How the free volume reduction freezes bulk amorphous lattice polymers

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The classical free volume theory of polymer glass transition assumed that the reduction of free volume would stop at a critical fraction around 0.025 upon glass transition in bulk amorphous polymers. The well-known WLF equation for the non-Arrhenius temperature-dependent viscosity above the glass transition temperature was thus derived. It is so far not yet clear whether there exists such an intrinsic frozen transition upon the reduction of only free volume. We hereby performed dynamic Monte Carlo simulations of bulk lattice polymers under athermal conditions, in which single vacant lattice sites serve as free-volume elements in the micro-relaxation model for mimicking the Brownian motions of polymers in the lattice space. We observed that the averaged diffusion constants of polymers linearly decay into zero upon the gradual reduction of free volume fractions down to zero. No sudden frozen transition occurs around the free volume fraction 0.025 as commonly observed in the practical experiments and the free volume theories, which implies other frozen mechanisms beyond the present case. Here the free-volume fraction was treated as a fixed geometric parameter, and volume relaxation was not included. The linear dependence could be attributed to the thermal fluctuation theorem of simple liquids, as evidenced by the linear dependence of diffusion constants on the reciprocal chain lengths under constant free volume fractions. Our observations demonstrated that, in this athermal lattice model, free-volume reduction alone does not generate an intrinsic frozen transition in bulk amorphous polymers.

Keywords: Polymer; Glass transition; Free volume theory; Diffusion coefficient; Dynamic Monte Carlo methods

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1 Introduction

The glass transition in polymeric materials denotes the macroscopic mechanical transformation of a polymer from the rubbery state to the glassy state. Early in 1950, Fox and Flory hypothesized [1] that the total volume of a liquid or an amorphous polymer could be phenomenologically decomposed into two distinct contributions: an occupied volume V_{occ} which was the volume physically excluded by the molecules themselves, and a free volume $V_f = V - V_{occ}$ which represented the unoccupied space distributed as irregular cavities or "holes" among the molecules. The fundamental premise was that molecular transport processes—including diffusion, viscous flow, and configurational relaxation—could occur only when a molecule or a polymer segment encountered an adjacent free-volume cavity of sufficient size to accommodate the displacement. Consequently, the rate of molecular transport was governed not only by temperature, but also by the fraction of free volume available to permit such displacements. The quantitative foundation of the theory was laid by Doolittle, who found empirically that [2] the viscosity of simple liquids such as *n*-alkanes followed an exponential dependence on

$$\eta = A \exp(B/f) \tag{1}$$

the relative free volume fraction $f = V_f/V_{occ}$, as given by

where A and B were empirical constants, with B typically closed to unity. The Doolittle equation formalized the central concept that viscosity increased precipitously and tended toward divergence as the available free volume approached zero: a small decrease in f produced a large increase in η. Cohen and Turnbull [3] subsequently provided a statistical-mechanical justification for this empirical law by assuming that molecular transport occurred only when a molecule encountered a void exceeding some critical size v^*, and that free volume was redistributed among molecules without energy cost. On the basis of these two simplifying assumptions, their model yielded the Doolittle functional form, thereby providing the theory with a more robust microscopic justification. Fox and Flory subsequently employed this framework in their analysis of polymer glass transition. They proposed that at high temperatures above the glass transition temperature T_g, free volume decreased linearly with the decrease of temperature, affording sufficient spatial freedom for the diffusion of polymer segments. Below T_g, the residual free volume was frozen into a constant fraction, no longer sufficient to sustain the cooperative motion of polymer segments.

By combining the Doolittle equation with the assumption that f freezes at a constant value f_g below T_g, Williams, Landel and Ferry made use of the empirical Doolittle equation for the free-volume dependence of viscosity η to derive the commonly referred WLF equation [4], as given by

$$log\frac{\eta(T)}{\eta(T_g)} = \frac{-C_1(T-T_g)}{C_2+T-T_g} \quad (2)$$

in which C_1 and C_2 denoted similar constants for more than 50 polymeric materials. The fitting constants provided an iso-free-volume fraction $f_g \approx 0.025$ at the glass transition temperature. This threshold implies a sudden reduction of diffusion coefficient of polymer chains as expected around the free volume fraction 0.025 for a common glass transition in the lattice polymer systems. The free volume theory was prevailing very well. However, it is important to recognize that the iso-free-volume hypothesis is a phenomenological assumption, not a first-principles result. It was introduced specifically to rationalize the form of WLF equation, and its physical origin has not yet been validated. The iso-free volume fraction remains as a hot issue in the literatures [5–13]. Berthier et al. provided a comprehensive overview of recent algorithmic advances aimed at the improving sampling efficiency and the accelerating equilibration, focusing on replica-exchange methodologies, cluster-based and swap Monte Carlo algorithms, as well as a range of related computational techniques [14]. However so far, whether there exists an intrinsic frozen transition of bulk amorphous polymer upon the reduction of free volume around its fraction 0.025 has not yet been clear.

To sum up, free-volume theory posited that polymer diffusion proceeds via the presence of monomer-sized vacancies, which underwent exchange with monomeric units. Above T_g, free volume decreased with decreasing temperature but still permitted segmental motion. Below T_g, the residual free volume was assumed to freeze at a critical fraction $f_g \approx 0.025$, leading to a sharp dynamic arrest. This iso-free-volume fraction constituted a

central assumption underlying WLF equation and its theoretical relationship to VFT equation (Vogel-Fulcher-Tammann equation, which will be mentioned in the *Result and Discussion* part). However, in real glass-forming polymer systems, densification is concomitant with modifications in intermolecular interactions, chain-packing efficiency, local activation energy barriers, and the extent of cooperative molecular rearrangements. Therefore, whether free-volume reduction alone could produce a frozen transition remains an open question.

The dominant advantage of the lattice models (including Ising model) is their ability to manipulate the entropy and enthalpy contributions in the condensed matter systems and to achieve a highly transparency control over the relevant parameters. Dynamic Monte Carlo simulations of lattice polymer systems have been developed with the micro-relaxation model to reproduce Brownian motions of lattice polymers, by making use of the single vacant lattice sites as free volume to swap with the occupying monomers, in company with local sliding diffusion along the chain if necessary [15]. Free-volume sites, in this work, refer to single vacant lattice sites created by removing polymer chains from a fully occupied lattice; they are not isolated point defects. The athermal lattice model isolates free volume as a geometric variable and deliberately excludes molecular interactions, chain stiffness, and volume relaxation. Therefore, the classical free volume theory demands the dynamic Monte Carlo simulations to check out the frozen transition of lattice polymers around the iso-free volume fraction 0.025.

In this work, we performed dynamic Monte Carlo simulations of bulk lattice polymers with free volume fractions decreasing over 0.025 under athermal conditions. We

observed that polymer diffusion coefficients showed no sudden transition around this free volume fraction. The free volume theory just made up such an assumption in order to derive WLF equation to describe the non-Arrhenius temperature dependence of viscosity in the highly elastic states of bulk amorphous polymers. The aim of this study was to evaluate whether a reduction exclusively in the free-volume fraction within an athermal bulk lattice polymer system could trigger an abrupt vitrification transition near $f \approx 0.025$.

2 Simulation techniques

We employed a discretized lattice framework of 64*64*64 cubic sites to accommodate the bulk polymer system with each chain containing 128 monomers. Each monomer and each free-volume element were separately assigned to the occupied and void single vacant lattice sites. In this simulation study, the cubic lattice spacing was adopted as the fundamental unit of length, and one Monte Carlo cycle was defined as the unit of time, corresponding to the total number of trial moves of micro-relaxation for all the monomers.

Since the fully occupation number of chains could be 2048, we began with the highest occupation system holding 2047 chains with the free volume fraction 0.00048828125, and relaxed the preset polymers under athermal conditions for 1×10^8 Monte Carlo cycles (MCs). This relaxation time was enough long for the preset ordered system to relax into equilibrium disordered state, as demonstrated in Figure 1. We then removed certain amounts of polymer chains from the higher occupation systems (smaller free volume fractions) and made athermal relaxation into the random coil states as well. A

series of free volume fractions spanned from 0.00048828125 to 0.091796875, crossing over the expected threshold 0.025. The free-volume fraction f was defined as the number of vacant lattice sites divided by the total number of lattice sites. It was implemented as a fixed geometric parameter by removing a prescribed number of polymer chains; it did not represent an equilibrium free volume governed by temperature or pressure, and volumetric relaxation was not modeled.

The microscopic relaxation of monomers was facilitated by more vacancy sites, which provided locations where monomers could swap in and out, consequently relieved chain-induced stress and decreased the total system energy. We introduced the excluded-volume effects in the micro-relaxation of polymers and prohibited simultaneous occupations of the same spatial position by two monomers, as well as spatial overlap of two distinct bonds. Periodic boundary conditions were applied throughout our simulation.

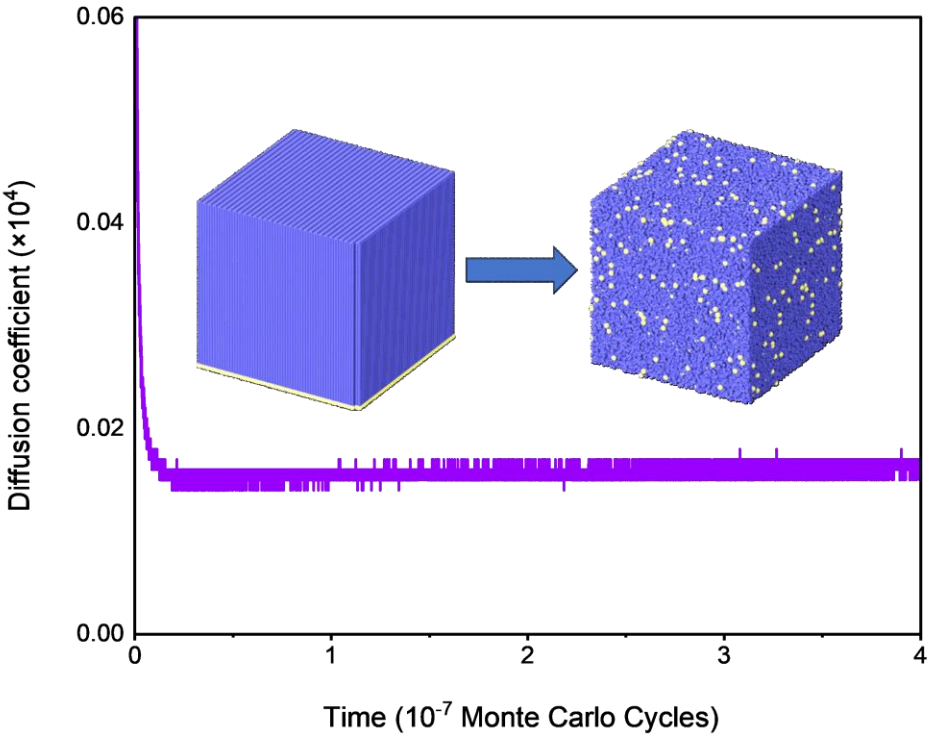


*Figure 1: Time evolution curve of segmental-time diffusion coefficients for the relaxation into the random coil state of the system with free volume fraction 0.00048828125 (only single 128-mer chain of 2048 chains removal from the fully occupation in 64*64*64 cubic lattice box). The inset snapshots demonstrate the preset ordered state and the relaxed random coil state. The yellow dots denote the chain ends of the polymer, and the blue elements represent the repeating units (monomers) along the 128-mer chains.*

The diffusion coefficient D of systems at each time period t (here 1000 MCs) was calculated by the mean square displacement of coil mass center $\overrightarrow{MC_i(t)}$ of the i^{th} chain at the time period t with n as the total number of chains, as given by

$$D = \frac{\sum_{i=1}^{n}[\overrightarrow{MC_i(t)} - \overrightarrow{MC_i(0)}]^2}{6tn} \quad (3)$$

The steady-state diffusion coefficient was determined as follows. For each system, $\boldsymbol{D(t)}$ was calculated over periods of 1000 MCs. When $\boldsymbol{D(t)}$ showed no systematic drift over at least $[\boldsymbol{N}]$ consecutive periods, the system was regarded as reaching a plateau. The reported $\boldsymbol{D}$ was averaged over these plateau periods. The error bars represent the standard deviation of the period-averaged $\boldsymbol{D}$ values within the plateau region. Unless otherwise stated, $[\boldsymbol{N}] = 100000$MCs.

3 Results and discussion

We conducted simulations on systems characterized by free volume fractions spanning from 0.00048828125 to 0.091796875, and calculated the corresponding diffusion coefficients as a function of time, as the results summarized in Figure 2. The shaking signal in the vertical direction reflected the thermal fluctuations in the system, and the amplitudes of the noise were also influenced by the free volume fractions: the lower the occupation density, the larger the fluctuations the system will experience at a given time.

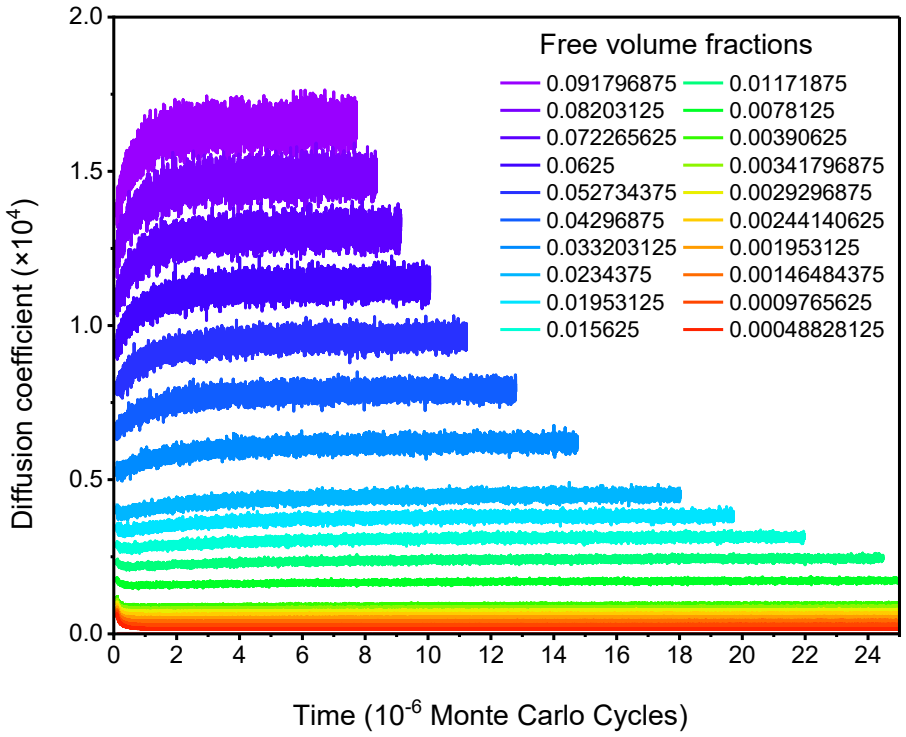


Figure 2: Time evolution of the diffusion coefficients at each period of 1000 MCs averaged over all the chains in the systems with various free volume fractions as labeled. The plateau value was identified when the period-averaged $D(t)$ showed no systematic drift over successive 100000 MCs periods. The average over the plateau region was taken as the steady-state diffusion coefficient.

In Figure 2, all of these diffusion coefficients eventually yield plateau values for time average. The isolated peak signals observed during the time evolution represented random fluctuations in the small systems, yet the plateau values were pronounced for all

the systems. We therefore interpreted these averaged final plateau values as the diffusion coefficients of the system in their steady states. This finding supports the robustness and reliability of our simulation approach.

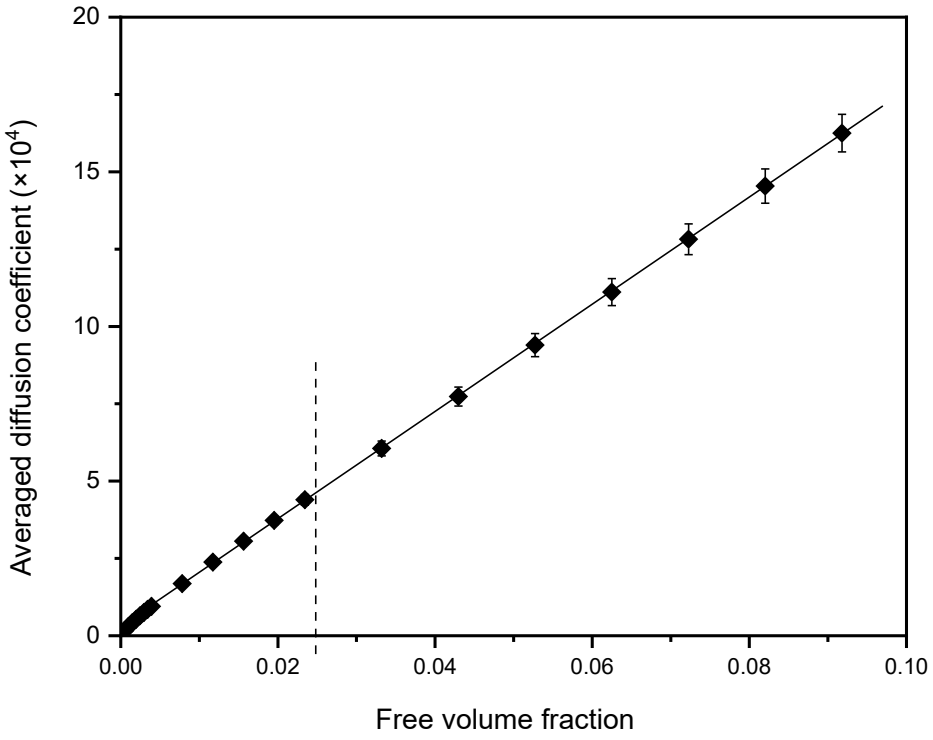


Figure 3: Averaged diffusion coefficients of bulk lattice polymers as a function of free-volume fraction. The dashed vertical line marks the iso-free-volume fraction $f = 0.025$. *Error bars are standard deviations of the period-averaged diffusion coefficients within the plateau region. The solid straight line is drawn as reference.*

In Figure 3, one can clearly see that the diffusion coefficients linearly decay with the free volume fraction down to the zero point. There is no occurrence of sudden frozen

transition around the free volume fraction 0.025, implying the failure of the fundamental assumption of the classical free volume theory in the simple athermal polymer systems. For the reflection of microscopic mechanisms of glass transition, the lattice model apparently needs other factors beyond the free volume. For instance, our recent MC simulations of stress relaxation of bulk lattice polymers demonstrated the frozen transition from high-temperature linear to low-temperature nonlinear viscoelasticity in bulk amorphous polymers [16-19].

The linear decay shown in Figure 3 persists down to $f = 0$. No abrupt change in D is observed at $f = 0.025$. These results indicate that, within the present athermal lattice model, a reduction in free volume alone is insufficient to induce a sharp freezing transition. This behavior is consistent with that of a simple liquid governed by Einstein's thermal fluctuation theorem. According to the well-known thermal fluctuation theorem, the averaged diffusion coefficient is given by

$$D = \frac{kT}{N\xi} \tag{4}$$

where *k* Boltzmann's constant, *T* temperature, *N* the number of monomers on each linear polymer chain, ξ the friction coefficient of each monomer and *f* the free volume fraction. In the lattice micro-relaxation model, a monomer moved by exchanging with a neighboring vacant site. The friction coefficient of each monomer ξ could be proportional to the reciprocal swapping probability, while the swapping probability was proportional to the free volume fraction *f*. In this sense, the higher free volume fraction allows the

$$D \propto \frac{kT}{N} f \tag{5}$$

higher extent of thermal fluctuations, resulting in the higher diffusion coefficient. Indeed, as shown in Figure 2, the segmental-time diffusion coefficients are fluctuating stronger with higher free volume fractions. At low f, the swapping probability is approximately proportional to f, so $\zeta \propto 1/f$. Therefore,

which rationalizes the linear dependence of D on f in Figure 3. This relation is expected to hold in the low-f, randomly distributed vacancy, local-swapping-dominated regime. At higher f, vacancy clustering, cooperative motion, and nonlinear effects might become important. Strictly speaking, D measured here is the long-time center-of-mass diffusion coefficient of chains. It should not be equated with segmental relaxation time, zero-shear viscosity, or the structural relaxation time that defines the glass transition. In experimental glass-forming polymers, the dramatic slowing down near $T_g$is usually probed by segmental relaxation, viscosity, stress relaxation, dynamic heterogeneity, and cooperative rearrangement size. Therefore, the absence of a sudden change in D at $f = 0.025$ does not imply that all dynamic quantities are free of transitions. These observations indicate that center-of-mass diffusion in the present athermal lattice model is consistent with simple-liquid behavior. For future investigations of free-volume mechanisms underlying the glass transition, more informative observables include the segmental mean-square displacement, bond-vector autocorrelation, stress relaxation modulus, zero-shear viscosity, and measures of dynamic heterogeneity.

Because the present simulations are performed in lattice units under athermal conditions, a direct quantitative comparison with experimentally measured diffusion coefficients is not warranted.

As additional evidence for the simple liquid holding the thermal fluctuation theorem, the diffusion coefficients D exhibited the reciprocal dependence of chain lengths N under constant free volume fraction in our further simulations, as shown in Figure 4.

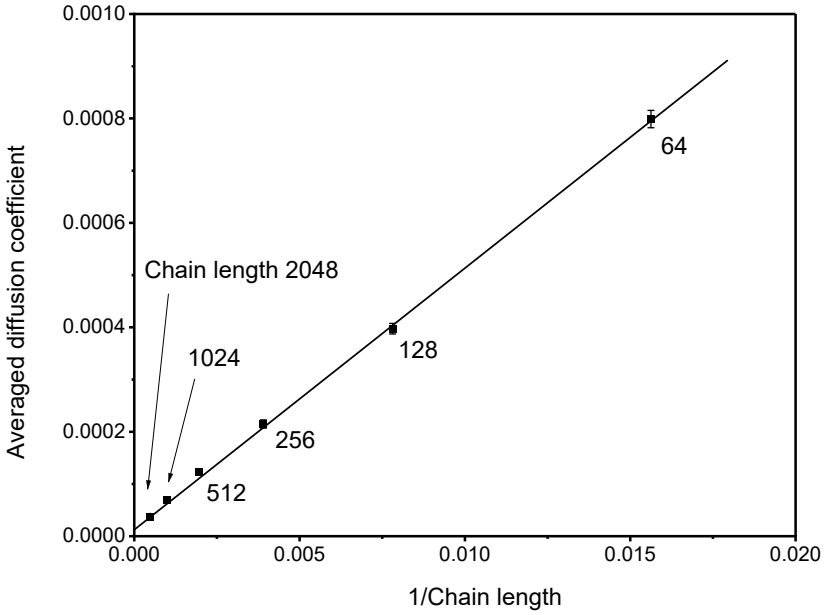


Figure 4: Diffusion coefficient versus the reciprocal chain length in the lattice polymer system with the same free volume fraction 0.0234375. The linear relationship was expected from the thermal fluctuation theorem. The straight line guides the eyes.

The assumption of free volume fraction stopping at the critical value upon glass transition actually brought a constant subtraction into the linear decaying of free volume fractions. When the free volume fraction was applied into the empirical Doolittle equation, the assumption effectively made a constant subtraction of temperature in Arrhenius equation,

and it served as Vogel temperature in Vogel-Fulcher-Tammann (VFT) equation to describe the non-Arrhenius fluid of the polymer elastic states. In this sense, the assumption was the key to derive WLF equation as a transformation of VFT, representing the non-Arrhenius behaviors of the elastic state in bulk amorphous polymers. In this sense, the classical free volume theory could be regarded as a phenomenological VFT theory. Our simulations indicate that the apparent arrest of free volume is not an inherent consequence of free-volume reduction alone within the athermal lattice model. This finding indicates that additional mechanisms—including specific intermolecular interactions, cooperative molecular rearrangements, and volumetric (structural) relaxation, etc., are likely to contribute to the sudden vitrification behavior in real glass-forming polymers.

4 Conclusion

In conclusion, we employed dynamic MC simulations of bulk lattice polymers to investigate the reduction of free volume for the frozen of bulk amorphous polymers under athermal conditions. We observed a linear decrease of diffusion coefficients with the reduction of free volume fractions down to both zeros, and no sudden transition of diffusion coefficients around the iso-free volume fraction 0.025 as commonly observed in the practical experiments and the free volume theories. The linear dependence could be attributed to the simple liquid holding Einstein's fluctuation-dissipation theorem, as evidenced also by the linear dependence of diffusion coefficients on the reciprocal chain lengths under constant free volume fractions.

Our results indicated that under ideal athermal conditions, the lattice model of bulk amorphous polymers reproduces the Brownian motions of simple liquid. Consequently, the reduction of free volume causes no sudden transition in the gradual decaying of diffusion coefficients. The assumption of a sudden frozen transition at the critical free volume fraction was employed in the classical free volume theory in order to derive the phenomenological VFT equation, i.e. WLF equation, for the description of non-Arrhenius fluid behaviors of bulk amorphous polymers in their highly elastic states.

Acknowledgements

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