IONS AT THE CRITICAL INTERFACE OF ^3He - ^4He MIXTURES

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Résumé.- Nous avons étudié des ions positifs et négatifs à l'interface des mélanges ^3He - ^4He . A cause de l'état critique le passage des ions par l'interface augmente fortement en approchant du point tricritique. Les temps de capture changent de trois décades dans un intervalle de température de seulement 20 mK et dépendent beaucoup du champ électrique.

Abstract.- Trapping of positive and negative ions at the interface of ^3He - ^4He mixtures has been studied. Due to the critical behavior the transmission of ions through the interface increases sharply as the tricritical points is approached. The trapping times for both types of ions vary by three orders of magnitude within temperature intervals of only 20 mK, and also depend strongly on the applied electric holding field.

1. INTRODUCTION.- The free surface of liquid helium has evolved as a nearly ideal substrate for studying electrons in 2 dimensions. The properties of such a sheet of surface state electrons, like cyclotron and plasmon resonances, have been investigated in detail [1]. Yet a number of predicted phenomena has until now escaped experimental verification, like the transition to an ordered state (Wigner crystal) [2], the dimples associated with the interaction of individual electrons with the helium surface [3], or the modification of the ripplon dispersion relation by the presence of surface state electrons [4,5]. Some of these phenomena should be much more easily detectable, if the perturbation of the surface due to the interaction with the Coulomb system could be increased, for instance by lowering the surface tension σ of the liquid substrate.

We have started to investigate such Coulomb systems, where σ is orders of magnitude less than at the free helium surface, namely ions at the interface of liquid ^3He - ^4He mixtures. Below the tricritical point (temperature $T_c = 0.867$ K, ^3He -concentration $X_c = 0.675$) a mixture with concentration X_c is phase separated with a ^3He -rich normal phase floating on top of a ^4He -rich superfluid phase. The boundary between the coexisting phases undergoes a critical softening near T_c , which manifests itself in a rapid decrease of the interfacial tension $\sigma_i \propto (T_c - T)^2$ [6].

The motion of ions in the mixture is strongly influenced by this interface. For temperatures far below T_c , where σ_i is large, it has been observed

that negative ions ("electron bubbles") do not penetrate from the upper to the lower phase because of a high energy barrier at the phase boundary. The barrier results mainly from the lower surface tension of the ^3He -rich phase and has been estimated to be $\Delta W \sim 220$ K below $T = 0.3$ K [7]. Thus it seems feasible to hold a layer of electron bubbles immediately above the interface at a distance of about the bubble radius $R \sim 20$ Å. On approaching the tricritical point the two coexisting liquid phases become more and more similar, and the barrier height decreases. Finally, when ΔW becomes comparable to kT , the ions will be able to pass the barrier by thermal activation.

For positive ions ("snowballs") the interface is expected to present 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. Therefore a layer of such snowballs should be formed just below the interface when an appropriate holding field is applied. Again, sufficiently close to the tricritical point the barrier height will become comparable to kT , and also the positive ions will pass into the other phase.

Apparently for a study of two-dimensional Coulomb systems interacting with a soft substrate one would like to approach the tricritical point very closely in order to have an interfacial tension as small as possible. On the other hand, for temperatures too close to T_c the ions will be trapped at the interface for a time too short to form a two-dimensional system in equilibrium. It is desi-

erable, therefore, to establish the temperature region where the transition from an impenetrable to a transparent interface takes place. We have investigated this transition separately both for negative and for positive ions as a function of temperature and applied electric holding field.

2. MODELS.- To illustrate roughly the conditions near the interface, we have plotted in figures 1 and 2 the energy of the ions in the ^3He - and ^4He -rich phase, as calculated from the snowball and bubble models /8/.

Fig. 1 : Variation of the potential of positive ions near the interface of ^3He - ^4He mixtures. The dotted line is calculated from equations (2) and (5), using $R_+ = 6.5 \text{ Å} / 8$, and $\Delta\epsilon = 3.1 \times 10^{-3} / 10$. The dashed line represent an electric holding field of $E = 50 \text{ V/cm}$ perpendicular to the interface, and the solid line is the sum of both contributions. The arrow indicates the potential minimum. For distances z from the interface smaller than the ion radius equation (5) is not applicable, and the dash-dotted line gives an estimate for the potential in this region

i) Positive ions are considered as $(\text{He}_2)^+$ -ions, surrounded by a core of solid helium with a radius R_+ of about $7 \text{ Å} / 8$. The energy of this complex is lowered by the polarization of the liquid surrounding the snowball

$$W = W_{\text{core}} - \frac{e^2}{R_+} \cdot \frac{(\epsilon_{3,4} - 1)}{2\epsilon_{3,4}} \quad (1)$$

where the energy W_{core} also contains the contribution of the solid-liquid surface tension, and the subscripts of the dielectric constant ϵ refer to the ^3He - and ^4He -rich phase. If we assume that the internal snowball structure does not change when going from one phase to the other, we obtain for the difference of the positive ion energies

$$W_4 - W_3 = - \frac{e^2}{R_+} \frac{(\epsilon_4 - \epsilon_3)}{2\epsilon_4 \epsilon_3} \quad (2)$$

Fig. 2 : Variation of the potential of negative ions near the interface of ^3He - ^4He mixtures as calculated from equations (4) and (5). The different lines have the same meaning as in figure 1. The parameters used are $R_- = 21 \text{ Å} / 8$, $\Delta\epsilon = 3.1 \times 10^{-3} / 10$, $\sigma_i = 6.5 \times 10^{-4} \text{ erg/cm}^2 / 6$, and $E = 50 \text{ V/cm}$. The potential wells $V_3 = 0.78 \text{ eV}$ and $V_4 = 0.85 \text{ eV}$ for the ^3He - and ^4He -rich phase, respectively, are obtained from the pure phases /11/ by linear interpolation. The dash-dotted line for $|z| < R_-$ is only a crude estimate, and the cusps at $z = \pm R_-$ are smeared out when the finite interfacial thickness is taken into account

ii) For negative ions, according to the bubble model the energy can be written as

$$W = \frac{\hbar^2 \pi^2}{2mR_-^2} \left[1 + \frac{\hbar}{(R_-^2 2mV)^{1/2}} \right]^{-2} + 4\pi R_-^2 \sigma + \frac{4\pi}{3} R_-^3 p - \frac{e^2 \cdot (\epsilon - 1)}{2R_- \epsilon} \quad (3)$$

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 polarization, respectively. Since the hydrostatic pressure and R_- are practically the same in both phases, the difference of the bubble energies is

$$W_4 - W_3 = \frac{\hbar^3 \pi^2}{R_-^3 (2m^3)^{1/2}} \cdot \left[\frac{1}{(V_3)^{1/2}} - \frac{1}{(V_4)^{1/2}} \right] + 4\pi R_-^2 \sigma_i - \frac{e^2 (\epsilon_4 - \epsilon_3)}{R_- \cdot 2\epsilon_4 \epsilon_3} \quad (4)$$

Here we have made use of Antonov's rule /9/, saying that the interfacial tension σ_i is equal to the difference of the surface tensions of the two phases in

equilibrium. For temperatures near the tricritical point, the resulting bubble energy is higher in the ^3He -rich phase, which at first sight seems to be contradictory to earlier estimates at low temperatures /7/. However, close to T_c the polarization term in (4) outweighs the other contributions.

Near the interface, the image potential

$$W_i = \frac{e^2}{4z} \cdot \frac{\epsilon_3 - \epsilon_4}{(\epsilon_3 + \epsilon_4)} \quad (5)$$

becomes important, and the resulting variation of the ion potentials with distance z is indicated by the dotted lines in figures 1 and 2. An electric holding field adds to these energies a term eEz . Note that for a field of, say, $E = 50$ V/cm at $T_c - T = 80$ mK the positive ion energy has a minimum at $z = 106$ Å below the interface. In contrast, negative ions in this model are located immediately above the interface even in the absence of a holding field.

So far the interface has been assumed as being infinitely sharp and rigid. This is certainly not correct near T_c , when the expected dimples in the critical interface and also the interfacial width become larger than the ion radii. Since no reliable estimate exists for these contributions until now, they have not been taken into account in the potentials of figures 1 and 2, which therefore should be regarded as rather qualitative. Actually, as will be seen in the discussion, the properties of the critical interface probably play an important role in the interpretation of the data.

3. EXPERIMENTAL.— In our initial experiments the ion current across the interface was measured as a function of temperature, with the applied fields being held constant. As an example, figure 3 shows the result for negative ions in a field of 85.7 V/cm. The current drops sharply to below the limit of detection within a temperature interval of only 20 mK, signaling the transition from a transmitting to an impenetrable interface around 60 mK below T_c .

As the equilibrium current I_0 decreases, the ions are trapped for a longer and longer time in the potential well near the interface. This trapping time yields a more unambiguous information than the current I_0 , which is disturbed by space charges and by fluctuations of the ion source efficiency.

The set-up we used for the ion trapping measurements is sketched in figure 4. After the inter-

Fig. 3 : Negative ion current across the interface of a phase separated ^3He - ^4He mixture in a field $E = 85.7$ V/cm. Above 0.82 K, the current is limited by the mobility of the ions in the bulk. Below, trapping at the interface becomes dominant.

Fig. 4 : 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.

face was charged, the source was switched off, and the number of ions at the interface began to decrease with a time constant τ equal to the trapping time. τ was determined in two complementary ways : First, the exponential decay of the current across the interface was measured with an electrometer /12/. This conventional method was applicable for trapping times between 1 and 100 s. For longer τ 's when the

currents became very small we applied a different method, using the fact that due to the electric holding field the ions exert a force upon the interface. This force leads to a macroscopic, but still very shallow deformation [13] proportional to the number of trapped ions (less than 10^{-2} mm deep for the fields and ion densities used here). When the light beam of a low-power laser is directed at the phase boundary at the limiting angle of total reflection, the deformation allows a small portion of light to leak into the upper half space, where it can be detected with a photomultiplier. In this way also extremely long trapping times can be measured quite sensitively. In the region of overlap, good agreement was found for electrically and optically determined τ 's.

4. RESULTS AND DISCUSSION.- The observed trapping times are plotted in figure 5 vs. temperature difference ($T_c - T$). Remarkable is the strong temperature dependence: τ varies by three orders of magnitude within a temperature interval of only 20 mK, both for negative and positive ions. Besides, the absolute value of τ is quite comparable for the two kinds of ions.

Fig. 5 : Trapping time τ of negative and positive ions vs. temperature. Electric holding fields are indicated; open and closed circles refer to electrical and optical data points, respectively. For clarity only a small fraction of the data is shown.

The data suggest a dependence

$$\tau \propto e^{\Delta W/kT} \quad (6)$$

- indicated by the straight lines - with an energy barrier ΔW at the interface varying roughly as

$\Delta W \propto (T_c - T)$. From the slopes the absolute value of ΔW can be estimated. Note that in terms of equation (6) the strong variation of τ is essentially due to the temperature dependence of ΔW , since kT changes by only 2.5 % in the investigated temperature interval.

As can be seen from the nearly constant slopes in figure 5 the electric field shows little effect upon the barrier height for either type of charge, but it has a marked influence on the absolute value of τ . This becomes more obvious from figure 6, where the variation of τ vs. E is plotted for constant temperature ⁽¹⁾. Qualitatively the decrease of τ with increasing E seems reasonable because at high fields the ions are drawn closer to the interface, and are therefore more likely to pass that barrier.

Fig. 6 : Trapping time vs. holding field E . $T_c - T = 73$ mK for negative and 70 mK for positive ions

A more quantitative comparison shows, however, that the simple snowball and bubble models outlined in section 2 are not sufficient to account for the observed trapping times :

i) Positive ions, due to the potential in figure 1, are located at a distance of the order of 100 Å below the interface. Since this is much larger than

(1) These measurements were checked in a different sample cell with a field configuration much more homogeneous than that in figure 4. Essentially the same dependence was observed.

the mean free path of these ions /8/, an adequate description for the ion transport across the phase boundary should be provided by Smoluchowski's equation for the diffusion of a particle over a potential barrier of height ΔW /14/ :

$$\tau^{-1} = \left[W''_{\max} \cdot W''_{\min} \right]^{1/2} (2\pi e)^{-1} \mu(T) \cdot e^{-\Delta W/kT} \quad (7)$$

where $\mu(T)$ is the ion mobility /15/, and $W''_{\max}$ and $W''_{\min}$ are the second derivatives of $W(z)$ at the maximum and minimum of the potential. The temperature dependence of τ is dominated here by the exponential factor, which justifies in retrospect deducing the energy barrier from the plots in figure 5. A significant discrepancy is found between ΔW_+ as calculated from the snowball model [equation (2)] and the energy barrier determined from a fit of the data to equation (7) with ΔW_+ as a variable. The experimental values are about a factor of two lower than predicted by (2), e.g. $\Delta W_+ \sim 20$ K instead of 40 K at $T_c - T = 80$ mK. Such a reduction is not quite unexpected because of the accumulation of ^4He atoms around the positive ions, which has also been observed in recent measurements of the positive ion mobility /15,16/.

Not only the absolute value of the potential barrier, but also its dependence on the applied electric field is not correctly reproduced by the simple snowball model. The variation of τ with E is stronger than estimated from figure 1, and it seems necessary to take the influence of the critical interface into account, like the reduction of the image force by the diffuse interfacial profile /6,7/, or the local deformation of the soft interface by the individual ions /3/.

(ii) For negative ions the distance from the phase boundary is expected to be very small. Hence it is not obvious that here the ion transport across the interface can again be described as a diffusion process ; indeed, a better model might be the thermal activation of a particle oscillating in a potential well. Since in this case, too, the predominant temperature dependence of τ is given by $e^{\Delta W/kT}$, we analyze our results in terms of such a relation (6), even though the details of the transport process are not known yet.

As for positive ions, also for bubbles the effect of the electric field on the trapping time is found to be much larger than expected from the calculated potential in figure 2, suggesting again the

influence of the critical interface. Besides, the temperature dependence of τ is only in poor agreement with the prediction of the bubble model. A quantitative analysis of the trapping times on the basis of the simple bubble model is very problematic, however, because the absolute value of the bubble energy W is about 10^3 K, whereas the difference $W_3 - W_4$ between the ^3He - and ^4He -rich phase is only of the order of a few K for the temperatures considered here. The calculated interfacial barrier is therefore very sensitive even to minor uncertainties in the various contributions to the bubble energy, like the surface tension or the potential well of the bubble.

In summary the present models do not provide a satisfactory description of the ion trapping at the phase boundary of ^3He - ^4He mixtures. Vice versa the trapping time data can serve as a sensitive test for more refined theories on ions at this critical interface and also for the interfacial structure /7/. In addition, our experiment has shown that both positive and negative ions can be trapped at the interface for times $\tau > 100$ s, as long as $(T_c - T) > 80$ mK. It should be possible therefore to study in more detail such two-dimensional Coulomb systems interacting with a soft substrate.

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