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Negative ions in non-polar liquids

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ABSTRACT

The structure and mobility of positive and negative ions in non-polar liquids are analyzed. The possibility of clusters and bubbles creation around ions of both signs is discussed. It is demonstrated that complexes formed around negative metal and halogen ions in superfluid helium have qualitatively different structures, although the measured values of the mobility were similar. In the case of Ba^- and Ga^- ions, which have low electron affinities, a bubble is formed around the ion; this bubble is similar to an electron bubble. In the case of Cl^-, F^-, and I^- ions, which have high electron affinities, a cluster is formed near the ion; this cluster is similar to the well-studied cluster at the He^+ ion.

1. Introduction: localization of electrons and positive ions in liquid dielectrics

The formation of isolated negative ions of molecules or atoms by electron capture and their properties have received continuing interest in recent years [1,2]. Quantum mechanical calculations have led to a detailed picture of the capture process [3]. Much less is known about the properties of negative ions in a dielectric non-polar liquid. Not many experimental and theoretical studies haven been published. The basic experimental information comes from drift mobility measurements. Some energetic information was obtained from photo detachment studies [4].

In the majority of non-polar dielectric liquids, electrons are quasifree and have mobilities several orders of magnitude higher than positive ions. But in liquid helium and several other dielectric liquids, an anomalous behavior of injected charged particles is observed (for review see [5–7]). The mobility of charges of both signs is significantly less than it could be expected from the classical Langevin theory. In addition, the electron mobility is several times less than the mobility of positive ions. An explanation of the anomalously low mobility of positive ions in liquid helium was proposed by Atkins [8]. He gave evidence that as a result of the polarization attraction between He^+(or rather $He_2{}^+$) and He atoms, a stable region of increased density is formed around the ion. The size of this ion complex (Atkins' snowball) is about 10–15a_0 ($a_0 = 5.3 \times 10^{-9}$ cm is the Bohr radius), the atom density near the ion corresponds to the density of crystalline helium, and the effective mass of the complex is about 50 masses of the helium atom.

Atkins' model is inapplicable for an explanation of the low electron mobility in liquid helium because the strong exchange repulsion between a free electron and electrons of the external shells of the He atoms prevents the creation of a shell of He atoms around the electron. A theory able to explain the anomalous properties of electrons in liquid helium was proposed by Kuper [9]. Kuper suggested that as result of the strong electron–atom exchange repulsion a void or bubble of radius of about 40a_0 is created around an electron. In an applied electric field, the bubble moves as a single entity with an electron inside. The electron bubble mobility is determined by the hydrodynamic resistance of matter which depends on the liquid viscosity and the size of the bubble. The possibility of the electron bubble creation in liquid dielectric is connected with the features of the electron–atom interaction. It consists of long-range polarization attraction and short-range exchange repulsion. The competition between them determines the value and sign of the energy of the bottom of the conduction band V_0 [10,11]. In liquids, whose atoms have a small polarizability (for example, ^{3}He, ^{4}He and Ne), the exchange interaction prevails and $V_0 > 0$. In these liquids, electrons are localized in empty voids which represent a potential well for the electrons. The formation of thermodynamically stable quasi-particles—electron bubbles takes place. Self-trapping results

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Table 1
Mobilities of positive impurity ions in liquid ^{4}He at $T = 1.3$ K [12]

Ion	He^+	K^+	Rb^+	Cs^+	Be^+	Ca^+	Sr^+	Ba^+
μ ($cm^2 V^{-1} s^{-1}$)	0.88	0.85	0.78	0.78	0.81	0.98	1.01	1.12

in a very small electron mobility of 10^{-2} to 10^{-3} $cm^2 V^{-1} s^{-1}$. In liquids, which have a negative V_0 (for example, Ar, Kr and Xe) the small compressibility of the liquids prevents the electron from localizing inside the fluctuations with a higher atomic density. As a result, the electrons stay in the free state and have a high mobility of about 10^3 $cm^2 V^{-1} s^{-1}$.

The mobility of the charged multiatomic complexes in normal liquids can be determined in the hydrodynamic regime by the Stokes law, $\mu = e/d\pi\eta R$, taking into account slipping ($d = 4$) or sticking ($d = 6$) boundary conditions at the bubble or cluster surface, correspondingly. In quantum liquids, at very low temperatures the applicability of the hydrodynamic approximation is violated, and the mobility of the bubbles is determined by collisions of the complex with collective excitations of the liquid, phonons and rotons [5].

In experiments with different positive impurity ions in liquid helium [12,13] deviations from the Stokes law and from the predictions of the Atkins model were detected. In Table 1, the mobilities of several positive impurity ions are presented. There is a qualitative difference between the mobilities of alkali and alkaline-earth metal ions: the mobilities of alkali metal ions are smaller than the mobility of a helium ion and the mobilities of the alkaline-earth metal ions are higher. In the case of alkaline-earth metal ions, the valence electrons have extended orbits and the formation of empty voids around the ions is possible [14]. This effect is connected with the strong exchange interaction of the valence electrons with the shell electrons of the atoms of the surrounding liquid. If one assumes a scattering process that depends only on the radius of the defects regardless if they are snowballs or bubbles (at the temperature region of this experiment, $T = 1.27$–1.66 K), the mobility is governed by scattering of the impurity ions on rotons [5], Ba^+should have a smaller defect radius in liquid helium than Ca^+. This was at a first glance surprising but could be qualitatively understood with the model of Cole and Bachman [14]. In their considerations, the ionic complex radius strongly depends on the extension of the wave function of the lone valence electron, which causes a repulsive interaction with the surrounding helium. In addition, the ion–dipole interaction of the positive core ion with the surrounding bulk helium causes an attraction. A competition between the repulsive and attractive forces results in different ion structures: around the Be^+ion the snowball is created (similar to He^+) but around the other alkaline-earth ions bubbles are created.

The mobility of some impurity ions has been reported for liquid xenon. Hilt et al. [15] generated defined positive ions of tetramethylsilane ($TMSi^+$) and n-pentane (n-pent$^+$) by positive charge transfer from parent ions of liquid Xe. The mobility of thallium$^{208}Tl^+$ and thorium $^{226}Th^+$ ions was studied in refs. [16] and [17], respectively. Preliminary results on Ba^+ions, were reported by Miyajima [18]. In addition, the mobility of impurity negative ions, $O_2{}^-$and $SF_6{}^-$were measured by Hilt et al. [15]. All mobility values of positive and negative ions in liquid Xe are summarized in Fig. 1. By analogy with the situation in liquid helium one can assume that in the case of n-pent$^+$and Tl^+Atkins' snowballs are created around the ions, while ions Th^+ most probably are localized inside bubbles similar to the bubbles around alkaline-earth metal ions in liquid helium. Probably, in the case of Ba^+ a transition from the bubble to snowball state takes place. With $TMSi^+$ ion the situation is more uncertain. In our paper [15], we considered that the low mobility of this ion is connected with snowball creation. However, the intermediate value of its mobility points to the possibility of bubble creation. This problem requires additional theoretical investigation.

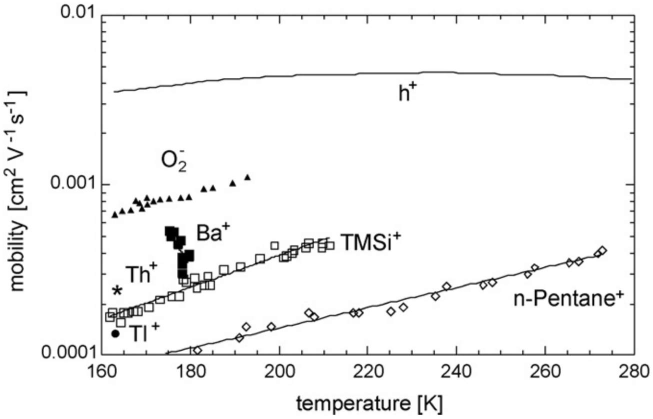

Fig. 1. Mobilities of defined ions in liquid Xe as a function of temperature [15–18](h^+ is the mobility of the positive hole).

2. Localization of negative ions in dielectric liquids

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 $O_2{}^-$ in Ar, Kr [19], and Xe [15,19] was investigated. In evaluating the structure of the negative ion, in addition to the effect of electrostriction only important for the majority of positive ions, one has to consider the exchange interaction between the lone electron of the negative ion and the electronic shells of the atoms of the liquid. The exchange interaction prevents a close approach of the neighboring atoms to the ion and can reduce significantly the effect of electrostriction [20–22]. A small exclusion sphere is formed from which the atoms are expelled. Outside of this sphere, the electrostriction leads to an increase of liquid density, but this increase is less than in the case of positive ion. This effect explains a significant difference in mobility of positive and negative ions in dense gases and liquids observed in experiments [5,15].

Experimental data on the mobility of electrons in liquid hydrogen and deuterium at the saturation line [23,24] are in a good agreement with the 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 at the low temperature region from 17 to 22 K in the experiment of Levchenko and Mezhov-Deglin [24] an anomalous high mobility of negative charge carriers was observed, which was 1.5 times higher than the mobility observed earlier by Sakai et al. [23]. Levchenko and Mezhov-Deglin interpret this distinction by the peculiarity of the experimental conditions. In the work of Sakai et al. [23], the excess electrons were injected in the liquid as result of photoemission from the cathode. The energy of such electrons is ∼ 1 eV, too small for the dissociation of the molecular hydrogen. In the work of Levchenko and Mezhov-Deglin [24], the excess electrons were created by β-decay of tritium atoms. The energy of such electrons is ∼ 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 β-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 in β-irradiated liquid hydrogen corresponds to the mobility of H^-ions. Levchenko and Mezhov-Deglin assumed that at low temperatures clusters are formed around the negative ions of atomic hydrogen which move

Table 2
Mobilities of negative impurity ions in liquid ^{4}He at $T = 1.3$ K [25]

Ion	e-Bubble	Cl^-	F^-	I^-	Ba^-	Ga^-
μ ($cm^2 V^{-1} s^{-1}$)	0.54	0.46	0.47	0.45	0.47	0.41

as a single entity in the liquid. However, calculations performed by Berezhnov et al. [22] have shown that the bubble creation around the negative ion H^- is energetically favored. The mobility of the ion bubble is higher, as was observed in the experiment [24].

3. Impurity negative ions in superfluid helium

Recently, the mobility of negative impurity ions in superfluid ^{4}He was measured [25]. The mobilities of the negative ions of both halogens (Cl^-, F^-, and I^-) and metals ($Ba^-$and Ga^-) were found to be lower than the mobilities not only of He^+ions but also of electron bubbles (see Tables 1 and 2). Evidently, only the formation of multiatomic complexes (clusters or bubbles) around the ions can be responsible for these low mobilities. Further down it will be shown that the structures of the resulting complexes in the case of halogens and metals are qualitatively different, although the mobilities are similar: solid clusters are formed near halogen ions, whereas the metal ions are localized in bubbles.

Let us consider at first a possibility of the bubble creation around a 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:

$$V_i(r) = \frac{-\alpha e^2}{2r^4}, r > R_c; \infty, r \le R_c \tag{1}$$

where α is the atomic polarizability, e 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 α 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, $\lambda \cong \sqrt{\hbar^2/2mE}$. The electron affinity E is usually much lower than the ionization potential I; because of this, the value of λ is much higher than the size of the corresponding atom. 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_l proposed by Stampfli [26].

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

Atom	α, a_0^3	E (eV)	I (eV)	R_c, a_0	C_6, a_0^6	R, a_0
He	1.39	–	24.6	–	1.31	32.2
Cl	15	3.61	12.97	0.92	9.76	5.71
F	3.76	3.40	17.42	0.51	2.94	5.05
I	24	3.06	10.45	1.13	13.49	6.35
Ba	283	0.14	5.21	4.08	93.27	20.7
Ga	33.6	0.41	6.00	1.52	12.42	19.8

The binding energy E_e 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 $V(r) = V_i(r) + V_l(r)$, and an optimum size of the cavity R was found provided that the free energy $F(R) = -E_e(R) + 4\pi\sigma R^2 + (4\pi/3)pR^3$ reached a minimum (σ is the surface tension coefficient and p is the pressure in the liquid). Table 3 summarizes the results of the calculation.

Although the experimentally measured mobilities of all the ions were similar, the size of the cavities around the halogen and metal ions were found to be significantly different. Initially, let us discuss the properties of Ba^- and Ga^- ions, which exhibit a low electron affinity E in a vacuum. According to our estimations, the electron binding energies E_e 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 λ 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 (electron bubble $\rightarrow Ba^- \rightarrow Ga^-$) 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 [5]. Bondarev [27] 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 Ba^- and 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 Ba^- and 1.4 K for Ga^-) and results in significant increase of the roton concentration near the ion bubbles. The estimation of the mobility of the ion complexes gives $\mu_r \approx 0.46$ and $0.44\, cm^2 V^{-1} s^{-1}$ for Ba^- and Ga^-, respectively. As can be seen in Table 2, this is consistent with the experimental values.

Let us turn to the discussion of the 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 ($5.6a_0$) is much smaller than the radii of solid clusters formed around positive He^+ions ($14.9a_0$) and alkali metal ions ($15.8a_0$) [12]. 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, let us invoke the reasoning that was used to explain the small differences in the mobilities of positive helium and alkali metal ions [14]. It was noted that, although the polarization interaction of an ion with helium atoms outside the cluster was 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. Indeed, 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

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

The van der Waals constant of the interaction of a He atom with an atom of the ion core C_6 was evaluated using the London formula [28]. Table 3 summarizes the constants C_6 thus calculated. Note that such an evaluation for the K^+ ion gives $C_6 \cong 7.42$. Thus, this effect can decrease the mobility of negative halogen ions by (5–10)% as compared to the mobility of the He^+ ion but hardly by a factor of 2. The decrease in the effective mass of a cluster due to the occurrence of a cavity around an ion, as well as due to a decrease in the local density of helium atoms within the cluster as a consequence of the exchange interaction of an electron with atoms, can be assigned to other effects that reduce the mobility of negative cluster ions. A sequential self-consistent consideration of all these phenomena is beyond the scope of this paper.

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