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Electron localization on a liquid-helium surface

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A theoretical treatment is given of the localization or self-trapping of the motion of electrons bound in extrinsic surface states on liquid helium. For a thin helium film (~ 100 Å) on a substrate we find a trapping energy of about 8 K. We investigate the breakdown of very thin films and show that in the bulk case an earlier estimate of the trapping energy by Shikin must be revised.

I. INTRODUCTION

When a charged particle approaches the surface of a dielectric medium it is attracted by long-range polarization forces (e.g., the image force). Near the surface shorter-range interactions come into play; for the case of an electron approaching liquid helium the effect of the short-range forces is to interpose an energy barrier $V_0 \approx 1$ eV, preventing the electron from entering the liquid. The net potential thus formed has a minimum near the surface which can bind electons: Their states have become known as external surface states. Theoretical work by Cole,[1] Shikin,[2] and others and a series of remarkable experiments[3-5] have given a clear picture of the states. The energy of binding to the surface of the liquid $\epsilon_\perp$ is about 0.65 meV, and the electronic wave function peaks at a distance $a_\perp = 76$ Å above the surface. In all observations thus far electons seem to be free to move parallel to the surface.

Shikin[2] pointed out the possibility that surface-state electrons could become localized on the helium. He argued that the presence of an electric field might make it energetically favorable to create a small dimple on the surface; a deep enough dimple would localize the particle and greatly reduce its mobility parallel to the surface. This is quite analogous to the three-dimensional self-trapping which is well known for electrons in solids. Shikin gave only rough estimates for the fields necessary to cause self-trapping (which we will argue, furthermore, are incorrect). The effect has not yet been observed. In this paper we reinvestigate the problem and point out situations in which observations of the self-trapping should be possible.

It will be shown that the electric fields necessary to give significant binding are very large (~10^4 V/cm). We suggest that this difficulty can be conveniently overcome by using the well-known tendency of helium to form films on substrates. If the film is not too thick, say, on the order of 100 Å, and if the substrate has a reasonable dielectric constant, the image field *due to the substrate* will lead to self-trapping. Accordingly, we consider the theory of an electron bound to a film on a substrate, though we will treat the bulk case as well.

In Sec. II we will discuss various contributions to the total energy of an electron on a "dimpled" helium surface in the presence of a substrate; the nature of the electronic wave function will also be considered. In Sec. III a variational solution will be given for the wave function and the deformation of the helium. Section IV will be devoted to proposals for experimental tests of the effects predicted.

II. ENERGY AND WAVE FUNCTION OF ELECTRON - HELIUM SYSTEM

Our treatment of the self-trapping problem will be variational. Accordingly, we must choose a reasonable form for the wave function of the system, and display the total energy as a functional of the wave function.

In what follows the helium will be treated as a classical incompressible fluid. The quantity playing the role of its wave function is its spatial configuration and, in particular, the surface deformation, to be denoted by δ. The fluid in the absence of deformation is flat; its surface will define the plane $z = 0$. We will use a set of cylindrical coordinates whose origin is on the undisturbed surface (exactly where will be defined more precisely below). We take δ to be a function of the radial coordinate r only. Thus the deformed surface whose shape is to be determined is specified by $z = \delta(r)$. The deformation δ is assumed to be small compared to $a_\perp$ and the thickness of the film. Also, it is assumed that $|d\delta/dr| \ll 1$ and that $\delta \to 0$ as $r \to \infty$.

For the flat surface the electronic wave function has the form

$$\psi = \varphi(z)\,\chi(r)\ . \tag{1}$$

For the flat film χ is a plane wave; here we seek conditions for which χ is localized. The origin of our cylindrical coordinate system, where $r=0$, is the centroid of the localized wave function. The assumption that χ and δ are both independent of angle is in accord with physical expectations, provided this origin is chosen.

A reasonable form for φ in the case of distortion is that of Shikin[2] which we adopt; we take the wave function which we would calculate for a flat surface and replace z by $z-\delta$. Thus, for example, if V_0 is taken to be an infinite barrier we can put $\varphi(0)=0$, and then ψ will vanish on the *distorted* surface $z=\delta$, as it must. It is implicit in our discussion that surface deformations never impart sufficient energy to cause significant mixing of φ's corresponding to different states. This will occur if the self-trapping energy $\epsilon_\parallel$ is always much less than $\epsilon_\perp$, as will turn out to be true.

We now display the total energy in terms of ψ and δ. The energy is referred to the situation in which the electron is at rest far enough from the helium so that all electric fields are essentially zero, and in which the fluid is undisturbed. We seek the largest nonvanishing contributions to the energy in terms of the small quantity δ and the wave function.

There are several terms in the energy of the system which we will now discuss, starting with the energy of the helium. First, the surface area of the distorted film is larger than that of the flat film. This gives a contribution to the energy of the fluid;

$$2\pi\sigma\int_0^\infty r\,dr\left\{\left[1+\left(\frac{d\delta}{dr}\right)^2\right]^{1/2}-1\right\} \approx \pi\sigma\int_0^\infty r\,dr\left(\frac{d\delta}{dr}\right)^2 . \tag{2}$$

In this equation σ is the surface tension of helium.

In our situation we consider the fluid to be acted on by body forces, i.e., the Van der Waals force which holds the film on the substrate and gravity. Let the total potential energy per unit volume be denoted by V. In our case

$$V=\rho g z - C/(z+d)^3 . \tag{3a}$$

Here d is the thickness of the film and ρ is the mass density of helium. The form of Eq. (3a) is standard for the van der Waals potential from a semi-infinite substrate. The constant C which we use below has been derived from the work of Anderson and Sabisky.[6]

The effect of V on the energy can be divided into two terms. The first is an energy due to the shifting of the liquid,

$$2\pi\int_0^\infty r\,dr\int_0^\delta V(z)\,dz . \tag{3b}$$

A second term must be derived from $V(z)$ because we have not, so far, satisfied the requirement that the total amount of fluid be conserved in the deformation; that is, a "dimple" at the origin must give rise to a small rise in liquid level elsewhere. It is straightforward to show that the energy which results is

$$-2\pi V(0)\int_0^\infty r\,dr\,\delta(r) . \tag{3c}$$

The sum of Eqs. (2), (3b), and (3c) gives the energy of the liquid, which we denote ϵ_L.

We now turn to the electronic energy and the interaction terms. The electronic kinetic energy arising from applying the Lapalacian in cylindrical coordinates to the product $\chi\varphi$ is

$$2\pi\int_0^\infty r\,dr\left(-\chi^*\frac{\hbar^2}{2m}\nabla_r^2\chi\right), \tag{4a}$$

$$\int_{-\infty}^\infty dz\left(-\varphi^*\frac{\hbar^2}{2m}\frac{d^2\varphi}{dz^2}\right). \tag{4b}$$

In addition there are terms resulting from applying the radial Laplacian ∇_r to $\varphi(z-\delta)$. These are several expressions involving first derivatives of φ, which may be converted to vanishing boundary terms, and a small term of order $|d\delta/dr|^2$, which we neglect.[2]

The potential energy of the electron arises in part from the electric fields it experiences. In our situation they may be applied externally or may arise from the image field of the helium or the substrate. We will postpone for the moment a discussion of the image field of the helium, and we will completely neglect the corrections due to "multiple images," i.e., due to the finite thickness of the film. Each such correction involves some power of the small factor $\kappa-1$, where κ is the dielectric constant of helium.

The remaining electric fields are lumped together and called $E_\perp$; the subscript indicates that only applied fields normal to the surface are to be considered. The substrate gives rise to an image field at the surface,

$$\tfrac14 e^2(\bar\kappa-1)/(\bar\kappa+1)\,d^2 , \tag{5a}$$

which contributes to $E_\perp$. Here $\bar\kappa$ is the dielectric constant of the substrate. The energy arising from $E_\perp$ is

$$2\pi\int_{-\infty}^\infty dz\int_0^\infty r\,dr\,|\varphi(z-\delta)|^2\,|\chi(r)|^2\,eE_\perp z = \int_{-\infty}^\infty dz\,|\varphi(z)|^2\,eE_\perp z + 2\pi\int_0^\infty r\,dr\,|\chi(r)|^2\,eE_\perp\delta(r) . \tag{5b}$$

In this equation we have neglected the dependence of $E_\perp$ on position and replaced it by its value at the surface. This is justified provided that $a_\perp$, the scale on which φ varies, is small compared with d. Recall that $a_\perp$ is ≈76 Å for bulk liquid; for a thin film the strong image fields further confine the electron and justify our assumption.

Collecting terms from Eqs. (4a) and (5b), we have an energy functional governing the motion of the electron parallel to the film,

$$\epsilon_e = 2\pi \int_0^\infty r\,dr(-\chi^* \nabla_r^2 \chi + eE_\perp \delta |\chi|^2). \qquad (6)$$

Finally, we turn to the energy terms associated with the electron-helium interaction. Part of this effect has already been mentioned, namely, the electric field which the electron experiences due to the induced polarization of the helium. At large distances from the helium this takes the form of the field due to an image charge, but close to the surface it changes form in a way which is poorly understood. Well inside the helium the interaction is well approximated by a large positive constant potential V_0.

It is fortunate for our purposes here that the nature of the interaction is not relevant to the self-trapping problem; that is, the associated energy is independent of δ. Specifically, we use our variational *Ansatz* and denote the interaction potential by U. For a flat surface U depends on z alone. For a deformed surface we argue that we can replace $U(z)$ with $U(z-\delta)$. For the short-ranged repulsive forces which the electron experiences when entering the liquid this replacement is clearly valid; for the longer-range forces outside it will hold only if the scale on which the deformation varies is very much larger than $a_\perp$; in this limit the electron sees a nearly flat surface at a position $z=\delta$ below it, instead of $z=0$. Shifting the coordinate by δ than properly changes U. In Sec. III we show that we are indeed in the proper limit.

The expectation value of $U(z-\delta)$ using the wave function $\chi(r)\varphi(z-\delta)$ is clearly independent of δ. Thus all the interaction terms do not depend on δ.

The conclusion we have just reached has consequences which will be useful below. Therefore we consider it worthwhile to point out that the result is more general than our variational *Ansatz.* For example, whenever the deformation is small enough that its effects can be considered in perturbation theory, we can draw the same conclusion. For, in perturbation theory, we must consider the quantity

$$\Delta\epsilon = 2\pi \int |\chi|^2 |\varphi|^2 r\,dr\,dz\,[\,U(z-\delta) - U(z)]. \qquad (7)$$

The first-order term in the expansion of $U(z-\delta)$ has the interpretation of a force, but the total force of the electron on the helium must vanish. Thus $\Delta\epsilon$ is exactly zero.

To make the result explicit consider the case of bulk helium and take a particular simple model for $U(z)$, namely, a barrier of infinite height at the liquid surface and a pure image force outside. The downward force on the helium surface gives a contribution to $\Delta\epsilon$ which may be expressed in terms of an "electron pressure,"

$$2\pi \int_0^\infty r\,dr\,\delta |\chi|^2 \frac{\hbar^2}{2m} \left| \frac{d\varphi(0)}{dz} \right|^2. \qquad (8a)$$

The long-range forces give

$$-2\pi \int_0^\infty r\,dr\,|\chi|^2 \delta \int_0^\infty dz\, \frac{\partial U}{\partial z} |\varphi|^2. \qquad (8b)$$

If the external field is zero, the coefficient of $\delta|\chi|^2$ may be calculated from the hydrogenic wave functions φ, which have often appeared in the literature[1,2]; it is in each case the same, $2Qe^2/a_\perp^2$, where $Q=(\kappa-1)/(\kappa+1)$. Thus the sum of Eqs. (8a) and (8b) vanishes. Parenthetically, we note that if the barrier at the surface is taken to be of finite height V_0, then the electron pressure is replaced by $V_0|\varphi(0)|^2$. We thus find a consistency requirement on the electronic wave function, $V_0|\varphi(0)|^2 = 2Qe^2/a_\perp^2$.

We have given stress to the stationary property of the interaction energy because we believe that the serious discrepancy between certain of the results given in Sec. III and the work of Shikin[2] may be traced to this point. In Shikin's work the electron pressure [Eq. (8a)] was used to derive a source term in an equation determining δ. But in doing this Shikin neglected the equal and opposite term of Eq. (8b).

We conclude this section by noting a very convenient feature of the results: The energy functional of Eq. (4b), the first term of Eq. (5b), and the interaction terms depend on φ but not on χ and δ. Thus the problem of the z motion may be solved, once and for all, for a flat surface, as has been done by Cole.[7] The self-trapping problem is completely independent and may be solved by minimizing $\epsilon_L + \epsilon_e = \epsilon_\parallel$. The determination of the minimum value of $\epsilon_\parallel$ and the associated wave function is the subject of Sec. III.

III. VARIATIONAL SOLUTION

Our strategy in this section will be to do a parametric variation of $\epsilon_\parallel$. We choose for $\delta(r)$ the form

$$\delta = -\delta_0/\cosh^2(\alpha r). \qquad (9)$$

Here δ_0 is the maximum depression of the surface and $1/\alpha$ is the distance scale for the depression; they are both positive variational parameters.

The wave function χ satisfies the Schrödinger equation derived by writing the Euler-Lagrange equation for ϵ_e. After the substitution $\chi = G/\sqrt{r}$, we have

$$\frac{d^2G}{dr^2} + \left(\frac{1}{4r^2} - \frac{2meE_\perp}{\hbar^2}\delta\right)G + \frac{2m\epsilon_e}{\hbar^2}G = 0. \qquad (10)$$

If the term $1/4r^2$ were replaced by $\frac{1}{4}\alpha^2 \sinh^2(\alpha r)$, Eq. (10) would be exactly soluble. In fact, in that case we have

$$G = D \tanh^{1/2}(\alpha r)[1 - \tanh^2(\alpha r)]^{(a-1)/2}, \qquad (11a)$$

$$\epsilon_e = -\frac{\hbar^2\alpha^2}{2m}(a-1)^2 = -\frac{\hbar^2\alpha^2}{2m}\left[\left(\frac{1}{4} + \frac{2meE_\perp\delta_0}{\hbar^2\alpha^2}\right)^{1/2} - 1\right]^2. \qquad (11b)$$

In Eq. (11a) D is a normalization constant. The replacement is justified if $\alpha r \ll 1$ within the region where G is large; this will turn out to be true for the variational parameters we find. We have further checked by using the difference between the two functions as a perturbing potential. The corrections to ϵ_e are always small.

All the terms in ϵ_L [Eqs. (2) and (3)] are simple integrals of $\delta(r)$ which can be expressed in terms of the variational parameters. For example, combining Eqs. (2) and (9) gives $0.168\pi\sigma\delta_0^2$ for the surface contribution to ϵ_L. The resulting parametric variation problem for $\epsilon_L + \epsilon_e$ is not difficult. Numerical calculation gives the results plotted in Fig. 1 for varying film thickness and several electric fields. The physical parameters used for the substrate, i.e., $\bar{\kappa}$ and C, are appropriate to CaF_2.[6] For example, for a film 100 Å thick $\epsilon_\parallel/k_B \simeq 8$ K. Note that we satisfy $\epsilon_\parallel \ll \epsilon_\perp$ by a large margin; for this thickness Cole[7] finds $\epsilon_\perp/k_B \simeq 200$ K.

There are several special cases of the general problem solved numerically above which are analytically tractable. For example, if no external field is applied and δ_0/d is small, we find

$$\epsilon_\parallel/k_B = -C_1/d^4, \qquad (12a)$$

$$\delta_0 = C_2/d^2, \qquad (12b)$$

$$1/\alpha = C_3 d^2. \qquad (12c)$$

The coefficients C_1, C_2, and C_3 are solutions of complicated transcendental equations, and we have been unable to give general expressions for them. However, for CaF_2, $C_1 = 8.3 \times 10^8$ K Å^4, $C_2 = 7.8 \times 10^4$ Å^3, $C_3 = 0.34$ Å^{-1}. We should point out that a substrate different from CaF_2 will not give rise to gross differences in the results. For example, a metal will have roughly the same van der Waals constant C and an image field only about one-third larger than that of the dielectric CaF_2.

Finally, we turn to the case of the surface of bulk helium ($d \to \infty$). This case is also analytically tractable. Note that there is no self-trapping unless an external field is applied. If a field is applied, the dimple becomes very large and shallow; $\epsilon_\parallel$ is well approximated by

$$\epsilon_\parallel = -0.47(eE_\perp)^2/\sigma, \qquad (13a)$$

$$\epsilon_\parallel/k_B \approx -2.5 \times 10^{-8} E_\perp^2. \qquad (13b)$$

In the last expression $\epsilon_\parallel/k_B$ is given in K and $E_\perp$ in V/cm. Equation (8) is in disagreement with Shikin's estimate, which is linear in $E_\perp$; our estimate is smaller for small $E_\perp$. The differences can be traced to our different treatment of certain terms in the energy which we have mentioned above.

In Sec. II we mentioned several conditions which had to be satisfied in order that our relatively simple discussion of the energy be valid. An examination of Fig. 1 shows that they all do hold. For example, in order to replace $U(z)$ by $U(z-\delta)$ we required that $a_\perp$ be much smaller than the extent of the deformation, i.e., than $1/\alpha$. Since $a_\perp \leq 76$ Å, Fig. 1 bears out our assumption even for very thin films.

IV. PROPOSED EXPERIMENTS

The theory we have outlined can hopefully be subjected to experimental test. The most direct

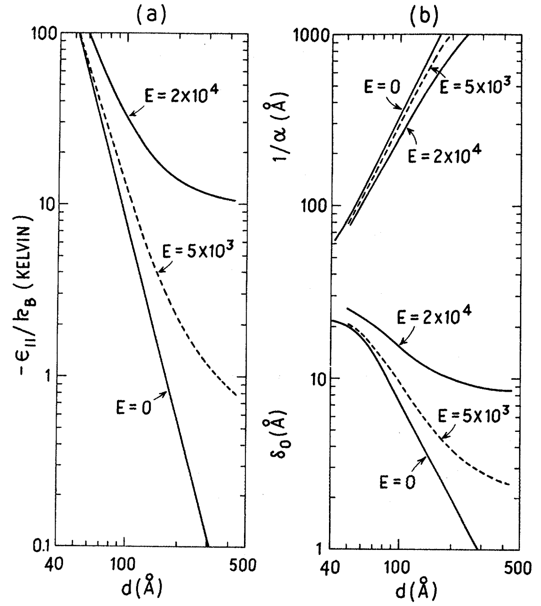

FIG. 1. (a) Dimpling energy and (b) parameters for films of various thickness. The lower curves in (b) represent δ_0, the upper $1/\alpha$. The applied electric fields are given in V/cm.

test would be to attempt to observe the mobility of the electron along the surface. When self-trapping sets in the mobility should greatly decrease; the self-trapped electron should have an effective mass on the order of a helium atomic mass because of the fact that it must drag the liquid deformation along as it moves.

The main obstacle to such an observation seems to be the small size of $\epsilon_{\parallel}$ for bulk fluids in moderate electric fields; we must have $\epsilon_{\parallel}/k_B > T$ if the electron is not to be thermally excited from its dimple. For thin films the situation should be quite different. Films 100 Å thick will have $\epsilon_{\parallel}/k_B \sim 8$ K; the mobility decrease should be observable in this case.

With our results in hand, we can also inquire about the breakdown of very thin helium films. Cole[7] found that a flat film would allow electrons to tunnel to the substrate at a thickness of about 10 Å. This result should be modified if for no other reason than that thinning of the film due to dimpling would assist tunneling. It seems likely, however, that another process should lead to breakdown at still larger thicknesses; namely, tunneling not directly to the substrate but to the bubble or negative-ion level in the liquid. The energy of the bubble is modified by the image field of the substrate and can be lowered from its usual position, about 0.1 eV above the vacuum, to equal $\epsilon_{\perp} + \epsilon_{\parallel}$. Suppose the bubble level is thus resonant with the extrinsic state for bubbles at some distance x above the substrate, and that $d - x$ is reasonably small. We might nevertheless predict that bubble formation would be very unlikely, since the electron must not only tunnel, but also nucleate a large (~15-Å radius) void in the liquid. However, if dimpling occurs as we have predicted, the electron will excavate, as it were, its own bubble, and remove the tunneling barrier as well; the dimple should be an efficient nucleation center. We argue that this "bubbling" process becomes favorable when $d - \delta_0 \simeq x$. From our results above, the criterion is satisfied for films with $d = 40$–50 Å. The prediction of breakdown at these reasonably large thicknesses could also be subjected to test.

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