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Generalizations of Boltzmann's Equation

G. R. Anstis

Department of Mathematical Physics, University of Adelaide, P.O. Box 498, Adelaide, S.A. 5001.

Abstract

A scheme is proposed for systematically generalizing Boltzmann's equation in order to describe the non-equilibrium behaviour of an arbitrarily dense gas. The method avoids the divergences that arise from considering the dynamics of groups of isolated particles by introducing appropriate damping terms. Transport coefficients are obtained from the kinetic equations by using the auto-correlation formulae. For a one-dimensional gas of impenetrable point particles, approximations to the coefficient of self-diffusion may be obtained readily from the proposed generalization. A first correction to Boltzmann's equation yields the self-diffusion coefficient to within 1% of its exact value.

1. Introduction

A long standing problem in non-equilibrium statistical mechanics is to determine the transport coefficients of a gas of arbitrary density. A dilute gas is adequately described in terms of the one-particle velocity distribution function which satisfies an equation first derived by Boltzmann. By his H-theorem, Boltzmann was able to show that the solution to the equation approaches the equilibrium velocity distribution for long times. Chapman and Enskog (Chapman and Cowling 1970) were the first to show how transport properties may be obtained from Boltzmann's equation. By their method of solution it is possible to calculate values for the coefficients of viscosity, thermal conductivity, self-diffusion etc. which are in good agreement with experiment for dilute gases.

Boltzmann's equation may be derived by assuming that the velocities of a pair of particles about to collide are uncorrelated. This is an approximation to the actual situation in a gas since two particles about to collide may have previously interacted but, through collision with other particles, may once again be on precollision trajectories. In this situation their velocities are certainly not independent. If collision sequences involving three or more particles are taken into account, it should be possible to derive an equation valid for a greater range of densities than is Boltzmann's equation. Generalizations of Boltzmann's equation proposed by various authors (Cohen 1973) systematically consider sequences of collisions among 2, 3, 4, ... isolated particles. In a formal fashion, equations for the one-particle distribution function can be derived in a form which enables the Chapman–Enskog methods to be applied. However, analysis of these equations shows that they contain infinite terms which can only be eliminated by taking into account collision sequences among an arbitrarily large number of particles, so that the original aim of describing the system in terms of the dynamics of small numbers of particles apparently has to be abandoned.

These 'renormalized' equations predict that, in two and three dimensions, the transport coefficients can be expressed as a power series in the density and in the logarithm of the density. However, it is not easy to see how these renormalization techniques can be applied systematically to describe a gas of arbitrary density. No generalization of Boltzmann's H-theorem has been proved either.

Nevertheless it is possible to obtain formally exact expressions for the transport coefficients in terms of the autocorrelation formulae first considered by Green (1954). To evaluate these formulae, one needs to be able to describe the position and velocity at all times of a single particle of a gas in equilibrium (Green 1961), and so the problem is equivalent to finding a generalization of Boltzmann's equation that is valid for all densities.

It is the purpose of this paper to show that Boltzmann's equation can be generalized systematically to enable the transport coefficients of an arbitrarily dense gas to be calculated. One difference between this work and previous schemes is that use is made of the autocorrelation formulae rather than the methods of Chapman and Enskog.

We restrict our considerations to a one-dimensional gas of impenetrable point particles, a model which has been considered in detail by Jepsen (1965), Lebowitz and Percus (1967) and Anstis *et al.* (1973). The coefficient of self-diffusion is known exactly for this model, and so we have the advantage of being able to test the validity of proposed generalizations of Boltzmann's equation. Extension of the present work to a gas of rigid discs or rigid spheres is straightforward, although complicated by the dynamics of such systems.

In Section 2 we define the distribution functions which enable us to determine the behaviour of a particle of a gas in equilibrium. In Section 3 we see that the one-particle velocity distribution function $h(v, t)$ satisfies an equation of the form

$$\partial h(v,t)/\partial t = U(t, \rho | h(t)) \tag{1}$$

or, alternatively, of the form

$$\partial h(v,t)/\partial t = \int_0^t \mathrm{d}t' \; V(t-t', \rho | h(t')), \tag{2}$$

where U and V are time-dependent functionals and ρ is the density of the gas.

Previous attempts to generalize Boltzmann's equation have been concerned with expressing the rate of change of the velocity distribution function as a time-independent functional. Such equations may be solved by the methods of Chapman and Enskog. In the present work, however, we calculate transport coefficients from equations of the form (1) or (2).

Evaluation of U and V requires that the complete dynamics of the system is known. We note that these functionals may be expressed as sums of contributions from the dynamics of subsystems involving either a finite or infinite number of particles. The two-body contributions lead to the Boltzmann collision operator. However, as is the case in two- and three-dimensional models, contributions from $3, 4, \ldots$-particle systems increase without limit as the time increases. Hence care must be taken to ensure that any approximations to equations (1) and (2) contain only finite expressions.

We outline two approaches for finding approximate equations for $h(v, t)$. One is to write the functionals in terms of the dynamics of 2, 3, ... particles interacting in

the fluid environment which contains an infinite number of particles. This approach, in effect, takes into account the fact that in an actual fluid there is a vanishing probability that a particle can avoid collisions for an arbitrarily long time. The functionals U and V are then expressed as sums of terms which remain finite for all times.

The alternative method of avoiding divergences comes from recognizing that the result of U and V acting on the equilibrium velocity distribution is zero. Hence, if the velocity distribution function $h(v,t)$ approaches its equilibrium value rapidly enough, the contributions to U and V from isolated groups of particles will be modified so that only finite terms are involved. As we show, the properties of the Boltzmann collision operator suggest that $h(v,t)$ does approach its equilibrium value rapidly enough.

In Section 4 we show how the transport coefficients may be obtained from the equations for $h(v,t)$ derived in the previous section by using the autocorrelation formulae. The self-diffusion coefficient may be calculated to within 1% of its exact value from a first correction to Boltzmann's equation. Finally, the implications of the present approach for two- and three-dimensional systems are examined in Section 5.

2. One-dimensional Model

The purpose of this section is to review some of the properties of a one-dimensional gas. We make use of some standard results of equilibrium and non-equilibrium statistical mechanics (for further details see Green and Leipnik 1970).

Consider a system of identical impenetrable point particles of mass m free to move on an infinite line. This gas can be described in terms of the properties of an ensemble of systems each of which is specified by the number of its particles and their positions and velocities at some time. The position and velocity of particle i are denoted by $z^{(i)} = (q^{(i)}, v^{(i)})$. The phase space distribution function F^N is defined as follows: $F^N(z^{(1)}, \ldots, z^{(N)}, t)\, \mathrm{d}z^{(1)} \ldots \mathrm{d}z^{(N)}$ denotes the fraction of N-particle systems of the ensemble in which at time t particle i is in the phase space element $\mathrm{d}z^{(i)}$ about the point $z^{(i)}$. The N-particle distribution function satisfies Liouville's equation

$$(\partial/\partial t + \kappa^N) F^N(z^{(1)}, \ldots, z^{(N)}, t) = 0, \tag{3}$$

where

$$\kappa^N = \sum_{i=1}^{N} \left(v^{(i)} \frac{\partial}{\partial q^{(i)}} - m^{-1} \frac{\partial \Phi_N}{\partial q^{(i)}} \frac{\partial}{\partial v^{(i)}} \right) \tag{4}$$

and Φ_N is the potential energy of the system. A formal solution to Liouville's equation is

$$\begin{aligned} F^N(z^{(1)}, \ldots, z^{(N)}, t) &= \exp(-\kappa^N (t - t_0))\, F^N(z^{(1)}, \ldots, z^{(N)}, t_0) \\ &\equiv S^{(N)}(z^{(1)}, \ldots, z^{(N)}, t - t_0)\, F^N(z^{(1)}, \ldots, z^{(N)}, t_0). \end{aligned} \tag{5}$$

We have introduced the streaming operator $S^{(N)}(z^{(1)}, \ldots, z^{(N)}, t - t_0)$, which transforms the coordinates $z^{(1)}, \ldots, z^{(N)}$ into the coordinates that the N particles would have had at a time $t - t_0$ earlier if they had interacted only among themselves.

In order to calculate transport coefficients we need to consider a sub-ensemble of the grand canonical ensemble for which the position and velocity of some particle, which we define as particle 1, are $q^{(1)} = 0$ and $v^{(1)} = v'$ at time t_0 (Green 1961).

The theory of equilibrium statistical mechanics enables us to write down the initial value of the N-particle distribution function as

$$F^{(N)}(z^{(1)}, ..., z^{(N)}, t_0) = \delta(q^{(1)})\,\delta(v^{(1)}-v')\,\Xi^{-1}\exp\left\{\beta\left(\mu(N-1) - \tfrac{1}{2}m\sum_{i=2}^{N}(v^{(i)})^2 + \Phi_N\right)\right\}. \tag{6}$$

The factor $\beta = 1/kT$ is related to the temperature T of the system, μ is the chemical potential, and Ξ is the grand canonical partition function, which is a normalization factor depending on β and μ.

The ensemble average of any property $G(z_1, ..., z_k, t)$ of the system is given by

$$\langle G(z_1, ..., z_k, t)\rangle = \sum_{N=0}^{\infty}\frac{1}{(N-1)!}\int dz^{(1)} ... \int dz^{(N)}\, F^N(z^{(1)}, ..., z^{(N)}, t)\, G(z_1, ..., z_k, t), \tag{7}$$

where, both here and below, the range of integration is not specified when it is unrestricted. This average is taken over all possible configurations of an N-particle system as well as over all possible values for the number of particles in the system. The factor $1/(N-1)!$ results from considering all particles, except for particle 1, as being identical. The grand partition function Ξ is chosen so that $\langle 1\rangle = 1$.

The n-particle velocity distribution functions are defined by

$$f^{(n)}(z_1, ..., z_n, t) = \sum_{1\neq i_2\neq ...\neq i_n}\langle\delta(z^{(1)}-z_1)\,\delta(z^{(i_2)}-z_2) ... \delta(z^{(i_n)}-z_n)\rangle, \tag{8}$$

where $f^{(n)}(z_1, ..., z_n, t)\,dz_1 ... dz_n$ is the fraction of systems of the ensemble in which at time t particle 1 is in the element dz_1 about the point z_1 of phase space and some other unspecified particles are in the elements $dz_2, ..., dz_n$ about the phase space points $z_2, ..., z_n$. From the definition (7) of the ensemble average, we obtain

$$f^{(n)}(z_1, ..., z_n, t) = \sum_{j=0}^{\infty}(j!)^{-1}\int dz_{n+1} ... \int dz_{n+j}\, F^{(n+j)}(z_1, ..., z_{n+j}, t). \tag{9}$$

Using this equation and the initial condition (6), we can show that

$$f^{(n)}(q_1, v_1, q_2, v_2, ..., q_n, v_n, t_0) = \rho^{n-1}\,h_0(v_2) ... h_0(v_n)\,\delta(q_1)\,\delta(v_1-v'), \tag{10}$$

where ρ is the density of particles in the system and $h_0(v)$ is the equilibrium velocity distribution:

$$h_0(v) = (\beta m/2\pi)^{\frac{1}{2}}\exp(-\tfrac{1}{2}\beta m v^2). \tag{11}$$

We now show that it is possible to write the n-particle velocity distribution function at time t in terms of the one-particle velocity distribution function at time t_0. First we note that the set of equations (9) implies the equations

$$F^{(n)}(z_1, ..., z_n, t) = \sum_{j=0}^{\infty}(-1)^j(j!)^{-1}\int dz_{n+1} ... \int dz_{n+j}\, f^{(n+j)}(z_1, ..., z_{n+j}, t). \tag{12}$$

This can be verified by direct substitution of equation (12) into equation (9). By using the formal solution (5) to Liouville's equation, we can write equation (9) as

$$f^{(n)}(z_1, ..., z_n, t) = \sum_{j=0}^{\infty}(j!)^{-1}\int dz_{n+1} ... \int dz_{n+j}\, S^{(n+j)}(t-t_0)\,F^{(n+j)}(z_1, ..., z_{n+j}, t_0). \tag{13}$$

Evaluating equation (12) at t_0, substituting it into equation (13) and invoking the initial condition (10), leads to

$$f^{(n)}(z_1, ..., z_n, t) = \rho^{n-1} \sum_{j=0}^{\infty} (j!)^{-1} \rho^j \sum_{k=0}^{j} (-1)^{j-k} \binom{j}{k} \times \int dz_{n+1} ... \int dz_{n+j} \, S^{(n+k)}(t-t_0) \, h_0(v_2) ... h_0(v_{n+j}) f^{(1)}(q_1, v_1, t_0). \tag{14}$$

It is convenient to write equation (14) in the form

$$f^{(n)}(z_1, ..., z_n, t) = \rho^n \sum_{j=0}^{\infty} (j!)^{-1} \rho^{j-1} \, T^{(n+j)}(z_1, ..., z_n, t-t_0) f^{(1)}(z_1, t_0), \tag{15}$$

where

$$T^{(n+j)}(z_1, ..., z_n, t-t_0) = \sum_{k=0}^{j} (-1)^{j-k} \binom{j}{k} \times \int dz_{n+1} ... \int dz_{n+j} \, S^{(n+k)}(t-t_0) \, h_0(v_2) ... h_0(v_{n+j}). \tag{16}$$

Thus we have achieved our aim of writing $f^{(n)}(t)$ in terms of $f^{(1)}(t_0)$.

The velocity distribution functions satisfy the hierarchy of equations (Anstis *et al.* 1973)

$$(\partial/\partial t + \kappa^{(n)}) f^{(n)}(z_1, ..., z_n, t) = \lim_{\varepsilon \to 0} \int dv_{n+1} \, |v_1 - v_{n+1}| \{ f^{(n+1)}(q_1^{\varepsilon}, v_{n+1}, z_2, ..., z_n, z_1, t) - f^{(n+1)}(z_1, z_2, ..., z_n, q_1^{\varepsilon}, v_{n+1}, t) \}, \tag{17}$$

where $q_1^{\varepsilon} = q_1 - \varepsilon \, \mathrm{sgn}(v_{n+1} - v_1)$, and $\kappa^{(n)}$ is the Liouville operator which includes only interactions between particle 1 and the other particles. All other collisions may be ignored, as the effect of such collisions is that the particles just exchange velocities.

Having written down the hierarchy of equations we can now state that the fundamental problem that we have to consider is how to obtain a closed equation for $f^{(1)}(t)$ from the infinite set of equations (17). One such closed equation may be obtained by assuming that

$$f^{(2)}(z_1, z_2, t) = \rho \, h_0(v_2) f^{(1)}(z_1, t) \tag{18}$$

for precollision values of z_1 and z_2, i.e. for $(q_1 - q_2)(v_1 - v_2) < 0_-$. Substituting equation (18) into (17) with $n = 1$ leads to Boltzmann's equation

$$\left(\frac{\partial}{\partial t} + v \frac{\partial}{\partial q} \right) f^{(1)}(q, v, t) = \rho B\{ f^{(1)}(q, v, t) \} \equiv \rho \int dw \, |v - w| \{ h_0(v) f^{(1)}(q, w, t) - h_0(w) f^{(1)}(q, v, t) \}. \tag{19}$$

Properties of the Boltzmann collision operator B are given in the Appendix.

The autocorrelation formula for the self-diffusion coefficient D is

$$D = \int_0^\infty \mathrm{d}t \int \mathrm{d}q \int \mathrm{d}v \int \mathrm{d}v'\, f^{(1)}(q, v, t)\, vv'\, h_0(v'). \tag{20}$$

We shall find it useful to define the quantities

$$h(v, t) = \int \mathrm{d}q\, f^{(1)}(q, v, t) \quad \text{and} \quad \phi(v) = \int_0^\infty \mathrm{d}t \int \mathrm{d}v'\; h(v, t)\, v'\, h_0(v'). \tag{21,22}$$

From equation (17) we see that $h(v, t)$ satisfies

$$\partial h(v, t)/\partial t = \int \mathrm{d}v_2\, |v - v_2| \{h^{(2)}(v_2, v, t) - h^{(2)}(v, v_2, t)\}, \tag{23}$$

where

$$h^{(2)}(v, v_2, t) = \lim_{\varepsilon \to 0} \int \mathrm{d}q\, f^{(2)}(q, v, q^\varepsilon, v_2, t). \tag{24}$$

For our one-dimensional model the self-diffusion coefficient can be evaluated exactly (Jepsen 1965). It is found to be

$$D = (2\pi\beta m)^{-\frac{1}{2}} \rho^{-1}. \tag{25}$$

All other transport coefficients are undefined for this system.

3. Equations for Velocity Distribution Function

In this section we show how to derive for the one-particle velocity distribution function $h(v, t)$ equations which have the forms (1) and (2). We first show that the two-particle velocity distribution function $f^{(2)}(t)$ can be expressed as a functional of $f^{(1)}(t)$ in two alternative ways and that, when these expressions are substituted into the first equation of the hierarchy of equations (17) and an integration over position is performed, we obtain equations of the desired form. That $f^{(2)}(t)$ can be expressed in terms of $f^{(1)}(t)$ follows from equation (14) which shows that both $f^{(1)}(t)$ and $f^{(2)}(t)$ may be expressed as functionals of $f^{(1)}(t_0)$. By writing $f^{(1)}(t_0)$ as a functional of $f^{(1)}(t)$ and substituting into the equation for $f^{(2)}(t)$ we obtain $f^{(2)}(t)$ in terms of $f^{(1)}(t)$.

The resulting expressions for the functionals $U(\rho, t)$ and $V(\rho, t)$ are sums of contributions from subsystems of particles to the time-evolution of the whole system. Thus we express U as a sum of contributions from the dynamics of small groups of particles. Although these contributions are unbounded in time, their contribution to U acting on $h(v, t)$ remains finite, and in fact approaches zero for large times. This is because the Boltzmann collision operator takes into account the interactions between an isolated group of particles and their environment. Hence it appears that it is possible to approximate U by retaining only the first few terms in the 2, 3, ... -body expression. On the other hand, we express V as a sum of many-body contributions. The 3, 4, ... -body contributions are modified by taking into account the possibility of a collision with another particle. Each term in the expansion of V remains finite

for all times, and we may approximate the functional by retaining just the first few terms.

If we consider equation (15) for $n = 1$, we have

$$f^{(1)}(z_1, t) = S^{(1)}(t-t_0) f^{(1)}(z_1, t_0) + \sum_{j=1}^{\infty} (j!)^{-1} \rho^j T^{(j+1)}(z_1, t-t_0) f^{(1)}(z_1, t_0). \tag{26}$$

This is an integral equation which can be solved for $f^{(1)}(t_0)$ in terms of $f^{(1)}(t)$ by iteration. The first two terms of the series expansion of the solution are

$$S^{(1)}(t-t_0) f^{(1)}(z_1, t_0) = f^{(1)}(z_1, t) - \rho \int dz_3 \{S^{(2)}(z_1, z_3, t-t_0) - S^{(1)}(z_1, t-t_0)\} \times S^{(1)}(z_1, -(t-t_0)) h_0(v_3) f^{(1)}(z_1, t) + \ldots. \tag{27}$$

If this expression is substituted into equation (15) for $n = 2$ we obtain $f^{(2)}(t)$ as a functional of $f^{(1)}(t)$:

$$f^{(2)}(z_1, z_2, t) = \rho S^{(2)}(z_1, z_2, t-t_0) S^{(1)}(z_1, -(t-t_0)) h_0(v_2) f^{(1)}(z_1, t) + \rho^2 \int dz_3 \{S^{(3)}(z_1, z_2, z_3, t-t_0) - S^{(2)}(z_1, z_3, t-t_0)\} \times S^{(1)}(z_1, -(t-t_0)) h_0(v_2) h_0(v_3) f^{(1)}(z_1, t) + \ldots. \tag{28}$$

The term proportional to ρ^2 in equation (28) is nonzero only for those configurations of the fluid in which particle 1 interacts with two other particles in the time interval $t-t_0$. In general the term associated with k-body collisions in the expansion (28) of $f^{(2)}(t)$ in terms of $f^{(1)}(t)$ is nonzero only when there are k collisions in the time interval $t-t_0$. Equation (28) is the one-dimensional analogue of a well-known expression for $f^{(2)}(t)$ obtained in higher dimensions (Cohen 1973).

Evaluating the effect of the streaming operators leads to the result

$$h^{(2)}(v_1, v_2, t) = \rho h_0(v_2) h(v_1, t) + \rho^2 (t-t_0) \int dv_3 \, \varepsilon((v_1-v_2)(v_2-v_3)) |v_2-v_3| \times h_0(v_1) \{h_0(v_3) h(v_2, t) - h_0(v_2) h(v_3, t)\} + \ldots. \tag{29}$$

Here $\varepsilon(x)$ denotes the step function

$$\varepsilon(x) = 1 \quad \text{for} \quad x > 0,$$
$$= 0 \qquad\quad x < 0.$$

The k-body term in expansion (29) contains the factor $(t-t_0)^{k-2}$. We note that if

$h(v,t) = h_0(v)$ then $h^{(2)}(t)$ assumes its equilibrium value. Substituting the above expression for $h^{(2)}(v_1, v_2, t)$ into the hierarchy equation (23) gives

$$\partial h(v_1,t)/\partial t = \rho \int \mathrm{d}v_2\, |v_1 - v_2| \{h_0(v_1)\, h(v_2,t) - h_0(v_2)\, h(v_1,t)\}$$

$$+\rho^2 (t-t_0) \int \mathrm{d}v_2 \int \mathrm{d}v_3\, \varepsilon((v_2-v_1)(v_1-v_3))\, |v_1-v_2|\, |v_1-v_3|\, h_0(v_2)$$

$$\times \{h_0(v_3)\, h(v_1,t) - h_0(v_1)\, h(v_3,t)\}$$

$$-\rho^2 (t-t_0) \int \mathrm{d}v_2 \int \mathrm{d}v_3\, \varepsilon((v_1-v_2)(v_2-v_3))\, |v_1-v_2|\, |v_2-v_3|\, h_0(v_1)$$

$$\times \{h_0(v_3)\, h(v_2,t) - h_0(v_2)\, h(v_3,t)\} + \ldots, \qquad (30)$$

which is of the form (1).

Let us now consider approximations to equation (30) obtained by retaining only $2, 3, \ldots, n$-body contributions to the operator $U(\rho, t)$. We may write this equation as

$$\partial h(v,t)/\partial t = \rho B[h] + \rho^2\, U_2(t)[h] + \ldots + \rho^n\, U_n(t)[h]. \qquad (31)$$

If we rewrite equation (31) as

$$h(v,t) = \exp(\rho B(t-t_0))\, h(v,t_0)$$

$$+ \int_{t_0}^{t} \mathrm{d}t' \exp(\rho B(t-t'))\{\rho^2\, U_2(t') + \ldots + \rho^n\, U_n(t')\}\, h(v,t'), \qquad (32)$$

we can see that the divergent $3, \ldots, n$-body contributions are damped by the Boltzmann term. In Section 4 below we solve this equation iteratively. As is shown in the Appendix, apart from the eigenvalue zero, the eigenvalues of the Boltzmann operator are less than $-\alpha(0)$, where $\alpha(v)$ is defined by equation (34) below. Each term of the iterative solution of equation (32) remains finite because of the damping factor $\exp \rho B t$. The sum of the terms also remains finite since, as can be seen from equation (31), the condition

$$\int h(v,t)\, \mathrm{d}v = 1$$

holds for all times.

Let us now derive an equation of the form (2). We express $V(\rho, t)$ in terms of certain many-body dynamical contributions because approximations to V must contain, at least approximately, effects of all particles of the system if finite values of the self-diffusion coefficient are to be obtained. Rather than start with equation (15) for the distribution functions, we derive new expansions by writing the hierarchy equations (17) as

$$\{\partial/\partial t + \kappa^{(n)} + \rho\alpha(v_1)\}\, f^{(n)}(z_1, \ldots, z_n, t)$$

$$= \lim_{\varepsilon \to 0} \int \mathrm{d}v_{n+1}\, |v_1 - v_{n+1}|$$

$$\times \{f^{(n+1)}(q_1^{\varepsilon}, v_{n+1}, z_2, \ldots, z_n, z_1, t) + \rho h_0(v_{n+1})\, f^{(n)}(z_1, \ldots, z_n, t)$$

$$- f^{(n+1)}(z_1, z_2, \ldots, z_n, q_1^{\varepsilon}, v_{n+1}, t)\}, \qquad (33)$$

with

$$\alpha(v) = \int \mathrm{d}w\, |v-w|\, h_0(w), \tag{34}$$

where $\rho\alpha(v)$ is the frequency of collisions experienced by a particle moving with velocity v in an equilibrium environment.

Equation (33) has the integral form

$$f^{(n)}(t) = \exp(-\{\rho\alpha(v_1)+\kappa^{(n)}\}(t-t_0))f^{(n)}(t_0)$$
$$+ \lim_{\varepsilon\to 0}\int_{t_0}^{t} \mathrm{d}t' \exp(-\{\rho\alpha(v_1)+\kappa^{(n)}\}(t-t')) \int \mathrm{d}v_{n+1}\, |v_1-v_{n+1}|$$
$$\times \{f^{(n+1)}(q_1^{\varepsilon}, v_{n+1}, \ldots, t') - f^{(n+1)}(z_1, \ldots, t') + \rho h_0(v_{n+1}) f^{(n)}(t')\}. \tag{35}$$

By a series of successive substitutions, expansions for the one- and two-particle velocity distribution functions are obtained:

$$f^{(1)}(z_1, t) = \exp(-\rho\alpha(v_1)(t-t_0))\, S^{(1)}(z_1, t-t_0) f^{(1)}(z_1, t_0)$$
$$+ \lim_{\varepsilon\to 0}\rho \int_{t_0}^{t} \mathrm{d}t' \exp(-\rho\alpha(v_1)(t-t'))\, S^{(1)}(z_1, t-t') \int \mathrm{d}v_3\, |v_1-v_3|$$
$$\times S^{(2)}(z_1^{\varepsilon}, z_1, t'-t_0)\, h_0(v_1) f^{(1)}(z_1^{\varepsilon}, t_0) + \ldots, \tag{36}$$

$$f^{(2)}(z_1, z_2, t) = \rho h_0(v_2) \exp(-\rho\alpha(v_1)(t-t_0))\, S^{(1)}(z_1, t-t_0) f^{(1)}(z_1, t_0)$$
$$+ \lim_{\varepsilon\to 0}\rho^2 \int_{t_0}^{t} \mathrm{d}t' \exp(-\rho\alpha(v_1)(t-t'))\, S^{(2)}(z_1, z_2, t-t') \int \mathrm{d}v_3\, |v_1-v_3|$$
$$\times S^{(3)}(z_1^{\varepsilon}, z_2, z_1, t'-t_0) f^{(1)}(z_1^{\varepsilon}, t_0) + \ldots, \tag{37}$$

where

$$z_1^{\varepsilon} = (q_1^{\varepsilon}, v_3).$$

From equations (36) and (37) we obtain

$$f^{(2)}(z_1, z_2, t) = \rho h_0(v_2) f^{(1)}(z_1, t)$$
$$+ \lim_{\varepsilon\to 0}\rho^2 \int_{t_0}^{t} \mathrm{d}t' \exp(-\rho\alpha(v_1)(t-t'))\, S^{(2)}(z_1, z_2, t-t')$$
$$\times \int \mathrm{d}v_3\, |v_1-v_3| \{S^{(3)}(z_1^{\varepsilon}, z_2, z_1, t'-t_0) - S^{(2)}(z_1^{\varepsilon}, z_1, t'-t_0)\}$$
$$\times h_0(v_1) h_0(v_2) f^{(1)}(z_1^{\varepsilon}, t_0) + \ldots, \tag{38}$$

where we have indicated only the first few terms of the expression.

We thus have obtained $f^{(2)}(t)$ as a linear functional of $f^{(1)}(t_0)$ which we write as

$$f^{(2)}(z_1, z_2, t) = \rho h_0(v_2) f^{(1)}(z_1, t) + \rho^2 K(z_1, z_2, t, \rho | f^{(1)}(t_0))$$
$$= \rho h_0(v_2) f^{(1)}(z_1, t) + \rho^2 \int_{t_0}^{t} \mathrm{d}t'\, K'(z_1, z_2, t-t', \rho | f^{(1)}(t_0)), \tag{39}$$

where K' is the time derivative of the functional K. We need to be able to express $f^{(1)}(t_0)$ as a functional of $f^{(1)}(t')$ if equation (39) is to lead to an equation of the type (2). By inverting equation (36) we obtain a suitable expression which, when substituted into equation (39), yields

$$f^{(2)}(z_1, z_2, t) = \rho h_0(v_2) f^{(1)}(z_1, t) + \rho^2 \int_{t_0}^{t} \mathrm{d}t' \, L(z_1, z_2, t-t', \rho | f^{(1)}(z_1, t')), \quad (40)$$

where L is a functional. Substitution of equation (40) into the first hierarchy equation and integration over position yields an equation of the desired form (2).

To obtain an explicit expression for V we first evaluate the effects of the streaming operators in equation (38) to obtain

$$\begin{aligned} h^{(2)}(v_1, v_2, t) = {} & \rho h_0(v_2) h(v_1, t) \\ & + \rho^2 \int_{t_0}^{t} \mathrm{d}t' \int \mathrm{d}v_3 \, \varepsilon((v_1 - v_2)(v_2 - v_3)) \, |v_2 - v_3| \, h_0(v_1) \\ & \times \{h_0(v_3) h(v_2, t_0) - h_0(v_2) h(v_3, t_0)\} \\ & \times \exp(-\rho \alpha(v_1)(t - t') \, |v_2 - v_3| / |v_1 - v_3|) + \ldots . \end{aligned} \quad (41)$$

The function $h(v, t_0)$ can be expressed in terms of $h(v, t')$ by equation (36). Substituting such an expression into equation (41) then enables us to write

$$\begin{aligned} \frac{\partial h(v_1, t)}{\partial t} = {} & \rho \int \mathrm{d}v_2 \, |v_1 - v_2| \{h_0(v_1) h(v_2, t) - h_0(v_2) h(v_1, t)\} \\ & + \rho^2 \int_{t_0}^{t} \mathrm{d}t' \int \mathrm{d}v_2 \int \mathrm{d}v_3 \, \varepsilon((v_2 - v_1)(v_1 - v_3)) \, |v_1 - v_2| |v_1 - v_3| \, h_0(v_2) \\ & \times \{h_0(v_3) h(v_1, t') - h_0(v_1) h(v_3, t')\} \exp(-\rho \alpha(v_2)(t - t') |v_1 - v_3| / |v_2 - v_3|) \\ & - \rho^2 \int_{t_0}^{t} \mathrm{d}t' \int \mathrm{d}v_2 \int \mathrm{d}v_3 \, \varepsilon((v_1 - v_2)(v_2 - v_3)) \, |v_1 - v_2| |v_2 - v_3| \, h_0(v_1) \\ & \times \{h_0(v_3) h(v_2, t') - h_0(v_2) h(v_3, t')\} \exp(-\rho \alpha(v_1)(t - t') |v_2 - v_3| / |v_1 - v_3|) \\ & + \ldots . \end{aligned} \quad (42)$$

We have thus indicated two of the terms in the expansion of $V(\rho, t)$. The exponential damping terms are contributions from those configurations of the fluid in which some particle of the gas interacts with a group of three particles with velocities v_1, v_2 and v_3.

The inclusion of multibody effects in each term of equation (42) ensures that each term approaches zero for long times. At this stage in the evolution of the system only the Boltzmann term may be nonzero but, by the H-theorem, we are assured that $h(v, t)$ will approach its equilibrium value. This argument also applies when equation (42) is approximated by retaining only the first few terms of the right-hand side. Such is not the case if many-body effects are not included. For instance, the equation which takes into account only two- and three-body contributions may be obtained by expanding the exponential terms in equation (42) in powers of the density and retaining terms in ρ and ρ^2 only. This is an equation also derived by Lebowitz and Percus (1967). However, it does not have the property that $\partial h / \partial t \to 0$ for long times.

4. Calculation of Self-diffusion Coefficient

We now show how the self-diffusion coefficient may be evaluated from the approximate equations for the above-derived velocity distribution function. The self-diffusion coefficient is given by the autocorrelation formula (20). For our one-dimensional model it can be evaluated *exactly* to obtain $D = 0{\cdot}282/\rho$, where we have taken $\beta m = 2$.

We first show that Boltzmann's equation leads to the value $D_B = 0{\cdot}328/\rho$. We next consider the approximation to equation (30) which results from retaining only two- and three-body contributions, and we show that this yields a value of $0{\cdot}317/\rho$. Finally the self-diffusion coefficient is calculated from equation (42), with only the explicitly indicated terms retained, and is shown to be just 1% off the exact value.

Starting with Boltzmann's equation (19), we can obtain

$$\int_0^\infty \mathrm{d}t \int \mathrm{d}v'\, v'\, h_0(v')\, \partial h(v,t)/\partial t = \rho \int \mathrm{d}v_2\, |v-v_2| \{h_0(v)\, \phi(v_2) - h_0(v_2)\, \phi(v)\}, \quad (43)$$

where $\phi(v)$ is defined by equation (22). Using the initial condition $h(v,0) = \delta(v-v')$ and the fact that $h(v,t) \to h_0(v)$ as $t \to \infty$, we obtain the integral equation

$$-v\, h_0(v) = \rho \int \mathrm{d}v_2\, |v-v_2| \{h_0(v)\, \phi(v_2) - h_0(v_2)\, \phi(v)\}. \quad (44)$$

The solution of this equation is given by equations (A9) and (A10) of the Appendix, with $s = 0$. The self-diffusion coefficient is then given by equation (20) which we write as

$$D = \int \mathrm{d}v\, \phi(v) v. \quad (45)$$

By numerical evaluation of the integral, we obtain $D_B = 0{\cdot}328/\rho$.

Let us now consider equation (30) which we approximate by retaining only two- and three-body contributions. Equation (32) may be solved iteratively for $h(v,t)$ to give

$$h(v,t) = \exp(\rho B t)\, h(v,0) + \int_0^t \mathrm{d}t' \exp(\rho B(t-t'))\, t' C \exp(\rho B t')\, h(v,0) + \ldots. \quad (46)$$

We have here taken $t_0 = 0$ and have written $U_3(t) = tC$, where C is a time-independent integral operator in velocity space and is given explicitly in equation (30).

From equation (46) we obtain the following expression for $\phi(v)$

$$\phi(v) = \rho^{-1}(1 + B^{-1} C B^{-1} + \ldots)\, B^{-1} \{v\, h_0(v)\}, \quad (47)$$

where B^{-1} is the inverse of the Boltzmann operator which is given by equations (A9) and (A10) of the Appendix. The expression (47) for $\phi(v)$ may be evaluated numerically. From equation (45) D is then found to be $0{\cdot}317/\rho$, a small correction to the Boltzmann value.

Finally we calculate the self-diffusion coefficient from the approximation to equation (42) in which only the indicated terms are retained. Putting $t_0 = 0$, we write the resultant equation as

$$\partial h(v,t)/\partial t = \rho B\{h(v,t)\} + \rho^2 \int_0^t \mathrm{d}t'\, A(t-t', \rho)\, h(v,t'). \quad (48)$$

Thus $\phi(v)$ now satisfies the equation

$$\left.\begin{aligned} -vh_0(v) &= \rho B\{\phi(v)\} + \rho^2 \int_0^\infty \mathrm{d}t \int_0^t \mathrm{d}t' \int \mathrm{d}v'\, v'\, h_0(v')\, A(t-t', \rho)\, h(v, t') \\ &= \rho B\{\phi(v)\} + \rho^2 \int_0^\infty \mathrm{d}t\, A(t, \rho)\, \phi(v). \end{aligned}\right\} \quad (49)$$

From equation (42) we see that, because of the exponential terms, the operator

$$\int_0^\infty \mathrm{d}t\, A(t, \rho)$$

is finite and is proportional to ρ^{-1}. Hence we can write equation (49) as

$$-v\, h_0(v) = \rho(B + \bar{A})\, \phi(v), \qquad \text{where} \qquad \bar{A} = \rho \int_0^\infty \mathrm{d}t\, A(t, \rho). \qquad (50a, b)$$

The solution to the integral equation (50a) is

$$\begin{aligned} \phi(v) &= -\rho^{-1}(1 + B^{-1}\bar{A})^{-1} B^{-1}\{vh_0(v)\} \\ &= -\rho^{-1}(1 - B^{-1}\bar{A} + B^{-1}\bar{A}B^{-1}\bar{A} + \ldots) B^{-1}\{vh_0(v)\}, \end{aligned} \quad (51)$$

which is an expression suitable for numerical evaluation. We find $D = 0{\cdot}280/\rho$, just 1% off the exact value.

5. Conclusions

In this paper we have shown that Boltzmann's equation may be generalized to describe a gas of arbitrary density. The one-particle velocity distribution function satisfies an exact equation which may be approximated to enable transport coefficients to be computed. By taking into account the dynamics of the whole system, at least statistically, we can be assured that each approximation contains only finite contributions. Alternatively we may approximate the exact equation by retaining only $2, 3, \ldots$-body contributions. In this case, $3, 4, \ldots$-body contributions are modified by the Boltzmann term which takes into account the interaction of an isolated group of particles with the rest of the system.

The present approach is general enough to apply to a gas of rigid discs or spheres but for more general interaction potentials, such as those for which bound states can occur, further generalization may well be necessary. In particular, equations of the type of (32) and (42) might be obtained, but the time dependence of the operators appearing in those equations would differ in an important way from the one-dimensional case. In two dimensions $U_3(t) \simeq \ln t$ as t becomes very large, while in three dimensions the four-body term $U_4(t)$ exhibits similar long time behaviour. We are then led to consider integrals of the type

$$\int_0^\infty \mathrm{d}t \exp(-\rho t) \int_0^t \mathrm{d}u\, (1+u)^{-1},$$

which for small values of ρ behaves like $\ln \rho$.

Two methods of modifying the contributions from isolated groups of particles have been proposed here for a one-dimensional model. Equations of the type (42),

in which the term $\exp(-\rho\alpha(v)t)$ is present, also lead to finite expressions in two and three dimensions. However, analysis of the two-dimensional Boltzmann operator suggests that the operator $\exp(\rho Bt)$ may not be adequate to provide the necessary convergence of the integrals that arise. This leads to the possibility that the self-diffusion coefficient may not exist in two dimensions. No such problem occurs for a gas of rigid spheres. Reference to the growing body of work on this problem may be found in an article by Cohen (1973).

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Appendix

The purpose of this appendix is to solve the one-dimensional form of Boltzmann's equation

$$\partial h(v,t)/\partial t = \rho \int \mathrm{d}w\, |v-w| \{h_0(v)\, h(w,t) - h_0(w)\, h(v,t)\}, \tag{A1}$$

which results from equations (19) and (21). We define

$$g(v,t) = \int \mathrm{d}v'\, v'\, h_0(v')\, h(v,t) \tag{A2}$$

and note that $h(v,t)$ is also a function of v'. In fact, we have $h(v,0) = \delta(v-v')$, so that $g(v,0) = vh_0(v)$ is an odd function of v. If we let

$$\bar{g}(v,s) = \int_0^\infty \mathrm{d}t \exp(-st)\, g(v,t) \tag{A3}$$

be the Laplace transform of $g(v,t)$ then $\bar{g}(v,s)$ satisfies the relation

$$s\bar{g}(v,s) - g(v,0) = \rho \int \mathrm{d}\omega\, |v-\omega| \{h_0(v)\, \bar{g}(\omega,s) - h_0(\omega)\, \bar{g}(v,s)\}. \tag{A4}$$

Since $g(v,0)$ is an odd function of v, the linear equation (A4) implies that $\bar{g}(v,s)$ is also odd.

Introducing the auxiliary function

$$G(v,s) = \int \mathrm{d}\omega\, |v-\omega|\, \bar{g}(\omega,s), \tag{A5}$$

we can write equation (A4) as

$$s\frac{\partial^2 G(v,s)}{\partial v^2} - 2g(v,0) = \rho\frac{\partial}{\partial v}\left(G(v,s)\frac{\mathrm{d}\alpha}{\mathrm{d}v} - \alpha(v)\frac{\partial G}{\partial v}\right) \tag{A6}$$

where $\alpha(v)$ is defined by equation (34). Integrating equation (A6) and using the boundary conditions

$$G(0,s) = 0 \qquad \text{and} \qquad \left.\frac{\partial G}{\partial v}\right|_{v=0} = -2\int_0^\infty \mathrm{d}\omega\, \bar{g}(\omega,s),$$

we obtain

$$G(v,s) = \{s+\rho\alpha(v)\}\int_0^v \mathrm{d}\omega\, f(\omega)\{s+\rho\alpha(\omega)\}^{-2}, \tag{A7}$$

where we have

$$f(v) = 2\int_0^v \mathrm{d}\omega\, g(\omega,0) - 2\{s+\rho\alpha(0)\}\int_0^\infty \mathrm{d}\omega\, \bar{g}(\omega,s), \tag{A8}$$

and hence

$$\bar{g}(v,s) = \tfrac{1}{2}\frac{\partial^2 G(v,s)}{\partial v^2} = \rho h_0(v)\int_0^v \mathrm{d}\omega\, f(\omega)\{s+\rho\alpha(\omega)\}^{-2} + g(v,0)\{s+\rho\alpha(v)\}^{-1}. \tag{A9}$$

The integral in the second term of the right-hand side of equation (A8), which is an unknown quantity in (A9), can be obtained by integrating (A9) to obtain

$$\left(1+2\{s+\rho\alpha(0)\}\int_0^\infty \mathrm{d}v\int_0^v \mathrm{d}\omega\, h_0(v)\{s+\rho\alpha(\omega)\}^{-2}\right)\int_0^\infty \mathrm{d}v\, \bar{g}(v,s)$$

$$= 2\rho\int_0^\infty \mathrm{d}v\, h_0(v)\int_0^v \mathrm{d}\omega\, \{s+\rho\alpha(\omega)\}^{-2}\int_0^\omega \mathrm{d}u\, g(u,0)$$

$$+ \int_0^\infty \mathrm{d}v\, g(v,0)\{s+\rho\alpha(v)\}^{-1}. \tag{A10}$$

The quantity $\phi(v)$ defined in equation (22) is given by equations (A9) and (A10) with $s = 0$.

If we now consider the eigenvalue equation

$$\lambda b(v) = B\{b(v)\}, \tag{A11}$$

we see that one solution is $b(v) = h_0(v)$ with $\lambda = 0$. To find other solutions we note that the eigenvalue equation has the form of equation (A4) with $g(v,0) = 0$ and $s/\rho = \lambda$. Hence its solution is given by equations (A9) and (A10). In particular the right-hand side of equation (A10) vanishes. By considering the left-hand side of this equation, we see that we have $\lambda < -\alpha(0)$.

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