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Structure of the Surface of Liquid He^4 at Zero Temperature*

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The ground-state wave function of a finite drop of liquid He^4 is taken as a product of two-body and one-body factors. The surface energy is calculated, taking into account the variation of the two-particle-correlation function in the surface region, and is minimized by a density profile which falls off outside the liquid with a scale length 0.7 Å and approaches the interior density with scale length 2 Å. The calculated surface tension is 10% higher than the observed value.

I. INTRODUCTION

Ground-state properties of an infinite sample of liquid He^4 have previously been calculated[1-5] quite successfully from a wave function of the Jastrow form

$$\Psi = \exp\frac{1}{2}\sum_{i<j} u(r_{ij}). \tag{1}$$

This wave function is readily generalized to describe a finite droplet by inclusion of one-body factors, and provides the basis for a "first-principles" calculation of the microscopic structure of the He^4 surface. Current interest in such calculations arises principally from Andreev's[6] proposal that the observed[7-11] surface tension of dilute solutions of He^3 in He^4 can be understood if some of the He^3 atoms live in bound states at the He^4 surface. Several calculations[12-14] confirm that the nature of these bound states depends in detail on the structure of the pure He^4 surface. Furthermore, the extension of Eq. (1) to inhomogeneous systems is intrinsically interesting because of the challenging technical problem of calculating the correlation function and kinetic energy density in a region of rapidly varying density. Early calculations[15,16] of the surface tension were based on very simple assumptions about these functions, which can now be seen to be insufficient for more than order of magnitude purposes. Shih and Woo[14] and Bowley[17] have made calculations similar in principle to the present one; the differences are discussed in subsequent sections.

To describe a finite drop of the liquid we have used the wave function

$$\Psi = Z \exp\left(\frac{1}{2}\sum_{i<j\leq N} u(r_{ij}) + \frac{1}{2}\sum t(\vec{r}_i)\right). \tag{2}$$

The function $t(\vec{r})$ controls the density. Far outside the drop $t \to -\infty$, and deep in the interior $t \to 0$ (provided u is sufficiently short range; a long-range u can necessitate a different behavior of t in the interior in order to avoid unphysical behavior of the density, as discussed in the Appendix). Z is a normalization factor. Ideally one would like u to depend on more than the scalar distance r_{ij}, so that u could change its form when $\vec{r}_i$ and $\vec{r}_j$ are near the surface, but calculations with such a u are prohibitively complicated. We have adopted the form of u used by Francis, Chester, and Reatto[4] (FCR) in their calculation of the bulk energy, namely,

$$u(r) = -(a/r)^5 - b/(r^2 + k_c^{-2}), \tag{3}$$

with $a = 2.990$ Å, $b = 6.987$ Å^2, and $k_c = 0.5$ Å^{-1}. The second term represents the zero-point fluctuations of the phonon field, and its inclusion was found by FCR to lower the ground-state energy slightly. Our most recent calculations, which will be reported in a subsequent paper, make us doubt that inclusion of the second term in Eq. (3) really lowers the energy, though such a term is necessary to produce the experimentally observed linear behavior of the x-ray structure factor $S(k)$ for small k.

II. METHOD OF CALCULATION

The density and the two-particle-correlation function are, in principle, obtained from the wave function by integrating

$$\rho(\vec{r}) = N\int \Psi^2(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)\, d\vec{r}_2 \cdots d\vec{r}_N, \tag{4}$$

$$\rho_2(\vec{r}, \vec{r}\,') = N(N-1)\int \Psi^2(\vec{r}, \vec{r}\,', \vec{r}_3, \ldots, \vec{r}_N) \times d\vec{r}_3 \cdots d\vec{r}_N. \tag{5}$$

We also define $\tilde{\rho}(\vec{r}) = \rho(\vec{r})/\rho_B$ (ρ_B is the number density in bulk) and $g(\vec{r}, \vec{r}\,') = \rho_2(\vec{r}, \vec{r}\,')/\rho(\vec{r})\rho(\vec{r}\,')$. The energy is the expectation value of the Hamiltonian $H = -(\hbar^2/2M)\sum \nabla_i^2 + \sum v(r_{ij})$ and, when the droplet is large, can be written as the sum of a volume term and a surface term $E = N\epsilon_B + A\Sigma$ (ϵ_B is the energy per atom in bulk, A is the surface area), where

$$\epsilon_B = -(\rho_B \hbar^2/8M) \int d\vec{r}_2 g_B(r_{12}) \nabla_2^2 u(r_{12}) + \tfrac{1}{2}\rho_B \int d\vec{r}_2 v(r_{12}) g_B(r_{12}), \tag{6}$$

$$\Sigma = -\frac{\rho_B \hbar^2}{2M} \int_{-\infty}^{\infty} dz \tilde{\rho}^{1/2}(z) \frac{d^2\tilde{\rho}^{1/2}(z)}{dz^2} + \rho_B \int_{-\infty}^{\infty} dz \tilde{\rho}(z)[\mathcal{E}(z) - \epsilon_B], \tag{7}$$

$$\mathcal{E}(\vec{r}_2) = -\frac{\rho_B \hbar^2}{8M}\left(\int d\vec{r}_1 \tilde{\rho}(\vec{r}_1) g(\vec{r}_1, \vec{r}_2) \nabla_1^2 u(r_{12}) + \int d\vec{r}_1 g(\vec{r}_1, \vec{r}_2) \nabla_1 u(r_{12}) \cdot \nabla_1 \tilde{\rho}(\vec{r}_1)\right) + \tfrac{1}{2}\rho_B \int d\vec{r}_1 \tilde{\rho}(\vec{r}_1) v(r_{12}) g(\vec{r}_1, \vec{r}_2). \tag{8}$$

We have assumed that $t(\vec{r})$ depends only on the coordinate z which measures distance normal to the surface; thus $\mathcal{E}(\vec{r})$ and $\rho(\vec{r})$ depend only on z. The function t has been eliminated by means of the relation

$$\nabla\rho(\vec{r}) = \rho(\vec{r})\nabla t(\vec{r}) + \int d\vec{r}' \rho_2(\vec{r}, \vec{r}') \nabla_{\vec{r}} u(\vec{r}, \vec{r}'), \tag{9}$$

which follows from the form of Ψ. The bulk energy ϵ_B depends only on u, which is not varied in our calculation. Instead of varying t so as to minimize the surface energy, we can vary $\rho(z)$. In principle, $\rho(z)$ and $u(r)$ determine $g(\vec{r}, \vec{r}')$, which is needed to calculate Eqs. (8) and (7).

The major calculational problem is to find the $g(\vec{r}, \vec{r}')$ which goes with a given $\rho(z)$ and $u(r)$. Even in the homogeneous fluid, approximate integral equations such as the Percus-Yevick (PY) equation[18] and the hypernetted-chain (HNC) equation[18] are insufficiently accurate for reliable calculations of ϵ_B. The energy (– 7.14 K/atom) consists of about 13-K/atom kinetic energy and – 20-K/atom potential energy. The above integral equations make errors in $g_B(r)$ which lead to errors of 1 or 2 K/atom in the kinetic and potential energies, and thus a large fractional error in the total energy.[19] These equations can be generalized to the case of an inhomogeneous fluid $[\rho_B \to \rho(z)]$, in which case accurate numerical solution becomes virtually impossible since g then depends on three variables (e.g., z_1, z_2, r_{12}). Even if the equations could be solved, there would be no reason to trust the results in view of the inaccuracy of these equations in the homogeneous fluid. Rather than deal with a numerically intractable approximate integral equation for $g(\vec{r}, \vec{r}')$ we elected to guess directly at the nature of the solution. Suppose we know the bulk correlation function $g_B(r; \rho)$ associated with the wave function (1) at every bulk density ρ. Then, in the inhomogeneous fluid described by (2), with density $\rho(z)$, we guess

$$g(\vec{r}, \vec{r}') = g_B\{|\vec{r} - \vec{r}'|; \tfrac{1}{2}[\rho(z) + \rho(z')]\} \tag{10a}$$

or (equally plausibly)

$$g(\vec{r}, \vec{r}') = g_B\{|\vec{r} - \vec{r}'|; \rho[\tfrac{1}{2}(z + z')]\}. \tag{10b}$$

We shall shortly discuss how to obtain accurate values of $g_B(r; \rho)$. Assuming that these are available, we calculate the surface energy (7) for a given $\rho(z)$, by means of (10a) and again by (10b). Calling the results Σ_a and Σ_b, we regard $|\Sigma_a - \Sigma_b|$ as a reasonable estimate of the error introduced by the approximation (10a) or (10b). In fact this error proves to be very small (3% or less in Σ). We note that the function $g_B(r; \rho)$ is calculated once and for all. When a new trial function $\rho(z)$ is chosen, $g(\vec{r}, \vec{r}')$ is found from (10a) or (10b) merely by consulting a table of $g_B(r; \rho)$. If it were necessary to solve an integral equation in three variables each time $\rho(z)$ is changed, the calculation would be impossible. Shih and Woo[14] proceed from a philosophy similar to ours, using the approximation

$$g(\vec{r}, \vec{r}') = g_B[|\vec{r} - \vec{r}'|; \rho^{1/2}(\vec{r})\rho^{1/2}(\vec{r}')], \tag{10c}$$

which undoubtedly[20] yields results in close agreement with (10a) and (10b). Their values for $g_B(r; \rho)$ are, however, obtained from the truncated Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy, which is even less accurate[21] than the PY and HNC equations.

III. CALCULATION OF BULK CORRELATION FUNCTION

To obtain $g_B(r; \rho)$ we have solved an integral equation which interpolates between the PY and HNC equations and is an order of magnitude more accurate than either when the interpolation parameter is properly chosen. One such equation has been proposed by Carley and Lado[22] and Rowlinson[23] and has been successfully used by Pokrant[2] to reproduce (with maximum error of 2%) the bulk correlation function which Schiff and Verlet[3] obtained by molecular dynamics for the "short range" $u(r) = -(2.990/r)^5$. Unaware of their work, we used a different interpolating equation, which also reproduces the Schiff-Verlet results with comparable accuracy. Both the PY and HNC equations make large fractional errors (as much as 25%) in the region where g is rising toward its first maximum, which lead to the previously mentioned errors in the bulk energy. With the use of an interpolating equation, the error in bulk energy induced by inaccurate calculation of g is reduced to 0.1 or 0.2 K/atom.

Curves A and B of Fig. 1 represent $g_{\text{PY}}(r) - g_{\text{SV}}(r)$

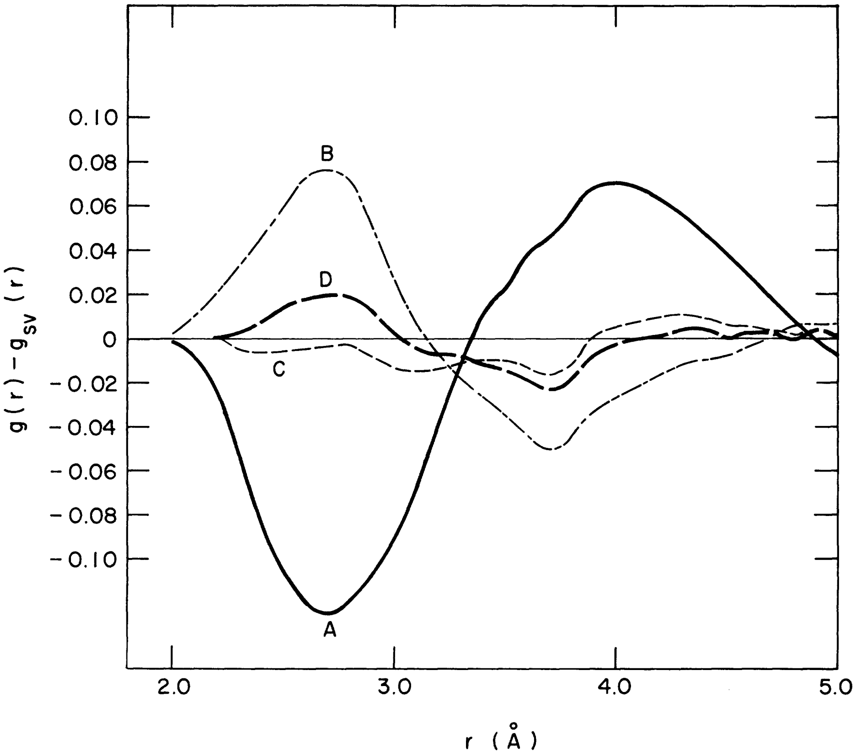

FIG. 1. Comparison of the Schiff-Verlet $g(r)$, computed by molecular dynamics, with solution of approximate integral equations. (A) Percus-Yevick equation; (B) hypernetted chain equation; (C) Eq. (15) with $\alpha = 0.59$; (D) Eq. (15) with $\alpha = 0.68$.

and $g_{\text{HNC}}(r) - g_{\text{SV}}(r)$, where $g_{\text{SV}}(r)$ is the Schiff-Verlet molecular-dynamics-correlation function $[u(r) = -(2.990/r)^5$, $\rho = 0.021\,85$ atom/Å$^3 \equiv \rho_0]$ and g_{PY} and g_{HNC} are the correlation functions which we have calculated from the PY and HNC equations for the same $u(r)$ and ρ. Since the figure shows that the PY and HNC equations make errors of opposite sign for essentially all r, the use of an interpolating equation seemed promising. Our interpolation procedure was suggested by writing the PY equation in the form

$$ge^{-u} = g - c \tag{11}$$

and the HNC equation in the form

$$ge^{-u} = e^{g-1-c}, \tag{12}$$

where $c(r)$ is the "direct-correlation function" defined by

$$g(\vec{r}) - 1 = c(\vec{r}) + \rho \int [g(\vec{r}\,') - 1]c(\vec{r} - \vec{r}\,')d\vec{r}\,' \tag{13}$$

or, in Fourier space,

$$S(k) = [1 - \rho c(k)]^{-1} \tag{14}$$

{where $\rho^{-1}[S(k) - 1]$ and $c(k)$ are the Fourier transforms of $g(\vec{r}) - 1$ and $c(\vec{r})$, respectively}. Our interpolating equation, which we call "the α equation," is

$$ge^{-u} = \frac{e^{\alpha(g-1-c)} - 1}{\alpha} + 1, \tag{15}$$

which reduces to (11) as $\alpha \to 0$ and (12) when $\alpha = 1$. We solved (15) for various α, and found that an excellent fit to $g_{\text{SV}}(r)$ is obtained for a rather wide range of α. Curves C and D of Fig. 1 show the accuracy of the fit for $\alpha = 0.59$ and $\alpha = 0.68$, respectively.

Of course one would like to determine the value of the interpolation parameter α without consulting the molecular dynamics calculations. Like Pokrant, we have done this by imposing the requirement of compressibility consistency, which is an easier to use variant of the pressure consistency requirement proposed by Rowlinson[23] and Lado.[24] Compressibility consistency states that

$$\frac{d}{d\rho}\left(\rho + \tfrac{1}{6}\rho^2 \int_0^\infty r g(r) u'(r) 4\pi r^2 dr\right) = \frac{1}{S(0)}, \tag{16}$$

the left and right sides being alternate expressions for the derivative with respect to density of the pressure p of a classical gas with interatomic potential $-u(r)$ at temperature $kT = 1$. At density ρ_0 we solved the system (14), (15) for $g(r; \rho, \alpha)$ and $\partial g(r; \rho, \alpha)/\partial \rho$. If the variation of α with ρ is neglected, then (16) determines α. The value of α thus found is $\alpha = 0.68$, which is within the region of good fit by eye to g_{SV}. The calculation was repeated at several other densities in order to estimate $d\alpha/d\rho$. The latter turns out to be small enough so that inclusion of the term $(\partial p/\partial \alpha)d\alpha/d\rho$ in (16) produces only a very small change in the

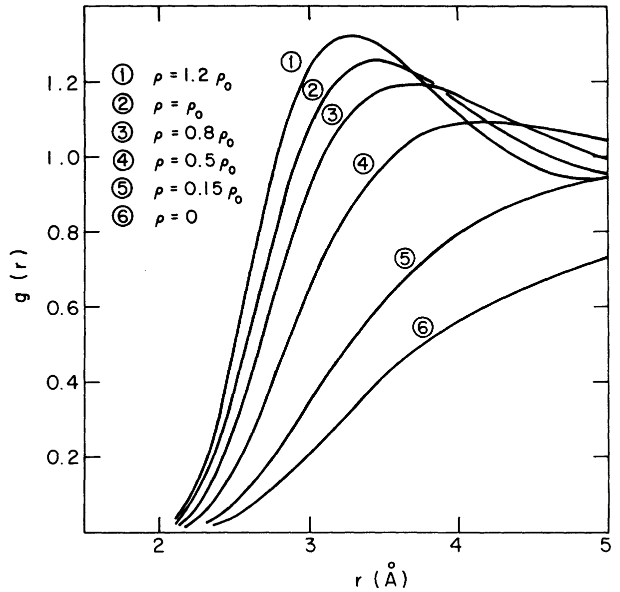

FIG. 2. Two-body-correlation function in bulk fluid, calculated from Eq. (15).

compressibility-consistent value of α. In the limit of zero density, the compressibility-consistent α can be determined analytically, and is $\alpha(\rho = 0) = 0.47$.

Equation (16) says nothing when the long-range u of Eq. (3) is used, since both sides of (16) are infinite for any α. However, the long-range part of u does not change g much, and it seems reasonable to use the previously determined (for short-range u) value of α. We actually used $\alpha = 0.59$ over the entire range $0 \leq \rho \leq 1.2\rho_0$. Considering that α does not vary much with ρ, and that g depends only weakly on α, and that PY and HNC become identical at low densities, it seems clear that our results would be negligibly affected by letting α vary with ρ. The bulk correlation function resulting from (3) and the α equation with $\alpha = 0.59$ is shown in Fig. 2. Calculations were carried out at density intervals $\Delta\rho = 0.05\,\rho_0$ and interpolation was used in evaluating (10a) and (10b).

As we mentioned earlier, our most recent culculations indicate that the inclusion of the long-range term in $u(r)$ does not lower the energy. Omission of this term would, of course, answer possible objections to the method of choosing the value of α. Comparison of the optimal surface shapes resulting from inclusion and omission of the long-range term in $u(r)$ will provide additional insight into the overall reliability of the calculation. In the early stages of this work we constructed an "experimental" bulk wave function by solving the α equation (with $\alpha = 0.59$) to find the u which produces the experimentally observed[25] g. The resulting bulk energy was slightly higher than that resulting from (3). If one believes this calculation, the conclusion is that the best Jastrow-type [Eq. (1)] wave function is not the one which yields the observed g. This might be direct evidence of the limitations of the Jastrow wave function, as discussed by Campbell and Feenberg[5] and Woo.[26]

IV. SHAPE OF THE SURFACE

Minimization of the surface energy (7) with respect to the function $\rho(z)$ makes sense only if, for the u chosen, the bulk energy ϵ_B has its minimum with respect to density at the physical density ρ_0. Otherwise, it is energetically advantageous to take matter out of the bulk and form an arbitrarily thick surface layer of matter at the density which minimizes ϵ_B [making the second term of (7) arbitrarily large and negative]. If $v(r)$ is taken to be the Lennard-Jones potential $v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ with the deBoer-Michels parameters $\sigma = 2.556$ Å and $\epsilon_0 = 10.22$ K, then the choice (3) of $u(r)$ leads to a minimum ϵ_B when $\rho = 0.9\rho_0$. We can either adopt the deBoer-Michels parameters and do a calculation at bulk density $\rho = 0.9\rho_0$, or alter the parameters in $v(r)$ in such a way that the bulk energy is minimum at $\rho = \rho_0$. We have done the latter with the choice $\sigma = 2.556$ Å and $\epsilon = 1.09\epsilon_0$. This results in a bulk energy $\epsilon_B = -7.43$ K/atom. Since this is close to the experimental value, one might expect the calculation to yield a fairly good value for the surface tension.

At this point it should be mentioned that Bowley[17] asserts that inclusion of a long-range (proportional to r^{-2}) term in $u(r)$ leads to a (negative) divergence in the surface energy. This arises because the integrand $\mathcal{E}(z) - \mathcal{E}_B$ in his counterpart of Eq. (7) dies off only as z^{-1} deep in the interior of the liquid when a long-range u is used, leading to a logarithmic divergence. Indeed, the first term on the right-hand side of (8) approaches its asymptotic interior value very slowly, the difference being proportional to z^{-1}; however, this z^{-1} term is exactly canceled by the second term on the right-hand side of (8) (which does not occur in Bowley's calculation) so that $\mathcal{E}(z) - \mathcal{E}_B$ dies off more rapidly than z^{-1}. In the Appendix we discuss the nature of Bowley's approximation, and how the term which cancels the divergence is lost in his calculation.

The first trial forms which we used for $\tilde{\rho}(z)$ were the exponential

$$\tilde{\rho}(z) = \tfrac{1}{2}e^{-\beta z}(z > 0);\ 1 - \tfrac{1}{2}e^{\beta z}(z < 0) \tag{17}$$

and the Fermi function

$$\tilde{\rho}(z) = (1 + e^{\beta z})^{-1}. \tag{18}$$

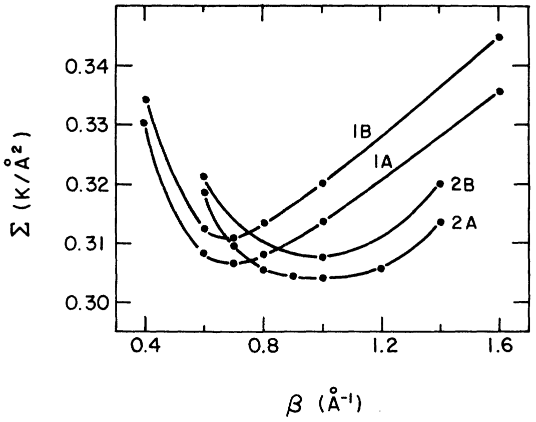

FIG. 3 Surface energy for exponential (1A, 1B) and Fermi (2A, 2B) density profiles. The scale length is β^{-1}. The A and B curves refer to different approximations for the correlation function in the inhomogeneous region.

The resulting surface energy is shown in Fig. 3. The curve 1A refers to the trial form (17), with the approximation (10a) used for $g(\vec{r}, \vec{r}')$; curve 1B refers to Eq. (17), with (10b) used for g; curves 2A and 2B refer to Eq. (18), plus (10a) and (10b), respectively. We note that the A and B curves agree within 1.5% near their minima, and that the difference between the two curves systematically decreases as β decreases. The latter is to be expected, since (10a) and (10b) become more nearly identical as the scale length in $\rho(z)$ increases.

The smallness of the difference between the A and B curves is surprising. The approximations (10a), (10b), and (10c) all become increasingly accurate when the length scale of ρ is large compared with the length scale of g (i.e., the interparticle spacing), but in fact our optimal $\rho(z)$ varies considerably over a distance of one interparticle spacing (about 3A). It is hard to make an *a priori* estimate of the error introduced by using (10a) or (10b) when $\rho(z)$ is not slowly varying. The smallness of the difference between the A and B curves leads us to conclude that this error is only one or two percent in our case.[20] We regard the agreement of the A and B curves as the measure of the internal consistency of the calculation. If the two approximations yielded significantly different surface energies, then neither approximation could be trusted. The good agreement arises as the result of the weak density dependence of g_B, and the fact that the surface energy functional depends on many different relative configurations of two particles. It appears almost self-evident to us that the true surface energy Σ lies in the range covered by Σ_a, Σ_b, and Σ_c. We cannot envision the mechanism by which all three approximations could yield almost the same surface energy, and yet all be far from the truth. When accurate Monte Carlo or molecular-dynamics calculations on inhomogeneous fluids become available, further investigation of the accuracy of these approximations will be possible. One might guess that it was not even necessary to take account of the density dependence of g, and that the crude approximation $g(\vec{r}, \vec{r}') = g_B(|\vec{r} - \vec{r}'|; \rho_0)$ would have sufficed. A few points were calculated with this approximation, and the resulting surface energy was 30–35% higher than that calculated with (10a) and (10b); we conclude that this approximation is much too crude to be used in a search for a minimum. The approximation (10a) was used in subsequent calculations.

Both Bowley[17] and Shih and Woo[14] have used a trial function of the form (2) in conjunction with a short-range $u(r)$. Bowley finds that the surface energy is minimum for $\beta = 2.2$ Å^{-1}, and Shih and Woo find $\beta = 1.67$ Å^{-1}, compared with our value $\beta = 1.0$ Å^{-1}. We ascribe the discrepancy principally to Bowley's use of the approximation $g(\vec{r}, \vec{r}') = g_B(|\vec{r} - \vec{r}'|; \rho_0)$ and Shih and Woo's use of the truncated BBGKY hierarchy to calculate the g_B which is used in (10c).

Having found the best Fermi function, we relaxed the condition of "particle-hole" symmetry $[\tilde{\rho}(-z) = 1 - \tilde{\rho}(z)]$ contained in Eqs. (17) and (18). We tried the "generalized Fermi function"

$$\tilde{\rho}(z) = (1 + e^{p(z)})^{-1}, \quad p(z) = \left(\frac{\beta_1 e^{\gamma z} + \beta_2 e^{-\gamma z}}{e^{\gamma z} + e^{-\gamma z}}\right) z, \tag{19}$$

which tends to a Fermi function with parameter β_1 for large positive z, and parameter β_2 for large negative z. With $\gamma = 1.0$ Å^{-1} and $\beta_1 = 1.0$ Å^{-1}, β_2 was varied, with a minimum Σ ($\Sigma = 0.296$ K/Å^2) occurring when $\beta_2 = 0.6$ Å^{-1}. Then β_1 was varied, keeping $\beta_2 = 0.6$, resulting in a minimum $\Sigma = 0.294$ when $\beta_1 = 1.4$. Then β_2 was varied again, with $\beta_1 = 1.4$, resulting in a minimum $\Sigma = 0.293$ when $\beta_2 = 0.5$. Variation of γ produced only a small change, the final minimum ($\Sigma = 0.2920$ K/Å^2) being obtained for $\gamma = 0.5$, $\beta_1 = 1.4$, $\beta_2 = 0.5$ (all in Å^{-1}). The experimental[9] value of Σ is 0.268 K/Å^2.

The possibility of overshoot [i.e., that $\rho(z)$ rises above its bulk value somewhere in the surface] was explored, and we found no indication that this is energetically favorable. This is in disagreement with a recent calculation by Regge,[27] who predicts overshoot on the basis of an essentially hydrodynamic calculation.

Calculations of the He^3 surface states, based on this work, are presently being carried out.

ACKNOWLEDGMENTS

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APPENDIX

An exact expression for the surface energy per unit area, before t is eliminated by means of (9), is

$$\Sigma = \rho_B \int dz\, \tilde{\rho}(z)[w(z) - w_B] - \frac{\rho_B \hbar^2}{8M} \int \tilde{\rho}(z) \frac{d^2 t}{dz^2}\, dz, \tag{A1}$$

where

$$w(z_1) = \frac{-\rho_B \hbar^2}{8M} \int d\vec{r}_2 \tilde{\rho}(\vec{r}_2) g(\vec{r}_1, \vec{r}_2) \nabla_2^2 u(r_{12}) + \tfrac{1}{2}\rho_B \int d\vec{r}_2 \tilde{\rho}(\vec{r}_2) v(r_{12}) g(\vec{r}_1, \vec{r}_2) \tag{A2}$$

and $w_B = w(-\infty) = \epsilon_B$ ($z \to -\infty$ far inside the drop). Bowley's equation (2.15) for Σ follows from (A1) and (A2) with the additional approximations

$$g(\vec{r}_1, \vec{r}_2) = g_B(|\vec{r}_1 - \vec{r}_2|) \tag{A3}$$

and

$$\tilde{\rho}(z) = e^{t(z)}\,. \tag{A4}$$

Although (A3) introduces substantial numerical error, it does not introduce spurious divergences into the calculation. Reasonable as (A4) may seem, we shall see that it is seriously in error when a long-range $u(r)$ is used, and that the approximation (A4) introduces a spurious divergence into Σ, which is not present in the exact expressions (A1) and (7).

With $u(r)$ given by Eq. (3), an elementary calculation of the asymptotic behavior of the first term on the right-hand side of (A2) yields

$$w(z) - w_B \approx \frac{-\rho_B \hbar^2}{4M} \frac{\pi b}{|z|} \tag{A5}$$

for large negative z. The first term on the right-hand side of (8) has identical behavior. The second term in (8) also behaves asymptotically as $|z|^{-1}$, with a coefficient exactly the negative of that in (A5), so that (7) exhibits no divergence. If Eq. (9) were used to eliminate the function $t(\vec{r})$ from (A1) [thus generating (7)], Bowley's calculation would contain no divergence. The approximation (A4) is equivalent to omitting the second term on the right-hand side of (9), which is precisely the term which cancels the divergence.

Of course (A1) is exact, and one is not *required* to eliminate t, as we have done. However, if the function t is physically reasonable [i.e., if the corresponding $\tilde{\rho}(z)$ tends to unity as $z \to -\infty$ and zero as $z \to \infty$], then the second term in (A1) will contain a divergence which cancels the divergence in the first term. The apparently reasonable choice

$$e^{t(z)} = (1 + e^{Bz})^{-1}, \tag{A6}$$

which Bowley has made, does not correspond to a reasonable $\tilde{\rho}(z)$. The second term on the right-hand side of (9) can be evaluated when $\vec{r}$ is far in the interior; letting the gradient operate on $\vec{r}\,'$ and integrating by parts (the integrated part vanishes on a surface which is entirely outside the droplet), the term becomes

$$\rho(\vec{r}) b \rho_B \int \frac{\hat{n}' dS'}{|\vec{r} - \vec{r}\,'|^2}\,, \tag{A7}$$

where we have assumed that $\nabla' \rho(\vec{r}\,')$ exists only near the surface. The integral in (A7) is a surface integral ($\hat{n}'$ is the outward normal), whose value depends on the sample size and shape. If the boundaries are planes at $z = 0$ and $z = -L$, and $\vec{r}$ is far in the interior but still "near" the $z = 0$ boundary (i.e., z large and negative, but $|z| \ll L$) then (A7) becomes $\rho(\vec{r}) b \rho_B 2\pi \ln L \hat{k}$, where $\hat{k}$ is a unit vector in the positive z direction. For a spherical droplet, $\ln L$ is replaced by $\ln R$. In this region, Eq. (9) becomes

$$\frac{d \ln \rho(z)}{dz} = \frac{dt}{dz} + B, \tag{A8}$$

where $B = 2\pi b \rho_B \ln L$. In order for ρ to be constant as $z \to -\infty$ we must have $t \sim -Bz$, so that e^t grows exponentially in the interior. Thus, (A4) is not reasonable deep in the interior. The next term on the right-hand side of (A8), which has been omitted, is proportional to $\ln|z|$. This gives rise to the divergence in the second term of (A1) which cancels the divergence in the first term.

If t has been eliminated from the calculation by (9), none of these troubles arises, since it is easy to make physically reasonable guesses for ρ. Bowley suggests that the divergence arises from the fact that u does not change its form near the surface, so that surface waves are treated inaccurately. As Bowley points out, the divergence which he found is a negative one; since the variational principle gives an upper bound on the energy, an "improved" choice of u would not cure the conceptual problem.

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[19] By "error" we mean not the difference between the calculated and experimental ϵ_B, but rather the error in the calculated ϵ_B introduced by using an approximate $g_B(r)$ which differs from what one would get by performing the integrations in (5).

[20] Subsequent to the submission of this paper we have calculated the surface energy Σ_c corresponding to our optimal density profile $\bar{\rho}(z)$, using the approximation (10c). The two surface energies Σ_c and Σ_a differ by 0.1%.

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