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Motion of Electrons in Liquid Argon*†

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The scattering of electrons moving through nonpolar liquids is discussed. The Hartree field of an atom is assumed not to change on passing from gas to liquid. The screening of the long-range polarization potential is given by a self-consistent local field, which is found in terms of the pair correlation function. A microscopic dielectric function follows as a byproduct. The overlap of atomic force fields in the liquid is handled by the use of an effective potential suggested by Cohen. Detailed calculations are made for electrons in liquid argon. The principal result is that the Ramsauer minimum no longer exists in the liquid. The drift velocity in a steady electric field is found from the solution of the Boltzmann equation given by Cohen and Lekner. Agreement between experiment and theory is good.

I. INTRODUCTION

EARLY studies[1,2] of conductivity pulses produced by ionizing radiation in liquid argon showed that the negative-charge carriers had mobilities three or four orders of magnitude larger than ionic mobilities. It was concluded that they were free electrons. They are in fact excited or excess electrons in the conduction band of the liquid, and the purpose of this paper is to give a microscopic description of their motion.

There are two main problems to resolve, namely (a) what is the effective atomic potential scattering the electron; and (b) how to calculate the transport properties when this potential is known. The latter has been examined by Cohen and myself[3]: A solution of the Boltzmann equation was given which included exactly the space–time correlations within the medium through the use of sum rules of the Van Hove spectral function $S(\mathbf{K},\omega)$. On the other hand, the question of the effective atomic potential acting on the electrons has either been left open,[2,4,5] or it was assumed that it is substantially the same as in scattering within the gas.[6] However, the long-range polarization force between an electron and a polarizable atom is screened by the presence of other polarizable atoms. The screening of the polarization interaction will be examined in Sec. III. There is considerable overlap of the polarization force fields of different atoms, and to a lesser extent, of the Hartree fields of nearest neighbors. This problem is considered in Sec. IV. A prerequisite for the discussion of screening and overlap in the liquid is a knowledge of the interaction between an electron and an isolated atom. A simplified discussion is given in Sec. II. The drift velocity of electrons in a steady electric field is calculated and compared with experiment in Sec. V. Finally, a simple extension of the results of Sec. III to the screening of the electric force between an electron and a hole in the liquid, which must be considered in the exciton problem, is given in the Appendix.

The screening, the effective potential, and the momentum-transfer cross section required for transport properties are all dependent on liquid structure through the pair correlation function $g(R)$ or the structure factor $S(K)$,

$$S(K)=1+n\int d^3R\, e^{i\mathbf{K}\cdot\mathbf{R}}[g(R)-1]. \tag{1}$$

An approximate structure factor in closed form is provided by the solution of the Percus-Yevick equation for the hard-sphere fluid[7]; it is compared with the neutron data of Henshaw[8] in Fig. 1. For our purposes this theoretical $S(K)$, and the $g(R)$ obtained from it by inverting (1), are sufficiently close to experiment and will be used in the calculations.

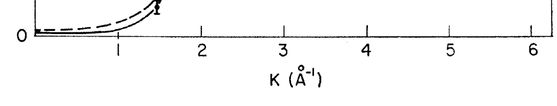

FIG. 1. Liquid-structure factor of argon at 84°K. The experimental points are from the neutron data of Henshaw, Ref. 8. The solid and dashed lines are theoretical structure factors for a hard-sphere fluid calculated from the Percus-Yevick equation with hard-sphere diameters of 3.44 and 3.25 Å, respectively.

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[2] M. S. Malkin and H. L. Schultz, Phys. Rev. **83**, 1051 (1951).

[3] M. H. Cohen and J. Lekner, Phys. Rev. (to be published).

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

[5] D. W. Swan, Nature **196**, 977 (1962); Proc. Phys. Soc. (London) **83**, 659 (1964).

[6] H. Schnyders, S. A. Rice, and L. Meyer, Phys. Rev. Letters **15**, 187 (1965).

[7] E. Thiele, J. Chem. Phys. **39**, 474 (1963); N. W. Ashcroft and J. Lekner, Phys. Rev. **145**, 83 (1966).

[8] D. G. Henshaw, Phys. Rev. **105**, 976 (1957).

II. SCATTERING OF ELECTRONS BY GASEOUS ARGON

In order to calculate the scattering of electrons in the liquid, we shall first give a simplified description of scattering in the gas. In the original paper on electron-argon scattering, Holtsmark[9] found phase shifts by integrating the radial part of the Schrödinger equation. The potential he used was the Coulomb potential of the nucleus screened by the Hartree distribution of electrons,[10] plus a polarization potential which was numerically adjusted[11] at short range to fit the data of Brüche.[12] The results presented here are essentially a reworking of the same problem with one modification, which is that the exchange and correlation effects are represented by the potential[13]

$$U_\alpha(R)=-\tfrac{1}{2}\alpha e^2/(R^2+R_\alpha{}^2)^2. \tag{2}$$

We have numerically[14] integrated Schrödinger's equation using the same Hartree field as Holtsmark,[10] and adjusting the parameter R_α in (2) to obtain the experimental scattering length deduced by Frost and Phelps[15] from their drift-velocity data. The presence of the long-range polarization potential requires modifications of the methods normally used in the extraction of phase shifts and of the scattering length.

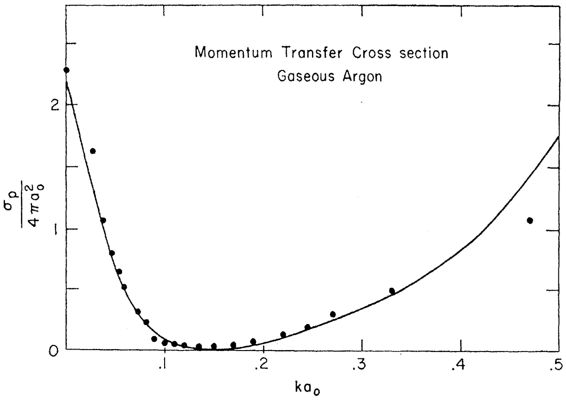

FIG. 2. Momentum-transfer cross section for electrons in argon gas. The points are cross sections extracted from drift-velocity measurements by Frost and Phelps (Ref. 15).

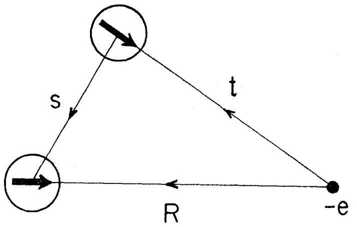

FIG. 3. Local fields in liquids. The field on the atom at **R** is the sum of the direct field plus the dipole fields of atoms at all other points **t**.

A. Scattering Length

At zero energy and for $R^2 \gg R_\alpha{}^2$ the L=0 partial wave satisfies

$$(d^2/dR^2+A^2R^{-4})u_0(R)=0, \tag{3}$$

where the length $A=(\alpha/a_0)^{1/2}$ is a measure of the strength of the polarization force.[16] The solution of (3) is

$$u_0(R)=R\{b\sin(A/R)+c\cos(A/R)\}. \tag{4}$$

Comparing the asymptotic form of this solution with the definition of the scattering length, $u_0 \to \mathrm{const}(R-a)$, gives a in terms of the coefficients b and c of the $k=0$ solution:

$$a=-(b/c)A. \tag{5}$$

The scattering length for electrons in argon has been obtained by O'Malley[17] by extrapolation of the Ramsauer and Kollath[18] data, and by Frost and Phelps,[15] from drift-velocity measurements. We fitted the parameter R_α of Eq. (2) so as to obtain the Frost-Phelps scattering length, $a=-1.5a_0$. The required value is $R_\alpha=1.22a_0$, or 0.65 Å.

B. Phase Shifts

The recent work of Levy and Keller[19] may be directly applied to the extraction of phase shifts due to a long-range potential. From Eqs. (40) and (46) of Ref. 19 it is easy to show that if the Lth partial wave passes through zero at a radius R, the phase shift $\delta_L \equiv \delta_L(\infty)$ is given by

$$\tan\delta_L(\infty)=\tan\delta_L(R)+\frac{1}{6kR}\left(\frac{A}{R}\right)^2\sec^2\delta_L(R) +O((kR)^{-2}), \tag{6}$$

where $\tan\delta_L(R)=j_L(kR)/n_L(kR)$, and j_L, n_L are the spherical Bessel and Neumann functions. At small energies the phases for $L \geqslant 1$ are determined entirely by the long-range polarization force[19]:

$$\tan\delta_L \simeq \frac{\pi(kA)^2}{(2L-1)(2L+1)(2L+3)}. \tag{7}$$

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[9] J. Holtsmark, Z. Physik **55**, 437 (1929).

[10] Reference 9, Table I. The entry at $r=0.02\ a_0$ is misprinted; it should read $2Zp=33.33$.

[11] Reference 9, Fig. 1. Because of an error in units, the asymptotic value of the polarization potential used by Holtsmark was too large by a factor of 2. This does not greatly affect the validity of Holtsmark's results, since he did not calculate cross sections at very low energies, where the polarization potential plays a major role.

[12] B. E. Brüche, Ann. Physik **1**, 93 (1929).

[13] B. Kivel, Phys. Rev. **116**, 926 (1959); Avco-Everett Research Laboratory, Everett, Massachusetts, Research Note No. 129, 1959 (unpublished).

[14] See *Modern Computing Methods* (Her Majesty's Stationery Office, London, 1961), 2nd ed. We have used the difference equation (27), p. 86, which is correct to fifth-order differences.

[15] L. S. Frost and A. V. Phelps, Phys. Rev. **136**, A1538 (1964).

[16] The polarizability α is 11 $a_0{}^3$ for argon, and $A=3.3\ a_0$. The scattering length of a polarization potential cutoff for $R<R_0$ is $a=-A\tan(A/R_0)$.

[17] T. F. O'Malley, Phys. Rev. **130**, 1020 (1963).

[18] C. Ramsauer and R. Kollath, Ann. Physik **12**, 837 (1932).

[19] B. R. Levy and J. B. Keller, J. Math. Phys. **4**, 54 (1963).

The phase shifts δ_L, $L=0$ to 3, were calculated from the corresponding partial waves from Eq. (6). The integrations of the partial waves $u_L(R)$ were carried out to distances ranging from $R=250a_0$ at low energies to $R=20a_0$ at energies of an electron volt or higher. Phase shifts determined from successive zeros of the wave functions always agreed to 0.5%, and usually to 0.1%. At zero energy $\delta_0=3\pi$, $\delta_1=2\pi$, and all higher phase shifts are zero, since there were three nodes in u_0, two in u_1 and none in u_2 and the higher partial waves.

In evaluating the momentum-transfer cross section[20]

$$\sigma_P=(4\pi/k^2)\sum_{L=0}^{\infty}(L+1)\sin^2(\delta_L-\delta_{L+1}),$$

we have used the calculated phase shifts for $L=0$ to 3, together with δ_4 and δ_5 estimated from Eq. (7). The resulting cross section is compared in Fig. 2 with the data extracted by Frost and Phelps[15] from drift-velocity measurements. Agreement is good up to about 2 eV. The drift velocities recalculated with our cross section are in excellent agreement (5% or better) with the data presented in Fig. 3 of Ref. 15 in the range $E/N=10^{-20}$ to 10^{-17} V cm^2.

III. SCREENING OF THE POLARIZATION INTERACTION

An electron at a distance R from an isolated atom of polarizability α induces on it a dipole of strength $\alpha e/R^2$, which in turn attracts the electron with a force of magnitude $2\alpha e^2/R^5$. The interaction potential is therefore $-\alpha e^2/2R^4$. Physically it is clear that the polarization force does not increase without limit as R tends to zero, and it must therefore be modified. This was done in the preceding section, where the effects of both exchange and correlation (polarization) were approximated at all distances of the potential (2). At small R this potential represents mainly exchange, since the polarization part goes to zero.[21] At large R ($\gg R_\alpha$) Eq. (2) gives the usual polarization term.

Now what is the polarization interaction between an electron and a particular atom in a liquid? The answer lies in finding the *local field* acting on the atom, which consists of the direct field and the sum of all other fields due to dipoles induced on neighboring atoms. In the case of external fields, or of light traveling through the medium, the induced dipoles are parallel in regions containing many atoms. Lorentz[22] has found the average local field for atoms arranged in a cubic lattice, and for a structureless fluid. For real liquids, Kirkwood[23] and Yvon[24] have solved the problem of dielectric polarization in a uniform external field. When the field is produced by charges within the liquid the induced atomic dipoles are no longer parallel. The screening is consequently more complicated, and becomes a function of the distance between electron and atom.

The problem is simplified by the fact that

$$v_A \ll v_e \ll v_{Ae}, \tag{8}$$

where v_A, v_e, and v_{Ae} are typical velocities of atoms in the liquid, of the free electrons, and of the atomic (bound) electrons. Thus the motion of the atoms can be ignored in calculating the mutual screening effect of neighbors, and the motion of the free electrons can be ignored in calculating the induced polarizations of the atomic electrons.

Consider now a point charge $-e$ in a liquid composed of atoms of polarizability α. In the absence of other nearby atoms, the electric field acting on an atom at $\mathbf{R}$ would be e/R^2 (see Fig. 3). By symmetry, the average local field acting on the atom at $\mathbf{R}$ is along $\mathbf{R}$, and a function of R only. Call it

$$(e/R^2)f(R), \tag{9}$$

i.e., define a function $f(R)$ such that the average local field acting on the atom is given by (9). Now this field is equal to the direct field e/R^2, plus the contribution to the field due to all the other induced atomic dipoles in the liquid. Given that an atom is located at some point in the fluid, the probability of finding another atom in the volume element $d\tau$ at distance s from the first is by definition $ng(s)d\tau$, where n is the number density of atoms, and g the pair-correlation function.[25] The field acting on this second atom (Fig. 3) is $(e/t^2)f(t)$, so that it has on it an induced dipole of average strength $\alpha(e/t^2)f(t)$. The component along $\mathbf{R}$ of the field at $\mathbf{R}$ due to this dipole is

$$(\alpha e f(t)/2Rs^3t^3)\left[\tfrac{3}{2}s^{-2}(s^2+t^2-R^2)(s^2+R^2-t^2)\right.$$
$$\left.+(R^2+t^2-s^2)\right]. \tag{10}$$

Integrating over all space in bipolar coordinates s, t ($d\tau=2\pi s\,ds\,t\,dt/R$), the self-consistency condition gives

$$f(R)=1-\pi n\alpha\int_0^\infty ds\, s^{-2}g(s)\int_{|R-s|}^{R+s}dt\, t^{-2}f(t)$$
$$\times\Theta(R,s,t), \tag{11}$$

where $\Theta(R,s,t)$ denotes the bracketed quantity in (10). The solution of the linear integral equation (11) then gives the required self-consistent, ensemble-average local field. In deriving (11) it is assumed that the average effect of the dipole at $\mathbf{t}$ is the same as the effect of the average dipole at $\mathbf{t}$, i.e., that fluctuations are negligible.

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[20] D. R. Bates, *Atomic and Molecular Processes* (Academic Press Inc., New York, 1962), p. 645.

[21] R. W. LaBahn and J. Callaway, Phys. Rev. **135**, A1539 (1964).

[22] H. A. Lorentz, *The Theory of Electrons* (Dover Publications, Inc., New York, 1952), Sec. 117 and notes 54, 55.

[23] J. G. Kirkwood, J. Chem. Phys. 4, 592 (1936).

[24] Y. Yvon, Actualités Sci. Ind., No. 543 (1937).

[25] If the charge is a free electron moving rapidly through the fluid, the atoms do not have time to react to the electrostrictive forces, and the fluid structure is unchanged by the presence of the charge.

For real liquids $g(s)=0$ for $s\leqslant\sigma$, where σ is the "hard-core diameter," or specifically the distance at which the repulsive potential energy between atoms becomes much greater than kT. For such systems $f(R)\rightarrow 1$ as $R/\sigma\rightarrow 0$. The local field in a *structureless fluid* can be obtained by setting

$$\begin{aligned} g(s)&=0 \quad s<\sigma \\ &=1 \quad s>\sigma, \end{aligned}$$

and taking the limit as σ tends to zero. We have

$$f(R)=1-\lim_{\sigma\rightarrow 0}\pi n\alpha\int_0^\infty ds\, s^{-2}\int_{|R-s|}^{R-s} dt\, t^{-2}f(t)\Theta(R,s,t).$$

Reversing the order of integration, we find that all the indirect contribution to the field at $\mathbf{R}$ comes from its immediate neighborhood:

$$f(R)=1-(8/3)\pi n\alpha f(R).$$

In the limit of a structureless fluid we therefore recover the Lorentz local field,[22]

$$f_L=[1+(8/3)\pi n\alpha]^{-1}. \quad (12)$$

For a given pair-correlation function, the local-field function can be found numerically by straightforward iteration of the integral equation (11). The solution corresponding to the $\sigma=3.44$ Å Percus-Yevick structure factor of Fig. 1 is shown in Fig. 4.

The local field takes into account the screening of the field producing the dipole moment on a given atom. Is there any further screening of the electron-atom interaction? This question may be resolved as follows[26]: The total energy of the induced atomic dipoles is

$$U=\tfrac{1}{2}\sum_i \mathbf{p}_i{}^2/\alpha-\sum_i \mathbf{p}_i\cdot\mathbf{E}_i{}^{(0)}-\tfrac{1}{2}\sum_{i,j}{}' \mathbf{p}_i\cdot\mathfrak{D}_{ij}\cdot\mathbf{p}_j. \quad (13)$$

The first term is the energy required to form dipoles of strength $\mathbf{p}_i$, the second is the dipole-field energy, and the third the dipole-dipole energy, with

$$\mathbf{p}_i\cdot\mathfrak{D}_{ij}\cdot\mathbf{p}_j=r_{ij}{}^{-3}[3(\mathbf{p}_i\cdot\mathbf{r}_{ij})(\mathbf{p}_j\cdot\mathbf{r}_{ij})/r_{ij}{}^2-\mathbf{p}_i\cdot\mathbf{p}_j].$$

The condition $\partial U/\partial\mathbf{p}_i=0$ gives the magnitude of each dipole,

$$\mathbf{p}_i=\alpha(\mathbf{E}_i{}^{(0)}+\textstyle\sum_j{}'\,\mathfrak{D}_{ij}\cdot\mathbf{p}_j)=\alpha\mathbf{E}_i{}^{(\mathrm{loc})}. \quad (14)$$

Therefore the total energy may be written

$$U=-\tfrac{1}{2}\textstyle\sum_i \alpha\mathbf{E}_i{}^{(\mathrm{loc})}\cdot\mathbf{E}_i{}^{(0)}. \quad (15)$$

This expression is the microscopic equivalent of

$$U=-\frac{1}{2}\int d\tau\mathbf{P}\cdot\mathbf{E}^{(0)},$$

which is the energy of a dielectric body in a field whose sources remain constant.[27]

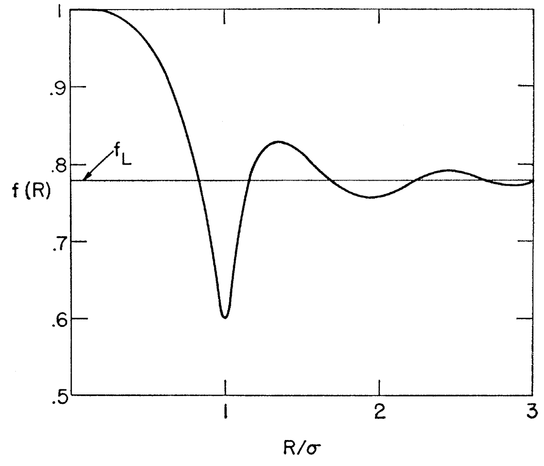

FIG. 4. Local-field function $f(R)$ due to point charge, calculated from the Percus-Yevick pair-correlation function $g(R)$ corresponding to liquid-argon density and a hard-core diameter $\sigma=3.44$ Å.

The form of the total energy in (15) shows that the screening effects are contained entirely in the local field. The polarization energy is the sum of energies

$$U_i=-\tfrac{1}{2}\alpha f(R_i)(e/R_i{}^2)^2. \quad (16)$$

Up to this point the discussion of the screening has been for the case of an electron moving among idealized atoms with constant polarizability α, acting as point dipoles. The point-dipole approximation does not lead to large error, since atoms in the liquid have vanishingly small probability of approaching closer together than the distance σ (i.e., $g(R)$ in Eq. (11) is zero for $R<\sigma$). We expect exchange and correlation to be important at distances of order R_α; by analogy with (2) the error involved in treating the atoms as point dipoles will be of order $2R_\alpha{}^2/\sigma^2$, i.e., about 5% for argon.

On the other hand, the distance between the electron and a given atom in the liquid can be small, and the polarizability cannot be taken to be constant for $R\lesssim R_\alpha$: this is implied by the use of (2). Equation (11) must be replaced by

$$f(R)=1-\pi n\int_0^\infty ds\, s^{-2}g(s)\int_{|R-s|}^{R+s} dt\, t^{-2}f(t)\alpha(t) \times\Theta(R,s,t). \quad (17)$$

The function $\alpha(R)$ is not known. We cannot simply define it so as to obtain (2), because (2) includes the effects of exchange as well as of correlation (polarization). We do expect $\alpha(R)$ to decrease rapidly for $R\lesssim R_\alpha$, i.e., as the electron penetrates into the atom. This will have a strong effect on $f(R)$ for small R. For example in a structureless fluid, instead of a constant Lorentz field we find

$$f(R)=[1+(8/3)\pi n\alpha f(R)]^{-1}. \quad (18)$$

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[26] I am indebted to Professor M. H. Cohen for this argument.

[27] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Company, Inc., New York, 1941), Sec. 2.10.

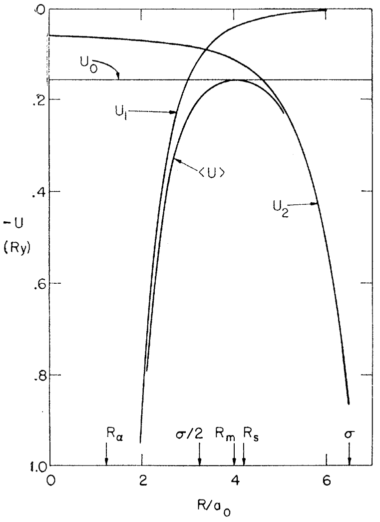

FIG. 5. Atomic potentials in liquid argon. U_0, U_1, and $\langle U\rangle$ are defined in the text. U_2 is the second part of the right-hand side of Eqs. (21) or (22).

We can use this result to estimate the error involved in neglecting the variation of polarizability with distance. At $R=0$ the difference between (18) and f_L is about 30% for argon. But there the correlation and exchange potential is swamped by the Coulomb potential, and in any case the screening goes to zero. The error in the total potential will be largest near $R=R_\alpha$. There it is of order $\pi n\alpha(U_\alpha/U_{\text{total}})R_\alpha$, which is 3% for argon.

We conclude that the local-field function $f(R)$ calculated from (11) will approximate the true local field quite well for $R \gtrsim 2R_\alpha$. At smaller distances the error in $f(R)$ can be large, but the error in the total potential should be everywhere less than about 10%. In the following we shall neglect the (unknown) variation in polarizability; by analogy with (16) we write for the electron-atom exchange and correlation potential in the liquid:

$$U_\alpha(R) = -\tfrac{1}{2}\alpha e^2 f(R)/(R^2+R_\alpha{}^2)^2\,, \qquad (19)$$

where $f(R)$ is found from (11). At small R this potential should be the same as in the gas, and it is, since $f(R)\to 1$ as $R/\sigma\to 0$. U_α becomes the dominant term for $R>2R_\alpha$; in this region the inaccuracy will come less from the idealizations discussed above than from uncertainties in the pair-correlation function, which are quite large (10 or 20%).

IV. THE EFFECTIVE POTENTIAL IN THE LIQUID

We shall assume that the change in the Hartree field of an atom on passing from gas to liquid is negligible. This is justified in part by the fact that the atomic polarizability of argon as determined from the Lorentz-Lorenz[28] expression for the refractive index changes by only 2% on condensation.[29] Since the molecular theory of the bulk refractive index[24] predicts a deviation from the Lorentz-Lorenz formula of the same magnitude, the change in electronic structure cannot be large.

Therefore, the single-atom potential seen by an electron in the liquid is the Coulomb field of the nucleus screened by the Hartree distribution of electrons, plus the screened exchange and polarization potential U_α of Eq. (19), with the *same* R_α that was used in the description of scattering in the gas:

$$U_1 = U_H + U_\alpha\,. \qquad (20)$$

This potential is shown in Fig. 5. The trouble with using it to calculate scattering in the liquid is that the potentials of neighboring atoms overlap. The electron therefore never is in free space, not even near the boundary of the Wigner-Seitz[30] sphere $R=R_s$, and we cannot calculate phase shifts. Kohn and Rostoker[31] deal with this problem by subtracting from the potential its value at R_s: the potential is nearly flat there, and the electron sees only differences in potential. Ziman[32] adds in the overlap of nearest neighbors in a "muffin-tin potential." A unique way of defining the effective potential near an atom at $\mathbf{R}_i$ is from the *ensemble average* of the total potential:

$$\langle U(|\mathbf{R}-\mathbf{R}_i|)\rangle = U_1(|\mathbf{R}-\mathbf{R}_i|) + \langle \textstyle\sum_j{}' U_1(|\mathbf{R}-\mathbf{R}_j|)\rangle\,. \qquad (21)$$

In bipolar coordinates, with the notation of Fig. 3,

$$\langle U(R)\rangle = U_1(R) + \frac{2\pi n}{R}\int_0^\infty ds\, s g(s)\int_{|R-s|}^{R+s} dt\, tU_1(t)\,. \qquad (22)$$

The effective potential U_{eff} is then defined as[33]

$$\begin{aligned} U_{\text{eff}} &= \langle U(R)\rangle - U_0 \quad && R<R_m \\ &= 0 && R>R_m\,, \end{aligned} \qquad (23)$$

where R_m and U_0 are defined by

$$[\partial\langle U\rangle/\partial R]_{R_m} = 0\,, \quad \langle U(R_m)\rangle = U_0\,. \qquad (24)$$

For argon, $R_m = 4.0a_0$ and $U_0 = -0.157$ Ry, or -2.13 eV (see Fig. 5). The idea behind U_{eff} is that the electron sees only differences in potential in its motion through the liquid. It is necessary (and we believe correct) to subtract out the constant part U_0 in order to calculate phase shifts in the usual way. It is however not clear that the momentum and energy transfers which the electron undergoes on scattering in the liquid are correctly given by the sum rules of $S(K,\omega)$, since U_{eff} combines the potentials of many atoms. This is an added assumption, which we are forced to make in order to use the solution of Boltzmann's equation given in Ref. 3.

Two cross sections are needed in the evaluation of

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[28] H. A. Lorentz, Ref. 22, Secs. 123, 124.

[29] C. P. Abbiss, C. M. Knobler, R. K. Teague, and C. J. Pings, J. Chem. Phys. **42**, 4145 (1965).

[30] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

[31] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

[32] J. M. Ziman, Proc. Phys. Soc. (London) **88**, 387 (1966).

[33] M. H. Cohen (private communication); M. H. Cohen and J. Jortner (to be published).

transport properties[3]:

$$\sigma_0(\epsilon)=2\pi\int_0^{\pi} d\theta\,\sin\theta(1-\cos\theta)\sigma(\epsilon,\theta) \tag{25}$$

$$\sigma_1(\epsilon)=2\pi\int_0^{\pi} d\theta\,\sin\theta(1-\cos\theta)\sigma(\epsilon,\theta)S(2k\,\sin\tfrac{1}{2}\theta)\,. \tag{26}$$

Here $\sigma(\epsilon,\theta)$ is the differential cross section, $\epsilon=\hbar^2k^2/2m$, and S is the structure factor given by (1). When there is no correlation among the scattering centers, as in a gas, $S(K)=1$ and σ_0 and σ_1 are the same as the cross section σ_p of Sec. II. In Fig. 6 we show the cross section σ_0 calculated from phase shifts with the unscreened potential, the screened potential U_1, and the effective potential defined above. The scattering lengths are, respectively, -1.48, -0.79, and $+1.44a_0$. The removal of overlap in the average potential changes the sign of the scattering length. The effective potential still binds three s states and two p states, but is not attractive enough to give a Ramsauer minimum.

V. DRIFT VELOCITY OF ELECTRONS IN LIQUID ARGON

The most recent data on the drift velocity of electrons in liquid argon is that of Swan[5] at high fields and of Schnyders, Rice, and Meyer[6] at low fields. There is a considerable gap in betweeen (see Fig. 7). The solution of Boltzmann's equation for electrons moving in a liquid is known.[3] The results may be written in terms of functions f_0 and f_1, where

$$\begin{aligned} f_0(\epsilon)&=\exp\left[-\int\frac{d\epsilon}{\epsilon+kTb(\epsilon)}\right],\\ f_1(\epsilon)&=-eE\Lambda_1 df_0/d\epsilon,\\ b(\epsilon)&=\tfrac{1}{3}(eE\Lambda_0)(eE\Lambda_1)/(2m/M)(kT)^2. \end{aligned} \tag{27}$$

Here Λ_0 and Λ_1 are "mean free paths" which determine the rates of energy and momentum transfer, respectively:

$$\Lambda_0^{-1}=n\sigma_0\,,\quad \Lambda_1^{-1}=n\sigma_1\,. \tag{28}$$

The mean energy and drift velocity are given in terms of f_0 and f_1 by

$$\begin{aligned} \langle\epsilon\rangle&=\int_0^\infty d\epsilon\,\epsilon^{3/2}f_0(\epsilon)\Big/\int_0^\infty d\epsilon\,\epsilon^{1/2}f_0(\epsilon)\,,\\ v_D&=\frac{1}{3}\left(\frac{2}{m}\right)^{1/2}\left(\int_0^\infty d\epsilon\,\epsilon f_1(\epsilon)\Big/\int_0^\infty d\epsilon\,\epsilon^{1/2}f_0(\epsilon)\right). \end{aligned} \tag{29}$$

In the weak-field region, the electrons have a Maxwellian distribution of energies, $f_0(\epsilon)=\exp(-\epsilon/kT)$, and the drift velocity is proportional to the field. In this region $\sigma_1\simeq4\pi a^2S(0)$, where a is the scattering length; the drift velocity is

$$v_D=\frac{2}{3}\left(\frac{2}{\pi mkT}\right)^{1/2}\frac{eE}{n4\pi a^2S(0)}\,. \tag{30}$$

This equation is equivalent to the expression (3.8) of Bardeen and Shockley[34] for the mobility of electrons in nonpolar crystals.

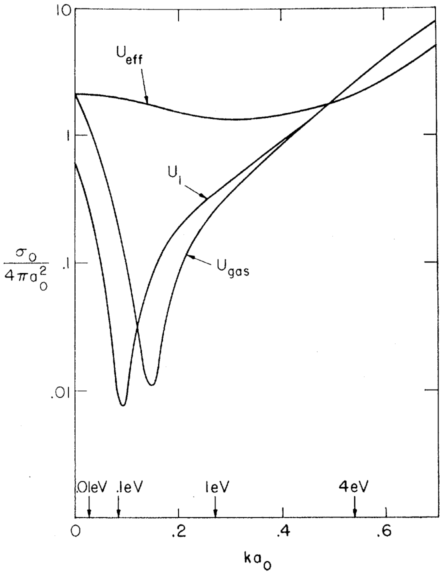

FIG. 6. Cross sections for electron scattering. The curves are labeled by the appropriate potential: $U_{\rm gas}$, U_1, and $U_{\rm eff}$. The cross sections are calculated from phase shifts, determined as in Sec. II. The near coincidence of the $U_{\rm gas}$ and $U_{\rm eff}$ cross sections at zero energy is fortuitous: The scattering lengths have opposite signs.

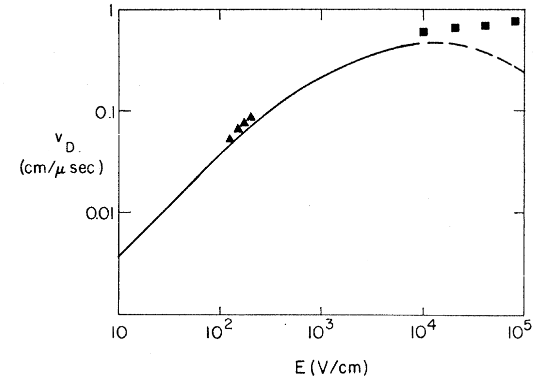

FIG. 7. Drift velocity of electrons in liquid argon. Squares: Swan's data at 90°K (Ref. 5); triangles: data of Schnyders, Rice, and Meyer at 85°K (Ref. 6); line: theory at 84°K. The line is dashed above 10^4 V/cm to indicate that the cross sections used are not accurate at these energies.

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[34] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950). The formula (30) for electron-drift velocity in liquids is certainly not new. It follows on substituting the Einstein-Smoluchowski scattering coefficient into the Lorentz (1905) formula (Ref. 22, p. 274). See also K. S. Krishnan and A. B. Bhatia, Nature **156**, 503 (1945).

TABLE I. Theoretical drift velocities in argon at 84°K. E is field in V/cm; v_D the drift velocity in cm/μsec; $\langle\epsilon\rangle$ the mean electron energy in eV; λ, Λ_0, and Λ_1 are the de Broglie wavelength, the energy transfer, and momentum-transfer mean free paths, all in Å.

E	v_D	$\langle\epsilon\rangle$	λ	Λ_0	Λ_1
10	0.0039	0.011	116	6.6	136
10^2	0.037	0.011	116	6.6	136
10^3	0.21	0.028	73	6.7	140
10^4	0.47	0.51	17	8.7	140
10^5	(0.25)	(2.4)	(8)	(9.0)	(60)

The results obtained for the drift velocity and mean energy of electrons in liquid argon at 84°K are shown in Fig. 7 and Table I. In the calculation we have used the potential U_{eff} defined in Sec. IV. The cross section σ_1 was evaluated with the $\sigma=3.25$ Å $S(K)$ of Fig. 1, since this has the correct long-wavelength limit, $S(0)=0.048$. The results will be discussed in the next section. First we need to estimate the effect of impurities in the liquid on the drift velocity.

The fractional energy loss per collision is of the order of m/M in elastic scattering, and of order unity for inelastic collisions. The fractional energy loss per unit path distance is therefore roughly $n^*\sigma^*$ for inelastic collisions, and $(m/M)n\sigma_0$ for elastic collisions. Here n^* and σ^* are the impurity number density and inelastic cross section. If impurities are to have negligible effect we must therefore have

$$n^*\sigma^* \ll (m/M)n\sigma_0. \tag{31}$$

A likely impurity in liquid argon is N_2, which can inelastically scatter electrons by excitation of the rotational[35] and vibrational[36] levels of the molecule. Rotational excitation can be important at low fields, when the electrons are thermalized. Vibrational excitation can only be important at high fields. In both cases the inelastic cross sections are of the order of Å^2 and thus the impurity level should be at about 10 ppm or less if the drift velocity in "pure" argon is to be measured. Swan's data is therefore on the borderline, since his argon contained about 50 ppm of impurities, which were primarily N_2. Schnyders, Rice, and Meyer purified their argon, and estimate their impurity level to be less than 1 ppm.

VI. DISCUSSION

To sum up, we have considered the motion of electrons in nonpolar liquids, specifically, liquid argon. The electron-atom potential is modified to include the effects of screening and overlap of the atomic force fields. The principal result is that the Ramsauer minimum no longer exists in the liquid. The drift velocity is calculated for electric-field strength varying by four orders of magnitude. The agreement with experiment is good except perhaps at very high fields. There both theory and experiment are uncertain; the former because the theoretical cross sections are inaccurate at electron energies above about 2 eV, and the latter because of the presence of impurities.

The results do not in any sense represent a fit to the data: The one adjustable parameter in the calculation ($R\alpha$) was fixed by the scattering in the gas. Therefore the comparison of theory with experiment gives a test of the assumptions we have made. Of these the main ones are: (1) that fluctuations in the screening and in the effective potential may be neglected. This is equivalent to assuming that the average over many events of scattering by a fluctuating potential is equal to the scattering by the average potential; (2) that the effect of multiple scattering is negligible; and (3) that the solution of the Boltzmann equation given in Ref. 3 is applicable when the scattering is calculated from the potential U_{eff}. The conclusion can be drawn that either the statements (1), (2), and (3) are correct, or that the errors involved partially cancel. We shall see that in fact *multiple-scattering* effects are strong but largely self-cancelling for electrons in liquid argon.

An estimate of the effect of multiple scattering can be made with the Wigner-Seitz[30] condition that the ground-state s wave function have zero gradient at $R=R_s$. The wave function calculated from U_{eff} satisfies this boundary condition at $k_0=0.35a_0^{-1}$. The electron at the bottom of the conduction band therefore has the energy $U_0+\hbar^2k_0^2/2m=-2.13$ eV$+1.67$ eV$=-0.46$ eV. This energy carries a large uncertainty however, since it is obtained as the difference between two larger energies, neither of which is known to better than 5%. We can therefore conclude only that the electron affinity of liquid argon will probably lie between 0.3 and 0.6 eV. This is in contrast to helium, where approximately 1 eV is needed to inject electrons into the liquid. Bardeen[37] has extended the Wigner-Seitz approach to the calculation of the effective mass at the bottom of the conduction band. It is determined by the gradient of the p wave at $R=R_s$. Using the p wave function calculated at $k=k_0$ we find $m_{\text{eff}}=0.50m$, which is in good agreement with the exciton effective mass deduced by Baldini[38] from exciton spectra in the solid i.e., $m_{\text{exciton}}=0.43m$.

These renormalization effects of multiple scattering, the ground-state energy and the effective mass, give a mobility which is also in good agreement with experiment. The single-scatterer mobility, 370 cm^2/V sec, is about 20% below the experimental mobility, 450 cm^2/V sec. The momentum-transfer cross section σ_1 increases by 1.37 in going from $k=0$ to $k=k_0$. The combined change in effective mass and cross section gives a mobility of 540 cm^2/V sec, which is about 20% above the experimental value.

ACKNOWLEDGMENTS

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[37] J. Bardeen, J. Chem. Phys. **6**, 367 (1938).

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throughout the course of this work. I am greatly indebted to Professor Morrel H. Cohen for criticism, ideas, and stimulus.

APPENDIX: MICROSCOPIC DIELECTRIC FUNCTION

In Sec. III we found the local field $f(R)e/R^2$ acting on an atom in the liquid at distance R from a free electron. Here we shall consider first the local field acting on atoms in the liquid due to charge q *on a given atom*, and then the field of this charge at an arbitrary point in the liquid, i.e., the dielectric function. As in Sec. III we make the point-dipole and constant polarizability assumptions. The extensions necessary to describe screening in the exciton problem will be briefly discussed.

In Fig. 3, replace the electronic charge $-e$ by an atom possessing a charge q, and define a function $F(R)$ such that the average local field acting on another atom at a distance R is $(q/R^2)F(R)$. By the arguments of Sec. III, $F(R)$ satisfies the integral equation

$$F(R)=1-\pi n\alpha\int_0^\infty ds\, s^{-2}\int_{|R-s|}^{R+s} dt\, t^{-2}F(t)\frac{g^{(3)}(R,s,t)}{g(R)}\times\Theta(R,s,t). \qquad \text{(A1)}$$

Here $g^{(3)}(R,s,t)$ is the triplet correlation function, for which the simplest approximation is the Kirkwood superposition product[39] of pair-correlation functions:

$$g_s^{(3)}(R,s,t)=g(R)g(s)g(t).$$

The local field $F(R)$ is similar to $f(R)$, except that the screening decreases more rapidly at small distances.

Consider now the field at a general point in the liquid at distance R from the atom with charge q. Denote this field by

$$(q/R^2)\kappa^{-1}(R), \qquad \text{(A2)}$$

where $\kappa(R)$ is the microscopic dielectric function. Summing over the fields at $\mathbf{R}$ produced by all the induced dipoles in the liquid, we find

$$\kappa^{-1}(R)=1-\pi n\alpha\int_0^\infty ds\, s^{-2}\int_{|R-s|}^{R+s} dt\, t^{-2}F(t)g(t)\Theta(R,s,t).$$

The integrand is singular at $s=0$. To obtain the electric field we exclude from the integration a small cylinder centered on $s=0$ with axis parallel to $\mathbf{R}$, and take the limit as the cylinder volume tends to zero. A straightforward calculation of the integral gives

$$4F(R)g(R)l/(l^2+\rho^2)^{1/2},$$

where l and ρ are the (infinitesimal) length and radius of the cylinder. As in the classical prescription for the average electric field in a dielectric medium,[40] we take $l\gg\rho$. Therefore

$$\kappa^{-1}(R)=1-4\pi n\alpha F(R)g(R). \qquad \text{(A3)}$$

Tbe same result is obtained by adding the potentials of the charge q and of all the induced dipoles, and differentiating with respect to R. For a structureless fluid, $F=[1+(8/3)\pi n\alpha]^{-1}$, so that we regain the Clausius-Mossotti dielectric constant,[22]

$$\kappa^{-1}=\frac{1-(4/3)\pi n\alpha}{1+(8/3)\pi n\alpha}.$$

In the exciton problem, the charge q is a "hole," due to the absence of an electron in the atom, and the field to be found is that sampled by the electron at $\mathbf{R}$. If the exciton mobility is low, the liquid structure will be changed in its neighborhood. This can be taken into account by appropriate changes in the correlation functions. The electron also polarizes the medium but, in the linear approximation, where $\mathbf{p}=\alpha(\mathbf{E}_{\text{hole}}^{(\text{loc})}+\mathbf{E}_{\text{electron}}^{(\text{loc})})$ the vector components of the atomic dipoles due to the electron all point toward the electron, giving a zero average field at the electron. The net field at the electron is therefore $(e/R^2)\kappa^{-1}(R)$.

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