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Thermodynamic signature of the dynamic glass transition in hard spheres

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Abstract

We use extensive event-driven molecular dynamics simulations to study the thermodynamic, structural and dynamic properties of hard-sphere glasses. We determine the equation of state of the metastable fluid branch for hard spheres with a size polydispersity of 10%. Our results show a clear jump in the slope of the isothermal compressibility. The observation of a thermodynamic signature at the transition from a metastable fluid to a glassy state is analogous to the abrupt change in the specific heat or thermal expansion coefficient as observed for molecular liquids at the glass transition. The dynamic glass transition becomes more pronounced and shifts to higher densities for longer equilibration times.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The amorphous or glassy state, a property of nearly all condensed matter systems, can be achieved by cooling or compressing the (supersaturated) liquid sufficiently rapidly beyond the glass transition. Glasses have a structure that is nearly indistinguishable from that of the liquid phase, but they can have dramatically different dynamical properties: molecules in a glass can move 10^{13} times slower than in a liquid phase [1]. How this is possible and whether this transition is gradual or sharp and accompanied by a structural change and diverging length scale is one of the main mysteries of glassy materials. Despite the huge amount of work devoted to glasses, the nature of the glass transition remains one of the deepest and most interesting unresolved problems in condensed matter physics [2].

Already in the 1930–1940s, it was shown by experiments that many molecular liquids show, at the glass transition, a rather abrupt change in measured thermodynamic quantities like the specific heat, thermal expansion coefficient and the isothermal compressibility [3]. The sudden drop in these so-called thermodynamic susceptibilities, which are directly related to thermodynamic fluctuations of the system or the long-wavelength static correlation functions, is found in many glass-forming systems, although it seems to be absent or very small in some others [4]. In the liquid phase, the particles vibrate at short times in the cages formed by their neighbors, while at longer times, cooperative structural relaxation occurs.

The latter relaxation slows down at the glass transition and the corresponding fluctuations no longer contribute to the thermodynamic susceptibilities of the system. The mechanism behind the freezing out of certain degrees of freedom can be thermodynamic or dynamic of origin. The thermodynamic mechanism arises from a structural change in the system, and the dynamic mechanism occurs because the observation time is too short for the system to reach equilibrium. According to Kauzmann, one can distinguish the thermodynamic from the dynamic mechanism by prolonging the observation time and studying whether the change in the thermodynamic quantities is still present at infinitely long times [3]. Whether the glass transition is of dynamic or thermodynamic origin has been hotly debated since then and has still not been settled.

In order to understand the glass transition, many investigations have been devoted to idealized model systems in which the particles behave as hard spheres. One might suppose that the issue is settled for such a simple model by computer simulations. While early simulation studies predict a thermodynamic transition [5, 6], as there is a discontinuity in the third or second derivative of the free energy, more recent studies show no discontinuity at all [7, 9, 10]. In these recent studies, large-scale molecular dynamics simulations were performed for long equilibration times, while monitoring the local crystalline order to obtain well-equilibrated, truly random configurations along the metastable fluid branch. No evidence of a second order or ideal glass transition was observed for the well-equilibrated fluid state points. The existence of a

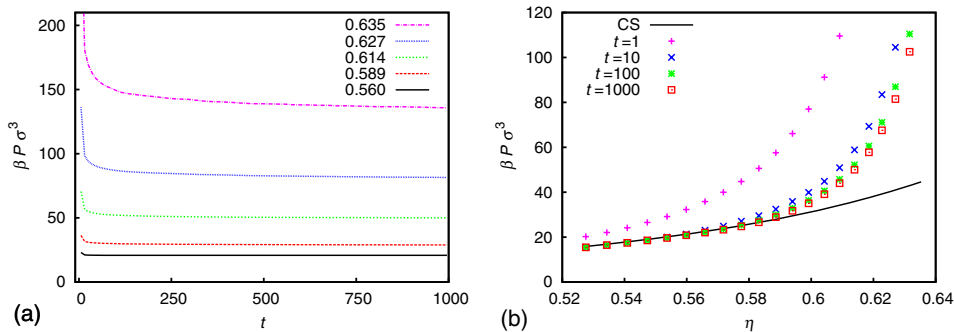


Figure 1. (a) The pressure $\beta P(t, \eta)\sigma^3$ of hard spheres with a polydispersity of 10% as a function of t in MD time units for varying packing fraction η (as labeled). (b) The pressure $\beta P(t, \eta)\sigma^3$ versus packing fraction η for varying time $t = 1, 10, 100$ and 1000. The solid line denotes the Carnahan–Starling (CS) equation of state.

thermodynamic glass transition is, on the other hand, proposed for hard spheres to avoid the paradox that the continuation of the equation of state of the stable liquid phase exhibits a divergence at unphysically high packing fractions, while one expects a divergence at random close packing ($\eta \simeq 0.64$) [15]. Experiments on colloidal hard spheres with diameter σ under Earth’s gravity exhibit a glass transition at a volume fraction $\eta = \pi \sigma^3 N / 6V \simeq 0.58$ with N the number of spheres and V the volume [11], while no glass transition is found without gravity [12, 13]. An ergodicity breaking transition is predicted by mode coupling theory due to slow relaxation [14]. It remains an open question as to whether there is, in the case of hard spheres, an abrupt change in a thermodynamic quantity at the glass transition, which one would expect on the basis of molecular glasses.

In this paper, we use extensive computer simulations to study the thermodynamic, dynamic and structural properties of hard-sphere glasses. Our results show evidence of a thermodynamic signature, i.e. an abrupt change in the slope of the isothermal compressibility, at the dynamic glass transition. Our findings are analogous to the abrupt change that has been found in the specific heat or thermal expansion coefficients at the glass transition of molecular liquids.

2. Method

We consider a system of hard spheres with a Gaussian diameter distribution yielding a size polydispersity of 10% to prevent crystallization. The distribution was cut off at five standard deviations. We have checked the formation of crystalline order by measuring the crystallinity [16]. We find no sign of crystalline order or fractionation in our simulations, which allows us to study the system for long times. We stress that simulations of pure hard spheres (and smaller polydispersities) do show crystallization for packing fractions $0.52 < \eta < 0.63$ [17] and that, for sufficiently long times and large system sizes, systems with a size polydispersity of 10% and $\eta > 0.54$ should partially crystallize as well [18].

We perform event-driven molecular dynamics (MD) simulations with fixed volume, energy and number of particles. We measure the pressure using the virial theorem [19]. We have checked that our results for the pressure agree

with the pressures obtained from the collision rate method and the value obtained from the contact value of the radial distribution function within statistical error. For our initial configuration, we employ the mechanical contraction method, which generates densely packed and highly jammed configurations [20]. The initial velocities of the particles are randomly chosen from a Maxwell–Boltzmann distribution. The time t is measured in MD time units defined as $\sqrt{m\sigma^2/k_B T}$, where $\sigma = (\sum_{i=1}^N \sigma_i^3 / N)^{1/3}$ is the average diameter, σ_i is the diameter of particle i and m is the mass of the particles.

3. Results

First, we study the equation of state of the metastable liquid branch. We perform simulations of 10^3 hard spheres for varying packing fractions. We measure the pressure $\beta P(t, \eta)\sigma^3$ as a function of time and we repeat the procedure for up to 100 independent starting configurations. In figure 1(a), we observe that the averaged pressure depends strongly on the age of the sample. The initial pressure is relatively high as the spheres are highly jammed in the initial configuration, but as the system evolves in time the particles rearrange to obtain more free volume and the pressure decreases rapidly. At a later stage, the particles diffuse less quickly as they are more caged and the pressure decays more slowly. We observe that only the short-time aging behavior is affected by the fine details of the protocol that is used to generate the initial configurations. The results obtained from an initial configuration generated with the event-driven Lubachevsky–Stillinger algorithm [8] yield long-time behavior which is indistinguishable from the simulations started with an initial configuration generated with the mechanical contraction method.

In figure 1(b), we plot the equation of state for different times obtained from figure 1(a). For comparison, we also plot the Carnahan–Starling (CS) equation of state for pure hard spheres [21]. At low η , our simulations for polydisperse hard spheres are almost indistinguishable from CS. Surprisingly, we find a clear deviation of our pressure data from CS, which shifts to higher packing fractions and becomes sharper when the system ages.

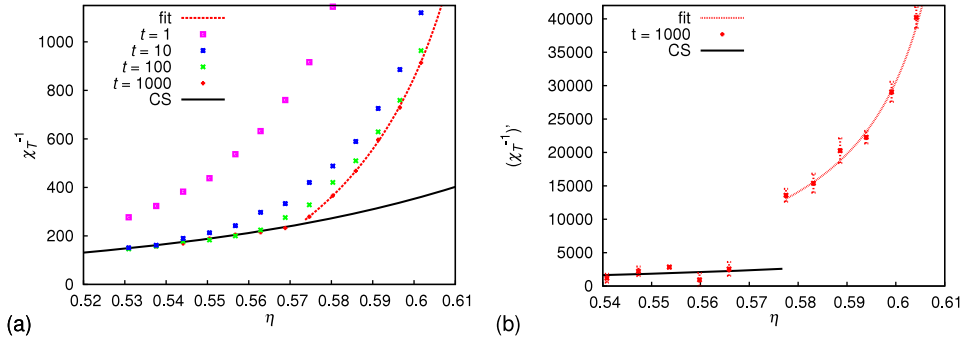


Figure 2. (a) The inverse compressibility χ_T^{-1} as a function of packing fraction η for time $t = 1, 10, 100$ and 1000 . The solid line denotes χ_T^{-1} obtained from the Carnahan–Starling equation of state, while the dashed lines are fits to guide the eyes. The statistical error is smaller than the symbol size. (b) The slope of the compressibility $(\chi_T^{-1})'$ as a function of η for time $t = 1000$. The solid line denotes $(\chi_T^{-1})'$ obtained from the Carnahan–Starling equation of state.

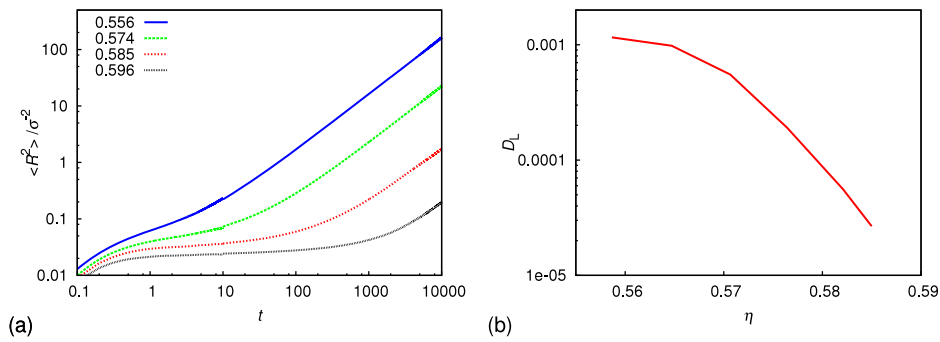


Figure 3. (a) The mean squared displacement $\langle R^2 \rangle / \sigma^2$ as a function of time in MD units for waiting time $t_w = 1 \times 10^5$ and varying packing fractions η as labeled. (b) The long-time diffusion coefficient D_L in units of $\sigma \sqrt{k_B T / m}$ as a function of η obtained from the mean squared displacements.

To investigate this deviation, we calculate numerically the derivative of our equation of state. The simplest form of a numerical derivative was used $df(x)/dx \approx (f(x + \Delta) - f(x - \Delta)) / (2\Delta)$ to obtain the inverse compressibility $\chi_T^{-1} = \rho(\partial\beta P\sigma^3/\partial\rho)$ and its derivative for time $t = 1, 10, 100$ and 1000 . We plot χ_T^{-1} versus η in figure 2(a). For comparison, we also plot χ_T^{-1} obtained from CS. We observe a sharp deviation from CS in the isothermal compressibility in figure 2(a) which becomes more pronounced and shifts to higher densities for longer aging times. In figure 2(b), we plot the derivative of the inverse compressibility $(\chi_T^{-1})'$ as a function of η for time $t = 1000$. We clearly observe a jump of nearly one order of magnitude in the slope of the compressibility, i.e. the third-order derivative of the free energy at $\eta \simeq 0.575$, which corresponds to the dynamic glass transition as observed experimentally [11]. The error bars were obtained by calculating the standard error of independent sets of simulations.

We wish to make a few remarks here. Instead of a jump in a second-order derivative of the free energy (e.g. the isothermal compressibility, specific heat) as in the case of many molecular glasses, we find indications of a jump in the third-order derivative of the free energy. In [5], it is speculated that the change in order of the transition is related to the absence of potential energy contributions in the case of hard spheres. The isothermal compressibility is related to density fluctuations, which consist of diffusional and vibrational contributions. At

the glass transition, diffusional contributions tend to zero, and hence the slope of the isothermal compressibility will change. For molecular glasses, potential energy fluctuations will disappear at the transition, yielding a discontinuity in the isothermal compressibility itself. It is interesting to investigate whether soft repulsive and attractive spheres yield a jump in a second-order derivative of the free energy (work along these lines is in progress). This might mean that the actual order of the dynamic glass transition is different for soft/attractive systems.

The next question is to determine which degrees of freedom are frozen at the glass transition. To this end, we determine the mean square displacement (MSD) $\langle R^2 \rangle / \sigma^2$ with $\langle \dots \rangle$ denoting an ensemble over all particles and configurations. From the MSD we obtained the long-time diffusion coefficients D_L for ‘aged’ systems, i.e. the measurement has been carried out after a waiting time $t_w = 1 \times 10^5$. Figure 3(a) shows that, for sufficiently high η , the MSD develops a plateau as the structural relaxation slows down. However, the plateau is finite for all η that we tested, which is to be expected as the equilibration times for these state points are shorter than $t = 10^5$. Figure 3(b) shows that D_L decreases upon increasing η , but it does not tend to zero at $\eta \simeq 0.58$, as was observed in experiments on colloidal systems in gravity [14]. Since gravity plays an important role in the formation of glasses [13, 12], the discrepancy is most likely caused by the absence of gravity in our simulations.

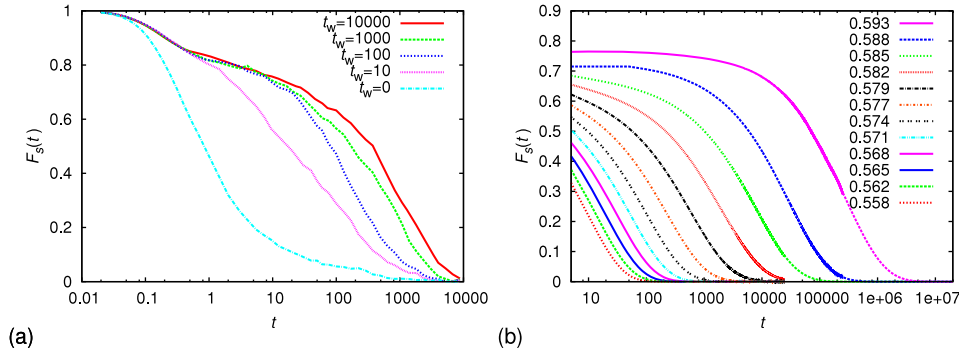


Figure 4. (a) The self-intermediate scattering function at a volume fraction of $\eta = 0.58$ for varying t_w (see labels). (b) The self-intermediate scattering function $F_s(t)$ for ‘aged’ systems ($t_w = 1 \times 10^5$ or 1×10^6) for varying η (see labels) and for $k\sigma = 8.2$.

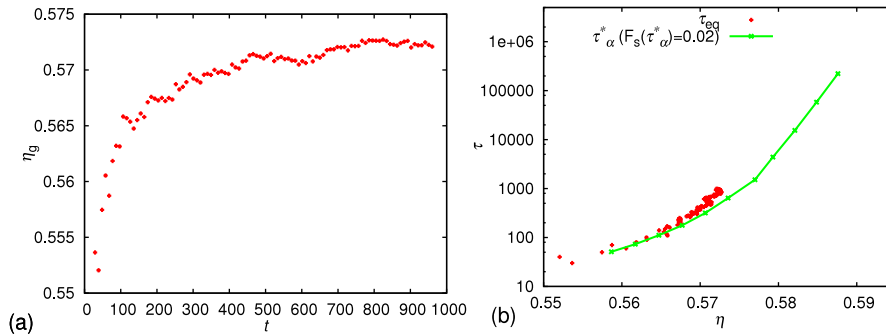


Figure 5. (a) The packing fraction η_g corresponding to the kink in χ_T^{-1} as a function of time t . (b) The equilibration time τ_{eq} and the relaxation time τ_α^* as a function of packing fraction η .

In addition, we calculate the self-intermediate scattering function $F_s(t)$ for a wavevector close to the main peak of the static structure factor, i.e. $k\sigma = 8.2$. We perform simulations of 2000 hard spheres with a polydispersity of 10%. Figure 4(a) shows that $F_s(t)$ has a clear aging behavior: the structural relaxation slows down dramatically for longer waiting times as the time window of the plateau of the correlation function increases. The particles get more arrested or caged upon prolonging the waiting time and the plateau in $F_s(t)$ grows in temporal extent when the system ages. For $\eta = 0.58$, $F_s(t)$ no longer changes between $t_w = 1 \times 10^5$ and $t_w = 1 \times 10^6$ and it is tempting to argue that the system reached the ‘equilibrium’ (but metastable with respect to a fractionated crystal phase) state. In order to eliminate the aging behavior, we perform long simulations of 1×10^7 time units. Figure 4(b) shows $F_s(t)$ for $k\sigma = 8.2$ and varying η for ‘aged’ systems ($t_w = 1 \times 10^5$ or 1×10^6). We clearly observe the development of a plateau, which is characteristic of structural relaxation, but the correlation function seems to decay to zero for all η . We note that the correlation function decays to zero within $t \simeq 1000$ for $\eta = 0.58$. However, for lower values of the wavevector $k\sigma$, the relaxation of $F_s(t)$ from the plateau value becomes slower and the time window of the plateau increases in contrast with the predictions of simple mode coupling theory.

As we find a strong aging behavior in the equation of state and its derivatives, we plot in figure 5(a) the packing fraction η_g corresponding to the kink in the isothermal compressibility as a function of ‘waiting’ time. As the kink in the isothermal

compressibility corresponds to a dynamic glass transition from a metastable fluid phase to a metastable glass state, one can identify the ‘waiting’ time as the time that is required to equilibrate the metastable fluid at $\eta \simeq \eta_g$. Figure 5(b) clearly shows that a longer ‘waiting’ time is required to equilibrate a system at increasing η . We now compare the equilibration time τ_{eq} with the relaxation time τ_α^* as defined by $F_s(\tau_\alpha^*) = 0.02$ for $k\sigma = 8.2$. We plot the equilibration time as a function of η along with τ_α^* in figure 5(b). We find that the equilibration time of the system as obtained from the kink in the isothermal compressibility (see figure 5(a)) agrees well with the relaxation time as obtained from the intermediate scattering function as shown in figure 4(b). We note that the normal definition of the relaxation time where $F_s(\tau_\alpha) = e^{-1}$ is always lower than the equilibration time obtained from the equation of state.

In conclusion, we find a clear jump in the slope of the compressibility, which becomes more pronounced and shifts to higher densities for longer aging times. According to Kauzmann, the glass transition is of thermodynamic origin, if the change in thermodynamics remains at infinite times. A thermodynamic ideal glass transition has been predicted at a Kauzmann packing fraction $\phi_K = 0.617$ on the metastable fluid branch in [15] using the replica method. However, the existence of a thermodynamic ideal glass transition is heavily debated. Our results show a nonequilibrium glass transition at a density range of 0.55–0.59, which is far below the theoretical predictions for the ideal glass transition. This is to be expected as the relaxation time diverges on approaching the

ideal glass transition [22], and hence it is impossible to reach ϕ_K , since already at lower densities, the fluid gets arrested in a nonequilibrium glass as the relaxation time becomes longer than the simulation time.

Although the simulations discussed here were based on polydisperse hard spheres, similar results were obtained with pure hard spheres: the pressure decays with a power law until crystallization sets in and diverges at a volume fraction that is slightly lower than the polydisperse case. At densities well below and above the glass transition we were able to obtain similar pressure data as for polydisperse hard spheres but, close to the glass transition, crystallization is so fast that we were not able to obtain accurate results for sufficiently long times.

The search for a structural change or a diverging length scale at the glass transition has been going on for a long time, but has not yielded any definite results. However, there is some evidence for a diverging length scale in dynamic correlation functions at the glass transition. For example, Weeks *et al* [23] have observed experimentally that clusters of fast moving colloidal particles are much larger in the metastable fluid than in the glass and that there is a sudden drop in cluster size at the glass transition. Benneman *et al* have found a diverging length scale of correlated motion at the glass transition in simulations of a polymer melt [24].

As we provide evidence for a clear thermodynamic signature at the dynamic glass transition, i.e. an abrupt change in the third-order derivative of the free energy, one might expect to find a structural change in one of the higher-body correlation functions when the system falls out of equilibrium. This can be understood from the virial expression that relates the pressure to the contact value of the pair correlation function. Subsequently, the first or second derivative of the pressure, i.e. the inverse compressibility or its slope, can then be expressed in terms of (the contact values of) a four-body or higher-body correlation function, respectively. In order to detect a discontinuity in the contact value of one of these higher-body correlation functions, which is a very subtle effect, one has to calculate these higher-body correlations with sufficient statistical accuracy so that one can extrapolate these correlation functions to the contact value with high precision. Unfortunately, our efforts to calculate these higher-body correlation functions were not sufficiently accurate close to the dynamic glass transition that we could detect such a discontinuity in the contact value. The main problem that we encounter is that, close to the dynamic glass transition, the system ages faster than that we were able to accumulate decent statistics for the correlation functions. When we try to increase our statistics by longer simulation times, the dynamic glass transition simply moves to higher packing fractions.

4. Conclusion

We have used extensive event-driven molecular dynamics simulations to study the thermodynamic, structural and dynamic properties of hard-sphere glasses. We have determined the equation of state of the metastable fluid branch for hard spheres with a size polydispersity of 10%. We demonstrated that the dynamic hard-sphere glass transition has a thermodynamic signature, i.e. there is an abrupt change in the second derivative of the equation of state. Hence, we have shown that the dynamic glass transition can be located by measuring the equation of state or derivatives thereof, as was already known for molecular glasses. Further we demonstrated that the equilibration time of the equation of state corresponds to the relaxation time as obtained from the self-intermediate scattering function.

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