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Surface excitations and surface tension of superfluid He^4[†]

D. O. Edwards, J. R. Eckardt[*], and F. M. Gasparini[‡]
Department of Physics, The Ohio State University, Columbus, Ohio 43210

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The Atkins theory of the temperature dependence of the surface tension α in superfluid He^4 has been improved by including the effects of compressibility, phonon dispersion, and Gibb's "surface adsorption" or "surface mass" in the calculation of the spectrum of the surface excitations or "ripplons." The theoretical ripplon spectrum is found to have a minimum close to the roton minimum in the empirical phonon spectrum. The results of the theory, which should be accurate up to a temperature of ~1.3 K, are presented in terms of the ripplon and phonon contributions to the surface entropy $(-d\alpha/dT)$. The ripplon spectrum and the surface entropy are found to depend on two phenomenological parameters: a length δ which is the surface mass per unit area divided by the density, and an area a which is the derivative of δ with respect to the curvature of the surface. In principle, both δ and a can be obtained from static measurements on curved surfaces. The theory is compared to new measurements of the surface entropy near 1 K and, assuming that δ is small, a is found to be about 1.5 Å^2.

I. INTRODUCTION

The purpose of this paper is to extend the simple "classical" theory of the surface excitations in superfluid helium, the so-called "ripplons," to higher wave numbers, where the effects of compressibility, phonon dispersion, and the curvature dependence of the surface tension become important. We also examine the ripplon (and phonon) contributions to the temperature-dependent part of the surface tension, $\Delta\alpha \equiv \alpha(T) - \alpha(0)$. At the end of the paper we compare the theory with some new measurements of the surface entropy $-d\alpha/dT$.

A ripplon contribution to the surface tension of liquids was first proposed by Frenkel,[1] following the work of Mandelstam[2] on light scattering. The idea was applied to liquid helium by Atkins[3] who treated the superfluid phase as a classical incompressible nonviscous liquid. In this case the relation between angular frequency ω and wave vector k is

$$\omega^2 = (\alpha_0/\rho_0)k^3\,, \tag{1}$$

where $\alpha_0 \equiv \alpha(0)$ is the surface tension at 0 K and ρ_0 the density at zero pressure. The ripplons produce a temperature-dependent contribution to the surface free energy (surface tension) which is given by

$$\Delta\alpha_R = k_B T \int \ln(1 - e^{-\beta\hbar\omega})\, d^2k/(2\pi)^2\,, \tag{2}$$

where $\beta \equiv 1/k_B T$. In an incompressible liquid there is no phonon contribution to the surface tension so that using Eq. (1) in Eq. (2) gives Atkins's result,

$$\Delta\alpha = \Delta\alpha_R = -0.1340(\rho_0/\alpha_0\hbar^2)^{2/3}(k_B T)^{7/3}\,. \tag{3}$$

With $\alpha_0 = 0.378$ erg cm^{-2},[4] this gives $\Delta\alpha = (-6.50 \times 10^{-3} T^{7/3})$ erg cm^{-2}.

In comparing theory and experiment, it is sometimes advantageous to consider the surface entropy (per unit area) $S^s = -d\alpha/dT$. According to Atkins's result $S^s = 0.01516 T^{4/3}$ erg cm^{-2} deg^{-1}. The general expression for the ripplon entropy per unit area is

$$S_R^s/k_B = \int [\beta\hbar\omega/(e^{\beta\hbar\omega} - 1) - \ln(1 - e^{-\beta\hbar\omega})]\, d^2k/(2\pi)^2\,. \tag{4}$$

Measurements of the surface tension[5-7] show a temperature dependence which is larger than that predicted by the Atkins formula. The assumptions in the Atkins theory were examined by Brouwer and Pathria,[8] but without reaching any definite conclusion about the disagreement with the observed temperature dependence of α.

Recently Reut and Fisher[9] have shown that better agreement with experiment is obtained if one introduces an additional rotonlike branch to the spectrum. Their analysis, which again neglects the compressibility of the liquid, suggests a minimum in this branch at about $\hbar\omega/k_B \sim 2$ K. The relation between these hypothetical "surface rotons" and the ripplon spectrum [Eq. (1)] is left open in their paper.

We shall see that the modifications of the Atkins theory presented here lead naturally to a minimum in the ripplon spectrum but at a much higher value of ω—in fact, close to the roton minimum in the bulk spectrum. We also demonstrate that an effect envisaged by Gibbs[10] in his general thermodynamic treatment of any liquid surface, namely, the existence of surface "adsorption" or surface mass even in a pure liquid, may account for some of the observed deviations from the Atkins theory.

In calculating the spectrum, we treat the liquid at the absolute zero so that all effects due to the vapor and normal fluid can be neglected. Seiden[11] has discussed the effect of the normal fluid on the surface waves quite extensively and has confirmed that, apart from damping, the normal fluid has a relatively small effect on the ripplon spectrum. The effect of finite temperature is further discussed at the end of this paper.

II. RIPPLES IN COMPRESSIBLE CLASSICAL LIQUID

We begin by considering the spectrum of small-amplitude ripples on a *compressible* irrotational nonviscous liquid of equilibrium density ρ_0. The velocity field can be represented by a velocity potential $\vec{v} = \text{grad}\phi$, and the linearized equation of continuity, the Euler equation, and the equation of state give

$$\frac{\partial\rho}{\partial t} + \rho_0 \nabla^2 \phi = 0\ , \tag{5}$$

$$-\rho_0 \frac{\partial\phi}{\partial t} = P = c^2(\rho - \rho_0)\ , \tag{6}$$

where P is the pressure and c is the velocity of sound.

In the usual treatment of the surface boundary condition the Kelvin (or Laplace) equation, $P = \alpha_0(r_1^{-1} + r_2^{-1})$, where r_1 and r_2 are the principal radii of curvature at the surface, combined with Eq. (6) and differentiated with respect to t, gives

$$\rho_0 \frac{\partial^2\phi}{\partial t^2} = -\alpha_0 \frac{\partial}{\partial z}\left(\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2}\right) \quad \text{at } z = 0\ . \tag{7}$$

Substituting $\phi = Ae^{lz}\sin(kx - \omega t)$ and eliminating ρ and P, Eqs. (5)–(7) give

$$\omega^2 = c^2(k^2 - l^2)\ , \tag{8}$$

$$\omega^2 = (\alpha_0/\rho_0)k^2 l\ . \tag{9}$$

The resulting spectrum $\omega(k)$ and the k dependence of the inverse penetration distance l are shown as the dashed curves in Figs. 1 and 2. For small k, $l \simeq k$ and we recover Eq. (1). For large k, that is $k\lambda \gg 1$, $\omega/k \to c$ and $l\lambda \to 1$, where the length $\lambda = \alpha_0/\rho_0 c^2 = 0.464$ Å for liquid helium.

In a more complete treatment of the surface boundary condition we must take into account the mass associated with the surface, which we call Γ (per unit area). This mass, originally introduced by Gibbs,[10] is usually neglected since it is of the order of the mass of a single layer of atoms. For instance, in liquid argon, Kirkwood and Buff[12] have calculated theoretically that the length δ, defined as $\delta = \Gamma/\rho$, is +3.5 Å. A δ equal to +0.7 Å has been used by Jortner, Kestner, Rice, and Cohen[13] in calculating the electron bubble radius in He II. (This value was based on the theory of a classical hard-sphere fluid of Reiss, Frisch, Helfand, and Lebowitz,[14] which cannot be quantitatively correct for liquid helium.) Γ and δ are related to the dependence of the surface tension on the curvature of the surface and they can be determined from the Gibbs adsorption equation[15]

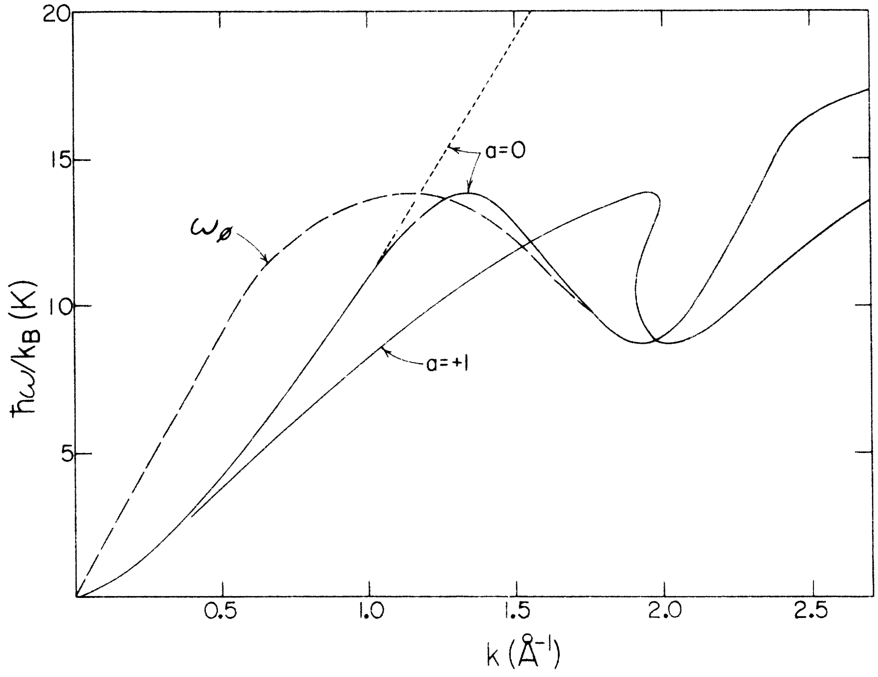

FIG. 1. Ripplon frequency expressed in degrees, $\hbar\omega/k_B$ vs the horizontal wave vector k. The empirical phonon spectrum $\omega_\phi(k)$ is shown for comparison. The other curves are short-dashed, calculated using $\omega = cq$ (constant velocity of sound); solid, calculated using the empirical phonon spectrum $\omega = \omega_\phi(q)$. The values of a are in Å^2; δ was assumed to be zero.

$$d\alpha = -\Gamma d\mu - S^s dT\,, \tag{10}$$

where μ is the chemical potential per unit mass. At $T=0$ this becomes

$$d\alpha = -\Gamma\, d\mu = -(\Gamma/\rho)\, dP = -\delta\, dP\,. \tag{11}$$

For instance, one could obtain δ by measuring the chemical potential or pressure in very small drops of liquid as a function of their mass.[16] As far as we know, there have been no experimental measurements of δ or Γ for any liquid; however, as we shall see, it may be possible to obtain a value for He II from the behavior of the ripplon spectrum.

The surface mass Γ arises in Gibbs's thermodynamic treatment[10,17] because the "surface of tension," whose area determines the surface energy, is not necessarily coincident with the "dividing surface," which is usually defined so that its volume times the bulk density of the liquid gives the correct total mass. The distance between these surfaces is just δ. For instance, in a small spherical drop the radius of the surface of tension would be obtained from the pressure using the Kelvin equation $r = 2\alpha/P$, while the radius calculated from the mass and the bulk density would be the radius of the dividing surface $(r+\delta)$.

In treating the surface boundary condition, taking the surface mass Γ into account, let us assume that the undisturbed surface of tension lies at $z=0$, and, in the presence of a small amplitude wave, at $z = \zeta(x, y, t)$. The linearized equation of continuity at the surface is

$$\rho_0\left(\frac{\partial\phi}{\partial z} - \dot{\zeta}\right) = \dot{\Gamma} + \Gamma\left(\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2}\right), \tag{12}$$

and the linearized equation of motion is

$$P = -\rho_0\frac{\partial\phi}{\partial t} = -\alpha_0\left(\frac{\partial^2\zeta}{\partial x^2} + \frac{\partial^2\zeta}{\partial y^2}\right) + \Gamma\ddot{\zeta}\,. \tag{13}$$

For a wave of the form $\phi = Ae^{lz}\sin(kx - \omega t)$, Eqs. (5) and (6) and (11)–(13) give

$$\omega^2 = c^2(k^2 - l^2)\,, \tag{8}$$

$$\omega^2 = [(\alpha_0/\rho_0)k^2 - \omega^2\delta](l + k^2\delta - a\omega^2\rho_0/\alpha_0)\,, \tag{14}$$

where we have defined the new quantity $a \equiv (\alpha/\rho_0^2) \times \partial\Gamma/\partial\mu = -\alpha(\partial^2\alpha/\partial P^2)$, which has the dimensions of an area. For a spherical drop of liquid a would be $\frac{1}{2}\partial\delta/\partial(1/r)$, where r is the radius of the drop.

Clearly Eq. (14) reduces to (9) when a and δ are both zero. Eliminating l between (8) and (14) and expanding to second order in k^2 we obtain

$$\omega^2 = (\alpha_0/\rho_0)k^3[1 - \tfrac{1}{2}\lambda k + k^2(\tfrac{1}{8}\lambda^2 + \lambda\delta - \delta^2 - a) + \dots]\,. \tag{15}$$

Since $\lambda \equiv \alpha_0/\rho_0 c^2$ is the only length which appears in the first-order correction term in the spectrum, it might be thought that the compressibility of the liquid would be the dominant effect in the corrections to the Atkins formula, Eq. (3). However, the contribution to α from the phonons tends to cancel the change in the ripplon contribution caused by compressibility, so that the final result for $\Delta\alpha$ is still sensitive to a and δ. Moreover, we find that to get accurate results for the surface entropy and $\Delta\alpha$, it is necessary to solve Eqs. (8) and (14) rather than use the approximate equation (15). The phonon contribution to the surface entropy is calculated in Sec. IV below; before pro-

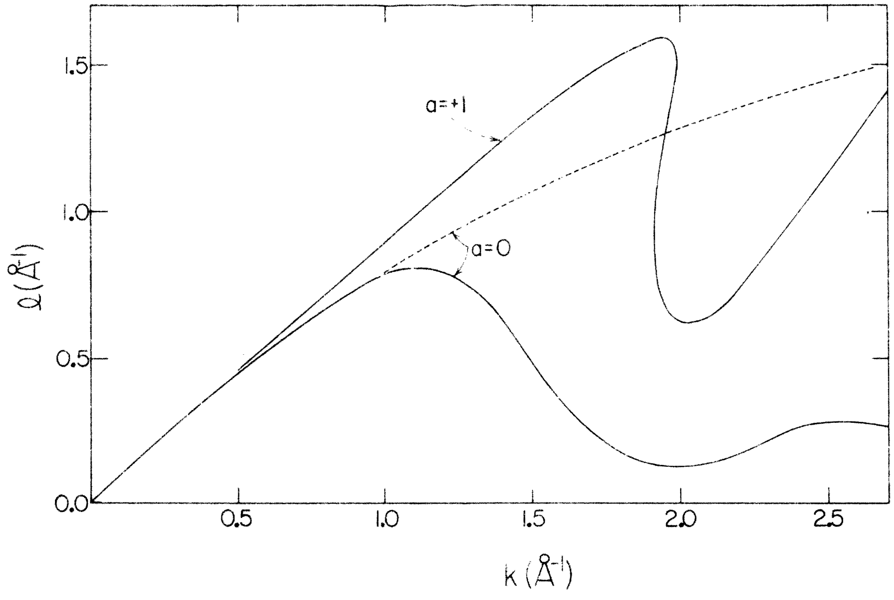

FIG. 2. Values of l, the inverse penetration distance, in Å^{-1} vs the horizontal wave vector k for the ripplon spectra shown in Fig. 1. The dashed line was calculated using a constant velocity of sound, $\omega = cq$; the full lines were calculated using the empirical phonon spectrum, $\omega_\phi(q)$.

ceeding with it we consider a generalization of the theory to take into account phonon dispersion.

III. MODEL WITH PHONON DISPERSION

Clearly, we cannot expect the theory described in Sec. II to resemble liquid helium for $k \gtrsim 0.5$ Å^{-1} since, as is shown by the well-known Landau spectrum[18] in Fig. 1, the phonons are then strongly dispersive and we cannot treat the velocity of sound c as a constant. To solve this problem we could use the semiphenomenological theory of liquid helium proposed by Ginzburg and Pitaevskii,[19] Gross,[20] and others, called the "Hartree liquid" theory. In this model the energy of the liquid is written as a functional of a single-particle "wave function" $\Psi(\vec{r}, t) = (\rho/m)^{1/2} e^{im\phi/\hbar}$, where $\rho(\vec{r}, t)$ and $\phi(\vec{r}, t)$ are the density and velocity potential, respectively, and m is the mass of a He^4 atom. The energy functional is[21]

$$E - E_0 = (\hbar^2/2m^2) \int (\nabla\sqrt{\rho})^2 \, d^3r + \tfrac{1}{2} \int \rho(\nabla\phi)^2 \, d^3r + (1/2m^2) \int\int [\rho(\vec{r}) - \rho_0] V(\vec{r}\,' - \vec{r}) \times [\rho(\vec{r}\,') - \rho_0] \, d^3r' \, d^3r . \tag{16}$$

The density and velocity potential fields at any time t are found by minimizing E subject to the normalization $\int (\rho - \rho_0) \, d^3r = 0$ and the equation of continuity, Eq. (5).

To make the frequency of small-amplitude density waves correspond to the empirical phonon frequencies $\omega_\phi(q)$, the potential $V(r)$ must have a Fourier transform V_q which satisfies the equation[21]

$$\omega_\phi(q) = [(\hbar q^2/2m)^2 + \rho_0 q^2 V_q/m^2]^{1/2} . \tag{17}$$

As is well known, this model gives values of the surface tension α_0 which are quite close to the empirical one. However, such calculations usually involve a rather artificial boundary condition; for instance, in the calculation of Amit and Gross[21] the density is put equal to zero on a plane $z = 0$ representing the surface. With this boundary condition, because of the so-called "quantum-pressure" term (the first term in the energy functional), the density function $\rho(z)$ which minimizes the energy drops smoothly to zero in a distance of the order of $\hbar/mc \sim 0.7$ Å of the boundary. The increase in the energy above the bulk value E_0 gives the surface tension. Since the boundary condition is rather artificial and because the calculations would be quite complicated, we have not attempted to solve the problem of a boundary undergoing ripple motion in the complete Hartree-liquid formalism. Instead, we have deleted the quantum-pressure term entirely, and we represent its effects by the classical Gibbsian surface tension specified by the parameters α_0, δ, and a.

In principle both δ and a can be determined from the Hartree-liquid model or more fundamental theories by solving the equations appropriate to a curved surface. Saam[22] has already made a rough estimate of δ from the Hartree-liquid theory and finds that $|\delta|$ is probably less than 0.1 Å. There have been no calculations of a, but one can estimate its order of magnitude by considering a single isolated He^4 atom as a spherical drop. The radius of the surface of tension r is given by $4\pi r^2 \alpha \simeq L$, where L is the latent heat per atom. The radius of the dividing surface $(r + \delta)$ is given by $\frac{4}{3}\pi\rho(r + \delta)^3 = m$. The result is $r \sim 1.5$ Å, $\delta \sim 0.6$ Å and, if one accepts Saam's estimate that, for a nearly flat surface $(r = \infty)$, $\delta \simeq 0$, then one concludes that $a = \frac{1}{2}\, \partial\delta/\partial(1/r) \sim +0.5$ Å^2.

Returning to our simplification of the Hartree-liquid theory [which we may call the "phonon-dispersive" (PD) model], since we omit the quantum-pressure term for consistency Eq. (17) must be modified to

$$\omega_\phi(q) = (\rho_0 V_q)^{1/2} q/m . \tag{18}$$

The normalization condition, the equation of continuity, and the minimization of the energy functional now lead to an Euler equation,

$$-\frac{\partial\phi}{\partial t} = \frac{1}{m^2} \int V(\vec{r} - \vec{r}\,')[\rho(\vec{r}\,', t) - \rho_0] \, d\vec{r}\,' , \tag{19}$$

which replaces Eq. (6) in the classical theory. These equations are satisfied by a solution of the form

$$\rho - \rho_0 = B e^{lz} \cos(kx - \omega t) , \quad \phi = A e^{lz} \sin(kx - \omega t) ,$$

provided

$$\omega = \omega_\phi(q) , \quad q^2 = k^2 - l^2 , \tag{20}$$

which takes the place of Eq. (8).

As far as the surface boundary condition is concerned, since we have decided to treat the surface according to the classical theory of surface tension, we have the same equation of continuity [Eq. (12)] and the same equation of motion [Eq. (13)] as in the classical theory. With Eqs. (5) and (11) we recover the classical result Eq. (14), so that the ripplon spectrum in the phonon dispersive theory is determined by Eqs. (20) and (14):

$$\omega = \omega_\phi(q) , \quad q^2 = k^2 - l^2 , \tag{20}$$

$$\omega^2 = (\alpha_0 k^2/\rho_0 - \omega^2\delta)(l + k^2\delta - a\omega^2\rho_0/\alpha_0) . \tag{14}$$

The result of solving these equations for $\omega(k)$ when a and δ are both zero is shown in Figs. 1 and 2 for comparison with the classical calculation with

$c = \text{const}$. The curve of $\omega(k)$ is asymptotic to the phonon spectrum $\omega_\phi(k)$ and has a minimum which is very close to the roton minimum. This feature is qualitatively independent of the values of a and δ, as is shown by the curve with $a = +1$ Å^2.

Of course at best the results of this calculation cannot be more than qualitatively correct at high wave numbers, particularly in the region where l^{-1}, the penetration distance, is predicted to be comparable to an atomic spacing. In addition, the curve for $a = +1$ Å^2 has unphysical features at high wave numbers in that, for large k, the ripplon frequency ω is multivalued, and the group velocity becomes infinite at two values of k. For $\delta < 0$, Eqs. (14) and (20) also have the unphysical solution $l = k = -\delta^{-1}$; $\omega = 0$. However, if $|\delta|$ is small this will occur at very high k. For all values of δ and a one can expect that the ripplon lifetime will become short for k greater than ~1 Å^{-1}.[23] In view of these limitations the main usefulness of the results in Eqs. (14) and (20) is in assessing the importance of phonon dispersion for comparatively low wave numbers, below 1 Å^{-1}, so that we can disentangle the effect of a and δ on the temperature dependence of α. This question is discussed further in Sec. V.

In Fig. 3 we show the ripplon contribution to the surface entropy calculated with representative values of δ and a using both the classical theory, with constant velocity of sound, and taking into account phonon dispersion using Eqs. (14) and (20) to obtain the ripplon frequency. These results were obtained by numerical integration up to $k = 2.9$ Å^{-1} using a Hewlett-Packard 9830A calculator. Where the ripplon frequency for $a = 1$ Å^2 is multivalued we have used only the lowest frequency.

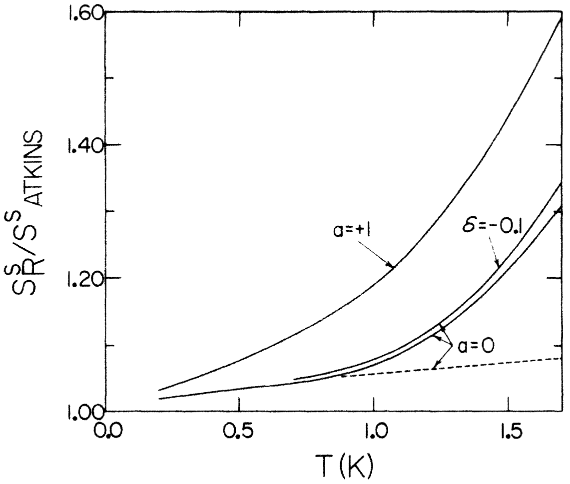

FIG. 3. Ripplon contribution to the surface entropy S^s_R compared to the value calculated from the Atkins formula $S^s_{\text{Åtkins}}$, as a function of temperature. The curves are dashed, calculated using $\omega = cq$ (constant velocity of sound); solid, calculated using the empirical phonon spectrum, $\omega_\phi(q)$. The values of a are in Å^2, δ is in Å; δ is zero unless otherwise stated.

IV. PHONON CONTRIBUTION TO SURFACE TENSION

So far we have ignored the effect of the surface on the phonon modes in the liquid. If one takes this into account one finds that the phonon modes are modified in the presence of a surface, thus giving rise to a surface energy which is in addition to the contribution due to the ripplons. To calculate this we consider a sample of liquid helium between two rigid parallel plane walls. A cut parallel to the walls and through the middle of the sample produces two free surfaces and, as well as introducing a set of ripplon modes, also changes the frequencies of the remaining phonon modes. If the new surfaces were completely free, i.e., if α_0, δ, and a were all zero, the boundary conditions on the velocity potential in either the classical case (Sec. II) or the quantum-hydrodynamic case (Sec. III) show that, on the average, each phonon mode has its wave vector $\vec{q}$ increased by a vector $\vec{\Delta}$ of magnitude $\pi/4H$ directed perpendicular to the surface. Here $2H$ is the thickness of the original sample of helium. At finite temperature T the resulting change in the phonon entropy and temperature-dependent free energy must be attributed to the introduction of the free surfaces, and forms part of the surface entropy and surface free energy. The phonon contribution to the surface tension using this "completely free" boundary condition is then[24]

$$\Delta\alpha^0_\phi = k_B T H \int \frac{\partial}{\partial\omega_\phi}\left[\ln(1 - e^{-\beta\hbar\omega_\phi})\right] \times (\text{grad}_q \omega_\phi) \cdot \vec{\Delta}\, \frac{d^3q}{(2\pi)^3} = \frac{\hbar}{16\pi}\int_0^\infty \frac{q^2\, d\omega_\phi}{e^{\beta\hbar\omega_\phi} - 1}, \tag{21}$$

which can also be written in the quasi-two-dimensional form

$$\Delta\alpha^0_\phi = -\frac{k_B T}{8\pi}\int_0^\infty \ln(1 - e^{-\beta\hbar\omega_\phi})\, q\, dq\,. \tag{22}$$

The corresponding contribution to the surface entropy (which is negative) is

$$S^{s,0}_\phi / k_B \simeq -\frac{1}{8\pi}\int_0^\infty \left(\frac{\beta\hbar\omega_\phi}{(e^{\beta\hbar\omega_\phi} - 1)} - \ln(1 - e^{-\beta\hbar\omega_\phi})\right) q\, dq\,. \tag{23}$$

For low temperatures where ω_ϕ may be set equal to cq the integral can be evaluated to give

$$S_\phi^{s,0}/k_B = -\frac{3\zeta(3)}{8\pi}\left(\frac{k_BT}{\hbar c}\right)^2 = -0.1435\left(\frac{k_BT}{\hbar c}\right)^2$$

$$= -5.98\times10^{-3}T^2 \text{ erg cm}^{-2}\text{deg}^{-1}. \qquad (24)$$

To take into account the real boundary condition, i.e., to include the effect of the surface tension α_0, we use the model described in Sec. III. The phonon modes correspond to solutions of the type

$$\phi = A\cos[\gamma(z+H)]\sin(kx-\omega t) \quad \text{with} \quad \omega=\omega_\phi(q),$$

$$q^2 = k^2+\gamma^2.$$

The surface boundary condition yields

$$\omega^2 = (\alpha_0 k^2/\rho_0 - \omega^2\delta)(-\gamma\tan\gamma H + k^2\delta - a\omega^2\rho_0/\alpha_0), \qquad (25)$$

which is the same as the classical result. In this case each phonon has its perpendicular wave vector γ increased by $\pi/4H$ plus an additional amount $\cot^{-1}(-\tan\gamma H)/H$, so that the phonon contribution to the temperature dependence of the surface tension is

$$\Delta\alpha_\phi = \Delta\alpha_\phi^0 + \left(\frac{\hbar}{2\pi^2}\right)\int_0^\infty \frac{q^2I(q)\,d\omega_\phi}{e^{\beta\hbar\omega_\phi}-1}, \qquad (26)$$

where

$$I(q) = \int_0^1 y\,dy\cot^{-1}\left[\left(\frac{1}{(\alpha_0(\rho_0)q^3(1-y^2)/\omega_\phi^2 - q\delta} - q\delta(1-y^2) - \frac{a\omega_\phi^2}{(\alpha/\rho_0)q}\right)\right] \qquad (27)$$

and $\omega_\phi(q)$ is the empirical phonon spectrum. The corresponding expression for the surface entropy is

$$S_\phi^s/k_B = S_\phi^{s,0}/k_B - \frac{1}{2\pi^2}\int_0^\infty \frac{xe^x}{(e^x-1)^2}I(q)q^2\,dx, \qquad (28)$$

where $x(q) = \beta\hbar\omega_\phi(q)$.

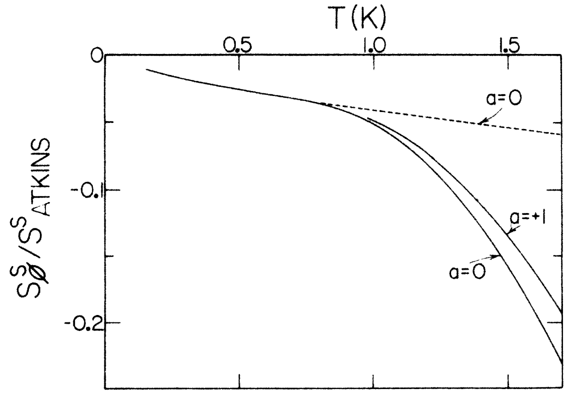

FIG. 4. Phonon contribution to the surface entropy S_ϕ^s, compared to the surface entropy calculated from the Atkins formula S^s_{Atkins}, as a function of temperature. The curves are dashed, calculated using $\omega = cq$ (constant velocity of sound); solid, calculated using the empirical phonon spectrum $\omega_\phi(q)$. The values of a are in Å^2, δ was assumed to be zero.

Figure 4 shows the phonon contributions to the surface entropy in various approximations for $a=0$ and $a=+1$ Å^2. The integrals with respect to k were evaluated numerically up to 2.9 Å^{-1}.

V. CONCLUSIONS AND SUMMARY

In Fig. 5 we show the theoretical surface entropy, including both the ripplon and phonon contributions in two approximations for $a=0$, $a=+1$ Å^2, and $a=1.5$ Å^2. We also show the effect of putting δ equal to −0.1 Å.

The experimental values in Fig. 5 are new results[6] which will be described in another paper.[7] The new data include measurements of $\Delta\alpha$ and $-d\alpha/dT$ and extend up to 2 K, so that only a small part of the experimental results is shown in Fig. 5. An account of the experimental method and the estimation of the errors will be given in a future paper.

Before discussing the theoretical curves in Fig. 5 in more detail we should examine the validity of the approximations we have made and estimate

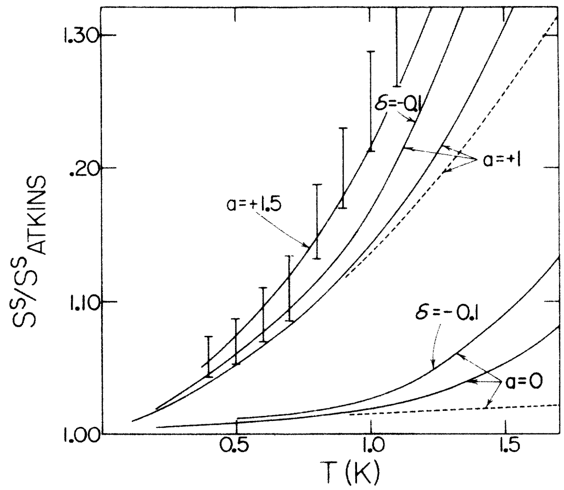

FIG. 5. Total surface entropy S^s compared to the value from the Atkins formula as a function of temperature. The values of a are in Å^2, δ is in Å; the value of δ is zero unless the curve is otherwise labeled. The dashed curves were calculated using $\omega = cq$ (constant velocity of sound); the full curves were calculated using the empirical phonon spectrum $\omega_\phi(q)$. The vertical bars are experimental data.

the temperatures at which these approximations may be expected to break down.

We first examine the "long-wavelength approximation," i.e., the assumption that the wavelength of the excitation is large compared to the characteristic atomic lengths in the liquid, which are of the order of 1 Å. An indication of the validity of this approximation can be obtained by comparing the results using the classical approximation $\omega = cq$ and using the (PD) theory with the empirical phonon spectrum $\omega = \omega_\phi(q)$. As Fig. 5 shows, this difference is quite small and amounts to about 2% at 1.3 K. At 1 K the difference is a fraction of a percent. Therefore we can have reasonable confidence in the PD results up to a temperature of at least 1.3 K.

Another approximation we have made is that the ripplons have well-defined energies and long lifetimes, and that the interactions between ripplons and between ripplons and phonons may be neglected. Saam[23] has calculated that the lifetime for a ripplon decaying into two or more ripplons with smaller wave vectors will become short for ripplons with $k \gtrsim 1$ Å^{-1}. However, his calculation is based on the spectrum for the incompressible liquid, Eq. (1). The fact that our spectrum has smaller positive curvature at high k will probably increase this lifetime. In any case, the contribution to the surface entropy from ripplons with $k \geqslant 1$ Å^{-1} is less than 2% at 1 K and ~4% at 1.2 K.

One may also think of the problem of the interaction of surface excitations as a deviation from the small-amplitude approximation we have assumed throughout our calculations. In the classical theory the mean-square angular deviation of the surface from flatness is of the order of $|\Delta\alpha/\alpha_0|$. The small-amplitude approximation will be valid as long as $|\Delta\alpha/\alpha_0|$ is small compared to unity. At 1 K $|\Delta\alpha/\alpha_0|$ is approximately 2% and at 1.3 K it is 4%.

The effect of interaction between the excitations can also be estimated by using a temperature-dependent ripplon spectrum in calculating the surface entropy. This procedure gives good results[25] up to ~1.8 K in calculating the bulk thermodynamic properties from the phonon spectrum measured by neutron scattering. Of course, we have no measurements of the ripplon spectrum or its temperature dependence, but we can estimate the order of magnitude of such an effect by using the empirical temperature-dependent surface tension $\alpha(T)$ and the temperature-dependent phonon spectrum $\omega_\phi(q, T)$ in our formulas, instead of α_0 and $\omega_\phi(q)$. Once again the effect is fairly small, amounting to an increase of ~1% of the surface entropy at 1 K and ~3% at 1.3 K.

We have also neglected the vapor contribution to the surface tension and surface entropy. Elementary estimates of the vapor contribution to α show it to be of order $P_{\text{sat}} h/(2\pi m k T)^{1/2}$, i.e., of the order of the thermal de Broglie wavelength times the saturated vapor pressure P_{sat}. This is negligible up to a temperature of at least 1.5 K. One must also remember that a ripplon with $\hbar_\omega/k_B$ greater than 7.2 K has enough energy to produce an evaporated atom. Again, the effect of this instability will presumably be confined to high temperatures.

From the above discussion we may have reasonable confidence in our theoretical results at a temperature of about 1 K. Referring to Figs. 3–5 at this temperature we notice that, although the ripplon contribution with $a = 0$ and $\delta = 0$ is quite a lot larger than the Atkins value, after adding the negative phonon contribution the total entropy is not significantly different (only 2%) from that predicted by Atkins's theory. Even at 1.5 K the difference is only 5%. This means that the net effects of compressibility and phonon dispersion are both small at 1 K and they cannot explain the observed deviations between the experiment and the Atkins theory at this temperature.

On the other hand, the effects of plausible nonzero values of δ and a are quite significant at 1 K, and they probably account for the observed behavior of the surface entropy. If Saam's estimate that $|\delta| \leqslant 0.1$ Å is correct, the principal effect is probably due to the quantity a, but it would be difficult to decide this experimentally. If $|\delta| \leqslant 0.1$ Å, then we can conclude that $a = 1.5 \pm 0.3$ Å^2 gives agreement between the theory and the experiment. This is not an unreasonable value of a, but it would be more satisfactory if we had theoretical estimates of both δ and a. Of course, in principle both a and δ could be obtained from static measurements on curved surfaces of liquid helium.

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[*] Present address: Logicon Corporation, 225 W. 5th St., San Pedro, Calif. 90733.

[‡] Present address: Physics Department, State University of New York at Buffalo, Buffalo, N.Y. 14214.

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[15] Note that according to Eq. (10) the usual equation $-d\alpha/dT = S^s$ for a pure substance must be replaced by $-d\alpha/dT = S^s + \Gamma d\mu/dT$. The correction term, neglecting the effect of the vapor, is just $\Gamma d\mu/dT = \delta s$, where s is the entropy density of the bulk liquid. However, since δ is probably much less than an atomic diameter this correction is usually small. In case δ is not small, we note that the theoretical equations for S^s in this paper are quite correct without this approximation, but the theoretical equations for $\Delta\alpha$ should contain an additional term $-\Gamma[\mu(0) - \mu(T)]$. To obtain the surface entropy from experimental values of $\alpha(T)$ one should use the equation $S^s = -d\alpha/dT - \Gamma d\mu/dT$.

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