dt_4 \left[\mathrm{e}^{-\zeta(x(t+\Delta t))(t_3-t_4)}\right]_{lm} \xi_n(t_4)\xi_k(t_2), \qquad (2.82) \\ I_i^{\zeta,\mathrm{aI}} &\equiv \frac{\partial \zeta_{jk}}{\partial x_l} b_{mn} b_{op} \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(x(t+\Delta t))(t_1-t_2)}\right]_{ij} \\ &\quad \times \int_{t_2}^{t+\Delta t} dt_3 \int_{-\infty}^{t_3} dt_4 \left[\mathrm{e}^{-\zeta(x(t+\Delta t))(t_3-t_4)}\right]_{lm} \xi_n(t_4) \\ &\quad \times \int_{-\infty}^{t_2} dt_5 \left[\mathrm{e}^{-\zeta(x(t+\Delta t))(t_2-t_5)}\right]_{ko} \xi_p(t_5). \qquad (2.83)\end{aligned}$$

Here arguments of $\zeta_{ij}(x(t+\Delta t))$ and $b_{ij}(x(t+\Delta t))$ are abbreviated only in this section. These integrals can be carried out in the same manner as Section 2.3 and one obtains

$$I_i^{b,\mathrm{aI}} = g_{ij}^{\dagger} \frac{\partial g_{jk}}{\partial x_k} \Delta t, \tag{2.84}$$

$$I_i^{\zeta,\mathrm{aI}} = -k_B T \frac{\partial L_{ij}}{\partial x_j} \Delta t. \tag{2.85}$$

The first term in the RHS of (2.81) converges to the anti-Ito multiplicative noise,

$$\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\zeta(x(t+\Delta t))(t_1-t_2)}\right]_{ij} b_{jk}(x(t+\Delta t))\xi_k(t_2) = g_{ij}(x(t+\Delta t))\Delta W_j. \tag{2.86}$$

Combining (2.84)–(2.86) with (2.81), the overdamped Langevin equation is obtained as

$$\Delta x_i = g_{ij}(x(t+\Delta t))\Delta W_j + \frac{1}{2}\left(g^\dagger_{ij}\frac{\partial g_{jk}}{\partial x_k} - \frac{\partial g^\dagger_{ij}}{\partial x_k}g_{jk}\right)\Delta t. \tag{2.87}$$

In contrast with one dimensional case (2.73), we have the correction terms proportional to Δt. Thus one finds that cancellation of the correction terms in one-dimensional case is just an accident and anti-Ito is not a special interpretation of multiplicative noise.

2.5 Stratonovich

One can also perform the expansion of b and ζ around $x^* = \frac{x(t)+x(t+\Delta t)}{2}$, which reads the Stratonovich convention of the multiplicative noise. We need to split $x(t_2)$ as

$$x(t_2) = x^* - \frac{1}{2}\left[x(t+\Delta t) - x(t_2)\right] + \frac{1}{2}\left[x(t_2) - x(t)\right]. \tag{2.88}$$

Then expansion of $b(x(t_2))$ around x^* becomes

$$\begin{aligned} b(x(t_2)) &= b\left(x^* - \frac{1}{2}\left[x(t+\Delta t) - x(t_2)\right] + \frac{1}{2}\left[x(t_2) - x(t)\right]\right) \\ &= b\left(x^*\right) - \frac{1}{2}\frac{\partial b(x)}{\partial x^*}\left[x(t+\Delta t) - x(t_2)\right] \\ &\quad + \frac{1}{2}\frac{\partial b(x)}{\partial x^*}\left[x(t_2) - x(t)\right] + \cdots, \end{aligned} \tag{2.89}$$

where $\frac{\partial b(x)}{\partial x^*} = \frac{\partial b(x)}{\partial x}\Big|_{x=x^*}$. Then the underdamped Langevin equation (2.9) can be expanded in powers of τ_p as

$$\begin{aligned} \ddot{x}(t_2) = &-\zeta(x^*)\dot{x}(t_2) + \frac{1}{2}\frac{\partial \zeta(x)}{\partial x^*}\left[x(t+\Delta t) - x(t_2)\right]\dot{x}(t_2) \\ &- \frac{1}{2}\frac{\partial \zeta(x)}{\partial x^*}\left[x(t_2) - x(t)\right]\dot{x}(t_2) \\ &+ b(x^*)\xi(t_2) - \frac{1}{2}\frac{\partial b(x)}{\partial x^*}\left[x(t+\Delta t) - x(t_2)\right]\xi(t_2) \\ &+ \frac{1}{2}\frac{\partial b(x)}{\partial x^*}\left[x(t_2) - x(t)\right]\xi(t_2) + \mathcal{O}(\tau_p). \end{aligned} \tag{2.90}$$

Then formal solution is given by

$$\begin{aligned}\Delta x &= \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(x^*)(t_1-t_2)} b(x^*)\xi(t_2) \\ &+\frac{1}{2}\frac{\partial \zeta(x)}{\partial x^*}\int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(x^*)(t_1-t_2)} \left[x(t+\Delta t)-x(t_2)\right]\dot{x}(t_2) \\ &-\frac{1}{2}\frac{\partial \zeta(x)}{\partial x^*}\int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(x^*)(t_1-t_2)} \left[x(t_2)-x(t)\right]\dot{x}(t_2) \\ &-\frac{1}{2}\frac{\partial b(x)}{\partial x^*}\int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(x^*)(t_1-t_2)} \left[x(t+\Delta t)-x(t_2)\right]\xi(t_2) \\ &+\frac{1}{2}\frac{\partial b(x)}{\partial x^*}\int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(x^*)(t_1-t_2)} \left[x(t_2)-x(t)\right]\xi(t_2) \quad (2.91)\end{aligned}$$

Clearly second term is half of correction appeared in anti-Ito expansion of ζ. Third is that appeared in Ito expansion, etc.. Thus we do not need to calculate them explicitly.

$$\begin{aligned}\Delta x &= \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 \mathrm{e}^{-\zeta(x^*)(t_1-t_2)} b(x^*)\xi(t_2) \\ &+\frac{1}{2}\left(I^{\zeta,\mathrm{aI}}+I^{\zeta,\mathrm{Ito}}+I^{b,\mathrm{aI}}+I^{b,\mathrm{Ito}}\right), \quad (2.92)\end{aligned}$$

By using the value of Is in (2.71), (2.32), (2.72) and (2.25), one arrives at

$$\text{(S)} \quad \dot{x} = g(x)\xi(t) + \frac{k_B T}{2}\frac{\partial L(x)}{\partial x}. \quad (2.93)$$

Here (S) stands for the Stratonovich interpretation of the multiplicative noise. Since the second term is already $\mathcal{O}(\Delta t)$ difference in choice of reference point is merely $\mathcal{O}(\Delta t^{3/2})$ and negligible. Thus we omit the argument of $\frac{\partial L}{\partial x}$ in second term. For multidimensional case it is easy to see that from (2.85), (2.55), (2.84) and (2.50), the correction terms are given by,

$$\frac{1}{2}\left(I_i^{\zeta,\mathrm{aI}}+I_i^{\zeta,\mathrm{Ito}}+I_i^{b,\mathrm{aI}}+I_i^{b,\mathrm{Ito}}\right) = \frac{1}{2}g_{ik}^{\dagger}\frac{\partial g_{kj}}{\partial x_j^*}\Delta t. \quad (2.94)$$

Thus the overdamp limit is

$$\text{(S)} \quad \dot{x}_i = g_{ij}(x)\xi_j(t) + \frac{1}{2}g_{ik}^{\dagger}\frac{\partial g_{kj}}{\partial x_j}. \quad (2.95)$$

2.6 General α convention

In this section we demonstrate the extension to arbitrary interpretation of the multiplicative noise in the overdamp limit. We set $x^* \equiv \alpha x(t+\Delta t) + (1-\alpha)x(t)$ and expand $\zeta(x(t_2))$ and $b(x(t_2))$ around x^*. We call this interpretation of noise α convention [55]. Here obeys an identity similar to (2.88).

$$x(t_2) = x^* - \alpha\left[x(t+\Delta t) - x(t_2)\right] + (1-\alpha)\left[x(t_2) - x(t)\right]. \tag{2.96}$$

Thus corrections to the multiplicative noise interpreted in this convention in the overdamp limit can be evaluated by a straightforward extension from the Stratonovich case, demonstrated in Section 2.5. By using (2.71), (2.32), (2.72) and (2.25), the correction terms are given by

$$\alpha\left(I^{\zeta,\mathrm{aI}} + I^{b,\mathrm{aI}}\right) + (1-\alpha)\left(I^{\zeta,\mathrm{Ito}} + I^{b,\mathrm{Ito}}\right) = (1-\alpha)k_BT\frac{\partial L}{\partial x^*}\Delta t. \tag{2.97}$$

Then the overdamp limit in one dimension is

$$\dot{x}(t) = g(x^*)\xi(t) + (1-\alpha)k_BT\frac{\partial L}{\partial x}. \tag{2.98}$$

This expression is identical with the overdamped Langevin equation proposed by Lau and Lubensky [55].

Extension to the multidimensional case is straightforward. The corrections are

$$\alpha\left(I_i^{\zeta,\mathrm{aI}} + I_i^{b,\mathrm{aI}}\right) + (1-\alpha)\left(I_i^{\zeta,\mathrm{Ito}} + I_i^{b,\mathrm{Ito}}\right) = \tag{2.99}$$
$$k_BT\,(1-\alpha)\,\frac{\partial L_{ij}}{\partial x_j}\Delta t + \frac{\alpha}{2}\left(g_{ik}\frac{\partial g^\dagger_{kj}}{\partial x_j} - \frac{\partial g_{ik}}{\partial x_j}g^\dagger_{kj}\right)\Delta t$$

by using (2.85), (2.55), (2.84) and (2.50). Thus the overdamp limit of the underdamped Langevin equation (2.36) in α convention is

$$(\alpha)\quad \dot{x}_i = g_{ij}(x)\xi_j(t) + (1-\alpha)\,k_BT\frac{\partial L_{ij}}{\partial x_j} + \frac{\alpha}{2}\left(g_{ik}\frac{\partial g^\dagger_{kj}}{\partial x_j} - \frac{\partial g_{ik}}{\partial x_j}g^\dagger_{kj}\right). \tag{2.100}$$

Here (ζ) stands for the general α interpretation of the multiplicative noise. $*$s in $\mathcal{O}(\Delta t)$ terms are omitted since difference in the choice of reference point is as small as $\mathcal{O}(\Delta t^{3/2})$. In the presence of external force $-\frac{\partial U}{\partial x_i}$ (2.100) becomes

$$\begin{aligned}(\alpha)\quad \dot{x}_i &= -L_{ij}(x)\frac{\partial U}{\partial x_j} + g_{ij}(x^*)\xi_j(t) \\ &\quad + T\,(1-\alpha)\,\frac{\partial L_{ij}}{\partial x_j} + \frac{\alpha}{2}\left(g_{ik}\frac{\partial g^\dagger_{kj}}{\partial x_j} - \frac{\partial g_{ik}}{\partial x_j}g^\dagger_{kj}\right).\end{aligned} \tag{2.101}$$

Again the expression is identical with that obtained in [55]. Note that by taking noise average (2.101) one finds that

$$\langle \dot{x}_i \rangle = \left\langle -L_{ij}(x)\frac{\partial U}{\partial x_j} \right\rangle + \left\langle T\frac{\partial L_{ij}}{\partial x_j} \right\rangle. \tag{2.102}$$

This equation means that average regression of fluctuation given in the left hand side (LHS) of (2.102) *does not* obey the macroscopic law (first term of the RHS of (2.102)). These quantities are identical in usual additive noise system, where L_{ij} is constant, called Onsager's regression hypothesis [57]. Now we find that the hypothesis is violated in the Brownian motion with the state-dependent Onsager coefficient.

2.7 Non-equilibrium case

Our procedure to adiabatically eliminate the fast relaxing momentum and obtain the overdamp limit directly from the underdamped Langevin equation works also in the non-equilibrium case. In such situations one cannot resort to the FDT: $b^2 = 2k_BT\zeta$. Here we only quote the final result for multidimensional case with α convention.

$$\begin{aligned} \dot{x}_i &= -L_{ij}(x)\frac{\partial U(x)}{\partial x_j} + \frac{\partial L_{ij}(x)}{\partial x_k}\zeta_{jl}(x)D_{lk}(x) \\ &\quad -\alpha\frac{\partial g_{ij}(x)}{\partial x_k}g^\dagger_{jk}(x) + g_{ij}(x^*)\xi_j(t), \end{aligned} \tag{2.103}$$

where we defined $\boldsymbol{D} \equiv \boldsymbol{g}\boldsymbol{g}^\dagger/2$. We assumed that $\boldsymbol{\zeta}\boldsymbol{b}\boldsymbol{b}^\dagger$ is a symmetric matrix. This condition is sufficient to ensure the existence of the overdamp limit. For details see the next section. One dimensional version of (2.103) is identical with [36, 54]. We left the detailed derivation in next section.

2.8 Curved space

In this section we consider the most general case, i.e., multidimensional, non-equilibrium and curved space in α convention. We demonstrate the calculation of overdamp limit in precise since the situation is quite general and the result will be used in Chapter 3.

Model

The underdamped Langevin equation is given by

$$\dot{x}_i = \left(m^{-1}(x)\right)_{ij} p_j, \tag{2.104}$$

$$\dot{p}_i = -\Gamma_{ij}(x)p_j - \frac{\partial H}{\partial x_j} + b_{ij}(x)\xi_j(t) \tag{2.105}$$

where we have defined $\boldsymbol{\Gamma} \equiv \boldsymbol{\zeta}\boldsymbol{m}^{-1}$. The Hamiltonian of the system H is given by

$$H = \frac{1}{2}p_i \left(m^{-1}(x)\right)_{ij} p_j + U(x). \tag{2.106}$$

The x dependence of mass matrix m_{ij} appears as a result of curved geometry of the generalized coordinate. We impose a following condition in order the system to have the overdamp limit.

$$\boldsymbol{\Gamma}^{-1}\boldsymbol{b}\boldsymbol{b}^{\dagger} = \boldsymbol{b}\boldsymbol{b}^{\dagger}\boldsymbol{\Gamma}^{-1,\dagger}. \tag{2.107}$$

As will be discussed later, this relation is a sufficient condition for the Kramers equation for joint probability distribution function for position and momentum to have a stationary solution for momentum.

Expansion by small parameter τ_p and Δt

First we expand $b_{ij}(x(t_2))$ and $\zeta_{ij}(x(t_2))$ around $x^* = \alpha x(t+\Delta t)+(1-\alpha)x(t)$. We make use of an identity for t_2 with $t < t_2 < t + \Delta t$,

$$x(t_2) = x^* - \alpha\left[x(t+\Delta t) - x(t_2)\right] + (1-\alpha)\left[x(t_2) - x(t)\right]. \tag{2.108}$$

Then we can expand $b_{ij}(x(t_2))$ around x^*

$$\begin{aligned} b_{ij}(x(t_2)) &= b_{ij}\left(x^* - \alpha\left[x(t+\Delta t) - x(t_2)\right] + (1-\alpha)\left[x(t_2) - x(t)\right]\right) \\ &= b_{ij}(x^*) - \alpha\frac{\partial b_{ij}}{\partial x_k^*}\left[x_k(t+\Delta t) - x_k(t_2)\right] \\ &\quad +(1-\alpha)\frac{\partial b_{ij}}{\partial x_k^*}\left[x_k(t_2) - x_k(t)\right] + \mathcal{O}(\Delta x^2), \end{aligned} \tag{2.109}$$

Since $x_k(t+\Delta t) - x_k(t_2)$ and $x_k(t_2) - x_k(t)$ are $\mathcal{O}(\Delta x) = \mathcal{O}(\Delta t^{1/2})$, this expansion, (2.109), can be interpreted as the power series expansion with respect to $\Delta t^{1/2}$. Similarly for Γ_{ij} one has

$$\begin{aligned} \Gamma_{ij}(x(t_2)) &= \Gamma_{ij}\left(x^* - \alpha\left[x(t+\Delta t) - x(t_2)\right] + (1-\alpha)\left[x(t_2) - x(t)\right]\right) \\ &= \Gamma_{ij}(x^*) - \alpha\frac{\partial \Gamma_{ij}}{\partial x_k^*}\left[x_k(t+\Delta t) - x_k(t_2)\right] \\ &\quad +(1-\alpha)\frac{\partial \Gamma_{ij}}{\partial x_k^*}\left[x_k(t_2) - x_k(t)\right] + \mathcal{O}(\Delta x^2). \end{aligned} \tag{2.110}$$

Substituting (2.109) and (2.110) into the underdamped Langevin equation (2.105) we have

$$\begin{aligned}\dot{p}_i(t_2) &= -\Gamma_{ij}(x^*)p_i(t_2) + \alpha\frac{\partial\Gamma_{ij}}{\partial x_k^*}\left[x_k(t+\Delta t) - x_k(t_2)\right]p_j(t_2) \\ &\quad -(1-\alpha)\frac{\partial\Gamma_{ij}}{\partial x_k^*}\left[x_k(t_2) - x_k(t)\right]p_j(t_2) - \frac{\partial H}{\partial x_i(t_2)} \\ &\quad +b_{ij}(x^*)\xi_j(t_2) - \alpha\frac{\partial b_{ij}}{\partial x_k^*}\left[x_k(t+\Delta t) - x_k(t_2)\right]\xi_j(t_2) \\ &\quad -(1-\alpha)\frac{\partial b_{ij}}{\partial x_k^*}\left[x_k(t_2) - x_k(t)\right]\xi_j(t_2). \qquad (2.111)\end{aligned}$$

One can solve it formally as

$$\begin{aligned}p_i(t_1) = \int_{-\infty}^{t_1} dt_2 G_{ij}^{12}\Bigg\{&-\frac{\partial H}{\partial x_j(t_2)} + b_{jk}(x^*)\xi_k(t_2) \qquad (2.112)\\ &+\alpha\frac{\partial\Gamma_{jk}}{\partial x_l^*}\left[x_l(t+\Delta t) - x_l(t_2)\right]p_k(t_2) \\ &-(1-\alpha)\frac{\partial\Gamma_{jk}}{\partial x_l^*}\left[x_l(t_2) - x_l(t)\right]p_k(t_2) \\ &-\alpha\frac{\partial b_{jk}}{\partial x_l^*}\left[x_l(t+\Delta t) - x_l(t_2)\right]\xi_k(t_2) \\ &+(1-\alpha)\frac{\partial b_{jk}}{\partial x_l^*}\left[x_l(t_2) - x_l(t)\right]\xi_k(t_2)\Bigg\},\end{aligned}$$

where the propagator G_{ij}^{12} is defined as

$$G_{ij}^{12} \equiv \left\{\exp\left[-\Gamma(x^*)(t_1 - t_2)\right]\right\}_{ij}. \qquad (2.113)$$

One can obtain the overdamp limit by discretizing the formal solution (2.112) as $\Delta x_i = x_i(t+\Delta t) - x_i(t)$ with $\Delta t \gg \Gamma^{-1}$,

$$\begin{aligned}
\Delta x_i = \int_t^{t+\Delta t} dt_1 \left(m^{-1}\right)_{ij}(x(t_1)) \int_{-\infty}^{t_1} dt_2 G^{12}_{jk} \\
\times \Bigg\{ -\frac{\partial H}{\partial x_k(t_2)} + b_{kl}(x^*)\xi_l(t_2) \\
+ \alpha \frac{\partial \Gamma_{kl}}{\partial x^*_m}\left[x_m(t+\Delta t) - x_m(t_2)\right] p_l(t_2) \\
- (1-\alpha)\frac{\partial \Gamma_{kl}}{\partial x^*_m}\left[x_m(t_2) - x_m(t)\right] p_l(t_2) \\
- \alpha \frac{\partial b_{kl}}{\partial x^*_m}\left[x_m(t+\Delta t) - x_m(t_2)\right] \xi_l(t_2) \\
+ (1-\alpha)\frac{\partial b_{kl}}{\partial x^*_m}\left[x_m(t_2) - x_m(t)\right] \xi_l(t_2) \Bigg\}. \qquad (2.114)
\end{aligned}$$

Since we are working on a curved coordinate the mass matrix is dependent of x. Thus we have to expand $\left(m^{-1}\right)_{ij}(x(t_1))$ in the first line of the RHS of (2.114) around x^* as

$$\begin{aligned}
\left(m^{-1}\right)_{ij}(x(t_1)) &= \left(m^{-1}\right)_{ij}(x^* - \alpha\left[x(t+\Delta t) - x(t_1)\right] + (1-\alpha)\left[x(t_1) - x(t)\right]) \\
&= \left(m^{-1}\right)_{ij}(x^*) - \alpha \frac{\partial m^{-1}_{ij}}{\partial x^*_k}\left[x_k(t+\Delta t) - x_k(t_1)\right] \\
&\quad + (1-\alpha)\frac{\partial m^{-1}_{ij}}{\partial x^*_k}\left[x_k(t_1) - x_k(t)\right] + \mathcal{O}(\tau_p^2), \qquad (2.115)
\end{aligned}$$

Recalling that the multiplicative noise is of $\mathcal{O}(\Delta t^{1/2})$ and others are of $\mathcal{O}(\Delta t)$, the leading contribution in the RHS of (2.114) comes from the second term in $\{\cdots\}$ of (2.114).

$$\begin{aligned}
\Delta x_i = \left(m^{-1}\right)_{ij}(x^*) \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G^{12}_{jk}\left[-\frac{\partial H}{\partial x_k(t_2)} + b_{kl}(x^*)\xi_l(t_2)\right] \\
+ \alpha I_i^{\zeta,\mathrm{aI}} + (1-\alpha) I_i^{\zeta,\mathrm{Ito}} + \alpha I_i^{b,\mathrm{aI}} + (1-\alpha) I_i^{b,\mathrm{Ito}} \\
+ \alpha I_i^{m,\mathrm{aI}} + (1-\alpha) I_i^{m,\mathrm{Ito}}, \qquad (2.116)
\end{aligned}$$

where I s are defined by

$$I_i^{\zeta,\mathrm{aI}} \equiv \left(m^{-1}\right)_{ij}(x^*)\frac{\partial \Gamma_{kl}}{\partial x^*_m}\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G^{12}_{jk}\left[x_m(t+\Delta t) - x_m(t_2)\right] p_l(t_2), \qquad (2.117)$$

$$I_i^{\zeta,\mathrm{Ito}} \equiv -\left(m^{-1}\right)_{ij}(x^*)\frac{\partial \Gamma_{kl}}{\partial x_m^*}\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G_{jk}^{12}\left[x_m(t_2)-x_m(t)\right] p_l(t_2), \tag{2.118}$$

$$I_i^{b,\mathrm{aI}} \equiv -\left(m^{-1}\right)_{ij}(x^*)\frac{\partial b_{kl}}{\partial x_m^*}\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G_{jk}^{12}\left[x_m(t+\Delta t)-x_m(t_2)\right] \xi_l(t_2), \tag{2.119}$$

$$I_i^{b,\mathrm{Ito}} \equiv \left(m^{-1}\right)_{ij}(x^*)\frac{\partial b_{kl}}{\partial x_m^*}\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G_{jk}^{12}\left[x_m(t_2)-x_m(t)\right] \xi_l(t_2), \tag{2.120}$$

$$I_i^{m,\mathrm{aI}} \equiv -\frac{\partial \left(m^{-1}\right)_{ij}}{\partial x_m^*}\int_t^{t+\Delta t} dt_1 \left[x_m(t+\Delta t)-x_m(t_1)\right] \int_{-\infty}^{t_1} dt_2 G_{jk}^{12} b_{kl}(x^*)\xi_l(t_2), \tag{2.121}$$

$$I_i^{m,\mathrm{Ito}} \equiv \frac{\partial \left(m^{-1}\right)_{ij}}{\partial x_m^*}\int_t^{t+\Delta t} dt_1 \left[x_m(t_1)-x_m(t)\right] \int_{-\infty}^{t_1} dt_2 G_{jk}^{12} b_{kl}(x^*)\xi_l(t_2). \tag{2.122}$$

These corrections are calculated by substituting $x_m(t+\Delta t)-x_m(t_2)$, $p_l(t_2)$ and $x_m(t_2)-x_m(t)$ in the lowest order in Δt, obtained by the formal solution (2.112) as

$$p_l(t_2) = b_{no}(x^*)\int_{-\infty}^{t_2} dt_3 G_{ln}^{23}\xi_o(t_3), \tag{2.123}$$

$$x_m(t+\Delta t)-x_m(t_2) = \left(m^{-1}\right)_{mp}(x^*) b_{qr}(x^*)\int_{t_2}^{t+\Delta t} dt_4 \int_{-\infty}^{t_4} dt_5 G_{pq}^{45}\xi_r(t_5), \tag{2.124}$$

$$x_m(t_2)-x_m(t) = \left(m^{-1}\right)_{mp}(x^*) b_{qr}(x^*)\int_{t}^{t_2} dt_4 \int_{-\infty}^{t_4} dt_5 G_{pq}^{45}\xi_r(t_5), \tag{2.125}$$

Calculation of corrections

In this subsection we perform calculation of corrections appeared in (2.117)–(2.122).

First, $I_i^{\zeta,\mathrm{Ito}}$ defined in (2.118) is evaluated by substituting (2.123) and (2.125) for $p_l(t_2)$ and $x_m(t_2)-x_m(t)$, yielding

$$\begin{aligned} I_i^{\zeta,\mathrm{Ito}} &= -\left(m^{-1}\right)_{ij}\frac{\partial \Gamma_{kl}}{\partial x_m}\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G_{jk}^{12} \\ &\quad \times \int_t^{t_2} dt_3 \int_{-\infty}^{t_3} dt_4 \left(m^{-1}\right)_{mp} G_{pq}^{34} b_{qr}\xi_r(t_4) \\ &\quad \times \int_{-\infty}^{t_2} dt_5 G_{ln}^{25} b_{no}\xi_o(t_5). \end{aligned} \tag{2.126}$$

Here quantities without time argument is evaluated at $x^* = \alpha x(t+\Delta t)+(1-\alpha)x(t)$. The quadratic term in the Gaussian white noise ξ can be replaced by its average according to (2.37). This replacement is correct in the mean square sense. In other words, the Fokker-Planck equation is not affected by this manipulation. Then,

$$\begin{aligned} I_i^{\zeta,\mathrm{Ito}} &= -\left(m^{-1}\right)_{ij} \frac{\partial \Gamma_{kl}}{\partial x_m} \left(m^{-1}\right)_{mp} \left(\boldsymbol{b}\boldsymbol{b}^\dagger\right)_{qn} \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G_{jk}^{12} \\ &\quad \times \int_t^{t_2} dt_3 \int_{-\infty}^{t_3} dt_4 G_{ln}^{24} G_{pq}^{34}. \end{aligned} \tag{2.127}$$

We split and exchange order of the double integral on t_3 and t_3 as

$$\int_t^{t_2} dt_3 \int_{-\infty}^{t_3} dt_4 = \int_t^{t_2} dt_4 \int_{t_4}^{t_2} dt_3 + \int_t^{t_2} dt_3 \int_{-\infty}^{t} dt_4. \tag{2.128}$$

We can ignore the contribution from the second term in the RHS of (2.128)since it is $\tau_p^{1/2}$ times smaller than the first term [33]. One can carry out the dt_3 integral as

$$\int_{t_4}^{t_2} dt_3 G_{pq}^{34} = \left[\boldsymbol{\Gamma} - \boldsymbol{\Gamma}\mathrm{e}^{-\boldsymbol{\Gamma}(t_2-t_4)}\right]_{pq}. \tag{2.129}$$

Substituting (2.129) into (2.127) and changing the variable from t_4 to $t_6 = t_2 - t_4$ reads

$$\begin{aligned} I_i^{\zeta,\mathrm{Ito}} &= -\left(m^{-1}\right)_{ij} \frac{\partial \Gamma_{kl}}{\partial x_m} \left(m^{-1}\right)_{mp} \left(\boldsymbol{b}\boldsymbol{b}^\dagger\right)_{qn} \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G_{jk}^{12} \\ &\quad \times \int_0^{\infty} dt_6 \left[e^{-\Gamma t_6}\right]_{ln} \left[\boldsymbol{\Gamma} - \boldsymbol{\Gamma}\mathrm{e}^{-\boldsymbol{\Gamma}t_6}\right]_{pq}. \end{aligned} \tag{2.130}$$

The second line is handled by the integration by parts as

$$\begin{aligned} \int_0^{\infty} dt_6 \left[e^{-\Gamma t_6}\right]_{ln} \left[\boldsymbol{\Gamma} - \boldsymbol{\Gamma}\mathrm{e}^{-\boldsymbol{\Gamma}t_6}\right]_{pq} &= -\left[\left[\boldsymbol{\Gamma}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}t_6}\right]_{ln} \left[\boldsymbol{\Gamma}^{-1} - \boldsymbol{\Gamma}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}t_6}\right]_{pq}\right]_{t_6=0}^{\infty} \\ &\quad + \int_0^{\infty} dt_6 \left[\boldsymbol{\Gamma}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}t_6}\right]_{ln} \left[\mathrm{e}^{-\boldsymbol{\Gamma}t_6}\right]_{pq} \\ &= \int_0^{\infty} dt_6 \left[\boldsymbol{\Gamma}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}t_6}\right]_{ln} \left[\mathrm{e}^{-\boldsymbol{\Gamma}t_6}\right]_{pq}. \end{aligned} \tag{2.131}$$

Here we ignored the surface term since it is $\tau_p^{1/2}$ times smaller than others. Then (2.130) is

$$\begin{aligned} I_i^{\zeta,\mathrm{Ito}} &= -\left(m^{-1}\right)_{ij} \frac{\partial \Gamma_{kl}}{\partial x_m} \left(m^{-1}\right)_{mp} \left(\boldsymbol{b}\boldsymbol{b}^\dagger\right)_{qn} \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G_{jk}^{12} \\ &\quad \times \int_0^{\infty} dt_6 \left[\boldsymbol{\Gamma}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}t_6}\right]_{ln} \left[\mathrm{e}^{-\boldsymbol{\Gamma}t_6}\right]_{pq}. \end{aligned} \tag{2.132}$$

One can perform the integral over t_1 and t_2 since the second line is independent of them. We ignore $-\infty < t_2 < t$ in dt_2 integral since it is $\tau_p^{1/2}$ time smaller than other contributions and make use of exchange of the double integral by using (2.26). Then,

$$\begin{aligned}\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G_{jk}^{12} &\cong \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_2 G_{jk}^{12} \\ &= \int_t^{t+\Delta t} dt_2 \int_{t_2}^{t+\Delta t} dt_1 G_{jk}^{12} \\ &= \int_t^{t+\Delta t} dt_2 \left[\mathbf{\Gamma}^{-1} - \mathbf{\Gamma}^{-1} \mathrm{e}^{-\mathbf{\Gamma}(t+\Delta t - t_2)}\right]_{jk} \\ &\cong \left(\Gamma^{-1}\right)_{jk} \Delta t. \end{aligned} \tag{2.133}$$

Applying (2.133) to (2.132) one arrives at

$$I^{\zeta,\mathrm{Ito}} = -\left(\zeta^{-1}\right)_{ij} \frac{\partial \Gamma_{jk}}{\partial x_l} m_{km} D_{ml} \Delta t, \tag{2.134}$$

where $\boldsymbol{D}$ is defined as

$$\boldsymbol{D} \equiv \int_0^\infty dt_6 \boldsymbol{\zeta}^{-1} \mathrm{e}^{-\mathbf{\Gamma} t_6} \boldsymbol{b}\boldsymbol{b}^\dagger \mathrm{e}^{-\mathbf{\Gamma}^\dagger t_6} \boldsymbol{m}^{-1}. \tag{2.135}$$

$\boldsymbol{D}$ plays a role of diffusion coefficient in equilibrium, since the FDT, $\boldsymbol{b}\boldsymbol{b}^\dagger = 2k_B T \boldsymbol{\zeta}$, leads to the Einstein relation $\boldsymbol{D} = k_B T \boldsymbol{\zeta}^{-1}$. We postpone to calculate the integral in $\boldsymbol{D}$ and proceed to calculate other corrections.

We next calculate $I_i^{m,\mathrm{Ito}}$ defined in (2.122). By substituting (2.125) for $x_m(t_1) - x_m(t)$,

$$\begin{aligned} I_i^{m,\mathrm{Ito}} &= \frac{\partial \left(m^{-1}\right)_{ij}}{\partial x_m} \int_t^{t+\Delta t} dt_1 \left(m^{-1}\right)_{mp} \int_t^{t_1} dt_3 \int_{-\infty}^{t_3} dt_4 G_{pq}^{34} b_{qr} \xi_r(t_4) \\ &\quad \times \int_{-\infty}^{t_1} dt_2 G_{jk}^{12} b_{kl} \xi_l(t_2). \end{aligned} \tag{2.136}$$

In the mean square sense,

$$I_i^{m,\mathrm{Ito}} = \frac{\partial \left(m^{-1}\right)_{ij}}{\partial x_m} \int_t^{t+\Delta t} dt_1 \left(m^{-1}\right)_{mp} \int_t^{t_1} dt_3 \int_{-\infty}^{t_3} dt_4 G_{pq}^{34} b_{ql} G_{jk}^{14} b_{kl}. \tag{2.137}$$

We ignore the contribution from $-\infty < t_4 < t$ in the integral over t_4 and change the order of the integral on t_3 and t_4 according to (2.128),

$$I^{m,\mathrm{Ito}} = \frac{\partial \left(m^{-1}\right)_{ij}}{\partial x_m} \left(m^{-1}\right)_{mp} \left(\boldsymbol{b}\boldsymbol{b}^\dagger\right)_{qk} \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_4 G_{jk}^{14} \int_{t_4}^{t_1} dt_3 G_{pq}^{34}. \tag{2.138}$$

Now we can carry out the integral over t_3.

$$I_i^{m,\mathrm{Ito}} = \frac{\partial \left(m^{-1}\right)_{ij}}{\partial x_m} \left(m^{-1}\right)_{mp} \left(\boldsymbol{b}\boldsymbol{b}^\dagger\right)_{qk} \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_4 G_{jk}^{14} \times \left[\boldsymbol{\Gamma}^{-1} - \boldsymbol{\Gamma}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}(t_1-t_4)}\right]_{pq}. \tag{2.139}$$

Change of variable from t_4 to $t_5 = t_1 - t_4$ and the integration by parts gives

$$\begin{aligned} I_i^{m,\mathrm{Ito}} &= \frac{\partial \left(m^{-1}\right)_{ij}}{\partial x_m} \left(m^{-1}\right)_{mp} \left(\boldsymbol{b}\boldsymbol{b}^\dagger\right)_{qk} \int_t^{t+\Delta t} dt_1 \int_0^{\infty} dt_5 \left[\boldsymbol{\Gamma}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}t_5}\right]_{jk} \left[\mathrm{e}^{-\boldsymbol{\Gamma}t_5}\right]_{pq} \\ &= \frac{\partial \left(m^{-1}\right)_{ij}}{\partial x_k} m_{jl} D_{lk} \Delta t. \end{aligned} \tag{2.140}$$

$I^{b,\mathrm{Ito}}$ defined in (2.120) vanishes as usual.

$$I^{b,\mathrm{Ito}} = 0. \tag{2.141}$$

The anti-Ito corrections given in (2.117), (2.119) and (2.121) are computed in almost the same way as others. First $I^{\zeta,\mathrm{aI}}$ is, using (2.124) and (2.123),

$$\begin{aligned} I^{\zeta,\mathrm{aI}} &= \left(m^{-1}\right)_{ij} \frac{\partial \Gamma_{kl}}{\partial x_m} \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G_{jk}^{12} \\ &\quad \times \int_{t_2}^{t+\Delta t} dt_3 \left(m^{-1}\right)_{mn} \int_{-\infty}^{t_3} dt_4 G_{no}^{34} b_{op} \xi_p(t_4) \int_{-\infty}^{t_2} dt_5 G_{lq}^{25} b_{qr} \xi_r(t_5). \end{aligned} \tag{2.142}$$

The mean square calculation leads to

$$\begin{aligned} I^{\zeta,\mathrm{aI}} &= \left(m^{-1}\right)_{ij} \frac{\partial \Gamma_{kl}}{\partial x_m} \left(m^{-1}\right)_{mn} \left(\boldsymbol{b}\boldsymbol{b}^\dagger\right)_{oq} \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G_{jk}^{12} \\ &\quad \times \int_{t_2}^{t+\Delta t} dt_3 \int_{-\infty}^{t_2} dt_5 G_{no}^{35} G_{lq}^{25}. \end{aligned} \tag{2.143}$$

The integral over t_3 is carried out as

$$\begin{aligned} \int_{t_2}^{t+\Delta t} dt_3 \boldsymbol{G}^{35} &= -\boldsymbol{\Gamma}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}(t+\Delta t-t_5)} + \boldsymbol{\Gamma}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}(t_2-t_5)} \\ &= \boldsymbol{\Gamma}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}(t_2-t_5)}. \end{aligned} \tag{2.144}$$

From the first and second line of (2.144) we used the fact that $\mathrm{e}^{-\boldsymbol{\Gamma}(t+\Delta t-t_5)}$ is exponentially small and negligible in the overdamp limit. Plugging (2.144) with (2.143) and performing change of variable $t_6 = t_2 - t_5$ one has

$$I^{\zeta,\mathrm{aI}} = \left(m^{-1}\right)_{ij} \frac{\partial \Gamma_{kl}}{\partial x_m} \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G_{jk}^{12} \left[\int_0^{\infty} dt_6 \boldsymbol{\zeta}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}t_6} \boldsymbol{b}\boldsymbol{b}^\dagger \mathrm{e}^{-\boldsymbol{\Gamma}^\dagger t_6}\right]_{ml} \tag{2.145}$$

since $[\cdots]$ is independent of t_1 and t_2 one can carry out the double integral over t_1 and t_2. Thus applying (2.133) to (2.145) and using the definition of $\boldsymbol{D}$ given in (2.135) one arrives at

$$\begin{aligned} I_i^{\zeta,\mathrm{aI}} &= \left(m^{-1}\right)_{ij}\left(\Gamma^{-1}\right)_{jk}\frac{\partial\Gamma_{kl}}{\partial x_m}\left(\boldsymbol{Dm}\right)_{ml}\Delta t \\ &= L_{ij}\frac{\partial\Gamma_{jk}}{\partial x_l}m_{km}D_{ml}\Delta t. \end{aligned} \tag{2.146}$$

Next we compute $I^{b,\mathrm{aI}}$ defined in (2.121). By using (2.124) for $x_m(t+\Delta t)-x_m(t_2)$

$$\begin{aligned} I^{b,\mathrm{aI}} &= -\left(m^{-1}\right)_{ij}\frac{\partial b_{kl}}{\partial x_m}\int_t^{t+\Delta t}dt_1\int_{-\infty}^{t_1}dt_2 G_{jk}^{12} \\ &\quad\times\int_{t_2}^{t+\Delta t}dt_3\left(m^{-1}\right)_{mn}\int_{-\infty}^{t_3}dt_4 G_{no}^{34}b_{op}\xi_p(t_4)\xi_l(t_2) \\ &= -\left(m^{-1}\right)_{ij}\frac{\partial b_{kl}}{\partial x_m}\int_t^{t+\Delta t}dt_1\int_{-\infty}^{t_1}dt_2 G_{jk}^{12}\int_{t_2}^{t+\Delta t}dt_3\left(m^{-1}\right)_{mn}G_{no}^{32}b_{ol} \\ &= -\left(m^{-1}\right)_{ij}\frac{\partial b_{kl}}{\partial x_m}\left(m^{-1}\right)_{mn}b_{ol}\int_t^{t+\Delta t}dt_1\int_{-\infty}^{t_1}dt_2 G_{jk}^{12}\int_0^{\infty}dt_5\mathrm{e}_{no}^{-\Gamma t_5}. \end{aligned} \tag{2.147}$$

Here we introduced $t_5=t_3-t_2$. Again the double integral on t_1 and t_2 can be carried out as (2.133). Then

$$I^{b,\mathrm{aI}} = -\left(\zeta^{-1}\right)_{ik}\frac{\partial b_{kl}}{\partial x_m}\left(m^{-1}\right)_{mn}b_{ol}\left(\Gamma^{-1}\right)_{no}\Delta t = -L_{ij}\frac{\partial b_{jk}}{\partial x_l}L_{lm}b_{mk}\Delta t. \tag{2.148}$$

Finally $I^{m,\mathrm{aI}}$ defined in (2.121) becomes by using (2.124),

$$\begin{aligned} I^{m,\mathrm{aI}} &= -\frac{\partial\left(m^{-1}\right)_{ij}}{\partial x_m}\int_t^{t+\Delta t}dt_1 m_{mp}^{-1}b_{qr}\int_{t_1}^{t+\Delta t}dt_4\int_{-\infty}^{t_4}dt_5 G_{pq}^{45}\xi_r(t_5) \\ &\quad\times\int_{-\infty}^{t_1}dt_2 G_{jk}^{12}b_{kl}\xi_l(t_2) \\ &= -\frac{\partial\left(m^{-1}\right)_{ij}}{\partial x_m}\int_t^{t+\Delta t}dt_1 m_{mp}^{-1}b_{ql}\int_{t_1}^{t+\Delta t}dt_4\int_{-\infty}^{t_1}dt_2 G_{jk}^{12}G_{pq}^{42}b_{kl}, \end{aligned} \tag{2.149}$$

by the mean square calculation. The integral on t_4 is carried out as (2.144),

$$\int_{t_1}^{t+\Delta t}dt_4\boldsymbol{G}^{42}\cong\boldsymbol{\Gamma}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}(t_1-t_2)}. \tag{2.150}$$

Then

$$I^{m,\mathrm{aI}} = -\frac{\partial\left(m^{-1}\right)_{ij}}{\partial x_m}\left(m^{-1}\right)_{mp} b_{ql}b_{kl}\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G^{12}_{jk}\left[\mathbf{\Gamma}^{-1}\mathrm{e}^{-\mathbf{\Gamma}(t_1-t_2)}\right]_{pq}$$
$$= -\frac{\partial\left(m^{-1}\right)_{ij}}{\partial x_k}\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\mathbf{\Gamma}(t_1-t_2)}\boldsymbol{bb}^\dagger \mathrm{e}^{-\mathbf{\Gamma}^\dagger(t_1-t_2)}\boldsymbol{\zeta}^{-1}\right]_{kj}. \quad (2.151)$$

Here by changing variable t_2 into $t_3 = t_1 - t_2$ again there appears $\boldsymbol{D}$.

$$I^{m,\mathrm{aI}} = -\frac{\partial\left(m^{-1}\right)_{ij}}{\partial x_k}\left(\boldsymbol{mD}\right)_{jk}\Delta t = -I_i^{m,\mathrm{Ito}}. \quad (2.152)$$

We have yet another correction due to the position dependence of the mass matrix. It enters in $-\frac{\partial H}{\partial x_k(t_2)}$ in the RHS of (2.116). It contributes to Δx_i as

$$\Delta U \equiv -\left(m^{-1}\right)_{ij}(x^*)\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G^{12}_{jk} p_l(t_2)\frac{\partial m^{-1}_{lm}}{\partial x_k}p_m(t_2), \quad (2.153)$$

By substituting (2.123) for ps we have

$$\Delta U = -L_{ij}\frac{\partial\left(m^{-1}\right)_{kl}}{\partial x_j}\left(\boldsymbol{bb}^\dagger\right)_{np}\int_0^\infty dt_5 \left[\mathrm{e}^{-\mathbf{\Gamma}t_5}\right]_{kn}\left[\mathrm{e}^{-\mathbf{\Gamma}t_5}\right]_{lp}\Delta t$$
$$= -\frac{1}{2}L_{ij}\frac{\partial\left(m^{-1}\right)_{kl}}{\partial x_j}\left[\boldsymbol{\zeta D m}\right]_{kl}. \quad (2.154)$$

In equilibrium FDT (or Einstein relation) : $\boldsymbol{\zeta D} = k_B T$ yields

$$\Delta U = \frac{1}{2}k_B T L_{ij}\frac{\partial}{\partial x_j}\ln\det m\Delta t. \quad (2.155)$$

Gathering the corrections

Now all the preparation has done to calculate the corrections appeared in (2.116). Let us first show how part of I^ζ and I^m cancel. by using (2.134), (2.140) and $\mathbf{\Gamma} = \boldsymbol{\zeta m}^{-1}$,

$$\begin{aligned} I_i^{\zeta,\mathrm{Ito}} + I_i^{m,\mathrm{Ito}} &= -L_{ij}\frac{\partial\Gamma_{jk}}{\partial x_l}\left(\boldsymbol{mD}\right)_{kl}\Delta t + \frac{\partial\left(m^{-1}\right)_{ij}}{\partial x_k}\left(\boldsymbol{mD}\right)_{jk}\Delta t \\ &= -L_{ij}\left(\frac{\partial\zeta_{jm}}{\partial x_l}\left(m^{-1}\right)_{mk} + \zeta_{jm}\frac{\partial\left(m^{-1}\right)_{mk}}{\partial x_l}\right)\left(\boldsymbol{mD}\right)_{kl}\Delta t \\ &\quad + \frac{\partial\left(m^{-1}\right)_{ij}}{\partial x_k}\left(\boldsymbol{mD}\right)_{jk}\Delta t \\ &= -L_{ij}\frac{\partial\zeta_{jm}}{\partial x_l}D_{ml}\Delta t = \frac{\partial L_{ij}}{\partial x_k}\left(\boldsymbol{\zeta D}\right)_{jk}\Delta t. \end{aligned} \quad (2.156)$$

Since $I_i^{\zeta,\mathrm{aI}}$ and $I_i^{m,\mathrm{aI}}$ is same as their Ito counterpart aside from signs, one has

$$I_i^{\zeta,\mathrm{aI}} + I_i^{m,\mathrm{aI}} = -\frac{\partial L_{ij}}{\partial x_k} \left(\boldsymbol{\zeta D}\right)_{jk} \Delta t. \tag{2.157}$$

Then plugging (2.156), (2.157), (2.148) and (2.141), one obtains the correction terms in (2.116)

$$\begin{aligned} &\alpha I_i^{\zeta,\mathrm{aI}} + (1-\alpha) I_i^{\zeta,\mathrm{Ito}} + \alpha I_i^{b,\mathrm{aI}} + (1-\alpha) I_i^{b,\mathrm{Ito}} + \alpha I_i^{m,\mathrm{aI}} + (1-\alpha) I_i^{m,\mathrm{Ito}} \\ &\qquad = (1-2\alpha) \frac{\partial L_{ij}}{\partial x_k} \left(\boldsymbol{\zeta D}\right)_{jk} \Delta t - \alpha L_{ij} \frac{\partial b_{jk}}{\partial x_l} \left(\boldsymbol{b}^\dagger \boldsymbol{L}^\dagger\right)_{kl} \Delta t \\ &= \frac{\partial L_{ij}}{\partial x_k} \left(\boldsymbol{\zeta D}\right)_{jk} \Delta t - \alpha \left[2 \frac{\partial L_{ij}}{\partial x_k} \left(\boldsymbol{\zeta D}\right)_{jk} + L_{ij} \frac{\partial b_{jk}}{\partial x_l} \left(\boldsymbol{b}^\dagger \boldsymbol{L}^\dagger\right)_{kl} \right] \Delta t. \end{aligned} \tag{2.158}$$

Contribution from the first term in the RHS of (2.116) becomes the multiplicative noise interpreted in α convention.

$$\left(m^{-1}\right)_{ij} (x^*) \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 G_{jk}^{12} b_{kl}(x^*) \xi_l(t_2) = g_{ij}(x^*) \Delta W_j. \tag{2.159}$$

This can be proven as follows. First we separate and change the order of double integral in the LHS of (2.159) as

$$\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 = \int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t} dt_2 + \int_t^{t+\Delta t} dt_2 \int_{t_2}^{t+\Delta t} dt_1. \tag{2.160}$$

Contribution from the first term in the RHS of (2.160) is approximately $\tau_p^{1/2}$ times smaller than that of second term and thus we can safely ignore it [33]. While for second term one can perform dt_1 integral and obtain

$$(\text{LHS of (2.159)}) = m_{ij}^{-1} b_{kl} \Gamma_{jm}^{-1} \int_t^{t+\Delta t} dt_2 \left[\delta - \mathrm{e}^{-\Gamma(t+\Delta t - t_2)}\right]_{mk} \xi_l(t_2), \tag{2.161}$$

here δ is Kronecker delta. Since we are concerned with the overdamp limit where Γ^{-1} is smaller than any other time scale $\mathrm{e}^{-\Gamma(t+\Delta t-t_2)}$ vanishes for almost all t_2 in integral range, except at the endpoint $t_2 = t + \Delta t$. Thus we can approximate

$$\delta - \mathrm{e}^{-\Gamma(t+\Delta t-t_2)} = \begin{cases} \delta & t_2 \neq t + \Delta t, \\ 0 & t_2 = t + \Delta t. \end{cases} \tag{2.162}$$

Then (2.161) is

$$\begin{aligned} m_{ij}^{-1} b_{kl} \Gamma_{jm}^{-1} \int_t^{t+\Delta t} dt_2 \left[\delta - \mathrm{e}^{-\Gamma(t+\Delta t-t_2)}\right]_{mk} \xi_l(t_2) &= L_{ij}(x^*) b_{jk}(x^*) \int_t^{t+\Delta t-0} dt_2 \xi_k(t_2) \\ &= g_{ij}(x^*) \left(W_{j,t+\Delta t-0} - W_{j,t}\right), \end{aligned} \tag{2.163}$$

here $t+\Delta t-0$ in the endpoint of integral means that the endpoint is excluded from integral. But this does not play any role in overdamp limit and we can write simply

$$g_{ij}(x^*)\left(W_{j,t+\Delta t}-W_{j,t}\right)=g_{ij}(x^*)\Delta W_j, \tag{2.164}$$

which is (2.159).

Now Let us consider the integral in the definition of $\boldsymbol{D}$ given in (2.135). Integration by part shows that

$$\boldsymbol{D}=\boldsymbol{g}\boldsymbol{g}^\dagger-\boldsymbol{D}^\dagger. \tag{2.165}$$

It is tempting to assume that $\boldsymbol{D}$ is symmetric and have

$$\boldsymbol{D}\stackrel{?}{=}\frac{1}{2}\boldsymbol{g}\boldsymbol{g}^\dagger, \tag{2.166}$$

since such term arises in the heuristic argument, presented in Appendix B.3. Also in equilibrium the FDT leads the Einstein relation $\boldsymbol{D}=k_BT\boldsymbol{L}$, which is symmetric. But it is clear that $\boldsymbol{D}$ is not symmetric by definition (2.135). This fact is essential in computation of the energy shift term (2.154).

$$[\boldsymbol{\zeta}\boldsymbol{D}\boldsymbol{m}]_{ij}=\int_0^\infty dt\left[\mathrm{e}^{-\boldsymbol{\Gamma}t}\boldsymbol{b}\boldsymbol{b}^\dagger\mathrm{e}^{-\boldsymbol{\Gamma}^\dagger t}\right]_{ij}=p_ip_j, \tag{2.167}$$

is symmetric as it should be since p_ip_j is symmetric matrix. It is also worth noting that (2.165) can be written as

$$\boldsymbol{D}+\boldsymbol{D}^\dagger=\boldsymbol{g}\boldsymbol{g}^\dagger. \tag{2.168}$$

Thus information on anti-symmetric part of $\boldsymbol{D}$ is lost in this relationship. The anti-symmetric part of $\boldsymbol{D}$, which vanishes in equilibrium might be able to characterize the degree of non-equilibrium. Let us split $\boldsymbol{D}$ into symmetric and anti-symmetric part by using following identity;

$$\begin{aligned}\boldsymbol{D} &= \frac{\boldsymbol{D}+\boldsymbol{D}^\dagger}{2}+\frac{\boldsymbol{D}-\boldsymbol{D}^\dagger}{2}\\ &\equiv \frac{\boldsymbol{g}\boldsymbol{g}^\dagger}{2}+\boldsymbol{D}^{\mathrm{as}}.\end{aligned} \tag{2.169}$$

here superscript "as" stands for anti-symmetric part of $\boldsymbol{D}$. This expression marks clear difference from $\boldsymbol{D}$ defined in the heuristic argument (B.55).

The second term in the RHS of (2.158), which is proportional to α, must cancel with the average of the multiplicative noise $\langle g_{ij}(x^*)\Delta W_j\rangle=$

$\alpha\frac{\partial g_{ij}}{\partial x_k}g^\dagger_{jk}\Delta t$. To see more precisely we use the decomposition of $\boldsymbol{D}$ (2.169). The terms proportional to α in the RHS of (2.158) become,

$$\begin{aligned}2\frac{\partial L_{ij}}{\partial x_k}\left(\boldsymbol{\zeta D}\right)_{jk}+L_{ij}\frac{\partial b_{jk}}{\partial x_l}\left(\boldsymbol{b}^\dagger\boldsymbol{L}^\dagger\right)_{kl}=&\frac{\partial L_{ij}}{\partial x_k}\left(\boldsymbol{\zeta g g}^\dagger\right)_{jk}+2\frac{\partial L_{ij}}{\partial x_k}\left(\boldsymbol{\zeta D}^{\rm as}\right)_{jk}\\&+L_{ij}\frac{\partial b_{jk}}{\partial x_l}g^\dagger_{kl}\\=&\frac{\partial g_{ij}}{\partial x_k}g^\dagger_{jk}+2\frac{\partial L_{ij}}{\partial x_k}\left(\boldsymbol{\zeta D}^{\rm as}\right)_{jk}.\end{aligned}\tag{2.170}$$

besides desirable first term, which cancels with $\langle g_{ij}(x^*)\xi_j\rangle$, we find that mysterious second term remains.

By applying (2.170), (2.154) and (2.159) to (2.116), the overdamped Langevin equation is given by

$$\begin{aligned}\dot{x}_i\;=\;&-L_{ij}\frac{\partial U}{\partial x_j}-L_{ij}\frac{\partial\left(m^{-1}\right)_{kl}}{\partial x_j}\left(\boldsymbol{\zeta D m}\right)_{kl}+g_{ij}(x^*)\xi_j\\&+\frac{\partial L_{ij}}{\partial x_k}\left(\boldsymbol{\zeta D}\right)_{jk}-\alpha\left[\frac{\partial g_{ij}}{\partial x_k}g^\dagger_{jk}+2\frac{\partial L_{ij}}{\partial x_k}\left(\boldsymbol{\zeta D}^{\rm as}\right)_{jk}\right].\end{aligned}\tag{2.171}$$

Now we faced two problems.

1. The Ito drift $\frac{\partial L_{ij}}{\partial x_k}\left(\boldsymbol{\zeta D}\right)_{jk}$ is different from that obtained by the heuristic argument. It was $\frac{\partial L_{ij}}{\partial x_k}\left(\boldsymbol{\zeta D}^{\rm s}\right)_{jk}$ with $\boldsymbol{D}^{\rm s}$ being symmetric part of $\boldsymbol{D}$.

2. Spurious correction $2\frac{\partial L_{ij}}{\partial x_k}\left(\boldsymbol{\zeta D}^{\rm as}\right)_{jk}$ appeared in the second term of $[\cdots]$ in the RHS of (2.171). This is more serious problem since term proportional to α must cancels with the average of the multiplicative noise $\langle g_{ij}(x^*)\xi_j\rangle=\alpha\frac{\partial g_{ij}}{\partial x_k}g^\dagger_{jk}$ so that the dependence on α in solution of the Langevin equation is avoided.

These difficulties on taking the overdamp limit without invoking FDT implies that we need to require a condition to the underdamped Langevin equation (B.51). Indeed, the momentum must relax to some stationary distribution, to ensure the existence of the overdamp limit in the case of the adiabatic elimination by means of Fokker-Planck equation. To understand this more clearly let us write down the Kramers equation for joint probability density $\Phi(X,P,t)\equiv\sum_{i=1}^N\langle\delta(X_i-x_i(t))\delta(P_i-p_i(t))\rangle$ for (2.104) and (2.105).

$$\frac{\partial\Phi(x,p,t)}{\partial t}=-\left\{H,\Phi\right\}+\zeta_{ij}(x)\left(p_j+B_{jk}(x)\frac{\partial}{\partial p_k}\right)\Phi,\tag{2.172}$$

where $B_{jk} \equiv \left(\boldsymbol{\Gamma}^{-1}\boldsymbol{b}\boldsymbol{b}^{\dagger}\right)_{jk}/2$ and $\{\cdot,\cdot\}$ is the Poisson bracket. In 1 dimension there is always 0 eigenfunction for operator $p+B(x)\frac{\partial}{\partial p}$, i.e., $\exp[-p^2/(2B(x))]$. This property is consistent with the fact that in 1 dimensional case one can compute the overdamp limit in any non-equilibrium situation. While for multi-dimensional case, if the system is in equilibrium, FDT $\boldsymbol{b}\boldsymbol{b}^{\dagger} = 2T\boldsymbol{\zeta}$ reads $B_{jk} = k_B T\delta_{jk}$, ensuring the stationary distribution $\exp[-p^2/(2k_BT)]$, but in general there does not exist the stationary solution of $\left(p_j + B_{jk}(x)\frac{\partial}{\partial p_k}\right)$. Thus in multidimensional case there does not always exist the stationary distribution for p and adiabatic elimination of momentum as a tool for taking the overdamp limit does not work. This fact implies that the computation of the direct overdamp limit within the Langevin equation also fails when momentum does not relax to the stationary distribution.

Then what is the necessary and sufficient condition for (2.172) to have stationary distribution for momentum? As one candidate we find that '$\boldsymbol{B}$ is a symmetric matrix' *sufficiently* ensures the existence of stationary solution: $\exp\left[-\frac{1}{2}p_i\left(B^{-1}\right)_{ij}p_j\right]$. Let us see what happens when this condition is satisfied. Can we compute the integral appears in the definition of $\boldsymbol{D}$ in (2.135)? Are problems arisen in (2.171) solved? The condition we require is

$$\boldsymbol{B} = \boldsymbol{B}^{\dagger} \quad \Leftrightarrow \quad \boldsymbol{\Gamma}^{-1}\boldsymbol{b}\boldsymbol{b}^{\dagger} = \boldsymbol{b}\boldsymbol{b}^{\dagger}\boldsymbol{\Gamma}^{-1,\dagger} \tag{2.173}$$

Indeed we have

$$\begin{aligned}
\boldsymbol{D} &= \int_0^{\infty} dt \boldsymbol{m}^{-1}\boldsymbol{\Gamma}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}t}\boldsymbol{b}\boldsymbol{b}^{\dagger}\mathrm{e}^{-\boldsymbol{\Gamma}^{\dagger}t}\boldsymbol{\Gamma}^{\dagger}\boldsymbol{\zeta}^{-1} \\
&= \int_0^{\infty} dt \boldsymbol{m}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}t}\boldsymbol{\Gamma}^{-1}\boldsymbol{b}\boldsymbol{b}^{\dagger}\boldsymbol{\Gamma}^{\dagger}\mathrm{e}^{-\boldsymbol{\Gamma}^{\dagger}t}\boldsymbol{\zeta}^{-1} \\
&= \int_0^{\infty} dt \boldsymbol{m}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}t}\boldsymbol{b}\boldsymbol{b}^{\dagger}\boldsymbol{\Gamma}^{-1,\dagger}\boldsymbol{\Gamma}^{\dagger}\mathrm{e}^{-\boldsymbol{\Gamma}^{\dagger}t}\boldsymbol{\zeta}^{-1} \\
&= \int_0^{\infty} dt \boldsymbol{m}^{-1}\mathrm{e}^{-\boldsymbol{\Gamma}t}\boldsymbol{b}\boldsymbol{b}^{\dagger}\mathrm{e}^{-\boldsymbol{\Gamma}^{\dagger}t}\boldsymbol{\zeta}^{-1} = \boldsymbol{D}^{\dagger}.
\end{aligned} \tag{2.174}$$

where we have made use of (2.173) from the second to the third line of (2.174). Plugging (2.168) and (2.174) immediately shows that

$$\boldsymbol{D} = \frac{\boldsymbol{g}\boldsymbol{g}^{\dagger}}{2}, \tag{2.175}$$

which is a symmetric matrix. Then the anti-symmetric part appeared in

(2.171) vanishes and we obtain

$$\begin{aligned}\dot{x}_i &= -L_{ij}\frac{\partial U}{\partial x_j} - L_{ij}\frac{\partial \left(m^{-1}\right)_{kl}}{\partial x_j}\left(\boldsymbol{\zeta D m}\right)_{kl} + g_{ij}(x^*)\xi_j \\ &\quad + \frac{\partial L_{ij}}{\partial x_k}\left(\boldsymbol{\zeta D}\right)_{jk} - \alpha\frac{\partial g_{ij}}{\partial x_k}g^\dagger_{jk}. \end{aligned} \tag{2.176}$$

$\boldsymbol{\zeta D m}$ in second term in the RHS of (2.176) came from $\boldsymbol{pp}$. Thus it must be a symmetric matrix. Let us check that.

$$\boldsymbol{\zeta D m} = \frac{1}{2}\boldsymbol{b b}^\dagger\boldsymbol{\zeta}^{-1}\boldsymbol{m} = \boldsymbol{B}^\dagger, \tag{2.177}$$

which is symmetric by the condition we required in (2.173). Thus all of the problems in (2.171) have been solved by the assumption (2.173). Note that this is a sufficient but not necessary condition at this stage. We do not know whether this condition is also necessary or a looser necessary and sufficient condition exists.

When there are no curvature on the coordinate x, the second term in the RHS of (2.176) is dropped and reduces to (2.103).

In equilibrium the FDT (2.58) holds and then the Einstein relation $\boldsymbol{D} = k_B T\boldsymbol{L}$ obeys. The final result becomes more beautiful. By using (2.155),

$$\dot{x}_i = L_{ij}\left(-\frac{\partial U^{\text{eff}}}{\partial x_j}\right) + g_{ij}(x^*)\xi_j(t) + T\frac{\partial L_{ij}}{\partial x_j} - \alpha\frac{\partial g_{ij}}{\partial x_k}g^\dagger_{jk}, \tag{2.178}$$

where energy shift $U \to U^{\text{eff}}$ is caused from the second term in the RHS of (2.176).

$$U^{\text{eff}} = U - \frac{1}{2}\ln\det m(x). \tag{2.179}$$

The equilibrium distribution for the Fokker-Planck equation for (2.178) is proportional to $\exp\left[-\beta U_{\text{eff}}\right]$. This energy shift naturally arises by integrating out the momentum from the Maxwell-Boltzmann distribution.

$$\int dp\, \mathrm{e}^{-\beta H(x,p)} \propto \sqrt{\det m(x)}\mathrm{e}^{-\beta U(x)} = e^{-\beta U_{\text{eff}}}. \tag{2.180}$$

Obtained expression of the overdamp limit in the curved space is used in Chapter 3. (2.178) is identical with that of adiabatic elimination of momentum on the Fokker-Planck equation obtained by Polettini [20].

It is interesting to note that the same result (2.176) is obtained by means of the formal solution not for p_i but $v_i = \dot{x}_i$, with slight change in cancellation of I^ζs and I^ms.

We also note that the results obtained from Section 2.2 to Section 2.6 are not new. Our calculation is just an alternative derivation of the overdamped Langevin equation for the system with the state-dependent friction coefficient. On the other hand, the extension of the calculation of the overdamp limit in arbitrary non-equilibrium situation is definitely new. The governing equations for non-equilibrium situations have been written only for the system with temperature gradient [33, 34, 52], and for one-dimensional case [36, 53, 54].

2.9 Hess-Klein and Sancho et al.

In this section we demonstrate the calculation of the overdamp limit within Langevin equation, proposed by Hess and Klein [40] and Sancho et al. [41]. The purpose of the present section is to stress that their calculation is incorrect but the result is somewhat correct. The difference from our derivation is roughly;

1. Overdamped Langevin equation is written in continuous time representation, although the discretization in time is mandatory to determine the interpretation of the multiplicative noise. Nonetheless they insist that the interpretation is given by the Stratonovich.

2. Expansion of the state-dependent friction coefficient $\zeta(x)$ is not performed.

We consider the case of one dimensional inertial system driven by white multiplicative noise according to Sancho's paper [41]. We start from following underdamped Langevin equation,

$$\ddot{x}(t) = -\zeta(x(t))\dot{x}(t) + b(x(t))\xi(t), \tag{2.181}$$

which is same as (2.9). Here $\zeta(x)$ is friction coefficient dependent on x. We assume that there exists $\zeta < \zeta(x)$ that defines lower bound of $\zeta(x)$ and ζ is sufficiently large so that time scale of inertia, $\tau_p \sim \zeta^{-1}$ is small compared with any other timescale we are interested in. $\xi(t)$ is the Gaussian white noise defined in (2.10). The FDT states that $b^2(x) = 2k_BT\zeta(x)$.

One can write down the formal solution of (2.181) as

$$\dot{x}(t) = \int_{-\infty}^{t} dt_1 G(t, t_1) b(x(t_1))\xi(t_1), \tag{2.182}$$

where $G(t, t_1)$ is a propagator defined by

$$G(t, t_1) \equiv \exp\left[-\int_{t_1}^{t} dt_4 \zeta(x(t_4)) \right]. \tag{2.183}$$

By further integrating (2.182) from time t_1 to t one has

$$\begin{aligned} x(t) - x(t_1) &= \int_{t_1}^{t} dt_2 \dot{x}(t_2) \\ &= \int_{t_1}^{t} dt_2 \int_{-\infty}^{t_2} dt_3 G(t_2, t_3) b(x(t_3)) \xi(t_3) \end{aligned} \tag{2.184}$$

The strategy of [40,41] is to expand the formal solution (2.182) in powers of τ_p and keep terms up to $\mathcal{O}(\tau_p)$. One can estimate the magnitude of each terms in the RHS of (2.182) in following manner.

1. $\int G = \mathcal{O}(\tau_p)$ since $\zeta^{-1} = \tau_p$ arises from an integration of exponential of ζ.

2. $b(x) = \mathcal{O}(\tau_p^{-1/2})$ by the FDT.

3. Noise $\xi(t)$ is implicitly $\mathcal{O}(\tau_p^{1/2})$ as shown below. $\xi(t)\xi(t')$ can be replaced by a delta function by its white Gaussian nature and one delta function reduce one time integral, inhibiting the gain of τ_p according to the rule 1. Then one finds that $\xi^2 = \mathcal{O}(\tau_p^{-1})$ and thus $\xi = \mathcal{O}(\tau_p^{-1/2})$. For example,
$$\int \int G\xi\xi \sim \int G \sim \mathcal{O}(\tau_p^{-1}). \tag{2.185}$$
Note that this rule has not been pointed out in [40, 41].

For example, by using these rules the multiplicative noise term, the third term of the RHS of (2.182) is estimated as

$$\int_{-\infty}^{t} dt_1 G(t, t_1) b(x(t_1)) \xi(t_1) \sim \mathcal{O}(\tau_p \tau_p^{-1/2} \tau_p^{-1/2}) = \mathcal{O}(\tau_p^0) \tag{2.186}$$

Similarly the order of $x(t) - x(t_1)$, given in (2.185) is

$$x(t) - x(t_1) = \int_{t_1}^{t} dt_2 \int_{-\infty}^{t_2} dt_3 G(t_2, t_3) b(x(t_3)) \xi(t_3) = \mathcal{O}(\tau_p^1). \tag{2.187}$$

We expand $b(x(t_1))$ in the RHS of (2.182) in powers of τ_p. Since $t_1 < t$,

$$\begin{aligned} b(x(t_1)) &= b(x(t) - x(t) + x(t_1)) \\ &= b(x(t)) - b'(x(t)) \left[x(t) - x(t_1)\right] + \mathcal{O}\left(b \left[x(t) - x(t_1)\right]^2\right) \\ &= b(x(t)) - b'(x(t)) \left[x(t) - x(t_1)\right] + \mathcal{O}(\tau_p^{3/2}) \end{aligned} \tag{2.188}$$

Note that this expansion is similar to what we have carried out in Section 2.4 with the anti-Ito expansion. Since $x(t) - x(t_2)$ is order of τ_p from (2.187) the expansion of $b(x(t_1))$ around $x(t)$ amounts power series expansion in τ_p.

Next we expand $G(t, t_1)$ in powers of τ_p by expanding $\zeta(x(t_4))$ in (2.183) around $x(t)$. Since $t_4 < t$,

$$G(t,t_1) = \exp\left[-\int_{t_1}^{t} dt_4 \left\{\zeta(x(t)) - \zeta'(x(t))\left[x(t) - x(t_4)\right] + \mathcal{O}(\tau_p^1)\right\}\right]. \tag{2.189}$$

Note that the neglected terms are $\mathcal{O}(\tau_p^1)$ since ζ itself is $\mathcal{O}(\tau_p^{-1})$. Since the second term in the exponential is $\mathcal{O}(\tau_p)$ one can further expand

$$\begin{aligned} G(t,t_1) =& \exp\left[-\zeta(x(t))(t-t_1)\right] \exp\left\{\zeta'(x(t)) \int_{t_1}^{t} dt_4 \left[x(t) - x(t_4)\right]\right\} \\ =& G^0(t,t_1) \\ & \times \left[1 + \zeta'(x(t)) \int_{t_1}^{t} dt_4 \left[x(t) - x(t_4)\right] + \mathcal{O}(\tau_p^2)\right]. \end{aligned} \tag{2.190}$$

Here we defined the bare propagator $G^0(t, t_1) \equiv \exp\left[-\zeta(x(t))(t - t_1)\right]$. By applying (2.188) and (2.190) to the formal solution (2.182)

$$\begin{aligned} \dot{x}(t) &= b(x(t)) \int_{-\infty}^{t} dt_1 G^0(t,t_1)\xi(t_1) \\ & \quad \times \left[1 + \zeta'(x(t)) \int_{t_1}^{t} dt_4 \left[x(t) - x(t_4)\right] + \mathcal{O}(\tau_p^2)\right] \\ & \quad \times \left[1 - b'(x(t))\left[x(t) - x(t_4)\right] + \mathcal{O}(\tau_p^2)\right] \end{aligned} \tag{2.191}$$

In [40, 41], the effect of the second term in second line in (2.191) is missing. We have to keep terms up to order of τ_p in right hand side of (2.191),

$$\begin{aligned} \dot{x}(t) =& b(x(t)) \int_{-\infty}^{t} dt_1 G^0(t,t_1)\xi(t_1) \\ & \times \left\{1 + \zeta'(x(t)) \int_{t_1}^{t} dt_4 \left[x(t) - x(t_4)\right] - b'(x(t))\left[x(t) - x(t_1)\right]\right\} \\ & + \mathcal{O}(\tau_p^2). \end{aligned} \tag{2.192}$$

We calculate two integrals which appear in the second and third term of $\{\cdots\}$ in the RHS of (2.192). We first calculate the third term, which is taken into account in [40, 41]. We set

$$I^{b,\mathrm{HS}} \equiv -b(x(t))b'(x(t)) \int_{-\infty}^{t} dt_1 G^0(t,t_1)\xi(t_1)\left[x(t) - x(t_1)\right]. \tag{2.193}$$

By substituting $x(t) - x(t_1)$ with (2.187) and replacing the quadratic term in noise ξ by δ function we have

$$I^{b,\mathrm{HS}} = -b(x(t))b'(x(t)) \int_{-\infty}^{t} dt_1 G^0(t,t_1) \int_{t_1}^{t} dt_2 \int_{-\infty}^{t_2} dt_3 G(t_2,t_3)\delta(t_1 - t_3) \tag{2.194}$$

We can replace G in the RHS of (2.194) by G^0 in the lowest order in τ_p. Then remaining time integral can be analytically carried out and one immediately has

$$I^{b,\mathrm{HS}} = -\frac{b(x(t))b'(x(t))}{2\zeta^2(x(t))} = \frac{k_B T}{2}\frac{\partial \zeta^{-1}(x)}{\partial x(t)}. \tag{2.195}$$

The second equality holds when one makes use of FDT: $b^2(x) = 2k_B T\zeta(x)$. Next we calculate the second term in $[\cdots]$ in the RHS of (2.192), which was neglected in [40, 41]. We set it $I^{\zeta,\mathrm{HS}}$, which is given by

$$I^{\zeta,\mathrm{HS}} \equiv b^2(x(t))\zeta'(x(t)) \int_{-\infty}^{t} dt_1 G^0(t,t_1)\xi(t_1) \int_{t_1}^{t} dt_4 \left[x(t) - x(t_4)\right]. \tag{2.196}$$

By substituting $x(t) - x(t_4)$ with (2.187) and replacing square of noise by its average and estimating ζ by its lowest order in τ_p and taking the overdamp limit $e^{-\zeta(x(t))t} \ll 1$ we have

$$\begin{aligned} I^{\zeta,\mathrm{HS}} &= b^2(x(t))\zeta'(x(t)) \int_{-\infty}^{t} dt_1 G^0(t,t_1) \int_{t_1}^{t} dt_4 \int_{t_4}^{t} dt_2 G^0(t_2,t_1) \\ &= -\frac{k_B T}{2}\frac{\partial \zeta^{-1}(x)}{\partial x(t)}. \end{aligned} \tag{2.197}$$

Note that although we performed the anti-Ito like expansion of ζ and b obtained corrections I^{HS}s are not the same as I^{aI}s in Section 2.4. See (2.72) and (2.71). They are just half values of anti-Ito corrections.

$$I^{b,\mathrm{HS}} = \frac{1}{2} I^{b,\mathrm{aI}} \quad \text{and} \quad I^{\zeta,\mathrm{HS}} = \frac{1}{2} I^{\zeta,\mathrm{aI}}. \tag{2.198}$$

So far we do not know the reason of these relationships.

Plugging (2.195) and (2.197) the formal solution (2.182) is

$$\begin{aligned} \dot{x}(t) &= b(x(t)) \int_{-\infty}^{t} dt_1 G^0(t,t_1)\xi(t_1) + I^{b,\mathrm{HS}} + I^{\zeta,\mathrm{HS}} + \mathcal{O}(\tau_p^2) \\ &= b(x(t)) \int_{-\infty}^{t} dt_1 G^0(t,t_1)\xi(t_1) + \mathcal{O}(\tau_p^2). \end{aligned} \tag{2.199}$$

Surprisingly term $I^{b,\mathrm{HS}}$ and $I^{\zeta,\mathrm{HS}}$ cancel each other. If first term on the RHS of (2.199) converges to the anti-Ito multiplicative noise (2.199) is the

correct overdamp limit. But apparently there is no logic one choose anti-Ito or a specific interpretation in the present derivation. If we do not perform expansion of $\zeta(x(t_4))$ in (2.190) one obtains

$$\dot{x}(t) = b(x(t)) \int_{-\infty}^{t} dt_1 G(t, t_1)\xi(t_1) + \frac{k_B T}{2} \frac{\partial \zeta^{-1}(x)}{\partial x(t)}. \tag{2.200}$$

Note that G is left unperturbed in this expression. This is correct if the first term in the RHS of (2.200) converges to the multiplicative noise interpreted by the Stratonovich rule, as [40, 41] have chosen. Again there is no reason to choose the Stratonovich.

2.10 Summary and conclusions

In this chapter we computed the overdamp limit for the Langevin equation with the multiplicative noises and the state-dependent transport coefficients by adiabatically eliminating the fast relaxing momentum from the underdamped Langevin equation. Mathematically, the overdamp limit is expressed as the situation where the time step of overdamp Langevin equation Δt and the relaxation time of the momentum τ_p are well separated. Our methodology is direct and far simpler than the derivation of overdamp limit through the Fokker-Planck equation. Advantages of our method are, that one can actively determine the interpretation of the multiplicative noises in the overdamp limit, and that it can be easily generalized into the multi-dimensional, non-equilibrium, and even into curved coordinate.

As the result of the first advantage we completely terminated the long standing Ito-Stratonovich dilemma. The dilemma occurs when one extend the overdamp Langevin equation with a constant friction coefficient and an additive noise into the one with a state-dependent friction and a multiplicative noise. The problem is that one cannot intuitively determine which interpretation of the multiplicative noise is *correct*, Ito or Stratonovich or else. Our answer is, no correct interpretation exists, when one try to extend the overdamp Langevin equation into state-dependent transport coefficient. Instead, one has to go back to the underdamped Langevin equation and take the overdamp limit faithfully to its definition.

It seems that sometimes it is wrongly understood, that there exists the *correct* interpretation of the multiplicative noises. In the experiments of the Brownian motion with the state-dependent friction coefficient, it is concluded that the anti-Ito is the correct interpretation of the multiplicative noise [17, 18]. But it is just an accidental result caused by the specialty of 1-dimensional system. As we have shown in (2.73) in Section 2.4 the correct

overdamp limit is identical with the result of ignoring inertia and interpreting the multiplicative noise in the anti-Ito sense for one-dimension. But in multi-dimensional system no choice of the interpretation of the multiplicative noise leads the correct overdamp limit with ignoring inertia (See (2.101)). We stress that one cannot insist that the anti-Ito is not special, by the computation of the overdamp limit within the Fokker-Planck equation or within the heuristic argument. Only our method can show that there are no preferred or special value of α, i.e., interpretation of multiplicative noise. Our calculation is not just an alternative derivation of overdamp limit, but brings a new insight in the interpretation of the multiplicative noise in the overdamped Langevin equation.

Throughout the chapter we assumed that the noise is white and thus its correlation time is zero. It is equivalent to the situation that noise is colored and has finite correlation time τ_n, but the correlation time is much smaller than the relaxation time of momentum: $\tau_n \ll \tau_p$. It is known that in the presence of such time scale separation the resulting multiplicative noise in overdamp limit $\tau_p \to 0$ becomes the Ito type, while in opposite limit, $\tau_n \gg \tau_p$, corresponds to the Stratonovich [30,33,38,58]. It looks contradicting since we have shown that in the situation $\tau_n \ll \tau_p$ one can choose any interpretation of the multiplicative noise. To resolve this question let us remind that in Section 2.2 the multiplicative noise term given by (2.19) splits into the Ito multiplicative noise and correction $I^{b,\mathrm{Ito}}$. $I^{b,\mathrm{Ito}} = 0$ holds in any situation including higher dimension and non-equilibrium case. And the average of the Ito multiplicative noise is always 0. Thus the average of the LHS of (2.19) is 0. This is nothing but that the multiplicative noise term appears in the overdamp limit (first term in the RHS of (2.17)) is the Ito type and there is no contradiction between our result and preceding studies.

Hess-Klein [40] and Sancho et al. [41] tried to compute the overdamp limit directly from the underdamped Langevin equation. But in their derivation the a correction term arisen from the x-dependence of the friction coefficient is missing. Furthermore, they did not discretize the overdamp Langevin equation in time. As the result they cannot determine the interpretation of the multiplicative noise in the overdamped Langevin equation. We solved this problem by discretizing the formal solution by means of finite time step Δt, which is much larger than τ_p, and by explicitly choosing the reference point at which the expansions of the state-dependent transport coefficient $\zeta(x)$ and the factor of the multiplicative noise $b(x)$ are performed. In [40,41], the expansion of $b(x)$ has been carried out but that of $\zeta(x)$ has not. If one carries out the expansion of $\zeta(x)$, the correction terms from b and ζ cancels (in 1-dimension. We have not checked for multi-dimension). It means that if one suppose the anti-Ito multiplicative noise the result is correct, but

apparently one do not have any logic of choosing specific interpretation. Hess implicitly and Sancho explicitly employed the Stratonovich convention, with disregarding the correction from $\zeta(x)$. This procedure somehow leads the correct overdamp limit. So far we do not have an answer to the reason why their "twofold error" acquires the correct result.

Ermak and MacCammon [13] was the first who succeeded to derive the overdamped Langevin equation directly from the underdamped Langevin equation with state-dependent friction coefficient. They implicitly employed the Ito expansion. In this sense our calculations performed in Section 2.2 and Section 2.3 themselves are not new. We stress that our new findings are, not the Langevin equation itself, but its generality of the methodology.

As we have pointed out in Section 2.6 the Onsager's regression hypothesis is violated in the overdamp limit with the state-dependent transport coefficient and a drift term $k_BT\frac{\partial L}{\partial x}$ comes up (see (2.102)). This drift term ensures the reciprocal relation in Onsager coefficient or proof of the FDT [55]. Thus the violation is mandatory to describe the fluctuation near the equilibrium system correctly.

As Sekimoto [33] has demonstrated for the system with temperature gradient, the method presented in this chapter is directly applicable to to the system out of equilibrium. In such situation, (2.103) is written as

$$\dot{x} = -\alpha\frac{\partial D(x)}{\partial x} + \sqrt{2D(x)}\xi(t), \tag{2.201}$$

if U is absent [33, 34]. $D(x) = k_BT(x)/\zeta$ is the state-dependent diffusion coefficient. This expression looks as if the temperature gradient does not cause the drift of the particle since the average of (2.201) leads to $\langle\dot{x}\rangle = 0$. This means that no thermodynamic force is acting on the Brownian particle. But once we translate (2.201) to the Fokker-Planck equation for the probability distribution function defined by $\rho(X,t) = \langle\delta(X - x(t))\rangle$, one finds that

$$\frac{\partial\rho}{\partial t} = \nabla(D\nabla\rho + D_T\nabla T), \tag{2.202}$$

where $D_T = D\rho/T$. This is the thermal diffusion equation for a dilute suspension with the Soret coefficient given by $S_T \equiv D_T/\rho D = 1/T$ and equivalent with the Fokker-Planck equation derived in [50]. This expression is consistent with that Dhont [59] has obtained, if the dilute limit of the colloidal particles is taken in his expression. But this coincidence is astonishing, since in our expression the effect of the thermodiffusion, second term in the RHS of (2.202), has purely dynamic origin, while the derivation by Dhont is based on the static arguments. We also note that the thermal diffusion of one colloidal

particle has been derived within more microscopic standpoint [60, 61] about 50 years ago. In these papers one more collection to the thermal diffusion coefficient is pointed out. Comparison with these theories is left for future works.

As we have noted in the introduction, the state-dependent transport coefficient appears in the Brownian motion with constraint conditions. In such case the motion of the Brownian particle becomes confined into the curved subspace. The calculation for such situation, presented in Section 2.8 will be used in Chapter 3.

Chapter 3

Langevin Dynamics with Rigid Constraints

3.1 Introduction

The Brownian motion under the constraint conditions appears in the broad subjects of physics. For example a polymer is made of monomers interconnected by the chemical bondings. Since the length of the chemical bondings is almost inextensible, one can approximate them as constraint conditions that distances between connected monomers are kept constant values [15, 62–66]. Dynamics of polymers in a solution is governed by the Brownian motion since the size of polymers is much larger than that of the solvent particles.

Recent developments in experimental techniques enable one to track the motion of a big protein molecule diffusing on a lipid membrane by using fluorescent molecules. This is the Brownian motion constrained on a 2-dimensional curved manifold. It is argued that one can extract the geometry of the membrane by observing the diffusion behavior of the protein molecules [21, 67, 68].

Spherical models are known as mean field, exactly solvable models of spin systems. A spherical model is imposed so called the spherical constraint condition, which enforces the sum of square of spin variables over all spins to be identical with the number of spins. The spherical model behaves as a mean field model since the spherical constraint condition inhibits each spins from changing their values independently and as a result it induces the effective long range interaction between all spins [69]. The advantage of the spherical model is not only its solubility. In the spherical model, spins can take any real values, in contrast with the Ising spins, which can only take discrete values 1 or -1. This feature of the spherical models reduces the difficulty

on analyzing the dynamics of spin systems. Thus the spherical models are appreciated as the very few models whose dynamics can be solved exactly, for both equilibrium and non-equilibrium case [25, 70]. A certain type of spin-glass version of the spherical model, called the p-spin spherical model, is expected to play a role of a mean field model for the glass transition of molecular liquids [5, 71, 72]. We will discuss this issue in Chapter 4.

In high energy physics, a method which maps the quantum field theory to a stochastic process is known, and it is called the stochastic quantization. Particularly, the quantization of the gauge fields is less trivial because of the existence of the gauge degree of freedom. For example let us recall the Lagrangian for the U(1) electro-magnetic field;

$$\mathcal{L} = -\frac{1}{4} F_{\mu\nu} F^{\mu\nu}, \quad \text{with} \quad F^{\mu\nu}(x) = \partial^\mu A^\nu(x) - \partial^\nu A^\mu(x). \tag{3.1}$$

Here A^μ is the vector potential and $\mu = 0, 1, 2, 3$. $\mu = 0$ stands for the time component in the Minkowski space and others are corresponding to the 3-dimensional space components. Because of anti-symmetric nature of $F^{\mu\nu}$ the Lagrangian does not depend on $\partial^0 A^0$, which is time derivative of A^0. The corresponding canonical momentum is

$$\pi_0(A, \partial A) = \frac{\partial \mathcal{L}}{\partial(\partial^0 A^0)} = 0. \tag{3.2}$$

This means that not all of the canonical variables, A^μs and π_μs are independent each other. Or it is expressed as an 'internal' constraint is emerged. In general a postulation of the gauge invariance into the Lagrangian causes the emergence of constraint conditions. In order to quantize the gauge theory within the stochastic quantization, a theory of the Brownian motion under constraint has been formulated [22, 56, 73, 74].

In the chemical physics, a method so called the blue moon sampling [23] is known as a computational tool to explore the complex free energy landscape of protein molecules. Let us imagine the situation that we know the configurations of the two local minima and want to determine which one is more stable. We further assume that the energy barrier between them is so high that the system cannot transit from one to another in a reasonable time scale of the computer simulation. The blue moon sampling works effectively for such situations. Let us introduce a reaction coordinate A and the free energy as a function of the reaction coordinate; $\mathcal{F}(A)$. Let A_i and A_f be the value of the reaction coordinate at the two minima. The problem is, which is smaller, $\mathcal{F}(A_i)$ or $\mathcal{F}(A_f)$. The blue moon sampling provides a numerical

realization of the thermodynamic integration.

$$\mathcal{F}(A_f) - \mathcal{F}(A_i) = \int_{A_i}^{A_f} dA \frac{\partial \mathcal{F}(A)}{\partial A} \cong \Delta A \sum_{n=1}^{N} \frac{\partial \mathcal{F}(A)}{\partial A_n}. \tag{3.3}$$

Between the second and third expression, we discretized the reaction path connecting A_i and A_f into N equidistant grid points with width ΔA. We assumed $A_1 = A_i$ and $A_N = A_f$. Then one performs simulations for each A_n. Here appears a constraint condition that fixes the value of the reaction coordinate $A = A_n$. For each simulations one measures the force acting on the system along with the reaction coordinate $f_n = \frac{\partial \mathcal{F}}{\partial A_n}$. Lastly by integrating f_n from $n = 1$ to $n = N$ one can can obtain the free energy difference between the start and the end point. The Brownian dynamics simulations are sometimes employed as a tool to investigate the morphology of the protein molecules, together with the blue moon sampling.

Length of the chemical bondings in the polymer or geometry of the membrane rapidly fluctuate around their average shape. Thus approximation of stiff chemical bonds as inextensible rigid rods is merely an idealization of the real systems. This idealization shall be justified when the time scales between the rapid vibration of bonds and dynamics of conformation of polymer are sufficiently disparate. But at the same time one has to be careful with the fact that the equilibrium distribution for the stiff and the rigid system are not identical [75]. It can be understood in a nutshell as follows. Since the total degree of freedom in rigid system is smaller than that of stiff, the total kinetic energy partitioned to each systems becomes different each other, by the equipartition theorem. For more detailed discussion, see [15, 75]. We also glance at this problem in Subsection 3.8.5. Throughout the chapter we concentrate on the rigid constraints.

Brownian motion under the constraint conditions is not only interested from its diversity of the examples, but also from a more conceptual reason. As a result of the constraint condition the motion of the Brownian particle becomes confined into a curved sub-manifolds. Hereafter we call such sub-manifolds 'constraint surface'. It is a long-standing problem, how to generalize the theory of the stochastic processes to the one on the curved manifolds [19, 20, 76–81].

Most of the examples of the constraint conditions illustrated above are written by equations with the position variables and do not explicitly depend on the velocity or the momentum or time[1]. Such constraint conditions are called the holonomic constraints. In this thesis we restrict our interest in the holonomic constraint.

[1] An exception is the case with the stochastic quantization. See (3.2)

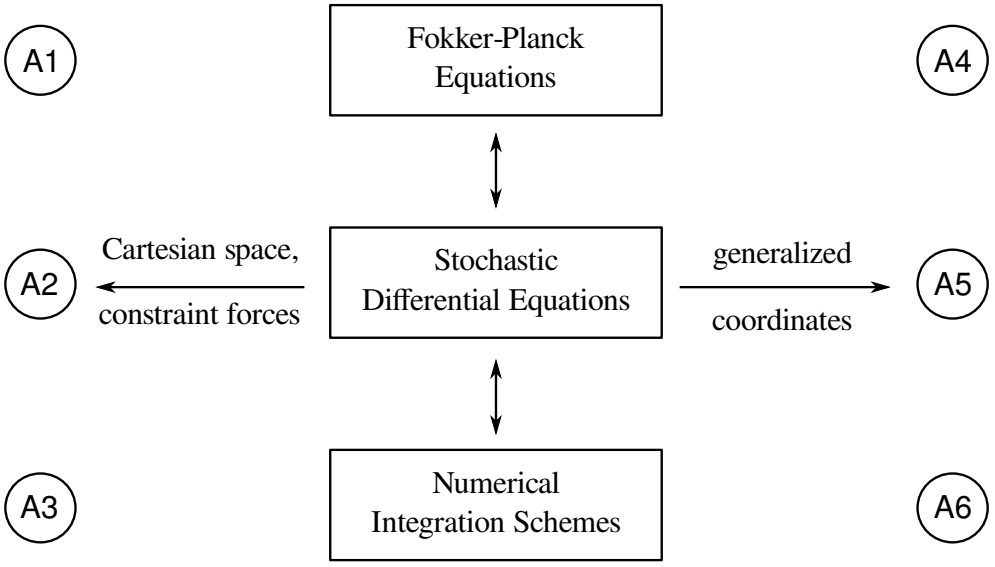

Figure 3.1: Classification of different approaches to rigidly constrained Brownian motion. The figure is brought from Öttinger's book [82].

In the Brownian motion one is often interested in the overdamp limit rather than the underdamped situation. In the polymeric fluids, the momenta of the monomers are expected to be relaxed to the Boltzmann distribution quickly. In other words, the overdamp limit can be taken, as long as one is interested in the long time limit where the time scale between rapid vibration of the chemical bondings and dynamics of the polymer are well separated. In the case with the blue moon sampling one is interested in the morphology of the protein molecules and information on their momentum are not needed. There are no momentum from the beginning in the case with the spherical spin models. In the community of the stochastic quantization both overdamp and underdamped Langevin equations are employed [73].

As we have thoroughly described, the Brownian motion under the constraint conditions is ubiquitous in physics. Hence, its formulation has been carried out in each communities. There are various ways to formulate it (See Figure 3.1). The Brownian motion can be formulated in two ways. One is to work on the Langevin equations which describe the time evolution of the stochastic variables like positions of monomers. The other is to work on the Fokker-Planck equation for the probability distribution function of positions of monomers. For each approaches, there are two ways to impose constraints. One is to formulate it within the effective degree of freedom where the actual motion of the particle under the constraints take place. We

call such degree of freedom the generalized coordinate. The other is to work on the Cartesian coordinate and apply the method of the Lagrange multiplier, which has been established in the classical mechanics. Bird, Curtiss, Armstrong and Hassager (BCAH) have derived the Fokker-Planck equation in the generalized coordinate [62]. Their strategy is categorized into A4 of Figure 3.1. Öttinger wrote down the Langevin equation which is equivalent with BCAH's Fokker-Planck equation and subsequently rewrote it in terms of the Cartesian coordinate [63, 82](A4→A5→A2) in order to accommodate the theory to the numerical simulation. Nonetheless, his Langevin equation is not closed within the Cartesian coordinate only and depends on the definition of the generalized coordinate, which completely spoils the merit in implementation to the numerical simulation. Furthermore, the derivation of the Fokker-Planck equation by BCAH, on which Öttinger's theory has based, is based on the theory called the phase space kinetic theory. It is a quite unfamiliar derivation of the Fokker-Planck equation (See Section 3.8.1). The results obtained by BCAH and Öttinger are all correct, but one needs to be very careful with the treatment of the curved coordinate. Thus we rather take another strategy. We start from the Langevin equation written in the Cartesian coordinate and impose the constraint condition by using the Lagrange multiplier. Hence our strategy is classified to A2 of Figure 3.1.

The strategy A2 has been tried to be realized by several authors [21–23, 43, 64, 65]. But most of their results conflict with Öttinger's theory. These failures tell us that it is difficult to impose a constraint on the overdamped Langevin equation. We deduce that this difficulty is caused by the non-covariance of the overdamped Langevin equation [20, 76]. Here covariance means that the equation of motion does not change its form by a change of coordinate. As pointed out in the previous paragraph, a constraint is closely related with a change of coordinate between the Cartesian and the generalized coordinate. Thus one can understand that the non-covariance of the overdamped Langevin equation makes the formulation of the constrained Brownian motion difficult (or impossible).

The purpose of this chapter is to disentangle those frustrated situations and give a simple and straightforward derivation of the Langevin equation for the constrained Brownian motion. All of the difficulties stated above are summarized in two points: the first is that derivation within the generalized coordinate is hard to understand, and the second is that the Lagrange multiplier method fails by the non-covariant nature when it is applied to the overdamped Langevin equation. To resolve these problems we start from the underdamped Langevin equation and realize the constraint condition by using the Lagrange multiplier method. Contrary to the overdamped Langevin equation, the underdamped one has covariance with respect to a change of

coordinate. Thus we expect that we do not face any difficulty in applying the method of Lagrange multiplier to the underdamped Langevin equation. Actually it is successfully done by Hinch [64]. Then by taking the overdamp limit from Hinch's Langevin equation, one obtains the correct Langevin equation for the Brownian motion under constraints.

This chapter is organized as follows. In Section 3.2 we introduce our model and constraint condition considered throughout the chapter. We define a curved space to describe the intrinsic dynamics of constrained system, called the generalized coordinate. In Section 3.3 we consider the system with constraints in the equilibrium state and derive the Maxwell-Boltzmann distribution both for the Cartesian coordinate and for the generalized coordinate. In Section 3.4 we demonstrate how the method of Lagrange multiplier works for the Hamilton mechanics. In Section 3.5 we apply the same procedure to the underdamped Langevin equation. The main part of this chapter is Section 3.6. We consider the overdamp limit for constrained Brownian motion in two different manners and check that indeed these results become identical. In Section 3.7 we extend our formulation into the non-equilibrium case, such as a system with temperature gradient. In Section 3.8 we summarize the preceding studies on Brownian motion with constraint, investigated in several communities, and make comparison with our theory. We summarize our results and make a conclusion in Section 3.9. Since the formulation requires one to introduce many symbols, we summarize them in Section 3.10.

3.2 Model and Geometry

In this section we introduce our model and constraint condition we are concerned with throughout the chapter. The constraint condition defines the two sub-manifolds: one is the intrinsic degree of freedom in which the motion of the particle is confined, or called the constraint surface. The other is the coordinate perpendicular to the constraint surface. We call these curved spaces altogether the generalized coordinate.

3.2.1 Without constraint

We consider a classical system written in the Cartesian coordinate. Let $x_i (i = 1, \ldots, N)$ be the position of ith coordinate and express its canonical conjugate by p_i. i stands for index of space and number of particles, etc. altogether. In the absence of the thermal fluctuation the particles obey the Newton equation of motion. Let us formulate it in the Hamilton form. The

Hamiltonian of the system is assumed to be given by

$$H = \frac{1}{2} p_i \left(m^{-1}\right)_{ij} p_j + U(x). \tag{3.4}$$

Hereafter we adopt the summation over repeated indices. m_{ij} is a mass matrix. When one is interested in the polymer with their mass of monomers being different each other it becomes

$$\boldsymbol{m} = \begin{pmatrix} m_1 & 0 & \cdots & 0 \\ 0 & m_2 & & \vdots \\ \vdots & & \ddots & 0 \\ 0 & \cdots & 0 & m_N \end{pmatrix}. \tag{3.5}$$

Bold symbol denotes a matrix. Mathematically there are no technical difference in treating a diagonal matrix with form of (3.5) and general m_{ij}. But the latter fits with the Einstein convention on the sum of suffixes and with the change of coordinate. Thus we employ a matrix form of the mass. $U(x)$ is the potential function of the system. Dynamics of the system is governed by the Hamilton equation.

$$\dot{x}_i = \{H, x_i\} = \left(m^{-1}\right)_{ij} p_j, \tag{3.6}$$

$$\dot{p}_i = \{H, p_i\} = -\frac{\partial U}{\partial x_i}. \tag{3.7}$$

Here overdot denotes the differentiation with respect to time and $\{\cdot, \cdot\}$ is the Poisson bracket defined by,

$$\{A, B\} \equiv \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial x_i} - \frac{\partial A}{\partial x_i}\frac{\partial B}{\partial p_i}. \tag{3.8}$$

In the presence of the thermal fluctuation, the governing equation changes from the Newton equation to the Langevin equation. The underdamped Langevin equation is obtained by adding the Stokes' drag force and the random force exerted by the solvent particles.

$$\dot{x}_i = \left(m^{-1}\right)_{ij} p_j, \tag{3.9}$$

$$\dot{p}_i = -\zeta_{ij}\dot{x}_j - \frac{\partial U}{\partial x_i} + f_i(t). \tag{3.10}$$

Here $\boldsymbol{\zeta}$ is the friction matrix. We assume that $\boldsymbol{\zeta}$ does not depend on x explicitly. In fact our theory can be directly applied to x-dependent friction matrix case. The reason why we start from the constant $\boldsymbol{\zeta}$ is to stress that

there inevitably arises the position-dependent friction by the implementation of the constraints. For detail the reader should refer to Section 3.6. $f(t)$ represents the random force. Its average is 0 and the variance is prescribed by the fluctuation-dissipation theorem (FDT),

$$\langle f_i(t)\rangle = 0, \quad \langle f_i(t)f_j(t')\rangle = 2k_BT\zeta_{ij}\delta(t-t'). \tag{3.11}$$

Here δ is Dirac's delta function. We further assume that $f_i(t)$ is a Gaussian noise and thus characterized by the moment upto the second order. Overdamped Langevin equation is given by

$$\dot{x}_i = L_{ij}\left(-\frac{\partial U}{\partial x_j} + f_j\right), \tag{3.12}$$

L_{ij} is the Onsager coefficient given by $\mathbf{L} = \boldsymbol{\zeta}^{-1}$. For the derivation of (3.12) see Appendix B.1 and Chapter 2. The dynamics of the p-spin spherical model obeys this overdamped Langevin equation [5, 6].

3.2.2 With constraints

Consider $M(< N)$ set of holonomic constraints. Holonomic means that the constraint conditions are expressed by equations written only within functions of the positions x and they do not explicitly depend on the velocity or the momentum or time. Namely,

$$F_\mu(x) = 0, \quad \mu = 1, \ldots, M \quad (M < N). \tag{3.13}$$

Hereafter we assume that x without index i abbreviates the N set of the position variables x_i. It is essential to restrict our scope into the holonomic constraints. Especially, existence of exact differential form is important. We will revisit this point in the end of this section.

The motion of the particles takes place within the curved $2(N-M)$-dimensional sub-phase space. It is convenient to define the basis of this sub-manifold. Discussion presented here is also found in [15, 22]. Let $q_\alpha(\alpha = 1, \ldots, N-M)$ be such coordinate. q_α, together with M constraint conditions, form a complete basis of N dimensional configurational space. As shown in Figure 3.2, q_α and F_μ must be orthogonal each other. Further we can request the orthonormality and completeness in each subspace. Given F_μ, these conditions are not sufficient to uniquely determine q_αs. Below we construct these basis and see how the arbitrarity emerges. We also exemplify some specific choices of the basis.

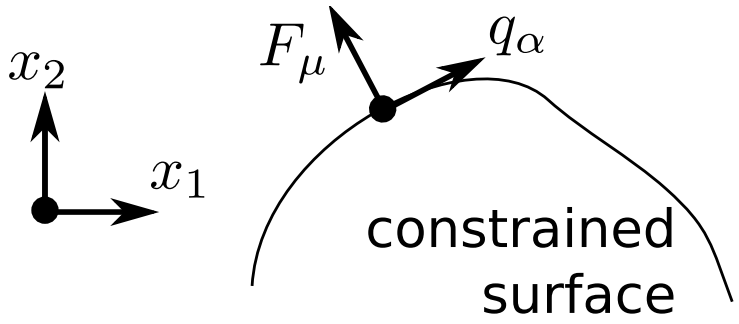

Figure 3.2: Geometry of the Cartesian coordinate and the generalized coordinate.

First of all one can define M set of N-dimensional basis vector perpendicular to the constraint surface from the constraint condition (3.13),

$$e_{\mu,i} \equiv \frac{\partial F_\mu(x)}{\partial x_i}. \tag{3.14}$$

It is natural to construct a reciprocal set of these basis following the spirit of the differential geometry. They also should satisfy the orthonormal and the complete conditions. The reciprocal vector in the space perpendicular to the constraint surface is defined by

$$e^\mu_j \equiv \frac{\partial x_i(F,q)}{\partial F_\mu}. \tag{3.15}$$

Since we have not defined q_α as a function of x yet, this reciprocal vector is not explicitly determined at this point. The orthonormality condition within the subspace perpendicular to the constraint surface reads,

$$e_{\mu,i}e^\nu_i = \delta^\nu_\mu. \tag{3.16}$$

These are $M \times M$ equations required to the basis vectors. Next we define the generalized coordinate parallel to the constraint surface, q_α. By construction it must be orthogonal to the perpendicular counterpart. Then one requires

$$0 = \frac{\partial F_\mu}{\partial q_\alpha} = \frac{\partial F_\mu}{\partial x_i}\frac{\partial x_i}{\partial q_\alpha} = e_{\mu,i}e^\alpha_i. \tag{3.17}$$

The reciprocal version of this orthogonal condition is automatically satisfied since it reads $\frac{\partial q_\alpha}{\partial F_\mu}$, which is equivalent with (3.17).

$$e^\mu_i e_{\alpha,i} = 0. \tag{3.18}$$

We assume that there exists $q_\alpha(x)$, $\alpha = 1, \ldots, N-M$ so that $e_i^\alpha = \frac{\partial x_i}{\partial q_\alpha}$ and $e_{\alpha,i} = \frac{\partial q_\alpha}{\partial x_i}$ satisfy (3.17) and (3.18) respectively. Then the completeness condition for set of F_μ and q_α is automatically satisfied.

$$e_{\mu,i}e_j^\mu + e_{\alpha,i}e_j^\alpha = \frac{\partial F_\mu(x)}{\partial x_i}\frac{\partial x_j(F,q)}{\partial F_\mu} + \frac{\partial q_\alpha(x)}{\partial x_i}\frac{\partial x_j(F,q)}{\partial q_\alpha} = \delta_{ij}, \tag{3.19}$$

by the chain rule of the differentiation. One require the orthonormality condition to the coordinate parallel to the constraint surface.

$$e_{\alpha,i}e_i^\beta = \delta_\alpha^\beta. \tag{3.20}$$

These are $(N-M)\times(N-M)$ requirements. Since we have required (3.16), (3.17) and (3.20), the total number of the requirements is,

$$\begin{aligned} M^2 + M(N-M) + (N-M)^2 &= N^2 + M^2 - NM \\ &= N^2 - M(N-M) < N^2. \end{aligned} \tag{3.21}$$

Now one sees that the total number of requirements is always smaller than the total degree of freedom: N^2. Thus one is quite free to choose the basis in the generalized coordinate. In the remaining part of the present section we introduce some examples of possible choices.

Example 1 In the presence of the momentum, i.e., in the Newtonian mechanics and the in the underdamped Langevin equation with mass matrix model, which will be considered in Section 3.4 and 3.5, it is natural to give [15],

$$e_i^\mu = \mathrm{M}_\perp^{\mu\nu} e_{\nu,j} \left(m^{-1}\right)_{ji}, \tag{3.22}$$

where $\mathrm{M}_\perp^{\mu\nu}$ is defined through its inverse as

$$\left(\mathrm{M}_\perp^{-1}\right)_{\mu\nu} = e_{\mu,i}\left(m^{-1}\right)_{ij} e_{\nu,j}. \tag{3.23}$$

One can define a projection operator onto the constraint surface as [15, 64]

$$P_{ij}^m \equiv \delta_{ij} - e_{\mu,i}e_j^\mu = \delta_{ij} - e_{\mu,i}\mathrm{M}_\perp^{\mu\nu} e_{\nu,k}\left(m^{-1}\right)_{kj}, \tag{3.24}$$

which is a rank $N-M$ matrix. It can be easily checked that $(\boldsymbol{P}^m)^2 = \boldsymbol{P}^m$ obeys and thus $\boldsymbol{P}^m$ is surely a projector. This projection operator naturally appears in the Newtonian dynamics and the underdamped Langevin equation under the constraints. The relation between superscript e_i^α and subscript $e_{\alpha,i}$ should be taken as

$$e_{\alpha,j} = \left(\mathrm{M}_\parallel^{-1}\right)_{\alpha\beta} e_i^\beta m_{ij}, \tag{3.25}$$

where we have defined

$$\mathrm{M}_{\parallel}^{\alpha\beta} = e_i^{\alpha} m_{ij} e_j^{\beta}. \tag{3.26}$$

One can check that the set of choices of (3.22) and (3.25) satisfies all the orthonormality conditions required above. By using the completeness relation (3.19) The projection operator $\boldsymbol{P}^m$ defined in (3.24) can be rewritten as

$$P_{ij}^m = e_{\alpha,i} e_j^{\alpha}. \tag{3.27}$$

Note that one can obtain a transpose of $\boldsymbol{P}^m$, say $(\boldsymbol{P}^m)^{\dagger}$, by inverting the order of superscript and subscript in (3.24) or in (3.27).

Example 2 As stated above there is freedom to choose the basis in the generalized coordinate. Thus Example 1 above is not the only choice. For example following choice between $e_{\mu,i}$ and e_i^{μ} also satisfies the orthonormality conditions.

$$e_i^{\mu} = \left(D^{-1}\right)^{\mu\nu} e_{\nu,i}, \quad D_{\mu\nu} = e_{\mu,i} e_{\nu,i}. \tag{3.28}$$

One can construct an another projection operator $\boldsymbol{P}$ as

$$P_{ij} = \delta_{ij} - e_{\mu,i} e_i^{\mu} = \delta_{ij} - e_{\mu,i} \left(D^{-1}\right)^{\mu\nu} e_{\nu,j}. \tag{3.29}$$

This projection operator arises when the mass or the Onsager coefficient are scalar [15, 22]. Note that in this choice the projection operator $\boldsymbol{P}$ becomes a symmetric matrix. For the perpendicular part of the generalized coordinate, the relation between e_i^{α} and $e_{\alpha,i}$ is given by

$$e_{\alpha,i} = \left(g^{-1}\right)_{\alpha\beta} e_i^{\alpha}, \quad g^{\alpha\beta} = e_i^{\alpha} e_i^{\beta}. \tag{3.30}$$

Example 3 In the overdamp limit, one will find that it is natural to construct the basis vectors by using the Onsager coefficient, rather than the mass matrix. We define

$$\Lambda_{\mu\nu}^{\perp} = e_{\mu,i} L_{ij} e_{\nu,j}, \tag{3.31}$$

and define superscript e_i^{μ}s as

$$e_i^{\mu} = L_{ik} e_{\nu,k} \left(\Lambda_{\perp}^{-1}\right)^{\nu\mu} \tag{3.32}$$

Then one can define the following projection operator

$$P_{ij}^L = \delta_{ij} - e_i^{\mu} e_{\mu,j} = \delta_{ij} - L_{ik} e_{\mu,k} \left(\Lambda_{\perp}^{-1}\right)^{\mu\nu} e_{\nu,j}. \tag{3.33}$$

This projector $\boldsymbol{P}^L$ naturally appears in the overdamp limit, see Section 3.6.

We summarize the recipe on the construction of the basis vectors for the generalized coordinate.

1. Give constraint conditions $F_\mu = 0$ and define $e_{\mu,i} \equiv \frac{\partial F_\mu}{\partial x_i}$, which behave as M set of N-dimensional basis vectors perpendicular to the constraint surface.

2. Introduce the reciprocal set e_i^μ and require the orthonormality condition.

3. Define the coordinate parallel to the constraint surface. Define e_i^α by using the orthogonality of parallel and perpendicular part of the generalized coordinate.

4. Again using the orthonormality (3.20) define subscript $e_{\alpha,i}$.

Let Q be the complete set of the N-dimensional generalized coordinate formed by F_μ and q_α.

$$\{Q\} = \{F_1, F_2, \ldots, F_M, q_1, q_2, \ldots, q_{N-M}\}. \tag{3.34}$$

Let $a = 1, \ldots, N$ be the suffix of Q, bundling α and μ.

In general a formulation of the system under the constraints becomes very complicated if one try to give concrete relations between q_α and x. For example let us consider a polymer depicted in Figure 3.3. In this case a set of coordinates parallel to the constraint surface might be given by polar angles θ and azimuthal angles ϕ for rigid bonds. Clearly, writing down all the e_i^αs and $e_{\alpha,i}$s explicitly is a complicated task. Moreover, since the choice of the generalized coordinate is not unique as shown above, it is not clear that the choice of θ and ϕ is appropriate to the situation. In fact in some situations, for example, the case that the mass is matrix or the Onsager coefficient is matrix, one has to introduce the generalized coordinate like the Example 1 and 3 above, respectively. Thus it is not smart to fix the parallel coordinate concretely. We do not need to give how q_αs can be written in terms of x. We just require the existence of such global coordinate and work on local conditions like (3.20). Here local means that the relationships between the Cartesian and the generalized coordinate are written in differential forms. One might think that one can construct the whole theory within the local coordinate only and can extend the scope of the constraint to differential forms like $e_{\mu,i}\delta x_i = 0$, instead of (3.13). But contrary to the expectation, it is not possible since we will repeatedly use the existence of $F_\mu(x)$ and $q_\alpha(x)$. For example the following relationships are mandatory for us to complete the calculations.

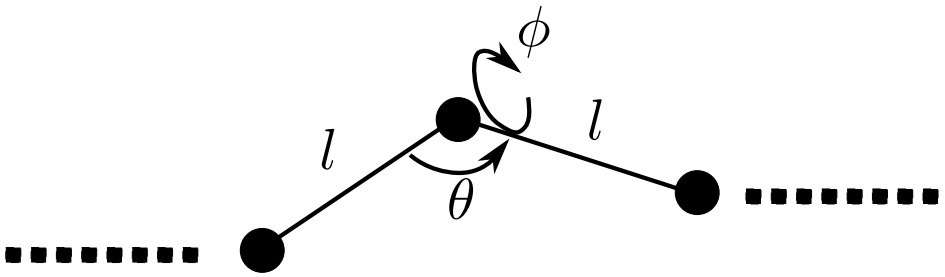

Figure 3.3: A model of a polymer. Distance between the monomers are fixed. Other degree of freedom, say polar angles θ and azimuthal angle ϕ are free to move, thus forms the coordinate parallel to the constraint surface.

$$\frac{\partial e_{\mu,i}}{\partial x_j} = \frac{\partial^2 F_\mu}{\partial x_i \partial x_j} = \frac{\partial e_{\mu,j}}{\partial x_i}, \tag{3.35}$$

$$\frac{\partial e_{\alpha,i}}{\partial x_j} = \frac{\partial^2 q_\alpha}{\partial x_i \partial x_j} = \frac{\partial e_{\alpha,j}}{\partial x_i}. \tag{3.36}$$

We noted in the beginning of this subsection that restricting the scope into the holonomic constraint is essential. Now that its reason is unveiled. Otherwise we cannot make use of (3.35).

3.3 Equilibrium statistical mechanics

In this section we consider how the constraint conditions affect the statistical property of the system, based on the argument by Kramers [83]. See also a recent review [84]. Basically this section does not contain any new result. The purpose of this section is twofold. One is to derive the correct equilibrium distribution function which works as a test to the dynamical theory. Any statistical dynamical theory must be consistent with the statistical mechanics. To check whether a dynamical theory is correct or not we need to know the equilibrium properties. The second is that arguments on statistical mechanical property of the constrained system give an important insight on choosing the generalized coordinate. In particular the choice of Example 1 in Section 3.2, equation (3.25) is inspired by the analysis presented in this section.

The starting point of Kramers' argument is simple. He assumed that the statistical measure of the system under the constraints is given by the small sub-phase space where the actual motion takes place, i.e., the coordinate parallel to the constraint surface and its conjugate momentum. The equilibrium distribution is given by the Boltzmann distribution with Hamiltonian

defined in this sub-phase space. Thus, the equilibrium distribution function for q_α and its conjugate momentum π^α is given by,

$$\tilde{\Psi}^{\rm eq}(q,\pi) = \mathcal{N}\exp\left[-\beta H(q,\pi)\right]. \tag{3.37}$$

Throughout the Chapter we put $\tilde{}$ to designate that the probability distribution function is for the generalized coordinate. We represent by Ψ the probability distribution function within the phase space and by Φ the one within the position variable only. $\mathcal{N}$ is a normalization constant and β is inverse temperature $1/(k_BT)$. In our settings we only know the Hamiltonian written in the Cartesian coordinate (3.4). We first have to rewrite it within the generalized coordinate. By using the chain rule of the differentiation,

$$\dot{x}_i = \frac{\partial x_i}{\partial Q_a}\dot{Q}_a = e_i^\mu \dot{F}_\mu + e_i^\alpha \dot{q}_\alpha. \tag{3.38}$$

Then the kinetic energy term in the Hamiltonian (3.4) becomes

$$K = \frac{1}{2}\dot{x}_i m_{ij}\dot{x}_j = \frac{1}{2}\dot{Q}_a \mathrm{M}^{ab}\dot{Q}_b, \tag{3.39}$$

where,

$$\mathbf{M} = \begin{pmatrix} e_i^\alpha m_{ij} e_j^\beta & e_i^\mu m_{ij} e_j^\beta \\ e_i^\alpha m_{ij} e_j^\nu & e_i^\mu m_{ij} e_j^\nu \end{pmatrix} = \begin{pmatrix} \mathrm{M}_\parallel^{\alpha\beta} & \mathrm{M}^{\mu\beta} \\ \mathrm{M}^{\alpha\mu} & \mathrm{M}_\perp^{\mu\nu} \end{pmatrix} \tag{3.40}$$

This matrix $\mathbf{M}$ can be block-diagonalized by choosing a suitable basis. Indeed Example 1 is the choice. Thus superscript e_i^μ and subscript $e_{\alpha,i}$ is given by (3.22) and (3.25) respectively. In this definition the off-diagonal block of matrix $\mathbf{M}$ drops as,

$$\mathrm{M}^{\mu\alpha} = e_i^\mu m_{ij} e_j^\alpha = \mathrm{M}_\perp^{\mu\nu} e_{\nu,k}\left(m^{-1}\right)_{ki} m_{ij} e_j^\alpha = \mathrm{M}_\perp^{\mu\nu} e_{\nu,k} e_k^\alpha = 0. \tag{3.41}$$

Here we have made use of the orthogonal condition (3.17). The another off-diagonal block $\mathrm{M}^{\alpha\mu}$ also vanishes by making use of the orthogonality (3.18). If one chooses the basis according to Example 2 or 3 the off-diagonal blocks of $\mathbf{M}$ do not vanish. This striking feature of the basis according to Example 1 enable us to construct the statistical mechanics within the phase space spanned by q_α and their canonical momenta. Let Π^μ be the conjugate momentum to F_μ. Since the constraint condition (3.13) must be satisfied time by time, it does not evolve with time. This consistency condition reads $\dot{F}_\mu = 0$ [85]. Thus, one see that the conjugate momentum Π^μ also vanishes.

$$\Pi^\mu \equiv \frac{\partial K}{\partial \dot{F}_\mu} = \mathrm{M}^{\mu a}\dot{Q}_a = \mathrm{M}_\perp^{\mu\nu}\dot{F}_\nu + \mathrm{M}^{\mu\alpha}\dot{q}_\alpha = 0. \tag{3.42}$$

Here we again used the fact that $\mathbf{M}$ is block-diagonal. It is very important fact, that $\dot{\Pi}^\mu = 0$ is ensured by the particular choice of the generalized coordinate. Then the dynamics under the constraints can be characterized by $2(N-M)$ dimensional parallel coordinate q_α and π^α. It can be also computed as

$$\pi^\alpha = \mathrm{M}_\parallel^{\alpha\beta}\dot{q}_\beta, \tag{3.43}$$

Thus the kinetic energy given in (3.39) becomes

$$K = \frac{1}{2}\pi^\alpha \left[\mathrm{M}_\parallel^{-1}(q)\right]_{\alpha\beta}\pi^\beta \tag{3.44}$$

Here we stress that $\mathbf{M}_\parallel$ depends on q. The potential energy $U(x)$ can be written only by means of q and we hereafter simply write $U(q)$. Then the Hamiltonian written within the parallel coordinate and their conjugate momentum is given by

$$H(q,\pi) = \frac{1}{2}\pi^\alpha \left[\mathrm{M}_\parallel^{-1}(q)\right]_{\alpha\beta}\pi^\beta + U(q). \tag{3.45}$$

We obtained an explicit form of the Hamiltonian appears in the Kramers' equilibrium distribution function (3.37).

We rewrite this equilibrium distribution function with the Cartesian coordinate for the later purpose. To this end we perform the change of coordinate from the generalized coordinate (3.37) to the Cartesian coordinate, together with its statistical measure. We denote $2(N-M)$ dimensional statistical measure in the generalized coordinate $dq_1\cdots dq_{N-M}d\pi^1\cdots d\pi^{N-M}$ by $dq_\alpha d\pi^\alpha$. Then,

$$\tilde{\Psi}^{\mathrm{eq}}(q_\alpha,\pi^\alpha)dq_\alpha d\pi^\alpha = \mathrm{e}^{-\beta H}dq_\alpha d\pi^\alpha. \tag{3.46}$$

The equilibrium distribution function for the Cartesian phase space variables x_i and p_i, $\Psi^{\mathrm{eq}}(x,p)$ can be derived as follows.

$$\tilde{\Psi}^{\mathrm{eq}}(q_\alpha,\pi^\alpha)dq_\alpha d\pi^\alpha = \mathrm{e}^{-\beta H}dq_\alpha d\pi^\alpha = \delta(F_\mu)\delta(\Pi^\mu)\mathrm{e}^{-\beta H}dq_\alpha d\pi^\alpha dF_\mu d\Pi^\mu \tag{3.47}$$

Here the constraint condition $F_\mu = 0$ and its consistency condition $\Pi^\mu = 0$ (shown in (3.42)) have been used. Next we use the following property of the delta function.

$$\delta(\Pi^\mu) = \delta(\mathrm{M}_\perp^{\mu\nu}\dot{F}_\nu) = \frac{1}{|\mathrm{M}_\perp|}\delta(\dot{F}_\mu) = \left|\mathrm{M}_\perp^{-1}\right|\delta(\dot{F}_\mu), \tag{3.48}$$

here $|\cdots|$ is determinant of $\cdots$. Plugging (3.48) and the Liouville's theorem $dQd\Pi = dxdp$ with the right hand side (RHS) of (3.47) one arrives at the equilibrium distribution function written in the Cartesian coordinate.

$$\Psi^{\rm eq}(x,p) = \delta(F_\mu(x))\delta(\dot{F}_\mu(x))\left|{\rm M}_\perp^{-1}\right|{\rm e}^{-\beta H}. \tag{3.49}$$

In the remaining part of this section we integrate out the momentum from the equilibrium distribution in the phase space to obtain the equilibrium distribution function within the position variables only. Results obtained here will be used for comparison with the stationary distribution function extracted from the overdamped Langevin equation under the constraints. We carry out the π^α integral in (3.46). It is a simple Gaussian integral since the kinetic energy is written in bilinear form,

$$\begin{aligned}\int d\pi^\alpha dq_\alpha e^{-\beta H} &\propto \sqrt{\left|{\rm M}_\parallel\right|}{\rm e}^{-\beta U}dq_\alpha = \delta(F_\mu)\sqrt{\left|{\rm M}_\parallel\right|}{\rm e}^{-\beta U}dq_\alpha dF_\mu \\ &= \left|\frac{\partial Q}{\partial x}\right|\delta(F_\mu)\sqrt{\left|{\rm M}_\parallel\right|}{\rm e}^{-\beta U}dx. \end{aligned}\tag{3.50}$$

The Jacobian $\left|\frac{\partial Q}{\partial x}\right|$ is a determinant of $N\times N$ matrix given by joining $e_{\alpha,i}$ and $e_{\mu,i}$, arisen from change of coordinate from Q to x. It is a student exercise to show that,

$$\left|\frac{\partial Q}{\partial x}\right|\sqrt{\left|{\rm M}_\parallel\right|} = \sqrt{|m|\left|{\rm M}_\perp^{-1}\right|}. \tag{3.51}$$

Proof Since a determinant of a multiple of matrices is a multiple of determinants of each matrices, the LHS of (3.51) can be written as

$$\left|\frac{\partial Q}{\partial x}\right|\sqrt{\left|{\rm M}_\parallel\right|} = \sqrt{|m|\left|\boldsymbol{e}\boldsymbol{m}^{-1}\boldsymbol{e}\right|\left|{\rm M}_\parallel\right|}. \tag{3.52}$$

Here we defined,

$$\boldsymbol{e} = (e_{\mu,i}, e_{a,i})\,. \tag{3.53}$$

Since $\boldsymbol{e}\boldsymbol{m}^{-1}\boldsymbol{e}$ is nothing but $\mathbf{M}$ defined in (3.40),

$$\begin{aligned}\boldsymbol{e}\boldsymbol{m}^{-1}\boldsymbol{e} &= \mathbf{M} = \begin{pmatrix} e_{\alpha,i}\left(m^{-1}\right)_{ij}e_{\beta,j} & e_{\alpha,i}\left(m^{-1}\right)_{ij}e_{\nu,j} \\ e_{\mu,i}\left(m^{-1}\right)_{ij}e_{\beta,j} & e_{\mu,i}\left(m^{-1}\right)_{ij}e_{\nu,j}\end{pmatrix} \\ &= \begin{pmatrix}\left({\rm M}_\parallel^{-1}\right)_{\alpha\beta} & 0 \\ 0 & \left({\rm M}_\perp^{-1}\right)_{\mu\nu}\end{pmatrix}. \end{aligned}\tag{3.54}$$

Since a determinant of block-diagonal matrix is a product of determinants of each blocks, we have that

$$\left|\boldsymbol{e}\boldsymbol{m}^{-1}\boldsymbol{e}\right| = \left|{\rm M}_\parallel^{-1}\right|\left|{\rm M}_\perp^{-1}\right|. \tag{3.55}$$

By substituting (3.55) into RHS of (3.52) one immediately have (3.51). Note that again the choice of basis according to Example 1 is essential to derive this relation. Otherwise (3.54) and (3.55) cannot hold and one cannot compute the determinant of $\boldsymbol{em}^{-1}\boldsymbol{e} = \mathbf{M}$. □

Plugging (3.51) into (3.50) yields,

$$\tilde{\Psi}^{\mathrm{eq}}(q_\alpha, \pi^\alpha) dq_\alpha d\pi^\alpha = \delta(F_\mu)\sqrt{|m|\left|\mathrm{M}_\perp^{-1}\right|}\mathrm{e}^{-\beta U} dx. \tag{3.56}$$

Then we arrived at the equilibrium distribution function within the position variables in the Cartesian coordinate.

$$\Phi^{\mathrm{eq}}(x) = \mathcal{N}\delta(F_\mu(x))\sqrt{\left|\mathrm{M}_\perp^{-1}(x)\right|}\mathrm{e}^{-\beta U(x)}. \tag{3.57}$$

We introduce following effective potential $U_{\mathrm{eff}}(x)$.

$$U_{\mathrm{eff}}(x) = U(x) - k_B T \ln\sqrt{\left|\left(\mathrm{M}_\perp^{-1}\right)(x)\right|} = U(x) + k_B T \ln\sqrt{|\mathrm{M}_\perp(x)|}, \tag{3.58}$$

By using U_{eff} the equilibrium distribution can be written as

$$\Phi^{\mathrm{eq}}(x) = \mathcal{N}\delta(F_\mu(x))\mathrm{e}^{-\beta U_{\mathrm{eff}}(x)} \tag{3.59}$$

This expression shows that the constraint conditions shift the potential in the equilibrium distribution from U to U_{eff}. How about the equilibrium distribution in the generalized coordinate? The answer is already derived in between the LHS and the RHS in (3.50). It is

$$\tilde{\Phi}^{\mathrm{eq}}(q) = \mathcal{N}\sqrt{\left|\mathrm{M}_\parallel\right|}e^{-\beta U(q)} = \mathcal{N}\exp\left[-\beta\tilde{U}(q)\right], \tag{3.60}$$

where $\tilde{U}(q)$ is defined as

$$\tilde{U}(q) = U(q) - k_B T \ln\sqrt{\left|\mathrm{M}_\parallel\right|}. \tag{3.61}$$

We summarize the results obtained in this section.

coordinate	with momentum	without momentum
generalized	$\exp[-\beta H]$	$\exp\left[-\beta\tilde{U}(q)\right]$
Cartesian	$\delta(F_\mu)\delta(\dot{F}_\mu)\left\|\mathrm{M}_\perp^{-1}\right\|\exp[-\beta H]$	$\delta(F_\mu)\exp[-\beta U_{\mathrm{eff}}]$

3.4 Canonical classical mechanics

In and after this section, we consider dynamics with constraints. As a first step we revisit the canonical classical mechanics under the constraint conditions, which is now established firmly. The Hamiltonian of the system is given by (3.4) and dynamics is given by the Hamilton equation (3.6) and (3.7). Constraint conditions are given by (3.13). We employ the method of Lagrange multiplier to realize the constraint conditions. A way to treat the constraint condition within the Canonical formalism is first discussed by Dirac in 1950 [85]. The method of the Lagrange multiplier was originally developed for the Lagrange formalism. Dirac's motivation to extend it to the Hamilton formalism was to treat constraints within the canonical quantization. Our motivation to work on the canonical mechanics is to extend it to the underdamped Langevin equation. The underdamped Langevin equation is simply obtained by adding a friction term and a random force term to the canonical mechanics.

The Hamiltonian of the system is shifted by introducing the Lagrange multiplier λ^μ as

$$H_c(x,p,\lambda) = H(x,p) - \lambda^\mu F_\mu(x). \tag{3.62}$$

The time evolution of the constraint condition $F_\mu(x)$ is given by

$$\frac{dF_\mu(x)}{dt} = \{H, F_\mu(x)\} - \lambda^\nu \{F_\nu(x), F_\mu(x)\}. \tag{3.63}$$

Since we have assumed that the constraint conditions are functions of x only and do not depend on p. Then the Poisson bracket in the second term in the RHS of (3.63) vanishes.

$$\frac{dF_\mu(x)}{dt} = \{H, F_\mu(x)\} = \frac{\partial H}{\partial p_i}\frac{\partial F_\mu(x)}{\partial x_i}. \tag{3.64}$$

Because of the consistency condition that the constraint condition must hold time by time $\dot{F}_\mu = 0$. In the present case the RHS of (3.64) does not depend on λ^μ and one cannot determine λ^μ. In such situation one need to impose further consistency conditions called 'secondary constraint' [85], which in the present case is $\ddot{F}_\mu = 0$. By further differentiating the both side of (3.64) one has

$$\begin{aligned}\frac{d}{dt}\left(\frac{\partial H}{\partial p_i}\frac{\partial F_\mu(x)}{\partial x_i}\right) &= \left\{H_c, \frac{\partial H}{\partial p_i}\frac{\partial F_\mu(x)}{\partial x_i}\right\} \\ &= \left\{H, \dot{F}_\mu(x)\right\} - \lambda^\nu \left\{F_\nu, \frac{\partial H}{\partial p_i} e_{\nu,i}\right\} = 0. \end{aligned} \tag{3.65}$$

The Poisson bracket $\left\{F_\nu, \frac{\partial H}{\partial p_i} e_{\nu,i}\right\}$ is none-zero thus it can be solved to obtain λ^μ. This Poisson bracket can be computed by using the explicit form of the Hamiltonian given in (3.4) as

$$\left\{F_\nu, \frac{\partial H}{\partial p_i} e_{\mu,i}\right\} = -e_{\mu,i}\frac{\partial^2 H}{\partial p_i \partial p_j} e_{\nu,j} = -\left(\mathrm{M}_\perp^{-1}\right)_{\mu\nu}. \tag{3.66}$$

The RHS of (3.66) is invertible $M \times M$ matrix. Otherwise not all of M constraints are independent and thus reducible. We assume that this reduction has already been done. Then λ^μ is determined as,

$$\lambda^\mu = -\mathrm{M}_\perp^{\mu\nu}\left\{H, \dot{F}_\nu\right\}. \tag{3.67}$$

The Poisson bracket in the RHS of (3.67) is computed as

$$\left\{H, \dot{F}_\nu(x)\right\} = \dot{x}_i \dot{x}_k \frac{\partial e_{\nu,i}}{\partial x_k} - \frac{\partial U}{\partial x_i}\left(m^{-1}\right)_{ij} e_{\nu,j}. \tag{3.68}$$

Substituting (3.68) into (3.67) and substituting it to the equation of motion

$$\dot{x}_i = \{H_c, x_i\}, \quad \dot{p}_i = \{H_c, p_i\}, \tag{3.69}$$

yields the canonical dynamics with the constraint conditions.

$$\dot{x}_i = \left(m^{-1}\right)_{ij} p_j, \tag{3.70}$$

$$\dot{p}_i = P_{ij}^m\left(-\frac{\partial U}{\partial x_j}\right) - e_{\mu,i}\mathrm{M}_\perp^{\mu\nu}\frac{\partial e_{\nu,j}}{\partial x_k}\dot{x}_j\dot{x}_k. \tag{3.71}$$

This is the main result of this section. Note that the second equation can be also written as,

$$P_{ij}^m\left(\dot{p}_j + \frac{\partial U}{\partial x_j}\right) = 0. \tag{3.72}$$

This implies that virtual displacement perpendicular to the constraint surface does not produce any virtual work, which is somewhat similar to the d'Alembert principle. To arrive at (3.72) we have used the following relationship.

$$\ddot{F}_\mu(x) = 0 = \frac{\partial e_{\mu,i}}{\partial x_j}\dot{x}_i\dot{x}_j + e_{\mu,i}\ddot{x}_i. \tag{3.73}$$

Equations (3.70) and (3.71) can be derived also on the generalized coordinate since the mechanics can be handled within any choice of canonical degree of freedom. In the present case the intrinsic motion of the particle

takes place in $2(N-M)$ dimensional phase space spanned by q_α and its canonical conjugate π^α. Thus the equation of motion is given by

$$\dot{q}_\alpha = \{H, q_\alpha\}_{N-M}, \quad \dot{\pi}^\alpha = \{H, \pi^\alpha\}_{N-M}. \tag{3.74}$$

We note that in (3.74) the Poisson bracket is defined within the $2(N-M)$ dimensional phase space. Thus $\{A, B\}_{N-M} = \frac{\partial A}{\partial \pi^\alpha}\frac{\partial B}{\partial q_\alpha} - \frac{\partial A}{\partial q_\alpha}\frac{\partial B}{\partial \pi^\alpha}$. We introduce the Lagrange multiplier to increase the total degree of freedom, as

$$H_c = H - \lambda^\mu F_\mu \tag{3.75}$$

With new Hamiltonian H_c, the canonical equation of motion is given by

$$\begin{aligned}
\dot{q}_\alpha &= \{H_c, q_\alpha\} = \{H, q_\alpha\} - \lambda^\mu \{F_\mu, q_\alpha\} = \{H, q_\alpha\} && (3.76)\\
\dot{F}_\mu &= \{H_c, F_\mu\} = \{H, F_\mu\} - \lambda^\nu \{F_\nu, F_\mu\} = \{H, F_\mu\} && (3.77)\\
\dot{\pi}^\alpha &= \{H_c, \pi^\alpha\} = \{H, \pi^\alpha\} - \lambda^\mu \{F_\mu, \pi^\alpha\} = \{H, \pi^\alpha\} && (3.78)\\
\dot{\Pi}^\mu &= \{H_c, \Pi^\mu\} = \{H, \Pi^\mu\} - \lambda^\nu \{F_\nu, \Pi^\mu\} = \{H, \Pi^\mu\} + \lambda^\mu && (3.79)
\end{aligned}$$

Since (3.77) does not depend on the multiplier λ^μ, the consistency condition equation $\dot{F}_\mu = 0$ cannot determine the value of λ^μ as was the case in the Cartesian coordinate. Rather it is determined from $\ddot{F}_\mu = 0$. To use this condition within the canonical formalism one has to fix the basis according to Example 1. of Section 3.3. In this choice of the basis, as we have shown in (3.42) the canonical momentum with respect to the constraint condition F_μ vanishes. Thus equating the RHS of (3.79) with 0 one can determine λ^μ as

$$\lambda^\mu = -\{H, \Pi^\mu\}. \tag{3.80}$$

Since we are now working on $2N$ dimensional phase space, one can compute the Poisson bracket by means of (x, p), instead of (q, F, π, Π). Then the multiplier given in (3.80) is computed as,

$$\lambda^\mu = -\frac{\partial H}{\partial p_i}\frac{\partial \Pi^\mu}{\partial x_i} + \frac{\partial H}{\partial x_i}\frac{\partial \Pi^\mu}{\partial p_i} = -\left(m^{-1}\right)_{ij} p_j \frac{\partial e_k^\mu}{\partial x_i} p_k + e_i^\mu \frac{\partial U}{\partial x_i}. \tag{3.81}$$

Here we have made use of the relation $\Pi^\mu = e_i^\mu p_i$. Thus the canonical equation of motion for the Cartesian variables x and p is given by

$$\begin{aligned}
\dot{x}_i(t) &= \{H_c, x_i\} = \left(m^{-1}\right)_{ij} p_j && (3.82)\\
\dot{p}_i(t) &= \{H_c, p_i\} = \{H, p_i\} - \lambda^\mu \{F_\mu, p_i\} \\
&= -P_{ij}^m \frac{\partial U}{\partial x_j} - \frac{\partial H}{\partial p_j}\frac{\partial e_k^\mu}{\partial x_j} p_k e_{\mu,i}. && (3.83)
\end{aligned}$$

Here we have made use of the following relationship,

$$\{F_\mu, p_i\} = -e_{\mu,i}. \tag{3.84}$$

Equations (3.82) and (3.83) are identical with that have been derived within the Cartesian coordinate: (3.70) and (3.71).

In order to check that the Lagrange multiplier method is correctly working for the canonical Hamilton mechanics, we derive the Liouville equation for the distribution function defined by

$$\Psi(x,p,t) = \left\langle \prod_{i=1}^{N} \delta(x_i - x_i(t))\delta(p_i - p_i(t)) \right\rangle. \tag{3.85}$$

The stationary solution to the Liouville equation must be identical to the equilibrium distribution function (3.49) derived in Section 3.3. Note that in (3.85) we distinguish the solution of the equation of motion represented by $x_i(t)$ and $p_i(t)$ with the value of the field x_i and p_i. Continuity of the probability distribution function reads,

$$\frac{\partial \Psi(x,p,t)}{\partial t} = -\frac{\partial}{\partial x_i}\left(\dot{x}_i \Psi\right) - \frac{\partial}{\partial p_i}\left(\dot{p}_i \Psi\right). \tag{3.86}$$

Here $\dot{x}_i$ and $\dot{p}_i$ in the RHS of (3.86) means the value of $\dot{x}_i(x(t), p(t))$ and $\dot{p}_i(x(t), p(t))$ given by the RHS of (3.82) and (3.83) whose arguments are replaced by the field variables x_i and p_i. Then by using (3.82) and (3.83) one sees that the Liouville equation is given by

$$\frac{\partial \Psi}{\partial t} = -\frac{\partial H}{\partial p_i}\frac{\partial \Psi}{\partial x_i} + \frac{\partial \ln |\mathrm{M}_\perp|}{\partial x_i}\frac{\partial H}{\partial p_i}\Psi + \frac{\partial H}{\partial x_j}P^m_{ij}\frac{\partial \Psi}{\partial p_i} - \frac{\partial H}{\partial p_j}\frac{\partial P^m_{ik}p_k}{\partial x_j}\frac{\partial \Psi}{\partial p_i}. \tag{3.87}$$

One can check that the stationary solution to (3.87) is nothing but (3.49) derived independently within the equilibrium statistical mechanics. Thus, one sees that the method of Lagrange multiplier works correctly for the Hamilton mechanics, since it is consistent with the equilibrium statistical mechanics.

3.5 Underdamped Langevin equation

In this section we extend the method of the Lagrange multiplier to the canonical mechanics into the case with fluctuations. The governing equation is the underdamped Langevin equation given in (3.9) and (3.10). To take into account the constraint conditions (3.13) we introduce the Lagrange multiplier λ^μ and have

$$\dot{p}_i(t) = -\zeta_{ij}\dot{x}_j - \frac{\partial U}{\partial x_i} + \lambda^\mu \frac{\partial F_\mu(x)}{\partial x_i} + f_i(t). \tag{3.88}$$

The consistency conditions states that $\dot{F}_\mu = \dot{x}_i(t)e_{\mu,i} = 0$ and $\ddot{F}_\mu(x) = \ddot{x}_i e_{\mu,i} + \dot{x}_i\dot{x}_j\frac{\partial e_{\mu,i}}{\partial x_j} = 0$. As was the case with previous section the first conditions do not determine λ^μ. It is determined by the second conditions. By substituting (3.88) into the second conditions,

$$\lambda^\mu = -\mathrm{M}_\perp^{\mu\nu} e_{\nu,i} \left(m^{-1}\right)_{ij} \left(-\zeta_{jk}\dot{x}_k - \frac{\partial U}{\partial x_j} + f_j\right) + \mathrm{M}_\perp^{\mu\nu}\frac{\partial e_{\nu,i}}{\partial x_j}\dot{x}_i\dot{x}_j \tag{3.89}$$

Substituting back into (3.88) yields the results which is parallel to the canonical mechanics given by (3.71).

$$\dot{x}_i = \left(m^{-1}\right)_{ij} p_j, \tag{3.90}$$

$$\dot{p}_i = P^m_{ij}\left(-\zeta_{jk}\dot{x}_k - \frac{\partial U}{\partial x_j} + f_j\right) - e_{\mu,i}\mathrm{M}_\perp^{\mu\nu}\frac{\partial e_{\nu,j}}{\partial x_k}\dot{x}_j\dot{x}_k. \tag{3.91}$$

We note that since $\boldsymbol{P}^m$ depends on the value of x the random force term becomes multiplicative even if one start from the Langevin equation with additive noise. As shown in Appendix A.4, in the underdamped case, appearance of the multiplicative noise causes no difficulty but one has to be careful in taking the overdamp limit, as we have thoroughly described in Chapter 2. Computation of the overdamp limit will be carried out in Section 3.6.

We transform (3.90) and (3.91) into the generalized coordinate. It can be straightforwardly carried out by using the chain rule of the differentiation. By choosing the basis of the generalized coordinate according to Example 1 of Section 3.2 one can see that $\dot{F}_\mu$ and its canonical momentum $\dot{\Pi}^\mu$ vanishes. For the parallel counterpart, q_α and π^α,

$$\dot{q}_\alpha = \frac{\partial q_\alpha}{\partial x_i}\dot{x}_i = e_{\alpha,i}\left(m^{-1}\right)_{ij} p_j. \tag{3.92}$$

The canonical conjugate to q_α is defined as

$$\pi^\alpha = \mathrm{M}_\parallel^{\alpha\beta}\dot{q}_\beta. \tag{3.93}$$

Here $\mathrm{M}_\parallel^{\alpha\beta}$ is defined in (3.26). Substituting (3.92) into (3.93) gives,

$$\pi^\alpha = \mathrm{M}_\parallel^{\alpha\beta} e_{\beta,i}\left(m^{-1}\right)_{ij} p_j = e_i^\alpha p_i. \tag{3.94}$$

Here we have made use of the relation between e_i^α and $e_{\alpha,i}$, given in (3.25). Further differentiation with respect to time leads the equation of motion

within the parallel counterpart of the generalized coordinate. By using (3.91)

$$\begin{aligned}\dot{\pi}^\alpha &= e_i^\alpha \dot{p}_i + \dot{e}_i^\alpha p_i \\ &= e_i^\alpha \left\{ P_{ij}^m \left(-\zeta_{jk} \left(m^{-1}\right)_{kl} p_l - \frac{\partial U}{\partial x_j} + f_j \right) \right. \\ &\qquad \left. - e_{\mu,i} \mathrm{M}_\perp^{\mu\nu} \frac{\partial e_{\nu,j}}{\partial x_k} \dot{x}_j \dot{x}_k \right\} + \frac{\partial e_i^\alpha}{\partial q_\beta} \dot{q}_\beta p_i. \end{aligned} \tag{3.95}$$

Note that the last term in $\{\cdots\}$ in the RHS of (3.95) vanishes by the orthogonality condition (3.17). The last term in the RHS of (3.95) can be written as follows,

$$\frac{\partial e_i^\alpha}{\partial q_\beta} \dot{q}_\beta p_i = -\frac{1}{2} \pi^\beta \frac{\partial \left(\mathrm{M}_\parallel^{-1} \right)_{\beta\gamma}}{\partial q_\alpha} \pi^\gamma. \tag{3.96}$$

Proof By using the formula for a derivative of a matrix inverse, $(A^{-1})' = -A^{-1}A'A^{-1}$, and (3.93), the RHS of (3.96) becomes

$$-\frac{1}{2} \pi^\beta \frac{\partial \left(\mathrm{M}_\parallel^{-1} \right)_{\beta\gamma}}{\partial q_\alpha} \pi^\gamma = \frac{1}{2} \dot{q}_\beta \dot{q}_\gamma \frac{\partial \mathrm{M}_\parallel^{\beta\gamma}}{\partial q_\alpha} \tag{3.97}$$

Substitution of definition of $\mathrm{M}_\parallel^{\alpha\beta}$ given by (3.93) into the RHS of (3.97) shows

$$\frac{1}{2} \dot{q}_\beta \dot{q}_\gamma m_{ij} \left(\frac{\partial e_i^\beta}{\partial q_\alpha} e_j^\gamma + e_i^\beta \frac{\partial e_j^\gamma}{\partial q_\alpha} \right) = \dot{q}_\beta \frac{\partial e^\beta}{\partial q_\alpha} m_{ij} e_j^\gamma \dot{q}_\gamma. \tag{3.98}$$

Since we have assumed in Section 3.2 that there exists the global $q_\alpha(x)$, but not in differential form, one has $\frac{\partial e_i^\beta}{\partial q_\alpha} = \frac{\partial^2 x_i}{\partial q_\alpha \partial q_\beta} = \frac{\partial e_i^\alpha}{\partial q_\beta}$. Further by using the consistency condition here obeys $p_i = m_{ij} e_j^\gamma \dot{q}_\gamma$. By applying this to the RHS of (3.98) one arrives at (3.96). □

By using (3.96) and $e_i^\alpha P_{ij}^m = e_j^\alpha$, holds from the fact that e_i^α is a vector parallel to the constraint surface, we arrive at the final expression,

$$\dot{q}_\alpha = \left(\mathrm{M}_\parallel^{-1} \right)_{\alpha\beta} \pi^\beta, \tag{3.99}$$

$$\dot{\pi}^\alpha = -Z_\parallel^{\alpha\beta} \left(\mathrm{M}_\parallel^{-1} \right)_{\gamma\delta} \pi^\delta - \frac{\partial H}{\partial q_\alpha} + f_\parallel^\alpha. \tag{3.100}$$

Here we have defined

$$f_\parallel^\alpha(q,t) = e_i^\alpha f_i(t), \quad Z_\parallel^{\alpha\beta} = e_i^\alpha \zeta_{ij} e_j^\beta. \tag{3.101}$$

Note that in the RHS of (3.100), the force term is not given by the gradient of U but by the gradient of H. The difference caused by the existence of last term in the RHS of (3.95). These expressions are used to derive the overdamp limit in Section 3.6.

We translate the underdamped Langevin equation with constraint into the Kramers equation for the probability distribution function (3.85). The recipe to derive the Kramers equation from the underdamped Langevin equation is described in Appendix A.2. Applying the same recipe to (3.90) and (3.91) gives

$$\begin{aligned}\frac{\partial \Psi}{\partial t} &= -\frac{\partial H}{\partial p_i}\frac{\partial \Psi}{\partial x_i} + \frac{\partial \ln |\mathrm{M}_\perp|}{\partial x_i}\frac{\partial H}{\partial p_i}\Psi + \frac{\partial H}{\partial x_j}P^m_{ij}\frac{\partial \Psi}{\partial p_i} - \frac{\partial H}{\partial p_j}\frac{\partial P^m_{ik}p_k}{\partial x_j}\frac{\partial \Psi}{\partial p_i} \\ &\quad + \left[\mathbf{P}^m\boldsymbol{\zeta}\right]_{ij}\frac{\partial}{\partial p_i}\left[\left(\frac{\partial H}{\partial p_j}\Psi + k_BTP^m_{kj}\frac{\partial}{\partial p_k}\right)\Psi\right]. \qquad (3.102)\end{aligned}$$

The first line in the RHS of (3.102) is exactly same as the case without the fluctuation, see the Liouville equation (3.87) in Section 3.4. The second line represents an effect of the fluctuation. Each lines become 0 when one substitute the equilibrium distribution function Ψ^{eq} given in (3.49). Thus again the result is consistent with equilibrium statistical mechanics performed in Section 3.3.

For the distribution function in the generalized coordinate defined by

$$\tilde{\Psi}(q,\pi,t) \equiv \left\langle \prod_{\mu=1}^{N-M} \delta(q_\alpha - q_\alpha(t))\delta(\pi^\alpha - \pi^\alpha(t)) \right\rangle, \qquad (3.103)$$

one can derive the Kramers equation in the same manner from (3.99) and (3.100).

$$\frac{\partial \tilde{\Psi}}{\partial t} = -\left\{H, \tilde{\Psi}\right\}_{N-M} + Z^{\alpha\beta}_{\parallel}\left[\left(\mathrm{M}^{-1}\right)_{\beta\gamma}\frac{\partial}{\partial \pi^\alpha}\pi^\gamma + k_BT\frac{\partial^2}{\partial \pi^\alpha \partial \pi^\beta}\right]\tilde{\Psi}. \qquad (3.104)$$

The first term in the RHS of (3.104) represents the effect of deterministic evolution, while the second term appears from the introduction of the fluctuation. The stationary solution of (3.104) is correctly given by the equilibrium distribution function (3.46).

3.6 Overdamped Langevin equation

The method of the Lagrange multiplier, performed in Section 3.4 and 3.5 does not work for the overdamped Langevin equation given in (3.12). Instead, we

perform an adiabatic elimination of the momentum from the constrained underdamped Langevin equation obtained in Section 3.5.

In Subsection 3.6.1 we perform the direct adiabatic elimination of the momentum from the underdamped Langevin equation with constraints, by applying the method we have developed in Chapter 2. In Subsection 3.6.2 we give an alternative adiabatic elimination of the momentum, by going through the Fokker-Planck equation for probability distribution function. This method is more established than the direct adiabatic elimination on the Langevin equation, thus works as the test of the result obtained in Subsection 3.6.1. In Subsection 3.6.3 we try to impose the constraint conditions to the system without momentum. The p-spin spherical model is the example for such situation.

3.6.1 Direct adiabatic elimination from underdamped Langevin equation

The overdamp limit is an approximation justified in a time scale much longer than the relaxation time of momentum: τ_π. Since in such situation τ_π can be regarded as a small parameter, one can perform a power series expansion with respect to τ_π. As shown in Chapter 2 the correct overdamp limit is obtained by taking order of τ_π upto τ_π^1 in the formal solution to the underdamped Langevin equation. It is widely misunderstood that the overdamp limit is identical to ignoring inertial term in the underdamped Langevin equation. But this is true only when the noise term is additive. In the presence of the constraint condition the noise term becomes multiplicative, as in (3.91) or in (3.100). In such situation we have to be more faithful to the definition of the overdamp limit [86]. We calculate this 'faithful overdamp limit' within the generalized coordinate since it does not work within the Cartesian expression. Its reason will be explained in the end of the derivation.

We set $\Gamma^\alpha_\beta \equiv Z_\parallel^{\alpha\gamma}\left(\mathrm{M}_\parallel^{-1}\right)_{\gamma\beta}$. It governs the relaxation time of momentum π^α. As stated above this relaxation time plays a role of the small parameter in the overdamp limit. Roughly speaking one can regard the matrix $\mathbf{\Gamma}$ very large. More mathematically τ_π is the maximum eigenvalue of $\mathbf{\Gamma}^{-1}$ and it is assumed to be much smaller than any other time scales appearing in the overdamp limit. As shown in Chapter 2, for $t_2 > t$ and $t_2 - t \gg \tau_\pi$, there holds $q(t_2) - q(t) \sim \mathcal{O}(\tau_\pi)$. Thus we can expand any function of q, say $f(q)$

in powers of τ_π.

$$\begin{aligned} f(q(t_2)) &= f(q(t) + [q(t_2) - q(t)]) \\ &= f(q(t)) + [q_\gamma(t_2) - q_\gamma(t)] \frac{\partial f(q)}{\partial q_\gamma} + \mathcal{O}(\tau_\pi^2). \end{aligned} \tag{3.105}$$

First we apply this expansion to $\mathbf{\Gamma}(q(t_2))$.

$$\Gamma^\alpha_\beta(q(t_2)) = \Gamma^\alpha_\beta(q(t)) + [q_\gamma(t_2) - q_\gamma(t)] \frac{\partial \Gamma^\alpha_\beta}{\partial q_\gamma(t)} + \mathcal{O}(\tau_\pi). \tag{3.106}$$

We substitute this expansion (3.106) into the underdamped Langevin equation (3.100) with time t_2.

$$\begin{aligned} \dot{\pi}^\alpha(t_2) &= -\Gamma^\alpha_\beta(q(t))\pi^\beta(t_2) - [q_\gamma(t_2) - q_\gamma(t)] \frac{\partial \Gamma^\alpha_\beta}{\partial q_\gamma(t)} \pi^\beta(t_2) \\ &\quad - \frac{\partial H}{\partial q_\alpha(t_2)} + e^\alpha_i(q(t_2)) f_i(t_2). \end{aligned} \tag{3.107}$$

The formal solution to (3.107) is given by

$$\begin{aligned} \pi^\alpha(t_1) &= \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\Gamma(q(t))(t_1 - t_2)} \right]^\alpha_\beta \\ &\quad \times \left\{ [q_\gamma(t_2) - q_\gamma(t)] \frac{\partial \Gamma^\beta_\delta}{\partial q_\gamma(t)} \pi^\delta(t_2) - \frac{\partial H}{\partial q_\beta(t_2)} + e^\beta_i(q(t_2)) f_i(t_2) \right\}. \end{aligned} \tag{3.108}$$

Here we assumed that $t_1 > t_2 > t$. Hereafter we drop the argument of $\Gamma(q(t))$ in the exponential in the first line of (3.108). We discretize the formal solution to obtain $\Delta q_\alpha \equiv q_\alpha(t + \Delta t) - q_\alpha(t)$ in the overdamp limit. Then

$$\begin{aligned} \Delta q_\alpha(t) &\equiv q_\alpha(t + \Delta t) - q_\alpha(t) \\ &= \int_t^{t+\Delta t} dt_1 \dot{q}_\alpha(t_1) = \int_t^{t+\Delta t} dt_1 \left[\mathrm{M}^{-1}_\parallel(q(t_1)) \right]_{\alpha\beta} \pi^\beta(t_1), \end{aligned} \tag{3.109}$$

We assume that the time increment Δt is infinitesimal but at the same time it is much larger than τ_π. In other words we are working on the double limit, first taking $\tau_\pi \to 0$ and subsequently $\Delta t \to 0$. Thus $\Delta t \gg \tau_\pi$ holds. By substituting the formal solution (3.108) into (3.109) one has

$$\begin{aligned} \Delta q_\alpha &= \int_t^{t+\Delta t} dt_1 \left[\mathrm{M}^{-1}_\parallel(q(t_1)) \right]_{\alpha\beta} \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\Gamma(t_1 - t_2)} \right]^\beta_\gamma \\ &\quad \times \left\{ [q_\delta(t_2) - q_\delta(t)] \frac{\partial \Gamma^\gamma_\epsilon}{\partial q_\delta(t)} \pi^\epsilon(t_2) - \frac{\partial H}{\partial q_\gamma(t_2)} + e^\gamma_i(q(t_2)) f_i(t_2) \right\}. \end{aligned} \tag{3.110}$$

The purpose of the present subsection is to write the RHS of (3.110) as functions of $q(t)$. To this end we have to express $\left[\mathrm{M}_{\parallel}^{-1}(q(t_1))\right]_{\alpha\beta}$, $[q_\delta(t_2)-q_\delta(t)]$, $\pi^\epsilon(t_2)$ and $e_i^\gamma(q(t_2))$ in terms of $q(t)$. For $\left[\mathrm{M}_{\parallel}^{-1}(q(t_1))\right]_{\alpha\beta}$ and $e_i^\gamma(q(t_2))$ one can apply the expansion (3.105).

$$\left[\mathrm{M}_{\parallel}^{-1}(q(t_1))\right]_{\alpha\beta} = \left[\mathrm{M}_{\parallel}^{-1}(q(t))\right]_{\alpha\beta} + [q_\gamma(t_1)-q_\gamma(t)]\,\frac{\partial\left(\mathrm{M}_{\parallel}^{-1}\right)_{\alpha\beta}}{\partial q_\gamma(t)} + \cdots, \tag{3.111}$$

$$e_i^\gamma(q(t_2)) = e_i^\gamma(q(t)) + [q_\delta(t_1)-q_\delta(t)]\,\frac{\partial e_i^\gamma}{\partial q_\delta(t)} + \cdots. \tag{3.112}$$

For π^ϵ one can recursively substitute the formal solution (3.108) in the leading order. Since the multiplicative noise term is the leading power in the formal solution it reads,

$$\begin{aligned}\pi^\epsilon(t_2) &= \int_{-\infty}^{t_2} dt_5\,\left[\mathrm{e}^{-\Gamma(t_2-t_5)}\right]_\alpha^\delta e_k^\alpha(q(t_5))f_k(t_5) + \mathcal{O}(\tau_\pi)\\ &= \int_{-\infty}^{t_2} dt_5\,\left[\mathrm{e}^{-\Gamma(t_2-t_5)}\right]_\alpha^\delta e_k^\alpha(q(t))f_k(t_5) + \mathcal{O}(\tau_\pi).\end{aligned} \tag{3.113}$$

Here we have used the expansion of $e_i^\gamma(q(t_5))$ given in (3.112) from the fist line to the second line in (3.113). $[q_\delta(t_2)-q_\delta(t)]$ in the leading order is obtained by integrating the formal solution from t to t_2,

$$\begin{aligned}q_\delta(t_2)-q_\delta(t) &= \int_t^{t_2} dt_3\,\left[\mathrm{M}_{\parallel}^{-1}(q(t_3))\right]_{\delta\alpha}\int_{-\infty}^{t_3} dt_4\,\left[\mathrm{e}^{-\Gamma(t_3-t_4)}\right]_\beta^\alpha e_j^\beta(q(t))f_j(t_4) + \mathcal{O}(\tau_\pi^2)\\ &= \int_t^{t_2} dt_3\,\left[\mathrm{M}_{\parallel}^{-1}(q(t))\right]_{\delta\alpha}\int_{-\infty}^{t_3} dt_4\,\left[\mathrm{e}^{-\Gamma(t_3-t_4)}\right]_\beta^\alpha e_j^\beta(q(t))f_j(t_4) + \mathcal{O}(\tau_\pi^2).\end{aligned} \tag{3.114}$$

We have made use of expansion (3.111) from the first to second line of (3.114).

Substituting (3.111) into the formal solution (3.110) yields

$$\begin{aligned}\Delta q_\alpha = \left[\mathrm{M}_{\parallel}^{-1}(q(t))\right]_{\alpha\beta}\int_t^{t+\Delta t} dt_1\int_{-\infty}^{t_1} dt_2\,\left[\mathrm{e}^{-\Gamma(t_1-t_2)}\right]_\gamma^\beta \\ \times\left\{[q_\gamma(t_2)-q_\gamma(t)]\,\frac{\partial\Gamma_\delta^\gamma}{\partial q_\gamma(t)}\pi^\delta(t_2) - \frac{\partial H}{\partial q_\gamma(t_2)} + e_i^\gamma(q(t_2))f_i(t_2)\right\} + I^{m,\mathrm{Ito}},\end{aligned} \tag{3.115}$$

where we have defined $I^{m,\mathrm{Ito}}$ by

$$I^{m,\mathrm{Ito}} \equiv \frac{\partial\left(\mathrm{M}_{\parallel}^{-1}\right)_{\alpha\beta}}{\partial q_\gamma(t)} \int_t^{t+\Delta t} dt_1 \left[q_\gamma(t_1) - q_\gamma(t)\right] \times \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\Gamma(t_1-t_2)}\right]_\delta^\beta e_i^\delta(q(t_2)) f_i(t_2). \quad (3.116)$$

Applying the expansion of $e_i^\gamma(q(t_2))$ and $[q_\gamma(t_1) - q_\gamma(t)]$ given in (3.112) and (3.114), $I^{m,\mathrm{Ito}}$ becomes

$$\begin{aligned} I^{m,\mathrm{Ito}} &= \frac{\partial\left(\mathrm{M}_{\parallel}^{-1}\right)_{\alpha\beta}}{\partial q_\gamma(t)} \left[\mathrm{M}_{\parallel}^{-1}(q(t))\right]_{\gamma\delta} e_j^\epsilon(q(t)) e_i^\kappa(q(t)) \\ &\quad \times \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_3 \int_{-\infty}^{t_3} dt_4 \left[\mathrm{e}^{-\Gamma(t_3-t_4)}\right]_\epsilon^\delta f_j(t_4) \\ &\quad \times \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\Gamma(t_1-t_2)}\right]_\kappa^\beta f_i(t_2). \end{aligned} \quad (3.117)$$

Since the noise f_i is white Gaussian one can replace the quadratic term by their average, according to (3.11). The integration over t_2 leads,

$$\begin{aligned} I^{m,\mathrm{Ito}} &= 2T \frac{\partial\left(\mathrm{M}_{\parallel}^{-1}\right)_{\alpha\beta}}{\partial q_\gamma(t)} \left[\mathrm{M}_{\parallel}^{-1}(q(t))\right]_{\gamma\delta} \\ &\quad \times \int_t^{t+\Delta t} dt_1 \int_t^{t_1} dt_3 \int_{-\infty}^{t_3} dt_4 \left[\mathrm{e}^{-\Gamma(u-t_4)}\right]_\epsilon^\delta Z_{\parallel}^{\epsilon\kappa}(q(t)) \left[\mathrm{e}^{-\Gamma(t_1-t_4)}\right]_\kappa^\beta. \end{aligned} \quad (3.118)$$

The remaining integrals are performed by integration by parts to give

$$I^{m,\mathrm{Ito}} = k_B T \frac{\partial\left(\mathrm{M}_{\parallel}^{-1}\right)_{\alpha\beta}}{\partial q_\gamma(t)} \left[\mathrm{M}_{\parallel}^{-1}(q(t))\right]_{\gamma\delta} Z_{\parallel}^{\beta\delta}(q(t)) \Delta t. \quad (3.119)$$

Back to the formal solution (3.115), let us compute the correction term appeared from the expansion of $\mathbf{\Gamma}$. It comes from the first term in $\{\cdots\}$ in the

RHS of (3.115).

$$\begin{aligned}\Delta q_\alpha &= \left[\mathrm{M}_\parallel^{-1}(q(t))\right]_{\alpha\beta}\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\Gamma(t_1-t_2)}\right]_\gamma^\beta \\ &\qquad \times\left\{-\frac{\partial H}{\partial q_\gamma(t_2)} + e_i^\gamma(q(t_2))f_i(t_2)\right\} \\ &\quad + I^{m,\mathrm{Ito}} + I^{\Gamma,\mathrm{Ito}}. \qquad (3.120)\\ I^{\Gamma,\mathrm{Ito}} &\equiv \left[\mathrm{M}_\parallel^{-1}(q(t))\right]_{\alpha\beta}\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\Gamma(t_1-t_2)}\right]_\gamma^\beta \\ &\qquad \times [q_\gamma(t_2)-q_\gamma(t)]\,\frac{\partial\Gamma_\delta^\gamma}{\partial q_\gamma(t)}\pi^\delta(t_2). \qquad (3.121)\end{aligned}$$

The new correction term $I^{\Gamma,\mathrm{Ito}}$ can be computed exactly the same way as for $I^{m,\mathrm{Ito}}$. By substituting the lowest order approximation for $[q_\gamma(t_2)-q_\gamma(t)]$ and $\pi^\delta(t_2)$ given by (3.114) and (3.113) and performing the integral, one arrives at

$$I^{\Gamma,\mathrm{Ito}} = -k_BT\left(Z_\parallel^{-1}\right)_{\alpha\beta}\frac{\partial\left(\Gamma^{-1}\right)_\gamma^\beta}{\partial q_\delta}\left(\Gamma^{-1}\right)_\delta^\gamma\Delta t. \qquad (3.122)$$

Next we compute the term appears from the q-dependence of the kinetic energy in the Hamiltonian. Since the Hamiltonian is given in (3.45) we split it to the kinetic and the potential term and have

$$\begin{aligned}\Delta q_\alpha &= \left[\mathrm{M}_\parallel^{-1}(q(t))\right]_{\alpha\beta}\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\Gamma(t_1-t_2)}\right]_\gamma^\beta \\ &\qquad \times\left\{-\frac{\partial U}{\partial q_\gamma(t_2)} + e_i^\gamma(q(t_2))f_i(t_2)\right\} \\ &\quad + I^{m,\mathrm{Ito}} + I^{\Gamma,\mathrm{Ito}} + \Delta U, \qquad (3.123)\\ \Delta U &\equiv -\left[\mathrm{M}_\parallel^{-1}(q(t))\right]_{\alpha\beta}\int_t^{t+\Delta t} dt_1 \int_{-\infty}^{t_1} dt_2 \left[\mathrm{e}^{-\Gamma(t_1-t_2)}\right]_\gamma^\beta \\ &\qquad \times\pi^\delta(t_2)\frac{\partial\left(\mathrm{M}_\parallel^{-1}\right)_{\delta\epsilon}}{\partial q_\gamma(t_2)}\pi^\epsilon(t_2). \qquad (3.124)\end{aligned}$$

ΔU can be computed by substituting the $\pi^\delta(t_2)$ for the formal solution (3.113) and taking the leading order. The result is,

$$\Delta U = k_BT\left(Z_\parallel^{-1}\right)_{\alpha\beta}\left(\frac{\partial}{\partial q_\beta}\ln\left|\mathrm{M}_\parallel\right|^{1/2}\right)\Delta t. \qquad (3.125)$$

Finally we expand $e_i^\gamma(q(t_2))$ in the second line of (3.123) around $q(t)$. The correction term arisen from this expansion vanishes, as shown in [33]. In the

notation on Chapter 2 it corresponds to $I^{b,\mathrm{Ito}} = 0$. In general this correction term, appeared from the state-dependence of the multiplicative noise in the underdamped Langevin equation, drops whenever one starts from the white noise setting. Thus one can replace $e_i^\gamma(q(t_2))$ by $e_i^\gamma(q(t))$. This term becomes the multiplicative noise in the overdamped Langevin equation. Remaining term, contribution from the first term in $\{\cdots\}$ in the second line in (3.123) becomes $-\left[Z_\parallel^{-1}(q(t))\right]_{\alpha\beta}\frac{\partial U}{\partial q_\beta}\Delta t$. Then,

$$\begin{aligned}\Delta q_\alpha &= \left[Z_\parallel^{-1}(q(t))\right]_{\alpha\beta}\left(-\frac{\partial U}{\partial q_\beta(t)} + \Delta f_\parallel^\beta(q(t),t)\right) \\ &\quad + I^{m,\mathrm{Ito}} + I^{\Gamma,\mathrm{Ito}} + \Delta U \end{aligned} \tag{3.126}$$

$I^{m,\mathrm{Ito}}$ and part of $I^{\Gamma,\mathrm{Ito}}$ cancel together, as $I^{m,\mathrm{Ito}} + I^{\Gamma,\mathrm{Ito}} = k_B T\frac{\partial\left(Z_\parallel^{-1}\right)_{\alpha\beta}}{\partial q_\beta(t)}\Delta t$. The correction ΔU shift the potential term from U to $\tilde{U}$. Thus the final expression is

$$\begin{aligned}\Delta q_\alpha &= \left[Z_\parallel^{-1}(q(t))\right]_{\alpha\beta}\left(-\frac{\partial \tilde{U}}{\partial q_\beta}\Delta t + \Delta f_\parallel^\beta(q(t),t)\right) \\ &\quad + k_B T\frac{\partial\left(Z_\parallel^{-1}\right)_{\alpha\beta}}{\partial q_\beta}\Delta t \end{aligned} \tag{3.127}$$

$$\Delta f_\parallel^\beta(q(t),t) = e_i^\beta(q(t))\Delta f_i, \tag{3.128}$$

$$\Delta f_i \equiv \int_t^{t+\Delta t} dt_1 f_i(t_1), \tag{3.129}$$

$$\tilde{U} \equiv U - k_B T \ln\left|\mathrm{M}_\parallel\right|^{1/2} \tag{3.130}$$

Here the interpretation of the multiplicative noise in the RHS of (3.127) should be the Ito type, since the RHS of (3.127) is solely written in $q(t)$, the value of q before kicked by the noise and the force. This feature resulted from the expansion of $e_i^\gamma(q)$, $\Gamma_\beta^\alpha(q)$ and $\left[\mathrm{M}_\parallel(q)\right]_{\alpha\beta}$ according to (3.105). By changing the reference point at which the expansion is performed one can obtain the multiplicative noise in any interpretations [86]. The equivalent overdamped Langevin equation can be obtained from the adiabatic elimination of momentum through the Fokker-Planck equation. Indeed such procedure is carried out in the community of Brownian motion on curved manifolds [20]. We also carry out this calculation in the next subsection, for comparison. But we stress that our strategy is much simpler since we can directly obtain the overdamped Langevin equation from the underdamped Langevin equation.

The last term in the RHS of (3.127) is called the Ito drift. This term never appears by the "overdamp limit" by ignoring inertia in (3.100). This term is mandatory to guarantee that the equilibrium distribution is given by $\tilde{\Phi}^{\rm eq}(q) \propto \exp\left[-\beta\tilde{U}(q)\right]$, in accordance with the result obtained in purely static argument in Section 3.3, equation (3.60). Indeed, the corresponding Fokker-Planck equation for probability distribution function

$$\tilde{\Phi}(q,t) \equiv \left\langle \prod_{\alpha=1}^{N-M} \delta(q_\alpha - q_\alpha(t)) \right\rangle, \tag{3.131}$$

can be derived straightforwardly from (3.127) as,

$$\frac{\partial\tilde{\Phi}}{\partial t} = \frac{\partial}{\partial q_\alpha}\left[\left(Z_\parallel^{-1}\right)_{\alpha\beta}\left(\frac{\partial\tilde{U}}{\partial q_\beta} + k_BT\frac{\partial}{\partial q_\beta}\right)\tilde{\Phi}(q,t)\right]. \tag{3.132}$$

The equilibrium distribution is not given by $\exp[-\beta U(q)]$. This difference was caused from the factor $\sqrt{|\mathrm{M}_\parallel|}$ caused from the Gaussian integral over the momentum. See Section 3.3. When the space is not curved and $\boldsymbol{m}$ is constant it merely causes a multiplication of a constant, which can be absorbed into the normalization factor. On the other hand when the space is curved, $\mathbf{M}_\parallel$ is dependent on the position variable q and it is not a constant anymore. This is the static origin of the factor $\sqrt{|\mathrm{M}_\parallel|}$. In the dynamics, presented in this section it has its origin in the last term in the RHS of (3.95). It turned out to be a gradient of kinetic energy by the formula (3.96), produced the correction term ΔU in (3.124) in the overdamp limit, realizing the energy shift from U to $\tilde{U}$.

The Fokker-Planck equation (3.132) is identical with that obtained by BCAH by using the phase space kinetic theory [62], see Subsection 3.8.1. Thus, the Langevin equation which Öttinger [63,82] has derived from BCAH's Fokker-Planck equation must be identical with our overdamped Langevin equation (3.127) and indeed it is.

Note also that the overdamp limit (3.127) contains the inverse of friction matrix in the parallel coordinate $\boldsymbol{Z}_\parallel$. It means that in order for the whole calculation being successful $\boldsymbol{Z}_\parallel$ must be invertible. This condition is always satisfied since otherwise not all the constraint condition is independent and they can be reduced. A more important notice is that one cannot perform the calculation of the overdamp limit within the Cartesian coordinate. In the Cartesian coordinate, the underdamped Langevin equation is given by (3.91) where the friction force is projected onto the constraint surface by the projection operator $\boldsymbol{P}^m$. A projection operator is not a full rank matrix

and therefore does not have an inverse. As the result, the friction matrix projected onto the constraint surface cannot be inverted. This is the reason why we must switch to the generalized coordinate on taking the overdamp limit.

We perform a change of coordinate from the generalized coordinate to the Cartesian coordinate. One should be careful with a peculiar property of the overdamped Langevin equation driven by white noise, i.e., the chain rule of differentiation for a composite function does not hold. For the Ito type Langevin equation (3.127) the Ito formula must be applied to obtain the time evolution of $x_i(q)$ [49],

$$\begin{aligned} \Delta x_i &\equiv x_i(t+\Delta t) - x_i(t) \\ &= \frac{\partial x_i}{\partial q_\alpha}\Delta q_\alpha + \frac{1}{2}\frac{\partial^2 x_i}{\partial q_\alpha \partial q_\beta}\Delta q_\alpha \Delta q_\beta + \mathcal{O}(\Delta t^{3/2}). \end{aligned} \tag{3.133}$$

A proof of the Ito formula is given in Appendix A.1. In a nutshell this formula can be understood as follows. The second term in the RHS of (3.133) usually becomes $\mathcal{O}(\Delta t^2)$ and is negligible in $\Delta t \to 0$ limit. But in the present case whiteness of the noise leads $\Delta q \sim \Delta t^{1/2}$. Then Δq^2 starts from Δt and contribute to the RHS of (3.133). This term is sometimes called the Ito correction. By substituting (3.127) into the Ito formula (3.133),

$$\begin{aligned} \Delta x_i &= e_i^\alpha \left[\left(Z_\parallel^{-1}\right)_{\alpha\beta} \left(-\frac{\partial \tilde{U}}{\partial q_\beta} + \Delta f_\parallel^\beta(q,t) \right) + k_B T \frac{\partial \left(Z_\parallel^{-1}\right)_{\alpha\beta}}{\partial q_\beta}\Delta t \right] \\ &\quad + \frac{1}{2}\frac{\partial e_i^\alpha}{\partial q_\beta}\left(Z_\parallel^{-1}\right)_{\alpha\gamma}\Delta f_\parallel^\gamma \left(Z_\parallel^{-1}\right)_{\beta\delta}\Delta f_\parallel^\delta \end{aligned} \tag{3.134}$$

Let us compute the RHS piecewise. First $\left(Z_\parallel^{-1}\right)_{\alpha\beta}$ is the inverse of $(N-M)\times(N-M)$ matrix $Z_\parallel^{\alpha\beta}$ and can be written as

$$\left(Z_\parallel^{-1}\right)_{\alpha\beta} = e_{\alpha,i}\widetilde{L}_{ij}e_{\beta,j}, \tag{3.135}$$

Here we have introduced following notations.

$$\widetilde{L}_{ij} \equiv L_{ij} - L_{ik}e_{\mu,k}\left(\Lambda_\perp^{-1}\right)^{\mu\nu}e_{\nu,l}L_{lj}, \tag{3.136}$$

$$\Lambda_{\mu\nu}^\perp \equiv e_{\mu,i}L_{ij}e_{\nu,j}, \tag{3.137}$$

$$L_{ij} = \left(\zeta^{-1}\right)_{ij}. \tag{3.138}$$

Clearly $\widetilde{\boldsymbol{L}}$ is a rank $N-M$ symmetric matrix and will play a role of the Onsager coefficient in the system under the constraints.

Proof We define the $N \times N$ extension of $\boldsymbol{Z}_{\|}$.

$$Z^{ab} \equiv e_i^a \zeta_{ij} e_j^b = \begin{pmatrix} Z_{\|}^{\alpha\beta} & Z^{\alpha\nu} \\ Z^{\mu\beta} & Z_{\perp}^{\mu\nu} \end{pmatrix}. \tag{3.139}$$

It works as the friction coefficient transformed into the generalized coordinate. One can define the Onsager coefficient $\boldsymbol{L} = \boldsymbol{\zeta}^{-1}$ written in the generalized coordinate.

$$\Lambda^{ab} \equiv e_{a,i} L_{ij} e_{b,j} = \begin{pmatrix} \Lambda_{\alpha\beta}^{\|} & \Lambda_{\alpha\nu} \\ \Lambda_{\mu\beta} & \Lambda_{\mu\nu}^{\perp} \end{pmatrix}. \tag{3.140}$$

Since we have fixed the basis of the generalized coordinate according to Example 1 of Section 3.2 in (3.40), the mass matrix in the generalized coordinate $\mathbf{M}$ is block-diagonal. In general $\boldsymbol{m}$ and $\boldsymbol{\zeta}$ cannot be block diagonalized at the same time and therefore $\boldsymbol{Z}$ and $\boldsymbol{\Lambda}$ are not block-diagonal matrices. In fact these properties of $\boldsymbol{Z}$ and $\boldsymbol{\Lambda}$ are essential in deriving the formula (3.135). By the orthonormality conditions (3.16), (3.18) and (3.20) $\boldsymbol{Z}^{-1} = \boldsymbol{\Lambda}$ holds as the relation between $N \times N$ matrix. We use following formula for inverse of block matrix [87],

$$\begin{aligned} E &= \begin{pmatrix} A & B \\ C & D \end{pmatrix}, \qquad (3.141) \\ E^{-1} &= \begin{pmatrix} (A - BD^{-1}C)^{-1} & A^{-1}B\left(D - CA^{-1}B\right)^{-1} \\ -\left(D - CA^{-1}B\right)^{-1} CA^{-1} & \left(D - CA^{-1}B\right)^{-1} \end{pmatrix}, \end{aligned}$$

where A and D are assumed to be square matrices. By applying it to $\boldsymbol{E} = \boldsymbol{\Lambda}$, the upper left block becomes

$$Z_{\|}^{\alpha\beta} = \left[\Lambda_{\alpha\beta}^{\|} - \Lambda_{\alpha\mu}\left(\Lambda_{\perp}^{-1}\right)^{\mu\nu}\Lambda_{\nu\beta}\right]^{-1}. \tag{3.142}$$

By taking the inverse of both side of (3.142), inverse of $Z_{\|}^{\alpha\beta}$ as a $(N - M) \times (N - M)$ matrix is obtained as

$$\begin{aligned} \left(Z_{\|}^{-1}\right)_{\alpha\beta} &= \Lambda_{\alpha\beta}^{\|} - \Lambda_{\alpha\mu}\left(\Lambda_{\perp}^{-1}\right)^{\mu\nu}\Lambda_{\nu\beta} \\ &= e_{\alpha,i}\left[L_{ij} - L_{ik}e_{\mu,k}\left(\Lambda_{\perp}^{-1}\right)^{\mu\nu} e_{\nu,l}L_{lj}\right] e_{\beta,j} \\ &= e_{\alpha,i}\widetilde{L}_{ij}e_{\beta,j}. \end{aligned} \tag{3.143}$$

Thus the formula (3.136) was proven. □

By using this formula the term come from the gradient of the potential in the RHS of (3.134) is computed as

$$- e_i^\alpha \left(Z_\parallel^{-1}\right)_{\alpha\beta} \frac{\partial \tilde{U}}{\partial q_\beta} = -e_i^\alpha e_{\alpha,j} \widetilde{L}_{jk} e_{\beta,k} e_l^\beta \frac{\partial \tilde{U}}{\partial x_l}. \tag{3.144}$$

Using the relationships $e_{\beta,k}e_l^\beta = P_{kl}^m$ and $(\boldsymbol{P}^m)^\dagger \widetilde{\boldsymbol{L}} \boldsymbol{P}^m = \widetilde{\boldsymbol{L}}$ gives,

$$(3.144) = -\widetilde{L}_{ij}\frac{\partial \tilde{U}}{\partial x_j} = P_{ij}^L L_{jk} \left(-\frac{\partial \tilde{U}}{\partial x_l}\right) \tag{3.145}$$

Here P_{ij}^L is a slightly different projection operator from P_{ij}^m and defined as

$$P_{ij}^L \equiv \delta_{ij} - L_{ik} e_{\mu,k} \left(\Lambda_\perp^{-1}\right)^{\mu\nu} e_{\nu,j} \tag{3.146}$$

Quite surprisingly the projection operator appeared in the underdamped Langevin equation with constraint, $\boldsymbol{P}^m$, has been replaced by $\boldsymbol{P}^L$ in the overdamp limit. The root of this replacement is nothing but the formula (3.135).

Next we compute the multiplicative noise term appearing in the second term of the RHS of (3.134). Plugging the formula (3.135) and $\Delta f_\parallel^\alpha = e_i^\alpha \Delta f_i$, it becomes

$$\begin{aligned} e_i^\alpha \left(Z_\parallel^{-1}\right)_{\alpha\beta} \Delta f_\parallel^\beta(q,t) &= e_i^\alpha e_{\alpha,j} \widetilde{L}_{jk} e_{\beta,k} e_l^\beta \Delta f_l(t) \\ &= P_{ij}^L L_{jk} \Delta f_k(t). \end{aligned} \tag{3.147}$$

The Ito drift and the Ito correction terms in the RHS of (3.134) is calculated aside from the factor $k_B T \Delta t$,

$$\begin{aligned} e_i^\alpha \frac{\partial \left(Z_\parallel^{-1}\right)_{\alpha\beta}}{\partial q_\beta} + \frac{\partial e_i^\alpha}{\partial q_\beta}\left(Z_\parallel^{-1}\right)_{\alpha\beta} &= \frac{\partial e_i^\alpha \left(Z_\parallel^{-1}\right)_{\alpha\beta}}{\partial q_\beta} \\ &= \frac{\partial \widetilde{L}_{ij} e_{\beta,j}}{\partial q_\beta}. \end{aligned} \tag{3.148}$$

by $\Delta f_\parallel^\alpha \Delta f_\parallel^\beta = 2k_B T Z_\parallel^{\alpha\beta} \Delta t$, (3.135) and $(\boldsymbol{P}^m)^\dagger \widetilde{\boldsymbol{L}} = \widetilde{\boldsymbol{L}}$. Since the present purpose is to write down the RHS of (3.134) in terms of x we rewrite the derivative with respect to q with x.

$$\frac{\partial \widetilde{L}_{ij} e_{\beta,j}}{\partial q_\beta} = e_k^\beta \frac{\partial \widetilde{L}_{ij}}{\partial x_k} e_{\beta,j} + \widetilde{L}_{ij} e_k^\beta \frac{\partial e_{\beta,j}}{\partial x_k}. \tag{3.149}$$

The completeness condition (3.19) states that $e_k^\beta e_{\beta,j} = \delta_{kj} - e_k^\mu e_{\mu,j}$. Applying it to the first term in the RHS of (3.149), it becomes

$$\frac{\partial \widetilde{L}_{ij}}{\partial x_j} - e_{\mu,j} e_k^\mu \frac{\partial \widetilde{L}_{ij}}{\partial x_k} + \widetilde{L}_{ij} e_k^\beta \frac{\partial e_{\beta,j}}{\partial x_k}. \tag{3.150}$$

$\widetilde{\boldsymbol{L}}$ is parallel to the constraint surface while $e_{\mu,i}$ is perpendicular. Then $L_{ij} e_{\mu,j} = 0$ holds. By differentiating both side of this relation one has $\frac{\partial \widetilde{L}_{ij}}{\partial x_k} e_{\mu,j} = -\widetilde{L}_{ij} \frac{\partial e_{\mu,j}}{\partial x_k}$. Applying this relation to the second term in (3.150),

$$(3.150) = \frac{\partial \widetilde{L}_{ij}}{\partial x_j} + \widetilde{L}_{ij} e_k^\mu \frac{\partial e_{\mu,j}}{\partial x_k} + \widetilde{L}_{ij} e_k^\alpha \frac{\partial e_{\alpha,j}}{\partial x_k} = \frac{\partial \widetilde{L}_{ij}}{\partial x_j} + \widetilde{L}_{ij} e_k^a \frac{\partial e_{a,k}}{\partial x_j}. \tag{3.151}$$

The second term in the RHS of (3.151) can be transformed as

$$e_k^a \frac{\partial e_{a,k}}{\partial x_j} = \frac{1}{2} \frac{\partial}{\partial x_k} \ln \left| \mathrm{M}^{-1} \right|, \tag{3.152}$$

with $|\mathrm{M}^{-1}|$ being the determinant of $N \times N$ matrix $\mathbf{M}^{-1}$ defined in (3.40).

Proof By using the relation between superscript e_i^a and subscript $e_{a,i}$, $e_{a,k} = \left(\mathrm{M}^{-1}\right)_{ab} e_i^b m_{ik}$, the left hand side (LHS) of (3.152) becomes

$$\begin{aligned} e_k^a \frac{\partial e_{a,k}}{\partial x_j} &= e_k^a \frac{\partial}{\partial x_j} \left(\mathrm{M}^{-1}\right)_{ab} e_i^b m_{ik} \\ &= \mathrm{M}^{ab} \frac{\partial \left(\mathrm{M}^{-1}\right)_{ab}}{\partial x_k} + e_{a,k} \frac{\partial e_k^a}{\partial x_j}. \end{aligned} \tag{3.153}$$

Here we make use of the differentiation of both side of the relation $e_{a,k} e_k^a = N = \text{const.}$,

$$\frac{\partial e_{a,k}}{\partial x_j} e_k^a + e_{a,k} \frac{\partial e_k^a}{\partial x_j} = 0. \tag{3.154}$$

Then one sees that the LHS and the second term in the RHS of (3.153) are identical aside from their signs, we have

$$e_k^a \frac{\partial e_{a,k}}{\partial x_j} = \frac{1}{2} \mathrm{M}^{ab} \frac{\partial \left(\mathrm{M}^{-1}\right)_{ab}}{\partial x_k} = \frac{1}{2} \frac{\partial}{\partial x_k} \ln \left| \mathrm{M}^{-1} \right|. \tag{3.155}$$

From the second to the third expression we applied the following formula for a derivative of a determinant [87].

$$\frac{\partial}{\partial x} |A| = |A| \left(A^{-1}\right)_{ij} \frac{\partial A_{ij}}{\partial x}. \tag{3.156}$$

Then (3.152) was proven. □

Plugging (3.152) with (3.151), the Ito drift and the Ito correction terms are,

$$k_B T \frac{\partial \widetilde{L}_{ij}}{\partial x_k} \Delta t + \frac{k_B T}{2} \widetilde{L}_{ij} \frac{\partial}{\partial x_j} \ln \left| \mathrm{M}^{-1} \right| \Delta t. \tag{3.157}$$

Plugging (3.145), (3.147) and (3.157) with (3.134) gives

$$\begin{aligned} \Delta x_i &= P^L_{ij} L_{jk} \left(-\frac{\partial \tilde{U}}{\partial x_k} \Delta t + \Delta f_k \right) + k_B T \frac{\partial \widetilde{L}_{ij}}{\partial x_j} \Delta t \\ &\quad + \frac{k_B T}{2} \widetilde{L}_{ij} \frac{\partial}{\partial x_j} \ln \left| \mathrm{M}^{-1} \right| \Delta t. \end{aligned} \tag{3.158}$$

Part of the second line and the energy shift in $\tilde{U} = U - k_B T \ln \left| \mathrm{M}_{\parallel} \right|^{1/2}$ cancels together as $\left| \mathrm{M}_{\parallel} \right| \times |\mathrm{M}^{-1}| = \left| \mathrm{M}_{\perp}^{-1} \right|$. Then by taking the $\Delta t \to 0$ limit we have

$$\text{(I)} \quad \dot{x}_i = P^L_{ij}(x) L_{jk} \left(-\frac{\partial U_{\text{eff}}}{\partial x_k} + f_j(t) \right) + k_B T \frac{\partial P^L_{ik} L_{kj}}{\partial x_j}, \tag{3.159}$$

$$U_{\text{eff}} \equiv U - k_B T \ln \left| \mathrm{M}_{\perp}^{-1} \right|^{1/2}, \tag{3.160}$$

$$\left(\mathrm{M}_{\perp}^{-1} \right)_{\mu\nu} \equiv \frac{\partial F_\mu}{\partial x_i} \left(m^{-1} \right)_{ij} \frac{\partial F_\nu}{\partial x_j}. \tag{3.161}$$

Here (I) in (3.159) stands for the Ito stochastic differential equation. This equation is the overdamp limit of Brownian motion with constraint, which is the final destination of this chapter. Note that (3.159)–(3.161) are written within x_i and F_μ only and do not depend on the details of q_α. The Fokker-Planck equation for the probability distribution function

$$\Phi(x,t) = \left\langle \prod_{i=1}^{N} \delta(x_i - x_i(t)) \right\rangle, \tag{3.162}$$

corresponding to (3.159) reads,

$$\frac{\partial \Phi}{\partial t} = \frac{\partial}{\partial x_i} \left[\widetilde{L}_{ij} \left(\frac{\partial U_{\text{eff}}}{\partial x_j} + k_B T \frac{\partial}{\partial x_j} \right) \Phi(x,t) \right], \tag{3.163}$$

ensuring the stationary distribution $\Phi^{\text{eq}}(x) \propto \prod_{a=1}^{M} \delta(F_\mu(x)) \exp\left[-\beta U_{\text{eff}}(x)\right]$. Again this is consistent with the equilibrium distribution function extracted from the purely static argument, (3.59) of Section 3.2.

Throughout the chapter we have assumed that the friction matrix and the Onsager coefficient are constant for two reasons. One is just for simplicity. The second is to demonstrate that one inevitably faces the multiplicative noise by imposing the constraint condition even if one starts from the Langevin equation driven by the additive noise. But the whole calculation can be applied to the situation with the state-dependent friction coefficient. The result is simply given by replacing $\boldsymbol{L}$ with $\boldsymbol{L}(x) = \boldsymbol{\zeta}^{-1}(x)$ in (3.159).

3.6.2 Derivation from Fokker-Planck equation

In this subsection we perform the adiabatic elimination of momentum by going through the Fokker-Planck equation, not directly from the underdamped Langevin equation. The derivation is a roundabout since one has to switch to the representation within the probability distribution function. The merit of this procedure is that it is well established. We summarized an example of 1-dimensional case in Appendix B.2. We start from the Kramers equation, i.e., the Fokker-Planck equation for the underdamped Langevin equation, written in the generalized coordinate, given in (3.104). Here we rewrite it as,

$$\frac{\partial \tilde{\Psi}}{\partial t} = \left(L_1 + \epsilon^{-1} L_0\right) \tilde{\Psi}(q, p, t). \tag{3.164}$$

We have introduced operators L_1 and L_2 defined as,

$$L_1 \cdot \equiv - \left\{H, \cdot\right\}_{N-M}, \quad \epsilon^{-1} L_0 \cdot \equiv Z_{\parallel}^{\alpha\beta} \left[\left(\mathrm{M}_{\parallel}^{-1} \right)_{\beta\gamma} \frac{\partial}{\partial \pi^{\alpha}} \pi^{\gamma} + k_B T \frac{\partial^2}{\partial \pi^{\alpha} \partial \pi^{\beta}} \right]. \tag{3.165}$$

Here a small parameter ϵ is introduced to remind that friction coefficient $\boldsymbol{Z}_{\parallel}$ is large. According to the recipe of the adiabatic elimination presented in Appendix B.2 we define a projection operator onto the position space.

$$\mathcal{P} \equiv \rho^{\mathrm{eq}}(\pi, q) \int dp, \quad \rho^{\mathrm{eq}}(\pi, q) \equiv \frac{1}{\mathcal{N}_p(q)} \exp\left[-\beta K(q, \pi)\right] \tag{3.166}$$

$$\mathcal{N}_p(q) \equiv \int d\pi \exp\left[-\beta K(q, \pi)\right] = (2\pi T)^{(N-M)/2} \left| \mathrm{M}_{\parallel}(q) \right|^{1/2}. \tag{3.167}$$

One can easily check a qualification of the projection operator $\mathcal{P}^2 = \mathcal{P}$. In the present case the mass matrix is dependent of the position variables q, which was not the case in the simple case demonstrated in Appendix B.2 but the methodology itself works as well. We set $\mathcal{Q} = 1 - \mathcal{P}$. The standard procedure to project the dynamics to the fast and slow counterpart shows that the slow dynamics $v \equiv \mathcal{P}\tilde{\Psi} = \rho^{\mathrm{eq}}(\pi, q)\tilde{\Phi}(q, t)$ obeys the following equation of motion, in the leading order to the small parameter ϵ.

$$\frac{\partial v}{\partial t} = \left[A - BF^{-1}C\right] v. \tag{3.168}$$

For derivation see (B.25) of Appendix B.2 or literature [39, 88] or review [8]. Here we set $A = B = \mathcal{P}L_1$, $C = \mathcal{Q}L_1$ and $F = L_0$. Av in the RHS drops as we show in the 1-dimensional example in Appendix. Below we demonstrate the calculation of $BF^{-1}Cv$ in the second term of the RHS of (3.168). First,

Cv is by definition,

$$\begin{aligned} Cv &= \mathcal{Q}L_1\mathcal{P}\tilde{\Psi} = (1-\mathcal{P})\,L_1\mathcal{P}\tilde{\Psi} = L_1\mathcal{P}\tilde{\Psi} - Av = L_1\mathcal{P}\tilde{\Psi} \\ &= -\left\{H, \rho^{\mathrm{eq}}(\pi,q)\tilde{\Phi}(q,t)\right\} \\ &= -\left(\mathrm{M}_{\|}^{-1}\right)_{\alpha\beta}\pi^{\beta}\left[\frac{\partial\rho^{\mathrm{eq}}(\pi,q)}{\partial q_\alpha}\tilde{\Phi} + \rho^{\mathrm{eq}}(q,\pi)\frac{\partial\tilde{\Phi}}{\partial q_\alpha}\right] \\ &\quad + \left[\frac{1}{2}\pi^{\beta}\frac{\partial\left(\mathrm{M}_{\|}^{-1}\right)_{\beta\gamma}}{\partial q_\alpha}\pi^{\gamma} + \frac{\partial U}{\partial q_\alpha}\right]\frac{\partial\rho^{\mathrm{eq}}(\pi,q)}{\partial\pi^{\alpha}}\tilde{\Phi}. \end{aligned} \tag{3.169}$$

The derivatives of the Boltzmann distribution $\rho^{\mathrm{eq}}(\pi,q)$ with respect to q and π appearing the RHS of (3.169) are given by

$$\frac{\partial\rho^{\mathrm{eq}}}{\partial q_\alpha} = -\left[\frac{\beta}{2}\pi^{\gamma}\frac{\partial\left(\mathrm{M}_{\|}^{-1}\right)_{\gamma\delta}}{\partial q_\alpha}\pi^{\delta} + \frac{1}{2}\frac{\partial|\mathrm{M}_{\|}|}{\partial q_\alpha}\right]\rho^{\mathrm{eq}}(\pi,q), \tag{3.170}$$

$$\frac{\partial\rho^{\mathrm{eq}}}{\partial\pi^{\alpha}} = -\beta\left(\mathrm{M}_{\|}^{-1}\right)_{\alpha\beta}\pi^{\beta}\rho^{\mathrm{eq}}(\pi,q). \tag{3.171}$$

Thus plugging (3.170) and (3.171) into the RHS of (3.169) shows that the contributions from the first term in $[\cdots]$ in the last line of (3.169) and from the first term in $[\cdots]$ in the RHS of (3.170) cancel together. Thus

$$Cv = \left(\mathrm{M}_{\|}^{-1}\right)_{\alpha\beta}\pi^{\beta}\rho^{\mathrm{eq}}(q,\pi)\left(\frac{\partial\beta\tilde{U}}{\partial q_\alpha} + \frac{\partial}{\partial q_\alpha}\right)\tilde{\Phi}(q,t). \tag{3.172}$$

Here the appearance of $\tilde{U}$ (defined in (3.61)) instead of U is caused by the second term in the RHS of (3.170) and its origin is the q dependence of the mass matrix.

Now we proceed to the second step. We compute $F^{-1}Cv$ by applying F^{-1} to both side of (3.172).

$$F^{-1}Cv = L_0^{-1}\left(\mathrm{M}_{\|}^{-1}\right)_{\alpha\beta}\pi^{\beta}\rho^{\mathrm{eq}}(q,\pi)\left(\frac{\partial\beta\tilde{U}}{\partial q_\alpha} + \frac{\partial}{\partial q_\alpha}\right)\tilde{\Phi}(q,t) \tag{3.173}$$

Since L_0 is defined in (3.165) one sees that it only acts on the function of the momentum π and passes through the function of position q. Thus L_0^{-1} in the RHS of (3.173) acts on $\pi^{\beta}\rho^{\mathrm{eq}}(q,\pi)$ only. It can be heuristically solved by picking up the relevant pieces from (3.173) as

$$L_0^{-1}\pi^{\alpha}\rho^{\mathrm{eq}}(\pi,q) = -\left(\mathbf{M}_{\|}\boldsymbol{Z}_{\|}^{-1}\right)_{\beta}^{\alpha}\pi^{\beta}\rho^{\mathrm{eq}}(\pi,q). \tag{3.174}$$

One can easily check that by applying L_0 to both side of (3.174). Then $F^{-1}Cv$ is given by

$$F^{-1}Cv = -\left(Z_{\parallel}^{-1}\right)_{\alpha\beta}\pi^{\beta}\rho^{\rm eq}(\pi,q)\left(\frac{\partial\beta\tilde{U}}{\partial q_{\alpha}}+\frac{\partial}{\partial q_{\alpha}}\right)\tilde{\Phi}(q,t). \tag{3.175}$$

Finally, we operate B on both side of (3.175) to obtain $BF^{-1}Cv$. Since B is defined as $B\cdot = \rho^{\rm eq}(\pi,q)\int d\pi'\,\{H(q,\pi'),\cdot\}_{N-M}$,

$$\begin{aligned} BF^{-1}Cv &= \rho^{\rm eq}(\pi,q)\int d\pi\left\{H,\pi^{\beta}\rho^{\rm eq}(\pi,q)\left(Z_{\parallel}^{-1}\right)_{\alpha\beta}\left(\frac{\partial\beta\tilde{U}}{\partial q_{\alpha}}+\frac{\partial}{\partial q_{\alpha}}\right)\tilde{\Phi}(q,t)\right\}_{N-M} \\ &= \rho^{\rm eq}(\pi,q)\left\{\left[\int d\pi\frac{\partial H}{\partial\pi^{\gamma}}\pi^{\beta}\frac{\partial\rho^{\rm eq}}{\partial q_{\gamma}}\right]+\left[\int d\pi\frac{\partial H}{\partial\pi^{\gamma}}\pi^{\beta}\rho^{\rm eq}\frac{\partial}{\partial q_{\gamma}}\right]\right. \\ &\quad \left.+\left[\int d\pi\frac{\partial^2 H}{\partial\pi^{\gamma}\partial q_{\gamma}}\pi^{\beta}\rho^{\rm eq}\right]\right\}\left(Z_{\parallel}^{-1}\right)_{\alpha\beta}\left(\frac{\partial\beta\tilde{U}}{\partial q_{\alpha}}+\frac{\partial}{\partial q_{\alpha}}\right)\tilde{\Phi}(q,t). \end{aligned} \tag{3.176}$$

Here three $[\cdots]$s in $\{\cdots\}$ in the RHS of (3.176) becomes the Gaussian integrals.

$$\int d\pi\left(\mathrm{M}_{\parallel}^{-1}\right)_{\gamma\delta}\pi^{\delta}\pi^{\beta}\frac{\partial\rho^{\rm eq}}{\partial q_{\delta}} = \left(\mathrm{M}_{\parallel}^{-1}\right)_{\lambda\sigma}\frac{\partial}{\partial q_{\gamma}}\left[\int d\pi\pi^{\delta}\pi^{\beta}\rho^{\rm eq}\right], \tag{3.177}$$

$$\int d\pi\left(\mathrm{M}_{\parallel}^{-1}\right)_{\gamma\delta}\pi^{\delta}\pi^{\beta}\rho^{\rm eq}\frac{\partial}{\partial q_{\gamma}} = \left(\mathrm{M}_{\parallel}^{-1}\right)_{\gamma\delta}\left[\int d\pi\pi^{\delta}\pi^{\beta}\rho^{\rm eq}\right]\frac{\partial}{\partial q_{\gamma}}, \tag{3.178}$$

$$\int d\pi\frac{\partial\left(\mathrm{M}_{\parallel}^{-1}\right)_{\gamma\delta}}{\partial q_{\gamma}}\pi^{\delta}\pi^{\beta}\rho^{\rm eq} = \frac{\partial\left(\mathrm{M}_{\parallel}^{-1}\right)_{\gamma\delta}}{\partial q_{\gamma}}\left[\int d\pi\pi^{\delta}\pi^{\beta}\rho^{\rm eq}\right]. \tag{3.179}$$

Then by using the following Gaussian integral,

$$\int d\pi\pi^{\delta}\pi^{\beta}\rho^{\rm eq} = k_B T\mathrm{M}_{\parallel}^{\delta\beta}, \tag{3.180}$$

one sees that the contributions from (3.177) and (3.179) cancel and (3.176) becomes

$$BF^{-1}Cv = \rho^{\rm eq}(\pi,q)\frac{\partial}{\partial q_{\beta}}\left[\left(Z_{\parallel}^{-1}\right)_{\alpha\beta}\left(\frac{\partial\tilde{U}}{\partial q_{\alpha}}+k_B T\frac{\partial}{\partial q_{\alpha}}\right)\tilde{\Phi}(q,t)\right]. \tag{3.181}$$

Substitution of (3.181) and $Av = 0$ into (3.168) and using $v = \rho^{\rm eq}(\pi,q)\tilde{\Phi}(q,t)$ leads the final result.

$$\frac{\partial\tilde{\Phi}(q,t)}{\partial t} = \frac{\partial}{\partial q_{\alpha}}\left[\left(Z_{\parallel}^{-1}\right)_{\alpha\beta}\left(\frac{\partial\tilde{U}}{\partial q_{\beta}}+k_B T\frac{\partial}{\partial q_{\beta}}\right)\tilde{\Phi}(q,t)\right], \tag{3.182}$$

which is identical with our (3.132). Note that the derivation demonstrated in this subsection is also performed by Polettini very recently [20]. A more non-systematic procedure is found in [66].

3.6.3 Formulation for the system without momentum

In this subsection we consider how to impose the constraints to the model without momentum. The p-spin spherical model is the most important example of such situation. Apparently one cannot resort to the adiabatic elimination of momentum from the underdamped Langevin equation. We will show that in subsection 3.8.2 basically the Lagrange multiplier method does not work for the overdamped Langevin equation. In this subsection we try to propose a possible workaround.

Contrary to the preceding sections we have to make use of the correct equilibrium distribution function to derive the constrained Brownian motion. We *assume* that it is given by

$$\begin{aligned} \Phi^{\mathrm{eq}}(x) &= \mathcal{N}\delta(F_\mu(x))\sqrt{|D|}\exp\left[-\beta U\right] \\ &= \mathcal{N}\delta(F_\mu(x))\exp\left[-\beta U^{\mathrm{od}}_{\mathrm{eff}}\right] \qquad (3.183) \\ U^{\mathrm{od}}_{\mathrm{eff}} &\equiv U - \frac{1}{2}k_B T \ln|D| \qquad (3.184) \\ D_{\mu\nu} &= \frac{\partial F_\mu}{\partial x_i}\frac{\partial F_\nu}{\partial x_i}. \qquad (3.185) \end{aligned}$$

This equilibrium distribution is identical with (3.59) for a scalar mass matrix case. There are no justification to choose this form. In some special conditions this can be "derived" within the Lagrange multiplier, see Subsection 3.8.2. But in general the Lagrange multiplier method applied to the overdamp Langevin equation leads a completely insane Fokker-Planck equation, where one cannot even find a stationary solution. This is also presented in Subsection 3.8.2. It seems that in principle one has to assume the form of the equilibrium distribution function when one impose the constraints on the overdamped Langevin equation. When one start from the underdamped Langevin equation one has the equipartition theorem which ensures the Maxwell-Boltzmann distribution as an equilibrium distribution function. In the overdamp limit we do not have such a guiding principle. We deduce this is why we do need to postulate the form of the equilibrium distribution like (3.183).

We consider the discretized overdamped Langevin equation with the Onsager coefficient being matrix:

$$\Delta x_i = L_{ij}\left(-\frac{\partial U}{\partial x_j}\Delta t + \Delta f_j\right), \qquad (3.186)$$

where Δf_i satisfies

$$\langle \Delta f_i \rangle = 0, \quad \langle \Delta f_i \Delta f_j \rangle = 2k_B T \left(L^{-1}\right)_{ij} \Delta t. \tag{3.187}$$

L_{ij} is a constant Onsager coefficient which depends on index i, j. We assume that in the presence of the holonomic constraints (3.13) the Langevin equation should be modified as

$$\Delta x_i = L_{ij} \left[-\frac{\partial U_{\rm eff}^{\rm od}}{\partial x_j} \Delta t + \Delta f_j + \frac{\partial F_\mu}{\partial x_j} \left(\lambda^\mu \Delta t + \nu_k^\mu \Delta f_k \right) + B_i \Delta t \right]. \tag{3.188}$$

Note that the forces exerted by the constraint conditions, represented by the introduction of λ^μ and ν_i^μ are perpendicular to the constraint surface. While B_i can be arbitrary. The introduction of such correction is mandatory to reproduce the desired equilibrium distribution function. Note also that we have shifted $U \to U_{\rm eff}^{\rm od}$. The difference caused by this shift can be absorbed into the definition of B_i. We expand $\Delta F_\mu(x)$ upto $\mathcal{O}(\Delta t)$ by using the Ito formula (A.24),

$$\begin{aligned} \Delta F_\mu &= \frac{\partial F_\mu}{\partial x_i} \Delta x_i + \frac{\partial^2 F_\mu}{\partial x_i \partial x_j} \Delta x_i \Delta x_j + \mathcal{O}(\Delta t^{3/2}) \qquad (3.189) \\ &= e_{\mu,i} L_{ij} \left(\delta_{jk} + e_{\nu,j} \nu_k^\nu \right) \Delta f_k + e_{\mu,i} L_{ij} \left(-\frac{\partial H}{\partial x_j} + e_{\nu,j} \lambda^\nu + B_i \right) \Delta t \\ &\quad + k_B T \frac{\partial e_{\nu,i}}{\partial x_j} L_{il} (\delta_{lk} + e_{\nu,l} \nu_k^\nu) \left(L^{-1}\right)_{kn} L_{jm} (\delta_{mn} + e_{\lambda,m} \nu_n^\lambda) \Delta t \\ &\quad + \mathcal{O}(\Delta t^{3/2}). \end{aligned}$$

We assume the RHS of (3.189) becomes 0 in each order of $\Delta t^{1/2}$ and Δt, separately. Then we have from $\mathcal{O}(\Delta t^{1/2})$ terms,

$$e_{\mu,i} L_{ij} \left(\delta_{jk} + e_{\nu,j} \nu_k^\nu \right) = 0. \tag{3.190}$$

Thus ν_i^μ is determined as

$$\nu_i^\mu = - \left(\Lambda_\perp^{-1} \right)^{\mu\nu} e_{\nu,i} L_{ij}, \tag{3.191}$$

where $\Lambda_{\mu\nu}^\perp$ is given in (3.31). Then by correcting $\mathcal{O}(\Delta t)$ term in (3.189) we obtain

$$e_{\mu,i} L_{ij} \left(-\frac{\partial U_{\rm eff}^{\rm od}}{\partial x_j} + e_{\nu,j} \lambda^\nu + B_j \right) + k_B T \frac{\partial e_{\mu,i}}{\partial x_j} \widetilde{L}_{ij} = 0. \tag{3.192}$$

where $\widetilde{L}_{ij}$ is defined in (3.136). The solution of (3.192) is given by

$$\lambda^\mu = \left(\Lambda_\perp^{-1} \right)^{\mu\nu} \left(e_{\nu,i} L_{ij} \frac{\partial U_{\rm eff}^{\rm od}}{\partial x_j} - e_{\nu,i} L_{ij} B_j - k_B T \frac{\partial e_{\nu,i}}{\partial x_j} \widetilde{L}_{ij} \right). \tag{3.193}$$

Then substituting ν_i^μ and λ^μ given in (3.191) and (3.193) into (3.188) we have

$$\begin{aligned}\Delta x_i &= \widetilde{L}_{ij}\left[-\frac{\partial U_{\rm eff}^{\rm od}}{\partial x_j}\Delta t + \Delta f_j + B_j\Delta t\right] - k_BTL_{ij}e_{\mu,j}\left(\Lambda_\perp^{-1}\right)^{\mu\nu}\frac{\partial e_{\nu,k}}{\partial x_l}\widetilde{L}_{kl}\Delta t \\ &= \widetilde{L}_{ij}\left[-\frac{\partial U_{\rm eff}^{\rm od}}{\partial x_j}\Delta t + \Delta f_j + B_j\Delta t\right] + k_BT\frac{\partial\widetilde{L}_{ij}}{\partial x_l}\left(L^{-1}\right)_{jk}\widetilde{L}_{kl}\Delta t. \quad (3.194)\end{aligned}$$

Here we have used $\widetilde{L}_{ij}e_{\mu,j} = e_{\mu,j}\widetilde{L}_{ji} = 0$ between the first and the second line of (3.194). The corresponding Fokker-Planck equation can be derived as

$$\begin{aligned}\frac{\partial\Phi(x,t)}{\partial t} &= \frac{\partial}{\partial x_i}\left[\widetilde{L}_{ij}\left(\frac{\partial U_{\rm eff}^{\rm od}}{\partial x_j} + k_BT\frac{\partial}{\partial x_j}\right)\Phi(x,t)\right. \\ &\qquad \left.+\widetilde{L}_{ij}\left(k_BT\frac{\partial\left(P^L\right)_{jk}^\dagger}{\partial x_k} - B_j\right)\Phi(x,t)\right]. \quad (3.195)\end{aligned}$$

$\boldsymbol{P}^L$ is defined in (3.33). If the second line vanishes the stationary solution to (3.195) is given by (3.183). Then as a sufficient condition, B_i is determined as

$$B_i = k_BT\frac{\partial\left(P^L\right)_{ij}^\dagger}{\partial x_j}. \quad (3.196)$$

Thus plugging (3.196) back into (3.194), we arrive at the Langevin equation with constraint,

$$\Delta x_i = \widetilde{L}_{ij}\left[-\frac{\partial U_{\rm eff}^{\rm od}}{\partial x_j}\Delta t + \Delta f_j\right] + k_BT\frac{\partial\widetilde{L}_{ij}}{\partial x_j}\Delta t. \quad (3.197)$$

where we have used $\widetilde{\boldsymbol{L}}\boldsymbol{L}^{-1}\widetilde{\boldsymbol{L}} = \widetilde{\boldsymbol{L}}$. The Fokker-Planck equation for the probability distribution function is thus

$$\frac{\partial\Phi(x,t)}{\partial t} = \frac{\partial}{\partial x_i}\left[\widetilde{L}_{ij}\left(\frac{\partial U_{\rm eff}^{\rm od}}{\partial x_j} + k_BT\frac{\partial}{\partial x_j}\right)\Phi(x,t)\right]. \quad (3.198)$$

We derive the Langevin equation in the generalized coordinate $Q = \{F_\mu, q_\alpha\}$ as it is used in Chapter 4. By construction the Langevin equation for the constraint condition is trivially given by $\Delta F_\mu = 0$. The Ito formula (A.24) for $q_\alpha(x)$ reads

$$\Delta q_\alpha = \frac{\partial q_\alpha}{\partial x_i}\Delta x_i + \frac{1}{2}\frac{\partial^2 q_\alpha}{\partial x_i\partial x_j}\Delta x_i\Delta x_j + \mathcal{O}(t^{3/2}) \quad (3.199)$$

Substituting Δx_i given in (3.197) yields

$$\text{(I)} \quad \Delta q_\alpha = \mathcal{L}_{\alpha\beta}\left(-\frac{\partial \tilde{U}^{\rm od}_{\rm eff}}{\partial q_\beta}\Delta t + \Delta \widetilde{f}^\beta\right) + k_B T \frac{\partial \mathcal{L}_{\alpha\beta}}{\partial q_\beta}\Delta t. \tag{3.200}$$

Here we defined

$$\mathcal{L}_{\alpha\beta} \equiv e_{\alpha,i}\widetilde{L}_{ij}e_{\beta,j}, \tag{3.201}$$

$$\Delta\widetilde{f}^\alpha \equiv e_i^\alpha \Delta f_i. \tag{3.202}$$

and $\tilde{U}^{\rm od}_{\rm eff} \equiv U(q) - k_B T \ln\sqrt{|g|}$ with $|g| = \det g^{\alpha\beta}$, $g^{\alpha\beta} = e_i^\alpha e_i^\beta$. $\mathcal{L}_{\alpha\beta}$ satisfies the same relation with $\left(Z_\parallel^{-1}\right)_{\alpha\beta}$ in (3.135). In subsection 3.6.1 we have fixed the relation between e_i^α and $e_{\alpha,i}$ by using (3.25). On the other hand in this subsection we have not chosen any particular basis. Thus here we distinguish them. The Fokker-Planck equation is given by

$$\frac{\partial \tilde{\Phi}(q,t)}{\partial t} = \frac{\partial}{\partial q_\alpha}\left[\mathcal{L}_{\alpha\beta}\left(\frac{\partial \tilde{U}^{\rm od}_{\rm eff}}{\partial q_\beta} + k_B T\frac{\partial}{\partial q_\beta}\right)\tilde{\Phi}(q,t)\right]. \tag{3.203}$$

Thus the stationary solution is given by

$$\tilde{\Phi}^{\rm eq}(q) = \mathcal{N}\exp[-\beta \tilde{U}^{\rm od}_{\rm eff}(q)]. \tag{3.204}$$

If we restrict ourselves to the case with a scalar Onsager coefficient case, i.e., $L_{ij} = L\delta_{ij}$, (3.197) becomes when we adopt the Stratonovich convention,

$$\text{(S)} \quad \dot{x}_i = P_{ij}L\left(-\frac{\partial U^{\rm od}_{\rm eff}}{\partial x_j} + f_j\right) + k_B T L P_{ij}\frac{\partial P_{jk}}{\partial x_k}. \tag{3.205}$$

Here (S) means that the multiplicative noise in the RHS of (3.205) is interpreted in the Stratonovich convention. We make use of following relationship,

$$P_{ij}\frac{\partial}{\partial x_j}\ln\sqrt{|D_{\mu\nu}|} = -P_{ij}\frac{\partial P_{jk}}{\partial x_k}. \tag{3.206}$$

Then the last term in the RHS of (3.205) and the gradient of the determinant term come from $U^{\rm od}_{\rm eff} = U - k_B T\ln\sqrt{|D_{\mu\nu}|}$ cancel together and one arrives at a simple result.

$$\text{(S)} \quad \dot{x}_i = P_{ij}L\left(-\frac{\partial U}{\partial x_j} + f_j\right). \tag{3.207}$$

This is the overdamped Langevin equation under constraint, obtained firstly by Namiki and co-workers [22] by applying the method of Lagrange multiplier

to the overdamped Langevin equation with the scalar Onsager coefficient. A simple result sometimes captures the correct physics and leads to a useful insights, but in the present case (3.207) is a misleading result. As we have shown in the matrix Onsager coefficient case it never can be generalized into the matrix Onsager coefficient model as

$$\text{(S)} \quad \dot{x}_i = \widetilde{L}_{ij}\left(-\frac{\partial U}{\partial x_j} + f_j\right), \tag{3.208}$$

but as

$$\text{(S)} \quad \dot{x}_i = \widetilde{L}_{ij}\left(-\frac{\partial U^{\rm od}_{\rm eff}}{\partial x_j} + f_j\right) + k_B T P^L_{ij}\frac{\partial \widetilde{L}_{jk}}{\partial x_k}. \tag{3.209}$$

3.7 Extension to non-equilibrium case

We have shown in Chapter 2 that the computation of the overdamp limit can be extended into the arbitrary non-equilibrium situation. Here we demonstrate that our derivation of the constrained Brownian motion can be also extended into the non-equilibrium system. Consider the case we do not have the FDT (3.11). The Underdamped Langevin equation is given by

$$\dot{x}_i = \left(m^{-1}\right)_{ij} p_j, \tag{3.210}$$

$$\dot{p}_i = -\zeta_{ij}\dot{x}_j - \frac{\partial U}{\partial x_i} + b_{ij}\xi_j(t). \tag{3.211}$$

ξ_i is the white Gaussian noise given by

$$\langle \xi_i(t)\rangle = 0, \quad \langle \xi_i(t_2)\xi_j(t_2)\rangle = \delta_{ij}\delta(t_1 - t_2). \tag{3.212}$$

In equilibrium, the FDT holds.

$$\boldsymbol{b}\boldsymbol{b}^\dagger = 2k_B T\boldsymbol{\zeta}. \tag{3.213}$$

We impose the holonomic constraint conditions,

$$F_\mu(x) = 0, \quad \mu = 1, \ldots, M. \tag{3.214}$$

In order to take into account the effect of the constraint conditions we introduce the Lagrange multiplier λ^μ and modify equation of motion (3.211) as

$$\dot{p}_i = -\zeta_{ij}\dot{x}_j - \frac{\partial U}{\partial x_i} + \lambda^\mu \frac{\partial F_\mu}{\partial x_i} + b_{ij}\xi_j, \tag{3.215}$$

Hereafter we use

$$e_{\mu,i} \equiv \frac{\partial F_\mu}{\partial x_i}. \tag{3.216}$$

The consistency condition that the constraint conditions are satisfied at each time reads

$$\ddot{F}_\mu = e_{\mu,i}\ddot{x}_i + \frac{\partial e_{\mu,i}}{\partial x_j}\dot{x}_i\dot{x}_j = 0. \tag{3.217}$$

Substitute (3.215) for $\ddot{x}_i$ and one can determine λ^μ as

$$\lambda^\mu = -e_i^\mu \left(-\zeta_{ij}\dot{x}_j - \frac{\partial U}{\partial x_i} + b_{ij}\xi_j \right) - \mathrm{M}_\perp^{\mu\nu} \frac{\partial e_{\nu,i}}{\partial x_j}\dot{x}_i\dot{x}_j, \tag{3.218}$$

where,

$$\left(\mathrm{M}_\perp^{-1}\right)_{\mu\nu} \equiv e_{\mu,i}\left(m^{-1}\right)_{ij} e_{\nu,j}, \tag{3.219}$$

$$e_i^\mu \equiv \mathrm{M}_\perp^{\mu\nu} e_{\nu,j}\left(m^{-1}\right)_{ji}. \tag{3.220}$$

Thus substituting (3.218) back into (3.215) yields

$$\dot{p}_i = P_{ij}^m \left(-\zeta_{jk}\dot{x}_k - \frac{\partial U}{\partial x_j} + b_{jk}\xi_k \right) - e_{\mu,i}\mathrm{M}_\perp^{\mu\nu} \frac{\partial e_{\nu,i}}{\partial x_j}\dot{x}_i\dot{x}_j, \tag{3.221}$$

where,

$$P_{ij}^m \equiv \delta_{ij} - e_{\mu,i}e_j^\mu, \tag{3.222}$$

is a projection onto the constraint surface.

Now we perform the transformation into the generalized coordinate defined by $N - M$ independent coordinate and M constraint conditions. We use q_α, $\alpha = 1, \ldots, N - M$ for the former. q_αs are constructed as follows. We first define the basis vector parallel to the constraint surface,

$$e_i^\alpha \equiv \frac{\partial x_i}{\partial q_\alpha}, \tag{3.223}$$

so that they are orthogonal to $e_{\mu,i}$ defined in (3.216).

$$e_i^\alpha e_{\mu,i} = \frac{\partial x_i}{\partial q_\alpha}\frac{\partial F_\mu}{\partial x_i} = 0. \tag{3.224}$$

The reciprocal set of e_i^α are chosen as

$$e_{\alpha,i} \equiv \left(\mathrm{M}_\parallel^{-1}\right)_{\alpha\beta} e_j^\beta m_{ji}, \tag{3.225}$$

$$\mathrm{M}_\parallel^{\alpha\beta} \equiv e_i^\alpha m_{ij} e_j^\beta. \tag{3.226}$$

Thus the basis of the generalized coordinate is chosen according to Example 1 of Section 3.2. It is easy to show that the canonical momenta for q_α, say π^α is given by

$$\pi^\alpha \equiv \mathrm{M}_\parallel^{\alpha\beta}\dot{q}_\beta = e_i^\alpha p_i \tag{3.227}$$

Then by differentiating both side of (3.227) with respect to time one has

$$\begin{aligned}
\dot{\pi}^\alpha &= e_i^\alpha \dot{p}_i + \dot{e}_i^\alpha p_i \\
&= e_i^\alpha P_{ij}^m \left(-\zeta_{jk}\dot{x}_k - \frac{\partial U}{\partial x_j} + b_{jk}\xi_k\right) + \frac{\partial e_i^\alpha}{\partial q_\beta} p_i q_\beta \qquad (3.228)\\
&= -Z_\parallel^{\alpha\beta}\left(\mathrm{M}_\parallel^{-1}\right)_{\beta\gamma}\pi^\gamma - \frac{\partial H}{\partial q_\alpha} + e_i^\alpha b_{ij}\xi_j, \qquad (3.229)
\end{aligned}$$

where we have defined

$$\begin{aligned}
Z_\parallel^{\alpha\beta} &\equiv e_i^\alpha \zeta_{ij} e_j^\beta, \qquad (3.230)\\
H &= \frac{1}{2}\pi^\alpha \left(M_\parallel^{-1}\right)_{\alpha\beta}\pi^\beta + U(q). \qquad (3.231)
\end{aligned}$$

Note that the existence of the last term in (3.228) ensures the shift from $\frac{\partial U}{\partial x_j}$ to $\frac{\partial H}{\partial x_j}$ in between (3.228) and (3.229).

Next we calculate the overdamp limit without invoking the FDT (3.213). The procedure is almost the same as that performed in Chapter 2. As shown in Section 2.8 we need to request a condition for fluctuation $\boldsymbol{b}$ and dissipation $\boldsymbol{Z}$ in order for the system to have the overdamp limit, which is (2.173). In this case it reads

$$\mathcal{B}^{\alpha\beta} \equiv \left(\Gamma^{-1}\right)_\gamma^\alpha e_i^\gamma \left(\boldsymbol{b}\boldsymbol{b}^\dagger\right)_{ij} e_j^\beta = \mathcal{B}^{\beta\alpha}. \tag{3.232}$$

The final result is (2.176). In the present notations,

$$\begin{aligned}
\dot{q}_\alpha &= \left(Z_\parallel^{-1}\right)_{\alpha\beta}\left[-\frac{\partial U}{\partial q_\beta} - \frac{1}{2}\frac{\partial\left(\mathrm{M}_\parallel^{-1}\right)_{\gamma\delta}}{\partial q_\beta}\left(\boldsymbol{Z}_\parallel\boldsymbol{\mathcal{D}}_\parallel\mathbf{M}_\parallel\right)^{\gamma\delta} + e_i^\beta(q^*)b_{ij}\xi_j\right]\\
&\quad + \frac{\partial\left(Z_\parallel^{-1}\right)_{\alpha\beta}}{\partial q_\gamma}\left(\boldsymbol{Z}_\parallel\boldsymbol{\mathcal{D}}_\parallel\right)_\gamma^\beta - \alpha\frac{\partial\mathcal{G}_{\alpha,i}}{\partial q_\beta}\mathcal{G}_{\beta,i}. \qquad (3.233)
\end{aligned}$$

Here we have defined

$$\begin{aligned}
\mathcal{G}_{\alpha,i} &\equiv \left(Z_\parallel^{-1}\right)_{\alpha\beta} e_j^\beta b_{ji}, \qquad (3.234)\\
\left(\mathcal{D}_\parallel\right)_{\alpha\beta} &\equiv \frac{\mathcal{G}_{\alpha,i}\mathcal{G}_{\beta,i}}{2}. \qquad (3.235)
\end{aligned}$$

$\boldsymbol{\mathcal{D}}_\parallel$ plays a role of diffusion coefficient in equilibrium case and in equilibrium FDT (3.213) states that

$$\boldsymbol{Z}_\parallel \boldsymbol{\mathcal{D}}_\parallel = T\boldsymbol{\delta}, \tag{3.236}$$

which is the generalized Einstein relation. In equation (3.233) the multiplicative noise is interpreted in general α-convention[2] defined in Chapter 2.

As the final step we transform (3.233) back to the Cartesian coordinate. We make use of the Ito formula (A.22) for the change of coordinate,

$$\begin{aligned}
\dot{x}_i &= e_i^\alpha \dot{q}_\alpha + \frac{1-2\alpha}{2}\frac{\partial e_i^\alpha}{\partial q_\beta}\dot{q}_\alpha \dot{q}_\beta \qquad (3.237)\\
&= e_i^\alpha \left(Z_\parallel^{-1}\right)_{\alpha\beta}\left[-\frac{\partial U}{\partial q_\beta} - \frac{1}{2}\frac{\partial\left(\mathrm{M}_\parallel^{-1}\right)_{\gamma\delta}}{\partial q_\beta}\left(\boldsymbol{Z}_\parallel \boldsymbol{\mathcal{D}}_\parallel \mathbf{M}_\parallel\right)^{\gamma\delta} + e_j^\beta(q^*) b_{jk}\xi_k\right]\\
&\quad + e_i^\alpha \frac{\partial\left(Z_\parallel^{-1}\right)_{\alpha\beta}}{\partial q_\gamma}\left(\boldsymbol{Z}_\parallel \boldsymbol{\mathcal{D}}_\parallel\right)_\gamma^\beta - \alpha e_i^\alpha \frac{\partial \mathcal{G}_{\alpha,j}}{\partial q_\beta}\mathcal{G}_{\beta,j} + \frac{1-2\alpha}{2}\frac{\partial e_i^\alpha}{\partial q_\beta}\mathcal{G}_{\alpha,j}\mathcal{G}_{\beta,j}.
\end{aligned}$$

The first term in $[\cdots]$ in the RHS of (3.237) is

$$-e_i^\alpha \left(Z_\parallel^{-1}\right)_{\alpha\beta}\frac{\partial U}{\partial q_\beta} = -P_{ij}^L L_{jk}\frac{\partial U}{\partial x_k}, \tag{3.238}$$

by using following formulae

$$\left(Z_\parallel^{-1}\right)_{\alpha\beta} = e_{\alpha,i}\widetilde{L}_{ij}e_{\beta,j}, \tag{3.239}$$

$$(P^m)_{ij}^\dagger \widetilde{L}_{jk} = \widetilde{L}_{ik} = P_{ij}^L L_{jk}. \tag{3.240}$$

The first formula is proven in Subsection 3.6.1. $\boldsymbol{P}^L$ is defined in (3.33). Similarly the contribution from the second term in $[\cdots]$ in the RHS of (3.237) is

$$-\frac{1}{2}\widetilde{L}_{ij}\frac{\partial\left(\mathrm{M}_\parallel^{-1}\right)_{\alpha\beta}}{\partial x_j}\left(\boldsymbol{Z}_\parallel \boldsymbol{\mathcal{D}}_\parallel \mathbf{M}_\parallel\right)^{\alpha\beta}. \tag{3.241}$$

By using (3.230), (3.235) and (3.226) we have

$$\left(\boldsymbol{Z}_\parallel \boldsymbol{\mathcal{D}}_\parallel \mathbf{M}_\parallel\right)^{\alpha\beta} = e_k^\alpha \left(\boldsymbol{b}\boldsymbol{b}^\dagger\right)_{kl} e_l^\gamma \left(Z_\parallel^{-1}\right)_{\gamma\delta}\mathrm{M}_\parallel^{\delta\beta}, \tag{3.242}$$

[2]Note that α is already used in the index of the parallel component of the generalized coordinate. But we decided to use the same α in another meaning, since it does not cause any confusion.

is a symmetric matrix with respect to index $\alpha\beta$ by the condition (3.232). In a meanwhile, by (3.226),

$$\frac{\partial \left(\mathrm{M}_{\parallel}^{-1}\right)_{\alpha\beta}}{\partial x_j} = \frac{\partial e_{\alpha,m}}{\partial x_j} \left(m^{-1}\right)_{mn} e_{\beta,l} + (\alpha \leftrightarrow \beta) \tag{3.243}$$

Thus by symmetric property of (3.242) the first and second term in the RHS of (3.243) has the same contribution to (3.241). Then,

$$\begin{aligned} \frac{\partial \left(\mathrm{M}_{\parallel}^{-1}\right)_{\alpha\beta}}{\partial x_j} \left(\boldsymbol{Z}_{\parallel}\boldsymbol{\mathcal{D}}_{\parallel}\mathbf{M}_{\parallel}\right)^{\alpha\beta} &= \frac{\partial e_{\alpha,m}}{\partial x_j} \left(m^{-1}\right)_{mn} e_{\beta,n} e_k^{\alpha} \left(\boldsymbol{b}\boldsymbol{b}^{\dagger}\right)_{kl} e_l^{\gamma} \left(Z_{\parallel}^{-1}\right)_{\gamma\delta} \mathrm{M}_{\parallel}^{\delta\beta} \\ &= \frac{\partial e_{\alpha,k}}{\partial x_j} e_k^{\delta} \left(Z_{\parallel}^{-1}\right)_{\delta\gamma} e_l^{\gamma} \left(\boldsymbol{b}\boldsymbol{b}^{\dagger}\right)_{lm} e_m^{\alpha} \\ &= 2\frac{\partial e_{\alpha,k}}{\partial x_j} e_l^{\alpha} \left(\boldsymbol{P}^L \boldsymbol{D}\boldsymbol{\zeta}\right)_{kl}. \end{aligned} \tag{3.244}$$

by using (3.225), (3.239) and (3.240). We have defined the diffusion matrix in the Cartesian coordinate as

$$\boldsymbol{D} \equiv \frac{1}{2}\boldsymbol{\zeta}^{-1}\boldsymbol{b}\boldsymbol{b}^{\dagger}\boldsymbol{\zeta}^{-1}. \tag{3.245}$$

One can check that the generalized Einstein relation $\boldsymbol{D} = k_B T \boldsymbol{\zeta}^{-1}$ holds when the FDT (3.213) is applied. The the second term in $[\cdots]$ in (3.237) contribute to its RHS as

$$(3.241) = -\widetilde{L}_{ij} \frac{\partial e_{\alpha,k}}{\partial x_j} e_l^{\alpha} \left(\boldsymbol{P}^L \boldsymbol{D}\boldsymbol{\zeta}\right)_{kl}. \tag{3.246}$$

The third term in the RHS of (3.237) is the multiplicative noise projected onto the constraint surface. Now it is straightforward to show that

$$e_i^{\alpha} \left(Z_{\parallel}^{-1}\right)_{\alpha\beta} e_j^{\beta} b_{jk}\xi_k = P_{ij}^L(x^*) L_{jk} b_{kl} \xi_l. \tag{3.247}$$

The fourth term in the RHS of (3.237) is the contribution from so called the Ito drift. This term and part of last term becomes

$$e_i^{\alpha} \frac{\partial \left(Z_{\parallel}^{-1}\right)_{\alpha\beta}}{\partial q_{\gamma}} \left(\boldsymbol{Z}_{\parallel}\boldsymbol{\mathcal{D}}_{\parallel}\right)_{\gamma}^{\beta} + \frac{1}{2}\frac{\partial e_i^{\alpha}}{\partial q_{\beta}} \mathcal{G}_{\alpha,j}\mathcal{G}_{\alpha,j} = \left(\frac{\partial \widetilde{L}_{il}}{\partial x_k} + \widetilde{L}_{ij}\frac{\partial e_{a,k}}{\partial x_j} e_l^a\right) \left[\boldsymbol{P}^L \boldsymbol{D}\boldsymbol{\zeta}\right]_{kl}. \tag{3.248}$$

Proof First we change derivatives with respect to q to x and use (3.235).

$$\text{(LHS of (3.248))} = e_i^\alpha \frac{\partial \left(Z_\parallel^{-1}\right)_{\alpha\beta}}{\partial x_j} \left(\boldsymbol{Z}_\parallel \boldsymbol{\mathcal{D}}_\parallel\right)_\gamma^\beta e_j^\gamma + \frac{\partial e_i^\alpha}{\partial x_j} D_{\alpha\beta}^\parallel e_j^\beta. \quad (3.249)$$

Next by using (3.239),

$$\begin{aligned}(3.249) \;=\; & e_i^\alpha e_l^\gamma \frac{\partial e_{\alpha,k}}{\partial x_l} \widetilde{L}_{kj} e_{\beta,j} \left(\boldsymbol{Z}_\parallel \boldsymbol{\mathcal{D}}_\parallel\right)_\gamma^\beta + (P^m)_{ik}^\dagger \frac{\partial \widetilde{L}_{kj}}{\partial x_l} e_j^\beta e_l^\gamma \left(\boldsymbol{Z}_\parallel \boldsymbol{\mathcal{D}}_\parallel\right)_\gamma^\beta \\ & + \widetilde{L}_{ij} \frac{\partial e_{\beta,j}}{\partial x_k} e_k^\gamma \left(\boldsymbol{Z}_\parallel \boldsymbol{\mathcal{D}}_\parallel\right)_\gamma^\beta + \frac{\partial e_i^\alpha}{\partial x_j} D_{\alpha\beta}^\parallel e_j^\beta. \quad (3.250)\end{aligned}$$

We perform some side calculations. It is easy to show by using (3.235), (3.239) and (3.240) that

$$e_l^\gamma \left(\boldsymbol{Z}_\parallel \boldsymbol{\mathcal{D}}_\parallel\right)_\gamma^\beta e_{\beta,j} = \left[\boldsymbol{P}^L \boldsymbol{D\zeta} \left(\boldsymbol{P}^m\right)^\dagger\right]_{lj}, \quad (3.251)$$

and

$$D_{\alpha\beta}^\parallel = e_{\alpha,i} P_{ij}^L D_{jk} \left(P^L\right)_{kl}^\dagger e_{\beta,l}. \quad (3.252)$$

Thus applying (3.251) and (3.252) to (3.250) leads

$$\begin{aligned}(3.250) =& e_i^\alpha \frac{\partial e_{\alpha,j}}{\partial x_k} \left(\boldsymbol{P}^L \boldsymbol{D\zeta} \widetilde{\boldsymbol{L}}\right)_{kj} + (P^m)_{ik}^\dagger \frac{\partial \widetilde{L}_{kj}}{\partial x_l} \left[\boldsymbol{P}^L \boldsymbol{D\zeta} \left(\boldsymbol{P}^m\right)^\dagger\right]_{lj} \\ & + \widetilde{L}_{ij} \frac{\partial e_{\beta,j}}{\partial x_k} \left(\boldsymbol{P}^L \boldsymbol{D\zeta}\right)_{kl} e_l^\beta + \frac{\partial e_i^\alpha}{\partial x_j} e_{\alpha,k} \left[\boldsymbol{P}^L \boldsymbol{D} \left(\boldsymbol{P}^L\right)^\dagger\right]_{kj}. \quad (3.253)\end{aligned}$$

Gathering the first and fourth term and splitting $(P^m)_{ik}^\dagger = \delta_{ik} - e_i^\mu e_{\mu,k}$ in second term gives

$$\begin{aligned}(3.253) \;=\; & \frac{\partial P_{ki}^m}{\partial x_j} \left[\boldsymbol{P}^L \boldsymbol{D} \left(\boldsymbol{P}^L\right)^\dagger\right]_{kj} + \frac{\partial \widetilde{L}_{ij}}{\partial x_l} \left[\boldsymbol{P}^L \boldsymbol{D\zeta} \left(\boldsymbol{P}^m\right)^\dagger\right]_{lj} \\ & - e_i^\mu e_{\mu,k} \frac{\partial \widetilde{L}_{kj}}{\partial x_l} \left[\boldsymbol{P}^L \boldsymbol{D\zeta} \left(\boldsymbol{P}^m\right)^\dagger\right]_{lj} + \widetilde{L}_{ij} \frac{\partial e_{\beta,j}}{\partial x_k} \left(\boldsymbol{P}^L \boldsymbol{D\zeta}\right)_{kl} e_l^\beta. \quad (3.254)\end{aligned}$$

The first and third term cancel together as shown below. By differentiating $e_{\mu,k}\widetilde{L}_{kj} = 0$ with respect to x_l one has $e_{\mu,k}\frac{\partial \widetilde{L}_{kj}}{\partial x_l} = -\frac{\partial e_{\mu,k}}{\partial x_l}\widetilde{L}_{kj}$. Then the third term in the RHS of (3.254) becomes

$$e_i^\mu \frac{\partial e_{\mu,k}}{\partial x_l} \widetilde{L}_{kj} \left[\boldsymbol{P}^L \boldsymbol{D\zeta} \left(\boldsymbol{P}^m\right)^\dagger\right]_{lj} = e_i^\mu \frac{\partial e_{\mu,j}}{\partial x_k} \left[\boldsymbol{P}^L \boldsymbol{D} \left(\boldsymbol{P}^L\right)^\dagger\right]_{kj}. \quad (3.255)$$

Thus plugging with the first term in the RHS of (3.254)

$$\left[\boldsymbol{P}^L\boldsymbol{D}\left(\boldsymbol{P}^L\right)^\dagger\right]_{kj}\left(\frac{\partial P^m_{ki}}{\partial x_j}+e^\mu_i\frac{\partial e_{\mu,j}}{\partial x_k}\right)=-\left[\boldsymbol{P}^L\boldsymbol{D}\left(\boldsymbol{P}^L\right)^\dagger\right]_{kj}e_{\mu,k}\frac{\partial e^\mu_i}{\partial x_j}=0. \tag{3.256}$$

here we used $P^m_{ki}=\delta_{ki}-e_{\mu,k}e^\mu_i$ and P^L is orthogonal to $e_{\mu,k}$. Then (3.254) becomes much simpler as

$$(3.254)=\frac{\partial\widetilde{L}_{ij}}{\partial x_k}\left[\boldsymbol{P}^L\boldsymbol{D}\boldsymbol{\zeta}\left(\boldsymbol{P}^m\right)^\dagger\right]_{kj}+\widetilde{L}_{ij}\frac{\partial e_{\beta,j}}{\partial x_k}\left(\boldsymbol{P}^L\boldsymbol{D}\boldsymbol{\zeta}\right)_{kl}e^\beta_l \tag{3.257}$$

Finally we split $(P^m)^\dagger$ in the first term as $(P^m)^\dagger_{lj}=\delta_{lj}-e^\mu_l e_{\mu,j}$. Then

$$\begin{aligned}(3.257) &= \frac{\partial\widetilde{L}_{ij}}{\partial x_k}\left[\boldsymbol{P}^L\boldsymbol{D}\boldsymbol{\zeta}\right]_{kj}-\frac{\partial\widetilde{L}_{ij}}{\partial x_k}e_{\mu,j}\left[\boldsymbol{P}^L\boldsymbol{D}\boldsymbol{\zeta}\right]_{kl}e^\mu_l\\ &\quad+\widetilde{L}_{ij}\frac{\partial e_{\alpha,j}}{\partial x_k}\left(\boldsymbol{P}^L\boldsymbol{D}\boldsymbol{\zeta}\right)_{kl}e^\alpha_l\\ &= \frac{\partial\widetilde{L}_{ij}}{\partial x_k}\left[\boldsymbol{P}^L\boldsymbol{D}\boldsymbol{\zeta}\right]_{kj}+\widetilde{L}_{ij}\frac{\partial e_{a,k}}{\partial x_j}e^a_l\left(\boldsymbol{P}^L\boldsymbol{D}\boldsymbol{\zeta}\right)_{kl}. \qquad (3.258)\end{aligned}$$

Between the first and second line we again used $e_{\mu,k}\frac{\partial\widetilde{L}_{kj}}{\partial x_l}=-\frac{\partial e_{\mu,k}}{\partial x_l}\widetilde{L}_{kj}$. Now the proof of (3.248) has done. □

The remaining terms in the RHS of the overdamped Langevin equation in the Cartesian coordinate (3.237) are terms dependent of the interpretation of the multiplicative noise. They becomes

$$-\alpha e^\alpha_i\frac{\partial\mathcal{G}_{\alpha,j}}{\partial q_\beta}\mathcal{G}_{\beta,j}-2\alpha\frac{\partial e^\alpha_i}{\partial q_\beta}D^\parallel_{\alpha\beta}=-\alpha\frac{\partial\widetilde{g}_{il}}{\partial x_k}\widetilde{g}_{kl}. \tag{3.259}$$

Here we defined

$$\widetilde{\boldsymbol{g}}=\widetilde{\boldsymbol{L}}\boldsymbol{b}. \tag{3.260}$$

Proof First we write $\mathcal{G}_{\alpha,i}$ in terms of the Cartesian coordinate.

$$\begin{aligned}\mathcal{G}_{\alpha,i} &= \left(Z^{-1}_\parallel\right)_{\alpha\beta}e^\beta_j b_{ji}=e_{\alpha,k}\widetilde{L}_{kl}e_{\beta,l}e^\beta_j b_{ji}\\ &= e_{\alpha,k}\widetilde{L}_{kl}P^m_{lj}b_{ji}=e_{\alpha,k}\widetilde{L}_{kj}b_{ji}=e_{\alpha,k}\widetilde{g}_{ki}. \qquad (3.261)\end{aligned}$$

Thus the first term on the LHS of (3.259) becomes, aside from a factor

$-\alpha$,

$$\begin{aligned} e_i^\alpha \frac{\partial \mathcal{G}_{\alpha,j}}{\partial q_\beta} \mathcal{G}_{\beta,j} &= e_i^\alpha e_l^\beta \frac{\partial}{\partial x_l} \left[e_{\alpha,k} \widetilde{g}_{kj} \right] e_m^\beta \widetilde{g}_{mj} \\ &= e_i^\alpha \left[\frac{\partial e_{\alpha,k}}{\partial x_l} \widetilde{g}_{kj} + e_{\alpha,k} \frac{\partial \widetilde{g}_{kj}}{\partial x_l} \right] \widetilde{g}_{lj} \\ &= e_i^\alpha \frac{\partial e_{\alpha,k}}{\partial x_l} \left(\widetilde{\boldsymbol{g}} \widetilde{\boldsymbol{g}}^\dagger \right)_{kl} + \left(P^m \right)_{ik}^\dagger \frac{\partial \widetilde{g}_{kj}}{\partial x_l} \widetilde{g}_{lj}. \end{aligned} \tag{3.262}$$

The second term on the LHS of (3.259) is

$$-2\alpha \frac{\partial e_i^\alpha}{\partial q_\beta} D_{\alpha\beta}^{\parallel} = \frac{\partial e_i^\alpha}{\partial x_j} e_{\alpha,k} \left(\widetilde{\boldsymbol{g}} \widetilde{\boldsymbol{g}}^\dagger \right)_{kj}, \tag{3.263}$$

by using (3.252). Then plugging (3.262) and (3.263) with the LHS of (3.259)

$$\begin{aligned} & e_i^\alpha \frac{\partial e_{\alpha,k}}{\partial x_l} \left(\widetilde{\boldsymbol{g}} \widetilde{\boldsymbol{g}}^\dagger \right)_{kl} + \left(P^m \right)_{ik}^\dagger \frac{\partial \widetilde{g}_{kj}}{\partial x_l} \widetilde{g}_{lj} + \frac{\partial e_i^\alpha}{\partial x_j} e_{\alpha,k} \left(\widetilde{\boldsymbol{g}} \widetilde{\boldsymbol{g}}^\dagger \right)_{kj} \\ &= \frac{\partial \left(P^m \right)_{ik}^\dagger}{\partial x_l} \left(\widetilde{\boldsymbol{g}} \widetilde{\boldsymbol{g}}^\dagger \right)_{kl} + \left(P^m \right)_{ik}^\dagger \frac{\partial \widetilde{g}_{kj}}{\partial x_l} \widetilde{g}_{lj} \\ &= \frac{\partial}{\partial x_k} \left[\left(\boldsymbol{P}^m \right)^\dagger \widetilde{\boldsymbol{g}} \right]_{il} \widetilde{g}_{kl} = \frac{\partial \widetilde{g}_{ij}}{\partial x_k} \widetilde{g}_{kj}, \end{aligned} \tag{3.264}$$

which is the RHS of (3.259). □

Now gathering all pieces in the overdamped Langevin equation (3.237), i.e., (3.238), (3.244), (3.247), (3.248) and (3.259) one obtains

$$\begin{aligned} (\alpha) \quad \dot{x}_i &= P_{ij}^L(x^*) L_{jk} \left[-\frac{\partial U}{\partial x_k} + \frac{\partial e_{\mu,l}}{\partial x_k} e_m^\mu \left(\boldsymbol{P}^L \boldsymbol{D} \boldsymbol{\zeta} \right)_{lm} + b_{kl} \xi_l \right] \\ &\quad + \frac{\partial \widetilde{L}_{ij}}{\partial x_k} \left(\boldsymbol{P}^L \boldsymbol{D} \boldsymbol{\zeta} \right)_{kj} - \alpha \frac{\partial \widetilde{g}_{ij}}{\partial x_k} \widetilde{g}_{kj}. \end{aligned} \tag{3.265}$$

Here (α) stands for general α convention for the multiplicative noise. This expression becomes identical with the result obtained in Section 3.6 when the FDT $\boldsymbol{D}\boldsymbol{\zeta} = k_B T \boldsymbol{\delta}$ is applied, as it should be.

For the system with the temperature gradient one can make use of $\boldsymbol{b}\boldsymbol{b}^\dagger = 2k_B T(x)\boldsymbol{\zeta}$ and (3.265) becomes

$$\begin{aligned} (\mathrm{I}) \quad \dot{x}_i &= P_{ij}^L L_{jk} \left(-\frac{\partial U}{\partial x_k} + T(x) \frac{\partial}{\partial x_i} \ln \left| \mathrm{M}^{-1} \right| + b_{kl} \xi_l \right) \\ &\quad + k_B T(x) \frac{\partial P_{ik}^L L_{kj}}{\partial x_j}. \end{aligned} \tag{3.266}$$

It can be translated into the expression within the probability distribution function. If we ignore the external force, it becomes

$$\frac{\partial \Phi(x,t)}{\partial t} = \nabla_i \left[D_{ij} \nabla_j \Phi + D_{ij} \nabla_j \left| \mathrm{M} \right| + D^T_{ij} \nabla_j T(x) \right], \tag{3.267}$$

where we have defined

$$D_{ij} = k_B T(x) \widetilde{L}_{ij}, \tag{3.268}$$

$$D^T_{ij} = D_{ij} \rho / T(x). \tag{3.269}$$

(3.267) is the thermal diffusion equation under the holonomic constraint condition. As an illustrative example, the systems of polymers or DNAs under the temperature gradient are interested in the biophysics [89]. It is known that the thermal diffusion coefficient D^T is dependent of the length of the polymer and one can segregate them by using the thermal gradient.

3.8 Preceding studies

As we have described in the introduction the constrained Brownian motion is ubiquitous and has been formulated in several communities. In this section we introduce them and make comparisons with their results and ours. The results identical with each other are collected in the same subsection.

3.8.1 BCAH and Öttinger

Here we derive the Smoluchowski equation for the probability distribution function in the generalized coordinate, according to the literature [62, 82] on polymer dynamics. A more refined argument is found in a review [15].

The sketch of the derivation is as follows.

1. Write down the Liouville equation in the phase space where the motion of the polymers takes place, i.e., the generalized coordinate.

2. Extract the dynamical evolution of the average of the momentum π^α from the Liouville equation and equate the time derivative of $\langle \pi^\alpha \rangle$ to 0. This is corresponding to the overdamp limit since one is interested in the time scale after the momentum is relaxed and its average does not evolve with time.

3. Apply the underdamped Langevin equation in the curved space. It gives a constitutive relation between the macroscopic current and the mean velocity.

4. By joining the constitutive relation and continuity equation for $\tilde{\Phi}(q,t)$ one arrives at the Smoluchowski equation for the probability distribution function in the generalized coordinate.

The derivation is an extension of Smoluchowski equation within so called the phase space kinetic theory into the curved coordinate.

The Liouville equation for phase space variables q, π or continuity equation is given by,

$$\frac{\partial \tilde{\Psi}(\pi,q,t)}{\partial t} = -\frac{\partial}{\partial q_\alpha}\left(\dot{q}_\alpha \tilde{\Psi}(\pi,q,t)\right) - \frac{\partial}{\partial \pi^\alpha}\left(\dot{\pi}^\alpha \tilde{\Psi}(\pi,q,t)\right). \tag{3.270}$$

By taking the Maxwell average after multiplying π^α to the both side of (3.270) one obtains the dynamics of average of the momentum.

$$\frac{d\langle \pi^\alpha \rangle_{\mathrm{M}}}{dt} = \langle \dot{\pi}^\alpha \rangle_{\mathrm{M}} - \frac{k_B T}{\tilde{\Phi}(q)} \frac{\partial \tilde{\Phi}(q)}{\partial q_\alpha}. \tag{3.271}$$

Here $\langle \cdots \rangle_{\mathrm{M}} = \int d\pi \cdots \exp[-\beta K(\pi,q)]$ is the Maxwell average. The kinetic energy $K(\pi,q) = \frac{1}{2}\pi^\alpha \left(\mathrm{M}_\parallel^{-1}\right)_{\alpha\beta} \pi^\beta$ is the same as that we have employed in (3.44). Since we are interested in the overdamp limit, the average of the momentum does not evolve with time. Thus the LHS of (3.271) vanishes.

$$\langle \dot{\pi}^\alpha \rangle_{\mathrm{M}} - \frac{k_B T}{\tilde{\Phi}(q)} \frac{\partial \tilde{\Phi}(q)}{\partial q_\alpha} = 0. \tag{3.272}$$

One need to extract $\langle \dot{\pi}^\alpha \rangle$. $\dot{\pi}^\alpha$ is governed by the underdamped Langevin equation

$$\dot{\pi}^\alpha = -Z_\parallel^{\alpha\beta} \dot{q}_\beta - \frac{\partial H}{\partial q_\alpha} + \widetilde{f}^\alpha. \tag{3.273}$$

This is the same as our (3.100). By substituting (3.273) into (3.272),

$$-Z_\parallel^{\alpha\beta} \langle \dot{q}_\beta \rangle_{\mathrm{M}} - \frac{\partial}{\partial q_\alpha}\left[\tilde{U}(q) + k_B T \ln \tilde{\Phi}(q)\right] = 0, \tag{3.274}$$

where we have used the fact that $\left\langle \widetilde{f}^\alpha \right\rangle = 0$. One can solve it for $\langle \dot{q}_\alpha \rangle_{\mathrm{M}}$ as,

$$\langle \dot{q}_\alpha \rangle_{\mathrm{M}} = -\left(Z_\parallel^{-1}\right)_{\alpha\beta} \frac{\partial}{\partial q_\alpha}\left[\tilde{U}(q) + k_B T \ln \tilde{\Phi}(q)\right]. \tag{3.275}$$

This equation relates the macroscopic velocity $\langle \dot{q}_\alpha \rangle_{\mathrm{M}}$ with the thermodynamic force. This is nothing but what is called the constitutive relation. In a

meanwhile the continuity equation of the probability distribution function $\tilde{\Phi}(q,t)$ reads,

$$\frac{\partial \tilde{\Phi}(q,t)}{\partial t} = -\frac{\partial}{\partial q_\alpha}\left(\dot{q}_\alpha \tilde{\Phi}(q,t)\right). \tag{3.276}$$

Replacing $\dot{q}_\alpha$ in the RHS of (3.276) by the RHS of constitutive relation (3.275) one arrives at the Smoluchowski equation for the generalized coordinate.

$$\frac{\partial \tilde{\Phi}(q,t)}{\partial t} = \frac{\partial}{\partial q_\alpha}\left[\left(Z_\parallel^{-1}\right)_{\alpha\beta}\left(\frac{\partial \tilde{U}}{\partial q_\beta} + k_B T \frac{\partial}{\partial q_\beta}\right)\tilde{\Phi}(q,t)\right]. \tag{3.277}$$

The stationary solution to (3.277) gives the correct Boltzmann distribution (3.60). The Smoluchowski equation (3.277) is consistent with our (3.132). Thus BCAH's formulation is consistent with ours.

Öttinger wrote down the equivalent Langevin equation with the Smoluchowski equation (3.277) in [63, 82], which is identical with our result.

3.8.2 Namiki-Hołyst-Ciccotti-Lelievre

In this subsection we follow the derivation of the overdamped Langevin equation with the constraint conditions, proposed by Namiki and co-workers, who belong to the community of the stochastic quantization [22]. The identical results are reported in the membrane community [21] and the blue moon sampling community [23, 90–92]. The method presented by these authors looks working for scalar Onsager coefficient case. But it is just an accident and if one consider the model with matrix Onsager coefficient their method immediately leads to a failure. The starting overdamped Langevin equation is given by

$$\dot{x}_i = L\left(-\frac{\partial U}{\partial x_i} + f_i(t)\right). \tag{3.278}$$

L is the Onsager coefficient. f_i is the Gaussian white noise and obeys the FDT (3.11). We consider the holonomic constraint conditions given in (3.13) and introduce the Lagrange multiplier λ^μ to satisfy the constraints. Then (3.278) becomes

$$\dot{x}_i = -\frac{\partial U}{\partial x_i} + \lambda^\mu \frac{\partial F_\mu}{\partial x_i} + f_i, \tag{3.279}$$

We can determine the multiplier λ^μ by imposing $\dot{F}_\mu(x) = 0$. Throughout this subsection we choose the Stratonovich calculus so that we can make use of

the chain rule of differentiation. Then $\dot{F}_\mu$ can be evaluated as

$$\begin{aligned}\dot{F}_\mu &= \frac{\partial F_\mu}{\partial x_i}\dot{x}_i \\ &= \frac{\partial F_\mu}{\partial x_i} L\left(-\frac{\partial U}{\partial x_i} + \lambda^\nu \frac{\partial F_\nu}{\partial x_i} + f_i\right) = 0. \end{aligned} \tag{3.280}$$

Then one can determine λ^μ as

$$\lambda^\mu = -(D^{-1})^{\mu\nu} e_{\nu,i} L\left(-\frac{\partial U}{\partial x_i} + f_i\right), \tag{3.281}$$

where we have defined

$$e_{\mu,i} \equiv \frac{\partial F_\mu}{\partial x_i}, \quad D_{\mu\nu} \equiv e_{\mu,i} e_{\nu,i}. \tag{3.282}$$

Substituting λ^μ back into (3.279) reads

$$\text{(S)} \quad \dot{x}_i = P_{ij} L\left(-\frac{\partial U}{\partial x_j} + f_j\right). \tag{3.283}$$

P_{ij} acts as a projection onto constraint surface, defined by

$$P_{ij} \equiv \delta_{ij} - e_{\mu,i}(D^{-1})^{\mu\nu} e_{\nu,j}. \tag{3.284}$$

If one chooses the another rule to differentiate F_μ in (3.280), say Ito, one can obtain the same result when one employ the correct rule of differentiation (A.24).

One can derive the Fokker-Planck equation for probability distribution function defined in (3.162), as

$$\frac{\partial \Phi(x,t)}{\partial t} = \frac{\partial}{\partial x_i}\left[P_{ij} L\left(\frac{\partial U_{\text{eff}}^{\text{od}}}{\partial x_j} + k_B T \frac{\partial}{\partial x_j}\right)\Phi(x,t)\right]. \tag{3.285}$$

where $U_{\text{eff}}^{\text{od}}$ is defined in (3.184). The stationary solution to (3.285) is given by (3.183). Note that in the present derivation the stationary distribution is "derived" by a deductive argument. As we noticed in subsection 3.6.3 the stationary distribution should be given when one starts from the overdamped Langevin equation. Thus the present derivation is mysterious. We also note that the equilibrium distribution function is different from that we have obtained by the static argument (3.59). It explicitly depended on the mass matrix while $U_{\text{eff}}^{\text{od}}$ is not since the starting overdamped Langevin equation (3.278) does not contain the mass. Thus in principle U_{eff} cannot be reproduced when one tries to impose the constraint to the overdamped Langevin

equation. This inconsistency in the equilibrium distribution does not necessarily mean Namiki is wrong. But when one tries to extend the Namiki's formalism to the matrix Onsager coefficient case one inevitably fails. Let us check this. We start from the Langevin equation with the matrix Onsager coefficient given in (3.12). By introducing the Lagrange multiplier we have

$$\dot{x}_i = L_{ij}\left(-\frac{\partial U}{\partial x_j} + \lambda^\mu e_{\mu,j} + f_j(t)\right). \tag{3.286}$$

We employ the Stratonovich differential. The consistency relation $\dot{F}_\mu = 0$ determines the value of the multiplier as

$$\lambda^\mu = -\left(\Lambda_\perp^{-1}\right)^{\mu\nu} e_{\nu,i} L_{ij}\left(-\frac{\partial U}{\partial x_j} + f_j\right). \tag{3.287}$$

Here as defined in (3.31), $\Lambda^\perp_{\mu\nu} \equiv e_{\mu,i} L_{ij} e_{\nu,j}$. Substituting (3.287) back into (3.286) gives

$$\text{(S)} \quad \dot{x}_i = \widetilde{L}_{ij}\left(-\frac{\partial U}{\partial x_j} + f_j\right). \tag{3.288}$$

$\widetilde{\boldsymbol{L}}$ is defined in (3.136). The corresponding Fokker-Planck equation is derived as

$$\begin{aligned}\frac{\partial \Phi(x,t)}{\partial t} &= \frac{\partial}{\partial x_i}\left\{\widetilde{L}_{ij}\left[\frac{\partial U^{\rm od}_{\rm eff}}{\partial x_j} + k_B T \frac{\partial}{\partial x_j}\right.\right. \\ &\qquad \left.\left. + k_B T\left(\frac{\partial\left(\boldsymbol{P}^L - \boldsymbol{P}\right)_{jk}}{\partial x_k}\right)\right]\Phi(x,t)\right\}\end{aligned} \tag{3.289}$$

If the second line of (3.289) is not present, one can obtain the equilibrium distribution function (3.183), as was the case with scalar Onsager coefficient model. In fact when $L_{ij} = L\delta_{ij}$, one has $\boldsymbol{P}^L - \boldsymbol{P} = 0$ and the second line vanishes. The Onsager coefficient is purely dynamic quantity and it must not change the equilibrium thermodynamic property. Thus if one construct the correct theory, the same equilibrium distribution must be derived both from the scalar and the matrix Onsager coefficient model. Therefore Namiki's method is clearly wrong. This means that one cannot impose the constraint condition to the overdamped Langevin equation by using the Lagrange multiplier. In other words, the forces exerted by the constraints cannot be expressed by linear combinations of $\frac{\partial F_\mu}{\partial x_i}$, which are perpendicular to the constraint surface. We deduce that this property is something to do with the non-covariance of overdamped Langevin equation or Smoluchowski equation. But so far we do not have a clear answer why Namiki's method fails.

3.8.3 Peters

In his thesis Peters has applied the heuristic argument proposed by Hasegawa [42] and Sancho et al. [41] to derive the overdamped Langevin equation with constraint [43]. The heuristic argument is reviewed in the Appendix B.3. We here describe its assertion briefly. It states that the overdamp limit can be taken by the following manner, from the underdamped Langevin equation driven by the multiplicative noise and the state-dependent friction coefficient.

1. Ignore the inertial term in the underdamped Langevin equation.
2. Interpret the multiplicative noise in the underdamped Langevin equation by the Ito convention.
3. The state-dependent friction coefficient is interpreted in the Stratonovich convention.

In order to combine the method of Lagrange multiplier with the heuristic argument Peters introduced a multiplier to the underdamped Langevin equation to project the noise term onto the constraint surface. Somehow the other forces, the friction and the external force, are not projected at this point. Subsequently he took the overdamp limit according to the heuristic argument and after that he again projected the forces onto the constraint surface. His method gives the correct result, as we will show, but apparently there is no reason to project the dynamics in twice. The procedure is already heuristic on taking the overdamp limit, but not only that, his implementation of the constraint makes the derivation more heuristic.

Below we follow the derivation by Peters. We start from the underdamp Langevin equation given in (3.9) and (3.10). We introduce the Lagrange multiplier in order to satisfy the constraint condition (3.13).

$$\dot{p}_i(t) = -\zeta_{ij}\dot{x}_j - \frac{\partial U}{\partial x_i} + \lambda^\mu_{\rm s}\frac{\partial F_\mu(x)}{\partial x_i} + f_i(t). \tag{3.290}$$

Here a subscript "s" in $\lambda^\mu_{\rm s}$ means that the multiplier is introduced to project the stochastic term and is different from our λ^μ in Section 3.5. The consistency condition states that

$$\begin{aligned}
\ddot{F}_\mu &= \frac{\partial e_{\mu,i}}{\partial x_j}\dot{x}_i\dot{x}_j + e_{\mu,i}\ddot{x}_i \\
&= \frac{\partial e_{\mu,i}}{\partial x_j}\dot{x}_i\dot{x}_j + e_{\mu,i}\left(m^{-1}\right)_{ij}\left(-\zeta_{jk}\dot{x}_k - \frac{\partial U}{\partial x_j} + \lambda^\nu_{\rm s}e_{\nu,j} + f_j\right) \\
&= 0.
\end{aligned} \tag{3.291}$$

$\dot{x}$ starts from $\mathcal{O}(\Delta t^{1/2})$ when it is discretized. The leading contribution comes from the white noise term. In (3.291) it is the last term in $(\cdots)$ in the second line. By assuming that the constraint condition is satisfied within order of $\Delta t^{1/2}$ one has

$$e_{\mu,i}\left(m^{-1}\right)_{ij}\left(\lambda_{\rm s}^{\nu}e_{\nu,j}+f_j\right)=0. \tag{3.292}$$

Since we assumed that $\lambda_{\rm s}^{\mu}$ corresponds to the stochastic term, it is $\mathcal{O}(\Delta t^{1/2})$. Then the multiplier is given by,

$$\lambda_{\rm s}^{\mu}=-{\rm M}_{\perp}^{\mu\nu}e_{\nu,i}\left(m^{-1}\right)_{ij}f_j. \tag{3.293}$$

Substituting (3.293) back into (3.290) yields

$$\dot{p}_i(t)=-\zeta_{ij}\dot{x}_j-\frac{\partial U}{\partial x_i}+P_{ij}^{m}f_j. \tag{3.294}$$

The projection operator $\boldsymbol{P}^m$ is given by $P_{ij}^m=\delta_{ij}-e_{\mu,i}{\rm M}^{\mu\nu}e_{\nu,k}\left(m^{-1}\right)_{kj}$, which is the same as our (3.24). Next we take the overdamp limit from (3.294) according to the heuristic argument. It reads,

$$\Delta x_i=\left(\zeta^{-1}\right)_{ij}\circ\left(-\frac{\partial U}{\partial x_j}\Delta t+P_{jk}^{m}\Delta f_k\right) \tag{3.295}$$

We have assumed in this chapter that ζ_{ij} is constant but the whole derivation can be straightforwardly extended to the case with the state-dependent $\zeta_{ij}(x)$. Peters intended to formulate the constrained Brownian motion to apply it to the dynamics of polymer solution. In polymer solution one should take into account the hydrodynamic interaction between polymers or monomers. Since the hydrodynamic interaction leads to the state-dependent friction matrix Peters considered such model from the beginning. We here follow him and assume that friction matrix depend on x. In (3.295) $\circ$ on ζ^{-1}'s right means that $\zeta^{-1}(x)$ is interpreted in the Stratonovich sense, by the rule 3 of the heuristic argument. P_{jk}^m in the RHS of (3.295) is interpreted in the Ito sense by rule 2. We introduce a new Lagrange multiplier to satisfy the constraint condition in $\mathcal{O}(\Delta t)$.

$$\Delta x_i=\left(\zeta^{-1}(x)\right)_{ij}\circ\left(-\frac{\partial U}{\partial x_j}\Delta t+\lambda_{\rm od}^{\mu}e_{\mu,j}\Delta t+P_{jk}^{m}\Delta f_k\right). \tag{3.296}$$

Here $\lambda_{\rm od}^{\mu}$ is a new Lagrange multiplier to be determined by using the consistency condition $\Delta F_\mu=0$. One has to choose a consistent formula to differentiate such composite function, according to the Ito formula (A.24). Here the interpretation of the multiplicative noise is given in Ito-Stratonovich mixed

manner in (3.296). We do not know how (A.24) is generalized in such case. But somehow Peters has adopted the Stratonovich differentiation. Following him,

$$\Delta F_\mu = e_{\mu,i}\Delta x_i = e_{\mu,i}\left(\zeta^{-1}(x)\right)_{ij} \circ \left(-\frac{\partial U}{\partial x_j}\Delta t + \lambda^\mu_{\rm od} e_{\mu,i}\Delta t + P^m_{ij}\Delta f_j\right) = 0. \tag{3.297}$$

Then one can obtain the value of the multiplier as

$$\lambda^\mu_{\rm od}\Delta t = -\Lambda^{\mu\nu}_\perp e_{\nu,i}\left(\zeta^{-1}\right)_{ij} \circ \left(\frac{\partial U}{\partial x_j}\Delta t + P^m_{ij}\Delta f_j\right) \tag{3.298}$$

Again substituting it back into (3.296) leads,

$$\Delta x_i = \widetilde{L}_{ij} \circ \left(-\frac{\partial U}{\partial x_j}\Delta t + P^m_{ij}\Delta f_j\right) \tag{3.299}$$

This is the overdamped Langevin equation with constraint obtained by Peters. Below we make a comparison with our result (3.159), by Ito-izing the multiplicative noise in (3.299). Since $\widetilde{\boldsymbol{L}}\boldsymbol{P}^m = \widetilde{\boldsymbol{L}}$, the Stratonovich part of (3.299) can be expanded as

$$\begin{aligned}\widetilde{\boldsymbol{L}}\left(x(t)+\frac{\Delta x}{2}\right) &= \widetilde{\boldsymbol{L}}(x(t)) + \frac{1}{2}\frac{\partial\widetilde{\boldsymbol{L}}}{\partial x_i(t)}\Delta x_i + \cdots \\ &= \widetilde{\boldsymbol{L}}(x(t)) + \frac{1}{2}\frac{\partial\widetilde{\boldsymbol{L}}}{\partial x_i(t)}\widetilde{L}_{ij}(x(t))\Delta f_j + \mathcal{O}(\Delta t)\end{aligned} \tag{3.300}$$

By substituting it into (3.299),

$$\Delta x_i = \widetilde{L}_{ij}\left(-\frac{\partial U}{\partial x_j}\Delta t + P^m_{ij}\Delta f_j\right) + \frac{\partial\widetilde{L}_{ij}}{\partial x_k}\widetilde{L}_{kl}\Delta f_l P^m_{jm}\Delta f_m \tag{3.301}$$

The last term in the RHS of (3.301) can be handled by the FDT (3.11) and one has

$$\frac{\partial\widetilde{L}_{ij}}{\partial x_k}\widetilde{L}_{kl}\Delta f_l P^m_{jm}\Delta f_m = T\frac{\partial\widetilde{L}_{ij}}{\partial x_k}P^m_{jk}\Delta t \tag{3.302}$$

Here we have used the identity $\boldsymbol{P}^L(\boldsymbol{P}^m)^\dagger = (\boldsymbol{P}^m)^\dagger$. Further by using $P^m_{jk} = \delta_{jk} - e_{\mu,j}e^\mu_k$,

$$\frac{\partial\widetilde{L}_{ij}}{\partial x_k}P^m_{jk} = \frac{\partial\widetilde{L}_{ij}}{\partial x_j} - \frac{\partial\widetilde{L}_{ij}}{\partial x_k}e_{\mu,j}e^\mu_k \tag{3.303}$$

Since $\widetilde{L}_{ij}$ and $e_{\mu,j}$ are orthogonal with each other, $\widetilde{L}_{ij}e_{\mu,j} = 0$. By differentiating the both side of this equation one has $\frac{\partial \widetilde{L}_{ij}}{\partial x_k}e_{\mu,j} = -\widetilde{L}_{ij}\frac{\partial e_{\mu,j}}{\partial x_k}$. Applying this to (3.303),

$$(3.303) = \frac{\partial \widetilde{L}_{ij}}{\partial x_j} + \widetilde{L}_{ij}\frac{\partial e_{\mu,j}}{\partial x_k}e^{\mu}_k = \frac{\partial \widetilde{L}_{ij}}{\partial x_j} + \widetilde{L}_{ij}\frac{\partial e_{\mu,k}}{\partial x_j}e^{\mu}_k. \tag{3.304}$$

Here we have made use of $\frac{\partial e_{\mu,j}}{\partial x_k} = \frac{\partial^2 F_\mu}{\partial x_j \partial x_k} = \frac{\partial e_{\mu,k}}{\partial x_j}$. The second term in the RHS of (3.304) can be simplified by using the following formula on a differential of a determinant [87],

$$\frac{\partial e_{\mu,k}}{\partial x_j}e^{\mu}_k = -\frac{1}{2}\frac{\partial}{\partial x_j}\ln\left|\mathrm{M}_\perp\right|. \tag{3.305}$$

Thus we arrive at the Ito-ized version of Peters' Langevin equation (3.299).

$$\begin{aligned}
\Delta x_i &= \widetilde{L}_{ij}\left(-\frac{\partial U}{\partial x_j}\Delta t + P^m_{ij}\Delta f_j\right) + T\frac{\partial \widetilde{L}_{ij}}{\partial x_j}\Delta t \\
&\quad -\frac{T}{2}\widetilde{L}_{ij}\frac{\partial}{\partial x_j}\ln\left|\mathrm{M}_\perp\right|\Delta t \\
&= \widetilde{L}_{ij}\left(-\frac{\partial U_{\mathrm{eff}}}{\partial x_j}\Delta t + \Delta f_j\right) + T\frac{\partial \widetilde{L}_{ij}}{\partial x_j}\Delta t.
\end{aligned} \tag{3.306}$$

This is identical with our result given in (3.159).

3.8.4 Hinch

Hinch has proposed the following overdamped Langevin equation, starting from the overdamped Langevin equation and imposing constraints by using the Lagrange multiplier [64]. His overdamped Langevin equation is (implicitly) written in Ito-Stratonovich mixed multiplicative noise.

$$\Delta x_i = -\widetilde{L}_{ij}\frac{\partial U}{\partial x_j}\Delta t + \widetilde{L}_{ij} \circ P_{jk}\Delta f_k. \tag{3.307}$$

Here $\widetilde{L}_{ij}$ in the RHS of (3.307) is interpreted in the Stratonovich sense, while the multiplicative noise $P_{jk}\Delta f_k$ is interpreted as Ito.

Corresponding Fokker-Planck equation can be obtained as

$$\frac{\partial \Phi(x,t)}{\partial t} = \frac{\partial}{\partial x_i}\left\{\widetilde{L}_{ij}\left[\frac{\partial U^{\mathrm{od}}_{\mathrm{eff}}}{\partial x_j} + k_B T\frac{\partial}{\partial x_j}\right]\Phi(x,t)\right\}, \tag{3.308}$$

which is equivalent with our (3.198) presented in Subsection 3.6.3. Thus the Langevin equation (3.307) is identical with (3.197).

3.8.5 Doi-Edwards

In this subsection we introduce the theory of the Brownian motion with constraint formulated in a famous literature on the polymer dynamics by Doi and Edwards [65]. The strategy of their derivation is starting from the Smoluchowski equation and imposing the constraint conditions by using the Lagrange multiplier. Thus their strategy is classified to A1 in Figure 3.1. We assume that the probability distribution function is driven by the thermodynamic force $\mathscr{F}$ given by gradient of the free energy $\mathscr{A}$,

$$\mathscr{F}_i = -\frac{\partial \mathscr{A}}{\partial x_i}, \tag{3.309}$$

$$\mathscr{A} = U(x) + k_B T \ln \Phi(x,t) - \lambda^\mu F_\mu(x). \tag{3.310}$$

The second term in the RHS of (3.310) represents an effect of the entropic diffusion. λ^μ is the Lagrange multiplier to be determined by a condition that the thermodynamic force keeps the constraint condition unchanged.

$$\dot{F}_\mu(x) = \frac{\partial F_\mu}{\partial x_i}\dot{x}_i = e_{\mu,i}\mathscr{V}_i = 0, \tag{3.311}$$

here velocity $\mathscr{V}_i$ is given by the constitutive equation,

$$\left(L^{-1}\right)_{ij}\mathscr{V}_j = \mathscr{F}_i. \tag{3.312}$$

L_{ij} is the Onsager coefficient. Then the Lagrange multiplier λ^μ is determined by substituting (3.312) into consistency condition (3.311) as

$$\lambda^\mu = -\left(\Lambda_\perp^{-1}\right)^{\mu\nu} e_{\nu,i} L_{ij}\left(\frac{\partial U}{\partial x_j} + k_B T \frac{\partial}{\partial x_j}\ln\Phi\right). \tag{3.313}$$

Substituting λ^μ back into (3.309) and (3.310) one sees that the thermodynamic force is given by

$$\mathscr{F}_i = -P^L_{ij}\left(\frac{\partial U}{\partial x_j} + k_B T \frac{\partial}{\partial x_j}\ln\Phi\right). \tag{3.314}$$

The continuity equation for probability distribution function in N dimensional phase space is given by

$$\frac{\partial}{\partial t}\Phi(x,t) = -\frac{\partial}{\partial x_j}\left(\mathscr{V}_i\Phi(x,t)\right). \tag{3.315}$$

By substitution of (3.314) into (3.315) one obtain

$$\frac{\partial}{\partial t}\Phi(x,t) = \frac{\partial}{\partial x_j}\left[\widetilde{L}_{ij}\left(\frac{\partial U}{\partial x_i} + k_B T\frac{\partial}{\partial x_j}\right)\Phi(x,t)\right]. \tag{3.316}$$

Note that substitution of (3.309) and (3.310) without introducing the Lagrange multiplier into the constitutive equation (3.312) and plugging with the continuity equation (3.315) yields the usual Fokker-Planck equation. Apparently the stationary solution to (3.316) is given by

$$\Phi^{\mathrm{eq}}(x) \propto \delta(F_\mu(x)) \exp\left[-\beta U\right], \tag{3.317}$$

which makes a striking difference with BCAH's or Kramers' results (3.57). The difference between them is an existence of $\ln|\mathrm{M}_\perp|$ term. It is known that in the stiff system with the infinite spring constraint the equilibrium distribution function is given by (3.317). Thus Doi-Edwards' derivation amounts to treating the stiff model system (although the title of the section in the literature is "Systems with rigid constraints"). Note that in polymer the stiff constraint is more realistic than rigid.

3.9 Summary and conclusions

In this chapter we have derived the overdamped Langevin equation under the holonomic constraint conditions by

1. Impose the constraints by using the Lagrange multiplier to the underdamped Langevin equation written in the Cartesian coordinate
2. Perform the change of coordinate into $(N-M)$-dimensional generalized coordinate
3. Take overdamp limit directly from the underdamped Langevin equation in the generalized coordinate
4. Turn it back to the representation in the Cartesian coordinate.

We successfully arrived at the correct result first proposed by BCAH and Öttinger. Our approach is far simpler than BCAH's one for which the complex treatment of the curved coordinate and careful application of the phase space kinetic theory is needed. Therefore our derivation can be easily extended into a more general situation, like non-equilibrium state, as performed in Section 3.7.

Öttinger has derived the overdamped Langevin equation under the constraints by a reduction from the BCAH's Smoluchowski equation, both for the generalized coordinate and for the Cartesian coordinate. His Langevin equation in the Cartesian coordinate depends on the choice of the generalized coordinate. While our (3.159) is solely written in the Cartesian coordinate

and the constraint conditions. In fact, Öttinger's and our Langevin equation represents the identical stochastic process, since the corresponding Fokker-Planck equation is the same. Thus one can eliminate the details on the generalized coordinate from Öttinger's expression and obtain our (3.159) within a small amount of mathematics. He was just not aware of the possibility that he can write down the final expression within the Cartesian coordinate and the constraint conditions only. On the other hand, this feature is naturally expected within our approach, since the method of Lagrange multiplier does not require one to introduce the parallel counterpart of the generalized coordinate and one can formulate the whole theory within the Cartesian coordinate and the constraint conditions. One of the advantages of our derivation is that we can expect this possibility from the beginning. Having a closed expression is a great merit particularly for the purpose of implementation to the computer simulations, while within the Öttinger's expression one always has to set the generalized coordinate explicitly, destroying the most of the merit working on the Cartesian coordinate.

Peters [43] derived the correct Langevin equation starting from the Cartesian Langevin equation and using the Lagrange multiplier to impose the constraint conditions. He first projected the noise term in order to satisfy the constraint within $\Delta t^{1/2}$ order. Then he took the overdamp limit according to the heuristic argument proposed in [41, 42]. Finally by again projecting the overdamp dynamics onto the constraint surface he obtained the correct overdamp Langevin equation under constraints. His calculation is simple since it does not require one to introduce the generalized coordinate. But as shown in Subsection 3.8.3 the derivation contains several heuristic and ambiguous points. For example there are no reason to introduce the Lagrange multiplier in twice. Moreover, adoption of the Stratonovich differential in (3.297) is also dubious. Our derivation is lengthier than Peters' but ours is more rigorous and contains no ambiguity.

If one starts from the overdamped Langevin equation in the Cartesian coordinate and implement the constraints by using the method of Lagrange multiplier, one inevitably fails to reproduce the correct equilibrium distribution since it contains the information of the mass matrix, see (3.57). In other words the two procedures, imposing the constraints and taking the overdamp limit are not commutable. The Lagrange multiplier method generally does not work for overdamped Langevin equation. That is to say, the force from the constraints cannot be expressed by the linear combination of vector perpendicular to the constraint surface. Quite misleadingly, it looks working for the scalar Onsager coefficient case [21–23]. But it cannot be generalized into the case with the matrix Onsager coefficient, as shown in (3.289).

In the literature by Doi and Edwards a method is illustrated to impose the constraints to the Smoluchowski equation (overdamped version of the Fokker-Planck equation) by using the Lagrange multiplier. But in this method one cannot obtain the determinant correction, which is the difference between U_{eff} and U. The stationary distribution becomes $\Phi^{\text{eq}}_{\text{Doi}}(x) \propto \prod_{\mu=1}^{M} \delta(F_\mu(x)) \exp\left[-\beta U(x)\right]$.

In Section 3.7, we extended our formalism to the general non-equilibrium situation. It can be applied for the thermodiffusion of polymers under the temperature gradient. Such systems are recently interested from the viewpoint of segregation of DNAs, since the thermodiffusion coefficient depends on the length of the polymer [89]. We put a theoretical first step toward understanding and controlling the thermodiffusion of macromolecules.

We showed that for the systems with momentum one can construct a rigorous theory to treat the holonomic constraint. But it is less clear how one can impose the constraints into the the spin systems, where the momentum is not present. We tried to answer it and proposed a tentative workaround in subsection 3.6.3, but we think a more refined treatment would be needed for future. The formalism constructed in subsection 3.6.3 is applied to the p-spin spherical model in Chapter 4.

3.10 Notations

Mathematical symbols

Symbol	Meaning	Introduced
$\boldsymbol{A}, \boldsymbol{B}, \cdots$	matrix	Sec. 3.2
$\boldsymbol{AB}$	product of matrix	
δ_{ij}	Kronecker's delta	
$\delta(t-t')$	Dirac's delta function	
$\lvert A \rvert$	determinant of matrix A	
$\{\cdot,\cdot\}$	Poisson bracket	(3.8)

Model quantities

Symbol	Meaning	Introduced
N	dimension of space(without constraint)	Sec. 3.2
H	Hamiltonian	(3.4)
U	potential energy	(3.4)
x_i	ith position in the Cartesian coordinate	Sec. 3.2
p_i	ith momentum in the Cartesian coordinate	Sec. 3.2
$\boldsymbol{m}$	mass matrix in the Cartesian coordinate	(3.5)
$\zeta_{ij}, \boldsymbol{\zeta}$	friction matrix in the Cartesian coordinate	(3.10)
$f_i(t)$	Gaussian white noise	(3.11)
k_B	Boltzmann constant	Sec. 3.2
T	temperature	Sec. 3.2
$L_{ij}, \boldsymbol{L}$	Onsager coefficient. $\boldsymbol{L} = \boldsymbol{\zeta}^{-1}$	(3.12)
$F_\mu(x)$	holonomic constraint condition	(3.13)
$\mu, \nu, \lambda, \ldots$	index of constraint condition. $\mu = 1, 2, \ldots, M$	(3.13)
M	number of constraints	Sec. 3.2
q_α	coordinate parallel to the constraint surface	Sec. 3.2
$\alpha, \beta, \gamma, \ldots$	index of coordinate parallel to constraint surface. $\alpha = 1, 2, \ldots, N - M$	Sec. 3.2
Q_a	generalized coordinate	(3.34)
$a, b, c, \ldots$	index of the generalized coordinate. $a = 1, 2, \ldots, N$.	Sec. 3.2
π^α	conjugate momenta to q_α	(3.43)
$\tilde{\Psi}(q, \pi, t)$	probability distribution function in the phase space spanned by the generalized coordinate	(3.103)
$\tilde{\Psi}^{\mathrm{eq}}(q, \pi)$	equilibrium probability distribution function in the generalized coordinate	(3.37)
$\Psi(x, p, t)$	probability distribution function in the Cartesian phase space	(3.85)
$\Psi^{\mathrm{eq}}(x, p)$	equilibrium probability distribution function in the Cartesian phase space	(3.49)

$\tilde{\Phi}(q,t)$	probability distribution function in the generalized coordinate	(3.131)
$\tilde{\Phi}^{\mathrm{eq}}(q)$	equilibrium probability distribution function in the generalized coordinate	(3.60)
$\Phi(x,t)$	probability distribution function in the Cartesian coordinate	(3.162)
$\Phi^{\mathrm{eq}}(x)$	equilibrium the probability distribution function in the Cartesian coordinate	(3.59)
$\mathcal{N}$	arbitrary normalization constant for the probability distribution function	(3.37)
K	kinetic energy	(3.39)
Π^{μ}	conjugate momenta to F_{μ}	(3.42)
ξ_i	Gaussian white noise	(3.212)
b_{ij}	factor of noise strength	(3.211)

Emerged quantities

Symbol	Meaning	Introduced
$e_{\mu,i}$	basis of the generalized coordinate, which is perpendicular to the constraint surface	(3.14)
e_i^{μ}	reciprocal set of $e_{\mu,i}$	(3.15)
e_i^{α}	basis of the generalized coordinate, which is parallel to the constraint surface	(3.17)
$e_{\alpha,i}$	reciprocal set of e_i^{α}	(3.18)
$\mathrm{M}_{\perp}^{\mu\nu}$	mass matrix projected onto the perpendicular coordinate	(3.23)
$\mathrm{M}_{\parallel}^{\alpha\beta}$	mass matrix projected onto the constraint surface	(3.26)
$P_{ij}^m, \boldsymbol{P}^m$	projection operator appears in the mechanics and the underdamped system	(3.24)

$D_{\mu\nu}$	metric tensor for coordinate perpendicular to the constraint surface	(3.28)
$g_{\alpha\beta}$	metric tensor for coordinate parallel to the constraint surface	
$P_{ij}, \boldsymbol{P}$	projection operator appearing in the overdamped system with scalar Onsager coefficient system	(3.29)
$\Lambda^{\perp}_{\mu\nu}$	Onsager coefficient projected onto the perpendicular coordinate	(3.31)
P^L_{ij}, $\boldsymbol{P}^L$	projection operator in the overdamped system with matrix Onsager coefficient system	(3.33)
U_{eff}	effective potential in the overdamped constrained system, derived from underdamp constrained system, appears in the Cartesian coordinate	(3.58)
$\tilde{U}$	effective potential in the overdamped constrained system, derived from underdamp constrained system, appears in the generalized coordinate	(3.61)
λ^{μ}	Lagrange multiplier	(3.62)
$f^{\alpha}_{\parallel}(q,t)$	noise in the constraint surface	(3.101)
$Z^{\alpha\beta}_{\parallel}$	friction coefficient projected onto the constraint surface	(3.101)
$\widetilde{L}_{ij}, \widetilde{\boldsymbol{L}}$	modified Onsager coefficient. rank $N-M$, $\widetilde{\boldsymbol{L}} = \boldsymbol{L}\boldsymbol{P}^L = \left(\boldsymbol{P}^L\right)^{\dagger}\boldsymbol{L}$	(3.136)
$U^{\text{od}}_{\text{eff}}$	effective potential in the overdamp limit	(3.184)
$\mathcal{G}_{\alpha,i}$	multiplicative factor in the overdamp limit, in the generalized coordinate	(3.261)
$\boldsymbol{\mathcal{D}}_{\parallel}$	diffusion matrix in the generalized coordinate	(3.235)
$\boldsymbol{D}$	diffusion matrix in the Cartesian coordinate	(3.245)
$\widetilde{\boldsymbol{g}}$	multiplicative factor in the Cartesian overdamp Langevin equation with constraint	(3.260)

Part II

Glassy dynamics with disparately separated time scales

Chapter 4

Dynamics of p-spin Spherical Model with Rigid Constraint

4.1 Introduction

A liquid below its freezing temperature is called supercooled liquid. The viscosity of supercooled liquids divergently grows upon cooling and stops flowing at finite temperature. This is the phenomenon called the glass transition. While more than ten orders of magnitude of slowing down of the dynamics its static structure remains indistinguishable from ordinary liquids. Thus in short the glass transition can be viewed as a solidification without crystallization. Understanding the origin of this slowing down is the ultimate goal of investigation of the glass transition. What makes the understanding of the glass transition difficult seems to be reduced to its randomness and the strong many body effect. Since the structure of the glass is as random as liquid it is hard to find the appropriate order parameter to characterize the slow dynamics. Furthermore since the glass transition occurs in high density liquid the dynamics of the constituent molecules becomes strongly correlated.

The Mode-Coupling Theory (MCT) is the one and only microscopic first-principles theory that has succeeded to describe the slow dynamics of supercooled liquid [1]. We believe that MCT plays a role of important milestone of the kinetic theory of supercooled liquids but at the same time it has some flaws. For instance MCT predicts a power law divergence of relaxation time of density correlation function of liquid at a finite temperature $T_{\rm d}$, called the dynamic transition. While in real liquid the relaxation time divergently grows as exponentially, at much lower temperature than $T_{\rm d}$. In other words MCT captures the slow dynamics of supercooled liquid qualitatively but not quantitatively. This is one reason why MCT is called "a mean field theory of

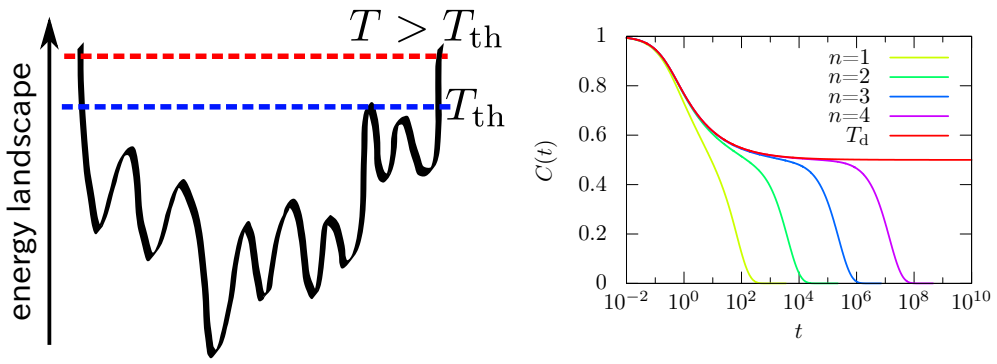

Figure 4.1: Left: The potential energy landscape of 1RSB spin glass model. Right: Dynamics of spin-spin correlation function $C(t)$ for the p-spin spherical model. Temperature is chosen as $T = T_{\rm d}(1 + 10^{-n})$.

the glass transition"[1]. The another reason comes from the similarity between MCT and the exact solution of a mean field spin glass model.

A certain class of spin glass models are the possible candidates which ease these two difficulties with keeping the phenomenology of slow dynamics without the crystallization. Spin glass model is the model with spins arranged on a prescribed lattice interacting randomly. Thus randomness is expected to be more controlled than molecular liquids. Among of them the p-spin spherical model (PSM) with $p \geq 3$ is a mean field spin glass model belonging to the 1-step Replica Symmetry Breaking (1RSB) universality class. The mean field character of the PSM suppresses the many body effect and allows one to handle it theoretically.

We briefly review physics of the 1RSB universality class. For complete review the reader should refer to [72]. Because of the frustration induced by the random interaction, the potential energy landscape of the system has exponential numbers of local minima (See left panel of Figure 4.1). When the temperature is sufficiently high the system can explore the whole phase space irrespective of the existence of minima (red dotted line). But by lowering the temperature the system becomes trapped at the local minima (blue dotted line). Since the model is mean field, the lifetime of the local minima diverges with the thermodynamic limit. Therefore, if the system starts to feel the existence of local minima at some threshold temperature, say $T_{\rm th}$, the system suddenly becomes non-ergodic. These properties of PSM are based on static arguments. On the other hand an analysis on the dynamic coun-

[1]Interestingly there have been reported both positive [93,94] and negative [95] evidence for this conjecture.

terpart of PSM revealed that it is described by an equation with the same structure as MCT and shares the most of important properties. For example the exact solution to the dynamic of PSM shows the power law divergence of the relaxation time at the dynamic transition temperature $T_{\rm d}$ (See the right panel of Figure 4.1). Astonishingly $T_{\rm d}$ and $T_{\rm th}$ coincide, although these values are determined by completely independent (i.e., dynamic and static) analysis. Thus one can make a statistical interpretation of $T_{\rm d}$. The dynamics of the system becomes no longer ergodic and the relaxation time diverges at $T_{\rm d} = T_{\rm th}$ since the system is trapped by exponential number of local minima. Thus the static and the dynamic arguments are consistent with each other. Since the exact solution of a mean field spin glass model and MCT is almost identical MCT is conjectured to be a mean field theory of the glass transition. This conjecture is called the mean field picture of the glass transition. Based on the mean field picture and on an attempt to go beyond it, there have been a large number of research carried out recently. For example one may expect that a statistical mechanical interpretation of the dynamic transition of MCT for supercooled liquid is possible since the dynamic transition $\sim$ threshold in energy minima [94, 96]. See also recent literature [97, 98] and reviews [72, 99–101].

MCT like dynamics of PSM is the only link between glass and spin glass. But its derivation has been carried out in an instrict way. PSM is imposed a holonomic constraint condition called the spherical constraint. It is given by

$$\sum_{i=1}^{N} \sigma_i^2 = N. \tag{4.1}$$

Here $\sigma_i \in \mathbb{R}$ is the value of ith spin and N is the total number of spins. In the original derivation of the dynamics of PSM [4] the spherical constraint is satisfied within "stiff" manner, introduced in Chapter 3. In the stiff treatment the constraint condition is realized by a steep harmonic potential around the constraint surface. Thus the constraint condition is not satisfied time by time but satisfied in average. In an another derivation by Crisanti et al., an even looser realization of the spherical constraint, say, "soft" has been employed [5]. They introduced a Lagrange multiplier to force the constraint but they had not determined it until the end of the calculation. In other words, the multiplier is determined after all the average have done. Again, the spherical constraint condition is satisfied only in average, i.e., not in time by time and not in each ensembles. We expressed "soft" is even looser than "stiff" since a dynamics of each ensemble in soft constraint need not satisfy the constraint conditions, while in the stiff case it is satisfied in the long time limit in each trajectories. In spite of these different treatments of the spheri-

cal constraint, [4] and [5] lead the identical result. The purpose of this chapter is to give a strict treatment of the spherical constraint, i.e., the constraint condition is satisfied in time by time and each ensembles, and see whether the similarity between MCT and the exact solution of PSM remains intact or not. Hereafter we call such realization of constraint conditions "rigid".

As stated in Chapter 3, Subsection 3.8.5, the stationary distribution for rigid and stiff constraint models differ by the logarithm of a determinant, see (3.59) and (3.317).

Technically speaking, the difference between soft and rigid models is the timing when one determines the value of the Lagrange multiplier. For rigid treatment it is fixed *before* taking average over noise or ensembles while in soft it is determined *after* all averages have been carried out. For the spherical model it is believed that the soft constraint is easier to be handled analytically [102]. For example the soft constraint has an advantage in a perturbative analysis since one can realize the constraint after the perturbative expansion. While in rigid model, it induces the nonlinear projection operator as shown in Chapter 3, which, in general, does not contain any small parameters. Even if one can perform a perturbation expansion with respect to this nonlinearity, the constraint condition will be violated. On the other hand, there is an advantage in rigid models. One cannot simulate soft models on computers since in general it is impossible to prepare the ensemble where the constraint condition is satisfied in average. While it is easy to implement the rigid constraint model on computer simulation. Note that since the spherical model is a mean field model one would be able to treat both soft and rigid models analytically. The introduction of the soft constrained spherical model, called the mean spherical model, is just an idealization of the original rigid model. Actually the static arguments for PSM, one of which is reviewed above, is carried out within the rigid treatment of the spherical constraint. Thus one should solve the dynamics of PSM with the rigid constraint.

It is known that in some case the difference between the mean spherical model and spherical model arises as a grave problem. This can be understood as a result of the inequivalence between the canonical and the grand-canonical ensembles for mean field models [103]. Since the spherical constraint (4.1) defines the value of number of spins N, rigid and soft constraint amounts to canonical and grand-canonical ensembles respectively. For the model of spherical ferromagnet it is shown that the expectation values of the magnetization differ from each other [104]. In the dynamics of spherical model it is known that even out of equilibrium there holds a proportional relationship between correlation and response function, which serves as a one of very few formulae known in the non-equilibrium system [70, 105]. The proportionality coefficient is called the effective temperature since in equilibrium it becomes

the actual temperature of the system, which is well known the fluctuation-dissipation theorem (FDT). It is known in the mean spherical model that the effective temperature is given uniquely for correlation and response for any physical quantities. But, on the other hand, in rigidly constrained spherical model the ratio between the correlation and response in non-equilibrium state depends on the choice of the physical quantities [25]. It means that the concept of the effective temperature is no longer applicable to the rigid constraint spherical models.

In [25], the dynamics of spherical ferromagnet with rigid constraint is analyzed by using the fact that the difference between soft and rigid is order of $N^{-1/2}$. Their method works when one can estimate the order of the difference, but in general it cannot be the case. In PSM, because of the randomness it is difficult to analyze the dynamics by splitting the difference between rigid and soft. Thus we employ the method for rigid constraint Brownian motion invented in the previous chapter to analyze the rigidly constrained PSM.

This chapter is organized as follows. In Section 4.2 we introduce the p-spin spherical model and its dynamics within rigid spherical constraint. In Section 4.3 we introduce a functional integral representation of the constrained Brownian motion where an average over random interaction is conveniently performed. In Section 4.4 we apply the formalism to the PSM and derive the dynamical equation for correlation and response. Section 4.5 is devoted to summary, discussion and conclusions.

4.2 Model

The Hamiltonian of PSM is defined for spin variables $\sigma_i \in \mathbb{R}$, $i = 1, \ldots, N$,

$$H = -\sum_{i_1 < \cdots < i_p}^{N} J_{i_1 \cdots i_p} \sigma_{i_1} \cdots \sigma_{i_p}. \tag{4.2}$$

Here summations over is are imposed for all pairs of spins. In other words, the interaction range is infinite and thus PSM is a mean field model. We assume that $p \geq 3$, since $p = 2$ corresponds to the another universality class of spin glass. $J_{i_1 \cdots i_p}$ is Gaussian random interaction with its average and variance given by,

$$\overline{J_{i_1 \cdots i_p}} = 0, \quad \overline{J_{i_1 \cdots i_p}^2} = 1/N^{p-1}. \tag{4.3}$$

Here $\overline{\cdots}$ represents average over randomness. The factor $1/N^{p-1}$ ensures the extensivity of the energy of the system since it leads $\sqrt{\overline{H^2}} \sim N$. We impose

the spherical constraint,

$$\sum_{i=1}^{N} \sigma_i^2 = N. \tag{4.4}$$

In the case of PSM, the spherical constraint guarantees the existence of lower bound of energy. We assume that the dynamics of spin variable σ_i in the absence of constraint condition is given by the model A [6],

$$\begin{aligned} \dot{\sigma}_i &= -\frac{\partial H}{\partial \sigma_i} + \eta_i, & (4.5)\\ \langle \eta_i(t) \rangle &= 0, & (4.6)\\ \langle \eta_i(t_1)\eta_j(t_2) \rangle &= 2k_B T \delta_{ij} \delta(t_1 - t_2). & (4.7) \end{aligned}$$

The dynamics under the spherical constraint can be extracted from the general expression given in (3.197).

$$\text{(I)} \quad \dot{\sigma}_i = P_{ij} \left(-\frac{\partial H}{\partial \sigma_j} + \eta_j \right) + k_B T P_{jk} \frac{\partial P_{ij}}{\partial x_k} \tag{4.8}$$

Here (I) stands for the Ito interpretation of the multiplicative noise appearing in the right hand side (RHS) of (4.8). The projection operator P_{ij} is given by

$$P_{ij} = \delta_{ij} - \frac{\sigma_i \sigma_j}{\sum_{i=1}^{N} \sigma_i^2} \approx \delta_{ij} - \frac{\sigma_i \sigma_j}{N}. \tag{4.9}$$

where $\approx$ represents "weak equality" which follows only after making use of constraint condition (4.4). Note that for instance in last term in the RHS of (4.8) a derivative of P_{ij} with respect to x must be performed before using the constraint condition. Thus the last term in the RHS of (4.8) reads,

$$P_{jk} \frac{\partial P_{ij}}{\partial x_k} \approx -\frac{N-1}{N} \sigma_i \to -\sigma_i. \tag{4.10}$$

The last equality holds in the thermodynamic limit $N \to \infty$.

We introduce the generalized coordinate $\varphi_\alpha (\alpha = 1, \ldots, N-1)$. In the case of PSM one can choose them as $N-2$ polar angles and 1 azimuthal angle in the N-dimensional polar coordinate. But we do not need to construct them explicitly, as shown in Chapter 3. The Langevin equation for φ_α reads from (3.200)

$$\text{(I)} \quad \dot{\varphi}_\alpha = -g_{\alpha\beta} \frac{\partial H}{\partial \varphi_\beta} + \xi_\alpha + k_B T e_{\beta,i} \frac{\partial e_{\alpha,j}}{\partial q_\beta}, \tag{4.11}$$

where $\xi_\alpha \equiv e_{\alpha,i} \eta_i$.

4.3 Functional Integral Representation

In this section we write down the functional integral representation of the constrained Brownian motion. We follow the notations introduced in Chapter 3 throughout this section. In the presence of M constraint conditions the motion of the Brownian particle is confined in the $(N-M)$-dimensional sub-manifold embedded in the N-dimensional Cartesian coordinate. One has to work on this sub-manifold since the statistical measure of the system is given in $N-M$ dimension. Langevin equation for these intrinsic variables are given in (3.200),

$$\Delta q_\alpha = \mathcal{L}_{\alpha\beta}\left(-\frac{\partial \tilde{U}^{\rm od}_{\rm eff}}{\partial q_\beta}\Delta t + \Delta \widetilde{f}^\beta\right) + k_B T \frac{\partial \mathcal{L}_{\alpha\beta}}{\partial q_\beta}\Delta t. \tag{4.12}$$

Following the same spirit with [4,5] we switch to the functional integral representation rather than the Langevin equation. We should keep in mind that number of independent variables is not N but $N-M$, due to the constraints. The functional integral representation gives the formal solution to the Fokker-Planck equation. Let $\Phi(q_1,t_1|q_0,t_0)$ be a conditional probability that q becomes q_1 at time t_1 under the condition of q_0 at time $t_0(<t_1)$. In the functional integral representation it is given by,

$$\Phi(q_1,t_1|q_0,t_0) = \int_{q_0}^{q_1} \mathrm{d}q \int \mathrm{d}\hat{q}\exp\left[S[q,\hat{q}]\right]. \tag{4.13}$$

The derivation is left in Appendix C. Here $S\left[q,\hat{q}\right]$ is so called Martin-Siggia-Rose(MSR) action functional [55, 106–108]. $\hat{q}$ is an auxiliary field which is hard to interpret physically. In the case of constrained Brownian motion, by using Langevin equation (4.12) the action S is given by

$$\begin{aligned} S[q,\hat{q}] = \int_{t_0}^{t_1} dt \Bigg[-\mathrm{i}\hat{q}^\alpha \left(\dot{q}_\alpha + \mathcal{L}_{\alpha\beta}\frac{\partial \tilde{U}^{\rm od}_{\rm eff}}{\partial q_\beta} - k_B T \frac{\partial \mathcal{L}_{\alpha\beta}}{\partial q_\beta}\right) \\ + k_B T \mathrm{i}\hat{q}^\alpha \mathcal{L}_{\alpha\beta}\mathrm{i}\hat{q}^\beta\Big]. \end{aligned} \tag{4.14}$$

By using the MSR action one can write down an expectation value of physical quantity $A(q)$ at time t under the condition that q took the value q_0 at time $t_0(<t)$.

$$\left\langle A(q(t))\right\rangle_{q_0,t_0} = \int \mathrm{d}q_1 A(q_1)\Phi(q_1,t_1|q_0,t_0). \tag{4.15}$$

For a two time quantity with $t_2 > t_1 > t_0$, similarly,

$$\begin{aligned} &\left\langle A_2(q(t_2))A_1(q(t_1))\right\rangle_{q_0,t_0} = \\ &\qquad \int \mathrm{d}q_2 \int \mathrm{d}q_1 A_2(q_2)\Phi(q_2,t_2|q_1,t_1)A_1(q_1)\Phi(q_1,t_1|q_0,t_0). \end{aligned} \tag{4.16}$$

If the system is at equilibrium at the initial time t_0 one can replace $\Phi(q_1, t_1|q_0, t_0)$ by $\Phi^{\rm eq}(q_1)$ in (4.16). Below we rewrite action $S[q, \hat{q}]$ by original Cartesian coordinate x_i since in most case we are interested in physical quantities defined in the Cartesian coordinate, not in q. We introduce $\mathrm{i}\hat{x}_i (i = 1, \ldots, N)$ as functions of $q, \hat{q}$ as

$$\mathrm{i}\hat{x}_i(q, \hat{q}) \equiv e_{\alpha,i}\mathrm{i}\hat{q}^\alpha. \tag{4.17}$$

Note that not all $\mathrm{i}\hat{x}_i$ are independent. The action functional (4.14) can be rewritten as

$$S[q, \hat{q}] = \int_{t_0}^{t_1} dt \left[-\mathrm{i}\hat{x}_i \left(\dot{x}_i + \widetilde{L}_{ij}\frac{\partial U}{\partial x_j} - k_B T \frac{\partial \widetilde{L}_{ij}}{\partial x_k} P_{jk} \right) + k_B T \mathrm{i}\hat{x}_i \widetilde{L}_{ij} \mathrm{i}\hat{x}_i \right]. \tag{4.18}$$

Hereafter we omit the argument $q, \hat{q}$ in $\hat{x}_i(q, \hat{q})$ as $\mathrm{i}\hat{x}$ as explicit function of $q, \hat{q}$ for simplicity.

We can derive the FDT [39] by using the functional integral formalism. Here we perform this as a warming up exercise on calculating the averages of the physical quantities written in the Cartesian coordinate. First, the linear response to the action (4.18) under the external field h_i is

$$S[q, \hat{q}, h] = S[q, \hat{q}] + \int \mathrm{d}t \mathrm{i}\hat{x}_i \widetilde{L}_{ij} h_j(t). \tag{4.19}$$

Hereafter we drop the endpoints of integration on time when they are not essential. The response function in the Cartesian coordinate $\chi_{ij}(t_1, t_2)$ is thus defined as

$$\begin{aligned} \chi_{ij}(t_1, t_2) &\equiv \left. \frac{\partial \langle x_i(t_1) \rangle^h}{\partial h_j(t_2)} \right|_{h=0} \\ &= \frac{\partial}{\partial h_j(t_2)} \int^{q(x(t_1))} \mathrm{d}q \int \mathrm{d}\hat{q} x_i(t_1) \exp\left[S[q, \hat{q}] + \int \mathrm{d}t \mathrm{i}\hat{x}_k \widetilde{L}_{kl} h_l(t) \right] \\ &= \left\langle x_i(t_1) \widetilde{L}_{jk}(x(t_2)) \mathrm{i}\hat{x}_k(t_2) \right\rangle. \end{aligned} \tag{4.20}$$

Next we extract the dynamics of the correlation and response functions. For convenience we rewrite the Langevin equations (3.197) and (3.200) as

$$\text{(I)} \quad \dot{x}_i = \widetilde{L}_{ij}\left(-\frac{\partial U}{\partial x_j} + f_j \right) + I_i, \tag{4.21}$$

$$\text{(I)} \quad \dot{q}_\alpha = e_{\alpha,i}\widetilde{L}_{ij}\left(-\frac{\partial U}{\partial x_j} + f_j \right) + \mathcal{I}_\alpha. \tag{4.22}$$

Here the multiplicative noise is interpreted in the Ito convention and we have defined following quantities.

$$I_i \equiv k_B T \frac{\partial \widetilde{L}_{ij}}{\partial x_k} P_{jk}, \quad \mathcal{I}_\alpha \equiv k_B T e_{\beta,j} \frac{\partial}{\partial q_\beta} \left(e_{\alpha,i} \widetilde{L}_{ij} \right). \tag{4.23}$$

Then relation between $\dot{x}_i$ and $\dot{q}_\mu$ are simply written as

$$\dot{x}_i = I_i + e_i^\mu \left(\dot{q}_\mu - \mathcal{I}_\mu \right), \tag{4.24}$$

$$\dot{q}_\alpha = e_{\alpha,i} \left(\dot{x}_i - I_i \right) + \mathcal{I}_\alpha. \tag{4.25}$$

We have to evaluate averages of functions of x with the integration measure $\mathrm{d}q\mathrm{d}\hat{q}$. This feature makes the calculation of averages bit cumbersome. For a function of x and $\hat{x}$, say $A(x, \hat{x})$, $\langle \dot{x}_i(t_1) A(x, \hat{x}) \rangle$ is evaluated as follows.

$$\begin{aligned} \langle \dot{x}_i(t_1) A(x, \hat{x}) \rangle &= \int \mathrm{d}q \int \mathrm{d}\hat{q} \dot{x}_i(t_1) A(x, \hat{x}) \exp\left[S[q, \hat{q}] \right] \\ &= \int \mathrm{d}q \int \mathrm{d}\hat{q} \left[I_i + e_i^\alpha \left(\dot{q}_\alpha - \mathcal{I}_\alpha \right) \right] A(x, \hat{x}) \\ &\times \exp\left\{ \int \mathrm{d}t \left[-\mathrm{i}\hat{q}^\alpha \left(\dot{q}_\alpha - \mathcal{I}_\alpha \right) - \mathrm{i}\hat{q}^\alpha \mathcal{L}_{\alpha\beta} \frac{\partial U}{\partial q_\beta} + \mathrm{i}\hat{q}^\alpha \mathcal{L}_{\alpha\beta} \mathrm{i}\hat{q}^\beta \right] \right\}, \end{aligned} \tag{4.26}$$

where we made use of (4.14) and (4.24). Since

$$\begin{aligned} -\frac{\partial}{\partial \mathrm{i}\hat{q}^\alpha(t_1)} \exp\left[-\int \mathrm{d}t \mathrm{i}\hat{q}^\alpha \left(\dot{q}_\alpha - \mathcal{I}_\alpha \right) \right] = \\ \left(\dot{q}_\alpha(t_1) - \mathcal{I}_\alpha \right) \exp\left[-\int \mathrm{d}t \mathrm{i}\hat{q}^\alpha \left(\dot{q}_\alpha - \mathcal{I}_\alpha \right) \right], \end{aligned} \tag{4.27}$$

(4.26) becomes,

$$\begin{aligned} \langle \dot{x}_i(t_1) A(x, \hat{x}) \rangle = &- \int \mathrm{d}q \int \mathrm{d}\hat{q} e_i^\alpha(t_1) \left\{ \frac{\partial}{\partial \mathrm{i}\hat{q}^\alpha(t_1)} \exp\left[-\int \mathrm{d}t \mathrm{i}\hat{q}^\alpha \left(\dot{q}_\alpha - \mathcal{I}_\alpha \right) \right] \right\} \\ &\times \exp\left[\int \mathrm{d}t \left(-\mathrm{i}\hat{q}^\alpha \mathcal{L}_{\alpha\beta} \frac{\partial U}{\partial q_\beta} + \mathrm{i}\hat{q}^\alpha \mathcal{L}_{\alpha\beta} \mathrm{i}\hat{q}^\beta \right) \right] \\ &+ \langle I_i(t_1) A(x, \hat{x}) \rangle. \end{aligned} \tag{4.28}$$

By integration by parts in $\int \mathrm{d}\hat{q}$,

$$\begin{aligned} \langle \dot{x}_i(t_1) A(x, \hat{x}) \rangle = &\int \mathrm{d}q \int \mathrm{d}\hat{q} e_i^\alpha(t_1) \left\{ A(x, \hat{x}) \left(-\mathcal{L}_{\alpha\beta}(t_1) \frac{\partial U}{\partial q_\beta(t_1)} \right) \right. \\ &\left. + 2k_B T \mathcal{L}_{\alpha\beta}(t_1) \mathrm{i}\hat{q}^\beta(t_1) + \frac{\partial A(x, \hat{x})}{\partial \mathrm{i}\hat{q}^\alpha(t)} \right\} \exp[S[q, \hat{q}]] \end{aligned}$$

$$
\begin{aligned}
& +\langle I_i(t_1)A(x,\hat{x})\rangle \\
= & -\left\langle e_i^\alpha(t_1)\mathcal{L}_{\alpha\beta}(t_1)\frac{\partial U}{\partial q_\beta(t_1)}A(x,\hat{x})\right\rangle \\
& +2k_BT\left\langle e_i^\alpha(t_1)\mathcal{L}_{\alpha\beta}(t_1)\mathrm{i}\hat{q}^\beta(t_1)A(x,\hat{x})\right\rangle \\
& +\left\langle e_i^\alpha(t_1)\frac{\partial A(x,\hat{x})}{\partial \mathrm{i}\hat{q}^\alpha(t_1)}\right\rangle + \langle I_i(t_1)A(x,\hat{x})\rangle \\
= & -\left\langle \widetilde{L}_{ij}(t_1)\frac{\partial U}{\partial x_j(t_1)}A(x,\hat{x})\right\rangle \\
& +2k_BT\left\langle \widetilde{L}_{ij}(t_1)\mathrm{i}\hat{x}_j(t_1)A(x,\hat{x})\right\rangle \\
& +\left\langle e_i^\alpha(t_1)\frac{\partial A(x,\hat{x})}{\partial \mathrm{i}\hat{q}^\alpha(t_1)}\right\rangle + k_BT\left\langle \frac{\partial \widetilde{L}_{ij}}{\partial x_k(t_1)}P_{jk}(t_1)A(x,\hat{x})\right\rangle.
\end{aligned}
\tag{4.29}
$$

Thus substituting $x_j(t_2)$ as $A(x,\hat{x})$ yields the dynamics of correlation function,

$$
\begin{aligned}
\frac{\partial C_{ij}(t_1,t_2)}{\partial t_1} &= \langle \dot{x}_i(t_1)x_j(t_2)\rangle \qquad (4.30)\\
&= -\left\langle \widetilde{L}_{ij}(t_1)\frac{\partial U}{\partial x_j(t_1)}x_j(t_2)\right\rangle + 2k_BT\chi_{ij}(t_2,t_1) \\
&\quad +k_BT\left\langle \frac{\partial \widetilde{L}_{il}}{\partial x_k(t_1)}P_{lk}(t_1)x_j(t_2)\right\rangle \\
&= -\left\langle \widetilde{L}_{ik}(t_1)\frac{\partial U_{\mathrm{eff}}^{\mathrm{od}}}{\partial x_k(t_1)}x_j(t_2)\right\rangle + 2k_BT\chi_{ij}(t_2,t_1) \\
&\quad +k_BT\left\langle \frac{\partial \widetilde{L}_{ik}}{\partial x_k(t_1)}x_j(t_2)\right\rangle.
\end{aligned}
$$

Similarly one can evaluate the time reversal of (4.30) as

$$
\begin{aligned}
\frac{\partial C_{ij}(-t_1,-t_2)}{\partial t_1} &= -\left\langle \widetilde{L}_{ik}(-t_1)\frac{\partial U_{\mathrm{eff}}^{\mathrm{od}}}{\partial x_k(-t_1)}x_j(-t_2)\right\rangle + 2k_BT\chi_{ji}(-t_2,-t_1) \\
&\quad +k_BT\left\langle \frac{\partial \widetilde{L}_{ik}}{\partial x_k(-t_1)}x_j(-t_2)\right\rangle. \qquad (4.31)
\end{aligned}
$$

We assume that x_i does not change sign in time reversal: $x_i(-t) = x_i(t)$. And since $\widetilde{L}_{ij}\frac{\partial U_{\mathrm{eff}}^{\mathrm{od}}}{\partial x_j}$ represents purely dissipative dynamics its time reversal

property is even. Thus (4.31) becomes

$$\begin{aligned}\frac{\partial C_{ij}(-t_1,-t_2)}{\partial t_1} &= -\left\langle \widetilde{L}_{ik}(t_1)\frac{\partial U_{\rm eff}^{\rm od}}{\partial x_k(t_1)}x_j(t_2)\right\rangle + 2k_BT\chi_{ij}(-t_1,-t_2) \\ &\quad +k_BT\left\langle \frac{\partial \widetilde{L}_{ik}}{\partial x_k(t_1)}x_j(t_2)\right\rangle. \end{aligned} \tag{4.32}$$

In equilibrium the two time correlation function depends only on the difference in two times. Thus comparing (4.30) and (4.32) we obtain the FDT. For $t>0$,

$$\frac{\partial C_{ij}(t)}{\partial t} = -k_BT\chi_{ij}(t). \tag{4.33}$$

4.4 Application to the p-spin spherical model

In this section we apply our formalism to the PSM. We follow the standard procedure in analyzing the dynamics of the PSM and employ the functional integral formalism for stochastic process [5]. We can immediately write down the MSR action from the Langevin equation (4.11). By using (4.18), the action functional is

$$\langle\cdots\rangle = \int {\rm d}\varphi{\rm d}\hat{\varphi}\cdots\exp\left[S[\varphi,\hat{\varphi}]\right], \tag{4.34}$$

$$S\left[\varphi,\hat{\varphi}\right] = \int {\rm d}t\left[-{\rm i}\hat{\sigma}_i\left(\dot{\sigma}_i+\frac{\partial H}{\partial\sigma_i}+k_BT\sigma_i\right)+k_BT{\rm i}\hat{\sigma}_i{\rm i}\hat{\sigma}_i\right] \tag{4.35}$$

where ${\rm i}\hat{\sigma}_i$ are defined as functions of $\varphi,\hat{\varphi}$ as

$${\rm i}\hat{\sigma}_i \equiv e_{\alpha,i}{\rm i}\hat{\varphi}^\alpha. \tag{4.36}$$

We perform the average over the random interaction for a self-averaging quantity $\cdots$ as

$$\overline{\langle\cdots\rangle} = \int {\rm d}\varphi{\rm d}\hat{\varphi}\cdots\overline{\exp[S[\varphi,\hat{\varphi}]]} = \int {\rm d}\varphi{\rm d}\hat{\varphi}\cdots\exp[\mathcal{L}_0+\mathcal{L}_J], \tag{4.37}$$

$$\begin{aligned}\mathcal{L}_0 &= \int {\rm d}t\left[-{\rm i}\hat{\sigma}_i\dot{\sigma}_i - k_BT{\rm i}\hat{\sigma}_i\sigma_i + k_BT{\rm i}\hat{\sigma}_i{\rm i}\hat{\sigma}_i\right], \\ \mathcal{L}_J &= \frac{pN}{4}\int {\rm d}t{\rm d}t'\left[Q_1(\sigma;t,t')Q_2^{p-1}(\sigma;t,t')\right. \\ &\qquad \left.+(p-1)Q_3(\sigma;t,t')Q_4(\sigma;t,t')Q_2^{p-2}(\sigma;t,t')\right]. \end{aligned} \tag{4.38}$$

In the last line of (4.37) we have defined following quantities

$$
\begin{aligned}
Q_1(\sigma;t,t') &= \frac{1}{N}\mathrm{i}\hat{\sigma}_i(t)\mathrm{i}\hat{\sigma}_i(t'), && (4.39)\\
Q_2(\sigma;t,t') &= \frac{1}{N}\sigma_i(t)\sigma_i(t'), && (4.40)\\
Q_3(\sigma;t,t') &= \frac{1}{N}\mathrm{i}\hat{\sigma}_i(t)\sigma_i(t'), && (4.41)\\
Q_4(\sigma;t,t') &= \frac{1}{N}\sigma_i(t)\mathrm{i}\hat{\sigma}_i(t'). && (4.42)
\end{aligned}
$$

which are formally same as soft constraint case.

Next we perform a Legendre transform of action functional $S[\varphi,\hat{\varphi}]$ into space of Qs and calculate the saddle point of the MSR action by using the mean field nature of the PSM. We insert

$$
\begin{aligned}
1 &= \int \mathrm{d}Q \prod_{\nu=1}^{4} \delta(Q_\nu(t,t') - Q_\nu(\sigma;t,t')) \\
&\propto \int \mathrm{d}Q\mathrm{d}\lambda \exp\left[-\int \mathrm{d}t\mathrm{d}t' i\lambda_\nu(t,t') \left(Q_\nu(t,t') - Q_\nu(\sigma;t,t')\right)\right], && (4.43)
\end{aligned}
$$

into (4.37) and obtain

$$
\begin{aligned}
\langle\cdots\rangle &= \int \mathrm{d}Q\mathrm{d}\lambda \exp\left\{ NG(Q,\lambda)\right. && (4.44)\\
&\quad \left. + \ln \int \mathrm{d}\varphi\mathrm{d}\hat{\varphi}\cdots \exp\left[\mathcal{L}_0 + N\int \mathrm{d}t\mathrm{d}t' i\lambda_\nu(t,t')Q_\nu(\sigma;t,t')\right]\right\}, \\
G(Q,\lambda) &\equiv \int \mathrm{d}t\mathrm{d}t' \left[\frac{p}{4}\left(Q_1(t,t')Q_2^{p-1}(t,t') + Q_3(t,t')Q_4(t,t')Q_2^{p-2}(t,t')\right)\right. \\
&\quad \left. - i\lambda_\nu(t,t')Q_\nu(t,t')\right]. && (4.45)
\end{aligned}
$$

Since quantities in exponential in (4.44) are all $\mathcal{O}(N)$ we can perform the steepest descent calculation on the integral over Q and λ, the result is

$$
\begin{aligned}
\langle\cdots\rangle &= \int \mathrm{d}\varphi\mathrm{d}\hat{\varphi}\cdots \exp\left[S_{\mathrm{eff}}[\varphi,\hat{\varphi}]\right], && (4.46)\\
S_{\mathrm{eff}}[\varphi,\hat{\varphi}] &= \int \mathrm{d}t \left[-\mathrm{i}\hat{\sigma}_i\left(\dot{\sigma}_i + k_BT\sigma_i\right) + T\mathrm{i}\hat{\sigma}_i\mathrm{i}\hat{\sigma}_i\right] \\
&\quad + \int \mathrm{d}t\mathrm{d}t' \left[\frac{p}{4} C^{p-1}(t,t')\mathrm{i}\hat{\sigma}_i(t)\mathrm{i}\hat{\sigma}_i(t')\right. \\
&\qquad + \frac{p(p-1)}{4}\left(\chi(t,t')C^{p-2}(t,t')\mathrm{i}\hat{\sigma}_i(t)\sigma_i(t')\right. \\
&\qquad \left.\left. + \chi(t',t)C^{p-2}(t',t)\mathrm{i}\hat{\sigma}_i(t')\sigma_i(t)\right)\right].
\end{aligned}
$$

Here we introduced the correlation and response functions as

$$\begin{aligned} C(t,t') &= \langle Q_2(t,t')\rangle = \frac{1}{N}\langle \sigma_i(t)\sigma_i(t')\rangle, \\ \chi(t,t') &= \langle Q_4(t,t')\rangle = \frac{1}{N}\langle \sigma_i(t)\mathrm{i}\hat{\sigma}_i(t')\rangle. \end{aligned} \tag{4.47}$$

and used the fact that

$$\begin{aligned} \chi(t,t') &= \frac{1}{N}\langle \sigma_i(t)P_{ij}(t')\mathrm{i}\hat{\sigma}_j(t')\rangle \\ &= \frac{1}{N}\left\langle \sigma_i(t)\left[\delta_{ij} - e_{\nu,i}(t')e^{\mu}_j(t')\right]e_{\alpha,j}(t')\mathrm{i}\hat{\varphi}^{\alpha}(t')\right\rangle = \frac{1}{N}\langle \sigma_i(t)\mathrm{i}\hat{\sigma}_i(t')\rangle \end{aligned} \tag{4.48}$$

by the orthogonality condition (3.18). Note that if there exists the underlining underdamped process and both mass matrix and Onsager coefficient are matrix this simplification does not occur. In such situation by (4.20)

$$\begin{aligned} \chi(t,t') &= \left\langle \sigma_i(t)\widetilde{L}_{ij}(t')\mathrm{i}\hat{\sigma}_j(t')\right\rangle \\ &= \left\langle \sigma_i(t)\left[L_{ij} - L_{ik}e_{\mu,k}(t')\left(\Lambda_{\perp}^{-1}\right)^{\mu\nu}(t')e_{\nu,l}(t')L_{lj}\right]e_{\alpha,j}(t')\mathrm{i}\hat{q}^{\alpha}(t')\right\rangle \end{aligned} \tag{4.49}$$

and the second term in $[\cdots]$ in the RHS of (4.49) cannot cancel with $e_{\alpha,j}$, since in the inertial case we have already fixed the coordinate according to Example 1 of Section 3.2.

The action S_{eff} is written in the bilinear form of σ and $\hat{\sigma}$ and thus it looks all of the non-linearity are renormalized. But since the measure of the functional integral is not $\mathrm{d}\sigma\mathrm{d}\hat{\sigma}$ but $\mathrm{d}\varphi\mathrm{d}\hat{\varphi}$, S_{eff} is non-linear in terms of $(\varphi,\hat{\varphi})$.

We derive the dynamic equation for correlation and response function. We make use of (4.24) for PSM:

$$\dot{\sigma}_i = e_i^{\mu}\left(\dot{\varphi}_{\alpha} - \mathcal{I}_{\mu}\right) - k_B T\sigma_i. \tag{4.50}$$

Then $\langle \dot{\sigma}_i(t_1)\cdots\rangle$ can be calculated along the same line with the derivation of (4.29) and get

$$\begin{aligned} \frac{\partial}{\partial t_1}C(t_1,t_2) &= 2T\chi(t_2,t_1) - k_B T C(t_1,t_2) \\ &\quad + \frac{p}{2}\int dt C^{p-1}(t,t_1)\langle P_{ij}(t_1)\mathrm{i}\hat{\sigma}_j(t)\sigma_i(t_2)\rangle/N \\ &\quad + \frac{p(p-1)}{2}\int \mathrm{d}t\chi(t_1,t)C^{p-2}(t_1,t)\langle P_{ij}(t_1)\sigma_j(t)\sigma_i(t_2)\rangle/N. \end{aligned} \tag{4.51}$$

Similarly, employing $\mathrm{i}\hat{\sigma}_j(t_2)$ as $\cdots$ gives dynamic equation for the response function

$$\begin{aligned}\frac{\partial}{\partial t_1}\chi(t_1,t_2) &= \delta(t_1-t_2)-k_BT\chi_{ij}(t_1,t_2) \\ &\quad +\frac{p}{2}\int dtC^{p-1}(t,t_1)\langle P_{ij}(t_1)\mathrm{i}\hat{\sigma}_j(t)\mathrm{i}\hat{\sigma}_i(t_2)\rangle/N \\ &\quad +\frac{p(p-1)}{2}\int \mathrm{d}t\chi(t_1,t)C^{p-2}(t_1,t)\langle P_{ij}(t_1)\sigma_j(t)\mathrm{i}\hat{\sigma}_i(t_2)\rangle/N.\end{aligned} \tag{4.52}$$

These equations are not closed within the correlation C and response χ themselves since the RHS contains 4-point correlations, for example,

$$\begin{aligned}\langle P_{ij}(t_1)\mathrm{i}\hat{\sigma}_j(t)\sigma_i(t_2)\rangle/N &= \left\langle \frac{\mathrm{i}\hat{\sigma}_i(t)\sigma_i(t_2)}{N}-\frac{\sigma_i(t_1)\sigma_i(t_2)\sigma_j(t_1)\mathrm{i}\hat{\sigma}_j(t)}{N^2}\right\rangle \\ &= \chi(t_2,t)-\left\langle\frac{\sigma_i(t_1)\sigma_i(t_2)\sigma_j(t_1)\mathrm{i}\hat{\sigma}_j(t)}{N^2}\right\rangle.\end{aligned} \tag{4.53}$$

Note that in the derivation with the soft constraint the dynamical equation for correlation and response function are already closed within C and χ after the steepest descent calculation [5]. We expect that, by mean field nature of PSM, the Gaussian approximation is exact and one can decouple 4-point correlation into product of 2-point functions. In order to consider whether one can justify the decoupling we go back to the action (4.46). We can extract the renormalized dynamic equation for φ_α as

$$\dot{\varphi}_\alpha(t)=\mathcal{I}_\alpha(t)-\frac{p(p-1)}{2}\int \mathrm{d}t'\chi(t,t')C^{p-2}(t,t')\sigma_i(t')e_{\alpha,i}(t)+e_{\alpha,j}(t)\eta_j^{\mathrm{eff}}(t), \tag{4.54}$$

where η_j^{eff} is the renormalized noise and its variance satisfies

$$\left\langle\eta_i^{\mathrm{eff}}(t_1)\eta_j^{\mathrm{eff}}(t_2)\right\rangle=\left[2k_BT\delta(t_1-t_2)+\frac{p}{2}C^{p-1}(t_1,t_2)\right]\delta_{ij}. \tag{4.55}$$

By multiplying $e_i^\alpha(t)$ to both side of (4.54) and using the relationships (4.50) we obtain the dynamic equation for σ_i.

$$\dot{\sigma}_i(t)=-k_BT\sigma_i(t)-\frac{p(p-1)}{2}\int \mathrm{d}t'\chi(t,t')C^{p-2}(t,t')\sigma_j(t')P_{ij}(t)+P_{ij}(t)\eta_j^{\mathrm{eff}}(t). \tag{4.56}$$

Note that this equation bears little resemblance to the soft constraint result (see (3.1) of [5]). Since $P_{ij}\approx\delta_{ij}-\frac{\sigma_i\sigma_j}{N}$ this cause the nonlinear term in the RHS of (4.56). Thus one can see that the nonlinearity has not been fully

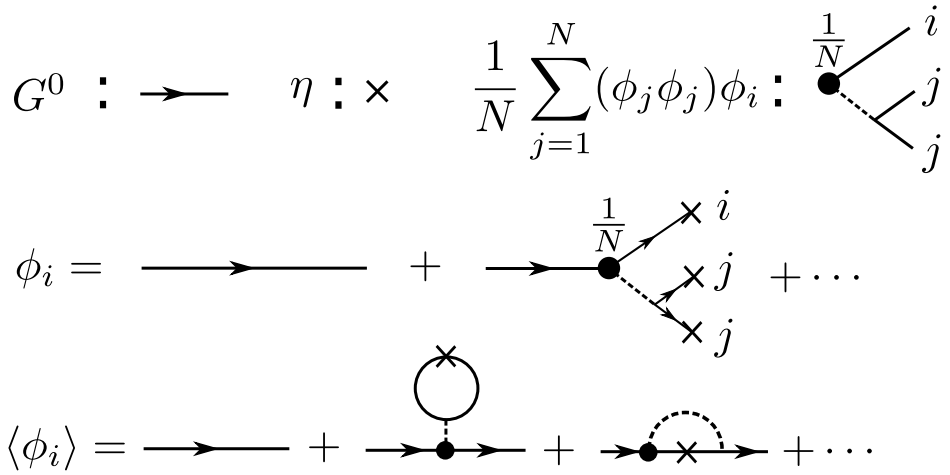

Figure 4.2: diagrammatic expansion of (4.57). The tadpole graph shown in second term in the RHS of the bottom line remains in $N \to \infty$ limit. Other diagrams such as third term in the RHS of the bottom line vanish as $1/N$.

renormalized yet. The nonlinear terms arisen from P_{ij} is proportional to $1/N$ and thus the dynamic equation (4.56) has same structure as critical dynamics of the N-vector model studied in [109]. In order to see the contribution from the nonlinear terms proportional to $1/N$ let us consider a schematic version of (4.56) for a field variable ϕ_i,

$$\dot{\phi}_i = -\mu\phi_i + \frac{1}{N}\sum_{j=1}^{N}(\phi_j\phi_j)\phi_i + \eta_i, \tag{4.57}$$

here we ignored the effect of memory term to concentrate on the problem of nonlinearity. By using the bare propagator

$$G^0 \equiv \left(\frac{\partial}{\partial t} + \mu\right)^{-1}, \tag{4.58}$$

one can expand the solution of (4.57) diagrammatically, as depicted in Figure 4.2. Here we employed so called 'faithful representation' of vertex in order to emphasize that 2 indices of 3 point vertex are the same [110]. As have shown in [109], the leading contribution from the nonlinear term, which remains finite in $N \to \infty$ limit, is so called the tadpole graphs only. In other words, diagrams produced by tying different index of vertex are sub-leading and vanish in $N \to \infty$ limit. The tadpole graph and non-tadpole graph are shown in the second and third terms in the last line of Figure 4.2. Collecting the

contribution from the all tadpole graphs cause a renormalization of 2-point functions such as the correlation and response functions. It replaces nonlinear term $\frac{1}{N}\sum_{j=1}^{N}(\sigma_j\sigma_j)\sigma_i$ with renormalized correlation $\frac{1}{N}\sum_{j=1}^{N}\langle\sigma_j\sigma_j\rangle\sigma_i$. This is equivalent with decoupling $\langle\sigma_i\sigma_i\sigma_j\sigma_j\rangle = \langle\sigma_i\sigma_i\rangle\langle\sigma_j\sigma_j\rangle$ in (4.51) and (4.52). We noted in the introduction that the rigid constraint in general produces a nonlinearity without any small parameters. But in the case of PSM, the nonlinearity arisen from the spherical constraint comes with a small parameter $1/N$. Thanks to this property of the PSM the dynamics with rigid constraint is now exactly solved.

As a result of the decoupling of the 4-point correlations to the multiple of 2-point correlations we arrive at the closed dynamic equations for the correlation function,

$$\begin{aligned}\frac{\partial C(t_1,t_2)}{\partial t_1} &= -\left[k_BT+\frac{p^2}{2}\int_{-\infty}^{t_1}dt\chi(t_1,t)C^{p-1}(t_1,t)\right]C(t_1,t_2)\\ &\quad+\frac{p(p-1)}{2}\int_{-\infty}^{t_1}\chi(t_1,t)C^{p-2}(t_1,t)C(t,t_2)\\ &\quad+\frac{p}{2}\int_{-\infty}^{t_2}dtC^{p-1}(t_1,t)\chi(t_2,t)+2k_BT\chi(t_2,t_1),\end{aligned}\tag{4.59}$$

and for the response function, by using $\mathrm{tr}P = N-1$,

$$\begin{aligned}\frac{\partial \chi(t_1,t_2)}{\partial t_1} &= \delta(t_1-t_2)\\ &\quad-\left[k_BT+\frac{p^2}{2}\int_{-\infty}^{t_1}dt\chi(t_1,t)C^{p-1}(t_1,t)\right]\chi(t_1,t_2)\\ &\quad+\frac{p(p-1)}{2}\int_{t_2}^{t_1}dt\chi(t_1,t)C^{p-2}(t_1,t)\chi(t,t_2),\end{aligned}\tag{4.60}$$

which are exactly same as the result of soft constraint calculation.

4.5 Discussion and conclusions

In this chapter we calculated the dynamics of PSM within the rigid constraint treatment. The result is the same as that has obtained within the soft constraint model. Thus the analogy between the dynamics of PSM and MCT for molecular liquids remain intact and the mean field picture has been saved.

We make a comparison with the stiff constraint derivation carried out by Kirkpatrick and co-worker [4]. As pointed out in Section 3.8.5 the difference

between the infinitely stiff and the rigid constraint is the existence of the logarithm of the determinant in the stationary distributions. In the PSM, constraint condition is given in (4.4) and thus $D = \frac{\partial F(x)}{\partial x_i}\frac{\partial F(x)}{\partial x_i} = 4N$. Thus $\ln|D| \sim \ln N$. In (3.184) energy U is extensive variable and scales as $\mathcal{O}(N)$, which is much larger than $\ln N$. Thus lndet term can be negligible in spherical constraint case in the thermodynamic limit. This is the reason why our result is the same as Kirkpatrick's one.

We point out one problem on our derivation. By substituting $A(x, \hat{x}) = \widetilde{L}_{ij}\mathrm{i}\hat{x}_j(t')$ in (4.29),

$$\begin{aligned}\left\langle \dot{x}_i(t)\widetilde{L}_{ij}(t')\mathrm{i}\hat{x}_j(t')\right\rangle &= -\left\langle \widetilde{L}_{ij}(t)\frac{\partial U}{\partial x_j(t)}\widetilde{L}_{ij}(t')\mathrm{i}\hat{x}_j(t')\right\rangle \\ &\quad +2k_BT\left\langle \widetilde{L}_{ik}(t)\mathrm{i}\hat{x}_k(t)\widetilde{L}_{ij}(t')\mathrm{i}\hat{x}_j(t')\right\rangle \\ &\quad +\left\langle e_i^\alpha(t)\widetilde{L}_{ij}(t')e_{\alpha,j}(t')\right\rangle\delta(t-t') \\ &\quad +k_BT\left\langle \frac{\partial\widetilde{L}_{ik}}{\partial x_l(t)}P_{kl}(t)\widetilde{L}_{ij}(t')\mathrm{i}\hat{x}_j(t')\right\rangle. \quad (4.61)\end{aligned}$$

By integrating both side of (4.61) from $t'-\epsilon$ to $t'+\epsilon$ with respect to t, one has

$$\chi(t'+\epsilon,t') - \chi(t'-\epsilon,t') = \frac{1}{N}\left\langle e_i^\alpha\widetilde{L}_{ij}e_{\alpha,j}\right\rangle + \mathcal{O}(\epsilon). \quad (4.62)$$

Taking the limit of $\epsilon \to 0$ and using the causality one has

$$\lim_{t'\to t-0}\chi(t,t') = \left\langle e_i^\alpha\widetilde{L}_{ij}e_{\alpha,j}\right\rangle/N. \quad (4.63)$$

In the case with PSM the RHS of (4.63) is $\langle \mathrm{tr}P\rangle/N = (N-1)/N \sim 1$ in the thermodynamic limit.

$$\lim_{t'\to t-0}\chi(t,t') = 1. \quad (4.64)$$

On the other hand, σ_i happens to be perpendicular to the constraint surface for the spherical constraint, while $\mathrm{i}\hat{\sigma}_i$ is in general parallel to constraint surface, by the definition (4.17). Thus $\sigma_i(t)\mathrm{i}\hat{\sigma}_i(t) = 0$, and

$$\chi(t,t) = \frac{1}{N}\langle\sigma_i(t)\mathrm{i}\hat{\sigma}_i(t)\rangle = 0. \quad (4.65)$$

(4.64) and (4.65) apparently contradict with each other. So far we do not know what is wrong.

As we have described in Subsection 3.6.3, the theory of the constrained Brownian motion for the systems without momentum has not been established yet, compared with the inertial systems (see Subsection 3.6.1 and 3.6.2). We stress that the present derivation of the dynamics of the PSM is based on such a fragile ground.

Chapter 5

Mode-Coupling Theory of Binary Mixture with Large Size Ratio

5.1 Introduction

In this chapter we report the numerical results on the binary mode-coupling theory (MCT), putting special emphasis on the time scale separation between the large and small species.

The binary mixtures show very rich glass phase behaviors. Switching the one-component system to the binary mixture introduces a new length scale to the system. The two length scales, sizes of the large and the small particles, make the nature of the glass transition very rich. When the size ratio between the large and small particles is not far from 1, it serves as a frustration against the crystallization, as depicted in (a) of Figure 5.1. To obtain a stable glassy state in computer simulations one has to prevent the crystallization. Hence, the binary mixtures with a moderate size ratio has been introduced as a model glass former. But if one change the size ratio far from 1, say $\delta \equiv \sigma_S/\sigma_L \sim 0.5$, with σ_S and σ_L being diameters of the small and large particles respectively, the size difference is not just a source of a frustration. Depending on the mixing ratio of the large or the small species, the leading player of the glass transition changes and a competition occurs in between two species [111–120]. Very exotic phase diagrams for binary mixture with large size ratio have been reported [2, 121–124].

Another interesting system closely related with binary mixture with large size ratio is randomly pinned system as a model of transport in confined pore [125–131]. This system is consist of completely frozen immobile parti-

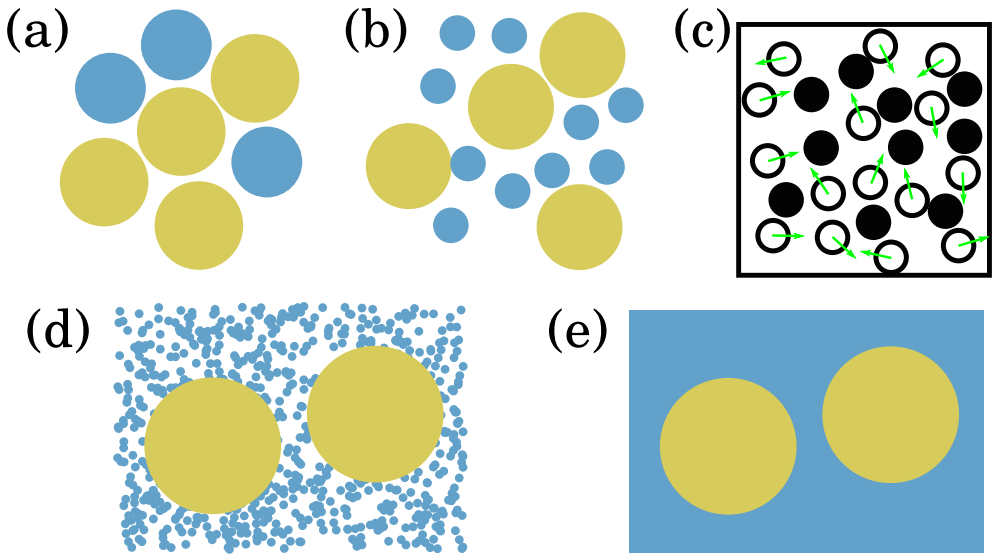

Figure 5.1: Several models of binary mixtures. (a) Size ratio between large and small particle is almost 1. Binary nature plays a role of a frustration against the crystallization. (b) Size ratio certainly differs from 1. Non-trivial geometry causes rich behavior for static and dynamics. (c) Limit of the infinite separation of the time scales leads to the system with mobile particle (white) and randomly pinned particles (black). (d) Binary mixture with disparate size ratio. Time scales between large and small species are decoupled and the effective one-component description shown in (e) is expected to be possible.

cles shown in black balls in (c) of Figure 5.1 and mobile white balls. When the size ratio goes disparately different from 1, the time scales between the large and small particles decouple. For the smaller particles, motion of the larger particles is so slow that it looks as if it is stopped. Therefore, the randomly pinned system is interpreted as the limit of infinite separation of time scales in the binary mixture. Such system has been introduced to investigate the rich behavior of the glass transition. The ordinary glass transition is characterized by a sudden emergence of a plateau in the density correlation function. This is called the type B glass transition. On the other hand, when there exist a lot of pinned particles (black ball in (c) of Figure 5.1), the glass transition of the mobile particles become continuous. This is called the type A glass transition. MCT for pinned system successfully captured this feature, showing its powerful predictive ability [132–138]. Recently the random pinning glassy system is attracting more and more interests from the viewpoint of a mean field picture of the glass transition. In this picture, the slow dynamics of the supercooled liquids is caused by large number of

metastable minima in the free energy landscape. In order to detect a length scale responsible for the minima, the idea of pinning has been introduced as a realization of the external force that attract the system to the minima [139,140]. The random pinning is one of the realizations of such external forces [141–144]. The effect of pinning decays with the distance from the pinned particles. From the decay of the correlation it is expected that one can extract a length scale responsible for a metastable state.

When the size ratio is disparate and the time scale between the large and small particles become separated one can adiabatically eliminate the freedom of the smaller particle and obtain an effective one-component system (see (d) and (e) of Figure 5.1). The adiabatic elimination considerably reduces the degree of freedom of the system and makes possible to simulate the system in reasonable computational costs. The effective description within larger particle in colloid-polymer mixture has succeeded to describe the experimental results [145, 146]. In colloid(large)-polymer(small) mixture, the osmotic pressure of the polymer causes a short range attractive interaction between colloidal particles. This interaction, called the Asakura-Oosawa (AO) potential, can be analytically obtained by the adiabatic elimination of the degree of freedom of polymer [147]. This short range strong force itself is interested from the viewpoint of controlling of interactions between the colloidal particles. Not only that, it dramatically enriches the dynamics and the glass transition of the colloidal suspensions. In ordinary colloidal system the glass transition undergoes because of their repulsive excluded volume. But in the case of colloid-polymer mixture the dynamics of colloids is trapped by the attractive pocket. The glass state realized by such interaction is called 'attractive glass'. This picture is first proposed within MCT [148] and later confirmed in experiment [149]. one-component system interacting with the effective AO potential is investigated by simulation [150–153], MCT [154–157] and experiments [149]. Thus the adiabatic elimination of the smaller particle and the resulting effective one-component theory gives us powerful predictions. But the static calculation of adiabatic elimination of smaller particle does not tell us how disparate time scale is needed to justify this approximation. If there exists the correct dynamical theory on binary mixture it will continue to the effective one-component theory in the limit of the disparate time scales and is able to tell us the quality of the adiabatic elimination. Therefore, the binary MCT can be tested with such perspective [158]. We also focus on this issue as a topic on the time scale separation.

Among the several theories of the glass transition, MCT for supercooled liquid excels other theories in the sense that it is a first-principles predictive theory [159] and is expected to play a role of a mean field theory of the glass transition [3]. It succeeded to describe the special feature of the dynamics

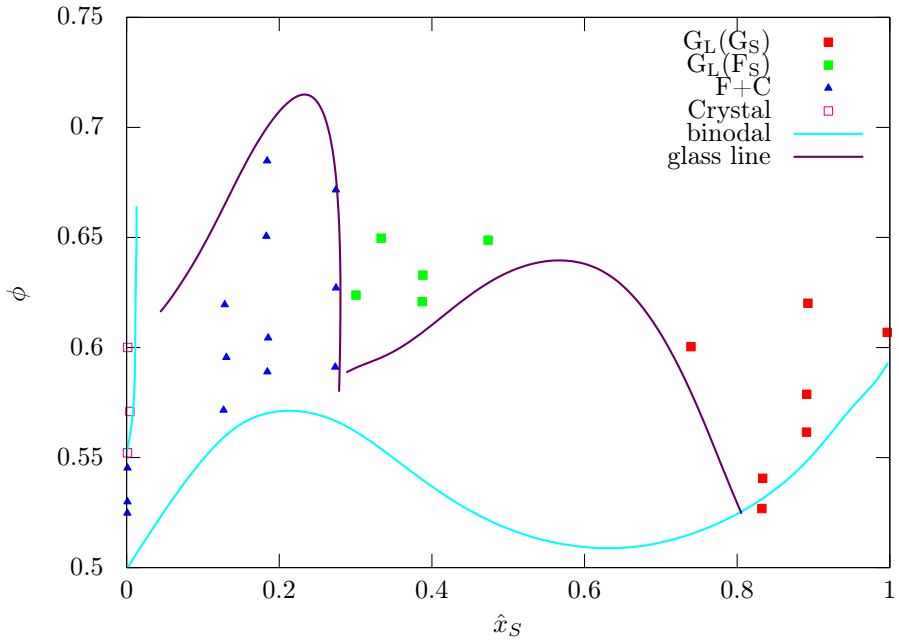

Figure 5.2: Experimental phase diagram for binary mixture of colloidal suspension with size ratio $\delta = 0.11$. Reproduced from [2]. Vertical and horizontal axis represent respectively the total packing fraction of colloidal suspension ϕ and volume fraction ratio of the smaller particle $\hat{x}_S$. Aqua and violet lines represents the fluid-solid binodal and the glass transition line. Open pink square is the crystal phase formed by the larger component. Filled blue triangle is sample phase-separated into fluid and crystal. Filled squares represents the glass phases.

of the density correlation function in supercooled liquids: the two step relaxation through a long plateau. But on the other hand it is known that MCT has several shortcomings. For example, MCT predicts the divergence of the relaxation time of the density correlation function at a finite temperature or a finite packing fraction, while such a divergence is not observed in experiments. This is called the dynamic transition of MCT. Although the transition itself is unphysical, it is appreciated to detect an onset of the slow dynamics of the supercooled liquid. As a graver example of the drawbacks, we focus on the time scale separation between the large and small particles in highly asymmetric binary mixtures.

MCT for binary mixtures can be derived as a straightforward extension of that of the monodisperse liquids [159]. But it has obvious difficulty in the limit that diameter of one species become infinitely smaller than another. In such limit one expects that the smaller particles can move around the

larger particles even if the large particles exhibit the glass transition. In fact, such phase is observed in an experimental system on the colloidal suspension [2, 121, 122]. As shown in Figure 5.2, when the volume fraction ratio of the smaller particle is not large, only the larger species undergoes the glass transition while smaller remains in the fluid phase (green symbol). In other words, the time scales between the large and small particles are separated. But when the smaller particles dominate the system, they form the glass phase by themselves and the larger becomes frozen-in the environment formed by the smaller particles (shown in red symbols). On the other hand, MCT for binary mixture predicts that the dynamic transition of collective motion of large and small particles occurs at the same parameter irrespective of the size ratio [160]. It suggests that the time scale separation between the large and the small particles is never achieved [123,161]. This prediction does not necessary hold for self correlations. Indeed, it is shown that in binary hard sphere mixture of $\delta \lesssim 0.2$, MCT predicts the existence of the phase at which the self motion of small particle is ergodic while other dynamic components, i.e., the self motion of the large particle and the collective motion of both species, exhibit the dynamic transition [113, 123]. So far the time scale separation between large and small particles is explained within the binary MCT by using the fact that the dynamic transition of the self correlation of small particle does not occur at the same parameter as the dynamic transition of the other correlations.

In this chapter we report that the binary MCT can describe the time scale separation between large and small particle only within the corrective density fluctuation. On the other hand, we also show that the binary MCT does not continue to the effective one-component theory in the limit of disparate size ratio. Note that the numerical result for the binary hard sphere mixtures is almost a reproduction of the result reported by Voigtmann [123]. We stress that our contribution is an another interpretation of his results.

The present chapter is organized as follows. In Section 5.2 we describe the model binary mixtures considered in this chapter and the MCT for binary mixtures. The numerical results are presented in Section 5.3. We summarize our results and give a discussion in Section 5.4.

5.2 Description of Model and Method

5.2.1 Binary mixture

The system of the binary mixture is uniquely determined by the size ratio δ, the total packing fraction ϕ, the packing fraction ratio of smaller particle $\hat{x}_S$. Other quantities are dependent of these three parameters. For example the number density ρ is given in 3-dimensional systems by

$$\rho = \frac{6\phi}{\pi}\left(\hat{x}_S\delta^{-3} + \hat{x}_L\right). \tag{5.1}$$

Here $\hat{x}_L = 1 - \hat{x}_S$ is the volume fraction ratio of the larger particles and we normalized the length scale of system by the diameter of the larger particle. In addition to $\hat{x}_S$ we shall introduce another parameter to represent degree of mixing:

$$x_S = \frac{\hat{x}_S}{\delta^3 + (1-\delta^3)\hat{x}_S}, \tag{5.2}$$

which is the mole fraction of the smaller particles.

The interaction between hard sphere i and j is given by

$$U = \begin{cases} 0 & r_{ij} > \sigma_{ij} \\ \infty & r_{ij} < \sigma_{ij} \end{cases} \tag{5.3}$$

with r_{ij} being distance between particle i and j. $\sigma_{ij} \equiv (\sigma_i + \sigma_j)/2$ and σ_i is diameter of ith particle. The Asakura-Oosawa (AO) model is the mixture of colloidal particle and polymer in the θ solvent. The polymers are modeled as ideal gas. Thus it is defined by [147]

$$\begin{aligned} U_{cc} &= \begin{cases} 0 & r_{ij} > \sigma_{ij} \\ \infty & r_{ij} < \sigma_{ij} \end{cases} && i \text{ and } j \text{ for colloid,} \\ U_{cp} &= \begin{cases} 0 & r_{ij} > \sigma_{ij} \\ \infty & r_{ij} < \sigma_{ij} \end{cases} && i \text{ for colloid, } j \text{ for polymer,} \\ U_{pp} &= 0 && i \text{ and } j \text{ for polymer.} \end{aligned} \tag{5.4}$$

5.2.2 Binary Mode-Coupling Theory

MCT provides the time evolution of the density correlation between each species:

$$\Phi_{\alpha\beta}(\boldsymbol{q}, t) \equiv \langle \delta\rho_\alpha(\boldsymbol{q}, t)\delta\rho^*_\beta(\boldsymbol{q}, 0)\rangle, \tag{5.5}$$

here Greek indices stand for species of particle. $*$ represents complex conjugate. For hard sphere system $\alpha, \beta = L, S$. L and S stand for large and small species. For the system of the AO model $\alpha, \beta = c, p$. c and p stand for colloid and polymer.

$$\delta\rho_\alpha(\boldsymbol{q}, t) = \frac{1}{\sqrt{N}} \sum_i^{N_\alpha} \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}_\alpha^i(t)} - (2\pi)^3\delta(q)\rho, \tag{5.6}$$

is the density fluctuation of species α in the Fourier space. $\boldsymbol{q}$ is wavenumber. $\boldsymbol{r}_\alpha^i(t)$ is the position of ith particle of species α at time t. N_α is number of particles of species α and N is the total number of particles.

In the time domain the dynamic equation of MCT for the overdamped system reads with adopting the dyadic abbreviation [162],

$$\boldsymbol{\tau}_q^0\dot{\boldsymbol{\Phi}}(q,t) + \boldsymbol{S}^{-1}(q)\boldsymbol{\Phi}(q,t) + \int_0^t dt' \boldsymbol{M}[\boldsymbol{\Phi}](q, t-t')\dot{\boldsymbol{\Phi}}(q,t') = 0, \tag{5.7}$$

where $\boldsymbol{\tau}_q^0$ and $\boldsymbol{S}(q)$ represent respectively the short time diffusion timescale and the static structure factor. We have to adopt these quantities as inputs since they are not determined within MCT. $\boldsymbol{M}[\boldsymbol{\Phi}](q,t)$ is the so called memory function which represents the nonlinear feedback of the density fluctuation in dense liquids and given by

$$M_{\alpha\beta}[\boldsymbol{\Phi}](q,t) = \frac{1}{2x_\alpha x_\beta \rho q^2} \int \frac{d^3\boldsymbol{k}}{(2\pi)^3} V^{\boldsymbol{q};\boldsymbol{kp}}_{\alpha\alpha'\alpha''} \Phi_{\alpha'\beta'}(k,t)\Phi_{\alpha''\beta''}(p,t)V^{\boldsymbol{q};\boldsymbol{kp}}_{\beta\beta'\beta''}. \tag{5.8}$$

Here summation over repeated indices is imposed and $\boldsymbol{p} = \boldsymbol{q} - \boldsymbol{k}$. We introduced the vertex function $V^{\boldsymbol{q};\boldsymbol{kp}}_{\alpha\alpha'\alpha''}$ as

$$V^{\boldsymbol{q};\boldsymbol{kp}}_{\alpha\alpha'\alpha''} = \hat{\boldsymbol{q}}\cdot\boldsymbol{k}\rho c_{\alpha\alpha'}(k)\delta_{\alpha\alpha''} + \hat{\boldsymbol{q}}\cdot\boldsymbol{p}\rho c_{\alpha\alpha''}(p)\delta_{\alpha\alpha'}, \tag{5.9}$$

where $\hat{\boldsymbol{q}} \equiv \boldsymbol{q}/q$ and $\boldsymbol{c}(q)$ is the direct correlation function which is related to the static structure factor by the Ornstein-Zernike (OZ) equation [163],

$$\rho c_{\alpha\beta}(q) = \frac{\delta_{\alpha\beta}}{x_\alpha} - \left[S^{-1}(q)\right]_{\alpha\beta}. \tag{5.10}$$

The dynamic transition point $\phi_\mathrm{d}(\delta, \hat{x}_S)$ is defined as a threshold packing fraction at which the density correlation function $\boldsymbol{\Phi}(q,t)$ becomes no longer ergodic. Therefore we may work on the long time limit of (5.7). The long time limit of the density correlation function is called the Debye-Waller (DW) factor: $\boldsymbol{F}(q) \equiv \lim_{t\to\infty}\boldsymbol{\Phi}(q,t)$. It satisfies

$$\boldsymbol{F}(q) = \boldsymbol{S}(q) - \left[\boldsymbol{S}^{-1}(q) + \boldsymbol{M}[\boldsymbol{F}](q)\right]^{-1}. \tag{5.11}$$

δ	q_c	N_q	Δq
0.4	200	512	0.391
0.3	200	512	0.391
0.2	300	1024	0.293

Table 5.1: Parameters associated with discretization of (5.7) and (5.11) for each investigated size ratio δ and region of volume fraction of small particle $\hat{x}_S$ for the systems of the hard sphere mixtures. q_c is a ultraviolet cutoff wave number and N_q is number of grid point. Δq is the grid spacing.

This is a self-consistent equation for the DW factor. Note that $\boldsymbol{\tau}_q^0$ is absent in (5.11) since a time derivative of the density correlation function always vanishes in the long time limit. Thus input to (5.11) is the static structure factor only. MCT also predicts the dynamics of the self intermediate scattering function. Its long time limit is called the Lamb-Mössbaur (LM) factor,

$$f_\alpha(q) = \lim_{t\to\infty} \left\langle \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}_\alpha(t)} \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}_\alpha(0)} \right\rangle. \tag{5.12}$$

Here $\boldsymbol{r}_\alpha$ without index of the particle i stands for the position of the tagged particle of species α. $f_\alpha(q)$ is evaluated within MCT as

$$f_\alpha = 1 - \left[1 + m_\alpha^s[\boldsymbol{F}, \boldsymbol{f}]\right]^{-1}, \tag{5.13}$$

$$m_\alpha^s[\boldsymbol{F}, \boldsymbol{f}] = \frac{1}{\rho q^2} \int \frac{d^3\boldsymbol{k}}{(2\pi)^2} V_{\alpha,\alpha'\beta'}^{s,\boldsymbol{qk}} F_{\alpha'\beta'}(k) f_\alpha^s(p), \tag{5.14}$$

$$V_{\alpha,\alpha'\beta'}^{s,\boldsymbol{qk}} = (\hat{\boldsymbol{q}}\cdot\boldsymbol{k})^2 \rho c_{\alpha\alpha'}(k) \rho c_{\alpha\beta'}(k). \tag{5.15}$$

Note that in (5.14) sum over only α' and β' are imposed.

We numerically solved (5.11) and determined the dynamic transition point. We discretized (5.11) on interval $q \in [\hat{o}\Delta q : q_c]$ where an offset $\hat{o} = 0.5$ is introduced to avoid the infrared singularity in memory function [164]. The grid spacing Δq is dependent of number of grid points N_q. We show in Table 5.1 the value of these parameters we have chosen for each size ratio δ for the hard sphere mixture system. Since the ultraviolet cutoff q_c must be much larger than the inverse of the shortest length scale of the system, the smaller δ, the larger q_c is needed. While for the AO model one need not to have a large q_c since the shortest length scale of the system is not δ but $\sigma_{cp} = (1+\delta)/2 \sim 1$ and does not much depend on δ. We employed an efficient numerical evaluation of the memory function called the Bengtzelius' trick [165] described in Appendix E. Note that a limit of the one-component system, $\hat{x}_S = 0$ or $\hat{x}_S = 1$, is singular as seen by the definition of the memory function (5.8). But this singularity can be avoided by transforming the

dynamic equation (5.7) or its long time limit (5.11) according to the method described in Appendix E.2.

We briefly describe the mathematical structure of the binary MCT which leads the dynamic transition for both species at the same parameter and forbids the complete time scale separation between the large and the small particles. For more complete discussion the reader should refer to [160, 166]. The equation we are concerned with, (5.11), is a self-consistent equation for DW factor $\boldsymbol{F}$, solved by substituting the value of the left hand side (LHS) iteratively to the right hand side (RHS). Let us denote the RHS of (5.11) as $\mathcal{I}[\boldsymbol{F}]$ and write

$$\boldsymbol{F} = \mathcal{I}[\boldsymbol{F}]. \tag{5.16}$$

The iterative procedure to obtain the numerical solution of (5.16) starts by choosing a candidate of the solution, say $\boldsymbol{F}^0$, and substitute it into the RHS of (5.16). Then one obtains $\boldsymbol{F}^1 = \mathcal{I}[\boldsymbol{F}^0]$. When a trial function $\boldsymbol{F}^n$ is sufficiently close to the genuine solution $\boldsymbol{F}$ the difference between $\boldsymbol{F}^n$ and $\boldsymbol{F}^{n+1}$, say $\delta\boldsymbol{F} = \boldsymbol{F}^{n+1} - \boldsymbol{F}^n$, will be small. Their difference can be computed within the linear order to $\delta\boldsymbol{F}$ as

$$\boldsymbol{F}^{n+2} - \boldsymbol{F}^{n+1} = \mathcal{I}(\boldsymbol{F}^{n+1}) - \mathcal{I}[\boldsymbol{F}^n] = \boldsymbol{C}[\delta\boldsymbol{F}] + \mathcal{O}(\delta\boldsymbol{F}^2), \tag{5.17}$$

with

$$\boldsymbol{C}[\boldsymbol{h}] \equiv 2\left(\boldsymbol{S} - \boldsymbol{F}\right)\boldsymbol{M}[\boldsymbol{F}, \boldsymbol{h}]\left(\boldsymbol{S} - \boldsymbol{F}\right). \tag{5.18}$$

Here $\boldsymbol{M}$ with two arguments is defined by

$$M_{\alpha\beta}[\boldsymbol{A}, \boldsymbol{B}] \equiv \frac{1}{2x_\alpha x_\beta \rho q^2} \int \frac{d^3\boldsymbol{k}}{(2\pi)^3} V^{qkp}_{\alpha\alpha'\alpha''} A_{\alpha'\beta'}(k) B_{\alpha''\beta''}(p) V^{qkp}_{\beta\beta'\beta''}. \tag{5.19}$$

Thus $\boldsymbol{M}[\boldsymbol{F}, \boldsymbol{F}]$ is the ordinary memory function defined in (5.8). $\boldsymbol{C}$ is called the stability matrix of a self-consistent equation (5.16) and it can be proven that $\boldsymbol{C}$ is positive definite matrix. It means that if $\boldsymbol{F}^n$ is positive definite $\boldsymbol{F}^{n+1}$ is also positive definite. Since usually $\boldsymbol{F}^0 = \boldsymbol{S}$ is chosen as a starting point and $\boldsymbol{S}$ is positive definite, the fixed point $\boldsymbol{F}$ becomes positive definite. This property forbids the solution to (5.16) to be

$$\boldsymbol{F}(q) = \begin{pmatrix} F_{LL}(q) & F_{LS}(q) \\ F_{SL}(q) & F_{SS}(q) \end{pmatrix} = \begin{pmatrix} F_{LL}(q) & F_{LS}(q) \\ F_{SL}(q) & 0 \end{pmatrix}. \tag{5.20}$$

In other words the positive definiteness of the stability matrix $\boldsymbol{C}$ forbids the complete time scale separation between large and small particles. If one choose a positive *semi*-definite $\boldsymbol{F}^0$ as a starting point the iterative procedure leads to a trivial fixed point $\boldsymbol{F} = 0$.

For later use we define the right and left eigenvector $\boldsymbol{e}$ and $\hat{\boldsymbol{e}}$ to the maximum eigenvalue of the stability matrix $\boldsymbol{C}$ [162, 166]. We impose following normalization to them.

$$\mathrm{tr}[\hat{\boldsymbol{e}}\boldsymbol{e}] = 1, \quad \mathrm{tr}\left[\hat{\boldsymbol{e}}\boldsymbol{e}(\boldsymbol{S}-\boldsymbol{F})^{-1}\boldsymbol{e}\right] = 1. \tag{5.21}$$

With these normalizations so called MCT exponent λ is defined by

$$\lambda \equiv \mathrm{tr}\left[\hat{\boldsymbol{e}}(\boldsymbol{S}-\boldsymbol{F})\boldsymbol{M}[\boldsymbol{e},\boldsymbol{e}](\boldsymbol{S}-\boldsymbol{F})\right]. \tag{5.22}$$

This exponent λ varies from 1/2 to 1 and characterize the types of the dynamic transition of MCT. In the case of mono-disperse hard sphere system with its static structure factor evaluated by using the Percus-Yevik (PY) approximation λ takes the value about 0.74.

5.2.3 Schematic Model

To focus on the mathematical structure of the binary MCT we consider a schematic version of (5.7). The schematic MCT is first introduced by Leutheusser to investigate the mathematical aspect of the one-component MCT, by ignoring the all the wavenumber dependence of the physical quantities [167]. It was quite successful in unveiling the mathematical structure of the dynamic transition of MCT [162]. The another advantage of the schematic models is that they are free from the approximation in the static input. In the full MCT one has to adopt the static structure factor. Obtaining the accurate static structure factor itself is very hard problem, particularly for dense liquids. So far no theory has succeeded to predict the static behaviour of liquids within a systematic approximation. Thus it is difficult to separate the origin of inaccuracy of the result obtained within MCT, static or dynamic.

We propose following dynamic equation of schematic binary MCT.

$$\boldsymbol{\tau}^0\dot{\boldsymbol{\Phi}}(t) + \boldsymbol{S}^{-1}\boldsymbol{\Phi}(t) + \int_0^t ds\boldsymbol{M}(t-s)\dot{\boldsymbol{\Phi}}(s) = 0. \tag{5.23}$$

Here, $\boldsymbol{\tau}^0$ represents the short time scale matrix and its $\alpha\beta$ component is given by $\tau^0_{\alpha\beta} = \tau^0_\alpha\delta_{\alpha\beta}$ (no sum over α), where τ^0_α represents diffusive time scale of particle of species α. Results obtained in this chapter do not depend on the choice of $\boldsymbol{\tau}^0$. $\boldsymbol{S} \equiv \boldsymbol{\Phi}(0)$ mimics the static structure factor. $\boldsymbol{M}(t)$ is the memory function in the "full" MCT. In our model it is assumed to be

$$M_{\alpha\beta} = \frac{1}{2x_\alpha x_\beta \rho} V_{\alpha\alpha'\alpha''}\Phi_{\alpha'\beta'}\Phi_{\alpha''\beta''}V_{\beta\beta'\beta''}, \tag{5.24}$$

with vertex tensor $V_{\alpha\beta\gamma}$. x_α and ρ are respectively the mole fraction of the small species and the density of the liquid. We assume following symmetries

$$V_{\alpha\beta\gamma} = V_{\alpha\gamma\beta}, \tag{5.25}$$
$$V_{\alpha\beta\beta} = 0 \quad (\alpha \neq \beta), \tag{5.26}$$
$$V_{\alpha\alpha\beta} = V_{\beta\beta\alpha}. \tag{5.27}$$

It can be checked that these symmetries hold also for the original vertices, see (5.9). These assumptions reduce the number of independent components of the vertices, to only three: $V_{LLL} = V_{LL}, V_{SSS} = V_{SS}, V_{LLS} = V_{LSL} = V_{SSL} = V_{SLS} = V_{LS}$.

Next we connect $\boldsymbol{V}$ with real fluid parameters, total packing fraction ϕ, size ratio δ and mole fraction of smaller particle x_S. The vertex functions for the original MCT are proportional to the direct correlation function $\rho\boldsymbol{c}(q)$. Thus we suppose that $V_{\alpha\beta} = \rho c_{\alpha\beta}$. We can impose some thermodynamic consistency constraints to each element of $\boldsymbol{c}$ [168].

1. In the limit $x_S = 0$ or $x_L = 0$ binary mixture continues to the mono-disperse system. Since $\boldsymbol{c}$ has dimension of [length]^3, it follows that

$$\delta^3 c_{LL}|_{x_S=0} = c_{SS}|_{x_S=1}. \tag{5.28}$$

2. The binary mixture with size ratio $\delta = 1$ must represent mono-disperse system. The direct correlation function is defined as $c_{\alpha\beta} = \delta^2 F_{\rm ex}/\delta\rho_\alpha\delta\rho_\beta$ where $F_{\rm ex}$ is the excess free energy functional, and $F_{\rm ex}$ for such system should become symmetric with respect to the interchange of the species. Thus we have for $\delta = 1$,

$$c_{LL} = c_{SS} = c_{LS} = c_{SL} \quad (\delta = 1). \tag{5.29}$$

3. The third constraint comes from the ideal gas limit of the smaller particles: $\delta = 0$. In such case the smaller particle does not contribute to $F_{\rm ex}$. Thus,

$$\frac{\delta F_{\rm ex}}{\delta\rho_S} = 0 \Rightarrow c_{SS} = c_{LS} = c_{SL} = 0 \quad (\delta = 0). \tag{5.30}$$

Taking these constraints into account we set $\boldsymbol{V}$ as

$$V_{LL} = \frac{\rho}{1-\phi}, \quad V_{SS} = \frac{\rho\delta^3}{1-\phi}, \quad V_{LS} = V_{SL} = \frac{\rho\delta^{3/2}}{1-\phi}. \tag{5.31}$$

In addition to above thermodynamic consistencies we have assumed that the vertices grow up proportional to $(1-\phi)^{-1}$, and that V_{LS} and V_{SL} is proportional to $\delta^{3/2}$.

Another static input is the static structure factor $\boldsymbol{S}$. In real liquid $\boldsymbol{S}$ is expressed in terms of $\boldsymbol{c}$ by using the OZ relation. But here we do not adopt it. If we use the OZ relation it reads roughly $\boldsymbol{S} \sim \boldsymbol{c}^{-1} \sim 1-\phi$. Thus $\boldsymbol{S}$ decrease with ϕ which is not realistic behavior as the model of the liquid [1]. Thus we assume $\boldsymbol{S}$ as increase with ϕ, like in real liquid[2].

$$S_{LL} = x_L + \hat{x}_L^2 \phi, \quad S_{SS} = x_S + \hat{x}_S^2 \phi, \quad S_{LS} = S_{SL} = \hat{x}_L \hat{x}_S \phi. \tag{5.32}$$

The first term in S_{LL} and S_{SS} mimic the large q asymptotic value of the static structure factor. The first term in S_{LS} and the second terms for S_{LL} and S_{SS} represent peak values of the static structure factor. Note also that these choices of $\boldsymbol{S}$ are consistent with the third thermodynamic consistency, but not with the first and the second.

One can evaluate the long time limit of (5.23) for the DW factor $\boldsymbol{F} \equiv \lim_{t\to\infty} \boldsymbol{\Phi}(t)$ as

$$\boldsymbol{F} = \boldsymbol{S} - \left[\boldsymbol{S}^{-1} + \boldsymbol{M}[\boldsymbol{F}]\right]^{-1}. \tag{5.33}$$

We distinguish glassy and liquid phase by the value of the DW factor, non-zero or zero respectively.

[1] One might argue that we have to take first $\boldsymbol{S}$ so that it grows with ϕ and eventually determine $\boldsymbol{c}$ by OZ relation. But in that way it is hard to require the thermodynamic consistency conditions, since $\boldsymbol{S}$ is dimensionless.

[2] This set is chosen by try and error.

5.3 Results

5.3.1 Hard Sphere mixture

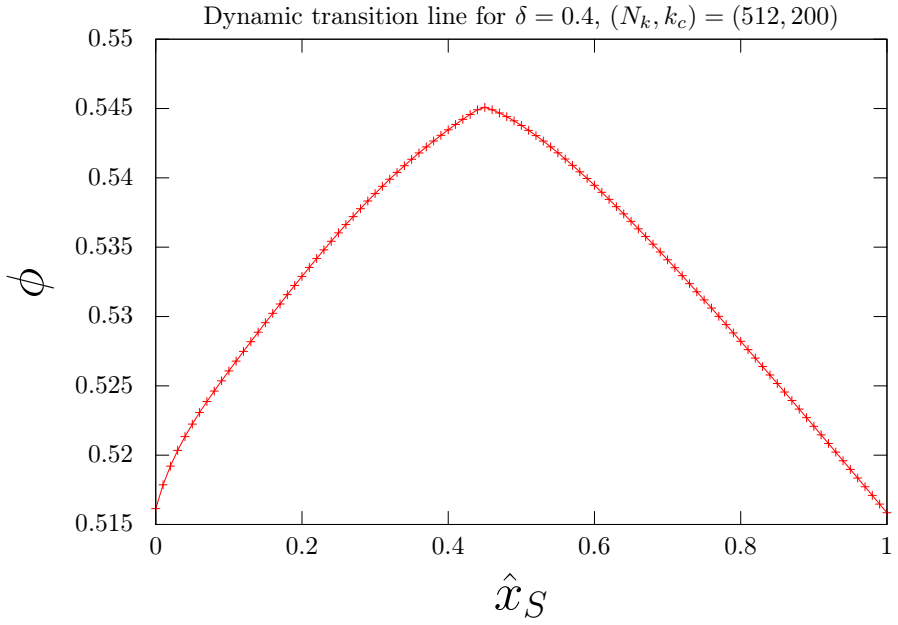

Figure 5.3: Dynamic phase diagram of binary hard sphere mixture with size ratio $\delta = 0.4$ within the binary MCT.

The case for $\delta = 0.4$

We estimate the dynamic transition point by using the bisection algorithm for packing fraction ϕ, by numerically evaluating (5.11) with the static structure factor evaluated by the analytical solution of Percus-Yevik(PY) approximation [169]. We show in Figure 5.3 the dynamic phase diagram obtained by MCT. A cross represents the dynamic transition point $\phi_{\rm d}$ for given δ and $\hat{x}_S$. Above $\phi_{\rm d}$ the DW factor is finite and the ergodicity is broken. Below $\phi_{\rm d}$ the DW factor $\boldsymbol{F} = 0$ and the system is in the liquid state. [3] The convex shape of the transition line shows that mixing of smaller particle with $\sigma_S = 0.4$ always

[3] As we stated in the introduction, although the dynamic transition itself is not observed in the experimental system, it is expected to indicate the onset of the slow dynamics of supercooled liquids. Hereafter sometimes $\phi > \phi_{\rm d}$ is called the glass phase in a conventional meaning.

shifts the transition line to the high packing fraction. Note that the convex shape of the transition line is qualitatively consistent with the experimental result on colloidal suspension with $\delta = 0.11$ [2] (See Figure 5.2).

We show in Figure 5.4 the MCT phase diagram together with the magnitude of the DW factors $F_{LL}(q)$ and $F_{SS}(q)$. The representative wavenumber is chosen as the peak wavenumber of $S_{LL}(q)$. They are normalized by their initial values, namely $S_{LL}(q)$ and $S_{SS}(q)$. Dynamic transition of F_{LL} is ordinary discontinuous one and its jump height becomes slightly larger as $\hat{x}_S$ increases. The jump height of F_{SS} changes more obviously with its composition. In small $\hat{x}_S$ region the discontinuity is relatively small. One can see a jump in the discontinuity at $\hat{x}_S \sim 0.5$. The small F_{SS} at $\phi_{\rm d}$ is seen not only for the representative wavenumber but also for other wavenumbers. We show in Figure 5.5 the DW factors at the dynamic transition point for several $\hat{x}_S$ as a function of wave number q. One can see that between $\hat{x}_S = 0.4$ and 0.5 there is a jump in DW factors for all q. This can be interpreted as localization(delocalization) of small(large) particle [111, 123].

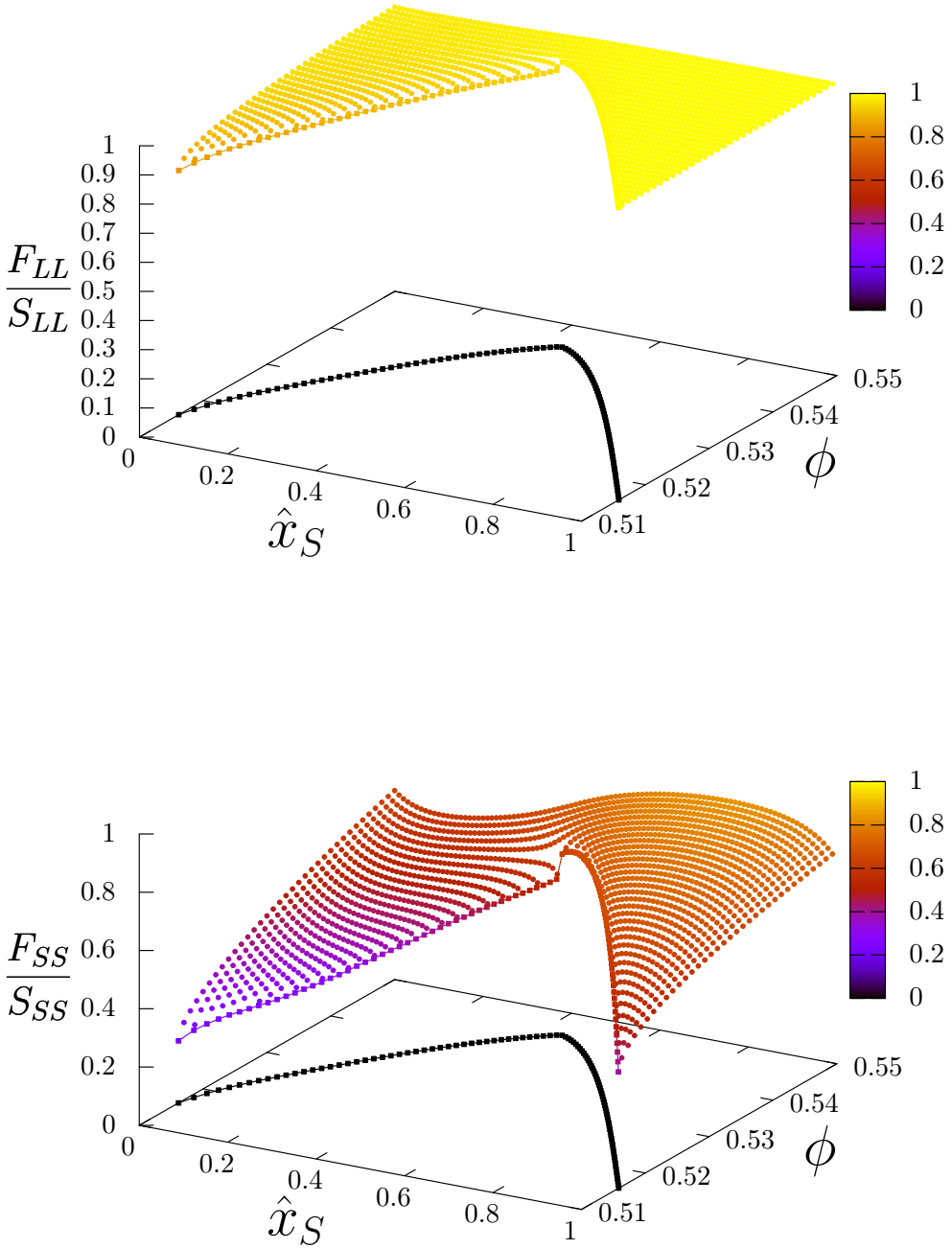

Figure 5.4: Color map of the DW factor for $\delta = 0.4$. The jump height of F_{SS} at the transition point is small compared with F_{LL}. The wave number q is chosen as peak wave number of S_{LL}.

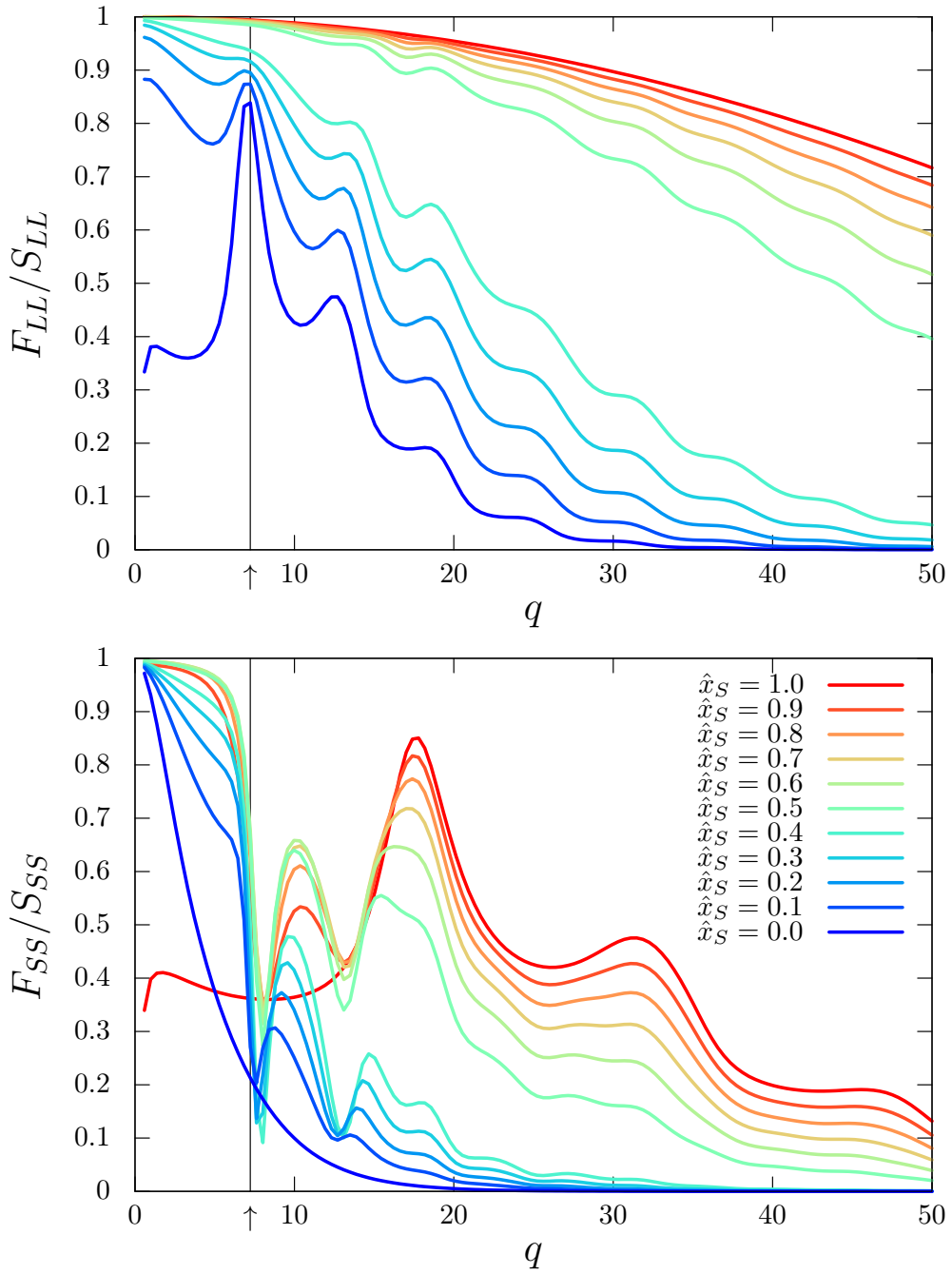

Figure 5.5: Wave number dependence of the DW factor at the dynamic transition point for several $\hat{x}_S$. Arrow indicates the representative wavenumber chosen in Figure 5.4.

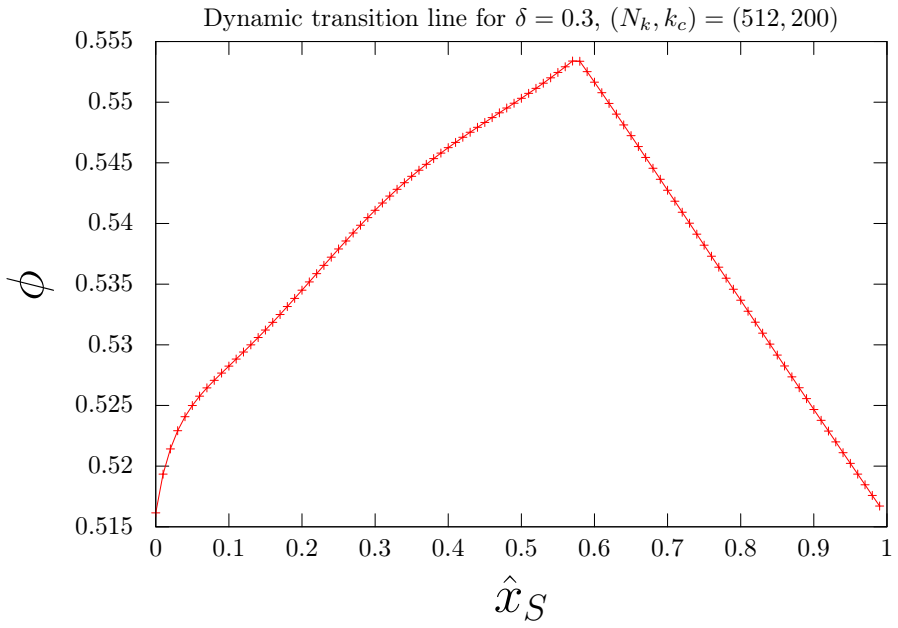

Figure 5.6: Dynamic phase diagram of binary hard sphere mixture with size ratio $\delta = 0.3$ within MCT.

The case for $\delta = 0.3$

Figure 5.6 and 5.7 shows the dynamic phase behavior and the DW factor for the systems of size ratio $\delta = 0.3$. F_{LL} shares the same qualitative trend as $\delta = 0.4$. While the small discontinuity at the dynamic transition point for F_{SS} is more pronounced. This behavior of F_{SS} indicates that the density correlation function $\Phi_{SS}(t)$ relaxes to almost zero even in the non-ergodic phase. Thus we expect that the small particles effectively behave as a fluid if the DW factor is too small to distinguish from zero. In order to check this idea, we numerically evaluated (5.7) to investigate the time evolution of the density correlation functions.

We show in the bottom panel of Figure 5.8 the dynamics of correlation functions near the dynamic transition point. The total packing fraction is taken as $\phi = \phi_{\mathrm{d}} \left(1 - 10^{-n/3}\right)$. Thus the larger the n, the closer to ϕ_{d}. The volume fraction of the smaller particles is chosen as $\hat{x}_S = 0.01$. One can see that both Φ_{LL} and Φ_{SS} slow down on approaching the dynamic transition point. But the height of the plateau for Φ_{SS} is much smaller than that of Φ_{LL}. From the numerical point of view a plateau with sufficiently small height can be regarded as 0. Then it is possible to argue that the smaller particles is in

the fluid phase even if the dynamics of the larger particle shows a two step relaxation. In other words, the larger particles exhibit the glass transition, while the small particles stay in a fluid phase. This observation does not conflict with the prediction by [160], which states that the F_{LL} and F_{SS} undergoes the dynamic transition at the same packing fraction, regardless of the magnitude of size ratio δ. The theorem does not tell the height of the DW factor at the dynamic transition point. We observe that when δ is sufficiently small and $\hat{x}_S$ is not so large, the jump height of the F_{SS} becomes negligibly small. Therefore, numerically speaking, the dynamics of Φ_{SS} does not slow down upon approaching the dynamic transition point, while the relaxation time of the larger particle divergently grows. In other words, the time scales between the large and the small particles is separated. Note that the height of the DW factor depends on the wavenumber, as shown in the top panel of Figure 5.8. One can see that the small F_{SS} is observed for the almost all wavenumbers when the volume fraction ratio of the smaller particle $\hat{x}_S$ is not too large. On the other hand when $\hat{x}_S \geq 0.2$ it is no longer the case.

In order to observe the time scale separation between the large and small particle more concretely, we extract the relaxation times of the correlation functions. The relaxation time is defined by the time when the correlation becomes 1/e of its initial value. They can be considered for each correlation functions in binary mixtures, i.e., Φ_{LL}, Φ_{SS} and Φ_{LS}. Let τ_L and τ_S be the relaxation times for Φ_{LL} and Φ_{SS}. Namely,

$$\Phi_{LL}(q, \tau_L(q)) = 1/\mathrm{e}, \quad \Phi_{SS}(q, \tau_S(q)) = 1/\mathrm{e}. \tag{5.34}$$

Note that the relaxation time is dependent of the wavenumber. We show this dependence for the binary mixture with size ratio $\delta = 0.3$, $\hat{x}_S = 0.01$, 0.02 and 0.03 in the left panel of Figure 5.9. Line color corresponds to the distance from the dynamic transition point measured by the packing fraction ϕ,

$$\phi = \phi_{\mathrm{d}} \left(1 - 10^{-n/3}\right), \quad n = 4, 5, 6, 7, 8. \tag{5.35}$$

One can see that for all $\hat{x}_S$ the relaxation time of the large-large correlation $\tau_L(q)$ grows with packing fraction for almost all wavenumber. On the other hand the behavior of $\tau_S(q)$ dramatically changes with $\hat{x}_S$. For $\hat{x}_S = 0.03$, $\tau_S(q \lesssim 2\pi)$ and $\tau_L(q \lesssim 2\pi)$ grow with increasing the packing fraction. It means that the time scales relevant with the length scale greater than the diameter of the larger particle slow down, both for large and small species. But when the volume fraction of the smaller particle is as small as $\hat{x}_S = 0.01$, $\tau_S(q \sim 2\pi)$ no longer grows like $\tau_L(q \sim 2\pi)$. In MCT it is known that the relaxation time from the plateau (not from the initial value) follows the power law divergence toward the dynamic transition point. Let us discriminate it

from our τ and call 'alpha-relaxation time' τ^α.

$$\tau^\alpha \propto (\phi - \phi_\mathrm{d})^{-\gamma}\,, \tag{5.36}$$

where γ is a system dependent, non-universal exponent. We plot our relaxation time $\tau(q)$ with the distance from ϕ_d in the bottom panel of Figure 5.9. For $\hat{x}_S = 0.01$, shown in the top right, τ_S shown in open symbols for several wavenumbers do not diverge toward ϕ_d, while $\tau_L(q = 2\pi)$ and $\tau_L(q = 2\pi/\sigma_{LS})$ follow (5.36). This result shows apparently the time scales for small particle are separated from the large particles, as observed in the experiment. We note that the whole behavior does not depend on the choice of the short time scale $\boldsymbol{\tau}^0$ in (5.7).

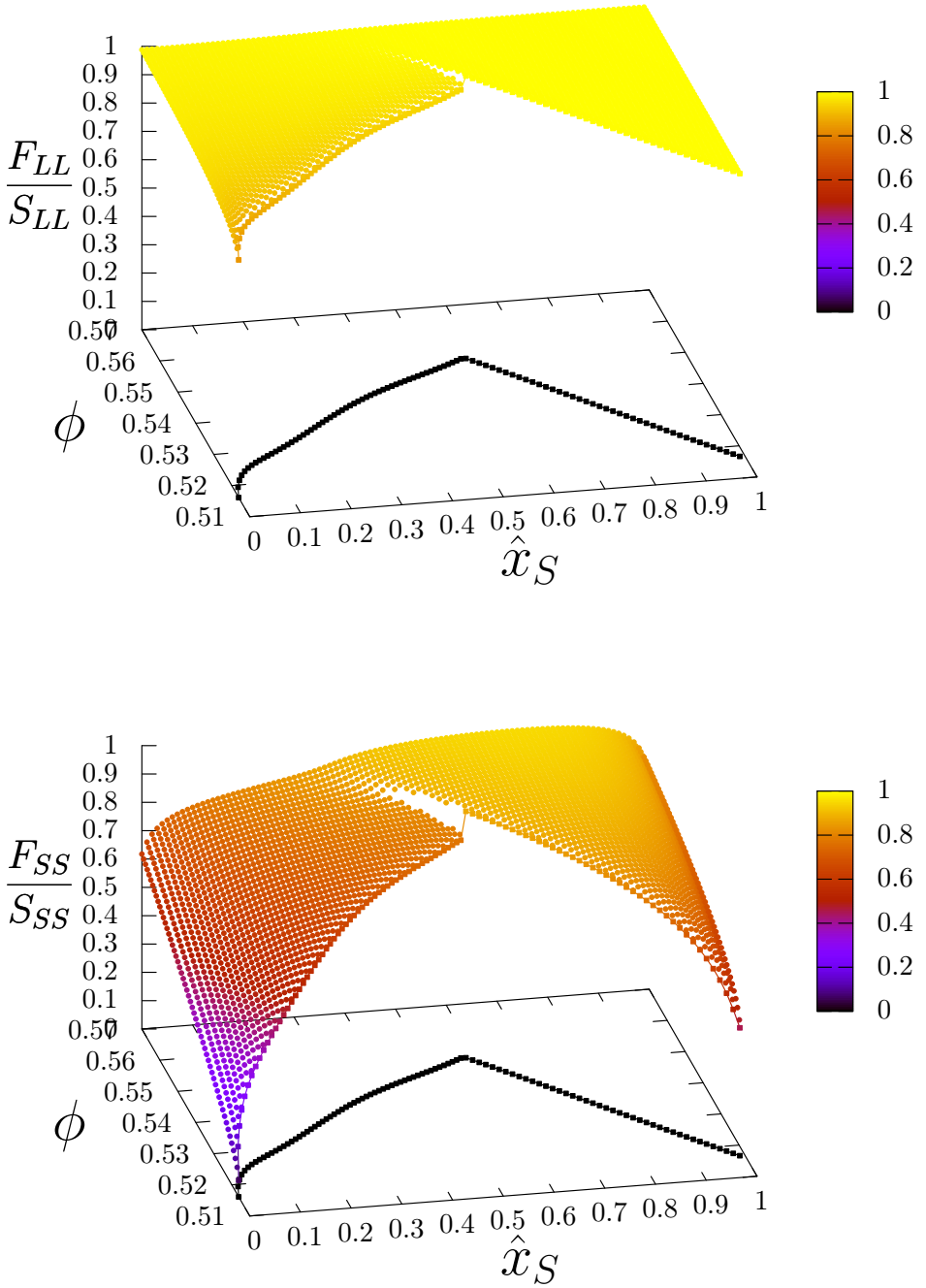

Figure 5.7: Color map of DW factor for $\delta = 0.3$. Its small-small component looks exhibiting a continuous transition in small $\hat{x}_S$.

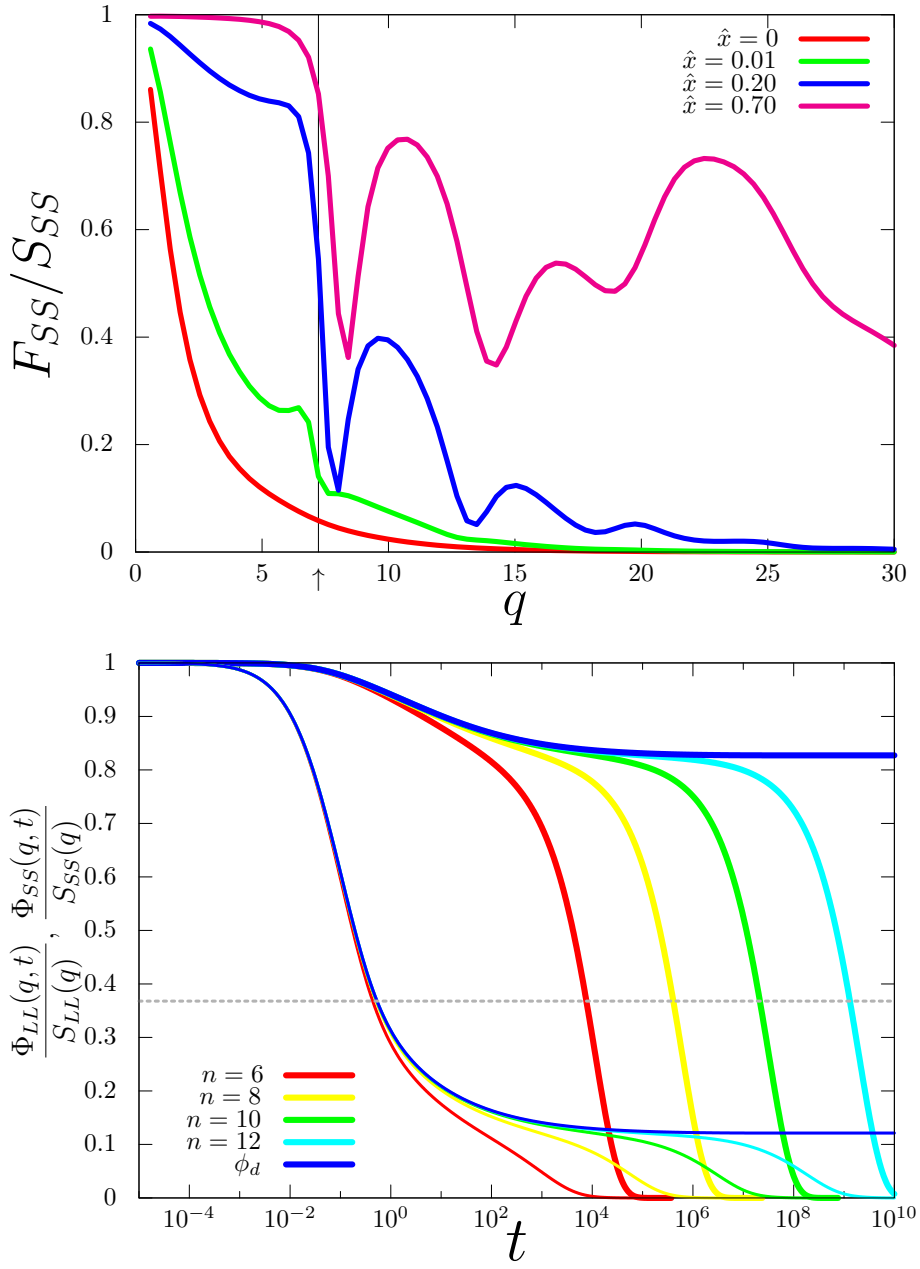

Figure 5.8: Top: The wave number dependence of the DW factor at $\phi_{\rm d}$ for $\hat{x}_S = 0$, 0.01, 0.2 and 0.7. Size ratio is $\delta = 0.3$. When the fraction of the smaller species is sufficiently small the DW factor of smaller particle is negligibly small. Arrow and vertical black line indicates the representative wavenumber chosen in Figure 5.7 and the bottom panel of this figure. Bottom: Dynamics of correlation function. Bold and thin line respectively corresponds to Φ_{LL} and Φ_{SS}. The wave number is chosen as the value indicated by the arrow in the top panel. Packing fraction is $\phi = \phi_{\rm d}\left(1 - 10^{-n/3}\right)$. $\hat{x}_S$ is chosen as $\hat{x}_S = 0.01$. Dotted horizontal line indicates the value of 1/e.

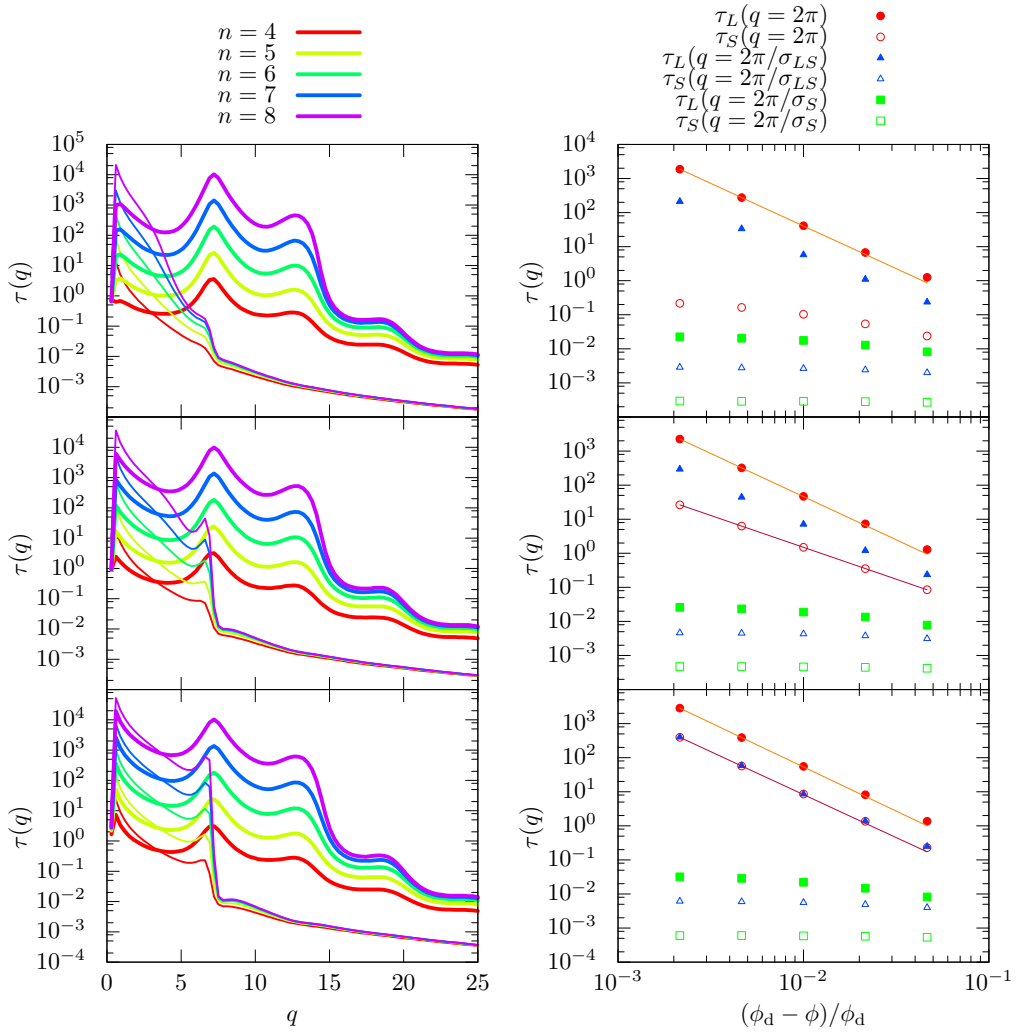

Figure 5.9: Left panel: Relaxation time for Φ_{LL} and Φ_{SS} as functions of wavenumber, defined in (5.34). Bold and thin lines represent respectively $\tau_L(q)$ and $\tau_S(q)$. Different color means different packing fraction according to (5.35). From top to bottom, volume fraction ratio of the small particle is chosen as $\hat{x}_S = 0.01$, 0.02 and 0.03. Right panel: Scaling plot of the relaxation times near the dynamic transition point ϕ_d.

The case for $\delta = 0.2$

Exploration for further disparate δ gives a useful insight to the origin of the time scale separation for small δ and small $\hat{x}_S$.

We first show the dynamic phase diagram obtained within the numerical evaluation of the long time limiting equation (5.11) in the top of Figure 5.10. The shape of the dynamic transition line starts to wind at small $\hat{x}_S$. So far we do not have a physical interpretation of this winding.

We show in Figure 5.11 color maps of the DW factors together with the phase diagram. As before, the peak wavenumber for $S_{LL}(q)$ is chosen as the representative q. The small jump for F_{SS} at the dynamic transition point for $\hat{x}_S \sim 0$ is even clearer than $\delta = 0.3$ case. Not only that, F_{SS} looks exhibiting a continuous transition at $\hat{x}_S = 0$, which is not the case in $\delta = 0.3$. To check this we plot F_{SS} at the dynamic transition point in the bottom panel of Figure 5.10. One can see that F_{SS} for $\hat{x}_S = 0$ is 0 for all wavenumber q, which is in contrast with the case for $\delta = 0.3$, see top panel of Figure 5.8. This feature clarifies the reason why the time scales between the large and small particles decouple for small δ and $\hat{x}_S$. The binary MCT continues to the one-component MCT for corrective density fluctuation and self correlation function when the volume ratio of one of two components becomes zero [166]. Thus in the limit $\hat{x}_S \to 0$ the equations we are dealing with continues to the MCT for $F_{LL}(q)$ and self correlation for small particle $f_S(q)$. As Voigtmann has shown in [123] for $\delta \leq 0.2$, the self correlation of small particle starts to decouple from other correlation functions when $\hat{x}_S$ is not too large. We stated that in Section 5.1 that in binary MCT for corrective density fluctuation $F_{\alpha\beta}(q)$, the dynamic transition occurs at $\phi_{\rm d}$ for all of the components [160]. While in general the self part f_α need not to undergo the dynamic transition at the same time. Indeed in the present situation, the small component of the self correlation function $f_S(q)$ remains 0 at the dynamic transition point. We show in Figure 5.12 the dynamic transition line for the LM factor for small particle together with the one for the DW factor. One sees that the transition of f_S indicated by the green line occurs at the higher packing fraction than the dynamic transition point for corrective fluctuation, indicated by the red line. As we stated, F_{SS} in corrective MCT for binary mixture continues to that for f_S when $\hat{x}_S$ is very close to 0. Thus for small $\hat{x}_S$, F_{SS} is expected to behave similarly with f_S. The numerical result shows that f_S is 0 at the dynamic transition point for corrective fluctuation. Thus F_{SS} at $\phi_{\rm d}$ becomes small, leading to the time scale separation between the large and small components. Note that for $\delta \geq 0.3$ the dynamic transition for $F_{\alpha\beta}$ and f_S occurs at the same packing fraction ϕ. The time scale separation in $\delta = 0.3$ shown in Figure 5.9 was

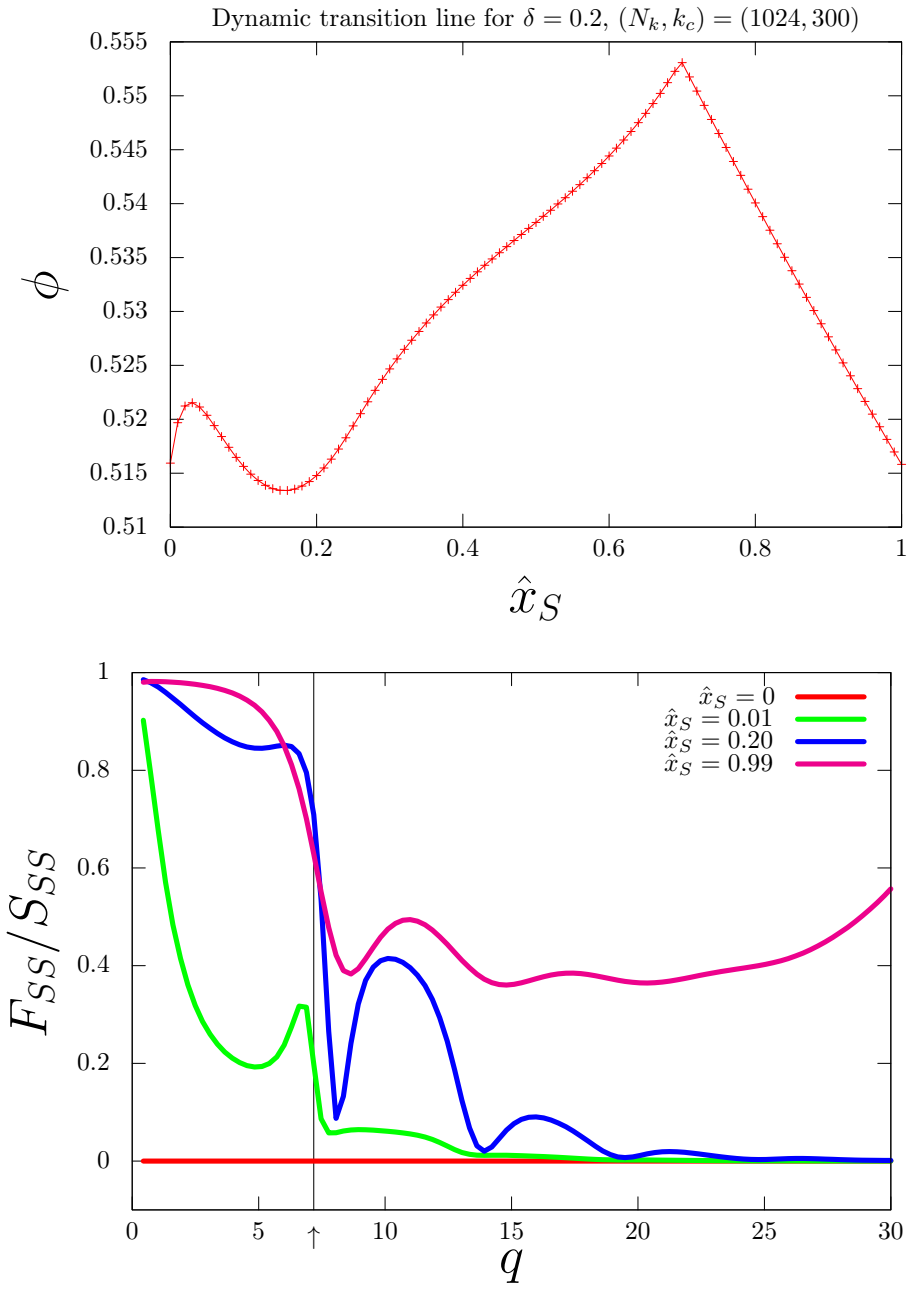

Figure 5.10: Top: Dynamic phase diagram of binary hard sphere mixture with size ratio $\delta = 0.2$. Bottom: Wave number dependence of DW factor at the dynamic transition point for several $\hat{x}_S$ for $\delta = 0.2$.

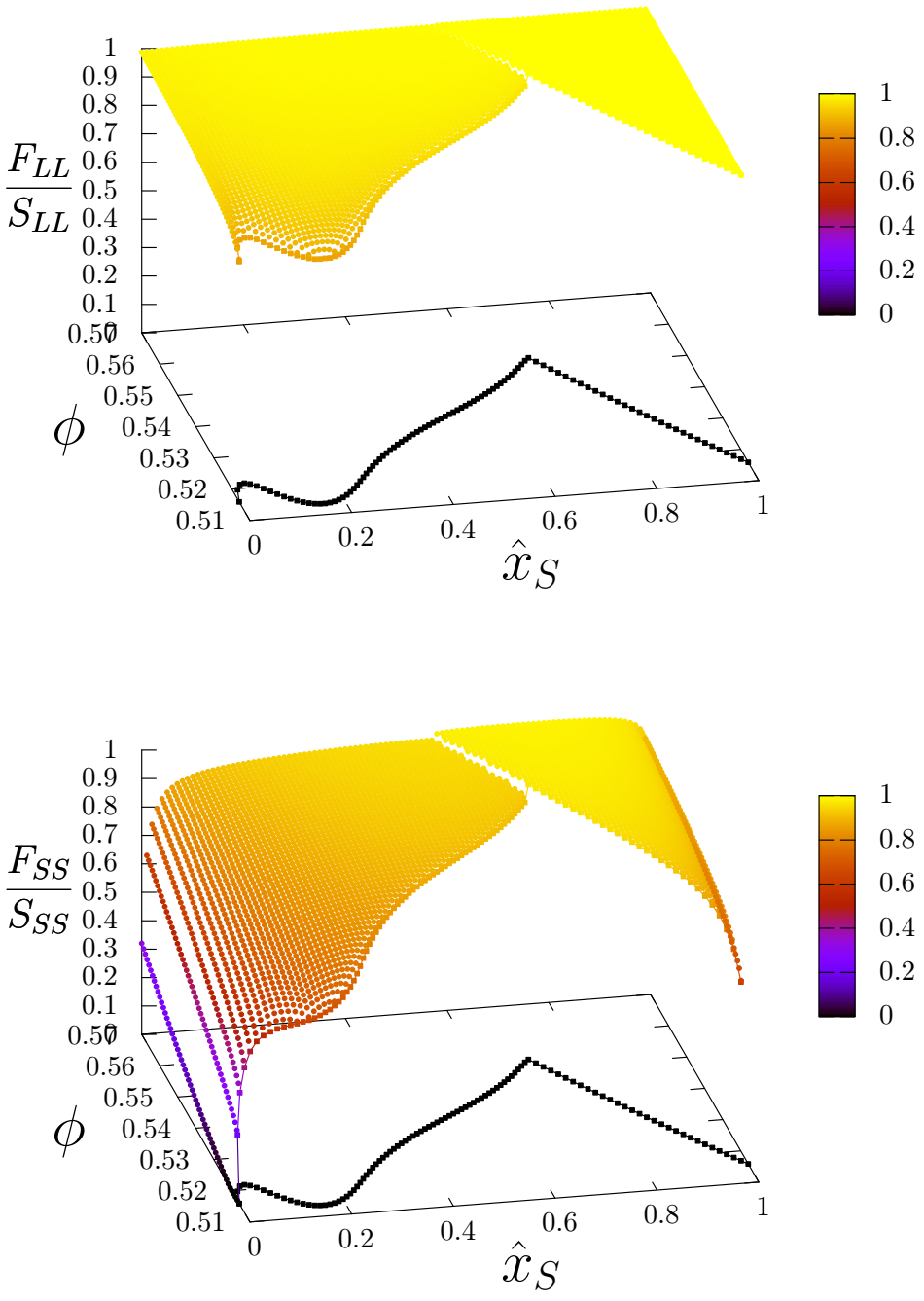

Figure 5.11: Color map of DW factor for $\delta = 0.2$.

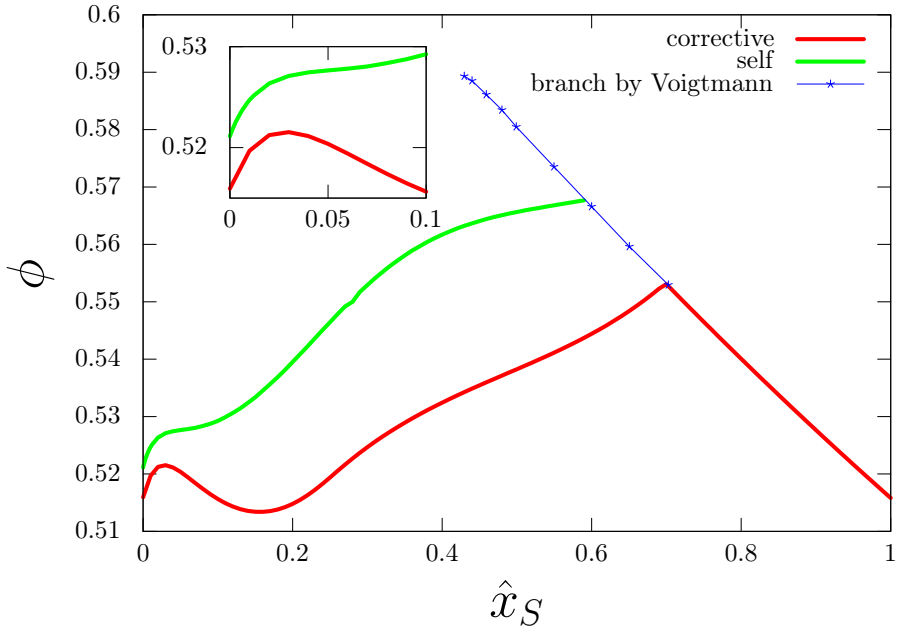

Figure 5.12: Dynamic phase diagram for binary hard sphere mixture with size ratio $\delta = 0.2$. Red and green line indicates the dynamic transition line for corrective fluctuation $F_{\alpha\beta}$ and self correlation for small particle f_S respectively. Blue line is a glass-glass transition characterized by the jump in the DW factor, observed in the bottom panel of Figure 5.11. Data for blue line is taken from [123]. Inset is the magnified phase diagram around small $\hat{x}_S$.

the asymptotic sign of the complete separation in the corrective and self correlation in $\delta = 0.2$.

5.3.2 Asakura-Oosawa model

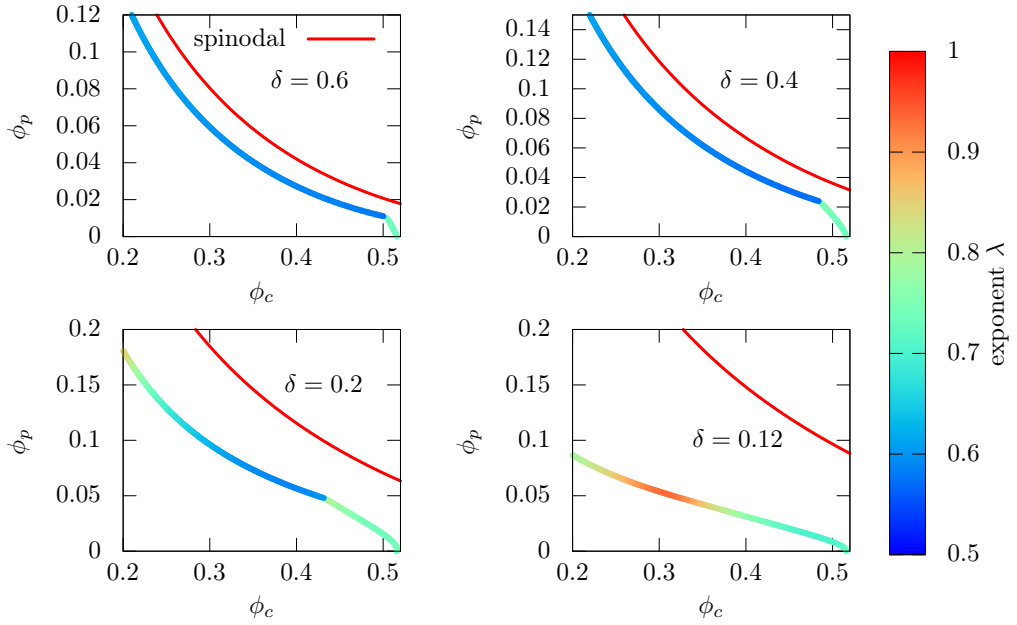

Figure 5.13: Static and dynamic phase diagrams of the AO model binary system within FMDFT and MCT. Line color indicates the MCT exponent λ at the dynamic transition (see text).

We have shown in Subsection 5.3.1 that the binary MCT is capable of describing effectively the time scale separation between large and small components. Then it is natural to expect that the binary MCT successfully continues to the effective one-component theory in the limit of disparate δ. The effective one-component theory is well studied in the AO model, rather than the hard sphere mixture [170,171]. As we mentioned in the introduction, the adiabatic elimination of small polymers induces the depletion interaction between big colloidal particles [147]. One-component MCT for the system of colloidal particle interacting with this effective AO potential was very successful [145]. Thus in this subsection we investigate the binary MCT for the AO model and compare the results with that of the effective one-component MCT. Note that this comparison has already been carried out by Zaccarelli et al., for very limited parameter space [158]. We here try to re-examine them more thoroughly.

We solve the long time limiting equation for the corrective and self density correlation function (5.11). We employed the static structure factor evaluated within the fundamental measure density functional theory (FMDFT)

for the AO model as input quantities [172]. We describe the details of analytical expression of the direct correlation function obtained in FMDFT in Appendix D. We show in Figure 5.13 the static and dynamic phase diagram for several size ratio $\delta = 0.6$, 0.4, 0.2, 0.12 in ϕ_c–ϕ_p plane. Red line is the spinodal for phase separation between the large colloids and the small polymers above which a mean field approximation used in FMDFT is violated[4]. $\phi_p = 0$ corresponds to the one-component hard sphere system, thus the system exhibits the dynamic transition at $\phi_c = 0.516$ for all δ. On adding polymer the transition line goes to the low density side for all investigated δ. Upon further increasing the amount of the polymer the dynamic transition line bends and starts to follow the shape of the spinodal line. Let us call the dynamic transitions before and after the kink "hard sphere type" and "spinodal driven type", respectively. As will be discussed later, the latter is caused by a precursor of the divergence in $\boldsymbol{S}(q = 0)$ at the spinodal point. It is believed that the dynamic transition for ordinary hard sphere model is caused by the growth of the first peak in the static structure factor $\boldsymbol{S}(q \sim 2\pi)$. The dynamic transition in the spinodal driven branch is clearly not of this type. Rather it looks an artificial transition. Note that for $\delta = 0.12$, all of the transitions are caused by the spinodal and one does not observe the kink anymore. In order to show the distinct signature of the two types of the dynamic transitions, we investigated the MCT exponent λ, defined in (5.22). The value of λ jumps at the kink of the dynamic transition line in Figure 5.13, indicating that the nature of the glass transition has been changed.

We investigate the structure of the two distinct dynamic transitions. We show in Figure 5.14 the DW factor, the LM factor and the static structure factor from top to bottom, for the binary AO model with $\delta = 0.4$. The left and right columns correspond to the quantities for colloid and polymer respectively. The four values of ϕ_p are chosen as, $\phi_p = 0$: 1-component hard sphere system, $\phi_p = 0.023$: the point just before the dynamic transition changes from the hard sphere type to the spinodal driven one, $\phi_p = 0.024$: just after the kink, and $\phi_p = 0.199$: the largest ϕ_p investigated in the present study. It is clear that at the kink of the dynamic transition line, the DW factor for large-large correlation changes discontinuously (see green and blue line in top left panel in Figure 5.14), while static structure stays pretty much the same, as shown in the bottom panel. Note also that the LM factor f_c and f_p become suddenly 0 at the kink. These qualitative features do not depend on the size ratio δ.

We compare our results with the phase diagram obtained within the effective one-component theory. We employ an effective one-component MCT for

[4]H. Löwen, private communication.

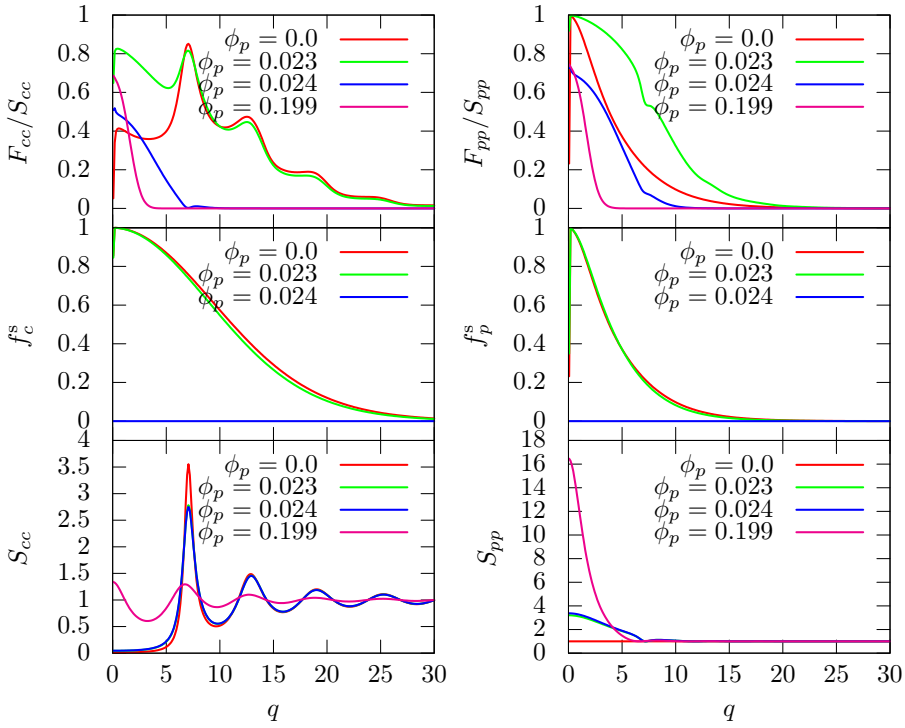

Figure 5.14: From top to bottom the DW factor, the LM factor and the static structure factor for $\delta = 0.4$ at the dynamic transition point are shown. Green and blue line indicates quantity corresponding to type 1 and 2 of dynamic transition, respectively. One sees that in phase 2 the LM factor is 0 for both species.

the AO system which is proposed and investigated by Zaccarelli et al. [158].

$$F = S - (S^{-1} - M)^{-1}, \tag{5.37}$$

$$M \equiv \frac{1}{2\rho_c q^2} \int \frac{d^3\boldsymbol{k}}{(2\pi)^3} V_{\text{eff}}^{\boldsymbol{qkp}} F(k) F(p), \tag{5.38}$$

$$V_{\text{eff}}^{\boldsymbol{qkp}} \equiv \hat{\boldsymbol{q}} \cdot \boldsymbol{k} \rho_c c^{\text{eff}}(k) + \hat{\boldsymbol{q}} \cdot \boldsymbol{p} \rho_c c^{\text{eff}}(p), \tag{5.39}$$

here $S = S_{cc}/x_c$. The effective direct correlation function c^{eff} is evaluated from $S(q)$ by using the OZ equation,

$$\rho_c c^{\text{eff}}(q) = 1 - \frac{1}{S(q)}. \tag{5.40}$$

We show in Figure 5.15 the comparison of phase diagram obtained within the effective one-component MCT (5.37) and binary MCT for AO model. One can see apparently these two theories contradict each other. For $\delta = 0.5$,

since the adiabatic elimination of small particle cannot be justified, the binary theory (green line) is expected to be accurate. In fact this is confirmed by the numerical simulation [158]. For $\delta = 0.15$ the dynamic transition line for effective one-component theory indicated by the red line in the bottom panel of Figure 5.15 goes to high ϕ_c region when one starts to add polymers to the pure hard sphere system. It means that the glass formed by the hard sphere "melts" by adding polymer and further adding polymer causes the glass transition again. This re-entrant transition is the one of the most important predictions of the effective one-component MCT and has been confirmed in experiment [148, 149]. Thus in $\delta = 0.15$ the adiabatic elimination of polymer is working. On the other hand, the binary MCT for $\delta = 0.15$ drastically deviates from the effective one-component MCT. As stated, most of the dynamic transition in the binary AO model is caused by the precursor of the phase separation spinodal. At the spinodal line the static structure factor for $q = 0$ becomes singular and as the precursor $S_{pp}(q \to 0)$ grows divergently on adding polymer. We show in Figure 5.16 the static structure factor S_{cc} and S_{pp} for two state points. One is just before the 'melting' point when one fixes the $\phi_c = 0.520$ and starts to add polymer to the pure hard sphere system, corresponds to $\phi_p = 0.0075$. Another is the state point at which the re-entry to the glass phase occurs, when one further increases the amount of polymer, corresponds to $\phi_p = 0.0530$. These state points are indicated by the pink squares in the bottom panel of Figure 5.15. In general, the dynamic transition of MCT causes when the total magnitude of the static structure factor exceeds some threshold value. Thus one can see that the dynamic transition in binary AO model with disparate size ratio is mainly caused by growing S_{pp}. Zaccarelli et al. have concluded that the discrepancy in phase diagram in $\delta = 0.15$ shown in Figure 5.15 is due to the incapability of time scale separation between the large and small particle in the binary MCT. Figure 5.16 implies that the discrepancy was caused from the sensitivity of S_{pp} to the spinodal. The possible explanation is either of,

- The binary MCT is wrong, as Zaccarelli et al. has argued. If there exists the correct version of binary MCT it has to be more insensitive to the growing S_{pp}.
- The FMDFT overestimates the S_{pp}.

Thus, in order to clarify whether the binary MCT continues to the effective one-component system, one should employ the model or static structure factor without spinodal instability, like binary hard sphere mixture approximated by the PY closure.

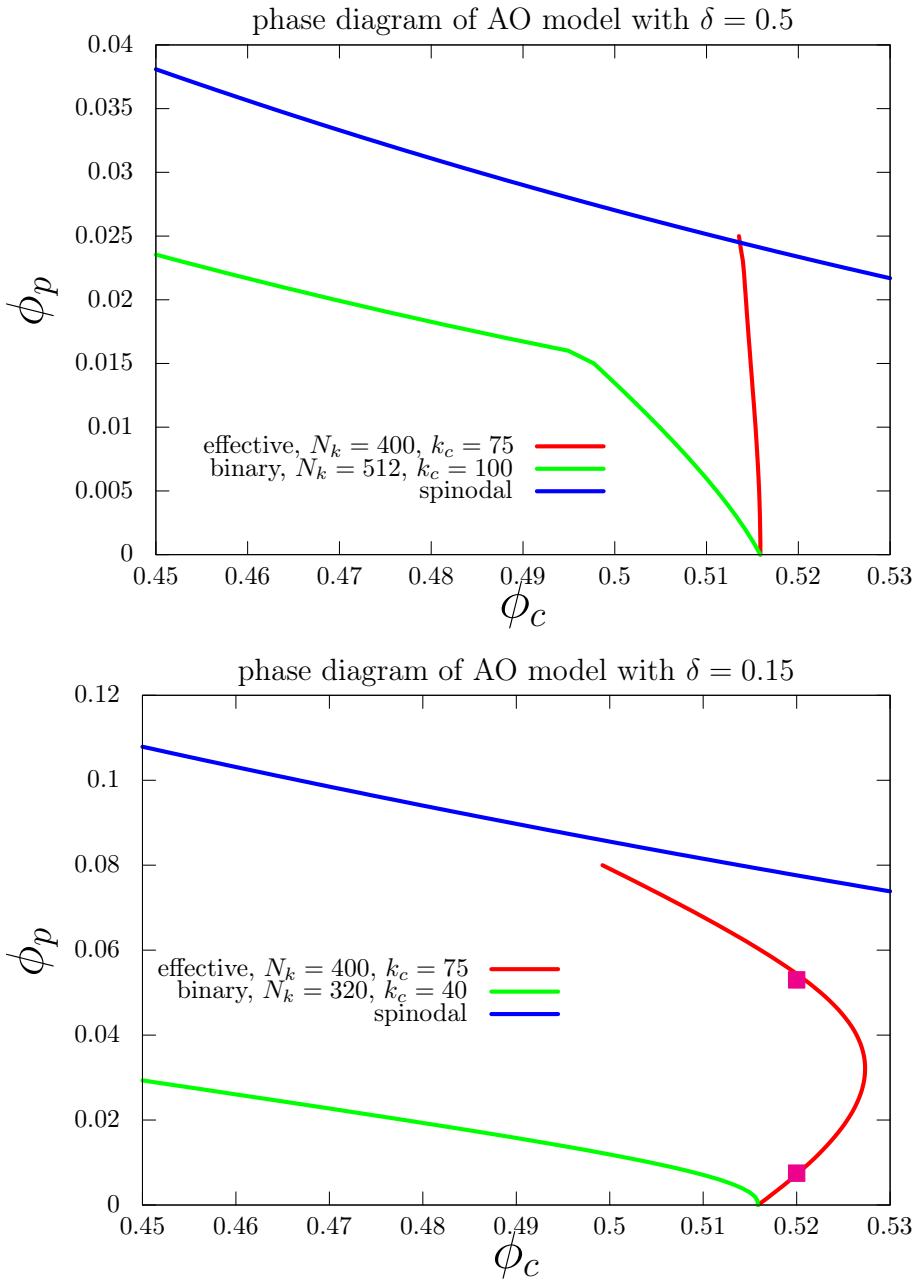

Figure 5.15: Phase diagram for the binary AO model and the effective one-component theory. Top: $\delta = 0.5$, Bottom: $\delta = 0.15$. These parameters are chosen according to [158]. Filled pink squares in the bottom panel represent the state points chosen in Figure 5.16.

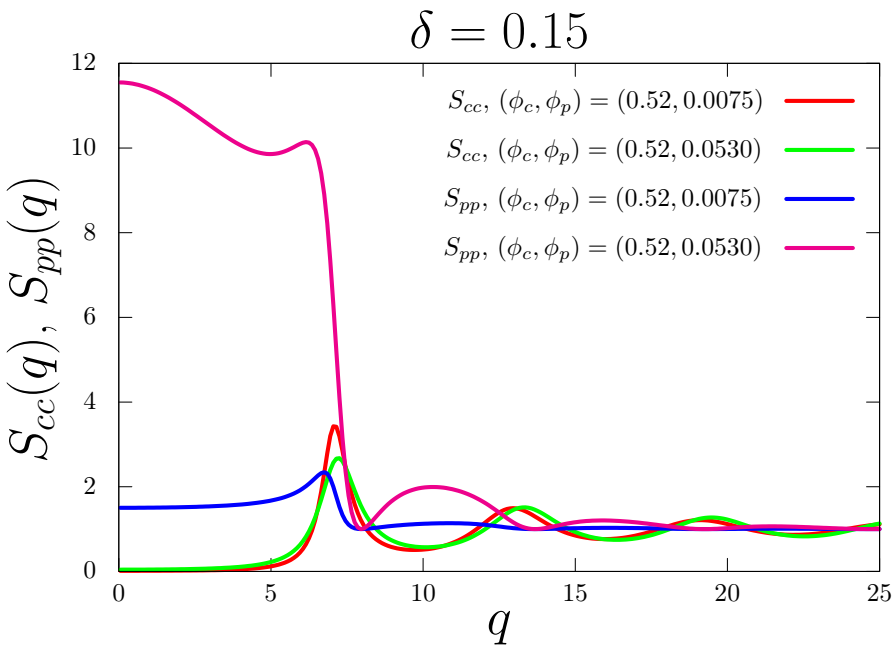

Figure 5.16: Static structure factor of the binary AO model for $\delta = 0.15$, $\phi_c = 0.520$. The packing fraction of the polymer is chosen as $\phi_p = 0.0075$ and 0.0530. These state points are indicated by the pink squares in the bottom panel of Figure 5.15.

5.3.3 Schematic model

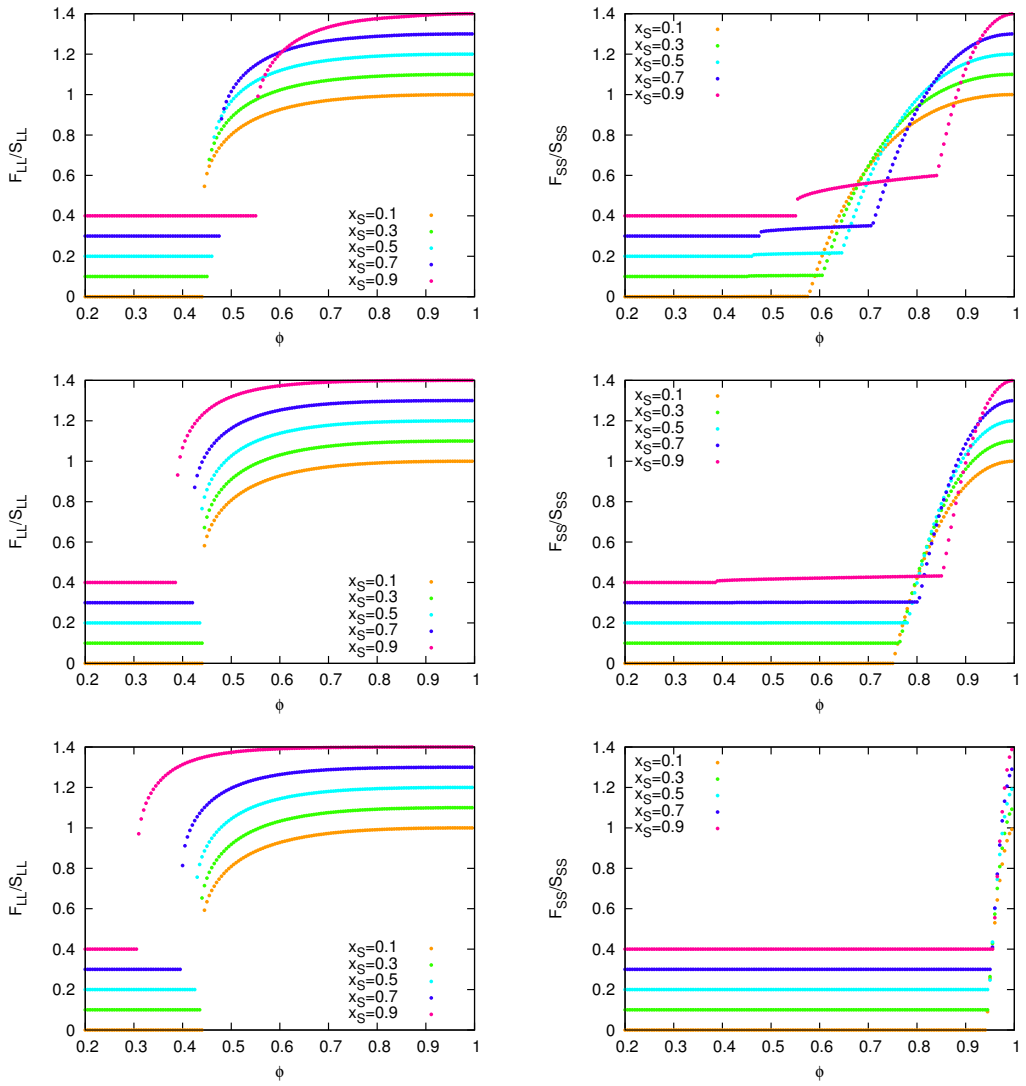

Figure 5.17: The DW factor for δ=0.5 (top), 0.3 (middle), 0.1 (bottom). In each rows, the left and right panel represents F_{LL} and F_{SS}. For visibility we vertically displaced plots for different x_S. We can see that for all δ, F_{SS} undergoes almost continuous transition at the dynamic transition points.

In order to investigate the mathematical structure of the binary MCT, and to clarify the origin of the time scale separation observed in Subsection 5.3.1 we analyze the schematic version of the binary MCT introduced in Subsection 5.2.3.

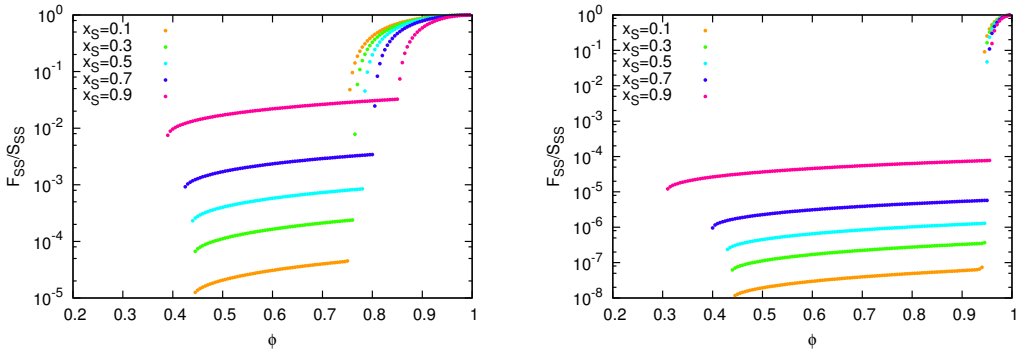

Figure 5.18: Semi-log plot for F_{SS} versus the packing fraction. Left: $\delta = 0.3$. Right: $\delta = 0.1$. The first transition at the lower ϕ occurs as the same time as F_{LL}.

We show in Figure 5.17 the DW factor as functions of the packing fraction ϕ for several δ and x_S, obtained by numerically solving (5.33). Our model achieves the dynamic transition upon increasing ϕ. The dynamic transition occurs for the all components of the DW factor $\boldsymbol{F}$ at the same parameter, due to the positive definiteness of the stability matrix. We observe an almost continuous transition of F_{SS} when δ is small. This is consistent with the experimental [2] and the full MCT [123] results. On the other hand, we do not observe a marked x_S dependence, contrary to the result obtained for the hard sphere mixtures.

When the size ratio becomes as disparate as $\delta = 0.1$, we can see that F_{SS} looks zero for almost all ϕ and x_S. In other words, the small particles can still move around even if the larger one is in the glassy phase, which means that the time scales between Φ_{LL} and Φ_{SS} are effectively decoupled. This is more apparent when one plots F_{SS} in semi-log vertical axis (See Figure 5.18). Upon increasing the packing fraction from 0 one first encounters a discontinuous dynamic transition for F_{LL} and F_{SS} at the same time. But the discontinuity of F_{SS} is so small that it can be only observed within the logarithmic plot. This feature is very similar to the result of full MCT. At higher ϕ one encounters a second glass-glass transition, which is apparent for F_{SS}. These two-step transitions are somewhat similar to that Franosch and Götze have observed in their schematic binary MCT, which is even simpler than our model [173]. For $\alpha = 1, 2$

$$F_\alpha = 1 - [1 + M_\alpha[\boldsymbol{F}]]^{-1}, \tag{5.41}$$
$$M_1 = vF_1^2 + v_1F_1F_2 + v_2F_2^2, \tag{5.42}$$
$$M_2 = wF_1^2 + w_1F_1F_2 + w_2F_2^2. \tag{5.43}$$

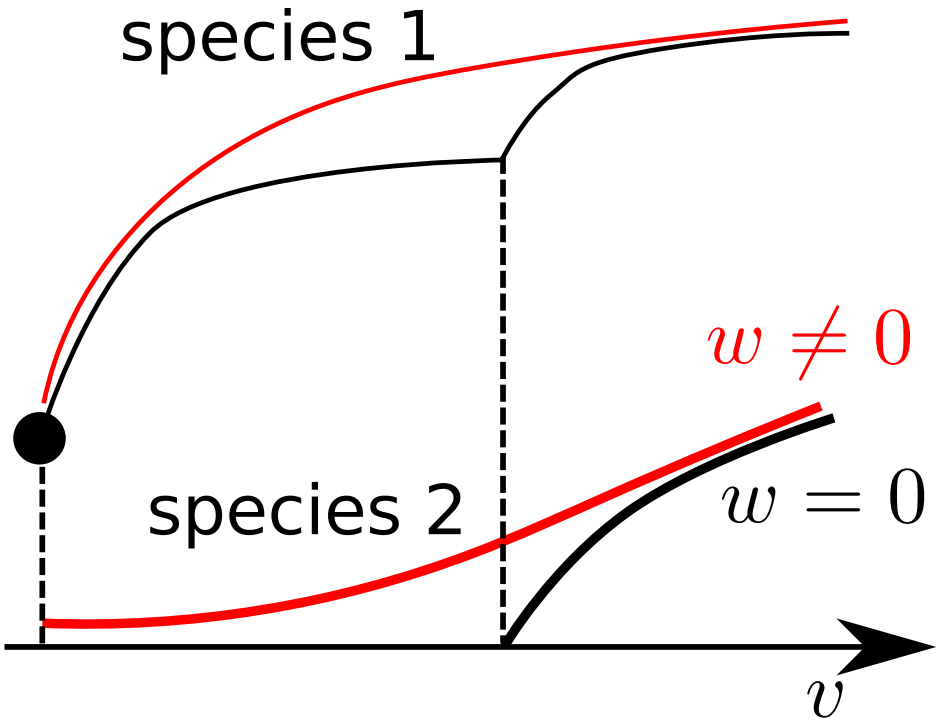

Figure 5.19: Schematic picture of the complete separation in the Franosch-Götze model.

Their model does not contain the cross correlation F_{LS}. When $w = 0$ and hence there are no bilinear feedback in M_2 by F_1, the model exhibits the phase at which species 1 is non-ergodic while 2 still remain ergodic (see the black line of Figure 5.19). Further increasing v, species 2 exhibits a continuous transition into the non-ergodic phase. This complete separation is smeared out by small but finite w. It causes a small jump height of F_2 at the first transition (see the red line of Figure 5.19). In this model the positive-definiteness of the stability matrix is broken for $w = 0$ and is recovered for finite w. One can check it by calculating the eigenvectors corresponding to the maximum eigenvalue of the stability matrix:

$$\boldsymbol{e} = \begin{pmatrix} e_1 \\ e_2 \end{pmatrix}. \tag{5.44}$$

e_1 is always positive while $e_2 = 0$ for $w = 0$ and non-zero for $w > 0$. $e_2 = 0$ is the result of the broken positive definiteness of the stability matrix.

We would expect that in our model small F_{SS} is achieved by small but nonzero e_{SS} since complete separation is prohibited by the positive definiteness of the stability matrix. We show in Figure 5.20 the ratio between LL

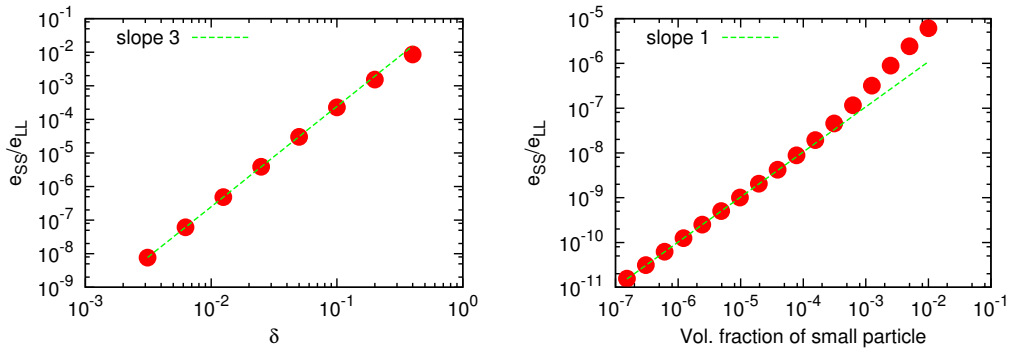

Figure 5.20: Left: Scaling plot of e_{SS}/e_{LL} near $\delta = 0$. The volume fraction ratio of the small particle is fixed to $\hat{x}_S = 0.20$. The eigenvector corresponding to the maximum eigenvalue of the stability matrix at the dynamic transition point goes to 0. Right: Scaling near $\hat{x} = 0$. Size ratio δ is fixed to 0.1.

component and SS component of the right eigenvector corresponding to the maximum eigenvalue to the stability matrix defined in (5.18). One can see from the left panel e_{SS}/e_{LL} goes to 0 when one decreases δ. It is a strong evidence that our model achieves the complete time scale separation between large and small particle in $\delta = 0$ limit by the same mechanism as Franosch-Götze model. Note also that as shown in the right panel of Figure 5.20 the limit of $\hat{x}_S = 0$ also continues to the complete scale separation. This fact is consistent with the result obtained in Subsection 5.3.1. In the hard sphere mixture for $\delta = 0.2$ the self correlation for small particle completely decoupled from other fluctuations. And since the binary MCT continues to the one-component MCT for F_{LL} and the self MCT for f_S in $\hat{x}_S \to 0$ limit, F_{SS} for small $\hat{x}_S$ behaves like f_S. This is the origin of the small F_{SS} in the full binary MCT. In our schematic binary MCT this decoupling starts from $\delta \lesssim 0.8$ (not shown).

5.4 Summary and conclusions

In this chapter we have investigated the binary MCT for the hard sphere mixtures, the AO model and the schematic model with the disparate size ratio. We found that although the dynamic transition for the collective motion of both species occurs at the same parameter, MCT can describe the time scale separation between the large and small particles when the size ratio is sufficiently disparate and the composition of the small particles is not large.

This comes from the almost continuous transition of the DW factor of small particle F_{SS}. $\Phi_{SS}(q,t)$ relaxes to very small value even nearby the dynamic transition point, since the height of plateau of $\mathbf{\Phi}(q,t)$ reflects the value of $\boldsymbol{F}(q)$ at the dynamic transition point. MCT predicts that the relaxation time *from* the plateau diverges toward the dynamic transition point, while the relaxation time *to* the plateau does not exhibit a marked ϕ dependence. Thus the actual relaxation time for small particle τ_S does not diverge when the dynamic transition is almost continuous, while τ_L grows rapidly as shown in Figure 5.9. This is the mechanism of the time scale separation achieved in the binary MCT. Then the next question is the origin of the almost continuous dynamic transition for F_{SS}. Investigation on the binary hard sphere mixture with $\delta = 0.2$ revealed that the complete decoupling between the self correlation of small particle f_S and other dynamical components achieves when δ is sufficiently small. In other words, the long time limit of the self correlation of the small particles remains 0, while other dynamical components of the DW factor and the LM factor undergo the dynamic transition. The binary MCT for the corrective correlation function continues to the MCT for the corrective correlation of the large particle F_{LL} and the one for the self correlation of the small particle f_S in the limit of volume fraction ratio of the small particle $\hat{x}_S$ goes to 0. Then F_{SS} with $\hat{x}_S \sim 0$ behaves like f_S, which is 0 at the dynamic transition point. Thus F_{SS} at ϕ_{d} becomes very small.

We have shown that in subsection 5.3.1 that the binary MCT for hard sphere mixtures is capable of describing the time scale separation between the large and small particles when the size ratio δ is sufficiently disparate. This fact implies that the binary MCT can handle the adiabatic elimination of small particles. In other words, the binary MCT continues to the effective one-component MCT when δ and $\hat{x}_S$ is sufficiently small. To check this hypothesis we numerically evaluated the binary MCT for the AO model and made a comparison with the corresponding effective one-component MCT in subsection 5.3.2. The result is negative. The dynamic transition line predicted by the binary MCT for the AO mixture considerably deviates from that of the effective one-component MCT. The dynamic transition in binary

MCT is driven by growing S_{pp} near the spinodal point and is almost nothing to do with S_{cc}, which is the only input to the effective one-component MCT. The reason why the binary MCT failed is either of (1) binary MCT is wrong and if there is the correct version of MCT the diverging S_{pp} does not affect the dynamic transition, or (2) The static structure evaluated by the FMDFT is wrong. True S_{pp} does not grow remarkably. Note that the hard sphere mixture with its static structure being evaluated by the PY approximation is free from a spinodal. It might be better to compare the binary and the effective one-component MCT for such system. Or, a qualification of the FMDFT for disparate δ is called for. To our knowledge, a comparison with a simulation data has been carried out only for S_{cc} [172], and S_{pp} is left untested.

Since essential and qualitative features of MCT are fully included in its schematic version [167], one can neglect the all q dependence and may be able to capture the origin of the time scale separation in MCT. Moreover, the schematic MCT is free from an approximation in the static structure factor. Thus one may not worry about the accuracy of the static structure factor and is able to concentrate on purely dynamic aspects of MCT. We proposed and worked on a binary schematic MCT in Subsection 5.2.3 and 5.3.3. Our schematic binary MCT successfully reproduced the effective time scale separation, observed in the full MCT for the systems of the hard sphere mixtures. The comparison with a more simplified schematic MCT proposed by Franosch and Götze revealed that the effective time scale separation is a precursor of the complete time scale separation in $\delta = 0$, or $\hat{x}_S = 0$ for sufficiently small δ. In these limits the positive-definite nature of the stability matrix is violated and it becomes positive *semi*-definite.

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Appendix A

Stochastic Calculus

In this appendix we summarize some basics on the stochastic calculus used frequently in the thesis, based on literature [48, 49]. Stochastic description or stochastic modeling of the system is widely used, from the Brownian motion, chemical reaction to the financial analysis. There are two ways to treat the stochastic process theoretically. One is on the stochastic differential equations (SDEs), which describe the time evolution of the stochastic variables. The other is the description on the Fokker-Planck equations (FPEs), which hold for the probability distribution functions (PDFs), rather than the stochastic variables. Description on the SDE sometimes faces a severe difficulty on applying the usual rule of the differentiation and integration since the origin of stochastic nature is indifferentiable random process. While in the FPE one is free from such mathematical subtlety since the random processes are averaged in the PDF. In spite of such mathematically non-trivial features, the SDE is commonly adopted to describe a stochastic process, as frequently as the FPE. We deduce its reasons as follows.

- In many case one can obtain the SDE by an intuitive discussion (see for example Appendix A.1). On the other hand it is not always clear how one can model a system by using the FPE. Thus the SDE is easier to derive when a system is given. As we have carried out in Chapter 3, imposing constraints into the stochastic systems becomes much simpler within the SDE.

- The SDE is easier to implement to the numerical simulation than the FPE. It is constructed simply by adding the random process to the ordinary differential equation. While one has to prepare a mesh grid to solve the FPE since it is a partial differential equation.

- One can write down and analyze the SDE regardless of the nature of

the random process. FPE can be derived only when the random process is Markov. When the property of the random processes is dependent of their past values, the description only withi the SDE is possible.

In Section A.1 we introduce the stochastic process and derive some mathematical formulae. In Section A.2 we describe how to map the SDE to FPE, by using the Kramers-Moyal expansion. We focus on the Brownian motion in Section A.3, where the origin of the random process is thermal fluctuation of the solvent. In the Brownian motion, magnitude of the fluctuation is severely restricted by the consistency with the equilibrium statistical mechanics and as a result several formulae like the fluctuation-dissipation theorem (FDT) hold. The random processes are classified into additive and multiplicative noises. Statistical properties of the additive noises do not depend on the value of the stochastic variables, while that of the multiplicative noises do. The additive noise can be treated in usual calculus but one has to be more careful with the multiplicative noise. For example, the extension of the Brownian motion into the case with the multiplicative noise fails in general. In Section A.4 we present an exception of this failure, which is our starting point of the calculation in Chapter 2.

A.1 Stochastic differential equation

The Langevin equation is a model SDE which has been introduced to describe the Brownian motion. For simplicity we consider one Brownian particle in a one-dimensional system. We use $x(t)$ to represent the position of the Brownian particle at time t. The forces acting on the Brownian particle are, i) the Stokes' drag force, ii) an external force, and iii) the random force exerted by the surrounding solvent particles. Thus the equation of motion for a Brownian particle is

$$m\ddot{x}(t) = -\zeta\dot{x}(t) - \frac{\partial U}{\partial x} + f(t). \tag{A.1}$$

Here m is the mass of the Brownian particle. Overdot represents the derivative with respect to time. $-\zeta\dot{x}$ is the Stokes' drag force and ζ is a friction coefficient. We assume that ζ is constant. $U(x)$ is potential and $f(t)$ represents the random force exerted by the solvent particles. It should be random in the sense that it satisfies

$$\langle f(t)\rangle = 0. \tag{A.2}$$

Here $\langle\cdot\rangle$ represents an average on many realizations of the random noise. The correlation time of this random stochastic process can be regarded as zero

since it is a model of the force arisen from the collision of the solvent particle, whose correlation time is order of picoseconds which is much smaller than the characteristic time of the Brownian particle. This property is expressed by $\langle f(t)f(t')\rangle \propto \delta(t-t')$. Here $\delta(t-t')$ is Dirac's delta function. It is known that the magnitude of the variance of the noise $f(t)$ is determined through the equipartition theorem $\left\langle m\dot{x}^2/2\right\rangle = k_BT/2$. Here we only quote the result and left the derivation in Appendix A.3.

$$\langle f(t)f(t')\rangle = 2k_BT\zeta\delta(t-t'). \tag{A.3}$$

Here k_B is the Boltzmann constant, T is the temperature of the solvent. Such noise is called 'white' since the spectrum of the noise correlation obtained by Fourier transform of (A.3) with respect to time shows that it is consist of spectra with all frequencies with the identical weights. Relation (A.3) connects the fluctuation of the solvent $f(t)$ and the dissipation ζ and called the FDT. We also assume that the PDF of the noise f is given by the Gaussian distribution. It considerably simplifies the manipulation of the stochastic processes since the noise is characterized by only within the first and second moment.

The white Gaussian noise is a mathematical idealization or an approximation of the real system. Below we describe its mathematical aspects. We consider a following white Gaussian stochastic process $\xi(t)$.

$$\langle \xi(t)\rangle = 0 \quad , \langle \xi(t)\xi(t')\rangle = \delta(t-t') \tag{A.4}$$

$\xi(t)$ is random and its value is nothing to do with its value in the past, thus it must be a non-continuous function for all t. While the position and velocity of the Brownian particle must be a continuous function of time. It means that any time integral of ξ must be continuous. A quantity

$$W_t - W_0 = \int_{W_0}^{W_t} dW_s \equiv \int_0^t ds\xi(s) \tag{A.5}$$

is called the Wiener process and must be continuous with respect to t. To define the integral measure dW_s mathematically more rigorous one has to discretize the integral range into n pieces with their width being Δt. Set $0 = t_0 < t_1 < \cdots < t_{n-1} = t$. For any function of time $G(s)$, the Ito integral is defined by [26]

$$\text{(I)} \int_0^t G(s)dW_s = \int_0^t G(s)\xi(s)ds \equiv \text{m.s.} \lim_{n\to\infty} \sum_{i=1}^{n} G(t_{i-1})\left[W_i - W_{i-1}\right], \tag{A.6}$$

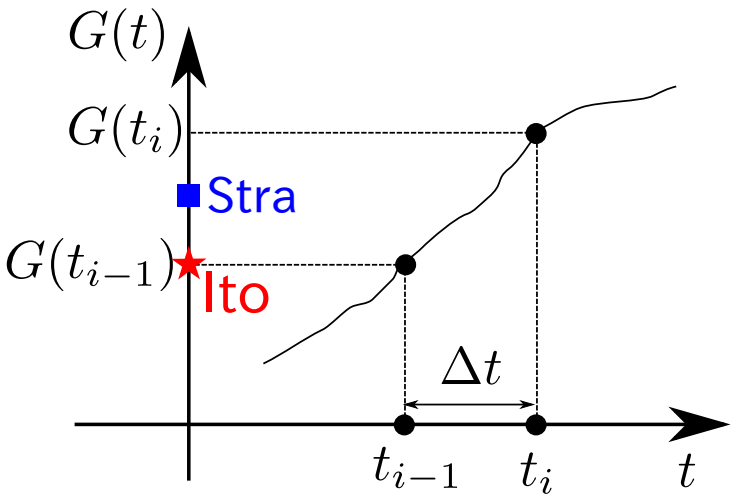

Figure A.1: Stochastic integral for Ito(red star) and Stratonovich(blue square) definition.

here 'm.s.' stands for the mean square limit. The mean square limit $A = \text{m.s.}\lim_{n\to\infty} A_n$ means that mean square of the difference between the left hand side (LHS) and the right hand side (RHS) goes to 0 in $n \to \infty$. Thus $\lim_{n\to\infty} \langle (A - A_n)^2 \rangle = 0$. One always has to resort to such an indirect definition of integral, otherwise the limit $n \to \infty$ or $\Delta t \to 0$ of the RHS of (A.6) does not converge. Hereafter we abbreviate $W_i = W_{t_i}$. The another type of integral has been proposed by Stratonovich [27]

$$(\text{S}) \int_0^t G(s) dW_s \equiv \text{m.s.} \lim_{n\to\infty} \sum_{i=1}^{n} G\left(\frac{t_i + t_{i-1}}{2}\right) [W_i - W_{i-1}] \tag{A.7}$$

These definitions of integrals are illustrated in Figure A.1. The two integrals are in general different each other, depending on the property of the integrand $G(t)$. If $G(t)$ depends on t through W_t, i.e., $G(t) = G(W_t, t)$ the different definition leads the different value of the integral. On the other hand $G(t)$ is merely a continuous function of t, for example $G(t) = 1$, two integrals coincide, which is the case with (A.5).

For both definition of the integral, following very important formula holds.

$$dW_t^2 = dt. \tag{A.8}$$

It looks somewhat peculiar since the LHS is stochastic while the RHS is deterministic. It comes from the fact that the integral is defined through an average.

Proof We abbreviate $G(\tau_i)$ with G_i for notational simplicity. Throughout the proof we employ the Ito integral. It is equivalent with (A.8) to show in

$$\begin{aligned}\int_{t_0}^{t} G(\tau)[dW(\tau)]^2 &\equiv \text{m.s.}\lim_{n\to\infty}\sum_{i}^{n} G_{i-1}(W_i - W_{i-1})^2 \\ &\equiv \text{m.s.}\lim_{n\to\infty}\sum_{i}^{n} G_{i-1}\Delta W_i^2, \end{aligned} \tag{A.9}$$

that A obeys

$$A \equiv \lim_{n\to\infty}\left\langle\left[\sum_{i}^{n} G_{i-1}(\Delta W_i^2 - \Delta t_i)\right]^2\right\rangle = 0. \tag{A.10}$$

Expanding $[\cdots]$ in (A.10) gives,

$$\begin{aligned} A &= \lim_{n\to\infty}\left[\left\langle\sum_{i}^{n}(G_{i-1})^2(\Delta W_i^2 - \Delta t_i)^2\right\rangle\right. \\ &\qquad \left. +2\left\langle\sum_{i<j}^{n} G_{j-1}(\Delta W_j^2 - \delta t_j)G_{i-1}(\Delta W_i^2 - \Delta t_i)\right\rangle\right] \\ &= \lim_{n\to\infty}\left[\sum_{i}^{n}\left\langle G_{i-1}^2\right\rangle\left\langle(\Delta W_i^2 - \Delta t_i)^2\right\rangle\right. \\ &\qquad \left. +2\sum_{i<j}^{n}\left\langle G_{j-1}(\Delta W_j^2 - \Delta t_j)G_{i-1}\right\rangle\left\langle(\Delta W_i^2 - \Delta t_i)\right\rangle\right]. \end{aligned} \tag{A.11}$$

Here we assumed that G_i is statistically independent with W_i. In other words, the value of G_i is not correlated with the value of the noise at the same time. This feature of G is called non-anticipating. Hereafter we only consider such physical quantities. By the definition of ΔW we have

$$\begin{aligned}\left\langle\Delta W_i^2\right\rangle &= \left\langle(W(t_i) - W(t_{i-1})^2)\right\rangle \\ &= \left\langle\left(\int_{t_{i-1}}^{t_i} d\tau\xi(\tau)\right)^2\right\rangle = \Delta t_i, \end{aligned} \tag{A.12}$$

and

$$\begin{aligned}\left\langle (\Delta W_i^2 - \Delta t_i)^2 \right\rangle &= \left\langle (\Delta W_i)^4 - 2(\Delta W_i)^2 \Delta t_i + (\Delta t_i)^2 \right\rangle \\ &= \left\langle \left(\int_{t_{i-1}}^{t_i} d\tau \xi(\tau) \right)^4 \right\rangle - 2\Delta t_i \Delta t_i + (\Delta t_i)^2 \\ &= \int_{t_{i-1}}^{t_i} \cdots \int_{t_{i-1}}^{t_i} d\tau_1 d\tau_2 d\tau_3 d\tau_4 \langle \xi(\tau_1)\xi(\tau_2)\xi(\tau_3)\xi(\tau_4) \rangle \\ &\quad - (\Delta t_i)^2. \end{aligned} \tag{A.13}$$

Since we assumed that ξ is Gaussian process, we can make use of the Wick's theorem,

$$\begin{aligned}\langle \xi(\tau_1)\xi(\tau_2)\xi(\tau_3)\xi(\tau_4) \rangle &= \langle \xi(\tau_1)\xi(\tau_2) \rangle \langle \xi(\tau_3)\xi(\tau_4) \rangle + 2\text{permutations} \\ &= \delta(\tau_1 - \tau_2)\delta(\tau_3 - \tau_4) + 2\text{permutations},\end{aligned}$$

Thus (A.13) becomes

$$\langle (\Delta W_i^2 - \Delta t_i)^2 \rangle = 2(\Delta t_i)^2. \tag{A.14}$$

Plugging (A.12) and (A.14) with (A.11) one has

$$A = 2 \lim_{n\to\infty} \sum_i^n \langle G_{i-1}^2 \rangle \Delta t_i^2 = 0. \tag{A.15}$$

Here we have used the fact that $\sum_i^n \propto n, \langle G^2 \rangle \sim \mathcal{O}(1), \Delta t_i \propto n^{-1}$. Thus the formula (A.8) has been proven. □

With these preparations one can define the Langevin equation or SDE with the multiplicative noise.

$$\dot{x}(t) = f(x(t), t) + g(x(t), t)\xi(t). \tag{A.16}$$

Here $f(x(t), t)$ and $g(x(t), t)$ are given functions of x and t. As shown below this equation does not uniquely determine a stochastic process $x(t)$. By integrating (A.16) from t to $t + \Delta t$, one has

$$\begin{aligned}x(t + \Delta t) - x(t) &= \int_t^{t+\Delta t} dt_1 \dot{x}(t_1) \\ &= \int_t^{t+\Delta t} dt_1 f(x(t_1), t_1) + \int_{W_t}^{W_{t+\Delta t}} dW_{t_1} g(x(t_1), t_1),\end{aligned} \tag{A.17}$$

The second term in the RHS of (A.17) depends on the definition of the stochastic integral, Ito (A.6) or Stratonovich (A.7). The difference between them is given by

$$\begin{aligned}(\mathrm{S})\int_{W_1}^{W_2} dW_{t_1} g(x(t_1),t_1) &= (\mathrm{I})\int_{W_1}^{W_2} dW_{t_1} g(x(t_1),t_1) \\ &\quad +\frac{1}{2}\int_{t_1}^{t_2} dt_1 g(x(t_1),t_1)\frac{\partial g(x,t_1)}{\partial x(t_1)}. \quad \text{(A.18)}\end{aligned}$$

The proof is almost the same as the calculation around (2.6). Thus one has to give a definition of the stochastic integral in the second term in the RHS of (A.17).

We introduce a parameter α with $0 \leq \alpha \leq 1$ so that we can handle the Ito and the Stratonovich together.

$$\begin{aligned} x^* &= \alpha x(t+\Delta t) + (1-\alpha)x(t) && \text{(A.19)}\\ &= x(t) + \alpha \Delta x && \text{(A.20)}\\ &= x(t+\Delta t) - (1-\alpha)\Delta x. && \text{(A.21)}\end{aligned}$$

The formula (A.8) is a relationship between integral measure. Here we translate it to the differential formula. It is called the Ito formula. The formula (A.8) implies that $\Delta W \sim \mathcal{O}(\Delta t^{1/2})$. Thus in order to differentiate a composite function of a stochastic variable one has to keep upto second order to Δx. For general function $f(x)$, one can expand $f(x(t+\Delta t))$ and $f(x(t))$ respectively as follows.

$$\begin{aligned} f(x(t+\Delta t)) &= f(x^* + (1-\alpha)\Delta x) && \text{(A.22)}\\ &= f(x^*) + (1-\alpha)\Delta x f'(x^*) + \frac{1}{2}(1-\alpha)^2(\Delta x)^2 f''(x^*) \\ &\quad +\mathcal{O}((\Delta x)^3), \\ f(x(t)) &= f(x^* - \alpha\Delta x) && \text{(A.23)}\\ &= f(x^*) - \alpha\Delta x f'(x^*) + \frac{1}{2}\alpha^2(\Delta x)^2 f''(x^*) + \mathcal{O}((\Delta x)^3).\end{aligned}$$

Thus subtracting these relations each other, one has

$$\begin{aligned}\Delta f &\equiv f(x(t+\Delta t)) - f(x(t)) \\ &= f'(x^*)\Delta x + \frac{1-2\alpha}{2} f''(x^*)(\Delta x)^2 + \mathcal{O}\left((\Delta x)^3\right). \quad \text{(A.24)}\end{aligned}$$

Keeping in mind that $(\Delta x)^2 \sim (\Delta W)^2 \sim \Delta t$ we take second order to Δx. Note that if one chooses the Stratonovich convention ($\alpha = 1/2$) the second term in the RHS of (A.24) vanishes, and ordinary chain rule of differentiation is recovered.

A.2 Kramers-Moyal expansion

We define the PDF $\Phi(X,t)$ by using the solution of SDE (A.40), $x(t)$, as

$$\Phi(X,t) \equiv \langle \delta(X - x(t)) \rangle. \tag{A.25}$$

The probability that x takes value X_1 at time t_1 under the condition that the value of x was X_0 at time t_0 is given by,

$$\Phi(X_1,t_1|X_0,t_0) = \langle \delta(X_1 - x(t_1)) \rangle_{X_0(t_0)}. \tag{A.26}$$

Here $\langle \cdots \rangle_{X_0(t_0)}$ means that the average is taken under the condition that $x(t_0) = X_0$. When the stochastic process is Markovian, i.e., driven by a white noise, the Chapman-Kolmogorov equation holds.

$$\Phi(X,t+\Delta t) = \int \mathcal{D}X_0 \Phi(X,t+\Delta t|X_0,t)\Phi(X_0,t). \tag{A.27}$$

By expanding the conditional probability in the RHS of (A.27) in powers of Δt, one obtains

$$\begin{aligned}
\Phi(X,t+\Delta t|X_0,t) &\equiv \langle \delta(X - x(t+\Delta t)) \rangle_{X_0,t} = \langle \delta(X - X_0 - \Delta x) \rangle_{X_0,t} \\
&= \delta(X - X_0) - \langle \Delta x \rangle \frac{\partial}{\partial X}\delta(X - X_0) \\
&\quad + \frac{1}{2}\langle \Delta x^2 \rangle \frac{\partial^2}{\partial X^2}\delta(X - X_0) + \cdots .
\end{aligned} \tag{A.28}$$

Here we set $\Delta x \equiv x(t+\Delta t) - X_0$. By substituting it into (A.27) and performing the integration by parts, one has

$$\begin{aligned}
\Phi(X,t+\Delta t) &= \Phi(X,t) - \frac{\partial}{\partial X}\left(\langle \Delta x \rangle_{X(t)} \Phi(X,t) \right) \\
&\quad + \frac{1}{2}\frac{\partial^2}{\partial X^2}\left(\left\langle (\Delta x)^2 \right\rangle_{X(t)} \Phi(X,t) \right).
\end{aligned} \tag{A.29}$$

By taking $\Delta t \to 0$ limit one arrives at following partial differential equation.

$$\begin{aligned}
\frac{\partial \Phi(X,t)}{\partial t} &= -\frac{\partial}{\partial X}\left(\lim_{\Delta t \to 0} \frac{\langle \Delta x \rangle_{X(t)}}{\Delta t} \Phi(X,t) \right) \\
&\quad + \frac{1}{2}\frac{\partial^2}{\partial X^2}\left(\lim_{\Delta t \to 0} \frac{\left\langle (\Delta x)^2 \right\rangle_{X(t)}}{\Delta t} \Phi(X,t) \right)
\end{aligned} \tag{A.30}$$

This method to derive the partial differential equation for PDF is called the Kramers-Moyal expansion. One can calculate $\langle \Delta x \rangle_{X(t)}$ and $\left\langle (\Delta x)^2 \right\rangle_{X(t)}$ from

the Langevin equation (A.16). We assume that the multiplicative noise in (A.16) is interpreted by the general α-convention. Then,

$$\lim_{\Delta t\to 0}\frac{\langle \Delta x\rangle_{X(t)}}{\Delta t} = f(X,t)+\alpha g' g(X,t), \tag{A.31}$$

$$\lim_{\Delta t\to 0}\frac{\left\langle (\Delta x)^2\right\rangle_{X(t)}}{\Delta t} = g^2(X,t). \tag{A.32}$$

By substituting (A.31) and (A.32) into (A.30) one obtains

$$\frac{\partial \Phi(X,t)}{\partial t} = -\frac{\partial}{\partial X}\left[f(X,t)+\alpha g' g(X,t)\right]\Phi + \frac{\partial^2}{\partial X^2}\left[\frac{g^2(X,t)}{2}\right]\Phi. \tag{A.33}$$

This equation describes the time evolution of PDF $\Phi(X,t)$, called the Fokker-Planck equation.

A.3 The Brownian motion

In Section A.1 and Section A.2 we developed the methodology to treat the stochastic processes mathematically. In this section we turn to the Brownian motion as a certain physical model described by the stochastic processes.

A.3.1 Underdamped Langevin equation

In this subsection we go back to (A.1) and show how the statistical mechanics constrains the form of governing equation. We start from

$$m\ddot{x}(t) = -\zeta \dot{x}(t) - \frac{\partial U}{\partial x} + f(t), \tag{A.34}$$

and keep variance of noise term $f(t)$ unspecified. We only assume that it is white Gaussian.

$$\langle f(t)\rangle = 0, \quad \langle f(t) f(t')\rangle = \Gamma\delta(t-t'). \tag{A.35}$$

Here Γ is a constant. One can solve (A.34) formally as

$$\dot{x}(t) = \frac{1}{m}\int_{-\infty}^{t} dt_1 \mathrm{e}^{-\frac{\zeta}{m}(t-t_1)}\left(-\frac{\partial U}{\partial x(t_1)} + f(t_1)\right). \tag{A.36}$$

We tentatively ignore the external force to make the discussion simple. Average kinetic energy $\left\langle m\dot{x}^2/2\right\rangle$ is calculated from (A.36) as

$$\begin{aligned}\left\langle \frac{m\dot{x}^2}{2}\right\rangle &= \left\langle \frac{1}{2m}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 \mathrm{e}^{-\frac{\zeta}{m}(2t-t_1-t_2)} f(t_1) f(t_2)\right\rangle \\ &= \frac{\Gamma}{4\zeta}.\end{aligned} \tag{A.37}$$

In between the first and second line of (A.37) we have made use of (A.35). These are purely dynamic argument. In statistical mechanics the equipartition theorem states that

$$\left\langle \frac{m\dot{x}^2}{2} \right\rangle = \frac{k_B T}{2}. \tag{A.38}$$

Thus we are forced to have

$$\Gamma = 2k_B T\zeta. \tag{A.39}$$

This is the FDT.

A.3.2 Overdamped Langevin equation

Overdamp limit is the situation where the timescale one is interested in is much longer than the relaxation time of momentum, and description only within the position variable is possible. For a simple model like (A.1) the overdamp limit is identical with ignoring inertial term in the LHS, but as pointed out in Chapter 2 it is no longer the case when noise is multiplicative. In this subsection we restrict ourselves in the case with the additive noise and examine its properties. The overdamp Langevin equation is given by

$$\dot{x}(t) = L\left(-\frac{\partial U}{\partial x(t)} + f(t)\right). \tag{A.40}$$

Here $L = 1/\zeta$ is the Onsager coefficient. For derivation of (A.40) the reader should refer to Appendix B.1. The FDT can be rewritten within the Onsager coefficient as

$$\langle f(t)f(t')\rangle = 2k_B T L^{-1}\delta(t-t'). \tag{A.41}$$

One can derive the corresponding FPE by using the Kramers-Moyal expansion introduced in Section A.2. The expansion coefficients are,

$$\begin{aligned}
\langle \Delta x\rangle &= \langle x(t+\Delta t) - X\rangle = \left\langle \int_t^{t+\Delta t} ds\dot{x}(s) \right\rangle \\
&= -L\frac{\partial U}{\partial X}\Delta t, &\text{(A.42)}\\
\left\langle (\Delta x)^2 \right\rangle &= 2k_B T L\Delta t. &\text{(A.43)}
\end{aligned}$$

Then plugging (A.42) and (A.43) into (A.30) one obtains

$$\frac{\partial \Phi(X,t)}{\partial t} = \frac{\partial}{\partial X}\left[L\left(\frac{\partial U}{\partial X} + k_B T\frac{\partial}{\partial X}\right)\Phi(X,t)\right]. \tag{A.44}$$

So far we have distinguished a stochastic variable $x(t)$ and its value X in deriving the FPE. But once it is derived we do not need to be careful of

the difference between them. Thus whenever it does not cause any confusion we just use x instead of X. A stationary solution of the FPE (A.44) is immediately found as

$$\Phi^{\rm eq}(X) = \mathcal{N} \exp\left[-\beta U(X)\right], \tag{A.45}$$

with $\mathcal{N}$ being a suitable normalization constant. One can derive the FPE from the SDE by using the Kramers-Moyal expansion and obtain a stationary solution given by the Maxwell-Boltzmann distribution. The latter is the consequence of the FDT, which bridges the noise intensity and friction coefficient and temperature. The FDT works as a starting point to construct a theory of Brownian motion. Here we describe another representation of the FDT. We define the equilibrium average as

$$\langle \cdots \rangle^{\rm eq} = \int \mathcal{D}X \Phi^{\rm eq}(X) \cdots . \tag{A.46}$$

Then it follows that

$$\langle \dot{x} \rangle^{\rm eq} = 0. \tag{A.47}$$

It means that the net current vanishes in the equilibrium state.

Proof By using the overdamp Langevin equation (A.40)

$$\langle \dot{x} \rangle^{\rm eq} = \left\langle -L\frac{\partial U}{\partial x} \right\rangle = -L\mathcal{N} \int \mathcal{D}X \exp[-\beta U(X)] \frac{\partial U}{\partial X}. \tag{A.48}$$

The RHS of (A.48) vanishes since here obeys $\mathrm{e}^{-\beta U}\frac{\partial U}{\partial X} = -k_B T \frac{\partial \mathrm{e}^{-\beta U}}{\partial X}$ and the integral becomes a surface term. Thus (A.47) is proven. □

The dynamics in the equilibrium state is also constrained by FDT. It states that a correlation function of a physical quantity is connected to the response to the external force. Sometimes this is called the 1st FDT. Consider an external force $h(t)$ conjugate to x. Then the Hamiltonian becomes,

$$U \to U - xh(t), \tag{A.49}$$

when h is sufficiently small. Under the weak external force h the distribution function will slightly deviate from the equilibrium distribution as

$$\Phi(x,t) = \Phi^{\rm eq}(x) + \Phi^h(x,t). \tag{A.50}$$

where Φ^h is assumed to be small. We can split the FPE in the presence with the external force in following manner.

$$\frac{\partial \Phi(x,t)}{\partial t} = \left(\mathsf{L}_0(x) + \mathsf{L}_h(x,t)\right) \Phi(x,t). \tag{A.51}$$

Here we have defined

$$\mathsf{L}_0(x)\cdot \equiv \frac{\partial}{\partial x}\left[L\left(\frac{\partial U}{\partial x}+k_BT\frac{\partial}{\partial x}\right)\cdot\right], \tag{A.52}$$

$$\mathsf{L}_h(x,t)\cdot \equiv -\frac{\partial}{\partial x}\left(Lh\cdot\right). \tag{A.53}$$

By definition we have

$$\mathsf{L}_0(x)\Phi^{\rm eq}=0. \tag{A.54}$$

Substituting (A.50) into (A.51) and keeping the lowest order to h, one obtains

$$\frac{\partial\Phi^h(x,t)}{\partial t}=\mathsf{L}_0(x)\Phi^h(x,t)+\mathsf{L}_h(x,t)\Phi^{\rm eq}(x), \tag{A.55}$$

It can be solved formally by regarding the first and second term in the RHS of (A.55) as a homogeneous and an inhomogeneous term,

$$\Phi^h(x,t)=\int_{-\infty}^{t}{\rm d}s\exp\left[(t-s)\mathsf{L}_0(x)\right]\mathsf{L}_h(x,s)\Phi^{\rm eq}(x). \tag{A.56}$$

By using this formal solution one can calculate an average of x in the presence of the external force,

$$\begin{aligned}\langle x(t_1)\rangle^h &= \int{\rm d}x x\Phi(x,t_1)=\int{\rm d}x x\left(\Phi^{\rm eq}(x)+\Phi^h(x,t)\right) \qquad (A.57)\\ &= \langle x\rangle^{\rm eq}+\int{\rm d}x x\Phi^h(x,t_1)\\ &= \langle x\rangle^{\rm eq}+\int{\rm d}x x\int_{-\infty}^{t}{\rm d}s\exp\left[(t_1-s)\mathsf{L}_0(x)\right]\mathsf{L}_h(x,s)\Phi^{\rm eq}(x)\\ &= \langle x\rangle^{\rm eq}-\int{\rm d}x x\int_{-\infty}^{t}{\rm d}s\exp\left[(t-s)\mathsf{L}_0(x)\right]\frac{\partial}{\partial x_k}\left(L_{kl}(x)h_l(s)\Phi^{\rm eq}(x)\right),\end{aligned}$$

where we have made use of (A.50), (A.53) and (A.56). Thus one can obtain the response function as

$$\begin{aligned}\chi(t_1,t_2) &\equiv \frac{\partial}{\partial h(t_2)}\left(\langle x(t_1)\rangle^h-\langle x\rangle^{\rm eq}\right)\\ &= -\int dx x\exp\left[(t_1-t_2)\mathsf{L}_0(x)\right]\frac{\partial}{\partial x}\left(L\Phi^{\rm eq}(x)\right). \qquad (A.58)\end{aligned}$$

Here we assumed $t_1>t_2$. By using the following identity

$$\left[x,\mathsf{L}_0\right]\Phi^{\rm eq}=-k_BT\frac{\partial}{\partial x}\left(L\Phi^{\rm eq}\right), \tag{A.59}$$

the response function can be rewritten as

$$\begin{aligned}\chi(t_1-t_2) &= \beta\int \mathrm{d}x x \exp\left[(t_1-t_2)\mathsf{L}_0(x)\right]\left[x,\mathsf{L}_0(x)\right]\Phi^{\mathrm{eq}}(x)\\ &= -\beta\int \mathrm{d}x x \exp\left[(t_1-t_2)\mathsf{L}_0(x)\right]\mathsf{L}_0(x)\left(x\Phi^{\mathrm{eq}}\right) \qquad \text{(A.60)}\\ &= -\beta\frac{\partial}{\partial(t_1-t_2)}\int \mathrm{d}x x \exp\left[(t_1-t_2)\mathsf{L}_0(x)\right]\left(x\Phi^{\mathrm{eq}}(x)\right).\end{aligned}$$

Here $\beta = (k_B T)^{-1}$ is the inverse temperature. The correlation function in the equilibrium state is defined by

$$\begin{aligned}C(t_1-t_2) &\equiv \left\langle x(t_1)x(t_2)\right\rangle_{\mathrm{eq}}\\ &= \int \mathrm{d}x \int \mathrm{d}x' x\Phi(x,t_1|x',t_2)x'\Phi^{\mathrm{eq}}(x'), \qquad \text{(A.61)}\end{aligned}$$

provided that $t_1 > t_2$. The conditional probability $\Phi(x,t_1|x',t_2)$ also satisfies the same FPE as the PDF. By using its formal solution

$$\Phi(x,t_1|x',t_2) = \exp\left[(t_1-t_2)\mathsf{L}_0(x)\right]\delta(x-x'), \qquad \text{(A.62)}$$

the correlation function becomes,

$$\begin{aligned}C(t_1-t_2) &= \int \mathrm{d}x \int \mathrm{d}x' x\left\{\exp\left[(t_1-t_2)\mathsf{L}_0(x)\right]\delta(x-x')\right\}x'\Phi^{\mathrm{eq}}(x')\\ &= \int \mathrm{d}x \int \mathrm{d}x' \left\{\exp\left[(t_1-t_2)\mathsf{L}_0^{\dagger}(x)\right]x\right\}\delta(x-x')x'\Phi^{\mathrm{eq}}(x')\\ &= \int \mathrm{d}x \left\{\exp\left[(t_1-t_2)\mathsf{L}_0^{\dagger}(x)\right]x\right\}x\Phi^{\mathrm{eq}}(x)\\ &= \int \mathrm{d}x x \exp\left[(t_1-t_2)\mathsf{L}_0(x)\right]\left[x\Phi^{\mathrm{eq}}(x)\right] \qquad \text{(A.63)}\end{aligned}$$

Here $\mathsf{L}^{\dagger}$ is a Hermite conjugate to L. By comparing (A.60) and (A.63) we arrive at the FDT of 1st kind,

$$\chi(t) = -\beta\frac{\partial}{\partial t}C(t). \qquad \text{(A.64)}$$

Here we introduced $t = t_1 - t_2$.

An extension to the multi-dimensional case is straightforward. The over-damp Langevin equation for $i = 1, \cdots, N$ is

$$\dot{x}_i = L_{ij}\left(-\frac{\partial U}{\partial x_j} + f_j\right). \qquad \text{(A.65)}$$

Hereafter summation over repeated indices is adopted. L_{ij} is the Onsager coefficient matrix and the noise f_i satisfies,

$$\langle f_i(t)\rangle = 0, \quad \langle f_i(t)f_j(t')\rangle = 2k_BT\left(L^{-1}\right)_{ij}\delta(t-t'). \tag{A.66}$$

The PDF of the variables X_i is defined as

$$\Phi(\boldsymbol{X},t) \equiv \left\langle \prod_{i=1}^{N} \delta(X_i - x_i(t)) \right\rangle. \tag{A.67}$$

Here $\boldsymbol{X}$ represents N set of X_i. $\Phi(\boldsymbol{X},t)$ satisfies the following Fokker-Planck equation, which is a straightforward extension from the one-dimensional case.

$$\frac{\partial\Phi(\boldsymbol{X},t)}{\partial t} = \frac{\partial}{\partial X_i}\left[L_{ij}\left(\frac{\partial U}{\partial X_j} + k_BT\frac{\partial}{\partial X_j}\right)\Phi(\boldsymbol{X},t)\right]. \tag{A.68}$$

Thus, the stationary solution to (A.68) is given by the Maxwell-Boltzmann distribution.

$$\Phi^{\mathrm{eq}}(\boldsymbol{X}) = \mathcal{N}\exp[-\beta U(\boldsymbol{X})]. \tag{A.69}$$

The FDT can be derived in the same manner as one-dimensional case.

$$\chi_{ij}(t) = -\beta\frac{\partial}{\partial t}C_{ij}(t). \tag{A.70}$$

A.4 Absence of the Ito-Stratonovich dilemma in underdamped Langevin equation

In this section we show that the choice of the interpretation of the multiplicative noises does not affect the solution of the Langevin equation for the underdamped Langevin equation. Thus there are no Ito-Stratonovich dilemma in the underdamped Langevin equation. This feature is essential for our theory in Chapter 2 and 3 to work properly. Consider a set of the underdamped Langevin equation in one dimension,

$$\dot{x}(t) = v(t), \tag{A.71}$$
$$\dot{v}(t) = -\zeta(x(t))v(t) + b(x(t))\xi(t). \tag{A.72}$$

Let us integrate these equations from t to $t+\Delta t$,

$$\Delta x = v(t)\Delta t, \tag{A.73}$$
$$\Delta v = -\zeta(x(t))v(t)\Delta t + b(x^*)\Delta W. \tag{A.74}$$

where $x^* = \alpha x(t + \Delta t) + (1 - \alpha)x(t)$. $b(x^*)$ in the RHS of (A.74) can be expanded around $x(t)$ as

$$b(x^*) = b(x(t)) + \alpha b'(x(t))\Delta x = b(x(t)) + \alpha b'(x(t))v(t)\Delta t. \tag{A.75}$$

Thus the difference between the α convention and the Ito is $\mathcal{O}(\Delta t)$. This is in contrast with the overdamped case, demonstrated in Section 2.1, equation (2.6). Then the multiplicative noise $b(x^*)\Delta W$ is

$$\begin{aligned} b(x^*)\Delta W &= b(x(t))\Delta W + \alpha b'(x(t))v(t)\Delta t\Delta W \\ &= b(x(t))\Delta W + \mathcal{O}(\Delta t^{3/2}). \end{aligned} \tag{A.76}$$

Thus difference in the different interpretation of the multiplicative noise vanishes faster than Δt. There is no Ito-Stratonovich dilemma in the underdamped Langevin equation.

Appendix B

Adiabatic Elimination

In this chapter we summarize the theories of the adiabatic elimination of the momentum in the Brownian motion. In Section B.1 we follow a derivation of the overdamp limit from the underdamped Langevin equation driven by the additive noise. For more general situation, for example, for the Brownian motion with the multiplicative noises, more sophisticated methods must be applied. We introduce such a method in Section B.2. In Section B.3 we review a heuristic argument on taking the overdamp limit.

B.1 Adiabatic elimination on linear process

We start from the underdamped Langevin equation given in (A.1) and derive the overdamped Langevin equation given in (A.40). The formal solution to (A.1) is given by

$$\dot{x}(t) = \frac{1}{m}\int_{-\infty}^{t} dt' \mathrm{e}^{-\frac{\zeta}{m}(t-t')}\left(-\frac{\partial U}{\partial x(t')} + f(t')\right). \tag{B.1}$$

Here $m/\zeta \equiv \tau_p$ is the time scale of damping of the momentum. The overdamp limit is the situation that the time scale one is interested in is much longer than τ_p. In other words, one can regard the friction ζ very large or the mass of the Brownian particle m is very small. Thus, the scale separation $t \gg \tau_p$ can be applied. In such situation the integral in the RHS of (B.1) is dominated by $t' = t$ and one can replace t' by t in $(\cdots)$ in the integrand. Then,

$$\frac{1}{m}\int_{-\infty}^{t} dt' \mathrm{e}^{-\frac{t-t'}{\tau_p}}\left(-\frac{\partial U}{\partial x(t')} + f(t')\right) = \frac{1}{m}\int_{0}^{\infty} du \mathrm{e}^{-\frac{u}{\tau_p}}\left(-\frac{\partial U}{\partial x(t)} + f(t)\right). \tag{B.2}$$

Here we set $u = t - t'$. One can carry out the integral over u and obtains

$$\int_0^\infty du \exp\left[-\frac{u}{\tau_p}\right] = \tau_p = \frac{m}{\zeta}. \tag{B.3}$$

Thus the formal solution (B.1) becomes

$$\dot{x}(t) = \zeta^{-1}\left(-\frac{\partial U}{\partial x} + f(t)\right). \tag{B.4}$$

This expression is identical with (A.40) if one adopts $L = \zeta^{-1}$. Note that this overdamp limit is identical with the underdamped Langevin equation (A.1) without the inertial term.

B.2 Kramers problem and projection method

In this section we summarize the method to adiabatically eliminate the fast relaxing momentum and obtain the overdamp limit within the FPE. The method is directly applicable to the models with the multiplicative noises and has been established already, see the literature [48, 49] or review [8]. Here we consider the following underdamped Langevin equation.

$$\dot{x} = m^{-1}p, \tag{B.5}$$

$$\dot{p} = -\zeta(x(t))\dot{x}(t) - \frac{\partial U}{\partial x} + f(x,t). \tag{B.6}$$

We assume that the friction coefficient is dependent of x and the noise becomes multiplicative since the FDT states that

$$\langle f(t)f(t')\rangle = 2k_B T\zeta(x(t))\delta(t-t'). \tag{B.7}$$

In the case of the underdamped Langevin equation the interpretation of the multiplicative noise does not affect the solution of SDE, as shown in Appendix A.4. One can derive the FPE (or Kramers equation) by using the Kramers-Moyal expansion presented in Appendix A.2 for the PDF

$$\Psi(x,p,t) = \langle\delta(x-x(t))\delta(p-p(t))\rangle, \tag{B.8}$$

as,

$$\frac{\partial\Psi(x,p,t)}{\partial t} = \frac{\partial}{\partial x}\left(-\frac{p}{m}\Psi\right) + \frac{\partial}{\partial p}\left(\frac{\zeta(x)}{m}p + \frac{\partial U}{\partial x}\right)\Psi + \frac{\partial^2}{\partial p^2}T\zeta(x)\Psi. \tag{B.9}$$

The problem to obtain the overdamp limit by adiabatically eliminating the fast relaxing momentum from the Kramers equation is called "Kramers problem" [10]. The goal of the problem is to write down the FPE for PDF for the position variables only, called the Smoluchowski equation. Here we introduce the projection method as a solution to the Kramers problem. The projection

method provides the way to split the dynamics of the PDF for the position and momentum to the fast and slow counterparts. The fast and slow motions are corresponding to the momentum and the position respectively. First we rewrite (B.9) as

$$\frac{\partial \Psi}{\partial t} = L_1 \Psi + \epsilon^{-1} L_0 \Psi. \tag{B.10}$$

Here we have defined L_1 and L_0 respectively as

$$L_1 = -m^{-1} p \frac{\partial}{\partial x} + \frac{\partial U}{\partial x}\frac{\partial}{\partial p} = -\{H, \}, \tag{B.11}$$

$$L_0 = \zeta(x)\left(\frac{1}{m}\frac{\partial}{\partial p} p + T\frac{\partial^2}{\partial p^2}\right), \tag{B.12}$$

and a symbol ϵ is introduced to remind that ζ is large and hence ζ^{-1} is small. One can check that the Boltzmann distribution for momentum is the 0 eigenfunction to the operator L_0:

$$L_0 \rho^{\mathrm{eq}}(p) = 0, \quad \rho^{\mathrm{eq}}(p) = \mathcal{N}_p^{-1} \exp\left[-\beta K(p)\right], \tag{B.13}$$

where $K(p)$ is the kinetic energy and $\mathcal{N}_p$ is the normalization factor defined as

$$K(p) = \frac{p^2}{2m}, \quad \mathcal{N}_p = \int dp \exp\left[-\beta K(p)\right] = \sqrt{mT}. \tag{B.14}$$

The relationship between the PDF for position and momentum $\Psi(x, p, t)$ and the PDF for position $\Phi(x, t)$ is simply given by

$$\Phi(x, t) = \int dp \Psi(x, p, t). \tag{B.15}$$

Thus one may expect that one can obtain the Smoluchowski equation by integrating both side of the Kramers equation (B.9) over p. But the Kramers problem is not as trivial as naively expected. We need to introduce a projection operator onto the slow dynamics.

$$\mathcal{P} \equiv \rho^{\mathrm{eq}}(p) \int dp. \tag{B.16}$$

It satisfies $\mathcal{P}^2 = \mathcal{P}$ and works as the projection operator to the slow counterpart of the PDF Ψ since

$$\mathcal{P}\Psi(x, p, t) = \rho^{\mathrm{eq}}(p)\Phi(x, t). \tag{B.17}$$

We define $\mathcal{Q} = 1 - \mathcal{P}$ and split the Kramers equation (B.10) following the spirit of the projection operator formalism.

$$\frac{\partial}{\partial t}\mathcal{P}\Psi = \mathcal{P}L_1\mathcal{P}\Psi + \mathcal{P}L_1\mathcal{Q}\Psi + \epsilon^{-1}\left(\mathcal{P}L_0\mathcal{P}\Psi + \mathcal{P}L_0\mathcal{Q}\Psi\right), \quad \text{(B.18)}$$

$$\frac{\partial}{\partial t}\mathcal{Q}\Psi = \mathcal{Q}L_1\mathcal{P}\Psi + \mathcal{Q}L_1\mathcal{Q}\Psi + \epsilon^{-1}\left(\mathcal{Q}L_0\mathcal{P}\Psi + \mathcal{Q}L_0\mathcal{Q}\Psi\right). \quad \text{(B.19)}$$

Since L_0 is proportional to $\frac{\partial}{\partial p}$ (see (B.12)), $\mathcal{P}L_0$ becomes the surface integral and drops. Then $\mathcal{P}L_0 = 0$ and $\mathcal{Q}L_0 = L_0$. Moreover, $L_0\rho^{\rm eq}(p) = 0$ leads $L_0\mathcal{P} = 0$. Then (B.18) and (B.19) are simplified as,

$$\frac{\partial}{\partial t}\mathcal{P}\Psi = \mathcal{P}L_1\mathcal{P}\Psi + \mathcal{P}L_1\mathcal{Q}\Psi, \quad \text{(B.20)}$$

$$\frac{\partial}{\partial t}\mathcal{Q}\Psi = \mathcal{Q}L_1\mathcal{P}\Psi + \mathcal{Q}L_1\mathcal{Q}\Psi + \epsilon^{-1}L_0\mathcal{Q}\Psi. \quad \text{(B.21)}$$

We rewrite them for visibility as

$$\frac{\partial v}{\partial t} = Av + Bw, \quad \text{(B.22)}$$

$$\frac{\partial w}{\partial t} = Cv + Dw + \frac{1}{\epsilon}Fw. \quad \text{(B.23)}$$

Namely, we defined

$$v = \mathcal{P}\Psi, \quad w = \mathcal{Q}\Psi,$$
$$A = B = \mathcal{P}L_1, \quad C = D = \mathcal{Q}L_1, \quad F = L_0. \quad \text{(B.24)}$$

Since w plays a role of the fast variable and its relaxation time is given by ϵ. $v = \rho^{\rm eq}(p)\Phi(x,t)$ is the slow variable. It can be shown that v obeys the following equation of motion in the leading order to ϵ.

$$\frac{\partial v}{\partial t} = \left[A - \epsilon BF^{-1}C\right]v. \quad \text{(B.25)}$$

Here we assumed that there exists F^{-1}.

Proof We switch to the Laplace representation. A Laplace transform of v is given by

$$\tilde{v}(z) \equiv \int_0^\infty dt e^{-zt}v(t). \quad \text{(B.26)}$$

Then (B.22) and (B.23) becomes

$$z\tilde{v}(z) - v(0) = A\tilde{v} + B\tilde{w}, \quad \text{(B.27)}$$

$$z\tilde{w}(z) - w(0) = C\tilde{v} + D\tilde{w} + \epsilon^{-1}F\tilde{w}. \quad \text{(B.28)}$$

One can solve (B.28) as

$$\tilde{w}(z) = \left[z + D - \epsilon^{-1}F\right]^{-1} \left(w(0) + C\tilde{v}(z)\right). \tag{B.29}$$

$[z + D - \epsilon^{-1}F]^{-1}$ in the RHS of (B.29) can be expanded in powers of ϵ as,

$$\left[z + D - \epsilon^{-1}F\right]^{-1} = -\epsilon F^{-1} - \epsilon^2 F^{-1}(z + D)F^{-1} + \mathcal{O}(\epsilon^3). \tag{B.30}$$

Then (B.29) becomes

$$\tilde{w}(z) = \left[-\epsilon F^{-1} - \epsilon^2 F^{-1}(z + D)F^{-1}\right] \left(w(0) + C\tilde{v}(z)\right) + \mathcal{O}(\epsilon^3). \tag{B.31}$$

By substituting this formal solution to the RHS of (B.27) one has

$$\begin{aligned} z\tilde{v}(z) - v(0) =& A\tilde{v}(z) + B\left[-\epsilon F^{-1} - \epsilon^2 F^{-1}(z + D)F^{-1}\right] \left(w(0) + C\tilde{v}(z)\right) \\ &+ \mathcal{O}(\epsilon^3) \qquad (B.32) \\ =& \left[A - \epsilon BF^{-1}C - \epsilon^2 BF^{-1}DF^{-1}C\right] \tilde{v}(z) \\ &- \epsilon^2 BF^{-2}Cz\tilde{v}(z) - \epsilon B\left(F^{-1} + \epsilon F^{-1}(z + D)F^{-1}\right) w(0). \end{aligned}$$

We recursively substitute $z\tilde{v}(z) = v(0) + A\tilde{v} + \mathcal{O}(\epsilon)$ to the first term in the last line of (B.32) and obtain

$$\begin{aligned} z\tilde{v}(z) - v(0) =& \left[A - \epsilon BF^{-1}C - \epsilon^2\left(BF^{-1}DF^{-1}C + BF^{-2}CA\right)\right] \tilde{v}(z) \\ &-\epsilon^2 BF^{-2}Cv(0) - \epsilon BF^{-1}(1 - \epsilon(z + D)F^{-1})w(0). \end{aligned} \tag{B.33}$$

In the present case it can be shown that $w(0) = 0$. In the overdamp limit one can choose as initial condition the equilibrium distribution in the PDF of the momentum.

$$\Psi(x, p, 0) = \rho^{\mathrm{eq}}(p)\Phi(x, 0). \tag{B.34}$$

Then one immediately finds

$$w(0) = \mathcal{Q}\rho^{\mathrm{eq}}(p)\Phi(x, 0) = \rho^{\mathrm{eq}}(p)\Phi(x, 0) - \rho^{\mathrm{eq}}(p)\int dp'\rho^{\mathrm{eq}}(p')\Phi(x, 0) = 0. \tag{B.35}$$

Thus the last term in the RHS of (B.33) drops. By performing the inverse Laplace transform of both side of (B.33), one has

$$\frac{\partial v}{\partial t} = \left[A - \epsilon BF^{-1}C\right] v + \mathcal{O}(\epsilon^2) \tag{B.36}$$

Now (B.25) has been proven. □

We compute piecewise the terms appearing in the RHS of (B.25). First Av is

$$\begin{aligned} Av &= \mathcal{P}L_1\mathcal{P}\Psi(x,p,t) \\ &= \rho^{\rm eq}(p)\int dp' \left[-\frac{p'}{m}\frac{\partial}{\partial x}+\frac{\partial U}{\partial x}\frac{\partial}{\partial p'}\right]\rho^{\rm eq}(p')\Phi(x,t). \end{aligned} \tag{B.37}$$

Here we have that

$$\frac{\partial \rho^{\rm eq}(p)}{\partial p} = -\frac{\beta p}{m}\rho^{\rm eq}(p). \tag{B.38}$$

Then the integrand in the RHS of (B.37) becomes an odd function to p' and thus Av vanishes. Next we calculate $BF^{-1}Cv$. A bit lengthy but it is straightforward to show that Cv is given by

$$\begin{aligned} Cv &= \mathcal{Q}L_1\mathcal{P}\Phi(x,p,t) = (1-\mathcal{P})\,L_1\mathcal{P}\Phi = L_1\mathcal{P}\Phi - Av = L_1\mathcal{P}\Phi \\ &= -\{H,\rho^{\rm eq}(p)\Phi(x,t)\} = -\rho^{\rm eq}(p)\frac{p}{m}\left(\frac{\partial \beta U}{\partial x}+\frac{\partial}{\partial x}\right)\Phi(x,t). \end{aligned} \tag{B.39}$$

Then, we operate F^{-1} on both side of (B.39).

$$F^{-1}Cv = -F^{-1}\rho^{\rm eq}(p)\frac{p}{m}\left(\frac{\partial \beta U}{\partial x}+\frac{\partial}{\partial x}\right)\Phi(x,t). \tag{B.40}$$

$F = L_0 = \zeta(x)\left(\frac{1}{m}\frac{\partial}{\partial p}p + T\frac{\partial^2}{\partial p^2}\right)$ acts on the function of p and pass through the function of x. In (B.40) it acts on $\rho^{\rm eq}(p)p$ only. Thus we have to solve

$$F^{-1}\rho^{\rm eq}(p)p \equiv u(x,p). \tag{B.41}$$

$u(x,p)$, which satisfies

$$Fu(x,p) = p\rho^{\rm eq}(p), \tag{B.42}$$

can be found heuristically as

$$u(x,p) = -mp\rho^{\rm eq}(p)\zeta^{-1}(x). \tag{B.43}$$

Then (B.40) becomes,

$$F^{-1}Cv = p\rho^{\rm eq}(p)\zeta^{-1}(x)\left(\frac{\partial \beta U}{\partial x}+\frac{\partial}{\partial x}\right)\Phi(x,t). \tag{B.44}$$

As the final step we operate B to the both side of (B.44).

$$\begin{aligned} BF^{-1}Cv &= \mathcal{P}L_1 p\rho^{\rm eq}(p)\zeta^{-1}\left(\frac{\partial \beta U}{\partial x}+\frac{\partial}{\partial x}\right)\Phi(x,t) \\ &= \rho^{\rm eq}(p)\int dp' \left[\frac{p'}{m}\frac{\partial}{\partial x}-\frac{\partial U}{\partial x}\frac{\partial}{\partial p'}\right]p'\rho^{\rm eq}(p') \\ &\qquad \times\zeta^{-1}(x)\left(\frac{\partial \beta U}{\partial x}+\frac{\partial}{\partial x}\right)\Phi(x,t) \end{aligned} \tag{B.45}$$

Here the second term in $[\cdots]$ in the RHS of (B.45) vanishes since it is a surface term. The first term is

$$\rho^{\rm eq}(p)\frac{1}{m}\int dp' p'^2 \rho^{\rm eq}(p')\frac{\partial}{\partial x}\zeta^{-1}(x)\left(\frac{\partial \beta U}{\partial x}+\frac{\partial}{\partial x}\right)\Phi(x,t). \tag{B.46}$$

Here dp' integral is simple Gaussian integral (or equivalently the equipartition theorem)

$$\int dp' p'^2 \rho^{\rm eq}(p') = mT. \tag{B.47}$$

Thus (B.46) becomes

$$BF^{-1}Cv = \rho^{\rm eq}(p)\frac{\partial}{\partial x}\zeta^{-1}(x)\left(\frac{\partial U}{\partial x}+T\frac{\partial}{\partial x}\right)\Phi(x,t). \tag{B.48}$$

By applying (B.48) and $Av = 0$ to the RHS of (B.25) and dividing both side by $\rho^{\rm eq}(p)$ one arrives at the Smoluchowski equation.

$$\frac{\partial \Phi(x,t)}{\partial t} = \frac{\partial}{\partial x}\zeta^{-1}(x)\left(\frac{\partial U}{\partial x}+T\frac{\partial}{\partial x}\right)\Phi(x,t). \tag{B.49}$$

This is a solution of the Kramers' problem. We summarize the recipe.

1. Write down the Kramers equation for PDF for position and momentum.

2. Split the RHS of the Kramers equation into L_0 and L_1.

3. Construct the projection operator for the slow part of the motion and split the Kramers equation into the fast and slow dynamics.

4. Evaluate the formal solution of the fast dynamics up to the order of ζ^{-1} and substitute it to the dynamic equation for the slow variable.

5. Compute the pieces appearing in the dynamical equation of the slow variable.

An extension to the multi-dimensional system is straightforward. In Subsection 3.6.2 we apply the formalism to the system with the curved multi-dimensional space.

B.3 The Heuristic argument

In this section we consider a following underdamp Langevin equation with the multiplicative noise.

$$\dot{x}_i = \left(m^{-1}\right)_{ij} p_j, \tag{B.50}$$

$$\dot{p}_i = -\zeta_{ij}(x)\dot{x}_j - \frac{\partial H}{\partial x_i} + b_{ij}(x)\xi_j(t). \tag{B.51}$$

The heuristic argument presented by Hasegawa et al. [42], Sancho et al. [41] and Peters [43] states that the overdamp limit for (B.51) is taken by the following recipe. Implicitly equivalent discussion is found in Yang and Ripoll [36] for system out of equilibrium.

- $\dot{p} = 0$. This is because in the derivation of the overdamp limit taken through the FPE we need to assume the existence of stationary distribution of p. This is nothing but that in overdamp limit the momentum is already damped to its equilibrium value and its average does not evolve with time.
- $\zeta(x)$ in the Stokes' drag force is interpreted in the Stratonovich.
- $b_{ij}(x)$ in the multiplicative noise reads in the Ito sense.

We are not aware of the complete proof of this argument. Here we cite some papers which might be relevant with the justification of the heuristic argument [38, 58].

Then the overdamp limit for (B.51) becomes

$$\Delta x_i = -\left(\zeta^{-1}\right)_{ij}(x^*)\frac{\partial H}{\partial x_j}\Delta t + \left(\zeta^{-1}\right)_{ij}(x^*) b_{jk}(x(t))\Delta W_k, \tag{B.52}$$

here $x^* = \frac{1}{2}\left(x(t+\Delta t) + x(t)\right) = x(t) + \frac{1}{2}\Delta x$. Let us rewrite the friction coefficient interpreted in the Stratonovich by the Ito form, so that we can obtain multiplicative noise written in the pure Ito interpretation.

$$\begin{aligned}
\left(\zeta^{-1}\right)_{ij}(x^*) &= \left(\zeta^{-1}\right)_{ij}(x(t)) + \frac{1}{2}\frac{\partial\left(\zeta^{-1}\right)_{ij}}{\partial x_k}\Delta x_k + \mathcal{O}(\Delta x^2) \\
&= \left(\zeta^{-1}\right)_{ij}(x(t)) + \frac{1}{2}\frac{\partial\left(\zeta^{-1}\right)_{ij}}{\partial x_k}\left(\zeta^{-1}\right)_{kl}(x^*) b_{lm}(x(t))\Delta W_m \\
&\quad + \mathcal{O}(\Delta t) \\
&= \left(\zeta^{-1}\right)_{ij}(x(t)) + \frac{1}{2}\frac{\partial\left(\zeta^{-1}\right)_{ij}}{\partial x_k}\left(\zeta^{-1}\right)_{kl}(x(t)) b_{lm}(x(t))\Delta W_m \\
&\quad + \mathcal{O}(\Delta t).
\end{aligned} \tag{B.53}$$

Substituting (B.53) into (B.52) and using the formula (A.8) one arrives at the Ito-ized overdamp Langevin equation.

$$\begin{aligned}\Delta x_i &= -\left(\zeta^{-1}\right)_{ij}(x(t))\frac{\partial H}{\partial x_j}\Delta t + \left(\zeta^{-1}\right)_{ij}(x(t))b_{jk}(x(t))\Delta W_k \\ &\quad + \frac{1}{2}\frac{\partial\left(\zeta^{-1}\right)_{ij}}{\partial x_k(t)}\left(\zeta^{-1}\right)_{kl}(x(t))b_{lk}(x(t))b_{jk}(x(t))\Delta t + \mathcal{O}(\Delta t^{3/2}) \\ &= -L_{ij}\frac{\partial H}{\partial x_j}\Delta t + g_{ij}(x(t))\Delta W_j + \frac{\partial L_{ij}}{\partial x_k}\left(\boldsymbol{\zeta}\boldsymbol{D}\right)_{jk}\Delta t, \end{aligned} \tag{B.54}$$

where

$$\boldsymbol{L} \equiv \boldsymbol{\zeta}^{-1}, \quad \boldsymbol{g} \equiv \boldsymbol{L}\boldsymbol{b}, \quad \boldsymbol{D} \equiv \frac{\boldsymbol{g}\boldsymbol{g}^\dagger}{2} = \frac{\boldsymbol{\zeta}^{-1}\boldsymbol{b}\boldsymbol{b}^\dagger\boldsymbol{\zeta}^{-1}}{2}. \tag{B.55}$$

Note that the last term in (B.54) is called the Ito drift, ensuring the FDT in multiplicative system. Although the reason is unclear but the heuristic argument leads the correct overdamp Langevin equation and the result is equivalent with our (2.103) with the Ito interpretation.

Appendix C

Martin-Siggia-Rose Formalism

In this appendix we summarize method of the functional integral formalism developed by Martin, Siggia and Rose (MSR) [55, 106, 174, 175]. It maps the Langevin equation to the path integral formalism and enable us to perform a systematic perturbation developed in the field theory.

C.1 1 Dimensional case

Consider the following one-dimensional Langevin equation.

$$\dot{x} = a(x) + b(x)\xi(t). \tag{C.1}$$

Here $\xi(t)$ is a Gaussian white noise and satisfies $\langle \xi(t) \rangle = 0$ and $\langle \xi(t)\xi(t') \rangle = \delta(t-t')$. Since the noise term is multiplicative, (C.1) is never defined uniquely unless the interpretation of the multiplicative noise is given. To this end we discretize (C.1) with time increment Δt.

$$\Delta x = x(t + \Delta t) - x(t) = a(x(t))\Delta t + b(x^*)\Delta W \tag{C.2}$$

We employ the general α-convention introduced in Appendix A.1. Thus x^* is defined by

$$x^* = \alpha x(t + \Delta t) + (1 - \alpha)x(t), \tag{C.3}$$

$0 \leq \alpha \leq 1$ is a real parameter and $\alpha = 0$ and $\alpha = 1/2$ respectively corresponds to the Ito and the Stratonovich interpretation.

$$\Delta W \equiv \int_t^{t+\Delta t} ds\xi(s). \tag{C.4}$$

is the discretized Wiener process. A conditional probability that the stochastic variable x takes the value X at $t + \Delta t$ under the condition that x took

X_0 at time t is defined as

$$\Phi(X, t+\Delta t|X_0, t) = \langle \delta(X - x(t+\Delta t)) \rangle_{X_0(t)}. \tag{C.5}$$

Here $\langle \cdots \rangle_{X_0(t)}$ denotes the conditional average under the condition that x took X_0 at time t. By substituting (C.2) into (C.5) one has

$$\Phi(X, t+\Delta t|X_0, t) = \langle \delta\left(X - X_0 - a(X_0)\Delta t - b(x^*)\Delta W\right) \rangle_{X_0(t)}. \tag{C.6}$$

We expand $b(x^*)$ around X_0 as,

$$\begin{aligned} b(x^*) &= b(X_0 + \alpha\Delta x) = b(X_0) + \alpha b'(X_0)\Delta x + \cdots \\ &= b(X_0) + \alpha b'(X_0)b(X_0)\Delta W + \mathcal{O}(\Delta t). \end{aligned} \tag{C.7}$$

Here $'$ denotes the differentiation with respect to x. By substituting (C.7) into (C.6) one has

$$\begin{aligned} \Phi(X, t+\Delta t|X_0, t) &= \langle \delta\left(X - X_0 - a(X_0)\Delta t - b(X_0)\Delta W \right. \\ &\quad \left. -\alpha b'(X_0)b(X_0)\Delta W^2 + \mathcal{O}(\Delta t^{3/2})\right) \rangle_{X_0(t)}. \end{aligned} \tag{C.8}$$

We use the Fourier representation of the delta function: $\delta(x) = \int \frac{dq}{2\pi} \mathrm{e}^{-iqx}$. Then,

$$\begin{aligned} \Phi(X, t+\Delta t|X_0, t) &= \left\langle \int \frac{d\hat{X}}{2\pi} \exp\left\{ -i\hat{X}\left[X - X_0 - a(X_0)\Delta t \right.\right.\right. \\ &\quad \left.\left.\left. -\alpha b' b(X_0)\Delta W^2 - b(X_0)\Delta W + \mathcal{O}(\Delta t^{3/2})\right]\right\} \right\rangle_{X_0(t)} \\ &= \int \frac{d\hat{X}}{2\pi} \exp\left\{ -i\hat{X}\left[X - X_0 - a(X_0)\Delta t\right]\right\} \\ &\quad \times \left\langle \exp\left[i\hat{X}\alpha b' b(X_0)\Delta W^2 + i\hat{X} b(X_0)\Delta W \right] \right\rangle_{X_0(t)}. \end{aligned} \tag{C.9}$$

One can carry out an average over noise appearing on the last line of (C.9) thanks to the Gaussian nature of ΔW.

$$\begin{aligned} \left\langle \exp\left[\alpha b' b(X_0)\Delta W^2 + b(X_0)\Delta W\right] \right\rangle_{X_0(t)} &= \\ \exp\left[\left(2i\hat{X}\alpha T b' b(X_0) + T(i\hat{X})^2 b^2(X_0) \right) \Delta t \right]. \end{aligned} \tag{C.10}$$

Applying (C.10) to (C.9),

$$\begin{aligned} \Phi(X, t+\Delta t|X_0, t) &= \\ \int \frac{d\hat{X}}{2\pi} \exp\left\{ \Delta t \left[-i\hat{X}\left(\frac{X - X_0}{\Delta t} - a(X_0) - 2\alpha T b' b(X_0) \right) \right.\right. \\ \left.\left. + T\left(i\hat{X}\right)^2 b^2(X_0) \right] \right\}. \end{aligned} \tag{C.11}$$

Since the noise correlation time is zero, the conditional probability $\Phi(X, t + \Delta t|X_0, t)$ depends only on X and X_0, and does not depend on the past value of the field. Such stochastic process is called the Markovian. For Markovian stochastic process the conditional probability obeys the following Chapman-Kolmogorov equation.

$$\Phi(X_f, t_f|X_0, t_0) = \int dX_{N-1} \cdots dX_1 \prod_{n=1}^{N} \Phi(X_n, t_n|X_{n-1}, t_{n-1}). \tag{C.12}$$

Plugging (C.11) with (C.12) and taking $\Delta t \to 0$ limit, one arrives at

$$\Phi(X_f, t_f|X_0, t_0) = \int_{X_0}^{X_f} \mathcal{D}X \int \mathcal{D}\hat{X} \exp\left[S[X, \hat{X}]\right]. \tag{C.13}$$

Here $\mathcal{D}X = \lim_{N\to\infty} dX_{N-1} \cdots dX_1$ represents the path integral. We defined the MSR action $S\left[X, \hat{X}\right]$ as

$$S\left[X, \hat{X}\right] = \int_{t_0}^{t_f} dt \left\{-i\hat{X}(t)\left[\dot{X} - a(X) - 2\alpha T b' b(X)\right] + T\left(i\hat{X}\right)^2 b^2(X)\right\}. \tag{C.14}$$

C.2 Multi-dimensional case

We note the result on multi-dimensional case. The Langevin equation is supposed to be given by

$$(\alpha) \quad \dot{x}_i = a_i(x) + b_{ij}(x^*, t)\xi_j(t). \tag{C.15}$$

Here (α) stands for general α-convention of the multiplicative noise. The MSR action $S[\boldsymbol{X}, \hat{\boldsymbol{X}}]$ is given by,

$$\begin{aligned} S[\boldsymbol{X}, \hat{\boldsymbol{X}}] \;=\; & \int_{t_0}^{t_f} dt \left[-i\hat{X}_i(t)\left(\dot{X}_i(t) - a_i(X) - 2\alpha T \frac{\partial b_{ij}}{\partial X_k} b_{kj}\right)\right. \\ & \left. + T i\hat{X}_i(t) i\hat{X}_j(t) b_{ik}(t) b_{jl}(t)\right] \end{aligned} \tag{C.16}$$

For the Brownian motion with the state-dependent Onsager coefficient given by (2.101) the MSR action is given by

$$S = \int_{t_0}^{t_f} dt \left[-i\hat{X}_i\left(\dot{X}_i(t) + L_{ij}(X)\frac{\partial U}{\partial X_j} - k_B T \frac{\partial L_{ij}}{\partial X_j}\right) + k_B T i\hat{X}_i L_{ij} i\hat{X}_j\right] \tag{C.17}$$

which does not depend on α, as it should be.

Appendix D

Fundamental Measure Density Functional Theory for Asakura-Oosawa Model

This is a brief note on the static structure of the Asakura-Oosawa (AO) model system [147] within the fundamental measure density functional theory (FMDFT) [172, 176]. The AO model is a model system of colloid-polymer mixture. The polymers are idealized as they do not interact each other, but has repulsive core with respect to the colloidal particles.

$$V_{cc}(r) = \begin{cases} 0 & r > \sigma_c \\ \infty & r < \sigma_c \end{cases}, \quad V_{cp}(r) = \begin{cases} 0 & r > (\sigma_c + \sigma_p)/2 \\ \infty & r < (\sigma_c + \sigma_p)/2 \end{cases}, \quad V_{pp}(r) = 0. \tag{D.1}$$

Here subscript c and p stand for colloid and polymer, respectively. $\sigma_\alpha (\alpha = c, p)$ is the interaction diameter of species α.

The AO system is uniquely determined by 3 parameters, i.e., packing fraction of the colloidal particle: ϕ_c, packing fraction of the polymer: ϕ_p and size ratio between colloid and polymer: $\delta = \sigma_p/\sigma_c$. Other quantities are extracted from these parameters. For example, total packing fraction $\phi = \phi_c + \phi_p$, number density of each species $\rho_\alpha = 6\phi_\alpha/(\pi\sigma_\alpha^3)$, number ratio of each particle $x_\alpha = \rho_\alpha/(\rho_c + \rho_p)$. We set the diameter of the colloidal particle as unity.

The FMDFT provides an approximation to the direct correlation function of liquids as,

$$c_{ij}(q) = \sum_{\nu,\mu} \left. \frac{\partial^2 \Phi}{\partial n_\nu^\alpha \partial n_\lambda^\beta} \right|_0 w_\nu^\alpha(\boldsymbol{q}) w_\lambda^\beta(-\boldsymbol{q}). \tag{D.2}$$

Here subscript $\nu, \lambda = 0, 1, 2, 3, v1, v2$ stands for "fundamental measure" and

ws, called the weight functions are give by

$$\begin{aligned} w_0^\alpha(q) &= j_0(qR_\alpha), & w_1^\alpha(q) &= R_\alpha j_0(qR_\alpha), \\ w_2^\alpha(q) &= 4\pi R_\alpha^2 j_0(qR_\alpha), & \boldsymbol{w}_{\mathrm{v}1}^\alpha(\boldsymbol{q}) &= R_\alpha \mathrm{i}\hat{\boldsymbol{q}} j_1(qR_\alpha), \\ \boldsymbol{w}_{\mathrm{v}2}^\alpha(\boldsymbol{q}) &= 4\pi R_\alpha^2 \mathrm{i}\hat{\boldsymbol{q}} j_1(qR_\alpha), & w_3^\alpha(q) &= 4\pi R_\alpha^3 \frac{j_1(qR_\alpha)}{qR_\alpha}. \end{aligned} \tag{D.3}$$

where $R_\alpha = \sigma_\alpha/2$ is radius of species α and $\hat{\boldsymbol{q}} = \boldsymbol{q}/q$. j_0 and j_1 are the 0th and 1st order spherical Bessel functions, respectively, which are defined as

$$j_0(x) = \frac{\sin(x)}{x}, \quad j_1(x) = -\frac{1}{x}\left(\cos(x) - \frac{\sin(x)}{x}\right). \tag{D.4}$$

The weighed density n is defined by

$$n_\nu^\alpha(\boldsymbol{x}) = \int d^3\boldsymbol{r} \rho_\alpha^{(1)}(\boldsymbol{r}) w_\nu^\alpha(\boldsymbol{x} - \boldsymbol{r}). \tag{D.5}$$

Subscript 0 in (D.2) means the derivatives at the homogeneous state: $\rho_\alpha(r) = \rho_\alpha$. In the homogeneous state the weighed densities becomes

$$\langle n_0^\alpha \rangle = \rho_\alpha, \quad \langle n_1^\alpha \rangle = R_\alpha \rho_\alpha, \quad \langle n_2^\alpha \rangle = 4\pi R_\alpha^2 \rho_\alpha, \tag{D.6}$$

$$\langle \boldsymbol{n}_{\mathrm{v}1}^\alpha \rangle = \langle \boldsymbol{n}_{\mathrm{v}2}^\alpha \rangle = 0, \quad \langle n_3^\alpha \rangle = \phi_\alpha. \tag{D.7}$$

Φ is the excess free energy density functional given by

$$\Phi = \Phi_1 + \Phi_2 + \Phi_3, \tag{D.8}$$

$$\Phi_1 = n_0^c \left[-\ln(1 - n_3^c + \frac{n_3^p}{1 - n_3^c}) \right] - n_0^p \ln(1 - n_3^c), \tag{D.9}$$

$$\begin{aligned} \Phi_2 = {} & (n_1^c n_2^c - \boldsymbol{n}_{v1}^c \cdot \mathbf{n}_{v2}^c) \left[\frac{1}{1 - n_3^c} + \frac{2n_3^p}{(1 - n_3^c)^2} \right] \\ & + \frac{n_1^p n_2^c - \boldsymbol{n}_{v1}^p \boldsymbol{n}_{v2}^c + n_1^c n_2^p - \mathbf{n}_{v1}^c \boldsymbol{n}_{v2}^p}{1 - n_3^c}, \end{aligned} \tag{D.10}$$

$$\begin{aligned} \Phi_3 = {} & \frac{(n_2^c)^3/3 - n_2^c (\mathbf{n}_{v2}^c)^2}{8\pi} \left[\frac{1}{1 - n_3^c} + \frac{2n_3^p}{(1 - n_3^c)^2} \right] \\ & + \frac{(n_2^c)^2 n_2^p - n_2^p (\boldsymbol{n}_{v2})^2 - 2n_2^c \mathbf{n}_{v2}^c \cdot \boldsymbol{n}_{v2}^p}{8\pi(1 - n_3^c)} \end{aligned} \tag{D.11}$$

We omit the q dependence of these quantities for brevity. The direct correlation function $\boldsymbol{c}$ is obtained by performing the derivatives in (D.2) and

substituting the homogeneous values (D.7). We shall write them all for note. Abbreviating $\left.\frac{\partial^2\Phi}{\partial n_\nu^\alpha \partial n_\lambda^\beta}\right|_0 = \Phi_{\nu\lambda}^{\alpha\beta}$, the nonzero and independent elements are,

$$\Phi_{03}^{cc} = \frac{1}{1-n_3^c}\left[1+\frac{n_3^p}{1-n_3^c}\right], \tag{D.12}$$

$$\Phi_{03}^{cp} = \frac{1}{1-n_3^c}, \tag{D.13}$$

$$\Phi_{13}^{cc} = \frac{1}{(1-n_3^c)^2}\left[n_2^c+n_2^p+\frac{2n_3^p}{1-n_3^c}\right], \tag{D.14}$$

$$\Phi_{13}^{cp} = \frac{n_2^c}{(1-n_3^c)^2}, \tag{D.15}$$

$$\begin{aligned}\Phi_{23}^{cc} = {} & n_1^c\left[\frac{1}{(1-n_3^c)^2}+\frac{2n_3^p}{(1-n_3^c)^3}\right]+\frac{n_1^p}{(1-n_3^c)^2} \\ & +\frac{(n_2^c)^2}{4\pi}\left[\frac{1}{(1-n_3^c)^3}+\frac{3n_3^p}{(1-n_3^c)^4}\right]+\frac{n_2^c n_2^p}{2\pi(1-n_3^c)^3},\end{aligned} \tag{D.16}$$

$$\Phi_{23}^{cp} = \frac{n_1^c}{(1-n_3^c)^2}+\frac{(n_2^c)^2}{4\pi(1-n_3^c)^3}, \tag{D.17}$$

$$\begin{aligned}\Phi_{33}^{cc} = {} & n_0\left[\frac{1}{(1-n_3^c)^2}+\frac{2n_3^p}{(1-n_3^c)^3}\right]+\frac{n_0^p}{(1-n_3^c)^2} \\ & +2n_1^c n_2^c\left[\frac{1}{(1-n_3^c)^3}+\frac{3n_3^p}{(1-n_3^c)^4}\right]+2\frac{n_1^p n_2^c+n_1^c n_2^p}{(1-n_3^c)^3} \\ & +\frac{(n_2^c)^3}{4\pi}\left[\frac{1}{(1-n_3^c)^4}+\frac{4n_3^p}{(1-n_3^c)^5}\right]+\frac{3(n_2^c)^2 n_2^p}{4\pi(1-n_3^c)^4},\end{aligned} \tag{D.18}$$

$$\Phi_{33}^{cp} = \frac{n_0^c}{(1-n_3^c)^2}+\frac{2n_1^c n_2^c}{(1-n_3^c)^3}+\frac{(n_2^c)^3}{4\pi(1-n_3^c)^4}, \tag{D.19}$$

$$\Phi_{v1v2}^{cc} = -\left[\frac{1}{1-n_3^c}+\frac{n_3^p}{(1-n_3^c)^2}\right] = -\Phi_{12}^{cc}, \tag{D.20}$$

$$\Phi_{v1v2}^{cp} = -\frac{1}{1-n_3^c} = -\Phi_{12}^{cp}, \tag{D.21}$$

$$\Phi_{v2v2}^{cc} = -\frac{n_2^c}{4\pi}\left[\frac{1}{(1-n_3^c)^2}+\frac{2n_3^p}{(1-n_3^c)^3}\right]-\frac{n_2^p}{4\pi(1-n_3^c)^2} = -\Phi_{22}^{cc}, \tag{D.22}$$

$$\Phi_{v2v2}^{cp} = -\frac{n_2^c}{4\pi(1-n_3^c)^2} = -\Phi_{22}^{cp}. \tag{D.23}$$

Here obeys the symmetry $\Phi_{\nu\lambda}^{\alpha\beta} = \Phi_{\lambda\nu}^{\alpha\beta}$ and $\Phi_{\nu\lambda}^{\alpha\beta} = \Phi_{\nu\lambda}^{\beta\alpha}$ thus we do not write down these dependent elements. And all other components are zero. One obtains $c_{\alpha\beta}(q)$ by substituting (D.12)–(D.23) and (D.3) into (D.2). The static

structure factor is obtained by making use of the Ornstain-Zernike equation,

$$[S^{-1}]_{ij}(q) = \delta_{ij} - \sqrt{\rho_i \rho_j} c_{ij}(q). \tag{D.24}$$

The static structure factor obtained within the FMDFT for the AO model is plotted in Figure 5.16 of Chapter 5.

Appendix E

Bengtzelius' trick

In this appendix we describe a method to compute the memory function in MCT in an efficient manner. The method is called the Bengtzelius' trick [165]. The trick reduces the computational load in evaluating the memory function for each q, from $\mathcal{O}(N_q^2)$ to $\mathcal{O}(N_q)$, where N_q is the number of grids.

E.1 Monodisperse case

We consider the long time limit of MCT for monodisperse liquid.

$$S(q) - F(q) = (S^{-1}(q) + M[F, F](q))^{-1}. \tag{E.1}$$

Here memory function M is defined as

$$M[F, F](q) = \frac{1}{2\rho q^2} \int \frac{d^3\boldsymbol{k}}{(2\pi)^3} V_{\boldsymbol{qkp}}^2 F_k F_p. \tag{E.2}$$

The vertex function $V_{\boldsymbol{qkp}}$ is

$$V_{\boldsymbol{qkp}} = \hat{\boldsymbol{q}} \cdot \boldsymbol{k} \rho c(k) + \hat{\boldsymbol{q}} \cdot \boldsymbol{p} \rho c(p), \tag{E.3}$$

here $\hat{\boldsymbol{q}} = \boldsymbol{q}/q$, $\boldsymbol{p} = \boldsymbol{q} - \boldsymbol{k}$ and $c(q)$ is the direct correlation function obeys the Ornstein-Zernike equation.

$$S^{-1}(q) = 1 - \rho c(q). \tag{E.4}$$

By using the rotational invariance of the integrand in (E.2) one can carry out the azimuthal integration (See left panel of Figure E.1.). Further by using the law of cosine,

$$\boldsymbol{q} \cdot \boldsymbol{k} = \frac{q^2 + k^2 - p^2}{2}, \quad \boldsymbol{q} \cdot \boldsymbol{p} = \frac{q^2 + p^2 - k^2}{2}, \tag{E.5}$$

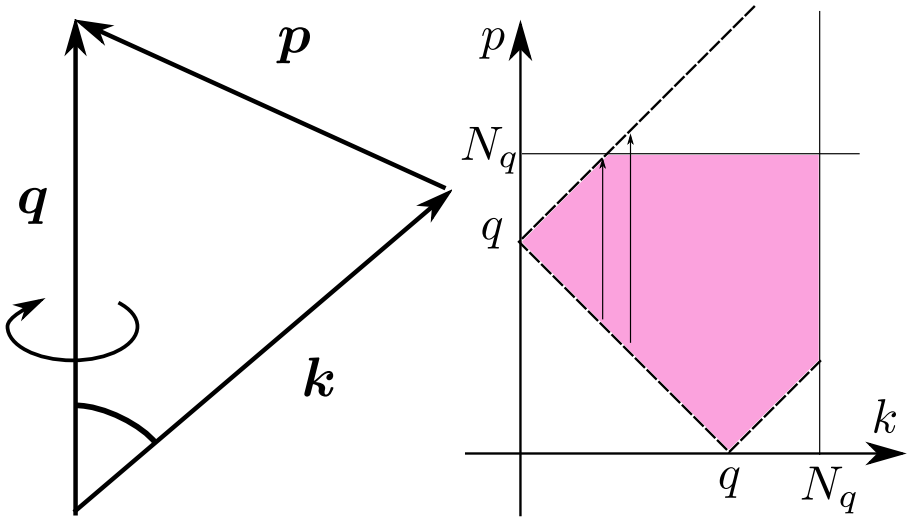

Figure E.1: Left: relation between $\boldsymbol{q}, \boldsymbol{k}, \boldsymbol{p}$. Right: Schematic picture for sum over p.

and

$$\int \frac{d^3\boldsymbol{k}}{(2\pi)^3} = \frac{1}{q}\int_0^\infty \frac{kdk}{2\pi}\int_{|q-k|}^{q+k}\frac{pdp}{2\pi}. \tag{E.6}$$

Thus

$$M[F,F] = \frac{1}{32\pi^2\rho q^2}\int_0^\infty dk\int_{|q-k|}^{q+k} dp\frac{kp}{q^3}V_{qkp}^2 F_k F_p. \tag{E.7}$$

The integrand can be decomposed into the multiple of the functions of k and q, p as,

$$\frac{kp}{q^3}V_{qkp}^2 \;=\; \sum_{n=1}^{9} a_k^{(n)} b_{q,p}^{(n)}, \tag{E.8}$$

where,

$$\begin{aligned}
a_k^{(1)} &= k^5\tilde{c}_k^2, & a_k^{(2)} &= 2k^3\tilde{c}_k^2, & a_k^{(3)} &= k\tilde{c}_k^2, \\
a_k^{(4)} &= 2k\tilde{c}_k, & a_k^{(5)} &= 4k^3\tilde{c}_k, & a_k^{(6)} &= -2k^5\tilde{c}_k, \\
a_k^{(7)} &= k^5, & a_k^{(8)} &= -2k^3, & a_k^{(9)} &= k.
\end{aligned} \tag{E.9}$$

$$\begin{aligned}
b_{q,p}^{(1)} &= q^{-3}p, & b_{q,p}^{(2)} &= q^{-3}p(q^2-p^2), & b_{q,p}^{(3)} &= q^{-3}p(q^2-p^2)^2, \\
b_{q,p}^{(4)} &= q^{-3}p(q^4-p^4)\tilde{c}_p, & b_{q,p}^{(5)} &= q^{-3}p^3\tilde{c}_p, & b_{q,p}^{(6)} &= q^{-3}p\tilde{c}_p, \\
b_{q,p}^{(7)} &= q^{-3}p\tilde{c}_p^2, & b_{q,p}^{(8)} &= q^{-3}p(q^2+p^2)\tilde{c}_p^2, & b_{q,p}^{(9)} &= q^{-3}p(q^2+p^2)^2\tilde{c}_p^2.
\end{aligned} \tag{E.10}$$

Then $M[A,B]$ can be evaluated by

$$M[A,B] = \frac{1}{32\pi^2\rho q^2}\sum_{n=1}^{9}\int_0^\infty dk a_k^{(n)} A_k \int_{|q-k|}^{q+k} dp b_{q,p}^{(n)} B_p. \tag{E.11}$$

By discretizing wave number integral on equidistant N_q grid points

$$M[A,B] = \frac{\Delta q^2}{32\pi^2\rho q^2}\sum_{n=1}^{9}\sum_{i_k=0}^{N_q-1} a_k^{(n)} A_k Z_{q,k}, \tag{E.12}$$

$$Z_{q,k}^{(n)} \equiv \sum_{i_p=|i_q-i_k|}^{i_q+i_k} b_{qp}^{(n)} B_p. \tag{E.13}$$

Z_{qk} can be evaluated in a recursive manner (See the right panel of Figure E.1)

$$Z_{q,0} = b_{q,q}^{(n)} B_q, \tag{E.14}$$

$$Z_{q,k} = Z_{q,k-1} + b_{q,q+k}^{(n)} B_{q+k} \begin{cases} +b_{q,q-k}^{(n)} B_{q-k} & (i_q \geq i_k) \\ -b_{q,k-q-1}^{(n)} B_{k-q-1} & (i_q < i_k) \end{cases}. \tag{E.15}$$

Thus the computation on sum over p can be carried out with $\mathcal{O}(1)$ computational load.

E.2 Multicomponent case

Before going into the Bengzelius' trick for binary MCT we transform the binary MCT described in Subsection 5.2.2 as follows. We define a hatted density correlation function as

$$\hat{\boldsymbol{\Phi}} \equiv \boldsymbol{X}^{-1/2}\boldsymbol{\Phi}\boldsymbol{X}^{-1/2}, \tag{E.16}$$

here $\boldsymbol{X}^{-1/2}$ is

$$\boldsymbol{X}^{-1/2} \equiv \begin{pmatrix} x_1^{-1/2} & 0 \\ 0 & x_2^{-1/2} \end{pmatrix}, \tag{E.17}$$

here x_α is mole fraction of species α. The memory function and the vertex function is transformed as,

$$\hat{M}_{\alpha\beta}(q) = \frac{1}{2\rho q^2}\int \frac{d^3\boldsymbol{k}}{(2\pi)^3}\hat{V}_{\alpha\alpha'\alpha''}^{\boldsymbol{qkp}}\hat{V}_{\beta\beta'\beta''}^{\boldsymbol{qkp}}\hat{\Phi}_{\alpha'\beta'}(k)\hat{\Phi}_{\alpha''\beta''}(p), \tag{E.18}$$

where $\boldsymbol{p} = \boldsymbol{q} - \boldsymbol{k}$ and $\hat{V}$ is

$$\hat{V}^{\boldsymbol{qkp}}_{\alpha\alpha'\alpha''} \equiv \hat{\boldsymbol{q}} \cdot \boldsymbol{k} \rho c_{\alpha\alpha'}(k) x^{1/2}_{\alpha'} \delta_{\alpha\alpha''} + \hat{\boldsymbol{q}} \cdot \boldsymbol{p} \rho c_{\alpha\alpha''}(p) x^{1/2}_{\alpha''} \delta_{\alpha\alpha'}. \tag{E.19}$$

Now one can see that the memory function is not singular at $x_S = 0$ or $x_L = 0$ (Cf. (5.8)). With these hatted quantities the dynamic equation of the binary MCT becomes

$$\hat{\boldsymbol{\tau}}^0_q \frac{\partial \hat{\boldsymbol{\Phi}}(q,t)}{\partial t} + \hat{\boldsymbol{S}}^{-1}(q) \hat{\boldsymbol{\Phi}}(q,t) + \int_0^t du \hat{\boldsymbol{M}}(t-u) \frac{\partial \hat{\boldsymbol{\Phi}}(q,u)}{\partial u} = 0, \tag{E.20}$$

where $\hat{\boldsymbol{\tau}}^0_q = \boldsymbol{X}^{1/2} \boldsymbol{\tau}^0_q \boldsymbol{X}^{1/2}$. Then the Debye-Waller factor $\boldsymbol{F}(q) \equiv \lim_{t\to\infty} \boldsymbol{\Phi}(q,t)$ satisfies

$$\hat{\boldsymbol{F}}(q) = \hat{\boldsymbol{S}}(q) - \left[\hat{\boldsymbol{S}}^{-1}(q) + \hat{\mathbf{M}}[\boldsymbol{F}](q) \right]^{-1}. \tag{E.21}$$

By the law of cosines (see Figure E.1), we have

$$\boldsymbol{q} \cdot \boldsymbol{k} = \frac{q^2 + k^2 - p^2}{2}, \quad \boldsymbol{q} \cdot \boldsymbol{p} = \frac{q^2 + p^2 - k^2}{2}. \tag{E.22}$$

Then one can integrate over the azimuthal angle of $\boldsymbol{k}$ since integrand is only dependent of p and k and one can transform integral as

$$\int \frac{d^3\boldsymbol{k}}{(2\pi)^3} = \frac{1}{q} \int_0^\infty \frac{kdk}{2\pi} \int_{|q-k|}^{q+k} \frac{pdp}{2\pi} \tag{E.23}$$

By substituting (E.22) into (E.19) and carrying out angular integral as (E.23) one has

$$\hat{M}_{\alpha\beta}(q) = \frac{1}{32\pi^2 \rho q^5} \int_0^\infty dk \int_{|q-k|}^{q+k} dp k p \tilde{V}^{qkp}_{\alpha\alpha'\alpha''} \tilde{V}^{qkp}_{\beta\beta'\beta''} \hat{\Phi}_{\alpha'\beta'}(k) \hat{\Phi}_{\alpha''\beta''}(p), \tag{E.24}$$

$$\tilde{V}^{qkp}_{\alpha\alpha'\alpha''} \equiv (q^2 + k^2 - p^2) \tilde{c}_{\alpha\alpha'} \delta_{\alpha\alpha''} + (q^2 + p^2 - k^2) \tilde{c}_{\alpha\alpha''} \delta_{\alpha\alpha'}, \tag{E.25}$$

$$\tilde{c}_{\alpha\beta}(k) \equiv \rho c_{\alpha\beta} x^{1/2}_\beta. \tag{E.26}$$

Since naive implementation of (E.24) for each q on N_q equidistant grid points yields $\mathcal{O}(N^2)$ computational load which dominates almost all of the computational time in analyzing the MCT. But as seen below sum over p can be reduced to $\mathcal{O}(1)$ by the Bengtzelius' trick [165]. First step of the Bengzelius' trick is decoupling of the sum over k and p. One sees that (complicated but straightforward)

$$\begin{aligned} M_{\alpha\beta}(q) = \frac{1}{16\pi^2 \rho q^5} \sum_{n=1}^{3} \Bigg[& \int_0^\infty dk a^{(n)}_{\alpha\gamma\beta\delta}(k) \hat{\Phi}_{\gamma\delta}(k) \int_{|q-k|}^{q+k} dp b^{(n)}(q,p) \hat{\Phi}_{\alpha\beta}(p) \\ & + \int_0^\infty dk c^{(n)}_{\alpha\gamma}(k) \hat{\Phi}_{\gamma\beta}(k) \int_{|q-k|}^{q+k} dp d^{(n)}_{\beta\delta}(q,p) \hat{\Phi}_{\alpha\delta}(p) \Bigg], \end{aligned} \tag{E.27}$$

where,

$$a^{(1)}_{\alpha\beta\gamma\delta}(k) = k^5\tilde{c}_{\alpha\beta}(k)\tilde{c}_{\gamma\delta}(k), \quad a^{(2)}_{\alpha\beta\gamma\delta}(k) = 2k^3\tilde{c}_{\alpha\beta}(k)\tilde{c}_{\gamma\delta}(k), \quad a^{(3)}_{\alpha\beta\gamma\delta}(k) = k\tilde{c}_{\alpha\beta}(k)\tilde{c}_{\gamma\delta}(k)$$
$$b^{(1)}(q,p) = p, \qquad b^{(2)}(q,p) = p(q^2-p^2), \qquad b^{(3)}(q,p) = p(q^2-p^2)^2$$
$$c^{(1)}_{\alpha\beta}(k) = k\tilde{c}_{\alpha\beta}(k), \qquad c^{(2)}_{\alpha\beta}(k) = -k^5\tilde{c}_{\alpha\beta}(k), \qquad c^{(3)}_{\alpha\beta}(k) = 2k^3\tilde{c}_{\alpha\beta}(k)$$
$$d^{(1)}_{\alpha\beta}(q,p) = p(q^4-p^4)\tilde{c}_{\alpha\beta}(p), \qquad d^{(2)}_{\alpha\beta}(q,p) = p\tilde{c}_{\alpha\beta}(p), \qquad d^{(3)}_{\alpha\beta}(q,p) = p^3\tilde{c}_{\alpha\beta}(p).$$

Then one discretize the sum over k and p on N_q grid points with distance Δq:

$$q = q_i = \Delta q\bar{i}_q, \quad \bar{i}_q = i_q + \hat{o}, \quad i_q = 0, 1, \ldots, N-1 \tag{E.28}$$

where offset $0 < \hat{o} < 1$ is introduced in order to avoid $q = 0$ singularity in $\hat{M}_{\alpha\beta}(q)$. In binary MCT such infrared divergence takes place while in one-component case there exists a finite $q = 0$ limit.

$$\hat{M}^{i_q}_{\alpha\beta} = \frac{\Delta q^3}{16\pi^2\rho\bar{i}_q^5}\sum_{n=1}^{3}\left[\sum_{i_k=0}^{N_q} a^{(n)}_{\alpha\gamma\beta\delta}(\bar{i}_k)\hat{\Phi}_{\gamma\delta}(\bar{i}_k)\sum_{i_p=|i_q-i_k|}^{i_q+i_k} b^{(n)}(\bar{i}_q,\bar{i}_p)\hat{\Phi}_{\alpha\beta}(\bar{i}_p)\right.$$
$$\left. + \sum_{i_k=0}^{N_q} c^{(n)}_{\alpha\gamma}(\bar{i}_k)\hat{\Phi}_{\gamma\beta}(\bar{i}_k)\sum_{i_p=|i_q-i_k|}^{i_q+i_k} d^{(n)}_{\beta\delta}(\bar{i}_q,\bar{i}_p)\hat{\Phi}_{\alpha\delta}(\bar{i}_p)\right] \tag{E.29}$$

Now we arrive at the most important part of the Bengtzelius' trick. Sum over i_p can be evaluated recursively (See Figure E.1).

$$Z_k(q) \equiv \sum_{p=q-k}^{q+k} w_p = Z_{k-1}(q) + w_{q+k} + \begin{cases} w_{q-k} & q \geq k \\ -w_{k-q-1} & q < k \end{cases}, \tag{E.30}$$
$$Z_0(q) = w_q, \tag{E.31}$$

with w_p being either of $b^{(n)}(\bar{i}_q,\bar{i}_p)\hat{\Phi}_{\alpha\beta}(\bar{i}_p)$ or $d^{(n)}_{\beta\delta}(\bar{i}_q,\bar{i}_p)\hat{\Phi}_{\alpha\delta}(\bar{i}_p)$. Then the sum over p can be evaluated within $\mathcal{O}(1)$ computational load. Put

$$A^{(n)}_{\alpha\beta}(k) \equiv a^{(n)}_{\alpha\gamma\beta\delta}(\bar{i}_k)\hat{\Phi}_{\gamma\delta}(\bar{i}_k), \quad B^{(n)}_{\alpha\beta}(k) \equiv \sum_{i_p=|i_q-i_k|}^{i_q+i_k} b^{(n)}(\bar{i}_q,\bar{i}_p)\hat{\Phi}_{\alpha\beta}(\bar{i}_p), \tag{E.32}$$

$$C^{(n)}_{\alpha\beta}(k) \equiv c^{(n)}_{\alpha\gamma}(\bar{i}_k)\hat{\Phi}_{\gamma\beta}(\bar{i}_k), \quad D^{(n)}_{\alpha\beta}(k) \equiv \sum_{i_p=|i_q-i_k|}^{i_q+i_k} d^{(n)}_{\beta\delta}(\bar{i}_q,\bar{i}_p)\hat{\Phi}_{\alpha\delta}(\bar{i}_p). \tag{E.33}$$

Then the memory function becomes

$$M^{i_q}_{\alpha\beta} = \frac{\Delta q^3}{16\pi^2\rho\bar{i}_q^5}\sum_{n=1}^{3}\sum_{i_k=0}^{N_q}\left[A^{(n)}_{\alpha\beta}(k)B^{(n)}_{\alpha\beta}(k) + C^{(n)}_{\alpha\beta}(k)D^{(n)}_{\alpha\beta}(k)\right]. \tag{E.34}$$

Sum over k and p is reduced from $\mathcal{O}(N_q^2)$ to $\mathcal{O}(N_q)$.