

Method for Finding the Density Expansion of Transport Coefficients of Gases

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This article presents a new method for finding the density expansion of certain transport coefficients of gases. Of these, the self-diffusion coefficient is the most important example. The method is to calculate the time-correlation function associated with the transport process. To lowest order in density, the results are identical with those found by Enskog's first-order perturbation solution of the Boltzmann equation. The first density correction requires the solution of a certain three-body problem. This problem is stated precisely, but is not solved.

1. INTRODUCTION

IT is well known, from the work of Green,¹ Kubo,² Mori,³ and others, that transport coefficients can be expressed as integrals of time-correlation functions. The simplest example is the self-diffusion coefficient D of an isotropic fluid

$$D = -\frac{1}{3} \lim_{\epsilon \rightarrow 0} \int_0^{\infty} dt e^{-\epsilon t} \left\langle \frac{\mathbf{p}_1(0)}{m} \cdot \frac{\mathbf{p}_1(t)}{m} \right\rangle_{av}, \quad (1.1)$$

where $\mathbf{p}_1(t)$ is the momentum of the diffusing molecule at time t , m is its mass, and the average is calculated with an equilibrium distribution of initial phase points.

Other transport coefficients, for example, the coefficients of viscosity and thermal conductivity, are not quite so simple. They involve time correlations of functions of position as well as momentum. We shall reserve a discussion of these coefficients for a later article. The most general transport coefficient considered in the present article have the form

$$\sigma = \lim_{\epsilon \rightarrow 0} \sigma(\epsilon),$$

$$\sigma(\epsilon) = \int_0^{\infty} dt e^{-\epsilon t} \langle J(\mathbf{p}_1(0)) J(\mathbf{p}_1(t)) \rangle_{av}, \quad (1.2)$$

where $J(\mathbf{p})$ is some function of momentum characteristic of the particular transport process. Clearly the self-diffusion coefficient is a special case of Eq. (1.2).

Mori⁴ has given a plausible argument that the calculation of transport coefficients from time-correlation functions, for gases at very low density, leads to results identical with those found by the customary solution of the Boltzmann equation. Montroll and Ward⁵ have shown how the time-correlation formula for electrical conductivity leads to the standard Boltzmann equation in the weak coupling limit; and they conjectured at some generalizations. They were not able to get entirely satisfactory results because of the extra complications of quantum statistics

and the apparent divergences characteristic of an electron gas.

We have discovered a method, somewhat like the virial expansion in equilibrium statistical mechanics, for finding higher terms in the density expansion of the momentum contributions to transport coefficients. The purpose of the present article is to describe this method and to give a preliminary argument concerning its validity.

We show that momentum transport coefficients can be calculated in the following way:

$$\sigma = \int d\mathbf{p}_1 \varphi(\mathbf{p}_1) J(\mathbf{p}_1) K(\mathbf{p}_1), \quad (1.3)$$

where $\varphi(\mathbf{p})$ is the equilibrium momentum distribution at temperature T ,

$$\varphi(\mathbf{p}) = \frac{\exp(-\mathbf{p}^2/2mkT)}{(2\pi mkT)^{3/2}}, \quad (1.4)$$

and $K(\mathbf{p}_1)$ is the solution of an operator equation in momentum space, of the form

$$(\rho \mathbf{B}_2 + \rho^2 \mathbf{B}_3 + \dots) \cdot K(\mathbf{p}_1) = J(\mathbf{p}_1), \quad (1.5)$$

where ρ is the density of the gas.

Equation (1.5) is a generalization of the integral equation arising in Chapman and Enskog's first-order perturbation solution of the Boltzmann equation. In particular, to the lowest order in density Eq. (1.5) is identical with Chapman and Enskog's integral equation.

The operator \mathbf{B}_3 contains the effects of triple collisions. The determination of this operator requires the solution of a certain well-defined three-body problem, described in Sec. 9.

The specific results of this article that we believe are new and significant are the following: (1) a general method for constructing higher order terms in the density expansion of the operator appearing in Eq. (1.5); (2) the reduction of the first correction \mathbf{B}_3 to a well-defined three-body problem; and (3) explicit demonstration that the method is free of divergences to the second order in density.

¹ M. S. Green, J. Chem. Phys. **20**, 1281 (1952); **22**, 398 (1954).

² R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

³ H. Mori, Phys. Rev. **112**, 1829 (1958).

⁴ H. Mori, Phys. Rev. **111**, 694 (1958).

⁵ E. W. Montroll and J. C. Ward, Physica **25**, 423 (1959).

2. HOW TO FIND THE OPERATORS B_n

In this section we present, without proof, the procedure for finding the operators B_n in Eq. (1.5). The rest of the article is concerned with a more detailed analysis of the first two terms, B_2 and B_3 .

Our method is based on explicit use of the Liouville operator L , Koopman's time displacement operator $\exp(iL)$, and the resolvent operator $(\epsilon - iL)^{-1}$. Koopman's operator has the following property: If $\alpha(\mathbf{R}, \mathbf{p})$ is some dynamical quantity, its value at time t is given as a function of initial values of \mathbf{R} and \mathbf{p} by the operator equation

$$\alpha(t) = \alpha(\mathbf{R}(t), \mathbf{p}(t)) = \exp(iL) \cdot \alpha(\mathbf{R}, \mathbf{p}). \quad (2.1)$$

By using this operator we may write Eq. (1.2) as

$$\sigma(\epsilon) = \int_0^\infty dt \exp(-\epsilon t) \langle J(\mathbf{p}_1) \exp(iL) J(\mathbf{p}_1) \rangle_{\text{av}}. \quad (2.2)$$

On performing the time integration, one obtains the resolvent operator $G(\epsilon)$, defined by

$$G(\epsilon) = \int_0^\infty dt \exp(-\epsilon t) \exp(iL) = (\epsilon - iL)^{-1}. \quad (2.3)$$

Thus, $\sigma(\epsilon)$ is

$$\sigma(\epsilon) = \langle J(\mathbf{p}_1) G(\epsilon) J(\mathbf{p}_1) \rangle_{\text{av}}. \quad (2.4)$$

The equilibrium average $\langle \rangle_{\text{av}}$ is performed in two stages. The first, denoted here by $\langle \rangle$ without the subscript av, is the equilibrium average over all coordinates, and over all momenta except \mathbf{p}_1 . The second stage is the average over \mathbf{p}_1 using the distribution $\varphi(\mathbf{p})$ defined in Eq. (1.4). We write this as

$$\langle \rangle_{\text{av}} = \int d\mathbf{p}_1 \varphi(\mathbf{p}_1) \langle \rangle. \quad (2.5)$$

Because the partial average $\langle \rangle$ does not touch the function $J(\mathbf{p}_1)$, $\sigma(\epsilon)$ is conveniently expressed as

$$\sigma(\epsilon) = \int d\mathbf{p}_1 \varphi(\mathbf{p}_1) J(\mathbf{p}_1) \langle G(\epsilon) \rangle J(\mathbf{p}_1). \quad (2.6)$$

Note that the operator $\langle G(\epsilon) \rangle$ is an intensive quantity: Although it is defined in a many-body system, it operates only in the space of functions of momentum of one molecule. We may therefore expect that it has a well-defined density expansion (of an unknown radius of convergence),

$$\langle G(\epsilon) \rangle = \Gamma_1(\epsilon) + \rho \Gamma_2(\epsilon) + \rho^2 \Gamma_3(\epsilon) + \dots \quad (2.7)$$

We suppose that the limit of an infinite system is taken at this stage of the calculation. That is, we let

$$\begin{aligned} N \rightarrow \infty, \quad V \rightarrow \infty, \\ \rho = N/V = \text{const}, \end{aligned} \quad (2.8)$$

where N is the number of molecules in the system, and V is the volume. This serves to eliminate the mathematically annoying but physically meaningless complications of recurrences at long times.

The operators $\Gamma_n(\epsilon)$ all diverge as $\epsilon \rightarrow 0$. In particular, the first one in the series is simply

$$\Gamma_1(\epsilon) = 1/\epsilon. \quad (2.9)$$

The divergence is not unexpected. If the limits existed, then σ would be expressed as a power series in density, containing only the zeroth and positive integral powers. But this is contrary to experience. We know, for example, that the self-diffusion coefficient is proportional to $1/\rho$ at low density, and therefore cannot be expanded in such a power series.

We consider now the operator $B(\epsilon)$, defined as the reciprocal of $\langle G(\epsilon) \rangle$,

$$[B(\epsilon)]^{-1} = \langle G(\epsilon) \rangle. \quad (2.10)$$

The formal density expansion (2.7) can be inverted (for nonzero ϵ) to yield a series expansion of $B(\epsilon)$,

$$B(\epsilon) = B_1(\epsilon) + \rho B_2(\epsilon) + \rho^2 B_3(\epsilon) + \dots \quad (2.11)$$

The coefficients can be found by elementary algebra. They are

$$\begin{aligned} B_1(\epsilon) &= [\Gamma_1(\epsilon)]^{-1} = \epsilon, \\ B_2(\epsilon) &= -\epsilon^2 \Gamma_2(\epsilon), \\ B_3(\epsilon) &= -\epsilon^2 \Gamma_3(\epsilon) + \epsilon^3 [\Gamma_2(\epsilon)]^2, \end{aligned} \quad (2.12)$$

and so forth.

We are going to demonstrate that the limits

$$\lim_{\epsilon \rightarrow 0} B_n(\epsilon) = B_n \quad (2.13)$$

exist when $n=2$ and $n=3$. We conjecture that they exist for all n , but this has not yet been proved. The operators B_n are just the ones appearing in Eq. (1.5).

Thus, the limit of $\langle G(\epsilon) \rangle$ is

$$\lim_{\epsilon \rightarrow 0} \langle G(\epsilon) \rangle = [\rho B_2 + \rho^2 B_3 + \dots]^{-1}. \quad (2.14)$$

This result, in combination with Eq. (2.6), leads to the prescription for calculating σ that was stated in Eqs. (1.3) and (1.5).

The rest of the article is concerned with a detailed proof of the existence of the limits B_2 and B_3 .

3. FOURIER REPRESENTATION

Investigation of the dependence of the averaged resolvent operator $\langle G(\epsilon) \rangle$ on ρ and ϵ will be considerably simplified by use of a Fourier expansion in space.

We use a box of volume V , and periodic boundary conditions. Then the well-known set of orthonormal functions

$$V^{-N/2} \exp(i\mathbf{k}\mathbf{R}) \quad (3.1)$$

is suitable for Fourier expansions. Here \mathbf{R} denotes the

set $(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$ of all N positions, and \mathbf{k} is the set $(\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N)$ of all N wave vectors. When \mathbf{R} and \mathbf{k} appear without subscripts, they are understood to refer to these complete sets of variables. When they appear with subscripts, they refer to individual molecules.

The matrix representation in \mathbf{k} space of an operator \mathbf{O} in position space is

$$\mathbf{O}(\mathbf{k}|\mathbf{k}') = V^{-N} \int d\mathbf{R} e^{-i\mathbf{k}\mathbf{R}} \mathbf{O} e^{i\mathbf{k}'\mathbf{R}}. \quad (3.2)$$

4. FOURIER EXPANSION OF $\langle \mathbf{G}(\epsilon) \rangle$

After one more bit of notation, we are able to write out the Fourier expansion of $\langle \mathbf{G}(\epsilon) \rangle$.

Because the partial average $\langle \rangle$ requires integration over momenta as well as positions, these have to be accounted for separately. We divide the canonical ensemble distribution function into momentum and position dependent factors,

$$\prod_{j=1}^N \varphi(\mathbf{p}_j) \times \rho(\mathbf{R}), \quad (4.1)$$

where $\varphi(\mathbf{p})$ is the one particle momentum distribution defined in Eq. (1.4), and $\rho(\mathbf{R})$ is the configurational distribution function. The latter is related to the total potential energy $U(\mathbf{R})$ of the configuration \mathbf{R} by

$$\rho(\mathbf{R}) = \frac{\exp[-U(\mathbf{R})/kT]}{\int d\mathbf{R} \exp[-U(\mathbf{R})/kT]}. \quad (4.2)$$

The averaged resolvent operator is

$$\langle \mathbf{G}(\epsilon) \rangle = \int d\mathbf{R} \rho(\mathbf{R}) \int \prod_{j=2}^N \varphi(\mathbf{p}_j) d\mathbf{p}_j \mathbf{G}(\epsilon). \quad (4.3)$$

The Fourier components of the configurational distribution are

$$P(\mathbf{k}) = \int d\mathbf{R} e^{i\mathbf{k}\mathbf{R}} \rho(\mathbf{R}). \quad (4.4)$$

Note that

$$P(0) = 1 \quad (4.5)$$

because of the normalization of $\rho(\mathbf{R})$.

The Fourier expansion of $\langle \mathbf{G}(\epsilon) \rangle$ is therefore

$$\langle \mathbf{G}(\epsilon) \rangle = \sum_{\mathbf{k}} P(\mathbf{k}) \int \prod_{j=2}^N \varphi(\mathbf{p}_j) d\mathbf{p}_j \mathbf{G}(\mathbf{k}|0), \quad (4.6)$$

where

$$\mathbf{G}(\mathbf{k}|0) = V^{-N} \int d\mathbf{R} e^{-i\mathbf{k}\mathbf{R}} \mathbf{G}(\epsilon). \quad (4.7)$$

Only the special matrix element $\mathbf{G}(\mathbf{k}|0)$ appear. This is because $\mathbf{G}(\epsilon)$ operates only on functions that are

independent of position, so that we can set $\mathbf{k}'=0$ in the definition (3.2) of the matrix.

To simplify an already cumbersome notation we shall often leave out the ϵ ; resolvent operators, binary collision operators, etc., all depend on ϵ unless the contrary is stated explicitly.

5. BINARY COLLISION EXPANSION

Another mathematical device which makes the following discussion considerably simpler is use of the binary collision expansion of the resolvent operator. Siegert and Teramoto⁶ have given an elementary derivation of the binary collision expansion of the quantum mechanical resolvent operator. Extension of their derivation to classical mechanics is trivial. We therefore just write down the necessary formulas without further justification.

We restrict our discussion to a model gas described by the Hamiltonian

$$H = \sum_{j=1}^N \mathbf{p}_j^2/2m + \frac{1}{2} \sum_{i \neq j} \phi(\mathbf{R}_i - \mathbf{R}_j), \quad (5.1)$$

where the potential of interaction ϕ depends only on the positions of the indicated molecules. The potential is assumed to be short ranged. We exclude Coulomb or dipolar forces. To avoid essentially irrelevant complications we assume also that the potential is spherically symmetric.

For the Hamiltonian (5.1) the Liouville operator splits into two parts,

$$\mathbf{L} = \mathbf{L}_0 + \mathbf{L}_1,$$

$$\mathbf{L}_0 = -i \sum_{j=1}^N \frac{\mathbf{p}_j}{m} \cdot \frac{\partial}{\partial \mathbf{R}_j}, \quad (5.2)$$

$$\mathbf{L}_1 = -\frac{1}{2} i \sum_{i \neq j} \mathbf{F}_{ij} \cdot \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right),$$

where the force \mathbf{F}_{ij} is

$$\mathbf{F}_{ij} = -\frac{\partial}{\partial \mathbf{R}_i} \phi(\mathbf{R}_i - \mathbf{R}_j). \quad (5.3)$$

Throughout this article a greek subscript will denote a specific pair of molecules, and a sum over a greek subscript will denote a sum over all distinct pairs. Thus,

$$\mathbf{L}_1 = \sum_{\alpha} \mathbf{L}_{\alpha}. \quad (5.4)$$

When α denotes the pair (ij) , then \mathbf{L}_{α} is

$$\mathbf{L}_{\alpha} = -i \mathbf{F}_{ij} \cdot \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right). \quad (5.5)$$

The free-particle resolvent operator is \mathbf{G}_0 ,

$$\mathbf{G}_0 = (\epsilon - i\mathbf{L}_0)^{-1}. \quad (5.6)$$

⁶ A. J. F. Siegert and E. Teramoto, Phys. Rev. **110**, 1232 (1958).

Unless otherwise indicated, \mathbf{L}_0 and \mathbf{G}_0 include all N molecules.

The binary collision operator \mathbf{T}_α plays a central role. This is defined as the solution of the equation

$$\mathbf{T}_\alpha = -i\mathbf{L}_\alpha + i\mathbf{L}_\alpha \mathbf{G}_0 \mathbf{T}_\alpha. \quad (5.7)$$

The operator \mathbf{T}_α describes the interaction of the specified pair of molecules, all others moving independently as free particles. The following section contains a summary of some useful properties of \mathbf{T}_α .

Now the binary collision expansion can be written out in detail,

$$\begin{aligned} \mathbf{G} = & \mathbf{G}_0 - \sum_{\alpha} \mathbf{G}_0 \mathbf{T}_\alpha \mathbf{G}_0 + \sum_{\alpha} \sum_{\beta \neq \alpha} \mathbf{G}_0 \mathbf{T}_\alpha \mathbf{G}_0 \mathbf{T}_\beta \mathbf{G}_0 \\ & - \sum_{\alpha} \sum_{\beta \neq \alpha} \sum_{\gamma \neq \beta} \mathbf{G}_0 \mathbf{T}_\alpha \mathbf{G}_0 \mathbf{T}_\beta \mathbf{G}_0 \mathbf{T}_\gamma \mathbf{G}_0 + \dots \end{aligned} \quad (5.8)$$

Note that any exclusion from a sum, for example $\beta \neq \alpha$, is to be interpreted strictly: Only the pair α , and no other, is to be excluded. This means that a general term in the expansion may contain many more factors \mathbf{T}_α than molecules, e.g.,

$$\mathbf{G}_0 \mathbf{T}_{12} \mathbf{G}_0 \mathbf{T}_{13} \mathbf{G}_0 \mathbf{T}_{12} \mathbf{G}_0 \mathbf{T}_{13} \mathbf{G}_0 \mathbf{T}_{23} \mathbf{G}_0. \quad (5.9)$$

Terms of the form of (5.9) actually correspond to the expansion of a triple collision in terms of binary collision operators. Later in the article we take advantage of this correspondence.

We use the Fourier representation of the binary collision expansion. The free-particle resolvent operator is a diagonal matrix in this representation,

$$\begin{aligned} \mathbf{G}_0(\mathbf{k}|\mathbf{k}') &= g(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}'); \\ g(\mathbf{k}) &= (\epsilon - i\mathbf{p} \cdot \mathbf{k}/m)^{-1}. \end{aligned} \quad (5.10)$$

Here \mathbf{p} denotes the set $(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$ of all N momenta. The symbol $\delta(\mathbf{k}-\mathbf{k}')$ is the Kronecker delta. Thus, (5.8) is replaced by

$$\begin{aligned} \mathbf{G}(\mathbf{k}|0) &= \epsilon^{-1}\delta(\mathbf{k}) - \epsilon^{-1} \sum_{\alpha} g(\mathbf{k})\mathbf{T}_\alpha(\mathbf{k}|0) \\ &+ \epsilon^{-1} \sum_{\alpha} \sum_{\beta \neq \alpha} \sum_{\mathbf{k}'} g(\mathbf{k})\mathbf{T}_\alpha(\mathbf{k}|\mathbf{k}') \\ &\quad \times g(\mathbf{k}')\mathbf{T}_\beta(\mathbf{k}'|0) \end{aligned} \quad (5.11)$$

Note the appearance of $1/\epsilon$ in each term. These factors come from the \mathbf{G}_0 at the right of each term in Eq. (5.8).

6. BINARY COLLISION OPERATOR

Here we summarize some properties of the operator \mathbf{T}_α that are useful in the following discussion. A more detailed treatment is given in the Appendix.

Property (1). \mathbf{T}_α is proportional to $1/V$ in the limit $V \rightarrow \infty$.

Property (2). Let α be, for example, the specific

pair (12). Then

$$\mathbf{T}_{12}(\mathbf{k}|\mathbf{k}') \propto \delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}'_1 - \mathbf{k}'_2) \prod_{n=3}^N \delta(\mathbf{k}_n - \mathbf{k}'_n). \quad (6.1)$$

That is, \mathbf{T}_α is diagonal in all wave vectors not directly involved in the pair α , and it is proportional to a Kronecker delta expressing wave vector conservation for the interacting pair.

Property (3). This relates the operator \mathbf{T}_α to the Boltzmann collision operator. Let $J(\mathbf{p}_1)$ be some arbitrary function of \mathbf{p}_1 ; then

$$\begin{aligned} \lim_{\epsilon \rightarrow 0} \lim_{V \rightarrow \infty} V \mathbf{T}_{12}(0|0) \cdot J(\mathbf{p}_1) \\ = - \int_0^{2\pi} d\psi \int_0^\infty b db \frac{|\mathbf{p}_1 - \mathbf{p}_2|}{m} [J(\mathbf{p}'_1) - J(\mathbf{p}_1)], \end{aligned} \quad (6.2)$$

where (b, ψ) are the standard impact variables of a binary collision, and \mathbf{p}'_1 is the momentum of molecule 1 after the collision, expressed as a function of the impact variables (b, ψ) and the momenta \mathbf{p}_1 and \mathbf{p}_2 before the collision.

7. DEPENDENCE ON ρ AND ϵ

So far we have found a general expression (4.6) for the partially averaged resolvent operator in the Fourier representation; and we have presented in (5.11) the binary collision expansion in the same representation. Now we combine these equations.

For convenience we write

$$\langle \mathbf{G}(\epsilon) \rangle = \mathbf{t}_0 + \mathbf{t}_1 + \mathbf{t}_2 + \dots, \quad (7.1)$$

where \mathbf{t}_n is the sum of all terms from the binary collision expansion containing exactly n binary collision operators. It has been noted already that this does not correspond directly to a density expansion. In this section we work out the ρ and ϵ dependence of the first few terms in the \mathbf{t} expansion (7.1).

The first term \mathbf{t}_0 is easy:

$$\mathbf{t}_0 = 1/\epsilon. \quad (7.2)$$

Note that it is independent of density. We shall see that the rest of the expansion (7.1) is at least of the first order in density. Thus,

$$\mathbf{t}_0 = \Gamma_1(\epsilon) = 1/\epsilon, \quad (7.3)$$

as was asserted in Eq. (2.9).

The second term \mathbf{t}_1 is

$$\mathbf{t}_1 = -\epsilon^{-1} \sum_{\mathbf{k}} P(\mathbf{k}) \int \prod_2^N \varphi(\mathbf{p}_j) d\mathbf{p}_j \sum_{\alpha} g(\mathbf{k})\mathbf{T}_\alpha(\mathbf{k}|0). \quad (7.4)$$

This is to operate on functions of \mathbf{p}_1 only. Then the pair α must include molecule 1. (The reason is that \mathbf{T}_α contains derivatives with respect to the momenta of the pair α , and if this pair does not include molecule 1,

the result of operating on a function of \mathbf{p}_1 vanishes.) Since there are $N-1$ equivalent pairs containing molecule 1, we can replace \mathbf{T}_α by \mathbf{T}_{12} , and replace the sum over α by the factor $N-1$.

A consequence of the second property of \mathbf{T}_α , as stated in Eq. (6.1), is that many of the \mathbf{k}_n in the set \mathbf{k} must vanish. Throughout the article we use the following convention: Whenever components of \mathbf{k} are written down explicitly, all components that are omitted are understood to vanish. For example,

$$\mathbf{T}_{12}(\mathbf{k}|0) = \mathbf{T}_{12}(\mathbf{k}_1, \mathbf{k}_2|0). \quad (7.5)$$

When we take account of wave vector conservation also, we get

$$\mathbf{t}_1 = -\epsilon^{-1}(N-1) \sum_{\mathbf{k}_1} P(\mathbf{k}_1, -\mathbf{k}_1) \int d\mathbf{p}_2 \varphi(\mathbf{p}_2) \times \left[\epsilon - i(\mathbf{p}_1 - \mathbf{p}_2) \cdot \mathbf{k}_1 / m \right]^{-1} \mathbf{T}_{12}(\mathbf{k}_1, -\mathbf{k}_1|0). \quad (7.6)$$

Further simplifications of \mathbf{t}_1 arise from the singular behavior in the sum (7.6) of the point $\mathbf{k}_1=0$. To see why this point is unusual, we have to analyze the quantity $P(\mathbf{k}_1, -\mathbf{k}_1)$. This is the Fourier transform of the pair distribution function of the gas.

We define the pair distribution function by

$$\rho^{(2)}(\mathbf{R}_1, \mathbf{R}_2) = \int \cdots \int d\mathbf{R}_3 \cdots d\mathbf{R}_N \rho(\mathbf{R}). \quad (7.7)$$

A well-known result of the theory of equilibrium distribution functions is that, in a large system,

$$\rho^{(2)}(\mathbf{R}_1, \mathbf{R}_2) = (1/V^2)(1 + U_{12}), \quad (7.8)$$

where U_{12} is a short-ranged "cluster" function of the separation \mathbf{R}_{12} . In a large system U_{12} depends on density but not on volume. Because of the cluster property of U_{12} , the Fourier integral P is

$$P(\mathbf{k}_1, -\mathbf{k}_1) = \delta(\mathbf{k}_1) + \frac{1}{V} \int d\mathbf{R}_{12} e^{i\mathbf{k}_1 \mathbf{R}_{12}} U_{12}. \quad (7.9)$$

To save space we abbreviate

$$u^{(2)}(\mathbf{k}_1) = \int d\mathbf{R}_{12} e^{i\mathbf{k}_1 \mathbf{R}_{12}} U_{12}. \quad (7.10)$$

The significant point here is that $P(\mathbf{k}_1, -\mathbf{k}_1)$ splits naturally into two parts having differing asymptotic behavior as $V \rightarrow \infty$. The part that is independent of V is important only for the single value $\mathbf{k}_1=0$. (We are still dealing with a finite, though large, system; this is why the Kronecker delta appears, and not the Dirac delta.) The other part of P is of order $1/V$, and it is important only for \mathbf{k}_1 of the order of $1/a$, where a is the distance over which the cluster function U_{12} does not vanish.

Thus \mathbf{t}_1 separates into two parts,

$$\mathbf{t}_1 = -\frac{N-1}{V} \frac{1}{\epsilon^2} \int d\mathbf{p}_2 \varphi(\mathbf{p}_2) V \mathbf{T}_{12}(0|0) - \frac{N-1}{V} \frac{1}{\epsilon} \int d\mathbf{p}_2 \varphi(\mathbf{p}_2) \sum_{\mathbf{k}_1} \frac{1}{V} u^{(2)}(\mathbf{k}_1) \times \left[\epsilon - i \frac{\mathbf{p}_1 - \mathbf{p}_2}{m} \cdot \mathbf{k}_1 \right]^{-1} V \mathbf{T}_{12}(\mathbf{k}_1, -\mathbf{k}_1|0). \quad (7.11)$$

In a large system the sum over \mathbf{k}_1 can be approximated by an integral, according to the well-known formula

$$\sum_{\mathbf{k}_1} \rightarrow \frac{V}{(2\pi)^3} \int d^3\mathbf{k}_1.$$

In this way \mathbf{t}_1 becomes

$$\mathbf{t}_1 = -\frac{\rho}{\epsilon^2} \int d\mathbf{p}_2 \varphi(\mathbf{p}_2) V \mathbf{T}_{12}(0|0) - \frac{\rho}{\epsilon} \int d\mathbf{p}_2 \varphi(\mathbf{p}_2) \frac{1}{(2\pi)^3} \int d^3\mathbf{k}_1 u^{(2)}(\mathbf{k}_1) \times \left[\epsilon - i \frac{\mathbf{p}_1 - \mathbf{p}_2}{m} \cdot \mathbf{k}_1 \right]^{-1} V \mathbf{T}_{12}(\mathbf{k}_1, -\mathbf{k}_1|0). \quad (7.12)$$

A factor V has been kept with \mathbf{T}_{12} because, as was observed earlier, \mathbf{T}_{12} is proportional to $1/V$ in a large system.

This calculation shows that \mathbf{t}_1 is proportional to ρ , and that it depends on higher powers of ρ through the quantity $u^{(2)}(\mathbf{k}_1)$ in the second term.

The rest of the expansion (7.1) turns out to be of order ρ^2 and higher. Therefore the second term in the density expansion (2.7) is

$$\Gamma_2(\epsilon) = \lim_{\rho \rightarrow 0} \mathbf{t}_1 / \rho. \quad (7.13)$$

The two parts of \mathbf{t}_1 depend on ϵ in significantly different ways. The first part contains ϵ explicitly in the factor $1/\epsilon^2$, and implicitly in \mathbf{T}_{12} . The second part contains ϵ explicitly in the factor $1/\epsilon$, and in the denominator of the free-particle resolvent operator inside the integral over \mathbf{k} space, and also implicitly in \mathbf{T}_{12} .

In the limit $\epsilon \rightarrow 0$, the ϵ dependence of the free-particle resolvent operator inside the \mathbf{k} -space integral does not cause any divergence trouble. This ϵ is "protected" by the integration over \mathbf{k}_1 . The same can be said of the ϵ dependence of \mathbf{T}_{12} .

The extra $1/\epsilon$ in the first part of \mathbf{t}_1 actually originated in a free-particle resolvent operator, $[\epsilon - i(\mathbf{p}_1 - \mathbf{p}_2) \cdot \mathbf{k}_1 / m]^{-1}$, for the special value $\mathbf{k}_1=0$. Because of the special character of the pair distribution function, expressed in Eq. (7.9), this single point

carries as much weight, in the limit of a large system, as the rest of \mathbf{k} space.

Exactly the same procedure can be applied to the term \mathbf{t}_2 which contains two binary collision operators,

$$\mathbf{t}_2 = \epsilon^{-1} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{\alpha} \sum_{\beta \neq \alpha} P(\mathbf{k}) \int \prod_2^N \varphi(\mathbf{p}_j) d\mathbf{p}_j \\ \times g(\mathbf{k}) \mathbf{T}_\alpha(\mathbf{k}|\mathbf{k}') g(\mathbf{k}') \mathbf{T}_\beta(\mathbf{k}'|0). \quad (7.14)$$

As before, β is replaced by the pair (12), and the sum over β is replaced by the factor $N-1$. Also, all \mathbf{k}' except \mathbf{k}_1' and \mathbf{k}_2' vanish, so that $g(\mathbf{k}')$ and \mathbf{T}_{12} depend on only the momenta \mathbf{p}_1 and \mathbf{p}_2 . The pair α must then include either molecule 1 or molecule 2. There are $N-2$ equivalent choices for the other member of the pair: We choose $\alpha=(13)$ or $\alpha=(23)$. Property (2) of the binary collision operator is used again, this time to eliminate $\mathbf{k}_4, \mathbf{k}_5, \dots, \mathbf{k}_N$. Then \mathbf{t}_2 becomes

$$\mathbf{t}_2 = (N-1)(N-2)\epsilon^{-1} \sum_{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 \mathbf{k}_1' \mathbf{k}_2'} P(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \\ \times \int \int d\mathbf{p}_2 d\mathbf{p}_3 \varphi(\mathbf{p}_2) \varphi(\mathbf{p}_3) g(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \\ \times [\mathbf{T}_{13}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3 | \mathbf{k}_1', \mathbf{k}_2', 0) + \mathbf{T}_{23}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3 | \mathbf{k}_1', \mathbf{k}_2', 0)] \\ \times g(\mathbf{k}_1', \mathbf{k}_2') \mathbf{T}_{12}(\mathbf{k}_1', \mathbf{k}_2' | 0). \quad (7.15)$$

Conservation of wave vectors adds two conditions on the sums,

$$\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0, \\ \mathbf{k}_1' + \mathbf{k}_2' = 0.$$

In \mathbf{T}_{13} there is the further condition $\mathbf{k}_2 = \mathbf{k}_2'$; and in \mathbf{T}_{23} there is the condition $\mathbf{k}_1 = \mathbf{k}_1'$. Therefore, only two sums over wave vectors remain out of the five indicated in Eq. (7.15).

Now we discuss the Fourier transform $P(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$ of the triplet distribution function

$$\rho^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = \int \dots \int d\mathbf{R}_4 \dots d\mathbf{R}_N \rho(\mathbf{R}). \quad (7.16)$$

The expansion analogous to (7.8) is

$$\rho^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) \\ = (1/V^3)(1 + U_{12} + U_{13} + U_{23} + U_{123}), \quad (7.17)$$

which defines the cluster function U_{123} . The functions U_{12} , U_{13} , and U_{23} are the same as in (7.8). It is known that U_{123} is a short-ranged function of each of the intermolecular distances R_{12} , R_{13} , and R_{23} . Consequently the Fourier transform separates into four parts,

$$P(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) \\ = \delta(\mathbf{k}_1) \delta(\mathbf{k}_2) \delta(\mathbf{k}_3) + (1/V) [\delta(\mathbf{k}_1 + \mathbf{k}_2) \delta(\mathbf{k}_3) u^{(2)}(\mathbf{k}_2) \\ + \delta(\mathbf{k}_2 + \mathbf{k}_3) \delta(\mathbf{k}_1) u^{(2)}(\mathbf{k}_3) + \delta(\mathbf{k}_3 + \mathbf{k}_1) \delta(\mathbf{k}_2) u^{(2)}(\mathbf{k}_1)] \\ + (1/V^2) \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3) u^{(3)}(\mathbf{k}_2, \mathbf{k}_3). \quad (7.18)$$

The final term contains a quantity $u^{(3)}$, which is defined by

$$u^{(3)}(\mathbf{k}_2, \mathbf{k}_3) = \int d\mathbf{R}_{12} \int d\mathbf{R}_{13} e^{i\mathbf{k}_2 \mathbf{R}_{12}} e^{i\mathbf{k}_3 \mathbf{R}_{13}} U_{123}. \quad (7.19)$$

From each term of P we get a corresponding contribution to \mathbf{t}_2 in (7.15). In the limit of large V , the first term is

$$\mathbf{t}_{2,1} = \rho^2 \frac{1}{\epsilon^3} \int \int d\mathbf{p}_2 d\mathbf{p}_3 \varphi(\mathbf{p}_2) \varphi(\mathbf{p}_3) \\ \times [V \mathbf{T}_{13}(0|0) + V \mathbf{T}_{23}(0|0)] V \mathbf{T}_{12}(0|0). \quad (7.20)$$

This term is of exactly the second order in density. Its behavior for small ϵ is dominated by the factor $1/\epsilon^3$, which can be traced back to the Kronecker deltas in the V -independent part of $P(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$.

The $1/V$ terms of Eq. (7.18) give rise to a number of contributions to \mathbf{t}_2 . Instead of writing them all in detail, we pick a typical one for illustration. This comes from the following part of (7.18):

$$(1/V) \delta(\mathbf{k}_3 + \mathbf{k}_1) \delta(\mathbf{k}_2) u^{(2)}(\mathbf{k}_1),$$

and from the $\mathbf{T}_{13} \mathbf{T}_{12}$ combination in (7.15). After accounting for conservation of wave vectors and all the Kronecker deltas, we get for this contribution

$$\mathbf{t}_{2,2} = \frac{(N-1)(N-2)}{V} \frac{1}{\epsilon^2} \sum_{\mathbf{k}_1} u^{(2)}(\mathbf{k}_1) \int \int d\mathbf{p}_2 d\mathbf{p}_3 \varphi(\mathbf{p}_2) \varphi(\mathbf{p}_3) \\ \times [\epsilon - i(\mathbf{p}_1 - \mathbf{p}_2) \cdot \mathbf{k}_1/m]^{-1} \\ \times \mathbf{T}_{13}(\mathbf{k}_1, -\mathbf{k}_1|0) \mathbf{T}_{12}(0|0). \quad (7.21)$$

In the limit of a large system, the sum is replaced by an integral, and a factor V is associated with each \mathbf{T} . The result is

$$\mathbf{t}_{2,2} = \rho^2 \frac{1}{\epsilon^2} \frac{1}{(2\pi)^3} \int d^3 \mathbf{k}_1 u^{(2)}(\mathbf{k}_1) \int \int d\mathbf{p}_2 d\mathbf{p}_3 \varphi(\mathbf{p}_2) \varphi(\mathbf{p}_3) \\ \times [\epsilon - i(\mathbf{p}_1 - \mathbf{p}_2) \cdot \mathbf{k}_1/m]^{-1} \\ \times V \mathbf{T}_{13}(\mathbf{k}_1, -\mathbf{k}_1|0) V \mathbf{T}_{12}(0|0). \quad (7.22)$$

This expression, like all the other contributions to \mathbf{t}_2 , is formally of order ρ^2 , and it includes higher order dependence implicitly through the quantities $u^{(2)}(\mathbf{k}_1)$ and $u^{(3)}(\mathbf{k}_2, \mathbf{k}_3)$.

The ϵ dependence of this term is dominated by the factor $1/\epsilon^2$. All other appearances of ϵ are protected by integration over \mathbf{k} space. The other contributions to \mathbf{t}_2 from the $1/V$ terms in Eq. (7.18) contain either the factor $1/\epsilon^2$ or the factor $1/\epsilon$. We do not write them out. Finally, the $1/V^2$ term in Eq. (7.18) gives the factor

$1/\epsilon$. All other appearances of ϵ are protected by integration.

To sum up, \mathbf{t}_2 is of order ρ^2 . The contribution $\mathbf{t}_{2,1}$ diverges in the limit $\epsilon \rightarrow 0$ according to $1/\epsilon^3$, and all other contributions are less strongly divergent.

Next we investigate the higher terms $\mathbf{t}_3, \mathbf{t}_4, \dots$ in the expansion (7.1). In \mathbf{t}_3 there are three binary collision operators. One of these must include molecule 1; out of the $N-1$ possibilities for the other, we choose molecule 2. The second operator must include either molecule 1 or 2; out of the $N-2$ possibilities for the other, we choose molecule 3. The third operator must include either molecule 1 or 2 or 3, and another that can either be distinct, so we choose to call it molecule 4, or it can duplicate a molecule already mentioned. Evidently the terms involving four distinct molecules are of order ρ^3 .

But the third binary collision operator does not have to introduce a new molecule. In fact, we can get contributions to \mathbf{t}_3 of order ρ^2 from the four combinations

$$\mathbf{T}_{12}\mathbf{T}_{13}\mathbf{T}_{12}; \quad \mathbf{T}_{23}\mathbf{T}_{13}\mathbf{T}_{12}; \quad \mathbf{T}_{12}\mathbf{T}_{23}\mathbf{T}_{12}; \quad \mathbf{T}_{13}\mathbf{T}_{23}\mathbf{T}_{12}.$$

Let us work out the first of these combinations as an illustration. We call this one $\mathbf{t}_{3,1}$:

$$\begin{aligned} \mathbf{t}_{3,1} = & -(N-1)(N-2) \frac{1}{\epsilon} \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''} P(\mathbf{k}) \int \prod_2^N \varphi(\mathbf{p}_j) d\mathbf{p}_j \\ & \times g(\mathbf{k})\mathbf{T}_{12}(\mathbf{k}|\mathbf{k}')g(\mathbf{k}')\mathbf{T}_{13}(\mathbf{k}'|\mathbf{k}'') \\ & \times g(\mathbf{k}'')\mathbf{T}_{12}(\mathbf{k}''|0). \end{aligned} \quad (7.23)$$

Because three molecules are involved, one needs the Fourier transform of the triplet distribution, Eq. (7.18). The first (volume independent) term of P leads to the following result in the limit of a large system,

$$\begin{aligned} & -\rho^2 \frac{1}{\epsilon^2} \frac{1}{(2\pi)^3} \int d^3\mathbf{k}_1 \int \int d\mathbf{p}_2 d\mathbf{p}_3 \varphi(\mathbf{p}_2)\varphi(\mathbf{p}_3)\mathbf{T}_{12}(0|\mathbf{k}_1, -\mathbf{k}_1) \\ & \times \left[\epsilon - i \frac{\mathbf{p}_1 - \mathbf{p}_2}{m} \cdot \mathbf{k}_1 \right]^{-1} \mathbf{T}_{13}(\mathbf{k}_1, -\mathbf{k}_1, 0|\mathbf{k}_1, -\mathbf{k}_1, 0) \\ & \times \left[\epsilon - i \frac{\mathbf{p}_1 - \mathbf{p}_2}{m} \cdot \mathbf{k}_1 \right]^{-1} \mathbf{T}_{12}(\mathbf{k}_1, -\mathbf{k}_1|0). \end{aligned} \quad (7.24)$$

The ϵ dependence is dominated by the factor $1/\epsilon^2$.

The other parts of P lead to less singular behavior, being dominated by the factor $1/\epsilon$. The same holds for all the other combinations of three binary collision operators: In all cases, the most singular behavior is dominated by the factor $1/\epsilon^2$.

Higher order terms $\mathbf{t}_4, \mathbf{t}_5, \dots$ can be investigated systematically by the same method. The contributions from sequences of operators involving just three molecules are always of order ρ^2 . The most singular behavior is always dominated by the factor $1/\epsilon^2$.

8. CANCELLATION OF DIVERGENCES

We are now in a position to verify the existence of the operators

$$\begin{aligned} \mathbf{B}_2 &= \lim_{\epsilon \rightarrow 0} [-\epsilon^2 \mathbf{\Gamma}_2(\epsilon)], \\ \mathbf{B}_3 &= \lim_{\epsilon \rightarrow 0} [-\epsilon^2 \mathbf{\Gamma}_3(\epsilon) + \epsilon^3 [\mathbf{\Gamma}_2(\epsilon)]^2]. \end{aligned} \quad (8.1)$$

The operator $\mathbf{\Gamma}_2(\epsilon)$ is given by Eqs. (7.12) and (7.13). It is easy to see that the limit exists,

$$\mathbf{B}_2 = \lim_{\epsilon \rightarrow 0} \int d\mathbf{p}_2 \varphi(\mathbf{p}_2) V \mathbf{T}_{12}(0|0). \quad (8.2)$$

The structure of \mathbf{B}_2 can be clarified by recalling property (3) of the binary collision operator, Eq. (6.2). When \mathbf{B}_2 operates on a function $J(\mathbf{p}_1)$ of the momentum \mathbf{p}_1 , the result is

$$\begin{aligned} \mathbf{B}_2 \cdot J(\mathbf{p}_2) = & - \int d\mathbf{p}_2 \varphi(\mathbf{p}_2) \int_0^{2\pi} d\psi \int_0^\infty b db \frac{|\mathbf{p}_1 - \mathbf{p}_2|}{m} \\ & \times [J(\mathbf{p}_1') - J(\mathbf{p}_1)]. \end{aligned} \quad (8.3)$$

Thus the structure of \mathbf{B}_2 is directly related to that of the Boltzmann collision operator. This result is of course not new; it was obtained by Mori,⁴ though by a less rigorous method. Also, Montroll and Ward⁵ very nearly obtained it.

We cannot give so thoroughly worked out an expression for the operator \mathbf{B}_3 . But from the information at hand it is easy to demonstrate that the limit $\epsilon \rightarrow 0$ exists. We do this now.

The calculations of the last section show that $\mathbf{\Gamma}_3(\epsilon)$ consists of many terms. First, there is a contribution from \mathbf{t}_1 ; this arises because the quantity $u^{(2)}(\mathbf{k}_1)$, in the second term of Eq. (7.12), depends on density. However, when this term is multiplied by ϵ^2 , it vanishes in the limit $\epsilon \rightarrow 0$ because its behavior is dominated by $1/\epsilon$.

Another contribution to $\mathbf{\Gamma}_3(\epsilon)$ comes from $\mathbf{t}_{2,1}$, which is given by Eq. (7.20). We note that this contribution diverges in the limit, because $\mathbf{t}_{2,1}$ is of order $1/\epsilon^3$ and is multiplied by ϵ^2 . This divergence must be cancelled exactly if the theory is correct.

The other contributions to $\mathbf{\Gamma}_3(\epsilon)$ are all dominated either by $1/\epsilon^2$ or by $1/\epsilon$. Because they are to be multiplied by ϵ^2 , they give no trouble in the limit. Consequently,

$$\begin{aligned} \epsilon^2 \mathbf{\Gamma}_3(\epsilon) = & \frac{1}{\epsilon} \int \int d\mathbf{p}_2 d\mathbf{p}_3 \varphi(\mathbf{p}_2)\varphi(\mathbf{p}_3) \\ & \times [V \mathbf{T}_{13}(0|0) + V \mathbf{T}_{23}(0|0)] V \mathbf{T}_{12}(0|0) \\ & + \text{"other terms,"} \end{aligned} \quad (8.4)$$

where the "other terms," which we do not write down explicitly, are well behaved in the limit.

We note further that the contribution to the divergent term of Eq. (8.4) from the combination $\mathbf{T}_{23}\mathbf{T}_{12}$ vanishes.

The reason is that

$$\lim_{\epsilon \rightarrow 0} \int d\mathbf{p}_2 \int d\mathbf{p}_3 \varphi(\mathbf{p}_2) \varphi(\mathbf{p}_3) V \mathbf{T}_{23}(0|0) J(\mathbf{p}_2) \quad (8.5)$$

vanishes for any function $J(\mathbf{p}_2)$ of \mathbf{p}_2 . This can be proved by using the Boltzmann property of $\mathbf{T}_{23}(0|0)$, together with microscopic reversibility. Thus we have

$$\epsilon^2 \mathbf{\Gamma}_3(\epsilon) = \frac{1}{\epsilon} \int d\mathbf{p}_2 \int d\mathbf{p}_3 \varphi(\mathbf{p}_2) \varphi(\mathbf{p}_3) V \mathbf{T}_{13}(0|0) V \mathbf{T}_{12}(0|0) + \text{"other terms."} \quad (8.6)$$

Now we consider the other part of \mathbf{B}_3 , coming from $\epsilon^3 [\mathbf{\Gamma}_2(\epsilon)]^2$. Equations (7.12) and (7.13) give $\mathbf{\Gamma}_2(\epsilon)$. Therefore

$$\epsilon^3 [\mathbf{\Gamma}_2(\epsilon)]^2 = \frac{1}{\epsilon} \left[\int d\mathbf{p}_2 \varphi(\mathbf{p}_2) V \mathbf{T}_{12}(0|0) \right]^2 + \text{"more other terms,"} \quad (8.7)$$

where "more other terms" denotes terms that are well behaved in the limit. We note that Eq. (8.7) contains a term diverging as $1/\epsilon$. Because

$$\left[\int d\mathbf{p}_2 \varphi(\mathbf{p}_2) V \mathbf{T}_{12}(0|0) \right]^2 = \int \int d\mathbf{p}_2 d\mathbf{p}_3 \varphi(\mathbf{p}_2) \varphi(\mathbf{p}_3) V \mathbf{T}_{13}(0|0) V \mathbf{T}_{12}(0|0), \quad (8.8)$$

this term cancels out exactly the divergent part of $\epsilon^2 \mathbf{\Gamma}_3(\epsilon)$. This demonstrates that the limit

$$\mathbf{B}_3 = \lim_{\epsilon \rightarrow 0} \{ \text{"other terms"} + \text{"more other terms"} \} \quad (8.9)$$

exists.

9. THREE-BODY RESOLVENT FORM OF \mathbf{B}_3

The operator \mathbf{B}_3 can be expressed quite simply in terms of resolvent operators of systems containing exactly two or three molecules.

Let \mathbf{L}_2 and \mathbf{L}_3 be the Liouville operators for systems of two and three molecules in the volume V . When it is desirable to specify the pair in \mathbf{L}_2 this is done explicitly; e.g., when the pair is (13) we write $\mathbf{L}_2(13)$. Let the corresponding resolvent operators be

$$\begin{aligned} \mathbf{G}_2 &= (\epsilon - i\mathbf{L}_2)^{-1}, \\ \mathbf{G}_3 &= (\epsilon - i\mathbf{L}_3)^{-1}. \end{aligned} \quad (9.1)$$

Also, let $\langle ; 2 \rangle$ and $\langle ; 3 \rangle$ denote canonical averages, over all positions and all momenta except \mathbf{p}_1 , calculated with the Hamiltonians for two and three molecules in the volume V .

Then \mathbf{B}_3 is given exactly by

$$\mathbf{B}_3 = \lim_{\epsilon \rightarrow 0} \lim_{V \rightarrow \infty} V^2 \left\{ \frac{1}{2} \epsilon^2 \langle \mathbf{G}_3 - \mathbf{G}_2(12) - \mathbf{G}_2(13) + \mathbf{G}_0; 3 \rangle - \epsilon^3 \langle [\mathbf{G}_2 - \mathbf{G}_0; 2] \rangle^2 \right\}. \quad (9.2)$$

This assertion can be verified easily by performing the binary collision expansion directly on \mathbf{G}_2 and \mathbf{G}_3 . We shall not give the details here.

Equation (9.2) shows that the calculation of the first density correction to the standard kinetic theory expressions for transport coefficients of the form (1.2) is equivalent to the solution of a well-defined three-body problem. The problem is specifically to evaluate the operator $\langle \mathbf{G}_3; 3 \rangle$.

In conclusion, I wish to thank Dr. J. Weinstock for his assistance in exploring an earlier version of this theory.

APPENDIX

The Appendix is concerned with a demonstration⁷ of the three properties of the binary collision operator that were stated in Sec. 6.

The binary collision operator \mathbf{T}_α was defined by Eq. (5.7). In Fourier representation this equation is

$$\mathbf{T}_\alpha(\mathbf{k}|\mathbf{k}') = -i\mathbf{L}_\alpha(\mathbf{k}|\mathbf{k}') + i \sum_{\mathbf{k}''} L_\alpha(\mathbf{k}|\mathbf{k}'') g(\mathbf{k}'') \mathbf{T}_\alpha(\mathbf{k}''|\mathbf{k}'). \quad (A1)$$

The matrix representation of \mathbf{L}_{12} [for explicitness we assume that the pair is (12)] is as follows:

$$\begin{aligned} -i\mathbf{L}_{12}(\mathbf{k}|\mathbf{k}') &= -V^{-N} \int d\mathbf{R} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}} \mathbf{F}(\mathbf{R}_1 - \mathbf{R}_2) \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2} \right). \end{aligned} \quad (A2)$$

The integrations over $\mathbf{R}_3, \mathbf{R}_4, \dots$ can be performed immediately, leading to Kronecker deltas. The integral over \mathbf{R}_2 can be replaced by an integral over the relative coordinate $\mathbf{R}_{12} = \mathbf{R}_1 - \mathbf{R}_2$. This gives

$$\begin{aligned} -i\mathbf{L}_{12}(\mathbf{k}|\mathbf{k}') &= -V^{-1} \int d\mathbf{R}_{12} e^{i(\mathbf{k}_1 - \mathbf{k}_1')\mathbf{R}_{12}} \mathbf{F}(\mathbf{R}_1 - \mathbf{R}_2) \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2} \right) \\ &\quad \times \prod_{n=3}^N \delta(\mathbf{k}_n - \mathbf{k}_n') \delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_1' - \mathbf{k}_2'). \end{aligned} \quad (A3)$$

Note that \mathbf{L}_{12} is diagonal in all \mathbf{k}_n except \mathbf{k}_1 and \mathbf{k}_2 , and that it contains a Kronecker delta expressing conservation of wave vectors, $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_1' + \mathbf{k}_2'$.

Property (2) of the binary collision operator is that \mathbf{T}_α is proportional to just the same Kronecker deltas as \mathbf{L}_α . The demonstration is elementary: One substitutes the assumed form of \mathbf{T}_α , and the calculated expression (A3) for \mathbf{L}_α , into the defining Eq. (A1).

Property (1) of \mathbf{T}_α states that it is proportional to $1/V$ in all limit of a large system. This is proved as follows. Because of all the Kronecker deltas in (A3),

⁷ A different method of finding the same results has been given by I. Prigogine and F. Henin, *Bull. Classe Sci. Acad. Roy. Belg.* **43**, 814 (1957). The present derivation, which we believe to be simpler and more direct, is based on ideas of J. G. Kirkwood, *J. Chem. Phys.* **15**, 72 (1947).

the sum over \mathbf{k}'' in (A1) reduces to a sum over a single wave vector. In the limit of a large system this sum can be approximated by an integral,

$$\sum_{\mathbf{k}''} \rightarrow \frac{V}{(2\pi)^3} \int d^3\mathbf{k}''.$$

The extra factor V picked up here cancels the $1/V$ associated with \mathbf{L}_α in the right-hand side of (A1). Therefore Eq. (A1) becomes

$$\begin{aligned} V\mathbf{T}_\alpha(\mathbf{k}|\mathbf{k}') &= -iV\mathbf{L}_\alpha(\mathbf{k}|\mathbf{k}') + i \frac{1}{(2\pi)^3} \int d^3\mathbf{k}'' V\mathbf{L}_\alpha(\mathbf{k}|\mathbf{k}'') \\ &\quad \times g(\mathbf{k}'') V\mathbf{T}_\alpha(\mathbf{k}''|\mathbf{k}'), \end{aligned} \quad (\text{A4})$$

in a large system. It is now evident that $V\mathbf{T}_\alpha$ is independent of volume, because its defining equation, (A4), does not contain the volume.

Now we consider property (3), which relates $\mathbf{T}_{12}(0|0)$ to the Boltzmann collision operator.

Suppose that \mathbf{T}_{12} operates on a function $J(\mathbf{p}_1)$ of \mathbf{p}_1 only. Because \mathbf{L}_{12} is diagonal in all \mathbf{k}_n except \mathbf{k}_1 and \mathbf{k}_2 , and because we are interested in only the matrix element $\mathbf{T}_{12}(0|0)$, we can set $\mathbf{k}_n=0$ for $n=3, 4, \dots$; Eq. (A1) is thereby simplified to

$$\begin{aligned} \mathbf{T}_{12}(\mathbf{k}_1, \mathbf{k}_2 | \mathbf{k}_1', \mathbf{k}_2') &= -i\mathbf{L}_{12}(\mathbf{k}_1, \mathbf{k}_2 | \mathbf{k}_1', \mathbf{k}_2') + i \sum_{\mathbf{k}_1''} \sum_{\mathbf{k}_2''} \mathbf{L}_{12}(\mathbf{k}_1, \mathbf{k}_2 | \mathbf{k}_1'', \mathbf{k}_2'') \\ &\quad \times g(\mathbf{k}_1'', \mathbf{k}_2'') \mathbf{T}_{12}(\mathbf{k}_1'', \mathbf{k}_2'' | \mathbf{k}_1', \mathbf{k}_2'). \end{aligned} \quad (\text{A5})$$

The important point here is that the free-particle resolvent operator g now contains only the momenta of the pair (12), so that $\mathbf{T}_{12}(\mathbf{k}_1, \mathbf{k}_2 | \mathbf{k}_1', \mathbf{k}_2')$ is just the binary collision operator in a two-body system.

This observation shows us how to calculate $\mathbf{T}_{12}(0|0)$ more directly. Let \mathbf{L}_2 be the Liouville operator for the two-body system, and let

$$\mathbf{G}_2 = (\epsilon - i\mathbf{L}_2)^{-1} \quad (\text{A6})$$

be its resolvent operator. Then the general binary collision expansion, (5.8), terminates at the second term,

$$\mathbf{G}_2 = \mathbf{G}_0 - \mathbf{G}_0 \mathbf{T}_{12} \mathbf{G}_0. \quad (\text{A7})$$

This can be solved for \mathbf{T}_{12} ,

$$\mathbf{T}_{12} = -\mathbf{G}_0^{-1} (\mathbf{G}_2 - \mathbf{G}_0) \mathbf{G}_0^{-1}. \quad (\text{A8})$$

The result of taking matrix elements, and operating on $J(\mathbf{p}_1)$, is

$$\begin{aligned} \mathbf{T}_{12}(0|0) \cdot J(\mathbf{p}_1) &= -\epsilon^2 \int \int d\mathbf{R}_1 d\mathbf{R}_2 (\mathbf{G}_2 - \mathbf{G}_0) J(\mathbf{p}_1). \end{aligned} \quad (\text{A9})$$

Now we write this in the form of a time integral,

$$\begin{aligned} &= -\epsilon^2 \frac{1}{V^2} \int_0^\infty dt \exp(-\epsilon t) \int \int d\mathbf{R}_1 d\mathbf{R}_2 \\ &\quad \times [\exp(i\mathbf{L}_2) - \exp(i\mathbf{L}_0)] J(\mathbf{p}_1). \end{aligned} \quad (\text{A10})$$

But $\exp(i\mathbf{L}_2)$ is the time displacement operator for the two-body system, and $\exp(i\mathbf{L}_0)$ does not change $J(\mathbf{p}_1)$, so that

$$\begin{aligned} &= -\epsilon^2 \int_0^\infty dt e^{-\epsilon t} \frac{1}{V^2} \int \int d\mathbf{R}_1 d\mathbf{R}_2 \\ &\quad \times [J(\mathbf{p}_1(t)) - J(\mathbf{p}_1)]. \end{aligned} \quad (\text{A11})$$

Here $\mathbf{p}_1(t)$ is the momentum at time t , given the initial values $\mathbf{R}_1, \mathbf{R}_2, \mathbf{p}_1, \mathbf{p}_2$ of all positions and momenta.

If the initial configuration is such that no collision has occurred up to time t , then $J(\mathbf{p}_1(t)) = J(\mathbf{p}_1)$, and the integrand vanishes. Thus, the entire spatial integral in (A11) depends on the volume of configuration space such that a collision has occurred between times 0 and t . Clearly only the relative positions are important, so the integral over \mathbf{R}_1 just gives a factor V . The integral over the relative coordinate \mathbf{R}_{12} is most conveniently expressed in cylindrical coordinates. The z axis is the direction of the initial relative velocity of the pair, the radial coordinate is the familiar impact parameter b , and the cylindrical angle is ψ . Then a volume element is

$$d^3\mathbf{R}_{12} = dz b db d\psi.$$

For a collision to occur during t , z must be of the order of $|\mathbf{p}_1 - \mathbf{p}_2|t/m$. Therefore (A11) is approximately

$$\begin{aligned} &= -\epsilon^2 \int_0^\infty dt e^{-\epsilon t} \frac{1}{V} \int_0^{2\pi} d\psi \int_0^\infty b db \frac{|\mathbf{p}_1 - \mathbf{p}_2|}{m} \\ &\quad \times t [J(\mathbf{p}_1') - J(\mathbf{p}_1)], \end{aligned} \quad (\text{A12})$$

where \mathbf{p}_1' is the momentum after the collision is completed, as a function of the initial momenta and the impact variables (b, ψ) .

This result is not entirely precise: An error has been made in the estimate of the configurational volume because no account has been taken of incomplete collisions. The error is of no importance, however, for t very much larger than the duration of a collision; and when the limit $\epsilon \rightarrow 0$ is taken in (A12), only very large t are significant.

On performing the time integration,

$$\epsilon^2 \int_0^\infty dt e^{-\epsilon t} = 1,$$

we obtain the final result,

$$\begin{aligned} \lim_{\epsilon \rightarrow 0} \mathbf{T}_{12}(0|0) \cdot J(\mathbf{p}_1) &= -\frac{1}{V} \int_0^{2\pi} d\psi \int_0^\infty b db \frac{|\mathbf{p}_1 - \mathbf{p}_2|}{m} [J(\mathbf{p}_1') - J(\mathbf{p}_1)]. \end{aligned} \quad (\text{A13})$$