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# The Minimum in the Mobility-Density Curve for Electrons Injected into Insulating Dense Gases

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Average force and force-force correlation formulae both point to the same result that the mobility  $\mu$  of electrons injected into dense gases like Ar, Xe, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> ought to exhibit at least gross regularities with respect to changes in gas density  $n$ . This is the motivation for focussing here on the mobility minimum characterized by  $d\mu/dn = 0$ . At this minimum, a formula for  $\mu_{\min}$  is obtained from which the scattering length  $a$  has been eliminated in favour of its density derivative ( $da/dn$ ). This density derivative, it is argued, must have the form  $\underline{a}_{\text{gas}}\Omega_t$ , where  $\Omega_t$  is a 'characteristic volume for transport' while  $\underline{a}_{\text{gas}}$  is the scattering length in the dilute gas limit. The Onsager continuum model, plus the Böttcher-Onsager formula for the dielectric constant, can be used as a first estimate of  $\Omega_t$ , which is shown to be proportional to the cube of the 'cavity radius' in this model. The formula for  $\mu_{\min}$  is finally brought into direct contact with experiment.

## 1 INTRODUCTION

Many data are now available for the mobility  $\mu$  of electrons injected into insulating fluids such as argon,<sup>1-3</sup> xenon,<sup>1,4</sup> methane<sup>5</sup> and ethane.<sup>6</sup> The general characteristics are remarkably similar at densities below that of the critical fluid;  $n\mu$  depends weakly on fluid density  $n$  for small  $n$ , but then exhibits a minimum, which for xenon, say, is at  $n \approx 0.8n_c$ ,

with  $n_c$  the critical density.<sup>4</sup> The theory of mobility has been discussed by a number of workers; we refer to papers by Lekner and Bishop,<sup>7</sup> and Basak and Cohen,<sup>8</sup> other references being given there.

It is natural to assume that the mobility  $\mu$  can be described theoretically by the scattering wave function  $\psi$  off a potential  $V(\mathbf{r})$  which is a sum of polarizable, localized, atomic-like potentials. Of course, the explicit calculation of  $\psi$  from such a 'disordered' potential is of considerable complexity, except in the limit of truly weak scattering.

Therefore in the present paper, we shall avoid the necessity for enquiring into the detailed form of  $\psi$  by focussing on the minimum in the mobility-density curve. Then, with a number of admittedly simplistic assumptions, we show that the momentum transfer cross-section  $\sigma_m$ , which we write following Gerjuoy<sup>9,10</sup> as an average force, should have density scaling properties which can be utilized rather directly at the minimum of the mobility-density curve.

## 2 MINIMUM OF MOBILITY-DENSITY CURVE RELATED TO AVERAGE FORCE

As is customary, we write the mobility  $\mu$  as

$$\mu = A[n\sigma_m S(0)]^{-1} \quad (2.1)$$

where  $\sigma_m$  is the momentum transfer cross section and  $S(0)$  the long wavelength limit of the fluid structure factor. Following Gerjuoy,<sup>9,10</sup>  $\sigma_m$  can be written in terms of an average force  $F$ , which is the gradient of the potential  $V(\mathbf{r})$ . With  $\psi$  denoting the wave function of the particle scattered from the potential  $V(\mathbf{r})$ , the momentum transfer cross section for the particle of energy  $E$  is explicitly

$$\sigma_m = \frac{1}{2E} \int \psi^* F \psi \, d\mathbf{r} \quad (2.2)$$

The Schrödinger equation which determines the scattered wave function  $\psi$  can be written in the equivalent integral equation form

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{1}{2\pi} \int G_0(|\mathbf{r} - \mathbf{r}'|) V(\mathbf{r}') \psi(\mathbf{r}') \, d\mathbf{r}' \quad (2.3)$$

where  $G_0$  is the free-particle Green function

$$G_0 = \frac{\exp(i\mathbf{k}|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} : E = \frac{\hbar^2 k^2}{2m} \quad (2.4)$$

where  $\hbar$  is Planck's constant divided by  $2\pi$  and  $m$  is the particle mass.

The point we wish to exploit here is that, when we write the explicit form of  $V(\mathbf{r})$  as

$$V(\mathbf{r}) = \sum_{\mathbf{R}_i} v(\mathbf{r} - \mathbf{R}_i) \quad (2.5)$$

then the usual assumption that  $v$  is atomic-like (structure independent) links density derivatives, entering through the atomic positions  $\mathbf{R}_i$ , with spatial derivatives of  $V(\mathbf{r})$ .

At the state of the system corresponding to the mobility minimum,  $\mu_{\min}$ , which is at a little higher density than the minimum of  $n\mu$  which is sometimes plotted, the mobility should be characterized fundamentally by  $V(\mathbf{r})$ , its spatial derivatives and structural correlation functions. We now return to Eq. (2.1) to obtain a formula for  $\mu_{\min}$ . This we shall then characterize, motivated by the above argument, by the density derivative of the scattering length  $a$ , introduced conveniently through  $\sigma_m = 4\pi a^2$ . Lumping the factor  $4\pi$  into the constant in Eq. (2.1) we can then write, after differentiating  $\mu$  with respect to  $n$  and putting  $d\mu/dn = 0$  at the mobility minimum:

$$4\left(\frac{\partial a}{\partial n}\right)_m^2 = \Omega_m^2 a_m^2 \left[ 1 + \frac{d \ln S(0)}{d \ln n} \right]_m^2 \quad (2.6)$$

where  $\Omega_m$  is the molecular volume  $(n_{\min})^{-1}$ . Returning to Eq. (2.1) we now eliminate the scattering length to obtain the mobility minimum in terms of the density derivative of the scattering length at the minimum,

$$\mu_{\min} = \frac{A\Omega^2 \left[ 1 + \frac{d \ln S(0)}{d \ln n} \right]_m^2}{4n_{\min} S(0)_m \left(\frac{\partial a}{\partial n}\right)_m^2} \quad (2.7)$$

At this stage, we exploit what was said above about the density being a dominant gross variable, and write

$$\left(\frac{\partial a}{\partial n}\right)_m^2 = a_{\text{gas}}^2 \Omega_t^2 \quad (2.8)$$

where  $a_{\text{gas}}$  is the scattering length in the dilute gas limit, essentially determined by the scattering properties of a single, polarizable atomic-like potential  $v(\mathbf{r})$  in Eq. (2.5). We shall refer to the volume  $\Omega_t$  in Eq. (2.8) as a 'characteristic volume for transport', or, if one wishes,  $\Omega_t^{1/3}$

can be defined as a characteristic length  $l_i$ . Returning to Eq. (2.7) we have therefore

$$\frac{(n_{\min} \mu_{\min})}{\lim_{n \rightarrow 0} (n_{\mu})} = \frac{1}{4} \left( \frac{\Omega_m}{\Omega_i} \right)^2 \frac{\left[ 1 + \frac{d \ln S(0)}{d \ln n} \right]_m^2}{S_m(0)} \quad (2.9)$$

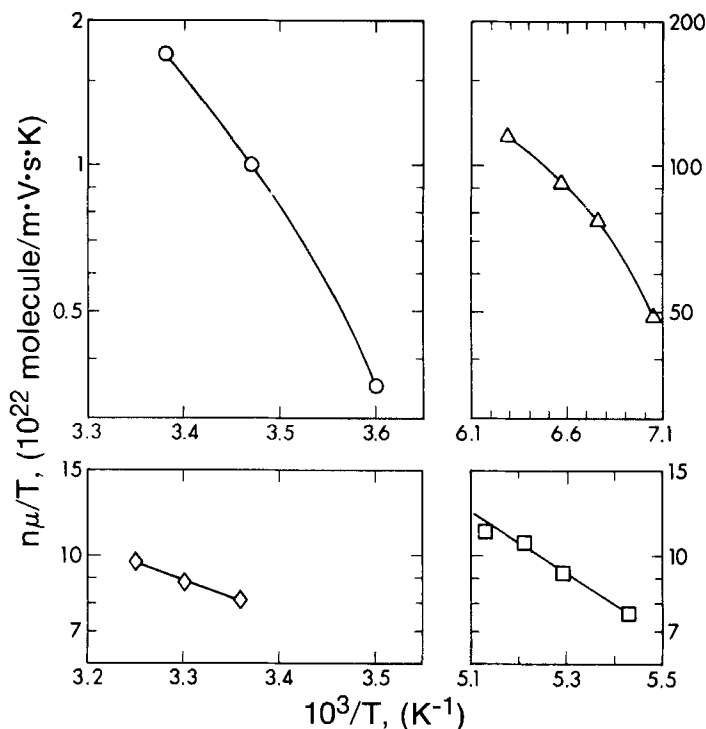
To obtain a mobility minimum, the ratio on the left side of Eq. (2.9) must be less than unity, which in turn implies

$$\left( \frac{\Omega_m}{\Omega_i} \right)^2 < \frac{4S_m(0)}{\left[ 1 + \frac{d \ln S(0)}{d \ln n} \right]_m^2} \quad (2.10)$$

As we shall see in the following section, the experimental value of the right-hand side of (2.10) is approximately two, and hence it follows that  $\Omega_m/\Omega_i \lesssim 1.5$ . In the Appendix, it is shown in the special case of the continuum model that  $\Omega_m$  is similar to the quantity  $(\frac{4}{3}\pi r^3)$ , where  $r$  is the cavity radius, since the static dielectric constant of the dense gas is  $\epsilon = 1.1-1.2$ .

Our interpretation of  $\Omega_i$  defined through  $(da/dn)_m^2 = a_{\text{gas}}^2 \Omega_i^2$  is that it is reflecting a characteristic volume involving the injected electron correlating with a cluster of fluid molecules. In this same context, it is worth adding that it is known from microscopic theory that the density derivative of the fluid structure factor representing pair correlations is related to the three-molecule correlation function  $g_3$ .<sup>11</sup> In a final, fully microscopic theory which has yet to be given, it is therefore already quite clear that multi-particle correlations will play an important role.

Because of this complex situation, we have thought it worthwhile to illustrate the above very general argument, leading inevitably to Eq. (2.9), by the specific example of the Onsager continuum model.<sup>12,13</sup> This is worked out in the Appendix where it is shown in this case that an equation having the form of Eq. (2.9) follows from the model,  $\Omega_i$  being, naturally enough, proportional to the cube of the 'cavity radius'  $r$  in that model as already mentioned above. We prefer, however, to view formula (2.9) as the fundamental one to bring into contact with experiment, both in relation to the magnitude of the characteristic volume  $\Omega_i$ , and its temperature dependence. This can be done in the general context of  $\Omega_i$  reflecting directly electron-molecular cluster correlations and in no way requires any commitment to a continuum model. What the Appendix shows, however, is that such a model is contained, naturally enough, as a special case fitting within the framework leading to Eq. (2.9).



**Figure 1** Arrhenius plots of  $n\mu/T$  for electrons in the dense gas somewhat below the density of  $\mu_{\min}$ , at temperatures near that of the vapor/liquid coexistence. The value of  $n/n_c$  and the Ref. no. are given in brackets: Xe,  $\circ$  (0.50, 4b); Ar,  $\triangle$  (0.37, 3);  $\text{CH}_4$ ,  $\square$  (0.48, 5b);  $\text{C}_2\text{H}_6$ ,  $\diamond$  (0.50, 6). The lowest temperature in each case is that of the coexistence vapor.

### 3 COMPARISON WITH EXPERIMENT

It remains to bring Eq. (2.9) into contact with experiment. First of all, we note that  $\mu_{\min}$  varies strongly with temperature. Using the result (2.2) with  $E$  replaced by the thermal energy  $k_B T$ , it seemed natural from Eq. (2.1) to plot  $\ln(n\mu/T)$  against  $1/T$  at a constant density near that of  $\mu_{\min}$ . Data are not available precisely at  $\mu_{\min}$ , so the nearest lower density was chosen. This led to the results shown in Figure 1; the approximate Arrhenius temperature coefficients of  $\mu/T$  are listed in Table 1. The values of  $E_{\mu/T}$  are relatively large and the behavior is quite general. The temperature coefficient of electron mobility in a dense gas near its vapor/liquid coexistence temperature increases with increasing density up to the critical. The values of the coefficient for different gases

**Table 1** Temperature dependences of electron mobility and structure factor functions in dense gases

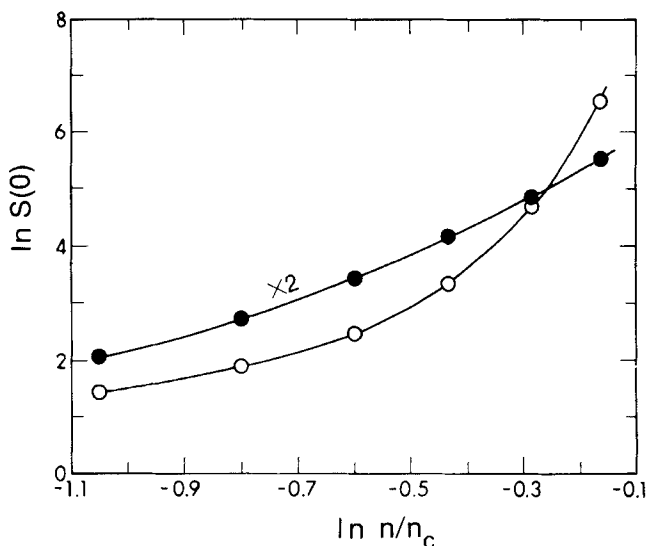
Gas	$n$ ( $10^{26}$ molecule/ $m^3$ )	$n/n_c^a$	$E_{int}^b$ (eV/ent)	Coexistence vapor				at $1.04 T_c$			
				$T$ (K)	$\mu$ ( $10^{-4}$ $m^2/V \cdot s$ )	$S(0)$	Ratio <sup>c</sup>	$T$ (K)	$\mu$ ( $10^{-4}$ $m^2/V \cdot s$ )	$S(0)$	Ratio <sup>c</sup>
Xe	25	0.50	0.66	279	4	8.8	0.56	301	28	4.7	0.60
Ar	30	0.37	0.12	142	230	4.6	0.63	157	570	3.0	0.62
CH <sub>4</sub>	29	0.48	0.13	184	48	8.0	0.58	198	86	4.4	0.60
C <sub>2</sub> H <sub>6</sub>	20	0.50	0.15	298	120	8.8	0.56	318	180	4.7	0.60
G <sup>d</sup>		0.60		0.982 $T_c$		17.0	0.47	1.04 $T_c$		6.7	0.67
		0.70		0.992 $T_c$		52.0	0.46	1.04 $T_c$		9.6	0.78
		0.80		0.996 $T_c$		260.0	1.04	1.04 $T_c$		14.0	1.06

<sup>a</sup> Temperature coefficients of electron mobilities are not available at the density of  $\mu_{min}$  precisely, so we report the closest on the low density side for which data are available, displayed in Figure 1. The value of  $n/n_c$  at which  $\mu_{min}$  occurs in saturated vapor (coexistent with liquid) is 0.8 in Xe, 0.6 in Ar, 0.7 in CH<sub>4</sub> and 1.0 in C<sub>2</sub>H<sub>6</sub>.

<sup>b</sup> Arrhenius temperature coefficient of electron  $\mu/T$ , from Figure 1. This energy is shared by an electron and the cluster of molecules with which it interacts at any given instant. The entity (ent) is the electron plus the scattering cluster and  $E_{int}$  seems to be largely associated with the change of the multi-particle correlation function of the cluster (decreasing the magnitude of the density fluctuations as the fluid is heated and removed from the coexistence region).

$$^c \frac{S(0)}{\left[1 + \frac{d \ln S(0)}{d \ln n}\right]^2}$$

<sup>d</sup> Each of the above gases.



**Figure 2** Density dependence of the structure factor  $S(0)$  in the coexistence vapor (○) and at a constant temperature  $1.04 T_c$  (●);  $n_c$  and  $T_c$  are the density and temperature of the critical fluid, respectively. Experimental data give the same curves for methane<sup>15a</sup> and the three isomers of pentane (*n*-pentane, 2-methylbutane and 2,2-dimethylpropane, Ref. 15b). The law of corresponding states is therefore valid and the curves apply also to xenon, argon and ethane.

are similar at a given  $n/n_c$ , independent of whether the molecules are polar or nonpolar, spherelike or nonspherelike.<sup>14</sup>

We also estimated from available data the variation of the factor  $S(0)/[1 + \{d \ln S(0)/d \ln n\}]^2$  at the densities of the mobilities in Figure 1. This ratio for the somewhat higher density at  $\mu_{\min}$  appears in Eqs (2.10) and (2.9). Relevant data<sup>15</sup> are shown in Figure 2 and listed in Table I. The ratio is nearly constant over the  $\sim 7\%$  increase of  $T$  of interest here, while the mobility increases rapidly. Since  $n_{\min}$  is expected to be only a weak function of  $T$ , it follows that  $\Omega_i$  must vary rather strongly with temperature. This might seem natural since  $\Omega_i$  represents a 'correlation volume' of the injected electron with its environmental 'molecular cluster'. On the other hand, in the Onsager continuum model this would predict that the cavity radius  $r$  should vary strongly with temperature. Baird, using a different method of analysis, concluded that  $r$  varied only weakly with temperature in the continuum framework.<sup>13,16</sup>

The value of  $S(0)$  is much more sensitive to vapor density and temperature than is that of the ratio  $S(0)/[1 + \{d \ln S(0)/d \ln n\}]^2$ . In the coexistence vapor the former increases from 4.6 at  $n/n_c = 0.37$  to 260 at



$n/n_c = 0.80$ , while the latter increases only from 0.63 to 1.04 (Table 1). Our treatment is only approximate, but it encourages further investigation of the implications of this ratio and  $\Omega_t$  for electron transport in dense gases.

The apparent value of  $\Omega_t$  is similar to the average volume  $\Omega_m$  occupied by a molecule in the dense gas, yet  $\Omega_t$  decreases with increasing temperature in a zone just above the vapor/liquid coexistence temperature. This is because  $n_{\min}$  is large enough that collective interactions have begun to decrease the effective scattering cross section of the molecules in the hard gas ( $T \gg T_{\text{coexistence}}$ ).

#### 4 SUMMARY

Taking the formula (2.1) as starting point, and representing the momentum transfer cross-section  $\sigma_m$  by an average force,<sup>9</sup> or equivalently a force-force correlation function,<sup>10</sup> one is led to a definition via Eq. (2.8) of a 'characteristic volume for electron transport',  $\Omega_t$ , in terms of the density derivative of the scattering length at the minimum of the mobility-density plot, in units of the scattering length in the dilute gas. Equation (2.9) then follows, which relates the product  $n_{\min}\mu_{\min}$ , in units of the Lorentz limit  $\lim_{n \rightarrow 0}(n\mu)$ , to the ratio  $(\Omega_m/\Omega_t)^2$  and the unperturbed liquid structure. This, however, appears through a density derivative, which in turn involves a three molecule correlation function. The value of  $\Omega_m/\Omega_t$ , representing the ratio of molecular volume to volume for transport, is  $\sim 1$  and has to be strongly temperature dependent if one is to fit  $\mu_{\min}$  against  $T$  data. If the Onsager continuum model is employed, this would imply the cavity radius  $r$ , usually assumed independent of density at constant temperature, to vary with temperature.

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## Appendix Characteristic volume $\Omega_t$ for electron transport, calculated in Onsager continuum model

In Eq. (2.8) we have given a definition of a characteristic volume  $\Omega_t$  for electron transport in insulating fluids. Eventually of course,  $\Omega_t$  must be calculated from first principles, using Eqs (2.2), (2.3) and (2.5). This remains a problem of considerable complexity because of (i) the intrinsic disorder and (ii) the need for detailed knowledge of the local molecular environment of the injected electron.

Therefore, it seemed of interest to illustrate Eq. (2.8) by using, in an approximate manner outlined below, the Onsager continuum model.<sup>12</sup> Within this model, we can adapt the recent discussion of the scattering length  $a$  by Baird<sup>16</sup> to bring it into contact with Eq. (2.8).

Baird chooses to write the scattering length  $a$  itself in the form

$$a = a_{\text{gas}} f_1(\varepsilon, u_1) \quad (\text{A1})$$

where  $\varepsilon$  is the fluid dielectric constant. This, as he points out, can be usefully approximated by the Böttcher-Onsager form. The variable  $u_1$  in the continuum model is  $\alpha/r^3$ , where  $\alpha$  is the polarizability and  $r$  is the 'cavity radius'. Baird's table contains the value  $u_1 = 8.34 \times 10^{-2}$  for Ar at  $T = 298^\circ\text{K}$ , and since this is substantially less than unity, we shall neglect it relative to unity in the formulae derived below.

Though complete results are complicated, we can make contact with the formula (2.8) as follows:

- i) Form  $\partial a / \partial n$  from Eq. (A1) as  $a_{\text{gas}} (\partial f_1 / \partial \varepsilon) \partial \varepsilon / \partial n$

ii) Evaluate  $(\partial f_1/\partial \varepsilon)$  at the place where  $f_1 = 0$ . This does not correspond to the mobility minimum, but rather to its maximum at a higher density. However, Baird's table shows that  $a$  is almost linear in  $n$  over a substantial range, so that little error is thereby introduced.

iii) Evaluate  $\partial \varepsilon/\partial n$  using the Böttcher-Onsager formula.<sup>12,13</sup>

As to step (i), one finds with  $u_1 \ll 1$

$$\left. \frac{\partial f_1}{\partial \varepsilon} \right|_{f_1=0} \simeq \frac{-1}{u_1 \varepsilon (2\varepsilon + 1)}. \quad (\text{A2})$$

Next we employ the Böttcher-Onsager formula, which can be written

$$\frac{12\pi \varepsilon n}{(\varepsilon - 1)(2\varepsilon + 1)} = \frac{1}{\alpha} - \frac{1}{r^3} \frac{(2\varepsilon - 2)}{(2\varepsilon + 1)} \quad (\text{A3})$$

Assuming again  $u_1 \ll 1$ , this yields

$$\frac{d\varepsilon}{dn} \simeq -12\pi\alpha\varepsilon^3/[\varepsilon + 2] \quad (\text{A4})$$

and hence it follows that

$$\frac{\partial a}{\partial n} = \frac{a_{\text{gas}} 12\pi\alpha\varepsilon^3}{u_1 \varepsilon [2\varepsilon + 1][\varepsilon + 2]} = \frac{3a_{\text{gas}}(4\pi r^3)\varepsilon^2}{[2\varepsilon + 1][\varepsilon + 2]} \quad (\text{A5})$$

Comparison with Eq. (2.8) establishes the desired point that in the Onsager model the 'characteristic volume for transport' is proportional to the cavity radius cubed.