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Density dependence of the conduction-band energy V_0 of excess electrons in fluid xenon

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The ground-state energy V_0 (relative to vacuum) of quasifree excess electrons in fluid xenon is calculated as a function of fluid density n. The calculations are performed within the framework of the Wigner-Seitz mean-field approximation for nonpolar fluids, using an accurate atomic pseudopotential to model the excess electron-xenon interaction. The calculated values of $V_0(n)$ are compared to experimental data and with other theoretical results.

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The study of the behavior of excess electrons injected into dielectric nonpolar fluids has recently received renewed attention, not only from a fundamental point of view but also with respect to the increasing development of liquid devices in a number of areas such as, for example, electrical insulation, pulsed-power technology, nuclear radiation spectroscopy, calorimetry, photochemistry, and radiation chemistry [1]. An important quantity for characterizing quasifree electron states in condensed systems is the conduction-band minimum energy V_0 (relative to the energy of an electron in vacuum) of injected particles. A great deal of work has been done during the past few years toward describing the evolution of electron energy bands in simple insulating classical fluids, such as argon, krypton, xenon, etc., as a function of fluid density n. In particular, the variation of $V_0(n)$ in rare-gas systems has been studied by means of various theoretical approaches, including the semiclassical percolation model [2], the path-integral Monte Carlo or molecular-dynamics simulation methods [3–5], the vacancy model [6], the reference-interaction-site model (RISM)-polaron theory [7], and the cellular polarizable fluid model [8]. In our previous papers, we calculated the density dependence of V_0 for quasifree excess electrons in the rare-gas fluids argon, krypton, helium, and neon [3,9], as well as in the molecular fluids methane and silane [10], by employing the Wigner-Seitz (WS) mean-field approximation for nonpolar fluids. In all cases studied, our results were found to reproduce very well the available experimental $V_0(n)$ data at all densities, including the solid phase.

In the present paper, we complete our work on fluid rare gases by extending our $V_0(n)$ WS calculations to the case of excess electrons in fluid xenon. The calculations have been carried out using an accurate atomic pseudopotential $V(r)$ similar to that previously developed by us [11] to study the elastic scattering of low-energy (0–20-eV) electrons from rare-gas atoms. Details of the construction of $V(r)$ can be found in Ref. [11]. For the case of the electron-xenon scattering system, the atomic polarizability and the first ionization potential of xenon, parameters that are involved in the calculation of the pseudopotential, are taken to be $\alpha = 4.5 \times 10^{-40}$ C m^2/V and $V_{\text{ion}} = 12.13$ eV, respectively [12]. The other two adjustable parameters intervening in the exchange potential part of $V(r)$, κ and λ, are chosen to give the best agreement between calculated and experimental elastic electron scattering cross sections [11]. For xenon, the values $\kappa = 1.55$ and $\lambda = 2.8$ (in atomic units, as in Ref. [11]) have been adopted in the present calculations, which yield a zero-energy electron scattering length of -0.329 nm, in very good agreement with the experimental value (-0.324 nm) determined by Steinberger *et al.* [13,14].

In the WS model [15] of a nonpolar fluid, each atom in the fluid is replaced by an equivalent atomic sphere of radius r_{WS}, given by

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

and the fluid structure is approximated by an average lattice structure with translational symmetry. In the sphere, the short-range excess electron-atom interaction is described by the atomic potential. The effect of the fluid mainly occurs through the many-body screening of the long-range excess electron-atom polarization interactions. The potential is assumed to be spherically symmetrical about any given atom, which, when combined with the average translational symmetry condition, amounts to neglecting fluctuations in the fluid and considering an ensemble-average potential acting on the excess electron [15,16]. This approximation for the fluid structure has recently been shown by Lopez-Castillo *et al.* [3] to be well suited for the calculation of $V_0(n)$ in simple fluids. In fact, using path-integral molecular-dynamics (PIMD) simulations, these authors demonstrated, for the case of the electron-argon system, that V_0 is only weakly sensitive to the actual fluid structure and to the changes of the coordination number with changing density in the fluid [3], as is done in WS-type mean-field calculations.

The total potential $U_{\text{WS}}(r)$ seen by the excess electron at a point $\mathbf{r}$ in the WS sphere can be expressed as the sum of $V(r)$ due to the atom at the origin ($\mathbf{r}=0$) and of the mean potential produced by the atoms lying outside the sphere [9,10],

$$U_{\text{WS}}(r) = V(r) + n \int V(|\mathbf{r}-\mathbf{r}'|) F(|\mathbf{r}-\mathbf{r}'|) g(r') d\mathbf{r}'. \tag{2}$$

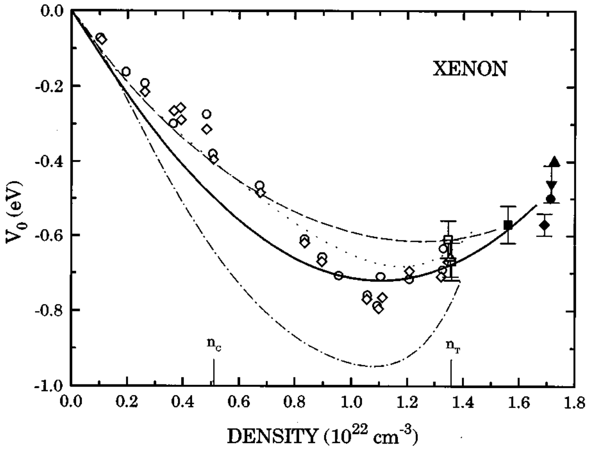

FIG. 1. Conduction-band minimum energy V_0 (relative to vacuum) of quasifree excess electrons in xenon as a function of fluid density n. Theoretical results: —, this work; · · · · ·, Ref. [2]; − − − −, Ref. [6]; —·—·—, Ref. [8]. Experimental results: ○, ◇, Ref. [20]; □, Ref. [21]; △, ■, Ref. [22]; ◆, Ref. [23]; ●, Ref. [24]; ▲, Ref. [25]; ▼, Ref. [26]. Note that filled symbols refer to $V_0(n)$ data for solid xenon. The densities at the critical (289.7 K) and triple (161.4 K) points are $n_C = 0.51\times10^{22}$ cm^{-3} and $n_T = 1.36\times10^{22}$ cm^{-3} (Ref. [27]), and are indicated by the short vertical lines.

Here the screening function $F(r)$ accounts for the polarization of the surrounding atoms in the fluid due to the presence of the excess electron. Our choice of $F(r)$ is the same as that employed in Ref. [16], and is given by (in SI units)

$$F(r)=\begin{cases} 1 & r\leq r_{\mathrm{WS}} \\ \left(1+\dfrac{2\alpha n}{3\varepsilon_0}\right)^{-1}, & r>r_{\mathrm{WS}}, \end{cases} \tag{3}$$

where ε_0 is the permittivity of the vacuum. The atom-atom pair-correlation function $g(r)$ is obtained by solving the Percus-Yevick equation [17] for a hard-sphere fluid model [18] with an atomic hard-sphere diameter $\sigma = 0.405$ nm [19]. The integration in Eq. (2) is over the whole space, with the condition that the excess electron is inside only one WS sphere at a time, that is $|\mathbf{r}-\mathbf{r}'|>r_{\mathrm{WS}}$.

Using the interaction potential $U_{\mathrm{WS}}(r)$ of Eq. (2), the ground-state energy V_0 of the quasifree excess electron is determined by numerically solving the Schrödinger equation for the lowest energy. This is done by subjecting the ground-state electron wave function $\Psi_0(r)$ to the WS periodic boundary condition $[d\Psi_0(r)/dr]=0$ at $r=r_{\mathrm{WS}}$, and by requiring $\Psi_0(r)$ to be regular at the origin. The results of our $V_0(n)$ calculations are shown as the solid curve in Fig. 1, along with the experimental data of Reininger *et al.* [20], Tauchert and co-workers [21], von Zdrojewski, Rabe, and Schmidt [22], Steinberger *et al.* [23], Bader *et al.* [24], Schwentner and co-workers [25], and Jortner and Gaathon [26]. The theoretical results of Simon, Dobrosavljević, and Stratt [2], Stampfli and Bennemann [6], and Iakubov and Pogosov [8] are also displayed in Fig. 1 for comparison. As one can see, the energy of the lowest lying electronic state (that is, the conduction-band minimum energy) is negative (relative to vacuum) over the whole density range considered, including the solid phase. V_0 reaches a minimum value of -0.72 eV at a liquid density of 1.1×10^{22} cm^{-3}. Overall, our results are found to reproduce very well the available experimental V_0 values [20–26].

A few remarks are in order here regarding the theoretical results of Simon, Dobrosavljević, and Stratt [2] and of Stampfli and Bennemann [6], with which we compare our $V_0(n)$ calculations. First, the percolation theory model of Ref. [2] for conduction-band energies in the heavy rare gases neglects the many-body screening of the long-range excess electron-atom polarization interactions. Such an assumption is contrary to the path-integral Monte Carlo or molecular-dynamics simulation results of Lopez-Castillo *et al.* [3], Space *et al.* [4], and Boltjes, de Graaf, and de Leeuw [5] for the electron-argon and electron-xenon systems, which clearly show that this screening effect does indeed play an essential role in the appearance of the observed minimum of $V_0(n)$. The importance of fully accounting for many-body polarization interactions in the problem at hand necessarily calls for a reexamination of the conclusion of universality reported by Simon, Dobrosavljević, and Stratt [2] in regard to the absolute density at which $V_0(n)$ passes through a minimum in the rare-gas systems. Second, the vacancy model proposed by Stampfli and Bennemann [6] uses the WS model, but relies on the approximation that the fluid can be treated as a face-centered-cubic solid with random vacancies, the effect of a decreasing density being due to an increasing number of vacant lattice sites. This approximation is in contrast to the PIMD simulation results of Lopez-Castillo *et al.* [3]. In fact, as mentioned above, these latter authors have demonstrated that V_0 is fairly insensitive to the degree of disorder, and that no effect is found to arise from the variation of the coordination number of the fluid [3]. Judging from these results, it therefore seems unlikely that the changes of the coordination number with changing density in the fluid can constitute a main factor in the determination of the density dependence of V_0. This, in turn, brings into question the reliability of the conclusion put forth by Stampfli and Bennemann [6] about the universal character of the vacancy model to estimate conduction-band energies in rare-gas fluids.

In closing, on the basis of the present results for xenon and of our previous work on atomic and simple molecular fluids [9,10], we should emphasize that the use of the Wigner-Seitz mean-field approximation for nonpolar fluids, along with an accurate electron-atom/molecule pseudopotential which properly reproduces available gas-phase scattering data, allows one to obtain theoretical $V_0(n)$ values that are in good agreement with experimental data, without invoking any adjustable parameter.

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