

COMMENTS AND ADDENDA

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Comments on the Theory of Electron Mobility in Simple Fluids

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The theory of Lekner for the scattering of excess electrons in fluid argon has been applied for densities lower than that at the triple point. We point out some discrepancies between the theory and recent experimental electron-mobility data in fluid argon.

In a recent paper from this laboratory¹ a comparison was made between experimental and theoretical²⁻⁴ zero field mobilities of an excess electron in fluid argon. It was shown that the electron mobility μ_0 could be related to an empirical effective scattering length $\tilde{\alpha}$. Given that single-scattering processes dominate the rate of dissipation of energy, and that the electrons remain in thermal equilibrium with the fluid (and hence have a Maxwell velocity distribution at temperature T), the effective scattering length can be calculated from the Lorentz-Lekner mobility relation²

$$\tilde{\alpha}_{\text{expt}} = \pm [(18\pi^3 k_B/e)^{1/2} m^{1/2} T^{3/2} n^2 \chi_T \mu_0]^{-1/2}. \quad (1)$$

Here m is the electron mass, χ_T the isothermal compressibility of the fluid, n the number density of the fluid, e the electronic charge, and k_B the Boltzmann constant. After noting that the calculated single-center e^- -Ar average scattering length at the triple point is positive,² while that for the free atom is negative, Lekner proposed^{3,4} a "zero scattering length" model to explain the mobility maxima which occur in excess-electron-heavy-rare-gas fluid systems. According to this model, the single-center average scattering length $\langle a \rangle$ passes through zero at n_{max} , the fluid density at the mobility maximum. The effective scattering length, as defined, includes a term due to average fluctuations in the scattering length $\langle \Delta a^2 \rangle$ as well

as $\langle a \rangle$. Even when $\langle a \rangle = 0$, $\langle \Delta a^2 \rangle$ is not zero, so that at n_{max} (0.012 \AA^{-3} for Ar¹), fluctuations in the local environment suffice to keep the mobility finite. The experimental scattering lengths for Ar, taken from Ref. 1, are plotted in Fig. 1, where we have assumed that the scattering length changes sign at n_{max} , according to Lekner's predictions. The estimated magnitude^{1,3} of the consequent fluctuations in the scattering length is in rough agreement with the apparent experimental value of $\pm \langle \Delta a^2 \rangle^{1/2} \approx \pm 0.1$ bohr. Thus, the zero-scattering-length model successfully accounts for the mobility behavior from the triple point to the mobility maximum in terms of the experimentally inferred effective scattering lengths.

In an effort to understand more clearly the mechanism responsible for the behavior of the effective scattering length, we have made theoretical calculations using a method proposed by Lekner.² Assuming that fluctuations may be neglected in first approximation, we have calculated the average scattering length for electrons in fluid argon at seven different densities; the results are displayed in Fig. 1 and Table I. It is clear that the theoretical and experimental effective scattering lengths disagree in magnitude and slope with respect to the fluid density. After a brief discussion of the procedure used to calculate these scattering lengths, we will consider the apparent reasons for the discrepancies.

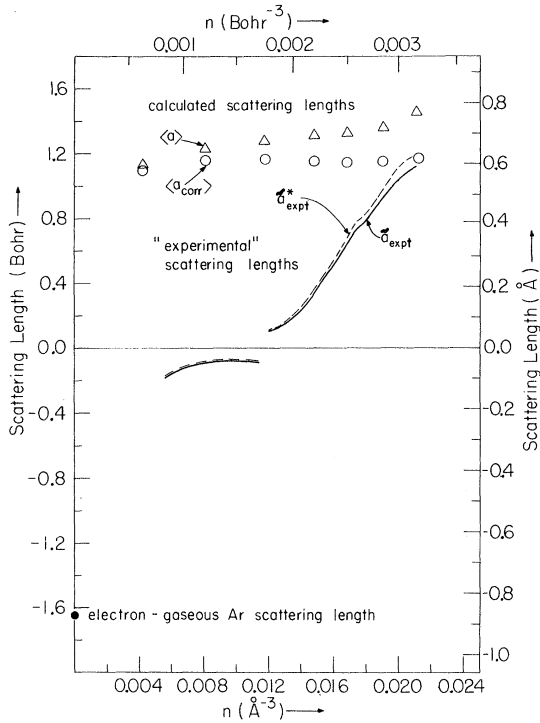


FIG. 1. Comparison of phenomenological scattering lengths \bar{a}_{expt} (\bar{a}_{expt}^*) and calculated average scattering lengths $\langle a \rangle$ ($\langle a_{\text{corr}} \rangle$) as a function of fluid number density n appropriate to the zero-field mobility of electrons in fluid argon.

In essence, Lekner² characterizes the field responsible for electron scattering in fluid argon by the muffin-tin approximation. The potential inside each muffin-tin sphere is taken to be the superposition of the single-site potentials $U_1(R)$:

$$U_{\text{eff}}(R) = U_1(R) + 4\pi n \int_0^\infty dr r^2 g(r) \int_0^\pi d\theta \sin\theta \times U_1(R^2 + r^2 - 2Rr \cos\theta)^{1/2} - U_0, \quad (2)$$

where $g(r)$ is the pair-distribution function of the fluid and U_0 is the value of the first maximum of the first two terms of Eq. (2), which occurs at the muffin-tin radius R_m . The single-site potential is taken to be the sum of the Hartree field of a neutral argon atom⁵ and the screened polarization potential:

$$2U_1(R) = 2U_{\text{Hartree}}(R) - \frac{\alpha/a_0 f(R)}{(R^2 + R_\alpha^2)^2} \text{Ry}, \quad (3)$$

where distance is measured in units of bohr (a_0). In these units the polarizability of Ar is $\alpha = 11 a_0^3$. The function $f(R)$ was defined by Lekner² to account for the average screening of the electron-induced dipole interaction by the dielectric medium. At large distances from the scattering center the screening is described by the Lorentz local-field $f_L = f(R \rightarrow \infty) = (1 + \frac{8}{3} \pi n \alpha)^{-1}$. At gaseous densities ($n \lesssim 10^{-5}$ atoms/ \AA^3) we have $f(R) \rightarrow 1$. Functional forms related to the polarizability interaction have been frequently used⁶ to extrapolate the exact second-order energy $[-(\alpha/a_0)/2R^4 + O(1/R^6)]$, which is valid only for positions outside the charge cloud of the atom, so as to obtain an effective interaction for electrons that penetrate inside the charge cloud of the atom. Lekner² chose the value $R_\alpha = 1.22 a_0$ in order that the cross sections calculated from $U_1(R)$ would be in agreement with those inferred from the drift-velocity measurements of Frost and Phelps.⁷ We find that with this value of the parameter R_α we are able to calculate total cross sections which agree with those determined in the more recent experimental measurements of Golden and Bandel⁸ to better than 20% for electron energies below 5 eV. Further details of the calculation of the ensemble-averaged effective potential $U_{\text{eff}}(R)$ are given in Ref. 2. The potentials used in the present calculations are shown in Fig. 2; they are replotted from Ref. 1 in terms of the ordinate $\log_{10}[-R U_{\text{eff}}(R)]$.

Phase-shift calculations were performed, using

TABLE I. Single-site parameters for express electron in fluid argon.

Fluid density		Muffin-tin radius	Wigner-Seitz radius	Lorentz screening factor	Maximum average potential	Calculated scattering length	Effective mass	Conduction-band minimum	
$n(\text{\AA}^{-3})$	$n(\text{bohr}^{-3})$	$R_m(\text{bohr})$	$R_s(\text{bohr})$	f_L	$-U_0(\text{Ry})$	$\langle a \rangle(\text{bohr})$	m^*/m	Wigner-Seitz approximation	Optical-potential approximation
								$k_0(\text{bohr}^{-1})$	$k_0^{\text{opt}}(\text{bohr}^{-1})$
(Hartree core potential for argon) ^a									
0.021 13	0.003 131	(5.00)	(∞)	(0.000)	(0.000)	2.233
0.019 03	0.002 820	4.00	4.24	0.774 ^b	0.157 ^b	1.458 ^c	0.75	0.330	0.239
0.016 82	0.002 492	4.16	4.39	0.794	0.121	1.360	0.78	0.295	0.219
0.014 82	0.002 196	4.25	4.58	0.813	0.109	1.334	0.81	0.270	0.204
0.011 76	0.001 743	4.29	4.77	0.832	0.099	1.309	0.84	0.248	0.190
0.008 08	0.001 197	4.38	5.16	0.862	0.087	1.279	0.88	0.213	0.167
0.004 22	0.000 625	4.54	5.84	0.901	0.070	1.232	0.92	0.167	0.136
(gas)	($\lesssim 4 \times 10^{-6}$)	4.82	7.25	0.945	0.047	1.136	0.97	0.110	0.094
(gas)	($\lesssim 4 \times 10^{-6}$)	(∞)	(∞)	(1.000)	(0.000)	-1.647 ^d

^aSee Ref. 5.

^bSee Ref. 2.

^cOur value differs from that calculated by Lekner by 1.3%.

^dSee Ref. 8.

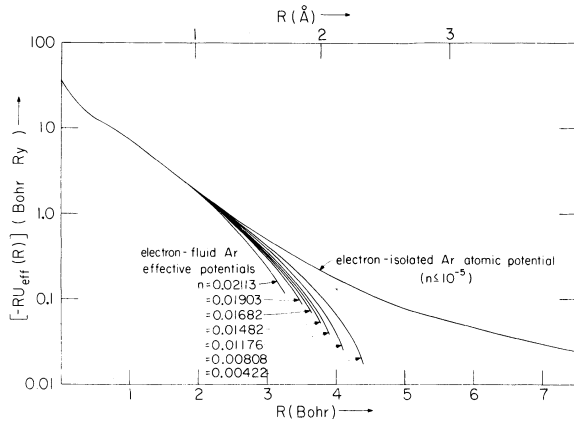


FIG. 2. Electron–fluid–argon single-center effective potentials at fluid number densities $n(\text{\AA}^{-3})$.

the effective potentials of Fig. 2, by numerically integrating the Schrödinger equation for fixed electron energy ϵ with Noumerov algorithm.⁹ The scattering phase shifts $\delta_l(\epsilon)$ were determined by matching the logarithmic derivative $\rho_l(R_m)$ of each calculated wave function to a linear combination of spherical Bessel and Neumann functions at the muffin-tin radius R_m . Momentum-transfer cross sections were then calculated from the relation

$$\sigma_1(\epsilon) = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} \sin^2[\delta_l(\epsilon) - \delta_{l+1}(\epsilon)], \quad (4)$$

where $k^2 = \epsilon(\text{eV})/13.6 \text{ bohr}^{-2}$.

It is found that for thermal-electron energies ($0.01 \text{ bohr}^{-1} \leq k \leq 0.05 \text{ bohr}^{-1}$), the cross sections $\sigma_1(\epsilon)$ are essentially energy independent and the s -wave phase shifts $\delta_0(\epsilon)$ dominate the other partial-wave phase shifts by at least two orders of magnitude. Therefore, the approximation

$$\sigma_1(\epsilon) \approx (4\pi/k^2) \sin^2 \delta_0(\epsilon) \approx 4\pi \langle a \rangle^2, \quad k \ll 1 \quad (5)$$

used to obtain Eq. (1) is indeed justified within this model. The resultant theoretical average scattering lengths

$$\langle a \rangle \equiv - \lim_{k \rightarrow 0} \left(\frac{\tan \delta_0(\epsilon)}{k} \right) \quad (6)$$

are plotted in Fig. 1. We estimate that these scattering lengths may vary up to 20–30% depending upon the details of the lengthy numerical calculations for the effective potentials (2). Agreement between experimental and theoretical mobilities is quite good at and near the triple-point density as has been noted previously.^{2,10,11} However, the slow variation of the scattering length with respect to fluid density is inherent in the muffin-tin model. From Fig. 2 it is evident that the “deep” part of the argon effective potential is very weakly dependent upon the density of the fluid. It may be pre-

dicted from the “shape-independent effective-range theory,”¹² that the low-energy cross sections for such a class of “finite range” potentials must be nearly equal, as we have empirically demonstrated. More precisely, the logarithmic derivative $\rho_0(R_m)$ of the s -wave function of the deep potential well is insensitive to small differences of energy near the top of the well. In addition, the spherical Bessel and Neumann functions, to which ρ_0 is matched at R_m , may be expanded to first order in their small argument kR_m . Consequently, in the limit of small k , Eq. (4) takes the energy-independent form

$$\sigma_1(\epsilon) \approx 4\pi \left(\frac{R_m^2 \rho_0}{R_m \rho_0 + 1} \right)^2 + O((kR_m)^2), \quad kR_m \ll 1. \quad (7)$$

It turns out that the cross sections (and scattering lengths) are even more constant with respect to fluid density than the above expression would imply, because the variations which do occur in R_m and $\rho_0(R_m)$ compensate each other. This analysis breaks down, however, when the scattering potentials have long range.

We first reexamine, qualitatively, the influence of the long-ranged polarizability interaction on the scattering cross section. The following argument suggests that when Eq. (2) is adopted the potential responsible for scattering is dominated by the core contribution, and hence is only accurate when the fluid is so dense that the superposed tails of interactions centered far from the region of interest have negligibly small spatial variation.

It has been shown¹³ that the polarizability interaction predominately determines the form of the electronic wave function and, consequently, the value of the phase shift, whenever the total electron energy is of comparable or lesser magnitude than the (classical) potential energy. That is, in the absence of screening, the polarizability interaction dominates for distances $R \lesssim d(\epsilon)$ from the Ar nucleus, where we have

$$d(\epsilon) \equiv \left(\frac{\alpha/a_0}{k^2} \right)^{1/4} \text{ bohr}. \quad (8)$$

This range can be very large when the electrons have low energy, such as we have assumed for the thermalized excess electrons in fluid Ar. For example, a 0.02 eV electron scattering from an isolated Ar atom has a “polarizability range” of $d(\epsilon = 0.02 \text{ eV}) \approx 9 \text{ bohr}$. Screening of the electron-induced dipole interaction by a dielectric medium only slightly reduces the range of the interaction. Using the Lorentz local-field function f_L , the polarizability range of the screened interaction at the same electron energy is approximately

$$d_{\text{screened}}(\epsilon) \approx d(\epsilon) f_L^{1/4} = d(\epsilon) \left(1 + \frac{8}{3} \pi n \alpha \right)^{-1/4}. \quad (9)$$

For fluid Ar at a density of $n \approx n_{\text{max}} = 0.012 \text{ \AA}^{-3}$, $f_L \approx 0.86$, and $d_{\text{screened}}(\epsilon) \approx 0.96 d(\epsilon)$. Now, in the

fluid, because we must consider the effects of the superposition of single-site potentials, we are led to compare the magnitudes of $d_{\text{screened}}(\epsilon)$ and R_m . According to Table I, for a fluid density of $n = 0.012 \text{ \AA}^{-3}$, $R_m \approx 4$ bohr. Thus, given the sensitivity of the cross section to the actual potential in the region $R > R_m$, we suspect that the average field defined in Eq. (2) is an inadequate characterization of the potential. After all, $g(R)$ has radial symmetry whereas the instantaneous potential "seen" by the electron, and responsible for scattering, does not. Deviations from radial symmetry increase in importance as the density decreases. Near the triple-point density the packing of atoms is sufficient to inhibit gross deviations in the arrangement of the centers of nearby atoms. Then the assumption that there exists a mean field with radial symmetry is a good approximation. As the density decreases, and more space is available for atomic motion, instantaneous configurations with nonradial symmetry become more and more probable. While it is always true that in the fluid the average environment of an atom has spherical symmetry, the instantaneous environment need not have said symmetry, and it is the instantaneous environment that defines the scattering potential. Thus, to obtain a more accurate single-scattering model it is necessary to use a more sophisticated averaging procedure than that inherent in Eq. (2).

It is also pertinent to question the use of the modified static Holtmark potential.⁵ It neglects many interactions, such as the exchange interaction, except insofar as the parameter R_a is chosen by the requirement that the potential reproduce the experimental low-energy electron-atom scattering cross sections. However, since the long-range polarizability interaction is known to dominate such cross sections, it is not clear that the core part of the potential, which is important for these fluid studies, is adequately tested by such a requirement. On the other hand, by the arguments given in the two preceding paragraphs, it seems unlikely that any simple modification of the fluid Ar single-center effective potential appropriate to this problem could achieve the strong density dependence implied by the experimental zero-field mobility.

Consider, now, the possible effects of multiple scattering. According to the simple approximations utilized by Lekner,² multiple scattering mainly changes the kinematics of the excess electron. A low-energy excess electron in a periodic lattice of Ar atoms would be expected to occupy the bottom of the conduction band at an energy ϵ_0 above $U_{\text{eff}}(R_m)$. In the perfect lattice there are no unoccupied states with energies $\epsilon < \epsilon_0$ available to the excess electron, since such states would be annihilated by the interference of the superposed wave functions from each scattering center. In the case of liquid

Ar at the same density n , we may suppose that states of $\epsilon < \epsilon_0$ have a low probability of occurrence because of similar interference effects. In the Wigner-Seitz approximation¹⁴ ϵ_0 is simply the energy at which the s -wave single-site radial wave function $\psi_0(R)$ has zero derivative at the Wigner-Seitz radius R_s , which is defined by the relation

$$\frac{4}{3} \pi R_s^3 \equiv 1/n. \quad (10)$$

The values of R_s appropriate to our problem are given in Table I. At all densities considered we have $R_s > R_m$. Consequently, the s -wave radial wave function in this case may be written

$$\begin{aligned} \psi_0(R) &= \frac{(\text{const})}{kR} (\sin kR - k \langle a \rangle \cos kR) \\ &= \frac{(\text{const})}{\cos \delta_0(\epsilon)} \frac{\sin k(R - \langle a \rangle)}{kR}, \quad R_s \geq R \geq R_m \end{aligned} \quad (11)$$

where $\langle a \rangle$ is the scattering length calculated according to Eq. (6).¹⁵ Then $k_0 \equiv (\epsilon_0(\text{eV})/13.6)^{1/2} \text{ bohr}^{-1}$ may be calculated by solving the equation

$$k_0 \tan k_0 R_s = \frac{R_s + \langle a \rangle}{(1/k_0^2) - R_s \langle a \rangle}. \quad (12)$$

Values of k_0 so calculated are given in Table I. Alternatively, we could estimate the energy of the lowest conduction band from the optical-potential approximation¹⁶

$$k_0^{\text{opt}} \equiv (4m \langle a \rangle)^{1/2} \text{ bohr}^{-1}. \quad (13)$$

For comparison, k_0^{opt} is also listed in Table I. The two estimates differ by only 30%.

The effect of raising the excess-electron energy appreciably above $U_{\text{eff}}(R_m)$ is mainly that the p phase shift now contributes and consequently the momentum-transfer cross sections (4) are reduced. Approximation (5) and, consequently, Eq. (1) are then no longer valid. We can roughly correct the relation between mobility and single-scattering amplitude by replacing the calculated scattering length $\langle a \rangle$ by $[\sigma_1(\epsilon_0)/4\pi]^{1/2}$. Values of these "corrected scattering lengths" $\langle a_{\text{corr}} \rangle$ are plotted in Fig. 1. Although this correction improves the agreement of theory and experiment at the triple-point density, it fails to do so at lower densities.

In the perfect lattice, the shape of the conduction band near ϵ_0 is well described by the effective mass approximation

$$\epsilon_k \approx \epsilon_0 + \frac{\hbar^2 k^2}{2m^*}. \quad (14)$$

The value of m^* may be estimated according to a method proposed by Bardeen¹⁷ in the framework of the Wigner-Seitz approximation. He finds

$$\frac{m^*}{m} = \frac{n}{\psi_0^2(R_s)/\eta^2 \{ [(R/P) (dP/dR)]_{R_s} - 1 \}}. \quad (15)$$

Here η is the normalization constant $\eta^2 \equiv [4\pi \times \int_0^{R_s} \psi_0^2(R) R^2 dR]^{-1}$, and $P(R)/R$ is the p -wave single-

site radial wave function, which may be expressed in terms of the p -wave phase shifts so that

$$\left(\frac{R}{P} \frac{dP}{dR}\right)_{R_s} = \frac{k_0 R_s + [(k_0 R_s)^2 - 1] \tan \delta_1(\epsilon_0) + [(k_0 R_s)^2 - k_0 R_s \tan \delta_1(\epsilon_0) - 1] \tan k_0 R_s}{\tan \delta_1(\epsilon_0) - k_0 R_s + [1 + k_0 R_s \tan \delta_1(\epsilon_0)] \tan k_0 R_s} \quad (16)$$

The calculated values of m^*/m are given in Table I. If one assumes that the energy-momentum relation (14) is preserved in fluid Ar at the same density n , the excess electron may be expected to achieve a modified Maxwell-Boltzmann velocity distribution in the fluid, with m^* replacing m and with the zero of energy at ϵ_0 above $U_{eff}(R_m)$. These new kinematics introduce a small correction factor to the experimentally inferred scattering-length formula (1):

$$\tilde{a}_{\text{expt}} \equiv (m/m^*)^{1/4} \tilde{a}_{\text{expt}} \quad (17)$$

The values of \tilde{a}_{expt} are plotted on the dotted line of Fig. 1. It is evident that this zero-order kinematic correction factor fails to appreciably improve the agreement between theory and experiment.

The single-scattering model with simple multiple-scattering corrections developed by Lekner has previously been shown^{2,10,11} to explain the experimentally observed drift velocity as a function of electric field of an excess electron in fluid heavy rare gases near their triple-point density. However, it has become clear in this work that this model inadequately describes the experimental observations made in the limit of zero electric field

over a wide range of densities of the fluid. Due to the failure of the single-center effective-potential model to give even a qualitatively correct understanding of the variation of the mobility with density, it appears to us that the problem requires a fresh analysis. We suggest that the important elements in such an analysis will be: (a) a more accurate description of instantaneous atomic configurations and their density dependence, and (b) a more accurate treatment of the effects of multiple-scattering processes.

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$$\lim_{R \rightarrow 0} [1 + \sum_i C_i(R) e^{-c_i R}] = 0 (R^n) \text{ with } n \geq 4.$$

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