1. Introduction

In this short review, we summarize experimental and theoretical studies of the properties of electrons in liquid helium. Electrons can be introduced into liquid helium by means of a radioactive source, by field-emission from a sharp tip, or by photoemission from the wall of a container. An electron entering helium loses kinetic energy by ionization and excitation of helium atoms (provided its energy is high enough) and by the production of elementary excitations of the liquid (rotons and phonons). After the electron has lost its kinetic energy it forces open a cavity in the liquid and becomes trapped in this cavity. This trapping occurs because the energy of the “bubble” state is lower than the energy that the electron would have if it were moving through uniform bulk liquid. We discuss the detailed calculation of the energy of these electron bubbles in the next section.

There are several reasons the study of these electron bubbles is of interest. The electron bubble is a unique system with no analogue. The bubbles form nanostructures of well defined geometry (almost perfectly spherical below 1 K). These nanostructures have the property that, unlike other quantum dots, when the electron is excited to a higher energy state there is a large change in the bubble size and shape. Thus it is interesting to study what happens when light is absorbed by an electron bubble. When the velocity of the bubble through the liquid exceeds a critical value, quantized vortices are produced, and the bubble can become trapped on a vortex.

2. Electron Bubble in the Ground State

We first consider why it is energetically favorable for an electron to become trapped in a bubble. The bubble state was first proposed by Careri et al.\textsuperscript{1) following an earlier proposal by Ferrell\textsuperscript{2) regarding the structure of positronium in liquid helium}. An electron entering helium has to overcome a potential barrier of height $U_{\text{b}}$. This object is referred to as an electron bubble, and has been studied experimentally and theoretically for many years. At first sight, it would appear that because helium atoms have such a simple electronic structure and are so chemically inert, it should be very easy to understand the properties of these electron bubbles. However, it turns out that while for some properties theory and experiment are in excellent quantitative agreement, there are other experiments for which there is currently no understanding at all.

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$$E_{\text{bubble}} = E_{\text{zp}} + E_{\text{S}} + E_{\text{V}} = E_{\text{zp}} + \alpha A + PV,$$

(1)

where $\alpha$ is the surface tension of helium, $A$ is the surface area, $P$ is the applied pressure, and $V$ is the volume of the bubble. Hence, for a spherical bubble of radius $R$ the energy is

$$E_{\text{bubble}} = \frac{h^2}{8mR^2} + 4\pi R^2\alpha + \frac{4}{3} \pi R^3 P,$$

(2)

where $m$ is the mass of the electron. In the absence of any applied pressure, the radius corresponding to the minimum energy is

$$R_{\text{min}} = \left( \frac{h^2}{32\pi m\alpha} \right)^{1/4},$$

(3)

and the bubble energy for this radius is

$$E_{\text{min}} = h \left( \frac{2\pi\alpha}{m} \right)^{1/2}.$$

(4)

The surface tension of helium at low temperatures is 0.375 erg cm\textsuperscript{-2}.\textsuperscript{4) Hence the radius $R_{\text{min}}$ is 18.9 Å and the energy is 0.21 eV. Thus, an electron in the bubble state has an energy considerably less than the energy $U_{\text{b}}$ of an electron moving through bulk liquid.

The calculation of the energy that has just been given is based on several simplifying assumptions. It has been assumed that the surface energy of the helium is simply proportional to the area of the surface. Clearly, for a bubble of radius 19 Å there may be significant corrections to the surface energy arising from the curvature of the surface. In the calculation of the zero-point energy of the electron, it has been assumed that the wave function $\psi$ of the electron goes to zero at the bubble wall. The penetration of the wave function into the wall gives a decrease in the electron energy. The degree to which this penetration takes place depends on the potential $U(r)$ experienced by the electron at the helium surface ($r$ is the distance from the center of the bubble). This potential depends on the density profile $\rho(r)$ of the helium in the vicinity of the bubble surface. The density profile $\rho(z)$ of the planar liquid–vapor interface for helium has been measured,\textsuperscript{3) and the width of the interface was found to be approximately 7 Å. The density profile $\rho(r)$ for the electron bubble differs from $\rho(z)$ because of the
curvature of the surface and because the interaction between the electron and the helium further modifies the helium profile. Thus, it is necessary to find a self consistent solution for $\psi(r)$ and $\rho(r)$. This problem has been tackled in a number of papers, mostly by using some form of density functional theory for the helium. As an example, we show in Fig. 1 the results of the recent calculation by Pi et al.\textsuperscript{10}

A further correction to the energy comes from polarization effects. The electron inside the bubble polarizes the surrounding helium and this lowers the total energy of the system. The simplest approximation is to take the electron as fixed at the center of the bubble; then this leads to a polarization energy of

$$E_{\text{pol}} = -\frac{(\varepsilon - 1)\psi^2}{2R}, \quad (5)$$

where $\varepsilon$ is the dielectric constant of the helium. In a more correct calculation, one can allow for the fact that the electron is not localized at the center of the bubble but has a probability $\psi^2 dV$ of being within some volume $dV$. Evaluation of the polarization energy averaged over all possible positions of the electron gives a value of $E_{\text{pol}}$ that is increased by a factor of 1.345 relative to the value given in eq. (5). For $R = 19\,\text{Å}$, this gives an energy of 0.028 eV, a 14% decrease in the total energy of the bubble. There is also a slight decrease in the equilibrium radius.

At a finite temperature, the shape of the bubble is modified due to thermal fluctuations. The normal modes of a spherical bubble can be classified by the usual quantum numbers $l$ and $m$. Each mode has a frequency $\omega_l$ (dependent only upon $l$) and the amplitude has a Gaussian probability distribution. Representative shapes are shown in Fig. 2. One can see that at a temperature of 1 K or below, the fluctuations in shape are small. The bubble shape is also modified if the pressure is more negative than a critical value $P_c$, there is no value of the radius at which the energy is a minimum and so beyond this point the bubble begins to grow very rapidly, i.e., “explodes”. This effect was first predicted by Akulichev and Boguslavskii\textsuperscript{14} and was observed experimentally by Classen \textit{et al.}\textsuperscript{15} A focusing ultrasonic transducer was used to generate a high amplitude pressure oscillation within a small volume of liquid helium. If there is an electron bubble within this volume, this bubble will explode and quickly grow to a size large enough to be detected by light scattering. The critical pressure $P_c$ is ap-
proximately −1.9 bars at low temperatures and changes with temperature primarily because of the variation in the surface tension. A comparison of the experimentally measured critical pressure2,15 with theory10 is shown in Fig. 4.

This technique in which a sound pulse is used to explode an electron bubble can be used to make a movie showing the motion of a single electron.16 This is technically more difficult than the experiment just mentioned because it is necessary to generate a sound wave that has an amplitude sufficient to exceed the critical pressure not just in a small focal region, but over a macroscopic volume (several cm). Sound pulses are applied at a repetition rate of 32 per second thereby causing the electron bubble to explode and become visible every 31 ms. The helium is illuminated with light from a flash lamp synchronized to the application of the sound. As an example of the sort of images that can be obtained, Fig. 5 shows a recording of the motion of an electron made in this way.

3. Excited States and Optical Transitions

To further test the theory described in the previous section, one can measure the optical absorption of the bubbles. For an electron confined in a spherical box, electric-dipole transitions from the ground state can occur to energy levels with angular momentum \( l = 1 \). If the potential is infinite outside the box, these levels have electron energy of

\[
E_{nl} = \frac{\hbar^2 \beta_{nl}^2}{2mR^2},
\]

where \( \beta_{nl} \) is the \( n \)-th zero of the spherical Bessel function \( j_l(x) \). Thus, optical transitions occur at photon energies of

\[
e_n = \frac{\hbar^2}{2mR^2} [\beta_{nl}^2 - \pi^2].
\]

Numerical values are \( \beta_{11} = 4.493 \) and \( \beta_{21} = 7.725 \). Then using a radius of 19 Å appropriate to liquid with zero applied pressure, the energies for the lowest two optical transitions are found to be 0.11 and 0.53 eV. Of course, these simple estimates do not take into account the corrections discussed in the previous section, such as the penetration of the wave function into the liquid, the width of the helium wall, etc. A detailed calculation allowing for these effects has been performed by Grau et al.17 using a density-functional method and the results obtained over a range of pressure are shown in Fig. 6.

The measurement of the optical absorption is very challenging. It is hard to have a high density of electron bubbles because even in the absence of an applied electric field, the space charge drives the electrons to the walls of the cell. The first measurements\(^{18,21}\) did not measure the absorption directly. It was discovered that when electron bubbles were illuminated with light of the correct wavelength to excite the electron, there was a change in the mobility of the bubbles. It was proposed that this change in mobility comes about because before illumination the electron bubbles are trapped on quantized vortices, and that the excitation of the electrons enables them to escape.\(^{18,19,22}\) We discuss this mechanism in more detail in §6. The first experiments in which the optical absorption was observed by direct measurement were performed by Grimes and Adams\(^{23}\) and by Pereversev and Parshin.\(^{24}\) The data of Grimes and Adams\(^{21,23}\) for the transition energy as a function of pressure are included in Fig. 6. It can be seen that the agreement between experiment and theory is excellent thereby confirming the basic assumptions about the physics of the bubble state.

In the optical absorption experiments, it is also possible to measure the width of the absorption line. One contribution to the width comes from the finite lifetime of the excited state; however, as we will show later, this contribution is negligible. The main contribution comes about because the shape of the bubble fluctuates and for each shape there is a slightly different photon energy required to make the optical transition. As mentioned earlier, a bubble has a spectrum of normal modes for shape oscillations; the amplitude of these modes is non-zero due to both zero-point and thermal fluctuations. The theory of the line width due to shape fluctuations was first considered by Fomin\(^{25}\) who gave only an order of magnitude estimate of the line width, specifi-
cally $10^{12} \text{s}^{-1}$ (=0.0007 eV), about 30 times smaller than the experimental result. Fowler and Dexter\textsuperscript{26} gave a more careful analysis but not including quantitatively the effect of all normal modes of vibration. They obtained a width of the 1S to 1P transition of 0.013 eV, still significantly less than the measured line width. A much more detailed theory of the effects of the different modes was then worked out by Maris and Guo.\textsuperscript{12} The line width arises from the mode with $l = 0$ (the “breathing mode”) and also the 5-fold degenerate $l = 2$ modes. A displacement of the bubble surface corresponding to the mode with $l = 0$ shifts each of the three 1P levels equally and by itself would lead to a Gaussian line shape. Displacements of the bubble surface due to the $l = 2$ vibrational modes, on the other hand, result in a splitting of the 1P electronic levels and lead to a non-Gaussian line shape. The final results of the calculation\textsuperscript{12} are in excellent agreement with the line-shape measurements of Grimes and Adams.\textsuperscript{21,23} The fluctuations in bubble shape should also give a significant absorption cross section for transitions from the 1S state to states with D symmetry.\textsuperscript{27}

Once the electron has made a transition to an excited state, the shape of the electron bubble undergoes a large change before reaching a shape of mechanical equilibrium. The pressure exerted on the bubble wall by the electron is

$$P_{el} = \frac{\hbar^2}{2m} \left( \nabla \psi \right)^2. \quad (7)$$

For mechanical equilibrium this pressure has to be balanced by the sum of the pressure $P$ that is externally applied to the liquid and the force due to surface tension. Hence

$$\frac{\hbar^2}{2m} \left( \nabla \psi \right)^2 = P + \alpha(k_1 + k_2), \quad (8)$$

where $k_1$ and $k_2$ are the principal curvatures. Thus, if the wave function changes, the curvature of the surface also has to change. For example, for P states the wave function vanishes everywhere in the $z = 0$ plane, and so the electron exerts no pressure on the wall in this plane. Thus, if the liquid pressure is zero, the sum of the curvatures $k_1$ and $k_2$ must be zero. Calculated bubble shapes for some of the low energy excited states are shown in Fig. 7.\textsuperscript{28} Note that these different states are labeled with reference to the quantum numbers of the electron in a spherical bubble. Thus, for example, the 1P state is the state that results by starting with a spherical bubble containing an electron with the wave function

$$\psi \propto \left[ \sin(\pi r/R) \cos(\pi r/R) \right] \cos \theta,$$

and then adiabatically adjusting the bubble surface and wave function so as to lower the total energy, i.e., the sum of the energy of the electron and the surface energy.

Investigations of these equilibrium shapes reveal a number of interesting effects. Because of the complexity of the problem, most of the calculations have used the simplest model, i.e., the bubble surface has been taken as having a sharp interface and the penetration of the electron wave function into the helium has been ignored. Some of the results obtained are as follows:

a) The discussion of the 1P state just given refers to a starting state $\psi_{110}$, i.e., a state with quantum numbers
$n = 1$ (no radial nodes), $l = 1$, and $m = 0$. Of course, for a spherical bubble there are also states with $m = \pm 1$. For these states the electron pressure $P_e$ still has axial symmetry and so at first sight one might expect that from this initial state the electron bubble could relax to an equilibrium shape with axial symmetry. However, it turns out that such shapes are unstable against small non-axially symmetric perturbations. One finds that once the possibility of such perturbations is allowed for, the bubble evolves into a shape that is identical to the $1P$ bubble shown in Fig. 7 but with the symmetry axis rotated.\(^{29}\) This has been investigated for the states with $n = 1$ and $l = 1$ but may possibly be a general result.

b) As the pressure is raised, the “waist” of the $1P$ bubble (see Fig. 7) decreases. By the time a pressure of 10 bars is reached, the radius of the waist has decreased to a few times the interatomic spacing, and so the use of the simple model with a sharp interface becomes questionable. Is the $1P$ bubble stable under these conditions? To investigate this it is necessary to use a reliable density functional for the helium. Lehtovaara and Eloranta\(^{11}\) have used a DF method to calculate the properties of the $1P$ bubble at zero pressure. It would be very interesting to extend this type of calculation to high pressures.

c) For the $2P$ bubble, a different type of instability occurs when the pressure is increased to 1.53 bar.\(^ {30}\) This instability occurs because the bubble shape becomes such that the $2P$ electron wave function is degenerate with the $1F$ state. Once the wave function has transitioned to $1F$ the waist of the bubble shrinks to zero and the bubble splits into two bubbles. The wave function inside each of these bubbles is of the $1P$ form.

d) For the starting $S$ states $\psi_{200}$ and $\psi_{300}$, there is again a surprise. The shape shown in Fig. 7 for the $2S$ state is based on the assumption that the bubble has spherical symmetry. However, Grinfeld and Kojima\(^ {11}\) showed that unless the pressure in the liquid is below $-1.23$ bar the $2S$ bubble is unstable against perturbations that lack axial symmetry. Since the bubble is unstable against a uniform radial expansion when the pressure is below $-1.33$ bar, this means that the bubble is spherical over only a very small pressure range. In the pressure range immediately above $-1.23$ bar, the bubble was shown to have tetrahedral symmetry (see Fig. 8). Above a pressure of $-0.65$ bar, the tetrahedral $2S$ bubble becomes unstable and relaxes to the $1D$ state. The $3S$ bubble has been studied Maris and Guo.\(^ {31}\) and has an even more complex behavior.

It would be very interesting to investigate all of these effects using a density functional approach. In addition, it should be noted that these calculations just described all the effects using a density functional approach. In addition, it would be very interesting to investigate all of these states and the results of a calculation\(^ {30}\) of the decay rates is shown in Fig. 9. Note that according to the Franck–Condon principle\(^ {32}\) these transitions between electronic states should be considered to take place while the shape of the bubble remains constant.

There are a number of experiments that could be performed to investigate the excited states. A measurement of the photon energies of the emitted light would provide a
Table I. Calculated values of the critical pressure at which electron bubbles explode. The calculation is described in ref. 35.

<table>
<thead>
<tr>
<th>Quantum state</th>
<th>Critical pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1S</td>
<td>−1.89</td>
</tr>
<tr>
<td>2S</td>
<td>−1.33</td>
</tr>
<tr>
<td>1P</td>
<td>−1.63</td>
</tr>
<tr>
<td>2P</td>
<td>−1.22</td>
</tr>
<tr>
<td>1D</td>
<td>−1.49</td>
</tr>
</tbody>
</table>

valuable test of the theory. This would require the detection of rather weak radiation in the far infrared but should be possible. A measurement of the mobility of bubbles (see next section) in excited states could give information about the bubble size but appears to be impossible to perform because of the short lifetime. One interesting way to test the theory is by means of cavitation experiments of the type described at the end of §2. As already mentioned, the 1S bubble becomes unstable and explodes at a critical pressure of −1.9 bar. Electron bubbles in an excited state will explode at a negative pressure of smaller magnitude, and the calculated values are listed in Table I. Thus, if a helium cell containing electron bubbles is illuminated with light of the appropriate wavelength, the threshold negative pressure for cavitation should be reduced. This effect has been detected and the measured reduction in the magnitude of the negative pressure is in agreement with theory.

4. Exotic Ions

In this and the following sections, we turn to consider a number of experiments that have given results that are not understood. The first experiments that we discuss are ion mobility measurements. To measure the mobility, electrons are first introduced into the liquid at the top of the experimental cell. They are prevented from moving into the main part of the cell by means of a negative potential applied to a grid. The voltage on this grid is then switched to allow a pulse of ions to pass into a drift region where they are subject to a uniform and known electric field. The time that it takes the ions to reach a collector electrode is measured and from this time, the mobility of the ions is determined. Schwarz has measured the mobility of electron bubbles over a wide temperature range using this time-of-flight method. The theory of the mobility has been studied by Barrera and Baym and by Bowley, and good agreement between theory and experiment was achieved. However, in another experiment performed in 1969, Doake and Gribbon detected negatively-charged ions that had a mobility substantially higher than that of the normal electron bubble negative ion. The ions were produced using an α source in the liquid. These “fast ions” were next seen in another time-of-flight experiment by Ihas and Sanders (IS) in 1971. They showed that the fast ion could be produced by either an α or β source, or by an electrical discharge in the helium vapor above the liquid. At 1 K, the mobility of the fast ions was about 7 times higher than the mobility of the normal ions. In addition, they reported the existence of two exotic ions with different mobilities. In their measurements, the mobility in large electric fields was studied, whereas IS had investigated the mobility in low fields. EM showed that, like the normal ion, the exotic ions nucleate vortices when their velocity reaches a critical value v*. This critical velocity was found to be larger for the exotic ions of higher mobility. The “fast ion” did not nucleate vortices. In another study, Williams et al. investigated how the production of the exotic ions was affected by the characteristics of the electrical discharge.

For ions moving in superfluid helium at a temperature around 1 K, the mobility is limited by scattering by rotons, and so the mobility should vary with temperature approximately as exp(Δ/kT), where Δ is the roton energy gap. One can see from Fig. 10 that log μ is indeed proportional to T−1. The slope of the plot of log μ vs T−1 is close to, but slightly larger than Δ. At 1 K the roton mean free path is
Table II. Radius of the fast ion (F) and some of the exotic ions estimated from their measured mobility as reported in ref. 42. This table is based on the assumption that the radius of the normal ion (N) is 19 Å.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>7.3</td>
</tr>
<tr>
<td>1</td>
<td>8.9</td>
</tr>
<tr>
<td>2</td>
<td>9.3</td>
</tr>
<tr>
<td>3</td>
<td>9.6</td>
</tr>
<tr>
<td>4</td>
<td>11.9</td>
</tr>
<tr>
<td>5</td>
<td>12.3</td>
</tr>
<tr>
<td>6</td>
<td>13.0</td>
</tr>
<tr>
<td>7</td>
<td>13.6</td>
</tr>
<tr>
<td>8</td>
<td>14.2</td>
</tr>
<tr>
<td>9</td>
<td>15.6</td>
</tr>
<tr>
<td>10</td>
<td>16.8</td>
</tr>
<tr>
<td>N</td>
<td>19</td>
</tr>
</tbody>
</table>

larger than the diameter of the ion, and so the drag exerted on the ion by the roton gas is roughly proportional to the cross-sectional area of the ion, i.e., proportional to the square of the radius. The normal electron bubble has a radius of around 19 Å, and since the measured mobility of the exotic ions is as much as 4 times the mobility of the normal ion, the radius of the exotic ions must lie in the range between about 10 and 19 Å. From the measurements of the mobility, the radius of the ions can be estimated as listed in Table II. The measurements by Eden and McClintock show that the critical velocity of an ion should increase with increasing radius of the ion. Thus, the measurements of the critical velocity also indicate that the exotic ions are smaller than normal electron bubbles.

So far it has not been possible to find any model that can explain the nature of these objects. If they were bubbles containing an electron in an excited state, the bubble would be larger and so the mobility would be lower. In addition, the lifetime of the excited states is much less than the time it takes for the exotic ions to drift the length of the experimental chamber. If the exotic ions were free electrons, i.e., electrons not trapped in a bubble, they should have a much larger mobility than that measured experimentally. In addition, a free electron is expected to form a bubble in a very short time. Helium negative ions do exist but also have a lifetime much less than that of the exotic. Sanders and Ihas have considered the possibility that the exotic ions could be bubbles containing two or more electrons. Such bubbles would be larger than normal electron bubbles, and so one would expect that the critical velocity for vortex nucleation would be smaller than for normal bubbles, in contrast to the experimental findings. In addition, calculations show that a bubble containing two electrons is unstable against fission into two bubbles each containing a single electron. Finally, one could fall back on the idea that the ions are some sort of impurity ion, but this too appears to be untenable. One would have to suppose that because of the electrical discharge in the vapor above the liquid, atoms are sputtered off of the electrodes that produce the discharge and off the walls of the experiment cell. The amplitudes of the signals due to the 13 exotic ions that are detected are roughly comparable, i.e., lie in a range spanning about a decade. Thus, the sputtered material would have to be composed of 13 different elements in roughly equal amounts. This seems very implausible. In addition, there are not many elements that when introduced into liquid helium as negative ions will form bubbles in the required size range. For the normal electron bubble one can consider that the bubble is prevented from collapsing by the outward pressure exerted on the wall by the wave function of the electron. Now consider, for example, a negative ion in which the last electron has a binding energy of $E_0$ when the ion is in vacuum. The electron wave function will fall off with distance as $\exp(-r\sqrt{2mE_0}/\hbar)$. If, for example, $E_0 = 1$ eV this means that the wave function will fall off as $\exp(-0.5r)$ where $r$ is measured in Angstroms. Thus, at a distance $r$ of 6 Å, for example, the wave function has already decreased to a very small value. Hence, when such an ion is placed in liquid helium the outermost electron cannot exert enough pressure to maintain a bubble with a radius of 10 to 15 Å. To explain the existence of a bubble in this size range, it is necessary to consider impurity atoms in which the last electron has a very weak binding, or even atoms which do not form bound negative ions in vacuum. This point has been made very clearly in a paper by Grigorev and Dyugaev. They show that to have a bubble radius larger than 12 Å, the electron affinity in vacuum has to be smaller than about 0.15 eV. There are a very limited number of elements that meet this condition and it is hard to believe that 13 of these elements could be present as impurities in the electrodes or cell walls.

It is important to note that the exotic ions have been seen only when the electrons are introduced through the use of a discharge in the vapor above the helium; this is not a necessary condition for the production of the fast ion. One could conjecture that some unknown charged complex is formed in the ionized vapor. Another possibility is that the intense light emitted from the discharge has some effect on the electron bubbles once they have been formed in the liquid.

5. Ions and Vortices

The idea that vorticity in a superfluid should be quantized was first put forward by Onsager and the concept of discrete quantized vortex lines was proposed by Feynman. The quantization of circulation was demonstrated in an elegant experiment by Vinen. Rayfield and Reif made the remarkable discovery that under some conditions an electron will move through superfluid helium at a velocity that decreases as the applied electric field increases. It was found that at a critical velocity a fast moving electron bubble nucleates a vortex ring and becomes attached to it. The work done on the electron by the electric field causes the vortex ring to increase in diameter and because of this increase the velocity of the ring decreases. A comprehensive review of theoretical and experimental work on vortices has been presented in a book by Donnelly. The theory of the nucleation of vorticity by a moving electron bubble has been developed by Muirhead, Vinen, and Donnelly. Their result for the critical velocity was
close to the value found experimentally, \(60\) It is generally accepted that the binding of an electron bubble to a vortex line comes about because when the bubble is located with its center on the core of the vortex line, it displaces superfluid that has a high kinetic energy. On this basis, the binding energy can be shown to be \(61\)
\[
V_0 = \frac{2\pi \rho_s \hbar^2 R}{m^2} \left[ \left( 1 + \frac{a^2}{R^2} \right)^{1/2} \sinh^{-1} \left( \frac{R}{a} \right) - 1 \right],
\]
(9)
where \(\rho_s\) is the superfluid density, \(R\) is the radius of the bubble, and \(a\) is the “healing length” estimated to be 1.46 Å. One can attempt to experimentally determine \(V_0\) from an analysis of the time \(\tau\) it takes for bubbles to escape after being trapped on vortices. This time is expected to vary with temperature as
\[
\tau^{-1} = \Gamma_0 \exp(-V_0/kT),
\]
(10)
where \(\Gamma_0\) is the attempt frequency for escape. Because \(\tau\) varies very rapidly with temperature, experimental data\(2,63\) can be obtained only over a very narrow temperature range; at saturated vapor pressure this range is from about 1.6 to 1.7 K. These data have been analyzed in different ways. Douglass\(62\) took \(\Gamma_0\) to be independent of temperature, and found that the temperature-dependence of \(\tau\) was best fit with \(V_0 = 140\) K. Pratt and Zimmerman obtained a similar value when they analyzed the temperature-dependence of their data.\(63\) Parks and Donnelly,\(61\) on the other hand, developed a theory of the prefactor and then chose \(V_0\) to give the measured magnitude of \(\tau\) in the center of the temperature range over which measurements were made. This gave a binding energy of about 45 K. For this to be consistent with eq. (9) the size of the bubble would have to be significantly less that the value of around 19 Å that is indicated by the optical absorption measurements. Several authors have tried to resolve this inconsistency. Pi et al.\(64\) have performed a density functional calculation using a functional scheme that has proven to be very accurate for the calculation of other properties of helium.\(65\) They find values for \(V_0\) of 104.5 K at \(T = 0\) and 97.4 at 1.6 K. Padmore\(66\) has suggested that the fluctuations in the position of the vortex line caused by the presence of the bubble will modify the temperature-dependence of the escape rate. This idea has been developed further in a series of papers by McCauley and Onsager,\(67\) but the overall situation remains unclear.

It appears likely that these difficulties are related to another problem. In §2 we described the ultrasonic experiments in which it was possible to measure the negative pressure \(P_c\) at which an electron bubble becomes unstable and explodes. In these experiments it is possible to also measure the explosion pressure \(P_{\text{UO}}\) for electrons that are trapped on vortices. The magnitude of \(P_{\text{UO}}\) was found to be about 13% less than the magnitude of \(P_c\).\(8,68\) Qualitatively, this difference is not surprising. The circulation of liquid around the core of the vortex gives a Bernoulli pressure which makes the pressure at the bubble lower than the pressure that is applied to the bulk liquid. However, the calculated difference between \(P_{\text{UO}}\) and \(P_c\) is only 4%. This difference has been obtained both from a simple theory along the same lines that leads to the result eq. (9) for the bubble energy,\(8\) and also by a detailed density functional theory.\(64\) Furthermore, it is curious that while theory appears to give too large a value for the binding energy, it gives too small a shift in \(P_c\). It would have seemed more likely that if there is something wrong with the general theoretical approach, the theory would either overestimate or underestimate the magnitude of both effects. Finally, we note that the theory of both effects are perhaps based on some unrealistic assumptions. In the calculation of the binding energy,\(63,64\) the calculated quantity \(V_0\) has been the difference in energy between two configurations. The first configuration can be considered to be a straight line vortex of length \(L\) running between two parallel plates a distance \(L\) apart, together with an electron bubble at a large distance from the vortex. The second configuration is with the vortex still running between the plates and the bubble centered on the vortex line. Thus, in the calculation it is assumed that when the bubble becomes attached to the vortex line the length of vortex line that is present decreases by approximately the diameter of the bubble. It would be more realistic to consider a vortex ring but then it is not obvious how much the length of vortex line will change when the bubble becomes attached. The same issue arises in the calculation of the change in the critical pressure.

The ultrasonic method has also revealed that there is another type of electron bubble (unidentified object UO).\(68\) This is found to explode at a critical pressure \(P_{\text{UO}}\) of magnitude significantly smaller than the magnitude of \(P_{\text{UO}}\), i.e., \(|P_c| > |P_{\text{UO}}| > |P_{\text{UO}}|\). Since the UO explodes at a smaller pressure, it appears likely that it is larger than the normal electron bubble. The UO has only been seen when the liquid contains a high density of vortices at low temperatures and so it is probable that the UO is an electron bubble attached in some way to a vortex, or possibly to more than one vortex. Two possible origins of the UO objects have been considered. The magnitude of the explosion pressure would be reduced if a bubble could be attached to a vortex line with two quanta of circulation. However, such vortices of higher circulation are believed to be unstable against decay into two normal vortices. A second possibility is that two vortices could be attached to a single electron bubble. This, again, would give a smaller explosion pressure. This has been investigated by Pi et al.\(69\) who find that the change in the explosion pressure is less than what is required to explain the experimental data.

Finally, we mention that the trapping of electrons provides a means to obtain information about the geometry of vortex lines. Packard and collaborators\(69\) were able to photograph the places where vortex lines in rotating helium reached the free surface of the liquid. More recently, in the movies made as described in §2, one can see some electrons that move on snake-like paths through the liquid.\(16\) It appears that these electrons are attached to quantized vortices and are sliding along the vortices as they move through the liquid. Current efforts are directed towards using this technique to obtain detailed images of the geometry of vortices.\(70\)

### 6. Dynamics of the Electron Bubble

In this review, we have so far mostly focused on the static properties of the electron bubbles such as the equilibrium shapes of bubbles in different quantum states. We now turn to consider situations in which the shape of the bubble changes rapidly with time. As a first example, consider the
“solvation process”, i.e., the initial formation of the bubble state. This has been discussed by Rosenblitt and Jortner.\textsuperscript{71) They consider an initial bubble of radius \( \sim 3 \) Å and find that the time \( \tau_{\text{expand}} \) for the bubble to reach full size is 3.9 ps. As the bubble grows, sound waves are radiated away into the surrounding liquid. In principle, the growth of the bubble could be measured by means of ultrafast optical techniques but this has not yet been done.\textsuperscript{72) The time \( \tau_{\text{expand}} \) can be estimated from measurements in which electrons are injected into liquid helium from a metal surface, and these estimates\textsuperscript{73) are in reasonable agreement with the theoretical value. If the electron is excited with light of sufficiently high photon energy, it will be ejected from the bubble into a free state, and the bubble will then collapse. Calculations give a time of 20 ps for this to happen.\textsuperscript{74) These calculations of Rosenblitt and Jortner treat the helium as a classical fluid without dissipation and the bubble is taken to have a sharp surface. It would be interesting to extend these calculations by using density functional methods and a first step in this direction has been taken by Eloranta and Apkarian.\textsuperscript{74)}

A more complicated dynamical problem arises when the electron is excited not out of the bubble but into the 1P or 2P states. As already mentioned, according to the Franck–Condon principle one should consider that the electronic transition occurs quickly, and the bubble begins to change shape after this transition has taken place. After excitation the electron exerts on the wall of the bubble a pressure as given by eq. (7), and the bubble evolves into a non-spherical shape. A full calculation of the evolution of the bubble shape should include allowance for the damping of the motion due to the normal fluid viscosity of the helium, the radiation of sound waves into the liquid, and the use of a density functional to correctly treat the density variation near the surface of the bubble. A calculation including all of these effects has not been done. In Fig. 11, we show the results of a calculation\textsuperscript{75) for a highly simplified model in which the liquid is treated as incompressible and inviscid. The electron is excited to the 1P state at time zero and the liquid moves as a result of the surface tension forces and the outward pressure exerted by the electron. After about 11 ps, the shape of the bubble is close to the equilibrium shape for the 1P bubble as shown in Fig. 7. However, at this instant the liquid at the poles is flowing away from the bubble center and the liquid at the waist is flowing inwards. As a result of this inertia, the bubble shape continues to change and at approximately 19.5 ps the bubble breaks into two pieces of equal size. The two pieces separate with a substantial velocity.

Now consider some of the limitations of this calculation. In the calculation leading to the results shown in Fig. 11, it has been assumed that the wave function has odd parity and that the bubble shape has even parity. As a consequence, each of the two baby bubbles that are produced has exactly the same size and contains electron wave function of equal amplitude. At first sight, one might argue that this is extremely unlikely to be the final state if a bubble in liquid helium at finite temperature is excited by light. Because of thermal fluctuations, the starting bubble will inevitably be somewhat distorted from spherical. Therefore as the point of fission is approached, it would seem that the electron wave function will simply move into whichever part of the bubble happens to be slightly larger and the other part will collapse. It turns out, however, that because of the peculiarities of quantum mechanics exactly the opposite happens.\textsuperscript{28) This is because the system is in an excited state and so the amplitude of the wave function is larger in the smaller bubble. This effect thus tends to drive the system towards a division of the bubble into two equal parts. Whether in fact this effect is large enough to cause a finite fraction of the wave function to end up in each baby bubble is not established. Elser,\textsuperscript{76) for example, has argued that before complete division of the bubble takes place the wave function of the electron will cease to deform adiabatically as the bubble shape develops and that, as a result, all the wave function will end up in one of the parts. This part will expand to become a conventional ground state bubble and the other part containing no wave function will collapse.

Clearly, if the energy loss due to the radiation of sound and the viscosity of the liquid is above a critical value, fission will not occur, and the bubble will relax to the equilibrium 1P shape. The loss due to sound radiation should not have a marked dependence on temperature and so one can certainly expect that the sum of these two energy loss mechanisms will increase with increasing temperature. There should also be a pressure effect. As already noted in discussing equilibrium shapes, the waist of a 1P bubble decreases markedly as the pressure is increased. Thus, for high pressures a time evolution that gives even a small overshoot of the equilibrium 1P shape will lead to fission and so fission should occur up to higher temperatures, perhaps even above the lambda transition. Thus, one can anticipate that fission will occur only in the region of the \( P-T \) plane as shown schematically in Fig. 12. Below the “fission line” 1P bubbles should be produced, whereas above the line fission should occur and so there will be no 1P bubbles resulting from optical illumination. A quantitative calculation of the boundary line in the \( P-T \) plane has not yet been reported.

The behavior indicated qualitatively in Fig. 12 has been detected using the ultrasonic technique\textsuperscript{77) and provides strong support for the theoretical ideas just described. If no pressure is applied to the liquid, 1P bubbles are produced even down to a temperature of 1.3 K. At a pressure of 1 bar,
1P bubbles are seen only above a temperature of approximately 1.5 K. Under the pressure–temperature conditions such that no 1P bubbles are produced by optical excitation, it appears that instead other objects are produced that require a larger negative pressure to explode. The nature of these objects is not understood at present.

Although this experiment provides strong evidence that fission of the bubble does occur, it does not determine what happens to the wave function of the electron. Jackiw et al.\(^{78}\) and Rae and Vinen\(^ {79}\) argue that even if some part of the wave function of the electron ends up in each of the baby bubbles, the final state of the system will always be one bubble containing all of the wave function of the electron, and that this bubble would be no different from an ordinary electron bubble. If this is really what happens and it happens in a very short time (e.g., a time of the order of the 10 ps), then under conditions of pressure and temperature such that fission of the bubble does occur, there should be no net effect of light on the electron bubbles, i.e., the bubbles should all return to their original state after the light is absorbed. However, this is not consistent with what is seen in the ultrasonic experiment just mentioned.\(^ {77}\)

Is there a connection between the fission process and the increase in mobility that is seen when bubbles in helium are illuminated with light of the right wavelength to excite optical transitions? Northby and Sanders\(^ {18}\) noted that the mobility enhancement was observed only for fields greater than about 1 kV cm\(^{-1}\) at 1.3 K, and suggested that it “may involve the interaction of the ion with turbulence or viscosity”. A field of 1 kV cm\(^{-1}\) at this temperature should give a velocity\(^ {80}\) of around 6 m s\(^{-1}\), much less than the critical velocity at which an electron bubble nucleates vortices, so it is not clear why the mobility enhancement occurs only above this field strength. But they also noted that the enhancement became unobservable above about 1.7 K. This certainly supports the idea that vortices are involved since it is known that at this temperature the trapping time for electron bubbles on vortices becomes very short. Zipfle and Sanders\(^ {19,20}\) studied the mobility enhancement as a function of pressure. They found that the temperature at which the signal disappeared decreased as the pressure was raised, becoming 1.34 K when the pressure reached 16 bar. This provides further support for the vortex interpretation because, from the results of Pratt and Zimmerman,\(^ {63}\) the escape time at zero pressure and 1.7 K (the condition at which the Northby–Sanders signal disappeared) is very close to the escape time at 16 bar and 1.34 K. These escape times are roughly 0.3 s. Grimes and Adams\(^ {21}\) also attributed the mobility enhancement that they saw to the escape of electron bubbles from vortices as a result of illumination, and again found that there was a strong correlation between the temperature at which the signal disappeared and the temperature at which the escape time dropped to a critical value. It is interesting to note, however, that Grimes and Adams could detect no enhancement at pressures below 1 bar, whereas Northby and Sanders, and Zipfle and Sanders, did detect a signal. It is possible that this is because Grimes and Adams were looking at the 1S → 1P transition whereas the other experiments studied the 1S → 2P transition. Elser\(^ {81}\) proposed that the signal in the Grimes and Adams experiment came about because after excitation to the 1P state the bubble undergoes fission, and the baby bubble that does not contain the electron collapses releasing heat. He proposed that if the pressure is below 1 bar, fission will not occur and so the amount of heat released will be reduced and not sufficient to enable the surviving bubble to escape from the vortex. The assumption that fission does not occur below a pressure of 1 bar is consistent with the ultrasonic experiments already mentioned.\(^ {77}\) Moreover, one would expect that for the 1S → 2P transition the amount of heat released should be larger, whether or not fission occurs, and so an excited bubble can escape even at zero pressure.

An alternative possibility is that the bubble escapes from the vortex “mechanically”. If fission occurs after the light is absorbed, the two baby bubbles will be ejected with a substantial velocity in opposing directions. Whether or not we accept the idea that one of them immediately collapses (whatever “immediately” means!), clearly the surviving bubble (or bubbles if each baby bubble contains a fraction of the wave function) has a chance of escaping from the potential binding it to the vortex just due to its high velocity. Since the ultrasonic experiments indicate that fission does not occur below 1 bar, one would not expect to see electron bubbles escaping from vortices in this pressure range. This is in agreement with experimental observations.

The initial experiments that we have been discussing did not provide an estimate of the probability that an electron bubble will escape from a vortex after absorbing a photon. This probability has now been measured\(^ {82}\) and found to be \( \sim 10^{-4} \); surprisingly small. This measurement was made at 1 K and a pressure of 1 bar. It would be very interesting to vary the temperature and the pressure and to check if this small probability is in fact consistent with the results of the mobility enhancement experiments.

The final question to discuss is the possible relation between fission and the exotic ions. The exotic ions are smaller than normal electron bubbles; could they be bubbles containing a fraction of the wave function of the electron?\(^ {28,29}\) As already noted, Jackiw et al.\(^ {78}\) and Rae and Vinen\(^ {79}\) have argued against this possibility. For this to be an explanation of the exotic ions there would need to be a mechanism by which bubbles containing at least 13 different fractions of the electron probability (integral of \(|\psi|^2\)) are produced. In the exotic ion experiments, the electrical discharge in the vapor above the liquid surface produces intense light over a broad region in which fission occurs and in which 1P bubbles are produced when light is absorbed.

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**Fig. 12.** Qualitative plot of the regions of the \( P-T \) plane in which fission occurs and in which 1P bubbles are produced when light is absorbed.
spectrum. This light will be absorbed by electron bubbles in the liquid and will cause different types of fission processes and will excite electrons out of the bubbles. It would be very valuable to perform more experimental studies of the exotic ions to investigate their properties more carefully. For example, the results reported so far indicate that the relative strength of the signals due to the different ions vary significantly with the position of the liquid level and the character of the light emitted in the electrical discharge. What is the correlation between the spectrum of the emitted light and the appearance of different ions? Is there a correlation between the intensities of different ions, e.g., when ion number 3 gives a strong signal is ion number 8 strong too, thereby implying some relation between their origins? This type of information cannot be extracted from the existing data and might give a clue to the origin of the ions.

7. Summary

We can summarize the current understanding of electron bubbles in liquid helium as follows:

a) The basic structure of these objects has been confirmed through accurate measurements of the photon energies required to cause optical absorption. The measured energies are in excellent agreement with detailed density functional calculations, and the shape of the absorption lines is well understood. The negative pressure at which the 1S ground state bubble becomes unstable has been measured and is in good agreement with theory.

b) The equilibrium shapes of electron bubbles in excited states have been calculated based on highly simplified models. It would be worthwhile to perform more detailed density-functional calculations of the properties of these objects and to detect the light that is emitted when they relax back to the ground state. The excited states undergo non-radiative decay by some unknown mechanism.

c) There are significant difficulties in understanding the interaction of electron bubbles with vortices. The calculated binding energy is not in agreement with experiment and the effect of vortices on the explosion pressure is not understood.

d) The exotic ions and the fast ion have been detected in several experiments by different groups. These ions are smaller than the normal electron bubble. There is still no understanding of the nature of these objects. This is remarkable when one considers that one is dealing here with electrons in a very pure liquid composed of atoms with no chemical properties. In addition to the exotic and fast ions, another object has been detected that is larger than the normal electron bubble. It is clear that more experiments are needed to study these fascinating objects.

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15) The experimental data shown in Fig. 4 are from ref. 6. Preliminary data [J. Classen, C.-K. Su, and H. J. Maris: Phys. Rev. Lett. 77 (1996) 2006] showed a somewhat larger negative pressure in the temperature range between 3 and 4 K.
48) This table is based on the radius estimate made by Ihas in his thesis. Ihas took the radius of the normal electron bubble to be 16.1 Å. We have multiplied Ihas' estimates of the radii of each exotic ion by a factor of 19/16.1 to allow for the fact that elsewhere in this review we...
have taken the radius of the normal electron bubble to be 19 Å. Note also that we have used a numbering scheme that is different from the system used in Ihas’ thesis.


50) As shown in ref. 30, the calculated lifetime of the excited states due to radiative decay is typically in the range between 10 and 100 μs, whereas the transit time in the ion mobility experiments is typically of the order of 10 ms. In addition, the lifetime of the 1P state has been measured to be considerably less than the calculated radiative decay lifetime (see ref. 33), indicating that the decay is dominated by some type of more rapid non-radiative decay process.


53) L. Onsager: Nuovo Cimento Suppl. 6 (1949) 249.


58) Humphrey Maris was born in England in 1939. He obtained his B. Sc. (1960) and Ph. D. (1963) degrees from Imperial College, London. He has been a research associate at Case Institute from 1963 to 1965. Since 1965 he has been a professor of physics at Brown University. He has worked in many areas of physics, including low temperature physics and liquid helium, ultrafast optics, neutrino detection, ultrasanics and the development of new techniques for semiconductor metrology.