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Mobility of Positive and Negative Charges in ^{3}He at the Critical Point

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Measurements of the mobility of positive and negative charges in the ^{3}He critical region are reported. The experimental data show that for the two probes there is a definite lowering of the mobility at the critical point. However, within the limits of our approach to the critical point ($\Delta T/T_c \simeq 6\times10^{-4}$; $\Delta p/p_c \simeq 3\times10^{-5}$), no evidence of dramatic decrease in the mobility is observed. The decrease in the mobility is $\approx 30\%$ for either probes; however, the influence of the critical phenomena on the shape of the mobility curve differs for the two probes probably because the positive and negative carriers differ in their effective radius. Some indication of the correct value of the ^{3}He critical temperature is also reported.

INTRODUCTION

THE behavior of transport coefficients near critical points is still an open question both theoretically and from an experimental point of view.[1] The friction coefficient plays an important role in nonequilibrium statistical mechanics, and it would be interesting to know to what extent its behavior is anomalous at critical points.

At the critical mixing point of a binary mixture the anomalous behavior of the transport coefficients is determined not only by the behavior of the friction coefficient but also by general thermodynamic arguments.[2] The situation is clearer at the liquid-vapor critical point, where the behavior of any mass transport (diffusion or Brownian motion) is determined mainly by the friction coefficient. Unfortunately the experimental situation is very confused. Until recently only three experiments with conflicting results have been reported.[3–5] For this reason we have measured the mobility of electric charges in ^{3}He near the critical point. Since the radius of the charged complex is greater than 10 Å, the data can be analyzed in terms of Brownian motion to yield some insight into the behavior of the friction coefficient.

Preliminary results, concerning electrons only, have been already published[6] and the experimental data indicate that the mobility decreases moderately ($\approx 30\%$) going through the critical region, without evidence of singularity.[3] In this paper we report the experimental data concerning the mobility of positive and negative carriers in ^{3}He near the critical point. Since positive and negative charge carriers in liquid ^{3}He are different in nature, we have the opportunity to investigate critical phenomena with two different probes using exactly the same experimental apparatus. Moreover, since a new determination of the ^{3}He critical temperature has recently been reported[7] and the new value is rather different from the accepted one,[8] we also explored this point in our mobility measurements.

EXPERIMENTAL APPARATUS AND RESULTS

The experimental setup is shown in Figs. 1 and 2. The mobility measurements are performed using a time-of-flight method,[9,10] which measures essentially the time of flight between the grid and the collector.

The distance from grid to collector is 4 mm. Therefore, as far as mobility measurements are concerned, our experimental vertical height is 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, the variation density is $\Delta\rho/\rho \simeq 10^{-2}$.[7,11] Since mobility measurements can be performed using a very small sample height, they are especially useful near the critical point where we have rather large density variation in the gravitational field due to the high values of the compressibility. The electric field between grid and collector (zero to peak voltage of the square wave) was either 150 or 75 V/cm; no difference was observed. Near the critical point the time of flight is ≈ 0.1 sec. The errors on the μ measurements are $\leqslant \pm 3\%$. Since the calculation of mobility from time-of-flight data is sensitive to grid-collector distance, from run to run we checked this distance by repeating some of the experimental results of the previous run.

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[1] J. V. Sengers, Natl. Bur. Std. (U.S.) Misc. Publ. No. 273 (1966).
[2] P. Debye, Phys. Rev. Letters 14, 783 (1965).
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[6] I. Modena and F. P. Ricci, Phys. Rev. Letters 19, 347 (1967).
[7] G. O. Zimmerman and C. E. Chase, Phys. Rev. Letters 19, 151 (1967).
[8] S. G. Sydoriak and R. H. Sherman, J. Res. Natl. Bur. Std. 68A, 547 (1964).
[9] S. Cunsolo, Nuovo Cimento 21, 76 (1961).
[10] P. De Magistris, I. Modena, and F. Scaramuzzi, in *Proceedings of the Ninth International Conference on Low-Temperature Physics*, edited by J. G. Daunt *et al.* (Plenum Press, Inc., New York, 1965), p. 349.
[11] R. H. Sherman and C. E. Chase have kindly supplied us with the *PVT* data.

The temperature regulation of the experimental cell (see Fig. 1) works according to the principle of balancing two thermal fluxes: A negative heat input is obtained by having the cell in poor thermal contact with a ^{4}He bath, boiling at a temperature slightly below that of the experiment, and a positive heat input comes from the heater wound around the cell. The cell is made quite light so as to respond quickly to temperature regulation. The ^{4}He temperature is fixed at 0.05°K lower than that of the ^{3}He and it is regulated by a bellow manostat within ± 0.005°K. The exchange gas (at a pressure ~ 1 Torr) cools the experimental cell. The heater is a manganin wire whose current is controlled by an electronic bridge. In one of the arms of the bridge there are two carbon resistors (33-Ω Allen-Bradley) imbedded in the copper wall of the experimental cell. The ^{3}He temperature is read by a carbon resistor (65-Ω Allen-Bradley) directly in contact with the ^{3}He sample. The power dissipated in this carbon resistor is $\leqslant 10^{-8}$ W and the sensitivity of the carbon resistor reading is $\pm 0.2\,\Omega$ at $1000\,\Omega$ which corresponds to $\Delta T/T \simeq 10^{-4}$. The calibration of the 65-Ω carbon resistor is made either through the ^{4}He vapor-pressure data (T_{58} temperature scale) when a small amount of ^{4}He is condensed in the experimental cell so as to have a vapor-pressure thermometer, or in the same way using ^{3}He instead of ^{4}He (T_{62} temperature scale). The pressure is read by a Texas Instruments quartz bourdon gauge (sensitivity ± 0.02 Torr). The carbon resistor calibration is repeated many times to insure against hysteresis, and the reproducibility is always within $\pm 2\times 10^{-3}$ °K.

The experimental cell is in contact with a ^{3}He reservoir through a Toepler pump so that the pressure can be varied continuously and it is possible to measure the quantity of ^{3}He gas admitted or taken away from the experimental cell in each step. In this way, one can calculate the density variation in the experimental cell in each step. The pressures are read using the above mentioned Texas quartz gauge. Correction for hydrostatic head is performed, using the temperature gradient along the filling tube, although the correction is always very small. The measurements are performed either at constant temperature varying the ^{3}He pressure (in both senses, decreasing and increasing pressure without finding any difference) or following isochores in order to measure $(\partial\mu/\partial T)_{\rho=\mathrm{const}}$.

In the isotherms around the critical point the pressure increments are $\leqslant 0.3$ Torr between subsequent experimental points. In any step near the critical point we waited more than 1 h after reaching equilibrium (pressure and temperature) before performing the mobility measurement. In isotherms near the critical isotherm, for points with density near the critical density, we repeated the measurement at 1 h intervals under the same conditions without observing any difference. The ^{3}He purity was 100.00% ^{3}He in He as supplied by Monsanto Research Corporation; and before being

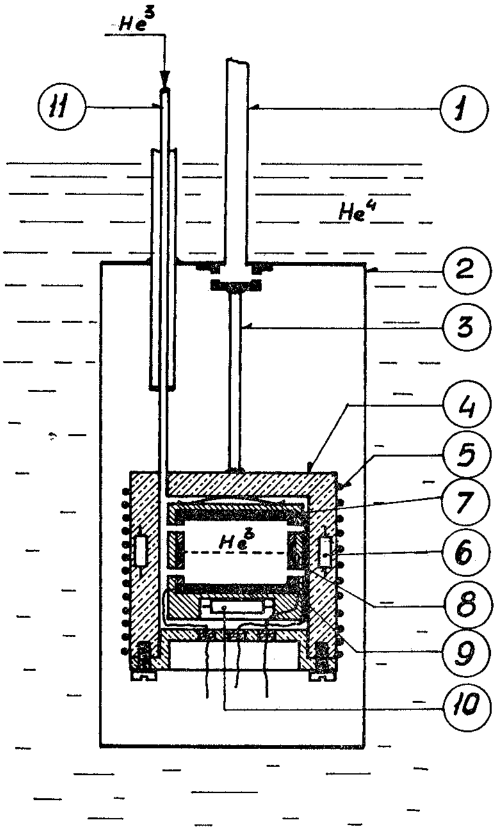

FIG. 1. Schematic view of the experimental cryostat: (1) inlet tube for exchange ^{4}He gas; (2) stainless steel container; (3) supporting tube; (4) copper block containing the ^{3}He cell; (5) heater; (6) two carbon resistors (33-Ω Allen and Bradley) incorporated within the walls of the copper block; (7) to (9) form a triode for mobility measurement; (7) source electrode coated with Po^{210}; (8) grid; (9) collector electrode; (10) carbon resistor (65-Ω Allen and Bradley) for measurement of the temperature of ^{3}He; (11) ^{3}He filling tube vacuum jacketed.

admitted in the experimental cell, ^{3}He is forced through a trap cooled at 4.2°K. At the end of the whole set of measurements reported in this paper, we checked the purity of the ^{3}He by mass spectrometer analysis and we found the ^{4}He impurity to be less than 0.05%.

The experimental results are reported in Figs. 3 and 4, which show the mobility versus pressure at various temperatures for negative and positive carriers, respectively. It is interesting to note in Figs. 3 and 4 the discontinuous jump in the $T=3.271$ and $T=3.258$°K isotherms which correspond to the first-order transition from liquid to vapor. Along the coexistence curve, while for negative carriers the mobility is always greater in the vapor than in the liquid, for positive carriers the situation is reversed. This is connected with the different structures of positive and negative carriers.

In Fig. 5 the coexistence curve of ^{3}He is reported together with the points where $(\partial\mu/\partial p)_{T=\mathrm{const}}$ changes sign for the isotherms of Figs. 3 and 4; it is apparent that these points lie on the extrapolation of the coexistence curve. Analogous results were already found

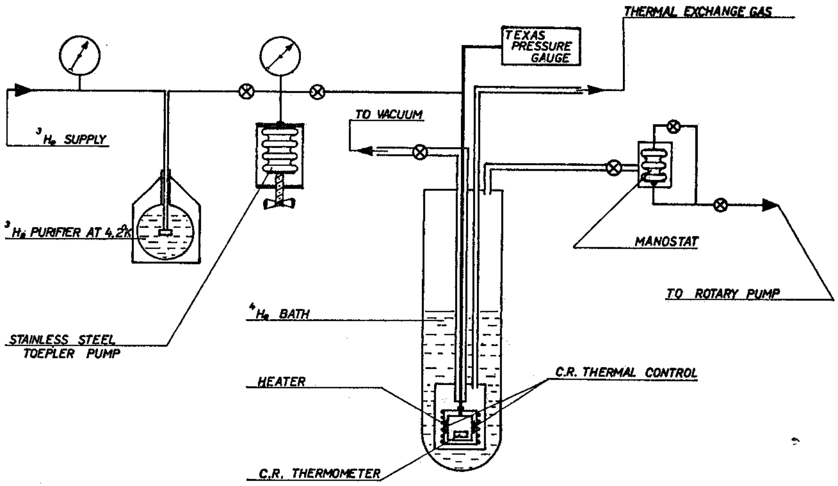

FIG. 2. Schematic view of the experimental setup.

for other critical phenomena.[12] We used the fact that the mobility exhibits a jump at first-order transitions (see isotherms $T=3.271$ and $T=3.258$°K in Figs. 3 and 4, respectively) to measure the ^{3}He critical temperature. In Fig. 4 we see that for isotherms at $T>3.314$°K, the mobility no longer exhibits a discontinuous jump.

Evidence for a first-order transition at $T=3.311$°K was obtained from mobility data of negative carriers (Fig. 6). The jump occurs at $p=862.5$ Torr. Therefore we have a strong indication that $3.311<T_c<3.314$°K, which is only slightly higher than the value of Ref. 7.

DISCUSSION

Since available molecular theories of mobility in dense fluids cannot be reliably applied to the critical region, we prefer to do a phenomenological analysis of the kind previously reported,[6] to interpret the mobility behavior at the critical point. In Figs. 7 and 8 we report the experimental results of the mobility as a function of the ^{3}He density for various isotherms. (^{3}He density was obtained from our measured pressure and temperature, using PVT data by Shermann[11] and by Chase.[11]) Moreover, in the density region $0.035\leqslant\rho\leqslant0.050$ g/cm^3 we can check the density since the mass added in each step is known. The agreement between these various ways of deducing the density turns out to be satisfactory.

First we can notice that for either positive or negative carriers the $\mu(T,\rho)$ isotherms generally have the same shape with some difference in detail. Since this is connected with the different structures of the two carriers we will consider them one at the time.

A. Negative Carriers

A discussion of the critical behavior for the mobility of electrons has been already given.[6] Here we would like

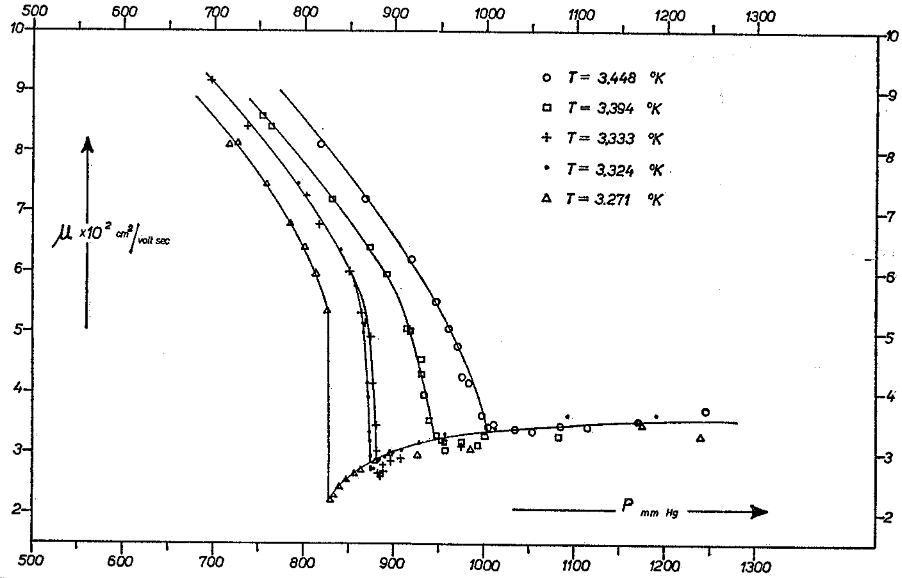

FIG. 3. Experimental results for negative carriers: The curves are smooth through the experimental points for each isotherm. The vertical line at $T=3.271$°K is drawn at the vapor pressure corresponding to this temperature.

[12] C. E. Chase, R. C. Williamson, and L. Tisza, Phys. Rev. Letters 13, 467 (1964).

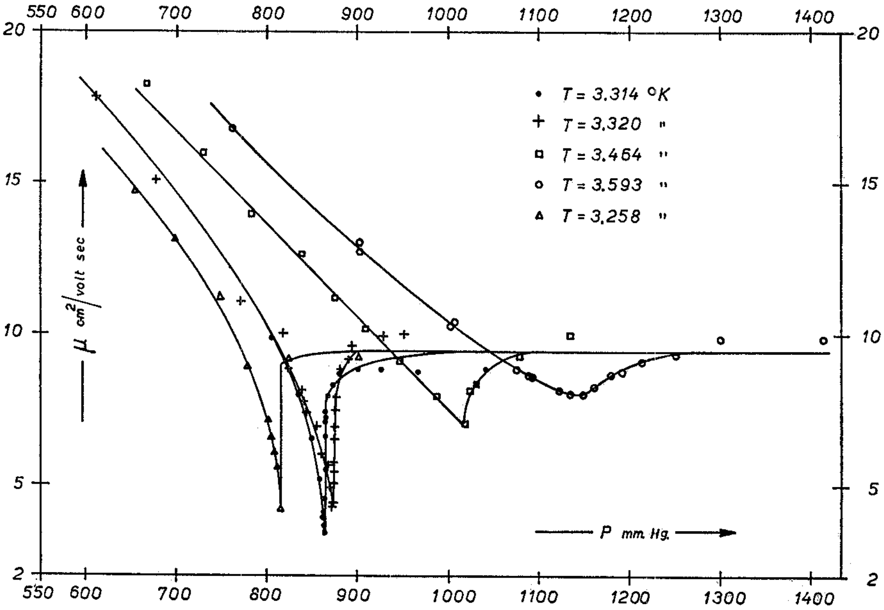

FIG. 4. Experimental results for positive carriers: The curves are smooth through the experimental points. The vertical line at $T = 3.258$°K is drawn at the vapor pressure corresponding to this temperature.

to discuss in some detail the analysis of the experimental data which we did in Ref. 6, showing the range of validity of this kind of analysis.

It is well known[13] that electrons do not form a bound state with a helium atom of the type He^- or He_n^-, and therefore, because of the low electron mass, they cannot be sharply localized. It has been shown[13,14] that for relatively dense helium the electron forms a bubble whose dimensions are fixed by a balance among the kinetic zero-point pressure of the electron, the resultant pressure due to the zero-point motion of ^{3}He atoms, the pressure due to the electrostatic interaction (electron-induced dipole on the ^{3}He atom), and the van der Waals contribution.

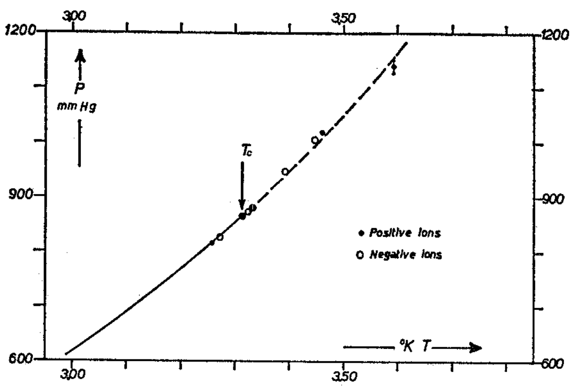

FIG. 5. Coexistence curve for ^{3}He (solid line). The dotted line represents an extrapolation of the coexistence curve. The points are the locus of mobility minima along the isotherms of Figs. 3 and 4.

[13] C. G. Kuper, Phys. Rev. **122**, 1007 (1961).

[14] J. L. Levine and T. M. Sanders, Jr., Phys. Rev. **154**, 138 (1967); J. Jortner, N. R. Kestner, S. A. Rice, and M. H. Cohen, J. Chem. Phys. **43**, 2614 (1965).

Taking London's expression[15] for the zero-point energy of the ^{3}He atoms, and for the other terms the expressions given by Kuper[13] adapted to ^{3}He case, we see that the bubble radius depends on the ^{3}He density,

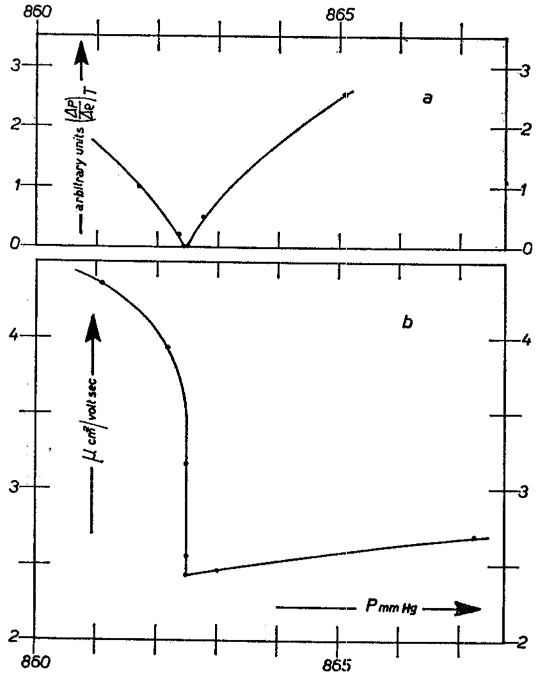

FIG. 6. (a) $(\Delta p/\Delta\rho)_{T=3.311°K}$ as a function of pressure. For three subsequent steps we lowered the average density in the experimental cell without noticing any change in the pressure. (b) Mobility versus pressure at $T = 3.311$°K. It is noticeable that this isotherm has a vertical part, i.e., a discontinuity in mobility at $p = 862.5$ Torr. This is the same pressure at which in (a) we found $\Delta\rho/\Delta p \simeq 0$.

[15] F. London, *Superfluids* (Dover Publications, Inc., New York, 1954), Vol. II, p. 30.

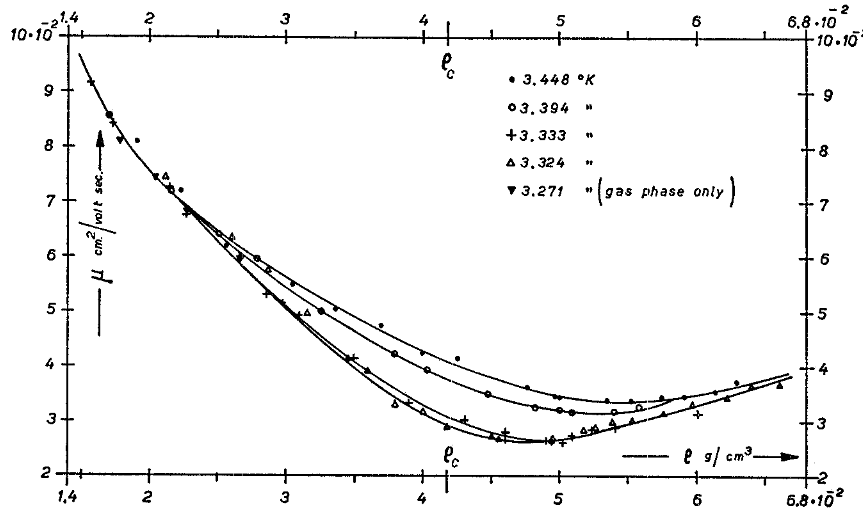

FIG. 7. Mobility of negative carriers as a function of density for various isotherms.

but at constant density it does not depend on the temperature range. Therefore, if we compare data at the same density, we can consider the bubble to have a constant radius. In the absence of critical phenomena, a 4% temperature variation at constant density should not lead to a detectable ($\Delta\mu/\mu\approx 1\%$) mobility variation. This conclusion follows from the two extreme theories: the friction-constant formalism[16] and the dilute-gas case.[17] Insensitivity of mobility to small temperature changes at constant density is also supported by experimental evidence, for the high-density region in the case of ^{4}He,[18] and for the low-density region from our present data in the density range $\rho\leqslant 0.020$ g/cm³ (see Fig. 7) and from Levine and Sanders's measurements (see Fig. 7 of Ref. 14). Figures 9 and 10 show the response of mobility to temperature changes in the critical regions, which was also reported previously. To the extent that the bubble model is correct, Figs. 9 and 10 estimate the width of the critical region as far as mobility measurements are concerned.

B. Positive Carriers

The structures of positive and negative carriers are quite different. Whereas the electron forms a rigid bubble, the positive ion builds up a cluster of ^{3}He atoms. The dimension of this cluster is obviously determined by a balance condition, at the cluster boundary, between kinetic energy and potential energy of a helium atom. When the surface tension γ is appreciable, the radius R of the cluster can be determined by the well-known formula used in cloud chambers[19] $\ln(p/p_s)$

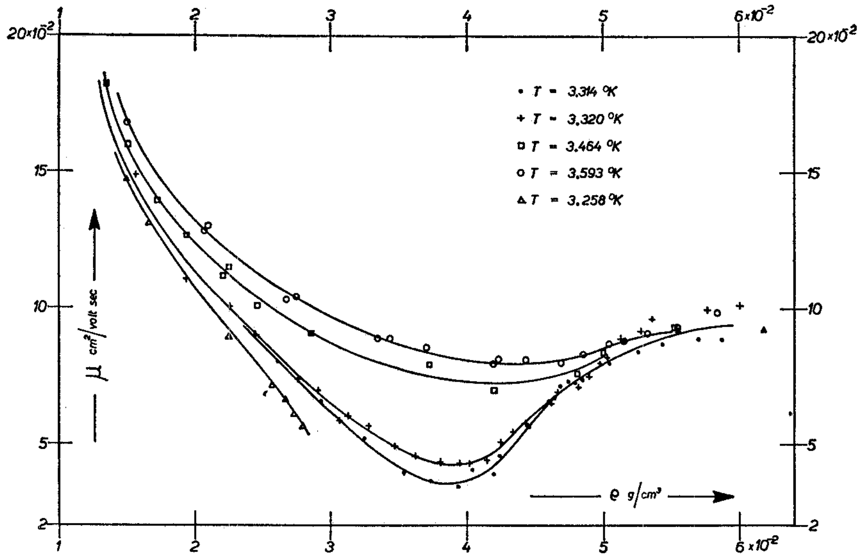

FIG. 8. Mobility of positive carriers as a function of density for various isotherms.

[16] S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience Publishers, Inc., New York, 1965).
[17] L. B. Loeb, *The Kinetic Theory of Gases* (Dover Publications, Inc., New York, 1961), p. 576.
[18] I. Modena and F. P. Ricci, Phys. Letters **25A**, 231 (1967).
[19] J. G. Wilson, *Cloud Chamber Technique* (Cambridge University Press, New York, 1951), p. 3.

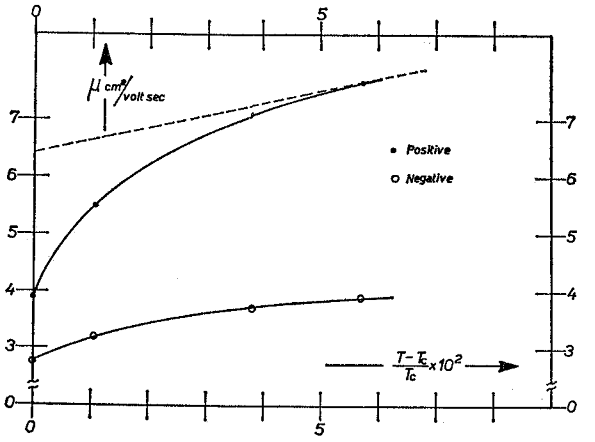

FIG. 9. Mobility versus temperature at $\rho \simeq \rho_c$ (Ref. 7). The dashed straight line has the same slope as the straight lines of Fig. 11. T_c has been taken at 3.312°K.

$=(nK_BT)^{-1}(2\gamma/R)-(\alpha e^2/2R^4K_BT)$, 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 is the Boltzmann constant. However, for temperatures higher than the critical temperature, where p_s and γ are meaningless, we can write the potential energy as the sum of the electrostatic (i.e., ion-induced dipole) interaction and a van der Waals contribution which originates from the density difference between the cluster and the helium bulk. Since the internal energy in a fluid can be written as proportional to some power of the density, we can write

$$\tfrac{1}{2}M\langle V^2\rangle=(N\alpha e^2/R^4)+C(\rho_{cl}{}^n-\rho_{He}{}^n)z\,, \qquad (1)$$

where M is the molecular weight, N is Avogadro's number, C and n are two constant peculiar to the ^{3}He, and ρ_{cl} and ρ_{He} refer to the density of the cluster and of the bulk ^{3}He, respectively. It is easy to see from Eq. (1) that at constant ^{3}He bulk density, in our small range of temperature, we can practically assume that R varies linearly on T. Therefore also μ should be linearly

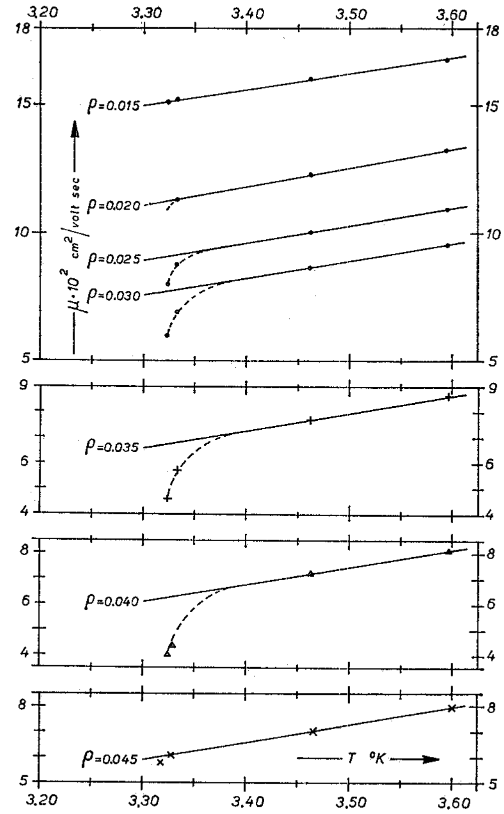

FIG. 11. Mobility versus temperature at various isopycnals for positive carriers. The straight lines give the normal temperature dependence due to the variation of the ion-cluster radius with temperature.

dependent on T if we are working at $\rho_{He}=$const. The zero-point motion would influence only the value of C and n. Therefore, if we plot the mobility as a function of T, taking the experimental data at constant density, we must have a straight line for points at temperatures above the critical temperature. Any deviation from this straight line is due to the critical phenomena. Figure 11 shows this kind of analysis. In Fig. 12, the deviation

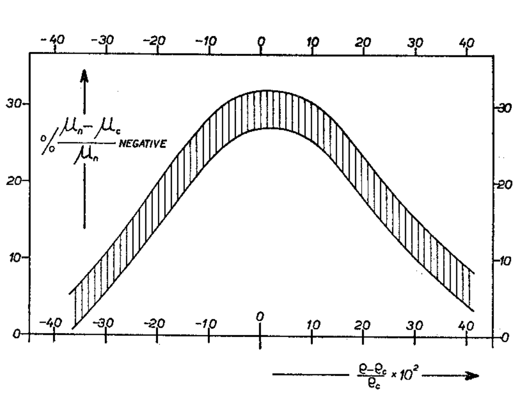

FIG. 10. Mobility defect in the critical region for negative carriers. The mobility defect is measured by the difference between a normal isotherm ($T=3.448$°K) and a nearly critical isotherm ($T=3.324$°K).

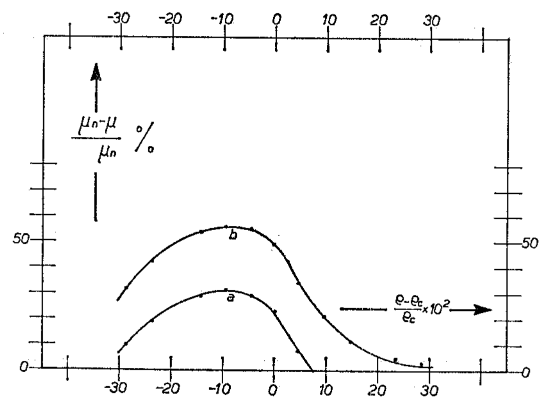

FIG. 12. Mobility defect in the critical region for positive carriers. The mobility defect [curve (a)] is measured by the deviation from the straight lines in Figs. 11 and 9. Curve (b) is just $\mu(T=3.593°\text{K})-\mu(T=3.314°\text{K})/\mu(T=3.593°\text{K})$.

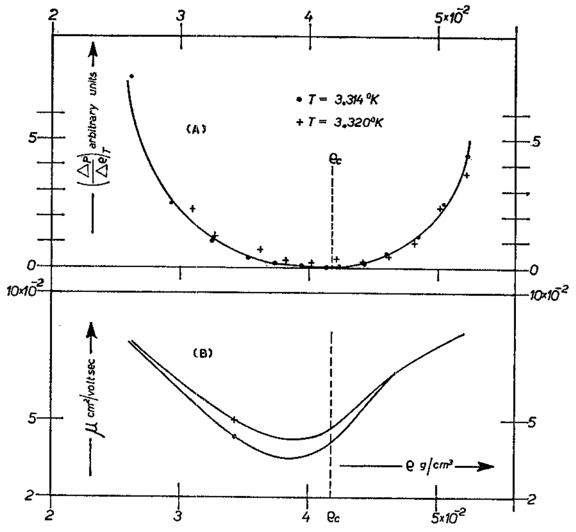

FIG. 13. (A) $(\Delta p/\Delta\rho)_{T=\text{const.}}$ as a function of density as from our measurements. The minimum of $\Delta p/\Delta\rho$ occurs at $\rho=\rho_c$ (Ref. 7). (B) Mobility versus density for the same isotherms as in (A). It is noticeable that the minima on the mobility curves occur at a density clearly lower than ρ_c (Ref. 7).

from the straight line, which is the normal behavior, is reported as a function of $(\rho-\rho_c)/\rho_c$, where ρ_c is the critical density [curve (a)].

Curve (b) represents the mobility difference between the isotherms at $T=3.593$ and $T=3.314$°K. Considering curves (a) and (b), it is clear that our correction to take into account the variation of R with the temperature at $\rho=$ const changes only the amount of the critical effect: The general shape of the curve (e.g., the asymmetric shape about the critical density) remains unaffected.

It is interesting to note that if we compare the plots of our experimental values of $(\partial p/\partial\rho)_{T=\text{const}}$ and of $\mu(T=\text{const})$ as a function of ρ, we can easily see from Figs. 13(A) and 13(B) that the density at maximum compressibility (which agrees also with the ρ_c value[7]) does not coincide with the density at minimum mobility, which in the positive ion case is also the point where $(\partial\mu/\partial p)_{T=\text{const}}$ changes sign.

CONCLUSIONS

From the previous analysis we can conclude that for both positive and negative probes, the mobility undergoes a decrease in the critical region. However, there is no evidence of a singularity as far as we were able to approach the critical point ($\Delta T/T_c \simeq 6\times10^{-4}$ and $\Delta p/p_c \simeq 3\times10^{-5}$). Therefore the qualitative conclusions of the previous paper[6] remain unchanged. Nevertheless, some minor differences are evident between the behavior of the two probes. The critical effect for the negative carriers (see Fig. 10) is centered at the critical density and is symmetric about it; while for positive carriers the curve (a) of Fig. 12 has the maximum shifted to lower density values and is clearly asymmetric. This fact could be due to a small perturbation in the external pressure from the electrostatic interaction. This effect is vanishingly small in the case of electrons owing to the larger size of the bubble with respect to the cluster. However, in order to put such an effect on a quantitative basis one should extrapolate a macroscopic quantity such as the compressibility to lengths of the order of angstroms.

ACKNOWLEDGMENTS

We wish to thank Dr. R. H. Sherman and Dr. C. E. Chase for sending us their experimental results before publication, and I. Cenciarelli for valuable help in construction of the apparatus.