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Density dependence of the conduction-band energy and of the effective mass of quasifree excess electrons in fluid neon and helium

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The conduction-band energy V_0 (relative to vacuum) and the effective mass m^* of quasifree excess electrons in fluid neon and helium are calculated as a function of number density n. The calculations are carried out within the framework of the Wigner-Seitz model for nonpolar fluids, using highly accurate pseudopotentials to represent the electron–rare-gas-atom interactions. The calculated values of $V_0(n)$ and $m^*(n)$ are found to be in good agreement with the available experimental data.

A detailed understanding of the behavior of excess electrons injected into dielectric nonpolar fluids is important 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 electrical insulation, pulsed-power technology, polymer physics, nuclear radiation spectroscopy, calorimetry, photochemistry and radiation chemistry, and so on.[1]

Two quantities of special interest in studies of electronic transport in nonpolar fluids are (i) the energy of the lowest extended state of a quasifree excess electron, which is generally referred to as the conduction-band energy V_0 (relative to the energy of the electron in vacuum), and (ii) the electron effective mass m^*. We have recently calculated V_0 and m^* as a function of number density n for several fluids—including argon, krypton, and xenon—which exhibit high electron mobilities.[2–5] $V_0(n)$ was found to be negative for all values of n with a minimum of a few tenths of an electron volt at intermediate liquid densities around $(1-1.2)\times10^{22}$ cm^{-3}. In contrast, $m^*(n)$ was found to decrease monotonically with increasing n, while approaching the free-electron mass (m_0) in the limit of zero density.

In the present work, we focus our attention on the fluids neon and helium. These fluids are interesting cases because the behavior of electrons injected into them differs greatly from that in the fluids considered before. In particular, electron mobility data reported for these systems reveal the coexistence of high- and low-mobility components, which are attributed to quasifree and localized (bubble) states of the excess electron,[6–8] respectively. In both helium and neon, the potential that the fluid exerts upon the excess electron is repulsive, so that quasifree conduction-band states are characterized by positive values of V_0.[9–11] Such states are unstable and induce local fluid dilatations, leading to the formation of bubble-trapped electron states below V_0.[1,12–14] In this paper, we are concerned only with the properties of the quasifree-electron states in these fluids, that is, those that give rise to the high-mobility component observed experimentally. As in our previous studies,[2–5] we calculate $V_0(n)$ for neon, and $m^*(n)$ for neon and helium, using the Wigner-Seitz (WS) (Ref. 15) model for nonpolar fluids. A brief description of our method of calculation is given below. The results of our $V_0(n)$ calculations for helium have already been published.[16]

In the WS model, each atom in the fluid is replaced by an equivalent atomic sphere of radius $r_{\rm WS}=(3/4\pi n)^{1/3}$, and the fluid structure is approximated by an average regular lattice structure for which the WS solution of the Schrödinger equation is valid.[13,15] At a point $\mathbf{r}$ in the WS sphere around an atom located at $\mathbf{r}=0$, the total potential $U(r)$ seen by an electron can be expressed as[2–5,16]

$$U(r)=V(r)+n\int V(|\mathbf{r}-\mathbf{r}'|)F(|\mathbf{r}-\mathbf{r}'|)g(r')d\mathbf{r}' , \qquad (1)$$

where $V(r)$ is the potential produced by the atom at the origin, $g(r)$ is the pair-correlation function of the fluid, and $F(r)$ is a screening function that accounts for the effect of the field of the induced dipoles of the surrounding atoms. The electron–rare-gas-atom interaction is represented by an accurate atomic pseudopotential, which was recently developed by the present authors to study the elastic scattering of low-energy (0–20 eV) electrons from helium[17] and neon.[18] The construction of these atomic pseudopotentials is based on the use of the highly accurate norm-conserving ionic pseudopotentials of Bachelet, Hamann, and Schlüter[19] and is described in detail in Refs. 17 and 18. At distances $r>r_{\rm WS}$, the screening is approximated by the Lorentz local-field function[13] $F(r)=[1+(8\pi/3)n\alpha]^{-1}$, where α is the atomic polarizability (1.384 and 2.669 a.u. for helium and neon,[20] respectively), while at $r<r_{\rm WS}$ we have $F(r)=1$. Finally, the radial distribution function $g(r)$ is obtained by solving the Percus-Yevick equation for a fluid of hard spheres,[21] using hard-sphere diameters equal to 2.556 and 2.749 Å for helium and neon,[22] respectively.

The ground-state energy V_0 of the quasifree excess electron in the undisturbed fluid is determined by solving numerically the Schrödinger equation inside the WS

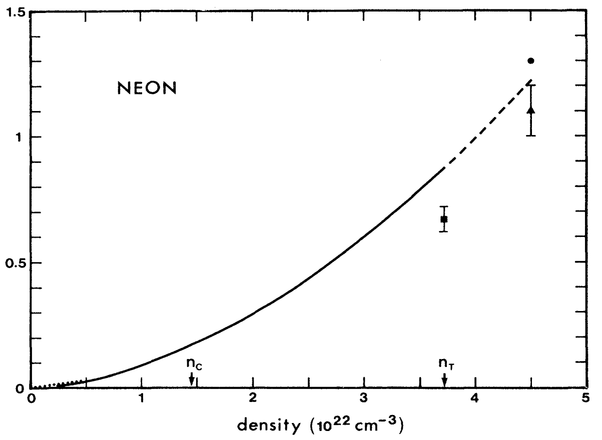

FIG. 1. Conduction-band energy V_0 as a function of fluid density n in neon. The solid line represents the $V_0(n)$ values calculated in this work. Experiment: ■ (liquid at the triple point, Ref. 10); ▲ (solid at 6 K, Ref. 25); ● (solid at 6 K, Ref. 26). The dashed line shown for densities above that at the triple point gives the results of our V_0 calculations for solid neon. The dotted straight line in the low-density gas region ($n < 0.5\times 10^{22}$ cm^{-3}) shows the density dependence of the electron-scattering Rydberg-state energy shift Δ_{sc} ($=V_0$) reported by Reininger *et al.* (Ref. 31). n_C and n_T denote the densities at the critical (44.4 K) and triple (24.55 K) points, respectively.

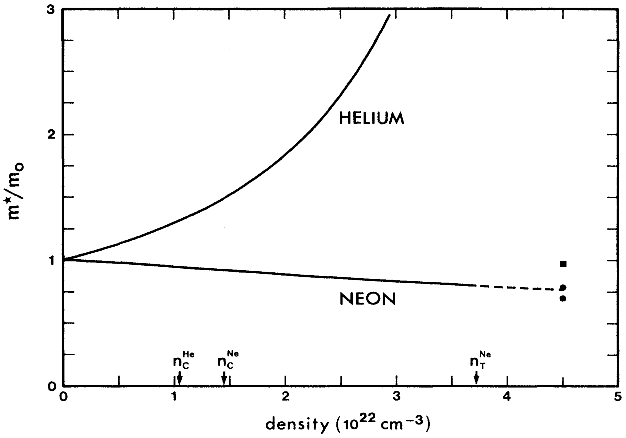

FIG. 2. Variation of m^*/m_0 as a function of density in fluid helium and neon: ——, present work; — — —, results of our m^*/m_0 calculations for solid neon. Experiment: ● (solid neon at 6 K, Ref. 32); ■ (solid neon at 6 K, Ref. 33). There are no experimental data of m^* in helium with which to compare our results. n_C^{He} and n_C^{Ne} denote the densities at the critical points of helium (5.19 K) and neon (44.4 K), respectively, and n_T^{Ne} denotes the density at the triple point of neon (24.55 K).

sphere with the interaction pseudopotential $U(r)$ given by Eq. (1) and with the ground-state electron pseudowave-function $\Psi_0(r)$ subjected to the WS boundary condition $d\Psi_0(r)/dr=0$ at $r=r_{WS}$.

The value of m^* is estimated according to a method proposed by Bardeen[23,24] in the framework of the WS approximation. It is given by

$$\frac{m^*}{m_0}=\frac{n}{[\Psi_0^2(r_{WS})/\eta^2]\left[\left(\frac{r}{P}\frac{dP}{dr}\right)_{r=r_{WS}}-1\right]}\ , \tag{2}$$

where η is the normalization constant

$$\eta^2=4\pi\int_0^{r_{WS}}[\Psi_0(r)]^2r^2dr\ , \tag{3}$$

and $P(r)/r$ is the p-wave single-site radial wave function, which is calculated directly from the radial Schrödinger equation with the potential $U(r)$ of Eq. (1).

The results of our $V_0(n)$ calculation for neon are given in Fig. 1 along with the available experimental data for both the liquid[10] and solid[25,26] phases. As we can see, there is good agreement between the calculated and experimental values. The dependence of V_0 on density very much resembles that obtained for helium.[16] The conduction-band energies in the liquid and in dense neon gas are positive with no minimum in $V_0(n)$. However, the values of V_0 are smaller (by factors of about 4–5) in neon than in helium fluid, which in turn indicates that the electron bubble state in neon is comparatively less stable than in helium.[9,13,27–29] For the sake of comparison, we have also shown in Fig. 1, at very low gas densities (where the WS model ought to be well approximated by the optical model[30]), the linear density dependence of the pressure-induced electron-scattering Rydberg-state energy shift Δ_{sc} ($=V_0$) obtained recently by Reininger *et al.*[31] from photoabsorption and photoconductivity measurements of C_6H_6 in neon. Our calculated $V_0(n)$ values in this density region are found to be slightly low as compared to those of Δ_{sc} (eV)$=0.54\times 10^{-23}n$ (n in cm^{-3}) reported by these authors.[31]

In Fig. 2 we present the results of our quasifree-electron effective-mass calculations performed for neon and helium for a wide range of densities. In the case of neon, the calculated effective mass is nearly the free-electron mass, decreasing very slowly with density in going from the gas to the solid phase (only 20% smaller than m_0 in the liquid at the triple point). It is worth noting that these density-dependent effective-mass results for neon bear a certain resemblance to those already reported for the heavier rare-gas fluids argon, krypton, and xenon.[5] As is apparent from Fig. 2, the values of m^* obtained in the solid phase compare remarkably well with those estimated from exciton spectroscopy experiments.[32,33] As far as we know, there are no experimental estimates of m^* in fluid (liquid or dense gas) neon with which to compare our results. In contrast to the neon and heavier rare-gas results, the quasifree-electron effective mass calculated for helium increases with increasing fluid density; $m^*(n)$ varies from m_0, in the limit of zero density, to about $3m_0$ at $n=3\times 10^{22}$ cm^{-3} (Fig. 2). Here again, there are no experimental values of m^* with which to compare our results.

In conclusion, we have reported in this paper an evaluation of the effective mass of quasifree excess electrons in neon and helium over a wide range of fluid densities. The calculations of $m^*(n)$ and $V_0(n)$ for fluid neon, extended to the solid phase, have given results that agree well with existing experimental data.

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