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Comment on the application of the Cohen-Lekner theory to excess electron mobility in liquid krypton

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The Cohen-Lekner theory of excess electron mobility in liquid rare gases is applied to liquid krypton at the triple point. A serious disagreement between the theory and experiment is pointed out and discussed.

The problem of the excess electron mobility in nonpolar liquids and especially in liquid rare gases has attracted considerable attention in recent years. Since the early experimental observations by Davidson and Larsh[1] and by Hutchinson,[2] a number of authors[3-10] have investigated experimentally the excess electron mobility in liquid Ar, Kr, and Xe over a wide range of the electric fields and liquid densities. These authors firmly established that electrons in liquid rare gases mentioned above are in extended (quasifree) states.

A detailed molecular theory of electron mobilities in liquid rare gases has been put forward by Cohen and Lekner.[11,12] These authors assumed that the principal scattering mechanism of free electrons is the elastic, single scattering from effective potentials of the muffin-tin type. Taking into account the interference of scattered electron waves, they obtained the appropriate Boltzmann equation and solved this equation for electrons moving in a steady electric field by a method due to Lorentz, Pidduck, and Davydov. In the weak-field region this solution takes the familiar Lorentzian form:

$$v_D = \frac{2}{3}\left(\frac{2}{\pi m k_B T}\right)^{1/2} \frac{eE}{4\pi a^2 S(0) n}, \tag{1}$$

where v_D is the electron drift velocity, m is the electron mass, k_B is the Boltzmann constant, T is the absolute temperature, e is the electron charge, E is the electric field, a is the scattering length, $S(0)$ is the liquid structure factor evaluated at zeroth electron wave number, and n is the number density of the liquid.

The problem of the evaluation of the scattering length a has been considered in details by Lekner.[12] He suggested the specific form of the effective scattering potential in which account is taken of the screening effect following from the interaction between dipoles excited in polarizable atoms by scattered electrons. The detailed numerical calculations of the electron mobility for argon at the triple point performed according to the Cohen-Lekner theory produced very good agreement with the experiment.[9,10,12] The Cohen-Lekner theory has been subsequently extended to the case of electron mobility in liquid hydrocarbons.[13,14]

Since the scattering length calculated by Lekner[12] for liquid argon at the triple point is positive and the scattering length for gaseous argon atoms is negative, it should pass through zero at some intermediate density. Thus, electron mobility should not be controlled by scattering from effective potentials (as introduced by Cohen and Lekner), but by other mechanisms (e.g., scattering from density fluctuations) in this region. This observation was used by Lekner[15,26] as a basis for a semiempirical model which qualitatively explained the excess electron mobility maxima established experimentally by Jahnke, Meyer, and Rice.[10] The detailed study of the density dependence of the scattering length for electrons in liquid argon, calculated according to the recipe provided by Cohen and Lekner[11,12] has been undertaken by Jahnke, Holtzwarth, and Rice.[16] They found quantitative and qualitative disagreement between the theory and experimental data[10] for argon densities lower than that at the triple point. This disagreement has been attributed by these authors to (i) neglect of the asymmetric instantaneous atomic configurations in a fluid at densities lower than that at the triple point, and (ii) neglect of an accurate treatment of the multiple scattering process.

The problem of the theoretical description of the excess-mobility maxima has been recently attacked by Boehm.[17] He observed that the mobility maxima appear in the vicinity of the critical density. The explanation of this phenomenon put forward by Boehm is based on the assumption that excess electrons in the critical region produce inhomogeneities which provide contiguous channels of relatively high conductivity. Boehm assumes that electron mobility in both the denser and the thinner regions of the fluid is controlled by essentially the same scattering mechanism proposed by Cohen and Lekner. In fact, Boehm[17] used in his calculations the formula (1) for both considered regions of the fluid, assuming the same scattering length but

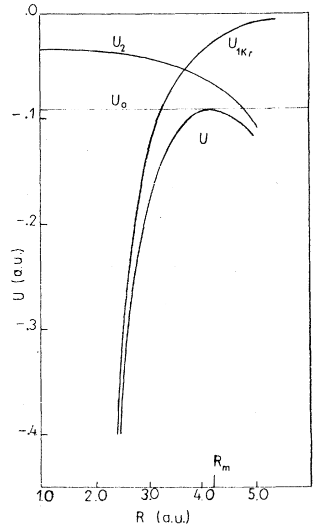

FIG. 1. Atomic potentials in liquid krypton. U_0, U_1, U_2, and $\langle U\rangle$ have the same meaning as in Ref. 12.

different structure factors and densities. Thus, Boehm avoided the problem of the density dependence of the scattering length raised by Jahnke, Holtzwarth, and Rice.[16]

The surprisingly good agreement between the Lekner calculations for liquid argon at the triple point[12] and experimental data[9,10] has been considered as a basis for further refinements[16] and generalizations[13,14] of the Cohen-Lekner theory. Since this theory is intended to describe all liquid rare gases in which free electrons are in the extended states (Ar, Kr, Xe), it would be very interesting to apply this theory to other rare gases at the triple-point density. Recent measurements of the krypton compressibility reported in the literature[18] make it possible for liquid krypton and this is the principal purpose of this Comment. We have calculated the scattering length, the electron drift mobility in a steady weak electric field, and the conduction-band minimum for krypton at the triple point (for $T = 117\,^\circ\mathrm{K}$, $n = 0.0176\ \mathrm{\AA}^{-3}$) using the Lorentzian expression for the drift velocity [Eq. (1)] and Cohen-Lekner method of calculation of the scattering length [applying the potential defined by Eqs. (22) and (23) in Ref. 12].

The calculations for liquid krypton have been performed with the use of an electron-atom potential of the form

$$U_{1\mathrm{Kr}} = U_{\mathrm{HF}} + U_\alpha\,, \qquad (2)$$

where U_{HF} is the Hartree-Fock potential given by Strand and Bohnam[20] and U_α is a polarization potential of the form

$$U_\alpha = -(\alpha/2r^4)\{1 - \exp[-(r/r_{\mathrm{eff}})^8]\}\,, \qquad (3)$$

where $\alpha = 16.8$ (a.u.) is the atomic polarizability of krypton,[19] and r_{eff} is the cutoff parameter accounting for the exchange interaction, which has been not explicitly taken into account in Eq. (2).

The potential $U_{1\mathrm{Kr}}$ is shown in Fig. 1. For krypton, $r_{\mathrm{eff}} = 1.325$ (a.u.). This value of r_{eff} has been found by numerically fitting the values of the total-scattering cross section obtained by the phase-shift method with the use of the potential $U_{1\mathrm{Kr}}$ [Eq. (2)] to the experimental data for the scattering of low-energy electrons [for electron wave vector $k \leq 0.15$ a.u. (see Fig. 2)]. The scattering length calculated with the use of the potential $U_{1\mathrm{Kr}}$ [Eq. (2)] with $r_{\mathrm{eff}} = 1.325$ a.u., that is for the dilute krypton gas, is -3.53 a.u. We have used in the calculations the radial distribution function $g(r)$, due to Clayton.[22]

The results of our calculations according to the Cohen-Lekner theory for liquid krypton at the triple point are displayed in Table I together with the results of the Cohen-Lekner theory for liquid argon and with the results for Ar and Kr inferred from the Springett-Jortner-Cohen theory.[23] Calculations for liquid krypton have been performed both with the value of $S(0) = 0.043$ inferred from the hard-sphere model[24] and the value $S(0) = 0.051$ obtained on the basis of the compressibility measurements.[18]

The data displayed in Table I lead to the conclusion that values of the scattering length and elec-

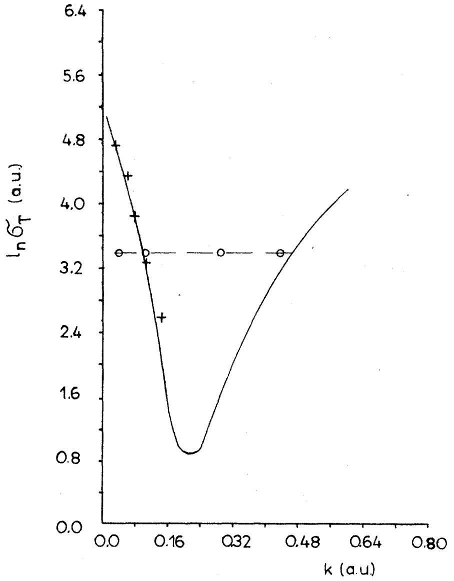

FIG. 2. Cross sections for electron scattering. Solid line, experimental data for gasous krypton (Ref. 21). Circles, data for liquid krypton at the triple point obtained by means of the Lekner theory. Crosses, data obtained with the use of the potential $U_{1\mathrm{Kr}}$ Eq. (2).

TABLE I. Calculations of the electron mobility and conduction-band minimum for liquid argon and krypton at the triple point.

	Cohen-Lekner theory			Springett-Jortner-Cohen theory	
Liquid	Scattering length (a.u.)	Mobility (cm^2/V sec)	Conduction-band minimum (eV)	Scattering length (a.u.)	Mobility (cm^2/V sec)
Argon	1.44^d	370^d 354^a	-0.65^e	1.74	246
Krypton	1.60	325^b 274^c	-1.20	2.02	204^b 172^c

[a] Calculated with the use of Eq. (1) and data due to Lekner (Ref. 12).

[b] Calculated for $S(0) = 0.043$ (Ref. 24).

[c] Calculated for $S(0) = 0.051$ (Ref. 18).

[d] See Ref. 12.

[e] See Ref. 16.

tron mobility calculated for liquid argon and krypton at the triple point with the use of both methods are rather close. This conclusion is in drastic disagreement with experiment for liquid krypton at the triple point, which gives the value of the electron mobility as $\mu = 1800$ cm^2/V sec.[9] We can see that this value is at least five times higher than the highest theoretical value ($\mu = 325$ cm^2/V sec) obtained with the use of the Cohen-Lekner theory. Thus, the case of liquid krypton at the triple point is in sharp contrast with the case of liquid argon for which the agreement between the Cohen-Lekner theory and experiment within 20% has been reached[12] for the electron mobility. It is interesting to note that both in the case of Ar and the case of Kr that phase shift calculated for the dilute gas limit has a different sign than that calculated for a liquid at the triple point. In the case of the conduction-band-minimum calculations both for liquid argon and krypton, the values found are much too high as compared with the experimental data (−0.20 eV for Ar and −0.40 eV for Kr).[23]

Very good agreement between theory and experiment concerning excess electron mobility in liquid argon at the triple point has convinced many authors that the Cohen-Lekner approach provides the accurate description of this phenomenon for liquid rare gases. The results for liquid krypton at the triple point given above indicate that this view is not quite correct. Among various possible deficiencies in the Cohen-Lekner theory discussed by Jahnke, Holtzwarth, and Rice,[16] the neglect of the accurate treatment of the multiple-scattering process seems to be the most important. A simple treatment of the multiple scattering has been already proposed by Lekner[12] in the form of a correction to the kinematics of excess electron in liquid rare gases. In the case of argon, this treatment did not change the results to a great extent. We would suggest one should consider the problem of multiple scattering in a more fundamental way, applying the t matrix expansion to the Kubo formula for the electron mobility in a manner similar to that adopted by Ashcroft and Schaich[25] to the problem of electrical conductivity in liquid metals. We hope to deal with this in a future paper.

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