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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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 $N_m = 96$ cm³ 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 He⁴ monolayers on graphite. Fractional coverages x are pluses, 0.60 ("critical coverage" $x_g = \frac{1}{3}$; 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 $\simeq 0.8Nk$ 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 $14^\circ-30^\circ$ 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, $17.6^{\circ} \le \theta \le 56^{\circ}$, changing consistently with x. Figure 2 presents Θ versus T for x < 1. Θ for each x is nearly constant at $T/\Theta \le 0.07$ 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(He)/N(graphite absorption)sites) = $x_{F} = \frac{1}{3}$.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, 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 He⁴,¹⁰ where the equivalent molecular area of the 3D solid is taken as a= $(molecular volume)^{2/3}$. 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. Latticegas ordering implies $C \propto \exp(-\operatorname{const}/T)$ 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 He⁴ 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 He³ at $x \simeq 1$. 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 He⁴ 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 firstorder 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 moleculararea 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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