What Does the Potential Energy Landscape Tell Us about the Dynamics of Supercooled Liquids and Glasses?

B. Doliwa[1] and A. Heuer[2]

[1]*Max Planck Institute for Polymer Research, Mainz, Germany*

[2]*Institute of Physical Chemistry, University of Münster, D-48149 Münster, Germany*

(Received 4 June 2003; published 2 December 2003)

For a model glass former we demonstrate via computer simulations how macroscopic *dynamic* quantities can be inferred from a potential energy landscape (PEL) analysis. The essential step is to consider whole superstructures of many PEL minima, called metabasins, rather than single minima. We show that two types of metabasins exist: some allowing for quasifree motion on the PEL (liquidlike), and the others acting as traps (solidlike). The activated, multistep escapes from the latter metabasins are found to dictate the slowing down of dynamics upon cooling over a much broader temperature range than is currently assumed.

DOI: 10.1103/PhysRevLett.91.235501 PACS numbers: 61.20.Ja, 61.43.Fs, 64.70.Pf, 66.30.–h

For the analysis of the still unsolved problem of supercooled liquids and glasses, the viewpoint of the potential energy landscape (PEL) has turned out to be very useful [1–4]. To this end, one considers the high-dimensional vector of all particle coordinates as a point moving on the surface of the total potential energy. At sufficiently low temperatures, the system resides near the local minima of the high-dimensional PEL. It has turned out that the PEL description of thermodynamics starts to work when cooling below approximately $T = 2T_c$, where T_c is the critical temperature of mode-coupling theory [5]. In this temperature regime the statistical properties of PEL minima fully determine all *thermodynamic* properties [6–9].

What is still lacking in the literature is a full quantitative understanding of *dynamics*, i.e., of the slowing down of molecular motion upon cooling. In this connection, the single-particle diffusion coefficient, $D(T)$, is a typical macroscopic quantity of interest. For a model glass former we have demonstrated via computer simulations that $D(T)$ can be inferred from a PEL analysis in a quantitative way. The essential step is to consider whole superstructures of many PEL minima, called metabasins [2,8,10–13], rather than single minima. Metabasins are reminiscent of protein-folding funnels [14] or related structures in small clusters [15].

The goal of this Letter is to derive physical consequences of this mapping between PEL and dynamics and thus to obtain a coherent picture of the glass transition. In particular we will dwell on the interpretation of the activation energies for fragile systems in the Arrhenius diagram, the concept of liquidlike and solidlike behavior [16], and the question of a possible crossover at T_c, as implied by the mode-coupling temperature and the analogy to p-spin models.

In what follows we analyze a binary mixture of Lennard-Jones particles (BMLJ). All details of the BMLJ have been reported in [10]. This system is designed to model a $Ni_{80}P_{20}$ mixture [17]. Langevin molecular dynamics have been employed with a simulation box of $N = 65$ particles at density $\rho = 1.2\sigma_{\mathrm{ref}}^{-3}$. Throughout the Letter, all quantities are given in reduced units, which, in the case of $Ni_{80}P_{20}$, correspond to $\sigma_{\mathrm{ref}} = 2.218$ Å, $\epsilon_{\mathrm{ref}} = 7.762$ kJ/mol, $t_{\mathrm{ref}} = 1.323$ fs, $T_{\mathrm{ref}} = 934$ K, and $D_{\mathrm{ref}} = \sigma_{\mathrm{ref}}^2/t_{\mathrm{ref}} = 0.372\ \mathrm{cm}^2/\mathrm{s}$. For the temperature regime of our analysis, a system size of $N = 65$ is provably sufficient to reproduce the dynamic properties of a macroscopic system [18,19]: We have checked, e.g., that $D(T)$ is the same for $N = 130$ within 10% for $T > T_c = 0.45T_{\mathrm{ref}}$. The minima are obtained by a steepest descent minimization. As usual we perform regular quenches of the system to monitor the energies of the corresponding energy minima. In addition, we use temporal interval bisectioning to resolve the elementary transitions between minima [12].

The definition of metabasins (MBs) is motivated by the observation that during the molecular dynamics in configuration space the system performs several back-and-forth jumps between adjacent minima until finally this region is left. The description of the transport may be simplified if these minima are regarded as a single superstructure, i.e., a MB [12]. Thus, the MBs correspond to an appropriate tiling of configuration space. Although irrelevant for the understanding of thermodynamic properties, they are of outstanding importance for dynamics. As shown in [20] it is possible to find a strict definition of MBs which can be also used in practice. Similarly to the previous consideration of energy minima the time evolution of the system may be regarded as a continuous sequence of MB visits with individual residence (waiting) times τ.

We briefly summarize the main results of our analysis which will be important throughout this Letter. They all hold for $T < 2T_c$. (i) Analyzing the escape characteristics from MBs by repeated simulations from the same MBs at different temperatures T [10], it turns out that the mean residence time in MBs of energy ϵ is given to a good approximation by

$$\langle \tau(\epsilon, T)\rangle \approx \tau_0(\epsilon)\exp[E(\epsilon)/k_B T]. \tag{1}$$

The Arrhenius form of $\langle \tau(\epsilon, T)\rangle$ suggests that the escapes from MBs are thermally activated, with a barrier height of $E(\epsilon)$, introduced here as a fitting parameter. The prefactor $\tau_0(\epsilon)$ turns out to be basically independent of ϵ. (We define ϵ as the energy of the lowest minimum within a MB.) (ii) $E(\epsilon)$ is directly related to the PEL barriers in the high-dimensional surrounding of the MBs. By a detailed discussion of this issue, incorporating the funnel-like nature of MBs, this was verified [10]. Thus, by analyzing the local topology of MBs, $E(\epsilon)$ can be predicted. We may interpret $E(\epsilon)$ as the depth of a MB of energy ϵ. The deeper the MB in the PEL, i.e., the lower ϵ, the higher the activation energy. In this analysis one has to take into account that the escape from a MB is a multistep process, i.e., generally comprises hops between several minima. (iii) A crucial quantity is the average residence time $\langle \tau(T)\rangle$. It is defined as the average over all MBs encountered at a specific temperature, i.e., $\langle \tau(T)\rangle = \int d\tau \tau \varphi(\tau, T)$. By $\varphi(\tau, T)$ and $\varphi(\epsilon, T)$, respectively, we denote the distribution of waiting times and energies of visited MBs. (iv) The *population* of MBs with energy ϵ is given by $p(\epsilon, T) = \langle \tau(\epsilon, T)\rangle \varphi(\epsilon, T)/\langle \tau(T)\rangle$. Numerically, it is indistinguishable from the population of minima, normally studied in this field and is purely Gaussian in the accessible energy range [21]. Using Eq. (1) the inverse average waiting time can be written as

$$\tau_0/\langle \tau(T)\rangle \approx \int d\epsilon\, p(\epsilon, T)\exp[-E(\epsilon)/k_B T]$$
$$\equiv \exp[-E_{\mathrm{eff}}(T)/k_B T], \tag{2}$$

where the energy dependence of $\tau_0(\epsilon)$ has been neglected. $E_{\mathrm{eff}}(T)$ can be interpreted as the typical barrier height, which grows upon cooling; see below. (v) A simple relation exists between $\langle \tau(T)\rangle$ and $D(T)$ via

$$D(T) \approx \frac{a^2}{6N\langle \tau(T)\rangle}, \tag{3}$$

with a temperature-independent effective jump length $a \approx 1.0\sigma_{\mathrm{ref}}$ [12]. Thus, the temperature dependence of $D(T)$ is *exclusively* determined by the average waiting time, whereas all spatial aspects of diffusion are temperature independent. Such a simple relation does not hold on the level of single minima. Actually, as a side effect it turns out that the dynamics can be basically described as a random walk between MBs, thus suggesting a nontopographic view. With the definition $D_0 \equiv a^2/6N\tau_0$ we can thus write

$$D(T) \approx D_0 \exp[-E_{\mathrm{eff}}(T)/k_B T]. \tag{4}$$

Note that the ingredients of the constant D_0, i.e., a and τ_0, have been obtained from the simulations mentioned above. In the units of our simulation we have $D_0 \equiv a^2/6N\tau_0 \approx 1.3 \times 10^{-5} D_{\mathrm{ref}}$. If the BMLJ is mapped on a $Ni_{80}P_{20}$ alloy this corresponds to $D_0 \approx 4.8 \times 10^{-6}\,\mathrm{cm}^2/\mathrm{s}$.

Here we discuss the relevant physical implications of Eqs. (1)–(4). In Fig. 1(a) we show the barrier height $E(\epsilon)$ as a function of MB energy, and the population of MB energies, $p(\epsilon, T)$, for different temperatures. From these quantities we obtain an estimate for the diffusion coefficient, denoted $D_{\mathrm{est}}(T)$. A comparison of the estimated with the true diffusion coefficient $D(T)$ (directly from molecular dynamics) is shown in (b). The very good agreement at $T_c \leq T \leq 2T_c$ reflects the consistency of our approach and shows that we can indeed understand the macroscopic dynamics from knowledge of the thermodynamics and the local barriers.

From the simulations, we know $p(\epsilon, T)$ and $E(\epsilon)$ for $\epsilon > -302\epsilon_{\mathrm{ref}}$. Both quantities do not display finite-size effects in this energy range [19]. Because of the Boltzmann weighting in Eq. (2) one may hope that the available information is sufficient to reliably estimate $D_{\mathrm{est}}(T)$ also for $T < T_c$. To check this hypothesis, we have calculated $D_{\mathrm{est}}(T)$ thereby using extreme candidates for possible ϵ extrapolations ($\epsilon < -302\epsilon_{\mathrm{ref}}$); see Fig. 1. It turns out that $D_{\mathrm{est}}(T)$ is very insensitive to $E(\epsilon)$. For $p(\epsilon; T)$ we have extended the Gaussian description but have set $p(\epsilon; T) = 0$ below different cutoff energies ϵ_{min}.

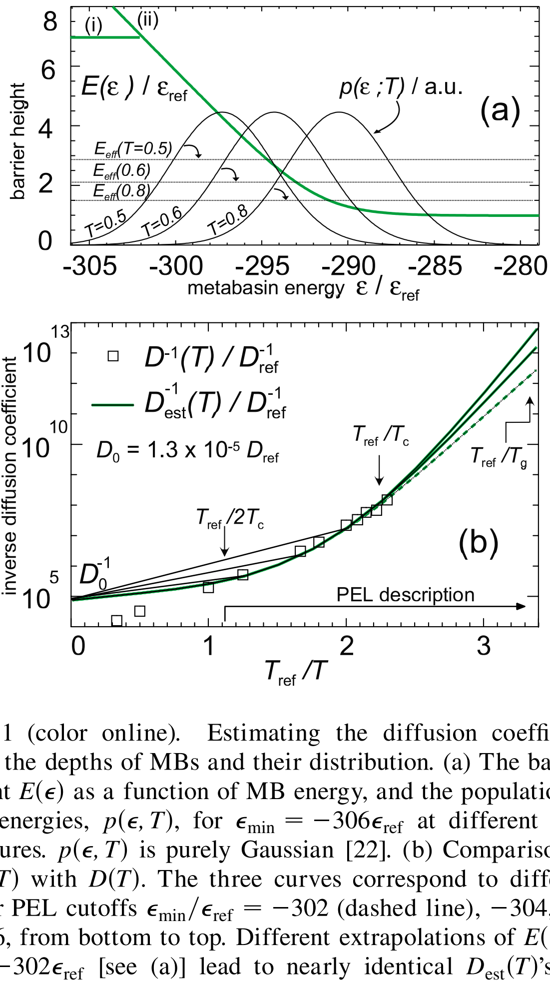

FIG. 1 (color online). Estimating the diffusion coefficient from the depths of MBs and their distribution. (a) The barrier height $E(\epsilon)$ as a function of MB energy, and the population of MB energies, $p(\epsilon, T)$, for $\epsilon_{\mathrm{min}} = -306\epsilon_{\mathrm{ref}}$ at different temperatures. $p(\epsilon, T)$ is purely Gaussian [22]. (b) Comparison of $D_{\mathrm{est}}(T)$ with $D(T)$. The three curves correspond to different lower PEL cutoffs $\epsilon_{\mathrm{min}}/\epsilon_{\mathrm{ref}} = -302$ (dashed line), -304, and -306, from bottom to top. Different extrapolations of $E(\epsilon)$ to $\epsilon < -302\epsilon_{\mathrm{ref}}$ [see (a)] lead to nearly identical $D_{\mathrm{est}}(T)$'s [no visible difference between the curves corresponding to (i) and (ii) in (a)]. We set $T_g \approx 0.3T_{\mathrm{ref}}$ [7].

(A lower bound for $\epsilon_{\min}$ is given by the condition that the number density of minima is of the order of $1/\epsilon_{\rm ref}$ [6]. This leads to $-306\epsilon_{\rm ref} \leq \epsilon_{\min} \leq -302\epsilon_{\rm ref}$ [21].) As shown in Fig. 1(b), the resulting uncertainty in the estimation of $D_{\rm est}(T)$ is small up to $T > 0.35T_{\rm ref}$ and becomes significant for lower temperatures. Since a cutoff at $-302\epsilon_{\rm ref}$ is probably far too drastic (see [21] for strong indications), however, the slowing down can be thus predicted semiquantitatively down to $T \approx T_g$, a region which very likely will never be accessible by molecular dynamics simulations.

Moreover, Eq. (4) implies that the activation energy which is obtained from connecting $(1/T = 0/T_{\rm ref}, D = D_0)$ and $[1/T, D(T)]$ in an Arrhenius plot by a straight line has a simple interpretation: it is the typical barrier height the system experiences at a given temperature [23]. This nontrivial interpretation has very recently been confirmed by hyperquench experiments [24], where the typical barrier height was measured by probing the specific heat during the reheating process.

To obtain a more detailed picture of MBs we have determined the distribution of waiting times, $\varphi(\tau, T)$, as shown in Fig. 2(a). By visual inspection, one can distinguish two different time regimes (separated by the vertical line at $\tau^* \approx 5000t_{\rm ref}$). In terms of energetics one expects that the long τ's arise from deep traps where the system is caught for a long time. In the opposite limit one may imagine that there are quite shallow MBs which do not strongly confine the system so that it will mainly stay close to the high-dimensional boundary of these MBs [see the sketches in (a)]. Thus, short waiting times correspond to just scratching the MBs. This expectation can be verified by analyzing the trajectory of the system during the MB visits; an example of such a computation is given in Fig. 1(b). There we plot $\langle \cos\alpha(\tau)\rangle$ over MBs of lifetime τ, where α is the angle between the entry point, the lowest minimum of the MB, and the exit point of the trajectory [see the sketches in (b)]. Again, two time regimes with a temperature-independent crossover time τ^* can be identified. Short visits to MBs lead to small values of α, meaning that the system indeed merely scratches these MBs. For $\tau > \tau^*$ the value of $\langle \cos\alpha(\tau)\rangle$ reaches a limiting value of ca. 0.2, indicating that entry and exit points are largely uncorrelated. This should be the case after a long residence inside a MB with many possible exits. Because of the difference in stability, we call the MBs with $\tau > \tau^*$ *solidlike*, the other MBs *liquidlike*. This notation has been borrowed from two-state models where these two types of configurations have been postulated [16].

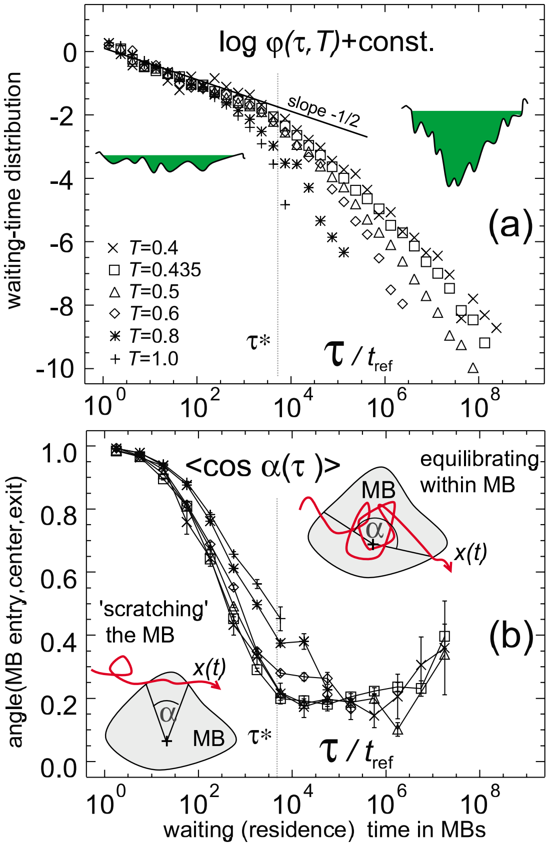

FIG. 2 (color online). Different exploration of MBs, as evidenced by the waiting-time distributions and the correlations between MB-entry and -exit points. (a) The distribution $\varphi(\tau, T)$ of waiting times at different temperatures. (b) Average value of $\langle \cos\alpha(\tau)\rangle$ over MBs of lifetime τ (see text and the sketches in (b), $x(t)$ symbolizes the high-dimensional trajectory of the system).

Clearly, the molecular slowing down upon cooling is caused by the enhancement of solidlike configurations. This can be quantified in two different ways. First, one may determine the fraction of solidlike configurations the system encounters, i.e., $\varphi_{\rm sol}(T) \equiv \int_{\tau^*}^{\infty} d\tau \varphi(\tau, T)$, where $\varphi_{\rm sol} < 0.5$ implies that more liquidlike than solidlike configurations are visited. Second, we can specify the *fraction of time* spent in solidlike configurations, which can be expressed as $p_{\rm sol}(T) \equiv \int_{\tau^*}^{\infty} d\tau p(\tau, T)$ with $p(\tau, T) = \tau\varphi(\tau, T)/\langle \tau(T)\rangle$. $p_{\rm sol} > 0.5$ implies that the system is mostly residing in solidlike configurations. In Fig. 3 we show the temperature dependence of $\varphi_{\rm sol}$ and $p_{\rm sol}$. Three different temperature regimes can be distinguished (see the sketch in Fig. 3): For $T > 2T_{\rm c}$ both quantities are smaller than 0.5. Thus, the system behaves liquidlike. Interestingly, this temperature regime (defined by *dynamics*) is exactly the temperature regime for which the minima no longer influence the *thermodynamic* properties of the system [4]. Below $2T_{\rm c}$, $p_{\rm sol}$ is larger than 0.5. Thus, the system mainly resides in solidlike MBs. Finally, below a temperature near $T_{\rm c}$, also $\varphi_{\rm sol}$ exceeds 0.5, i.e., we have a trap-to-trap motion. This crossover, however, is very gradual.

With Eq. (2) we can also analyze the question in which temperature regime the dynamics are dominated by activated processes. We call a process activated if the activation energy $E(\epsilon)$ is larger than $5k_{\rm B}T$. To this end, we consider the fraction of $\langle \tau(T)\rangle$ which is made up by activated hops, i.e.,

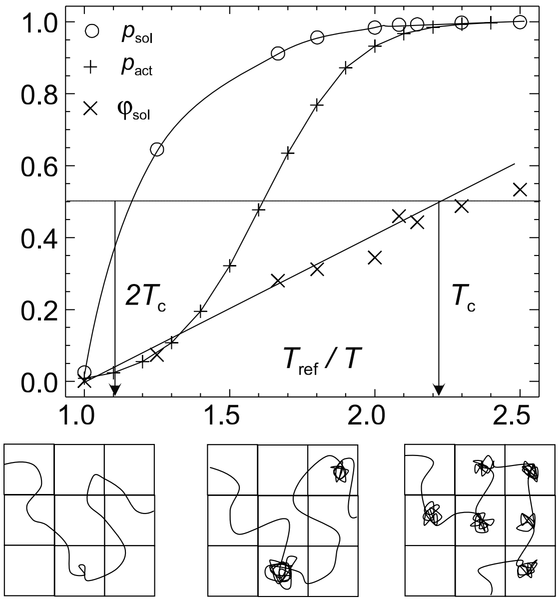

FIG. 3. The temperature dependence of p_{sol} (the fraction of time spent in solidlike configurations), φ_{sol} (the fraction of solidlike configurations encountered during the time evolution), and p_{act} (a measure for the contribution of activated processes to the diffusion coefficient; see text). In the lower part we depict schematic plots of the scenarios in the three temperature regimes. The squares symbolize the different MBs.

$$\langle \tau(T)\rangle^{-1} \int_{E(\epsilon)>5k_BT} d\epsilon \langle \tau(\epsilon, T)\rangle \varphi(\epsilon, T) \equiv p_{act}(T),$$

as shown in Fig. 3. The crossover temperature for which $p_{act} = 0.5$ is close to $1.5T_c$ (which is not very sensitive to the definition of p_{act}). Thus, already significantly above T_c, the dynamics are dominated by activated processes. Please note that the MBs contributing to the above integral are solidlike since they fulfill $\langle \tau(\epsilon, T)\rangle \gtrsim \tau^*$ (see [10]). This is why $p_{act}(T) \leq p_{sol}(T)$.

The present results seem to be at variance with the current understanding that activated transitions between PEL minima set in at T_c, whereas above T_c they are irrelevant. The latter scenario is motivated by the properties of p-spin models [25] and has been backed by the observations that the number of free directions (obtained via instantaneous-normal-mode analyses [26,27]), is directly related to the diffusion coefficient and that above T_c the system is close to transition states rather than close to minima [28,29]. In our earlier publication [10], we have already pointed out the problems with the latter kind of investigation. More importantly, though, the above-cited works do not incorporate the MB structure of configuration space. In doing so, one has focused on the vast majority of *intra*-MB transitions, which, however, are irrelevant for relaxation.

Finally, we note that the results of our work with respect to the crossover to activated behavior as well as the nontopographic nature of inter-MB dynamics is compatible with the implications obtained from a recent analysis of spin-facilitated models of the glass transition [30].

We thank C. A. Angell, L. Berthier, J. P. Garrahan, and H.W. Spiess for helpful discussions.

---

[1] M. Goldstein, J. Chem. Phys. **51**, 3728 (1969).
[2] F. H. Stillinger, Science **267**, 1935 (1995).
[3] P. G. Debenedetti and F. H. Stillinger, Nature (London) **410**, 259 (2001).
[4] S. Sastry, P. G. Debenedetti, and F. H. Stillinger, Nature (London) **393**, 554 (1998).
[5] W. Götze and L. Sjogren, Rep. Prog. Phys. **55**, 241 (1992).
[6] S. Sastry, Nature (London) **409**, 164 (2001).
[7] F. Sciortino, W. Kob, and P. Tartaglia, Phys. Rev. Lett. **83**, 3214 (1999).
[8] S. Büchner and A. Heuer, Phys. Rev. Lett. **84**, 2168 (2000).
[9] E. La Nave, S. Mossa, and F. Sciortino, Phys. Rev. Lett. **88**, 225701 (2002).
[10] B. Doliwa and A. Heuer, Phys. Rev. E **67**, 031506 (2003).
[11] R. A. Denny, D. R. Reichman, and J.-P. Bouchaud, Phys. Rev. Lett. **90**, 025503 (2003).
[12] B. Doliwa and A. Heuer, Phys. Rev. E **67**, 030501 (2003).
[13] T. F. Middleton and D. J. Wales, Phys. Rev. B **64**, 024205 (2001).
[14] J. D. Bryngelson, J. N. Onuchic, N. D. Socci, and P. G. Wolynes, Proteins **21**, 167 (1995).
[15] K. D. Ball, R. S. Berry, R. E. Kunz, F. Y. Li, A. Proykova, and D. J. Wales, Science **271**, 963 (1996).
[16] E.W. Fischer, A. Bakai, A. Patkowski, W. Steffen, and L. Reinhardt, J. Non-Cryst. Solids **307**, 584 (2002).
[17] T. A. Weber and F. H. Stillinger, Phys. Rev. B **31**, 1954 (1985).
[18] S. Büchner and A. Heuer, Phys. Rev. E **60**, 6507 (1999).
[19] B. Doliwa and A. Heuer, J. Phys. Condens. Matter **15**, S849 (2003).
[20] A. Saksaengwijit, B. Doliwa, and A. Heuer, J. Phys. Condens. Matter **15**, S1237 (2003).
[21] B. Doliwa, Ph.D. thesis, Shaker Verlag, Aachen, 2003.
[22] A. Heuer and S. Büchner, J. Phys. Condens. Matter **12**, 6535 (2000).
[23] J. C. Dyre, Phys. Rev. B **51**, 12 276 (1995).
[24] C. A. Angell, Y. Z. Yue, L. M. Wang, J. R. D. Copley, S. Borick, and S. Mossa, J. Phys. Condens. Matter **15**, S1051 (2003).
[25] A. Crisanti and F. Ritort, Physica (Amsterdam) **280A**, 155 (2000).
[26] E. La Nave, H. E. Stanley, and F. Sciortino, Phys. Rev. Lett. **88**, 035501 (2002).
[27] J. Chowdhary and T. Keyes, Phys. Rev. E **65**, 026125 (2002).
[28] L. Angelani, R. D. Leonardo, G. Ruocco, A. Scala, and F. Sciortino, Phys. Rev. Lett. **85**, 5356 (2000).
[29] T. S. Grigera, A. Cavagna, I. Giardina, and G. Parisi, Phys. Rev. Lett. **88**, 055502 (2002).
[30] L. Berthier and J. P. Garrahan, J. Chem. Phys. **119**, 4367 (2003).