More complicated wave structures and less ideal-ized dynamics need to be considered, as do the effects of small-angle collisions in disrupting the adiabatic structure. Preliminary crude estimates indicate that when Eq. (18) is well satisfied, colli-sional effects may not lead to more rapid diffu-sion than in the absence of the fluctuations. This point may require computational verification.

In summary, by applying the results of Aamodt and Lieberman and Lichtenberg we show that a single, constant-amplitude electrostatic mode, resonant at some point with a multiple of the ion gyrofrequency (e.g., a velocity-space instability like the drift-cone mode), will lead to a stochas-tic velocity-space diffusion given by Eq. (8) and eventual particle loss if its amplitude is above a certain critical value given by Eq. (18). Below this amplitude a "superadiabaticity" exists in the sense that over many bounces the excursions in magnetic moment remain bounded.

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# Motional Narrowing in Monolayer-He³-Film NMR*

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NMR linewidth measurements have been made on He³ monolayer films adsorbed on graphite. A melting transition and transition to an ordered lattice gas are identified. Mobile, ideal-gas behavior above the transition temperature is observed with the gas phase persisting to low temperatures for coverages outside the transition regions. The present measurements indicate that helium films adsorbed on graphite provide a fruitful system for the study of NMR in two dimensions.

A subject of considerable current interest is the behavior of matter of reduced dimensionality. Monolayer helium films provide a particularly at-tractive model of two-dimensional behavior be-cause they are inert and monatomic, thus avoid-ing the complications of chemisorption and mo-lecular rotation. Thermal properties,[1] for exam-ple specific heat and heat of adsorption, com-prise the majority of measurements on monolay-er films. Several NMR studies have been made,[1] but it has not been possible to make a very close connection between NMR and specific-heat ob-servations. In part this has been due to the lack of any dramatic signatures in either measure-ment. Recent experiments with helium adsorbed on graphite[2-5] have revealed monolayer film be-havior not observed in previous studies. Sharp heat-capacity peaks were found which have been attributed to phase transitions. The present measurements give direct evidence that these phase transitions are accompanied by changes in adatom mobility.

The NMR measurements were made using graphitized carbon black[6] as a substrate. Origi-nally Grafoil similar to that used in the specific-heat work was tried but the signal was severely distorted, apparently because of rf shielding. The graphitized carbon black is in the form of fine particles ~0.2 $\mu$m in diameter. Electron microscopy shows the particles to be polyhedra with the basal plane exposed. Adsorption proper-ties of the graphitized carbon black and Grafoil are similar.[7] The graphitized black was enclosed in a quartz sample tube which was mounted in the cryostat and baked under vacuum at 1000°C for three days. A liquid-nitrogen trap in the fill line containing a Union Carbide 13× molecular sieve removed impurities in the He³ gas. A monolayer capacity of 3.17 cm³ STP was determined by a He³ isotherm at 4.2 K, accurate to about 3%. The spectrometer, of standard Rollins design with lock-in detection, operated at 20.5 MHz. The low signal-to-noise ratio made it necessary to average the widths of ten traces at each tem-perature to reduce the uncertainty.

Data taken between 1.4 and 4.2 K for fractional monolayer coverages $0.3 \leq x \leq 0.9$ are shown in Fig. 1. The linewidth $\delta H$ is the difference be-tween the maximum and minimum of the signal derivative. The general features of the width as
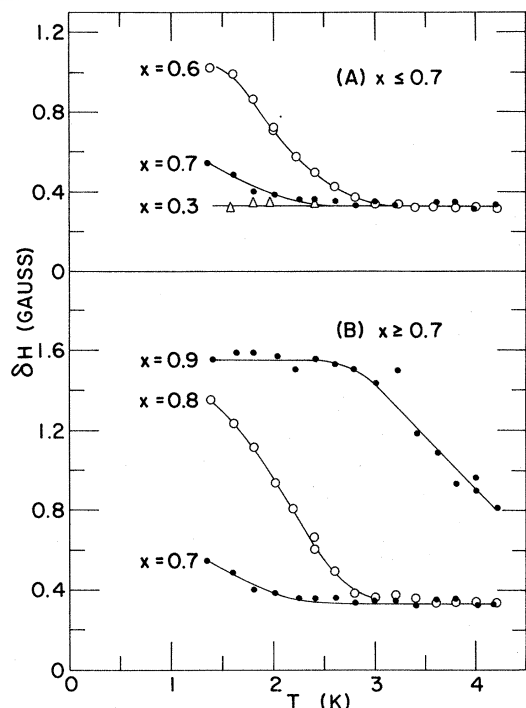
FIG. 1. Experimental linewidth as a function of temperature. $x$ is the fractional He$^3$ monolayer coverage.
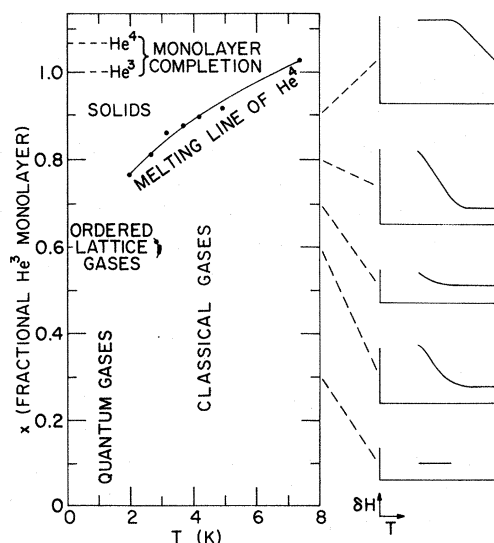


FIG. 2. Phase diagram for monolayer helium films (see Ref. 10). Data points denote peaks in the specific heat. The diagrams to the right are schematic representations of the data in Fig. 1.

a function of temperature are as follows: At high temperature the width is temperature independent and equal to 0.33 G for all $x \leq 0.8$. It is felt that this width is instrumentally determined. At low temperature the linewidth varies considerably with coverage and temperature. For several coverages a broad line is seen at 1.4 K which narrows at higher temperatures with the narrowing temperature dependent on coverage. For $x$ = 0.7 the line has almost completely narrowed by 1.4 K, while the lowest coverage line is narrow at all temperatures.

This narrowing of the resonance line at increased temperature is interpreted as being due to a relatively higher mobility of the helium adatoms along the surface, the well-known motional narrowing.[8] On the basis of this interpretation one can see from the data of Fig. 1(b) that for coverages near monolayer completion the film changes to a state of higher mobility at temperatures increasing monotonically with coverage. For $x$ = 0.7 this change is nearly complete at 1.4 K. At lower coverages [$x \leq 0.7$, Fig. 1(a)] distinctly different behavior is observed. A low mobility state is observed below 3 K for $x$ = 0.6, while for *both lower and higher* coverages the low-temperature mobility is *greater*. Thus in this coverage range an *increase* as well as a decrease in the number of ad-

sorbed atoms results in an *increase* in the film mobility.

To interpret these mobility changes further it is necessary to consider the heat-capacity results previously mentioned. As Resing[9] has pointed out, for adsorbed systems the NMR alone is not sufficient to show that an abrupt transition has taken place, but only indicates that the mobility has changed. In this respect the specific-heat measurements are most valuable. The data revealed very sharp peaks, attributed to phase transitions, which form the basis of the phase diagram[10] shown in Fig. 2. The NMR results, shown schematically on the right of the figure, can now be interpreted in light of this phase diagram. Near monolayer coverage the specific heat indicates a two-dimensional "melting."[4] This is based on a correspondence with bulk helium of the melting and Debye temperatures as a function of atomic density. The NMR results provide direct evidence of a mobility change, substantiating the specific-heat interpretation. Although the melting line shown in Fig. 2 is for data taken on He$^4$ films, the heat capacity of one He$^3$ film with $x \simeq 1$ was measured, revealing a similar peak.

At 0.6 monolayers a sharp heat-capacity peak is observed at 3 K for both helium isotopes,[3,5] while for higher and lower coverages the peak is absent. At this coverage the helium film is in registry with the graphite substrate structure with one helium atom for every three potential

minima. It was proposed that a transition took place to an ordered "lattice gas," with the substrate providing the lattice. The NMR results show clearly that this transition also involves a change in mobility, and is thus not a simple lattice-gas order-disorder transition. It is also seen that for coverages away from the "critical" coverage the lack of film-substrate registry allows the film mobility to persist to lower temperatures.

Using the fact that for $x = 0.6$ the helium atoms are ordered on the substrate potential, for which the lattice structure is known, the second moment was calculated using Van Vleck's formula.[11] Since the signal-to-noise ratio was too small to allow a direct measurement of the second moment, the measured linewidth was related to the second moment by assuming a Gaussian line shape. For a triangular array with interatomic spacing $r_{ij} = 4.26$ Å, the calculated rigid lattice linewidth, allowing for instrumental broadening, is 0.99 G. Within experimental uncertainty this is consistent with the measured value, although the temperatures attained in the experiment were not sufficiently low to assure that this is the experimental rigid lattice width. If it is assumed that the film with $x = 0.9$ also orders in a triangular array (not, of course, in registry with the substrate) so that $1/r_{ij} \sim x^{1/2}$, a rigid lattice width of 1.76 G is calculated. This is larger than is observed, although by scaling down the calculated linewidth, which would be the case if the measured line shape had some Lorentzian character, both sets of data can be fitted within experimental uncertainty. It must be noted, however, that no account has been taken here of exchange, known to have a large effect on the linewidth in bulk solid helium. Possibly for $x = 0.9$ there is some exchange narrowing, while for $x = 0.6$ the registry with the substrate causes sufficient localization of the helium atoms that exchange is unimportant. Questions such as this are too detailed for these preliminary results.

The data for $x = 0.6$ were fitted by the expression[12]

$$\delta\omega^2 = \delta\omega_0'^2 + \delta\omega_0^2 2\pi^{-1} \tan^{-1}(\delta\omega \, \tau_c),$$

where $\delta\omega_0'$ is the high-temperature linewidth, $\delta\omega_0$ is the rigid lattice width, and $\tau_c$ is the spin-spin correlation time. Assuming a form for $\tau_c$ of

$$\tau_c = \tau_0 e^{V/kT},$$

a fairly good fit to the data could be made with $\tau_0 = 9.2 \times 10^{-8}$ sec and $V/k = 14°$. This expression is only a very rough approximation, providing or-

der-of-magnitude estimates of the quantities involved. It must be stressed that the data are not sufficiently accurate to rule out other functional forms for $\tau_c$. Furthermore, the expression for $\delta\omega^2$ was derived for three-dimensional systems and should properly be modified for use in two dimensions. To the author's knowledge only one attempt has been made[13] to calculate the effects of two-dimensional diffusion on the NMR and the result does not appear to be applicable to the present case.

These measurements, when combined with the previous specific-heat work, provide a fairly detailed picture of the properties of a monolayer helium film adsorbed on graphite. It has been possible to relate mobility changes observed in the NMR to sharp peaks in the specific heat, giving strong evidence of the existance of several phases. It will now be necessary to extend the measurements to include spin-lattice relaxation times in order to probe more deeply the dynamic properties of two-dimensional systems.

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