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

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(Dated: November 1, 2018)

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.

PACS numbers: 61.20.Ja, 02.70.Ns, 02.70.Uu, 61.43.Fs, 64.70.Pf

As a liquid is cooled below its melting temperature \( T_m \) (supercooled liquid) the structural time \( \tau \) increases considerably. In a small temperature interval, \( \tau \) changes by more than 13 order of magnitude. When \( \tau \) reaches values bigger than 100s 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 \[1, 2, 3\], experimentally \[4, 5, 6\] and numerically \[7, 8, 9, 10\]. Both thermodynamics \[2\] and dynamic \[16\] 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 \[11\]). Simulation stretching in the ns time window have 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 \[12, 13\] even for network forming liquids \[14, 15\].

The analysis of numerical data has been also 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 \( \epsilon_{IS}(T) \) is a decreasing function of \( T \) \[16\]. The number of explored local PES minima, commonly named inherent structures (IS) — the exponential of the configurational entropy in the inherent structure formalism \[13, 15, 16\] — decreases also on cooling. Numerical studies on aging liquids \[21, 22\] 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 control the equilibration time scale: (i) the timescale for escape from a selected basin (a timescale depending on the kinetic energy) and (ii) the timescale 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 slow down beyond the ns time scale can not 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 \[22, 23, 24, 25\].

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 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 non-interacting 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 de-
scribed by an Hamiltonian

$$H_m(\vec{q}_m, \vec{p}_m) = \sum_{i=1}^{N} \frac{1}{2m} \vec{p}_i^2 + \Lambda_m(t)E(\vec{q}_m) + \frac{1}{2}Q \left( \frac{s_m}{s_m} \right)^2 + \frac{(3N - 3)}{k_B T_0} \ln(s_m)$$

(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 $m = 0,...,M - 1$ set the $M$ different temperatures of the $M$ replicas [27] at time 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:

$$H = \sum_{m=1}^{M} H_m.$$  

(2)

As discussed in detail in Ref. [27] and [30], the choice of $\Lambda_m(0)$ must guarantee a significant overlap in the energy distributions of different replicas, a requirement which oblige to keep $M$ proportionally to the system size.

In this article we focus on the time requested 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 can 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 manybody anti-crystalline potential designed to inhibit crystallization [31]. The $\epsilon$ and $\sigma$ parameter of the LJ potential are chosen as unit of energy and length respectively. The LJ potential is truncated and shift at 2.5. The potential energy, which includes the anti-crystalline potential is

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

(3)

where $V_{LJ}$ is the LJ part of the potential and the sum is over all $\vec{k}$ such that $k_{\text{max}} - \Delta k < ||\vec{k}|| < k_{\text{max}} + \Delta k$. The other terms in Eq. (3) set in only when any of the wavevector around the structure factor peak increases beyond the value $S_0$ and act by damping the unwanted crystalline like density fluctuation. We chose a number density $\rho = 1$, and $S_0 = 10$, $k_{\text{max}} = 7.12$, $\alpha = 0.83$ and $\Delta k = 0.34$ for the anti-crystalline parameters as proposed in Ref. [31]. The integration timestep is 0.0025, in time units of $\sqrt{m\sigma^2/\epsilon}$. The dynamics for this model has been previously studied [22]. It has been shown that a fast decrease of the structural times takes place below $T = 1$. The $T$ dependence of $\tau$ follows a power law in $T - T_x$, with $T_x \approx 0.475$. $T_x$ has been identified with the ideal MCT for this model, an hypothesis supported also by an analysis of the $T$ dependence of the diffusive directions [29].

The PT algorithm is identical to that encoded in Ref. [30] and we refer to that paper for details on the technique. The algorithm we implement uses $M = 14$ identical non-interacting replicas each composed of $N = 256$ particles. The 14 temperatures are chosen to span an 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, 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 $\Lambda$ 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 requested 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 run lasts two million time step. Hence, in the PT part of the work, the equation of motion have been integrated more than 40 million times.

The same starting configurations ($T = 1.05$) are also used as initial configurations for conventional constant temperature MD simulations at several 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.

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 decreases of the vibrational energy — corresponding to the fast equilibration to the new bath $T$ of the intra-basin vibrational motions — is observed. This fast change is followed by a much slower decrease which 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 which has been proven fruitful to separate large fast component and 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 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 — being the intra-basin vibrational part 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.

Fig. 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 article no improvement in equilibration rates is achieved by implementing the PT algorithm.

For the related model of binary mixture Lennard Jones [11], the number of basins with depth $e_{1S}$, in the range of $e_{1S}$ values characteristic of the PES region explored above $T_x$ is well represented by a gaussian distribution. The total number of basins has been shown to scale with the size $N$ of the system as $e^{\alpha N}$ with $\alpha \approx 0.8$ [14]. For our 256 atom case, this correspond 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! In this respect, it is possible that the rate of equilibration at low temperatures is significantly controlled by a simple entropic effect. 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 modes analysis [33] 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 requested in this condition to change local basin.

It would be interesting to find out if 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 [14] and for which activated processes are dominant at low $T$. Preliminary indications [33] 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 $e_{1S}(t)$ for PT and MD in clusters with different disconnectivity graph types.

The fact that in the explored $T$-region equilibration times are not improved in the PT case is consistent with recent finding in the field of protein simulations. This analogy is not at all surprising due to the significant similarities in the problem of glass formation and protein folding [34]. Again, the similarity points to the structure of the PES as key element in the control of the characteristic times.

To conclude, we like to call the reader attention on the fact that to study a fixed $T$-range, the PT technique requires a number of replicas which 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 which may well be several order of magnitude smaller than the one of the top temperature. 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. Of course, bookkeeping facilities are enhanced in the PT case.

Acknowledgments

The authors warmly thank Walter Kob for useful discussions. We acknowledge support from INFM - Iniziativa Calcolo Parallelo and INFM PRA HOP.
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