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Optimized Monte Carlo Method for glasses

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Abstract

A new Monte Carlo algorithm is introduced for the simulation of supercooled liquids and glass formers, and tested in two model glasses. The algorithm thermalizes well below the Mode Coupling temperature and outperforms other optimized Monte Carlo methods.

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1. Introduction

The lack of structural or thermodynamic changes at the glass transition [1] is a major problem for its investigation. The only standard feature, as compared with second-order phase transitions [2], is the dramatic dynamical slowing down at the critical temperature. A fairly standard mechanism for slow dynamics in a homogeneous system at finite temperature is the divergence of a correlation length (*critical slowing down* [2]). Slowness arises from the need of configurational changes to propagate over increasingly large regions (the critical origin of the Mode Coupling singularity[3] has been recently recognized[4]). It has been recently proposed [5] to study this growing length-scale in glass-formers through the finite size behaviour of small systems [2]. Note that experiments in films and nanopores[6, 7] show that the glass transition changes in samples with one or more dimensions of nanometric scale. In particular, the specific heat is most sensitive to the size of the confining pore when temperatures are close to the glass transition[8].

Numerical simulations are an important tool for the study of the glass transition. Their worse drawback is the shortness of the times that may be simulated in today computers (roughly speaking, microseconds). As a consequence, the computer model goes out of equilibrium by the Mode-Coupling temperature, $T_{\rm mc}$, rather than the actual glass temperature, $T_{\rm c}$. To approach $T_{\rm c}$, one may resort to optimized Monte Carlo (MC) methods [9, 10, 5], namely methods implementing unphysical dynamical rules that strongly reduce the equilibration times. When thermalization is achieved, optimized MC allow one to study *equilibrium* mean values and their temperature (or pressure) derivatives, although the purely dynamic features of these methods are interesting in their own right [5].

In this conference note, we give the first full description of the local swap algorithm [5]. We compare the performance of the local swap dynamics with the standard MC and with the microcanonical algorithm [10]. We conclude that local swap yield equilibrium data at temperatures where the microcanonical algorithm no longer thermalizes. Finally, we address the fishy issue of estimating the specific heat in a *metastable* liquid state. We give here details about the strategy followed in [5], where tiny but clearly measurable finite-size effects were observed in the specific heat.

2. Models and observables

We consider two similar models of fragile glass formers, namely binary mixtures of soft spheres. The first model, extensively studied in Ref. [5], is a 50% mixture of particles interacting through the pair potential $V_{\alpha\beta}(r) = \epsilon[(\sigma_\alpha + \sigma_\beta)/r]^{12} + C_{\alpha\beta}$, where $\alpha, \beta = A, B$, with a cutoff at $r_{\rm c} = \sqrt{3}\sigma_0$. The choice $\sigma_{\rm A} = 1.2\sigma_{\rm B}$ hampers crystallization, as compared with the $\sigma_{\rm A} = \sigma_{\rm B}$ model. We impose $(2\sigma_{\rm A})^3 + 2(\sigma_{\rm A} + \sigma_{\rm B})^3 + (2\sigma_{\rm B})^3 = 4\sigma_0^3$ where σ_0 is the unit length. Constants $C_{\alpha\beta}$ are chosen to ensure continuity at $r_{\rm c}$. We work at constant volume, with particle density fixed to σ_0^{-3} and temperatures in the range $[0.897T_{\rm mc}, 10.792T_{\rm mc}]$. We use periodic boundary conditions in a cubic box in systems with $N = 512, 1024, 2048$ and 4096 particles. For argon parameters, $\sigma_0 = 3.4$Å, $\epsilon/k_B = 120$K and $T_{\rm mc} = 26.4$K.

In the second model [11, 10] the choice $\sigma_{\rm B} = 1.4\sigma_{\rm A}$ is made. Naming $x = r/(\sigma_\alpha + \sigma_\beta)$, the pair potential in units $\epsilon = 1$ is $V(x) = x^{-12} + x - 13/12^{12/13}$ if $x < 12^{1/13}$ and zero otherwise (thus, the cut-off distance depends on the type of interacting species). We study density $1.08\sigma_0^{-3}$, as in Refs. [11, 10].

Since the potential energy per particle, e shows the slowest excitations [5, 11], we shall focus here only in this observable, the internal energy being $\frac{3}{2}k_{\rm B}T + \langle e \rangle$ (for other quantities, see Ref. [5]). The constant-volume specific heat, C_v, is:

$$e = \frac{1}{2N} \sum_{j,k \neq j} V(\vec{r}_k - \vec{r}_j)\,, \quad C_v = \frac{3}{2} + \frac{N}{T^2}\left[\langle e^2 \rangle - \langle e \rangle^2\right] \quad \text{(units } \epsilon = k_{\rm B} = 1\text{)}. \tag{1}$$

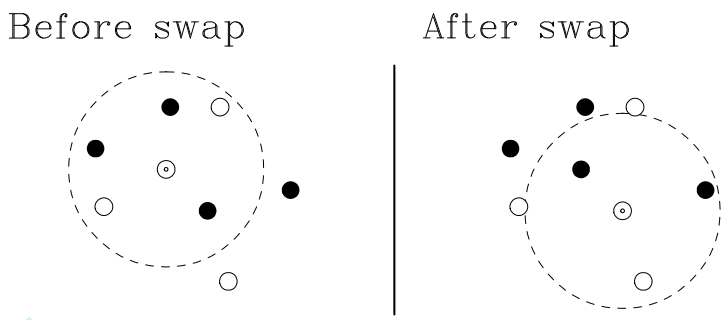

Figure 1: The local swap move. The A particles are depicted by full symbols, while B particles are open symbols. The (say) B particle picked randomly (signaled by a central mark) may be swapped with any one of the three A particles inside the sphere shown in the left part of the plot. After the swap (right), only two B particles could be exchanged with the picked B particle.

3. The local swap Monte Carlo algorithm

The Grigera-Parisi swap algorithm[9] consists in picking randomly a pair of particles of distinct type, A and B, try to exchange their positions, and accepting this move with probability $\min\{1, \mathrm{e}^{-\Delta E/T}\}$ (ΔE is the total potential energy change produced by the swap). If combined with standard MC, it is very effective in reducing the equilibration time. The caveat is that the acceptance of the swap move is very small (see below, and Fig. 4—right). Actually, the probability of accepting a swap move decreases with the distance of the swapped particles, being almost asymptotic already at r_{c}. For the nearest picked particles, at $T = T_{\mathrm{mc}}$, the probability of accepting the swap is about 10 times larger than for distant particles. In large systems, one seldom picks neighboring particles for the swap. To cure this problem, we have proposed the local swap.

In the local swap, the elementary MC step is either (with probability p) a single-particle displacement attempt or (with probability $1-p$) an attempt to *swap* particles. Therefore, for $p = 1$ the algorithm reduces to standard MC. From here on we call local swap to the algorithm with $p = 0.5$. The time unit t_0 is N/p elementary steps. Our swap consists in picking a particle at random (the *picked* particle) and trying to interchange its position with that of a particle of opposite type (the *swapped* particle), chosen at random among those at distance smaller than $0.6r_{\mathrm{c}}$ for the $\sigma_{\mathrm{A}}/\sigma_{\mathrm{B}} = 1.2$ model and $0.73r_{\mathrm{c}}$ for the $\sigma_{\mathrm{A}}/\sigma_{\mathrm{B}} = 1.4$ one (see Fig. 1). Note that this distance may not decrease arbitrarily, since no swappable particles would be eventually found. The optimal choice for the swap distance is the one that maximize the number of actually performed swap moves in a given simulation time. Yet, there is an intrinsic lack of symmetry. Indeed, let N_{old} be the number of swappable particles around the picked particle in its original position, and N_{new} the number of swappable particles for the picked particle in its final position. The probability of choosing the swapped particle is $1/N_{\mathrm{old}}$ in the original configuration, while it would be $1/N_{\mathrm{new}}$ in the final configuration. Detailed balance (see e.g. [2]) holds only if this asymmetry is incorporated in the probability of accepting the swap:

$$p_{\text{accept swap}} = \min\{1, \frac{N_{\mathrm{old}}}{N_{\mathrm{new}}} \mathrm{e}^{-\Delta E/T}\}\,. \tag{2}$$

The performance of the local swap below T_{mc} is far superior to the standard MC (Fig. 2) and to the microcanonical method of Ref. [10] (Fig. 3). Furthermore, for both the $\sigma_{\mathrm{A}}/\sigma_{\mathrm{B}} = 1.2$ and the $\sigma_{\mathrm{A}}/\sigma_{\mathrm{B}} = 1.4$ models, local swap finds a crystallization phase transition. A previous simulation of the $\sigma_{\mathrm{A}}/\sigma_{\mathrm{B}} = 1.2$ model [12], using the Grigera-Parisi global swap, found crystals with up to 60 particles. The local swap, (Fig. 4—left), does find crystals even for systems with 1024 particles. For the $\sigma_{\mathrm{A}}/\sigma_{\mathrm{B}} = 1.4$ model, we find disordered bcc crystals, not reported in previous studies [11, 10]. Actually,

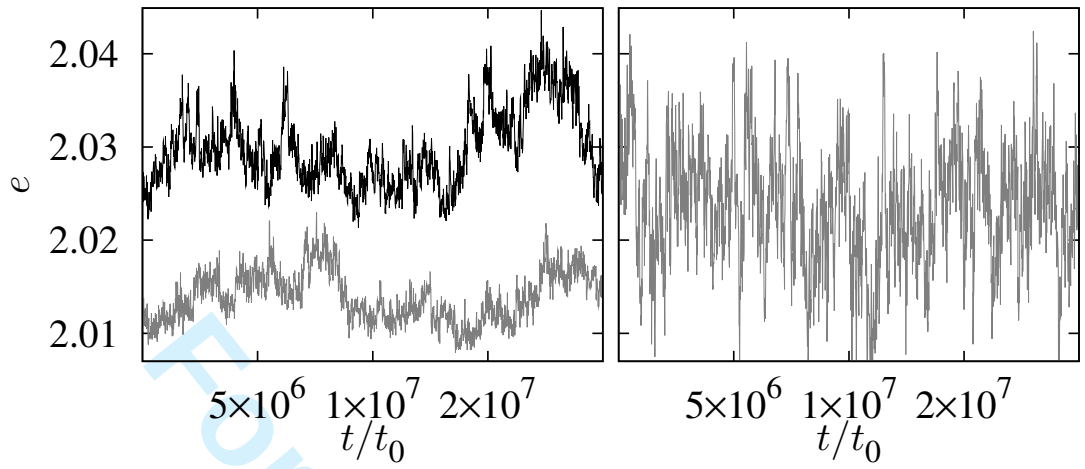

Figure 2: Comparison of the performance of the local swap (right) and standard Monte Carlo (left), as shown by the Monte Carlo history of the potential energy per particle (data points are the average of $10^4 t_0$ successive steps), for the $\sigma_A/\sigma_B = 1.2$ model at $T = 0.897 T_{mc}$ and 1024 particles. The two standard Monte Carlo runs had as starting points thermalized configurations obtained with local swap. In our time window, the two standard simulations do not explore the same energy range. Instead the single local swap simulation explores the full energy range.

with 54 particles, we found a perfect bcc crystal (the A and B particles formed two interleaving single cubic lattices).

The acceptances of the Grigera-Parisi global swap and the local swap algorithms in the fluid phase are compared for the $\sigma_A/\sigma_B = 1.4$ model in Fig. 4—right, for a $N = 32$ and a $N = 256$ system. We have checked that, for $N = 256$ particles, the acceptance for the global swap is already in the thermodynamic limit (the acceptance of the local swap is N independent). For this model, the acceptance probability decreases by three orders of magnitude with decreasing temperature, in the plotted range. In the thermodynamic limit, local swap outperforms the global swap by a factor 4 at 2.13 T_c, that improves to a gain factor of 8 at 0.9 T_c. For the model $\sigma_A/\sigma_B = 1.2$, the local swap acceptance varies linearly in T^{-4} from 0.74% at $0.9 T_{mc}$ up to 6% at $2 T_{mc}$. For the global swap, the acceptance in the thermodynamic limit for the $\sigma_A/\sigma_B = 1.2$ model range from 0.53% at 0.9 T_{mc} up to 4.7% at $2 T_{mc}$.

4. Studying the metastable phase

The liquid is metastable in our soft-sphere models. Thus, the question arises of how to study the thermodynamic properties of a supercooled liquid. We give here details about the strategy we followed in Ref. [5]. The underlying assumption is that the equilibration time (specifically, the exponential autocorrelation time for the energy [5]) for the metastable liquid phase is much smaller than the crystallization time. Our strategy has been to run several MC runs (up to 400 at the lowest temperatures [5]). In each run, the equilibrated metastable liquid is neatly separated from the crystallizing system (see Fig. 4-left). In the analysis we only consider histories whose metastable liquid part was self-consistently found to be longer than 100 exponential energy autocorrelation times (to avoid bias, we also discarded some 20 autocorrelation times *before* crystallization). Note that the central MC history in Fig. 4-left does not meet this criterion (at this low temperature the autocorrelation time was $10^5 t_0$).

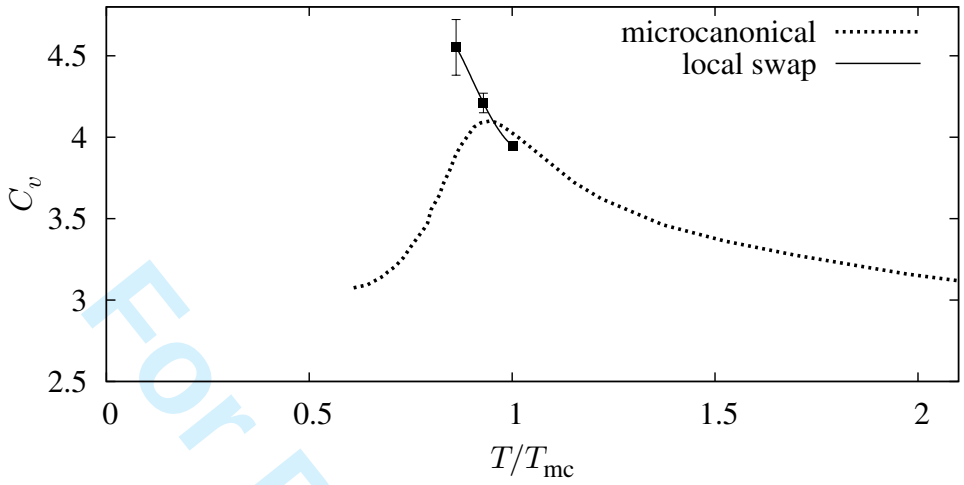

Figure 3: Specific heat of the $\sigma_{\rm A}/\sigma_{\rm B} = 1.4$ model with 128 particles, as a function of temperature, as obtained with local swap ($10^9 t_0$ steps) and with the microcanonical method [10] (error estimates were not provided in Ref. [10]). Local swap produces a significantly larger estimate of the specific heat at our lowest simulated temperatures, signaling better sampling of configuration space and indicating that the microcanonical method is unable to thermalize at such low temperatures.

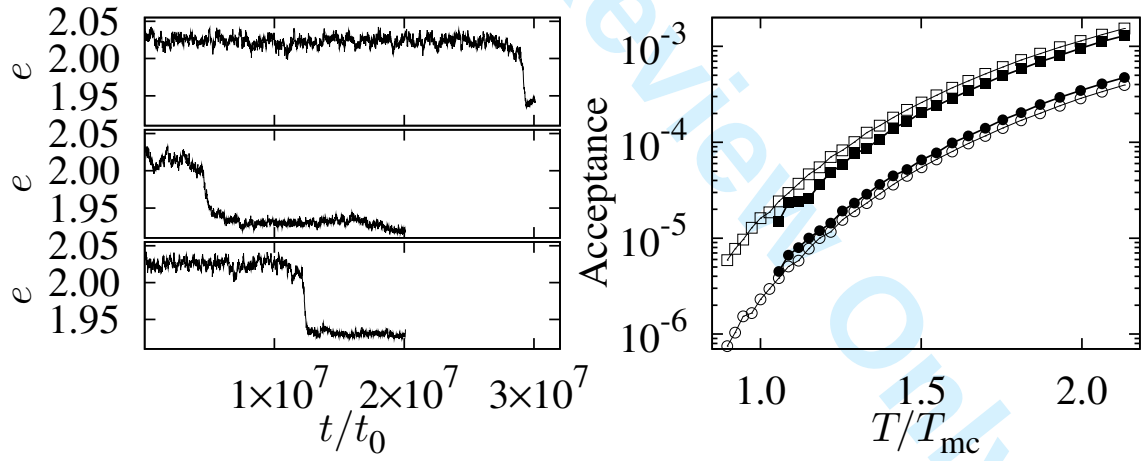

Figure 4: (Left) Examples from the 100 generated (local swap) Monte Carlo histories for the potential energy density of the $\sigma_{\rm A}/\sigma_{\rm B} = 1.2$ model with 1024 particles at $T = 0.897 T_{\rm mc}$. One may clearly distinguish the metastable liquid from the crystallizing system, that starts as a sharp energy drop in all three runs. (Right) Swap probability acceptance for the here explained local algorithm (squares) and the global Parisi Grigera swap (circles), for the $\sigma_{\rm A}/\sigma_{\rm B} = 1.4$ model in the fluid phase, as a function of temperature. We show results for $N = 32$ particles (filled symbols) and $N = 256$ particles (open symbols). The latter coincides within errors with those for $N = 1024$ particles.

5. Conclusions

We give the first full description of the local swap algorithm [5], that is compared with the Grigera-Parisi global swap [9]. The swap acceptance for the local swap algorithm is neatly superior. We compare as well the performance of the local swap dynamics with the standard MC and with the microcanonical algorithm [10], concluding that local swap yield equilibrium data at temperatures where the microcanonical algorithm no longer thermalizes. Furthermore, local swaps finds crystal states not reported in previous work for the $\sigma_A/\sigma_B = 1.4$ model [10, 11]. We have given details about how to estimate the specific heat in a *metastable* liquid state [5].

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