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SURFACE TENSION OF He II NEAR THE λ POINT AND THE BOUNDARY CONDITION OF THE ORDERING PARAMETER ON THE FREE SURFACE

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Thermodynamic considerations and the results of experiments on vapor dragging over the surface of superfluid helium under conditions of purely superfluid motion, and of thermal counterflow of the normal and superfluid components, are used to substantiate the boundary condition $\Psi = 0$ for the ordering parameter in He II at the free surface. It is shown that if $\Psi = 0$ at the surface with the vapor, the surface tension of the He II should contain an additional contribution which varies with the temperature near the λ point as $\Delta\sigma = \Delta\sigma_0\,(T_\lambda - T)^{4/3}$. This results is in qualitative agreement with the experimental data.

In the phenomenological theories of superfluidity,[1–6] an important role is played by the boundary conditions for the macroscopic complex order parameter $\Psi(\mathbf{r})$ which describes the superfluid state. As an initial variant of the Ginzburg–Pitaevskiĭ phenomenological theory,[1] arguments were brought forward according to which $\Psi(\mathbf{r})$ should vanish on the boundary with the solid wall. Experiments on the shift of the λ point in narrow slits and capillaries confirm the validity of this boundary condition. To the contrary, the problem of the condition for $\Psi(\mathbf{r})$ at the free surface remains an open question today, although it has recently been shown that the experimental data on the shift of the λ point in thin unsaturated helium films[7, 8] favor the condition $\Psi = 0$ rather than the alternative condition $(d\Psi/dx) = 0$, which is also admissible as a possibility in the Ginzburg–Pitaevskiĭ theory.

The present paper has a double purpose. On the one hand, we shall show that as $T \to T_\lambda$ the boundary condition $\Psi = 0$ at the free surface can be obtained from very general considerations which assume only the continuity of the change in $\Psi(\mathbf{r})$ in the surface layer. On the other hand, as soon as Ψ vanishes on the free surface, an additional surface energy ought to be connected with this change in Ψ. As a result, the surface tension of He II should contain an additional contribution in comparison with the surface tension of normal He I, and the curve for the dependence of the surface tension $\sigma(T)$ on the temperature should undergo some jump at the λ point. The corresponding behavior of $\sigma(T)$ has actually been observed experimentally in the researches of Atkins and Narahara,[9] who noted a significant change in the slope of the curve $\sigma(T)$ on going through the λ point. Inasmuch as the contribution to the surface tension from other factors (change in density, capillary waves) has no singularity at the λ point, the aforementioned experiments reinforce the conclusion that $\Psi = 0$ on the free surface.

1. We first consider the problem of the boundary condition for the ordering parameter near the λ point. We shall prove that on the liquid-vapor interface Ψ takes on the value[1] Ψ_0, where $0 \leq \Psi_0 \leq \Psi_e$, $\Psi_e \sim \epsilon^{\beta}$ is the equilibrium value of the ordering parameter in the liquid phase far from the surface and $\epsilon = T_\lambda - T$. The index β as well as the other critical indices used in what follows, is defined in the usual way (see, for example, [10]). In the liquid phase, the coherence length $\xi_l(\epsilon)$, which defines the characteristic size of the inhomogeneity associated with the deviation of Ψ from its equilibrium value, is equal to $\xi_l(\epsilon) = \xi_{l0}\epsilon^{-\nu'}$. The inhomogeneity of Ψ is connected with the surface energy.

$$\Delta F_s^{(l)} \sim (\partial^2 F^{(l)}/\partial\Psi^2)_e(\Psi_e - \Psi_0)^2\xi_l(\varepsilon) \sim \varepsilon^{\gamma' - \nu'}(\Psi_e - \Psi_0)^2. \tag{1}$$

Here we have used the standard definition of the critical index γ^{-1}: $\chi_l^{-1} = (\partial^2 F^{(l)}/\partial\Psi^2)_e \sim \epsilon^{\gamma'}$. On the other hand, in the gaseous phase,[2] which is not superfluid, Ψ must decay to zero from the value Ψ_0 on the boundary at distances ξ_g on the order of the interatomic distance, and the surface energy associated with the change of Ψ in the gaseous phase

$$\Delta F_s^{(g)} \sim (\partial^2/F^{(r)}/\partial\Psi^2)_0\Psi_0^2\xi_g \tag{2}$$

can depend on the temperature only through Ψ_0.

Combining (1) and (2) and minimizing with respect to Ψ_0, we obtain the result that the minimum of the total surface energy $\Delta F_s = \Delta F_s^{(l)} + \Delta F_s^{(g)}$ is achieved when

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[1] In the case of an immobile liquid, which we have in mind everywhere below, Ψ can be regarded as a real quantity.

[2] We regard the gas phase as a weakly non-ideal Bose gas, in which the superfluidity (Ψ different from zero near the surface) is "induced" by the quantum proximity effect. The situation here is completely analogous to what takes place in the case of the contact of superconducting and normal metals, [11] or, even more closely, the case of contact of the normal and superfluid phases of helium in the case for example, in which a gravitational field acts on the column of liquid He^4 near the transition point. [12]

$$\Psi_0/\Psi_e \sim (\chi_g/\chi_l)(\xi_l/\xi_g) \sim \varepsilon^{\gamma'-\nu'}. \tag{3}$$

In helium, $\nu' = 2/3$, and the value $4/3$ is usually taken for γ'.[3)] We thus see that $\Psi_0/\Psi_e \sim \epsilon^{2/3} \to 0$ as $T \to T_\lambda$.

Here the total surface-tension contribution associated with the change in Ψ, is

$$\Delta\sigma = \Delta F_s \sim \chi_l^{-1}\Psi_e^2\xi_l \sim \varepsilon^{\gamma'+2\beta-\nu'} \tag{4}$$

or, if we use similarity relations $\gamma' = 2 - \alpha + 2\beta$ and $\nu' = (2 - \alpha')/3$, then

$$\Delta\sigma \sim \varepsilon^{2(2-\alpha')/3} \sim \varepsilon^{4/3}. \tag{5}$$

We have set α' equal to its experimental value: $\alpha' = 0$.

We note that while the rate of decrease of Ψ_0 as it approaches the λ point depends on the specific meaning attached to the ordering parameter (see footnote 3), the behavior of the surface tension does not depend on the index β and is completely determined, within the framework of the similarity hypothesis, by the character of the singularity in the heat capacity.

For the relative contribution to the surface tension from the gaseous phase, using (2) and (3), we get

$$(\Delta F_s^{(g)}/\Delta F_s) \sim (\chi_l/\chi_g)(\xi_g/\xi_l)(\Psi_0/\Psi_e)^2 \sim \Psi_0/\Psi_e. \tag{6}$$

Thus, $(\Delta F_s^{(g)}/\Delta F_s) \to 0$ if $(\Psi_0/\Psi_e) \to 0$. This makes it possible, in the case of more specific estimates of the value of the contribution to the surface tension brought about by the ordering parameter (see Sec. 3), to limit ourselves to the calculation of $\Delta F_s^{(l)}$, setting $\Psi = 0$ in this case.

Everywhere above, we have neglected the finiteness of the thickness of the separation boundary, assuming that the liquid density changes discontinuously at the boundary. The finiteness of the thickness of the separation boundary could be taken into account within the framework of a more concrete phenomenological model (the expansion (7), Sec. 3), assuming that the coefficients A, B, ... in this expansion change smoothly at some distance ξ from their values A_l and B_l ... in the liquid phase of the values $A_g < 0$, B_g, ... in the gaseous phase. However, this allowance is essential only when the characteristic scale for the change in the order parameter is equal in order of magnitude to the characteristic scale for the change in the density. If $\xi_l(\epsilon) \gg \xi_\rho$, then the principal contribution to the surface tension, as can be established, will be given as before by the larger distances $r \sim \xi_l(\epsilon)$

2. The considerations set forth above are suitable only near the λ point. However, we can introduce arguments which show that far from the λ point Ψ goes to zero on the boundary with the vapor, but smoothly and without a discontinuity. This conclusion is arrived at from the results of the experiments of Binakker (unpublished; see [15]) and Osborn[15] on the measurements of the velocity of the vapor over a surface of moving He II under conditions when only the superfluid component moves and in the case of counterflow of the normal and superfluid components,[15] as well as from experimental estimates[16, 17] of the value of the coefficient of condensation in He II. It was shown in the experiments of Binakker and Osborn that the vapor is dragged over the surface of superfluid helium only by the normal component. On the basis of the Binakker experiment, Osborn[15] estimates that the maximal value of the coefficient of momentum transfer from the superfluid component to the vapor is less than 10^{-6}, and draws the conclusion that exchange of momentum and energy between the superfluid component and the vapor generally does not take place. At the same time, experimental measurements of the condensation coefficient[16, 17] show that this coefficient is of the order unity in He II, i.e., an atom of vapor incident on the surface of the liquid adheres to it with a probability of order unity.

Discussing these two results, Hunter and Osborn[17] point out that the attempt at their joint microscopic interpretation runs into difficulties: the condensing atom, as experiment shows, cannot transfer part of its energy and momentum to the superfluid component. On the other hand, the transfer of energy and momentum to the normal component by direct creation of a roton or a group of phonons, or of a roton and phonons, cannot be realized, inasmuch as it is impossible here to satisfy the laws of conservation of energy and momentum simultaneously. We are therefore obliged to turn to processes in which the creation of a roton or of phonons takes place through the medium of already existing, sufficiently energetic, thermal excitations. The probability of the latter, however, is small and, what is especially important, must change strongly with changing temperature. Experimentally, the condensation coefficient is near unity over a sufficiently wide range of temperatures.

The difficulties that have been pointed out are clearly removed if we admit that $\Psi = 0$ on the boundary with the vapor and consequently the layer of atoms of the liquid immediately adjacent to the surface, through which exchange with the vapor is effected, is completely normal. The fact that the mean kinetic energy of the atoms evaporating from the helium is greater than the temperature of the liquid in the volume[18] is not astonishing from this point of view; the effective temperature of the dense, strongly interacting gas of excitations near the surface can be very high—although other interpretations of this question are possible.[19-22]

Thus the indicated experiments give us a basis for assuming that $\Psi = 0$ on the free surface, independently of the closeness of the λ point. For this case, the specific law according to which Ψ vanishes can, of course, depend on a number of factors (in particular, the shape of $\Psi(x)$ should depend strongly on the character of the changes of the total density near the boundary. In each case, the possibility of change of $\Psi(x)$ close to the free surface should be assumed in the construction of a systematic microscopic theory of the surface tension of He II at low temperatures, as well as in the consideration of other surface effects.

[3)] The value of γ' depends on what meaning attaches to the order parameter. For $\Psi(r)$ we take its usual definition as a quantity proportional to the square root of the density of the superfluid component. In the Wong variant [4] (see also [13]), $\Psi(r)$ is given another definition, and γ' is set equal to unity. Actually, using similarity considerations, we can show that $\gamma' - \nu' > 0$ if the index η which characterizes the departure of the correlation function $\langle\Psi(r)\,\Psi(r')\rangle \sim r^{-(1+\eta)}$ at the transition point from the Ornstein-Zernike law, is less than unity. Usually, $\eta \ll 1$. [14] In the Wong variant, $\eta = 1/2$.

3. We now turn to the problem of the surface tension of He II near the λ point. We shall carry out a more accurate estimate of the numerical value of the contribution of the ordering parameter to the surface tension on the basis of some specific types of phenomenological expansion. Let us write the density of the free energy of He II in the form[1–6, 23]

$$F_{\text{II}}(\varepsilon,\Psi)=F_{\text{I}}(\varepsilon)+\frac{\hbar^2}{2m}(\nabla\Psi)^2-A(\varepsilon)\Psi^2+\frac{B(\varepsilon)}{2}\Psi^4+\frac{C(\varepsilon)}{3}\Psi^6+\ldots,\qquad(7)$$

where, following [2–6], we shall assume that $A(\epsilon) = A_0\epsilon^{4/3}$, $B(\epsilon) = B_0\epsilon^{2/3}$, $C(\epsilon) = C_0\epsilon^0$, ... For Ψ we preserve the same meaning as in the Ginzburg–Pitaevskiĭ theory:[1]

$$\rho_s=m|\Psi|^2.\qquad(8)$$

Ψ(x) obeys the equation (x is the coordinate normal to the surface):

$$\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}=-A(\varepsilon)\Psi+B(\varepsilon)\Psi^3+C(\varepsilon)\Psi^5+\ldots,\qquad(9)$$

which, in the case that we have considered, has the first integral

$$\frac{\hbar^2}{2m}\left(\frac{d\Psi}{dx}\right)^2=A(\Psi_e^2-\Psi^2)-\frac{1}{2}B(\Psi_e^4-\Psi^4)-\frac{1}{3}C(\Psi_e^6-\Psi^6)-\ldots.\qquad(10)$$

Then, finding dΨ/dx, substituting in (7), integrating $\Delta F = F_{11}(\epsilon, \Psi) = F_{11}(\epsilon, \Psi_e(\epsilon))$ and making the substitution dx → (dx/dΨ)dΨ under the integral, we get

$$\Delta\sigma(\varepsilon)=2\int_0^{\Psi_e}\left[A(\Psi_e^2-\Psi^2)-\frac{1}{2}B(\Psi_e^4-\Psi^4)-\frac{C}{3}(\Psi_e^6-\Psi^6)-\ldots\right]^{1/2}d\Psi\qquad(11)$$

or, going to the nondimensional variable $y = \Psi/\Psi_e$ under the integral sign

$$\Delta\sigma(\varepsilon)=\left(\frac{\hbar}{m}\right)^2\left(\frac{\rho_s(\varepsilon)}{\xi(\varepsilon)}\right)\int_0^1\left[(1-y^2)-\frac{1}{2}L(1-y^4)-\frac{1}{3}M(1-y^6)-\ldots\right]^{1/2}dy.\qquad(12)$$

Here $L = B(\epsilon)\Psi_e^2(\epsilon)/A(\epsilon)$, $M = C\Psi_e^4(\epsilon)/A(\epsilon)$, ... are constants which no longer depend on the temperature, and satisfy the relation $L + M + \ldots = 1$ and $\xi(\epsilon) = \hbar/\sqrt{2mA(\epsilon)}$.

For the following, we assume that we can restrict ourselves in (5) to only the first three terms in the expansion of the volume portion of the free energy density. This assumption includes most of the variants of the phenomenological theory that have been discussed to date in the literature. The integral in (12) depends in this case only on the single parameter L and is easy to evaluate. We shall give the value of the coefficient $\Delta\sigma_0$ in the temperature dependence of $\Delta\sigma(\epsilon) = \Delta\sigma_0\epsilon^{4/3}$ for the most interesting cases:

1) L = 1 (the Mamaladze variant[2])

$$\Delta\sigma_0=9.15\cdot10^{-2}\ \text{erg-cm}^{-2}\text{-deg}^{-4/3};$$ [4]

2) L = 0 (the Slyusarev–Strzhemechnyĭ variant[6])

$$\Delta\sigma_0=9.60\cdot10^{-2}\ \text{erg-cm}^{-2}\text{-deg}^{-4/3}$$

3) L = −850 (the Amit variant[3]),

$$\Delta\sigma_0=10.7\cdot10^{-2}\ \text{erg-cm}^{-2}\text{-deg}^{-4/3}$$

From these values, we can see that $\Delta\sigma_0$ does not depend very much on the higher terms of the expansion. So far as a comparison with experiment is concerned, all three theoretical curves agree, within the limits of experimental error, with the data of Atkins and Narahara,[9] although preference is given here to values of L close to unity (the Mamaladze variant).

4. Summing up, we can say that both the theoretical considerations given above and experiment[7–9, 15, 16] indicate that Ψ = 0 in He II at the free surface. Here the surface tension of He II should have an additional contribution, absent in the normal phase. The temperature dependence of this contribution near the λ point can be associated, by means of similarity relations, with the singularity in the heat capacity. New, more exact measurements of the surface tension near the λ point are necessary in order to test this relation. Measurements of the surface tension can also be used as another criterion in the selection of the particular variant of the phenomenological expansion of the free energy near the λ point.

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[4] Such a value of $\Delta\sigma_0$ is also obtained in the Wong variant, [4] which reduces in the given case to the Mamaladze variant by means of the substitution $\Psi \to \Psi\epsilon^{1/6}$.

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