

Finite size effects in the specific heat of glass-formers

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Abstract. We report clear finite size effects in the specific heat and in the relaxation times of a model glass former at temperatures considerably smaller than the Mode Coupling transition. A crucial ingredient to reach this result is a new Monte Carlo algorithm which allows us to reduce the relaxation time by two order of magnitudes. These effects signal the existence of a large correlation length in static quantities.

INTRODUCTION

When compared to experiments, numeric simulations of glass-forming systems present severe limitations. In fact, while the actual physical origin of the phenomenon termed generically as *glass transition* is still a matter of debate, its investigation is limited by the practical impossibility to reach thermodynamic equilibrium when the relaxation time τ of a sample glass in a laboratory becomes of order of 10^2 seconds or when the τ of a model glass in a modern computer becomes of $\sim 10^{-8}$ seconds. Thus the glass temperature T_g is conventionally defined in experiments and numeric simulations cannot get very close to it¹. Furthermore, the statistical accuracy in experiments is fairly larger, because the time-length \mathcal{L} of typical experiments is many decades larger than in simulations. Indeed, statistical errors decrease roughly as $1/\sqrt{\mathcal{N}_{ind}}$ where the number of *independent* configurations \mathcal{N}_{ind} is given by $\mathcal{N}_{ind} \sim \mathcal{L}/\tau$. This problem is particularly serious in the study of time correlators, whose peculiar behavior is one of the most clear signature of the glass transition. For every observable, O , the normalized time correlator is

$$C_O(t) = \frac{\langle O(0)O(t) \rangle - \langle O \rangle^2}{\langle O^2 \rangle - \langle O \rangle^2}. \quad (1)$$

The region $C \sim 0$ is very interesting, since it allows to estimate the relaxation time (see below). On the other hand, in that region the relative error from a *single* measurement grows as C^{-1} hence a very large \mathcal{N}_{ind} is needed to get some significant signal over the noise. As a consequence, most of previous numeric work was confined to

$C > 0.1$, while in experiments one is able to explore far lesser values of C .

Despite those limitations, numeric simulations turn out to be quite useful in many respects, mostly in the key issue of identifying the quantity suffering the largest spatial fluctuations at the glass transition.[1, 2, 3, 4, 5] In fact, unlike standard phase transitions the equilibration time of glass-formers (supercooled liquids, polymers, proteins, superconductors, etc.) diverges without dramatic changes in their structural properties[6, 7, 8], challenging the interpretation of the slowing down as a critical phenomenon[9]. A possible way out has been found in the *heterogeneous dynamic scenario*, which postulate that *local* time correlators (i.e where O is a local quantity) are correlated over diverging length scales. The possible advantages of numeric simulations with respect of experiment are twofold. First, they are more suitable to investigate local quantities. Second, they allow an easier implementation of Finite Size Scaling techniques, a powerful tool to detect diverging correlation length.[10, 11, 12] New, fast algorithms for numerical simulation are therefore needed in order to get as close as possible to the experimental regime, while retaining all the advantages provided by numerics.

TRANSLATIONAL INVARIANT QUANTITIES

In this numeric work, we wish to ask the following question: Are there static observables whose correlation length ξ diverge at the glass transition? (Note that experimental clues are not available). In other words we wonder if a standard second order phase transition is behind the glass transition. We borrow from the dynamic heterogeneity scenario the hypothesis that a diverging cor-

¹ e.g. in SiO_2 Molecular Dynamics simulation have been performed only down to $T \sim 2200K$ while $T_g = 1500K$.

relation length would show up in four-particle correlation function and focus on translational invariant quantities.

Little attention has been paid so far to such quantities. In fact experiments (e.g. elastic scattering for the spatial correlations and dielectric response for the dynamic behavior) and simulations typically investigate quantities which are not invariant under an uniform displacement of the coordinates, $\vec{r}_i = \vec{r}_i + \vec{\Delta}$, namely the density fluctuations of generic momentum \vec{Q} :

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

where $\rho(0)$ is the particle density and it is constant because of mass conservation. Density fluctuations at small \vec{Q} are surely slow modes of the system, their time-correlator decaying exponentially with characteristic time $\tau \sim D^{-1}Q^{-2}$ (D is the diffusivity). We have no guarantee whatsoever though that they are the only relevant slow modes.

How to expand the space of observables investigated taking into account even quantities which preserve the translational symmetry? For the sake of definiteness we limit to the NVT ensemble and introduce energy density fluctuations:

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

where V_{kj} is the interaction energy $V(\vec{r}_k - \vec{r}_j)$ between particles k and j . Note that $\rho_e(0)$ is the non-conserved potential energy density, which we call e (the internal energy is then $\frac{3}{2}k_B T + \langle e \rangle$). A general way to obtain translationally invariant observables consists in multiplying densities with wave-vectors \vec{q} and $-\vec{q}$:

$$\mathcal{S}(\vec{q}) = \rho(\vec{q})\rho(-\vec{q}), \quad \mathcal{S}_e(\vec{q}) = \rho_e(\vec{q})\rho_e(-\vec{q}). \quad (4)$$

We see then that the correlation functions of these translational invariant quantities involve the positions of four particles. Moreover the mean value of $\mathcal{S}(\vec{q})$ is the static structure factor $S(\vec{q})$, while $\langle \mathcal{S}_e(0) \rangle$ is related to the constant-volume specific heat, C_V as $T^2 C_V = N(\sigma_0)^6 [\langle \mathcal{S}_e(0) \rangle - \langle e \rangle^2]$.

THE LOCAL SWAP MONTE CARLO ALGORITHM

We study a 50% mixture of particles interacting through the pair potential $V_{\alpha\beta}(r) = \varepsilon[(\sigma_\alpha + \sigma_\beta)/r]^{12} + C_{\alpha\beta}$, where $\alpha, \beta = A, B$, with a cutoff at $r_c = \sqrt{3}\sigma_0$ (σ_0 is the unit length). The choice $\sigma_B = 1.2\sigma_A$ hampers crystallization. We impose $(2\sigma_A)^3 + 2(\sigma_A + \sigma_B)^3 + (2\sigma_B)^3 =$

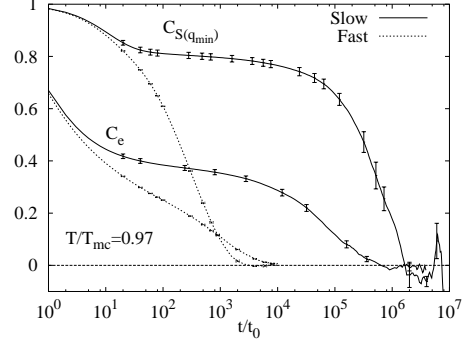


FIGURE 1. Correlators for two translationally invariant quantities: the potential energy density, e , and the square of the density fluctuation, $\mathcal{S}(q_{\min})$, at the minimal momentum allowed by the boundary conditions (1024 particles, below T_{mc}). The local swap algorithm decorrelates faster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

$4\sigma_0^3$. Constants $C_{\alpha\beta}$ are chosen to ensure continuity at r_c . The simulations are at constant volume, with particle density fixed to σ_0^{-3} and temperatures in the range $[0.897T_{\text{mc}}, 10.792T_{\text{mc}}]$, where T_{mc} is the Mode Coupling temperature[13]. 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 $N = 512, 1024, 2048$ and 4096 particles. For argon parameters, $\sigma_0 = 3.4\text{\AA}$, $\varepsilon/k_B = 120\text{K}$ and $T_{\text{mc}} = 26.4\text{K}$.

We modify the Grigera-Parisi swap algorithm[14] to make it *local*, in order to keep the algorithm in the dynamic Universality Class[9] 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 distance 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 $0.9T_{\text{mc}}$ up to 6% at $2T_{\text{mc}}$. 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.

In fig. (1) we show that the time-correlator of the local swap is in general different from the one of the standard MC. The main difference is given by the absence of the cage effect when the particles are allowed to swap. This is seen by the absence of the plateau in the time correlator in the swap dynamics. This implies that Mode Coupling transition is rather ill-defined within the swap dynamics. In fact, at mean field level Mode Coupling singularity is seen as due to the divergence of the caging time scale [13]. The Theory of Critical Phenomena suggests that the decay of time correlators of two different

TABLE 1. Stretching exponent β of the time correlator of the energy at different temperatures. The fit to a stretched exponential form has been performed in the region $C < 0.1$

T	$2.13T_{mc}$	$1.08T_{mc}$	$1.02T_{mc}$	$0.97T_{mc}$	$0.92T_{mc}$	$0.89T_{mc}$
β	0.99(3)	0.99(8)	0.98(12)	0.89(13)	0.83(4)	0.93(12)

dynamics sharing both the local nature and the conservation laws is given by the same function of the correlation length ξ (up to non universal numerical prefactors). They are said in fact to belong to the same dynamic Universality Class [9]. Since at *very long* times that decay is expected to be exponential it is possible to define the *exponential autocorrelation time* [15] which identifies the longest characteristic relaxation time τ :

$$C_O(t) \xrightarrow[t \rightarrow \infty]{} e^{-t/\tau}. \quad (5)$$

where

$$\tau \sim \xi^z \quad (6)$$

the dynamic exponent z depending only on the Class of the dynamics.

In a critical phenomenon one expects that eventually all the observables with the same symmetry decay with the same rate $1/\tau$ since they are all coupled to the slowest mode. The order parameter is supposed to be such slowest mode and its decay is purely exponential. In fig. (2) we show the large time decay of different translational invariant quantities obtained with the local swap. At high temperatures the exponential time is clearly the same, on the other hand at lower temperatures this is more difficult to show, since the point where in log-linear representation all the curves become parallel moves at lower and lower values of C . Actually, in literature the time decay of glass-former is more often described by stretched exponentials like $C_O(t) \sim \exp - (t/\tau)^\beta$, with $\beta < 1$. The stretching would arise from the contribution of many regions relaxing with different time scales. For the quantities we study in this work the stretched exponential fit nicely the time correlators only at intermediate times while, as we show in table 1, in the asymptotic region $C < 0.1$ the decay is in fact purely exponential. It would be very difficult to get this result with standard algorithm since at large t the correlator is *very* noisy.

The advantage of local swap over standard MC is not limited to the lack of the cage effect. This would be of no use if the exponential time of the two dynamics was the same. We see instead in Fig. (3) that, although the τ of the local swap seems to diverge, it remains always two order of magnitude smaller than the exponential time for the standard MC. Because of eq. (6) the fact that this ratio is roughly constant at all temperatures suggests that z is the same for both dynamics and then that they belong to the

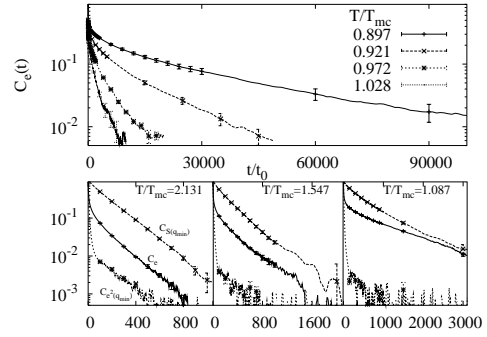


FIGURE 2. Time correlators for $N = 1024$ particles ($N = 2048$ at $T/T_{mc} = 0.897$) with the swap algorithm. Top panel: temperature variation of the correlator of e , close to T_{mc} . Bottom panels: correlators of several translational invariant quantities. Asymptotically, three parallel straight lines should be found, with slope $-1/\tau_{exp}$. At the highest temperature, (bottom, left), this is clearly observed. At lower temperatures (bottom, right) we do not have enough independent measurements to see clearly this common slope.

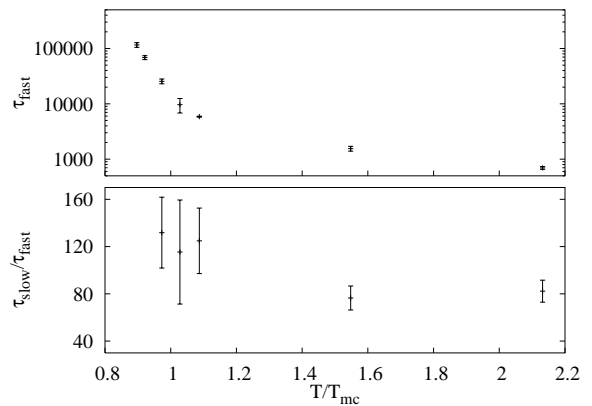


FIGURE 3. Top: exponential time τ_{fast} of the translational invariant quantities with the swap dynamics for $N = 1024$ particles ($N = 2048$ at $T/T_{mc} = 0.897$). Bottom: the ratio of the exponential times for standard MC (τ_{slow}) and local swap dynamics (τ_{fast}).

same Universality class. As anticipated in the introduction, reducing τ allows us to obtain results with a higher statistical accuracy. We show in fact in table 2 some parameters describing a selection of recent numeric simulations using standard algorithms (molecular dynamics)

TABLE 2. Statistical accuracy in the most recent Molecular Dynamics studies of simple glass-formers

Paper	Size*	Lowest T^\dagger	Time**
Yu & Carruzzo [16]	512	$1.01T_{mc}$	10^\ddagger
Berthier[17]	1372	$0.97T_{mc}$	100
Lacevic et al.[18]	8000	$1.03T_{mc}$	222

* Number of particles.

† Lowest temperature where the authors equilibrated the system.

** simulation length in units of relaxation time.

‡ the main finding of this paper is that the specific heat yields a thermalization time about 100 times larger than the alpha correlation time. In our simulations, this is the relaxation time considered.

TABLE 3. Statistical accuracy reached by means of the new local swap

Temperature	Size	Time
$0.97T_{mc}$	1024	100000
$0.897T_{mc}$	1024	27000
$0.897T_{mc}$	2048	3000
$0.897T_{mc}$	4096	400

to be compared in table 3 with the results that we were able to obtain with the local swap algorithm.

FINITE SIZE EFFECTS

Since the possible order parameter of the glass transition is unknown, a direct measure of the correlation length is difficult, but one may detect it indirectly through Finite-Size Scaling[11] by performing numeric simulations of system with different sizes. In fact, in the critical region, quantities related with fluctuations (such as the specific heat) depend on the size of the system. Under the hypothesis that the order parameter belongs to the class of translational invariant quantities, its exponential time τ has to grow with system size as a power law (the exponent being z) until the correlation length becomes smaller than the linear size of the system. Thus, in general, Eq. (6) holds in the thermodynamic limit while it has to be modified in systems of finite size [15]:

$$\tau \sim \max(L, \xi)^z. \quad (7)$$

Another quantity of interest is the specific heat C_v . As a matter of fact it must show a critical behavior if a second order phase transition is the responsible for the glass transition. In this case the approach to the thermodynamic value is rather expected to be exponential in the regime where $L < \xi$.

In Fig. (4) we show then the relaxation time and the specific heat dependence on the size of the simulation

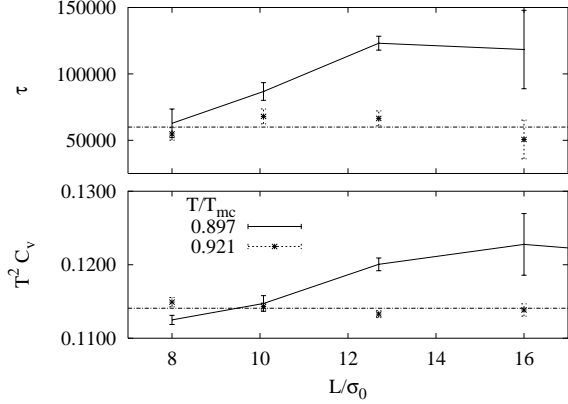


FIGURE 4. Top: size dependence of the exponential time at the two smallest temperatures studied, $T/T_{mc} = 0.921, 0.897$. Bottom: size dependence of the specific heat.

box, L . The main result is that at the smallest studied temperature $T = 0.897T_{mc}$, a noticeable growth of both quantities with L is found up to $L \sim 12.7\sigma_0$ ($\sim 4.3\text{nm}$ for argon parameters) which is our estimation of the correlation length ξ . The quantity defined by eq. (5) represents the *largest* relaxation time, which is the one affected by criticality. Of course, different time-scales (e.g. the plateau of intermediate scattering functions) might display a different dependence on L [19].

The correlation length that we have found is comparable with the experimental domain size for cooperative dynamics[20, 21], and well above previous simulations[17]. Aiming to estimate to dynamic exponent z one needs the value of ξ at larger temperatures, however up to $T = 0.921T_{mc}$ no finite-size effects are detected for both quantities. We believe that one should study smaller system to find them, but unfortunately they crystallize quickly below $2.13T_{mc}$. Taking $8\sigma_0$ as upper bound for ξ at $T = 0.921T_{mc}$ and utilizing the values of τ at the two smallest temperature we derive from Eq. (6) $z \sim 1.2$ as a rough estimate of the upper bound for the dynamic exponent.

CONCLUSIONS

Our findings are relevant in a twofold way.

Fast Monte Carlo algorithm We have shown that fast algorithms may open for numeric simulation a window on the phenomenology of the glass transition that was previously available only to experiments. On the other hand, the local swap dynamics introduced works quite well with the simple model studied here but it becomes less effective when the parameters of the model change. In a similar soft

sphere model [16] with $\sigma_B = 1.4\sigma_A$, the swap acceptance reduces of two order of magnitudes.

Finite size effects Having looked for a diverging correlation length we must at the moment content with a static correlation length that, close to the glass transition, is an order of magnitude larger than the range of the interactions. This challenges the common view that in glasses only dynamic quantities become correlated at large scales. More importantly, 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 [16, 22] are an appealing possibility to estimate the potential energy relaxation time, the correlation-length could be studied by Finite-Size Scaling of the specific-heat and of relaxation times in films or in larger pores than previously used to confine glass-formers. In fact experiments in films [23] and nanopores [24] show that the glass transition changes in samples with one or more dimensions of nanometric scale ². Interestingly, the specific-heat of toluene confined on pores of diameter 8.7 nm [24], close to its glass temperature, is significantly smaller than for bulk toluene, which could signal a correlation length well above the nanometric scale.

At a qualitative level one may note that a second order phase transition is not the only scenario predicting Finite Size effects in the specific heat. In fact, in the random first order transition picture of the glass transition [25] recently revised by Biroli and Bouchaud [26] the contribution to the specific heat from the configurational entropy $s_c(T)$ (the logarithm of the number of metastable states) is sizeable only when the system is large enough to contain many regions in different states. This happens when

$$L^d s_c(t) > 1. \quad (8)$$

To discriminate between the two interpretations a direct measurement of the correlation length of the energy would be needed. Nevertheless, in [27] we have shown some evidence for a singular behavior of the specific heat, consistent with the second order phase transition interpretation.

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² although it is difficult to disentangle Finite-Size Scaling from the effects of the interaction with the substrate.

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