

Mobility of Ions in Liquid He⁴I and He³ as a Function of Pressure and Temperature*

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In this paper we present an experimental study of the pressure and temperature dependence of the mobility of the positive and negative species of charged particles in liquid He⁴ above the λ transition and in liquid He³. The mobility of the positive species in He⁴ decreases linearly with increasing density, and the Stokes radius of the positive species is inversely proportional to $T^{\frac{1}{2}}$. The mobility of the negative species initially increases with increasing density and then falls off linearly with further increase in density. The Stokes radius of the negative species increases with increasing temperature. At constant density the mobilities of both species in He⁴ and He³ vary very slowly with temperature. At the vapor pressure and around 2.2°K there is a larger temperature dependence than indicated above, but this is probably due to the approach of the λ transition. The mobility of the positive species in He⁴ and He³ at 3.0°K is a linear function of density, independent of the isotope.

Feynman has suggested (and Kuper detailed) a model for the negative species in which an electron is trapped in a bubble of radius b . Comparison with our data shows that this model is not

able to account for the temperature and pressure dependence of the observed mobility. In the Appendix, we show that an electron would not diffuse by quantum mechanical tunneling from cavity to cavity.

Davis, Rice, and Meyer have derived an expression for the mobility of the negative species by assuming (a) that the negative species is a free electron and (b) that scattering is determined by a small pseudopotential equal to the polarization potential outside an atom and zero inside the atom. They predict a mobility which initially increases with increasing density at constant temperature, but they cannot predict the decrease of mobility with further increase in density unless they assume a density dependent effective mass of the electron. The effective mass necessary to fit theory to experiment is approximately 100 electron masses and is proportional to the square of the density. This model is promising, but more detailed calculations of the effective mass must be made before the mechanism of negative charge transport may be considered to be completely understood.

I. INTRODUCTION

IT has been shown that ions can be successfully used as microscopic probes into superfluid helium.¹⁻⁴ Since the drift velocity of ions as a function of the applied electric field can be measured quite accurately for very low ion concentrations (10^3 cm^{-3}), it is possible to perform an idealized hydrodynamic experiment in which a body is dragged through the fluid and its velocity measured as a function of the force applied. In the present paper, experiments are reported wherein the mobility of ions has been used to study the transport properties of the simple fluids, liquid HeI and He³, as a function of temperature and pressure.

The theoretical analysis of transport phenomena in simple fluids has made considerable progress recently,⁵⁻⁷ but much experimental data is needed both to test the theory and to guide future development. The two helium isotopes have in their liquid form an unusually low density (due to zero point motion) and their

properties may be expected to be between the extremes of gas-like and liquid-like behavior. The two isotopes obey different statistics and it is interesting to see whether or not the statistics influence transport phenomena, even in the nondegenerate state. Furthermore, the nature of the charged particles in liquid helium is still rather obscure,⁸⁻¹⁰ since a He⁻ ion does not seem stable enough to act as a charge carrier in the fluid. Finally, the large compressibility of the liquid helium isotopes allows one to cover a considerable density range within a moderate pressure range.

II. EXPERIMENTAL METHOD

The method used to determine the charge mobility consisted of a direct time of flight measurement of the drift velocity of the ions as a function of the applied electric field. The method used and apparatus required have been reported earlier.^{3,11} One minor change became necessary: the drift velocities measured in HeII were so high that the frequency of the square wave potential applied to the electric gates was at least 100 cps. In HeI and liquid He³ this frequency was reduced by more than a factor of 10 for a drift space of about 1 cm and low fields. The ac coupling between the square wave generator and the grid system of Fig. 1 of reference 3 was replaced by a dc coupling shown diagrammatically in Fig. 1. A Hewlett-Packard function generator (No. 202A) superseded the oscillator-squaring circuit for use at low frequencies. The frequency of the function

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¹ R. L. Williams, Can. J. Phys. **35**, 134 (1957).

² G. Careri, *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. III, p. 58.

³ F. Reif and L. Meyer, Phys. Rev. **119**, 1164 (1960).

⁴ L. Meyer, *Proceedings of the Seventh International Conference on Low-Temperature Physics* (Toronto University Press, Toronto, 1960), p. 487.

⁵ For a recent review, see S. A. Rice and H. L. Frisch, Ann. Rev. Phys. Chem. **11**, 187 (1960).

⁶ H. T. Davis, S. A. Rice, and J. V. Sengers, J. Chem. Phys. **35**, 2210 (1961).

⁷ H. T. Davis, S. A. Rice, and L. Meyer (to be published).

⁸ K. R. Atkins, Phys. Rev. **116**, 1339 (1959).

⁹ C. G. Kuper, Phys. Rev. **122**, 1007 (1961).

¹⁰ R. Abe and K. Aizu, Phys. Rev. **123**, 10 (1961).

¹¹ L. Meyer and F. Reif, Phys. Rev. **123**, 727 (1961).

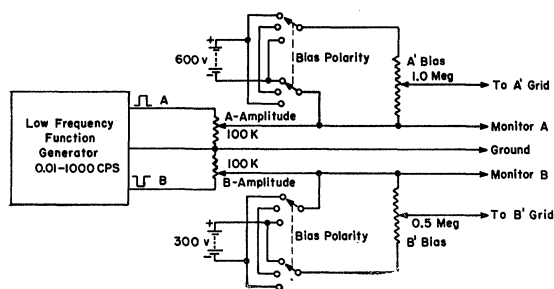


FIG. 1. A'-B' biasing circuit for low frequencies.

generator was checked against a No. 522B Hewlett-Packard electronic counter.

The apparatus corresponded to Fig. 2 of reference 3 with the high pressure attachments described in reference 11. The He³ refrigerator was not used; the vacuum chamber between the outer helium bath and the experimental chamber contained a small amount of exchange gas. The temperature of the experimental chamber was determined with a calibrated carbon thermometer; temperatures derived from the bath pressure and from the resistance thermometer agreed within 0.001°K. The electric field was limited to less than 200 v/cm in the drift space, because of the danger of electrical breakdown in the parts of the apparatus where the

leads pass through spaces containing low-pressure helium gas. In this range the drift velocity, v_i , was proportional to the electric field, \mathcal{E} , so that the data are reported only as the mobility $\mu_i = v_i/\mathcal{E}$. The relative accuracy is again, as in reference 3, about 2% (only two points deviate by 5%), with the possibility that the error in the absolute values might be somewhat higher.

The He³ used in the experiment was kindly loaned to us by Professor R. H. Hildebrand, to whom we are greatly indebted for his help and cooperation. The gas was pressurized by cryogenic pumping; the He³ was first condensed in a stainless steel cylinder at about 1.2°K, after passing through a trap filled with bronze wool at 4.2°, in order to remove traces of tritium. After warming up the stainless steel cylinder, the gas was under approximately 1500-psi pressure; the high-pressure He³ was then condensed in the experimental chamber as described in reference 11. The amount of He³ available was unfortunately not large enough to pressurize the liquid in the experimental chamber at the lowest temperature (1.2°), because of the 30% increase in the fluid density between the boiling point and 1.2°.

III. EXPERIMENTAL RESULTS

A. He⁴I

The mobilities determined in He⁴I are displayed in Table I and shown graphically in Figs. 2 through 7. Figures 2 and 3 show the mobility of the positive and negative ions, respectively, as a function of pressure for different temperatures. Figures 4 and 5 display the same data as a function of density using the pressure-

TABLE I. He⁴ data.

T (°K)	P (atm)	$\mu_+ \times 10^2$ (cm ² volt ⁻¹ sec ⁻¹)	$\mu_- \times 10^{-2}$ (cm ² volt ⁻¹ sec ⁻¹)
2.2	1.0	5.28	3.87
2.2	1.0	5.22	3.73
2.2	1.0	4.95	3.57
2.2	7.4	3.69	3.47
2.2	8.1	3.96	
2.2	8.2		3.66
2.2	14.0	2.90	2.88
2.2	14.3	2.82	2.78
2.2	14.4	3.09	3.01
2.2	20.9	2.47	
2.2	20.6		2.62
2.2	27.5	1.90	2.08
2.2	27.6	1.83	2.04
3.0	1.0	4.61	2.55
3.0	1.0	4.14	2.70
3.0	7.3	3.73	2.75
3.0	7.5	3.32	2.78
3.0	13.9	2.67	2.51
3.0	14.0	3.05	2.51
3.0	21.0	2.55	2.24
3.0	21.1	2.35	2.30
3.0	27.6	1.97	2.10
3.0	27.7	2.24	2.06
4.2	1.0	5.43	2.35
4.2	1.0	5.29	1.98
4.2	7.4	4.17	
4.2	7.6		2.80
4.2	8.5	4.30	
4.2	8.3		2.88
4.2	14.6	3.73	2.74
4.2	14.8	3.39	2.51
4.2	19.9	3.19	2.65
4.2	20.9	3.32	2.54
4.2	27.8	2.86	2.37

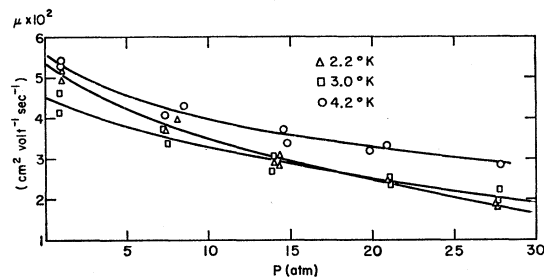


FIG. 2. Mobility of the positive species in HeI as a function of pressure at 2.2, 3.0, and 4.2°K.

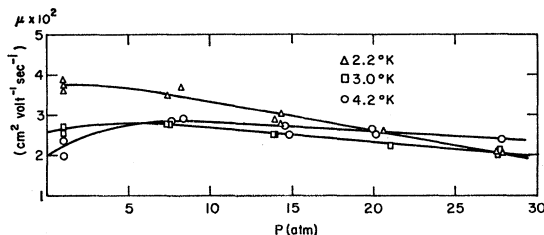


FIG. 3. Mobility of the negative species in HeI as a function of pressure at 2.2, 3.0, and 4.2°K.

density data of Keesom¹² and the data of Lounasmaa and Kaunisto.¹³ Figures 6 and 7 present the mobilities, μ_+ and μ_- , respectively, as a function of temperature for different densities. These are derived from the curves of Figs. 4 and 5 by taking, for three densities which were attainable at all temperatures, smoothed values of the ionic mobilities.

B. Liquid He³

The mobilities determined in He³ are displayed in Table II. In the last column of Table II the densities of He³ at the temperature and pressure of our experiments (according to Sherman and Edeskuty¹⁴) are listed.

IV. DISCUSSION

As can be seen immediately from the figures and tables, the mobility depends strongly on the density and only slightly on the temperature. The mobility of the positive ions (μ_+) is, at constant temperature, essentially a linear decreasing function of the density. The slope of this line becomes steeper with decreasing temperature: $(\partial\mu_+/\partial\rho)$ has the values 0.57 at 4.2°, 0.71 at 3.0°, and 1.1 cm⁵/g-volt-sec at 2.2°K. The behavior of the mobility of the negative ions (μ_-) is much more complex. Qualitatively, μ_- behaves in a manner similar to that observed below the λ point in reference 11, i.e., at low pressures the mobility increases with increasing density, whereas at higher pressures μ_- approaches

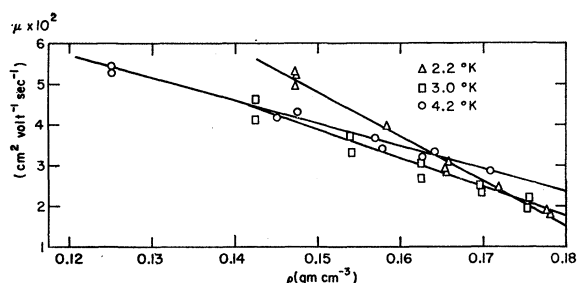


FIG. 4. Mobility of the positive species in HeI as a function of density at 2.2°, 3.0°, and 4.2°K.

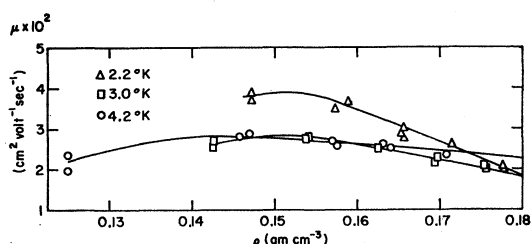


FIG. 5. Mobility of the negative species in HeI as a function of density at 2.2°, 3.0°, and 4.2°K.

¹² W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., Amsterdam, 1942), p. 240.

¹³ O. V. Lounasmaa and L. Kaunisto, *Ann. Acad. Sci. Fennicae AVI* (1960).

¹⁴ R. H. Sherman and E. J. Edeskuty, *Ann. Phys.* **9**, 522 (1960).

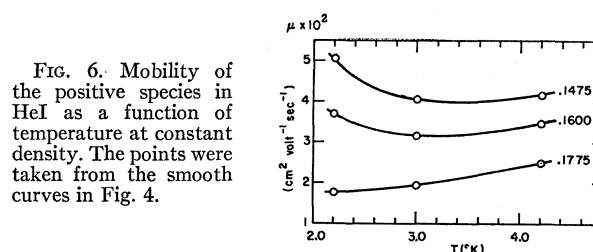
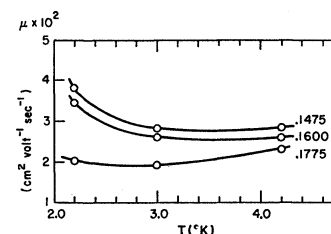


FIG. 6. Mobility of the positive species in HeI as a function of temperature at constant density. The points were taken from the smooth curves in Fig. 4.



μ_- . Below the λ point and above 7 atm, $\mu_+ = \mu_-$ within the experimental error. In these experiments the pressure and density range was limited by the low melting pressure (~ 25 atm) at the low temperature. A comparison of Figs. 4 and 5 shows that above the λ point μ_- always differs somewhat from μ_+ . At 4.2°K μ_- always remains smaller than μ_+ in the density range investigated; however, at 2.2° and a density of 0.18 g cm⁻³ it appears that $\mu_- > \mu_+$. If the trend of Fig. 4 and Fig. 5 were continued, at sufficiently high densities, μ_- would become greater than μ_+ at 4.2°. A more detailed comparison of the ratio (μ_-/μ_+) below and above the λ point does not seem possible, since completely different scattering mechanisms are involved. Below the λ point the ions are scattered chiefly by collisions with rotons after a considerable mean free flight, whereas above the λ point the mean free path is only of the order of an atomic distance and the scattering mechanism is rather complex and not known in detail.

In Fig. 8, the values of μ_+ and μ_- for liquid HeI and He³ at about 3°K are plotted as a function of the number density. The values of μ_+ for He³ lie approximately on a line drawn through the μ_+ values in HeI and extrapolated to the much lower densities of He³,

TABLE II. He³ data.

T (°K)	P (atm)	$\mu_+ \times 10^2$ (cm ² volt ⁻¹ sec ⁻¹)	$\mu_- \times 10^2$ (cm ² volt ⁻¹ sec ⁻¹)	ρ (g cm ⁻³)
1.21	1.15	7.65	3.64	0.0842
1.79	1.63	8.25	4.04	0.0834
2.15	2.05	8.17		0.0830
2.25	2.11		4.06	0.0826
2.94	3.10	8.28		0.0810
2.94	3.14		4.32	0.0812
3.15	3.41	8.14		0.0803
3.10	3.41		4.04	0.0803
2.94	1.34	9.36	3.50	0.0714
3.20	1.09	8.83	3.09	0.0629

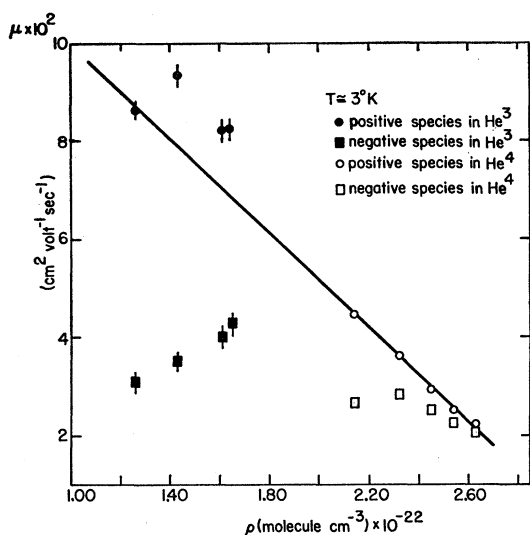


FIG. 8. Mobilities of the positive and negative species in He^4 and He^3 as a function of density at approximately 3°K . Note that the mobility of the positive species seems to be a linear function of the density independent of the isotope.

but this is not true for μ_- . This plot shows again that the number density is the most important factor influencing the mobility, rather than temperature or statistics.

Figures 6 and 7 and the data for He^3 show in detail how small the temperature dependence of the mobility is. The increase in μ_+ and μ_- in HeI at 2.2°K and low densities over that expected is probably due to the nearness of the λ point. Dash and Taylor¹⁵ found a similar effect on the viscosity of HeI , and Grenier,¹⁶ on the heat conductivity on approaching the λ point. μ_- seems to be somewhat more sensitive to the approach to the λ point than μ_+ . At our highest density, the λ point is shifted to lower temperature by almost half a degree. It is, therefore, not surprising that under these conditions no anomalous increase in mobility at 2.2° has been observed.

The extremely small temperature dependence of the mobility rules out any activated step in the motion of the ions through the fluid, i.e., the possibility that the ion has to jump over energy barriers before reaching a new position. A similar conclusion was reached by Garwin and Reich¹⁷ from their measurements of the self-diffusion of He^3 (which also shows a very small temperature dependence). However, below 0.55°K Hart and Wheatley¹⁸ observed a marked increase of diffusion with decreasing temperature. Unfortunately, we did not reach such low temperatures so that we are not able to make a comparison with their data. The mobility may be connected with the diffusion coefficient

D by the Einstein relation:

$$\mu/D = e/kT, \quad (1)$$

where e is the charge of the ion, k the Boltzmann constant, and T the absolute temperature. The diffusion coefficient (D_i) for the positive ions derived from the measured mobilities in liquid He^3 by using Eq. (1) is about 5 times smaller than the self-diffusion coefficient (D_s) measured by Garwin and Reich. This is by no means surprising, since the positive ion is a much more massive particle (the mass is estimated to be about 100 He^4 masses; cf. references 8 and 9) than a He^3 atom. The temperature and pressure dependence of D_i and D_s are rather similar. The relationship between D_i and D_s observed is in complete agreement with the relationship between positive ion diffusion and self diffusion in liquid Ar.^{18a} Garwin and Reich suggested that the small temperature dependence of D_s might be due to tunneling of the He^3 atoms during diffusion. The fact that D_i and D_s behave in a similar way seems to exclude this mechanism because the ion is much too heavy for a tunneling process.

The mobilities at 1.20° in He^3 seem to be somewhat lower than expected from the trend at higher temperatures. This may be due to a change in the density isotherm, since Rives and Meyer¹⁹ find a maximum in density at slightly lower temperatures than considered herein.

V. SOME SIMPLE MODELS

The simplest interpretation of our data uses Eq. (1) and the Stokes-Einstein relation,

$$D = kT/6\pi\eta a, \quad (2)$$

where η is the viscosity and a the radius of a rigid sphere representing the diffusing particle, to obtain

$$\mu\eta = \text{const}, \quad (3)$$

TABLE III. $\mu\eta$ at different temperatures along the vapor pressure curves for He^4 and He^3 (arbitrary units).

T ($^\circ\text{K}$)	4.2	3.2	3.0	2.2	1.2	Fluid
$\mu_+\eta$	1.93		1.73	1.54		HeI
$\mu_-\eta$	0.79		0.94	1.08		HeI
$\mu_+\eta$		1.68			2.25	He^3
$\mu_-\eta$		0.6			1.0	He^3

^{18a} Note added in proof. Interpretation of the decreased mobility of the ion as due to an increased mass is incomplete. Davis, Rice, and Meyer [J. Chem. Phys. (to be published)] have studied positive ion mobility in liquid Ar, Kr, and Xe and also found the ion mobility to correspond to a diffusion coefficient five times smaller than that of an atom. They have also developed a molecular theory valid for these classical fluids which is in quantitative agreement with experiment. It is concluded that the positive ion is likely Ar_2^+ , \dots Xe_2^+ and that although electrostriction increases the local density, no freezing occurs and the increased friction arises from enhancement of the dissipation by short range forces. This enhancement is due to the increase in local density.

¹⁹ J. E. Rives and H. Meyer, Phys. Rev. Letters 7, 217 (1961).

¹⁵ R. D. Taylor and J. G. Dash, Phys. Rev. 106, 398 (1957).

¹⁶ C. Grenier, Phys. Rev. 83, 598 (1951).

¹⁷ R. L. Garwin and H. A. Reich, Phys. Rev. 115, 1478 (1959).

¹⁸ H. R. Hart and J. C. Wheatley, Phys. Rev. Letters 4, 3 (1960).

a relation known in electrochemistry as Walden's rule. Using the data of Dash and Taylor¹⁵ for the viscosity of HeI and He³, one obtains the figures displayed in Table III. Peshkov and Zinov'eva^{20,21} have also measured the viscosity of HeI and He³. The temperature dependence of the viscosity as found by Dash and Taylor agrees with the temperature dependence of Peshkov's and Zinov'eva's data, while in absolute magnitude Peshkov's and Zinov'eva's data are about 10% lower than those of Dash and Taylor. Hence, for the purposes of examining the temperature dependence of the product, $\mu\eta$, both sets of data yield the same trend.

One possible interpretation of the slight increase of $\mu_+\eta$ with temperature in HeI is that the ion is not a perfectly rigid sphere; any softer repulsive potential will allow particles of high thermal energy to penetrate deeper than particles of low thermal energy causing the radius to decrease slightly with rising temperature. A similar effect was observed in reference 3 (cf. p. 1167, where the experimental results for the ion-roton scattering required a somewhat temperature dependent ion-roton collision cross section in order to be consistent with theoretical predictions). In HeI, $\mu_+\eta$ is a linear function of $T^{1/2}$ within the error of the experiments. The Stokes diameter of the positive ion would then decrease with $T^{1/2}$ or be inversely proportional to the thermal velocity. The opposite trend of $\mu_-\eta$ does not fit any simple picture.

Another interesting feature is that $\mu_+\eta$ for HeI and He³ are the same at 3°K within the experimental error. Even the difference in $\mu_-\eta$ for the two isotopic fluids is not very great. The Stokes radii computed from the mobility data and Eqs. (1) and (2) are in HeI, 4.3 Å for positive, and 8.5 Å for negative ions. These are surprisingly reasonable values for such an oversimplified and primitive model. (Compare the theoretical estimates in references 8 and 9.) In He³ the Stokes radius for the positive ions is about 5 Å at 3.2°K and somewhat lower at 1.2°, showing again the very similar character and behavior of the positive charge carrier in both isotopes. The corresponding values for the negative ions are: 14 Å at 3.2° and 9 Å at 1.2°K. All these computations refer to the saturated vapor pressure curve, since it is only under these conditions that viscosity measurements for He³ have been performed.

The drift velocities were derived from recordings of the ion current as a function of the frequency of the square wave field applied to the electric gates. This current is a maximum when the time the ions need to drift from the entrance gate across the drift space to the exit gate just equals an integral multiple of the period of the square wave field. In the case that there are several charge carriers present with differing drift velocities, more than one set of peaks should appear

in the plot of current vs frequency. No indication of more than one set of peaks was found, either in the experiments of references 3 and 11 or in the present work. The form of the peaks corresponded reasonably well with the form derived theoretically in Appendix B of reference 3. Thus, even a second species of not greatly differing drift velocity can be ruled out. This is of special importance for the region where μ_- shows a maximum as a function of density or pressure. Any explanation of this maximum as indicating a gradual change in the character of the negative ions, e.g., from the "bubble" where an electron is trapped in the fluid to something like He_n^- , can be ruled out. In the transition region both of these forms would be present in measurable amounts. They would have to have different mobilities in order to produce the extremum in the mobility vs density curve, and either several peaks or rather, distorted peaks should have been observed. A model combining features of the "bubble" and of the "iceberg" might be juggled to explain the data, but we prefer to avoid this kind of parameterization.

A quasi-molecular model of the negative species was suggested by Feynman and Kuper⁹ has worked out the details. In this model it is assumed that the electron is trapped in a rigid bubble of radius b , with b approximately 12 Å. One would expect a bubble this large to obey Stokes law. However, the bubble radius as calculated by Kuper is not very sensitive to pressure and remains almost constant over the pressure range from one to thirty atmospheres, while the Stokes radius, as determined from μ_- and experimental values of the viscosity^{15,22} decreases by about 35%. Also, the bubble radius is not very sensitive to a temperature change in the range from 2.2°K to 4.2°K, while the experimental Stokes radius varies by about 35% with temperature over this range. We must then conclude that, if an "electron bubble" exists, the mechanism of charge transport is not that of dragging the bubble through the liquid.

Another possibility suggests itself. If by a fluctuation a cavity appears in the neighborhood of the bubble containing the electron, the electron could jump or "tunnel" from its cavity to the adjacent cavity. According to this model, the mobility would be determined by the jump frequency and the probability of a suitable volume fluctuation. However, rough calculations presented in the Appendix indicate that the mobility predicted by this model is vanishingly small, and, therefore, that this is an inefficient transport mechanism. Around the bubble there is a sizeable density increase due to electrostriction and, as a consequence, there is a non-negligible work of compression necessary for the electron to jump irreversibly from bubble to cavity. This acts as a retarding influence on the jumping electron. Also, since the equilibrium

²⁰ K. N. Zinov'eva, Soviet Phys.—JETP 7, 421 (1958).

²¹ V. P. Peshkov and K. N. Zinov'eva, *Reports on Progress in Physics* (The Physical Society, London, 1959), Vol. 22, p. 504.

²² B. Welber, Phys. Rev. 119, 1816 (1960).

radius of the bubble is rather large, the probability of a suitable cavity fluctuation is small. With the combined effect of these two inhibiting factors the predicted mobility is of the order 10^{-61} , or for all practical purposes, it is of the order zero.

VI. PSEUDOPOTENTIAL SCATTERING

In addition to the fact that the models mentioned in the preceding section do not agree with experiment, there is a more fundamental feature which is objectionable. Within the framework of these models we must assume that wave function describing an electron is localized about a chosen point in the liquid. However, a chemically unbound electron should be described by a wave function of large extension in space with approximately equal charge density throughout the system, as in the case of a polaron in an ionic crystal. This difficulty is avoided, if we treat the electron as free except for single scattering by the atoms.

The nearly-free electron is by no means a new idea. This concept has, of course, been very successful in predicting the observed properties of metals in both the liquid and solid states, alloys, and conjugated hydrocarbons. However, the reason that such a crude model should work for these systems has only recently been explained (Phillips and Kleinman²³ and later Cohen and Heine²⁴). It has been pointed out that even though there is a very strong negative potential energy well for an electron near an atomic nucleus, it is approximately cancelled by the high kinetic energy associated with the rapid oscillations of the wave function within the region of the ion core. These oscillations are seen to arise from the requirement that the wave function of the free electron be orthogonal to all the occupied electron orbitals.

Davis, Rice, and Meyer⁷ have derived an expression for the mobility of an electron in a nonpolar liquid assuming the interaction potential at position \mathbf{r} , to be given by

$$V(\mathbf{r}) = -e^2 \sum_{i=1}^N \frac{\alpha(\epsilon+2)}{2} \left(\frac{\epsilon+2}{3\epsilon} \right)^2 U_i(|\mathbf{r}-\mathbf{R}_i|), \quad (4)$$

where,

$$U_i(|\mathbf{r}-\mathbf{R}_i|) = \begin{cases} 1/|\mathbf{r}-\mathbf{R}_i|^4, & |\mathbf{r}-\mathbf{R}_i| \geq a/2 \\ 0, & |\mathbf{r}-\mathbf{R}_i| < a/2 \end{cases} \quad (5)$$

\mathbf{R}_i is the vector position of the i th atom in the fluid, α the atomic polarizability, ϵ the dielectric constant, and e the electronic charge. The parameter a is taken to be an atomic diameter, about 2.6 \AA for helium. It is also assumed that the concentration of free electrons is very small and, thus, that Boltzmann statistics are satisfactory.

Treating the electrons as plane waves scattered by the above defined pseudopotential, it is found that the

electronic mobility is given by

$$\mu = \frac{2e\pi^{1/2}\hbar^4}{3\sqrt{2}m^*(kT)^{3/2}\rho_N^2\kappa_L|U_K|^2}, \quad (6)$$

where m^* is the effective mass of the electron, T the absolute temperature, ρ_N the number density of the fluid, κ_L the compressibility of the fluid, and $|U_K|$ is defined by

$$|U_K| = \frac{4\pi\alpha(\epsilon+2)^2}{a} \left(\frac{\epsilon+2}{3\epsilon} \right) e^2. \quad (7)$$

The above equation [Eq. (4)] is valid in the limit of slow electrons so that it should hold for electrons moving with thermal velocity in liquid helium. Actually, the Fourier transform of the radial distribution function of the liquid, $a(K)$, should appear in the denominator of Eq. (4), but at these temperatures and densities the electron wavelength is so long that only the zeroth component of $a(K)$ makes a contribution. $a(K=0)$ is given by $a(0) = kT\rho_N\kappa_L$. In this sense the scattering of the electron is analogous to light scattering.

Experimentally we have seen that the mobility of the negative species in He^3 increased with increasing density at constant temperature, and in He^4 the mobility initially increases with increasing density and then begins to decrease linearly with density. If we assume the effective mass to be independent of density the mobility as predicted by Eq. (6) increases with increasing density and the effective mass as determined using the experimental value of μ_- at 4.2°K and 1 atm pressure is about 60 times the mass of an electron.

However, the mobility given by Eq. (6) does not decrease with increasing density as found experimentally in HeI . If the free electron model as described above is assumed to be correct, the deviation of the predicted mobility from that found experimentally can be interpreted as a density dependent effective mass. Substituting into Eq. (6) the experimental values of μ_- at 4.2°K and 1, 10, and 30 atmospheres and solving for the effective mass for each of these conditions we find $m^*/m_e(4.2^\circ\text{K}, 1 \text{ atm}) = 62$, $m^*/m_e(4.2^\circ\text{K}, 10 \text{ atm}) = 80$, and $m^*/m_e(4.2^\circ\text{K}, 30 \text{ atm}) = 108$. The effective mass to electron mass ratio is proportional to the square of the density.

As the electron moves through the liquid, it experiences a retardation due to the polarization forces. That is, the electron motion is coupled with local density fluctuations. The velocity with which a density fluctuation can occur is roughly equal to the velocity of sound (10^4 to 10^5 cm/sec) in HeI . The thermal velocity of a free electron in HeI [$v = (3kT/m_e)^{1/2}$] is about 10^5 to 10^6 cm/sec so that we cannot expect any calculation of an electrostrictive density increase about a static charge in a fluid to be valid for the prediction of the effective mass of the electron.

A more accurate treatment of the electron-medium coupling can probably be given by using techniques

²³ J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

²⁴ M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

resembling those used in polaron theory.^{25,26} The electron-medium coupling can give rise to local density fluctuations and to a local dielectric constant which differs from the dielectric constant of the unperturbed fluid. The extent of the coupling and, hence, the effective mass will probably depend on the velocity of the electron (temperature) and the density of the liquid.

Using second-order perturbation techniques, detailed calculations of the dynamical coupling or effective mass of the electron in a nonpolar liquid such as helium are underway at present. These calculations will probably give some information concerning the general validity of the pseudopotential scattering in a nonpolar liquid.

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APPENDIX

In the following analysis, we shall assume an electron is classically trapped in a bubble of diameter c . By "classically trapped," we mean that the electronic kinetic energy $\hbar^2/2mc^2$, is less than the potential barrier keeping the electron in the cavity. Furthermore, we shall postulate that the electron migrates through the fluid by tunneling from hole to hole with each tunneling step in a direction uncorrelated with the preceding step. The holes are produced by local fluctuations of the free volume v_f , with the free volume defined as the difference between the molecular volume and the Van der Waals volume per molecule. The electronic migration, which would result in no net charge displacement in the absence of external fields, is biased by the electric field to produce a net drift of electrons in the direction of the field.

Making use of the Einstein relations, we can express the mobility as

$$\mu = \frac{e}{kT} D = \frac{e}{6kT} \langle \nu R^2 \rangle, \quad (\text{A1})$$

with μ , e , and D the mobility, charge, and diffusion coefficient of the electron, R the separation of the electron bubble and the nearest neighbor cavity, and with the average performed over an equilibrium ensemble. ν is the jump frequency of the electron. Taking the probability of density of finding a nearest-neighbor cavity at the distance R , $p(R)$, to be independent of the probability of a suitable volume fluctuation, $p(v^*)$, we can write

$$\mu = \frac{e}{6kT} \int \nu(R) R^2 p(R) p(v^*) e^{-\Delta g/kT} dR, \quad (\text{A2})$$

with $p(v^*)$ the probability of a volume fluctuation producing a cavity with a volume, v^* , equal to at least $\frac{4}{3}\pi(c/2)^3$, and Δg the work of compression necessary for the electron to jump irreversibly from bubble to cavity.

In the neighborhood of the bubble the atoms are polarized by the electric field of the electron, and the resulting electrostatic interaction produces an electrostrictive increase in local density and, consequently, local pressure. The work of compression, Δg , is then given by $\int_{v^*}^{\infty} (p - p_0) dv$, where p_0 is the pressure of the unperturbed liquid and p is the local pressure. As calculated by Atkins,¹⁰ the density perturbation, $\rho - \rho_0$, is inversely proportional to the fourth power of the distance from the center of the electron bubble, and hence, with the aid of the equation of state, we can calculate Δg .

To determine the jump frequency of the electron we can represent the medium by a square potential barrier of height V_0 , through which the electron must tunnel to get to the next cavity. Since the kinetic energy of an electron in a bubble of radius $c/2$ is $E = \hbar^2/2mc^2$ we express the jump frequency as

$$\nu(R) = (1/c)(E/2m)^{\frac{1}{2}} T(R), \quad (\text{A5})$$

where $T(R)$ is the tunneling coefficient or the probability that an electron impinging upon the bubble wall will penetrate the barrier V_0 between the bubble and the next nearest neighbor, and the factor $(1/c)(E/2m)^{\frac{1}{2}}$ is the frequency with which the electron oscillates across the bubble. Neglecting nonspherical states, the tunneling coefficient²⁷ is given by the relation

$$T(R) = \frac{1}{1 + [1 + \frac{1}{4}(\kappa/k_e - k_e/\kappa)] \sinh^2 \kappa(R - c)}, \quad (\text{A6})$$

where

$$\kappa = [(2m/\hbar^2)(V_0 - E)]^{\frac{1}{2}}, \quad k_e = [(2m/\hbar^2)E]^{\frac{1}{2}}. \quad (\text{A7})$$

Considering the interactions of the helium atoms with one another to be of a rigid core nature, one can use the formula derived by Cohen and Turnbull²⁸ for $p(v^*)$, namely,

$$p(v^*) = e^{-\gamma v^*/v_f}, \quad (\text{A8})$$

where γ is a numerical factor accounting for the overlap of free volume; it should lie between $\frac{1}{2}$ and 1. We have assumed the electron will not jump to a cavity of radius smaller than $c/2$ since the kinetic energy of an electron trapped in a cavity goes up with the inverse square of the cavity radius.

$p(R)$ is a more difficult quantity to calculate, but we can obtain a crude form for it by imagining that the fluid is composed of a continuum plus holes of density ρ_h . In our actual model this hole density would be the

²⁵ H. Fröhlich, H. Pelzer, and S. Zienau, *Phil. Mag.* **41**, 221 (1950).

²⁶ H. Fröhlich, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 325.

²⁷ See, for example, L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, New York, 1958).

²⁸ M. H. Cohen and D. Turnbull, *J. Chem. Phys.* **31**, 1164 (1959).

average number of cavities per unit volume. We can estimate ρ_h by considering the incompressible (solid) state to be free of holes while the liquid is fractionally of solid density and fractionally holes. Then, the fraction of the system which is holes would be $\theta = (v_l - v_s)/v_l$, where v_l and v_s are the molar volumes of the liquid and solid states, respectively. It can then be shown²⁹ that the probability density of finding a nearest-neighbor bubble at a distance R from the electron bubble is

$$p(R) = 4\pi R^2 \rho_h \exp\left[-\frac{4}{3}\pi(R^3 - c^3)\rho_h\right], \quad \begin{matrix} R \geq c \\ R < c \end{matrix} \quad (A9)$$

where we have neglected the overlap of cavities, since this would result in the formation of a new bubble rather than aiding in charge transport.

Combining relevant equations as given above, the expression for mobility becomes

$$\mu = \frac{e\hbar k_e}{6mkTc} \exp\left[-\frac{\gamma v^*}{v_f} - \frac{\Delta g}{kT}\right] \times \int_c^\infty \exp\left[-\frac{4}{3}\pi\rho_h(R^3 - c^3)\right] T(R) 4\pi R^4 \rho_h dR. \quad (A10)$$

By making the substitution $u = \frac{4}{3}\pi\rho_h(R^3 - c^3)$, defining $\vartheta = \frac{4}{3}\pi c^3 \rho_h$, and evaluating the constants in Eq. (A10), we obtain

$$\mu = 4.2 \times \frac{10^6}{T} \exp\left[-\frac{\gamma v^*}{v_f} - \frac{\Delta g}{kT}\right] \times \int_0^\infty e^{-u} \left(\frac{u}{\vartheta} + 1\right)^{\frac{2}{3}} T\left[c\left(\frac{u}{\vartheta} + 1\right)^{\frac{1}{3}} - c\right] du, \quad (A11)$$

²⁹ S. A. Rice, Discussions Faraday Soc. **32**, 181 (1962).

where the units of μ are $\text{cm}^2 \text{statvolt}^{-1} \text{sec}^{-1}$. The integral in Eq. (A11) is a function of ϑ , κ , and c . We note that $\frac{4}{3}\pi(c/2)^3 \rho_h$ can be estimated as approximately equal to the quantity we defined as θ and, thus, we obtain $\vartheta = 8\theta$. Over the temperature range from 2.2 to 4.2°K and the pressure range from 1 to 30 atm, θ takes on values ranging from a maximum of about $\frac{1}{2}$ to a minimum of about $\frac{1}{10}$. In order to estimate the integral in Eq. (A11), numerical calculations were carried out for several values of θ , ranging from $\frac{1}{2}$ to $\frac{1}{10}$. We also varied κ over a wide range as follows: For simplicity we let $V_0 = E = n\hbar^2/2mc^2$, where n varied from 1 (just bound state) up to 100. This corresponds to κc varying from $\kappa c = 0$ to $\kappa c = 14\pi$. The integral varies rather slowly with both κ and ϑ (8θ) and ranges at most from about 0.7 to 0.2 for the above mentioned values of the parameters. Thus, to estimate the magnitude of μ as given by Eq. (A11), we do not have to be disturbed by lack of knowledge of κ .

Choosing Kuper's radius, $b = c/2 = 12 \times 10^{-8}$ cm, $\Delta g \propto 1/b$ as given by Atkins, $\gamma = \frac{1}{2}$, and Van der Waals' radius, $a = 1.3 \times 10^{-8}$ cm, we find $\mu \sim 10^{-61}$ at 1 atm and 4.2°K. In these cgs units, the experimental value for μ is about 6.0. The terms $e^{-\gamma v^*/v_f}$ and $e^{-\Delta g/kT}$ contribute about equally in the above calculation with $e^{-\gamma v^*/v_f} \sim 10^{-35}$ and $e^{-\Delta g/kT} \sim 10^{-32}$. Even if we assumed we had overestimated b by a factor of 2, that is, if $b = 6 \times 10^{-8}$ cm instead of 12×10^{-8} cm, we still get $\mu \sim 10^{-62}$, where the term $e^{-\Delta g/kT}$ now contributes 10^{-64} to μ while $e^{-\gamma v^*/v_f}$ contributes only $10^{-4.4}$. Thus, we conclude that it is virtually impossible for an electron to diffuse by tunneling: If the bubble were small enough for the probability of a suitable fluctuation to be of the appropriate order, the work of compression would be so large that $e^{-\Delta g/kT} \sim 0$, and to reduce the work of compression suitably the radius of the bubble would be so large that $e^{-\gamma v^*/v_f} \sim 0$.