

A THERMODYNAMIC TREATMENT OF ANISOTROPIC DIFFUSION IN AN ELECTRIC FIELD

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Abstract

Non-equilibrium thermodynamics is used to analyse the diffusive processes associated with a swarm of charged particles (ions or electrons) drifting in a neutral gas under the influence of an electric field. A simple approximate phenomenological relationship connecting components of the diffusion tensor with the drift velocity of the swarm is derived and the utility of the formula is illustrated in several cases where previous analyses have been carried out using the Boltzmann equation.

I. THEORY

The anisotropic character of the diffusive processes associated with a swarm of charged particles drifting in a neutral gas under the influence of an electric field was first predicted by Wannier (1953). Recently, this phenomenon has been observed for electrons (Wagner, Davis, and Hurst 1967) and subsequently a number of theoretical investigations have been carried out involving solution of the Boltzmann equation (Lowke and Parker 1968, 1969; Parker and Lowke 1969; Skullerud 1969; Huxley 1972). The Boltzmann analysis requires certain assumptions concerning statistical and microscopic properties of the system; for example, in dealing with electrons, a knowledge of the electron-neutral momentum-transfer cross section is required. On the other hand, a macroscopic theory developed through thermodynamics could avoid such assumptions and would be therefore completely general. However, while the kinetic theory analysis via the Boltzmann equation furnishes actual numerical values for the transport coefficients, thermodynamics is capable of providing only phenomenological relationships between experimentally measurable quantities.

In the present work, non-equilibrium thermodynamics is used to establish phenomenological relationships connecting components of the diffusion tensor with the drift velocity of the swarm for both electron-gas and ion-gas systems (equations (14) and (23) respectively). In general the formulae derived are only approximate since, strictly speaking, the domain of non-equilibrium thermodynamics is restricted to situations where deviations from equilibrium are not large, and where quantities such as entropy and temperature are defined in the thermodynamic sense (De Groot and Mazur 1962). However, as we shall see, the thermodynamic treatment given here is useful for predicting diffusion coefficients from a given set of drift velocities (of either theoretical or experimental origin) under even highly non-equilibrium (high field) conditions. Questions concerned with the accuracy of the formulae and the connection with the kinetic theory approach are discussed in Section II.

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We first of all specifically consider electrons. The modifications necessary for a thermodynamic treatment of anisotropic diffusion of ions are discussed in Section III. As is conventional in non-equilibrium thermodynamics, we start from the entropy production ϑ associated with the irreversible transport process. Using the methods outlined by De Groot and Mazur (1962, Ch. 13), it can be shown that for small deviations from equilibrium the entropy production for an electron-gas system at (common) temperature T is given by

$$T\vartheta = Ne\mathbf{W}_{av} \cdot (\mathbf{E} - \nabla\mu/e) \geq 0, \quad (1)$$

where $\mathbf{E}$ denotes the electric field and N , e , $\mathbf{W}_{av}$, and μ are the density, charge, average velocity, and chemical potential per particle of the electrons respectively. It has been assumed that the concentration of electrons is very small and that the average velocity of the neutral particles is zero. Furthermore, collisions between electrons and neutrals have been assumed to be elastic.

Normally it is postulated from equation (1) that there exists a linear phenomenological relation between the thermodynamic flux $Ne\mathbf{W}_{av}$ and the force

$$\mathbf{X} \equiv \mathbf{E} - \nabla\mu/e, \quad (2)$$

and this is sufficient for dealing with near-equilibrium situations (De Groot and Mazur 1962). However, since we wish to consider the more general problem where the field may be strong, and the deviation from equilibrium substantial, we assume that the *form* (1) of entropy production remains applicable under all conditions, with T now denoting the electron temperature. The accuracy of this assumption depends upon the applicability of the Gibbs equation for entropy (from which (1) is derived) under highly non-equilibrium conditions (De Groot and Mazur 1962). A more definitive determination of accuracy can be achieved by appealing to kinetic theory (Section II). In addition, it is postulated that the flux depends in general upon the force in a non-linear manner (Callen 1960), that is,

$$Ne\mathbf{W}_{av} = \mathbf{L}^{(1)} \cdot \mathbf{X} + \mathbf{L}^{(2)} : \mathbf{X}\mathbf{X} + \mathbf{L}^{(3)} : \mathbf{X}\mathbf{X}\mathbf{X} + \dots, \quad (3)$$

where the phenomenological coefficients $\mathbf{L}^{(j)}$ are cartesian tensors of rank $j+1$.

Equation (3) can be reduced to a more simplified form by noting that:

- (i) parity considerations require even terms in $\mathbf{X}$ to be excluded, that is, $\mathbf{L}^{(2j)} = 0$, and
- (ii) the tensors $\mathbf{L}^{(j)}$ must be independent of $\mathbf{X}$ and therefore, since the properties of the system are isotropic, they must reduce to scalar multiples of unit tensors.

Hence equation (3) becomes

$$\mathbf{W}_{av} = \sum_j (L^{(2j+1)} X^{2j}) \mathbf{X}, \quad (4)$$

where the factor Ne has been absorbed into the new (scalar) phenomenological coefficients $L^{(2j+1)}$.

If we assume that spatial gradients are always small, regardless of the strength of the electric field, then to first order in $\nabla\mu$, we have from equation (2)

$$X^{2j} \approx E^{2j} \left(1 - 2j \mathbf{E} \cdot \frac{\nabla\mu/e}{E^2} \right). \quad (5)$$

For an ideal gas mixture, it can be shown that (see Appendix)

$$\nabla\mu = kT N^{-1} \nabla N \quad (6)$$

for a system in which temperature is uniform (k is Boltzmann's constant). Substitution of equations (5) and (6) into (4) then gives

$$W_{av} = K\mathbf{E} - \mathbf{D} \cdot N^{-1} \nabla N, \quad (7)$$

where the mobility coefficient and diffusion tensor are defined respectively by

$$K(E) = \sum_j L^{(2j+1)} E^{2j} \quad (8)$$

and

$$\mathbf{D}(E) = (kT/e) \sum_j L^{(2j+1)} E^{2j} (\mathbf{I} + 2j \hat{\mathbf{E}} \hat{\mathbf{E}}). \quad (9)$$

In a coordinate system in which the z axis is parallel to $\mathbf{E}$, it can be seen that $\mathbf{D}$ has the form

$$\mathbf{D} = \begin{pmatrix} D_T & 0 & 0 \\ 0 & D_T & 0 \\ 0 & 0 & D_L \end{pmatrix}, \quad (10)$$

where

$$D_T = (kT/e)K \quad \text{and} \quad D_L = (kT/e)(K + E \partial K / \partial E) \quad (11a, b)$$

denote the transverse and longitudinal diffusion coefficients respectively. The ratio of diffusion coefficients parallel and perpendicular to the field is therefore

$$D_L/D_T = \partial(\ln W)/\partial(\ln E), \quad (12)$$

where

$$W \equiv K\mathbf{E} \quad (13)$$

is the average velocity under spatially uniform conditions. The latter quantity is conventionally referred to simply as the drift velocity of the swarm.

II. COMPARISON WITH RESULTS OF KINETIC THEORY

Equations (11) and (12) are exact only as long as the Gibbs equation is applicable. The latter equation can be shown to hold only if the distribution function of the electrons is nearly Maxwellian appropriate to temperature T (De Groot and Mazur 1962). It is found that the Boltzmann equation gives such a distribution function

only for the so-called Maxwell or mean free time model of interaction (obtained by setting $l = -1$ in equation (15) below; Crompton 1969). Thus the accuracy of equations (11) and (12) under highly non-equilibrium conditions depends upon how closely the momentum-transfer cross section approximates to this model.

We consider below the results of calculation of D_L/D_T via equation (12). While individual calculation of D_L and D_T is possible from equations (11), this requires a knowledge of T as well as of W . It should be noted that (11a) is in the form of an Einstein relation; again, this is known to hold only for the Maxwell model of interaction (Crompton 1969).

It is well known (Wannier 1953) that the Boltzmann equation predicts that W depends upon E and the gas density N_0 solely through the ratio E/N_0 . Assuming W to have this property, it follows that equation (12) becomes

$$D_L/D_T = \partial(\ln W)/\partial\{\ln(E/N_0)\}. \quad (14)$$

Equation (14) is in a suitable form for rapid computation of D_L/D_T , since it is simply a matter of determining the slope of the drift velocity versus field curve with logarithmically scaled axes.

(a) *Model Cross Sections*

If the momentum-transfer cross section Q is assumed to be of the form

$$Q(\epsilon) = Q_0 \epsilon^{l/2}, \quad (15)$$

where ϵ is the electron energy, then it can be shown (Wannier 1953) that under *high* field conditions the Boltzmann equation yields for the drift velocity

$$W = \text{const.}(E/N_0)^{1/(l+2)}. \quad (16)$$

Substitution of (16) into (14) gives

$$D_L/D_T = 1/(l+2). \quad (17)$$

In addition to solving the Boltzmann equation for cross sections of the form (15), Parker and Lowke (1969) derived an expression for D_L/D_T via a semiquantitative treatment based upon a balance equation for energy. They obtained the result

$$D_L/D_T = (l+3)/2(l+2). \quad (18)$$

Since equation (17) derives from (1), which in turn is based upon balance equations for mass, momentum, and entropy as well as for energy (De Groot and Mazur 1962), it is to be expected that this thermodynamic formula will be more accurate than the Parker-Lowke semiquantitative result (18). Comparison with the numerical results obtained by Parker and Lowke in solution of the Boltzmann equation do indeed indicate that this is the case (see Table 1).

While it is evident that the thermodynamic result (17) is more accurate than (18), it is also clear that the error associated with the former increases as the cross section deviates from the Maxwell model ($l = -1$), i.e. as the distribution function becomes farther removed from Maxwellian.

TABLE 1

COMPARISONS OF CALCULATED RATIOS OF LONGITUDINAL TO TRANSVERSE DIFFUSION COEFFICIENTS
(HIGH FIELD LIMIT)

The ratios D_L/D_T derived by Parker and Lowke (1969) from both a semiquantitative model (equation (18)) and numerical solution of the Boltzmann equation are compared with the results obtained from thermodynamics for cross sections of the form (15)

l	Parker and Lowke (1969)		Thermodynamics Equation (17)
	Equation (18)	Boltzmann equation	
$-3/2$	$3/2$	1.95	2
-1	1	1	1
0	$3/4$	0.495	$1/2$
1	$2/3$	0.29	$1/3$
2	$5/8$	0.18	$1/4$

(b) *Realistic Cross Sections*

Lowke and Parker (1968, 1969) have calculated longitudinal and transverse diffusion coefficients for electrons in a number of gases using cross sections inferred from measurements of drift velocity. Their results have been compared (in cases

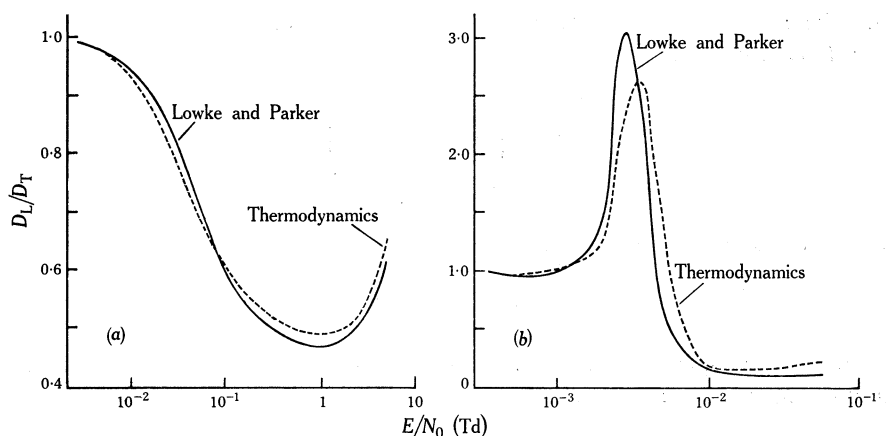


Fig. 1.—Comparisons between the results derived by Lowke and Parker (1969) and those obtained from thermodynamics (equation (14)) for the ratio D_L/D_T for electrons in (a) helium gas at a temperature of 293 K and (b) argon gas at 77 K. (Note that 1 townsend (Td) $\equiv 10^{-17}$ V cm 2 .)

where collisions can be considered elastic) with values computed from equation (14), and the curves of D_L/D_T versus E/N_0 for helium and argon are shown in Figures 1(a) and 1(b) respectively. Values of W used in the right-hand side of (14) are those derived by Lowke and Parker (1968).

It is evident that equation (14) provides at least a very good qualitative estimate of D_L/D_T over a wide range of field strengths. The discrepancies are worst for argon, and there it is known that the cross section is a strong function of energy (Engelhardt and Phelps 1964). Thus for argon the electron distribution function is highly non-Maxwellian and consequently the thermodynamic equations as developed here can be expected to suffer more from inaccuracies in this particular case. Similar agreement between the thermodynamic and Boltzmann treatments has been found for xenon and krypton.

III. ANISOTROPIC DIFFUSION OF IONS

For electrons, the smallness of the electron-neutral molecule mass ratio ensures a near spherically symmetric distribution function (Robson and Kumar 1971), with the result that there is an effective equipartitioning of energy. Thus, it is possible to ascribe a temperature T to the electrons for use in the thermodynamic equations even under high field conditions. However, for ions, whose mass is more nearly comparable with the neutral particles, equipartitioning of energy is not realized even at low and intermediate field strengths. We now consider how the equations for D_L and D_T derived in Section II must be modified in order to remain applicable for ions.

It is shown in the Appendix that if $\frac{1}{2}kT_{\parallel}$ and $\frac{1}{2}kT_{\perp}$ represent the mean random energies of the ions in directions parallel and perpendicular to the field respectively then the gradient of chemical potential is given by

$$\nabla\mu = k\mathbf{T} \cdot N^{-1} \nabla N, \quad (19)$$

where, for a coordinate system in which the field is directed along the z axis, the tensor $\mathbf{T}$ has the form

$$\mathbf{T} = \begin{pmatrix} T_{\perp} & 0 & 0 \\ 0 & T_{\perp} & 0 \\ 0 & 0 & T_{\parallel} \end{pmatrix}. \quad (20)$$

The ion "temperature" may then be defined as

$$T = \frac{1}{3} \text{trace } \mathbf{T}.$$

Replacing equation (6) by (19) and carrying out the algebra as before, we obtain the modified formulae for ions:

$$D_T = (kT_{\perp}/e)K, \quad D_L = (kT_{\parallel}/e)(K + E \partial K / \partial E), \quad (21a, b)$$

$$D_L/D_T = (T_{\parallel}/T_{\perp}) \partial(\ln W) / \partial(\ln E). \quad (22)$$

Furthermore, if W is obtained from the Boltzmann equation then equation (22) becomes

$$D_L/D_T = (T_{\parallel}/T_{\perp}) \partial(\ln W) / \partial\{\ln(E/N_0)\}. \quad (23)$$

As an example, for the Maxwell model of interaction we have from equations (16)

and (23) that

$$D_L/D_T = T_{\parallel}/T_{\perp}, \quad (24)$$

a result which has previously been deduced by Wannier (1953) through solution of the Boltzmann equation.*

Figure 2 shows the results of calculation of D_L/D_T from equation (23), together with values obtained directly through numerical solution of the Boltzmann equation (Robson 1972), for potassium ions in helium gas interacting through an assumed potential

$$\phi(r) = \epsilon \left\{ \frac{1}{2}(1+\gamma)(r_m/r)^{12} - 2\gamma(r_m/r)^6 - \frac{3}{2}(1-\gamma)(r_m/r)^4 \right\}, \quad (25)$$

with $\gamma = 0.34$, $\epsilon = 0.024$ eV, and $r_m = 2.73$ Å. Values of W and $T_{\parallel}/T_{\perp}$ used in the right-hand side of (23) were obtained by solution of the Boltzmann equation under

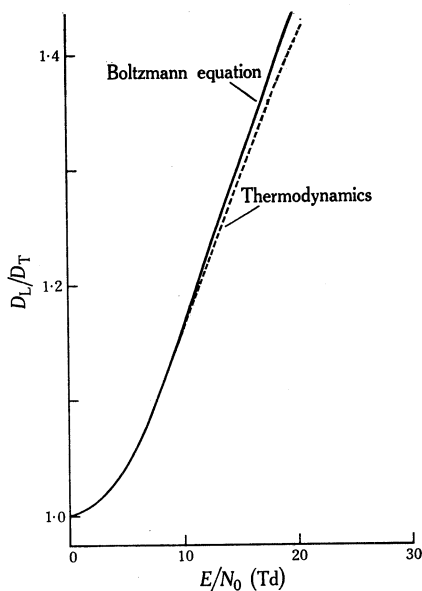


Fig. 2.—Comparison of results for the ratio D_L/D_T , for potassium ions in helium gas at a temperature of 303 K, calculated from thermodynamics (equation (23)) and from numerical solution of the Boltzmann equation for a (12-6-4) interaction potential (equation (25)).

spatially uniform conditions. It can be seen that the agreement is good (to within a few per cent) over the range of field considered. It should be noted that it is the factor $T_{\parallel}/T_{\perp}$ which dominates the behaviour of the right-hand side of (23), since in this particular case W is very nearly linear in E/N_0 . Thus, the disparity of diffusion coefficients is mainly attributable to the anisotropic character of the ion velocity distribution function, and the field dependence of the drift velocity (equivalently, the nature of the ion-neutral interaction) plays very little part in determining the qualitative dependence of D_L/D_T upon field strength. This is in direct contrast to the cases of electron diffusion considered in Section II, where the anisotropy in velocity space is negligible (that is, $T_{\parallel}/T_{\perp} \approx 1$).

* Wannier (1953) also conjectured that a relation between D_L and K similar to equation (21b) should be approximately true in general.

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APPENDIX

A proof of equation (6) is given here, and equation (19) is obtained through a suitable generalization of the procedure.

The functional dependence of chemical potential upon temperature and pressure is given through the Gibbs–Duhem relation (De Groot and Mazur 1962)

$$-\sum_k N_k S_k \delta T + \delta p = \sum_k N_k \delta \mu_k, \quad (\text{A1})$$

where T and p denote the temperature and pressure and N_k , S_k , and μ_k denote the density, entropy, and chemical potential per particle of component k respectively. This equation is only strictly valid for equilibrium or quasi-equilibrium situations, but we shall assume here that it also holds (at least approximately) under less restrictive conditions.

For the electron–gas system, in which the temperature as well as the properties of the neutral gas are uniform, we have from equation (A1) that

$$\nabla p = N \nabla \mu, \quad (\text{A2})$$

where all quantities now pertain to the electrons. If the mixture is assumed to be ideal then the partial pressure of the electrons is given by the well-known expression

$$p = \frac{2}{3} N \times \bar{E}_e = N k T, \quad (\text{A3})$$

where $\bar{E}_e$ is the mean random energy of the electrons and T now denotes the electron

temperature. Substitution of (A3) into (A2) then gives

$$\nabla\mu = kT N^{-1} \nabla N,$$

which is equation (6).

In the ion-gas system, the pressure must be considered to be a tensor of the form (taking a coordinate system with the z axis parallel to the field)

$$\mathbf{P} = \begin{pmatrix} P_{\perp} & 0 & 0 \\ 0 & P_{\perp} & 0 \\ 0 & 0 & P_{\parallel} \end{pmatrix}. \quad (\text{A4})$$

Again for an ideal system we have that

$$P_n = 2N \times \bar{E}_{in} \equiv NkT_n, \quad (\text{A5})$$

where $\bar{E}_{in}$ is the mean random energy of the ions in the direction n . The generalization of equation (A2) in this case is

$$\nabla \cdot \mathbf{P} = N \nabla\mu. \quad (\text{A6})$$

Substitution of equations (A4) and (A5) into (A6) then yields equation (19), namely

$$\nabla\mu = k\mathbf{T} \cdot N^{-1} \nabla N,$$

where $\mathbf{T}$ is defined by equation (20).

