

The Surface of Liquid ^4He , Based on the Idea That $\prod_{i<j} f(r_{ij})$ Describes a Droplet

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We argue that the wave function $\prod f(r_{ij})$ describes the ground state of a droplet of liquid ^4He . With this wave function, expressions for the surface energy ϵ and the surface tension σ of liquid ^4He at $T=0$ are derived. Choosing particular $f(r)$ and density profile, and the simplest pair correlation function, we plot the variation of ϵ and σ with surface thickness t . For slow variation of density at the surface, ϵ becomes proportional to t . The surface thickness is found to be about 4 \AA . The inclusion of phonon zero-point motion correlations in the wave function leads (at $T=0$) to a $-R^2 \log R$ term in the energy of a droplet of radius R , implying a logarithmic divergence in both ϵ and σ . At $T>0$ the phonon correlations give a $\log T$ dependence of ϵ and σ and a negative bulk specific heat. Suggestions as to the reason for these problems are explored, but no definite conclusions are reached.

1. INTRODUCTION

The ground state of a drop of liquid helium is usually approximated by a Bijl-Jastrow product over pairs times a Hartree factor, namely

$$\prod_{i<j}^N f(r_{ij}) \prod_i^N s(r_i)$$

The function $s(r_i)$ is used to control the density variation at the surface, and is determined variationally.¹⁻⁴

In this paper we put forward the view that the function

$$\Psi(1, \dots, N) = \prod_{i<j}^N f(r_{ij}) \quad (1)$$

already describes a droplet, and thus necessarily has a surface. There are three arguments to support this: First we note that Ψ is both translationally

and rotationally invariant, so that it could describe only spherically symmetric self-bound systems. Second, we can argue by analogy with a classical fluid consisting of atoms interacting with pairwise central forces. This has a probability density proportional to

$$\exp \left\{ -\frac{1}{T} \sum_{i < j} u(r_{ij}) \right\}$$

and thus has the same form as Ψ^2 , the quantum probability density. For temperatures and pressures lying between the triple and the critical points, this probability density will describe a drop in equilibrium with its vapor. [We note in passing that this classical analogy implies that the function $f(r)$ should not be monotonically increasing (as is usually assumed) if it is to describe a self-bound system, since a classical system does not have condensation unless the pair potential $u(r)$ contains an attractive part. A similar view has been expressed recently by De Michelis and Reatto.⁵] The third argument in favor of our assertion that $\prod f(r_{ij})$ describes a droplet is provided cumulatively by the results of this paper, where we calculate the surface energy and the surface tension of the Bijl-Jastrow product (1). The results, both analytically and numerically, are entirely satisfactory provided we leave out the r^{-2} correlations, which Reatto and Chester⁶ assert must exist in the bulk pair function f for all Bose systems that have phonon excitations.

Our calculation of the surface energy and tension with the wave function Ψ of Eq. (1) can be regarded as the zeroth-order approach to the problem. It is *not* a variational calculation, because the pair function f is determined by minimizing the total energy, which is dominated by the bulk energy when the radius of the drop is macroscopic. That is, we take whatever function minimizes the bulk energy, and calculate the consequent surface energy and tension. There is no doubt that the inclusion of a variational factor such as $s(r)$ will lower the total energy and hence probably give a better description of the surface. We believe, however, that our zeroth-order calculation is simpler and yet both analytically and numerically not very far from reality.

In Section 2 we calculate the surface energy of a spherical drop at $T=0$ directly from the expectation value of the Hamiltonian in the state Ψ . By letting the radius of the drop tend to infinity, we discuss the simpler case of a plane surface with gravity and wall forces absent. Extensive use is made of results previously derived for monatomic classical liquids (Lekner and Henderson,⁷ referred to below as LH).

In Section 3 our results for ϵ (surface energy per unit area) together with experimental values for ϵ and the binding energy per atom in the bulk

are used to calculate the surface thickness of liquid ^4He . We find a 10–90 thickness of about 3.9 \AA , in good agreement with recent estimates.

In Section 4 we use the Toda⁸ and Brout and Nauenberg⁹ expression for the surface tension σ of a quantum fluid to obtain σ for the wave function Ψ . Curves of σ and ε vs. λ (a length characterizing the density variation at the surface) are computed, using the simplest approximation for the pair correlation function $g(r)$. Since $\sigma = \varepsilon$ at absolute zero, the curves should intercept at the value of λ that corresponds to the actual density profile. Despite the crude $g(r)$, this method yields a surface thickness in good agreement with Section 3 (about 3.4 \AA).

Finally, in Section 5 we find that the inclusion of Reatto and Chester's phonon factor leads to unphysical results, namely divergences in ε and σ and a negative bulk specific heat. We conclude that one of the following is incorrect: the phonon factor, or our assumption that the wave function Ψ is enough to describe a surface.

2. SURFACE ENERGY OF $\prod f(r_{ij})$

The expectation value of the Hamiltonian

$$H = \frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j}^N \sum_{i<j}^N u(r_{ij}) \quad (2)$$

when the wave function is of the form (1) may be written as (see, for example, Lekner¹⁰)

$$\langle H \rangle = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1, \mathbf{r}_2) \left[u(r_{12}) - \frac{\hbar^2}{4m} \left(\phi''(r_{12}) + \frac{2}{r_{12}} \phi'(r_{12}) \right) \right] \quad (3)$$

where the two-particle density correlation function is defined by

$$n(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \Psi^2 / \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi^2 \quad (4)$$

and where we have written

$$f(r) = \exp \left[\frac{1}{2} \phi(r) \right] \quad (5)$$

To extract the surface part of (3), we make the approximation

$$n(\mathbf{r}_1, \mathbf{r}_2) = n(r_1)n(r_2)g(r_{12}) \quad (6)$$

where $n(r_1)$ is the single-particle density measured relative to the center of mass, and $g(r_{12})$ is the pair correlation function. Equation (6) really has two approximations in it: The first is that we have broken the translational invariance of the system described by Ψ of Eq. (1), and have by some

means localized the center of mass of the droplet at the origin. The second approximation is that we have assumed that the pair correlation function is a function of r_{12} only, which can only be true inside the liquid. This second approximation has been discussed by LH (Section 3) in the classical context; for our purposes the disadvantage of its numerical inaccuracy is outweighed by the simplicity of the analytic results which it makes possible.

With the approximation (6), then, the expectation value of the energy becomes

$$\langle H \rangle = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 n(r_1)n(r_2)h(r_{12}) \quad (7)$$

where

$$h(r) = g(r) \left\{ u(r) - \frac{\hbar^2}{4m} \left[\phi''(r) + \frac{2}{r} \phi'(r) \right] \right\} \quad (8)$$

In bipolar coordinates (Hill, ¹¹ p. 203), Eq. (7) reads

$$\langle H \rangle = (2\pi)^2 \int_0^\infty dr_1 r_1 n(r_1) \int_0^\infty dr_2 r_2 n(r_2) \int_{|r_1-r_2|}^{r_1+r_2} dr r h(r) \quad (9)$$

By successive interchange of the order of integration, the energy may be written as

$$\langle H \rangle = 2\pi \int_0^\infty dr r^2 h(r) Q(r) \quad (10)$$

where

$$Q(r) = (2\pi/r) \int_0^\infty dr_1 r_1 n(r_1) \int_{|r-r_1|}^{r+r_1} dr_2 r_2 n(r_2) \quad (11)$$

The function Q is proportional to the volume overlap of two identical spherical density distributions whose centers are separated by distance r . The function $Q(r)$ may be evaluated analytically for simple density variations. The simplest of these is the step function

$$n(r_1) = \begin{cases} n_0, & r_1 < R \\ 0, & r_1 > R \end{cases} \quad (12)$$

For the step-function density, Q becomes n_0^2 times the volume common to two spheres of radius R separated by distance r . This function is well known (Hill, ¹¹ p. 210):

$$Q_0(r) = \begin{cases} \frac{4}{3}\pi R^3 n_0^2 \left[1 - \frac{3}{2} \left(\frac{r}{2R} \right) + \frac{1}{2} \left(\frac{r}{2R} \right)^3 \right], & (r < 2R) \\ 0, & (r > 2R) \end{cases} \quad (13)$$

We have thus shown that the expectation value of the energy of a droplet with a step-function density (radius R) is

$$\begin{aligned}
 E(R) = & \left(\frac{4}{3}\pi R^3\right)2\pi n_0^2 \int_0^{2R} dr r^2 h(r) \quad (\text{volume term}) \\
 & - (4\pi R^2)(\pi/2)n_0^2 \int_0^{2R} dr r^3 h(r) \quad (\text{surface term}) \\
 & + \frac{1}{6}\pi^2 n_0^2 \int_0^{2R} dr r^5 h(r) \quad (\text{constant term}) \quad (14)
 \end{aligned}$$

When $h(r)$ is short-ranged the upper limit may be replaced by infinity in each case, and we regain the usual volume energy

$$E/N = 2\pi n_0 \int_0^\infty dr r^2 h(r) \quad (15)$$

plus a step-function contribution to the energy per unit area of the surface,

$$\varepsilon_0 = -\frac{1}{2}\pi n_0^2 \int_0^\infty dr r^3 h(r) \quad (16)$$

When $h(r)$ varies as r^{-4} due to the zero-point vibration of the phonons, the separation into volume, surface, and constant terms is lost. We shall return to this problem in Section 5.

Having shown how we can extract a surface energy from Ψ for spherical symmetry, we turn to the simpler case of a plane geometry, which is the $R \rightarrow \infty$ limit of the spherical case. For the plane geometry we can use our work on the surface energy of a classical liquid-vapor interface (LH, Section 3), since there is mathematically a one-to-one correspondence between a classical system with probability distribution

$$\exp \left\{ -\frac{1}{T} \sum_{i<j}^N \sum^N u(r_{ij}) \right\}$$

and our quantum system with probability distribution given by

$$\Psi^2 = \exp \left\{ \sum_{i<j}^N \sum^N \phi(r_{ij}) \right\}$$

From (3), with the plane surface approximation

$$n(\mathbf{r}_1, \mathbf{r}_2) = n(z_1)n(z_2)g(r_{12}) \quad (17)$$

we have for the surface energy per unit area [cf. LH,⁷ Eqs. (69), (70)]

$$\epsilon = \pi n_0^2 \int_0^\infty dr rh(r) \left[-\frac{1}{2}r^2 + q_1(r) + q_2(r) \right] \tag{18}$$

with

$$\begin{aligned} q_1(r) &= -2 \int_{-r}^r dz z \delta f(z) - 2r \left[\int_r^\infty dz \delta f(z) - \int_{-\infty}^{-r} dz \delta f(z) \right] \\ q_2(r) &= \int_{-\infty}^\infty dz_1 \delta f(z_1) \int_{z_1-r}^{z_1+r} dz_2 \delta f(z_2) \end{aligned} \tag{19}$$

The function δf is defined by

$$n(z)/n_0 = f(z) = f_0(z) + \delta f(z) \tag{20}$$

where f_0 is a step function (see Fig. 1).

The location of the surface is not arbitrary, since the derivation of (18) and (19) depends on the property

$$\int_{-\infty}^\infty dz \delta f(z) = 0 \tag{21}$$

which defines the (Gibbs) dividing surface. In the above formulas the dividing surface is at $z = 0$.

The first term of (18) has already been derived [Eq. (16)]; the spherical counterparts of the other terms can also be derived and can be shown to be the same as (19) in the limit of large R , as expected.

For an exponential density variation

$$n(z) = \begin{cases} n_0(1 - \frac{1}{2} e^{z/\lambda}), & z < 0 \\ \frac{1}{2} n_0 e^{-z/\lambda}, & z > 0 \end{cases} \tag{22}$$

or

$$\delta f(z) = \frac{1}{2} \operatorname{sgn} z \exp(-|z|/\lambda) \tag{23}$$

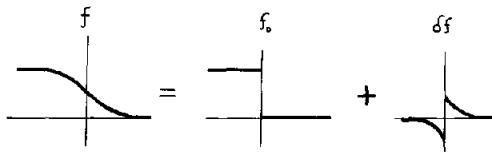


Fig. 1. The functions f and δf defining the density profile.

the surface energy becomes (LH, Section 4)

$$\epsilon = -\frac{1}{2}\pi n_0^2 \int_0^\infty dr rh(r)\{r^2 + \lambda^2[4 - e^{-r/\lambda}(4 + r/\lambda)]\} \quad (24)$$

For a Fermi function density variation,

$$n(z) = n_0/(e^{z/\delta} + 1) \quad (25)$$

or

$$\delta f(z) = (\text{sgn } z)/(e^{|z|/\delta} + 1) \quad (26)$$

it is straightforward to show (compare with Bowley's¹ result)

$$\epsilon = -\frac{\pi}{2}n_0^2 \int_0^\infty dr rh(r)\left\{r^2 + 4\delta^2 \int_0^{r/\delta} dx \frac{x}{e^x - 1}\right\} \quad (27)$$

As the surface thickness (proportional to λ and δ in the two chosen densities) goes to zero, we regain the step-function result, Eq. (16), from both (24) and (27). As the surface thickness becomes large compared to the range of $h(r)$, we have the limiting forms

$$\epsilon \rightarrow \epsilon_\infty = -\frac{3}{2}\pi n_0^2 \lambda \int_0^\infty dr r^2 h(r) \quad (28)$$

and

$$\epsilon \rightarrow \epsilon_\infty = -2\pi n_0^2 \delta \int_0^\infty dr r^2 h(r) \quad (29)$$

The fact that in the limit of large surface thickness the surface energy becomes proportional to the thickness of the liquid-vacuum interface can be shown more generally by a Taylor expansion method (LH, Section 5). One finds that, neglecting second-order and higher derivatives of the density, the surface energy is given by

$$\epsilon \approx 2\pi n_0^2 \int_0^\infty dr r^2 h(r) \left\{ \int_{-\infty}^\infty dz [\delta f(z)]^2 - 2 \int_0^\infty dz \delta f(z) \right\} \quad (30)$$

When the density variation is characterized by a single length (such as λ or δ) both of the integrals in the curly brackets are proportional to this length; in particular, on inserting (23) or (26) into (30), we regain (28) or (29).

In Fig. 2 we have plotted the integrands of the expressions (16), (24), and (28) for the surface energy. The full expression (24) and the slowly varying density limit (28) are both plotted for $\lambda = d$, where d is the hard-core diameter of the Lennard-Jones potential

$$u(r) = 4v[(d/r)^{12} - (d/r)^6]$$

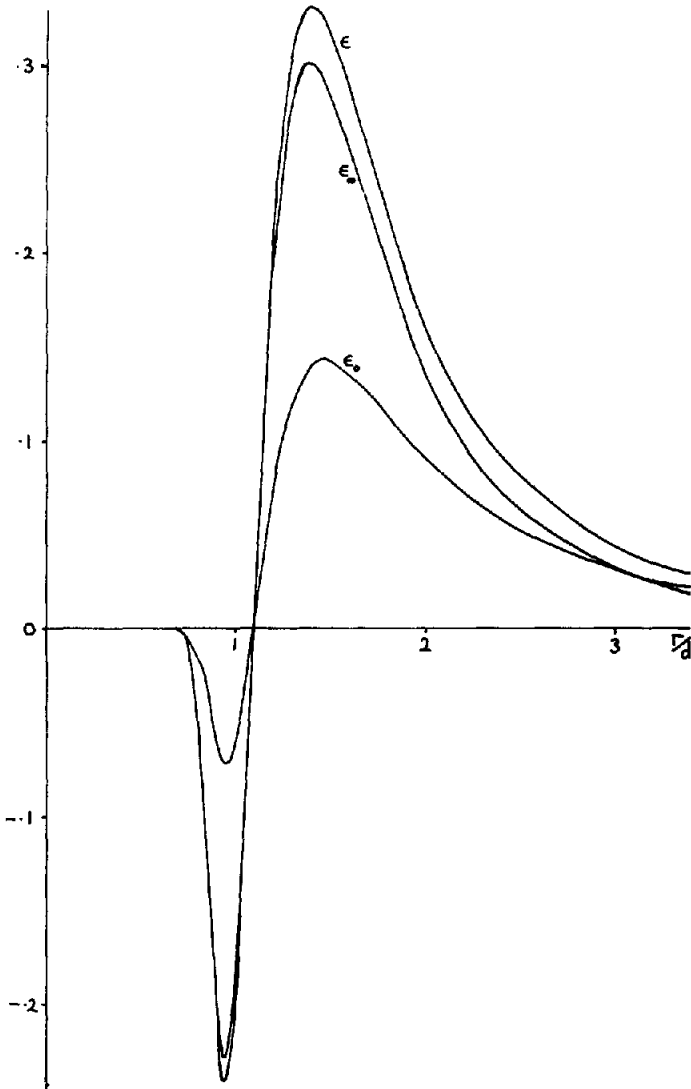


Fig. 2. Integrands of the exponential density expressions for ϵ and ϵ_∞ at $\lambda = d$, together with the integrand for the limiting expression ϵ_0 . We took $d = 2.6 \text{ \AA}$ and $v = 10.3 \text{ K}$. The areas under the curves times $2\pi n_0^2 d^4 v$ ($= 1.431 \text{ K/\AA}^2$ or 1.975 erg/cm^2) give the surface energies.

The function ϕ was taken to be $-2(d/r)^5$ [this is close to the optimum among forms of the type $-a(b/r)^n$ tried by McMillan¹²]. The pair correlation function was approximated by e^ϕ .

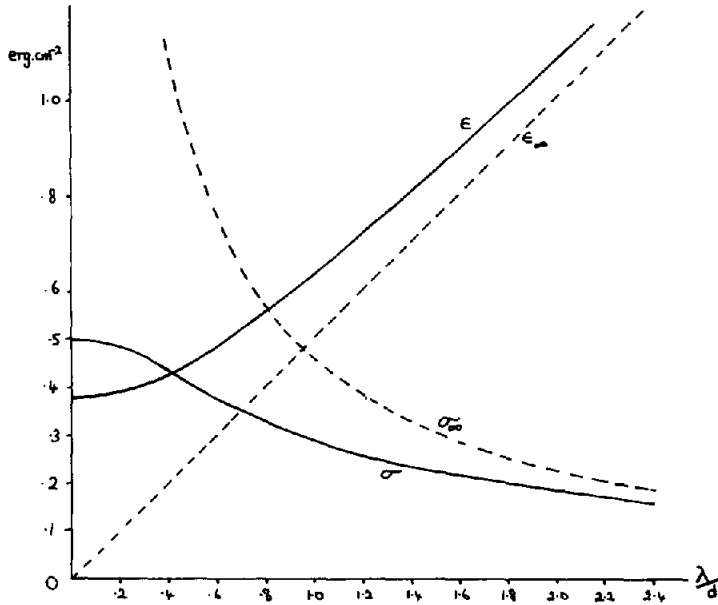


Fig. 3. Surface energy and surface tension for the exponential density profile. ϵ and ϵ_∞ from Eqs. (24) and (28); σ and σ_∞ from Eqs. (44) and (45).

In Fig. 3 the values of the surface energy obtained for the exponential density variation are shown as a function of λ/d . We see that ϵ is greater than ϵ_∞ , and increases monotonically with λ . The fact that ϵ does not show even a local minimum at some physical value of λ/d need not surprise us, since we are not doing a variational calculation. However, we should issue a word of caution that the choice of g has a large effect on the curves in Fig. 3. From Fig. 2 it can be seen that the magnitude of g in the region $r \leq d$ affects the negative part of the integrand, while the first maximum, which is present in a realistic g , affects the positive part. It so happens that the crude approximation

$$g = \exp[-2(d/r)^5]$$

contains canceling errors that lead to a very reasonable result. If a more realistic pair correlation function is used in order to include the effect of a maximum, then equal care must be exercised in the $r \leq d$ region.

3. THE SURFACE THICKNESS

The problem of assigning one length as the thickness of the surface has no unique solution when one is comparing different density profiles. The

length we have found most useful for numerical comparisons is the 10–90 thickness, which is the distance in which the density rises from 10% of its bulk value of 90% of its bulk value. If we call this thickness t , then for the exponential and Fermi function profiles we have

$$t = 2\lambda \log 5 \approx 3.22\lambda$$

and

$$t = 2\delta \log 9 \approx 4.39\delta$$

In terms of this definition we see that the exponential and Fermi profiles give the same thickness when

$$\lambda/\delta = (\log 9/\log 5) \approx 1.365$$

Consider the slowly varying density limiting expressions (28) and (29) for the surface energy. From (14) we note that these can be written as

$$\varepsilon_\infty = -\frac{3}{4}\lambda E/V \quad (31)$$

and

$$\varepsilon_\infty = -\delta E/V \quad (32)$$

where E/V is the bulk energy per unit volume. [Note that these expressions are the same when $\lambda = (4/3)\delta$, which compares well with the 10–90 equivalence condition $\lambda = 1.365\delta$.] We are now in a position to evaluate the surface thickness from our $\varepsilon(\lambda)$ curve and experimental data: Rewrite (31) as

$$\lambda = -\frac{4}{3} \left(\frac{\varepsilon}{E/V} \right) \frac{\varepsilon_\infty}{\varepsilon} \quad (33)$$

For the quantities in the parentheses we can substitute the experimental values $\varepsilon = 0.373 \text{ erg/cm}^2$ (Atkins and Narahara¹³) and $E/N = -0.99 \times 10^{-15} \text{ erg/atom}$, $N/V = n_0 = 2.2 \times 10^{22} \text{ atoms/cm}^3$; this gives $\lambda \approx 2.3(\varepsilon_\infty/\varepsilon) \text{ \AA}$. With $d = 2.6 \text{ \AA}$ we then find

$$\varepsilon_\infty/\varepsilon \approx 1.14 \lambda/d \quad (34)$$

In Fig. 4 we plot this line, together with the ratio $\varepsilon_\infty/\varepsilon$ obtained from results of Fig. 3. The line (34) and the curve $\varepsilon_\infty/\varepsilon$ intercept at $\lambda/d \approx 0.46$, which gives a 10–90 thickness

$$t = 3.9 \text{ \AA}$$

This estimate has the advantage that nature evaluates two very difficult integrals for us (ε and E/N), and all we have had to find is the ratio $\varepsilon_\infty/\varepsilon$, which we expect to be insensitive to the errors in our choice of the pair

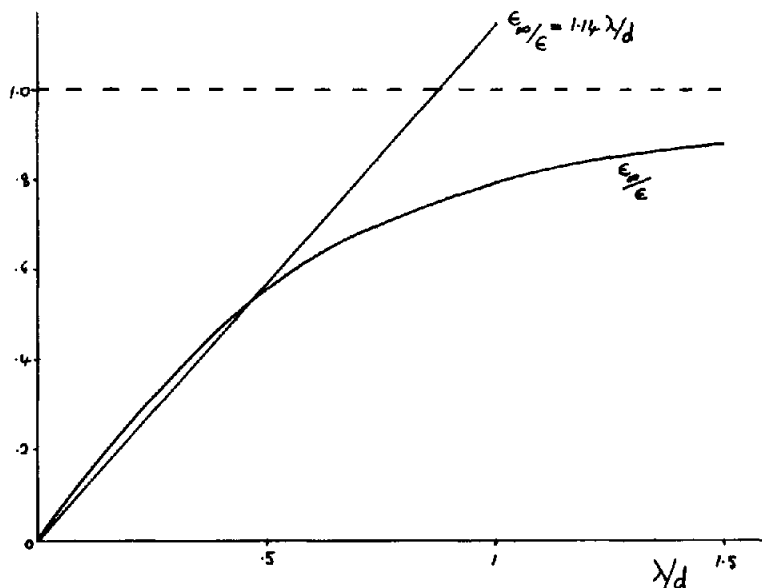


Fig. 4. Determination of the surface thickness from Eq. (34) and the results of Fig. 3.

correlation function g and the pair function f . The agreement with recent estimates, based on a comparatively enormous amount of numerical work, is good: Chang and Cohen³ obtained $\lambda \approx 1.4 \text{ \AA}$ and $\delta \approx 1.0 \text{ \AA}$, giving $t \approx 4.6$ and 4.4 \AA , respectively, while Liu *et al.*⁴ calculate $t \approx 5 \text{ \AA}$.

We conclude this section by pointing out the physical meaning of the slowly varying density limits, Eqs. (31) and (32). Consider Eq. (31) first and let A be the area of the surface. Then, according to (31), the surface energy is

$$\Delta E = A\varepsilon \approx -\frac{3}{4}\lambda A(E/V)$$

The 10–90 thickness of the surface is 3.22λ , so that the volume ΔV of the interface is approximately $3.22\lambda A$. The number of atoms in the interface is $\Delta N \approx \frac{1}{2}n_0 \Delta V$, so that

$$\Delta E \approx -\frac{3}{4}(2/3.22)(\Delta N)E/N \approx -\frac{1}{2}(\Delta N)E/N$$

The same approximate relation follows from the Fermi-function limiting form (32). The physical meaning of (31) and (32) is thus clear: The positive surface energy corresponds to the loss of approximately one-half the binding energy per atom for every atom in the surface layer.

4. SURFACE TENSION OF $\Pi f(r_{ij})$

Toda⁸ and Brout and Nauenberg⁹ have derived general expressions for the surface tension of a quantum liquid. Their result is the sum of a potential energy contribution σ_p and a kinetic energy contribution σ_k :

$$\sigma = \sigma_p + \sigma_k \quad (35)$$

where, at $T = 0$,

$$\sigma_p = \frac{1}{4L_x L_y} \int d\mathbf{r}_1 \int d\mathbf{r}_2 n(\mathbf{r}_1, \mathbf{r}_2) \frac{r_{12}^2 - 3z_{12}^2}{r_{12}} \frac{du(r_{12})}{dr_{12}} \quad (36)$$

and

$$\sigma_k = \frac{1}{L_x L_y} \left(-\frac{N\hbar^2}{m} \right) \left\langle \frac{\partial^2}{\partial z_1^2} - \frac{\partial^2}{\partial x_1^2} \right\rangle \quad (37)$$

The above formulas have been written for a plane interface in the x - y plane, of area $L_x L_y$. The potential energy contribution is the classical expression evaluated in LH, and the kinetic energy term may be put into the same form as the potential energy term when the wave function is a product of pair functions. We have, with

$$\Psi = e^{\Phi/2}, \quad \Phi = \sum_{i < j} \phi(r_{ij})$$

the result

$$\begin{aligned} \left\langle \frac{\partial^2}{\partial z_1^2} \right\rangle &= \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi \frac{\partial^2}{\partial z_1^2} \Psi \\ &= \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi \left[\frac{1}{4} \left(\frac{\partial \Phi}{\partial z_1} \right)^2 + \frac{1}{2} \frac{\partial^2 \Phi}{\partial z_1^2} \right] \end{aligned}$$

Integrating the rhs of the first equality by parts, we also have

$$\left\langle \frac{\partial^2}{\partial z_1^2} \right\rangle = - \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \left(\frac{\partial \Psi}{\partial z_1} \right)^2 = -\frac{1}{4} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi^2 \left(\frac{\partial \Phi}{\partial z_1} \right)^2$$

Therefore

$$\begin{aligned} \left\langle \frac{\partial^2}{\partial z_1^2} \right\rangle &= \frac{1}{4} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi^2 \frac{\partial^2 \Phi}{\partial z_1^2} \\ &= \frac{N-1}{4} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \frac{1}{r_{12}} \left\{ \frac{d\phi(r_{12})}{dr_{12}} + z_{12}^2 \frac{d}{dr_{12}} \left[\frac{1}{r_{12}} \frac{d\phi(r_{12})}{dr_{12}} \right] \right\} \Psi^2 \quad (38) \end{aligned}$$

Thus

$$\begin{aligned} \sigma_k &= \frac{1}{4L_x L_y} \left(-\frac{\hbar^2}{m} \right) N(N-1) \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \frac{z_{12}^2 - x_{12}^2}{r_{12}} \frac{d}{dr_{12}} \left[\frac{1}{r_{12}} \frac{d\phi(r_{12})}{dr_{12}} \right] \Psi^2 \\ &= \frac{1}{4L_x L_y} \left(-\frac{\hbar^2}{2m} \right) \int d\mathbf{r}_1 \int d\mathbf{r}_2 n(\mathbf{r}_1, \mathbf{r}_2) \frac{3z_{12}^2 - r_{12}^2}{r_{12}} \frac{d}{dr_{12}} \left[\frac{1}{r_{12}} \frac{d\phi(r_{12})}{dr_{12}} \right] \end{aligned} \quad (39)$$

For a plane surface we can write

$$n(\mathbf{r}_1, \mathbf{r}_2) = n(z_1)n(z_2)g(r_{12}, z_1, z_2) \quad (40)$$

and then the surface tension reduces to (cf. LH, Section 2)

$$\begin{aligned} \sigma &= \frac{\pi}{2} \int_{-\infty}^{\infty} dz_1 n(z_1) \int_{-\infty}^{\infty} dz_2 n(z_2) \int_{|z_{12}|}^{\infty} dr g(r, z_1, z_2) \\ &\quad \times [r^2 - 3z_{12}^2] \left[u' + \frac{\hbar^2}{2m} \left(\frac{\phi'}{r} \right)' \right] \end{aligned} \quad (41)$$

If $g(r, z_1, z_2)$ is approximated by $g(r)$, we get [cf. Eq. (50) of LH]

$$\sigma = \frac{\pi}{2} n_0^2 \int_0^{\infty} dr g(r) \left[u' + \frac{\hbar^2}{2m} \left(\frac{\phi'}{r} \right)' \right] \left[\frac{1}{4} r^4 + p_1(r) + p_2(r) \right] \quad (42)$$

where

$$\begin{aligned} p_1(r) &= -2 \int_{-r}^r dz \delta f(z) z (r^2 - z^2) \\ p_2(r) &= \int_{-\infty}^{\infty} dz_1 \delta f(z_1) \int_{z_1-r}^{z_1+r} dz_2 \delta f(z_2) (r^2 - 3z_{12}^2) \end{aligned} \quad (43)$$

For the exponential density profile (23) we have from LH, Eq. (77)

$$\begin{aligned} \sigma &= \frac{\pi}{2} n_0^2 \int_0^{\infty} dr g(r) \left[u' + \frac{\hbar^2}{2m} \left(\frac{\phi'}{r} \right)' \right] \\ &\quad \times \left\{ \frac{r^4}{4} + \lambda^4 \left[18 - \frac{2r^2}{\lambda^2} - e^{-r/\lambda} \left(18 + 18 \frac{r}{\lambda} + \frac{7r^2}{\lambda^2} + \frac{r^3}{\lambda^3} \right) \right] \right\} \end{aligned} \quad (44)$$

which has the large- λ limit [cf. LH, Eq. (80)]

$$\sigma \rightarrow \sigma_{\infty} = \frac{\pi}{30} n_0^2 \frac{1}{\lambda} \int_0^{\infty} dr g(r) \left[u' + \frac{\hbar^2}{2m} \left(\frac{\phi'}{r} \right)' \right] r^5 \quad (45)$$

For the Fermi-function density profile (26) we use the methods of LH

(Section 4) to evaluate p_1 and p_2 . We find

$$\begin{aligned} \sigma = & \frac{\pi}{2} n_0^2 \int_0^\infty dr g(r) \left[u' + \frac{\hbar^2}{2m} \left(\frac{\phi'}{r} \right)' \right] \\ & \times \left\{ \frac{r^4}{4} + 2\delta^4 \int_0^{r/\delta} dx \frac{x}{e^x - 1} \left(3x^2 - \frac{r^2}{\delta^2} \right) \right\} \end{aligned} \quad (46)$$

The large- δ limit is

$$\sigma \rightarrow \sigma_\infty = \frac{\pi}{45} n_0^2 \frac{1}{\delta} \int_0^\infty dr g(r) \left[u' + \frac{\hbar^2}{2m} \left(\frac{\phi'}{r} \right)' \right] r^5 \quad (47)$$

Note that the exponential and Fermi profiles give the same σ_∞ if $\lambda = \frac{3}{2}\delta$, whereas the surface energies were equal in this limit when $\lambda = \frac{4}{3}\delta$.

The limiting results obtained above are special cases of the general formula for slowly varying density [cf. LH, Eq. (83)]

$$\sigma = \frac{2\pi}{15} \int_0^\infty dr g(r) \left[u' + \frac{\hbar^2}{2m} \left(\frac{\phi'}{r} \right)' \right] r^5 \int_{-\infty}^\infty dz \left(\frac{dn}{dz} \right)^2 \quad (48)$$

which is obtained by a Taylor expansion of the density, neglecting fourth-order and higher derivatives of the density. As in the case of surface energy, the odd derivative terms in the expansion give zero contribution, so that correction terms are two orders higher in the gradient. In Fig. 5 we have plotted, in the manner of Fig. 2, the integrand of the step-function limit for the surface tension

$$\sigma_0 = \frac{\pi}{8} n_0^2 \int_0^\infty dr g(r) \left[u' + \frac{\hbar^2}{2m} \left(\frac{\phi'}{r} \right)' \right] r^4 \quad (49)$$

along with integrands of the exponential density expression (44) and its large- λ limit (45), at $\lambda = d$.

The values of surface tension as a function of λ/d , obtained with the zeroth-approximation pair correlation function $g = e^\phi$, are shown in Fig. 3. The curves for ε and σ intersect at $\lambda = 0.41d$ and since $\varepsilon = \sigma$ at absolute zero, provided the location of the surface is defined by (21) (see Section 3 of LH), we have another estimate of the surface thickness: $t = 3.22\lambda \approx 3.4 \text{ \AA}$. This value is likely to be less accurate than our previous estimate of Section 3, since it is based on a first principles calculation with a crude g and no direct experimental input. Nevertheless, the intercept energy 0.43

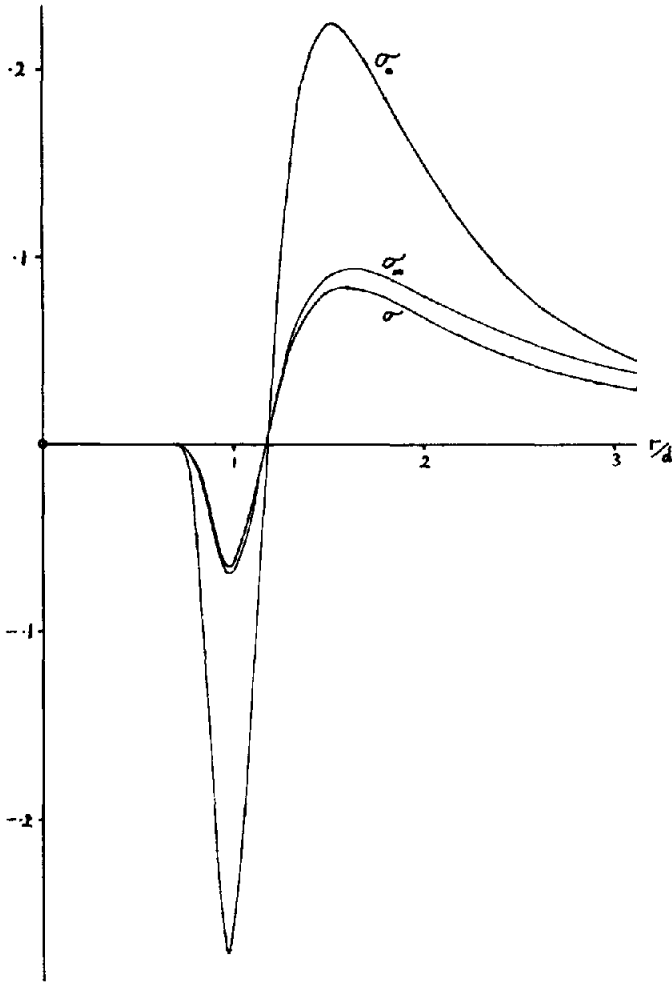


Fig. 5. The surface tension integrands, plotted in the same way as the energy integrands of Fig. 2. The areas under the curves times $2\pi n_0^2 d^4 v$ give the surface tensions.

erg/cm^2 is remarkably close to the experimental value of 0.37 erg/cm^2 , implying that the severe approximations that we made to obtain the curves of Fig. 3 contain canceling errors (see discussion at the end of Section 2).

Sections 2-4 support our initial assertion that $\prod_{i<j} f(r_{ij})$ describes a droplet, but we should remember that these results are based on the assumption that $\phi(r)$ decays rapidly at large r .

5. PROBLEMS WITH $\prod f(r_{ij})$ WHEN ZERO-POINT MOTION OF PHONONS IS INCLUDED

In the previous sections we found that the wave function

$$\prod_{i < j} e^{\phi(r_{ij})/2} \quad (50)$$

gave good results for the surface energy and thickness of liquid helium provided $\phi(r)$ tends to zero rapidly as $r \rightarrow \infty$. In particular, the McMillan form

$$\phi(r) = -2(d/r)^5 \quad (51)$$

led to reasonable results.

However, Reatto and Chester⁶ have shown that the existence of phonon excitations in liquid helium implies that a factor of the ground-state wave function is of the form (50), with

$$\phi(r) \rightarrow \phi_p = -(b^2/r^2) \quad (52)$$

where

$$b = \frac{1}{\pi} \left(\frac{mc}{n_0 \hbar} \right)^{1/2} \approx 2.6 \text{ \AA} \quad (53)$$

The term ϕ_p leads to a logarithmic divergence (to minus infinity) of both our surface energy and surface tension expressions, (18) and (42). This divergence has appeared in previous formulations for the surface energy of liquid helium, and varying attempts have been made at understanding it (see Bowley¹ and Chang and Cohen,³ both of which are discussed below). Note also that the divergence invalidates the derivations of the large-surface-width expressions ϵ_∞ and σ_∞ . To see clearly the consequences of the phonon factor, let us return to the droplet of Section 2 and consider contributions to the total energy coming from particle separations greater than $2a$, where a is (say) 5 \AA ; then we can take $\phi = \phi_p$, $g = 1$, and $u = 0$ to obtain the asymptotic value

$$h(r) \rightarrow \frac{\hbar^2 b^2}{2m} \frac{1}{r^4} \quad (54)$$

which can be regarded as an effective repulsive $1/r^4$ interaction. Inserting (54) into (14), we find that the direct contribution of the infinite-range

correlations arising out of the zero-point motion of the phonon modes is

$$\begin{aligned}\Delta E &= \frac{4}{3}(\hbar cn_0)R^3 \int_{2a}^{2R} dr r^{-2} \left[1 - \frac{3}{2} \left(\frac{r}{2R} \right) + \frac{1}{2} \left(\frac{r}{2R} \right)^3 \right] \\ &= \frac{2}{3}(\hbar cn_0)R^2 \left[\frac{R}{a} - \frac{3}{2} \log \left(\frac{R}{a} \right) - \frac{3}{4} - \frac{1}{4} \frac{a^2}{R^2} \right]\end{aligned}\quad (55)$$

For a flat surface of area L^2 , (54) similarly leads to a positive volume term and a $-L^2 \log(L/a)$ term. So at $T=0$ the long-range part of the phonon correlations raises the bulk energy (i.e., from a variational point of view they should be left out to lower the total energy), and produces a negative $R^2 \log(R/a)$ term, as well as a negative R^2 term. The bulk energy is raised by $\hbar c/2\pi a$ (≈ 0.58 K when $a = 5 \text{ \AA}$) per atom, which is small in comparison with the experimental bulk energy, -7.16 K per atom. On the other hand, the "surface" energy is lowered by $(\hbar cn_0/4\pi)[\log(R/a) + \frac{1}{2}]$, which is approximately 0.63 erg/cm^2 when $R = 0.5 \text{ mm}$ and $a = 5 \text{ \AA}$. Thus for R large enough we have that at $T=0$ the "surface" energy would be negative, which seems impossible to accept.

It is known that at finite temperatures the long-range correlations due to the zero-point motion are exponentially damped, so one might hope that the above problems in the ground state would disappear at finite temperature. However we find that this is not so. Reatto and Chester⁶ have shown that the diagonal part of the density matrix has the form of a product wave function, with the long-range part due to phonon zero-point motion. The probability density is thus of the same form as before, with

$$\phi_p(r, T) \rightarrow -\frac{b^2}{r^2} \frac{\pi Tr/\hbar c}{\sinh(\pi Tr/\hbar c)} \quad (56)$$

and so the kinetic energy term

$$-(\hbar^2/4m)\nabla^2\phi_p$$

in the total energy again has the form of a repulsive interaction. The screening length $\hbar c/\pi T$ is approximately 5.8 \AA at 1 K. Inserting (56) into (14) and considering contributions from particle separations greater than $2a$, we find that the finite-temperature phonon zero-point motion contribution to the bulk energy is (when $2\pi TR/\hbar c \gg 1$)

$$\Delta E_v = \frac{2}{3}(\hbar cn_0) \frac{R^3}{a} F\left(\frac{2\pi Ta}{\hbar c}\right) \quad (57)$$

where

$$F(x) = \frac{1}{2} \frac{x}{\sinh x} \left(1 + \frac{x \cosh x}{\sinh x} \right) \quad (58)$$

The low-temperature expansion gives a negative contribution to the specific heat proportional to T^3 , since

$$F(x) = 1 - (7/360)x^4 + O(x^6) \quad (59)$$

In fact, the slope of F is always negative, so the screened zero-point motion contributes a negative specific heat, with a maximum magnitude at $T \approx 0.45\hbar c/a$. This result is in accord with our statement above that the correlations due to the zero-point motion of the phonon modes are equivalent to an effective repulsive r^{-4} interaction which is screened thermally, because the higher the temperature, the better the screening, and so the energy due to the zero-point motion of the phonons decreases with T . For a of order of the atomic diameter or greater, this negative T^3 specific heat is an order of magnitude larger than the normal T^3 term due to thermal excitation of phonons, so the total bulk specific heat is negative up to $T \approx \hbar c/a \approx 1$ K. This indicates an instability in the system, since if the energy decreases with temperature in any region, a spontaneous positive temperature fluctuation will decrease the total energy and thus release heat, further increasing the temperature, which will in turn decrease the energy, and so on. Similarly, a negative temperature fluctuation will induce a continual decrease in temperature.

The surface energy contribution of the zero-point motion of the phonon modes is readily obtained from (56) and (14). We find

$$\Delta\varepsilon = -\frac{\hbar cn_0}{8\pi} \left[\frac{x}{\sinh x} + 2F(x) - 2 \log \tanh \frac{x}{2} \right] \quad (60)$$

where $x = 2\pi Ta/\hbar c$. The derivation of this expression is valid only when the total surface energy is greater than zero, since a spherical shape is assumed in (14). The low-temperature ($2\pi T \ll \hbar c/a$) expansion is

$$\Delta\varepsilon = -\frac{\hbar cn_0}{4\pi} \left[\log \left(\frac{\hbar c}{\pi Ta} \right) + \frac{3}{2} + O\left(\frac{\pi Ta}{\hbar c} \right)^2 \right] \quad (61)$$

The above expressions are again limited to the region $2\pi TR/\hbar c \gg 1$. From (61) we see that the surface contribution to the specific heat is positive, varies as T^{-1} , and will become larger than the previously noted negative T^3 bulk contribution when $T \leq (\hbar c/3a)(a/R)^{1/4}$. This temperature is of the order of 10^{-2} K for a droplet of millimeter size.

The consequences of the long-range correlations arising out of the zero-point motion of the phonons thus appear to be (i) a negative bulk specific heat; (ii) a term in the energy varying as $-R^2 \log(R/a)$ at $T = 0$; and (iii) a logarithmic temperature dependence of the surface energy at low

temperatures, with measurable temperature variation at about 10^{-1} K and zero ε at about 10^{-3} K.

Bowley,¹ who first met one of the difficulties associated with the long-range phonon correlations (he found a divergence to minus infinity in the surface energy at $T=0$ when these correlations were included), has postulated that the inclusion of the zero-point motion of the surface modes would remove this problem. The correlations due to surface-mode zero-point motion have yet to be evaluated explicitly, though Chang and Cohen¹⁴ have written down an expression for their contribution to the ground-state wave function. We feel that it is unlikely that the surface-wave zero-point motion can remove a problem that arises from the existence of bulk modes, since we expect the correlations due to the surface modes to be of a different kind, and additional to the phonon modes, rather than canceling them in a substantial part of the interior.

Another approach to these difficulties is that of Chang and Cohen,³ who use the wave-function

$$\Psi = \prod_{i < j} \exp \left[\frac{1}{2} \phi(r_{ij}) \right] \prod_k \exp \left[\frac{1}{2} t(\mathbf{r}_k) \right] \quad (62)$$

where the function $t(\mathbf{r})$ is optimized variationally, as in Bowley's work. However, instead of parametrizing t , as Bowley did, they eliminate t in favor of the density n , and parametrize n . [We note in passing that Bowley's assumption that $n = n_0 e^t$ leads to the same expression for ε as our work based on $\prod e^{\phi/2}$, plus a small term $-(\hbar^2/8m) \int d\mathbf{r} n(r) \nabla^2 t(r)$. We will generalize Chang and Cohen's result for the energy and give a similar treatment for the surface tension. The expectation value of the Hamiltonian (2) taken with the trial function (62) is readily shown to be [cf. (3)]

$$\begin{aligned} \langle H \rangle = & \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1, \mathbf{r}_2) \{ u(r_{12}) - (\hbar^2/4m) \nabla_1^2 \phi(r_{12}) \} \\ & - (\hbar^2/8m) \int d\mathbf{r}_1 n(\mathbf{r}_1) \nabla_1^2 t(\mathbf{r}_1) \end{aligned} \quad (63)$$

The Yvon equation

$$\nabla_1 n(\mathbf{r}_1) = n(\mathbf{r}_1) \nabla_1 t(\mathbf{r}_1) + \int d\mathbf{r}_2 n(\mathbf{r}_1, \mathbf{r}_2) \nabla_1 \phi(r_{12}) \quad (64)$$

obtained by differentiating the defining relation for the density

$$n(\mathbf{r}_1) = N \int d\mathbf{r}_2 \cdots d\mathbf{r}_N \Psi^2 / \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi^2 \quad (65)$$

can now be used to rewrite the last term in (63) in terms of the density n

and the pair function ϕ . Then, defining

$$n(\mathbf{r}_1, \mathbf{r}_2) = n(\mathbf{r}_1)n(\mathbf{r}_2)g(\mathbf{r}_1, \mathbf{r}_2) \quad (66)$$

and

$$g(\mathbf{r}_1, \mathbf{r}_2) = \exp[\phi(r_{12}) + \gamma(\mathbf{r}_1, \mathbf{r}_2)] \quad (67)$$

the expectation value of the total energy becomes

$$\begin{aligned} \langle H \rangle = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1, \mathbf{r}_2) & \left(u(r_{12}) + \frac{\hbar^2}{4m} \{ [\nabla_1 \phi(r_{12})]^2 \right. \\ & \left. + \nabla_1 \phi(r_{12}) \nabla_1 \gamma(\mathbf{r}_1, \mathbf{r}_2) \right) + \frac{\hbar^2}{8m} \int d\mathbf{r}_1 n(\mathbf{r}_1) [\nabla_1 \log n(\mathbf{r}_1)]^2 \end{aligned} \quad (68)$$

In a uniform fluid, the HNC and PY equations for the pair correlation function may be used to evaluate γ (see, for example, Feenberg,¹⁵ p. 695)

$$\gamma(\mathbf{r}_1, \mathbf{r}_2) = \begin{cases} P(r_{12}) & \text{(HNC)} \\ \log[1 + P(r_{12})] & \text{(PY)} \end{cases} \quad (69)$$

where

$$\begin{aligned} P(r) &= \frac{1}{(2\pi)^3 n_0} \int d\mathbf{k} [\exp(-i\mathbf{k} \cdot \mathbf{r})] \frac{[S(k) - 1]^2}{S(k)} \\ &= \frac{1}{2\pi^2 n_0 r} \int_0^\infty dk k (\sin kr) \frac{[S(k) - 1]^2}{S(k)} \end{aligned} \quad (70)$$

and

$$S(k) = 1 + n_0 \int d\mathbf{r} [\exp(i\mathbf{k} \cdot \mathbf{r})] [g(r) - 1] \quad (71)$$

is the structure factor. The large- r variation of $P(r)$ (and hence of γ) is determined by the small- k variation of $S(k)$. If we accept the correctness of the usual form, $S(k) \rightarrow \hbar k / 2mc$,^{15,16} then integrating the right-hand side of (70) by parts and substituting for $S(k)$ gives for the asymptotic form of $P(r)$

$$P(r) \rightarrow \frac{mc}{\pi^2 \hbar n_0} \frac{1}{r^2} - \frac{1}{2\pi^2 n_0} \frac{\hbar}{mc} \frac{1}{r^4} + \dots \quad (72)$$

Thus we have that

$$\gamma(r) \rightarrow P(r) = (b^2/r^2) + O(r^{-4}) = -\phi_p(r) + O(r^{-4}) \quad (73)$$

i.e., using the HNC or PY equations, the contributions of the zero-point phonon correlations cancel in the first term of (68), at least deep inside the liquid. [We should, however, note that the equivalent classical fluid ($u =$

$-T\phi$) corresponding to the product wave function (1) when $\phi \rightarrow -b^2/r^2$ has energy per particle and pressure both proportional to the size of the system, and thus the validity of the HNC and PY equations needs to be reexamined for this very singular case.] In fact, provided γ goes to zero no slower than r^{-1} , (68) will not diverge.

A similar result follows for the surface tension. We find, for the wave function (62), that the surface tension is given by (42), the expression derived for the wave function (1), plus the term

$$\Delta\sigma = \frac{1}{L_x L_y} \left(-\frac{\hbar^2}{4m} \right) \int d\mathbf{r}_1 t''(z_1) n(z_1) \tag{74}$$

(in this case we find it simpler to work with a plane surface). When we again eliminate t by using the Yvon equation, we find

$$\begin{aligned} \Delta\sigma = & \frac{\hbar^2}{4m} \int dz n(z) \left[\frac{d}{dz} \log n(z) \right]^2 \\ & + \frac{\hbar^2}{4m L_x L_y} \times \text{surface part of} \int d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1, \mathbf{r}_2) \\ & \times \{ \nabla_1^2 \phi(r_{12}) + [\phi'(r_{12})]^2 + \nabla_1 \phi(r_{12}) \cdot \nabla_1 \gamma(\mathbf{r}_1, \mathbf{r}_2) \} \end{aligned} \tag{75}$$

The singular part of the second term in (75) has the form [cf. (3) and (18)]

$$-\frac{\pi n_0^2 \hbar^2}{4 m} \int_0^\infty dr r^3 g(r) \left(\phi_p'' + \frac{2}{r} \phi_p' \right) \tag{76}$$

while the singular part of (42) is

$$\frac{\pi n_0^2 \hbar^2}{16 m} \int_0^\infty dr r^4 g(r) \left(\frac{\phi_p'}{r} \right)' \tag{77}$$

and when ϕ_p varies as r^{-2} , these cancel.

Thus it appears that by using the wave function (62) instead of (1), the divergence in the surface tension and the surface energy has either been removed, or has been shifted to the density gradient term

$$\int d\mathbf{r} n(\mathbf{r}) [\nabla \log n(\mathbf{r})]^2 \tag{78}$$

Chang and Cohen¹⁴ argue that when a physically reasonable density is chosen, this term will not be divergent. However, it is not clear whether the long-range correlation ϕ_p in the ground state gives such a physically reasonable density.

To sum up, we have shown that good results for the energy, tension, and thickness of the surface of liquid ${}^4\text{He}$ are obtained with the wave function $\prod f(r_{ij})$, provided r^{-2} correlations due to phonon zero-point motion are left out. When the phonon correlations are included serious problems arise that may only be overcome by using the method of Chang and Cohen and the wave function $\prod f(r_{ij}) \prod s(r_i)$. The question of whether it is the wave function $\prod f(r_{ij})$ or the phonon correlation factor that is at fault remains unanswered, however, since the exact density profiles that follow from the suggested wave functions are not yet known.

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