

Transport Phenomena in the Presence of Reactions: Definition and Measurement of Transport Coefficients

R. E. Robson

Physics Department, James Cook University,
Townsville, Qld 4811, Australia.

Abstract

Transport coefficients defined as constants of proportionality in flux-gradient relationships generally differ, in the presence of reactions, from coefficients of gradient terms appearing in balance equations such as the diffusion equation. Consequently, experiments sampling fluxes have to be interpreted differently from those sampling bulk properties. This difference is analysed here from the perspective of swarm experiments, which are surveyed and analysed with the help of a phenomenological transport theory. Standardisation in terminology and reporting of transport coefficients, along the lines suggested by Blevin and Fletcher (1984), is strongly supported.

What's in a name? That which we call a rose by any other name would smell as sweet.

(W. Shakespeare *ca* 1596)

1. Introduction

In the protracted and sometimes vigorous debate concerning the definition and measurement of transport coefficients conducted at informal gatherings of swarm physicists in recent times, these words from 'Romeo and Juliet' may have had a soothing effect. Although there has been a measure of consensus among the participants of a recent Japan–Australia Workshop on Gaseous Electronics (Blevin 1988; Robson 1988; Tagashira 1988), it would be fair to say that a division still exists in the ranks over the identification of a fundamental set of transport quantities in terms of which all swarm experiments can and should be analysed. An unusual feature of the debate is that the matter has not yet been presented to the general physics community in a universally accessible published form, and so this very important, fundamental question has presumably escaped the attention of transport theorists and experimentalists at large, and indeed has been lost on just about anyone outside the swarm fraternity who uses flux-gradient relationships. This paper seeks to put matters right in respect of the latter and at the same time puts the case of what the author considers to be the majority in the above-mentioned debates. Hopefully, the 'feud' can, in this way, be brought to a speedier and more satisfactory conclusion than its more famous literary counterpart referred to above.

The basic question is really: 'What is a transport coefficient, how is it defined and how is it measured? To answer this, one ought to take a general perspective, rather than the particular viewpoint of gaseous electronics, as is so often the case. Traditionally speaking, transport coefficients $\mathcal{L}_{ij}$ are *defined* through near-equilibrium *linear* relationships between fluxes Γ_i and the thermodynamic forces X_j which produce them (Chapman and Cowling 1970; Batchelor 1967; de Groot and Mazur 1969; Mason and McDaniel 1988):

$$\Gamma_i = \sum_j \mathcal{L}_{ij} X_j. \quad (1)$$

Examples include Fourier's law of heat conduction, Newton's law of viscosity and Fick's law of diffusion where the forces correspond to (the negative of) gradients in temperature, fluid velocity and particle density respectively. The important qualification here is that the gradients are assumed to be small and the transport coefficients $\mathcal{L}_{ij}$ therefore constant. The typical experiment is designed with this assumption in mind: Whether or not it is actually realised is another question. Similarly, when it comes to theoretical analysis, such as the Chapman-Enskog solution of Boltzmann's equation (Chapman and Cowling 1970), density gradients are assumed weak and transport coefficients are calculated on the basis of definition (1). In nonequilibrium thermodynamics (de Groot and Mazur 1969), the same circumstances pertain, although transport coefficients appear there as phenomenological parameters, related perhaps by time-reversal (Onsager) and/or geometrical symmetries (de Groot and Mazur 1969; Robson 1970), but otherwise purely empirical.

We now consider reactive effects, used here as a generic term to describe all types of non-particle conserving collisions, including ionisation, attachment, annihilation and so on. Equation (1) may still be used to define transport coefficients $\mathcal{L}_{ij}$ and these quantities may be determined by any experiment which measures fluxes and forces separately and preserves the conditions underlying the validity of (1). [Note that an electrode inserted into an electron swarm (Lowke *et al.* 1977; Robson 1981) for the purpose of collecting current most definitely does *not* satisfy this latter criterion.] However, an experiment which samples *bulk properties* of the system will yield *different* values L_{ij} of transport coefficients, as explained below. In the absence of reactive effects the 'flux' and 'bulk' transport coefficients are the same, i.e. symbolically.

$$L_{ij} \xrightarrow{\text{no reactions}} \mathcal{L}_{ij}.$$

Thus, there are two fundamental sets of transport coefficients, as first observed by Tagashira *et al.* (1977), in the context of electron swarm experiments. Explicit, general expressions for reactive corrections were given by Kumar *et al.* (1980) in their formal solution of Boltzmann's equation for particle swarms. Blevin and Fletcher (1984) and Blevin (1988) argued that although swarm transport parameters may indeed depend upon the type of experiment in which they are measured, there are strong grounds for selecting the 'bulk' quantities as representing the standard.

The present article strongly supports the call by Blevin and Fletcher for standardisation, our thesis being that:

- (i) most swarm experiments involve determination of 'bulk' transport properties;
- (ii) the presence of boundaries in measurements of fluxes may undermine the validity of (1) and hence 'flux' transport properties may be difficult to measure in practice.

We would also suggest that:

- (iii) it is misleading to associate the name of any experiment with transport coefficients, flux or bulk, as these quantities have an existence and a definition independent of any particular experimental arrangement.

We discuss all these points in the context of a brief survey of the types of swarm experiments and an even more concise description of the theory used in their analysis.

2. Outline of Swarm Theory and Survey of Swarm Experiments

(a) Theory

In the interests of brevity, we give a purely macroscopic outline of the relevant theory of particle swarms in a neutral gas subject to an electric field $\mathbf{E}$. Experiment and theory are linked by the equation of continuity

$$\partial_t n + \nabla \cdot \mathbf{\Gamma} = S, \quad (2)$$

where $\mathbf{\Gamma} = n\mathbf{v}$ is the swarm particle flux and n , $\mathbf{v}$ and S denote swarm number density, average velocity and production rate per unit volume respectively. All these quantities generally depend upon position $\mathbf{r}$ and time t . In classical near-equilibrium theories the flux is usually expressed in the form (1), namely

$$\mathbf{\Gamma}(\mathbf{r}, t) = n(\mathbf{r}, t) \mathcal{K} \mathbf{E} - \mathcal{D} \nabla n(\mathbf{r}, t), \quad (3)$$

where $\mathcal{K}$ and $\mathcal{D}$ are classical mobility and diffusion coefficients respectively. We shall follow conventional definitions of transport coefficients and assume that the *hydrodynamic limit* pertains, so that all space-time dependence is expressible through linear functionals of $n(\mathbf{r}, t)$. If nonhydrodynamic conditions prevail (e.g. near boundary walls), then conventional transport coefficients cannot be defined.

Equation (3) can be generalised for strong fields to

$$\mathbf{\Gamma}(\mathbf{r}, t) = \sum_{j=0}^{\infty} \mathbf{\Gamma}^{(j)} \otimes \nabla^j n(\mathbf{r}, t) \quad (4)$$

and the source term can be decomposed similarly:

$$S(\mathbf{r}, t) = \sum_{j=0}^{\infty} S^{(j)} \otimes \nabla^j n(\mathbf{r}, t). \quad (5)$$

Here $\mathbf{\Gamma}^{(j)}$ and $S^{(j)}$ are field-dependent tensors of rank j and $\otimes$ denotes a j -fold scalar product. Equations (4) and (5) are sufficient but not necessary conditions for the existence of the hydrodynamic limit.

By analogy with the classical prescription (3), we could define a 'flux' diffusion tensor

$$\underline{\mathcal{D}} \equiv -\Gamma^{(2)} = \begin{pmatrix} \mathcal{D}_\perp & . & . \\ . & \mathcal{D}_\perp & . \\ . & . & \mathcal{D}_\parallel \end{pmatrix},$$

where $\mathbf{w} = \mathcal{K}\mathbf{E} = \Gamma^{(1)}$ defines 'flux' mobility $\mathcal{K}$ and 'flux' drift velocity $\mathbf{w}$, and $\nu = S^{(0)}$ is an average production rate of swarm particles, e.g. by ionisation.

On the other hand substitution of (4) and (5) into (2) yields the generalised diffusion equation

$$\partial_t n + \mathbf{W} \cdot \nabla n - \mathbf{D} : \nabla \nabla n + \sum_{j=3}^{\infty} \omega^{(j)} \otimes \nabla^j n = n\nu, \quad (6)$$

where $\omega^{(j)} = \Gamma^{(j)} - S^{(j)}$ and

$$\mathbf{W} = \mathbf{w} - S^{(1)}, \quad \mathbf{D} = \underline{\mathcal{D}} + S^{(2)} = \begin{pmatrix} D_\perp & . & . \\ . & D_\perp & . \\ . & . & D_\parallel \end{pmatrix}. \quad (7)$$

Here $\mathbf{W}$ and $\mathbf{D}$ denotes the reaction-corrected 'bulk' drift velocity and 'bulk' diffusion tensor respectively. Bulk mobility is given by $K = W/E = \mathcal{K} - S^{(1)}/E$. The sets $\{\mathcal{K}, \underline{\mathcal{D}}\}$ and $\{K, \mathbf{D}\}$ correspond to the quantities $\mathcal{L}_{ij}$ and L_{ij} respectively referred to in the Introduction.

The physical origin of the corrections $S^{(j)}$ can be easily understood (Robson 1986, 1988), and explicit formulas involving distribution functions are well known (Kumar *et al.* 1980). An approximate expression for $S^{(1)}$, obtained from momentum transfer theory, is given by (14) below.

(b) Survey of Experiments

(i) The *Cavalleri* (C) experiment (Huxley and Crompton 1974; Robson 1976) measures total number $N(t)$ of electrons in a diffusion chamber as a function of time, usually with $E = 0$. Setting $W = 0$, $\omega^{(2j+1)} = 0$, and $D_\parallel = D_\perp \equiv D$ in (6), the solution with $n = 0$ on the boundaries gives (Robson 1976)

$$N(t) = \int n(\mathbf{r}, t) d^3r \sim e^{-t/\tau}$$

at sufficiently long times, where $\tau^{-1} = -\nu + \Lambda^{-2} D_{\text{eff}}$, and where

$$D_{\text{eff}} = D \left(1 - \frac{\omega^{(4)}}{\Lambda^2 D} + \frac{\omega^{(6)}}{\Lambda^4 D} \dots \right) \quad (8)$$

is an effective coefficient and Λ is a 'diffusion length', comparable with the dimensions of the chamber. Since $\omega^{(j)}/D$ scales as n_0^{2-j} , equation (8) defines the function $D_{\text{eff}}(k)$, where $k = (n_0 \Lambda)^{-1}$. Thus $n_0 D_{\text{eff}}$ depends upon the geometry of the diffusion chamber and (nonlinearly) upon gas pressure.

However, it has long been recognised that the fundamental property is the thermal equilibrium coefficient $D = D_{\text{eff}}(0)$, obtained experimentally by raising gas pressure sufficiently high such that $k \rightarrow 0$. The series representation (8), which derives from the density gradient expansions (4) and (5), is valid only for sufficiently small k . A full kinetic theoretical treatment (Robson 1976) yields $D_{\text{eff}}(k)$ for all k .

(ii) In the *Townsend-Huxley* experiment (Huxley and Crompton 1974), the ratio of currents arising from a steady stream of electrons in the z -direction falling on a split anode furnishes the transverse diffusion coefficient $D_{\perp}$. The analysis is based on the second-order diffusion equation [retain only the first three terms on the left side of (6)]

$$\partial_t n + W \partial_z n - D_{\parallel} \partial_z^2 n - D_{\perp} (\partial_x^2 + \partial_y^2) n = n\nu, \quad (9)$$

with $\partial_t n = 0$ everywhere and the boundary condition $n = 0$.

(iii) In what have been labelled *pulsed radiolysis drift tube* (PRDT) experiments (Cassidy 1981), electrons are produced by a finite pulse of X-radiation uniformly in the gas confined by two plane electrodes and the total electron population $N(t)$ is monitored as a function of time. If the experiment is analysed in terms of (9), it yields W , with diffusion effects appearing as small correction terms.

(iv) In the *pulsed Townsend* (PT) experiment (Huxley and Crompton 1974; Tagashira *et al.* 1977; Blevin and Fletcher 1984), electrons are produced by UV radiation at the cathode and a displacement current

$$I(t) \sim w \int n(\mathbf{r}, t) d^3r$$

flows in the external circuit. Although w could in principle be obtained in this way, the experimental value found is in fact W .

(v) In the *time-of-flight* (TOF) experiment (Huxley and Crompton 1974) a pulse of particles is introduced into a drift chamber at $z = 0$, $t = 0$. The solution of (9) in one dimension is

$$n(z, t) = \frac{n_0}{(4\pi D_{\parallel} t)^{1/2}} \exp[\nu t - (z - Wt)^2 / 4D_{\parallel} t], \quad (10)$$

showing that W is the centroid velocity, ν is the overall growth rate and $(4D_{\parallel} t)^{1/2}$ is the longitudinal dispersion. Experiments infer $n(z, t)$ and W , $D_{\parallel}$ and ν may be found by comparison of (10) with data at various z and t .

(vi) In the *steady-state Townsend* (SST) experiments (Tagashira *et al.* 1977; Blevin and Fletcher 1984; Phelps and Pitchford 1985), a steady stream of electrons emitted from the cathode ionises the gas and at a sufficiently large distance z from the cathode it is usually assumed that

$$n(z) \sim \exp(\alpha z), \quad (11)$$

where α is the first Townsend ionisation coefficient. Substitution of (11) in to (4) and (6) gives

$$v_z = \Gamma_z/n = w \left(1 - \frac{\alpha D_{||}}{w} + \frac{\alpha^2 \Gamma^{(3)}}{w} + \dots \right), \quad (12)$$

$$\alpha(W - \alpha D_{||} + \alpha^2 \omega^{(3)} + \dots) = \nu \quad (13)$$

respectively, from which α and v_z may (at least in principle) be found to the desired accuracy by taking sufficient terms in the expansions. Problems of convergence of these series could arise if α were not sufficiently small. Thus, just as in the Cavalleri experiment, it appears that a kinetic theory treatment (Phelps and Pitchford 1985) based on the hydrodynamic limit but avoiding a density gradient expansion is desirable. However, unlike the Cavalleri experiment, there appears to be no obvious empirical means of extracting any of the transport coefficients appearing in parentheses in (12) and (13) as a limiting case, e.g. at high pressure. This is because α scales as n_0 and all terms in the series (12) and (13) are therefore independent of n_0 . Of course, α itself may be found by direct comparison of (11) with the empirical density profile, and v_z could, in principle, be obtained if the flux Γ were measureable in some way which did not disturb the free-space density distribution (11). We must therefore regard this experiment as furnishing quantities v_z and α which occupy a unique position in the hierarchy of transport coefficients.

3. Discussion

We firstly observe that the reactive correction $S^{(1)}$ of equation (7) is given by the approximate relation (Robson 1986)

$$S^{(1)} = -\frac{kT_{||}}{e} \frac{\partial \nu}{\partial E}, \quad (14)$$

so that if the collision frequency for nonconservative collisions is independent of energy, and the average production rate ν is consequently independent of E/n_0 , W and w are identical (but different from v_z). If collisions are conservative, $\nu = 0$, $\alpha = 0$ by (13) and consequently $W = w = v_z$. In general, however, all three differ. Notice that $S^{(1)}$ can be either positive or negative. Similar corrections for diffusion coefficients are given by Robson (1986). This multiplicity of transport coefficients in nonconservative conditions (ionisation, attachment, etc.) can give rise to difficulties in interpretation unless care is taken in the definition, measurement, calculation and reporting of drift velocities. The sort of difficulties which can arise otherwise are apparent in a recent paper of Ingold (1989) who effectively compared v_z (w_0 in the notation of Ingold) with w of Robson (1986). As these are fundamentally different quantities, it is not surprising that such significant discrepancies are observed, even in the case of a constant momentum-transfer collision frequency. The criticisms contained in Ingold's paper are therefore quite misplaced. Robson (1986) and Robson and Ness (1988) did not 'overlook' the importance of the density gradient, as claimed by Ingold, but rather we have expanded in terms

of it, as in equations (4) and (5), and identified transport coefficients in the manner described above. There is no reason to doubt the validity of any of the results reported by Robson (1986) or Robson and Ness (1988). Braglia *et al.* (1990) have introduced further 'conventional' transport coefficients, but these are artificial constructs, inconsistent with any conventional definition that we know of and not measurable in any case (Ness and Brennan 1992).

Blevin (1988) suggested that a transport property can be usefully defined only if:

- (i) it is *measurable* and not an artifact of a particular theoretical model or method of analysis;
- (ii) it is a *universal* quantity, independent of the method of measurement or the particular experimental arrangement. The SST parameters v_z and α do not appear to qualify, since they are related to a specific experimental arrangement.

In principle, the 'flux' or PT drift velocity w also satisfies these conditions, but its determination also requires an independent measurement of the number of electrons in a swarm. Only the 'bulk' quantities W , v , $D_{||}$ and $D_{\perp}$ satisfy the above stipulations. Looked at from another perspective, only these parameters appear in the diffusion equation (9), which is used to analyse the majority of experiments. We therefore suggest that W be designated as *the* drift velocity and $D_{||}$, $D_{\perp}$ as *the* diffusion coefficients, as these are the parameters which are in fact measured. The corresponding flux-derived parameters w , $\mathcal{D}_{||}$ and $\mathcal{D}_{\perp}$ are not measured in present-day experiments.

These considerations should also be taken into account wherever transport processes are accompanied by reactive effects, in fluid mechanics, plasma physics, micrometeorology, engineering applications and so on. The scope for discussion is very broad.

Acknowledgment

Helpful discussions with Drs K. Ness and K. Kumar are gratefully acknowledged.

References

- Batchelor, G. K. (1967). 'An Introduction to Fluid Mechanics' (Cambridge Univ. Press).
- Blevin, H. A. (1988). Proc. Japan-Aust. Workshop on Gaseous Electronics (Eds M. Hayashi and R. W. Crompton), p. 84 (CSIRO: Sydney).
- Blevin, H. A., and Fletcher, J. (1984). *Aust. J. Phys.* **37**, 593.
- Braglia, G. L., Diligenti, M., Wilhelm, J., and Winkler, R. (1990). *Nuovo Cimento D* **12**, 257.
- Cassidy, R. A. (1981). *Aust. J. Phys.* **34**, 677.
- Chapman, S., and Cowling, T. G. (1970). 'The Mathematical Theory of Non-uniform Gases', 3rd edn (Cambridge Univ. Press).
- de Groot, S. R., and Mazur, P. (1969). 'Nonequilibrium Thermodynamics' (North Holland: Amsterdam).
- Huxley, L. G. H., and Crompton, R. W. (1974). 'The Diffusion and Drift of Electrons in Gases' (Wiley: New York).
- Ingold, J. (1989). *Phys. Rev. A* **40**, 3855.
- Kumar, K., Skullerud, H. R., and Robson, R. E. (1980). *Aust. J. Phys.* **33**, 343.
- Lowke, J. J., Parker, J. H., and Hall, C. A. (1977). *Phys. Rev. A* **15**, 1237.

- Mason, E. A., and McDaniel, E. W. (1988). 'Transport Properties of Ions in Gases' (Wiley: New York).
- Ness, K. F., and Brennan, M. J. (1992). *Nuovo Cimento* (submitted).
- Phelps, A. V., and Pitchford, L. C. (1985). *Phys. Rev. A* **31**, 2932.
- Robson, R. E. (1970). *Ann. Phys. (New York)* **60**, 46.
- Robson, R. E. (1976). *Phys. Rev. A* **13**, 1536.
- Robson, R. E. (1981). *Aust. J. Phys.* **34**, 223.
- Robson, R. E. (1986). *J. Chem. Phys.* **85**, 4486.
- Robson, R. E. (1988). Proc. Japan-Aust. Workshop on Gaseous Electronics (Eds M. Hayashi and R. W. Crompton), p. 80 (CSIRO: Sydney).
- Robson, R. E., and Ness, K. F. (1988). *J. Chem. Phys.* **89**, 4815.
- Tagashira, H. (1988). Proc. Japan-Aust. Workshop on Gaseous Electronics (Eds M. Hayashi and R. W. Crompton), p. 76 (CSIRO: Sydney).
- Tagashira, H., Sakai, Y., and Sakamoto, S. (1977). *J. Phys. D* **10**, 1051.

Manuscript received 21 June, accepted 13 September 1991