Absence of a structural glass phase in a monatomic model liquid predicted to undergo an ideal glass transition

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Abstract. We study numerically a two-dimensional monodisperse model of interacting classical particles predicted to exhibit a static liquid–glass transition. Using a dynamical Monte Carlo method we show that the model does not freeze into a glassy phase at low temperatures. Instead, depending on the choice of the hard-core radius for the particles, the system either collapses trivially or a polycrystalline hexagonal structure emerges.

Keywords: classical Monte Carlo simulations, structural glasses (theory)
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1. Introduction

There has been considerable progress in the physics of structural glasses in the last few years [1, 2]. While experimentally as well as numerically new insights have been gained, theoretical studies of simple glass-forming models lag behind. A structural glass is a solid state characterized by ‘random’ particle positions such that it is not possible to identify symmetries, i.e., no long-range order exists. The nature of the transition from a liquid to such a disordered phase is still an open problem (see for example [3, 4]). A popular microscopic approach is that of mode-coupling theory which predicts a purely dynamical transition, i.e., a change in the dynamics from ergodic to non-ergodic behavior (see for example [5]). In contrast, a static glass transition arises from an equilibrium classical statistical mechanics approach using a replica formulation [6, 7], based on the assumption of an entropy crisis scenario [8]. It is important to note that this approach assumes that the system is in a uniform phase, thereby ignoring a crystal state from the very outset. A static glass transition may therefore only arise in systems where a crystal state does not dominate the low-temperature phase, e.g., by being separated from the glass phase by a large energy barrier.

The replica technique has been applied to a variety of systems, such as identical hard spheres [9], a Lennard-Jones binary mixture [10] and to a monatomic model with attractive two-body interactions [11]. The last study has the advantage over conventional glass-forming models in that exact replica calculations can be performed, thus potentially being able to deliver new insights into this complex field. The authors of [11] consider a system of $N$ classical particles in $D$ dimensions which interact via a two-body potential which is non-zero for a given distance $R$ between the particles and zero otherwise (see figure 1).

Analytical [12, 13] and numerical studies [14] report the absence of a static glass phase in monodisperse hard spheres in two and three dimensions, respectively. Therefore it would be of interest to test whether the model proposed in [11] has a static glass transition even though the model is intrinsically monodisperse (see equation (2) below). In this work we study the model proposed by Dotsenko and Blatter [11] numerically in two space dimensions ($D = 2$) and find that for various combinations of the model parameters the

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1 Note that for polydisperse systems the existence and nature of the glass phase are still controversial (see [18, 19]).

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Figure 1. Schematic plot of the interaction potential $U(r)$ (equation (2)) between two particles with relative distance $r = |r_i - r_j|$. For $r \in [R - r_0, R + r_0]$ the particles feel an attraction; otherwise the potential is zero. Note that the model is defined in the limit $1 \ll r_0 \ll R$. (a) The interaction potential as introduced in [11] with a hard-core radius $h = 1$. (b) The interaction potential modified in order to avoid a trivial particle collapse with a hard-core radius $R/4 < h < R/2$.

system crystallizes immediately. We thus conclude that some amount of disorder must be introduced in order to stabilize the glass phase.

2. Model

We study the monatomic glass former proposed in [11]. The model describes $N$ particles in $D$ space dimensions with a two-body interaction potential

$$U = \sum_{i<j} U(r_i, r_j),$$

where

$$U(r_i, r_j) = \frac{1}{r_0^2} (|r_i - r_j| - R)^2 - 1$$

for $R_- < |r_i - r_j| < R_+$. Here $R_\pm = R \pm r_0$, where $R$ is the ‘interaction radius’ of the potential and $r_0$ the width of the parabolic potential well (see figure 1 for details). The particle size is set to unity, which is equivalent to a hard-core radius of $h = 1$. In these units the results obtained in a mean-field approximation are valid in the parameter regimes $1 \ll r_0 \ll R$ and for an average particle distance which equals approximately those of the crystal and the liquid phase, i.e. $\rho^{-1/D} \approx R$ ($\rho$ denotes the density). The liquid and glass phases are predicted to be separated [11] by a critical temperature

$$T_c \sim 1/\ln(DR/r_0).$$

The disordered nature of the phase for temperatures below $T_c$ is identified by means of a replica correlator which quantifies the correlations between particles in two or more replicas.

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3. Numerical method and results

We use a Metropolis Monte Carlo (MC) method (see for example [15] for details). Without loss of generality we study particles in two space dimensions with periodic boundary conditions in a box of size \( L_x \times L_y \). A MC step consists of choosing a new configuration of particle positions and accepting this move with probability \( p = \min[1, \exp(-\Delta U/T)] \), where \( \Delta U \) is the difference in potential energy between the old and new configurations of particles. Two kinds of local moves are applied: a random particle and a random direction are chosen, and the particle is moved in this direction by a distance uniformly drawn from either the interval \([0, r_0]\) or the interval \([R_-, R_+]\). The resulting local dynamics serves as a model for the realistic dynamics of the system in renormalized physical time. In the absence of ergodicity breaking, the method also allows one to study the thermodynamic phase of the system: after a sufficient number of MC steps, configurations are distributed according to the equilibrium distribution \( \exp(-U/T) \). Clearly, if no disordered phase is found after relatively few MC steps, the use of optimized non-local MC updates which allow the system to assume low-energy configurations in a much faster manner will certainly not lead to a disordered phase either. The simulation is started with a random configuration of particles. The temperature \( T \) for the simulation is chosen such that \( T < T_c \), where \( T_c \) is given by equation (3). Since the system starts from a quenched configuration, the cooling rate is thus infinitely high, as required in [11].

For the glass phase to be stable Dotsenko and Blatter [11] give clear restrictions on the parameters of the model glass former, i.e., \( 1 \ll r_0 \ll R \). Simulating the system with the standard hard-core radius \( h = 1 \) and for temperatures \( T < T_c \) yields a trivial collapse where all particles approach each other up to a minimum distance of \( 2h \). We have tested this scenario for various choices of all system parameters. The same trivial

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Figure 3. Configuration snapshot after $3 \times 10^9$ Monte Carlo steps for $r_0 = 10$, $R = 100$, $h = 30$ (i.e., $T_c \approx 0.33$), $T = 0.1$, $N = 1200$ and an average particle distance $\rho^{-1/2} \approx 108$ (i.e., a smaller density than in figure 2). A polycrystalline structure with randomly oriented patches of hexagonal crystal is found.

Collapse is found for any hard-core radius which satisfies $h < R/4$. To avoid this behavior, we increase the size of the hard-core radius to values $R/2 > h > R/4$. Note that the size of the hard-core radius $h$ is irrelevant in the analytic calculations of [11, 16].

For the modified interaction potential (figure 1(b)) a hexagonal crystal structure emerges: if $L_x$, $L_y$ and $N$ are chosen appropriately, a perfect crystal develops as shown in figure 2. If the density is lower than the density of the hexagonal crystal, the particles organize in a polycrystalline structure: small hexagonal crystal patches with random orientations form, as can be seen in figures 3 and 4(d). In figures 4(a)–(d) we show how the crystalline structure forms as a function of time measured in Monte Carlo steps, starting from a low-density random configuration (panel (a)). We have also measured the replica correlator (equation (62) in [11]) whose finite value would be indicative of a glassy state. However, in our simulations, it takes a large value close to the linear system size squared, which means that particles in two replicas are completely uncorrelated (not shown). For large systems and various densities, ranging from those of the crystal state (figure 2) to ones for much more dilute systems (figures 3 and 4), our results are in stark contrast to the predictions of [11]: while a glassy ‘network-like’ structure with an average number of nearest neighbors which is significantly smaller than in a crystalline state is predicted, our results are locally crystal-like and show a high degree of order.$^2$.$^3$. We have measured the structure factor of the system which suggests an underlying crystalline structure (peaks) and does not show the typical ring-like feature found for a disordered system such as a glass or liquid.

$^2$ We have also measured the probability of creating a crystal germ to overcome the surface energy cost grows linearly with system size. This means that for a large enough system a germ will form which eventually will spread over a macroscopic volume of the system (depending on the particle density it can be the whole system volume). Quoting Werner Krauth: ‘Schwupp-di-wupp the whole box is a crystal’.

$^3$ The probability of creating a crystal germ to overcome the surface energy cost grows linearly with system size.
Figure 4. Particle configurations for $N = 1000$ particles ($r_0 = 10, R = 100, h = 30, T = 0.05 \ll T_c$) in a system with average particle distance $\rho^{-1/2} \approx 167$. (a) Initial random configuration, (b) configuration snapshot after $2 \times 10^7$ MC steps, (c) configuration snapshot after $2 \times 10^8$ MC steps, and (d) after $5 \times 10^9$ MC steps. As in figure 3, a polycrystalline structure emerges.

varied the system parameters, in particular increasing the ratio of $R$ and $r_0$, but the results were qualitatively similar to the ones shown in the figures. Therefore, if a glass phase exists in the model, it cannot be observed, since crystallization takes place very quickly.

4. Conclusions

In conclusion, our results from Monte Carlo simulations are in agreement with previous predictions [12,13] that monatomic systems in two space dimensions with two-body interactions, such as the recent proposal [11] studied here in detail, cannot form a glassy structure at low temperatures. Instead, the system forms a polycrystalline structure and does not show an ideal liquid–glass transition. This is unfortunate since the proposed monatomic model is analytically solvable and thus holds promise for delivering new insights to the physics of glass formers. It might be of interest to verify whether the model is still analytically solvable if, for example, many-body interactions between the particles [17] are added to the Hamiltonian, or Gaussian randomness is introduced into the distance $R$ to suppress the crystal state and favor a glassy phase. Assuming that the
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crystal structure is better suppressed in higher space dimensions, it might be conceivable to find a glass structure for $D > 2$ and thus possibly determine a lower critical dimension of the model.

While the simulations are performed for finite systems, we believe that the number of particles studied will not influence the conclusions found. In particular, we have scanned the vast parameter space in detail and have performed simulations for many different particle numbers and densities, always obtaining similar results.

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