Comments and Addenda

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Localized excess-electron states in simple classical fluids: Quasilocalization

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One of the results of recent interesting calculations on electron states in the rare-gas fluids has been reinterpreted and verified by experiment. The extent of electron quasilocalization in dense argon gas near the critical region is less than that in xenon at the same relative density n/n_c and temperature T/T_c.

In a recent interesting treatment of localized states of excess electrons in rare-gas (noble) fluids,[1] calculations indicated that the decrease of the density normalized mobility μn in xenon vapor near the critical region[2] was not due to the formation of dropletlike localized states. However, another interpretation of the calculation results is that, if the decrease of μn were due to the formation of dropletlike states, the extent of localization would be smaller in argon than in xenon at the same relative density n/n_c and temperature T/T_c. Measurements in argon show that such is the case.

The parameter used by Ebner and Punyanitya[1] that requires discussion here is a, which characterizes the strength of the coupling between the electron and the atoms of the fluid. Although the authors recognized that the value of a should be density dependent, they used at all densities the value estimated for the liquid at its triple point. However, by analogy with the electron scattering lengths of argon and xenon,[3,4] a can be expected to decrease algebraically with decreasing density, reaching a limiting value for the dilute gas. At high densities a becomes less negative due to interference of the single atom interactions.

Ebner and Punyanitya[1] estimated that to produce stable droplets in the vapor near the critical point the value of a in xenon would have to decrease from -0.96 Å in the liquid at the triple point to -1.2 Å in the dense gas, while in argon the change would have to be from -0.20 Å in the liquid at the triple point to -0.6 Å in the dense gas. The required relative change is 200% in argon, but only 25% in xenon. One might therefore expect to find a smaller contribution of dropletlike states in argon than in xenon.

The total effect of these states upon the average electron mobility is not large,[2] and the trap depth is only $\sim kT$. The states are not very stable, so they are more aptly described as quasilocalized[5] than as localized. The density fluctuations that serve as trapping centers in the dense gas are not true droplets, and they might be better termed quasidroplets.

The thermodynamics of the quasilocalization process can be presented in terms of the following equations.

$$\text{medium} \rightleftharpoons \text{site}, \tag{1}$$

$$e^-_{qf} + \text{site} \rightleftharpoons e^-_{ql}, \tag{2}$$

where e^-_{qf} and e^-_{ql} represent quasifree and quasilocalized electrons respectively. The density normalized mobility at any fluid density n (molecule/cm^3) and $T(K)$ is:

$$\mu n = n\mu_n^0 f, \tag{3}$$

where μ_n^0 is the quasifree electron mobility at density n, and f is the fraction of electrons in the quasifree state.

$$f = (e^-_{qf})/[(e^-_{qf}) + (e^-_{ql})] = [1 + (\text{site})K_2]^{-1}, \tag{4}$$

where the parentheses represent concentrations and K_2 is the equilibrium constant of reaction 2. It follows that

$$(n\mu_n^0/\mu n) - 1 = \exp(\Delta S'/k)\exp(-\Delta H'/kT), \tag{5}$$

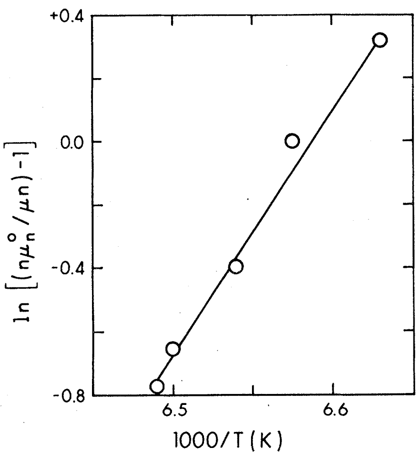

FIG. 1. Plot of $\ln[(n\mu_n^0/\mu n) - 1]$ against T^{-1} for argon at the critical density and just above the critical temperature. $n_c = 8.1 \times 10^{21}$ molecule/cm^3, $T_c = 150.9$ K, $\mu_{n_c}^0 = 380$ cm^2/Vs.

where k is Boltzmann's constant, the overall standard entropy change is $\Delta S' = \Delta S_1^0 + \Delta S_2^0$ and the standard enthalpy change is $\Delta H' = \Delta H_1^0 + \Delta H_2^0$.

It is possible to estimate the value of μ_n^0 in the critical fluid of xenon, although cell explosions prevented the direct measurement. The Ramsauer-Townsend minimum in the electron scattering cross section of xenon is normally considered to be a low-density gas phase phenomenon, but it persists into the critical fluid and to densities somewhat higher than the critical n_c.[2] The value of μ_n^0 is therefore somewhat less than the maximum μ_{max} in a plot of μ against field strength at n_c.[2] Hence, $\mu_{n_c}^0 \approx 40$ cm^2/V s.

From Eq. (5) and data reworked from Ref. 2, we obtain for xenon at n_c and temperatures just above T_c: $\Delta H' \approx -1.0$ eV, $\Delta S' \approx -3.4$ meV/K and $\Delta G' \approx -0.04$ eV. The large negative values of $\Delta H'$ and $\Delta S'$ are attributed mainly to site formation, reaction(1). It is a condensationlike process which produces large spacial and temporal fluctuations in the microscopic density of the medium. The molar equivalent of $\Delta H'$ is equal to the heat of condensation of eight mols of xenon at its normal boiling point[6] and of many more mols than that under the present conditions. Thus, of the order of a hundred molecules are involved in a quasidroplet that quasilocalizes an electron.

A similar treatment of recent measurements in argon (Fig. 1) gives, at n_c and temperatures just above T_c: $\Delta H' = -0.67$ eV, $\Delta S' = -4.4$ meV/K and $\Delta G' = -0.01$ eV. The molar equivalent of $\Delta H'$ is equal to the heat of condensation of nine mols of argon at its normal boiling point. As in xenon, one concludes that of the order of a hundred molecules are involved in the quasilocalization of one electron. However, the extent and energy of quasilocalization are smaller in argon than in xenon.

[1]C. Ebner and C. Punyanitya, Phys. Rev. A 19, 856 (1979).
[2]S. S.-S. Huang and G. R. Freeman, J. Chem. Phys. 68, 1355 (1978).
[3]T. F. O'Malley, Phys. Rev. 130, 1020 (1963).
[4]J. Lekner, Phys. Rev. 158, 130 (1967).
[5]J. Jortner and A. Gaathon, Can. J. Chem. 55, 1801 (1977).
[6]A. C. Jenkins, in *Argon, helium and the rare gases*, edited by G. A. Cook (Interscience, New York, 1961), Vol. 1, p. 392.