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<td>Author(s)</td>
<td>Yamamoto, R; Kob, W</td>
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<tr>
<td>Citation</td>
<td>PHYSICAL REVIEW E (2000), 61(5): 5473-5476</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2000-05</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/50116">http://hdl.handle.net/2433/50116</a></td>
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<tr>
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<tr>
<td>Type</td>
<td>Journal Article</td>
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<td>Textversion</td>
<td>publisher</td>
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Kyoto University
Replica-exchange molecular dynamics simulation for supercooled liquids

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(Received 4 January 2000)

We investigate to what extent the replica-exchange Monte Carlo method is able to equilibrate a simple liquid in its supercooled state. We find that this method does indeed allow us to generate accurately the canonical distribution function even at low temperatures and that its efficiency is about 10–100 times higher than the usual canonical molecular dynamics simulation.

PACS number(s): 65.20.+w, 61.43.Fs, 02.70.Lq, 02.70.Ns

If a liquid is cooled to a temperature close to its glass transition temperature, its dynamical properties show a drastic slowing down. At the same time, a crossover from highly unharmonic liquidlike behavior to harmonic solidlike behavior is expected in its static (thermodynamic) properties at a certain temperature $T_K$, the Kauzmann temperature [1]. Very recently the value of $T_K$ of simple model liquids have been determined analytically [2] and numerically [3,4] and some possibilities of a thermodynamic glass transition at $T_K$ have been discussed. Although the values of $T_K$ obtained with the different methods are consistent with each other, it was necessary for the numerical calculations of $T_K$ to extrapolate high-temperature data ($T \approx 0.45$) of the liquid and disordered solid branches of the configurational entropy $S(T)$ down to significantly lower temperatures ($T_K=0.3$).

We construct a system consisting of $M$ noninteracting subsystems (replicas), each composed of $N$ particles, with a set of arbitrary particle configurations $\{q_1, \ldots, q_M\}$ and momenta $\{p_1, \ldots, p_M\}$. The Hamiltonian of the $m$th subsystem is given by

$$H_m(p_m, q_m) = K(p_m) + \Lambda_m E(q_m),$$

where $K$ is the kinetic energy, $E$ is the potential energy, and $\Lambda_m \in \{\lambda_1, \ldots, \lambda_M\}$ is a parameter to scale the potential. (ii) A MD simulation is done for the total system, whose Hamiltonian is given by $\mathcal{H} = \sum_{m=1}^{M} H_m$, at a constant temperature $T = \beta_0^{-1}$ using the constraint method [20]. Step (ii) generates a canonical distribution $P(q_1, \ldots, q_M, \beta_0) = \Pi_{m=1}^{M} P(q_m : \Lambda_m \beta_0) \propto \exp[-\beta_0 \sum_{m=1}^{M} \Lambda_m E(q_m)]$ in configuration space [21]. (iii) At each time interval $\Delta t_{RX}$, the exchange of the potential scaling parameter of the $m$th and $n$th subsystem are considered, while $\{q_1, \ldots, q_M\}$ and $\{p_1, \ldots, p_M\}$ are unchanged. The acceptance of the exchange is decided in such a way that it takes care of the condition of detailed balance. Here we use the Metropolis scheme, and thus the acceptance ratio is given by

$$w_{m,n} = \begin{cases} 1, & \Delta_{m,n} = 0 \\ \exp(-\Delta_{m,n}), & \Delta_{m,n} > 0 \end{cases}$$

where $\Delta_{m,n} = \beta_0 (\Lambda_n - \Lambda_m) [E(q_m) - E(q_n)]$. (iv) Repeat steps (ii) and (iii) for a sufficiently long time. This scheme leads to canonical distribution functions $P(E; \beta_i)$ at a set of inverse temperatures $\beta_i = \lambda_i \beta_0$. To make a measurement at an inverse temperature $\beta_i$ one has to average over all those subsystems ($i \in [1, \ldots, M]$) for which we have (temporarily) $\beta_i = \lambda_i \beta_0$. Usually canonical molecular dynamics (CMD) simulations are realized if we skip step (iii).

In the present simulation, we take $M = 16$, $\beta_0 = 0.45^{-1}$, $\lambda_i = 1-0.0367(i-1)$, and thus cover a temperature range $0.45T \leq T \leq 1$. Exchange events are examined only between subsystems that have scaling parameters $\lambda_i$ and $\lambda_{i+1}$ that are nearest neighbors; the events with $i=1,3,5,\ldots$ or $i=2,4,6,\ldots$ are repeated alternatively every $\Delta t_{RX}$ intervals. We find that the highest average acceptance ratio for this
between be made more similar by optimizing the different gaps be-

to the temperature variation in the RXMD method, the sys-

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FIG. 1. (a) Typical walks of the subsystems in temperature space. (b) Time dependence of the mean squared displacement. The solid line shows \( \Delta R^2(t) \) for \( A \) component from RXMD for a subsystem which at \( t=0 \) was at \( T=0.45 \) \((m=1)\), and the dashed line is \( \Delta R^2(t) \) from CMD at \( T=0.45 \). The two curves have been calculated by starting from the same initial configuration.

type of move is 0.186 for the exchange of \( \lambda_1 \) and \( \lambda_2 \), and

FIG. 2. The canonical distribution function \( P_i(E) \) at various
temperatures \( T_i \) \((1 \leq i \leq 16)\) obtained by a single RXMD simulation. Here \( T_1 = 0.45 \) and \( T_{16} = 1.0 \).

\[
\Delta R^2(t) = \frac{1}{N} \left[ q_m(t) - q_m(0) \right]^2
\]  

\[
\frac{dE}{N} \int dE' P_i(E') \exp \left[ (\lambda_i - \lambda_j) \beta_0 E' \right]
\]  

obtained by a single RXMD simulation. For adjacent

\[
P_i(E; \lambda_i, \beta_0) = P(E; \lambda_i, \beta_0)
\]  

for the RXMD \((m=1)\) and for the CMD performed at

\[
\lambda_i, \beta_0 \text{ obtained from RXMD}
\]  

\[
\lambda_i, \beta_0 \text{ obtained from RXMD}
\]  

\[
\exp \left[ (\lambda_i - \lambda_j) \beta_0 E' \right]
\]  

at a new temperature \( T_i = (\lambda_i \beta_0)^{-1} \) from any \( P_i(E) \). Note

\[
\frac{P_i(E) \exp \left[ (\lambda_i - \lambda_j) \beta_0 E \right]}{\int dE' P_i(E') \exp \left[ (\lambda_i - \lambda_j) \beta_0 E' \right]}
\]  

that in equilibrium the left-hand side should be independent

In Fig. 3 we plot different \( P_i(E; \lambda_i, \beta_0) \), using as input the
distributions \( P(E; \lambda_i, \beta_0) \) for \( 1 \leq i \leq 8 \), obtained from RXMD
(a) and CMD (b) simulations. (Both simulations extended
over 8.7 \times 10^4 \text{ time units.}) We see that in the case of the
RXMD the different distributions \( P_i \) fall nicely on top of
each other in the whole energy range, thus giving evidence
that the system is indeed in equilibrium. In contrast to this,
the different distributions of the CMD, Fig. 3(b), do not superimpose at low energies (or at low temperatures), thus demonstrating the lack of equilibration. This can be seen more clearly by comparing Figs. 3(c) and 3(d), where $P_i(E;\lambda_i\beta_0)$ is plotted.

Figure 4 shows the temperature dependence of the potential energy $E(T)$ obtained from RXMD simulations via

$$E(T) = \int dE' P(E';\lambda_i\beta_0) E'. \quad (6)$$

For the sake of comparison we have also included in this plot data from CMD with the same length of the production run as well as data from CMD simulations which were significantly longer (about one order of magnitude) [3]. The solid line is a fit to the RXMD results with the function $E(T) = E_0 + AT^{0.6}$, a functional form suggested by analytical calculations [5]. One can see that RXMD and CMD results coincide at higher temperatures, but deviations become significant at low temperatures (see the Inset in Fig. 4). Furthermore, we see that the present RXMD results agree well with the CMD data of the longer simulations.

As a final check to see whether the RXMD is indeed able to equilibrate the system also at low temperatures, we have

FIG. 3. The canonical distribution function at $T = (\lambda_4\beta_0)^{-1} = 0.506$ by reweighting $P_i(E)$ for $1 \leq i \leq 8$ obtained by RXMD (a) and standard CMD (b) simulations. The numbers in parentheses present temperatures at which simulations were done. The same function at $T = (\lambda_4\beta_0)^{-1} = 0.45$ obtained by RXMD (c) and CMD (d). Note that in both simulations the length of the runs is the same (8.7×10^4 time units).

FIG. 4. Temperature dependence of the potential energy $E(T)$ obtained via RXMD (○) and CMD (+) of runs with the same length. * presents values from much longer CMD runs. The solid line is the best fit to the RXMD data with a fit function $E = E_0 + AT^{0.6}$, where $E_0 = -8.656$ and $A = 2.639$ are fit parameters.
calculated the temperature dependence of the (constant volume) heat capacity \( C_v(T) \) via the two routes

\[
C_v(T) = \frac{\partial E(T)}{\partial T},
\]

and plot the results in Fig. 5. Again we see that within the accuracy of our data the two expressions give the same answer, thus giving evidence that the system is indeed in equilibrium.

Summary. We have done replica-exchange molecular dynamics and canonical molecular dynamics simulations for a binary Lennard-Jones mixture in order to check the efficiency of the replica-exchange method for a structural glass former in the strongly supercooled regime. We find that at low temperatures the RXMD is indeed significantly more efficient than the CMD, in that the effective diffusion constant of the particles is around 100 times larger in the RXMD. However, accurate simulations are still difficult for \( T<0.45 \) even with RXMD. Finding an optimal choice of \( M, \{ \lambda_1, \ldots, \lambda_M \} \), and \( \Delta t_{RX} \) may be important in order to allow simulations also for \( T<0.45 \) within reasonable computation times. Furthermore, it might be that the efficiency of RXMD improves even more if one uses it below the critical temperature of mode-coupling theory [24], since there is evidence that below this temperature the nature of the energy landscape is not changing anymore [25].

The authors acknowledge the financial support from the DFG through Grant No. SFB 262. R.Y. acknowledges the Grants in Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan and thanks Professor B. Kim for valuable discussions. Calculations have been performed at the Human Genome Center, Institute of Medical Science, University of Tokyo.

[17] For very small systems, \( N \leq 36 \), this method has been applied to structural glasses also by B. Coluzzi and G. Parisi, J. Phys. A 31, 4349 (1998).
[22] If \( \Delta t_{RX} \) is large, it obviously slows down the algorithm since the number of exchange trials in a single simulation is inversely proportional to \( \Delta t_{RX} \). On the other hand, if an exchange event between \( \lambda_i \) and \( \lambda_{i+1} \) (or \( \lambda_{i-1} \)) has occurred at \( t=0 \), the properties of the subsystem at temperature \( \lambda_i \beta_0 \) for \( t>0 \) will depend for a characteristic (aging or equilibration) time \( \tau_m \) on whether it previously was at temperature \( \lambda_i \beta_0 \) or \( \lambda_{i-1} \beta_0 \). So \( \Delta t_{RX} \) should be larger than \( \tau_m \) for efficient random walks in the temperature space, otherwise strong memory effects will make the exchanges inefficient. The value of \( \tau_m \) depends strongly on the details of the system considered and is possibly very large in our system, particularly at low temperatures. Actually with a choice of \( \Delta t_{RX} = 200 \Delta t \), the subsystems initially at the lowest three temperatures do not reach the highest temperature state within our simulation time.