Ions at helium interfaces

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Abstract. The boundaries between different phases of condensed helium provide an interesting testing ground for studying ions in a quantum matter matrix. Here we consider the simplest positive and negative ions in helium – snowballs and electron bubbles, respectively – being trapped at the liquid-liquid interface of phase-separated ^3He - ^4He mixtures and at the liquid-solid interface of ^4He . A comparison of experimental results for the trapping with predictions of the snowball and the bubble models shows that the models are in qualitative accord with the observations, but disagree in detail. It is suggested to use such studies for refinements of the ion models. In addition multielectron bubbles (= mesoscopic ions) and electrons on helium films are briefly discussed.

1. Introduction

The condensed phases of helium provide a variety of very clean, well-defined interfaces which in the past have been studied both for their own sake and as model systems for condensed matter in general. The interface between liquid and solid He, e.g., is one of the best understood systems displaying a roughening transition, and subtle but important details have been measured there [1], which in other systems so far have not been experimentally accessible. Likewise, liquid mixtures of the two stable helium isotopes ^3He and ^4He in the vicinity of their consolute critical point (at a temperature $T_c = 0.867\text{ K}$ and a ^3He concentration $x_c = 0.67$) represent one of the most ideal and best-studied systems exhibiting a higher order (in this case tri-)critical point, and the interface between the two co-existing helium phases – a superfluid ^4He -rich and a normal ^3He -rich phase – has been the topic of detailed investigations, in particular with respect to its critical behavior [2]. Moreover, the most easily accessible helium interface, namely the “free” surface between liquid and gas, has also been studied in a number of experiments.

In the course of these investigations ions have played an important role for several reasons:

- i) ions can be used as very sensitive and convenient probes not only for bulk, but in particular also for interfacial and surface properties;
- ii) vice versa, interfaces can be used to test models for the various ion species in liquid and solid helium;
- iii) the ions, being charged particles, form novel 2-dimensional Coulomb systems which due to their interaction have interesting collective properties.

Whereas the first aspect, ions as an interfacial and surface probe, has been reviewed already in several articles [3] and will therefore not be considered here further, there exist hardly any publications on the exploitation of helium interfaces for testing models of the ion structures. This will hence be the central topic of the present paper. The last aspect, phenomena arising from the Coulomb interaction between charges at the interface, is treated in the contribution by W.F. Vinen in this volume and will only be shortly addressed at the end of this paper.

The ions we shall deal with are the two types that are most easily generated in liquid helium [4], e.g. by irradiation with energetic particles: The negative ion in this case simply consists of an electron inside a spherical cavity in the liquid, the so-called electron bubble, which has a diameter of about 35 Å and is stabilized essentially by the equilibrium between the forces due to surface tension (pointing inward) and zero point motion of the electron (pointing outward). Positive He ions in liquid helium, on the other hand, are considered as solid “snowballs”, which form under the influence of the electrostrictive pressure due to the central charge of the snowball, and have a diameter around 15 Å .

In spite of these – in principle – simple pictures we shall see that the behavior of these ions at interfaces cannot be described in a quantitative way, if the crude models existing for bubbles and snowballs are applied. Such discrepancies, derived from the trapping of ions at interfaces, have been pointed out already one and a half decades ago [5,6]. Since then, however, considerable progress has

been made in experimental techniques, one of the most spectacular being the application of laser spectroscopy, as evidenced in various contributions to this symposium. These new experiments certainly will give rise to more refined versions of the ion models, and existing results for ions at interfaces can then serve as a sensitive testing ground for these models. Moreover, it has been shown [3] that it is possible to accumulate considerable ion densities ($\sim 10^9 \text{ cm}^{-2}$) at the interfaces, hence it should be possible to study the ions directly in this environment by spectroscopic means.

In the following we shall treat in chapter 2 the trapping of ions at the interface between the coexisting ^3He - and ^4He -rich phases of liquid ^3He - ^4He mixtures near the tricritical point. Chapter 3 deals with ions at the interface between liquid and crystalline ^4He . Finally, in chapter 4 charges at the liquid-gas interface are considered, mainly the mesoscopically sized multielectron bubbles and electrons on He films.

2. Ions at the liquid-liquid interface of ^3He - ^4He mixtures

As already mentioned, a ^3He - ^4He mixture with concentration x , is phase-separated below the tricritical temperature, with a ^3He -rich normal phase floating on top of a ^4He -rich superfluid one. The boundary between the two coexisting phases undergoes a critical softening near T_c , which manifests itself in a rapid decrease of the interfacial tension $\sigma_i \propto (T_c - T)^2$ [2]. The motion of the ions is strongly influenced by this interface: For electron bubbles it has been observed that at temperatures far below T_c , where σ_i is large, the charges do not penetrate from the upper into the lower phase due to a high energy barrier at the phase boundary [7]. The barrier results mainly from the lower surface tension of the ^3He -rich phase and has been estimated to be $\Delta W \approx 220 \text{ K}$ for temperatures below 0.3 K . Thus electron bubbles can be trapped above the interface at a distance of about the bubble radius. On approaching the tricritical point the two coexisting liquid phases become more and more similar, and the barrier height decreases rapidly. Eventually, when ΔW becomes comparable to $k_B T$, the ions will be able to pass the barrier by thermal activation.

For positive He "snowballs" the interface was shown to represent a barrier in the reverse direction, from the lower to the upper phase, because the positive ion energy (dominated by the polarizability) is lower in the superfluid phase [5]. Thus a layer of such snowballs can be trapped just below the interface when an appropriate holding field is applied. (Polarization effects also provide a potential barrier for the negative ions going from the denser to the less dense phase, similar to the situation at the free ^4He surface [8], hence at low enough temperatures bubbles can also be trapped below the ^3He - ^4He interface). Again, sufficiently close to the tricritical point the barrier height becomes comparable to $k_B T$, and also the positive ions will pass into the other phase.

Since the energy barrier ΔW depends on the structure of the ions, a determination of the characteristic trapping time τ at the interface (which is essentially determined by ΔW) can serve as a sensitive consistency check for the

models used to describe the ion structure. Measurements of the trapping times have been carried out [5] either by following directly the decay of the current after charging the interface or by optically measuring the deformation of the interface caused by the electrostatic pressure of the trapped ion pool (see Fig. 1). Results for τ in the vicinity of the tricritical point are shown in Fig. 2a for positive and in 2b for negative ions as a function of temperature. Obviously the trapping time varies quite rapidly with temperature, so that the range of τ which is easily accessible – about 1 to 1000 s for the two experimental techniques mentioned above – restricted the measurements to a temperature interval $T_c - T$ from 70 to 90 mK. In addition to the pronounced temperature dependence there exists also a variation of the absolute value of τ with the applied electric holding field E . For both kinds of ions τ decreases as E is raised, which qualitatively is the expected dependence. Quite unexpectedly, however, both the absolute value and the temperature dependence of τ for positive and negative ions are very similar. By contrast, the existing snowball and bubble models suggest very different behaviors:

i) for *negative ions* one can estimate the energy barrier ΔW by considering the main contributions to the bubble energy

$$W = \hbar^2 \pi^2 / [2m R^2 (1 + \hbar / (R^2 2m V)^{1/2})^2] + 4\pi R^2 \sigma + (4\pi/3) R^3 p - e^2 (\epsilon - 1) / 2\epsilon R. \quad (1)$$

resulting from the energy of an electron in a spherical potential well of depth V and radius R , from the surface tension σ , the hydrostatic pressure p and the polarisation of the surrounding medium with a dielectric constant ϵ . A comparison of these contributions for the ^3He - and the ^4He -rich phase shows that only a relatively small energy barrier on the order of 2 K should exist at a temperature $T_c - T = 80 \text{ mK}$.

ii) for *positive ions*, an estimate for ΔW can be obtained by taking into account the polarisation of the liquid surrounding the snowball:

$$W = W_{\text{core}} - (e^2 / R_+) (\epsilon_4 - \epsilon_3) / 2\epsilon_3 \epsilon_4 \quad (2)$$

where the energy W_{core} contains the energy of the snowball itself and the contribution of the liquid-solid surface tension (the indices refer to the ^4He - and ^3He -rich phase, respectively). If we assume for simplicity that the internal snowball structure does not change when passing from one phase to the other, we obtain for the difference of the positive ion energies

$$W_4 - W_3 = - (e^2 / R_+) (\epsilon_4 - \epsilon_3) / 2\epsilon_3 \epsilon_4 \quad (3)$$

In this case the value calculated for the energy barrier ΔW is 40 K at a temperature $T_c - T = 80 \text{ mK}$, a factor of 20 higher than for negative ions. Since $\epsilon_4 - \epsilon_3$ varies linearly with $T_c - T$ one expects a dependence

$$\tau \propto \exp[(T_c - T) / k_B T] \quad (4)$$

Indeed, an exponential relationship of this form, indicated by the straight lines in Fig. 2a, is in accord with the

Fig. 1. Experimental set-up for measurements of the trapping time of negative ions. When the ion source (here a field emission tip) is switched off, an exponential decay of both the collector current and the light intensity at the photomultiplier is observed. The ring is charged such that loss of ions to the wall is prevented. For positive ions the sample cell was inverted, and a radioactive source was used (after [5])

Fig. 2. Trapping time τ of positive and negative ions at the interface of a phase separated liquid ^3He - ^4He mixture in the vicinity of the tricritical temperature $T_c \approx 0.867\text{ K}$. Electrical holding fields are indicated. Open and closed circles refer to electrical and optical measurements (see Fig. 1)

experimental data. Yet the model cannot fully account for the observed trapping times of the positive ions, because the theoretical value of the coefficient b and hence the calculated absolute value of ΔW is about twice as large as derived from the data in Fig. 2a.

For negative ions, on the other hand, the theoretical prediction for ΔW , as calculated from (1), is smaller than the experimental value. The disagreement in the absolute value in this case even amounts to nearly one order of magnitude.

Since the experimental uncertainty in τ is well below these discrepancies, the simple ion models used here are obviously insufficient to account for a quantitative description, and more refined approaches appear to be necessary. One might hope that improvements based on the recent progress on ion studies could help to solve this puzzle. In this context the measured dependence of the trapping time on the holding field E (Fig. 6 in [5]), which so far is also lacking a quantitative interpretation, might be a valuable check of more sophisticated models.

3. Ions at the liquid-solid interface of ^4He

It is known from a number of experiments, that the formation of electron bubbles is not restricted to the liquid phase, but that this kind of negative ions also exists in solid ^4He [9]. Using a calculation similar to (1) the bubble energy in solid ^4He at the melting pressure can be estimated to be about 200 K higher than in the coexisting liquid phase [10]. Therefore it should be possible to trap electron bubbles at the liquid-solid interface. Experimentally it has been demonstrated that this is indeed the case; actually the trapped ion pool has been used in various experiments, e.g. to determine the growth coefficient of ^4He crystals [11]. Nevertheless, the details of the bubble structure at the interface are far from being clear: If an electron bubble is pulled against the liquid-solid interface from the liquid side by an external electric field and is hence in contact with the crystal, its surface is partly liquid and partly solid (Fig. 3). Nothing is known to date about details of the bubble shape in such an anisotropic environment. As for the liquid-liquid interface discussed before the spectroscopy of bubbles trapped on solid helium appears as a promising tool to shed light on this peculiar system.

For positive ions at the liquid-solid interface the knowledge is even more sparse. It is not clear, e.g., whether they are trapped at all at this boundary when approaching the crystal surface from the liquid phase. At first glance one might expect that the snowballs, due to their solid core, can easily penetrate from the liquid side into the crystal. However, the structure of the snowball is expected to be incompatible with the crystal structure of hcp ^4He . Therefore one might have a large angle of contact between the surfaces of the snowball and the crystal, just as for ^4He crystals in contact with the disordered solid ^4He layer covering "usual" sample cell walls [12]. This phenomenon of incomplete wetting between ordered and disordered solid ^4He should give rise to a surface barrier for the snowball at the liquid-solid interface. Yet diffusion processes in the contact region might locally rearrange the ^4He atoms, as for the drift of the snowballs in the crystalline phase under the influence of an external electric field [13], so that upon closer investigation the wetting argument might not hold. In fact, preliminary measurements seem to indicate that snowballs do enter the crystal from the liquid

Fig. 3. Existence of an electron bubble at a liquid-solid He interface

phase (14), but more conclusive experiments are required for a definite answer.

5. Electrons at the liquid - gas interface

In this chapter we consider electrons trapped above the surface of liquid He. Hence we are not really dealing with ions but with quasi-free electrons, moving parallel to the surface in the potential well resulting from the superposition of the attractive image potential induced by the electrons in the dielectric substrate (helium), the external electrostatic potential which provides charge neutrality of the whole system, and the short range Pauli repulsion due to the closed electron shell of the He atoms. The surface state electrons thus form a two-dimensional Coulomb crystal with intriguing properties, such as the formation of a solid "Wigner crystal" phase at low enough temperatures (15).

Since the electrons, under the influence of the externally applied electric field, exert an electrostatic force upon the He, the liquid surface is slightly depressed in the region of the electron pool. As the electron density is raised, this depression increases in depth until finally the surface undergoes an electrohydrodynamic (ehd) instability, where the electrons penetrate into the liquid in the form of multiply charged gas bubbles (16, 17). In a narrow transition region one in addition observes the formation of stable periodic structures on the surface, the so called dimple lattice, which results from a soft mode in the spectrum of surface excitations (ripples) in the presence of charges (18).

6.1. Multielectron bubbles

The multielectron bubbles which are generated during the ehd instability are determined in their size essentially by

Fig. 4. Schematic set up for electrical and optical detection of multielectron bubbles. The video camera for the optical measurement was focused on the volume between anode and glass tube, at an angle of 50° with respect to the laser beam, to pick up light scattered from the bubbles in nearly isotropic direction.

Fig. 5. Displacement current due to a train of multielectron bubbles in liquid He recorded at the anode (see Fig. 4) at a temperature of 4.5 K. Each peak corresponds to one multielectron bubble (Z = number of electrons in the bubble).

the equilibrium between surface tension and electrostatic pressure, just as for single electron bubbles. The electronic term now is dominated by the mutual Coulomb repulsion of the electrons located at the inner surface of the bubble. A typical bubble charge is some 10^4 elementary charges, the corresponding bubble diameter several μm (17).

Due to their microscopic size, these multielectron bubbles can easily be detected by light scattering techniques. With the set-up schematically sketched in Fig. 4 it was also possible to generate regular trains of bubbles, as shown in Fig. 5. Excited by their motion through the liquid the bubbles exhibit pronounced oscillations (Fig. 6) which sometimes get strong enough that the bubble undergoes a "Coulomb explosion" and separates into two smaller fragments.

Multielectron bubbles, like trapped single ions, present many open problems regarding their behavior at interfaces. Even their stability at interfaces has not yet been investigated, but one might imagine various scenarios. If

Fig. 6. Track of a single multi-electron bubble moving from the liquid He surface to the anode tip. The illumination time is 20 ms (one video frame). Modulations along the track are due to oscillations of the bubble. In the upper part of the track a fairly regular oscillation can be seen (a frequency of about 2 kHz as determined in an independent measurement), which then develops into a superposition of several oscillation modes giving rise to larger, irregular spacings.

we consider a multi-electron bubble being dragged, e.g. towards the liquid-solid He interface (or, perhaps easier to realize, the interface between liquid He and solid hydrogen), it might disintegrate into individual single-electron bubbles, caused by the deformation of the large bubble when it is in contact with the solid. If the perturbation generated by the solid wall is small enough, on the other hand, the multi-electron bubble could remain stable, and one could in this way have a convenient trap to study a bubble in detail with respect to its eigenmodes [19], the properties of the electron system on its surface, etc. As an interesting aspect of the multi-electron bubbles the electron density on their surface can be rather large, well beyond the limit of $2.4 \times 10^{11} \text{ cm}^{-2}$ [3] on a flat liquid He surface given by the onset of the chd instability mentioned above. This increase is possible because the bubble due to its small radius of curvature can balance a large electrostatic pressure of the electron system inside it.

4.2. Electrons on He films

As an alternative way of circumventing the chd instability one can use the van der Waals force, acting from a solid substrate upon a thin He film and thus stabilize the He surface even at very high electron densities up to 10^{12} e/cm^2 and beyond. This range, where quantum corrections to the classical behavior of the 2D electron system are expected to become relevant, has been demonstrated to be experimentally accessible already some time ago [26]. However, pinning of the electrons to the surface roughness of the solid substrate below the He film (like glass plates or polymer foils) reduced the electron mobility, which for a long time hampered the experiments with

Fig. 7. Microwave absorption *a* and susceptibility *b* of a 2-dimensional sheet of electrons on a thin He film (supported by an oxidized Si wafer) at a temperature of 1.3 K. The electron density was estimated from the thickness of the oxide (about 1000 Å) and the applied holding voltage. The kinks in the curves at an electron density of 10^{11} cm^{-2} (arrow *a*) see a signature for the transition from a 2D electron fluid to the 2D Wigner solid phase [13]. The abrupt signal changes at $n = 0.5 \times 10^{11} \text{ cm}^{-2}$ (arrow *b*) might indicate the phase transition from the Wigner solid to the degenerate 2D Fermi gas.

these systems. In spite of such difficulties microwave measurements have very recently revealed striking features in the electron susceptibility and absorption at high electron densities (see Fig. 7) [21], which might be interpreted as the long-sought phase transition from the Wigner crystal to the degenerate Fermi gas in the quantum regime of a 2D Coulomb system. More detailed experiments are presently underway to find additional evidence for such a transition.

5. Conclusion

In this brief article on ions at helium interfaces only a few of the various aspects of these interesting systems could be touched. It is evident that for most questions that arise

due to the presence of an interface only qualitative, if any, answers exist, and that some of the present arguments are rather speculative. Nevertheless the combination of ions and quantum matter interfaces appears as a promising and sensitive tool to investigate a fascinating field at the borderline between atomic and condensed matter physics. There are good chances that results from these systems, in particular in view of new experimental developments, can serve as a useful guideline for theoretical efforts towards a more complete understanding of ions in helium.

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