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Various charged complexes at the surface of liquid helium*

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Abstract

We propose and study the properties of several new systems at the surface of liquid He. Negative ions of a large radius absorbed on the surface behave like a system of heavy electrons. The charged complexes of a bound electron on the surface and a neutral cluster below the surface give a chance of a direct measuring the Wigner crystal of electrons. Surface states of He atoms are very important for the properties of liquid He surface. The temperature dependence of surface tension of liquid He is strongly affected by these surface states.

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1. Properties of electrons on the surface and in the bulk of liquid helium have been extensively studied for more than 30 years [1]. An electron on the helium surface has a very high mobility due to high purity of helium at low temperatures when all outside particles quit the quantum liquid. In

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the bulk of helium an electron has a low mobility due to the formation of bubbles with a large radius ~ 17Å. Positive ions under the helium surface [2] and the system of diplons (bound states of an electron on and a positive ion below the helium surface) [3] have also been considered. In the present note we propose and study the properties of three new types of charged particles at the surface of liquid helium.

The first objects to be studied are charged clusters under the helium surface consisting of a neutral cluster with one electron attracted to the cluster by the polarization potential [4] (see Fig. 1).

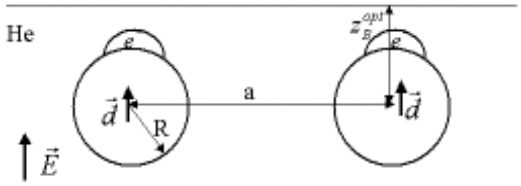

Figure 1: The schematic view of charged clusters below the helium surface.

There are several experimental methods to introduce an outer particle into liquid helium. Atoms, molecules and small clusters are created inside helium by the laser ablation. Larger clusters of radius $R > 50$Å are instilled into helium through its surface [5]. At high concentration of these clusters in helium an iceberg is formed. This was studied experimentally in [6] by injecting clusters of $\sim 10^3$ molecules into liquid helium. Large clusters of air or hydrogen were observed as a fog, slowly precipitating to the bottom of the vessel with the speed of 10^{-2} cm/sec. Below the λ-point of helium the clusters coagulate in flakes of a "snowfall" [6].

The binding energy of an electron to the cluster is usually very large: $E_{Be} \sim 0.1 - 1$ eV. The electric field E_{ex} presses these heavy charges to the surface of helium, where they form a two-dimensional system. The optimal distance z_B^{opt} of these heavy charged particles to the surface is determined by the minimum of potential energy:

$$V_{cl}(z_B) = eE_{ex}z_B + \frac{e^2}{z_B}2\nu_1 - Mgz_B + \frac{(\vec{E}_{ex}R_*^3)^2}{z_B^3}\nu_1 + V_{vdW}, \qquad (1)$$

where

$$\nu_1 \equiv \frac{1}{8}\frac{\varepsilon_h - 1}{\varepsilon_h + 1} \approx 1/300.$$

The first term in (1) is caused by the external field. The second term is the image potential of a charge near the surface. The third gravitational term is important only for very big clusters of the radius $R > 10^4$Å; usually one can neglect this term. The fourth term in (1) is the image potential of the cluster dipole moment. Rigorously, this moment $\vec{d}$ is generated both by the external field $\vec{E}_{ex}$ and by the field of attracted electron. However, the image potential due to electron-generated dipole moment of the cluster is always smaller than the second term in (1) by a factor of $[(\varepsilon_B - 1)R/(\varepsilon_B + 1)z_B]^2/2 < 1/2$. Therefore for the estimation of z_B we shall take into account only the dipole moment $\vec{d} = \vec{E}_{ex}R_*^3$ generated by the external field. The last term in (1) is the van der Waals potential. This term prevents the cluster to emerge from helium. It is $\propto 1/z_B^3$ and becomes important only when the cluster is very close to the surface.

Now we have to separate two different cases. First we consider small clusters when $e/R^2 \gg E_{ex}$ or $R \ll \sqrt{e/E_{ex}} \approx 700$Å for a field $E_{ex} = 3000$V/cm. The gravitational field, the dipole image potential and the van der Waals potential are then much weaker than the first two terms in (1). Therefore to find the optimal z-coordinate of the bound electron z_B we restrict to these two (pure electronic) terms. By differentiating $V_{cl}(z_B)$ with respect to z_B, we find

$$z_B^{opt} = \sqrt{2\nu_1 e/E_{ex}}. \tag{2}$$

For a field of $E_{ex} = 3000$ V/cm we get $z_B^{opt} \approx 60$Å. If $z_B^{opt} < R$, the cluster will be close to the surface but not emerge from helium because of the short-range van der Waals attraction forces between the cluster and helium atoms.

The opposite case of a large cluster ($e/R^2 \ll E_{ex}$ or $R \gg 700$Å) is even more interesting. Here we also have to consider the dipole-dipole image potential of the cluster increasing as R^6. The optimal distance z_B^{opt} is now determined by the quadratic equation

$$\frac{dV_{cl}}{dz_B} = eE_{ex} - \frac{e^2}{z_B^2}2\nu_1 - 3\frac{(\vec{E}_{ex}R_*^3)^2}{z_B^4}\nu_1 = 0, \tag{3}$$

which gives

$$z_B^{opt} = \sqrt{\frac{\nu_1 e}{E_{ex}}}\left[1 + \sqrt{1 + \frac{3}{\nu_1}\left(\frac{E_{ex}R_*^2}{e}\right)^3}\right]^{1/2}. \tag{4}$$

At $E_{ex}R_*^2/e \gg 1$ this becomes

$$z_B^{opt} \approx \sqrt{\frac{\nu_1 e}{E_{ex}}} \left(\frac{3}{\nu_1}\right)^{1/4} \left(\frac{E_{ex}R_*^2}{e}\right)^{3/4} . \qquad (5)$$

Now the optimal distance $z_B^{opt} \propto (E_{ex})^{1/4} R^{3/2}$, and one can reach $z_B^{opt} > R$ by increasing E_{ex} and R. At $\varepsilon_B = 80 \approx \infty$ and $E_{ex} = 5000$ V/cm this condition is fulfilled only for huge clusters $R \geq 5000$ Å$= 0.5\mu$m .

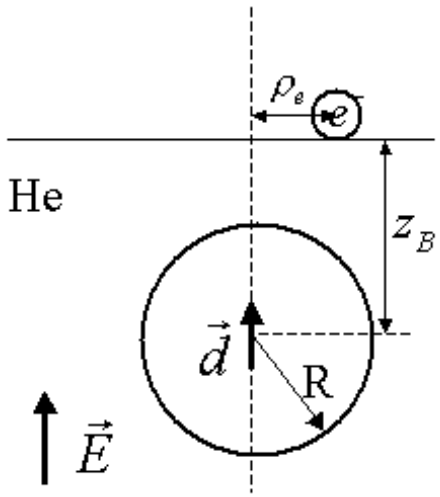

Figure 2: The schematic view of neutral clusters below helium surface and a bound electron above the cluster.

One can also put an electron on the helium surface and a neutral cluster under the surface [7] (see Fig. 2). The neutral cluster is attracted to the electron due to the cluster dipole moment induced by the electron and the external electric field (which is usually applied to the system of electrons on the surface of liquid helium). However, the cluster does not emerge to the surface of helium because of van der Waals and image dipole-dipole repulsion from the surface. The electron above the neutral cluster is also confined to the surface plane by the attraction potential. Electric field in this case must have an opposite direction in order for the system to be stable. The size of neutral cluster can vary from nanoscale (few nanometers) to micrometers. The electron forms bound states above the cluster due to the electrical interaction with the cluster dipole moment that creates a confining

potential for the electron in the surface plane:

$$V_{eB}(\rho_e, z_e, z_B) = -\frac{eER_*^3(z_B + \bar{z}_e)}{[(z_B + \bar{z}_e)^2 + \rho_e^2]^{3/2}} - \frac{e^2R_*^3}{2\left[(z_B + \bar{z}_e)^2 + \rho_e^2\right]^2}. \quad (6)$$

This potential for the lowest electron energy levels can be approximated by a quadratic function [7]:

$$V_{eB}(\rho_e, z_e, z_B) = -\left[\frac{eER_*^3}{z_B^2} + \frac{e^2R_*^3}{2z_B^4}\right] + \frac{\rho_e^2}{z_B^2}\left[\frac{3eER_*^3}{2z_B^2} + \frac{e^2R_*^3}{z_B^4}\right]. \quad (7)$$

The electron energy levels in this harmonic oscillator potential are given by the frequency:

$$\omega_0^2 = \frac{2}{mz_B^2}\left[\frac{3eER_*^3}{2z_B^2} + \frac{e^2R_*^3}{z_B^4}\right]. \quad (8)$$

The optimal distance of the cluster from the helium surface can be obtained by minimizing the total energy approximately given by [7]

$$V(z_B) \approx \frac{(E_{tot}R_*^3)^2}{8z_B^3}\frac{\epsilon_h - 1}{\epsilon_h + 1} - \frac{eER_*^3}{z_B^2} + \frac{e^2R_*^3}{z_B^4}\left[0.11(2\epsilon_h + \epsilon_B) - 1/2\right]. \quad (9)$$

where $E_{tot} = E + e/z_B^2$. For an ice cluster $\epsilon_B = 80$. In this case the expression in square brackets is positive. Since $(\epsilon_h - 1)/(\epsilon_h + 1) \approx 1/300$, one can neglect the first term in (9). Minimizing (9) we get an estimate for the optimal distance of the cluster from the surface z_{B0} as a function of external electric field (in SGSE units)

$$z_{B0} = \frac{10^{-4}}{\sqrt{E}}. \quad (10)$$

For a cluster with $R_* = 500$ Å, the condition $z_{B0} \gg R$ is fulfilled at $E \ll 30000$ V/cm, i.e. at all available fields. One can show that for clusters of smaller size $R_* = 100$ Å there is also a wide interval of the external field where these charged clusters are stable.

We have just argued the possibility to realize a 2D system of charged clusters below helium surface. The dipole moment and electric charge of each cluster allow clusters to be fixed at a macroscopic distance $z_0 > R$ below the helium surface. At low helium temperatures any thermal fluctuations of the positions of these heavy charges are small. Let us now consider the Wigner crystallization of these charges.

The interaction of two charged clusters at the distance a is described by the potential energy

$$V_{int}(a) = \frac{e^2}{a} + \frac{(\vec{E}_{ex} R_*^3)^2}{a^3} \equiv V_e + V_d. \tag{11}$$

The dipole-dipole part V_d of the interaction between clusters becomes dominant ($V_d > V_e$) if $ae < E_{ex} R_*^3$. At $E_{ex} = 5 \cdot 10^3$ V/cm, $R_* = 5000$ Å and $a = 10R_*$ (this corresponds to the average cluster density $n_s = 1/a^2 = 4 \cdot 10^6 \mathrm{cm}^{-2}$) one gets

$$V_e = 3\mathrm{K}; \quad \mathrm{V_d} = 300\mathrm{K}. \tag{12}$$

Accepting the empirical criterion $V(a) > 100 k_B T$ of a 2D Wigner crystal to melt we come to the conclusion of the possibility to observe the liquid-to-crystal phase transition at rather high temperature $T \sim 3$K. The oddity of the situation at hand is that the crystal lattice is formed by the short-range dipole forces ($V_d \gg V_e$), and the long-range Coulomb interaction appears in the existence of long-wave plasma oscillations. An observation of these effects should be possible by using the method first applied 50 years ago [8] (for more recent references see [6]). The neutral clusters come to helium through its surface and go down slowly to the bottom of the helium vessel where the electron source is maintained. The electrons from the injector are drawn up by the electric field. In the bulk of helium some of the clusters bind one electron and form a 2D charged system below the surface. Other clusters glue to the bottom of the vessel by the van der Waals forces. The excess electrons will finally make a quantum tunnel transition through the helium surface to the vacuum where electrons have a lower energy. The energy of big charged clusters is, on the contrary, lower inside the helium because of the short-range van der Waals attraction of the cluster to the atoms of liquid. This gain of the van der Waals energy is roughly proportional to the cluster surface.

To study stability of 2D charged system of clusters one has to consider also their van der Waals attraction to each other at the mean distance a. At a large distance, the van der Waals potential energy of two atoms is [9]

$$V_{vdW}(a) = \frac{23\hbar c}{4\pi a^7} \beta^2, \tag{13}$$

where β is the atomic polarizability of clusters. It is related to the dielectric constant $\varepsilon_B = 1 + 4\pi\beta n$, where n is the density of the cluster medium. Integration of (13) over the cluster volume gives

$$V_{BB}(a) = \frac{23\hbar c R^6}{36\pi a^7} (\varepsilon_B - \varepsilon_H)^2. \tag{14}$$

For a cluster consisting of H_2O molecules with $\varepsilon_B \approx 80$, $R = 5000$ Å and $a = 10R$ (the same as in (12)) we get from (13) the estimate of $V_{BB}(a) = 0.6$K. Since $V_{BB}(a) \ll V_d(a)$, there is a wide range of parameters where the 2D system under study is stable against coagulation (sticking together) of clusters.

It is much easier to detect the Wigner lattice of huge charged clusters than that of electrons. The Wigner lattice of electrons permits only an indirect method for experimental studies [10]. On the other hand, the Wigner crystallization of charged clusters can be detected directly by neutron or X-ray scattering. If the charged clusters are very large ($R \gg 5000$Å), they can be visually observed.

The third object we want to note is the system of negative ions on the liquid helium surface.

The quantum effects in 2D electron gas on the helium surface attract great attention. For distinguishing the role of these quantum effects it would be very useful to be able to change the electron mass. For example, this would help to find out if the quantum melting of electron Wigner crystal was indeed observed in [11]. Such an opportunity is given by negative ions on the helium surface [12]. We show that the negative Ca- and Ba- ions of large radii are adsorbed on the helium surface. Ions on the free liquid helium surfaces have not been studied previously due to a seeming impossibility to confine them on the surface. Ca- and Ba- ions have very low binding energies and hence, like electrons, form bubbles of large radius in the bulk of helium, the energy of which is higher than on the surface. The behavior of ions on the surface exhibits a number of previously unknown features owing to their large masses and strong localization in the horizontal plane. Even in the absence of a confining electric field, a hole is formed below an ion due to the polarization attraction between the liquid helium and the charged ion. This hole formation reduces the ion mobility by several orders of magnitude and increases its effective mass several times more [12]. The critical density of electrons and ions is approximately the same on the surfaces of thin and thick helium films.

The last objects on the liquid helium surface we want to mention, are the bound states of helium atoms. The concentration of helium vapor above liquid helium falls down exponentially as the temperature decreases. The temperature dependence of surface tension and the mobility of surface electrons at such low temperature is determined (according to the common opinion) only by surface waves – ripplons. However, there is another surface object that strongly influences both of these observable quantities even in pure helium isotopes. These are the surface states of helium atoms. The

energy difference of this surface state and the chemical potential of helium atoms in the bulk is $\approx$ 0.2K for ^{3}He and $\approx$ 3K for ^{4}He. This is much less than the corresponding difference for the He vapor ($\approx$ 7.15K for ^{4}He). Therefore, these surface states have some essential occupation by He atoms (which form a 2D gas on the surface) and influence all properties of the liquid He surface. This idea has been proposed only recently in [13] where the effect of these surface states on the surface tension of pure He isotopes has been calculated and compared with the experimental data obtained in Japan [14].

In closing, we note that the considered effects are not very sensitive to the type of quantum liquid. They could also be observed in liquid hydrogen, where $\varepsilon_H = 1.28$.

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