Evidence for Anomalous Dynamic Heterogeneities in Isostatic Supercooled Liquids

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Upon cooling, the dynamics of supercooled liquids exhibits a growing transient spatial distribution of relaxation times that is known as dynamic heterogeneities. The relationship between this now well-established crucial feature of the glass transition and some underlying liquid properties remains challenging and elusive in many respects. Here we report on computer simulations of liquids with a changing network structure (densified silicates), and show that there is a deep and important link between the mechanical nature characterized by topological constraints and the spatial extent of such fluctuations. This is not only revealed by a maximum in the dynamic correlation length ξ_4 for fluctuations when the liquid becomes isostatically rigid, but also by a contraction of the volume of relaxing structural correlations upon the onset of stressed rigidity.

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Once crystallization has been avoided under fast cooling, the viscosity of many liquids is found to increase dramatically to reach $\eta = 10^{12}$ Pa · s at a reference temperature that is defined as the glass transition temperature T_g. This empirical definition signals that below T_g a liquid will be too viscous to flow on a laboratory time scale, and the resulting material will be identified as a glass, i.e., a material that displays all the salient microscopic features of a liquid but has the macroscopic characteristics of a solid.

Both recent experiments [1,2] and computer simulations [3–5] indicate that nontrivial spatiotemporal fluctuations emerge during the course of this slowing down of these so-called dynamic heterogeneities, and these features are not restricted to supercooled liquids satisfying $T > T_g$ because they can be observed in jammed systems [1], colloids [2], or polymers [6] as well, underscoring the general character of the physical behavior [7]. Such investigations have detected that a small part of the liquid evolves more rapidly, but have also verified that "rapid" regions have a collective behavior that strongly controls the dynamics. For the particular case of supercooled liquids, it has been furthermore established that such dynamic fluctuations become stronger as the liquid gets closer to T_g, and these can be characterized [8] by a growing dynamic correlation length ξ_4 that seems to diverge in a fashion similar to typical length scales close to a critical point in ordinary phase transitions [9]. Another important feature signaling an increased complexity of the fluid dynamics in the vicinity of the glass transition is the detection of a dramatic change in the connection between translational and rotational diffusivity and viscosity that is valid in equilibrated liquids, and quantified by the Stokes-Einstein (SE) relation: $\eta \propto T/D$. Once T is sufficiently low, this relation breaks down [10], and the diffusivity becomes much higher than its value expected from the viscosity using the SE relation. The reasons for this breakdown remain an unanswered question, although connections with dynamic heterogeneities have been stressed [11].

We adopt in the present Letter a slightly different approach, albeit in line with previous simulation work on, e.g., soft sphere liquids [12] or silica [13] regarding dynamic heterogeneities. Network glass-forming liquids [14,15] under different thermodynamic conditions afford, indeed, a unique venue for exploring the dynamics and understanding ultimately the origin of the nontrivial relaxation events linked to dynamic heterogeneity. Such systems are dominated by important structural features given the ionocovalent nature of bonds and short range order motifs, e.g., tetrahedra such as in silica. Secondly, one can tune the thermodynamic conditions (composition, pressure) in a continuous fashion, and compositional trends in physical properties can be compared, leading to the establishment of new correlations. This choice may be particularly interesting since another key quantity of the glass transition, fragility, is known to change nonmonotically in such network-forming liquids with a fragile-strong-fragile evolution upon, e.g., appropriate alloying [16].

Here, we show that these features encoded in various quantities emphasizing the onset of a heterogenous dynamics are dominated by the elastic nature of the supercooled liquid structure. This picture can be cast in a rather simple form by using topological constraints [17], which derive from rigidity theory, while also revealing that particular liquids display an enhanced ease to collective dynamics. It is found, indeed, that isostatic liquids fulfilling the Maxwell stability criterion display a certain number of anomalous behaviors that highlight their critical nature and the one of corresponding glasses. The number of topological constraints n_c is evaluated from the relevant bond-stretching and bond-bending interactions and compared to available degrees of freedom per atom [18]. Results indicate that when the supercooled liquid is optimally constrained ($n_c \simeq 3$), the dynamic correlation length for fluctuations is maximum, whereas the volume on which structural relaxation is correlated contracts as the liquid becomes stressed rigid ($n_c > 3$). Secondly, the obtained trends with pressure or constraints also permit us to investigate in detail the validity of the SE relation in connection with the rigid nature of the network structure. The target system is a prototypal network-forming liquid, $2SiO_2$-Na_2O (NS2), which is known to undergo a rigid to flexible transition induced by pressure, and the focus is on two temperatures at 2000 and 1500 K in order to eventually separate effects due to the viscous slowing down from rigidity. For details regarding the simulation procedure [19], successful comparison with experimental data [19,20], and the estimate of topological constraints [15], we refer the reader to the relevant articles.

To establish our conclusions, we have first built on the framework for characterizing dynamic heterogeneity introduced by Lačević *et al.* [21]. The spatially heterogeneous dynamics for the densified liquids under consideration can be easily decoded from accumulated atomic scale snapshots by comparing two structures at two different times via the measure of an overlap function that is defined by

$$Q(t) = \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathbf{r}_i(0) - \mathbf{r}_j(t)), \tag{1}$$

out of which a fluctuation $\chi_4(t) = \beta V[\langle Q^2(t)\rangle - \langle Q(t)\rangle^2]/N^2$ can be determined that represents the volume on which structural relaxation processes are correlated, χ_4 being also expressed in terms of a "coarse-grained" four-point time dependent density correlation functions $g_4(r,t)$ measuring correlations of motions between time $t = 0$ and t arising at two points $\mathbf{r}$ and $\mathbf{0}$ [21].

Using the simulated trajectories, we first represent in Fig. 1 the behavior of the overlap function $Q(t)$ that exhibits the usual complex decay, also found in the intermediate scattering function $F_s(k,t)$. The trend with pressure is, in fact, rather close to the one obtained at the same pressures for $F_s(k,t)$ [15]; i.e., $\langle Q(t)\rangle$ decays at long times but for some intermediate pressures (6 GPa) a typical relaxing time is found to be substantially reduced. By choosing a fixed value [i.e., $\langle Q(t)\rangle = 1/e$], at 2000 K we find, indeed, a typical time $\tau_Q = 35$, 11, and 45 ps for 0, 6, and 22 GPa, respectively. These values are close to those found from $F_s(k,t)$. As the temperature decreases to 1500 K, the relaxation time increases substantially as expected (see below). The fluctuation of $Q(t)$ [i.e., $\chi_4(t)$, inset] not only indicates that correlated motions are time dependent and $\chi_4(t)$ is zero at short times but also displays a maximum at $t = t_4^{\max}$ that is also pressure dependent.

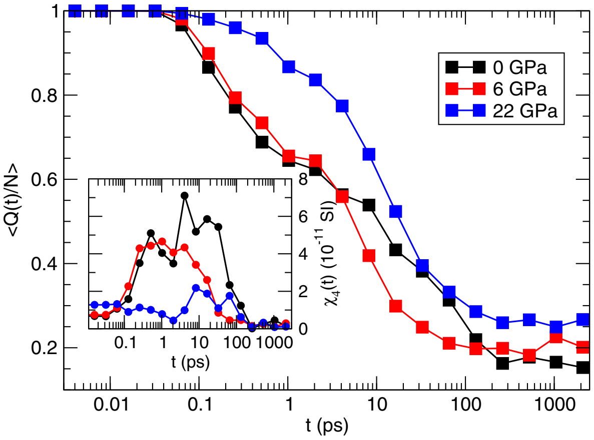

FIG. 1. Behavior of the overlap order parameter $Q(t)$ for three selected pressures in densified liquid NS2 for $T = 2000$ K. The inset shows the corresponding fluctuations of $Q(t)$ embedded in the time-dependent order parameter $\chi_4(t)$.

Next, we determine the link with structural correlations. From the calculated function $g_4(r,t)$, by Fourier transform one can obtain the four-point structure factor $S_4(k,t)$, which is represented in Fig. 2 for the time $t = t_4^{\max}$, and which increases at small k for all pressures. The low wave vector part of $S_4(k,t)$ usually permits us to extract a correlation length ξ_4 that describes, e.g., density fluctuations near a liquid-gas transition in the Ornstein-Zernike theory [9]:

$$S_4^{\mathrm{ol}}(k,t) = \frac{S_4^{\mathrm{ol}}(0)}{1 + k^2 \xi_4(t)^2}. \tag{2}$$

From Eq. (2) and the different trajectories, the correlation length $\xi = \xi_4(t_4^{\max})$ can be represented as a function of pressure (inset of Fig. 2). Interestingly, ξ_4 goes through a broad maximum found at $\simeq 4.8$ Å for both 2000 and 1500 K. This maximum is approximatively defined between 2 and 12 GPa, signaling that in this pressure range, the supercooled liquids display a rather different dynamics as compared to low or high pressure, with enhanced correlated motions of atoms, and an obvious anomaly. Similarly, we find (not shown but see below) an anomalous behavior for both $t_4^{\max}$ and $\xi_4(t_4^{\max})$, which display a minimum and a maximum in the same pressure interval, respectively.

What is the origin of these nonmonotonic trends? Our key result is the identification that these nonobvious features in dynamic heterogeneities are driven by aspects of rigidity.

To support this claim, we evaluate for all obtained trajectories at given P and T the density n_c of rigid topological constraints from calculating the radial and

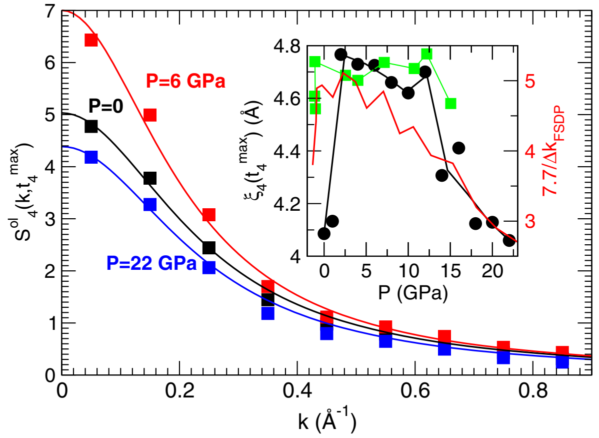

FIG. 2. Small k behavior of $S_4^{\mathrm{ol}}(k,t_4^{\max})$ for selected pressures in liquid NS2 at 2000 K, fitted by Eq. (2) (solid lines). The inset shows the Ornstein-Zernicke fitted correlation length ξ_4 as a function of pressure for 2000 K (filled black circles) and 1500 K (filled green boxes). Right axis (red) shows the Si–O coherence length $7.7/\Delta k_{\mathrm{FSDP}}$ obtained from the static structure factor [22] in the glassy state (300 K). See text for details.

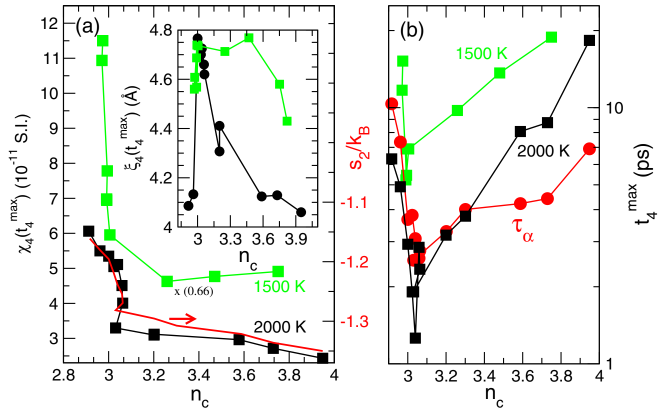

FIG. 3. (a) Behavior of $\chi_4(n_c)$ determined from Fig. 1 as a function of the number of constraints n_c. Right axis (red curve): pair correlation entropy $s_2(n_c)$. The inset represents the correlation length $\xi_4(t_4^{\max})$ (same as the inset of Fig. 2) but this time represented as a function of n_c. (b) $t_{\max}$ as a function of the number of constraints n_c for 2000 and 1500 K. The red curve is a direct calculation of τ_α [15].

angular excursions between pairs or triplet of atoms [14,15]. This enumeration is directly inspired by the classical mechanics view of topological constraints associating large or small radial or angular motion with the absence or presence of corresponding bond-stretching and bond-bending restoring forces. In the literature, such an analysis for amorphous networks and glasses has led to the recognition that the Maxwell stability criterion for isostaticity fulfilled when $n_c = 3$ in 3D is associated with an elastic phase transition [18], the locus of the transition being determined by the presence of structures that are optimally constrained. At low (zero) temperature, this transition separates a flexible phase having low energy deformation modes [23] from a stressed rigid phase with a large bond or interaction density, these salient features being now also observed in jammed solids [24,25] and biological networks [26]. The extension to liquids from phenomenological models [17,27] or MD simulations [14] permits us to study the effect of such rigidity transitions also in the liquid phase, and we build on these below.

Figure 3(a) (inset) shows the behavior of ξ_4, now represented as a function of the constraint density n_c. The location of the maximum noticed previously (Fig. 2, inset) is found to coincide with the criterion $n_c = 3$ typical of isostatic liquids. Remarkably, the behavior of ξ_4 with temperature also highlights the fact that the dynamical correlation length displays only a limited variation for $n_c = 3$, whereas ξ_4 increases substantially when $n_c \neq 3$ as also observed in some other glass-forming liquids [7]. Mousseau and co-workers [28] have suggested that the addition or destruction of single bonds close to the isostatic condition induces important variations in the size of macroscopic regions of the network, suggesting that the system is maintained in a critical state as $n_c \simeq 3$. As a result, the volume over which structural correlations emerge is found to also display an anomalous behavior that is revealed by a dramatic decrease of χ_4 [Fig. 3(a)]. This quantity reduces, indeed, by more than a factor 2, and underscores the presence of a percolative phase transition, as also observed at low temperature [18,24]. It involves a rapid decrease of local structural ordering as reflected by the similar evolution of the calculated pair correlation entropy s_2 [20,29]. In flexible networks, the absence of rigid structures and the possibility of low energy deformation modes permit us to avoid the emergence of large scale correlations, whereas in stressed rigid liquids, both internal eigenstress and a large bond density prevent a dynamic evolution of the structural correlations. Furthermore, it is also recognized that the dynamic correlation length ξ_4 is of the same order as the one related to the first sharp diffraction peak (FSDP) (red curve, inset of Fig. 2) [22,30] found at low temperature (300 K) in static correlations of network-forming species (Si–O). The width of this peak leads to a coherence length for ordering $7.7/\Delta k_{\mathrm{FSDP}}$ [31] that is indicative of an average cluster size, following the Scherrer equation for microcrystals. Importantly, given the same trend and the same order of distances, one is led to believe that the dynamic correlation length ξ_4 is associated with this repetitive characteristic distance between (Si,O) atoms. It builds up in isostatic systems and give rise to the first sharp diffraction peak in the static structure factor $S(k)$ of corresponding glasses.

In addition, the typical time for maximal correlated motions (i.e., $t_4^{\max}$) is seen to be minimal when the liquid is isostatic, and for 2000 K the trend with n_c is found to nearly parallel the one obtained [15] from a separate computation of the viscosity η and G_∞ from the shear strain or shear stress response using $\tau_\alpha = \eta/G_\infty$, where G_∞ is a plateau shear modulus, once the intermediate time (β relaxation) processes have been relaxed [15,32]. The maximum value for ξ_4 that results from clusters with an enhanced cooperative motion turns out to induce a facilitation for a local structural relaxation as revealed by the minimum of $t_{\max}$ for the isostatic liquids.

The present results have a certain number of consequences regarding aspects driving the glass transition, and its connection with the rigidity of the underlying liquid, while also indicating features of criticality in the high temperature liquid as revealed by the cusplike behavior of ξ_4 close to $n_c \simeq 3$. It is usually believed that rigidity controls the fragility of network-forming melts, and isostatic systems lead to a strong (Arrhenius) behavior for the viscosity dependence [16], and involve a homogeneous spatial distribution of constraints. This, furthermore, leads to thermally reversing windows (Boolchand phases) with a minimal change in enthalpy across the glass transition [33] when $n_c \simeq 3$ [15]. Such reversible liquids usually display a strong character with minimum values for the fragility [16]. The correlations are only partially met in the present NS2 liquid because the evolution of the fragility [34] cannot be easily linked with the variation of ξ_4. In fact, NS2 glasses having reversible character [15] are also those that exhibit a maximal correlation length scale ξ_4 for dynamic heterogeneity and a critical nature in model networks [28], although the fragility does not show any anomaly [34]. One, thus, arrives at the conclusion that such isostatic liquids located at the flexible-to-stressed rigid elastic phase transitions lead to a rapid variation of dynamic heterogeneities that impacts the transport and relaxation properties: relaxation time, viscosity, diffusivity, and, ultimately the enthalpic relaxation at the glass transition. The generalized susceptibility χ_4 being related to the fluctuations in the number $Q(t)$ of the overlapping particles, one, finally, acknowledges that the onset of a stressed rigid liquid will induce a strong reduction of the volume of correlated motions. In parallel, the maximum of the correlation length ξ_4 associated with the overlapping particles indicates that isostatic liquids display a tendency to an onset of caging given that flexible regions are now significantly reduced and surrounded by an overconstrained network structure. This is usually also detected when ξ_4 increases on densification [4,8].

Although there are some conflicting conclusions on this issue [10,11,35,36], we finally discuss the connection of the dynamic heterogeneities with the breakdown of the SE relationship. A popular means to detect this breakdown is to represent calculated diffusivities as a function of η/T (Fig. 4). At low temperature, the representation deviates from the high temperature behavior $D \propto \eta/T$, and instead one usually uses a fractional SE exponent ζ such as $D \propto (\eta/T)^\zeta$ with $\zeta \simeq 0.6$–0.9 in many supercooled liquids [10,35,36]. Our results [20] indicate that the silicon diffusivity D_{Si} verifies, in fact, $D \propto \eta/T$, this observation being valid for all investigated temperatures or pressures [Fig. 4(a)], including the lowest one at 1500 K, and consistent with a compilation of data on silica [37]. However, the behavior of diffusivities D_{Na} of the more mobile Na atoms differs markedly from D_{Si} because a breakdown of the SE relationship can be detected at low temperatures. In addition, for a fixed temperature and when the rigidity nature of the liquid is tuned by pressure, even the fractional SE relationship is found to be partially valid only. As the rigidity analysis is performed (gray zone), it is found, indeed, that typical fractional SE exponents encountered in supercooled liquids can only fit the stressed rigid liquids having $n_c > 3$ [$\zeta \simeq 0.65(9)$, broken line in Fig. 4(b)], whereas flexible liquids involve fractional exponents of the order of $\zeta \simeq 0.2$, and the isostatic liquids an important variation of ζ with n_c. In addition, one now detects that for a fixed temperature flexible and isostatic liquids with changing pressure exhibit an increase of D_{Na}

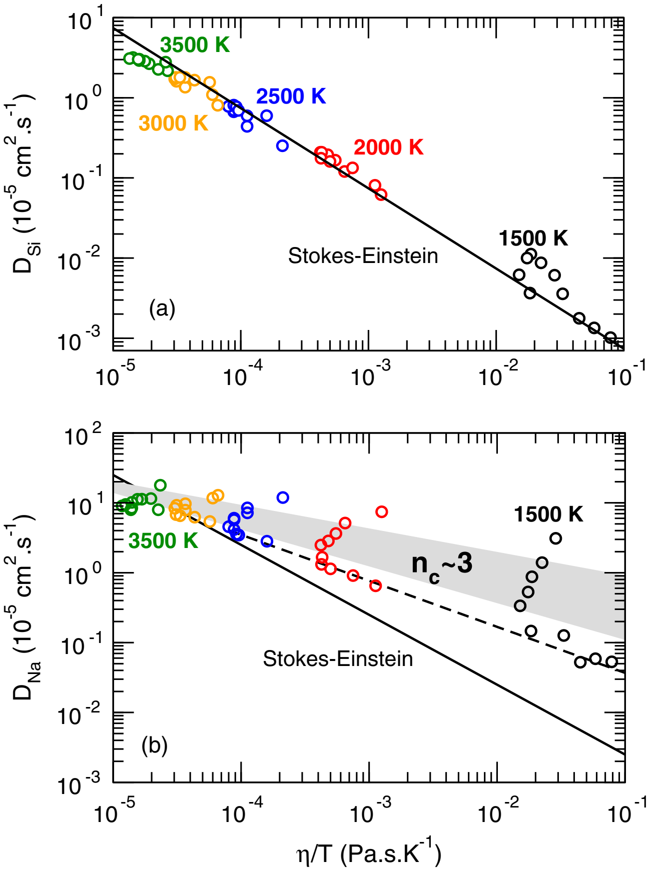

FIG. 4. SE plot showing calculated silicon (a) and sodium diffusivities (b) as a function of Green-Kubo calculated η/T for different sets of liquid temperatures and pressures or constraints. The solid line corresponds to the SE relationship (ζ) whereas the broken line in panel (b) corresponds to a fractional SE with $\zeta = 0.65(9)$. See text for details. The gray zone in panel (b) represents the zone of isostatic liquids, calculated using Refs. [14,15].

with increasing viscosity, and given the fragile or strong nature of such liquids [16], a proposed correlation [38] between SE deviation and fragility does not hold in the present case.

In conclusion, we have shown that the heterogeneous dynamics associated with the glass transition is linked with aspects of rigidity, and isostatic liquids are found to be at the critical edge of very different behaviors. While flexible (low-connected) and stressed rigid (highly connected) liquids exhibit larger relaxation times towards equilibrium, and a reduced dynamic correlation length, isostatic liquids fulfilling $n_c \simeq 3$ not only lead to an enhanced dynamic correlation that manifests by a maximum of ξ_4 but also display a dramatic variation in the volume of correlated motions. Given the reported connections between isostatic character and reversibility windows at T_g, the present anomalous features on dynamic heterogeneities in the liquid state are believed to drive well-known anomalies at the glass transition and in the glassy state occurring at the rigidity transition. It would be interesting to check the general character of these findings by focusing on other typical glass-forming systems known to undergo a rigidity transitions, including those (Ge–Se) that display also an anomaly in the fragility variation. Work in this direction is in progress.

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