

Chapter 2. THEORIES OF GLASS TRANSITION AND SLOW DYNAMICS

The volume and enthalpy of glass-forming liquids are continuous function of temperature even in the supercooled-glass transition region. However, their temperature derivative, thermal expansion coefficient and the specific heat, change in a discontinuous manner at T_g . The relaxation properties such as relaxation time and viscosity have features of gradual transition at T_g . The explanation of this gradual transition from liquid-like to solid-like properties is very complex and still not well understood and remains as an open problem.

This glass transition is ascribed to the slowing down which is caused by the increase of the density of molecular packing and the reduction of the thermal energy which occurs during the cooling. The geometrical aspect of molecular rearrangement in a densely packed state made an appearance of the concept of cooperativity which is advocated by Adam and Gibbs [9]. It means that the molecular rearrangement occurs by cooperative movement in an extended region than by independent motion of individual molecules. This cooperative region is known as cooperatively rearranging regions (CRR), domain, cluster or spatial heterogeneity.

The basics of several theories or models will be introduced in this chapter with relation to the cooperativity and slow dynamics.

2.1 Free volume theory

Fox and Flory first postulated that the liquid-glass transition resulted from the decrease of the free volume of the amorphous phase below some critical value v_c [27]. The subsequent derivation of Doolittle's fluidity equation [28] within the free volume theory is based on four simple assumptions [7] which can be summarized as follows:

- 1) It is possible to associate a local volume v of molecular scale with each other.
- 2) When v reaches some critical value v_0 , the excess can be regarded as free.
- 3) Molecular transport occurs only when voids have volume greater than some critical value v^* formed by the redistribution of the free volume.
- 4) No energy is required for free volume distribution.

From these assumptions, the Vogel-Tammann-Fulcher (VTF) law was first derived from the free volume assumption in 1959 and has been developed for the glass transition problem [7].

2.1.1 Vogel-Tammann-Fulcher (VTF) law

The free volume v_f can be defined by,

$$v_f = \langle v \rangle - v_0, \quad (2.1)$$

where $\langle v \rangle$ is the average volume per molecule in the liquid and v_0 is the constant molecular volume which is independent of temperature. For the system with N molecules of total volume V , the average free volume fraction f to total volume is given by,

$$f = \frac{V_f}{V} = \frac{Nv_f}{V}, \quad (2.2)$$

where V_f is the total free volume.

It is assumed that the free volume fraction has a linear temperature dependence above the glass transition temperature T_g ,

$$f = f_g + \alpha_f(T - T_g), \quad (2.3)$$

where α_f is the difference between the thermal expansion coefficients of the liquid and glass.

From the assumption 3), the diffusion coefficient D is proportional to the fraction of molecules having a free volume larger than the critical v^* [28], then D is given by,

$$D \propto \int_{v^*}^{\infty} \exp\left(-\frac{v}{v_f}\right) dv = D_0 \exp\left(-\frac{v^*}{v_f}\right) \quad (2.4)$$

The diffusion coefficient D can be derived by inserting Eqs. (2.2) and (2.3) into Eq. (2.4) as follows,

$$\begin{aligned}
D &= D_0 \exp\left(-\frac{v^*}{v_f}\right) = D_0 \exp\left(-\frac{v^* N}{fV}\right) \\
&= D_0 \exp\left(-\frac{v^* N}{\alpha_f V} \frac{1}{T + \frac{f_g}{\alpha_f} - T_g}\right) \\
&= D_0 \exp\left(-\frac{B}{T - T_0}\right)
\end{aligned} \tag{2.5}$$

where $B = \frac{v^* N}{\alpha_f V}$ and $T_0 = T_g - \frac{f_g}{\alpha_f}$

This equation is well-known VTF law which well explain the relaxation behavior of supercooled liquid.

2.1.2 Molecular weight effect on glass transition temperature

The molecular weight (M_w) affects T_g . The free volume is proportional to the chain ends.

A polymer can be represented by

$$A(X)_nB, \tag{2.6}$$

where X is the repeat unit which there are n in the chain and A and B are the chain ends. When $n = 1$, the monomer can be represented as AXB. For this system, the molar volume, $v(n)$, at constant temperature may be divided into two types of volume, namely occupied volume and free volume, the latter allowing mobility of the molecules. The volume of chain end may be assigned to free volume. It is assumed that total $V(n)$ with any repeat chain n can be given by,

$$V(n) = V_m \times n + V_f, \tag{2.7}$$

where V_m is the volume of a X unit in the chain and V_f is the total volume of the both chain ends. Similarly, the molecular weight M_w will be given by,

$$M_w = m_m \times n + m_f, \tag{2.8}$$

where m_m is the weight of a X unit and m_f is the combined weight of the two chain ends. The molar volume $v(n)$ can be obtained by dividing Eq. (2.7) by Eq. (2.8):

$$v(n) = v(\infty) + \frac{V_f - m_f v(\infty)}{M_w}, \tag{2.9}$$

where $v(\infty) = V_m / m_m$ is the limiting specific volume for a chain with infinite length. Eq. (2.9) is able to be written for the monomer which $M_w = m_m + m_f$,

$$v(n) - v(\infty) = [v(1) - v(\infty)] \frac{m_m + m_f}{M_w}, \quad (2.10)$$

where $v(1)$ is the specific volume of the monomer.

It is assumed that the specific volume changes linearly with temperature T ,

$$v(n) = v_0(n) + \alpha_n T, \quad (2.11)$$

where $v_0(n)$ is the extrapolated specific volume at $T = 0$ K and α_n is the slope, $dv(n)/dT$, of the $v(n)$ vs. T curve. For the limit cases for both monomer and infinite chain, it follows that,

$$\begin{aligned} v(1) - v(\infty) &= [v_0(1) - v_0(\infty)] + [\alpha_1 - \alpha_\infty]T \\ &= \Delta v_0 + \Delta \alpha T \end{aligned} \quad (2.12)$$

The temperature dependence of specific volume can be obtained from Eqs. (2.10), (2.11) and (2.12),

$$v(n) = v_0(\infty) + \alpha_\infty T + \frac{(m_m + m_f)(\Delta v_0 + \Delta \alpha T)}{M_w} \quad (2.13)$$

This equation expresses the relationship among volume, temperature and molecular weight of a polymer.

The specific volume at T_g has a linear relationship with T_g given by,

$$v_g = v_g(\infty) - B[T_g(\infty) - T_g], \quad (2.14)$$

where $v_g(\infty)$ and $T_g(\infty)$ are the values of specific volume and T_g of infinite chain and B is a constant.

The Eq. (2.13) for infinite chain with infinite molecular weight at T_g , $v_g(\infty)$, is able to be substituted into Eq. (2.14), then T_g can be written in this form,

$$\begin{aligned} T_g &= T_g(\infty) \left[\frac{\alpha_\infty - B - \frac{(m_m + m_f)\Delta v_0}{T_g(\infty)M_w}}{\alpha_\infty - B + \frac{(m_m + m_f)\Delta \alpha}{M_w}} \right] \\ &= T_g(\infty) - \left[\frac{(m_m + m_f)(\Delta \alpha T_g(\infty) + \Delta v_0)}{\alpha_\infty - B + \frac{(m_m + m_f)\Delta \alpha}{M_w}} \right] \frac{1}{M_w} \end{aligned} \quad (2.15)$$

At sufficiently high M_w , this relationship reduces to,

$$T_g = T_g(\infty) - \frac{K}{M_w}, \quad (2.16)$$

where $K = \frac{(m_m + m_f)(\Delta \alpha T_g(\infty) + \Delta v_0)}{\alpha_\infty - B}$ is a constant.

From T_g in Eq. (2. 16) and T_0 in Eq. (2. 5), the ratio T_g/T_0 is given by,

$$\frac{T_g}{T_0} = \frac{T_g}{T_g - \frac{C_0}{\alpha}} = \frac{T_{g^\infty} - \frac{K}{M_w}}{T_{g^\infty} - \frac{K}{M_w} - \frac{C_0}{\alpha}} \quad (2. 17)$$

2.2 Adam-Gibbs theory

- Configurational entropy model

Adam and Gibbs introduced the temperature variation of the size of the cooperatively rearranging region (CRR) to explain the temperature dependence of relaxation behavior in glass-forming liquids [9]. It is assumed that the supercooled liquid consists of CRR which grows to infinite size at Vogel-Fulcher temperature or Kauzmann temperature. The fraction of regions where cooperative rearrangement is possible is then proportional to the transport coefficient.

2.2.1 Transition probability

A subsystem of the sample which can rearrange into another configuration independently of its environment is defined as CRR. The number of molecules or monomer segments in polymer in CRR is denoted by z . The size of z depends on the sufficient fluctuation in energy or enthalpy.

To evaluate the transition probability of cooperative rearrangements, we assume N is independent, equivalent and distinguishable. Since the subsystems are in both mechanical and thermal contact with each other, N subsystems is an isobaric-isothermal ensemble. Each subsystem has z molecules. Only n subsystems, however, are in states of allowing a cooperative rearrangement.

The Gibbs free energy of ensemble is given by $G = z\mu = -kBT \ln \Delta(z, P, T)$. Here k_B is the Boltzmann constant, T is temperature and Δ is isobaric-isothermal partition function which is given by,

$$\Delta(z, P, T) = \sum_{E, V} w(z, E, V) \exp\left(-\frac{E}{kT}\right) \exp\left(-\frac{PV}{kT}\right) \quad (2.18)$$

where w is the degeneracy of energy E and volume V of the subsystem with pressure P .

In the same manner, the Gibbs free energy for allowing a cooperative rearrangement subsystem is $G = z\mu' = -kT \ln \Delta'(z, P, T)$.

Then the fraction of the states permitting rearrangement among all subsystem is given by,

$$\begin{aligned}\frac{n}{N} &= \frac{\Delta'}{\Delta} = \exp\left[-\frac{(G' - G)}{kT}\right] \\ &= \exp\left[-\frac{z(\mu' - \mu)}{kT}\right] = \exp\left[-\frac{z\Delta\mu}{kT}\right],\end{aligned}\quad (2. 19)$$

where $\Delta\mu$ is the potential energy hindering the cooperative rearrangement per molecule or monomer segment and independent on T and z .

The transition probability $W(T)$, which permits cooperative rearrangement, is proportional to n/N and then given by,

$$W(T) = A \frac{n}{N} = A \exp\left[-\frac{z\Delta\mu}{kT}\right] \quad (2. 20)$$

The transition probability $\langle W(T) \rangle$ is the sum over all possible corresponding to different z . There is a critical lower limit z^* to the size of cooperative regions that can yield nonzero transition probabilities. Thus $\langle W(T) \rangle$ is given by,

$$\begin{aligned}\langle W(T) \rangle &= \sum_{z=z^*}^{\infty} A \exp\left[-\frac{z\Delta\mu}{kT}\right] \\ &= \frac{A}{1 - \exp\left(-\frac{\Delta\mu}{kT}\right)} \exp\left(-\frac{z^* \Delta\mu}{kT}\right)\end{aligned}\quad (2. 21)$$

As $\exp\left(-\frac{\Delta\mu}{kT}\right)$ in the denominator is nearly equal to zero, the denominator is negligibly dependent on temperature in comparison with the numerator. Eq. (2. 21) can be rewritten with new frequency factor A' ,

$$\langle W(T) \rangle = A' \exp\left(-\frac{z^* \Delta\mu}{kT}\right) \quad (2. 22)$$

The results state simply that the overwhelming majority of transitions are undergone by regions whose size differs negligibly from the smallest size z^* that permits a transition at all. It is an expression of the fact that the transitions of these smallest cooperative regions involve the smallest number z^* of monomer units surmounting, essentially and simultaneously, the individual barriers restricting their arrangement.

2.2.2 Critical size of CRR

In order to evaluate a critical lower limit z^* to the size of cooperative regions, we consider the configurational entropy S_c given by,

$$S_c = k \ln W_c \quad (2. 23)$$

where W_c is the number of configurations of the macroscopic supersystem.

On the other hand, the configurational entropy S_c of a macroscopic supersystem composed of N subsystem is generally given by,

$$S_c = N s_c, \quad (2. 24)$$

where s_c represents the configurational entropy of a subsystem of z monomer units. The configurational entropy of a cooperative subsystem can be expressed by combining Eqs. (2. 23) and (2. 24),

$$s_c = k \ln (W_c^{1/N}) \quad (2. 25)$$

For the macroscopic system to consist of a mole of monomers or segments, the number of subsystem is given by $z = N_A/N$, where N_A is Avogadro's number. Then from the Eq. (2. 25), s_c can be written as the function of z ,

$$s_c = k \ln (W_c^{z/N_A}) \quad (2. 26)$$

It means that the configurational entropy of a subsystem increases monotonically with the size of the subsystem for a given temperature and pressure.

There must be a lower limit z^* to the size of a cooperative subsystem that can perform a rearrangement into another configuration. For this lower limit, the available number of configurations of this subsystem is $W_c^{z^*/N_A}$. Then, the critical configurational entropy s_c^* of the representative CRR with size z^* is given by,

$$s_c^* = k \ln (W_c^{z^*/N_A}), \quad (2. 27)$$

and then the critical size z^* can be expressed in terms of the molar configurational entropy S_c ,

$$z^* = N_A s_c^* / S_c \quad (2. 28)$$

Substituting this result into the expression for the average transition probability, Eq. (2. 22), yields new equation,

$$\langle W(T) \rangle = A' \exp \left(- \frac{N_A s_c^* \Delta \mu}{k T S_c} \right) \quad (2. 29)$$

2.2.3 VTF equation

The temperature dependence of $S_c(T)$ can be evaluated from the general equation relating the entropy and specific heat capacity,

$$S_c(T) - S_c(T_0) = \int_{T_0}^T \frac{\Delta C_p(T)}{T} dT, \quad (2. 30)$$

where $\Delta C_p(T)$ is the difference in specific heat capacity between equilibrium liquid and the glass. It is assumed that the system is frozen at T_0 , called ideal glass transition

temperature or Vogel-Fulcher temperature, therefore,

$$S_c(T) = \int_{T_0}^T \frac{\Delta C_p(T)}{T} dT \quad (2.31)$$

To calculate $S_c(T)$, the hyperbolic postulation, $\Delta C_p(T) = T_g \Delta C_p(T_g)/T$, was used [29, 30], i.e., the configurational entropy is

$$S_c(T) = \int_{T_0}^T \frac{T_g \Delta C_p(T_g)}{T^2} dT = T_g \Delta C_p(T_g) \frac{T - T_0}{TT_0} \quad (2.32)$$

Substituting this equation into Eq. (2.29) yields another relationship,

$$\begin{aligned} \langle W(T) \rangle &= A' \exp \left(- \frac{T_0 N_A s_c^* \Delta \mu}{k T_g \Delta C_p(T_g) T - T_0} \right) \\ &= A' \exp \left(- \frac{B}{T - T_0} \right) \end{aligned} \quad (2.33)$$

where $B = \frac{T_0 N_A s_c^* \Delta \mu}{k T_g \Delta C_p(T_g)}$.

As the diffusion coefficient D is related to the transition probability, i.e., $D(T) \propto \langle W(T) \rangle$, diffusion coefficient is given by,

$$D(T) = D_0 \exp \left(- \frac{B}{T - T_0} \right) \quad (2.34)$$

This equation is the VTF one.

This theory links the relaxation properties with thermal properties through diffusion coefficient and entropy and results in the VTF equation.

2.3 Domain model

The cooperative domain model for the polymers was proposed in 1991 [10]. This model proposed that a segmental relaxation requires intermolecular cooperativity to discuss the molecular and thermodynamic factors that affect the relaxation behavior around T_g .

2.3.1 Domain and conformer

The smallest segmental unit of rotation is called as conformer. The domain size of cooperativity is the number of conformer that must relax simultaneously with its close neighbors. As the volume is decreased by change of temperature, the domain size grows and the conformational entropy decreases.

At an enough high temperature, most conformers are allowed to relax independently each other by the expanded volume. The temperature of this limit is defined as T^* , where the domain size is unity. At an extreme low temperature, on the other hand, there is a temperature where the domain size has grown infinitely so that all conformers move together. The conformational entropy disappears at this temperature called T_0 . Between these two limit temperatures, T^* and T_0 , the domain size denoted Z has a finite value and is dependent upon the temperature, i.e., $Z = Z(T)$.

Now, we suppose that a conformer can take the value of W_z as the number of states. As each conformer relaxes individually at T^* , the conformational entropy, s^* , of 1 mole of conformers is,

$$s^* = N_A k_B \ln W_z, \quad (2.35)$$

where N_A is the Avogadro's number and k_B is the Boltzmann constant. One domain contains Z conformers. When there are N_z domains in a mole of conformers, the conformational entropy, S_c , is given by,

$$S_c = N_z k_B \ln W_z \quad (2.36)$$

As $Z = N_A / N_z$,

$$Z = \frac{N_A k_B \ln W_z}{N_z k_B \ln W_z} = \frac{s^*}{S_c} \quad (2.37)$$

On cooling below T^* , the conformational entropy S_c will decrease and reach 0 at T_0 with meshing of the conformers. On the other hand, when each conformer relaxes independently without cooperativity, S_c reaches 0 at 0 K. The comparison between the cases of relaxations without cooperativity and with cooperativity is represented in Fig. 2. 1 in terms of excess enthalpy vs. temperature. Curve A represents the temperature dependent excess enthalpy, $h^*(T)$, for the former and Curve B, $H_c^*(T)$, of the latter.

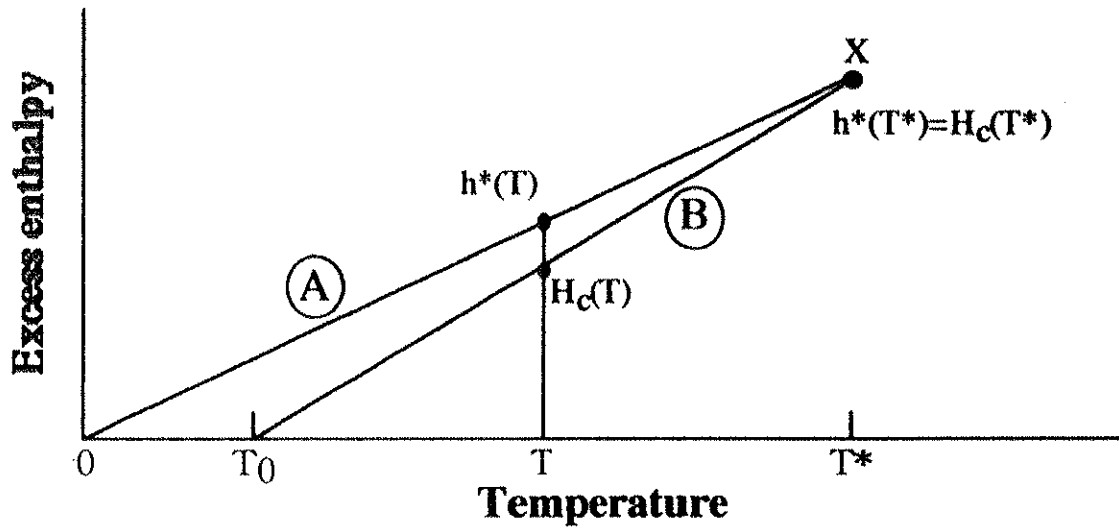


Fig. 2.1 The temperature variation of excess enthalpy in cases that molecules relax a) without cooperativity and b) with cooperativity

If we assume that curves A and B have similar shape but differ only in the temperature scale, curve B can be obtained by compressing curve A through a change in the temperature scale from $[0 \rightarrow T^*]$ to $[T_0 \rightarrow T^*]$, i.e. $\Delta X_{0T^*} \approx \Delta X_{T_0T^*}$, so that the relationship can be obtained,

$$\frac{H_c(T)/H_c(T^*)}{h_c(T)/h_c(T^*)} \approx \frac{(T - T_0)/(T^* - T_0)}{T/T^*} \quad (2.38)$$

There is another relationship between enthalpy and entropy,

$$\frac{H_c(T)}{h_c(T)} \approx \frac{TSc}{Ts^*} \quad (2.39)$$

Form Eqs. (2.38) and (2.39), we obtain,

$$\frac{Sc}{s^*} = \frac{T^*}{(T^* - T_0)} \frac{(T - T_0)}{T} \quad (2.40)$$

This equation follows the temperature dependent domain size, Z , combining with Eq (2.37),

$$Z = \frac{(T^* - T_0)}{T^*} \frac{T}{(T - T_0)}, \quad (2.41)$$

which shows the properties of Z such as $Z = 1$ at T^* and $Z \rightarrow \infty$ at T_0 .

2.3.2 Derivation of the VTFlaw

If each conformer can relax independently, the activation energy barrier $\Delta\mu$ would be constant. The relaxation time τ would follow the Arrhenius-like temperature dependence,

$$\ln \frac{\tau}{\tau^*} = \frac{\Delta\mu}{kT} - \frac{\Delta\mu}{kT^*}, \quad (2.42)$$

where τ^* is the relaxation time at T^* . When Z conformers in a domain can relax simultaneously, their relaxation time grows at a faster rate with temperature than shown by Eq. (2.42). The transition probability for the simultaneous relaxation is then the Z th power of the probability for an independent conformer. The relaxation time at T is obtained by the formula,

$$\begin{aligned} \ln \frac{\tau}{\tau^*} &= \frac{Z\Delta\mu}{kT} - \frac{\Delta\mu}{kT^*} \\ &= \frac{\Delta\mu}{k} \left(\frac{s^*}{TSc} - \frac{1}{T^*} \right) \\ &= \frac{\Delta\mu}{k} \left(\frac{T^* - T_0}{T^*} \frac{1}{T - T_0} - \frac{1}{T^*} \right) \end{aligned} \quad (2.43)$$

At $T \rightarrow \infty$, Eq. (2.43) is given by,

$$\ln \frac{\tau_0}{\tau^*} = \frac{\Delta\mu}{k} \left(-\frac{1}{T^*} \right) \quad (2.44)$$

Combining Eqs.(2.43) and (2.44) to eliminate τ^* term gives the VTF law,

$$\begin{aligned} \ln \frac{\tau}{\tau_0} &= \frac{\Delta\mu}{k} \left(\frac{T^* - T_0}{T^*} \frac{1}{T - T_0} \right) \\ &= \frac{\Delta\mu^*}{k_B} \frac{1}{T - T_0}, \end{aligned} \quad (2.45)$$

where $\Delta\mu^* = \Delta\mu \left(\frac{T^* - T_0}{T^*} \right)$ is the activation energy for an independently relaxing conformer. The well-known VTF law is derived from the temperature dependence of domain size Z .

2.4 Two order parameter model

Two order parameter model is based on the Ginzberg-Landau type model and connects the physical picture of structural glass and spin glass in a natural way [11, 12]. According to this model, the frustration in glass-forming liquids can be clarified by two order parameters, density order parameter ρ and bond order parameter S . As a demonstration of this model, the unusual thermodynamic behavior of water has been explained [12].

2.4.1 Frustration of two order parameter

It is focused on the effective attractive interaction potential between molecules. The potential is generally given by the superposition form of isotropic part of the interaction \bar{V} and its anisotropic part ΔV ,

$$V(r, \Omega) = \bar{V}(r) + \Delta V(r, \Omega) \quad (2.46)$$

where r is the distance from the center of mass of the molecule and Ω represents the orientation. The latter anisotropic part causes a locally favored structure which consists of a molecule and its neighboring n molecules. Two different types of symmetry are generally favored in a liquid. One is favored by \bar{V} and the other is favored by ΔV . The former maximizes density and represents the long-range density ordering, while the latter maximizes the local bonds. In liquid, the locally favored structure by ΔV is not identical with any crystallographic symmetry. The local bond formation causes fluctuation in the intermolecular interaction and symmetry-breaking random fields. It plays the role of random disordering field against crystallization and favors vitrification.

The density ρ and the bond order S of liquids can be expressed by the fluctuation form, $\rho = \bar{\rho} + \delta\rho$ and $S = \bar{S} + \delta S$, respectively. The Hamiltonian associated with density fluctuation $\delta\rho$ is given by,

$$\beta H_\rho = \int dr \left[\frac{\tau}{2} \delta\rho(r)^2 - \frac{a_3}{3} \delta\rho(r)^3 + \frac{a_4}{4} \delta\rho(r)^4 \right], \quad (2.47)$$

where $\tau = a_2(T - T^*_\rho)$ and T^*_ρ is the density ordering temperature. In the same manner, the Hamiltonian associated with bond ordering fluctuation ΔS is also given by,

$$\beta H_S = \int dr \left[\frac{\kappa}{2} \delta S(r)^2 - \frac{b_3}{3} \delta S(r)^3 + \frac{b_4}{4} \delta S(r)^4 \right], \quad (2.48)$$

where $\kappa = b_2(T - T^*_s)$ and T^*_s is the bond ordering temperature. For the physical feature of the phase transition of liquids, the gradient terms and the couplings between ρ and S are added to the above Hamiltonians, so that the following Hamiltonian is obtained,

$$\begin{aligned} \beta H_T = & \beta H_\rho + \frac{K_\rho}{2} \int dr |\nabla \delta \rho(r)|^2 + \beta H_S + \frac{K_S}{2} \int dr |\delta S(r)|^2 \\ & - \int dr \left[c_{1\rho} \delta \rho(r) S(r) + c_{1S} \rho(r) \delta S(r) + \frac{c_{2\rho}}{2} \delta \rho(r)^2 S(r) + \frac{c_{2S}}{2} \rho(r) \delta S(r)^2 \right] \end{aligned} \quad (2.49)$$

The coupling terms between ρ and S indicate the frustration effects between them. There are two types of frustration. One is the negative coupling with $c_i < 0$. It means that the formation of bonds leads to a decrease of density and also to the decrease of the ordering temperature. The other is the positive coupling with $c_i > 0$. For this case, the formation of bond leads to an increase in density and to an increase of the ordering temperature. For example, the ordering temperatures, $T^{**\rho}$ and T^{**s} , are shifted up or down according to positive or negative coupling of $c_{2\rho}$ or c_{2s} by the relations of $T^{**\rho} = T^*\rho + (c_{2\rho}/a_2)\bar{S}$ and $T^{**s} = T^*s + (c_{2s}/b_2)\bar{\rho}$, respectively. The sign of coupling between ρ and S gives a criterion on whether molecules crystallize or vitrify. For the positive coupling, molecules should crystallize without vitrification, while for the negative coupling, vitrification can occur.

There are two types of origins about the glass-liquid transition: (1) the anisotropic interactions that are not consistent with the crystallographic symmetry and (2) the quenched disorder in structures of particle or molecules. The temperature and strength of disorder path of the vitrification is shown in Fig. 2. 2.

2.4.2 Relaxation features

Fig. 2. 2 is the schematic phase diagram of the liquid-glass or liquid-crystal transition [11]. \bar{S} is the measure of disorder strength. This value is the spatially averaged value of S , given by $\bar{S} = S_0 \exp(n\Delta V/k_B T)$, where n is the number of near neighboring molecules, ΔV is the bonding energy and k_B is the Boltzmann constant. The density-ordering temperatures, $T_m^*(0) = T_m^*$ and $T_m^*(\bar{S})$, represent the melting temperature of a real

defect free crystal formed as a result of density of ordering and that of a hypothetical crystal with disorder. The relaxation behavior of liquid above T_m^* obeys the Arrhenius law, $\tau = \tau_0 \exp(\Delta E/kBT)$ where ΔE is the activation energy, and the relaxation function is exponential, $\Phi(t) = \exp(-t/\tau)$.

Between T_m^* and $T_0(\bar{S})$, the relaxation is characterized by the slow dynamics. It comes from the spatial islands having a higher molecular density than the liquid in the valley of free energy hypersurface. The valleys whose state are metastable are separated by the finite barriers. In order to complete the slow relaxation, the molecules must overcome the barriers. This phase is similar to the Griffith phase known in spin glass system. The relaxation in this Griffith-like phase can be characterized by the KWW function, usually called stretched exponential, $\Phi(t) = \exp[-(t/\tau)^{\beta_{KWW}}]$ instead of the exponential relaxation. The parameter is a monotonically increasing function of temperature and reach $\beta_{KWW} = 1$ at T_m^* . The slow dynamics of Griffith-like phase may be completely freezing-in at the Vogel-Fulcher temperature T_0 due to the infinite energy barriers. Therefore, the relaxation time diverges at T_0 . T_0 is equivalent to the Kauzmann temperature T_K . The glass transition occurs at the temperature where the metastable islands having sufficiently high energetic barriers do percolate. Therefore, the glass transition temperature exists between T_m^* and T_0 .

This model predicts some relaxational features. (1) Below T_m^* , the energy barrier height E_B between islands given by $E_B = \frac{BT}{T-T_0}$ gives us well-known VTF law. The crossover from Arrhenius to VTF at T_m^* (near T_m) is predicted. (2) The disorder strength \bar{S} determines the temperature interval between T_m^* and T_0 . (3) A stronger glass suffers from stronger disorder effects. It is consistent with the fact that a) the change in specific heat across T_g is weaker for a stronger glass, b) a longer interval between T_g and T_0 and c) the larger β_{KWW} at T_g for a stronger glass.

2.5 Mode coupling theory

The development of mode coupling theory (MCT) leads to the topics of recent research on liquid-glass transition. This theory pointed out that crucial point of structural glass transitions in simple liquids is the transition from ergodic to non-ergodic dynamics of density fluctuations with wave vectors of microscopic scale. The density correlation function $\Phi(t)$ at the wave vector q is given by,

$$\phi_q(t) = \frac{\langle \delta\rho_q^*(t) \delta\rho_q(0) \rangle}{\langle \delta\rho_q^*(0) \delta\rho_q(0) \rangle} \quad (2. 50)$$

For liquid, it shows an ergodic dynamics. In other word, the density correlation function of liquid reaches zero at the infinite time. On the other hand, the density correlation function of glass has a finite value even when $t \rightarrow \infty$, which means non-ergodicity.

The theory is successfully applied to the understanding of dynamical behavior in the fragile glass-forming liquid. According to MCT, the fast β relaxation process is assigned to the rapid motion of a molecule inside the cage and α relaxation is usually assigned to the lifetime of cage. This theory predicts a dynamical glass transition from an ergodic to nonergodic behavior at a critical temperature T_c . The existence of the crossover temperature T_c was supported by the anomalous decrease in the Debye-Waller factor at T_c [17, 31]. The critical temperature T_c , however, is not consistent with the calorimetric glass transition temperature T_g . T_c is usually 30 - 50 K above T_g .

This theory evaluate the temperature dependence of the viscosity given by,

$$\eta = \eta_0 (T - T_c)^{-\gamma} \quad (2. 51)$$

It reveals that viscosity diverges at T_c , however, it is inconsistent with the experimental results.

It also predicts that the shape parameters in Havrilliak-Negami (HN) function [33] are independent on the temperature so that the β_{KWW} in stretched exponential relaxational function does not depend on the temperature. However, the value of β_{KWW} is an increasing function of temperature.