Nonlinear Diffusion of Ions in a Gas. II*
Diffusion in Finite Enclosures

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Abstract

The connection between nonlinear diffusion and diffusion cooling of ions in a bounded gas is examined using the BGK model kinetic equation.

Introduction

The evolution in time of the density distribution of an ensemble of ions in a neutral gas subject to an electrostatic field has been studied by several authors (see Part I (Robson 1975) and references therein) with particular regard being paid to the nonlinear character of the diffusion process when density gradients are steep. For zero field and an unbounded gas, the ions tend eventually to be distributed uniformly and to reach thermal equilibrium with the neutral molecules. The presence of boundaries, however, has a profound effect upon the properties of the ion swarm at long times and thus, for instance, thermal equilibrium is never achieved. This phenomenon of 'diffusion cooling' (Biondi 1954) is shown in the present paper to be associated with the persistence of nonuniformity in the ion density and with non-linear diffusive effects.

As in Part I, we take a model kinetic equation for the ions, namely, the BGK model equation (Bhatnagar *et al.* 1954). This model cannot be justified *a priori*, but it does make the problem mathematically tractable. A similar approach was adopted by Grewal (1964) in studying the analogous problem of Brownian motion, although he did not consider the effects of boundaries. The limitations of the BGK model were discussed in Part I, and we note here that it is perhaps best suited to describing cases where collisional exchange phenomena are important (Whipple *et al.* 1975; H. R. Skullerud, personal communication).

Theory

For mathematical simplicity we take plane-parallel geometry, and hence work in one dimension with spatial and velocity coordinates x and u respectively. The BGK model kinetic equation (Bhatnagar *et al.* 1954) for the ion distribution function $f(u, x, t)$ is then

$$\frac{\partial f}{\partial t} + u \frac{\partial f}{\partial x} = -v\{f - n\, w(\alpha, u)\}, \tag{1}$$

where v is the ion–neutral collision frequency,

$$n(x, t) = \int_{-\infty}^{\infty} du\, f(u, x, t) \tag{2}$$

is the ion number density,

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

is the Maxwellian distribution function for the ions in thermal equilibrium with the neutral gas molecules (temperature T), and

$$\alpha^2 \equiv m/\kappa T,$$

κ being Boltzmann's constant and m the ion mass.

In solving equation (1), we assume that the *net* ion particle current away from the walls is zero, that is,

$$\int_{0}^{\infty} du\, u\, f(u, x = 0, t) = 0 = \int_{-\infty}^{0} du\, u\, f(u, x = L, t), \tag{3a}$$

where L is the distance between the walls. This, however, is only an approximation to the exact boundary conditions:

$$f(u > 0, x = 0, t) = 0 = f(u < 0, x = L, t), \tag{3b}$$

which signify that no ions whatever are reflected back into the gas (McDaniel 1964). Another approximation made here is to assume a solution of the form (one spatial Fourier mode approximation):

$$f(u, x, t) = \exp(-\omega t)\{A(u)\sin(kx) + B(u)\cos(kx)\}, \tag{4}$$

where ω and k are constants (Corngold 1964).

Substituting equation (4) in (1), we find that

$$A(u) = v\, w(\alpha, u)\{a(v - \omega) + kbu\}C(u) \tag{5a}$$

and

$$B(u) = v\, w(\alpha, u)\{b(v - \omega) - aku\}C(u), \tag{5b}$$

where

$$C(u) = \{(ku)^2 + (v - \omega)^2\}^{-1}, \qquad a = \int_{-\infty}^{\infty} du\, A(u) \qquad \text{and} \qquad b = \int_{-\infty}^{\infty} du\, B(u), \tag{6a, b, c}$$

while

$$n(x, t) = \exp(-\omega t)\{a\sin(kx) + b\cos(kx)\}. \tag{7}$$

The equations (5) have a nontrivial solution only if

$$1 - v(v - \omega)\int_{-\infty}^{\infty} du\, w(\alpha, u)\, C(u) = 0,$$

which is the 'dispersion relation' connecting ω and k. This can be conveniently written in terms of the well-known plasma dispersion function (Fried and Conte 1961):

$$1 + \mathrm{i}(k\lambda)^{-1} Z(\mathrm{i}\zeta) = 0, \tag{8}$$

where $\zeta = (k\lambda)^{-1}(1 - \omega/v)$ and $\lambda = \sqrt{2}/\alpha v$ is the ion mean free path. The constant k is to be fixed by the boundary conditions (3).

Equation (8) is of the same form as equation (11) of Part I for ions diffusing in an unbounded neutral gas in the absence of an electrostatic field. (There is a slight difference in notation: to obtain the equations in Part I, ω is to be replaced here by $\mathrm{i}\omega$.) In the present case, k is 'quantized' by virtue of the presence of boundaries. The physical significance of equation (8) and its connection with the equation of continuity is discussed in Part I. The boundary conditions (3), together with equations (4), (5) and (8), yield the following equation for k:

$$\tan(kL) = 2(b/a)\{(b/a)^2 - 1\}, \qquad \text{where} \qquad b/a = \sqrt{\pi}(\omega/v)\zeta^{-1}\exp(-\zeta^2)/E_1(\zeta^2), \tag{9a, b}$$

and E_1 is the exponential integral.

In most practical cases, the ion number density varies very slowly over distances comparable with the mean free path. Nevertheless, we allow for moderate variations and assume that

$$k\lambda < 1 \qquad \text{and} \qquad \zeta > 1. \tag{10}$$

If we use the asymptotic expansions for the plasma dispersion function and the exponential integral, equations (8) and (9b) become respectively

$$\omega/v = \tfrac{1}{2}(k\lambda)^2\{1 - \tfrac{1}{2}(k\lambda)^2 + ...\} \tag{11}$$

and

$$b/a = \tfrac{1}{2}\sqrt{\pi}\,k\lambda + O((k\lambda)^5). \tag{12}$$

Equations (7) and (11) taken together show that n satisfies the following 'diffusion equation'

$$\frac{\partial n}{\partial t} = D_0\frac{\partial^2 n}{\partial x^2} + \delta\lambda^2\frac{\partial^4 n}{\partial x^4} + ... = (D_0 - \delta k^2\lambda^2 + ...)\frac{\partial^2 n}{\partial x^2} \equiv D\frac{\partial^2 n}{\partial x^2}, \tag{13}$$

where $D_0 = \tfrac{1}{2}\lambda^2 v$ is the thermal equilibrium diffusion coefficient occurring in Fick's linear law of diffusion, while

$$D = D_0(1 - \delta k^2\lambda^2/D_0 + ...) \tag{14}$$

is an 'effective diffusion coefficient' for the ions and $\delta = \tfrac{1}{2}D_0$ is a higher order transport coefficient. Clearly, we have $D < D_0$, although the difference decreases as $k\lambda \to 0$; that is, as the density gradient becomes weaker, Fick's law of diffusion applies. The quantity $k\lambda$ can be made small by increasing the neutral gas pressure (i.e. by reducing λ) or by enlarging the enclosure. From equations (9a) and (12), it follows that the allowed values for k are

$$k = m\pi/(L + \sqrt{\pi}\,\lambda), \qquad \text{where} \qquad m = 1, 2, 3, \dots. \tag{15}$$

The expression for $n(x, t)$ therefore consists of a summation over terms like those on the right-hand side of equation (7), each corresponding to different modes m of diffusion. The lowest-order mode ($m = 1$) dominates at long times, since $\omega(k)$ increases with k (see equation 11), and only this mode is considered here.

Extrapolating $n(x, t)$ linearly beyond the physical boundary, we find the distance at which n vanishes (linear extrapolation distance) to be given by

$$d = \left| n\left(\frac{\partial n}{\partial x}\right)^{-1}_{x=0,L} \right| = b/ka = \tfrac{1}{2}\sqrt{\pi}\,\lambda. \tag{16}$$

The ratio $d/\lambda = \tfrac{1}{2}\sqrt{\pi} \approx 0\cdot89$ compares with values of $0\cdot67$ obtained by simplified mean free path arguments and $0\cdot71$ obtained from Boltzmann transport theory (McDaniel 1964, and references therein).

For an unbounded gas, the ions eventually reach thermal equilibrium with the neutral gas molecules, whatever the initial density distribution. However, the presence of boundaries and the resulting loss of ions by diffusion result in the mean ion energy reaching a steady value, uniform throughout the enclosure, but *below* the thermal equilibrium value of $\tfrac{1}{2}\kappa T$. By equations (4), (5a), (5b) and (8) we have

$$\langle \tfrac{1}{2}mu^2 \rangle = \{1/n(x,t)\} \int_{-\infty}^{\infty} du \, \tfrac{1}{2}mu^2 f(x,u,t) = \tfrac{1}{2}m(\omega-v)\omega/k^2 \tag{17}$$

and, assuming $k\lambda < 1$, it follows from (11) that

$$\langle \tfrac{1}{2}mu^2 \rangle = \tfrac{1}{2}\kappa T\{1 - (k\lambda)^2 + ...\} < \tfrac{1}{2}\kappa T. \tag{18}$$

Clearly, $\langle \tfrac{1}{2}mu^2 \rangle \rightarrow \tfrac{1}{2}\kappa T$ as the enclosure is enlarged or the gas pressure increased.

Discussion

The phenomenon of diffusion cooling was first observed by Biondi (1954) for electrons in the afterglow of low pressure argon and neon discharges.* The physical explanation involves the preferential leakage of high energy particles to the walls, with the remaining particles having a lower average energy. We have seen in the present paper that diffusion cooling for ions is significant when the mean free path is not negligible compared with the dimensions of the enclosure, under which conditions nonlinear diffusive processes occur, leading to a lower effective ion diffusion coefficient. It should be noted that, although we have taken plane-parallel geometry for simplicity, the main results of this paper are actually applicable to all geometries (although the value of k and the spatial form of n will differ).

It is to be emphasized that we have used a model kinetic equation as the starting point and hence the derived formulae should be regarded as being only qualitatively correct. Some deficiencies of the BGK model are discussed by Grewal (1964) and in Part I. There are two important effects which are missing from this model:

(i) The collision frequency v is assumed here to be a constant, independent of energy. Recent investigations (Robson 1976) for electrons indicate that 'diffusion heating' can occur if v varies more rapidly than linearly with energy. However, we have $D < D_0$ in all cases.

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* Diffusion cooling also occurs for neutrons in thermal reactors (Beckurts and Wirtz 1958).

(ii) The model is inadequate for dealing with charged particles whose mass is greatly different from that of the neutral molecules, and thus is not suitable for electrons. The parameter determining the importance of nonlinear diffusion effects and hence diffusion cooling is actually $k\lambda_\varepsilon$, where λ_ε is the mean free path for energy transfer. Since for electrons $\lambda_\varepsilon/\lambda \gg 1$, while for ions $\lambda_\varepsilon/\lambda \approx 1$, it is clear that, at a given pressure, diffusion cooling may be significant for electrons but not for ions. It should be noted that the extrapolation distance $d \approx \lambda$ in all cases, and thus it may be neglected for electrons even when diffusion cooling is strong. A more detailed discussion of the theory for electrons was given by Leemon and Kumar (1975), and an analysis of the recent experiment of Rhymes and Crompton (1975) for electrons in mixtures of neutral gases was given by Robson (1976).

Finally we note that, if the approximations (3a) and (4) are not made, there results an integral equation for the ion density:

$$n(x) = \int_0^L d\xi \, K(\,|\,x - \xi\,|\,)\, n(\xi),\tag{19}$$

where the kernel,

$$K(\eta) = v \int_0^\infty du \, \{w(\alpha, u)/u\} \exp\{-(v - \omega)\eta/u\},\tag{20}$$

must be evaluated numerically (Abramowitz 1953; Abramowitz and Stegun 1965). Thus, although the form of the solution (4) is clearly incompatible with the rigorous boundary conditions (3b), and the less stringent conditions (3a) imply a negative (and therefore unphysical) distribution function for certain velocities u, these approximations are essential to keep the problem mathematically tractable. A rigorous numerical solution of the integral equation (19) could have an intrinsic mathematical interest but may not be of much use for elucidating the more important physical aspects of the problem.

Acknowledgment

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