

String-like collective motion in the α - and β -relaxation of a coarse-grained polymer melt

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Relaxation in glass-forming liquids occurs as a multi-stage hierarchical process involving cooperative molecular motion. First, there is a “fast” relaxation process dominated by the inertial motion of the molecules whose amplitude grows upon heating, followed by a longer time α -relaxation process involving both large-scale diffusive molecular motion and momentum diffusion. Our molecular dynamics simulations of a coarse-grained glass-forming polymer melt indicate that the fast, collective motion becomes progressively suppressed upon cooling, necessitating large-scale collective motion by molecular diffusion for the material to relax approaching the glass-transition. In each relaxation regime, the decay of the collective intermediate scattering function occurs through collective particle exchange motions having a similar geometrical form, and quantitative relationships are derived relating the fast “stringlet” collective motion to the larger scale string-like collective motion at longer times, which governs the temperature-dependent activation energies associated with both thermally activated molecular diffusion and momentum diffusion. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5009442>

I. INTRODUCTION

The relaxation of glass-forming (GF) molecular liquids characteristically occurs as a two-stage process. First, there is a “fast” or “ β -relaxation” process, having a weakly temperature-dependent relaxation time on the order of picoseconds (ps),^{1,2} followed by the “primary” or “ α -relaxation” process having a relaxation time ranging from ps to even minutes as fluids are cooled towards their glass-transition temperature, T_g . The α -relaxation time τ_α attracts the most attention since it has central significance for understanding and controlling the properties of condensed materials near their processing temperatures and for understanding many material properties under field-use conditions. However, the β -relaxation of non-crystalline materials becomes increasingly important in the glassy state since the α -relaxation time scale typically exceeds the experimental time scales by a substantial factor. In particular, “two-level” excitations, which have been suggested to be associated with the β -relaxation dynamics of glass-forming liquids,^{3–7} are widely thought to be responsible for the “anomalous” temperature dependence of the specific heat, thermal conductivity, and other low temperature properties of glassy materials.^{8–11}

Neither the α - nor the β -relaxation processes are normally observed to be “simple,” in the sense of involving exponential time dependence of relaxation functions, and the theoretical description for the occurrence, mathematical nature, and physical origin of these rather universally observed relaxation processes in GF materials remains widely debated. That said, many experimental and simulation studies have provided important insight into these relaxation processes and

the nature of glass formation. For example, it is now generally appreciated that GF liquids are inherently dynamically heterogeneous,¹² and it is also generally accepted that this heterogeneity impacts relaxation in GF materials. In particular, the β -relaxation process can be observed (see Fig. 2) in the short-time decay of the collective and self-intermediate scattering functions, and it is known that the β -relaxation involves a combination of molecular oscillatory motion, as in crystalline materials, and some type of “quasi-elastic” β -relaxation process that leads to significant stress relaxation, even in the glass regime.^{3,13–16} (For clarity, the “fast β -relaxation” referred to above is distinct from the “Johari-Goldstein” or “slow- β relaxation” process that is observed in dielectric and mechanical relaxation measurements,^{17–20} the fast- β relaxation is also distinct from the theoretical β -relaxation process predicted by mode-coupling theory,²¹ which relates to an intermediate time scale associated with the breaking of molecular cages.)

Neutron scattering measurements^{6,22} and molecular dynamics simulations^{23–30} on a broad range of GF liquids suggest that this “quasi-elastic” β -relaxation involves collective atomic exchange motions on a ps time scale taking the form of groups of atoms moving coherently in the form of “string-like” displacements. Similarly, the absence of the isotope effect on the diffusion of atoms in metallic glasses²⁸ and the Boson peak of glass-forming liquids have been rationalized as being due to string-like collective motion on a ps time scale.^{5,13,31–33} This short time scale cooperative motion should not be confused with the string-like displacements that are correlated with molecular diffusion and the α -relaxation process.^{34–39} However, it is natural to expect that these

string-like exchange motions are somehow related,⁴⁰ and the present work seeks to understand the relationship between the collective dynamics in the α - and β -relaxation regimes and to better quantify the nature and physical significance of collective dynamics in the β -relaxation regime.

II. SIMULATIONS AND METHODS

A. Molecular dynamics

In order to study the α - and β -relaxation dynamics, we use a well-known model for glass-forming materials, the Kremer-Grest model of a glass-forming polymer melt. We consider chains with $N_{\text{poly}} = 20$ monomers which interact via the Lennard-Jones (LJ) potential with strength ε , mass m , diameter σ , and are truncated and shifted to zero beyond a cutoff distance $r_c = 2.5\sigma$. Neighboring monomers are connected by a finitely extensive nonlinear elastic (FENE) potential with a bond strength $k_p = 30\varepsilon/\sigma^2$ and bond length $R_0 = 1.5\sigma$. Our simulation cell contains $N_{\text{chain}} = 400$ chains and we simulate along an isobaric path of pressure $P = 1.0$, covering a temperature T range, $0.42 < T < 1.5$. For each T , we first equilibrate the system at fixed pressure to determine the equilibrium volume; we then further equilibrate each system with volume fixed at the determined equilibrium value. Trajectory data are then collected with fixed volume, to avoid any complications of fluctuating simulation dimensions. Our results are expressed in reduced units, ε energy, σ length, m mass, time $\sigma\sqrt{m/\varepsilon}$, and temperature in ε/k_B where k_B is Boltzmann's constant. We emphasize that we only consider systems in equilibrium in order to avoid complications associated with non-equilibrium aspects of glass-formation. The chain length that we have chosen is sufficiently long that dynamics of glass-formation are only weakly sensitive to chain length but not so long that chain entanglement effects are prevalent.

Although the simulation of glass-formation in polymeric fluids is technically more complicated than the binary Lennard-Jones mixture model that is often utilized as a “minimal model” of glass-formation, our polymer model has advantages as a general model of molecular glass-formation since it is not subject to phase separation between the components and crystallization after long computational times.^{41–43} In addition to these practical advantages, molecular glass-forming liquids by definition have molecular bonds, and the coupling of molecular cohesive interactions and bond stiffness is expected to be an essential feature in real molecular glass-forming liquids.

B. Mean-squared displacement and relaxation

The time dependence of the mean-square displacement $\langle r^2(t) \rangle$ for all T simulated is shown in Fig. 1. The mean amplitude of local particle motion within a dynamic “cage” of surrounding molecules, $\langle u^2 \rangle$, is defined by $\langle r^2(t) \rangle$ at the “caging time” defined by the emergence of a minimum in the logarithmic derivative of $\langle r^2(t) \rangle$ with respect to t .^{37,38,44,45} Since this caging time criterion also defines the β -relaxation time, τ_β ,^{46,47} we have the definition, $\langle u^2 \rangle = \langle r^2(\tau_\beta) \rangle$. We

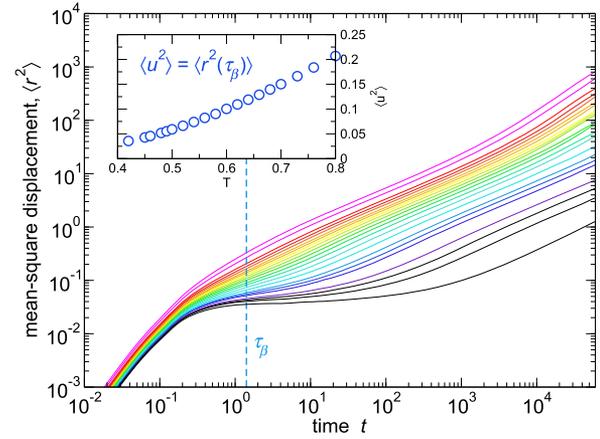


FIG. 1. Time dependence of the mean square displacement of the monomer $\langle r^2(t) \rangle$. The dotted line indicates the β time scale $\tau_\beta \approx 1.4$, and the intersection with this line defines $\langle u^2 \rangle = \langle r^2(\tau_\beta) \rangle$. Inset shows the resulting T dependence of $\langle u^2 \rangle$.

refer to $\langle u^2 \rangle$ as the “Debye-Waller factor,” even in the case where the “particle” is a chain statistical segment rather than an individual atom within a molecule or an isolated atom. In our polymer model, $\tau_\beta \approx 1.4$, and this characteristic time is nearly independent of T ,³⁸ which in laboratory units corresponds to a time scale on the order of 1 ps. The constancy of this precisely defined caging time for polymer liquids is consistent with previous simulation observations on the “caging time” by Leporini and co-workers.^{44,45} Many previous experimental observations have also indicated that τ_β is on the order of 1 ps and weakly temperature dependent.^{1,2}

We obtain the characteristic α -relaxation time τ_α by computing the coherent intermediate scattering function [shown in Fig. 2(a)],

$$F_{\text{coh}}(q_0, t) \equiv \frac{1}{NS(q_0)} \left\langle \sum_{j,k=1}^N e^{-iq_0 \cdot [r_k(t) - r_j(0)]} \right\rangle, \quad (1)$$

where r_j is the position of monomer j , $S(q_0)$ is the static structure factor, q_0 is the location of the first peak in $S(q)$, $q_0 \approx 7$, and N is the number of particles. We define the characteristic structural relaxation time τ_α by the criterion $F(q_0, \tau_\alpha) = 0.2$. Similarly, the incoherent (or self-) intermediate scattering function equals

$$F_{\text{inc}}(q_0, t) \equiv \frac{1}{N} \left\langle \sum_j^N e^{-iq_0 \cdot [r_j(t) - r_j(0)]} \right\rangle. \quad (2)$$

Figure 2(b) shows that $F_{\text{inc}}(q_0, t)$ is quite similar to F_{coh} . However, the relaxation time of $F_{\text{inc}}(q_0, t)$ is somewhat smaller [inset of Fig. 2(b)] since the incoherent part excludes the contributions from correlations between pairs. $F_{\text{coh}}(q_0, t)$ provides a measure of the relaxation of collective density fluctuations in the fluid at the scale q_0 , while $F_{\text{inc}}(q_0, t)$ characterizes the displacement motion of individual particles in the fluid. Both $F_{\text{coh}}(q_0, t)$ and $F_{\text{inc}}(q_0, t)$ are routinely measured by elastic and inelastic neutron scattering measurements, respectively, and these properties are central to characterizing relaxation in liquids from both experimental and computational standpoints.

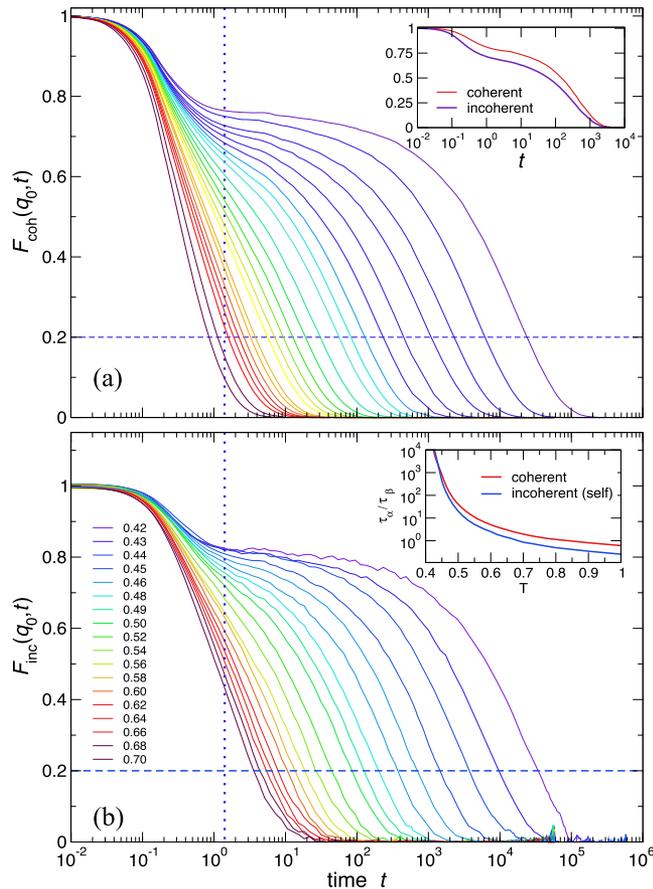


FIG. 2. (a) Coherent intermediate scattering function, $F_{\text{coh}}(q_0, t)$. The inset illustrates a comparison of both scattering functions for $T = 0.46$. For both main figures, the intersection with horizontal dashed line defines the relaxation time τ_α and the intersection with the vertical dotted line defines their respective non-ergodicity parameter. (b) Incoherent intermediate scattering function, $F_{\text{inc}}(q_0, t)$. The inset illustrates the T dependence of τ_α obtained from the $F_{\text{inc}}(q_0, t)$ and from the coherent intermediate scattering function $F_{\text{coh}}(q_0, t)$, normalized by τ_β .

C. Collective string-like motion associated with α - and β -relaxation

To identify the strings formed by highly mobile particles, we follow the procedures originally developed in Ref. 34 and later adapted for the specific polymer model that we study.^{37,48} Specifically, we consider two mobile monomers i and j to be in the same string if, over an interval t , one monomer has replaced the other within a radius $\delta = 0.55$ although the results are not strongly sensitive to this choice for reasonable values of δ . This definition allows us to evaluate the average number of particles undergoing string-like displacements $L(t)$ over any time interval t , as shown in Fig. 3. Naturally, the string size has a limiting value of unity at both extremely short and long times, where monomer displacements are non-cooperative.

We examine the magnitude of the extent of collective motion $L(t)$ at two characteristic times: the string lifetime t_L and τ_β . $L(t)$ exhibits a maximum at a time that we identify at the characteristic string “lifetime” t_L , and we refer to the peak value of L as the “string length.” The string lifetime t_L is generally similar to that of the peak in the non-Gaussian parameter t^* , and it exhibits similar temperature dependence.³⁷ In small

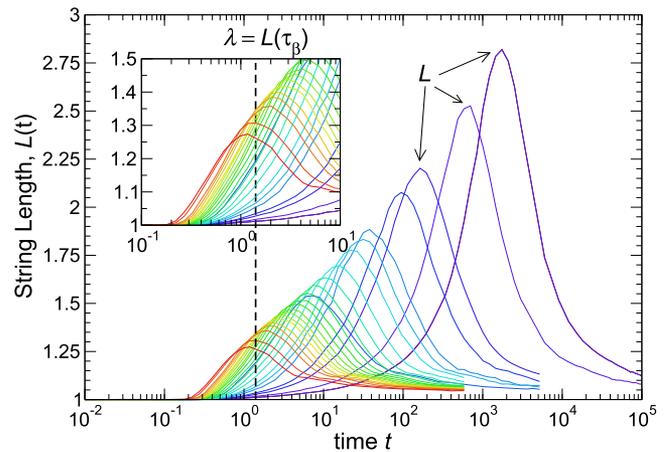


FIG. 3. Time dependence of the mean string size $L(t)$, which exhibits a peak value L near the time scale of diffusive relaxation. We further define the “stringlet” size $\lambda = L(t = \tau_\beta)$ in a similar fashion except we consider the scale of collective motion at τ_β , the same “caging time” at which the Debye-Waller factor $\langle u^2 \rangle$ is defined. For our polymeric model, we find that τ_β is nearly independent of T and on the order of 1 ps. This time is nearly independent of T and has $\mathcal{O}(1 \text{ ps})$ in laboratory units, consistent with previous simulation estimates for polymers^{44,45} and experimental observations.^{1,2}

molecule liquids, the time scale t^* has been observed to scale inversely with the diffusion coefficient so that this time can be interpreted as “diffusive time scale.”^{37,49–52} Of course, this interpretation is more complicated in polymer fluids because of chain connectivity, and in such fluids, t^* is a relaxation time associated with segmental displacement motion. The characteristic time t^* is generally shorter than the α -relaxation time, τ_α , but longer than τ_β . To characterize collective motion at τ_β , we define the “stringlet length” $\lambda = L(t_\beta)$. The onset temperature T_A for non-Arrhenius temperature dependence coincides with the first emergence of molecular caging, and the supplementary material of Ref. 38 discusses in detail the determination of T_A for our polymer model. Alternatively, a simpler and physically appealing definition of T_A is the temperature at which the α and β relaxation times become equal, i.e., $\tau_\alpha = \tau_\beta$.⁵³ Above T_A , τ_β cannot be readily defined from $\langle r^2(t) \rangle$.

III. BACKGROUND

We first briefly review what we already know about the string-like collective motion at time scales required for the establishment of molecular diffusion, and the phenomenological relationship between this collective motion and the amplitude of molecular vibrations on the β -relaxation time scale, characterized by the Debye-Waller factor. These observations have been discussed at greater length in Ref. 39.

The seminal work of Adam and Gibbs⁵⁴ proposed the view that the α -relaxation in GF fluids is an activated process,

$$\tau_\alpha \propto \exp[\Delta G(T)/k_B T], \quad (3)$$

where the temperature-dependence activation free energy barrier ΔG grows in proportion to the number of atoms or molecules necessary for a cooperative rearrangement to occur. Thus, $\Delta G(T) = z(T)\Delta\mu$, where z is the size (mass) of the cooperatively rearranging region (CRR), and $\Delta\mu = \Delta H_a - T\Delta S_a$

is the activation energy in the high temperature regime where the fluid is (relatively) dynamically homogeneous. Unfortunately, Adam and Gibbs offered no molecular definition of a CRR. Consistent with the abstract notion of a CRR, simulations and experiments for materials ranging from polymers to metallic glasses have shown the existence of mobile atoms or particles that progressively cluster in cooled liquids, and that these clusters are composed of string-like clusters of particles undergoing collective exchange motion.^{34,35,37,48,55–59} The average length L of these “strings” (defined by the peak value shown in Fig. 3) is relevant to the approach of Adam and Gibbs since L has been observed to increase in direct proportion to the activation free energy $\Delta G(T)$ of the structural relaxation time determined from $F_{coh}(q, t)$ (or other relaxation functions).^{35–38,60,61} Accordingly, the string model of glass-formation³⁸ generalizes the Adam-Gibbs model [Eq. (3)], where τ_α can be quantitatively described by

$$\tau_\alpha(T) = \tau_0 \exp \left[\frac{(L(T)/L_A)\Delta\mu}{k_B T} \right], \quad (4)$$

which identifies $z(T) = L(T)/L_A$, where $L_A \equiv L(T_A)$ is the mean string length at the onset temperature T_A of non-Arrhenius relaxation; the relaxation time prefactor $\tau_0 = \tau_\beta \exp[-\Delta\mu(T_A)/k_B T_A]$.³⁹ (Note that $L_A \approx \lambda_A$ since the α - and β -relaxation times are nearly equal at T_A .) Figure 4 illustrates the applicability of this description for the present coarse-grained polymer fluid. (Details of fitting our simulation data to Eq. (4) are described in Refs. 38 and 60, which has also been validated for a range of model systems at various thermodynamic conditions.^{36–38,53,60–63}) Equation (4) describes τ_α quantitatively, where the high temperature activation free energy $\Delta\mu$ (the only free parameter) is determined by fitting Eq. (4) to simulation data. Freed has recently provided theoretical support for Eq. (4) by extending transition state theory to account for multiple particle collective barrier crossing events,⁶⁴ and the

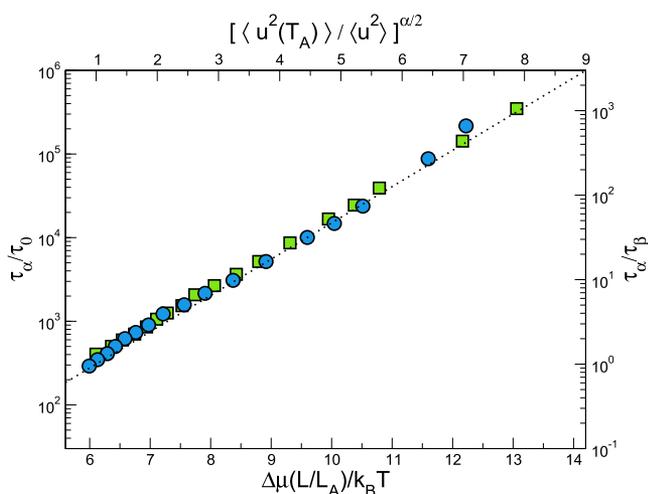


FIG. 4. Universal relationships for our model of GF liquid (a) α -relaxation and string length L as stated in Eq. (4) and (b) τ_α and $\langle u^2 \rangle$ as in Eq. (5). The relaxation time approaches the minimal “vibrational” relaxation time, τ_0 . The approach of τ_α to τ_0 defines another characteristic temperature, the Frenkel temperature, beyond which the fluid acquires the thermodynamic and dynamic properties of a gas.^{66–68} This limiting temperature normally occurs in the supercritical fluid regime, making it physically inaccessible in most polymeric materials.

random first-order transition (RFOT) theory of glass formation is based on very similar ideas.⁶⁵

As an alternate approach to explain the non-Arrhenius temperature dependence of the α -relaxation in GF materials, a variety of models based on the vibrational behavior due to the elastic response of the fluid have been developed.^{39,44,45,69–72} In particular, τ_α can be well described by the relation³⁹

$$\tau_\alpha = \tau_\beta \exp \left[\left(\frac{\langle u^2(T_A) \rangle}{\langle u^2 \rangle} \right)^{\alpha/2} - 1 \right], \quad (5)$$

where $\langle u^2(T_A) \rangle$ is the Debye-Waller factor determined at T_A , and $\alpha \approx 3.4$ for the GF liquid considered in the present paper. Figure 4 illustrates the applicability of Eq. (5) to our polymer segmental relaxation time data, and equivalent relations have been tested for a variety of systems.^{49,51,72} The molecular volume defining the range of thermally excited atomic motion $\langle u^2 \rangle^{3/2}$ can be interpreted as the volume of the region explored by the center of mass of the particles over the time scale τ_β .^{71,73} Equation (5) can then alternatively be interpreted as a kind of “free volume” expression for τ_α , where the constant α in this equation accounts for the fact that these free volume regions can have a complicated shape,⁷¹ especially in the case of polymeric fluids because the polymer segments themselves often have an asymmetric shape. Consistent with this geometrical interpretation, α is found to be nearly 3 for ZrCu metallic glasses, when the free volume regions are plausibly nearly spherical, and $\alpha = 1.9$ in recent simulations based on a near planar molecular model. That said, this geometrical interpretation of α requires further study before being accepted uncritically. Moreover, we must distinguish the rattle volume quantified by $\langle u^2 \rangle$ from actual void regions in the fluid not occupied by molecules, as probed, for example, by positron annihilation measurements. Despite the different physical nature of these types of “free volume,” their experimental estimates seem to track each other phenomenologically.⁷⁴

The fact that the string-like cooperative rearrangements (on the time scale of molecular rearrangement) and the Debye-Waller factor (on the time scale of vibrations) both provide accurate predictions for the α relaxation time provides the backdrop to frame our investigation. Accordingly, one of our goals is to develop a more precise relationship between string size and the Debye-Waller factor.

IV. RESULTS

How is collective motion on the time scale of molecular reorganization related to the fast relaxation dynamics captured by the Debye-Waller factor? To address this question, we begin by examining the nature of collective motions on the vibrational time scale and develop a formal theoretical relationship between collective motion on the vibrational and diffusive time scales.

A. Strings and stringlets

We identify string-like collective motions on the scale of the β -relaxation—which we term “stringlets”—based on the same approach used to define strings on the diffusive

time scale. Specifically, the stringlet size $\lambda = L(t = \tau_\beta)$, as described in Sec. II C. Although the string-like collective motion observed in simulations in both the β - and α -relaxation regimes exhibits a superficial resemblance in terms of a general “string-like” geometry, these dynamic structures should not be naively equated. Figure 5(a) compares these measures of the scale of collective motion in the α - and β -relaxation regimes. We find that $\lambda(T)$ grows upon heating, while $L(T)$ becomes smaller upon heating. The inverted T dependence of L and λ is expected based on prior studies: Schober and co-workers^{75,76} first identified growing stringlet size on heating. Other studies have also indicated that the stringlets exhibit an exponential size distribution.^{4,26} Figure 5(a) further shows that $L(T)$ and $\lambda(T)$ become *equal* near the onset temperature, T_A , the T at which $\tau_\alpha \approx \tau_\beta$. It is then apparent that $L(T)$ grows as the extent of collective motion at short time scales becomes reduced, presumably due to a progressive inhibition of fast coherent collective motion due to increased molecular caging upon cooling. In other words, as the molecules become increasingly “stuck” by surrounding molecules upon cooling, larger scale of collective motion mediated by large scale molecular diffusion is required to achieve structural relaxation. We suggest that this is the origin of the dual relationship between strings and stringlets.

To develop a formal theoretical relationship between strings and stringlets (and ultimately between α and β scale

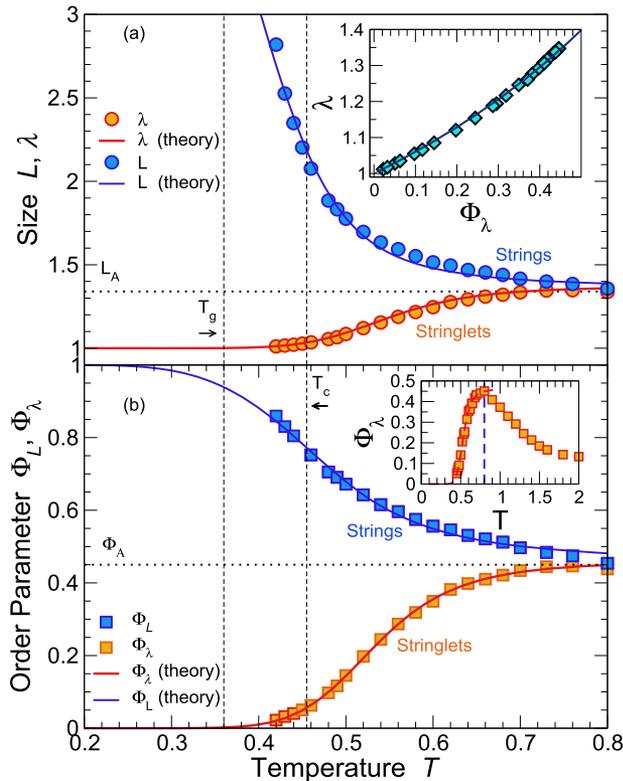


FIG. 5. (a) Temperature dependence of length of the strings L and stringlets λ . The lines from the theory for stringlets are a result of a combination of Eqs. (6) and (7). For strings, the theory is from Ref. 38. The inset shows λ and Φ_λ parametric relationship [Eq. (7)]. (b) Temperature dependence of the order parameters for string Φ_L and stringlet Φ_λ formation. The red line for Φ_λ is the two-state description [Eq. (6)], and the theory for Φ_L is from Ref. 38. The inset shows the full T dependence of Φ_λ . The dashed line indicates that Φ_λ peaks at “onset” temperature of glass formation T_A .

relaxation), we use an approach employed in previous work,³⁸ where we established that the strings arising in glass-forming liquids can be quantitatively described in terms of an initiated equilibrium polymerization model.^{77,78} The string model of glass formation predicts the size distribution of strings, the T dependence of their average length, and the order parameter of the assembly process (defined by the fraction of mobile monomer in the “condensate-like” state of collective motion).³⁸ Here, we show that the growth of the stringlets can be likewise described *phenomenologically* by an equilibrium polymerization process. However, in this case, the polymerization occurs upon *heating* rather than cooling, as found in the polymerization of sulfur and actin^{79–83} and in vortex “blowout” upon heating (growth of vortex length with increasing temperature) in type II superconductors.^{84,85}

An important element of this polymerization description of stringlet size is the order parameter of the stringlet self-assembly process, which we define by the fraction Φ_λ of mobile particles that undergo collective stringlet motion. This definition parallels the polymerization description of the strings,³⁸ where there is an equivalent order parameter Φ_L for the extent of string assembly. Figure 5(b) shows the T dependence of both Φ_L and Φ_λ , which correspond to string-like exchange motions underlying the α and β -relaxation processes, respectively. $\Phi_L(T)$ and $\Phi_\lambda(T)$ follow the normal variation for equilibrium polymerization upon cooling and heating. More specifically, the increase of Φ_λ with temperature is consistent with the increase in stringlet size λ (polymerization on heating),^{79–83} while the increase of Φ_L follows that of string size L on cooling (polymerization on cooling). For $T < T_A$, $\Phi_\lambda(T)$ can be well described by a simple two-state model,

$$\Phi_\lambda(T) = \frac{\Phi_\lambda(T_A)}{[1 + \exp[(\Delta H - T\Delta S)/T]]}, \quad (6)$$

where $\Delta H = 5.9$ and $\Delta S = 11$ are the two-state energetic parameters. The resulting fit is indicated by the red line in Fig. 5(b). We also show the full T dependence of Φ_λ (including $T > T_A$) in the inset of Fig. 5(b). Φ_λ has a maximum at T_A , coincident with the merging of the α and β process at high T . The variation of Φ_λ with T is typical for an activated equilibrium polymerization processes occurring upon heating.^{79–83}

We obtain expressions linking scales of collective motion associated with the α - and β -relaxation by considering the short-time collective motion as an activated polymerization process and check the consistency of this model with our simulation observations. We can relate the stringlet size λ to the extent of assembly Φ_λ , similar to what was done previously for the strings; this will allow us to provide an explicit prediction for the T dependence of λ . Based on the theory for activated polymerization,⁸⁶ the order parameter Φ_λ relates to the size of the stringlets λ by

$$\lambda(T) = \frac{2 - A_\lambda}{2 - A_\lambda - \Phi_\lambda(T)}, \quad (7)$$

where A_λ varies for the type of polymerization model (activated, initiated, etc.) and molecular properties (change stiffness, etc.).⁸⁶ (These constraints on equilibrium polymerization must in practice be clarified through experimental studies.) The inset of Fig. 5(a) shows that this expression accurately

describes the relation between λ and Φ_λ for our data, from which we find $A_\lambda = 0.246$.

We next link the theoretical description of the stringlets to that of the strings. In the polymerization theory for collective motion on the α time scale,³⁸ we showed that L and Φ_L obey an equation similar to Eq. (7), namely,

$$L(T) = \frac{2 - A_L}{2 + A_L - 2\Phi_L(T)} L_A, \quad (8)$$

where $A_L = \Phi_L(T_A)$ and $L_A = L(T_A)$ (so that both parameters are directly defined from simulation data). The inset to Fig. 6 shows one-to-one relationship between Φ_L and Φ_λ implying a one-to-one relation between L and λ . In particular, we notice Φ_L and Φ_λ are empirically related,

$$\Phi_\lambda = \Phi_\lambda(T_A) \exp\left[-\frac{(\Phi_L(T) - A_L)^2}{2\sigma^2}\right], \quad (9)$$

where $\sigma = 0.14$. Based on this observation, along with Eq. (7) and Eq. (8), we parametrically relate the fast (λ) and slow (L) collective motion by the closed analytic form

$$\lambda = \frac{2 - A_\lambda}{2 - A_\lambda - \Phi_\lambda(T_A) \exp[-((1 - L_A/L)(1 - \Phi_L(T_A)/2))^2/2\sigma^2]}, \quad (10)$$

which is consistent with our simulated data in Fig. 6 to a good approximation. Given that the relationship of L to λ is rather complicated, it is helpful to recognize that below T_A , the string length and stringlet length are related by the simple empirical relation

$$L \approx L_0 + b_0/(\lambda - 1)^{1/2}, \quad T < T_A, \quad (11)$$

where $b_0 = 0.17$ and $L_0 = 1.18$ are the fitting constants. For $T < T_A$, Eq. (11) describes our simulation data for L and λ nearly as well as the estimate based on the polymerization model. Thus, we have established a direct relationship between the sting and stringlet size. We next discuss the physical picture of glass-formation implied by the relationship between L and λ .

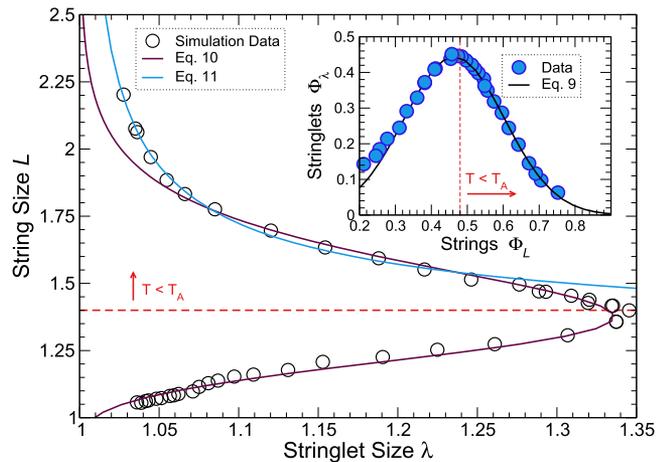


FIG. 6. Competition between stringlet and string growth. The main panel shows the parametric relation between the α time scale string-like excitations L and the short time collective motion λ . The dark line illustrates Eq. (10) and the red curve shows the low- T approximation of Eq. (11). The inset shows the corresponding relation between the string Φ_L and stringlet Φ_λ order parameters. The solid line illustrates the analytical model for Φ_λ from Eq. (9). The dashed lines separate the low- T from high- T behavior.

The qualitative increase in the average stringlet length λ upon heating can be rationalized from the inertially dominated motion of the particles in the fast dynamics regime.^{71,87,88} In particular, the amplitude of these inertial correlated motions becomes amplified upon heating simply because the molecules have a greater kinetic energy at higher T , leading to the observed increase in the amplitude of the β -relaxation upon heating rather than cooling.¹ The predominantly inertial character of the β -relaxation is also reflected in the form of the initial decay of the $F(q_0, t)$ approaching the vibrational plateau, which decays as a “stretched Gaussian” or “compressed exponential” with an β exponent value near $3/2$ over a wide range of temperatures.⁷¹ This functional form for $F_{coh}(q_0, t)$ holds to an excellent approximation for polymer nanocomposites⁸⁷ and thin polymer films,⁸⁸ and we have checked that this phenomenon is also found in small molecule liquids such as water. A purely inertial decay of $F(q_0, t)$ at very short times corresponds to a β exponent equals 2, but dynamic heterogeneity (stringlets) apparently reduces the β exponent in the fast relaxation process, leading to a somewhat reduced value of β ,⁷¹ a “stretched Gaussian.” This reduction is parallel to the case of α relaxation process at longer times, where the “stretching exponent” β becomes reduced from the reference value of 1, corresponding to the ubiquitous “stretched exponential” α -relaxation of glass-forming materials.

B. Stringlets and Debye-Waller factor

The increased amplitude of molecular motion upon heating is also reflected in the mean amplitude of atomic motion $\langle u^2 \rangle$. An examination of $\langle u^2 \rangle$ of particles within a string cluster over the time scale over which the string persists, i.e., the peak time of the non-Gaussian parameter t^* , reveals how the stringlet collective motion influences $\langle u^2 \rangle$. Figure 7 shows a time series of $\langle u^2 \rangle$ for a representative monomer of a string composed of 7 particles, while the inset shows the T dependence of $\langle u^2 \rangle$. We see that $\langle u^2 \rangle$ for the string “monomers” exhibits much larger values than for monomers that are not in

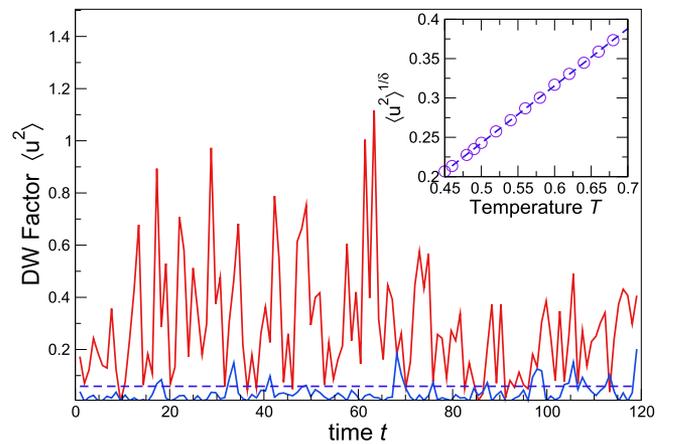


FIG. 7. Time series of $\langle u^2 \rangle$ for a representative monomer in a string representative string have a length $s = 7$ (in red) and a representative monomer that is not in a string (blue). The inset shows $\langle u^2(T) \rangle$ illustrating the highly anharmonic nature of the T variation of $\langle u^2 \rangle$, where $\delta = 2.9$ ($\delta = 1$ for the harmonic case).

the strings.⁸⁹ Since particles in the strings are by far the most mobile chain segments, they make the predominant contribution to the magnitude of $\langle u^2 \rangle$, even though there are relatively few such particles, i.e., $\approx 5\%$. We support this statement by showing the contribution of particles to the average value of $\langle u^2 \rangle$ from particles that are not in the “activated” string state (dashed line in Fig. 7), which show a much smaller $\langle u^2 \rangle$.

Since molecules exhibiting string-like collective motion in the β -relaxation regime should exhibit larger values of $\langle u^2 \rangle$ than “unexcited” molecules, we can also anticipate a relationship between λ and $\langle u^2 \rangle$. The particles moving collectively in a string-like manner on ps time scales are indeed predominantly responsible for the degree of structural relaxation in the fast dynamics regime as quantified by the measurable non-ergodicity parameter. These fast-collective motions are evidently highly anharmonic in nature, and we may quantify this by determining how much the T dependence of $\langle u^2 \rangle$ deviates from a linear T scaling that is characteristic of harmonically localized particles. The inset in Fig. 7 shows that $\langle u^2 \rangle^{1/\delta}$ is nearly linear in T where $\delta = 2.9$ and extrapolates to zero near the Vogel-Fulcher-Tammann temperature of our system, $T_0 \approx 0.2$.^{37,39} Evidently, $\langle u^2(T) \rangle$ is nearly cubic in T , and this non-linear variation is broadly consistent with previous experimental and computational studies of glass-forming liquids.⁵¹ However, the exponent δ is not universal and a value of δ near 1 has been observed for metallic glasses.⁵¹

We can empirically relate Φ_λ to $\langle u^2 \rangle$ for $T < T_A$ by invoking the two-state model for the T dependence of Φ_λ , described by Eq. (6), and shown in Fig. 5(b). Based on the nearly cubic temperature dependence of $\langle u^2(T) \rangle$, we can replace $T \approx (\langle u^2 \rangle / a_0)^{1/\delta}$ in Eq. (6), where $a_0 = 0.43$ and $\delta = 2.9$. Figure 8 shows that this argument leads to a very reasonable approximation for the parametric relation between $\langle u^2(T) \rangle$ and $\Phi_\lambda(T)$. Furthermore, given that Eq. (7) directly relates the stringlet size to Φ_λ , we have an implicit relation between $\langle u^2(T) \rangle$ and $\lambda(T)$, and Fig. 8 demonstrates that this relation describes the simulation data rather well. Thus, we have provided direct connections among $\langle u^2 \rangle$, λ , and L .

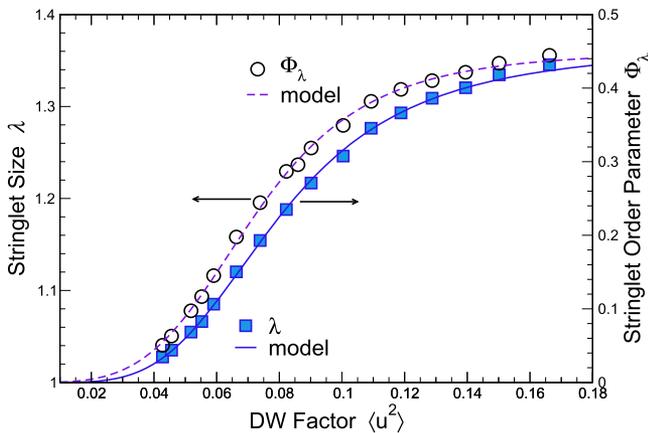


FIG. 8. Relationship between the short time collective motion λ and the Debye Waller Factor $\langle u^2 \rangle$. The symbols represent the simulation data and the lines represent the mathematical model; the dashed line uses Eq. (6) to relate Φ_λ and $\langle u^2 \rangle$, and the solid line combines Eqs. (7) and (6) to relate λ to $\langle u^2 \rangle$.

Finally, we consider how these collective stringlet motions may relate to the quasi-elastic relaxation by considering how such particles contribute to the decay of the incoherent (or self part) intermediate scattering function $F_{\text{inc}}(q_0, t)$ in the β -relaxation regime where $q_0 = 7$ where q_0 corresponds to a length scale $2\pi/q_0$ on the order of an interparticle distance. We first point out that the extent of this decay can be directly related to the Debye-Waller factor, $\langle u^2 \rangle$. In particular, the non-Gaussian parameter,

$$\alpha_2 = \frac{3}{5} \frac{\langle r(t)^4 \rangle}{\langle r(t)^2 \rangle^2} - 1, \quad (12)$$

is small throughout the β -relaxation regime. This means that the behavior of $F_{\text{inc}}(q_0, t = 1)$ (the ps scale), which defines the *fixed time* incoherent “non-ergodicity parameter” h_{inc} , is well approximated by a Gaussian approximation, $h_{\text{inc}} = \exp[-q_0^2 \langle u^2 \rangle / 6]$. We can also define a non-ergodicity parameter for the coherent scattering function F_{coh} . Because the incoherent (self-) component of the scattering function is the dominant contribution to the overall coherent scattering function $F_{\text{coh}}(q_0, t)$ at this time scale, the *fixed time* non-ergodicity parameter h_{coh} can be approximated by a similar expression

$$h_{\text{coh}} \approx \exp[-A \langle u^2 \rangle + B], \quad (13)$$

where the constants $A = 1.54$ and $B = 0.43$ are empirically determined.⁹⁰ Figure 9 shows this approximation and the T dependence of both non-ergodicity parameters. h_{coh} quantifies the plateau of the dynamical structure factor at the particle caging time, and thus, the degree of quasi-elastic structural relaxation. Consequently, the basic significance of $\langle u^2 \rangle$ for understanding collective β -relaxation is evident. In addition, we can understand qualitatively the reason why the intensity of the contribution of the β -relaxation grows upon heating while that for the α -relaxation grows upon cooling. This also helps explain the origin of the strong correlation of the β -relaxation intensity with the rattle “free volume” $\langle u^2 \rangle^{3/2}$.

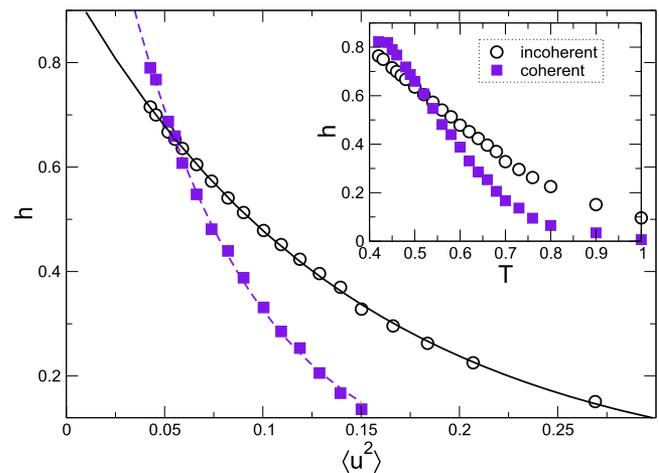


FIG. 9. Non-ergodicity parameter and $\langle u^2 \rangle$. The circled symbols represent the incoherent non-ergodicity parameter h_{inc} and the squared symbols represent the coherent counterpart, h_{coh} . The dashed line illustrates the Gaussian approximation $h_{\text{inc}} = \exp[-q_0^2 \langle u^2 \rangle / 6]$ from incoherent scattering function, where $q_0 \approx 7$ (peak position in static structure, corresponding to average intersegmental distance) and the solid line represents $h_{\text{coh}} \approx \exp[-A \langle u^2 \rangle + B]$ from the coherent intermediate scattering function analog.

V. DISCUSSION AND CONCLUSION

We have described a quantitative relation between the collective motion in the β - and α -relaxation processes of GF liquids by considering the nature of collective molecular motion in these dynamical regimes. Curiously, the geometrical form of the collective motion is similar in both these dynamical regimes. In each relaxation regime, the excitations predominantly take the form of strings, but the temperature variation of the average string length and the fraction of mobile particles in these relaxation processes is inverted, reflecting a coupling of these collective motions. Our analysis suggests a new picture for the origin of extensive collective motion underlying the rapidly growing α -relaxation time and the variation of the non-ergodicity parameter governing the extent of quasi-elastic relaxation at short times. In particular, the progressive suppression of collective relaxation in the β -relaxation regime upon cooling requires relaxation to occur through larger scales and particle displacements at long time scales to enable the ultimate structural relaxation of the material. At the glass transition, the fast collective channels of relaxation are presumably sufficiently suppressed that the material begins to “seize up” into a non-equilibrium glass state.⁷³ We have also gained insight into recent observations relating other experimentally accessible fast dynamics properties to the α -relaxation time by considering how the stringlet motion contributes to the *fixed time* non-ergodicity parameter and the Debye-Waller factor. The stringlets’ motion is part of the sub-dynamics of the strings observed at longer time scales. Relaxation in cooled liquids then occurs by a cascade of relaxation processes involving collective motion starting from inertially dominated motions at short times, slower mass diffusion cooperative shuffling of particles over relatively high energy barriers, and finally slow momentum diffusion processes mediated by numerous mass diffusion events mediated by strings. When polymers are entangled, new layers of dynamical heterogeneity emerge, and the hierarchy of relaxation processes extends to much longer time and spatial scales.

What about the slow β or Johari-Goldstein β -relaxation? How does this universal relaxation process of glass-forming liquids relate to the usual α and β -relaxation processes described above? The slow β process is observed in mechanical and dielectric relaxation processes, but it is not apparent in $F(q_0, t)$, explaining why we have said little about this relaxation process in the present paper. Cicerone and co-workers have suggested that the Johari-Goldstein relaxation process corresponds to transition events between metabasins in the potential energy landscape⁹¹ and further that the rate of these transitions governs the rate of molecular diffusion.⁹² This proposed interpretation of the Johari-Goldstein relaxation process, and the finding that t^* scales inversely to the molecular diffusion coefficient in small molecule fluids,^{37,49–52} would suggest that t^* might be identified with the Johari-Goldstein or slow β -relaxation process. This is a curious possibility that would naturally explain the observed decoupling relation between τ_α and t^* found in previous simulation studies.^{37,53} This relationship would also be consistent with the string motions corresponding to *intra*basin

inherent transition events,⁹¹ while the stringlets would then reflect intrabasin motions within the potential energy landscape. This scenario of exploring local inherent structure minima as a basic feature of the fast dynamics of liquids, followed by “metabasin” transitions responsible for molecular diffusion to distances on the order of the interparticle distance at longer time scales accords with Heuer’s hierarchical view of the dynamics of glass-forming liquids.^{93,94}

Structural relaxation requires yet another process, momentum diffusion, at still longer times. The α -relaxation time process correlates in molecular fluids with the shear relaxation time, which relates to the rate of momentum diffusion rather than mass diffusion. This time scale is generally much longer than the diffusive time t^* in cooled liquids and many diffusive events are then necessary to achieve structural relaxation. This is a rather generic consequence of the existence of dynamic heterogeneity, which is widely believed to lead to the breakdown of the Stokes-Einstein (SE) equation, though alternate explanations exist that do not invoke heterogeneity, such as the temperature dependence of the waiting time distribution for molecular displacements. A fractional Stokes-Einstein (FSE) relation can be derived from effective medium theory if immobile particle heterogeneities in the fluid persist on a diffusive time scale.^{95,96} The observed emergence of such a FSE relation implies that the structural relaxation time τ_α tends to be much larger than the mass diffusion time t^* at temperatures well below T_A so that numerous string events associated with mass diffusion are required to allow for the structural relaxation of the cooled liquid. The resulting FSE fractional power-law relation between t^* and τ_α and Eq. (4) mathematically implies that the string length L controls the change in the relative value of *both* the activation free energies of both diffusion (t^*) and structural relaxation (τ_α).^{37,38} This explains why the string model is applicable to the description of structural relaxation, a highly complex relaxation process governed predominantly by the rate of momentum diffusion rather than the rate of mass diffusion. As first shown by Alder and Wainwright,^{97,98} and more recently by Anikeenko and Naberukhin,^{99,100} momentum diffusion in liquids occurs through the formation and movement of vortices that have scales and lifetimes much larger than the scale of the strings associated with the activated mass diffusion transport. The strings are substructures of these fluid vortices and the stringlets are substructures of the strings.

Based on these observations and arguments, we suggest that the appearance of both the Johari-Goldstein β -relaxation and α -relaxation processes in dielectric and mechanical measurements arises from a mode coupling of the mass and momentum diffusion processes in the autocorrelation function corresponding quantitatively to these relaxation processes. This is a natural consequence of dynamic heterogeneity and a similar coupling between mass and momentum diffusion processes is found in relaxation fluids near their critical point.¹⁰¹ At any rate, structural relaxation in glass-forming liquids seems to occur through a hierarchical cascade of relaxation processes and we look forward to better quantifying how these relaxation processes interrelate in the future.

Note added in proof. Mesoscale vortex excitations also arise in turbulent fluids at high rates of flow and these excitations have also been modeled in terms of polymeric structures.¹⁰²

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- ⁸⁹The inherent structure analysis of molecular trajectories in cooled molecular glass-forming liquids^{25,26} provides further insights into this motion where string-like particle exchange events mediate large scale inherent structure transitions and where these transition events occur on intervals having a roughly ps on time scales. Normally, an extremely large number of such stringlet events occur before the diffusive time t^* at T well below T_A .
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