Size-Dependent Properties of a Two-Dimensional Solid near Melting

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The behavior of a two-dimensional solid near melting is analyzed by the molecular-dynamics technique. Two size-dependent properties are determined: the mean amplitude of vibration (θ) from the lattice positions and the elasticity (shear modulus μ), which vary logarithmically with system size. When the size is increased to give $\theta \approx 0.18$ the particles begin to diffuse and the elasticity is close to its predicted melting value. The result demonstrates that previous computer models have been too small to simulate bulk solid near melting.

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The thermodynamic and dynamic behaviors of a two-dimensional (2D) system at melting have been the subject of controversy for a long time.[1] Computer-simulated systems show a traditional first-order phase transition. On the other hand, new experimental data[2] support the theory[3-5] that melting in 2D could be continuous. A continuous transition is associated with long-range correlations which are suppressed in the small computer models,[6] and in the present Letter I have analyzed size-dependent properties of a 2D solid near (or at) melting. The system consists of particles which interact with repulsive Lennard-Jones forces [Weeks-Chandler-Andersen (WCA) system[7]] and the 2D medium is simulated by the molecular-dynamics (MD) technique.[6,7]

There are several reasons for choosing the WCA system. The main reason is that I want to study the indirect influence of the system size on the local structure and behavior, and in the WCA system a particle interacts only with its nearest neighbors. Systems with pure short-range forces have already been studied. The advantage, however, of the WCA system is that the WCA system is not in the "high-temperature limit," since it does not scale, but depends thermodynamically on both temperature, T, and density, ρ, and the abnormal melting behavior might only be present at low temperatures.[4] The MD calculations are performed at the relatively low temperature $kT/\epsilon=1$. Systems of $N=256$ and $N=1024$ exhibit the usual first-order melting behavior (Fig. 1). The tie line of equal chemical potential between fluid and solid (dot-dashed line) is calculated with use of the data in Ref. 6 and by gradually "switching off" the attractive potential (λ expansion[8,9]). The tie line pressure, $pr_m^2/\epsilon = 13.1_3$, is higher than directly observed and is believed to be an upper limit[10,11] above which the stable state should be the triangular solid, no matter how large the system is. The solid state in this (T, ρ) region is analyzed by varying the size of the system. Two size-dependent properties are determined: the mean amplitude of vibration from the lattice positions and the elasticity (shear modulus), which both show a logarithmic size dependence.

The logarithmic divergence in a 2D system has been known for a long time.[12-14] A simple Debye theory gives a logarithmic divergence of the relative mean amplitude of vibrations, or Lindemann's ratio, θ, and in itself it is not alarming, since if the modes do not couple, the system might be astronomically large before a particle has changed lattice position; the divergence has been considered as a property of the ordered state in

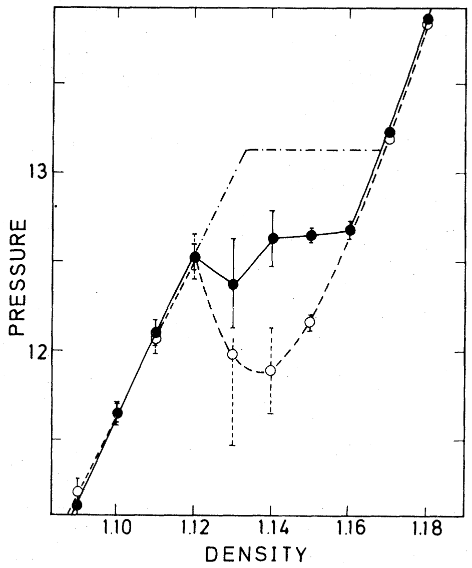

FIG. 1. $kT/\epsilon=1$ pressure vs density isotherm. The full line and the solid points are for $N=1024$; the dotted line and the circles are for $N=256$. The tie line between bulk solid and fluid with equal chemical potential is also shown (dot-dashed line).

2D. The ratio θ is obtained as

$$\theta = \{\langle N^{-1}\sum_{i}^{N}[\vec{r}_i(t) - \langle \vec{r}_i\rangle]^2\rangle\}^{1/2}/d \qquad (1)$$

by time averaging, where $d(\rho)$ is the lattice distance. This definition does not refer to a certain structure, and so frozen defects do not obscure the result that when the system size at constant ρ and T is increased to a point where $\theta \gtrsim 0.18$ a fraction of the particles diffuse and θ diverges with time. Figure 2 shows isochores of θ at $kT/\epsilon = 1$ as a function of $\ln N$. The isochores $\rho r_m^2 = 1.15$ (inverted triangles) and 1.16 (crosses) correspond to points of state in the coexisting phase region (Fig. 1), and the system should indeed melt when the size of the system is increased, as observed. On the other hand, the isochore $\rho r_m^2 = 1.17$ should be above the coexisting solid-state density ($\rho r_m^2 \approx 1.16$) where the system is stable. This might not be the case, however. In a system of $N = 8100$ particles at $\rho r_m^2 = 1.17$, the particles began to diffuse, but first after 50 000 time steps.

Figures 3(a) and 3(b) give a dynamic and topological picture of the onset of diffusion in this system. Figure 3(a) shows the locations of particles which, in 10^4 steps, have changed lattice positions. The diffusion is located in four regions (a, b, c, and d) and shows up as consecutive jumps. Figure 3(b) shows the crystal defects[15] after the 10^4 steps, where a, b, c, and d refer to the defects associated with the diffusion. Detailed analysis of Figs. 3(a) and 3(b) and corresponding pictures for the next 2×10^4 steps showed that regions with consecutive jumps always contain defects—often in small loops of ≈ 10 particles—but as Fig. 3(b) demonstrates, there are also defects and loops elsewhere. Diffusion in 3D crystals is well knonw and so one could argue that the present calculations only show that the system exhibits bulk diffusion for a size which allows for vacancies, interstitials, etc. But the new state in 2D appears at a certain value of a mean parameter (θ) which indicates a thermodynamic change and results in consecutive jumps —or diffusion with a very high frequency, e.g., corresponding to the order of 3×10^{23} jumps/s cm^2 for a noble-gas monolayer.

Another indication that 2D melting of soft particles depends on the size of the system is obtained by calculating the Lamé coefficient, μ.

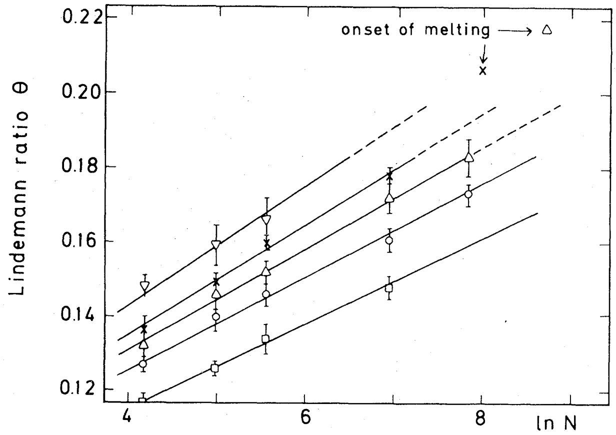

FIG. 2. The relative mean amplitude of vibration, θ, as a function of system size, $\ln N$. The isochores are $\rho r_m^2 = 1.15$ (inverted triangles), 1.16 (crosses), 1.17 (triangles), 1.18 (circles), and 1.20 (squares), and are obtained from more than 4×10^4 time steps per point. However, the two points which show onset of melting are obtained from only 2×10^3 steps (cross) and 7×10^3 steps (triangle), respectively, since at melting θ diverges slowly with time.

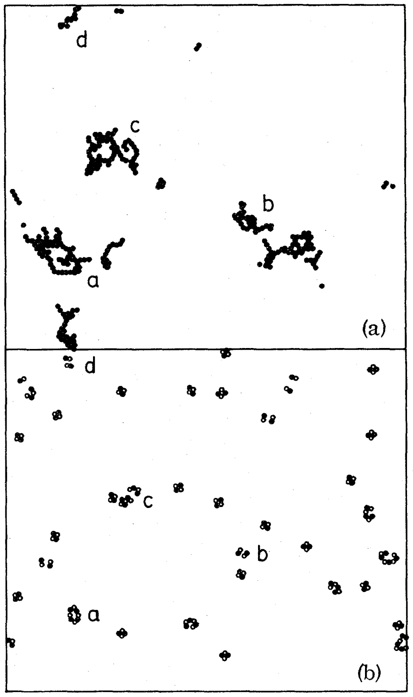

FIG. 3. (a) The mean positions of particles, which, within 10^4 time steps, diffuse. (b) The crystal defects obtained from the positions after the 10^4 steps ($\approx 10^{-10}$ s). Particles with coordination numbers 5 and 7 (and 8) are given by solid and open circles, respectively. There is a correspondence in locations a, b, c, and d between regions with diffusion and with crystal defects.

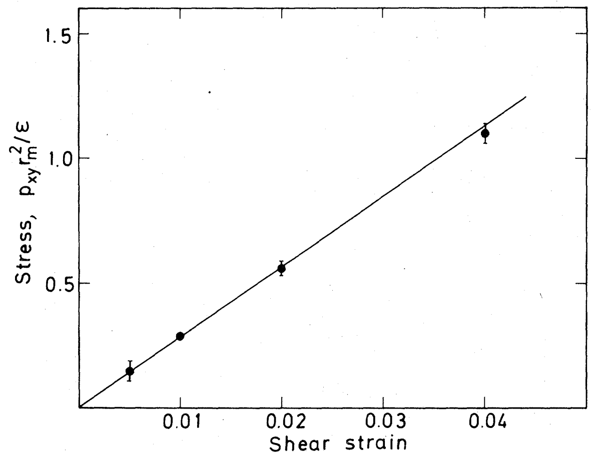

FIG. 4. The stress p_{xy} in a $N=64$-particle system at the density $\rho r_m^2=1.18$. The points for the strain 0.005, 0.02, and 0.04 are obtained for 10^5 time steps. The point for 0.01 is for 2.5×10^6 steps.

The coefficient is determined as described in Ref. 11, by applying a small homogeneous shear strain. It is calculated for $N=64$, 256, and 1024 at $\rho r_m^2=1.17$ and 1.18. The crystals were only subjected to small strains (±0.005 for $\rho r_m^2=1.17$ and ±0.005 and ±0.01 for $\rho r_m^2=1.18$). Figure 4 demonstrates that the obtained stress is well inside the linear regime for these small values. The instantaneous value of μ fluctuates,[16] which necessitates very long calculations in order to obtain a significant result. The lengthy computation was carried out for different starting configurations and for different signs of the strain and,[17] at the end of the calculations the systems were observed to relax to their unconstrained equilibrium configurations within a few hundred time steps by releasing the shear strain, with all the particles maintained at their original lattice positions.

Figure 5 gives μ as a function of $\ln N$. The uncertainties are the rms deviations from the means and are obtained from the independent subsets. The six points show a logarithmic size dependence. According to Nelson and Halperin[4] a certain combination, K, of the elastic coefficients takes on the universal value $16\pi\approx50$ at melting. For the triangular lattice[11]

$$K=\frac{(8/\sqrt{3})\beta\mu/\rho}{1+\mu/(\rho\,\partial p/\partial\rho)}. \qquad (2)$$

The pressure, p, increases a little with increasing size (Fig. 1), but the compressibility, determined from the isotherms near melting, is almost independent of N. Thus, as a consequence of the size dependence of the shear modulus, K decreases logarithmically. Previous computer simulations show melting for a slightly higher value of K (≈55–60). By extrapolation of the result in Fig. 5, K is estimated to reach a value ≈55 for $N\approx40\,000$ for $\rho r_m^2=1.17$, but the estimate is uncertain.

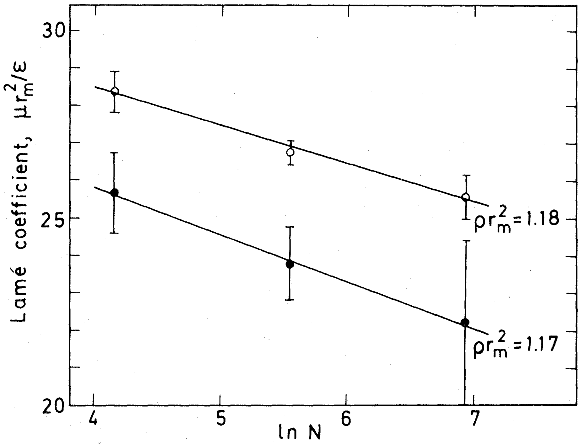

FIG. 5. Shear modulus, μ, as a function of $\ln N$.

To conclude, the present calculations primarily show that computer systems of the order of a thousand particles are too small to simulate melting in soft-disk systems. With an increase of the system size for a solid near melting, the particles begin to diffuse. This state must be included in a statistical mechanical equilibrium average before the nature of the transition can be determined. The onset of diffusion is observed at a system size where the combination K of the elastic coefficients is near its predicted melting value. Secondly, small computer systems cannot be used to test melting theories which treat the 2D system as an elastic medium since the shear modulus for the small systems shows a significant size dependence. Finally it should be pointed out that the established number dependence of μ and θ does not permit an extrapolation to larger N and/or lower temperatures since many other, and converging, functions fit the few data for the shear modulus and since the critical value of θ might be temperature dependent. Thus the present result does not resolve the problem of the order of the melting transition in 2D.

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[1] See, e.g., papers in *Ordering in Two Dimensions*,

edited by S. K. Sinha (North-Holland, Amsterdam, 1980), and references therein.

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[17] The numbers of time steps for $\rho r_m^2 = 1.18$ are for $N = 64$, 2.5×10^6; for $N = 256$, 8×10^5; and for $N = 1024$, 1.6×10^5. The reason for obtaining the means of p_{xy} from independent subsets, instead of one long computation, was to avoid a small undetected drift in the angular moment that would cause a drift in p_{xy}.