Journal of Statistical Physics, Vol. 13, No. 1, 1975

Long-Range Correlations in Kinetic Theory[1]

Chelluri C. A. Sastri[2]

Received February 3, 1975

It is shown that macroscopic correlations in a fluid are conserved for macroscopically long times. The equations of conservation can be written in a form independent of the density of the fluid and are therefore valid for a liquid as well as for a gas. The possibility of developing a kinetic theory of turbulence on the basis of these equations (along the lines of V. N. Zhigulev and of S. Tsugé) is indicated.

KEY WORDS: Kinetic theory; macroscopic correlations; conservation; turbulence.

1. INTRODUCTION

The purpose of this paper is to study the propagation of two-point, long-range (macroscopic) correlations in a fluid. We consider a fluid whose intermolecular potential has a finite range and distinguish between long-range and short-range correlations as follows: When the distance of separation between any two molecules is of the order of the range of the intermolecular force, we say the correlation between the molecules is short range; when it is considerably larger, the correlation is long range. Short-range correlations are studied in the theory of dense gases; long-range correlations usually

---

[1] The contents of this paper formed part of the Ph.D. thesis submitted by the author under the supervision of Prof. Harold Grad to the Department of Mathematics, New York University and issued as NYU—Courant Institute of Mathematical Sciences Technical Report MF-72, October 1973.

[2] Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario, Canada.

appear in a context apparently unrelated to their microscopic nature, namely, in turbulent fluid dynamics. One of our aims is to clarify this connection.

Contributions to the long-range correlation between any two molecules come from their initial correlation and their interaction with other molecules, past and present. The Boltzmann equation (see Ref. 1 for a derivation), which describes a rarefied gas, is based on the assumption that long-range correlations are negligible. (It is sometimes(2) even stated that, over macroscopic times, correlations are destroyed by collisions.) The question naturally arises whether this assumption is correct. It was conjectured by Grad(3) that it cannot be, and we verify this conjecture. More precisely, the result is that long-range correlations are conserved over macroscopic times (i.e., times much longer than the mean free time, such as are relevant on a fluid-dynamic scale) in the sense that when they are expressed as correlations between any two conserved macroscopic quantities—such as mass and mass, or mass and energy—they obey conservation equations just like the ordinary fluid dynamic quantities. Thus if the macroscopic correlations are large initially, they will continue to be large for macroscopically long times.[3]

Long-range microscopic correlations can be transformed into correlations between macroscopic quantities as follows. By introducing a probability density on the phase space of the system (i.e., the fluid, regarded as a large collection of molecules) and by localizing, with respect to the molecules, the macroscopic quantities of interest—such as mass, momentum, and energy—one can calculate their densities at a point in 3-space as well as the joint densities of any two of them at any two points. Given any two macroscopic quantities, one gets the correlation between them by subtracting the products of their densities from their joint density. Our result is that if each of the two macroscopic quantities is conserved and if the distance between the two points chosen is larger than a few times the range of the intermolecular force, then the correlation is conserved.

Some of the macroscopic correlation equations for a rarefied gas have been given by Zhigulev(6) and Tsugé.(7,8) Tsugé also raised the question of the validity of the Boltzmann equation in the presence of turbulence. It is clear that the equation is valid as long as macroscopic correlations are small, i.e., as long as the motion of the fluid is not turbulent. When there is turbulence, all the derivations of the equation break down, but it is not clear whether the equation itself remains valid. At any rate, in order to obtain the correct macroscopic correlation equations for a rarefied gas, one should replace the Boltzmann equation by a kinetic equation or sequence of equations which

[3] Correlations, which we shall study here, refer to one time and two or more positions, whereas fluctuations, which we shall not study here, refer to two or more times (and any number of positions). Fluctuations, like correlations, can be studied either from the point of view of fluid dynamics(4) or from that of kinetic theory.(5)

includes correlations. This we shall do in a subsequent paper. Our work could thus be interpreted as a further step toward a kinetic theory of turbulence along the lines of Zhigulev and Tsugé.[4]

A few remarks are now in order. Conventional thermodynamics is based on the assumption that the system has only two time-independent integrals, namely, mass and energy. If the system has other integrals, the thermodynamics that ensues differs from conventional thermodynamics and has been discussed by Grad(10,11) and Lewis.(12) Fluid dynamics, however, is based on the existence of another integral, namely, momentum. Systems whose angular momentum is conserved are also sometimes considered.(10,11,13,14) For the sake of generality, we consider a system whose molecules have internal degrees of freedom and which has any or all of the above types of integrals. Also, our derivation is valid even when the intermolecular forces are velocity dependent, though we require that the divergence of the force with respect to velocity vanish.

The method we use is essentially the same as that developed by Grad(11) in his generalization of Irving and Kirkwood's(15) derivation of the conservation equations of fluid dynamics. Grad's method is more general than that of Irving and Kirkwood in two ways: (1) Instead of considering only mass, momentum, and energy as Irving and Kirkwood did, he considered general integrals which are purely additive—as mass and momentum are—or which have a purely additive part and a part that consists of two-body interactions, as energy does. (2) He considered systems which have internal degrees of freedom.

Because of the generality, Grad's method is readily applicable to our problem. It consists in computing the density in 3-space of an arbitrary integral and, by using the Liouville equation, its rate of change. In order to show that the equation for the rate of change is a conservation equation, one has to just show that the terms other than the convective derivative of the density are divergences of appropriate[5] vector functions. To derive the conservation equations for macroscopic correlations, we proceed in a similar manner. We first compute the joint density of a pair of integrals and then, by multiplying the Liouville equation by the appropriate quantity and integrating with respect to everything except the two space coordinates involved, obtain an equation for the rate of change of the density. Using this and the equations for the conservation of the density of each of these integrals, we get the conservation equation for the correlation between them.

We assume that the molecules of the fluid obey the laws of classical mechanics. Our notation is essentially the same as in Ref. 11. Moreover, for

---

[4] The idea that microscopic correlation functions can be used to describe turbulence occurs in Ref. 9, but no equations for macroscopic correlations are derived.

[5] See Section 4.

the sake of completeness of presentation, Section 4 is reproduced from this reference.

2. NOTATION AND CONVENTIONS

We consider a system consisting of N particles, each of which has s degrees of freedom, three external and $s - 3$ internal. We denote the coordinates of the ith molecule by

$$P_i = (x_i, \xi_i, q_i, p_i)$$

where x_i is the position vector of the center of mass of the molecule and $\xi_i = dx_i/dt$ is the velocity vector of the center of mass. The q_i denote internal coordinates and the $p_i = dq_i/dt$ denote internal velocities.

Let

$$P = (P_1, P_2, P_3, \ldots, P_N)$$

denote a point in the $2Ns$-dimensional phase space of the system. We introduce a probability density $f(P, t)$ on this space and normalize it:

$$\int f(P, t)\, dP = 1$$

where the integration extends over the entire phase space. Whenever we suppress the time coordinate—as we did above—we mean that all the quantities appearing are considered at one instant of time, namely t. Now, we consider a one-phase, one-component system, so that all the molecules are identical. We therefore assume that f is symmetric in all the particles, and define the reduced or marginal densities—called the one-particle distribution function, the two-particle distribution function, etc.—by

$$f_1(P_1) = \int f\, dP_2\, dP_3 \cdots dP_N$$

$$f_{12}(P_1, P_2) = \int f\, dP_3\, dP_4 \cdots dP_N$$

and so on. Since we will need only the first four or five distribution functions, we adopt the convention that if r is the total number of subscripts of a distribution function, then it is the r-particle distribution function; the subscripts themselves indicate the arguments of the function. For instance, f_{245} is the three-particle distribution function of the particles labeled 2, 4, and 5. Clearly, the reduced densities are symmetric and normalized to 1.

The density f changes in time but in such a way that it satisfies the Liouville equation:

$$\frac{\partial f}{\partial t} + \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \cdot \xi_i + \frac{\partial f}{\partial \xi_i} \cdot F_i + \frac{\partial f}{\partial q_i} \cdot p_i + \frac{\partial f}{\partial p_i} \cdot G_i \right) = 0 \qquad (1)$$

where $F_i = d\xi_i/dt$ is the acceleration of the center of mass and $G_i = dp_i/dt$ is the internal acceleration of the ith molecule. Here, the refers to summation over the three external, or the $s - 3$ internal, degrees of freedom.

We write

$$F_i = \sum_{j=1}^{N} F_{ij}, \qquad G_i = \sum_{j=1}^{N} G_{ij} \tag{2}$$

where F_{ij} is the acceleration of the center of mass of the ith molecule due to the jth molecule; similarly for G_{ij}. The F_{ii} and G_{ii} are the accelerations of the ith particle due to external forces. We assume that

$$\begin{aligned} F_{ii} &= F_{11}(P_i), & G_{ii} &= G_{11}(P_i) \\ F_{ij} &= F_{12}(P_i, P_j), & G_{ij} &= G_{12}(P_i, P_j) \end{aligned} \tag{3}$$

We consider two cases; an integral ϵ can be of type (a):

$$\epsilon = \sum_{i=1}^{N} \epsilon_i, \qquad \epsilon_i = \epsilon_1(P_i)$$

or type (b):

$$\epsilon = \sum_{i=1}^{N} \epsilon_i + \sum_{\substack{i,j=1\\ i<j}}^{N} \epsilon_{ij}, \qquad \epsilon_i = \epsilon_1(p_i), \qquad \epsilon_{ij} = \epsilon_{12}(P_i, P_j)$$

We assume that $\epsilon_{ij} = \epsilon_{ji}$ and that ϵ_{ij} has a finite range. If ψ is any phase function, i.e., if $\psi = \psi(P_1, P_2, \ldots, P_N)$, we define two mean values:

$$\bar{\bar{\psi}}(x_1) = N \int \psi f \frac{dP_1\, dP_2 \cdots dP_N}{dx_1}$$

and

$$\bar{\psi}(x_1, x_2) = N(N-1) \int \psi f \frac{dP_1\, dP_2 \cdots dP_N}{dx_1\, dx_2}$$

Here the convention is that the integration is performed with respect to all the variables except those appearing in the denominator. The expected value $\langle\psi\rangle$ of ψ is defined by

$$\langle\psi\rangle = \int \psi f\, dP$$

3. DENSITIES

In order to calculate the amount of ϵ in any region D, one has to localize it. This we do as follows: ϵ_i is localized at x_i, the center of the molecule, and

ϵ_{ij} is localized half at x_i and half at x_j. Now suppose ϵ is of type (a) and let ϕ denote the characteristic function of the set D. Then the amount ϵ_D of ϵ in D is $\sum_i \phi(x_i)\epsilon_i$ and

$$\langle \epsilon_D \rangle = \int \sum_i \phi(x_i)\epsilon_i f \, dP = N \int_{x_1 \in D} f_1 \epsilon_1 \, dP_1 \tag{4}$$

Hence if D_ϵ denotes the density of ϵ, $D_\epsilon = N \int \epsilon_1 f_1 \, (dP_1/dx_1)$ in case (a). A similar calculation gives

$$D_\epsilon = N \int \epsilon_1 f_1 \frac{dP_1}{dx_1} + \frac{N(N-1)}{2} \int \epsilon_{12} f_{12} \frac{dP_1 \, dP_2}{dx_1} \tag{5}$$

in case (b).

Before we compute the joint density of a pair of integrals, we notice that there are three cases: (1) both integrals are of type (a); (2) one integral is of type (a) and the other is of type (b); (3) both integrals are of type (b). Strictly speaking, case 3 subsumes cases 1 and 2. Nevertheless, for the sake of convenience and clarity, we shall consider them separately. Now, let ϵ', ϵ'' be integrals. As in the case of the ordinary density, we calculate ϵ'_{D_1} and ϵ''_{D_2}, the amounts of ϵ' and ϵ'' in regions D_1 and D_2, respectively. If $J_{\epsilon'\epsilon''}$ denotes the joint density of ϵ' and ϵ'', calculation of $\langle \epsilon'_{D_1} \epsilon''_{D_2} \rangle$ gives

$$J_{\epsilon'\epsilon''} = N\delta(x_1 - x_2) \int \epsilon_1' \epsilon_1'' f_1 \frac{dP_1}{dx_1} + N(N-1) \int \epsilon_1' \epsilon_2'' f_{12} \frac{dP_1 \, dP_2}{dx_1 \, dx_2} \tag{6}$$

in case 1.

Similarly one obtains

$$\begin{aligned} J_{\epsilon'\epsilon''} = {} & N\delta(x_1 - x_2) \int \epsilon_1' \epsilon_1'' f_1 \frac{dP_1}{dx_1} + N(N-1) \int \epsilon_1' \epsilon_2'' f_{12} \frac{dP_1 \, dP_2}{dx_1 \, dx_2} \\ & + \frac{N(N-1)}{2} \delta(x_1 - x_2) \int \epsilon_1' \epsilon_{12}'' f_{12} \frac{dP_1 \, dP_2}{dx_1} \\ & + \frac{N(N-1)}{2} \int \epsilon_1' \epsilon_{12}'' f_{12} \frac{dP_1 \, dP_2}{dx_1 \, dx_2} \\ & + \frac{N(N-1)(N-2)}{2} \int \epsilon_1' \epsilon_{23}'' f_{123} \frac{dP_1 \, dP_2 \, dP_3}{dx_1 \, dx_2} \end{aligned} \tag{7}$$

in case 2, and

$$\begin{aligned} J_{\epsilon'\epsilon''} = {} & N\delta(x - x_2) \int \epsilon_1' \epsilon_1'' f_1 \frac{dP_1}{dx_1} + N(N-1) \int \epsilon_1' \epsilon_2'' f_{12} \frac{dP_1 \, dP_2}{dx_1 \, dx_2} \\ & + \frac{N(N-1)}{2} \delta(x_1 - x_2) \int \epsilon_1' \epsilon_{12}'' f_{12} \frac{dP_1 \, dP_2}{dx_1} \end{aligned}$$

$$
\begin{aligned}
&+ \frac{N(N-1)}{2} \int \epsilon_1{}' \epsilon''_{12} f_{12} \frac{dP_1\, dP_2}{dx_1\, dx_2} \\
&+ \frac{N(N-1)(N-2)}{2} \int \epsilon_1{}' \epsilon''_{23} f_{123} \frac{dP_1\, dP_2\, dP_3}{dx_1\, dx_2} \\
&+ \frac{N(N-1)}{2}\, \delta(x_1 - x_2) \int \epsilon'_{12} \epsilon''_1 f_{12} \frac{dP_1\, dP_2}{dx_1} \\
&+ \frac{N(N-1)}{2} \int \epsilon'_{12} \epsilon''_2 f_{12} \frac{dP_1\, dP_2}{dx_1\, dx_2} \\
&+ \frac{N(N-1)(N-2)}{2} \int \epsilon'_{13} \epsilon''_2 f_{123} \frac{dP_1\, dP_2\, dP_3}{dx_1\, dx_2} \\
&+ \frac{N(N-1)}{4}\, \delta(x_1 - x_2) \int \epsilon'_{12} \epsilon''_{12} f_{12} \frac{dP_1\, dP_2}{dx_1} \\
&+ \frac{N(N-1)(N-2)}{4}\, \delta(x_1 - x_2) \int \epsilon'_{12} \epsilon''_{13} f_{123} \frac{dP_1\, dP_2\, dP_3}{dx_1} \\
&+ \frac{N(N-1)}{4} \int \epsilon'_{12} \epsilon''_{12} f_{12} \frac{dP_1\, dP_2}{dx_1\, dx_2} \\
&+ \frac{N(N-1)(N-2)}{4} \int \epsilon'_{13} \epsilon''_{21} f_{123} \frac{dP_1\, dP_2\, dP_3}{dx_1\, dx_2} \\
&+ \frac{N(N-1)(N-2)}{4} \int \epsilon'_{12} \epsilon''_{23} f_{123} \frac{dP_1\, dP_2\, dP_3}{dx_1\, dx_2} \\
&+ \frac{N(N-1)(N-2)}{4} \int \epsilon'_{13} \epsilon''_{23} f_{123} \frac{dP_1\, dP_2\, dP_3}{dx_1\, dx_2} \\
&+ \frac{N(N-1)(N-2)(N-3)}{4} \int \epsilon'_{13} \epsilon''_{24} f_{1234} \frac{dP_1\, dP_2\, dP_3\, dP_4}{dx_1\, dx_2} \qquad (8)
\end{aligned}
$$

in case 3.

The joint densities consist of three parts. The terms containing the δ-function give rise to self-fluctuations or autocorrelations. Those in which the molecules at x_1 and x_2 interact with each other either directly or via a third molecule express short-range correlations. The rest of the terms refer to long-range correlations. Since we are interested only in long-range correlations, we assume that the molecules labeled 1 and 2 are far apart. More specifically, if σ denotes the range of the intermolecular force, we assume that in case 1, particles 1 and 2 are separated by a distance larger than σ. Then Eq. (6) becomes

$$J_{\varepsilon'\varepsilon''} = N(N-1) \int \epsilon_1{}' \epsilon''_2 f_{12} \frac{dP_1\, dP_2}{dx_1\, dx_2} \qquad (9)$$

Similarly, if we assume that particles 1 and 2 are separated by a distance greater than 2σ in case 2 and 3σ in case 3, Eqs. (7) and (8) become

$$
\begin{aligned}
J_{\epsilon'\epsilon''} = {} & N(N-1)\int \epsilon_1{}'\epsilon''_2 f_{12}\,\frac{dP_1\,dP_2}{dx_1\,dx_2} \\
& + \frac{N(N-1)(N-2)}{2}\int \epsilon_1{}'\epsilon''_{23} f_{123}\,\frac{dP_1\,dP_2\,dP_3}{dx_1\,dx_2}
\end{aligned}
\tag{10}
$$

and

$$
\begin{aligned}
J_{\epsilon'\epsilon''} = {} & N(N-1)\int \epsilon_1{}'\epsilon''_2 f_{12}\,\frac{dP_1\,dP_2}{dx_1\,dx_2} \\
& + \frac{N(N-1)(N-2)}{2}\int (\epsilon_1{}'\epsilon''_{23} + \epsilon''_2\epsilon'_{13}) f_{123}\,\frac{dP_1\,dP_2\,dP_3}{dx_1\,dx_2} \\
& + \frac{N(N-1)(N-2)(N-3)}{4}\int \epsilon'_{13}\epsilon''_{24} f_{1234}\,\frac{dP_1\,dP_2\,dP_3\,dP_4}{dx_1\,dx_2}
\end{aligned}
\tag{11}
$$

respectively.

4. SOME IDENTITIES AND A FORMULA OF IRVING AND KIRKWOOD

Let ϵ be an integral. Introduce the notation

$$(i,j) = \frac{\partial\epsilon_i}{\partial\xi_i}\cdot F_{ij} + \frac{\partial\epsilon_i}{\partial p_i}\cdot G_{ij}$$

and

$$(i,j,k) = \frac{\partial\epsilon_{ij}}{\partial\xi_i}\cdot F_{ik} + \frac{\partial\epsilon_{ij}}{\partial p_i}\cdot G_{ik}$$

There is no summation on repeated indices. Suppose the system is isolated and consists of only one particle. Then $d\epsilon_1/dt = 0$, which gives

$$\frac{\partial\epsilon_1}{\partial x_1}\cdot\xi_1 + \frac{\partial\epsilon_1}{\partial q_1}\cdot p_1 = 0 \tag{12}$$

This is an identity that limits the class of functions ϵ_1 that make ϵ an integral. If the system is isolated and consists of two particles, then $(d/dt)(\epsilon_1 + \epsilon_2) = 0$ in case (a) and $(d/dt)(\epsilon_1 + \epsilon_2 + \epsilon_{12}) = 0$ in case (b). Using (12), one gets

$$(1,2) + (2,1) = 0 \tag{13}$$

in case (a) and

$$
\begin{aligned}
& (1,2) + (2,1) + (1,2,2) + (2,1,1) \\
& \quad + \frac{\partial\epsilon_{12}}{dx_1}\cdot\xi_1 + \frac{\partial\epsilon_{12}}{\partial x_2}\cdot\xi_2 + \frac{\partial\epsilon_{12}}{\partial q_1}\cdot p_1 + \frac{\partial\epsilon_{12}}{\partial q_2}\cdot p_2 = 0
\end{aligned}
\tag{14}
$$

in case (b).

Now suppose that the system is isolated and consists of three particles. Consider case (b). One has $(d/dt)(\epsilon_1 + \epsilon_2 + \epsilon_3 + \epsilon_{12} + \epsilon_{13} + \epsilon_{23}) = 0$, and, on using identities (12) and (14), one obtains

$$(1,2,3) + (2,1,3) + (2,3,1) + (3,2,1) + (3,1,2) + (1,3,2) = 0 \qquad (15)$$

We remark that no new identities are obtained by considering systems consisting of more than three particles. Actually, even when a system of three particles is considered, no new information is obtained in either case (a) or case (b), provided one assumes in the latter case that the intermolecular forces are independent of velocities.

One can verify the following formula of Irving and Kirkwood(15) by direct differentiation: If x_1, x_2 are vectors and K is a vector function defined by

$$K(x_1) = \tfrac{1}{2}\int x_2 \int_0^1 \phi(x_1 - \alpha x_2, x_1 + (1 - \alpha)x_2)\, d\alpha\, dx_2 \qquad (16)$$

where ϕ is some smooth function and where the x_2-integration extends over the whole space, then

$$\operatorname{div} K \equiv (\partial/\partial x_1)\cdot K = \tfrac{1}{2}\int [\phi(x_1, x_2) - \phi(x_2, x_1)]\, dx_2 \qquad (17)$$

Conversely, the right-hand side of (17) is the divergence of K [as defined by (16)] plus some divergenceless vector function, as yet undetermined.

We shall make repeated use of this formula to identify certain terms as divergences and the corresponding flow vectors with vectors of the form (16). We choose this definition of K out of an infinity of choices. In order to show that this is reasonable, one has to calculate the flow of ϵ across the surface of a domain D. It is necessary for this purpose to localize the flow of ϵ. For the part of ϵ that is carried by the molecules, this has already been done by the localization of ϵ. For the part due to intermolecular forces, we assume that the flow between any two molecules is along their line of centers. With this assumption, one can show that the flow vector is exactly of the form (16) if D is a half-space; if D is any other domain, it differs from a vector of the form (16) by one which, though it depends on D, is small and localized. Moreover, the difference has zero divergence and therefore makes no contribution to the total flow of ϵ into the domain when integrated over the boundary.

5. CONSERVATION EQUATIONS FOR CORRELATIONS

In order to obtain the equations for correlations, we shall need the conservation equation for a general integral, which was derived in Ref. 11.

But we need some notation to write it down. We shall adopt the convention that if a quantity appears with subscript i, it is evaluated at x_i. The mass density ρ_1 and the macroscopic velocity u_1 of the fluid are defined by

$$\rho_1 = mN\int f_1 \frac{dP_1}{dx_1}, \qquad \rho_1 u_1 = mN\int \xi_1 f_1 \frac{dP_1}{dx_1}$$

The peculiar velocity c_1 of particle 1 is defined by $c_1 = \xi_1 - u_1$. With this notation and in case (a), the conservation equation takes the form

$$\frac{\partial \bar{\bar{\epsilon}}_1}{\partial t} + \frac{\partial}{\partial x_1}\cdot(\bar{\bar{\epsilon}}_1 u_1) + \frac{\partial}{\partial x_1}\cdot Q_{1\mathrm{a}} = 0 \tag{18}$$

where

$$Q_{1\mathrm{a}} = \overline{\overline{c_1\epsilon_1}} - N(N-1)K_{1\mathrm{a}} \tag{19}$$

where $K_{1\mathrm{a}}$ is given by (16) in terms of

$$\phi_{1\mathrm{a}} = \int \left(\frac{\partial \epsilon_1}{\partial \xi_1}\cdot F_{12} + \frac{\partial \epsilon_1}{\partial p_1}\cdot G_{12}\right) f_{12}\, \frac{dP_1\, dP_2}{dx_1\, dx_2}$$

In case (b), let $\epsilon_{12}^* = \epsilon_1 + \frac{1}{2}(N-1)\epsilon_{12}$. Then the equation is

$$\frac{\partial \overline{\overline{\epsilon_{12}^*}}}{\partial t} + \frac{\partial}{\partial x_1}\cdot\overline{\overline{(\epsilon_{12}^* u_1)}} + \frac{\partial}{\partial x_1}\cdot Q_{1\mathrm{b}} = 0 \tag{20}$$

where

$$Q_{1\mathrm{b}} = \overline{\overline{c_1\epsilon_{12}^*}} - N(N-1)K_{1\mathrm{a}} - \tfrac{1}{3}N(N-1)(N-2)K_{1\mathrm{b}} \tag{21}$$

where $K_{1\mathrm{a}}$ is the same as before and K_{1b} is given by (16), with

$$\phi_{1\mathrm{b}} = \int \left(\frac{\partial \epsilon_{13}}{\partial \xi_1}\cdot F_{12} + \frac{\partial \epsilon_{13}}{\partial p_1}\cdot G_{12} + \frac{\partial \epsilon_{13}}{\partial \xi_3}\cdot F_{32} + \frac{\partial \epsilon_{13}}{\partial p_3}\cdot G_{32}\right) f_{123}\, \frac{dP_1\, dP_2\, dP_3}{dx_1\, dx_2}$$

Now we shall derive the equation for the joint density of a pair of integrals ϵ', ϵ''. Recall that there are three cases: (1) both integrals are of type (a); (2) one integral is of type (a) and the other is of type (b); (3) both integrals are of type (b). Recall also that if

$$Q_{12} = \epsilon_1{}'\epsilon_2'' \qquad \text{in case 1}$$

$$Q_{12} = \epsilon_1{}'\epsilon_2'' + \tfrac{1}{2}(N-2)\epsilon_1{}'\epsilon_{23}'' \qquad \text{in case 2}$$

and

$$\begin{aligned} Q_{12} = {} & \epsilon_1{}'\epsilon_2'' + \tfrac{1}{2}(N-2)(\epsilon_1{}'\epsilon_{23}'' + \epsilon_2''\epsilon_{13}') \\ & + \tfrac{1}{4}(N-2)(N-3)\epsilon_{13}'\epsilon_{24}'' \qquad \text{in case 3} \end{aligned}$$

then, in each case, $\bar{Q}_{12}$ is the joint density in 3-space of ϵ' and ϵ'' when x_1 and x_2 are far apart.

We shall assume throughout that the system is isolated.

Case 1. On multiplying Eq. (1) (the Liouville equation) by $N(N-1)Q_{12}$ and integrating with respect to $dP/dx_1\, dx_2$, one gets

$$\begin{aligned}
&\frac{\partial \bar{Q}_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1\bar{Q}_{12}) + \frac{\partial}{\partial x_1}\cdot(\overline{c_1 Q_{12}}) + \frac{\partial}{\partial x_2}\cdot(u_2\bar{Q}_{12}) + \frac{\partial}{\partial x_2}\cdot(\overline{c_2 Q_{12}}) \\
&\quad - \overline{\frac{\partial \epsilon_1{}'}{\partial x_1}\cdot\xi_1\epsilon_2''} - \overline{\frac{\partial \epsilon_1{}'}{\partial q_1}\cdot p_1\epsilon_2''} - \overline{\frac{\partial \epsilon_2''}{\partial x_2}\cdot\xi_2\epsilon_1{}'} \\
&\quad - \overline{\frac{\partial \epsilon_2''}{\partial q_2}\cdot p_2\epsilon_1{}'} - \overline{\left(F_{12}\cdot\frac{\partial \epsilon_1{}'}{\partial \xi_1} + G_{12}\cdot\frac{\partial \epsilon_1{}'}{\partial p_1}\right)\epsilon_2''} \\
&\quad - \overline{\left(F_{21}\cdot\frac{\partial \epsilon_2''}{\partial \xi_2} + G_{21}\cdot\frac{\partial \epsilon_2''}{\partial p_2}\right)\epsilon_1{}'} - (N-2)\left[\overline{\left(F_{13}\cdot\frac{\partial \epsilon_1{}'}{\partial \xi_1} + G_{13}\cdot\frac{\partial \epsilon_1{}'}{\partial p_1}\right)\epsilon_2''}\right. \\
&\quad \left. + \overline{\left(F_{23}\cdot\frac{\partial \epsilon_2''}{\partial \xi_2} + G_{23}\cdot\frac{\partial \epsilon_{''}^{2}}{\partial p_2}\right)\epsilon_1{}'}\right] = 0
\end{aligned} \tag{22}$$

If identity (12) is used and if it is assumed that $|x_2 - x_1| > \sigma$, Eq. (22) becomes

$$\begin{aligned}
&\frac{\partial \bar{Q}_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1\bar{Q}_{12}) + \frac{\partial}{\partial x_2}(u_2\bar{Q}_{12}) + \frac{\partial}{\partial x_1}\cdot(\overline{c_1 Q_{12}}) + \frac{\partial}{\partial x_2}\cdot(\overline{c_2 Q_{12}}) \\
&\quad - (N-2)\left[\overline{\left(F_{13}\cdot\frac{\partial \epsilon_1{}'}{\partial \xi_1} + G_{13}\cdot\frac{\partial \epsilon_1{}'}{\partial p_1}\right)\epsilon_2''} + \overline{\left(F_{23}\cdot\frac{\partial \epsilon_2''}{\partial \xi_2} + G_{23}\cdot\frac{\partial \epsilon_2''}{\partial p_2}\right)\epsilon_1{}'}\right] = 0
\end{aligned} \tag{23}$$

The set over which the assumption that $|x_2 - x_1| > \sigma$ fails is a strip of width 2σ in six-dimensional space. But σ is a small parameter, and ultimately we will take a limit in which $\sigma \to 0$. We believe it can be shown by considering the initial value problem that if the terms dropped are small initially, they will remain small over a finite, macroscopic amount of time. Intuitively, this means that if two specific particles are far apart initially, they have a very small probability of coming close to each other within such a time.

On using identity (13) and the formula of Irving and Kirkwood, (23) can be written as a conservation equation:

$$\begin{aligned}
&\frac{\partial \bar{Q}_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1\bar{Q}_{12}) + \frac{\partial}{\partial x_2}\cdot(u_2\bar{Q}_{12}) + \frac{\partial}{\partial x_1}\cdot(\overline{c_1 Q_{12}}) + \frac{\partial}{\partial x_2}\cdot(\overline{c_2 Q_{12}}) \\
&\quad - N(N-1)(N-2)\left(\frac{\partial}{\partial x_1}\cdot\kappa^{(1)} + \frac{\partial}{\partial x_2}\cdot\kappa^{(2)}\right) = 0
\end{aligned} \tag{24}$$

where

$$\kappa^{(1)} = \int \epsilon_2'' K^{(1)}(x_1, P_2)\,\frac{dP_2}{dx_2}$$

with

$$\phi^{(1)}(x_1, x_3) = \int \left(\frac{\partial \epsilon_1{}'}{\partial \xi_1} \cdot F_{13} + \frac{\partial \epsilon_1{}'}{\partial p_1} \cdot G_{13} \right) f_{123} \frac{dP_1 \, dP_3}{dx_1 \, dx_3} \tag{25}$$

and

$$\kappa^{(2)} = \int \epsilon_1{}' K^{(2)}(P_1, x_2) \frac{dP_1}{dx_1}$$

with

$$\phi^{(2)}(x_2, x_3) = \int \left(\frac{\partial \epsilon_2''}{\partial \xi_2} \cdot F_{23} + \frac{\partial \epsilon_2''}{\partial p_2} \cdot G_{23} \right) f_{123} \frac{dP_2 \, dP_3}{dx_2 \, dx_3}$$

Case 2. One first multiplies the Liouville equation by $N(N-1)Q_{12}$ and integrates with respect to $dP/dx_1 \, dx_2$. Then one observes that the bar denotes integration (with respect to everything except x_1 and x_2) and that, under the integral sign, the dummy indices can be interchanged at will. For example,

$$\overline{F_{24} \cdot \frac{\partial \epsilon_2''}{\partial \xi_2} \epsilon_1'} = \overline{F_{23} \cdot \frac{\partial \epsilon_2''}{\partial \xi_2} \epsilon_1'}$$

If, further, one uses identities (12)–(14) and assumes that $|x_2 - x_1| > 2\sigma$, one gets an equation which, on using identity (15) and the Irving–Kirkwood formula, gives

$$\begin{aligned} &\frac{\partial \bar{Q}_{12}}{\partial t} + \frac{\partial}{\partial x_1} \cdot (u_1 \bar{Q}_{12}) + \frac{\partial}{\partial x_2} \cdot (u_2 \bar{Q}_{12}) + \frac{\partial}{\partial x_1} \cdot (\overline{c_1 Q_{12}}) + \frac{\partial}{\partial x_2} \cdot (\overline{c_2 Q_{12}}) \\ &\quad - N(N-1)(N-2) \left(\frac{\partial}{\partial x_1} \cdot \kappa^{(1)} + \frac{\partial}{\partial x_2} \cdot \kappa^{(2)} \right) \\ &- \frac{N(N-1)(N-2)}{2} \frac{\partial}{\partial x_1} \cdot \kappa^{(3)} - \frac{N(N-1)(N-2)(N-3)}{3} \frac{\partial}{\partial x_2} \cdot \kappa^{(6)} = 0 \end{aligned} \tag{26}$$

where $\kappa^{(1)}$ and $\kappa^{(2)}$ are the same as in (24) and

$$\kappa^{(3)} = \int \epsilon_{23}'' K^{(3)}(x_1, P_2, P_3) \frac{dP_2 \, dP_3}{dx_2}$$

with

$$\phi^{(3)} = \int \left(\frac{\partial \epsilon_1{}'}{\partial \xi_1} \cdot F_{14} + \frac{\partial \epsilon_1{}'}{\partial p_1} \cdot G_{14} \right) f_{1234} \frac{dP_1 \, dP_4}{dx_1 \, dx_4}$$

and

$$\kappa^{(6)} = \int \epsilon_1{}' K^{(6)}(P_1, x_2) \frac{dP_1}{dx_1}$$

with

$$\phi^{(6)} = \int \left(\frac{\partial \epsilon_{23}''}{\partial \xi_2} \cdot F_{24} + \frac{\partial \epsilon_{23}''}{\partial p_2} \cdot G_{24} + \frac{\partial \epsilon_{23}''}{\partial \xi_3} \cdot F_{34} + \frac{\partial \epsilon_{23}''}{\partial p_3} \cdot G_{34} \right) f_{1234} \frac{dP_2 \, dP_3 \, dP_4}{dx_2 \, dx_4}$$

Case 3. On multiplying the Liouville equation by $N(N-1)Q_{12}$ and integrating with respect to $dP/dx_1\,dx_2$, and following the same type of reasoning as in cases 1 and 2 (with the exception that it is assumed that $|x_2 - x_1| > 3\sigma$), one gets

$$\begin{aligned}\frac{\partial \bar{Q}_{12}}{\partial t} &+ \frac{\partial}{\partial x_1}\cdot(u_1\bar{Q}_{12}) + \frac{\partial}{\partial x_2}\cdot(u_2\bar{Q}_{12}) + \frac{\partial}{\partial x_1}\cdot(\overline{c_1 Q_{12}}) + \frac{\partial}{\partial x_2}\cdot(\overline{c_2 Q_{12}}) \\ &- N(N-1)(N-2)\left(\frac{\partial}{\partial x_1}\cdot\kappa^{(1)} + \frac{\partial}{\partial x_2}\cdot\kappa^{(2)}\right) \\ &- \frac{N(N-1)(N-2)(N-3)}{2}\left(\frac{\partial}{\partial x_1}\cdot\kappa^{(3)} + \frac{\partial}{\partial x_2}\cdot\kappa^{(4)}\right) \\ &\quad \frac{N(N-1)(N-2)(N-3)}{3}\left(\frac{\partial}{\partial x_1}\cdot\kappa^{(5)} + \frac{\partial}{\partial x_2}\cdot\kappa^{(6)}\right) \\ &- \frac{N(N-1)(N-2)(N-3)(N-4)}{6}\left(\frac{\partial}{\partial x_1}\cdot\kappa^{(7)} + \frac{\partial}{\partial x_2}\cdot\kappa^{(8)}\right) = 0\end{aligned} \tag{27}$$

where $\kappa^{(1)}$, $\kappa^{(2)}$, $\kappa^{(3)}$, and $\kappa^{(6)}$ are the same as before, and

$$\kappa^{(4)} = \int \epsilon'_{13}K^{(4)}(P_1, x_2, P_3)\,\frac{dP_1\,dP_3}{dx_1}$$

with

$$\phi^{(4)} = \int \left(\frac{\partial\epsilon''_2}{\partial\xi_2}\cdot F_{24} + \frac{\partial\epsilon''_2}{\partial p_2}\cdot G_{24}\right) f_{1234}\,\frac{dP_2\,dP_4}{dx_2\,dx_4}$$

and

$$\kappa^{(5)} = \int \epsilon''_2 K^{(5)}(x_1, P_2)\,\frac{dP_2}{dx_2}$$

with

$$\phi^{(5)} = \int \left(\frac{\partial\epsilon_{13}}{\partial\xi_1}\cdot F_{14} + \frac{\partial\epsilon'_{13}}{\partial p_1}\cdot G_{14} + \frac{\partial\epsilon'_{13}}{\partial\xi_3}\cdot F_{34} + \frac{\partial\epsilon'_{13}}{\partial p_3}\cdot G_{34}\right) f_{1234}\,\frac{dP_1\,dP_3\,dP_4}{dx_1\,dx_4}$$

and

$$\kappa^{(7)} = \int \epsilon''_{24} K^{(7)}(x_1, P_2, P_4)\,\frac{dP_2\,dP_4}{dx_2}$$

with

$$\phi^{(7)} = \int \left(\frac{\partial\epsilon'_{13}}{\partial\xi_1}\cdot F_{15} + \frac{\partial\epsilon'_{13}}{\partial p_1}\cdot G_{15} + \frac{\partial\epsilon'_{13}}{\partial\xi_3}\cdot F_{35} + \frac{\partial\epsilon'_{13}}{\partial p_3}\cdot G_{35}\right) f_{12345}\,\frac{dP_1\,dP_3\,dP_5}{dx_1\,dx_5}$$

and

$$\kappa^{(8)} = \int \epsilon'_{13} K^{(8)}(P_1, x_2, P_3) \frac{dP_1\, dP_3}{dx_1}$$

with

$$\phi^{(8)} = \int \left(\frac{\partial \epsilon''_{24}}{\partial \xi_2} \cdot F_{25} + \frac{\partial \epsilon''_{24}}{\partial p_2} \cdot G_{25} + \frac{\partial \epsilon''_{24}}{\partial \xi_4} \cdot F_{45} + \frac{\partial \epsilon''_{24}}{\partial p_4} \cdot G_{45} \right) f_{12345} \frac{dP_2\, dP_4\, dP_5}{dx_2\, dx_5}$$

Before we can write down the conservation equations for correlations, we have to introduce some notation:

$$\psi_{12} = f_{12} - f_1 f_2$$

$$\psi_{123} = f_{123} - f_1 f_2 f_3 - [f_1 \psi_{23}]^3$$

and

$$\psi_{1234} = f_{1234} - f_1 f_2 f_3 f_4 - [f_1 \psi_{234}]^4 - [f_1 f_2 \psi_{34}]^6 - \alpha [\psi_{12} \psi_{34}]^3$$

where α is some number[6] and where the square brackets indicate a symmetric sum; the number appearing above each sum indicates the number of terms in it. For example,

$$[f_1 \psi_{23}]^3 = f_1 \psi_{23} + f_2 \psi_{13} + f_3 \psi_{12}$$

The above formulas serve as definitions of ψ_{12}, ψ_{123}, etc. In analogy with the definition of the r-particle distribution function, $\psi_{12\ldots r}$ is called the r-particle correlation.

The notation introduced above makes it possible to express the r-particle correlation function in terms of the r-particle distribution function and lower order correlations or, equivalently, lower order distribution functions.

If ϵ', ϵ'' are any integrals, we shall denote the correlation between them by c_{12} and its convective flow by a_{12} and b_{12}.[7] Specifically, in case 1

$$c_{12} = \bar{Q}_{12} - \overline{\overline{\epsilon_1{}'}}\, \overline{\overline{\epsilon''_2}} = N^2 \int \epsilon_1{}' \epsilon''_2 \psi_{12} \frac{dP_1\, dP_2}{dx_1\, dx_2}$$

$$a_{12} = \overline{c_1 Q_{12}} - \overline{\overline{c_1 \epsilon_1{}'}}\, \overline{\overline{\epsilon''_2}} = N^2 \int c_1 \epsilon_1{}' \epsilon''_2 \psi_{12} \frac{dP_1\, dP_2}{dx_1\, dx_2}$$

and

$$b_{12} = \overline{c_2 Q_{12}} - \overline{\overline{\epsilon_1{}'}}\, \overline{\overline{c_2 \epsilon''_2}} = N^2 \int c_2 \epsilon_1{}' \epsilon''_2 \psi_{12} \frac{dP_1\, dP_2}{dx_1\, dx_2}$$

---

[6] Different choices of α give rise to different ways of truncating f_{1234}. For instance $\psi_{1234} = 0$ and $\alpha = 1$ gives the well-known Mayer truncation; $\alpha = 0$ gives a truncation suggested by Grad (private communication).

[7] In expressing these quantities, we shall put $N \simeq N - 1 \simeq N - 2 \simeq N - 3 \simeq N - 4$.

In case 2

$$
\begin{aligned}
c_{12} &= \bar{Q}_{12} - \overline{\overline{\epsilon_1{}'}}\,\overline{\overline{\epsilon_2''}} - \frac{N}{2}\overline{\overline{\epsilon_1{}'}}\,\overline{\overline{\epsilon_{23}''}} \\
&= N^2 \int \epsilon_1{}'\epsilon_2''\psi_{12}\,\frac{dP_1\,dP_2}{dx_1\,dx_2} \\
&\quad + \frac{N^3}{2}\int \epsilon_1{}'\epsilon_{23}''(\psi_{123} + f_2\psi_{13} + f_3\psi_{12}) \\
&\quad \times \frac{dP_1\,dP_2\,dP_3}{dx_1\,dx_2}
\end{aligned}
$$

a_{12} and b_{12} are defined by inserting c_1 and c_2, respectively, in the integrands in the definition of c_{12}.

In case 3

$$
\begin{aligned}
c_{12} = \bar{Q}_{12} - \overline{\overline{\epsilon_1{}'}}\,\overline{\overline{\epsilon_2''}} - \frac{N}{2}(\overline{\overline{\epsilon_1{}'}}\,\overline{\overline{\epsilon_{23}''}} + \overline{\overline{\epsilon_2''}}\,\overline{\overline{\epsilon_{13}'}}) - \frac{N^2}{4}\overline{\overline{\epsilon_{13}'}}\,\overline{\overline{\epsilon_{24}''}} \\
= N^2 \int \epsilon_1{}'\epsilon_2''\psi_{12}\,\frac{dP_1\,dP_2}{dx_1\,dx_2} \\
+ \frac{N^3}{2}\int \epsilon_1{}'\epsilon_{23}''(\psi_{123} + f_2\psi_{13} + f_3\psi_{12})\,\frac{dP_1\,dP_2\,dP_3}{dx_1\,dx_2} \\
+ \frac{N^3}{2}\int \epsilon_2''\epsilon_{13}'(\psi_{123} + f_1\psi_{23} + f_3\psi_{12})\,\frac{dP_1\,dP_2\,dP_3}{dx_1\,dx_2} \\
+ \frac{N^4}{4}\int \epsilon_{13}'\epsilon_{24}''(\psi_{1234} + [f_1\psi_{234}]^4 + f_1f_2\psi_{34} + f_1f_4\psi_{23} + f_2f_3\psi_{14} \\
+ f_3f_4\psi_{12} + \alpha\psi_{12}\psi_{34} + (\alpha - 1)\psi_{13}\psi_{24} + \alpha\psi_{23}\psi_{14})\,\frac{dP_1\,dP_2\,dP_3\,dP_4}{dx_1\,dx_2}
\end{aligned}
$$

a_{12} and b_{12} are defined the same way as in cases 1 and 2.

We are now ready to write down the equations for the correlations.

Case 1. Using Eqs. (18) and (25), we get

$$
\begin{aligned}
\frac{\partial c_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1c_{12}) + \frac{\partial}{\partial x_2}\cdot(u_2c_{12}) + \frac{\partial}{\partial x_1}\cdot a_{12} \\
+ \frac{\partial}{\partial x_2}\cdot b_{12} + \frac{\partial}{\partial x_1}\cdot\kappa^{(1)'} + \frac{\partial}{\partial x_2}\cdot\kappa^{(2)'} = 0
\end{aligned}
\qquad (28)
$$

where

$$
\kappa^{(1)'} = -N^3\kappa^{(1)} + \overline{\overline{\epsilon_2''}}N^2K_{1a}, \qquad \kappa^{(2)'} = -N^3\kappa^{(2)} + \overline{\overline{\epsilon_1{}'}}\,N^2K_{2a}
$$

Case 2. Using Eqs. (18), (20), and (26), we get

$$\frac{\partial c_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1 c_{12}) + \frac{\partial}{\partial x_2}\cdot(u_2 c_{12}) + \frac{\partial}{\partial x_1}\cdot a_{12} + \frac{\partial}{\partial x_2}\cdot b_{12} + \frac{\partial}{\partial x_1}\cdot(\kappa^{(1)'} + \kappa^{(3)'}) + \frac{\partial}{\partial x_2}\cdot(\kappa^{(2)'} + \kappa^{(6)'}) = 0 \tag{29}$$

where $\kappa^{(1)'}$ and $\kappa^{(2)'}$ are the same as before, and

$$\kappa^{(3)'} = -\tfrac{1}{2}N^4\kappa^{(3)} + \tfrac{1}{2}N^3\overline{\overline{\epsilon''_{23}}}K_{1a}, \qquad \kappa^{(6)'} = -\tfrac{1}{3}N^4\kappa^{(6)} + \tfrac{1}{3}N^3\overline{\overline{\epsilon_1{}'}}K_{2b}$$

Case 3. Using Eqs. (20) and (27), we get

$$\frac{\partial c_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1 c_{12}) + \frac{\partial}{\partial x_2}\cdot(u_2 c_{12}) + \frac{\partial}{\partial x_1}\cdot a_{12} + \frac{\partial}{\partial x_2}\cdot b_{12} + \frac{\partial}{\partial x_1}\cdot(\kappa^{(1)'} + \kappa^{(3)'} + \kappa^{(5)'} + \kappa^{(7)'}) + \frac{\partial}{\partial x_2}\cdot(\kappa^{(2)'} + \kappa^{(4)'} + \kappa^{(6)'} + \kappa^{(8)'}) = 0 \tag{30}$$

where $\kappa^{(1)'}$, $\kappa^{(2)'}$, $\kappa^{(3)'}$, and $\kappa^{(6)'}$ are the same as before, and

$$\kappa^{(4)'} = -\tfrac{1}{2}N^4\kappa^{(4)} + \tfrac{1}{2}N^3\overline{\overline{\epsilon'_{13}}}K_{2a}, \qquad \kappa^{(5)'} = -\tfrac{1}{3}N^4\kappa^{(5)} + \tfrac{1}{3}N^3\overline{\overline{\epsilon''_2}}K_{1b}$$

$$\kappa^{(7)'} = -\tfrac{1}{6}N^5\kappa^{(7)} + \tfrac{1}{6}N^4\overline{\overline{\epsilon''_{24}}}K_{1b}, \qquad \kappa^{(8)'} = -\tfrac{1}{6}N^5\kappa^{(8)} + \tfrac{1}{6}N^4\overline{\overline{\epsilon'_{13}}}K_{2b}$$

We emphasize that all the foregoing calculations apply to a fluid of any density and that rarefaction has nothing to do with correlations. But when a gas is rarefied, the terms containing the intermolecular potential explicitly can be dropped. The equations for the correlations take the form

$$\frac{\partial c_{12}}{\partial t} + \frac{\partial}{\partial x_1}\cdot(u_1 c_{12}) + \frac{\partial}{\partial x_2}\cdot(u_2 c_{12}) + \frac{\partial}{\partial x_1}\cdot a_{12} + \frac{\partial}{\partial x_2}\cdot b_{12} = 0$$

where the quantities c_{12}, a_{12}, and b_{12} are defined as in case 1. For a rarefied gas, the correlation equations corresponding to Euler's equations have been derived by Zhigulev(6) and those corresponding to the Navier–Stokes equations by Tsugé.(7,8) Finally, we shall consider some special cases of Eqs. (28)–(30).

Mass–Mass. $\epsilon_1{}' = m$, $\epsilon_2{}' = m$, and

$$c_{12} = N^2m^2\int \psi_{12}\,\frac{dP_1\,dP_2}{dx_1\,dx_2}$$

$$a^i_{12} = N^2m^2\int c_1{}^i\psi_{12}\,\frac{dP_1\,dP_2}{dx_1\,dx_2}, \qquad b^i_{12} = N^2m^2\int c_2{}^i\psi_{12}\,\frac{dP_1\,dP_2}{dx_1\,dx_2}$$

$\kappa^{(1)'i}$ and $\kappa^{(2)'i}$ vanish. Equation (28) becomes

$$\frac{\partial c_{12}}{\partial t} + \frac{\partial}{\partial x_1{}^i}(u_1{}^i c_{12}) + \frac{\partial}{\partial x_2{}^i}(u_2{}^i c_{12}) + \frac{\partial a^i_{12}}{\partial x_1{}^i} + \frac{\partial b^i_{12}}{\partial x_1{}^i} = 0 \tag{31}$$

Mass–Momentum. $\epsilon_1' = m$, $\epsilon_2''^j = m\xi_2{}^j$, and

$$c_{12}^j = N^2 m^2 \int \xi_2{}^j \psi_{12} \frac{dP_1\, dP_2}{dx_1\, dx_2}$$

$\kappa^{(1)'ij} = 0$ and

$$\kappa^{(2)'ij} = -N^3 \kappa^{(2)ij} + \rho_1 N^2 K_{2a}^{ij}, \qquad \kappa^{(2)ij} = m \int K^{(2)ij}(P_1, x_2) \frac{dP_1}{dx_1}$$

with

$$\phi^{(2)j} = m \int F_{23}^j f_{123} \frac{dP_2\, dP_3}{dx_2\, dx_3}$$

Let $y^j = x_3{}^j - x_2{}^j$. Then, if the intermolecular forces are central, F_{23}^j depends only on $r = |y|$:

$$F_{23}^j = y^j F^*(r)$$

where $F^*(r)$ is some function of r. Let

$$g_{123}(P_1, x_2, x_3) = \int f_{123} \frac{dP_2\, dP_3}{dx_2\, dx_3}$$

Then

$$\phi^{(2)j} = m y^j F^*(r) g_{123}$$

and

$$K^{(2)ij} = \tfrac{1}{2} m \int y^i y^j F^*(r) \int_0^1 g_{123}(x_2 - \lambda y, x_2 + (1 - \lambda) y)\, d\lambda\, dy$$

where we have suppressed the dependence of g_{123} on P_1.

Recalling that

$$K_{2a}^{ij} = \tfrac{1}{2} m \int y^i y^j F^*(r) \int_0^1 n_{23}(x_2 - \lambda y, x_2 + (1 - \lambda) y)\, d\lambda\, dy$$

we obtain

$$\kappa^{(2)'ij} = -\tfrac{1}{2} m^2 N^3 \int y^i y^j F^*(r) \int_0^1 (\psi_{123} + f_2 \psi_{13} + f_3 \psi_{12})\, d\lambda\, dy \frac{dP_1}{dx_1}$$

where the integrand of the inner integral has already been integrated with respect to $dP_2\, dP_3/dx_2\, dx_3$ and is evaluated at $(x_2 - \lambda y, x_2 + (1 - \lambda) y)$.

Mass–Angular Momentum. $\epsilon_1' = m$, $\epsilon_2''^{jk} = m(x_2{}^j \xi_2{}^k - x_2{}^k \xi_2{}^j) + \mu_2^{jk}$, where μ_2 is the internal angular momentum of molecule 2 (if i, j, k are cyclic, we denote the ith component of μ_2 by μ_2^{jk}). We have

$$c_{12}^{jk} = N^2 m^2 \int (x_2{}^j \xi_2{}^k - x_2{}^k \xi_2{}^j) \psi_{12} \frac{dP_1\, dP_2}{dx_1\, dx_2} + N^2 m \int \mu_2^{jk} \psi_{12} \frac{dP_1\, dP_2}{dx_1\, dx_2}$$

$$\kappa^{(1)'ljk} = 0, \qquad \kappa^{(2)'ljk} = -N^3 \kappa^{(2)ljk} + N^2 \rho_1 K_{2a}^{ljk}$$

Momentum–Momentum. $\epsilon_1'^j = m\xi_1{}^j$, $\epsilon_2''^k = m\xi_2{}^k$, and

$$c_{12}^{jk} = N^2m^2 \int \xi_1{}^j\xi_2{}^k\psi_{12}\, \frac{dP_1\, dP_2}{dx_1\, dx_2}$$

If the intermolecular forces are central, we proceed in the same way as in the mass–momentum case and obtain ($y^i = x_3{}^i - x_1{}^i$, $r = |y|$)

$$\kappa^{(1)'ijk} = -\frac{m^2N^3}{2} \int y^iy^j\xi_2{}^kF^*(r) \int_0^1 (\psi_{123} + f_1\psi_{23} + f_3\psi_{12})\, d\lambda\, dy\, \frac{dP_2}{dx_2}$$

and ($y^i = x_3{}^i - x_2{}^i$, $r = |y|$)

$$\kappa^{(2)'ijk} = -\frac{m^2N^3}{2} \int y^iy^k\xi_1{}^jF^*(r) \int_0^1 (\psi_{123} + f_2\psi_{13} + f_3\psi_{12})\, d\lambda\, dy\, \frac{dP_1}{dx_1}$$

ACKNOWLEDGMENTS

I take this opportunity to express my sincere gratitude to my teacher, Prof. Harold Grad, who not only suggested the problem but also provided constant encouragement and guidance. I also wish to thank Prof. J. K. Percus for his kind interest in the work and for his helpful suggestions. The work was supported by the Air Force Office of Scientific Research, USAF, under Grant No. AFOSR-71-2053.

REFERENCES

1. H. Grad, "Principles of the Kinetic Theory of Gases," in *Handbuch der Physik*, S. Flugge, ed., Springer Verlag, Berlin (1958), Vol. XII.
2. M. N. Kogan, *Rarefied Gas Dynamics*, Plenum Press, New York (1969).
3. H. Grad, "Singular Limits of Solutions of Boltzmann's Equation," NYU—Courant Institute of Mathematical Sciences Report, MF-77, 1972; also in *Proc. Eighth Int. Symp. on Rarefied Gas Dynamics*, Stanford University, July 1972.
4. L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*, Pergamon Press, (1959).
5. R. F. Fox and G. E. Uhlenbeck, *Phys. Fluids* **13**:2881 (1970).
6. V. N. Zhigulev, *Doklady Akad. Nauk SSSR* **165**:502 (1965) [English transl.: *Soviet Phys.—Doklady* **10**:1003 (1966)].
7. S. Tsugé, *Phys. Letters* **33A**:145 (1970).
8. S. Tsugé, "The Boltzmann and Klimontovich Formalisms with Reference to Turbulence Resolution," in *Proc. Eighth Int. Symp. on Rarefied Gas Dynamics*, Stanford University, July 1972.
9. S. K. Srinivasan, "A New Approach to the Kinetic Theory of Fluids—Onset of Turbulent Motion," in *Symposia on Theoretical Physics and Mathematics*, A. Ramakrishnan, ed., Plenum Press, New York (1968), Vol. 7; and references cited therein.
10. H. Grad, *Comm. Pure Appl. Math.* **5**:455 (1952).
11. H. Grad, *J. Phys. Chem.* **56**:1039 (1952).
12. R. M. Lewis, *Arch. Ratl. Mech. Anal.* **5**:355 (1960).
13. J. S. Dahler, *J. Chem. Phys.* **30**:1447 (1959).
14. A. C. Eringen, *Int. J. Eng. Sci.* **2**:205 (1964).
15. J. H. Irving and J. G. Kirkwood, *J. Chem. Phys.* **18**, No. 6 (1950).