

Theory of the energy spectrum of excess electrons in highly polarizable fluids

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The energy of the bottom of the conduction zone and the effective mass of excess electrons injected into a nonpolar fluid with high polarizability is considered. Pseudopotential theory of electrons in a cellular medium is extended to conditions where polarization attraction predominates over electron-fluid interaction. The solution is obtained in the Wigner-Seitz cell for the case where the scattering length of electron in the fluid is negative. The calculated density dependences of the conduction-zone bottom and effective mass of electron in noble fluids are in satisfactory agreement with available experimental data.

I. INTRODUCTION

The problem of the excess-electron state in fluids has attracted the attention of many researchers for a long time. A noble fluid with excess electrons is the simplest system with strong interaction between charged particles and a dense medium. Here two opposite effects manifest themselves. In weakly polarizable fluids the electron is self-trapped; in fluids with high polarizabilities thermal electrons have high mobility and may be considered almost free. The last phenomenon is a result of the counterbalance of the polarization attraction and the core repulsion in a dense medium and allows one to speak about the "conduction zone" for the electron motion. Today the physics of the almost free state seems to be clear. However, some important questions remain open for discussion (see the recent reviews given by Schmidt¹ and Christophorou²).

The ground-state energy of the electron (the energy of the conduction-zone bottom) passes through a wide minimum with decreasing density.³⁻⁶ Recently, this dependence was successfully described in a number of interesting papers.⁷⁻¹² However, some strong assumptions were made. Explicit representations of the electron-atomic potential, the short-range component of which is unknown, are especially questionable (see the corresponding criticism given in Refs. 11 and 12). As a result, it turns to be impossible to describe by the same approach the density dependences of both the bottom energy and the electron mobility. The last dependence passes over a sharp maximum and is very sensitive to any inaccuracy. The position of the mobility maximum is very close to the position of the minimum of the bottom energy.

These difficulties may be avoided by using a pseudopotential theory developed on the basis of the ideas of Springett, Cohen, and Jortner.¹³ In Refs. 14-16 the pseudopotentials were constructed for *s* and *p* waves of electron scattering from a unit cell of the fluid. The analytical expression for the density dependence of the scattering length was obtained. In agreement with the Lekner prediction¹⁷ the calculated scattering length, being negative in a gas, becomes positive at high densities. The density dependences of the electron mobility and en-

ergy of the bottom of the conduction zone were calculated without any adjusted parameters and were in satisfactory agreement with experimental data. The inputs to the theory are the scattering length (i.e., *s*-wave phase shift) on an isolated atom, its polarizability, and the binary correlation function of the liquid, which are known experimentally.

In this paper the peculiarities of the energy spectrum are considered. The ground-state energy and electron effective mass are calculated for the whole liquid-density regime with the use of a cellular model without adjustable parameters. For this purpose a solution of the wave equation for an electron in the Wigner-Seitz cell is obtained for the case of negative electron scattering length. It extends the possibility of description of electron states in a fluid, while the average environment of an atom has a spherical symmetry. The electron effective mass is calculated in the same approach. It is proved that the density dependence of the reduced effective mass tends to unity with decreasing density, not monotonically but passing through a maximum which exceeds unity. So the effective mass tends to unity from above in a diluted gas.

In Sec. II below, we review the cellular description of electron states and obtain the solution for the case of negative scattering length. The density dependence of the ground-state energy is calculated. In Sec. III, the relevant expression for the effective mass is obtained and a qualitative analysis of the density dependence of the effective mass is given. In Sec. IV, effective masses in Ne, Ar, and Xe are calculated. This requires the knowledge of *p*-wave phase shifts. The dependences of the *p*-wave shift on electron energy and fluid density are obtained.

II. ELECTRON IN A CELLULAR HIGHLY POLARIZABLE FLUID

Consider the ground state of an electron in the Wigner-Seitz cell with the radius $\bar{r} = (4\pi N/3)^{-1/3}$, where *N* is the atomic density. It is convenient to write down the wave equation for the radial wave function $\chi(r)$,

$$d^2\chi/dr^2 + [q^2 - 2m\hbar^{-2}U(r)]\chi = 0, \quad (1)$$

where $\chi(r) = r\psi(r)$, $\psi(r)$ is the electron wave function,

and q is the wave number. The ground-state wave function is symmetrical about any atom (i.e., the center of the cell), so that the following boundary condition has to be satisfied: $(d\psi/dr)=0$ at $r=\bar{r}$. In a dense medium the electron finds itself in a muffin-tin potential field $U(R)$. Within the Wigner-Seitz cell $U(r)$ is represented by the electron interaction with an atom situated at the center of the cell, and with the mean interaction with the cell environment. At short distances from the cell center $U(r)$ is known. However, pseudopotential theory does not introduce explicitly the electron-fluid interaction potential.¹⁸ If the scattering length of the electron from a cell, L , is small, one can follow the approach of the zero-radius potential, and use the second boundary condition in the form $\psi(L)=0$. In the case $L > 0$, this results in the widely used solution (e.g., Ref. 13)

$$\psi(r) = A (q_0 r)^{-1} \sin[q_0(r-L)], \quad (2)$$

where A is the normalization constant. The eigenvalue of the wave number q satisfies the equation

$$\tan[q_0(\bar{r}-L)] = q_0 \bar{r}. \quad (3)$$

This solution is used successfully in the electronics of fluids. The energy of the conduction-zone bottom¹³ is

$$V_0 = u_0 + \hbar^2 q_0^2 / 2. \quad (4)$$

Here u_0 is the result of the mean polarization of the medium.

The potential $U(r)$ inside every cell has a short-range repulsive component and a long-range attractive one. The last component represents the nonuniformities of polarization of the fluid. At high densities the strong overlap of the electron-atomic polarization potentials smooths out the potential field considerably. That leads to weakening of the attractive component of $U(r)$. Because of it the short-range repulsion dominates at high densities, and the scattering length is positive. In highly polarizable liquids with decreasing density the attraction strengthens and the scattering length becomes negative.^{13,17} In this case, Springett, Cohen, and Jortner¹³ modified Eqs. (2) and (3). They described the short-range repulsive component of $U(r)$ by some scattering length L_c , which is positive, and replaced the second boundary condition by $\psi(L_c)=0$. As to the long-range component of $U(r)$ it was smeared inside the cell. This simplified approach helps one to understand some important relationships. However, it is too ambiguous to give an accurate description. Moreover, it does not describe the observed minimum in the density dependence of V_0 .^{11,12}

Fortunately, another more reasonable approach may be proposed for the case when the scattering length is negative but its absolute value is small. The ground-state energy is negative now. We denote it $(-\hbar^2 \kappa_0^2 / 2m)$. The wave equation in the same approach of the zero-radius potential is reduced to

$$d^2 \chi(r) / dr^2 - \kappa_0^2 \chi(r) = 0. \quad (5)$$

With the boundary condition $\psi(L)=0$, the solution of (5) takes the form

$$\psi(r) = A (\kappa_0 r)^{-1} \sinh[\kappa_0(r-L)]. \quad (6)$$

The eigenvalue κ_0 satisfies the equation

$$\tanh[\kappa_0(\bar{r}-L)] = \kappa_0 \bar{r}. \quad (7)$$

The energy of the ground state is negative, and the momentum is imaginary:

$$\hbar q = i \hbar \kappa_0. \quad (8)$$

Instead of Eq. (4), we have

$$V_0 = u_0 - \hbar^2 \kappa_0^2 / 2m. \quad (9)$$

Equation (6) gives the approximate solution of the wave equation. It does not satisfy the condition $\psi(0)=0$. On the contrary, the solution diverges at the origin. However, if the domain of the pseudodescription is small compared with the cell volume ($|L|^3 \ll \bar{r}^3$), the divergence is not important. It does not prevent the normalization of $\psi(r)$:

$$A^2 = \frac{4}{3} (\kappa_0 \bar{r})^{-3} \{ \sinh[2\kappa_0(r-L)] + \sinh(2\kappa_0 L) - 2\kappa_0 \bar{r} \}. \quad (10)$$

If it is necessary, one can use some methods to eliminate the divergence of $\psi(r)$ at the origin.

There are two consequences of the relation (7). First, we have the inequality

$$\hbar^2 \kappa_0^2 / 2m \leq \hbar^2 / 2m \bar{r}^2. \quad (11)$$

This means that the electron will not be localized in the potential well of the unit cell. Second, a transition exists in the Fermi optical approach at low densities,

$$-\kappa_0^2 / 2 = 3L / 2\bar{r}^3. \quad (12)$$

The correct low-density limit is a feature of some well-known Wigner-Seitz formulas, although the cellular approach loses the validity of course.

Calculations of ground-state energy require the dependence of the scattering length on atomic density. Scattering lengths extracted from measured mobilities¹⁹⁻²⁰ are used below, and calculated¹⁴ $L(N)$ for densities where experimental L are absent.

Table I contains the input data. Figure 1 demonstrates the calculated dependences of electron scattering length and ground-state energy on the density of fluid argon. The ground-state energy is positive at high densities, where $L > 0$, passes through zero at the density N^* , where L becomes zero, and becomes negative with decreasing density.

TABLE I. Atomic polarizability α , scattering length on solitary atom L_0 , distance of the closest approach σ , and calculated radius of pseudopotential core for p waves.

Fluid	α (a_0^3)	L_0 (a_0)	σ (a_0)	r_1 (a_0)
Neon	2.663	0.20	5.25	1.65
Argon	11.08	-1.63	6.50	2.36
Xenon	27.11	-5.90	7.66	3.10

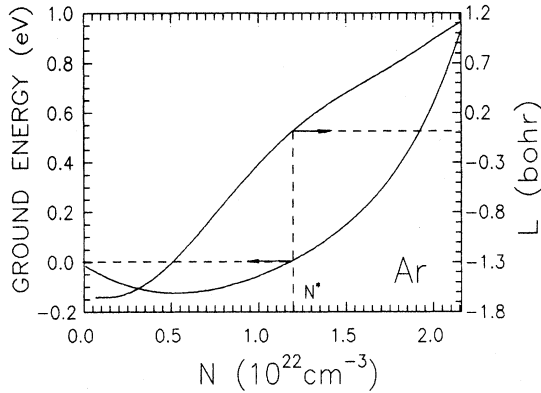


FIG. 1. Density dependences of scattering length L and ground-state energy of electrons in Ar.

Now it is possible to calculate the energy of the bottom of the conduction zone in a wide range of fluid densities. The second component of V_0 is given by the expression^{13,14}

$$\begin{aligned} u_0 &= -3\alpha e^2 (2\bar{r}^3)^{-1} f \int g(R) R^{-2} dR \\ &\cong -3\alpha e^2 I_0 (2\sigma\bar{r}^3)^{-1} f, \end{aligned} \quad (13)$$

where $g(R)$ is the binary correlation function of the medium, σ is the distance of the closest interatomic approach (the parameter of the Lennard-Jones potential), and $f = (1 + 2\alpha\bar{r}^{-3})^{-1}$ is the Lorentz local-field correction.¹⁷ The integral

$$I_0 = \int g(R) R^{-2} dR$$

is calculated using the Verlet radial distribution functions $g(r)$ of the Lennard-Jones fluid.²¹ These functions describe adequately the real structure of simple liquids in a wide range of densities. So in Eq. (13) the changes in interatomic correlation with the density variations are taken into account, including the reduction of the number of nearest neighbors. The integral $I_0 \cong 1.2$ in the domain of

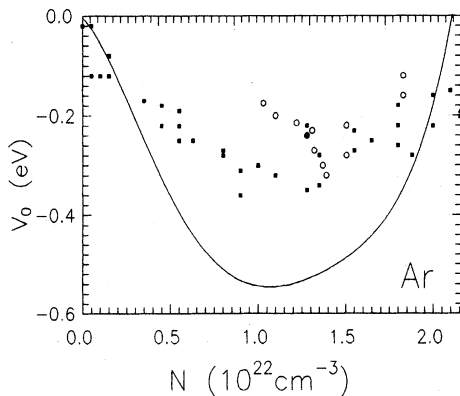


FIG. 2. Density dependences of energy V_0 in fluid Ar. Circles (Ref. 6), squares (Ref. 4), and triangles (Ref. 3) are experimental data.

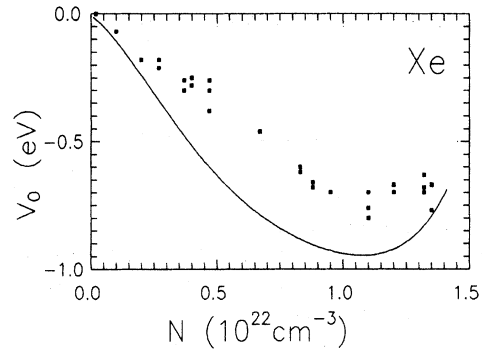


FIG. 3. Density dependences of energy V_0 in Xe. Squares (Ref. 5) are experimental data.

\bar{r} which is less than σ .¹⁴ If $\bar{r} > \sigma$, the following estimate can be used: $u_0 \cong -3\alpha e^2 (2\bar{r}^4)^{-1} f$.

The calculated results are shown in Figs. 2 and 3 and compared with the experimental data. The theory describes the passage of V_0 through the minimum, but it underestimates V_0 systematically. We discuss this in the last section of the paper.

III. EFFECTIVE-MASS DENSITY DEPENDENCE

The wave function of an almost free electron in a liquid can be represented as a free-electron wave, modulated by the cellular functions (2). The kinetic energy of excess electrons $\epsilon(k) = \hbar^2 k^2 / 2m_{\text{eff}}$ is counted from V_0 , where m_{eff} is the electron effective mass and $\hbar k$ is the electron momentum. The effective mass of such an electron can be calculated by the method proposed by Bardeen and described in Ref. 22. It is a perturbation theory which uses the expansion in powers of $(k/q_0)^2$. Hence the validity domain of the theory is limited to kinetic energies which are small in comparison with the ground-state energy in the Wigner-Seitz cell. As to the calculated effective mass, it has to differ not too much from the free-electron mass.

The Bardeen formula reads

$$(m_{\text{eff}}/m)^{-1} = \psi^2(\bar{r}) [d \ln \chi_1(\bar{r}) / d \ln \bar{r} - 1], \quad (14)$$

where $\chi_1(r)$ is the single-site radial p -wave function of an electron at the bottom of the conduction zone and $\chi_1(\bar{r})$ is taken at the cell boundary. In the case $L > 0$, Eq. (14) was used in Ref. 23. It was converted to a form suitable for calculations:

$$\begin{aligned} d \ln \chi_1 / d \ln \bar{r} &= (q_0 \bar{r})^2 \tan(q_0 \bar{r} + \delta_1) \\ &\times [\tan(q_0 \bar{r} + \delta_1) - q_0 \bar{r}]^{-1} - 1, \end{aligned} \quad (15)$$

where $\delta_1 \equiv \delta_1(q_0)$ is the p -wave phase shift.

Consider now the case $L < 0$, where the ground-state energy is equal to $(-\hbar^2 \kappa_0^2 / 2m)$. The wave function $\chi_1(r)$ is the solution of the wave equation which we consider in the approach of the zero-radius potential,

$$d^2 \chi_1 / dr^2 + [2r^{-2} - \kappa_0^2] \chi_1 = 0. \quad (16)$$

Here it is supposed that the phase shift δ_1 is a result of

the potential action at distances which are smaller than \bar{r} . The solution has the form

$$\chi_1 = \sinh(\kappa_0 r + \delta_1) / \kappa_0 r - \cosh(\kappa_0 r + \delta_1). \quad (17)$$

Let us remember that the considered state is the state with imaginary momentum $i\kappa_0$. The function δ_1 is defined on the plane of complex momenta.²⁴ The function $\delta_1(i\kappa)$ represents the analytic continuation of the function $\delta_1(q)$, determined at the axis of real momenta q , to the axis of imaginary momenta $i\kappa$. On the imaginary axis the phase shift from the short-range potential is totally imaginary. Note that for the sake of space Eq. (17) contains $\delta_1 \equiv \text{Im}\delta_1(i\kappa_0)$, i.e., the symbol Im is omitted.

Hence in Eq. (14) we should substitute $\psi(r)$ (6) and the derivative

$$d \ln \chi_1(r) / d \ln \bar{r} = -(\kappa_0 \bar{r})^2 \tanh(\kappa_0 \bar{r} + \delta_1) \times [\tanh(\kappa_0 \bar{r} + \delta_1) - \kappa_0 \bar{r}]^{-1} - 1. \quad (18)$$

We discuss now the density dependence of m_{eff}/m in a wide range of liquid densities. Near the triple point, where the electron-liquid interaction is repulsive ($L > 0$), m_{eff}/m is smaller than unity. It grows with decreasing density, i.e., with growth in \bar{r} . At some density N^* the scattering length passes through zero. This corresponds to the maximum in the electron mobility. For example, in xenon the peak mobility is nearly four orders of magnitude larger than the low-density value. It is clear that the electron is almost free here and its effective mass must be very close to the mass of the free electron, m . Using Eqs. (14), (2), and (15) and (14), (6), and (18), we obtain the following relationships near $\bar{r}^* = (4\pi N^*/3)^{-1/3}$:

$$m_{\text{eff}}/m|_{\bar{r}^* - \epsilon} \cong 1 - 9\delta_1(q_0)(q_0 \bar{r}^*)^{-3}, \quad (19)$$

$$m_{\text{eff}}/m|_{\bar{r}^* + \epsilon} \cong 1 + 9 \text{Im}\delta_1(i\kappa_0)(\kappa_0 \bar{r}^*)^{-3}, \quad (20)$$

where $\epsilon \rightarrow 0$. Hence the ratio m_{eff}/m is close to unity. At $\bar{r} = \bar{r}^*$ the derivative of m_{eff}/m is given by

$$d(m_{\text{eff}}/m)/d\bar{r}|_{\bar{r}^*} \cong -(3/2\bar{r}^*)dL/d\bar{r}^* - 9d[\delta_1(q_0)(q_0 \bar{r}^*)^{-3}]/d\bar{r}^*. \quad (21)$$

It is positive because $dL/d\bar{r}^* < 0$. Hence m_{eff}/m grows with decreasing density and exceeds unity. At smaller densities m_{eff}/m after passing over the maximum begins to decrease and in a gas approaches unity from above.

In reality the formulas given above lose their validity somewhat earlier because the cellular model of fluids fails in a gas.

IV. p PHASE SHIFT AND EFFECTIVE-MASS CALCULATIONS

The pseudopotential approach does not use the explicit form of the potential $U(r)$ at small distances. Adequate information about the short-range interaction can be extracted from the phase shifts of partial waves scattered on an isolated atom. It allows one to describe the electron-fluid interaction with high accuracy.^{14,15} How-

ever, here we chose a somewhat simpler way of calculation. Consider the ensemble-averaged potential consisting of three components: the hard core of radius r_1 , the polarization potential of the central atom, and the environment potential. Therefore outside the core we have

$$U(r) = V(r) + u(r), \quad r_1 \leq r \leq \bar{r}, \quad (22)$$

$$V(r) = -\alpha e^2 / (2r^4),$$

$$u(r) \cong -\frac{3\alpha e^2}{2\bar{r}^3 \sigma} f \left[I_2 \frac{2r^2}{3\sigma^2} + I_4 \frac{3r^4}{5\sigma^4} \right]. \quad (23)$$

Integrals I_2 and I_4 are calculated in the same way as I_0 in Eq. (13). If $\bar{r} < \sigma$, $I_2 \cong 1.6$ and $I_4 \cong 1.8$. If $\bar{r} > \sigma$, parameter σ has to be replaced by \bar{r} in Eq. (23), and factors I_2 and I_4 by unity.

In this case the p -wave shift is given by

$$\delta_1 = \delta_1^c + \delta_1^p + \delta_1^n, \quad (24)$$

where δ_1^c is given by the textbook formula for a hard sphere of radius r_1 and δ_1^p and δ_1^n are generated by the potential (22). The potential well does not contain a bound state, so the Born approach may be used:²⁵

$$\delta_1^p + \delta_1^n = (2m/\hbar^2 k^2) \int_{r_1}^{\bar{r}} U(kr) J_{3/2}^2(kr) dr. \quad (25)$$

It may be refined by the replacement of one of the functions of free motion by the pseudofunction $\chi_1(r)$, which vanishes at $r = r_1$ and contains the phase function $\delta_1(r)$,

$$\delta_1^p + \delta_1^n = -(2m/\hbar^2 k^2) \int_{x_1}^{\bar{x}} U(x) (\sin x/x - \cos x) \times \{ \sin[x - \delta_1(x)]/x - \cos[x - \delta_1(x)] \} dx, \quad (26)$$

where $x = kr$, $\bar{x} = k\bar{r}$, and $x_1 = kr_1$.

As the first approximation it is possible to use δ_1^c as the phase function, $\delta_1(x) \cong \delta_1^c \cong -x_1^3/3$. If $\bar{x} \ll 1$, one obtains in this case

$$\delta_1^p \cong (\alpha k^3 \bar{r} / 9a_0) \{ 1 - 3r_1 / (2\bar{r}) + (r_1 / \bar{r})^3 / 2 - x_1^2 (2r_1 / 5\bar{r}) \ln(\bar{r} / r_1) - \bar{x}^2 [1 - (r_1 / \bar{r})^3] / 15 \}. \quad (27)$$

This formula amends the formula for δ_1^p which was given earlier in Ref. 15. For scattering on a cell environment we use the expression from Ref. 15:

$$\delta_1^n \cong (2\alpha k^3 \bar{r} / 63a_0) (\bar{r} / \sigma)^3 f \times \{ I_2 [1 - \frac{7}{45} \bar{x}^2] + \frac{7}{10} I_4 (\bar{r} / \sigma)^2 [1 - \frac{9}{35} \bar{x}^2] \}. \quad (28)$$

For determination of r_1 it is necessary to calculate the p -wave scattering on an isolated atom. In this case, $\delta_1 = \delta_1^c + \delta_1^p$. The last term may be calculated by moving the upper limit of the integral in Eq. (26) to infinity. It is convenient to calculate r_1 using the position of the zero of δ_1 as a function of momentum, $\delta_1(k^*) = 0$. With k^* from Ref. 26, the value of r_1 for argon is equal to $2.36a_0$. At the triple point, $(r_1 / \bar{r})^3 \cong 0.16$. It is small even at the

triple point, and the pseudopotential core may be introduced.

Calculated phase shifts are given in Fig. 4. At the triple point, where the polarization is weakened significantly, scattering on the core dominates and $\delta_1 < 0$. At smaller densities the components of δ_1 almost cancel and the phase shift becomes small. With further decrease in density the attractive interaction continues to increase, and δ_1 becomes positive as in a gas. The values given by the series (27) and (28) compare well to the results of numerical integration in (26).

For Xe this approximation is insufficient because of the high polarizability of the Xe atom. An attempt was undertaken to refine the procedure of calculation. The following phase function was inserted in (26):

$$\delta_1(r) = \delta_1^c - (2m/\hbar^2 k^2) \int_{x_1}^x U(y) (\sin y/y - \cos y) \times \{ \sin[y - \delta_1(y)]/y - \cos[y - \delta_1(y)] \} dy, \quad (29)$$

and self-consistent calculations of δ_1 with the use of Eqs. (26) and (29) were carried out. The self-consistent core radius $r_1 = 3.1a_0$. The calculated δ_1 are compared in Fig. 5 with the results of the simpler approach which was used for argon. One can see how self-consistency modifies the results.

The reduced effective masses m_{eff}/m are given in Figs. 6 and 7. The m_{eff}/m density dependences demonstrate the qualitative peculiarities which are discussed in the

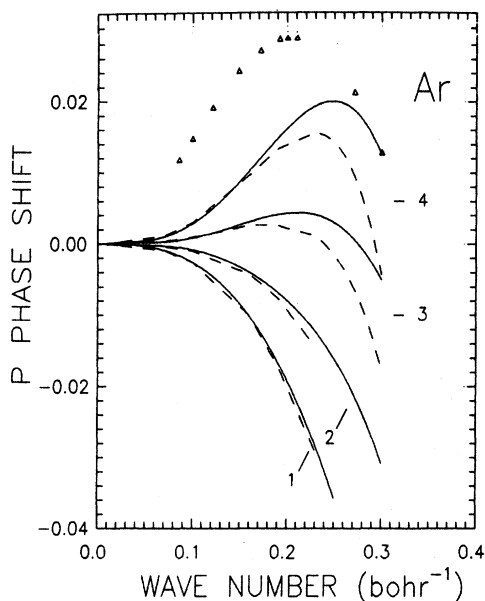


FIG. 4. Wave-number dependences of p -wave phase shifts in argon. Atomic number densities in units of 10^{22} cm^{-3} : curve 1, 2.16; curve 2, 1.20; curve 3, 0.80; curve 4, 0.60. Solid lines, result of numerical integration. Dashed lines, expansion of $\delta_1(k)$ in powers of wave number. Triangles, isolated Ar atom (Ref. 24).

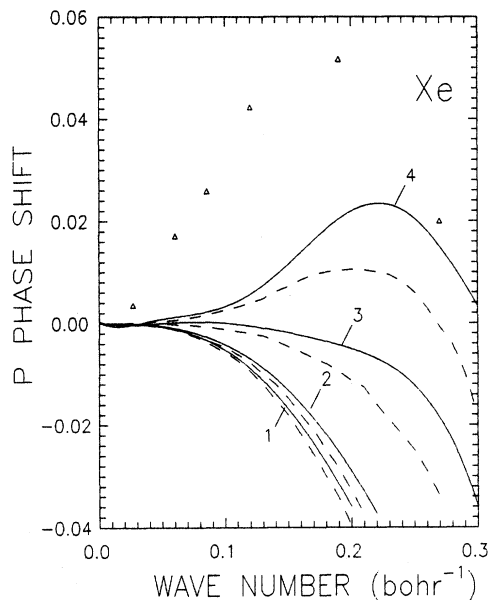


FIG. 5. Wave-number dependences of p -wave phase shifts in xenon. Atomic number densities in units of 10^{22} cm^{-3} : curve 1, 1.41; curve 2, 1.20; curve 3, 1.00; curve 4, 0.80. Solid lines, result of self-consistent calculations. Dashed lines, calculations by Eq. (26). Triangles, isolated atom (Ref. 27).

previous section. However, in xenon m_{eff}/m passes through unity at a Xe density which is considerably lower than $N^* \approx 1.2 \times 10^{22} \text{ cm}^{-3}$. We cannot affirm that p phase shifts are calculated for Xe so satisfactorily as for Ar.

Finally, consider an electron in neon. The scattering length on an isolated atom is positive and small, $L_0 = 0.17a_0$. In neon, depending on density and temperature, electrons can be observed in highly mobile states as

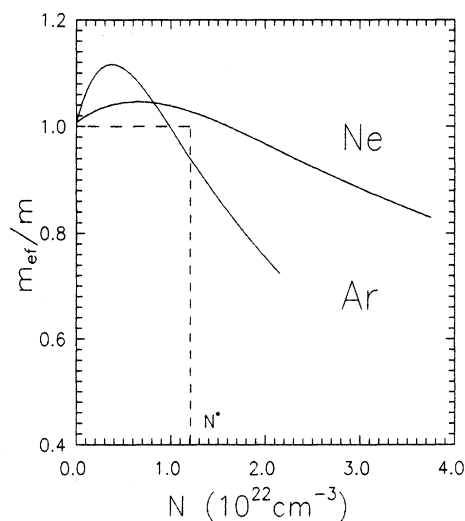


FIG. 6. Density dependences of reduced effective masses in Ar and Ne. Square, experiment (Ref. 28). Position of zero of scattering length in Ar is indicated.

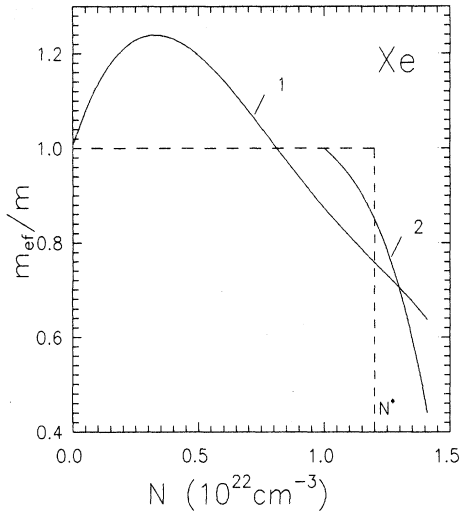


FIG. 7. Density dependences of reduced effective mass in Xe: curve 1, result of calculation; curve 2, dependence obtained from measured data (Refs. 29,30).

well as being self-trapped electrons.^{31,32}

The scattering length of an almost free electron in fluid Ne (Fig. 8) increases due to the weakening of the attractive component of $U(r)$ with the increase in density. At the triple point, L attains $0.74a_0$. The energy of the conduction-zone bottom demonstrates the specific behavior. It is positive at the triple point in accordance with measured data.³ With decreasing density the energy fails and becomes small at $N \cong 1.7 \times 10^{22} \text{ cm}^{-3}$. Remaining small, V_0 passes through zero, and becomes negative.

It is worth mentioning here that the problem of excess electron in a dense medium differs from the Fermi problem of weakly bound electron-ion pair. The energy V_0 is represented by the sum of two terms, namely, $\hbar^2 q_0^2 / 2m$ and u_0 . Both of them are induced by an injected electron.¹³ In diluted neon values of $\hbar^2 q_0^2 / 2m \cong 2\pi\hbar^2 L / 2m$ are positive but small, and u_0 , which is negative, prevails.

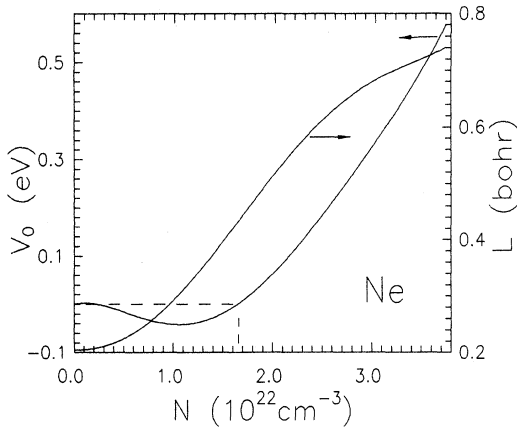


FIG. 8. Scattering length L and energy of conduction-zone bottom V_0 as functions of Ne density.

As to the reduced effective mass in neon, it is close to unity at the density range $N \leq 1.7 \times 10^{22} \text{ cm}^{-3}$, where V_0 is small. Calculated values of m_{eff}/m exceed unity slightly at low densities. The increase over unity cannot be considered as something exotic. For example, the reduced effective mass of the positron, injected into condensed matter, exceeds unity.³⁴ However, we cannot say now that this peculiarity in neon is not a result of our approximations.

V. DISCUSSION

The modeling of the electron-liquid potential field is the basic problem for every investigation of excess-electron behavior. The problem requires answers to two questions. First, how do we describe the short-range interaction with atoms of the fluid? Second, how do we build the potential field in the interatomic space taking account of the structure of the medium?

The short-range component of the electron-atomic potential is unknown. Explicit introduction of it leads inevitably to introduction of adjusted parameters. However, it is the set of scattering phase shifts which is required, not the potential itself. This is the starting point for the pseudopotential theory. The phase shifts caused by the short-range component of the interaction may be calculated from the phase shifts of partial waves scattered by isolated atom. These phase shifts remain unchanged in dense media.

The structure of the electron-liquid potential field in interatomic space is determined by the polarization of the liquid by an injected electron in the framework of the cellular model. The cellular (or muffin-tin) model uses the averaged symmetry of a simple liquid. The radius of a spherical cell has to be equal to the mean interatomic spacing. The field inside a cell has to be calculated with the use of the radial distribution functions of the liquid.

The pseudopotential theory was suggested by Springett, Cohen, and Jortner in Ref. 13 and it was used successfully by a number of authors. In Refs. 14–16 and in the present paper the theory is extended, and now it helps to describe a large body of experimental data obtained during the last decade in a wide range of densities.

However, the theory is a mean-field theory and does not account for fluctuations of the potential field due to the density fluctuations. Apparently, this is a reason for the overestimation of the calculated $|V_0|$ which one can see in Figs. 2 and 3.

Consider for a start the mean squared fluctuation of the energy of the medium polarization,

$$\overline{\delta u_0^2} = (\frac{du_0}{dN})^2 \overline{\delta N^2} \approx (u_0/N)^2 \overline{\delta N^2}, \quad (30)$$

where $\overline{\delta N^2}$ is the mean squared fluctuation of the density. An *a priori* estimate of $\overline{\delta N^2}$ is not obvious, because the volume of optimal fluctuation is not clear. Fortunately, the value of $\overline{\delta N^2}$ can be obtained from the measured maximum value of the electron mobility in the liquid, μ_{max} , at the density $N = N^*$. The thing is that the value of μ_{max} is determined by the fluctuations of the scattering length $\overline{\delta L^2}$.³⁵ The measured mobility data²³ allow one to evalu-

ate $(\overline{\delta L^2}) \approx 0.11a_0^2$ in argon. On the other hand, we can write

$$\overline{\delta L^2} = (dL/dN)^2 \overline{\delta N^2}. \quad (31)$$

Hence

$$\overline{\delta u_0^2} = (u_0/N)^2 (dL/dN)^{-2} \overline{\delta L^2}. \quad (32)$$

This results in $(\overline{\delta u_0^2})^{1/2} \approx 0.09$ eV at the minimum of the density dependence of V_0 in argon.

Now it is possible to estimate the influence of the small density fluctuations on the ground-state energy of an electron in the unit cell, $T_0 = \hbar^2 q_0^2 / 2m$. Small density fluctuations are given by the Gauss distribution

$$F(N) = (2\pi\overline{\delta N^2})^{-1} \exp[-(N - \overline{N})^2 / \overline{\delta N^2}], \quad (33)$$

where N is the mean particle density. Near the density $\overline{N} = N^*$

$$T_0 \approx 2\pi\hbar^2 m^{-1} N L(N). \quad (34)$$

Taking into account the almost linear dependence $L(N)$ (Fig. 1), T_0 may be approximated by

$$T_0 \approx 2\pi\hbar^2 m^{-1} N(N - N^*) dL/dN. \quad (35)$$

The value of T_0 at the mean density $N = N^*$ is equal to zero, but the mean value $T_0(N^*)$ is finite. Straightforward averaging of (35) over the distribution (33) leads to

$$\overline{T_0(N^*)} = 2\pi\hbar^2 m^{-1} \overline{\delta L^2} (dL/dN^*)^{-1}, \quad (36)$$

where $\overline{\delta L^2}$ and dL/dN^* are taken at $\overline{N} = N^*$, and may be evaluated from the measured mobilities.²³ This yields the significant value $\overline{T_0(N^*)} \approx 0.024$ eV.

We emphasize, however, that the given analysis accounts for spherically symmetric fluctuations of the cell environment and does not account for the development of asymmetry. So the influence of fluctuations is considerably bigger, and it is comparable to the overestimations of V_0 in Fig. 2.

A theoretical model which properly accounts for fluctuations is based on the Feynman path-integral (PI) approach. It was proposed by Chandler and Wolynes.³⁶ The partition function for the quantum-electron-classical-liquid system was written as the integral of the path-dependent action over all paths in imaginary time. Monte Carlo (MC) and molecular-dynamics (MD) techniques were then used to evaluate the path integral. Results have been reported for an electron in fluid helium,³⁷ in helium, and in xenon.^{38,39} Considerable progress was achieved later.^{9,29,40}

In principle, path-integral and MC or MD calculations can yield results with high precision which take account of the inherent disorder of the fluid. Note that the theory requires an explicit form of the electron-atomic potential as input. The potential has to reproduce faithfully the scattering of electrons from the atom. In the opposite case, PIMC and PIMD calculations would not give an adequate description. The first calculations for xenon used an inaccurate potential and could not describe the minimum in the density dependence of V_0 . It is not sufficient to require a good reproduction of the cross section. The potential must reproduce the phase shifts of partial electron waves scattered from the atom and do it

at low energies, lower than $|V_0|$.

Up to now correlation functions for quantum electrons are in general difficult to calculate over the complete range of densities, using the present computation techniques. That is why the RISM polaron theory is attractive.⁴¹ RISM theory was originally introduced by Chandler to study the structure of liquids. By joining the Feynman polaron approximation with RISM theory, a method was given which ignores fluctuations of large amplitudes, but provides a practical procedure for attacking a number of problems. Chen and Miller⁴² explained by what approximations the results of PIMC calculations can be reproduced by the RISM polaron theory in the difficult problem of self-trapping in highly polarizable liquids.

In Ref. 7 a semiclassical attempt was made to explore the problem including disorder. Considerations are based on the semiclassical idea that a particle of sufficiently high energy (exceeding V_0) may percolate throughout the sample. The idea was used by the theory of electron self-trapping. A corresponding criticism is given by Hernandez.⁴³ The relation between such a classical percolation threshold and quantum delocalization is not established.

If the ground-state energy is calculated, one may be interested in the determination of the effective mass. The calculated effective masses are shown in Figs. 6 and 7. They agree satisfactorily with experimental data near the triple points of Ar and Xe and in xenon at densities down to 0.9×10^{22} cm⁻³. The Reshotko *et al.* measurements of exciton creation energies²⁹ were combined with the Nakagawa *et al.* experimental data on the continuum edge³⁰ to obtain the experimental dependence of m_{eff}/m on xenon density.

A somewhat different density dependence of m_{eff}/m was calculated in Ref. 44. The reported m_{eff}/m increase monotonically with decreasing density from the triple point, so they arrive at unity in a diluted gas only. It is impossible to indicate unambiguously the reason for such a behavior because the procedure of the calculations is entirely numerical and phase shifts δ_0 and δ_1 are not displayed. However, it is clear that it would be impossible to describe the observed maximum in excess-electron mobility using these phase shifts.

In a diluted gas our calculations describe the approach of m_{eff}/m to unity. The wide range of densities examined in this exploration extends well beyond reasonable physically values, but it helps to highlight the qualitative trends. We understand that another formalism is required here for reliable quantitative calculations. It is the Green function method of many-particle theory. We intend to consider this question later.

The values of m_{eff}/m given in Figs. 6 and 7 do not differ much from unity. Therefore the requirement of validity of the approach of almost free electrons, used by the Bardeen theory, is satisfied.

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