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Computer simulation of melting in a two-dimensional Lennard-Jones system

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The melting in a two-dimensional Lennard-Jones system is investigated by the molecular-dynamics technique. "Final-size" effects on the melting are analyzed by performing calculations for systems with up to 3600 particles. The phase transition is weakly first order, but analysis of the crystal shows that there is a weak increase in the density of crystal defects as the size of the system is increased. The defects appear in large loops just before melting. The size effect on the defects in the lattice will weaken the first-order transition further when the size of the system is increased.

I. INTRODUCTION

The properties of two-dimensional (2D) systems at high densities have been the subject of controversy for a long time. Originally, Peierls[1] and Landau[2] showed that conventional long-range order does not exist in such a "solid" system due to the long-wavelength phonons. However, despite the missing translational long-range order, orientational long-range order can still be present.[3] This exact result[3] only concerns the structure of the dense state and not the way in which it can be reached from the low-density fluid state, e.g., by performing phase transition(s). Recently, Halperin, Nelson,[4] and Young[5] (HNY) have derived a theory for the phase changes in 2D media in which they predict that if the melting is not of first order thermodynamically, then two second-order phase transitions are necessary to come from the isotropic low-density state to the high-density state with orientational long-range order.

On the other hand, 2D computer models show a first-order melting. Alder and Wainwright[6] first performed molecular dynamics (MD) calculations on 870 hard disks and found that the pressure isotherm exhibits a van der Waals loop when the system melts. Later Hoover and Ree[7] derived a method, the "single-occupancy method" (SO), to determine the free energy of the ordered solid state and calculated[8] the tie line between fluid and solid states with equal chemical potential. The melting pressure determined in this way agrees with the value obtained by Alder and Wainwright. Recently, a series of computer simulations[9–15] for various systems with soft repulsive potentials has confirmed this first-order behavior. The soft-disk systems exhibit such characteristics as hysteresis[9] and nonuniform solid-fluid particle distribution at the phase transition,[10–12] and the location of the observed transition agrees fairly well with the location of the calculated "tie line" between the fluid and solid of equal chemical potential.[13] On the other hand, the systems have properties which are (qualitatively) in accordance with the theory derived in Refs. 4 and 5.[12,15]

In the present article we report some very long and accurate MD calculations on systems of different numbers (N) of Lennard-Jones particles with N up to 3600, in order to investigate the melting mechanism and the influence of the size of the system on the phase transition. The calculations (see the Appendix) are performed for the temperature $kT/\epsilon=1$. This temperature is well above the 2D critical liquid-gas temperature, but on the other hand the attractive part of the potential is still important at this temperature.

II. LOCATION OF THE MELTING ZONE

The melting zone was located (dynamically) as the density zone in which the pressure isotherm exhibited a van der Waals loop. The loops were obtained by starting the system in a triangular lattice state at the density $\rho\sigma^2=(2/\sqrt{3})2^{1/3}\approx 0.9165$, and scaling the systems down to lower densities. The results of the calculations are given in Tables I and II and shown in Fig. 1. Both the small system of

TABLE I. Pressure and energy per particle for the $N=256$ Lennard-Jones system at $kT/\epsilon=1$.

$\rho\sigma^2$	$p\sigma^2/\epsilon$	u/ϵ	Number of time-steps (10^3)
0.5953	0.91	−0.620	10
0.6350	1.10	−0.744	10
0.7143	1.89	−0.960	10
0.7540	2.48	−1.072	10
0.7937	3.39	−1.163	10
0.8135	3.94	−1.196	10
0.8334	4.55	−1.232	10
0.8413	4.79	−1.248	10
0.8493	5.11	−1.256	80
0.8572	5.34	−1.279	10
0.8651	5.60±0.08	−1.30±0.02	50
0.8731	5.0±0.4	−1.43±0.04	50
0.8810	4.87	−1.495	10
0.8880	5.16	−1.494	35
0.8937	5.52	−1.501	10
0.9048	5.88	−1.521	10
0.9165	6.50	−1.528±0.002	14

256 particles (○) and the large system of 3600 particles (●) display a loop in the pressure iostherm; however, whereas the small system exhibits large pressure fluctuations in the melting zone, the pressure only fluctuates a little in the 3600-particle system and the loop is more smoothed out. The uncertainties in pressure and energy in the large system at melting were 0.04 and 0.005, and outside the loop the corresponding uncertainties in both systems were of the order 0.02 and 0.004, respectively. The systems exhibited hysteresis; when the large system was rescaled to a higher density the pressure converged very slowly to the equilibrium value, at the solid branch of the loop.

The melting zone was also located thermodynamically by calculating the points of fluid and solid states with equal chemical potential. In order to calculate the free energy and chemical potential of the solid state, we need to know the free energy of the solid in the (starting) state $kT/\epsilon=1$, $\rho\sigma^2=0.9165$. It was obtained by the SO technique as described in Ref. 16, and the points of state for the single-occupancy cell system are given in Table III. The three-dimensional SO system exhibits a kink in the pressure $p(\rho)$ at a density below the solid density at melting and this second-order phase transition is interpreted as the density above which the particles are constrained to their cells;

TABLE II. Pressure and energy per particle for the $N=3600$ Lennard-Jones system at $kT/\epsilon=1$.

$\rho\sigma^2$	$p\sigma^2/\epsilon$	u/ϵ	Number of time-steps (10^3)
0.8493	5.08	−1.258	3
0.8572	5.32	−1.280	4
0.8651	5.51	−1.309	5
0.8731	5.55	−1.354	10
0.8810	5.44	−1.420	10
0.8880	5.37	−1.471	10
0.8953	5.48	−1.504	5
0.9010	5.73	−1.514	5
0.9165	6.54	−1.522±0.003	5

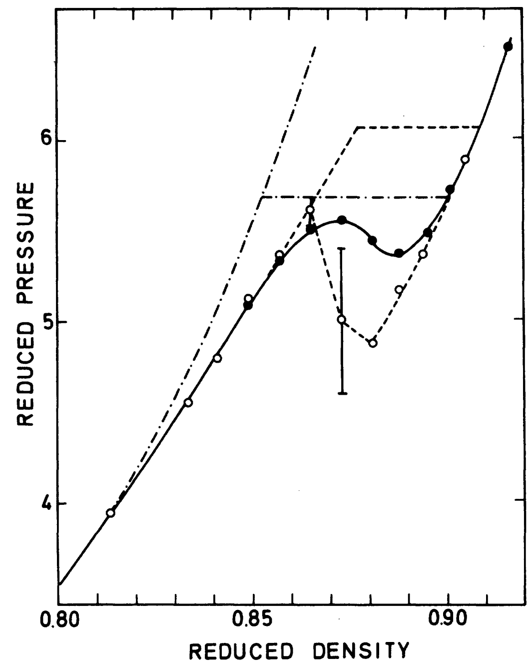

FIG. 1. The pressure as a function of density at $kT/\epsilon=1$. The full line and the points ● give the pressure in the large system, and the dotted line and the points ○ give the corresponding pressure in the small system. Also shown is the extension of the fluid pressure and the tie line in the small system (dotted line) together with the virial expansion pressure and its tie line (— • — • — •) taken from Ref. 13.

not by the Wigner-Seitz cell walls but by their nearest neighbors. The transition is more fuzzy in 2D (Ref. 8) and the present long calculations show that it is a continuous taking over of another "constraint mechanism". This conclusion is obtained by counting the number of reflections per particle at the cell walls as a function of density, which was found to decline exponentially with increasing density with two different slopes (well) above and below a certain density region $\rho\sigma^2 \approx 0.75$. Analysis of the particle structure shows that the SO system contains (bound) disclinations[17] both above and below the transition zone $\rho\sigma^2 \approx 0.75$ and an explanation of the fuzzy transition in the 2D soft-disk system could be that it is the disclinations which are gradually excluded in the lattice as the density is increased.

The dependence on the size of the SO system was analyzed by performing a calculation for $N=576$. At low density the SO system is independent of N, and *a priori* we would expect a possible size dependence to begin to show up in the regime $\rho\sigma^2 \approx 0.75$, and have performed a MD calculation for $N=576$ and $\rho\sigma^2=0.75$. No size dependence is registered within the accuracy of the calculations which is estimated to be 0.005 in the pressure below $\rho\sigma^2=0.75$ and of the order 0.01 above. The convergence of the MD calculations was slower above $\rho\sigma^2=0.75$ and long runs were performed. However, different starting conditions gave the same pressure so the SO method is still ergodic in this region. When the cell was removed at $\rho\sigma^2=0.9165$ no change was observed in the pressure within the accuracy of the calculations, and the points of state in Table III thus serve as a reversible path from the low-density region from which the free energy F is calculated.[18] We find good agreement with the corresponding value obtained by Barker *et al.*[13] who calculated F by integrating from $T \approx 0$ and using the "quasiharmonic" approximation. At $\rho\sigma^2=0.9165$ and $kT/\epsilon=1$,

Present calculation $F/N\epsilon=-0.14_3$,

Ref. 13 $F/N\epsilon=-0.13_6$.

The thermodynamic location of the melting zone can now be determined. Figure 1 shows the calculated tie line (dotted line) between fluid and solid with equal chemical potential for the $N=256$ particle system. The thermodynamic location of the phase transition appears at higher pressure than actually observed in both the small and the large system. Also shown in the figure is the Padé extrapolation of the virial expansion and the calculated tie line taken from Ref. 13 (— • — • — •). The Padé approximant fails systematically above $\rho\sigma^2=0.80$ by giving too high a pressure. This shortcoming of the virial expansion with 5–6 virial coefficients is also observed for hard disks.[8] We have analyzed this quality further by compressing (scaling) the systems rapidly from $\rho\sigma^2=0.80$. The systems were compressed to the freezing density during 40–80 timesteps ($\lesssim 10^{-12}$ s) which is shorter than the transit time for a sound wave and thus, no long-range correlations could take place during this time. The pressure just after the compression was higher than the equilibrium pressure but lower than the Padé approximant pressure, from which we conclude that the shortcoming of the truncated virial expansion is not due to a freezing phenomena (or to the appearance of a hexatic phase[4,5]). However, it means that the first-order nature is less pronounced than found in Ref. 13, and it implies that the tie line appears at a higher pressure.

The calculated tie line (dotted line) appears at a higher melting pressure than actually observed in both systems, but the uncertainty must be rather

TABLE III. Pressure and energy per particle for the single-occupancy system of $N = 256$ Lennard-Jones particles at $kT/\epsilon = 1$.

$2^{1/3}\rho\sigma^2$	$p\sigma^2/\epsilon$	u/ϵ	Number of time-steps (10^3)
0.1	0.073		15
0.2	0.125		10
0.3	0.148		5
0.4	0.149	+0.316	5
0.5	0.144	+0.078	5
0.6	0.174	−0.187	7
0.7	0.293	−0.460	14
0.8	0.606	−0.736	5
0.85	0.878	−0.879	5
0.9	1.277	−1.009	5
0.925	1.520	−1.072	5
0.95	1.84	−1.132	15
0.975	2.16	−1.196	15
1	2.52	−1.258	17
1.025	2.91	−1.319	15
1.05	3.36	−1.377	22
1.075	3.89	−1.433	30
1.09	4.26	−1.463	13
1.10	4.50	−1.482	16
1.11	4.81	−1.490	13
1.1188	5.07	−1.508	25
1.14	5.85	−1.526	10
1.1547	6.50	−1.528	15

high due to the small density change at the transition, which means that the curves $\mu_s(p)$ and $\mu_l(p)$ for the solid and fluid chemical potential at the crossing point have almost the same slope.[19] The uncertainty in μ comes from the MD simulations, the extrapolation of the equation of state for the fluid, and from the calculated free energy. For example, an error in the free energy of the solid state: $\Delta F/N\epsilon \approx 0.01$ will result in change in the melting pressure on $\Delta p\sigma^2/\epsilon \approx 0.25$. The calculated melting pressure is $p\sigma^2/\epsilon = 6.06$, and the melting pressures in the two systems estimated from a (crude) "equal-area" construction of $p(\rho^{-1})$ are ≈ 5.20 and ≈ 5.50, respectively, for the small and large system and we believe that the difference between the calculated and the observed melting pressure is not greater than can be explained by the uncertainty of the calculations.

III. THE PHASE TRANSITION

The phase transition, as it appears in both the small and the large system, is of course first order but the question is whether it is an artifact caused either by the size of the system or by insufficient time averaging. In order to answer the first question we have performed a more extensive analysis of size effects both in the fluid and solid state. The result of the analysis of the fluid state is that there is no significant size effect here. The calculations were performed for systems of $N = 256$, 576, 1024, and 3600 particles at the density $\rho\sigma^2 = 0.8493$ and gave the same pressure within the accuracy of the calculations. The solid state, however, exhibits a weak size dependence. At the density $\rho\sigma^2 = 0.9165$, which corresponds to a dense solid in both systems, the energy per particle is significantly greater in the large system and the density of crystal defects per particle were found to be 0.0031 ± 0.0006 and 0.0100 ± 0.0010, respectively, for the small and large system. This effect is increased when the transition is approached: Table IV gives the result of the calculations for the density $\rho\sigma^2 = 0.8880$, which is also analyzed by Tobochnik and Chester.[12] The present calculations show that the point of state $\rho\sigma^2 = 0.8880$, $kT/\epsilon = 1$ lies on the thermodynamically unstable part of the van der Waals loop and represent an over-expanded crystal close to the spinoidal point. This fact explain the narrow melting temperature interval at the isochores in Ref. 12.

TABLE IV. Size effect on pressure, energy, and lattice defects at the metastable state $\rho\sigma^2=0.8880$ and $kT/\epsilon=1$.

N	$p\sigma^2/\epsilon$	u/ϵ	Disclinations per particle	Number of timesteps (10^3)
~ 1(SO)	5.07 ± 0.03	-1.508	0	25
56	5.11 ± 0.06	-1.499	<0.01	50
256	5.16 ± 0.02	-1.494 ± 0.002	0.02_6	35
576	5.21 ± 0.05	-1.489 ± 0.005	0.02_9	75
1024	5.26 ± 0.04	-1.484 ± 0.005	0.03_4	28
3600	5.37 ± 0.03	-1.471 ± 0.004	0.05_2	10

The question whether equilibrium states of the systems can be obtained in time intervals of $\approx 10\,000$ timesteps is difficult to answer. The transit time of a sound wave gives only a lower limit for the necessary time interval. Another test can (in principle) be performed by compressing the systems from a fluid state, since if the points shown in Fig. 1 represent equilibrium states the systems should freeze and end in the starting state by compression. However, as already mentioned, the large system showed hysteresis and converged very slowly at the "solid" branch of the loop: When compressing from the density 0.8880 to 0.9010 the pressure after 8000 timesteps was 5.81 ± 0.04 and in the next 5000 steps it only decreased a little. A structure analysis showed that the state contained a higher concentration of crystal defects than the corresponding state given in Table III. We believe that the system had not reached equilibrium and that the necessary time would have been very long. However, if this state has to be included in an appropriate averaging over equilibrium configurations the pressure and the density discontinuity at the phase transition will only change a little.

In the HNY theory[4,5] the lattice defects before melting are assumed to appear in pairs of bound dislocations with opposite Burger vectors. By melting into a possible "hexatic phase" the dislocations dissociate and destroy the (algebraic) long-range lattice order. The dislocation itself consists of pairs of bound disclinations, e.g., disclinations with coordination numbers 5 and 7, and at the melting of the hexatic phase into an isotropic fluid the disclinations dissociate and finally destroy the long-range order between pairs of particles. This theory is developed from the Kosterlitz-Thouless[20] (KT) theory for melting in 2D, which has been supported both by computer simulations and experiments.[21] The present calculations of lattice defects in the solid show that the majority of defects consist of quadruplets of disclinations with coordination number (5757) as assumed in the HNT-KT theory, but also of small loops of disclinations (575757. . .). Figure 2 shows a typical picture of lattice defects at the density $\rho\sigma^2=0.8953$, which corresponds to a density just above the melting density determined from an equal-area construction of $p(\rho^{-1})$ in Fig. 1. At higher densities the pictures are qualitatively the same. As the density is decreased the defects are found to cluster together in loops and clusters as also observed in Refs. 12 and 15. Figure 3(a) shows a typical picture of defects at $\rho\sigma^2=0.8880$. We find, not surprisingly, that the size effects given in Table IV are associated with creation of these loops and clusters which are prevented in the small systems with periodic

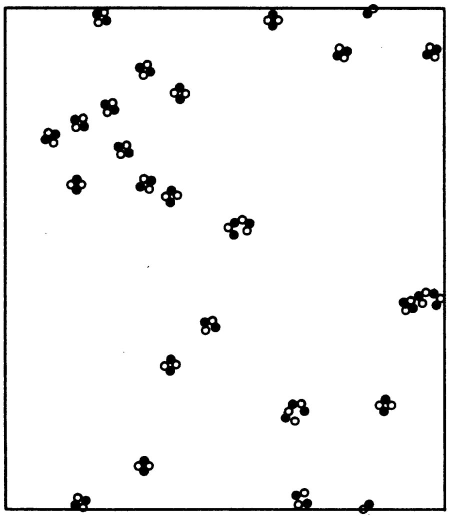

FIG. 2. Particles in the large system at $\rho\sigma^2=0.8953$ with coordination numbers different from 6 (disclination center). Particles with coordination numbers 5 and 7 are given by ⊗ and ○, respectively.

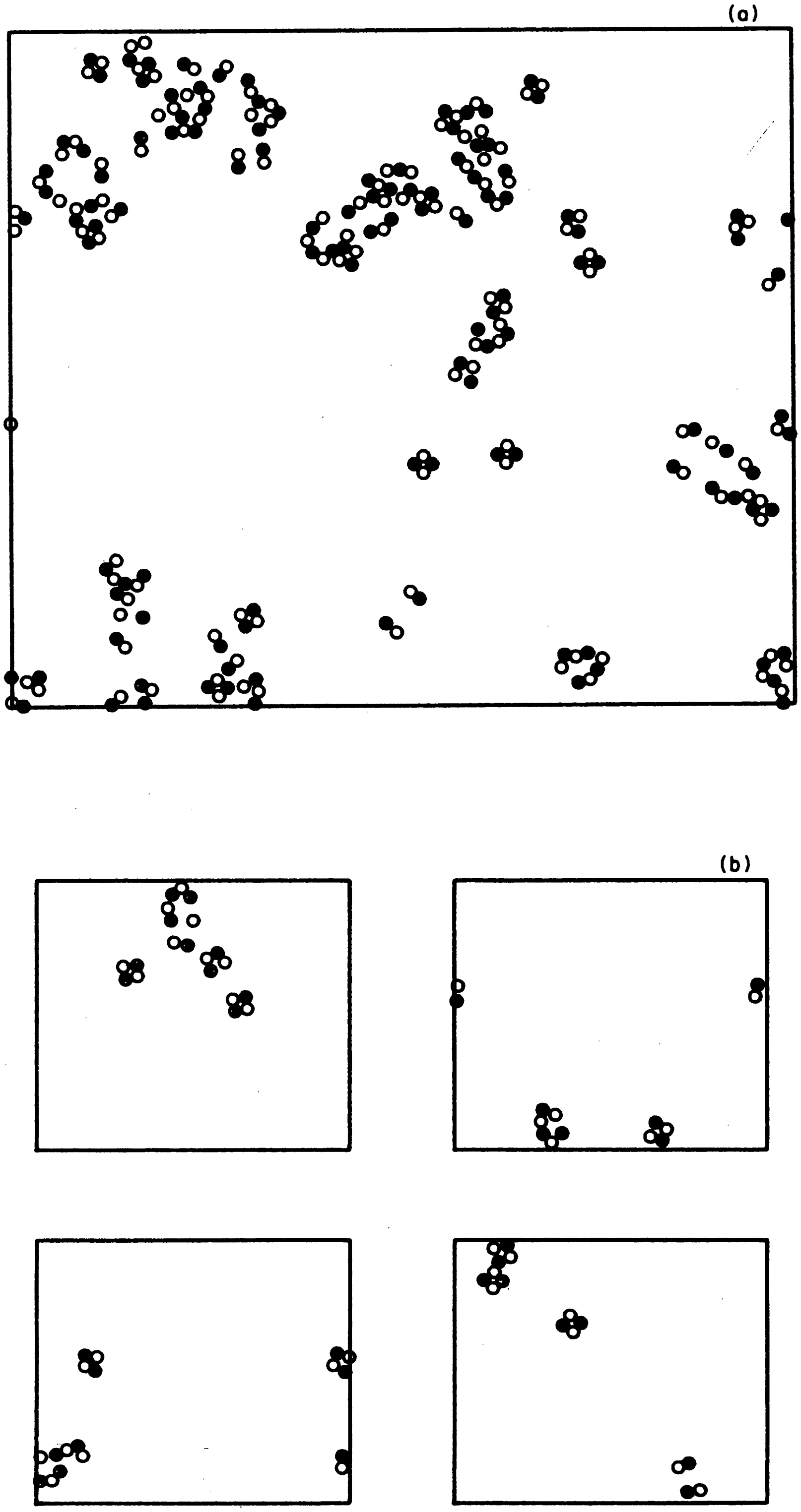

FIG. 3. (a) Disclinations in the large system at $\rho\sigma^2=0.8880$. (b) Four (subsequent) pictures at $\rho\sigma^2=0.8880$ of disclinations in the $N=576$ system. Pairs of dislocations are more dominating in the smaller system.

boundaries. Figure 3(b) shows four subsequent pictures of defects in the system of $N=576$ particles also at $\rho\sigma^2=0.8880$.

The HNY theory gives a quantitative description of 2D melting. One of the predictions is that the product of the Lamé elastic constants, λ and μ, should approach a certain value at melting. They predict that lim$K$:

$$\lim_{T\to T_m} \frac{4\mu(\mu+\lambda)}{2\mu+\lambda}\frac{d^2}{kT}=16\pi\approx 50\ , \tag{1}$$

where T_m is the solid-state melting temperature and d is the lattice constant of the triangular lattice. The Lamé coefficients were calculated accordingly to the formula derived by Squire *et al.*[22] The value of K was found to be significantly greater than 50 at the points where the crystals ($N=256,3600$) melt due to thermodynamical instability, but it was of the order 50 at the densities where the two systems melted.

The conclusion of these calculations is that the phase transition in the computer systems is first order. The KT melting theory describes melting at the spinoidal point and the melting may occur not due to unbinding dislocations, but due to generation of loops of disclinations (grain boundaries in 2D). Whether this result holds in the thermodynamic limit is of course, in principle, impossible to say from two sets of calculations. Hoover and Alder[23] have estimated the number dependence of the melting pressure in a hard-disks system and found that the variation with N could be explained as originating in the number dependence of the communal entropy which varies as $-\ln(2\pi N)^{1/2}/N$. This effect will result in an increase in the melting pressure of ≈ 0.3 when the number is changed from $N=256$ to 3600 as actually observed, and the melting pressure, due to this effect, should only change marginally (≈ 0.01) when $N\to\infty$. But the calculation is based on the assumption that the density discontinuity $\rho_l^{-1}-\rho_s^{-1}$ is not number dependent. Furthermore, in a Lennard-Jones system we need not only consider entropy effects but also energy effects, and the solid-state energy is found to be weakly number dependent due to an increase of the density of crystal defects as N is increased. This number dependence will weaken the transition and may change the nature of the transition in the thermodynamic limit.

Compared to real systems, e.g., monolayer adsorbed on solid surfaces, the computer systems are rather small. The diameter of the box in the large computer system corresponds only to ~ 250 Å; in that case it simulates a noble-gas monolayer. The real systems suffer from surface and interface defects caused by the edges of the crystal adsorption planes; an imperfection the computer systems do not have. On the other hand, the periodical boundaries even prevent rather small density fluctuations and it is these fluctuations which must cause the bulk 2D crystal defects which finally melt the system.

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APPENDIX

The systems consist of N particles in a rectangular cell with the ratio $3^{1/2}/2$ between the edge lengths. The density is ρ and the particles interact through a Lennard-Jones potential

$$u(r)=4\epsilon[(r/\sigma)^{-12}-(r/\sigma)^{-6}]\ , \tag{A1}$$

truncated at $r_c=2^{1/6}2.5\sigma\approx 2.8\sigma$. The MD calculations were performed as described in Refs. 10 and 16 by integrating the equations of motion and using the "Verlet algorithm" with a timestep

$$\Delta t=2^{1/6}0.005\sigma(m/\epsilon)^{1/2}\approx 10^{-14}\ \text{s}\ .$$

The pressure p, energy per particle u, and temperature were obtained as the time average of the virial of the forces, the potential energy, and kinetic energy, respectively. In addition we obtained the derivative of pressure and energy from the fluctuations in pressure and kinetic energy according to the formula (in 2D)[24]

$$N\langle \delta T^2\rangle = T^2(1-c_v^{-1})\ , \tag{A2}$$

and

$$-N\left\langle \delta\left[\frac{p}{\rho}-T\right]\delta T\right\rangle=\frac{T^2}{c_v}\left[\frac{1}{\rho}\left[\frac{\partial p}{\partial T}\right]_\rho-1\right]\ , \tag{A3}$$

where the brackets are time average and $\delta x\equiv x(t)-\langle x(t)\rangle$.

The calibration (of kinetic energy) to $kT/\epsilon\approx 1$

was continued until none of the observed quantities T, p, u, $\partial p/\partial T$, and c_v showed any systematic variation with time. In addition we have used another criteria for the necessary time for calibration and subsequent time for averaging, namely, that these time intervals should be much larger than the time it takes an adiabatic soundwave to traverse half the system. (The half, due to the periodical boundaries). The sound velocity c was obtained as

$$c = \left[\left[\frac{\partial p}{\partial \rho} \right]_T + \frac{T}{c_v \rho^2} \left[\frac{\partial p}{\partial T} \right]_\rho \right]^{1/2} \tag{A4}$$

from (A2) and (A3), and by numerical differentiation of $p(\rho)$ near—but not at—the phase transition. This traversion time was found to be $\approx 10^3$ timesteps for the large 60×60 particle system.

After the calibration the equilibrium pressure and energy were obtained from the subsequent time interval and fine corrected to $kT/\epsilon = 1$ by means of $\partial p/\partial T$ and c_v. The temperatures for the generated equilibrium points of state deviated less than 1% from $kT/\epsilon = 1$, and the fine corrections were less than, or at the order of the estimated uncertainties in p and u. Finally, the pressure and energy per particle were corrected for contributions due to the truncated "tail" of the potential. For 2D we have

$$p_{as} \simeq -\tfrac{1}{2}\pi\rho^2 \int_{r_c}^{\infty} dr\, g(r) r^2 u'(r), \tag{A5}$$

$$u_{as} \simeq \pi\rho \int_{r_c}^{\infty} dr\, g(r) r u(r), \tag{A6}$$

where $g(r)$ is the radial distribution function for the system of particles interacting through the truncated pair potential. For $\rho\sigma^2 < 0.8$ the formula were simplified further by setting $g(r) = 1$. For $\rho\sigma^2 > 0.8$ $g(r)$ was first approximated by unity for $r > 2^{1/6}4\sigma$.

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[17] Concerning the definition and calculation of crystal defects in 2D, see Ref. 15.

[18] See Ref. 16. The (ρ, p) data in Table III agree with the previous less accurate and extensive points used in Ref. 16. We have, however, found an error in the computer program for the calculation of the free energy, used in Ref. 16, which had lead to a small but systematic error in the calculated free energy in Ref. 16, at high temperature $kT/\epsilon \gtrsim 1$, and to a too low melting pressure for these temperatures.

[19] Since $\partial\Delta\mu/\partial p = \rho_l^{-1} - \rho_s^{-1}$.

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