SHORT COMMUNICATIONS

ON A CONJECTURE ABOUT DIFFUSION OF GASEOUS IONS

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Abstract

A previous conjecture by the author about the diffusion coefficient of gaseous ions is restated more precisely, thereby eliminating, in particular, an error of a factor of two which seemed to be contained in it in certain cases. The conjecture, which is essentially an extension of the Nernst–Einstein relation to situations not close to equilibrium, is made plausible by a Langevin-type derivation.

A much earlier extensive article on the motion of charged carriers in gases (Wannier 1953; hereinafter referred to as Paper I) contained a number of relations which although only semi-quantitatively correct were easy to use. These relations have been widely applied (Eiber and Kandel 1968; Bloomfield and Hasted 1969; Naidu and Prasat 1970; Johnsen *et al.* 1970; Young *et al.* 1970; Parkes 1971). The same article included results on ionic and electronic diffusion which have also been extensively used (Gatland and McDaniel 1970; McDaniel and Mosley 1970; Volz *et al.* 1971; Woo and Whealton 1971; Woo and Young 1971). The work on diffusion could be summed up approximately in the form of a rule for diffusion coefficients which was essentially an extension of the Nernst–Einstein relation (Nernst 1888). Through my contact with the Australian group (Robson 1972*a*) I have become aware that the rule needs restatement. If it is applied superficially, it appears to be in error by a factor of $\frac{1}{2}$ for transverse diffusion in the high field region when the scattering cross section is approximately constant. Such an error would indeed be serious as the formula is meant to be semiquantitatively correct. However, the present work will show that we are not really dealing with an error but with an incorrect interpretation of the rule. A more precise formulation of the old conjecture is given here which sets this right. In addition, a quasi-derivation is presented which is an adaptation of the Langevin (1908) procedure to the present situation. The derivation is, of course, not meant to replace precise theoretical work such as that of Skullerud (1969) on the same subject.

The rule in question is that defined by equation (148) of Paper I. The formulation involved a lack of precision in the concept of "mobility". In the context of the work performed there the correct choice was the longitudinal differential mobility. This choice must be modified if diffusion transverse to the field is to be considered, since

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comparisons with the transverse differential mobility are then required. The conjecture should therefore read

$$\frac{\text{diffusion coefficient along } n}{\text{differential mobility along } n} = \frac{2 \times \text{mean random energy along } n}{e}. \tag{1}$$

It can be quickly verified that this formulation furnishes the missing factor of 2 for transverse diffusion when the mean free path is constant. In the longitudinal direction the differential mobility is indeed $\mathrm{d}\langle c_z \rangle/\mathrm{d}E$, as implied in Paper I, but in the transverse direction the differential mobility deals with a differential shift in the angle, and this yields for the mobility the expression $\langle c_z \rangle/E$. When $\langle c_z \rangle$ is proportional to $E^{\frac{1}{2}}$, as it is in the high field region, the second expression is larger than the first by a factor of 2, as required.

We shall now present a derivation of the rule (1) which is in direct analogy with the procedure used by Langevin (1908) for the equilibrium case. Suppose that there is a relation between the viscous force F and the mean drift velocity $\bar{v}$ which is arbitrary except that each is a single valued function of the other, and that this relation is isotropic:

$$F = \Phi(\bar{v}), \tag{2a}$$

or in vectorial form

$$\boldsymbol{F} = (\bar{\boldsymbol{v}}/\bar{v})\Phi(\bar{v}). \tag{2b}$$

Differentiation of equation (2b) gives

$$\mathrm{d}\boldsymbol{F} = \frac{\mathrm{d}\bar{\boldsymbol{v}}}{\bar{v}}\Phi(\bar{v}) - \frac{\bar{\boldsymbol{v}}}{\bar{v}^2}\Phi(\bar{v})\,\mathrm{d}\bar{v} + \frac{\bar{\boldsymbol{v}}}{\bar{v}}\frac{\mathrm{d}\Phi(\bar{v})}{\mathrm{d}\bar{v}}\mathrm{d}\bar{v}. \tag{3}$$

In order to explore a local region of the $\boldsymbol{F}$ versus $\bar{\boldsymbol{v}}$ relation, we consider $\boldsymbol{F}$ and $\bar{\boldsymbol{v}}$ to be fixed and at the same time replace $\mathrm{d}\boldsymbol{F}$ by an incremental force $\boldsymbol{G}$ and $\mathrm{d}\bar{\boldsymbol{v}}$ by an incremental velocity $\boldsymbol{w}$. Equation (3) then takes the form

$$\boldsymbol{G} = \frac{\Phi(\bar{v})}{\bar{v}}\boldsymbol{w} - \frac{\bar{\boldsymbol{v}}}{\bar{v}^3}\Phi(\bar{v})(\bar{\boldsymbol{v}}\,.\,\boldsymbol{w}) + \frac{\bar{\boldsymbol{v}}}{\bar{v}^2}\frac{\mathrm{d}\Phi()\bar{v}}{\mathrm{d}\bar{v}}(\bar{\boldsymbol{v}}\,.\,\boldsymbol{w}). \tag{4}$$

The general relation (2b) between $\boldsymbol{F}$ and $\bar{\boldsymbol{v}}$ has now been transformed into a local linear relation between $\boldsymbol{G}$ and $\boldsymbol{w}$. Equation (4) assumes a more transparent form if we separate out the longitudinal and transverse components

$$G_{\parallel} = \frac{\mathrm{d}\Phi(\bar{v})}{\mathrm{d}\bar{v}}w_{\parallel}, \qquad G_{\perp} = \frac{\Phi(\bar{v})}{\bar{v}}w_{\perp}. \tag{5a, b}$$

In the following treatment we shall write $\Phi'(\bar{v})$ for the constant of proportionality, with the understanding that $\Phi'(\bar{v})$ is to be interpreted as $\mathrm{d}\Phi/\mathrm{d}\bar{v}$ if we are dealing with motion longitudinal to $\bar{\boldsymbol{v}}$ and as $\Phi(\bar{v})/\bar{v}$ for motion transverse to $\bar{\boldsymbol{v}}$. The subsequent developments are to apply either to equation (5a) or (5b), but not to both simultaneously.

In order to obtain something like a derivation for the rule (1), we follow Langevin (1908) and separate the total force acting on an individual ion into a steady component given by (5a) or (5b) and a random component $A(t)$ whose time average is zero,

$$m\dot{w} = -\Phi'(\bar{v})\,w + A(t). \tag{6}$$

We now consider the relation (6) in a coordinate system moving with velocity $\bar{v}$. This makes no difference if we are dealing with equation (5b) but redefines the longitudinal displacement as one measured with respect to $\bar{v}t$. If we denote this displacement by x, we then have by definition $w = \mathrm{d}x/\mathrm{d}t$. Multiplying equation (6) by x then leads to the expression

$$mx\,\mathrm{d}^2x/\mathrm{d}t^2 = -\Phi'(\bar{v})\,x\,\mathrm{d}x/\mathrm{d}t + x\,A(t)$$

or

$$\tfrac{1}{2}m\,\mathrm{d}^2(x^2)/\mathrm{d}t^2 - m(\mathrm{d}x/\mathrm{d}t)^2 = -\tfrac{1}{2}\Phi'(\bar{v})\,\mathrm{d}(x^2)/\mathrm{d}t + x\,A(t). \tag{7}$$

By now taking a coarse average of this equation and assuming x to be uncorrelated with A, we finally obtain

$$\tfrac{1}{2}m\,\mathrm{d}^2\langle x^2\rangle/\mathrm{d}t^2 + \tfrac{1}{2}\Phi'(\bar{v})\,\mathrm{d}\langle x^2\rangle/\mathrm{d}t = m\langle w^2\rangle. \tag{8}$$

We are to solve this equation subject to the initial condition that x is known to be zero at $t = 0$. The first derivative of x^2 is then also known to be zero while, on the other hand, w^2 has a time-independent average computable from the velocity distribution function. With these initial and side conditions the solution of equation (8) is found to be

$$\langle x^2\rangle = \frac{2m\langle w^2\rangle}{\Phi'(\bar{v})}\left\{t - \frac{m}{\Phi'(\bar{v})} + \frac{m}{\Phi'(\bar{v})}\exp\left(-\frac{\Phi'(\bar{v})\,t}{m}\right)\right\}. \tag{9}$$

If we accept for the diffusion coefficient the definition

$$D_x = \lim_{t\to\infty}(\langle x^2\rangle/2t),$$

we see that diffusion is the long-term phenomenon contained in the first term of equation (9), and that the factor outside the braces is twice the diffusion coefficient

$$D = m\langle w^2\rangle/\Phi'(\bar{v}),$$

which means that for diffusion in the longitudinal direction

$$D_{\parallel} = m\langle(v_{\parallel}-\bar{v})^2\rangle\,\mathrm{d}\bar{v}/\mathrm{d}F, \tag{10a}$$

while for diffusion in the transverse direction

$$D_{\perp} = m\langle v_{\perp}^2\rangle\,\bar{v}/F. \tag{10b}$$

Equations (10a) and (10b) are identical with the clarified conjecture (1).

The derivation presented here shows that thermal equilibrium does not play as crucial a role in the validity of the Nernst–Einstein relation as is generally supposed. Of course, there exist exact derivations for the case of equilibrium which cannot be duplicated in the present instance, and the relation (1) is only approximately true. However, in many instances this will still be very useful information. The error inherent in the above derivation is twofold: firstly the linearized relation (6) was extended beyond its natural range of validity, and secondly the last term in equation (7) was omitted in the averaging. With respect to the first approximation, circumstances happen to be favourable for the linearization to be valid in that, for heavy ions in a light gas, departures from the mean are unlikely while, for electrons, the anisotropy of the velocity distribution is weak and the next term in equation (8) would contain $\langle xw^2 \rangle$ which is odd in x. The least favorable case is probably the one with equal masses, where indeed a discrepancy of 18% in the rule (1) has been found (Wannier 1953). The omission of the last term in equation (7) is more easily justified. We need not deny the existence of a correlation between force and velocity but only between force and position. A direct correlation between force and position clearly cannot exist in a uniform medium. It can, however, arise indirectly, in the sense that if the position is abnormal the velocity must have been also abnormal for some time, and there is no reason why the force should not correlate with velocity. Thus a correlation between force and position is present, but the indirect nature of it is a fair argument for it being numerically small. We conclude therefore that both equations (10) are plausible and probably semi-quantitatively correct. A look at Skullerud's (1969, 1973) results confirms this expectation.

It is hoped that this amended conjecture, reinforced by the plausible but not rigorous derivation above, will prove to be as useful as the original conjecture has been. The practical consequences of the revised rule have already been explored by Robson (1972*b*).

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