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Experimental behaviour of Ionic Structures in Liquid Helium - II.

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Summary. — Experiments have been performed to select a proper model among some proposed structures for helium ions in liquid helium. The apparatus is essentially a diode, where the ions are produced by α-rays and the currents can be measured in the bulk liquid, in the liquid-vapour interphase and in the bulk solid. By the quite different behaviour of the positive and negative ions in the interphase experiments one is led to picture the positive ion as a cluster of polarized atoms around one charge, and the negative ion as a large cage where the electron is self-trapping.

1. – Introduction.

The increasing interest in the use of ions in liquid helium as a tool for the investigation of the properties of liquid helium itself, calls attention to the nature of ionic structures. It is the purpose of this paper to discuss the possible structures, and then to describe an experiment which shows some evidence for these model structures for the positive and negative ions.

2. – Possible structures of ions in liquid helium.

In this Section we will briefly review and elaborate on the structures which have been proposed by us [1] and independently calculated by ATKINS [2].

2·1. *The positive ion.* – It is well known that in He gas the He_2^+ ion is a stable entity, and elementary calculations indicate that in a dense medium

[1] G. CARERI, F. SCARAMUZZI and J. O. THOMSON: *Nuovo Cimento*, **13**, 186 (1959).
[2] K. R. ATKINS: Univ. of Pennsylvania Techn. Rep. no. 3, Contract no. 551 (28).

a cluster He_n^+ must easily be formed, the n atoms sorrounding the positive ion being attached to it by polarization forces. These polarization forces are actually so large that the co-ordinated atoms will stick together at a distance much less than the average atomic distance, behaving like a highly compressed solid droplet. On this ground ATKINS has calculated the mass of a cluster due to this electrostrictive effect to amount to about 50 ^{4}He mass units. We point out here that this mass excess must be considered as a static effect, and has nothing to do with any hydrodynamical effective mass which may exist in specific situations, and may eventually be added to the above indicated static mass. Quite soundly ATKINS also observes that these clusters should be stable as long as the ion moves with a velocity lower than the sound velocity, the sound velocity being that rate at which a compression in the medium can propagate. For larger velocities the charge may leave the cluster and its mobility under an external electric field may then sharply increase, but it is not known if this will be at all the case due to possible creation of excitations by the hot charge cluster.

However we are faced with another possibility. The positive hole may migrate, jumping from one atom to another by random walk, as happens in similar situations in crystalline mediums. The jumping of the positive charge is, of course, in reality the transferring of an electron from a neutral atom to the positive ion, creating an ion from the formerly neutral atom. As ATKINS points out, the electrostrictive effect will soon be obliterated and we will have a quite different entity, a charge distribution in a quite large volume of low density. ATKINS discards this possibility with the argument that this could be the case only if the positive ion were monoatomic. In a cluster, he says, the jumping of a hole is no longer possible since this would involve rearrangement of the massive nuclei, and this cannot occur with a velocity greater than the zero point velocity of the He atoms.

It is our opinion, instead, that the charge may well escape the potential barrier which keeps it in the denser material, by some kind of tunnelling effect. Therefore the question of the possible structures of the positive ion is still an open one, and one has to choose between two limiting models:

I) the positive ion is a solid cluster of He atoms polarized around a positive charge, which may change site while still remaining inside the cluster;

II) the positive ion is a charge distributed in a large region with density comparable to that of the liquid, the charge continuously jumping from one atom to another.

2·2. *The negative ion.* – It is also well known that in He the He^- is unstable, and He_2^- must be loosely bound if it forms at all. It may be that He_n^- has some

stability, and the resulting structure would then be similar to the I) structure proposed above for the positive ion.

However, if the electron likes to stay in the empty space, then the interesting possibility exists that it might remain free in an effective cage, big enough to reduce its zero point motion, and self-trapping inside this cage by polarization forces. It seems that this possibility has been first independently pointed out by FERRELL [3] to explain the anomalous large life of positronium in liquid helium; as a matter of fact, in this way a positronium atom is able to avoid contact with the liquid and increase its lifetime. For this model ATKINS calculated that the extra mass associated with it may be as large as 280 ^{4}He atoms, the negative cloud extending over a region encompassing many helium atoms.

However, here again a tunnelling effect may exist, which could let the electron leave the shell-like cage of polarized atoms, and diffuse in a large region. Therefore we are still faced with the following possibilities:

I) The negative ion is a solid cluster, like the structure I) proposed for the positive ion.

II) The negative ion is a cloud of charge in a cage, self-trapped by the shell of polarized atoms.

III) The negative ion is a free electron moving in a large region, of the density of the liquid, escaping by tunnelling any trapping which might occur.

To the above possibilities, we must add the following one, suggested by WILLIAMS [4] and supported by analogies in the gas:

IV) The negative ion is actually a charged impurity (probably oxygen) which can form a cluster in the same way as the structure I) of the positive ions.

3. - Experimental.

In this Section we will describe an experiment of a qualitative nature, which in our opinion cap help one to choose between the ionic structures above outlined. In this experiment the ions are accelerated by the uniform electric field between the plates of a parallel plate capacity and the current thereby

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[3] R. A. FERRELL: *Phys. Rev.*, **108**, 167 (1957).

[4] R. L. WILLIAMS: *Canad. Journ. Phys.*, **35**, 134 (1957).

produced is measured as a function of the applied voltage. The gap between the horizontal plates would be filled with liquid or solid helium, or else partially filled with liquid so that the liquid-gas phase boundary was parallel to and between the plates.

3·1. *The apparatus.* – The apparatus is essentially a diode where the ions are produced by a layer of polonium at one plate, and collected on the other plate by a suitable electric field. Different diodes have been employed and here in the following we give their dimensions in cm (the symbols are shown in Fig. 1) and the relative current density J in units of 10^8 ions/s cm^2, as measured at the standard condition of 2 °K and 200 V/cm.

The plates were made of silver except for the diode No. 1 where platinum was employed. The polonium source was obtained simply by letting one drop of 0.5 normal nitric solution to evaporate on the plate. It is estimated that 10^{11} ion pairs per second were also produced, but the recombination in the liquid was so effective to get current densities ranging only between 10^{-15} to 10^{-10} A/cm^2 s. Incidentally, the range of α-particles in the liquid was lower than 0.3 mm.

The diode was protected sometimes by a plexiglass can, and the whole unit could be moved in the dewar by means of « O » ring seals to follow the bath level when the two phase system was investigated.

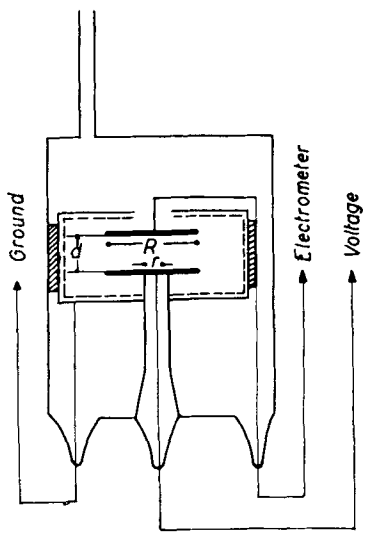

Fig. 1. – The diode used for the liquid and liquid-vapour phases. The helium cryostat is not shown.

The electrometer and other technical devices used here were the same as in the experiments described by CARERI, SCARAMUZZI and THOMSON (1).

	R	r	d	J
no. 1	1	0.25	0.5	2.0
no. 2	1	0.25	0.5	2.5
no. 3	1	0.13	0.8	3.0

A somewhat different diode was used for measuring the current in solid helium, due to the need of applying on high pressure. However, the changes were only matter of technical details.

3·2. *Experimental results*:

A) Classical liquids. As a reference view-point for the behaviour of the diodes we have investigated some non-polar classical liquids. CCl_4 and N_2 were chosen for matter of experimental convenience (Fig. 2 and 3).

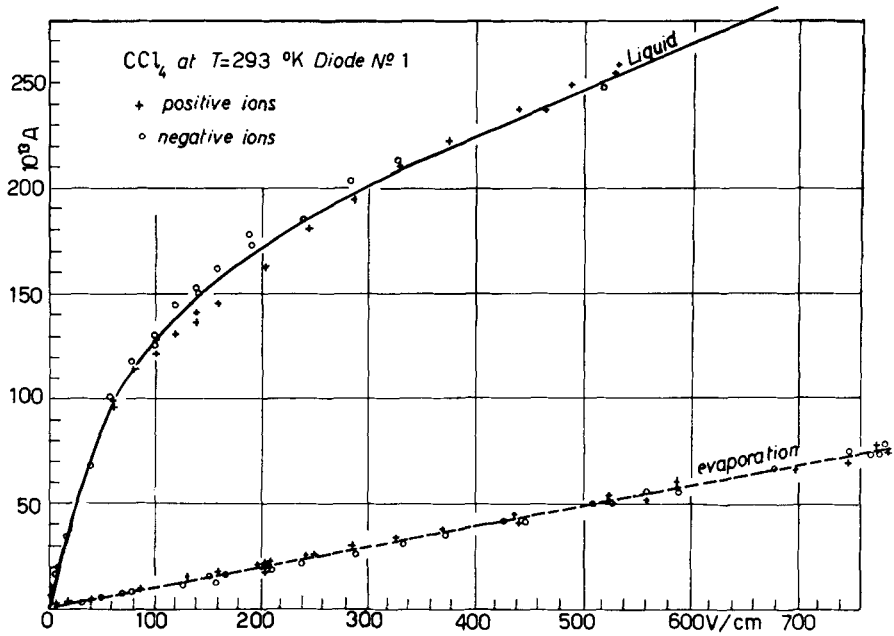

Fig. 2. – The ionic currents in carbon tetrachloride versus the applied field.

The curves labelled « liquid » have been obtained with both the electrodes below the liquid level of the bath, and the curves labelled « evaporation » have been obtained when the upper electrode was above the bath level and the lower one containing the radioactive layer below. The name « evaporation » is a short and improper one for a phenomenon which is a non-equilibrium process of ion extraction from a liquid surface by means of an electric field perpendicular to the surface.

A glance to these curves shows that the behaviour is just the one we should expect, namely:

a) There is no difference between positive and negative ions both in the liquid and in evaporation.

b) By increasing the voltage in the liquid the current increases without approaching a saturation value, in accordance with previous works; this is due to large recombination in the columns.

c) The temperature has a slight influence in the sense of increasing the current with the increasing temperatures as expected in any process involving an activation energy.

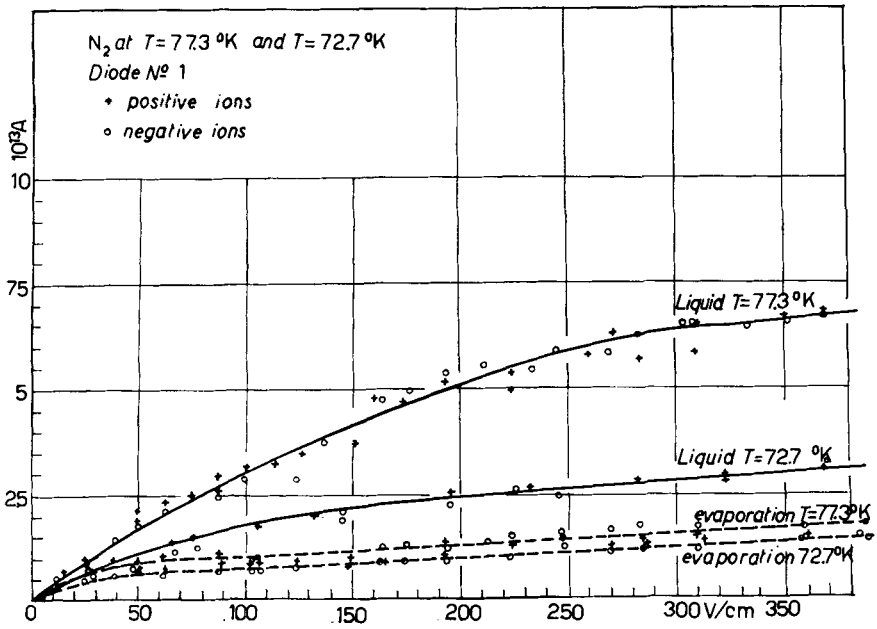

Fig. 3. – The ionic currents in nitrogen versus the applied field at two temperatures.

d) The evaporation currents are lower than the liquid ones, at given voltage and temperature, since the polarization forces keep the ions in the denser medium.

e) Finally, there is not a qualitative difference between CCl_4 and N_2.

B) Liquid helium. The same runs have been performed in liquid helium, and some important differences are at once noticed. The data were well reproducible working with different diodes; only some selected examples are shown in the following.

The evaporation curves also show some important new features, as may be seen in Figs. 4, 5, 6, 7 and 8 that may be summarized as follows:

a) Above T_λ the evaporation curves are the same as the liquid ones and are the same for ions of both signs.

b) Below T_λ the evaporation curve of the positive ions is always lower than the one of the negative ions, the liquid curves remaining the same for both; the difference between evaporation and liquid curves is most drastic for the positive ions just below T_λ.

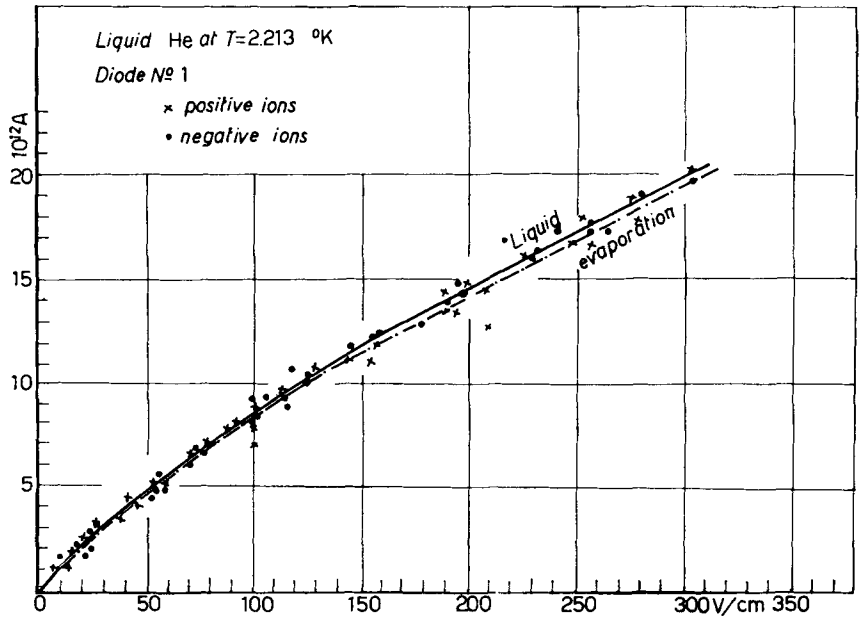

Fig. 4. – The ionic currents in helium versus the applied field, soon above the λ transition.

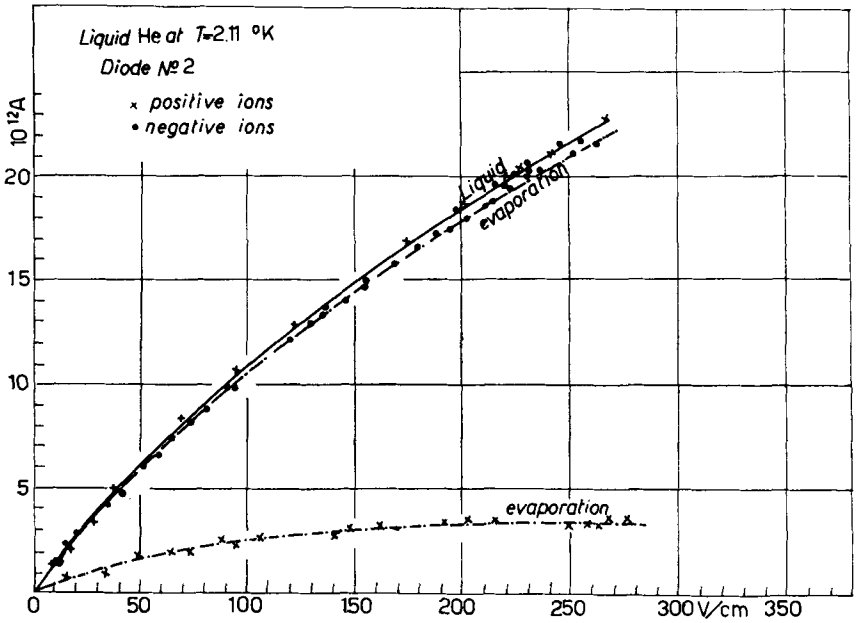

Fig. 5. – The ionic currents in helium versus the applied field, soon below the λ transition. Note the strong effect on the evaporation of the positive ions.

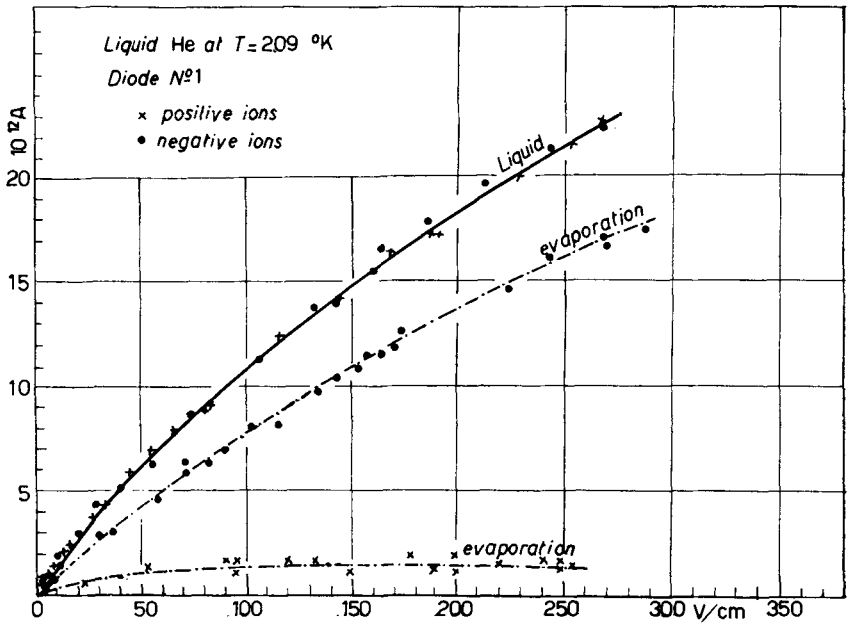

Fig. 6. – The same as Fig. 5, at a lower temperature.

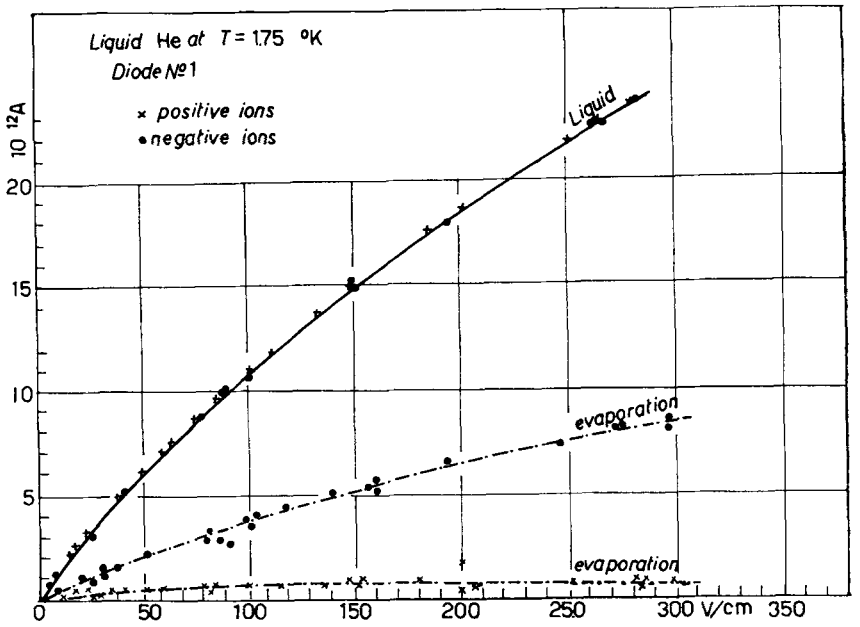

Fig. 7. – The same as Fig. 5, at a lower temperature.

d) At the lowest temperatures the evaporation curves approach very small values which have been proved to be due to leakage current, radioactive contamination of the plexiglas and other similar effects.

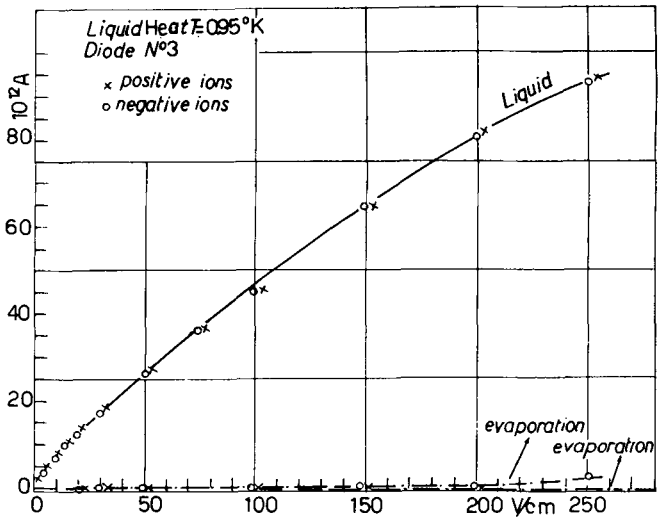

Fig. 8. – The same as Fig. 5, at a lower temperature.

C) Solid helium. When the pressure on the helium in the cell containing the diode was increased to the melting pressure, the current at once fell to an extremely low value, not distinguishable from the electrometer background noise.

Since the experiment necessarily deals with ions of both signs at the same time, we can only say that this result means that at least one of the two species of ions could not move. This would cause the total current to vanish because of the polarization of one electrode. It seems that the negative ion if it is a free electron ought to be mobile in solid helium as in any dielectric. We then interpret the vanishing of the total current as an indication that the current of positive ions is neagligible in the solid.

4. – Discussion.

The above quoted results of the inter-phase experiment may be qualitatively understood in terms of the current picture of liquid helium. The rapid fall of the ionic evaporation below the λ temperature is then due to the rapid fall in the number of excitations, since excitations are needed to let the ions across the liquid-vapour surface. Therefore this extraction mechanism in liquid helium is not much different from the evaporation mechanism of any liquid, where the molecule to evaporate has to pick up some energy from the

sorrounding molecules during a local fluctuation of the collisions, in order to overcome the binding energy with the neighbour molecules. In the case of the ions we presume this binding energy to be much larger due to the strong forces ion-polarized molecules, and the ions will have definite preference to stay inside the liquid medium.

Once this picture is accepted, then we deduce that the positive and negative ions must be quite different entities, and that it is easier to push the negative ion out of the surface than the positive one. We conclude that the negative ion cannot have the same or a more massive structure than the positive, and therefore the structures I and IV must be discarded. We stress the practical importance of discarding IV because that means that in liquid helium the concentration of impurities is really negligible, or at least that they do not contribute at all in these experiments with ions.

Next we consider the absence of extraction currents for negative ions in the low temperature runs. This indicates that for negative ions tunnelling effects are negligible, an important result which rules out its possible structure III.

Finally the solid helium experiment shows that for the positive ion the structure II involving jumps eventually by tunnelling must also be discarded.

5. - Conclusion.

The only structures left are then I for the positive ion and II for the negative ion, or briefly the positive ion is a cluster and the negative is an empty bubble. We believe this to be in agreement with all other experimental information concerning the mobility, since the mobility of the negative ions is lower than the positive ones ([1]). This is due to the larger extension of the shell surrounding the negative cloud in comparison with the solid droplet surrounding the positive charge, as indicated in 1.

It is hoped that future theoretical and experimental work may lay better foundations on the structures, which have been adopted here on the basis of the experimental evidence so far at hand.

RIASSUNTO

Sono stati eseguiti degli esperimenti per scegliere un modello adatto fra alcune strutture possibili per gli ioni di elio in elio liquido. L'apparecchio è essenzialmente un diodo, dove gli ioni sono prodotti da raggi α e le correnti possono essere misurate in fase liquida, solida e in interfase liquido-vapore. Tramite il differente comportamento degli ioni positivi e negativi negli esperimenti in interfase, si è portati a ritenere lo ione positivo come un raggruppamento di atomi polarizzati intorno ad una carica, e lo ione negativo come una cavità dove l'elettrone si auto-intrappola.