Three-Body Scattering Operator in Nonequilibrium Statistical Mechanics

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A method is presented for calculating the time-dependent irreducible clusters, $\beta_s(t)$ which appear in the kernel of the equation of evolution derived in the preceding article. The clusters $\beta_1(t)$ and $\beta_2(t)$—which correspond to binary and ternary collisions, respectively—are calculated in detail. They are each found to divide into the two following parts: (1) a "completed" collision part which corresponds to collisions which are eventually completed (scattering processes) and (2) an "incompleted" part which corresponds to those collisions not completed by time t. The incompleted collision parts contribute to the "memory" of the equation of evolution and are shown to be relatively small when t is large. The completed collision parts, which play a central role in the theory of transport coefficients, are time-independent scattering operators in momentum space and do not contribute to the memory. By means of the "binary-collision expansion" a systematic method is presented for the calculation of the three-body scattering operator $[\lim_{t\to\infty} t^{-1}\beta_2(t)]$ which is directly applicable to interaction forces with infinite repulsions. An approximate formula is then derived for this scattering operator in a form which can be readily used to calculate the density correction to transport coefficients which arise from ternary collisions.

I. INTRODUCTION

THE kernel of the equation of evolution derived in the preceding article[1] involved time-dependent irreducible cluster integrals $\beta_s(t)$ which correspond to multiplet collisions in configuration space. The purpose of the present article is to indicate how these time-dependent cluster integrals (collision integrals, scattering operators) are calculated in general, and to calculate $\beta_1(t)$ (binary collisions) and $\beta_2(t)$ (ternary collisions) in detail.

These cluster integrals are important for two reasons: (1) The kinetics of approach to equilibrium is determined by the time dependence of the cluster integrals $\beta_s(t)$.[1] (2) Macroscopic transport coefficients may be determined by the scattering operator

$$\lim_{t\to\infty} \sum_{s=1}^{\infty} \beta_s'(t).$$

Several authors[2] have discussed various forms of the asymptotic three-body operator $\beta_2'(\infty)$. By integrating $\beta_2'(\infty)$ over all particle momenta but one, we obtain the operator which appears as the density correction in Green's Boltzmann equation. The relationship between the latter operator and the first density correction to transport coefficients for homogeneous systems has been derived by Choh and Uhlenbeck, and a comparable result for transport coefficients has been recently obtained by Zwanzig, from a different approach. The three-body operator discussed by Resibois may be viewed as the expansion of Green's operator in powers of the interaction potential.

In none of the above references, it will be noted, has an attempt been made to calculate the three-body scattering operator, nor has the time dependence of the general operator $\beta_2'(t)$ been considered.

In this article we shall present a systematic method for the calculation of the three-body scattering operator $\beta_2'(\infty)$ which is directly applicable to interaction potentials with infinite repulsions. We shall then obtain an approximation for $\beta_2'(\infty)$ in a form which can be readily used to calculate the density correction to transport coefficients which arise from ternary collisions.

We shall also determine the time dependence of $\beta_1(t)$ and $\beta_2(t)$ by means of the binary-collision expansion. We shall find that $\beta_1(t)$ and $\beta_2(t)$ each divide into a completed collision part and an incompleted collision part. The completed collision part corresponds to scattering processes and plays a central role in the theory of transport coefficients. The incompleted collision part corresponds to those collisions which are not completed by time t and contribute to the "memory" of the equation of evolution. The latter part is shown to be relatively small when t is large.

In Sec. IIA and IIB we calculate $\beta_1(t)$ and $\beta_2(t)$. In Sec. III we determine the explicit relationship between incompleted collisions and the memory of the equation of evolution. There we also find disagreement with Resibois'[2] claim that only situations in which all three particles are *simultaneously* interacting play a role in the asymptotic three-body scattering operator. In Sec. IV we devote our attention to the three-body scattering operator

$$\beta_2'(\infty)=\lim_{t\to\infty}[t^{-1}\beta_2(t)].$$

II. CALCULATION OF TIME-DEPENDENT CLUSTER INTEGRALS $\beta_k(t)$

A. Calculation of $\beta_1(t)$

The cluster integral $\beta_1(t)$ has previously been calculated under the assumption that binary collisions are instantaneous.[3] This is equivalent to calculating

[1] J. Weinstock, preceding paper, Phys. Rev. **132**, 454 (1963).

[2] M. S. Green, Physica **24**, 393 (1958); S. T. Choh and G. E. Uhlenbeck, Navy Theoretical Physics, Contract No. Nonr 1224(15), University of Michigan, 1958; R. Zwanzig, Phys. Rev. **129**, 486 (1963); P. Resibois, J. Math. Phys. **4**, 166 (1963).

[3] R. Brout, Physica **22**, 509 (1956).

$\lim_{t\to\infty} t^{-1}\beta_1(t)$. We shall not make this assumption. Instead, we shall calculate $\beta_1(t)$ very carefully and determine the effects of the finite duration of a binary collision upon the time dependence of $\beta_1(t)$ as follows.

We combine Eqs. (26) and (12) of Ref. (1) to obtain, with $g(0)\equiv g(\mathbf{P}_1,\mathbf{P}_2,\cdots)$ denoting any function of the initial momenta of the particles of a system such that $\beta_1(t)g(0)$ converges,

$$\beta_1(t)g(0)\equiv\sum_{i<j} V^{-1}\int d\mathbf{R}_{ij}[G_{ij}(t)-G_0(t)]g(0)$$

$$=\sum_{i<j} V^{-1}\int d\mathbf{R}_{ij}$$

$$\times[g(\mathbf{P}_1,\cdots\mathbf{P}_i(t)\cdots\mathbf{P}_j(t)\cdots)-g(0)]. \quad (1)$$

Here, in the notation of Ref. 1,

$$G_{ij}(t)\equiv e^{it(L_N^0+L_{ij})},$$

$$G_0(t)\equiv e^{itL_N^0},$$

$$L_N^0\equiv i\sum_{k=1}^{N} m^{-1}\mathbf{P}_k\cdot\partial/\partial\mathbf{R}_k,$$

$$L_{ij}\equiv i[\partial/\partial(\mathbf{R}_i-\mathbf{R}_j)]V(\mathbf{R}_i-\mathbf{R}_j)\cdot(\partial/\partial\mathbf{P}_i-\partial/\partial\mathbf{P}_j),$$

so that $G_{ij}(t)$ involves the formal Green function solution of the equation of motion for the pair of interacting particles i and j [$V(\mathbf{R}_i-\mathbf{R}_j)$ is their interaction potential] and satisfies

$$G_{ij}(t)g(0)=g(\mathbf{P}_1\cdots\mathbf{P}_i(t)\cdots\mathbf{P}_j(t)\cdots),$$

where $\mathbf{P}_1(t)$ and $\mathbf{P}_j(t)$ denote the momenta of the two interacting particles i and j (considered isolated) at time t, given that at time zero they were at a relative separation $\mathbf{R}_{ij}$ with initial momenta $\mathbf{P}_i$ and $\mathbf{P}_j$. That is, $\mathbf{P}_i(t)$ and $\mathbf{P}_j(t)$ are the solutions of the two-body problem.

Obviously, the integrand of (1) is nonzero only if particles i and j are aimed to collide within time t in which case

$$\mathbf{P}_i(t)\neq\mathbf{P}_i, \quad \mathbf{P}_j(t)\neq\mathbf{P}_j.$$

If i and j do not collide within time t, then

$$\mathbf{P}_i(t)=\mathbf{P}_i, \quad \mathbf{P}_j(t)=\mathbf{P}_j,$$

so that the integrand of (1) will be zero. Since t, $\mathbf{P}_i$, and $\mathbf{P}_j$ are all fixed parameters in (1) it follows that whether or not a collision will take place is determined by $\mathbf{R}_{ij}$.

The region of $\mathbf{R}_{ij}$ space from which a collision between i and j will be "aimed" to take place within time t is called a *collision cylinder*[3] and is denoted by $\Omega(ij;t)$. This cylinder has its axis along $\mathbf{P}_{ij}$, its length equal to $m^{-1}P_{ij}t$, and its cross section equal to the total scattering cross section σ_T of the collision defined by

$$\sigma_T\equiv\int_{4\pi} d\omega\,\sigma(P_{ij},\omega)=\int d\phi\int d\theta\,\sigma(P_{ij},\theta,\phi)\sin\theta,$$

where $\sigma(P_{ij},\omega)$ denotes the differential scattering cross section, and ω denotes the "solid" scattering angle (azimuthal angle ϕ and scattering angle θ). In addition, we note that the collision cylinder has hemispherical "caps" at both its ends.

Particles i and j will not collide within time t if $\mathbf{R}_{ij}$ lies outside $\Omega(ij;t)$ and, hence, the integrand of (1) will vanish when $\mathbf{R}_{ij}$ lies outside of $\Omega(ij;t)$. We may, thus, restrict the region of integration over $\mathbf{R}_{ij}$ to lie within $\Omega(ij;t)$. We may then divide the integration over $\mathbf{R}_{ij}$ into integrations over the components of $\mathbf{R}_{ij}$ parallel to and perpendicular to $\mathbf{P}_{ij}$ ($R_{\parallel}$ and $R_{\perp}$) so that

$$\int_{\text{all space}} d\mathbf{R}_{ij}[G_{ij}(t)-G_0(t)]g(0)$$

$$=\int_{\Omega(ij;t)} d\mathbf{R}_{ij}[g(\cdots\mathbf{P}_i(t),\cdots\mathbf{P}_j(t),\cdots)-g(0)]$$

$$=\int_{\epsilon}^{-m^{-1}P_{ij}t-\epsilon} dR_{\parallel}\int_{\sigma_T} dR_{\perp}$$

$$\times[g(\cdots\mathbf{P}_i(t),\cdots\mathbf{P}_j(t),\cdots)-g(0)], \quad (2)$$

where

$$\epsilon\equiv[a^2-|\mathbf{R}_{ij}\times\mathbf{P}_{ij}|^2P_{ij}^{-2}]^{1/2}$$

and a is equal to the range of the force.

The calculation of (2) is quite simple in cylindrical coordinates. We transform the variable $R_{\parallel}$ into the variable t_1^0 by means of the transformation equation

$$t_1^0\equiv-mP_{ij}^{-1}(R_{\parallel}+\epsilon),$$

so that t_1^0 is the time at which i and j "begin" to collide. If, in addition, the integration over $R_{\perp}$ is transformed into an integration over the *solid* scattering angle ω we find that (2) becomes

$$V^{-1}\int d\mathbf{R}_{ij}[G_{ij}(t)-G_0(t)]g(0)$$

$$=V^{-1}\int_{-2\epsilon mP_{ij}^{-1}}^{t} dt_1^0\int_{4\pi} d\omega\,\sigma(P_{ij},\omega)$$

$$\times[g(\cdots\mathbf{P}_i(t),\cdots\mathbf{P}_j(t),\cdots)-g(0)]. \quad (3)$$

The negative lower limit $(-2\epsilon mP_{ij}^{-1})$ accounts for the case in which i and j are initially within each other's force field.

When t_1^0 lies within the interval

$$0\leqslant t_1^0\leqslant t-\tau_c,$$

where τ_c is a time interval on the order of the duration of a binary collision, then at time t particles i and j

will have completely passed through each other's force field, and they will be moving away from each other with their asymptotic momenta. In such an event we say that the collision between i and j has been "completed." Under these circumstances the momenta $\mathbf{P}_i(t)$ and $\mathbf{P}_j(t)$ will only depend upon the scattering angle ω. These momenta will not depend upon t_1^0 (or R_{11}). In fact, $\mathbf{P}_i(t)$ and $\mathbf{P}_j(t)$, after a completed collision, are given by

$$\begin{aligned}\mathbf{P}_i(t)&=\mathbf{P}_i-\mathbf{P}_{ij}\cdot\mathbf{ll},\\ \mathbf{P}_j(t)&=\mathbf{P}_j+\mathbf{P}_{ij}\cdot\mathbf{ll},\quad (0\leqslant t_1^0\leqslant t-\tau_c)\end{aligned}\tag{4}$$

where $\mathbf{l}$ is the unit vector in the perihelion direction.

If, on the other hand, t_1^0 lies within the intervals

$$-2\epsilon mP_{ij}^{-1}<t_1^0<0,\quad t-\tau_c<t_1^0<t,$$

then i and j will either begin or end up within each others force fields and, hence, $\mathbf{P}_i(t)$ and $\mathbf{P}_j(t)$ will depend upon t_1^0 (or R_{11}).

If we substitute (4) into (3) and then introduce the operator $A_{ij}(\mathbf{l})$ (momentum substitution operator) defined by

$$\begin{aligned}A_{ij}(\mathbf{l})g(\mathbf{P}_1\cdots\mathbf{P}_i\cdots\mathbf{P}_j\cdots)\\ =g(\mathbf{P}_1,\cdots\mathbf{P}_i-\mathbf{P}_{ij}\cdot\mathbf{ll},\cdots\mathbf{P}_j+\mathbf{P}_{ij}\cdot\mathbf{ll},\cdots),\end{aligned}\tag{5a}$$

we find

$$\begin{aligned}V^{-1}\int d\mathbf{R}_{ij}[G_{ij}(t)-G_0(t)]g(0)\\ =V^{-1}\int_0^{t-\tau_c}dt_1^0\,m^{-1}P_{ij}\int d\omega\,\sigma[A_{ij}(\mathbf{l})-I]g(0)\\ +V^{-1}\int_{-2\epsilon mP_{ij}^{-1}}^{0}dt_1^0\,m^{-1}P_{ij}\int d\omega\\ \times\sigma[g(\cdots\mathbf{P}_i(t)\cdots)-g(0)]\\ +V^{-1}\int_{t-\tau_c}^{t}dt_1^0\,m^{-1}P_{ij}\int d\omega\\ \times\sigma[g(\cdots\mathbf{P}_i(t)\cdots)-g(0)].\end{aligned}\tag{5b}$$

The t_1^0 integral in the first term on the right-hand side of (5) may be carried through immediately to obtain for (5)

$$\begin{aligned}V^{-1}\int d\mathbf{R}_{ij}[G_{ij}(t)-G_0(t)]g(0)\\ =(t-\tau_c)\Lambda_{ij}g(0)+M_{ij}(t)g(0),\end{aligned}\tag{6a}$$

where Λ_{ij} is the time-independent scattering operator defined by

$$\Lambda_{ij}\equiv V^{-1}m^{-1}P_{ij}\int d\omega\,\sigma[A_{ij}(\mathbf{l})-I]\tag{6b}$$

and

$$\begin{aligned}M_{ij}(t)\equiv V^{-1}\left(\int_{-2\epsilon mP_{ij}^{-1}}^{0}dt_1^0+\int_{t-\tau_c}^{t}dt_1^0\right)\\ \times m^{-1}P_{ij}\int d\omega\,\sigma[G_{ij}(t)-G_0(t)].\end{aligned}\tag{6c}$$

To obtain the order of magnitude of $M_{ij}(t)$ we apply the mean value theorem to the t_1^0 integral in (6c) and so obtain, since $(\epsilon mP_{ij}^{-1})=O(\tau_c)$,

$$M_{ij}(t)=O(\tau_c\Lambda_{ij})\ll t\Lambda_{ij}\quad(\text{large } t).\tag{7}$$

The scattering operator $(V\Lambda_{ij})$ is just the binary-collision integral which appears in the well-known Boltzmann equation. We see, from the derivation of (6a), that Λ_{ij} corresponds to completed collisions of a finite duration—not necessarily to instantaneous collisions.

The operator $M_{ij}(t)$ arises from "incompleted" collisions and, as can be seen in (7), is much smaller than $t\Lambda_{ij}$ for large t $(t\gg\tau_c)$.

To obtain $\beta_1(t)$ we substitute (6) into (1),

$$\begin{aligned}\beta_1(t)g&=[(t-\tau_c)\sum_{i<j}\Lambda_{ij}+\sum_{i<j}M_{ij}(t)]g\\ &\equiv[(t-\tau_c)\Lambda_{(1)}+M_{(1)}(t)]g,\end{aligned}\tag{8}$$

which is exact for all t. When t is large we see from (7) that the incompleted collision term $M_{(1)}(t)$ is relatively small.

$$M_{(1)}(t)=O(\tau_c\Lambda_{(1)})\ll t\Lambda_{(1)}.$$

Differentiating (8) with respect to t we obtain

$$\beta_1'(t)=\Lambda_{(1)}+M_{(1)}'(t),\quad \beta_1'(\infty)=\lim_{t\to\infty}t^{-1}\beta_1(t)=\Lambda_{(1)}.$$

The scattering operator $\Lambda_{(1)}$ is the "master" binary collision operator which appears in the low-density limit of the master equation.

From Eq. (38) of the previous paper we see that the incompleted collision operator $M_{(1)}(t)$ contributes to the non-Markoffian memory of the exact master equation. The scattering operator $\Lambda_{(1)}$ for completed collisions does not contribute to the memory. This operator is relevant to zero-frequency transport coefficients. The frequency dependence of transport coefficients may be obtained from the time dependence of $M_{(1)}(t)$.[4]

B. Calculation of $\beta_2(t)$

In this section we shall calculate the ternary collision integrals $\beta_2(ijk;t)$ [see Eq. (26) of Ref. 1]. We shall

[4] The formal frequency and density dependence of various transport coefficients can be obtained by combining the Laplace transform solution of the generalized master equation [Eq. (36) of Ref. 1] with the corresponding autocorrelation functions.

find that

$$(\partial/\partial t)\beta_2(123;t)=\Lambda_{123}+(\partial/\partial t)M_{123}(t),$$
$$=\Lambda_{123}+O(t^{-1}\tau_c\Lambda_{123}),$$

where Λ_{123} is a time-independent scattering operator for ternary collisions and is the three-particle analog of the binary-collision scattering operator Λ_{12}. The scattering operator Λ_{123} corresponds to completed ternary collisions just as Λ_{12} corresponds to completed binary collisions. The time-dependent operator $(\partial/\partial t)M_{123}(t)$ arises from incompleted ternary collisions and approaches zero as t approaches infinity.

To begin the calculation of $\beta_2(123;t)$ we first obtain its binary-collision expansion. Thus, we combine Eqs. (26), (15), and (7) [with $N=3$] of Ref. 1 to obtain

$$\beta_2(123;t)\equiv V^{-2}\int d\mathbf{R}_{12}d\mathbf{R}_{13}\,V_2(123;t)$$
$$=V^{-2}\int d\mathbf{R}_{12}d\mathbf{R}_{13}\sum_{n=3}^{\infty}\sum_{\{\alpha\}}^{123}f_{\alpha_1}f_{\alpha_2}\cdots f_{\alpha_n}G_0. \quad (9)$$

This expansion contains time-dependent irreducible clusters of three particles such as $f_{12}f_{13}f_{12}$, $f_{12}f_{13}f_{23}f_{13}$, $f_{12}f_{13}f_{12}f_{23}f_{13}f_{12}$, $f_{12}f_{13}f_{23}$.

We shall first calculate the integral of the simplest cluster, $f_{12}f_{13}f_{12}$, in detail. We shall then find that all the other cluster integrals in (9) have the same time dependence as the integral of $f_{12}f_{13}f_{12}$.

We thus consider [see Ref. 1, Eq. (6)], with the integral of $f_{12}f_{13}f_{12}$ denoted by $I_{(12)(13)(12)}$,

$$I_{(12)(13)(12)}g\equiv V^{-2}\int d\mathbf{R}_{12}d\mathbf{R}_{13}\,f_{12}f_{13}f_{12}g$$
$$\equiv V^{-2}\int d\mathbf{R}_{12}d\mathbf{R}_{13}\int_0^t dt_1\int_{t_1}^t dt_2\int_{t_2}^t dt_3\,G_{12}(t)iL_{12}$$
$$\times G_{13}(t_2-t_1)iL_{13}G_{12}(t_3-t_2)iL_{12}G_0(t-t_3)g. \quad (10)$$

It has been proven[5] that the time integrations in (10) may be exactly performed for the special case of hard-sphere interactions to yield

$$I_{(12)(13)(12)}g=V^{-2}\int d\mathbf{R}_{12}d\mathbf{R}_{13}\lim_{\tau_2\to t-t_1{}^0}[G_{12}(t)-G_0(t)]$$
$$\times\lim_{\tau_2\to -t_2{}^0}G_0(-\tau_1)[G_{13}(\tau_1)-G_0(\tau_1)]$$
$$\times G_0(-\tau_2)[G_{12}(\tau_2)-G_0(\tau_2)], \quad (11)$$

where $t_k{}^0$ is simply the instant of time at which an isolated pair of particles α_k [$\alpha_1=(12)$, $\alpha_2=(13)$, $\alpha_3=(12)$] will collide if their initial separation and relative momentum are $\mathbf{R}_{\alpha_k}$ and $\mathbf{P}_{\alpha_k}$, respectively, and is defined by the relation

$$t_k{}^0\equiv -mP_{\alpha_k}{}^{-1}\{\mathbf{R}_{\alpha_k}\cdot\mathbf{P}_{\alpha_k}P_{\alpha_k}{}^{-1}+(a^2-|\mathbf{R}_{\alpha_k}\times\mathbf{P}_{\alpha_k}|^2P_{\alpha_k}{}^{-2})^{1/2}\}.$$

[5] J. Weinstock, Phys. Rev. **126**, 341 (1962).

[We shall use Eq. (11) to calculate $I_{(12)(13)(12)}$ with the understanding that it is only exact for hard-sphere interactions. At the conclusion of this section we shall show that the main results may be carried over to more general interaction potentials.]

To evaluate (11) we recall, from the previous section, that the term $[G_{ij}(t)-G_0(t)]$ is nonzero for only those initial values of $\mathbf{R}_{ij}$ which lead to a collision between particles i and j within time t; i.e., for only those values of $\mathbf{R}_{ij}$ which lie within a collision cylinder. The binary collision propagator $G_{ij}(t)$ "prescribes" the changes in momenta of particles i and j corresponding to this collision, whereas the free-particle propagator $G_0(t)$ "prescribes" no changes in momenta. [$G_0(t)$ "prescribes" i and j to pass "through" each other without changing momenta, as if they were free particles.] For this reason, when integrating $[G_{ij}(t)-G_0(t)]$ over a collision cylinder, we say that $G_{ij}(t)$ produces a *real* collision between i and j, whereas $G_0(t)$ produces a *hypothetical*[6] collision between i and j.

In the cluster function in the integrand of (11) we see that the binary collision propagators $G_{ij}(t)$ always occur together with the free-particle propagator $G_0(t)$ in the combination $[G_{ij}(t)-G_0(t)]$. Each such combination is only nonzero for that region of $\mathbf{R}_{ij}$ space which leads to a collision between particle i and j within the interval t. For this reason the integrand in (11) is nonzero *for only those regions of* $\mathbf{R}_{12}$ *and* $\mathbf{R}_{13}$ *space which lead to the sequence of three binary collisions (both real and hypothetical) in which a collision between 1 and 2 is followed by a collision between 1 and 3 followed by a recollision between 1 and 2.* [Since each collision in this sequence may be real or hypothetical there will be eight combinations of these successive collisions depending on whether a given collision is real or hypothetical. These eight combinations correspond to the eight terms which are obtained by multiplying out the integrand in (11)—see Figs. 1 and 2.] The evaluation of (11) essentially consists of determining the regions of $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$ for which this sequence, (12)(13)(12), of successive collisions takes place.[7]

The first and second collision in this sequence will occur when $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$ lie within appropriate collision cylinders. Whether or not the third collision (the recollision between 1 and 2) takes place will depend upon the specific values of $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$ within these collision cylinders. That is, once specific values of $\mathbf{R}_{12}$

[6] M. S. Green, J. Chem. Phys. **25**, 836 (1956). This reference introduces the notion of hypothetical collisions of which our use is a specialization.

[7] The point of view of this calculation resembles that of Ref. 3. Our calculation involves an extension of the calculations in Ref. 3 to what is there referred to as a "correlated" sequence of binary collisions. These "correlated" collision terms are actually the clusters which appear in the binary collision expansion of the time-dependent irreducible, $\beta_k(t)$, and they correspond to three or more particle collisions. [See also R. Mazo, J. Chem. Phys. **35**, 831 (1961).]

and $\mathbf{R}_{13}$ are chosen the future relative motions of 1, 2, and 3 are determined for all time, and one can calculate whether or not the third collision will take place. We shall find that when $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$ are restricted to lie within certain regions of the collision cylinders then, and only then, will the third collision take place.

The calculation of (11) will, thus, consist of first finding the collision cylinders which lead to the first and second collisions, and then determining the regions of these collision cylinders which lead to the third collision.

1. *First and Second Collisions*

In this section we shall calculate the regions of $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$ space (collision cylinders) for which the operators in (11) which correspond to the first two collisions do not vanish. Thus, the operator $[G_{12}(t)-G_0(t)]\cdots$ (corresponding to the first collision) will vanish and, hence, the integrand of (11) will vanish unless particles 1 and 2 are aimed to collide within time t. Consequently,

$$\int_{\text{all space}} d\mathbf{R}_{12}[G_{12}(t)-G_0(t)]\cdots = \int_{\Omega(12;t)} d\mathbf{R}_{12}[G_{12}(t)-G_0(t)]\cdots, \quad (12)$$

where the region of integration $\Omega(12;t)$ is the collision cylinder whose length is $m^{-1}|\mathbf{P}_1-\mathbf{P}_2|t$ and whose cross section is $\sigma_T(|\mathbf{P}_1-\mathbf{P}_2|)$. Substituting (12) into (11), and then dividing the right side of (11) into two parts according to whether the first collision is real, $G_{12}(t)$, or hypothetical, $G_0(t)$, we obtain

$$I_{(12)(13)(12)}g=\int_{\Omega(12;t)} d\mathbf{R}_{12}\int d\mathbf{R}_{13}\, G_{r(12)(13)(12)}g - \int_{\Omega(12;t)} d\mathbf{R}_{12}\int d\mathbf{R}_{13}\, G_{h(12)(13)(12)}g, \quad (13)$$

where we have defined

$$G_{r,h(12)(13)(12)}\equiv \lim_{\tau_1\to t-t_1^0} G_{12,0}(t) \lim_{\tau_2\to -t_2^0} G_0(-\tau_1) \times[G_{13}(\tau_1)-G_0(\tau_1)]G_0(-\tau_2)[G_{12}(\tau_2)-G_0(\tau_2)]. \quad (14)$$

[The integrand, $G_{r(12)(13)(12)}g$, of the first multiple integral on the right-hand side of (13) contains the operator $G_{12}(t)$ and, hence, corresponds to a real first collision between 1 and 2. That is, if $f(\mathbf{P}_1,\mathbf{P}_2,\mathbf{P}_3)$ is any function of $\mathbf{P}_1$, $\mathbf{P}_2$, and $\mathbf{P}_3$, then when $\mathbf{R}_{12}$ lies within $\Omega(12;t)$ we must have

$$G_{12}(t)f(\mathbf{P}_1,\mathbf{P}_2,\mathbf{P}_3)=f[\mathbf{P}_1(1),\mathbf{P}_2(1),\mathbf{P}_3],$$

where $\mathbf{P}_1(1)$ and $\mathbf{P}_2(1)$ are the momenta of 1 and 2 after the first collision.]

In the first multiple integral on the right side of (13) we have the operator

$$\lim_{\tau_1\to t-t_1^0} G_{12}(t)G_0(-\tau_1)[G_{13}(\tau_1)-G_0(\tau_1)]\cdots,$$

(corresponding to the second collision when the first is real), which will vanish unless 1 and 3 are aimed to collide between the time t_1^0 (at which the first collision occurred) and the time t. Hence, just as for (12), we must have

$$\int_{\text{all space}} d\mathbf{R}_{13} \lim_{\tau_1\to t-t_1^0} G_{12}(t)G_0(-\tau_1)[G_{13}(\tau_1)-G_0(\tau_1)]\cdots = \int_{\Omega_r(13;t-t_1^0)} d\mathbf{R}_{13} \lim G_{12}(t)G_0(-\tau_1) \times[G_{13}(\tau_1)-G_0(\tau_1)]\cdots, \quad (15)$$

where $\Omega_r(13;t-t_1^0)$ is the collision cylinder whose length is $m^{-1}|\mathbf{P}_1(1)-\mathbf{P}_3|(t-t_1^0)$ and whose cross section is $\sigma_T(|\mathbf{P}_1(1)-\mathbf{P}_2|)$. [The subscript "$r$" denotes that, due to the operator $G_{12}(t)$, 1 and 2 have undergone a real collision so that the momentum $G_{12}(t)\mathbf{P}_1=\mathbf{P}_1(1)$ appears instead of $\mathbf{P}_1$.]

Similarly, we see that the second multiple integral on the right side of (13) contains the operator

$$\lim_{\tau_1\to t-t_1^0} G_0(t)G_0(-\tau_1)[G_{13}(\tau_1)-G_0(\tau_1)]\cdots$$

(corresponding to the second collision when the first is hypothetical), which will vanish unless 1 and 3 are aimed to collide between time t_1^0 and time t. Hence,

$$\int_{\text{all space}} d\mathbf{R}_{13} \lim_{\tau_1\to t-t_1^0} G_0(t)G_0(-\tau_1)[G_{13}(\tau_1)-G_0(\tau_1)]\cdots = \int_{\Omega_h(13;t-t_1^0)} d\mathbf{R}_{13} \lim G_0(t)G_0(-\tau_1) \times[G_{13}(\tau_1)-G_0(\tau_1)]\cdots, \quad (16)$$

where $\Omega_h(13;t-t_1^0)$ is the collision cylinder whose length is $m^{-1}|\mathbf{P}_1-\mathbf{P}_3|(t-t_1^0)$ and whose cross section is $\sigma_T(|\mathbf{P}_1-\mathbf{P}_3|)$. [The subscript "$h$" denotes that the previous collision between 1 and 2, in this integral, is hypothetical so that $\mathbf{P}_1$ appears instead of $\mathbf{P}_1(1)$. That is, $G_0(t)\mathbf{P}_1=\mathbf{P}_1$.]

Substituting (15) and (16) into (13) we obtain

$$I_{(12)(13)(12)}g=\int_{\Omega(12;t)} d\mathbf{R}_{12}\int_{\Omega_r(12;t)} d\mathbf{R}_{13}\, G_{r(12)(13)(12)}g - \int_{\Omega(12;t)} d\mathbf{R}_{12}\int_{\Omega_h(13;t-t_1^0)} d\mathbf{R}_{13}\, G_{h(12)(13)(12)}g. \quad (17)$$

To facilitate the calculation of (17) it is convenient to transform the variables of integration $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$

into cylindrical coordinates as was done in (3). Accordingly, the component of $\mathbf{R}_{12}$ parallel to $\mathbf{P}_{12}$ is transformed into the time of the first collision $t_1{}^0$ and the component of $\mathbf{R}_{12}$ perpendicular to $\mathbf{P}_{12}$ is transformed into the solid scattering angle of the first collision ω_1. Similarly, for the first term on the right of (17) the component of $\mathbf{R}_{13}$ parallel to $[\mathbf{P}_1(1)-\mathbf{P}_3]$ is transformed into the time $t_2{}^*$ at which the second collision is aimed to take place (when the first collision is real, and the component of $\mathbf{R}_{13}$ perpendicular to $[\mathbf{P}_1(1)-\mathbf{P}_3]$ is transformed into the solid scattering angle ω_2. In the second term on the right of (17) the component of $\mathbf{R}_{13}$ parallel to $\mathbf{P}_{13}$ is transformed into the time $t_2{}^0$ at which the second collision is aimed to take place (when the first collision is hypothetical), and the component of $\mathbf{R}_{13}$ perpendicular to $\mathbf{P}_{13}$ is transformed into the solid scattering angle ω_2. Making these changes of variables to cylindrical coordinates in (17) we find

$$I_{(12)(13)(12)}g=m^{-2}V^{-2}\int_0^t dt_1{}^0\int_{t_1{}^0}^t dt_2{}^*\int d\omega_1\int d\omega_2$$
$$\times P_{12}|\mathbf{P}_1(1)-\mathbf{P}_3|\sigma_{12}(\omega_1,P_{12})\sigma_{13}(\omega_2,\ |\mathbf{P}_1(1)-\mathbf{P}_3|)$$
$$\times G_{r(12)(13)(12)}g-m^{-2}V^{-2}\int_0^t dt_1{}^0\int_{t_1{}^0}^t dt_2{}^0\int d\omega_1\int d\omega_2$$
$$\times P_{12}P_{13}\sigma_{12}\sigma_{13}G_{h(12)(13)(12)}g\,, \quad (18)$$

and we wish to emphasize that the set of variables $t_1{}^0$, t_2, ω_1, ω_2 is entirely equivalent to the set of variables $\mathbf{R}_{12}$, $\mathbf{R}_{13}$.

2. *Third Collision*

The integrands $[G_{r(12)(13)(12)}g$ and $G_{h(12)(13)(12)}g]$ in (18) both contain the operator $\cdots[G_{12}(\tau_2)-G_0(\tau_2)]$ which will vanish unless 1 and 2 are aimed to recollide [the third collision in the sequence (12)(13)(12)]. We may, thus, restrict $t_1{}^0$, t_2, ω_1, and ω_2 in (18) to lie within those regions of the collision cylinders which lead to the third collision. This may be accomplished as follows:

We note that $\mathbf{P}_1$, $\mathbf{P}_2$, and $\mathbf{P}_3$ are fixed parameters in (18), so that once specific values of $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$ $(t_1{}^0,t_2,\omega_1,\omega_2)$ are selected, the relative motions of particles 1, 2, and 3 are determined for all time. Since $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$ are restricted to lie within collision cylinders, the first two collisions will be aimed to take place. But, at the instant following the second collision, particles 1 and 2 will be at a relative distance $\mathbf{R}_{12}(2)$ with a relative momentum $\mathbf{P}_{12}(2)$ and, hence, particles 1 and 2 will recollide only if, at that instant, they are moving towards each other with an impact parameter b_3,

$$b_3\equiv|\mathbf{R}_{12}(2)\times\mathbf{P}_{12}(2)|P_{12}(2)^{-1},$$

which is less than the range of force a (hard-sphere diameter a). That is, particles 1 and 2 will recollide, within time t, if and only if at the instant following the second collision their relative distance $\mathbf{R}_{12}(2)$ and momentum $\mathbf{P}_{12}(2)$ satisfy

$$|\mathbf{R}_{12}(2)\times\mathbf{P}_{12}(2)|P_{12}(2)^{-1}<a\,, \quad (19a)$$
$$\mathbf{R}_{12}(2)\cdot\mathbf{P}_{12}(2)<0\,, \quad (19b)$$
$$t_3{}^*<t\,, \quad (19c)$$

where (19a) ensures that their impact parameter is less than the range of force, (19b) ensures that they are moving towards each other rather than away from each other, and (19c), with $t_3{}^*$ denoting the time at which this third collision takes place, ensures that the collision sequence occurs within time t. But $\mathbf{R}_{12}(2)$, $\mathbf{P}_{12}(2)$, and $t_3{}^*$ are uniquely and, as we shall see, easily determined functions of $t_1{}^0$, t_2, ω_1, and ω_2:

$$\mathbf{R}_{12}(2)=\mathbf{R}_{12}(t_1{}^0,t_2,\omega_1,\omega_2)\,,$$
$$\mathbf{P}_{12}(2)=\mathbf{P}_{12}(t_1{}^0,t_2,\omega_1,\omega_2)\,,$$
$$t_3{}^*=t_3{}^*(t_1{}^0,t_2,\omega_1,\omega_2)\,,$$

so that the inequalities (19a,b,c) exactly define the only regions of $t_1{}^0$, t_2, ω_1, and ω_2 for which the third collision will follow the first two collisions.

This means that the inequalities define the only regions of $t_1{}^0$, t_2, ω_1, ω_2 for which $G_{r(12)(13)(12)}$ and $G_{h(12)(13)(12)}$ are nonvanishing. Consequently, we may write (18) as

$$I_{(12)(13)(12)}g=\int_0^t dt_1{}^0\int_{t_1{}^0}^t dt_2{}^*\int d\omega_1\int_{V_r} d\omega_2\, C_rG_{r(12)(13)(12)}g$$
$$-\int_0^t dt_1{}^0\int_{t_1{}^0}^t dt_2{}^0\int d\omega_1\int_{V_h} d\omega_2\, C_hG_{h(12)(13)(12)}g$$
$$\equiv I_{r(12)(13)(12)}g-I_{h(12)(13)(12)}g\,, \quad (20)$$

where V_r and V_h denote those regions in the spaces of $t_1{}^0$, $t_2{}^*$, ω_1, ω_2 and $t_1{}^0$, $t_2{}^0$, ω_1, ω_2 which satisfy (19a)–(19c) when the first collision is real and hypothetical, respectively, so that

$$\cdots\int_{V_r} d\omega_2 \quad \text{and} \quad \cdots\int_{V_h} d\omega_2$$

mean that the integration over $t_1{}^0$, $t_2{}^*$ (or $t_2{}^0$), ω_1, and ω_2 must be restricted to the regions of the collision cylinders which satisfy (19a)–(19c) when the first collision is real (or hypothetical); and where we have defined, for convenience,

$$C_r\equiv V^{-2}m^{-2}P_{12}|\mathbf{P}_1(1)-\mathbf{P}_3|$$
$$\times\sigma_{12}(\omega_1,P_{12})\sigma_{13}(\omega_2,|\mathbf{P}_1(1)-P_3|)\,, \quad (21)$$
$$C_h\equiv V^{-2}m^{-2}P_{12}P_{13}\sigma_{12}(\omega_1,P_{12})\sigma_{13}(\omega_2,P_{13})\,.$$

The calculation of $I_{(12)(13)(12)}$ now consists of four steps: (1) to determine $\mathbf{R}_{12}(2)$, $\mathbf{P}_{12}(2)$, and $t_3{}^*$ as functions of $t_1{}^0$, t_2, ω_1, and ω_2; (2) to solve (19a)–(19c) [for those regions of $t_1{}^0$, t_2, ω_1, and ω_2 which lead to all three collisions]; (3) to explicitly restrict the integrations in (20) to the regions of t_1^0, t_2, ω_1, and ω_2 which are determined by step (2); and (4) to replace the propagators $G_{ij}(\tau)$ which appear in (20) by their corresponding momentum substitution operators $A_{ij}(\mathbf{l})$.

The details of this calculation are given in Appendix A where it is found that $I_{(12)(13)(12)}(t)g$ is given, exactly, by

$$I_{(12)(13)(12)}(t)g=[t\Lambda_{(12)(13)(12)}+M_{(12)(13)(12)}(t)]g, \quad (22)$$

where $\Lambda_{(12)(13)(12)}$ is a time-independent scattering operator for *completed collisions* defined by

$$\Lambda_{(12)(13)(12)} \equiv \int_0^{\tau_{rc}} d\tau_r \int_{D_r} d\omega_1 d\omega_2\, C_r A_{12}(\mathbf{l}_1) A_{13}(\mathbf{l}_2)[A_{12}(\mathbf{l}_{3r})-I] - \int_0^{\tau_{hc}} d\tau_h \int_{D_h} d\omega_1 d\omega_2\, C_h A_{13}(\mathbf{l}_2)[A_{12}(\mathbf{l}_{3h})-I]. \quad (23)$$

[Here D_r and D_h denote regions of integrations over ω_2 and are defined as those regions of ω_2 which satisfy $\mathbf{l}_1\cdot\mathbf{P}_{r12}(2)<0$ and $\mathbf{l}_2\cdot\mathbf{P}_{h12}(2)$, respectively; $\mathbf{l}_1=\mathbf{l}_1(\omega_1)$ and $\mathbf{l}_2=\mathbf{l}_2(\omega_2)$ are the unit vectors in the perihelion direction of the first and second collision, respectively, and are known functions of the solid scattering angles ω_1 and ω_2; $\mathbf{l}_{3r}$ and $\mathbf{l}_{3h}$ are unit vectors in the perihelion direct of the third collision when the first collision is real and hypothetical, respectively, and are given by (A23); $P_{r12}(2)$ and $\mathbf{P}_{h12}(2)$ are the relative momenta of particles 1 and 2 at the instant following the second collision when the first collision is real and hypothetical, respectively, and are given by (A3) and (A17); τ_{rc} and τ_{hc} are time intervals of the duration of a binary collision and are explicitly given in (A6); and $\tau_r\equiv t_2^*-t_1^0$, $\tau_h\equiv t_2^0-t_1^0$.]

The time-dependent operator $M_{(12)(13)(12)}(t)$ corresponds to an *incompleted* sequence of collisions and is defined by (A20), (A13), and (A18). [We note that the integration $\int d\omega_1 d\omega_2$ in the definition of $M_{(12)(13)(12)}(t)$ contains the restriction $t_3^*>t$. This restriction means that the last collision, in the collision sequence (12)(13)(12), must occur after time t and, hence, is referred to as an incompleted collision.]

Equation (22) expresses the fact that the collision integral $I_{(12)(13)(12)}(t)$ divides into a completed and an incompleted collision part. The notion of completed and incompleted collisions is quite general and is a useful concept with which to understand the kinetics of approach to equilibrium and the frequency dependence of transport coefficients.

The completed collision part $\Lambda_{(12)(13)(12)}$ is a "simple" scattering operator which may prove useful in calculating transport coefficients. The more complicated incompleted collision part $M_{(12)(13)(12)}(t)$ is relatively small when t is large. This is because of the restriction $t_3^*>t$ upon the region of integration over ω_1 and ω_2. This restriction can not be satisfied when t is infinite and leads to a relatively small value of $M_{(12)(13)(12)}(t)$ when t is large. The asymptotic time dependence of $M_{(12)(13)(12)}(t)$ can be shown to be given by

$$M_{(12)(13)(12)}(t)=E\ln t+E', \quad (24)$$

where E and E' are independent of t and have their order of magnitude given by $O(t_c\Lambda_{(12)(13)(12)})$ [the logarithmic time dependence in (24) is a consequence of the fact that the volume of ω_1 and ω_2 space which satisfies $t_3^*>t$ is proportional to t^{-2} when t is large] so that

$$I_{(12)(13)(12)}(t)g\sim t\Lambda_{(12)(13)(12)}g \quad (t\gg\tau_c).$$

3. *Time Dependence of the Remaining Three-Particle Cluster Integrals*

To complete the calculation of β_2 we must determine the time dependence of the remaining cluster integrals of particles 1, 2, 3,

$$I_{(\alpha_1)\cdots(\alpha_n)}\equiv V^{-2}\int d\mathbf{R}_{12}d\mathbf{R}_{13}\, f_{\alpha_1}f_{\alpha_2}\cdots f_{\alpha_n}G_0 \quad (25)$$

[for example: $I_{(12)(13)(12)(13)(23)(13)(23)}$], which appear in the binary-collision expansion of $\beta_2(123;t)$, Eq. (9). This is done in Appendix B where it is found that

$$I_{(\alpha_1)\cdots(\alpha_n)}g=[t\Lambda_{(\alpha_1)\cdots(\alpha_n)}+M_{(\alpha_1)\cdots(\alpha_n)}(t)]g. \quad (26)$$

Here, $\Lambda_{(\alpha_1)\cdots(\alpha_n)}$ is a (time-independent) scattering operator for the *completed* sequence of successive binary collisions, in which a collision between the pair of particles α_1 is followed by a collision between α_2 and so on up to α_n. This scattering operator is explicitly expressed in (B8). The time-dependent operator $M_{(\alpha_1)\cdots(\alpha_n)}(t)$ corresponds to an incompleted sequence of binary collisions and is defined in (B9). [This operator is associated with incompleted collisions because it contains the restriction $t_n^*>t$, where t_n^* is the time at which occurs the last collision in the sequence $(\alpha_1)(\alpha_2)\cdots(\alpha_n)$.] It can be shown that

$$M_{(\alpha_1)\cdots(\alpha_n)}(t)=O(\ln t), \quad (\text{large } t)$$

so that $t\Lambda_{(\alpha_1)\cdots(\alpha_n)}$ is the dominant part of $I_{(\alpha_1)\cdots(\alpha_n)}$ for large t.

The "full" triple-collision integral $\beta_2(123;t)$ is obtained by simply substituting (26) and (25) into (9). We thus obtain

$$\beta_2(123;t)=t\Lambda_{123}+M_{123}(t), \quad (27)$$

where Λ_{123} is a ternary-collision scattering operator for completed collisions,

$$\Lambda_{123}\equiv\sum_{n=3}^{\infty}\sum_{\{\alpha\}}^{123}\Lambda_{(\alpha_1)\cdots(\alpha_n)} = \lim_{t\to\infty} t^{-1}\beta_2(123;t), \quad (28)$$

and

$$M_{123}(t) \equiv \sum_{n=3}^{\infty} \sum_{\{\alpha\}}^{123} M_{(\alpha_1)\cdots(\alpha_n)}(t)$$
$$= O(\ln t) \qquad (29)$$

corresponds to incompleted ternary collisions.

Equation (27) is exact for all t. It expresses the fact that the ternary-collision integral (three-particle cluster integral) $\beta_2(123;t)$ divides into a completed ternary-collision part (dominant part) and an incompleted collision part. The completed ternary-collision part Λ_{123} is a scattering operator analogous to the binary-collision scattering operator Λ_{12}. It occurs in the Markoffian limit of the generalized master equation and will play a central role in the calculation of density dependent transport coefficients. The more complicated incompleted part $M_{123}(t)$ is relatively small when t is large. The time dependence of $M_{123}(t)$ is relevant to the kinetics of approach to equilibrium as well as to the frequency dependence of transport coefficients. We shall discuss the connection between $\beta_2(123;t)$ and the master equation in the next section.

Thus far, we have only proven (27) for hard-sphere potentials. An equation of the same form as (27) may be derived for any repulsive pair force of finite range. This is because when (τ_c/t) is small we may use the mean value theorem to expand $\beta_2(123;t)$ in the small parameter (τ_c/t). The first term of such an expansion will be asymptotic to (27) [for large t] and the remaining terms will be relatively small for large t. We thus find that following is exact for repulsive forces.

$$\beta_2(123;t) = t\Lambda_{123} + M_{123}(t), \qquad (30)$$

providing Λ_{123} and $M_{123}(t)$ are defined by the formal relations

$$\Lambda_{123} \equiv \lim_{t\to\infty} t^{-1}\beta_2(123;t) = \beta_2'(123;\infty),$$
$$M_{123}(t) \equiv \beta_2(123;t) - t\Lambda_{123}. \qquad (31)$$

In view of (31), $M_{123}(t)$ satisfies

$$\lim_{t\to\infty} t^{-1} M_{123}(t) = 0.$$

III. TERNARY-COLLISION OPERATOR AND THE NON-MARKOFFIAN BEHAVIOR OF THE EQUATION OF EVOLUTION

We wish to elucidate the connection between incompleted collisions and the non-Markoffian memory of the master equation. The master equation for the evolution of ϕ involves the "master" ternary collision operator $\beta_2(t)$ which is obtained by summing $\beta_2(ijk;t)$ over all of the particles of the system. That is,

$$\beta_2(t) \equiv \sum_{i<j<k} \beta_2(ijk;t) \qquad (32)$$

appears in the non-Markoffian kernel of the master equation.

Substituting (30) into (32) we obtain

$$\beta_2(t) = t\Lambda_{(2)} + M_{(2)}(t), \qquad (33)$$

where $\Lambda_{(2)}$ and $M_{(2)}$ are "master" ternary-collision operators defined by

$$\Lambda_{(2)} \equiv \sum_{i<j<k} \Lambda_{ijk}, \quad M_{(2)}(t) \equiv \sum_{i<j<k} M_{ijk}(t).$$

Differentiating (33) with respect to t gives

$$\beta_2'(t) = \Lambda_{(2)} + M_{(2)}'(t).$$

From Eq. (38) of the previous paper we see that the non-Markoffian memory of the master equation contains $M_2'(t)$ but not Λ_2. But, from (B9) we see that $M_2(t)$ is entirely due to incompleted ternary collisions $(t_n^* > t)$. This, indeed, shows that non-Markoffian behavior arises from incompleted collisions.

We further note that *instantaneous* ternary collisions do not contribute to the three-body scattering operator Λ_{123}. To understand why we consider Λ_{123} expressed in terms of $\Lambda_{(\alpha_1)\cdots(\alpha_n)}$, in (28), we recall that $\Lambda_{(\alpha_1)\cdots(\alpha_n)}$ is the scattering operator for a sequence of successive binary collisions among 1, 2, and 3 in which pair α_1 collide at time t_1^0, pair α_2 collide at time t_2^*, and so on up to time t_n^*. In order for this sequence of collisions among particles 1, 2, and 3 to be instantaneous we must obviously require that

$$t_1^0 = t_2^* = \cdots = t_n^*,$$

that is, the time interval during which this sequence occurs must vanish. But we see from (B8) that if $t_2^* - t_1^0 \equiv \tau_2 = 0$, then $\Lambda_{(\alpha_1)\cdots(\alpha_n)} = 0$ and, hence, from (28)

$$\Lambda_{123} = 0 \quad (t_2^* = t_1^0).$$

This proves that the three-body scattering operator vanishes for those collisions which are literally instantaneous or, in other words, instantaneous ternary collisions do not contribute to the three-body scattering operator.

The essence of ternary collisions, then, is not that of a single instantaneous event but one in which three particles collide, successively, many times in a highly correlated fashion. For example, see Figs. 1 and 2. (Hence, if an experiment could be devised which would measure the kinetic energy of a particle undergoing a ternary collision we would find that a curve representing the kinetic energy of such a particle as a function of time shows several local maxima and minima.) The duration of such a ternary collision will, in general, be larger than the duration of a single binary collision. Furthermore, it is not necessary that all three particles in such a collision be simultaneously interacting—particularly if the pair force is short ranged—hard spheres, for example.

This contradicts Resibois' claim that only situations in which the three particles are *simultaneously* interacting play a role in the asymptotic three-body scattering operator Λ_{123}. This is immediately clear for the simple example of hard spheres, since then simultaneous ternary collisions are necessarily instantaneous, and, as we have shown, instantaneous ternary collisions do not contribute to Λ_{123} at all. (It is obvious that the cross section, or region of configuration space, for three hard spheres to come simultaneously into contact is equal to zero.)

Finally, the above discussion supports our assertion that it is the concept of completed collisions of a finite duration, rather than instantaneous collisions, which is fundamental in understanding nonequilibrium phenomena.

IV. TRANSPORT COEFFICIENTS

In view of the role played by the scattering operator Λ_{123} in the calculation of transport coefficients it is desirable that it be cast into a form that is readily amenable to calculations. Since Λ_{123} involves the solution of the three-body problem, one must inevitably consider approximate methods. Approximations based upon expansions in the interaction strength are to be avoided since all the terms, in such an expansion, diverge for infinite repulsions. The binary-collision expansion, on the other hand, is well suited to infinite repulsions. In this section we shall use the binary-collision expansion to obtain an approximate expression for Λ_{123} in such a form that it may be readily applied to calculate transport coefficients.

The binary-collision expansion of Λ_{123} is given by (31) and (9)

$$\begin{aligned}\Lambda_{123}&\equiv\lim_{t\to\infty}t^{-1}\beta_2(123;t)\,,\\&=\lim_{t\to\infty}t^{-1}V^{-2}\int d\mathbf{R}_{12}d\mathbf{R}_{13}\sum_{n=3}^{\infty}\sum_{\{\alpha\}}^{123}f_{\alpha_1}\cdots f_{\alpha_n}\,,\\&=\sum_{n=3}^{\infty}\sum_{\{\alpha\}}^{123}\Lambda_{(\alpha_1)\cdots(\alpha_n)}\,,\end{aligned}\tag{34}$$

where the scattering operator $\Lambda_{(\alpha_1)\cdots(\alpha_n)}$ for hard spheres is given exactly by (B8). [Equation (B8) is a good approximation for other interactions when the corresponding cross sections are used.]

But, the summand in (34) decreases with n. That is, it can be seen from (B8) and (B2) that

$$\Lambda_{(\alpha_1)\cdots(\alpha_{n-1})}>\Lambda_{(\alpha_1)\cdots(\alpha_{n-1})(\alpha_n)}\,.\tag{35}$$

This is because the region of integration over τ_2, ω_1, and ω_2 (over $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$ space) in $\Lambda_{(\alpha_1)\cdots(\alpha_{n-1})}$ is greater than the region of integration in $\Lambda_{(\alpha_1)\cdots(\alpha_{n-1})(\alpha_n)}$. That is, $\Lambda_{(\alpha_1)\cdots(\alpha_{n-1})(\alpha_n)}$ contains all the restrictions implied by (32) with $k=3, 4, \cdots(n-1)$, and n, whereas $\Lambda_{(\alpha_1)\cdots(\alpha_{n-1})}$ only contains the restriction with $k=3, 4, \cdots(n-1)$.

Taking advantage of the fact that (34) is a decreasing series in n, we approximate (34) by

$$\Lambda_{123}\approx\sum_{\{\alpha\}}^{123}\Lambda_{(\alpha_1)(\alpha_2)(\alpha_3)}\,.\tag{36}$$

The rate at which (34) converges and, hence, the validity of (36) is a matter that could and should be investigated since it may lead to a good approximate solution of the three-body scattering problem in classical gases.

The scattering operator $\Lambda_{(12)(13)(12)}$ in (36) is explicitly given by (23), and the various quantities contained there are given in the Appendix. Equations (23) and (36) may be directly used to calculate an approximate first-order density correction to transport coefficients by means of the autocorrelation function method.

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APPENDIX A: CALCULATION OF $I_{(12)(13)(12)}(t)g$

The calculation of $I_{(12)(13)(12)}(t)g$ from Eq. (20) involves the four steps enumerated in Sec. B2. Since, however, $\mathbf{P}_{12}(2)$ will depend upon whether the first and second collisions are real or hypothetical, we must make a separate, but similar, calculation for each of the four possible cases. The number of cases may be immediately reduced to two since there can be no contribution when the second collision is hypothetical. This is because a hypothetical second collision, in the sequence (12)(13)(12), implies that 1 and 2 will collide two times with each other without either of them suffering any momentum change in between. This is clearly impossible for hard-sphere collisions. That is, the following hypothetical second collision terms in (20) must vanish:

$$\int_{\Omega(12;t)}d\mathbf{R}_{12}G_{12,0}(t)\lim_{\tau_2\to-t_2^0}G_0(-\tau_2)\times[G_{12}(\tau_2)-G_0(\tau_2)]\tag{A1}$$

and, hence, we may replace $G_{r,h(12)(13)(12)}$ in (20) by

$$G'_{r,h(12)(13)(12)}=\lim_{\tau_1\to t-t_1^0}G_{12,0}(t)\lim_{\tau_2\to-t_2^0}G_0(-\tau_1)\times G_{13}(\tau_1)G_0(-\tau_2)[G_{12}(\tau_2)-G_0)\tau_2)]\,.\tag{A2}$$

There thus remains two cases depending upon whether the first collision is real or hypothetical. We shall first focus our attention upon the real first collision term $I_{r(12)(13)(12)}g$ in (20). If we let the subscripts r and h denote that the first collision is real and hypothetical, respectively, then for step one we find the relative momenta of 1 and 2 at the instant following the second collision (when the first collision is real) is given by (see Fig. 1)

$$\mathbf{P}_{r12}(2)=\mathbf{P}_{r12}(1)-[\mathbf{P}_{13}-\mathbf{P}_{12}\cdot\mathbf{l}_1\mathbf{l}_1]\cdot\mathbf{l}_2\mathbf{l}_2, \quad \text{(A3)}$$
$$\mathbf{P}_{r12}(1)=\mathbf{P}_{12}-2\mathbf{P}_{12}\cdot\mathbf{l}_1\mathbf{l}_1,$$
$$\mathbf{R}_{r12}(2)=m^{-1}(t_2^*-t_1^0)\mathbf{P}_{r12}(1)+a\mathbf{l}_1, \quad \text{(A4)}$$

where $\mathbf{l}_1=\mathbf{l}_1(\omega_1)$ and $\mathbf{l}_2=\mathbf{l}_2(\omega_2)$ are unit vectors in the perihelion direction of the first and second collisions and are known functions of the solid scattering angles ω_1 and ω_2, respectively.

According to step two in the calculation of $I_{r(12)(13)(12)}g$ we substitute (A3) and (A4) into (19a) and solve for $(t_2^*-t_1^0)$ to obtain[8]

$$t_2^*-t_1^0<\tau_{rc}=\tau_{rc}(\omega_1,\omega_2), \quad \text{(A5)}$$

where τ_{rc} is of the order of the duration of a binary collision and is given as a function of $\mathbf{l}_1$ and $\mathbf{l}_2$ (or, equivalently, of ω_1 and ω_2) by

$$\begin{aligned}\tau_{rc}\equiv ma|\mathbf{P}_{r12}(1)\times\mathbf{P}_{r12}(2)|^{-2}\\ \times\{[(\mathbf{l}_1\times\mathbf{P}_{r12}(2)\cdot\mathbf{P}_{r12}(1)\times\mathbf{P}_{r12}(2))^2\\ +(\mathbf{l}_1\cdot\mathbf{P}_{r12}(2))^2|\mathbf{P}_{r12}(2)\times\mathbf{P}_{r12}(1)|^2]^{1/2}\\ -\mathbf{l}_1\times\mathbf{P}_{r12}(2)\cdot\mathbf{P}_{r12}(1)\times\mathbf{P}_{r12}(2)\}. \quad \text{(A6)}\end{aligned}$$

The inequalities (19a) and (19b) are partially redundant and it can be shown that the inequality

$$\mathbf{l}_1\cdot\mathbf{P}_{r12}(2)<0 \quad \text{(A7)}$$

together with (A5) are exactly equivalent to the two inequalities (19a) and (19b).

For step three in the calculation we substitute (A5) and (A7) into $I_{r(12)(13)(12)}g$ in (20) to obtain, with the change of variables $t_2^*-t_1^0\equiv\tau_r$,

$$I_{r(12)(13)(12)}g=\int_0^t dt_1^0\int_0^{t-t_1^0}d\tau_r\int_{D_1}d\omega_1 d\omega_2 \; C_rG_r'{}_{(12)(13)(12)}g, \quad \text{(A8)}$$

where D_1 is the region of τ_r, ω_1, ω_2 which satisfies $\tau_r<\tau_{rc}$, $\mathbf{l}_1\cdot\mathbf{P}_{r12}(2)<0$, $t_3^*<t$. (The region D_1 is, of course, the same as V_r.) But

$$t_3^*\equiv(t_3^*-t_2^*)+\tau_r+t_1^0\geqslant\tau_r+t_1^0,$$

so that

$$\int_0^{t-t_1^0}d\tau_r\int_{D_1}d\omega_1d\omega_2=\int_0^{\tau_{rc}}d\tau_r\int_{D_2}d\omega_1d\omega_2,$$

[8] Inequality (A5), which follows directly from (19a), is the most significant relationship of this derivation. It states that in order to satisfy the condition of "impact parameter small enough for the third collision to occur" [Eq. (19a)] the time interval $(t_2^*-t_1^0)$ between the instants at which the first and second collision occur must be bounded by τ_{rc}. Since τ_{rc} is of the order of the duration of a binary collision it follows that during the time interval between the first and second collision all three particles must be relatively close to each other—close within orders of magnitude of molecular size. This, in fact, is the essence of a ternary collision.

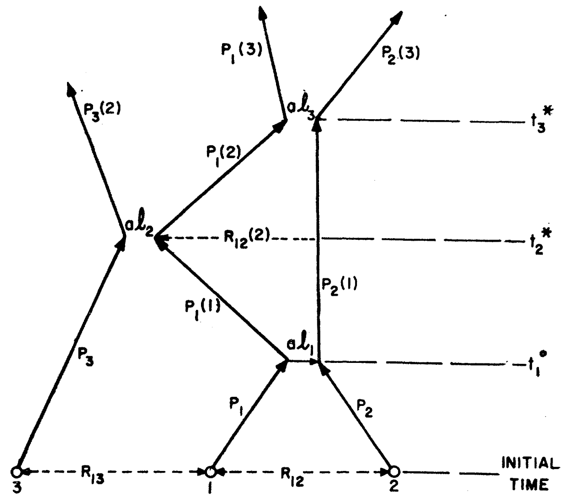

FIG. 1. Schematic diagram of particle trajectories for a three successive binary-collision term which contributes to the three-particle scattering operator.

where D_2 denotes the region for which $\mathbf{l}_1\cdot\mathbf{P}_{r12}(2)<0$, $t_3^*<t$ and, hence, (A8) becomes

$$I_{r(12)(13)(12)}g=\int_0^t dt_1^0\int_0^{\tau_{rc}}d\tau_r\int_{D_2}d\omega_1d\omega_2 \times C_rG'_{r(12)(13)(12)}g. \quad \text{(A9)}$$

We see in (A9) that t_1^0, τ_r, ω_1, and ω_2 have been restricted to those regions for which all three collisions in the sequence (12)(13)(12) are aimed to take place within time t. This means that the binary-collision propagators G_{12} and G_{13} which appear in $G'_{r(12)(13)(12)}$ will produce the real momentum changes corresponding to these collisions and, hence, these propagators may be replaced by their corresponding momentum operators (A_{12} and A_{13}). The free-particle propagators produce no changes in momenta and may be replaced by identity operators. We thus have, for an initial phase point in which all three collisions are aimed to take place within time t,

$$\begin{aligned}G'_{r(12)(13)(12)}=A_{12}(\mathbf{l}_1)A_{13}(\mathbf{l}_2)[A_{12}(\mathbf{l}_3)-I]\\ \equiv S_{r(12)(13)(12)}. \quad \text{(A10)}\end{aligned}$$

The momentum operator $S_{r(12)(13)(12)}$ is a time-independent scattering operator in momentum space and not a propagator. This operator merely transforms the momenta of a group of particles from the momenta that they have before they interact with each other to the momenta they will have after they interact with each other in a sequence of binary collisions.

We next substitute (A10) into (A9), divide the resulting integral into two parts by dividing the region of integration into two parts $[\int_{D_2}=\int_{D_r}-\int_{D_{r3}}$, where D_r is the region of ω_2 which satisfies $\mathbf{l}_1\cdot\mathbf{P}_{r12}(2)=0$, and D_{r3} is the region of ω_2 and τ_r which satisfies both

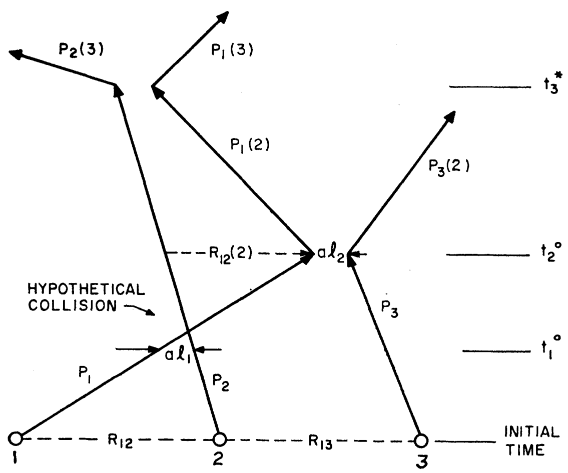

FIG. 2. Schematic diagram of particle trajectories for three successive binary collisions in which the first collision is *hypothetical.*

$\mathbf{l}_1\cdot\mathbf{P}_{r12}(2)<0$ and $t_3^*>t]$[9], and then freely integrate over t_1^0 in the first part (D_r) to obtain

$$I_{r(12)(13)(12)}g=[t\Lambda_{r(12)(13)(12)}+M_{r(12)(13)(12)}(t)]g\,, \quad \text{(A11)}$$

where $\Lambda_{r(12)(13)(12)}$ is defined by

$$\Lambda_{r(12)(13)(12)}\equiv\int_0^{\tau_{rc}}d\tau_r\int_{D_r}d\omega_1 d\omega_2\, C_r S_{r(12)(13)(12)} \quad \text{(A12)}$$

and is a time-independent scattering operator for completed collisions.

The operator $M_{r(12)(13)(12)}(t)$ corresponds to incompleted collisions $(t_3^*>t)$ and is defined by

$$M_{r(12)(13)(12)}\equiv-\int_0^t dt_1^0\int_0^{\tau_{rc}}d\tau_r\int_{D_{r3}}d\omega_1 d\omega_2\; C_r S_{r(12)(13)(12)}\,. \quad \text{(A13)}$$

[The t_1^0 integration in $M_{r(12)(13)(12)}(t)$ is complicated by the fact that the region of integration depends upon t_1^0 through the inequality $t_3^*>.]t$

[9] This division of the collision integral in (A9) into two parts, according to

$$\cdots\int_{t_3^*<t}d\omega_1 d\omega_2=\cdots\int d\omega_1 d\omega_2-\cdots\int_{t_3^*>t}d\omega_1 d\omega_2\,,$$

separates out incompleted collision events $(t_3^*>t)$. The integration over $\tau_r\equiv\tau_2^*-t_1^0$ in all these integrals is bounded by τ_{rc} which, for most of ω_1 and ω_2, is of the order of the duration of a binary collision. This means that in the first integral on the right (completed collisions) the main contribution corresponds to sequences of collisions in which the time interval between successive collisions is relatively small and, hence, for which all three particles are simultaneously close to each other at some time. In the second integral on the right (incompleted collisions), however, there is the restriction $t_3^*>t$ which, when t is large, can only be satisfied for a very small region of ω_1 and ω_2 space for which, it turns out, τ_{rc} is very large. In this integral, then, τ_r may assume large values and, hence, the dominant contribution corresponds to large time intervals between successive collisions. In this case all three particles will not be simultaneously close to each other at any time.

Thus far, we have only calculated the real first collision term $I_{r(12)(13)(12)}g$ in (20). There still remains the calculation of $I_{h(12)(13)(12)}g$ which corresponds to a hypothetical first collision. The operator $I_{h(12)(13)(12)}$ may be calculated in the same way as $I_{r(12)(13)(12)}$. The only difference is that in the hypothetical collision case the particle momenta do not change as a result of the first collision (see Fig. 2) so that the results of the real collision case may be carried over to the hypothetical collision case by merely changing the appropriate particle momenta. It is thus found that

$$I_{h(12)(13)(12)}g=[t\Lambda_{h(12)(13)(12)}+M_{h(12)(13)(12)}(t)]g\,, \quad \text{(A14)}$$

where $\Lambda_{h(12)(13)(12)}$ is a scattering operator for completed collisions defined by (with $\tau_h\equiv t_2^0-t_1^0$)

$$\Lambda_{h(12)(13)(12)}\equiv\int_0^{\tau_{hc}}d\tau_h\int_{D_h}d\omega_1 d\omega_2\times C_h A_{13}(\mathbf{l}_2)[A_{12}(\mathbf{l}_{3h})-I]. \quad \text{(A15)}$$

Here D_h is the region of ω_2 which satisfies $\mathbf{l}_1\cdot\mathbf{P}_{h12}(2)<0$, and τ_{hc} is given by (A6) when the momenta $\mathbf{P}_{r(12)}(1)$ and $\mathbf{P}_{r12}(2)$ are replaced by

$$\mathbf{P}_{h12}(1)=\mathbf{P}_{12}\,, \quad \text{(A16)}$$

$$\mathbf{P}_{h12}(2)=\mathbf{P}_{12}-\mathbf{P}_{13}\cdot\mathbf{l}_2\mathbf{l}_2\,. \quad \text{(A17)}$$

The operator $M_{h(12)(13)(12)}(t)$ for incompleted collisions is given by

$$M_{h(12)(13)(12)}\equiv-\int_0^t dt_1^0\int_0^{\tau_{hc}}d\tau_h\int_{D_{h3}}d\omega_1 d\omega_2\times C_h A_{13}(\mathbf{l}_2)[A_{12}(\mathbf{l}_{3h})-I]\,, \quad \text{(A18)}$$

where D_{h3} is the region of τ_h and ω_2 which satisfies $\mathbf{l}_1\cdot\mathbf{P}_{h12}(2)<0$, $t_3^0>t$.

The entire cluster integral $I_{(12)(13)(12)}g$ in (20) may be finally obtained by subtracting (A14) from (A11). Thus,

$$I_{(12)(13)(12)}g=[t\Lambda_{(12)(13)(12)}+M_{(12)(13)(12)}(t)]g\,, \quad \text{(A19)}$$

where

$$\begin{aligned}\Lambda_{(12)(13)(12)}&\equiv\Lambda_{r(12)(13)(12)}-\Lambda_{h(12)(13)(12)}\,,\\ M_{(12)(13)(12)}&\equiv M_{r(12)(13)(12)}-M_{h(12)(13)(12)}\,.\end{aligned} \quad \text{(A20)}$$

We have thus far computed all the quantities in $\Lambda_{(12)(13)(12)}$ as functions of ω_1, ω_2, and $\tau_{r,h}$ [in terms of $\mathbf{l}_1(\omega_1)$ and $\mathbf{l}_2(\omega_2)$] except for $\mathbf{l}_{3r}$ and $\mathbf{l}_{3h}$. To compute $\mathbf{l}_3$ ($\mathbf{l}_{3r}$ or $\mathbf{l}_{3h}$) we refer to Fig. 3 and denote the scattering angle and "vector" impact parameter of the third collision by θ_3 and $\mathbf{b}_3$, respectively. We then find, after a little algebra,

$$\mathbf{l}_3=\cos(\tfrac{1}{2}\theta_3)b_3^{-1}\mathbf{b}_3+\sin(\tfrac{1}{2}\theta_3)P_{12}(2)^{-1}\mathbf{P}_{12}(2)\,, \quad \text{(A21)}$$

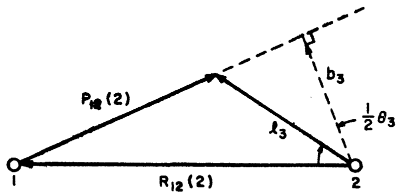

FIG. 3. Vector diagram for the third collision.

where [with (A4)]

$$\mathbf{b}_3 \equiv P_{12}(2)^{-2}\{a\mathbf{P}_{12}(2)\times[\mathbf{l}_1\times\mathbf{P}_{12}(2)] + \tau\mathbf{P}_{12}(2)\times[\mathbf{P}_{12}(1)\times\mathbf{P}_{12}(2)]\}. \quad \text{(A22)}$$

The scattering angle θ_3 is related to the impact parameter b_3 by the law of force and, hence, $\mathbf{l}_3$ must be computed separately for each law of force. For hard spheres we have simply

$$b_3 = a\cos(\tfrac{1}{2}\theta_3),$$

so that (A21) becomes

$$\mathbf{l}_3 = a^{-1}\mathbf{b}_3 + (1-b_3^2a^{-2})^{1/2}P_{12}(2)^{-1}\mathbf{P}_{12}(2). \quad \text{(A23)}$$

The unit vectors $\mathbf{l}_{3r}$ and $\mathbf{l}_{3h}$ are obtained from (A23) by replacing $\mathbf{P}_{12}(2)$ by $\mathbf{P}_{r12}(2)$ and $\mathbf{P}_{h12}(2)$, respectively, and replacing τ by τ_r and τ_h, respectively.

APPENDIX B: CALCULATION OF $I_{(\alpha_1)\cdots(\alpha)_n}(t)g$

The calculation of $I_{(\alpha_1)\cdots(\alpha_n)}$,

$$I_{(\alpha_1)\cdots(\alpha_n)} \equiv V^{-2}\int d\mathbf{R}_{12}d\mathbf{R}_{13}\, f_{\alpha_1}\cdots f_{\alpha_n}G_0, \quad \text{(B1)}$$

proceeds in the same way as $I_{(12)(13)(12)}$. The integrand $[f_{\alpha_1}f_{\alpha_2}\cdots f_{\alpha_n}]$ of $I_{(\alpha_1)\cdots(\alpha_n)}$ is a nonzero for only those regions of $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$ which lead to that sequence of n successive binary collisions between particles 1, 2, and 3 [Ref. 1 Eq. (6) and Ref. 5 Eq. (25)] which we denote by $(\alpha_1)\cdots(\alpha_n)$. Each collision may be real or hypothetical, and the sequence must be completed by time t.

We, thus, restrict $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$, in $I_{(\alpha_1)(\alpha_2)\cdots(\alpha_n)}$, to lie within collision cylinders so as to ensure that the first two collisions occur. For the third collision we must require, similar to (19a,b), that $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$, in $I_{(\alpha_1)\cdots(\alpha_n)}$, satisfy

$$|\mathbf{R}_{\alpha_3}(2)\times\mathbf{P}_{\alpha_3}(2)|P_{\alpha_3}(2)^{-1}<a, \quad \mathbf{R}_{\alpha_3}(2)\cdot\mathbf{P}_{\alpha_3}(2)<0.$$

Similarly, for the kth collision to take place we must have, for all k,

$$\begin{aligned}&|R_{\alpha_k}(k-1)\times P_{\alpha_k}(k-1)|P_{\alpha_k}(k-1)^{-1}<a,\\ &R_{\alpha_k}(k-1)\cdot P_{\alpha_k}(k-1)<0, \quad (3\leqslant k\leqslant n)\end{aligned} \quad \text{(B2)}$$

where $\mathbf{R}_{\alpha_k}(k-1)$ and $\mathbf{P}_{\alpha_k}(k-1)$ denote the relative position and momentum of the pair α_k at the instant following the $(k-1)$th collision. Furthermore, since the sequence of collision must be completed by time t we must require that the time, t_n^*, of the last collision satisfy

$$t_n^*<t.$$

The integration of $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$ over collision cylinders now proceeds as for $I_{(12)(13)(12)}$. We transform the $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$ integrations into integrations over scattering angles and times of collisions, and then divide the integral into a real and a hypothetical first collision part, exactly as for $I_{(12)(13)(12)}$. Equation (B1) then becomes, in condensed notation,

$$I_{(\alpha_1)\cdots(\alpha_n)}g = \int_0^t dt_1^0\int_{t_1^0}^t dt_2^*\int_{V_{1r},V_{1h}} d\omega_1 d\omega_2[C_r'S_r - C_h'S_h]g,$$

where we have defined

$$\begin{aligned}C_r' &\equiv m^{-2}V^{-2}P_{\alpha_1}P_{\alpha_2}(1)\sigma(\omega_1,P_{\alpha_1})\sigma(\omega_2,P_{\alpha_2}(1)),\\ C_h' &\equiv m^{-2}V^{-2}P_{\alpha_1}P_{\alpha_2}\sigma(\omega_1,P_{\alpha_1})\sigma(\omega_2,P_{\alpha_2}),\end{aligned}$$

and V_{1r} or V_{1h} denotes those regions of t_1^0, t_2, ω_1, and ω_2 which satisfy (B2) for all $k(3<k<n)$, when the first collision is real or hypothetical, and which also satisfy $t_n^*<t$. We have also replaced the propagators in $f_{\alpha_1}\cdots f_{\alpha_n}$ by their corresponding momentum operators in S_r and S_h, since when (B2) is satisfied for all k then all collisions in the sequence will be aimed to take place and, hence, the corresponding momentum changes will occur. The scattering operators S_r and S_h are thus given by

$$\begin{aligned}S_r &\equiv A_{\alpha_1}(\mathbf{l}_1)[A_{\alpha_2}(\mathbf{l}_2)-I]\cdots[A_{\alpha_n}(\mathbf{l}_n)-I],\\ S_h &\equiv I[A_{\alpha_2}(\mathbf{l}_2)-I]\cdots[A_{\alpha_n}(\mathbf{l}_n)-I],\end{aligned} \quad \text{(B3)}$$

where $\mathbf{l}_n$ is the unit vector in the perihelion direction of the nth collision.

From the solution of (B2) with $k=3$ we obtain a restriction of the same form as (A5)—just as we did for $I_{(12)(13)(12)}$. That is, the solution of (B2) with $k=3$ yields

$$t_2 - t_1^0 < \tau_c' = \tau_c'(\omega_1,\omega_2), \quad \text{(B4)}$$

so that (B3) may be written, with the change of variables $t_2 - t_1^0 \equiv \tau_2$,

$$I_{(\alpha_1)\cdots(\alpha_n)}g = \int_0^t dt_1^0\int_0^{t-t_1^0} d\tau_2\int_{V'_{1r,h}} d\omega_1 d\omega_2 \times C_r'S_r - C_h'S_h]g, \quad \text{(B5)}$$

where $V'_{1r,h}$ denotes the regions of τ_2, ω_1, ω_2 which satisfy $\tau_2<\tau_c'$, Eq. (B2), and $t_n^*<t$. [The region $V'_{1r,h}$ is the same as $V_{1r,h}$—the dependence upon τ_2 has simply been made explicit in $V'_{1r,h}$.]

We may now divide the time integrations in (B5) into two parts, as in (A11),

$$\cdots\int_0^{t-t_1^0} d\tau_2\int_{V'_{1r,h}} d\omega_1 d\omega_2=\cdots\int_0^{\tau_c'} d\tau_2\int_{D'_{r,h}} d\omega_1 d\omega_2 -\cdots\int_0^{\tau_c'} d\tau_2\int_{D'_{r3,h3}} d\omega_1 d\omega_2\,, \tag{B6}$$

where $D'_{r,h}$ denote the regions of τ_2, ω_1, ω_2 which satisfies Eq. (B2), and $D'_{r3,h3}$ denote the regions of τ_2, ω_1, ω_2 which satisfies Eq. (B2) as well as $t_n^*>t$.

Furthermore, we note that the restrictions upon the region of integration in (B5) which come from (B2) with $k\geqslant 4$ will be independent of t_1^0. This is because $\mathbf{R}_{\alpha_k}(k-1)$ and $\mathbf{P}_{\alpha_k}(k-1)$ are independent of t_1^0 [$\mathbf{R}_{\alpha_k}(k-1$, and $\mathbf{P}_{\alpha_k}(k-1)$ only depends upon τ_2, ω_1, and ω_2]. We may, thus, freely integrate the first term on the right-hand side of (B6) over t_1^0 to finally obtain

$$I_{(\alpha_1)\cdots(\alpha_n)}g=[t\Lambda_{(\alpha_1)\cdots(\alpha_n)}+M_{(\alpha_1)\cdots(\alpha_n)}]g\,, \tag{B7}$$

where $\Lambda_{(\alpha_1)\cdots(\alpha_n)}$ is the time-independent scattering operator for completed collisions defined by

$$\Lambda_{(\alpha_1)\cdots(\alpha_n)}\equiv\int_0^{\tau_c'} d\tau_2\int_{D'_{r,h}} d\omega_1 d\omega_2[C_r'S_r-C_h'S_h] \tag{B8}$$

and $M_{(\alpha_1)\cdots(\alpha_n)}(t)$ is an operator which corresponds to those initial phase points which lead to incompleted collisions ($t_n^*>t$). This operator is given by

$$M_{(\alpha_1)\cdots(\alpha_n)}(t)\equiv-\int_0^t dt_1^0\int_0^{\tau'} d\tau_2\int_{D'_{r3,h3}} d\omega_1 d\omega_2 \times[C_r'S_r-C_h'S_h]\,. \tag{B9}$$

The asymptotic time dependence of $M_{(\alpha_1)\cdots(\alpha_n)}(t)$ can be shown to satisfy

$$M_{(\alpha_1)\cdots(\alpha_n)}(t)=O(\ln t)\quad(\text{large } t)\,. \tag{B10}$$

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Coupling-Constant Sum Rules*

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Coupling-constant sum rules are derived assuming that the violation of unitary symmetry transforms like the eighth component of "unitary spin." This parallels the derivation of the mass sum rule.

I. INTRODUCTION

A MODEL of strong interaction symmetry in which both mesons and baryons transform like the eight-dimensional irreducible representation of $SU(3)$ was proposed by Gell-Mann and Nee'man.[1] The immediate prediction of such a model—that the mesons are degenerate and the baryons are degenerate—is clearly false. Nevertheless, the symmetry scheme appears useful.[2] The success of the Gell-Mann mass formula[3] indicates that the breakdown of symmetry occurs in a particularly simple way. In this paper, we apply similar considerations to coupling constants, and we derive coupling-constant sum rules analogous to the Gell-Mann mass formula.

II. COUPLING CONSTANT SUM RULES

The only effective-mass Lagrangian invariant under $SU(3)$ is

$$\mathcal{L}_M=M\,\mathrm{Tr}\bar{B}B\,, \tag{1}$$

where

$$B=\begin{pmatrix} \dfrac{\Sigma^0}{\sqrt{2}}+\dfrac{\Lambda}{\sqrt{6}} & \Sigma^+ & n \\ \Sigma^- & -\dfrac{\Sigma^0}{\sqrt{2}}+\dfrac{\Lambda}{\sqrt{6}} & p \\ \Xi^0 & \Xi^- & -\dfrac{2}{\sqrt{6}}\Lambda \end{pmatrix}. \tag{2}$$

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† Alfred P. Sloan Foundation Fellow.

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