RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 46, NUMBER 17 1 NOVEMBER 1992-I

First-order melting transition of the hard-disk system

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(Received 4 June 1992)

We present a very strong evidence for a first-order melting transition in the hard-disk system by exploiting the finite-size scaling of the bulk free-energy barrier. We use isobaric Monte Carlo simulations to allow fluctuations in the volume of the system, which lead, in the presence of a first-order transition, to a double-peaked structure in the volume distribution. We also find that the system melts directly from a two-dimensional solid with long-range orientational order to an isotropic liquid with no intervening hexatic phase.

The nature of the two-dimensional melting transition[1] has been a matter of hot controversy for the past two decades. Halperin and Nelson, and Young[2] (following the basic ideas of Kosterlitz and Thouless, and Berenzinskii[3]) demonstrated the possibility that the transition between two-dimensional solid and isotropic liquid can occur via two second-order transitions corresponding, respectively, to dissociation of dislocations and disclinations. The low-temperature solid phase is characterized by algebraic decay of translational order (long-range translational order is absent in two-dimensional solids) and long-range bond-orientational order. The intermediate phase displays exponential decay of translational order and algebraic decay of bond-orientational order and is called the hexatic phase. A conventional first-order transition between the two-dimensional solid and isotropic liquid is also a possibility.

Even for a very simple system like hard disks, the issue of the order of the melting transition has not been previously settled. Conventional methods for identifying the order of a phase transition in computer simulations have not been very successful as they are subject to ambiguity. As an example, observation of hysteresis has often been invoked as evidence for a first-order transition but hysteresis depends strongly on system sizes and the heating and cooling rates. A systematic analysis of size dependence is required to determine the nature of the melting transition. However, previous approaches[4] to analyzing the size dependence have not led to conclusive results.

In this paper, we present, from isobaric Monte Carlo (MC) simulations, very convincing evidence for a first-order melting transition in the hard disk system. We follow the finite-size scaling method of Lee and Kosterlitz.[5]

We consider $N=L^2$ hard disks of radius $\frac{1}{2}$ in a two-dimensional box of volume $V=\sqrt{3}/2L^2v$, where $v\geq 1$ is the reduced volume and $v=1$ corresponds to the most compact state. The density of the system is simply related to v as $\rho=N/V=2/\sqrt{3}v$. We imposed periodic boundary conditions on the system and the aspect ratio of $2/\sqrt{3}$ was chosen to fit the perfect triangular lattice. The partition function of the system can be written as[10] $Z(\beta,p)=\mathrm{Tr}V^N\exp\{-\beta[pV+\sum_{\langle i,j\rangle}U(i,j)]\}$, where p is the pressure of the system, $\beta=1/kT$, and $U(i,j)$ ($=0$ for $|i-j|\geq 1$, infinity otherwise) is the pair-potential energy of hard disks. The sum is over all pairs. Since the only allowed potential energy for the system is zero, $p^*\equiv\beta p$ enters as a single effective parameter, which controls the volume of the system. The partition function now can be written as $Z(p^*)=\mathrm{Tr}'\exp(N\ln V-p^*V)$, where Tr′ represents a sum over all possible configurations satisfying the hard-disk potential. It is easy to see that small p^* will lead to large v corresponding to an isotropic (disordered) phase and large p^* will compress the system to $v\rightarrow 1$. The high-p^* phase is a two-dimensional solid, which has long-range bond-orientational order but translational disorder. Therefore we expect that the two-dimensional solid will melt for intermediate p^*. Should the transition be first order, the volume of the system will show a discontinuity at $p^*=p_c^*$ in the thermodynamic limit. Since the obvious choice for the order parameter is the volume of the system, which is a kind of conjugate variable to p^*, we allow the system to change its volume during the process of the simulation.

We performed constant pressure (actually constant $p^*=p/kT$) MC simulations in which each step consisted of the following two parts: (1) The rearrangement of the hard disks through individual particle moves. The trial movement of each disk is chosen as a combination of random changes of position in both x and y directions with fixed maximum amplitude. Only movements satisfying $|i-j|\geq 1$ for all pairs (i,j) are accepted. We find that a maximum amplitude of 0.09 gives about a 45% acceptance rate. (2) A random isotropic change of the volume of the system. If the distance between any two disks gets smaller than 1, the trial is always rejected. If the trial volume V' is smaller than the present volume V, it is always accepted. Larger volume is accepted with probability $\exp[-p^*(V'-V)+N\ln(V'/V)]$, which is less than 1 for the interesting range of $p^*=7-8$. Volume changes were attempted 40–200 times for each set of individual disk moves. For convenience in data storage we discretized the volume in advance. The mesh size was chosen to get a 40–50% acceptance rate for changing the volume by one unit.

In the hard-disk system the volume plays a role analogous to that of internal energy in the usual temperature-

driven first-order transitions of statistical systems. Therefore, if the system undergoes a first-order transition, in the thermodynamic limit we expect the distribution of volume $N(v)$ at the critical value p_c^* to consist of two δ functions located at the corresponding bulk values. However, for finite systems the two δ functions will be rounded, and instead we will observe a double-peaked structure $N(v)$ near an effective critical pressure $p_c^*(L)$, which is shifted from p_c^*.

The Lee-Kosterlitz method[5–9] has been very successful in identifying very weak first-order transitions even with available system sizes much less than the correlation length ($L<0.05\xi$). The basic idea of the method is as follows: Whether the double-peaked structure in a histogram of the order parameter is an artifact of finite system size can be determined by observing the size dependence of the bulk-free-energy barrier ΔF (corresponding to the excess free energy of an interface between competing states). Under the assumption that L is sufficiently large so that irrelevant fields have scaled away so that the only fields left are those relevant at the critical point, the Lee-Kosterlitz method constitutes an unambiguous method of numerically detecting a first-order transition. Right at a critical point, ΔF remains independent of system size. Near the critical point it increases (decreases) as $gL^{1/\nu}$ for first-order (continuous) transition, where g measures the distance from the critical point and ν is the correlation length exponent along the g direction. ΔF diverges as L^{d-1} for strong first-order transitions ($\xi \gg L$).

We performed about 10^7 MC steps as described above, for various system sizes $L=10,12,14,16,20$. Indeed we find a double-peaked structure in $N(v)$ for $L=10$ near $p=7.29$ as shown in Fig. 1. To measure $\Delta F(L)$ the logarithm of $N(v)$ was smoothed by fitting with an eighth-order polynomial and extrapolating using the histogram method[11] to $p_c^*(L)$ defined as the pressure for which the two peaks are of equal height. In Fig. 2, we show ΔF as a function of L^{-1}. The monotonic increase in ΔF, signifying a first-order transition, is unambiguous as we increase the number of particles. We find that ΔF is increasing faster than L^{d-1}. For $L<\xi$, $\Delta F(L)$ increases (if the transition is first order) as $L^{1/\nu}$, where ν is a correlation length exponent in the extended parameter space. But

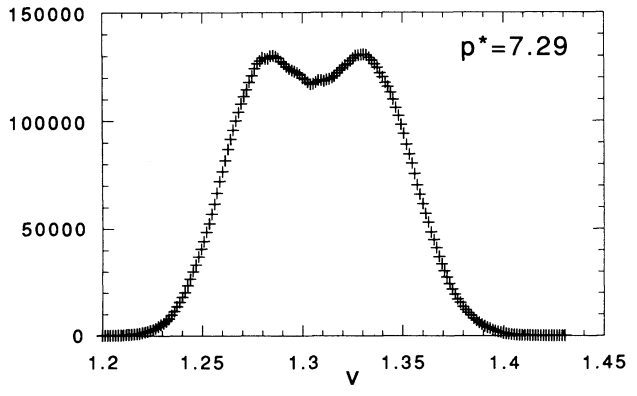

FIG. 1. $N(v)$ for $L=10$ after 10^7 MC steps. Simulations were carried on at $p^*=7.30$ and extrapolated to $p^*=7.29$, where double peaks are of equal height.

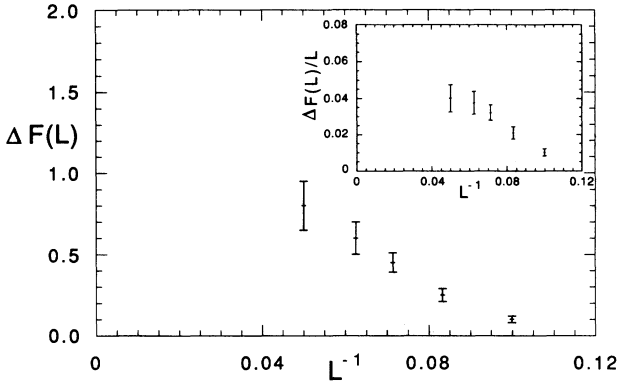

FIG. 2. ΔF vs L^{-1}. The inset shows that ΔF is increasing faster than L^{d-1} for small L. For larger L it seems to saturate to L^{d-1}.

for $L \gg \xi$, $\Delta F(L)$ will eventually cross over to L^{d-1}, as can perhaps be seen for the larger sizes in the inset of Fig. 2. We estimate the correlation length at the transition as $\xi \sim 25$ from[11] $\Delta F(L=\xi)=1$. System sizes were limited by the computing resources and increasing time scale for fluctuations, but we find that $10 \leq L \leq 20$ is sufficiently large to identify the hard-disk melting transition as first order.

Next we want to identify the two bulk states just below and above p_c^*. A common scenario for first-order melting is that as soon as the dislocations are dissociated they may expedite the excitation of unbound disclinations. Therefore, the existence of the first-order transition could be taken to imply that the transition is directly between solid and isotropic liquid. But, in principle, there exists the possibility of a first-order solid-hexatic transition. To investigate this matter, we performed fixed volume MC simulations at the volumes corresponding to the two competing phases, while computing the bond-orientational order parameter, which we define as $\psi_6^2=\langle |(1/N)\sum_l (1/n_l)\sum_j e^{6i\theta_{lj}}|^2 \rangle$, where the sum on l is over all particles, the sum on j is over nearest neighbors, n_l is the number of nearest neighbors of particle l, and N is the number of particles in the system. The Voronoi construction is necessary to define the nearest neighbors in a rigorous manner. However, a cutoff between the first two peaks of the pair-distribution function determines them adequately for our purpose.

As shown in Fig. 3, we find that the two competing states correspond to solid and isotropic liquid states, respectively. For the solid state, we find the peak position moves to larger values of the order parameter as system size is increased. This result is rather surprising but is consistent with the fact that ΔF is increasing faster than L^{d-1}. We note that for each system size the appropriate competing volumes are determined by the position of the peaks in $N(v)$ for that system size.

In order to apply the Lee-Kosterlitz method, the system must adequately sample both competing phases. However, with our present simulation algorithm, the time required to fluctuate between competing states increases surprisingly rapidly with system size. For exam-

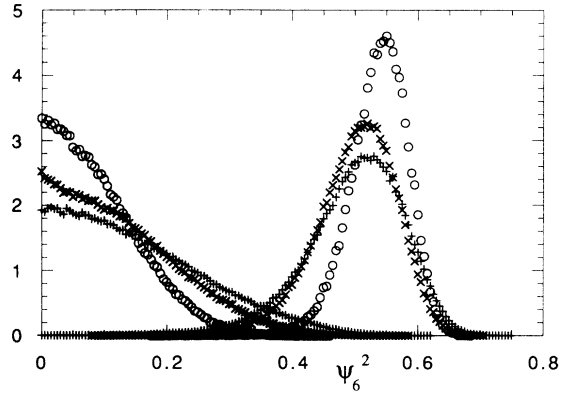

FIG. 3. Distribution of ψ_6^2 from fixed volume MC simulations at volumes corresponding to the peaks of $N(v)$ for $L=10$ (+), 12 (×), and 16 (○). The distribution is normalized after $(1-3)\times 10^6$ MC steps. It is clear that the two competing states correspond to a two-dimensional solid and an isotropic state.

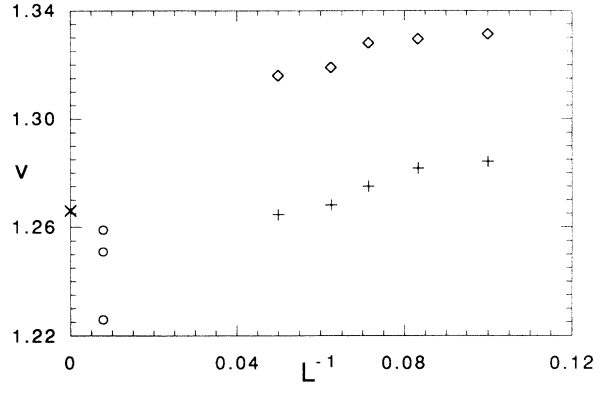

FIG. 5. Peak positions v_1 (+), v_2 (◇) at $p_c^*(L)$ vs L^{-1}. Errors are about the size of symbol. For comparison, we include the data points of Zollweg, Chester, and Leung (Ref. 14) (○). Their assumed value (Ref. 13) of $v_1(L=\infty)=1.266$ is also shown as ×. $v=1.259$ (and possibly $v=1.251$) seems to be inside the coexistence region.

ple, we observe only 4–5 jumps between solid and fluid for our largest size during 10^7 MC steps. We believe this inefficient sampling may be understood as a failure of importance sampling for the hard-disk system. For most interaction potentials, the Metropolis algorithm for a constant pressure simulation leads to importance sampling of both the many particle arrangements possible within a given volume and of the volume itself. In the hard-disk system, however, for a given volume the significant states are selected purely entropically from among those satisfying the hard-disk constraint. Thus importance sampling of the particle rearrangements is meaningless. In addition, the importance sampling of the volume is anomalous, since the probability distribution for volume fluctuations depends solely on the shortest distance between disks.

There exist no phase transitions in finite systems. But we can define various characteristic $p_c^*(L)$, all of which tend, as $L\to\infty$, to the bulk critical pressure p_c^* with finite-size corrections of $O(L^{-d})$ when $L\gg\xi$. For the given small system sizes, it is difficult to pinpoint p_c^* with accuracy, since we are not yet in the scaling regime. We roughly estimate $p_c^*\simeq 8.0$ from Fig. 4. An accurate estimate would simply require larger simulations.

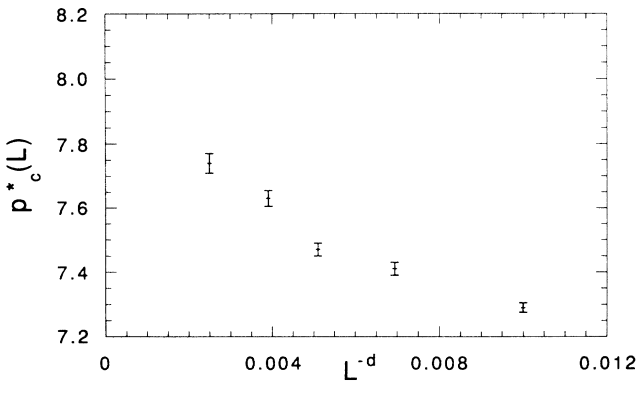

FIG. 4. $p_c^*(L)$ vs L^{-d}. For $L\gg\xi$ it should approach p_c^* with correction of $O(L^{-d})$. We roughly estimate the critical pressure as $p_c^*=8.0$, but one has to take it with caution, since the data are not in the asymptotic region yet.

We show our estimates of the competing volumes as a function of L in Fig. 5. These estimates should scale as L^{-1} for a strong first-order transition.[12] A previous estimate by Alder and Wainwright[13] of $v_1=1.266$ ($\rho_1=0.912$) is indicated as well. Even though our data are not in the scaling regime yet, it seems clear that the melting density is somewhat higher than previously believed. Thus the observation by Zollweg, Chester, and Leung[14] in very large simulations (up to $L=128$) of nonsolidlike behavior at $v=1.259, 1.251$ ($\rho_1=0.917, 0.923$) is perhaps not surprising. Zollweg and Chester[15] have recently performed further simulations of this very large system throughout the transition. Their observation of large pressure fluctuations leads them to suggest that the transition is continuous. However, we believe that our scaling analysis shows conclusively that, although the transition is weakly first order, it is first order.

A study of two-dimensional melting in more general potentials would be of great interest. In particular, the existence of a tricritical point in the (T,p) parameter space has been suggested for the Lennard-Jones system. Logarithmic and r^{-3} potentials would have potential relevance to recent experimental results on high-T_c superconductors[16] and magnetic bubble arrays.[17] The method presented here can be directly applied to those systems by measuring the appropriate order parameter. The efficiency of the simulation may be better for these systems, since importance sampling could be more effective.

In conclusion, we present a very strong evidence for a first-order phase transition in the hard-disk system by exploiting the finite-size scaling of the bulk free energy barrier between competing states, from which the intermedi-

ate states are shown to be an artifact of finite system size. We also find that the competing bulk states are two-dimensional solid and isotropic liquid. We present preliminary results for the finite-size behavior of the critical pressure and volume of each competing phase. More accurate results can be obtained only by simulating larger system sizes.

We are grateful to J. M. Kosterlitz, D. Kim, and K.-C. Lee for stimulating discussions. This work was supported by the U.S. Department of Energy under Contract No. W-31-109-ENG-38.

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