TABLE I. Superconducting energy gap measured as function of frequency for 99.9% lead for longitudinal waves along the ⟨111⟩ direction.

Frequency Mc/sec	Energy gap $2\epsilon_0(0)k_BT_c$
1030	4.8
950	5.2
290	5.4
210	4.9
110	5.0

TABLE II. Superconducting energy gap measured as function of sound pulse amplitude for 99.9% pure lead at 510 Mc/sec for longitudinal waves along the ⟨111⟩ direction

Sound pulse amplitude	Energy gap $2\epsilon_0(0)k_BT_c$
Lowest possible	4.7
3000 times higher in power	5.2

tables of Mühlschlegel[10] of $\epsilon_0(T)/\epsilon_0(0)$ in terms of T/T_c. Here α_s and α_n are the values of the attenuation in the superconducting and normal states, respectively, $\epsilon_0(T)$ is the energy gap as function of the temperature T, $\epsilon_0(0)$ is the limiting gap at 0°K, and k_B is Boltzmann's constant. Figure 1 shows a typical graph of α_s/α_n as a function of the reduced temperature T/T_c, where T_c is the superconducting transition temperature. The energy gap values $\epsilon_0(0)$ obtained in the range from 50 to 1050 Mc/sec are presented in Table I.

This table does not include measurements performed at 510 Mc/sec. At this frequency data were obtained at rather higher sound pulse amplitudes and at the lowest convenient pulse amplitude. The difference in the amplitudes corresponded to a change of 25 dB or a factor of 3000 in the power output of the transmitter. The data were analyzed in a similar manner as before to obtain the corresponding energy-gap values. These are summarized in Table II. This result points to the fact that there is some evidence of an amplitude dependence although it is very weak. Since it is estimated that the measurements at the other frequencies were performed at low or intermediate amplitudes, the energy-gap values can be viewed as having an approximate error of ±0.3 maximum where the error of −0.3 is favored.

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Ground-State Properties of a Model of a Two-Dimensional System of Liquid Helium-3[†]

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An investigation is made of the low-temperature behavior of a two-dimensional many-fermion system parametrized to serve as a model of a monomolecular layer of liquid He^3. The calculations are made using the Λ_{00} approximation of the Martin-Schwinger thermodynamic Green's function theory. A Herzfeld potential is used for the two-body interaction in order that the resulting T-matrix equation can be solved exactly. Three sets of the three parameters of this potential are chosen by requiring that they reproduce either the experimental and theoretical low-temperature second virial coefficient, the phase shifts calculated from the 6–12 potential, or the experimental binding energy and density of the three-dimensional system. The chemical potential, energy per particle, density, and specific heat are calculated. Of the three sets of parameters the maximum binding energy for the two-dimensional system results from the potential which predicts the correct three-dimensional experimental energy and density. The maximum binding in this case is 0.68°K at a density corresponding to $r_0=2.9$ Å. Three-dimensional calculations were made with the several sets of parameters, with the result that the virial-coefficient and phase-shift sets predict too little attraction.

I. INTRODUCTION

A THEORETICAL calculation of the low-temperature properties of a two-dimensional system of He^3 is of interest because of recent experimental work[1] on monomolecular layers of liquid helium. This paper reports the results of a calculation of the binding energy, density, chemical potential, and specific heat of a two-dimensional model of liquid He^3 in the zero-

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temperature limit. The calculations are based on Puff's Λ_{00} approximation of the Martin-Schwinger thermodynamic Green's function theory and the numerical work has been done on an electronic computer.

A brief discussion of the Green's function equations and the approximations used here in solving them is contained in Sec. II. The Λ_{00} theory requires a transition (T) matrix analogous to the K matrix of Brueckner theory. A two-body potential is chosen that will allow us to solve the integral T-matrix equation exactly. This potential is the Herzfeld potential, an infinite repulsive core plus an attractive square well. The determination of the parameters of this potential is discussed in Sec. III. Section IV presents numerical results for the low temperature properties of interest and contains a discussion of the specific heat. Finally Sec. V contains a discussion of these results. In the case of the two-dimensional fermion system used as a model of a monolayer of He^3 the implicit assumption is made that the substrate is sufficiently smooth on the atomic scale so that no bound states exist and so that the effective mass of the single-particle states is not greatly altered. Also, in the calculation of the specific heat, strong adhesive forces are assumed so that the excitations which determine the low-temperature limit of specific heat are the excitations of the two-dimensional many-body system. These assumptions are discussed further in Sec. V.

II. GREEN'S-FUNCTION EQUATIONS

The Martin-Schwinger Green's-function approach to the many-body problem[2] will yield the exact ground-state properties of the system if the exact one-particle Green's function can be obtained. However, each Green's function of a given order is obtained from the Green's function of the next higher order, and so the entire hierarchy of equations must be solved to obtain the exact G_1. In coordinate space the first two of these equations are

$$G_1(1,1')=G_1^0(1,1')+G_1^0(1,2)V(2,3)G_2(23,3^+1'), \quad (1)$$

$$G_2(12,1'2')=G_1^0(1,1')G_1(2,2')-G_1^0(1,2')G_1(2,1')+G_1^0(1,3)V(3,4)G_3(234,4^+1'2'). \quad (2)$$

Here G_1^0 is the solution of the differential equation of motion for G_1 with no interaction term. The numerical indices denote position, time, and spin. Integration over space and time and summation over spin is intended for repeated indices. The time dependence of V is simply

$$V(2,3)=iv(\mathbf{r}_2-\mathbf{r}_3)\delta(t_2-t_3). \quad (3)$$

The usual approximation made is to truncate the infinite chain of equations above by factoring the G_3 of Eq. (2) into symmetrized products of G_1 and G_2, keeping correlations between particles interacting through V. This is a low-density approximation and means in words that when two particles are interacting their motion is independent of all other particles in the medium. This can be expressed analytically as

$$V(2,3)G_3(123,1'2'3')\approx V(2,3)[G_1(1,1')G_2(23,2'3')-G_1(1,2')G_2(23,1'3')+G_1(1,3')G_2(23,1'2')]. \quad (4)$$

Substituting this expression for G_3 into Eq. (2) yields what is called the Λ_{10} approximation. The resulting equation for G_2 is

$$G_2(12,1'2')=G_1(1,1')G_1(2,2')-G_1(1,2')G_1(2,1')+\tfrac{1}{2}[G_1^0(1,3)G_1(2,4)+G_1(1,3)G_1^0(2,4)]\times V(3,4)G_2(34,1'2'). \quad (5)$$

A further approximation can also be made, which consists of replacing the G_1's in the square brackets with G_1^0's. This is called the Λ_{00} approximation, and this theory has been investigated thoroughly for nuclear matter by Puff[3] and subsequently by Falk and Wilets[4] and Reynolds and Puff.[5] The difference between Λ_{00} and Λ_{10} has been investigated for nuclear matter[6,7] with the result that Λ_{10} predicts slightly less binding than does Λ_{00}. This paper will rely solely on the Λ_{00} theory.

Equation (5) can be converted into an integral equation for a T matrix, defined by $VG_2=TG_1G_1$, which is analogous to the K matrix used by Brueckner. In the zero-temperature limit of the Λ_{00} theory, with the condition that the chemical potential μ be negative, the integral equation in momentum space is

$$\langle\mathbf{k}_1\mathbf{k}_2|T_K(\omega)|\mathbf{k}_1\mathbf{k}_2\rangle=\langle\mathbf{k}_1\mathbf{k}_2|v-v_{\mathrm{ex}}|\mathbf{k}_1\mathbf{k}_2\rangle+\int\frac{d\mathbf{k}''}{(2\pi)^3}\langle\mathbf{k}_1\mathbf{k}_2|v|\mathbf{k}_1''\mathbf{k}_2''\rangle\left[\omega-\frac{\hbar^2}{2m}(2k''^2+\tfrac{1}{2}K^2)\right]^{-1}\times\langle\mathbf{k}_1''\mathbf{k}_2''|T_K(\omega)|\mathbf{k}_1\mathbf{k}_2\rangle, \quad (6)$$

where K and k'' are the center-of-mass and relative momenta, respectivey.

Once this T matrix has been obtained the bulk properties of the system can be calculated using the following equations self-consistently:

$$V(k_1,\omega)=\int\frac{d\mathbf{k}_2}{(2\pi)^3}\hat{\rho}(k_2)\langle\mathbf{k}_1\mathbf{k}_2|T_K(\omega+\omega_0(k_2))|\mathbf{k}_1\mathbf{k}_2\rangle, \quad (7)$$

$$\omega_0(k_1)=\frac{\hbar^2k_1^2}{2m}+V(k_1,\omega_0(k_1)), \quad (8)$$

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$$\hat{\rho}(k_1)=\theta(k_F-k_1)\left[1-\frac{\partial V(k_1,\omega)}{\partial\omega}\bigg|_{\omega=\omega_0(k_1)}\right]^{-1}, \tag{9}$$

$$E/N=(2/\rho)\int\frac{d\mathbf{k}_1}{(2\pi)^3}\hat{\rho}(k_1)\frac{1}{2}\left[\frac{\hbar^2k_1{}^2}{2m}+\omega_0(k_1)\right], \tag{10}$$

$$\rho=2\int\frac{d\mathbf{k}_1}{(2\pi)^3}\hat{\rho}(k_1). \tag{11}$$

$$\mu=\omega_0(k_F) \tag{12}$$

Equations (6), (7), (10), and (11) can be converted easily to apply to a two-dimensional system by changing the integrations from

$$\int\frac{d^3k}{(2\pi)^3}\quad\text{to}\quad\int\frac{d^2k}{(2\pi)^2}.$$

II. TWO-BODY INTERACTION

Equation (6) for the T matrix can be solved exactly for either a sum of square wells or a sum of separable potentials. We have chosen the Herzfeld potential for calculational purposes in order to avoid the nonlocal nature of the separable potential while keeping the numerical aspects of the problem tractable. The He^3-He^3 interaction is then parametrized by three quantities (a_1, the hard-core radius; a_2, the radius of the outer edge of the attractive well; and V_0, the well depth). These parameters can be determined by requiring that they reproduce the second virial coefficient in the low-temperature range.

There are experimental data for the second virial coefficient $B(T)$ in the range from 1.5 to 4°K, and outside that range values have been calculated using the 6–12 and exponential-six potentials. The general expression for the second virial coefficient is

$$B(T)=\frac{1}{32}\left(\frac{2\pi\hbar^2}{KTm/2}\right)^{3/2}+\tfrac{3}{4}\sum_{l\text{ odd}}(2l+1)\left(\frac{2\pi\hbar^2}{KTm/2}\right)^{3/2}\left\{\frac{1}{\pi}\int_{E=0}^{\infty}\eta_l d[\exp(-E/KT)]-\sum_{\text{discrete}}\exp(-E_{nl}/KT)\right\}$$
$$+\tfrac{1}{4}\sum_{l\text{ even}}(2l+1)\left(\frac{2\pi\hbar^2}{KTm/2}\right)\left\{\frac{1}{\pi}\int_{0}^{\infty}\eta_l d[\exp(-E/KT)]-\sum_{\text{discrete}}\exp(-E_{nl}/KT)\right\}. \tag{13}$$

Here η_l is the phase shift for the lth partial wave, E is the energy of the relative motion of the two particles, m is the He^3 atomic mass (5.0076×10^{-24} g), T is the absolute temperature, K is Boltzmann's constant, and the E_{nl} are the energies of the bound states. There were no bound states for the range of the parameters investigated so the sum over discrete states can be neglected.

In practice it is convenient to use Kihara's method[8] in which $B(T)$ is calculated as a function of the new parameters

$$g=a_2/a_1,$$
$$s=|V_0|(m/\hbar^2)a_1{}^2[4(g-1)^2/\pi^2],$$
$$\tau=\frac{\pi^2sK}{4(g-1)^2|V_0|}T.$$

The parameter s is the effective depth parameter used in nuclear physics by Blatt and Jackson.[9] An electronic computer was used to calculate a quantity $f(\tau)$ which was proportional to $T^{3/2}B(T)$ and independent of the T/τ ratio. For a particular g value, calculations were performed for various s values which gave minimum values of $f(\tau)$ in the vicinity of the theoretically expected minimum value. The lateral spread of the calculated curve when plotted against T is, of course, dependent on the T/τ ratio. Thus if $f(\tau)$ is normalized to be equal to $T^{3/2}B(T)$ and the ratio T/τ is chosen so that the best comparison is obtained for the two curves the third parameter τ is then determined. To check the computation a calculation was first made for He^4 with $g=1.5$, $s=1.0$, and agreement was obtained with the results of Kihara.

The He^3 virial coefficients can be compared with a few measured values in the range of 1.5-4°K[10] and with theoretical curves calculated for the 6–12 potential and the exponential-six potential.[11] Results of the fittings indicate that there is a range of g values over which for some s value a fit can be found to the observed data and to the theoretical curves for $B(T)$ in the temperature range from 1 to 10°K. Figure 1 is a typical comparison of the calculated virial coefficients of the Herzfeld potential with the experimental and theoretical values for He^3. In Table I the parameters of the Herzfeld

TABLE. I. Herzfeld potential parameters determined by fitting of second virial coefficient.

g	s	T/τ	a_1(Å)	a_2(Å)	$V_0(K^0)$
1.5	0.895	2.39	2.594	3.89	−21.11
1.75	0.865	2.85	2.386	4.16	−10.82
2.0	0.845	3.37	2.185	4.370	− 7.03
2.25	0.825	3.81	2.055	4.624	− 4.96
2.5	0.810	4.23	1.95	4.89	− 3.76
2.75	0.798	4.57	1.88	5.16	− 2.93

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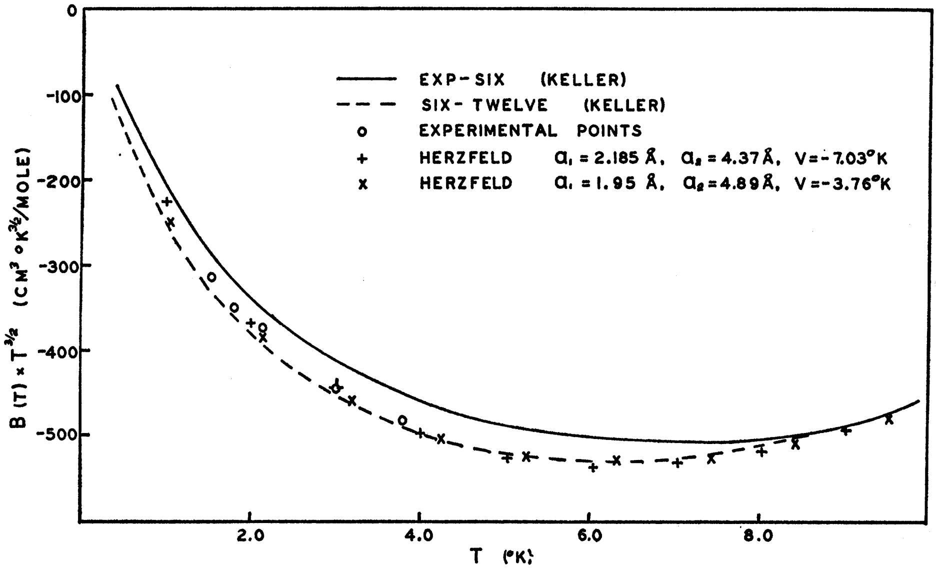

FIG. 1. A comparison of the second virial coefficient multiplied by $T^{3/2}$ calculated for the Herzfeld potentials with the experimental values and with the theoretical values for the exponential-six and for the 6–12 potential.

potential are listed for various fittings. A general conclusion can be drawn that as g becomes smaller the calculated $B(T)$ curve has excessive curvature and tends to lift up from the He^3 and the six-twelve values in the region of 10 deg and of 0 deg. As g becomes larger the Herzfeld $B(T)$ curve is too broad. The conclusion is that the best set of parameters from the basis of the second virial coefficients alone is that of $g=2.0$: i.e., $a_1=2.18$ Å, $a_2=4.37$ Å, $V_0=-7.03$°K.

Certainly the second virial coefficients themselves are not a reliable determination for the parameters of a crude potential such as the Herzfeld potential. The virial coefficient expansion is a low-density expansion, and the virial coefficients are most sensitive to the long range part of the potentials. It is certainly desirable, therefore, to use other criteria for the parameterization of the He^3-He^3 interaction.

We know that scattering data for momenta up to values of order k_F are important in the Λ_{00} theory, and we can impose an additional restriction on the potential. We require that the parameters reproduce $B(T)$ fairly well in the low-temperature region and that they also give the proper phase shifts for the lower partial waves near k_F. The set of parameters corresponding to $g=2.5$ is the best of all the sets in Table I in this respect.

A third set of parameters has also been chosen by the criterion that they should reproduce the experimental binding energy and density when a Λ_{00} calculation is performed. Taking a binding energy of 2.53°K per particle and a density parameter r_0 (defined by $1/\text{density}=(4/3)\pi r_0^3$) equal to 2.43 Å we find a suitable choice of parameters to be

$$a_1=1.85\text{ Å},$$
$$a_2=3.95\text{ Å},$$
$$V_0=-10.7\text{°K}.$$

This potential is intended to phenomenologically compensate for errors inherent in the Λ_{00} approximation and in the use of the Herzfeld potential. The strength parameter for this potential is $s=1.19$, which indicates the presence of a bound state. This is contrary to most data on the He^3-He^3 interaction and indicates that the calculations with potentials determined from virial coefficient and scattering data will yield insufficient binding.

There is of course more than one set of three potential parameters which will yield the two experimental quantities of binding energy and density. We find that the core radius is very important in determining the proper density for the system but that the energy can be fit over a range of a_2 and V_0 values. No attempt was made to find a physical reason for choosing one particular pair of a_2 and V_0 values in preference to the others, and calculations are presented for one member of this set only.

IV. RESULTS

Van Leeuwen and Reiner[12] have solved the three-dimensional T-matrix equation exactly for a potential made up of an arbitrary number of step potentials in general and for a Herzfeld potential in particular. Their analysis can be applied to the two-dimensional system and the result is the same as if the normalized spherical Bessel functions in their result are replaced by cylindrical Bessel functions and the square of a_1 or of a_2 at any point is simply replaced by a_1 or a_2, respectively. Having the exact T matrix enables us to solve Eqs. (7) to (9) self-consistently to obtain the zero-temperature bulk properties of the system. This was first done for the three-dimensional system and values of E/N and μ were found as functions of r_0. For the pure virial-

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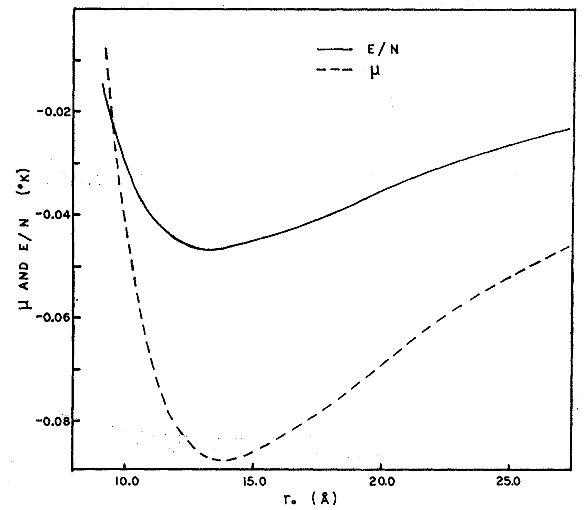

FIG. 2. Variation of μ and E/N with the separation parameter r_0 Herzfeld potential ($a_1=1.95$ Å, $a_2=4.89$ Å, $V_0=-3.76$°K).

coefficient potential corresponding to $g=2.0$ the energy per particle remains positive and has values of $0.1\leqq E/N\leqq 0.2$°K at densities corresponding to $3.5\leqq r_0\leqq 4.0$ Å. The potential based on considerations of both virial coefficient and phase shifts yields slightly more attraction, with $E/N\approx -0.1$°K at $r_0\approx 3.25$ Å at the energy minimum. Thus the Λ_{00} approximation with the Herzfeld potential fitted to virial coefficients and phase shifts does not seem to be a good approximation applied to the three-dimensional system. These results are in agreement with those of Beck[13] who used separable potentials fit to de Boer phase shifts in a Λ_{00} calculation. He finds the system is self-bound with a binding energy of -0.04°K at a density corresponding to $r_0=3.25$ Å. Brueckner and Gammel[14] in a different calculation using a realistic two-body potential find $E/N=-0.9$°K at $r_0\approx 2.6$ Å.

When two-dimensional calculations are done with the same potentials the general feature of very weak attraction persists, but maximum binding does not occur until extremely large interparticle separations. The virial-coefficient potential ($g=2.0$) yields a minimum energy per particle of -0.03°K at $r_0=14.8$ Å. The virial-coefficient–phase-shift potential ($g=2.5$) yields a minimum of energy at $E/N=-0.047$°K and $r_0=13.3$ Å. Figure 2 illustrates the variation of the energy per particle and the chemical potential with r_0 for the latter potential. Finally when the potential parameters which yield the experimental bulk properties for the three-dimensional system were used an energy minimum of $E/N=-0.68$°K at $r_0=2.9$ Å is found.

Puff and Reiner[15] have obtained an expression for the specific heat of a system of interacting fermions based on the Λ_{00} approximation. Their result is made up of one term equal to the usual effective-mass term multiplied by the momentum distribution factor $\rho(k_F)$ plus temperature-dependent correction terms which can give a contribution at absolute zero. Most theoretical calculations of the specific heat rely on the effective-mass approximation and, because of the inherent limitations of our approximation, we also will obtain the specific heat from

$$C=\left[1+\frac{m}{\hbar^2 k_F}\frac{dV(k_1,\omega_0(k_1))}{dk_1}\bigg|_{k_1=k_F}\right]^{-1}C_{\text{free}}, \tag{14}$$

$$\frac{C}{C_{\text{free}}}=\frac{m^*}{m}=\frac{\hbar^2 k_F}{m}\left[\frac{d\omega_0(k)}{dk}\bigg|_{k=k_F}\right]^{-1} \tag{15}$$

The ratio of C/C_{free} was calculated at the energy minimum for the three-dimensional system and the results are $m^*/m=1.25$ for the $g=2.5$ set of parameters, $m^*/m=1.27$ for the $g=2.0$ set, and $m^*/m=1.1$ for the "physical set". These numbers are to be compared to $\mathrm{m}^*/m=1.88$, obtained by Brueckner and Gammel.

The calculations in two dimensions are done over a range of densities and our two-dimensional specific heat as a function of r_0 is pictured in Fig. 3 for the $g=2.5$ potential. In this case m^*/m is less than one and approaches one as the density goes to zero. At the point of maximum binding the results are $C/C_{\text{free}}=m^*/m=0.86$ for the above set of parameters, $m^*/m=0.88$ for the $g=2.0$ set, and $m^*/m=1.49$ for the "physical set."

V. DISCUSSION

The Λ_{00} theory is an approximation in which an attempt is made to treat two-particle correlations in the medium while replacing the effects of the other

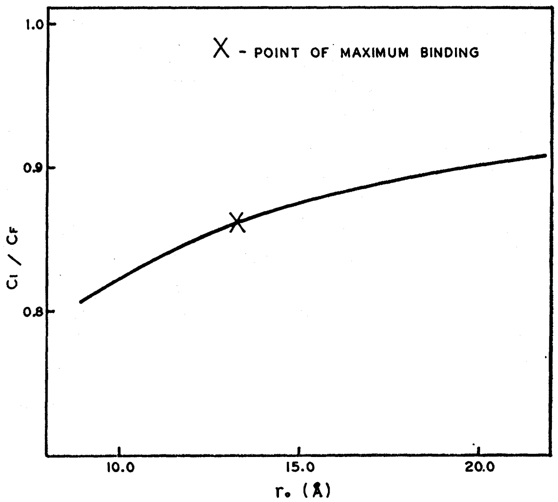

FIG. 3. Variation of specific heat with the separation parameter r_0 expressed as the ratio of the interacting to the free Fermi gas for the Herzfeld potential ($a_1=1.95$ Å, $a_2=4.89$ Å, $V_0=-3.76$°K).

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particles by an average field. For a dilute system this should be a good approximation and indications are that it is valid for nuclear matter. Helium is however significantly denser than nuclear matter when expressed relative to the respective close-packed densities figured according to the respective repulsive-core sizes. The calculations presented here along with those of Brueckner and Gammel indicate that corrections to the two-body theory must be incorporated before a theory can be applied to liquid He^3. Bethe[16] has shown that when the three-particle problem is treated correctly the result reduces to the two-particle result except when the three particles are close to one another. In that case the wave function is reduced to $\frac{1}{3}$ of the more elementary value corresponding to the fact that the wave function can be excluded from the strong repulsive core only once.

However, the two-dimensional system is less dense than the three-dimensional system and a two-particle theory such as Λ_{00} may be expected to have more validity in this situation. Our results for the two-dimensional system probably bracket the true behavior of the system, with the virial coefficient potential indicating too little attraction and the potential based on the three-dimensional physical properties indicating too much.

There is a considerable difference between the density of the monolayers measured by Goodstein and the densities calculated at maximum binding with the Λ_{00} approximation. This is not a basic disagreement between theory and experiment since a great range of densities is available to the monolayer. With sufficient attraction the substrate could bind the system even though the two-dimensional system by itself would not be bound at the same density. Goodstein *et al.* report a coverage corresponding to $r_0 \approx 2.0$ Å. Even with the very attractive phenomenological potential the calculated μ is positive for $r_0 < 2.1$ Å. Our calculations are not applicable at greater densities since a positive μ results in a more complicated kernel in the T-matrix equation. The energy per particle can be extrapolated to go positive near an r_0 of 2.0 Å and to increase with a decreasing r_0 at a rate in excess of a °K/Å. If there is, therefore, any validity in the Λ_{00} model the He^3 atoms in the observed monolayer are close enough together to experience strong mutual repulsion with the large adhesive forces of the substrate holding the layer together.

The calculated quantity that is to be compared directly with experiment is the specific heat at the same density as in the experiment. Unfortunately the only experimental data available are far into the positive-μ region of density. The significant thing is that Goodstein *et al.* report a specific heat proportional to the square of the temperature. The most direct explanation of this is a two-dimensional Debye model with collective, phonon-like excitations. The Λ_{00} calculation is, of course, based on single-particle-like excitations, and the calculated specific heat would be proportional to T. The question arises as to whether a collective-state-excitation model would be appropriate at high densities while a Fermi-liquid theory as Λ_{00} might become valid as low densities are approached. To answer this question experiments are needed with He^3 monolayers with coverages that range from those of Goodstein down to those which correspond to r_0 values of 12 Å or more. An observation of a change in the temperature dependence of specific heat as the coverages are decreased would be the most direct evidence of such a change of behavior.

The search for a specific heat linear in T at low densities would be futile if the surface of the substrate is so rough that the ground-state wave function of a He^3 atom on the substrate were localized. In that case a two dimensional Fermi-liquid model would not apply however low the density. The most direct interpretation of the T^2 specific heat would be that collective excitations occur so that the helium atoms are interacting with each other and are not found to be in localized ground states in which case an exponential specific heat would be expected.

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The authors are indebted to Professor L. Wilets for originally suggesting the subject of this paper and for many helpful conversations during the course of the work. They wish to thank Professor R. Puff for helpful discussions and comments. One of us (T.C.F.) would like to acknowledge the hospitality of the Physics Department at the University of Washington where this work was begun. Numerical calculations were performed on the IBM 7094 computer at the University of Washington, where a grant of computer time was given, and on the CDC 3600 computer at the University of California, San Diego.

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