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Equilibration times in numerical simulation of structural glasses: Comparing parallel tempering and conventional molecular dynamics

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Generation of equilibrium configurations is the major obstacle for numerical investigation of the slow dynamics in supercooled liquid states. The parallel tempering (PT) technique, originally proposed for the numerical equilibration of discrete spin-glass model configurations, has recently been applied in the study of supercooled structural glasses. We present an investigation of the ability of parallel tempering to properly sample the liquid configuration space at different temperatures, by mapping the PT dynamics into the dynamics of the closest local potential energy minima (inherent structures). Comparing the PT equilibration process with the standard molecular dynamics equilibration process we find that the PT does not increase the speed of equilibration of the (slow) configurational degrees of freedom.

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As a liquid is cooled below its melting temperature T_m (supercooled liquid) the structural time τ increases considerably. In a small temperature interval, τ changes by more than 13 order of magnitude. When τ reaches values bigger than 100 s the liquid behaves as an amorphous solid, i.e., a glass.

In recent years, a considerable interest has been devoted to the study of the supercooled state of matter, both theoretically [1–3], experimentally [4–6] and numerically [7–10]. Both thermodynamic [2] and dynamic [1] theories have been proposed to explain the rich phenomenology of glassy systems. Molecular dynamics (MD) simulations have proved to be a powerful tool for studying simple models for liquids in supercooled states (for a review, see Ref. [11]). Simulation stretching in the nanosecond time window has offered the possibility of a detailed comparison between theoretical predictions and "exact" numerical results. So far, such comparisons have been limited to weakly supercooled states, i.e., to the temperature region where characteristic times are at most of the order of 10 ns. In this region, mode coupling theory (MCT) has shown its ability in correctly predicting the numerical results [9,12,13] even for network forming liquids [14,15].

The analysis of numerical data has also been very fruitful in the study of the potential energy surface (PES)—the so-called energy landscape—of several models [3]. These studies have provided evidence that in equilibrium the average basin depth $e_{IS}(T)$ is a decreasing function of T [16]. The number of explored local PES minima, commonly named inherent structures—the exponential of the configurational entropy in the inherent structure formalism [17–19]—decreases also on cooling. Numerical studies on aging liquids [20,21] have shown that the equilibration process is related to the slow search for deeper and deeper basins on the potential energy surface. In the PES framework at least two different factors controlling the equilibration time scale: (i) the time scale for escape from a selected basin (a time scale depending on the kinetic energy) and (ii) the time scale for finding deeper basins (a time scale depending on the number of accessible basins). Which of the two factors is the leading one is still an open question.

Presently, the interesting region where dynamics slows down beyond the nanosecond time scale cannot be studied numerically since the generation of equilibrated configurations requires prohibitive computational times. The possibility of disposing of equilibrium configuration could open the possibility of studying, if not the entire structural relaxation process, at least the initial part of it, where several interesting phenomena related to the dynamics in disordered structures are taking place [22–25].

Several algorithms have been developed to improve the equilibration times in numerical simulations of glassy systems [26,27]. A study by Kob and Yamamoto suggests that the parallel tempering (PT) may become an important tool to provide independent equilibrium configurations for structural glasses. The claim was based on a comparison of the MD mean square displacement (MSD) with the same quantity calculated during the PT run. The PT-MSD turns out to be significantly larger than the corresponding MD-MSD. While in conventional MD, the MSD has a physical meaning for its long time limit being controlled by the diffusion coefficient of the atoms, in PT, the MSD is only a measure of the difference between the original configuration and the configuration at time t since the configuration is changing T during its evolution. Hence the MSD value in PT is basically controlled by the diffusivity at the highest studied T but carries no information on the equilibration rate. Indeed, both the initial configuration and the configuration at time t can be nonequilibrium configurations but very different from each other. For this reason, in this paper we focus on a more sensitive indicator of the equilibrium properties of the system, i.e., on the evolution in time of the inherent structure e_{IS}.

The PT technique [27] was developed for dealing with the slow dynamics of disordered spin systems. The PT algorithms simultaneously simulates a set of M identical noninteracting replicas of the system, each of them at a different *T*. Pairs of replica swap their temperatures according to a Monte Carlo procedure. The basic idea is that each replica performs a random walk among the *M* different *T*. Hence, when the replica explores the high *T* states, the probability to escape from its basin is enhanced.

Each of the *M* replicas, composed by *N* atoms, is described by a Hamiltonian

$$H_m(\vec{q}_m,\vec{p}_m)=\sum_{i=1}^{N}\frac{1}{2m}\vec{p}_i^{\,2}+\Lambda_m(t)E(\vec{q}_m)+\frac{1}{2}Q\left(\frac{\dot{s}_m}{s_m}\right)^2+\frac{(3N-3)}{k_BT_0}\ln(s_m), \qquad (1)$$

where $E(\vec{q}_m)$ is the potential energy of the system. $\Lambda_m(t)$ is a scaling parameter for the potential energy, which effectively sets the temperature *T* of the *m*th replica to the value $T_0/\Lambda_m(t)$, where T_0 indicates the lowest studied temperature. Consequently, the values $\Lambda_m(0)$, for $m=0,\ldots,M-1$ set the *M* different temperatures of the *M* replicas [27] at time $t=0$. The degree of freedom s_m [last two terms in Eq. (1)] are relative to the Nosé thermal bath [28]. The thermostat constrains the average kinetic energy of each replica to the value $3/2Nk_BT_0$.

The whole Hamiltonian is then

$$H=\sum_{m=1}^{M}H_m. \qquad (2)$$

As discussed in detail in Refs. [27,29], the choice of $\Lambda_m(0)$ must guarantee a significant overlap in the energy distributions of different replicas, a requirement that obliges to keep *M* proportionally to the system size.

In this paper, we focus on the time required to find the low inherent structure configurations visited in equilibrium. More specifically, to evaluate if the PT technique is a viable candidate to equilibrate structural glasses, we compare the PT and the conventional MD dynamics by computing the inherent structure energy as a function of the simulation time. Since e_{IS} is a much more sensitive indicator of equilibrium than the total potential energy, we put the PT technique under stringent test.

I. MODELS AND DETAILS OF SIMULATION

The system we investigated is the monoatomic Lennard-Jones (LJ) model modified by adding a many-body anticrystalline potential designed to inhibit crystallization [30]. The ϵ and σ parameters of the LJ potential are chosen as units of energy and length, respectively. The LJ potential is truncated and shifted at 2.5. The potential energy, which includes the anticrystalline potential is

$$E(\vec{q}_m)=V_{LJ}(\vec{q}_m)+\frac{1}{2}\alpha\sum_{\vec{k}}\theta(S_m(\vec{k})-S_0)[S_m(\vec{k})-S_0]^2, \qquad (3)$$

where V_{LJ} is the LJ part of the potential and the sum is over all values of $\vec{k}$ such that $k_{max}-\Delta k<\|\vec{k}\|<k_{max}+\Delta k$. The other terms in Eq. (3) set in only when any wave vector around the structure factor peak increases beyond the value S_0 and acts by damping the unwanted crystallinelike density fluctuation. We chose a number density $\rho=1$, and $S_0=10$, $k_{max}=7.12$, $\alpha=0.83$, and $\Delta k=0.34$ for the anticrystalline parameters as proposed in Ref. [30]. The integration time step is 0.0025, in time units of $\sqrt{m\sigma^2/\epsilon}$. The dynamics for this model has been previously studied [31]. It has been shown that a fast increase of the structural times takes place below $T=1$. The *T* dependence of τ follows a power law in $T-T_x$, with $T_x\approx0.475$. T_x has been identified with the ideal MCT for this model, a hypothesis supported also by an analysis of the *T* dependence of the diffusive directions [32].

The PT algorithm is identical to that encoded in Ref. [29] and we refer to that paper for details on the technique. The algorithm we implement uses $M=14$ identical noninteracting replicas each composed of $N=256$ particles. The 14 temperatures are chosen to span over a range from $T=1.05$ down to 0.485, in particular the temperatures we used are the following: 0.485, 0.518, 0.534, 0.562, 0.597, 0.646, 0.694, 0.745, 0.80, 0.85, 0.90, 0.95, 1.0, and 1.05.

The Hamiltonian of one replica is that of Eq. (1). All replicas evolve according to the standard Nosé constant temperature MD simulation. Every 1000 steps an attempt to exchange the scaling parameter of all pair of replicas with adjacent temperatures (swap of the Λ values) is performed using the following criterion: an exchange is accepted in Metropolis fashion, i.e., the acceptance ratio is

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

where $\Delta_{m,n}=\beta_0(\Lambda_n-\Lambda_m)[E(q_m)-E(q_n)]$. The events with $i=0,2,4,\ldots$ or $i=1,3,5,\ldots$ are repeated alternatively every 1000 integration steps.

The outcome of such calculation are, in principle, equilibrium configurations in the canonical ensemble at the *M* different temperatures.

To estimate the time required to the PT algorithm to equilibrated all replicas we start our PT algorithm with *M* replicas extracted from a previously generated ensemble of equilibrium configurations at $T=1.05$. At this *T*, the structural relaxation time is of the order of 1000 steps and hence generation of equilibrium configurations with conventional MD does not pose any problem. By starting with this ensemble of configurations, the PT equilibration time is, by construction, 0 for the highest temperature. We performed 20 of such independent PT runs to improve the statistic. Each of such runs last two million time steps. Hence, in the PT part of the work, the equations of motion have been integrated $40\times M$ million times.

The same starting configurations ($T=1.05$) are also used as initial configurations for conventional constant temperature MD simulations at the *M* bath temperatures *T*, to compare the rate of equilibration of PT and conventional MD algorithms. For each temperature of these MD simulations, we performed 16 independent runs to improve statistics. Hence, in the MD part of the work, the equation of motion has been integrated $32\times M$ million times.

Local minima configurations have been calculated via conjugate gradient minimization. The minimization process is considered completed when the potential energy change associated with one iteration is less than 10^{-15} to ensure a great accuracy.

II. RESULTS

We focus here on the evolution in time of the inherent structure energy e_{IS}, comparing the PT and MD procedures. Recent work [20,21,33] has provided evidence that following a T change, the system response is characterized by two different time scales. A short time scale, related to the equilibration of the system within a well-defined basin of the energy landscape and a slow time scale related to the search for basin of the "right" depth. The evolution of one-time quantities carries on information on these two time scales. After a sudden change of T a very fast decrease of the vibrational energy—corresponding to the fast equilibration to the new bath T of the intrabasin vibrational motions—is observed. This fast change is followed by a much slower decrease that corresponds to the slow decrease of the basin's depth. The absolute change in e_{IS} during the aging process is significantly smaller than the change in the total potential energy and hence it requires a careful analysis to be detected. A way that has been proven fruitful to separate the large fast component and the small slow component is to monitor directly the evolution of e_{IS}. Building on the expertise developed in recent years, we adopt this indicator as an effective tool to monitor the equilibration of the system in configuration space.

We note on passing that, since e_{IS} is a small component of the potential energy—the intrabasin vibrational part being dominating—a nice scaling of the total potential energy distribution may not guarantee perfect equilibration.

Figure 1 compares the time evolution of the inherent structure energy in the conventional MD (top) and in the PT (bottom) runs. In both cases, by construction, the initial e_{IS} coincides with the equilibrium value of e_{IS} at $T=1.05$. As time goes on, each replica starts to explore larger and larger parts of the configuration space selecting configuration with lower and lower values of e_{IS}. The equilibration process lasts until the equilibrium value of e_{IS} is reached. The same picture applies to the conventional MD case, where the simulation indeed reproduces the aging process following a T jump from $T=1.05$ to the new bath temperature. Crucial to the result of the paper is the meaning of time scale used in Fig. 1 and the associated corresponding CPU time. The computational effort (in terms of CPU) is identical in MD and in PT. Indeed, by running a PT code based on M replicas one obtains simultaneously results like the one presented in Fig. 1 for M different values of T. The total number of simulated steps is then $M\times 210^6$. To produce the same M temperature data with MD, again, one has to run $M\times 210^6$ different simulations. Averages over l different runs to improve the statistics simply multiply by l the single run CPU time for both MD and PT. In both PT and MD cases, parallel coding can be implemented in a very efficient way, running on different CPUs the M different values of T and indeed calculations were carried out on a parallel architecture.

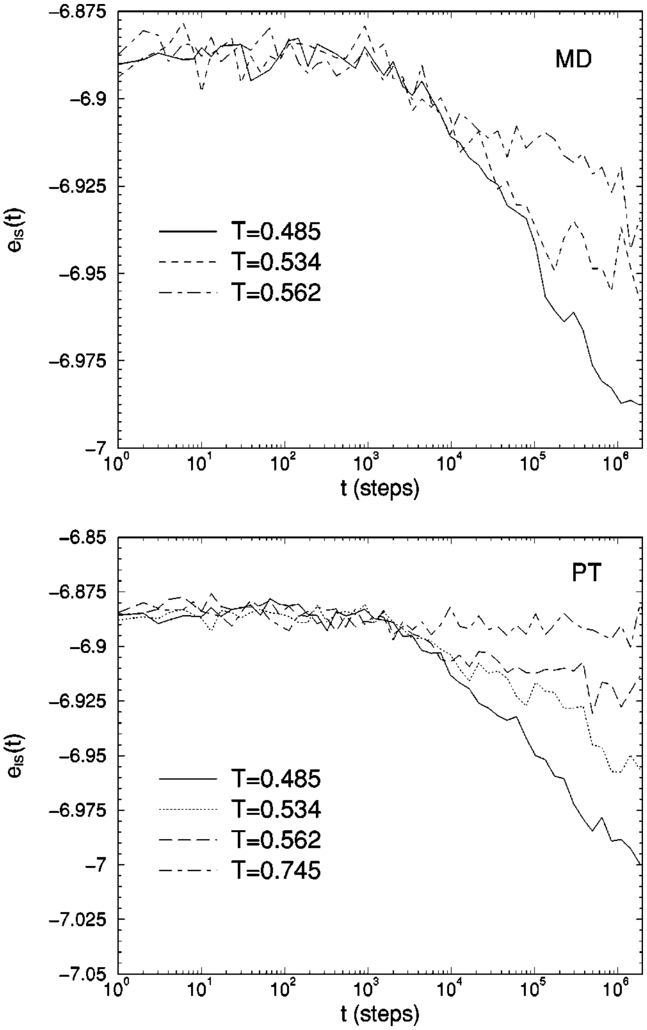

FIG. 1. Inherent structure energies as a function of time for MD (top) and PT (bottom). Time is measured in number of integration steps for both MD and PT. In PT, a conventional MD run is performed between the T swaps and hence the CPU time per step is identical in both procedures.

Figure 2 compares the time evolution of e_{IS} for PT and MD simulations at three different temperatures. In all cases, we find clear indications that the equilibration of the slow degrees of freedom does not depend on the procedure adopted.

III. DISCUSSION

The data shown in Fig. 2 very clearly show that for the Lennard-Jones case investigated in this paper no improvement in equilibration rates is achieved by implementing the PT algorithm.

For the related model of binary mixture of Lennard-Jones [11], the number of distinct basins with depth e_{IS}, in the

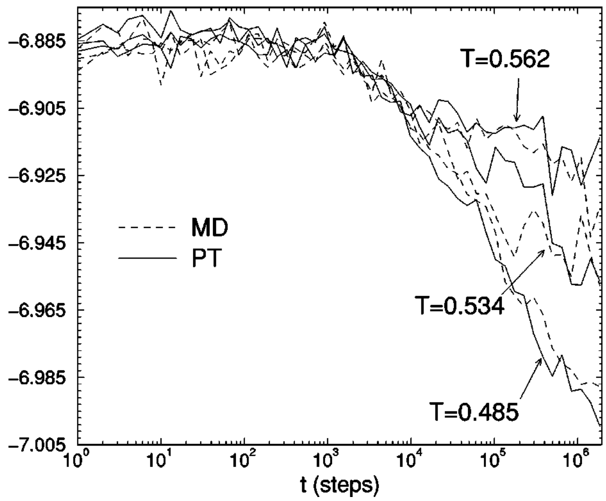

FIG. 2. Inherent structure energies as a function of time: comparison between MD and PT.

range of e_{IS} values characteristic of the PES region explored above T_x is well represented by a Gaussian distribution. The total number of distinct basins has been shown to scale with the size N of the system as $e^{\alpha N}$ with $\alpha \approx 0.8$ [18]. For our 256 atom case, this corresponds to about 10^{87} basins. Under such complicated potential energy landscape conditions, an unbiased search for the location of the deepest basin would require an order of 10^{87} attempts. While the hypothesis of a completely unbiased search is an extreme one, the possibility of a significant role of entropic (as opposed to energetic) effects may be valid. In this respect, it is possible that the rate of equilibration at low temperatures is significantly controlled by entropy. This could explain why the possibility of overcoming barriers with higher probability offered by PT does not favor a faster equilibration process. This picture is also consistent with the fact that in the T region explored (which is still above T_x) saddle dominated dynamics is dominant. Recent instantaneous normal mode analysis [34] has indeed provided evidence that above T_x the system explore mostly regions of the potential energy landscape, which are characterized by a large number of negative curvature directions. No activated processes are required in this condition to change local basin. A further support to the hypothesis of a significant role of entropy in controlling dynamics and equilibration in supercooled liquids comes from the experimental evidence of a linear relation between $\ln(\tau)$ and $1/TS_{conf}(T)$—where S_{conf} is the so-called configurational entropy—as first proposed by Adam and Gibbs (AG) [35]. In the energy landscape thermodynamic formalism [17] $S_{conf}(T)$ is proportional to the logarithm of the number of basins explored at temperature T, or equivalently, to the logarithm of the number of basins of depth $e_{IS}(T)$. The recently observed validity of the AG relation also in the region above T_x [19,36,37] points out towards an important role of the entropic search in the equilibration process.

It would be interesting to find out whether the PT algorithm may be valuable in studying strong liquids, for which less relevant changes in the PES are taking place on cooling as compared to fragile liquids [37] and for which activated processes are dominant at low T. Preliminary indications [38] seems to suggest that this may be the case. It would also be important to correlate the efficiency of PT with the structure of configuration space and connectivity between distinct potential energy surface basins. A possible line of research could be to compare $e_{IS}(t)$ for PT and MD in clusters with different disconnectivity graph [39] types.

To conclude, we like to call the reader's attention on the fact that to study a fixed T range, the PT technique requires a number of replicas that increases linearly with the system size, to guarantee proper overlap in the potential energy distributions of adjacent replicas and hence a significant replica exchange rate. Moreover, all replicas have to be simulated for the same total time interval. This time is fixed by the lowest temperature, which is characterized by a relaxation time that may well be several order of magnitude smaller than the one of the highest temperatures. Both effects concur in making PT a not very convenient algorithm for simulating structural glasses as compared to conventional MD. Indeed, in MD, the total simulation time at each temperature can be chosen to scale with the structural relaxation time.

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