

## Critical behavior of the specific heat in glass formers

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We show numeric evidence that, at low enough temperatures, the potential energy density of a glass-forming liquid fluctuates over length scales much larger than the interaction range. We focus on the behavior of translationally invariant quantities. The growing correlation length is unveiled by studying the finite-size effects. In the thermodynamic limit, the specific heat and the relaxation time diverge as a power law. Both features point towards the existence of a critical point in the metastable supercooled liquid phase.

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The glass transition differs from standard phase transitions in that the equilibration time of glass formers (polymers, supercooled liquids, colloids, granulars, superconductors, etc.) diverges without dramatic changes in their structural properties. Indeed elastic neutron scattering experiments show that the static structure factor of polymers and supercooled liquids undergoes marginal modifications when approaching the glass transition. Yet, their equilibration time  $\tau$ , as obtained, for instance, from the  $\alpha$  peak in the AC dielectric susceptibility, grows by many orders of magnitude close to the transition [1]. Reconciling the two faces of the glass transition is a major challenge for condensed matter physics.

A general mechanism producing a divergence of the equilibration time of a homogeneous system at finite temperature is the divergence of a correlation length (*critical slowing down* [2]). Slowness is due to the fact that configurational changes need to propagate over increasingly large regions (the critical origin of the mode coupling singularity [3] has been recently recognized [4]). Within this framework, a key problem is identifying the quantity with the largest spatial fluctuations close to the glass transition. Since equal-time correlation functions do not reveal statistical fluctuations over large length scales, it has been suggested that two-time correlation functions must be studied [4–8]. The goal is to extend beyond the mean-field level the mode coupling view of the glass transition as a purely dynamic phenomenon.

Strong space fluctuations of the relaxation properties (*dynamic heterogeneities*) have been found experimentally [9,10] and numerically [11]. However, the size of the correlated domains is not larger than a few nanometers (a few angstroms, in simulations).

Here we report numeric simulations for a fragile glass-forming liquid [12,13] showing large scale fluctuations in the specific heat, an equal-time correlation function. Thus, we claim that the dynamical features of the glass transition are due to a critical slowing down arising from a continuous phase transition suffered by the metastable liquid. The diffi-

culty in recognizing it is due to the fact that standard scattering experiments are not devised to detect spatial fluctuations in the energy density. Yet, a large correlation length can be studied through finite-size effects [14]. Note that experiments in films [15] and nanopores [16] show that the glass-transition changes in samples with one or more dimensions of nanometric scale, although it is difficult to disentangle finite-size scaling from the effects of the interaction with the substrate. However, the specific heat of toluene confined on pores of a diameter 8.7 nm [16], close to its glass temperature, is significantly smaller than for bulk toluene, which could signal a correlation length well above the nanometric scale.

We study a 50% mixture of particles interacting through the pair potential  $V_{\alpha\beta}(r) = \epsilon[(\sigma_\alpha + \sigma_\beta)/r]^{12} + C_{\alpha\beta}$ , where  $\alpha, \beta = A, B$ , with a cutoff at  $r_c = \sqrt{3}\sigma_0$ . The choice  $\sigma_B = 1.2\sigma_A$  hampers crystallization. We impose  $(2\sigma_A)^3 + 2(\sigma_A + \sigma_B)^3 + (2\sigma_B)^3 = 4\sigma_0^3$ , where  $\sigma_0$  is the unit length. Constants  $C_{\alpha\beta}$  are chosen to ensure continuity at  $r_c$ . The simulations are at a constant volume, with the particle density fixed to  $\sigma_0^{-3}$  and temperatures in the range  $[0.897T_{mc}, 10.792T_{mc}]$ , where  $T_{mc}$  is the mode coupling temperature [3]. We use periodic boundary conditions on a box of size  $L$  (which discretizes momenta in units of  $q_{min} = 2\pi/L$ ) in systems with 512, 1024, 2048, and 4096 particles. From the molecular dynamics van Hove self-correlation function [17], one has for argon parameters,  $\sigma_0 = 3.4 \text{ \AA}$ ,  $\epsilon/k_B = 120 \text{ K}$ , and  $T_{mc} = 26.4 \text{ K}$ . We shall obtain equilibrium data below  $T_{mc}$ .

We modify the Grigera-Parisi swap algorithm [13] to make it *local*, in order to keep the algorithm in the dynamic universality class [2] of standard Monte Carlo (MC). The elementary MC step is either (with probability  $p$ ) a single-particle displacement attempt or (with probability  $1-p$ ) an attempt to *swap* particles. The swap is made by picking a particle at random and trying to interchange its position with that of a particle of opposite type, chosen at random *among those at distances smaller than  $0.6r_c$* . Detailed balance requires that the Metropolis test include not only the energy variation but the change in the number of neighbors. The swap acceptance is independent of system size and grows from 0.74% at  $0.9T_{mc}$  up to 6% at  $2T_{mc}$ . In this work we use  $p=0.5$  (named *local swap* from here on) and  $p=1.0$  (named standard MC). The time unit  $t_0$  is  $N/p$  elementary steps.

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Although time correlators differ for different dynamics, when studying static quantities (e.g., specific heat) the choice of Monte Carlo dynamics is a matter of practical convenience. We study local swap *time* correlators only in order to explore *static* properties. Yet, the asymptotic decay of time correlators of two dynamics belonging to a single dynamic universality class is given by the same function (up to a rescaling) of the correlation length [2]. Since standard and swap MC are both local and share the same conservation laws, we expect the ratio of their autocorrelation times, Eq. (4), to be essentially constant, even if their time correlators differ at intermediate times.

We assume that equilibrium behavior can be meaningfully studied in a *metastable* phase [18] (i.e., the equilibration time for the metastable liquid phase is much smaller than the crystallization time). At the lowest temperatures we simulate up to 400 independent MC runs. In the analysis we only consider histories longer than 100 exponential autocorrelation times (see below). We use the jackknife method to estimate errors [14].

The study of a stochastic classical dynamics is mathematically equivalent to the diagonalization of a quantum Hamiltonian [19], related to the Fokker-Planck (FP) operator, whose eigenvalues yield the relaxation time scales. Translational invariance of the FP operator induces a classification of physical quantities according to their wave vector,  $Q$ . The small  $Q$  density fluctuations are ruled by the hydrodynamic law stemming from mass conservation  $\tau(Q) \propto Q^{-2}$  [20], which become singular at  $Q=0$ . Yet, the dynamics of the translationally invariant quantities ( $Q=0$  sector) may be studied for nonconserved quantities such as the potential energy.

A generic observable  $O$  is said to belong to the  $Q$  sector if it transforms as  $O \rightarrow e^{i\vec{Q}\cdot\vec{\Delta}}O$  under a uniform displacement of the coordinates,  $\vec{r}_i \rightarrow \vec{r}_i + \vec{\Delta}$ . A well-known example are the Fourier transforms [ $V_{kj} \equiv V(\vec{r}_k - \vec{r}_j)$ ]:

$$\rho(\vec{Q}) = \frac{\sigma_0^{-3}}{N} \sum_{j=1}^N e^{i\vec{r}_j \cdot \vec{Q}}, \quad \rho_e(\vec{Q}) = \frac{\sigma_0^{-3}}{2N} \sum_{j,k \neq j} e^{i\vec{r}_j \cdot \vec{Q}} V_{kj}. \quad (1)$$

Note that  $\rho(0)$  is the (conserved) particle density, while  $\rho_e(0)$  is the (nonconserved) potential energy density, which we call  $e$  (the internal energy is then  $\frac{3}{2}k_B T + \langle e \rangle$ ).

Multiplying densities with wave vectors  $\vec{q}$  and  $-\vec{q}$  yields translationally invariant observables:

$$S(\vec{q}) = \rho(\vec{q})\rho(-\vec{q}), \quad S_e(\vec{q}) = \rho_e(\vec{q})\rho_e(-\vec{q}). \quad (2)$$

The mean value of  $S(\vec{q})$  is the static structure factor  $S(\vec{q})$ , while  $\langle S_e(0) \rangle$  is related to the constant-volume specific heat,  $C_V$  as  $T^2 C_V = N(\sigma_0)^6 [\langle S_e(0) \rangle - \langle e \rangle^2]$ . For every observable,  $O$ , we consider the normalized time correlator

$$C_O(t) = [\langle O(0)O(t) \rangle - \langle O \rangle^2] / (\langle O^2 \rangle - \langle O \rangle^2). \quad (3)$$

The theory of critical phenomena [2] suggests that, at *very long* times, time correlators decay exponentially.<sup>1</sup> We con-

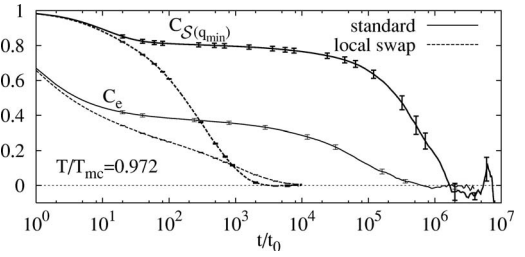


FIG. 1. Correlators for two translationally invariant quantities: the potential energy density  $e$  and the square of the density fluctuation,  $S(q_{\min})$ , at the minimal momentum allowed by the boundary conditions (1024 particles, below  $T_{mc}$ ). The local swap algorithm decorrelates faster than standard MC.

sider two autocorrelation times [21], the integrated time  $\tau_{\text{int},O}$  and the exponential time  $\tau_{\text{exp},O}$ :

$$\tau_{\text{int},O} = \int_0^\infty C_O(t) dt, \quad C_O(t) \xrightarrow[t \rightarrow \infty]{} e^{-t/\tau_{\text{exp},O}}, \quad (4)$$

with different meanings. The  $\tau_{\text{int},O}$  of  $Q=0$  quantities is related to transport properties (e.g., viscosity is  $\tau_{\text{int}}$  for some components of the energy-stress tensor [20]). The  $\tau_{\text{exp},O}$  is the longest characteristic time and depends only on the  $Q$  sector to which  $O$  belongs.

In Fig. 1 we show the time correlator for the potential energy density and  $S(\vec{q}_{\min})$ . While at short times standard MC and local swap dynamics yield the same correlators, the swap does not present the mode coupling plateau (hence significance of  $T_{mc}$  for swap MC is unclear), allowing a better study of the long time decay. Following this decay is difficult. The numerical (or experimental) effort to obtain the correlator  $C$  with prescribed accuracy grows as  $C^{-2}$  when  $C \rightarrow 0$ . In fact, most of previous work was confined to  $C > 0.1$ , while we are able to explore the range  $0.01 < C < 0.1$  (Fig. 2).

In Fig. 2 we show a semilogarithmic plot of the time correlators versus time. For long times, a straight line of slope  $-1/\tau_{\text{exp}}$  should be found. In Fig. 2(a) we show that  $\tau_{\text{exp}}$  obtained from  $e$  grows fast near the mode coupling temperature. The lower panels of Fig. 2 confirm that  $\tau_{\text{exp}}$  is actually a property of the  $Q=0$  sector. When our statistics are good enough to follow the correlator for three decades, the estimate for the exponential time does not depend on the chosen correlator. At low temperature one must be content with choosing the most convenient observable to extract  $\tau_{\text{exp}}$ . Every observable within a symmetry class has some overlap with the slowest mode of that class. The one which shows the smaller slope at shorter times is closer to the slowest mode, allowing more precise studies of  $\tau_{\text{exp}}$ .

The growth of  $\tau_{\text{exp}}$  is shown in Fig. 3(a). Close to a critical point, one expects a power law divergence of  $\tau_{\text{exp}}$ . This hypothesis accounts for our data, with an estimate for the critical temperature  $0.84T_{mc} < T_c < 0.89T_{mc}$ .

Universality requires that  $\tau_{\text{exp}} \propto A(T - T_c)^{-z\nu}$ , with  $T_c$  and the combination of critical exponents  $z\nu$  independent of the dynamics. Interestingly enough, in Fig. 3(a) we find that the

<sup>1</sup>Stretched exponentials fit nicely in intermediate times [1].

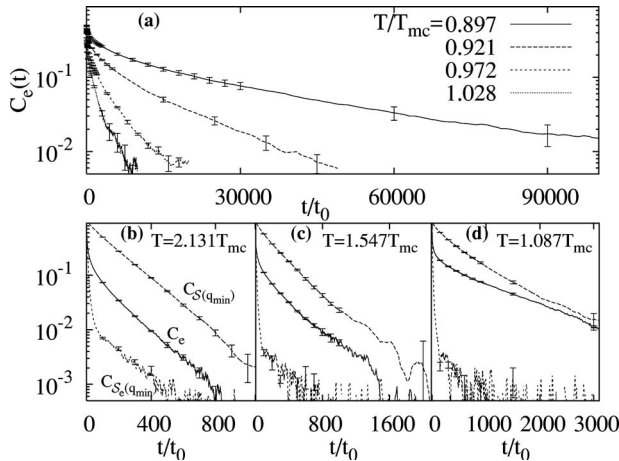


FIG. 2. Correlators for  $N=1024$  particles ( $N=2048$  at  $T/T_{mc}=0.897$ ) with the swap algorithm. Panel (a): temperature variation of the correlator of  $e$ , close to  $T_{mc}$ . Panels (b)–(d): correlators of several  $Q=0$  quantities. Asymptotically, three parallel straight lines should be found, with slope  $-1/\tau_{exp}$ . At the highest temperature (b), this is clearly observed, as well as in (c). In (d) we do not have enough independent measurements to see clearly this common slope.

ratio of  $\tau_{exp}$  for the swap and the standard MC dynamics is constant within errors, in spite of the enormous difference on their short-time behaviors.

A crucial issue is identifying the quantity with largest spatial fluctuations. For local dynamics, this quantity is closely related to the slowest mode (whose relaxation is purely exponential). Closeness can be quantified by the ratio of the integrated autocorrelation time to the exponential one, Eq. (4). The challenge is to find the observable that maximizes this ratio in the  $Q=0$  sector ( $\tau_{int}/\tau_{exp}=1$  only for the slowest mode). In Fig. 3(b) we show the ratio  $\tau_{int}/\tau_{exp}$  for the potential energy and for  $S(q_{min})$ , obtained with the swap dynam-

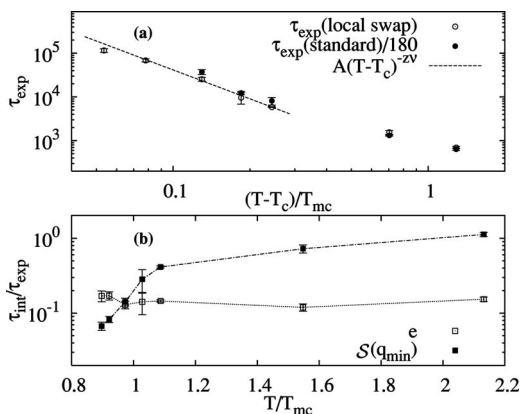


FIG. 3. Panel (a):  $\tau_{exp}$  vs reduced temperature (line is a fit of the swap data to a critical divergence). Note universality with respect to changes in the dynamics (the two  $\tau_{exp}$  differ in a constant factor). With standard MC one is restricted to  $T \geq 0.973T_{mc}$ . (b): ratio  $\tau_{int}/\tau_{exp}$  for swap dynamics. The participation of  $S(q_{min})$  in the slowest mode decreases upon approaching  $T_c$ , while the share of  $e$  slightly increases. We use  $N=1024$  but for  $T/T_{mc}=0.897$ , where  $N=2048$ .

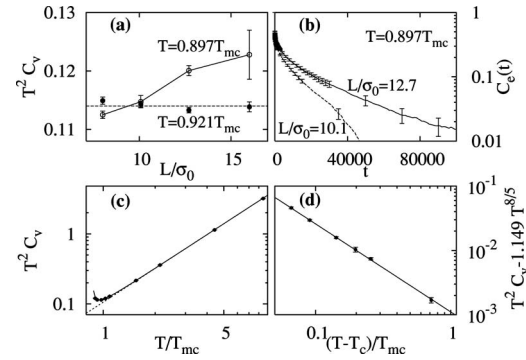


FIG. 4. Panel (a): unlike internal energy (not shown), the specific heat is a growing function of the simulation box size, until the system becomes much larger than the correlation length [14]. This is visible for  $L < 12\sigma_0$  at  $T=0.897T_{mc}$ , but not at  $T=0.921T_{mc}$ . The correlation length grows quickly close to  $T_c$ , which is confirmed by the time correlator for the potential energy (b). Panel (c): infinite volume specific heat vs temperature. The dashed line is the  $T^{8/5}$  Rosenfeld-Tarazona law. Deviations from the  $T^{8/5}$  law can be fitted by a critical divergence [full line in (d)] yielding  $T_c=0.86T_{mc}$ .

ics. We observe that  $S(q_{min})$  seems a very good candidate at high temperatures but the ratio  $\tau_{int}/\tau_{exp}$  sinks near  $T_{mc}$ . Fortunately, the potential energy displays a modest but constant ratio (even slightly increasing at low temperatures). This is a strong indication that critical behavior can be investigated in the fluctuations of the potential energy, namely the specific heat, and that a diverging correlation length would show up in four-particle correlators.

For the local dynamics studied here, diverging autocorrelation times suggest diverging correlation lengths, that should show up in static properties as well. Since the order parameter is unknown, a direct measure of the correlation length is difficult, but one may detect it indirectly through finite-size scaling [14]. The time correlators have taught us that energy fluctuations are promising candidates. We studied, Fig. 4(a), the specific-heat dependence on the size of the simulation box,  $L$ . Unfortunately, small systems crystallize quickly below  $2.13T_{mc}$ . On the other hand, the metastable liquid can be studied with  $N=512$  particles, using local swap, down to  $T=0.897T_{mc}$ . Up to  $T=0.921T_{mc}$  no finite-size effects are detected. However, for  $T=0.897T_{mc}$ , a noticeable growth of the specific heat with  $L$  is found up to  $L=12\sigma_0$  ( $\sim 4$  nm for argon parameters). This length is comparable with the experimental domain size for cooperative dynamics [9,10], and well above previous simulations [11]. The  $\tau_{exp}$  show a similar effect, Fig. 4(b).

The next step is the study of critical behavior in the infinite-volume specific heat itself, displayed in Fig. 4(c). Generally speaking, critical divergences for the specific heat are difficult to study numerically due to the presence of a large noncritical background (see, e.g., Ref. [22]). Fortunately, in our case the background is given by the Rosenfeld-Tarazona law [23],  $T^2 C_V \propto T^{8/5}$ , which should be followed by a noncritical dense fluid at low temperatures. We have checked that from  $T=2T_{mc}$  to beyond  $10T_{mc}$  the  $T^{8/5}$  law is extremely accurate. Interestingly, at lower temperatures (where the agreement with the  $T^{8/5}$  law should be

still better in the absence of criticality) *deviations* start to be significant. They are well described by a power law divergence  $\propto(T-T_c)^{-\alpha}$ . To estimate errors in  $T_c$  and  $\alpha$  is difficult. Excluding the two extremal points in Fig. 4(c), the fit yields  $\alpha=0.9$  and  $T_c=0.86T_{mc}$ . Including any of the extremal points in the fit,  $\alpha$  slightly grows. Taking into account the bound  $\alpha < 1$  imposed by the continuity of the internal energy, we estimate  $0.9 < \alpha < 1.0$  and  $0.84T_{mc} < T_c < 0.86T_{mc}$ .

In summary, we studied the equilibrium static and dynamic properties of a model of a fragile supercooled liquid, with emphasis on the dynamics of translationally invariant quantities. We claim that critical slowing down is behind the structural arrest of glass formers, which have then universal properties. We find that time correlators with a complicated structure relax exponentially at very long times. The study of the time correlators is a powerful, unprejudiced method of identifying the physical quantities suffering fluctuations over the largest length scale. The potential energy, rather than density fluctuations, emerges as the candidate for the study of this critical phenomenon. Experiments measure the constant pressure specific heat, that is obtained from the

constant volume one by adding a term that is smooth in the absence of critical density fluctuations (not found here). The critical temperature obtained from the divergence of the specific heat and of the autocorrelation times lies in the range  $T/T_{mc}=0.83-0.88$ . The study of the dynamics of translationally invariant quantities appears as a challenge to experimentalists. While measurements of the frequency dependence of the specific heat [24,25] are an appealing possibility to estimate the potential energy relaxation time, the correlation length could be studied by the finite-size scaling of the specific-heat and of relaxation times in films [15] or in larger pores than previously used to confine glass formers [16].

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