B 7, 4491, 4502 (1973).

[14] U. Landman and M. Shlesinger, Phys. Rev. B 16, 3389 (1977), and Ref. 8(d), 27, and 36 therein.

[15] E. W. Montroll, J. Math. Phys. (N.Y.) 10, 753 (1969).

[16] U. Landman and M. Shlesinger, Bull. Am. Phys. Soc. 23, 211 (1978), and Solid State Commun. 27, 939 (1978).

Has Two-Dimensional Superfluidity Been Seen in Real ^{4}He Films?

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The theory of two-dimensional superfluidity by Nelson and Kosterlitz is examined in the context of ideal interacting ^{4}He films. It is shown that superfluid onset in a film on a uniform surface would have a critical-temperature gap due to phase condensation. No experiments on uniform or heterogeneous substrates have disclosed any gap, indicating that superfluid onset in experimental films may have another origin.

In a recent Letter Nelson and Kosterlitz[1] predict that, if recent theories of phase transitions in the planar *XY* model are applicable to uniform two-dimensional ^{4}He films, the areal density of superfluid will undergo a universal jump ρ_s as the critical temperature T_c is approached from below. The predicted relation is a linear dependence, with theoretical slope independent of the wall potential, coverage, and other details:

$$\lim_{T\to T_c^-}\left(\frac{\rho_s}{T}\right)=2m^2k_B/\pi\hbar^2 = 3.49\times10^{-9}\ \mathrm{g/cm^2\ K}. \qquad (1)$$

Recent experiments by Bishop and Reppy[2] using a torsional oscillator and re-examination of third-sound experiments by Rudnick[3] are in quantitative agreement with Eq. (1). In addition Bishop and Reppy cite third-sound results obtained by Mochel and by Hallock which are consistent with Refs. 2 and 3. The correspondence appears to confirm the theory and, at the same time, the judgment that the experimental films were indeed uniform two-dimensional (2D) systems. However, in this Letter I cite contrary evidence that makes it extremely unlikely that the films in question could have been uniform. On this basis, we are faced with (at least) two alternative explanations: (a) 2D superfluidity is not strongly affected by the kind of heterogeneity present in the experimental films, or (b) the agreement is fortuitous and an explanation of the data must be sought elsewhere.

Virtually all solid surfaces are heterogeneous in adsorption except for atomically clean and well-ordered crystals having a single class of crystal facet exposed to the adsorbed gas.[4] Unless the uniformity of the substrate is demonstrated for the particular gas, physical property, coverage, and temperature conditions in question, then it is prudent to suspect it as heterogeneous. There are no reported studies demonstrating that the several substrates Mylar,[2] glass,[3] argon-coated glass,[3] and polished CaF_2 [3] used in the torsional oscillator and third-sound experiments are uniform in adsorption, and therefore the uniformity of the films has to be doubted. But even in the event that all of the substrates were ideal, the ^{4}He films themselves would be nonuniform *in the plane*. This nonuniformity arises from the interactions between the He atoms themselves, which causes monolayers adsorbed on uniform surfaces to condense into 2D liquid phase at low temperature and, if the density is sufficiently high, to form 2D solid. In the following I discuss the experimental results for ^{4}He on uniform surfaces, and explore the consequences of the theory of 2D superfluidity applied to such films.

Monolayer and multilayer films of ^{4}He have been studied for many years. During the earlier period the substrates were typically heterogeneous adsorbents, and on these surfaces the films showed little evidence of any layer structure or phases within layers. The absence of structure is now understood to result from strong lateral fields due to substrate heterogeneity. However, since 1970 film studies on more uniform substrates have disclosed a succession of distinct regimes within the first and second adsorbed layers of ^{4}He, ^{3}He, and ^{4}He-^{3}He mixtures.[5-12] These adsorbents have been various high-area basal-plane graphite substrates and basal-plane graphite plated with monolayers of noble gases. The different phases are understood as arising from combinations of the He-He interactions and interactions with the substrate, and quantitative theories[13-15] based on the known potentials and structures of the surfaces agree well with experiment.

The simplest phase diagram that has been observed for ^{4}He monolayers is that of the second layer on graphite, which shows only 2D gas and liquid phases and no registered phase. The immediate substrate for the second layer is a monolayer of close-packed 2D solid helium, which provides a nearly inert and smooth surface. This system appears to be the closest realization of 2D ^{4}He that has been produced to date. However, although the condensation is limited to just the second-layer atoms, their interactions are mediated to some extent by the underlying substrate, and therefore the critical properties and exact location of the 2D vapor-liquid phase boundary depend on the substrate. Several mechanisms for substrate mediation are possible. In the case of second-layer ^{4}He compared to the first layer on graphite the principal mechanism is believed to be the magnitude of the adsorption potential which controls the amplitude of surface-normal motion.[16,17] The surface-normal motion reduces the average surface-parallel interaction between He atoms and hence the 2D critical temperature. The effect is of comparable importance on Ne-plated graphite.[9]

Experimental observations of superfluidity require continuous flow paths over macroscopic areas. Dimensions depend on instrumental details, but are typically on the order of 1 cm^2. In a two-phase film with only one-phase superfluid, experimental detection requires long-range connectivity of that phase, which depends on the fractional area covered and its spatial distribution. In ideal systems two phases separate into just two homogeneous regions but on realistic uniform substrates phases can be finely dispersed, being nucleated at imperfections. When the average density of the film is low, 2D liquid is in relatively small patches surrounded by 2D vapor, their sizes and placement depending on the distribution of nucleation centers and the treatment history of the film. Thus there should be no universal relation for superfluid onset in macroscopic films on all surfaces and with all experimental methods, even if the fundamental relation governing onset in a uniform 2D film were universal. However, if the theory is correct for uniform films, then certain general features emerge which should lead to qualitatively similar aspects in the presence of phase condensation. To illustrate these I assume specific phase boundaries. Figure 1(a) shows the 2D liquid-vapor phase boundary for the second layer of ^{4}He on graphite, as given by Polanco and Bretz.[12] In addition I show a line corresponding to Eq. (1), here marking the maximum transition temperature at each density of a single uniform phase. According to theory[1] this limit corresponds to uniform films in which there is no depletion of superfluid below T_c^- due to processes other than vortex depairing. In most of the range the limiting normal-superfluid boundary lies wholly in the two-phase region. In this region to the left of the normal-superfluid boundary the liquid is superfluid but the vapor is not. Thus the film at low temperature and low coverage consists of isolated 2D superfluid patches and hence the film as a whole does not display superflow at any temperature down to $T = 0$. With increasing coverage the average patch size increases. Neighboring close patches coalesce to form larger patches

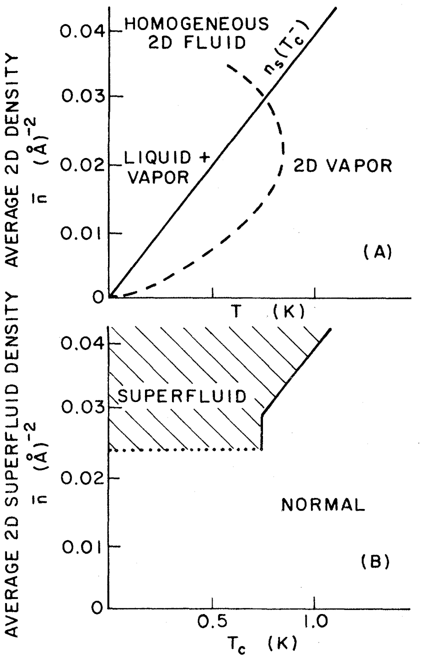

FIG. 1. (a) Phase diagram of a ^{4}He monolayer on a uniform surface, showing a two-phase liquid-vapor coexistence region with outlines corresponding to the second layer on basal-plane graphite (Ref. 12). Also shown is the superfluid density–critical-temperature relation according to the theory of Nelson and Kosterlitz (Ref. 1), assuming no depletion due to excitations. (b) Superfluid onset temperatures of films having phase boundaries shown in (a).

until at a coverage whose value depends on the details of the substrate and the measurement, the film develops a continuous 2D liquid path extending over the entire experimental area, and superflow appears. In Fig. 1(b) I show its appearance at a coverage of $\frac{2}{3}$ of the liquid density. The transition from normal to superfluid is in this case a 2D percolation transition, whose nature should be different from a transition brought about by a change in density of a uniform fluid. The critical temperature of the percolation transition is that of the critical end point, where the normal-superfluid line and the phase coexistence boundary intersect. On increasing the coverage the connectivity of the film increases but T_c remains the same until the average density exceeds the density of the critical end point. Above this coverage the film is a uniform fluid at the temperature of the transition, and therefore T_c increases linearly thereafter, with slope appropriate to the uniform film.

Changes in either the normal-superfluid line or the two-phase boundary affect the parameters of detection of superflow. For example, depletion of the superfluid density before the Nelson-Kosterlitz transition causes onset temperatures to be depressed. However, the overall shape remains similar to Fig. 1(b), with a gap, a constant-temperature section, and section with variable T_c at higher density. The variable section need not be linear or even monotonically increasing if depletion varies with temperature and density. In all of these variants there is a region of transition temperatures that is inaccessible to experiment, between 0 and the T_c corresponding to the density of the 2D liquid in equilibrium with its vapor. This situation is analogous to that in 3D, where there are no transition temperatures between 0 and T_λ of saturated liquid. Presumably there could be a transition in the 3D vapor if it could be cooled below the Bose-Einstein transition temperature corresponding to its density. However, the density of the vapor decreases more rapidly than $T^{3/2}$ so that it is always in its normal phase all the way to $T=0$. If in contrast to Fig. 1(a) the phase condensation were depressed so far that the normal-superfluid transition line did not cross the two-phase boundary [Fig. 2(a)], superfluidity would appear at low coverages in an isolated region of temperatures not extending to $T=0$, as in Fig. 2(b). The two distinct regions of superfluid and normal behavior correspond to homogeneous 2D phases (A) and to two-phase coexistence regimes (B) separated from the A regions by lines of percolation transitions.

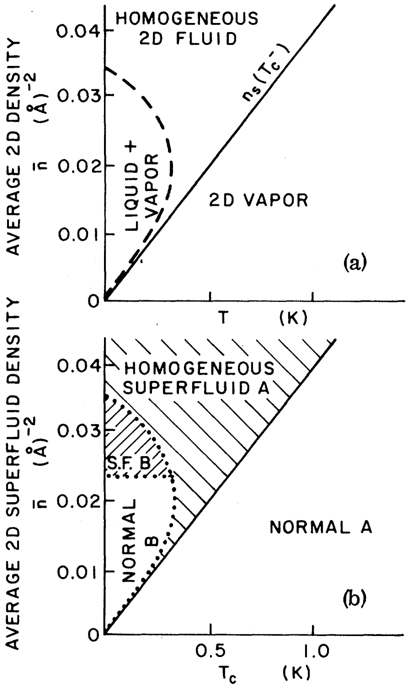

FIG. 2. (a) Phase diagram of a ^{4}He monolayer with a liquid-vapor condensation region having temperatures below the superfluid onset line. (b) Superfluid onset temperatures corresponding to the boundaries of (a). There are two normal and two superfluid regimes, corresponding to uniform and phase condensed regions. Percolation transitions are shown as dotted lines.

It is noteworthy that these arguments relating phase condensation and superfluidity in monolayers ought to be relevant to any mechanism of 2D superfluidity in uniform films, and are not limited to the Nelson-Kosterlitz theory. The recent experiments[2,3] show superfluid onset temperatures varying linearly with coverage over the full experimental range from 1.9 to 0.3 K, and additional third-sound data extends T_c's down to 0.1 K.[19] The thicknesses range from 1.55 to 0.72 layers on top of an inert film of about 1.4 layers which is presumed to be immobilized by substrate heterogeneity. The thicknesses of the active layers are in the range where, if the films were uniform, they would undergo phase condensation within the surveyed temperature range.

If the superfluid transitions that are observed are to be understood in terms of a 2D theory, then the absence of a critical-temperature gap implies that phase condensation is either nonexistent or irrelevant. It is not obvious that either case is reasonable, and it would therefore seem necessary that they be examined in detail. To be convincing, the theory would have to deal with realistic models of heterogeneity, involving wide ranges of magnitudes and scale lengths to model the variety of substrates used in the cited experiments.

An alternative explanation is that superfluid onset is not strictly a uniform-film phenomenon. If the films undergo phase condensation before superfluid onset and if superfluidity involved a collective state of the two-phase system then a critical-temperature gap would not necessarily appear. Such a state is quite different from that discussed by Nelson and Kosterlitz.[1] It is, however, consistent with the theory of clustering and percolation,[20,21] which has been proposed to explain results obtained on more uniform surfaces.[22,23]

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[1] D. R. Nelson and J. M. Kosterlitz, Phys. Rev. Lett. 39, 1201 (1977). See also J. M. Kosterlitz and D. J. Thouless, J. Phys. C 6, 1181 (1973).

[2] D. J. Bishop and J. D. Reppy, Phys. Rev. Lett. 40, 1727 (1978).

[3] I. Rudnick, Phys. Rev. Lett. 40, 1454 (1978).

[4] J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975).

[5] M. Bretz *et al.*, Phys. Rev. A 8, 1589 (1973).

[6] R. L. Elgin and D. L. Goodstein, Phys. Rev. A 9, 2657 (1974).

[7] R. J. Rollefson, Phys. Rev. Lett. 29, 410 (1972); B. P. Cowan *et al.*, Phys. Rev. Lett. 38, 165 (1977).

[8] S. V. Hering, S. W. Van Sciver, and O. E. Vilches, J. Low Temp. Phys. 25, 793 (1976).

[9] S. B. Crary and O. E. Vilches, Phys. Rev. Lett. 38, 973 (1977); S. B. Crary, O. Ferreira, and O. E. Vilches, unpublished.

[10] K. Carneiro, W. D. Ellenson, L. Passell, J. P. McTague, and H. Taub, Phys. Rev. Lett. 37, 1695 (1976).

[11] M. Bretz, Phys. Rev. Lett. 38, 501 (1977).

[12] S. E. Polanco and M. Bretz, Phys. Rev. B 17, 151 (1978).

[13] C. E. Campbell and M. Schick, Phys. Rev. A 3, 691 (1971).

[14] M. D. Miller and C. W. Woo, Phys. Rev. A 7, 1322 (1973).

[15] R. L. Siddon and M. Schick, Phys. Rev. A 9, 907 (1974).

[16] L. M. Sander, M. Bretz, and M. W. Cole, Phys. Rev. B 14, 61 (1976).

[17] A. D. Novaco, Phys. Rev. B 13, 3194 (1976).

[18] M. Schick, J. Walker, and M. Wortis, Phys. Rev. B 16, 2205 (1977).

[19] J. H. Scholz, E. O. McLean, and I. Rudnick, Phys. Rev. Lett. 32, 147 (1974).

[20] J. G. Dash, Phys. Rev. B 15, 3136 (1977).

[21] B. A. Huberman and J. G. Dash, Phys. Rev. B 17, 398 (1978).

[22] J. A. Herb and J. G. Dash, Phys. Rev. Lett. 29, 846 (1972).

[23] M. Bretz, Phys. Rev. Lett. 31, 1447 (1973).

Adsorption and Dissociation of Nitric Oxide on the Ru(001) Surface

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The adsorption of nitric oxide and its dissociation on the Ru(001) surface have been studied through the vibrational energies of the adsorbed layer. The inelastic electron scattering measurements show that two distinct states of molecular NO are adsorbed at 130 K. The dissociation of a bridged NO is complete at 316 K, whereas a linear form remains on the surface until 500 K. This is explained by a difference in activation energies for dissociation of NO and by the blocking of sites by nitrogen and oxygen adatoms.

The adsorption and reaction of NO on metal surfaces is a subject of obvious interest in surface chemistry. In addition to the industrial importance of the catalytic reduction of NO, the wide variety of NO complexes in metal nitrosyls suggests that the surface chemistry of NO will be a fertile area of research.[1] In this work, we report the first vibrational measurements of NO on the Ru(001) surface and direct evidence of two forms of adsorbed NO with differing activation energies for dissociation.

Previous studies have been made of NO chemisorbed on the Ru(101) and Ru(100) surfaces as well as on a Ru field-emission tip.[2-6] The photoemission measurements of NO adsorbed on the Ru(100) surface by Bonzel and Fischer were car-