

Are Monte Carlo simulation results affected by sample shape? An investigation based on the Lebwohl–Lasher model

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We investigate the sample shape dependence of periodic boundary conditions and cluster Monte Carlo simulation results for a Lebwohl–Lasher model with 1000 particles. We find marked differences between the two simulations, with pronounced shape effects when using periodic boundary conditions and we discuss their significance.

1. Introduction

Computer simulation methods can only study finite and often rather small samples, typically consisting of a few hundred to a few thousand particles [1,2]. On the other hand, if one sets out to study bulk materials, it is to be hoped and maybe to be expected that the results should not depend very significantly on the sample size and shape since these are accessories to the calculation certainly not present in a truly bulk sample. The same kind of argument also applies to the choice of boundary conditions for the sample. As long as they are irrelevant in our real bulk sample we are free to choose them to reproduce bulk behaviour at best. There are of course cases where the interest is in studying a truly small system. For instance, if we intend to study submicron size droplets of a liquid crystal in empty space or dispersed in, say, a polymeric medium, the boundary conditions should reflect the actual surface conditions [3].

However, if our target is really bulk behaviour then boundary conditions that allow a correct approximation of macroscopic properties in a fashion that depends as little as possible on size and shape should be sought. An appreciation and an appropriate treat-

ment of boundary conditions is particularly important in systems with a normal temperature existence range not too far from a transition, such as liquid crystals.

While size effects are rather well studied [4,5], much less is known on the effects of sample shape, although some studies on Ising, Heisenberg [6,7] and hard disk systems [8] have been published and typically cubic samples or anyway samples consistent with a convenient unit cell are used.

The sample we would ideally like to have corresponds to a “virtual box” in a macroscopic sample. This box would just relate to our observation, e.g. be the part of the sample that we actually visualize, but at the same time be a subset of a large system so it would not have real interfaces. The behaviour of the molecules in the observation box would be determined by all the molecules outside (and thus out of view) as well as by those inside, so shape and size effects should be smeared and relatively unimportant. In other words, we expect the results obtained to be representative of bulk behaviour, more or less independently of the shape of the observation window.

In a computer simulation the boundary conditions

are normally provided by creating a suitable set of "ghost" particles surrounding the necessarily finite sample box where calculations are performed and letting them interact with the particles of the sample proper. In practice the methods of correcting for surface effects are essentially of two kinds:

(i) The ghosts are independent of what happens inside the sample (e.g. they are fixed, or they are changed in a way uncorrelated to the current molecular organization in the box).

(ii) The ghosts are updated using information on the configurations of the particles inside the box to construct the environment outside. The typical example is periodic boundary conditions (PBC), where replicas of the box are used and continuously updated. In computer simulations, both Monte Carlo (MC) and molecular dynamics, PBC are routinely used when investigating bulk properties [1,2]. While extremely useful, easy to program and definitely better than having an empty space outside, PBC inevitably introduce spurious local correlations that can in turn induce a shape dependence. An alternative to PBC, proposed some time ago by one of us [9] is cluster Monte Carlo (CMC). This method tries to use the information on the configuration inside the box to create a set of ghosts that have the same average properties, in particular order parameters, as those of the sample, while not having an identical configuration as in PBC. The method, described in ref. [9] and applied in various other works (see, e.g., refs. [10,11]) will be briefly summarized here. First we recall that the essence of the MC method is to calculate averages and that the desired bulk average of a quantity A can be exactly written as an average over external "world" configurations $[W]$ of the average values $\langle A \rangle_{[W]}$ calculated for a fixed configuration of the "world" outside the sample box. In practice a finite set M_w of external ghost configuration samplings is used and a single Monte Carlo average is approximated with an average of MC results obtained for a fixed environment $[W]$,

$$\langle A \rangle \approx \frac{1}{M_w} \sum_{[W]} \langle A \rangle_{[W]}. \quad (1)$$

The needed outside world configurations $[W]$, i.e. the orientations of the virtual neighbours, are sampled from an orientational distribution function con-

structed, using maximum entropy principles, from the order parameters calculated inside the sample:

$$\langle P_L \rangle_{\text{LAB}} = \frac{1}{N} \sum_i^N P_L(\cos \beta_i), \quad L=0, 2, \dots, L', \quad (2)$$

where β_i is the angle between the axis of particle i and the preferred direction and P_L is a Legendre polynomial. The best information theory [12] inference for the orientational distribution of the particles outside the sample based on these observables is

$$P(\cos \beta) = \exp\left(\sum_{L=0}^{L'} a_L P_L(\cos \beta)\right), \quad (3)$$

where the coefficients a_L are determined from the constraint that the available $\langle P_L \rangle$ be reobtained by averaging $P_L(\cos \beta)$ over the distribution, with a_0 given by the normalization condition of $P(\cos \beta)$. Here we have used the first two relevant order parameters, $\langle P_2 \rangle$ and $\langle P_4 \rangle$.

In practice a standard Metropolis Monte Carlo procedure [13] is used to update the lattice for a certain number of cycles, i.e. of sets of N attempted moves, while monitoring the order parameters $\langle P_2 \rangle_{\text{LAB}}$, $\langle P_4 \rangle_{\text{LAB}}$ inside the sample, calculated over M_k cycles. When these become different from those calculated over the outside ghosts, $\langle P_L \rangle_{\text{out}}$, beyond a certain threshold, the ghost configuration is updated. Thus the coefficients a_2 , a_4 are calculated and $P(\cos \beta)$ in eq. (3) is determined. A set of orientations for the ghost particles outside the box are then sampled from this distribution, using a standard rejection technique and checking that the order parameters $\langle P_L \rangle_{\text{out}}$ relative to the particles outside are the same as those inside to an acceptable threshold and repeating the generation otherwise [9,10]. The energy of the system is then recalculated, a small number (typically 10–20) of micro re-equilibration sweeps is discarded, then the new MC trajectory for the new $[W]$ configuration is followed in the usual way.

The thresholds for ghost update are tuned to ensure on the one hand that we do not choose incorrect order parameters outside and leave them unchanged

and that on the other hand the updating is done only when really needed and not on every cycle or on the basis of some wild fluctuation [9,10]. The method provides the correct bulk asymptotic limit for the angular pair correlation function [13,14] as a function of distance (i.e. the order parameter squared) based on information over the whole sample. Cluster Monte Carlo method aims to estimate *bulk* properties on a sample of a given finite size more closely than periodic boundary conditions on a sample of the same size.

2. The model

In the Lebwohl-Lasher (LL) model [13-15] particles are placed at the sites of a cubic lattice and interact through a pair potential,

$$U_{ij}(\beta) = -\epsilon_{ij} P_2(\cos \beta_{ij}), \quad (4)$$

with ϵ_{ij} an attractive positive constant that takes the value ϵ if i and j are nearest neighbours and 0 otherwise; P_2 is the second Legendre polynomial and β_{ij} is the relative angle between the long axis of the i th and j th particles. The LL model presents a weakly first order orientational phase transition at the reduced temperature $T^* \equiv kT/\epsilon = 1.1232$ [14].

3. Monte Carlo simulations

3.1. Periodic boundary conditions

We have studied, employing the standard Monte Carlo Metropolis method with periodic boundary conditions (see, e.g. ref. [13]), systems with $N_x \times N_y \times N_z$ particles containing approximately 1000 molecules. We have examined the full temperature dependence of the following four systems (cf. fig. 1): $10 \times 10 \times 10$, $5 \times 5 \times 40$ and $3 \times 3 \times 110$, $2 \times 2 \times 250$. The simulations were completely independent of each other, the run at the lowest temperature studied for each system was initiated from a completely aligned system. The calculations at the other temperatures were started from an equilibrium configuration at the nearest lower temperature. The energy was evaluated as usual and the heat capacity per site was obtained by differentiation of the energy with respect

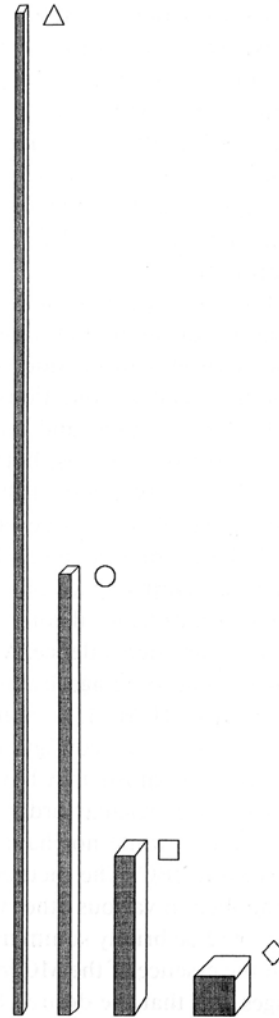


Fig. 1. A sketch of the sample shapes used: $2 \times 2 \times 250$ (Δ), $3 \times 3 \times 110$ (\circ), $5 \times 5 \times 40$ (\square) and $10 \times 10 \times 10$ (\diamond).

to temperature. Second rank order parameters referred to the instantaneous director, $\langle P_2 \rangle_\lambda$, have been determined by diagonalization of the ordering matrix [13] and fourth rank order parameters $\langle P_4 \rangle_\lambda$ have been computed with the algorithm introduced in ref. [14]. Results for the specific heat C_V^* and for $\langle P_2 \rangle_\lambda$ are reported in figs. 2a and 2b. We see profound changes induced by the shape changes. While the cubic sample has the usual [15] well defined transition with the attendant rapid change in $\langle P_2 \rangle_\lambda$, the $5 \times 5 \times 40$ and $3 \times 3 \times 110$ systems show a much more continuous and smooth change and eventually

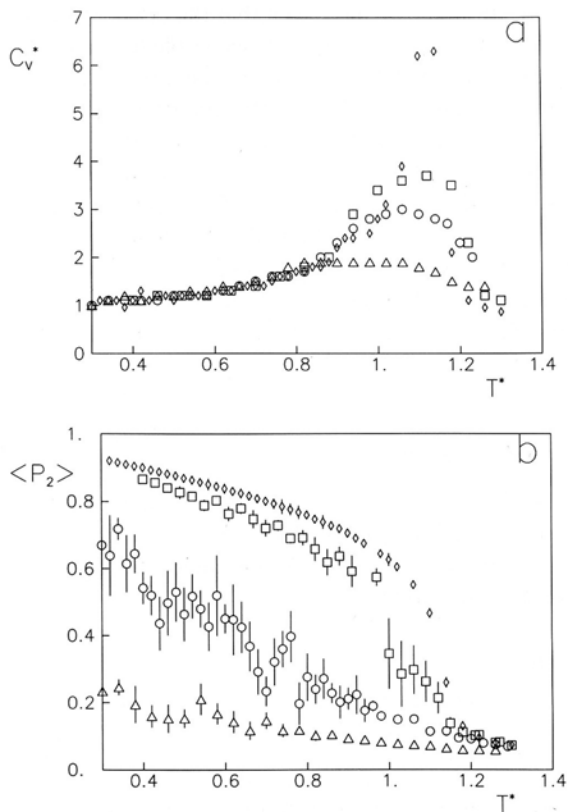


Fig. 2. The dimensionless heat capacity per particle C_v^* (a) and second rank order parameter $\langle P_2 \rangle$ (b) against reduced temperature $T^* \equiv kT/\epsilon$ for a $2 \times 2 \times 250$ (Δ), $3 \times 3 \times 110$ (\circ), $5 \times 5 \times 40$ (\square) and $10 \times 10 \times 10$ (\diamond) Lebwohl-Lasher sample studied with periodic boundary conditions.

the $2 \times 2 \times 250$ system behaves very similarly to a one-dimensional system [16]. The other observables, e.g. $\langle P_4 \rangle_\lambda$, present a similar behaviour and thus are not shown for reasons of space. A similar picture of shape induced disordering is shown in table 1 by performing calculations for a number of other systems at the single reduced temperature $T^*=1$ and after a sufficiently long equilibration (typically 40000 cycles).

3.2. Cluster boundary conditions

We have simulated the same four systems studied with PBC with cluster boundary conditions and we have obtained the results shown in fig. 3 for the heat capacity and the second rank order parameter. It is apparent that there is a large difference between the

Table 1

The values of the order parameter $\langle P_2 \rangle_\lambda$ and of the energy per particle $\langle U^* \rangle$ at $T^*=1$ for various lattice shapes studied with PBC. N_v is the number of particles in the system and N_s is the number of particles belonging to the surface.

System	N_v	N_s	$\langle P_2 \rangle_\lambda$	$\langle U^* \rangle$
$10 \times 10 \times 10$	1000	488	0.63	-1.593
$9 \times 9 \times 12$	972	482	0.63	-1.599
$8 \times 8 \times 15$	960	492	0.63	-1.603
$7 \times 7 \times 20$	980	530	0.61	-1.587
$6 \times 6 \times 27$	972	572	0.56	-1.590
$5 \times 5 \times 40$	1000	658	0.35	-1.569
$4 \times 4 \times 62$	992	752	0.34	-1.588
$3 \times 3 \times 110$	990	882	0.17	-1.572
$2 \times 2 \times 250$	1000	1000	0.08	-1.604
$1 \times 1 \times 1000$	1000	1000	0.035	-1.994

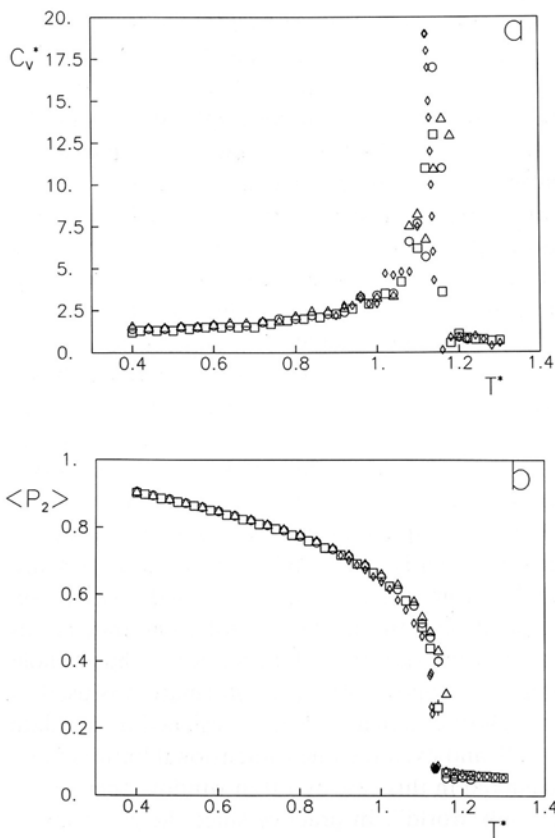


Fig. 3. The dimensionless heat capacity per particle C_v^* (a) and second rank order parameter $\langle P_2 \rangle_\lambda$ (b) plotted against reduced temperature T^* for a $2 \times 2 \times 250$ (Δ), $3 \times 3 \times 110$ (\circ), $5 \times 5 \times 40$ (\square) and $10 \times 10 \times 10$ (\diamond) Lebwohl-Lasher sample studied with cluster Monte Carlo boundary conditions.

Table 2

Position T^* and peak value of heat capacity anomaly C_V^* in reduced units for Lebwohl-Lasher model systems of different shape studied with PBC and CMC simulations.

System	$(T^*)_{CV}^{PBC}$	$(C_V^*)_{max}^{PBC}$	$(T^*)_{CV}^{CMC}$	$(C_V^*)_{max}^{CMC}$
$2 \times 2 \times 250$	0.90	2.1	1.16	14.9
$3 \times 3 \times 110$	1.10	3.1	1.14	17.4
$5 \times 5 \times 40$	1.12	4.8	1.14	13.8
$10 \times 10 \times 10$	1.14	6.2	1.12	19.1

results provided by the PBC and CMC algorithms. Here the results are essentially independent of sample shape even for the very long and thin samples.

4. Discussion and conclusions

Upon comparing PBC and CMC results we notice in particular a pronounced dependence upon sample shape for PBC, while the CMC results for the different cases are quite similar. Upon decreasing the breadth and width of the sample while keeping the volume constant, we approach, when using PBC, the limit of a one-dimensional model. Indeed we have in this case PBC results that become similar to the analytical solution of Vuillermot and Romerio [17], where no long range order exists. Thus the shortest size in a non-cubic sample is limiting the accuracy of the calculation as a means of approximating bulk behaviour, while of course the calculation can be appropriate to other, lower dimension, physical systems. It is clear that this is due to the spurious correlations introduced by the particle by particle copying of sample information to the outside ghost. Quite differently, in CMC ghost orientations are sampled from a distribution generated, using maximum entropy, on the basis of order parameters calculated as averages over all the particles. Thus "whole sample" as opposed to point information is used to create ghosts. Actually CMC is designed to simulate the bulk and even the one-dimensional limit is to be considered in this case as a thin window opening on the "bulk world". In practice since the ghost molecules are generated on the basis of orientational information gathered from the whole sample, not just locally, and consequently the results do not change as dramatically as for periodic boundary conditions simulations.

In summary we have seen that the effect of sample shape can be practically non-negligible for model liquid crystal systems containing even a relatively large number of particles. At least for the Lebwohl-Lasher model, which incidentally has short range interactions, this applies to samples with a number of particles of the order of one thousand. The shape effect is quite noticeable with periodic boundary conditions and we expect that this effect could have implications in simulations of a variety of fluid [18] and lattice systems, especially with longer range interactions.

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