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On the Extension of the Boltzmann Equation to Include Pair Correlations

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The derivation of kinetic equations, including the effects of pair correlations, for a gas of particles interacting via purely repulsive forces is reported. An additional assumption on the form of the two-particle distribution function yields the Enskog equation for a dense hard-sphere gas. However, the true two-particle distribution function is not of this form.

KEY WORDS: Boltzmann equation; pair correlations; kinetic equations.

Recently a new derivation of the Boltzmann transport equation has been presented[1,2] which has several advantages over existing ones. In particular, the method can be extended to yield equations of more generality than the standard Boltzmann equation. In this note we report one such generalization, namely the inclusion of pair correlations for the case of purely repulsive interactions of short range.

To state these new equations we denote the reduced one-particle distribution function for a gas of N particles by $f_1(1) = f_1(\mathbf{r}_1, \mathbf{p}_1, t)$ and write the two-particle distribution function as

$$f_2(1, 2) = f_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t) = f_1(1)f_1(2) + \sigma(1, 2) \tag{1}$$

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where $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ and $\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N$ are the positions and momenta of the N particles of time t. In addition let

$$H^{(1)}(1) = p_1^2/2m, \qquad H^{(2)}(1, 2) = p_1^2/2m + p_2^2/2m + V_{12} \tag{2}$$

be the one- and two-body Hamiltonians, respectively, where the interparticle potential $V_{12} = V(\mathbf{r}_1 - \mathbf{r}_2)$ is assumed to be purely repulsive and of short range, and let $[X, Y]$ denote the Poisson bracket defined by

$$[X(1, 2, \ldots, N),\ Y(1, 2, \ldots, N)] = \sum_{l=1}^{N} \left(\frac{\partial X}{\partial \mathbf{r}_l} \cdot \frac{\partial Y}{\partial \mathbf{p}_l} - \frac{\partial Y}{\partial \mathbf{r}_l} \cdot \frac{\partial X}{\partial \mathbf{p}_l} \right) \tag{3}$$

Let $\mathbf{b}_{ij}$ be the impact-parameter vector of a binary collision between particles i and j with relative speed v_{ij}. The post-collision configuration $(\mathbf{r}_i, \mathbf{p}_i, \mathbf{r}_j, \mathbf{p}_j)$ is assumed to be given; it is such that $|\mathbf{r}_i - \mathbf{r}_j| = r_0$ (the range of the interaction) and $(\mathbf{r}_i - \mathbf{r}_j)\cdot(\mathbf{p}_i - \mathbf{p}_j) > 0$. The pre-collision configuration $(\mathbf{r}_i', \mathbf{p}_i', \mathbf{r}_j', \mathbf{p}_j')$ is obtained by tracing backward in time across the collision sphere, all other particles being assumed to be outside range of particles i and j, until we reach the entrance to the collision sphere. The "free-drift pre-collision configuration" $(\mathbf{r}_i'', \mathbf{p}_i'', \mathbf{r}_j'', \mathbf{p}_j'')$ is obtained similarly, but in the tracing back process the interaction potential V_{ij} is also set to zero, i.e., the paths are straight lines. We shall denote the two pre-collision configurations by i', j' and i'', j'', respectively, for short. Then the functions $f_1(1)$ and $\sigma(1, 2)$ satisfy the pair of integrodifferential equations

$$\begin{aligned} \partial f_1(1)/\partial t &= -[u(1), H^{(1)}] + \int d^3p_3 \int d^2b_{13} \\ &\quad \times v_{13}\{u(1')u(3') - u(1'')u(3'') + \sigma(1', 3') - \sigma(1'', 3'')\} \end{aligned} \tag{4}$$

$$\begin{aligned} \partial \sigma(1, 2)/\partial t &= -[\sigma(1, 2), H^{(2)}] - [u(1)u(2), V_{12}] \\ &\quad + \int d^3p_3 \int d^2b_{23} v_{23}\{\sigma(1, 2')u(3') \\ &\quad - \sigma(1, 2'')u(3'') + \sigma(1, 3')u(2') - \sigma(1, 3'')u(2'')\} \\ &\quad + (1 \rightleftarrows 2) \end{aligned} \tag{5}$$

where $(1 \rightleftarrows 2)$ indicates the double integral of the same form with the roles of particles 1 and 2 interchanged, and where the function u is related to f_1 and σ by

$$u(1) = f_1(1) - \int_{r<r_0} \sigma(1, 2)\, d\tau_2 \tag{5a}$$

The distance r_0 is the range of the interaction. u differs from f_1 by omission of that contribution from $\int \sigma(1, 2)\, d\tau_2$ in which particles 1 and 2 are within range of one another.

A full derivation of these equations will be given elsewhere and we only give a brief outline here. The basic assumption is a generalization of the ansatz of Blatt and Opie[1,2] for the N-particle distribution function at time t to the form (assuming N even)

$$\begin{aligned} F_N(1, 2, \ldots, N; t) = C_N\{ & g(1)g(2) \cdots g(N) \\ & + h(1, 2)g(3) \cdots g(N) + \text{permutations} \\ & + h(1, 2)h(3, 4)g(5) \cdots g(N) + \text{permutations} \\ & + \cdots \\ & + h(1, 2)h(3, 4) \cdots h(N-1, N) + \text{permutations}\} \end{aligned} \tag{6}$$

where C_N is a normalization constant and the functions $g(1)$ and $h(1, 2)$ can be related to $f_1(1)$ and $f_2(1, 2)$ by the standard definitions of the reduced distribution functions. As in the earlier work, one now allows F_N to evolve following the N-particle Liouville equation for a time interval Δt, which is (a) appreciably longer than the duration of a collision, but (b) much shorter than the mean free time between collisions. After this time interval, F_N will no longer be of the form (6). However, it is possible to find functions $g(1)$ and $h(1, 2)$ such that F_N can be approximated by the form (5) at time $t + \Delta t$ and still yield the correct one- and two-particle distribution functions. This procedure yields equations for

$$\Delta g = g(\mathbf{r}_1, \mathbf{p}_1, t + \Delta t) - g(\mathbf{r}_1, \mathbf{p}_1, t) \tag{7a}$$

and

$$\Delta h = h(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t + \Delta t) - h(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, t) \tag{7b}$$

Equations (4) and (5) then follow by a series of further approximations, which amount to neglecting all ternary and higher-order collisions (i.e., three or more particles interacting at the same time) and approximating time derivatives by differences over Δt.

In conclusion we make several comments on Eqs. (4) and (5) and their immediate consequences.

(i) Since in the absence of external forces

$$[f_1(1), H^{(1)}] = (\mathbf{p}_1/m) \cdot \nabla_{\mathbf{r}_1} f_1(\mathbf{r}_1, \mathbf{p}_1, t) \tag{8}$$

we recover the standard Boltzmann equation if $\sigma \equiv 0$, which is seen, via (1), to be equivalent to the molecular chaos assumption on $f_2(1, 2)$. We note that the integral $\iint \sigma(1, 2)\, d\tau_1\, d\tau_2$ is of order N, not of order N^2. Thus this integral, and all effects involving $\sigma(1, 2)$, becomes zero in the so-called Boltzmann–Grad limit.[3,4]

(ii) On the other hand, if we *assume* that $\sigma(1, 2)$ is of the form

$$\sigma(1, 2) = f_1(1)f_1(2)[Y(\mathbf{R}_{12}) - 1] \tag{9}$$

where $\mathbf{R}_{12} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ is the center-of-mass position vector of particles one and two and the function Y is independent of momenta, (4) becomes

$$\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}_1}{m}\cdot\nabla_{\mathbf{r}_1} f_1 = \int d^3\mathbf{p}_3 \int d^3\mathbf{b}_{13} v_{13}[Y(R'_{13})f_1(1')f_1(3') - Y(R_{13})f_1(1)f_1(3)] \tag{10}$$

If we now specialize to a hard-sphere interaction, this result reduces to Enskog's equation for a dense hard-sphere gas.[5,6]

(iii) However, as several authors have noted (see, e.g., Chapman and Cowling[6]), the Enskog theory is insufficient to describe the effect of pair correlations on transport properties. This failure can be traced back to the inadequacy of assumption (9). Indeed, one can use (5) to show that $\sigma(1, 2)$ contains extremely strong correlations between the vectors $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ and $\mathbf{p}_{12} = \mathbf{p}_2 - \mathbf{p}_1$. Hence $\sigma(1, 2)$ cannot be approximated by (9) with Y independent of momenta. Some of the consequences of this observation are elaborated in the next paper in this issue.

(iv) The restriction to binary collisions can be relaxed and the effects of ternary and even higher order events included. However the analysis, already of some complexity, becomes considerably more difficult.

(v) Finally, it is informative to note that (4) and (5) can be deduced from the BBGKY hierarchy (see, e.g., Liboff,[7] Ch. 2.5). To do so we assume F_N has the form (6) at all times, calculate $f_3(1, 2, 3)$ in terms of $g(i)$ and $h(i, j)$, and thereby truncate the hierarchy. If again only binary collisions are considered and the collision terms reduced in the standard way (see, e.g., Liboff,[7] Ch. 4.3) to Boltzmann-like collision integrals, (4) and (5) result with f_2 related to σ by (1). This truncation procedure is different from other schemes, for example, the Rice–Allnatt theory (see, e.g., Rice and Gray,[8] Ch. 5), where the hierarchy is truncated by a "molecular chaos" assumption of $f_3(1, 2, 3)$ directly. The resulting equations (4) and (5) are consequently significantly different from the Rice–Allnatt equations (ignoring their soft-attractive potential contributions). The application of the former equations to the transport properties of moderately dense gases and fluids will be reported in subsequent publications.

However, it should be stressed that the original method of derivation outlined above possesses important advantages over the alternative derivation from the BBGKY hierarchy. These include the possibility of extension to systems containing attractive forces capable of forming bound states, as well as allowing for ternary and higher order collisions.

(vi) The referee has called our attention to related work by Kritz *et al.*[9] and Pomeau.[10] Their method of approach differs from ours, and so does their result. To obtain their theory from ours, it is necessary to omit the collision integrals in our Eq. (5). These collision terms allow for modification of a scattering correlation by subsequent collisions of particle 1 or 2 with other particles in the gas. It is the absence of these terms which causes the correlation peak in Ref. 9 to remain at constant height as time goes on (see Fig. 2, p. 320, of Ref. 9). In our theory, this peak height decays exponentially, following the law: $\exp[-(g_1 + g_2)(r_{12}/v_{12})]$, where g_1 is the inverse mean free time of particle 1, momentum p_1, against collision with other particles, and similarly for g_2.

The paper by Pomeau is written very lucidly, and it is therefore possible to locate the source of the difference precisely. In his Appendix A he uses an approximation for the three-particle reduced distribution function f_3. As he says: "The condition (A1) expresses that, in the low density limit, the binary correlations arise from the *direct* interaction between particles only, and that any effect of the surrounding particles on this correlation is of a lowest order in n." Because of the omission of the effect of surrounding particles, Eq. (2.14) in Ref. 10 needs to be corrected by a multiplicative factor, equal to the probability that the point $\mathbf{r}$ in his region Δ_1 can be reached without intercepting some other scattering center on the way. This is the origin of our exponentially decaying factor.

Pomeau's main conclusion, that the hydrodynamic modes lead to infinite-range correlations, can be traced to this omission; in our theory $\sigma(1, 2)$ has a finite range under all conditions.

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