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ABSTRACT

An unexpected rise in the constant-volume heat capacity of bcc He\textsuperscript{4} is observed in the 0.02°K interval below the discontinuity at melting, giving thermodynamic evidence for the appearance of new modes of motion associated with the break-up of the crystal. The appearance of slipping motion in molecular dynamics computer experiments with hard-particle systems allows the nature of these instabilities to be examined.

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Melting usually appears in thermodynamic measurements as a sharp transition at a density that is well approximated by the empirical Lindemann law.\(^1\) At the melting density a process which can break up the long range order of the crystal and cause the disappearance of low frequency shear waves in the fluid becomes sufficiently probable. It is therefore natural to propose that at the melting point the crystal becomes unstable to a long wavelength transverse shear mode.\(^2\) The problem associated with any instability criterion is that it can apply only at a point beyond the thermodynamic stability limit and lead to van der Waals like behavior as, for example, in the infinite compressibility criterion. Furthermore it is not possible to identify the stable phase that the instability leads to; it could be another crystal structure. Nevertheless, the difference in the ability to support a long wavelength transverse mode is the only general way to distinguish between a solid and a fluid; the frequently used alternative of the degree of order does not distinguish between a solid and a fluid in two dimensions.\(^3\)

The lack of experimental evidence in favor of associating instabilities with melting is not surprising in view of the difficulty of detecting the appearance of one or a few highly cooperative low-frequency modes, particularly by measurement of thermodynamic properties which are usually dominated by the more abundant high-frequency modes. In helium, however, the melting temperature is so low that the high frequency modes are not yet fully excited and the heat capacity contribution of an excitation appearing just prior to melting is relatively more significant. Furthermore, it should be particularly prominent in
the bcc phase because the transverse (110) mode is well known to be of low frequency.4

We have measured the heat capacity \( C_V \) of He\(^4\) at a number of densities in the bcc and low-density hcp phases. The samples were contained in a pressure cell that was sealed by a remotely operated valve located at the cell itself. Problems associated with the use of a plug of solid He to seal the filling tube were thus avoided. A typical result for one sample passing through the bcc phase is shown in Figure 1.

The expected discontinuous increase of \( C_V \) at the melting temperature of the bcc phase is preceded by a rapid but smooth increase beginning 0.02°K lower, which is accompanied by an increase in the thermal relaxation time of the sample. This behavior is independent of the thermal history of the sample and was even observed when the heat capacity points were taken with decreasing temperature (by balancing a negative heat leak with a power input that was interrupted to produce a decrease in sample temperature). Edwards and Pandorf\(^5\) observed a similar effect but attributed it to pressure gradients in their sample and did not report their data in this region. Their cell was filled with sintered copper powder leaving an average pore diameter of 10 \( \mu \) and they observed other effects indicative of pressure gradients. However, the other effects disappeared after a half-hour anneal but the premelting "tail" in \( C_V \) did not. In the measurements reported here there is no reason to expect pressure gradients in the sample and no affects attributable to them were observed. We have searched for, but have been unable to identify, experimental errors which could produce this effect, and we therefore conclude that it must be characteristic of the melting process.
The transition of the hcp phase to liquid (I or II) or to bcc solid yields no obvious rise in $C_v$ similar to that accompanying melting of the bcc phase. However, careful analysis of the data in reduced form does show the presence of a similar, but much smaller, effect within $0.02^\circ K$ of each type of transition.

A model of the melting process which suggests an explanation of the helium results has been previously proposed to account for the behavior of hard disks as observed by molecular dynamics computer experiments in the phase transition region. In this simple model, which leads to nearly quantitative agreement with the computer results, alternative rows of particles are allowed to move relative to each other, the melting instability corresponding to the possibility of rows of particles suddenly being able to slide past each other at a critical density. The existence of such sliding motion has now been confirmed by computer experiments in a narrow density range of about 2% previous to melting.

Extensive computer runs in this narrow density range have led to the observation of a rarely occurring motion in which of the order of 10 successive nearest neighbors are shifted in a closed loop. The sequence of displacements tends to move in close-packed rows. A good example is the slipping motion of 7 particles in 870 disk system at a volume relative to close-packing of 1.265 (melting occurs at about 1.27) in which 2 adjacent rows of 3 and 4 particles moved antiparallel to each other while the pressure of the system remained virtually that of the solid phase. This slipping motion takes place in a relatively short time scale (on the order of 100 collisions per particle) comparable to the melting process itself.
It has not been possible to generalize the above simple model to 3 dimensions, nor has it been possible to study large enough systems of spheres on the computer to establish co-existing fluid and solid phases. Hence it is only possible presently to investigate motion in the metastable solid branch at a density slightly higher than the highest density at which the system is able to jump discontinuously to the fluid phase. In that region motion similar to the disk phase was observed; that is, the motion is primarily confined to close-packed planes in either a fcc or hcp crystal. About 20 such events involving anywhere from 3 to 30 moving particles in crystals consisting of a few hundred particles have been observed. The motion appears to be more planar and to involve fewer particles as the density is further removed from melting. Several circulatory motions of nearest neighbors have also been observed at a density at which the system subsequently melted and these show nearly as many nearest neighbor jumps in different planes as in the same plane.

In conclusion it appears that in these very anharmonic systems--hard spheres and helium--melting is preceded by the testing of a new region of phase space which becomes accessible upon melting. This testing can consist of either large scale collective oscillations of the particle about their lattice sites in certain favorable directions or an actual displacement of a set of particles to nearest neighbor sites. In the presence of attractive forces energy is absorbed into these modes leading to an increased heat capacity. Close to melting the displacements appear to become more complex. At melting they are no longer closed loops and thus rapidly propagate throughout the entire crystal. To confirm these partially supported conjectures, scattering and sound wave attenuation experiments should be carried out.
REFERENCES

FIGURE CAPTION

Figure 1. The constant-volume heat capacity of He$^4$ at a volume of 20.903 cm$^3$/mole. The dashed line shows the observed behavior in the hcp-bcc mixed phase region. The six lowest-temperature points were obtained on supercooled bcc phase.
Fig. 1

The graph shows the specific heat capacity ($C_v$) as a function of temperature ($T$) in units of J/mole-K. The phase transition from hcp to bcc structure is indicated by the label "hcp-bcc" and the transition from bcc structure is labeled "bcc." The temperature range is from 1.68 to 1.76 °K.
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