PHYSICAL REVIEW B VOLUME 29, NUMBER 9 1 MAY 1984

Binding of ^{3}He in ^{4}He films

Francis M. Gasparini, Bidyut Bhattacharyya, and Michael J. DiPirro*
Department of Physics and Astronomy, State University of New York at Buffalo, Amherst, New York 14260

(Received 19 September 1983)

We present for the first time a calculation of the binding of ^{3}He to films of ^{4}He. We follow a variational procedure which has been used successfully for calculating the binding of ^{3}He to the surface of bulk ^{4}He. Our main modifications consist of the inclusion of the substrate van der Waals field as a local pressure within the film and as an attractive tail in the vacuum region above the surface. We compare the solution for the bound-state energies with experimental results for films and find reasonable agreement for the binding energy. Our calculation and experimental results suggest that models of ^{3}He in films of ^{4}He, where the ^{3}He is assumed to be in a continuum of three-dimensional states, are not strictly correct.

I. INTRODUCTION

When ^{3}He is added to liquid ^{4}He, it is energetically favorable for the ^{3}He to reside in a state localized at the liquid-vacuum interface. The first observation of this phenomenon came from measurements of the surface tension.[1] These measurements showed a decrease of the surface tension at low temperatures when the surface state become appreciably occupied with ^{3}He. The correct interpretation of these data was provided by Andreev,[2] who suggested the existence of such a state for the ^{3}He. There have been a number of experiments since then which have shown that at the bulk surface a single state exists at an energy of 2.22 K below solution into bulk ^{4}He. The ^{3}He in this state behaves very nearly as an ideal two-dimensional (2D) Fermi gas of quasiparticles with an effective mass about 1.5 times the bare mass m_3. The experimental as well as the theoretical situations have been the subject of a recent review.[3]

In the case of films of ^{4}He, it has been found that the ^{3}He is still bound at the free surface, but its behavior is more complicated. It is found, for instance, that the binding energy is a strong function of the two-dimensional ^{3}He density,[4] and that for sufficiently thin films, the ^{3}He at the surface separates into a dense phase.[5] More detailed discussion of these observations is planned to be the subject of other publications. In this paper we want to present an extension of a theoretical model to represent the zero-coverage limit for ^{3}He in films of ^{4}He. In the case of bulk ^{4}He this model has been applied successfully to calculate the binding energy for ^{3}He at the free surface. This is a variational calculation which follows an ansatz due to Feynman.[6] It was applied to ^{4}He with a free surface by Lekner,[7] who showed that the solution for the ^{3}He bound states can be reduced to a one-dimensional Schrödinger equation with an effective potential. Saam[8] was the first to construct such a potential and solve for what turned out to be a single bound state. More recently, Mantz and Edwards[9] have improved on this calculation by incorporating in the effective-potential information from atomic scattering at the surface[10] and adding the liquid-surface—^{4}He-atom van der Waals attraction for the vacuum region above the surface.

We show in this paper that this theory can be extended to the case of ^{4}He films by incorporating the effect of the substrate's van der Waals field in the effective potential. When we solve for the bound states in this potential, we find a discrete spectrum with only a few states. This is in contrast to models which have often been used for ^{3}He in ^{4}He films, where it has been assumed that the ^{3}He in the film is in a three-dimensional continuum.[11,12] We compare the results of our calculation with results of our experiments extrapolated to zero ^{3}He coverage. These are measurements of heat capacity for helium films formed on Nuclepore filters.[4,5] We find numerical agreement for the binding energy, the energy difference between the ground state and the first excited state, to roughly the same precision as has been found for the calculation of this energy for the bulk surface.

II. THEORY AND THE EFFECTIVE POTENTIAL

Lekner[7] was the first to extend the variational theory of Feynman[6] to the case of ^{4}He with a free surface. In this theory the wave function describing one ^{3}He atom at $\vec{r}_1$ and $N-1$ ^{4}He atoms at $\vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N$ is written as

$$\psi(\vec{r}_1,\ldots,\vec{r}_N)=\phi(\vec{r}_1)\left[\frac{\rho_0}{\rho(\vec{r}_1)}\right]^{1/2}\psi_0(\vec{r}_1,\ldots,\vec{r}_N)\;, \tag{1}$$

where ψ_0 is the ground-state wave function of the ^{4}He atom, ρ_0 is the bulk ^{4}He density at zero pressure, $\rho(\vec{r}_1)$ is the local density, and $\phi(\vec{r}_1)$ is a function to be varied to achieve the minimum energy. This minimization results in a one-dimensional Schrödinger-like equation, which for the liquid surface as the x-y plane is given by

$$-\frac{\hbar^2}{2m_3}\frac{d^2\phi(z_1)}{dz_1^2}+V_3(z_1)\phi(z_1)=\epsilon\phi(z_1)\;. \tag{2}$$

The effective potential for the ^{3}He, $V_3(z)$, is given in terms of the ground-state properties of the ^{4}He. Motion of the ^{3}He in the x-y plane remains as that of a free particle.

Saam[8] was the first to construct $V_3(z)$ and obtain a solution for the energy ϵ. More recently, Mantz and Edwards[9] (ME) have redone this calculation and incorporated in $V_3(z)$ experimental results for $\rho(z)$ obtained from scattering experiments. These authors also include the proper asymptotic behavior of $V_3(z)$ in the region of the vacuum. They find $\epsilon=4.64$ K, in quite good agreement with the experimental result of 5.00 ± 0.03 K.

Following the notation of ME, the effective potential can be written as

$$V_3(z_1)=\frac{\hbar^2}{2m_3}\frac{a''(z_1)}{a(z_1)}-L_4+\left[\frac{m_4}{m_3}-1\right]t(z_1)\ , \qquad (3)$$

where $a(z)=[\rho(z)/\rho_0]^{1/2}$, L_4 is the latent heat at zero temperature, and $t(z)$ is the kinetic energy per particle in the ^{4}He ground state. This quantity can be constructed by observing the asymptotic behavior of $V_3(z)$ in the vacuum and in the liquid regions, and assuming, as was pointed out by Saam, that in the region of the surface changes in $t(z)$ stem mainly from density variations. In the liquid region just below the surface $t(z)$ is related to properties of solutions of ^{3}He in ^{4}He. These two approaches for $t(z)$, from the liquid and the vacuum sides, join smoothly through the surface region and with the first term in Eq. (3) provide the potential which binds the ^{3}He at the surface of bulk ^{4}He.

To extend this calculation to ^{3}He in a film of ^{4}He, one must incorporate in $V_3(z)$ the influence of the substrate van der Waals field, which is responsible for the formation of the film. This field, to the extent that the ^{3}He is concerned, reflects itself in three ways. In the vacuum region a ^{3}He atom, instead of seeing just the van der Waals attraction from the ^{4}He surface, is also affected by that of the substrate. This gives a more attractive tail to $V_3(z)$ in the vacuum. In the surface region, the ^{4}He density profile is modified, hence the "well" region of the potential is changed. More importantly, however, in the liquid region of the film there is an increase of the local pressure as one approaches the solid substrate. This reflects itself in a repulsive, hard-core—type region for $V_3(z)$ which is not present in the bulk-surface case. This feature, of course, affects most strongly the spectrum of excited states available to the ^{3}He. The spectrum becomes a discrete set of 2D states as opposed to the continuum of three dimensional (3D) states available in the liquid region for the bulk-surface case. We describe now how we have constructed $V_3(z)$ and solved for the energy spectrum. We have done this for three films of thickness equal to those we have studied experimentally.

A. $V_3(z)$ for films of ^{4}He

To construct the effective potential, we have treated the liquid-film region and the surface-vacuum region separately, and then joined the potential in a smooth way. This is similar to, but a bit different from, what is done for the bulk surface case. We consider the liquid-film region first. Following ME, we write $V_3(z)$ as

$$V_3(z_1)=V_4(z_1)+(L_4-E)a^{2n}(z_1)\ , \qquad (4)$$

where

$$V_4(z_1)=\frac{\hbar^2}{2m_4}\frac{a''(z_1)}{a(z_1)}-L_4\ , \qquad (5)$$

and the exponent n is related to properties of ^{4}He and dilute mixtures of ^{3}He in ^{4}He. Equation (4) can be taken as valid in the whole region of the surface, even though the $a^{2n}(z)$ term is strictly applicable to the liquid region just below the surface. The point is that this term becomes rapidly negligible as one goes into the low-density region. Here, the $a''(z)$ term dominates. All the terms in Eq. (4) are functions of pressure, which we calculate as follows. We consider the film as a uniform fluid and use the relationship between the pressure P and the substrate's van der Waals potential U,[11]

$$-v\,dP=dU\ . \qquad (6)$$

We have parametrized the variations of the molar volume v as a polynomial in P and integrated Eq. (6) to obtain

$$P^3-9.37P^2+1.85\times10^4P=9.59\times10^7\left[\frac{1}{z^3}-\frac{1}{d^3}\right]\ , \qquad (7)$$

where P is in units of atmospheres and z and d are in Å. The pressure is made to go to 0 at $z=d$, the liquid surface. To relate to the experimental value of d,[13] we note that experimentally the film thickness is determined from the amount of ^{4}He condensed and the adsorption area available. Experiments indicate that the first layer, a solid, forms a thickness of about 3 Å, and that subsequent helium atoms form a fluid film at very nearly the bulk density.[14] This is not strictly self-consistent with a density which varies as a function of position from the substrate, but is a reasonable approximation when considering just the determination of the film thickness. We will refer to this as the nominal thickness and identify this as the d of Eq. (7).

With the pressure variation of the film known from Eq. (7), the dependence of L_4, E_3, and a on z can be input in Eq. (4).[15] For the exponent n, we have found that it varies by only 6% in the range of pressures up to 20 atm. We have taken this number as a constant. The potential which results from this calculation is shown in Fig. 1 for the case of two films, $d=13$ and 21.8 Å. The rise of the potential as one approaches the solid substrate at $z=0$ is due mainly to the decrease in L_4 with pressure. Near the free surface, where the pressure goes to 0, the potential approaches $-E_3=2.78$ K. This is the energy of the lowest state for ^{3}He in bulk ^{4}He at zero pressure.

To construct $V_3(z)$ through the surface region and in the vacuum, we must know the density profile at the free surface. We have taken $a(z)$ to behave as a Fermi function

$$a(z)=1/(e^{p(z)}+1)\ . \qquad (8)$$

The function $p(z)$ determines the sharpness of the surface, and, as used by ME, contains parameters β, λ, γ, and δ,

$$p(z)=\beta z+\gamma+\frac{\lambda}{4\beta}(z^2+\delta^2)^{-1}\ . \qquad (9)$$

Among these parameters, $\gamma=-2.5$ and $\delta^2=8.5$ Å^2 are

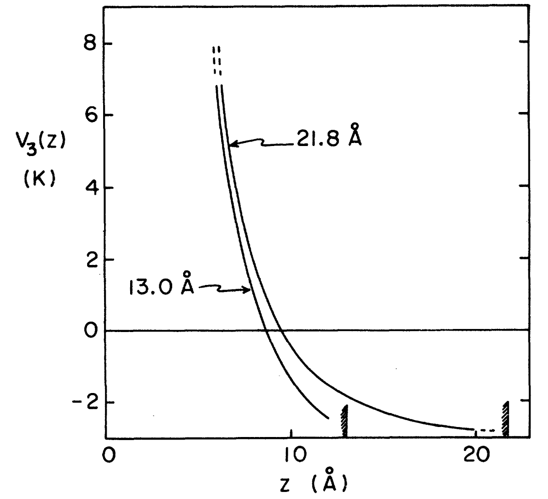

FIG. 1. ^{3}He effective potential in the liquid region for films with nominal thickness of 21.8 and 13.0 Å. The substrate is at $z=0$. The nominal thickness is indicated by the shaded vertical lines.

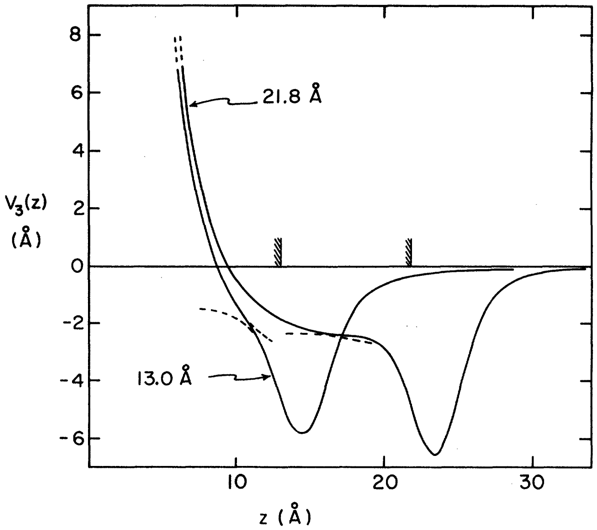

FIG. 2. Full ^{3}He effective potential for two films of ^{4}He. Two regions are joined together to form this potential, the "vacuum" and the "film" region. The extrapolation of these potentials beyond the region where they are joined is indicated by dashed lines. The vertical shaded lines are at the nominal film thickness.

fixed by fitting data from the elastic scattering experiments of ^{4}He atoms at the liquid surface.[10] The remaining parameters are fixed by requiring that in the region above the surface $V_4(z)$ have the van der Waals form

$$V_4=-\frac{\alpha_0}{z^3}\,, \tag{10}$$

where α_0 is the He-atom—He-surface van der Waals constant. This yields $\lambda \cong 20$ Å. The requirement that Eq. (10) be satisfied also fixes β,

$$\beta=\left[\frac{2m_4L_4}{\hbar^2}\right]^{1/2}=1.087 \tag{11}$$

in units of Å^{-1}.

For the case of a film of ^{4}He, taking the origin at the solid substrate, we have written $p(z)$ as

$$p(z)=\beta(z-d)+\gamma+\frac{\lambda}{4\beta}\{[(z-d)^2+\delta^2]^{-1}+\lambda'/z^2\}\,, \tag{12}$$

where $\lambda'=\alpha/\alpha_0$ is the ratio of He-substrate to He—He-surface van der Waals constants. This ensures that above the film one has the correct asymptotic behavior:

$$\lim_{z\to\text{large}} V_3(z)=V_4(z)=-\frac{\alpha_0}{(z-d)^3}-\frac{\alpha}{z^3}\,. \tag{13}$$

Numerically, we have $\lambda=20$ Å as in ME, and $\lambda'=14.6$. This latter is obtained by using 2.4×10^{-37} erg cm^3 as the value of α for the He—Nuclepore-filter van der Waals constant.[14] We have retained the remaining parameters in Eq. (12), γ and δ^2, at the same value as for the bulk surface. This, of course, is not strictly correct, but there are no scattering experiments in the case of films from which these parameters could be obtained independently. We will return to this point later.

With an expression for $p(z)$, and hence, $a(z)$, we can now construct, via Eqs. (4) and (5), $V_3(z)$ for the surface-vacuum region. This potential should join in a smooth way with the potential shown in Fig. 1, constructed from the liquid properties. In fact, not surprisingly, this does not happen; rather, a small discontinuity exists where one would expect these potentials to join. To take care of this, we note that in our calculation of $V_3(z)$ for the surface region we have used $L_4=7.16$ K, the zero-pressure value for the ^{4}He binding energy. In fact, this number is a function of pressure, and should be smaller when the potential is made to match $V_3(z)$ constructed from the liquid side. We find that these potentials join smoothly if for Eq. (11) we take $L_4=6.8$, 6.47, 6.2 K for the 21.8-, 15.3-, and 13.0-Å films, respectively. With this proviso, the full potentials for the same two films shown in Fig. 1 are now shown in Fig. 2. The dashed lines show the continuation of the "liquid side" and the "vacuum side" through the region where they match. These potentials have a minimum in a region slightly above $z=d$, the nominal surface. This feature is very similar to the situation with the bulk surface.

B. Solution for the bound states

To solve Eq. (2) for the eigenvalues and eigenfunctions, we have used the boundary condition that ϕ vanishes at $z=3$ Å. This is to reflect the fact that the dense solid layer of ^{4}He at the substrate is impenetrable to the ^{3}He. For large z, we have forced the wave function to vanish at $z=53$ Å. Both of these restrictions have a negligible effect on the lowest bound states and are just a convenient interval in which to integrate Eq. (2). We have checked this by increasing and decreasing this range by 10 Å, as well as forcing ϕ to vanish at 6 Å rather than 3 Å. The difference between ground state and first excited states changed by only $\sim$0.10 K. Limiting the integration interval does introduce the artificial result that the energy spectrum is discrete even for positive energies, i.e., the vacuum region. Here the ^{3}He should be a free particle. This feature of the solution is understood and is of no interest.

To solve Eq. (2) numerically, we have divided the region of integration into 100 intervals and used a procedure given by Cooney *et al.*[16] We have checked this procedure for the case where $V_3(z)$ is the bulk surface potential. In this case, we have taken the integration interval as 80 Å, i.e., ±40 Å of the surface. We find a single bound state at at energy -4.67 K. This is to be compared with the result of ME of -4.64 K. The slight discrepancy we attribute to the numerical method.

For the case of the films, we show in Fig. 3 the solution for the ground-state and first-excited-state probability densities superimposed over the ^{4}He density profile. The simplest feature of the solution is that the lowest bound state is, indeed, mostly localized at the surface. The first excited state, however, has a substantial probability density in the surface region as well. Clearly the distinction of surface state versus film state is not as meaningful as in the case of the bulk surface where one speaks of a surface state and bulk states. There is a tendency, which can be noted in Fig. 3, for the thicker films to have the excited state more extended into the liquid region. This trend should continue with further increase of thickness until the excited states become a three-dimensional continuum. Another simple feature suggested by Fig. 3 is that the effective mass m^* of the ^{3}He quasiparticle in the excited state should be larger than in the ground state. This comes from the simple hydrodynamic argument that the excited state sees proportionately more of the liquid region than the ground state. Experimentally, one finds that this is so. The ground state has in the limit of zero ^{3}He coverage $m^* \cong (1-2)m_3$, while the excited state has $m^* \cong (6-7)m_3$. These results are planned to be discussed in greater detail in a subsequent publication.

We list in Table I the lowest bound states which result from our calculation.[17] These are compared with results which are obtained by extrapolating experimental values of ϵ_1, ϵ_2, and $\Delta\epsilon$ to zero coverage.[4,5] In the case of the 21.8-Å film, this extrapolation cannot be done reliably and is omitted from the table. We also note that the behavior of ϵ_1 and ϵ_2 with coverage is not as smooth as $\Delta\epsilon$, and hence, the extrapolation to zero coverage is not particularly reliable. In one way, this is expected since the heat capacity from which these results are obtained are most sensitive to $\Delta\epsilon$ rather than the absolute values of the energies. The errors shown in this table reflect the uncertainty in the extrapolation.

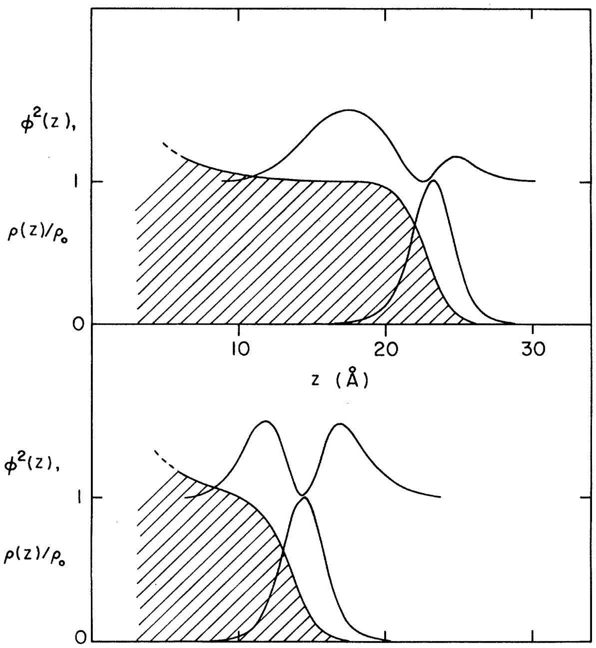

FIG. 3. Density profile, shaded region, and the probability densities for the ground-state and first excited state for ^{3}He in two films of ^{4}He. The first 3 Å near $z=0$ are taken as solid ^{4}He. The probability densities are in arbitrary units.

In the case of $\Delta\epsilon$, we see from this table that the results of our calculation are not out of line with the experimental results. There seems to be a systematic tendency for the model to underestimate the value of $\Delta\epsilon$. This is most obvious for the thinnest film, but is also true for the bulk surface. In the cases of ϵ_1 and ϵ_2, the results for the 13-Å film are in reasonable agreement with calculations, while for the 15.3-Å case the experimental results seem markedly higher.

TABLE I. Theoretical and experimental results for the bound-state energies of ^{3}He in ^{4}He films and in bulk ^{4}He.

Film thickness (Å)	ϵ_1 (K) Theory	ϵ_1 (K) Expt.	ϵ_2 (K) Theory	ϵ_2 (K) Expt.	$\Delta\epsilon$ (K) Theory	$\Delta\epsilon$ (K) Expt.
13.0	-3.93	-5.0 ± 0.6	-1.05	-1.0 ± 0.6	2.88	4.1 ± 0.3
15.3	-4.14	-7.1 ± 0.6	-1.38	-3.6 ± 0.6	2.76	3.1 ± 0.2
21.8	-4.40		-1.97		2.43	
∞	-4.67	-5.00 ± 0.03[a,b]	-2.79[c]	-2.785 ± 0.01[a]	1.88[d]	2.22 ± 0.03[b]

[a] Reference 15.

[b] Reference 3.

[c] W. E. Massey, C. W. Woo, and H. T. Tan, Phys. Rev. A 1, 519 (1970).

[d] Reference 9.

III. COMMENTS AND CONCLUSIONS

The principal distinction in the effective potential between ^{3}He in a film and at the surface of bulk ^{4}He is the repulsive part which stems from the higher pressure in the film due to the substrate's van der Waals field. At the surface, even though we do have a modification from the substrate, the effect is not very strong. In addition, we have retained in our calculation the parameter γ and δ^2, which are determined from bulk-surface properties. To see how sensitive our calculation is to these parameters, we have changed these in a range of 20—40%. We have found that $\Delta\epsilon$ changes only of the order of ± 0.01 K. One can vary these parameters, however, more drastically and actually induce oscillations in the density on the vacuum side of the surface and hence obtain a double-well type of potential. This does not seem very reasonable. Overall, we can say that the treatment of the density profile at the surface is the weakest link in the calculation. From the experimental values of ϵ_1, for instance, one would expect the well region at the surface to be deeper. We also note at this point that our procedure of joining the two sides of the potential in a smooth way need not have been done, or could have been done by "lowering" the liquid side of the potential. Both of these procedures yield more negative values for the energies, but do not affect $\Delta\epsilon$ to an appreciable extent.

We feel the merit of our calculation is that it is a rather simple extension of the theory applied to the bulk surface, and nevertheless picks up some important features of the experimental results. Not the least important among these is the fact that the excited states for the ^{3}He are also 2D in character and form a discrete spectrum for motion in the z direction. This is in agreement with the earlier observations of DiPirro and Gasparini[4,18] and is to be constrasted with models where this spectrum is treated as a 3D continuum.

ACKNOWLEDGMENTS

This research is supported in part by the National Science Foundation, Grants Nos. DMR-8007302 and DMR-8305742.

---

[*] Present address: NASA, Goddard Spaceflight Center, Greenbelt, Maryland 20771.

[1] B. N. Esel'son, V. G. Ivantsov and A. D. Shvetz, Zh. Eksp. Teor. Fiz. 44, 483 (1963) [Sov. Phys.—JETP 17, 330 (1963)]; K. R. Atkins and Y. Narahara, Phys. Rev. 138, A437 (1965).

[2] A. F. Andreev, Zh. Eksp. Teor. Fiz. 50, 1415 (1966) [Sov. Phys.—JETP 23, 939 (1966)].

[3] D. O. Edwards and W. F. Saam, in *Progress in Low Temperature Physics,* edited by D. R. Brewer (North-Holland, Amsterdam, 1978), Vol. VIIA, Chap. 4.

[4] M. J. DiPirro and F. M. Gasparini, Phys. Rev. Lett. 44, 269 (1980); B. Bhattacharyya and F. M. Gasparini (unpublished).

[5] B. Bhattacharyya and F. M. Gasparini, Phys. Rev. Lett. 49, 919 (1982).

[6] R. P. Feynman, Phys. Rev. 94, 262 (1954).

[7] J. Lekner, Philos. Mag. 22, 669 (1970).

[8] W. F. Saam, Phys. Rev. A 4, 1278 (1971).

[9] I. B. Mantz and D. O. Edwards, Phys. Rev. B 20, 4518 (1979).

[10] D. O. Edwards and P. P. Fatouros, Phys. Rev. B 17, 2147 (1978).

[11] M. Chester, J. P. Laheurte, J. P. Romagnan, Phys. Rev. B 14, 2812 (1976).

[12] J. P. Laheurte, J. P. Romagnan, and W. F. Saam, Phys. Rev. B 15, 4214 (1977).

[13] In previous work, we have often quoted thicknesses 3 Å less than the values used in this paper. These thicknesses referred to the liquid portion of the film.

[14] T. P. Chen, M. J. DiPirro, A. A. Gaeta, and F. M. Gasparini, J. Low Temp. Phys. 26, 927 (1977).

[15] For the molar volume, L_4 and E_3 as functions of pressure, we have used values tabulated in C. Ebner and D. O. Edwards, Phys. Lett. 26, 79 (1971).

[16] P. J. Cooney, E. P. Kanter, and Z. Vagur, Am. J. Phys. 49, 76 (1981).

[17] The two thinnest films have one additional state which is barely bound at -0.03 and -0.15 K, respectively. The 21.8-Å film has two additional states at -1.05 and -0.10 K.

[18] M. J. DiPirro and F. M. Gasparini, in *Ordering in Two Dimensions,* edited by S. K. Sinha (North-Holland, New York, 1980).