On the static length of relaxation and the origin of dynamic heterogeneity in fragile glass-forming liquids

S. Davatolhagh
Department of Physics, College of Sciences, Shiraz University, Shiraz 71454, Iran

(Dated: March 23, 2022)

PACS numbers: 64.70.Pf

I. INTRODUCTION

In the glassy phenomenology, it is the super-Arrhenius slowing down of the transport properties that is most striking \[1, 2\]. We refer to the so-called fragile liquids \[3\], which are distinguished by a highly temperature-dependent effective energy barrier, $E_{\text{eff}}(T)$, in their thermally activated expression for structural or $\alpha$ relaxation time

$$\tau_\alpha(T) = \tau_\infty \exp(E_{\text{eff}}(T)/k_B T),$$

(1)

where $\tau_\infty \approx 10^{-15}$s is a high-$T$ relaxation time, and $k_B$ is the Boltzmann constant. The temperature variation of $\tau_\alpha(T)$ for fragile supercooled liquids is described over a wide range of temperatures by the empirical Vogel-Fulcher temperature, Eq. (2), is called the Vogel-Fulcher temperature, and of-

$$\tau_\alpha(T) = \tau_\infty \exp[A/(T - T_0)].$$

(2)

The apparent divergence temperature $T_0$ appearing in Eq. (2), is called the Vogel-Fulcher temperature, and is often found to be very close to the Kauzmann temperature $T_K$ \[5\], where the configurational entropy of the liquid appears to vanish, if it were to stay in equilibrium \[6\]. Although $T_K$ is not a rigorous lower-bound, it is a fairly good indication as to the lowest temperature a liquid can be supercooled \[7\]. We note that Eq. (2) automatically predicts a phase transition at $T_0$ \[8, 9\]. It is the case that in finite dimensions, and short-range interactions, a diverging time is normally accompanied by a diverging length. In fact, the large activation energy barrier $E_{\text{eff}}(T_g) \approx 50$ $k_B T_g$ observed for weakly bonded fragile liquids at the laboratory glass temperature $T_g$, is regarded as an indication for the cooperative nature of the relaxation dynamics \[10\]. Several equilibrium theories of the structural glass transition, invoke an increasing static correlation length that diverges at $T_K (\approx T_0)$ \[11, 12, 13\]. As the dynamics is activated, even a small correlation length leads to macroscopic values for $\tau_\alpha$ exceeding the observation time: thus, the falling out of equilibrium of the liquid at the laboratory glass temperature $T_g (> T_0)$, which is conveniently defined as that temperature where $\tau_\alpha(T_0) \sim 10^8$s \[8\].

The most puzzling aspect of this super-Arrhenius dynamic slow down is that it is not seen to be accompanied by any obvious change in the static structure of the liquid. The static structure factor (i.e. Fourier transform of the pair correlation function) obtained by X-ray and neutron scattering experiments reveals only marginal changes in the local density profile of polymers and molecular supercooled liquids \[14\]. In other words, an ‘extended’ short-range order of less than a nanometer in size begins to appear as the liquid is cooled toward $T_g$. This occurs while the $\alpha$ relaxation time as obtained from viscosity and a.c. dielectric susceptibility measurements increases by as much as 12 orders of magnitude. It is reconciling the above two aspects of the structural glass transition, i.e. structure versus dynamics, which remains a major challenge in the condensed matter physics \[15\]. Clearly, there is no detectable growing length associated with the density fluctuation. However, there are general arguments in favor of the fourth-order potential energy density correlation function and associated thermal susceptibility, the structural specific heat, as the ideal quantities for studying the static properties in fragile \[10\] and model glass-forming liquids \[15\]. Although in experiments the contribution of the potential energy is difficult to separate from the kinetic contributions to the specific heat, it is accessible in computer simulations of model glass-formers such as prototype Binary Mixture of Lennard-Jones (BMLJ) particles \[16, 17\].

From another perspective, and unlike the simple liquids treated as homogeneous \[21\], deeply supercooled liquids are also distinguished by dynamic heterogeneous domains \[21, 22\], a few nanometers across, with widely different relaxation times (varying by five orders of magnitude). Recent multi-dimensional Nuclear Magnetic Resonance (NMR) measurements are found to favor a heterogeneity size, $\xi_{\text{het}} = 2$–3 nm, i.e. 5 or more atomic diameters \[21, 23\]. Results obtained from the fluctuation...
theory \cite{24} using the Heat Capacity Spectroscopy (HCS) data \cite{25} are similar—though some times higher \cite{21}. As for their dependence on the temperature, more recent experimental procedures have discovered a growing dynamic length accompanying the glass formation in colloidal and molecular liquids \cite{27}. However, the origin of this dynamic heterogeneity remains unclear to date. Do dynamic heterogeneous domains correspond to any static correlation in the structure? The heterogeneity of time suggests possible heterogeneity in the structure. Thus, a knowledge of the typical size of the static and/or dynamic lengths, their temperature dependencies and correlation (if any) can go a long way in resolving the structural glass problem \cite{21}.

In a previous work \cite{16,28}, we proposed a Bond Ordering (BO) scenario for the glass transition in which the cooperative relaxation of bonds in terms of energy, uncorrelated with density ordering or crystallization \cite{21,50}, has been discussed. In this bond ordering picture, the structural component of the specific heat arising from the potential energy fluctuation, plays the central role as the thermal susceptibility associated with the static length for cooperative relaxation \cite{10}. This static relaxation length, $\xi_{BO}$, is defined as that length-scale over which energy fluctuations are correlated. It may also be regarded as an operational definition for the average linear size of Cooperatively Rearranging Regions (CRRs) discussed in the context of Adam-Gibbs-DiMarzio theory of cooperative relaxation \cite{11,12}. The scenario predicts a growing (and possibly diverging) structural specific heat with the lowering temperature for the fragile liquids, which has been in part corroborated by more recent Monte Carlo (MC) simulations of a Lennard-Jones binary mixture \cite{15}, by Fernandez et al. They found that local potential energy fluctuations are in fact correlated over distances much larger than the short range of the inter-atomic interactions. This is made evident by studying finite-size effects at normally inaccessible temperatures $T < T_{MCT}$, where $T_{MCT}$ is the apparent mode coupling transition temperature \cite{31}. Temperatures as low as 0.895 $T_{MCT}$ are accessed and studied in equilibrium using a local swap MC dynamics that is insensitive to the ‘cage-effect’, and thus drastically reduces the equilibration time.

Our aim in this paper is to make evident the correlation between the static relaxation length, $\xi_{BO}$, defined as the average length over which energy fluctuation is correlated, and the typical linear size of the dynamically heterogeneous domains, $\xi_{MCT}$, which close to $T_g$ is five or more atomic diameters \cite{21,27}. This is done in an attempt to clarify the physical origin of dynamic heterogeneity.

The rest of this paper is organized as follows: In Section \textbf{IV} we briefly review the implication for the static correlation length, of the theories of structural glass that invoke an underlying ideal glass transition. Prominent examples are the Adam-Gibbs-DiMarzio entropy model, and discontinuous mean-field spin glass models that have a random first-order transition in the mean-field formalism. We also discuss the potential-energy-landscape view of dynamics in supercooled liquids in section \textbf{II}. This paves the way in section \textbf{III} for a phenomenological determination of the structural contribution to the specific heat, $C_s$, and the corresponding static length of relaxation, $\xi_{BO}$, for the fragile supercooled liquids. The thermal behavior of $\xi_{BO}$ is derived from that of $C_s$ via an energy version of the Fisher scaling law. In section \textbf{IV} we discuss the implication of this novel approach with regard to the physical origin of dynamic heterogeneity, and its apparent relation to the mean field models of structural glass transition. A brief summary of the main results appears in section \textbf{V}.

\section{II. IMPLICATION OF PREVIOUS THEORETICAL WORK FOR STATIC CORRELATION LENGTH}

\subsection{A. Adam-Gibbs entropy model}

By considering the liquid to be made up of identical clusters of size $z$, each capable of undergoing independent rearrangement, Adam and Gibbs (AG) \cite{11} arrived at an activated expression for $\tau_a(T)$ where the effective energy barrier is given by $E_{\text{eff}}(T) = z^*(T)\Delta\mu$. $\Delta\mu$ is to be largely interpreted as the ‘potential energy barrier’ per atom against rearrangement in a cluster composed of $z^*(T)$ atoms, and taken to be a constant. $z^*(T)$ is the minimum ‘critical’ size of a CRR, allowing a transition between two configurations. By definition, the configurational entropy of this minimal CRR is given by $s^*_c \equiv k_B \ln 2$. It is easy to see that the ratio of the total number of atoms $N$ to the size of minimal CRR $z^*$, should be equal to the ratio of the total configurational entropy $S_c$ to the minimum entropy of a CRR $s^*_c$: $N/z^*(T)/S_c(T)/s^*_c$ \cite{22}. Thus, $z^*(T)$ is expressed in terms of the configurational entropy of the system

$$z^*(T) = Nk_B \ln 2/S_c(T).$$ \hspace{1cm} (3)

Furthermore, by assuming a hyperbolic form $\Delta C_p = C/T$ for the excess specific heat of the liquid over the equilibrium crystal \cite{1}, an approximate expression for the configurational entropy is obtained by the thermodynamic integration

$$S_c(T) = \int_{T_K}^{T} dT \Delta C_p(T) = C(T - T_K)/T.$ \hspace{1cm} (4)$$

On substitution into Eq. \textbf{3}, this results in VF equation being recovered. We also note that $z^*(T) \propto T/(T - T_K)$. Letting $z^*(T) \sim \xi_{AG}^*$, a (minimal) static relaxation length is obtained

$$\xi_{AG}(T) = \xi_\infty[1 - (T_K/T)]^{-1/3},$$ \hspace{1cm} (5)$$

where $\xi_\infty$ is constant and should be regarded as the typical inter-atomic spacing or an atomic diameter.
In fact the concept of the increasing size of cooperative regions with the lowering temperature, dates back to considerations by Jenckel in 1939 [32]. However, the thermal variation of cooperativity was formulated in terms of the atomic packing energy, while AG theory emphasizes the role of configurational entropy. It should also be pointed out that the central results of the Adam-Gibbs theory could be obtained without recourse to the concept of configurational entropy [33], with only the assumption of a diverging $z^*(T)$ as $T \to T_g$, where $T_g$ is a second-order phase transition point. For instance it has been found that the ratio $T_g/T_D = 1.28 \pm 0.08$ in agreement with the AG prediction $T_g/T_K = 1.30 \pm 0.04$. As may be seen from Table I, the static length of cooperativity at $T_g$ obtained from Eq. (5) in fact is too small to define cooperative regions. Adam-Gibbs arguments give rearranging units with at most 10 atoms near $T_g$. Considerations based on mean-field models of structural glass transition, lead to bigger cooperative regions, as described next.

B. Discontinuous mean-field spin glass models

From the notion of droplet fluctuations together with the concept of random first-order transition observed in discontinuous mean-field spin glass models [32, 33], a correlation length is predicted that varies as $\xi_{MF} \sim (T - T_K)^{-2/d}$, where $d$ is the space dimensions. To illustrate this mean-field result we follow the more direct approach presented in [32, 33]. An statistical mechanical analysis based on replica method [34, 36] reveals in mean-field models of structural glass transition (p-spin models, Potts glass, etc.) that there are in fact two distinct transitions at $T_D$ and $T_K$ ($T_D > T_K$), the first of which at $T_D$ is a dynamical transition akin to ideal mode coupling transition [31]. This dynamical transition at $T_D$ appears only in the mean-field, and is reduced to a crossover temperature in finite dimensions by the nucleation process or activated hopping between the multitude of the glassy metastable states, $N(T) \approx \exp[N\sigma(T)]$, in the range of temperatures $T_K < T < T_D$. Thus, the configurational entropy, $S_c(T) \equiv k_B \ln N(T)$, maintains its extensive character for $T_K < T < T_D$, as $N(T)$ is exponential in the number of particles $N$ in this temperature range. However, as the thermodynamic transition point $T_K$ is approached from above, the configurational entropy vanishes linearly, $S_c = S_{\infty}[(T/T_K) - 1]$, and the system stays in a glassy configuration indefinitely. It should also be pointed out that the replica overlap order parameter changes discontinuously despite the lack of a latent heat. The replica approach [34, 36] further indicates that

$$N(T < T_K) \propto \exp \left( \frac{T_K}{T_K - T} \right),$$

$$N(T > T_K) \propto \exp \left[ N \left( \frac{T}{T_K} - 1 \right) \right].$$  \hspace{2cm} (6)

A correlation length for the thermodynamic transition at $T_K$ is obtained by matching Eqs. (6) in the critical region, giving $N \sim (T - T_K)^{-2}$, and letting $N \sim \xi_{MF}^d$. Thus,

$$\xi_{MF}(T) = \xi_{\infty}[1 - (T_K/T)]^{-2/d}. \hspace{2cm} (7)$$

The correlation length exponent predicted is $\nu = 2/3$ in $d = 3$ dimensions.

We note, however, that the cooperative regions obtained from Eq. (7) involve at most 90 particles at $T_g$ [37]. This is a significant improvement over the AG result, but falls short of the size of dynamic heterogeneous domains observed at $T_g$, which typically comprise a few hundred atoms [28]. Another difficulty with this mean-field picture is that its glassy behavior is greatly modified in the short-range versions when studied numerically in three dimensions [38, 39]. MC simulations of a short-range version of p-spin glass model in three dimensions [38], indicate a continuous/second-order transition to the glassy phase accompanied by a diverging susceptibility or correlation length. The finite-size scaling results are found to be in favor of a correlation length exponent $\nu = 1$ (see, Fig. 3 in [38]). Similar behavior is observed in a short-range frustrated Ising Lattice Gas (FILG) model [38], which also is known to have a random first-order transition in the mean-field. The correlation length exponent is found to be unity for FILG too. In view of Harris criterion for the relevance of disorder in a second-order phase transition [40], which requires $\nu \geq 2/d$, and the above observations, we believe that mean-field $\nu = 2/3$ should be regarded as a lower-bound estimate of the correlation length exponent for the fragile glass-forming liquids. In section III we shall also argue for a correlation length exponent $\nu = 1$ for the fragile systems, using a different argument.

C. Dynamics as an activated potential energy barrier crossing

It is a long held view that in supercooled liquids, dynamics is dominated by the topographic properties of the system’s Potential Energy Landscape (PEL) [41, 42]: long-time $\alpha$ relaxation is dictated by thermally activated crossing of the potential energy barriers separating different valleys of the potential energy surface $\Phi(r_1, \ldots, r_N)$, which is defined over the $3N$-dimensional configurational space of the liquid comprising $N$ atoms. It is also argued that activated transport over the potential energy barriers begins to dominate at low temperatures, where $E_{\text{eff}}(T) \geq 5k_BT$ [41]. This description of dynamics in terms of the $(3N + 1)$-dimensional PEL, facilitates the study of collective phenomena in viscous liquids, and helps to unify in a simple way some of the static and kinetic phenomena associated with the glass transition [43].

More recently, it has been demonstrated using molecular dynamics simulations of model glass-forming li-
uities that the concept of activated hopping between whole super-structures of many PEL minima, called PEL Metabasins (MBs), is central to a quantitative description of the long-time dynamics in glass-forming liquids 14, 15. Here, the time evolution of the system is regarded as a sequence of MB visits each with a residence time \( \tau \). The mean residence/escape time from MB of energy \( e \) is given by \( \langle \tau(e, T) \rangle = \tau_c \exp(E(e)/k_BT) \), where \( e \) is defined as the energy of the lowest local minimum within the MB. In fact the activation barrier, \( E(e) \), is found to depend on the depth of MB in PEL, \( e \), in a rather simple way 13, 14: \( E(e) \approx -e \). The lower the \( e \), the higher is the activation barrier \( E(e) \). A suitable average over the MBs visited by the representative point at a given temperature, gives the average residence time \( \langle \tau(T) \rangle \), which is to be regarded as \( \tau_n(T) \):

\[
\tau_\infty/\langle \tau(T) \rangle = \int de \, p(e, T) \exp(-E(e)/k_BT) = \exp(-E_{\text{eff}}(T)/k_BT),
\]

where \( p(e, T) \) is the fraction of MBs within the range \( e \) to \( e+d \) visited by the representative point at \( T \). Clearly, \( E_{\text{eff}}(T) \) may be interpreted as some suitable average over the potential energy barriers \( E(e) \approx -e \) encountered by the liquid at a given temperature 15. An spectacular demonstration of this assertion is the concurrence between the crossover to super-Arrhenius relaxation and the commencement of the variation with temperature of \( \langle e(T) \rangle \) in an 80:20 BMLJ model liquid (see, Fig. 1 in 19). In order to better illustrate the close correlation between \( E_{\text{eff}}(T) \) and \( \langle e(T) \rangle \), in Fig. 1 we plot \( k_BT \ln(\tau_n/\tau_\infty) \) (\( \equiv E_{\text{eff}}(T) \)) against the average value of PEL minima, \( \langle e(T) \rangle \), for the temperatures accessed using the data of Ref. 19. The correlation is rather impressive. This indicates among other things that the effective activation energy barrier embodied in the empirical VF equation, may also be taken as an estimate for the thermal variation of \( \langle e(T) \rangle \), or that of the configurational energy density \( \langle \Phi(T) \rangle/N \), of the liquid 10:

\[
E_{\text{eff}}(T) \sim -\langle \Phi(T) \rangle/N.
\]

We use this result to estimate the temperature variation of the structural specific heat for the fragile glass-forming liquids.

III. IMPLICATION OF BOND ORDERING SCENARIO FOR STATIC LENGTH OF RELAXATION

In an attempt to clarify the physical origin of the dynamic heterogeneity observed in deeply supercooled liquids, we expand on the concept of bond ordering 23 and the associated correlation length 10. As pointed out in section 11, \( \xi_{\text{MF}}(T_g) \) is a significant improvement over \( \xi_{\text{AG}}(T_g) \), but consistently smaller than the typical linear size of the dynamic heterogeneous domains, \( \xi_{\text{het}}(T_g) \). As it turns out another static correlation length, \( \xi_{BO}(T_g) \), defined as the length-scale over which the potential energy fluctuation is correlated, is in perfect agreement with the experimental observation.

By bond ordering we refer to the correlated relaxation of bonds into their low-lying energy states, where interatomic bonds (as opposed to atoms) are treated as distinct objects possessing internal degrees of freedom or energy levels. The length-scale over which the energy fluctuations are correlated thus defines the static length of relaxation, \( \xi_{BO} \). The fourth-order correlation function in terms of the local density \( \rho(r) \), which may also be interpreted as a two-point energy correlation function in terms of the local potential energy density \( \phi(r) \), is defined by 17:

\[
G_E(r) = \langle \phi(r)\phi(0) \rangle - \langle \phi \rangle^2 \sim g(r/\xi_{BO})/r^{d-2+\eta'}.
\]

\( G_E(r) \) is a fourth-order correlator as \( \phi(r) \propto \rho(r)^2 \). The exponent \( \eta' \), is related to the structural specific heat exponent \( \alpha \), via a fluctuation-response equation

\[
C_s = \frac{1}{k_BT^2} \int d^d r G_E(r) \sim \int \xi_{BO}^d d^d r / r^{d-2+\eta'} \sim \xi_{BO}^{2-\eta'},
\]

where \( \xi_{BO} \) is the static correlation length beyond which the correlation function rapidly vanishes. From Eq. 11, where the link between the structural specific heat \( C_s \) and the static relaxation length \( \xi_{BO} \) becomes apparent, an energy version of the Fisher scaling 18 is obtained:

\[
\alpha = (2-\eta')\nu.
\]

Assuming \( \eta' = 0 \) for the fragile glass-forming liquids, which has been corroborated by the numerical studies of short-range versions of mean-field structural glass models 58, 59, we get

\[
\nu = \alpha/2.
\]

The structural specific heat \( C_s \) is in fact the temperature rate of change of the configurational energy. In view of Eq. 6, it is approximated by

\[
C_s = -\frac{\partial E_{\text{eff}}}{\partial T}.
\]

Using the effective energy barrier implied by equation 24, i.e., \( E_{\text{eff}}(T) = Ak_BT/(T - T_0) \), we have

\[
C_s = Ak_B(T/T_0 - 1)^2.
\]

Eq. 15 implies a power law temperature variation for the structural specific heat of the fragile supercooled liquids, with an exponent \( \alpha = 2 \). A critical power-law increase for the structural specific heat, has been recently reported in MC simulations of a BMLJ model liquid 17.
The exponent $\nu$ is thus given by $\nu = \alpha/2 = 1$. Hence, with the effective potential energy barrier embodied in the empirical Vogel-Fulcher equation, we have

$$\xi_{BO}(T) = \xi_\infty T / (T - T_0).$$

In fact, the quantity $F \equiv T_g / (T_g - T_0) = \xi_{BO}(T_g) / \xi_\infty$ is some times regarded as a measure of the fragility of the liquid. Its range of values for intermediate to most fragile of the liquids is $3 < F < 7.5$. Thus, more fragile the liquid, the larger is the static length of relaxation at $T_g$. Using Eq. (16), and $T_g/T_0 = 1.28 \pm 5.8\%$, the static length of relaxation at $T_g$ is determined to be in the range $3.4$–$7.0$ inter-atomic spacings. This is indeed in perfect agreement with the typical linear size of the dynamic heterogeneous domains observed at $T_g$.

IV. DISCUSSION

In Table I we compare the values obtained for static lengths $\xi_{BO}$, $\xi_{MF}$ and $\xi_{AG}$ at $T_g$. This is done using the ratio $T_g/T_0 = 1.28 \pm 5.8\%$. We find $\xi_{BO}(T_g) = 3.4$–$7.0$ atomic diameters in excellent agreement with $\xi_{MF}(T_g) \gtrsim 5$ atomic diameters. We also note that (energy) fluctuations of all linear sizes $x \lesssim \xi_{BO}$ must be possible, and indeed probable. (A similar, but stronger, effect arising from density fluctuations is believed to be the cause of critical opalescence observed in fluids near their critical point.) Thus, one expects heterogeneous domains with a distribution of relaxation times at $T_g$, or not too far above $T_0$, such that the bigger domains have longer life-times $\tau$. By assuming an activated form $\tau \sim e^\Delta$, and $x$ to vary by a factor of 10, we have $\tau$ values that vary by 4 decades. This therefore explains the existence of dynamic heterogeneities near $T_g$ whose life-times differ by several orders of magnitude.

We see that the correlated relaxation of bonds in terms of energy, can be viewed as the physical origin of the dynamic heterogeneity observed in deeply supercooled liquids.

It also is a matter of considerable interest that the BO exponent, $\nu = 1$, is in perfect agreement with that obtained from three-dimensional simulations of models of structural glass that exhibit a random first-order transition in the mean-field. In fact, it appears that bond ordering scenario provides a physical interpretation for the replica symmetry breaking transition observed in theory and simulation, where members of coupled replica tend to sit in front of each other in the low temperature glassy phase. Let us consider $m$ coupled replica constrained to be in the same state. This resembles a liquid consisting of (super)molecular structures with every molecule composed of $m$ number of coupled atoms. This is an artifact of the attractive coupling among the replica, and can be viewed as a theoretical indication for the local ordering of bonds in the realistic systems. A detailed investigation of this apparent analogy will be presented elsewhere.

V. SUMMARY

To summarize, the exponent governing the thermal behavior of the static relaxation length in fragile supercooled liquids, $\nu = 1$, implies a stronger temperature dependence for cooperativity than previously thought. The static relaxation length estimated at $T_g$ is in perfect agreement with the typical size of the dynamic heterogeneous domains in deeply supercooled liquids. Furthermore, this larger static length also explains the wide distribution of relaxation times associated with the heterogeneities, which is central to explaining the stretched exponential relaxation, and the decoupling of self-diffusion from viscosity in deeply supercooled liquids.

The correlated relaxation of bonds in terms of energy is therefore identified as the origin of dynamic heterogeneity in fragile supercooled liquids.

[1] M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. 100, 13200 (1996); C. A. Angell, Curr. Opin. Solid State Mater. Sci. 1, 578 (1996).
[2] P. G. Debenedetti, Metastable Liquids (Princeton University Press, Princeton, 1996).
[3] C. A. Angell, J. Non-Cryst. Sol. 131-3, 13 (1991); 102, 205 (1988).
[4] H. Vogel, Phys. Z. 22, 645 (1921); G. S. Fulcher, J. Am. Ceram. Soc. 8, 339 (1925).
[5] W. Kauzmann, Chem. Rev. 43, 219 (1948); F. E. Simon, Z. Anorg. Allgemein. Chem. 203, 217 (1931).
[6] C. A. Angell, J. Res. Natl. Inst. Stand. Tech. 102, 171 (1997); R. Richert and C. A. Angell, J. Chem. Phys. 108, 9016 (1999).
[7] S. R. Elliott, Physics of Amorphous Materials, 2nd Edn. (Longman Scientific, London, 1990).
[8] D. Kivelson, G. Tarjus, X. Zhao, and S. A. Kivelson, Phys. Rev. E 53, 751 (1996).
[9] M. Mezard, “First steps in glass theory” in More is different, M. P. Ong and R. N. Bhatt (eds.), (Princeton University Press, Princeton, 2001).
[10] G. Tarjus, D. Kivelson, and P. Viot, J. Phys.: Condens. Matter 12, 6497 (2000).
[11] G. Adam and J. H. Gibbs, J. Chem. Phys. 43, 139 (1965).
[12] J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys. 28, 373 (1958).
[13] T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, Phys. Rev. A 40, 1045 (1989).
[14] R. L. Leheny, N. Menon, S. R. Nagel, D. L. Price, K. Suzuya, and P. Thiyagarajan, J. Chem. Phys. 105, 7783 (1996); A. van Blaaderen and P. Wiltzius, Science 270, 1177 (1995).
[15] P. W. Anderson, Science 267, 1615 (1995).
[16] S. Davatolhagh, J. Phys.: Condens. Matter 17, 1275
(2005).
[17] L. A. Fernandez, V. Martin-Mayor, and P. Verrocchio, Phys. Rev. E 73, 020501 (2006).
[18] W. Kob, and H. C. Anderson, Phys. Rev. E 51, 4626 (1995).
[19] S. Sastry, P. G. Debenedetti, F. H. Stillinger, T. B. Schroder, J. C. Dyre, and S. C. Glotzer, Physica A 270, 301 (1999).
[20] J. P. Hansen and I. R. McDonald, Theory of Simple Liquids (Academic Press, London, 1986).
[21] M. D. Ediger, Annu. Rev. Phys. Chem. 51, 99 (2000).
[22] H. Sillescu, J. Non-Cryst. Solids 243, 81 (1999).
[23] U. Tracht, M. Wilhelm, A. Heuer, H. Fang, K. Schmidt-Rohr, H. W. Spiess, Phys. Rev. Lett. 81, 2727 (1998).
[24] L. D. Landau and E. M. Lifshitz, Statistical Physics (Pergamon, London, 1980).
[25] E. Douth, J. Non-Cryst. Solids 53, 325 (1982).
[26] E. Douth, H. Huth, and M. Beiner, J. Phys.: Condens. Matter 13, 451 (2001).
[27] L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. ElMasri, D. L’Hote, F. Ladieu, and M. Pierno, Science 310, 1797 (2005).
[28] S. Davatolhagh and B. R. Patton, Phys. Rev. B 64, 224206 (2001).
[29] H. Tanaka, J. Phys.: Condens. Matter 10, L207 (1998); ibid 11, L159 (1999).
[30] See, also, H. Tanaka, J. Chem. Phys. 111, 3163 (1999); ibid 111, 3175 (1999).
[31] W. Gotz and L. Sjogren, Rep. Prog. Phys. 55, 241 (1992); E. Leutheusser, Phys. Rev. A 29, 2765 (1984).
[32] E. Jenckel, Z. Physik. Chem. 184, 309 (1939).
[33] U. Mohanty, J. Chem. Phys. 100, 5905 (1994); Adv. Chem. Phys. 89, 89 (1994).
[34] T. R. Kirkpatrick and P. G. Wolynes, Phys. Rev. B 36, 8552 (1987).
[35] T. R. Kirkpatrick and D. Thirumalai, Transp. Theor. Stat. Phys. 24, 927 (1995).
[36] D. Thirumalai and T. R. Kirkpatrick, Phys. Rev. B 38, 4881 (1988).
[37] X. Xia and P. G. Wolynes, Proc. Natl. Acad. Sci. 97, 2990 (2000).
[38] M. Campellone, B. Coluzzi, and G. Parisi, Phys. Rev. B 58, 12081 (1998).
[39] A. de Candia and A. Coniglio, Phys. Rev. E 65, 16132 (2001).
[40] A. B. Harris, J. Phys. C 7, 1671 (1974).
[41] M. Goldstein, J. Chem. Phys. 51, 3728 (1969).
[42] F. H. Stillinger and T. A. Weber, Phys. Rev. A 25, 978 (1982); Science 225, 983 (1984).
[43] F. H. Stillinger, Science 267, 1935 (1995).
[44] S. Buchner and A. Heuer, Phys. Rev. Lett. 84, 2168 (2000); Phys. Rev. E 60, 6507 (1999).
[45] B. Doliwa and A. Heuer, Phys. Rev. Lett. 91, 235501 (2003); Phys. Rev. E 67, 031506 (2003).
[46] A. Saksaengwijit, B. Doliwa, and A. Heuer, J. Phys.: Condens. Matter 15, 1237 (2003).
[47] See, e.g., S. Davatolhagh, Am. J. Phys. 74, 441 (2006); and references therein.
[48] M. E. Fisher, J. Math. Phys. 5, 944 (1964).
[49] A. B. Bestul and S. S. Chang, J. Chem. Phys. 40, 731 (1964).
[50] H. E. Stanley, Introduction to phase transitions and critical phenomena (Oxford University Press, Oxford, 1971).
[51] See, e.g., X. Xia and P. G. Wolynes, Phys. Rev. Lett. 86, 5526 (2001).
FIG. 1: Dynamical activation energy $E_{\text{eff}}(T)$ is plotted against the average depth of PEL $\langle e(T) \rangle$ for temperatures accessed using the data of Ref. [19] in order to illustrate their correlation. Solid line is the least squares fit to the data points.
TABLE I: The static correlation lengths $\xi_{BO}$, $\xi_{MF}$ and $\xi_{AG}$ at $T_g$ are tabulated for comparison. The observed linear size of dynamic heterogeneous domains $[21, 27]$, $\xi_{\text{het}}(T_g)/\xi_{\infty} \gtrsim 5$, is in excellent agreement with the prediction based on bond ordering picture.

| Model                 | $\nu$ | $\xi(T_g)/\xi_{\infty}$ |
|-----------------------|-------|--------------------------|
| Bond Ordering         | 1     | 3.4–7.0                  |
| Mean Field            | 2/3   | 2.3–3.7                  |
| Adam and Gibbs        | 1/3   | 1.5–1.9                  |