Efficient Monte Carlo simulation of a glass forming binary mixture

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We propose and use a novel, hybrid Monte Carlo algorithm that combines configurational bias particle swaps with parallel tempering. We use this new method to simulate a standard model of a glass forming binary mixture above and below the so-called mode-coupling temperature, $T_{MCT}$. We find that an ansatz that was used previously to extrapolate thermodynamic quantities to temperatures below $T_{MCT}$ breaks down in the vicinity of the mode-coupling temperature. Thus, previous estimates of the so-called Kauzmann temperature need to be reexamined. Also, we find that the Adam-Gibbs relations $D \propto \exp(-a/T S_c)$ and $\tau \propto \exp(b/T S_c)$, which connect the diffusion coefficient $D$ and the relaxation time $\tau$ with the configurational entropy $S_c$, are valid for all temperatures for which the configurational and vibrational contributions to the free energy decouple.

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Understanding the nature of the glass transition has been of great interest for several decades. One of the earliest paradigms [1, 2], that has recently been reformulated [3] and subsequently received considerable attention, assumes the existence of an “ideal” glass transition which occurs when the entropy of the supercooled liquid becomes equal to the entropy of a disordered solid. This paradigm has stimulated several simulational studies [4, 5] which have confirmed both the qualitative description of supercooled liquids’ dynamics and even the quantitative, numerical prediction of the transition temperature, the so-called Kauzmann temperature $T_K$, for a popular model of a glass forming binary mixture. However, these simulational investigations were restricted to temperatures above the so-called mode-coupling temperature, $T_{MCT}$. Thus, in these previous studies, in order to investigate the equality of the liquid and disordered solid entropies, one had to extrapolate higher temperature data obtained directly from simulations to significantly lower temperatures (for example, for the binary mixture studied in Refs. [1, 2] it was found that $T_{MCT}/T_K \approx 1.45$). The commonly used extrapolations were questioned in a recent investigation of the configurational entropy [6]. This study is unique in that it accessed directly the low temperature region below $T_{MCT}$.

It showed that the commonly used extrapolations break down below $T_{MCT}$ and the existence of the Kauzmann temperature was put in doubt. Reference [6] used a novel density-of-states Monte Carlo method. Also, it used a binary mixture model that was somewhat different [7] than the model used in most of the previous simulations. Finally, although several system sizes were considered in Ref. [6], the largest system (216 particles) was significantly smaller than systems used in previous studies (the largest ones had 1000 particles).

The goal of our investigation was to address the question of the existence of the Kauzmann temperature for the original model studied in Refs. [1, 2]. Since the long relaxation times below $T_{MCT}$ makes equilibration of molecular and Brownian dynamics simulations very difficult, we propose and use a novel, specialized Monte Carlo algorithm designed to decrease the time between independent measurements of strongly supercooled liquids. This new method allows us to obtain accurate thermodynamic quantities for temperatures below the mode-coupling temperature. We find that the previously used extrapolations of thermodynamic quantities to estimate the Kauzmann temperature break down in the vicinity of the mode-coupling temperature. Furthermore, by using the results of Brownian dynamics simulations, we demonstrate that the Adam-Gibbs relations [2] are valid for low temperatures. We propose using the Adam-Gibbs relation and the results of the Monte Carlo simulation to predict the diffusion coefficient.

To directly access temperatures below the mode-coupling temperature, we combined non-local trial moves with parallel tempering. Non-local trial moves, identity exchanges, have been effective in speeding up simulations with different size particles [8, 9]. However, high density and large size disparity drastically reduce the acceptance rate of identity exchanges [8], which decreases their usefulness in dense glass forming liquids at low temperatures. To overcome this, we used parallel tempering, which attempts to exchange replicas of the system which are being simulated at different temperatures. This allows configurations which are trapped in a deep potential energy minimum at low temperatures to change considerably by being simulated at higher temperatures. A variation of this technique, which combines replica exchange with molecular dynamics, has been shown to speed up the equilibration of the system studied in this work [10].

We simulated an 80:20 binary mixture introduced by W. Kob and H. Andersen [11]. The interaction potential is $V_{\alpha \beta}(r_{ij}) = 4\epsilon_{\alpha \beta}[(\sigma_{\alpha \beta}/r_{ij})^{12} - (\sigma_{\alpha \beta}/r_{ij})^{6}]$ where $\alpha, \beta \in \{A, B\}$, $\epsilon_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\epsilon_{BB} = 0.5$, $\sigma_{AA} = 1.0$, $\sigma_{AB} = 0.8$, and $\sigma_{BB} = 0.88$. The results are presented in reduced units with $\epsilon_{AA}$ and $\sigma_{AA}$ being the units of energy and length, respectively. We simu-
lated 1000 particles in a fixed cubic box with a box length of 9.4. We performed a parallel tempering Monte Carlo simulation and a series of Brownian dynamics simulations. The Monte Carlo simulation was performed using the following set of temperatures, \( T = 0.62, 0.59, 0.56, 0.53, 0.50, 0.48, 0.46, 0.44, 0.43, 0.42, 0.41, \) and 0.40. The Brownian dynamics simulations were performed at \( T = 5.0, 3.0, 2.0, 1.5, 1.0, 0.9, 0.8, 0.6, 0.55, 0.5, 0.47, 0.45, \) and 0.44.

The details and results of the Brownian dynamics simulation have been presented elsewhere. Here we briefly describe the Monte Carlo simulation. We utilize three trial moves: a standard, local single particle displacement, a configurational bias particle swap, and parallel tempering. The configuration bias particle exchange attempts to swap two particles of different sizes. The smaller particle will always fit in the space left by the larger particle, but, since the density is high, the converse is rarely true. To increase the acceptance rate, 50 trial configurations are explored for the larger particle around the former position of the smaller particle. One of the trial positions is chosen with a probability which depends on the potential energy, and the move is accepted with a probability so that detailed balance is maintained.

The configurational bias increases the acceptance rate, but the acceptance rate for the particle swaps is still very small, around 10^{-8} at \( T = 0.5 \), which is the lowest temperature in which the swaps were attempted. It has been shown that identity exchange can decrease the equilibration time of a simulation dramatically even if the acceptance rate is very small. Parallel tempering consists of an attempted exchange of particle positions between adjacent temperatures. Thus, the configurational bias particle swaps can decrease the correlation time for the configurations which begin the simulation at the temperatures in which the swaps are not attempted.

To estimate the efficiency of our algorithm, we compared the energy correlation time measured in Monte Carlo moves per particle with the energy correlation time in the Brownian Dynamics simulation measured in Brownian Dynamics time steps. We found that the former time increases slower with decreasing temperature than the latter time. The energy correlation time for the Monte Carlo simulation at \( T = 0.4 \) corresponds to generating one statistically independent configuration approximately every five days for a parallel algorithm using four threads on a hyperthreaded dual-processor 3.2 GHz Pentium workstation.

We used a variety of different checks for equilibration: monitoring the running average of the potential energy \( U(N) = \left< U \right>_N \), where \( U_i \) is the potential energy for step \( i \) (\( U(N) \) does not show any systematic drift), comparing specific heat calculated using the derivative of the energy and energy fluctuations (they agree, see Fig. 2), comparing the temperature assumed in the simulation algorithm with the so-called configurational temperature (they agree), etc.

Here we discuss in some detail a stringent equilibration test introduced by Yamamoto and Kob. This so-called re-weighting procedure relies upon the fact that an equilibrium distribution of the energy for a temperature \( T_1 \) can be determined from an equilibrated simulation at a different temperature \( T_0 \). Shown in Fig. 1a and Fig. 1b are the re-weighted probability distributions of the potential energy for \( T = 0.44 \) and 0.5, respectively. The filled circles in the figures are the probability distributions calculated from simulation runs at \( T = 0.44 \) and 0.5, respectively. The other symbols are the re-weighted probability distributions, and the solid lines are Gaussian distributions determined from the average energies and the specific heats calculated at the respective temperatures. Note that there is a slight systematic deviation from a Gaussian distribution at the lowest temperatures. This deviation is within the uncertainty of the calculation, thus it is not clear whether it has any significance. In any case, it should be noted that the re-weighted probability distributions still superimpose very well. Thus, at all temperatures there is good overlap between the re-weighted distributions and this fact provides strong evidence that the Monte Carlo simulation has properly equilibrated.

The specific heat calculated from energy fluctuations and from the derivative of the energy determined from the Brownian dynamics and the Monte Carlo simulation is shown in Fig. 2. Note that a correction due to the finite simulation time \( T_0 \) has been applied to the specific heat calculated from the energy fluctuations. The agreement between the Monte Carlo, the Brownian dynamics, and the two methods of calculating the specific heat is very good except for the derivative of the energy for the Brownian dynamics simulation at the lowest temperature. There is a peak in the specific heat around \( T \approx 0.45 \), which is close to the usually cited

![Figure 1](image-url)
The mode-coupling temperature $T_{MCT} \approx 0.435$ determined from fits to the diffusion coefficient and the relaxation time. It is clear from Fig. 2 that the extrapolation that was used in prior studies is violated below the mode-coupling temperature. A similar violation was observed in a recent investigation of a different binary mixture. Recall that the former studies only simulated systems at temperatures higher than $T_{MCT}$, whereas the latter one was able to access temperatures below $T_{MCT}$.

In Fig. 3 we show the total liquid entropy, $S$, and the so-called disordered solid entropy, $S_{vib}$. To find the total entropy $S$ we performed a standard thermodynamic integration along the $T = 5.0$ isotherm and then along the $V_0 = (9.4)^3$ isochore. For $T \geq 0.62$ we utilized a commonly used fit for the specific heat shown as a solid line in Fig. 2. For $T < 0.62$ we numerically integrated the specific heat. The results of the numerical integration are shown as triangles in Fig. 3a. The solid line going through the circles for $T > 0.45$ and slightly deviating from them for $T < 0.45$ is the standard extrapolation that relies on using the fit shown as a solid line in Fig. 2 for all temperatures.

To evaluate the disordered solid entropy we followed the procedure used in previous studies. First, we determined the inherent structures by quenching 500-1000 configurations. Then we checked that for $T \leq 0.62$ the system can be described by a configurational and a vibrational part. We calculated the entropy of the disordered harmonic solid by diagonalizing the Hessian matrix calculated at the inherent structures and determined the vibrational frequencies $\omega_i$. Next, we calculated the vibrational contribution to the entropy $S_{vib} = \left\langle \sum_{i=1}^{3N-3} \left[ 1 - \ln(\beta \omega_i) \right] \right\rangle'$ where $\cdot ' \cdot$ denotes an average over the inherent structures (note that throughout this paper we set Planck’s constant equal to one). The results are shown as circles and squares in Fig. 3a. The solid line going through the circles and squares is obtained by fitting $\left\langle \sum_{i=1}^{3N-3} \ln(\omega_i) \right\rangle'$ to a polynomial in $T$ of degree 2. This quantity, which is the contribution to $S_{vib}$ that originates from the the vibrational frequencies, is almost temperature-independent.

In Fig. 3b, we show the configurational entropy $S_c = S - S_{vib}$. Note that $S_c$ was only calculated for temperatures for which the system can be divided into a configurational and a vibrational part. We used the extrapolation results in the Kauzmann temperature $T_K = 0.29$, which is very close to previous estimates. Note that below the mode-coupling temperature our results deviate from this extrapolation. Thus, the previous estimates of the Kauzmann temperature have
to be reexamined. The peak in the specific heat indicates that the total entropy is larger than the previous estimate, and that the Kauzmann temperature, if it exists at all, is lower. Our results are consistent with those obtained in Ref. \[2\] for a different binary mixture.

We examined the Adam-Gibbs relations $D \propto \exp(-a/TS_c)$ and $\tau \propto \exp(b/TS_c)$ [1]. Shown in Fig. 4 are the logarithms of the diffusion coefficients and the relaxation times (the relaxation times are obtained from the self-intermediate scattering function in the usual way [11, 12]) plotted as a function of $1/TS_c$ for $T \leq 0.6$. The diffusion coefficients and the relaxation times are determined from the Brownian dynamics simulations. The configurational entropy is determined from the Monte Carlo simulation and the Brownian dynamics simulations. Although some curvature can be seen in the relaxation time data, the fits are very good and verify the Adams-Gibbs relation for this temperature range. Assuming that the Adam-Gibbs relation holds at lower temperatures, we can predict the diffusion coefficient down to $T = 0.4$ from the results of the Monte Carlo simulation; see the inset in Fig. 4.

In summary, we propose and use a novel, hybrid Monte Carlo algorithm which allows accurate calculation of equilibrium quantities below the mode-coupling temperature. Our method combines non-local configuration bias particle swaps and parallel tempering. The results obtained with this algorithm put in doubt the commonly used extrapolation of the supercooled liquid entropy and previous estimates of the Kauzmann temperature. Moreover, we show that the Adam-Gibbs relations $D \propto \exp(-a/TS_c)$ and $\tau \propto \exp(b/TS_c)$ hold for all temperatures for which the configurational and vibrational contributions to the free energy decouple.

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