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Theory of electron mobility in dense gases*

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A new extended theory of electron transport in dense gases is presented. It is shown that positive and negative density effects can be explained in terms of a single unifying theory. The agreement between theory and experiment is extremely good over a wide range of pressure and temperature in gases with a negative effect, such as He and H_2. Some further improvements of the theory in gases with elevated polarizability seem to be necessary for a better quantitative agreement with experimental data, even if the agreement in Ar makes us confident that the proposed theoretical approach can be correct. In the light of our unifying theory, previous theoretical models are analyzed and it is shown that almost all can be obtained under special conditions.

I. INTRODUCTION

The density dependence of the electron drift velocity W in dense gases at a given (small) field-to-density ratio E/N, is an established experimental phenomenon first observed almost twenty years ago.[1] Since then, positive and negative effects (i.e., drift velocities that increase or decrease with the density N) have been observed in a number of gases under different conditions of pressure and temperature. For the most part, these results have been already reviewed.[2-6] In Sec. VI, those experimental data that are particularly significant as a test of our theoretical approach will be reported.

As concerns theory, several more or less debated models have been proposed in the last years to explain the experimental evidence. However, because of the difficulties the problem presents from the analytical and, even more, from the interpretative points of view, the situation still appears to be rather unsatisfactory. In this paper, after a brief analysis of the theoretical models proposed up to now, we shall present a multiple-scattering theory which in our opinion gives a satisfactory answer to the conceptual problem. It is shown, in fact, how positive and negative effects can be (quantitatively) explained in terms of a *single unifying theory* in which localization phenomena, which appear so evident in these systems, are also taken into correct consideration. In order to reduce formal difficulties and in an attempt to give a more satisfactory answer to the conceptual problem, the restriction to thermal electrons will be retained. On the other hand, no rigorous attempt has yet been done to develop a transport theory for hot electrons. The proposed extensions[7,8] to elevated E/N of some theories developed for thermal electrons appear to be reasonable simple ways to solve the problem, but they still need sound mathematical justifications.

II. THEORETICAL MODELS OF THE LITERATURE

The first experimental observations of a density dependence of electron drift velocity were all relative to gases (i.e., N_2, H_2, CO_2, D_2, C_2H_6) where the effect is negative.[1-6] Frommhold[9] suggested that the lower drift velocities at higher densities were due to the thermal electrons spending part of their transit time as negative ions, trapped in postulated Feshbach resonances associated with excited rotational states of the molecules.[2] This model, however, which only provides negative effects in molecular gases, was soon found to be inconsistent with the discovery that the effect is positive in CH_4 and that positive and negative effects are possible in monoatomic gases.[2-6]

Legler[10] proposed an alternative model based on the observation that, under the conditions of some experiments (where $N \gtrsim 10^{20}\ \text{cm}^{-3}$), the wavelength of the low-energy electrons becomes of the same order as the mean-free path. For this reason, Legler suggested that the gas can be treated as a continuous medium and that multiple-scattering rather than single-scattering theory must be used. Legler applied multiple-scattering theory in the form of a *shift of the kinetic energy* which, according to a theory of Fermi,[11] can be related to the scattering length. This, in turn, leads to an explanation of both negative and positive effects according to the sign of the scattering length. Also, this theory had only a limited success as it was unable to correctly account for the experimental results if not in exceptional cases,[2] at extremely elevated values of N.

Atrazev and Yakubov[7] presented two distinct interpretative models for positive and negative effects. The positive effect in gases with large polarizability is explained in terms of a density-dependent attenuation of the polarizability α by a factor of $(1+8\pi\alpha N/3)$, as a consequence of the dipole-dipole interactions induced by the electrons on the atoms, which finally leads to a new effective cross section

$$q_{\text{eff}}=q(1+2\pi^2\alpha^2 N/3a_0 r_0 a)^2 ,$$

where a (<0) is the scattering length, a_0 the Bohr radius, and r_0 is a not-well-defined "atomic radius," which is fixed by imposing agreement between theory and experiment at a given N. On the contrary, the negative effect (in atoms with low polarizability) is explained in terms of a quantum-mechanical multiple-scattering model *apparently* leading to a collision frequency increased by a factor of $(1+\lambda qN/\pi)$, λ being the electron wavelength. The reduced electron drift velocity W/W_0 is then written to change with N according to the equation

$$\frac{W}{W_0}=1-\frac{1}{2\sqrt{\pi}}Nq\lambda , \qquad (2.1)$$

where $\lambda=h/\sqrt{2mkT}$ and where $W_0=W(N\rightarrow 0)$ is the classical drift velocity. The momentum-transfer cross section q is also given a constant value when writing W/W_0 in this form. Equation (2.1) agrees well with the experimental data in slightly dense gases where negative effects have been observed. However, in spite of this success, the derivation of Eq. (2.1) seems to be incorrect. In fact, according to a theory developed by Yakubov,[12] the corrective term should be divided by about a factor of 2. But even the good agreement with experimental data in Ar and CH_4 did not seem to be a sufficient support to the theory of positive effect presented by Atrazev and Yakubov. In fact, the presence of a parameter r_0, whose choice is somewhat critical, is a weakness of the theory.

Almost simultaneously and independently, Braglia and Dallacasa[8] proposed a quantum-mechanical model of both negative and positive effects. The theory, in a sense, extends Fermi's theory of Legler's model[13] and also is based on the observation that multiple-scattering effects can be properly accounted for in terms of scattering amplitude (or t matrix). Braglia and Dallacasa[8] also arrived at Eq. (2.1) for the low-density negative effect and at an apparently satisfactory explanation of the positive effect in Ar. In our opinion, this theory still remains as that which better explains the low-density negative effects from the conceptual and mathematical points of view, despite an assumption of the energy dependence of the scattering amplitude which, probably because of an insufficient justification, gives place to some criticism. But we shall return to this question below. The positive effect in Ar still is explained in terms of a kinetic-energy shift and an effective scattering length. Of course, the limits of similar assumptions will also be reconsidered below. Here, we shall limit ourselves to mention that Gryko and Popielawski,[14] on the line of a previous work,[15] have recently attempted to extend the Braglia and Dallacasa[8] theory for Ar to higher powers of N than the first. However, it seems to us that on the basis of our theory developed below, this extension is not fully consistent with the orders of the approximations underlying our mentioned first-order theory.

Schwarz[6] applied the Eggarter and Cohen percolation model with a proper extension of the technique for the electronic-trapping calculation. In this way, Schwarz is apparently led to a satisfactory interpretation of the experimental results in He at very low temperatures, but in terms of a distance (over which the potential fluctuations occur) as a parameter which must be fixed empirically. In spite of this weakness of the theory and the apparent substantial difference with our approach, we believe that the two approaches have many more points of contact than suspected *a priori*. Therefore, we shall return briefly to this subject below.

The last theoretical approach that remains to be mentioned at this point is due to O'Malley[16] who proposed an interpretative model of positive and negative effects. Really, apart from the choice of the shift and the quantitative agreement with experimental data, the positive effect still is explained in terms of a kinetic-energy shift in the electron-collision frequency. Therefore, from a conceptual point of view the interpretation of the phenomenon is on the same lines of previous models. However, the equation that O'Malley arrived at with speculative arguments seems to find better theoretical justification in our theory, for not-too-small values of N. This will be shown below. As concerns the negative effect, the phenomenon is explained in terms of a modification of the electron energy distribution to take account of a supposed electron trapping in spatially localized states with negative kinetic energies, as a consequence of the uncertainty principle. In this way, O'Malley is led to write that[17]

$$W=\frac{4}{3}\frac{eE}{m\sqrt{\pi}}(kT)^{-5/2}$$

$$\times\int_0^\infty \epsilon^{3/2}\nu^{-1}(\epsilon)\exp\left[-\frac{(\epsilon+\Gamma)}{kT}\right]d\epsilon\ , \qquad (2.2)$$

$$\simeq W_0\exp\left[-\bar{\Gamma}/kT\right]\ , \qquad (2.3)$$

where e is the electron charge, m the electron mass, k the Boltzmann constant, T the gas temperature, $\nu(\epsilon)\equiv N\sqrt{2\epsilon/m}\,Q(\epsilon)$ the total electron-collision frequency, and $\Gamma=(h/\pi\sqrt{2m})NQ\sqrt{\epsilon}$. Here, Q is the total electron cross section and h the Planck constant. As suggested by O'Malley, in Eq. (2.3) Γ is taken outside the integral as an average. In the light of the theory presented below, Eq. (2.2) finds its justification at the lower densities.

After this brief analysis of the various approaches that have been proposed over the last ten years, in spite of the disagreement between the different theoretical models, one is led to conclude that a correct explanation of the phenomenon must be possible in terms of a multiple-scattering theory (both for the positive and the negative effects). In fact, almost all the authors seem to indicate that this is the direction that must be taken. Below, we shall try to show how the positive and negative density effects can be explained in terms of a general unifying theory. The conditions will also be discussed under which the theoretical models presented above can be obtained from the general theory.

III. FORMALISM AND APPROXIMATION OUTLINE

A few elements of the mathematical formalism, which are needed for a better comprehension of the electron transport theory developed in Sec. IV, will be given first together with an outline of the approximations that are useful for effective calculations.

A. The Green operator approximation

To start with, we introduce the Green operator $G(\epsilon)$ defined as

$$G(\epsilon)=(\epsilon+i\eta-H)^{-1}\ , \qquad (3.1)$$

where $\eta=0_+$ is an infinitesimal positive quantity and $H=p^2/2m+V(\vec{r})$ is the Hamiltonian of an electron in the potential $V(\vec{r})$. For an electron in a gas, $G(\epsilon)$ is a function of the atom positions through $V(\vec{r})$. Since the atoms are statistically distributed, it is useful to introduce the configurational average of $G(\epsilon)$, for example, $\mathcal{G}(\epsilon)=\langle G(\epsilon)\rangle$. More, in particular, Eq. (3.1) is conveniently rewritten as[17]

$$\mathcal{G}(\epsilon)=\mathcal{G}_0(\epsilon)+\mathcal{G}_o(\epsilon)\mathcal{T}(\epsilon)\mathcal{G}_0(\epsilon)\ , \qquad (3.2)$$

where $\mathcal{G}_0(\epsilon)=G_0(\epsilon)\equiv[G(\epsilon)]_{V=0}$, and $\mathcal{T}(\epsilon)=\langle T(\epsilon)\rangle$ with the t matrix $T(\epsilon)$ defined by the equation

$$T(\epsilon)=V+VG_0T(\epsilon)\ . \qquad (3.3)$$

When writing that $V=\sum_i V_i$, V_i being the contribution to the potential V from the ith atom (localized at $\vec{R}_i$), Eq. (3.3) leads to the following development of $T(\epsilon)$[18]:

$$T(\epsilon)=\sum_i t_i+\sum_{i\neq j} t_iG_0t_j$$

$$+\sum_{\substack{i\neq j\\ j\neq k}} t_iG_0t_jG_0t_k+\cdots\ , \qquad (3.4)$$

t_i being the t matrix of the ith atom. The contributions from atomic correlations are represented by the multiple sums of the right-hand side (rhs). Now, the quantity of major interest for our discussion of Sec. IV, is the diagonal representation $\mathcal{G}(\vec{k},\epsilon)$ of $\mathcal{G}(\epsilon)$ on the $\vec{k}$ basis, i.e., $\mathcal{G}(\vec{k},\epsilon)=\mathcal{G}_{\vec{k}\vec{k}}(\epsilon)$, which will be given here in the canonical form

$$\mathcal{G}(\vec{k},\epsilon)=[\epsilon+i\eta-\epsilon_{\vec{k}}-\Sigma(\vec{k},\epsilon)]^{-1}\ , \qquad (3.5)$$

where $\epsilon_{\vec{k}}=(\hbar^2/2m)\vec{k}^2$ is the electron (kinetic) energy and $\Sigma(\vec{k},\epsilon)$ is the self-energy[17] (note that $\Sigma\mathcal{G}=\langle VG\rangle$). The appropriate expression of $\Sigma(\vec{k},\epsilon)$ can be obtained from Eqs. (3.2) and (3.4) or, directly, from Eq. (3.1). Generally, this is a difficult problem but useful approximations can be more simply obtained in some significant cases.

The first case is one where the atom number density N is sufficiently low so that the correlation terms may be neglected in Eq. (3.4). In this case, $\mathcal{T}(\vec{k},\epsilon)=Nt(\vec{k},\epsilon)$ and from Eq. (3.2), we may also expect that

$$\mathcal{G}(\vec{k},\epsilon)=(\epsilon+i\eta-\epsilon_{\vec{k}})^{-1}$$

$$+(\epsilon+i\eta-\epsilon_{\vec{k}})^{-2}Nt(\vec{k},\epsilon)\ , \qquad (3.6a)$$

$$\simeq[\epsilon+i\eta-\epsilon_{\vec{k}}-Nt(\vec{k},\epsilon)]^{-1}\ , \qquad (3.6b)$$

where $t(\vec{k},\epsilon)=t_{\vec{k}\vec{k}}(\epsilon)$ is the t matrix (in the momentum-basis representation) of a single atom. A comparison of Eq. (3.6b) with Eq. (3.5) then leads one to write that, in the low-density limit,

$$\Sigma(\vec{k},\epsilon)=Nt(\vec{k},\epsilon)\ . \tag{3.7}$$

This result will also be used below to study electron transport in gases, but its range of validity is generally very restricted.[17] When N is increased from very low values, approximation (3.6b) becomes invalid and correlations can also become important.

Another important case is one where the atom density still is sufficiently low that the position $\mathcal{T}(\vec{k},\epsilon)=Nt(\vec{k},\epsilon)$ is permitted, but elevated enough to make Eq. (3.7) to fail. This assumption is generally justified with good accuracy for the physical situations of interest in this paper as the correlation terms are expected to contribute to $\mathcal{T}(\epsilon)$ when the electron wavelength is of the same order as the mean-free path l. But situations where this happens for a non-negligible fraction of electrons are only found for the uppermost densities and the lowest temperatures in the experiments of our interest. In fact, for electrons in gases, it turns out that atomic correlations can still be neglected at values of N so elevated that the *eikonal* approximation[19] can be retained. In this case, the large random variations of the potential over a de Broglie wavelength will, in a Fourier representation, only affect the short-wavelength part of the spectrum and thus be unimportant for the scattering. Under these conditions, one can assume that the self-energy, following from a comparison of Eqs. (3.5) and (3.6a), is a slowly varying function of $\vec{k}$ such that $\Sigma(\vec{k},\epsilon)\simeq\Sigma(\vec{k}_0,\epsilon)$, $\vec{k}_0=\vec{k}_0(\epsilon)$ being an effective momentum which satisfies the equation[20]

$$\epsilon-\epsilon_{\vec{k}_0}-\Delta(\vec{k}_0,\epsilon)=0\ , \tag{3.8}$$

where $\Delta(\vec{k}_0,\epsilon)=\mathrm{Re}\Sigma(\vec{k}_0,\epsilon)$. Similar approximations and their limits of validity have already been discussed in the literature.[19] Here we are interested to observe that two distinct solutions of Eq. (3.8) exist; that is,

$$\Delta(\vec{k}_0,\epsilon)=-N\delta(\vec{k}_0,\epsilon)$$

or $\hfill$ (3.9a)

$$\epsilon_{\vec{k}_0}=\epsilon+N\delta(\vec{k}_0,\epsilon)\ ,$$

and

$$\Delta(\vec{k}_0,\epsilon)=N\delta(\vec{k}_0,\epsilon)=0$$

or $\hfill$ (3.9b)

$$\epsilon_{\vec{k}_0}=\epsilon\ ,$$

where $\delta(\vec{k}_0,\epsilon)=\mathrm{Re}t(\vec{k}_0,\epsilon)$. There is no reason to reject *a priori* one of these solutions. So, both cases will be studied in detail when the specific problem of electron transport in gases will be considered.

B. *T*-matrix approximation

Below, the t matrix $t(\vec{k},\epsilon)$ will be approximated by its value $t(\epsilon_{\vec{k}})$ on the energy shell for any density N of interest in this paper. This simplification could be too drastic for atoms with strong polarization. For instance, in gases such as Ar, it could represent only a first approximation. However, the assumption appears to be entirely justified for gases where the cross sections are weakly dependent on the electron energy. But we shall return to this comment below. Here, we shall restrict ourselves to the observation that for low electron energies the following standard result is valid[17,20]:

$$\delta(\epsilon_{\vec{k}})=\delta(\vec{k}_0,\epsilon)\,|_{\,\text{shell}}=\frac{2\pi\hbar^2}{m}a+O(\epsilon_{\vec{k}})\ , \tag{3.10}$$

where the $O(\epsilon_{\vec{k}})$ are generally much smaller than the reported term proportional to the scattering length a. However, for higher energies, the development (3.10) must be modified. To this end, we refer ourselves to the dispersion relation satisfied by $t(z)$ on the complex plane, that is,[20]

$$Nt(z)=\langle V\rangle+\frac{\hbar N}{\sqrt{2m}}\frac{1}{\pi}\int_0^\infty\frac{\sqrt{\epsilon'}Q(\epsilon')}{z-\epsilon'}d\epsilon'+R(z)\ , \tag{3.11}$$

where $z=\epsilon+i\eta$ $(\eta=0_+)$, and where $\langle V\rangle=\int d\vec{r}\,V(\vec{r})$ is the average potential, $Q(\epsilon)$ is the total electron-collision cross section, and $R(z)$ is the contribution from bound states which for our purposes can be neglected. Since $t(z)$ is an analytical function on the complex plane (apart from the real positive axis), and the integral of Eq. (3.11) is a Cauchy integral, the derivative $t'(z)$ will exist for $z\neq\epsilon\geq 0$. After some algebra t' is found to be given by the equation

$$t'(z)=\frac{1}{2}\frac{t(z)-\delta(0)}{z}+\frac{1}{\pi}\frac{\hbar N}{\sqrt{2m}}\int_0^\infty\frac{Q'(\epsilon')}{Q(\epsilon')}\frac{\sqrt{\epsilon'}Q(\epsilon')}{z-\epsilon'}d\epsilon'\ . \tag{3.12a}$$

Now letting $z=\epsilon+i\eta$ and $\eta\rightarrow 0$, we find the following real part of $t'(z)$:

$$\delta'(\epsilon)\simeq\left[\frac{1}{2\epsilon}+\frac{Q'(\epsilon)}{Q(\epsilon)}\right][\delta(\epsilon)-\delta(0)]\ . \qquad (3.12\text{b})$$

The approximation (3.12a) to (3.12b) is valid for not-too-small energies and slowly varying $Q'(\epsilon)$. In this case, integration of $\delta'(\epsilon)$ leads to the following real part of $t(z)$:

$$\delta(\epsilon)=\langle V\rangle+A\frac{2\hbar}{\sqrt{2m}}\sqrt{\epsilon}Q(\epsilon)\ . \qquad (3.13)$$

Under the conditions of our interest (scattering from potential fluctuations), the constant A can be obtained by having recourse to the localization criterium $\delta'(\epsilon_c)=1$, ϵ_c being the mobility edge proposed in some localization theories.[21,22] According to the Yoffe and Regel principle,[23] this is equivalent to assuming that the electron wavelength $\lambda\!\!\!^{-}=\hbar/\sqrt{2m\epsilon}$ and the electron mean-free path $l=1/NQ(\epsilon)$ are equal for $\epsilon=\epsilon_c$. The result is that

$$A=1/[1+2\epsilon_c Q'(\epsilon_c)/Q(\epsilon_c)]\ .$$

However, in all of the cases considered in this paper it can also be assumed that $A\simeq 1$. In fact, the contribution from the term involving the logarithmic derivative of $Q(\epsilon)$ can be neglected with good approximation. It is interesting to observe that Eq. (3.13) can also constitute a rigorous result for certain cross sections which permit a direct integration of the dispersion relation (3.11). So for instance, if $Q(\epsilon)=Q_0(\epsilon_1/\epsilon)^n$ for $\epsilon>\epsilon_1$ and $Q(\epsilon)=Q_0$ for $\epsilon<\epsilon_1$, where n is a positive integer and ϵ_1 is a fixed (arbitrary) energy, from Eq. (3.11) it is found that

$$\delta(\epsilon)=\begin{cases} t_1(0)+B\epsilon \quad (\epsilon<\epsilon_1) & (3.14)\\ \langle V\rangle+A\dfrac{2\hbar}{\sqrt{2m}}\sqrt{\epsilon}Q(\epsilon) \quad (\epsilon>\epsilon_1) & (3.15)\end{cases}$$

where $B=2nQ_0/(\frac{1}{2}+n)\sqrt{\epsilon_1}$ is a constant. This result also shows that Eq. (3.13) is only appropriate for higher energies than those required for the validity of Eq. (3.10).

As a final observation, it will be noted that in the presence of a resonance at $\epsilon=\epsilon_R$, the two previous representations of $\delta(\epsilon)$ given in Eqs. (3.10) and (3.13) both become invalid. The dispersion relation (3.11), however, preserves its validity and may be used for the study of $t'(z)$. To obtain an analytical result very simply, a model cross section is assumed such that $Q(\epsilon)=Q_1$ for $\epsilon<\epsilon_R-\Gamma_R/2$, $Q(\epsilon)=Q_2$ for $\epsilon>\epsilon_R+\Gamma_R/2$, and $Q(\epsilon)=Q_0$ in the resonance energy region with Q_1 and $Q_2\ll Q_0$. In this case, it is found that

$$t'(z)=\frac{t(z)-\delta(0)}{2z}+\frac{1}{\pi}\frac{\hbar N}{\sqrt{2m}}\left[\frac{\sqrt{\epsilon_R-\Gamma_R/2}}{z-(\epsilon_R-\Gamma_R/2)}-\frac{\sqrt{\epsilon_R+\Gamma_R/2}}{z-(\epsilon_R+\Gamma_R/2)}\right]Q_0\ , \qquad (3.16)$$

and if $z\simeq\epsilon_R$,

$$\delta'(z)\simeq\delta'(\epsilon_R)=\nu_R\tau_R\ , \qquad (3.17)$$

where $\nu_R=\sqrt{2\epsilon_R/m}\,NQ_0$ is the electron-collision frequency at the resonance and $\tau_R=4\hbar/(2\pi\Gamma_R)$ approximately corresponds to the mean life of the resonant state. This result appears to be a special case also deducible in the context of the scattering theory in terms of the time of delay in the collision,[24] which is here assimilated to τ_R.

IV. DRIFT VELOCITY

The electron drift velocity in the limit $E/N\to 0$, i.e., for thermal electrons, can be obtained by using the linear response theory of disordered systems. We shall discuss now two different formulations which both have recourse to the Green's function we have discussed in Sec. III.

(1) According to Rubio's theory,[25] the drift velocity can be given the form

$$W=eE\frac{\sqrt{2m}}{3\pi^3\hbar^3}\int_{-\infty}^{+\infty}d\epsilon\left[-\frac{df}{d\epsilon}\right]\times\int_0^\infty d\epsilon_{\vec{k}}\,\epsilon_{\vec{k}}^{3/2}\tau(\epsilon,\vec{k})\rho(\epsilon,\vec{k})\ , \qquad (4.1)$$

where (note that here δ is Dirac's δ function)

$$\rho(\epsilon,\vec{k})=\frac{\Gamma(\vec{k},\epsilon)}{[\epsilon-\epsilon_{\vec{k}}-\Delta(\vec{k},\epsilon)]^2+\Gamma^2(\vec{k},\epsilon)}$$

$$\simeq\pi\delta(\epsilon-\epsilon_{\vec{k}}-\Delta(\vec{k},\epsilon))\ , \qquad (4.2)$$

since $\Gamma(\vec{k},\epsilon)=\mathrm{Im}\Sigma(\vec{k},\epsilon)\propto N$ is small for the atomic densities considered here. Moreover, $\tau(\epsilon,\vec{k})$

is a time of flight which is given by the equation

$$\tau^{-1}(\epsilon,\vec{k})=\frac{m\sqrt{2m}}{(2\pi)^2}\int\int d\omega\, d\epsilon_{\vec{k}'}\sqrt{\epsilon_{\vec{k}'}}\,\Omega(\vec{k},\vec{k}')\times(1-\cos\vartheta)\rho(\epsilon,\vec{k}')\ , \tag{4.3}$$

$d\omega=2\pi\sin\vartheta\, d\vartheta$ being an element of solid angle in the $\vec{k}'$ direction. The transition probability density Ω is the kernel of a Bethe-Salpeter equation[15–25] which can be given in terms of the matrix elements of $\mathcal{T}_{\vec{k}\vec{k}'}(\epsilon)$. To the order of the approximations of this paper, i.e., consistently with Eq. (3.7), it is

$$\mathcal{T}_{\vec{k}\vec{k}'}(\epsilon)=Nt_{\vec{k}\vec{k}'}(\epsilon)\ ,$$

so that[15–25]

$$\Omega(\vec{k},\vec{k}')\simeq N\,|t_{\vec{k}\vec{k}'}|^2 S(\vec{k}-\vec{k}')\ , \tag{4.4}$$

where $t_{\vec{k}\vec{k}'}(\epsilon)$ are the matrix elements of the t matrix of a single atom, and $S(\vec{k}-\vec{k}')$ is the static structure factor of the gas. Then, in light of this result and of Eq. (4.2), it can be written that

$$\tau^{-1}(\epsilon,\vec{k})=\nu(\epsilon)\simeq\sqrt{(2/m)[\epsilon-\Delta(\vec{k}_0,\epsilon)]}\,Nq(\epsilon-\Delta(\vec{k}_0,\epsilon))S(0)\left|1+\frac{\partial\Delta(\vec{k}_0,\epsilon)}{\partial\epsilon_{\vec{k}_0}}\right|^{-1}\ , \tag{4.5}$$

where q is the momentum-transfer cross section. As concerns the momentum $\vec{k}_0$, it is found to be the root of the equation

$$\epsilon-\epsilon_{\vec{k}}-\Delta(\vec{k},\epsilon)=0\ , \tag{4.6}$$

which follows from the δ-function approximation of Eq. (4.2) and agrees with Eq. (3.8). This means that $\vec{k}_0$ is the effective momentum we mentioned above.

(2) When the atom number density is sufficiently low, it is possible to obtain W under the condition (3.7) that $\Sigma(\vec{k},\epsilon)=Nt(\vec{k},\epsilon)=Nt(\epsilon)$. In this case $S(0)\simeq 1$, while from Eq. (4.5) it follows that

$$\nu(\epsilon)=\sqrt{(2/m)[\epsilon-N\delta(\epsilon)]}\times Nq(\epsilon-N\delta(\epsilon))\ , \tag{4.7}$$

which permits us to write

$$W=\frac{eE}{N}\frac{m}{3\pi^2\hbar^3}\times C\beta\int_{\epsilon_0}^{+\infty}d\epsilon\frac{[\epsilon-Nt(\epsilon)]}{q(\epsilon-Nt(\epsilon))}e^{-\beta\epsilon}\ , \tag{4.8}$$

ϵ_0 being the solution of the equation $\epsilon-N\delta(\epsilon)=0$, $Ce^{-\beta\epsilon}$ the normalized (Maxwellian) electron-energy distribution and $\beta=1/kT$. Introduction of the new integration variable $u=\epsilon-Nt(\epsilon)$ leads us to write

$$W\simeq\frac{eE}{N}\frac{m}{3\pi^2\hbar^3}C\beta\int_0^{\infty}du\left[1+N\frac{dt(u)}{du}\right]\frac{u}{q(u)}\times e^{-\beta[u+Nt(u)]}\ . \tag{4.9}$$

(3) As mentioned, better approximations at higher densities are provided by Eqs. (3.9) for $\Delta(\vec{k}_0,\epsilon)$. In this case, we have the two solutions, $\epsilon_{\vec{k}_0}=\epsilon$ and $\epsilon_{\vec{k}_0}=\epsilon+N\delta(\vec{k}_0,\epsilon)$, which by virtue of Eq. (4.5), lead to the following alternative equations for the drift velocity:

$$W=eE\frac{\sqrt{2m}}{3\pi^2\hbar^3}C\beta\int_0^{\infty}d\epsilon_{\vec{k}}\frac{\epsilon_{\vec{k}}^{3/2}}{\nu(\epsilon_{\vec{k}}-T_{1\vec{k}})}\times e^{-\beta(\epsilon_{\vec{k}}-T_{1\vec{k}})}\ , \tag{4.10}$$

with $T_{1\vec{k}}=N\delta(\epsilon_{\vec{k}})$ and

$$W=eE\frac{\sqrt{2m}}{3\pi^2\hbar^3}C\beta\int_{\epsilon_0}^{\infty}d\epsilon_{\vec{k}}\frac{\epsilon_{\vec{k}}^{3/2}}{\nu(\epsilon_{\vec{k}}+T_{1\vec{k}})}\times\left[1-\frac{dT_{1\vec{k}}}{d\epsilon_{\vec{k}}}\right]e^{-\beta\epsilon_{\vec{k}}}\ , \tag{4.11}$$

where now $T_{1\vec{k}}=N\delta(\epsilon_{\vec{k}}+T_{1\vec{k}})$. The energy ϵ_0 in the latter equation is the zero of $1-dT_{1\vec{k}}/d\epsilon_{\vec{k}}=0$. It corresponds to the mobility edge,[23–26] which shows that Eq. (4.11) can describe situations where localization phenomena from potential fluctuations are possible.[6] Of course, Eqs. (4.10) and (4.11) appear to be mutually excluding equations since Eq. (4.10) becomes meaningless for $T_{1\vec{k}}>0$ (as it happens in He, N_2, and H_2), while Eq. (4.11) becomes meaningless for $T_{1\vec{k}}<0$ (as in Ar). Then, it sounds natural to associate Eqs. (4.10) and (4.11) to the two distinct real cases where $T_{1\vec{k}}<0$ and $T_{1\vec{k}}>0$, respectively. However, it is possible that the general solution really corresponds to a weighted average of the two drift velocities.

(4) It is worth noting that Eqs. (4.10) and (4.11) in general do not lead to Eq. (4.9) in the limit as $N\rightarrow 0$. This result confirms that the approxima-

tions underlying the two results (4.10) and (4.11) correspond to a different higher range of density than that involved by Eq. (4.9). However, Eq. (4.11) can lead to the same Eq. (4.9) in the particular case when use is made of Eq. (3.13) with $\langle V \rangle = 0$ (potential fluctuations). In fact, for $T_{1\vec{k}} > 0$, to the lowest order in N, both Eqs. (4.9) and (4.11) can be given the form

$$W = eE \frac{\sqrt{2m}}{3\pi^2\hbar^3} C\beta \int_0^\infty du \frac{u^{3/2}}{\nu(u)} e^{-\beta[u+\tilde{\Gamma}(u)]} , \tag{4.12}$$

where

$$\tilde{\Gamma}(u) = \frac{2}{3} \frac{h}{\pi} \frac{\sqrt{u}}{\sqrt{2m}} NQ(u) .$$

To obtain this result it is also supposed that $Q \simeq$ const. Equation (4.12) is in agreement with the proposal (2.2) by O'Malley[16] according to which the uncertainty principle allows the electrons to assume negative kinetic energies, i.e., $u < 0$, in a range of the order of $\tilde{\Gamma}(u)$ with a consequent reduction $e^{-\beta\tilde{\Gamma}}$ of the electron population $e^{-\beta u}$, which contributes to the drift speed W. In light of the present theory, a similar interpretation appears to be only justified at the lower values of N while it fails as N is increased.

(5) As mentioned above, we have been led to our conclusions by following two distinct approaches. The alternative method which can be used for the calculation of electron drift velocity is that based on the coherent potential approximation (CPA) developed by Velicky,[27] according to which W can be given the form

$$W = \frac{eE}{2\pi} \frac{2\sqrt{2m}}{3\pi^3\hbar^3} \int_{-\infty}^{+\infty} d\epsilon \left[-\frac{df}{d\epsilon} \right] \times \int_0^\infty d\epsilon_{\vec{k}} \epsilon_{\vec{k}}^{3/2} \rho^2(\epsilon, \vec{k}) . \tag{4.13}$$

With the use of the same approximation (4.2) for $\rho(\epsilon, \vec{k})$, Eq. (4.13) can be given the form

$$W = \frac{eE}{2\pi} \frac{\sqrt{2m}}{3\pi^3\hbar^3} \int_0^\infty d\epsilon_{\vec{k}} \epsilon_{\vec{k}}^{3/2} \times \int_{-\infty}^{+\infty} \left[-\frac{df}{d\epsilon} \right] \frac{\rho(\epsilon, \vec{k})}{\Gamma(\epsilon, \vec{k})} . \tag{4.14}$$

Finally, using the optical theorem, as proposed by Rubio,[25] in the form

$$\Gamma(\epsilon, \vec{k}) = \frac{1}{(2\pi)^3} \int d\vec{p}\, \Omega(\vec{k}, \vec{p}) \rho(\epsilon, \vec{p}) , \tag{4.15}$$

one sees that Eq. (4.13) agrees with Eqs. (4.1) and (4.3) of Rubio's theory for isotropic scattering,[14] in which case the contribution from the $\cos\vartheta$ term in Eq. (4.3) vanishes. For atoms with a total cross section different from that for momentum transfer, the equivalence of the two theories, which apparently is not complete, is restored by assuming that the scattering processes are isotropic and that the total cross section equals the momentum-transfer cross section.

V. ANALYSIS OF THE RESULTS AND COMPARISON WITH OTHER THEORETICAL MODELS

In this section we shall present a more detailed analysis of the equations for W obtained in Sec. IV and a comparison with other theoretical models of the literature will also be done.

(1) The low-density limit will be considered first. On the basis of Eqs. (3.10) or (3.14) for $\delta(u)$, Eq. (4.9) easily leads us to write that

$$\frac{W}{W_0} = 1 + O(N) . \tag{5.1}$$

The constant C of Eq. (4.9) is determined by the normalization condition

$$C \int_{-\infty}^{+\infty} e^{-\beta\epsilon} \rho(\epsilon) d\epsilon = 1 \tag{5.2a}$$

with a density of states

$$\rho(\epsilon) = \frac{1}{(2\pi)^3} \int d\vec{k}\, \rho(\epsilon, \vec{k}) = \left[\frac{m}{2} \right]^{1/2} \frac{1}{\pi\hbar^3} \sqrt{\epsilon - Nt(\epsilon)} , \tag{5.2b}$$

which is correct under the approximate condition $\Sigma(\vec{k}, \epsilon) \simeq Nt(\epsilon)$ used to obtain Eq. (4.9). As shown by Eq. (5.1), depending on the value of $O(N)$, the density effect is expected to be very small if not completely negligible under the conditions of validity of Eq. (4.9). This conclusion seems to be confirmed by experiments. For instance, Crompton and Robertson[28] find that in He the density effect is zero, within the error of 1%, up to a pressure of 700 torr at 77 K. A very small effect is also observed under the same conditions in parahydrogen and, particularly, in normal hydrogen. There is, in fact, a different effect in p-H_2 and n-H_2 which, in the context of the theory we have developed, would have to be ascribed to a different value of the range B, depending on the rotational states of the molecule. Finally, vanishing density effects at sufficiently low pressures have also been observed by Freeman and co-workers[29] in a number of saturated vapors near the critical point. Our theory also does not contrast with these and similar effects which have been recently observed in gases such as Ar by Huang and Freeman.[29]

(2) Let us now turn our attention to the high-density limit. We shall first consider Eq. (4.10). Equations (3.10) and (3.14) can be used with the restriction that $T_{1\vec{k}} < 0$, i.e., that $a < 0$, since

$$T_{1\vec{k}} = N\delta(\epsilon_{\vec{k}}) \simeq 2\pi(\hbar^2/m)Na \ .$$

In fact, in the contrary case, Eq. (4.10) becomes meaningless. In this way, Eqs. (5.2) lead us to write that

$$W = \frac{4}{3}\frac{eE}{m\sqrt{\pi}}\beta^{5/2}\int_0^\infty d\epsilon_{\vec{k}}\frac{\epsilon_{\vec{k}}^{3/2}e^{-\beta\epsilon_{\vec{k}}}}{\nu(\epsilon_{\vec{k}} - N\delta(\epsilon_{\vec{k}}))} \ , \tag{5.3}$$

which under the condition $\delta(\epsilon_{\vec{k}}) \simeq \delta(0)$ agrees with the equation proposed by O'Malley,[16] on the basis of speculative physical argumentations. Equation (5.3) is then expected to be valid for atoms with negative scattering length and therefore, in the same measure as $T_{1\vec{k}}$ may be approximated by its value on the shell, for atoms with a (pronounced) Ramsauer minimum. Another limit of Eq. (5.3) is, as mentioned, the atom density N which must be sufficiently elevated since Eq. (5.3) does not lead to the results (4.9) as $N \to 0$, even to the lowest order in N.

(3) It remains to analyze the consequences of Eq. (4.11) (potential fluctuations). The t matrix of interest in this case is calculated at energies greater than $\epsilon_{\vec{k}} \sim kT$ so that the low-energy representation (3.10) does not appear to be so appropriate as Eq. (3.13). If we limit ourselves to consider cross sections that are weakly dependent on the electron energy, we may write that

$$T_{1\vec{k}} = N^*\delta(\epsilon_{\vec{k}}) \tag{5.4}$$

with

$$\begin{aligned} N^* &= N\frac{\delta(\epsilon_{\vec{k}} + N^*\delta(\epsilon_{\vec{k}}))}{\delta(\epsilon_{\vec{k}})} \\ &\simeq N\frac{\delta(\epsilon_{\vec{k}} + N^*\delta(kT))}{\delta(\epsilon_{\vec{k}})} \ . \end{aligned} \tag{5.5}$$

In this equation, the last step involves a negligible error for not too elevated densities. The normalization constant C is now properly calculated using a density of states

$$\rho(\epsilon) = \left[\frac{m}{2}\right]^{1/2}\frac{1}{\pi\hbar^3}\sqrt{\epsilon} \ ,$$

which finally leads us to write

$$W = \frac{4}{3}\frac{eE}{m\sqrt{\pi}}\beta^{5/2}\int_{\epsilon_0}^\infty d\epsilon_{\vec{k}}\frac{\epsilon_{\vec{k}}^{3/2}e^{-\beta\epsilon_{\vec{k}}}}{\nu(\epsilon_{\vec{k}} + N^*\delta(\epsilon_{\vec{k}}))} \times \left[1 - N^*\frac{d\delta(\epsilon_{\vec{k}})}{d\epsilon_{\vec{k}}}\right] \ , \tag{5.6}$$

ϵ_0 being the root of the equation $1 - N^* \times dt(\epsilon_0)/d\epsilon_0 = 0$. It is of interest to observe that if the choice $\delta(\epsilon_{\vec{k}}) \simeq$ const would be appropriate, Eq. (5.6) would lead to the same equation proposed by Legler[10] for gases with negative density effect since $N^* \simeq N$. But the presence of the mobility edge imposes that $k > 1/l$ (with the electron mean-free path satisfying the condition $1/l \gtrsim 5\times 10^4$ cm^{-1} for the typical situations where $N \gtrsim 10^{20}$ cm^{-3}). Accordingly, Eq. (3.13) seems to become more appropriate than Eq. (3.10) valid at (very) low energies. In fact, the choice of Legler leads to an unsatisfactory agreement with experiments while Eq. (3.13), as we shall see, leads to an almost perfect agreement. In this latter case, from Eq. (5.5) it is obtained that

$$N^* = N\left[1 + 2\frac{\hbar}{\sqrt{2mkT}}N^*Q(kT)\right]^{1/2} \ , \tag{5.7}$$

which makes Eq. (4.6) well defined for explicit calculations. Finally, it can be observed that our previous first-order theory also is a particular case of the above equations. With the choice (5.7) and neglecting higher-order terms so that $N^* \simeq N$, from Eq. (5.6) it is easy to find Eq. (7) of our previous paper[8], which we proposed for $a > 0$. For $a < 0$, the linear terms with respect to N of Eq. (5.3) can be given the form (10) of our previous paper[8] when using the appropriate effective scattering length.

(4) Another interesting situation which is also described by our theory, and in particular by Eq. (5.6), is one where the density effect is due to resonance trapping of the electrons. If we limit our considerations to the lowest-order terms in N, so that $N^* \simeq N$, and suppose the phenomenon to be dominated by the resonance, we may use the result (3.17). Under these conditions, it is reasonable to

neglect $\delta(\epsilon)$ but not $d\delta/d\epsilon_{\vec{k}}$ and infer from Eq. (5.6) that

$$\frac{W}{W_0}=1-\nu_R\tau_R\ , \tag{5.8}$$

which agrees with the equation proposed in the presence of resonance trapping[30] and, in particular, with Frommhold's theory[3]. Before concluding our comparisons with other theoretical models, it still remains to mention the points of contact that exist between our high-density theory and the percolation theory of Schwarz.[6] Both are, in fact, semiclassical theories leading in particular to a mobility which vanishes continuously as the electron energy tends to the mobility edge. This is a known result of the percolation theory[31] and also follows from our Eq. (5.6) because of the factor $(1-N^*d\delta/d\epsilon_{\vec{k}})$. However, our theory does not involve free parameters. It is directly deduced from a rigorous transport theory, contrary to what happens for the theories of Eggarter[31] and Eggarter and Cohen.[32] In spite of this, we believe that, really, we are concerned with the same theory as the basic assumptions are the same.

VI. COMPARISON WITH EXPERIMENTAL RESULTS

On the basis of the theory presented in Secs. IV and V, and in particular of Eqs. (4.9), (4.10), and (4.11), we have seen that it is possible to give theoretical justification (in terms of t matrix) of a number of models proposed by various authors. This confirms the original idea of our previous paper[8] (where Kubo's formula for W was developed in the low-density limit, for situations of interest in dense gases) that the theory of the density effect can be entirely based on properties of the t matrix and the static structure factor. In this section we shall present a comparison between theory and experimental data, which not only permits us to assess the exact limits of our extended theory but also to test the quantitative agreement with previous theoretical models.

The first comparison is with experimental data in He. In Fig. 1 the comparison is with data from Schwarz[6] at 4.2 K, while in Fig. 2 the data at 77.6 K are from Bartels.[3,33] In this latter figure, some points at 293 K from Grünberg[34] are also reported. As concerns the theoretical predictions, dashed curves M are introduced to represent the drift velocities provided by Eq. (2.2). These curves do not correspond exactly to those given by O'Malley[16] since ours have been obtained by direct numerical integration of Eq. (2.2) without taking Γ outside the integral as an average, as indicated in Eq. (2.3). Curve L is from Legler's theory[10] with the appropriate scattering length. Finally, curves P (solid lines) are used to represent the predictions of our extended theory, i.e., of Eqs. (5.6) and (5.7). For comparison, curves S, which are obtained by assuming the Wigner-Seitz correction for the gas density, are also reported, in which case N^* is numerically estimated using appropriate equations given by Eggarter.[30] As one can see, the agreement between our extended theory and experiments is extremely good

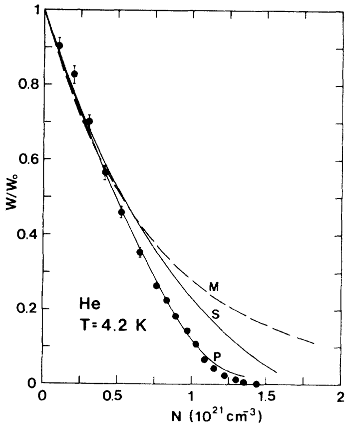

FIG. 1. Comparison between theory and experimental data (●) in He at 4.2 K. Curve M, Eq. (2.2); curve S, present theory with Wigner-Seitz correction for the gas density; curve P, present extended theory with N corrected according to Eq. (5.7).

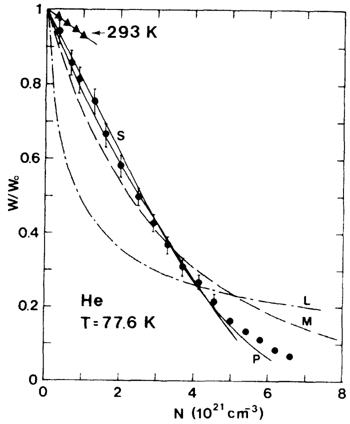

FIG. 2. Same quantities as in Fig. 1 but for $T=77.6$ K. Curve L is from Legler's theory. A comparison is also reported of our extended theory with a few experimental points at 293 K.

and not only to the lower densities. This conclusion is also confirmed by the results of Figs. 3 and 4 where the same quantities of Figs. 1 and 2 are reported in logarithmic scale. This is done in order to show to what extent theoretical models agree with experiments in the region of the pronounced fall off of the electron mobility at elevated values of N. Only for the higher densities is there a discrepancy between curves P and experimental points, which is also expected, as our extended theory still remains an approximate theory. In fact, multiple-scattering corrections are only approximately introduced through the use of an appropriate N^*. Moreover, a constant value for Q is assumed in the corrective terms. In any case, the agreement of curves P with experimental data is always much better than that of curves relative to other theoretical models. For comparison, Figs. 3 and 4 report (represented by dashed curves M') results obtained by O'Malley[16] from the approximate Eq. (2.3), where Γ is given an average value $\bar{\Gamma}$ and $\exp(-\beta\bar{\Gamma})$ is taken outside the integral. As one can see, the agreement between theory and experiment, at least in this case, is worse when Eq. (2.2) is used in place of its approximate form (2.3). The agreement in any case is good at moderate and low densities.

In Fig. 4 a comparison is also reported between our extended theory and experimental data from Bartels[3,33] in H_2 at 77.6 K. The agreement still is very good. This is also confirmed by the results of Fig. 5. In order to also give the reader an indication of the extents of the corrections for multiple scattering and structure factor, in Fig. 5 a curve is reported (i.e., $P1$) obtained with $S(0)=1$ and $N^*=N$ and a curve (i.e., $P2$) obtained with $S(0)=1$, and the correct value of N^* as given by Eq. (5.7). As concerns the structure factor, it must be noted that the correction is introduced by writing that $S(0)=1-2NB$, where B is the second virial coefficient, or directly (as in Ar and CH_4) using results for $S(0)$ of the literature.[35]

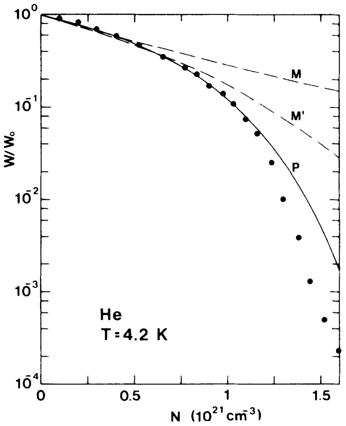

FIG. 3. Some quantities of Fig. 1 are here reported in logarithmic scale. Curve M' is from Eq. (2.3).

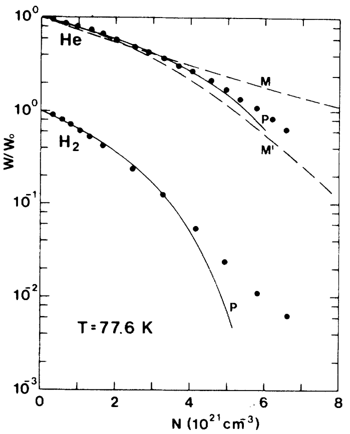

FIG. 4. Some quantities of Fig. 2 are here reported in logarithmic scale. Curve M' is from Eq. (2.3). Also reported in this figure is a comparison between our extended theory and experimental data in H_2 at 77.6 K.

Let us turn now our attention to gases where the drift velocity is found to increase with N. In Fig. 6 the comparison between theory and experiment is relative to Ar at 297 K. Of course, the notations are the same we adopted in previous figures. Therefore, curve L is from Legler's theory[10] when using the appropriate scattering length (as obtained by Milloy and co-workers[36]). Curve P is from our ex-

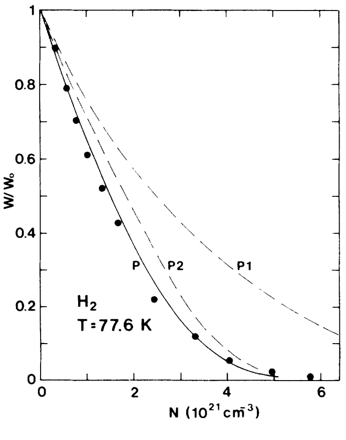

FIG. 5. Same comparison between theory and experiment in H_2 at 77.6 K as reported in Fig. 4 but on a different scale. Here, Curve $P1$ is obtained with $S(0)=1$ and $N^*=N$ while curve $P2$ is obtained with $S(0)=1$ and N^* from Eq. (5.7).

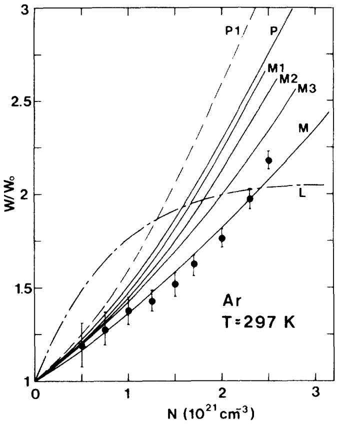

FIG. 6. Comparison between theory and experiment in Ar at 297 K. Curve P, present extended theory; curve $P1$, extended theory with $S(0)=1$; curve L, Legler's theory with MCRR scattering length; curves $M1$,$M2$,$M3$, O'Malley. Curve M is obtained from $M3$ when introducing the correction for structure factor.

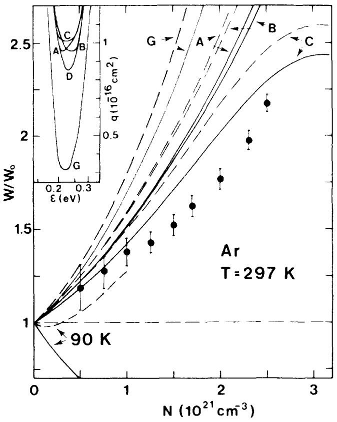

FIG. 7. Theoretical dependence of $W(N)$ on N in Ar at 297 K in correspondence of the various cross sections reported in the inset. Dashed lines are obtained under the condition $S(0)=1$ while the solid lines are obtained with the correct structure factor. Data at 90 K relative to cross section D of MCRR are also reported.

tended theory, i.e., from Eq. (5.3). It is obtained by using the cross section of Milloy and co-workers[36] (referred to as MCRR cross section) and a proper correction for the structure factor. On the contrary, $P1$ is the result one obtains under the condition $S(0)=1$. The three curves $M1$, $M2$, and $M3$ are the same curves reported by O'Malley.[16] Apart from the apparent discrepancy, they should be obtained with the same equation leading to our curve $P1$ but with cross sections which differ from that of Milloy and co-workers[36] in the region of the Ramsauer minimum of small extents, so that the modifications of the classical drift velocity W_0 are always maintained within 1% with respect to the correct value. In this context, it is particularly interesting to observe that, when correcting $M3$ with the proper structure factor,[34] a curve M is obtained which perfectly agrees with the experimental points from Bartels.[37] As one can see from the results reported in this figure, the theoretical curves strongly depend on the behavior of the cross section up to, and in particular at, the minimum. This is even more clearly shown by the results of Fig. 7 where four different curves obtained with four different cross sections are reported. As shown in the inset, three cross sections differ only in the region of the Ramsauer minimum from that of MCRR, represented by curve D. In particular, cross sections A and B correspond to an increase of the minimum of D of 12% and cross section C to an increase of 18%. Finally, cross section G is that of Golden.[38] As expected, the results of this figure show a better agreement between experiment and theory if the depth of the minimum is reduced. Also reported in Fig. 7 are the theoretical predictions obtained with cross section D of MCRR at 90 K where the effect in Ar has been found to be negative,[39] at least up to 700 torr.

To this point, we have presented a picture of substantial agreement between theory and experiment. This makes us confident that our extended theory is conceptually correct. The agreement is particularly good in gases presenting negative effects such as He and H_2. But there are other considerations, that we have already done in part, which support our model. For instance, the suprisingly small effect observed in a number of gases at sufficiently small values of N (Refs. 28 and 29) seems also to be in accord with our model. Only in Ar does the predicted effect tend to be systematically elevated, indicating in this way that probably the approximations introduced are slightly too crude or even that different effects take place simultaneously. Really, this conclusion seems necessary to explain the poor agreement between theory and experiment that we have observed in CH_4. In part this disagreement is certainly due to the imperfect knowledge of the cross section, but this is not the only reason. As shown in Fig. 8, we have analyzed the results obtained with three different cross sections of the literature: (1) a model cross section first used by Kleban and Davis[40] which is sometimes adopted when studying

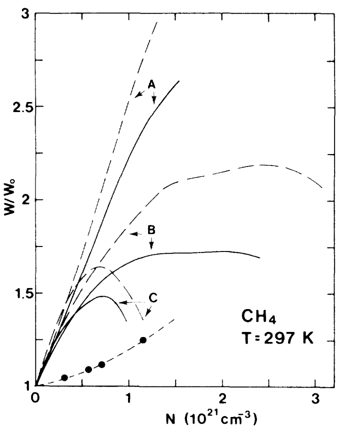

FIG. 8. Comparison between theory and experiment in CH_4. Dashed and solid lines are obtained with $S(0)=1$ and the correct structure factor, respectively. Curve A, model cross section of Kleban and Davies; curve B, total cross section of Ramsauer and Kollath; curve C, momentum-transfer cross section of Pollock.

electron transport in this gas[41] (curves A), (2) the total cross section of Ramsauer and Kollath[42] (curves B), and (3) the momentum-transfer cross section obtained by Pollock[43] from swarm data (curves C). In all cases, the predicted dependence of W on N is much more pronounced than observed experimentally. As suggested by Atrazev and Yakubov,[7] a partial balancing between positive and multiple-scattering negative effects cannot be excluded. Also, the use of an effective (i.e., lower) scattering length can eliminate the discrepancy and could probably find justification. But it must also be taken into account that, as a rule, use has been made of the on-shell approximation for the scattering amplitude. It is reasonable to suppose that this is an insufficient approximation in the presence of strong polarization forces.

VII. CONCLUSIONS

The main conclusions which follow from the analysis presented in this paper are as follows:

(1) Both positive and negative gas-density effects on the electron mobility can be explained in terms of a single (unifying) multiple-scattering theory, which can be deduced from a general (rigorous) transport theory in a consistent mathematical way.

(2) For arbitrary values of the gas density N, the mobility theory is very complicated for both positive and negative effects but it becomes much simpler in the limit of very low and sufficiently high densities, to which we turn special attention in this paper.

(3) Apart from one or two exceptions, i.e., the theories of positive effect of Legler[10] and Atrazev and Yakubov,[7] all the theoretical models previously proposed to explain positive and/or negative effects can be deduced from our extended theory under appropriate conditions.

(4) The agreement with experimental data is extremely good for gases such as He and H_2, where the electron mobility decreases with N, over a wide range of gas densities and for all the gas temperatures used in the experiments. For gases, such as Ar, where the electron mobility increases with N, the theory leads to a final equation which agrees well with models recently proposed by other authors, but the agreement with experiments remains not so perfect and becomes poor for gases such as CH_4. Different reasons could explain the discrepancy, but there are elements to suspect that it is due to approximations which fail in the presence of strong polarization forces.

(5) In the low-density limit, on the basis of our extended theory, the extremely small effect (null effect) which has been experimentally observed in a number of gases is (qualitatively) explained for the first time.

As concerns the open problems, we have already seen that the agreement between theory and experiments is not as good for the positive as it is for the negative effects. An analysis of the consequences of the "on the energy shell" approximation for the matrix elements of the t matrix, in the presence of strong polarization forces, would be necessary. Also we must emphasize that our theory requires sufficiently elevated or sufficiently low gas densities. Even if the range of pressures which is not so well covered by our treatment seems of limited practical importance, the extension of our treatment would be of interest. Finally, another open problem remains that of extending the theory to higher values of E/N to (quantitatively) explain the density dependence of the drift velocity for nonthermal electrons. Almost certainly, this extension will not change the interpretative part of the phenomenon.[8,12] However, in spite of that, the formulation of a rigorous transport theory of electron mobility for hot electrons remains a difficult open problem to which we intend to turn our attention in another paper.

[*] A synthesis of this paper has been presented at the Second International Seminar on Swarm Experiments in Atomic Collision Research, Oak Ridge, Tennessee, July, 1981 (invited talk) [cf. *Electron and Ion Swarms*, edited by L. G. Christophorou (Pergamon, New York, 1981)].

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