

A Theoretical Interpretation of Free Volume at Glass Transition*

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Abstract We devise a relaxed lattice model (RLM) to study the mechanism of glass transition, which unifies the cage-effects from particle-particle interaction and entropy. By analyzing entropy in RLM with considering the influence of interactions on equilibrium, we demonstrate that glass transition is a second-order phase transition. For a perfect one-dimensional linked particle system like linear polymer under normal pressure, the free volume at glass transition is rigorously deduced out to be 2.6%, which provides a theoretical basis for the iso-free volume of 2.5% given by Willian, Landel and Ferry (WLF) equation. Extending to system with dead particles linked with higher dimensions like branched or cross-linked chains under positive or negative pressure, free volume at glass transition is varied, based on which we construct a phase diagram of glass transition in the space of free volume-dead particle-pressure. This demonstrates that free volume is not the single parameter determining glass transition, while either dead particles like cross-linked points or external force fields like pressure can vary free volume at the glass transition.

Keywords Glass transition; Iso-free volume; Relaxed lattice model; Predicted phase diagram

INTRODUCTION

The liquid-glass transition of polymer and other materials is a long-standing challenge in condensed matter physics^[1–13]. Gas, liquid and crystal can be differentiated by inter-particle position or radial distribution function, while the difference between liquid and glass lies mainly in particle motion rather than position. Approaching glass transition temperature T_g , liquid experiences kinetic slowdown with orders increase of relaxation time τ but without obvious structural change. To bridge static thermodynamic property and kinetic slowdown, the Adam-Gibbs theory^[12] derives a relation between configuration entropy and relaxation time τ , and predicts an ideal glass transition as a second order phase transition. Meanwhile, another class of explanation on kinetic slowdown, such as free volume theory^[13–17] and dynamic theories^[18–20], emphasizes volume change and density fluctuation, where strong particle-particle interactions or “links” construct a “cage effect” and restrict free motion. Probably both of them play their roles in glass transition and impose constraints on particle motion.

Among all these theoretical efforts, the free-volume model is a simple but useful picture in describing viscosity in the vicinity of glass transition, which is initially proposed by Doolittle^[21, 22]. Based on the initial concept, different models of free volume have been developed by Fox and Flory^[23–25], Simha and Boyer^[26], Cohen and Turnbull^[15] and Cohen and Grest^[16], Williams, Landel and Ferry (WLF)^[27], White and Lipson^[28, 29] and others^[10, 30–35]. A recent perspective of White and Lipson^[36] discussed each models in detail. One important

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and elegant idea is the iso-free volume at glass transition for all polymers and other materials, initially proposed by Fox and Flory^[23–25] and later obtained to be about 2.5% by WLF on fitting experimental viscosities. The iso-free volume is a conjecture still waiting for a microscopic theory to confirm.

Moreover, as the WLF iso-free volume of 2.5% is excess free volume, it is not possible to measure directly by experiment. Experimental techniques like positron annihilation spectroscopy^[37–42] acquire total free volume, which includes excess and vibration free volumes. Lacking of a theoretical basis and direct experimental confirmation, whether an iso-free volume exists for all materials at glass transition remains an open debating issue. Nevertheless, considering the success of WLF equation, the iso-free volume of about 2.5% should not be simply attributed to a mystery accident, which may have its first-principle physics origin.

In this work, we study glass transition with a modified lattice model, in which particle-particle interactions and relaxation process or equilibrium have been considered at the first place. Thus we name this model relaxed lattice model (RLM). Free volume originally introduced by Doolittle^[21, 22] is taken as a precondition for particle motion. By analyzing entropy of one-dimensional linked particles like linear polymer under normal pressure, we demonstrate that glass transition is a second order phase transition. For the first time, the fascinating constant of iso-free volume of about 2.5% at glass transition, initially obtained by WLF^[27] through fitting experimental data, is rigorously deduced to be 2.6%. At the end, extending the model to particles linked with higher dimensions like branch or cross-linked polymers (named as dead particles) and at positive or negative pressure, we have drawn a phase diagram of glass transition in the space of free volume-dead particle-pressure. This demonstrates that free volume is not the single parameter controlling glass transition, which is in-line with the suggestion of locally correlated lattice model and experimental observations. Note that “free volume” discussed in this work is excess free volume and denoted as V_f .

THEORY

Glass Transition of Linear Polymer

In our relaxed lattice model (RLM), three different particles are introduced to fill the lattice, namely motor particle (MP), dead particle (DP) and free volume particle (FVP). Motor particle (MP) represents structural unit of materials restricted by links (strong but short range interactions like chemical bond which are defined as “links”) no more than 2 that can move freely when sufficient free volume is available, while dead particle (DP) is structural unit of materials restricted by links more than 2 and cannot exchange position with free volume particle. Free volume particle (FVP) occupies one unit volume of free volume. From Doolittle’s concept of free volume, transport of motor particles occurs only when the volume of a single free volume particle is no less than that of a motor particle. Note that this judgment condition is only held for normal system while system under positive or negative pressure will be discussed in the last part of this work. We define a parameter $\theta = v_p/v_f$, where v_p and v_f are volumes of one motor particle and one free volume particle, respectively. When $\theta < 1$, the free motion ability of particle is too strong to be changed into low motion ability state: glass state. Thus glass transition can only occur in the regions of $\theta > 1$ and $\theta = 1$. Here $\theta > 1$ means that neighbor particles cannot exchange their positions with each other through a single free volume particle but only move in a space smaller than their own size. Based on concept of free volume and Doolittle’s assumption, we make a definition for glass transition temperature T_g : the transition temperature from $\theta > 1$ to $\theta = 1$. Note that the definition of $\theta = 1$ corresponds to $B = 1$ in Vogel-Tammann-Fulcher (VTF)^[43–45] equation $\eta = Ae^{B/(T-T_0)}$ or Doolittle’s equation^[21, 22] $\eta = Ae^{BV_{fc}/V_{free}}$ under normal pressure, which was taken by WLF to obtain the iso-free volume of 2.5% at glass transition. The conditions $\theta = 1$ and $B = 1$ describe the same physical picture: motor particles are just able to exchange their positions. $B = 1$ means that the kinetic energy of motion particle is sufficient to overcome the activation energy of diffusion, while $\theta = 1$ implies that the space (free volume) is large enough allowing motor particle to exchange their positions.

Before solving the question of general material, we first study glass transition in one-dimensional linked particles like linear polymeric chains under normal condition. Taking Flory’s lattice model^[46] but considering the

influence of particle-particle interactions on entropy, the lattice changes. The schematic diagram in the case of $\theta = 1$ is shown in Fig. 1. The total number of lattices is defined: $n_0 = \frac{V_0}{V_f} = n_1 + \theta n_2$, where n_1 is the number of free volume particles (grey spots), n_2 is the number of chains, x is the number of motor particles (blue spots) in one single chain, $\beta = \frac{V_f}{V_0} = \frac{n_1}{n_0}$ is the excess free volume percentage. The pressure is defined as equilibrium pressure P_e , which stands for the conditions that the boundary particles have the same situation with the inner ones.

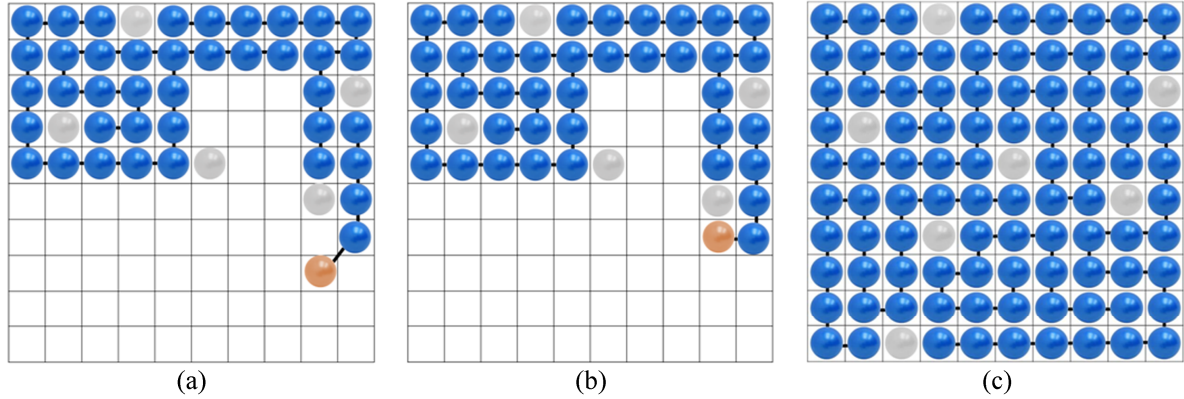


Fig. 1 Relaxed lattice model (RLM) with $\theta = 1$: (a) putting a new particle into the lattice; (b) new particle moving during relaxation time to be balanced; (c) all particles having been set and balanced (The grey spots represent the free volume particles; the blue ones are motor particles linked into lines. The online version is colorful.)

Considering that i chains have been placed, let us set the next particle to complete the lattice in Fig. 1(a). If the relaxation time is neglected in counting the ways of arrangements of the new particle, then we get Fig. 1(c) directly after we set all the particles. Flory has first provided the answer in the condition of $\theta = 1$ with entropy expressed as $S = k \ln \left(\frac{n_0!}{(n_0 - n_2 x)!} \right) + k n_2 (x-1) \ln \left[\frac{z-1}{n_0} \right]$.

If we consider particle-particle interaction and the relaxation process in Fig. 1(b), the entropy will be different. Considering that i chains have been placed, the number of adjacent lattices to the ix motor particle is $z\theta$. Of course, one of them is the $ix-1$ motor particle, and the rest lattices has a chance of $1-f_i$ to be an available lattice for setting the new motor particle. The $1-f_i$ of Flory is $1-f_i = 1 - \frac{xi}{n_0}$. However, if the motor particle has

experienced a relaxation process, it would move to the position closer to other motor particles because of particle-particle interactions in Fig. 1(b). Therefore, a new correction parameter r is proposed here to represent the effect of particle-particle interactions on the configuration of linear chains. The new motor particle has the probabilities locating either adjacent to motor particles with particle-particle interactions or adjacent to free volume particles without interactions and parameter r is expressed as the ratio between these two probabilities.

The $1-f_i$ of ours is $1-f_i = 1 - \frac{xi}{n_0} \cdot r$. Before figuring out the true value of r , we first solve the entropy.

Using mathematical abilities learned from Flory, the number of ways for placement of the $i+1$ chain is: $W = (n_0 - r\theta xi)(z\theta - 1)^{x\theta-1} \frac{(n_0 - r\theta xi)^{x\theta-1}}{n_0^{x\theta-1}}$. Then we get the new entropy:

$$S = \frac{k}{r} \ln \left(\frac{n_0!}{(n_0 - r\theta n_2 x)!} \right) + k\theta n_2 (x-1) \ln \left(\frac{z\theta - 1}{n_0} \right) \quad (1)$$

where k is Boltzmann constant, z is 6^[46].

Set the part of denominator $n_0 - r\theta n_2 x$ equal to y . y means the number of lattices available for adding a new motor particle. Thus, $y \geq 0$ is from both physics and mathematics:

$$y = \begin{cases} n_0 - r\theta n_2 x > 0, T > T_1 \\ 0, T \leq T_1 \end{cases} \quad (2)$$

where T_1 is the highest temperature point in condition of $y = 0$. The entropy S can be written as:

$$S = \begin{cases} \frac{k}{r} \ln \left(\frac{n_0!}{(n_0 - r\theta n_2 x)!} \right) + k\theta n_2 (x-1) \ln \left(\frac{z\theta - 1}{n_0} \right), T > T_1 \\ \frac{k}{r} \ln(n_0!) + k\theta n_2 (x-1) \ln \left(\frac{z\theta - 1}{n_0} \right), T \leq T_1 \end{cases} \quad (3)$$

Two different entropy functions indicate two different disordered states in Eq. (3). Moreover, $\begin{cases} S_{T_1^+} = S_{T_1^-} \\ \left. \frac{\partial S}{\partial T} \right|_{T_1^-} \neq \left. \frac{\partial S}{\partial T} \right|_{T_1^+} \end{cases}$

points out that T_1 is a second order thermodynamic transition temperature. Then we will prove that $T_g = T_1$ at

$\begin{cases} y = 0 \\ \theta = 1 \end{cases}$. If $\begin{cases} y = 0 \\ \theta = 1 \end{cases}$ presents a temperature region, then $T_g \neq T_1$; if it is only a point, then $T_g = T_1$. Therefore, $\begin{cases} y = 0 \\ \theta = 1 \end{cases}$ is the answer of physics of glass transition, which is solved in the following lines.

The motor particles at the middle of the chains are more difficult to reach free volume particles compared to the ones at the tails or nails. An accurate correction has to be established to address this issue^[47–49]. Here $y = 0$ is named as the judgment equation:

$$y = n_0 - r\theta n_2 x = 0 \implies 1 - \frac{r \left(n_2 x \theta - \frac{2n_2 \theta (x-1)}{z\theta} \right)}{n_0 - \frac{2n_2 \theta (x-1)}{z\theta}} = 0 \implies \frac{3}{1-\beta} = \left(3 - \frac{1}{\theta} \right) r + \frac{1}{\theta} \quad (4)$$

To analyze the judgment Eq. (4), a precise definition should be given to the parameter r . The illustration of the definition of r is drawn in Fig. 2. We can imagine that the links connecting motor particles into chains are cut off by a ‘micro-scissor’ in an isolated system without changing the structure of each motor particle itself. The kinetic energy of each particle after ‘cut-off’ is equal to the energy of motion before ‘cut-off’. The motor particles then become ‘free’ spots. The mobility of these spots increases largely and the whole system expands because of the increase of degree of freedom and the change of motion modes (the interactions between spots are balanced by micro-scissor project to create a reversible expansion process). The mean-free-length of the motion of motor particles after ‘cut-off’ is referred as parameter l . The probability of motor particle adjacent to motor particle with particle interactions, p_1 , is inversely proportional to the third power of l in three dimensions ($p_1 = \frac{c}{l^3}$, where c is a constant). For the system without interactions ($r = 1$ in this system, the number of motor particles adjacent to free volume particles is equal to that of the ones adjacent to motor particles), the number of free volume particles will stay the same after the ‘cut-off’ because no energy will be released. Mean-free-length l is then almost equal to the size of motor particle b . Therefore, the probability of motor particle adjacent to free volume particle without particle interactions, p_2 , is inversely proportional to the third power of size of motor particle b ($p_2 = \frac{c}{b^3}$). Then, the parameter r could be defined as:

$$r = \frac{p_1}{p_2} = \frac{c/l^3}{c/b^3} = \frac{b^3}{l^3} \quad (5)$$

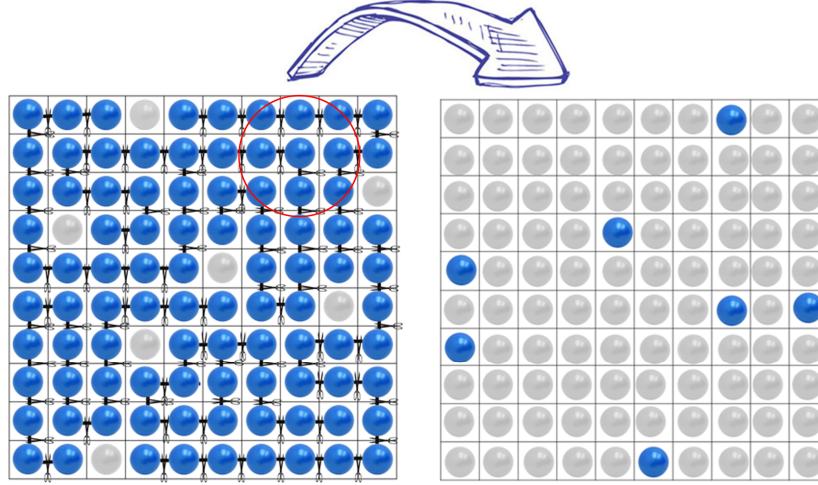


Fig. 2 RLM before and after “cut-off” (in the case of $\theta = 1$)

The left graph represents the RLM before “cut-off” thought experiment. The right graph represents that all the chain bond links are cut-off by micro-scissors and the whole lattice expands.

For $\theta = 1$, let us figure out the meaning of parameter r at the glass transition point. The free volume of the system could be regarded as equivalent to the “free volume” contributed from the movements of motor particles^[13–17]. From the mean-free-length model, free volumes before and after expansion are $n_1 b^3$ and $n_2 x l^3$, respectively. Considering the whole lattice as a constrained system, the free volume expands 36 times (Based on analytic mechanics, 6 comes from the increase of activation mode and another 6 comes from the reduction of centroid mass and centroid displacement; details see Appendix) after “cut-off” due to the increasing mobility of motor particles. Then $n_2 x l^3 = 36 n_1 b^3$. Thus:

$$r = \frac{b^3}{l^3} = \frac{n_2 x b^3}{n_2 x l^3} = \frac{n_2 x b^3}{36 n_1 b^3} = \frac{1 - \beta}{36 \beta} \quad (6)$$

Combining Eq. (6) with Eq. (4) it results:

$$\frac{3}{1 - \beta} = 2 \frac{1 - \beta}{\beta} \frac{1}{36} + 1 \quad (7)$$

The simple form of Eq. (7) is:

$$\beta = \frac{-19 + 3\sqrt{42}}{17} \approx 2.6\% \quad (8)$$

2.6% is the number that WLF equation needs for years and the direct proof to Flory’s iso-free volume (note that initial fitting with WLF equation on experimental data is 2.5%). Yet it may be the most general factor of glass transition and now is proved rigorously. Let us discuss the neighborhood of entropy to make the physics meaning of 2.6% clear. Combining Eq. (6) with Eq. (1), the entropy S would be:

$$S = \frac{k}{r} \ln \left(\frac{n_0!}{\left(n_0 - \frac{(1 - \beta)^2 n_0}{18 \beta (2 + \beta)} \right)!} \right) + k \theta n_2 (x - 1) \ln \left(\frac{z \theta - 1}{n_0} \right) \quad (9)$$

The neighborhood of temperature at the point of $\beta = \frac{-19+3\sqrt{42}}{17} \approx 2.6\%$ can be defined as $(T_{2.6\%} - \delta, T_{2.6\%}, T_{2.6\%} + \delta)$, which is equivalent with the neighborhood of free volume β $(2.6\% - \delta, 2.6\%, 2.6\% + \delta)$. Thus, the neighborhood of entropy is calculated to be S $(\infty, \frac{k}{r} \ln(n_0!) + k\theta n_2(x-1) \ln\left(\frac{z\theta-1}{n_0}\right), \text{Finite value})$. The appearance of this infinite value indicates that $\begin{cases} y=0 \\ \theta=1 \end{cases}$ is only a temperature point but not an area. And now, we accomplished the demonstration of $T_1 = T_g = T_{2.6\%}$.

Prediction of RLM: Glass Transition for General Materials

In order to analyze the glass-transition process of general materials, the particles with 0 or 1 chain-bond link are neglected, because these particles can only serve as a plasticizer. The motor particles with 2 chain-bond links are the main participants which we refer to as motor particles, while the motor particles with 3 or more chain-bond links are named dead particles due to restricted motion. We consider the whole system consisting of n_1 free volume particles and n_2 “variable chains”. To be simpler without loss of generality, the percentage of motor particles on each variable chain is a constant ζ . Thus $n_0 = n_1 + (\theta x + \theta' x') n_2 = n_1 + n_2 \theta x / r_2 = n_1 + n_2 \theta' x' / (1 - r_2)$, where x' is the number of dead particles in one single chain, $\theta' = \frac{v_{dp}}{v_f}$ (v_{dp} is the volume of single dead particle). Then, the entropy for general materials (derivation is the same as for linear chain) is:

$$S = \frac{k\zeta}{r} \ln\left(\frac{n_0!}{(n_0 - r\theta n_2 x / \zeta)!}\right) + \frac{k(1-\zeta)}{r'} \ln\left(\frac{n_0!}{[n_0 - r'\theta' n_2 x' / (1-\zeta)]!}\right) + k\theta n_2(x-1) \ln\left(\frac{z\theta-1}{n_0}\right) + k\theta' n_2(x'-1) \ln\left(\frac{z\theta-z_0}{n_0}\right) + kn_2 \ln(C_{\theta x + \theta' x'}^{\theta x}) \quad (10)$$

The last term is a constant, $(z_0 + 1)$ is number of chain bond links of a dead particle. The part of entropy contributed from motor particles, “motor part”, is:

$$S_1 = \frac{k\zeta}{r} \ln\left(\frac{n_0!}{(n_0 - r\theta n_2 x / \zeta)!}\right) + k\theta n_2(x-1) \ln\left(\frac{z\theta-1}{n_0}\right) \quad (11)$$

And so is the “dead part”:

$$S_2 = \frac{k(1-\zeta)}{r'} \ln\left(\frac{n_0!}{[n_0 - r'\theta' n_2 x' / (1-\zeta)]!}\right) + k\theta' n_2(x'-1) \ln\left(\frac{z\theta-z_0}{n_0}\right) \quad (12)$$

Obviously, the “motor part” and “dead part” are independent of each other. Here, the demonstration that “dead particles” cannot participate in glass transition is given by the reduction to absurdity. Assuming that the dead particles could take part in glass transition, the transition temperature of dead particles is different from the one of motor particles because of the independence of S_1 and S_2 . Thus, the “dead part” entropy S_2 determines this transition and hence means we could model the transition in such a system that only contained dead particles and could be described by S_2 . So, from the derivation above, there must be $\frac{3}{1-\beta} = 2\frac{1-\beta}{\beta} \frac{1}{g} + 1$, and $g = \frac{\text{mobility of particles after cut-off}}{\text{mobility of particles before cut-off}}$. But after cut-off, the system is zero-dimensional linked and its degree

of freedom is $6^{n_2x'}$. And before cut-off, the system is usually three-dimensional or sometimes two-dimensional linked one, and the degree of free volume is about $3n_2x'$, which is too small. Thus the parameter $g = 0$, which means that the equation $\frac{3}{1-\beta} = 2\frac{1-\beta}{\beta} \frac{1}{g} + 1$ does not really exist and neither does the transition. Therefore, glass-transition can only take place in a system of plenty of motor particles with just two chain bond links and the nature of glass-transition for general materials is then of course same as linear polymeric chains.

Glass transition of general materials occurs in motor particles only. From Eqs. (11) and (12), the Eq. (7) of free volume and Eq. (6) at glass transition would change into Eqs. (13) and (14):

$$\frac{\beta + 2 + \theta' \frac{n_2x'}{n_0}}{2 - 2\left(\beta + \theta' \frac{n_2x'}{n_0}\right)} = r \quad (13)$$

$$r = \frac{1 - \beta - \theta' \frac{n_2x'}{n_0}}{36\beta} \quad (14)$$

Combining Eq. (13) with Eq. (14), it results:

$$\beta = \frac{1}{17}(-19 - 8 \times \rho + 3\sqrt{3}\sqrt{14 + 10 \times \rho + 3 \times \rho^2}) \quad (15)$$

where $\rho = \theta' \frac{n_2x'}{n_0}$, the occupation percentage of dead particles.

Equation (15) is quantitatively illustrated in Fig. 3(a), which is essentially the phase diagram of glass transition of general materials. Here glass transition is caused and controlled by entropy, which shows no significant structural change. However, there may be another kind of glass transition which is caused by energy gap, which can be explained by “crystal kernel”-like theories.

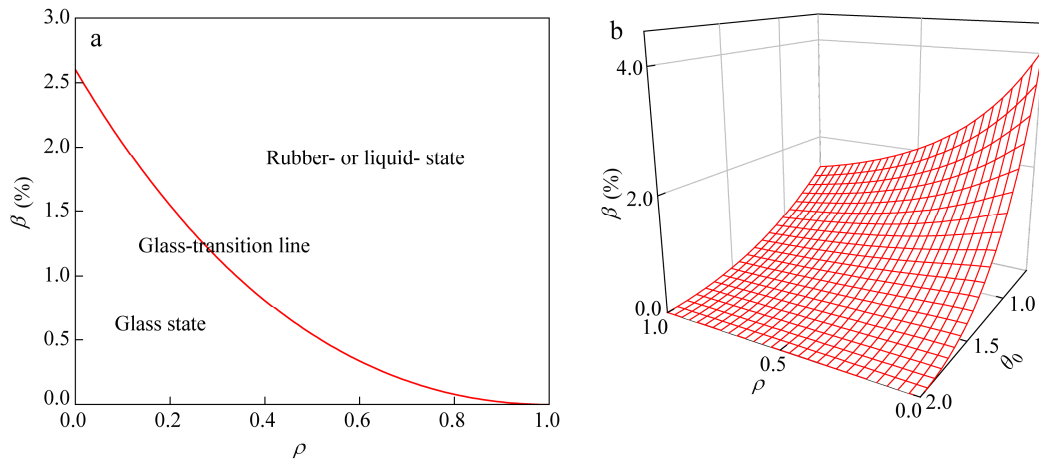


Fig. 3 Prediction: (a) Phase diagram of glass-transition explained by Eq. (15); (b) Phase diagram of glass-transition explained by Eq. (18)

β and ρ present percentages of free volume and dead particles, respectively; θ is the relative free volume size which allows motor particles to transport.

Prediction: Glass Transition under External Field

The influence of external force field on glass transition can also be explained by our RLM. Let us extend the

normal pressure RLM to a system under positive or negative pressure. Back to Fig. 1(a), if the external force is oriented or partly oriented^[50–53] (or thermomechanical history^[54]), the arrangements should be rather different from what has been shown. Here, we only discuss an easier situation: disoriented external force field or static pressure.

Free volume is sensitive to pressure because the equilibrium process described by Fig. 1(b) would be harder under positive pressure (or easier under negative pressure). As mentioned earlier, the definition of $\theta = 1$ corresponds to $B = 1$ in Vogel-Tammann-Fulcher (VTF) equation $\eta = Ae^{B/(T-T_0)}$ or Doolittle's equation $\eta = Ae^{BV_{hc}/V_{fcc}}$ under normal pressure P_e , where the activation energy $\Delta E_{p_e} = kT_{p_e}$ is just sufficient to drive the exchange of motor particle positions. Assuming the work imposed by pressure P is W_p , the activation energy required to drive motor particle motion can be expressed as:

$$\Delta E_p = kT_{p_e} - W_p = kT_p \theta_p \quad (16)$$

Therefore, the precondition of free volume size which allows motor particles to transport (similar to Doolittle's definition) changes from 1 to θ_p . Interestingly, the entropy function shows no change, but the line between glass and liquid states changes from $\begin{cases} y=0 \\ \theta=1 \end{cases}$ to $\begin{cases} y=0 \\ \theta=\theta_p \end{cases}$. With this new judgment condition for glass transition, we obtain

$$\frac{1-\beta-\rho}{36\beta\theta_p} = \frac{\frac{\theta_p}{1-\beta-\rho} - \frac{1}{3}}{\theta_p - \frac{1}{3}} \quad (17)$$

Thus we get Eq. (18) and a much useful phase diagram of glass transition is presented in Fig. 3(b).

$$\beta@T_g = \frac{1-\rho+15\theta_p-15\rho\theta_p-54\theta_p^2+6\sqrt{3}\sqrt{2\theta_p^2-5\rho\theta_p^2+3\rho^2\theta_p^2-15\theta_p^3+15\rho\theta_p^3+27\theta_p^4}}{1+33\theta_p} \quad (18)$$

From Eqs. (16) and (18), when the pressure is positive, W_p is positive, $\theta_p < 1$ and decreases with the increase of pressure, and the iso-free volume point increases with pressure increase. The situation of negative pressure is on the opposite.

DISCUSSION

Based on the entropy analysis, we demonstrate that glass transition is a second order thermodynamic phase transition, which is in line with the theory of Adam-Gibbs but deduced out from different theoretical approach. The iso-free volume of 2.6% for glass transition does exist for linear polymer at normal condition, while system containing dead particles or at positive or negative pressure may have different fraction of free volume at glass transition. As the concept of iso-free volume at glass transition has been questioned from different aspects, we discuss some issues related to the fitting of WLF for obtaining free volume of 2.5%, which have been systematically analyzed in recent perspectives.

The first issue challenges WLF's iso-free volume is related to the value of B in Doolittle's equation: $\eta = Ae^{BV_{hc}/V_{fcc}}$. Doolittle's constant is on the order of unity and WLF simply takes B to be 1. The parameter $B = 1$ means that the motion energy of motor particle is just enough to cross the energy gap of viscosity, which corresponds to $\theta = 1$. In other words, the sizes of single free volume particle and motor particle are equal. The calculation of iso-free volume of 2.6% at glass transition for linear chains is precisely based on $\theta = 1$ at normal pressure. In the WLF's calculation, free volume at glass transition is related to C_1 , while C_2 is assumed to connect the difference between thermal expansion coefficients above and below glass transition temperature,

where C_1 and C_2 are assumed to be constants in WLF equation $\ln\left[\frac{\eta}{\eta_g}\right] = \frac{-C_1(T-T_g)}{C_2+T-T_g}$. As discussed by

Angell^[55], C_1 is rather constant about 17 ± 2 , which supports the existence of iso-free volume at glass transition. The second challenge on the WLF's iso-free volume at glass transition is related to C_2 , which does not keep a universal constant for different polymers. The variation of C_2 is attributed to fragility of different polymers explained by Angell^[55]. WLF relates C_2 to the difference between thermal expansion coefficients above and below glass transition temperature, which, however, may also be affected by reference temperature. The variation or the physical attribution of C_2 seems to be not affecting the universality of constant C_1 and the iso-free volume at glass transition. Note that the iso-free volume of 2.6% at glass transition is only valid for linearly linked motor particle system under normal pressure (without dead points and external force), which, nevertheless, still has its universality for diverse materials as WLF equation suggested.

The fraction of free volume β at glass transition indeed varies with the percentage of dead particles ρ and external field like pressure as illustrated in Fig. 3, which demonstrates that free volume is not the single parameter to determine glass transition. This is in line with the suggestion of local correlated lattice model and may also account for experimental observations on variation of free volume at glass transition. Under high pressure, glass transition may occur at lower β . Thus the concept of iso-free volume may indeed exist but only for linear systems under specific conditions. Taking into account of dead particle and pressure, free volume at glass transition is not a single "iso-free volume point" but rather a curved plane in the space of free volume-dead particle-pressure. Experiments show that oriented force like tensile deformation may also enhance mobility of particles, which can activate flow. As current RLM is based on the equilibrium consideration, how to incorporate directional forces or non-equilibrium field in the model is still a challenge, which is still waiting for further exploring.

CONCLUSIONS

The mechanism of glass transition is studied with a relaxed lattice model (RLM), where the influence of particle interaction on entropy is taken into account. Analysis on entropy shows that glass transition is a second order phase transition. The free volume of perfect one-dimensional linked chain system at glass transition is 2.6% under equilibrium pressure, which is amazingly consistent with the iso-free volume fitted on experimental data with WLF equation. To emphasize here, the 2.6% of RLM could be not only applied to polymers, but also used in other material fields just like WLF equation. Free volume at glass transition is further discussed to vary with the multiple link restrictions or the content of dead particles like branched or crosslinked polymers and pressure, which indicates that free volume is not the single parameter controlling glass transition. Based on the result a phase diagram of glass transition is predicted in free volume-dead particle-pressure.

APPENDIX

The old lattice model only includes the translational freedom, and the early free volume is defined from that angle. But our excess free volume is based on White and Lipson's lately work published on Macromolecules, in which all the freedoms of motions could contribute a part of free volume due to the first principle model of locally correlated lattice (LCL)^[28, 29].

Because the number of particles of each chain is very large, we ignore the end effect. Two assumptions are proposed to simplify the deduction without loss of generality. The assumptions will not change the final mathematical answer if the end effect is ignored, but would make the deduction easier.

Assumption 1:

Free volume is contributed by all the motor particles, and each motor particle has the same kinetic energy and contributes the same part of free volume.

Assumption 2:

The degree of freedom of each motor particle is the same, and after choosing the axis, the free volume contributed by each freedom is the same.

Deduction:

The total free volume could be expressed as:

$$V_f = n_f \times v_{0f} \quad (19)$$

V_f is the total free volume, n_f is total degree of freedom, v_{0f} is the volume contributed by each freedom. The number of particles is n_2x .

The expansion rate could be:

$$\frac{V_{f, \text{ after cut-off}}}{V_{f, \text{ before cut-off}}} = \frac{n_{f, \text{ after cut-off}}}{n_{f, \text{ before cut-off}}} \times \frac{v_{0f, \text{ after cut-off}}}{v_{0f, \text{ before cut-off}}} \quad (20)$$

(a) The $\frac{n_{f, \text{ after cut-off}}}{n_{f, \text{ before cut-off}}}$

After cut-off, every particle is free, and the degree is 6, which includes 3 kinds of independent translational motions, 2 kinds of independent rotations and 1 kind of vibration. The number of particles is n_2x .

So, we get $n_{f, \text{ after cut-off}} = 6^{n_2x}$.

We can reconnect the cut-off particles to trace the freedom before cut-off. When the first particle was reconnected with the second particle, 6 independent constitutive equations were built; 3 of them described the balance of translational motions of the two particles, 2 rest of them described rotation behaviors, and the last one revealed the total vibration. So, the degree of freedom changed from 6^2 to 6^{2-1} . Then, we consider that the third particle was reconnected. From the lattice model, the motion of the third particle is independent with the centroid of the first particle and the second particle. So, the degree of freedom changed from 6^{2-1} to 6^{3-1} . Reconnecting all the rest of particles, we can get: $n_{f, \text{ before cut-off}} = 6^{n_2x-1}$. Therefore,

$$\frac{n_{f, \text{ after cut-off}}}{n_{f, \text{ before cut-off}}} = 6 \quad (21)$$

(b) The $\frac{v_{0f, \text{ after cut-off}}}{v_{0f, \text{ before cut-off}}}$

Considering the micro-scissor thought experiment, the particles would expand after cut-off with works provided by micro-scissor model. So, the kinetic energy of each motor particle is the same in those three states:

State I: the equilibrium state before cut-off, kinetic energy is E_I , position function is R_I , free volume contributed by motion of one freedom is v_{0f-I} ;

State II: the non-equilibrium state just after cut-off, kinetic energy is E_{II} , position function is R_{II} , free volume contributed by motion of one freedom is v_{0f-II} ;

State III: the equilibrium state after expansion, kinetic energy is E_{III} , free volume contributed by motion of one freedom is v_{0f-III} .

Translations between different states:

State I to State II: Cut-off, equilibrium state to non-equilibrium state, dynamic process without change of kinetic energy.

State II to State III: Reversible change or quasi-static process, expansion without change of kinetic energy, non-equilibrium state to equilibrium state.

Therefore:

$$\left\{ \begin{array}{l} E_I = E_{II} = E_{III} \\ R_I = R_{II} \end{array} \right. \quad \text{II} \xrightarrow{\text{Reversible expansion}} \text{III} \quad (22)$$

E is kinetic energy, R is particle position. Because of $\text{II} \xrightarrow{\text{Reversible expansion}} \text{III}$, from thermodynamic laws, the volume contributed by one motion of freedom of state III (v_{0f-III}) is the largest volume of all states. For state II is non-equilibrium one but has the same structure with state III, every freedom in state II has chance to reach such large free volume as (v_{0f-III}). Therefore:

$$v_{0f-III} = \text{Max}(v_{0f-II})$$

The contribution of each rotational freedom can be expressed as: $C_t u^2 L$, where u is velocity, L is the length of axis. C_t is a parameter representing dynamic volume of motor particle, which is proportional to the square of relaxation time (τ^2) of particle. At non-equilibrium condition, the relaxation time τ is time and particle dependent. When the relaxation time of one particle reaches its maximum at equilibrium or any other states in chance, C_t gets its maximum C_e , at which the maximum contribution of each rotational freedom is $C_e u^2 L$. Because of no change of chemical structure and physical parameters in the micro-scissor thought experiment, C_e is the same at states I–III.

At the end, we get:

$$\left\{ \begin{array}{l} E_I = E_{II} = E_{III} \\ R_I = R_{II} \\ v_{0f-III: \text{rotation}} = C_e u_{III}^2 L_{III} = \text{Max}(v_{0f-II}) = \text{Max}(C_t u_{II}^2 L_{II}) \\ C_{e@I} = C_{e@II} = C_{e@III} \end{array} \right. \quad (23)$$

For the first particle, we choose the second motor particle to be its origin point to analyze the free volume of state II and then use the equation set (23) to get:

$$\frac{v_{0f: \text{after cut-off}}}{v_{0f: \text{before cut-off}}} = \frac{v_{0f-III}}{v_{0f-I}} = \frac{\text{Max}(v_{0f-II})}{v_{0f-I}} \quad (24)$$

Considering the mode of which the first motor particle revolved around the second motor particle, after cut-off the equivalent centroid's mass changed from $\left(m + m + \frac{1}{2}m + \frac{1}{4}m + \dots\right)$ to m (m is the mass of one motor particle) and the axis of rotation changed from half of chain bond to whole chain bond. The $(m + m)$ is the total mass of the first and the second particles, the $\frac{1}{2}m$ is the correction of equivalent mass of the third particle because the motion of the third particle influenced the position of the second particle or origin point, and $\frac{1}{4}m$ is the correction of the fourth particle, and so on. The lengths of rotation axis of the centroid before cut-off and just after cut-off are $L/2$ and L , respectively.

Therefore, considering the $E_I = E_{II} = E_{III}$:

$$\frac{1}{2} \left(m + m + \frac{1}{2}m + \frac{1}{4}m + \dots \right) u_I^2 = \frac{1}{2} m u_{II}^2 \quad (25)$$

u_I and u_{II} are velocities of states I and II. Combining (25) and (24), for the first particle:

$$\frac{v_{0f: \text{after cut-off}}}{v_{0f: \text{before cut-off}}} = \frac{v_{0f-III}}{v_{0f-I}} = \frac{\text{Max}(v_{0f-II})}{v_{0f-I}} = \frac{C_e u_{II}^2 L}{C_e u_I^2 L/2} = \frac{C_e 3u_I^2 L}{C_e u_I^2 L/2} = 6 \quad (26)$$

For the second particle, pick the third particle to be its origin point, and we get the same result of 6. Neglecting the few motor particles at the tail of the chains (the ratio varies from 6 to 4), the ratio $\frac{v_{0f: \text{after cut-off}}}{v_{0f: \text{before cut-off}}}$ for all particles is 6.

Combining Eqs. (21) and (26) with Eq. (20), the total expansion rate is

$$\frac{V_{f: \text{after cut-off}}}{V_{f: \text{before cut-off}}} = \frac{n_{f: \text{after cut-off}}}{n_{f: \text{before cut-off}}} \times \frac{v_{0f: \text{after cut-off}}}{v_{0f: \text{before cut-off}}} = 6 \times 6 = 36 \quad (27)$$

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