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Theory of Negative Ions in Liquid Helium*

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It is shown that Atkins' electrostriction model gives reasonable values for the mobility of positive ions in liquid helium. However, that model cannot account for the observed difference between positive- and negative-ion mobilities. Arguments are advanced in support of the "bubble" model; the negative ion is believed to be a free electron in a cavity of radius about 12 A. The bubble model leads to a mobility in fair agreement with experiment.

I. INTRODUCTION

THERE have been several experimental investigations recently into the behavior of ions in liquid helium.[1-3] At sufficiently low fields a field-independent mobility is observed, varying with temperature as $e^{\Delta/kT}$ over a temperature range from below 1° to 2°K. Here Δ is nearly Landau's[4] roton threshold energy, and the results have naturally been interpreted in terms of a roton-ion scattering mechanism.

Atkins[5] has given a "static" theory of the structure of an ion in the liquid, based on the idea that the ion polarizes its neighboring atoms, and that the resulting electrostatic interaction produces an electrostrictive increase in the local density. He finds a "solid" core of radius b_+,[6] surrounded by a density field ρ, with

$$\rho-\rho_0 \propto r^{-4}. \tag{1}$$

Since rotons are unable to propagate in the solid, the scattering of rotons by the core will be approximately "hard sphere" scattering. Landau and Khalatnikov[7] give the effective radius of a roton (from roton-roton scattering) as about 4 A, so that we expect the closest distance of approach l of a roton to an ion to be about 10.3 A. At such a large distance, the electrostriction will make only a small contribution to the scattering,[8] so that the scattering cross section should be πl^2.

The experiments do not measure cross sections directly, but mobilities, and in order to compare these with theoretically predicted cross sections, we need the effective mass of the ion complex. Atkins shows that the excess mass contained in the density field of the electrostriction model is about $40M$ (where M is the mass of a He atom). But the effective mass which is relevant to a mobility calculation has to be considerably larger than this. In the "solid" core, all matter, and not merely excess matter, has to move with the ion. Moreover there is a "hydrodynamic" mass, to take into account the kinetic energy of the liquid flowing around the solid core.[9] These two contributions together amount to

$$(1+\tfrac{1}{2})\tfrac{4}{3}\pi b_+^3\rho_0 M, \tag{2}$$

where b_+ is the solid core radius, and ρ_0 is the unperturbed number density, $=2.17\times10^{22}$ cm^{-3}. Hence the

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

[2] G. Careri, J. Reuss, F. Scaramuzzi, and J. O. Thomson, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958), p. 155; G. Careri, F. Scaramuzzi, and J. O. Thomson, Nuovo cimento **13**, 186 (1959); G. Careri, S. Cunsuolo, and F. Dupré, Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960 (to be published).

[3] L. Meyer and F. Reif, Phys. Rev. **110**, 279 (1958); Phys. Rev. Letters **5**, 1 (1960), Phys. Rev. **119**, 1164 (1960); Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960 (to be published).

[4] L. D. Landau, J. Phys. (U.S.S.R.) **5**, 71 (1941); **11**, 91 (1947).

[5] K. R. Atkins, Phys. Rev. **116**, 1339 (1959).

[6] Below the λ point, $b_+\sim 6.3$ A.

[7] L. D. Landau and I. M. Khalatnikov, Zhur. Eksp. i Teoret. Fiz. **19**, 637 (1949).

[8] See Sec. IV.

[9] E.g., H. Lamb, *Hydrodynamics*, (Cambridge University Press, New York, 1932), 6th ed., p. 124.

effective mass is

$$M_{\text{eff}}=M(40+2\pi b_+{}^3\rho_0)\simeq 100M. \tag{3}$$

With this effective mass, the experimental data[2] give a cross section $\sigma_+=0.57\times10^{-13}$ cm^2 for positive ions and $\sigma_-=0.93\times10^{-13}$ cm^2 for negative ions. Using Atkins' model, we should predict $\sigma=0.33\times10^{-13}$ cm^2, in fair agreement with the experimental values for positive ions.[10] However, Atkins' model cannot account for the difference between the behavior of positive and negative ions.

The suggestion has been made[11] that the negative ion consists of an electron in the center of a "bubble" in the liquid. The author will advance some theoretical considerations in support of this model, which will be shown to yield mobilities in fair accord with experiment.

II. CORRELATIONS PRODUCED BY THE SHORT-RANGE REPULSIONS

Neither He^- nor $He_2{}^-$ is a stable system,[5] and it seems rather implausible that any complex, $He_n{}^-$, is stable. It will, therefore, be assumed that the negative ion is a free electron whose interactions with the atoms of the liquid are primarily short-range repulsions. These will be approximated by a hard core of radius $a=1.3$ A. In addition, there will be an attractive interaction of longer range, arising from the electrostatic polarization of the atoms. The appropriate potential is

$$\begin{aligned} V_e&=-\alpha e^2r^{-4}, \quad r>a;\\ V_e&=0, \quad r<a, \end{aligned} \tag{4}$$

where α is the atomic polarizability; the molar polarizability, $N_0\alpha=0.125$. If we approximate to the effect of the hard core by a pseudopotential,[12,13]

$$V_{\text{core}}=2\pi\hbar^2am^{-1}\delta(r), \tag{5}$$

then we see that all Fourier components satisfy $V_{\text{core}}(k)\gg V_e(k)$. Thus for s-wave scattering the attractive forces may be neglected; in the first instance, they will be neglected entirely.

In order to see how the positions of atoms in the liquid are correlated with the electron position, let us localize the electron within a sphere of radius b_-. The electronic wave function is then $\psi_e\sim b_-{}^{-\frac{3}{2}}$ inside the sphere and very small outside it. If now an atom is within the sphere, the wave function has in addition to vanish at the surface of the atomic core. This condition requires an energy $E_{\text{intrusion}}$:

$$E_{\text{intrusion}}\simeq\int\psi_e{}^*V_{\text{core}}\psi_e d^3x\simeq 2\pi\hbar^2a/mb_-{}^3. \tag{6}$$

This energy is very large compared with the zero-point kinetic energy E of a helium atom in the liquid, if b_- is of the same order as the normal interatomic spacing. Even if b_- is as large as 15 A, $E_{\text{intrusion}}$ is still 3×10^{-14} erg, while the zero-point kinetic energy $E_0\simeq40$ cal/mole $\simeq3\times10^{-15}$ erg/atom.[14] Hence, the electron wavepacket represents a potential barrier, nearly impenetrable to atoms of the liquid.

III. THE BUBBLE MODEL

In view of the considerations of Sec. II, it is clear that there will be an optimum degree of localization of the electron. If b_- is too small, then the electronic kinetic energy will be very large, while if b_- is too large (subject still to the condition that it is small enough to have $E_{\text{intrusion}}\gg E_0$), then the work done, against the zero-point pressure, in removing all the atoms from the localization region, becomes large. Provided that the equilibrium radius of the electron wave packet turns out to be less than $\sim$15 A, this "bubble" model should be a good approximation. *Outside* the bubble, Atkins' electrostriction theory should apply, but because the bubble will turn out to be quite large, the electrostrictive effects will be relatively unimportant.

The size of the bubble is now to be determined, by minimizing the total energy, or, equivalently, by requiring that the pressure exerted outward by the electron on the liquid be equal to the inward pressure exerted by the atoms on the electron. If the van der Waals' attractions were of sufficiently long range compared to the bubble size, then the pressure exerted by the atoms on the bubble would be their kinetic energy per unit volume, $E_0\rho_0=6\times10^7$ d cm^{-2}=60 atm. In the actual situation, this condition is rather far from the truth, and a calculation of the van der Waals' pressure is necessary. The result (see Appendix) is

$$p_{\text{vdW}}=-38(1-c^2/b_-{}^2), \tag{7}$$

where p_{vdW} is in atmospheres, and $c=3.6$ A is the mean interatomic distance (i.e., $\rho_0{}^{-1}=\frac{4}{3}\pi c^3$). There is also a small pressure term arising from the electrostatic attraction between the electron and the polarized atoms,

$$p_{es}=\rho_e{}^2\alpha/2b_-{}^4=5.2\times10^4 \text{ atm A}^4/b_-{}^4. \tag{8}$$

The outward pressure exerted by the electron is the volume derivative of its kinetic energy. If, for definiteness, the electron wave function is taken

$$\psi\propto r^{-1}\sin(\pi r/b_-), \tag{9}$$

[10] J. de Boer and A. t'Hooft [Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto 1960 (to be published)], using a Born approximation and neglecting the effect of the central solid core, find 90×10^{-13} cm^2. However, the effective potential in their calculation has a range $\sim$5 A only, so that the large apparent cross section corresponds to the breakdown of the Born approximation. Near the center of the sphere of electrostriction, their effective potential becomes very large and cannot be treated perturbatively.

[11] R. P. Feynman (unpublished), reported by G. Careri, F. Scaramuzzi, and J. O. Thomson, footnote 2.

[12] J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley & Sons, New York, 1952), p. 76.

[13] Here m is the electronic mass (strictly, the *reduced* mass).

[14] L. Goldstein, Phys. Rev. **100**, 98 (1955); L. Goldstein and J. Reekie, *ibid.* **98**, 857 (1955).

then this kinetic energy is $\pi^2\hbar^2/2mb_-^2$, and the pressure the electron exerts is

$$p_{\rm kin}=\pi\hbar^2/4mb_-^5=7.9\times10^6 \text{ atm A}^5/b_-^5. \qquad (10)$$

The equilibrium condition is

$$E_0\rho_0+p_{\rm vdW}=p_{\rm kin}-p_{es}. \qquad (11)$$

The two sides of Eq. (11) have been plotted in Fig. 1, and the equilibrium radius is seen to be $b_-=12.1$ A.

The effective mass of the negative ion is the sum of its electrostriction mass and its hydrodynamic mass. Atkins[5] comments that half of the electrostriction mass of a point charge lies outside 10 A, so that outside $b_-=12.1$ A, the electrostrictive mass is about $17M$. The hydrodynamic mass is

$$M_{\rm hyd}=\tfrac{1}{2}\times\tfrac{4}{3}\pi b_-^3\rho_0\simeq 82M, \qquad (12)$$

and the total effective mass is

$$M_{\rm eff}=M_{es}+M_{\rm hyd}\simeq 100M, \qquad (13)$$

(fortuitously) very close to the effective mass of the positive ion [see Eq. (3)].

IV. THE SCATTERING AND MOBILITY OF IONS

Although the central core of a negative ion in liquid helium now looks very different from the central core of a positive ion, neither the effective mass nor the cross section will be drastically different. Both the solid sphere at the center of the positive ion and the bubble of the negative ion will behave primarily as rigid scattering centers. Also, in both cases the core is surrounded by Atkins' electrostrictive density field (1). The analysis of the present section will apply to both kinds of ions, provided b is interpreted as b_+ or b_- as required. In the first instance, only the "rigid sphere" scattering will be considered; it will then be shown that the electrostriction effects make only a small correction.

The expressions for the scattering cross section of a rigid sphere are simple in the limiting cases of low and high energy.[15] If $\hbar k$ is the incident momentum and the radius of the sphere is l, then the "low-energy" region is defined by the condition $kl<1$. In the "high-energy" region, defined by $kl\gg1$, the cross section is twice geometrical, $\sigma=2\pi l^2$. However, half of the scattering is *forward* scattering[15] while the remainder is approximately isotropic. The forward scattering will play no role in a gas-kinetic calculation of the mobility, so that the cross section which we should use is just the classical one,

$$\sigma=\pi l^2. \qquad (14)$$

For a thermal roton, k will always be close to the minimum in the excitation spectrum, $k_0=2$ A^{-1}. To determine $l=b+b_0$, use is made of Landau and Khalatnikov's[7] estimate of the roton radius $b_0=4$ A, as indicated in Sec. I. We see that $kl_+\simeq20$, $kl_-\simeq30$, so that all roton-ion collisions are "high energy." In Table I, the cross sections, calculated from (14), are compared with values calculated by Careri *et al.*[16] from the experimental data, assuming $M_{\rm eff}=100M$.

TABLE I. Comparison of theoretical values of the roton cross section, calculated from Eq. (14), with experimental values of Careri *et al.*[a]

	Roton cross section (cm²) Theoretical	Experimental
Positive ion	0.33×10^{-13}	0.57×10^{-13}
Negative ion	0.82×10^{-13}	0.93×10^{-13}

[a] See the work cited in footnote 16.

In order to estimate the importance of the electrostrictive region on the cross section, use will be made of Langevin's theory of the mobility of ions in a polarizable gas.[17] The interaction potential between an ion and a roton, outside the central core region, may be taken

$$V=\left(\frac{\partial\Delta}{\partial\rho}\right)_{\rho_0}\delta\rho=\frac{\rho_0}{\Delta}\left(\frac{\partial\Delta}{\partial\rho}\right)_{\rho_0}\Delta\frac{\delta\rho}{\rho_0}=-\tfrac{1}{3}\Delta\frac{\delta\rho}{\rho_0} \qquad (15)$$

[see de Boer and t'Hooft[10]; the term in $(\delta\rho/\rho)^2$ will not be required, since outside the core $\delta\rho/\rho\ll1$]. In view of (1), this represents an attractive force varying as r^{-5}, so that the situation is completely analogous to the one discussed by Langevin. If we write p for the "roton pressure" and, from (1) and (15),

$$V=-\gamma r^{-4}, \qquad (16)$$

and define

$$\lambda^2=4pl^4/N_0\gamma=(8/3)kTl^4/\gamma=\frac{2kT}{\Delta}\frac{\rho_0}{\delta\rho(l)}, \qquad (17)$$

then the parameter λ, representing the relative importance of the core and the outer region, has the same significance as Langevin's λ. The cross section is then

$$\sigma=\pi l^2[3/4\lambda A(\lambda)], \qquad (18)$$

where $A(\lambda)$ has been tabulated[17]; for large λ, $3/4\lambda A(\lambda)=1+0.21\lambda^{-2}$. To get a numerical estimate, we note that $\delta\rho/\rho_0=0.14$ at the solidification pressure, i.e., at $r=b_+=6.3$ A.

TABLE II. Correction factor $3/4\lambda A$ in Eq. (18).

Temperature	2°K	1.5°K	1°K
λ_+	23	17	12
$(3/4\lambda A)_+$	1.009	1.012	1.017
λ_-	120	90	60
$(3/4\lambda A)_-$	1.002	1.002	1.003

[15] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, New York, 1949), p. 38.

[16] G. Careri, F. Scaramuzzi, and J. O. Thomson, reference 2.

[17] P. Langevin, Ann. chim. et phys., Ser. 8, 5, 245 (1905); H. R. Hassé, Phil. Mag. 1, 139 (1926).

TABLE III. Comparison of geometrical and experimental ratios of the cross section for ion-He^3 scattering to that for ion-roton scattering.

	(He^3 cross section)/(roton cross section) Geometrical	Experimental
Positive ion	0.55	0.09
Negative ion	0.68	0.30

Table II shows the small corrections produced by the factor $3/4\lambda A$ in (18).

V. DISCUSSION

It has been suggested[18] that the negative ions present in liquid helium are really impurity ions (e.g., O^-). This hypothesis will not explain the difference between the positive- and negative-ion mobility, since the Atkins model should apply to a heavy impurity. The contribution of the ion itself to the effective mass of the complex is quite small. On the other hand, the bubble model explains the difference in a natural way.

The present model could, of course, be improved. The assumption that the bubble is "rigid" is not essential. In a more complete theory it will be capable of oscillation, and there will be resonance contributions to the cross section. The frequency for radial pulsations, for example, will be of the order of 10^{12} cps so that resonances may well be important both for roton and particularly for phonon scattering. Reif and Meyer[3] find that the phonon cross section of a negative ion is about five times greater than that of a positive ion.

An important discrepancy between theory and experiment which still remains is the ion-He^3 atom scattering. Reif and Meyer[3] have observed the mobility at temperatures below 1°K, where roton scattering is frozen out. They varied the amount of He^3 present as an impurity in He^4 and were able to find the ion-He^3 cross sections. The "geometrical" cross sections will differ from those for the roton-ion systems only in the substitution of the He^3 radius, say 1.3 A, for the roton radius of 4 A. The geometrical cross sections are too large by up to a factor 6 (see Table III). However, the situation is rather more complicated; the scattering of He^3 atoms is not "high-energy" scattering in the sense of Sec. IV. At first sight, this will make matters even worse, since for a rigid sphere the low-energy cross section is $4\pi l^2$. But at temperatures $\sim\frac{1}{2}$°K, $kl\sim 1$ for thermal He^3 atoms; it is, therefore, possible for the s-wave phase shift to come close to π. The s-wave partial cross section will then be anomalously small (Ramsauer effect). Provided that the attractive forces can keep the phase shifts for higher partial waves small, this gives a possible explanation for the small He^3-ion cross section.

ACKNOWLEDGMENTS

I wish to thank Professors L. Meyer, J. R. Schrieffer, and G. D. Whitfield for valuable discussions.

[18] D. W. Swan, Proc. Phys. Soc. (London) **76**, 36 (1960).

APPENDIX

The van der Waals' Pressure at the Surface of a Negative Ion

It will be assumed that outside the "bubble" the radial distribution function $g(|\mathbf{r}_i-\mathbf{r}_j|)$ is unaffected by the presence of the bubble. Then, if $V(|\mathbf{r}_i-\mathbf{r}_j|)=-\beta/|\mathbf{r}_i-\mathbf{r}_j|^6$ is the two-particle van der Waals' potential, the potential of an atom at a point $\mathbf{r}$ in the liquid is

$$W(\mathbf{r})=\int g(|\mathbf{r}-\mathbf{r}_i|)V(|\mathbf{r}-\mathbf{r}_i|)d^3r_i, \tag{19}$$

where the integral is to be taken over the whole liquid, *except* the region inside the bubble. It is convenient to make the following approximation for $g(r)$:

$$g(r)=0,\quad r<c$$
$$=\rho_0,\quad r>c. \tag{20}$$

Then (see Fig. 2),

$$W(r)-W_0=4\pi\int_{\mathrm{Max}[c,\,r_1-b]}^{r_1+b}\frac{\beta}{r^6}r^2dr\int_{\xi(r)}^{1}d\cos\theta, \tag{21}$$

where $\xi(r)$, the lower limit on the angular integration, is given by

$$\xi=(-b^2+r_1^2+r^2)/2r_1r, \tag{22}$$

and W_0 is the mean van der Waals' potential in bulk liquid. The potential near the surface of the bubble will be obtained by setting $r_1-b=\delta\ll b$. Evaluation of the integral in this limiting case gives

$$W=4\pi\beta\rho_0\left(\frac{1}{3c^3}-\frac{1}{4c^2b}-\frac{1}{4}\frac{\delta}{c^4}(1-c^2/b^2)\right), \tag{23}$$

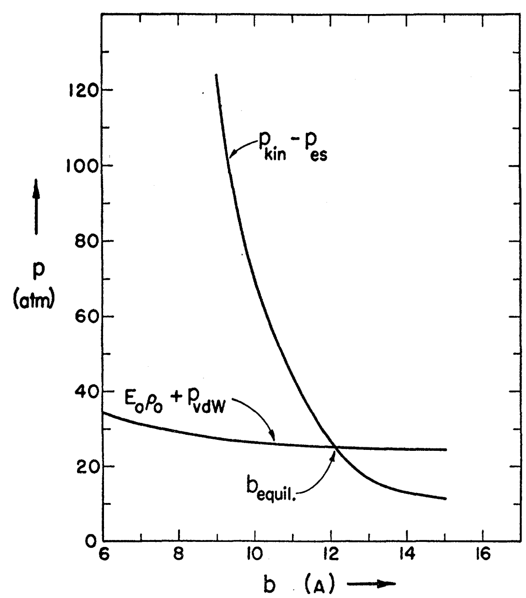

FIG. 1. Graphical solution of Eq. (11).

(neglecting powers of c/b higher than the second). The force exerted on an atom at the surface is obtained by differentiating with respect to δ and setting $\delta=0$; finally the van der Waals' pressure is

$$p_{\mathrm{vdW}}=-\left(\frac{3}{4\pi}\right)^{\frac{1}{3}}\rho_0^{\frac{2}{3}}\pi\beta\rho_0 c^{-4}(1-c^2/b^2)$$
$$=-38(1-c^2/b^2)\text{ atm.} \qquad (7)$$

To test the reasonableness of the approximation (20), we may note that, for a plane surface ($b=\infty$), the potential *at* the surface is $\frac{1}{2}W_0$, and that $|W_0|-E_0$ should be the latent heat per atom, $\sim\frac{1}{4}E_0$. Inserting numerical values in (23) gives $|W_0|-E_0\sim\frac{1}{6}E_0$.

Notes added in proof. (1) Experiments by Meyer and Reif (to be published) show that under pressure the roton-negative ion cross section decreases, until at a pressure of about 7 atm, the negative and positive ion cross sections become equal. This phenomenon provides striking confirmation of the bubble model below 7 atm.

(2) The considerations advanced in this paper should apply equally in pure He^3. At moderate temperatures (e.g., above 1°K), the bubble (or Atkins sphere) should obey Stokes' Law. The mobility should then be

$$\mu=e/6\pi\eta b,$$

where η is the viscosity at the same temperature.

(3) Reif (private communication) has criticized the values of the "experimental" cross sections, since, in their derivation from the measured mobilities, the "persistence of velocity" in a collision was neglected. The corrections to the roton-ion cross sections are slight, in view of the high intrinsic momentum of a roton, so that the agreement in Table I is not impaired. However, for the ion-He^3 cross section, when the persistence of velocity is taken into account, Meyer and Reif find the much augmented values $\sigma=\pi s^2$, where $S_-=26$ A and $S_+=10$ A. These are in reasonable agreement with the theoretical values $\sigma=4\pi l^2$, with $l=13.4$ A and $l_+=7.6$ A.

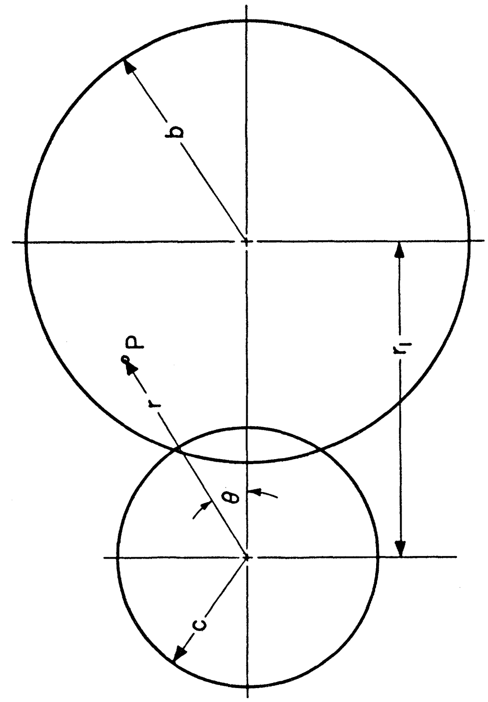

FIG. 2. The domain of integration of Eq. (21) is over the sphere of radius b, except for its overlap with the sphere of radius c.