

Electron scattering in atomic liquids: Application to the maximum of electron mobility

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The phenomenon of the maximum of the electron mobility in liquids with a high atomic polarizability at the density N_m is explained by the suggestion of weakness of the s -wave scattering at this density. The model of the electron scattering by short-range potentials limited within the Wigner-Seitz cells is used. This model describes the change of the scattering length and predicts a zero value of the scattering length at the density N_m . The s - and p -wave phase shifts are calculated for this density. It is found that the cross section of the Wigner-Seitz cell is proportional to the electron energy squared and is negligible for slow electrons. Fluctuations of the liquid density result in fluctuations of the Wigner-Seitz cell radius. The s - and p -wave phase shifts and the mean cross section for *the electron scattering by fluctuations* are calculated. The phase shifts for an isolated atom are used as initial parameters. The mean cross section has a small but finite value for slow electrons and it decreases with the growth of the electron energy. It is shown that slow electrons are scattered by the fluctuations of the liquid density, and fast electrons are scattered by the Wigner-Seitz cells.

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I. INTRODUCTION

Electronic states in dense and strongly correlated systems such as liquefied noble gases have been already studied by many researchers.¹⁻⁴ After being injected into liquids with a high atomic polarizability (liquid argon, krypton, and xenon) the electrons are highly mobile and therefore can be considered as virtually free electrons. The zero-field mobility of electrons measured in liquids of this kind is a nonmonotonic function of liquid density.⁵⁻¹¹ With the growth of the liquid density N , the electron mobility $\mu(N)$ reaches its maximum. These maxima were detected in liquid Ar, Kr, and Xe at densities N_m , which are close to 10^{22} cm⁻³. According to Lekner¹² the peak value of the electron mobility μ_{\max} is determined by the electron scattering on fluctuations of the liquid density. Such scattering restricts the electron mobility at the density N_m .

In liquids, electrons move among strongly correlated scatterers. The basic theory developed by Lekner and co-worker^{13,14} takes into account the spatial correlation of atoms in the kinetic approximation of the electron mobility in atomic liquids. In this approach, like in the case of gaseous state, the main free path of electrons is much longer as compared to both the electron wavelength and the interatomic distance. It allows the kineticlike description of the electron behavior in liquids to be developed. This approach introduces an effective electron scattering cross section in liquids. As shown in Ref. 13 the cross section in liquids differs significantly from well-known cross sections in rarefied gases. For zero-energy electrons the cross section is determined by the scattering length. For isolated atoms of Ar, Kr, and Xe, scattering lengths are usually negative, $L_{\text{atom}} < 0$. This results from the predominant long-range polarization attraction between the isolated atom and the electron. In dense fluids the interatomic distance is small enough to make overlapped “tails” of the polarization potentials of neighboring atoms. This “muffin-tin” potential is realized in liquids. Each cell of this potential is a short-range scatterer with a positive scattering length, $L_{\text{cell}} > 0$. This is the direct result of

the competition between polarization electron-to-atom attraction and short-range repulsion. Being dominant in gases, the long-range polarization attraction is reduced in liquids due to the superposition of several electron-atomic potentials. In liquids the short-range repulsion evidently dominates, so with the increase of the medium’s density from gas to liquid, the effective scattering length $L_{\text{cell}}(N)$ surpasses the zero value and becomes positive.¹³ This change of sign of the scattering length results in the maximum of the electron mobility.

The effective cross section of electron scattering in liquids can be calculated using the electron-atom pseudopotential for liquids.^{13,15} In the framework of the pseudopotential method, the background energy $V_0(N)$, the effective electron mass $m_{\text{eff}}(N)$, the zero-field mobility $\mu(N)$, and the effective cross section as functions of the density were previously calculated.^{16,17} Parameters of the pseudopotential were determined from characteristics of the isolated atom such as polarizability α and the atomic scattering length L_{atom} . In the framework of this approach only low-energy s -wave scattering was taken into account to calculate the mobility of zero-energy electrons. The scattering length of the isolated atom is a basic parameter of the pseudopotential.

Another approach to describe the scattering of fast electrons in liquids with high atomic polarizability was proposed in Ref. 18. It requires additional information about partial phase shifts of wave functions of electrons scattered by the isolated atom. In the framework of this method the phase shifts for s and p waves were calculated by the variable-phase method¹⁹ for the single cell of the muffin-tin potential. The Schrödinger equation for an electron wave function in the Wigner-Seitz cell of the muffin-tin potential was solved in Refs. 20–22. Parameters of the electron energy spectrum, V_0 and m_{eff} , in liquids were calculated as functions of the liquid density. The electron mobility was not determined in these calculations. In these works the authors used complex electron-atom potentials. In the variable-phase method developed in Ref. 18 the electron-atom potential is substituted by more accessible data^{23–28} such as partial waves phase shifts

$\delta_\ell(\kappa)$ of the isolated atom with complete information about the electron-atom scattering. It allows us to calculate the phase shifts for the atomic potential inside the Wigner-Seitz cell. Mathematical aspects of the problem were considered in Ref. 18.

According to Lekner's theory¹² the maximum mobility is limited by electron scattering on density fluctuations. The present paper describes this phenomenon. First, density-dependent phase shifts of electron scattering waves are calculated for the electron-atom potential that is cut off outside of the muffin-tin cell. Second, phase shifts of the scattering on density fluctuations as functions of the electron energy are obtained by the variable-phase method. In the following section we discuss the scattering of electrons in dense atomic media with high polarizability. In order to obtain the effective transport cross sections the phase shifts of partial s and p waves ($\ell = 0, 1$) are calculated, and estimations of higher harmonics with $\ell > 2$ are made. The Wigner-Seitz cell, whose radius depends on the density of media, is a single scatterer in liquids. The phase shifts calculated in the present paper are functions of both the electron energy (wave number κ) and the density of media through the density-dependent radius of the cell, r_c . Expressions for phase shifts of electron scattering by Wigner-Seitz cells in conditions where the effective scattering length $L_{\text{cell}}(N)$ equals zero are obtained and the cross section of the cell is calculated. Then, the expressions for the mean-squared values of the s - and p -wave phase shifts for electron scattering by density fluctuations are obtained. As it will be shown below, such scattering prevails over the scattering by an individual cell for low-energy electrons. The magnitude of the fluctuation scattering cross section decreases with the growth of the electron wave number κ (electron energy) and becomes negligible in the case of hot electrons. Therefore, the single cell is the main scatterer for hot electrons.

Here we propose a model that allows fluctuation cross sections of low-energy electrons to be calculated. The expression for the cross section contains an unknown parameter. The physical meaning of this parameter is the volume of fluctuations that scatter the electrons. The mobility of electrons scattered by the fluctuations matches the maximum mobility measured experimentally. So, the value of the unknown parameter can be obtained by matching the calculated mobility with the experimental values of $\mu(N)$ in the vicinity of the maximum. The whole procedure is demonstrated by the example of the electron mobility in liquid xenon.

II. SCATTERING OF ELECTRONS BY A SINGLE MUFFIN-TIN CELL

In the liquid, electrons interact with the average field created by the atoms of the liquid. This potential field forms a muffin tin and each element of this potential can be modeled by surrounding each atom with the Wigner-Seitz cell. The cell has the density-dependent radius $r_c = (3/4\pi N)^{1/3}$; here N is the density number of atoms in the liquid. So, the liquid is considered as a set of Wigner-Seitz cells, and each cell acts as a single scatterer for electrons. Inside the cell the electrons interact with the central atom by the potential $V_{\text{atom}}(r)$,

which is a truncated electron-atom potential. Far from the center of the cell, the potential has a polarization form

$$V_{\text{pol}}(r) = -\frac{\alpha e^2}{2r^4}, \quad (1)$$

where r is the distance between the cell center and the electron, α is the atomic polarizability. The polarization potential, Eq. (1), is the well-known long-range part of the electron-atom potential, $V_{\text{atom}}(r)$. To consider the scattering of electrons by the cell, the phase-shift technique in the form of the variable-phase method¹⁹ has been used. In this method, it is not necessary to solve the Schrödinger equation for wave functions of electrons scattered by the potential $V(r)$ and to calculate phase shifts of the asymptotic form of wave functions. The phase shifts $\delta_\ell(\kappa)$ for the potential $V(r)$ are obtained as asymptotical solutions, $\eta_\ell(\kappa, r \rightarrow \infty)$, of the equation for phase functions,

$$\frac{d\eta_\ell(r, \kappa)}{dr} = -\frac{2mV(r)}{\hbar^2\kappa} [\cos \eta_\ell j_\ell(\kappa r) - \sin \eta_\ell n_\ell(\kappa r)]^2, \quad (2)$$

with boundary condition $\eta_\ell(0, \kappa) = 0$. Here $j_\ell(\kappa r)$ and $n_\ell(\kappa r)$ are the spherical Bessel and Neumann functions, respectively. In order to solve Eq. (2) with such a problem statement, the shape of the scattering potential $V(r)$ must be determined over all the considered area including the vicinity of zero.

It is easy to verify that $\eta_\ell(r, \kappa)$ is the phase shift of the partial ℓ -wave function scattered by the potential $V(r)$ cut at the distance r from the center. When r approaches infinity, the phase function tends to reach the value of the phase shift

$$\lim_{r \rightarrow \infty} \eta_\ell(\kappa, r) = \delta_\ell(\kappa), \quad (3)$$

at the full potential, which can be the nonrestricted potential, as the long-range polarization potential, Eq. (1). Therefore, calculations of phase shifts for the electron-atom potential cut off at the cell boundary r_c become equivalent to calculations of phase functions $\eta_\ell(r_c, \kappa)$. The phase shifts for the Wigner-Seitz cell can be obtained correctly by solving the phase equation, Eq. (2), with boundary conditions, Eq. (3), where $\delta_\ell(\kappa)$ are known partial phase shifts of an isolated atom. No specific information about the short-range part of the electron-atom potential is required in this approach. It is enough to solve Eq. (2) in the interval (r_c, ∞) , where the boundary conditions, Eq. (3), are valid for the right boundary of this interval ($r \rightarrow \infty$), and the function $\eta_\ell(r_c, \kappa)$ is obtained for the left boundary of the interval ($r = r_c$). There is only the long-range polarization part, Eq. (1), of the electron-atom potential within this interval. The phase shifts $\delta_\ell(\kappa)$ contain all the information about the short-range part of the potential $V_{\text{atom}}(r)$. These phase shifts can be taken from previous works.²³⁻²⁸

The modified-effective-range theory (MERT) developed by O'Malley²⁹ can be used to obtain phase shifts for an isolated atom. The four-parameter MERT expansions for scattering phase shifts are given by³⁰

$$\tan \delta_0 = -L_{\text{atom}} \ell \left[1 + \frac{4\alpha}{3a_0} \ell^2 \ln(\ell a_0) \right] - \frac{\pi\alpha}{3a_0} \ell^2 + D\ell^3 + F\ell^4, \quad (4)$$

$$\tan \delta_1 = \frac{\pi\alpha}{15a_0} \ell^2 - a_1 \ell^3,$$

$$\tan \delta_\ell = \frac{\pi\alpha\ell^2}{(2\ell+3)(2\ell+1)(2\ell-1)a_0}. \quad (5)$$

Here a_0 is the Bohr radius; ℓ is the electron wave number in units of a_0^{-1} [ℓ is related to the electron energy ϵ (eV) as $\epsilon = 13.6(\ell a_0)^2$]; ℓ is the angular momentum quantum number; L_{atom} and α are the atomic scattering length and polarizability; D , F , and a_1 are adjustable parameters taken from Ref. 30 for an Xe-like atom: $L_{\text{atom}} = -6a_0$, $\alpha = 27a_0^3$, $D = 490a_0^3$, $F = -628a_0^4$, and $a_1 = 22a_0^3$. The higher-order phase shifts, $\ell > 1$, were obtained by the Born approximation for the polarization potential. The MERT expansion for the phase shifts is valid only for a limited range of electron energies, $\epsilon < 0.75$ eV.

Some characteristics of the phase shifts of the Wigner-Seitz cell can be considered in the approximation of small values for the wave number ℓ . For example, the potential of the Wigner-Seitz cell is limited by the cell boundary r_c and turns out to be a short-range potential. In that case the Blatt-Jackson expansion for the ℓ -wave phase shift in terms of wave number ℓ is valid^{31,18} and leads to an s -wave phase-shift expansion in odd powers of the wave number,

$$\eta_0(r_c, \ell) = -L_{\text{cell}}(r_c)\ell - A(r_c)\ell^3, \quad (6)$$

here $L_{\text{cell}}(r_c)$ is the effective scattering length in the liquid. Coefficients $L_{\text{cell}}(r_c)$ and $A(r_c)$ are functions of the cell radius. The equation for the coefficients $L_{\text{cell}}(N)$ and $A(r_c)$ can be obtained by the substitution of expansion Eq. (6) into Eq. (2) for $\ell = 0$ with the polarization potential, Eq. (1), and by a comparison of the terms within one power of the wave number ℓ . The equation for $L_{\text{cell}}(N)$ was solved correctly by quadratures¹⁸ and the solution becomes

$$L_{\text{cell}}(r_c) = \left\{ \frac{1}{r_c} + \sqrt{\frac{a_0}{\alpha}} \tan \left[\arctan \left(\sqrt{\frac{\alpha}{a_0}} \frac{1}{L_{\text{atom}}} \right) - \sqrt{\frac{\alpha}{a_0}} \frac{1}{r_c} \right] \right\}^{-1}. \quad (7)$$

It is important to note that the scattering length of the Wigner-Seitz cell, $L_{\text{cell}}(r_c)$, obtained by this approach (the mean potential of the environment was not taken into consideration) describes qualitatively all features that are characteristic for electron scattering in atomic liquids. At larger distances r_c (or at lower densities N), the function $L_{\text{cell}}(r_c)$ tends to the value L_{atom} , which is the negative scattering length of the isolated atom. As the density increases (which

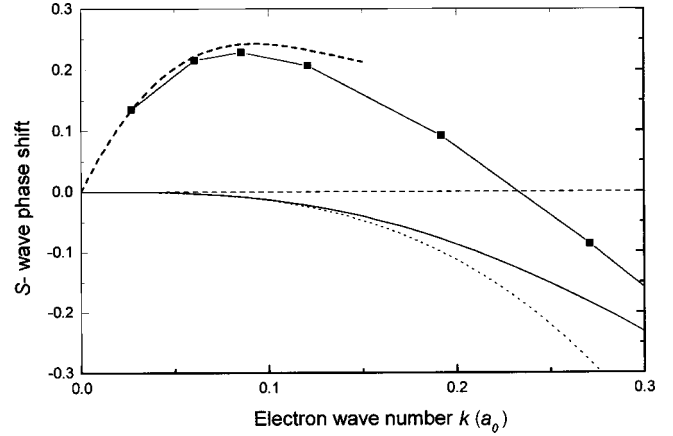


FIG. 1. s -wave phase shifts vs the wave number k for the isolated Xe atom, and for the Wigner-Seitz cell with radius $r_m = 6.06a_0$ and with the Xe atom in the center. $\delta_0(\ell)$ for the atom: points, data (Ref. 27); dashed line, the MERT approximation, Eq. (4). $\eta_0(\ell, r_m)$ for the cell: solid line, calculations by the variable-phase method; dotted line, calculations by the expansion (6).

corresponds to the decrease of r_c) the scattering length grows and changes its sign. According to Eq. (7), $L_{\text{cell}}(r_c)$ passes through zero at

$$r_m = \sqrt{\frac{\alpha}{a_0}} \left[\frac{\pi}{2} + \arctan \left(\sqrt{\frac{\alpha}{a_0}} \frac{1}{L_{\text{atom}}} \right) \right]^{-1}; \quad (8)$$

here $r_m = 6.06a_0$ for $L_{\text{atom}} = -6a_0$ and $\alpha = 27a_0^3$.

In a fluid with the density N_m corresponding to the radius r_m of the Wigner-Seitz cell, s -wave scattering is determined by the second term in the expansion, Eq. (6). With the density N_m and the radius r_m , the expression for $A(r_m)$ has a form¹⁸

$$A(r_m) = \frac{\alpha r_m}{3a_0} \left[1 - \beta \left(2 \sqrt{\frac{\alpha}{a_0}} \frac{1}{r_m} \right) \right], \quad \beta(z) = z \int_0^\infty \frac{\sin x}{(x+z)} dx. \quad (9)$$

The magnitude of $A(r_m)$ is $13a_0^3$ for $r_m = 6.06a_0$. The expansion Eq. (6) is significantly different from the MERT expansion, Eq. (4), for s -wave phase shifts of the nonlimited polarization potential, where the term quadratic in power ℓ , $\pi\alpha\ell^2/3a_0$, coexists with odd power terms. This is the result of the spatial limitation of the Wigner-Seitz cell potential. The results of the calculations of the s -wave phase shifts under conditions where the effective scattering length equals zero are shown in Fig. 1, together with s -wave phase shifts for the Xe atom calculated in Ref. 27 and by the MERT approximation. The phase shift for the isolated atom is positive for small ℓ and increases further in proportion to ℓ . Then, $\delta_0(\ell)$ falls down and passes zero. That leads to the Ramsauer effect for electron scattering in heavy noble gases. The Ramsauer effect disappears in these liquids.³² As it follows from Fig. 1, the s -wave phase shift is a negative monotonic function of ℓ until the Wigner-Seitz cell radius reaches r_m . The magnitude of the s -wave phase shift is far less than the magnitude of the phase shift of the isolated atom for small wave numbers.

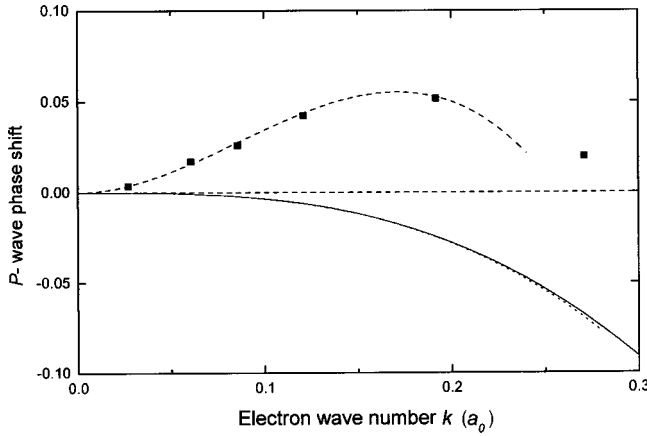


FIG. 2. p -wave phase shifts vs the wave number k for the isolated Xe atom and the Wigner-Seitz cell with radius $r_m = 6.06a_0$ and with the Xe atom in the center. $\delta_1(k)$ for the atom: points, data (Ref. 27); dashed line, the MERT approximation, Eq. (5). $\eta_1(k, r_m)$ for the cell: solid line, calculations by the variable-phase method; dotted line, calculations by the expansion (10).

According to the Blatt-Jackson expansion for the phase shifts for a short-range potential³¹ in terms of wave number k , the first term of this expansion for p -wave shifts has the same power of wave number k as the second term of the expansion for s -wave phase shifts,

$$\eta_1(r_c, k) = -a_1(r_c)k^3 + O(k^5). \quad (10)$$

The p -wave phase shift for the Wigner-Seitz cell with the radius r_m is calculated by Eq. (2) for $\ell = 1$. Data²⁷ for $\delta_1(k)$ are used for the boundary condition, Eq. (3). The results presented in Fig. 2 also contain the atomic phase shift. The last one is a positive nonmonotonic function of the wave number that increases as k^2 for small k . It results from the long-range polarization interaction between an electron and a single atom. For the short-range potential of the Wigner-Seitz cell with the radius r_m , the quantity $\eta_1(r_m, k)$ is a monotonic negative function and varies as k^3 for small k according to the expansion Eq. (10). It has been verified that $\lim_{k \rightarrow 0} [\eta_1(r_m, k)/k^3]$ is a constant as long as $a_1(r_m) = 3.5a_0^3$. So, in liquids with the density N_m , where $L_{\text{cell}}(N_m) = 0$, s - and p -wave phase shifts are proportional to k^3 and their values are less than the values for the corresponding phase shifts for an isolated atom.

The following d -wave phase shift $\eta_2(k, r_m)$ for the Wigner-Seitz cell can be estimated for small wave numbers using the Born approximation while considering only the polarizing interaction of the electron with the central atom,

$$\eta_2(k, r_m) = \frac{\pi \alpha k^2}{2a_0} \int_0^{r_m k} J_{5/2}^2(x) x^{-3} dx \approx \frac{\alpha}{1728 a_0 r_m^2} (k r_m)^5. \quad (11)$$

Here $J_{5/2}(x)$ is the spherical Bessel function, and the final expression is obtained for $k r_m \ll 1$. The phase shift for the d wave is proportional to k^5 for a short-range potential. The expression Eq. (11) is the first term of the Blatt-Jackson expansion for the d -wave phase shift. The d -wave phase shift

for the cell is much less than the d -wave phase shift for an isolated atom obtained in the same approximation, $\delta_2(k) = \pi \alpha k^2 / 105 a_0$. Hence, the d -wave scattering is negligible for the calculations of cross sections.

Transport properties of electrons (mobility, diffusion coefficient, etc.) are determined by the momentum-transfer cross section of electron scattering by the atoms of the medium. In our model electron scatterers are Wigner-Seitz cells. Each cell has the atom at its center. Therefore, spatial locations of the cells correspond to the positions of atoms in the liquid and they are correlated due to atom-to-atom interaction. According to the Cohen-Lekner theory¹⁴ the structure factor of the liquid $S(k)$ should be taken into account when calculating the momentum-transfer cross section. The structure factor $S(k)$ can be obtained from the experimental data of neutron³³ and x-ray scattering in liquids or by computer simulations. A long-wave limit of the structure factor $S(0)$ is in the relationship with the isothermal compressibility χ_T of the liquid, $S(0) = N T \chi_T$, and can be obtained from thermodynamic properties of the liquid. For slow electrons the $S(0)$ factor can be used in calculations of the momentum-transfer cross section, which is determined by the partial phase shifts η_ℓ ,

$$q_{\text{cell}}(r_c, \epsilon) = \frac{4\pi}{k^2} S(0) \sum_{\ell=0}^{\infty} (\ell+1) \sin^2(\eta_\ell - \eta_{\ell+1}). \quad (12)$$

The partial phase shifts $\eta_\ell(k, r_c)$ depend on the cell radius r_c . As a rule, the phase shift with $\ell = 0$ is the dominant shift in the case of slow electrons. This s -wave phase shift is a linear function for small k : $\eta_0(k, r_c) = -L_{\text{cell}}(r_c) k$. It leads to expression for the effective cross section of individual scattering of slow electrons by the single cell,

$$q_{\text{cell}}(N) = 4\pi S(0) L_{\text{cell}}^2(N). \quad (13)$$

In a liquid with the density N_m , at the maximum of electron mobility, the effective scattering length equals zero and the individual s -wave scattering is weak. In order to calculate the individual scattering cross section of the cell at the density N_m , we take into account the second term of the series for the s -wave phase-shift expansion by powers of the wave number and the first term of the corresponding series for the p -wave phase shift. It leads to a more accurate expression for the cross section of the single Wigner-Seitz cell in a liquid [as compared to Eq. (13)],

$$\begin{aligned} q_{\text{cell}}(\epsilon) &= \frac{4\pi S(0)}{k^2} (\eta_0^2 - 2\eta_1\eta_0 + 3\eta_1^2) \\ &= 4\pi S(0) k^4 [A^2(r_m) - 2A(r_m)a_1(r_m) + 3a_1^2(r_m)]. \end{aligned} \quad (14)$$

Here phase shifts are assumed to be less than unity, and only s - and p -wave phase shifts are taken into account for small wave numbers k . The cross section for slow electrons is proportional to the electron energy squared. This effective cross section is shown in Fig. 3 together with the cross section of an isolated atom of Xe. We restrict our considerations

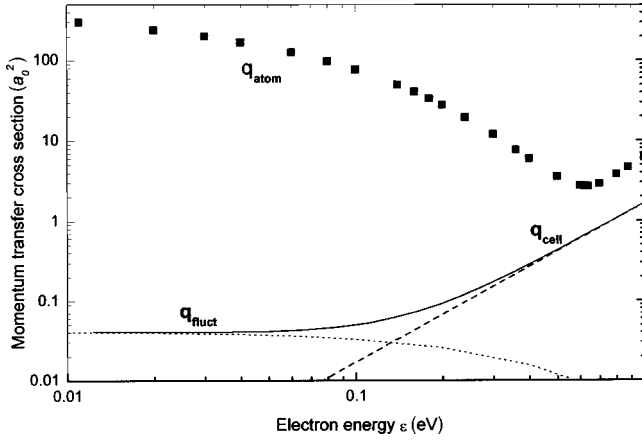


FIG. 3. Momentum-transfer cross section vs the electron energy. Points, isolated Xe atom (Ref. 30); dashed line, isolated Wigner-Seitz cell; dotted line, density fluctuations; solid line, the total cross section for the density N_m .

by electron energies that do not exceed 1 eV. Within this energy interval the expansion of phase shifts in terms of the wave number powers Eqs. (6) and (10) is valid. The effective cross section is negligible for slow electrons. So, in the liquid with the density N_m , low-energy electrons are not scattered by the single Wigner-Seitz cell with radius $r_c = r_m$, and their mobility seems to be infinite. Nevertheless, values of the peak mobility, $\mu_{\max}(N_m)$, measured in experiments are high, but limited. To explain this fact, the electron scattering by density fluctuations needs to be involved into our model.

III. SCATTERING OF ELECTRONS BY DENSITY FLUCTUATIONS

In this section electron scattering by density fluctuations is considered. In real liquids, there are density fluctuations ΔN , and their mean-squared value $(\Delta N)^2$ has a nonzero value. The mean-squared value of the density fluctuations, $(\Delta N)^2 = N^2 T \chi_T \Omega^{-1}$, is in a relationship with the isothermal compressibility of liquid, χ_T , and the volume of fluctuations, Ω . The cell radius $r_c(N)$ varies correspondingly with fluctuations. The mean-squared value of randomly fluctuating radius of the cell $(\Delta r_c)^2$ also has a nonzero value. For low-energy electrons, the cross section is determined by the partial-wave phase shift squared, and the mean-squared s -wave phase shift differs from zero for cells with the mean radius r_m . We consider the fluctuation having the linear dimension much larger than the mean interatomic distance, r_c . Fluctuations of the cell radius, $\Delta r_c = -r_c \Delta N / 3N$, lead to fluctuations of partial-waves phase shifts $\Delta \eta_\ell(r_c, \ell)$ of scattering by the Wigner-Seitz cell

$$\Delta \eta_\ell(r_c, \ell) = -\frac{r_c}{3} \frac{d\eta_\ell(r_c, \ell)}{dr_c} \frac{\Delta N}{N}. \quad (15)$$

The mean value of density fluctuations, (ΔN) , equals zero and the mean value of the phase-shift fluctuation, $\Delta \eta_\ell(\ell, r_s)$, equals zero as well. The expression for the cross section, Eq. (14), contains the phase shift squared. The mean

value of $[\Delta \eta_\ell(\ell, r_s)]^2$ is connected with $(\Delta N)^2$ and has a nonzero value. So, the momentum-transfer cross section includes both the contribution of individual scattering by single cell $q_{\text{cell}}(\epsilon, N_m)$, Eq. (14), and the contribution of scattering by density fluctuations,

$$q_{\text{fluct}}(\epsilon, N_m) = \frac{4\pi}{\ell^2} [(\Delta \eta_0)^2 + 3(\Delta \eta_1)^2 - 2(\Delta \eta_0 \Delta \eta_1)]. \quad (16)$$

The terms in the right-hand side of Eq. (16) are proportional to the mean-squared value of density fluctuations, $(\Delta N)^2$, and as it follows from Eq. (15) that they contain derivatives from phase shifts of the cell radius. To calculate these derivatives, the variable-phase method was used. Rewriting Eq. (2) for the phase shifts $\eta_\ell(\ell, r)$ of scattering on the polarization potential $V_{\text{pol}}(r)$, one obtains

$$\begin{aligned} \frac{d\eta_\ell(\ell, r_c)}{dr_c} = & -\frac{\pi\alpha}{2a_0 r_c^2} [J_{\ell+1/2}(\ell r_c) \cos \eta_\ell \\ & + (-1)^\ell J_{\ell+1/2}(\ell r_c) \sin \eta_\ell]^2. \end{aligned} \quad (17)$$

Substituting Eq. (17) into Eq. (15), one can obtain mean-squared values of ℓ -wave phase shifts

$$(\Delta \eta_\ell)^2 = \left[\frac{\pi\alpha}{6a_0 r_m^2} \right]^2 \frac{T\chi_T}{\Omega} J_{\ell+1/2}^4(\ell r_m). \quad (18)$$

Here it was assumed that the phase shifts η_ℓ are negligible in comparison with ℓr_m for considered values of wave numbers. The spherical Bessel function in the right-hand side of Eq. (18) defines $(\Delta \eta_\ell)^2$ as a function of the wave number ℓ . So, at the density N_m the partial cross sections of s - and p -waves scattering by density fluctuations are

$$(q_0)_{\text{fluct}} = \frac{4\pi(\Delta \eta_0)^2}{\ell^2} = 4\pi(\overline{\Delta L})^2 \left(\frac{\sin \ell r_m}{\ell r_m} \right)^4, \quad (19a)$$

$$\begin{aligned} (q_1)_{\text{fluct}} = & \frac{4\pi}{\ell^2} 3(\Delta \eta_1)^2 \\ = & 12\pi(\overline{\Delta L})^2 \left(\frac{\sin \ell r_m - \ell r_m \cos \ell r_m}{(\ell r_m)^2} \right)^4. \end{aligned} \quad (19b)$$

For low electron energies when $\ell r_m \ll 1$, the constant partial cross section for s -wave scattering is

$$(q_0)_{\text{fluct}} = 4\pi(\overline{\Delta L})^2, \quad (20)$$

here $(\overline{\Delta L})^2$ is the mean-squared value of the random scattering length due to density fluctuations,

$$(\overline{\Delta L})^2 = \left[\frac{\alpha}{3a_0 r_m} \right]^2 \frac{T\chi_T(N_m, T)}{\Omega}. \quad (21)$$

There is the adjustable parameter Ω in this expression, which is the volume of the fluctuation. We do not know how to justify the choice of this parameter. The first that comes to mind is to assume that the linear dimension of the optimal

fluctuation is equal to the electron wavelength. For thermal electrons in liquid Xe at $T=223$ K one obtains $\Omega=6.7 \times 10^4 a_0^3$. In the present calculations the experimental data⁷ for Xe were used. According these data the mobility maximum in Xe occurs at $T=223$ K and $N_m=1.2 \times 10^{22} \text{ cm}^{-3}$, where $S(0)=\overline{TN\chi_T}=0.18$. It was obtained that $S(0)/N_m\Omega=0.0015$ and $(\Delta L)^2=0.0033a_0^2$.

In the framework of our model, it is possible to obtain the cross section of fluctuations as a function of the wave number k . The partial s -wave cross section $(q_0)_{\text{fluct}}$ decreases with the growth of the electron energy according to Eq. (19a). The partial p -wave cross section, Eq. (19b), is proportional to the squared electron energy for slow electrons,

$$(q_1)_{\text{fluct}}=4\pi(\Delta L)^2\frac{(\ell r_m)^4}{27}. \quad (22)$$

The magnitude of this cross section is negligible in comparison with the s -wave cross section $(q_0)_{\text{fluct}}$ for $\ell r_m < 1$. The p -wave partial cross section of scattering by fluctuation, $(q_1)_{\text{fluct}}$ Eq. (22), is the same function of the electron wave number k as the cross section of the individual scattering by the single cell, Eq. (19). The magnitude of the later is much higher than that for $(q_1)_{\text{fluct}}$.

Following Eq. (18), the d -wave phase shift with $\ell=2$ for scattering of slow electrons by density fluctuations is proportional to k^5 , and the magnitude of the d -wave partial cross section of fluctuation is negligibly small.

The expression (16) for the cross section of scattering by density fluctuations has the crossing term

$$\begin{aligned} & -\frac{4\pi}{k^2}\overline{2(\Delta\delta_0\Delta\delta_1)} \\ & =-8\pi(\Delta L)^2\left[\frac{\sin\ell r_m(\sin\ell r_m-\ell r_m\cos\ell r_m)}{(\ell r_m)^3}\right]^2 \\ & \approx-8\pi(\Delta L)^2\frac{(\ell r_m)^2}{9}. \end{aligned} \quad (23)$$

The last equation was derived for small wave numbers, $\ell r_m \ll 1$. The contribution from this term reduces the fluctuation cross section, Eq. (16), which for the small k decreases with growth of the wave number (or electron energy) as

$$q_{\text{fluct}}(\ell, r_m)=4\pi(\Delta L)^2\left(1-\frac{8}{9}(\ell r_m)^2\right). \quad (24)$$

The cross section of fluctuations as a function of the wave number k is shown in Fig. 3, dotted line. For slow electrons with $\ell r_m \ll 1$, this cross section remains a constant. Then the cross section decreases with the growth of the electron energy according to Eq. (24).

The summary momentum-transfer cross sections $q(\epsilon, N_m)=q_{\text{cell}}(\epsilon, N_m)+q_{\text{fluct}}(\epsilon, N_m)$ of electron scattering by the Wigner-Seitz cells and by density fluctuations are shown in Fig. 3, solid lines. The partial s - and p -wave cross sections of the Wigner-Seitz cell depend on the electron energy as ϵ^2 and they are very small for low energies. For slow electrons, s -wave scattering by density fluctuations gives the main contribution to the summary cross section. So, the

momentum-transfer cross section is constant for small energies and is determined by scattering by the density fluctuations. For electrons with higher energies the cross section $q_{\text{fluct}}(\epsilon, N_m)$ decreases, Fig. 3, dotted line, and the summary cross section increases monotonically due to scattering by the Wigner-Seitz cells. The cross section of hot electrons is determined by scattering by Wigner-Seitz cells and increases as the square of electron's energy, Fig. 3, dashed line.

IV. DISCUSSION

Earlier Lekner¹² assumed in his qualitative explanation of the nature of the maximum mobility in liquid Ar that s -wave scattering of slow electrons by atoms is negligible in liquids at the density N_m . This means that the mean scattering length becomes zero and scattering of slow electrons occurs only by fluctuations of the liquid density at N_m . On the other side, the theory advanced in Ref. 13 does not include the density-dependent effective scattering length $L_{\text{cell}}(N)$, so in order to estimate the cross section of fluctuations, Lekner considered a spatial displacement of atoms in the electron environment.¹² This approximation considers only the influence of the fluctuating potential of atoms surrounding the cell.

In the present paper, we undertake further development of Lekner's theory but our approach to the problem is slightly different. The method we used is also capable of describing the passage of the function $L_{\text{cell}}(N)$ through zero at $N=N_m$. The model proposed in this paper describes electron scattering in media where individual electron-atom s -wave scattering vanishes in the first order of the expansion in powers of the wave number k . We also discuss next terms of the partial-wave phase-shifts expansion. Electrons are scattered by the Wigner-Seitz cells and each cell is characterized by the average radius r_c and the potential acting on the electron inside the cell. Scattering of slow electrons is determined through the constant cross section, Eq. (13), in the low-energy limit of the s wave. The scattering length of the cell equals zero at density N_m , so the scattering of slow electrons by the cell is totally determined by the next terms of s - and p -wave scattering. In the present work we calculated the phase shifts for s - and p -partial waves. Other partial phase shifts (d wave, etc.) are small for electrons with energies $\epsilon \leq 1$ eV, which results in the expression for the cross section of scattering by the Wigner-Seitz cell. This cross section is proportional to the electron energy squared, Eq. (14), and is negligible for low electron energies. It means that the mobility of electrons scattered by the cells becomes infinite as the density reaches N_m . Experiments demonstrate large but nevertheless the finite value of the peak mobility. We consider scattering of electrons by extensive fluctuations of the fluid density that can change the radius of the Wigner-Seitz cell. As a result, scattering phase shifts vary randomly. The mean-square scattering length $(\Delta L)^2$ in the expression for the atomic cross section is not zero. As is shown, the mean-square value of the s -wave phase shift provides a major contribution to the cross section $q_{\text{fluct}}(\epsilon)$, Eq. (16), for low-energy electrons. In the framework of our model, the cross section of scattering by density fluctuations becomes a con-

stant for zero-energy electrons, Eq. (20). The mean-squared scattering length characterizes the cross section. Our expression for the scattering length, Eq. (21), contains the unknown parameter Ω that reflects the total volume of fluctuations. We assume that the size of the density fluctuation is equal to the wavelength of the electron. Validation of this assumption was carried out by comparison of our calculations with experimental data.

The partial s -wave scattering by density fluctuations must be taken into account for the calculation of the mobility of slow electrons. This scattering determines a magnitude of the electron peak mobility at $N=N_m$. Earlier Lekner³⁴ proposed the Lorentz formula for the mobility

$$\mu_{\max} = \frac{2}{3} \left(\frac{2}{\pi m T} \right)^{1/2} \frac{e}{N_m 4 \pi ((\Delta L)^2 + S(0) L_{\text{cell}}^2(N))}, \quad (25)$$

and predicted the Lorentzian shape of the peak as a function of the density. Now we use this expression for the mobility of slow electrons in the vicinity of N_m substituting in Eq. (25) the values of $(\Delta L)^2$, Eq. (21), and L_{cell}^2 where $L_{\text{cell}}(N) = (dL_{\text{cell}}/dN)_m (N - N_m)$. The derivative $(dL_{\text{cell}}/dN)_m$ was calculated with the function obtained, Eq. (7): $(dL_{\text{cell}}/dN)_m = (\alpha/3r_m a_0) N_m^{-1}$. In this approximation the mobility maximum has the Lorentzian form predicted by Lekner,

$$\mu_{\max} = \frac{2}{3} \left(\frac{2}{\pi m T} \right)^{1/2} \frac{e}{N_m 4 \pi \left(\frac{\alpha}{3a_0 r_m} \right)^2 S(0)} \times \frac{N_m \Omega}{\left(1 + \frac{(N - N_m)^2}{N_m^2} N_m \Omega \right)}. \quad (26)$$

The Lorentzian shape of the mobility maximum is determined by the parameter $N_m \Omega$. The higher is the maximum, the narrower it is. Experimental data⁶ for Ar and Xe do confirm this statement: the mobility maximum in Ar is lower and wider than this maximum in Xe. The real function $\mu(N)$ measured in liquid Ar, Kr, and Xe in the vicinity of N_m is still far from the Lorentzian shape. In order to compare our calculations with experimental data, Eq. (25) should be used. The structure factor $S(0)$ dependence on the liquid density and the temperature should also be taken into account. The measurements^{6,7,9} were conducted in the vicinity of the vapor-liquid coexistence line, where $S(0)$ changes significantly. Figure 4 shows the data⁷ along with the calculation results for $N_m \Omega = 120$. For the experimental conditions⁷ (Xe

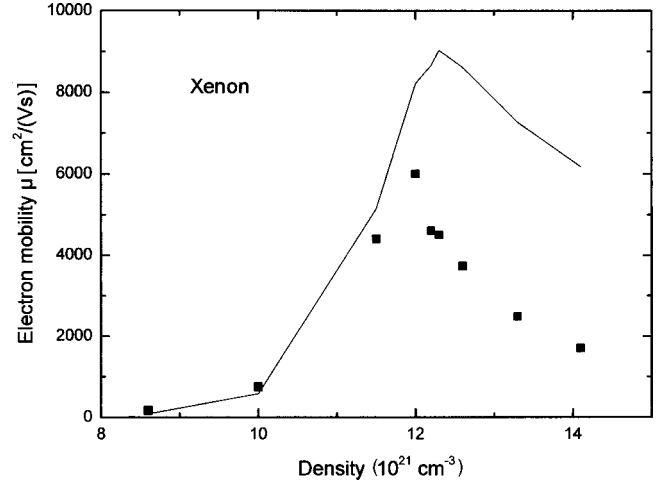


FIG. 4. The electron mobility maximum in liquid Xe Points, data (Ref. 7); solid line, calculations using Eq. (25).

at the vapor-liquid coexistence line) we use the density and temperature dependence of the isothermal compressibility in our present calculations.

In order to come to general conclusions we have developed a model for electron scattering in liquids with high atomic polarizability for the conditions when s -wave scattering is weak and the electron mobility goes through the maximum as a function of the liquid density. Electron scattering by fluctuations of the liquid density totally determines the magnitude of the peak mobility. Such fluctuations contain about hundred atoms. The cross section of the fluctuation obtained $q_{\text{fluct}}(\epsilon)$, is a function of the electron energy and drops as the electron energy increases. For high electron energies the scattering by fluctuations is replaced by scattering by the Wigner-Seitz cells. Both types of scatterings give contribution to the summary cross section. This cross section coincides with the cross section q_{fluct} for low energies of electrons. As the electron energy grows, the contribution from the scattering by individual cells $q_{\text{cell}}(\epsilon)$ gradually becomes predominant in the summary cross section. As a result, the cross section combined starts to increase with the growth of the energy of hot electrons. This understanding of the behavior of the cross sections allows transport coefficients of both thermal and hot electrons to be calculated.

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