The Mathematical Theory of Electrical Discharges in Gases. B. Velocity-Distribution of Positive Ions in a Static Field*†

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1. INTRODUCTION

IN the present paper we treat the stationary velocity distribution, especially drift velocity, of ions in a static, homogeneous electric field in the absence of a magnetic field.

Our main assumption is that the number-density of ions,

$$n=\int f(\mathbf{c})d\mathbf{c}\equiv\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}f(\mathbf{c})dudvdw, \quad (1.1)$$

is much smaller than that of gas molecules,

$$N=\int f_1(\mathbf{c}_1)d\mathbf{c}_1. \quad (1.2)$$

Here $\mathbf{c}(u,v,w)$ and $f(\mathbf{c})$ are the velocity and the velocity-distribution function of the ions; $\mathbf{c}_1(u_1,v_1,w_1)$ and $f_1(\mathbf{c}_1)$ are those of the gas molecules.

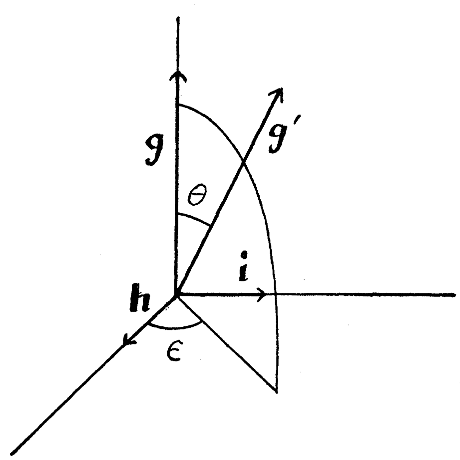

FIG. 1. Vector representation of relative velocity.

Under this assumption, f_1 takes the Maxwellian distribution,

$$f_1=N\left(\frac{m_1}{2\pi kT}\right)^{\frac{3}{2}}\exp\left(-\frac{m_1c_1^2}{2kT}\right),\quad c_1=|\mathbf{c}_1|, \quad (1.3)$$

which remains unchanged by the electric field. Here m_1 is the mass of a gas molecule; k and T are the Boltzmann constant and the absolute temperature, respectively. Moreover, the Boltzmann equation becomes linear with respect to f:

$$\frac{eE}{m}\frac{\partial f}{\partial w}=\int\int\int(f'f_1'-ff_1)gI(g,\theta)\sin\theta d\theta d\epsilon d\mathbf{c}_1,$$
$$E=|\mathbf{E}|,$$

when the z axis is taken in the direction of the electric field $\mathbf{E}$. Here e and m denote the charge and the mass of the ion, respectively; $f'f_1'-ff_1$ is the abbreviation for $f(\mathbf{c}')f_1(\mathbf{c}_1')-f(\mathbf{c})f_1(\mathbf{c}_1)$, $\mathbf{c}'$ and $\mathbf{c}_1'$ are the final velocities of the ion and the gas molecule encountering with initial velocities $\mathbf{c}$ and $\mathbf{c}_1$ with diffraction angle θ for the orbit of relative motion; $I(g,\theta)\sin\theta d\theta d\epsilon$ indicates the differential cross section for scattering into the solid angle $\sin\theta d\theta d\epsilon$ for the relative speed $g=|\mathbf{c}-\mathbf{c}_1|=|\mathbf{c}'-\mathbf{c}_1'|$ (see Fig. 1).

In terms of the function

$$f^{(0)}\equiv n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\exp\left(-\frac{mc^2}{2kT}\right),\quad c=|\mathbf{c}|, \quad (1.4)$$

to which f would reduce in case of no electric field, let

$$f=f^{(0)}(1+\Phi). \quad (1.5)$$

Then the Boltzmann equation can be expressed as

$$\frac{eE}{m}\frac{\partial f}{\partial w}=-Nf^{(0)}\mathrm{J}\Phi. \quad (1.6)$$

Here J is a linear operator operating on any function $\phi(\mathbf{c})$ of the velocity of ions,

$$\mathrm{J}\phi=\frac{1}{N}\int\int\int f_1(\phi-\phi')gI(g,\theta)\sin\theta d\theta d\epsilon d\mathbf{c}_1, \quad (1.7)$$

$\phi-\phi'$ being the abbreviation for $\phi(\mathbf{c})-\phi(\mathbf{c}')$.

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† In my previous article of the same title (T. Kihara, Revs. Modern Phys. **24**, 45 (1952)), hereafter referred to as A, I quoted several passages from my book *Imperfect Gases*. This book was originally written in Japanese and published in 1949. Although the whole text was translated into English in the United States (by U. S. Air Force in U. S. Air Force Technical Reports), the distribution of the translation is unfortunately limited. Therefore, I want to publish a revised version of the parts to which the previous article is related. In consequence, references in footnotes 2, 3, and 5 of Part A are to be rewritten as Eq. (3.1), Eq. (2.8), and Section 2 of Part B, respectively.

When we define the inner product of two functions, $\phi(\mathbf{c})$ and $\psi(\mathbf{c})$, by

$$(\phi, \psi)=\frac{1}{n}\int f^{(0)}\phi\psi d\mathbf{c}, \tag{1.8}$$

the operator J is symmetric,

$$(\psi, \mathrm{J}\phi)=(\phi, \mathrm{J}\psi), \tag{1.9}$$

and positive-definite,

$$(\phi, \mathrm{J}\phi)\geqq 0. \tag{1.10}$$

Multiplying both sides of (1.6) by $-\phi(\mathbf{c})d\mathbf{c}$ and integrating, we have

$$-\frac{eE}{m}\int \frac{\partial f}{\partial w}\phi d\mathbf{c}=N\int f^{(0)}\phi \mathrm{J}\Phi d\mathbf{c}.$$

Integrating by parts on the left side and using the relation $\mathrm{J}(1+\Phi)=\mathrm{J}\Phi$ and the symmetric property of J on the right side, we obtain

$$\frac{eE}{m}\int f\frac{\partial\phi}{\partial w}d\mathbf{c}=N\int f\mathrm{J}\phi d\mathbf{c}.$$

With average value symbols defined by

$$\langle\psi\rangle_{\mathrm{Av}}=\frac{1}{n}\int f\psi d\mathbf{c},$$

this relation becomes

$$\frac{eE}{m}\left(\frac{\partial\phi}{\partial w}\right)_{\mathrm{Av}}=N\langle \mathrm{J}\phi\rangle_{\mathrm{Av}}. \tag{1.11}$$

In particular, when w is taken for ϕ, we have

$$eE/m=N\langle \mathrm{J}w\rangle_{\mathrm{Av}}. \tag{1.12}$$

2. HEAVY IONS IN A LIGHT GAS

First,

$$\mathrm{J}\mathbf{c}=\frac{1}{N}\int\int\int f_1(\mathbf{c}-\mathbf{c}')gI(g,\theta)\sin\theta d\theta d\epsilon d\mathbf{c}_1 \tag{2.1}$$

will be transformed generally.

In terms of the velocity of the center of mass and the relative velocity before encounter,

$$\mathbf{G}=\frac{m_1}{m_1+m}\mathbf{c}_1+\frac{m}{m_1+m}\mathbf{c},\quad \mathbf{g}=\mathbf{c}-\mathbf{c}_1, \tag{2.2}$$

we have

$$\mathbf{c}=\mathbf{G}+\frac{m_1}{m_1+m}\mathbf{g},$$

and, since $\mathbf{G}$ remains unchanged by the collision,

$$\mathrm{J}\mathbf{c}=\frac{1}{N}\frac{m_1}{m_1+m}\int\int\int f_1(\mathbf{g}-\mathbf{g}')gI(g,\theta)\sin\theta d\theta d\epsilon d\mathbf{c}_1,$$

where $\mathbf{g}'$ is the relative velocity after encounter.

Taking two unit vectors perpendicular to $\mathbf{g}$ and to each other, we can express $\mathbf{g}'$ as

$$\mathbf{g}'=\mathbf{g}\cos\theta+g\mathbf{h}\sin\theta\cos\epsilon+g\mathbf{i}\sin\theta\sin\epsilon$$

(see Fig. 1). Therefore,

$$\mathrm{J}\mathbf{c}=\frac{2\pi}{N}\frac{m_1}{m_1+m}\int\int f_1\mathbf{g}(1-\cos\theta)gI(g,\theta)\sin\theta d\theta d\mathbf{c}_1.$$

In terms of effective collision cross sections between the ion and the molecule, which are defined by

$$\phi^{(l)}=\int_0^\pi(1-\cos^l\theta)gI(g,\theta)\sin\theta d\theta,\quad l=1, 2, \cdots, \tag{2.3}$$

we have

$$\mathrm{J}\mathbf{c}=\frac{2\pi}{N}\frac{m_1}{m_1+m}\int f_1\mathbf{g}\phi^{(1)}d\mathbf{c}_1,$$

namely

$$\mathrm{J}\mathbf{c}=\frac{2\pi}{N}\frac{m_1}{m_1+m}\int f_1(\mathbf{c}-\mathbf{c}_1)\phi^{(1)}d\mathbf{c}_1, \tag{2.4}$$

or, in terms of the z component,

$$\mathrm{J}w=\frac{2\pi}{N}\frac{m_1}{m_1+m}\int f_1(w-w_1)\phi^{(1)}d\mathbf{c}_1. \tag{2.5}$$

Up to this point no approximations have been made in the calculations.

Now, we treat the special case where the mass of an ion is sufficiently large in comparison with that of a gas molecule, i.e., $m\gg m_1$. Let us consider the problem on the condition that the drift velocity of the ions is much smaller than the thermal velocity of the gas molecules; i.e.,

$$(\langle w\rangle_{\mathrm{Av}})^2\ll kT/m_1. \tag{2.6}$$

The effective cross section $\phi^{(1)}$ is a function of the reduced mass $m_1m/(m_1+m)$ and the relative speed g. In the present case the former can be put equal to m_1, and the latter is

$$g=(c_1^2-2\mathbf{c}_1\cdot\mathbf{c}+c^2)^{\frac{1}{2}}\doteqdot c_1-\mathbf{c}_1\cdot\mathbf{c}/c_1.$$

Hence the cross section becomes

$$\phi^{(1)}(g)=\phi^{(1)}(c_1)-\frac{\mathbf{c}\cdot\mathbf{c}_1}{c_1}\frac{\partial\phi^{(1)}}{\partial c_1}.$$

Inserting this in (2.5) and denoting $\phi^{(1)}(c_1)$ by $\phi^{(1)}$

anew, we obtain

$$\frac{N}{2\pi}\frac{m_1+m}{m_1}\mathrm{J}w=w\int f_1\phi^{(1)}d\mathbf{c}_1+w\int f_1\frac{\partial\phi^{(1)}}{\partial c_1}\frac{w_1^2}{c_1}d\mathbf{c}_1,$$

the integrals of odd functions of $\mathbf{c}_1$ vanishing. The first term on the right-hand side is equal to

$$4\pi w\int_0^\infty f_1\phi^{(1)}c_1^2dc_1,$$

and the second term is

$$\frac{1}{3}w\int f_1\frac{\partial\phi^{(1)}}{\partial c_1}c_1d\mathbf{c}_1=\frac{4\pi}{3}w\int_0^\infty f_1\frac{\partial\phi^{(1)}}{\partial c_1}c_1^3dc_1$$

$$=-4\pi w\int_0^\infty f_1\phi^{(1)}c_1^2dc_1+\frac{4\pi}{3}w\frac{m_1}{kT}\int_0^\infty f_1\phi^{(1)}c_1^4dc_1.$$

We have, therefore,

$$\mathrm{J}w=\frac{2\pi}{N}\frac{m_1}{m_1+m}\frac{4\pi}{3}w\frac{m_1}{kT}\int_0^\infty f_1\phi^{(1)}c_1^4dc_1$$

$$=\frac{16}{3}\frac{m_1}{m_1+m}w\pi^{\frac{1}{2}}\int_0^\infty \exp(-V^2)V^4\phi^{(1)}dV,$$

$$V=(m_1/2kT)^{\frac{1}{2}}c_1.$$

In terms of weighted mean values of the effective cross sections, defined as

$$\Omega^{(l)}(r)=\pi^{\frac{1}{2}}\int_0^\infty \phi^{(l)}V^{2r+2}\exp(-V^2)dV,\qquad r=l,\,l+1,\,\cdots,$$

$$V=\left(\frac{m_1m}{m_1+m}\frac{1}{2kT}\right)^{\frac{1}{2}}g, \tag{2.7}$$

we obtain finally

$$\mathrm{J}w=\lambda w,\quad \lambda=\frac{16}{3}\frac{m_1}{m_1+m}\Omega^{(1)}(1). \tag{2.8}$$

Inserting (2.8) into (1.12), we have

$$\langle w\rangle_{\mathrm{Av}}=\frac{eE}{mN\lambda}=\frac{3}{16}\frac{m_1+m}{m_1m}\frac{eE}{N\Omega^{(1)}(1)}. \tag{2.9}$$

The mobility of heavy ions in a light gas is independent of the field strength, so long as our condition (2.6) holds.

Let us find the velocity distribution function. First,

$$\mathrm{J}(w^p)=\frac{1}{N}\int\int\int f_1(w^p-w'^p)gI(g,\theta)d\theta d\epsilon d\mathbf{c}_1$$

will be evaluated for any positive integer p. Considering

$$w^p-w'^p=\left(G_z+\frac{m_1}{m_1+m}g_z\right)^p-\left(G_z+\frac{m_1}{m_1+m}g_z'\right)^p$$

$$\doteqdot p\frac{m_1}{m_1+m}(g_z-g_z')G_z^{p-1},$$

we have, after a procedure similar to that used in obtaining (2.5),

$$\mathrm{J}(w^p)=\frac{2\pi}{N}\frac{m_1}{m_1+m}p\int f_1g_zG_z^{p-1}\phi^{(1)}d\mathbf{c}_1$$

$$=\frac{2\pi}{N}\frac{m_1}{m_1+m}p\int f_1(w-w_1)\times\left(w+\frac{m_1}{m_1+m}w_1\right)^{p-1}\phi^{(1)}d\mathbf{c}_1.$$

Bearing in mind that mw^2 and $m_1w_1^2$ are of the same order of magnitude, we can carry out calculations similar to the above and obtain

$$\mathrm{J}(w^p)=\lambda\left[pw^p-p(p-1)w^{p-2}\frac{kT}{m}\right], \tag{2.10}$$

where λ is the same as in (2.8), which is a special case of (2.10). When this is rewritten as

$$\mathrm{J}(w^p)=\lambda\left[w\frac{d(w^p)}{dw}-\frac{kT}{m}\frac{d^2(w^p)}{dw^2}\right],$$

it is easy to see that the relation

$$\mathrm{J}\Phi=\lambda\left(w\frac{d\Phi}{dw}-\frac{kT}{m}\frac{d^2\Phi}{dw^2}\right) \tag{2.11}$$

holds for any function Φ which is expressed by a power series in w and does not depend on the other components of $\mathbf{c}$.

Anticipating that Φ in (1.5) and (1.6) is an analytic function of w only, and does not depend on the other components, u and v, we make use of (2.11). After some manipulation, we have

$$\frac{eE}{m}\frac{\partial f}{\partial w}=N\lambda\left(\frac{kT}{m}\frac{\partial^2 f}{\partial w^2}+w\frac{\partial f}{\partial w}+f\right),$$

or, in terms of $\langle w\rangle_{\mathrm{Av}}$,

$$\frac{kT}{m}\frac{\partial^2 f}{\partial w^2}+(w-\langle w\rangle_{\mathrm{Av}})\frac{\partial f}{\partial w}+f=0.$$

From this differential equation it is evident that f can be obtained by replacing w in $f^{(0)}$ by $w-\langle w\rangle_{\mathrm{Av}}$. Namely, we obtain

$$f=n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\exp\left[-\frac{m}{2kT}\{u^2+v^2+(w-\langle w\rangle_{\text{Av}})^2\}\right], \quad (2.12)$$

in accordance with our anticipation. *The velocity distribution of heavy ions in a light gas is Maxwellian around the drift velocity*, so long as (2.6) holds.

3. MAXWELLIAN MODEL OF COLLISION CROSS SECTIONS

The Maxwellian model is defined by the idealization that the scattering coefficient $I(g,\theta)$ is inversely proportional to the relative speed g. For this model each $\phi^{(l)}$ becomes independent of g, and the mathematical handling is simple without any assumption as regards the ratio of the mass of an ion to that of a molecule.

In this case, (2.5) is reduced to

$$\mathrm{J}w=2\pi\phi^{(1)}\frac{m_1}{m_1+m}w. \quad (3.1)$$

Hence we have, by use of (1.12),

$$\langle w\rangle_{\text{Av}}=\frac{eE}{2\pi\phi^{(1)}N}\frac{m_1+m}{m_1m}. \quad (3.2)$$

For the Maxwellian model, the mobility times gas density, $N\langle w\rangle_{\text{Av}}/E$, is independent of the field strength and the temperature.

When $\phi^{(1)}$ does not depend on the relative speed, $\Omega^{(1)}(1)$ is equal to $3\pi\phi^{(1)}/8$, and Eq. (3.2) can be rewritten as

$$\langle w\rangle_{\text{Av}}=\frac{3}{16}\frac{m_1+m}{m_1m}\frac{eE}{N\Omega^{(1)}(1)}, \quad (3.3)$$

which is identical with (2.9). This formula, which is valid in these two idealized cases, is the first approximation to a more detailed expression to be derived in the next section.

Equation (3.1) indicates that w is one of the eigenfunctions of the symmetric linear operator J, and the corresponding eigenvalue is $2\pi\phi^{(1)}m_1/(m_1+m)$. Let us make a little preparation to investigate other eigenfunctions and eigenvalues.

Sonine polynomials $S_m^{(n)}(x)$ are defined by the expression

$$(1-s)^{-m-1}\exp\left(-\frac{xs}{1-s}\right)=\sum_{n=0}^{\infty}S_m^{(n)}(x)s^n, \quad (3.4)$$

where $0<s<1$, and x and m are real. In particular,

$$S_m^{(0)}=1, \quad S_m^{(1)}(x)=m+1-x. \quad (3.5)$$

Since

$$(1-s)^{-m-1}(1-t)^{-m-1}\times\int_0^\infty\exp\left[-x\left(1+\frac{s}{1-s}+\frac{t}{1-t}\right)\right]x^mdx$$
$$=(1-s)^{-m-1}(1-t)^{-m-1}\int_0^\infty\exp\left[-\frac{x(1-st)}{(1-s)(1-t)}\right]x^mdx$$
$$=(1-st)^{-m-1}\Gamma(m+1),$$

we obtain, by equating coefficients of s^pt^q, the orthogonality relation,

$$\int_0^\infty e^{-x}S_m^{(p)}(x)S_m^{(q)}(x)x^mdx=\frac{\Gamma(m+p+1)}{p!}\delta_{pq}, \quad (3.6)$$

where δ_{pq} is unity for $p=q$ and zero for $p\neq q$. Differentiating each side of (3.4) with respect to x, we have

$$\frac{d}{dx}S_m^{(n)}(x)=-S_{m+1}^{(n-1)}(x). \quad (3.7)$$

Multiplying each side of (3.4) by $1-s$, we have a recursion formula,

$$S_{m-1}^{(n)}=S_m^{(n)}-S_m^{(n-1)}. \quad (3.8)$$

By differentiating (3.4) with respect to s and replacing m by $m-1$, and n by $n-1$, we have another relation

$$mS_m^{(n-1)}(x)-xS_{m+1}^{(n-1)}(x)=nS_{m-1}^{(n)}(x). \quad (3.9)$$

Finally, by combining (3.8) and (3.9), we have

$$mS_m^{(n)}(x)-xS_{m+1}^{(n-1)}(x)=(m+n)S_{m-1}^{(n)}(x). \quad (3.10)$$

In terms of these Sonine polynomials, we define functions of $\mathbf{c}$ by

$$\psi_l^{(r)}=\left(\frac{mc^2}{2kT}\right)^{l/2}P_l\left(\frac{w}{c}\right)S_{l+\frac{1}{2}}^{(r)}\left(\frac{mc^2}{2kT}\right), \quad (3.11)$$
$$l,r=0,1,2,\cdots,$$

P_l being Legendre polynomials. Then each $\psi_l^{(r)}$ is a polynomial of degree $l+2r$ in the components of $\mathbf{c}$; and the orthogonality relation is given by

$$(\psi_l^{(r)},\psi_{l'}^{(r')})=\frac{1}{n}\int f^{(0)}\psi_l^{(r)}\psi_{l'}^{(r')}d\mathbf{c}$$
$$=\frac{2}{2l+1}\frac{1}{\pi^{\frac{1}{2}}}\frac{1}{r!}\Gamma(l+r+\tfrac{3}{2})\delta_{ll'}\delta_{rr'}. \quad (3.12)$$

Let us specialize ϕ in (1.11) to $\psi_l^{(r)}$. Since, by use of (3.7) and (3.10) and similar relations for the Legendre polynomials, the relation

$$(l+\tfrac{1}{2})\left(\frac{2kT}{m}\right)^{\frac{1}{2}}\frac{\partial\psi_l^{(r)}}{\partial w}=l(l+\tfrac{1}{2}+r)\psi_{l-1}^{(r)}-(l+1)\psi_{l+1}^{(r-1)}$$

$(\psi_{l+1}^{(-1)}\equiv 0)$ can be derived, we obtain generally

$$(l+\tfrac{1}{2})\langle J\psi_l^{(r)}\rangle_{Av}=\mathcal{E}[l(l+\tfrac{1}{2}+r)\langle\psi_{l-1}^{(r)}\rangle_{Av}-(l+1)\langle\psi_{l+1}^{(r-1)}\rangle_{Av}], \quad (3.13)$$

where

$$\mathcal{E}\equiv(eE/mN)(m/2kT)^{\frac{1}{2}}. \quad (3.14)$$

In particular, for the Maxwellian model each $\psi_l^{(r)}$ is an eigenfunction of the operator J:

$$J\psi_l^{(r)}=\lambda_r(l)\psi_l^{(r)}. \quad (3.15)$$

This can be directly ascertained for $l+2r$ small; in terms of

$$W\equiv\left(\frac{m}{2kT}\right)^{\frac{1}{2}}w, \quad C^2\equiv\frac{mc^2}{2kT},$$

and

$$M_1\equiv\frac{m_1}{m_1+m}, \quad M_2\equiv\frac{m}{m_1+m}, \quad (3.16)$$

the eigenfunctions and eigenvalues for $l+2r\leqq 3$ are as follows:

$\psi_0^{(0)}=1, \quad \lambda_0(0)=0;$

$\psi_1^{(0)}=W, \quad \lambda_0(1)=2\pi M_1\phi^{(1)};$

$\psi_0^{(1)}=\tfrac{3}{2}-C^2, \quad \lambda_1(0)=4\pi M_1M_2\phi^{(1)};$

$\psi_2^{(0)}=\tfrac{3}{2}W^2-\tfrac{1}{2}C^2,$

$\lambda_0(2)=\pi M_1(4M_2\phi^{(1)}+3M_1\phi^{(2)});$

$\psi_1^{(1)}=W[(5/2)-C^2],$

$\lambda_1(1)=2\pi M_1(M_1^2\phi^{(1)}+3M_2^2\phi^{(1)}+2M_1M_2\phi^{(2)});$

$\psi_3^{(0)}=(5/2)W^3-\tfrac{3}{2}WC^2,$

$\lambda_0(3)=\pi M_1(-3M_1^2\phi^{(1)}+6M_2^2\phi^{(1)}+9M_1M_2\phi^{(2)}+5M_1^2\phi^{(3)}).$

In general,

$$\lambda_r(l)>0 \quad \text{for} \quad l+2r>0.$$

Inserting (3.15) into (3.13), we have

$$(l+\tfrac{1}{2})\lambda_r(l)\langle\psi_l^{(r)}\rangle_{Av}=\mathcal{E}[l(l+\tfrac{1}{2}+r)\langle\psi_{l-1}^{(r)}\rangle_{Av}-(l+1)\langle\psi_{l+1}^{(r-1)}\rangle_{Av}], \quad (3.17)$$

from which it is evident that $(-1)^r\langle\psi_l^{(r)}\rangle_{Av}$ is positive and proportional to E^{l+2r}.

By this system of equations each $\langle\psi_l^{(r)}\rangle_{Av}$ can be expressed in terms of the $\lambda_r(l)$:

$$\langle\psi_l^{(0)}\rangle_{Av}=l!\mathcal{E}^l/\lambda_0(1)\lambda_0(2)\cdots\lambda_0(l), \quad l=1,2,\cdots,$$

$$\langle\psi_0^{(1)}\rangle_{Av}=-2\mathcal{E}^2/\lambda_0(1)\lambda_1(0),$$

$$\langle\psi_1^{(1)}\rangle_{Av}=-\frac{2}{3}\frac{\mathcal{E}^3}{\lambda_0(1)\lambda_1(1)}\left[\frac{4}{\lambda_0(2)}+\frac{5}{\lambda_1(0)}\right],$$

etc. Since

$$\frac{m}{2kT}\langle u^2\rangle_{Av}-\tfrac{1}{2}=\frac{m}{2kT}\langle v^2\rangle_{Av}-\tfrac{1}{2}$$

$$=-\tfrac{1}{3}(\langle\psi_0^{(1)}\rangle_{Av}+\langle\psi_2^{(0)}\rangle_{Av})$$

$$=\frac{2}{3}\frac{\mathcal{E}^2}{\lambda_0(1)}\left[\frac{1}{\lambda_1(0)}-\frac{1}{\lambda_0(2)}\right]$$

$$=2\pi\phi^{(2)}\mathcal{E}^2M_1^2/\lambda_0(1)\lambda_1(0)\lambda_0(2)>0,$$

and

$$\frac{m}{2kT}\langle(w-\langle w\rangle_{Av})^2\rangle_{Av}-\tfrac{1}{2}$$

$$=\tfrac{1}{3}(2\langle\psi_2^{(0)}\rangle_{Av}-\langle\psi_0^{(1)}\rangle_{Av}-3\langle\psi_1^{(0)}\rangle_{Av}^2)$$

$$=\frac{1}{3}\frac{\mathcal{E}^2}{\lambda_0(1)}\left[\frac{4}{\lambda_0(2)}+\frac{2}{\lambda_1(0)}-\frac{3}{\lambda_0(1)}\right]$$

$$=\frac{2\pi M_1^2\mathcal{E}^2}{\lambda_0(1)\lambda_1(0)\lambda_0(2)}[M_1\phi^{(2)}+2M_2(2\phi^{(1)}-\phi^{(2)})]>0,$$

it follows that *the velocity distribution is less sharp than the Maxwellian distribution corresponding to the same temperature.*

In order to argue more in detail, let us assume between an ion and a gas molecule an attractive potential, inversely proportional to the fourth power of the distance. For this type of Maxwellian model we have the following numerical values:[1]

$$\phi^{(2)}/\phi^{(1)}=0.70, \quad \phi^{(3)}/\phi^{(1)}=1.2.$$

By use of these it can be shown that

$$\langle(w-\langle w\rangle_{Av})^2\rangle_{Av}-\langle u^2\rangle_{Av}>0,$$

and

$$\langle(w-\langle w\rangle_{Av})^3\rangle_{Av}>0.$$

These inequalities provide information concerning the deviations from spherical symmetry and plane symmetry of the velocity distribution: *the distribution of the z component of ion velocities is less sharp than that of the other components; its rate of decrease in the rear is steeper than that in the front, the maximum taking place at a negative z component of the velocity.*

4. GENERAL THEORY OF MOBILITY

In the two preceding sections we have treated special cases; the general case will be dealt with in this section.

Except for the Maxwellian model, the $\psi_l^{(r)}$ defined by (3.11) are not necessarily eigenfunctions of the linear operator J. However, since J is spherically symmetric, we can let

$$J\psi_l^{(r)}=\sum_s a_{rs}(l)\psi_l^{(s)}, \quad (4.1)$$

[1] The first value is taken from H. R. Hassé, Phil. Mag. **1**, 139 (1926); H. R. Hassé and W. R. Cook, Phil. Mag. **3**, 977 (1927).

with

$$a_{rs}(l) = (\psi_l^{(s)}, J\psi_l^{(r)})/(\psi_l^{(s)}, \psi_l^{(s)}). \qquad (4.2)$$

In particular, $a_{rr}(l) \geqq 0$, since J is positive-definite.

Inserting (4.1) into (3.13), we have

$$(l+\tfrac{1}{2})\textstyle\sum_s a_{rs}(l)\langle\psi_l^{(s)}\rangle_{\mathrm{Av}} = \mathcal{E}[l(l+\tfrac{1}{2}+r)\langle\psi_{l-1}^{(r)}\rangle_{\mathrm{Av}} - (l+1)\langle\psi_{l+1}^{(r-1)}\rangle_{\mathrm{Av}}] \qquad (4.3)$$

$(\psi_{l+1}^{(-1)} \equiv 0)$, from which it is evident that $\langle\psi_l^{(r)}\rangle_{\mathrm{Av}}$ is an even function of E for l even and an odd function of E for l odd. Hence the drift velocity and the mobility are odd and even, respectively. Equation (4.3) can be solved by means of successive approximations as follows:

The nondiagonal coefficients, $a_{rs}(l)$ for $r \neq s$, are considered to be small, since they vanish in the case of the Maxwellian model. Therefore, we can determine the first approximation, which will be referred to as $\langle\psi_l^{(r)}\rangle_{\mathrm{AvI}}$, from

$$(l+\tfrac{1}{2})a_{rr}(l)\langle\psi_l^{(r)}\rangle_{\mathrm{AvI}} = \mathcal{E}[l(l+\tfrac{1}{2}+r)\langle\psi_{l-1}^{(r)}\rangle_{\mathrm{AvI}} - (l+1)\langle\psi_{l+1}^{(r-1)}\rangle_{\mathrm{AvI}}]. \qquad (4.4)$$

It is evident that $(-1)^r\langle\psi_l^{(r)}\rangle_{\mathrm{AvI}}$ is positive and proportional to the $(l+2r)$th power of the field strength.

In particular,

$$a_{00}(1)\langle\psi_1^{(0)}\rangle_{\mathrm{AvI}} = \mathcal{E},$$

or

$$\langle w\rangle_{\mathrm{AvI}} = \frac{eE}{Nm}\frac{1}{a_{00}(1)}. \qquad (4.5)$$

The second approximation can be determined from the equation to which (4.3) reduces when the first approximations are inserted into terms with nondiagonal coefficients. That is,

$$\langle\psi_1^{(0)}\rangle_{\mathrm{AvII}}[a_{00}(1) + a_{01}(1)\langle\psi_1^{(1)}\rangle_{\mathrm{AvI}}/\langle\psi_1^{(0)}\rangle_{\mathrm{AvI}} + \cdots] = \mathcal{E},$$

or

$$\langle w\rangle_{\mathrm{AvII}} = \frac{eE}{Nm}\left[\sum_{r=0}^{\infty} a_{0r}(1)\frac{\langle\psi_1^{(r)}\rangle_{\mathrm{AvI}}}{\langle\psi_1^{(0)}\rangle_{\mathrm{AvI}}}\right]^{-1}. \qquad (4.6)$$

Now we must evaluate

$$a_{0r}(1) = (\psi_1^{(r)}, \mathrm{J}\psi_1^{(0)})/(\psi_1^{(r)}, \psi_1^{(r)}) = \frac{3}{2}\frac{\pi^{\frac{1}{2}}r!}{\Gamma[r+(5/2)]}(\psi_1^{(r)}, \mathrm{J}\psi_1^{(0)}). \qquad (4.7)$$

By the definition of the Sonine polynomials, $(\psi_1^{(r)}, \mathrm{J}\psi_1^{(0)})$ is the coefficient of s^r in the expansion of

$$\frac{m}{2kT}\frac{1}{n}(1-s)^{-(5/2)}\int f^{(0)}\exp\left(-\frac{s}{1-s}\frac{mc^2}{2kT}\right)w\mathrm{J}wd\mathbf{c}, \qquad (4.8)$$

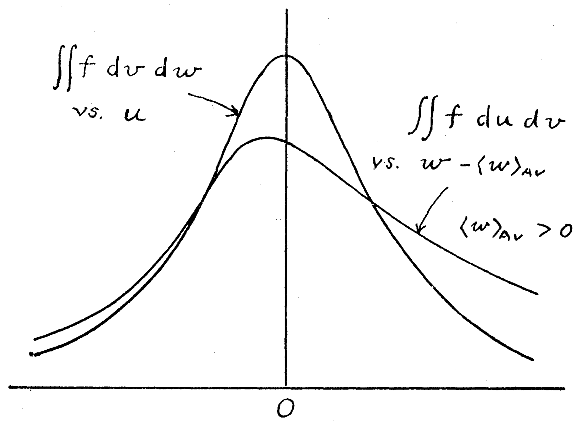

FIG. 2. Asymmetry of the velocity distribution of ions with a positive drift velocity.

which is equal to, by virtue of (2.5), (1.3), and (1.4),

$$\frac{\pi}{kT}\frac{m_1m}{m_1+m}\frac{(m_1m)^{\frac{3}{2}}}{(2\pi kT)^3}(1-s)^{-(5/2)} \times \int\int \exp(-A)w(w-w_1)\phi^{(1)}d\mathbf{c}d\mathbf{c}_1,$$

where

$$A \equiv \frac{m_1c_1^2}{2kT} + \frac{1}{1-s}\frac{mc^2}{2kT}.$$

In terms of the velocity of the center of mass, $\mathbf{G}$, and the relative velocity, $\mathbf{g}$, given by (2.2), we have

$$A = \frac{1}{1-s}\frac{m_1+m}{2kT}[(1-M_1s)G^2 + M_1M_2(1-M_2s)g^2 + 2M_1M_2s\mathbf{G}\cdot\mathbf{g}]$$

$(G = |\mathbf{G}|,\ g = |\mathbf{g}|)$, where M_1 and M_2 are given by (3.16). By use of a new variable

$$\mathbf{G}' = \mathbf{G} + \frac{M_1M_2s}{1-s}\mathbf{g}, \quad G' = |\mathbf{G}'|,$$

this can be transformed into a quadratic form:

$$A = \frac{1-M_1s}{1-s}\frac{m_1+m}{2kT}G'^2 + \frac{1}{1-M_1s}\frac{1}{2kT}\frac{m_1m}{m_1+m}g^2.$$

Since

$$\frac{\partial(\mathbf{G}, \mathbf{g})}{\partial(\mathbf{c}, \mathbf{c}_1)} = \frac{\partial(\mathbf{G}', \mathbf{g})}{\partial(\mathbf{G}, \mathbf{g})} = 1,$$

we can substitute $d\mathbf{G}'d\mathbf{g}$ for $d\mathbf{c}d\mathbf{c}_1$. Furthermore, for

$$w(w-w_1) = (G_z + M_1g_z)g_z = \left(G_z' + \frac{1-s}{1-M_1s}M_1g_z\right)g_z$$

we can substitute

$$\frac{1}{3}\frac{1-s}{1-M_1 s}M_1 g^2,$$

because $\phi^{(1)}$ is a function of g. By use of all these realtions, and by integration with respect to $\mathbf{G}'$, (4.8) is transformed into

$$\frac{8}{3}M_1\pi^{\frac{1}{2}}\int_0^\infty (1-M_1 s)^{-(5/2)} \times\exp\left(-\frac{V^2}{1-M_1 s}\right)V^4\phi^{(1)}dV, \quad (4.9)$$

$$V=\left(\frac{m_1 m}{m_1+m}\frac{1}{2kT}\right)^{\frac{1}{2}}g.$$

Consulting the definition of $\Omega^{(1)}(1)$, (2.7), we see that (4.9) divided by $8M_1/3$ is equal to $\Omega^{(1)}(1)$ in which T is replaced by $T(1-M_1 s)$. (4.9) is, therefore, equal to

$$\frac{8}{3}M_1\sum_{r=0}^{\infty}\frac{(-1)^r}{r!}(M_1 sT)^r\frac{d^r}{dT^r}\Omega^{(1)}(1).$$

Hence it follows that

$$(\psi_1^{(r)}, J\psi_1^{(0)})=\frac{8}{3}M_1\frac{(-1)^r}{r!}(M_1 T)^r\frac{d^r}{dT^r}\Omega^{(1)}(1). \quad (4.10)$$

(Making use of the relation

$$T\frac{d}{dT}\Omega^{(l)}(r)=\Omega^{(l)}(r+1)-(r+\tfrac{3}{2})\Omega^{(l)}(r),$$

or from (4.9) directly, we can express (4.10) in terms of $\Omega^{(1)}(1)$, $\Omega^{(1)}(2)$, $\cdots$, $\Omega^{(1)}(r+1)$. We prefer, however, not to rewrite for the present purpose.)

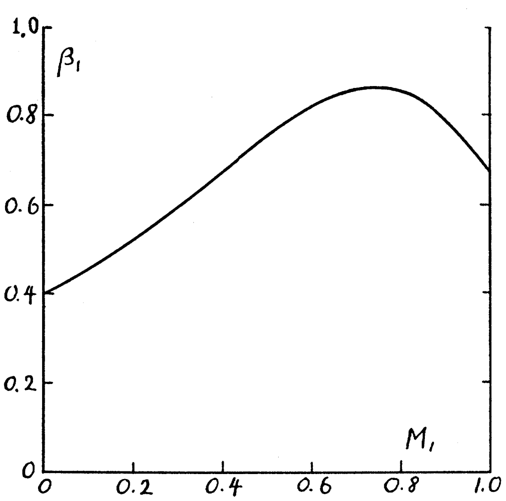

FIG. 3. Values of the factor β_1 in the coefficient b_1.

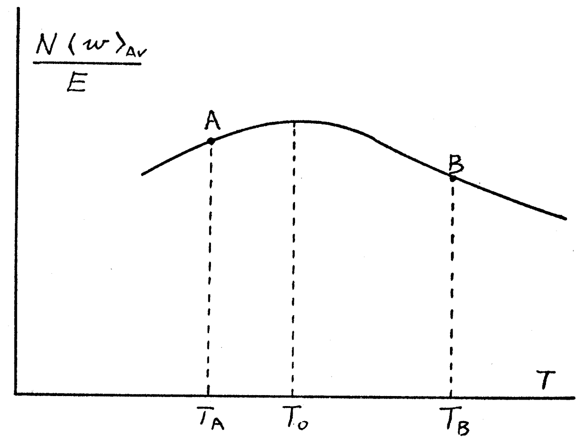

FIG. 4. Mobility times gas density for infinitesimal field strength as a function of temperature. Points A and B correspond to A and B in Fig. 5, respectively.

Inserting (4.10) into (4.7), and consulting (4.5) and (4.6), we obtain finally

$$\langle w\rangle_{\mathrm{AvI}}=\frac{3}{16}\frac{m_1+m}{m_1 m}\frac{eE}{N\Omega^{(1)}(1)}, \quad (4.11)$$

$$\langle w\rangle_{\mathrm{AvII}}=\frac{3}{16}\frac{m_1+m}{m_1 m}\frac{eE}{N}\left[\sum_{r=0}^{\infty}\frac{(b_r T)^r}{r!}\frac{d^r}{dT^r}\Omega^{(1)}(1)\right]^{-1}, \quad (4.12)$$

where

$$(b_r)^r=\frac{3}{4}\frac{\pi^{\frac{1}{2}}r!}{\Gamma[r+(5/2)]}\frac{(-1)^r\langle\psi_1^{(r)}\rangle_{\mathrm{AvI}}}{\langle\psi_1^{(0)}\rangle_{\mathrm{AvI}}}(M_1)^r. \quad (4.13)$$

The b_r are positive and proportional to E^{2r}, except that $b_0=1$.

In the case of the Maxwellian model, for which $\Omega^{(l)}(r)$ is independent of T, our first and second approximations coincide with each other. For heavy ions also, subject to the condition (2.6), the second approximation becomes identical with the first, because b_1, b_2, $\cdots$, which can be expressed in the form

$$b_r=\frac{m_1}{2kT}(\langle w\rangle_{\mathrm{Av}})^2\beta_r, \quad r=1, 2, \cdots,$$

with β_r remaining finite for the limit $M_1\to 0$, vanish. In these two cases the first approximation is exact, as we already know.

In general cases let us content ourselves with the second approximation. The mobility is then given by the right-hand side of (4.12) divided by E. The relationship shows that an increase of E^2 and an increase of T have a somewhat similar effect on the mobility. The weaker the field is, the more accurately holds the similarity. *For a sufficiently weak field, mobility times density is a function of one variable,* $T(1+b_1)$.

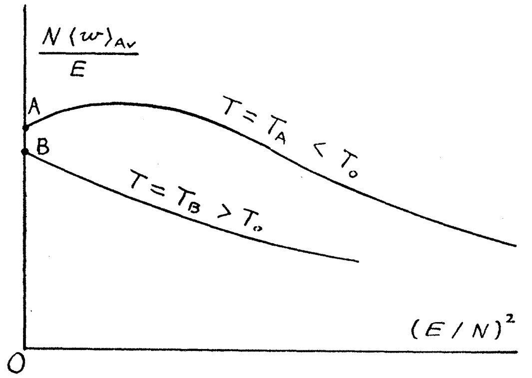

FIG. 5. Mobility times gas density as functions of $(E/N)^2$, E and N being the field strength and the number-density of gas molecules, respectively (see Fig. 4).

As regards

$$b_1=\frac{m_1}{2kT}(\langle w\rangle_{Av})^2\beta_1, \tag{4.14}$$

we obtain

$$\beta_1=\frac{4}{15}M_2\left[\frac{a_{00}(1)}{a_{11}(1)}\left(4\frac{a_{00}(1)}{a_{00}(2)}+5\frac{a_{00}(1)}{a_{11}(0)}\right)\right],$$

which can be approximated by the value for the Maxwellian model

$$\beta_1=\frac{4}{15}M_2\left[\frac{\lambda_0(1)}{\lambda_1(1)}\left(4\frac{\lambda_0(1)}{\lambda_0(2)}+5\frac{\lambda_0(1)}{\lambda_1(0)}\right)\right]$$
$$=\tfrac{2}{5}(12M_2+5M_1\phi^{(2)}/\phi^{(1)})\times(4M_2+3M_1\phi^{(2)}/\phi^{(1)})^{-1}\times(M_1^2+3M_2^2+2M_1M_2\phi^{(2)}/\phi^{(1)})^{-1}.$$

Figure 3 shows β_1 for $\phi^{(2)}/\phi^{(1)}=0.70$.

According to experimental results, the temperature variation of the mobility times gas density for infinitesimal field strength has a maximum at a certain temperature, T_0, as shown in Fig. 4, indicating that $\Omega^{(1)}(1)$ has a minimum at that temperature. Consulting this fact, our theory can predict the following field variation of the mobility.

For temperatures a little lower than T_0, the mobility first increases with the field strength, then takes a maximum and finally decreases; for temperatures higher than T_0, the mobility decreases from the beginning (see Fig. 5).

The temperatures T_0 are such as are given in Table I. Since T_0 is usually higher than room temperatures, the mobility usually must first increase with the field strength. In fact, measurements by Mitchell and Ridler[2] on the mobility of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_3^+, $Na^+(NH_3)$, and N_2^+ in N_2 as well as those by Hershey[3] on the mobility of K^+ in H_2, He, Ne, and A correspond to the case $T<T_0$. It is regrettable that many recent measurements made at the Bell Telephone Laboratory[4] are lacking in weak field regions and cannot be used for the present purpose.

Recently Wannier[5] at the Bell Telephone Laboratory tackled the same problem as the present article. After he treated some special cases, such as the case of an extremely high field and the case of the Maxwellian cross section, he concluded: "It is to be hoped that a more satisfactory way of proceeding can be found." The present author hopes that the way of proceeding developed in this section will be satisfactory.

5. MOBILITY IN A WEAK FIELD

When the electric field is infinitesimal, both the first and the second approximations of the drift velocity are given by the right-hand side of (4.11). The aim of this section is to derive a more accurate formula in this case, chiefly in order to have some information about the accuracy of our formula (4.12). (We can use the experimental results of the mobility in a weak field for the purpose of determining the force between an ion and a molecule. An accurate expression is desirable for this purpose, too.)

When the electric field is sufficiently weak, Eq. (4.3) reduces to

$$\textstyle\sum_s a_{rs}(l)\langle\psi_l^{(s)}\rangle_{Av}=\mathcal{E}\delta_{r0}\delta_{l0},$$

or

$$\langle\psi_l^{(r)}\rangle_{Av}=0 \quad\text{for}\quad l\neq 1 \tag{5.1}$$

and for $l=1$,

$$\textstyle\sum_s a_{rs}\langle\psi_1^{(s)}\rangle_{Av}=\mathcal{E}\delta_{r0}, \tag{5.2}$$

where

$$a_{rs}\equiv a_{rs}(1).$$

Let the first approximation, $\langle\psi_1^{(r)}\rangle_{AvI}$, be determined by

$$a_{rr}\langle\psi_1^{(r)}\rangle_{AvI}=\mathcal{E}\delta_{r0},$$

and the nth approximation, $\langle\psi_1^{(r)}\rangle_{Avn}$, be determined by

$$a_{rr}\langle\psi_1^{(r)}\rangle_{Avn}+\textstyle\sum_s(1-\delta_{rs})a_{rs}\langle\psi_1^{(s)}\rangle_{Avn-1}=\mathcal{E}\delta_{r0}$$

TABLE I. The temperatures corresponding to the minimum of $\Omega^{(1)}(1)$.

	T_0	Reference
He^+ in He	*ca* 300°K	a
N_2^+ in N_2	*ca* 700	a
Cs^+ in He	210	b
Na^+ in He	*ca* 600	b
Li^+ in He	*ca* 700	c
K^+ in A	400	c

[a] A. M. Tyndall and A. F. Pearce, Proc. Roy. Soc. (London) **A149**, 426 (1935).
[b] A. F. Pearce, Proc. Roy. Soc. (London) **A155**, 490 (1936).
[c] K. Hoselitz, Proc. Roy. Soc. (London) **A177**, 200 (1941).

[2] J. H. Mitchell and K. E. W. Ridler, Proc. Roy. Soc. (London) **A146**, 911 (1934).

[3] A. V. Hershey, Phys. Rev. **56**, 908 (1939).
[4] J. A. Hornbeck, Phys. Rev. **84**, 615 (1951); R. N. Varney, Phys. Rev. **88**, 362 (1952); **89**, 708 (1953).
[5] G. H. Wannier, Phys. Rev. **83**, 281 (1951); **87**, 795 (1952).

($n=$II, III, $\cdots$). Then we obtain, for instance,

$$\langle\psi_1{}^{(r)}\rangle_{\text{Av III}}=\frac{\mathcal{E}}{a_{rr}}\Bigg[\delta_{r0}-(1-\delta_{r0})\frac{a_{r0}}{a_{00}}+\sum\nolimits_s (1-\delta_{rs})(1-\delta_{s0})\frac{a_{rs}a_{s0}}{a_{ss}a_{00}}\Bigg].$$

In particular, for $r=0$

$$\langle w\rangle_{\text{Av III}}=\langle w\rangle_{\text{Av I}}\left[1+\sum_{s=1}^{\infty}\frac{a_{0s}a_{s0}}{a_{ss}a_{00}}\right]. \tag{5.3}$$

Let us adopt

$$\langle w\rangle_{\text{Av I}}(1+a_{01}a_{10}/a_{11}a_{00})$$

as an approximation to $\langle w\rangle_{\text{Av}}$. Since we have

$$\frac{a_{01}a_{10}}{a_{11}a_{00}}=\frac{a_{00}}{a_{11}}\cdot\frac{a_{01}}{a_{00}}\frac{a_{10}}{a_{00}}=\frac{2}{5}\frac{a_{00}}{a_{11}}M_1{}^2\left(\frac{T}{\Omega^{(1)}(1)}\frac{d\Omega^{(1)}(1)}{dT}\right)^2,$$

and a_{00}/a_{11} can be approximated by the value for the Maxwellian model,

$$\frac{\lambda_0(1)}{\lambda_1(1)}=(M_1{}^2+3M_2{}^2+2M_1M_2\phi^{(2)}/\phi^{(1)})^{-1},$$

we obtain

$$\langle w\rangle_{\text{Av}}\doteqdot\langle w\rangle_{\text{Av I}}(1+\Delta), \tag{5.4}$$

where

$$\Delta=\tfrac{2}{5}(M_1{}^2+3M_2{}^2+2M_1M_2\phi^{(2)}/\phi^{(1)})^{-1}\times\left(M_1\frac{d\ln\Omega^{(1)}(1)}{d\ln T}\right)^2, \tag{5.5}$$

in which 0.7 can be substituted for $\phi^{(2)}/\phi^{(1)}$.

The Δ is large when $M_2=1-M_1$ is small. For M_2 sufficiently small, we have

$$\Delta=\frac{2}{5}\left(\frac{d\ln\Omega^{(1)}(1)}{d\ln T}\right)^2,$$

which takes the value

$$\Delta=\frac{1}{10}\left(1-\frac{4}{s}\right)^2, \tag{5.6}$$

when the inverse power potential

$$u(r)=\lambda r^{-s} \tag{5.7}$$

is assumed between the ion and the molecule.

Moreover, in the case of $M_2\ll 1$, the problem can be treated exactly.[6] The precise value when (5.7) is adopted is related to the first approximation as

$$\frac{\langle w\rangle_{\text{Av}}}{\langle w\rangle_{\text{Av I}}}=\frac{16}{9\pi}\Gamma\left(3-\frac{2}{s}\right)\Gamma\left(2+\frac{2}{s}\right). \tag{5.8}$$

The numerical values of (5.8) and $1+\Delta$, obtainable from (5.6), are as follows:

s	∞	12	4	2
$1+\Delta$	1.100	1.044	1	1.100
(5.8)	1.132	1.056	1	1.132

Since the actual case corresponds to such values of s as $4\lesssim s\lesssim 12$, the accuracy of (5.4) is satisfactory, and Eq. (4.12) is accurate within the error of $6M_1{}^2$ percent, at least for weak fields.

ERRATA FOR PART A

In the second term on the left-hand side of (2.2), change $\partial\mathbf{c}$ to $\partial\mathbf{r}$.

Four lines above Eq. (A.1), change $\langle\mathbf{c}^2\rangle_{\text{Av}}$ to $|\langle\mathbf{c}\rangle_{\text{Av}}|^2$.

Five lines above Eq. (A.2), change $1-\cos l\theta$ to $1-\cos^l\theta$.

First column of Table II, change He, He, $\cdots$ to He, Ne, $\cdots$.

Eqs. (10.1) and (10.5), take out the absolute value symbols.

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[6] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, London, 1939), p. 187.