mination of optical anisotropies. There is no doubt that one or more effects, not related to the reorientation and redistribution phenomena, rise to disparities in this case. New theoretical work on the dc Kerr effect, such as that recently published by Hellwarth,[1] is of great importance.

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[1] R. W. Hellwarth, J. Chem. Phys. 52, 4, (1970); 52, 2128 (1970).

[2] V. A. Zamkov, Opt. i Spektroskopiya 15, 654 (1963) [Opt. Spectry. (USSR) 15, 355 (1963).

[3] M. F. Vuks, Opt. i Spektroskopiya 23, 6 (1966); 697 (1966)[Opt. Spectry. (USSR) 23, 697 (1966)].

[4] G. Mayer and F. Gires, Compt. Rend. 258, 2039 (1964).

[5] S. Kielich, Acta Phys. Polon. 30, 4 (1966); 30, 683 (1966).

[6] M. Pauthenier, Ann. Phys. (Paris) 14, 239 (1920).

[7] F. Gires, Ann. Radioelec. 23, 281 (1968).

[8] P. Langevin, Le Radium 7, 9 (1910); 7, 249 (1910).

[9] I. E. Tamm, *Fundamentals of Electrical Theorie* (Moscow, 1954), p. 145.

[10] L. Landau and E. Lifchitz, *Electrodynamique des Milieux Continus* (Editions de Moscou, Moscow, 1969), p. 77.

[11] M. Paillette, Ann. Phys. (Paris) 4, 671 (1969).

[12] J. R. Lalanne, J. Phys. (Paris) 20, 643 (1969).

[13] The correlation coefficient r^2 is defined by $r^2 = \sum_i (y_i - \bar{y})^2 - \sum_i (y_i - y_i')^2 / \sum_i (y_i - \bar{y})^2$, where y_i is the experimental value of $(\Delta I/I)^{1/2}$, $\bar{y}$ the mean value of the y_i, and y_i' the adjusted value of y_i by using a linear relation between $(\Delta I/I)^{1/2}$ and P. See for example, E. Morice and F. Chartier, *Méthode Statistique* (Imprimerie Nationale, Paris, 1954), Vol. 2, p. 289.

[14] P. Bothorel, J. Colloid Sci. 27, 529 (1968).

[15] C. Such, C. Clement, and P. Bothorel, Compt. Rend. 271C, 228 (1970).

[16] France patent, CNRS, No. 102 348 (1967).

[17] S. Kielich, J. R. Lalanne, and F. B. Martin, Compt. Rend. B 272, 731 (1971).

[18] S. Kielich, Acta Phys. Polon. 19, 149 (1960); 22, 299 (1962).

[19] R. W. Hellwarth, Phys. Rev. 152, 156 (1966).

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Origin of Bound States of He^3 Atoms on Free Superfluid He^4 Surfaces

W. F. Saam
Department of Physics, Ohio State University, Columbus, Ohio 43210

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An approximate theory of the motion of a He^3 atom in the vicinity of a superfluid He^4 surface is presented. The theory predicts a bound state of the He^3 atom in the vicinity of the surface, in accord with experimental results. The theoretical value for the energy of this state (measured with respect to the He^4 chemical potential) is within 35% of the experimentally determined value.

I. INTRODUCTION

The existence of bound states of He^3 atoms on free superfluid He^4 surfaces was first proposed by Andreev[1] in order to explain the observed drop[2-4] in the surface tension of dilute solutions of He^3 in He^4 at low temperatures. Andreev did not, however, explain the existence of these surface states. Recently Lekner[5] has derived, using the variational principle, a simple one-dimensional Schrödinger equation governing the motion of a single He^3 atom near a free He^4 surface at zero temperature. Assuming a plane surface in the x-y plane, he took a trial wave function of the form $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = [\psi(z_1)/n^{1/2}(z_1)] \times \psi_0(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$. Here $\vec{r}_1$ is the coordinate of the He^3 atom and $\vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N$ are the coordinates of $N-1$ He^4 atoms. $\psi_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ is the ground-state wave function for N He^4 atoms with a surface in the x-y plane, and $n(z)$ is the number density associated with ψ_0. Application of the variational principle give the equation

$$\frac{d^2\psi(z)}{dz^2} + [\lambda - U(z)]\psi(z) = 0 \qquad (1)$$

for $\psi(z)$. The effective potential $U(z)$ is given by

$$U(z) = \left(1 - \frac{m_3}{m_4}\right)t(z) + n^{-1/2}(z)\frac{d^2 n^{1/2}(z)}{dz^2} \ . \qquad (2)$$

$(\hbar^2/2m_4)t(z)$ is the kinetic energy per particle in pure He^4, the bulk of the He^4 atoms being located at $z > 0$. m_3 and m_4 are the masses of He^3 and He^4 atoms, respectively. The surface-energy levels $\epsilon_s = (\hbar^2/2m_3)\lambda$ are measured with respect to the chemical potential in pure bulk He^4.

Equation (1) was not solved by Lekner, although he did point out that $U(z)$ can have an attractive region if $t(z)$ and $n(z)$ decrease monotonically as the surface is approached from the bulk. In this paper we show that the asymptotic values of $U(z)$ far from the surface can be determined exactly. Then we construct a simple analytic form for $U(z)$ by interpolating between these values and solve numerically the resulting equation. The equation has a single bound surface state with an eigenvalue about 35% above the experimentally determined value. This discrepancy is understandable if we note that the bare He^3 mass is used in the kinetic energy part of Eq. (1). This must lead to an overestimate of the kinetic energy contribution to ϵ_s.

II. DETERMINATION OF EFFECTIVE POTENTIAL

The determination of $U(z)$ proceeds from the fact, proven in the Appendix, that the ground-state wave function $\psi_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ for N He^4 atoms with a surface (the bulk being located at $z > 0$) has the asymptotic behavior

$$\lim_{z_1 \to -\infty} \psi_0(\vec{r}_1, \ldots, \vec{r}_N) \sim e^{\alpha z_1/2} g(\vec{r}_2, \ldots, \vec{r}_N), \tag{3}$$

where

$$\alpha/2 = [(2m_4 \epsilon_B/\hbar^2)]^{1/2} . \tag{4}$$

ϵ_B is the binding energy per atom for pure He^4. This is just what we expect on intuitive grounds if we think of each He^4 atom as being bound in a well of depth ϵ_B.

From (2) we may easily find the limit of $U(z)$ as $z \to -\infty$. The density $n(z)$ is defined by

$$n(z) = L^2 \int dr^{N-1} \psi_0^2(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N), \tag{5}$$

L being the dimension of the system parallel to the surface and dr^{N-1} being a compact notation for $d^3r_2 d^3r_3 \ldots d^3r_N$. Using (3) in (5), we obtain

$$n(z) \xrightarrow[z \to -\infty]{} L^2 e^{\alpha z} \int dr^{N-1} g^2(\vec{r}_2, \ldots, \vec{r}_N). \tag{6}$$

It follows immediately that

$$n^{-1/2}(z) \frac{d^2 n^{1/2}(z)}{dz^2} \xrightarrow[z \to -\infty]{} \frac{\alpha^2}{4} = \frac{2m_4}{\hbar^2} \epsilon_B . \tag{7}$$

Since

$$n(z)\, t(z) \equiv -L^2 \int dr^{N-1} \psi_0 \nabla_1^2 \psi_0, \tag{8}$$

we may use (3) to find

$$\left(1 - \frac{m_3}{m_4}\right) t(z) \xrightarrow[z \to -\infty]{} -\frac{\alpha^4}{4} \left(1 - \frac{m_3}{m_4}\right)$$

$$= -\frac{2m_4}{\hbar^2} \epsilon_B \left(1 - \frac{m_3}{m_4}\right) . \tag{9}$$

Combining (2), (7), and (9) gives

$$\frac{\hbar^2}{2m_3} U(z) \xrightarrow{\quad} +\epsilon_B , \tag{10}$$

as one might expect, especially if we note that in this limit Lekner's trial wave function (see Sec. I) $\psi(\vec{r}_1, \ldots, \vec{r}_N)$ decouples, becoming proportional to $\psi(z_1) g(\vec{r}_2, \ldots, \vec{r}_N)$.

The limit of (2) as $z \to +\infty$ is, clearly,

$$\frac{\hbar^2}{2m_3} U(z) \xrightarrow[z \to +\infty]{} \frac{\hbar^2}{2m_3} \left(1 - \frac{m_3}{m_4}\right) t_0 \equiv \epsilon_{30} , \tag{11}$$

where $(\hbar^2/2m_4) t_0$ is the kinetic energy per particle in bulk He^4. This approximate result was originally derived by Baym[6] for the energy ϵ_{30} of a He^3 atom in superfluid He^4 at $T = 0$.

We can now construct a reasonable form for $U(z)$. Assuming a surface symmetric about $z = 0$, we write

$$n(z) = n_0/(1 + e^{-\alpha z}). \tag{12}$$

This agrees with (6) and with the bulk value n_0 which $n(z)$ must take on as $z \to \infty$. It also makes precise the definition of the surface. Further, we approximate $t(z)$ by

$$\frac{\hbar^2}{2m_3} \left(1 - \frac{m_3}{m_4}\right) t(z) = \epsilon_{30} - \frac{\epsilon_{30} + \epsilon_B/3}{1 + a e^{\alpha z}} . \tag{13}$$

This agrees with the limits (9) and (11), using $m_3 = (\frac{3}{4}) m_4$. The coefficient a is determined by requiring that far inside the liquid ($z \to +\infty$), where $\nabla n(z)$ is small, we have

$$\frac{\hbar^2}{2m_3} \left(1 - \frac{m_3}{m_4}\right) \nabla t(z) \xrightarrow[z \to \infty]{} \frac{\partial \epsilon_{30}}{\partial n} \nabla n(z). \tag{14}$$

The term $d^2 n^{1/2}(z)/dz^2$ contributes no terms linear in $\nabla n(z)$ to this limit. Combining (12)–(14) gives

$$a = \left(1 + \frac{\epsilon_B}{3\epsilon_{30}}\right) \bigg/ \frac{n}{\epsilon_{30}} \frac{\partial \epsilon_{30}}{\partial n} . \tag{15}$$

We use the experimental values $\epsilon_B = 7.15$ K [7] and $\epsilon_{30} = 4.36$ K, [8] expressing energies in temperature units. Further, since ϵ_{30} is the zero-He^3-concentration limit of the He^3 chemical potential μ_3 in He^4, we have

$$\frac{\partial \epsilon_{30}}{\partial n} = \frac{\partial \mu_3}{\partial n} = (1 + \hat{\alpha}) \frac{\partial \mu_4}{\partial n} = (1 + \hat{\alpha}) \frac{m_4 s^2}{n} , \tag{16}$$

where s^2 is the sound velocity in He^4 and $\hat{\alpha} = 0.28$ is the fractional excess volume of He^3 in superfluid He^4 at $T = 0$.[9] Using $m_4 s^2 = 27.2$ K, and putting all of these results together, we find

$$a = 0.89. \tag{17}$$

Combining (2), (12), (13), and (17) we obtain

$$U(z) = \frac{\alpha^2}{4} \left[\frac{1 - 2e^{\alpha z}}{(1 + e^{\alpha z})^2} + \frac{8m_3}{\hbar^2 \alpha^2} \left(\epsilon_0 - \frac{\epsilon_0 + \epsilon_B/3}{1 + 0.89 e^{\alpha z}}\right)\right] . \tag{18}$$

$U(z)$ is plotted in Fig. 1 along with the wave function of its single bound state.

III. NUMERICAL RESULTS AND COMMENTS

For numerical work, it is most convenient to cast (1) in the dimensionless form

$$\frac{d^2 \psi(x)}{dx^2} + [\hat{\lambda} - \hat{U}(x)] = 0, \tag{19}$$

with $x \equiv \alpha z$. Then we have

$$\hat{\lambda} = \lambda/\alpha^2 = 3\epsilon_s/16\epsilon_B , \tag{20}$$

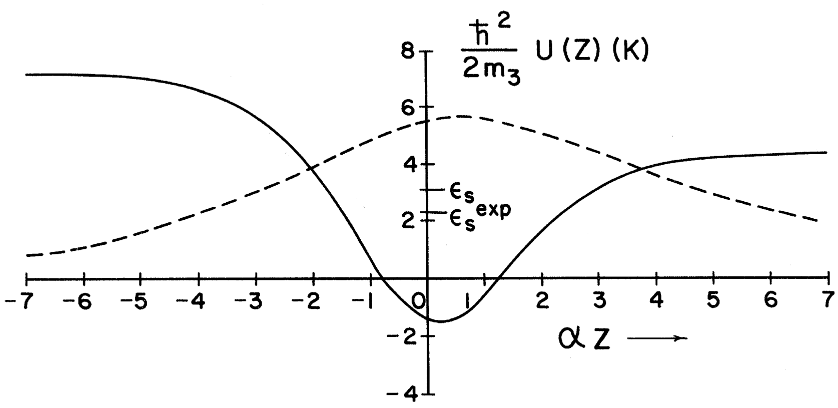

FIG. 1. Potential $(\hbar^2/2m_3)U(z)$ in K (solid line) and the wave function for its bound state (dashed line) in arbitrary units. The theoretical (ϵ_s) and the experimental values (ϵ_s^{exp}) values of the He^3 surface energy are indicated.

and, putting in numbers,

$$\hat{U}(x)=\frac{1}{4}\left(\frac{1-2e^x}{(1+e^x)^2}+0.458-\frac{0.708}{1+0.89\,e^x}\right)\quad . \tag{21}$$

Equation (19) is rather easily integrated numerically with the result that U has one bound state with energy

$$\epsilon_s=3.1\text{ K}. \tag{22}$$

The most recent experimental result is[4]

$$\epsilon_s^{\exp}=2.32\text{ K}. \tag{23}$$

Both values for the surface energy are indicated in Fig. 1.

We conclude with some commentary on our theory. First, the fact that our value (22) for ϵ_s is only about 35% above the experimental value probably indicates that we have gotten the essential physics right. The He^3 atom is bound to the surface because its excess kinetic energy relative to a He^4 atom, the term proportional to $t(z)$ in (2), falls off near the surface more rapidly than the effective single-particle potential $n^{-1/2}(z)n^{1/2\prime\prime}(z)$ rises near the surface. [Note that if $m_3=m_4$, (1) is solved by $\psi(z)=n^{1/2}(z)$, just what we expect in this case for the single-particle wave function.] In other words, a He^3 atom finds it advantageous to sit on the surface because it gains in reduction of kinetic energy relative to its large bulk value more than it loses in increasing its energy due to its attraction to the He^4 bath. Nevertheless, our theory is still quite crude. The assumption of a symmetric surface [see (12)] is certainly open to question. In fact, if we replace (12) by

$$n(z)=n_0/(1+be^{\alpha z}) \tag{24}$$

and try to lower ϵ_s by varying b, we can reduce ϵ_s by a maximum of 0.3 K.[10] This seems to be about the best which a simple theory using the bare He^3 mass can do. Physically, it is clear that (1) should reduce, as $z\to+\infty$, to

$$\frac{d^2\psi}{dz^2}+\left(\lambda-\frac{2m_3^*}{\hbar^2}\epsilon_{30}\right)\psi=0, \tag{25}$$

where $m_3^*\approx 2.34m_3$ is the effective mass for He^3 quasiparticle motion in bulk He^4. Qualitatively, then, in the region of the surface we should use a mass varying between m_3 and m_3^*. This would reduce ϵ_s further by lowering the kinetic energy of the surface quasiparticle. It is not worthwhile, however, to attempt this in view of the approximations already made. In point of fact it is not in principle clear how to consistently include a position-dependent effective mass.

Finally, it is perhaps surprising that the effective potential (see Fig. 1) becomes negative near the surface. One expects this potential to be greater than the corresponding one for a He^4 atom, which must rise as $z\to-\infty$ because of the surface energy. However, there is nothing in principle preventing such a He^4 potential from dropping near the surface before rising as $z\to-\infty$. In fact, if one uses the variational principle to derive the equation analogous to (1) for the motion of a He^4 atom, taking care to symmetrize the trial wave function,[11] one finds

$$\frac{d^2\psi(z)}{dz^2}-n^{1/2}(z)\,\frac{d^2n^{1/2}(z)}{dz^2}\,\psi(z)=-\lambda\int_{-\infty}^{\infty}dz'S(z,z')\,\psi(z'), \tag{26}$$

where the structure factor $S(z,z')$ is defined by

$$\sum_{i,j=1}^{N}\int dr^N\,\frac{\psi(z_i)\psi(z_j)}{[n(z_i)n(z_j)]^{1/2}}\,\psi_0^2(\vec{r}_1,\ldots,\vec{r}_N)\equiv\int dz_1dz_2\,\psi(z_1)S(z_1,z_2)\,\psi(z_2). \tag{27}$$

In the limit as $z\to\infty$, Eq. (26) gives the well-known Feynman[12] result for the excitation spectrum in pure He^4, while for $z\to-\infty$, it reduces to a free-particle equation. The potential term $n^{-1/2}n^{1/2\prime\prime}$ appears both in (1) and (26), and it is this term which causes the potential in Fig. 1 to be negative near the surface.

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APPENDIX

Here we examine the asymptotic behavior of the ground-state wave function $\psi_0(\vec{r}_1, \ldots, \vec{r}_N)$ for N He^4 atoms with a surface near $z=0$, the bulk located at $z>0$. ψ_0 solves the Schrödinger equation

$$H\psi_0 = \left(-\sum_{i=1}^{N} \frac{\hbar^2 \nabla_i^{\,2}}{2m_4} + \frac{1}{2} \sum_{i \neq j} V(\vec{r}_i - \vec{r}_j)\right) \psi_0 = E_N \psi_0 . \quad \text{(A1)}$$

For z_1 large and negative and all other $z_i \gg z_1$, ψ_0 must be of the form

$$\psi_0(\vec{r}_1, \ldots, \vec{r}_N) = f(z_1) g(\vec{r}_2, \ldots, \vec{r}_N). \quad \text{(A2)}$$

Since ψ_0 may be chosen to be real and non-negative, we may choose f and g real and non-negative. Putting (A2) in (A1) and noting that $V(\vec{r}_1 - \vec{r}_i)$ falls off rapidly when $\vec{r}_1$ is far from $\vec{r}_i$, we obtain

$$-\frac{\hbar^2}{2m_4} \frac{d^2 f(z_1)}{dz_1^2} g$$

$$= E_N f g - f\left(-\sum_{i=2}^{N} \frac{\hbar^2 \nabla_i^{\,2}}{2m_4} + \frac{1}{2} \sum_{i \neq j \neq 1} V(\vec{r}_i - \vec{r}_j)\right) g. \quad \text{(A3)}$$

When $-z_1$ is sufficiently large (A3) can be solved for all $z_i \gg z_1$ $(i \neq 1)$ only if

$$\left(-\sum_{i=2}^{N} \frac{\hbar^2 \nabla_i^{\,2}}{2m_4} + \frac{1}{2} \sum_{i \neq j \neq 1} V(\vec{r}_i - \vec{r}_j)\right) g(\vec{r}_2, \ldots, \vec{r}_N)$$

$$= E g(\vec{r}_2, \ldots, \vec{r}_N), \quad \text{(A4)}$$

where E is a constant. Since g is real and non-negative, it must then be the ground-state wave function for $N-1$ He^4 atoms with a surface, and

$$E = E_{N-1} . \quad \text{(A5)}$$

Combining (A3)–(A5) and noting that $E_{N-1} - E_N = \epsilon_B$, the binding energy per atom in He^4 at $T=0$, gives

$$+\frac{\hbar^2}{2m_4} g \frac{d^2 f(z_1)}{dz_1^2} = \epsilon_B f(z_1) g, \quad \text{(A6)}$$

so that as $z_1 \to -\infty$ we have

$$\psi_0 = g f(z_1) \sim e^{z_1 \alpha/2} g(\vec{r}_2, \ldots, \vec{r}_N), \quad \text{(A7)}$$

with $\alpha \equiv 2[2m_4 \epsilon_B / \hbar^2]^{1/2}$.

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[1] A. F. Andreev, Zh. Eksperim. i Teor. Fiz. 50, 1415 (1966) [Sov. Phys. JETP 23, 939 (1966)].

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

[3] K. N. Zinovyeva and S. T. Boldarev, in *Proceedings of the Eleventh International Conference on Low Temperature Physics*, edited by J. F. Allen (University of St. Andrews Printing Department, St. Andrews, Scotland, 1969).

[4] H. M. Guo, D. O. Edwards, R. E. Sarwinski, and J. T. Tough, Bull. Am. Phys. Soc. 16, 87 (1971); and (unpublished). These authors use ϵ_0 to denote what we call $\epsilon_{30} - \epsilon_s$.

[5] J. Lekner, Phil. Mag. 22, 669 (1970).

[6] G. Baym, Phys. Rev. Letters 17, 952 (1966); see also J. Bardeen, G. Baym, and D. Pines, Phys. Rev. 156, 207 (1967).

[7] H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. A 64, 1 (1960).

[8] P. Seligman, D. O. Edwards, R. E. Sarwinski, and J. T. Tough, Phys. Rev. 181, 415 (1969).

[9] D. O. Edwards, E. M. Ifft, and R. E. Sarwinski, Phys. Rev. 177, 380 (1969).

[10] Note that this is not a valid application of the variational principle.

[11] Here one uses $\psi(\vec{r}_1, \ldots, \vec{r}_N) = \sum_{i=1}^{N} [\psi(z_i)/n^{1/2}(z_i)] \times \psi_0(\vec{r}_1, \ldots, \vec{r}_N)$ as the trial wave function.

[12] R. P. Feynman, Phys. Rev. 94, 262 (1954).