

Brillouin results seem to be systematically lower than the ultrasonic data and lower than the theoretical integral $J(\omega^*)$.¹⁵ We also find that the theoretically predicted dispersion is too small at large ω^* values. Probably the same argument about the assumption of the Ornstein-Zernike form should be invoked here. It should, however, be emphasized that the previously reported⁷ large discrepancies between the Brillouin and ultrasonic dispersion results have disappeared and that a reasonably good agreement with theory can now be obtained.

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¹²It should be noted here that for the investigated temperature range $B(\epsilon)$ turned out to be almost constant. The theoretical expression for $\pi B(\epsilon)$ is the same as that for the B in Eq. (6) of Ref. 4. The value of $\pi B(\epsilon)$ varied in our new analysis between 2.0 and 1.8. This should be compared with the constant value of 1.9 which was adopted for B in Ref. 4.

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¹⁵It has been pointed out to us by H. L. Swinney that in the derivation of the integrals given in Eqs. (11) and (12), only the critical part of the Rayleigh linewidth is introduced. The maximum difference in the value for the integrals between the assumption that the total linewidth equals the critical linewidth or equals only the background value is however not more than 20% at $\omega^* \approx 5$. The effect is much smaller for $I(\omega^*)$ than for $J(\omega^*)$.

Solid Phase of He⁴ Monolayers: Debye Temperatures and "Melting" Anomalies*

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Specific heats of He⁴ monolayers on graphite indicate two-dimensional solid phases. Debye temperatures Θ range from 17.6° to 56° systematically with coverage. Anomalies are identified with melting, but the melting process is a continuous transition. Films and bulk solid He⁴ at equal values of interatomic spacing have nearly the same Θ 's and melting temperatures.

Low-coverage He monolayers on basal-plane graphite surfaces behave as two-dimensional (2D) quantum gases.^{1,2} At higher densities, He³ and He⁴ display sharp second-order heat-capacity peaks attributed to lattice-gas-ordering transitions.³ In this Letter we describe new features at still higher coverages: a 2D solid regime closely analogous to bulk solid He⁴ which melts by a continuous process.

This study was made with the same apparatus and procedures as before. The films were twelve samples of He⁴, at coverages x between 0.7 and 1.16. We define $x \equiv N/N_m$, where $N_m = 96 \text{ cm}^3 \text{ STP}$ is the He⁴ monolayer capacity of the graphite calorimeter at low T . Film specific heats C/Nk are given in Fig. 1, much of the data being omitted for greater clarity. We include data near 3° for He⁴ at the "critical coverage" x_c of the ordering

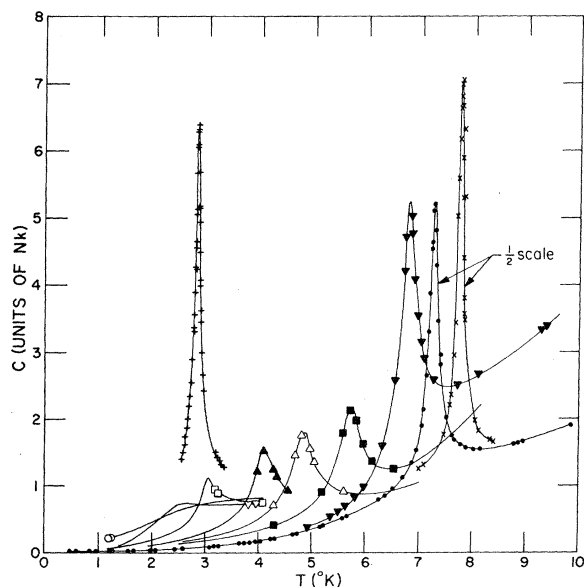


FIG. 1. Specific heats of He^4 monolayers on graphite. Fractional coverages x are pluses, 0.60 ("critical coverage" $x_c = \frac{1}{3}$); open circles, 0.07; open inverted triangles, 0.76; open squares, 0.81; closed triangles, 0.85; open triangles, 0.87; closed squares, 0.91; closed inverted triangles, 0.94; closed circles, 1.0; crosses, 1.16. For greater clarity only part of the data is shown.

transition to emphasize changes to a new regime at $x > x_c$. The critical quantity $N_c = 53.4 \text{ cm}^3 \text{ STP}$ was determined within 1% by a detailed survey of the critical region, and corresponds to the N at which peak height and temperature are maximized. Above x_c the ordering peak weakens rapidly until by $x = 0.7$ no trace remains: Here $C(T)$ is sigmoid, varying as low powers of T below 1.5° and tending to a constant $\approx 0.8Nk$ above 3° . With further increases of coverage to $x = 0.72$, an abrupt kink appears at 1.93° , and for $x = 0.76$ a cusp-shaped maximum is seen at 2.65° . The anomalies in C progressively strengthen and shift to higher T , resulting in the spectacular peaks at $x \sim 1$ with temperatures above 7° and heights considerably greater than the 3° ordering peak. A significant feature of these films is that C varies as T^2 for temperatures well below the anomalies.

T^2 heat capacities of He films on other substrates⁴⁻⁷ have been interpreted as signatures of 2D solids. 2D Debye temperatures of 14° – 30° have been reported, but changes of Θ with x conflict with models of uniform films. Roy and Halsey,⁸ citing the strong heterogeneity of most ad-

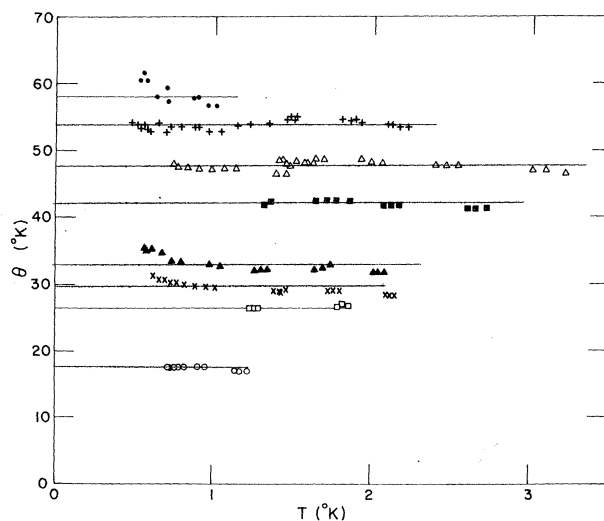


FIG. 2. 2D "Debye" temperatures Θ for $T/\Theta \leq 0.07$. Fractional coverages x are open circles, 0.72; open squares, 0.81; crosses, 0.82; closed triangles, 0.85; closed squares, 0.91; open triangles, 0.94; pluses, 0.99; closed circles, 1.0.

sorbents, attribute the "pseudo Debye" behavior to long-range variations in binding energy, which force adatoms into dense islands. On graphite we now find a wider range of magnitudes, $17.6^\circ \leq \Theta \leq 56^\circ$, changing consistently with x . Figure 2 presents Θ versus T for $x < 1$. Θ for each x is nearly constant at $T/\Theta \leq 0.07$ and decreases at high T . For $x = 1$ there is no constant region. This may be due to desorption and thermal promotion to the second layer, effects which are less important at lower x . For $x = 1.16$, $C(1^\circ)$ can be represented by a first layer with $\Theta = 56^\circ$ and a partial second layer of 2D gas.

Figure 3 displays the dependence of $\Theta(1^\circ)$ on coverage. For this plot we use a quantitative gauge of molecular area a based on the identification of the transition at x_c as ordering to a regular array at density $N(\text{He})/N(\text{graphite absorption sites}) \equiv x_c = \frac{1}{3}$.³ The crystallographic parameters of basal-plane graphite⁹ and the N_c for our cell yield a more precise value for adsorption area than the conventional method based on N_2 and Ar vapor-pressure isotherms: The two values disagree by 7%, consistent with the absolute accuracy of the isotherm method. Figure 3 includes the Θ 's at $T/\Theta \ll 1$ of hcp He^4 ,¹⁰ where the equivalent molecular area of the 3D solid is taken as $a = (\text{molecular volume})^{2/3}$. The two sets of Θ 's agree within 2% in a over the common range. Although some correspondence is reasonable, complete coincidence is totally unexpected.

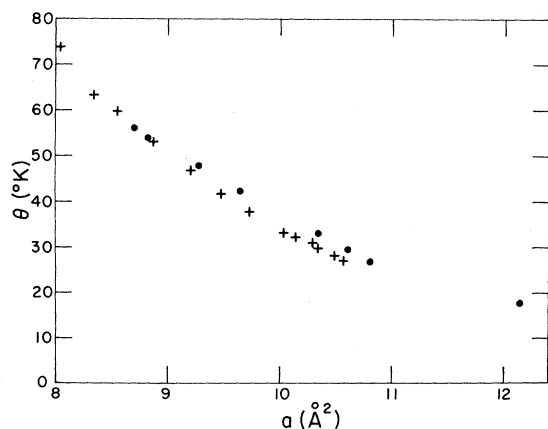


FIG. 3. Debye temperatures of He^4 monolayers (closed circles) and hcp He^4 (Ref. 10) (pluses) on a molecular-area scale.

Several mechanisms for the anomalies were considered, including melting, lattice-gas ordering, superfluidity, lateral condensation, and interlayer transitions. All but melting were discarded, for reasons outlined as follows. Lattice-gas ordering implies $C \propto \exp(-\text{const}/T)$ at low T rather than the observed T^2 . Peak heights would be greatest at x_g values corresponding to simple fractions, but x_g ranges from 0.42 to 0.58 (after desorption corrections), with no reversal of trend at $x_g = \frac{1}{2}$. Furthermore, we find comparable behavior in He^4 films on Xe-plated graphite, where the symmetry and density of sites are different. Superfluidity was ruled out by finding a strong peak above 7° in He^3 at $x \approx 1$. Lateral condensation requires very large 2D binding energies, over an order of magnitude greater than estimated,¹¹ and phase coexistence at lower x (which is not seen). Interlayer transitions are essentially single-particle processes, but the sharp peaks indicate collective behavior.

The melting hypothesis suggests a comparison of the temperatures of the film anomalies and melting temperatures of solid He^4 on a molecular area scale (see Fig. 4).¹⁰ The two sets of data are nearly parallel over the common range, film values lying at areas higher by 10–15%. The correspondence, although not as close as for the Θ 's, seems to confirm the melting hypothesis. The shift to higher areas is consistent with the idea of steric hindrance of atoms constrained to a plane.¹²

If film melting is correct, the process must be different from melting of 3D crystals. A first-order transition would cause discontinuities in

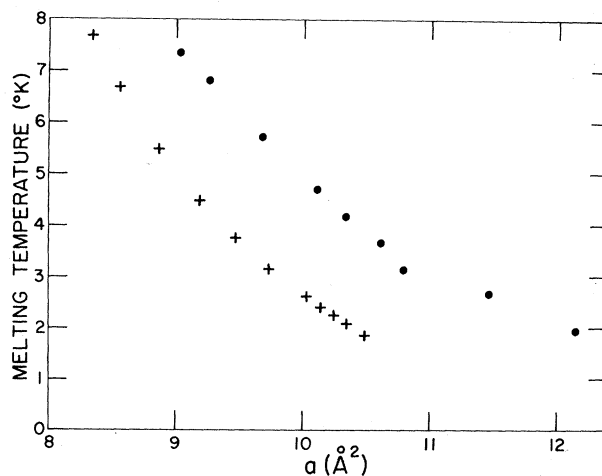


FIG. 4. Temperatures of the specific-heat anomalies in He^4 monolayers (closed circles) and melting temperatures of hcp He^4 (Ref. 10) (pluses) on a molecular-area scale.

$C(T)$ at the boundaries of the two-phase regions. In the films, melting appears to be a continuous function of T . This suggests a connection with general theories of the influence of dimensionality on long-range order^{13,14} which predict that in 2D the range of crystalline order changes gradually with T .

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