



## Probing a Liquid to Glass Transition in Equilibrium

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We use computer simulations to investigate the static properties of a simple glass-forming fluid in which the positions of a finite fraction of the particles have been frozen. By probing the equilibrium statistics of the overlap between independent configurations of the liquid, we find strong evidence that this **random pinning induces a glass transition**. At low temperatures, our numerical findings are consistent with the existence of a random first-order phase transition rounded by finite size effects.

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Experiments allow us to measure the increase of the viscosity of liquids approaching the glass transition over more than 15 decades. Despite this broad range, it is at present not known whether this phenomenon is controlled by an underlying phase transition, or whether relaxation times progressively increase down to zero temperature [1]. There is not even agreement on the microscopic mechanisms at work, despite the fact that glassy dynamics is commonly observed in a large variety of materials, from simple liquids, network forming liquids, to soft and biological matter [2]. Because supercooled liquids inevitably fall out of equilibrium at the experimental glass temperature  $T_g$ , amorphous solids form without encountering any singularity.

The existence of a thermodynamic transition at a finite temperature  $T_K < T_g$  is highly debated [2]. Such a singularity was first discussed by Kauzmann [3] who pointed out that **experimental data for the configurational entropy extrapolate to zero at  $T_K$ , the “Kauzmann temperature.”** This implies that for  $T > T_K$  there exist exponentially many (in the number of particles) equilibrium states (neglecting vibrations), whereas **below  $T_K$  this number becomes subexponential and the system forms an “ideal” glass.** This view is supported by the analysis of the  $T$  dependence of the relaxation times, which seem to diverge at a temperature  $T_0 > 0 \approx T_K$  [4]. However, so far  $T_0$  and  $T_K$  have been determined only by uncontrolled extrapolations of the behavior of macroscopic observables, thus leaving much room for debate [5,6].

The existence of a true liquid-glass phase transition is appealing from a theoretical perspective, since a number of analytical results suggest the existence of a **“random first-order transition”** (RFOT) occurring in glass-forming materials [7,8], which provides a close connection to Kauzmann’s entropy crisis. However, the mean-field starting point of the RFOT, the technical difficulties posed by finite-dimensional fluctuations [9,10], and the difficulty to directly probe the microscopic foundations of the theory explain why RFOT is only one among several theoretical scenarios for the glass transition [2]. In the following we demonstrate that it is indeed possible **to make an**

**equilibrium study of a liquid-glass transition whose nature is very similar to the one possibly occurring at  $T_K$  in bulk glass-formers** [11,12]. This allows us to probe numerically the nature of the phase transition and the microscopic properties of the glass phase at thermal equilibrium without any uncontrolled extrapolations.

We consider a binary mixture of harmonic spheres [13,14] of diameter ratio 1.4 at density  $\rho = 0.675$ , which we study using molecular dynamics [see Supplemental Material (SM) [15] for methodological details]. This quasi-hard sphere system is a good glass-former and can be simulated efficiently. It has an onset temperature around  $T_{\text{on}} \approx 10$ , and a mode-coupling temperature  $T_{\text{mct}} \approx 5.2$  [14]. All quantities are expressed in appropriate reduced units (see SM [15]). To sample the equilibrium thermodynamic properties of the system, we use replica exchange molecular dynamics [16]. This numerical method enables us to perform an efficient equilibrium sampling of the configuration space in the  $NVT$  canonical ensemble. We ensure thermalization and equilibrium sampling by requiring that all particles move several times across the entire simulation box for each state point and that all replicas properly explore the configuration space. Within our simulations, the system did not show any sign of crystallization.

Our central idea is **to induce a glass transition by increasing the strength of a random pinning field in a thermalized dense liquid** [11,12]. We first equilibrate the liquid at a given temperature  $T$ , before freezing permanently the position of a certain set of particles. Among various other pinning geometries [12,17,18], here we select a finite concentration of particles,  $c$ . Working at constant total number density  $\rho$ , we then study the equilibrium properties of the model in the  $(c, T)$  phase diagram. For each state point, we average the results over independent realizations of the random pinning field [17]. Intuitively, pinned particles constrain the available phase space of the remaining fluid particles, thus impacting their static and dynamic properties. Indeed, we find that the dynamics slows down dramatically with increasing  $c$  at constant  $T$ ; see Fig. SM1 [15]. While earlier studies had reported similar slowing down [12,19–21], no direct equilibrium

study of the liquid-glass transition with random pinning has been reported (see Ref. [22] for a different type of transition).

Note that freezing particles at the positions they occupy at equilibrium does not perturb the interaction part of the Hamiltonian. Indeed, any ensemble averaged static correlation function measured in the pinned liquid takes the same value as in the bulk system at  $c = 0$  [17,23]. Theoretical studies have shown that increasing  $c$  at low enough temperature affects the configurational space in the same way as decreasing temperature does for the bulk liquid [11,24]. In particular, the RFOT occurring at  $T_K^0$  for  $c = 0$  becomes a transition line  $T_K(c) \geq T_K^0$  with equivalent properties. Note that other types of pinning fields [22,25,26] produce qualitatively different results, because they perturb the Hamiltonian and possibly affect the nature of the glass transition [24].

Figure 1 provides a qualitative illustration of our strategy: An equilibrium glass state is obtained at constant temperature,  $T = 4.8$ , if the concentration  $c$  is increased. In these snapshots the large spheres are the pinned particles in a typical realization of the disorder whereas the small dots stem from the superposition of a large number of

independent, equilibrium configurations visited by the fluid particles. For  $c = 0$ , the dots look like mist homogeneously filling the simulation box. For  $c = 0.0625$ , Fig. 1(a), the fluid particles are basically unconstrained and still have access to a large number of distinct configurations. Thus the dots form fuzzy clouds. **An increase to  $c = 0.1875$ , Fig. 1(b), condenses the dots into well-defined patches, which represent the highly constrained positions occupied by the free particles. This qualitative observation illustrates that increasing  $c$  leads to a collective localization of the fluid particles.** We emphasize that during the replica exchange simulations, all fluid particles diffuse and explore the entire simulation box. However, **particles move in such a way that collective density fluctuations are frozen.** Thus, the system is in a glass state characterized by a frozen amorphous density profile [2].

We now study in more detail the transition between the fluid and glass states. Figure 1 suggests that the number of available states, and thus the configurational entropy, considerably decreases with increasing  $c$ . A quantitative determination of the configurational entropy is, however, difficult and has several shortcomings [2]. Therefore we use a microscopic order parameter to characterize the transition from fuzzy clouds to small patches seen in Fig. 1. An appropriate quantity is the overlap  $q_{\alpha\beta}$  measuring the degree of similarity between two arbitrary configurations  $\alpha$  and  $\beta$ , which has been used in spin glass models displaying a RFOT [7]. In practice, we discretize space into cubic boxes of linear size  $\ell = 0.55$ , and define  $n_i^{(\alpha)} = 1$  if box  $i$  in configuration  $\alpha$  is occupied by a particle, and  $n_i^{(\alpha)} = 0$  if not. Then,

$$q_{\alpha\beta} = \frac{1}{N_b} \sum_{i=1}^{N_b} n_i^{(\alpha)} n_i^{(\beta)}, \quad (1)$$

where the sum runs over the  $N_b$  boxes that do not contain pinned particles. By definition  $q_{\alpha\alpha} = 1$ , while a small overlap is obtained for independent configurations ( $q_{\text{rand}} \approx 0.11 \approx \rho \ell^3$  on average for an ensemble of independent configurations). In the remainder of the paper, we characterize the transition by analyzing the statistical properties of the overlap for a broad range of control parameters.

In Fig. 1(c), we show the  $c$  dependence of the average overlap,  $\langle q \rangle = \langle q_{\alpha\beta} \rangle$ , where the brackets stand for thermal and disorder averages. Above the onset temperature,  $\langle q \rangle$  increases gradually with  $c$ . For  $T \lesssim 8.0$ , the growth remains modest at low  $c$ , but this initial regime is followed by a rapid increase in the range  $\langle q \rangle \approx 0.25$ – $0.4$ . Finally, if  $T$  is decreased even further this rapid growth occurs for lower values of  $c$  and becomes sharper. At  $T = 4.8$  it is sufficient to reach just  $c \approx 0.11$  to abruptly localize the fluid particles,  $\langle q \rangle > 0.5$ .

These observations show that at low  $T$  the glass state is reached at a sharply defined  $c$  value, whereas pinning acts quite smoothly at high  $T$ . The  $T$  dependence of  $\langle q \rangle$  is

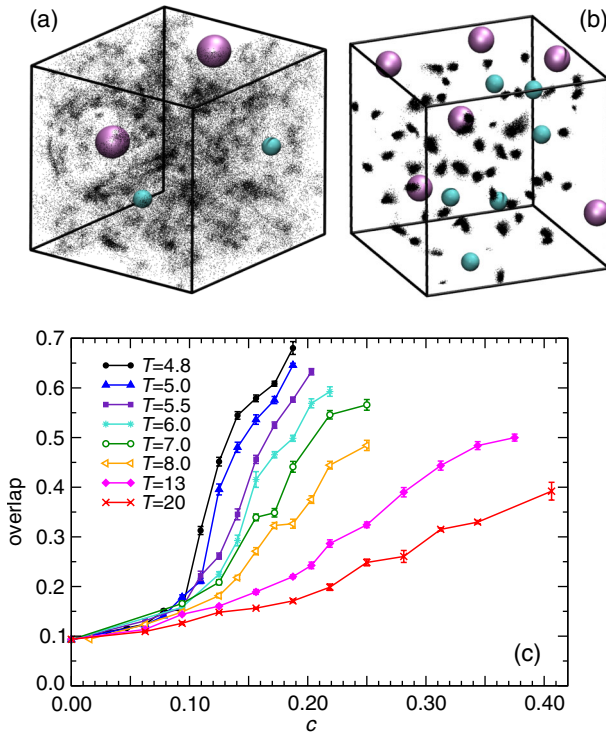


FIG. 1 (color online). (a), (b): Large spheres represent pinned particles (rescaled in size by a factor 0.5), small dots are the superposition of the position of fluid particles obtained from a large number of independent equilibrium configurations at  $T = 4.8$  for  $c = 0.0625$  (a) and  $c = 0.1875$  (b). The total number of particles is  $N = 64$ . (c) Average overlap  $\langle q \rangle$  as a function of concentration  $c$  of pinned particles for  $N = 64$  and different temperatures.

consistent with the emergence of a discontinuous jump at low temperatures,  $T \lesssim 8.0$ , but the relatively small system size shown in Fig. 1(c),  $N = 64$ , will smear out such a discontinuity. To overcome this difficulty we have determined the fluctuations of  $\langle q \rangle$  and in Fig. 2 we show its distribution function,  $P(q) = \langle \delta(q - q_{\alpha\beta}) \rangle$ .

At high temperatures,  $T = 13$  in Fig. 2(a),  $P(q)$  evolves smoothly from distributions peaked at small  $q$  for small  $c$  to distributions peaked at large  $q$  values at large  $c$ . This is consistent with  $P(q)$  becoming a delta function for  $N \rightarrow \infty$  for all  $c$ , and with the smooth increase of  $\langle q \rangle = \int_0^1 P(q)q dq$  at high  $T$  shown in Fig. 1(c). A qualitatively different behavior is observed at low  $T$ ; see Fig. 2(b). A narrow peak is still present for small and large  $c$ , but  $P(q)$  is *bimodal* for intermediate  $c$ . The presence of two peaks implies that it is equally probable that two independent thermalized configurations are either very similar or very different. The former situation is favored at larger  $c$  because too few distinct configurations exist, while the latter holds at small  $c$  when the pinning field is not strong enough to prevent the system from exploring a large configuration space. Bimodal distributions of the order parameter can be interpreted as the phase coexistence between the low- $q$  liquid and the high- $q$  glass phases,

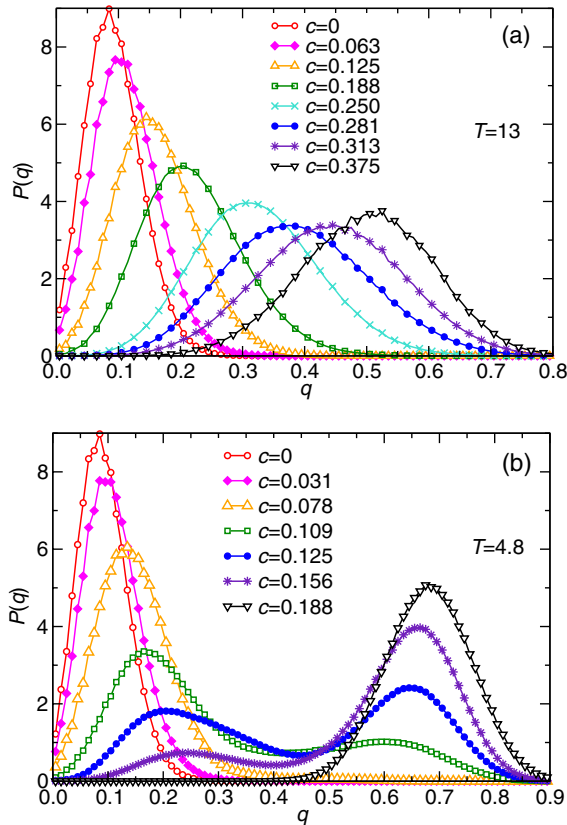


FIG. 2 (color online). Probability distribution of the overlap,  $P(q)$ , for different values of the concentration of pinned particles at high and low  $T$  [(a), (b), respectively]. Note the presence of a double peak structure at low temperatures.

and the two-peak structure of  $P(q)$  is suggestive of a first-order transition for the order parameter  $\langle q \rangle$ , rounded by finite size effects.

To estimate the location of this putative transition, we have measured various moments of the distribution  $P(q)$ . From the second moment  $\langle q^2 \rangle = \int_0^1 P(q)q^2 dq$ , we define the static susceptibility,  $\chi(c, T) = N(1 - c)[\langle q^2 \rangle - \langle q \rangle^2]$ . Figure 3(a) shows that at high temperatures  $\chi$  has a mild  $c$

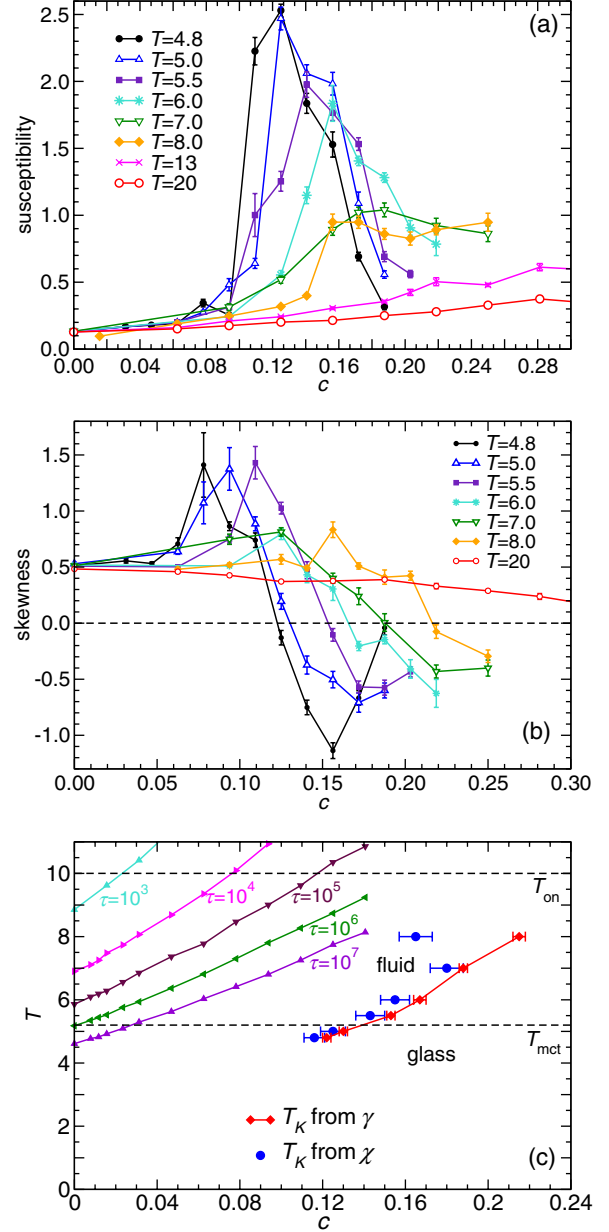


FIG. 3 (color online). (a) The static susceptibility  $\chi$  as a function of concentration  $c$  for different temperatures. (b)  $c$  dependence of the skewness  $\gamma$  for different  $T$ . (c) The equilibrium phase diagram determined from the position of the peak in the susceptibility  $\chi$  and from the root of the skewness  $\gamma$  showing the location of the fluid and glass phases. Also included are curves of constant relaxation time as determined from the self-intermediate scattering function.

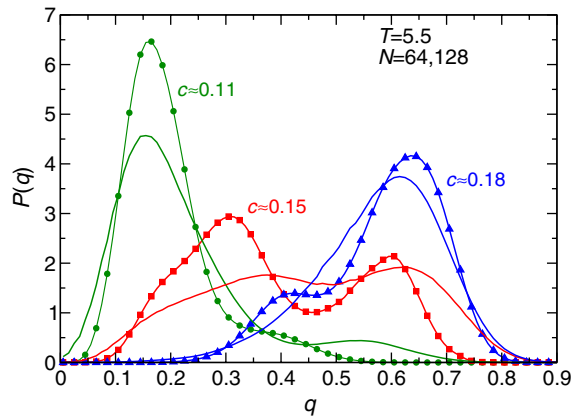


FIG. 4 (color online). System size dependence of the overlap distribution function for  $T = 5.5$  and three values of  $c$  below (green), near (red), and above (blue) the transition for  $N = 64$  (lines) and  $N = 128$  (lines with symbols). The peak susceptibility increases from  $\chi \approx 1.8$  for  $N = 64$  to  $\chi \approx 2.7$  for  $N = 128$  (data not shown).

dependence, whereas it develops a well-defined peak for  $T \leq 7.0$  whose height and location, respectively, increases and shifts to smaller  $c$  if  $T$  decreases. The observed growth of the peak  $\chi(c, T)$  at low  $T$  is direct evidence of increasing static correlations in the bulk system [12,27]. The location of this peak allows us to estimate the value of the critical concentration at the given temperature. Figure 3(b) shows that an even more accurate location is obtained by considering the skewness  $\gamma(c, T)$  of the distribution  $P(q)$ ,  $\gamma = \langle (q - \langle q \rangle)^3 \rangle / \langle (q - \langle q \rangle)^2 \rangle^{3/2}$ , since  $\gamma$  crosses zero when the distribution is symmetric, i.e., precisely at coexistence. From the location of the peak in  $\chi(c, T)$  and the zero-crossing point of  $\gamma(c, T)$ , we can locate the fluid-glass coexistence line [Fig. 3(c)]. These two quantitative estimates become reliable if  $T \leq 8.0$ , i.e., when bimodal distributions are present, and we see that they agree with each other within error bars (estimated using the jackknife method). In the context of Fig. 3(c), the existence of a Kauzmann temperature at  $c = 0$  would rely on extrapolating our finite  $c$  transition points (determined without extrapolation) to the limit  $c \rightarrow 0$ .

Our results show that random pinning induces a glass transition with nontrivial thermodynamic signatures that are consistent with the existence of an equilibrium RFOT [11]. However, since our results have been obtained for a rather small system size,  $N = 64$ , they do not establish its existence in the thermodynamic limit. Since the parallel tempering algorithm becomes less efficient when  $N$  is increased we cannot access very low  $T$ 's for larger  $N$ . However we can investigate the  $N$  dependence at higher  $T$ 's. Our results for larger systems confirm that no sharp transition exists for  $T \geq 8.0$ , while we obtained clear signs of enhanced bimodality and static susceptibility when  $T < 6.0$  (see Fig. 4 for  $T = 5.5$ ). The small dip in  $P(q)$  for  $N = 64$  and intermediate  $c$  values becomes more

pronounced for  $N = 128$ , while the peaks at low and large overlaps become sharper. Such system-size dependence is typical of first-order transitions. A more extensive finite-size scaling analysis would be useful, since it yields direct microscopic insight into the surface tension between the two phases, but is at present beyond the computational means.

In contrast to conventional studies of the glass transition, our approach allows us to study both liquid and glass phases at thermal equilibrium, it does not require uncontrolled extrapolations, and we characterize the glass formation by means of a microscopic order parameter. We expect that similar results could be obtained with other numerical models. Our work thus demonstrates the feasibility of systematic equilibrium studies of the nature of the liquid to glass transition. Also, by using optical tweezers it will be possible to use this method to study colloidal glasses and thus to produce experimentally what is often considered as “impossible-to-reach ideal glass states” [28]. Random pinning in the context of granular glass transitions [29,30] is another promising perspective. Therefore our work opens the door for a new generation of direct, systematic studies of the nature of the glass state and for the production of novel amorphous materials.

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