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Hybrid Monte Carlo simulation of a glass-forming binary mixture

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We propose a different, hybrid Monte Carlo algorithm that combines configurational bias particle swaps with parallel tempering. We use this algorithm 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. We also find that the Adam-Gibbs relations $D \propto \exp(-a/TS_c)$ and $\tau \propto \exp(b/TS_c)$, which connect the diffusion coefficient D and the relaxation time τ 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] assume the existence of an “ideal” glass transition which occurs at a temperature T_K when the entropy of the supercooled liquid becomes equal to the entropy of the disordered solid [3]. This paradigm has recently been reformulated [4], and has stimulated several simulational studies [5,6]. However, these simulational investigations were restricted to temperatures above the so-called mode-coupling temperature $T_{MCT} > T_K$. Thus, 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. [5,6] it was found that $T_{MCT}/T_K \approx 1.45$. The commonly used extrapolations of the configurational entropy were questioned in a recent investigation [7], which is unique in that it accessed directly the low temperature region below T_{MCT}. It showed that these extrapolations break down below T_{MCT} and the existence of the Kauzmann temperature was put in doubt. Reference [7] used a novel density-of-states Monte Carlo method to simulate a model of a binary mixture that was somewhat different [8] than the model used in most of the previous simulations. Moreover, although several system sizes were considered in Ref. [7], the largest system was significantly smaller than systems used in previous studies.

The goal of our investigation was to examine the validity of the commonly used extrapolation procedure for the original model studied in Refs. [5,6] and to address the question of the existence of the Kauzmann temperature. Since the long relaxation times below T_{MCT} make the equilibration of molecular and Brownian dynamics simulations very difficult, we use a specialized Monte Carlo algorithm designed to decrease the time needed to generate independent configurations. This method allows us to obtain accurate thermodynamic quantities for temperatures below the mode-coupling temperature. We find that the extrapolations of thermodynamic quantities, which were previously used to estimate the Kauzmann temperature, break down in the vicinity of T_{MCT}. 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 at temperatures in which it is not possible to equilibrate the Brownian dynamics simulations.

We simulated an 80:20 binary mixture introduced by Kob and Andersen [9]. 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 ϵ_{AA} and σ_{AA} being the units of energy and length, respectively. We simulated 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 [10,11]. Here we briefly describe the Monte Carlo simulation. We utilize three trial moves: a standard, local single particle displacement, a configurational bias particle exchange, 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 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 [12,13]. The configurational bias increases the acceptance rate, but the acceptance rate for the particle swaps is still small. At the lowest temperature in which the identity exchanges were attempted, $T=0.50$, about four identity exchanges were accepted every 10^5 attempts per particle. At $T=0.62$, about one identity exchange was accepted every 10^3 attempts per particle. These acceptance rates are small, but it has been shown that identity exchange can decrease the

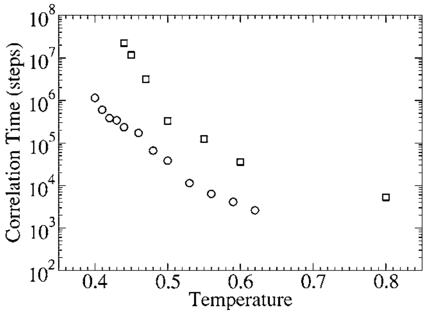

FIG. 1. The energy correlation time. The open circles are the results of the Monte Carlo simulation described in this paper. The squares are the results of Brownian dynamic situations [10,11].

equilibration time of a simulation dramatically [12,14] even if the acceptance rate is small. Parallel tempering consists of an attempted exchange of particle positions between adjacent temperatures [13]. Without parallel tempering, the configurations which begin the simulation below $T=0.50$ would not benefit from the configurational bias particle exchange. With parallel tempering, the particle exchange can decrease the number of Monte Carlo moves needed to produce effectively independent configurations for all temperatures.

In Fig. 1 we compare the energy correlation times of the Monte Carlo simulation and the Brownian dynamics simulations. The former is measured in Monte Carlo moves per particle and the latter in Brownian dynamics time steps (note that each time step advances the positions of all of the particles). We found that the former time increases slower with decreasing temperature. At $T=0.60$ the Monte Carlo is approximately 9 times more efficient, but at $T=0.44$, it is around 95 times more efficient. In real time, the entire Monte Carlo simulation $(0.40 \leq T \leq 0.62)$ was about 25% shorter than the Brownian dynamics simulation at the two lowest temperatures, 0.45 and 0.44.

We used a variety of different checks for equilibration: monitoring the running average of the potential energy $U(N)=(1/N)\Sigma_{i=1}^{N} U_i$, 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. 3), comparing the temperature assumed in the simulation algorithm with the so-called configurational temperature [15] (they agree), etc. [16]. Here we discuss in some detail a stringent equilibration test introduced by Yamamoto and Kob [17]. This so-called reweighting procedure relies upon the fact that an equilibrium distribution of the energy for a temperature T can be determined from an equilibrated simulation at a different temperature T'. Shown in Figs. 2(a) and 2(b) are the reweighted 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 open symbols are the reweighted 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. However, the reweighted probability distributions still superimpose very well. Thus, at all temperatures there is good overlap between the reweighted distributions and this fact provides strong evidence that the Monte Carlo simulation has properly equilibrated.

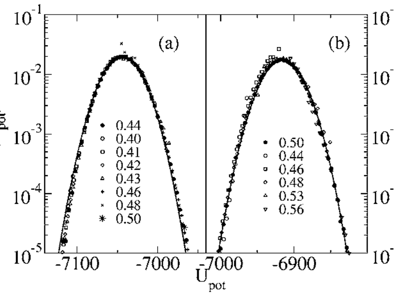

FIG. 2. The reweighted potential energy probability distributions. The solid line is a Gaussian distribution $\sqrt{1/[2\pi k_B C_{V,pot}(T)T^2]}\exp[-(U_{pot}-\langle U_{pot}\rangle)^2/(2k_B C_{V,pot}(T)T^2)]$ for $T=0.44$ and $T=0.50$.

To examine the previously employed procedures, we used the results from the Monte Carlo and the Brownian dynamics simulations for temperatures above $T_{MCT}=0.435$ and extrapolated these high temperature results to temperatures below T_{MCT}. To perform the extrapolation, we followed the same procedure as previous authors and assumed that the temperature dependence of the energy is given by $E(T)=aT^{3/5}+b$ [18]. The extrapolations are shown as solid lines in Figs. 3 and 4. Our main finding is that a comparison of these extrapolations with the results obtained directly from the Monte Carlo simulation for temperatures below T_{MCT} shows that the extrapolations are not valid below T_{MCT}.

In Fig. 3 we show the specific heat calculated from energy fluctuations and from the derivative of the energy. Results from both the Brownian dynamics and the Monte Carlo

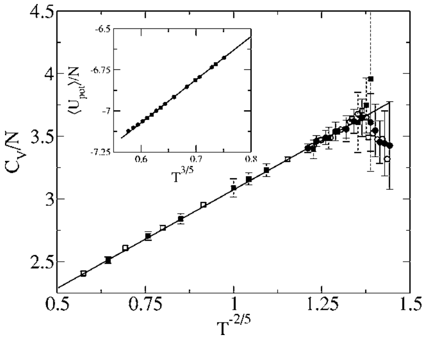

FIG. 3. The specific heat per particle as a function of $T^{-2/5}$ calculated from energy fluctuations (closed symbols) and the derivative of the energy (open symbols) for the Brownian dynamics (squares) and the Monte Carlo (circles). The solid line is $C_V/N=0.6aT^{-2/5}+1.5$, where a was obtained from fitting the average potential energy $\langle U_{pot}\rangle$ to a function of the form $aT^{3/5}+b$ (the a and b parameters obtained from the fit are $a=2.6362$ and $b=-8.6547$). Inset: the average potential energy per particle as a function of $T^{3/5}$; the solid line is the $aT^{3/5}+b$ fit.

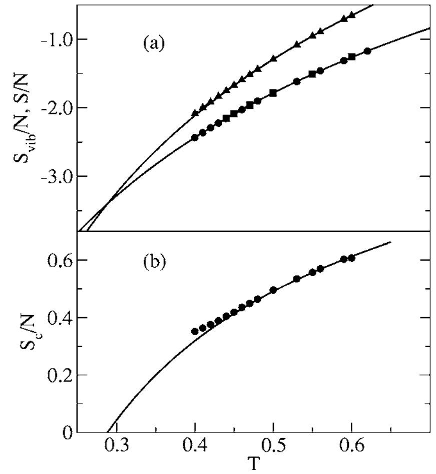

FIG. 4. (a) The total entropy per particle S/N (triangles) and the disordered solid entropy per particle S_{vib}/N. The latter entropy has been calculated using the inherent structures obtained from the Monte Carlo (circles) and the Brownian dynamics (squares) simulations. The solid lines are the commonly used extrapolations described in the text. (b) The configurational entropy per particle, $S_c/N=S/N-S_{vib}/N$. The solid line is the extrapolation obtained from the difference of the extrapolations shown in (a). The error bars for S/N, S_{vib}/N, and S_c/N are smaller than the size of the symbols.

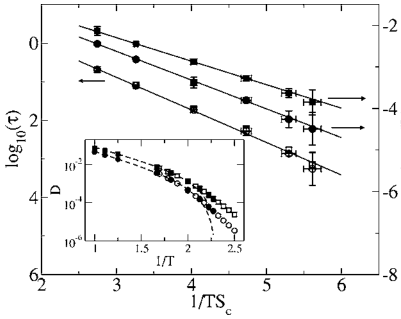

FIG. 5. Test of the Adam-Gibbs relations $D \propto \exp(-a/TS_c)$ (solid symbols and right vertical axis) and $\tau \propto \exp(b/TS_c)$ (open symbols and left vertical axis) for the A (circles) and the B particles (squares). Inset: The diffusion coefficient determined directly from the Brownian dynamics simulations (closed symbols) and predicted using the Adam-Gibbs relation (open symbols) for the A (circles) and B particles (squares). The Adam-Gibbs prediction uses S_c determined from the Monte Carlo simulations. The dashed curves are mode-coupling theory power law fits $a(T-0.435)^{\gamma}$ over the temperature range $0.5 \leq T \leq 0.8$.

simulation are shown. Note that a correction due to the finite simulation time [19–21] 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 Brownian dynamics simulation for $T<0.45$. However, the specific heat is still within the statistical uncertainty of the calculation. There is a peak in the specific heat around $T \approx 0.45$, which is close to the usually cited mode-coupling temperature $T_{MCT} \approx 0.435$ [9]. It is clear from Fig. 3 that the extrapolation that was used in prior studies [5,6] is violated below the mode-coupling temperature. A similar violation was observed in a recent investigation of a different binary mixture [7]. 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. 4(a) we show the total liquid entropy and the disordered solid entropy. To find the total entropy S we performed a thermodynamic integration along the $T=5.0$ isotherm and then along the $V_0=(9.4)$ (Ref. [4]) isochore. For $T \geq 0.62$ we utilized a commonly used fit for the specific heat shown as a solid line in Fig. 3. For $T<0.62$ we numerically integrated the specific heat. The results of the numerical integration are shown as triangles in Fig. 4(a). The solid line going through the triangles for $T>0.45$ and slightly deviating from them for $T<0.45$ is the standard extrapolation [5,6] that relies on using the fit shown as a solid line in Fig. 3 for *all* temperatures.

To evaluate the disordered solid entropy S_{vib} we followed the procedure used in previous studies [5,22–26]. First, we determined the inherent structures by quenching 500–1000 configurations at each temperature. Then we checked that for $T \leq 0.62$ the system can be described by a configurational and a vibrational part [5]. Next, we diagonalized the Hessian matrix calculated at the inherent structures, determined the vibrational frequencies ω_i, and calculated the vibrational contribution to the entropy $S_{vib}=\langle \sum_{i=1}^{3N-3}[1-\ln(\beta\hbar\omega_i)]\rangle'$ where $\langle\,\rangle'$ denotes an average over the inherent structures (note that Planck's constant has been set equal to 1). The results are shown as circles and squares in Fig. 4(a). The solid line going through the circles and squares is obtained by fitting $\langle \sum_{i=1}^{3N-3}[\ln(\omega_i)]\rangle'$ to a polynomial in T of degree 2. This quantity, which is the contribution to S_{vib} that originates from the vibrational frequencies, is almost temperature independent.

In Fig. 4(b) we show the configurational entropy $S_c=S-S_{vib}$. Note that S_c was only calculated at temperatures for which the system can be divided into a configurational and a vibrational part, i.e., for $T \leq 0.62$. In Fig. 4(b) we also compare our results (symbols) with the previously used extrapolation (solid line) of the configurational entropy. This extrapolation results in the Kauzmann temperature $T_K=0.29$, which is very close to previous estimates of $T_K=0.297 \pm 0.02$ [5], and $T_K \approx 0.28$ [6]. Our main result is that below T_{MCT} the commonly used extrapolation fails. 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. [7] for a different binary mixture.

We examined the Adam-Gibbs relations $D \propto \exp(-a/TS_c)$ and $\tau \propto \exp(b/TS_c)$ [2]. Shown in Fig. 5 are the logarithms of the diffusion coefficients D and the relaxation times τ [27] obtained from the Brownian dynamics simulations plotted as a function of $1/TS_c$ for $0.44 \leq T \leq 0.6$. Although some curvatures 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. 5.

In summary, we propose and use a different Monte Carlo algorithm which allows accurate calculation of equilibrium quantities below the mode-coupling temperature. Our method combines nonlocal configuration bias particle swaps and parallel tempering. The results obtained with this algorithm show that the commonly used extrapolation of the supercooled liquid entropy fails and puts in doubt previous estimates of the Kauzmann temperature. Moreover, we show that the Adam-Gibbs relations hold at all temperatures for which the configurational and vibrational contributions to the free energy decouple.

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