THEORY OF ELECTRONIC AND IONIC MOBILITY IN LIQUID He⁴I AND LIQUID He³

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(Received June 11, 1962)

There have been a number of recent studies of the mobilities of charge carriers in liquid He.[1,2] From these investigations we may draw the following conclusions:

(a) In the temperature region below the λ point of He⁴ the mobility, μ, is of the form

$$\mu \propto \exp(\Delta/kT), \tag{1}$$

with Δ/k having the values 8.8°K and 8.1°K for positive and negative ions, respectively. This observation suggests strongly that the dominant mechanism of dissipation involves interaction between ions and rotons.

(b) Below about 0.65°K scattering due to ion-phonon interactions and He³ impurities becomes important.

(c) Above the λ point of He⁴ and in He³ above 2.2°K the dissipative mechanism is very different. In this region the mobility appears to depend on the density and not on the statistics of the fluid.

Two models have been proposed to explain the experimental observations. These involve the localization of an electron in a bubble (Kuper[3]) and local freezing due to electrostriction (Atkins[4]). Neither of these models accounts for the pressure and temperature variations of the ion mobility.[2]

Moreover, it is common practice to assume the mobility to be functionally related to an effective mass, m^*, and a collision cross section, σ, by

$$\mu = (q/m^*) \cdot (1/n\sigma\langle v \rangle), \tag{2}$$

with q the unit charge, n the number density of scatters, and $\langle v \rangle$ the average relative velocity of ion and scatterer. Equation (2) is valid only for a dilute gas. Further, in this formulation m^* and σ are both unknown. It has been common practice to assume m^* to be from one to fifty helium atomic masses and then to compute σ from the observed mobility. The choice of a large effective mass (that is, $m^* \sim 10^5 m_e$), which derives from the models of Atkins and Kuper, we shall show to be unjustified.

In this note we wish to summarize a theory of the mobility of electrons (assumed to be the negative charge carriers) and of He₂⁺ ions (assumed to be the positive charge carriers) in liquid He³ and He⁴I. The theory is in quantitative agreement with experiment, as can be seen from Tables I and II, and differs considerably from all previous attempts to describe the behavior of the ions.

An electron will interact with a dense fluid medium in two ways. First, the electron polarizes

Table I. Comparison of observed and calculated effective masses of an electron in liquid helium.

Isotope	T (°K)	p (atm)	μ_- (obs) (cm² sec⁻¹ volt⁻¹)	$(m^*/m_e)_{obs}$	$(m^*/m_e)_{calc}$	α_{obs}	α_{calc}
He⁴	4.20	1.0	2.16×10^{-2}	128	149	8.9	9.27
He³	3.00	2.0	3.70×10^{-2}	97	105	8.4	8.5

Table II. Comparison of observed and calculated mobilities of the positive ion in liquid helium.

$\zeta_H = 21.0 \times 10^{-12}$ g sec^{-1}	
$\zeta = 9.60 \times 10^{-12}$ g sec^{-1}	For positive ion in He^{4}I,
μ_+ (calc) $= 5.2 \times 10^{-2}$ cm^2 volt^{-1} sec^{-1}	$T = 2.2°$K,
μ_+ (obs) $= 5.6 \times 10^{-2}$ cm^2 volt^{-1} sec^{-1}	$p = 1$ atm

its surroundings and this polarization must follow, to a greater or lesser extent, the motion of the electron. As a result, the effective mass of the electron is greater that that of an electron in vacuum. Second, the quasi-free electron will be scattered from the atoms comprising the fluid. The coherence of the scattering is determined by the spatial distribution of atomic centers, and in this manner the liquid geometry determines the electron mobility.

The ability of the polarization to follow the motion of the electron depends upon the frequency of the Fourier components of the density fluctuation describing the local atomic distribution. If it is assumed that (a) for a nondispersive medium (such as He) the velocity with which the electrorestrictive density increase can occur is governed by the velocity of sound, and (b) the time dependence of the local density fluctuations can be described by one frequency, ω, then there is a one-to-one correspondence between the coupling of an electron to a fluid medium and the coupling of an electron to a polar lattice.[5] Following the arguments of Feynman,[6] one finds

$$m^*/m_e = 1 + 0.02\,\alpha^4,$$

$$\alpha = \tfrac{1}{2}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon}\right)\frac{q^2}{\hbar}\left(\frac{2m_e}{\hbar\omega}\right)^{1/2},$$

$$\omega = (kT/\hbar)(464/C_v)^{1/3}, \tag{3}$$

with m_e the free electron mass, ϵ_∞ the bulk dielectric constant, ϵ the dielectric constant corresponding to the local density (using Clausius–Mosotti relationship), and C_v the specific heat at constant volume.

The physical justification for the two assumptions made arises from the observation that the density increase due to polarization is of relatively short range (of order 10 Å). Therefore the Fourier components of the density fluctuation of most importance are those involving relative motion of neighboring atoms. Because the spe-

cific heat of He is accurately described by a phonon spectrum at low T, we take ω to be defined by the velocity of sound, i.e., the Debye frequency. For a nondispersive medium it is probably accurate enough (since α depends on $\omega^{-1/2}$) to assume that even the high frequency Fourier components have very similar time variations, and therefore the representation of the polarization time dependence by one harmonic frequency is a reasonable approximation.[7] Thus, density fluctuations which lead to polarization fluctuations and thereby to a local dielectric constant differing from the bulk dielectric constant cause an enhancement of the inertial reaction of the electron to an imposed field. The resultant effective mass is of the order of 100 electron masses.

The quasi-free electron $(m^* \neq m_e, \psi \sim e^{i\vec{k}\cdot\vec{R}})$ is scattered from an atom by a potential, V. This potential is assumed to have the form of a Coulomb polarization at large separations and a repulsive spherical barrier pseudopotential[8,9] inside the atom. When the electron density is very low a simple calculation based on the Boltzmann equation leads to

$$\mu_- = \frac{4\pi q\beta}{3}\left(\frac{\hbar}{m^*}\right)^2\left(\frac{\beta\hbar}{2\pi m^*}\right)^{3/2}\int_0^\infty e^{-(\beta\hbar^2 k^2/2m^*)}k^4\,\tau(k)\,dk,$$

$$1/\tau(k) = \int (1 - \cos\theta)Q(k,\theta)\,\sin\theta\,d\theta\,d\varphi,$$

$$Q(k,\theta) = \frac{2\pi}{\hbar}\left|\langle\vec{k}'|V|\vec{k}\rangle\right|^2\frac{m^* \upsilon k}{4\pi\hbar^2}, \tag{4}$$

with $\beta = (kT)^{-1}$, $\vec{k}$ the electron wave vector, υ the volume of the system, and all other symbols have their customary meaning. For the case that the electrons have thermal velocities, $ka \ll 1$, with a the diameter of the scattering atom. It is then easily shown that

$$\mu_- = \frac{q\hbar^4\beta^{3/2}a^2}{24\sqrt{2}\,\pi^{3/2}m^{*5/2}\rho_N^2\kappa_L C^2},$$

$$C = \tfrac{1}{2}(\alpha_p)[(\epsilon + 2)/3\epsilon]^2 q^2, \tag{5}$$

with ρ_N the number density of atoms, κ_L the isothermal compressibility, and α_p the atomic polarizability.

Calculations based on Eqs. (5) and (3) are shown in Table I. As can be seen, there is excellent agreement between calculation and experiment.[2]

Consider now the mobility of the positive ion, herein assumed to be He$_2^+$. Mazo and Kirkwood[10] have presented a theory of quantum fluids taking as the starting point the equation of motion for the Wigner function. As in the classical case, the

theory of the dense fluid is complicated by the coupling between the equations for the distribution of pairs, triplets, $\cdots$ of molecules. With the use of the superposition approximation and an asymptotic approximation to the momentum current density in the configuration space of pairs, it may be shown that the properties of a quantum fluid correspond to those of a classical fluid at the same volume but at a temperature, τ_Q, defined by the quantum-mechanical mean momentum current density. At $0°K$, $\tau_Q = 12.9°K$ for He^4.

The analysis of transport phenomena in dense fluids presented by Rice and Allnatt[11] can be re-derived using Wigner functions and the approximations of Mazo and Kirkwood. The result is

$$\mu_+ = \frac{q}{\frac{8}{3}\rho_N \sigma_i^2 g_2(\sigma_i)[2\pi m_i m k \tau_Q/(m_i + m)]^{1/2} + \zeta},$$

$$= q/(\zeta_H + \zeta),$$

$$\zeta = (4\pi m c^3 \rho_m)^{-1}[\tfrac{1}{3}\rho_m \int \nabla^2 V(R) g_2(R) d\mathfrak{v}]^2, \quad R > \sigma_i;$$

(6)

where $g_2(R)$ is the pair correlation function, σ_i the contact diameter of the ion-atom pair, ρ_m the mass density of the fluid, m_i the mass of the ion and m the mass of an atom, $V(R)$ the potential energy of interaction between ion and atom, and c the velocity of sound. A comparison of the observed[2] and calculated positive ion mobility in He^4 at $2.2°$ is displayed in Table II. The calculations show excellent agreement with experiment. As in other studies of positive ion mobility in the liquids Ar, Kr, and Xe,[12] the Coulomb potential gives rise to an electrostrictive local density increase which enhances the dissipation of energy by the short-range forces. For He, the direct dissipation by

the Coulomb interaction is about one-half that due to short-range interactions, whereas for Ar, Kr, and Xe the contribution is much smaller.

The calculations presented herein do not involve adjustable parameters, and therefore the agreement with experiment may be considered a significant test of the theory and not merely a test of functional form. Studies of the extension of the theory of mobility presented to the superfluid region are now in progress.

*National Science Foundation Predoctoral Fellow.

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