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SURFACE EXCITATIONS IN LIQUID He^4

L. S. REUT and I. Z. FISHER

Odessa State University

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It is shown that Atkins formula for the surface tension of pure liquid He^4 is exact up to a temperature of 0.6°K, if a correction is introduced for the dependence of the static part of the surface tension on the density. It is assumed that a roton part exists in the spectrum of surface elementary excitations. It is shown that the experimental data on the surface tension of He^4 up to 1.4°K agree with this assumption and the parameters for the roton part of the spectrum are determined.

1. INTRODUCTION

In 1953, Atkins proposed a theory of the temperature dependence of the surface tension of pure liquid He^4 in the low temperature region, starting from a representation of capillary waves on the free surface of the liquid as longwave surface elementary excitations.[1,2] His final result has the form

$$\sigma(T)=\sigma_0-\frac{0,1340}{\hbar^{4/3}}\left(\frac{\rho}{\sigma}\right)^{2/3}(kT)^{7/3}, \tag{1}$$

where σ_0 is the surface tension at T = 0, ρ the density of the liquid, and the values of ρ and σ in the second term can be replaced by the values at T = 0 with sufficient accuracy. However, in the exact measurements in the temperature range from 0.4 to 1.4°K in [3], the impossibility of satisfying the experimental data was observed, for any choice of the constant σ_0 in Eq. (1). As a result, doubt was cast on the validity of this equation.

The idea of noninteracting surface elementary excitations as the reason for the temperature contributions to the surface tension of liquid He^4 is physically reasonable and very attractive. Arguing by analogy with the theory of the bulk properties of liquid He^4,[2] this idea can lead to valid results up to comparatively high temperatures of the order of 1.5–1.8°K, above which it is no longer possible to avoid the interaction of the elementary excitations. On the other hand, the same analogy indicates that the longwave approximation in the estimate of the spectrum of elementary excitations leads to correct thermodynamic consequences only for sufficiently low temperatures, for example, up to 0.5–0.6°K. Therefore, it is natural to attempt to explain the negative conclusions of [3] because of the use of the simple formula (1) outside its region of applicability, and not because of the incorrectness of the original idea of the theory.

One of the problems of the present work is the establishment of the bounds of applicability of the Atkins equation (1). It is shown that this equation can be assumed to be exact up to temperatures 0.6–0.65°K and leads to excellent agreement with the available experimental data. Here the meaning of the term σ_0 in Eq. (1) should be made more precise. At higher temperatures, it is necessary to know the spectrum of shortwave surface excitations for the correct estimate of the surface tension of liquid He^4. It is shown below that the assumption of the existence of surface excitations of the roton type is in excellent agreement with the experimental data of [3] over the entire range of temperatures studied there, and an approximate estimate is obtained of the parameters of the roton part of the spectrum of elementary excitations.

2. REMARKS ON THE STATIC CONTRIBUTION TO THE SURFACE TENSION

We take up the idea of the surface tension in liquid He^4 up to comparatively high temperatures as the sum of a static contribution $\sigma = \sigma_0(\rho)$ and a contribution from the noninteracting surface elementary excitations. If κ is the wave number of the excitations and $\omega = \omega(\kappa)$ is their frequency, then the general expression for the surface tension is[1,2]

$$\sigma(\rho,T)=\sigma_0(\rho)-\frac{\hbar}{4\pi}\int_0^\infty\frac{(d\omega/d\varkappa)\varkappa^2d\varkappa}{\exp(\hbar\omega/kT)-1}. \tag{2}$$

Equation (1) is then obtained in the capillary wave approximation:

$$\omega(\varkappa)=(\sigma/\rho)^{1/2}\varkappa^{3/2}. \tag{3}$$

We have emphasized the dependence of the surface tension of the liquid on its volume density, which is important for the exact comparison of the theoretical calculations with the experimental data, and an explanation is needed. The surface tension on the separation boundary of two phases and, phenomenologically, on the molecular level also, can be determined from only the single condition of the mechanical equilibrium of the boundary of the phases.[4] For a one-component system, this leads to the surface tension as a function of the temperature and pressures: $\sigma = \sigma(p, T)$. The usual confirmation that $\sigma = \sigma(T)$ then follows from the additional requirement of not only mechanical, but also total thermodynamic equilibrium of the two bounding phases. This determines $p = p(T)$ along the curve of phase equilibrium and leads to $\bar{\sigma}(T) = \sigma(p(T), T)$. If the second phase is a rarefied gas, then one can give the density of the liquid with great accuracy in place of the pressures, and neglect the density of the gas. Then, in the general case, for the surface tension of the liquid, we get $\sigma = \sigma(\rho, T)$, and especially along the liquid-gas equilibrium curve, which is determined by the equation $\rho = \rho(T)$, we get $\sigma(T) = \sigma(\rho(T), T)$.

On the other hand, it is clear from the method of derivation of Eqs. (1) and (2) that both terms on the right hand sides are determined independently of the conditions of complete phase equilibrium of the liquid-gas, as the free energy of the boundary of liquid He^4 for specified volume density ρ. Therefore, one must assume $\sigma_0 = \sigma(\rho, 0) = \sigma_0(\rho)$ in Eq. (1), as is clearly shown in Eq. (2). Inasmuch as all the current experiments on the surface tension of liquid He^4 refer to the liquid-gas equilibrium line with the law for liquid density variation $\rho = \rho(T)$ along this line, and not to the isochore ρ = const, they must be compared with Eqs. (1) or (2) for $\sigma_0 = \sigma_0(\rho(T))$, and not for σ_0 = const. Thus, along the phase equilibrium curve, there is in Eqs. (1) an additional temperature dependence of the surface tension, which should be taken into account.

Unfortunately, almost nothing is known about the function $\sigma_0(\rho)$ in Eq. (2). In [5] the problem of the determination of $\sigma_0(\rho)$ was solved by starting out from an equation of the Hartree type for the effective wave function of superfluid helium filling a half-space. Assuming a contact interaction of the atoms and using the variational method of solution, they obtained

$$\sigma_0(\rho) = 0.7\,\hbar c\rho / m, \tag{4}$$

where m is the mass of the He^4, c the sound velocity for T = 0. Substitution of the numerical values of the quantities on the right side of (4) leads to the good result $\sigma_0 = 0.38$ erg/cm^2 at low pressures. A more exact determination of $\sigma_0(\rho)$ has not been carried out.

3. SURFACE TENSION OF He^4 AT LOW TEMPERATURES

The absence of reliable information on the function $\sigma_0(\rho)$ forces us to use approximations. We take

$$\sigma_0(\rho) = 0.6818\,\hbar c\rho / m \tag{5}$$

for all values of c and ρ in the low temperature range. The coefficient in (5) was chosen somewhat smaller than in (4), which does not contradict the variational procedure of determination of the surface energy in [5], allowing improvement of the estimate in the direction of its decrease. The four digits of the coefficient are so chosen that for T = 0.4°K, the simultaneous use of Eq. (5) and the Atkins temperature contribution from (1) would lead to the exact coincidence with the experimental value of $\sigma(T)$ from [3], to the same number of digits. It is then seen that up to a temperature of 0.6°K inclusive, the simultaneous use of (1) and (5) leads to complete agreement of the calculated and experimental values of $\sigma(T)$ with the same accuracy at all points. The divergence of the calculated and experimental values of $\sigma(T)$, which extends to three units of the fourth decimal place is noted, while the computed data are shown to be greater than the experimental. For experimental data, we have used the weighted average given in [3] for a very large number of experimental points. Evidence on $\sigma(T)$ for $T < 0.4$°K in [3] is lacking. Data on the temperature dependence of the density and sound velocity along the liquid-gas equilibrium curve were taken from [6,7]. Thus, in the range up to $T \approx 0.65$°K, the theoretical estimates for the surface tension of liquid He^4, in the model of capillary waves, should be assumed to be very good (if the experiment does not lead to unexpected results in the investigated range $T < 0.4$°K).

We note that in the range $0.4°\mathrm{K} \le T \le 0.6°\mathrm{K}$, the product $c\rho$ in Eq. (5) depends very slightly on the temperature. Therefore, the initial Atkins assumption σ_0 = const, with suitable choice of the constant, together with Eq. (1), is seen here to be almost as good as the approximation (5). Failures in the selection of the value of σ_0 in [3] are due to the attempt to cover by Eq. (1) with σ_0 = const the entire experimentally studied temperature interval up to T = 1.4°K; however, there is no basis for such an attempt.

The best estimate for σ_0 = const in the temperature interval from 0.4° to 0.6°K is the value $\sigma_0 = 0.3728$ erg/cm^2. For such a choice of σ_0, the divergence between the values computed from Eq. (1) and the experimental data from [3] does not exceed one unit in the fourth decimal place in $\sigma(T)$. However, at temperatures somewhat greater than 0.6°K, this divergence becomes significant and exceeds by a factor of about two the corresponding divergence for the approximation (5). It is also shown that upon extrapolation of Eq. (1) in the range of high temperatures, up to 1.4°K, the choice (5) is closer to the experimental points than the choice σ_0 = const for all temperatures.

A result which is equivalent to that pointed out above should be obtained by using several terms of the expansion of the unknown function $\sigma_0(\rho_0 + \Delta\rho(T))$ in a power series in $\Delta\rho = \rho - \rho_0$ in place of the approximation (5). Here, one would have to determine at least two unknown coefficients from the experimental data in place of one in (5).

4. SURFACE EXCITATIONS OF THE ROTON TYPE

For the description of the temperature dependence of the surface tension of liquid He^4 at temperatures above 0.65°K, account of only one longwave surface excitation in Eq. (2) is insufficient. The real path of the dispersion law $\omega = \omega(\kappa)$ of the surface excitations for large κ is unknown. By analogy with the theory of bulk properties of liquid He^4, it is natural to assume the existence of a roton part on the dispersion curve

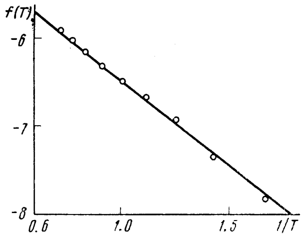
$$\hbar\omega(\varkappa) = \Delta + \hbar^2(\varkappa - \varkappa_0)^2 / 2\mu \tag{6}$$

and to attempt to explain the observed divergence between the values of $\sigma(T)$ along the liquid-gas equilibrium curve, computed from Eq. (1) and measured experimentally, at $T > 0.65$°K. The parameters Δ, κ_0, and μ should depend only on the density (or pressure) of the liquid. We shall assume this dependence to be weak and neglect it. In order that the roton portion of the spectrum $\omega(\kappa)$ have meaning, the clear differentiation of from the longwave portion of the capillary waves (3) is necessary. This leads to the requirement $\hbar\omega^{\mathrm{cap}}(\kappa_0) > \Delta$, and we get the inequality

$$\varkappa_0 > (\rho / \sigma)^{1/3}(\Delta / \hbar)^{2/3}. \tag{7}$$

In other respects, the parameters Δ, κ_0, and μ are as yet unknown. Substituting Eq. (6) in Eq. (2), and assuming $\Delta \gg kT$, we obtain an estimate for the additional contribution to the surface tension, equal to

$$\sigma^{\mathrm{rot}}(\rho, T) \approx -\frac{\varkappa_0}{\hbar}\left(\frac{\mu}{2\pi}\right)^{1/2}(kT)^{3/2} e^{-\Delta/kT}. \tag{8}$$



Dependence of the function f(T) on 1/T. $\sigma_0 = 0.3728$ erg/cm^2.

Thus, we finally obtain, for not too high temperatures,

$$\sigma(\rho, T) = \sigma_0(\rho) + \sigma^{\text{cap}}(\rho, T) + \sigma^{\text{rot}}(\rho, T). \tag{9}$$

For states along the liquid-gas equilibrium line, we equate the left hand side of this expression with the experimental values of the coefficient of surface tension and, for simplicity of writing, introduce the function

$$f(T) = \ln\{\sigma_0(T) + \sigma^{\text{cap}}(T) - \sigma^{\text{exp}}(T)\} - {}^3/_2 \ln T. \tag{10}$$

It then follows from Eq. (8) that one should have

$$f(T) = B - \frac{\Delta}{kT}, \quad B = \ln\left[\frac{\varkappa_0}{\hbar}\left(\frac{\mu}{2\pi}\right)^{1/2} k^{3/2}\right]. \tag{11}$$

Thus, the surface excitations of the roton type should lead to a contribution to the surface tension of liquid He^4, assuring a linear variation of the function f(T) when plotted as a function of 1/T.

For strict verification of the prediction (11), one must know the function σ_0(T), which is not known to us in the region of high temperature. The choice of the "best" constant value $\sigma_0 = 0.3728$ erg/cm^2 (see above) leads to the result shown in the figure. The linearity of the curve f(T) over the entire temperature range from T ≈ 0.6°K to T = 1.4°K is completely satisfactory. A small systematic departure from linear variation of f(T) is possible in the range 0.8-0.9°K, connected with the approximation of the estimate σ_0 = const. The possibility of the use of the approximation (5), extrapolated to the range of high temperatures, is also tested. The results turned out to be unsatisfactory.

Treatment of the data of the drawing by relations (7) and (11) leads to the following estimates

$$\Delta = 1{,}95^\circ\,\text{K} = 2{,}7 \cdot 10^{-16}\ \text{erg},$$
$$\varkappa_0\sqrt{\mu} = 1{,}77 \cdot 10^{-5}\ \text{g}^{1/2}/\text{cm}, \ \varkappa_0 > 0{,}30\ \text{Å}^{-1},$$
$$\mu < 0{,}052\, m.$$

where m is the mass of the He^4 atom. The condition $\Delta \gg kT$ is not very well satisfied here and the correction terms should be taken into account in Eq. (8). However, it makes no sense to do this without the simultaneous account of the departure of σ_0(T) from a constant value in the temperature range of interest to us. The value $\Delta \approx 2$°K that is found is close to the value of the analogous parameter for impurity surface excitations from the Andreev theory.[8] The probable value of κ_0 evidently lies close to 0.5 Å^{-1} and below the analogous quantity for volume rotons. The effective mass of the surface roton in this case is seen to be of the order of several hundredths of the mass of the He^4 atom and less than the effective mass of the volume roton.

Thus the assumption as to the existence of surface excitations of the roton type is very plausible. For greater accuracy in the determination of the parameters Δ, κ_0, and μ, reliable theoretical estimates of the function $\sigma_0(\rho)$ are necessary.

In our approach, the interesting problem as to whether the "capillary phonons" and "rotons" considered above comprise two portions of the same branch in the spectrum of surface excitations or whether these are portions of different branches of the excitations remains unresolved. In connection with the decay character of the excitation spectrum (3) for increasing κ, the first possibility is doubtful and the entire problem needs special investigation.

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