PHYSICAL REVIEW E **88**, 022313 (2013)

Overlap fluctuations in glass-forming liquids

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(Received 7 June 2013; published 22 August 2013)

We analyze numerically thermal fluctuations of the static overlap between equilibrium configurations in a glass-forming liquid approaching the glass transition. We find that the emergence of slow dynamics near the onset temperature correlates with the development of non-Gaussian probability distributions of overlap fluctuations, measured using both annealed and quenched definitions. Below a critical temperature, a thermodynamic field conjugate to the overlap induces a first-order phase transition, whose existence we numerically demonstrate in the annealed case. These results establish that the approach to the glass transition is accompanied by profound changes in the nature of thermodynamic fluctuations, deconstructing the view that glassy dynamics occurs with little structural evolution.

DOI: 10.1103/PhysRevE.88.022313 PACS number(s): 64.70.Q−, 05.20.Jj, 05.10.−a

Theoretical approaches to the physics of glass-forming materials are broadly organized in two categories [1]. A first class of theories concentrates on thermodynamic aspects, typically starting from a description of (assumed) relevant structural features of viscous liquids (configurational entropy, geometrical motifs, free volume), from which slow dynamics is predicted to emerge [2]. A second class of models is based on the opposite view that the thermodynamics of viscous liquids is not evolving in any essential way and focuses directly on relaxational aspects. This dynamical viewpoint is justified by the observation that the structure of viscous liquids does not seem to differ drastically from that of simple liquids, at least at the level of two-body static correlations. In recent years, this view gained support because it can directly be connected to detailed studies of dynamic heterogeneity in glassy materials [3], which have unambiguously established that nontrivial spatiotemporal fluctuations accompany the glass transition [4].

In this work, we show that nontrivial, measurable thermodynamic fluctuations develop in supercooled liquids approaching the glass transition. We characterize their nature and show that they are also intimately related to dynamics. To obtain these results, we analyze the thermal fluctuations of a thermodynamic quantity, the overlap between equilibrium configurations. The physical motivation is that if the glass transition is controlled by a sharp decrease in the number of available metastable states [5] possibly leading to the entropy crisis first discussed by Kauzmann [6], it should then become more likely for two independent equilibrium configurations to belong to the same state and thus to have a large mutual overlap. Therefore, thermal fluctuations of the overlap, just like the more technical construction of point-to-set correlations [7], should directly reveal and quantify the emergence of growing structural correlations in glass-forming liquids approaching the glass transition.

In the context of supercooled liquids, the fluctuations of the overlap Q between equilibrium configurations have first been analyzed for spin glass models displaying a random first-order transition (RFOT) [8,9], where the overlap distribution is needed to characterize the low-temperature phase. However, the overlap is also useful *above* the glass transition, because it allows the introduction of a Landau free energy $V(Q)$, also called "effective potential" [10]. The potential was shown theoretically to capture the temperature evolution of RFOT free energy landscapes. In the mean-field limit where these concepts are well-defined, $V(Q)$ loses convexity when metastable states first appear; it then develops a local minimum at the mode-coupling singularity, which becomes the global one at the "ideal" or Kauzmann glass transition [10]. Direct measurements of $V(Q)$ in finite dimensions are scarce and conflicting [11–14]. It was found to display none of the mean-field features in two lattice glass models [12,13], while a recent investigation using soft spheres suggests a change in the convexity of $V(Q)$ near the mode-coupling temperature [14].

The potential $V(Q)$ also serves as a starting point for field-theoretical calculations attempting to extend RFOT results to finite dimensions [15–19]. These calculations additionally suggest that the RFOT mean-field landscape is highly fragile with respect to finite-dimensional fluctuations [20], which could even affect the universality class to be considered [21]. Since these findings directly challenge the relevance of a thermodynamic perspective to supercooled liquids, detailed studies of $V(Q)$ in finite dimensions are needed.

A more direct interpretation of the effective potential is obtained from its definition as a "large deviation" function for the equilibrium fluctuations of the overlap,

$$P(Q) \sim \exp[-\beta N V(Q)], \tag{1}$$

where $P(Q)$ is the probability distribution of equilibrium overlap fluctuations in a system with N particles at temperature $T = \beta^{-1}$ (we set Boltzmann's constant to unity). Equation (1) shows that the temperature evolution of $V(Q)$ directly affects the nature of thermal fluctuations of the overlap and also suggests a conceptually simple way of measuring $V(Q)$. Interestingly, Eq. (1) provides a direct connection with dynamical views of glasses. Recently, large deviations of *dynamical* observables have been analyzed [22]. The emergence of spatially heterogeneous dynamics was related to the appearance of non-Gaussian (nearly exponential) probability distributions of dynamic fluctuations. Equivalently, these broad tails imply that a field conjugated to the dynamic activity should induce a nonequilibrium first-order phase transition between two phases with distinct dynamics, as observed numerically [23,24]. While the existence of long-lived metastable states (as in RFOT) is sufficient to explain these dynamic fluctuations and nonequilibrium transitions [25], alternative explanations with trivial thermodynamics also exist [23]. Therefore, establishing the existence of thermodynamic observables obeying a phenomenology similar to that of dynamic ones will provide a concrete bridge between static and dynamic viewpoints [26].

We use computer simulations to analyze static fluctuations of the overlap in a simple numerical model of a glass-forming material. We consider a 50:50 binary mixture of harmonic spheres [27] of diameter ratio 1.4, which we study using Monte Carlo dynamics. The Hamiltonian reads $H(\{\mathbf{r}\}) = \sum_{j>i} v(\frac{|\mathbf{r}_i - \mathbf{r}_j|}{\sigma_{ij}})$, with the harmonic pair interaction $v(r \leqslant 1) = \frac{E}{2}(1-r)^2$, truncated for distances larger than the mean diameter $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$, and $\{\mathbf{r}\} \equiv (\mathbf{r}_1, \ldots, \mathbf{r}_n)$. For the density $\rho = 0.675$ (using the small particle diameter as the unit length), this model behaves as a binary hard sphere mixture [28], which is a well-established model to analyze the glass transition. It is characterized by an onset temperature around $T_{\rm on} \approx 10$ and a mode-coupling temperature $T_{\rm mct} \approx 5.2$, with temperatures expressed in units of $10^{-4}E$ [29]. The overlap Q_{12} between configurations 1 and 2 is defined as

$$Q_{12} = \frac{1}{N} \sum_{i,j=1}^{N} \theta(a - |\mathbf{r}_{1,i} - \mathbf{r}_{2,j}|), \tag{2}$$

where $\theta(x)$ is the Heaviside function, $\mathbf{r}_{1,i}$ denotes the position of particle i within configuration 1, and we take $a = 0.3$. By definition, $Q_{11} = 1$, while Q_{12} is small for uncorrelated configurations. (of order $\approx \frac{4}{3}\pi\rho a^3 \equiv Q_{\rm rand} \ll 1$). Note that exchanging the positions of two particles does not decrease Q_{12}. Therefore, the overlap represents an "agnostic" measure of the degree of similarity between two amorphous density fields, with no reference to a specific type of structural order.

By definition, $V(Q)$ represents the free energy cost to maintain two thermalized copies of the liquid at a fixed value of their mutual overlap. Formally, this amounts to performing the following *quenched* calculation:

$$V_{\rm q}(Q) = -\frac{T}{N} \int d\mathbf{r}_2 \frac{e^{-\beta H_2}}{Z_2} \log \int d\mathbf{r}_1 e^{-\beta H_1} \delta(Q - Q_{12}), \tag{3}$$

where $H_1 \equiv H(\{\mathbf{r}_1\})$ and $H_2 \equiv H(\{\mathbf{r}_2\})$, while Z_2 is the corresponding partition functions. In Eq. (3), the thermal fluctuations of Q_{12} are first probed for a fixed configuration 2 drawn from the equilibrium distribution, and then the logarithm of the probability distribution is averaged by sampling independent configurations.

This procedure is numerically demanding because it requires two successive averages. A simpler, but approximate, procedure is to use an *annealed* definition:

$$V_{\rm a}(Q) = -\frac{T}{N} \log \iint d\mathbf{r}_2 d\mathbf{r}_1 e^{-\beta(H_2+H_1)} \delta(Q - Q_{12}), \tag{4}$$

where configurations 1 and 2 are fluctuating simultaneously, and no disorder average is needed.

Direct measurements of $V(Q)$ are difficult because typical fluctuations of Q are small compared to the average value $\approx Q_{\rm rand}$. To probe large deviations of the overlap, we use umbrella sampling techniques to measure the statistical weight of untypical values of the overlap. In practice, we use for each temperature T a series of n independent simulations, each simulation being biased by a Gaussian perturbation to the original Hamiltonian, $W_i(Q) = k_i(Q - Q_i)^2$, for $(i = 1, \ldots, n)$, which biases the overlap towards a desired value $Q_i \in [Q_{\rm rand}, 1]$. We make sure that each independent simulation first reaches the (biased) equilibrium and that simulations are long enough that they can properly sample equilibrium fluctuations in the biased phase space. Thus, each simulation returns the measurement of the (biased) probability distribution functions, $P_i(Q)$. We then use multihistogram reweighting methods to reconstruct the unbiased probability $P(Q)$ from the n independently measured $P_i(Q)$ [30],

$$P(Q) = \frac{\sum_{i=1}^{n} P_i(Q)}{\sum_{i=1}^{n} e^{-\beta W_i}/Z_i}, \tag{5}$$

where the Z_i are defined self-consistently as

$$Z_i = \int_0^1 dQ' \frac{\sum_{j=1}^{n} P_j(Q')}{\sum_{j=1}^{n} e^{\beta(W_i - W_j)}/Z_j}. \tag{6}$$

We find that up to 16 independent simulations are needed to accurately reconstruct $P(Q)$ over the entire relevant range, depending on the system size studied, $N = 64$, 108, and 256, and on the temperature, $T \geqslant 7$. We were not able to properly sample fluctuations for $T < 7$ (and thus closer to $T_{\rm mct}$). The more demanding simulations are for large Q, large N, and low T. Up to 40 independent samples were used for the disorder average in Eq. (3). Finally, note that using biasing potentials $W_i(Q)$ efficiently solves the problem (first discussed in Ref. [11]) of translational and rotational invariances in Eqs. (3) and (4).

We present in Fig. 1 the numerical results obtained for both $V_{\rm q}(Q)$ and $V_{\rm a}(Q)$ in harmonic spheres for a range of temperatures, $T \geqslant 7$, which thus encompasses the onset of slow dynamics. These results indicate that thermal fluctuations of the overlap become broader as temperature is lowered and deviate increasingly from a Gaussian behavior, which would correspond, via Eq. (1), to a parabolic $V(Q)$. As suggested by the dashed lines, the fluctuations are well described for temperatures $T \lesssim 10$ and for intermediate Q by an exponential behavior. Note that for the annealed case at the lowest T the potential is clearly not convex, at least for this moderate system size [31]. Overall, this behavior is in excellent agreement with results obtained within mean-field models displaying a RFOT, where the convexity of $V_{\rm q}(Q)$ is lost below $T_{\rm on}$. For finite-dimensional systems, convexity should be restored through the emergence of interfaces and phase separation between high-Q and low-Q phases [14], therefore yielding exponential decay in $P(Q)$, and thus linear behavior for $V(Q) \sim -T \log P(Q)$, as observed in Fig. 1. We find quantitative, rather than qualitative, differences between $V_{\rm a}$ and $V_{\rm q}$. The main effect of the quenched disorder in these data is to introduce an additional source of fluctuations which depresses slightly the emergence of exponential decay from $T \approx 10$ for the annealed case to $T \approx 8$ for the quenched case.

It is remarkable that $V(Q)$, which quantifies the thermal fluctuations of a *purely static* observable, loses convexity near (or slightly below) the onset temperature. Below $T_{\rm on}$, time correlation functions develop a two-step decay, and dynamics become spatially heterogeneous. Our results

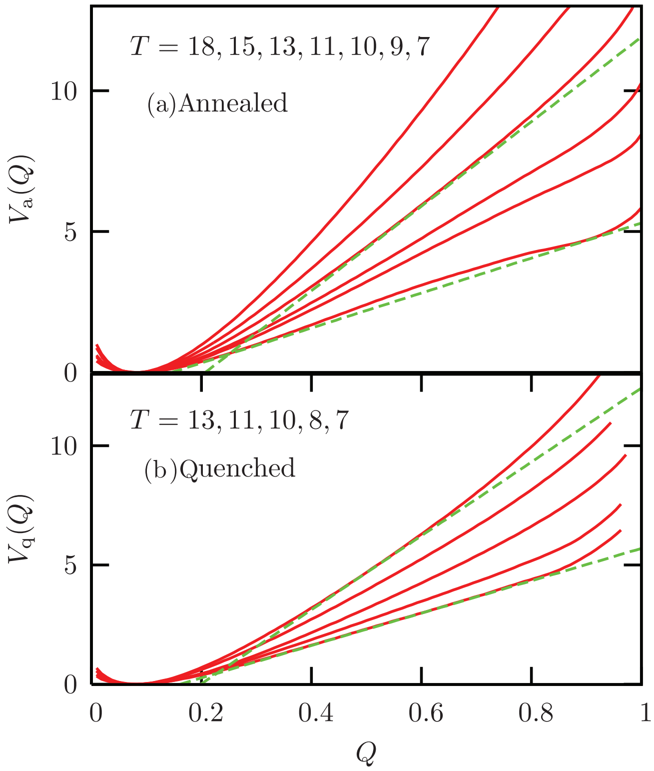

FIG. 1. (Color online) Temperature evolution of effective potential using (a) annealed and (b) quenched averages, for $N = 108$ particles. Very similar behavior is obtained for $N = 64$ and $N = 256$ (not shown). Data are vertically shifted data at different T such that $V(Q) = 0$ at the low-Q mininum. Dashed lines represent straight lines, and temperature decreases from top to bottom.

are thus qualitatively distinct from the emergence of non-Gaussian fluctuations of dynamic observables [22], and they demonstrate that thermodynamic fluctuations are (at least) as relevant as dynamic ones. The physical interpretation of the behavior of $V(Q)$ offered by RFOT is that $T_{\rm on}$ marks the emergence of many metastable states, whose number decreases as temperature is lowered further. This makes it more and more likely for two configurations drawn at random to belong to the same state and thus to have a large mutual overlap, as observed in Fig. 1. This also suggests that the driving force for structural relaxation is reduced at low T, which is the RFOT theory explanation for the slowing down of the dynamics [32].

A direct, but spectacular, consequence of the loss of convexity of $V(Q)$ is that a field conjugated to the overlap should induce an *equilibrium* first-order phase transition [10,33–36], because its main effect is to "tilt" the potential towards large Q values. Physically, this amounts to studying the phase diagram of two coupled copies of the same system:

$$H_{\rm tot}(\{\mathbf{r}_1\},\{\mathbf{r}_2\}) = H(\{\mathbf{r}_1\}) + H(\{\mathbf{r}_2\}) - \epsilon Q_{12}. \qquad (7)$$

In the quenched version, copy 2 is drawn from the equilibrium distribution, the thermal properties of copy 1 are measured and then averaged over independent copies 2. In the annealed scheme, the copies evolve simultaneously under the influence of $H_{\rm tot}$ in Eq. (7). Generalizing Eq. (5) to take into account the presence of the thermodynamic field ϵ, we directly estimate $P(Q,\epsilon)$ from the set of numerical simulations described above. We can then explore relevant features of the (T,ϵ) phase diagram.

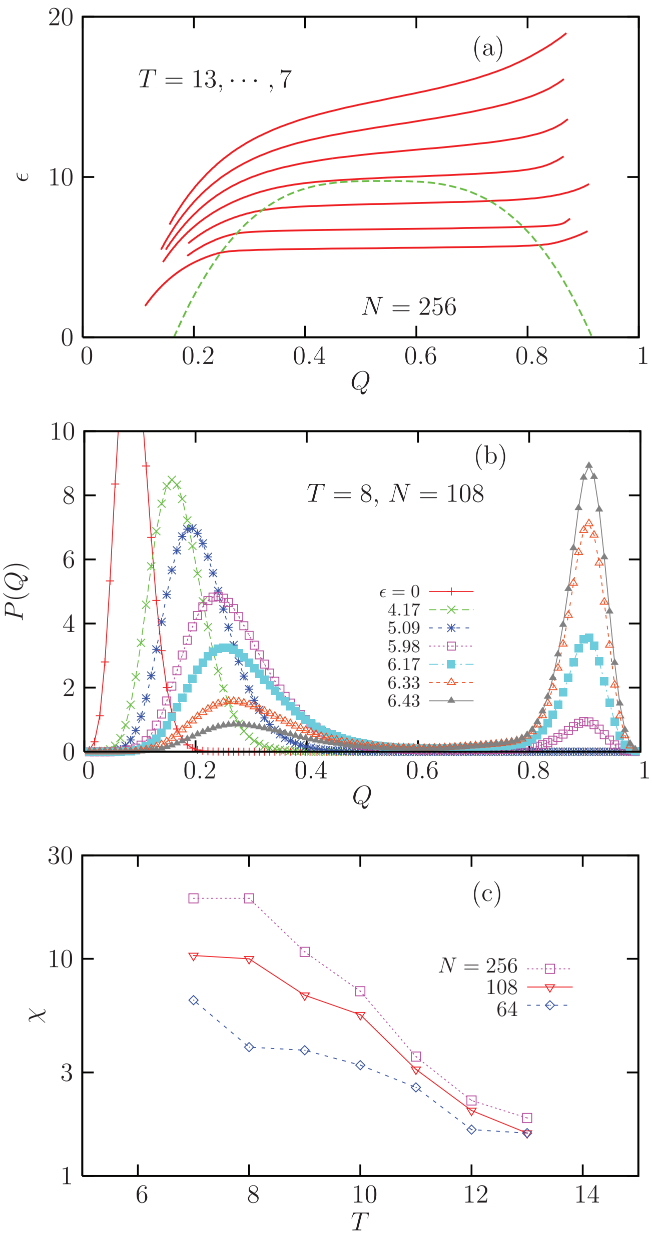

FIG. 2. (Color online) Numerical indications of a thermodynamic first-order equilibrium phase transition ending at a critical point near ($T_c \approx 9.8$, $\epsilon_c \approx 10$). (a) Isotherms $\epsilon(Q)$ for $N = 256$. The dashed coexistence line is drawn using the $d = 3$ Ising model critical exponent. (b) Probability distribution of overlap fluctuations across the first-order transition at $T = 8$ and $N = 108$, the coexistence occurring near $\epsilon \approx 6.17$. (c) Temperature evolution of the maximum of the static susceptibility for different system sizes.

We present in Fig. 2 our main findings for the annealed case, which establish the existence of first-order phase transition terminating at a second-order critical point. Figure 2(a) shows the evolution of isotherms $\epsilon(Q)$, in a representation which underlies the analogy with the standard liquid-gas coexistence region. While Q increases smoothly with ϵ at high temperature, it develops a sharp jump as temperature becomes lower than $T \approx 10$. By construction, this must correspond to the temperature where $V_{\rm a}(Q)$ loses convexity in Fig. 1. A stronger indication of the emergence of a first-order phase transition is obtained by measuring the fluctuations of the overlap at finite ϵ, as shown in Fig. 2(b). While the fluctuations are nearly Gaussian for small and large values of the coupling field, they are clearly *bimodal* at intermediate ϵ, with peak positions revealing the values of the overlap in the coexisting two phases. Finally, Fig. 2(c) presents data for the static susceptibility $\chi(Q,\epsilon) = N[\langle Q^2\rangle - \langle Q\rangle^2]$. Increasing ϵ at constant T we find that χ displays a maximum at a well-defined value of the field, which coincides with the value for which $P(Q)$ is bimodal. We report the temperature evolution of this maximum for various system sizes in Fig. 2(c). These data indicate that fluctuations are enhanced with increasing N at low enough temperature, supporting the existence of a first-order phase transition in the thermodynamic limit below a critical temperature $T_{\rm c}$, which is expected to be in the same universality class as the $d = 3$ Ising model [37]. Indeed, our data are compatible with $\chi \sim L^d$ at low T, while the data for $\chi/L^{\gamma/\nu}$ cross near $T_{\rm c} \approx 9.8 \pm 1$ when using the 3d Ising values of the critical exponents. We note that the isotherms in Fig. 2(a) are well described below $T_{\rm c}$ by a jump in Q increasing as $\Delta Q \sim (\epsilon_c - \epsilon)^\beta$ using again the Ising value for β and $\epsilon_c \approx 10$. By contrast, the quenched coupling is believed to be in a different universality class, the one of the random-field Ising model [38]. We would need data at lower temperature to test this interesting prediction, a task we leave for future work.

The present results unambiguously demonstrate the emergence of strongly non-Gaussian thermodynamic fluctuations in a three-dimensional, bulk supercooled liquid approaching its glass transition. This is also revealed by the existence, which we establish using finite-size scaling analysis, of an equilibrium first-order phase transition in the (T,ϵ). Such a phase transition was hinted at in earlier numerical studies [14,35,36], but thermalization and sampling issues, finite-size effects, the location of the critical point, and its connection with the onset of slow dynamics had not been discussed.

This shows that the nature of $V(Q)$ in finite-dimensional liquids is compatible with the mean-field RFOT starting point used in field-theoretical calculations and seems to contradict the claim that a different form of the potential should be used [21]. It also shows, somewhat surprisingly, that mean-field results are more robust for real liquids than for more abstract spin glass models [20].

Interestingly, the present first-order transition is more easily studied numerically than the transition induced by a random pinning field recently analyzed for the same model [39]. While both transitions result from the unique properties of RFOT free energy landscapes, only the latter corresponds to an ideal glass transition line [40], of the type possibly occurring in bulk liquids at low temperature. It would be interesting to perform a finite-size scaling analysis of the type presented here for the random pinning case as well.

Although of purely thermodynamic origin, the present phase transition shares in fact many similarities with the nonequilibrium transition induced by a field conjugate to the dynamic activity [23]. Both are first-order transitions induced by an external biasing field and differ qualitatively from the bulk glass transition. Their qualitative similarity is further demonstrated by the observation that the jump in the overlap reported in Fig. 2(a) is accompanied by a sharp change in the dynamics. We find, for instance, a decrease of 3 decades of the self-diffusion constant for $T = 9$ when the overlap jumps from 0.25 to 0.7. This shows that a first-order change of the dynamic activity can, in fact, be easily triggered by a thermodynamic field under fully equilibrium conditions. Combined with the results in Ref. [25], our work suggests that nonequilibrium first-order transitions in space-time are natural consequences of the emergence of a nontrivial effective potential, $V(Q)$, which efficiently captures the complexity of the underlying free energy landscape.

More generally, the parallel evolution of static and dynamic fluctuations unveiled here suggests that the temperature evolution of thermodynamic fluctuations drives the slow dynamics in glass-forming liquids, deconstructing the familiar view that glassy dynamics occurs with little structural evolution.

I thank D. Coslovich for helping me set up the numerical simulations and several useful discussions and G. Parisi for pointing out an inconsistency in temperature units in an earlier version of the manuscript. I also thank G. Biroli, S. Franz, R. Jack, J. Kurchan, G. Szamel, G. Tarjus, and F. Zamponi for additional exchanges. The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013)/ERC Grant Agreement No. 306845.

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[1] L. Berthier and G. Biroli, Rev. Mod. Phys. **83**, 587 (2011).

[2] K. Binder and W. Kob, *Glassy Materials and Disordered Solids* (World Scientific, Singapore, 2011).

[3] M. D. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).

[4] *Dynamical Heterogeneities in Glasses, Colloids and Granular Materials*, edited by L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, and W. van Saarloos (Oxford University Press, Oxford, 2011).

[5] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).

[6] W. Kauzmann, Chem. Rev. **43**, 219 (1948).

[7] J.-P. Bouchaud and G. Biroli, J. Chem. Phys. **121**, 7347 (2004).

[8] M. Mézard, G. Parisi, and M. Virasoro, *Spin Glass Theory and Beyond* (World Scientific, Singapore, 1988).

[9] T. R. Kirkpatrick and D. Thirumalai, Phys. Rev. Lett. **58**, 2091 (1987).

[10] S. Franz and G. Parisi, Phys. Rev. Lett. **79**, 2486 (1997).

[11] B. Coluzzi and G. Parisi, J. Phys. A: Math. Gen. **31**, 4349 (1998).

[12] K. A. Dawson, S. Franz, and M. Sellitto, Europhys. Lett. **64**, 302 (2003).

[13] G. Parisi, arXiv:0911.2265.

[14] C. Cammarota, A. Cavagna, I. Giardina, G. Gradenigo, T. S. Grigera, G. Parisi, and P. Verrocchio, Phys. Rev. Lett. **105**, 055703 (2010).

[15] J. Yeo and M. A. Moore, Phys. Rev. E **86**, 052501 (2012).

[16] M. Dzero, J. Schmalian, and P. G. Wolynes, Phys. Rev. B **72**, 100201 (2005).

[17] S. Franz, J. Stat. Mech. (2005) P04001.

[18] C. Cammarota, G. Biroli, M. Tarzia, and G. Tarjus, Phys. Rev. Lett. **106**, 115705 (2011).

[19] S. Franz, G. Parisi, and F. Ricci-Tersenghi, J. Stat. Mech. (2013) L02001.

[20] C. Cammarota, G. Biroli, M. Tarzia, and G. Tarjus, Phys. Rev. B **87**, 064202 (2013).

[21] M. A. Moore and B. Drossel, Phys. Rev. Lett. **89**, 217202 (2002).

[22] M. Merolle, J. P. Garrahan, and D. Chandler, Proc. Natl. Acad. Sci. U.S.A. **102**, 10837 (2005).

[23] J. P. Garrahan, R. L. Jack, V. Lecomte, E. Pitard, K. van Duijvendijk, and F. van Wijland, Phys. Rev. Lett. **98**, 195702 (2007).

[24] L. O. Hedges, R. L. Jack, J. P. Garrahan, and D. Chandler, Science **323**, 1309 (2009).

[25] R. L. Jack and J. P. Garrahan, Phys. Rev. E **81**, 011111 (2010).

[26] T. Speck, A. Malins, and C. P. Royall, Phys. Rev. Lett. **109**, 195703 (2012).

[27] L. Berthier and T. A. Witten, Europhys. Lett. **86**, 10001 (2009).

[28] L. Berthier and T. A. Witten, Phys. Rev. E **80**, 021502 (2009).

[29] W. Kob, S. Roldan-Vargas, and L. Berthier, Nat. Phys. **8**, 164 (2012).

[30] D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (Academic Press, San Diego, 2001).

[31] As for ordinary first-order phase transitions, a nonconvex potential is obtained in the mean-field limit which only considers homogeneous systems. In finite dimensions, the potential becomes convex because the system creates an interface between the two phases, which restores convexity in the thermodynamic limit. The nonconvexity found numerically here is therefore a finite-size effect, not a direct signature of the mean-field result.

[32] T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, Phys. Rev. A **40**, 1045 (1989).

[33] J. Kurchan, G. Parisi, and M. A. Virasoro, J. Phys. I **3**, 1819 (1993).

[34] M. Mézard, Physica A **265**, 352 (1999).

[35] S. Franz and G. Parisi, Phys. A **261**, 317 (1998).

[36] S. Franz, M. Cardenas, and G. Parisi, J. Chem. Phys. **110**, 1726 (1999).

[37] C. Cammarota and G. Biroli, J. Chem. Phys. **138**, 12A547 (2013).

[38] G. Biroli and G. Tarjus (private communication); S. Franz and G. Parisi, arXiv:1307.4955.

[39] W. Kob and L. Berthier, Phys. Rev. Lett. **110**, 245702 (2013).

[40] C. Cammarota and G. Biroli, Proc. Natl. Acad. Sci. U.S.A. **109**, 8850 (2012).