Mobility of positive ions in He^3-He^4 solutions

V. N. Bondarev and I. Z. Fisher

Odessa State University

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The mobility of positive ions in a dilute solution of He^3 in liquid He^4 at low temperatures and in weak external fields is calculated. A nonlinear dependence of the ion velocity on field strength, which is due to interaction between the He^3 atoms and superfluid flow in which the impurity moves, is obtained. The results of the calculations are compared with the experimental data.

1. INTRODUCTION

At low temperatures ($T \lesssim 0.3°K$) the mobility of ions in dilute He^3—He^4 solutions is governed primarily by the collisions with the impurity atoms. The experimentally determined mobility of negative ions decreases weakly with increasing field and is approximately equal to the mobility calculated using a simple model of collisions between impurities and hard spheres of suitable dimensions and mass. In the case of positive ions, the velocity rises nonlinearly with the applied field even in the weak-field range. In stronger fields this ion velocity rises more slowly, passes through a peak and begins to fall. In this case, the model of collisions with hard spheres is completely unsuitable. The experimental results are reported in[1-4]. A detailed discussion of the observations is given in[1,2].

From the point of view of the collision dynamics the most interesting observation is the "anomalous" (in respect of the sign) nonlinear variation of the mobility of positive ions in weak external fields. It is suggested in[2] that this is due to an effect predicted by Reut and Fisher,[5] in which impurities are sucked into a region of higher superfluid velocities formed around an ion moving across a solution. We shall give an approximate calculation of the mobility of a positive ion in a dilute He^3—He^4 solution for low ion velocities, in accordance with the model suggested in[2]. We shall compare the calculations with the experimental results. We shall check the collision model suggested in[2] and the effect predicted in[5]. The concentration of the He^3 atoms will be assumed to be so small that the mobility of an ion is governed by a sum of independent collisions with separate He^3 atoms.

The interaction of an He^3 atom with a positive ion comprises three main contributions, which can be described approximately as follows.

1. The ion can be regarded as a hard sphere so there is a hard-core potential

$$V_0(r) = \begin{cases} +\infty, & \text{if } (r) < a, \\ 0, & \text{if } (r) > a, \end{cases} \tag{1}$$

where a is the sum of the radii of the ion and the He^3 atom, and r is the instantaneous distance between the centers of the two particles.

2. In the vicinity of the ion there are polarization forces which result in the repulsion of He^3 atoms and this repulsion is described by the potential[2,6]

$$V_1(r) = \frac{\alpha e^2}{2r^4}\left(\frac{v_3}{v_4} - 1\right) \equiv \frac{\varkappa}{2r^4}, \quad r > a, \tag{2}$$

where e is the electronic charge, α is the polarizability of the He atom, v_3 and v_4 are the average atomic volumes of He^3 and He^4 in solution ($v_3 > v_4$).

3. The motion of the spherical ion across a solution at rest gives rise to a flux of the liquid which flows around the ion. The square of the velocity of the superfluid component of this flux, deduced from the classical hydrodynamics of an ideal liquid, is

$$v_s^2(\mathbf{r}) = \frac{a^6 U^2}{4r^6}(1 + 3\cos^2\gamma), \quad r > a, \tag{3}$$

where U is the velocity of the ion, r is the distance measured from the instantaneous position of the center of the ion, γ is the angle between $\mathbf{r}$ and $\mathbf{U}$, and the difference between the ionic radius a_0 and the "radius" a in Eq. (1) is ignored. The presence of a field $v_s^2(\mathbf{r})$ gives rise to, in accordance with[5], an attraction between the impurity atoms in accordance with the law

$$V_2(\mathbf{r}) = -Bv_s^2(\mathbf{r}), \quad B > 0, \quad r > a. \tag{4}$$

According to the estimates given in[5], the coefficient B is

$$B = \frac{m_3}{2}\left[\frac{m_3^*}{m_4} + \rho_s \frac{\partial}{\partial c}\left(\frac{1}{\rho}\right)\right]. \tag{5}$$

Here, c is the concentration (by weight) of the impurity atoms, m_3 and m_3^* are the true and effective masses of an He^3 atom in solution, ρ and ρ_s are the total and superfluid densities. Equation (5) has been derived in the thermodynamic limit but we may assume that it is also approximately true in our case.

The total potential of the interaction between an atom of He^3 and a positive ion is the sum of the expressions (1), (2), and (4). All the estimates represented by Eqs. (1)—(4) are rigorously true only at large distances from the ion. At distances $r \approx a$ one should introduce various corrections, mainly because of changes in the field of ρ, ρ_s, and v_s under the influence of the polarization forces. Calculations of these corrections are given in[7]. However, at low ion velocities and low temperatures the main contribution to the ion mobility is made by long-range collisions with He^3 atoms and we can use the estimates given above. Moreover, the extreme idealization of the structure of the ion, implied in Eq. (1), is unnecessary.

All this also applies to negative ions in He^3—He^4 solutions. However, the true radii of these ions are large and, therefore, the contributions of $V_1(\mathbf{r})$ and $V_2(\mathbf{r})$ to the interaction are now only small corrections to the main interaction $V_0(\mathbf{r})$.

2. TRANSPORT COLLISION CROSS SECTION

The main task is to calculate the total transport cross section for the scattering of the He^3 atoms by a positive ion, considered as a function of the ion velocity and of the relative velocity of the colliding particles. We shall restrict ourselves to the approximate classical case when a rigorous allowance for the quasiclassical nature of the scattering in the range of velocities of interest to us is not satisfied very well. Nevertheless, it is shown in[2] that the classical calculations of the ion mobility without allowance for the interaction (4) give quite satisfactory results for the constant part of the mobility.

The absence of a spherical symmetry of the potential $V_2(\mathbf{r})$ given by Eq. (4) presents a considerable difficulty. We shall replace approximately the exact expression (4) by the average over the directions of the relative velocities of the particles before a collision. We can easily see that in the case of very high and very low ion velocities, compared with the average thermal velocity of the He^3 atoms, this is equivalent to the retention in Eq. (4) of the angular dependence of the potential. In the intermediate range of velocities we can use a smooth interpolation between these two extreme cases. In this way, we obtain

$$\tfrac{1}{2}(1+3\overline{\cos^2\gamma})=\varphi(y), \tag{6}$$

where

$$y=U\sqrt{\frac{m}{2k_BT}},\quad \varphi(y)=2-\frac{3}{2y^2}+\frac{3}{4y^3}\frac{1}{\sqrt{\pi}}\int_0^\infty\frac{dx}{x}\left[e^{-(x-y)^2}-e^{-(x+y)^2}\right], \tag{6'}$$

and m is the reduced mass of the ion-impurity system. If $\varphi \lesssim 1$, we obtain

$$\varphi(y)=1+\frac{2}{5}y^2-\frac{4}{35}y^4+\frac{8}{315}y^6-\frac{16}{3465}y^8+\ldots \tag{7}$$

and $\varphi(y) \to 2$ for $y \to \infty$. The total potential (1)—(4) together with Eq. (6) is

$$V_0(r)+\frac{\varkappa}{2r^4}-\frac{a^6BU^2}{2r^6}\varphi(y). \tag{8}$$

For large values of U the potential (8) ceases to be a monotonic function of r. The critical value of U when this happens is approximately 30 m/sec at $T \sim 0.3°K$. We shall assume that the ion velocity does not exceed this critical value.

The standard methods of the classical theory of scattering by a spherically symmetric potential[8] yield the following equation for the angle of scattering in the center-of-mass system, considered as a function of the impact parameter b:

$$\chi=\pi-2b\int_{r_0}^\infty\frac{dr}{r^2}\left[1-\frac{b^2}{r^2}-\frac{f^2}{r^4}+\frac{d^2}{r^6}\right]^{-1/2}, \tag{9}$$

where $r_0 = \max(a, r_m)$, r_m is the highest of the zeros of the radicand,

$$f^2=\frac{\varkappa}{mg^2},\quad d^2=\frac{a^6BU^2}{mg^2}\varphi(y). \tag{10}$$

m and g are the reduced mass and relative velocity of the ion-impurity system. In the $r_m > a$ case, the integral in Eq. (9) reduces to a complete elliptic integral of the first kind, so that we obtain

$$\chi=\pi-2\sqrt{\frac{1-\omega+\lambda}{1+\omega}}K\left(\sqrt{\frac{\lambda+\omega}{1+\omega}}\right). \tag{11}$$

The parameters λ and ω are restricted by the conditions

$$0\leqslant\lambda\leqslant1,\quad \lambda/(1+\lambda)\leqslant\omega\leqslant1+\lambda \tag{12}$$

and related to the smallest positive root of the equation

$$1-u_0^2-\frac{f^2}{b^4}u_0^4+\frac{d^2}{b^6}u_0^6=0 \tag{13}$$

by the expressions

$$\begin{aligned}\omega&=\tfrac{1}{2}\{\sqrt{(1-u_0^2)^2+4d^2u_0^6/b^6}+1-u_0^2\},\\ \lambda&=\tfrac{1}{2}\{\sqrt{(1-u_0^2)^2+4d^2u_0^6/b^6}-1+u_0^2\}.\end{aligned} \tag{14}$$

In the case $r_m < a$ [i.e., $au_0/b > 1$ in accordance with Eq. (13)], the lower limit in Eq. (9) is $r_0 = a$ and instead of Eq. (11) we obtain

$$\chi=\pi-2\sqrt{\frac{1+\lambda-\omega}{1+\omega}}F\left(\arcsin\sqrt{\frac{1+\omega}{(au_0/b)^2+\omega}},\sqrt{\frac{\lambda+\omega}{1+\omega}}\right), \tag{15}$$

where F(x, k) is an incomplete elliptic integral of the first kind. We shall be interested in the case of low drift velocities and, therefore, we shall use Eq. (11) in our calculations.

It is difficult to obtain the explicit form of the function $\chi(b)$ from the formulas given above. In the case of low ion velocities, the problem simplifies considerably if all the quantities are expanded as series in powers of d^2/f^3. In this way, instead of the two-parameter representation (11)—(14), we obtain the one-parameter expression

$$\begin{aligned}\chi=\pi&-2\sqrt{1-2k^2}K(k)+\frac{d^2}{f^3}\frac{\sqrt{1-2k^2}}{k\sqrt{1-k^2}}[(1-k^2)(2-k^2)K(k)\\ &-2(1-k^2+k^4)E(k)]-\frac{1}{4}\frac{d^4}{f^6}\frac{\sqrt{1-2k^2}}{k^2(1-k^2)}\Big[(16-48k^2+35k^4\\ &-22k^6-13k^8+8k^{10})K(k)-\\ &-\frac{16-56k^2+56k^4-32k^6-36k^8+56k^{10}-16k^{12}}{1-k^2}E(k)\Big]+\ldots\end{aligned} \tag{16}$$

$$b^2=f(1-2k^2)/k(1-k^2)^{1/2},\quad 0\leqslant k\leqslant1/\sqrt{2}, \tag{17}$$

where E(k) is a complete elliptic integral of the second kind. Hence, with the same precision we obtain the following expression for the transport cross section:

$$\sigma_{tr}=2\pi\int_0^\infty[1-\cos\chi(b)]b\,db=J_0f-J_1\frac{d^2}{f^2}-J_2\frac{d^4}{f^5}+\ldots, \tag{18}$$

where J_0, J_1, J_2, ... are numbers given by (the expression for J_2 in terms of the integral is not given because it is too cumbersome)

$$\begin{aligned}J_0&=2\pi\int_0^{1/\sqrt{2}}\frac{dk}{k^2(1-k^2)^{3/2}}\cos^2[\sqrt{1-2k^2}K(k)]=3{,}75,\\ J_1&=-\pi\int_0^{1/\sqrt{2}}\frac{dk\sqrt{1-2k^2}}{k^3(1-k^2)^2}\sin[2\sqrt{1-2k^2}K(k)][(1-k^2)(2-k^2)K(k)\\ &-2(1-k^2+k^4)E(k)]=1{,}48,\quad J_2=1{,}24.\end{aligned} \tag{19}$$

3. CALCULATION OF THE ION MOBILITY AND DISCUSSION

The mobility of a positive ion can be calculated from the general theory of collisions in a gaseous mixture of particles having very different masses. Replacing everywhere the reduced mass of the system formed by a positive ion and an atom of He^3 with the effective mass of an atom of He^3 in a solution ($m = m_3^*$), we obtain—in accordance with[9]—an equation for the relationship between the ion velocity U and the applied electric field $\mathscr{E}$:

$$\frac{e\mathscr{E}}{m_3^*n_3}=U\sqrt{\frac{2k_BT}{\pi m_3^*}}e^{-y^2}\int_0^\infty e^{-y^2x^2}[2y^2x\,\mathrm{ch}(2y^2x)-\mathrm{sh}(2y^2x)]\sigma_{tr}x^2\,dx, \tag{20}$$

where n_3 is the number density of the impurity atoms, $x = g/U$, and for the sake of simplicity the ion velocity is expressed in the dimensionless form $y = U(m_3^*/2k_BT)^{1/2}$. Using Eq. (18) for σ_{tr} and calculating the integrals, we obtain

$$\frac{e\mathscr{E}}{m_3^* n_3} = 3{,}75\sqrt{\frac{\varkappa}{m_3^*}}\,U\left\{1 - 0{,}844\frac{\sqrt{k_BT}\,Ba^6}{\varkappa^{3/2}}U^2\varphi(y)\psi(y)\right.$$
$$\left. - 1.67\frac{k_BTB^2a^{12}}{\varkappa^3}U^4\left(1+\frac{2}{5}y^2\right)\varphi^2(y) + \ldots\right\}, \qquad (21)$$

where $\varphi(y)$ is obtained from Eqs. (6′) and (7) and there is a new function

$$\psi(y) = \frac{3}{2}\left\{e^{-y^2} + \frac{1}{4}\int_0^1 [(2y^2-1)+(6y^2-1)x^2]e^{-y^2x^2}dx\right\}. \qquad (22)$$

If $y \lesssim 1$, we obtain

$$\psi(y) = 1 + \frac{1}{5}y^2 - \frac{1}{70}y^4 + \frac{1}{630}y^6 - \frac{1}{5544}y^8 + \ldots. \qquad (23)$$

The expression (21) solves the problem formulated above. Using Eq. (21), we can calculate the ion mobility to within terms of order of $\mathscr{E}^4$. We can see that the sucking in of impurity atoms into a region adjoining a moving ion does indeed raise the ion mobility, as predicted in in[2].

We shall now give numerical estimates and compare them with the experimental results. We used the following values taken from[2,1]: $m_3^* = 2.35m_3$, $(v_3/v_4) = 1.28$, $\alpha = 2.06 \times 10^{-25}$ cm^3. The constant part of the mobility calculated from Eq. (21), $\mu(0) = 14.9/\tilde{c}$ cgs esu, where $\tilde{c}$ is the molar concentration of the impurities, has already been considered in[2] and is in satisfactory agreement with the experimental results. The theoretical value is 10% higher than the experimental mobility taken from[1,2] and approximately 10% smaller than the results given in[3,4]. The ion velocity $U = \mu(0)E$ obtained theoretically on the basis of Eq. (21) is represented by the dashed curves in Fig. 1. The nonlinear part of the mobility was calculated directly from the complete formula (21). The exact value of a^6B was not known. According to the thermodynamic estimate (5), the theoretical value B for solutions with low concentrations of impurity atoms should be

$$B = {}^1/_2[m_3m_3^*/m_4 + m_4(v_3/v_4 - 0{,}75)] \approx 1.24m_3. \qquad (24)$$

If $a \sim 7$ Å and B is given by Eq. (24), we find that $a^6B \sim 10^{-66}$ g·cm^6. The nonlinear part of the mobility was calculated by selecting the best value of a^6B in the expected range given above: this was done by comparing the calculations with the experimental data given in[1-4]. The constant value of the mobility was taken from the experimental data in each case. It was found that the best agreement between the calculations and the results reported in[1-4] was obtained for $a^6B = 0.39 \times 10^{-65}$ g·cm^6. When this estimate of B was employed, the radius of a positive ion was found to be a = 9.3 Å. For the cited value of a^6B and $U \leq 25$ m/sec the terms of the series in Eq. (21) decrease rapidly, ensuring a satisfactory precision of the calculations. A comparison of the results of our calculations (continuous curves) with the experimental data taken from[2] and[3,4] is given in Fig. 1.

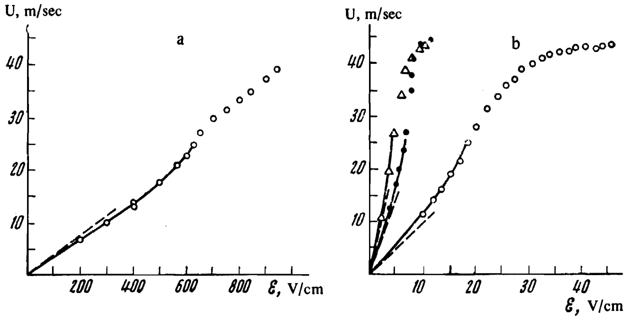

FIG. 1. Dependences of the drift velocity of positive ions on the electric field applied to He^3-He^4 solutions with the following amounts of He^3: a) 1.3%, T = 0.37°K; [2] b) ○—0.0502% and T = 0.3°K, ●—0.017% and T = 0.29°K, △—0.0106% and T = 0.37°K.

The obtained value of the ionic radius exceeds somewhat (by about 2—2.5 Å) the usually accepted value of this radius. This discrepancy may be due to the difference between the "true" and effective hydrodynamic radii of an ion (see[7]).

In all cases, the experimental dependences $U = U(\mathscr{E})$ plotted in Fig. 1 have an inflection in the region of $U \sim 30$ m/sec. Our model of the interaction between a positive ion and an atom of He^3, represented by Eqs. (1)—(4), predicts such an inflection because at high relative velocities of the particles we can expect direct scattering by the hard-core potential of an ion given by Eq. (1). A simple estimate based on Eqs. (1)—(4) predicts the correct position of the inflection point. However, more rigorous calculations for the $U \gtrsim 30$ m/sec have not yet been carried out.

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