

Deformation-potential theory for the mobility of excess electrons in liquid argon

Soumen Basak and Morrel H. Cohen

James Franck Institute and Department of Physics, University of Chicago, Chicago, Illinois 60637

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We investigate the motion of a slow electron in a simple classical fluid in the context of low-field mobility measurements of excess electrons in liquid argon, reported by Jahnke, Meyer, and Rice (JMR). The electron is described in terms of an effective Hamiltonian which is a generalization of the effective-mass Hamiltonian of an electron in a crystal. It is proposed that the primary source of electron scattering is a deformation potential produced by long-wavelength fluctuations of the fluid density. A semiphenomenological theory of the mobility is constructed on this basis. The dependence of the leading deformation-potential coefficient on the fluid density is obtained by fitting the data of JMR to the theory. A calculation of this coefficient based on a previous analysis by Jahnke, Holzworth, and Rice agrees well with that emerging from the data fitting.

I. INTRODUCTION

For ten years there have been intermittent experimental and theoretical investigations of the motion of excess electrons injected into simple insulating liquids such as argon, krypton, etc. which attempt to elucidate the nature of electronic states in fluids. One quantity of interest is the zero-field mobility of excess electrons in these fluids, where the mobility is defined as $\mu_0 = \lim(V_d/E)$ as $E \rightarrow 0$, where V_d is the electron drift velocity in a steady applied electric field E . Jahnke, Meyer, and Rice¹ (hereafter called JMR) have published extensive data on μ_0 from measurements carried out in liquid argon over a wide range of pressure and density. These data are summarized in their Fig. 11, reproduced here as Fig. 1. The mobility exhibits a maximum at a number density of fluid atoms n, n_{\max} , of approximately 0.012 \AA^{-3} (0.81 g cm^{-3}) for five different isobars ranging from 50 to 70 atmospheres. In this paper we propose an explanation for these mobility maxima, starting from a specific model for the description of electron scattering in the liquid.

A few years prior to the publication of the JMR data, Lekner² had advanced a theory of the motion of electrons in liquid argon. Lekner postulated that the electrons scatter off an *effective* potential built up of a superposition of screened-electron-single-argon-atom potentials, as in the muffin-tin approximation.³ It was essentially a single scattering approximation and gave a good accounting of the experimental data⁴ on the field dependence of the electron drift velocity at the triple point of argon, 85 K. To explain the observed mobility maxima, Lekner subsequently proposed⁵ that the average *effective* scattering length for an electron in the fluid, called $\langle a \rangle$, was a function of n and passed through zero at n_{\max} . The environmental fluctuations in $\langle a \rangle$ were suggested as the mechanism

responsible for keeping the mobility finite when $\langle a \rangle$ was zero. Using a semiempirical expression for the mobility derived by Lekner, JMR then showed that the zero scattering length model did describe correctly their mobility data, but only for densities greater than 0.014 \AA^{-3} .

In order to verify the behavior proposed by Lekner for the scattering length, Jahnke, Holzworth, and Rice⁶ (JHR) calculated $\langle a \rangle$ as a function of n from Lekner's theory and compared their result with the experimental scattering length a_{expt} , as given by the Lorentz-Lekner mobility relation [see Eq. (1) of JHR]. They found that the calculated scattering length, besides being nonzero at all densities of interest around n_{\max} , disagreed with a_{expt} in both magnitude and slope with respect to n . These authors thus were led to conclude that Lekner's single-center effective-potential model

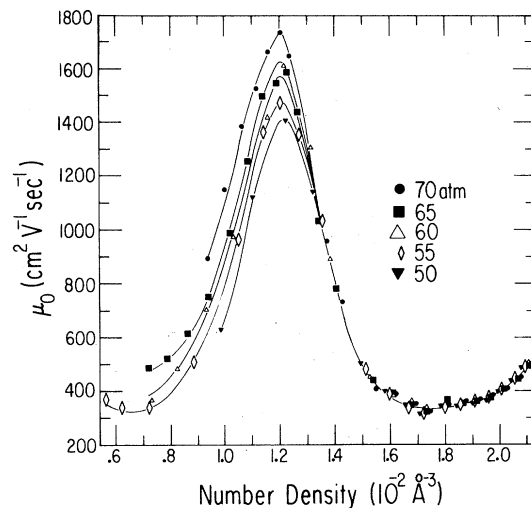


FIG. 1. Summarized data of JMR (Ref. 1) on zero-field electron mobilities as a function of number density in fluid argon.

does not give even a qualitatively correct understanding of the variation of the mobility with density.

The principal reason for the failure of Lekner's theory appears to be its neglect of the effects of multiple scattering processes. Consider an excess electron in thermal equilibrium in the otherwise empty conduction band of a simple insulating liquid. Assuming an effective mass of the order of unity for an electron within the liquid, its thermal de Broglie wavelength λ_T will be of the order of 100 molecular separations. The electron wave function must, therefore, be strongly influenced by multiple scattering from the molecules of the liquid, which are arranged without long-range order and are in motion. However, the mobility data, when interpreted in terms of the simplest version of kinetic theory, yield mean free paths (l) substantially larger than λ_T for the case of argon and other simple liquids. Apparently, the electron propagates almost freely in the material. These two contradictory observations, about strong interaction with the medium and yet a free-particle-like behavior, can be reconciled by introducing the concept of an effective Hamiltonian

$$\mathcal{H}_{\text{eff}} = p^2/2m^* + V_0. \quad (1)$$

This Hamiltonian was first introduced by one of the present authors and his coworkers⁷ in analogy with its counterpart in the effective-mass theory for electron motion in crystals. Here \vec{p} is the electronic quasimomentum, m^* is its effective mass, and V_0 is the energy at the bottom of the conduction band. It was suggested (Ref. 7) that V_0 consists of two parts. One, the kinetic energy ϵ_0 associated with the exclusion of the electron from the interiors of the molecules, can be estimated in the Wigner-Seitz approximation,⁸ which includes multiple scattering effects in a simple way. The other is the attractive polarization potential U_0 experienced by the electron between the atoms, which Lekner² estimated in a self-consistent manner.

It is useful at this point to classify and separate the effects of the different scattering processes on the electronic wave function. The wave function should be nearly as smooth as is possible under the constraints imposed by the presence of the atoms. These introduce large amplitude Fourier components on the scale of the inverse interatomic separation. Propagation of the electron through the material with occasional scattering introduces large amplitude Fourier components on the scale of the thermal wave number. Since these two regions of wave-number space are widely separated, it is possible to introduce a partition between them in a region where the amp-

litude of the Fourier coefficients of the wave function is small. Thus if q_c denotes a cutoff to the long-wavelength part of Fourier space, it should have a value in the range $2\pi/\lambda_T \ll q_c \ll 2\pi/2r_s$, where r_s is the radius of the Wigner-Seitz⁸ sphere of a fluid atom. However, the exact value of q_c is not expected to be a sensitive parameter in the theory.

The effective Hamiltonian given by Eq. (1) depends upon the local environment of the electron. The effective mass m^* and the kinetic energy term ϵ_0 in V_0 are both determined by the scattering of the electron from the fluid atoms in its vicinity. Only the wave vector \vec{k} (where $\vec{p} = \hbar\vec{k}$) is the exception, since it characterizes the slowly varying pseudo-wave-function of the electron. The molecular configuration is a function of position within the fluid, and so is each of the above parameters in H_{eff} . However, because of the smallness of p (for an electron with energy within $k_B T$ of the bottom of the conduction band), any term in H_{eff} with joint position and momentum dependence can be ignored. m^* thus can be put equal to its average value within the fluid, and the position dependence of H_{eff} restricted to that of V_0 . Thus we get

$$\mathcal{H}_{\text{eff}}(\vec{r}) = p^2/2m^* + V_0(\vec{r}), \quad (2)$$

which is a straightforward generalization of Eq. (1).

It is now easy to identify the physical origin of the scattering mechanism that determines the mobility of the electron in the fluid. Fluctuations of the local fluid density, $n(\vec{r})$, either inherent or temperature induced, will produce changes in the local environment of the electron, and thus in the potential $V_0(\vec{r})$ seen by it. It is thus fluctuating potential which scatters the electron, just as lattice deformation-potentials from acoustic phonons scatter carriers in semiconductors. The scattering potential is obtained by expanding $V_0(\vec{r})$ about its mean value \bar{V}_0 in powers of the density fluctuations

$$\Delta n(\vec{r}) = n(\vec{r}) - \bar{n}, \quad (3)$$

where \bar{n} is the average density of the fluid. Thus we arrive at the following expression for the electron scattering potential:

$$\begin{aligned} \Delta V_0(\vec{r}) &= V_0(\vec{r}) - \bar{V}_0 \\ &= V_0' \Delta n(\vec{r}) + \frac{1}{2} V_0'' [\Delta n(\vec{r})]^2 \\ &\quad + \frac{1}{6} V_0''' [\Delta n(\vec{r})]^3 + \dots, \end{aligned} \quad (4)$$

where V_0' , V_0'' , etc. are derivatives of V_0 with respect to \bar{n} and are themselves functions of \bar{n} . These derivatives are analogous to deformation-potential coefficients, coupling the density fluctua-

tions to potential fluctuations.

The preceding discussion provides us with the basis for the construction of the theory of the mobility, which we shall do in Sec. II. We shall treat the electron scattering in the Born approximation, which is valid as long as $\lambda_T \ll l$. In Sec. III we shall describe the results of fitting the data of JMR to the theory of Sec. II. In Sec. IV we examine the validity of neglecting the higher-order terms in the Born series for the electron scattering cross section. Two model calculations of the density dependence of the quantity V'_0 are described in Sec. V, where use is made of the results previously obtained by JHR. There have been measurements of the electron mobility in other liquids, yielding results which lend support to the physical picture emerging from this work. In Sec. VI, mention will be made of these experiments, which suggest the interesting possibility of a Ramsauer effect in fluids.

II. THEORY OF ELECTRON MOBILITY

Consider a small number of electrons injected into a simple insulating liquid such as argon, where they populate the low-energy states in the conduction band. From the discussions of the last section and the form of the effective Hamiltonian given by Eq. (2), these electrons can be regarded as essentially free, each having an energy $E_k = \hbar^2 k^2 / 2m^*$ measured from the conduction band minimum V_0 . Solving the Boltzmann transport equation for such an electron in the presence of a dc electric field \vec{E} and under the assumptions of

(i) elastic scattering and (ii) a small perturbation of the electron distribution proportional to the field E , one arrives at the following expression⁹ for the zero-field mobility:

$$\mu_0 = (2e/3m^*k_B T) \langle \tau_k E_k \rangle_0, \quad (5)$$

where e is the electronic charge, k_B is the Boltzmann constant, $\langle \rangle_0$ denotes average with respect to the Maxwellian energy distribution of thermalized excess electrons inside the liquid at the temperature T , and τ_k is the relaxation time defined by

$$\tau_k^{-1} = \sum_{\vec{k}'} W_{\vec{k}\vec{k}'} \left(1 - \frac{\vec{k}' \cdot \vec{E}}{\vec{k} \cdot \vec{E}} \right). \quad (6)$$

In Eq. (6), $W_{\vec{k}\vec{k}'}$ is the transition probability per unit time for scattering between plane-wave electronic states \vec{k} and \vec{k}' , given by

$$W_{\vec{k}\vec{k}'} = (2\pi/\hbar) |t_{\vec{k}\vec{k}'}|^2 \delta(E_k - E_{k'}), \quad (7)$$

where $t_{\vec{k}\vec{k}'}$ is the t matrix for the scattering and the δ function ensures that energy is conserved in the process.

One can evaluate $|t_{\vec{k}\vec{k}'}|^2$ from its usual definition, using the scattering potential $\Delta V_0(\vec{r})$ of Eq. (4). In doing this, it is possible to neglect the time dependence of $\Delta V_0(\vec{r})$, since a scattering event takes place on a time scale much smaller than that on which the density fluctuations change. The expression for $W_{\vec{k}\vec{k}'}$ that follows then consists of a series of terms, arising out of two different expansions: The expansion of $\Delta V_0(\vec{r})$ in powers of $\Delta n(\vec{r})$ as given by Eq. (4), and the Born series for the perturbation expansion of $t_{\vec{k}\vec{k}'}$, given by

$$t_{\vec{k}\vec{k}'} = \langle \vec{k} | \Delta V_0 | \vec{k}' \rangle + \sum_{\vec{k}''} \frac{\langle \vec{k} | \Delta V_0 | \vec{k}'' \rangle \langle \vec{k}'' | \Delta V_0 | \vec{k}' \rangle}{E_k - E_{k''} + i0} + \sum_{\vec{k}'', \vec{k}'''} \frac{\langle \vec{k} | \Delta V_0 | \vec{k}'' \rangle \langle \vec{k}'' | \Delta V_0 | \vec{k}''' \rangle \langle \vec{k}''' | \Delta V_0 | \vec{k}' \rangle}{(E_k - E_{k''} + i0)(E_{k''} - E_{k'''} + i0)} + \dots \quad (8)$$

We present here a simple version of the theory that incorporates the essential physics without being mathematically cumbersome. To this end, we retain only the first term in the t -matrix expansion and truncate the resulting series for $W_{\vec{k}\vec{k}'}$, keeping terms involving the product of up to four $\Delta n(\vec{r})$'s. The first simplification is justified if the scattering potential is weak. We shall check this requirement later by examining the contributions of the higher-order terms in the t -matrix series. The truncation in Δn was necessary because higher-order density-density correlations cannot be evaluated exactly. Hence, besides the two terms for which exact expressions are available, only the first two of these terms that had to be approximately calculated have been included in $W_{\vec{k}\vec{k}'}$. From Eqs. (4), (7), and (8) and the foregoing discussion, one has

$$W_{\vec{k}\vec{k}'} = (2\pi/\hbar) \delta(E_k - E_{k'}) [T_1(\vec{k}, \vec{k}') + T_2(\vec{k}, \vec{k}') + T_3(\vec{k}, \vec{k}') + T_4(\vec{k}, \vec{k}')], \quad (9)$$

where

$$\begin{aligned} T_1 &= V_0'^2 \langle \vec{k} | \Delta n(\vec{r}) | \vec{k}' \rangle \langle \vec{k}' | \Delta n(\vec{r}') | \vec{k} \rangle, \\ T_2 &= V_0' V_0'' \text{Re} \langle \vec{k} | \Delta n(\vec{r}) | \vec{k}' \rangle \langle \vec{k}' | [\Delta n(\vec{r}')]^2 | \vec{k} \rangle, \\ T_3 &= \frac{1}{4} V_0''^2 \langle \vec{k} | [\Delta n(\vec{r})]^2 | \vec{k}' \rangle \langle \vec{k}' | [\Delta n(\vec{r}')]^2 | \vec{k} \rangle, \\ T_4 &= \frac{1}{8} V_0' V_0''' \text{Re} \langle \vec{k} | \Delta n(\vec{r}) | \vec{k}' \rangle \langle \vec{k}' | [\Delta n(\vec{r}')]^3 | \vec{k} \rangle, \end{aligned} \quad (10)$$

and Re indicates the real part of an expression. As shown below T_1, \dots, T_4 depend on \vec{k} and \vec{k}' only through $\vec{q} = \vec{k} - \vec{k}'$, which is the momentum transfer in the scattering. In relating $W_{\vec{k}\vec{k}'}$ to an experimentally measured quantity such as the mobility, one has to take the thermodynamic averages of the terms defined by Eqs. (10) over all possible

amplitudes of the density fluctuations. This can be conveniently done by reexpressing these terms in terms of $\rho_{\vec{q}}$'s, the Fourier components of $\Delta n(\vec{r})$, given by

$$\Delta n(\vec{r}) = \frac{1}{\Omega} \sum_{|\vec{q}| < q_c} e^{i\vec{q} \cdot \vec{r}} \rho_{\vec{q}}, \quad (11)$$

where Ω is the volume of the system and q_c is the cutoff introduced in Sec. I. This cutoff is necessary since the local density has meaning only for distances greater than the interatomic separation, and because the effects of scattering occurring on an atomic scale have already largely been included in the effective mass and V_0 entering Eq. (2). Assuming that the plane-wave electronic states $|\vec{k}\rangle$ are normalized in the volume Ω , we have from the first of Eqs. (10) and Eq. (11)

$$\begin{aligned} \langle\langle T_1(\vec{q}) \rangle\rangle &= (V_0'^2/\Omega^2) \langle\langle \rho_{\vec{q}} \rho_{-\vec{q}} \rangle\rangle \\ &= (V_0'^2/\Omega) n S_2(q), \end{aligned} \quad (12)$$

where $\langle\langle \rangle\rangle$ represents the thermodynamic average, n is the average particle density of the system, and $S_2(q)$ its static structure factor.¹⁰ The momentum transfer q has a magnitude of the order of the thermal wave number of the electrons, for which $S_2(q)$ is essentially the same as $S_2(0)$.¹¹ This justifies our earlier *ansatz* that the electronic mobility is determined by scattering from the long-wavelength density fluctuations. We shall eventually make use of this by taking the limit $q \rightarrow 0$ in evaluating the terms in Eqs. (10). Using the well known result $S_2(0) = nk_B T \chi_T$, we then have from Eq. (12) in the limit of $q \rightarrow 0$:

$$\langle\langle T_1(0) \rangle\rangle = \lim_{q \rightarrow 0} \langle\langle T_1(q) \rangle\rangle = V_0'^2 \frac{nk_B T \chi_T}{\Omega}, \quad (13)$$

where χ_T is the isothermal compressibility of the fluid.

The next term in Eqs. (10) is

$$\langle\langle T_2(\vec{q}) \rangle\rangle = \frac{V_0' V_0''}{\Omega^3} \text{Re} \sum_{\vec{q}_1} \langle\langle \rho_{\vec{q}_1} \rho_{\vec{q} - \vec{q}_1} \rho_{-\vec{q}} \rangle\rangle,$$

where the cutoff q_c in the q -space sum has been omitted and will be implied from now on. The average of the product of three q -space density amplitudes can be exactly evaluated only in the $q \rightarrow 0$ limit; the result is¹⁰

$$\begin{aligned} \langle\langle T_2(0) \rangle\rangle &= \lim_{q \rightarrow 0} \langle\langle T_2(q) \rangle\rangle \\ &= V_0' V_0'' \frac{n}{\Omega^2} \sum_{\vec{q}_1} \left[S_2'(0) S_2(q_1) \right. \\ &\quad \left. + nk_B T \left(\frac{\partial S_2(q_1)}{\partial p} \right)_T \right], \end{aligned} \quad (14)$$

where p is the pressure.

Using the fact that

$$\left(\frac{\partial S_2(q)}{\partial p} \right)_T = n \chi_T \left(\frac{\partial S_2(q)}{\partial n} \right)_T$$

and transforming the discrete sum in q space into and integral, Eq. (14) can be written as

$$\langle\langle T_2(0) \rangle\rangle = V_0' V_0'' (n^2 k_B T \chi_T / \Omega) \alpha, \quad (15)$$

where

$$\alpha = \frac{1}{2\pi^2} \int_0^{q_c} dq q^2 \left[S_2(q) + n \left(\frac{\partial S_2(q)}{\partial n} \right)_T \right]. \quad (16)$$

Equations (13) and (15) represent the only two terms in the series for $W_{\vec{k}\vec{k}}$, for which one has exact expressions. The next two terms each involve a product of four $\Delta n(\vec{r})$'s and can only be approximately evaluated, even in the $q \rightarrow 0$ limit. From Eqs. (10), they are

$$\langle\langle T_3(\vec{q}) \rangle\rangle = \frac{V_0''^2}{4\Omega^4} \sum_{\vec{q}_1, \vec{q}_2} \langle\langle \rho_{\vec{q}_1} \rho_{\vec{q} - \vec{q}_1} \rho_{\vec{q}_2} \rho_{-\vec{q} - \vec{q}_2} \rangle\rangle,$$

$$T_4(\vec{q}) = \frac{V_0' V_0''}{3\Omega^4}$$

$$\times \text{Re} \sum_{\vec{q}_1, \vec{q}_2} \langle\langle \rho_{\vec{q}} \rho_{\vec{q}_1} \rho_{\vec{q}_2} \rho_{-\vec{q} - \vec{q}_1 - \vec{q}_2} \rangle\rangle. \quad (17)$$

To evaluate these, we have adopted the Gaussian approximation, according to which the free energy of the system containing a given set of Fourier amplitudes $\rho_{\vec{q}}$ is a sum over q of terms proportional to $|\rho_{\vec{q}}|^2$ only. The probability distribution for any $\rho_{\vec{q}}$ is then a Gaussian, and the average of a product of four $\rho_{\vec{q}}$'s can be broken up into all possible combinations of products of averages of two $\rho_{\vec{q}}$'s. For example

$$\begin{aligned} \langle\langle \rho_{\vec{q}_1} \rho_{\vec{q} - \vec{q}_1} \rho_{\vec{q}_2} \rho_{-\vec{q} - \vec{q}_2} \rangle\rangle &\approx \langle\langle \rho_{\vec{q}_1} \rho_{\vec{q} - \vec{q}_1} \rangle\rangle \langle\langle \rho_{\vec{q}_2} \rho_{-\vec{q} - \vec{q}_2} \rangle\rangle \\ &\quad + \langle\langle \rho_{\vec{q}_1} \rho_{\vec{q}_2} \rangle\rangle \langle\langle \rho_{\vec{q} - \vec{q}_1} \rho_{-\vec{q} - \vec{q}_2} \rangle\rangle \\ &\quad + \langle\langle \rho_{\vec{q}_1} \rho_{-\vec{q} - \vec{q}_2} \rangle\rangle \langle\langle \rho_{\vec{q} - \vec{q}_1} \rho_{\vec{q}_2} \rangle\rangle. \end{aligned} \quad (18)$$

Using now the definition¹⁰

$$\langle\langle \rho_{\vec{q}_1} \rho_{\vec{q}_2} \rangle\rangle = n \Omega S_2(q_1) \delta_{\vec{q}_1 + \vec{q}_2, 0},$$

one has from Eqs. (17) and (18)

$$\langle\langle T_3(\vec{q}) \rangle\rangle \approx \frac{V_0''^2}{2} \frac{n^2}{\Omega^2} \sum_{\vec{q}_1} S_2(q_1) S_2(|\vec{q} - \vec{q}_1|), \quad (19)$$

$$\langle\langle T_4(\vec{q}) \rangle\rangle \approx V_0' V_0'' \frac{n^2}{\Omega^2} S_2(0) \sum_{\vec{q}_1} S_2(q_1),$$

where use has been made of the fact that $\vec{q} \neq 0$ in the expression for $\langle\langle T_3(\vec{q}) \rangle\rangle$. In the long-wavelength limit $q \rightarrow 0$, these equations can be written in the form

$$\begin{aligned}\langle\langle T_3(0) \rangle\rangle &= \lim_{q \rightarrow 0} \langle\langle T_3(\vec{q}) \rangle\rangle = V_0''^2 (n^2 / \Omega^2) \beta, \\ \langle\langle T_4(0) \rangle\rangle &= \lim_{q \rightarrow 0} \langle\langle T_4(\vec{q}) \rangle\rangle \\ &= V_0' V_0''' (n^2 / \Omega^2) n k_B T \chi_T \lambda,\end{aligned}\quad (20)$$

where

$$\begin{aligned}\beta &= \frac{1}{2\pi^2} \int_0^{q_c} dq q^2 S_2(q), \\ \gamma &= \frac{1}{4\pi^2} \int_0^{q_c} dq q^2 [S_2(q)]^2.\end{aligned}\quad (21)$$

Collecting together the relevant results from Eqs. (9) through (21), one arrives at the following expression for the thermodynamically averaged transition probability

$$\begin{aligned}\langle\langle W_{\vec{k}\vec{k}'} \rangle\rangle &= (2\pi/\hbar) \delta(E_{\vec{k}} - E_{\vec{k}'}) (n^2 / \Omega) \\ &\times (V_0''^2 k_B T \chi_T + V_0' V_0'' k_B T \chi_T \alpha \\ &+ V_0''^2 \beta + V_0' V_0''' n k_B T \chi_T \gamma).\end{aligned}\quad (22)$$

In calculating τ_k^{-1} using Eqs. (6) and (22), it is necessary to sum over \vec{k}' states of a given spin only, since the scattering does not flip the electron spin. The final expression for the mobility, obtained from Eq. (5), is rewritten in a form convenient for comparison with the experimental data:

$$\begin{aligned}\mu_0^{-1} n^{-2} T^{-1/2} &= \frac{3m_e^2}{2c\hbar^4} \left(\frac{m_e k_B}{2\pi} \right)^{1/2} \left(\frac{m^*}{m_e} \right)^{5/2} \\ &\times (V_0''^2 k_B T \chi_T + V_0' V_0'' k_B T \chi_T \alpha \\ &+ V_0''^2 \beta + V_0' V_0''' n k_B T \chi_T \gamma),\end{aligned}\quad (23)$$

where m_e is the mass of the free electron.

III. COMPARISON WITH EXPERIMENTAL DATA

Equation (23) expresses the implicit dependence of the electronic mobility on the fluid density n , through both the thermodynamic variables T and χ_T and the phenomenological deformation-potential coefficients $V_0'(n)$, $V_0''(n)$, and $V_0'''(n)$. We have extracted the density dependence of the latter coefficients required to fit the data of JMR to Eq. (23), using the thermodynamic data provided by them. The integrals contained in α , β , and γ were performed numerically using the closed form expression for $S_2(q)$ given by Ashcroft and Lekner,¹¹ with the hard-sphere diameter of the fluid argon atom taken as 3.44 Å.¹² The upper limit q_c in these integrals was also a phenomenological parameter whose value was adjusted for best fit to the data. As mentioned before, q_c was introduced to eliminate density fluctuations of wavelength smaller than the mean interatomic spacing $2r_s$, where r_s is the Wigner-Seitz radius⁸ defined through $4\pi r_s^3/3 = 1/n$. Thus q_c was put equal to A/r_s in the integrals in α , β , and γ and the param-

eter A varied to obtain a best fit to the data. To be consistent with the assumptions made in introducing q_c , the optimum value of A should be significantly smaller than π .

The factor involving m^*/m was ignored in the data fitting. As calculated by JHR, this quantity decreases monotonically with increasing n by a factor of 1.6 over the range of densities involved in the fit and so does not affect the results in any significant manner.

The left-hand side of Eq. (23) contains the experimentally measured mobility μ_0 as well as the fluid state variables n and T , while the right-hand side contains all the phenomenological parameters besides n , T , χ_T . The aim of the fitting procedure was to find an empirical analytic form for V_0' as a function of n which, together with its derivatives $V_0''(n)$ and $V_0'''(n)$, when substituted in Eq. (23) would match the two sides of it for all densities covered by the data. The goodness of the fit was judged by the value of χ^2 , calculated from the 5% uncertainty in the μ_0 values and the 1% uncertainty of the thermodynamic data quoted by JMR.

Several polynomial forms in n were tried as the desired representation for $V_0'(n)$, progressing from a linear dependence of V_0' on n , through quadratic to cubic. The goodness of the fit increased less rapidly as the degree of the polynomial used for $V_0'(n)$ increased. After examining the behavior of the individual terms on the right-hand side of Eq. (23) as the form used for V_0' was varied, it was decided to use the following empirical function to represent $V_0'(n)$ for fitting the data:

$$V_0'(n) = a + b \tanh[c(n - n_0)], \quad (24)$$

where a , b , c , and n_0 are the variable parameters in the fit. It should be remarked that the detailed density dependence of $V_0'(n)$ emerging from the data-fitting should not be taken seriously since it depends on the empirical form given by Eq. (24), which was chosen only for convenience. The important things to observe in this empirical V_0' are its order of magnitude and the density at which it changes sign, which can be compared with similar features of the $V_0'(n)$ emerging from model calculations.

The mobility data at 70 atm pressure were fitted to Eq. (23) in three stages: (i) first, only those two terms on the right-hand side which involve V_0'' and $V_0''^2$ were used in the fit; (ii) then the term involving the product $V_0' V_0''$ was added to the first two, and (iii) finally the fourth term involving $V_0' V_0'''$ was included. The best-fit forms for V_0' as a function of n in these three cases are shown in Fig. 2. The smooth curves in Figs. 3(a)–3(c) show the actual fit of the right-hand side of Eq. (23) to its left-hand side, represented in these

figures by the points with experimental error bars assigned to them. Good fits to the data at other pressures (viz. $P = 50, 55, 60,$ and 65 atm) were obtained with essentially the same $V'_0(n)$.

Figure 2 shows that $V'_0(n)$ changes appreciably not in magnitude but in slope in going from case (i) to case (iii). At the same time, the quality of the fit to Eq. (23) deteriorates, as shown in Figs. 3(a)–3(c). The possible conclusion emerging from these observations is that the first two terms on the right-hand side of Eq. (23) are sufficient to reproduce the essential features of the mobility data, such as the order of magnitude of μ_0 and the maximum in μ_0 at the intermediate density. The inclusion of more terms on the right-hand side of Eq. (23), done for the sake of making the theory more rigorous, points to the inadequacy of such a simple empirical form for $V'_0(n)$ as given by Eq. (24).

The best-fit values of the parameter A are 3.2, 2.8, and 2.2 in cases (i), (ii), and (iii), respectively. The first value corresponds very nearly to a cutoff of π/r_s in the q -space integrals, thus effectively eliminating density fluctuations of wavelength smaller than the mean interatomic spacing $2r_s$. With the inclusion of more terms on the right-hand side of Eq. (23), this cutoff systematically shifts to longer wavelengths, which is the right direction with respect to the consistency criterion $q_0 \ll \pi/r_s$ mentioned earlier.

The following observations hold for all the three

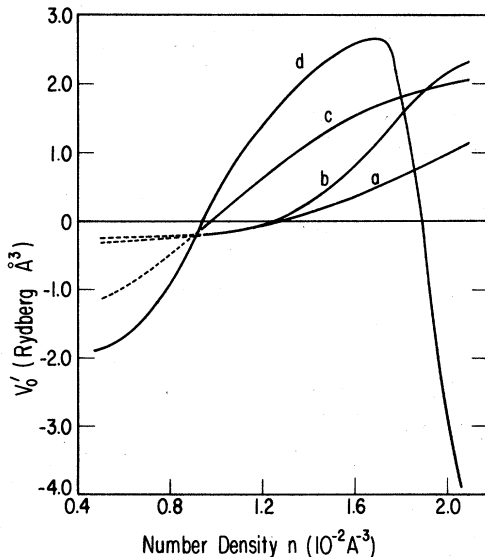


FIG. 2. Curves (a), (b), and (c) represent the empirical $V'_0(n)$ which give the best fit of the JMR data to Eq. (23) for the three cases discussed in Sec. III. The dotted portions of these curves are extrapolations to densities lower than those at which the fits were made. Curve (d) represents the $V'_0(n)$ obtained using the Wigner-Seitz approximation, as discussed in Sec. V.

cases (i)–(iii): At the highest densities considered, the series represented by the four terms on the right-hand side of Eq. (23) converged adequately with the first term making the dominant contribution. The contribution of the fourth term tended to be larger than those of the second and third terms, perhaps because the last term at which the series for W_{EG} is cutoff bears the weight of the omitted terms and thus contributes disproportionately to Eq. (23). At the lower densities, the convergence was marginal, the first

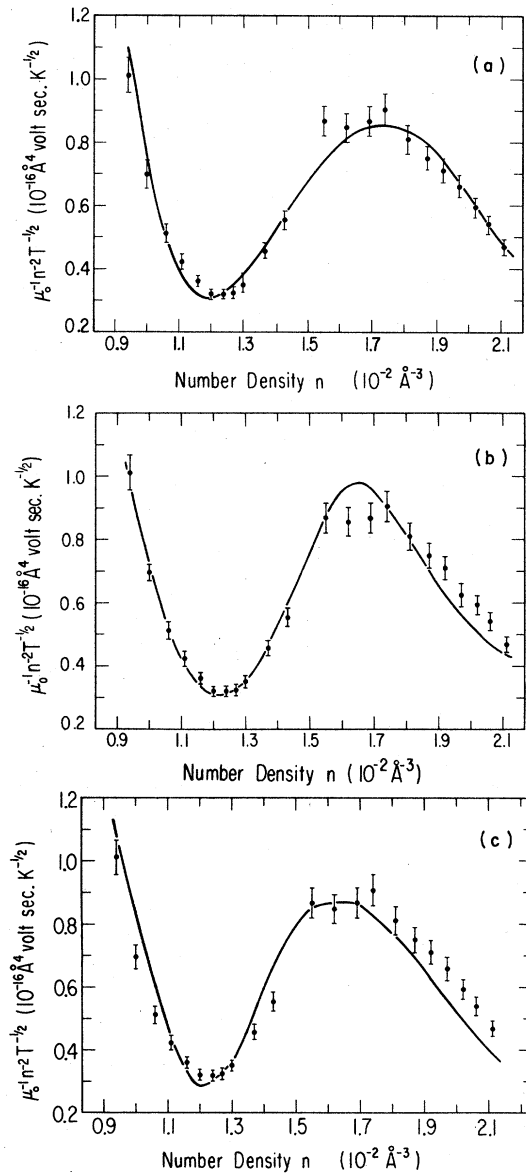


FIG. 3. (a)–(c). Fit of the JMR data to Eq. (23) using the empirical $V'_0(n)$ shown in Fig. 2 and for the three cases (i)–(iii) discussed in Sec. III. In each case, the solid line represents the right-hand side of Eq. (23) and the circles the left-hand side.

term dominating near the mobility maximum and with all other terms being of similar magnitudes elsewhere.

Although the data fitting has been carried out over the entire range of densities covered by the mobility data, Figs. 3(a)–3(c) show the results only down to about $n=0.0100 \text{ \AA}^{-3}$. Below this density the quality of the fit becomes considerably worse than that shown in these figures. The reason why the fit goes bad is probably not the inadequacy of the theory as it stands, but the use of erroneous information on the structure factor of a fluid. The structure factor of a hard-sphere fluid, as evaluated from the closed form expression given by Ashcroft and Lekner,¹¹ has a very small constant value for a considerable range of q from 0 to about 0.5 \AA^{-1} at all densities. However, as the data of Mikolaj and Pings¹³ and others¹⁴ on the scattering of x rays from fluid argon show, at low densities the structure factor increases with decreasing q near $q=0$. This maximum in $S_2(q)$ at small q is quite pronounced at densities close to the critical point in the liquid-gas phase diagram of argon, and is caused by strong density fluctuations that become increasingly prominent as the critical point is approached. The use of the Ashcroft and Lekner solution for the structure factor has thus led to estimates of α , β , and γ , which are quite far removed from what they actually are for liquid argon. It is our belief that the fit goes bad at low densities because of these wrong estimates for α , β , and γ . That the fit should be good at higher densities is also consistent with this argument. The data of Mikolaj and Pings¹³ show that the low scattering-angle peak in $S_2(q)$ becomes less prominent as the density gets higher, thus making the hard-sphere model estimates of α , β , and γ close to what they should actually be for liquid argon.

We have tried to incorporate the correct experimental information on the structure factor into the data-fitting scheme. The experimental data^{13,14} on $S_2(q)$ exist only at a few densities and pres-

ures. We have made rough interpolations and extrapolations of this data to obtain $S_2(q)$ at all the pressures and densities at which the mobility measurements were made. When the mobility data was fitted to Eq. (23) with the same empirical form for $V'_0(n)$ as given by Eq. (24), and with this new input on the structure factor, a fit as good as that shown in Figs. 3(a)–3(c) was not found. Obviously, the empirical form for $V'_0(n)$ was inadequate, and it was not considered worth looking for another suitable form for $V'_0(n)$ due to the approximate nature of the information on $S_2(q)$. However, one thing did emerge from this new effort on fitting the data. It is that the best-fit value of the parameter A was further reduced to 0.8, which lends good support to the basic assumption of scattering of electrons by long-wavelength density fluctuations.

In summarizing this section, it is thus possible to state that the order of magnitude of the mobility and its maximum around $n=0.0120 \text{ \AA}^{-3}$ are well represented by Eq. (23) with the empirical $V'_0(n)$ shown in Fig. 2. The mobility data at densities lower than 0.0100 \AA^{-3} may also be reproduced when accurate information on the structure factor of the fluid becomes available. A slightly different $V'_0(n)$ would be required.

IV. CONVERGENCE OF THE BORN APPROXIMATION FOR $W_{\vec{k}\vec{k}'}$

In this section we examine the effect of neglecting all terms except the first in the Born series for $t_{\vec{k}\vec{k}'}$, as has been done in writing down Eq. (9) for $W_{\vec{k}\vec{k}'}$. For reasons already cited preceding that equation, we again confine our attention to only those terms in the series for $W_{\vec{k}\vec{k}'}$ which involve the product of up to four Δn 's but this time include also the contributions of the second- and third-order terms in the Born series for $t_{\vec{k}\vec{k}'}$, shown in Eq. (8). The complete series for the averaged $W_{\vec{k}\vec{k}'}$, truncated at the order mentioned, then stands as follows:

$$\begin{aligned}
 \langle\langle W_{\vec{k}\vec{k}'} \rangle\rangle &= \frac{2\pi}{\hbar} \delta(E_{\vec{k}} - E_{\vec{k}'}) \left(\frac{V_0'^2}{\Omega^2} \langle\langle \rho_{\vec{q}} \rho_{-\vec{q}} \rangle\rangle + \frac{V_0' V_0''}{\Omega^3} \text{Re} \sum_{\vec{q}} \langle\langle \rho_{\vec{q}} \rho_{\vec{q}_1} \rho_{-\vec{q} - \vec{q}_1} \rangle\rangle \right. \\
 &+ \frac{V_0''^2}{4\Omega^4} \sum_{\vec{q}_1, \vec{q}_2} \langle\langle \rho_{\vec{q}_1} \rho_{\vec{q}_2} \rho_{-\vec{q} - \vec{q}_2} \rho_{\vec{q} - \vec{q}_1} \rangle\rangle + \frac{V_0' V_0''}{3\Omega^4} \text{Re} \sum_{\vec{q}_1, \vec{q}_2} \langle\langle \rho_{\vec{q}} \rho_{\vec{q}_1} \rho_{\vec{q}_2} \rho_{-\vec{q} - \vec{q}_1 - \vec{q}_2} \rangle\rangle \\
 &+ \frac{2V_0'^3}{\Omega^3} \text{Re} \sum_{\vec{q}_1} \frac{\langle\langle \rho_{\vec{q}} \rho_{\vec{q}_1} \rho_{-\vec{q} - \vec{q}_1} \rangle\rangle}{E_{\vec{k}'} - E_{\vec{k}' + \vec{q}_1} + i0} + \frac{V_0'^2 V_0''}{\Omega^4} \text{Re} \sum_{\vec{q}_1, \vec{q}_2} \frac{\langle\langle \rho_{\vec{q}_1} \rho_{\vec{q}_2} \rho_{\vec{q} - \vec{q}_1} \rho_{-\vec{q} - \vec{q}_2} \rangle\rangle}{E_{\vec{k}'} - E_{\vec{k}' + \vec{q}_2} + i0} \\
 &+ \frac{V_0'^2 V_0''}{\Omega^4} \text{Re} \sum_{\vec{q}_1, \vec{q}_2} \frac{\langle\langle \rho_{\vec{q}} \rho_{\vec{q}_1} \rho_{\vec{q}_2} \rho_{-\vec{q} - \vec{q}_1 - \vec{q}_2} \rangle\rangle + \langle\langle \rho_{\vec{q}} \rho_{\vec{q}_1} \rho_{-\vec{q}_2} \rho_{\vec{q}_2} \rho_{-\vec{q} - \vec{q}_1} \rangle\rangle}{E_{\vec{k}'} - E_{\vec{k}' + \vec{q}_1} + i0} \\
 &+ \frac{2V_0'^4}{\Omega^4} \text{Re} \sum_{\vec{q}_1, \vec{q}_2} \frac{\langle\langle \rho_{\vec{q}} \rho_{\vec{q}_1} \rho_{-\vec{q}_2} \rho_{\vec{q}_2} \rho_{-\vec{q} - \vec{q}_1} \rangle\rangle}{(E_{\vec{k}'} - E_{\vec{k}' + \vec{q}_1} + i0)(E_{\vec{k}'} - E_{\vec{k}' + \vec{q}_2} + i0)} \\
 &+ \left. \frac{V_0'^4}{\Omega^4} \text{Re} \sum_{\vec{q}_1, \vec{q}_2} \frac{\langle\langle \rho_{\vec{q}_1} \rho_{\vec{q}_2} \rho_{-\vec{q} - \vec{q}_1} \rho_{\vec{q} - \vec{q}_2} \rangle\rangle}{(E_{\vec{k}'} - E_{\vec{k}' + \vec{q}_1} + i0)(E_{\vec{k}'} - E_{\vec{k}' - \vec{q}_2} - i0)} \right). \tag{25}
 \end{aligned}$$

It is seen that the Born approximation result for $W_{\mathbf{k}\mathbf{k}'}$, as given by Eq. (9), is reproduced here in the first four terms of Eq. (25). We shall examine in the following the magnitudes of two representative terms from the rest of the present series

$$\begin{aligned} \langle\langle T_5(q) \rangle\rangle &= \frac{2V_0'^4}{\Omega^3} \operatorname{Re} \sum_{\mathbf{q}_1} \frac{\langle\langle \rho_{\mathbf{q}} \rho_{\mathbf{q}_1} \rho_{-\mathbf{q}-\mathbf{q}_1} \rangle\rangle}{E_{\mathbf{k}'} - E_{\mathbf{k}' + \mathbf{q}_1} + i0} \\ &\approx \frac{2V_0'^3}{\Omega^3} \frac{2m_e}{\hbar^2} \frac{\Omega}{(2\pi)^3} \operatorname{Re} \int_0^{q_c} dq_1 q_1^2 \langle\langle \rho_{\mathbf{q}} \rho_{\mathbf{q}_1} \rho_{-\mathbf{q}-\mathbf{q}_1} \rangle\rangle \int_{-1}^1 \frac{d\mu \times 2\pi}{-2k'q_1\mu - q_1^2 + i0} \\ &= \frac{2V_0'^3}{\Omega^2} \frac{2m_e}{\hbar^2} \frac{1}{4\pi^2} \int_0^{q_c} dq_1 q_1^2 \langle\langle \rho_{\mathbf{q}} \rho_{\mathbf{q}_1} \rho_{-\mathbf{q}-\mathbf{q}_1} \rangle\rangle \frac{1}{2k'q_1} \ln \left| \frac{q_1 - 2k'}{q_1 + 2k'} \right|. \end{aligned}$$

The quantity $\langle\langle \rho_{\mathbf{q}} \rho_{\mathbf{q}_1} \rho_{-\mathbf{q}-\mathbf{q}_1} \rangle\rangle$ can be taken out of the integral over μ in the approximation that either q or q_1 is small. The integral above cannot be exactly evaluated, since $\langle\langle \rho_{\mathbf{q}} \rho_{\mathbf{q}_1} \rho_{-\mathbf{q}-\mathbf{q}_1} \rangle\rangle$ is unknown. To make an order of magnitude estimate, we broke up the interval of integration into two parts: one from zero to q_0 over which $\langle\langle \rho_{\mathbf{q}} \rho_{\mathbf{q}_1} \rho_{-\mathbf{q}-\mathbf{q}_1} \rangle\rangle$ can be approximately replaced by $\langle\langle \rho_{\mathbf{q}} \rho_{\mathbf{q}_1} \rho_{-\mathbf{q}} \rangle\rangle$, and the other from q_0 to q_c over which the ln term can be approximated by $-4k'/q_1$. For the purpose of estimation let us take $q_0 = 4k_{\text{th}} \approx 4k'$, where k_{th} is the wave number corresponding to the thermal de Broglie wavelength of the electron. Then for the $q \rightarrow 0$ limit we get, making use of Eq. (14),

$$\langle\langle T_5(0) \rangle\rangle \approx -(2m_e V_0'^3 / \pi^2 \hbar^2) (n^2 / \Omega) k_B T \chi_T \kappa,$$

where

$$\begin{aligned} \kappa &= q_0 \left[S_2(0) + \lim_{q \rightarrow 0} n \left(\frac{\partial S_2}{\partial n} \right)_q \right] \\ &\quad + \int_{q_0}^{q_c} dq \left[S_2(q) + \frac{q}{3} \left(\frac{\partial S_2}{\partial q} \right)_n + n \left(\frac{\partial S_2}{\partial n} \right)_q \right]. \end{aligned}$$

The ratio of the contributions to the right-hand side of Eq. (23) of this term, had it been incorporated in Eq. (9) for $W_{\mathbf{k}\mathbf{k}'}$, and the similar term $\langle\langle T_2(0) \rangle\rangle$ is

$$R_1 = - \frac{2m_e}{\pi^2 \hbar^2} \frac{V_0'^2}{V_0''} \frac{\kappa}{\alpha}. \quad (26)$$

We have examined this ratio for values of V_0' , V_0'' , and A which best fit the data of JMR to Eq. (23), as given by curve (c) in Fig. 2. R_1 is negative for all densities and its magnitude, starting at 0.003 at a density of 0.0094 \AA^{-3} , increases steadily (i.e., it is 0.094 at $n = 0.0127 \text{ \AA}^{-3}$) to reach the value 1.40 at the highest density, i.e., at 0.0211 \AA^{-3} . Consider next the term,

$$\langle\langle T_6(q) \rangle\rangle = \frac{V_0'^2 V_0''}{\Omega^4} \operatorname{Re} \sum_{\mathbf{q}_1, \mathbf{q}_2} \frac{\langle\langle \rho_{\mathbf{q}} \rho_{\mathbf{q}_1} \rho_{\mathbf{q}_2} \rho_{-\mathbf{q}-\mathbf{q}_1-\mathbf{q}_2} \rangle\rangle}{E_{\mathbf{k}'} - E_{\mathbf{k}' + \mathbf{q}_2} + i0}$$

which, in the Gaussian approximation described

for $W_{\mathbf{k}\mathbf{k}'}$ relative to the ones already used in constructing the theory in Sec. II. In doing this, we will use for V_0' , V_0'' , and V_0''' the values obtained for the best fit of the JMR data to Eq. (23), as explained in Sec. III. Consider the term

before and in the $q \rightarrow 0$ limit, is

$$\langle\langle T_6(0) \rangle\rangle \approx 2V_0'^2 V_0'' \frac{2m_e}{\hbar^2} \frac{n^2}{\Omega^2} \sum_{\mathbf{q}_1} \frac{[S_2(q_1)]^2}{k'^2 - |\mathbf{k}' + \mathbf{q}_1|^2 + i0}.$$

Converting the q_1 sum into an integral and breaking up the interval of integration into two parts as before, we arrive at the approximate result

$$\langle\langle T_6(0) \rangle\rangle \approx -(2m_e / \pi^2 \hbar^2) V_0'^2 V_0'' (n^2 / \Omega) \xi,$$

where

$$\xi = q_0 [S_2(0)]^2 + \int_{q_0}^{q_c} dq [S_2(q)]^2.$$

We have examined the ratio of the contributions of this term and $\langle\langle T_3(0) \rangle\rangle$ to Eq. (23), which is

$$R_2 = \frac{-2m_e}{\pi^2 \hbar^2} \frac{V_0'^2}{V_0''} \frac{\xi}{\beta}. \quad (27)$$

This ratio varies from 0.003 at $n = 0.0094 \text{ \AA}^{-3}$ through 0.111 at $n = 0.0127 \text{ \AA}^{-3}$ to 2.186 at $n = 0.0211 \text{ \AA}^{-3}$, and is always negative.

The contributions of the other terms of Eq. (25) to Eq. (23) can be similarly calculated and compared with those already included in the latter equation; all such contributions are of the same order of magnitude. Thus, the higher Born approximation corrections appear unimportant at low densities, where T_2 and T_3 are important, and are comparable to or larger than T_2 and T_3 at densities at which the latter are small compared to T_1 . We conclude that the Born series for $t_{\mathbf{k}\mathbf{k}'}$ is not rapidly convergent; however, the corrections introduced into Eq. (23) on this account will not be significant.

V. MODEL CALCULATIONS OF $V_0(n)$ AND $V_0'(n)$

In this section we have estimated, using two different models, the energy $V_0(n)$ of the conduction band minimum for an excess electron in liquid argon for several values of the density n . From

these estimates the quantity $V'_0(n)$ is obtained as a function of n and compared with the $V'_0(n)$ emerging from the data fitting.

As mentioned earlier, V_0 consists of two parts. One of these is the background potential U_0 , which includes² the effects of (i) the screening of the polarization part of the electron-argon-atom interaction by the surrounding atoms, and (ii) the overlapping of neighboring atomic fields. JMR have evaluated U_0 for liquid argon at several densities extending over the range of fluid states covered by their experiments. The other is the kinetic energy term ϵ_0 ; this we shall estimate in two different models, each of which represents the liquid only approximately.

First, as in Lekner's theory,² we consider the liquid as a collection of atoms which scatter weakly and singly; the kinetic energy term can then be written as $\epsilon_0 = \hbar^2 k_{\text{opt}}^2 / 2m_e$, where $k_{\text{opt}} = (4\pi n \langle a \rangle)^{1/2}$ in the single-scattering, optical-model,¹⁵ approximation. This gives for the conduction band minimum

$$V_0(n) = (\hbar^2 / 2m_e) 4\pi n \langle a \rangle + U_0, \quad (28)$$

where both $\langle a \rangle$ and U_0 are functions of the fluid density n . Using the values of U_0 and $\langle a \rangle$ given by JHR, we have calculated k_{opt} , ϵ_0 , and V_0 in this model at a number of densities and displayed them in Table I. From Eq. (28) we can write

$$V'_0(n) = (\hbar^2 / 2m_e) 4\pi \langle a \rangle + (\hbar^2 / 2m_e) 4\pi n \langle a \rangle' + U'_0, \quad (29)$$

where primes denote derivatives with respect to n . It should be pointed out that had we set the scattering potential ΔV_0 equal to $V'_0 \Delta n$ in Eq. (4) and neglected the terms involving $\langle a \rangle'$ and $U'_0(n)$ in the expression for $V'_0(n)$ given by Eq. (29), we would

have arrived at the same expression for the mobility as that obtained by Lekner.² To show qualitatively what is wrong with this procedure, we have used the results of Table I to estimate V'_0 numerically as a function of density as obtained by (i) neglecting the density dependences of $\langle a \rangle$ and U_0 and (ii) including such density dependences. The results are shown in Fig. 4. It is seen that curve (a), which represents the single term $\hbar^2 4\pi \langle a \rangle / 2m_e$, increases slowly and monotonically over the experimental range of densities, thereby ruling out any chance of leading to the mobility maxima in the framework of Lekner's theory.² However, curve (b), representing the full expression for V'_0 in Eq. (29), does show a minimum, albeit very flat, around a density of 0.012 \AA^{-3} . This result can, in principle, reproduce the observed maxima in the density dependence of the mobility. But the exact shapes of the mobility curves and the magnitudes of the mobilities so obtained do not compare well with experiment. Thus, the foregoing analysis only has value in pointing out that a successful interpretation of the mobility data requires incorporating into the theory the nontrivial density dependence of the average potential U_0 and the effective scattering length $\langle a \rangle$.

The optical-model¹⁵ approximation used above is good only in the limit of a low density of scatterers. In the range of higher densities pertaining to real liquids, strong multiple scattering of the excess electron from neighboring fluid atoms becomes the predominant factor which sets the energy scale of the electron. We incorporate this into our analysis most simply by replacing k_{opt} with k_0 in evaluating ϵ_0 , where k_0 is determined via the Wigner-Seitz approximation⁸ from the relation $\tan k_0(r_s - \langle a \rangle) = k_0 r_s$. The values of k_0 and V_0 calculated in this model are also dis-

TABLE I. Conduction-band minimum energy of an excess electron in liquid argon (V_0).

Fluid density n (\AA^{-3})	Calculated scattering length $\langle a \rangle$ (\AA)	Maximum average potential $-U_0$ (Ry.)	Optical-model approximation			Wigner-Seitz approximation		
			$k_{\text{opt}} = (4\pi n \langle a \rangle)^{1/2}$ (\AA^{-1})	$\epsilon_0 = \frac{\hbar^2 k_{\text{opt}}^2}{2m}$ (Ry.)	Cond.-band minimum energy $-V_0$ (Ry.)	k_0^a (\AA^{-1})	$\epsilon_0 = \frac{\hbar^2 k_0^2}{2m}$ (Ry.)	Cond.-band minimum energy $-V_0$ (Ry.)
0.004 22	0.601 ^b	0.047 ^c	0.178 ^b	0.009	0.038	0.208 ^d	0.012	0.035
0.008 08	0.652	0.070	0.257	0.018	0.052	0.319	0.029	0.041
0.011 76	0.677	0.087	0.316	0.028	0.059	0.410	0.047	0.040
0.014 82	0.693	0.099	0.359	0.036	0.063	0.482	0.065	0.034
0.016 82	0.706	0.109	0.386	0.042	0.067	0.529	0.078	0.031
0.019 03	0.720	0.121	0.414	0.048	0.073	0.584	0.095	0.026
0.021 13	0.772	0.157	0.452	0.057	0.100	0.667	0.125	0.032

^a See Sec. V of text.

^b See Reference 6.

^c See Reference 1.

^d Our value differs somewhat from that calculated in Ref. 6, especially at the higher densities.

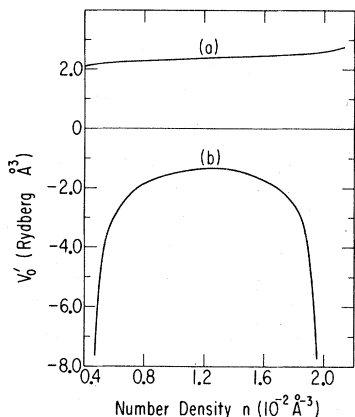


FIG. 4. Curve (a) represents $V'_0(n)$ obtained using the optical-model approximation, as given by Eq. (29); curve (b) represents only the first term on the right-hand side of Eq. (29).

played in Table I and are used to estimate numerically the corresponding $V'_0(n)$. The curve (d) in Fig. 2 is a plot of this V'_0 against the density, which is reasonably close in magnitude and shape to the curve (c) for the empirical form of V'_0 in the range of densities between 0.010 \AA^{-3} and 0.016 \AA^{-3} . That the Wigner-Seitz model estimate of V'_0 then deviates considerably from the empirical V'_0 is, we believe, due to erroneous estimates by JMR of $\langle a \rangle$ and U_0 at high densities. It will be observed from Table I that at the higher densities V'_0 is a small difference between two large contributions, ϵ_0 (repulsive) and U_0 (attractive). Any small errors in these contributions are likely to be magnified in V'_0 .

In closing, we remark that these two models for V_0 (and V'_0) are both approximate and represent, at best, two opposite extremes of the true physical picture of a liquid. The optical model approximation can be expected to be good only for dilute gases, while the Wigner-Seitz approximation can really be applied with confidence only to close packed solids. However, of the two, the latter seems to us to be a more plausible approximation because of the importance of the multiple scattering effect in liquids, which the Wigner-Seitz approximation represents well.

VI. DISCUSSION

In this paper we have proposed a theory for the mobility of excess electrons in a simple insulating liquid based on the scattering of such electrons from long-wavelength density fluctuations. The electronic motion couples to these fluctuations through a deformation-potential V'_0 which is a function of the density of the liquid. As Fig. 2 shows, the V'_0 which gives a best fit of the data to this theory goes through zero at a density close to

that at which the maxima in the mobility occur. This is one of the important results suggested by our work, namely that the maximum in the mobility is caused by the vanishing of the leading deformation potential coefficient. A similar idea was proposed by Lekner,⁵ who claimed that the *effective* scattering length $\langle a \rangle$ vanishes at the density of the maxima. However, the calculations of JHR clearly showed that $\langle a \rangle$ did not show the right density dependence for this purpose, at least within the context of Lekner's theory of an *effective* scattering potential. On the other hand $V'_0(n)$, as obtained from the two model calculations shown in this paper, exhibits very strong density dependence and in one case passes through zero at almost the same density at which does the empirical $V'_0(n)$. It thus appears that Lekner's idea of a Ramsauer minimum¹⁶ in the scattering of electrons in liquid argon may indeed be true, provided the scattering is described in terms of a deformation-potential appropriate for fluids.

There is evidence for this type of generalized Ramsauer effect occurring in other fluids. Holroyd and Cipollini¹⁷ have reported maxima in the excess electron mobility in liquid neopentane and TMS at densities where the conduction band energy V_0 shows a minimum in these liquids. The authors have suggested that around the minimum of V_0 , the potential fluctuations caused by density fluctuations will be minimal, causing a minimum in the electron scattering and a maximum in the mobility. This is a physical statement of the interesting result mentioned in the last paragraph. Such correspondence between the maxima in the excess electron mobility and the minimum in V_0 have also been suggested¹⁸ in the case of fluid hydrocarbons such as methane and ethane.

Although there is qualitative agreement between the results of Secs. III and V, there is a number of ways in which the work described here can be improved. The term ϵ_0 has been evaluated using two simplified models, none of which really applies to a liquid. The short-wavelength multiple scattering of an electron from its neighbors is important in a liquid, but the molecular packing is not necessarily dense or regular enough to warrant the use of the Wigner-Seitz approximation. This method assumes the electron to be in the field of a fluid atom which is at the center of the Wigner-Seitz sphere formed by its close-packed neighbors. Disorder in the packing geometry of atoms in a liquid can cause (i) deviation in the shape of the volume enclosed by nearest neighbors from a sphere and (ii) displacement of the central atom from the geometrical center of the enclosed volume. In order to arrive at reliable quantitative results in the present case, one therefore requires a

more detailed analysis of the multiple scattering problem than use of the Wigner-Seitz approximation.

Another direction of improvement of the theory lies in the construction of the potential underlying the calculation of U_0 and of $\langle a \rangle$. The calculations of JMR were done following the prescriptions of Lekner for screening and for averaging the potential of the surrounding atoms. Both of these are simplified, but as yet we have nothing better. Any errors originating here may be magnified by the fact that the contributions of U_0 and ϵ_0 to V_0 are of opposite sign. Finally, the convergence of the series for $\Delta V_0(\vec{r})$ and $t_{\vec{k}\vec{k}'}$, though satisfactory, is not excellent. Any effort to improve this by reformulating the problem will certainly help place the present theory on firmer grounds.

In conclusion, it appears that our model of an electron residing in a quasi-free-state in the conduction band of a liquid and getting occasionally scattered by density fluctuations represents quite

accurately the motion of an excess electron in a simple liquid. The deformation-potential coefficients show density dependence strong enough to produce the observed structure in the mobility curves, thereby removing the need for any further manipulation of the scattering length $\langle a \rangle$, which has been shown⁶ to have a density dependence which is much too weak for this problem. The present work needs refinement, however, in the way of a more careful evaluation of V_0 . At the same time, this work gives rise to the interesting notion of a generalized Ramsauer effect¹⁶ in condensed media.

ACKNOWLEDGMENT

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