Structure and mobility of negative ions in dense gases and nonpolar liquids

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The structure of negative ions in dense gases and nonpolar liquids is investigated. It is shown that the competition between the polarization attraction and the exchange repulsion between the outer electron of a negative ion and the atoms of the medium can lead to the formation near the negative ion of a cavity surrounded by a denser layer. The dependence of the cavity radius and the structure of the denser layer on the temperature and density of the medium leads to anomalous behavior of the negative ion mobility. Estimates of the mobility of the O_2^- ion in helium and neon agree well with the available experimental results. © *1995 American Institute of Physics.*

1. INTRODUCTION

Over several decades, numerous investigators have been drawn to study the transport properties of charged particles injected into a dielectric medium. The transport properties of electrons in gases and liquids have been most fully studied.[1–4] In the interaction of an electron with the atoms or molecules of a medium, polarization attraction is predominant at large distances, while at short distances exchange repulsion takes over. This has the consequence that in media with predominant repulsion (for example, He, Ne, and H_2), it may be thermodynamically advantageous for an electron to be localized at density fluctuations (rarefactions) with subsequent formation of a bubble. In media with high polarizability, the localization of an electron may occur at fluctuations of concentration type and lead to the formation of multiatomic charged clusters, as appears to happen in dense gaseous Xe (Ref. 5). Clusters are also formed in the case of self-trapping (localization) of positrons, since in this case there is no exchange interaction.[6]

The structure and transport properties of positive ions have also been well studied. Because of the electrostriction effect, the local properties of the medium (density, pressure, viscosity) are strongly changed near an ion, and under certain conditions this leads to solidification of the liquid near the ion[7,1] and to the formation of a cluster. This explains the rather low mobility of positive ions in liquid helium and some other liquids at low temperatures, and the weak dependence of the mobility on the species of the positive ion.

Much less is known about the structure and transport properties of negative ions. Of particular interest is the O_2^- ion, since oxygen is present as an impurity in essentially all experiments. Thus, in Bartels's study[8] not only electrons but also negative oxygen ions were investigated in strongly supercritical helium. The mobility of O_2^- ions has also been measured in supercritical dense neon,[9] and in liquid argon, krypton,[10] and xenon.[10,11]

The electrostriction effect does not depend on the sign of the charge. Therefore, the model proposed by Atkins[7] to explain the transport properties of positive ions has also been used in the case of negative ions. However, the authors of Refs. 8–10 encountered serious difficulties. For example, Bartels[8] unsuccessfully attempted to explain the anomalous mobility by proposing the existence in He of an O_n^- complex. Borghesani *et al.*,[9] using one of the modifications of Atkins's model, proposed that a cluster of Ne atoms is formed around the O_2^-, and they took into account the local change in the properties of the medium around the cluster to calculate the mobility. However, they did not take into account the short-range repulsive part of the ion–atom interaction and were forced to use the cluster radius as a fitting parameter. In Refs. 10 and 11 there was also no convincing explanation of the differences between the mobilities of positive and negative ions.

In this paper, we show that the short-range repulsion of an outer weakly bound electron of a negative ion leads as a result of interaction with the atoms of the medium to the formation around the O_2^- of a cavity rather than a cluster. This is due to the fact that the outer electron is localized in a spatial region with a characteristic size appreciably greater than that of the electron shells of the oxygen molecule. Such an electron interacts actively with the atoms of the surrounding medium. As in the case of free electrons, the competition between the long-range polarization attraction and the short-range exchange repulsion can lead to the formation of an almost empty cavity in the immediate vicinity of the ion, the cavity being surrounded by a denser layer. The density of the atoms in this layer may appreciably exceed the mean density of the atoms in the medium.

We first consider a very simple model that completely ignores electrostriction effects and takes into account only the exchange repulsion between the outer O_2^- electron and the atoms of the medium. The model can be used in the case of gases whose atoms have low polarizability and at sufficiently high temperatures, for example, in He under the conditions of Bartels's experiment.[8] Further, in the framework of the self-consistent field method with allowance for interaction between the atoms, we find the connection between the

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concentration of the atoms of the medium near the negative ion and the wave function of the outer electron of the negative ion. We determine the effective interaction potential between the negative ion and the atoms of the medium. We calculate the density profiles of the atoms near the O_2^- ions and their mobility in He and Ne. The results of the calculations are compared with the available experimental data and the theoretical calculations of Refs. 8 and 9.

2.RECTANGULAR WELL MODEL

The binding energy of an electron in the oxygen molecule is fairly low: $\varepsilon=0.46$ eV. Therefore, the orbit of the outer electron of the molecular ion O_2^- is appreciably more extended than the orbits of the inner electrons ($R_i \sim \hbar/\sqrt{2m\varepsilon} \cong 4.2a_0$, where a_0 is the Bohr radius). The interaction of this electron with the atoms of the medium is a polarization interaction only at large distances. At short distances the repulsion associated with the exchange interaction of the outer electron of the negative ion with the electrons of the outer shells of the atoms of the medium is predominant. It is the presence of the exchange repulsion that is the most important reason for the difference between the properties of positive and negative ions in dense media. It leads to the appearance of a cavity near a negative ion. This effect is most clearly seen in dense helium, in which the low polarizability of the atoms has the consequence that the electrostriction effect plays a secondary role. The situation is similar to the case of electron and positron bubbles in gaseous and liquid helium and neon,[1,2,4,6] the bubbles around excited atoms,[12] and around positive ions of rare-earth metals[13] in liquid helium. In the latter two cases, the analogy is most complete, since the bubbles are formed by the interaction with the ambient atoms of localized electrons that are also in extended orbits.

As in the case of free electrons, the interaction of the weakly bound outer O_2^- electron with the atoms of the medium can be considered in the framework of the optical model.[14] This interaction leads to a shift in the energy of the bottom of the electron conduction band by an amount V_0, which is a function of the density of the medium. Therefore, the fluctuations of the density lead to fluctuations of V_0. In helium, the exchange repulsion is predominant, V_0 is positive, and the density fluctuations of rarefaction type lead to a local lowering of the electron potential energy. In the case of free electrons, this is the main reason for self-trapping when the electron binding energy in the potential well of a fluctuation is greater than the work needed to create the fluctuation. In the case of negative ions, the electron is localized even in the absence of fluctuations. However, its binding energy is changed inside a fluctuation whose characteristic diameter is comparable with that of the electron wave function. The optimum shape of the fluctuation can be determined by minimizing the free energy or, in other words, by maximizing the difference between the increase in the binding energy of the electron in the negative ion and the work needed to create the corresponding fluctuation.

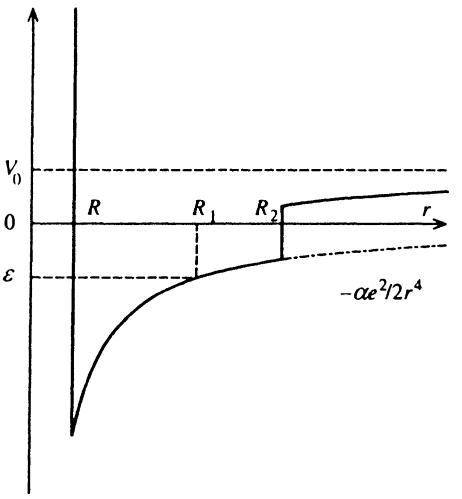

FIG. 1. Model of the potential that acts on an electron in a negative ion.

Before we turn to a more detailed analysis of the effect of the medium on the spectrum of the outer electron in a negative ion, we discuss the main properties of the isolated negative ion. This can be done by means of the simplified model potential shown in Fig. 1:

$$U(r)=\begin{cases} -\dfrac{\alpha e^2}{2r^4} & \text{for } r>R, \\ \infty & \text{for } r\leqslant R, \end{cases} \tag{2.1}$$

where α is the polarizability of an atom or molecule, and R is the effective radius of the short-range hard core. This potential has the correct long-range polarization asymptotic behavior and takes into account the short-range exchange repulsion. As was shown in Ref. 15, the energy spectrum of an electron in the potential (2.1) can be determined with good accuracy from the condition of matching of the logarithmic derivatives of the short-range asymptotic behavior of the radial electron wave function

$$\chi(r)=Ar\,\sin\left[\sqrt{\frac{\alpha}{a_0}}\left(\frac{1}{r}-\frac{1}{R}\right)\right] \tag{2.2}$$

to its long-range asymptotic behavior

$$\chi(r)=Be^{-\gamma_1 r}, \quad \gamma_1^2=\frac{2m\varepsilon}{\hbar^2} \tag{2.3}$$

at the point

$$R_1=\left(\frac{\alpha}{a_0\gamma_1^2}\right)^{1/4}. \tag{2.4}$$

In (2.2)–(2.4), A and B are numerical constants, and ε is the binding energy of the electron in the atom or molecule. The relationship between R, α, and ε is given by

$$\cot\left[\sqrt{\frac{\alpha}{a_0}}\left(\frac{1}{R_1}-\frac{1}{R}\right)\right]-R_1\sqrt{\frac{a_0}{\alpha}}=1. \tag{2.5}$$

In the case of the O_2^- ion, the binding energy is $\varepsilon=0.46$ eV, and the polarizability of the O_2 molecule is $\alpha=10.6a_0^3$. The solution of Eq. (2.5) gives $R\cong0.93a_0$. Note that the exact solution of the Schrödinger equation for the potential (2.1) gives the very similar result $R\cong0.92a_0$. In the derivation of

(2.5), we assumed that the binding energy ε is small compared with the depth $\alpha e^2/2R^4$ of the potential well; it is readily seen that this assumption is easily satisfied in O_2^- ion.

We now turn to a discussion of the effect of fluctuations in the density of the atoms of the medium on the spectrum of the negative ion. We consider the simplest model, in which the fluctuation is a cavity with radius R_2. In this case, by analogy with (2.1) and with allowance for the influence of the atoms of the medium, the model potential in which the electron is localized can be represented in the form

$$U(r)=\begin{cases} V_0-\dfrac{\alpha e^2}{2r^4} & \text{for } r\geqslant R_2, \\ -\dfrac{\alpha e^2}{2r^4} & \text{for } R<r<R_2, \\ \infty & \text{for } r\leqslant R. \end{cases} \tag{2.6}$$

This potential is also shown in Fig. 1. Note that in this model we do not take into account the effect of the polarization interaction of the electron with the atoms of the medium either on the form of the potential within the cavity or on the distribution of the atoms outside the cavity. The validity of this approximation for helium will be discussed below.

As before, the wave function of the outer electron $\chi(r)$ near the core will be the same as (2.2). At large distances $(r\gg R_2)$, $\chi(r)$ will be equal to the function (2.3) if γ_1 is replaced in it by γ_2 determined by the expression

$$\gamma_2^2=\gamma_1^2+\frac{2mV_0}{\hbar^2}. \tag{2.7}$$

In the intermediate region $(R_1<r<R_2)$, the wave function has the form

$$\chi(r)\cong C_1e^{\gamma_1 r}+C_2e^{-\gamma_1 r}. \tag{2.8}$$

Matching the logarithmic derivatives of the wave functions at the points $r=R_1$ and $r=R_2$, we obtain an equation relating the electron binding energy ε in the negative ion to the cavity radius R_2:

$$\cot\left[\sqrt{\frac{\alpha}{a_0}}\left(\frac{1}{R_1}-\frac{1}{R}\right)\right]-R_1\sqrt{\frac{a_0}{\alpha}} = \frac{\left(1+\dfrac{\gamma_2}{\gamma_1}\right)e^{-\gamma_1(R_1-R_2)}-\left(1-\dfrac{\gamma_2}{\gamma_1}\right)e^{\gamma_1(R_1-R_2)}}{\left(1+\dfrac{\gamma_2}{\gamma_1}\right)e^{-\gamma_1(R_1-R_2)}+\left(1-\dfrac{\gamma_2}{\gamma_1}\right)e^{\gamma_1(R_1-R_2)}}. \tag{2.9}$$

In the limit $V_0\to 0$ or $R_2\to\infty$, there is a transition to the case of an isolated ion, and Eqs. (2.9) and (2.5) are indeed identical.

Upon formation of a bubble around the negative ion, the free energy F of the system is reduced by the increase in the electron binding energy in the negative ion and increased by the work done against volume and surface forces:

$$\Delta F=-\Delta\varepsilon(R_2)+\frac{4\pi}{3}pR_2^3+4\pi\sigma R_2^2, \tag{2.10}$$

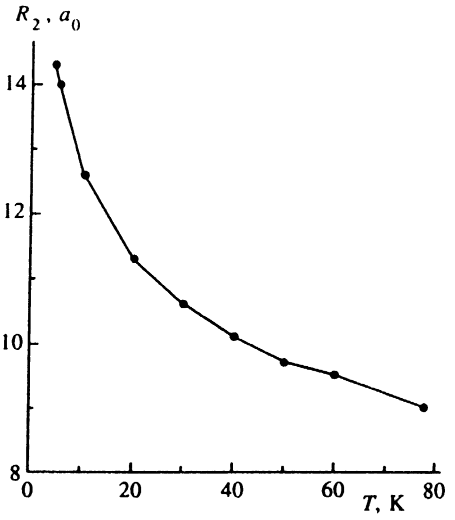

FIG. 2. Radius of the cavity formed around an ion in helium as a function of the temperature for density $N=2.5\cdot 10^{21}$ cm^{-3} of the medium.

where σ is the coefficient of surface tension. The optimum bubble radius is determined by minimizing the free energy: $d\Delta F/dR_2=0$.

Having in mind a subsequent comparison of our calculations with Bartels's results on the mobility of O_2^- ions in dense gaseous helium (see Sec. 4), we calculated R_2 under the conditions of this experiment[8] at $T=77.6$ K and at densities from $2.5\cdot 10^{21}$ to $7.5\cdot 10^{21}$ cm^{-3}. We also varied V_0 from 0.08 to 0.24 eV (Ref. 16). The cavity radius under these conditions was found to be essentially constant and equal to $9a_0$.

The dependence of the cavity radius on the temperature is shown in Fig. 2. As the temperature is reduced, there is a tendency for the bubble radius to increase. For example, in saturated He vapor at $T\cong 4.2$ K the bubble radius is $R_2\cong 20a_0$. However, the estimates of R_2 in this model at such low temperatures must be treated with caution. The fact is that, as will be shown below, the importance of the polarization attraction increases strongly with decreasing temperature, and this leads to the formation of a significant density enhancement of the medium around the cavity, allowance for which is necessary but complicated in our simplified model.

We now discuss the limits of applicability of the proposed model associated with the neglect of polarization attraction. This effect can be nominally subdivided into three components. Above all, the polarization attraction directly affects the value of V_0. For example, in a sufficiently rarefied gas V_0 can be estimated in the framework of the optical model, $V_0\approx 2\pi\hbar^2L_aN/m$, where N is the density of the medium. The polarization interaction can be taken into account here by means of the electron scattering length L_a for scattering by an atom of the medium:[6,17]

$$L_a\cong\left(\frac{\alpha_a}{a_0}\right)^{1/2}\cot\left[\left(\frac{\alpha_a}{a_0}\right)^{1/2}\frac{1}{R_a}\right], \tag{2.11}$$

where α_a is the polarizability of an atom of the medium, and R_a is the radius of its core. The scattering length is an integrated characteristic of the scattering process and takes into account both the exchange repulsion and the polarization attraction.

On the other hand, the polarization interaction changes the energy of the electron level in the negative ion. In our model, this change $\Delta\varepsilon_p$ can be estimated as a function of the cavity radius:

$$\Delta\varepsilon_p \approx \frac{2\pi e^2 \alpha_a N}{R_2}. \tag{2.12}$$

The possibility of ignoring this effect is determined by the condition

$$\Delta\varepsilon_p \ll V_0. \tag{2.13}$$

Using the optical model for a rough estimate of V_0, we obtain from (2.12) and (2.13) the condition

$$\frac{\alpha_a}{a_0 R_2 L_a} \ll 1, \tag{2.14}$$

which when satisfied allows us to ignore the direct effect of the polarization interaction on the binding energy of the electron in the negative ion. It is easy to show that in He the condition (2.14) is satisfied ($L_{\mathrm{He}} \sim 1a_0$). However, already in Ne ($\alpha_{\mathrm{Ne}} \cong 2.67a_0^3$, $L_{\mathrm{Ne}} \cong 0.45a_0$), this condition ceases to hold.

In addition, because of electrostriction a denser layer forms around the cavity, and, as will be shown below, its importance increases as the temperature is decreased. The influence of this effect is negligible if

$$\lambda_T^2 \frac{\alpha_a}{a_0 R_2^4} \ll 1, \tag{2.15}$$

where $\lambda_T = \hbar/\sqrt{2mT}$ is the thermal electron wavelength. At $T=77$ K in He, the condition (2.15) is easily satisfied, and the role of the denser layer can be ignored. At lower temperatures in He, the condition (2.15) is violated. For example, at $T=4.2$ K, $\lambda_T^2\alpha_a/a_0R_2^4 \geqslant 1$, and this effect must be taken into account. In Ne at $T=45$ K, the condition (2.15) is also not satisfied ($\lambda_T^2\alpha_a/a_0R_2^4 \cong 1.9$).

Bearing in mind the facts noted above, in what follows we shall use the self-consistent field model to take into account more correctly the interaction of the electron with the medium.

3. SELF-CONSISTENT FIELD APPROXIMATION

We now turn to the consideration of a model that can be regarded as a generalization of the self-consistent field method (which is widely used in the theory of self-trapping of free electrons[2,4]) to the case of an electron localized in the field of an atom or a molecule and forming a negative ion. The use of this approach makes it possible to take into account correctly the polarization effects mentioned in the previous section and enables us to describe from a consistent point of view states with both strong rarefaction and appreciable concentration of the medium near the ion.

We shall assume that the electron is in the ground state in the field of a complex formed by an O_2^- molecule and a fluctuation in the density of the atoms of the environment with binding energy ε measured from the lower boundary of the conduction band V_0 of the free electron:

$$V_0 = N\int\int V(\mathbf{r}-\mathbf{r}')|\Psi(\mathbf{r})|^2 d\mathbf{r}d\mathbf{r}', \tag{3.1}$$

where $V(\mathbf{r})$ is the two-body potential of the interaction between the electron and an atom of the medium. In Eq. (3.1), V_0 is also the average field that acts on a free electron in the case of a uniform distribution of the atoms of the medium.

We also assume that the electron interacts simultaneously with a large number of atoms:

$$N\nu \gg 1, \quad \nu = 4\pi a^3/3, \tag{3.2}$$

where a is the characteristic range of the electron–atom forces. Then the averaged Schrödinger equation for the electron has the form

$$-\frac{\hbar^2}{2m}\Delta\Psi(\mathbf{r}) + U(\mathbf{r})\Psi(\mathbf{r}) + \left\{\int V(\mathbf{r}-\mathbf{r}')[N(\mathbf{r}') - N]d\mathbf{r}'\right\}\Psi(\mathbf{r}) = -\varepsilon\Psi(\mathbf{r}), \tag{3.3}$$

where m is the electron mass. The averaged electron wave function $\Psi(\mathbf{r})$ reproduces the general behavior of the real wave function but does not have irregularities near the centers of the atoms. The difference between (3.3) and the corresponding equations known in the theory of electron self-trapping[2,4] consists of the introduction into this equation of the field $U(\mathbf{r})$ (2.1) of the molecule in which the electron is localized. The expression in the curly brackets in (3.3) determines the potential of the mean field, the emergence of which is due to the deviation of the concentration of the atoms of the medium near the ion from the mean value. The formation of a fluctuation of atoms of the medium leads to a change ΔS in the entropy of the ion–medium system. At the same time, the work $T\Delta S$ is expended on the formation of such a fluctuation.

In a dense gas, it is necessary to take into account the correlations of the atoms of the medium with each other. These correlations can be taken into account approximately by the means of the lattice gas model, which leads to the following expression for the free energy of the ion–medium system:[2]

$$\beta F = -\beta\varepsilon + \int\left[N(\mathbf{r})\ln\frac{N(\mathbf{r})}{N} + \frac{1-N(\mathbf{r})b}{b}\ln\frac{1-N(\mathbf{r})b}{1-Nb}\right] \times d\mathbf{r} - a\beta\int[N(\mathbf{r})-N]^2 d\mathbf{r}. \tag{3.4}$$

Here $b=1/2N_c$ and $a=T_c/N_c$ are, respectively, responsible for the repulsive and attractive interactions of the atoms of the medium with each other (T_c and N_c are the critical parameters of the lattice gas). Variation of (3.4) with respect to all possible distributions $N(\mathbf{r})$ of the atoms of the medium around the ion gives an equation for the local density:

$$\frac{N(\mathbf{r})}{N}=\frac{(1+\xi)\exp[-\beta\tilde{V}(\mathbf{r})+2a(N(\mathbf{r})-N)]}{1+\xi\exp[-\beta\tilde{V}(\mathbf{r})+2a(N(\mathbf{r})-N)]},$$

$$\xi=\frac{N}{2N_C-N}. \tag{3.5}$$

At high densities, the expression (3.5) takes into account the fact that the density of the atoms cannot exceed the close-packing density $2N_c$ in the lattice model. In (3.5), $\tilde{V}(\mathbf{r})$ is the effective potential of the interaction of the electron with an atom of the environment, and it is the quantum-mechanical expectation value of the potential of the electron–atom interaction $V(\mathbf{r}-\mathbf{r}')$, where $\mathbf{r}$ is the position vector of the atom of the medium, and $\mathbf{r}'$ is the position vector of the electron:

$$\tilde{V}(\mathbf{r})=\int V(\mathbf{r}-\mathbf{r}')|\Psi(\mathbf{r}')|^2d\mathbf{r}'. \tag{3.6}$$

On the other hand, since the interaction of the electron with an atom or the molecule of a negative ion through the potential $U(\mathbf{r})$ is included in (3.2) and influences the form of the electron wave function in (3.5), $\tilde{V}(\mathbf{r})$ can be regarded as the effective potential of the interaction of the negative ion with the atoms of the environment.

Thus, to establish the structure of the complex around the negative ion, it is necessary to solve the self-consistent system of equations (3.3)–(3.5), taking into account (2.1) and (3.6). In view of the complexity of the problem, we shall seek the solution of this system by the direct variational method on the class of test wave functions that do not have zeros at $r>R$:

$$\Psi(\mathbf{r})=C\,\frac{r-R}{r^2}\cdot\exp(-r/\lambda), \tag{3.7}$$

where C is a normalizing constant, and λ is a variational parameter that determines the characteristic distance over which the wave function varies. The preexponential part of (3.7) models the behavior of the function near the atomic core and takes into account the fact that at the core $\Psi(R)=0$. In the limit $r\rightarrow\infty$, (3.7) gives the correct asymptotic behavior of the wave function: $\Psi\propto\exp(-r/\lambda)/r$. The use of (3.7) for the O_2^- molecule in vacuum to calculate the radius of the hard core of the electron–molecule interaction with effective potential (2.1) leads to very slight changes in $R(R\cong0.907a_0)$ compared with the exact value $R\cong0.92a_0$.

We now specialize the electron–atom potential $V(\mathbf{r})$ in (3.6) and consider the scattering of a slow electron by this potential. Following Ref. 2, we decompose $V(\mathbf{r})$ into two components:

$$V(\mathbf{r})=V_1(\mathbf{r})+V_2(\mathbf{r}), \tag{3.8}$$

where

$$V_1(\mathbf{r})=\begin{cases}\infty, & r\leqslant R_a,\\ 0 & r>R_2,\end{cases}$$

$$V_2(\mathbf{r})=\begin{cases}0 & r<R_2,\\ -\alpha_a e^2/2r^4, & r\geqslant R_a.\end{cases} \tag{3.9}$$

Here α_a is the polarizability of an atom of the medium, and R_a [like R in (2.1)] is the effective radius of the short-range core of an atom of the medium; it is related to the scattering length for scattering of the electron by the atom by the relation (2.11). Assuming that the condition $\lambda\gg R_a$ holds, as $V_1(\mathbf{r})$ we can use the effective Fermi potential

$$V_1(\mathbf{r})=\frac{2\pi\hbar^2R_a}{m}\,\delta(\mathbf{r}). \tag{3.10}$$

Here R_a is the electron scattering length corresponding to the potential $V_1(\mathbf{r})$. This immediately gives for $\tilde{V}$ in (3.6)

$$\tilde{V}_1(\mathbf{r})=\frac{2\pi\hbar^2R_a}{m}\,|\Psi(\mathbf{r})|^2. \tag{3.11}$$

We use the asymptotic representation well-known in scattering theory for the zeroth scattering phase shifts of an electron in a centrally symmetric field:[14]

$$\sin(\delta_0-\delta_{01})\cong-\frac{2mk}{\hbar^2}\int_0^\infty V_2(r)\varphi_0(r)\varphi_{01}^*(r)dr. \tag{3.12}$$

Here k is the modulus of the electron wave vector, δ_0 and φ_0 are the phase shift and radial wave function of the electron in the field $V(\mathbf{r})$ with orbital angular momentum $l=0$, and δ_{01} and φ_{01} are the analogous quantities in the truncated potential $V_1(\mathbf{r})$.

In the Born approximation, φ_0 in (3.12) can be replaced by φ_{01}. However, this requires fulfillment of the condition $R_a^2\gg\alpha_a/a_0$, which is violated in practically all the inert gases except for helium. Already in neon $R_a^2\cong\alpha_a/a_0$, and it is necessary to substitute the exact electron wave function φ_0 in (3.12). Following Ref. 15, we approximate the electron wave function by functions that are identical to the exact one near the core and at infinity:

$$\varphi_0=\begin{cases}Dr\,\sin\sqrt{\dfrac{\alpha_a}{a_0}}\left(\dfrac{1}{r}-\dfrac{1}{R_a}\right), & r<r_1,\\ \sin\dfrac{k(r-L_a)}{k}, & r>r_1,\end{cases} \tag{3.13}$$

where L_a is the scattering length of a slow electron scattered by the atom. The point of separation r_1 is determined from the condition of equality of the kinetic and potential energies of the electron and is the point at which the two asymptotic behaviors of the wave functions are matched:

$$r_1=(\alpha_a/a_0k^2)^{1/4}. \tag{3.14}$$

As $k\rightarrow0$, we have $r_1\rightarrow\infty$, and the condition of matching of the wave functions gives

$$D=-\left[\sin\sqrt{\frac{\alpha_a}{a_0R_a^2}}\right]^{-1}.$$

Substituting (3.13) in (3.12), we can obtain the approximate connection between the zeroth scattering phase shift and the electron wave number.

We now turn to the calculation of the effective potential of the polarization interaction:

$$\tilde{V}_2(\mathbf{r})=\int_{|\mathbf{r}-\mathbf{r}'|>R_a}V_2(\mathbf{r}-\mathbf{r}')|\Psi(\mathbf{r}')|^2d\mathbf{r}'. \tag{3.15}$$

Here $\Psi(\mathbf{r}')$ is a smoothed electron wave function and does not take into account the behavior near the cores of the atoms of the medium. Allowance can be made for this by analogy with (3.13), and then (3.15) can be represented in the form

$$\tilde{V}_2(\mathbf{r})=\int_{|\mathbf{r}-\mathbf{r}'|>R_a} V_2(\mathbf{r}-\mathbf{r}')\chi^2(\mathbf{r}-\mathbf{r}')|\Psi(\mathbf{r}')|^2 d\mathbf{r}', \tag{3.16}$$

$$\chi(\mathbf{r}-\mathbf{r}')=D\sin\left[\sqrt{\frac{\alpha_a}{a_0}}\left(\frac{1}{|\mathbf{r}-\mathbf{r}'|}-\frac{1}{R_a}\right)\right]. \tag{3.17}$$

By analogy with (3.13), this function takes into account the exact behavior of the electron wave function near the atomic core. In addition $\chi^2(\mathbf{r}-\mathbf{r}')\rightarrow 1$ as $|\mathbf{r}-\mathbf{r}'|\rightarrow\infty$. Calculation of $\tilde{V}_2(\mathbf{r})$ in the form of (3.16) is difficult due to the presence of the angle dependence $|\mathbf{r}-\mathbf{r}'|\geqslant R_a$ in the limit of integration. This difficulty can be eliminated by extending the region of integration to the complete space $r'\geqslant R$ (R is the radius of the core of the O_2^- molecule) by introducing the cutoff function

$$f(\mathbf{r}-\mathbf{r}')=\exp(-R_a/|\mathbf{r}-\mathbf{r}'|). \tag{3.18}$$

Then from (3.16) we obtain

$$\tilde{V}_2(\mathbf{r})\cong\int_{r'>R} V_2(\mathbf{r}-\mathbf{r}')\chi^2(\mathbf{r}-\mathbf{r}')f(\mathbf{r}-\mathbf{r}')|\Psi(\mathbf{r}')|^2 d\mathbf{r}'. \tag{3.19}$$

The significance of the introduction of the cutoff function is to prevent penetration of the electron into the region of the core of an atom of the medium and to eliminate the divergence of the integral (3.16) at $r=r'$. The choice of the cutoff function is fairly arbitrary. For example, the investigation of electron self-trapping in polar liquids in Ref. 18 used a different cutoff function, though, admittedly, this did not free the authors from the need for a numerical integration and the use of fitting parameters. In this paper, we propose a consistent method for introducing the cutoff function.

Indeed, the introduction of the cutoff function in (3.16) to calculate the effective potential affects the characteristics of the electron scattering by an atom and, in particular, the scattering length. To take into account these changes, it is necessary to introduce the cutoff function $f(\mathbf{r})$ in the equation for the zeroth phase shift (3.12) too, extending the integration to the complete region. Thus, for the scattering length of a slow electron scattered by an atom we obtain the zeroth approximation in k

$$L_a=R_a+\frac{2m}{\hbar^2}\int_0^\infty V_2(r)f(r)\varphi_0(r)\varphi_{01}^*(r)dr. \tag{3.20}$$

Taking into account (3.13) and noting that $\varphi_{01}=\sin k(r-R)/k$, we obtain

$$L_a=R_a-\frac{\alpha e^2 m}{\hbar^2}D\int_0^\infty\frac{dr}{r^3}(r-R_a)\times\exp\left(-\frac{R_a}{r}\right)\sin\left[\sqrt{\frac{\alpha_a}{a_0}}\left(\frac{1}{r}-\frac{1}{R_a}\right)\right]. \tag{3.21}$$

Knowing the electron–atom scattering length L_a from experiment, we can use (3.21) to determine the radius of the core of the exchange repulsion with allowance for the error introduced by the use of the cutoff function.

Having determined R_a and using the explicit form of the smoothed electron wave function (3.7), we can calculate the total effective potential by means of (3.11) and (3.19). Substituting this potential in (3.5) and finding the local density of the medium $N(r)$ near the ion as a function of the variation parameter λ, we can minimize the free energy functional (3.4) of the ion–medium system and find λ_m, the optimum length of variation of the smoothed electron wave function in the medium. Finally, substituting λ_m in (3.5), we can find the optimum profile of the density fluctuation of the medium around the negative ion. It turns out that λ_m depends very weakly on the temperature, density, and species of the atoms of the gas. Therefore, although the self-consistent field theory takes into account only the averaged configurations of the atoms, the influence of the fluctuations of the concentration of the atoms λ_m can be ignored. Below, to simplify the estimates, we shall also ignore the fluctuations in the size and shape of the complex. This is entirely justified, since the number of particles in a complex is usually large, and under the conditions in which we are interested ΔF has a sharp minimum, max $\beta|\Delta F|\gg 1$.

4. DISCUSSION OF THE RESULTS

We first consider helium under the conditions of Bartels's experiment (Ref. 8): $T=77.6$ K, $2.5\cdot 10^{21}$ cm$^{-3}\leqslant N\leqslant 7.5\cdot 10^{21}$ cm^{-3}. The experimentally known scattering length for scattering of a slow electron by a helium atom is $L_a\cong 1.16a_0$, and the polarizability of the helium atom is $\alpha_a\cong 1.39a_0^3$ (see, for example, Ref. 2). Equation (3.21) gives $R_a\cong 1.68a_0$, and the condition of applicability of the Born approximation, $R_a^2\gg\alpha_a/a_0$, can be regarded as satisfied. For the given parameters, the minimization of the free energy of the ion–medium system gives the value $\lambda_m\cong 4.8a_0$ for the optimum length of variation of the electron wave function. Thus, the condition $R_a\ll\lambda_m$ can also be assumed to be satisfied.

The calculated profiles of the local density as functions of the distance from the center of the ion are shown in Fig. 3. The radius of the cavity formed around the negative O_2^- ion in helium is approximately $9a_0$ and depends weakly on the density of the medium, completely confirming the conclusions drawn in Sec. 2 by means of the simpler model. As can be seen from Fig. 3, the increase in the density of the medium near the cavity at $T=77.6$ K is very slight and can be ignored. In this case, the exchange repulsion plays the main role and determines the cavity radius. The polarization attraction on its background is slight and can be ignored. The bubble radius is in fact determined by the radius of the hard core of the effective potential of the interaction of the negative ion with the atom of the medium.

The situation is different in helium at lower temperatures. Here, as was pointed out in Sec. 2, $\lambda_T^2\alpha_a/a_0R_2^4\geqslant 1$, and, as can be seen from Fig. 3, the increase in the density that arises near the bubble is appreciable.

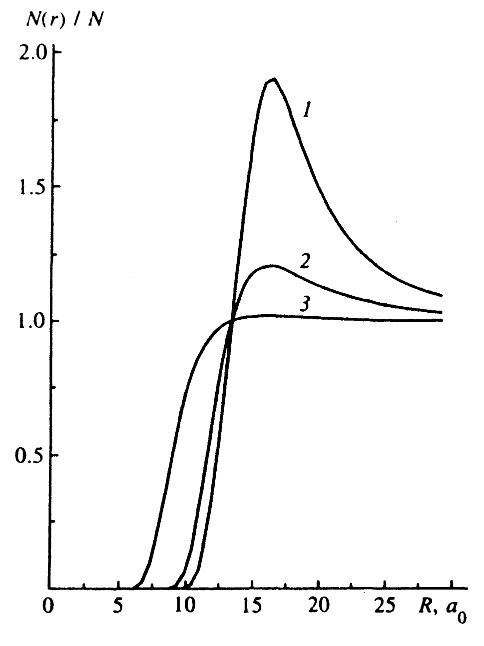

FIG. 3. Local density as a function of the distance from the center of the O_2^- ion in He constructed for a density $N=2.5\cdot10^{21}$ cm^{-3} of the medium in the unperturbed state and for different temperatures: *1*) 5, *2*) 10, *3*) 77.6 K.

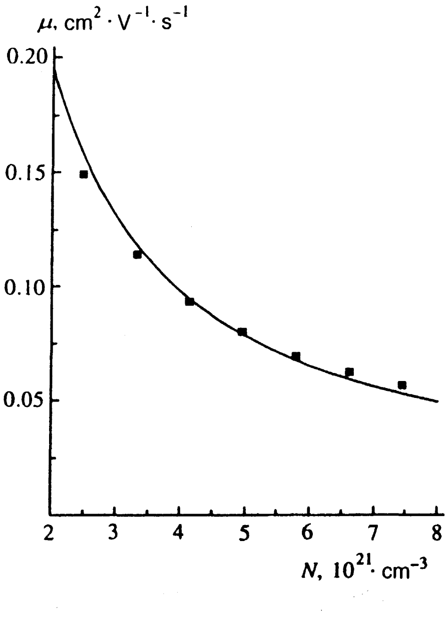

FIG. 4. Mobility of the O_2^- ion in He at $T=77.6$ K. The curve is calculated in accordance with (4.1), and the points are the experimental results of Ref. 8.

Under the conditions given above of the experiment of Ref. 8, the mean free path exceeds the cavity radius. To calculate the mobility, we can use the solution of Boltzmann's equation for a heavy particle moving in an ideal gas. The cross section for scattering of a helium atom by the cavity surrounding the negative ion is approximately $4\pi R_2^2$. In reality, in a sufficiently rarefied gas it is not particularly meaningful to speak of the formation of a cavity or bubble. However, the ion kinetics will, as before, be determined by the scattering of the atoms of the medium by the effective potential of the negative ion, which is determined above all by the value of R_2. Thus, to estimate the mobility in the so-called Knudsen regime, we use the expression[2]

$$\mu=\frac{3e}{8NR_2^2\sqrt{2\pi MT}}, \tag{4.1}$$

where M is the mass of an atom of the medium. The results of calculation in accordance with this expression are presented in Fig. 4. It can be seen that they are in good agreement with the experimental results of Ref. 8.

We now consider dense neon under the conditions of the experiment of Ref. 9: $T=45$ K, $2.5\cdot10^{21}$ cm$^{-3}\leqslant N\leqslant2.5\cdot10^{22}$ cm^{-3}. The scattering length for a slow electron scattered by a neon atom is $L_a\cong0.45a_0$, and the neon polarizability is $\alpha_a\cong2.67a_0^3$. Using (3.21), we obtained $R_a\cong1.34a_0$ and $\lambda_m\cong4.8a_0$. The results of the calculations of the profiles of the relative local density as a function of the distance from the center of the negative ion are shown in Fig. 4, in which the values of $N(r)/N$ are plotted for different densities of the medium in the unperturbed state. It can be seen from Fig. 5 that the radius of the cavity around the ion is, as before, close to $10a_0$ and is essentially independent of the density of the medium. On the other hand, the increase in the density around the cavity depends strongly on the density of the medium, this being due to the change in the nature of the interatomic correlation when N is changed. Thus, once it has reached its greatest value, the maximum of the density enhancement begins to decrease with increasing N, this being due to the sharp decrease in the compressibility of the medium. At the mostly liquid density $N\cong2.5\cdot10^{22}$ cm^{-3}, the density enhancement disappears essentially completely. Since in this range of densities the mean interatomic separation is much less than the characteristic radius of the cavity

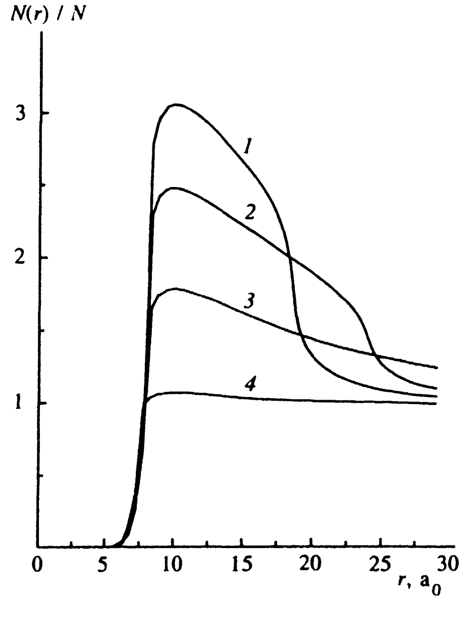

FIG. 5. Local density of Ne atoms as a function of the distance to the center of the O_2^- ion plotted for $T=45$ K and different densities of the medium in the unperturbed state: *1*) $8\cdot10^{21}$, *2*) 10^{22}, *3*) $1.4\cdot10^{22}$, *4*) $2.5\cdot10^{22}$ cm^{-3}.

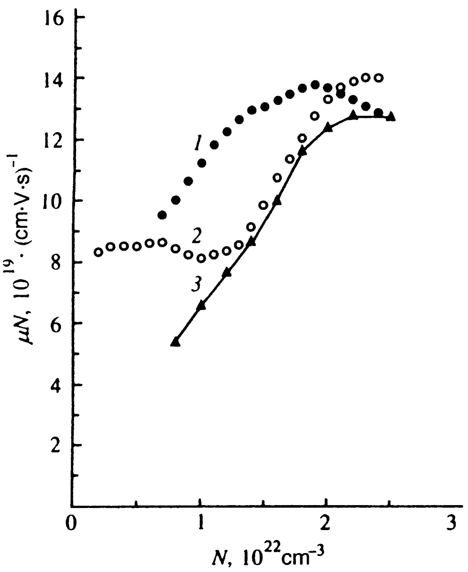

FIG. 6. Reduced mobility μN of the O_2^- ion in Ne as a function of the density of the medium: *1*) the theoretical calculations of Ref. 9; *2*) the experimental results of Ref. 9; *3*) the results of our estimates.

formed around an ion, to estimate the O_2^- mobility in neon at $T=45$ K we can use the well-known expression for the Stokes mobility:

$$\mu=\frac{e}{6\pi\eta R_i}, \tag{4.2}$$

where η is the viscosity of the medium, and R_i is the radius of the complex. As R_i in this expression, we can choose the radius of the maximum of the density profile, and as η the viscosity of the medium at this point. The result of our calculations is given in Fig. 6. We have plotted here the experimental results and the theoretical calculations of Ref. 9. It can be seen from Fig. 6 that our results are in good qualitative agreement with the experiment. More accurate calculations of the mobility require allowance for the profiles of the local density and viscosity in the solution of the Navier–Stokes equation.

Thus, we have shown that the competition between the polarization attraction and the exchange repulsion leads to the formation around the negative O_2^- ion of a complicated complex in the form of a cavity surrounded by a denser layer. In a rarefied gas at sufficiently high temperatures and in a liquid the density enhancement is rather small, and for estimates one can use the model of an empty bubble with rectangular potential walls. In the general case, it is necessary to use the self-consistent field method. The dependence of the cavity radius and the structure of the denser layer on the temperature and density of the medium have made it possible to explain the anomalous behavior of the mobility of the O_2^- ion in helium and neon.

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