

PHYSICAL REVIEW LETTERS

VOLUME 11

15 SEPTEMBER 1963

NUMBER 6

COOPERATIVE MOTION OF HARD DISKS LEADING TO MELTING

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(Received 8 July 1963)

None of the approximate integral equations¹⁻³ for the radial distribution function has yet given any insight into the observed⁴ hard-sphere and hard-disk phase transitions. Only the integral equations based on the superposition approximation have been shown to give singularities in the hard-sphere equation of state, but the connection between the singularities and the phase transition has not been established.

On the other hand, some insight into the hard-disk phase transition can be gained by study of the computer-generated oscilloscope traces of disk trajectories in the two-phase region. These pictures suggest that an important feature of the cooperative motion leading to melting is the sliding of rows of particles past each other. This sliding motion is incorporated into a simple model and is shown to lead to a phase transition for disks at approximately the right pressure and density. Furthermore, this model leads to an accurate description of the solid phase of disks near close packing. Finally, the model suggests that, for particles which do not have a hard core, a solid-fluid critical point will be observed.

In previous models of the solid phase⁵ a central particle is allowed to wander in a cell in which the neighbors are strictly confined to lattice positions. This is illustrated in Fig. 1 for hard disks; the free area, a_f , accessible to the center of the wanderer is the central cross-hatched region. In this model the probability density in configuration space is expressed as a product of single-particle probability densities⁶; that is, the

motions of neighboring particles are uncorrelated.

The other extreme, treated here, in which some neighboring particles are perfectly correlated will also lead to a theory of the cell type, as shown in Fig. 1. The unit crystallographic cell of the hexagonal lattice (dashed rectangle) can be thought of as containing two kinds of particles, both of which are periodically repeated. One kind of particle (open circles) includes the central wanderer and some of its correlated neighbors. These move in unison (indicated by arrows) relative to the other kind of neighboring particle (cross-hatched

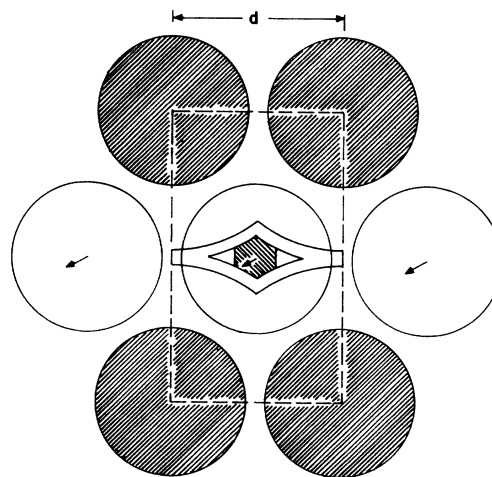


FIG. 1. Configurations of the cell of elastic disks. The shaded particles are fixed. Free areas available to the central wanderer are shown.

circles) which are fixed at lattice positions. Considering the lattice to be generated by a single unit cell with periodic boundary conditions, so that identical motion occurs in each cell, the cooperative behavior corresponds to one sublattice (in this case a row of atoms) sliding relative to another sublattice. This correlated cell model is, of course, unrealistic because the perfect correlation of neighbors does not, in fact, extend over an infinite range but, as suggested by the oscilloscope pictures, only over some ten particle diameters. Nevertheless, the model describes the solid phase quite accurately; it is not expected to describe the fluid phase.

The correlated cell-model free area (central diamond shape region) is larger than the ordinary cell-model free area, as shown in Fig. 1. For the correlated cell model,

$$a_f = (3d^4)^{1/2} - \frac{1}{2}(4d^2 - d^4)^{1/2} - 2 \sin^{-1}(\frac{1}{4}d^2)^{1/2} - \frac{1}{2}(12d^2 - 9d^4)^{1/2} + 2 \cos^{-1}(3d^2/4)^{1/2}$$

for $1 < d^2 < \frac{4}{3}$, (1)

where d is the nearest-neighbor distance relative to the particle diameter σ . The equation of state obtained from

$$pA/NkT = \partial(\ln a_f)/\partial(\ln A) = \partial(\ln a_f)/\partial(\ln d^2) \quad (2)$$

is shown in Fig. 2. At $d^2 = \frac{4}{3}$ the functional form of a_f changes since at that point rows can slide past each other. The free area for $d^2 > \frac{4}{3}$ is indicated in Fig. 1 by the larger central diamond-shaped region with cutoff corners. The expression for it is merely the first three terms of Eq. (1). At low densities, the definition of a_f depends explicitly upon boundary conditions, which here have been taken such that the central particle is confined to the area per particle.

It should be pointed out that the portion of the equation of state with a positive $(\partial p/\partial A)_T$ which leads to the first-order phase transition by the Maxwell construction is obtained entirely from Eq. (1), and hence is not an artifact due to the sudden appearance of new regions accessible to the wanderers. In fact, a number of similar models have similar characteristic equations of state. As examples, a two-dimensional square lattice in which the wanderer is confined by four stationary particles at the corner of a square exhibits a phase transition near twice the close-packed area, and a hexagonal lattice which has arbitrarily three alternate neighboring particles correlated with the central particle exhibits a

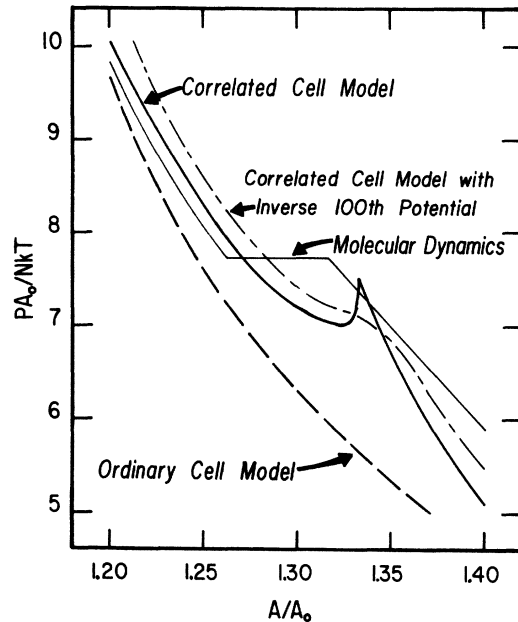


FIG. 2. The equation of state of elastic disks in the phase-transition region. A/A_0 is the area relative to the close-packed area, A_0 . Light solid line, molecular dynamics; dashed line, ordinary cell model; heavy solid line, correlated cell model; dash-dot line, correlated cell model with a repulsive potential falling off as the inverse 100th power of the distance.

phase transition very similar to the case previously treated where two neighbors were correlated. In the case of three correlated neighbors, the lattice is generated by a box with periodic boundary conditions containing six particles (three unit cells wide). These six atoms are not all independent but subdivided into two stationary particles (the one at the center and the ones in the corners) and four correlated ones. Sliding of rows is quite feasible in this model also. If the six atoms had been treated as all uncorrelated, a phase transition would not likely be observed, since boxes containing four or twelve independent particles did not lead to one⁷ by molecular dynamics computer calculations. The reason for this is that density fluctuations are so restricted in such systems that the probability of parallel sliding of rows is drastically reduced at the density of the phase transition.

In the limit of close packing, the correlated cell-model isotherm reduces to the ordinary cell-model isotherm which has been shown to be exact for finite systems.⁸ Presuming that away from close packing, the equation of state can be expanded in

$\alpha = A/A_0 - 1$, as

$$pA/NkT = (2/\alpha) + C_0 + C_1\alpha + C_2\alpha^2 + \dots, \quad (3)$$

the value of C_0 for the ordinary cell model is $\frac{14}{9} = 1.56$, for the correlated cell model $\frac{17}{9} = 1.89$, while the molecular dynamic result gives 1.86 ± 0.03 for either 72 or 870 particles. The values of C_1 are $-\frac{7}{81} = -0.086$, $\frac{82}{81} = 0.765$, and 0.9 ± 0.2 , respectively. This quantitative success of the correlated cell model near close packing, as well as in the phase transition, as shown in Fig. 2, indicates its general validity in the high-density region. Figure 2 also shows that for a very steep inverse power-law repulsive potential of the form $kT(\sigma/r)^{100}$ the phase transition disappears. Also, no phase transition was obtained when the repulsive power was four or twelve. For these potentials the integral occurring in the free area of the cooperative cell model was evaluated numerically. A study now in progress involving other potentials,

further models, and three-dimensional systems should help answer the question whether the mechanism of melting in real systems is similar to that of elastic disks.

*This work was performed under the auspices of the U. S. Atomic Energy Commission.

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OPTICAL TRANSITIONS IN WHICH CRYSTAL MOMENTUM IS NOT CONSERVED*

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(Received 29 July 1963)

Photoemissive studies may give detailed information concerning optical transitions in solids. In particular, the absolute energy of the initial and final states involved in the optical transition can be deduced from the distribution in energy of the emitted electron. Results in good agreement with theory have been obtained from Si.¹ Since optical transitions between valence- and conduction-band states depend on both the energy-band structure and the optical selection rules, photoemission has been used here to obtain information concerning both of these quantities. In Si, in spectral regions of high absorption coefficient and photoemissive yield, only transitions in which \vec{k} is directly conserved are of importance.^{1,2} It is the purpose of this Letter to report and discuss data in which no evidence for a selection rule requiring the conservation of \vec{k} was found. The valence-band structure of the materials studied has also been deduced and related to the atomic spin-orbit splitting.

The materials reported on here are IA-VB compounds, Cs₃Bi, Cs₃Sb, Na₂K₃Sb, K₃Sb, and Rb₃Sb which have been rather extensively studied.³⁻⁵ It has been established that photoemission from

these materials is a bulk process. It has also been shown that in many of them a large percentage of the optical transitions produce photoelectrons. The experimental techniques used have been described elsewhere.⁶

If the energy distribution produced by photons of energy $h\nu$ (see Fig. 1) is plotted against the energy of the electron in vacuum, E , minus $h\nu$, the distribution is referred to the valence-band states, at energy E_ν , from which it was excited.⁷ If only direct optical transitions are important, the energy of the valence-band state from which the electron is excited will change with $h\nu$. As a result, a change in $h\nu$ cannot produce an equal change in E if the valence band has finite width.^{1,8} Only if the valence band is flat with negligible width or if the conservation of \vec{k} is not an important optical selection rule, will $\Delta E = \Delta h\nu$. Under these conditions structure in the energy distribution due to the valence band will fall at the same place when the energy distributions for various values of $h\nu$ are plotted versus $E_\nu = E - h\nu$.

In Fig. 1, experimental energy distributions obtained from Cs₃Bi are plotted versus E_ν . For the sake of comparison, the curves obtained for