Transport of Electrons in Atomic Liquids in High Electric Fields

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ABSTRACT

To describe the transport properties of hot electrons in high electric fields, a theory for the scattering of excess electrons in atomic liquids with high atomic polarizability is proposed. The theory is based on the variable phase method and it does not require information about the short-range part of the electron-atom potential. The scattering of electrons by density fluctuations in a liquid of a given macroscopic density (the liquid density) is taken into account in the framework of the theory. Mobility, mean and characteristic energies of electrons as functions of the electric field strength are calculated for different liquid densities. The results are presented for liquid Ar at the triple point, and at the density at which the scattering of electrons by density fluctuations is predominant.

1 INTRODUCTION

BEGINNING in the sixties, extensive experimental data for excess electron transport in liquefied noble gases were obtained [1–9]. If the polarizability of the atoms of the liquid is high (liquefied Ar, Kr, and Xe), the excess electrons have a high mobility. Zero-field mobility of electrons in these liquids has a strong density dependence. The theoretical aspects of this problem concern a most striking phenomenon, the nonmonotonic dependence of zero-field electron mobility as a function of density in liquid Ar [10, 11]. In these papers it has been shown that the increase in electron mobility with decrease of liquid density corresponds to the weak scattering of slow electrons for low liquid densities.

Under the action of an external electric field, the electrons become heated and their mobility decreases with increasing electric field strength. At present there are experimental data both for the zero-field mobility of thermal electrons and for the mobility of hot electrons in strong electric fields. With increasing electric field strength, the mobility of electrons decreases. Such a dependence is obtained for electric field strengths E larger than some threshold value E_h. The value E_h for the electric field is required for the onset of electron heating. At higher field values, electrons become hot. Transport coefficients of hot electrons such as the mobility μ, the diffusion coefficients $D_{||}$ and $D_{\perp}$, along and perpendicular to the electric field, the mean electron energy ϵ_m, and the longitudinal $\epsilon_\lambda = D_{||}/\mu$ and transverse $\epsilon_{tr} = D_{\perp}/\mu$ characteristic energies depend on the electric field strength. The transverse characteristic energy was measured in liquid Ar and Xe.

For an analysis of the electron transport experimental data, a theory has been proposed by Cohen and Lekner [12]. According to this theory, the transport properties of free electrons in a liquid are described in the framework of a kinetic theory: an energy distribution function of electrons, and the Boltzmann equation for this function, which takes into account scattering of electrons in a liquid. Spatial correlation between atoms is taken into account by the structure factor of a liquid. The kinetic properties of the hot electrons in liquid Ar [11] and other heavy noble liquids [13] have been calculated for the liquid states near the triple points in the framework of this theory. The cross section for electron scattering has been assumed to be a constant for slow electrons; for electrons with large energies the cross section in the liquid tends to the cross section of an isolated atom. This assumption needs proof, and its justification will be verified below in this paper by the calculation of electron scattering in liquids.

A theoretical model for electron scattering in liquid Ar, Kr, and Xe at different densities, including the density of the triple point N_{tp} and the density N_m where a maximum in mobility occurs, is presented in this paper. The theory is based on the variable phase method and needs no information about the short-range part of the electron-atom potential. In the framework of this theory, scattering phase shifts for electrons in the liquid are calculated as a function of the electron energy. The phase shifts obtained are used to produce of a density dependent cross section of electrons in the liquid. Then, in the frame of the Cohen-Lekner theory, this cross section can be used to describe of the transport coefficients of hot electrons and their heating by a strong external electric field. So far the calculation of hot electron mobility has been carried out only for the triple point of the liquid. In this paper, the calculations of hot electron transport coefficients for smaller densities, including the density at which the mobility maximum is observed, are reported. The results of these calculations show the change of the transport coefficients over a wide range of electric fields and of liquid densities. At the present moment, complete experimental data have been obtained for the electron mobility. Measurements of the transverse characteristic energy have been carried out only for the triple point in liquid Ar and Xe. Therefore a comparison of the calculated results with the experimental data

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is performed for these conditions only for the electron mobility.

2 SCATTERING OF ELECTRONS IN ATOMIC LIQUIDS WITH HIGH POLARIZABILITY

2.1 ELECTRON SCATTERING BY AN ISOLATED ATOM

The quantum theory treats electron scattering in terms of the partial wave functions and their phase shifts. For an isolated atom the partial wave phase shifts $\delta\lambda(k)$ for $l = 0, 1 \ldots$ and the cross section $q(\epsilon)$ of an atom depend on the wave number k and the electron energy. The wave number k is related to the electron energy ϵ by the expression $\epsilon = 13.6k^2$ eV where k is measured in atomic units (a_0^{-1}), and $a_0 = \hbar^2/e^2m = 5.3\times10^{-9}$ cm is the Bohr radius, which is formed from the Planck constant $\hbar$, and the electron charge e and the mass m. For slow electrons, the homogeneous (s-wave) scattering with $l = 0$ is the predominant one. In this case the low energy limit $\epsilon \to 0$ of the cross section is determined by the scattering length L_a of the atom

$$q_a(0) = 4\pi L_a^2 \tag{1}$$

For the isolated atom the cross section for slow electrons is thus constant.

The scattering of an electron by isolated Ar, Kr or Xe atoms is determined by competition between a short-range repulsion and a long-range polarization attraction. The negative sign of the scattering length of atoms and the Ramsauer minimum in their energy dependent cross-section results from this competition. For larger electron energies, the next partial waves (p-wave with $l = 1$, d-wave with $l = 2$, *etc.*) have to be taken into account and the momentum transfer cross section of atom $q(\epsilon)$ as a function of electron energy ϵ is determined by the expression

$$q(\epsilon) = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(l+1)\sin^2(\delta_l - \delta_{l+1}) \tag{2}$$

For moderate energies s- and p-wave scattering can only be taken into account in the equation

$$q(\epsilon) = \frac{4\pi}{k^2}\left[\delta_0^2(k) - 2\delta_0\delta_1 + 3\delta_1^2(k)\right] \tag{3}$$

The low energy limit Equation (1) is obtained because

$$\delta_0(k) = -L_a k \tag{4}$$

for small wave numbers, and $\delta_0(k) \gg \delta_1(k)$. The s-wave phase shift $\delta_0(k)$ for an isolated Ar atom is shown as points in Figure 1. For the small wave number k, the phase shift $\delta_0(k)$ is positive because the scattering length for Ar, Kr, and Xe atoms are negative, and it means that the electron-atom polarization attraction plays the more important role. For larger values of k, the s-wave phase shift of the atom decreases with electron energy increase, and it becomes negative for $k > k_* = 0.15a_0^{-1}$. In this energy domain the short-range repulsion between an atom and an electron predominates. For the electron energy 0.3 eV, which corresponds to the wave number k_*, the s-wave partial scattering is weakened and in a gas, the cross section as a function of electron energy is small.

Therefore, the sign of the s-wave phase shift correlates with the atom-electron interaction: the positive value of $\delta_0(k)$ means that the attraction predominates, and the negative value of $\delta_0(k)$ infers the predominance of the electron-atom repulsion. This opposition produces the

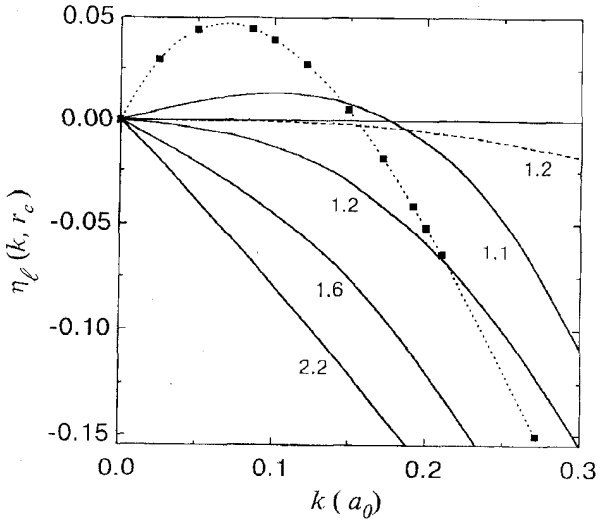

Figure 1. Partial phase shifts $\eta_l(k, N)$ as a function of the wave number k for isolated Ar atom (points and dotted line) and liquid Ar with different densities: Solid lines, s-wave $\eta_0(k, N)$, $N = 1.1\times10^{22}$ cm^{-3}, 1.2×10^{22} cm^{-3}, 1.6×10^{22} cm^{-3}, 2.2×10^{22} cm^{-3}. Dashed line, p-wave $\eta_1(k, N_m)$ at the density $N_m = 1.2\times10^{22}$ cm^{-3}.

Ramsauer effect in noble gases with high values of atomic polarizability (Ar, Kr and Xe). The effect, consisting in the weakening of electron scattering with energies between 0.3 and 0.5 eV in the gases, is a result of the competition of the long-range polarization attraction and the short-range repulsion, which leads to their considerable mutual compensation. The attraction dominates at low energies, but with increasing energy the repulsion takes over, and the cross section of an electron as a function of energy has the well pronounced Ramsauer minimum. However in the corresponding liquids the Ramsauer effect is absent [14]. In dense media the overlapping of the long-range polarization potentials of the nearest atoms weakens the attraction, and the repulsion dominates even at low energies. The absence of the Ramsauer effect in liquids near their triple points was discovered long ago [11]. The evolution of the character of electron scattering with the density variation from liquid to gas was investigated in [14]. Below, it is pointed out that the Ramsauer effect appears when the density of liquid is decreased. To show this, we shall consider the features of electron scattering in liquids.

2.2 ELECTRON SCATTERING IN AN ATOMIC LIQUID.

In liquids the mean distance between neighboring atoms is $r_c = \sqrt[3]{3/4\pi N}$, where N is the particle density of the liquids, $N \simeq 1$ to 2×10^{22} cm^{-3}. For these densities, $r_c = (4.3 \text{ to } 5.4)a_0$. This distance is larger than the size of an atom, but considerably smaller than the radius of significant electron-atom polarization attraction. Hence, at a transition from a rare gas to a liquid the short-range part of atom-electron potential remains unchanged, but the polarization part of the potential is noticeably diminished. The average field affecting an electron in the liquid is related to a 'muffin-tin' potential. One can model an element of this potential by surrounding each atom of the liquid by the Wigner-Seitz sphere with a radius r_c. The Wigner-Seitz cell plays the role of the unified scatterer of electrons in the liquid. The potential

$V(r)$ affecting an electron inside the cell is the sum of the potential of a centered atom $V_a(r)$ and the mean potential of the surrounded atoms $\langle V_p(r)\rangle$

$$V(r) = V_a(r) + \langle V_p(r)\rangle \qquad r \leqslant r_c \tag{5}$$

The short-range repulsive part of the electron-atom potential is not well known, but the long-range polarization attraction has the known asymptotic form $V_a(r \to \infty) = -\alpha e^2/2r^4$, where α is the polarizability of the atoms.

The potential of the surroundings is created by the atoms outside the cell which are at distances from the cell center larger than r_c. We can write the potential of the surroundings in the form [15]

$$\begin{aligned}\langle V_p(r)\rangle &= -\frac{3\alpha e^2}{2r_c^3}\int_{r_c}^{\infty}\frac{g(R)r^2(2R^2-r^2)f(r-R)\,dR}{R^2(R^2-r^2)^2} \\ &\approx -\frac{3\alpha e^2}{2r_c^3\sigma}f\frac{r^2}{\sigma^2}\left(1+\frac{r^2}{\sigma^2}\right)\end{aligned} \tag{6}$$

where σ is the parameter of the Lennard-Jones potential responsible for an inter-atomic repulsion. Here the sum over the ensemble of the surrounding atoms is replaced by an integration over a continuous density distribution in the liquid with the pair correlation function $g(R)$. The parameter σ of the inter-atomic attraction in a liquid is included in an expression for $g(R)$. The factor f is taken outside the cell and it equals the Lorentz-Lorenz factor of the local field [11], $f = (1+8\pi\alpha N/3)^{-1}$. The mean environment potential given by Equation (6) is smaller than the potential of a centered atom $V_a(r)$ everywhere in a cell, except in a domain close to a cell boundary. Thus, scattering of electrons by the Wigner-Seitz cell is determined by the potential $V_a(r)$ which is cut off at the boundary of a cell. The cell potential $V(r)$ is a short-range one and its range is limited by r_c. The scattering cross section of electrons in the liquid is determined by this potential. Scattering of electrons by the short-range cell potential given by Equation (5) is different from scattering by the spatial infinite polarization potential of an isolated atom.

For calculation of the cross section, the variable phase method is used [16]. The partial phase shifts $\delta_l^c(k, r_c)$ for the atom-electron potential $V_a(r)$, which is cut off at the boundary of the Wigner-Seitz cell r_c, can be obtained by the numerical solution of the phase function equation

$$\begin{aligned}\frac{d\delta_l^c(k,r)}{dr} = -\frac{2mV_a(r)}{\hbar^2 k}\big[&j_l(kr)\cos\delta_l^c(k,r) \\ &- n_l(kr)\sin\delta_l^c(k,r)\big]^2\end{aligned} \tag{7}$$

which is equivalent to the Schrödinger equation, where $j_l(kr)$ and $n_l(kr)$ are the spherical Bessel and Neumann functions respectively, and m is the electron mass. The boundary condition is an asymptote of the phase shift

$$\lim_{r\to\infty}\delta_l^c(k,r) = \delta_l(k) \tag{8}$$

The partial phase shift $\delta_l(k)$ for an isolated atom is included in the boundary condition. We suppose that the partial phase shifts $\delta_l(k)$ as a function of wave number k are known for the scattering of electrons by an isolated atom. So, the corresponding phase shifts for scattering by the centered atom of the isolated Wigner-Seitz cell can be calculated.

The mean potential $\langle V_p(r)\rangle$ can be taken into account in the framework of a perturbation approximation. The partial s-wave phase shift $\eta_0(k, r_c)$ of the Wigner-Seitz sphere potential $V(r)$ with radius r_c is

$$\eta_0(k,r_c) = \delta_0^c - \frac{2m}{\hbar^2 k}\int_0^{r_c}\langle V_p(r)\rangle\sin^2\left[kr+\delta_0^c(k,r)\right]dr \tag{9}$$

where $\delta_0^c(k, r_c)$ is the s-phase shift for the atom-electron potential which is cut off at the boundary of a cell. For the s-wave phase shift $\delta_0^c(k, r_c)$, the phase function Equation (7) and the boundary condition (8) have the form

$$\begin{aligned}\frac{d\delta_0^c(k,r)}{dr} &= -\frac{\alpha}{a_0 r^4}\frac{\sin^2\left[kr+\delta_0^c(k,r)\right]}{k} \\ \lim_{r\to\infty}\delta_0^c(k,r) &= \delta_0(k)\end{aligned} \tag{10}$$

The calculated partial phase shifts $\eta_l(k, r_c)$ are a function of both the wave number k and the cell radius r_c. The last means that the phase shifts obtained are functions of the fluid density.

The s-wave phase shifts for Ar with different values of r_c (for different values of liquid density) are presented in Figure 1. For an isolated atom ($r_c \to \infty$) the s-phase shift $\delta_0(k)$ is positive for small k and has zero value at $k_* = 0.15a_0^{-1}$. This means that the scattering length for an isolated Ar atom is negative and the cross section has a minimum (the Ramsauer effect) as a function of electron energy at $\epsilon = 0.3$ eV. At the triple point ($N_{tp} = 2.2\times10^{22}$ cm^3, $r_c = 4.18a_0$) $\eta_0(k, r_c)$ is negative (see Figure 1). It means that the scattering length is positive at this density. The phase shift $\eta_0(k, r_c)$ is a monotonic function of the wave number k, and there is no Ramsauer minimum in electron-scattering cross section in the liquid. For density $N_m \simeq 1.2\times10^{22}$ cm^{-3}, the $\eta_0(k, r_c)$ curve has no linear length for small k. This signifies that the scattering length is equal zero, and the mobility of thermal electrons has a maximum at this density [10].

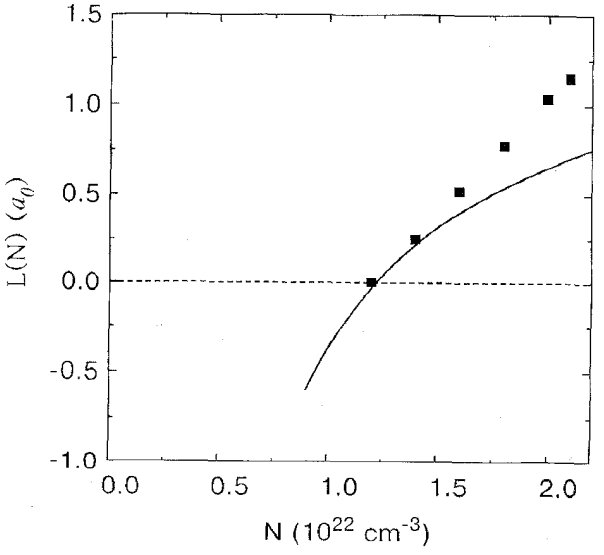

Figure 2. Scattering length in liquid Ar *vs.* density (solid line). Squares, experimental data [3].

The scattering length of the Wigner-Seitz cell having the potential $V(r)$, Equation (5), is shown in Figure 2 as a function of the density of the liquid. The function $L(N)$ decreases monotonically from positive values for a liquid near its triple point to negative values for a gas. At the density $N_m = 1.2\times10^{22}$ cm^{-3}, the function $L(N)$ crosses zero

and the corresponding low-energy cross section Equation (1) is zero. In this case, the scattering of low energy electrons is determined by both an energy dependent s-wave partial cross section and a p-wave cross section.

The cell potential $V(r)$, Equation (5), is a short-range one and the Blatt-Jackson expansion of a partial wave phase shift $\eta_l(k, r_c)$ in term of the wave number k is valid, *i.e.*

$$\tan \eta_l(k, r_c) = -k^{2l+1}\left[a_l(r_c) + b_l(r_c)k^2\right] \quad (11)$$

where the parameters a_l and b_l are functions of the cell radius r_c. For the s-wave phase shift $\eta_0(k, r_c)$, the expansion Equation (11) can be written in the form

$$\eta_0(r_c, k) = -L(r_c)k - A(r_c)k^3 \quad (12)$$

where $L(r_c)$ is the scattering length in a liquid. The coefficient $A(r_c)$ can be calculated over a wide range of densities [18]. For argon at the density N_m this parameter has a magnitude $A(r_m) = 6a_0^3$. The p-wave phase shift has the cube power dependence on wave number and is given by

$$\eta_1(k, r_c) = -a_1(r_c)k^3 + O(k^5) \quad (13)$$

The parameter $a_1(r_c)$ as a function of the cell radius r_c is calculated by the variable phase functions method. For Ar at the density $N_m \simeq 1.2\times10^{22}$ cm^{-3}, $a_1(r_m) = 0.67a_0^3$, and $a_1(r_{tp}) = 3.4a_0^3$ at the density $N_{tp} = 2.2\times10^{22}$ cm^{-3} near the triple point. The result of calculations of p-wave phase shift using Equation (13) for $r_m = 5.11a_0$ is shown in Figure 1 as a dashed line.

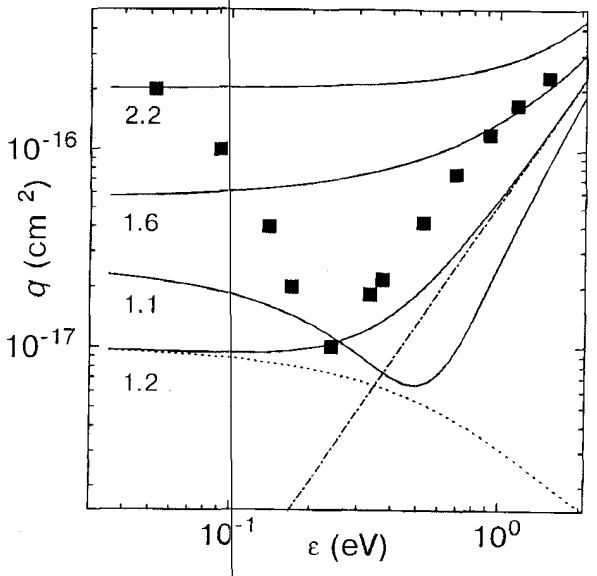

Figure 3. Elastic scattering cross section as a function of electron energy for an isolated Ar atom (squares) and for liquid Ar at different densities: $N = 1.1\times10^{22}$ cm^{-3}, 1.2×10^{22} cm^{-3}, 1.6×10^{22} cm^{-3}, 2.2×10^{22} cm^{-3} (solid lines). Dashed line - individual scattering by unit cell $q_{cell}(\epsilon, N_m)$ at the density $N_m = 1.2\times10^{22}$ cm^{-3}. Dotted line, scattering by density fluctuation $q_f(\epsilon, N_m)$, Equation (17).

In Figure 3 the cross section for an isolated Ar atom is compared with the cross sections calculated by means of Equation (3) for liquid Ar, using the partial wave phase shifts $\eta_0(k, r_c)$ and $\eta_1(k, r_c)$. At the triple point the cross section depends weakly on the energy. Such dependence is typical for a short-range scatterer. Initially, the cross section in liquid Ar at its triple point was calculated and taken into account by Lekner [11]. The energy dependence of the cross section for $N = 1.6\times10^{22}$ cm^{-3} is almost identical with that for the triple point, but the magnitude of the cross section $q(\epsilon)$ is smaller, because the scattering length is smaller too. Finally, for the density $N = 1.1\times10^{22}$ cm^{-3} the energy dependence of the cross section exhibits the Ramsauer effect. At this density the scattering length is negative, and the competition between the electronmedium attraction and repulsion is clearly displayed as the Ramsauer minimum in the cross section.

2.3 ELECTRON SCATTERING BY FLUCTUATIONS OF FLUID DENSITY

It is interesting to analyze the N_m case in more detail, when the scattering length equals zero and scattering by a single cell is weak. The s- and p-wave phase shifts are proportional to k^3. As the s-wave and p-wave phase shifts are proportional to k^3, the cross section of individual scattering by a single cell Equation (3) as a function of the electron energy ϵ is proportional to ϵ^2 and is very small for small ϵ. The magnitude of the mobility at its maximum is large, but limited. Experiments show that the magnitude of mobility not so large as would follow from consideration of the individual cross section only. So, a different mechanism of electron scattering exists in a liquid, and it is predominant at density N_m where individual s-wave scattering of electron by the isolated Wigner-Seitz cell is weakened. Scattering of electrons by density fluctuations has to be taken into account [10]. This scattering determines the magnitude of the mobility maximum at $N_m \simeq 1.2\times10^{22}$ cm^{-3}.

In real liquids, there are fluctuations of liquid density ΔN and their mean-squared value $\overline{(\Delta N)^2}$ is not equal to zero. The cell radius $r_c(N)$ fluctuates due to the density fluctuations. The mean-squared value of the random radius $r_c(N)$ is also not equal to zero. For low-energy electrons, the cross section is determined by the partial wave phase shift squared, and the mean-squared s-wave phase shift is not equal to zero for a cell with a mean radius r_m. Taking into account s-wave and p-wave phase shifts only, we obtain for the cross section of electron scattering by the density fluctuations

$$q_f(\epsilon, N_m) = \frac{4\pi}{k^2}\left[\overline{(\Delta\eta_0)^2} + 3\overline{(\Delta\eta_1)^2} - 2\overline{(\Delta\eta_0\Delta\eta_1)}\right] \quad (14)$$

where ϵ is the electron energy, and k is the corresponding wave number. The values of $\overline{(\Delta\eta_0)^2}$ and $\overline{(\Delta\eta_1)^2}$ are the mean-squared values of the fluctuations of the s-wave and p-wave phase shifts, given by

$$\overline{(\Delta\eta_l)^2} = \left(\frac{4\pi}{9}r_c^4\frac{d\eta_l(k, r_c)}{dr_c}\right)^2\overline{(\Delta N)^2} \quad (15)$$

To calculate the derivatives from the phase shifts $\eta_l(k, r_c)$ of cell radius r_c, the variable phase method is used. According to that method, the phase shift $\eta_l(k, r_c)$ for scattering by the cell potential $V(r)$, cut off at the distance r_c, satisfies the equation

$$\frac{d\eta_l(k, r)}{dr} = -\frac{2mV(r)}{\hbar^2 k}\times \left[j_l(k, r)\cos\eta_l(k, r) - \eta_l(k, r)\sin\eta_l(k, r)\right]^2 \quad (16)$$

where $j_l(k, r)$ and $n_l(k, r)$ are spherical Bessel and Neumann functions respectively, and the potential $V(r)$ affecting an electron inside the cell, Equation (5). Equations (14) to (16) can be used to obtain the cross section for scattering by density fluctuations as a function of the

wave number k. Thus,

$$q_f(\epsilon, r_m) = 4\pi\overline{(\Delta L)^2}\left\{\left(\frac{\sin kr_m}{kr_m}\right)^4 + 3\left(\frac{\sin kr_m - kr_m\cos kr_m}{(kr_m)^2}\right)^4 - 2\left(\frac{\sin kr_m(\sin kr_m - kr_m\cos kr_m)}{(kr_m)^3}\right)^2\right\} \quad (17)$$

Equation (17) is written for the case for which the mean cell radius equals r_m and the mean scattering length is zero, *i.e.* $L(r_m) = 0$. The mean-squared value of the random scattering length due to density fluctuations is

$$\overline{(\Delta L)^2} = \left(\frac{2m}{3\hbar^2}V(r_m)r_m^3\right)^2\frac{\overline{(\Delta N)^2}}{N_m^2} \quad (18)$$

Here $\overline{(\Delta N)^2} = \chi_T N^2 T\Omega^{-1}$ is the squared mean fluctuation of the density of a liquid of volume Ω and χ_T is the isothermal compressibility of the liquid. The cross sections of scattering by a cell $q_{cell}(\epsilon, N_m)$ in a liquid Ar having the density N_m and of scattering by fluctuations $q_f(\epsilon, N_m)$ are shown in Figure 3 by dashed and dotted lines. For small electron energies the cross section of the fluctuations is constant. Its magnitude contains the unknown parameter Ω, which is determined from the experimental value of the mobility peak at density N_m. With increase of electron energy, the cross section of density fluctuations decreases. Thus, low energy electrons are scattered by the density fluctuations. Fast electrons with energy larger than 0.4 eV are scattered by the Wigner-Seitz cells. The summarized cross section for electron in liquid Ar with a cell radius r_m is shown in Figure 3 as a solid line.

Thus, the variable phase function method allows us to describe the scattering of electrons in dense fluids such as liquefied Ar, Kr and Xe over a wide range of densities. For the liquids near their triple points, scattering of electrons occurs by the Wigner-Seitz cells. The scattering length of the cell is positive, and the s-wave phase shift $\eta_0(k, r_c)$ is a linear function of wave number for large values of k. So, the cross section of electrons in the liquid at such densities is constant for high electron energies, Figure 3. At this density the contribution of electron scattering by fluctuations Equations(17) and (18), is negligible compared with individual scattering by the cells. As the density of a liquid decreases, the scattering length of the cell becomes smaller and equals zero at the density N_m. In this case s-wave and p-wave scattering by an isolated cell is very small and scattering of electrons by density fluctuations plays a significant role. The cross section for this scattering is constant for small electron energies and is determined by the volume of the most effective fluctuation. This cross section decreases as electron energy increases, and the individual scattering of electrons by a cell, growing with electron energy, becomes predominant for fast electrons with energy > 0.4 eV. In this case, at density N_m, slow electrons are scattered by the density fluctuations and fast electrons are scattered by the Wigner-Seitz cells. Let us consider how these features of electron scattering are manifested in electron transport properties.

3 THE MOBILITY AND HEATING OF ELECTRONS

The cross section obtained for electrons as a function of their energy in liquid Ar at different densities can be used for the calculation of electron transport properties, such as mobility, and the mean and characteristic energies in the framework of Cohen-Lekner theory [12]. Electrons are scattered in a liquid, and lose their energy and momentum in these collisions. The energy transfer from an electron to atoms of the liquid occurs by elastic electron-atom collisions and electron energy losses are determined by the relation $\delta = 2m/M$, where m is the electron mass and M is the atom mass. According to the Cohen-Lekner theory, in the case of individual scattering by cells the spatial correlation of atoms must be taken into account in the momentum transfer cross section. Every cell has an atom of the liquid at its center. Therefore, the spatial positions of cells correspond to the positions of atoms of a liquid. The structure factor $S(k)$ of the liquid must be taken into account in the calculation of the momentum transfer cross section of scattering by cells [12]. For electron energies < 2 eV, the long-wave limit $S(0)$ of the structure factor $S(k)$ is contained in the momentum transfer cross section $q_s(\epsilon)$ as a factor, so that $q_s(\epsilon) = S(0)q_{cell}(\epsilon)$. The structure factor $S(k)$ can be obtained from experimental data of neutron and X-ray scattering in liquids and from computer simulations. The long-wave limit of the structure factor $S(0)$ is related to the isothermal compressibility χ_T of a liquid by the expression $S(0) = NT\chi_T$. The motion and heating of electrons in liquids under the action of an external electric field are determined by two electron-energy dependent parameters, namely the frequency of energy transfer ν_ϵ and the frequency of momentum transfer ν_m, so that

$$\begin{aligned}\nu_\epsilon &= \delta N q(\epsilon, N)(2\epsilon/m)^{1/2}\\ \nu_m &= N q_s(\epsilon, N)(2\epsilon/m)^{1/2}\end{aligned} \quad (19)$$

Here N is the particle density of the liquid, ϵ is the electron energy, $\delta = 2m/M$ is the doubled electron-atom mass ratio, *i.e.* the fraction of electron energy losses at the elastic collision

$$q(\epsilon, N) = q_{cell}(\epsilon, N) + q_f(\epsilon, N) \quad (20)$$

is the effective cross section for the elastic collisions of electrons in the liquid, and $q_s(\epsilon, N)$ is the momentum transfer cross section

$$q_s(\epsilon, N) = S(O, N)q_{cell}(\epsilon, N) + q_f(\epsilon, N) \quad (21)$$

These cross sections are the sum of the contributions to scattering by density fluctuations $q_f(\epsilon, N)$ and to scattering by cells $q_{cell}(\epsilon, N)$. The scattering of electrons by density fluctuations is not coherent. Hence the fluctuation momentum transfer cross section does not contain the structure factor of a liquid.

The state of a liquid Ar with the density $N_{tp} = 2.2\times10^{22}$ cm^{-3} is near the triple point and is reasonably far from the critical point. From data of isothermal compressibility [3], the long-wave limit of the structure factor $S(0)$ can be calculated as being 0.056 for this state. The dependence of $S(k)$ on the wave number k begins for electron energies > 2 eV [13]. So, we may use the long-wave value $S(0)$ for momentum transfer cross section if the mean energy of electrons is < 2 eV.

The situation is different for the Ar state at the density N_m. The states with density $N_m = 1.2\times10^{22}$ cm^{-3} and at 5 to 7 MPa (the temperature being near 150 K) [3] are close to the critical point for Ar (150.9 K, 483 MPa). The long-wave structure factor for liquid Ar at these

states is in excess of unity, $S(0) \approx 2.7$. It is the result of the contribution of long-range fluctuations in liquid density, which are typical in the vicinity of the critical point. The size of the long-range fluctuations is typified by a length which is larger than the inter-atomic spacing r_c. So, the k dependent structure factor $S(k)$ increases rapidly from the value $S(0)$ to unity in a narrow interval of very small k values. This region makes a small contribution to expressions for transport coefficients. Therefore in the following calculations we shall assume $S(0) = 1$ for Ar at the density N_m.

In the framework of a kinetic theory, transport coefficients of electrons are determined by the energy distribution function $f(\epsilon)$. In the zero-field limit, the function is the Maxwell distribution function with the temperature T of the liquid. If the electric field strength E is sufficiently large to satisfy the inequality

$$T \leqslant \frac{2e^2E^2}{3m_{eff}\nu_\epsilon(T)\nu_m(T)} \tag{22}$$

the function becomes the field-strength dependent non-Maxwellian distribution function $f(\epsilon, E)$. In that case, the electrons are 'hot' and their mean energy is larger than that corresponding to the liquid temperature. Transport coefficients of hot electrons such as the mobility μ, the diffusion coefficients parallel $D_\parallel$ and perpendicular $D_\perp$ to the field direction, and the longitudinal $\epsilon_l = eD_\parallel/\mu$ and transverse $\epsilon_{tr} = eD_\perp/\mu$ characteristic energies, depend on the field strength.

For low energies which correspond to the case of thermal electrons, the cross sections q_s and q are constant. At the density $N_{tp} = 2.2\times10^{22}$ cm^{-3}, the cross section $q_{cell}(\epsilon, N_{tp})$ of the Wigner-Seitz cells is more larger than the cross section $q_f(\epsilon, N_{tp})$ of the density fluctuations, because the scattering length $L(N_{tp})$ is larger than the root-mean-square value $[\overline{(\Delta L)^2}]^{1/2}$. In this condition, electron scattering by density fluctuations gives a small contribution to the cross sections $q(\epsilon, N_{tp})$ and $q_s(\epsilon, N_{tp})$. One can obtain from the inequality (22) the boundary field strength E_h, in excess of which electrons begin to heat, namely

$$E_h = e^{-1}N_{tp}T\sqrt{3\delta S(0)}4\pi L^2(N_{tp}) \tag{23}$$

At the density $N_m = 1.2\times10^{22}$ cm^{-3}, scattering of slow electrons by cells is very small and is determined by scattering due to density fluctuations. In this case the threshold field strength E_h is given by

$$E_h = e^{-1}N_mT\sqrt{3\delta}4\pi\overline{(\Delta L)^2} \tag{24}$$

Calculations using Equations (23) and (24) give $E_h(N_m) = 14$ V/cm and $E_h(N_{tp}) = 73$ V/cm. The last value is lower than $E_h = 200$ V/cm which is measured in reported experiments [6, 8]. This is a consequence of the discrepancy between experimental and theoretical values of the scattering length (see Figure 2). The experimental value $L(N_{tp}) = 1.1a_0$ is 1.5× the theoretical value of $0.7a_0$. It is not a large discrepancy for a theory without adjustable parameters. The expression (23) for E_h contains the scattering length squared, and the experimental value of E_h is twice the theoretical one. Below we use the experimental magnitude $L(N_{tp}) = 1.1a_0$ for calculations of electron transport coefficients in liquid Ar near its triple point.

The results of these calculations are represented in Figure 4, where the electron mobility, the mean energy, and the transverse and longitudinal characteristic energies, are shown as a function of electric field

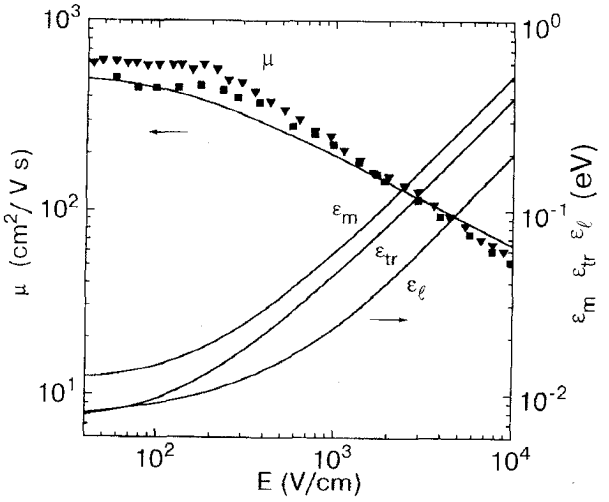

Figure 4. Transport coefficients of electrons in liquid Ar near the triple point ($N_{tp} = 2.2\times10^{22}$ cm^{-3}) as a function of electric field strength. Points, experimental data for mobility [6, 8]; solid lines, the calculated mobility μ, the mean electron energy ϵ_m, and the transverse ϵ_{tr} and the longitudinal ϵ_l characteristic energies.

strength. For field strengths $< E_h$ the transport coefficients are constant: the mobility of thermal electrons $\mu(0) = 500$ cm^2/Vs, the mean electron energy $\epsilon_m = 3T/2$, and the characteristic energies $\epsilon_{tr} = \epsilon_l = T$. As the electric field strength increases above E_h, electrons begin to heat and their transport coefficients depend on the field strength. For liquid Ar near its triple point the elastic cross section $q_{cell}(\epsilon, N_{tp})$ is constant for electron energies $\leqslant 1$ eV. For constant $q(\epsilon)$ and $q_s(\epsilon)$ it is easy to calculate the transport coefficients of hot electrons at $E > E_h$, where it is possible to neglect the liquid temperature T in the expression for the energy distribution function. In this case the mobility decreases as $E^{1/2}$ and the mean and characteristic energies are proportional to E [13], as given by

$$\begin{aligned} \mu(E) &= 1.1\mu(0)\sqrt{(E_h/E)} \\ \epsilon_m &= 1.05T(E/E_h) \\ \epsilon_{tr} &= 0.8T(E/E_h) \\ \epsilon_l &= 0.5\epsilon_{tr} \end{aligned} \tag{25}$$

These asymptotic expressions for transport coefficients are in good agreement with experimental data for mobility at electric field strengths $> 10^3$ V/cm.

For liquid Ar at the density $N_m = 1.2\times10^{22}$ cm^{-3}, the cross section of slow electrons is also constant and is determined by the scattering of electrons due to fluctuations in liquid density. The calculated results for electron transport coefficients at the density N_m are shown in Figure 5 together with experimental data for mobility. An initiation of heating occurs when there is a constant cross section, as in the case of Ar near the triple point. Then, as the heating field strength E increases, the electron mean energy becomes > 0.3 eV. Scattering by cells begins to play a significant role in the cross sections $q(\epsilon, N_m)$ and $q_s(\epsilon, N_m)$ (see the dashed line in Figure 3). When the field strength becomes large enough, individual scattering with cross section proportional to ϵ^2 prevails over scattering by density fluctuations. It leads to a weakening of electron heating, *i.e.* the dependence of $\epsilon_m(E)$ becomes consider-

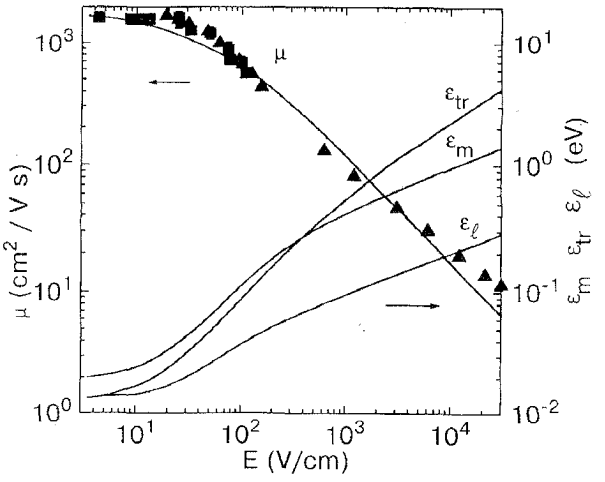

Figure 5. Transport coefficients of electrons in liquid Ar at the density $N_m = 1.2{\times}10^{22}$ cm^{-3} as a function of electric field strength. Points, experimental data for mobility [1, 6, 9]; solid lines, the calculated mobility, the mean electron energy ϵ_m, and the transverse ϵ_{tr} and the longitudinal ϵ_l characteristic energies.

ably weaker than linear. When the field strength reaches 10^3 V/cm, the electron mean energy attains the value 0.5 eV. In this condition most of the electrons are affected by collisions with cells. The cross section of these collisions is proportional to the square of electron energy *i.e.* $q_{cell}(\epsilon, N_m) \sim \epsilon^2$. The electron mobility as a function of the field strength decreases as $E^{-5/6}$. The mean energy of electrons grows as $E^{1/3}$, which is slower than the growth of electron heating with E at the triple point.

Let us call attention to the large divergence between characteristic and mean energy at high electric field strengths. The transverse characteristic energy is several times higher than the mean energy of an ensemble of electrons. It results from a large growth in the individual cross section with increasing electron energy. Due to the increase of the cross section $q_{cell}(\epsilon)$ as a function of electron energy, the growth in the mean energy of electrons $\epsilon_m(E)$ becomes slower. At the same time $\epsilon_{tr}(E)$ increases continuously, regardless of the increase of $q_{cell}(\epsilon)$. The magnitude of the transverse characteristic energy ϵ_{tr} is very sensitive to values of low energy cross section even for high field strengths. Therefore, in the case of strong growth in the cross section, the mean energy and longitudinal characteristic energy increase slowly with growth in field strength, but the transverse characteristic energy maintains its growth which is stronger than the $\epsilon_m(E)$ and $\epsilon_l(E)$ growth. The ratio between the transverse and longitudinal characteristic energies increases with growth in field strength and it reaches a factor 10 for strong fields. This phenomenon has been found by an analysis of the heating of electrons in the liquid near the triple point [13]. In this case the difference occurs for more larger field strengths, and a sharp growth in structure factor of a liquid as a function of electron energy produces this phenomenon. This difference is exhibited for field strengths larger than those shown in Figure 4.

4 CONCLUSION

A first attempt to provide a description of excess electron transport properties in noble liquids for a wide range of liquid densities and external electric field strengths is presented. It is possible to do so due to the adoption of a unified approach to electron scattering in these liquids. The scattering of electrons is caused both by atoms of the liquid and by fluctuations in the liquid density. The potential of the interaction between an electron and an atom inside the liquid is modeled by a 'muffin tin' potential, each cell being the Wigner-Seitz sphere surrounding every atom of liquid. This approach makes it possible to consider electron scattering in liquids with different densities and to describe the maximum of electron mobility as a function of liquid density.

The variable phase function approach is used for the investigation of electron scattering in a liquid. It makes it possible to calculate partial wave phase shifts and scattering cross sections as a function of electron energy for liquids with different densities. As a result, an explanation of the disappearance of the Ramsauer minimum of cross section as a function of electron energy is obtained for liquid Ar.

A peak in electron mobility is observed at the specific density N_m. In this case scattering of electrons by the Wigner-Seitz cells is small, and scattering by fluctuations of liquid density plays the major role. The cross section of scattering by density fluctuations is obtained as a function of electron energy. Scattering of electrons with large energy by density fluctuations weakens, and individual scattering by the Wigner-Seitz cells begins to play a major role for these energies.

These features of electron scattering in the liquid with different densities are manifested in an electric field dependence of electron transport coefficients. Near the triple point of Ar, electron scattering by density fluctuations is small and the cross section of scattering by the Wigner-Seitz cells varies weakly with electron energy. Therefore, as the heating of electrons in the external electric field increases, the electron mobility decreases with the field strength as $E^{-1/2}$, and the mean and characteristic energies increase proportionally with the field strength. At the density N_m at which the mobility peak is observed, the cross section as a function of electron energy increases, beginning at smaller energy values, because a fast electron scattering mechanism by cells replaces a slow electron scattering mechanism by density fluctuations. Therefore, a sharper decrease of the electron mobility $\mu \sim E^{-5/6}$ with field strength, and a weak heating $\epsilon_m \sim E^{1/3}$ are predicted. The difference between the mean and characteristic energies is related to the increase in cross section. Earlier, this divergence has been predicted for noble liquids at the triple point for higher field strengths. Measurements of the transverse characteristic energy have been carried out at the triple point of Ar only. It would be interesting to expand the scope of these measurements to include low liquid densities.

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