

Nonlinear Diffusion of Ions in a Gas

R. E. Robson

Department of Physics, James Cook University of North Queensland, Qld 4811.

Abstract

The evolution in time of an initially closely bunched group of ions in a neutral gas is examined by solving a model kinetic equation, and limits to the validity of the linear law of diffusion (Fick's law) are established. The implications of nonlinear diffusion processes for determination of ion transport coefficients in drift tube experiments are discussed.

1. Introduction

Determination of transport coefficients from ion and electron swarm experiments in neutral gases has in the past relied upon the linear law of diffusion (Fick's law) to describe the charged particles in transit through the neutral gas. The particle flux in this approximation is thus written as

$$\mathbf{J} = nK\mathbf{E} - \mathbf{D} \cdot \nabla n,$$

where n is the ion density, K the mobility coefficient, $\mathbf{E}$ the electric field and $\mathbf{D}$ the diffusion tensor with components $D_{\parallel}$ and $D_{\perp}$ parallel and perpendicular to the field respectively. However, density gradients in experiments may be large and a linear theory of diffusion based upon the assumption of weak variations in n is clearly inadequate.

Ideally, one would like to solve Boltzmann's equation in which $\mathbf{E}$ appeared as an arbitrary parameter and spatial variations in density were not assumed small from the outset. As yet, only special cases have been dealt with, where the mathematical problems are not so severe: Skullerud (1974) examines the case of electrons under the assumption that the distribution of velocities is very nearly spherically symmetric (the well-known 'two-term' approximation; see e.g. Robson and Kumar 1971) and finds significant corrections to the earlier predictions of Parker and Lowke (1969) for the so-called time-of-flight experiment; Whealton (1975) shows that shock-wave phenomena arise from nonlinear diffusion of heavy ions in a gas. It appears that a solution to the general problem is a long way off, as even the weak gradient situation is very difficult to handle for strong enough electric fields (Kumar and Robson 1973).

An alternative to the rigorous analytic approach is to simulate the electron or ion swarm on a computer (McIntosh 1974). This has proved particularly useful in demonstrating the pear-shaped asymmetry of the swarm which must arise from nonlinear diffusive effects (Kumar and Robson 1973). Yet another alternative is to replace the collision term in the Boltzmann equation by an approximate expression which accounts for collisions in a phenomenological way; thus a simple relaxation-time model, often used in the kinetic theory of gases (Bhatnagar *et al.*

1954), is proposed to describe the collisions between ions and neutral molecules. What is lost in precision (it must be acknowledged that the model is very approximate) is balanced by the fact that an analytic solution is obtained and the physical understanding of the evolution of the ion swarm in time is consequently enhanced. This approach therefore provides a useful picture to complement the purely numerical work seemingly inevitable in any rigorous theory.

The problem specifically dealt with here is the idealized time-of-flight experiment, in which the ions are injected into the gas as a sharp pulse. We first derive exact expressions (valid at all times) for the position of the centroid and the mean square width of the pulse (equations (13a) and (13b) respectively). In Section 3, we examine the asymptotic behaviour of the swarm in time and as a result find small, but nevertheless significant, corrections to the predictions of the classical linear theory.

2. Theory

Solution of Model Kinetic Equation

Assume an unbounded neutral gas into which a tenuous pulse of n_0 ions of mass m and charge e are injected at the origin of coordinates at time $t = 0$. The ion velocity distribution function $f(\mathbf{r}, \mathbf{c}, t)$ is assumed to obey a relaxation-time model kinetic equation of the form

$$\partial f / \partial t + \mathbf{c} \cdot \nabla f + \mathbf{a} \cdot \partial f / \partial \mathbf{c} = -\nu(f - n w(\alpha, c)), \quad (1)$$

where ν is the ion-neutral collision frequency,*

$$n(\mathbf{r}, t) = \int d\mathbf{c} f(\mathbf{r}, \mathbf{c}, t)$$

is the ion number density,

$$w(\alpha, c) = (\alpha^2 / 2\pi)^{3/2} \exp(-\frac{1}{2}\alpha^2 c^2)$$

is the Maxwellian velocity distribution function appropriate to the gas temperature T , and

$$\alpha^2 = m/\kappa T \quad \text{and} \quad \mathbf{a} = e\mathbf{E}/m,$$

κ being the Boltzmann constant.

The solution of equation (1) via Fourier transformation in real space and in velocity space, together with Laplace transformation in time, yields for the transformed distribution function:

$$\begin{aligned} \bar{f}(\mathbf{k}, \mathbf{s}, \omega) &= \int_0^\infty dt \int d\mathbf{c} \int d\mathbf{r} f(\mathbf{r}, \mathbf{c}, t) \exp\{-i(\mathbf{k} \cdot \mathbf{r} + \mathbf{s} \cdot \mathbf{c} - \omega t)\} \\ &= -\exp\{i\mathbf{s}_\parallel(\frac{1}{2}\mathbf{s}_\parallel \mathbf{a}_\parallel + \mathbf{s}_\perp \cdot \mathbf{a}_\perp - \Omega)/k\} \\ &\quad \times \int^{s_\parallel} d\sigma \frac{1}{k} \left[\bar{n}(\mathbf{k}, \omega) \exp\left(-\frac{\sigma^2 + s_\perp^2}{2\alpha^2}\right) + f_0(\mathbf{k}, \sigma, s_\perp) \right] \\ &\quad \times \exp\left(-\frac{i\sigma(\frac{1}{2}\sigma \mathbf{a}_\parallel + \mathbf{s}_\perp \cdot \mathbf{a}_\perp - \Omega)}{k}\right) \Bigg], \end{aligned} \quad (2)$$

* Ion-ion interactions are neglected in comparison with ion-neutral interactions. Strictly speaking, ν is not the true collision frequency but some other closely related parameter; however, the distinction can be ignored for our purposes.

where

$$\begin{aligned}s_{\parallel} &= (\mathbf{s} \cdot \mathbf{k})k/k^2, & s_{\perp} &= \mathbf{s} - s_{\parallel}, \\ \mathbf{a}_{\parallel} &= (\mathbf{a} \cdot \mathbf{k})\mathbf{k}/k^2, & \mathbf{a}_{\perp} &= \mathbf{a} - \mathbf{a}_{\parallel}, \\ \Omega &= \omega + iv,\end{aligned}\quad (3)$$

and the transformed ion density and initial distribution function are given respectively by

$$\bar{n}(\mathbf{k}, \omega) = \int dt \int d\mathbf{r} n(\mathbf{r}, t) \exp\{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} = \bar{f}(\mathbf{k}, s=0, \omega) \quad (4)$$

and

$$f_0(\mathbf{k}, s) = \int d\mathbf{r} \int d\mathbf{c} f(\mathbf{r}, \mathbf{c}, t=0) \exp\{-i(\mathbf{k} \cdot \mathbf{r} + s \cdot \mathbf{c})\}. \quad (5)$$

The ions are initially supposed to have a gaussian distribution of velocities,

$$f(\mathbf{r}, \mathbf{c}, t=0) = n_0 \delta(\mathbf{r}) w(\mathbf{c}),$$

where $\alpha'^2 = m/\kappa T'$ and T' is the initial temperature of the ions. The transform (5) of the initial distribution function is therefore also gaussian:

$$f_0(\mathbf{k}, s) = n_0 \exp\{-s^2/2\alpha'^2\}. \quad (6)$$

Equations (2) and (4) together yield the expression for the Fourier-Laplace transform of the ion density:

$$\bar{n}(\mathbf{k}, \omega) = n_0 \beta' Z(\zeta') \{i\sqrt{2k}(1 + iv\beta Z(\zeta)/\sqrt{2k})\}^{-1}, \quad (7)$$

where Z is the plasma dispersion function, which is well known in the theory of wave propagation in plasmas (Fried and Conte 1961); it is defined by

$$Z(\zeta) = \pi^{-\frac{1}{2}} \int_{-\infty}^{\infty} dx \exp\{-x^2/(x-\zeta)\}, \quad \text{Im}(\zeta) > 0, \quad (8)$$

and by the analytic continuation of this function for $\text{Im}(\zeta) < 0$. The other new symbols appearing in equation (7) are defined by

$$\beta^{-2} = \alpha^{-2} + k^{-2} \mathbf{a} \cdot \mathbf{k} \quad \text{and} \quad \zeta = \Omega\beta/\sqrt{2k}, \quad (9)$$

β' and ζ' being similarly defined in terms of α' .

The first step in obtaining $n(\mathbf{r}, t)$ from $\bar{n}(\mathbf{k}, \omega)$ is to carry out the inversion of the Laplace transform. This leaves us with the Fourier transform $\tilde{n}(\mathbf{k}, t)$ of the ion density. Thus from equation (7) we have

$$\begin{aligned}\tilde{n}(\mathbf{k}, t) &= \int d\mathbf{r} n(\mathbf{r}, t) \exp(-i\mathbf{k} \cdot \mathbf{r}) \\ &= (2\pi)^{-1} \int_C d\omega \bar{n}(\mathbf{k}, \omega) \exp(-i\omega t),\end{aligned}\quad (10)$$

where C is a contour in the complex ω -plane lying above the singularities of the

integrand. These singularities are poles arising from the vanishing of the denominator of equation (7); hence we have the 'dispersion relation'

$$1 + i\nu\beta Z(\zeta)/\sqrt{2k} = 0. \quad (11)$$

Once the zeros of this expression, $\omega = \omega_k$, are known, the contour integral (10) can be determined by the usual method of residues. We do this specifically in the limit of small k (weak density gradient approximation) in the following subsection.

Centroid and Mean Square Width of Pulse

The quantities determined by experiment are the position of the centroid and the mean square width of the pulse, denoted respectively here as

$$\langle r \rangle = n_0^{-1} \int dr n(r, t) r$$

and

$$\langle RR \rangle = n_0^{-1} \int dr n(r, t) R R = \langle rr \rangle - \langle r \rangle \langle r \rangle,$$

where $R = r - \langle r \rangle$ is the position of an ion relative to the centroid. Since these 'moments' of the density are simply related to $\tilde{n}(k, t)$ by

$$n_0 \langle r \rangle = i \left(\frac{\partial \tilde{n}}{\partial k} \right)_{k=0} \quad \text{and} \quad n_0 \langle rr \rangle = - \left(\frac{\partial^2 \tilde{n}}{\partial k \partial k} \right)_{k=0}, \quad (12)$$

we can find the quantities of experimental interest directly by differentiation of equation (10). There is no need to solve the dispersion relation (11) if this is all the information required.

After some lengthy but straightforward calculation, we thus obtain

$$\langle r \rangle = a v^{-1} t - a v^{-2} + a e^{-\nu t} v^{-2}, \quad (13a)$$

$$\begin{aligned} \langle rr \rangle = 21 \{ (\alpha^2 v)^{-1} t + (\alpha' v)^{-2} - 2(\alpha v)^{-2} + e^{-\nu t} [\{ (\alpha v)^{-2} - (\alpha' v)^{-2} \} \nu t + 2(\alpha v)^{-2} - (\alpha' v)^{-2}] \} \\ + a a v^{-4} \{ v^2 t^2 - 6 + 2e^{-\nu t} (v^2 t^2 + 3\nu t + 3) \}. \end{aligned} \quad (13b)$$

In the absence of neutral molecules, the ions would suffer a uniform acceleration a (provided ion-ion interactions could be ignored); even when neutrals are present, the pulse will exhibit a similar behaviour immediately after it is released, before many collisions have occurred. Thus, for times $t \ll \nu^{-1}$ equation (13a) gives

$$\langle r \rangle \approx \frac{1}{2} a t^2.$$

After only a few collision periods, that is, $t \gtrsim \nu^{-1}$, the exponential terms can be neglected, and the resulting expressions show that the experimentally determined quantities behave linearly with time in this limit:

$$\langle r \rangle = a v^{-1} t - a v^{-2}, \quad (14a)$$

$$\langle RR \rangle = 2 \{ \{ 1(\alpha^2 v)^{-1} + a a v^{-3} \} t + 1 \{ (\alpha' v)^{-2} - 2(\alpha v)^{-2} \} - \frac{7}{2} a a v^{-4} \}. \quad (14b)$$

The coefficients of t in equations (14a) and (14b) are just the drift velocity W and twice the diffusion tensor D respectively (see equations (26) below). The constant terms become negligible after many collisions (for times $t \gg \nu^{-1}$) and thus the expressions for the centroid position and the mean square width as predicted by the diffusion equation (see equations (19) below) are regained in this limit. The conditions prevailing in drift tube experiments are such that the ions do in fact make many collisions with neutrals in transit between the emitter and the collector. On the basis of this model equation calculation, it would thus seem plausible to take transport coefficients as being given directly by the centroid position and the mean square width of the pulse measured at the collector. The traditional theoretical interpretation of the time-of-flight experiment is thus supported.

It must be emphasized that this model does not include the ion-neutral mass ratio m/M . For very light ions (or electrons), this parameter is most important and the indications are (Skullerud 1974) that it is the so-called collision frequency for energy transfer, $(2m/M)\nu$, which ought to appear in place of ν . In this case, the constant terms in equations (14) may be significant (McIntosh 1974; Skullerud 1974). However, when ion and neutral molecule masses are not very much different, these expressions should be at least qualitatively correct.

3. Long-time Behaviour of Ion Swarm

Review of Macroscopic Diffusion Theory

Deviations from Fick's linear law of diffusion have been accounted for in a phenomenological way by Whealton (1974) and others by assuming a particle flux of the form

$$\mathbf{J} = n\mathbf{W} - D \cdot \nabla n + \mathbf{Q} : \nabla \nabla n + \dots, \quad (15)$$

where $\mathbf{Q}$ is a third rank tensor. This together with the equation of continuity,

$$\partial n / \partial t + \nabla \cdot \mathbf{J} = 0,$$

yields the following differential equation for ion number density

$$\partial n / \partial t + \mathbf{W} \cdot \nabla n - D : \nabla \nabla n + \mathbf{Q} : \nabla \nabla \nabla n + \dots = 0. \quad (16)$$

We refer to (16) as the diffusion equation, although this terminology is usually reserved for the second-order equation only, in which $\mathbf{Q}$ is neglected.

The same technique as that used in solving equation (1) is again used for equation (16), together with the initial condition $n(\mathbf{r}, t=0) = n_0 \delta(\mathbf{r})$. Thus, the Fourier-Laplace transform of the ion density is found to be

$$\bar{n}(\mathbf{k}, \omega) = i n_0 / (\omega - \omega_k^{(0)}),$$

where

$$\omega_k^{(0)} = \mathbf{W} \cdot \mathbf{k} - i D : \mathbf{k} \mathbf{k} - \mathbf{Q} : \mathbf{k} \mathbf{k} \mathbf{k} - \dots, \quad (17)$$

and the dispersion relation is simply $\omega = \omega_k^{(0)}$. Inversion of the Laplace transform then gives

$$\bar{n}(\mathbf{k}, t) = n_0 \exp(-i \omega_k^{(0)} t), \quad (18)$$

from which the classical expressions for the centroid position and the mean square

width of the pulse follow:

$$\langle r \rangle = Wt, \quad \langle RR \rangle = 2Dt, \quad (19)$$

where $R = r - Wt$. All these expressions are without any constant terms (cf. equations 13). It is also a result of this macroscopic approach that the tensor $\mathbf{Q}$ plays no role in determining the quantities (19) of experimental interest.

The expression for the density is found from equation (18) to be

$$n(r, t) = n_0(2\pi)^{-3} \int d\mathbf{k} \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega_k^{(0)} t)\}, \quad (20)$$

and this was the starting point in the theory of Kumar and Robson (1973). Setting $\mathbf{Q} = 0$ in the expression (17) for $\omega_k^{(0)}$ (i.e. making the linear assumption) leads to the well-known result

$$\begin{aligned} n(r, t) = n_0 P(R, t) &= n_0 \int d\mathbf{k} \exp(i\mathbf{k} \cdot \mathbf{R} - \frac{1}{2} \mathbf{k} \mathbf{k} : \mathbf{R} \mathbf{R}) \\ &= n_0 (2\pi)^{-3/2} |\langle \mathbf{R} \mathbf{R} \rangle|^{-1} \exp\{-\mathbf{R} \mathbf{R} : (2\langle \mathbf{R} \mathbf{R} \rangle)^{-1}\}. \end{aligned} \quad (21)$$

This describes a spheroidal pulse symmetrical about the centroid position, which is drifting with mean velocity $\mathbf{W} = \mathbf{KE}$ and spreading in time. (Pulse widths are proportional to $(D_{\parallel} t)^{\frac{1}{2}}$ and $(D_{\perp} t)^{\frac{1}{2}}$ in directions parallel and perpendicular to $\mathbf{E}$ respectively.)

Kumar and Robson (1973) pointed out that the inclusion of $\mathbf{Q}$ destroys the symmetry about the centroid, thus resulting in a 'pear-shaped' pulse. Whealton (1974) has solved equation (16) without neglecting $\mathbf{Q}$, and has verified this asymmetry. He has also found that physically meaningful results are obtainable only for sufficiently small values of $Q^2/D_{\parallel} t$, thus illustrating directly that equation (15) and the equivalent expansion (17) are correct only asymptotically at long times when gradients in the density are weak.

Model Kinetic Equation Calculations

It is assumed for mathematical simplicity that ions when released have the same temperature as the gas. (Note that the macroscopic theory of the preceding subsection does not distinguish between various possible initial energy distributions for the ions.) Thus we have $\alpha' = \alpha$, $\beta' = \beta$ and $\zeta' = \zeta$ in equation (10).

Suppose that $\omega = \omega_k$ is any one of the zeros of the dispersion relation (11). The residue $b(\omega_k, t)$ of the integrand of equation (10) corresponding to the pole at ω_k can be shown to be given by

$$2\pi i b(\omega_k, t) = -n_0 i \{(k^2 \alpha^{-2} + i \mathbf{a} \cdot \mathbf{k})/v\omega_k\} \exp(-i\omega_k t), \quad (22)$$

and $\tilde{n}(\mathbf{k}, t)$ will be a sum of such terms. The dominant residue at long times will correspond to the smallest pole. Explicitly, we seek the major contribution to $\tilde{n}(\mathbf{k}, t)$ at times $t > v^{-1}$, that is, after many collisions have occurred. Hence we solve the dispersion relation (11) with the requirement

$$|\omega| < v. \quad (23)$$

Now it can be shown that equation (11) admits such solutions only for small k . Since small wave numbers k correspond to weak density gradients ∇n , this observation confirms the intuitive notion that spatial variations in density must tend to become smoothed out after a sufficiently large number of collisions, regardless of the initial sharpness of the pulse.

For small k , the argument of the plasma dispersion function is large, that is,

$$|\zeta| = |\Omega\beta/\sqrt{2k}| > 1, \quad (24)$$

and the asymptotic expansion of $Z(\zeta)$ is therefore appropriate (Fried and Conte 1961). Thus the dispersion relation (11) becomes

$$1 - i\nu\Omega^{-1}\{1 + k^2/\Omega^2\beta^2 + 3(k^2/\Omega^2\beta^2)^2 + 15(k^2/\Omega^2\beta^2)^3 + \dots\} = 0. \quad (25)$$

The small- ω solution is obtained by successive iterations (starting with $\omega = 0$) and this yields once again the 'multipole expansion' (17), in which the coefficients appear explicitly as

$$W = av^{-1}, \quad D = 1(\alpha^2v)^{-1} + aaav^{-3}, \quad Q = 2\{a1(\alpha^2v^3)^{-1} + 2aaaav^{-5}\}. \quad (26)$$

The condition for the validity of equation (17) (and hence the validity of the diffusion equation (16) is the relation (24), which for small ω can be written approximately as

$$|2k^2/\Omega^2\beta^2| = 2v^{-2}|k^2/\alpha^2 + ia \cdot k| < 1.$$

This can always be written in the form $k\lambda < 1$ where, for example, for very weak fields

$$\lambda = \sqrt{2}/v\alpha = (2\kappa T/m)^{\frac{1}{2}}v^{-1}$$

is the mean free path of an ion in the gas under thermal equilibrium conditions, and for very strong fields (or zero gas temperature)

$$\lambda = 2av^{-2}$$

is twice the distance the ion swarm drifts as a whole during one collision period. Thus the ion density must vary only slowly over distances comparable with λ and, in particular, the width of the pulse must significantly exceed λ if the diffusion equation (16) is to hold. Obviously, equation (16) must not be used to describe the initial, sharp pulse (times $t < v^{-1}$); this is the source of error in the expression (18) for $\tilde{n}(k, t)$ and is why Whealton (1974) found physically meaningless results at short times. To sum up, the classical diffusion equation (or its modified form 16) can be used to describe the asymptotic behaviour of the pulse, but the initial condition $n(r, t) = n_0 \delta(r)$ must not be employed in its solution.

Having solved the dispersion relation, we can now write down the expression for the Fourier-transformed ion density. From equation (22),

$$\begin{aligned} \tilde{n}(k, t) &= 2\pi i \sum_{\omega_k} b(\omega_k, t) \\ &\approx n_0 [v^{-1}a \cdot k - ik^2(\alpha^2v)^{-1}]/\omega_k^{(0)} \exp(-i\omega_k^{(0)}t), \quad vt > 1. \end{aligned} \quad (27)$$

This differs from the classical result (18) through the factor in square brackets.

Significantly, however, this factor approaches unity in the limit $k \rightarrow 0$, so that for very weak gradients there is no distinction between the two results. (Note that the density function $n(\mathbf{r}, t)$, whose Fourier transform is given by (27), also satisfies the diffusion equation.)

To second order in k , equation (27) can be written as

$$\tilde{n}(\mathbf{k}, t) = n_0 \exp(-i\mathbf{k} \cdot \langle \mathbf{r} \rangle - \frac{1}{2} k k : \langle \mathbf{R} \mathbf{R} \rangle), \quad (28)$$

where the expressions for the centroid position and mean square width are given by equations (14a) and (14b) respectively. Errors of order k^3 will not affect these results. Thus the ion density is approximately of the form (21) again, that is, the swarm has a spheroidal shape symmetrical about the centroid position $\langle \mathbf{r} \rangle$. Higher order corrections will lead to an asymmetric pulse, but the experimentally measured quantities $\langle \mathbf{r} \rangle$ and $\langle \mathbf{R} \mathbf{R} \rangle$ are independent of whether the pulse is pear-shaped or not. Moreover, for very long times ($vt \gg 1$), equations (14) show that $\langle \mathbf{r} \rangle$ and $\langle \mathbf{R} \mathbf{R} \rangle$ tend to their classical values (19). Thus, as long as the drift tube in a time-of-flight experiment is long enough, the classical diffusion equation can continue to be used to predict transport coefficients accurately.

4. Concluding Remarks

The theory given here is for the time-of-flight experiment with no boundary effects. It is envisaged that other experiments, such as the Townsend-Huxley arrangement for transverse diffusion, in which boundary effects are so important, could also be usefully analysed through the model kinetic equation approach. In that case, the Fourier transformation methods used here would not be appropriate and some other method of solution would have to be found.

We have seen that a macroscopic description of the ion swarm is possible only after times that are long compared with the mean free time v^{-1} . (This is sometimes called the hydrodynamic regime.) It is inconsistent to use the diffusion equation in conjunction with the initial condition for ion density, even though this does in fact give the correct expression for density at very long times (such that $vt \gg 1$). Strictly speaking, we must have some additional information about the swarm at a later time $t_0 > v^{-1}$ which can be used when solving the diffusion equation. This would involve difference measurements in the time-of-flight experiment. These observations are in broad agreement with the results of Skullerud's (1974) study of electron swarms from the Boltzmann equation.

The simple Krook model (1) used here has several deficiencies: persistence-of-velocity effects, which are of importance for heavy ions, are lost, as are effects due to the difference between energy and momentum relaxation times, which are of importance for light ions or electrons. By taking a speed-independent collision frequency ν we have further restricted the quantitative applicability of the results, but it appears that consideration of a more elaborate model would lead to prohibitive mathematical difficulties. Models which take these effects into account are described by Morse (1964) and Holway (1966).

Note added in proof

The BGK model predicts a field-independent lateral diffusion coefficient $D_{\perp}$ (equations 26). The origin of this rather anomalous result has been pointed out by

H. R. Skullerud (personal communication): In the derivation of equation (1) (Bhatnagar *et al.* 1954), it is assumed that the ions are scattered after a collision with a Maxwellian distribution of velocities at the gas temperature T . Energy gained in the field direction is therefore never transferred to perpendicular directions and hence the lateral random energy (and therefore $D_{\perp}$) does not depend upon the field strength. This model should perhaps best fit ions in the parent gas where resonant charge transfer dominates the interaction (McDaniel and Mason 1973). However, the range of validity of the BGK equation is by no means well established and it must therefore be stressed that the results obtained here should be viewed only as providing a qualitative description of the true physical situation (whether or not charge transfer processes are important).

References

- Bhatnagar, P. L., Gross, E. P., and Krook, M. (1954). *Phys. Rev.* **54**, 511.
Fried, B. D., and Conte, S. D. (1961). 'The Plasma Dispersion Function' (Academic: New York).
Holway, L. H. (1966). *Phys. Fluids* **9**, 1658.
Kumar, K., and Robson, R. E. (1973). *Aust. J. Phys.* **26**, 157.
McDaniel, E. W., and Mason, E. A. (1973). 'The Mobility and Diffusion of Ions in Gases' (Wiley: New York).
McIntosh, A. I. (1974). *Aust. J. Phys.* **27**, 59.
Morse, T. F. (1964). *Phys. Fluids* **7**, 2012.
Parker, J. H., and Lowke, J. J. (1969). *Phys. Rev.* **181**, 290.
Robson, R. E., and Kumar, K. (1971). *Aust. J. Phys.* **24**, 835.
Skullerud, H. R. (1974). *Aust. J. Phys.* **27**, 195.
Whealton, J. H. (1974). *J. Phys. B* **7**, 1602.
Whealton, J. H. (1975). *Phys. Rev. A* **11**, 297.

Manuscript received 2 December 1974

