New Theory of Electron Drift Velocity in Gases

G. CAVALLERI AND G. SESTA
Laboratori C.I.S.E. (Centro Informazioni Studi Esperienze), Segrate, Milano, Italy
(Received 15 May 1967; revised manuscript received 22 December 1967)

The electron drift velocity is usually obtained on the assumptions that: (i) the velocity variation due to the electric field is small compared to the thermal velocity, and (ii) the inelastic collision rate is negligible with respect to the elastic collision rate. By introducing the distribution function $f_0(c_0)$ of the velocities c_0 immediately after a collision ("initial" distribution function), we develop a new theory which obviates the above assumptions and is therefore particularly suitable in the case of high values of the ratio between the electric field and the gas pressure. The drift velocity is obtained by two successive steps. First we obtain a rigorous expression for the drift velocity $w(c_0)$ of electrons having initial velocity c_0. By expanding this expression to first order under assumption (i) only, the usual expression for $w(c_0)$ is found again, and its validity is therefore extended even to the case of inelastic collisions, since assumption (ii) has not been used. In order to obtain the drift velocity W, the expression for $w(c_0)$ must be averaged over the initial distribution function $f_0(c_0)$. The initial velocity distribution, not being affected by the electric field, is isotropic when the differential collision cross section is isotropic. Therefore, the resulting integral equation for $f_0(c_0)$, though rigorous, has the same simplicity as the usual first-order expansion of the Boltzmann equation.

1. INTRODUCTION

IN the presence of a constant and uniform electric field $\mathbf{E}$, the velocity distribution function of the electrons in a gas may be represented by $F(c,\vartheta)$, where c is the magnitude of the velocity and ϑ is the angle between $\mathbf{c}$ and $\mathbf{E}$, the dependence of F on the spatial coordinates being neglected. Consequently, the drift velocity W is given by

$$W=\int_0^{\pi}\int_0^{\infty} c\cos\vartheta F(c,\vartheta)dcd\vartheta. \tag{1}$$

However, the function $F(c,\vartheta)$ of the two variables c and ϑ has never been deduced, since Boltzmann's integrodifferential equation is practically intractable in the case of a function of two variables. Therefore, all authors expand $F(c,\vartheta)$ in spherical harmonics[1] (Legendre functions) of $\cos\vartheta=c_z/c$, or in some other way,[2] in order to have for the unknown a function $f(c)$ of only one variable (the magnitude of the velocity). With the exception of Wannier[3] (who, however, assumed that the collisions were only elastic, since he considered ions), all authors[1,2,4] have retained only the zero- and first-order terms of the expansion. This is equivalent to the following two simplifying assumptions, corresponding to a small anisotropy of $F(c,\vartheta)$: (i) The velocity variations Δc_E between two successive collisions, due to the accelerating field E, are small with respect to the thermal velocity c, i.e., $\Delta c_E \ll c$; (ii) the inelastic collision frequency ν_{in} is small with respect to the elastic collision frequency ν_{el}, i.e., $\nu_{\text{in}} \ll \nu_{\text{el}}$.

Using the distribution function $f(c)$ of the velocity magnitude, the expression for the drift velocity W is given by

$$W=\int_0^{\infty} w(c)f(c)dc, \tag{2}$$

where $w(c)$ is an approximate drift velocity of monoenergetic electrons. Notice that $w(c)$ exhibits the dependence of W on characteristic parameters, and may be approximated by W if one deals with mean values, as in Compton's theory.[5] We are particularly interested in a complete expression for $w(c)$ and will first examine the various "theories"[6] developed for deducing $w(c)$, since we have not found a completely satisfactory critical review of this subject in the literature. Moreover, some fundamental concepts, clarified in the following examination, will be used in the next section. The various theories leading to an expression for $w(c)$ may be classified as belonging to one of two different types: (a) theories deducing $w(c)$ from the first-order expan-

[1] G. Hertz, Z. Physik **32**, 298 (1925); M. J. Druyvensteyn, Physica **10**, 69 (1930); J. A. Smit, *ibid.* **3**, 543 (1936); H. Margenau, Phys. Rev. **69**, 508 (1946); T. Holstein, *ibid.* **70**, 367 (1946); D. Barbiere, *ibid.* **84**, 653 (1951); W. P. Allis, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 21, p. 413; N. P. Carleton and L. R. Megill, Phys. Rev. **126**, 2089 (1962).

[2] C. Maroli, Nuovo Cimento **41**, 208 (1966); P. Caldirola, O. De Barbieri, and C. Maroli, *ibid.* **42**, 266 (1966).

[3] G. H. Wannier, Bell System Tech. J. **32**, 211 (1953).

[4] See, for example, A. E. D. Heylen and T. J. Lewis, Proc. Roy. Soc. (London) **271**, 531 (1963). These authors have calculated the distribution function $f(c)$ for He, Ne, and Ar, taking into account inelastic collisions and subtracting the inelastic collision cross sections from the total cross section in order to calculate the mean free path to be introduced into Eq. (4).

[5] J. M. Benade and K. T. Compton, Phys. Rev. **11**, 184 (1910); K. T. Compton, *ibid.* **22**, 333 (1923); K. T. Compton and I. Langmuir, Rev. Mod. Phys. **2**, 219 (1930).

[6] See, for example, L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley, 1955), Chaps. 1 and 3; L. G. H. Huxley and R. W. Crompton, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 335; A. von Engel, *Ionized Gases* (Clarendon Press, Oxford, England, 1965), 2nd ed., Chap. IV, Sec. 2, p. 122; W. P. Allis (Ref. 1). These authors consider only the case of constant mean free path and elastic collisions (Compton theory of Ref. 5) and the final viewpoint of the theories here classified as belonging to type (a). For the theories belonging to type (b) see the original papers (they are not critical reviews) quoted in Refs. 11–13.

sion of $F(c,\vartheta)$; (b) theories deducing $w(c)$ from the study of a generic electron motion.

Both types retain the simplifying assumption (i). The theories of type (a) also use assumption (ii), and therefore give an expression for $w(c)$ in which only the elastic collision cross section is introduced.[4] All theories (b) make use of a further assumption, namely: (iii) The mean free path λ is independent of the thermal velocity c.

The theories of type (a) make use of the Lorentz treatment[7] of electric conduction in metals. This treatment, by use of assumptions (i), (ii), and (iii), leads to

$$w(c)=(2a/3)\lambda/c, \tag{3}$$

where $a=eE/m$ is the acceleration of an electron (or ion) of charge e and mass m, and subjected to an electric field E. Morse, Allis, and Lamar[8] generalized Lorentz's method by including the case of a collision-cross-section dependence on c. They implicitly arrived at the usual formula which was explicitly given for the first time by Davidson[9] and reads

$$w(c)=\tfrac{1}{3}a\left(\frac{\lambda}{c}+\frac{d\lambda}{dc}\right)=\frac{a}{3c^2}\frac{d(c^2\lambda)}{dc}. \tag{4}$$

Recently Huxley and Crompton[10] have deduced Eq. (4) by a slightly different procedure.

Group (b) includes Drude's theory,[11] the first theory of Langevin,[12] and Townsend's theory.[13] Drude's theory, besides retaining assumptions (i) and (iii), does not consider the distribution of the free paths given by

$$P(s)ds=-\frac{dn}{n}=\frac{1}{\lambda}\exp\left(-\frac{s}{\lambda}\right)ds, \tag{5}$$

where dn is the number of electrons colliding between s and $s+ds$. This distribution must be taken into account in the theories of type (b), which consider the motion of a generic electron between two successive collisions, and therefore with a generic path s. Moreover, Drude's theory is not correct because it assumes, as a mean velocity vector, the expression

$$\mathbf{W}=\sum_1^n{}_k\,\mathbf{c}_k/n, \tag{6}$$

taken over a set of particles with equal density for every direction in velocity space. This is incorrect, since the particles which follow different orientations with respect to the accelerating field have different times of flight. The correct expression is

$$\mathbf{W}=\left(\sum_1^n{}_k\,\mathbf{s}_k/\sum_1^n{}_k\,t_k\right)=\sum_1^n{}_k\,\mathbf{c}_k t_k/\sum_1^n{}_k\,t_k, \tag{7}$$

where the sum is extended through the history of a single particle; that is, over the successive paths $\mathbf{s}_k$ between collisions. In this case the various velocity vectors must be weighted with the corresponding times of flight, t. The $w(c)$ evaluated by Eq. (7) leads to the Lorentz expression (3).

Because of the error mentioned above, Drude[11] obtained

$$w(c)=(a/2)\lambda/c. \tag{8}$$

The same error is included in the first theory of Langevin,[12] who assumed, for the mean displacement s_E in the direction of E, the expression corresponding to Eq. (8), in the case of a generic path s, i.e.,

$$s_E=(\tfrac{1}{2}a)t^2=(\tfrac{1}{2}a)s^2/c^2, \tag{9}$$

which is equivalent to $w(c)s/c$ with $w(c)$ given by Eq. (8). Then Langevin[12] averaged over the distribution of free paths given by Eq. (5) and, multiplying by the mean collision frequency $\bar{c}/\lambda$ (he assumed $\lambda=$ const and $\Delta c_E \ll c$), he obtained

$$w(c)=a\lambda/c. \tag{10}$$

Notice that expressions (9) and (10) are correct only for paths perpendicular to $\mathbf{E}$. On the other hand, if we consider a set of successive paths along E (half of them parallel to E, and the others antiparallel) and with λ independent of c, the mean displacement vector $\bar{\mathbf{s}}$ and the contribution to the drift velocity would be zero. The fact that flights of different orientations contribute differently to $w(c)$ has been taken into account in Townsend's theory[13] even though use is still made of assumptions (i) and (iii).

To conclude this review, we may say that Eq. (4) obtained by theories of type (a) is the most complete formula so far deduced under assumptions (i) and (ii).[14] The simplifying assumption (i) implies a lower limit on

[7] H. Lorentz, *Theory of Electrons* (B. G. Tuebner, Leipzig, 1916), p. 267; H. Lorentz, Proc. Amst. **7**, 438 (1905); **7**, 585 (1905); **7**, 684 (1905); P. Debye, Ann. Phys. (Paris) **33**, 441 (1910).

[8] P. M. Morse, W. P. Allis, and E. S. Lamar, Phys. Rev. **48**, 412 (1935).

[9] P. M. Davidson, Proc. Phys. Soc. (London) **67**, 159 (1954); see also the footnotes of J. A. Smit (Ref. 1).

[10] L. G. H. Huxley and R. W. Crompton, Australian J. Phys. **10**, 118 (1957); **13**, 587 (1960); **13**, 718 (1960). See also D. R. Bates (Ref. 6).

[11] P. Drude, Ann. Phys. (Paris) **1**, 566 (1900); **3**, 369 (1900); **7**, 687 (1902); E. Rieche, Physik Z. **10**, 508 (1909).

[12] P. Langevin, Ann. Chem. Phys. **28**, 435 (1903); J. S. E. Townsend, *Electrons in Gases* (Hutchinson's, London, 1947), Chap. 1.

[13] J. S. E. Townsend, Phil. Mag. **22**,1 45 (1936); see also Ref. 7.

[14] Notice also, that Wannier (see Ref. 3), who integrated Boltzmann's equation and therefore used Eq. (2), considered high fields, but only for ions, for which inelastic collisions are negligible even in the case of the high fields considered by Wannier. Consequently, assumption (ii) has been retained by Wannier, who maintained even assumption (i). In particular, for ion masses much larger than molecule masses, Wannier (see Ref. 3) approximated the distribution function of the magnitudes of ion velocity by a Dirac delta function centered at a velocity c of the same order as the drift velocity w, so that the assumption $c \simeq w \gg \Delta c_E$ is well satisfied. Only in the case of ion masses of the same order as molecular masses did Wannier (see Ref. 14) dispense with assumption (i). Yet in this case, he did not seek a theoretical expression, but used the "almost empirical" Monte Carlo method (see Sec. II D of Ref. 3).

c, and therefore Eq. (4) is not reliable for low-energy electrons. Assumption (ii) implies that only the mean free path corresponding to the elastic collision cross section[4] has to be introduced into Eq. (4).

In Sec. 2 we remove assumptions (i), (ii), and (iii) by a method which may be thought of as a generalization of Townsend's theory.[13] Consequently an expression of $w(c)$ more complete than Eq. (4) will be found.

2. DEDUCTION OF $w(c)$ WHEN $\sigma(c,\vartheta)$ IS ISOTROPIC

In this section we shall consider the case of isotropic differential collision cross sections $\sigma(c,\vartheta)$. Our method consists of the calculation of the average path length $S(c_0)$ along the field direction and the average time of flight $T(c_0)$ between two successive collisions, for electrons having the same initial velocity magnitude c_0. It results in a drift velocity for monoenergetic electrons

$$w(c_0)=S(c_0)/T(c_0), \tag{11}$$

where $S(c_0)$ and $T(c_0)$ have been obtained as an average over all the initial angles ϑ_0 and all the possible flight times t, as shown generally in Eq. (7).

The above procedure is possible if the number dn of the electrons scattered into the solid angle $d\Omega$ with initial velocity c_0 is independent of ϑ_0, that is, when $\sigma(c,\vartheta)$ is isotropic. Let us clarify this fact, together with the other fact that, in order to obtain the drift velocity W, we must average $w(c_0)$ given by Eq. (11) over the distribution function of the velocity magnitudes immediately after collisions. This "strange" distribution function is a particular case of a more general one here called a "partial" distribution function, defined as follows. Let us "photograph" (at any instant) the position and the velocities of all electrons and consider the electrons which are, at the instant considered, in a shell between r and $r+dr$ from the previous centers of scattering. The distribution function of these particular electrons is here called the *partial* distribution function $F_r(c,\vartheta)$. It is related to the usual "total" distribution function $F(c,\vartheta)$ by the relationship

$$\int_0^\infty F_r(c,\vartheta)dr=F(c,\vartheta). \tag{12}$$

The most interesting and the only practically useful partial function is the one corresponding to $r=0$, here called the "initial" distribution function and represented by $F_0(c_0,\vartheta_0)$. Instead of the other partial distribution functions defined by Eq. (12), we use in the following a normalized initial distribution function, i.e.,

$$\int_0^\pi\int_0^\infty F_0(c_0,\vartheta_0)dc_0d\vartheta_0=1. \tag{13}$$

The advantage of using $F_0(c_0,\vartheta_0)$ is that, in the case of the isotropic cross section $\sigma(c,\vartheta)$, the initial distribution function is isotropic because it is not affected by the electric field. Consequently, it may be split into the following product:

$$F_0(c_0,\vartheta_0)=f_0(c_0)\Pi_0(\vartheta_0), \tag{14}$$

where $f_0(c_0)$ is the initial distribution function of the velocity magnitudes and $\Pi(\vartheta_0)$ is the initial angular distribution function. The splitting given by Eq. (14) is possible not only under assumption (i) of Sec. 1, as is true for the usual $F(c,\vartheta)$, but in the general case, even in the presence of very high electric fields. Moreover [always when $\sigma(c,\vartheta)$ is isotropic], the initial angular distribution function is known completely, since it is isotropic, i.e.,

$$\Pi_0(\vartheta_0)=\tfrac{1}{2}\sin\vartheta_0. \tag{15}$$

Notice that, under assumption (i), the "average" angular distribution function defined as

$$\Pi(\vartheta)=\int_0^\infty F(c,\vartheta)dc \tag{16}$$

is almost isotropic, but it is just the residual small degree of anisotropy which is responsible for W. By contrast, because of the very high ratio between molecular masses and electron mass, $\Pi_0(\vartheta_0)$ is practically isotropic when $\sigma(c,\vartheta)$ is isotropic, even when the partial angular distribution function immediately before collisions is completely anisotropic, as it is for high fields.[15] In this case the very small degree of anisotropy of $\Pi_0(\vartheta_0)$ may be neglected, since W is of the same order as c. Generally, when $\sigma(c,\vartheta)$ is isotropic, the degree of anisotropy of $\Pi_0(\vartheta_0)$ is much lower than one of the average angular distribution function $\Pi(\vartheta)$ defined by Eq. (16).

Let us give a mathematical form to the above concepts. After a time of flight t, the velocity of an electron having initial velocity c_0 and subjected to an acceleration $a=eE/m$ is given by

$$c(c_0,\vartheta_0,t)=[(c_0\cos\vartheta_0+at)^2+c_0^2\sin^2\vartheta_0]^{1/2}, \tag{17}$$

where ϑ_0 is the angle between $\mathbf{c}_0$ and $\mathbf{E}$. The projection s_E of the displacements s of the same electron in the direction of $\mathbf{E}$ is given by

$$s_E(c_0,\vartheta_0,t)=c_0t\cos\vartheta_0+\tfrac{1}{2}at^2. \tag{18}$$

The distribution of the free paths s is somewhat different from the usual Eq. (5), which is valid only for λ independent of c. With the same notation as in Eq. (5), but with $\lambda(c)$, we may now calculate the distribution function $P(c_0,\vartheta_0,s)$ for the free paths. This is defined by

[15] In such a case, the electrons that are scattered at large angles immediately after collisions rapidly deviate because of the applied field, so that, after a very short time following a collision, the angular distribution becomes very narrow.

the relationship

$$P(c_0,\vartheta_0,s)ds=-dn/n_0. \tag{19}$$

As in Eq. (5), $-dn$ is the number of electrons colliding between s and $s+ds$, and n_0 the initial number of electrons. On the other hand, it can easily be seen that the elementary number $-dn$ of collisions is given by

$$-dn=nds/\lambda[c(c_0,\vartheta_0,s)]. \tag{20}$$

Integrating Eq. (20), we have

$$n=n_0\exp\left(-\int_0^s\frac{ds}{\lambda[c(c_0,\vartheta_0,s)]}\right). \tag{21}$$

Hence, by substituting Eq. (21) into the right-hand side of Eq. (20), and the result into Eq. (19), we obtain

$$P(c_0,\vartheta_0,s)=\frac{1}{\lambda[c(s)]}\exp\left(-\int_0^s\frac{ds}{\lambda[c(s)]}\right). \tag{22}$$

Instead of considering the distribution function $P(c_0,\vartheta_0,s)$ of the free paths, it is convenient to change the variables and introduce the distribution function Q of the times of flight, since s_E and c are very simple functions of c_0, ϑ_0, and t [see Eqs. (17) and (18)], but not of c_0, ϑ_0, and s. The new function Q is defined by

$$P(c_0,\vartheta_0,s)ds=Q(c_0,\vartheta_0,t)dt=-dn/n.$$

We get

$$Q(c_0,\vartheta_0,t)=\frac{c}{\lambda(c)}\exp\left(-\int_0^t\frac{cdt}{\lambda[c(t)]}\right)$$

$$=-\frac{d}{dt}\left\{\exp\left(-\int_0^t\frac{cd\tau}{\lambda(\tau)}\right)\right\}. \tag{23}$$

Weighting the displacement s_E given by Eq. (18) over the distribution of the times of flight given by Eq. (23) and over the angular distribution function of the initial directions given by Eq. (15), we obtain the total displacement $S(c_0)$ in the direction of the electric field of the electrons having initial velocity c_0. Weighting in the same way the times of flight t, we obtain the total time of flight $T(c_0)$ of the same electrons. Then, by means of Eqs. (11), (15), (17), (18), and (23) we get

$$w(c_0)=\frac{\displaystyle\int_0^\pi\sin\vartheta_0d\vartheta_0\int_0^\infty(c_0t\cos\vartheta_0+\tfrac{1}{2}at^2)d/dt\left\{\exp\left(-\int_0^t[(c_0\cos\vartheta_0+a\tau)^2+c_0^2\sin^2\vartheta_0]^{1/2}d\tau/\lambda(\tau)\right)\right\}dt}{\displaystyle\int_0^\pi\sin\vartheta_0d\vartheta_0\int_0^\infty t(d/dt)\left\{\exp\left(-\int_0^t[(c_0\cos\vartheta_0+a\tau)^2+c_0^2\sin^2\vartheta_0]^{1/2}d\tau/\lambda(\tau)\right)\right\}dt}. \tag{24}$$

Equation (24) is the required expression and is valid without any simplifying assumption. In order to calculate the drift velocity W we must average $w(c_0)$ given by Eq. (24) over the initial distribution function $f_0(c_0)$ of the velocity magnitudes:

$$W=\int_0^\infty w(c_0)f_0(c_0)dc_0. \tag{25}$$

Note that, whereas Eq. (2) is valid under the simplifying assumptions (i) and (ii) of Sec. 1, Eq. (25) is valid without retention of these assumptions.

For a better understanding of this theory, let us present it in a slightly different form. Instead of considering an instantaneous "photograph" of electron velocities, let us examine the history of a generic electron. The distribution of the successive velocities taken by this electron (and in particular the distribution of the initial speeds) is equal to that obtained by a photograph, since an almost stationary situation for electrons is considered, i.e., an "almost" Lorentz gas with a stationary mean molecular energy, lower than the stationary electron energy. In other words, we assume ergodicity, which is usually accepted in this case (see for example Sec. II D of Ref. 3), and which simply means that there are no privileged electrons. Consequently, if the successive initial speeds [i.e., $f_0(c_0)$] and their angular distribution [which is isotropic and is given by Eq. (15)] are known, the displacement of the electron considered can be easily calculated, both its trajectories (the motion is uniformly accelerated and therefore the trajectories are parabolas) and the length distribution of the parabolic arcs [given by Eq. (13)] being known. In the same way we calculate the total time of flight of the paths considered. Everything concerning the trajectories of the electrons having initial speed c_0 is taken into account by $w(c_0)$ given by Eq. (24). The initial speeds of the successive paths are taken into account by $f_0(c_0)$. Hence Eq. (25) gives the mean displacement per unit time of the electron considered, i.e., drift velocity.

By this second picture one can immediately see that the initial speeds do not form a zero-measure set, since there is an initial speed for any path. Obviously, the initial speeds must be taken at a distance from the last center of scattering (molecule) just beyond the sphere of interaction between electron and molecule. The smallest value of the applied external field E that perturbs appreciably the electron motion inside the

interaction sphere is the upper limit for our theory. Fortunately, the maximum values of E and of the characteristic ratio E/p (p being the gas pressure) are far beyond the E/p values pertaining to the physics of the gaseous state, even extended up to $E/p \simeq 1000$ V cm^{-1} Torr^{-1}.

Leaving to Sec. 5 the formulation of the equation governing the initial distribution function $f_0(c_0)$, in Secs. 3 and 4 some consequences of the exact expression (24) are considered.

3. APPLICATION OF THE GENERAL FORMULA IN THE CASE OF CONSTANT FLIGHT TIMES

Since usually the mean value of c/λ is finite, we have

$$\left| t \exp\left\{ -\int_0^t \frac{c\,d\tau}{\lambda(\tau)} \right\} \right|_0^\infty = 0. \tag{26}$$

Taking Eq. (26) into account, an integration by parts of Eq. (24) with respect to t gives

$$w(c_0) = \frac{\displaystyle\int_0^\pi \sin\vartheta_0 d\vartheta_0 \int_0^\infty (c_0\cos\vartheta_0 + at)\exp\left\{ -\int_0^t [(c_0\cos\vartheta_0 + a\tau)^2 + c_0^2\sin^2\vartheta_0]^{1/2} d\tau/\lambda(\tau) \right\} dt}{\displaystyle\int_0^\pi \sin\vartheta_0 d\vartheta_0 \int_0^\infty \exp\left\{ -\int_0^t [(c_0\cos\vartheta_0 + a\tau)^2 + c_0^2\sin^2\vartheta_0]^{1/2} d\tau/\lambda(\tau) \right\} dt}. \tag{27}$$

Two evident particular examples satisfying (26) are given by $\lambda/c = \text{const} = \tau_0$ and $\lambda = \text{const}$. In the case of $\lambda/c = \tau_0$, the integration of Eq. (27) is very simple and gives

$$w(c_0) = \frac{\displaystyle\int_0^\pi \sin\vartheta_0 d\vartheta_0 \int_0^\infty (c_0\cos\vartheta_0 + at)\exp(-t/\tau_0) dt}{\displaystyle\int_0^\pi \sin\vartheta_0 d\vartheta_0 \int_0^\infty \exp(-t/\tau_0) dt} = a\tau_0 = a\frac{\lambda}{c}, \tag{28}$$

which is the same result obtained from Eq. (4) for $\lambda/c = \text{const}$. Therefore, in this case, Eq. (4) is valid even for very high fields, i.e., not only under assumptions (i) and (ii). Note that the same result was found by Langevin[12] [see Eq. (10)]. In fact Langevin[12] used Eq. (6), which is valid only when the time intervals relative to different paths are equal, as occurs for $\lambda/c = \text{const}$; in this case Eq. (7) reduces to Eq. (6).

4. FIRST-ORDER EXPANSION OF EQ. (24) UNDER ASSUMPTION (i)

Let us retain the simplifying assumption (i) of Sec. 1, but not assumptions (ii) and (iii). In our case assumption (i) means

$$at \ll c_0 \simeq c, \quad \vartheta_0 \simeq \vartheta. \tag{29}$$

Therefore we may expand c [given by Eq. (17)] and λ to first order with respect to the variable t, obtaining

$$\begin{aligned} c(c_0,\vartheta_0,t) &\simeq c_0 + at\cos\vartheta, \\ \lambda[c(c_0,\vartheta_0,t)] &\simeq \lambda_0 + at\cos\vartheta\,(d\lambda/dc)_{c=c_0}, \end{aligned} \tag{30}$$

where $\lambda_0 = \lambda(c_0)$. Substituting Eqs. (30) in Eq. (23) and expanding Eq. (23) to first order, we obtain

$$Q(c_0,\vartheta_0,t) \simeq \frac{c_0 + at\cos\vartheta}{\lambda_0 + at\cos\vartheta\, d\lambda/dc} \exp\left\{ -\int_0^t \frac{(c_0 + a\tau\cos\vartheta)d\tau}{\lambda_0 + a\tau\cos\vartheta\,(d\lambda/dc)} \right\} \simeq \left(\frac{c_0}{\lambda_0} + \frac{at}{\lambda_0}\cos\vartheta - \frac{c_0 at}{\lambda_0^2}\cos\vartheta\frac{d\lambda}{dc} \right)$$

$$\times \exp\left(-\frac{c_0}{\lambda_0}t - \frac{a\cos\vartheta}{2\lambda_0}t^2 + \frac{c_0}{\lambda_0^2}a\cos\vartheta\frac{d\lambda}{dc}\frac{t^2}{2} \right) \simeq \frac{c_0}{\lambda_0}\left[1 - \frac{at^2\cos\vartheta}{2\lambda_0}\left(1 - \frac{c_0}{\lambda_0}\frac{d\lambda}{dc} \right) + \frac{at\cos\vartheta}{c_0}\left(1 - \frac{c_0}{\lambda_0}\frac{d\lambda}{dc} \right) \right] \exp\left(-\frac{c_0}{\lambda_0}t \right). \tag{31}$$

By substituting Eq. (31) in Eq. (24) and taking into account Eq. (29) (i.e., $a\lambda_0/c_0 \ll c_0$, which implies $a^2\lambda_0^2/c_0^3 \ll a\lambda_0/c_0$), we obtain after some calculations

$$w(c_0) \simeq w(c) \simeq \frac{\displaystyle\int_0^\pi \sin\vartheta d\vartheta [\lambda_0\cos\vartheta + a(\lambda_0^2/c_0^2)(1-\cos^2\vartheta) + a\cos^2\vartheta(\lambda_0/c_0)(d\lambda/dc)]}{\displaystyle\int_0^\pi \sin\vartheta d\vartheta [(\lambda_0/c_0) - (1/c_0)(\lambda_0/c_0)^2 a\cos\vartheta(1 - (c_0/\lambda_0)(d\lambda/dc))]} = (\tfrac{1}{3}a)(2\lambda/c + d\lambda/dc). \tag{32}$$

This equation coincides with Eq. (4), but here it has been found without using assumption (ii), whereas, so far, all theories of type (a) (see Sec. 1) have deduced Eq. (4) under that assumption. These theories were therefore forced to take the mean free path λ to be introduced into Eq. (4) as that corresponding to only the elastic collision cross section σ_{el}.

Some authors consider high fields (see, in particular, Figs. 4–6 of Heylen and Lewis[4]) for which assumption (ii) is no longer valid. These authors[4] subtract the inelastic cross section from the total collision cross sections in order to have a value of λ to introduce into Eq. (4). By contrast, Eq. (27) has been deduced by using the mean free path λ corresponding to the total collision cross section and the same cross section must be used in Eq. (32) since this equation has been deduced from Eq. (24) under assumption (i) only.

5. INITIAL DISTRIBUTION FUNCTION OF THE VELOCITY MAGNITUDES

In order to complete the theory we must find the expression for the initial distribution function $f_0(c_0)$ not subject to assumptions (i) and (ii).

Let us consider a number dn_0 per unit volume of particles having initial velocities with magnitudes between c_0 and c_0+dc_0, and directions within the solid angle $d\Omega=2\pi\sin\vartheta_0 d\vartheta_0$. When $\sigma(c,\vartheta)$ is isotropic, and because of Eqs. (14) and (15), dn_0 is given by

$$dn_0=F_0(c_0,\vartheta_0)dc_0 d\vartheta_0=f_0(c_0)dc_0\tfrac{1}{2}\sin\vartheta_0 d\vartheta_0. \quad (33)$$

The quantity $dn_0\times Q(c_0,\vartheta_0,t)dt$, where the time-of-flight distribution $Q(c_0,\vartheta_0,t)$ is given by Eq. (23), represents the fraction of the electrons considered that collide between t and $t+dt$ and that have a velocity c given by Eq. (17). Because of the collision, the velocity c changes to a new initial velocity c_0'. Let us denote by $G(c\rightarrow c_0')$ the scattering kernel, i.e., the probability density for speed changing from c to the new initial velocity c_0' upon scattering. Then integrating $dn_0Q(c_0,\vartheta_0,t)dtG(c\rightarrow c_0')$ over c_0, ϑ_0, and t, we obtain

$$f_0(c_0')=\int_0^\infty f_0(c_0)dc_0\int_0^\pi \tfrac{1}{2}\sin\vartheta_0 d\vartheta_0\int_0^\infty G(c\rightarrow c_0')\frac{c}{\lambda}\times\exp\left(-\int_0^t\frac{c}{\lambda}d\tau\right)dt. \quad (34)$$

This equation is a Fredholm homogeneous integral equation of the second kind in which the unknown is a function $f_0(c_0)$ of only one variable. Therefore, the difficulty of integration is of the same order as that arising in integrating Boltzmann's integrodifferential equation, where the function $F(c,\vartheta)$ of two variables is expanded to first order, so as to have as unknown a function $f(c)$ of only one variable. Such a procedure implies the simplifying assumptions (i) and (ii) of Sec. 1, which are not retained in Eq. (34).

We leave research on the solutions of Eq. (34) to the future, giving here some specifications of the scattering kernel $G(c\rightarrow c_0')$.

In the case of inelastic collisions, $G(c\rightarrow c_0')$ can be expressed, taking into account the conservation of energy, by Dirac's delta functions

$$G(c\rightarrow c_0')=\frac{1}{\sigma_{tot}(c)}\sum_i\sigma_{in}{}^i(c)\delta\left[c-\left(c_0'^2+\frac{2}{m}\epsilon_i\right)^{1/2}\right], \quad (35)$$

where $\sigma_{in}{}^i(c)$ and ϵ_i are the cross section and the excitation energy of the ith inelastic level, respectively, and $\sigma_{tot}(c)=\sigma_{el}(c)+\sum_i\sigma_{in}{}^i(c)$, where $\sigma_{el}(c)$ is the elastic cross section.

For E/p values (p being the gas pressure) higher than the value for which the mean electron energy (as calculated taking into account elastic collision only) is greater than the lowest inelastic level, the effect of the speed changes due to elastic collisions is negligible.[16] In this case it is sufficient to introduce Eq. (35) into (34), and one integration is done immediately because of the Dirac delta functions. Therefore our theory becomes particularly fitted for high E/p values.

For intermediate E/p values, even in the case of elastic collisions, it seems sufficient to approximate the relevant scattering kernel $G_{el}(c\rightarrow c_0')$ by a Dirac delta function centered on the mean value[17] of the velocities which, because of collisions, transform into the new initial velocity c_0', i.e.,

$$G_{el}(c\rightarrow c_0')=\frac{\sigma_{el}(c)}{\sigma_{tot}(c)}\delta\left[c-\frac{m+M}{(m^2+M^2)^{1/2}}c_0'\right], \quad (36)$$

where M is the mass of the molecules. Therefore, even for intermediate E/p values we may immediately make an integration by substituting the sum of Eqs. (35) and (36) in Eq. (34). Equation (36) seems acceptable because, for electron energies corresponding to intermediate E/p values, the velocity distribution function is almost isotropic when $\sigma(c,\vartheta)$ is isotropic.

The degree of isotropy is still better at low and very low E/p values, for which Eq. (34), together with Eq. (36) only, may be used instead of Boltzmann's equation. However, at low E/p values the usual procedure[1,2] may be used. But whereas assumption (ii) is always verified at low E/p values, assumption (i) is not verified for electrons having very low initial velocities. This implies a small error in the low-energy tail of $f(c)$ calculated by the usual procedure.[1,2] A greater error in the calculation of W by means of Eq. (2) comes from $w(c)$, because the usual expression (4) diverges for $c\rightarrow 0$. In this case we suggest averaging the exact expression of $w(c_0)$, given by Eq. (24), over $f(c)$ calculated by the usual procedure. Notice that in this case $w(c_0)$ given by Eq. (24) is

[16] This occurs for $E/p>1$–5 V cm^{-1} Torr^{-1}.

[17] E. W. McDaniel, *Collision Phenomena in Ionized Gases* (J. Wiley & Sons, Inc., New York, 1964), p. 19.

almost equal to $w(c)$ given by Eq. (4) (as shown in Sec. 4), with the exception of the very low initial velocities c_0, for which assumption (i) is not valid.

6. CASE OF ANISOTROPIC DIFFERENTIAL COLLISION CROSS SECTION

In this case it is well known,[18] in the so-called transport approximation, that the Boltzmann equation remains the same as in the case of an isotropic collision cross section $\sigma(c,\vartheta)$, provided one substitutes for the mean free path λ the "transport (or diffusion) mean path" (or "mean free path for momentum transfer") λ_d, defined by the relationship

$$1/\lambda_d(c)=N\sigma_d(c)=N\int_0^\pi \sigma(c,\vartheta)(1-\cos\vartheta)\tfrac{1}{2}\sin\vartheta d\vartheta$$
$$=N\sigma(c)[1-\alpha(c)]=[1-\alpha(c)]/\lambda(c). \quad (37)$$

In order to calculate $w(c)$, the λ_d given by Eq. (37) may also be used. Yet, so far, only $\sigma_{el}(c)=\sigma_{tot}-\sigma_{in}$ has been introduced into Eq. (37) in order to obtain λ_d for use in Eq. (4). Moreover, the differential cross section $\sigma_{in}(c,\vartheta)$ for inelastic collisions is usually considered as isotropic. When this condition is no longer valid we may use the expression found by Altshuler,[19] i.e.,

$$\frac{1}{\lambda_d(c)}=N\sigma_d(c)=N\int_0^\pi \sigma(c,\vartheta)$$
$$\times\{1-\cos\vartheta[1-(c_{12}/c)^2]^{1/2}\}\tfrac{1}{2}\sin\vartheta d\vartheta, \quad (38)$$

where c is the speed before the collision, and c_{12} is given by the relationship

$$\tfrac{1}{2}mc_{12}^2=\epsilon_2-\epsilon_1=\epsilon, \quad (39)$$

ϵ_1 and ϵ_2 being the energy levels of two quantum states and ϵ the excitation energy of the inelastic level considered. Since

$$c^2=c_0^2+c_{12}^2, \quad (40)$$

where c_0 is the initial velocity, we may put Eq. (38) into the form

$$\frac{1}{\lambda_d(c)}=N\int_0^\pi \sigma(c,\vartheta)[1-(c_0/c)\cos\vartheta]\tfrac{1}{2}\sin\vartheta d\vartheta$$
$$=N\sigma(c)[1-\alpha(c)\beta(c)]. \quad (41)$$

When c_0/c does not depend on ϑ, the quantity $\beta(c)$ is simply given by $\beta(c)=c_0/c$. In this case we suggest another argument in favor of Eq. (41) by generalizing a procedure used by Huxley and Crompton[20] to find Eq. (4).

We use the same notation as in Ref. 20 [where inelastic collisions were not considered]. For an inelastic encounter, the velocities r and R relative to the centroid are deflected through the angle ϑ to have $r'=\beta(c)r$ and $R'=\beta(c)R$ (instead of $r'=r$ and $R'=R$ as occurs in an elastic encounter). Consequently the mean value of r' is $r\beta(c)\cos\vartheta=r\alpha(c)\beta(c)$. The product $\alpha\beta$ appears instead of α, and hence the same product appears in Eq. (14) of Ref. 20. This is acceptable, since we have proved in Sec. 4 that Eq. (4) [which is equal to Eq. (15) of Ref. 19] is valid even when there are inelastic collisions. Moreover it can be seen immediately that the use of the mean free path λ_d as given by Eq. (41) is correct in the limiting case of $\alpha(c)\to 1$ and $\beta(c)\to 0$. In fact, the substitution of Eq. (37) in Eq. (4), when $\alpha(c)\to 1$ gives $w(c)\to\infty$, whereas when $\beta(c)=0$, the direction of the emerging electron is of no concern in determining $w(c)$.

Finally, since the mean free path as given by Eq. (37), which appears in Eq. (15) of Ref. 20, is the same as the one used in Boltzmann's equation, by similar reasoning we suggest using the mean free path as given by Eq. (41) in Eqs. (24) and (34).

7. CONCLUSIONS

The method here presented consists essentially in referring to the initial velocity c_0, since the corresponding initial distribution function $F_0(c_0,\vartheta_0)$, being unaffected by the electric field, is isotropic when the differential collision cross section $\sigma(c,\vartheta)$ is isotropic, and therefore $F_0(c_0,\vartheta_0)=\frac{1}{2}f_0(c_0)\sin\vartheta_0$. This allows us to exploit the knowledge of the integrated equation of motion and the flight-time distribution, which is easily obtained and is given by Eq. (23) of Sec. 2. The drift velocity W is given by $W=\int_0^\infty w(c_0)f_0(c_0)dc_0$, and this expression is not subjected to the simplifying assumptions used by the previous theories, since we have obtained $w(c_0)$ directly and not by a first-order perturbation method.

The quantity $w(c_0)$ is the drift velocity of electrons having initial velocity c_0, and may be compared with the corresponding approximate expression for $w(c)$

[18] A. M. Weinberg and P. Wigner, *The Physical Theory of Neutron Chain Reactors* (The University of Chicago Press, Chicago, 1958), Chap. VIII, p. 196; K. U. Beckurts and K. Wirtz, *Neutron Physics* (Springer-Verlag, Berlin, 1964), Part II, p. 95; S. Glasstone and M. C. Edlung, *The Elements of Nuclear Reactor Theory* (D. Van Nostrand Co., Inc., New York, 1952), Chap. V, Sec. 5.26, p. 98; see also Ref. 19.

[19] S. Altshuler, J. Geophys. Res. 68, 4707 (1963). Notice that the speed denoted by v in Eqs. (17) and (18) of Altshuler's paper must be changed into v', since, in the remainder of the paper, Altshuler has denoted by v' the speed immediately before collisions. The use of v instead of v' in Eqs. (15)–(18) is due to the following change of variable: $vdv=v'dv'$ [performed between Eqs. (13) and (14)]. The speed v (or v') is then considered as an integration variable. But when Altshuler exploited $Q_{12}(v)$ [in our notation $\sigma_{in}(c)$], he should have replaced v by v'.

[20] L. G. H. Huxley and R. W. Crompton, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 342.

obtained by the various theories mentioned in Sec. 1. In the particular case of $\lambda/c=$const, the "complete" expression for $w(c_0)$ calculated in Sec. 2, gives, as shown in Sec. 3, the same result obtainable from Eq. (4) (which is the most complete expression obtained by the other theories) but without having to rely on simplifying assumptions.

Therefore, in the particular case of $\lambda/c=$const, we prove that Eq. (4) is valid not only for low fields but also for high fields. In the general case (Sec. 4), the expansion of $w(c_0)$ to first order in time, together with use only of the assumption that the speed variation between two successive collisions is small with respect to the thermal velocity, again gives Eq. (4). The validity of this equation can therefore be extended even to inelastic collisions by simply considering λ as the actual mean free path corresponding to the total (elastic+inelastic) collision cross section. In Sec. 5 an integral equation for the initial distribution function $f_0(c_0)$ of the velocity magnitudes is given. This equation has the same difficulty as Boltzmann's equation, in which an expansion to first order has been performed, since we have as unknown a function $f_0(c_0)$ of a single variable. The dependence on the variable ϑ has been eliminated since the initial distribution function is isotropic. In Sec. 6 the case of anisotropic $\sigma(c,\vartheta)$ is considered. In the usual transport approximation, we suggest using the mean free path for momentum transfer given by Eq. (41), which also takes into account the case of anisotropic inelastic collisions.

ACKNOWLEDGMENTS

The authors wish to thank Professor E. Gatti, Professor R. Bonalumi, and Professor F. T. Arecchi for useful critical discussions during the development of this work.

PHYSICAL REVIEW VOLUME 170, NUMBER 1 5 JUNE 1968

Variational Method for the Ground State of Multispecies Quantum Fluids*

K. R. Allen and Tucson Dunn
Department of Physics and Astronomy, University of Florida, Gainesville, Florida
(Received 22 November 1967)

A series expansion for the ground-state energy of a multispecies quantum fluid is obtained. This expansion is derived by assuming that the ground-state wave function for the fluid can be approximated by the symmetrized ground-state wave function for a mixture of quantum ideal gases times a product of pair functions. The lowest-order approximation to the energy is minimized with respect to variations in these pair functions in order to obtain an approximation to the ground-state wave function for the system. In principle, this variational procedure can be carried out to any desired order in the energy expansion, and the machinery for doing so is explicitly exhibited. The results of this variation in the lowest order are applied to a two-species system consisting of electrons and nuclei. The results are consistent at high densities.

I. INTRODUCTION

In recent years, a great deal of attention has been given to the thermodynamic properties of the quantum electron gas. A fair number of techniques have been developed for the treatment of this problem. Some of these are the perturbation expansion which used the Green's-function technique[1–3] and another developed by Bohm and Pines[4] which uses the random-phase approximation (RPA). These techniques give good results at high densities. A variational method has been developed by Gaskell,[5] who uses collective coordinates and the RPA, which is also good at high densities. Hedin[6] has combined the RPA and the Martin-Schwinger integral equation to obtain good results in the intermediate density range. The lattice-gas approach[7,8] holds at low densities.

While attempts have been made to apply the Green's-function technique to systems composed of more than one species of particle,[9] the results are very restricted. A variational method for determining the ground-state properties of multispecies quantum systems is presented in this paper. The method developed here is similar to that used by Gaskell[5] in his treatment of the quantum electron gas. We assume that the ground-state wave function can be approximated by

$$\psi=\psi_0 \exp\{-\tfrac{1}{2}\theta\}, \qquad (1.1)$$

* Work supported by the National Aeronautics and Space Administration and the National Science Foundation.

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