PHYSICAL REVIEW A VOLUME 2, NUMBER 6 DECEMBER 1970

Three-Particle Collisions in a Gas of Hard Spheres

W. R. Hoegy
Laboratory for Planetary Atmospheres, Goddard Space Flight Center, Greenbelt, Maryland 20771

and

J. V. Sengers
Institute for Molecular Physics, University of Maryland, College Park, Maryland 20742
(Received 30 July 1970)

The triple-collision integrals which determine the first density correction to the transport coefficients are derived for a gas of hard spheres using the binary-collision expansion. This expansion provides a convenient technique for classifying the contributions in terms of sequences of successive binary collisions between three molecules. Such sequences contain both interacting and noninteracting collisions. It is demonstrated that for three hard spheres all sequences terminate after four successive collisions, independent of the interacting or noninteracting nature of the collisions. As a consequence, the collision integrals are related to a limited number of sequences with three and four collisions only. It is shown that equivalent results are obtained from the surface-integral form of the triple-collision operator, derived earlier by Green and Sengers.

I. INTRODUCTION

Nonequilibrium statistical mechanics predicts that the first density correction to the transport coefficients of a gas can be represented by a term linear in the density n. That is, the thermal conductivity λ and the shear viscosity η can be written as[1,2]

$$\lambda = \lambda_0 + \lambda_1 n + \cdots \quad , \qquad (1.1)$$
$$\eta = \eta_0 + \eta_1 n + \cdots \quad .$$

As is well known, the transport coefficients λ_0 and η_0 in the low-density limit are determined by the solution of the linearized Boltzmann equation. The Boltzmann equation takes into account only uncorrelated binary collisions. The transport coefficients λ_0 and η_0 can be expressed in terms of collision integrals which involve the velocities of two molecules before and after a binary collision.

In the past decade many investigators have derived the integral equation for the coefficients λ_1 and η_1 of the first density correction. For a discussion and a bibliography we refer to a recent review article by Ernst, Haines, and Dorfman.[1] This integral equation leads to collision integrals for the coefficients λ_1 and η_1 that involve the effects of collisions between three molecules. For a gas of hard spheres it was shown by Green[3] and Sengers[4] that the triple-collision integrals can be reduced to a surface-integral form, analogous to the binary-collision integrals determining λ_0 and η_0. That is, the integrals could be expressed in terms of the initial and final velocities of three particles in specified sequences of successive correlated collisions. Thus, the problem was completely reduced to a study of the dynamics of three spheres.

In the earlier formulation,[3,4] the dynamics of the molecules was described with the aid of a time-displacement or streaming operator $S_{-t}(1, \ldots, l)$. The operator $S_{-t}(1, \ldots, l)$ is a substitution operator which replaces the phase variables of l particles at a given time by their values at a time t earlier. As an alternative approach several investigators have proposed to describe the dynamics using a binary-collision expansion.[5]

Here we reconsider the reduction of the triple-collision integrals for a gas of hard spheres from the point of view of the binary-collision expansion. This expansion enables us to decompose the triple-collision integrals into a series of terms consisting of increasing numbers of successive binary collisions. The decomposition, thus obtained, differs in appearance from the decomposition derived earlier by the surface-integral method.[4] Nevertheless, we shall show in Sec. V that the two decompositions are completely equivalent. One of the advantages of the binary-collision expansion is that certain properties of the triple-collision operator, such as its symmetry, can be readily demonstrated. More importantly, we shall use the binary-collision expansion formalism to eliminate those collision sequences that cannot occur according to the laws of mechanics.

The generalization of the Boltzmann equation to include the effect of three-particle collisions is obtained from a cluster expansion of the Liouville operator. As a consequence, the collision sequences involve not only interacting collisons, but also noninteracting collisions. In the latter type of collision the particles pass through one another instead of exchanging their momenta. We shall prove that all sequences of binary collisions between three hard spheres terminate after four successive collisions. Several sequences of three and four successive collisions can also be ruled out as being physically impossible. Thus the triple-collision integrals will be decomposed into a limited number of sequences with three and four collisions only.

II. TRIPLE-COLLISION OPERATOR

A formal solution of the integral equation which describes the effect of triple collisions yields for the coefficients λ_1 and η_1[6,7]

$$\lambda_1 = (1/3kT^2)\int d\vec{p}_1 \vec{A}(\vec{p}_1)\cdot I_3\vec{A}(\vec{p}_1)\ ,$$
$$\eta_1 = (1/10kT)\int d\vec{p}_1 \overleftrightarrow{B}(\vec{p}_1) : I_3 \overleftrightarrow{B}(\vec{p}_1). \tag{2.1}$$

The functions $\vec{A}(\vec{p}_1)$ and $\overleftrightarrow{B}(\vec{p}_1)$ which are functions of the momentum $\vec{p}_1$ only, represent the solutions of the linearized Boltzmann equations

$$I_2\vec{A}(\vec{p}_1) = -\phi(1)\left(\frac{p_1^2}{2m} - \frac{5}{2}kT\right)\frac{\vec{p}_1}{m}\ ,$$
$$I_2\overleftrightarrow{B}(\vec{p}_1) = -\phi(1)\frac{\vec{p}_1^{\,0}\vec{p}_1}{m}\ . \tag{2.2}$$

The mass of a molecule is denoted by m and $\phi(i)$ is the normalized Maxwell distribution function

$$\phi(i) = (2\pi mkT)^{-3/2}\, e^{(-p_i^2/2mkT)}\ . \tag{2.3}$$

The tensor $\vec{p}_1^{\,0}\vec{p}_1$ is the traceless tensor associated with with the dyadic $\vec{p}_1\vec{p}_1$. The operators I_2 and I_3 are linearized binary- and triple-collision integral operators. In the cluster expansion method developed by Green[8] and Cohen,[9] these operators can be related to the streaming operators S_{-t},

$$I_2 = \int dx_2\, \theta_{12}\, \mathcal{S}(12)\phi(1)\phi(2)\sum_{i=1}^{2} P_{1i}\ , \tag{2.4}$$

$$I_3 = \int dx_2\, dx_3 \theta_{12}\{\mathcal{S}(123) - \mathcal{S}(12)\mathcal{S}(13) - \mathcal{S}(12)\mathcal{S}(23) + \mathcal{S}(12)\}\phi(1)\phi(2)\phi(3)\sum_{i=1}^{3} P_{1i}, \tag{2.5}$$

with

$$\mathcal{S}(1,\ldots,l) = \lim_{t\to\infty} S_{-t}(1,\ldots,l)\prod_{i=1}^{l} S_{+t}(i). \tag{2.6}$$

We use the notation dx_i to indicate an integration over the momentum $\vec{p}_i$ and the position $\vec{r}_i$ of particle i. The permutation operator P_{1i} interchanges the indices 1 and i. The operator θ_{ij} is a differential operator

$$\theta_{ij} = \frac{\partial U_{ij}}{\partial \vec{r}_i}\cdot\frac{\partial}{\partial \vec{p}_i} + \frac{\partial U_{ij}}{\partial \vec{r}_j}\cdot\frac{\partial}{\partial \vec{p}_j}\ , \tag{2.7}$$

where U_{ij} is the pair potential of particles i and j.

Equation (2.5) was the starting point of the previous reduction of the triple-collision operator.[4,6] However, for the binary-collision expansion it is more convenient to use the ϵ method, first introduced by Zwanzig.[10] This method uses resolvent operators $G(1,\ldots,l)$ which are the Laplace transforms of the streaming operators

$$G(1,\ldots,l) = \int_0^\infty dt\, e^{-\epsilon t} S_{-t}(1,\ldots,l)$$
$$= [\epsilon + \mathcal{H}(1,\ldots,l)]^{-1}, \tag{2.8}$$

where $\mathcal{H}(1,\ldots,l)$ is the Liouville operator for the l particles

$$\mathcal{H}(1,\ldots,l) = \mathcal{H}_0(1,\ldots,l) - \sum_{1\le i<j\le l}\sum \theta_{ij} \tag{2.9}$$

and

$$\mathcal{H}_0(1,\ldots,l) = \sum_{i=1}^{l}\frac{\vec{p}_i}{m}\cdot\frac{\partial}{\partial\vec{r}_i}\ . \tag{2.10}$$

We also need the resolvent operator $G_0(1,\ldots,l)$ which generates the free streaming of the particles

$$G_0(1,\ldots,l) = [\epsilon + \mathcal{H}_0(1,\ldots,l)]^{-1}\ . \tag{2.11}$$

The equivalence of the two methods to describe the first density correction was demonstrated for hard spheres by Ernst, Haines, and Dorfman.[1] Using their notation, one finds

$$I_2 = \lim_{\epsilon\to 0}\epsilon B_2(\epsilon)\ , \tag{2.12}$$

$$I_3 = \lim_{\epsilon\to 0}\epsilon B_3(\epsilon)\ , \tag{2.13}$$

where[11]

$$\epsilon B_2(\epsilon) = \int dx_2 \theta_{12} G(12)\, W(12)\, G_0^{-1}(12) \times\phi(1)\phi(2)\sum_{i=1}^{2} P_{1i}, \tag{2.14}$$

$$\begin{aligned}\epsilon B_3(\epsilon) = \int dx_2\, dx_3 \{&\theta_{12}G(12)(\theta_{13}+\theta_{23})G(123)\,W(123)\\ &+\theta_{12}G(12)g(12;3)\\ &-\theta_{12}G(12)\,W(12)\,\theta_{13}G(13)\,W(13)\\ &-\theta_{12}G(12)\,W(12)\,\theta_{23}G(23)\,W(23)\}\\ &\times G_0^{-1}(123)\phi(1)\phi(2)\phi(3)\sum_{i=1}^{3}P_{1i}\ .\end{aligned} \tag{2.15}$$

The statistical factors $W(1,\ldots,l)$,

$$W(1,\ldots,l) = \prod_{1\le i<j\le l}(1+f_{ij})\ , \tag{2.16}$$

are related to the Mayer functions f_{ij},

$$f_{ij} = e^{-U_{ij}/kT} - 1. \tag{2.17}$$

The function $g(12;3)$ is given by

$$g(12;3) = W(12)f_{13}f_{23}\ . \tag{2.18}$$

It is understood that the limit $\epsilon\to 0$ is taken after all other operations have been performed.

The self-diffusion coefficient can be expressed in terms of the same operators, provided one deletes the permutation operators P_{1i}.

The first term of $B_3(\epsilon)$ can be simplified using the relation

$$\theta_{12}G(12)(\theta_{13}+\theta_{23})G(123) = \theta_{12}G(123)-\theta_{12}G(12). \qquad (2.19)$$

We find it convenient to symmetrize the operator $B_3(\epsilon)$ so that all three particles play the same role. For this purpose we interchange the integration variables 2 and 3. Furthermore, we add the corresponding term starting with θ_{23}, since they vanish upon integration over $\vec{p}_2$ and $\vec{p}_3$. Thus we obtain

$$\epsilon B_3(\epsilon)=\tfrac{1}{2}\int dx_2 dx_3\, T(123,\epsilon) \times\phi(1)\phi(2)\phi(3)\sum_{i=1}^{3}P_{1i} \qquad (2.20)$$

with

$$T(123,\epsilon) = \Big\{(\theta_{12}+\theta_{13}+\theta_{23})G(123)W(123)-\sum_{\alpha}\theta_\alpha G(\alpha)W(\alpha) -\sum_{\alpha_1\neq\alpha_2}\sum\theta_{\alpha_1}G(\alpha_1)W(\alpha_1) \times[f_{\alpha_2}+\theta_{\alpha_2}G(\alpha_2)W(\alpha_2)]\Big\}G_0^{-1}(123). \qquad (2.21)$$

The summations are to be taken over the three pairs 12, 13, and 23.

We express the θ_{ij} operators in terms of resolvent operators

$$\theta_{12}+\theta_{13}+\theta_{23}=G_0^{-1}(123)-G^{-1}(123), \qquad (2.22)$$

$$\theta_{12}=G_0^{-1}(12)-G^{-1}(12)=G_0^{-1}(123)-G^{-1}(12), \qquad (2.23)$$

so that

$$T(123,\epsilon)=\Big\{G_0^{-1}(G(123)-G_0)W(123) -\sum_{\alpha}G_0^{-1}(G(\alpha)-G_0)W(\alpha) -\sum_{\alpha_1\neq\alpha_2}\sum G_0^{-1}(G(\alpha_1)-G_0)W(\alpha_1) \times[f_{\alpha_2}+G_0^{-1}(G(\alpha_2)-G_0)W(\alpha_2)]\Big\}G_0^{-1}. \qquad (2.24)$$

From now on we omit the arguments of the free streaming operator G_0.

It is our purpose to decompose this operator into a sum of operators each of which transforms the initial momenta of the particles to the momenta after a specific sequence of collisions. The equations quoted in this section apply to molecules interacting with any spherical symmetric short-range repulsive pair potential. The remainder of this paper is specifically concerned with a gas of hard-sphere molecules.

III. BINARY-COLLISION EXPANSION

A detailed study of the binary-collision expansion for the case of hard spheres was recently presented by Ernst, Dorfman, Hoegy, and Van Leeuwen.[5] The resolvent operators $G(1,\ldots,l)$ can be related to binary-collision operators by

$$G(1,\ldots,l)W(1,\ldots,l) =[G_0+G_0\textstyle\sum_\alpha \overline{T}_\alpha G(1,\ldots,l)]W(1,\ldots,l), \qquad (3.1)$$

$$W(1,\ldots,l)G(1,\ldots,l) =W(1,\ldots,l)[G_0+G(1,\ldots,l)\textstyle\sum_\alpha T_\alpha G_0]. \qquad (3.2)$$

While $G(1,\ldots,l)$ and $W(1,\ldots,l)$ do commute, the binary-collision operators to be used depend on whether the overlap exclusion is written to the left or to the right.

The binary-collision operators T_α and $\overline{T}_\alpha$ contain an interacting and a noninteracting term[12]

$$T_\alpha=T^i_\alpha+T^n_\alpha, \qquad (3.3)$$

$$\overline{T}_\alpha=T^i_\alpha+\overline{T}^n_\alpha. \qquad (3.4)$$

To describe the effect of the binary-collision operators we consider the parameters that specify a collision between two hard spheres 1 and 2 with diameter σ (see Fig. 1). An impact vector $\vec{b}_{12}$ is defined by

$$\vec{b}_{12}=\vec{r}_{12}-\vec{r}_{12}\cdot\hat{v}_{12}\hat{v}_{12}, \qquad (3.5)$$

where $\vec{r}_{12}=\vec{r}_1-\vec{r}_2$ is the relative position, $\vec{v}_{12}=\vec{v}_1-\vec{v}_2$ the relative velocity, and $\hat{v}_{12}$ the unit vector in the direction of $\vec{v}_{12}$. For $b_{12}<\sigma$, we define a perihelion vector

$$\sigma\vec{k}=\vec{b}_{12}+\hat{v}_{12}(\sigma^2-b_{12}^2)^{1/2} \qquad (3.6)$$

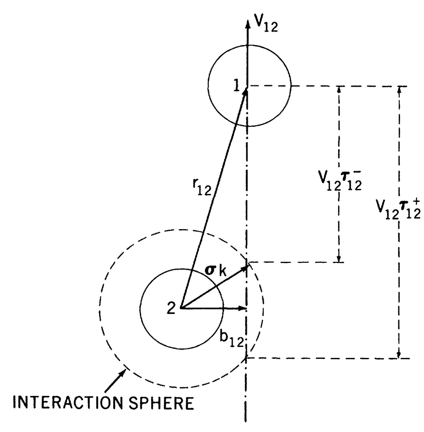

FIG. 1. Geometry of a collision between two hard spheres.

and two contact times

$$\tau_{12}^{\pm} = [\vec{r}_{12} \cdot \hat{v}_{12} \pm (\sigma^2 - b_{12}^2)^{1/2}]/v_{12} . \quad (3.7)$$

The operators T_{12} and $\overline{T}_{12}$ are defined by[5]

$$T_{12}^{i} = \theta(\sigma - b_{12})\,\delta(\tau_{12}^{-})\mathcal{R}_{12} , \quad (3.8)$$

$$T_{12}^{n} = -\,\theta(\sigma - b_{12})\,\delta(\tau_{12}^{-}) , \quad (3.9)$$

$$\overline{T}_{12}^{n} = -\,\theta(\sigma - b_{12})\,\delta(\tau_{12}^{+}) , \quad (3.10)$$

where $\theta(x) = 1$ for $x > 0$, $\theta(x) = 0$ for $x < 0$, and $\delta(\tau)$ is the Dirac δ function. The operator $\mathcal{R}_{12}$ transforms the velocities $\vec{v}_1$ and $\vec{v}_2$ into the velocities $\vec{v}_1'$ and $\vec{v}_2'$ before the collision[13]

$$\mathcal{R}_{12}\vec{v}_1 = \vec{v}_1' = \vec{v}_1 - \vec{v}_{12} \cdot \vec{k}\vec{k} ,$$
$$\mathcal{R}_{12}\vec{v}_2 = \vec{v}_2' = \vec{v}_2 + \vec{v}_{12} \cdot \vec{k}\vec{k} . \quad (3.11)$$

A product of T and G_0 operators can be interpreted in terms of a collision sequence when read from left to right. For example, Fig. 2 shows the collision sequences associated with the four terms of $T_{12}G_0T_{13}$. Since we consider backward streaming, the diagrams are to be read from top to bottom. The operators T_{12}^{i} and T_{12}^{n} are only different from zero when the particles 1 and 2 are in contact at the top of the diagram. The terms in $T_{12}G_0T_{13}$ require that the conditions for two successive collisions be satisfied, such that $\tau_{12}^{-} < \tau_{13}^{-}$. (Note that $T_{12}^{n}G_0T_{13}^{i}$ and $T_{12}^{n}G_0T_{13}^{n}$ may include situations where 1 and 3 are colliding while particles 1 and 2 are still overlapping.) For $\overline{T}_{12}^{n}$ and $\overline{T}_{13}^{n}$ the time ordering refers to the contact time τ_{12}^{+} and τ_{13}^{+}, respectively. The

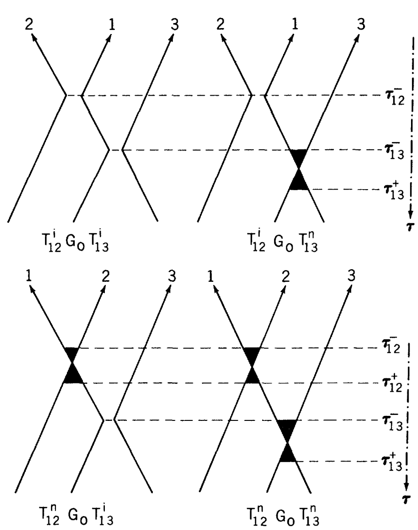

FIG. 2. The four collision sequences associated with the four terms of $T_{12}G_0T_{13}$. The lines represent particle trajectories and the shaded areas indicate regions where two particles overlap. Diagrams are to be read from top to bottom.

operator product transforms the velocities of the particles at the top of the diagram to the initial velocities at the bottom of the diagram. A minus sign is associated with each noninteracting collision.

We mention some relationships between the T operators and the Mayer functions,

$$f_\alpha T_\alpha = 0, \quad \overline{T}_\alpha f_\alpha = 0 \quad (3.12)$$

and

$$T_\alpha f_\beta = f_\beta T_\alpha, \quad \overline{T}_\alpha f_\beta = f_\beta \overline{T}_\alpha \quad (\alpha \neq \beta). \quad (3.13)$$

We shall also need the commutation relation

$$G_0 f_\alpha - f_\alpha G_0 = G_0(T_\alpha - \overline{T}_\alpha)G_0 = G_0(T_\alpha^n - \overline{T}_\alpha^n)G_0. \quad (3.14)$$

For a proof of these relations we refer to Ernst *et al.*[5]

The binary-collision expansion is generated by successive iteration of Eqs. (3.1) and (3.2). For the two-particle resolvent operator, this procedure terminates after one iteration,

$$G(\alpha)\,W(\alpha) = G_0 + G_0\overline{T}_\alpha G_0 , \quad (3.15)$$

$$W(\alpha)\,G(\alpha) = G_0 + G_0\,T_\alpha G_0 , \quad (3.16)$$

since[14]

$$T_\alpha G_0 T_\alpha = 0, \quad \overline{T}_\alpha G_0 T_\alpha = 0, \quad \overline{T}_\alpha G_0 \overline{T}_\alpha = 0. \quad (3.17)$$

Substitution of (2.23) and (3.15) into the expression (2.14) for $\epsilon B_2(\epsilon)$ yields

$$\epsilon B_2(\epsilon) = \int dx_2\, \overline{T}_{12}\,\phi(1)\,\phi(2) \sum_{i=1}^{2} P_{i1} , \quad (3.18)$$

which reduces to the familiar form of the Boltzmann collision operator.

Similarly, we substitute Eq. (3.1) for $l = 3$ and Eq. (3.15) into the expression (2.24) for the triple-collision operator

$$T(123, \epsilon) = [\sum_\alpha \overline{T}_\alpha\, G(123)\, W(123) - \sum_\alpha \overline{T}_\alpha G_0 - \sum\sum_{\alpha_1 \neq \alpha_2} \overline{T}_{\alpha_1}\, G_0(f_{\alpha_2} + \overline{T}_{\alpha_2} G_0)]\, G_0^{-1} . \quad (3.19)$$

As mentioned earlier, for a dynamical interpretation we read the terms from left to right. Therefore, we prefer to bring the overlap conditions $W(123)$ and f_{α_2} to the left. Using the commutator (3.14) we obtain

$$T(123, \epsilon) = [\sum_\alpha \overline{T}_\alpha W(123) G(123) - \sum_\alpha \overline{T}_\alpha G_0 - \sum\sum_{\alpha_1 \neq \alpha_2} \overline{T}_{\alpha_1}(f_{\alpha_2} G_0 + G_0 T_{\alpha_2} G_0)]\, G_0^{-1}. \quad (3.20)$$

In order to express $T(123, \epsilon)$ as a sum of terms that are convergent individually, we iterate (3.2) twice,

$$W(123)G(123) = W(123)\,[G_0 + \sum_\alpha G_0 T_\alpha G_0 + G(123)$$

$$\times \sum_{\alpha_1 \neq \alpha_2}\sum T_{\alpha_1} G_0 T_{\alpha_2} G_0] \,, \tag{3.21}$$

so that

$$T(123,\epsilon) = \sum_{\substack{\alpha \\ (\alpha\neq\beta\neq\gamma\neq\alpha)}} f_\beta f_\gamma \overline{T}_\alpha + \sum_{\substack{\alpha_1\neq\alpha_2 \\ (\alpha_1\neq\beta\neq\alpha_2)}}\sum f_\beta \overline{T}_{\alpha_1} G_0 T_{\alpha_2} + \sum_{\alpha_1\neq\alpha_2\neq\alpha_3}\sum\sum \overline{T}_{\alpha_1} W(123)\, G(123)\, T_{\alpha_2} G_0 T_{\alpha_3} \,. \tag{3.22}$$

In Equation (3.22) we have indicated explicitly that the indices in two successive T operators refer to different pairs of particles. However, this condition is also satisfied automatically as a result of (3.17). Each term in (3.22) involves at least three conditions on the phases of the particles. In the first term $f_\beta f_\gamma \overline{T}_\alpha$, two pairs of particles overlap; we refer to this term as the double overlap term. The double overlap term is the contribution according to the theory of Enskog[15]: It is the Boltzmann collision operator associated with one pair of particles multiplied with the excluded volume of the third particle.[4] The second sum in (3.22) is a collection of terms that contain a single overlap condition. However, it should be remarked that the products of three T operators also include single overlap configurations implicitly.[16]

The triple-collision operator can be expanded into sequences with increasing numbers of successive correlated collisions by further iteration of (3.21). Noting that

$$\overline{T}_{\alpha_1} W(123)\, G_0 T_{\alpha_2} = (1+f_\beta)\, \overline{T}_{\alpha_1} G_0 T_{\alpha_2} \,, \quad (\alpha_1 \neq \beta \neq \alpha_2) \tag{3.23}$$

we obtain

$$T(123,\epsilon) = \sum_{s=3}^{\infty} T^{(s)}(123,\epsilon) \,, \tag{3.24}$$

with

$$T^{(3)}(123,\epsilon) = \sum_{\substack{\alpha \\ (\alpha\neq\gamma\neq\gamma\neq\alpha)}} f_\beta f_\gamma \overline{T}_\alpha + \sum_{\substack{\alpha_1\neq\alpha_2 \\ (\alpha_1\neq\beta\neq\alpha_2)}}\sum f_\beta \overline{T}_{\alpha_1} G_0 T_{\alpha_2} + \sum_{\substack{\alpha_1\neq\alpha_2\neq\alpha_3 \\ (\alpha_1\neq\beta\neq\alpha_2)}}\sum\sum (1+f_\beta)\, \overline{T}_{\alpha_1} G_0 T_{\alpha_2} G_0 T_{\alpha_3} \,, \tag{3.25}$$

$$T^{(4)}(123,\epsilon) = \sum_{\substack{\alpha_1\neq\alpha_2\neq\alpha_3\neq\alpha_4 \\ (\alpha_1\neq\beta\neq\alpha_2)}}\sum\sum\sum (1+f_\beta)\, \overline{T}_{\alpha_1} G_0 T_{\alpha_2} \times G_0 T_{\alpha_3} G_0 T_{\alpha_4} \,, \tag{3.26}$$

$$T^{(5)}(123,\epsilon) = \sum_{\substack{\alpha_1\neq\alpha_2\neq\alpha_3\neq\alpha_4\neq\alpha_5 \\ (\alpha_1\neq\beta\neq\alpha_2)}}\sum\sum\sum\sum (1+f_\beta)\, \overline{T}_{\alpha_1} G_0 T_{\alpha_2} \times G_0 T_{\alpha_3} G_0 T_{\alpha_4} G_0 T_{\alpha_5} \,, \tag{3.27}$$

etc.

In the derivation of (3.24) we have not used explicitly the fact that the operator $T(123,\epsilon)$ operates on a function of the momenta alone. We shall show in Sec. V that with the latter restriction, $T^{(3)}(123,\epsilon)$ can also be written in the more compact form

$$T^{(3)}(123,\epsilon) = \sum_{\substack{\alpha_1\neq\alpha_2\neq\alpha_3 \\ (\alpha_1\neq\beta\neq\alpha_2)}}\sum\sum (1+f_\beta)\, T_{\alpha_1} G_0 T_{\alpha_2} G_0 T_{\alpha_3} . \tag{3.28}$$

Each term $T^{(s)}(123,\epsilon)$ in the expansion (3.24) corresponds to sequences of s correlated binary collisions between the three particles.

IV. REDUCTION OF TRIPLE-COLLISION OPERATOR

A decision as to when the expansion (3.24) terminates requires a study of the dynamics of three particles. We first mention some rules that are immediate consequences of the definition of the T operators

$$\overline{T}_\alpha G_0 T_\beta^n G_0 T_\alpha = 0 \,, \qquad T_\alpha G_0 T_\beta^n G_0 T_\alpha = 0 \,. \tag{4.1}$$

These equations express the fact that a pair of particles cannot recollide after a collision, unless the trajectory of at least one of the two particles is deflected by an interacting collision with the third particle:

$$\overline{T}_{\alpha_1} G_0 T_{\alpha_2}^n G_0 T_{\alpha_3}^n G_0 T_{\alpha_4} = 0 \,, \qquad T_{\alpha_1} G_0 T_{\alpha_2}^n G_0 T_{\alpha_3}^n G_0 T_{\alpha_4} = 0 \,. \tag{4.2}$$

The reason for (4.2) is that in the given sequence none of the pairs is aimed to collide after the first three collisions.

We list a number of lemmas, each of which expresses the impossibility of a specific collision sequence for three hard spheres.

Lemma 1: $\overline{T}_{\alpha_1} G_0 T_{\alpha_2}^i G_0 T_{\alpha_3}^i G_0 T_{\alpha_4}^i G_0 T_{\alpha_5} = 0 \,.$ (4.3)

The lemma that three hard spheres of equal mass and diameter cannot undergo more than four successive collisions was stated by Sandri *et al.*[17] and proved in detail by Murphy and Cohen.[18,19] However, in the original formulation of the lemma, no distinction was made between real collisions and interacting collisions. A real collision is a collision with the condition that it is not preceded by a noninteracting collision.[20] Strictly speaking, in order for three spheres not to undergo more than four collisions, it would be necessary to prove

$$\overline{T}_{\alpha_1}(1+G_0T_{\beta_1}^n)\, G_0 T_{\alpha_2}^i (1+G_0T_{\beta_2}^n) G_0 T_{\alpha_3}^i (1+G_0T_{\beta_3}^n) \times G_0 T_{\alpha_4}^i (1+G_0T_{\beta_4}^n)\, G_0 T_{\alpha_5} = 0 \,. \tag{4.4}$$

The factors $1+G_0T_\beta^n$ ensure that the succeeding interacting collision is considered only when it is real. Equation (4.3) implies (4.4), but not vice versa. The reason is that according to (4.4) the conditions for five successive interacting collisions conceivably could be met, in which case the sequence would be rendered hypothetical as a result of the interference of a noninteracting collision. An examination of Murphy's proof shows that the latter argument is never used and that the conditions for five successive interacting collisions indeed cannot be satisfied regardless of whether the collisions are real or hypothetical. Thus Murphy's proof justifies the stronger conclusion (4.3).[21]

In the formulation of the subsequent lemmas, we denote the three pairs of particles by α, β, and γ. Thus we shall always use the convention $\alpha \neq \beta \neq \gamma \neq \alpha$;

Lemma 2: $$\overline{T}_\alpha G_0 T_\beta^i G_0 T_\alpha^i G_0 T_\beta = 0 \,, \tag{4.5}$$

Lemma 3: $$\overline{T}_\alpha G_0 T_\beta^i G_0 T_\gamma^i G_0 T_\alpha = 0 \,. \tag{4.6}$$

Lemmas 2 and 3 express the fact that these particular four collision sequences cannot occur.[17,19] Again we use the stronger interpretation for four successive interacting collisions, independent of whether they are real or hypothetical, justified on the basis of Murphy's proof;

Lemma 4: $$\overline{T}_\alpha G_0 T_\beta^i G_0 T_\gamma^n G_0 T_\alpha = 0 \,, \tag{4.7}$$

$$\overline{T}_\alpha G_0 T_\beta^i G_0 \overline{T}_\gamma^n G_0 T_\alpha = 0, \tag{4.8}$$

Lemma 5: $$\overline{T}_\alpha G_0 T_\gamma^n G_0 T_\beta^i G_0 T_\alpha = 0, \tag{4.9}$$

$$\overline{T}_\alpha G_0 \overline{T}_\gamma^n G_0 T_\beta^i G_0 T_\alpha = 0, \tag{4.10}$$

TABLE I. Terms in $T^{(5)}$ (123, ϵ).

Collision sequence	Lemma
$\overline{T}_\alpha G_0 T_\beta^i G_0 T_\alpha^i G_0 T_\beta^n G_0 T_\gamma = 0$	2
$\overline{T}_\alpha G_0 T_\beta^i G_0 T_\alpha^i G_0 T_\gamma^n G_0 T_\beta = 0$	2, 4
$\overline{T}_\alpha G_0 T_\beta^i G_0 T_\gamma^i G_0 T_\alpha^n G_0 T_\beta = 0$	3, 4
$\overline{T}_\alpha G_0 T_\beta^i G_0 T_\gamma^i G_0 T_\beta^n G_0 T_\alpha = 0$	3
$\overline{T}_\alpha G_0 T_\beta^i G_0 T_\alpha^n G_0 T_\gamma^i G_0 T_\alpha = 0$	3
$\overline{T}_\alpha G_0 T_\beta^i G_0 T_\alpha^n G_0 T_\gamma^i G_0 T_\beta = 0$	5
$\overline{T}_\alpha G_0 T_\beta^i G_0 T_\gamma^n G_0 T_\alpha^i G_0 T_\beta = 0$	2, 5
$\overline{T}_\alpha G_0 T_\beta^i G_0 T_\gamma^n G_0 T_\alpha^i G_0 T_\gamma = 0$	4
$\overline{T}_\alpha G_0 T_\beta^n G_0 T_\gamma^i G_0 T_\alpha^i G_0 T_\beta = 0$	5
$\overline{T}_\alpha G_0 T_\beta^n G_0 T_\gamma^i G_0 T_\alpha^i G_0 T_\gamma = 0$	2, 5
$\overline{T}_\alpha G_0 T_\beta^n G_0 T_\gamma^i G_0 T_\beta^i G_0 T_\alpha = 0$	3
$\overline{T}_\alpha G_0 T_\beta^n G_0 T_\gamma^i G_0 T_\beta^i G_0 T_\gamma = 0$	2
$\overline{T}_\alpha G_0 T_\beta^n G_0 T_\gamma^i G_0 T_\alpha^n G_0 T_\beta = 0$	5
$\overline{T}_\alpha G_0 T_\beta^n G_0 T_\gamma^i G_0 T_\beta^n G_0 T_\alpha = 0$	4, 5

Lemma 6: $$f_\gamma T_\alpha G_0 T_\beta^i G_0 T_\alpha = 0 \,, \tag{4.11}$$

$$f_\gamma \overline{T}_\alpha G_0 T_\beta^i G_0 T_\alpha = 0 \,, \tag{4.12}$$

Lemma 7: $$f_\gamma T_\alpha G_0 T_\beta G_0 T_\gamma = 0 \,, \tag{4.13}$$

$$f_\gamma \overline{T}_\alpha G_0 T_\beta G_0 T_\gamma = 0 \,. \tag{4.14}$$

Lemmas 4–7 are new. They are various representations of a theorem which says that once the conditions for a recollision $T_\alpha G_0 T_\beta^i G_0 T_\alpha$ are satisfied, pair γ cannot be in contact during the entire recollision process. A proof of the lemmas 4–7 is given in the Appendix.

The lemmas presented above are to be supplemented with the following rules. First, the lemmas are valid when the left- and right-most T operators are either interacting or noninteracting. Second, since a noninteracting collision does not change any of the velocities, the lemmas remain valid upon addition of any number of noninteracting collisions.

From these lemmas, we deduce the following theorem:

$$T^{(s)}(123, \epsilon) = 0, \quad \text{for } s \geq 5 \,. \tag{4.15}$$

Proof[22]: First we note that in each term of $T^{(s)}(123, \epsilon)$, for $s > 5$, the subgroup of five left-most operators is equal to a term in $T^{(5)}(123, \epsilon)$. Thus, it is sufficient to prove that each individual term of $T^{(5)}(123, \epsilon)$ vanishes.

For this purpose we consider all possible combinations of five T operators. From lemma 1 we conclude that at least one of the intermediate collisions must be noninteracting. Equation (4.1) says that such a noninteracting collision cannot be inserted between two T operators with the same index. Equation (4.2) rules out the possibility that two successive intermediate collisions are both noninteracting. The remaining combinations are listed in Table I. Upon inspection, we conclude that all terms vanish since each contains a subgroup of four collisions that are ruled out by the lemmas. The appropriate lemmas for the individual terms are listed in the second column of Table I. The term

$$\overline{T}_\alpha G_0 T_\beta^n G_0 T_\gamma^i G_0 T_\beta^i G_0 T_\gamma$$

vanishes according to lemma 2, since T_β^n can be replaced with $-T_\beta^n G_0 \overline{T}_\beta^n$.

As a next step we investigate the terms of $T^{(4)}(123, \epsilon)$. The various combinations of four T operators are listed in Table II. Again we conclude that several sequences are impossible. Thus (3.26) reduces to

$$T^{(4)}(123, \epsilon) = \sum_{\alpha \neq \beta} \sum (1 + f_\gamma) [\overline{T}_\alpha G_0 T_\beta^i G_0 T_\alpha G_0 T_\gamma + \overline{T}_\alpha G_0 T_\beta G_0 T_\gamma^i G_0 T_\beta] \,. \tag{4.16}$$

TABLE II. Terms in $T^{(4)}$ (123, ϵ).

Collision sequence	Lemma
$\overline{T}_\alpha G_0 T^i_\beta G_0 T^i_\alpha G_0 T_\beta = 0$	2
$\overline{T}_\alpha G_0 T^i_\beta G_0 T^i_\alpha G_0 T_\gamma \neq 0$	
$\overline{T}_\alpha G_0 T^i_\beta G_0 T^i_\gamma G_0 T_\alpha = 0$	3
$\overline{T}_\alpha G_0 T^i_\beta G_0 T^i_\gamma G_0 T_\beta \neq 0$	
$\overline{T}_\alpha G_0 T^i_\beta G_0 T^n_\alpha G_0 T_\gamma \neq 0$	
$\overline{T}_\alpha G_0 T^i_\beta G_0 T^n_\gamma G_0 T_\alpha = 0$	4
$\overline{T}_\alpha G_0 T^n_\beta G_0 T^i_\gamma G_0 T_\alpha = 0$	5
$\overline{T}_\alpha G_0 T^n_\beta G_0 T^i_\gamma G_0 T_\beta \neq 0$	

Furthermore, the terms with f_γ can be deleted as a result of lemmas 6 and 7. In the terms of $T^{(3)}(123, \epsilon)$ containing three T operators, we can delete the overlap exclusion for the same reason. Summarizing our results we find

$$T(123, \epsilon) = T^{(3)}(123, \epsilon) + T^{(4)}(123, \epsilon) , \qquad (4.17)$$

with

$$T^{(3)}(123, \epsilon) = \sum_{\substack{\alpha \\ (\alpha \neq \beta \neq \gamma \neq \alpha)}} f_\beta f_\gamma \overline{T}_\alpha + \sum_{\substack{\alpha_1 \neq \alpha_2 \\ (\alpha_1 \neq \beta \neq \alpha_2)}} \sum f_\beta \overline{T}_{\alpha_1} G_0 T_{\alpha_2}$$
$$+ \sum_{\substack{\alpha_1 \neq \alpha_2 \\ (\alpha_1 \neq \beta \neq \alpha_2)}} \sum (\overline{T}_{\alpha_1} G_0 T^i_{\alpha_2} G_0 T_{\alpha_1}$$
$$+ \overline{T}_{\alpha_1} G_0 T_{\alpha_2} G_0 T_\beta), \qquad (4.18)$$

$$T^{(4)}(123, \epsilon) = \sum_{\substack{\alpha_1 \neq \alpha_2 \\ (\alpha_1 \neq \beta \neq \alpha_2)}} \sum (\overline{T}_{\alpha_1} G_0 T^i_{\alpha_2} G_0 T_{\alpha_1} G_0 T_\beta$$
$$+ \overline{T}_{\alpha_1} G_0 T_{\alpha_2} G_0 T^i_\beta G_0 T_{\alpha_2}) . \qquad (4.19)$$

Thus the dynamics is restricted to a limited number of collision sequences with at most four successive collisions.

V. COMPARISON WITH SURFACE-INTEGRAL METHOD

The fact that the triple-collision operator can be decomposed into a sum of operators, each of which is related to a particular collision sequence, was demonstrated earlier by one of the authors.[4] That derivation started from the expression (2.5) for I_3 in terms of the streaming operators $\mathcal{S}(1, \ldots, l)$. This operator was symmetrized following the same arguments as those used in the derivation of (2.20). For the configurational part of the integral we considered the positions of the three particles along their free trajectories. A surface integral was obtained by integrating over τ^-_α which is the time relative to the time of the first collision enountered when streaming backwards. The result was

$$I_3 = \tfrac{1}{2} \int dx_2 dx_3 \sum_{\alpha_1 \neq \alpha_2} \sum \delta(\tau^-_{\alpha_1})$$
$$\times \sum_\mu T_\mu(\alpha_1; \alpha_2) \phi(1) \phi(2) \phi(3) \sum_{i=1}^{3} P_{1i}, \qquad (5.1)$$

where the summation over μ represents a summation over the six diagrams of Fig. 3, indicated by R1, R2, C1, C2, H1, and H2. Just as in Fig. 2, the diagrams should be read from top to bottom. For convenience, we have retained the δ function to indicate that the integrand is evaluated at the time $\tau^-_\alpha = 0$ of the first collision. The successive collisions are time ordered according to the contact times τ^-. Although not indicated explicitly, the trajectories in R1 and C1 should be continued until no further interacting collisions are encountered. The effect of the operator associated with each diagram is to transform the velocities at the top of the diagram into the velocities at the bottom. In this convention each diagram of Fig. 3 represents actually two diagrams: one in which the third collision is interacting and another in which the third collision is noninteracting. The operator has a minus sign when the number of noninteracting collisions is odd. For a derivation of this surface-integral form of the triple-collision operator we refer to the earlier publications.[4,6,23]

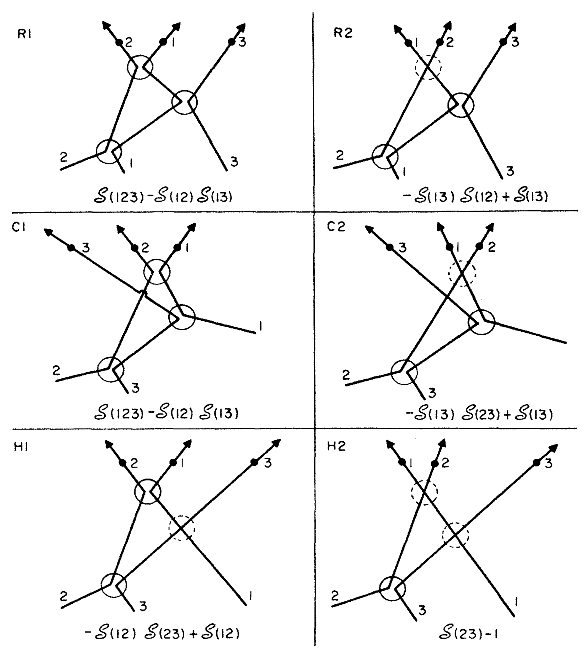

FIG. 3. The six collision sequences associated with the surface integral form of the triple-collision operator (Refs. 4, 6, 23). The lines represent particle trajectories and the circles indicate collisions between the two particles whose trajectories are enclosed. The dotted circles indicate noninteracting collisions.

It should be noted that the diagrams of Fig. 3 do not specify the collision sequences completely, but that in addition some auxiliary conditions have to be imposed. The first auxiliary condition requires that the phases of the particles at the surface $\tau_{\alpha_1}^- = 0$ should be restricted not only to nonoverlapping configurations, but also to receding phases. Thus any collisions that might occur when the trajectories are extended into the future should be excluded. The second auxiliary condition says that all collisions up to and including the first noninteracting collision should be *real*. Lastly, as mentioned earlier, the three collisions of R1 and C1 could be followed by a fourth interacting collision.

On comparing (5.1) with (2.20) we see that

$$\lim_{\epsilon \to 0} T(123, \epsilon)$$

should be identified with

$$T(123) = \sum_{\alpha_1 \neq \alpha_2} \sum \delta(\tau_{\alpha_1}^-) \sum_{\mu} T_\mu(\alpha_1; \alpha_2) \ . \qquad (5.2)$$

The six diagrams of Fig. 3 represent a decomposition of the triple-collision operator which differs in appearance from the decomposition (4.17) derived from the binary-collision expansion. It can be shown that the auxiliary conditions mentioned above represent a concise formulation of the combined effect of all operators $T^{(s)}(123, \epsilon)$ in (3.24) for $s \geq 3$, regardless of the validity of the lemmas quoted in Sec. IV. For convenience, we shall demonstrate the equivalence by considering only those collision sequences that are dynamically possible. Thus, we first investigate how the lemmas simplify the $T_\mu(\alpha_1; \alpha_2)$ operators.

To specify the auxiliary conditions explicitly, we introduce the following functions:

$$A_\alpha = \theta(\sigma - b_\alpha)\,\theta(\tau_\alpha^-) \ , \qquad (5.3)$$

$$Z_\alpha = \theta(\sigma - b_\alpha)\,\theta(-\tau_\alpha^+) \ , \qquad (5.4)$$

$$N_\alpha = \theta(b_\alpha - \sigma) \ . \qquad (5.5)$$

Thus $A_\alpha = 1$ when pair α is aimed to collide in the past, $Z_\alpha = 1$ when pair α is aimed to collide in the future, and $N_\alpha = 1$ when pair α is not aimed to collide in either direction. These functions were used previously by one of us in a discussion of the Lorentz gas.[24] Since f_α can be written as

$$f_\alpha = -\theta(\sigma - b_\alpha)\,\theta(-\tau_\alpha^-)\,\theta(\tau_\alpha^+) \ , \qquad (5.6)$$

we note

$$A_\alpha + Z_\alpha + N_\alpha - f_\alpha = 1 \ . \qquad (5.7)$$

The $T_\mu(\alpha_1; \alpha_2)$ operators can be transcribed in terms of these functions and the binary-collision operators used in the previous sections. As an example we consider $T_{R1}(12; 13)$:

$$\delta(\tau_{12}^-)\,T_{R1}(12; 13) = (A_{13} + N_{13})(A_{23} + N_{23})\,T_{12}^i(1 + G_0 T_{23}^n)\,G_0 \times T_{13}^i(1 + G_0 T_{23}^n)\,G_0(T_{12} + T_{12}^i G_0 T_{23}) \ . \qquad (5.8)$$

The factor $(A_\gamma + N_\gamma)$ guarantees that the receding phase condition is satisfied for pair γ. The function $\delta(\tau_{12}^-)$ is incorporated in the first T_{12} operator. The factors $1 + G_0 T_{23}^n$ guarantee that the second and third collisions are real. The last term $T_{12}^i G_0 T_{23}$ gives the correction if a fourth collision is encountered. Lemma 2 implies that such a collision can only involve particles 2 and 3. Again it is understood that the limit $\epsilon \to 0$ is taken just as in the preceding paragraphs. Similarly, the other $T_\mu(12; 13)$ operators can be represented by

$$\delta(\tau_{12}^-)\,T_{R2}(12; 13) = (A_{23} + N_{23})\,T_{12}^n G_0 T_{13}^i G_0 T_{12} \ , \qquad (5.9)$$

$$\delta(\tau_{12}^-)\,T_{C1}(12; 13) = (A_{13} + N_{13})(A_{23} + N_{23})\,T_{12}^i(1 + G_0 T_{23}^n)G_0 \times T_{13}^i(1 + G_0 T_{12}^n)G_0(T_{23} + T_{23}^i G_0 T_{13}), \qquad (5.10)$$

$$\delta(\tau_{12}^-)\,T_{C2}(12; 13) = (A_{23} + N_{23})\,T_{12}^n G_0 T_{13}^i G_0 T_{23}, \qquad (5.11)$$

$$\delta(\tau_{12}^-)\,T_{H1}(12; 13) = (A_{13} + N_{13})(A_{23} + N_{23})\,T_{12}^i G_0 T_{13}^n G_0 T_{23}, \qquad (5.12)$$

$$\delta(\tau_{12}^-)\,T_{H2}(12; 13) = T_{12}^n G_0 T_{13}^n G_0 T_{23} \ . \qquad (5.13)$$

In describing T_{R1} and T_{C1} we have used the fact that only one particular collision could be added to the three successive interacting collisions. Lemmas 4 and 5 lead to further simplifications in T_{R1} and T_{C1}:

$$\delta(\tau_{12}^-)\,T_{R1}(12; 13) = (A_{13} + N_{13})(A_{23} + N_{23})\,T_{12}^i G_0 T_{13}^i G_0(T_{12} + T_{12}^i G_0 T_{23}), \qquad (5.14)$$

$$\delta(\tau_{12}^-)\,T_{C1}(12; 13) = (A_{13} + N_{13})(A_{23} + N_{23})\,T_{12}^i G_0[T_{13}^i G_0 T_{23} + T_{23}^n G_0 T_{13}^i G_0 T_{23} + T_{13}^i G_0 T_{12}^n G_0 T_{23} + T_{13}^i G_0 T_{23}^i G_0 T_{13}] \ . \qquad (5.15)$$

Note that the term

$$T_{12}^i G_0 T_{23}^n G_0 T_{13}^i G_0 T_{23}^i G_0 T_{13}$$

in (5.10) vanishes according to lemma 2, since T_{23}^n can be replaced with $-T_{23}^n G_0 \overline{T}_{23}^n$.

In contrast to the derivation of (4.17), the surface integral (5.2) was derived under the explicit assumption that the operator operates on a function of momenta, as is the case for the triple-collision integrals (2.1). Therefore, the two decompositions of the triple-collision operator (4.17) and (5.2) will only yield identical results in the spatially homogeneous case. Since

$$\int dx_2 dx_3 G_0^{-1} F(\vec{r}_{21}, \vec{r}_{31}, \vec{p}_1, \vec{p}_2, \vec{p}_3) = 0 \qquad (5.16)$$

if F is a function of the relative positions $\vec{r}_{21}$ and $\vec{r}_{31}$, we can use a simplified version of the commutator (3.14)

$$(T_\alpha^n - \overline{T}_\alpha^n) G_0 = f_\alpha. \qquad (5.17)$$

Furthermore, we note that

$$(A_{23} + N_{23}) T_{12} = (1 + f_{23} - Z_{23}) T_{12}$$

$$= (1 + f_{23} + \overline{T}_{23}^n G_0) T_{12}. \qquad (5.18)$$

The replacement of $-Z_{23}T_{12}$ by $\overline{T}_{23}^n G_0 T_{12}$ represents a shift of the surface from $\tau_{12}^- = 0$ to $\tau_{23}^+ = 0$, which is again justified in the spatially homogeneous case. Similarly, $A_{13} + N_{13}$ can be replaced with

$$A_{13} + N_{13} = 1 + \overline{T}_{13}^n G_0, \qquad (5.19)$$

where the term with f_{13} vanishes due to the presence of the succeeding T_{13} operator. By substituting (5.18) and (5.19) into the expressions for $T_\mu(12;13)$ and working out the products, we can express $T(123)$ in terms of products of T operators.[25] However, many terms vanish, again as a result of the lemmas quoted in Sec. IV. Since the arguments are precisely the same as those used in the reduction of $T^{(4)}(123, \epsilon)$ and $T^{(5)}(123, \epsilon)$ we do not discuss the intermediate steps, but simply state the result:

$$T(123) = \sum_{\alpha_1 \neq \alpha_2}\sum \delta(\tau_{\alpha_1}^-) \sum_\mu T_\mu(\alpha_1; \alpha_2)$$

$$= T^{(3)}(123) + T^{(4)}(123), \qquad (5.20)$$

with

$$T^{(3)}(123) = \sum_{\substack{\alpha_1 \neq \alpha_2 \\ (\alpha_1 \neq \beta \neq \alpha_2)}}\sum (T_{\alpha_1} G_0 T_{\alpha_2}^i G_0 T_{\alpha_1} + T_{\alpha_1} G_0 T_{\alpha_2} G_0 T_\beta), \qquad (5.21)$$

$$T^{(4)}(123) = \sum_{\substack{\alpha_1 \neq \alpha_2 \\ (\alpha_1 \neq \beta \neq \alpha_2)}}\sum (\overline{T}_{\alpha_1} G_0 T_{\alpha_2}^i G_0 T_{\alpha_1} G_0 T_\beta + \overline{T}_{\alpha_1} G_0 T_{\alpha_2} G_0 T_\beta^i G_0 T_{\alpha_2}). \qquad (5.22)$$

The terms of $T^{(3)}(123)$ are precisely the terms associated with the six diagrams of Fig. 3 if the auxiliary conditions are disregarded. The terms of $T^{(4)}(123)$ which are identical to those in (4.19) represent the effects of the auxiliary conditions.

In order to show that $T^{(3)}(123)$ is identical to (4.18) we need to shift the surface from $\tau_{\alpha_1}^- = 0$ to $\tau_{\alpha_1}^+ = 0$, when the first collision is noninteracting. Using (5.17) we obtain

$$T^{(3)}(123) = \sum_{\substack{\alpha_1 \neq \alpha_2 \\ (\alpha_1 \neq \beta \neq \alpha_2)}}\sum (\overline{T}_{\alpha_1} G_0 T_{\alpha_2}^i G_0 T_{\alpha_1} + \overline{T}_{\alpha_1} G_0 T_{\alpha_2} G_0 T_\beta) + \sum_{\substack{\alpha_1 \neq \alpha_2 \\ (\alpha_1 \neq \beta \neq \alpha_2)}}\sum f_{\alpha_1} T_{\alpha_2} G_0 T_\beta. \qquad (5.23)$$

Repeating the procedure once more for the last term, we find

$$\sum_{\substack{\alpha_1 \neq \alpha_2 \\ (\alpha_1 \neq \beta \neq \alpha_2)}}\sum f_{\alpha_1} T_{\alpha_2} G_0 T_\beta = \sum_{\substack{\alpha_1 \neq \alpha_2 \\ (\alpha_1 \neq \beta \neq \alpha_2)}}\sum (f_{\alpha_1} \overline{T}_{\alpha_2} G_0 T_\beta + f_{\alpha_1} f_{\alpha_2} T_\beta). \qquad (5.24)$$

In the double overlap term $f_{\alpha_1} f_{\alpha_2} T_\beta$ we can replace T_β with $\overline{T}_\beta$, since both operators reduce to the Boltzmann operator in the spatially homogeneous case. Therefore, on comparing these results with (4.18) we confirm the identity of the two forms of the triple-collision operator.

The operator can be transformed into a form which elucidates more clearly its symmetry upon time reversal. For this purpose we rearrange the terms of $T^{(3)}(123)$,

$$T^{(3)}(123) = \sum_{\substack{\alpha \\ (\alpha \neq \beta \neq \gamma \neq \alpha)}} f_\beta f_\gamma \overline{T}_\alpha + \sum_{\substack{\alpha_1 \neq \alpha_2 \\ (\alpha_1 \neq \beta \neq \alpha_2)}}\sum [\overline{T}_{\alpha_1} G_0 T_{\alpha_2}^i G_0 T_{\alpha_1} + \overline{T}_{\alpha_1} (f_{\alpha_2} G_0 + G_0 T_{\alpha_2} G_0) T_\beta], \qquad (5.25)$$

where from (3.14)

$$f_{\alpha_2} G_0 + G_0 T_{\alpha_2} G_0 = G_0 f_{\alpha_2} + G_0 \overline{T}_{\alpha_2} G_0. \qquad (5.26)$$

Using (5.26) and lemma 7, $T^{(4)}(123)$ can be written

$$T^{(4)}(123) = \sum_{\substack{\alpha_1 \neq \alpha_2 \\ (\alpha_1 \neq \beta \neq \alpha_2)}}\sum (\overline{T}_{\alpha_1} G_0 T_{\alpha_2}^i G_0 T_{\alpha_1} G_0 T_\beta + \overline{T}_{\alpha_1} G_0 \overline{T}_{\alpha_2} G_0 T_\beta^i G_0 T_{\alpha_2}). \qquad (5.27)$$

The time-reversed operator is obtained by reversing the order of the operators and interchanging T and $\overline{T}$. As mentioned above, the double overlap term $f_\beta f_\gamma \overline{T}_\alpha$ is itself symmetric when operating on a function of momenta. Thus $T^{(3)}(123)$ is symmetric upon time reversal according to (5.25) and (5.26) and $T^{(4)}(123)$ according to (5.27). This time symmetry is not sufficient to prove a generalized H theorem, but it does ensure that the matrix elements of the triple-collision operator in a Sonine polynomial representation[4] are symmetric.

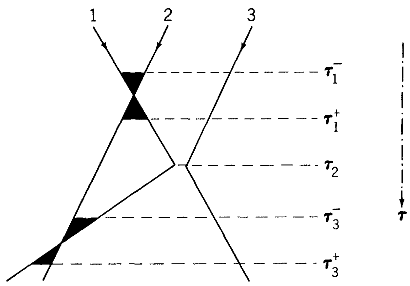

FIG. 4. A recollision sequence $T_{12}^n G_0 T_{13}^i G_0 T_{12}^n$.

VI. SUMMARY

Using the binary-collision expansion we have decomposed the triple-collision operator into a series of terms related to collision sequences involving increasing numbers of successive correlated binary collisions. The expansion turns out to be equivalent with a decomposition of the triple-collision operator derived previously by a surface-integral method. We have presented some dynamical lemmas which imply that all collision sequences between three hard spheres terminate after four successive collisions regardless of whether the collisions are interacting or noninteracting. This is a generalization of a lemma presented by previous authors which stated that three equal spheres cannot undergo more than four interacting collisions. The dynamical lemmas lead also to some interesting simplifications in the sequences of three and four successive collisions.

ACKNOWLEDGMENTS

The authors are indebted to Dr. D. T. Gillespie and Dr. M. H. Ernst for some stimulating discussions. Part of the research was supported by the Arnold Engineering Development Center, Tenn., Contract No. F 40600-69-C0002. The research was initiated while Dr. Hoegy was a National Research Council Postdoctoral Research Associate at the National Bureau of Standards.

APPENDIX

Our proof of the new lemmas 4–7 is based on an analysis of the recollision sequence $T_{12}^n G_0 T_{13}^i G_0 T_{12}^n$ (see Fig. 4). The contact times of the three collisions are indicated by τ_1^-, τ_1^+, τ_2, τ_3^-, τ_3^+. For convenience we follow the motion in the forward time direction. Lemmas 4–7 are consequences of the following theorem:

$$r_{32}(\tau) > \sigma, \quad \text{for } \tau_1^- \le \tau \le \tau_3^+ . \qquad \text{(A1)}$$

In view of the symmetry of the recollision sequence, it is sufficient to prove $r_{32}(\tau) > \sigma$ for $\tau_2 \le \tau \le \tau_3^+$.

The theorem is most easily proved by examining the actual trajectories of the three particles in three-dimensional space. For this purpose we consider a coordinate system with the center of the action sphere of 1 at the origin O for times $\tau_1^- \le \tau \le \tau_2$. The coordinate system is oriented such that for times $\tau > \tau_1^-$ sphere 2 is in the XZ plane, moving in the positive Z direction (see Fig. 5).

The relative separation of pair 21 at time τ_1^+ is the vector from O to A,

$$OA = \vec{r}_{21}(\tau_1^+) = (\sigma\cos\theta_1,\ 0,\ \sigma\sin\theta_1), \quad 0 \le \theta_1 \le \pi/2. \qquad \text{(A2)}$$

The center of sphere 2 is at point A at $\tau = \tau_1^+$. For times $\tau > \tau_1^+$ it moves along line AB in the positive Z direction.

At time $\tau = \tau_2$, the center of sphere 3 lies at point C on the action sphere of 1,

$$OC = \vec{r}_{32}(\tau_2) = (-\sigma\cos\phi\,\sin\theta_2,\ \sigma\sin\phi,\ \sigma\cos\phi\,\cos\theta_2), \qquad \text{(A3)}$$

where ϕ is the angle that OC makes with the XZ plane and θ_2 is the angle between the Z axis and the projection of OC onto the XZ plane.

In a collision between two hard spheres, the velocity components along the line of centers are exchanged. Therefore, for times $\tau > \tau_2$ the center of sphere 1 moves along the extension of line CO, i.e., from O toward D and the center of sphere 3 moves in the plane perpendicular to CO at C.

We examine the conditions on the location of point C (the center of sphere 3 at time $\tau = \tau_2$) such that pairs 12 and 32 aim to collide at some time $\tau > \tau_2$. Since at time $\tau = \tau_2$ the center of 1 is at O and the center of 2 is between A and B, 1 aims to collide with 2 only when the path of 1 is directed toward the tangent plane perpendicular to OA at point A; this requires C to lie in the opposite hemisphere from A. Now, since at time $\tau = \tau_2$ the center of 3 is at point C and the center of 2 is between A and B, and A and C lie in opposite hemi

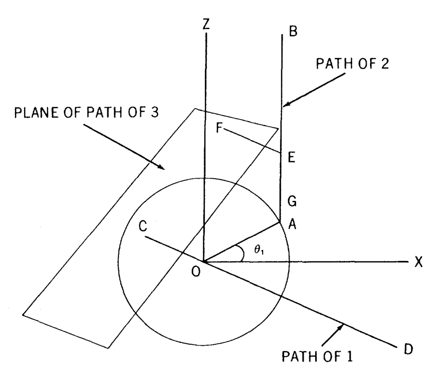

FIG. 5. Geometrical representation of a recollision showing the particle trajectories.

spheres, it follows that $r_{32}(\tau_2) > \sigma$. Therefore, 3 can aim to collide with 2 only when the plane of the path of 3 intersects line AB. The above conditions imply for θ_2 and ϕ

$$\theta_1 < \theta_2 < \pi/2, \quad -\pi/2 < \phi < +\pi/2 . \qquad (A4)$$

Consider the distance from the points on the path of 2 to the plane of the path of 3. Since the plane of the path of 3 intersects AB, there are two points on line AB whose distance to the plane of the path of 3 is σ. We denote as point E the position of 2 at the earlier time τ_E, when the distance $EF = \sigma$. For all times $\tau < \tau_E$, $r_{32}(\tau) > \sigma$, so that the time τ_4^- of first contact of pair 32 is greater than or equal to τ_E,

$$\tau_4^- \geq \tau_E . \qquad (A5)$$

Next we consider the distance from the points on the path of 2 to the plane through the Y axis and line OD. Since the distance from point A to the plane is $\sigma \sin(\theta_2 - \theta_1) < \sigma$, at some time $\tau_G > \tau_1^+$ the center of 2 is at point G, such that the distance from G to the plane of OD and the Y axis is equal to σ. Thus the time τ_3^+ of the last contact of pair 12 must be smaller than or equal to τ_G,

$$\tau_3^+ \leq \tau_G . \qquad (A6)$$

We examine the distance from point E to the plane of the Y axis and line OD. This distance is given by the line EO. Line EO lies in the XZ plane and is therefore perpendicular to the Y axis; it is also parallel to CF and hence perpendicular to line OD. The length of EO is

$$|EO| = \sigma \cos\theta_1 / \cos\theta_2 , \qquad (A7)$$

and thus, according to (A2) and (A4), $EO > \sigma$. This implies $AE > AG$ and hence

$$\tau_E > \tau_G . \qquad (A8)$$

On comparing (A8) with (A5) and (A6) we conclude

$$\tau_4^- > \tau_3^+ . \qquad (A9)$$

An equivalent statement is

$$r_{32}(\tau) > \sigma, \quad \text{for } \tau_2 \leq \tau \leq \tau_3^+ . \qquad (A10)$$

Lemmas 4–6 and Eqs. (4.7)–(4.12) follow from (A1) since they involve the recollision sequence $\alpha\beta\alpha$ with pair γ in contact or overlapping during the recollision sequence. Lemma 7 also follows from (A1) since T_β must be an interacting T operator in Eqs. (4.13) and (4.14), which results in the recollision sequence $\gamma\beta\gamma$ with contact of pair α during the sequence.

---

[1]M. H. Ernst, L. K. Haines, and J. R. Dorfman, Rev. Mod. Phys. 41, 296 (1969).

[2]The next term which is proportional to $n^2 \log n$ is not considered here.

[3]M. S. Green, Phys. Rev. 136, A905 (1964).

[4]J. V. Sengers, Phys. Fluids 9, 1333 (1966).

[5]M. H. Ernst, J. R. Dorfman, W. R. Hoegy, and J. M. J. Van Leeuwen, Physica 45, 127 (1969) and references contained therein.

[6]J. V. Sengers, *Boulder Lectures in Theoretical Physics, Vol.* 9C (Gordon and Breach, New York, 1967), p. 335.

[7]We do not consider the effect of binary collisions on the first density correction.

[8]M. S. Green, J. Chem. Phys. 25, 836 (1956).

[9]E. G. D. Cohen, Physica 28, 1025 (1962).

[10]R. Zwanzig, Phys. Rev. 129, 486 (1963).

[11]Note that $\epsilon B(\epsilon) = B(\epsilon)\, G_0^{-1}$ when operating on a function of momenta.

[12]Contrary to Ref. 5, we make a distinction between interacting collisions and real collisions.

[13]We use backward streaming operators.

[14]Note that $T_\alpha G_0 \overline{T}_\alpha = T_\alpha^n G_0 \overline{T}_\alpha^n$ may differ from zero.

[15]S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge U. P., London, England, 1939), Chap. 16.

[16]An analysis and evaluation of the overlap terms will be presented in a subsequent publication.

[17]G. Sandri, R. D. Sullivan, and P. Norem, Phys. Rev. Letters 13, 743 (1964); G. Sandri and A. H. Kritz, Phys. Rev. 150, 92 (1966).

[18]E. G. D. Cohen, *Boulder Lectures in Theoretical Physics, Vol.* 8A (University Colorado Press, Boulder, Co., 1966), Appendix II, p. 170.

[19]T. J. Murphy (unpublished).

[20]The concept of a real collision was introduced in Ref. 4. A hypothetical collision is a collision that *is* preceded by a noninteracting collision. Note that real and hypothetical collisions can be either interacting or noninteracting.

[21]The authors are indebted to Professor T. J. Murphy for a stimulating discussion on this topic.

[22]Using the same arguments one can show that the lemmas 1–3 alone imply that $T^{(s)}$ (123, ϵ) = 0 for $s \geq 6$.

[23]J. V. Sengers, in *Symposium on Kinetic Equations, Cornell University*, 1969, edited by R. Liboff and N. Rostoker (Gordon and Breach, New York, 1970), p. 137.

[24]W. R. Hoegy, Phys. Rev. 185, 210 (1969).

[25]In substituting (5.18) and (5.19) care must be exercised in transforming the terms $Z_{13} Z_{23}$ and $-Z_{13} f_{23}$; see Ref. 24 for details.