Comments

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Comment on "Molecular-dynamics simulation of excess-electron transport in simple fluids"

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A recent treatment of the saturation drift velocity v_{sat} of electrons in dense, supercritical argon [Leycuras and Levesque, Phys. Rev. A 32, 1180 (1985)] gives positive values of dv_{sat}/dn at $n/n_c = 1.2$—1.6, whereas the experimental values are negative in both the supercritical gas and the liquid at these densities [Jahnke, Meyer, and Rice, Phys. Rev. A 3, 734 (1971); Huang and Freeman, Phys. Rev. A **24**, 714 (1981)]. Other difficulties are mentioned.

A recent treatment of the saturation drift velocities v_{sat} of extra electrons in dense, supercritical argon[1] does not fit certain features of the experimental data.[2,3] In particular, the change of v_{sat} with density, dv_{sat}/dn, is predicted to be positive in the density range $n/n_c = 1.2$—1.6 (n_c is the density of the critical fluid),[1] whereas it is observed to be negative in both the supercritical gas[2] and the liquid[3] at these densities. Several comments are offered.

(1) At constant density, increasing the temperature to change from the liquid to the supercritical gas increases v_{sat} slightly but does not alter the value of dv_{sat}/dn (Fig. 1, experimental points from Refs. 2 and 3).

(2) Figure 3 of Ref. 1 displays calculated values of $v_{sat} = 400$—900 m/s over the argon density range $n = 9.6$—14.4 (10^{27}molecule/m^3). Experimentally, at $n = 8.1$—12.9 (10^{27}molecule/m^3) a plateau in the drift velocity occurs at 900—600 m/s, at fields $E \approx 10$—30 kV/m.[3] This appears to be the plateau to which Leycuras and Levesque[1] refer. At higher densities, $n \geq 14.8\times10^{27}$ molecule/m^3, this plateau does not exist;[3] it has collapsed into the long, gentle increase of drift velocity with field that occurs at high fields in argon at all densities.[3–5] The plateau at intermediate fields at $n \leq 13\times10^{27}$ molecule/m^3 is attributed to electron heating by the field and the rapid rise of the momentum-transfer cross section σ_m on the high-energy side of the Ramsauer-Townsend (RT) minimum.[6] At $n > 13\times10^{27}$ molecule/m^3 the electron-molecule separation distance is continually too small to allow the RT effect to occur.[3]

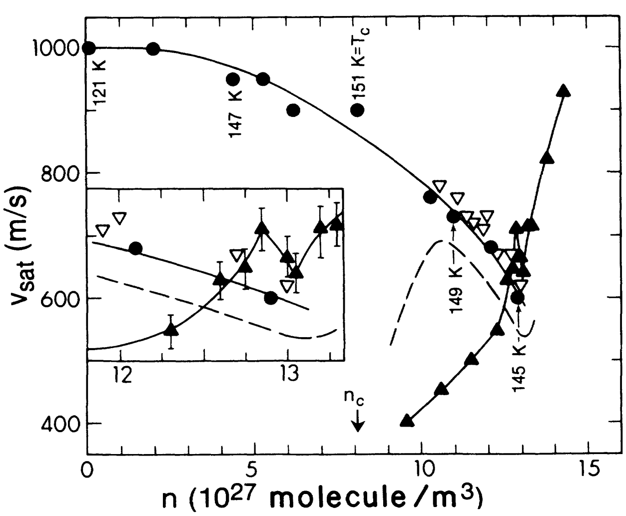

FIG. 1. Saturation drift velocity of electrons in argon as a function of density: ∇, supercritical gas, 155 ±3 K, experimental, Ref. 2; ▲, supercritical gas, ~155 K, theoretical, Ref. 1; ●, coexistence gas and liquid at indicated temperatures, experimental, Ref. 3; — — —, Ref. 2 as quoted in Ref. 1. 2.69×10^{25} molecule/m^3 = 1 amagat (Leycuras and Levesque response).

(3) In argon at $n < 13\times10^{27}$ molecule/m^3 the experimental value of dv_{sat}/dn is negative in both the supercritical gas and the liquid (Fig. 1), whereas that predicted by Leycuras and Levesque for the supercritical gas is positive.[1] Values of v_{sat} in the supercritical gas, displayed in Ref. 2, are included in Fig. 1. No velocity plateau was obtained at $n < 10.6\times10^{27}$ molecule/m^3;[2] the S curve attributed[1] to that reference seems to be in error, since there is not an experimental value $v_{sat} = 600$ m/s at 0.0096 atoms/Å^3.[2]

(4) The 10% dip in v_{sat} indicated in the calculated values at n near 13.1×10^{27} molecule/m^3 is within the reported 10% uncertainty of the calculations.[1] The dip is also too narrow to be credible (Fig. 1). The uncertainties in the calculated results can also be assessed from the earlier report.[7]

(5) In liquid argon near the triple point, where $n = 21\times10^{27}$ molecule/m^3, a much higher velocity plateau occurs at a much higher field strength: $v_{sat} = 8000$ m/s at $E = 7$—9 MV/m.[5] This plateau does not occur at low densities and is due to a different mechanism than that discussed in the above item (2). The mechanism probably involves inelastic processes of relatively high-energy electrons. The Leycuras mechanism predicted a value of v_{sat} only 50% of the observed.[7]

(6) The model in Ref. 1 includes the assumption that the extra electron is localized on a single argon atom. It attributes the maximum electron-transfer rate, and hence the value of v_{sat}, to the molecule-molecule collision rate. This is contrary to the observation that v_{sat} is slightly higher in the low-density gas than in the dense gas or low-density liquid.[3] The localization model for electrons in supercritical or liquid argon, whether the electron is assumed to be localized on one or several molecules,[8] has been argued to be untenable.[6,9] The arguments need not be repeated here. Quasilocalization of electrons occurs in dense gases and low-density liquids at temperatures near the vapor-liquid coexistence curve, if the applied electric field is not too high.[3,10–12] At the field strengths required to attain v_{sat}, quasilocalization does not occur.[3,10(b)] Quasilocalization does not occur even at low field strengths in argon at $n \geq 14\times10^{27}$ molecule/m^3;[3] extra electrons reside in a conduction band.[3,10,13–15]

(7) The statement that "one can easily verify that for every gas the abrupt decrease of the mobility (less pronounced in methane) occurs at a density for which the onset of localization is predicted by the Mott expression $\langle k\Lambda\rangle = k(n\langle\bar{\sigma}_m\rangle)^{-1}$, where k is the wave number associated with the electron in thermal equilibrium with the fluid, Λ is the mean free path, n the number density of the fluid, and $\langle\bar{\sigma}_m\rangle$ the thermal average of the momentum transfer cross section at the fluid temperature" has recently been shown to be untrue.[16] In helium at $2.7\text{K} \leq T \leq 293$ K, and in hydrogen at 78 K $\leq T \leq 293$K, the density-normalized mobility $n\mu$ decreases at much lower densities than predicted by the Mott expression. The value of $n\mu$ has decreased to 0.72 of the low-density gas limit $(n\mu)_0$ at a density 6.3 times smaller than that, n_M, predicted by the Mott expression.[16] Electron behavior in many dense gases has recently been assessed[16] with respect to the Mott expression[17] and that of Ioffe and Regel.[18] The latter applies cleanly to electrons in helium and hydrogen, where the electron-molecule interaction is repulsive. Neither expression applies cleanly to gases in which the interaction with thermal electrons is attractive (argon, xenon, ammonia, water, ethane, and so on).[16]

(8) The methane vibrational phase-relaxation results of Marsault cited in Ref. 19 display a maximum in bandwidth at the critical density n_c and a minimum near $2n_c$. They are reminiscent of the bulk viscosity of argon, which has a maximum at n_c and a minimum near $2n_c$.[20] While the vibrational bandwidth and the bulk viscosity reflect the molecular dynamics in the fluid, they do not support either the conduction-band model or the attachment model of electron transport, because they could be consistent with both types of model. In the deformation potential version[14,15] of the conduction-band model, electron mobility is determined by fluid-density fluctuations, as are the changes of vibrational bandwidth in methane[19] and bulk viscosity of argon.[20]

(9) The localization of an electron on a single argon atom proposed in Ref. 1 is very different from the quasilocalization of a thermal electron by a large density fluctuation in a dense gas near the vapor-liquid coexistence curve.[10,21] The latter has been demonstrated to occur in many gases, but under limited conditions.[3,10,11,21,22]

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