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Ions in Liquid Helium*

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The mobility of an ion in liquid He⁴ is known to be appreciably less than the mobility of a He³ atom and varies in a different way with temperature. It is suggested that the essential difference is that electrostriction effects increase the liquid density over a large region surrounding the ion, so that the ion drags around with it about 50 He⁴ atoms. The density field of the positive ion is calculated in a semiclassical approximation. A possible difference between the density fields for positive and negative ions is briefly discussed. Various experimental ways of checking this picture of an ion are suggested.

I. INTRODUCTION

THE mobility of ions in liquid He⁴ has been measured by Williams,¹ by Careri, Reuss, Scaramuzzi, and Thomson,² and by Meyer and Reif.³ For field strengths less than 200 volt cm⁻¹ the mobility is field independent.³ Below the λ point it varies approximately as $1/\rho_n$, suggesting that it is due primarily to collisions of the ion with rotons. Above the λ point it is approximately inversely proportional to the viscosity of the liquid. The mobility of the positive ion is about 50% larger than that of the negative ion, the exact ratio varying somewhat with temperature. At higher field strengths^{1,2} the mobility varies approximately as E^{-1} .

Assuming that the ions obey classical Boltzmann statistics their diffusion coefficient D can be deduced from their mobility μ by the Nerst-Einstein relation,

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

In this way the diffusion coefficient of the positive ion at 1.2°K is found to be 1.5×10^{-4} cm² sec⁻¹, which should be compared with a value of about 2×10^{-2} cm² sec⁻¹ for the diffusion coefficient of He³ in dilute He³-He⁴

mixtures.⁴ One might expect an ion and a He³ atom in solution to be very similar entities. The fact that the diffusion coefficient of the ion is many times smaller suggests that there may be a fundamental difference. The purpose of this article is to suggest that there is a large region surrounding the ion in which the density of the liquid is appreciably increased and it is this density field which determines the mobility. One consequence of this picture is that the ion drags around with it a large number of He⁴ atoms and therefore has a very large effective mass.

II. ELECTROSTRICTION

When a polarizable fluid is distributed throughout a nonuniform electric field, its pressure and density increase with increasing field. An ion in liquid helium produces a very strong field in its vicinity and one might anticipate that the mean density of the surrounding liquid steadily increases as the ion is approached. Treating the liquid as a classical continuum, we shall estimate the magnitude of this electrostriction effect and show that it is probably very important. Since the

⁴ Beenakker, Taconis, Lynton, Dokoupil, and van Soest, *Physica* **18**, 433 (1952); see also J. J. M. Beenakker and K. W. Taconis, *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1955), Vol. 2, Chap. VI. R. L. Garwin and H. A. Reich [*Phys. Rev.* **115**, 1478 (1959)], using a spin echo technique, have obtained diffusion coefficients much smaller than those of Beenakker *et al.*, but still several times larger than for an ion. It is not yet clear whether this is because Garwin and Reich were using much more concentrated solutions and were working at higher pressures.

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

² Careri, Reuss, Scaramuzzi, and Thomson, *Low-Temperature Physics and Chemistry*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958), p. 155; *Nuovo cimento* **13**, 186 (1959).

³ L. Meyer and F. Reif, *Phys. Rev.* **110**, 279 (1958).

He⁴ atom is nonpolar, very stable, spherically symmetrical and has a low electric polarizability, and since the atoms are well separated in the liquid so that their wave functions overlap very little, the classical approximation may not be too bad, except perhaps within a distance of a few angstrom units in the immediate vicinity of the ion. We shall see that the effects are large even if the immediate vicinity of the ion is ignored.

The dielectric constant, ϵ , of the liquid is given by the Clausius-Mosotti formula⁵

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \frac{\rho}{M} N\alpha_0. \quad (2)$$

ρ is the liquid density, M the molecular weight, N Avogadro's number, and α_0 the molecular polarizability. ϵ is only slightly larger than 1 and no appreciable error is introduced if the equation is simplified to

$$\epsilon = 1 + (4\pi\rho/M)N\alpha_0. \quad (3)$$

The polarization per mole in an electric field \mathbf{E} is

$$\mathbf{P} = N\alpha_0\mathbf{E}. \quad (4)$$

The molar polarizability, $N\alpha_0 = 0.1245$, will be assumed to be independent of density.⁶ This is true if the distortion of the atomic wave function produced by the electric field is independent of the distortion produced by interaction with neighboring atoms. It is known that the molar polarizability changes very little between gaseous densities and the density of the liquid at the saturated vapor pressure, but this may no longer be so at the density of closest packing, which may possibly be approached very close to the ion.

The partial potential of the liquid at a point where the electric field is E is

$$\mu = U - TS + pV - EP. \quad (5)$$

The first and second laws of thermodynamics give the equation

$$TdS = dU + p dV - EdP. \quad (6)$$

Differentiating Eq. (5) and making use of Eq. (6)

$$d\mu = -SdT + Vdp - PdE. \quad (7)$$

When the liquid is in equilibrium in a nonuniform field, the partial potential must be the same everywhere ($d\mu = 0$) and, if there are no temperature gradients ($dT = 0$),

$$Vdp = PdE. \quad (8)$$

If the pressure is p_0 at the point where $E = 0$,

$$\int_{p_0}^p Vdp = \int_0^E PdE. \quad (9)$$

Substituting the value of P from Eq. (4),

$$\int_{p_0}^p Vdp = \frac{1}{2} N\alpha_0 e^2. \quad (10)$$

At a distance r from a singly charged ion,

$$E = e/er^2, \quad (11)$$

where the dielectric constant ϵ is obtained by substituting the local value of the density in Eq. (3). Finally, then

$$\int_{p_0}^p Vdp = \frac{1}{2} N\alpha_0 e^2 / r^4 \left(1 + \frac{4\pi\rho}{M} N\alpha_0 \right). \quad (12)$$

$E = 0$ when $r = \infty$ and p_0 is therefore the external pressure on the liquid. Given the equation of state ($V = M/\rho$ as a function of p at constant T), Eq. (12) allows p and ρ to be calculated as a function of r .

For sufficiently large values of r , p is only slightly larger than p_0 and the integral may be written approximately as $V_0(p - p_0)$. Also

$$(p - p_0) = u_1^2(\rho - \rho_0)/\gamma, \quad (13)$$

where u_1 is the velocity of first sound and γ the ratio of specific heats. Hence,

$$\begin{aligned} \rho - \rho_0 &= \frac{\gamma N\alpha_0 e^2}{2V_0 u_1^2 \epsilon_0^2 r^4} \\ &\propto 1/r^4. \end{aligned} \quad (14)$$

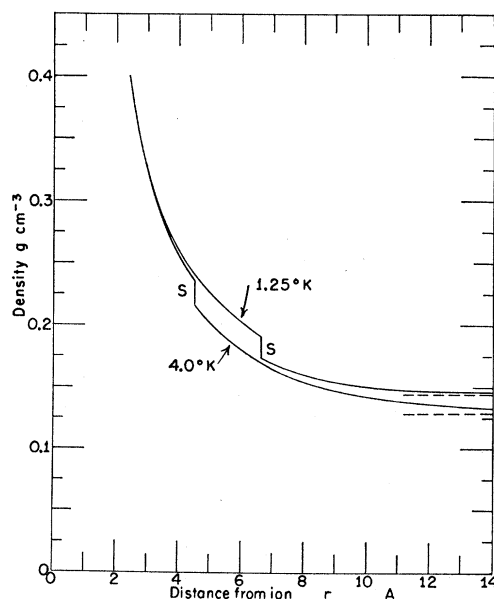


Fig. 1. Variation in density of liquid near a localized point charge. These curves are based on a classical calculation for a continuum and the surface energy at the solid-liquid boundary has been ignored.

⁵ H. Frohlich, *Theory of Dielectrics* (Oxford University Press, New York, 1949), p. 169.

⁶ M. H. Edwards, *Can. J. Phys.* 34, 898 (1956).

The extra mass associated with the presence of the ion is

$$M_e = \int_0^{\infty} 4\pi r^2 (\rho - \rho_0) dr. \quad (15)$$

The extra mass outside a sphere of radius r_c large enough that Eq. (14) applies is

$$M_e' = \frac{2\pi\gamma N\alpha_0 e^2}{V_0 u_1^2 \epsilon_0^2 r_c}. \quad (16)$$

The external pressure p_0 was first taken to be equal to the saturated vapor pressure. The pressure in the vicinity of the ion was calculated from Eq. (12), using the equation of state of Keesom and Keesom.⁷ At a distance of 2 or 3 Å from the ion the pressure was found to rise to the order of magnitude of 1000 atmospheres, which is greatly in excess of the melting pressure, and so it was necessary to assume that the helium was solid in the immediate vicinity of the ion. The melting pressure data were taken from Swenson⁸ and the equation of state of the solid from Dugdale and Simon.⁹ Once the pressure was known as a function of r , the equation of state could be used to determine the density, giving curves such as those shown in Fig. 1.

The point S on each curve represents the boundary of a solid sphere surrounding the ion. However, we have ignored the fact that the melting pressure of a small solid sphere is greater than for bulk solid because of surface tension effects. If $p_m(r)$ is the pressure in the liquid just outside a solid sphere of radius r and σ_{sl} is the surface tension between solid and liquid, then the pressure just inside the sphere is $p_m(r) + 2\sigma_{sl}/r$. A simple thermodynamic argument shows that

$$p_m(r) - p_m(\infty) \simeq \frac{V_s}{V_l - V_s} \frac{2\sigma_{sl}}{r}, \quad (17)$$

where V_s and V_l are the molar volumes of solid and liquid at the melting pressure. The effect of surface tension is to reduce the radius of the solid sphere, but its importance cannot be estimated until the value of σ_{sl} is known. In any case the dimensions are so small that any theory based on the properties of bulk liquid and solid is likely to break down, and it is quite uncertain whether any solid-like structure is formed, although there is obviously good reason to believe that the density is very high within a few angstroms of the ion.

Disregarding these subtleties, curves such as those of Fig. 1 can be used to calculate the extra mass of liquid associated with the ion. Equation (15) must be used for $r < 10$ Å but the simplified form of Eq. (16) can

be used for larger radii (about half the extra mass is outside a radius of 10 Å). The total extra mass is shown as a function of temperature in Fig. 2. The outstanding feature, of course, is that, if this analysis is true, the ion drags around with it about 40 He⁴ atoms. Since density changes can be propagated with the velocity of sound, the extra mass will in fact remain attached to the ion as long as the velocity of the ion does not exceed the velocity of sound. We must not assume, however, that this total extra mass M_e is identical with the "effective mass" M_i of the ion in transport phenomena, although there is every reason to believe that they have the same order of magnitude. It is possible, though, that several atoms in the immediate vicinity of the ion are so tightly held that we must count the total density there, rather than the extra density. This would certainly be true if the ion were surrounded by a small solid sphere.

An interesting possibility suggested by these ideas is that, when the external pressure is just below the melting pressure, the ion might become the center of quite a large solid sphere. For example, the work of Swenson⁸ suggests that it might be possible to maintain the pressure steady at a value only 0.01 atmosphere below the melting pressure. At 1.25°K the pressure would increase to the melting pressure at a distance of about 50 Å from the ion and the resulting solid sphere would contain about 10⁴ He⁴ atoms. However, a surface tension of 0.1 erg cm⁻² would reduce the radius of the sphere to about 6.5 Å, and so a final decision on this point must await an estimate of the magnitude of the surface tension.

III. CORE OF THE DENSITY HUMP

The above classical treatment applies to a localized point charge. The actual ion, whatever its nature, must be described by a wave function extending over a finite region of space. If the average velocity of the ion inside this region were appreciably greater than u_1 , the velocity

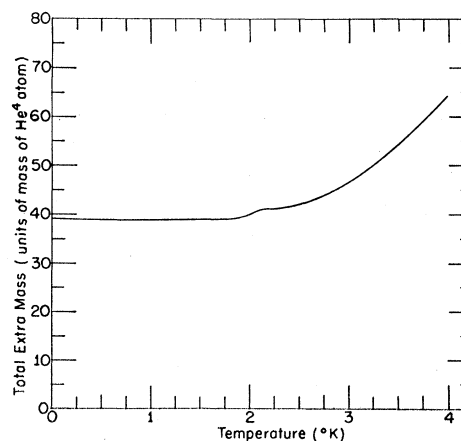


FIG. 2. The total extra mass associated with an ion as a function of temperature. This curve is based on the classical continuum approach.

⁷ W. H. Keesom, *Helium* (Elsevier Publishing Company, Amsterdam, 1942), p. 237.

⁸ C. A. Swenson, *Phys. Rev.* **79**, 626 (1950).

⁹ J. S. Dugdale and F. E. Simon, *Proc. Roy. Soc. (London)* **A218**, 291 (1953).

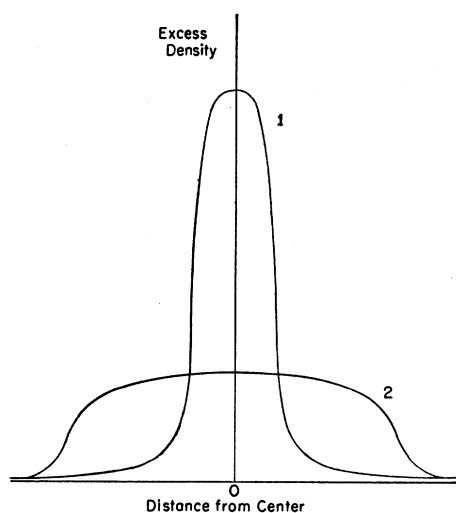


FIG. 3. Schematic representation of the liquid density in the vicinity of an ion. Curve 1: all ions heavier than helium, positive helium ion. Curve 2: almost free electrons. In both cases it has been assumed that the ion complex moves through the liquid with a velocity less than that of sound.

of sound in the liquid, the electrostriction effects in the surrounding liquid would not be able to follow the motion of the ion, which would therefore be more nearly equivalent to a charge distribution of finite diameter. Outside the effective diameter of this cloud of charge, the electric field would be almost the same as for a point charge and the electrostriction effects would be unaltered. Inside the cloud, however, the electric field would be reduced and the electrostriction effects would be smaller. We must therefore consider this point carefully.

The velocity of sound u_1 and the zero-point velocity of a He^4 atom in the liquid both have an order of magnitude $\hbar/m_4\delta$, where m_4 is the mass of the atom and δ is the average interatomic distance. This is a simple consequence of the fact that the gradient of the wave function is of order $1/\delta$; it must change from zero to a maximum and back to zero again as an atom is moved through a distance of the order of δ .¹⁰ A similar argument applies to an ion of a foreign atom. If this ion is heavier than a He^4 atom, its zero-point velocity can exceed the velocity of sound only if it is trapped within a cell of dimensions less than δ . Our previous approximation of a localized point charge is then adequate. Of course the ion can drift through the liquid with a thermal velocity $v_i = (3kT/M_i)^{1/2}$, but since its effective mass M_i must be greater than m_4 , v_i is always appreciably less than u_1 .

If the positive monatomic helium ion, He^+ , can exist in the liquid, the following interesting possibility arises. The above argument can be applied to the motion of the He^+ nucleus, but there is the additional possibility

that the positive hole might jump to one of the neighboring neutral He atoms. This would occur after an average time interval $\tau \sim \hbar/2z\Delta E$, where z is the number of neighboring atoms (the equivalent of a coordination number) and ΔE is the energy separation between the nuclear-symmetric and nuclear-antisymmetric wave functions for a He^+ ion at the appropriate distance from a neutral He atom. Taking $z \sim 5$ and $\Delta E \sim 0.1$ eV,¹¹ we obtain $\tau \sim 3 \times 10^{-15}$ sec and the "velocity" for a single jump $\delta/\tau \sim 10^7 \gg u_1$. The subsequent motion is a random walk and the distance travelled after n jumps is on the average $n^{1/2}\delta$. The effective velocity is therefore $n^{1/2}\delta/n\tau = \delta/n^{1/2}\tau$. When this velocity falls to a value comparable with u_1 , the electrostriction effects can begin to follow the motion. This happens when

$$\begin{aligned} n &\sim (\delta/u_1\tau)^2 \\ &\sim 10^5. \end{aligned} \quad (18)$$

The effective radius of the charge cloud would then be

$$\begin{aligned} R &\sim n^{1/2}\delta \\ &\sim \delta^2/u_1\tau \\ &\sim 300\delta \\ &\sim 10^{-5} \text{ cm}. \end{aligned} \quad (19)$$

Distribution of the charge over such a large volume would almost completely obliterate the electrostriction effects.

However, it is unlikely that the positive ion is monatomic. The He_2^+ molecule ion is known to have a dissociation energy of 2.5 eV,¹¹ which is very large compared with all the other forms of energy involved in the problem. Moreover, He_2^+ ions are more numerous than He^+ ions in the gas at high pressures.¹² It therefore seems probable that the positive ion is He_n^+ where n is a small integer. It is probably a compact unit; the internuclear distance in He_2^+ is 1.1 Å, as compared with $\delta = 3.6$ Å for the liquid. We have already seen that such a massive entity is highly localized from our point of view. Moreover, rapid jumping of the hole is no longer possible since it would involve rearrangement of the massive nuclei and this obviously cannot occur with a velocity greater than the zero-point velocity of the He atoms. We conclude that the electrostriction theory given in the previous section may be a reasonable approximation for the positive ion.

The negative monatomic helium ion, He^- , is probably unstable.¹³ The neutral diatomic molecule, He_2 , is on the verge of stability. The He_2^- ion, if formed, must be very loosely bound. It is possible that a small compact polyatomic ion He_n^- is the stable form in the liquid, and if this is so the electrostriction theory is valid as in the case of the positive ion. It is then difficult to

¹⁰ R. P. Feynman, *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1955), Vol. I, Chap. II.

¹¹ L. Pauling, *J. Chem. Phys.* **1**, 56 (1933).

¹² A. V. Phelps and S. C. Brown, *Phys. Rev.* **86**, 102 (1952).

¹³ Ta-You Wu, *Phil. Mag.* **22**, 837 (1936); E. Haloien and J. Midtal, *Proc. Phys. Soc. (London)* **A68**, 815 (1955).

understand the difference in mobility between positive and negative ions. However, another possibility is that the electron moves almost freely in the regions between the widely spaced atoms. This presents a difficult many-body problem, but is probably within the capabilities of current techniques. A rough analysis,¹⁴ in which the electron is treated as though it were at the bottom of the conduction band in an insulator, suggests a density distribution in the liquid of the type shown in Fig. 3, corresponding to an electron wave function spreading over a region containing many He⁴ atoms. It is hoped that a more rigorous analysis will be published later. The effective mass of the negative ion may be even greater than that of the positive ion, but in any case the density field appears to be different.

Once the density field is known, the mobility well below the λ point can be calculated by considering the scattering of rotons in this density field. The interaction is a consequence of the fact that the roton parameters Δ , p_0 , and μ vary with density. Such calculations are proceeding.

IV. FURTHER DISCUSSION

Assuming the ions to be almost independent systems and their number density to be small enough so that there is no doubt that they obey classical statistics, they can be treated like an ideal gas and shown to drift through the liquid with a mean thermal velocity

$$v_t = (3kT/M_i)^{1/2}, \quad (20)$$

where M_i is the effective mass including the mass of the He⁴ atoms dragged along with the ion. At 1.5°K, if M_i is about 40 times the mass of a He⁴ atom (Fig. 2) then $v_t \sim 1.5 \times 10^3$ cm sec⁻¹. This is much less than the velocity of sound, $u_1 \sim 2.4 \times 10^4$ cm sec⁻¹.

In the presence of an electric field there is a uniform drift velocity $v_d = \mu E$ superimposed on these random thermal velocities. As long as $v_d \ll v_t$ the mobility is given by

$$\mu = el/M_i v_t, \quad (21)$$

where l is a mean free path, and μ is therefore field independent. However, when $v_d \gg v_t$, then

$$v_d = (2elE/M_i)^{1/2}, \quad (22)$$

and the mobility should vary as $E^{-1/2}$. In the experiments of Meyer and Reif,³ in which the mobility was field independent, the drift velocity never exceeded 100 cm sec⁻¹ at 1.5°K. In the experiments of Williams¹ the

drift velocity was always greater than 10^3 cm sec⁻¹ at 1.5°K and the mobility varied approximately as $E^{-1/2}$. This is consistent with the previously quoted value of 1.5×10^3 cm sec⁻¹ for v_t . Obviously a careful investigation of the field dependence of the mobility could be used to determine the effective mass.

One of the most direct methods of measuring the effective mass would be cyclotron resonance. In order that the relaxation time should be long enough, it is necessary to have $\mu H/c > 1$. With $H \sim 10^4$ oersteds this implies $\mu > 10^4$ cm² sec⁻¹ volt⁻¹ as compared with the largest measured value of 2 cm² sec⁻¹ volt⁻¹ at 1.2°K. This very high mobility might be attainable at a temperature of the order of 0.1°K if the dominant mechanism continues to be scattering by phonons and rotons. At sufficiently low temperatures the principal scatterers might be the He³ atoms which are always present in small amounts even in well helium, and it might be necessary to reduce the number of these. The resonant frequency would be in the vicinity of 100 kc/sec. Since the recombination rate of the ions is not known, it is difficult to estimate whether it would be possible to achieve a sufficiently high concentration of ions to give a detectable signal.

The ions form part of the normal component² and might therefore be investigated by the conventional methods which give information about the normal component. Near 0°K the normal component would be composed almost entirely of ions and the velocity of second sound would be

$$u_2 = (5kT/3M_i)^{1/2}. \quad (23)$$

In the absence of ions, second sound pulses would be considerably elongated because of mean free path effects, but the introduction of the ions would sharpen up the pulses and considerably reduce the velocity. Such phenomena are observed when He³ atoms are introduced.¹⁵ At higher temperatures the density of the normal component would be mainly due to phonons and rotons, but their interaction with the ions might be strong enough to produce a detectable change in the viscosity of the normal component or the attenuation of first or second sound.

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¹⁴ K. R. Atkins, Office of Naval Research Technical Report No. 3, Contract N-onr 551 (28) (unpublished).

¹⁵ J. C. King and H. A. Fairbank, Phys. Rev. **93**, 21 (1954).