

Picosecond Dynamic Heterogeneity, Hopping, and Johari-Goldstein Relaxation in Glass-Forming Liquids

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We show that incoherent quasielastic neutron scattering from molecular liquids reveals a two-state dynamic heterogeneity on a 1 ps time scale, where molecules are either highly confined or are free to undergo relatively large excursions. Data ranging from deep in the glassy state to well above the melting point allows us to observe temperature-dependent population levels and exchange between these two states. A simple physical picture emerges from this data, combined with published work, that provides a mechanism for hopping and for the Johari-Goldstein (β_{JG}) relaxation, and allows us to accurately calculate the diffusion coefficient, D_T , and characteristic times for α , and β_{JG} relaxations from ps time scale neutron data.

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The dynamics of liquids is not completely understood but seems to be quite complex. In addition to viscosity and the closely related α relaxation, there are at least two other apparently universal relaxation processes, denoted as “fast β ” (β_{fast}) and “Johari-Goldstein β ” (β_{JG}) [1]. All three have been topics of investigation for decades, yet many questions about the individual processes and their inter-relationship are unresolved.

It seems that each of these processes may be influenced by short-time-scale dynamic heterogeneity. The β_{fast} process, which occurs at ≈ 1 ps, has been historically considered to arise only from uniform vibrational motion, but was recently shown to also contain a signature of collective motion [2]. An influence of short-time dynamic heterogeneity on α relaxation was suggested by Goldstein [3], who proposed a thermally induced hopping over saddle points on a potential energy landscape (PEL). Mode coupling theory (MCT) also seems to require a phenomenon such as hopping to properly account for α relaxation below a critical temperature (T_c) [4]. The connection of the β_{JG} process to short-time dynamic heterogeneity is less well established, but evidence for a connection seems to be building [5–7]. In particular, β_{JG} relaxation appears to involve interbasin transitions in the PEL formalism, similar to α relaxation. It is argued that the former should, thus, also feel influence from dynamic heterogeneity [7].

We present analysis of incoherent quasielastic neutron scattering (QENS) that provides a molecular mechanism, rooted in ps time scale dynamic heterogeneity, for the β_{JG} process and its relation to hopping and to α and β_{fast} relaxation.

We have performed QENS on five liquids, propylene carbonate (PC), propylene glycol (PG), glycerol, orthoterphenyl (OTP), and sorbitol. $S(q, \omega)$ data from each material was obtained over a momentum transfer range of (0.2 to 2.5) \AA^{-1} and energy transfer range of (0.19 to 4.5) meV,

and was transformed to $F(q, t)$ for fitting. Care was taken to avoid potential artifacts due to multiple scattering and crystallization; this, along with fitting details are discussed in the Supplemental Material [9]. Figure 1 shows the intermediate scattering function [ISF, $F(q, t)$] data from propylene glycol at 1 ps (approximate time scale for β_{fast} relaxation), and fits to a two-state model [12,13]

$$F_s(q) = (1 - \Phi)e^{(-\pi^2\sigma_{TC}^2q^2)} + \Phi e^{(-\pi^2\sigma_{LC}^2q^2)}. \quad (1)$$

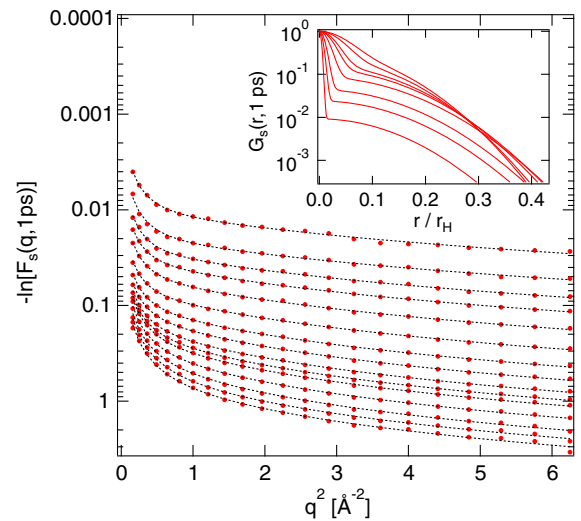


FIG. 1 (color online). ISF at 1 ps for PG at $T = 60, 90, 120, 150, 180, 210, 240, 265, 290, 307, 320, 350, 375, 400,$ and 425 K (circles, top to bottom), with fits to Eq (1) (dashed lines). Inset: van Hove function with abscissa normalized by PG hydrodynamic radius corresponding to fits at $T = 60, 120, 180, 240, 290, 320, 375,$ and 425 K (bottom to top). Data were collected at the NIST neutron center on NG4 [8] with an energy resolution of $200 \mu\text{eV}$ and $\lambda = 4.0 \text{\AA}$.

where σ_{TC} and σ_{LC} indicate characteristic length scales of motion, and Φ represents the fraction of molecules exhibiting motion characterized by σ_{LC} . The parameters σ_{LC} and σ_{TC} have very low covariance (see the Supplemental Material [9]) because their fit values are well separated. Further, $\sigma_{LC} < q_m < \sigma_{TC}$, where q_m is the peak in the structure factor, $\approx 1.4 \text{ \AA}^{-1}$ for these liquids. Thus, σ_{LC} and σ_{TC} , respectively, describe intramolecular and highly localized motion. The two distinct length scales of motion are easily visualized in the single particle van Hove correlation function calculated from the fit parameters and shown in the inset of Fig. 1 as $G_s(r) = (1 - \Phi)e^{(-r^2/\sigma_{TC}^2)} + \Phi e^{(-r^2/\sigma_{LC}^2)}$. Thus, we observe that the β_{fast} process has two components. One is a localized, vibrationlike motion of tightly caged (TC) molecules, and the other is a relaxation executed by more loosely caged (LC) molecules. The latter have been associated with collective motion through the q dependence of the coherent structure factor, $S(q, \omega)$ [2].

Figure 2 shows, in solid symbols, σ_{TC} and σ_{LC} values obtained at 1 ps and normalized by the high-temperature hydrodynamic radius (r_H) of each of the molecular species [14–17] as indicated in panels 2(a)–2(e). The hollow symbols are normalized σ_{LC} values obtained at 10 ps. The magnitudes of σ_{LC} fall in the range 0.1 to 0.3 r_H , consistent with fast collective motions seen in colloids [18], simulation [19], and ionic systems [2]. We note that the collective motions characteristic of the LC regions must occur on a time scale ≈ 1 ps or less, since $\sigma_{LC} = \sigma_{LC, 10 \text{ ps}}$ in all cases (except PC and PG at high temperature, which are likely influenced by α relaxation at 10 ps).

The temperature dependence of σ_{TC} values is consistent with expectations for a localized component, changing markedly in the vicinity of T_c and T_g . We ascribe the anomalously high σ_{TC} values for OTP to ring libration, and note that the characteristic length scale of this motion is small compared to σ_{LC} , again attesting to the intermolecular nature of the latter. Unfortunately, this excess scattering prevents us from using the OTP σ_{TC} data in the quantitative analysis at the end of this Letter.

Figure 3 shows Φ , the fraction of molecules participating in LC states during a particular time window. The solid and hollow symbols are Φ values at 1 and 10 ps, respectively, for each of the liquids. At low temperatures, $\Phi_{10 \text{ ps}} = \Phi_{1 \text{ ps}}$, indicating that the LC states are long-lived. On the other hand, $\Phi_{10 \text{ ps}} > \Phi_{1 \text{ ps}}$ at higher temperatures, where we can conclude that these LC domains transiently visit regions of space, allowing molecules there to undergo large excursions before the LC domain moves on, consistent with Keys *et al.* [20]. We observe $\Phi_{10 \text{ ps}} = 1$ at high temperature, indicating that all molecules are eventually involved in LC domains. The lower inset of Fig. 3 shows that the amount of exchange between TC and LC states is significant on a time scale of a few ps only at $T \geq T_c$.

Having established the presence of two exchangeable dynamic states, we now consider our results in the context of

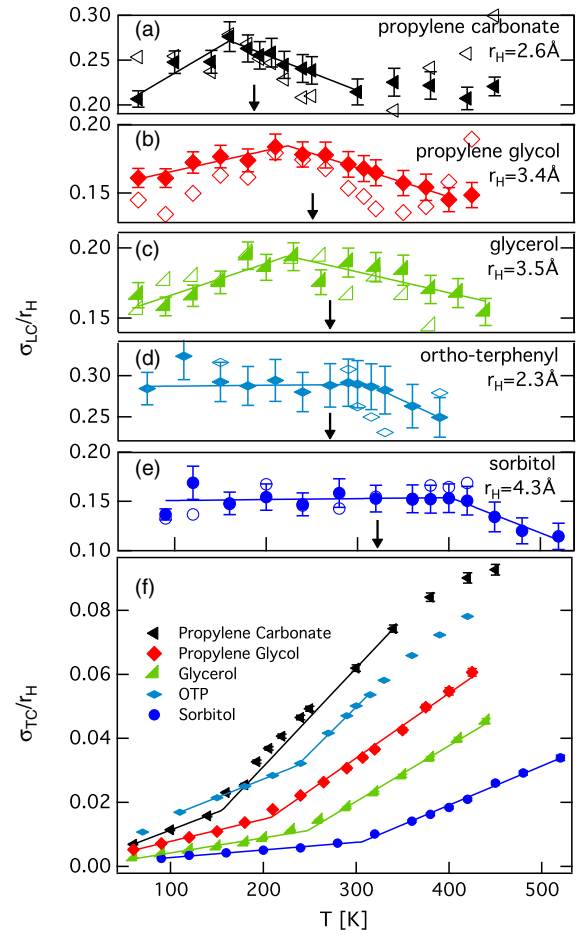


FIG. 2 (color online). Confinement length scales for LC (a)–(e) and TC (f) molecules in the two-state model at 1 ps (solid symbols) and 10 ps (hollow symbols). Solid lines are best fits. Arrows indicate T_c for each material. Error bars indicate uncertainties in parameters at one standard deviation.

previous findings and formulate a physical picture of the underlying dynamics. Thermally activated [3] and phonon-assisted [4] hopping processes were proposed, and evidence for hopping was later observed in simulation where particles were typically localized but occasionally moved in a relatively small number of steps to distinct positions where they again became localized [21]. Similar behavior is now observed routinely in simulation and model systems [18,19,22–25], and the basic mechanism for this hopping can be gleaned from results of these studies as follows. (1) The rapid excursions involve discrete cooperative rearrangements of particles from one locally preferred structure (metabasin) to another. (2) On a ps time scale, these rearrangements generally involve only a small number of particles (≈ 2 to 4), resulting in relocation by typically 0.2 to 0.3 particle radii. (3) For time $\gg 1$ ps, cooperative motion of larger groups of particles is asynchronous, being made up of ps time scale rearrangements of smaller groups.

The correspondence between the hopping behavior seen in simulation and the behavior reported here in the LC and

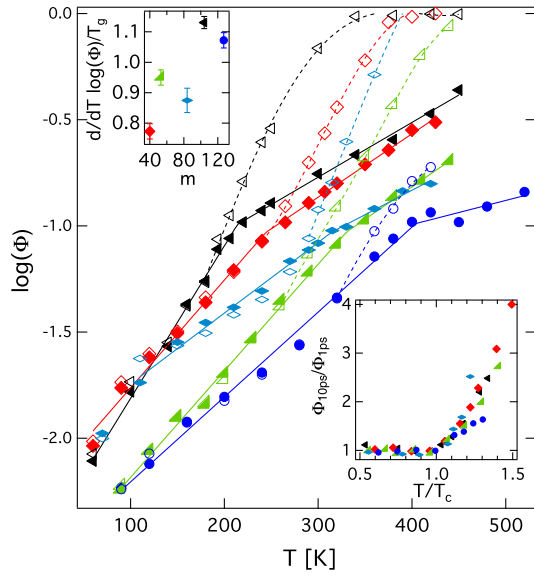


FIG. 3 (color online). Φ at 1 ps (solid symbols), and Φ at 10 ps (hollow symbols). Symbols have same association as in Fig. 2. Solid and dashed lines are guides to the eye. The insets are described in the text.

TC states is clear. We observe that, on a 1 ps time scale, and for $T < T_c$, most molecules are immobile and confined to within $0.02 r_H$. On the other hand, a small fraction ($< 10\%$) are free to move relatively large distances, up to $0.3 r_H$, probably through cooperative motion. Because of the time-dependent exchange between the LC and TC populations, the average molecule will be highly localized, then be transiently associated with a LC domain and freed to move away from its initial position. Subsequently, it will be relocalized as the LC domain passes to a new region of space. These conditions are sufficient to yield the hopping behavior and will necessarily do so provided that (1) the wait time between excursions is much longer than the time required for reorganization in a LC state (≈ 1 ps), and (2) molecules make unusually large excursions as a LC domain passes through a region of space (i.e., $\sigma_{LC} > \sigma_{TC}$). Both of these conditions are manifestly fulfilled at $T < T_c$ for all the systems studied, and appear to hold even for $T < 1.5T_c$.

The hopping mechanism described above requires only transient domains of rapid, cooperative motion. It is not obvious how these domains arise, but their origin must be due either to dynamics (kinetic energy fluctuations) or structural heterogeneity. A dynamic origin was initially proposed [3,4]. While difficult to imagine how it might physically occur [26], dynamically induced hopping was indirectly supported by a lack of correlation between structure and dynamics when the latter was averaged over a time comparable to the structural relaxation time, τ_α at $T \geq T_c$ [27,28]. The data of Fig. 3 suggest that dynamic states change on a time scale of a few ps at $T > T_c$, so, in retrospect, it is not surprising that no correlation was found

between structure and dynamics. Recent work has shown that a correlation between structure and dynamics is found when dynamics are measured over times $< \tau_\alpha$ [29,30]. Further, two aspects of our data suggest a predominately structural origin for hopping. First, we observe a linear temperature dependence in $\log(\Phi)$ (see Fig. 3), whereas a dynamic origin would yield a $-1/T$ dependence from $\Phi \propto e^{-E/kT}$. Second, the fact that σ_{LC} is temperature insensitive and remains large, even at 60 K, strongly suggests a structural origin.

Putting aside the origin of the dynamic states, we now show that their behavior can be used to derive the key dynamic signatures of liquids. A system with two exchanging dynamic states such as is discussed above may have as many as three dynamic signatures. Dynamics at the fast and slow extremes (β_{fast} and α) will arise from motion in the LC and TC states, respectively. A third dynamic signature may arise on an intermediate time scale from exchange between the TC and LC states. Importantly, the exchange process and TC relaxation will merge if all molecules exchange between states on a time scale comparable to or shorter than the intrinsic TC relaxation time. We propose that the intermediate time scale process, the TC-LC exchange, corresponds to β_{JG} relaxation.

Within the proposed framework, we expect that $\langle x^2 \rangle = \sqrt{\pi} \Phi \sigma_{LC}^2 / 2 = 6D_T \tau_{\beta_{JG}}$ if we assume that translation occurs primarily in LC domains (since $\sigma_{LC} \gg \sigma_{TC}$), and that new displacements will occur at a rate proportional to the TC-LC exchange rate. We also expect that β_{JG} relaxation (TC-LC exchange) will facilitate α relaxation when the intrinsic TC relaxation is sufficiently slow. In this limit, α relaxation would be facilitated by first passage of an LC domain, $\log(\tau_\alpha) \propto \log(\tau_{\beta_{JG}}) / \gamma$, where $\gamma < 1$ would arise from spatial correlations in the relaxation process [31], due to the “stringlike” nature of the mobile particle arrangements at short time [23]. We expect the TC-LC exchange to be only weakly cooperative, so treat it as a simple activated process, with activation energy, $E_a \propto 1/\sigma_{TC}$, for rearrangement of TC particles at a TC-LC interface. Under these assumptions, we write expressions for these relaxation and transport processes

$$\tau_{\beta_{JG}} = \tau_{ex} = \tau_0 \exp \left[\frac{\delta}{kT \bar{\sigma}_{TC}} \right], \quad (2)$$

$$\frac{\tau_\alpha}{\tau_c} = \left(\frac{\Phi_c \tau_{\beta_{JG}}}{\Phi \tau_c} \right)^{1/\gamma}, \quad (3)$$

$$D_T = \frac{\sqrt{\pi} \Phi \sigma_{LC}^2}{12g \tau_{\beta_{JG}}}, \quad (4)$$

where τ_0 is an inverse attempt rate, associated with β_{fast} relaxation, $\bar{\sigma} = \sigma / r_H$, τ_c and Φ_c are the α relaxation time and Φ value at T_c (we assume $\tau_\alpha \approx \tau_{\beta_{JG}}$ at T_c), and g , a fitting factor, is expected to be $O(1)$.

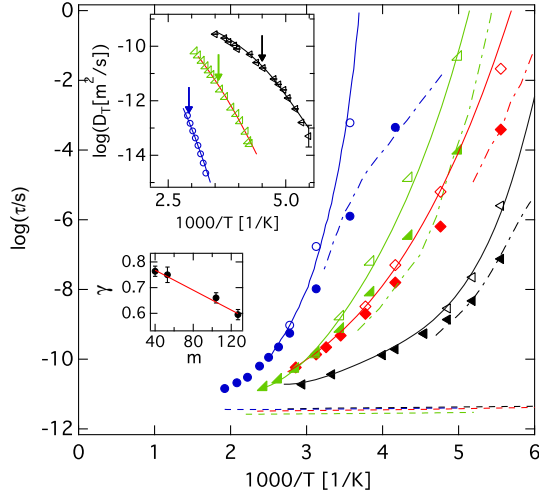


FIG. 4 (color online). Calculated relaxation times: $\tau_{\beta,JG}$ (solid symbols), τ_{α} (hollow symbols), $\tau_0 = \tau_{\beta,fast}$ (dashed lines). Measured relaxation times: τ_{α} (solid lines) [32,34,35], $\tau_{\beta,JG}$ (dashed-dotted lines) [32,34]. The upper inset shows D_T values for PC [14], glycerol [33] and sorbitol [17] (symbols), and fits to Eq. (4) (solid lines). The arrows indicate T_c for these liquids. Symbols have the same association with samples as in previous figures. The lower inset shows the correlation between γ and fragility.

Figure 4 shows experimentally measured values of τ_{α} and $\tau_{\beta,JG}$ for four of the five liquids studied here, as well as fits to Eqs. (2) and (3). We vary τ_0 , δ , and γ to find simultaneously optimal fits to the α and β_{JG} data. We obtain excellent fits with all measurements, except for β_{JG} measurements of glycerol between 220 and 270 K. Those data were extracted from a weak β peak largely buried under a strong α peak [32]. Table I gives fit parameters. The parameter τ_0 has values expected for $\tau_{\beta,fast}$, and we find that δ and γ correlate strongly with the melting temperature, T_m , and the fragility index, m , respectively. We obtain the relations $\delta = -25 + 8.6 \times 10^4/T_m$ with correlation coefficient $r^2 = 0.97$ and $\gamma = 0.85 - 2.0 \times 10^{-3}m$, with $r^2 = 0.99$. The relationship between γ and m is shown in the lower inset of Fig. 4.

Results from Eq. (4) are plotted in the upper inset of Fig. 4, along with direct measurements of D_T for glycerol [33] and PC [14], and an estimate of D_T for sorbitol [17]. Although these materials have a large variation in fragility and degree to which the Stokes-Einstein relation is violated, the model produces the correct temperature dependence for all systems for which we have diffusion data. It further gives correct absolute values within a factor of 5 before correction by the multiplicative fitting parameter, g . Additionally, the values of g are very similar for the two systems for which D_T has been directly measured.

The model and data we present provide an explanation for the the β_{JG} relaxation and suggest a straightforward relation between $\langle \tau_{\beta,JG} \rangle$ and σ_{TC} , which depends only on T_m ; properly scaled with T_m , all the $\langle \tau_{\beta,JG} \rangle$ data will very nearly coincide. The data further suggest that β_{JG} and hopping arise from a structural phenomenon such as

TABLE I. Fit parameters.

	τ_0 (ps)	δ (kJ/mol)	γ	g	T_m	m
PC	2.0 ± 0.4	380 ± 12	0.66 ± 0.2	$0.23 \pm .04$	218	104
PG	2.5 ± 0.4	377 ± 10	0.76 ± 0.2	...	214	40
Glycerol	2.5 ± 0.4	248 ± 8	0.74 ± 0.3	0.38 ± 0.02	291	53
Sorbitol	3.2 ± 0.4	212 ± 9	0.59 ± 0.2	4.5 ± 0.4	383	127

frustrated packing, indicating that these should occur in any liquid or noncrystalline solid.

The model and data also suggest that α relaxation derives primarily from the β_{JG} process at the temperatures we have investigated. At $T > T_c$, more than 10% of molecules are involved in LC domains at any time, and, since these domains should contain no more than three to four molecules [2,23], most molecules are within 1.5 molecular diameters of an LC domain. In this regime, the entire system should relax on roughly the time scale for exchange of molecules into and out of LC domains, giving $\tau_{\alpha} \approx \tau_{\beta,JG}$. At $T < T_c$, Φ drops and LC domains become more scarce, so that it takes increasingly longer for β_{JG} exchange events to accomplish α relaxation, leading to a bifurcation of these relaxation times. If the exchange events occurred randomly in space, the simple relation $\tau_{\alpha} = \tau_{\beta,JG}/\Phi$ would hold. The exponent, γ , relating changes in τ_{α} and $\tau_{\beta,JG}$ arises because the LC domains move through the material to generate stringlike mobile domains [23], so TC-LC exchange events will have nontrivial spatial correlations. It seems that essentially all fragility-related information is contained in γ , and Φ , since $\langle \tau_{\beta,JG} \rangle$ appears to be nearly universal when temperature is scaled by T_m . In the upper inset to Fig. 3, we find a loose correlation between m and the temperature dependence of Φ .

In addition to TC-LC exchange, α relaxation should occur via a parallel intrinsic TC relaxation processes. The fact that we have accounted only for the latter but still obtain excellent fits indicates that the former is relatively slow, and this is consistent with the MCT result that the intrinsic α relaxation diverges [4]. We suggest that intrinsic TC relaxation may not contribute significantly until higher temperatures and that the anomalies observed near T_A may be due to changes in the relative importance of TC and TC-LC exchange to α relaxation.

The mechanism we propose for β_{JG} relaxation provides a rationale for many known features of this relaxation process. For example, it justifies the close connection between β_{JG} relaxation and translational diffusion [36,37], provides a temperature-dependent activation energy as required by Dyre *et al.* [38], and provides a mechanism for the relevant PEL to be similar to that of the α relaxation [7]. It also provides for a connection between β_{JG} and low- T heat capacity anomalies [39], since the LC domains persist at low temperature [40]. Further, the drop in Φ at low temperature explains the negative temperature dependence in the strength of β_{JG} [41].

Finally, we note that the presence of regions of extended mobility as evidenced here could give rise to an excess density of states and, thus, could be related to the boson peak. On the other hand, the relationship would not be trivial, since the amplitude of the boson peak and the magnitude of Φ observed by us have very different temperature dependencies.

Based on our QENS data and literature cited herein, we have presented a simple two-state dynamic model that ties α , β_{JG} , and β_{fast} relaxations, and translational diffusion to ps time scale dynamic heterogeneity in liquids. The model allows simple and quantitative calculation of time scales for each of these processes, and provides a molecular mechanism for hopping and for the Johari-Goldstein β process. We advocate a structural origin for the LC state related to packing frustration and, thus, expect the proposed model to be generic.

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