Numerical Investigation of the Entropy Crisis in Model Glass Formers

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Abstract

We investigate numerically the low temperature equilibration of glassy systems via non-local Monte Carlo methods. We re-examine several systems that have been studied previously and investigate new systems in order 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 re-evaluated. 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. 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 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 coworkers 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 postulated that a second order transition occurs at $T_K$ while theories based upon mean-field spin glass ideas contain a random first order transition at $T_K$. Stillinger has argued that localized defects must destroy a second order ideal glass transition. 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. While 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 kinetic facilitated models successfully explain many of the features exhibited by supercooled liquids without invoking the notion of configurational entropy. The difficulty of directly probing slowly cooled, low temperature glassy configurations, either experimentally or computationally, has made 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, histogram re-weighting and the use of specific non-local MC moves. 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, while Santen and Krauth have shown that a two dimensional hard-sphere system displays no such signature. It has been difficult to obtain further insight into these phenomena, as the simulation methodologies are highly system specific. Although extremely useful for several systems, the cluster algorithm of Krauth has been hard to generalize to more complex and three dimensional systems, while 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.

In this paper, we re-examine claims in favor 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 system studied by Santen and Krauth in both two and three dimensions. A critical assessment is made concerning the ability of various non-local 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 and against an entropy crisis in all systems studied to date must be re-evaluated.

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 $T_c$, but have not been useful in obtaining well equilibrated configurations significantly below this temperature. Other techniques, such as expanded ensemble methods, multi-canonical algorithms, and the density-of-states Monte Carlo approach 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
Conventional Monte Carlo techniques augmented with non-local 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 comprised of its neighbors) that would take many local Monte Carlo moves to achieve. Recently, two types of non-local Monte Carlo methods have been applied to the study of glassy systems: The cluster pivot algorithm (CPA) of Krauth and coworkers\textsuperscript{14} and the swap Monte Carlo (SMC) algorithm applied by Grigera and Parisi to the study of the entropy crisis\textsuperscript{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 only swapped 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, as 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 $\sigma_1/\sigma_2 = 1.2$, $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$ 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\textsuperscript{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 two dimensional hard-sphere system of Santen and Krauth\textsuperscript{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 $\Delta$. Isothermal compressibilities are calculated both by finite difference of the volume with respect to pressure, $\kappa_{\text{diff}} = -\frac{1}{\langle V \rangle} \frac{\partial \langle V \rangle}{\partial P}$, and by fluctuations of the volume, $\kappa_{\text{fluc}} = \frac{\langle V^2 \rangle - \langle V \rangle^2}{\langle V \rangle}$. If the system is well equilibrated and the data well averaged, $\kappa_{\text{diff}} = \kappa_{\text{fluc}}$. This provides a necessary (but not sufficient) test for equilibration that, together with convergence and stability of thermodynamic averages, is applied throughout. We also applied the Flyvberg-Petersen method\textsuperscript{29} to determine accurate estimates of the statistical error, which were well below 0.1% of the heat capacity, even at extremely low temperatures.

Lastly, a polydisperse soft-sphere system is studied with $\sigma_i = 1 + \Delta * i$ where $1 \leq i \leq N$ and $\Delta$ is chosen so that $R_{\text{max}} = 20$, 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 $\Gamma = \rho T - \frac{D}{12}$, where $D$ is the dimensionality of the system). Constant volume is chosen so that $\rho_{\text{poly}} = \frac{\frac{4}{3} \sum_{i=1}^{N} \pi r_i^3}{L^3} = 1$. For all of the systems, up to $1 \times 10^8$ steps of equilibration and $1 \times 10^9$ 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 coworkers\textsuperscript{5,6}. Harmonic solid entropies are calculated for $N$ particles in $D$ dimensions as

$$S_{\text{sol}}^{(a)} = \frac{N D}{2} \left(1 + \log \left(\frac{2\pi}{\beta}\right) - \left(\frac{1}{N_{\text{pos}}} \sum_{i=1}^{N_{\text{pos}}} \log(\lambda_i)\right)\right),$$

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

\[ S_{\text{liq}} = S_{\text{liq}}^0 + \beta E_{\text{liq}}(\beta) - \int_0^\beta d\beta' E_{\text{liq}}(\beta'), \]  

(4)

where \( S_{\text{liq}}^0 \) represents the ideal gas entropy in the \( \beta \to 0 \) limit and \( E_{\text{liq}}(\beta) \) is the average energy at inverse temperature \( \beta \). Liquid entropies are extrapolated into the glassy regime by fitting the data as \( S_{\text{liq}}(T) = aT^{-2/5} + b \), a well known fitting form for the entropy of simple liquid. Inherent structures, when needed, are found by steepest descent quenches for the binary soft-sphere system, and a combination of steepest descent and conjugate gradient for the polydisperse system. Data is 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 Sec. 2. 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 and the inherent structure-based method of Buchner and Heuer. The approach of Buchner and Heuer is similar to that of Sciortino, Kob and Tartaglia, 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 Sec. 2, we find \( \Gamma_K = 1.72 \) \( (\Gamma = \rho T^{-\frac{D}{H}}) \) while the method of Buchner and Heuer yields \( \Gamma_K = 1.69 \). A previous estimate using the random first order approach by Coluzzi et. al. 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. While for large system sizes they could not equilibrate the system at low temperatures (large \( \Gamma \)), 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 Fig. 1a. The agreement between the values of the specific heat calculated from fluctuations and derivatives of the average energy suggest that the equilibration of configurations has been achieved. In the inset of Fig. 1, we display an expanded view of the specific heat for the 34 particle system that includes higher
temperatures (lower $\Gamma$ values). A second interesting signature in the specific heat appears near $\Gamma = 1.25$. This signature becomes sharper for larger systems, as shown in Fig. 1B. The sharpness of this peak, together with its system-size dependence, strongly support the view that this feature is thermodynamic in nature. It is interesting to note that $\Gamma = 1.25$ is close to the onset of supercooling at $\Gamma_0 \approx 1.335$. 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.

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 Fig. 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 $\Gamma$, 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 $\Gamma_c$, the location of the mode-coupling temperature (density)$^{36}$. In Fig. 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 by direct differentiation of the average energy diverge from each other 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 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) vanish, 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 \( \Gamma_c \approx 1.7 \) coincides with the gap between defective crystal
states and the ground state is purely accidental. Furthermore, we find that, while SMC
is more efficient than methods like 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 re-investigate the completely polydisperse two dimensional
hard-sphere system studied by Santen and Krauth\textsuperscript{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 two dimensional hard-sphere
system via the SSMC approach. In Fig. 4 we show \( \kappa^{-1} \) vs. \( \rho \) 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, as the SSMC approach works in arbitrary
dimensions, while 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 accurately yield relaxation times in two dimensional systems\textsuperscript{38} and meaningful
quantities in the \( \alpha \)-relaxation regime\textsuperscript{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 $\rho_K$ in the system of Santen and Krauth by noting that a conservative guess for the ratio of mode-coupling to Kauzmann densities from the $\rho T^{-\frac{2}{3}}$ dependence in an “equivalent” soft-sphere system would imply that $\rho_K$ is about 10 percent larger than $\rho_c$. While this estimate is crude, it implies that 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 further explore the properties of this two dimensional hard-sphere system, we address the nature of the phase space available to the smaller discs. While, at the highest densities 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 Fig. 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 due to 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. 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 an 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.

Since the system studied by Santen and Krauth is both athermal and two dimensional, we have also studied a three dimensional soft-sphere version of this system. In Fig. 6 we show the specific heat of a small ($N=34$) version of the polydisperse three dimensional soft-sphere system discussed in the introduction. Interestingly, while the data shows that the heat capacity calculated via fluctuations and by 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 close inspection of instantaneous and inherent structures make it clear that particles of similar size have bunched together. In Fig. 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 three dimensional 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 non-local Monte Carlo methods provide equilibrated results is not broad enough to investigate deeply glassy states, while 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, two dimensional 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 non-local 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 two dimensional 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, since 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 non-local moves still cannot equilibrate systems under conditions where the number
of available configurations become sparse. Interestingly, while the Monte Carlo methods investigated here greatly increase the rate of equilibration for temperatures (densities) near $T_c$ ($\rho_c$) 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.

While 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 non-local Monte Carlo studies on small systems whose potentials are tailored to strongly penalize structures with intermediate and long range order\textsuperscript{41}. It would also be interesting to re-investigate larger versions of the systems studied here with the more powerful Wang-Landau approach\textsuperscript{24,26}. We are currently pursuing these directions.

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Figure Captions

Fig. 1: (a) The heat capacity per particle for a 34 particle binary soft-sphere system. The inset extends this calculation to higher temperatures (lower $\Gamma$), where a second smaller peak is evident. $C_V$ as calculated by fluctuations is plotted as (x) and finite difference as (*), a convention which is maintained throughout the paper. Swap moves were attempted on average every ten moves, and data was collected for between $1 \times 10^7$ and $1 \times 10^9$ steps, with longer runs for lower temperatures. (b) The heat capacity per particle for the same system and computational details as in part (a), but with 60 particles. The heat capacity as calculated by fluctuations and derivatives is shown. The 34 particle peak is included (solid line) to facilitate direct comparison.

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

Fig. 3: The 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 ten moves, and data was collected for between $1 \times 10^8$ and $1 \times 10^9$ steps.

Fig. 4: The converged inverse isothermal compressibility $\kappa^{-1}$ vs. $\rho$ for the polydisperse hard-sphere system of Santen and Krauth. The system was equilibrated by SSMC. Swap moves were attempted on average every ten moves and data was collected for $1 \times 10^9$ steps, though such a long run was only necessary for extremely high pressures.

Fig. 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 is taken at $P = 0.09$, which corresponds to $\rho \approx 0.861$.

Fig. 6: The heat capacity per particle for a 34 particle polydisperse soft-sphere system. The peak arises due to a phase separation process that induces intermediate range order in the system. Swap moves are attempted on average every ten steps and data was collected for $1 \times 10^7$ to $6 \times 10^8$ steps.

Fig. 7: An 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 inside (not behind) the large cluster. Similar clustering and the beginnings of phase separation can be found in all low temperature structures of this system.
Fig. 1a

A graph showing the relationship between $C/N$ and $\Gamma$. The graph includes an inset with a more detailed view of the data points.
Fig. 2

(a) (b)
Fig. 3

The graph shows the relationship between $C_V/N$ and $\Gamma$. The data points are plotted as crosses and stars. The $x$-axis represents $\Gamma$ ranging from 1 to 1.8, while the $y$-axis represents $C_V/N$ ranging from 0 to 4.
Fig. 4

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4}
\end{figure}
\begin{align*}
\langle (r(t) - r(0))^2 \rangle &= 1.149 \\
r_i &= 1.5216 \\
r_i &= 19.776 \\
r_i &= 19.851
\end{align*}
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