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Multiple-scattering theory of excess electrons in simple fluids

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A formalism is developed to study the dependence on the density n of the conduction-band energy minimum $V_0(n)$ (relative to vacuum) of excess electrons in simple fluids in the framework of the multiple-scattering theory. Focusing our attention on the low-density expansion of $V_0(n)$, it is suggested that V_0 is not an analytic function of n because of the contribution of infinitely remote atoms of the fluid. This expansion is investigated within the random-phase approximation (RPA). In its simplest form, the RPA treatment predicts an analytic behavior generalizing Fermi's linear law. Taking the case of excess electrons in fluid argon as an example, we calculate the term of order n^2, which appears to be due to excluded-volume effects and is very sensitive to the temperature and the interatomic potential. The inclusion of multiple-scattering effects is investigated through a higher-order RPA treatment, which is shown to present the same nonanalytic behavior of $V_0(n)$ as the "exact" result. In order to explore this behavior experimentally, it is proposed that accurate $V_0(n)$ measurements be performed at very low fluid densities along isotherms.

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I. INTRODUCTION

Studies of the properties of excess electrons in a variety of insulating fluids have been under way for many years [1]. Recently, a great deal of effort has been devoted to this subject from a numerical point of view, especially in simple fluids, such as, for example, heavy rare gases (argon, krypton, and xenon) and simple hydrocarbons (methane) [2,3]. One important feature of excess electrons in these simple fluids is the variation of the conduction-band energy minimum V_0 (relative to vacuum) with density n. As the fluid goes from the gas phase to the liquid near the triple point, $V_0(n)$ is found to exhibit a minimum at a density that approximately coincides with the density at which one observes a maximum of the electron mobility [1]. The only exact result, established by Fermi [4], concerns the limiting behavior of V_0 at very low densities and is expressed, in atomic units, as

$$V_0(n)=2\pi a n \ , \tag{1}$$

where a is the electron scattering length for a single atom of the fluid.

Fermi's limiting law [Eq. (1)] has been consistently used at low densities to interpret experimental results of the shift of the vertical ionization potential of a molecular impurity doped into a number of nonpolar gases as a function of the host density [5–7]. As shown in a recent investigation performed in low-density argon doped with CH_3I, this law, when extrapolated to higher densities, accounts for a remarkable fraction of the measured V_0 value even at densities close to the critical point [5]. Moreover, in Ref. [2], it has been proven, using path-integral molecular-dynamics simulations of the electron-argon system, that V_0 is only weakly sensitive to the structure and the coordination number of the fluid. Such observations suggest that including structure and multiple-scattering effects to the lowest order in density in addition to Fermi's leading contribution could provide a good estimate of the overall conduction-band energy curve and eventually afford an explanation of the existence of the V_0 minimum in the liquid region near the critical point.

This paper is organized as follows. In Sec. II we present a theory of $V_0(n)$ that is an extension of Fermi's formula to all fluid densities and is based on the multiple-scattering theory of Foldy [8] and Lax [9]. The result is a hierarchy of equations that cannot be solved in a closed form. Section III describes a random-phase approximation (RPA) that allows for an asymptotic expansion of $V_0(n)$ at low fluid densities. Taking the case of an excess electron in fluid argon as an example, we show in Sec. IV that, within the single-scattering approximation, the departure from the ideal gas structure is responsible for a correction of V_0 that is quadratic in n. In contrast, Sec. V suggests that, for an ideal gas, the departure from the single-scattering approximation gives rise to a nonanalytic correction to $V_0(n)$. A conclusion is given in Sec. VI. We use atomic units in this paper unless otherwise specified.

II. MULTIPLE-SCATTERING THEORY

We consider a monatomic fluid composed of a very large number of atoms (N) with coordinates $\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_N$, in a volume Ω, with density $n=N/\Omega$. An excess electron at the bottom of the fluid's conduction band is characterized by an extended (percolating) state Ψ and the (lowest) energy V_0 (relative to vacuum), such that

$$\left\{\frac{\mathbf{p}^2}{2}+\sum_{i=1}^{N} V(|\mathbf{r}-\mathbf{R}_i|)\right\}\Psi(\mathbf{r})=V_0\Psi(\mathbf{r}) , \tag{2}$$

where $\mathbf{p}$ is the conjugate momentum to the position of the electron $\mathbf{r}$ and V is the potential describing the electron's interaction with a single fluid atom. In relation to large disordered systems [10], we make the central assumption that V_0 is a self-averaged quantity in the same way as, for example, the electronic density of states. It is then appropriate to carry out the average of Eq. (2) over all fluid configurations. Since Ψ is an extended state, its average value is a nonvanishing constant and it is convenient to set this value equal to one. Under these conditions, the average kinetic-energy term vanishes and we get

$$V_0(n)=n\int_{\Omega} d\mathbf{r}\, V(r)\Psi_1(r) , \tag{3}$$

where Ψ_1 is the configuration average of Ψ keeping one atom at the origin. It is easy to show that Ψ_1 obeys the inhomogeneous equation

$$\left\{\frac{p^2}{2}+V(r)\right\}\Psi_1(r)+n\int_{\Omega} d\mathbf{R}\, g_2 V(|\mathbf{r}-\mathbf{R}|)\Psi_2(\mathbf{r},\mathbf{R}) = V_0\Psi_1(r) , \tag{4}$$

where g_2 is the pair distribution function of the fluid and Ψ_2 is the configuration average of Ψ keeping one atom at the origin and a second atom at $\mathbf{R}$.

Equation (4) is the first of a hierarchy of equations that relate configuration averages of Ψ with P and $P+1$ atoms in fixed positions (Ψ_P and Ψ_{P+1}, respectively), namely,

$$\left\{\frac{\mathbf{p}^2}{2}+\sum_{i=1}^{P} V(|\mathbf{r}-\mathbf{R}_i|)\right\}\Psi_P(\mathbf{r}) +n\int_{\Omega} d\mathbf{R}_{P+1} g_{P+1} V(|\mathbf{r}-\mathbf{R}_{P+1}|)\Psi_{P+1}(\mathbf{r}) = V_0\Psi_P(\mathbf{r}) , \tag{5}$$

where g_{P+1} is the distribution function of the atom $P+1$ when atoms $1,\ldots,P$ are kept fixed. This hierarchy of equations is familiar in multiple-scattering theory, but here the emphasis is put on the determination of V_0. Because of the simple way by which the density enters Eqs. (3)–(5), it seems natural to consider the inhomogeneous terms as perturbations and consequently develop an asymptotic density expansion of V_0 about $n=0$. This could be done, for instance, by assuming a power-series expansion for V_0 and the Ψ_P ($P=1,2,\ldots$) configuration averages and by identifying the coefficients of the same power in n. In order to obtain Ψ_1 to order P in n, it would be sufficient to truncate the hierarchy at the same level P, that is, to neglect the influence of the fluid in Eq. (5) so that Ψ_P would have to be known only to zeroth order in n and be given by

$$\left\{\frac{\mathbf{p}^2}{2}+\sum_{i=1}^{P} V(|\mathbf{r}-\mathbf{R}_i|)\right\}\Psi_P(\mathbf{r})=0 . \tag{6}$$

However, a closer look at the iterative equations would show that this procedure is incorrect, because the terms in the expansion of Ψ_1 would be secular and increasingly divergent as $r\rightarrow\infty$ with increasing order. This behavior, in turn, is symptomatic of a singular perturbation problem [11] and, consequently, of the nonanalytic character of V_0 at low densities.

The correct perturbative treatment of the complete hierarchy is a formidable task that we do not intend to undertake in this work. Instead, we present in the following sections a RPA treatment of this system of equations, which presents a similar singularity at low densities. The resulting expansion is thus expected to share the same analytical properties as the exact solution to the hierarchy and eventually very similar values for the coefficients of the expansion. In particular, we will show that fluid-structure effects lead to an analytic perturbation series, while the correction due to multiple scattering is not analytic.

III. RANDOM-PHASE APPROXIMATION

The RPA is a low-density approximation appropriate to the perturbative treatment we are seeking. In its simplest form, the RPA two-center wave function $\Psi_2(1,2)$ is approximated by

$$\Psi_2(1,2)=\Psi_1(1)\Psi_1(2) , \tag{7}$$

where the numbers 1 and 2 in parentheses refer to the coordinates $\mathbf{R}_1$ and $\mathbf{R}_2$ of the atoms 1 and 2, respectively, while the subscripts refer to the number of centers considered. For clarity of presentation, this simplified notation will be used in the following. It must be noted that Eq. (7) is exact when atoms are infinitely remote.

Before studying this first-order random-phase approximation (RPA1), we describe the next level of approximation (RPA2), which we will consider below. We first introduce a correction to Eq. (7), namely,

$$\begin{aligned}\Psi_2(1,2)&=\Psi_1(1)\Psi_1(2)+\delta\Psi_2(1,2)\\ &=\Psi_1(1)\Psi_1(2)\{1+\varphi(1,2)\} ,\end{aligned} \tag{8}$$

and then apply the RPA to the three-center wave function

$$\Psi_3(1,2,3)=\Psi_1(1)\Psi_1(2)\Psi_1(3) \times\{1+\varphi(1,2)+\varphi(1,3)+\varphi(2,3)\} . \tag{9}$$

Substituting Eqs. (3) and (8) into Eq. (4) gives

$$H_1(1)\Psi_1(1)=n\Psi_1(1)\int_{\Omega} d2(1-g_2)V(2)\Psi_1(2) -n\int_{\Omega} d2\, g_2 V(2)\delta\Psi_2(1,2) , \tag{10}$$

where it is seen that the inhomogeneous term consists of two very distinct contributions. The first one is called the "excluded-volume" term because it vanishes for an ideal gas ($g_2=1$). The second one is the multiple-scattering term, which goes beyond the RPA1 of Eq. (7).

Neglecting both terms on the right-hand side in Eq. (10) corresponds to the single-scattering approximation, which leads to the Fermi relation of Eq. (1). For the purpose of the following discussion, we introduce the corresponding solution Ψ_0 defined by

$$H_1(1)\Psi_0(1)=0\ , \tag{11}$$

which is related to the scattering length a by the relation

$$a=2\int V(r)\Psi_0(r)r^2dr\ . \tag{12}$$

Fermi's result can then be deduced by a comparison of Eqs. (3) and (12).

The second equation of the hierarchy of Eq. (5) gives Ψ_2, according to

$$\left\{\frac{p^2}{2}+V(1)+V(2)\right\}\Psi_2(1,2) \\ +n\int_\Omega d3\,g_3V(3)\Psi_3(1,2,3)=V_0\Psi_2(1,2)\ , \tag{13}$$

and terminates the hierarchy. Substituting Eqs. (3) and (9) into Eq. (13) yields

$$\begin{aligned}H_2(1,2)\Psi_2(1,2)=&\,n\Psi_2(1,2)\int_\Omega d3(1-g_3)V(3)\Psi_1(3)\\ &-n\Psi_1(1)\int_\Omega d3\,g_3V(3)\delta\Psi_2(2,3)\\ &-n\Psi_1(2)\int_\Omega d3\,g_3V(3)\delta\Psi_2(1,3)\ ,\end{aligned} \tag{14}$$

where again the inhomogeneous term is seen to consist of contributions from both excluded-volume and multiple-scattering terms.

The system of Eqs. (10) and (14) is very difficult to solve, partly because of the appearance of the unknown distribution functions g_2 and g_3. This situation is not much improved by using the Kirkwood superposition approximation [12] to connect these two distributions. More simplifications are therefore needed in order to proceed further.

IV. FIRST-ORDER RPA

In this approximation (RPA1), Eq. (10) reduces to

$$H_1(1)\Psi_1(1)=n\Psi_1(1)\int_\Omega d2(1-g_2)V(2)\Psi_1(2)\ , \tag{15}$$

which is a nonlinear, integro-differential equation for Ψ_1. We have already presented, in the preceding section, the solution (Ψ_0) of Eq. (11), which corresponds to the simple case of an ideal fluid ($g_2=1$). Since we are interested in the limit of low fluid densities (that is, when $n\rightarrow 0$), it is legitimate to take g_2 as [12]

$$g_2(R)\approx e^{-\beta U(R)}\ , \tag{16}$$

where $\beta=1/(k_BT)$, k_B is Boltzmann's constant, T is the temperature, and U is the interatomic potential. Equations (15) and (16) readily show the importance of the temperature on Ψ_1 and hence on V_0.

Let us assume the density expansion

$$\Psi_1=\Psi_0+n\delta\Psi_1+\cdots\ . \tag{17}$$

Then, substituting Eq. (17) into Eq. (14) and retaining terms to first order in n, we get

$$H_1(1)\delta\Psi_1(1)=\Psi_0(1)\int_\Omega d2(1-g_2)V(2)\Psi_0(2)\ . \tag{18}$$

In contrast to Eq. (15), Eq. (18) is now an ordinary differential equation for $\delta\Psi_1$.

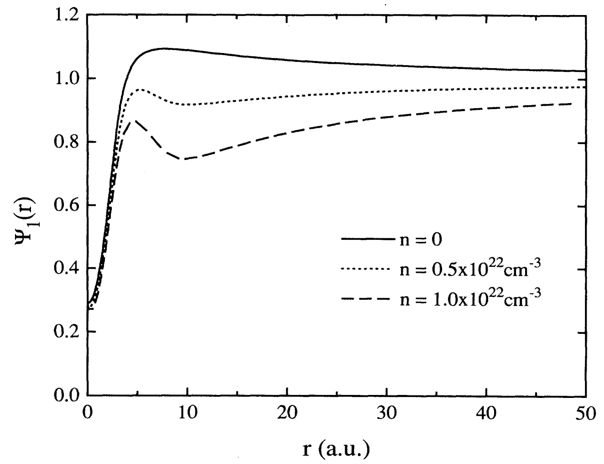

FIG. 1. Plot of the averaged electron wave function $\Psi_1(r)$ in the hard-sphere fluid model, calculated from Eqs. (17) and (18) for three fluid argon densities, namely, $n=0$, 0.5×10^{22}, and 10^{22} cm^{-3}. For $n=0$, $\Psi_1(r)$ reduces to $\Psi_0(r)$, which corresponds to the solution of Eq. (11) for the simple case of an ideal fluid.

We now consider, as an example, the case of an excess electron injected in fluid argon. To represent the electron-argon interaction, we use the pseudopotential $V(r)$ of Li, Broughton, and Allen [13], which has been successfully used in the path-integral molecular-dynamics $V_0(n)$ calculations of Ref. [2]. $\Psi_0(r)$ is shown in Fig. 1 and the corresponding electron scattering length, calculated from Eq. (12), is $a=-1.428$ a.u., in good agreement with experimental results [14]. Two fluid models, namely, the hard-sphere model (HSM) and the Lennard-Jones model (LJM), are successively examined below.

A. Hard-sphere model

In the HSM, the low-density pair distribution function is given by

$$g_2(R)=\begin{cases}0 & \text{if } R<\sigma\\ 1 & \text{if } R>\sigma\ ,\end{cases} \tag{19}$$

where σ is the hard-sphere diameter ($\sigma=6.437$ a.u. for argon [2]). Figure 1 shows the first-order averaged wave function $\Psi_1(r)$ calculated from Eqs. (17) and (18) for three fluid argon density values ranging from $n=0$ [in this limit, $\Psi_1(r)$ reduces to $\Psi_0(r)$] to the liquid near the critical point. Substituting Eq. (17) into Eq. (3) and using Eq. (12), we derive the V_0 expansion

$$V_0(n)=2\pi na+bn^2+\cdots\ , \tag{20}$$

where b is independent of temperature in the present case and is expressed from the solution $\delta\Psi_1$ of Eq. (18) by

$$b=4\pi\int_0^\infty V(r)\delta\Psi_1(r)r^2dr\ . \tag{21}$$

Using the pseudopotential $V(r)$ of Li, Broughton, and Allen [13] in Eq. (21) yields the value $b=956$ a.u. To appreciate the scope of this result, it is instructive to compare the $V_0(n)$ expansion of Eq. (20) with the experimentally measured values of V_0. Before doing that, however, we must bear in mind that the whole procedure presented here assumes a density-independent pair potential to describe the electron-fluid interaction. In Ref. [2], it has been shown that the many-body screening of the long-range electron-atom polarization potential plays an important role in accounting for a large fraction of the total $V_0(n)$ curve in the argon system. The correction $\delta V_0(n)$ to the "unscreened" V_0 values can be calculated analytically as [2]

$$\delta V_0(n)\approx 2\pi n\alpha(1-f_\infty)/r_{\rm WS}\ , \tag{22}$$

where α is the atomic polarizability ($\alpha=10.56$ a.u. for argon [13]), $r_{\rm WS}$ is the Wigner-Seitz radius defined by

$$\frac{4\pi}{3}r_{\rm WS}^3=\frac{1}{n}\ , \tag{23}$$

and f_∞ is the Lorentz screening factor at infinite electron-atom separation

$$f_\infty=\left[1+\frac{8\pi n\alpha}{3}\right]^{-1}\ . \tag{24}$$

Combining Eqs. (22) and (20) thus gives

$$V_0(n)\approx 2\pi na+bn^2+[2\pi n\alpha(1-f_\infty)/r_{\rm WS}]\ . \tag{25}$$

Note that, in contrast to Eq. (20), Eq. (25) is no longer an exact asymptotic expansion, but only gives an approximate analytical expression for $V_0(n)$. A plot of $V_0(n)$, calculated from Eq. (25), is presented as the solid line in Fig. 2, along with experimental data [5,15] and with the $V_0(n)$ simulation results of Ref. [2]. As we can see, the agreement is remarkable within the whole range of densities up to the triple point. Considering that these results have not been fit to experiment in any way, such an agreement suggests that Eq. (25) contains most of the physical factors intervening in the determination of V_0. However, the reason for Eq. (25) to be all that accurate over a large density range is not clear at present and further analysis is necessary to investigate the roots of its success.

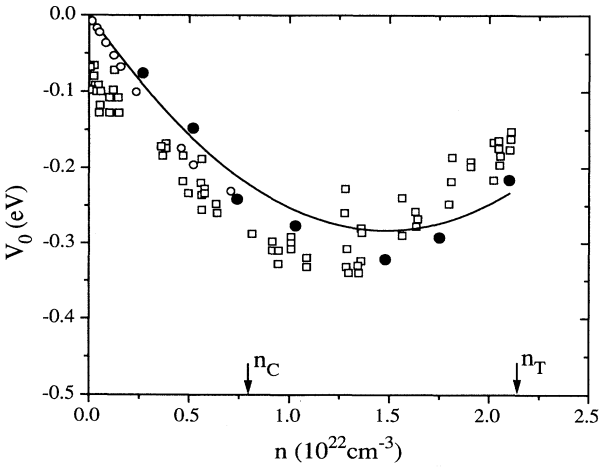

FIG. 2. Comparison of the present results of $V_0(n)$ calculated from Eq. (25) (solid line) with the experimental data of Ref. [5] (open circles) and Ref. [15] (open squares). Also shown are the results of path-integral molecular-dynamics calculations of Ref. [2] (solid circles). The densities of argon at the critical and triple points are $n_C=0.80\times10^{22}$ cm^{-3} (150.7 K) and $n_T=2.13\times10^{22}$ cm^{-3} (83.8 K) [16].

At this point, it is interesting to mention a previous calculation of the coefficient b of the n^2 term in Eq. (25) due to Foldy and Walecka [17]. Using an optical-potential approximation, these authors obtained the analytical expression $b_{\rm FW}=(2\pi a\sigma)^2$, which yields, for argon, $b_{\rm FW}=3335$ a.u. (instead of our value $b=956$ a.u.). Clearly, $b_{\rm FW}$ overestimates the curvature of the $V_0(n)$ curve observed experimentally.

B. Lennard-Jones model

In the LJM, the interatomic potential is given by

$$U(R)=4\varepsilon\left[\left[\frac{\sigma}{R}\right]^{12}-\left[\frac{\sigma}{R}\right]^{6}\right]\ , \tag{26}$$

where, for argon, $\varepsilon=3.796\times10^{-4}$ a.u. (that is, $\varepsilon/k_B=119.8$ K) [2] and σ has the same value as in the HSM.

The pair distribution function g_2 is now dependent on the temperature and so are the density expansions of Ψ_1 and $V_0(n)$. We thus reexpress Eqs. (17) and (25) as

$$\Psi_1=\Psi_0+n\delta\Psi_1(T)+\cdots \tag{27}$$

and

$$V_0(n)=2\pi na+b(T)n^2+[2\pi n\alpha(1-f_\infty)/r_{\rm WS}]\ . \tag{28}$$

Figure 3 shows the first-order derivative function $\delta\Psi_1(r)$ calculated from Eq. (18) at three different values of T for the LJM, along with the corresponding function for the HSM. As we can see, the $\delta\Psi_1$ perturbation of the LJM is generally more important than that of the HSM and is progressively closer to this latter as the temperature increases.

Table I presents values of b for a set of selected temperatures ranging from 50 to 1000 K. It is seen that b is strongly dependent on the temperature since even its sign may change with T. As noted above for $\delta\Psi_1(T)$, the coefficient $b(T)$ of the LJM approaches that of the HSM as T increases. In contrast to what we did for Eq. (25), here it is not worth plotting Eq. (28) in order to compare $V_0(n)$ against experimental data. In fact, the HSM is clearly closer to the experimental data than the LJM (with $\varepsilon/k_B=119.8$ K). This result may appear somewhat surprising since one expects the Lennard-Jones potential to provide a more realistic description of the fluid than the hard-sphere potential. There is an argument, however, in favor of the HSM, based upon the fact that the ex-

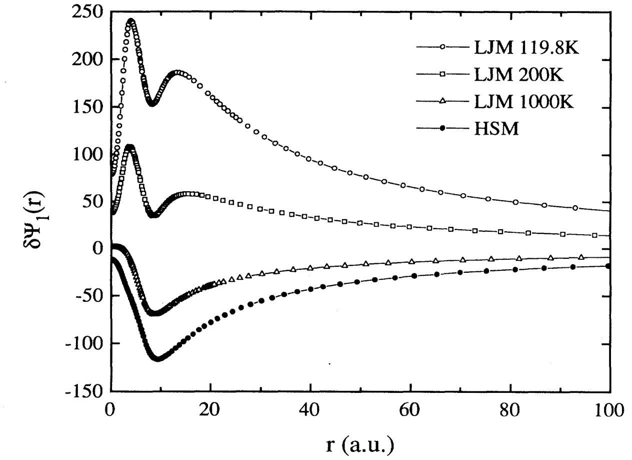

FIG. 3. Plot of the first-order derivative function $\delta\Psi_1(r)$ calculated from Eq. (18) at three different temperatures (namely, 119.8, 200, and 1000 K) for the Lennard-Jones fluid model (LJM), along with the corresponding function for the hard-sphere fluid model (HSM).

perimental $V_0(n)$ data shown in Fig. 2 correspond to measurements performed along the liquid-vapor coexistence line rather than along isotherms. Under these conditions, one can in fact observe [2] that the function g_2 calculated from Eq. (16) for the HSM gives a better description of the low-density pair distribution function of the fluid than that calculated for the LJM, even if the interatomic potential is not as good. Clearly, Eq. (28) is not appropriate to make comparisons with existing experimental data, but the strong sensitivity of b with respect to temperature is an incentive to carry out $V_0(n)$ measurements along isotherms.

V. SECOND-ORDER RPA

The preceding section was devoted to the investigation of fluid structure on the low-density dependence of $V_0(n)$, neglecting multiple-scattering effects. Here we make the opposite assumptions, that is, we neglect fluid-structure effects and concentrate on multiple scattering. In this approximation (RPA2), we have $g_2=g_3=1$ and hence Eqs. (10) and (14) simplify to

$$H_1(1)\Psi_1(1)=-n\int_\Omega d2\,V(2)\delta\Psi_2(1,2) \tag{29}$$

and

$$\begin{aligned}H_2(1,2)\Psi_2(1,2)=&-n\Psi_1(1)\int_\Omega d3\,V(3)\delta\Psi_2(2,3)\\&-n\Psi_1(2)\int_\Omega d3\,V(3)\delta\Psi_2(1,3)\ .\end{aligned} \tag{30}$$

Comparing the right-hand sides of Eqs. (29) and (30), Eq. (30) can be rewritten in the form

$$H_2(1,2)\Psi_2(1,2)=\Psi_1(1)H_1(2)\Psi_1(2)+\Psi_1(2)H_1(1)\Psi_1(1)\ . \tag{31}$$

Upon substituting Eq. (8) into Eq. (31) and grouping with Eq. (29), we then get the system of equations

$$H_1(1)\Psi_1(1)=-n\int_\Omega d2\,V(2)\delta\Psi_2(1,2)\ , \tag{32a}$$

$$H_2(1,2)\delta\Psi_2(1,2)=-\mathbf{p}\Psi_1(1)\cdot\mathbf{p}\Psi_1(2)\ , \tag{32b}$$

with the boundary conditions $\Psi_1\rightarrow 1$ and $\delta\Psi_2\rightarrow 0$ when $r\rightarrow\infty$.

In the remainder of this section, we will be concerned with the asymptotic analysis of Eqs. (32a) and (32b) as $n\rightarrow 0$. For the sake of simplicity of the foregoing mathematical development, we will assume that the electron-atom potential $V(r)$ is truncated, that is, vanishes after some cutoff radius, which may be chosen arbitrarily large. Under this assumption, our asymptotic analysis will remain essentially the same provided that the "real" interaction potential falls off sufficiently rapidly with r. This is the case for the present polarization potential, which decays as r^{-4} [2,13], but would not be the case for a dipolar interaction.

Before proceeding with the analysis, it is interesting to note that the actual RPA2 system of equations exhibits the same mathematical singularity as the complete hierarchy of Eq. (5). To see that Eqs. (32a) and (32b) represent a singular perturbation problem, let us consider an iterative construction of the solution $\delta\Psi_2$. We start with the estimate $\Psi_1=\Psi_0$, which we substitute into Eq. (32b). As $R\rightarrow\infty$, in the neighborhood of atom 2, Eq. (32b) may be rewritten as

$$H_1(2)\delta\Psi_2(1,2)=\Psi_0'(1)\Psi_0'(2)\cos(\theta_{12})\ , \tag{33}$$

where θ_{12} is the angle between the vectors $\mathbf{r}$ and $\mathbf{r}-\mathbf{R}$ and $\Psi_0'(1)$ is of the order of $1/R^2$ so that $\delta\Psi_2$ is also of order $1/R^2$. Looking now at Eq. (32a) when $r\rightarrow\infty$, we see that the only contribution to the integral on the right-hand side comes from atoms in the neighborhood of r [we recall that the potential $V(r)$ is of finite range], that is, from atoms with $R\rightarrow\infty$. This implies that the integral itself behaves as $1/r^2$. As a consequence, the next estimate of Ψ_1 behaves as $\ln(r)$, which is actually a secular behavior (grows with increasing r). It is not difficult to see, by the same kind of argument, that the next iteration will give rise to secular terms of order $r\ln(r)$ and that the situation will get worse as we continue the iterative procedure. Clearly, this behavior is similar to that presented by the complete hierarchy of Eq. (5) and indi-

TABLE I. Variation of the coefficient b (in a.u.) of the n^2 term in the density expansion of $V_0(n)$ for fluid argon at selected temperatures, within the RPA1 [Eqs. (25) and (28)]. The results concern the Lennard-Jones (LJM) and hard-sphere (HSM) fluid models.

	LJM						HSM
T (K)	50	119.8	200	300	400	1000	
$b(T)$	−4466	−509.4	141.2	417.1	538.2	728.7	956.0

cates that the correct asymptotic expansion of $V_0(n)$ in the present RPA2 will certainly be of the same nature as that of the "exact" problem.

To pursue now with the correct perturbative analysis of Eqs. (32a) and (32b), we use the boundary-layer theory [11]. From the previous analysis, we know that there is a boundary layer at $r=\infty$. As a first step, let us concentrate on the inner solution by looking at the asymptotic behavior of Eqs. (32a) and (32b) as $r \rightarrow \infty$. By analogy with the above analysis, when $R \rightarrow \infty$, we have

$$\delta\Psi_2(1,2) \approx \Psi_1'(R)\chi(2) , \tag{34}$$

where we have introduced the function χ defined by

$$H_1(2)\chi(1,2) = \Psi_0'(2)\cos(\theta_{12}) . \tag{35}$$

Substituting Eq. (34) into Eq. (32a) gives, when $r \rightarrow \infty$,

$$p^2\Psi_1 \approx n\lambda\Psi_1' , \tag{36}$$

where λ is given by

$$\lambda = -2\int d2\, V(2)\chi . \tag{37}$$

With the restriction that $\lambda > 0$, the solution of Eq. (36) that satisfies the boundary condition $\Psi_1(\infty)=1$ is

$$\Psi_1 \approx 1 + C\int_\infty^r dr' \frac{1}{r'^2} e^{-n\lambda r'} , \tag{38}$$

where C is a constant of interaction to be determined later by asymptotic matching. The remarkable point about Eq. (38) is the exponential behavior of the electron wave function, which contrasts with the usual $1/r$ behavior of a single atom scattering wave function. The effect of the fluid is thus to destroy the long-range correlation of the electron wave function. It is clear that, far from the central atom, the behavior of the wave function must be entirely determined by the surrounding fluid, whatever the density. The type of exponential decay found here for $\Psi_1(r)$ is obviously due to the introduction of a cutoff radius in $V(r)$; it would be different (a power law, in fact) for the real polarization potential, but our conclusions would remain essentially the same.

As a second step, we examine the outer solution. Near the origin, at zero density, this solution is

$$\Psi_1 \approx \Psi_0 . \tag{39}$$

Finally, by matching the inner and outer solutions of Eqs. (38) and (39) in the limiting conditions $r \rightarrow \infty$, $nr \rightarrow 0$, and $n \rightarrow 0$, we obtain $C = a$ (the scattering length) and hence the uniform asymptotic approximation to $\Psi_1(r)$

$$\Psi_1 = \Psi_0 + a\int_\infty^r dr' \frac{1}{r'^2}(e^{-n\lambda r'} - 1) . \tag{40}$$

Unfortunately, this approximation is only of zeroth order in n, the error being of order $n\ln(n)$, and introduces an artificial $r\ln(r)$ behavior near the origin. Going beyond this approximation is considerably more difficult. At this time, the result may only be "guessed," giving an asymptotic expansion to $V_0(n)$ that is likely of the form $n^2\ln(n)$. We should note here that the existence of logarithmic terms has already been predicted in the low-density expansions for the mobility of excess electrons in helium gas [18] and for the ground-state energies of many-boson and many-fermion interacting systems of hard spheres [19]. This result is important because it suggests that multiple scattering gives rise to a nonanalytic expansion of $V_0(n)$ at very low fluid densities, which would dominate over excluded-volume effects (we recall that the latter are of order n^2 only).

VI. CONCLUSION

In this paper, we have developed a general formalism to study the density dependence of the conduction-band energy minimum $V_0(n)$ of excess electrons in simple fluids within the framework of the multiple-scattering theory. This theory only assumes a density-independent pair potential to describe the electron-fluid interaction. The complete treatment of the problem is extremely difficult and it has been shown that a random-phase approximation may be useful to study the asymptotic behavior of $V_0(n)$ at low fluid densities. In its simplest form, the RPA1 treatment has been remarkably successful in the description of the experimental $V_0(n)$ data in fluid argon, although its reliability rests on the evaluation of the importance of multiple-scattering effects. We have presented arguments indicating that these effects enter through nonanalytic terms in the density expansion of $V_0(n)$ about $n=0$. This point still remains to be investigated in more detail. As a preliminary remark on that point, let us note the following peculiarity presented by argon. In fact, we have stressed that, for the argon system, Fermi's linear law remarkably describes the variation of $V_0(n)$ in a wide range of densities. This is note the case, however, for many other fluids (for example, this is particularly untrue for the case of xenon). We have noted that the dimensionless parameter controlling V_0 is given by na^3 and is indeed very different in argon and xenon [20]. This distinct behavior, which illustrates the strength of the electron-atom potential, should be accounted for by inclusion of multiple-scattering effects, but in that case, we have also shown, through a higher-order RPA treatment (RPA2), that a nonanalytic correction to $V_0(n)$ is then expected.

Recently, Meyer and Reininger [5] have reported accurate data for V_0 from the shift of the vertical ionization potential of a molecular impurity (CH_3I) doped into fluid argon. This experimental accuracy, however, does not seem sufficient to convincingly analyze the low-density $V_0(n)$ data in the spirit of the present work. Moreover, the question of the analyticity of V_0 at low fluid densities must be addressed by means of measurements performed along isotherms rather than along the liquid-vapor coexistence line. It is our opinion that such measurements would be very useful for providing significant information on the electron-atom interaction, as well as on the interatomic potential through the pair distribution function. In particular, the strong sensitivity of the n^2 term in the low-density expansion of $V_0(n)$ with respect to temperature should allow for an easy experimental observation.

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