reproduced by the second and first terms of $\mathcal{G}_l^0$, respectively.

It is easily seen that the scattering Green's function $\mathcal{G}_l^{(\pm)}$ contains only outgoing waves: The asymptotic behavior of the Hankel functions is[31]

$$H_l^{(1)}(kr) \to (2/\pi kr)^{1/2} \exp[i\{kr-\tfrac{1}{2}(l+\tfrac{1}{2})\pi\}]$$
$$H_l^{(2)}(kr) \to (2/\pi kr)^{1/2} \exp[-i\{kr-\tfrac{1}{2}(l+\tfrac{1}{2})\pi\}]. \quad \text{(B9)}$$

The scattered waves have an exponential time dependence $\mathcal{U}_l^{(\pm)} \approx \exp[\mp iE_{k\kappa}t]$, so that both positive- and negative-energy solutions contain outgoing cylindrical waves of the form $r^{-1/2}\exp[\pm i(kr-E_{k\kappa}t)]$.

With the explicit form of $\mathcal{G}_l^0$, it is possible to prove the relation between the reaction matrix and the phase shift [Eq. (60)].[39] The standing-wave solution $\mathcal{W}_l$ satisfies an integral equation

$$\mathcal{W}_l(r)=\mathcal{Y}_l(r)+\int_0^\infty r'dr'\mathcal{G}_l^0(r,r')\mathcal{V}_l(r')\mathcal{W}_l(r'). \quad \text{(B10)}$$

[39] Reference 24, pp. 303–306.

In the limit of large r, only the first term of Eq. (B6) contributes, and we find

$$\mathcal{W}_l(r) \to \mathcal{Y}_l(r)+\frac{\pi m}{2}\left[1+\frac{E_{k\kappa}\tau^{(3)}-\mu\tau^{(1)}}{\mu+(2m)^{-1}(k^2+\kappa^2)}\right]Y_l(kr) \times\int_0^\infty r'dr'J_l(kr')\mathcal{V}_l(r')\mathcal{W}_l(r'). \quad \text{(B11)}$$

The quantity in square brackets may be rewritten with Eqs. (10), (11), and (51) as $(2\rho/m)\mathfrak{N}^{(+)}\mathfrak{N}^{(+)\dagger}$. If $J_l(kr)$ and $Y_l(kr)$ are replaced by their asymptotic forms,[31] Eq. (B11) then becomes

$$\mathcal{W}_l(r) \to \mathfrak{N}^{(+)}(2/\pi kr)^{1/2}[\cos\{kr-\tfrac{1}{2}(l+\tfrac{1}{2})\pi\} +\pi\rho R_l \sin\{kr-\tfrac{1}{2}(l+\tfrac{1}{2})\pi\}]. \quad \text{(B12)}$$

Comparison of Eqs. (61) and (B12) shows that

$$\pi\rho R_l=-\tan\delta_l, \quad \text{(B13)}$$

which is Eq. (60).

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Nonanalyticity of Transport Coefficients and the Complete Density Expansion of Momentum Correlation Functions

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The complete "formal" density expansion of any momentum autocorrelation function—at any frequency—is derived from the density expansion of the generalized master equation. (The sth term in this expansion is explicitly defined in terms of the time-displacement operator of $s+1$ particles and involves the dynamics of $s+1$ isolated particles.) The entire derivation consists of only a few algebraic steps, and is valid for noncentral (polar) pair forces as well as central forces. It is then shown that the third and higher order terms in the *zero-frequency* limit of the density expansion diverge—although the first two terms and the entire sum coverage (the density expansion "breaks down"). This suggests that transport coefficients are not analytic functions of the density. It is suggested that a partial resummation (renormalization)—analogous to that used in the electron-gas problem—be used to calculate the nonanalytic behavior of transport coefficients.

I. INTRODUCTION

THE subject of autocorrelation functions has been receiving a great deal of recent attention. This is primarily because the study of certain autocorrelation functions provides a convenient means for calculating transport coefficients from first principles.[1,2] In view of this it is somewhat surprising to find that there has been little significant advance in the calculation of transport coefficients for classical systems since the work of Choh and Uhlenbeck.[3] They used the Bogolioubov approach to obtain formulas for the first density correction to transport coefficients, that is, for the effects of triple collisions on transport coefficients. Derivations of comparable results from the autocorrelation-function approach have since been presented in Refs. 4–8, and a systematic method for analytically calculating the triple-collision operators in these density corrections of transport coefficients has been given in Ref. 8. Still remaining to be determined are the formulas for higher order terms (general term) in the density expansion of transport coefficients, the frequency dependence of

[1] M. S. Green, J. Chem. Phys. **22**, 308 (1954).
[2] R. Kubo, J. Phys. Soc. **12**, 570 (1957).
[3] S. T. Choh and G. E. Uhlenbeck, Navy Theoretical Physics, Contract No. Nonr. 1224 (15), University of Michigan, 1958 (unpublished).
[4] S. Ono and T. Shizume, J. Phys. Soc. (Japan) **18**, 29 (1963).
[5] R. Zwanzig, Phys. Rev. **129**, 486 (1963).
[6] E. Cohen and M. Ernst, Phys. Letters **5**, 192 (1963).
[7] K. Kawasaki and I. Oppenheim, Phys. Rev. **136**, A1519 (1964).
[8] J. Weinstock, Phys. Rev. **132**, 470 (1963).

transport coefficients, and the basic question of whether or not the higher order terms converge in the limit of zero frequency (infinite time).

The purpose of this communication is to derive the complete "formal" density expansion of the autocorrelation of any function of momenta—at any frequency—from the density expansion of the master equation[9,10] (the coefficient of the sth term in this expansion is in terms of propagators which involve the dynamics of $s+1$ isolated particles similar to those in Ref. 9). The entire derivation consists of a few algebraic steps and is very simple. Furthermore, it is valid for noncentral pair forces as well as for central forces. (The master-equation approach has also been used by Mori[11] and Swenson[12] to obtain the first term—binary-collision term—in the density expansion of transport coefficients.)

The density expansion of autocorrelation functions at *zero frequency* is examined in Sec. III where attention is drawn to a peculiar and, perhaps, profound result for transport coefficients, namely, that although the first- and second-order terms (these terms are asymptotic collision operators for binary and ternary collision, respectively) in the density expansion converge, the third and higher order terms diverge at infinite times (zero frequencies). This was first noted in Ref. 9 (Sec. IIIA). The asymptotic time dependence of these divergent terms is, in fact, shown in Sec. III to be given by

$$\partial\beta_s(t)/\partial t \underset{t\to\infty}{=} O(t^{s-3}\ln t)\,,\quad (s\geqslant 3)\,.$$

A similar result for $\beta_3(t)$ has been independently obtained by Dorfman and Cohen, and by R. J. Swenson.[13] This has been further verified by Sengers[14] who has calculated the "two-dimensional" triple-collision operator in some detail. He finds that this "two-dimensional" operator also diverges and that the coefficient of the divergent part does not vanish. The fact that the density expansion of transport coefficients breaks down at zero frequency suggests that transport coefficients are not analytic functions of the density and, hence, the theory of transport coefficients for dense, or moderately dense, gases would appear to be even more complicated than had been widely anticipated. It is suggested, however, that a partial resummation procedure (renormalization), analogous to that used in the electron-gas problem,[15] be used to calculate the nonanalytic dependence of transport coefficients.

II. DENSITY EXPANSION OF AUTOCORRELATION OF ANY FUNCTION OF MOMEMTUM—FROM THE GENERALIZED MASTER EQUATION

Let $\mathbf{R}_i$ and $\mathbf{P}_i$ denote the position and momentum, respectively, of particle i, $\{\mathbf{R}\}$ denote the positions of all N particles of the system and $\{\mathbf{P}\}$ denote the momenta of all N particles of the system. If we further let $\psi\equiv\psi(\{\mathbf{P}\})\equiv\psi(\mathbf{P}_1,\cdots\mathbf{P}_N)$ denote any function whatsoever of the momenta of all N particles, then the autocorrelation of ψ is defined by

$$a(t)\equiv\langle\psi e^{-itL}\psi\rangle\equiv\int d\{\mathbf{P}\}d\{\mathbf{R}\}\psi e^{-itL}\psi D_N \qquad (1)$$

where L is the Liouville operator defined by

$$L\equiv L_0+\sum_{j<k}L_{jk}\,,$$
$$L_0\equiv -i\sum_{j=1}^{N}m^{-1}\mathbf{P}_j\cdot\partial/\partial\mathbf{R}_j\,, \qquad (2)$$
$$L_{jk}\equiv i(\partial V_{jk}/\partial\mathbf{R}_{jk})\cdot(\partial/\partial\mathbf{P}_j-\partial/\partial\mathbf{P}_k)\,.$$

D_N is the normalized thermal distribution function of the system defined by

$$D_N\equiv e^{-\beta H}\bigg/\int d\{\mathbf{R}\}d\{\mathbf{P}\}e^{-\beta H}. \qquad (3)$$

H is the Hamiltonian of the system defined by

$$H\equiv\sum_{j=1}^{N}(2m)^{-1}P_j^2+\sum_{j<k}V_{jk}$$
$$\equiv H_0+\sum_{j<k}V_{jk}\,. \qquad (4)$$

β^{-1} is the product of the temperature with Boltzmann's constant, and V_{jk} is the interaction potential (not necessarily central) between particles j and k.

We shall consider the Laplace transform of $a(t)$, denoted by $\bar{a}(E)$, which is given by taking the Laplace transform of both sides of (1)

$$\bar{a}(E)\equiv\int_0^\infty dt\, e^{-Et}\int d\{\mathbf{P}\}d\{\mathbf{R}\}\psi e^{-itL}\psi D_N\,. \qquad (5)$$

Denoting the quantities $e^{-itL}\psi D_N$ and $\int d\{R\}e^{-itL}\times\psi D_N$ by $F_N(t)$ and $\phi(t)$, respectively,

$$F_N(t)\equiv e^{-itL}\psi D_N\equiv e^{-itL}F_N(0)\,,$$
$$\phi(t)\equiv\int d\{\mathbf{R}\}e^{-itL}\psi D_N\equiv\int d\{\mathbf{R}\}F_N(t)\,, \qquad (6)$$

and assuming commutation of integrations, Eq. (5)

[9] J. Weinstock, Phys. Rev. **132**, 454 (1963).
[10] J. Weinstock, Phys. Rev. **140**, A98 (1965).
[11] H. Mori, Phys. Rev. **111**, 694 (1958).
[12] J. A. McLennan and R. J. Swenson, J. Math. Phys. **4**, 1527 (1963).
[13] J. Dorfman and E. Cohen (private communication). R. J. Swenson (private communication).
[14] J. V. Sengers (private communication).
[15] J. Weinstock, Phys. Rev. **133**, A673 (1964). [See also K. R. Goldman and E. Frieman, Bull. Am. Phys. Soc. **11**, 531 (1965).] K. Kawasaki and I. Oppenheim have also obtained this result for the diffusion coefficient (private communication).

for $\bar{a}(E)$ can now be written in the suggestive form

$$\bar{a}(E)=\int d\{\mathbf{P}\}\psi\int dt\, e^{-Et}\int d\{\mathbf{R}\}e^{-itL}F_N(0)$$

$$\equiv\int d\{\mathbf{P}\}\psi\int dt\, e^{-Et}\phi(t). \qquad (7)$$

The $\{\mathbf{R}\}$ integral in Eq. (7), it will be noted, is the *time-dependent momentum distribution function of N particles* —the formal solution of the master equation—defined by $\int d\{\mathbf{R}\}e^{-itL}F_N(0)$.

We can now easily obtain the density expansion of $\bar{a}(E)$ from the density expansion of the master equation which is exactly given in Ref. 10, Eq. (5) [see Eq. (29) of Ref. 9] by

$$\partial\phi(t)/\partial t=\sum_{s=1}^{\infty}\beta_s'(t)\mathbf{O}_D F_N(0)$$

$$+\int_0^t dy[\sum_{s=1}^{\infty}\beta_s''(t-y)]\phi(y) \quad (N, V\to\infty) \qquad (8)$$

where $\beta_s(t)$ is defined in Ref. 9 as a function of L_0, L_{ij}, and t through the time-displacement operators of $(s+1)$ particles (primes denote derivatives). The properties of β_s which are of present concern are that it is proportional to the sth power of the particle density (N/V) and it involves the dynamics of $s+1$ isolated particles in an explicit and well defined way. Further details about the properties, and definition, of β_s will be found in Refs. 9 and 8.

The term $\sum_s\beta_s'(t)\mathbf{O}_D F_N(0)$ vanishes when $F_N(0)$ is independent of particle configurations since[10]

$$\mathbf{O}_D F_N(0)\equiv F_N(0)-V^{-N}\int d\{\mathbf{R}\}F_N(0).$$

It thus describes the effects of initial "correlations" in configuration space upon the evolution of $\phi(t)$ and, providing the "correlations" are of finite extent, it vanishes in the limit of infinite t, i.e.,

$$\lim_{t\to\infty}\sum_s\beta_s'(t)\mathbf{O}_D F_N(0)=0. \qquad (9)$$

[Equation (8) differs from Eq. (29) of Ref. 9 in that it is valid for arbitrary $F_N(0)$ whereas Eq. (29) of Ref. 9 is only valid when $\mathbf{O}_D F_N(0)=0$ and, hence, does not contain the term $\sum_s\beta_s'(t)\mathbf{O}_D F_N(0)$.]

If we denote the Laplace transforms of $\beta_s(t)$ and $\phi(t)$ by $\bar{\beta}_s(E)$ and $\bar{\phi}(E)$, respectively, then the solution of (8) for $\bar{\phi}(E)$—obtained by taking the Laplace transform of both sides of (8)—is easily shown to be

$$\bar{\phi}(E)\equiv\int_0^\infty dt e^{-Et}\int d\{\mathbf{R}\}e^{-itL}F_N(0)$$

$$=[E-E^2\sum_{s=1}^{\infty}\bar{\beta}_s(E)]^{-1}$$

$$\times[\phi(0)+\sum_{s=1}^{\infty}E\bar{\beta}_s(E)\mathbf{O}_D F_N(0)] \qquad (10)$$

where we have used the fact that[9] $\beta_s(0)=\beta_s'(0)=0$.

Substituting (10) into (7) we obtain the desired result

$$\bar{a}(E)=\int d\{\mathbf{P}\}\psi\{1/[E-E^2\sum_{s=1}^{\infty}\bar{\beta}_s(E)]\}$$

$$\times[\phi(0)+E\sum_{s=1}^{\infty}\bar{\beta}_s(E)\mathbf{O}_D F_N(0)], \qquad (11)$$

where, from (6), $\phi(0)$ is defined by

$$\phi(0)\equiv\psi D_N^0$$

and

$$D_N^0\equiv e^{-\beta H_0}\Big/\int d\{\mathbf{P}\}e^{-\beta H_0}.$$

Equation (11) is the complete "formal" density expansion of any momentum autocorrelation function at any frequency. At nonzero frequencies ($E\neq 0$), however, it can be seen that Eq. (11) actually involves a double expansion in the density. The momentum operator $\bar{\beta}_s(E)$, as we have mentioned, is proportional to $(N/V)^s$, involves the time-displacement operator of no more than $s+1$ isolated particles (it involves the dynamics of $s+1$ isolated particles) and is defined in Ref. 9. The explicit expression for $\beta_1(t)$, $\beta_2(t)$, and $\beta_3(t)$ is also given, for the reader's convenience, in Appendix A of the present article.

To obtain $\bar{a}(E)$ to a given order in the density one can terminate the series $\sum_{s=1}^{\infty}\bar{\beta}_s(E)$ at the corresponding s—providing E is large enough (see Sec. III for complications at small E).

To evaluate $\bar{a}(E)$ numerically—to order n, let us say—one must be able to calculate the quantity

$$[E-E^2\sum_{s=1}^{n}\bar{\beta}_s(E)]^{-1}\phi(0)\equiv K(n) \qquad (12)$$

which obviously satisfies

$$[E-E^2\sum_{s=1}^{n}\beta_s(E)]K(n)=\phi(0) \qquad (13)$$

and involves the numerical solution of the dynamical $(n+1)$-body problem. Life would be easy if $\phi(0)$ were an eigenvector of $E^2\beta_s(E)$, with eigenvalue $\lambda_s(E)$, since then $K(n)$ would be given by

$$K(n)=\phi(0)/\left[E-\sum_{s=1}^{n}\lambda_s(E)\right], \tag{14}$$

$$\lambda_s(E)=\int d\{\mathbf{P}\}\phi(0)E^2\bar{\beta}_s(E)\phi(0)\Big/\int d\{\mathbf{P}\}\phi(0)^2. \tag{15}$$

More likely, for transport coefficients, $\phi(0)$ is an approximate eigenvalue of $E^2\bar{\beta}_s(E)$ and (15) is a good first approximation. This cannot yet be justified, but has already been shown to be the case for $[E^2\bar{\beta}_1(E)]_{E=0}$ (binary collision operator) by Mori[11] who used an expression comparable to (15) to obtain the usual results for transport coefficients to lowest order in the density.

III. ZERO-FREQUENCY LIMIT—NONANALYTICITY OF TRANSPORT COEFFICIENTS AND DIVERGENCE OF $\beta_s'(\infty)$

In this section we shall examine the zero-frequency limit of autocorrelation functions, and shall point out an unusual and, perhaps, profound result for transport coefficients, namely, that although $\beta_1'(\infty)$ and $\beta_2'(\infty)$ converge, the four-body and higher terms $\beta_s'(\infty)(s>3)$ do not converge.[9]

The zero-frequency limit of $\bar{a}(E)$ is obtained immediately and exactly from (11) and (9) [the magnitude of $\beta_s(E)\mathbf{O}_D F_N(0)$ must have a finite upper bound since the spatial "correlation" length of $F_N(0)$ is finite]. Thus,

$$\bar{a}(0)=\int d\{\mathbf{P}\}\psi\{1/[\lim_{E\to 0}-\sum_{s=1}^{\infty}E^2\bar{\beta}_s(E)]\}\psi D_N{}^0. \tag{16}$$

But, since $\beta_s'(t)]_{t=0}=\beta_s(t)]_{t=0}=0$,[9] we have

$$\lim_{E\to 0}E^2\bar{\beta}_s(E)=\lim_{E\to 0}\int_0^\infty dte^{-tE}\beta_s''(t)$$
$$=\beta_s'(\infty) \tag{17}$$

so that (16) can be written

$$\bar{a}(0)=\int d\{\mathbf{P}\}\psi\{1/[\lim_{t\to\infty}-\sum_{s=1}^{\infty}\beta_s'(t)]\}\psi D_N{}^0 \tag{18}$$

or

$$\bar{a}(0)=\int_0^\infty dt\int d\{\mathbf{P}\}\psi\exp[t\lim\sum_{s=1}^{\infty}\beta_s'(t)]\psi D_N{}^0. \tag{19}$$

Equation (19) expresses $\bar{a}(0)$ in the familiar relaxation form, and is exact for any momentum autocorrelation function with any pair interaction potential between particles. An immediate consequence of (19), previously noted by others,[16,17] is that one only needs the asymptotic forms of the master-equation operators (scattering operators) to calculate transport coefficients.

[16] R. Balescu, Physica **27**, 693 (1961).
[17] R. J. Swenson, Physica **29**, 1174 (1963).

Equation (19), or (16) or (18), is the density expansion of the "kinetic parts" of transport coefficients provided $\beta_s'(\infty)\equiv\lim_{t\to\infty}d\beta_s(t)/dt$ exists. It has already been proven[8] that $\beta_1'(\infty)$ exists and $\beta_2'(\infty)$ exists. It turns out, however, that $\beta_s'(\infty)$ does not exist for every s—as was previously pointed out.[9] In fact, it is shown in Appendix B that

$$\beta_s'(t)\underset{t\to\infty}{=}O(t^{s-3}\ln t),\quad (s\geqslant 3). \tag{20}$$

The fact that the third and higher coefficients of the density expansion of the "kinetic parts" of transport coefficients diverge at zero frequency suggests that transport coefficients are not analytic functions of the density (the density expansion breaks down). It is important to note here, however, that although $\beta_s'(\infty)$ diverges the infinite sum

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

converges—very rapidly. The proof of this convergence is somewhat complicated (and not terribly relevant here) and will be published separately.

It is important to note that Eqs. (8), (11), and (19) are each valid, despite Eq. (20), since they contain the convergent infinite sum of collision operators. [It is their usefulness as a density expansion for dense gases that is jeopardized by Eq. (20).] We have simply established that the limit can not be interchanged with the sum.

In view of Eq. (20) it appears that the theory of transport coefficients is even more complicated than had been widely anticipated. To circumvent this difficulty one can expand $\sum_{s=1}^{\infty}\beta_s'(t)$ into "binary collision operators"[9] and then partially resum the resultant terms into convergent groups—in a manner similar to what has been done for the electron gas.[15] The details of this "renormalization" will be the subject of a future communication.

APPENDIX A

Formulas for $\beta_1(t)$, $\beta_2(t)$, and $\beta_3(t)$ are obtained from Eqs. (26), (11), (12), and (16) of Ref. 9. Thus, with $N,\,V\to\infty$,

$$\beta_1(t)\equiv\sum_{1\leq i<j\leq N}V^{-1}\int d\mathbf{R}_{ij}[G_{ij}(t)-G_0(t)], \tag{A1}$$

$$\beta_2(t)\equiv\sum_{1\leq i<j<k\leq N}V^{-2}\int d\mathbf{R}_{ij}d\mathbf{R}_{ik}V_2(ijk,t)$$
$$\equiv\sum_{i<j<k}V^{-2}\int d\mathbf{R}_{ij}d\mathbf{R}_{ik}[G_{ijk}(t)+2G_0(t)-G_{ij}(t)$$
$$-G_{ik}(t)-G_{jk}(t)-\sum_{\left\{\substack{a<b,\,c<d\\ ab\neq cd}\right\}}^{ijk}\int_0^t dt_1\int_{t_1}^t dt_2$$
$$\times G_{ab}(t_1)iL_{ab}G_{cd}(t_2-t_1)iL_{cd}G_0(t-t_2), \tag{A2}$$

$$\beta_3(t)\equiv\sum_{i<j<k<l}V^{-3}\int d\mathbf{R}_{ij}d\mathbf{R}_{ik}d\mathbf{R}_{il}[G_{ijkl}(t)-G_0(t)$$
$$-\sum_{a<b}^{ijkl}\int_0^t dt_1[G_{ab}(t_1)-G_0(t_1)]G_{ijkl}(t-t_1;\neq ab)$$
$$-\sum_{a<b<c}^{ijkl}\int_0^t dt_1V_2(abc;t_1)G_{ijkl}(t-t_1;\neq abc)\,,\quad\text{(A3)}$$

where G_0, G_{ij}, G_{ijk}, and G_{ijkl} are the time-displacement operators for free particles, two interacting particles, three interacting particles and four interacting particles, respectively, defined by

$$G_0\equiv e^{itL_0}\,,$$
$$G_{ij}\equiv e^{it(L_0+L_{ij})}\,,$$
$$G_{ijk}\equiv e^{it(L_0+L_{ij}+L_{ik}+L_{jk})}\,,\quad\text{(A4)}$$
$$G_{ijkl}\equiv\exp[it(L_0+\sum_{a<b}^{ijkl}L_{ab})]\,,$$

and $G_{ijkl}(t;\neq abc)$ and $G_{ijkl}(t;\neq ab)$ are defined, with $a=i$, $b=j$, $c=k$, for example, by

$$G_{ijkl}(t;\neq ijk)\equiv G_0+G_{il}+G_{jl}+G_{kl}\,,$$
$$G_{ijkl}(t;\neq ij)\equiv G_{ikl}+G_{jkl}-3G_0-G_{kl}-G_{ik}-G_{il}-G_{jk}-G_{jl}+e^{it(L_0+L_{ik}+L_{jl})}+e^{it(L_0+L_{il}+L_{jk})}\,.$$

The sum $\sum_{a<b}{}^{ijkl}$ means, for example,

$$\sum_{a<b}^{ijkl}L_{ab}\equiv L_{ij}+L_{ik}+L_{il}+L_{jk}+L_{jl}+L_{kl}\,.$$

Equations (A1), (A2), and (A3) are explicit definitions of the first three terms in the density expansion of momentum autocorrelation function ("kinetic parts" of transport coefficients) in terms of the time-displacement operators for zero, two, three, and four interacting particles. They involve the solution of the two-body, three-body, and four-body problems, respectively, in an explicit and well-defined manner.

APPENDIX B

The asymptotic time dependence of the four-particle collision operator $\beta_3(t)$ can be calculated by the binary-collision-expansion method of Refs. (9) and (8) [which was used there to obtain the asymptotic time dependence of $\beta_2(t)$]. This method consists of expanding $\beta_3(t)$ in a sum of ordered products of binary-collision operators, each term of which corresponds to an ordered sequence of successive binary collisions among four isolated particles, and then calculating the asymptotic time dependence of each term—which we shall now do.

Thus, a leading term in the binary collision expansion of $\beta_3(t)$[8,9] is

$$I_{(12)(13)(14)(12)}$$
$$\equiv V^{-3}\int d\mathbf{R}_{12}d\mathbf{R}_{13}d\mathbf{R}_{14}\int_0^t dt_1G_{12}(t_1)iL_{12}$$
$$\times\int_{t_1}^t dt_2G_{13}(t_2-t_1)iL_{13}\int_{t_2}^t dt_3G_{14}(t_3-t_2)iL_{14}$$
$$\times\int_{t_3}^t dt_4G_{12}(t_4-t_3)iL_{12}G_0(t-t_4)$$
$$\equiv V^{-3}\int d\mathbf{R}_{12}d\mathbf{R}_{13}d\mathbf{R}_{14}f_{12}f_{13}f_{14}f_{12}G_0\quad\text{(B1)}$$

where f_{12} has been defined in Ref. 9.

It has been established in Ref. 8 that $f_{12}f_{13}f_{14}f_{12}$ corresponds to a sequence of successive binary collisions in which a collision between particles 1 and 2, is followed by a collision between 1 and 3, followed by a collision between 1 and 4 followed by a collision (recollision) between 1 and 2. That is, $f_{12}f_{13}f_{14}f_{12}$ is different from zero for only those regions in the space of $\mathbf{R}_{12}$, $\mathbf{R}_{13}$, and $\mathbf{R}_{14}$ which lead to a collision between 1 and 2 followed by successive collisions between 1 and 3, 1 and 4, and 1 and 2 in that order.

Hence, as in Ref. 8, we note that $f_{12}f_{13}f_{14}f_{12}$ is zero when $\mathbf{R}_{12}$, $\mathbf{R}_{13}$, and $\mathbf{R}_{14}$ lie outside the "collision cylinders[8]" for the first, second, and third collision in the sequence, respectively, so that, as in Ref. (8), we can restrict the integrations over $\mathbf{R}_{12}$, $\mathbf{R}_{13}$, and $\mathbf{R}_{14}$ to lie within the respective "collision cylinders," and then we can transform these integrals into integrals which are parallel and perpendicular to the axes of the respective collision cylinders to obtain[8]

$$V^{-3}\int d\mathbf{R}_{12}d\mathbf{R}_{13}d\mathbf{R}_{14}f_{12}f_{13}f_{14}f_{12}G_0$$
$$=\int_0^t dt_1{}^*\int_{t_1{}^*}^t dt_2{}^*\int_{t_2{}^*}^t dt_3{}^*\int d\omega_1\int d\omega_2\int d\omega_3C\,.\quad\text{(B2)}$$

Here $t_1{}^*$, $t_2{}^*$, and $t_3{}^*$ are the instants of time at which the first, second, and third collisions in the sequence are "aimed" to take place,[8] ω_1, ω_2, and ω_3 are the solid scattering angles for the first, second, and third collisions, and C has been defined by

$$C\equiv V^{-3}m^{-3}P_{12}\sigma_{12}P_{13}(1)\sigma_{13}P_{14}(2)\sigma_{14}f_{12}f_{13}f_{14}f_{12}G_0$$

where $\mathbf{P}_{ij}(k)$ is the relative momentum between i and j, immediately after the kth collision of the sequence has taken place, σ_{ij} is the differential scattering cross section for the collision between i and j, and m is the particle mass.

The $\mathbf{R}_{12}$, $\mathbf{R}_{13}$, and $\mathbf{R}_{14}$ integrations in (B2) have been restricted to "collision cylinders" which ensure that the first three collisions in the sequence will take place.

But $f_{12}f_{13}f_{14}f_{12}$, and C, can still vanish for those regions of the "collision cylinders" which do not eventually lead to the fourth and last collision in the sequence. Hence, the regions of integration on the right-hand side of (B2) can be further reduced to ensure that the fourth collision takes place. This can be done by restricting the solid angle ω_3 to that region for which the impact parameter of particles 1 and 2 at the instant following the conclusion of the third collision (this impact parameter is a function of t_1^*, t_2^*, t_3^*, ω_1, ω_2, and ω_3) is less than the diameter of the particles. That is, we must require that

$$\mathbf{R}_{12}(3)\cdot\hat{P}_{12}(3)\leq a \tag{B3}$$

where $\mathbf{R}_{12}(3)$ is the distance between 1 and 2 at the instant following the third collision, $\hat{P}_{12}(3)$ is a unit vector in the direction of the relative momentum between 1 and 2 at that instant, $\mathbf{R}_{12}(3)\cdot\hat{P}_{12}(3)$ is the impact parameter between 1 and 2 at that instant, and a is the diameter of the particles. The distance $\mathbf{R}_{12}(3)$ can be expressed as[8]

$$\mathbf{R}_{12}(3)=(t_2^*-t_1^*)m^{-1}\mathbf{P}_{13}(1)+(t_3^*-t_2^*)m^{-1}\mathbf{P}_{14}(2)+\boldsymbol{\varepsilon} \tag{B4}$$

where the magnitude of $\boldsymbol{\varepsilon}$ is of pzrticle size and is independent of time (for hard spheres $\boldsymbol{\varepsilon}$ is simply the product of the particle diameter with the unit vector in the perihelion direction of the first collision in the sequence).

But as t approaches infinity we see that for most of the integration region in (B2) $(t_3^*-t_2^*)$ and $(t_2^*-t_1^*)$ will be very large and, hence, $\mathbf{R}_{12}(3)$ will be very large in relation to the particle diameter. Hence, we see from (B3) that to ensure that the fourth collision is aimed to take place, the direction of the relative velocity between 1 and 2 at the conclusion of the third collision must lie within a very small solid angle of order of magnitude:

$$O(a^2/R_{12}(3)^2)\,,\quad (\text{large } t)\,.$$

It then follows—since the direction of the relative velocity between 1 and 2 at the conclusion of the third collision depends on ω_3—that the integration over ω_3 in (B2) must be restricted to lie within a small solid angle of order of magnitude $a^2R_{12}(3)^{-2}$ in order to ensure that the fourth collision takes place (i.e., that $f_{12}f_{13}f_{14}f_{12}$ does not vahish) when t is large. In other words

$$\int d\omega_3 C=O(a^2/R_{12}(3)^2)C\quad (\text{large } t \text{ for 4th collision}). \tag{B5}$$

Substituting (B5) into (B2) and making use of the *mean-value theorem we have*

$$I_{(12)(13)(14)(12)}=\int_0^t dt_1^*\int_{t_1^*}^t dt_2^*\int_{t_2^*}^t dt_3^*\int d\omega_1\int d\omega_2 \times C_0 O\left(\frac{a^2}{R_{12}(3)^2}\right) \tag{B6}$$

where C_0 means that C must be evaluated at a value of ω_3 which lies within the *restricted* solid angle and satisfies the mean-value theorem.

We can now substitute (B4) into (B6), differentiate, and carry out the indicated time integrations to obtain the desired result.

$$(\partial/\partial t)I_{(12)(13)(14)(12)}=O(\ln t)\,,\quad \text{large } t)\,. \tag{B7}$$

Since the higher order terms in the binary collision expansion of $\beta_3(t)$ can not be larger than $I_{(12)(13)(14)(12)}$ it follows that[8]

$$\partial\beta_3(t)/\partial t=O(\ln t)\,. \tag{B8}$$

For the general $(s+1)$-particle collision operator $\beta_s(t)$ we write the leading term in its binary collision expansion as

$$I_{(12)\cdots(1S)(12)}\equiv V^{-s}\int d\mathbf{R}_{12}\cdots\int d\mathbf{R}_{1S}f_{12}\cdots f_{1S}f_{12}G_0 \tag{B9}$$

which at large t becomes [for the same reason as in (B6)]

$$I_{(12)\cdots(1S)(12)}\equiv\int_0^t dt_1^*\cdots\int_{t_{s-1}^*}^t dt_S^* O\left(\frac{a^2}{R_{12}(3)^2}\right), \tag{B10}$$

where t_s^* is the time at which the sth binary collision in the sequence (12), (13)$\cdots$(1S), (12) is aimed to take place, and $\mathbf{R}_{12}(s)$ is the distance between 1 and 2 at the conclusion of the sth collision and can be expressed as

$$\mathbf{R}_{12}(s)=m^{-1}\sum_{k=2}^{s}(t_k^*-t_{k-1}^*)\mathbf{P}_{1,k+1}(k-1)+\boldsymbol{\varepsilon}. \tag{B11}$$

Carrying out the time integrations in (B10) we find

$$(\partial/\partial t)I_{(12)\cdots(1S)(12)}=O(t^{s-3}\ln t) \tag{B12}$$

so that

$$\partial\beta_s(t)/\partial t=O(t^{s-3}\ln t)\,. \tag{B13}$$

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