tering of x-rays is negligible and also, the scattering is very nearly elastic. However, the experiment of Orton, Shaw, and Williams failed to cover the region relevant to the integration, their lowest value for x being 0.7. The earliest determination of $a(x)$ was made by Trimble and Gingrich[11] using x-ray transmission. However, the experimental techniques available 25 years ago, such as the microphotometry of film, are far less accurate than modern counting techniques. Although previous determinations of $a(x)$ indicated deviations between α_{calc} and α_{expt}, a point which had been emphasized by Greene and Kohn,[6] we believe that the nature of these earlier determinations of $a(x)$ was such that the existence of a discrepancy had not been conclusively established.

In summary, we believe that our measurements of $a(x)$ clearly demonstrate that a serious disagreement between the best accepted current theory and experiment exists. In the absence of some other convincing explanation for this discrepancy, we conclude that these results are evidence for the breakdown of the Born approximation in liquid metals.

We wish to thank Professor Volker Heine for suggesting this experiment, and we express our gratitude to Professor Walter Kohn and Professor J. M. Luttinger for several illuminating discussions. We also wish to thank Dr. Nathan Wiser and Dr. Paul Soven for many useful conversations. Finally, we wish to acknowledge the help received from Dr. George Brady and Professor Boris W. Batterman on the experimental aspects of the problem.

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LAMBDA TRANSITION IN ADSORBED HELIUM AT $T > T_\lambda$†

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A growing recent interest in the properties of adsorbed helium[1-8] has led us to re-examine an unsolved problem in earlier work. Our measurements indicate that a phase transition corresponding to the lambda transition in bulk He^4 occurs in the adsorbed film at temperatures above T_λ for pressures below the bulk vapor pressure (hereafter P_0). The temperature and pressure coordinates of the transitions form a curve in the P-T plane which is an extension of the lambda line into the region of the unsaturated film (i.e., at $P < P_0$).

In 1949 the heat capacity of multilayer films of adsorbed He^4 was measured by Frederikse.[9] He found that the maximum in the heat capacity due to the lambda transition was depressed in temperature, and the anomaly broadened with decreasing coverage. In 1951 Morrison and Drain[10] found substantially similar results for adsorbed argon near the melting point of the bulk solid. Meyer and Long[11] then pointed out that for such systems the surface tension must be treated as an additional intensive thermodynamic variable—a two-dimensional analog of pressure. This allows for the coexistence of three phases, two adsorbed phases and the vapor, along a line in the P-T plane at $P < P_0$. The heat capacities are measured at constant molar area, analogous to constant molar volume in three dimensions, so that coexistence of phases of different density is possible for a fixed coverage over a range of temperatures. Since there is only a single coexistence line in P-T regardless of coverage, this means that the isosteres (P-T curves at constant coverage) for adjacent coverages must overlap. Morrison, Drain, and Dugdale[12] subsequently showed that nitrogen films exhibited heat-capacity characteristics near the melting point similar to those for argon, but also reported that no common isostere existed for either transition, thus apparently contradicting the prediction of Meyer and Long. The class of film transitions exhibiting these heat-capacity characteristics includes methane[13] and other vapors,[14] but no explanation for these phenomena has been forthcoming.[14]

If the melting transitions do not obey the prediction of Meyer and Long, it may be due to conditions peculiar to melting. For example, Landau has pointed out[15] that a crystalline state might be precluded in two dimensions. Since He^4 undergoes a transition of a different type, we have undertaken to search for a common isostere near T_λ. This was done by taking adsorption isotherms, in which a phase change would be expected to show up as a departure from the smooth curve of coverage versus pressure and overlapping isosteres would be indicated by a vertical rise.

The substrate for the present measurements consisted of copper precoated with a monolayer of argon.[8] Adsorption isotherms were measured in the temperature range 2.08 to 2.77°K. The temperature was controlled by means of a mechanical manostat[16] and monitored by mercury and differential oil manometers. All temperatures quoted are ±0.005°K.

The results are displayed in Fig. 1. It may be seen that irregularities occur at $P \approx 39$ mm Hg for temperatures just above T_λ. An inflection similar to these was observed by Mastrangelo and Aston[17] in a careful isotherm taken on TiO_2 in conjunction with a repetition of Frederikse's measurement. In that case it was attributed to the onset of a new layer. However, we find that these irregularities occur at many times the B. E. T.[18] monolayer capacity for this surface (15.8 cm³ STP at $P \approx 10^{-3}$ mm Hg and $T = 4.21$°K), so that it does not seem reasonable to attribute them to layer formation.

Meyer and Long pointed out that the occurrence of heat-capacity maxima at $T < T_\lambda$ is not necessarily inconsistent with a transition at $T > T_\lambda$.[11] This is because adsorption isotherms reflect conditions at the top of the film, where all three phases are in equilibrium, but the heat capacity is a property of the entire film. There are large gradients in the forces between helium atoms and the wall within a few atomic distances of the wall, and these gradients cause variations in all the thermodynamic properties of the first few layers. Therefore, the heat capacity of a thick film is a composite of the various curves. Measurements of the thermal conductivity and mass-flow properties of the unsaturated film[19] have indicated superfluidity onset temperatures below T_λ. The connection between those transport properties and the type of transition apparently implied by the present results, however, is not yet clear.

In Fig. 2(a), P at the position of the irregularity is plotted against T. The highest temperature point is that of Mastrangelo and Aston.[17] By plotting P/P_0 against T/T_λ, as in Fig. 2(b), it is seen that these points may be fitted by

$$(P/P_0)_{\text{eq}} = [T_0 - T]/[T_0 - T_\lambda]; \quad T_0 = 2.7\text{°K}. \tag{1}$$

No explanation is yet offered for this simple behavior.

Treating the lambda point as a second-order

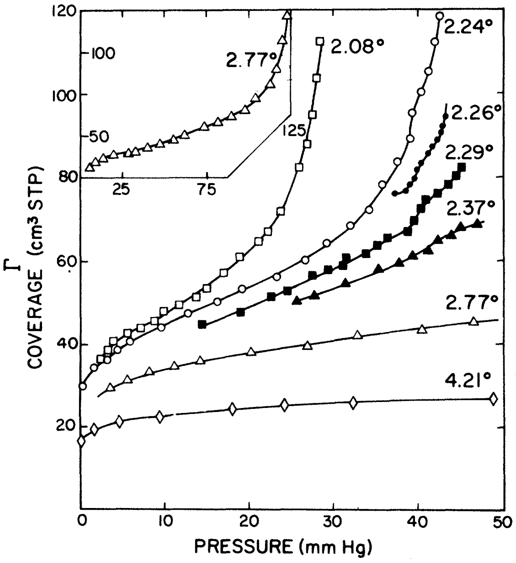

FIG. 1. Adsorption isotherms, He^4 on argon-coated copper.

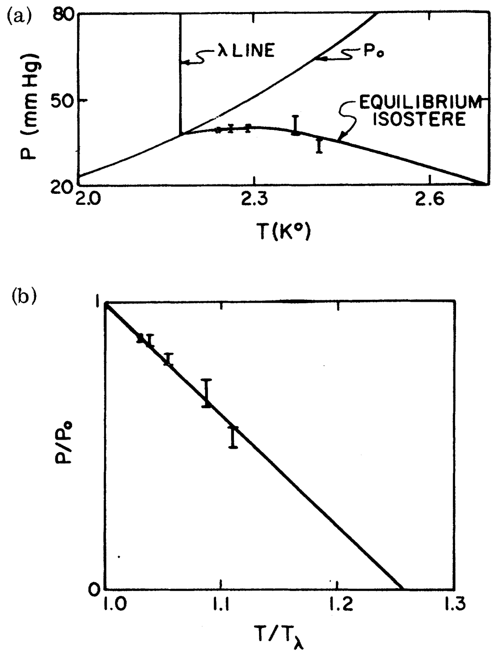

FIG. 2. Phase diagram in the P-T plane.

transition, Meyer and Long derive, for the equilibrium isostere,

$$\left(\frac{dP}{dT}\right)_{\text{eq}}=\frac{1}{V_g}\left\{S_g-S_a+A\frac{\partial S_2/\partial T-\partial S_1/\partial T}{\partial A_2/\partial T-\partial A_1/\partial T}\right\}, \qquad (2)$$

where V, A, and S are molar volume, area and entropy, and subscripts g, a, 1, and 2 refer to gas, over-all adsorbed phase, and adsorbed phases 1 and 2. As the isostere passes to just below P_0, the film is very thick and the properties of the adsorbed phases cannot be very different from bulk liquid He. Using $(1/A)(\partial A/\partial T)=(\frac{2}{3})(1/V)(\partial V/\partial T)$ and $\partial S_2/\partial T-\partial S_1/\partial T=\Delta C/T$, and making use of the Ehrenfest relations,[20] Eq. (2) becomes

$$\left(\frac{dP}{dT}\right)_{\text{eq}}=\left(\frac{dP_0}{dT}\right)_{\lambda}+\frac{3}{2}\frac{V_l}{V_g}\left(\frac{dP_\lambda}{dT}\right)_{\lambda}, \qquad (3)$$

where $(dP_\lambda/dT)_\lambda$ is the slope of the lambda line for $P>P_0$. This yields $(dP/dT)_{\text{eq}}=-0.9$ atm deg^{-1} compared to $+0.03$ atm deg^{-1} from Eq. (1). Although this disagreement is based on an extrapolation of the data to infinite film thickness, it should be emphasized that the observed coordinates of the transition, $P\gtrsim 39$ mm Hg at 2.24°, means that the slope of the isostere must necessarily be positive for fairly thick films. Thus, whereas Meyer and Long correctly predicted that the transition in unsaturated films would occur at $T>T_\lambda$, their treatment yielded the wrong magnitude and sign for the slope of the isostere for thick films. This seems to imply that, in contrast to the situation in bulk liquid helium,[21] the phase transition in the film cannot be treated as second order. We are currently undertaking researches designed to further investigate the nature and properties of this phase change.

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QUANTUM CORRECTIONS TO CRITICAL-POINT BEHAVIOR

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Recent experimental evidence[1-3] suggests that the behavior of He^3 and He^4 at their critical points deviates qualitatively from that observed with "classical" gases for which the de Boer parameter $\Lambda^* = h/(m\epsilon\sigma^2)^{1/2}$ is small. (m, ϵ, and σ measure the mass, potential well depth, and collision diameter, respectively.) In particular, while the coexistence curves of Xe and CO_2 may be described accurately over a wide range of T approaching T_c by

$$R(T) = (\rho_{\mathrm{liq}} - \rho_{\mathrm{gas}})/2\rho_c \approx D[1-(T/T_c)]^\beta \tag{1}$$

with β lying in the range 0.33 to 0.36,[4-6] the apparent value of β (e.g., on a log-log plot) for He^3 and He^4 seems to increase to values in the range 0.40-0.50 when $T/T_c \geqslant 0.98$.[1,2] Similar changes towards "Van der Waals-like" behavior appear to take place also in the other critical-point exponents (γ and γ' for the compressibility above and below T_c, etc.).[3,5,7]

Sherman and Hammel[7] have discussed these effects from the viewpoint of de Boer's theory of corresponding states. They implicitly suggested that the exponents $\beta(\Lambda^*)$, $\gamma(\Lambda^*)$, etc., are continuous smoothly varying functions of Λ^*. The purpose of this note is to argue, on the contrary, that the ideal critical-point exponents defined[5,8] in the limit $T \to T_c$ are probably discontinuous functions of Λ^* with, for example, $\beta = \beta_0$ for $\Lambda^* = 0$, $\beta = \beta_1$ for $0 < \Lambda^* < \Lambda^*_1$, and, possibly, $\beta = \beta_2$ for $\Lambda^* > \Lambda^*_1$. The implications of this conclusion for the shapes of coexistence curves, etc., will be discussed.

For pair interactions of the form $\varphi(r) = \epsilon f(r/\sigma)$, where $f(x)$ is a "universal" shape factor, the Hamiltonian of an N-body system may be written

$$\mathcal{H}_N = \epsilon(\mathcal{H}_0 + g\mathcal{H}_1), \tag{2}$$

where $\mathcal{H}_0$ is the reduced potential energy and $\mathcal{H}_1$ the reduced kinetic energy $-\frac{1}{2}\sum_i \partial^2/\partial x_i^2$, while the coupling constant is

$$g = (\Lambda^*/2\pi)^2 = (\bar{\lambda}^*)^2. \tag{3}$$

For a classical gas ($g=0$), the analogy with a spin-$\frac{1}{2}$ Ising ferromagnet via the lattice-gas model is well known[8,9] and may be expressed by

$$\epsilon \equiv J^{\parallel}, \quad \varphi(0) = +\infty, \quad \varphi(r) \equiv -J(r),$$

$$\epsilon\mathcal{H}_0 + \mu N \equiv \mathcal{H}_{\mathrm{Ising}}, \quad \rho/\rho_c \equiv 1-(M/M_{\mathrm{sat}}),$$

$$\text{and } \mu_c - \mu \equiv 2H,$$

μ being the chemical potential and H the reduced magnetic field. As noticed by a number of authors,[10-15] there is a corresponding analogy between a quantum-mechanical Bose lattice gas and an anisotropic Heisenberg-Ising magnet. The reduced kinetic energy becomes the transverse interaction

$$\mathcal{H}_1 = \mathcal{H}^{\perp} = \sum_i (S_i^x S_j^x + S_i^y S_j^y), \tag{4}$$

where the sum runs over nearest-neighbor pairs, and the coupling constant is

$$g = J^{\parallel}/J^{\perp} \equiv (2d\sigma^2/qa^2)(\bar{\lambda}^*)^2, \tag{5}$$

where d is the dimensionality, q the coordination number, and a the lattice spacing. In the simplest ferromagnetic nearest-neighbor model,[15] $J(r)$ vanishes for $r > a$, and one may take $\sigma \simeq a$ so that the prefactor in (5) lies between $\frac{1}{2}$ and 1 for most lattices. The pure isotropic Heisenberg model then corresponds to $g=1$ or $\bar{\lambda}^* = \bar{\lambda}_1^* \simeq 1-\sqrt{2}$.

Numerical evidence for the simple $d=3$ Ising model[16] shows that $\beta(0) = 0.31 \simeq 5/16$ and $\gamma(0) = 1.25 \simeq 5/4$, whereas for the Heisenberg model $T_C(1) < T_C(0)$ and $\gamma(g=1) = 1.33 \simeq \frac{4}{3}$ is indicated.[17] These changes are actually away