Vibrational Modes of a Negative Ion in Liquid Helium*

V. Celli
University of Virginia, Charlottesville, Virginia
and
Morrel H. Cohen
The James Franck Institute, University of Chicago, Chicago, Illinois
and
M. J. Zuckerman
Solid State Theory Group and Department of Physics, Imperial College, London S. W. 7, England
(Received 15 April 1968)

A general expression is obtained for the breathing mode and the surface-distortion modes of a negative ion or electron bubble in liquid He^4 at low temperatures. The electron is assumed to be in a spherical potential well of finite depth. The modes are damped because of the excitation of compressional waves in the surrounding fluid. Numerical calculations indicate that the breathing mode gives rise to a broad resonance in the vicinity of 10^{11} sec^{-1} and that there is a rather sharp quadrupole distortion mode with frequency varying from 1.6×10^{11} to 5.6×10^{11} sec^{-1} as the external pressure varies from 0 to 20 atm.

I. INTRODUCTION

The problem of excess electrons in liquid helium has been the subject of considerable research.[1-3] The theory due to Ferrell[1] and Kuper[2] suggests that the excess electron is not in direct contact with the liquid. Instead it creates an almost macroscopic spherical bubble for itself by quantum kinetic pressure, which balances the surface tension and hydrostatic pressure at the surface of the bubble. The radius of the bubble varies from 10 to 16 Å with hydrostatic pressure.[3] The depth of the potential well for the electron is found to be approximately 1.0 eV from photo-ionization experiments.[4] Periodic discontinuities in the mobility of both positive and negative ions in He II have been found by Careri and others.[5] It has been suggested that these discontinuities are due to the formation of quantized vortex rings found in the wake of these ions by Rayfield and Reif.[6] However Cope and Gribbon[7] propose that head-on collisions between rotons and vibrating electron bubbles can also give rise to such discontinuous steps in the mobility. The expression they use for the modes of vibration of the bubble is due to Rayleigh[8] for the surface vibrations of a spherical droplet of incompressible fluid. This model is too simple since it ignores the quantum nature of the electron inside the bubble. In this paper we develop a theory of the vibrations of the bubble taking into account the quantum kinetic pressure of the electron. The results are radically different from Cope and Gribbon's and do not support the explanation of the Careri mobility steps suggested by these authors. Other recent work based on a somewhat different bubble model[9] is in qualitative agreement with our results.

A general expression for the breathing and surface modes of the bubble is derived in Sec. 2. The electron is assumed to be at the center of a spherical potential well of depth V_0. The surrounding helium liquid is treated as a compressible fluid and classical expressions are used for the energy due to the surface tension and the hydrostatic pressure of the liquid. The driving force which activates the surface modes of the bubble can be either an electromagnetic field or a sound wave, in the z direction. The resultant radial deformation $\Delta(\theta)$ of the bubble may then be expressed as a function of the polar angle. The Hamiltonian of the electron is next perturbed to second order in $\Delta(\theta)$ and the resultant change in kinetic pressure is calculated in terms of the electronic wave functions of the unperturbed spherical well. Use of the boundary conditions at the surface of the bubble and the Born-Oppenheimer approximation yields a general expression for the modes of vibration of the bubble. Section 3 gives the results of numerical calculations of the frequency and damping constant for the breathing mode and the quadrupole surface mode. Similar work has been done by Gross and Tung-Li[9] in the limit of an infinite spherical potential well and an incompressible fluid.

II. THE GENERAL EQUATION FOR THE MODES OF VIBRATION OF AN ELECTRON BUBBLE

Let the shape of the bubble be described in spherical coordinates by the equation

$$r = a + \Delta(\theta) \qquad (2.1)$$
$$\Delta(\theta) = {\sum_n}' a_n P_n(\cos\theta)$$

where the prime indicates that the sum over n begins with $n = 1$. The coefficients a_n will be regarded as infinitesimal. To second order, the surface area S and the volume V of the bubble are given by Rayleigh[8];

$$S = 4\pi a^2 + 2\pi {\sum_n}' (2n+1)^{-1}(n^2+n+2)a_n^{\,2}, \qquad (2.2)$$

$$V = (4\pi/3)a^3 + 4\pi a {\sum_n}' (2n+1)^{-1} a_n^{\,2}. \qquad (2.3)$$

The Hamiltonian of the trapped electron is to second order in a_n

$$H(a) - V_0[\delta(r-a)\Delta(\theta) - \tfrac{1}{2}\delta'(r-a)\Delta(\theta)^2] \qquad (2.4)$$

where δ is the Dirac delta function, a prime indicates differentiation, and $H(a)$ is the Hamiltonian of an electron trapped in a spherical well of depth V_0 and radius a.

At equilibrium under a uniform pressure p the bubble is spherical, all the coefficients a_n vanish, and the equilibrium value of a is determined by the condition that the total energy $E_{tot}(a)$ be a minimum. This leads to the equation

$$-dE_{00}(a)/da \equiv V_0 R_{00}{}^2(a) = 8\pi\sigma a + 4\pi p a^2 \qquad (2.5)$$

where $R_{00}(r)/r$ is the normalized radial wave function and E_{00} the eigenvalue in the ground state of $H(a)$. When p equals the external hydrostatic pressure p_e, the solution of (2.5) will be denoted by a_e. Similarly, the equilibrium values of S and V are denoted by S_e and V_e. Deviations from static equilibrium are described quite generally by letting the shape of the bubble vary according to (2.1), where we now insert

$$a = a_e + a_0 \,. \qquad (2.6)$$

The pressure on the surface of the bubble becomes $p_e + \Delta p(\theta)$, with

$$\Delta p(\theta) = \sum_n p_n P_n(\cos\theta). \qquad (2.7)$$

The unprimed sums in (2.7) and in the following include $n=0$. The total energy E_{tot} of the ion can now be expanded around the equilibrium values. We have, to second order in a_n and p_n,

$$E_{tot} = E_{el} + \sigma S + p_e V + S_e \int_0^\pi \Delta p(\theta)\Delta(\theta)\sin\theta d\theta, \qquad (2.8)$$

where E_{el} is the ground-state expectation value of (2.4). It should be noticed that terms linear in a_0 actually vanish because of the equilibrium condition (2.5). The total energy (2.8) is then

$$E_{tot} = E_{00} + \sigma S_e + p_e V_e + \sum_n (2n+1)^{-1} \times (\tfrac{1}{2}K_n a_n{}^2 + 4\pi a_e{}^2 p_n a_n), \qquad (2.9)$$

where E_{00} is the ground state energy of $H(a_e)$ and the effective spring constants K_n are computed from (2.2), (2.3), and (2.4). The result is

$$K_n = 4\pi\sigma(n^2+n+2) + 8\pi p_e a_e - 2V_0 R_{00} R_{00}' + 2V_0{}^2 \sum_j \frac{R_{00}{}^2 R_{jn}{}^2}{(E_{00} - E_{jn})}, \qquad (2.10)$$

where E_{jn} and $R_{jn}(r)/r$ are, respectively, the energy and the radial wave function for the jth state of $H(a_e)$ belonging to the nth spherical harmonic. Here and in the following a prime denotes differentiation with respect to r and all functions of r are to be evaluated at $r = a_e$ if no explicit argument appears. For $n=0$ the term $j=0$ is not included in the sum in (2.10).

If the shape of the bubble and the pressure at its surface are allowed to vary with time, a time-dependent disturbance will result in the surrounding liquid. Such a disturbance is described generally enough by a linear combination of kinetic potentials of the type

$$\varphi_n h_n(kr) e^{-i\omega t} P_n(\cos\theta), \qquad (2.11)$$

where k and ω are related through the sound velocity c

$$\omega = kc \,. \qquad (2.12)$$

In (2.11) and in the following h_n is short for $h_n{}^{(1)}$, the spherical Hankel function corresponding to the boundary condition of outgoing waves at infinity. The normal component of the velocity at the surface of the bubble should equal the time derivative of (2.1). This implies

$$\varphi_n h_n{}' = -i\omega a_n \,. \qquad (2.13)$$

The pressure exerted by the liquid on the surface of the bubble is of the form (2.7), with

$$p_n = i\omega\rho\varphi_n h_n \,, \qquad (2.14)$$

where ρ is the density of the undisturbed liquid. It can be verified *a posteriori* that the Born-Oppenheimer approximation is valid, so that at each instant the bubble takes the equilibrium shape under the pressure $p(\theta)$. This implies that E_{tot} is stationary with respect to a_n, or

$$K_n a_n + 4\pi a_e{}^2 p_n = 0. \qquad (2.15)$$

Equations (2.12) through (2.15) lead to an eigenvalue equation for the vibration frequencies ω_n, which are in general complex. The corresponding solutions for the kinetic potential decay exponentially in time and increase without bound with the distance from the bubble, because of (2.12). Although such solutions in themselves are devoid of physical significance, a knowledge of the complex eigenfrequencies is quite useful. Thus, if an external driving force is added, it is found that there are resonances in the response of the system. Physically, the external driving force may be an electromagnetic field acting on the trapped electron or an incoming acoustic wave (see Wang[10]).

It can be shown that the partial wave amplitudes b_n of the scattered acoustic wave for unit incident intensity are given by

$$b_n = (2n+1)i^{n-1} \frac{xj_n + x_n{}^2 dj_n(x)/dx}{xh_n + x_n{}^2 dh_n(x)/dx} \,, \qquad (2.16)$$

where $x = ka_e = \omega a_e/c$, and x_n is given by (3.1) below. We expect then to observe the vibrational modes of the bubble as resonances in the amplitudes of the scattered acoustic wave. [Compare (2.16) with (3.2) below.]

The spring constant K_n can easily be evaluated in closed form as follows. First we eliminate σ in favor of the experimentally accessible quantity p_e by using (2.5). Then (2.10) can be rewritten, for $n \neq 0$, omitting from now on the subscript e, since all quantities are evaluated at equilibrium

$$K_n = -2\pi p a(n+2)(n-1) + (2V_0 R_{00}{}^2/a) \times [\tfrac{1}{4}(n^2+n+2) - aR_{00}{}'/R_{00} - V_0 a^3 G_n(a,a;E_{00})] \,. \qquad (2.17)$$

We have introduced here the notation $G_n(r,r';E)$ for the radial coefficient of the nth spherical harmonic with zero azimuthal quantum number in the expansion of the Green's function for a spherical well, at energy E. The coefficient G_n obeys the differential equation

$$\left\{-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}-\frac{n(n+1)}{r^2}\right]+V(r)-E\right\}$$
$$\times G_n(r,r';E)=\frac{1}{r^2}\delta(r-r'), \tag{2.18}$$

where $V(r)$ equals $-V_0$ for $r<a$ and vanishes for $r>a$. For $r'=a$, the solution of (2.18) with appropriate boundary conditions is

$$\begin{aligned} G_n &= Aj_n(\alpha r) \quad r<a \\ &= Bh_n(i\beta r) \quad r>a, \end{aligned} \tag{2.19}$$

with

$$\begin{aligned} \hbar^2\beta^2/2m &= -E \\ \hbar^2\alpha^2/2m &= V_0+E. \end{aligned} \tag{2.20}$$

Matching the two solutions at $r=a$, we obtain

$$G_n(a,a;E)=-(2m/\hbar^2a^2)(h_n'/h_n-j_n'/j_n)^{-1}. \tag{2.21}$$

When $E=E_{00}$, α and β are related by

$$\alpha\cot\alpha a=-\beta \tag{2.22}$$

and a manageable expression can be obtained for K_n.

For $n=1$, we expect on physical grounds to find no restoring force, because it can be seen that K_1 is proportional to the second-order energy change when the bubble is rigidly shifted; this change must of course be zero. One can also verify explicitly that K_1 vanishes after substituting G_1 as given by (2.19) into (2.17).

For $n=0$, formula (2.17) should be modified by replacing $G_0(a,a;E_{00})$, which diverges, by the limit (for E going to E_{00}) of

$$G_0(a,a;E)-R_{00}^2/a^2(E-E_{00}). \tag{2.23}$$

The resulting expression is also derived by a more direct method in the next section.

III. NUMERICAL EVALUATIONS OF THE BREATHING AND QUADRUPOLE MODES

For the following it is convenient to introduce the dimensionless variable $x=ka=\omega a/c$. The natural frequencies of the problem, in dimensionless units, are

$$x_n=(a/c)(K_n/4\pi\rho a^3)^{1/2}. \tag{3.1}$$

Then the eigenvalue equation for ω is, from (2.15) and preceding equations,

$$x\,dh_n(x)/dx=-(x/x_n)^2h_n(x). \tag{3.2}$$

We now proceed to an evaluation of the complex frequencies of the lowest modes of vibration.

Breathing Mode

For $n=0$, the eigenvalue equation (3.2) can be solved explicitly to give the eigenfrequency

$$w_0=(cx_0/a)[(1-\tfrac{1}{4}x_0^2)^{1/2}-\tfrac{1}{2}ix_0]. \tag{3.3}$$

The spring constant K_0 is most easily evaluated directly from the formula

$$K_0=d^2E_{00}/da^2+8\pi(\sigma+pa), \tag{3.4}$$

from which once again we can eliminate σ by use of the equilibrium condition (2.5). Putting

$$\gamma=\beta a/(1+\beta a), \tag{3.5}$$

we have from (2.20) and (2.22)

$$V_0R_{00}^2(a)=-dE_{00}/da=\gamma\hbar^2\alpha^2/ma, \tag{3.6}$$

and we obtain

$$K_0=(\hbar^2\alpha^2/ma^2)[2\gamma+6\gamma^2-2(\alpha a)^2/(1+\beta a)^2]+4\pi pa, \tag{3.7}$$

$$K_0\to 8\hbar^2\pi^2/ma^4+4\pi pa \text{ for } \beta a\to\infty. \tag{3.8}$$

Representative values of K_0 and of the real and imaginary parts of ω_0 are given in Table I for the values of a determined experimentally by Springgett and Donnelly.[11] It should be noticed that the values of ω_0 are very sensitive functions of a, varying approximately as $a^{-7/2}$. Thus uncertainties in a affect rather seriously the estimated value of ω_0. The results are also somewhat dependent on the sound velocity c. For consistency, we take the values of c at 1.5°K, the temperature at which a was determined.[11] With all these limitations in mind, the only conclusion to be drawn from the results of this subsection is simply that there exists a broad resonance in the neighborhood of $\omega_0=10^{11}$ sec^{-1}, the maximum of the resonance shifting to higher frequencies with increasing pressure.

Quadrupole Oscillations

Next we look for solutions of (2.17) for $n=2$, since, as we saw, there are no modes with $n=1$. The value of K_2 in the limit $\beta a\to\infty$ can be ob-

TABLE I. The stiffness constant K_0 and the real and imaginary parts of the frequency ω_0 of the breathing mode, as a function of pressure at $T=1.5$°K.

p (atm)	ρ (g/cm^3)	c/a (10^{11} sec^{-1})	K_0 (erg/cm^2)	Reω_0 (10^{11} sec^{-1})	$-$Imω_0 (10^{11} sec^{-1})
0	0.1452	1.472	48.5	0.777	0.222
4	0.1508	1.985	93.1	1.35	0.526
8	0.1562	2.374	129	1.75	0.770
12	0.1607	2.715	162	2.11	1.00
16	0.1648	3.036	198	2.46	1.26
20	0.1685	3.356	238	2.84	1.57

tained independently of the theory of Sec. 2 by noticing that to first order a quadrupole distortion is identical to a spheroidal distortion. The use of Moszkowski's calculation[12] for the second-order electronic energy change due to the spheroidal distortion gives the following result for K_2:

$$K_2 = 64.94\hbar^2/ma^4 - 8\pi pa. \tag{3.9}$$

This agrees with the result of Gross and Tung-Li.[9] More generally, K_2 can be obtained for finite V_0 from (2.17) and (3.3). After some algebra, the result is

$$K_2 = \frac{2\hbar^2\alpha^2}{ma^2}\frac{\beta a}{(1+\beta a)^2} \times \left((\alpha a)^2 \frac{(\beta a)^2 + 3\beta a + 3}{3(1+\beta a)} - 1\right) - 8\pi pa. \tag{3.10}$$

From this, (3.9) is recovered in the limit $\beta a \to \infty$, $\alpha a \to \pi$. The eigenvalue equation (3.2) now becomes:

$$x_2^2(ix^3 - 4x^2 - 9ix + 9) = -x^2(x^2 + 3ix - 3). \tag{3.11}$$

This equation must be solved numerically for the values of x_2^2 at hand, which are somewhat larger than unity. The results are given in Table II, the values used for c and a being the same as for Table I. The roots come in pairs, with equal and opposite real parts and equal imaginary parts. One pair of roots are almost pure imaginary, the other almost real. Only the value of $\omega_2 = cx/a$ pertaining to the latter is given in Table II, as the former does not correspond to a sharp resonance.

TABLE II. The stiffness constant K_2 and the real and imaginary parts of the frequency ω_2 of the quadrupole distortion mode, as a function of pressure at $T = 1.5$°K.

p (atm)	K_2 (erg/cm^2)	Reω_2 (10^{11} sec^{-1})	$-$Imω_2 (10^{11} sec^{-1})
0	75.2	1.60	0.0434
4	143	2.67	0.122
8	198	3.48	0.208
12	249	4.16	0.296
16	303	4.84	0.399
20	364	5.56	0.532

CONCLUSIONS

We conclude that the model considered indicates the existence of a rather sharp resonance for quadrupole distortions. It is hoped that experimental evidence will be forthcoming to check the calculations of this section. In particular, data from acoustic attenuation and Raman scattering off liquid helium in the presence of negative ions should show peaks from which the vibrational frequencies of the bubble can be obtained. Work is in progress to calculate the expected results of such experiments using the model presented in this paper, which is more manageable than the description of the bubble "from first principles" employed by Gross and Tung-Li.[9] In fact the two descriptions are quite closely related and in a way complementary. Our model has an unphysical discontinuity of the fluid density at the boundary; Gross and Tung-Li avoid this, but they constrain the electron in a well of infinite depth. Either of these approximations however has little effect on the answers obtained. The main difference between the two approaches is that we allow the vibrational energy of the bubble to be carried away by exciting phonons in the surrounding fluid.[10] Physically, this must be so, although a description of the dynamics of the fluid in terms of undamped phonons may not be appropriate for the short wavelengths involved.

ACKNOWLEDGMENTS

The authors wish to thank Professor B. Deaver, Professor L. M. Falicov, Professor N. Cabrera, and Dr. F. Moss for stimulating discussions, and B. Duvall for undertaking the calculations leading to the results of Tables I and II.

*Sponsored by the Air Force Office of Scientific Research, United States Air Force, under grant/contract AFOSR-1138-66 and by the National Science Foundation and the Office of Naval Research.

[1]R. Ferrell, Phys. Rev. 108, 167 (1957).

[2]C. G. Kuper, Phys. Rev. 122, 1007 (1961).

[3]B. E. Springett, Morrel H. Cohen, and Joshua Jortner, Phys. Rev. 159, 183 (1967).

[4]J. A. Northby and T. M. Sanders, Jr., Phys. Rev. Letters 18, 1184 (1967).

[5]For recent work in this area, including references to previous publications, see L. Bruschi, P. Mazzoldi, and M. Santini, Phys. Rev. 167, 203 (1968).

[6]G. W. Rayfield and F. Reif, Phys. Rev. 136, A1194 (1964).

[7]J. A. Cope and P. W. F. Gibbon, Phys. Letters 16, 128 (1965).

[8]Lord J. W. S. Rayleigh, *Theory of Sound* (Dover Publications, Inc., New York, 1945), p. 364.

[9]E. P. Gross and H. Tung-Li, Phys. Rev. 170, 190 (1968).

[10]S. Wang, Ph.D. dissertation, University of Michigan, 1967 (unpublished).

[11]B. E. Springett and R. J. Donnelly, Phys. Rev. Letters 17, 364 (1966).

[12]M. Moszkowski, Phys. Rev. 99, 803 (1955).