Pseudopotential theory for the state of an electron in liquids with a high polarizability

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We propose a pseudopotential theory for the state of an electron injected into a nonpolar liquid. We use for the initial data quantities known experimentally—the scattering length for an isolated atom, its polarizability, and the pair correlation function of the liquid. We obtain an expression for the scattering length of the electron for the scattering by a Wigner–Seitz cell of the liquid. The calculated density dependence of the electron mobility and of the ground state energy are found to be in satisfactory agreement with experiments. © *1995 American Institute of Physics.*

1. INTRODUCTION

The state of a charged particle in a dense medium is the subject of many studies. Its description gives a clue to the solution of a variety of physical problems. An electron injected into an atomic liquid is the simplest realization of such a system and is suitable for detailed experimental investigations. It is well known that in that case various effects show up.

A most striking phenomenon is observed in weakly polarizable liquids—the electron self-localizes. States appear in which the electron is bound to the substance (for recent surveys see Ref. 1).

In liquids which have a high polarization the electron remains free and acquires a mobility which is higher than in a gas. This effect was already observed in the sixties. It was explained that it occurs as the result of the competition between the polarization attraction between the electron and the atoms of the liquid and the short-range repulsion. The polarization attraction which predominates in a gas is weakened in a liquid due to the overlap of the electron-atom potentials to such an extent that in a liquid the repulsion dominates. This manifests itself in the change in sign of the electron scattering length from negative to positive. The theory developed at the same time explained the observed effects in the vicinity of the triple point of liquid argon, but for krypton and xenon it was already untenable (see the reviews in Refs. 2 and 3).

In recently performed experiments measurements were carried out in a wide range of densities—from liquids to gases. The density dependence of the electron ground state passes through a minimum. The electron mobility passes through a maximum and its position is the same as the position of the minimum of the ground state energy. It is obvious to connect this fact with the vanishing of the scattering length. However, the existing theory does not describe the behavior of the scattering length as a function of the density.

This difficulty gave rise to a number of studies.[4–9] However, in all those the starting point is giving the explicit form of the electron-atom interaction potential. The short-range component of this potential is not known. Hence, fitting parameters necessarily appear. The inconsistencies which then arise have been discussed in detail in Refs. 8 and 9. At the same time these papers were inherently incomplete—the minimum of the ground state energy is described but not the maximum of the mobility.

We start from the fact that one needs not give explicitly the short-range component of the electron-atom potential. The necessary information about it is contained in the length L_0 for scattering by an isolated atom and its polarizability α, which are known from experiments. The phase shift of an s-wave scattered by the short-range component of the atomic potential remains the same for an atom in a liquid. As to the long-range polarization component, it is renormalized. The theory given below refers to a pseudopotential type theory and develops ideas expounded in a paper by Springett, Cohen, and Jortner.[10]

In what follows we construct the profile of the potential field in which the electron moves. We evaluate the scattering length for scattering by a Wigner–Seitz cell of that potential. Next we discuss the possibility for using kinetic theory and describe the mobility maximum. In the last section we calculate the ground state energy as function of the density (the affinity of the electron to the substance). We give a comparison with experiments.

2. SCATTERING OF AN ELECTRON IN A LIQUID

The average field in which the electron interacts in the liquid is a muffin tin potential.[11] One can model an element of this potential by surrounding each atom by a Wigner–Seitz cell of radius $\bar{r} = (4\pi N/3)^{-1/3}$, where N is the atomic density of the liquid. In the liquid the electron interacts with the atoms of the cell and also with its surroundings. We shall assume that the short-range component of the electron-atom potential has a range a which is much smaller than the size of the cell. At distances larger than a the interaction with the central atom will then be a polarization interaction,

$$V_p(r) = -\alpha e^2/(2r^4). \tag{1}$$

The potential of the surroundings is created by the atoms outside the cell which are at distances from the center close to σ, where σ is the parameter of the Lennard–Jones potential responsible for the interatomic repulsion. It is given in Table I. Restricting ourselves to relatively high densities such that $\bar{r} < \sigma$ holds, we can write the potential of the surroundings in the form[10]

TABLE I.

Substance	α, a_0^3	L_0, a_0	a, a_0	σ, a_0
Argon	11.1	−1.63	1.68	6.4
Xenon	27.1	−5.9	2.15	7.66

$$u(r) = \sum_j f(r) V_p(\mathbf{r} - \mathbf{R}_j) = -\frac{3\alpha e^2}{2\bar{r}^3} f \int \frac{R^2 g(R) dR}{(R^2 - r^2)^2}. \tag{2}$$

Here the sum over the ensemble of the surrounding atoms is replaced by an integration over a continuous density distribution in the liquid with a pair correlation function $g(R)$. The function $f(R)$ is outside the cell equal to the Lorenz–Lorentz factor of the local field,[12] $f = (1 + 8\pi\alpha N/3)^{-1}$.

We shall see in what follows that it is sufficient to use $u(r)$ in the form of an expansion of the integrand in (2) in R/r, retaining the first terms. We then have

$$u(r) = -\frac{3\alpha e^2}{2\bar{r}^3\sigma} f\left(I_0 + I_2 \frac{2}{3} \frac{r^2}{\sigma^2} + I_4 \frac{3}{5} \frac{r^4}{\sigma^4}\right) = u_0 + u_2 + u_4,$$

$$I_n = (1+n) \int g(x) x^{-(2+n)} dx, \quad n = 0, 2, 4. \tag{3}$$

If we assume $g(R) = 0$ for $R < \sigma$ and that for $R > \sigma$, we find that the I_n are equal to unity. When one uses real $g(R)$ known for Lennard–Jones liquids[13] I_0, I_2, and I_4 are practically constant in the range of densities considered, $I_0 = 1.2$, $I_2 = 1.6$, and $I_4 = 1.8$. The constant u_0 is equal to the average polarization energy of the medium and $u_2(r)$ and $u_4(r)$ are components of the cell potential determined by its surroundings.

The pseudopotential of the cell is the sum of the electron-atom potential cut off at the boundary of the cell and the averaged potential (3) of the surrounding atoms. We consider the problem of the scattering length $L(\bar{r})$ for such a potential. To do this we use the well known expression[14] for the change in the phase shift of an s-wave caused by a change in the potential,

$$(\tilde{\chi}_0\chi_0' - \tilde{\chi}_0'\chi_0)|_{r=\infty} = \frac{2m}{\hbar^2} \int_0^\infty [V(r) - \tilde{V}(r)] \chi_0\tilde{\chi}_0 dr, \tag{4}$$

where $\chi_0(r)$ and $\tilde{\chi}_0(r)$ are wavefunctions with wavenumber $k = 0$ for the perturbed potential $V(r)$ and the potential $\tilde{V}(r)$. The perturbed potential will be the cell pseudopotential:

$$V(r) = \begin{cases} V_a(r) + u_2(r) + u_4(r, & r \leqslant \bar{r}, \\ 0, & r > \bar{r}. \end{cases} \tag{5}$$

As the unperturbed potential we use the potential of an isolated atom $\tilde{V}(r) = V_a(r)$. The wavefunctions are normalized such that

$$\chi_0(r) = r - L, \quad \tilde{\chi}_0(r) = r - L_0, \quad r \to \infty, \tag{6}$$

where L_0 is the scattering length for an isolated atom and L is the required scattering length for the cell pseudopotential. The integral on the right-hand side of (4) can be split into two—over the interior of the cell and outside it:

$$L - L_0 = \frac{2m}{\hbar^2} \int_0^{\bar{r}} [u_2(r) + u_4(r)] \chi_0(r) \tilde{\chi}_0(r) dr$$

$$- \frac{2m}{\hbar^2} \int_{\bar{r}}^\infty \left(-\frac{\alpha e^2}{2r^4}\right) \chi_0(r) \tilde{\chi}_0(r) dr, \tag{7}$$

where we have used the fact that for $r > \bar{r}$ the electron-atom potential is equal to the polarization potential (1). As the wavefunction $\tilde{\chi}_0(r)$ we take the well known wavefunction for the polarization potential,[15]

$$\tilde{\chi}_0 = Ar \sin\left(\frac{1}{r} \sqrt{\frac{\alpha}{a_0}} - \Delta\right),$$

$$A = -\sqrt{1 + L_0^2 \frac{a_0}{\alpha}}, \quad \cot \Delta = L_0 \sqrt{\frac{a_0}{\alpha}}. \tag{8}$$

Here Δ is the phase shift caused by the short-range component of the potential. The normalization constant A corresponds to the asymptotic behavior of (6) and a_0 is the Bohr radius.

The wavefunction $\tilde{\chi}_0(r)$ describes the scattering by an isolated cell of the muffin tin potential. Outside the cell $r \geqslant \bar{r}$ it is the same as its asymptotic form (6). Inside the cell we use for the function $\chi_0(r)$ the polarization wavefunction (8) smoothly joined to the asymptotic form (6) at the boundary of the cell, $\chi_0(\bar{r}) = \bar{r} - L$. We then have for $\chi_0(r)$

$$\chi_0(r) = \begin{cases} \left\{ r\left(1 - \frac{L}{\bar{r}}\right) \sin\left(\frac{1}{r} \sqrt{\frac{\alpha}{a_0}} - \kappa\right) \left[\sin\left(\frac{1}{\bar{r}} \sqrt{\frac{\alpha}{a_0}} - \kappa\right)\right]^{-1} \right\}, \\ r \leqslant \bar{r}, \quad r - L, \quad r > \bar{r}, \end{cases} \tag{9}$$

where the phase shift κ is determined by the equation:

$$\cot\left(\frac{1}{\bar{r}} \sqrt{\frac{\alpha}{a_0}} - \kappa\right) = -\sqrt{\frac{a_0}{\alpha}} \frac{L\bar{r}}{\bar{r} - L}. \tag{10}$$

We carry out the integration over the volume of the cell in (7) approximately, assuming that the main contribution to the integral comes from the vicinity of the upper limit of integration. The second integral in (7) is calculated exactly. Solving the equation obtained for L we find:

$$L = \frac{L_c - \bar{r}A(1 - L_c/\bar{r})}{1 - A(1 - L_c/\bar{r})}. \tag{11}$$

Here L_0 is the scattering length for the polarization potential cut off at $\bar{r}$,

$$L_c = \left\{ \frac{1}{\bar{r}} + \sqrt{\frac{a_0}{\alpha}} \tan\left[\sqrt{\frac{\alpha}{a_0}} \left(\frac{1}{a} - \frac{1}{\bar{r}} \right) \right] \right\}^{-1}, \quad (12)$$

where we have used the notation

$$\Delta = a^{-1} \sqrt{\alpha / a_0}. \quad (13)$$

The contribution of the averaged potential of the surroundings of the cell is determined by the parameter

$$A = \frac{2}{5} \frac{\alpha \bar{r}}{a_0 \sigma^3} f \left[I_2 + \frac{9}{14} I_4 \frac{\bar{r}^2}{\sigma^2} \right]. \quad (14)$$

The assumption made in the calculations, that the wavefunction $\chi_0(r)$ is only a little distorted inside the cell by the potential $u(r)$ of the surroundings, requires that the inequality $A \ll 1$ be satisfied. In the triple point of argon we have $A = 0.114$.

Another important inequality must reflect the assumption that the fraction of the cell volume in which the short-range component of the potential dominates is small. We note that the length a defined in (13) is a measure of the range of that component. It is thus necessary to require that

$$(a/\bar{r})^3 \ll 1. \quad (15)$$

In argon we have $a = 1.68$ and at the triple point we have $(a/\bar{r})^3 = 0.064$.

The function $L(N)$ calculated using Eqs. (11), (12), and (13) is shown in Fig. 1. The calculated scattering length of an electron in a liquid vanishes for a density which is close to the density N^* corresponding to the maximum of $\mu(N)$. The fact that the function $L(N)$ passes through zero was first noted in Ref. 12, but subsequent calculations carried out in a number of papers did not describe this effect although it had been confirmed experimentally.[16,17] We show in Fig. 1 the values of $L(N)$ obtained from the experimental mobility $\mu(N)$.[16] The agreement between calculation and experiment is good if one takes into account that the quantities L_0 and α, which are well known for isolated atoms, are the only parameters entering in the calculation of the function $L(N)$. One could hardly expect greater accuracy from a theory which does not use free parameters. One must rather consider it a success to get an accurate vanishing of the calculated function $L(N)$ in the point N^* corresponding to the maximum value of the mobility.

The expression for $L(N)$ has the correct limit for low densities, $L(N \to 0) \to L_0$. To obtain it one must change to the gas approximation in (14), replacing the parameter σ of the interatomic potential by the average interatomic distance $\bar{r}$.

3. MAXIMUM OF THE ELECTRON MOBILITY IN A LIQUID

In a weak electric field excess thermal electrons are in partial equilibrium with the medium. Their kinetic energy is much smaller than the characteristic scale on which the potential changes. The interaction of these electrons with the medium is thus determined by the s-wave scattering, the phase of which is linear in the wavenumber k, $\delta_0 = -Lk$. The
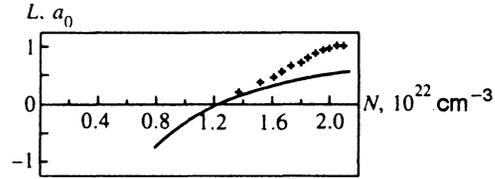
parameter characterizing the interaction of the electron with the medium is the scattering length $L(N)$. In kinetic theory one can consider the motion of an electron in a liquid as consecutive acts of scattering by elementary cells, characterized by the scattering length $L(N)$. If we take the spatial correlation of the cell into account,[18] the mean free path of an electron is

$$l = [4\pi L^2(N) N S(0)]^{-1}. \quad (16)$$

The long-wavelength structure factor of the liquid is small near the triple point, $S(0) \simeq 0.05$. When the density decreases the increase in $S(0)$ will be compensated by the decrease in the scattering length $L(N)$. As a result the mean free path l is large for almost the whole range of liquid densities. In order that kinetic theory be applicable one must require that the Ioffe-Regel parameter which is equal to the ratio of the electron wavelength to its mean free path be small:

$$4\pi L^2 N S(0) \lambda \ll 1. \quad (17)$$

We can rewrite this inequality using the gas kinetic expression for the mobility μ in another form,

$$e\hbar / Tm\mu \ll 1. \quad (18)$$

For temperatures in the region of 100 K this corresponds to $\mu \gg 10^2$ cm^2/V·s. Such high values of the mobility have, indeed, been observed (Fig. 2).

We write the expression for the mobility in a Lorentzian form

$$\mu(N) = \frac{2}{3} \sqrt{\frac{2e^2}{\pi T m_{\text{eff}}}} \{ N[4\pi L^2(N) S(0) + 4\pi \overline{(\delta L)^2}] \}^{-1}, \quad (19)$$

where $m_{\text{eff}} \simeq m$ is the effective mass of the electron in the liquid. In the denominator of expression (19) we have taken into account the fluctuations in the scattering length when the liquid density fluctuates.[19,20]

The scattering length depends significantly on the density in a medium with a strong interaction. The maximum of the electron mobility as function of the liquid density, connected with the weakening of its scattering, is caused by the decrease in the average scattering length up to where it vanishes. Near that density the electrons "do not see" the separate scatterers and the scattering occurs by density fluctuations which contain many atoms.

The scattering of electrons by fluctuations determines the magnitude of the mobility maximum. We shall calculate $\overline{(\delta L)^2}$ as follows
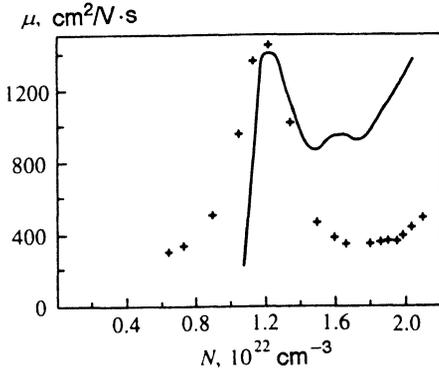
FIG. 2. Mobility of an electron in liquid argon as function of the density. The curve is the calculated function and the points are experimental data from Ref. 16.

$$\overline{(\delta L)^2} = \left(\frac{dL}{dN}\right)^2 \overline{(\delta N)^2}, \tag{20}$$

where $\overline{(\Delta N)^2} = NS(0)/\Omega$ are the mean square liquid density fluctuations occurring in a volume Ω. Substituting (11) into (20) we get

$$\overline{(\delta L)^2} \approx \frac{S(0)}{N^*\Omega} \left[\frac{\alpha}{3a_0\bar{r}^*}\left(1 + 2I_2 f \frac{\bar{r}^{*3}}{\sigma^3}\right)\right]^2. \tag{21}$$

Equation (21) contains a free parameter—the fluctuation volume Ω. We use Eq. (19) to derive its value from the experimental value of μ_{max}. The size $\Omega^{1/3}$ turns out to be close to 6.5σ for Ar and Xe. It is significantly larger than the size of the minimum fluctuation necessary to form the potential of the surroundings. Apparently, fluctuations which violate the spherical symmetry of the cell are very important. They are neglected in Eq. (20).

The results of calculating the mobility of electrons in liquid Ar and the experimental data of Ref. 16 are shown in Fig. 2. The theory satisfactorily describes the mobility maximum. The large value of the product $N^*\Omega$ which occurs in the denominator of (21) makes the scattering by the fluctuations $\overline{(\delta L)^2}$ given by (21) larger than the contribution to the scattering by separate cells (taking their spatial correlation into account) only in a narrow range near the value N^*. The shape of the extremum of the mobility $\mu(N)$ is thus determined by the functions $L(N)$ and $S(0,N) = NT\chi_T$, where χ_T is the isothermal compressibility of the liquid.

We discuss the mobility on the "wings" of the function $\mu(N)$. The decrease of the mobility with increasing N (for $N > N^*$) is determined by the growth of the scattering length $L(N)$. However, later the function $S(0,N)$ becomes the decisive factor and the measured mobility starts to increase. This is the consequence of the density dependence of the structure factor $S(0)$ which decreases when the density increases due to the decrease of the isothermal compressibility. In solid argon ($N = 2.5 \times 10^{22}$ cm^{-3}) the measured mobility reaches 3800 cm^2/V·s. The calculated mobility increases too steeply due to an underestimate by a factor two of the calculated scattering length which was discussed in the preceding section.

When the density decreases, $N < N^*$, the structure factor $S(0,N)$ increases with decreasing density and the calculated mobility drops off steeply. For the calculated values the inequalities (17) and (18) are here violated and the kinetic theory used by us is inapplicable. However, under the same conditions the measured mobility remains rather large. Clearly it is here insufficient to take into account the spatial correlation of the cells in the simplest form of the long-wavelength structure factor. Taking the dependence of $S(k,N)$ on small k into account in that region awaits further considerations.

4. GROUND STATE ENERGY

The ground state energy $\varepsilon = \hbar^2 q_0^2/2m$ of the electron is an eigenvalue of the solution of the Schrödinger equation in the Wigner–Seitz cell,

$$d^2\chi/dr^2 + [q_0^2 - 2m\hbar^{-2}U(r)]\chi = 0 \tag{22}$$

with the boundary condition $\chi(\bar{r}) = \bar{r}\chi'(\bar{r})$. In the zero-radius potential approximation we can use $\chi(L) = 0$ as the second boundary condition. As a result the wavefunction

$$\psi(r) = \chi(r)/r = A(q_0 r)^{-1} \sin[q_0(r-L)], \tag{23}$$

and the eigenvalue of the wavenumber satisfy the following condition for $L > 0$:

$$\tan[q_0(\bar{r}-L)] = q_0\bar{r}. \tag{24}$$

This Wigner–Seitz solution has often been used in the literature.

The solution given here is unsuitable under conditions in which the attraction dominates over the repulsion, i.e., for $L < 0$. Under those conditions, starting with Ref. 10, the second boundary condition has been written down using some scattering length which was estimated for the short-range repulsive component, and the polarization component of the potential was averaged. This procedure, which admits considerable latitude, nevertheless gave values for the ground state energy in the triple point. However, the fact that the ground state energy passes through a minimum was not described.[8,9] We obtain a correct solution of this problem.

Under conditions when the scattering length is negative the ground state energy $\varepsilon = -\hbar^2\kappa_0^2/2m$ is also negative. The Schrödinger equation has the form

$$d^2\chi/dr^2 - [\kappa_0^2 + 2m\hbar^{-2}U(r)]\chi = 0. \tag{25}$$

It is natural to use for its solution, if L has a small absolute magnitude, the same zero-radius potential approximation, i.e., the boundary condition $\psi(L) = 0$. The solution has the following form,

$$\psi(r) = A(\kappa_0 r)^{-1} \sinh[\kappa_0(r-L)]. \tag{26}$$

The eigenvalue κ_0 satisfies the relation

$$\tanh[\kappa_0(\bar{r}-L)] = \kappa_0\bar{r}. \tag{27}$$

The obtained solution does not satisfy the condition $\psi(0) = 0$. However, if the pseudopotential region is small,
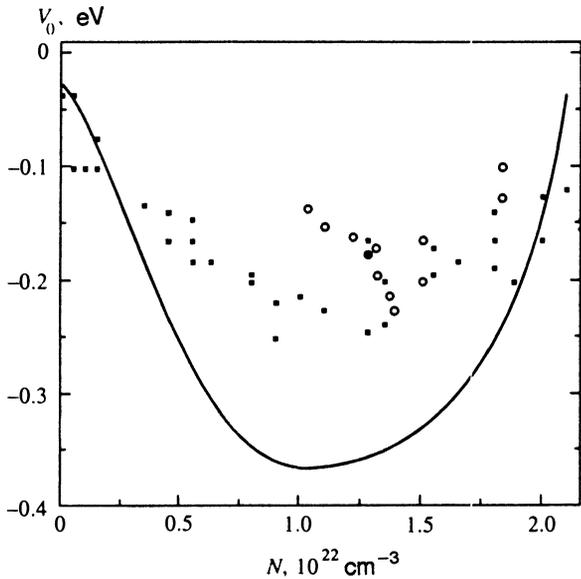
$$(|L|/\bar{r})^3 \ll 1, \tag{28}$$

FIG. 3. Ground state energy of an electron in liquid argon as function of the density, $V_0(N)$. The curve is the calculated function, the experimental data are from Ref. 21 (■), Ref. 22 (O), and Ref. 23 (▲).

the divergence of ψ at the origin is not important. It does not prevent normalization,

$$A^2 = (4/3)(\kappa_0 \bar{r})^{-3}\{\sinh[2\kappa_0(r-L)]$$
$$+ \sinh(2\kappa_0 L) - 2\kappa_0 \bar{r}]\}^{-1}. \tag{29}$$

It follows from Eq. (27) that

$$\hbar^2 \kappa_0^2/2m \leqslant \hbar^2/2m\bar{r}^2. \tag{30}$$

This means that the electron cannot be localized in the region of a single cell.

For lower densities as in the case $L>0$ there is a transition to Fermi's optical approximation,[15] $\kappa_0^2/2 = -(3/2)L\bar{r}^{-3}$. The quantity measured is not the energy ε but the energy V_0 of the affinity of the electron to the liquid. It differs from ε by a shift equal to the energy of the average polarization of the substance,

$$V_0 = u_0 + \epsilon, \tag{31}$$

where u_0 is given by Eq. (3).

The function $V_0(N)$ calculated for argon is given in Fig. 3 with the results of the measurements of Refs. 21–23. The calculated curve is obtained by using the measured function $L(N)$ for densities where there are such results and the calculated $L(N)$ where there are no such results. At low densities the values of V_0 are matched to the optical approximation when we have

$$V_0 = -3\alpha e^2(2\bar{r}^4)^{-1} + 3e^2 L_0 a_0(2\bar{r}^3)^{-1}. \tag{32}$$

There exists a region of intermediate densities in which neither the optical nor the cell approximation applies.

The theory satisfactorily describes the minimum in the function $V_0(N)$. However, the calculated values of $|V_0|$ are larger than the experimental ones. This can possibly be ex-

plained by the fact that the proposed theory is a mean-field theory and does not take into account the effect of density fluctuations. A description of a liquid in terms of the pair correlation function enables us to consider spherically symmetric fluctuations but not spherically asymmetric fluctuations, which certainly play an important role, especially in the lower density region. Taking these effects into account is, apparently, possible in numerical experiments. A numerical method of studying the state of a light quantum particle in a classical liquid requires giving the electron-atom potential explicitly both at large and at small distances.[24,25] The results of such calculations published so far contain adjustable parameters and are therefore doubtful. Our work shows that the short-range part of this interaction can be given in the simplest form, for instance, in the form of a hard core at a distance a. One should verify that then the phase shift δ_0 is satisfactorily reproduced at low energies. We note that the proposed pseudopotential satisfies this condition only for s-wave scattering. It is possible that this turns out to be sufficient.

In conclusion one should note that the proposed theory enables us to describe satisfactorily the two experimentally determined functions $\mu(N)$ and $V_0(N)$ over a relatively broad range of liquid densities. Earlier papers described only one of these functions. Here we have presented calculations referring to argon. The theory describes krypton and xenon in a similar way.

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