Phase Transition in a System of Hard Disks by Monte Carlo Simulation

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The discrepancy shown by the methods of Monte Carlo and molecular dynamics in hard-disk systems concerning the solid-liquid coexistence region is analyzed. Using a system containing 224 disks we were able to obtain the van der Waals–type loop curve which has so far only been obtained by the molecular-dynamics procedure for 870 hard disks. This result is due to an improvement in the choice of the most representative configurations in the Monte Carlo procedure.

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Recently, improved simulations of Monte Carlo (MC) and molecular dynamics (MD) simulations have provided data with accuracy of 1 part in 10^4 for the equation of state of the classical hard-disk fluid system,[1] when $\tau=\rho_0/\rho$ ranges from $\tau=1.4$ to 30, where ρ is the number density and ρ_0 refers to the closest-packing configuration. However, when τ is reduced the same accuracy is not easily achievable and, in fact, for $\tau\simeq 1.32$ it has been shown[2] that a system of 870 hard disks undergoes a freezing transition. The fluid-solid transition was located by the observation of a van der Walls–type loop at $1.26\lesssim\tau\lesssim 1.32$, by means of the MD procedure. Further extensive MC calculations were carried out[3,4] and the van der Waals loop could not be reproduced, presumably because of the lack of completeness of the averaging over all admissible configurations at any one density on the loop. In this Letter this disagreement is reconsidered and we show in what way it is possible to reproduce the van der Waals–type loop for 224 hard-disk systems, recovering a few characteristic results of the successful MD simulation for the 870–hard-disk system.[2]

The basic idea of the improvement presented here is to make use, in a peculiar way, of the important sampling technique[5] introduced by Metropolis *et al.*,[6] but (ironically) never fully used in their simulation of the hard-disk system.

In order to reach adequate chain length, keeping in mind an economical use of computer time, we take advantage of the very short-ranged potential, and instead of examining all $N-1$ interactions of the displaced disk with the other disks, we consider only some much smaller class of neighbors. However, the gist of our method (still) is to seek, among all configuration of a canonical ensemble, the most representative configurations. Although it is clear that certain classes of configurations are more important than others, on the strength of having more elements, the game of chance on $\exp(-\Delta E/kT)$ is inefficacious since all configurations with nonoverlapping hard disks have the same weight ($\Delta E=0$ for any move). In fact, it seems that in the interval of confusion, $1.29<\tau<1.36$, the disks are susceptible to being captured by topological traps, and hence the consequent manifestation of ergodic difficulties.[4]

The method presented here has the same aim as the method used by Hansen and Verlet[7] in the case of a Lennard-Jones system, i.e., to inhibit density fluctuations by constraining the system to remain fairly homogeneous in the transition region.

Let us start by considering an arbitrary large system of volume V, containing N particles. 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 N/r particles. If we consider a particular cell c_n, the equilibrium value $\langle A\rangle$ of any intensive quantity A of interest may be expressed by

$$\langle A\rangle_c=\frac{\sum_{(s)}A(s)\exp[-\beta(E_s-\mu N_s)]}{\sum_{(s)}\exp[-\beta(E_s-\mu N_s)]}, \tag{1}$$

where the subscript c in $\langle A\rangle_c$ stands for cell ensemble averaging and the sum runs over the set of all states: $\sum_{(s)}\equiv\sum_{N_s}\int\{dq\}$ (state being defined here by a given point in the configuration space, spanned by all canonical coordinates of systems with $0,1,2,\ldots$ particles); $\beta=1/kT$ where k is the Boltzmann constant and T is the absolute temperature, and μ is the excess chemical potential measured relatively to μ_0 of a perfect gas with the same particle mass, density, and temperature.[8,9]

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:

$$\{\mathbf{X}_k\}_V=\{\mathbf{x}_i\}_{c_1}\otimes\{\mathbf{x}_j\}_{c_2}\otimes\cdots\otimes\{\mathbf{x}_p\}_{c_r}. \tag{2}$$

Thus, a particular point $\mathbf{X}_k$ in the modified configuration space is given by our choosing a particular state from each cell and multiplying them. Because of the macroscopic size of the cells, the cell grand-canonical ensemble average $\langle A\rangle_c$ is identical to the modified canonical ensemble average $\langle A\rangle_v$, i.e., $\langle A\rangle_c=\langle A\rangle_v$. Note that, in spite of the fluctuation of the number of particles n_i in each cell, we have imposed the conservation law $\sum_{n_i}=N$ with $dN(t)/dt=0$.

Our MC procedure follows the steps outlined above,

i.e., 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. (2), using transition probabilities

$$T_{ij}=T_{ij}((\mathbf{x}_i)_{c_a}(\mathbf{x}_i)_{c_d}\in\mathbf{X}_i\rightarrow(\mathbf{x}_j)_{c_a}(\mathbf{x}_j)_{c_d}\in\mathbf{X}_j)$$

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 to j due to a single move of a particle, for instance, belonging to cell c_d (donor cell) which goes to another cell c_a (acceptor cell).[10] Therefore, at most two cells may be involved in the transition $\mathbf{X}_i\rightarrow\mathbf{X}_j$ and the space $\{\mathbf{X}_k\}_v$ is explored by walking through the phase space $\{\mathbf{x}_i\}_c$ for all cells.

In order to define quantitatively T_{ij} for a system of hard disks we concern ourselves initially with the construction of the transition probabilities $W_c((\mathbf{x}_i)_{c_p}\rightarrow(\mathbf{x}_j)_{c_p})$, from one point $(x_i)_{c_p}$ in the phase space of the cell c_p to another one $(\mathbf{x}_j)_{c_p}$ in the following way: $W_c=\min[\exp(-a),1]$ where $a=\beta(\Delta E-\mu n_{ij})$. The quantity ΔE is the change in energy of the system, i.e., $\Delta E=0$ or ∞, and $n_{ij}=n_j-n_i$ where n_j is the number of particles in the state $\mathbf{x}_j$. Therefore, the probability to have simultaneously two specific configurations in the cells c_a and c_d, relatively to a configuration $(\mathbf{x}_0)_c$ with $(n_{c_a}+n_{c_d})/2$ particles taken as reference, is

$$P_i=W_c((\mathbf{x}_0)_c\rightarrow(\mathbf{x}_i)_{c_a})W_c((\mathbf{x}_0)_c\rightarrow(\mathbf{x}_i)_{c_d}).$$

T_{ij} is therefore defined as $\min(P_j/P_i,1)$, which assumes the values 0, $\exp(-\beta\mu)$, or 1.

We used $N=224$ initially in a trigonal lattice and divided the initial volume into 56 smaller boxes, each one containing four disks. The conventional periodic boundary condition was used on the bigger box. In order to make the transitions from one cell to others with a higher number of disks even more difficult, an extra bias was used, i.e., we convert μ into $\mu\Delta n$ in the exponential above. Δn is the difference between the number of disks in the acceptor and donor cells after and before the move, respectively. Thereby our aim was to calculate the average number $\bar{n}$ of disks which surround each one, enabling us to write the equation of state[6]: $\phi=P/\rho kT=(1+\pi d_0^2\bar{n}/2)$, where 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

$$\phi_k=\frac{\Delta}{m}\sum_{i=p_k(\Delta)q_k}\phi(t_i), \tag{3}$$

where $\phi(t_i)$ is the reduced pressure due to the ith-generated configuration, $P_k=m(k-1)+1$, $q_k=mk$ and $p_k(\Delta)q_k$ meaning "from p_k to q_k with increment of Δ MCSS," i.e., Δ MCSS are discarded between each two $\phi(t_i)$ considered. In order to get better statistically independent configurations, $\Delta=5$ was used for both cases, i.e., $\mu=0$ and $\mu\neq0$, giving therefore a meaningful error estimate.[11] The MC estimate for the average $\langle A\rangle$ then reduces to

$$\bar{\phi}=\frac{1}{M}\sum_{k=1}^{M}\phi_k. \tag{4}$$

In Table I we list the values of the equation of state for a few values of τ and μ,[12] together with results from MCMD calculations.[1] We did not investigate the dependence of μ on the system size and number of subunits. However, since the pressure in the fluid phase should not be affected strongly by these parameters —less than 1% in our case[1,13] at $\tau=1.4$— we use the Erpenbeck-Luban[1] result in order to foretell μ roughly for each τ. For too small μ, increasing ergodicity difficulties are observed, as τ decreases from 1.4 toward the transition region. On the other hand, for too large μ the relaxation to equilibrium is very sluggish. Indeed, the values of μ which bring the pressure near to MCMD results[1] are those which make the pressure to reach equilibrium faster. The dependence of μ on the system constraints will be the subject of future work.

In Fig. 1, we show the results for the pressure against τ for $\beta\mu=0.0$ (open squares) and $\beta\mu=1.5$ (full dots). The continuous curve drawn for τ between 1.25 and 1.40, for the case $\beta\mu=0.0$ (i.e., reducing our approach to the canonical-ensemble MC procedure), shows two disconnected branches, namely, the high- and low-pressure branches.[4] 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.[2] Our results for the location and equilibrium pressure at the melting transition, the horizontal line in Fig. 1, cannot be compared to the results obtained by Alder and Wainwright since the dependence on the system size and chemical potential have not been clarified. The open dots (dashed lines) represent two-

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 the 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 $\tau\rightarrow\infty$, $\beta\mu\rightarrow0$.

		$\beta\mu$				
τ	Erpenbeck and Luban[a]	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 1.

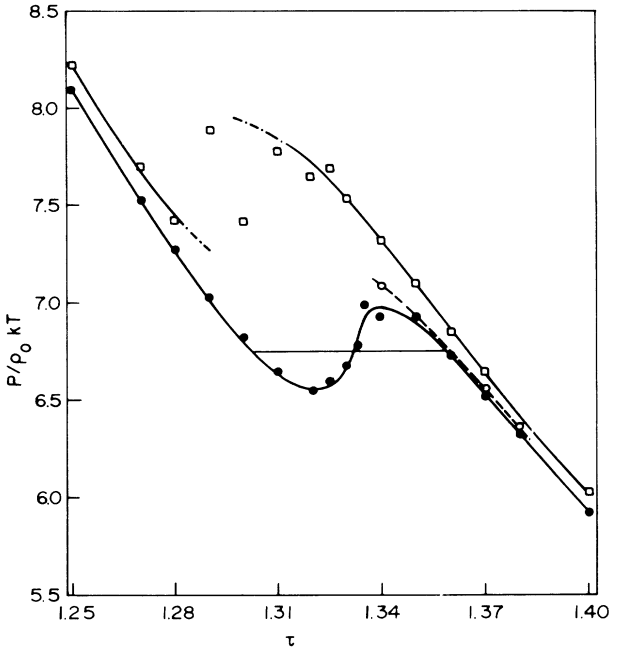

FIG. 1. Reduced presure ϕ against reduced volume τ. The dots represent the reduced pressure for $\beta\mu = 1.5$. The open ones, adjusted by the dashed line, presented "two-step" relaxation. Open squares represent the reduced pressure for $\beta\mu = 0.0$. The dash-dotted line segments indicate a region of canonical average with a poor estimate. The accuracy is discussed in the text.

step relaxation with the manifestation of a long-living metastable state[14]: 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).

The probability distribution $p(\phi_k)$ 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 the estimates for the average pressure were typically within 1%, but in a few cases ($\tau = 1.33$ to 1.34) were within 2%. Different 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 ($M = 800$).

The main consequence of the approach described above is to restrain the progression of configurations which result in distributions too far away from uniform ones. Therefore, the chance of the system's being captured by topological traps is reduced in a significant way.

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