so that (B3) through (B5) are easily evaluated in terms of G_l. The same results hold for $F(p,p')$.

From (B1) one then finds

$$\left.\frac{\partial^2\epsilon^0(p)}{\partial p^2}\right|_{p_F}=\frac{1}{m}-\frac{1}{3}\frac{F_1}{m^*}=\frac{1}{m^*},\tag{B7}$$

$$\left.\frac{\partial^3\epsilon^0(p)}{\partial p^3}\right|_{p_F}=\frac{1}{3}\frac{F_1}{m^*p_F},\tag{B8}$$

and from (B2),

$$\left.\frac{\partial\gamma(p)}{\partial p}\right|_{p_F}=\gamma(p_F)G_1/p_F\tag{B9}$$

and

$$\left.\frac{\partial^2\gamma(p)}{\partial p^2}\right|_{p_F}=0,\tag{B10}$$

where we have restricted ourselves to the $l=0$ and 1 coefficients in the expansion (B6).

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On the Surface Tension of Liquid Helium II†

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The "intrinsic" surface tension of liquid He II, arising from the structural energy of the free surface, is calculated on the basis of Gross and Pitaevski's imperfect-gas model. The resulting expression, when supplemented by the contribution arising from the presence of quantized surface modes of vibration, gives a value of 0.28 erg cm^{-2} for the surface tension of liquid helium in the limit T → 0°K. This value compares well with the experimental estimate of 0.37 erg cm^{-2}. It is also demonstrated that the so-called boundary effects, which arise from a better enumeration of the density of states in a bounded statistical system, do not make a significant contribution to the temperature dependence of the surface tension. The dominant contribution is again the one due to the quantized surface modes.

I. INTRODUCTION

RECENT experimental work by Atkins and Narahara[1] on the determination of the surface tension of liquid He^4 for temperatures down to 0.35°K has shown that the temperature dependence of the surface tension can be expressed by an empirical relationship of the form

$$\sigma(T)=\sigma(0)-aT^n,\tag{1.1}$$

where $\sigma(0)$ is the limiting value of the surface tension as $T\rightarrow 0°\mathrm{K}$, while a and n are adjustable parameters. The best fit, using the method of least squares, was obtained with $\sigma(0)=0.3729$ erg cm^{-2}, $a=0.0081$ erg cm^{-2}°K^{-n}, and $n=2.5\pm0.2$. A complete theoretical understanding of the observed behavior of $\sigma(T)$, as depicted by Eq. (1.1), is, however, still lacking.

The most satisfactory theory we have had so far of the surface tension of liquid HeII is the one due to Atkins, who, in an earlier paper,[2] suggested that the major contribution to the surface energy of this liquid comes from the quantized surface modes of vibration (also referred to as "ripplons"). Atkins assumed these surface modes to be similar in nature to the macroscopic capillary waves which have a frequency-dependent phase velocity as given by[3]

$$u=(2\pi\sigma\nu/\rho)^{1/3},\tag{1.2}$$

where σ is the surface tension of the liquid, ρ is its density, and ν is the frequency of the wave. In the spirit of the Debye theory of solids, Atkins chose a cutoff frequency ν_c such that the total number of normal modes of vibration in the surface was equal to the total number of atoms in a monomolecular layer (of thickness δ) at the surface. This fixed the cutoff frequency at about 10^{11} sec^{-1} and the corresponding characteristic temperature $\theta_c(=h\nu_c/k)$ at a few degrees Kelvin.

Thus, according to Atkins's theory, a part of the observed surface tension $\sigma(T)$ of liquid helium arises from the presence of quantized surface modes, which themselves arise due to the surface tension of the liquid. Accordingly, we must invoke an "intrinsic" surface tension, $\sigma_i(T)$ say, of the liquid, with the result that the observed surface tension $\sigma(T)$ can be written as

$$\sigma(T)=\sigma_i(T)+\sigma_v[T,\sigma_i(T)],\tag{1.3}$$

where σ_v is the contribution arising from the vibrational modes of the surface which would depend upon the temperature of the liquid explicitly as well as implicitly,

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[1] K. R. Atkins and Y. Narahara, Phys. Rev. **138**, A437 (1965).

[2] K. R. Atkins, Can. J. Phys. **31**, 1165 (1953).

[3] C. G. Kuper, Physica **22**, 1291 (1956); K. R. Atkins, *ibid.* **23**, 1143 (1957).

the latter through the T dependence of σ_i itself. Of course, it will be natural for us to look for the origin of $\sigma_i(T)$ in the basic interactions among the atoms of the fluid. A study of this aspect of the problem constitutes the main theme of the present investigation.

In the limit of 0°K, Eq. (1.3) reduces to[2]

$$\sigma(0)=\sigma_i(0)+\frac{\hbar}{7\pi^{1/4}}\left(\frac{8\sigma_i(0)}{\rho\delta^7}\right)^{1/2}, \tag{1.4}$$

the second term on the right-hand side representing the zero-point contribution of the surface modes. In order to appreciate the relative magnitudes of the two terms in (1.4), we note that to obtain the experimental estimate of 0.37 erg cm^{-2} for $\sigma(0)$, we require $\sigma_i(0)$ to be about 0.14 erg cm^{-2}, leaving about 0.23 erg cm^{-2} for $\sigma_v(0)$. The contribution of the surface modes is, therefore, more than appreciable.

At nonzero temperatures, especially for $T\ll\theta_c$, the added contribution of the surface modes (as arising from the explicit dependence on temperature) turns out to be[2]

$$-1.55\left(\frac{\rho}{\sigma(0)}\right)^{2/3}\frac{k^{7/3}}{\hbar^{4/3}}T^{7/3} = -6.5\times10^{-3}T^{7/3}\text{ erg cm}^{-2}. \tag{1.5}$$

The exponent 7/3 is quite consistent with the empirical value of 2.5±0.2; however, the numerical factor here is about 20% lower than the corresponding empirical value. It is, however, quite imaginable that the temperature dependence of σ_i itself could, to some extent, account for the remainder.

An alternative explanation of the temperature dependence of the surface tension of liquid helium has been attempted by Singh,[4] who adopted the ideal-gas model for this liquid but made use of a better enumeration of the eigenfunctions in the bounded continuum—an enumeration which takes into account the so-called surface effects in the expression for the density of states. Singh thereby obtained for the temperature-dependent part the expression

$$-\pi mk^2T^2\zeta(2)/2\hbar^2=-7.5\times10^{-3}T^2\text{ erg cm}^{-2}; \tag{1.6}$$

here m is the mass of a helium atom, while the Riemann function $\zeta(2)$ is equal to $\frac{1}{6}\pi^2$. Comparing (1.6) with the empirical result of Atkins and Narahara, one finds that the numerical factor now is much closer to the corresponding empirical value, but the exponent is significantly low. From the point of view of agreement with the experimental data, therefore, there is not much reason to choose one or the other of the two alternatives (1.5) and (1.6). From a physical point of view, however, we note that whereas the theoretical basis for (1.5) is sufficiently sound, the adequacy of using the ideal-gas model for liquid helium, which led to (1.6), is hardly acceptable. Of course, Singh's argument does advocate a closer examination of the surface effects than has hitherto been done; however, in studying the contribution of these effects to the density of states and hence to the free energy of liquid helium we must consider a gas of actual excitations, namely, phonons and rotons, rather than one of noninteracting atoms. Moreover, in the absence of interatomic interactions one cannot understand why $\sigma_i(0)$, and hence $\sigma(0)$, should at all be nonzero.

The only way out of this dilemma lies in taking into account the interatomic interactions in the fluid and in turn studying their contribution to the surface energy of the system. However, before we proceed to do so, we prefer to settle once and for all the issue with regard to the surface effects that arise from a proper enumeration of the density of states in the gas of elementary excitations. This is done in Sec. 2, where the surface-energy contributions made by phonons and rotons have been explicitly evaluated. It is important to note that these contributions are nonzero only for $T\neq0$; moreover, in magnitude, they turn out to be negligible in comparison with the contribution made by the surface modes of vibration.[5] Now, since the ideal-gas model does not appear to be relevant to the study of liquid helium, the contribution of the surface modes of vibration to the temperature-dependent part of the surface tension remains the most dominant one.

In Sec. 3 we attempt to explain the existence of the limiting surface tension $\sigma(0)$ on the basis of the interatomic interactions. The theoretical model employed for this investigation consists of a dilute, *imperfect* gas of bosons, interacting through a two-body potential $V(\mathbf{r}-\mathbf{r}')$ which can be replaced by a pseudopotential $V_0\delta(\mathbf{r}-\mathbf{r}')$, where[6]

$$V_0=4\pi a\hbar^2/m, \tag{1.7}$$

a being the relevant scattering length. It is well known that this model has been successfully employed by Gross[7] and by Pitaevski[8] to demonstrate the possibility of the existence of quantized vortex motion in a Bose fluid. The basic feature of this model is to endow the system with an inhomogeneity in space which extends over regions of the order of $(n_0|a|)^{-1/2}$, where n_0 is the mean particle density, and which results, in a very natural way, in an increase in the energy of the system. We have employed this model to investigate the nature of the inhomogeneity at the free surface of a Bose liquid and compute thereby the energy associated with a unit area of the surface. This leads to a nonvanishing

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[4] A. D. Singh, Phys. Rev. **125**, 802 (1962).

[5] It appears worthwhile to state here in clear terms that the latter contribution is an exclusively surface phenomenon, whereas the former ones are in the nature of surface effects (or rather surface corrections) supplementing the customary bulk values.

[6] K. Huang and C. N. Yang, Phys. Rev., **105**, 767 (1957).

[7] E. P. Gross, Nuovo Cimento **20**, 454 (1961).

[8] L. P. Pitaevski, Zh. Eksperim. i. Teor. Fiz. **40**, 646 (1961) [English transl.: Soviet Phys.—JETP **13**, 451 (1961)].

value of the intrinsic surface tension $\sigma_i(0)$, whence follows the vibrational part $\sigma_v(0)$, so that finally we have an estimate for the observed surface tension at absolute zero, viz., $\sigma(0)$ of Eq. (1.4). The resulting theoretical value of 0.28 erg cm^{-2} compares favorably with the experimental estimate of 0.37 erg cm^{-2}.

2. SURFACE EFFECTS IN A GAS OF EXCITATIONS

For studying the physical properties of a statistical system, a knowledge of the asymptotic distribution of single-particle states, which are eigenfunctions of the Schrödinger equation

$$\nabla^2\psi+k^2\psi=0, \quad (\mathbf{k}=\mathbf{p}/\hbar), \tag{2.1}$$

is essential. Customarily, the number of eigenstates $g(p)$ with momenta not exceeding a particular value p is approximated by the familiar Rayleigh-Weyl expression

$$g(p)\simeq V\tfrac{4}{3}\pi(p/h)^3, \tag{2.2}$$

where V is the volume of the enclosure. Of course, the validity of this expression rests on the assumption that the linear dimensions of the enclosure are much larger than the characteristic wavelength h/p. A more rigorous study of the density of states, as allowed by (2.1), shows that the second term of the asymptotic expression for $g(p)$, of which (2.2) is the main term, is directly proportional to the surface area S of the enclosure.[9,10] This surface term is naturally of a very direct physical interest to us, for, when taken into account in calculating the extensive properties of a physical system, it leads to what might be called a "surface contribution" to the customary bulk values of these properties.

For the sake of generality, we consider the enclosure to be an n-dimensional domain, $D^{(n)}$ say; this will enable us to study the case of ripplons without any extra calculation. For such a domain, Fedosov[9] has established the following asymptotic formula:

$$\int_0^K (K-k)^\xi dg(k)=\sum_{i=n}^{1} a_i\frac{\xi!i!}{(\xi+i)!}K^{\xi+i}+O(K^{n-1}), \tag{2.3}$$

so that, with $\xi=0$, one obtains

$$g(K)=\sum_{i=n}^{1} a_iK^i+O(K^{n-1}). \tag{2.4}$$

The coefficients a_i here are related to certain geometrical measures of the domain, viz.,

$$a_n=\text{mes}_nD^{(n)}/2^n\pi^{n/2}(\tfrac{1}{2}n)! \tag{2.5}$$

and

$$a_{n-1}=\mp\frac{\sum_j \text{mes}_{(n-1)}S_j{}^{(n-1)}}{2^{n+1}\pi^{\frac{1}{2}(n=1)}[\frac{1}{2}(n-1)]!}, \tag{2.6}$$

where $S_j{}^{(t)}$ is a t-dimensional "face" of the domain; the upper (lower) sign corresponds to the Dirichlet (Neumann) boundary condition, i.e., everywhere at the boundary $\psi=0$ $(d\psi/dn=0)$.

For a three-dimensional domain of *arbitrary* shape, Eqs. (2.5) and (2.6) yield the formula

$$g(K)=(K^3/6\pi^2)V\mp(K^2/16\pi)S+O(K^2). \tag{2.7}$$

Now, the error term as such rather appears to vitiate the role of the surface term in the expression for $g(K)$. However, Pathria[10] has provided sufficient computational evidence to show that the error term in (2.7) is in effect much inferior to the surface term, so that Eq. (2.7) may be replaced by

$$g(K)=(K^3/6\pi^2)V\mp(K^2/16\pi)S+o(K^2). \tag{2.8}$$

This implies that the correction term in (2.4) may also be written as $o(K^{n-1})$. With this understanding, we can readily evaluate the surface contributions to the free energy of liquid helium as arising from phonons, rotons, and ripplons. The resulting free energy per unit area will then be interpreted as the temperature-dependent part of the surface tension of this liquid.

Now, the free energy F of a Bose-Einstein gas of (noninteracting) quasiparticles below the transition temperature T_λ is given by the formula

$$F=kT\sum_\epsilon \ln(1-e^{-\epsilon/kT}). \tag{2.9}$$

One can convert the summation here into an integral by employing the expression (2.4), along with (2.5) and (2.6), for the density of states. Again, for generality, we take the energy-momentum relation for the quasiparticles to be $\epsilon=\alpha p^s$. We then obtain for the free energy

$$F=-\frac{\pi^{n/2}(n/s)!\zeta(n/s+1)V_n}{(\frac{1}{2}n)!h^n\alpha^{n/s}}(kT)^{n/s+1}$$
$$\pm\frac{\pi^{(n-1)/2}[(n-1)/s]!\zeta[(n-1)/s+1]A_n}{4[\frac{1}{2}(n-1)]!h^{n-1}\alpha^{(n=1)s}}(kT)^{(n-1)/s+1}. \tag{2.10}$$

Considering only the surface term, we have, as a check, for the ideal-gas particles $(n=3;\ \alpha=1/2m,\ s=2)$,

$$\begin{aligned}F_s/A&=\pm[\pi m\zeta(2)/2h^2](kT)^2\\&=\pm7.5\times10^{-3}T^2\text{ erg cm}^{-2},\end{aligned} \tag{2.11}$$

which is Singh's result.[4] It is instructive to note that Eq. (2.11) can also be derived without making use of the explicit expression for $g(K)$. In that case one works with the summations as such and arrives at the desired results by applying the θ-function transformation to the

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[9] B. V. Fedosov, Dokl. Akad. Nauk. SSSR, **151**, 786 (1963); **157**, 536 (1964) [English transl.: Soviet Math.—Doklady 4, 1092 (1963); **5**, 988 (1964)].

[10] R. K. Pathria, Nuovo Cimento Suppl. 4, 276 (1966).

sums; for details, see the Appendix. Still another way of deriving this result is through the construction of the Mellin transforms of the relevant summands.[11]

(a) For the phonons ($n=3$; $\alpha=c$, $s=1$), one obtains[12]

$$F_s/A=\pm[\pi\zeta(3)/2\hbar^2c^2](kT)^3$$
$$=\pm 1.96\times 10^{-4}T^3 \text{ erg cm}^{-2}. \quad (2.12)$$

(b) For ripplons, the energy-momentum relationship, when the effect of the gravitational field can be neglected, is[3]

$$\epsilon=(\sigma/\rho\hbar)^{1/2}p^{3/2}, \quad (2.13)$$

so that we have $\alpha=(\sigma/\rho\hbar)^{1/2}$, $s=\frac{3}{2}$. Since ripplons constitute a surface phenomenon (rather than a correction to some bulk value), the desired result in this case follows from the main term of the formula (2.10) with $n=2$ and $V_2=A$. One thus obtains

$$F/A=-\pi(\rho/2\pi\sigma)^{2/3}\hbar(kT/\hbar)^{7/3}\Gamma(7/3)\zeta(7/3)$$
$$=-6.5\times 10^{-3}T^{7/3} \text{ erg cm}^{-2}. \quad (2.14)$$

This is precisely the result obtained earlier by Atkins.[2]

(c) For rotons, it is necessary to make a separate calculation because their energy-momentum relationship does not fall in the category discussed above. One has, in this case, $\epsilon=\Delta+(p-p_0)^2/2\mu$. A straightforward calculation, making use of the density of states formulas (2.4)–(2.6), gives

$$F_s/A=\pm kT\frac{\pi}{2\hbar^2}\int_{-\infty}^{\infty}e^{-[\Delta+(p-p_0)^2/2\mu]/kT}p\,dp$$
$$=\pm[(2\pi^3\mu)^{1/2}/2\hbar^2]p_0\,e^{-\Delta/kT}(kT)^{3/2}$$
$$=\pm 3.1\times 10^{-2}\,e^{-\Delta/kT}T^{3/2} \text{ erg cm}^{-2}. \quad (2.15)$$

A comparison of (2.12) with (2.14) readily shows that the surface effect of the phonon component, at $T\simeq 1°\text{K}$, is hardly a few percent of the direct contribution of the ripplons. The surface effect of the roton component, as given by (2.15), is still less, by another factor of 10 or more. Moreover, a basic difficulty with the surface effects (2.12) and (2.15) is that they are so strongly dependent on the nature of the boundary conditions used that it appears somewhat awkward to ascribe to them any definite physical significance. Thus, we see that the observed temperature dependence of the surface tension of liquid helium is, in the main, given by the direct surface energy of the ripplons.

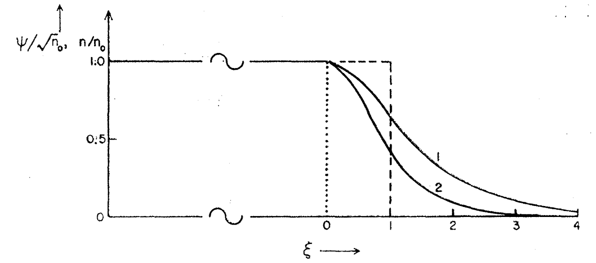

FIG. 1. Variation of the superfluid wave function (curve 1) and of the superfluid density (curve 2) at the free surface. The dashed line indicates the spatial extent of the fluid if the density were uniform throughout.

3. THE IMPERFECT GAS MODEL ($T=0°\text{K}$)

We now examine the nature of the nonuniformity of distribution of atoms in the region of the free surface of the Bose fluid; this study will enable us to calculate the free energy associated with a unit area of the surface and to obtain thereby a theoretical estimate for the observed surface tension. The imperfect gas model to be employed for this investigation has already been studied in detail by some authors,[7,8] who have shown that the spatial variation of the particle density $n(\mathbf{r})(\equiv|\psi(\mathbf{r})|^2)$ in the system is given by the nonlinear equation

$$\{-(\hbar^2/2m)\nabla^2+4\pi a\hbar^2/m|\psi|^2\}\psi=\mu\psi, \quad (3.1)$$

where a is the scattering length of the interaction and μ is the increase in the energy of the system consequent upon the addition of one more particle to it. We shall apply Eq. (3.1) to study only the surface part of the fluid, for it is in this part alone that we have a variation of $n(r)$ from the bulk value n_0 to a vanishingly small value, over a region characterized by some sort of a "healing length." It is, however, important to note right in the beginning that the existence of a free surface, which is one of the basic characteristics of a liquid (as opposed to a gas), necessarily requires that the atoms in the surface region experience a predominantly attractive force towards the interior of the fluid; consequently, the effective scattering length of interaction for atoms in this so-called "surface layer" must be negative,[13] i.e., $a=-|a|$.

Now, considering a free surface normal to the x axis, so that the operator ∇^2 in (3.1) is merely d^2/dx^2, and denoting the value of $n(x)$ at the point of inflexion (see Fig. 1) by n_s, we obtain for the parameter μ

$$\mu=(4\pi a\hbar^2/m)n_s. \quad (3.2)$$

Equation (3.1) can then be written as

$$d^2\psi/dx^2+8\pi|a|\psi^3=8\pi|a|n_s\psi. \quad (3.3)$$

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[11] See S. Franchetti, Nuovo Cimento **5**, 183 (1957), Eq. (22); this calculation corresponds to the Dirichlet boundary condition. Using the same method, A. D. Singh and R. K. Pathria, Progr. Theoret. Phys. (Kyoto) 24, 229 (1960), carried out a calculation for the Neumann boundary condition as well; see Eq. (10) of the Appendix I of their paper.

[12] This result can also be derived by the method of Mellin transforms; see S. Franchetti, Ref. 11, Eq. (28).

[13] A negative scattering length for atomic interactions in liquid helium has also been used by M. Girardeau, Phys. Fluids **5**, 1468 (1962); see also K. Huang, Phys. Rev. **119**, 1129 (1960).

Introducing the reduced variables

$$\psi_0(x)=\psi(x)/n_s^{1/2}, \quad \xi=x/l, \tag{3.4}$$

where $l=(8\pi n_s|a|)^{-1/2}$, our differential equation becomes

$$d^2\psi_0/d\xi^2+\psi_0^3-\psi_0=0. \tag{3.5}$$

The relevant solution of this equation would be the one that vanishes as $\xi\rightarrow\infty$ and has a vanishing slope at, say, $\xi=0$; for all $\xi<0$, i.e., everywhere in the bulk of the liquid, we shall take $n(x)=n(0)\equiv n_0$. We find that

$$\psi_0=\sqrt{2}\,\mathrm{sech}\,\xi \tag{3.6}$$

is such a solution; accordingly,

$$n(x)=2n_s\,\mathrm{sech}^2(x/l). \tag{3.7}$$

As $x\rightarrow 0$, the particle density approaches the value $2n_s$, which should be equal to the bulk value n_0. Thus, the point of inflexion of the (ψ_0,ξ) curve (see Fig. 1) corresponds to a particle density exactly $\frac{1}{2}$ of the bulk value, which is clearly a very satisfactory situation. The dashed line in the graph indicates the spatial region which would be occupied by the particles now constituting the nonuniform surface layer if they were spread out uniformly with a density equal to n_0. Thus, $l[=(4\pi|a|n_0)^{-1/2}]$ is a measure of the extent of the spatial inhomogeneity in the free surface; in magnitude, it is comparable to the lateral dimension of the "core" of a quantized vortex.

The structural energy per unit area associated with the nonuniformity in the free surface can be determined by calculating the difference between the energy per unit area of the surface layer *as it is* and that of the corresponding layer if the distribution were uniform. One thereby has

$$\begin{aligned}\frac{F-F_0}{A}=\frac{E-E_0}{A}&=\frac{\hbar^2}{2m}\int_0^\infty\left|\frac{d\psi}{dx}\right|^2dx\\&\quad+\frac{2\pi a\hbar^2}{m}\left[\int_0^\infty|\psi(x)|^4dx-\int_0^l n_0^2dx\right]\\&=\tfrac{1}{3}\hbar^2n_0/ml=(2\pi^{1/2}\hbar^2/3m)n_0^{3/2}|a|^{1/2}.\end{aligned} \tag{3.8}$$

Using Girardeau's[13] estimate for $|a|$, viz., 2Å, we obtain from the foregoing

$$\sigma_i(0)=0.09 \text{ erg cm}^{-2}. \tag{3.9}$$

The existence of the intrinsic surface tension would lead to the presence of ripplons on the free surface, which, in turn, would give rise to a zero-point free energy. Atkins has carried out this calculation earlier, with the result[2]

$$\begin{aligned}\sigma_v(0)&=\int_0^{\nu_c}(\tfrac{1}{2}h\nu)g(\nu)d\nu\\&=(h/7\pi^{1/4})[8\sigma_i(0)/\rho\delta^7]^{1/2},\end{aligned} \tag{3.10}$$

which, on substitution from (3.8), becomes

$$\sigma_v(0)=\frac{8\pi}{7\sqrt{3}}\frac{\hbar^2}{m}\frac{n_0^{1/4}|a|^{1/4}}{\delta^{7/2}}. \tag{3.11}$$

Substituting the relevant numbers in this expression, we get

$$\sigma_v(0)=0.19 \text{ erg cm}^{-2}. \tag{3.12}$$

Combining (3.9) and (3.12), we obtain for the observed surface tension $\sigma(0)$ of He^4 an estimate of 0.28 erg cm^{-2}; the corresponding experimental estimate is 0.37 erg cm^{-2}.

Of course, on the basis of a gaseous model, though interacting, we cannot expect to understand the physical behavior of a liquid quantitatively, especially when the numerical value used for the scattering length is not very reliable. Qualitatively, the theory developed here indeed appears to be a step in the right direction.

Finally, we remark that since the temperature dependence of the surface tension of liquid helium is reasonably well explained by the surface-energy contribution from the ripplons, the intrinsic surface tension σ_i may not be expected to be strongly temperature-dependent. Nevertheless, this aspect of the problem is also being pursued.

APPENDIX

We derive here expression (2.11) without replacing the summation over states by an integration; accordingly, we shall not make use of any explicit formula for $g(K)$. Let us consider a gas of noninteracting particles, each of mass m, confined to a volume V, which for simplicity is taken to be a cube of side a. The energies of the stationary states of any one particle are given by

$$\epsilon=(h^2/8ma^2)(s^2+t^2+u^2), \tag{A1}$$

where s, t, and u can take only positive integral values in the case of the Dirichlet boundary condition, but can also take the value zero in the case of the Neumann boundary condition.

We then have for the logarithm of the grand partition function

$$\ln\mathcal{Q}=-\sum_{s,t,u}\ln[1-ze^{-\mu(s^2+t^2+u^2)}], \tag{A2}$$

where $\mu=h^2/(8ma^2kT)$ and z is the fugacity of the system. The internal energy U can then be determined by the relationship

$$U=-[\partial\log\mathcal{Q}/\partial\beta]_{z,V}, \tag{A3}$$

where $\beta=1/kT$. Carrying out the expansion (A2) in powers of z and the differentiation as required by (A3) we obtain

$$U=\frac{h^2}{8ma^2}\sum_{s,t,u}\sum_{j=1}^{\infty} z^j(s^2+t^2+u^2)\,e^{-\mu j(s^2+t^2+u^2)}$$

$$\equiv\frac{3h^2}{8ma^2}\sum_{j=1}^{\infty} z^j\Big[\sum_s s^2\,e^{-\mu j s^2}\Big]\Big[\sum_t e^{-\mu j t^2}\Big]^2. \qquad \text{(A4)}$$

The sums involved here can be evaluated by using Poisson's formula[14]

$$\sum_{s=-\infty}^{\infty} e^{-\mu j s^2}=\left(\frac{\pi}{\mu j}\right)^{1/2}\sum_{s=-\infty}^{\infty} e^{-\pi^2 s^2/\mu j}, \qquad \text{(A5)}$$

and the one resulting from (A5) by a differentiation with respect to (μj), namely,

$$\sum_{s=-\infty}^{\infty} s^2\,e^{-\mu j s^2}=\left(\frac{\pi}{(\mu j)^3}\right)^{1/2}\sum_{s=-\infty}^{\infty}\left[\tfrac{1}{2}-\frac{\pi^2 s^2}{\mu j}\right]e^{-\pi^2 s^2/\mu j}. \qquad \text{(A6)}$$

From (A5) and (A6) it follows that, in the limit $\mu\rightarrow 0$,

$$\sum_{\substack{s=1\\ 0}}^{\infty} e^{-\mu j s^2}\equiv\frac{1}{2}\left[\left(\frac{\pi}{\mu j}\right)^{1/2}\sum_{s=-\infty}^{\infty} e^{-\pi^2 s^2/\mu j}\mp 1\right]$$

$$\simeq\tfrac{1}{2}\big[(\pi/\mu j)^{1/2}\mp 1\big], \qquad \text{(A5}')$$

and

$$\sum_{\substack{s=1\\ 0}}^{\infty} s^2\,e^{-\mu j s^2}\equiv\tfrac{1}{2}\sum_{s=-\infty}^{\infty} s^2\,e^{-\mu j s^2}\simeq\tfrac{1}{4}\big[\pi/(\mu j)^3\big]^{1/2}. \qquad \text{(A6}')$$

Accordingly, (A4) becomes

$$U\simeq\tfrac{3}{2}(V/\lambda^3)kTg_{5/2}(z)\mp\tfrac{1}{4}(A/\lambda^2)kTg_2(z), \qquad \text{(A7)}$$

where $\lambda=h/(2\pi mkT)^{1/2}$ and the function

$$g_n(z)=\sum_{j=1}^{\infty} j^{-n}z^j.$$

The free energy of the system can be calculated by means of the formula

$$F=-T\int_0^T\frac{U}{T^2}dT, \qquad \text{(A8)}$$

whence we finally get

$$F=(-V/\lambda^3)kTg_{5/2}(z)\pm\tfrac{1}{4}(A/\lambda^2)kTg_2(z). \qquad \text{(A9)}$$

For $T<T_\lambda$, $z\simeq 1$; then, for $n>1$, $g_n(z)\simeq\zeta(n)$. The second term in (A9) thereby gives precisely the expression (2.11) for F_s/A.

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[14] See D. Menzel, *Fundamental Formulas of Physics*, (Dover Publications, Inc., New York, 1960), p. 77. This is also referred to as the θ-function transformation: see R. H. Fowler and H. Jones, Proc. Camb. Phil. Soc. 34, 573 (1938).

Errata

Effect of Molecular Redistribution on the Nonlinear Refractive Index of Liquids. R. W. HELLWARTH [Phys. Rev. **152**, 156 (1966)]. We have discovered an important error in the sign of a term calculated in the Appendix. As a result, the question raised in this paper as to the accuracy of the Kirkwood superposition approximation for calculating certain configurational averages for liquids can now be answered: The approximation gives the wrong sign at liquid densities for the nonlinear free-energy term and also for other quantities whose signs are known on general grounds. Specifically, in Eq. (A17), for I_3 the factor $(l^2+2\pi^2/3)$ should be $(l^2-2\pi^2/3)$. Also, in (A21) the factor 0.5066 should be replaced by 0.922 and in (A22) the factor -0.117 should be replaced by -0.467. We have re-examined the small correction K_4 and ascertained that its sign is negative, so that it contributes, though very little, to the worsening of the failure of the superposition approximation. With these corrections, the superposition approximation gives, instead of the existing Eq. (38),

$$\begin{aligned}U_{22}/(NE'^4\rho^2\alpha^4)=(l^2+2\pi^2/3)\Delta-2\pi^2/3\\ +\pi^2(32+136\Delta+167\Delta^2)/(45\rho\tau)\\ +1.13\rho\tau(1+K_4/4).\end{aligned} \qquad (38)$$

From the definition (28b), U_{22} must be positive. For symmetric molecules $(\Delta=0)$, the right-hand side is seen to fail to stay positive as the density ρ increases beyond $1.6/\tau$, where $\tau/8$ is the molecular volume. Normal liquid densities run between $2/\tau$ and $3/\tau$. The above change in U_{22} requires that the expression (41) for n_2 be altered to

$$n_2=\frac{\pi\rho\alpha^2\beta}{n(1-4\pi\rho\alpha/3)^4}\left[\Delta+\frac{4\pi^2\rho\alpha^2}{45\tau}(32+136\Delta+167\Delta^2)+\frac{8\pi^2\rho^2\alpha^2(\Delta-1)}{3}+4.51\alpha^2\rho^3\tau\right], \qquad (41)$$