A new technique for grand canonical Monte Carlo simulation: Application in a hard disk system

A. Caliri, M. A. A. da Silva, and B. J. Mokross

Citation: The Journal of Chemical Physics **91**, 6328 (1989); doi: 10.1063/1.457400
View online: http://dx.doi.org/10.1063/1.457400
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/91/10?ver=pdfcov
Published by the AIP Publishing

A new technique for grand canonical Monte Carlo simulation: Application in a hard-disk system

A. Caliri[a)]
IBILCE-UNESP-S. J. Rio Preto, São Paulo, Brazil

M. A. A. da Silva[a)]
FC-UNESP-Bauru, São Paulo, Brazil

B. J. Mokross
IFQSC-USP-São Carlos, São Paulo, Brazil

(Received 27 February 1989; accepted 22 June 1989)

We present a new Monte Carlo approach which is capable to reduce significantly the two-phase coexistence region by constraining the system to remain fairly homogeneous in the transition region. This is achieved by introducing the chemical potential as an extra intensive thermodynamic variable in the canonical average. The technique developed was applied in a system containing 224 hard disks. The approach can, on the other hand, be applied in a general way to other systems.

I. INTRODUCTION

This article is a more extensive and complete version of a recent letter by the same authors.[1] The central motivation for this work is an old problem concerning a discrepancy between results from Monte Carlo (MC) and Molecular Dynamics (MD) simulations on hard-disk systems. However, the approach here developed can be applied, in a general way, to other systems.

Regardless the studies on thermodynamics properties of hard spheres and disks to be in appearance not more than an academic problem, it is of great importance not only in physics but also in biology, chemistry, metallurgy, ceramics, soil science, as well in mathematics and many branches of engineering.[2–5] For example, it is fundamental in microscopic theory of fluids, where hard-spheres systems are used as reference systems for perturbation theories.[5]

The refered lack of agreement concerns to the solid–liquid coexistence region.[1] In the following we give a brief general review of the problem. For $\tau \cong 1.32$, $\tau = \rho_0/\rho$ where ρ is the number density and ρ_0 refers to the closed-packing configuration, it has been shown[6,7] that a system of hard disks undergoes a freezing transition. The fluid–solid transition was located by the observation of a van der Waals-type loop, in the pressure × volume plot, at $1.26 < \tau < 1.32$, by means of the MD procedure. The two-phase coexistence could be observed in a direct way,[6] following the particle trajectory in the system. Further extensive MC calculations were carried out[8,9] and the van der Waals loop could not be reproduced,[10] presumably due to lack of completeness of the averaging over all admissible configurations at any one density on the loop. Very early work[11] already pointed out the very poorly estimated canonical average obtained in the transition region, due to ergodic difficulties. In fact, the manifestation of ergodic difficulties in the interval of confusion,[9] $1.29 < \tau < 1.36$,[1] seem to be due to the slow but strong fluctuation of domains of random (or irregular) close packing, which serve as long-living topological traps. In this context we note that random close packing can occur in two ways: dense and loose packing.[12]

Our aim in this work is, through a kind of "economical ensemble," to avoid (or more rigorously, to reduce significantly to a small interval of densities) the two-phase coexistence and so to show in what way it is possible to reproduce, by MC computation, the van der Waals-type loop for 224-hard-disk system, recovering a few characteristic results of the successful MD simulation for the 870-hard-disk system.[6]

The method has as general purpose to inhibit density fluctuations[13] by constraining the system to remain fairly homogeneous in the transition region. This is achieved by introducing, in a peculiar manner, the chemical potential as an extra intensive thermodynamic variable in the canonical average. In the Sec. II of this paper, we treat the pressure for a classical system as a thermodynamic quantity derived from either, canonical and grand canonical ensemble, emphasizing the significance of the suitable choice among the possible ensembles, for finite systems. Section III presents the economical ensemble for a general system, and since this new ensemble imitates the grand canonical one, we will call it by "mimetic grand canonical ensemble". In Sec. IV the approach is applied to a system of hard disks, and in Sec. V we present the results with reference to the calculation on the hard-disk system and comments.

II. CANONICAL AND GRAND CANONICAL ENSEMBLE

A. Pressure

The system we consider here will be described in classical terms. Thus the canonical (or NVT) partition function

$$Z_N = \sum_{\{s\}} \exp(-E_s/kT), \tag{1}$$

$Z_N = Z_N(V,T)$, for a D-dimensional system of N particle of mass m contained in volume V, interacting pairwise through the total potential energy $U(\{\mathbf{r}_i\})$, at absolute temperature T, is given by

$$Z_N = \frac{1}{h^{DN}N!}\int \cdots \int \exp(-\epsilon/kT)d\{\mathbf{q}_i\}, \tag{2}$$

[a)] Present address: FCFRP/USP-Depto. Física e Química Universidade de São Paulo Av. do Café S/N 14049 Ribeirão Preto, SP-Brazil.

 0021-9606/89/226328-09$02.10

where h and k are, respectively, the Planck and Boltzmann's constant, $d\{\mathbf{q}_i\} = d\{\mathbf{r}_i\}d\{\mathbf{p}_i\}$ and $\epsilon = \epsilon(\mathbf{q}_i)$, a function of all positions $\mathbf{r}_i$ and momenta $\mathbf{p}_i$, is

$$\epsilon = \sum_{i=1}^{DN} \frac{\mathbf{p}_i^2}{2m} + U(\{\mathbf{r}_i\}), \tag{3}$$

The multiple integral in Eq. (2) breaks into a product of integral over momenta and over coordinates, resulting

$$Z_N = \Lambda^{-DN} Q_N, \tag{4}$$

where $Q_N = Q_N(V,T)$ is the configurational integral

$$Q_N = \frac{1}{N!}\int \cdots \int \exp(-U(\{\mathbf{r}_i\})/kT) d\{\mathbf{r}_i\} \tag{5}$$

and $\Lambda = h/\sqrt{2\pi mkT}$ is the so called thermal de Broglie wavelength of the particles. Only for the one-dimensional case, $D = 1$, the configurational integral can be solved exactly.[14]

On the other hand, the grand canonical (or μVT) partition function

$$\mathcal{Z} = \sum_{\{s\}} \exp[-(E_s - \mu N_s)/kT] \tag{6}$$

with $\mathcal{Z} = \mathcal{Z}(\mu,V,T)$ and μ being the chemical potential, is given by

$$\mathcal{Z} = \sum_{N=0}^{\infty} \Lambda^{-DN} z^N Q_N, \tag{7}$$

where z, the fugacity, is

$$z = \exp(\mu/kT). \tag{8}$$

The pressure in the canonical ensemble is given by

$$P = -\frac{\partial F}{\partial V} \tag{9}$$

with $F = F(V,T)$ being the Helmholtz free energy, defined as

$$-\beta F = \lim_{N\to\infty} \log Z_N, \tag{10}$$

where $\beta = 1/kT$.

In the grand canonical ensemble, the pressure is directly related to the Landau potential

$$\Omega = -PV \tag{11}$$

with $\Omega = \Omega(\mu,V,T)$ being defined by

$$\beta\Omega = -\log \mathcal{Z}. \tag{12}$$

For the particular case of hard particles, the total potential energy can assume only two values, i.e., $U(\{\mathbf{r}_i\}) = \infty$ when $r_{ij} < \sigma$ for at least one pair (i,j), where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and σ is the particle diameter, and $U(\{\mathbf{r}_i\}) = 0$ when $r_{ij} \geqslant \sigma$ for all pairs (i,j). Thus, the temperature does not play any role on Q_N and in spite of the free energy F to be highly nontrivial for $D \geqslant 2$—because Eq. (5)—the nonideal gas contribution to the equation of state, Eqs. (4,5, 9, and 10), is temperature independent, i.e., the second virial coefficient, third virial coefficient, so on, are temperature independent. However, the Landau potential, Eqs. (12), suggests that the pressure depends on the temperature, and so the resultant conclusion from the previous analyses on the canonical ensemble, here, no longer is so manifest.

In any case, the equation of state cannot depend on the particular choosen ensemble, and consequently one must show that in the thermodynamic limit, the ensembles are equivalent. Actually, the Van Hove's theorem[16] ensures that the equation of state in the canonical ensemble is the same as that in the grand canonical ensemble, but for finite systems—and this, of course, is the case in simulation—one specific choice among the alternative ensembles may result to be more convenient, mainly because of nonnegligible strong fluctuations in small systems.

In MC simulations, the search for the more adequate ensemble has been a subject of interest.[17–19] To this aim careful computations on hard disks were gone by Wood.[20,21] He did calculations in the isothermal–isobaric ensemble (NPT-ensemble) for $N = 48$ and 90 molecules systems. However he did not succeed in one of the original objectives, i.e., to eliminate the disagreement between the MC and MD simulation results in the region of freezing. He concluded that, in this case, the NPT-ensemble appears to give fairly convergent results in contrast to the canonical ensemble (NVT-ensemble), but due more to the use of higher speed machinery than to any inherent advantage of NPT method, although it has been emphasized[22] that in general, for small finite systems, the alternative ensembles give results for averages which are different at least by $O(N^{-1})$.

B. Thermodynamic average

The equilibrium value $\langle A \rangle$ of any extensive quantity A of interest may be expressed by

$$\langle A \rangle = \mathcal{Z}^{-1} \sum_{\{s\}} A(s) \Lambda^{-DN_s} Z^{N_s} Q_{N_s}, \tag{13}$$

where the sum runs over the set of all states $\{s\}$. Assuming $A(s)$ as a function only of the particle positions and using the result for the average number of particle $\overline{N}$ of a perfect gas of the same particle mass m, density and temperature,

$$\overline{N} = \Lambda^{-D} V \exp(-\mu_0/kT), \tag{14}$$

where μ_0 is the chemical potential of the perfect gas, the grand canonical ensemble average becomes

$$\langle A \rangle = \frac{\sum_{N=0}^{\infty} e^{N\log\overline{N} - \log N!} e^{N\mu'/kT} \int \cdots \int A(\{\mathbf{r}_i\}) e^{-\beta U} d\{\mathbf{r}_i\}}{\sum_{N=0}^{\infty} e^{N\log\overline{N} - \log N!} e^{N\mu'/kT} \int \cdots \int e^{-\beta U} d\{\mathbf{r}_i\}}, \tag{15}$$

where $\mu' = \mu - \mu_0$ is the excess chemical potential and $U = U(\{\mathbf{r}_i\})$.

One may use this exact equation in a MC procedure[23] by using $\mu'/kT + \log \overline{N}$ as an applied parameter—the MC calculation determines $\overline{N}$ and consequently μ'/kT—but making the approximation $N \log \overline{N} = \log N!$, an even simpler MC procedure is obtained, i.e., we obtain for the grand canonical ensemble average

$$\langle A \rangle = \frac{\sum_{N=0}^{\infty} \int \cdots \int A(\{\mathbf{r}_i\}) e^{-\beta(U - N\mu')} d\{\mathbf{r}_i\}}{\sum_{N=0}^{\infty} \int \cdots \int e^{-\beta(U - N\mu')} d\{\mathbf{r}_i\}}, \tag{16}$$

Both equations, the exact ensemble, Eq. (15), and the modified ensemble, Eq. (16), were used by Adams[17] in order to determine the excess chemical potential for a system of hard spheres. Both are in agreement with each other and give good consistency with the values obtained by others methods.

When, in a system of hard spheres,—$\Delta U(\{\mathbf{r}_i\}) = 0$ or ∞—one uses the modified ensemble, one particle is removed with probability

$$\exp(-\mu'/kT) \tag{17}$$

while the attempt to add one particle is always made, i.e., only the change in the energy is checked.

Now, using the exact ensemble, one particle is removed with probability

$$\min\left[\frac{N}{\overline{N}}\exp(-\mu'/kT),1\right] \tag{18}$$

and added, if there is room for it [i.e. $U(\{\mathbf{r}_i\}) = 0$], with probability

$$\min\left[\frac{\overline{N}}{N+1}\exp(-\mu'/kT),1\right]. \tag{19}$$

III. MIMETIC GRAND CANONICAL ENSEMBLE

In the simulation of a fluid at constant density, in the two-phase coexistence region, the finite size of the system significantly disturbs the results that one should expect in the thermodynamic limit, e.g., a correction to the internal energy, due to interface between the domain of the minority phase and majority phase, of $O(N^{-1/D})$ arises.[23] The natural remedy for this situation is to study the problem in the grand canonical (μVT) ensemble, because in this ensemble all independent thermodynamic variables are intensive and so, the two-phase coexistence appears an an improbable region, in which one never observes any stable equilibrium state. However, simulations in the μVT-ensemble usually are distinctly slower than simulations in the NVT-ensemble. Therefore, at this point we concern ourselves with the introduction of the mimetic grand canonical (MGC) ensemble. Let us start by considering an arbitrary large system of defined volume V, containing exactly N particles and at fixed temperature T. We divide this volume into a large number r of subunits (identical cells), with a volume $v = V/r$, each of which is statistically large and contains on the average $\overline{N} = N/r$ particles. If we consider a particular cell C_n, the equilibrium value of the extensive quantity A will be expressed by $\langle A \rangle_C$, where the subscript C stands for cell ensemble averaging.

Now let us represent the set of all states of the cell C_n by $\{\mathbf{x}_i\}_{C_n}$ and then form a modified canonical ensemble through the following Cartesian product of replicas:

$$\{\mathbf{X}_k\}_V = \{\mathbf{x}_i\}_{C_1} \otimes \{\mathbf{x}_j\}_{C_2} \otimes \cdots \otimes \{\mathbf{x}_l\}_{C_r}. \tag{20}$$

Each particular point $\mathbf{X}_k$ in the modified configuration space is obtained choosing a specific state from each cell and multiplying them. Note that in spite of the fluctuation of the number of particle N_i in each cell, we imposed the conservation law $\Sigma_i N_i = N$ with $dN(t)/dt = 0$. Due to the supposed macroscopic size of the cells, the grand canonical ensemble average $\langle A \rangle_C$ is identical to the modified ensemble average $\langle A \rangle_V$, i.e., $\langle A \rangle_C = \langle A \rangle_V$. According to this, the prescription hinted by the Eq. (20) does not show advantages in the thermodynamic limit; but for finite systems, a systematic study on a set of systems of different sizes, can reveal distinct "routes" of the finite size effect on the simulation results, for each distinct ensembles.

Thus, recalling the fact that the usefulness of the MC method rests on the (empirical) knowledge that through this method is has been possible to simulate accurately the thermodynamic properties of macroscopic systems using finite systems, in practice, our MC procedure consist of the following process: we go through the points of $\{\mathbf{x}_i\}_C$ of each cell, constructing a random walk of points $\{\mathbf{X}_k\}_V$ defined by Eq. (20), using transition probabilities

$$T_{ij} = T_{ij}\left[(\mathbf{x}_i)_{C_a}(\mathbf{x}_i)_{C_d} \in \mathbf{X}_i \rightarrow (\mathbf{x}_j)_{C_a}(\mathbf{x}_j)_{C_d} \in \mathbf{X}_j\right] \tag{21}$$

from one configuration to another and take the average $\langle A \rangle$ over $\{\mathbf{X}_k\}_V$. The quantities in brackets indicate transitions from the state $i \rightarrow j$ due to a single move of a particle, for example, belonging to cell C_d (donor cell) which goes to another cell C_a (acceptor cell). Therefore at most two cells may be involved in the transition $\mathbf{X}_i \rightarrow \mathbf{X}_j$ and the phase space $\{\mathbf{X}_k\}_V$ is explored walking through the phase space $\{\mathbf{x}_i\}_C$ for all cells. Note additionally that the conservation law $dN/dt = 0$ is automatically taken in account in this prescription.

A picture of what is going on (in the MC realization) is the following: when a particle belonging to one particular cell is moved in order to produce a new configuration, everything happens as if this specific cell were a subsystem of a much larger system (whose physical description is given specifying its volume V, number of particle N, temperature T, and (consequently) the chemical potential μ) with the remainder cells forming the medium. For moves inside the same cell, our approach is reduced to the standard one, i.e., the importance sampling technique[24] introduced by Metropolis *et al.*,[25,26] and so the move is accepted with probability $\min[\exp(-\Delta E/kT),1]$. However, if the move drives the particle from one cell to another cell, we distinguish two events which we consider as independent ones, although simultaneous: (*i*) the *exit* of one particle from a particular cell, and (since the total number of particle, N, in the system as a whole is maintained fixed), (*ii*) the *entrance* of the same particle in another neighboring cell. In each case (*i*) and (*ii*), the involved cells, each one at its own time, are considered as the subsystem with the remainder cells constituting the medium. Under these conditions the move is accept with probability

$$p = \min\left[\frac{N_d}{\overline{N}}\exp\left(\frac{-\Delta E_d - \mu'}{kT}\right),1\right] \times \min\left[\frac{\overline{N}}{N_a+1}\exp\left(\frac{-\Delta E_a + \mu'}{kT}\right),1\right], \tag{22}$$

where N_d and N_a are, respectively, the number of particles in the donor and acceptor cell, and $\overline{N}$ is the average number of

particles in the cells; ΔE_d and ΔE_a are, respectively, the energy change in the donor and acceptor cell.

It is important to note that when the ratio $N_d/\bar{N}$ and $\bar{N}/(N_a+1)$ are small enough (strong inhomogeneity) Eq. (22) becomes

$$p=\frac{N_d}{N_a+1}\exp(-\Delta E/kT), \tag{23}$$

where $\Delta E=\Delta E_d+\Delta E_a$. Note that the increase of inhomogenity is made difficult. Similarly, if the ratio $N_d/\bar{N}$ and $\bar{N}/(N_a+1)$ are large enough (again, strong inhomogeneity) we obtain

$$p=1 \tag{24}$$

which helps to reduce the inhomogenity.

On the other hand, if the system remains fairly homogeneous, in general four distinct situations must be verified:

$$p=\begin{cases}\dfrac{N_d}{N_a+1}\exp(-\Delta E/kT), & \text{if } u \text{ and } v<1\\ u, & \text{if } u<1 \text{ and } v\geqslant 1\\ v, & \text{if } u\geqslant 1 \text{ and } v<1\\ 1, & \text{if } u \text{ and } v>1\end{cases} \tag{25}$$

where $u=(N_d/\bar{N})\exp[-(\Delta E_d+\mu')/kT]$ and $v=(\bar{N}/(N_a+1))\exp[-(\Delta E_a-\mu')/kT]$.

IV. APPLICATION OF THE MGC METHOD TO A SYSTEM OF HARD DISKS

Now we return to the hard-disk problem. Using Eq. (25), T_{ij}, the transition probability from one configuration (i) to another (j), assume the values 0,p or 1, with $p=(N_d/\bar{N})\exp(-\mu'/kT)$. The value $T_{ij}=0$ is applied for moves which give $\Delta E=\infty$, i.e., overlapping of disks; $T_{ij}=p$ is used when the move results in $\Delta E=0$ and drives the particle to outside of its original cell; finally, $T_{ij}=1$ is applied for moves which give $\Delta E=0$ and restrict the particle into the same cell.

In order to make the transitions from one cell to others with higher number of disks even more difficult, (i.e., to turn the inhomogeneity even more inviable) an extra bias was used: we converted $p=\exp(-\mu'/kT+\Delta\eta)$ into $p=\exp(-\Delta n\mu'/kT)$ where $\Delta\eta=\log N_d-\log\bar{N}$ and Δn is the difference between the number of disks in the acceptor and donor cells after and before the move, respectively. In the previous work[1] we adopted an alternative procedure to obtain the same result: we started considering the modified ensemble described by Eq. (16) and (17) and the transition probability T_{ij} was determined, for the especial case of a system of hard disks, considering only the two cells involved in the movement of the disk and then respective configurations together with a related special configuration taken as reference.

In our simulation we used a system containing $N=224$ disks, initially in a trigonal lattice and the initial volume was divided into 56 smaller boxes, each one containing four disks. The conventional periodic boundary condition was used on the bigger box. With the intent of reaching adequate chain length, keeping in mind an economical use of computer time, one can take advantage of the very short-ranged potential involved, and instead of examining all $N-1$ interactions of the displaced disk with the others, only a much smaller class of neighbors has to be considered. This was accomplished by updating a table of neighbors for each particle. The standard "no-bias" acceptance ratio of 0.5 was not used; instead, acceptance ratio between 0.35 and 0.45, depending on τ, was used.[28,29] Thereafter our aim was to determine the average number $\bar{n}$ of disks which surround each one, enabling us to write the equation of state[25]

$$\phi=1+\frac{\pi d_0^2\bar{n}}{2}, \tag{26}$$

where $\phi=P/\rho kT$, P is the pressure, and d_0 the disk diameter. The total number of configurations generated was initially broken up into some number M of successive sequences of m Monte Carlo steps per site (MCSS) each and then we calculate

$$\phi_r=\frac{\Delta}{m}\sum_{i=p_r(\Delta)q_r}\phi(t_i), \tag{27}$$

where $\phi(t_i)$ is the reduced pressure due to the ith-generated configuration, $p_r(\Delta)q_r$ meaning "from p_r to q_r with incrment of Δ," Δ MCSS are discarded between each two $\phi(t_i)$ considered, and $p_r=m(r-1)+1$, $q_r=mr$ with $m=50$ and $r=1(1)M$. In order to get better statistically independent configurations, apart an initial discard, $\Delta=5$ was used, giving therefore a meaningful error estimate.[27] The MC estimate for the average $\langle A\rangle$ then reduces to

$$\bar{\phi}=\frac{1}{M}\sum_{r=1}^{M}\phi_r. \tag{28}$$

V. RESULTS AND COMMENTS

In this section we present the results of an extensive calculation using the MGC ensemble for a hard-disk system. In Table I, we list the values of the equation of state for several values of τ and μ, together with the Erpenbeck and Luban results[30] from Monte Carlo and molecular dynamics (MCMD) simulations, which have provided data with accuracy of 1 part in 10^4 for the equation of state of the hard-disk fluid system, for $1.4\leqslant\tau\leqslant 30$. We did not investigate yet the dependence of μ' on the system size, number, and shape of the subunits. However, since the pressure in the fluid phase should not be affected strongly by these parameters—

TABLE I. Values of $\phi=P/\rho kT$ for hard disks as a function of the reduced volume τ, for different values of $\beta\mu'$. Note that as τ increases, the value of $\beta\mu'$ which brings the pressure near to the Erpenbeck and Luban results decreases, in agreement with the fact that as $\tau\to\infty$, $\beta\mu'\to 0$.

τ	Erpenbeck–Luban[a] $-\beta\mu'=$	0.0	0.5	1.0	1.5	2.0
1.4	8.306	8.44	8.42	8.34	8.31	8.29
1.5	6.6074	6.71	6.64	6.62	6.59	···
1.6	5.4963	5.59	5.52	5.48	5.43	···
5.0	1.4983	1.50	1.47	1.44	1.44	···
10.0	1.2106	1.20	1.18	1.18	1.18	···
20.0	1.0974	1.09	1.08	1.07	1.07	···

[a] Reference 30.

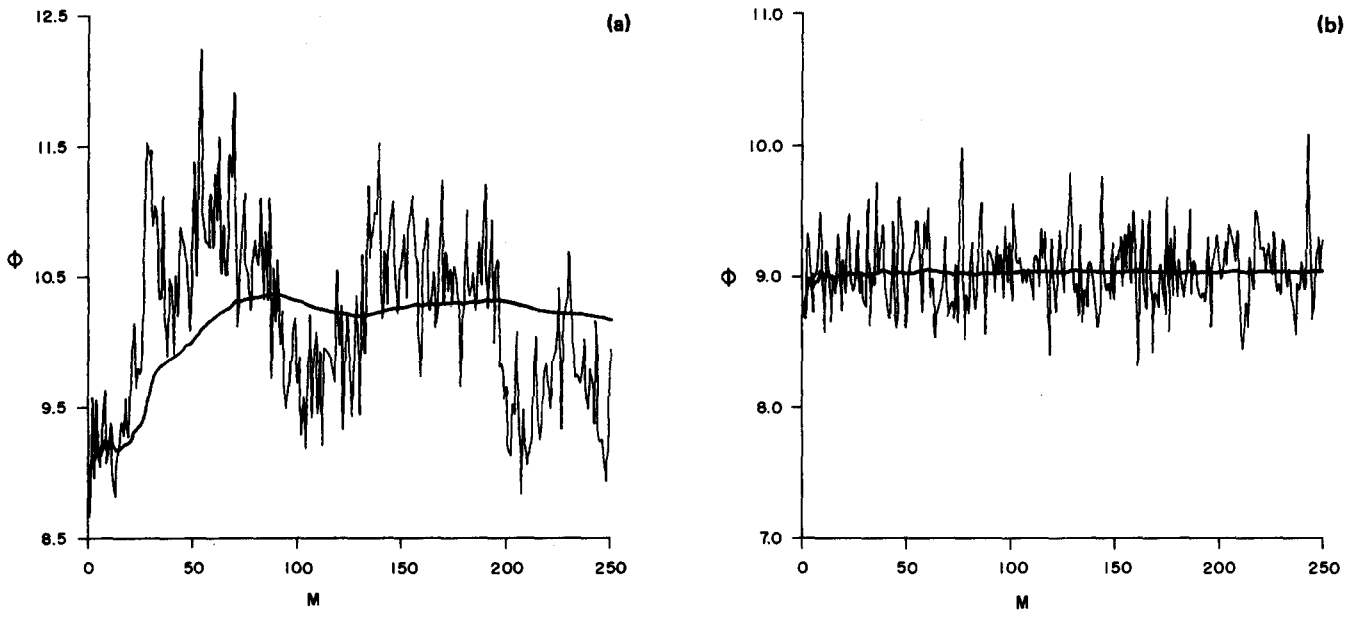

FIG. 1. (a) Evolution of the average pressure; $\tau = 1.29$ and $M = 250$ for $\beta\mu' = 0.0$. Heavy line: reduced pressure evolution. Light line: reduced pressure ϕ_r. (b): Same for $\beta\mu' = 1.5$.

less than 1% in our case[30,31] at $\tau = 1.4$—we use the Erpenbeck–Luban[30] result in order to foretell μ' roughly for each τ. Indeed for too small $\beta\mu'$, increasing ergodicity difficulties are observed, as τ decreases from 1.4 toward the transition region. On the other hand, for too large $\beta\mu'$ the relaxation to equilibrium is very sluggish. In the Figs. 1 and 2 we show the evolution of the reduced pressure average for $\tau = 1.29$ and 1.40, respectively. In the former is shown the result for $\beta\mu' = 0$ and 1.5; in the latter, $\beta\mu' = 1.5$ and 15.0.

In the interval of confusion, $1.29 < \tau < 1.36$, strong fluctuations determine a very poor estimate of the canonical ($\beta\mu' = 0$) average pressure. Fluctuations in this case should be a natural consequence of the finite size of the system, determining persistent transitions between the solid and fluid phase, but, eventual topological traps—presumably occasioned by representative configurations concerning nucleation of (dense or loose) random packing—introduce spurious bias toward higher pressure, as suggested by Fig. 1(a). Indeed, for any case of packing, ordered, or random, each particle touches several others. Thus, if eventually a particular configuration with a significant fraction of disks near enough to random packing one is reached, it can stay in

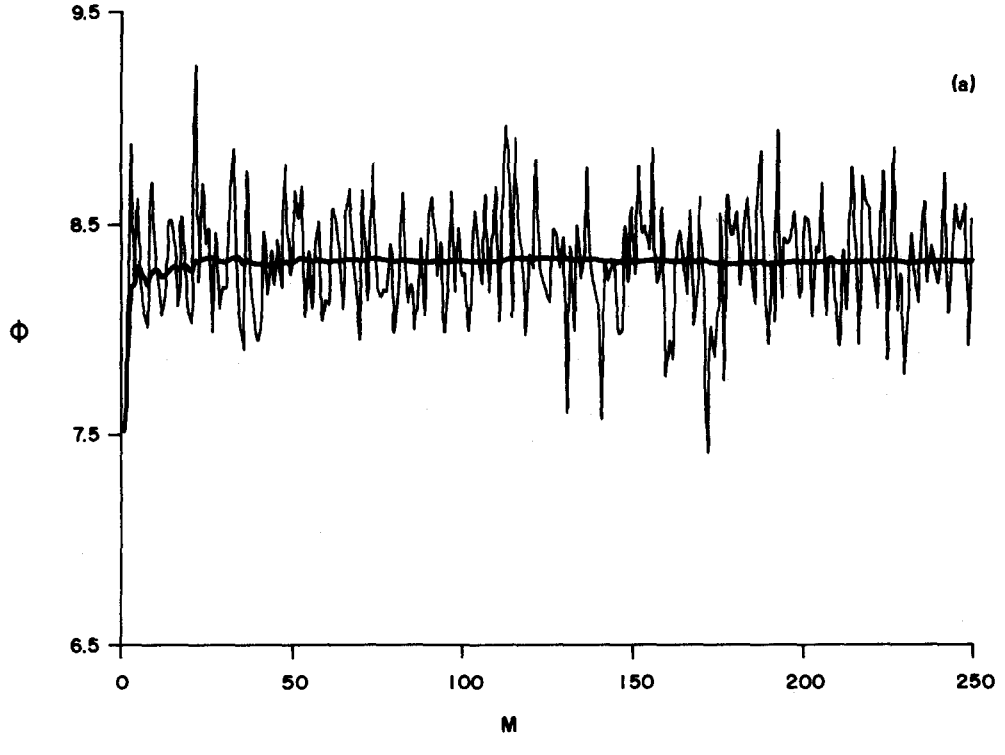

FIG. 2. (a) Evolution of the average pressure; $\tau = 1.40$ and $M = 250$ for $\beta\mu' = 1.5$. Heavy line: reduced pressure evolution. Light line: reduced pressure ϕ_r. (b): Same for $\beta\mu' = 15.0$

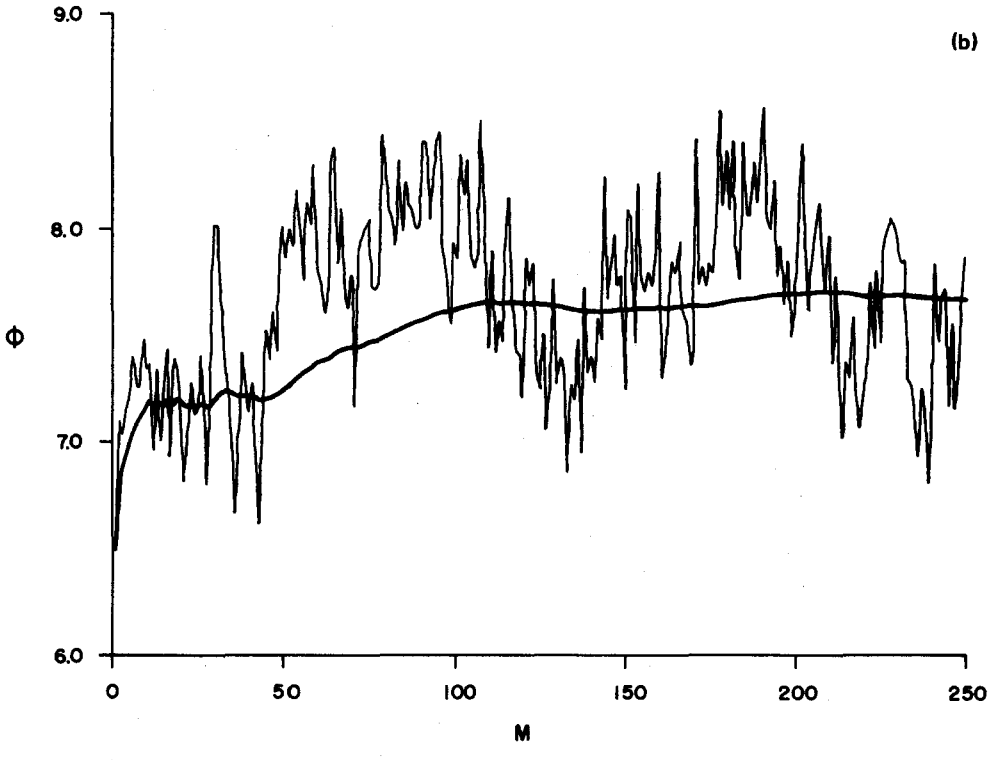

FIG. 2. (*continued*).

such classes of configurations for a long "time," characterizing in this way the manifestation of ergodic difficulties.

With the application of the MGC procedure, the nucleation (fading) of such clusters of random packing is made difficult (facilitated) by the requirement of homogeneity, induced by the method. Figure 1(b) shows explicitly how quick the equilibrium is reached.

For too large $\beta\mu'$ the system behaves as a collection of cells juxtaposed, each one with (practically) four disks—since, in this case, the disks cannot easily escape from the cells. Thus, except by influences of exotic boundary conditions on each cell, one should expect, for the evolution of the average pressure, similar behavior with respect to small systems with $\beta\mu' = 0$. However, as one can observe in Fig. 2(b), for $\beta\mu'$ too large the impoverishment of the estimates is determined by the increase in the correlations among the configurations generated (keeping $\Delta = 5$) producing a kind of modulation on the average.

We extended the calculation for the case $\tau = 1.4$ for several values of $\beta\mu'$ with $M = 250$ and the interesting result is exhibited in the Fig. 3 plotting $\phi \times \beta\mu'$. We can identify clearly at least two distinct regions: $\beta\mu' < 5.0$ and $\beta\mu' \geqslant 5$.

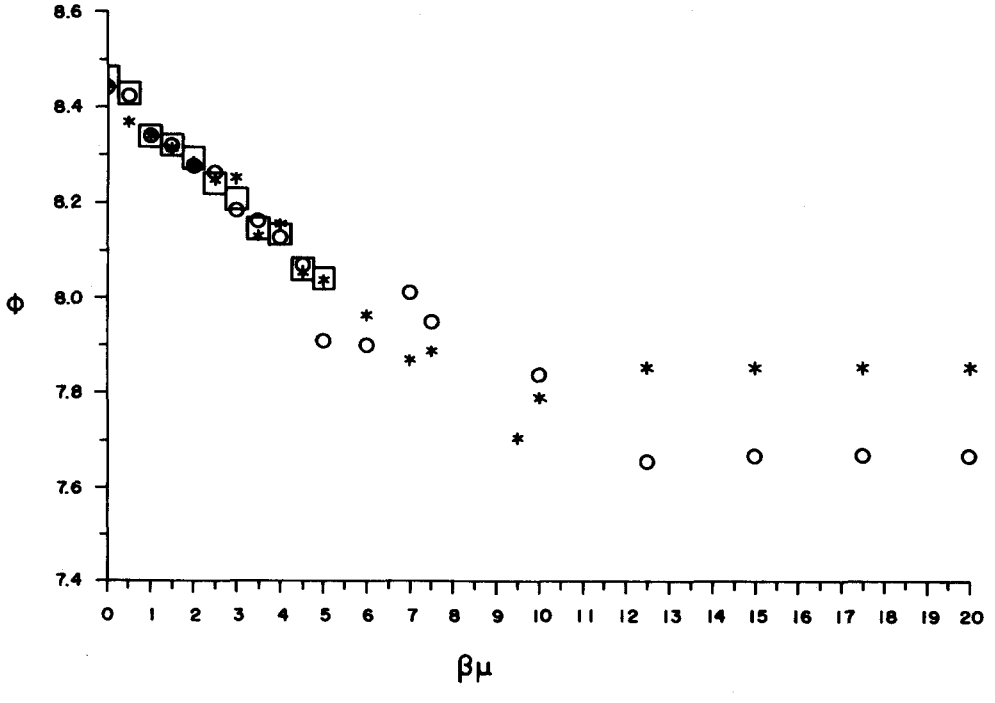

FIG. 3. Pressure as function of $\beta\mu'$ for $\tau = 1.4$. Circles, stars, and boxes correspond to calculated values for three distinct initial conditions (different seeds). The accuracy is discussed in the text.

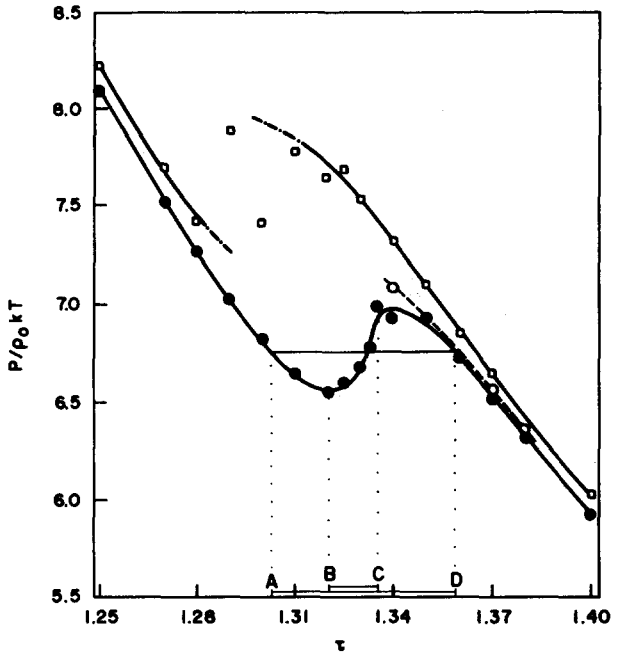

FIG. 4. Reduced pressure ϕ against reduced volume τ. The dots represent the reduced pressure for $\beta\mu' = 1.5$. The open ones, adjusted by the dashed line, represent two-step relaxation. Open squares represent the reduced pressure for $\beta\mu' = 0.0$. The dash–dotted line segments indicate a region of canonical average with a poor estimate. The accuracy is discussed in the text.

While in the region of smaller values for $\beta\mu'$ the accuracy of the estimates were typically within 1% (Note the remarkable independence of the relaxed pressure values with respect to the initial conditions for values of $\beta\mu' = 1.0$, 1.5, and 2.0), in the other extreme region, the average pressure suffers severe influence of the initial conditions. This can be understood through a direct inspection of Fig. 2(b), which revels (for $\beta'\mu = 15.0$) the strong correlation among the consecutive configurations generated, ruining the meaning of the error estimate.

In Fig. 4, we show the results for the pressure ϕ against τ for $\beta\mu' = 0$ (open squares) and 1.5 (full dots). The continuous curve drawn for τ between 1.25 and 1.40, for the case $\beta\mu' = 0$ (i.e., reducing our approach to canonical ensemble MC procedure), shows two disconnected branches, namely, the high- and low-pressure branches.[9] The dash–dotted line segments indicate a region ($1.28 < \tau < 1.31$) of canonical average that is very poorly estimated. For $\beta\mu' = 1.5$ the continuous curve drawn through the full dots reproduces a van der Waals-type loop for a finite system, as first found by Alder and Wainwright.[6] The open dots (dashed line) represent two-step relaxation with the manifestation of a long-living metastable state.[32] The pressure reaches equilibrium at values indicated by the open dots, then a sudden jump occurs and the pressure relaxes at lower values (corresponding full dots).

In Fig. 5 we show the pressure evolution for $\tau = 1.34$ and $\beta\mu' = 1.5$. It is important to note that the transition does not occur directly from the set of configurations corresponding to the first plateau, to the set of configurations corresponding to the second plateau. An analysis of the individual contribution to average pressure, Fig. 6, reveals that configurations concerning much lower pressure are visited before the set of configurations corresponding to the second plateau is reached.

The probability distribution $p(\phi)$ was verified as being approximately Gaussian with a bigger width for τ between 1.31 and 1.35. Those cases with $\tau < 1.335$ presented a longer tail toward higher pressure and the opposite (longer tail toward lower pressure) was observed for $\tau > 1.335$. The tails disappear for $\tau < 1.29$ and $\tau > 1.36$. The accuracy of estimates for the average pressure were typically within 1%, but in a few cases ($\tau = 1.33$ to 1.34) were within 2%. Different

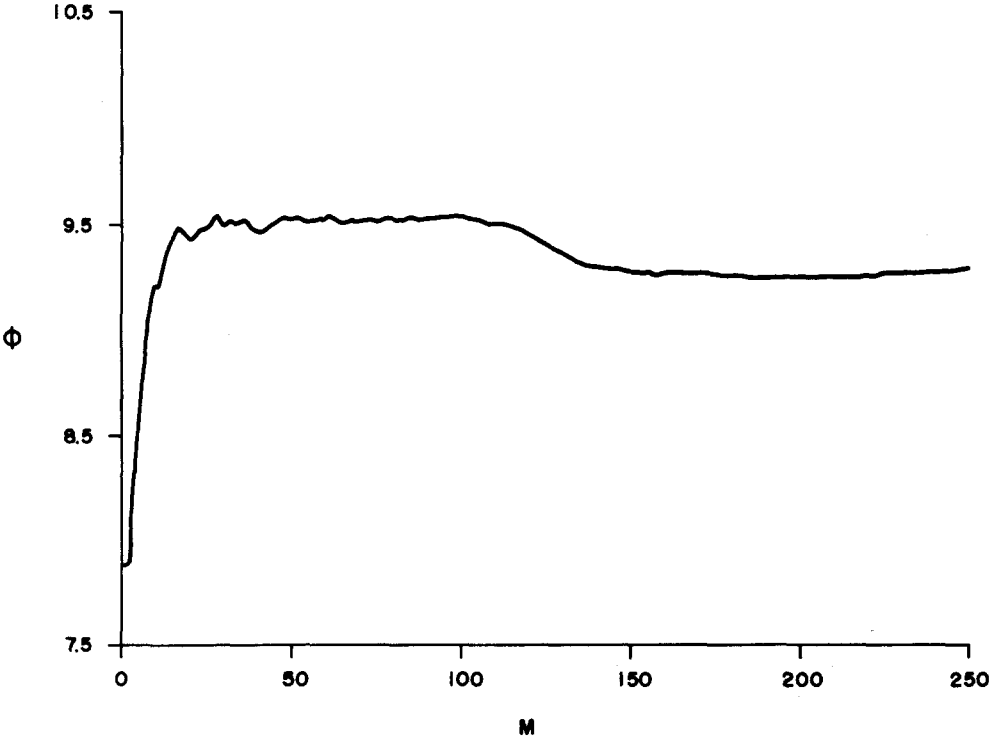

FIG. 5. Two-step relaxation behavior; $\tau = 1.34$ and $\beta\mu' = 1.5$.

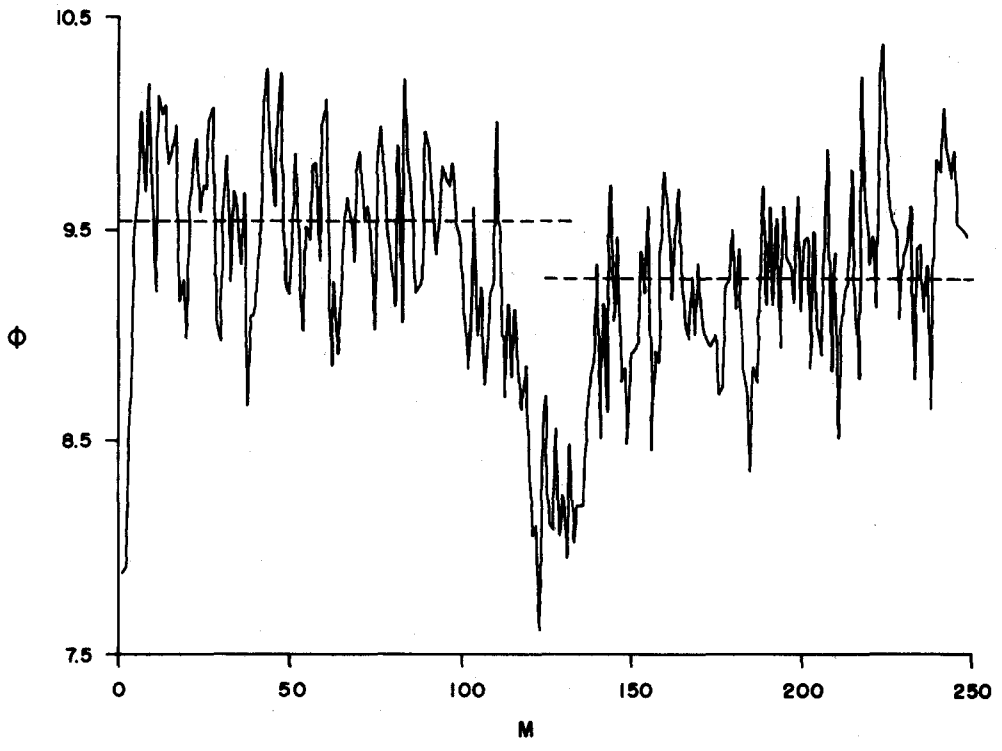

FIG. 6. Individual contribution to the pressure for $\tau = 1.34$ and $\beta\mu' = 1.5$.

values for M and the initial discarded length were used depending on τ. For a few cases, as $\tau = 1.3325$, 1.34, and 1.35 special attention was paid when the total number of configurations generated reached 50×10^6 ($M = 800$).

Finally we discuss the meaning of the van der Waals-type loop. In a truly μVT-ensemble calculation, the region of two-phase coexistence, approximately the length of the horizontal line in Fig. 4 (segment AD), is a "forbidden region" for the corresponding densities. If simulation is forced to go on in this region,—as we really did by imposing the conservation law $dN/dt = 0$—the relaxed states obtained cannot correspond to a thermodynamic equilibrium state; they are rather, long-living metastable states. In the Fig. 7 we sketch what should be expected for the pressure in a truly μVT-ensemble: starting the simulation from low-density (higher values of τ) the system may reach and stay on the metastable liquid branch (dashed line) until it nucleates (or reaches some limit of stability—point "1") and jumps to the stable solid branch, above the freezing density, represented by τ_1. The opposite, i.e., from high to low density direction, system tries to stay on the solid branch to as high value of τ as possible, than, jump to the stable liquid branch below the melting density, represented by τ_2.

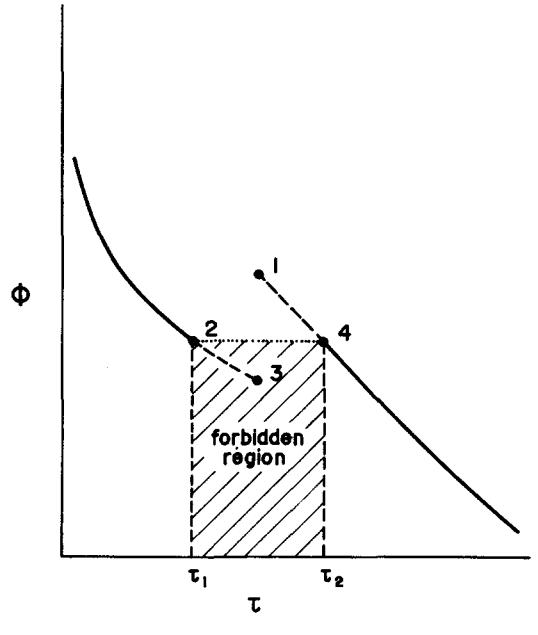

FIG. 7. Schematic function of state in the grand canonical (μVT) ensemble. The continuous lines describe solid and liquid states. The dashed line segments indicate metastable states with points "1" and "3" representing limits of stabilities. The points "2" and "4" correspond to a unique set of parameters at which the pressure of the solid equals the pressure of the liquid, at the same temperature and chemical potential, and so locates the phase transition point.

On the other hand in a NVT-ensemble calculation the allowed co-existence of phases introduces an extra contribution to the free energy: besides the bulk pure phases contribution, the interfacial contribution must be included. For each density the condition of extreme (minimum) over the free energy determines the interface shape and size. Thus the resulting isotherm is found to have loops.[33]

In the MGC-ensemble calculation, the coexistence of phases is not totally exclude, but rather its occurrence is limited to a smaller interval of densities—segment BC in Fig. 4. Then, the existence of the loop is due to both: long-living metastable states and the small interval of densities where the method did not succeed to eliminate completely the co-existence of different phases.

ACKNOWLEDGMENTS

The authors are grateful to Dr. R. V. Calheiros from IPMET-Bauru, SP, for computational facilities. Part of this

work has been supported financially by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP).

During the last part of this work, financial support through a special credit from CNPq, as well the friendly hospitality of Dr. O. Baffa Filho, at FFCLRP/USP-Ribeirão Preto, SP, was crucial. For all that, one of us, A. C., is fully acknowledged.

[1]M. A. A. da Silva, A. Caliri, and B. J. Mokross, Phys. Rev. Lett. **58**, 2312 (1987).
[2]S. Jasty, M. Al-Naghy, and M. de Llano, Phys. Rev. A **35**, 1376 (1987).
[3]M. Ross and B. J. Alder, Phys. Rev. Lett. **16**, 1077 (1966); C. S. Cargil J. Appl. Phys. **41**, 2289 (1970).
[4]N. J. A. Sloano, Sci. Am. **116**, Page (1984).
[5]J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 584 (1976).
[6]B. J. Alder and T. E. Wainwright, Phys. Rev. **127**, 359 (1962).
[7]W. G. Hoover and F. H. Ree, J. Chem. Phys. **49**, 3609 (1968).
[8]A. Rotemberg, New York University Report No. *NYO-1480-3, 1964 (unpublished).
[9]W. W. Wood, in *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbroke (North-Holland, Amsterdam, 1968), Chap. 5, p. 176.
[10]D. Levesque, J. J. Weis, and J. P. Hansen, in *Monte Carlo Method in Statistical Physics*, edited by K. Binder (Springer, Berlin, 1978), Chap. 2, p. 62.
[11]W. W. Wood and J. D. Jacobson, J. Chem. Phys. **27**, 1207 (1957).
[12]J. G. Berryman, Phys. Rev. A **27**, 1053 (1983).
[13]J. Hansen and L. Verlet, Phys. Rev. **184**, 151 (1969).
[14]K. F. Herzfeld and M. G. Mayer, J. Chem. Phys. **2**, 38 (1934); see also Ref. 15.
[15]L. Tonks, Phys. Rev. **50**, 955 (1936).
[16]K. H. Huang, *Statistical Mechanics* (Wiley, New York, 1963), Chap. 8, p. 168 and p. 321.
[17]D. J. Adams, Mol. Phys. **28**, 1241 (1974).
[18]M. Creutz, Phys. Rev. Lett. **50**, 1411 (1983).
[19]See Ref. 10, Chap. 10 and Ref. 9, Chap. 5.
[20]W. W. Wood, J. Chem. Phys. **48**, 415 (1968).
[21]W. W. Wood, J. Chem. Phys. **52**, 729 (1970).
[22]I. E. Farquhar, *Ergodic Theory in Statistical Mechanics* (Interscience, New York, 1964), p. 37.
[23]H. Furukawa and K. Binder, Phys. Rev. A **26**, 556 (1982).
[24]L. D. Fosdick, Methods Comput. Phys. **1**, 295 (1963).
[25]N. Metropolis, A. W. Rosembluth, M. N. Rosembluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).
[26]H. L. Anderson, J. Stat. Phys. **43**, 731 (1986).
[27]H. Muller-Krumbhaar and K. Binder, J. Stat. Phys. **8**, 25 (1973).
[28]M. Rao, C. Pangali, and B. J. Berne, Mol. Phys. **37**, 1773 (1979).
[29]W. Chapman and N. Quirke, Physica, B **131**, 34 (1985).
[30]J. J. Erpenbeck and M. Luban, Phys. Rev. A **32**, 2920 (1985).
[31]W. G. Hoover and B. J. Alder, J. Chem. Phys. **46**, 686 (1967).
[32]D. P. Landau and K. Binder, Phys. Rev. B **17**, 2328 (1978).
[33]J. E. Mayer and W. W. Wood, J. Chem. Phys. **42**, 4268 (1965).