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SURFACE TENSION OF WEAK HELIUM ISOTOPE SOLUTIONS

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The change in the surface tension of liquid helium, due to dissolution of small amounts of an impurity, is determined. The change is negative or positive, depending on the presence of surface impurity levels. The experimental data indicate the presence of surface levels in solution of He^3 and apparently their absence in solutions of He^4 in He^3.

LIQUID He^4 is a quantum liquid at low temperatures. This circumstance exerts a strong influence on the behavior of impurity particles dissolved in it (in practice this impurity is always the isotope He^3). Indeed, the impurity atom placed in the liquid behaves like an excitation with dispersion law (see[1,2])

$$E = \Delta + p^2/2M, \tag{1}$$

where E is the excitation energy, p the momentum, and Δ and M are constants, the first of which is equal in order of magnitude to the boiling temperature of liquid helium and the second to the mass of the helium atom[1]). At sufficiently low temperatures T, the main contribution to all phenomena is made by excitations whose wavelength $\lambda = \hbar/p \sim \hbar/\sqrt{mT}$ is much larger than the interatomic distance.

The purpose of the present paper is to show that the quantum character of the liquid makes it possible to change the variation of its surface tension when sufficiently small amounts of the impurity are dissolved. Relation (1) is valid at large distances from the boundary of the liquid. It constitutes an expansion of the excitation energy in powers of $(pa)^2$ (a is the interatomic distance). Near the boundary, besides the correction for Δ (proportional to p^2), there appears a correction U which depends on z (we assume that the liquid fills the region $z > 0$). When $z \gg a$, the latter is small compared with Δ, but can be larger than $p^2/2M$. The Hamiltonian of the impurity has therefore, for $z \gg a$, the following form:

$$H = \Delta + p^2/2M + U(z). \tag{2}$$

The dependence of U on the momentum p can, of course, be neglected. The presence of the energy U(z) is connected with the long-range forces of electromagnetic (van der Waals) or acoustic origin (see[4]). We can therefore state that U depends on z in power-law fashion:

$$U(z) = U_0(a/z)^n \quad (n > 2), \tag{3}$$

where U_0 is a constant of the order of Δ.

On the basis of (2) we can write an equation for the wave function of the impurity with energy E:

$$\nabla^2\psi + 2M\hbar^{-2}[E - \Delta - U(z)]\psi = 0. \tag{4}$$

By virtue of the homogeneity of the problem in the directions x and y, the wave function is of the form $f(z)\exp(ik_x x + ik_y y)$. Substituting this in (4), we obtain

$$d^2f/dz^2 + [q^2 - \beta(a/z)^n]f = 0;$$
$$q^2 = 2M\hbar^{-2}(E - \Delta - k_x^2 - k_y^2), \quad \beta = 2M\hbar^{-2}U_0. \tag{5}$$

In region $1/q \gg z \gg a$ we can neglect the two last terms in (5). Indeed, if this is done, we obtain

$$f(z) = A + Bz, \tag{6}$$

where A and B are constants that depend on the form of U(z) at atomic distances. Regarding now the discarded terms as a perturbation, we can readily see that the first of them makes a contribution of the order of $(qz)^2 \ll 1$, and the second of the order of $(a/z)^{n-2} \ll 1$. Since the quantity q does not enter in the equation at all in the region under consideration, the ratio of the constants A and B does not depend on q. When $z \gg a$ we can neglect only the last term in (5). We then obtain

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[1]) The value of the effective mass M of the He^3 atom in liquid He^4 is known [2]. The value of Δ can be determined from an analysis of the experimental data on the dependence of the saturated-pressure over a weak solution of He^3 in He^4 on the temperature. The corresponding processing of the results of Sommers [3] gives a value $\Delta \approx -2.7°K$.

$$f = \text{const}\cdot\sin(qz + \delta).$$

The phase δ is determined from the condition for joining with (6) when $qz \ll 1$, from which we get that $\delta \propto q$.[2] At the small values of q of interest to us, we can therefore put $\delta = 0$.

Thus, the system of solutions of the wave equation (4), describing reflection of excitations from the boundary, consists of the functions $\sin(qz) \cdot \exp(ik_x x + ik_y y)$, with energy $E = \hbar^2(q^2 + k_x^2 + k_y^2)/2M$. The square of the modulus of the wave function

$$|\psi_q(z)|^2 \propto \sin^2 qz \tag{7}$$

determines the probability density of the different values of the coordinate of the impurity in a state with given q. To find the coordinate dependence of the density of the number of impurities n(z), expression (7) must be averaged over states with different values of q. Recognizing that the probability of the given value of q is proportional to $\exp(-\hbar^2 q^2/2MT)$, we obtain

$$n(z) = \text{const}\cdot \int_0^\infty \sin^2 qz \cdot \exp(-\hbar^2 q^2/2MT)\, dq. \tag{8}$$

Further, carrying out simple integration and determining the constant from the condition $n(\infty) = c\rho/m$, where c is the concentration of the solution, ρ the density of the liquid He^4, and m the mass of its atom, we have

$$n(z) = c\rho m^{-1}[1 - \exp(-2MTz^2/\hbar^2)] \tag{9}$$

We see from this formula that the density of the impurities is much below the value for $z \to \infty$ at distances of the order of $\hbar/\sqrt{MT}$ from the boundary, that is, at a distance of the order of the excitation wavelength.

Let us calculate the excess number of impurities per unit surface area:

$$n_s \equiv \int_0^\infty [n(z) - n(\infty)]\, dz. \tag{10}$$

With the aid of (9) we readily obtain

$$n_s = -c\frac{\hbar\rho}{2m}\left(\frac{\pi}{2MT}\right)^{1/2}. \tag{11}$$

This exhausts all the excess number of impurities only in the case when there are no surface levels, that is, levels with energy lower Δ localized at atomic distances from the boundary. We assume that such levels exist, and denote their minimal energy by $\Delta - \epsilon_0$ ($\epsilon_0 > 0$). Near this energy we have, obviously,

$$E = \Delta - \varepsilon_0 + k^2/2\mu, \tag{12}$$

where k is the two dimensional momentum in the plane of the boundary of the liquid and μ is a certain constant equal in order of magnitude to M.

With the aid of well known thermodynamic formulas and relation (12) we can easily calculate the chemical potential ζ_s of the impurities at the surface levels. We obtain

$$\zeta_s = \Delta - \varepsilon_0 - T\ln(\mu T/\pi\hbar^2 N_s), \tag{13}$$

where N_s is the number of impurities at the surface levels per unit area. From the condition that ζ_s be equal to the chemical potential of the impurities in the volume

$$\zeta = \Delta - T\ln\left[\frac{2m}{c\rho}\left(\frac{MT}{2\pi\hbar^2}\right)^{3/2}\right] \tag{14}$$

we obtain

$$N_s = c\frac{\hbar\rho}{m}\frac{\mu}{M}\left(\frac{2\pi}{MT}\right)^{1/2} e^{\varepsilon_0/T}. \tag{15}$$

It is assumed here that the concentration c is sufficiently small to be able to use Boltzmann statistics.

The total excess number of impurities is equal to the sum $N_s + n_s$. However, comparing (15) with (11) we see that $N_s/n_s \sim \exp(\epsilon_0/T) \gg 1$, so that the surface levels, if they exist, make the main contribution.

The surface-tension coefficient α of the solution is connected with $N_s + n_s$ by a simple relation[6]:

$$\left(\frac{\partial\alpha}{\partial c}\right)_T = -\frac{T}{c}(N_s + n_s). \tag{16}$$

If the surface levels change, then we obtain with the aid of (16) and (15)

$$\alpha = \alpha_0 - c\frac{\hbar\rho}{m}\frac{\mu}{M}\left(\frac{2\pi T}{M}\right)^{1/2} e^{\varepsilon_0/T}, \tag{17}$$

where α_0 is the surface tension of the pure solvent. In the absolute case we have on the basis of (11) and (16)

$$\alpha = \alpha_0 + c\frac{\hbar\rho}{2m}\left(\frac{\pi T}{2M}\right)^{1/2}. \tag{18}$$

We see from the obtained formulas, the surface tension decreases with increasing impurity concentration if there exist surface levels, and increases if there are none. Comparison with the available experimental data[7] gives grounds for concluding the presence of surface levels for the He^3 atom in liquid He^4. Thus, it is necessary to apply the formula (17) to weak solutions of He^3 in He^4.

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[2] We note that the situation arising here is similar to the well known problem of scattering of slow particles [5].

Comparing (17) with the data of Essel'son and Bereznyak[7], we can determine the unknown constants ϵ_0 and μ:

$$\varepsilon_0 \approx 3.1^\circ, \quad \mu \approx M.$$

If we take into consideration the temperature dependence of the surface tension of pure He^4, obtained by Atkins[8]

$$\alpha_0 = \alpha_{00} - A\left(\frac{\rho}{\alpha}\right)^{2/3}\frac{T^{7/3}}{\hbar^{4/3}} \tag{19}$$

(where A is a constant of the order of unity and α_{00} is the value of α_0 at T = 0), then we readily note that α does not depend monotonically on the temperature. Namely, the function $\alpha(T)$ for the solution has a maximum. For the temperature of the maximum we obtain from (19) and (17):

$$T \approx \frac{\varepsilon_0}{\ln(B/c)}, \quad B \sim \frac{m^{3/2}\varepsilon_0^{11/6}}{\alpha^{2/3}\rho^{1/3}\hbar^{7/3}}. \tag{20}$$

We note that such a maximum was observed by Atkins and Narahara[9].

Finally, we write out an inequality that limits the region of concentrations from which formula (17) is valid:

$$c \ll \frac{m}{\rho}\left(\frac{mT}{\pi\hbar^2}\right)^{3/2} e^{-\varepsilon_0/T}. \tag{21}$$

It expresses the fact that we should have $T_0 \ll T$, where T_0 is the degeneracy temperature of the impurities situated at the surface levels.

We now stop to discuss the case of weak solutions of He^4 in liquid He^3. The reasoning that has led us to formulas (17) and (18) remains fully in force in this case, too. In order to establish which of the two possibilities—(17) or (18)—is realized in such solutions, that is, whether or not there exist surface levels for the He^4 atom on the surface of liquid He^3, we must turn again to the experimental data. Although these data are not available at present for weak solutions, measurements of the surface tension of concentrated solutions[10] nevertheless make it quite probable that the derivative $\partial\alpha/\partial c$ is positive for small concentrations of He^4. This means that formula (18) should be applicable to weak solutions of He^4 in liquid He^3, provided c is taken to mean the concentration of He^4, ρ and m the density and mass of the He^3, and M the effective mass of the He^4 atom. We note that in this case the expression for the surface tension does not contain at all any constants characterizing the properties of the surface.

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