Negative ions in liquid helium

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Structure of negative ions in liquid $^4$He is analyzed. The possibility of cluster or bubble formation around impurity ions of both signs is discussed. It is demonstrated that in superfluid helium, around negative alkaline-earth metal ions, bubbles are formed and, around halogen ions, clusters are formed. The nature of “fast” and “exotic” negative ions is also discussed. It is assumed that the “fast” ions are negative ions of helium excimer molecules localized inside bubbles. The “exotic” ions are stable negative impurity ions, which are always present in small amounts in gas discharge plasma. Around such ions, bubbles or clusters are created with radius smaller the radius of electron bubbles.

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Keywords: liquid helium, negative ions, electron and ion bubbles.

1. Introduction

The positive helium ions and electrons in liquid helium exhibit very low mobilities. This is due to the fact that a spherical region of solid helium with a radius of about 0.7 nm is formed around the ion because of a polarization interaction with the atoms of the liquid, whereas the electron is localized in a bubble, whose radius is close to 2 nm, because of a strong exchange interaction (e.g., see [1–3]). The mobility was also measured for a number of positive impurity ions in superfluid $^4$He [4–6]. A qualitative difference between the mobilities of alkali and alkaline-earth metal ions was found (see Table 1): the mobilities of alkali metal ions were smaller than the $\text{He}^+$ mobility and decreased with the atomic number, but the mobilities of the alkaline-earth metal ions (other than $\text{Be}^+$) were higher than the $\text{He}^+$ mobility and increased with the atomic number. These differences cannot be interpreted in terms of the simple electrostatic model proposed by Atkins [7], in which the structure of a complex depends only on the ionic charge. Cole and Bachman [8] gave a qualitative explanation for the effects observed. In their considerations the radius of the ionic complex strongly depends on the extension of the wave function of the lone valence electron, which causes a repulsive interaction with the surrounding helium. In the case of alkali metal ions the van der Waals interaction of the ion core with helium atoms plays an appreciable role. This interaction results in an increase in the radius of a solid ion complex and in the dependence of this radius on the atomic number. In the case of alkaline-earth metal ions, the valence electrons have extended orbitals and the formation of empty voids around the ions is possible. This effect is connected with the strong exchange interaction of the valence electrons with the shell electrons of the atoms of the surrounding liquid.

Table 1. Mobilities of positive impurity ions in liquid $^4$He at $T = 1.3$ K [5]

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\text{He}^+$</th>
<th>$\text{K}^+$</th>
<th>$\text{Rb}^+$</th>
<th>$\text{Cs}^+$</th>
<th>$\text{Be}^+$</th>
<th>$\text{Ca}^+$</th>
<th>$\text{Sr}^+$</th>
<th>$\text{Ba}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$, cm$^2$/V·s</td>
<td>0.88</td>
<td>0.85</td>
<td>0.78</td>
<td>0.78</td>
<td>0.81</td>
<td>0.98</td>
<td>1.01</td>
<td>1.12</td>
</tr>
</tbody>
</table>

The structure and transport properties of electrons and positive ions in low temperature atomic liquids have been well studied. Much less is known about the properties of negative ions. Only in a few works the mobility of $\text{O}_2^-$ in Ar, Kr [9], and Xe [9,10] was investigated. Berezhnov et al. [11] discussed a possibility of the bubble creation around $\text{H}^-$ ions in liquid hydrogen. Experimental data on the mobility of electrons in liquid hydrogen and deuterium at the saturation line [12,13] are in a good agreement with the electron bubble model in the region of relatively high temperatures from 22 to 32 K for liquid hydrogen and in deuterium at all temperatures. However in liquid hydrogen, in the low temperature region from 17 to 22 K, in the experiment of Levchenko and Mezhov-Deglin [13] an anomalous high mobility of negative charge carriers was observed, which was 1.5 times higher than the mobility...
observed earlier by Sakai, Bötcher, and Schmidt [12]. Levchenko and Mezhov-Deglin interpret this distinction by the peculiarity of the experimental conditions. In the work of Sakai et al. [12] the excess electrons were injected in the liquid as result of photoemission from the cathode. The energy of such electrons is $\sim 1$ eV, too small for the dissociation of the molecular hydrogen. In the work of Levchenko and Mezhov-Deglin [13] the excess electrons were created by $\beta$-decay of tritium atoms. The energy of such electrons is $\sim 10$ keV, large enough not only for ionization but also for multiple dissociation of molecular hydrogen. Therefore, in the latter experiment a significant concentration of hydrogen atoms was generated near the track of the $\beta$-particle in the liquid. These atoms are able to form stable negative ions in contrast to hydrogen molecules. The anomalous mobility of the negative charges at low temperatures is energetically more favored than the mobilities not only of Ar ions but also of electron bubbles (see Tables 1 and 2). Evidently, only the formation of multiatomic complexes (clusters or bubbles) around the atoms can be responsible for these low mobilities.

Table 2. Mobilities of negative impurity ions in liquid $^4$He at $T = 1.3$ K [14]

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\mu$, cm$^2$/(V·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cl}^-$</td>
<td>0.54</td>
</tr>
<tr>
<td>$\text{F}^-$</td>
<td>0.46</td>
</tr>
<tr>
<td>$\text{I}^-$</td>
<td>0.47</td>
</tr>
<tr>
<td>$\text{Ba}^-$</td>
<td>0.45</td>
</tr>
<tr>
<td>$\text{Ga}^-$</td>
<td>0.47</td>
</tr>
<tr>
<td>$\text{O}_2^-$</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Properties of negative impurity ions in liquid helium were investigated in [11,15–19]. In these studies, it was found that the binding energy $E$ of the outer-shell electron in a negative ion (electron affinity) in a liquid dielectric increases by about 1 eV and a spherical cavity is formed around the ion. The radius of this cavity depends not only on the thermodynamic parameters of the liquid but also on the characteristics of the negative ion. The negative ion in vacuo is formed by a long-range polarization attraction and a short-range exchange repulsion between the outer-shell electron and the ion core. The following simplest model potential can be used as a potential for the interaction of an electron with its atom:

$$V(r) = \begin{cases} \frac{\alpha e^2}{2r^4}, & r > R_c, \\ \mu, & r \leq R_c, \end{cases}$$

where $\alpha$ is the atomic polarizability, $e$ is the electron charge, and $R_c$ is the radius of the solid atomic core, which occurs due to the exchange interaction of the outer-shell electron with electrons of internal atomic shells. Table 3 summarizes the solid core radii $R_c$ obtained by solving the Schrödinger equation for an electron in potential (1) with known polarizability $\alpha$ and electron affinity $E$. The asymptotic behavior of a wave function away from a repulsion center has the form $\psi(r) = r^{-1} \exp(-r/\lambda)$. The characteristic size of the region of the spatial electron localization depends on the attachment energy, $\lambda \approx \sqrt{\hbar^2/2mE}$. The electron affinity $E$ is usually much lower than the ionization potential $I$; because of this, the value of $\lambda$ is much higher than the size of the corresponding atom or molecule. A weakly bound electron spends the majority of time away from the ion core and interacts with the atoms of the surrounding liquid similarly to a free electron. The exchange interaction results in the formation of a spherical cavity of radius $R$ around the ion. The electron potential energy undergoes a jump of approximately 1 eV at the boundary of a cavity. In our calculations we use the model potential of the interaction of the outer-shell electron of a negative ion with the atoms of the liquid $V_I$ proposed by Stampfl [20]. The binding energy $E_I$ of the outer-shell electron of a negative ion placed in a cavity of the liquid was found by solving the Schrödinger equation with the resulting potential $V(r) = V_I(r) - V_I(R)$, and an equilibrium radius of the cavity $R$ was found provided that the free energy

$$F(R) = -E_I(R) + 4\pi\sigma R^2 + (4\pi/3)pR^3$$

reached a minimum ($\sigma$ is the surface tension coefficient and $p$ is the pressure in the liquid). Table 3 summarizes the results of the calculation.

Table 3. Atomic core polarizability $\alpha_c$, electron affinity $E$, core ionization potential $I$, solid core radius $R_c$, van der Waals constant $C_6$ for the interaction of the core with helium atoms, and radius $R$ of the cavity around the negative ion

<table>
<thead>
<tr>
<th>Core</th>
<th>$\alpha_c^3$</th>
<th>$E$, eV</th>
<th>$I$, eV</th>
<th>$R_c$, a$_0$</th>
<th>$C_6$, a$_0^6$</th>
<th>$R$, a$_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>15</td>
<td>3.61</td>
<td>12.97</td>
<td>0.92</td>
<td>9.8</td>
<td>5.71</td>
</tr>
<tr>
<td>F</td>
<td>3.8</td>
<td>3.40</td>
<td>17.42</td>
<td>0.51</td>
<td>2.9</td>
<td>5.05</td>
</tr>
<tr>
<td>I</td>
<td>24</td>
<td>3.06</td>
<td>10.45</td>
<td>1.13</td>
<td>13.5</td>
<td>6.35</td>
</tr>
<tr>
<td>Ba</td>
<td>283</td>
<td>0.14</td>
<td>5.21</td>
<td>4.08</td>
<td>93.3</td>
<td>20.7</td>
</tr>
<tr>
<td>Ga</td>
<td>33.6</td>
<td>0.41</td>
<td>6.00</td>
<td>1.52</td>
<td>12.4</td>
<td>19.8</td>
</tr>
<tr>
<td>$\text{He}^2_6$</td>
<td>316</td>
<td>0.18</td>
<td>4.77</td>
<td>1.79</td>
<td>67.0</td>
<td>15.4</td>
</tr>
<tr>
<td>O$_2$</td>
<td>10.6</td>
<td>0.46</td>
<td>12.1</td>
<td>0.91</td>
<td>6.6</td>
<td>11.0</td>
</tr>
<tr>
<td>O</td>
<td>5.4</td>
<td>1.46</td>
<td>13.6</td>
<td>0.63</td>
<td>3.6</td>
<td>6.8</td>
</tr>
<tr>
<td>H</td>
<td>4.5</td>
<td>0.75</td>
<td>13.6</td>
<td>0.60</td>
<td>3.0</td>
<td>8.5</td>
</tr>
</tbody>
</table>
One can see that the sizes of the cavities around the halogen and alkaline-earth metal ions are significantly different. First, let us discuss properties of complexes formed around the negative ions of halogens. In terms of our model, the radius of the cavities in which these ions are localized \((5−6)a_0\) is much smaller than the radii of solid clusters formed around \(\text{He}^+\) ions \((14.9a_0)\) and alkali metal positive ions \((15.8a_0)\) [5]. This suggests that clusters are formed near the negative ions of halogens. In this case, the presence or absence of a cavity within a cluster is of little importance for the determination of the radius of these clusters: as in the case of positive ions, the negative ions at the center of a cluster can be considered as point ions. To understand the reason for the considerable difference between the mobilities of the He\(^+\) ion, on the one hand, and negative halogen ions, on the other hand, Khrapak [17] invoke the reasoning that was used to explain the small differences in the mobilities of positive helium and alkali metal ions [8]. It was noted that, although the polarization interaction of an ion with helium atoms outside the cluster is equal for all the ions, the additional van der Waals interaction of helium atoms with the ion core depends on its atomic number. An excess pressure results in an increase in the cluster radius and a decrease in the cluster mobility. This effect is even more important in the case of negative ions. The potential energy of the interaction of a helium atom arranged near the surface of a cluster with a point ion placed at the center of the cluster takes the form

\[
V_a(r) = -\frac{\alpha_{\text{He}}e^2}{2r^4} - \frac{C_6}{r^6}, \quad C_6 = \frac{3}{2} \frac{I_{\text{He}}I_a}{I_{\text{He}} + I_a} \alpha_{\text{He}}\alpha_a. \quad (3)
\]

Here \(C_6\) is the van der Waals constant of the interaction of helium atoms with the atom of the ion core, which was evaluated using the London formula [21]. Table 3 summarizes the constants \(C_6\) thus calculated. With growth of the constant \(C_6\) the cluster radius has to increase and the mobility has to decrease in agreement with small mobility changes observed in experiment [14]. However, this effect can decrease the mobility of negative halogen ions by \((5−10)\%\) as compared to the mobility of the \(\text{He}^+\) ion but hardly by a factor of 2.

In the case of alkaline-earth metal ions \(\text{Ba}^-\) and \(\text{Ga}^-\), which exhibit a low electron affinity in the vacuum, the bubble radius is large enough and creation of the solid shell around the bubbles is unlikely. According to our estimations, the electron binding energies \(E_c\) for these ions in liquid helium at \(T = 1.3\) K are similar and equal to 1.42 and 1.46 eV, respectively. The difference between the characteristic size of wave functions \(\lambda\) for these ions is small; this fact is ultimately responsible for the observed similarity of the ion mobilities. At first glance, the fact that the mobility decreases with decreasing bubble radius \((\text{Ba}^- \rightarrow \text{Ga}^-)\) is surprising. However, note that, at \(T = 1.3\) K on the saturation line of liquid \(^4\)He, the mobility of ion complexes depends on scattering by rotons [1]. Bondarev [22] had shown that the density of rotons increases with decreasing distance to the ion complex as result of the polarization attraction. In the case of the electron bubbles this effect does not play a significant role because of the large value of their radius. In the case of \(\text{Ba}^-\) and \(\text{Ga}^-\) ions the polarization interaction of the helium atoms situated in the vicinity of the bubble surface plays an important role \((\alpha e^2/2R^4 = 1.2\) K for \(\text{Ba}^-\) and 1.4 K for \(\text{Ga}^-\)) and results in significant increase of the roton concentration near the ion bubbles. This effect can be responsible for difference of the mobilities of \(\text{Ba}^-\) and \(\text{Ga}^-\) ions. However, a question why mobilities of alkaline-earth metal ions are less than the mobility of the \(\epsilon\)-bubble is still open.

### 3. Fast and exotic ions

In addition to “usual” electron bubbles in superfluid helium two kinds of negative charge carriers were observed: “fast” [23–27] and “exotic” [24–27] ions. The mobility of the fast ions was about 7 times higher than the electron bubble mobility and mobilities of several different exotic ions lay in between. For production of ions different methods were used: the \(\alpha\) source placed in liquid [23], the \(\beta\) source and gas discharge placed above the liquid [24,25,26], and only the gas discharge above the liquid [26,27]. Mobility of the electron bubbles at temperature around 1 K is determined by collisions with rotons and is proportional to square of the bubble radius \(R\). If one suggests, that around fast and exotic ions, voids or clusters are created, then one may estimate the radius of these complexes assuming that their mobility is proportional to the radius square [3,25,26]. It lies between 30.4\(a_0\) (electron bubbles) and 11.8\(a_0\) (fast ions). At low electric fields electron bubbles are in the thermal equilibrium with the gas of scatters (rotons) and the bubble drift velocity is proportional to the electric field. Under increasing the electric field the bubble energy is also increased and the field dependence of the drift velocity became weaker. Finally, at some critical electric field the drift velocity demonstrates an abrupt change, known as giant fall or giant discontinuity (see, for example, [28]). It is the result of the creation of a charge-carrying quantized vortex rings in the superfluid. The same effect is observed with the exotic ions but not with the fast ions [26]. This may be an evidence for the different nature of fast and exotic ions. The measurements show that the critical velocity \(v_c\) for the nucleation of vortex rings by exotic ions is larger than for electron bubbles, and that amongst the different exotic ions, \(v_c\) increases as the mobility increases. Theory predicts that the critical velocity of an ion should increase with decreasing of the ion radius [29]. Thus, the measurements of the critical velocity also indicate that the exotic ions are smaller than the normal electron bubbles.

It is strange, but the nature of the fast and exotic ions is still unknown. Several models were proposed for these
negative charge carriers [24,30] but none of them could interpret all experimental data [3,31]. Below we suggest a new model. It follows from experiments that fast and exotic ions have different nature. Both kinds of ions were not observed in usual experiments, both kinds were observed in gas discharge experiments, and exotic ions were not observed in experiments with radioactive sources. Let us consider their properties separately.

We suggest that fast ions represent a bubbles created around negative ions of the excimer He* in the triplet state. In contrast to “usual” experiments, in which electrons are photo-injected in liquid helium with an energy of the order of 1 eV, using of radioactive sources or gas discharges produces not only ionization but also excited atoms and molecules as well. Both the singlet atomic and molecular excitations decay rapidly to the ground electronic state, but the long-living triplet species quickly thermalize and form bubbles around themselves. With 15 μs time constant the triplet He* combines with another helium atom to produce He* in a highly excited vibrational state (ν = 16). This state relaxes to its ground vibrational state with time constant about 30 μs [32]. The lowest electronically excited state in liquid helium is the triplet excimer He* which lies at 17.8 eV above the ground state. Due to the very weak spin-orbit coupling in He, this state is metastable with a large intrinsic lifetime of about 15 s [33–35]. Spectroscopic studies result in a conclusion that eximers occur in bubble states. The bubble model was employed by Hickman et al. to analyze spectral shifts of He* [36] and He* [37] in liquid He. Results of early studies have been validated in the later spectroscopic studies [38–40]. Theoretical estimations of the bubble radius give about 12a0 for He* [41] and 13a0 for He* [42].

The long-lived metastable negative excimer ion He* was first observed in 1984 [43] and now its properties in vacuum are well known. The 4Πg state has electronic configuration 2πg1σg2πg2σg, the electron affinity E is 0.18±0.03 eV, the lifetime is 135±15 μs, only ν = 0 vibrational state is responsible for this long-lived state [44]. This ion can exist in liquid helium as result of excitation by α or β particles, or as result of the diffusion through the surface from the gas-discharge plasma. However properties of He* ions in condensed helium are quite unknown. It is sufficiently evident that like excimer He*, the ion He* is localized inside empty void. Size of the void can be estimated in frames of the model used in previous section for impurity negative ions. For this, it is necessary to estimate parameters α*, R*, and C6 of the interaction potential. The main contribution to the polarizability of the excimer He* gives the excited atom He*, αHe* ≈ αHe*. The atomic polarizability can be estimated from its ionization potential, α ≈ a−3 ≈ I−3, where a is the radius of the atom. The excitation energy of the helium atom is 19.82 eV and the ionization potential IHe = 24.59−19.82 = 4.77 eV. Thus

\[ \alpha_{He^*} \approx \alpha_{He} \left( \frac{I_{He}}{I_{He^*}} \right)^3 \approx 204a_0^3. \]  

(4)

The core radius R* is determined by solution of the Schrödinger equation with known E and αHe*. This gives R* = 1.79a0. The constant of the van der Waals interaction of the core (He*) with helium atoms can be estimated by the London formula

\[ C_6 \approx \frac{3}{2} \frac{I_{He}}{I_{He^*}} \alpha_{He} \alpha_{He^*} \approx 67a_0^6. \]  

(5)

Figure 1 shows the free energy of a spherical bubble created around He* ion as a function of its radius. The equilibrium bubble radius is equal 15.4a0, more than twice smaller than the radius of the e-bubble. Notice that the wave function of the 4Πg state of He* does not possess spherical symmetry. As a result a form of the bubble has to obtain a characteristic two-lobe peanut structure similar to the excited e-bubble in 1P state [45]. This effect could reduce the roton scattering cross-section of the bubble and explain observed rise of the fast ions mobility.

The issue remains open about the lifetime of the He* ion in condensed helium. The drift time in the experiments [24–27] is about 1 ms, several times greater than the vacuum lifetime of the ion. However the wave function of the outer electron of the He* ion undergoes significant alternations which can result in increasing of the ion lifetime. Another possibility to adjust the difference between the short lifetime and long drift time consists in following: during the drift time between electrodes electrons have a possibility several times to escape from the ionic complex with subsequent capture by another excited molecule. After escaping from the ion with an energy of about 19 eV, the electron is thermalized during approximately 1 ps [2] and after that it can be captured by a next excitation or it can create an e-bubble. If concentration of the excimer molecules He* in liquid helium is high enough, then electrons practically all time will be localized in He* inside.
Exotic ions were observed in superfluid helium only when ionization of helium was produced by gas discharge above the liquid surface. There is good reason to believe that these ions are stable negative impurity ions, which are always present in small amounts in the gas discharge plasma. Despite the fact that in superfluid helium all impurities are frozen out, atomic and molecular impurities may be present in the discharge plasma as a consequence of the etching from the experimental cell walls and electrodes. Unfortunately the plasma composition in experiments [24–27] is unknown and below we present results of our estimations for several most probable candidates for the role of the exotic ions, such as O$_2^-$, O$^-$, and H$^-$. All these ions are localized inside bubbles. Dependencies of the free energy on the bubble radius for these ions are shown in Fig. 2. Values of the equilibrium radii of these ions are listed in Table 3. The size of the O$_2^-$ bubble is three times less the radius of the e-bubble and this ion can be responsible for mobility of one of the fastest exotic ions. The size of O$^-$ bubble or cavity is much smaller than the radius of cluster usually formed around positive helium ion. As in the case of negative ions of halogens, this points to the formation of a solid cluster around the O$^-$ ion, with a void inside. The size of this complex has to be closed to that of He$^+$ cluster (14.9$\alpha_0$), and its mobility has to exceed about two or three times the e-bubble mobility. The ion H$^-$ represents an intermediate case: the bubble is surrounded by a layer of dense but probably not solid helium. For the determination of its structure and that of similar exotic ions more detailed and complex investigations are needed.

4. Conclusions

In this work we have addressed the properties of different negative impurity ions in liquid helium. With help of a simple model it was found that owing to the strong exchange interaction of the outer electron of a negative ion a void is always created around the ion. In the case of ions with a large enough electron affinity a layer of solid helium can be formed around the void, and the complex represents a cluster rather than a bubble. It was demonstrated that complexes formed around negative alkaline-earth metals and halogens have qualitatively different structure (bubbles and clusters, correspondingly), although the measured values of their mobility were similar. It was substantiated that the “fast” ions represent negative ions of the excimer He$_2^+$ localized in non-spherical bubble. Concerning the “exotic” ions, an assumption was made that they are formed in the gas discharge plasma as result of the etching of the cell walls and electrodes and are then injected into the liquid.

Additional experimental and theoretical investigations are necessary for better understanding of properties of impurity negative ions in superfluid helium and other dielectric liquids.

In the experiment by Kasimov et al. [14] the mobility of negative impurity ions injected in liquid helium was smaller than the mobility of the e-bubbles. But in this work the well known mobility of e-bubbles (see, for example, [1,46]) was not measured. According to our estimations the radius of these charged complexes is about 15$\alpha_0$ (halogen negative ion clusters) or 20$\alpha_0$ (alkaline-earth metal negative ion bubbles). As a result the mobility of impurity ions has to be several times higher than the e-bubble mobility in contradiction with the experiment. Additional experiments with simultaneous measurement of the ion and e-bubble mobility as well as with more wide nomenclature of ions are desirable. The measurements of the critical velocity for nucleation of vortex rings by impurity ions could also give important information about size of these ionic complexes.

The interest to the theoretical investigations of the properties of He$_2^-$ ions in liquid helium is self-evident. It would be rewarding to perform density-functional calculations of the equilibrium shape of the non-spherical bubble similar to the recent calculations for excited e-bubbles [19,42,45]. Knowledge of the bubble shape and of the outer electron wave function will give the possibility to estimate the lifetime of the He$_2^-$ ion in liquid helium. Kinetics of the bubble formation around He$_2^-$ and possible electron trapping by excimer He$_3^+$ are worthy of investigation.

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