Negative impurity ions in liquid ^{4}He

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We present theoretical results, based on zero-temperature density-functional theory, for the formation and properties of a negative impurity ion in bulk liquid ^{4}He. We first consider Ca which, due to its very low electron affinity, does not easily form a negative ion in vacuum. We show that a neutral Ca atom in bulk liquid ^{4}He can easily capture a nearby electron bubble leading to the exothermic formation of a Ca^- ion trapped inside a spherical cavity of ~15 Å radius. The Ca negative ion in bulk ^{4}He turns out to be a metastable state, the lowest-energy configuration being represented instead by a weakly bound Ca^- ion floating over the nearly unperturbed free surface of liquid ^{4}He. We have computed the threshold negative pressure at which the trapped Ca^- ion bubble explodes and we discuss our results in light of recent experimental measurements. We have also considered the possible ion formation in the case of a Ne atom, i.e., an atomic impurity that does not form a negative ion in vacuum. Despite the long-range attraction between the electron bubble and the Ne atom due to polarization forces, in the minimum-energy configuration the electron bubble and the Ne atom rather than merge together remain spatially separated in bulk liquid ^{4}He, forming a weakly bound state that has no analog in vacuum.

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I. INTRODUCTION

Negative ions in liquid He have been the subject of intense experimental and theoretical studies since many years. An excess electron in bulk liquid ^{4}He is trapped inside a bubblelike cavity[1] void of helium atoms of radius R approximately 19 Å, see Ref. 2 for a recent review of electrons in liquid ^{4}He. Electron bubbles have been investigated extensively through mobility measurements and optical spectroscopy studies, and their behavior is rather well understood. Numerous theoretical calculations of the structure of electron bubbles in liquid ^{4}He have been reported, ranging from the simplest model calculations[1,3] to more refined schemes.[4] More recently, theoretical calculations based on density-functional (DF) theory have provided a detailed account of the basic energetic and structural properties of electron bubbles,[5–7] whose structure has been confirmed through accurate measurements of the infrared-absorption spectrum.[3,8] The measured energies are in excellent agreement with detailed density-functional calculations[7,9] and the shape of the absorption lines is well understood.[10] Electron bubbles in superfluid ^{4}He have been also studied in cavitation experiments.[11] The negative pressure at which the $1S$ ground-state bubble becomes unstable has been measured and theoretical results are in good agreement with experiment.[12]

Below a temperature of 1 K, electron bubbles have been observed that explode at less negative pressures than those required to destabilize usual electron bubbles.[13] These objects appear to be bigger than the normal electron bubble and are associated with the presence of quantized vortices in the liquid to which they are attached. The results of theoretical calculations are only in semiquantitative agreement with the experiments,[14] this remaining an open issue.

In addition to these bubbles, there have been several observations of other negatively charged objects whose physical nature is still a mystery. These include the so-called fast ion and exotic ions. Because they have a higher mobility than the normal electron bubble, these objects are believed to be small, probably with radius in the approximate range R ~10–16 Å.[15] The exotic ions and the fast ion have been detected in several experiments by different groups.[16,17]

No satisfactory explanation has been given so far for the existence of exotic ions. They cannot be electron bubbles in an excited state since they would be larger than normal electron bubbles. Since different species of such exotic ions were observed at the same time in ^{4}He, it is unlikely that these are negative ions of impurity atoms. A more radical proposal has been put forward, where such objects are thought to be bubbles where only some fraction of the electron wave function is trapped.[18] The trapping might occur, for instance, when a normal bubble is excited from the ground state to a higher quantum state and the bubble then undergoes fission.[19,20] The existence of these electron fractions, however, has been criticized in Refs. 21–23.

Although 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 impurity ions. In a few early experimental studies the mobility of O_2^- in Ar, Kr, and Xe was investigated.[24,25] In evaluating the structure of the negative ion, besides the effect of electrostriction, 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 ^{4}He atoms to the ion and can reduce significantly the effect of electrostriction.[26] A small exclusion sphere is formed from which the atoms of the fluid are expelled. Outside of this sphere, electrostriction leads to an increase in the liquid density, but this increase is usually much less than in the case of positive ions. This effect ex-

plains the significant differences in the measured mobilities of positive and negative ions in dense gases and liquids observed in experiments.[25,27]

Recently, the mobilities of the negative ions of both halogens (Cl, F, and I) and metals (Ba and Ga) were measured[28] and found to be smaller than the mobilities not only of He^+ ions but also of electron bubbles. All the above species show a lower mobility than electrons in superfluid ^{4}He, in spite of the fact that their radius is smaller than that of the electron bubble.

The structure and mobility of negative ions in nonpolar liquids have been analyzed[29] in a model calculation using a simple electron-atom pseudopotential. The possibility of cluster and bubble formation 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 are similar. In the case of Cl, F, and I negative ions, which have high electron affinities,[30] a cluster is formed near the ion; this cluster is similar to the well-studied cluster formed around the He^+ ion. The situation is quite different for Ba^- and Ga^- due to their lower electron affinity. Here the extra electron is loosely bound to the atom and it interacts strongly with the electronic shells of the surrounding helium. Just as in the case of an excess electron in liquid helium, a void is generated around the electron of the metal anions. The void radius is smaller than in the case of the free electron.

Somewhat intermediate is the case of ^{3}He impurities in liquid ^{4}He, which are present even in the isotopically purest ^{4}He liquid. Due to its low solubility in ^{4}He, ^{3}He is expected to be in a surface (Andreev) state[31] with respect to ^{4}He. When a ^{3}He impurity atom approaches an electron bubble, there is a competition between the tendency to condense on the inner surface of the bubble cavity and the ^{3}He-electron repulsion. As a result,[32] a bound state of ^{3}He on the surface of the bubble cavity indeed occurs, with an energy 1.3 K lower than the chemical potential in a bulk solution, confirming an earlier suggestion made by Dahm.[33] ^{4}He bubbles coated by ^{3}He atoms are described, e.g., in Ref. 34.

To explain the existence of a bubble in the size range of exotic ions, it is necessary to consider impurity atoms in which the excess electron has a very weak binding, or even atoms which do not form bound negative ions in vacuum. This point has been clarified in Ref. 35, where it has been shown that to have a bubble radius larger than, say, 12 Å, the impurity electron affinity in vacuum has to be less negative than about −0.15 eV. Recent theoretical estimates[36] confirm this trend. There are very few atoms that meet this criterion, one such impurity (Ca) will be studied in the present work.

Because of the very weak interaction of the loosely bound excess electron, this fragile atomic negative ion has a finite and short lifetime in vacuum due to the very small amount of energy required to knock out the extra electron. As we will show in the following, the situation is quite different for negative impurity ions in liquid ^{4}He, where they not only can be created rather easily but, because of the energy barrier preventing the escape of the electron from the bubble, they are quite robust.

We present here DF calculations, at zero temperature (T) and pressure, of negative impurity ions in liquid ^{4}He. We will consider two atomic impurities, one characterized by a small negative electron affinity (Ca), and a rare-gas atom (Ne) which, due to its closed-shell electronic structure, has no electron affinity. Ca has perhaps the lowest-negative value of electron affinity among atoms thus it is expected to have quite a delocalized extra electron. A stable Ca^- ion exists in vacuum, despite previous believing that negative ions of alkali-earth atoms are unstable. It is however fairly difficult to produce and detect it. Experimental evidence for the existence of a stable Ca^- ion is presented in Ref. 37.

Ca neutral atoms are known to have a solvated state in bulk liquid ^{4}He although their most stable state is on the surface of ^{4}He.[38,39] When an electron bubble is also present in the helium system, one might expect that the impurity atom will be drawn toward the electron bubble by the polarization forces with potential $-\alpha e^2/2r^4$, where α is the atomic polarizability.

Our calculations, based on the $T=0$ density-functional approach that has been used in the past to study, among other helium problems, the localization and properties of electron bubbles in He,[5,7] show that a Ca atom trapped in liquid ^{4}He is indeed attracted toward a nearby electron bubble and eventually is drawn inside the cavity in a seamless way, capturing the electron and forming a Ca^- ion bubble. This seems to point toward a facile way of producing negative ions in liquid ^{4}He even if the electron-capture cross section is small in the gas phase. On the other hand, an atomic impurity with no electron affinity, exemplified in the present work by a Ne atom, does not merge with the bubble but forms instead a new state, where an almost undisturbed electron bubble is weakly bound to the solvated neutral Ne atom by long-range polarization forces.

II. METHOD

Our approach follows Refs. 7, 14, and 40, and we briefly summarize the main ingredients of DF calculations for ^{4}He in the following. The total energy E of the electron-helium system under study here can be written as a functional of the electron wave function $\Phi(\mathbf{r})$ and the ^{4}He effective macroscopic wave function $\Psi(\mathbf{r})=\sqrt{\rho(\mathbf{r})}$, $\rho(\mathbf{r})$ being the ^{4}He particle density

$$E[\Psi,\Phi] = \frac{\hbar^2}{2m_{^4\mathrm{He}}}\int d\mathbf{r}|\nabla\Psi(\mathbf{r})|^2 + \int d\mathbf{r}\mathcal{E}(\rho) + \frac{\hbar^2}{2m_e}\int d\mathbf{r}|\nabla\Phi(\mathbf{r})|^2 + \int d\mathbf{r}|\Phi|^2 V_{e\text{-He}}(\rho) + \int d\mathbf{r}'\rho(\mathbf{r}')V_{X\text{-He}}(|\mathbf{r}_{ion}-\mathbf{r}'|) + \int d\mathbf{r}|\Phi(\mathbf{r})|^2 V_{X\text{-}e}(|\mathbf{r}_{ion}-\mathbf{r}|). \quad (1)$$

In this equation, $\mathcal{E}(\rho)$ represents the zero-temperature potential energy DF described in Ref. 40. Inclusion of the electron-helium interaction is done as in Ref. 7, where the

electron-He density-dependent interaction proposed by Cole and co-workers[41] is used. Such interaction, which is local in nature, does not take fully into account the long-range polarization tail of the e-He interaction at large distances. However, test calculations have shown that the inclusion of the missing nonlocal part (which is much more computationally expensive than the local interaction) does not appreciably alter the calculated structural properties of the e-bubble as computed using only the local part.

The impurity atom is treated as a fixed external potential described by a suitable atom-He pair interaction $V_{X\text{–He}}$. V_{X-e} represents the interaction potential between an excess electron and the neutral impurity atom. The variational minimization of the zero temperature constrained grand potential $E(\Psi,\Phi)-\mu\int d\mathbf{r}\rho(\mathbf{r})-\varepsilon\int d\mathbf{r}|\Phi(\mathbf{r}\ |^2$, where μ is the helium chemical potential and ε the electron eigenvalue, yields two coupled Euler-Lagrange equations that have to be self-consistently solved

$$-\frac{\hbar^2}{2m_{^4\text{He}}}\Delta\Psi+\left\{\frac{\delta\mathcal{E}}{\delta\rho}+|\Phi|^2\frac{\partial V_{e\text{–He}}(\rho)}{\partial\rho}+V_{X\text{–He}}\right\}\Psi=\mu\Psi, \tag{2}$$

$$-\frac{\hbar^2}{2m_e}\Delta\Phi+\{V_{e\text{–He}}(\rho)+V_{X-e}\}\Phi=\varepsilon\Phi. \tag{3}$$

The iterative solution of the above equations gives the minimum eigenenergy ε and electron wave function $\Phi(\mathbf{r})$, as well as the ^{4}He density $\rho(\mathbf{r})$, the chemical potential μ being known in advance from the bulk liquid equation of state. One essential ingredient in our calculations (besides the well-established theoretical tools to describe liquid ^{4}He and its interaction with neutral impurities and electrons) is the electron-impurity interaction. We chose to describe this interaction by means of a suitable pseudopotential acting on the extra electron, constructed in such a way that it gives the experimental value for the electron-atom binding energy. We have partially followed the prescription of Refs. 42 and 43. We describe here the procedure for the case of Ca. The pseudopotential describing the interaction between a Ne atom and an excess electron will be described later. We write

$$V_{X-e}=V_H+V_{pol}+V_x+V_c, \tag{4}$$

where V_H is the static, mean-field Coulomb interaction between the excess electron and the Ca-electron distribution, which can be written as $V_s=-[Z-y_0(r)]e/r$, where Z is the atomic number,[43] and

$$y_0(r)=\sum_{i=1}^{N}\left[\int_0^r P_i^2(r')dr'+r\int_r^\infty\frac{P_i^2(r')}{r'}dr'\right]. \tag{5}$$

For the bound electronic orbitals P_i appearing in Eq. (5) we took the analytic Hartree-Fock wave functions of Clementi and Roetti.[44] The electron density is given in terms of these orbitals by $n_e(r)=(1/4\pi r^2)\Sigma_{i=1}^N P_i^2(r)$.

The polarization potential due to charge-dipole dispersion interactions is $V_{pol}=-\alpha_d e^2/2r^4$, where α_d is the atom dipole polarizability ($\alpha_d=169a_0^3$ for Ca). For the exchange potential V_x we took the simple Slater "$X\alpha$ potential" $V_x=-(3\alpha/2\pi)[3\pi^2\rho(\mathbf{r})]^{1/3}$ with $\alpha\sim0.7$, a value which is found to apply to most atoms in the periodic table.[43] The short-range part of the correlation potential V_c (which at large distances goes as $V_c\sim-\alpha_d e^2/2r^4$) is here a purely phenomenological part which accounts for short-range correlation effects, including the orthogonality constraints, and it has been chosen in the form $V_c=A/r^n$ with $A>0$. The repulsive character of V_c is justified by the orthogonality constraint of the extra electron wave function with respect to the Ca occupied electron orbitals. The parameters (A,n) in V_c are adjusted to reproduce, after integrating the radial Schrödinger equation for an electron in the presence of V_{X-e}, the experimental eigenenergy of the extra electron in the Ca^- ion, $\varepsilon=-0.018$ eV.[45] We find that the value $n=6$ provides the best fit to the experimental result.

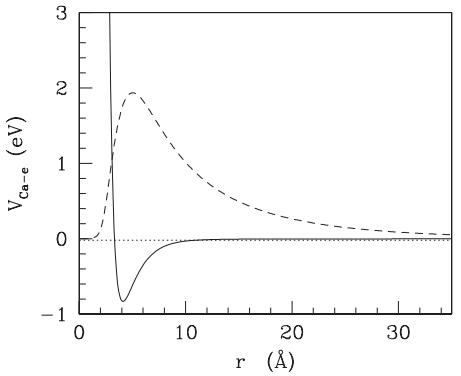

FIG. 1. Electron-Ca pseudopotential (solid line). The dashed line shows the radial wave function for the excess electron in the Ca negative ion. The dotted line represents the experimental-negative eigenenergy.

We show in Fig. 1 the computed electron-Ca pseudopotential, together with the radial wave function of the excess electron. The horizontal line shows the experimental electron eigenvalue that we used as an input in our construction. Our computed wave function for the excess electron compares well with that calculated with a different method in Ref. 46 for the outer electron in Ca^-.

III. RESULTS AND DISCUSSION

We first consider the case of a neutral Ca atom interacting with an electron bubble in liquid ^{4}He. To describe the Ca-He interaction $V_{X\text{–He}}$ we have used the pair potential computed in Ref. 47. The effect of the quantum motion of the impurity on its solvation energies in liquid ^{4}He has been investigated in Ref. 39. We have estimated here the Ca zero-point energy by computing the energy as a function of small displacements of the atom within the frozen ^{4}He cavity corresponding to the ground-state-density configuration. We have found such contribution to be rather small, of about 5 K. For this reason we do not consider explicitly the quantum nature of the impurity and treat it instead as an infinitely massive particle described by the external potential $V_{X\text{–He}}$.

We first consider separately the three possible structures for the Ca-electron bubble system, namely, one corresponding to (i) an isolated Ca atom solvated inside liquid ^{4}He, (ii)

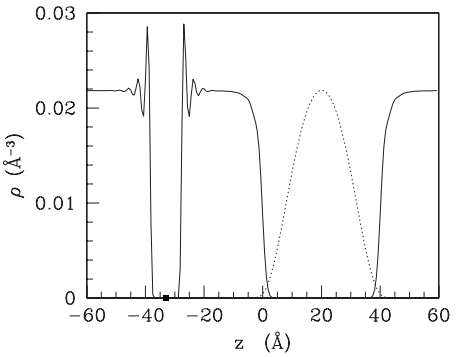

FIG. 2. ^{4}He density profile for a neutral Ca atom near an electron bubble. The black square indicates the position of the Ca neutral atom. The dotted line shows the electron probability density $|\Phi|^2$ in arbitrary units.

an isolated electron bubble, and (iii) the combined system corresponding to a Ca^- ion trapped in liquid He. At zero pressure, the configuration (i) has a grand potential (GP) $\Omega = E - \mu N$ of −97 K, the configuration (ii) has a GP of 2290 K, and the configuration (iii) has a GP of 1011 K, making it energetically more stable than the separated Ca atom and

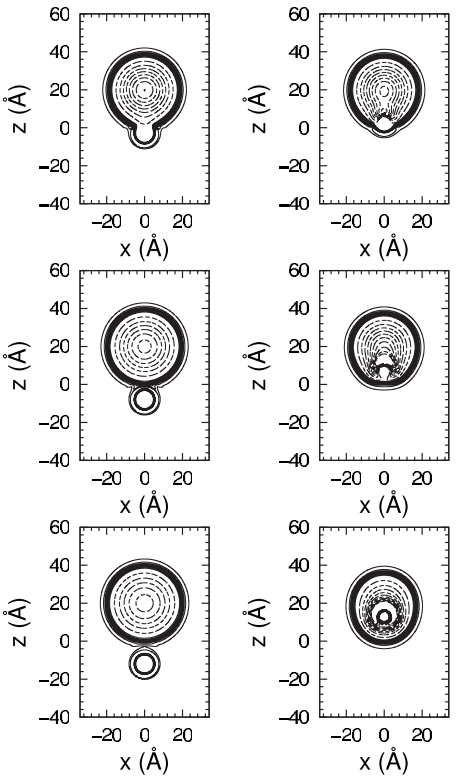

FIG. 3. Sequence of equal density contour plots showing, starting from the bottom left panel, clockwise, the capture of a neutral Ca atom by a nearby electron bubble, eventually leading to the formation of a Ca negative ion. The equidensity lines for the ^{4}He density (solid lines) are plotted for values between $0.1\rho_b$ and $0.9\rho_b$, in steps of $0.1\rho_b$, $\rho_b = 0.0218$ Å^{-3} being the ^{4}He bulk liquid density. The equidensity lines for the electron density (dashed lines) are plotted using nine lines between zero and the maximum value of $|\Phi|^2$.

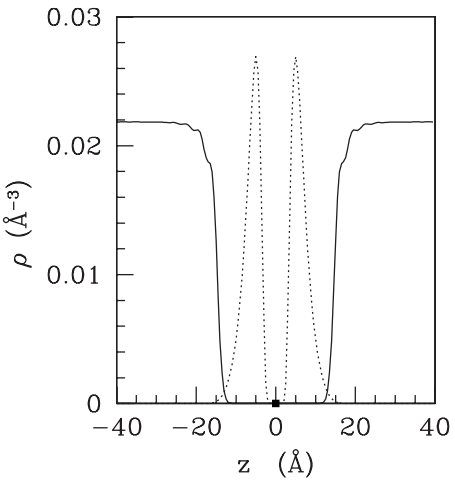

FIG. 4. Density profile showing the Ca negative ion trapped inside the helium cavity. The dotted line represents the excess electron probability density $|\Phi|^2$ in arbitrary units and the solid line the ^{4}He density. The black square indicates the position of the Ca atom.

electron bubble. Although the Ca^- ion is not globally stable, having a positive GP, it is nevertheless the preferred structure when a Ca impurity interacts with an electron bubble. The energy gain is due to the binding of the extra electron to the Ca atom and to the reduction in surface energy due to the smaller size of the cavity hosting the Ca^- ion. A typical configuration is shown in Fig. 2, where a solvated Ca neutral atom (left part of the figure) is nearby an electron bubble (right part of the figure).

Figure 3 displays a sequence of snapshots showing a few configurations as the Ca neutral atom approaches the nearby electron bubble until the Ca^- ion is formed by capture of the electron. These configurations are obtained during the imaginary time evolution that we use to minimize the energy density functional. These results suggest that the whole process of merging a neutral Ca impurity with a nearby e bubble, which is driven initially by long-range polarization forces, occurs spontaneously, indicating the absence of an activation barrier for the process. We have checked this issue by performing a series of additional calculations, where during the minimization we kept fixed the relative distance between the impurity and the e bubble, and found that indeed there is no energy barrier separating the initial and final configurations shown in Fig. 3.

Figure 4 shows the final, lowest-energy configuration for the Ca^- ion trapped inside the ^{4}He. The configuration has radial symmetry around the position of the trapped impurity atom. The cavity entrapping the Ca^- ion has a $R = 14.7$ Å radius. We have not found evidence of the state proposed in Ref. 48 on the basis of a simplified description of the system, where the impurity atom is predicted to reside in the bubble cavity, at a distance of about $R/2$ from the center, where the electric field produced by an electron at the center of the bubble would reach its largest value.[48] According to our calculations, instead, once the Ca atom enters the ^{4}He cavity interface, it is drawn inside toward the center of the bubble, while the extra electron is eventually spherically distributed around it.

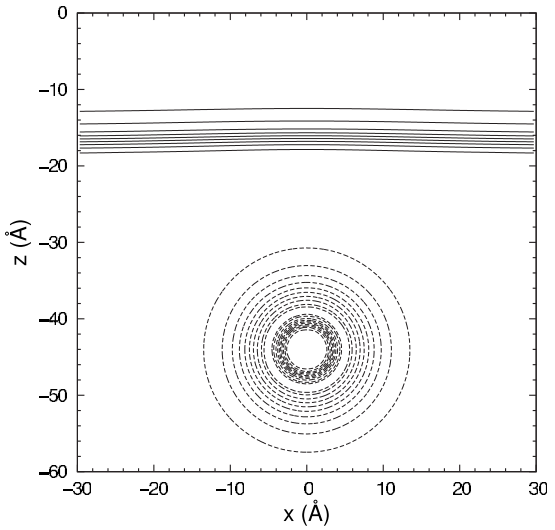

FIG. 5. Contour density plot showing the equilibrium configuration for a Ca^- ion on the surface of liquid ^{4}He. The circular lower contours represent the excess electron probability density $|\Phi|^2$ while the upper part of the figure is occupied by ^{4}He. The horizontal lines represent the free surface region of the superfluid. The contour line values are the same as in Fig. 3.

Although the trapped Ca^- ion described above has a lower energy than the separated neutral Ca and electron bubble pair, it is however a metastable state, the most stable state being the one where the Ca^- ion floats above the ^{4}He surface, being hold to it only by very weak polarization forces. We have studied the latter configuration, i.e., a Ca^- ion placed just outside the ^{4}He surface, simulated here using a slab geometry,[49] and show in Fig. 5 the resulting minimum-energy configuration for the Ca^- ion on the surface of liquid ^{4}He (in this figure the ^{4}He occupies the upper part of the displayed region, the almost horizontal contour lines showing the ^{4}He surface barely perturbed by the Ca^- ion) It appears from Fig. 5 that the extended electron cloud around the Ca^- ion keeps it fairly away from the ^{4}He surface thus reducing the net Ca-He attraction while the effect of the long-range attractive potential on the electron due to helium is not enough to distort its distribution around the Ca atom. As a result, a nearly undistorted Ca^- ion floats above the ^{4}He surface, at a distance $z_0 \sim 28$ Å measured from the point where the ^{4}He density equals half of its bulk liquid value. A very shallow dimple, barely visible in the scale of Fig. 5, develops just beneath the Ca^- ion.

In order to determine an accurate value for the binding energy of the Ca^- ion on the surface of ^{4}He we have corrected the value calculated using our slab geometry by adding a contribution ΔE due to the image potential of a semi-infinite ^{4}He at a distance (z_0+z_{slab}) from the Ca^- ion, where z_0 is the Ca^--surface equilibrium distance and $z_{slab}=60$ Å is the slab thickness, i.e., $\Delta E=-e^2(\epsilon-1)/[4(\epsilon+1)(z_0+z_{slab})]$, $\epsilon=1.0588$ being the dielectric constant of liquid ^{4}He. The resulting binding energy, $E_b=11$ K, is comparable with the binding energy of a free electron on the surface of liquid ^{4}He, about 8 K.[41]

Negative ions of large radius (Ca^- and Ba^-) have been studied in Ref. 35, finding a stable surface state. In this reference, the formation of a hole, i.e., a deep dimple, underneath the adsorbed ion on the ^{4}He surface is predicted due to the attraction of polarization forces. This dimple of 3.3 Å deep is found to reduce the ion mobility by several orders of magnitude. The separation between the levitating Ca^- ion and the surface was found to be 20 Å, and the radius of the bubble in bulk helium was found to be 14.1 Å.[35] As discussed before, our calculations predict instead the formation of a very shallow, almost negligible dimple, which cannot have any important effect on the surface mobility of the ion. The predictions of Ref. 35 are likely affected by a simplified e-atom pseudopotential and by the neglecting of the ^{4}He surface thickness.

It is interesting to compute the negative pressure at which the trapped Ca^- ion bubble explodes. One can anticipate that due to its smaller radius compared with that of the electron bubble, a Ca^- ion is expected to become unstable at a more negative pressure than that needed to destabilize an electron bubble, which is $P_c \sim -2$ bar.[11,13]

We have performed a series of calculations where a negative fixed value for the ^{4}He pressure is imposed on the system as done in previous density-functional calculations for electron bubbles.[7,12,14] We have found that the threshold for the mechanical instability of the Ca^- ion is about $P_c \sim -3$ bar. Since a similar behavior is expected for other negative ions, where the ^{4}He cavity trapping them is even smaller than for Ca^-, this rules out negative impurity ions as possible candidates to explain the anomalous negative ions that are observed to explode at a smaller $|P_c|$. We have also computed, for the sake of comparison, such a pressure for the case of a neutral Ca atom immersed in liquid He, finding $P_c \sim -9$ bar.

The structure of a negative ion differs intrinsically from that of neutral atoms due to the short-range nature of the force that binds the outer excess electron. The resulting potential well is so shallow that it can typically support no more than one bound state. Thus, conventional spectroscopic studies involving transitions between bound states are not possible on negative ions. The situation for a negative ion trapped in liquid helium is quite different since excited states can be sustained and hopefully observed by measuring the infrared-absorption spectrum thus providing a potential signature for the presence of a given negative impurity ion in the liquid.

To provide an estimate of the relevant transition energies in a spectroscopic optical-absorption measurement of a Ca^- ion in liquid ^{4}He, we have computed the absorption energies for the $1S \rightarrow 1P$ and $1S \rightarrow 2P$ transitions by finding, in the spirit of Franck-Condon principle, the excited states of the excess electron in the frozen ground-state helium configuration.[7,9] The calculated energies are 0.158 eV for the $1S \rightarrow 1P$ transition, and 0.64 eV for the $1S \rightarrow 2P$ transition. The corresponding values for the electron bubble are 0.11 and 0.49 eV, respectively.[3,7] Hence, the infrared absorption of Ca^- bubbles would not be mistaken for that of electron bubbles present in the same sample. We have also computed the oscillator strengths for such transitions and have found that the $1S \rightarrow 1P$ one accounts for 92% of the total strength, whereas a small contribution with strength 7% is associated with the $1S \rightarrow 2P$ transition. These two transitions together

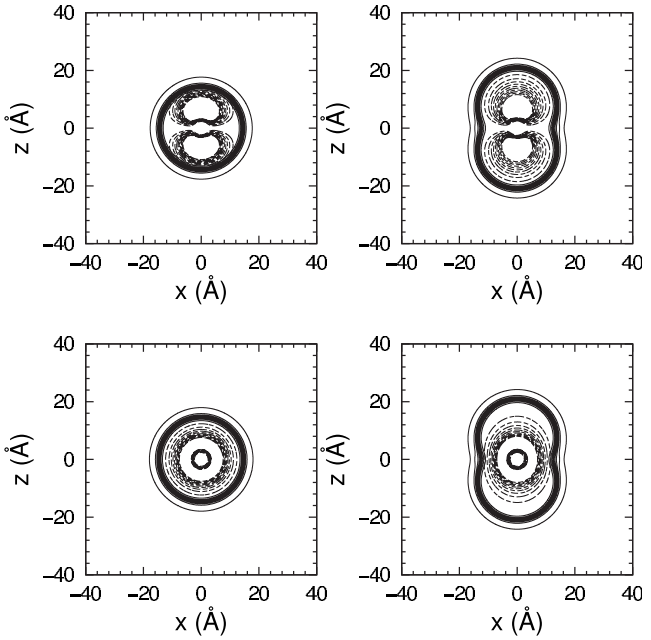

FIG. 6. ^{4}He equidensity contour plots showing the Ca^- excitation/deexcitation configurations and the corresponding electron probability distributions. The contour line values are the same as in Fig. 3.

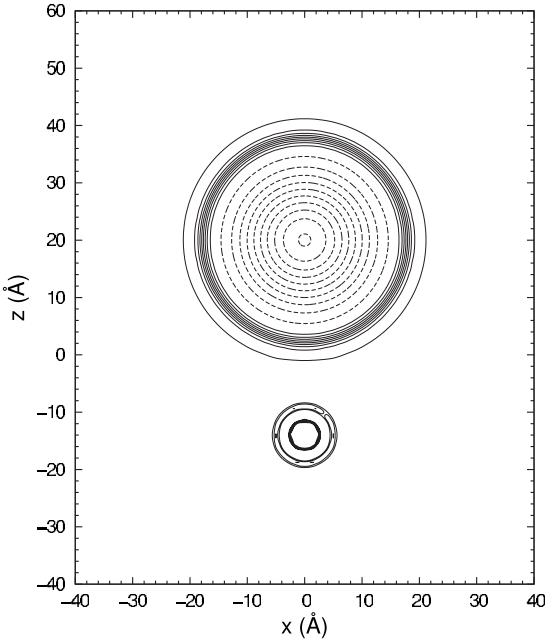

FIG. 7. Contour density plot showing the bound state formed by a solvated Ne impurity (lower contour lines) and an electron bubble (upper contour lines). The contour line values are the same as in Fig. 3.

account for 99.4% of the Thomas-Reiche-Kuhn sum rule.

During the excited electron lifetime, the superfluid has time to relax around it until the latter eventually decays to its deformed ground state in a ^{4}He environment which is different from the spherical one initially hosting the ion.[50,51] Neglecting dynamical effects, we can estimate the energy of the emission process by finding the deformed ^{4}He density configurations and associated Ca^- wave functions.

We show in Fig. 6 the four relevant configurations which characterize the $1S \rightarrow 1P$ absorption and subsequent $1P \rightarrow 1S$ emission. The bottom-left panel shows the probability density of the ground-state configuration for the Ca^- ion. The upper left panel shows that of the excess electron excited into the $1P$ state, in the frozen ground-state ^{4}He cavity. We then allow for ^{4}He relaxation in the presence of the excited state, as shown in the upper-right panel. The lower-right panel shows the electron probability density for the $1S$ state in the deformed ^{4}He cavity. The electron energy difference for the two configuration on the left gives the excitation energy while the electron energy difference for the two configurations on the right gives the emission energy. For the emission energy, we find in this way a value of 0.111 eV. Consequently, about 545 K energy are released into the superfluid during the absorption-emission cycle. We remark that the above treatment is only approximate because it completely neglects any dynamical coupling between the helium and the excited electron: ultrafast nonradiative transitions to the ground-state electron configuration might be possible though, as in the case for solvated electrons in liquid ^{4}He.[52]

We have also considered the interaction between an atomic impurity and an electron bubble in the case where the impurity atom does not bind an extra electron in vacuum. We have chosen Ne which, due to the relatively strong Ne-He interaction, is easily solvated in bulk liquid ^{4}He. We have proceeded in quite the same way as we have done for Ca. Two different ingredients are required for these calculations, namely, a reliable representation of the Ne-He and Ne-electron interactions in Eqs. (1)–(3). We have taken the Ne-He interaction from Ref. 51, where accurate potential curves for different combinations of rare-gas atom pairs were computed. For the Ne-electron interaction we have used a pseudopotential developed in Ref. 42, which accurately describes the dominant, s-wave scattering properties of the Ne-electron pair.

At variance with the case of Ca, where the spontaneous formation of a negative ion in liquid ^{4}He occurs, in the case of Ne our calculations show that the complex made of two fairly apart electron bubble and Ne atom does constitute a bound system. Indeed, we have computed the binding energy of such a complex defined as $E_b = \Omega_{\mathrm{Ne}} + \Omega_e - \Omega_{\mathrm{Ne}+e}$ and have found a very small positive value. This binding, which has no analog in vacuum, is very weak being only due to polarization forces.

In order to find the equilibrium configuration of this complex and its weak binding energy, we have performed a series of imaginary time minimizations where the Ne atom is initially placed at different distances from the electron bubble. The resulting equilibrium configuration is shown in Fig. 7.

The distance between Ne and the center of the electron bubble is about 34 Å and their binding energy is $E_b \sim 4$ K. It is remarkable that no such bound state exists in vacuum due to the positive Ne-electron-scattering length. We have also checked that there exists a metastable configuration where the Ne atom sits at the center of the electron bubble, being surrounded by a spherically symmetric excess elec-

tron, whose energy is 50 K higher than that of the weakly bound, separated Ne and electron bubble pair. As a final comment, since the electron bubble is practically undisturbed by the nearby Ne atom, this complex is expected to explode at the same negative pressure than the electron bubble, i.e., −2 bar.

IV. SUMMARY

We have carried out density functional calculations for the formation and properties of two impurity ions in liquid ^{4}He, one obtained from an atom with negative electron affinity (Ca) and another one from an atom with no electron affinity (Ne). We have found that Ca^- may be trapped inside a spherical cavity of about 15 Å radius, forming a metastable state. The equilibrium state consists of the Ca^- anion floating on top of the superfluid free surface. Our calculations for the equilibrium surface state rule out the existence of any sizeable dimple at the helium surface that might produce a sensible change in the mobility of the anion on the free surface, as proposed recently. Our calculations for the metastable Ca^- ion bubble rule out that the impurity atom permanently resides off the bubble center although zero-point motions which we have not taken into account may of course produce some wandering of the anion inside the bubble. Interestingly, the Ne atom and electron bubble form a complex weakly bound by polarization forces.

Within our model, we have calculated the absorption energies of the $1S \rightarrow 1P$ and $1S \rightarrow 2P$ transitions for the Ca^- bubble and have found that they are significantly different from those of the electron bubble, facilitating, in principle, their experimental determination in spite of the difficulties of infrared-absorption spectroscopy experiments.

Finally, we have determined the critical pressure for the explosion of the Ca^- bubble and have found a more negative value than for the electron bubble. Since Ca has one of the lowest values for the electron affinity, this seems to rule out the possibility that some unexplained events found in cavitation experiments are caused by the presence of negative impurity ions in liquid helium.

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