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R. Cantelli, I. Modena and F. P. Ricci: MOBILITY OF POSITIVE AND NEGATIVE CHARGES IN ^3He AT THE CRITICAL POINT.-

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INTRODUCTION. -

The behaviour of the transport coefficients near the critical points is still an open question either theoretically or from an experimental point of view[1]. Quite an important role in the non equilibrium statistical mechanics is that of the friction coefficient, and the real question is how much its behaviour is anomalous at the critical points.

At the critical mixing point of a binary mixture the anomalous behaviour of the transport coefficients is dictated not only by the behaviour of the friction coefficient but also by general thermodynamical arguments[2]. Whereas the situation is much clear at the liquid-vapour critical point where the behaviour of any mass transport (diffusion or Brownian motion) is mainly dictated by the friction coefficient. Unfortunately the experimental situation is very confused. Only three experiments were available in the literature on this subject[3, 4, 5] with results strongly conflicting. (This

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situation could be due to the fact that people too often underestimate the errors coming from gravitational effects). For this reason we started recently in measuring the mobility of electric charges in ^{3}He near the critical point and in the published paper[6], concerning only electrons, we found indeed a decrease ($\sim$30%) in the mobility through the critical point but no evidence of any dramatic lowering[3]. Taking in mind the dimension in Helium of the charged complex ($>$ 10 Å), when we measure the mobility we have the same kind of information as in the Brownian motion experiment and therefore some insight on the behaviour of the friction coefficient.

In this report we summarize all our experimental data concerning the mobility of positive and negative carriers in ^{3}He around the critical point. Positive ions are rather interesting being different from the negative carriers and giving us the opportunity to investigate the critical phenomena with two different probes using exactly the same experimental apparatus. We will also discuss in some detail the experimental apparatus since in this type of experiments many experimental features come into play.

EXPERIMENTAL APPARATUS. -

The temperature regulation of the experimental cell works according to the principle of balancing two thermal fluxes: a negative heat input obtained by having the cell in bad thermal contact with a ^{4}He bath, boilding at a temperature slightly below that of the experiment, and a positive heat input coming from the heater wound around the cell. Fig. 1 and 2 show schematically the experimental apparatus. The cell was made quite light so to have a good time constant in the temperature regulation. The ^{4}He temperature is fixed at 0.05°K lower than the ^{3}He one and is regulated by a bellow manostat within $\pm$0.005°K. The exchange gas (at a pressure $\sim$1 torr) provides the cooling of the experimental cell. The heater is a manganin wire, and the power in the heater is controlled through an electronic bridge. In one of the arms of the bridge there are two C.R. (33 Ω Allen Bradley) imbedded in the copper wall of the experimental cell. The ^{3}He temperature is read by a C.R. (65 Ω Allen Bradley) directly in contact with the ^{3}He sample. The power dissipated in this C.R. is $\leqslant 10^{-8}$W and the sensitivity of the C.R. reading is $\pm$0.2 Ω if the C.R. is in the range of 1000 Ω which corresponds to $\Delta T/T \simeq 10^{-5}$. The calibration of the 65 Ω C.R. was made either through the ^{4}He vapor pressure data (T_{58} temperature scale) when a small amount of ^{4}He was condensed in the experimental cell so to have a vapor pressure thermometer, or in the same way using, however, ^{3}He (T_{62} temperature scale). The pressures were read by a Texas instrument quartz bourdon gauge (sensitivity $\pm$0.02 torr). The calibration was repeated many times to be sure against hysteresis and the reproducibility was always within $\pm 2 \times 10^{-3}$°K.

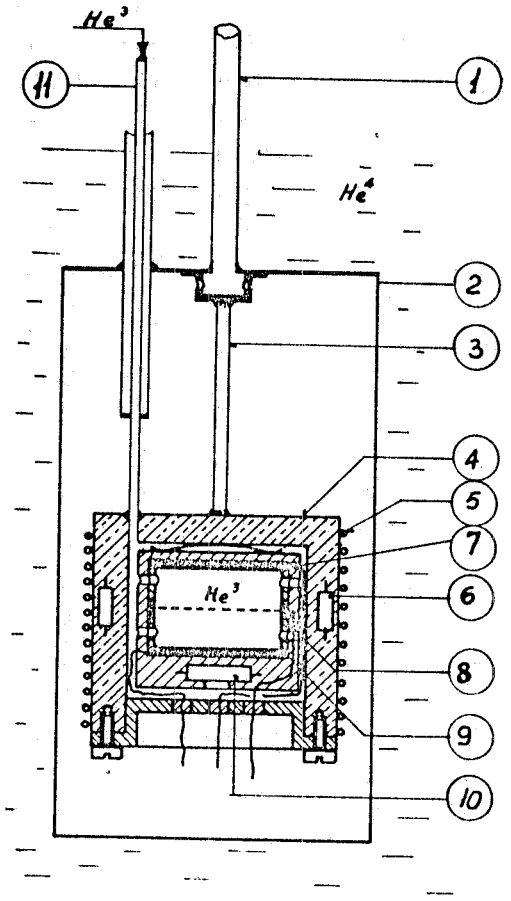

FIG. 1 - Schematic view of the experimental cryostat:

1 Inlet tube for exchange He^4 gas
2 Stainless steel container
3 Supporting tube
4 Copper block containing the He^3 cell
5 Heater
6 Two carbon resistors incorporated within the walls of the copper block
7 , 8 and 9 form a triode for mobility measurement
7 Source electrode coated with Po^{210}
8 Grid
9 Collector Electrode
10 Carbon resistor for measurement of the temperature of He^3
11 He^3 filling tube vacuum jacketed.

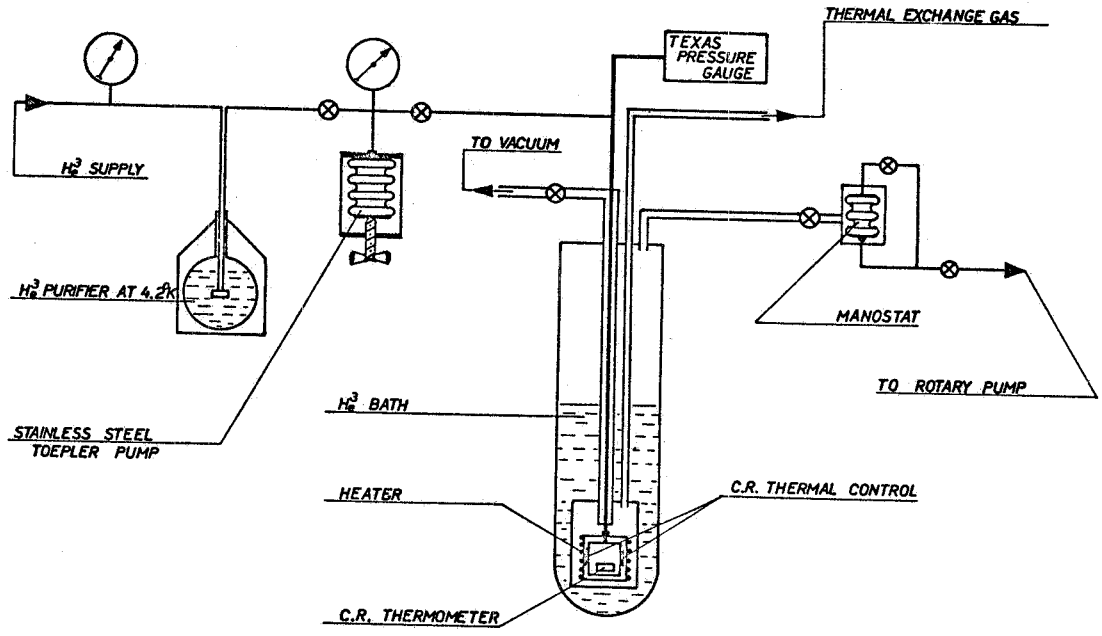

FIG. 2 - Schematic view of the experimental set.

The experimental cell is in contact with a ^{3}He resevoir so the pressure can be varied continuously. The pressures were read using the above mentioned Texas quartz gauge. Correction for hydrostatic head were performed, using the temperature gradient along the filling tube, although they were always very small. The mobility measurements were performed using a time of flight method[7, 8], which measure essentially the time of flight between the grid and the collector. The distance grid-collector was 4 mm. Therefore, as far as mobility measurments, our experimental vertical height was 4 mm. Taking into account the ^{3}He density, along this height we have a pressure variation $\Delta p \lesssim 0.02$ torr and therefore, at the critical point, an indetermination in density $\Delta\varrho/\varrho \simeq \simeq 10^{-2}$.

We want to stress that a mobility measurement has this particular advantage of very small experimental space and therefore it is particularly useful in the critical experiments.

The electric field between grid and collector (zero peak voltage of the square wave) was either 150 V/cm or 75 V/cm; no difference was observed. For thermodynamical states around the critical point the time of flight result ~ 0.1 sec. The errors on the μ measurements were $\leq \pm$ $\pm$ 3%. Since the mobility value is strongly dependent on the grid-collector distance, from run to run we checked this distance by repeating some experimental results of the previous run. The measurements were performed either at constant temperature varying the ^{3}He pressure (in both sense decreasing and increasing pressure without finding any difference) or following isochores which was particularly useful to measure $(\partial\mu/\partial T)_{\varrho} = \text{cost}$.

In the isotherms, around the critical point the pressure increments were ≤ 0.3 mm Hg between successive experimental points. In any step, around the critical point, we waited more than 1 hour after equilibrium (pressure and temperature) was reached before performing the mobility measurement. At the critical point[9] we repeated the measurement at 1 hour intervals in the same thermodynamical conditions without observing any difference. The ^{3}He purity was 100.00 % ^{3}He in ^{4}He as supplied by Monsanto Res. Corp. and before to be admitted in the experimental cell, it was forced through a trap cooled at 4.2°K.

EXPERIMENTAL RESULTS. -

The experimental results are reported in Figs.3, 4, 5 and 6. Figs.3 and 4 show the mobility versus pressure at various temperatures for negative and positive carriers respectively. Fig. 5 is an enlarged plot of the mobility versus pressure for positive carriers around the critical point. It is interesting to note in Figs.3 and 4 the discontinuous jump in the T = = 3.271 and T = 3.258 isotherms which correspond to the liquid vapour first

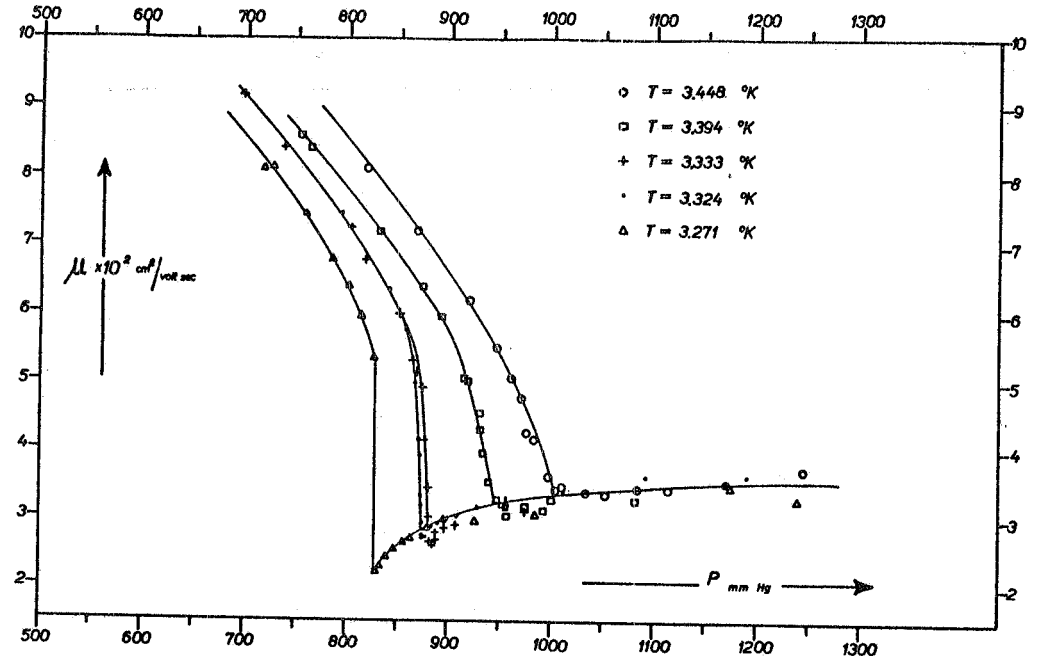

FIG. 3 - Experimental results for negative carriers: the curves are smooth through the experimental points for each isotherm; the vertical line at T = 3.271 °K is set at the vapor pressure corresponding to this temperature.

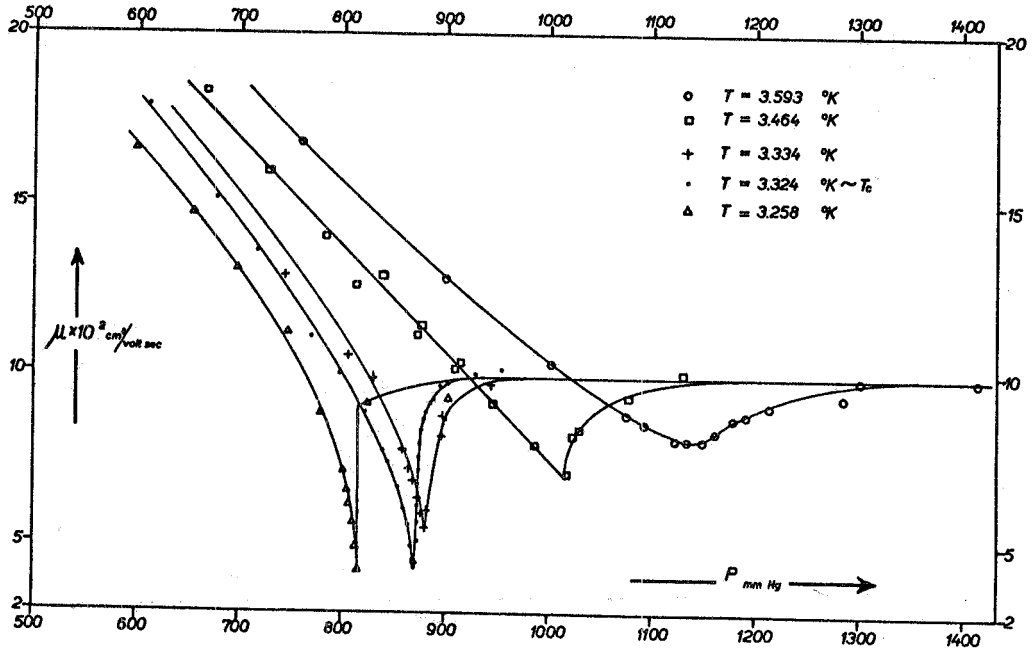

FIG. 4 - Experimental results for positive carriers: the curves are smooth through the experimental points; the vertical line at T = 3.258°K is set at the vapor pressure corresponding to this temperature.

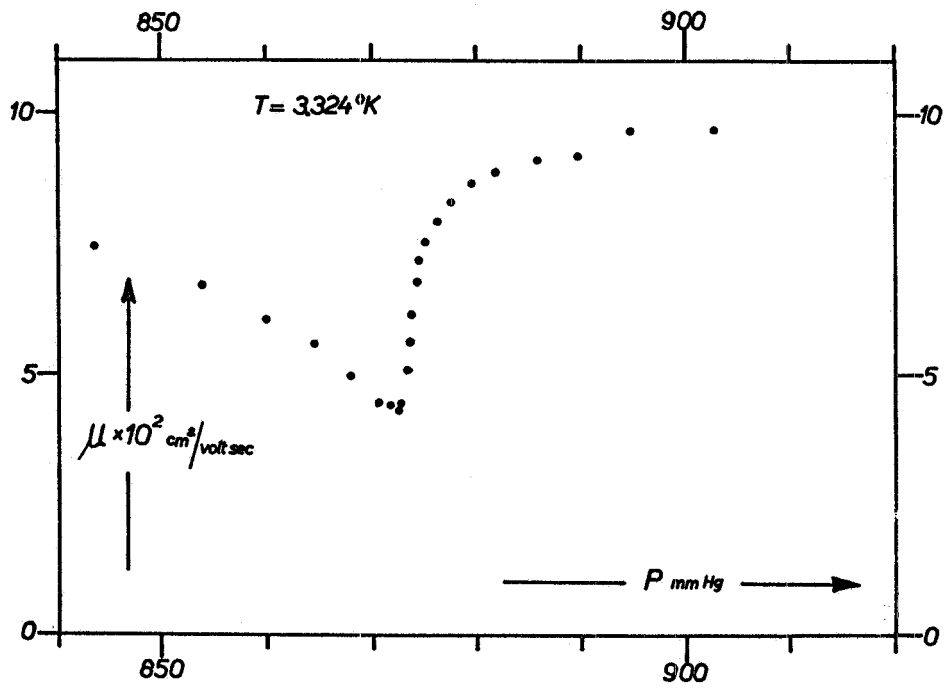

FIG. 5 - Experimental results at the critical isotherm from Fig. 4 expanded in the temperature axis for positive carriers.

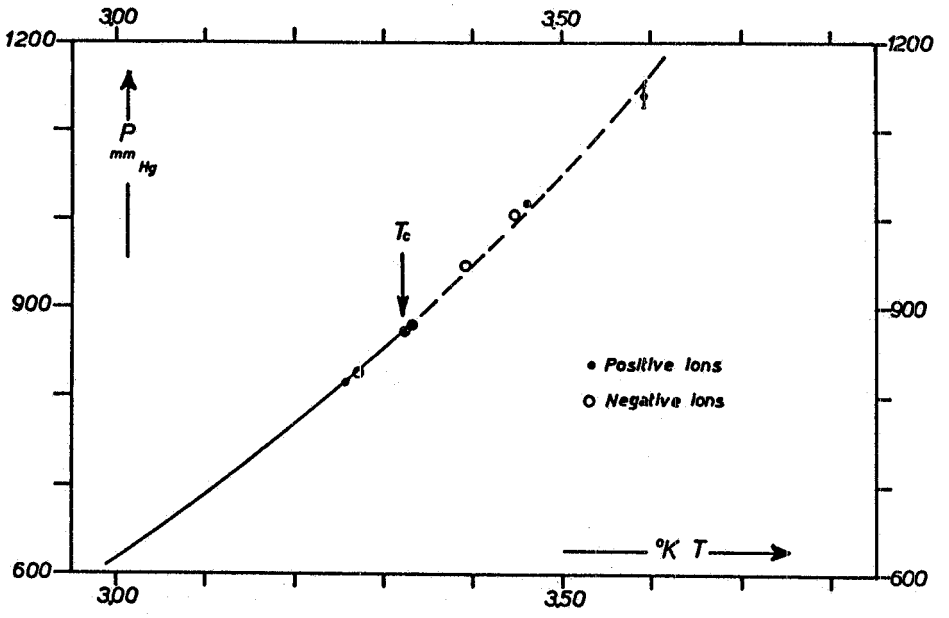

FIG. 6 - Coexistence curve for He^3 (solid line); the dotted line represents an extrapolation of the coexistence curve. The points are the locus of mobility minima along the isotherms of the Fig. 3 and 4.

order transition. Along the coexistence curve, while for negative carriers the mobility is always greater in the vapour than in the liquid, for positive carriers the situation is viceversa. This is connected with the different structure of positive and negative carriers.

In Fig. 6 the coexistence curve of ^3He is reported together with the points were the $(\partial\mu/\partial p)_{T=cost.}$ change sign for the isotherms of Fig. 3 and 4; it is noticeable that these points lie on the extrapolation of the coexistence curve as was already found in other critical phenomena[10].

DISCUSSION. -

Since there are not molecular theories of the mobility in dense fluid which are at the level to give figures to be compared with experimental results, we prefer to do a phenomenological analysis of the kind previously reported[6], to deduce the critical peculiarity in the mobility behaviour. In Fig. 7 and 8 we report the experimental results of the mobility as a function of the ^3He density for various isotherms. (The translation of Fig. 3 and 4 in Fig. 7 and 8 has been done using PVT data by R. H. Shermann, cited in ref. 9 and kindly obtained as private communication). First we can notice that either for positive or for negative carriers the $\mu(T, \varrho)$ isotherms look generally of the same shape although with some differences in the details. Since that is connected with the different structure of the two carriers we will consider tham one at the time.

A) - Negative carriers. -

A discussion of the critical peculiarity for the mobility of electrons has been already given using a kind of data treatment[6]. In this report we would like to discuss mainly the reason for that data treatment showing its range of validity.

It is well known[11] that electrons do not form a bound state with an Helium atom of the type He^- or He_n^- and therefore, due to the light mass, they cannot be sharply localized. Many times has been shown[12] that for not very rarefied Helium the electron form a bubble the dimension of which are fixed by a balance of the kinetic zero point pressure of the electron with the sum of the pressure due to the zero point motion of ^3He atoms, plus the pressure due to the electrostatic interaction electron polarized ^3He atom, plus the van der Waals contribution.

Taking for the zero point energy of the ^3He atoms the London's expression[13] and for the other terms the expressions given by Kuper[11], translated for the ^3He case, we see that the bubble radius depends on the ^3He density but at constant density does not depend on the temperature in our temperature range. Therefore if we compare data at the same

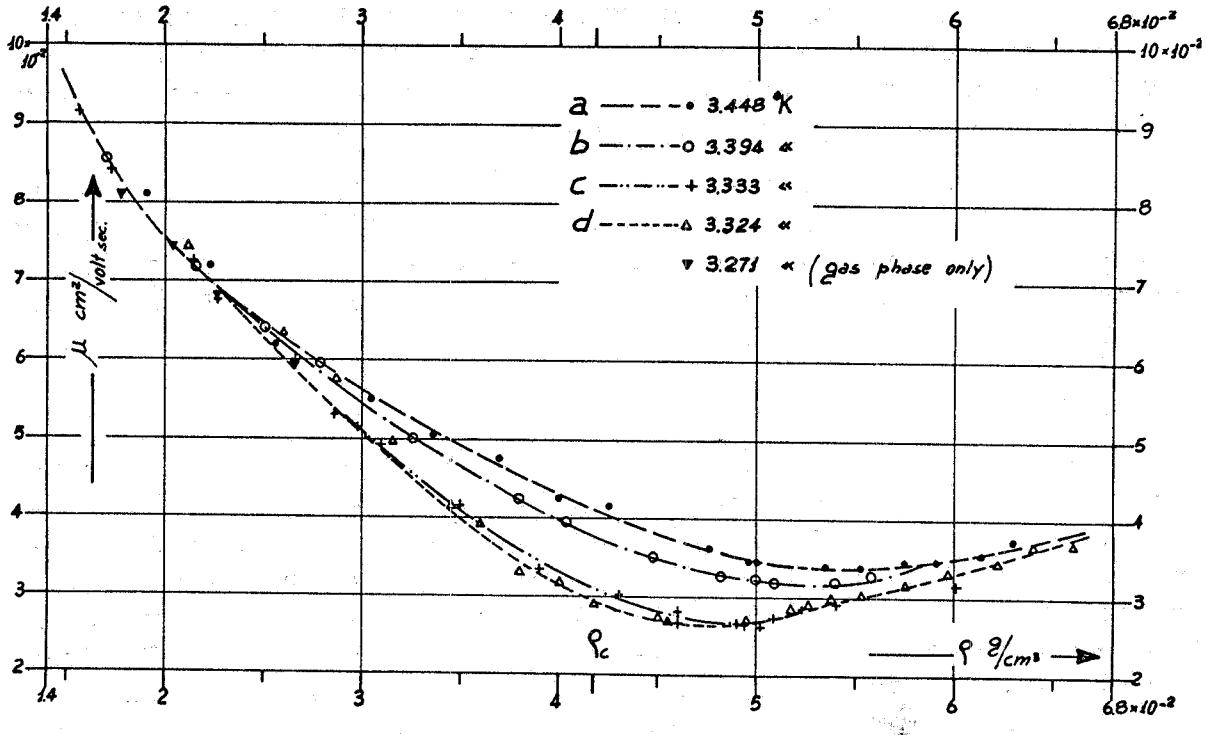

FIG. 7 - Mobility of negative carriers as a function of density for various isotherms.

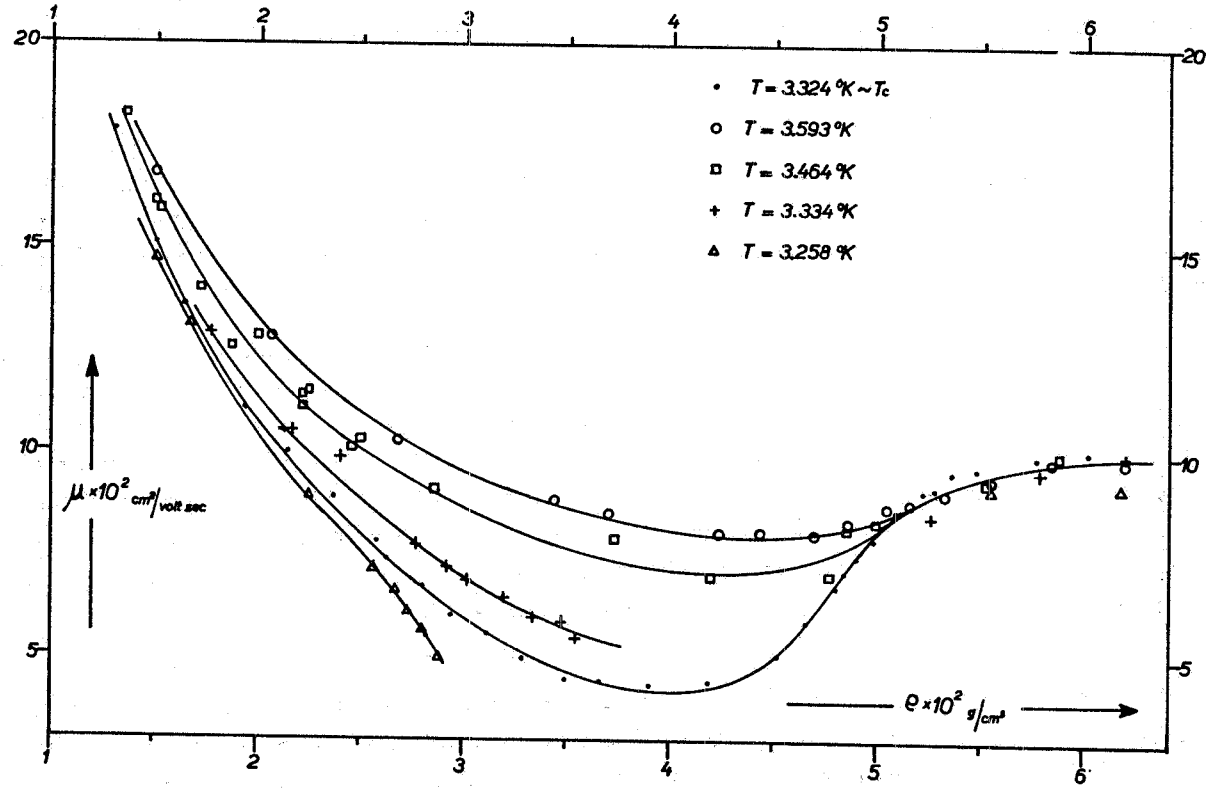

FIG. 8 - Mobility of positive carriers as a function of density for various isotherms.

density we can think the bubble as to have a constant radius. Now if we have to do with a constant radius particle and we are asking about the behaviour of the mobility at constant density as a function of temperature over a temperature variation $\Delta T/T = 0.04$, we can safely infer than any theory of mobility would predict (in absence of critical phenomena) a $\Delta\mu/\mu$ much less than 1% which is well inside our experimental errors. In fact we have this results from the two extreme theories: the friction constant formalism[14] and the dilute gas case[15]. The insensitivity to the temperature when we are at constant density is also supported by experimental evidence as has been shown for the high density region in the case of ^4He[16] and for the low density region from our present data in the density range 0.020 gr/cm^3 (see Fig. 7). Having clear this behaviour the obvious analysis to do, to evidentiate the critical phenomena, is just that reported in Fig. 9 and 10a which we already discussed in the previous work[6]. We want to stress that as far as the bubble model for electrons in Helium is correct our analysis is safe since always involves comparison between experimental data at the same density. Therefore the conclusion already achieved[6] about the width of the critical region and the behaviour of the mobility at the critical point is confirmed.

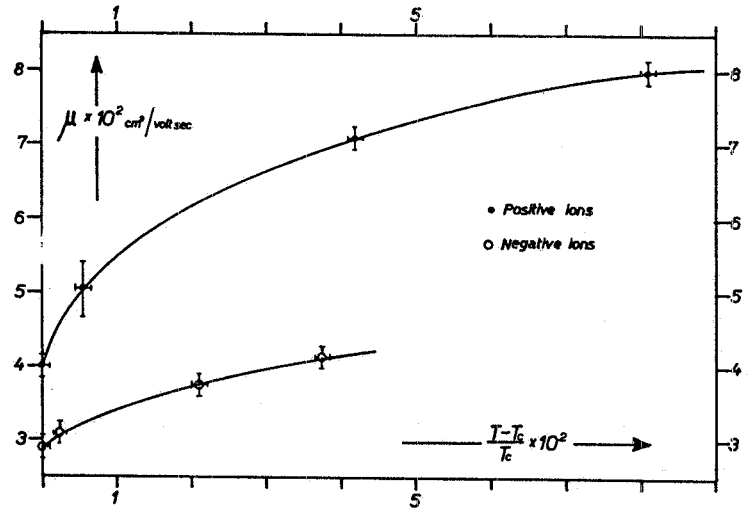

FIG. 9 - Mobility versus temperature at $\rho = \rho_c$. The points are read on the smooth lines of fig. 7 and 8. The errors give the degree of confidence of the smooth curves.

B) - Positive carriers. -

If in this case we want to repeat the kind of analysis we did in the case of electrons we must discuss first the structure of the positive carriers in helium. In fact the structure of positive and negative carriers are quite different. Whereas the electrons form a rigid bubble the positive ion builds up a cluster of ^3He atoms. The dimension of this cluster it is obviously determined by a balance condition, at the cluster boundary, between kinetic energy and potential energy of an helium atom. When the surface tension γ is appreciable the radius R of the cluster can be deter-

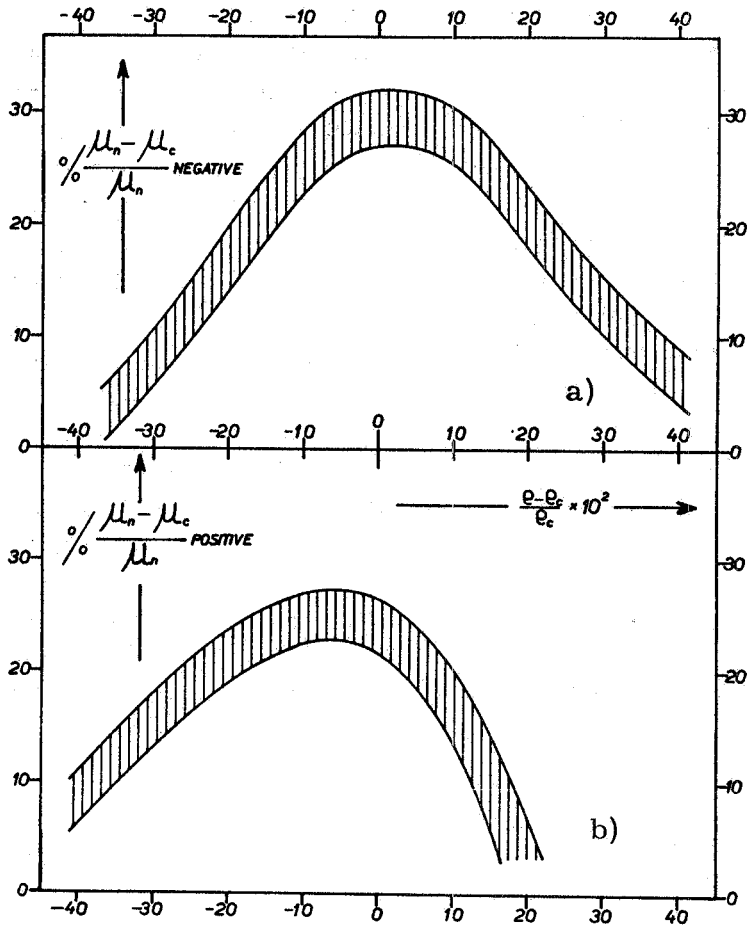

FIG. 10 - Mobility difference between the mobility at the critical temperature (μ_c) and mobility at a "normal" isotherm versus density. In Fig. 10a) the "normal" isotherm is that at T = 3.448°K. In Fig. 10b) the "normal" isotherm is the point on the straight line in Fig. 11 at T = T_c.

mined by the well known formula used in cloud chamber[17] $\ln(p/p_s) = (nK_BT)^{-1}\ (2\gamma/R) - (\alpha e^2/2R^4K_BT)$ where p is the actual pressure of the Helium gas, p_s is the saturation pressure at the same temperature, α is the Helium polarizability and K_B the Boltzman constant. However for temperatures higher than the critical one, where p_s and γ loose meaning, we can write the potential energy as the sum of the electrostatic one (i.e. ion-induced dipole interaction) and of a Van der Waals contribution which originates from the different density between the cluster and the Helium bulk. Since the internal energy in a liquid is nearly proportional to the square of the density, using the ^{3}He heat vaporization data, we can write

$$(1) \qquad \frac{1}{2} M \langle V^2 \rangle = \frac{N \alpha e^2}{R^4} + 2.72 \times 10^{10} \left(\rho^2_{\text{cluster}} - \rho^2_{H_e} \right)$$

where M is the molecular weight, N is the Avogadro number and all quantities must be expressed in CGS units. Putting $\rho_{\text{cluster}} \simeq 0.07$ gr/cm^3 we have for R a dependence on ρ_{He} as well as on T. The dependence of R on ρ_{He} at 3.3°K seems to be very mild, just few percent over our density range, as we can see from eq. (1). The temperature depen

dence of R at ρ_{He} = const. turns out to be

$$(2) \qquad \left[\frac{\partial R}{\partial T}\right]_{\rho_{He}=\text{const.}} = \frac{\left[3 - 6.37\,\frac{1}{\rho_{cl}}\left(\frac{\partial \rho_{cl}}{\partial T}\right)_{\rho_{He}=\text{const.}}\right] \cdot 10^7 \cdot R^5}{0.96\, N \alpha e^2}$$

Having the uncertainty on the exact value of $1/\rho_{cl}(\partial\rho_{cl}/\partial T)_{\rho_{He}=\text{const.}}$ we can only say that the order of magnitude of $(\partial R/\partial T)_{\rho_{He}=\text{const.}}$ from eq. (2) is in agreement with the experimental results. However what is important is that in our temperature and density range $[\partial R/\partial T]_{\rho_{He}=\text{const.}}$ does not depend either on the temperature or on the density. Therefore if we plot the mobility μ as a function of T, taking experimental data at constant density, we must have a straight line for points at temperature above the critical one. Any deviation from this straight line is due to the critical phenomena. Fig. 11 shows this kind of analysis from the experimental data of Fig. 8. In Fig. 10b the deviation from the straight line, which is the normal behaviour, is reported as a function of $(\rho - \rho_c)/\rho$, where ρ_c is the critical density.

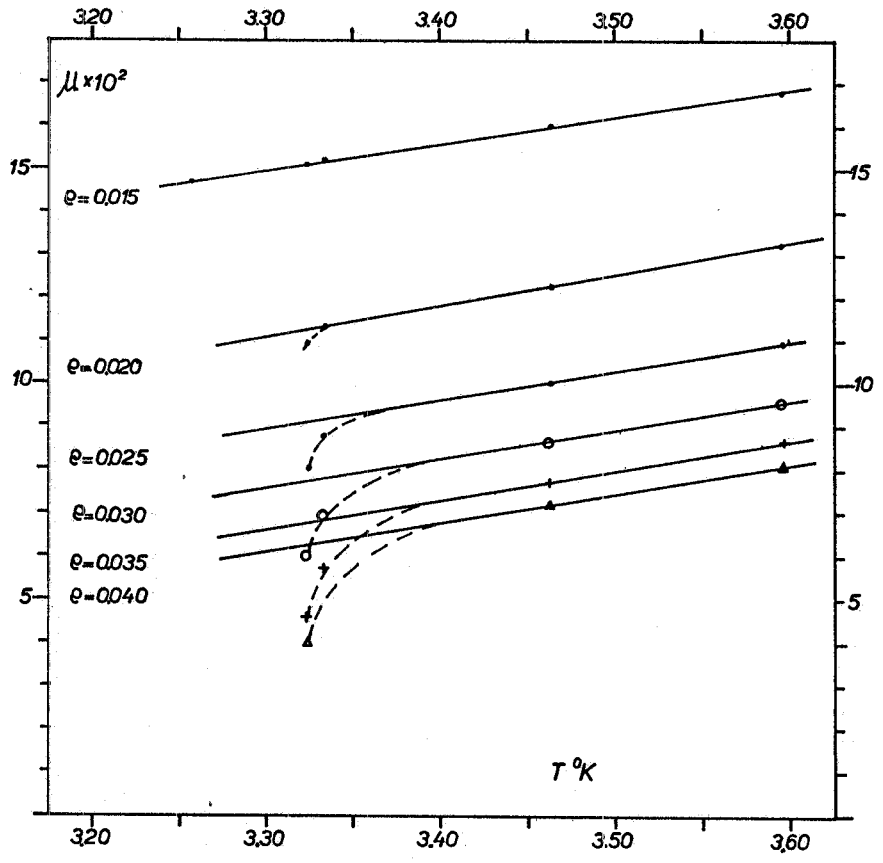

FIG. 11 - Mobility versus temperatures at various isopycnals for positive carriers.

CONCLUSION. -

From the previous analysis we can construct Figures 10a) and 10b) which show the amount of the critical anomalies in the mobility of electric charges. First one must notice that the anomaly has the same shape and it is of the same amount for both positive and negative charges although the cluster around the positive charge has a radius something like a factor 1/2 of the bubble radius. Secondly we do not find big anomalies as previously reported[3]. This point can be questioned on the basis that we are not very close to the critical temperature, however we disagree because the general trend of Fig. 9 does not indicate the possibility of big variation in our conclusion even if we go to an isotherm something like $0.01^{o}K$ lower than $3.324^{o}K$.

Some more works seem necessary to understand the real reason for the discrepancy of the available experimental results[3, 4, 5].

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