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1974 J. Phys. A: Math. Nucl. Gen. 7 1895

(http://iopscience.iop.org/0301-0015/7/15/015)

J. Phys. A: Math., Nucl. Gen., Vol. 7, No. 15, 1974. Printed in Great Britain. © 1974

Non-equilibrium statistical mechanics I. The Boltzmann transport equation

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Received 28 March 1974

Abstract. By using a new method, the Boltzmann transport equation is deduced from the Liouville equation. The method involves an assumption of a statistical nature, which can be relaxed so as to yield equations more general than the Boltzmann equation, or than presently known extensions of the Boltzmann equation. The method also clarifies the origin of the time irreversibility of the Boltzmann equation.

1. Introduction

Approximately one hundred years ago, Ludwig Boltzmann set up his transport equation for dilute gases (Boltzmann 1872, 1875) by using intuitive arguments. The Boltzmann equation is the basis for nearly all discussions of transport properties in dilute gases, and there is excellent agreement between its prediction and experiment.

Nonetheless, problems remain even one hundred years later; the most important ones are:

(i) The Boltzmann equation leads to time irreversibility, ie, the forward sense of time is distinguished, and memory of the initial state of the system at time $t = 0$ is lost as the solution proceeds towards thermal equilibrium. By contrast, the equations of classical dynamics are reversible in time, and the question arises how one can derive an equation with irreversible results (Boltzmann's equation) from a time-reversible basic equation (Liouville's equation for the full distribution function). In Boltzmann's own derivation, the irreversibility can be traced back to a statistical assumption about the probability of collisions (the '*Stosszahlansatz*'); but it would be more satisfactory to have the statistical assumption appear directly related to quantities involved in the Liouville equation itself.

(ii) The Boltzmann equation is restricted to very dilute gases; extension to encompass transport properties of somewhat denser gases has proved extremely difficult. The methods used to date lead to expansions which contain divergent coefficients (Ernst *et al* 1969), and are therefore unsatisfactory.

(iii) The Boltzmann equation does not allow for ternary or higher-order collisions, only for binary collisions. In a chemical reaction such as

$$\mathrm{H}+\mathrm{H} \leftrightarrow \mathrm{H}_2 \tag{1.1}$$

binary collisions are of no effect, since the energy in the centre of mass system (which is conserved in a binary collision) is positive for the left-hand side, negative for the right-hand side. An extension of the Boltzmann equation to allow for the possibility of chemical reactions is needed; if developed, it would automatically provide a fundamental theory of the rate of chemical reactions in gases.

In a series of papers we shall address ourselves to these problems, employing a new method to obtain, firstly, the Boltzmann equation and then extensions to it. The present paper emphasizes the principle of the new method. Other authors have described derivations of the Boltzmann equation starting from the Liouville equation (these include Kirkwood 1946, Bogoliubov 1946, Born and Green 1949, Hollinger and Curtiss 1960, Hoffman and Green 1965) but we feel that the approach given here provides the clearest answer to the above three problems. A summary of this material was reported in a previous communication (Blatt and Opie 1974).

The remainder of the introduction establishes notation. The N-particle, full distribution function is normalized by

$$\int \rho(\boldsymbol{r}_1,\boldsymbol{p}_1,\boldsymbol{r}_2,\boldsymbol{p}_2,\ldots,\boldsymbol{r}_N,\boldsymbol{p}_N,t)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\ldots\mathrm{d}\tau_N = N! \tag{1.2}$$

where

$$\mathrm{d}\tau_i = \mathrm{d}^3\boldsymbol{r}_i\,\mathrm{d}^3\boldsymbol{p}_i = \mathrm{d}x_i\,\mathrm{d}y_i\,\mathrm{d}z_i\,\mathrm{d}p_{xi}\,\mathrm{d}p_{yi}\,\mathrm{d}p_{zi}. \tag{1.3}$$

The distribution function is assumed to satisfy the Liouville equation

$$\frac{\partial\rho}{\partial t} = -[\rho, H_N] \tag{1.4}$$

where H_N is the N-particle hamiltonian, the particles being confined to a rigid box of volume V, and the bracket on the right-hand side denotes a Poisson bracket.

The Boltzmann equation is an equation for the one-particle projection of ρ, defined by

$$f(\boldsymbol{r}_1,\boldsymbol{p}_1,t) = \frac{N\int\rho(1,2,3,\ldots,N)\,\mathrm{d}\tau_2\,\mathrm{d}\tau_3\ldots\mathrm{d}\tau_N}{\int\rho(1,2,3,\ldots,N)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\ldots\mathrm{d}\tau_N} \tag{1.5}$$

where we have abbreviated the arguments $(\boldsymbol{r}_i,\boldsymbol{p}_i)$ simply by 'i'. Within the Boltzmann equation, one term describes the effect of binary collisions. The momentum symbols for the particles before the collision are primed, $\boldsymbol{p}'_1$ and $\boldsymbol{p}'_2$, and after the collision unprimed, $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$, respectively†. The impact parameter vector $\boldsymbol{b}$ (after the collision) is the component of $\boldsymbol{r}_2-\boldsymbol{r}_1$ at right angles to the direction of $\boldsymbol{p}_2-\boldsymbol{p}_1$, ie,

$$\boldsymbol{b} = (\boldsymbol{r}_2-\boldsymbol{r}_1)-\frac{(\boldsymbol{r}_2-\boldsymbol{r}_1)\cdot(\boldsymbol{p}_2-\boldsymbol{p}_1)}{|\boldsymbol{p}_2-\boldsymbol{p}_1|^2}(\boldsymbol{p}_2-\boldsymbol{p}_1). \tag{1.6}$$

The vectors $\boldsymbol{p}_2-\boldsymbol{p}_1$, and $\boldsymbol{p}'_2-\boldsymbol{p}'_1$ lie in one plane: the scattering angle in the CM system is the angle between the vectors $\boldsymbol{p}_2-\boldsymbol{p}_1$ and $\boldsymbol{p}'_2-\boldsymbol{p}'_1$ and these two vectors have the same magnitude. The relative speed of the two particles is given by

$$v_{12} = \frac{|\boldsymbol{p}_2-\boldsymbol{p}_1|}{m}. \tag{1.7}$$

For meaningful collisions, the impact parameter vector $\boldsymbol{b}$ has magnitude of the order of the range r_0 of the inter-atomic forces, which is assumed to be small compared to all

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† It is to be noted that the allocation of primes is the reverse of that normally used: this choice is most convenient for the present method.

other lengths of interest in a dilute gas. The impact parameter vector $\boldsymbol{b}$ determines the relation between 'before collision' and 'after collision' values:

$$\boldsymbol{p}'_1 = \boldsymbol{p}'_1(\boldsymbol{p}_1, \boldsymbol{p}_2, \boldsymbol{b}) \qquad \boldsymbol{p}'_2 = \boldsymbol{p}'_2(\boldsymbol{p}_1, \boldsymbol{p}_2, \boldsymbol{b}) \tag{1.8}$$

where the detailed functional forms depend on the inter-atomic force law. Except for this effect of $\boldsymbol{b}$, distances of atomic dimensions are ignored in the Boltzmann equation (eg, if the particles just emerging from a collision are located at $\boldsymbol{r}''_1$ and $\boldsymbol{r}''_2$, say, these two vectors are identified and just called $\boldsymbol{r}_1$). Similarly, the time duration of a collision is ignored. The resulting Boltzmann equation has the form:

$$\frac{\partial f}{\partial t} = -[f, H_1] + \int \mathrm{d}^3 \boldsymbol{p}_2 \int \mathrm{d}^2 \boldsymbol{b}\, v_{12}(f(\boldsymbol{r}_1, \boldsymbol{p}'_1) f(\boldsymbol{r}_1, \boldsymbol{p}'_2) - f(\boldsymbol{r}_1, \boldsymbol{p}_1) f(\boldsymbol{r}_1, \boldsymbol{p}_2)) \tag{1.9}$$

where H_1 is the one-particle hamiltonian. For simplicity, we shall ignore external forces on the system, so that $H_1 = (\boldsymbol{p}_1)^2/2m$ and the Poisson bracket becomes

$$[f, H_1] = \frac{\boldsymbol{p}_1}{m} \operatorname{grad}_{\boldsymbol{r}} f(\boldsymbol{r}, \boldsymbol{p}_1, t). \tag{1.10}$$

In the collision term (second term on the right-hand side) of (1.9), the integration over $\boldsymbol{b}$ is only two dimensional, since the vector $\boldsymbol{b}$ is restricted to lie in the plane perpendicular to $\boldsymbol{p}_2 - \boldsymbol{p}_1$. The integral is often written in the form

$$\int \mathrm{d}^2 \boldsymbol{b} \ldots = 2\pi \int_0^\infty b\, \mathrm{d}b \ldots. \tag{1.11}$$

This completes the establishment of notation. In § 2, we shall derive equation (1.9) from equation (1.4) by making suitable statistical assumptions. The new derivation and its consequences will be discussed in § 3.

2. The new derivation

In general, the distribution function $\rho(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{r}_2, \boldsymbol{p}_2, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_N, t)$ includes the description of correlated behaviour of the particles making up the system. If, however, it should happen at some time t that the particles are statistically uncorrelated, this would be described by means of an N-particle distribution function which is a product of single-particle functions, $g(\boldsymbol{r}, \boldsymbol{p}, t)$, which we can normalize (without loss of generality) by means of:

$$\int g(\boldsymbol{r}, \boldsymbol{p}, t)\, \mathrm{d}^3 \boldsymbol{r}\, \mathrm{d}^3 \boldsymbol{p} = V \tag{2.1}$$

where V is the volume of the container. Given the normalization (1.2) of ρ, the N-particle distribution function of an uncorrelated system has the form:

$$\rho(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{r}_2, \boldsymbol{p}_2, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_N, t) = \frac{N!}{V^N} g(\boldsymbol{r}_1, \boldsymbol{p}_1, t) g(\boldsymbol{r}_2, \boldsymbol{p}_2, t) \ldots g(\boldsymbol{r}_N, \boldsymbol{p}_N, t). \tag{2.2}$$

The concepts of *correlation* and *dynamical interaction* between particles are distinct, and must be kept apart in thinking about a system of particles. For example, if the

N-particle hamiltonian has the form

$$H_N = T_N + V_N \tag{2.3}$$

with

$$T_N = \sum_{k=1}^{N} \frac{(\boldsymbol{p}_k)^2}{2m} \tag{2.4}$$

and

$$V_N = \sum_{i<j} \phi(r_{ij}) \tag{2.5}$$

then V_N represents the dynamical interaction, and the system is an independent-particle system if $\phi(r_{ij}) = 0$. However, an ensemble of such systems may have been started off in such a way that the particles are correlated with each other at time $t = 0$. Then ρ is *not* of form (2.2) at time $t = 0$, and if ρ obeys the Liouville equation (1.4), ρ is then *not* of form (2.2) at any future time t, in spite of the absence of interactions in the hamiltonian. This is therefore an example of correlations without dynamical interactions.

Conversely, even if the dynamical interactions exist (V_N is not zero), it is possible in principle to prepare an ensemble of systems in such a way that *at time* $t = 0$ the distribution function is of the uncorrelated form (2.2), ie, such that

$$\rho(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{r}_2, \boldsymbol{p}_2, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_N, 0) = \frac{N!}{V^N} g_0(\boldsymbol{r}_1, \boldsymbol{p}_1) g_0(\boldsymbol{r}_2, \boldsymbol{p}_2) \ldots g_0(\boldsymbol{r}_N, \boldsymbol{p}_N). \tag{2.6}$$

The function $g_0(\boldsymbol{r}, \boldsymbol{p})$ is in the nature of an initial condition, and is restricted only by the normalization condition (2.1). This distribution function represents an ensemble of systems, each with dynamical interactions present, but with the particles being statistically uncorrelated at time $t = 0$.

Of course, this state of affairs cannot last. If the hamiltonian contains interactions, then the very first collision after $t = 0$ introduces correlations, and as a result, the N-particle distribution function ρ at any time other than $t = 0$ does *not* have the uncorrelated form (2.2). Formally, this shows itself by the fact that the *form* (2.2) is inconsistent with the Liouville equation (1.4), unless the system is an independent-particle system ($V_N = 0$). An independent-particle system, and only such a system, has solutions of (1.4) of the form (2.2) at all times.

Let us consider a time interval Δt which is: (*a*) much longer than the duration of one collision; and (*b*) much shorter than the mean free time of a typical particle between successive collisions. If the gas is sufficiently dilute, such a time interval Δt can be found. If ρ at time $t = 0$ has the form (2.6), ρ at time Δt does *not* have the form (2.2), no matter what we choose to be the function $g(\boldsymbol{r}, \boldsymbol{p}, \Delta t)$.

However, we can now ask the question: 'How should the function $g(\boldsymbol{r}, \boldsymbol{p}, \Delta t)$ be chosen so that (2.2) represents the best approximation to the true function ρ at time $t = \Delta t$?' This becomes a sensible question as soon as we decide what we mean by 'best'. Since the purpose of statistical mechanics is to calculate expectation values of physical quantities Q over ensembles, we shall phrase our criterion of 'best' in terms of such expectation values:

$$\langle Q \rangle = \frac{\int Q\rho \, d\tau_1 \, d\tau_2 \ldots d\tau_N}{\int \rho \, d\tau_1 \, d\tau_2 \ldots d\tau_N}. \tag{2.7}$$

Here Q is any desired function of $\boldsymbol{r}_1, \boldsymbol{p}_1, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_N$.

We would like to demand that *all* expectation values come out right; but this is clearly too much, since it leads to the exact N-particle distribution function ρ, and no other. Hence, if we want an approximation of form (2.2) for ρ, we must be less ambitious in what we demand by way of a fit.

Physical quantities Q can be classified as one-particle, two-particle, three-particle, etc, quantities, in the usual way. For example, the kinetic energy T_N, equation (2.4), is classified as a one-particle quantity, since it is a sum of N separate terms, each term involving the position and momentum of no more than one particle. The potential energy V_N, equation (2.5), is classified as a two-particle quantity, since it is a sum of $N(N-1)/2$ terms, each term involving the coordinates of two particles (particles i and j).

We can now state our criterion for a 'best approximation'. In this hierarchy of one-particle, two-particle, ..., k-particle quantities, we want to get *agreement between the exact and the approximate expectation values for all one-particle quantities.* With the approximate form (2.2) for ρ, we can achieve no more, and we shall see that this condition leads directly to the Boltzmann equation. If, on the other hand, we are willing to go to approximate N-particle distribution functions of forms more complicated than (2.2), we can sharpen up our condition for a 'best approximation'—for instance, we may be able to demand agreement between the exact and the approximate expectation values for all one-particle *and* for all two-particle quantities (but perhaps not for three-particle quantities). This is the subject of later papers in this series.

The general one-particle quantity has the form

$$Q = \sum_{i=1}^{N} q(\boldsymbol{r}_i, \boldsymbol{p}_i) \tag{2.8}$$

and a simple calculation shows that its expectation value (2.7) can be expressed in terms of the one-particle projection of ρ, ie, of f defined in equation (1.5):

$$\langle Q \rangle = \int q(\boldsymbol{r}_1, \boldsymbol{p}_1) f(\boldsymbol{r}_1, \boldsymbol{p}_1, t)\, \mathrm{d}^3\boldsymbol{r}_1\, \mathrm{d}^3\boldsymbol{p}_1 . \tag{2.9}$$

Thus, our criterion of 'best' approximation means that we must choose the function g in (2.2) in such a way that the one-particle projection of the approximate ρ, (2.2), is equal to the one-particle projection f of the exact ρ at time $t = \Delta t$. A simple calculation from (1.5) and (2.2) shows that the one-particle projection of (2.2) equals $(N/V)g(\boldsymbol{r}, \boldsymbol{p}, t)$, and thus our condition reads:

$$\frac{N}{V} g(\boldsymbol{r}, \boldsymbol{p}, \Delta t) = f(\boldsymbol{r}, \boldsymbol{p}, \Delta t) \tag{2.10}$$

where the right-hand side is to be computed from the exact distribution function at time Δt, obtained by solving the Liouville equation (1.4) with initial condition (2.6), and then doing the projection (1.5).

Let us now carry out this programme. We shall be interested, not in $g(\boldsymbol{r}, \boldsymbol{p}, \Delta t)$ but rather in the difference:

$$\Delta g \equiv g(\boldsymbol{r}, \boldsymbol{p}, \Delta t) - g_0(\boldsymbol{r}, \boldsymbol{p}). \tag{2.11}$$

Straightforward combinations of (1.2), (1.5) and (2.10) with (2.11) gives:

$$\Delta g = \frac{V}{N!} \int (\rho(\boldsymbol{r}_1, \boldsymbol{p}_1, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_N, \Delta t) - \rho(\boldsymbol{r}_1, \boldsymbol{p}_1, \ldots, \boldsymbol{r}_N, \boldsymbol{p}_N, 0))\, \mathrm{d}\tau_2\, \mathrm{d}\tau_3 \ldots \mathrm{d}\tau_N . \tag{2.12}$$

The solutions of the Liouville equation can be written in terms of dynamical configurations. Let $\{r'_1, p'_1, r'_2, p'_2, \ldots, r'_N, p'_N\}$ be that initial configuration at time $t = 0$ which makes the system reach the desired final configuration $\{r_1, p_1, \ldots, r_N, p_N\}$ at time $t = \Delta t$, under the action of the N-particle hamiltonian H_N. Then (1.4) is solved by:

$$\rho(r_1, p_1, r_2, p_2, \ldots, r_N, p_N, \Delta t) = \rho(r'_1, p'_1, r'_2, p'_2, \ldots, r'_N, p'_N, 0). \tag{2.13}$$

In this way, both integrands in (2.12) are reduced to the known (by assumption) N-particle distribution function at time $t = 0$, given by (2.6). Substitution of (2.13) and (2.6) into (2.12) gives:

$$\Delta g = V^{1-N} \int (g_0(r'_1, p'_1) g_0(r'_2, p'_2) \ldots g_0(r'_N, p'_N) - g_0(r_1, p_1) g_0(r_2, p_2) \ldots g_0(r_N, p_N))\, \mathrm{d}\tau_2\, \mathrm{d}\tau_3 \ldots \mathrm{d}\tau_N. \tag{2.14}$$

This expression is exact, and its evaluation yields the best possible Δg, and hence the best possible $g(r, p, \Delta t)$, to represent the true N-particle distribution function by the approximation (2.2) at time $t = \Delta t$, in our sense of 'best possible'.

We now proceed to an approximate evaluation of (2.14) for dilute gases. For given momenta $p_1, p_2, \ldots, p_N$, and a given position r_1 of the first particle, the domain of integration in the multiple integral over $r_2, r_3, \ldots, r_N$ can be broken up into subdomains, according to the number of 'other' particles which have interacted with particle 1 during the time interval Δt. Let $\Delta V_i, i = 2, 3, \ldots, N$, be the 'excluded volume' for particle number i, ie, that region of r_i such that particle i, with given momentum p_i, must have interacted with particle 1, momentum p_1, during the time interval Δt. The value of ΔV_i will be deduced later; in general, ΔV_i is a function of p_1 and p_i.

We now break up the multiple integration over the r coordinates as follows:

$$\begin{aligned}
\int \mathrm{d}^3 r_2\, \mathrm{d}^3 r_3 \ldots \mathrm{d}^3 r_N
&= \int_{V-\Delta V_2} \mathrm{d}^3 r_2 \int_{V-\Delta V_3} \mathrm{d}^3 r_3 \ldots \int_{V-\Delta V_N} \mathrm{d}^3 r_N \\
&+ \int_{\Delta V_2} \mathrm{d}^3 r_2 \int_{V-\Delta V_3} \mathrm{d}^3 r_3 \ldots \int_{V-\Delta V_N} \mathrm{d}^3 r_N + \text{permutations} \\
&+ \int_{\Delta V_2} \mathrm{d}^3 r_2 \int_{\Delta V_3} \mathrm{d}^3 r_3 \int_{V-\Delta V_4} \mathrm{d}^3 r_4 \ldots \int_{V-\Delta V_N} \mathrm{d}^3 r_N + \text{permutations} \\
&+ \ldots .
\end{aligned} \tag{2.15}$$

The first line on the right-hand side of (2.15), a single term, gives the contribution of configurations in which none of particles $2, 3, \ldots, N$ collide with particle 1 during the time interval Δt. The second line of (2.15) contains $N-1$ terms altogether, each of which represents exactly one other particle colliding with particle 1 during time Δt; the term written out explicitly is for a (1, 2) collision, and the permutations represent (1, 3), (1, 4), …, (1, N) collisions. The third line of (2.15) contains $(N-1)(N-2)/2$ terms, each representing a ternary collision.

When the integral in (2.14) is separated according to the scheme (2.15), we obtain the series

$$\Delta g = \Delta g^{(1)} + \Delta g^{(2)} + \Delta g^{(3)} + \ldots \tag{2.16}$$

where the superscript of each term represents the order of the collisions involved, ie, $\Delta g^{(2)}$ is the contribution from binary collisions.

We now evaluate $\Delta g^{(1)}$. By assumption, particle 1 does not collide during time t, hence we have

$$\boldsymbol{r}'_1 = \boldsymbol{r}_1 - \frac{\boldsymbol{p}_1}{m}\Delta t \qquad \boldsymbol{p}'_1 = \boldsymbol{p}_1. \tag{2.17}$$

The relationship between $\boldsymbol{r}'_i$ and $\boldsymbol{r}_i$ for $2 \leqslant i \leqslant N$ is much more complicated, since all these other particles may collide with each other. Fortunately, we do not need these relations, because we can use the Liouville theorem:

$$\mathrm{d}\tau_2\,\mathrm{d}\tau_3\ldots\mathrm{d}\tau_N = \mathrm{d}\tau'_2\,\mathrm{d}\tau'_3\ldots\mathrm{d}\tau'_N. \tag{2.18}$$

This relation between the phase-space volume elements holds for an isolated system, and by assumption particles $2, 3, \ldots, N$ form an isolated system (isolated from particle 1) here. When we carry out the integrations, we encounter the integral:

$$\int \mathrm{d}^3\boldsymbol{p}_i \int_{V-\Delta V_i} \mathrm{d}^3\boldsymbol{r}_i\, g_0(\boldsymbol{r}_i, \boldsymbol{p}_i) \simeq V - \frac{\Delta V}{N} n_0(\boldsymbol{r}_1) \tag{2.19}$$

where ΔV is a suitable average of the excluded volume $\Delta V_i(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{p}_i)$ over the momenta $\boldsymbol{p}_i$ (see equation (2.33) later on), and $n_0(\boldsymbol{r}_1)$ is the number density irrespective of momentum:

$$n_0(\boldsymbol{r}_1) = \frac{N}{V}\int \mathrm{d}^3\boldsymbol{p}_1 g_0(\boldsymbol{r}_1, \boldsymbol{p}_1). \tag{2.20}$$

Combination of (2.19), (2.16), (2.15) and (2.14) gives the result:

$$\Delta g^{(1)} \simeq (g_0(\boldsymbol{r}'_1, \boldsymbol{p}'_1) - g_0(\boldsymbol{r}_1, \boldsymbol{p}_1))\left(1 - \frac{\Delta V}{N} n_0(\boldsymbol{r}_1)\right)^{N-1}. \tag{2.21}$$

Let us discuss the second factor first. Using the identity

$$\lim_{N\to\infty}\left(1 - \frac{x}{N}\right)^N = \exp(-x) \tag{2.22}$$

the second factor is essentially equal to $\exp(-\Delta V n_0(r_1))$. Later on, in the discussion at the end of this section, we shall show that this is equal to $\exp(-\Delta t/t_{\mathrm{f}})$ where t_{f} is the mean free time of particle 1 (position $\boldsymbol{r}_1$, momentum $\boldsymbol{p}_1$) between consecutive collisions with other particles. By our basic assumption of a dilute gas and our choice of Δt, this exponential can be replaced by unity.

This leaves us with the first factor in (2.21). Substitution of (2.17) then gives the result:

$$\frac{\Delta g^{(1)}}{\Delta t} = -\frac{\boldsymbol{p}_1}{m}.\operatorname{grad} g_0. \tag{2.23}$$

We have therefore recovered the 'drift term' of the Boltzmann equation, in essence, and we have done so in an intuitively plausible way, by considering the contribution of those configurations of the system in which particle 1 just drifts along during the time interval Δt, without suffering any collisions.

Next, we turn to the evaluation of $\Delta g^{(2)}$, the contribution from binary collisions of particle 1 with one other particle. The $N-1$ terms in the second line of (2.15) all give the same result, so we take the term written explicitly (a (1, 2) collision in time Δt) and multiply the result by $N-1$. Particles $3, 4, \ldots, N$ can be eliminated as before; those integrations give the same exponential factor, which we again ignore for a dilute gas. We are therefore left with the expression:

$$\Delta g^{(2)} \simeq \frac{N-1}{V} \int_{\Delta V_2} d\tau_2 (g_0(\boldsymbol{r}_1', \boldsymbol{p}_1') g_0(\boldsymbol{r}_2', \boldsymbol{p}_2') - g_0(\boldsymbol{r}_1, \boldsymbol{p}_1) g_0(\boldsymbol{r}_2, \boldsymbol{p}_2)). \tag{2.24}$$

The integration is to extend over all those configurations $(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{r}_2, \boldsymbol{p}_2)$ which arise from the binary collision at some time t_c in the interval $0 \leqslant t_c \leqslant \Delta t$. A schematic picture is shown in figure 1.

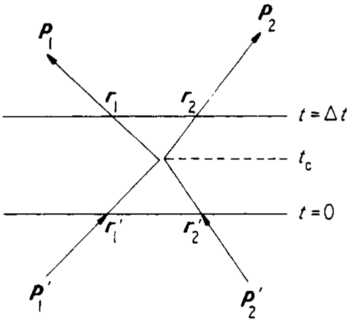

Figure 1. The binary collision at time t_c transforms the configuration $(\boldsymbol{r}_1', \boldsymbol{p}_1', \boldsymbol{r}_2', \boldsymbol{p}_2')$ at time $t = 0$ into the configuration $(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{r}_2, \boldsymbol{p}_2)$ at time $t = \Delta t$.

To define the 'collision instant' t_c more precisely, we shall extrapolate backwards from time $t = \Delta t$ on a straight-line path. We define:

$$\boldsymbol{r} = \boldsymbol{r}_2 - \boldsymbol{r}_1 \qquad \boldsymbol{v}_{12} = \boldsymbol{v}_2 - \boldsymbol{v}_1 = \frac{\boldsymbol{p}_2 - \boldsymbol{p}_1}{m} \tag{2.25}$$

and

$$\boldsymbol{s}(t) = \boldsymbol{r} - (\Delta t - t)\boldsymbol{v}_{12} \tag{2.26}$$

$\boldsymbol{s}(t)$ is the displacement vector from particle 1 to particle 2, obtained by straight-line extrapolation, ie, ignoring the actual collision. We now define the collision instant t_c as that value of the time t for which $\boldsymbol{s}(t)$ has minimum absolute value. A simple calculation yields:

$$t_c = \Delta t - \frac{\boldsymbol{r} \cdot \boldsymbol{v}_{12}}{(\boldsymbol{v}_{12})^2}. \tag{2.27}$$

Furthermore, the extrapolated displacement $\boldsymbol{s}(t_c)$ at this moment is identical with the impact parameter vector $\boldsymbol{b}$ defined by equation (1.6). Solving (2.26) for $\boldsymbol{r} = \boldsymbol{r}_2 - \boldsymbol{r}_1$ with t set equal to t_c yields the relation

$$\boldsymbol{r}_2 = \boldsymbol{r}_1 + \boldsymbol{b} + (\Delta t - t_c)\boldsymbol{v}_{12}. \tag{2.28}$$

The vector $\boldsymbol{r}_2$ has three components: x_2, y_2, z_2. The vector $\boldsymbol{b}$ has only two independent components (both perpendicular to $\boldsymbol{v}_{12}$), which we shall call b_ξ and b_η respectively. The relation (2.28) makes it clear that a specification of t_c, b_ξ and b_η suffices to deduce x_2, y_2 and z_2, for given values of $\boldsymbol{r}_1$, $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$.

The integration in (2.24) is a sixfold integral $\int d^3p_2 \int d^3r_2$. We shall carry out the integrations over x_2, y_2 and z_2 first, with p_2 fixed. r_1 and p_1 are free variables, not dummy variables of integration, and are therefore certainly fixed. We can thus replace the three dummy variables of integration x_2, y_2, z_2 by the alternative three variables: t_c, b_ξ, b_η. The jacobian of this transformation is obtained easily from (2.28). Without loss of generality, we may assume v_{12} to be in the direction of z_2, so that the vector equation (2.28) assumes the simple form

$$x_2 = x_1 + b_\xi \qquad y_2 = y_1 + b_\eta \qquad z_2 = z_1 + (\Delta t - t_c)v_{12}. \tag{2.28a}$$

The jacobian determinant is now trivial and is equal to $-v_{12}$. Thus we have

$$\int d^3r_2 = \int dx_2\, dy_2\, dz_2 = \int dt_c\, db_\xi\, db_\eta\, v_{12}. \tag{2.29}$$

Since the collision instant t_c is now one of the dummy variables of integration (this is the essential point!), we get the desired contribution, ie, the contribution of binary collisions during the time interval Δt, precisely by imposing the limits of integration $0 \leqslant t_c \leqslant \Delta t$ on this integral. Thus (2.24) is replaced by

$$\Delta g^{(2)} \simeq \frac{N-1}{V} \int d^3p_2 \int_0^{\Delta t} dt_c \int d^2b v_{12}(g_0(r'_1, p'_1)g_0(r'_2, p'_2) - g_0(r_1, p_1)g_0(r_2, p_2)). \tag{2.30}$$

We now make the following further approximations: (*a*) $N-1$ is replaced by N; (*b*) the integration over t_c is done by the mean-value theorem, to give just a factor Δt; (*c*) the small differences between the positions r'_1, r'_2, r_2 and r_1 are ignored†.

To get the Boltzmann equation, we now need merely to write

$$\frac{\partial g}{\partial t} \simeq \frac{\Delta g^{(1)} + \Delta g^{(2)}}{\Delta t} \tag{2.31}$$

and to multiply both sides of this by the factor (N/V). By equation (2.10), this gives $\partial f/\partial t$ on the left-hand side, and by (2.23) and (2.30) we get exactly the right-hand side of equation (1.9), the Boltzmann equation.

For completeness, we provide the estimate of the average excluded volume ΔV in equation (2.19). For given momenta p_1 and p_i, the excluded volume ΔV_i can be obtained by integration from (2.29). Let us assume that the interatomic force law has a well defined range of action r_0, beyond which the force vanishes. Then

$$\Delta V_i(p_1, p_i) = \int_0^{\Delta t} dt_c \int_0^{r_0} 2\pi b\, db\, v_{1i} = (\pi r_0^2)v_{1i}\,\Delta t. \tag{2.32}$$

Actual interatomic forces do not have a sharply defined range of action r_0. However, the factor πr_0^2 in (2.32) is simply the total collision cross section $\sigma_{\mathrm{tot}}(p_1, p_i)$. When calculated quantum mechanically rather than from classical mechanics, this total cross section is a well defined, finite quantity even for a force law which decreases for large r like $1/r^6$, for example.

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† A more careful discussion shows that what we are ignoring here is not nearly as big as all that: most of this displacement is taken care of by the drift term in the Boltzmann equation; what we are really ignoring is similar to the 'collisional transfer' term of Enskog's theory of transport in dense gases, and to the 'duration of the collision' or 'collisional delay time' of Felix Smith (Enskog 1921, Smith 1972). Both are effects which vanish in the dilute gas limit.

The 'suitable average' ΔV to be inserted in (2.19) is then

$$\Delta V(\boldsymbol{r}_1,\boldsymbol{p}_1)=\frac{\int \mathrm{d}^3\boldsymbol{p}_i\,\sigma_{\mathrm{tot}}(\boldsymbol{p}_1,\boldsymbol{p}_i)v_{1i}g_0(\boldsymbol{r}_1,\boldsymbol{p}_i)}{\int \mathrm{d}^3\boldsymbol{p}_i\,g_0(\boldsymbol{r}_1,\boldsymbol{p}_i)}\Delta t. \tag{2.33}$$

The exponent $x = \Delta V n_0(\boldsymbol{r}_1)$ in (2.22) is then equal to $\Delta t/t_{\mathrm{f}}$ where t_{f} is the mean free time of particle 1 between consecutive collisions, defined by

$$\frac{1}{t_{\mathrm{f}}}=\frac{N}{V}\int \mathrm{d}^3\boldsymbol{p}_i\,\sigma_{\mathrm{tot}}(\boldsymbol{p}_1,\boldsymbol{p}_i)v_{1i}g_0(\boldsymbol{r}_1,\boldsymbol{p}_i). \tag{2.34}$$

By construction Δt is much less than this mean free time, so the ratio $x = \Delta t/t_{\mathrm{f}}$ is small compared to unity, and $\exp(-x)$ can be replaced by unity.

3. Discussion

3.1. *Irreversibility*

Our new derivation of the Boltzmann equation exhibits the origin of the time irreversibility immediately and directly. The replacement of the exact N-particle distribution function $\rho(\boldsymbol{r}_1,\boldsymbol{p}_1,\ldots,\boldsymbol{r}_N,\boldsymbol{p}_N,\Delta t)$ by the approximate form (2.2) clearly throws away information about the state of the ensemble at time $t = \Delta t$, information which is essential to recover the initial state precisely. As we go forward in time by successive time intervals Δt, the loss of information builds up, until no memory of the initial state remains apart from absolute constants of motion.

While there are considerable doubts whether the Liouville equation represents any real thermal system adequately (Blatt 1959), it should be noted that the fundamental loss of information about the initial state, occasioned by thermal motion of the walls of the system, is *not* represented correctly by the drastic approximation (2.2) which is to hold everywhere in the interior of the gas. Thus, it is not unreasonable to expect real physical correlation effects, *not* included in the Boltzmann equation, even in very dilute gases. Such effects do exist, and will be derived in later papers in this series.

3.2. *Minor extensions and corrections*

Throughout the derivation in § 2, we have made minor approximations appropriate to a very dilute gas. For example, equation (2.31) ignores the effects of ternary and higher-order collisions (the terms $\Delta g^{(3)}$, $\Delta g^{(4)}$, etc). These approximations are not inherent in the basic assumption (2.2), and could be improved. For example, ternary collisions could be included if desired.

However, there is considerable doubt whether such effects should be included, or at least are worth including, without a more fundamental improvement in the basic assumption (2.2). The assumption of no correlated behaviour at all is extremely restrictive and doubtful. Rather than working out the consequences of that assumption to the finest deail, it is probably preferable to investigate the consequences of somewhat less restrictive assumptions.

3.3. Major extensions

The most obvious and immediate extension of this theory is to include some (but of course not all) correlations, so as to generalize the ansatz (2.2). In equilibrium statistical mechanics, the Ursell expansion is well known in the derivation of the virial series (Ursell 1927). It is true, though less generally known, that the Ursell expansion also leads to a treatment of equilibrium in chemical reactions (Schafroth *et al* 1957, Blatt 1964), and to a theory of the superconducting state of metals (Schafroth 1954, Schafroth *et al* 1957, Blatt 1964).

The first extension along these lines is to include pair correlations, described by a function $h(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{r}_2, \boldsymbol{p}_2, t)$ with the property

$$\int h(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{r}_2, \boldsymbol{p}_2)\, \mathrm{d}\tau_1\, \mathrm{d}\tau_2 = \text{Order } V \qquad \text{(rather than of order } V^2\text{)}. \tag{3.1}$$

The property (3.1) ensures that the pair correlations included in h are of 'finite range', ie particles at opposite ends of the volume V are not correlated statistically. The ansatz (2.2) is then augmented to the form:

$$\begin{aligned}\rho(1, 2, 3, \ldots, N) = C\{&g(1)g(2)g(3)\ldots g(N) + h(1,2)g(3)g(4)\ldots g(N) + \text{permutations} \\ &+ h(1,2)h(3,4)g(5)g(6)\ldots g(N) + \text{permutations} + \ldots \\ &+ h(1,2)h(3,4)h(5,6)\ldots h(N-1,N) + \text{permutations}\}.\end{aligned} \tag{3.2}$$

Following our basic programme, we assume that ρ is of this form, precisely, at time $t = 0$; we follow the time development of ρ by means of the Liouville equation, for a short time Δt; and we ask for the 'best' approximation of the form (3.2) to the exact N-particle distribution function ρ at time Δt. Since the ansatz (3.2) is more flexible than (2.2), we can demand correspondingly more from a 'best' approximation. It turns out that it is possible to demand that the *expectation values of all one-particle quantities and of all two-particle quantities* can be fitted by the 'best' approximation of form (3.2); and conversely, this requirement determines the time development of the functions g and h uniquely. The detailed calculation is by no means simple, and the results are not such as one would be likely to obtain by purely intuitive arguments similar to those of Boltzmann.

The development of equations based upon (3.2), and their discussion, forms the subject matter of future papers in this series.

Other major extensions are possible. There is no reason to restrict ourselves to transport phenomena in gases. In any thermodynamic system, the true density matrix (or classically, the true distribution function) can be replaced by some approximation containing one or more arbitrary functions (such as the functions $g(\boldsymbol{r}, \boldsymbol{p}, t)$ and $h(\boldsymbol{r}_1, \boldsymbol{p}_1, \boldsymbol{r}_2, \boldsymbol{p}_2, t)$ in (3.2)). We can then again employ the basic idea of deriving a 'best' approximation of specified functional form by demanding exact agreement for the expectation values of some, but not all, physical quantities. For instance, transport properties of spin systems can be approached in this fashion.

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