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Theory of excess-electron mobility in compressed argon

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The purpose of this paper is to calculate the mobility of excess electrons in compressed argon (20–100 atm) both in single-scattering and multiple-scattering approximations. Calculations in the single-scattering approximation are carried out with the aid of the Cohen-Lekner theory. A new formula for the mobility of excess electrons in the multiple-scattering approximation is derived from the Kubo-Greenwood relation for electric conductivity. Numerical results inferred from this formula and from the Cohen-Lekner theory are compared with the experimental data reported in the literature. The results obtained in this paper indicate that the Cohen-Lekner theory is applicable only at very low densities of gaseous argon and that inclusion of the long-range part of the electron-atom potential gives a significant improvement in the theoretical results. The multiple-scattering corrections have been estimated to be about (10–25)% of the value of mobility calculated in the single-scattering approximation.

I. INTRODUCTION

The problem of the excess electrons (EE) in liquid rare gases and other nonpolar fluids has been considered by many authors both experimentally[1-4] and theoretically.[5-8] The experimental data lead to the conclusion that the EE in rare gases (Ar, Kr, and Xe) and some hydrocarbons are in extended (quasifree) states. The single-scattering theory of the mobility of EE has been elaborated by Cohen and Lekner[5] (CL). This theory is based on the Boltzmann equation for the momentum distribution function $f(\vec{p})$ of electrons moving in the set of muffin-tin potentials. Taking into account the correlation between scattering centers Cohen and Lekner solved the appropriate Boltzmann equation for this case by the expansion of $f(\vec{p})$ in a series of Legendre polynomials (Pidduck's method). Lekner[6] was the first, who applied this theory to the case of EE in liquid argon at the density near the triple point and found that theoretical value of mobility of EE agrees well with the experimental data. However, Jahnke, *et al.*[7] have pointed out large discrepancies between the theory and experiment for densities of argon lower than the density at the triple point. Also, for EE in liquid krypton at the density at the triple point, the theoretical result for the electron mobility is at least five times lower than the experimental value.[9] A very good agreement between the theory and experiment for liquid argon at the density of the triple point is, in fact, rather surprising. One should rather expect a good agreement between the theory and experiment for low densities of the fluid. This conclusion is due to fact that the CL theory neglects the multiple scattering and in the limit of low densities of fluid proceeds smoothly into the theory of electron mobility in dilute gases.[10] Therefore, it would be interesting to test the CL theory in the low-density region of fluid. The existing experimental data[11] concerning the velocity of EE in low electric fields make it possible for compressed argon for pressures ranging from 20 to 100 atm at $T=297\,^{\circ}\mathrm{K}$. This problem will be considered in Sec. II, where we also give an outline of the CL theory and discuss the details of the electron-argon atom interaction potential.

One of the most serious shortcomings of the CL theory, considered by Lekner[6] as well as by Jahnke *et al.*[7] is the fact that it neglects the multiple-scattering contributions to the mobility of EE. Lekner[6] proposed a simple estimation of these contributions, based on the Wigner-Seitz model. These corrections, however, do not change substantially the theoretical result of the CL theory for densities lower than the density of the argon triple point, so a qualitative disagreement still exists between the CL theory and the experimental data. In this paper we propose to approach the multiple-scattering problem with the aid of the Kubo-Greenwood relation for electric conductivity. This will be a starting point for the derivation of a formula for the mobility of EE within the multiple-scattering approximation (Sec. III). The formula obtained in the lowest order of the scattering potential is formally identical with the zero-electric-field limit of the CL theory. Next, we use this formula to calculate the mobility of EE in the compressed argon in the range from 20 to 100 atm and estimate the contribution due to multiple scattering. Finally in Sec. IV we summarize and discuss the results obtained in this paper.

After this paper was completed the work of Braglia and Dallacasa[12] came to our attention. These authors deal with the problem of theory of the density dependence of electron drift velocity in gases (including argon). They do not consider explicitly the electron-atom potentials and they claim that the multiple-scattering corrections are disregarded in their approach. The final formula in the paper of Braglia and Dallacasa[12] [Eq. (4)] clearly goes beyond the standard mobility formula obtained from the Boltzmann equation. This observation shows that the final formula of these authors seems to be inconsistent with the simplified Kubo-Greenwood formula used as a starting point of their theory. The simplified Kubo-Greenwood formula [Eq. (2)] is wrong if one is to deal with terms of higher-order density than one. The paper of Braglia and Dallacasa[12] contains a number of unjustified assumptions and approximations among which the assumption that the electron momentum cross section is equal to the total cross section seems to be the most important. We hope to deal with the paper of Braglia and Dallacasa[12] in a separate Comment.

II. SINGLE-SCATTERING APPROXIMATION

A. Cohen-Lekner theory (Ref. 5)

Now, for the sake of completeness we summarize the main points of the CL theory. First we define the single-scattering approximation, which in terms of scattering amplitude can be stated as follows: total scattering amplitude for transition of EE from state $\vec{k}$ into state $\vec{k}'$, $F(\vec{k}\to\vec{k}')$ is the coherent sum of the amplitudes singly scattered on each scattering center, i.e.,

$$F(\vec{k}\to\vec{k}') = \sum_j F_s \exp[-i(\vec{k}'-\vec{k})\vec{R}_j] \;, \tag{2.1}$$

where F_s is the singly scattered amplitude and $\vec{R}_j$ is the space coordinate of the jth center. The collision integral of the Boltzmann equation will contain the square of modulus of $F(\vec{k}\to\vec{k}')$, configurationally averaged over coordinates $\vec{R}_j$ of the system. For randomly distributed $\vec{R}_j$ this average will be proportional to the number density n of the scattering centers, but for liquids, where the correlations between atoms or molecules are very important, the factor of proportionality will be, in general $nS(\vec{k}-\vec{k}', \omega)$, instead of n. Here $S(\vec{k}, \omega)$ is the dynamical structure factor of liquid, $\vec{K}$ and ω being the change of momentum and energy of scattered electron, respectively. The occurrence of the energy-independent structure factor $S(\vec{K})$ in the CL theory leads to the substantial change of the numerical results of the mobility of EE for liquids as compared with the random systems.

Taking into account Eq. (2.1) and assuming that the Boltzmann equation is valid for the case of EE, Cohen and Lekner[5] have established a set of differential equations for the coefficients of expansion of $f(\vec{p})$ into series of Legendre polynomials.

Their result for the mobility of EE takes in the limit of small electric fields the following form:

$$v_D = \tfrac{2}{3}(2/\pi m k_B T)^{1/2}[eE/4\pi a^2 S(0) n] \;, \tag{2.2}$$

where v_D is the drift velocity, m and e are electron mass and charge, respectively, E is the electric field, k_B is the Boltzmann constant, T is the absolute temperature, and a is the scattering length. The structure factor $S(\vec{K})$ is evaluated at the zeroth electron wave vector. In order to calculate the scattering length a, the detailed form of scattering potential $U_{\mathrm{MT}}(r)$ is required. According to Lekner[6] this potential can be defined as follows:

$$U_{\mathrm{av}}(r) = v(r) + \left\langle\!\!\left\langle \sum_{i=2} v(\vec{r}-\vec{R}_i) \right\rangle\!\!\right\rangle \tag{2.3}$$

$$U_{\mathrm{MT}}(r) = \begin{cases} U_{\mathrm{av}}(r) - U_0 & \text{for } r<R_m \\ 0 \quad \text{for } r>R_m \end{cases} \tag{2.4}$$

where $v(r)$ is the electron-atom interaction potential and quantities R_m and U_0 are defined by the equation:

$$\left.\frac{dU_{\mathrm{av}}(r)}{dr}\right|_{r=R_m} = 0; \quad U_0 = U_{\mathrm{av}}(R_m) \;. \tag{2.5}$$

The symbol $\langle\langle\ \rangle\rangle$ denotes the configurational average, i.e., for any site dependent quantity $A(\vec{R}_1, \ldots, \vec{R}_s)$ we have:

$$\langle\langle A\rangle\rangle = \int P_s(\vec{R}_1,\ldots,\vec{R}_s) A(\vec{R}_1,\ldots,\vec{R}_s) d\vec{R}_1 \ldots d\vec{R}_s \;, \tag{2.6}$$

where $P_s(\mathbf{R}_1, \ldots, \vec{R}_s)$ is the sth order distribution function of liquid.

The Lekner's definition of the scattering potential $U_{\mathrm{MT}}(r)$, Eqs. (2.3)–(2.5), is to some extent quite arbitrary, i.e., the form of the $U_{\mathrm{MT}}(r)$ (except of its range) is not connected in any way with the formalism leading to Eq. (2.2). For example, it is possible to modify the potential defined by Eq. (2.4) replacing R_m by R_s given by $\frac{4}{3}\pi R_s^3 n = 1$. This modification ensures that space in the fluid is covered (on the average) exactly once.

B. Electron-atom interaction potential

As we are interested in the calculations of the mobility of EE in compressed argon we confine our considerations to the potential electron-argon atom. This potential has a one or more parameters, and their values are numerically adjusted to ensure the agreement between calculated and experimental momentum transfer cross section Q_M in some range of energy.[6] Sometimes, the total cross section Q_T is used when Q_M is unavailable. Lekner[6] and Jahnke *et al.*[7] have used a simple potential being a sum of the

Hartree and a polarization potentials with one adjustable parameter. This simple potential (further denoted as P_1) enables us to fit quite accurately the experimental values of Q_M due to Braglia *et al.*[13] but cannot fit recently published data due to Milloy *et al.*[14] Therefore we decided to suggest the electron-atom potential in the form:

$$v(r) = U_{\mathrm{HF}}(r) + U_{\mathrm{ex}}(r) + U_{\mathrm{pol}}(r)\,, \qquad (2.7)$$

where $U_{\mathrm{HF}}(r)$ is the Hartree-Fock potential, given by Strand and Bonham,[15] $U_{\mathrm{pol}}(r)$ is the polarization potential in the form[16]:

$$U_{\mathrm{pol}}(r) = -(\alpha/2r^4)\{1 - \exp[-(r/r_\alpha)^8]\} \qquad (2.8)$$

where α is the static polarizability of argon atom, $\alpha = 11$ a.u., r_α is the adjustable parameter. The adopted form of the exchange potential, $U_{\mathrm{ex}}(r)$ is the same as that proposed by Riley *et al.*,[17] namely,

$$U_{\mathrm{ex}}(r) = -(2/\pi)K_F(r)\chi(\eta)\,, \qquad (2.9)$$

where

$$\chi(\eta) = \tfrac{1}{2} + [(1-\eta^2)/4\eta]\ln|(1+\eta)/(1-\eta)|\,,$$

$$\eta = K(r)/K_F(r)\,,$$

$$K_F(r) = (3\pi\hat{\rho}(r))^{1/3}\,,$$

$$K^2(r) = 2[\epsilon + I\exp(-e_1 r)] + K_F^2(r)\,,$$

where $\hat{\rho}(r)$ is the density of electron charge of atom, ϵ is the energy of EE, I is the first ionization potential of argon atom and e_1 is the adjustable parameter, chosen to ensure correct behavior of the function $K(r)$ for large r ($e_1 > 0$). This potential has two adjustable parameters, r_α and e_1. The most satisfactory fit of calculated Q_M with the experimental data of Milloy *et al.*[14] is for the following values of parameters: $r_\alpha = 4.475$ a.u. and $e_1 = 0.6$ a.u. (further, the potential given by Eqs. (2.7)–(2.9) with the values of parameters given above will be denoted by P_2). However, our potential is energy dependent (through the quantity ϵ) and therefore is very cumbersome in practical use, so we have decided to fix energy ϵ ($\epsilon = 0.0085$ eV) and this energy-independent form of P_2 has been used in further calculations. Figure 1 compares the calculated values of Q_M both of P_1 and P_2 together with experimental data of Braglia *et al.*[13] and of Milloy *et al.*[14] Also, *ab initio* calculations of Thompson[18] are displayed.

C. Numerical results of the CL theory for compressed argon (20-100 atm)

The calculations of the mobility of EE in compressed argon have been performed with the radial distribution function $g(r)$ in the form

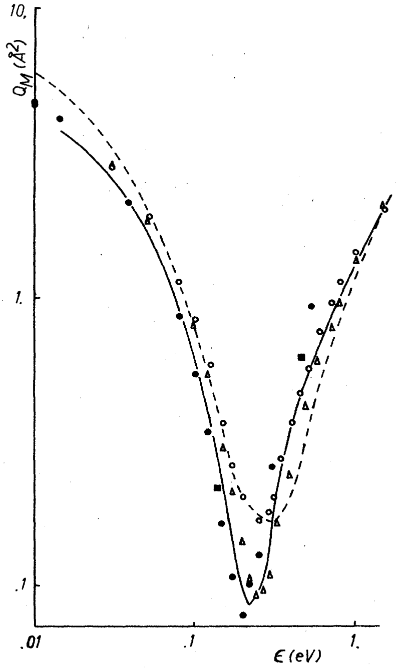

FIG. 1. Calculated and experimental momentum transfer cross section Q_M for argon. ---- experimental (Ref. 13); —— experimental (Ref. 14); ○ theoretical using P_1; △ theoretical, using P_2 (energy-independent form); ● theoretical, using P_2 (energy-dependent form), ■ theoretical (Thompson, Ref. 18).

$$g(r) = \exp[-\beta U_{LJ}(r)][1 + ng_1(r)]\,, \qquad (2.10)$$

where $U_{LJ}(r)$ is the Lennard-Jones potential for argon,[27] $\beta = 1/k_B T$, and g_1 is the first term of the virial expansion for $g(r)$ calculated with the use of $U_{LJ}(r)$. The structure factor $S(K)$ has been taken as the Fourier transform of the radial distribution function given above. The results of calculations of the mobility of EE for both potentials P_1 and P_2 are displayed in Table I, together with the experimental data due to Bartels.[11] Let us observe, that theoretical values of mobility for both potentials P_1 and P_2 are rather close, but are far too small as compared with the experimental data. Also the results obtained with the use of the modified Lekner potential with R_m replaced by R_s do not agree with the experimental data. In fact, these results are even worse than those obtained in the framework of original CL theory, probably due to inclusion of the positive part of the average electron-atom potential. This disagreement between the theory and experiment cannot be attributed to the neglect of the multiple scattering processes in the CL theory. It seems to us that much more important is cutting off the long-range polarization potential inherent in the CL theory [Eqs.

TABLE I. Mobility μ of EE in compressed argon according to the CL theory.

Number density ($\mathrm{\AA}^{-3}$)	Potential P_1						Potential P_2			Experimental value of μ ($\mathrm{cm^2/V\,s}$)
	R_m (a.u.)	$U_{av}(R_m)$ (a.u.)	μ^a ($\mathrm{cm^2/V\,s}$)	R_s (a.u.)	$U_{av}(R_s)$ (a.u.)	μ^b ($\mathrm{cm^2/V\,s}$)	R_m (a.u.)	$U_{av}(R_m)$ (a.u.)	μ^a ($\mathrm{cm^2/V\,s}$)	
0.0005	5.974	−0.007 01	1061.9	14.770	−0.008 16	1841.9	6.244	−0.008 13	818.1	2928.6
0.0010	5.616	−0.009 66	438.8	11.723	−0.016 36	185.6	5.932	−0.011 71	317.7	1700.0
0.0015	5.402	−0.011 86	263.3	10.241	−0.024 72	63.0	5.746	−0.014 78	182.9	1214.3
0.0020	5.258	−0.013 85	184.1	9.304	−0.033 32	31.9	5.602	−0.017 58	124.2	1075.0
0.0025	5.146	−0.015 72	140.2	8.637	−0.042 05	19.9	5.486	−0.020 22	92.5	1057.1

[a] μ is the mobility calculated with the effective potential given by Eqs. (2.3)–(2.5).

[b] μ is the mobility calculated with the effective potential (2.4) with R_m replaced by R_s and $U_0 = U_{av}(R_s)$.

(2.3)–(2.5)]. The comparison of the values of R_m displayed in Table I leads to the conclusion that the muffin-tin potential $U_{\mathrm{MT}}(r)$ [Eq. (2.4)] has a short range even at such small density as 0.0005 $\mathrm{\AA}^{-3}$. Therefore the CL theory practically does not account for the long-range polarization potential, which is very important in the scattering of electrons on the single argon atom. This problem will be considered in Sec. IV. Now we proceed to the discussion the mobility of EE in the multiple-scattering approximation.

III. MULTIPLE-SCATTERING APPROXIMATION

A. Derivation of the basic mobility formula

In the one-electron approximation, the Hamiltonian of EE in the fluid can be written in the form:

$$H = H_0 + U = H_0 + \sum_i v(\vec{r} - \vec{R}_i)\,, \tag{3.1}$$

where H_0 is the kinetic energy operator of EE and $v(\vec{r} - \vec{R}_i)$ is the scattering potential, located at $\vec{R}_i$. For the case considered in this paper $v(\vec{r} - \vec{R}_i)$ is the potential of electron-free argon atom, modified by introduction of so-called polarization screening function $f(r)$ (for details see Ref. 6) in order to account the interaction between EE and the dipoles induced on the atoms of fluid.

The Green operator for the above Hamiltonian is defined by the relation:

$$G^{\pm} = G_0^{\pm} + G_0^{\pm} U G^{\pm}\,, \tag{3.2}$$

where $G_0^{\pm}$ is the free-electron Green operator, defined as

$$G_0^{\pm}(\epsilon) = \frac{1}{\epsilon - H_0 \pm i\eta} \quad \eta \to 0^+\,. \tag{3.3}$$

The Kubo-Greenwood formula for electric conductivity of any system with Hamiltonian (3.1) can be written in terms of Green operator $G^{\pm}$ as[19]:

$$\sigma_{\mu\nu} = \frac{\hbar}{\Omega\pi} \int d\epsilon \frac{df}{d\epsilon} \left(\mathrm{Re\,tr} \langle\langle j_\mu G^+ j_\nu G^+ - j_\mu G^+ j_\nu G^- \rangle\rangle\right)\,, \tag{3.4}$$

where $\sigma_{\mu\nu}$ is the conductivity tensor, $\hbar$ is the Planck constant, Ω is the volume of the system, f is the Fermi-Dirac distribution function, and j_μ is the one-electron current operator. It is evident from the equation given above that the calculation of electric conductivity is reduced to the study of quantity $\langle\langle GjG \rangle\rangle$, i.e., configuration average of the product of two Green functions. The quantity of this form satisfies the Bethe-Salpeter equation, which for the case of homogeneous and isotropic fluid can be written in the form[19]: (in the momentum representation)

$$\langle\langle G(\epsilon) j G(\epsilon')\rangle\rangle(\vec{k}) = \langle\langle G(\epsilon)\rangle\rangle(\vec{k})\langle\langle G(\epsilon')\rangle\rangle(\vec{k})\cdot\left(j(\vec{k}) + \frac{\Omega}{8\pi^3}\int d\vec{k}' W(\epsilon,\epsilon',\vec{k},\vec{k}')\cdot\langle\langle G(\epsilon) j G(\epsilon')\rangle\rangle(\vec{k})\right) \tag{3.5}$$

where $W(\epsilon,\epsilon',\vec{k},\vec{k}')$ is the vertex function. We consider the vertex function for $\epsilon = \epsilon + i\eta$, $\epsilon' = \epsilon - i\eta$, $\eta \to 0^+$ and therefore we denote: $W(\epsilon,\vec{k},\vec{k}') = W(\epsilon,\epsilon',\vec{k},\vec{k}')$. An analog of the Bethe-Salpeter equation for the configuration average of the single Green function is the Dyson equation[19]

$$\langle\langle G\rangle\rangle = G_0 + G_0\Sigma\langle\langle G\rangle\rangle\,, \tag{3.6}$$

where we introduced the self-energy operator Σ. There is close connection between Σ and W. This is the so-called optical theorem or Ward identity,[19,20] which can be stated as follows:

$$\Gamma(\epsilon,\vec{k}) = -\frac{1}{\pi}\,\mathrm{Im}\Sigma(\epsilon,\vec{k}) = \frac{\Omega}{8\pi^3}\int d\vec{p}\,W(\epsilon,\vec{k},\vec{p})\rho(\epsilon,\vec{p})\,, \tag{3.7}$$

where we introduced a function $\rho(\epsilon,\vec{p})$ defined as follows:

$$\rho(\epsilon,\vec{p}) = -(1/\pi)\,\mathrm{Im}\langle\langle G(\epsilon,\vec{p})\rangle\rangle\,. \tag{3.8}$$

This function is the kind of dispersion relation between energy ϵ and wave vector $\vec{p}$. For free electrons there is a "sharp" relation $\epsilon = \hbar^2k^2/2m$, therefore, for this case:

$$\rho(\epsilon,\vec{k}) = \delta(\epsilon - \hbar^2k^2/2m) = (m/\hbar^2k_\epsilon)\delta(k - k_\epsilon)\,;\quad \hbar^2k_\epsilon^2/2m = \epsilon\,. \tag{3.9}$$

For the case of EE it seems to be reasonable that relation (3.9) is valid, at least as a first approximation. This is due to large mobility of EE which is observed experimentally.[1-4] Also, in the theory of liquid metals this approximation is commonly used.[21]

Now we consider the problem of evaluation of the conductivity formula Eq. (3.4) which can be rewritten for isotropic fluid in a more tractable form in terms of the functions Γ and ρ [Eqs. (3.7) and (3.8)].

$$\sigma = -\frac{\hbar}{3\pi}\int\frac{df}{d\epsilon}\,d\epsilon\int\frac{d\vec{k}}{8\pi^3}\left\{\frac{3e^2}{m}\frac{\rho(\epsilon,\vec{k})}{\Gamma(\epsilon,\vec{k})}\left(\epsilon - \frac{\hbar^2k^2}{2m} - \mathrm{Re}\Sigma(\epsilon,\vec{k})\right) + j(\vec{k})\langle\langle G^+ j G^-\rangle\rangle(\vec{k})\right\} \tag{3.10}$$

Substituting the approximation (3.9) for function $\rho(\epsilon,\vec{k})$ in the right side of Eq. (3.5) we get (denoting: $\rho(\vec{k}) \equiv \rho(\epsilon,\vec{k})$; $\Gamma(\vec{k}) \equiv \Gamma(\epsilon,\vec{k})$)

$$\langle\langle G^+ j G^-\rangle\rangle(k) = \frac{\rho(\vec{k})}{\Gamma(\vec{k})}\left(j(\vec{k}) + C\int k_\epsilon^2 d\omega' W(\epsilon,k,k_\epsilon')j(k_\epsilon') + C^2\int\int d\omega' d\omega'' k_\epsilon^4 W(\epsilon,k,k_\epsilon')W(\epsilon,k_\epsilon',k_\epsilon'')j(k_\epsilon'') + \dots\right) \tag{3.11}$$

where $C = [\Omega m/8\pi^3\hbar^2k_\epsilon\Gamma(\epsilon,k_\epsilon)]$ and integration is performed over angles ω, ω'' which defines the directions of vectors $\vec{k}'$, $\vec{k}''$, $\vec{k}'''\cdots$ Using the relation[22]

$$\int d\omega_{\vec{k}'}\,j(\vec{k}')W(\epsilon,\vec{k},\vec{k}') = j(\vec{k})\int d\theta\,\sin\theta\cos\theta\,W(\epsilon,k_\epsilon,\theta)d\varphi\,, \tag{3.12}$$

where $|\vec{k}| = |\vec{k}'| = k_\epsilon$, after a little algebra we can show that Eq. (3.10) can be rewritten in the form

$$\sigma = -\frac{2}{3}\frac{me^2}{\hbar^3\pi^2}\int\epsilon\frac{df}{d\epsilon}\frac{1}{\Lambda_1^{-1}(\epsilon)}\,d\epsilon\,, \tag{3.13}$$

where we have introduced the quantity $\Lambda_1^{-1}(\epsilon)$ which is defined by equation

$$\Lambda_1^{-1}(\epsilon) = 2n\pi\int_0^\pi \sin\theta(1-\cos\theta)\frac{m^2}{4\pi^2\hbar^4}\times|V(\epsilon,k_\epsilon,\theta)|^2 S(2k_\epsilon\sin\tfrac{1}{2}\theta)\,d\theta \tag{3.14}$$

The function $V(\epsilon,k_\epsilon,\theta)$ is directly related to the vertex function $W(\epsilon,k_\epsilon,k_\epsilon,\theta)$:

$$W(\epsilon,k_\epsilon,k_\epsilon,\theta) = (n/\Omega)|V(\epsilon,k_\epsilon,\theta)|^2 S(2k_\epsilon\sin\tfrac{1}{2}\theta)\,. \tag{3.15}$$

In the lowest order of the scattering potential the quantity $\Lambda_1^{-1}(\epsilon)$ is reduced to the quantity given by Eq. (17) in the paper due to Cohen and Lekner.[5] For small densities of fluid $1/n\Lambda_1^{-1}(\epsilon)$ is equal to Q_M—the momentum transfer cross section.[6] One can also verify, that Eq. (3.13) gives the correct result in the lowest order of scattering potential for liquid metals (i.e., Ziman's formula). Indeed, using $df/d\epsilon = -\delta(\epsilon - \epsilon_F)$, ϵ_F is the Fermi energy and Eq. (3.14) in the lowest order with respect to the potential, we can easily obtain:

$$\sigma = \frac{n_e e^2\hbar}{2\pi m}\left(\int\frac{d\vec{k}'}{8\pi^3}S(\vec{k}-\vec{k}')|\hat{v}(\vec{k},\vec{k}')|^2 \times(1-\cos\theta)\delta(\epsilon-\epsilon_F)\right)^{-1}, \tag{3.16}$$

where n_e is the number density of electrons in liquid metals and $\hat{v}(\vec{k},\vec{k}')$ is the Fourier transform of the potential v [Eq. (3.1)].

In the case of EE in the fluids the correctly normalized Boltzmann distribution function should be used. This is due to very low density of EE and small external electric fields. This function has the form:

$$f = n_e 4\pi^3 \hbar^3 (1/2\pi k_B T m)^{3/2} \exp(-\epsilon/k_B T) . \qquad (3.17)$$

After substitution of the function given above to Eq. (3.13) we obtain the CL result for the EE mobility in the limit of small electric fields (assuming, that Λ_1^{-1} is energy independent):

$$\mu = \tfrac{2}{3} e (2/m k_B T \pi)^{1/2} (1/\Lambda_1^{-1}) , \qquad (3.18)$$

where μ is the EE mobility.

On the basis of Eqs. (3.13)–(3.15) we can conclude that the problem of calculation of the EE mobility in fluids is reduced to the calculation the function $V(\epsilon, k_\epsilon, \theta)$. In order to obtain the equation concerning this function we consider a diagrammatic expansion for the vertex W. Using the well-known cluster functions $H_s(\vec{R}_1, \ldots, \vec{R}_s)$ (for details see Ref. 23) we conclude on the basis of the Bethe-Salpeter equation (3.5) that vertex W can be defined as the sum of all irreducible diagrams, shown in Fig. 2. Generally, such expressions as displayed in Fig. 2 cannot be summed up. In order to sum this expression we select diagrams with only one black point, so we can write the expression for the vertex W in the closed form:

$$W = \int \sum_{l,s=0} v(\langle\langle G \rangle\rangle v)^l v(\langle\langle G^* \rangle\rangle v)^s \times H_{l+s+2}(\vec{R}_1, \ldots, \vec{R}_{l+s+2}) d\vec{R}_1 \cdots d\vec{R}_{l+s+2} . \qquad (3.19)$$

Now we use the momentum representation and define

$$v(\vec{k}_1, \vec{k}_2) = (1/\Omega) \exp[-i(\vec{k}_1 - \vec{k}_2)\vec{R}_i] \cdot \hat{v}(\vec{k}_1, \vec{k}_2)$$

$$\hat{v}(\vec{k}_1, \vec{k}_2) = \int \exp[-i(\vec{k}_1 - \vec{k}_2)\vec{r}]\, v(\vec{r}) d\vec{r} \qquad (3.20)$$

$$S_s(\vec{q}_1, \ldots, \vec{q}_s) = \frac{1}{N} \int \exp[-i(\vec{q}_1\vec{R}_1 + \ldots + \vec{q}_s\vec{R}_s)] \times H_s(\vec{R}_1 \ldots \vec{R}_s) d\vec{R}_1 \ldots d\vec{R}_s \cdot \delta(\vec{q}_1 + \ldots + \vec{q}_s, 0) .$$

Using the definitions given above we can rewrite the (l, s) term of Eq. (3.19) in the form

$$W_{l,s}(\epsilon, \vec{k}, \vec{p}) = \frac{(8\pi^3)^{-(l+s)}}{\Omega^2} N \int d\vec{k}_1 \ldots d\vec{k}_{s+l}\, \hat{v}(\vec{k}, \vec{k}_1) \langle\langle G(\vec{k}_1) \rangle\rangle \ldots \hat{v}(\vec{k}_l, \vec{p}) \hat{v}(\vec{p}, \vec{k}_{l+1}) \cdot \langle\langle G^*(\vec{k}_{l+1}) \rangle\rangle \ldots \hat{v}(\vec{k}_{s+l}, \vec{k}) S_{l+s+2}(\vec{k} - \vec{k}_1, \ldots, \vec{k}_s - \vec{p}, \vec{p} - \vec{k}_{s+1}, \ldots, \vec{k}_{s+l} - \vec{k}) , \qquad (3.21)$$

where N is the number of atoms in the system. Unfortunately, the expression given above still contains unknown Fourier transform of the cluster function H_{l+s+2}. We use the geometric approximation for this function,[23] i.e.,

$$S_s(\vec{q}_1, \ldots, \vec{q}_s) = S_2(\vec{q}_1) \ldots S_2(\vec{q}_1 + \ldots \vec{q}_{s-1}) ;$$
$$S_2 \equiv S . \qquad (3.22)$$

Using Eqs. (3.15), (3.19), (3.21), and (3.22) and the momentum representation we obtain for function $V(\epsilon, \vec{k}, \vec{p})$ the following equation:

$$V(\epsilon, \vec{k}, \vec{p}) = \sum_{s=0} \langle \vec{k} | v(\langle\langle G \rangle\rangle S v)^s | \vec{p} \rangle = \hat{v}(\vec{k}, \vec{p}) + \int \frac{d\vec{q}}{8\pi^3} V(\epsilon, \vec{k}, \vec{q}) \langle\langle G(\vec{q}) \rangle\rangle \times S(\vec{k} - \vec{q}) \hat{v}(\vec{q}, \vec{p}) . \qquad (3.23)$$

This equation can be rearranged to a more convenient form:

$$V(\epsilon, \vec{k}, \vec{p}) = \hat{t}(\vec{k}, \vec{p}) + \int \frac{d\vec{q}}{8\pi^3} V(\epsilon, \vec{k}, \vec{q}) \langle\langle G(\vec{q}) \rangle\rangle \times [S(\vec{k} - \vec{q}) - 1] \hat{t}(\vec{q}, \vec{p}) . \qquad (3.24)$$

where we have introduced the scattering matrix $\hat{t}$ containing averaged Green function $\langle\langle G \rangle\rangle$. The matrix $\hat{t}$ is defined by the equation:

$$\hat{t} = v + v \langle\langle G \rangle\rangle \hat{t} . \qquad (3.25)$$

This is an analog of the well-known Lippmann-Schwinger equation for ordinary scattering matrix, t:

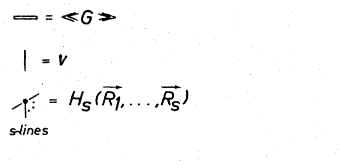

FIG. 2. Some low-order diagrams contributing to the vertex function W.

$$t = v + vG_0 t \ . \qquad (3.26)$$

The comparison of Eqs. (3.23) or (3.24) with the similar results obtained by Ashcroft and Schaich[24] leads to the conclusion that the approximate proposed here in the framework of the diagrammatic method is equivalent to the van Howe's "irreducible diagonal" condition.

B. Results of numerical calculations

In order to calculate the mobility of EE in compressed argon in the multiple-scattering approximation with the use of formulas derived in Sec. III A we should first calculate the scattering matrix $\hat{t}$. The direct evaluation of $\hat{t}$ from the Lippmann-Schwinger equation (3.25) is, however, impossible, as we do not know the average Green's function, $\langle\langle G \rangle\rangle$ of the system. Therefore, we approximate the matrix $\hat{t}$ by the matrix t defined by Eq. (3.26). This is equivalent with the replacement of the averaged Green's function $\langle\langle G \rangle\rangle$ by free-electron Green's function G_0. From Eqs. (3.25) and (3.26) we obtain, after a little algebra:

$$\hat{t} = t + t(\langle\langle G \rangle\rangle - G_0)\hat{t} \qquad (3.27)$$

so we see that the proposed approximation for $\hat{t} \cong t$ is the first term of iteration expansion of the exact equation (3.27) for $\hat{t}$. Consequently, recalling the expansion of the self-energy into series of $\hat{t}$ matrix[23] we approximate:

$$\Sigma \cong nt \ . \qquad (3.28)$$

The calculations have been performed with the potential P_2, defined in Sec. II. However, we should modify this potential in order to account the dipole interaction between EE and atoms of fluid. This has been done exactly as in the CL theory, i.e., by modification of the polarization part of potential, $U_{\mathrm{pol}}(r)$ with the aid of polarization screening function $f(r)$ introduced by Lekner.[6] Having defined potential v, we solve Eq. (3.26) for matrix t by the matrix inversion method using formulas derived by Watson and Nuttall.[25] The numerical solution of Eq. (3.24) for the function $V(\epsilon, \vec{k}, \vec{p})$ is straightforward if we make the expansion of $V(\epsilon, \vec{k}, \vec{p})$ into series of Legendre polynomials (we truncate this series after the two first terms). The obvious approximation for V is $V = t$, as it can be seen from Eq. (3.24). This approximation can be called the single-scattering approximation, as it leads directly to the Lekner's formula for the EE mobility, Eq. (3.18). Recalling the well-known relation between scattering matrix t and the scattering amplitude F_s and taking into account Eq. (2.1) we observe, that approximation $V = t$ is the equivalent to a reformulation of the single-scattering approximation in terms of the vertex function W. The results of our calculations of the mobility of EE for $V = t$ and for V obtained by numerical solution of Eq. (3.24) are displayed in Table II.

TABLE II. Mobility of EE in the multiple-scattering approximation.

Number density (Å^{-3})	μ^s (Ref. a) (cm^2/V s)	μ^m (Ref. b) (cm^2/V s)
0.0005	1882.9	2051.8
0.0010	970.3	1101.8
0.0015	666.9	777.6
0.0020	547.3	654.7
0.0025	431.6	580.8

[a] μ^s is the mobility calculated with the function $V = t$.

[b] μ^m is the mobility calculated with the function V obtained from numerical solution of Eq. (3.24).

IV. DISCUSSION

In this paper we have calculated the mobility of EE in compressed argon using both the CL theory and the formula derived in Sec. III A. The results obtained with the use of the CL theory for the mobility of EE are far too low as compared with the experimental values. On the other hand, the results obtained within the multiple-scattering approximation proposed in this paper agree much better with the experiment, although a considerable gap between theory and experiment still exists. The comparison of the data from Table II with two last columns of Table I shows that the mobility calculated with the full potential (including the long-range polarization potential) is much more close to the experimental data than values obtained using the muffin-tin potential $U_{\mathrm{MT}}(r)$ proposed by Lekner.[6] However, introduction of such long-range potential means, that the potentials centered on the neighbor atoms overlap to some extent. This gives rise to the unsymmetrical interaction of EE with the atoms of fluid. This point has not been considered in this paper, but we hope that this effect is not very important at the densities of fluid considered in this paper.

The multiple-scattering contributions to the EE mobility can be defined as the difference between the mobility calculated with $V = t$ and the mobility calculated with the function V obtained from Eq. (3.24). The multiple-scattering corrections defined in such a way are of order about 10% to 25% of the mobility of EE calculated within the single-scattering approximation. Therefore, we conclude that these corrections are significant even at such low densities of fluid as those considered in this paper.

The theory presented in this paper suffers from many deficiencies and therefore its results are about 1.5–2 times lower than the experimental values of mobility of EE. Here we briefly discuss the most important approximations made in the process of calculations with the aid of the theory developed in Sec. III A.

(i) The electron-atom potential defined by Eq. (2.7) together with the parameters chosen in the way described in Sec. II is a very crude approximation of the true electron-atom potential. The much better would be fitting of function given by Eq. (2.7) with more adjustable parameters to the differential cross section for a set of energies, but at present such fitting is rather impossible due to the lack of extensive experimental data concerning the differential cross section for argon at low energies.

(ii) The use of geometric approximation for higher correlation functions [Eq. (3.22)] permits an overlapping of two or more atoms of fluid, which is certainly untrue for real fluids. Unfortunately the calculations involving the more advanced approximations, for example, the superposition approximation, lead to very complicated expressions even for averages of quantities depending only on the single Green's function operator.[26]

(iii) The numerical values displayed in Table II have been obtained with the approximation for the matrix $\hat{t}$ and self-energy Σ, discussed in Sec. III B. One can see that these approximations are, respectively, zero and first order in the density of fluid, and therefore should be valid at low densities of fluid, but we have not estimated the contribution of higher powers of density to matrix $\hat{t}$ and self-energy Σ.

(iv) The estimation of the effect of overlapping potentials, mentioned previously is very difficult. We can only say, on the basis of comparison of the data contained in Tables I and II, that permission for overlapping of potentials gives considerably less error than the use of the muffin-tin potential of Lekner, $U_{\rm MT}(r)$ [Eq. (2.4)]. This statement is probably true only at low densities of fluid, where the overlapping is rather negligible, but may be wrong for high densities of fluid.

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[1] H. Schnyders, S. A. Rice, and L. Meyer, Phys. Rev. 150, 127 (1966).

[2] B. Halperin, S. A. Rice, and R. Gomer, Phys. Rev. 156, 351 (1967).

[3] J. A. Jahnke, L. Meyer, and S. A. Rice, Phys. Rev. A 3, 734 (1970).

[4] H. T. Davis and R. G. Brown, Adv. Chem. Phys. 31, 329 (1975).

[5] M. H. Cohen and J. Lekner, Phys. Rev. 158, 305 (1967).

[6] J. Lekner, Phys. Rev. 158, 130 (1967).

[7] J. A. Jahnke, N. A. W. Holtzwarth, and S. A. Rice, Phys. Rev. A 5, 463 (1972).

[8] R. Boehm, Phys. Rev. A 12, 2189 (1975).

[9] J. Gryko and J. Popielawski, Phys. Rev. A 16, 1333 (1977).

[10] L. G. Huxley and R. W. Crompton, *The Diffusion and Drift of Electrons in Gases* (Wiley, New York, 1974).

[11] A. K. Bartels, Ph.D. thesis, University of Hamburg, 1974.

[12] G. L. Braglia and V. Dallacasa, Phys. Rev. A 18, 711 (1978).

[13] G. L. Braglia, G. M. de Munari, and G. Mambriani, in Com. Naz. Energia Nucl. RT/F160 (1965).

[14] H. V. Milloy, R. W. Crompton, J. A. Rees, and A. G. Robertson, Aust. J. Phys. 30, 61 (1977).

[15] T. G. Strand and R. A. Bonham, J. Chem. Phys. 40, 1686 (1964).

[16] W. A. Garret and R. A. Mann, Phys. Rev. 130, 650 (1963).

[17] M. E. Riley and D. G. Truhlar, J. Chem. Phys. 63, 2182 (1975).

[18] D. G. Thompson, Proc. R. Soc. London A 294, 160 (1966).

[19] J. Rubio, J. Phys. C 2, 288 (1969).

[20] P. L. Leath, Phys. Rev. B 2, 3078 (1970).

[21] T. E. Faber, *An Introduction to the Theory of Liquid Metals* (Cambridge University, Cambridge, England, 1972).

[22] G. V. Chester and A. Thellung, Proc. Phys. Soc. London 73, 745 (1959).

[23] L. E. Ballentine, Adv. Chem. Phys. 31, 263 (1975).

[24] N. W. Ascroft and W. Schaich, Phys. Rev. B 1, 1370 (1970).

[25] K. M. Watson and J. Nuttal, *Topics in Several Particle Dynamics* (Holden-Day, San Francisco, 1967).

[26] M. Watabe and F. Yonezawa, Phys. Rev. B 11, 4753 (1975).

[27] J. P. Hansen and J. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1976), p. 68.