Confinement as a Tool to Probe Amorphous Order

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We study the effect of confinement on glassy liquids using random first order transition theory as a framework. We show that the characteristic length scale above which confinement effects become negligible is related to the point-to-set length scale introduced to measure the spatial extent of amorphous order in supercooled liquids. By confining below this characteristic size, the system becomes a glass. Eventually, for very small sizes, the effect of the boundary is so strong that any collective glassy behavior is wiped out. We clarify similarities and differences between the physical behaviors induced by confinement and by pinning particles outside a spherical cavity (the protocol introduced to measure the point-to-set length). Finally, we discuss possible numerical and experimental tests of our predictions.

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The search for a growing static length accompanying the slowing down of the dynamics of supercooled liquids is a *leitmotiv* and a key open issue in the study of the glass transition. The super-Arrhenius behavior of the relaxation time is indeed a hint that such a length exists: a growing energy barrier should be related to an increasing cooperativity, as first conjectured a long time ago by Adam and Gibbs and then firmly advocated within random first order transition (RFOT) theory [1,2]. Recently, this intuition was put on a rigorous basis by Montanari and Semerjian [3]. Their result was obtained using the cooperative length scale, ℓ_{PS}, that measures the spatial extent of amorphous order and that was originally introduced in Ref. [4] to characterize the spatial structure of the so-called mosaic state envisioned for supercooled liquids by the RFOT theory [2]. The definition of ℓ_{PS} called the point-to-set (PS) length is the following: take a typical equilibrium configuration, freeze the positions of all particles outside a sphere centered around a given point, and study how the thermodynamics of the remaining particles inside the sphere is influenced by this amorphous boundary condition [4,5]; ℓ_{PS} is the smallest radius of the sphere at which the boundary has no longer any effect on the configuration at the center. As its definition above makes clear, ℓ_{PS} is quite difficult to measure. It can be obtained by numerical simulations but for rather high temperatures only [6–10] because of equilibration problems [9,11]. Therefore, one can only access its first increase in a regime where it should not play an important role in determining the dynamics; only in the deeply supercooled activated regime should ℓ_{PS} be directly linked to the growth of the relaxation time [12,13]. The way out of this impasse would be to measure such a length in experiments on molecular liquids close to the glass transition. However, no experimental way for doing that has been devised so far.

Actually, there might be an alternative and simpler way to measure a growing static length in supercooled liquids: studying the role of spatial confinement on glassy dynamics [1,2]. Indeed, if the glass transition is related to the growth of a static length, the study of confined liquids may unveil the existence of such a length by measuring the smallest confinement linear size, ℓ_C, such that bulk behavior is recovered. As for finite size scaling in critical phenomena, the idea is to use the possibility of varying the system size as an investigation tool. Unfortunately, the interaction between the boundary and the confined fluid and the possible change of density inside the confining region lead to nonuniversal behavior even for the simpler case of the melting-freezing transition [14]. In the case of confined supercooled liquids, the glass transition temperature has been found to either increase or decrease as a function of the confinement length scale depending on the experimental system [14,15]; no clear indication of a growing static length could be found. It was not understood, however, whether this is due to an intrinsic inability of confinement to probe the growing static length characterizing the glass transition or just to the practical complications cited above. Results obtained in numerical simulations and for colloidal systems point toward the latter possibility [16,17]. Theoretically, the distinction between ℓ_C and ℓ_{PS} is subtle and boils down to the difference in the boundary conditions used to study the behavior of a confined fluid. For ℓ_{PS}, the boundary (henceforth called amorphous and denoted AB) is obtained by freezing particles from an equilibrium configuration at temperature T—the hunch is that this protocol quenches very subtle correlations and, hence, the pinned particles at the boundary act as a pinning field that forces the configuration inside the cavity to be in a given amorphous state for $\ell < \ell_{PS}$. For ℓ_C, instead, the boundary (henceforth called random and denoted RB) is essentially formed by a rough wall that only induces trivial short-range correlations due to steric constraints. In this Letter, we clarify similarities and differences in the physical behaviors of confined liquids with random and amorphous boundary conditions using RFOT theory as a framework [12,13]. We have found that ℓ_C and ℓ_{PS} increase in a similar fashion (the former being smaller than the latter) but that the corresponding confined systems behave very differently below ℓ_C and ℓ_{PS}. Our results, which are also relevant for recent studies on pinning particles from equilibrium and from random configurations [9,18–28], demonstrate that confinement is indeed a way to probe the length scale associated with the spatial extent of amorphous order in supercooled liquids.

Let us start with some heuristic arguments that will be backed later by analytical computations. RFOT theory is based on the competition between the huge number of possible amorphous states in which a liquid can freeze, measured by the configurational entropy density $s_c(T)$, and the tendency to sample states with low free energy [12,13]. By pinning all particles outside a spherical cavity, the number of possible states in which the particles inside the cavity can arrange is diminished. Correspondingly, the total configurational entropy inside the cavity decreases and reads at leading order in ℓ: $s_c(4\pi/3)\ell^3 - 4\pi Y_{PS}\ell^{\theta_{PS}}$ [29]. The last term is a surface contribution, hence, $\theta_{PS} \leq 2$ (the 4π is included in reference to the simplest case $\theta_{PS} = 2$). It is thought to originate from the boundary free-energy mismatch between the subset of states which are incompatible at the boundary with the initial configuration used to pin particles. By decreasing ℓ, fewer and fewer states remain compatible. For $\ell < \ell_{PS}$, only the one corresponding to the initial configuration survives. The point-to-set length is therefore directly related to the configurational entropy and reads $\ell_{PS} = (3Y_{PS}/s_c)^{1/(3-\theta_{PS})}$. It represents, within RFOT, the typical linear size over which the system is amorphously ordered—"the mosaic's tile length." The confinement setup is very similar to the previous one but with the crucial difference that the boundary is featureless, i.e., it equally disfavors all states. The total configurational entropy is expected to decrease also in this case as $s_c(4\pi/3)\ell^3 - 4\pi Y_C\ell^{\theta_C}$ (as found for the one-dimensional Kac random energy model in Ref. [30]). It is reasonable to assume, and it is in agreement with our analytical findings, that $\theta_C = \theta_{PS}$ and $Y_C \lesssim Y_{PS}$; i.e., confinement leads to a decrease of configurational entropy similar to the AB case. We define the confinement length as the value of ℓ at which the configurational entropy inside the cavity vanishes, which leads to the result $\ell_C = (3Y_C/s_c)^{1/(3-\theta_C)}$. In the AB case, and for $\ell < \ell_{PS}$, the system is frozen in the only state compatible with the boundary condition; whereas instead in the RB case, for $\ell < \ell_C$, it can sample all the lowest free energy states available, whose free energy difference is $O(1)$. This regime is exactly the analog of the one expected below T_K, the so-called one step replica symmetry breaking phase. Thus, decreasing the confinement length is tantamount to lowering the temperature for bulk systems with the important difference that, since the system is finite, only a crossover and not a true phase transition happens at

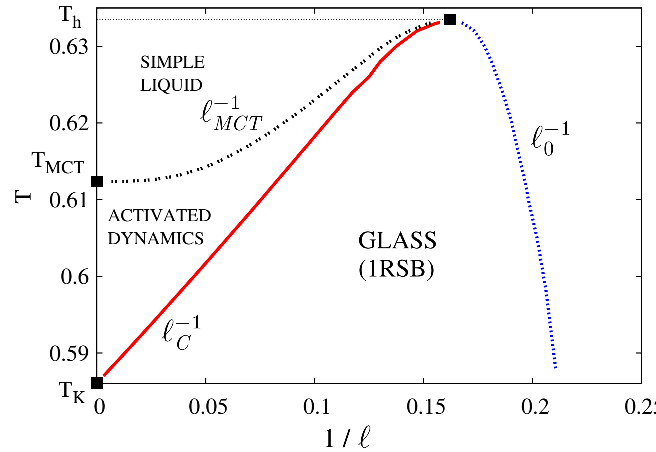

FIG. 1 (color online). Confinement "phase diagram": the continuous line (red) denotes a finite size glass transition at ℓ_C, the dashed line on the left (black) is the mode-coupling theory (MCT) crossover at ℓ_{MCT}, and the dotted one on the right (blue) indicates a continuous glass transition at ℓ_0.

$\ell = \ell_C$. This analogy suggests that a mode-coupling crossover should also take place at a length ℓ_{MCT} ($> \ell_C$), as indeed found in microscopic computations in Ref. [21]. Our previous arguments suggest that although $\ell_C < \ell_{PS}$, these length scales are proportional to each other and increase similarly when the configurational entropy diminishes: if $s_c(T) \propto T - T_K$ for $T \to T_K$ then they both diverge as $1/(T - T_K)^{1/(3-\theta)}$. We expect that by decreasing ℓ the relaxation time increases, first because of mode-coupling effects and then because of the RFOT-Adam-Gibbs mechanism [12,13] that relates the decrease of s_c to the increase of the relaxation time. When ℓ becomes of the order of ℓ_{PS} or ℓ_C, in the AB and RB cases, respectively, the relaxation time scale should start decreasing—faster in the AB case because the system has just to sample one given state [11], slower in the RB case where collective rearrangements corresponding to interstate dynamics still go on but involve a smaller number of particles (see the Supplemental Material [31] and Ref. [32]). Collective glassy behavior is expected to disappear at very high temperature or very small ℓ. A sketch of the resulting phase diagram, which actually corresponds to the analytical solution that we shall present later, is shown in Fig. 1.

We now present our analytical investigation of confinement with RB conditions; the AB case was treated in Ref. [33]. Our starting point is the replica free energy functional $F[q_{ab}(x)]$ already used several times to analyze the glass transition [12]; the spatially varying field $q_{ab}(x)$ is defined for $a < b$, where a and b denote the replica indices which run over n different values (with $n \to 0$). Note that the random boundary condition acts as an external quenched disorder, this is why one ends up with the $n \to 0$ analytic continuation of the replicated functional even for a system that does not contain any quenched disorder. In previous analyses, two forms have been used:

a Ginzburg-Landau one [34] and another obtained by an analysis based on the Kac limit [35]. We focus on the latter because it has the advantage of corresponding to a well-defined model—a disordered p-spin Kac system (see [35] and the Supplemental Material for details [31]). Since the Ginzburg-Landau action can be recovered making a gradient and a field expansion, our results are not restricted to this specific choice of $F[q_{ab}(x)]$. For the p-spin Kac model the random boundary condition can be explicitly taken into account by requiring that all the spins outside the cavity are equal to a random configuration, i.e., sampled from the infinite temperature Boltzmann measure. One can also show that taking instead a configuration with, e.g., all spins up is statistically equivalent. This is natural because from the point of view of an amorphous state, a random boundary condition or a nondisordered one are statistically equal. The analog for particle systems of this result is that random boundary conditions (obtained from high T configurations) or rough walls should all be equivalent as far as collective glassy effects are concerned. From the replica point of view, the random boundary conditions lead to the constraint $q_{ab}(x) = 1\ \forall\ a, b$ outside the cavity. As in previous studies, we focus on two *Ansätze* for the form of $q_{ab}(x)$: one is replica symmetric (RS) $q_{ab}(x) = q_0\ \forall\ a, b$, and the other is one step replica symmetry breaking (1RSB); i.e., replica are collected in n/m groups and $q_{ab}(x) = q_1(x)$ for replica inside the same group and $q_{ab}(x) = q_0(x)$ otherwise. The physical meaning of these solutions are the usual ones: when only the RS solution is present, the liquid is simple and not glassy. When the 1RSB solution at $m = 1$ appears, an exponential number of metastable states emerges (this is related to the mode-coupling transition). From the derivative of $F[q_{ab}(x)]$ in $m = 1$ [36], one can obtain the configurational entropy which vanishes when the 1RSB solution with $m < 1$ starts to extremize $F[q_{ab}(x)]$, i.e., the system is in the glass phase. The form of $F[q_{ab}(x)]$ within the 1RSB *Ansatz* (the RS can be recovered imposing $q_0 = q_1$) reads $F[q_{ab}(x)] = \int d^3x \mathcal{L}_{1\mathrm{RSB}}(q_0(x), q_1(x), m)$ where

$$\mathcal{L}_{1\mathrm{RSB}} = (1-m)\frac{\beta^2}{2}f(q_1 * \psi) + m\frac{\beta^2}{2}f(q_0 * \psi) - \frac{1}{2}\frac{q_0}{1-(1-m)q_1 - mq_0} - \frac{m-1}{2m}\log(1-q_1) - \frac{1}{2m}\log[1-(1-m)q_1 - mq_0],$$

and $\psi(x)$ is a normalized three-dimensional Gaussian, and $f(q)$ is a function defined as $f(q) \equiv q^p/2$ with $p = 3$ (we considered the $p = 3$ Kac-spin model). The notation $q * \psi(x)$ indicates the convolution $\int d^3y \psi(y-x)q(x)$. By extremizing $F[q_{ab}(x)]$ with respect to q_0, q_1, and m, assuming spherical symmetry around the origin and using the boundary conditions $q_0 = q_1 = 1$ outside the cavity, one obtains the inhomogeneous equations determining the RS and 1RSB solutions (more details in Ref. [33] and the Supplemental Material [31]). We now present the results that lead to the phase diagram reported in Fig. 1. At very high temperature we only find the RS solution for any value of ℓ, i.e., confinement does not induce any glassy behavior. Below a certain temperature denoted T_h in Fig. 1, and above T_{MCT}, we find that the cavity radius ℓ plays a role similar to the temperature. By decreasing ℓ, first the system undergoes a MCT transition at $\ell = \ell_{\mathrm{MCT}}$, as also found in Ref. [21], and then the configurational entropy vanishes at $\ell = \ell_C$. In Fig. 1, we have called "simple liquid" the region where only the RS solution is present, "activated dynamics," the one characterized by a finite configurational entropy, where the dynamics is activated and (within RFOT) follows an Adam-Gibbs law, and "glass" the one where replica symmetry is broken and the ideal glass phase sets in. Figure 1 shows that the glass transition line becomes continuous and bends downwards. By confining the system below ℓ_C, the system eventually exits from the glassy phase for a radius equal to ℓ_0. In this regime, the effect of the boundary is overwhelming and destroys the nontrivial free energy landscape. At $\ell = \ell_0$, q_0 and q_1 approach one another continuously while m remains less than 1. These results provide a microscopic derivation of the heuristic arguments put forward previously and allow us to determine $\theta_C = 2$ and Y_C, which is temperature dependent: it is of the order of 0.1 close to T_K, and smaller than Y_{PS} of approximatively 10%. In Fig. 2 we report the behaviors of ℓ_C and ℓ_{MCT} that look very similar even quantitatively to the analogous ones obtained in the AB case [33]. This is in agreement with what was found in simulations of supercooled liquids for the dynamical length scale [17]. A direct comparison of ℓ_C and ℓ_{PS} is presented in the inset of Fig. 2; they both diverge as a power law $1/(T - T_K)$, but ℓ_C is slightly smaller than ℓ_{PS}.

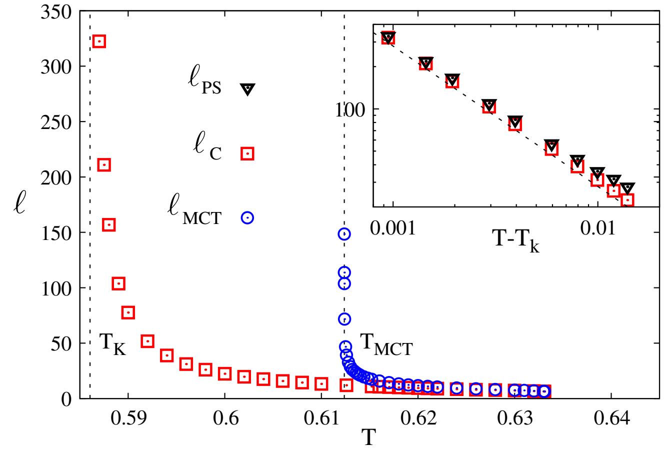

FIG. 2 (color online). The lengths ℓ_C (squares) and ℓ_{MCT} (circles) are plotted as a function of T in the case of random boundaries. The divergence of ℓ_{MCT} is proportional to $1/(T - T_{\mathrm{MCT}})^{1/4}$ (not shown). Inset: the behavior of ℓ_C (squares) as a function of $T - T_K$ is compared to that of ℓ_{PS} (triangles): the straight line indicates the common power law $1/(T - T_K)$.

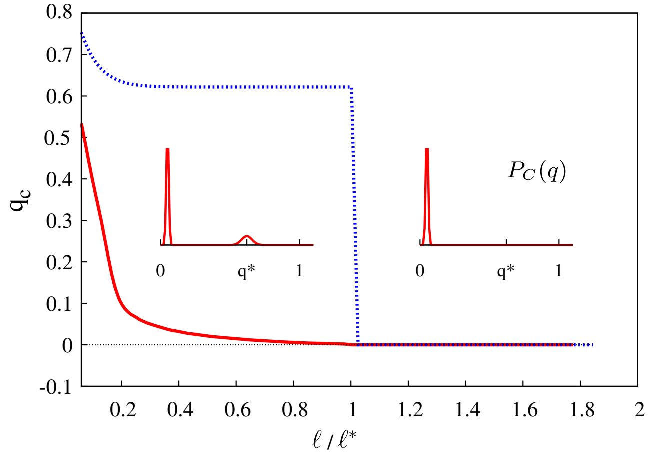

FIG. 3 (color online). Main: average overlap at the center of the cavity $q_c(\ell/\ell^*)$ as a function of the rescaled cavity radius ℓ/ℓ^* for random boundary (continuous line), $\ell^* = \ell_c$, and amorphous boundary (dashed line), $\ell^* = \ell_{\mathrm{PS}}$ (in this case $T = 0.594$, $\ell_c = 38.85$, $\ell_{\mathrm{PS}} = 43.9$). The difference in the confined systems overlap distribution $P_C(q)$ between the regime $\ell < \ell_C$ and $\ell > \ell_C$ is shown pictorially.

The other quantity of interest is the behavior of the average overlap, $\langle q^{(\mathrm{cen})}\rangle$, between two independent equilibrium configurations (in the presence of the same boundary) at the center of the cavity. In the AB case, the average overlap jumps discontinuously from a low to a high value at ℓ_{PS}, whereas in the RB case it starts to increase in a continuous way (with a discontinuous derivative) at ℓ_C, see Fig. 3. Physically, this is due to the nature of the 1RSB phase and to the probabilistic meaning of its parameter m: in the ideal glass (1RSB) phase two equilibrium configurations belong to different states (and have overlap q_0) with probability m and belong to the same state (and have an overlap q_1) with probability $1 - m$, contrary to the AB case where as soon as the configurational entropy vanishes only one stable configuration is left. Since $m \to 1$ for $\ell \uparrow \ell_C$, the average overlap at ℓ_C joins smoothly the one corresponding to the regime $\ell > \ell_C$, where two configurations are in different states with probability 1. Since the curve $\langle q^{(\mathrm{cen})}\rangle(\ell)$ is smooth and does not follow a scaling function $f(\ell/\ell_C)$ contrary to the AB case [it goes as $f(\ell/\ell_C)/\ell$ for $\ell < \ell_C$ and is exponentially small in ℓ for $\ell > \ell_C$, see the Supplemental Material [31]], $\langle q^{(\mathrm{cen})}\rangle(\ell)$ is not suitable to determine ℓ_C numerically. A better observable is instead the probability distribution of the overlap, which should show for $\ell < \ell_C$ two peaks, one at a value $q_0^{(\mathrm{cen})}$ with weight m and one at a value $q_1^{(\mathrm{cen})}$ with weight $1 - m$, and for $\ell > \ell_C$ only one peak centered in $q_0^{(\mathrm{cen})}$ (fluctuations of Y_C [7] are expected to make the crossover between these two regimes smooth in real systems). In experiments, the easiest protocol to study the effect of confinement consists of measuring the relaxation time that should first increase substantially approaching ℓ_C, since the system undergoes a "finite-size glass transition" and then decreases (see the Supplemental Material [31] and Ref. [32] for a more detailed discussion).

An interesting question relevant for numerical simulations is whether periodic boundary conditions are more AB or RB like. A reasonable working hypothesis is that they resemble more the latter since they do not favor any particular state. Recent numerical simulations have indeed found a nonmonotonic dependence of the relaxation time on the system size [37] and an Adam-Gibbs relation between relaxation time and the size-dependent configurational entropy [38] for supercooled liquids with periodic boundary conditions.

This work based on RFOT theory shows that "simple" confinement allows us to probe the length associated to amorphous order in supercooled liquids. We found that the best observables to extract the confinement length are the overlap distribution (which can be likely measured only in simulations) and the relaxation time. We clarified similarities and differences with the case of amorphous boundary conditions, which are actually analogous to the ones found for particles pinned at random from equilibrium and random configurations (see, in particular, the similarity between phase diagrams [18]). The conclusion of our work is that confinement studies are a route worth pursuing further since they provide direct access to the length associated to the spatial extent of amorphous order in supercooled liquids. The interaction between the boundary and the confined fluid is irrelevant as far as collective glassy effects are concerned when ℓ_{PS} and ℓ_C are large compared to molecular scales. This is not the case in experiments where these large length scales are not large enough. Therefore, it would be crucial to make the confining surface "neutral," i.e., with an interaction fluid-boundary as similar as possible to the fluid-fluid one, and to work at fixed density, for example, adapting the external pressure.

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