Numerical Investigation of the Entropy Crisis in Model Glass Formers†

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We investigate numerically the low-temperature equilibration of glassy systems via nonlocal Monte Carlo methods. We reexamine several systems that have been studied previously and investigate new systems to test the performance of such methods near the putative Kauzmann temperature, T_K, where the configurational entropy is presumed to vanish. Our results suggest that previous numerical claims in favor of and against a thermodynamic transition at a finite T_K must be reevaluated. Our work provides some guidelines and suggestions for future numerical investigations of disordered systems at high densities and low temperatures.

I. Introduction

The nature of the glass transition is one of the great unsolved problems in condensed-matter physics. The kinetic glass transition (occurring at temperature T_g) is phenomenologically defined to occur when a liquid reaches a threshold viscosity.[1] It has long been speculated that a thermodynamic transition to a disordered solid would occur if the liquid could be cooled infinitely slowly without crystallizing. Kauzmann[2] argued that extrapolating the supercooled liquid entropy into the glassy regime implies that a temperature (known as the Kauzmann temperature, T_K) exists where the configurational entropy of the liquid becomes less than that of the crystal. Gibbs and co-workers[3] resolved this crisis by suggesting that a phase transition to an "ideal glass" occurs at T_K. Many theories of glassy behavior contain thermodynamic transitions to an ideal glass state. Gibbs and Di Marzio[4] postulated that a second-order transition occurs at T_K whereas theories based upon mean-field spin glass ideas contain a random first-order transition at T_K.[5−7] Stillinger has argued that localized defects must destroy a second-order ideal glass transition.[8] In general, localized excitations (non-mean-field effects) should round any transition that would occur at T_K, and recent arguments have been put forward to access the conditions under which the signatures of mean-field behavior survive.[9] Although the above theories in some sense *presuppose* the existence of a transition at T_K that drives the formation of a disordered solid, other theoretical models of glassy behavior completely avoid the notion of an underlying thermodynamic transition. In particular, a large class of kinetically facilitated models successfully explain many of the features exhibited by supercooled liquids without invoking the notion of configurational entropy.[10] The difficulty of directly probing slowly cooled, low-temperature glassy configurations, either experimentally or computationally, has made the resolution of the issue of the entropy crisis extremely difficult.

Advances in simulation techniques have made the low-temperature equilibration of certain model systems possible. These techniques include parallel tempering,[11] histogram reweighting,[12] and the use of specific nonlocal MC moves.[13−15] Recent studies of model systems have produced seemingly conflicting results regarding the possible existence of an entropy crisis. Grigera and Parisi have demonstrated that a soft-sphere mixture displays a distinct signature of a thermodynamic transition near the Kauzmann temperature predicted by the random first-order phase-transition scenario,[15] and Santen and Krauth have shown that a 2D hard-sphere system displays no such signature.[14] It has been difficult to obtain further insight into these phenomena because the simulation methodologies are highly system-specific. Although extremely useful for several systems,[14,16−18] the cluster algorithm of Krauth[19] has been hard to generalize to more complex and 3D systems, and the swapping method used by Grigera and Parisi fails for systems with attractive interactions. Other methods, such as simulated annealing and parallel tempering, have been found to equilibrate slowly in the glassy regime.[20]

In this paper, we reexamine claims in favor of and against the existence of an entropy crisis at a temperature T_K. We carefully explore the nature of the thermodynamic signature in the heat capacity of the soft-sphere system studied by Grigera and Parisi and study thermalized versions of a system studied by Santen and Krauth in both two and three dimensions. A critical assessment is made concerning the ability of various nonlocal Monte Carlo techniques to equilibrate liquids under conditions necessary to probe the putative entropy crisis. Our conclusions suggest that strong claims for numerical evidence both in favor of and against an entropy crisis in all systems studied to date must be reevaluated.

II. Computational Details

When a liquid is deeply supercooled, its microscopic motion is characterized by rapidly growing relaxation times. This slow relaxation renders the use of conventional molecular dynamics and Monte Carlo techniques impractical for obtaining well-equilibrated configurations near the glass-transition temperature. Recently, several methodologies have been introduced in an effort to overcome the problems associated with the rapid onset of sluggish dynamics that hinder equilibration with local simulation techniques. Parallel tempering methods have been shown to speed up equilibration above the mode-coupling temperature T_c [21] but have not been useful in obtaining well-equilibrated configurations significantly below this temperature.[20] Other techniques, such as expanded ensemble methods,[22]

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multicanonical algorithms,[23] and the density-of-states Monte Carlo approach,[24,25] may provide routes to obtaining equilibrated configurations at low temperatures, although few systematic studies have been performed for glassy systems with these techniques and we will not discuss them further here.[26,27]

Conventional Monte Carlo techniques augmented with nonlocal moves offer a powerful approach to overcoming ergodicity problems associated with rough free-energy landscapes. These methods allow for moves that interchange particles or groups of particles while still maintaining detailed balance. Even if such moves are rarely accepted, they greatly accelerate sampling by providing routes for relaxation (e.g., the hopping of a particle out of the cage composed of its neighbors) that would take many local Monte Carlo moves to achieve. Recently, two types of nonlocal Monte Carlo methods have been applied to the study of glassy systems: the cluster pivot algorithm (CPA) of Krauth and co-workers[14] and the swap Monte Carlo (SMC) algorithm applied by Grigera and Parisi to the study of the entropy crisis.[15]

In this work, we introduce a trivial modification of the SMC approach, called swap-sector Monte Carlo (SSMC), that is optimized for equilibrating polydisperse systems. As with SMC, the positions of particles of different sizes are swapped at varying intervals. Noting that the probability of swapping falls off quickly as the ratio of particle sizes differs from 1, we introduce a swap sector where particles are swapped only with those that differ in radius by less than a tunable parameter $\Delta\sigma$. In the limit of large $\Delta\sigma$, standard SMC is recovered. $\Delta\sigma$ can be optimized for efficiency; a large $\Delta\sigma$ yields a low acceptance ratio, and a small $\Delta\sigma$ allows pairs of particles to be swapped back and forth repeatedly. This method has been used to equilibrate both hard- and soft-sphere polydisperse systems, facilitating direct comparison between the two. Three different systems are simulated in this work. The first is a binary soft-sphere system identical to that studied by Grigera and Parisi, with

$$V = \sum_{i \neq j}^{N} \left(\frac{\sigma_i + \sigma_j}{|\mathbf{r}_i - \mathbf{r}_j|} \right)^{12} \tag{1}$$

where $\sigma_1/\sigma_2 = 1.2$, $\sigma_{12} = {}^1/_2(\sigma_1 + \sigma_2)$, and $\epsilon_1 = \epsilon_2 = 1$. The units are set by choosing $\sigma_1 = 1$. Runs are executed by varying the temperature with constant volume, chosen so that $\rho^* = \rho\sigma_x^3 = 1$, where

$$\sigma_x^3 = \frac{1}{4}\sigma_1^3 + \frac{1}{2}\sigma_{12} + \frac{1}{4}\sigma_2^3 \tag{2}$$

is the effective radius defined by conformal solution theory.[28] All simulations in this work employ periodic boundary conditions. Systems of 34, 60, 70, and 258 particles are studied, consistent with previous studies. Although clearly too small to study dynamics in a regime where the dynamical correlation length is noticeably growing, our studies should provide a useful probe of the underlying thermodynamic behavior.

The second system is the 2D hard-sphere system of Santen and Krauth,[14] run in the NPT ensemble. The 256 particles have radii ranging from $R_1 = 1$ to $R_{256} = 20$, with $R_i - R_{i-1} = \Delta$ for constant Δ. Isothermal compressibilities are calculated both by the finite difference of the volume with respect to pressure, $\kappa_{\mathrm{diff}} = -(1/\langle V\rangle)(\partial\langle V\rangle/\partial P)$, and by fluctuations of the volume, $\kappa_{\mathrm{fluc}} = \langle V^2\rangle - \langle V\rangle^2/\langle V\rangle$. If the system is well equilibrated and the are data well averaged, then $\kappa_{\mathrm{diff}} = \kappa_{\mathrm{fluc}}$. This provides a necessary (but not sufficient) test for equilibration that, together with the convergence and stability of the thermodynamic averages, is applied throughout. We also applied the Flyvberg–Petersen method[29] to determine accurate estimates of the statistical error, which were well below 0.1% of the heat capacity even at extremely low temperatures.

Last, a polydisperse soft-sphere system is studied with $\sigma_i = 1 + \Delta^* i$ where $1 \leq i \leq N$ and Δ is chosen so that $R_{\max} = 20$, providing a thermal version of the Santen and Krauth system. Runs are executed by both varying the temperature with constant volume and varying the volume with constant temperature to confirm the validity of the results. (Excess thermodynamic properties in soft-sphere systems depend only on the parameter $\Gamma = \rho T^{-D/12}$, where D is the dimensionality of the system.) Constant volume is chosen so that

$$\rho_{\mathrm{poly}} = \frac{\frac{4}{3}\sum_{i=1}^{N}\pi r^3}{L^2} = 1$$

For all of the systems, up to 1×10^8 steps of equilibration and 1×10^9 steps of data collection are used, providing well-converged data. Data accuracy and convergence properties were established through numerous shorter runs.

In several cases presented below, it is useful to have an estimate of the location of the putative Kauzmann temperature as calculated through the random first-order theory. Here we follow Parisi and co-workers.[5,6] Harmonic solid entropies are calculated for N particles in D dimensions as

$$S_{\mathrm{sol}}^{(\mathrm{a})} = \frac{ND}{2}\left(1 + \log\left(\frac{2\pi}{\beta}\right) - \left\langle \frac{1}{N_{\mathrm{pos}}}\sum_{i=1}^{N_{\mathrm{pos}}} \log(|\lambda_i|)\right\rangle\right) \tag{3}$$

where N_{pos} denotes the number of positive eigenvalues λ_i of the instantaneous Hessian. These are averaged over 100–200 different configurations for each temperature, each separated by 1×10^4 steps, which is more than enough to obtain good statistics. Liquid entropies are calculated by thermodynamic integration as

$$S_{\mathrm{liq}} = S_{\mathrm{liq}}^0 + \beta E_{\mathrm{liq}}(\beta) - \int_0^\beta \mathrm{d}\beta'\, E_{\mathrm{liq}}(\beta') \tag{4}$$

where S_{liq}^0 represents the ideal gas entropy in the $\beta \to 0$ limit and $E_{\mathrm{liq}}(\beta)$ is the average energy at inverse temperature β. Liquid entropies are extrapolated into the glassy regime by fitting the data as $S_{\mathrm{liq}}(T) = aT^{-2/5} + b$, a well-known fitting form for the entropy of simple liquids.[6,30] Inherent structures, when needed, are found by steepest descent quenches for the binary soft-sphere system and by a combination of the steepest descent and conjugate gradient for the polydisperse system. Data are averaged over thousands of such configurations for each temperature.

III. Binary Soft-Sphere System

The first system that we investigate is the binary soft-sphere liquid defined in section II. To demonstrate the robustness of estimates of the Kauzmann temperature in this system, we calculate T_{K} via the random first-order theory of Mezard and Parisi[5,6] and the inherent structure-based method of Buchner and Heuer.[31,32] The approach of Buchner and Heuer is similar to that of Sciortino, Kob, and Tartaglia[33,34] and yields nearly the same estimate of T_{K}. Using the approach of Mezard and Parisi and the definitions of the entropy of the liquid and disordered solid discussed in section II, we find that $\Gamma_{\mathrm{K}} = 1.72$

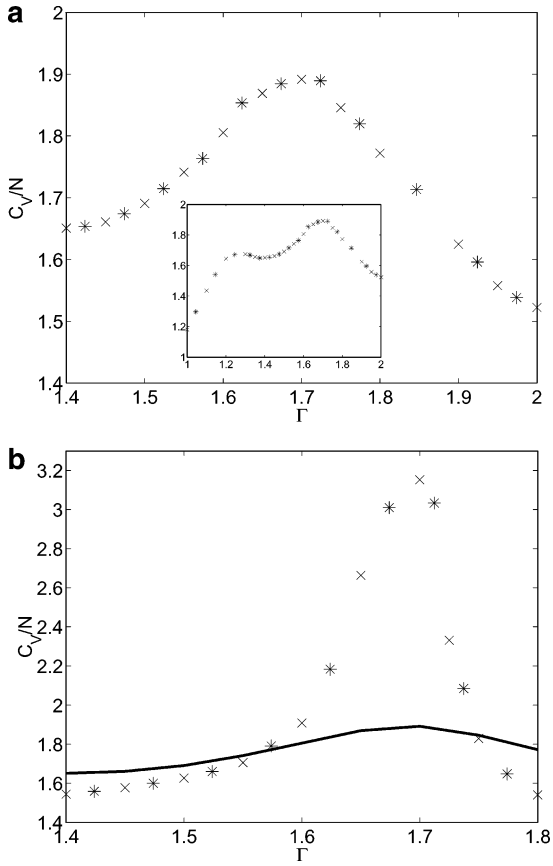

Figure 1. (a) Heat capacity per particle for a 34-particle binary soft-sphere system. The inset extends this calculation to higher temperatures (lower Γ), where a second smaller peak is evident. C_V (×) as calculated by fluctuations and the finite difference (*) are plotted; this symbol convention is maintained throughout the paper. Swap moves were attempted on average every 10 moves, and data were collected for between 1×10^7 and 1×10^9 steps, with longer runs for lower temperatures. (b) Heat capacity per particle for the same system and computational details as given in part a, but with 60 particles. The heat capacity as calculated by fluctuations and derivatives is shown. The 34-particle peak is included (—) to facilitate direct comparison.

($\Gamma = \rho T^{-D/12}$) whereas the method of Buchner and Heuer yields $\Gamma_K = 1.69$. A previous estimate using the random first-order approach by Coluzzi et al.[6] yielded $\Gamma_K = 1.65$ analytically and $\Gamma_K = 1.75$ from simulation data. It is unclear why our estimate differs from that of Coluzzi et al., but it is most likely due to slight differences in numerical implementation. Regardless of these differences, a consistent estimate of $\Gamma_K \approx 1.7$ emerges from these approaches.

Recently, Grigera and Parisi implemented the SMC procedure for the soft-sphere mixture. Although for large systems they could not equilibrate the system at low temperatures (large Γ), they found a peak in the specific heat of a small (34-particle) system at $\Gamma \approx 1.7$. We have reproduced this calculation in Figure 1a. The agreement between the values of the specific heat calculated from fluctuations and derivatives of the average energy suggests that the equilibration of configurations has been achieved. In the inset of Figure 1, we display an expanded view of the specific heat for the 34-particle system that includes higher temperatures (lower Γ values). A second interesting signature in the specific heat appears near $\Gamma = 1.25$. This signature becomes sharper for larger systems, as shown in Figure 1b. The sharpness of this peak together with its system-size dependence strongly supports the view that this feature is thermodynamic in nature. It is interesting that $\Gamma = 1.25$ is close to the onset of supercooling at $\Gamma_0 \approx 1.3$.[35] For systems that are larger still ($N > 70$), the signature near $\Gamma = 1.25$ vanishes, as does the ability to equilibrate the system with the SMC method for $\Gamma > 1.5$ for reasonable trajectory lengths.

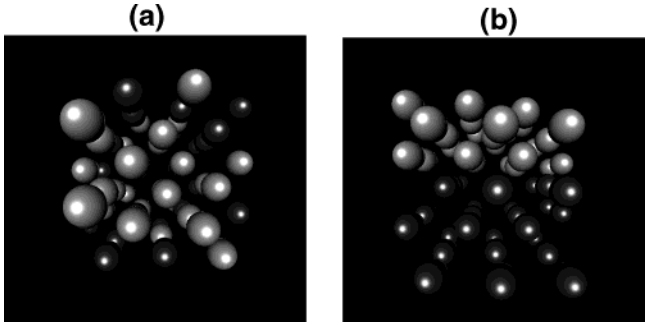

Figure 2. Crystalline structures found by SMC. (a) Inherent configuration of a 60-particle binary soft-sphere system sampled at $\Gamma = 1.3$, near the first heat-capacity peak and (b) instantaneous structure sampled at $\Gamma = 1.8$, near the second peak.

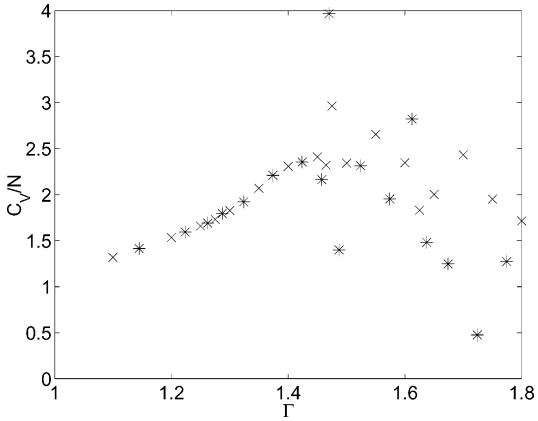

Figure 3. Heat capacity per particle for the 70-particle binary soft-sphere system. Equilibrated samples are obtained only up to $\Gamma = 1.45$. Swap moves were attempted on average every 10 moves, and data were collected for between 1×10^8 and 1×10^9 steps.

The appearance of secondary features in thermodynamic quantities suggests that perhaps the specific heat peak near $\Gamma = 1.7$ is not the result of the type of entropy crisis envisioned in the random first-order theory of glassy thermodynamics. To investigate this further, we examine the structures obtained from SMC in small systems that display a specific heat peak near $\Gamma = 1.7$. In Figure 2, we show representative configurations of the system obtained by SMC at $\Gamma = 1.3$ and 1.8. The system is clearly not an amorphous solid but a phase-separated crystal with substitutional defects and, at very low temperatures, the phase-separated crystal itself.

The ground-state structure found by SMC is a phase-separated crystal. By examining the inherent structure configurations sampled at various values of Γ, we conclude that the peak in the specific heat results from a gap in the density of states between the set of all defective crystal configurations and the ground state of the system. As the system size increases, defective crystalline configurations become harder to locate relative to the set of amorphous configurations, and the sharp features in the specific heat vanish, as does the ability of SMC to equilibrate the system significantly below the estimated value of Γ_c, the location of the mode-coupling temperature (density).[36] In Figure 3, we plot the specific heat for 70 particles obtained from the SMC method. Note that the agreement between the heat capacity calculated via fluctuations and direct differentiation of the average energy diverges near $\Gamma_c \approx 1.45$.

We thus conclude that the specific heat peak found in the binary soft-sphere system is not a direct consequence of an ideal

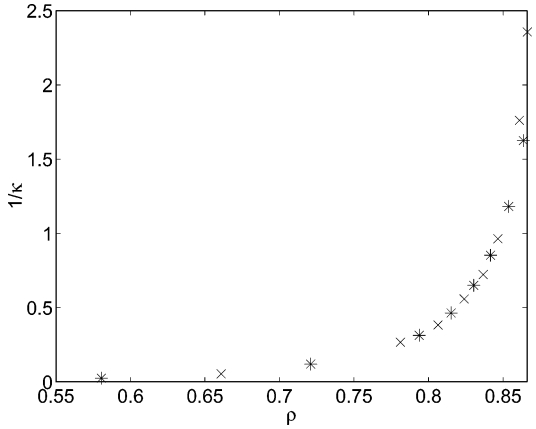

Figure 4. Converged inverse isothermal compressibility κ^{-1} vs ρ for the polydisperse hard-sphere system of Santen and Krauth. The system was equilibrated by SSMC. Swap moves were attempted on average every 10 moves, and data were collected for 1×10^9 steps, though such a long run was necessary only for extremely high pressures.

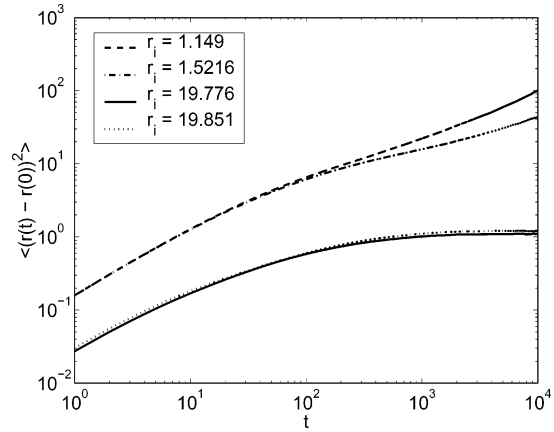

Figure 5. Mean square displacement vs MC time for two small and two large particles chosen at random from the polydisperse hard-sphere system of Santen and Krauth. The data are taken at $P = 0.09$, which corresponds to $\rho \approx 0.861$.

glass transition. One may speculate that the gap between defective crystalline states and the ground state occurs near $\Gamma_K = 1.7$ because the number of amorphous configurations at these energy values (nearly) vanishes, and thus the peak at $\Gamma_K = 1.7$ is indeed an indirect consequence of the vanishing of the configurational entropy associated with glassy states. The fact that slightly larger systems (i.e., $N > 70$) than those for which converged specific heats may be obtained cannot be equilibrated significantly below $\Gamma_c \ll \Gamma_K$ makes this reasoning suspect. It still remains to be determined if the fact that the predicted Kauzmann value of $\Gamma_c \approx 1.7$ coincides with the gap between defective crystal states and the ground state is purely accidental. Furthermore, we find that whereas SMC is more efficient than methods such as parallel tempering for $\Gamma \approx \Gamma_c$ neither approach is able to equilibrate large systems significantly below the mode-coupling temperature (density) in this system.

IV. Polydisperse Systems

Having seen that states with crystalline order interfere with a direct investigation of the entropy crisis in the binary soft-sphere system, we now turn to the analysis of polydisperse systems. The first goal will be to reinvestigate the completely polydisperse 2D hard-sphere system studied by Santen and Krauth.[14] Here we will examine systems in three dimensions as well as systems at finite temperatures to address concerns that might arise with Santen and Krauth's particular system.

First, we calculate the compressibility of a 256-particle 2D hard-sphere system via the SSMC approach. In Figure 4, we show κ^{-1} versus ρ for this system. Our results agree with those of Santen and Krauth, although we were able to equilibrate the system at slightly higher densities. Interestingly, we have found that our implementation of SSMC is more efficient than the cluster algorithm of Santen and Krauth, although this may indeed be a result of our own inefficient optimization of their technique. Regardless, the similarity in the convergence of the two methods is significant because the SSMC approach works in arbitrary dimensions, but the method of Santen and Krauth is difficult to generalize, particularly to systems with $D > 2$.[37] By fitting the diffusion constant of the larger discs to a power law form, $D(\rho) \approx (\rho - \rho_c)^\gamma$, Santen and Krauth extract a glass-transition density of $\rho_c \approx 0.805$. These diffusion constants are measured by short-time local Monte Carlo dynamics, which has been shown to yield accurate relaxation times in 2D systems[38] and meaningful quantities in the α-relaxation regime.[39] This means of extracting a critical density should actually yield the mode-coupling density and not the glass-transition density. Thus, it is not surprising that there is no thermodynamic signature in the compressibility near $\rho_c = 0.805$. One can make a rough estimate of the location of ρ_K in the system of Santen and Krauth by noting that a conservative guess for the ratio of mode coupling to Kauzmann densities from the $\rho T^{-D/12}$ dependence in an "equivalent" soft-sphere system would imply that ρ_K is about 10% larger than ρ_c. Although this estimate is crude, it implies that an exploration of the putative entropy crisis in the system studied by Santen and Krauth is out of reach of both the SSMC and cluster algorithm used by Santen and Krauth.

To explore further the properties of this 2D hard-sphere system, we address the nature of the phase space available to the smaller discs. Whereas at the highest densities that we can probe the largest discs are completely trapped for long Monte Carlo times, the smaller discs are diffusive and do not even show a significant cage effect. In Figure 5, we show the mean square displacement of large and small discs, illustrating that part of the system remains fluid even at the highest densities. From the standpoint of the standard definition of configurational entropy, it would appear that the polydisperse hard-sphere system studied by Santen and Krauth cannot experience a strict entropy crisis in principle because of the disparity of disc sizes. Recent work by Kumar et al. suggests that a reasonable correlation should exist between the density of random close-packing and the Vogel density in a hard-sphere system.[40] If we crudely interchange the Vogel density and the Kauzmann density, then we expect that the ideal glass transition, if one occurs at all, will occur close to the random close-packed density. If, as in the polydisperse system of Santen and Krauth, the larger spheres freeze while the smaller spheres remain mobile, then the existence of the mobile, incompressible background fluid will always prevent the effective close-packing of the larger spheres. It is not clear what signatures of an entropy crisis might exist in systems where a finite fraction of particles may still undergo diffusive motion while the remaining particles are frozen, but it would appear that the very concept of an entropy crisis in such a system is perhaps ill-defined.

Because the system studied by Santen and Krauth is both athermal and 2D, we have also studied a 3D soft-sphere version of this system. In Figure 6, we show the specific heat of a small ($N = 34$) version of the polydisperse 3D soft-sphere system discussed in the Introduction. Interestingly, although the data shows that the heat capacity calculated via fluctuations and by

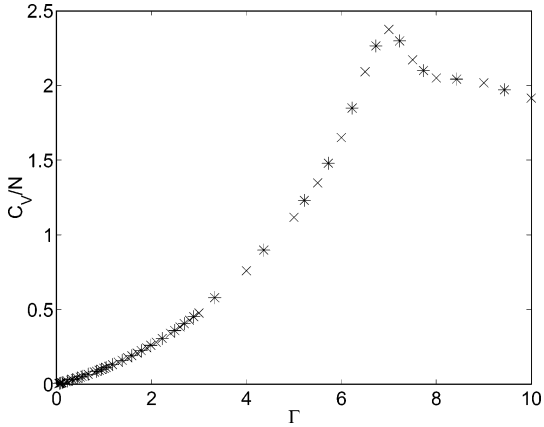

Figure 6. Heat capacity per particle for a 34-particle polydisperse soft-sphere system. The peak arises from a phase-separation process that induces intermediate-range order in the system. Swap moves are attempted on average every 10 steps, and data are collected for 1×10^7 to 6×10^8 steps.

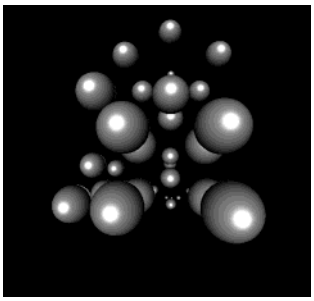

Figure 7. Inherent structure of the 34-particle polydisperse soft-sphere system at $\Gamma = 10.0$. A cluster of large particles lies in the foreground, and a cluster of small particles lies inside (not behind) the large cluster. Similar clustering can be found in all low-temperature structures of this system.

derivatives of the average energy agree there is a sharp thermodynamic feature in the heat capacity at low temperatures. One would naively expect that this system cannot exhibit a state with intermediate-range order and therefore this peak must be related to a glassy phenomenon, but this is not the case. Subtle features in the radial distribution function as well as a close inspection of instantaneous and inherent structures make it clear that particles of similar size have bunched together with local order. In Figure 7, we show one such inherent configuration found via SSMC at low temperatures.

We conclude once again that the peak in the heat capacity is the result of an exotic crystallization phenomena. In this sense, our 3D thermalized version of the system studied by Santen and Krauth is similar to the binary soft-sphere system studied by Grigera and Parisi. For larger systems, the range of thermodynamic parameters for which nonlocal Monte Carlo methods provide equilibrated results is not broad enough to investigate deeply glassy states, whereas smaller systems show thermodynamic signatures consistent with the formation of defective or phase-separated crystals. Interestingly, we could not find evidence of this type of phase separation in small, 2D polydisperse hard- or soft-sphere systems; however, we were still limited to densities and temperatures that differ significantly from those at which an entropy crisis might be expected.

V. Conclusions

In this work, we have taken a closer look at the recent use of nonlocal Monte Carlo methods to investigate the nature of low-temperature glassy thermodynamics. We have found that claims for and against the existence of an entropy crisis that have been recently reported in the literature must be reconsidered. The peak in the specific heat found by Grigera and Parisi through the SMC approach can be attributed to an energy gap between the manifold of defective crystalline configurations and the phase-separated ground state of the system. The use of SSMC (optimized SMC) performs at least as well as the cluster algorithm of Santen and Krauth for the 2D polydisperse hard-sphere system, but both are unable to probe this system at high enough densities to render strong claims about the behavior of the configurational entropy meaningful. Furthermore, because this system has a very wide range of particle radii, a macroscopic portion of the system remains fluid at the highest densities. This fact further clouds the discussion of a possible entropy crisis in this system. It is not surprising that even powerful Monte Carlo methods that make use of nonlocal moves still cannot equilibrate systems under conditions where the number of available configurations becomes sparse. Interestingly, whereas the Monte Carlo methods investigated here greatly increase the rate of equilibration for temperatures (densities) near T_c (ρ_c), they are not efficient at lower temperatures (higher densities). Completely polydisperse systems are an exception to this finding, but these systems are pathological in the sense that there is always significant phase space for a finite fraction of the system to explore even when part of the system is configurationally frozen. In general, we have found that one has to be careful to avoid the subtle phase separation and the corresponding sharp features in thermodynamic quantities that may occur in these systems.

Although the findings presented here are somewhat negative, they do provide important guidelines and warning signs for any computational investigation of the entropy crisis in systems with realistic potentials. It would be interesting to perform nonlocal Monte Carlo studies on small systems whose potentials are tailored to penalize structures with intermediate and long-range order strongly.[41] It would also be interesting to reinvestigate larger versions of the systems studied here with the more powerful Wang−Landau approach.[24,26] We are currently pursuing these directions.

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