Absence of Thermodynamic Phase Transition in a Model Glass Former

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The glass transition can simply be viewed as the point at which the viscosity of a structurally disordered liquid reaches \(10^{13}\) Poise [1]. This definition is operational but sidesteps fundamental controversies about the glass: Is the transition a purely dynamical phenomenon [2]? This would mean that ergodicity gets broken, but that thermodynamic properties of the liquid remain unchanged across the transition if determined as thermodynamic equilibrium averages over the whole phase space. The opposite view [3–6] claims that an underlying thermodynamic phase transition is responsible for the dramatic slowdown at the liquid-glass boundary. Such a phase transition (which shows up in proper equilibrium phase space averages) would trigger the dynamic standstill, and then get masked by it. A recent Monte Carlo algorithm introduces non-local moves for hard-core systems in a way which preserves micro-reversibility. Here we use this method to equilibrate a two-dimensional hard disc system far within its glassy phase. We show that indications of a thermodynamic transition are lacking up to very high densities, and that the glass is indistinguishable from the liquid on purely thermodynamic grounds.

We considered polydisperse hard discs \(i = 1, \ldots, N\) with radii \(r_i\) \((r_i - r_{i-1} = \Delta/(N - 1))\) in a square box of volume \(V = L^2\) with periodic boundary conditions. The polydispersity \(\Delta/r_1\) was kept fixed and the system studied as a function of the density \(\rho = \pi \sum_i r_i^2/L^2\). Note that hard-core systems are athermal: the phase diagram and the dynamics (up to a trivial rescaling) are independent of temperature. The external control parameters are the density (for the [NV] ensemble) or the pressure (for [NP]).

Conventional, local-move Monte Carlo simulations in the [NV] ensemble were used to compute effective diffusion constants [8] at densities for which the local algorithm was still ergodic, cf. fig. 1. We failed to detect any finite-size effects by comparing runs with 256 and 1024 discs at density \(\rho = 0.764\), but we noticed strong dependence of the diffusivities on the disc size. For each disc \(i\) we found its diffusivity \(D_i\) to agree very well with [9]

\[
D_i(\rho) \sim (\rho - \rho_G^G)^\alpha.
\]

For the \(\sim 180\) largest discs we found no systematic dependence of \(\rho_G^G = \rho^G \equiv 0.805 \pm 0.01\) (with a best fit \(\alpha \approx 2.4\)). For the smallest discs \(i\), the extrapolated values for \(\rho_G^G\) increased slowly. Our result for \(\rho_G^G\) agrees with what was found in a related system (B. Doliwa, Diploma Thesis, University of Mainz (1999)).

We next performed simulations with the cluster Monte Carlo algorithm [10]. There, groups of discs are swapped around a ’pivot’ (cf. fig. 4) in a way which represents an alternative Markov-chain sampling of the Boltzmann distribution. The correctness of both implementations was validated by comparing structural quantities (pair correlation functions) and thermodynamic variables in the manifestly liquid regime, where the local algorithm still converges well. We found that the cluster Monte Carlo algorithm does not slow down as we pass \(\rho_G\).

FIG. 1. Effective diffusion constants as a function of the radius for polydisperse hard discs. **Upper 6 curves:** 256 discs with polydispersity \(\Delta/r_1 = 19\) were simulated using the local-move Monte Carlo algorithm at densities at which the algorithm equilibrated. The effective diffusion constants were calculated via \(D_i = \langle (x_i(t_0 + t) - x_i(t_0))^2 \rangle / (4t)\), for \(x_i(t_0 + t) - x_i(t_0) \gg r_N\). The time was measured in Monte Carlo sweeps. Only the motion relative to the largest disc was taken into account. These asymptotic constants agree (up to a rescaling of the time unit) with what would be obtained in a molecular dynamics simulation [6]. **Lowest curve:** as above, but equilibrated initial configurations were provided by the cluster Monte Carlo algorithm. We observe that the smallest \(\sim 50\) discs are able to pass through the blocked matrix made up of the largest \(\sim 200\) discs. These findings are well consistent with the estimated values of the transition densities.
FIG. 2. Equilibrium compressibility. System as before was simulated using the cluster Monte Carlo algorithm. Equilibrium equation of state (inset) and inverse compressibility $\kappa^{-1}$ (main figure) were obtained in the [NP] ensemble. $\kappa$ was obtained from the fluctuations of the volume (points with error bars) and from the derivative of the best $V(P)$ fit according to the functional form $V(P) - \text{const} = aP^{-b}$ (Parameters of the best fit are $\text{const} = 84.3, a = 254, b = 0.69$). Indications of an equilibrium phase transition are lacking. The gray lines indicate the localization of the glass transition as extrapolated from fig. 1.

We used the cluster Monte Carlo algorithm to compute the equation of state in the [NP] ensemble. For pressures corresponding to the glass transition density $\rho_G^c$, we reached a relative precision for $V$ of 0.05% during a one-week simulation on a single processor workstation ($N = 256$). The compressibility of the system was obtained both by deriving the algebraic fit to $V(P)$ (cf. inset of fig. 2) and by computing the volume fluctuations:

$$\kappa = -\frac{1}{V} \frac{\partial (V)}{\partial P} = \frac{\langle V^2 \rangle - \langle V \rangle^2}{\langle V \rangle} \tag{2}$$

The agreement of the two methods (main fig. 2) testifies to the excellent convergence of the cluster Monte Carlo algorithm. Some of the compressibility data at high density were obtained from several independent runs with identical results. In contrast, the local Monte Carlo algorithm yielded non-reproducible (generally lower) compressibilities.

The results presented in fig. 2 allow us to draw far-reaching conclusions:

i) In the polydisperse hard-disc system considered, the glass is indistinguishable from the liquid on purely thermodynamic grounds, as we find no indication of a phase transition.

ii) Furthermore, the glass remains thermodynamically stable. No tendency towards crystallization or phase separation was detected. At smaller values of the polydispersity $\Delta/r_1$, a crystalline state is present, and can be readily detected in the equation of state \[10\]. In a related two-dimensional system of binary mixtures, phase separation was evidenced by the cluster Monte Carlo algorithm \[11\].

iii) Finally, the smooth behaviour of the compressibility as we cross $\rho_G^c$ indicates that the ergodicity of the cluster Monte Carlo algorithm is preserved up to the highest densities studied.

FIG. 3. Distribution of inherent structure densities for 15 discs with polydispersity $\Delta/r_1 = 19$. Equilibrium configurations were generated during a long run of the cluster Monte Carlo algorithm. The corresponding inherent structures were obtained by iterating a rescaling of the particle radii and local Monte Carlo moves (“rattling”) until a jamming state (of density $\rho_{IS}$) was reached. As $\rho$ increases, inherent structures with higher $\rho_{IS}$ become more probable. The same inherent structures with very large values of $\rho_{IS}$ were found in the simulation at $\rho = 0.82$ and $\rho = 0.84$.

Beyond the above point iii), the cluster Monte Carlo algorithm has passed an extremely stringent ergodicity test in a system with 15 polydisperse discs (where we also identified a density $\rho_G^c$ of complete dynamical standstill): A large number of equilibrated configurations were stored during single cluster-simulation runs in the [NV] ensemble at various densities $\rho$. For each stored configuration we then alternated very small up-scaling of each radius $r_i \rightarrow (1 + \epsilon)r_i$ ($i = 1, \ldots, N$) with a few local Monte Carlo moves (“rattling”). The procedure was repeated until a jamming state (with unchanged polydispersity $\Delta/r_1$) was reached. This state represents an inherent structure (IS), generalised from what is done in thermal systems by a quench to zero temperature \[12\]. Histograms of the IS densities $\rho_{IS}$ for different values of $\rho$ show that the algorithm explores the remaining regions of phase space as the density $\rho$ is increased, cf. fig. 3.
FIG. 4. Example of a cluster move at high density. The (+) denote the randomly chosen ‘pivot’ with respect to which the cluster (grey discs) can be flipped [7]. Periodic boundary conditions are indicated. The inherent structure related to the configuration a) is conjectured to yield the closest packed state for \( N = 15, \Delta/r_1 = 19 \).

A non-ergodic algorithm would get stuck in one or a few IS (during a single run) as regions of phase space become dynamically inaccessible. We observed the contrary: almost identical sets of IS with extremely large values of \( \rho_{IS} \gg \rho \) appeared in simulations at different, very high, values of \( \rho \). For intermediate values of \( \rho_{IS} \), the match could no longer be achieved, simply because of the very large number of different IS, even in a system with 15 discs, cf. fig. 3. Figure 4a) shows a configuration at \( \rho = 0.86 \), which can be blown up into the densest IS which we were able to find at polydispersity \( \Delta/r_1 = 19 \) (\( \rho_{IS} = 0.8938 \)). This IS (as many others) occurred frequently during a single run both at \( \rho = 0.84 \) and at \( \rho = 0.82 \). We conjecture that the IS related to fig. 4a) solves the closest-packing problem for \( N = 15 \) and \( \Delta/r_1 = 19 \).

In conclusion, our results show that the new Monte Carlo algorithm (which can be generalised to incorporate a smooth potential) works extremely well at densities at which the local method is totally stuck. Besides the calculation of thermodynamic quantities, the algorithm can also be used to study the finite-time dynamics (starting from equilibrated samples) at \( \rho \gtrsim \rho^C \). This is how the lowest curve in fig. 1 was obtained. As the initial condition is thermalised, we gain access to unbiased dynamical information in a regime which used to be out of reach of rigorous simulations because not all discs can be properly equilibrated with the local algorithm. Clearly, the method represents a very powerful tool to study glasses.

[1] Angell, C. A. Formation of Glasses from Liquids and Biopolymers. Science 267, 1924–1935 (1995).
[2] Götz, W. & Sjörgen, L. Relaxation Processes in Supercooled Liquids. Rep. Prog. Phys. 55, 241–376 (1992).
[3] Kauzmann, W. The nature of the glassy state and the behavior of liquids at low temperatures. Chem. Rev. 43, 219–256 (1948).
[4] Gibbs, J. H. & DiMarzio, E. A. Nature of the Glass Transition and the Glassy State. J. Chem. Phys. 28, 373–383 (1958).
[5] Adam, G. & Gibbs, J. H. On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids. J. Chem. Phys. 43, 139–146 (1965).
[6] Menon, N. & Nagel, S. R. Evidence for a Divergent Susceptibility at the Glass Transition. Phys. Rev. Lett. 74, 1230–1233 (1995).
[7] Dress, C. & Krauth, W. Cluster Algorithm for hard spheres and related systems. J. Phys. A: Math Gen 28, L597–L601 (1995).
[8] Hansen, J. P. & McDonald, I. R. Theory of Simple Liquids. (Academic, London, 1986).
[9] Fuchs, M., Götz, W., & Mayr, M. R. Asymptotic laws for tagged-particle motion in glassy systems. Phys. Rev. E 58, 3384–3399 (1998).
[10] Alder, B. J. & Wainwright, T. E. Phase Transition in Elastic Disks. Phys. Rev. 127, 359–361 (1962).
[11] Buhot, A. & Krauth, W. Phase separation in two-dimensional additive mixtures. Phys. Rev. E 59, 2939–2941 (1999).
[12] Stillinger, F. H. & Weber, T. A. Packing structures and transitions in liquids and solids. Science 225, 983–989 (1984).
[13] Sastry, S., Debenedetti, P. G. & Stillinger, F. H. Signatures of distinct dynamical regimes in the energy landscape of a glass-forming liquid. Nature 393, 554–557 (1998).
[14] Malherbe, J. G. & Amokrane, S. Asymmetric mixture of hard particles with Yukawa attraction between unlike ones: a cluster algorithm simulation study. Mol. Phys. 97, 677–683 (1999).

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