FREE PATH FORMULAE FOR THE COEFFICIENT OF DIFFUSION D AND VELOCITY OF DRIFT W OF IONS AND ELECTRONS IN GASES

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Summary

In derivations of formulae for D and W for electrons by the method of free paths (Huxley 1957*a*, 1957*b*) the assumption was made that along a number of successive free paths an electron travels at essentially the same speed c. As this assumption is not true of ions it would not be legitimate to apply the formulae to the motion of ions in gases without further discussion. However, the formulae are in fact valid for ionic motion and in what follows they are established in a more general form.

I. Coefficient of Diffusion D

Consider a large number p of free paths $x_1, x_2, \ldots, x_n$ all traversed at the same speed c by the ion or electron, but not necessarily consecutively.

If l_0 is the mean free path then

$$pl_0 = \sum_1^n x_k.$$

Let $\bar{g}$ be the mean speed of the ion (with speed c) relative to the molecules which move at random and let N be the number of molecules in unit volume.

The sum of the times spent in traversing the paths x_k is $t = pl_0/c$, that is to say, $p = ct/l_0$. But $p = \bar{g}tN\pi\sigma^2$, consequently $l_0 = (c/\bar{g})N\pi\sigma^2 = l_0(c)$. For electrons $\bar{g} = c$; $l_0 = 1/N\pi\sigma^2$. σ is the limiting value of the impact parameter beyond which deflections of the ions are unimportant.

Consider a diffusing group of n electrons or ions. In the absence of an electric or magnetic field the rate of increase of the mean of the squares of the distance of the n particles from a fixed origin is given by the well-known formula $\mathrm{d}\overline{r^2}/\mathrm{d}t = 6D$.

In time t let the kth particle traverse a succession of free paths $\mathbf{x}_{k,m}$ so that its vector position changes from $\mathbf{r}_{0k}$ at time $t=0$ to $\mathbf{r}_k$ at time t. That is,

$$\mathbf{r}_k = \mathbf{r}_{0k} + \sum_{m=1} \mathbf{x}_{k,m}.$$

Also, if $\mathbf{r}_0$ is the position of the centroid of the group,

$$n\mathbf{r}_0 = \sum_{k=1}^{n} \mathbf{r}_k = \sum_{k=1}^{n} \mathbf{r}_{0k}\,; \qquad \sum_{k=1} \sum_{m=1} \mathbf{x}_{k,m} = 0,$$

$$\sum_{k=1} r_k^2 = \sum_k \mathbf{r}_k \cdot \mathbf{r}_k = \sum_{k=1} r_{0k}^2 + 2\mathbf{r}_0 \sum_{k=1} \sum_{m=1} \mathbf{x}_{k,m} + \Big(\sum_{k=1} \sum_{m=1} \mathbf{x}_{k,m}\Big) \cdot \Big(\sum_{k=1} \sum_{m=1} \mathbf{x}_{k,m}\Big).$$

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The total increment in the squares of the distances r_k is, therefore, since the middle term on the right-hand side is zero in the mean,

$$\Delta r^2 = \sum_{k=1}^{n} (r_k^2 - r_{0k}^2) = (\sum_{k=1} \sum_{m=1} \mathbf{x}_{k,m}) \cdot (\sum_{k=1} \sum_{m=1} \mathbf{x}_{k,m})$$
$$= \sum_{k=1} \{ \sum_{m=1} x_{k,m}^2 + 2 \sum_{m=1} x_{k,m}(x_{k,(m+1)} \cos (\theta_1)_{k,m} + x_{k,(m+2)} \cos (\theta_2)_{k,m} + \ldots +)\},$$

where $(\theta_j)_{k,m}$ is the angle between the mth free path and the $(m+j)$th free path of the kth particle.

Of the total number T of free paths $\mathbf{x}_{k,m}$ let the proportion of those traversed at speeds lying between c and $(c+\mathrm{d}c)$ be $f\mathrm{d}c$.

The contribution of such free paths to

$$\sum_{k=1} \sum_{m=1} x_{k,m}^2$$

is $T2l_0^2 f\mathrm{d}c$, where, as explained above,

$$l_0 = l_0(c) = \left(\frac{c}{\bar{g}}\right)\left(\frac{1}{N\pi\sigma^2}\right), \text{ and } \int_0^\infty f\mathrm{d}c = 1.$$

Their contribution to

$$2 \sum_{k=1} \sum_{m=1} x_{k,m}(x_{k,m+1} \cos (\theta_1)_{k,m} + x_{k,m+2} \cos (\theta_2)_{k,m} + \ldots)$$

is $(Tf\mathrm{d}c)2l_0S$; where S is the mean value of the sum in the bracket, namely,

$$[\sum_{j=1} \overline{x_{k,m+j} \cos (\theta_j)_{k,m}}]_c,$$

associated with those free paths x_m traversed at speed c. In general the free paths $x_{k,m+j}$ in S are not traversed at speed c.

Thus the contribution to Δr^2 by those free paths traversed at speed c is $\Delta r_0^2 = (Tf\mathrm{d}c)2l_0(l_0+S)$, and the average increment over a free path of that quantity is $2l_0(l_0+S)$. Since the average time spent over a free path is l_0/c, the mean rate of increase is $2c(l_0+S)$ from each particle moving at speed c. It follows that the rate of increase of the mean of the squares of the distances r_k taken over the distribution of velocities over the whole group of n particles is

$$\frac{\mathrm{d}}{\mathrm{d}t}\overline{r^2} = \overline{2c(l_0+S)} = 6D.$$

Thus

$$D = \tfrac{1}{3}\overline{(l_0+S)c} = \tfrac{1}{3}\overline{lc}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where

$$l = l_0 + S\,; \quad l_0 = \left(\frac{c}{\bar{g}}\right)\left(\frac{1}{N\pi\sigma^2}\right); \quad \text{and } S = [\sum_{j=1} \overline{x_{k,m+j} \cos (\theta_j)_{k,m}}]_c \equiv S(c).$$

The evaluation of S is simplified in the case of diffusing electrons because, if the free path $x_{k,m}$ is traversed at speed c, the succeeding paths $x_{k,m+j}$ are also traversed at almost the same speed.

Thus $S=l_0(\overline{\cos\theta_1}+\overline{\cos\theta_2}+\ldots+\overline{\cos\theta_j}+\ldots)$, where $\overline{\cos\theta_j}$ is the mean value of the cosine of the angles θ_j between a free path traversed at speed c and its jth succession.

Consider $\overline{\cos\theta_2}$; if the angle between the second and third free paths is α, then $\theta_2=(\theta_1+\alpha)$, and $\cos\theta_2=\cos\theta_1\cos\alpha-\sin\theta_1\sin\alpha$, and $\overline{\cos\theta_2}=(\overline{\cos\theta_1})(\overline{\cos\alpha})=(\overline{\cos\theta_1})^2$, the term in the sines disappearing in the mean. Proceeding thus, it follows that $(\overline{\cos\theta_j})=(\overline{\cos\theta_1})^j$.

Consequently, $S=l_0\,\overline{\cos\theta_1}/(1-\overline{\cos\theta_1})$ and

$$D=\tfrac{1}{3}(\overline{lc})\text{ with }l=l_0/(1-\overline{\cos\theta_1})\text{ and }l_0=1/N\pi\sigma^2. \qquad \ldots\ldots (2)$$

If the ions and electrons are scattered isotropically, then $\overline{\cos\theta_j}=0$ for all values of j.

It may be remarked that S is also the mean value of the corresponding sum for the free paths preceding a free path $x_{k,m+j}$ traversed at speed c, since the reversed sequence is dynamically possible.

II. Velocity of Drift in a Uniform and Constant Electric Field

In the absence of an electric field the number of free paths in a large group of n_0 free paths all traversed at speed c, whose lengths lie between x and $x+\mathrm{d}x$, is (with $NA_0(c)=1/l_0=(N\pi\sigma^2)\bar{g}/c$)

$$\mathrm{d}n_1=-n_0NA_0(c)\exp\left(-NA_0(c)x\right)\mathrm{d}x=-NA_0(c)n_1\mathrm{d}x,$$

where $n_1=n_0\exp\left(-NA_0x\right)$.

When, however, an electric field $\mathbf{E}$ is present the velocity of the ions or electrons changes over the course of a free path and at a distance x along a free path the velocity has become $c+\Delta c(x)$ where $\Delta c(x)$ is proportional to E. In what follows it will be assumed that $\Delta c(x)/c\ll 1$ and terms dependent on E^2 are rejected.

Thus at the end of a free path of length x, the collisional cross section has become $A_0(c)+\{\mathrm{d}A_0(c)/\mathrm{d}c\}\Delta c(x)$. Consequently,

$$\frac{\mathrm{d}n_1}{\mathrm{d}x}=-\left[NA_0(c)+N\frac{\mathrm{d}A_0}{\mathrm{d}c}\Delta c(x)\right]n_1,$$

so that the number of free paths that exceed x in length is

$$n_1=n_0\exp\left[-NA_0x-N\frac{\mathrm{d}A_0}{\mathrm{d}c}\int_0^x\Delta c(x)\mathrm{d}x\right],$$

and the number of free paths whose lengths lie between x and $x+\mathrm{d}x$ becomes

$$\mathrm{d}n_1=n_0\left[NA_0+N\frac{\mathrm{d}A_0}{\mathrm{d}c}\Delta c(x)\right]\left[\exp\left(-NA_0x-N\frac{\mathrm{d}A_0}{\mathrm{d}c}\int_0^x\Delta c(x)\mathrm{d}x\right)\right]\mathrm{d}x.$$

Consequently,

$$\frac{\mathrm{d}n_1}{n_0}\doteqdot\left\{NA_0+N\frac{N\mathrm{d}A_0}{\mathrm{d}c}\left(\Delta c(x)-NA_0\int_0^x\Delta c(x)\mathrm{d}x\right)\right\}\exp\left(-NA_0x\right)\cdot\mathrm{d}x. \qquad \ldots\ldots\ldots\ldots (3)$$

In terms of the mean free path $l_0=1/NA_0$ equation (**3**) becomes

$$\frac{\mathrm{d}n_1}{n_0}=\exp\left(-\frac{x}{l_0}\right)\left\{\frac{1}{l_0}+\frac{1}{l_0^2}\cdot\frac{\mathrm{d}l_0}{\mathrm{d}c}\left(\frac{1}{l_0}\int_0^x \Delta c(x)\mathrm{d}x-\Delta c(x)\right)\right\}\mathrm{d}x. \qquad \ldots\ldots\ldots \quad (\mathbf{4})$$

Consider a group of n ions or electrons moving in a steady state of motion and let the number whose speeds lie between c and $c+\mathrm{d}c$ be $\mathrm{d}n_c=nf(c)\mathrm{d}c$. In the course of each free path the ion or electron is displaced by the field **E** by a small amount in the direction of **E** so that the centroid of the group drifts with a velocity **W**.

In travelling at speed c at an angle θ to **E** along a free path of length x, an ion is deflected a distance $\frac{1}{2}(Ee/m)(x/c)^2 \sin\theta$ at right angles to the direction θ and is on this account advanced a distance $\frac{1}{2}(Ee/m)(x\sin\theta/c)^2$ in the direction of the force **E**e.

In addition it travels the distance $x\cos\theta$ as in free flight without **E**. The increment in speed due to **E** is $\Delta c(x)=(Ee/m)(x/c)\cos\theta$ in the direction θ, the proportion of those free paths that begin in direction θ and are terminated between x and $x+\mathrm{d}x$ is obtained by substituting this value of $\Delta c(x)$ in equation (**4**).

The mean displacement along a single free path of an ion of the group $\mathrm{d}n_c$ taken over all directions θ and free paths x is, therefore,

$$\frac{1}{2}\int_0^\pi\int_0^\infty\left\{\frac{Ee}{2m}\left(\frac{x}{c}\right)^2\sin^2\theta+x\cos\theta\right\}\left\{\frac{1}{l_0}+\frac{1}{l_0^2}\,\frac{\mathrm{d}l_0}{\mathrm{d}c}\left(\frac{x}{2l_0}-1\right)x\cos\theta\cdot\frac{Ee}{mc}\right\}$$
$$\times\exp\left(-\frac{x}{l_0}\right)\sin\theta\mathrm{d}\theta\mathrm{d}x$$
$$=\frac{2}{3}\frac{Ee}{m}\left(\frac{l_0}{c}\right)^2+\frac{1}{3}\frac{Ee}{m}\,\frac{l_0}{c}\,\frac{\mathrm{d}l_0}{\mathrm{d}c}=\frac{1}{3}\frac{Ee}{m}\,\frac{l_0}{c}\,\frac{1}{c^2}\,\frac{\mathrm{d}}{\mathrm{d}c}(l_0c^2). \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{5})$$

The average time taken to traverse a single free path at speed c is l_0/c, consequently the mean speed of drift of the centroid of the $\mathrm{d}n_c$ electrons of the group n is

$$W_c=\frac{1}{3}\frac{Ee}{m}\,\frac{1}{c^2}\,\frac{\mathrm{d}}{\mathrm{d}c}(l_0c^2).$$

It remains to consider the contribution to W_c of the equivalent mean extension of the free paths x that arises when the scattering of ions or electrons in encounters with molecules is not isotropic so that $\overline{\cos\theta_1}$ is not zero. This extension was defined in Section I and was denoted by $S\equiv S(c)$.

In effect, the displacement in the direction of **E** of an ion traversing a free path x between encounters at an angle θ with **E** is increased from $x\cos\theta$ to $(x+S)\cos\theta$, but this quantity vanishes in the mean taken over all directions θ. Nevertheless, the extension S is responsible for an addition to the mean displacement as given in expression (**5**). The field **E** produces a change in direction of the velocity **c** at the end of a free path x, of an amount $\Delta\theta=(Ee/m)(x/c^2)\sin\theta$ and an increase in the speed by an amount $\Delta c(x)=(Ee/m)(x/c)\cos\theta$. Thus S is increased to $S+(\mathrm{d}S/\mathrm{d}c)\Delta c(x)$, and through the operation of the field **E** along x the ion or electron receives an additional displacement $\{S+(\mathrm{d}S/\mathrm{d}c)\Delta c(x)\}\Delta\theta\cdot\sin\theta$

in the direction of **E**. The mean value of this displacement for all free paths of length x and direction θ is

$$\tfrac{1}{2}\int_0^{\pi}\int_0^{\infty}\left\{S\,\frac{Ee}{m}\,\frac{x}{c^2}\sin^2\theta+\frac{\mathrm{d}S}{\mathrm{d}c}\,\frac{Ee}{m}\,\frac{x}{c}\cos\theta\sin\theta\right\}\frac{1}{l_0}\exp\left(-\frac{x}{l_0}\right)\sin\theta\mathrm{d}\theta\mathrm{d}x$$
$$=\tfrac{1}{3}\frac{Ee}{m}\,\frac{l_0}{c}\left(\frac{2S}{c}+\frac{\mathrm{d}S}{\mathrm{d}c}\right)=\tfrac{1}{3}\frac{Ee}{m}\,\frac{l_0}{c}\,\frac{1}{c^2}\,\frac{\mathrm{d}}{\mathrm{d}c}(Sc^2). \qquad \text{(6)}$$

The total mean displacement of an electron or ion traversing a free path at speed c is the sum of the final terms in expressions (**5**) and (**6**), namely,

$$\tfrac{1}{3}\frac{l_0}{c}\,\frac{Ee}{m}\,\frac{1}{c^2}\,\frac{\mathrm{d}}{\mathrm{d}c}\{(l_0+S)c^2\}=\tfrac{1}{3}\frac{l_0}{m}\,\frac{Ee}{m}\,\frac{1}{c^2}\,\frac{\mathrm{d}}{\mathrm{d}c}(lc^2),$$

where $l=l_0+S$ as defined in equation (**1**). The mean time to traverse a free path is (l_0/c), consequently the speed of drift of the centroid of those ions or electrons moving at speeds c is

$$W_c=\tfrac{1}{3}\frac{Ee}{m}\,\frac{1}{c^2}\,\frac{\mathrm{d}}{\mathrm{d}c}(lc^2).$$

Consequently, the velocity of the centroid of the group as a whole is,

$$\mathbf{W}=\tfrac{1}{3}\frac{\mathbf{E}e}{m}\,\overline{\frac{1}{c^2}\,\frac{\mathrm{d}}{\mathrm{d}c}(lc^2)}=\tfrac{1}{3}\frac{\mathbf{E}e}{Nm}\,\overline{\frac{1}{c^2}\,\frac{\mathrm{d}}{\mathrm{d}c}\left(\frac{c^2}{A}\right)}, \qquad \text{(7)}$$

where the equivalent collisional cross section is $A=1/Nl$ and the average is taken with respect to the distribution of speeds c (Huxley 1957*a*, where the derivation of the formula is restricted to the motions of electrons).

From the expressions for the coefficient of diffusion D and velocity of drift **W** (equations (**1**) and (**7**)) it can be seen that the ratio W/D is given by

$$\left.\begin{aligned}\frac{W}{D}&=\frac{Ee}{m}\left(\overline{c^{-2}\frac{\mathrm{d}}{\mathrm{d}c}(lc^2)}\right)/(\overline{lc})\\&=\frac{Ee}{\frac{1}{2}m\overline{c^2}}\left\{\frac{\overline{c^2}}{2}\cdot\overline{c^{-2}\frac{\mathrm{d}}{\mathrm{d}c}(lc^2)}/(\overline{lc})\right\}\\&=\frac{Ee}{\frac{1}{2}m\overline{c^2}}F.\end{aligned}\right\} \qquad \text{(8)}$$

Consider the expression $\overline{c^{-2}\mathrm{d}(lc^2)/\mathrm{d}c}$ in the special case in which the speeds of agitation of the ions or electrons are distributed according to the law of Maxwell, that is to say, $\mathrm{d}n_0/n=(4/\alpha^3\sqrt{\pi})\exp(-c^2/\alpha^2)c^2\mathrm{d}c$.

The mean value required is, therefore,

$$\frac{4}{\alpha^3\sqrt{\pi}}\int_0^{\infty}\exp\left(-\frac{c^2}{\alpha^2}\right)\frac{\mathrm{d}}{\mathrm{d}c}(lc^2)\mathrm{d}c=\frac{4}{\alpha^3\sqrt{\pi}}\,\frac{2}{\alpha^2}\int_0^{\infty}\exp\left(-\frac{c^2}{\alpha^2}\right)lc^3\mathrm{d}c$$
$$=(2/\alpha^2)(\overline{lc})$$
$$=3(\overline{lc})/\overline{c^2}.$$

The formula for W/D in this case reduces to

$$\frac{W}{D}=\frac{3}{2}\left(\frac{Ee}{\frac{1}{2}m\overline{c^2}}\right). \qquad (9)$$

Suppose instead, that the dependence $l(c)$ of l upon c is of the form $l \propto c$ (inverse fifth power interaction), then the factor F also reduces to 3/2 and equation (**9**) is again valid. In general, however, equation (**9**) is not exact since F assumes values other than 3/2 when the law of distribution is not that of Maxwell or $l(c)$ is not proportional to c. In general, for electronic motion, $F \neq 3/2$.

III. References

Huxley, L. G. H. (1957*a*).—*Aust. J. Phys.* **10**: 118.
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