[1] B. B. Kadomtsev and O. P. Pogutse, Zh. Eksp. Teor. Fiz. 51, 1734 (1966) [Sov. Phys. JETP 24, 1172 (1967)], and Dokl. Akad. Nauk SSSR 186, 553 (1969) [Sov. Phys. Dokl. 14, 470 (1969)].

[2] G. M. Zaslavskii and N. N. Filonenko, Zh. Eksp. Teor. Fiz. 54, 1590 (1968) [Sov. Phys. JETP 27, 851 (1968)].

[3] T. H. Stix, in *Proceedings of the Third Symposium on Plasma Heating in Toroidal Devices, Varenna, Italy, 1976* (Editrice Compositori, Bologna, to be published).

[4] A. B. Rechester and T. H. Stix, Phys. Rev. Lett. 36, 587 (1976).

[5] G. M. Zaslavskii and B. V. Chirikov, Usp. Fiz. Nauk 105, 3 (1971) [Sov. Phys. Usp. 14, 549 (1972)]; B. V. Chirikov, *Research Concerning the Theory of Non-linear Resonance and Stochasticity* (CERN, Geneva, 1971).

[6] B. B. Kadomtsev and O. P.Pogutse, Vopr. Teor. Plazmy 5, 209 (1967) [Rev. Plasma Phys. 5, 249 (1970)].

[7] T. M. O'Neil, Phys. Fluids 8, 2255 (1965).

[8] J. B. Taylor and E. W. Laing, Phys. Rev. Lett. 35, 1306 (1975).

[9] G. R. Smith and A. N. Kaufman, Phys. Rev. Lett. 34, 1613 (1975).

[10] N. T. Gladd and D. W. Ross, Phys. Fluids 16, 1706 (1973).

[11] P. F. Byrd and M. D. Friedman, *Handbook of Elliptic Integrals for Engineers and Scientists* (Springer, New York, 1971).

[12] A good review is given by D. A. Ehst, Ph.D. thesis, Massachusetts Institute of Technology, 1976 (unpublished).

[13] B. Coppi and A. Taroni, Plasma Phys. 16, 161 (1974), and 17, 951 (1975).

[14] M. Dobrowolny and P. Negrini, Phys. Rev. Lett. 28, 132 (1972).

Modification of the Low-Density Phases of Adsorbed Helium Monolayer Films Produced by Changes in the Adsorbing Substrate*†

S. B. Crary and O. E. Vilches
Department of Physics, University of Washington, Seattle, Washington 98195

(Received 14 February 1977)

The specific heats of monolayer ^{4}He and ^{3}He films adsorbed on Ar-plated Grafoil show profound differences from films on bare Grafoil. The apparent liquefaction temperature of ^{4}He is doubled, and the interacting Fermi gas behavior of ^{3}He is modified to show either condensation or strong band effects.

Surface phases of monolayer helium films adsorbed on Grafoil[1-6] have been the subject of considerable experimental study since the work of Bretz and Dash.[7] Some of these phases have been successfully described in terms of two-dimensional (2D) models. Heat capacity measurements of two-layer films[8,9] have provided some information on the behavior of helium adsorbed on a solid substrate other than Grafoil. The adsorbent is then helium-plated Grafoil. The "second layer" studies have shown a marked *decrease* in the 2D ^{4}He condensation temperature, almost no change in the thermodynamic behavior of ^{3}He, the absence of ordering transitions for both isotopes, and the appearance of melting at densities comparable to those of the first layer.

In this Letter we report specific-heat measurements of both ^{4}He and ^{3}He monolayers adsorbed on a radically different surface, argon-plated Grafoil. Argon plating increases the depth and the variation of the depth and changes the translational symmetry of the adsorbing potential while still providing a well-characterized surface. Our measurements show that by modifying the substrate it is possible to change the thermodynamic properties of the adsorbed films. We have produced a 1-K *increase* in the apparent condensation temperature of ^{4}He. In addition, we have observed either condensation or the existence of band-type effects in ^{3}He.

Previous experimental work on argon-plated Grafoil has consisted of measurements of adsorption isotherms at $T \geq 4.2$ K.[10,4] The 4.2-K results for ^{4}He have been theoretically analyzed by Novaco,[11] who deduced the second virial coefficient. In addition, the density of states of a single adsorbed helium atom on rare-gas–plated graphite has been calculated,[12] as has the effect of the substrate potential on the ground state of adsorbed helium.[13]

Measurements were carried out using a well-characterized Grafoil cell (cell *B* of Ref. 2) plated at nitrogen temperature with 85 cm^3 of argon. The argon monolayer capacity of this cell at 77 K is 82± 3 cm^3. Helium coverages were prepared by admitting known quantities of gas to the cell at 4.2 K. The adsorbed film was annealed at 8 K for two hours and then cooled slowly to the experimental range.

Our ^{4}He results are displayed in Fig. 1(a). The runs at areal densities $n = 0.0093$, 0.0233, 0.0846, and 0.0887 Å^{-2} contain most of the data taken at these coverages. A similar number of specific-heat points were taken for all other coverages, but for clarity only smooth lines with a few experimental points are shown. The dominant feature is a rounded specific-heat peak that moves to higher temperature as the coverage is increased, the strongest peak ($C/Nk \cong 3.5$) occurring for $n = 0.0233$ Å^{-2} and $T = 2.28$ K. The positions of these peaks in the density-versus-temperature plane are shown in Fig. 1(b), where peak positions for ^{4}He on unplated Grafoil are also shown. The phase for ^{4}He on bare Grafoil on the high-temperature side of the boundary is a 2D interacting Bose gas.[2] For T lower than the dashed line, the phases are believed to be a 2D liquid for $n < 0.05$ Å^{-2}, a substrate registered lattice gas for $n \cong 0.06$ Å^{-2}, and a 2D solid above 0.08 Å^{-2}. The small region between 0.07 and 0.08 Å^{-2} could be a substrate-ordered phase or a region of coexisting substrate-ordered and solid phases.[6] The peaks measured using the Ar-plated Grafoil fall on a curve very different from those on the unplated substrate, except for the highest two densities where the same melting line appears to be followed. This agreement may be coincidental. For $T < T_{\text{peak}}$ the temperature dependence of the specific heat at $n = 0.0846$ Å^{-2} is the same as that of the lower-density coverages, while the $n = 0.0887$ Å^{-2} data show approximately T^2 behavior with $\theta_{\text{Debye}} \simeq 31$ K, higher than for a similar coverage on unplated Grafoil.

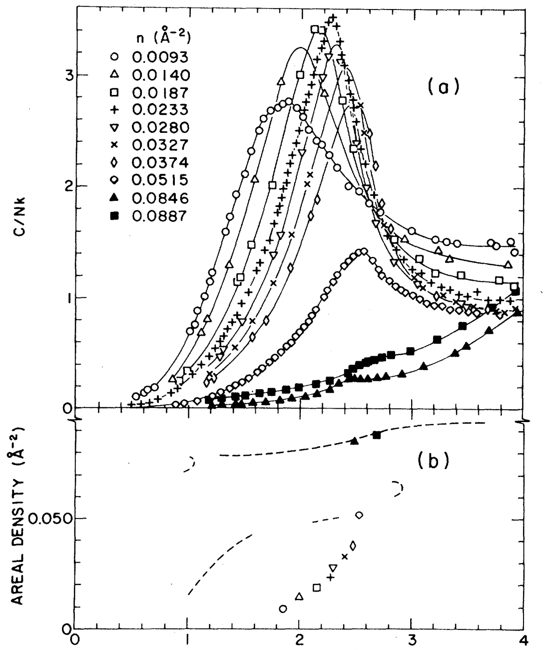

FIG. 1. (a) C/Nk vs T for ^{4}He on Ar-plated Grafoil. (b) Location of heat-capacity peaks in the n-T plane. Dashed line, ^{4}He on bare Grafoil (from Refs. 2, 3, 6, and 14).

We have taken heat capacity data for two ^{3}He coverages. We chose the coverage that had given the highest peak for ^{4}He, and one substantially larger but still in the range measured by Hickernell, McLean, and Vilches[14] on unplated Grafoil. Their results show that the heat capacity of ^{3}He on bare Grafoil for $T > 0.5$ K and lower densities is like that of an interacting 2D Fermi gas. At lower temperature, a rounded anomaly at $T \cong 0.2$ K shows the effect of strong ^{3}He-^{3}He interactions. Results for the Ar-plated substrate are shown in Fig. 2. At temperatures above 1 K there is no evidence of the type of peaks seen for ^{4}He. For $n = 0.0233$ Å^{-2} a peak was found at $T = 0.75$ K. This peak decreases in height (almost disappears) for the higher coverage. This last coverage, the only one taken to 0.13 K, also shows some evidence of the behavior observed by Hickernell, McLean, and Vilches[14] below 0.3 K.

We now compare our results to the behavior of films on unplated Grafoil. For helium adsorbed on unplated Grafoil at low densities, Siddon and Schick[15] have shown that the experimental re-

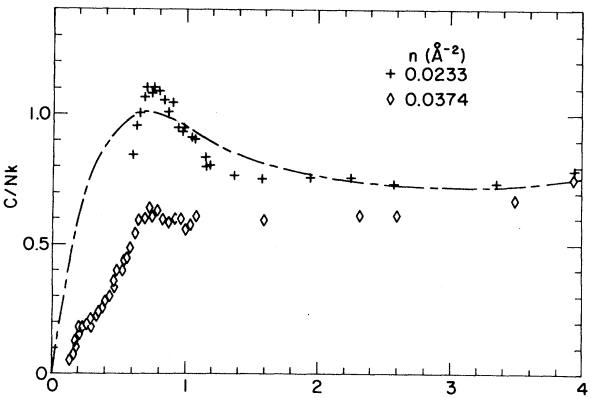

FIG. 2. C/Nk vs T for ^{3}He adsorbed on Ar-plated Grafoil. Dashed line, calculation of Novaco and Milford (Ref. 12) for $n = 0.027$ Å^{-2}.

sults can be adequately described by

$$C/Nk = 1 - n\beta^2 d^2B/d\beta^2, \qquad (1)$$

where B is the second virial coefficient and $\beta = (kT)^{-1}$. They calculated $B(T)$ and its derivatives for both ^{4}He and ^{3}He ignoring the substrate potential. When results are correctly described by Eq. (1), the expression $[(C/Nk) - 1]n^{-1}$ is a function of T alone. Siddon and Schick plotted the ^{4}He and ^{3}He data of Refs. 7 and 14 in this way and found that for all coverages below one-half monolayer and temperatures above any anomalies the experimental points for each isotope describe a common curve, in good agreement with their theory.

In Fig. 3 we present our ^{4}He results for plated Grafoil plotted in this manner. Our intermediate-coverage data appear to fall on a different common curve than the one for unplated Grafoil, indicating a substantial change in the virial coefficient. Deviations from the common curve for the lowest-density data are due to a small amount of substrate heterogeneity. The same trend can be seen in low-density data for ^{4}He on unplated Grafoil.[16]

For $T < T_{\text{peak}}$ and for all ^{4}He coverages except $n = 0.0887$ Å^{-2}, the specific heat displays a power-law dependence on T between 0.5 and 2.0 K. From a log-log plot of the data we obtain an exponent of 3.3 ± 0.2. For comparison, the unplated system gives 2.2 ± 0.2. The unplated results are in reasonable agreement with a theoretical calculation of 2D liquid ^{4}He by Miller and Woo[17] which ignored the substrate potential.

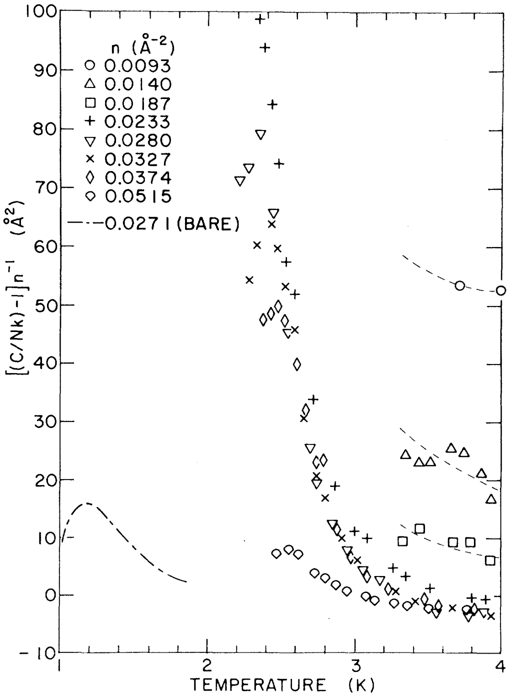

FIG. 3. ^{4}He data above the peak temperature plotted as $[(C/Nk) - 1]n^{-1}$ vs T.

All previous helium monolayer work on Grafoil has shown, in agreement with theory, that except for a narrow range of densities ($0.055 < n < 0.078$ Å^{-2}) the periodic variation of the graphite substrate is not very important. Our experimental results show that modifications of the adsorbing potential strongly affect the thermodynamic behavior of the films, including the effective interactions between helium atoms. For ^{4}He the results are a modification of the temperature dependence of the second virial coefficient and an apparent increase in the 2D condensation temperature. Furthermore, the substantial change in the temperature dependence of the specific heat below the observed peaks ($T^{3.3}$) gives a strong indication that these films are not strictly 2D in character. The experimental results of Bretz and Polanco[8] for the second layer of ^{4}He adsorbed on Grafoil also show changes from strictly 2D character. The shift in the condensation temperature, opposite to the one we measure, has been interpreted by Sander, Bretz, and Cole[18] as produced by the surface-normal motion of the second-layer atoms. This motion changes the effective interaction between two adsorbed atoms, accounting for a substantial fraction of the observed change. A calculation of the effective interaction between helium atoms at finite temperature on different substrates has not been made.

Band calculations for noninteracting helium on argon-plated surfaces (graphite and copper) predict rounded peaks in the specific heat for both isotopes at $T \simeq 0.8$ K.[12,19] We do not expect ^{4}He, for which adatom-adatom interactions are strong above 1 K for both plated and unplated surfaces, to be well described by the noninteracting model. For ^{3}He on the other hand, the noninteracting model may be appropriate at low densities, the model becoming less appropriate as the density, and hence the importance of interactions, increases. The peak seen in our data at $T = 0.75$ K and $n = 0.0233$ Å^{-2} is in good agreement with Novaco and Milford's band calculations (Fig. 2).[12] Furthermore, their analysis[19] predicts that for increased coverages the magnitude of this rounded peak should decrease somewhat (~ 10% for a change of density from $n = 0.027$ Å^{-2} to $n = 0.043$

Å^{-2}), reflecting features in the density of states. Our higher-density data show a peak diminished in height by about 40%. Whether the greater change in peak height observed in the data can be explained by interactions is not known, and needs further investigation.

The possibility also exists that the peak in the ^{3}He data is due to the same effect which produces the ^{4}He peak at $T \simeq 2$ K (e.g., condensation[20]) and that band effects are playing a secondary or negligible role. This latter interpretation is strengthened by the observation that the deviation of C/Nk from unity for the ^{3}He films is proportional to density above 1 K, in agreement with the virial equation [Eq. (1)], whereas band calculations[19] predict deviations from unity independent of n. If this is the case, two-dimensional liquid ^{3}He would be a new quantum system to study.

In conclusion, substrate effects are an important determinant of the film thermodynamics, and the plated Grafoil system provides a reliable way to investigate these effects. Both ^{4}He and ^{3}He measurements should be extended over the entire range of densities and to low temperatures in an effort to reach a better understanding of both the substrate effects and the new properties described here. In addition, calculations of the He-He interactions in the presence of a periodic adsorbing potential should be made and tested against the experimental results.

We are grateful to Professor J. G. Dash and Professor M. Schick for valuable discussions, and to Mr. C. Kohan for help in taking the data.

---

*Research supported in part by the National Science Foundation.

†Some of this work was presented at a recent conference [Workshop on Physical Adsorption, Brookhaven National Laboratory, Upton, N. Y., December 1976 (unpublished)]. At this conference, C. N. Koutsogeorgis and J. G. Daunt presented ^{4}He specific-heat results on a similar substrate. Their results and ours agree for some coverages.

[1] Grafoil is the trademark of an exfoliated graphite product marketed by Union Carbide Carbon Products Division, 270 Park Avenue, New York, N. Y.

[2] M. Bretz, J. G. Dash, D. C. Hickernell, E. O. McLean, and O. E. Vilches, Phys. Rev. A 8, 1589 (1973), and Phys. Rev. A 9, 2814(E) (1974).

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

[4] G. J. Goellner, J. G. Daunt, and E. Lerner, J. Low Temp. Phys. 21, 347 (1975).

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

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

[7] M. Bretz and J. G. Dash, Phys. Rev. Lett. 26, 963 (1971).

[8] M. Bretz and S. Polanco, *Low Temperature Physics LT-14*, edited by M. Krusius and M. Vuorio (North Holland, Amsterdam, 1975), Vol. 1, p. 451.

[9] S. W. Van Sciver, *Low Temperature Physics LT-14*, edited by M. Krusius and M. Vuorio (North-Holland, Amsterdam, 1975), Vol. 1, p. 368.

[10] E. Lerner and J. G. Daunt, J. Low Temp. Phys. 10, 299 (1973).

[11] A. D. Novaco, J. Low Temp. Phys. 21, 359 (1975).

[12] A. D. Novaco and F. J. Milford, Phys. Rev. A 5, 783 (1972).

[13] A. D. Novaco and C. E. Campbell, Phys. Rev. B 11, 2525 (1975).

[14] D. C. Hickernell, E. O. McLean, and O. E. Vilches, Phys. Rev. Lett. 28, 789 (1972).

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

[16] M. Bretz, Ph.D. thesis, University of Washington, 1971 (unpublished).

[17] M. D. Miller and C.-W. Woo, Phys. Rev. A 7, 1322 (1973). A factor of 4 error in the calculation is mentioned in J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975).

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

[19] F. J. Milford and A. D. Novaco, Phys. Rev. A 14, 1136 (1971).

[20] The possibility of condensation of quasi-two-dimensional ^{3}He when adsorbed on argon was suggested by J. G. Dash and M. Bretz, Phys. Rev. 174, 247 (1968).