Logarithmic divergence in the virial expansion of transport coefficients of hard spheres. I

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The expansion of transport coefficients of gases in powers of the density makes a logarithmic divergence appear in the second-order correction to the Boltzmann order term. This divergence arises from the sequences of four collisions among four isolated hard spheres. The number of distinct sequences may be reduced to 10 in the cases of the shear viscosity and the heat conductivity and to 9 for the self-diffusion coefficient. For these three transport coefficients the contributions of two sequences are computed in the first Enskog approximation and given in terms of elementary functions.

I. INTRODUCTION

It is now widely recognized that an expansion of transport coefficients of gases in powers of the density does not exist very probably beyond some finite order.[1] In d-dimensional systems, the coefficient of this expansion diverges logarithmically at the order n^{d-1} for the shear viscosity and the heat conductivity and at the order n^{d-2} for the self-diffusion coefficient (n is the number density). However, to our knowledge, the computation of the coefficients in front of these diverging quantities has not been carried out explicitly for three-dimensional gases—except for the particular case of the perfect Lorentz gas.[2] This paper is the first one of a series, where this calculation will be done for the above-mentioned transport coefficients (i.e., the shear viscosity, the heat conductivity, and the self-diffusion coefficient) of a gas of hard spheres.

This calculation could be relevant in a study of the *actual* low-density behavior of transport coefficients. In fact, in a renormalized theory of this low-density expansion, the diverging factor $\ln\epsilon$, where ϵ is approximately the inverse duration of a collision sequence between four spheres, should be replaced by $\ln n$, as this duration cannot exceed too largely the mean free flight time.[1] As the power expansion of the heat conductivity, for instance, reads

$$K = K_0 + K_1 n + K_2' n^2 \ln\epsilon + \cdots,$$

the renormalized theory should yield

$$K = K_0 + K_1 n + K_2'' n^2 \ln n,$$

where K_2'' is still the coefficient in front of the $n^2 \ln\epsilon$ term of the power expansion. This conjecture is true in the case of the perfect Lorentz gas with hard spheres as scatterers,[2] but is still unproved in general.

In the present paper, we shall consider explicitly all kinds of sequences of four collisions between hard spheres that contribute to K_2' and in Sec. II their number will be reduced to 10. In Sec. III, two contributions to K_2' will be reduced to constants in the first Enskog approximation. We shall give also the corresponding contributions to the shear viscosity and the self-diffusion coefficient. The forthcoming paper will be devoted to the computation of the other contributions, much more involved than the ones considered in the present work.

II. RING COLLISION SEQUENCES BETWEEN FOUR SPHERES AND THEIR SYMMETRIES

A. Generalities

The Green-Kubo formula for the heat conductivity reads

$$K = \lim_{\epsilon \to 0} \lim_{\substack{N,V \to \infty \\ N/V = n}} K(\epsilon),$$

with

$$K(\epsilon) = \frac{m}{3k\tau^2 V} \int_0^\infty dt\, e^{-\epsilon t} \langle \vec{\mathcal{J}}(0) \cdot \vec{\mathcal{J}}(t) \rangle, \qquad (1)$$

where $\langle \cdots \rangle$ denotes a canonical equilibrium average at temperature τ on the ensemble of initial conditions for a system of N hard spheres in a box of volume V, and where $\vec{\mathcal{J}}(t)$ is the value at time t of the fluctuating heat current in the system.

Expanding formally $K(\epsilon)$ in powers of n, we get

$$K(\epsilon) = \sum_{l=0}^{\infty} n^l K_l(\epsilon),$$

where the computation of the lth term involves[1] the knowledge of the dynamics of $(l+1)$ particles.

It has been shown[3] that $K_0(\epsilon)$ exists, as being the Boltzmann order value of the heat conductivity, while $K_1(\epsilon)$ behaves[4] near $\epsilon = 0$ like $K_1(\epsilon = 0) + O(\epsilon \ln\epsilon)$ and has a finite limit for small ϵ. But a logarithmic divergence occurs for $K_2(\epsilon)$ and more generally $K_l(\epsilon) \sim 1/\epsilon^{l-2}$ $(l \geq 3)$. Using Kawasaki-Oppenheim arguments,[5] the resummation of the most divergent contributions at every order in this density expansion should yield a convergent value of $K(0)$:

$$K = K_0(0) + K_1(0)n + K_2' n^2 \ln n \,.$$

The purpose of this paper and a subsequent one is to calculate K_2'.

Some of the contributions to $K_2(\epsilon)$ arise from the dynamical correlations created by collision sequences between four isolated molecules. As shown above, one class of these collisions, the "ring events" (as the one drawn in Fig. 1), is

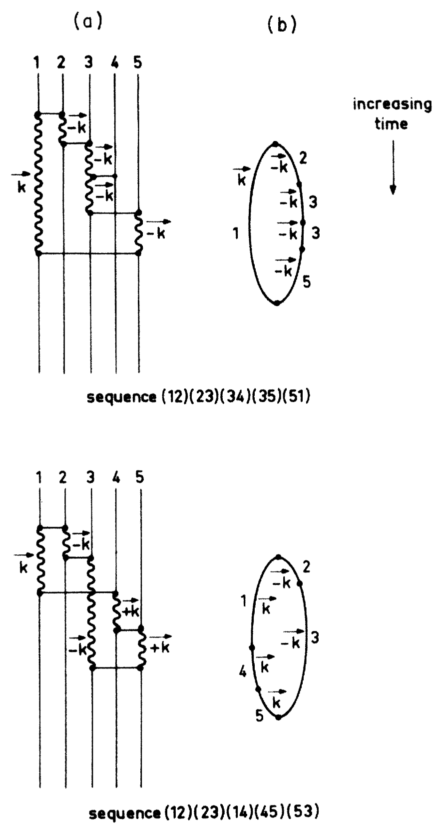

FIG. 1. Some irreducible ring events of 5 particles. Time increases downwards. (a) Each binary collision is represented by a horizontal line between the two particles involved; $\vec{k}$ (or $-\vec{k}$) is the carried momentum. (b) Schematization of the sequences of (a); only the particle carrying a nonzero "momentum" ($+\vec{k}$ or $-\vec{k}$) is labelled. The two representations are taken from Kawasaki and Oppenheim (Ref. 5).

responsible for the logarithmic divergence of $K_2(\epsilon = 0)$. The other contributions to K_2 arise from the virial expansion of the equilibrium weight in (1) or from the potential part of the heat current $\vec{\mathcal{J}}$. As shown in Appendix A, it may be assumed that these contributions do not diverge.

Let us briefly sketch the derivation of the virial expansion of $K_2(\epsilon)$. As this becomes quite complicated beyond the first term, we shall consider part of this expansion only, and neglect both the potential part of the heat current and any effect of the equilibrium correlations, so that the heat current $\vec{\mathcal{J}}$ is reduced to its kinetic part, i.e., $\sum_i \vec{j}_i$ with $\vec{j}_i = \vec{v}_i\,(\frac{1}{2}mv_i^2 - \frac{5}{2}kT)$. Let us define a Liouville evolution operator that acts on any function of the dynamical variables of the system as

$$e^{iLt}\vec{\mathcal{J}}(0) = \vec{\mathcal{J}}(t)\,;$$

thus we may write (1) as

$$K(\epsilon) = \frac{n}{3kT^2}\left\langle \vec{j}_1 \cdot G(\epsilon) \sum_i \vec{j}_i \right\rangle \tag{2}$$

with $G(\epsilon) = (\epsilon - iL)^{-1}$, and $K(\epsilon)$ stands here and from now on for that part of the heat conductivity under consideration, the average $\langle \cdots \rangle$ is carried over an equilibrium weight of a system of noninteracting particles. Expanding $G(\epsilon)$ by means of the binary-collision operator, one gets the following renormalized density expansion for $K(\epsilon)$:

$$K(\epsilon) = \frac{n}{3kT^2}\int d\vec{v}_1\, \Phi(\vec{v}_1)\vec{j}_1 \cdot [\epsilon + n\Lambda_B + n^2\Lambda_{CU}(\epsilon) - n^3\Lambda_{SCU}(\epsilon) + O(n^4)]^{-1} \cdot \vec{j}_1\,, \tag{3}$$

where

$$\Phi(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right)$$

is the Boltzmann statistical factor; Λ_B is the linearized Boltzmann collision operator, Λ_{CU} the linearized Choh-Uhlenbeck operator, and Λ_{SCU} the linearized "super-Choh-Uhlenbeck" collision operator; they involve, respectively, the dynamics of two, three, and four isolated molecules and may be defined by means of matrix elements of the binary operator T_{ij} to be defined below.

The linearized Boltzmann collision operator Λ_B acts on any function ψ of the velocity as

$$\Lambda_B\psi = \int d\vec{v}_2\, \Phi(\vec{v}_2)\langle 0,0|T_{12}|0,0\rangle[\psi(\vec{v}_1) + \psi(\vec{v}_2)]\,.$$

The linearized Choh-Uhlenbeck collision operator Λ_{CU} involves a series of products of three and more binary collision operators, their indices being chosen among three particles only. The super-Choh-Uhlenbeck operator Λ_{SCU} that will be considered in this work involves a product of at least four collision operators with four particles; one of these contributions is

$$\Lambda_{SCU}(\epsilon)\psi = \int \prod_{i=2}^{4} d\vec{v}_i\, \Phi(\vec{v}_i) \frac{1}{(2\pi)^3} \int d\vec{q} \langle 0,0 | T_{12} | \vec{q}, -\vec{q}\rangle (\epsilon - i\vec{q}\cdot\vec{v}_{12})^{-1} \langle -\vec{q}, 0 | T_{23} | -\vec{q}, 0\rangle (\epsilon - i\vec{q}\cdot\vec{v}_{12})^{-1}$$

$$\times \langle \vec{q}, 0 | T_{14} | \vec{q}, 0\rangle (\epsilon - i\vec{q}\cdot\vec{v}_{12})^{-1} \langle \vec{q}, -\vec{q} | T_{12} | 0, 0\rangle \sum_{i=1}^{4} \psi(\vec{v}_i) + (\text{similar terms}).$$

A priori, the binary expansion of Λ_{SCU} is infinite, even for hard spheres. However our objective is *not* a computation of the complete super-Choh-Uhlenbeck contribution to some transport coefficient; we are only interested in the divergence of the density expansion of transport coefficients, and the more "catastrophic" divergences are expected to arise from the ring collision events which involve the minimum number of collisions for each collision operator, i.e., four collisions at the super-Choh-Uhlenbeck order (order n^2 in the virial expansion for the heat conductivity), five collisions at the order n^3, and so on. Of course we do not claim that the higher-order terms in the binary collision expansion do not yield divergences too, but either they are less "catastrophic" than the ring divergences, or they are due to some reason as yet unknown. From Eq. (3), the super-Choh-Uhlenbeck contribution to the heat conductivity is in the first Enskog approximation

$$K_2(\epsilon) = \frac{2}{75} \frac{m^2 \tau K_0^2}{(k\tau)^5} \int \prod_{i=1}^{4} d\vec{v}_i\, \Phi(\vec{v}_i)$$

$$\times (\vec{j}_1 + \vec{j}_2) \cdot \Lambda_{SCU}(\epsilon) (\vec{j}_1 + \vec{j}_2 + \vec{j}_3 + \vec{j}_4), \tag{4}$$

where

$$K_0 \equiv K_0(\epsilon = 0) = \frac{75}{64} \frac{k}{a^2} \left(\frac{k\tau}{\pi m}\right)^{1/2} \tag{5}$$

for hard spheres, and it will be understood that $\Lambda_{SCU}(\epsilon)$ accounts for the ring events only and so is replaced by the first term in its binary collision expansion:

$$\sum_{\alpha,\beta,\gamma} T_{12} G_0 T_\alpha G_0 T_\beta G_0 T_\gamma ,$$

where, as usual G_0 is the resolvent of the noninteracting Hamiltonian; T_{ij} is the binary collision operator, and α, β, γ stand for any nonordered pair of indices (i,j) $(i \neq j,\ 1 \leq i,j \leq 4)$. We have used the freedom in the labeling of particles to call (12) the pair colliding at the beginning of the sequence; as we assume that time increases from the left to the right, (12) is the first collision of the ring event.

B. List of the collisions

From the summation $\sum_{\alpha,\beta,\gamma}$ there should be $\binom{4}{2}^3 = 216$ different terms in $\Lambda_{SCU}(\epsilon)$. However, this number is lowered by the following rules:

Rule a. Two consecutive pairs of indices cannot be the same: $\alpha \neq (12)$, $\beta \neq \alpha$, $\gamma \neq \beta$. This is due to the resummation carried out in the binary-collision operator, and for hard spheres expresses the simple property that two particles cannot recollide unless one of them has met a third particle.

Rule b. The set of indices $\{(12), \alpha, \beta, \gamma\}$ cannot be split into two (or eventually more) nonempty subsets so that particles belonging to different parts are not connected by a binary-collision operator. For instance $T_{12}G_0T_{34}G_0T_{12}G_0T_{34}$ is rejected, as there is no common collision between subsets (12) and (34). More generally, any term vanishes when no quantity containing i or j appears on the right (or the left) of T_{ij}. This rule derives from the property that $T_{34}G_0T_{12}f(\vec{v}_1, \vec{v}_2) = 0$ for any function f.

Rule c. The sequences are "irreducible": a particle cannot meet a first subset of particles, leave them, and interact with another subset having no collision event in common with the first one because the contributions arising from these "reducible" diagrams are products of irreducible factors and so disappear[1] in the inverted series for the collision operator. This rule rejects the sequence $T_{12}G_0T_{13}G_0T_{34}G_0T_{12}$ or the sequence $T_{12}G_0T_{23}G_0T_{31}G_0T_{14}$; in the present case this rule states that a particle colliding only once does it in an intermediate collision.

With the above restrictions we are now able to list the allowed sequences for $\Lambda_{SCU}(\epsilon)$. One of the particles, 1 or 2, must occur in the second collision (rule b) but not both (rule a); then a new particle, say 3, must appear in α, the fourth particle occurs in the third collision (rule c), and so the product $T_{12}T_{\alpha}T_{\beta}T_{\gamma}$ takes the form

$$T_{12}T_{23}T_{i4}T_{jk} \quad (i=1,2,3;\, j,k=1,2,3,4)\,,$$

and the allowed sequences are

$$(12)(23)(14)(12)\,,\ (12)(23)(14)(13)\,,$$
$$(12)(23)(14)(24)\,,\ (12)(23)(14)(34)\,,$$
$$(12)(23)(24)(12)\,,\ (12)(23)(24)(14)\,,$$
$$(12)(23)(34)(13)\,,\ (12)(23)(34)(14)\,.$$

The third sequence is the time-reversed expression of the second one (this can be seen through the substitution of indices 1, 2, 3, $4 \to 2$, 4, 1, 3); from elementary properties of the operator T_{ij} they give the same contribution; the same remark holds for the sixth and seventh sequences. So, there are only six distinct sequences $s_1, \ldots, s_6$ defined as

$$\begin{aligned} s_1 &= (12)(23)(14)(12)\,,\\ s_2 &= (12)(23)(14)(13)\,,\\ s_3 &= (12)(23)(14)(34)\,,\\ s_4 &= (12)(23)(24)(12)\,,\\ s_5 &= (12)(23)(34)(13)\,,\\ s_6 &= (12)(23)(34)(14)\,, \end{aligned} \tag{6}$$

and the contribution of the sequences s_2 and s_5 to $K_2(\epsilon)$ are to be multiplied by 2. The six processes are symbolized in Fig. 2.

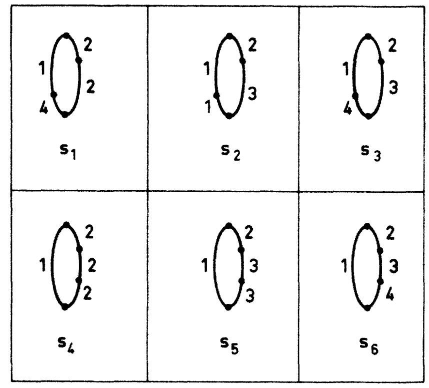

FIG. 2. Diagrams representing the six possible sequences $s_1, \cdots, s_6$ of four-particle irreducible ring events for the heat conductivity or the shear viscosity. The conventions are the same as in Fig. 1(b).

C. Real and virtual collisions

We now make explicit the "matrix element" of T_α. This element describes the action of T_{12} on any function of the general form

$$e^{i\vec{k}\cdot\vec{r}_1}e^{i\vec{k}'\cdot\vec{r}_2}\psi(\vec{v}_1,\vec{v}_2)\,.$$

For a hard-sphere potential, T_{12} may be split into a "virtual" and a "real" part as[6,7]

$$T_{12} = T_{12}{}^{R} - T_{12}{}^{V}\,,$$

with

$$\langle \vec{k}+\vec{q}, \vec{k}'-\vec{q}\,|\, T_{12}{}^{V} |\vec{k},\vec{k}'\rangle \psi(\vec{v}_1,\vec{v}_2) = v_{12}\int d\vec{b}\, e^{-i\vec{q}\cdot\vec{\rho}(\vec{b},\vec{v}_{12})}\psi(\vec{v}_1,\vec{v}_2)\,, \tag{7a}$$

$$\langle \vec{k}+\vec{q}, \vec{k}'-\vec{q}\,|\, T_{12}{}^{R} |\vec{k},\vec{k}'\rangle \psi(\vec{v}_1,\vec{v}_2) = v_{12}\int d\vec{b}\, e^{-i\vec{q}\cdot\vec{\rho}(\vec{b},\vec{v}_{12})}\psi(\vec{v}_1{}',\vec{v}_2{}')\,, \tag{7b}$$

where $\vec{\rho}(\vec{b},\vec{v}_{12})$ is the distance between the centers of the spheres at the instant of the collision

$$\vec{\rho}(\vec{b},\vec{v}_{12}) = \vec{b} + (\vec{v}_{12}/v_{12})(a^2-b^2)^{1/2}\,, \tag{8}$$

and $\vec{b}$ is the impact parameter, orthogonal to $\vec{v}_{12}$ and moving inside the circle of radius a (a is the *diameter* of the hard spheres); and where $\vec{v}_1{}'$, $\vec{v}_2{}'$ are the velocities after collision and $\vec{v}_{12} = \vec{v}_1 - \vec{v}_2$.

As an useful example, we get from Eqs. (7) and (8) the action of T_{12} on the heat current:

$$\langle \vec{q}, -\vec{q}\,|\, T_{12}|0,0\rangle (\vec{j}_1+\vec{j}_2) = v_{12}\int d\vec{b}\, e^{-i\vec{q}\cdot\vec{\rho}(\vec{b},\vec{v}_{12})}\Delta\vec{J}(\vec{b};\vec{v}_1,\vec{v}_2)\,, \tag{9}$$

with

$$\Delta\vec{J}(\vec{b};\vec{v}_1,\vec{v}_2) = \tfrac{1}{2}m\{\vec{v}_{12}(\vec{v}_{12}\cdot\vec{V}) - \vec{w}(\vec{b},\vec{v}_{12})[\vec{w}(\vec{b},\vec{v}_{12})\cdot\vec{V}]\}\,, \tag{10}$$

and

$$\vec{V} = \tfrac{1}{2}(\vec{v}_1+\vec{v}_2) = \tfrac{1}{2}(\vec{v}_1{}'+\vec{v}_2{}')\,, \tag{11a}$$

$$\vec{w}(\vec{b},\vec{v}_{12}) = \vec{v}_1{}' - \vec{v}_2{}' = -\vec{v}_{12}\left(1-\frac{2b^2}{a^2}\right) - \frac{2\vec{b}}{a^2}(a^2-b^2)^{1/2}v_{12}\,. \tag{11b}$$

Using Eqs. (7)–(11), we may write a contribution to $K_2(\epsilon)$, from the sequence s_1 for example, as:

$$+\frac{2m^2\tau K_0^2}{75(k\tau)^5}\int\prod_{i=1}^{4}\Phi(\vec{v}_i)\,d\vec{v}_i\int\frac{d\vec{q}}{(2\pi)^3}\int\frac{d\vec{b}\,v_{12}}{\epsilon-i\vec{q}\cdot\vec{v}_{12}}e^{i\vec{q}\cdot\vec{\rho}(\vec{b},\vec{v}_{12})}\,\Delta\vec{J}(\vec{b};\vec{v}_1,\vec{v}_2)\cdot\langle-\vec{q},0\,|\,T_{23}\,|-\vec{q},0\rangle\frac{1}{\epsilon-i\vec{q}\cdot\vec{v}_{12}}$$

$$\times\langle\vec{q},0\,|\,T_{14}\,|\,\vec{q},0\rangle\frac{1}{\epsilon-i\vec{q}\cdot\vec{v}_{12}}v_{12}\int d\vec{b}'''\,e^{-i\vec{q}\cdot\vec{\rho}(\vec{b}''',\vec{v}_{12})}\,\Delta\vec{J}(\vec{b}''';\vec{v}_1,\vec{v}_2)\,,$$

where we have used the Hermicity of the T operator to make the left T_{12} operator act on its left. The intermediate T operators (T_{23} and T_{14} in the above example) must be split into their virtual and real parts, and so the contribution to $K_2(\epsilon)$ of any one of the sequences s_i ($i=1,2,\ldots,6$) listed in Eqs. (6), will be the sum of four terms:

$$S_i=S_i^{VV}-S_i^{VR}-S_i^{RV}+S_i^{RR}$$

where $+[2m^2\tau K_0^2/75(k\tau)^5]S_i$ is the contribution of sequence s_i to $K_2(\epsilon)$, and where the superscripts R and V, written in the chronological order, mean, respectively, "real" and "virtual" and refer to the part of the intermediate T operator we consider. For instance, S_1^{RV} is the contribution of the sequence s_1 when the collision (23) is real and the collision (14) is virtual. Each of the six sequences S_i being divided into four contributions RR, RV, VR and VV, we should have 24 terms to compute. Actually, their number can be reduced by the following considerations:

(i) If the two particles colliding at the beginning and end of the sequence are the same (cases s_1 and s_4), the two intermediate collisions cannot be virtual as the velocity of at least one of the particles 1 and 2 must be modified during the sequence in order to allow a recollision. This obvious point could be verified by an explicit computation of S_1^{VV} and S_4^{VV}. Thus

$$S_1^{VV}=S_4^{VV}=0\,.$$

(ii) Some real-virtual sequences are time-reversed from each other and

$$S_1^{RV}=S_1^{VR},\quad S_3^{RV}=S_3^{VR},$$
$$S_4^{RV}=S_4^{VR},\quad S_6^{RV}=S_6^{VR}.$$

(iii) Let us introduce a new classification among the intermediate collisions. We shall say that there is *no transfer* of correlation if the new particle appearing in this collision does not occur again on the right of this collision. For instance, particles 3 and 4 appear only once in the sequence (12), (23), (14), (12), and, roughly speaking, the correlation between particles 1 and 2 created in this sequence by the left collision (12) is "scattered" (but not "transferred") by collisions (23) and (14); this makes invalid the Stosszahlansatz for the last collision (12), leading to a correction to the Boltzmann theory. On the other hand, we shall say that a *transfer* of correlation takes place in an intermediate collision, say (23), if the new particle occurring in this collision, say particle 3, does appear again on the right, although the collided particle, 2, disappears. In the sequence (12) (23) (14) (13), the correlation created by the *first collision* (12) is transferred from particle 2 to 3 at collision (23), and due to this new correlation, the Stosszahlansatz breaks down for the last collision (13).

The interest of this splitting into collisions with or without transfer is the following one: *when the intermediate collision is real*, due to the isotropy of the scattering cross section between hard spheres, the integration over the impact parameter makes any distinction between the two particles after the collision almost disappear, except for the shift between the centers of the spheres at the instant of the collision. But it may be understood that this shift of order a, becomes unimportant when one considers large collision sequences, as the one yielding the $\ln\epsilon$ behavior of $K_2(\epsilon)$. Henceforth, it is of interest to consider the behavior of a diverging contribution to $K_2(\epsilon\to 0)$ under the transformation of an intermediate real collision *with* transfer into a real collision *without* transfer and conversely. This transformation acts on a collision sequence as follows: when an intermediate collision $(i,\,j)$ is real, make on its right the substitution $i\longleftrightarrow j$, anything else being kept fixed [for short this transformation will be called (transfer)$\longleftrightarrow$(no transfer)]. For instance, this yields from (12) $(23)^R$ $(14)^R$ (12), the sequences (12) $(23)^R$ $(14)^R$ (13), (12) $(23)^R$ $(14)^R$ (43), and (12) $(23)^R$ $(14)^R$ (42).

As shown in Appendix B for a large class of collision sequences, this transformation does not modify the contribution to the diverging part of $K_2(\epsilon\to 0)$, and using the results of Appendix C, this result may be straightforwardly extended to any four-particle ring collision event with intermediate real collisions.

Let us point out again that this is due to the isotropy of the differential cross section for hard spheres. A similar property probably does not hold for other potentials, and it is surely not true for two-dimensional systems as can be seen from the calculation by Sengers of the first diverging term for the viscosity of hard discs.[8] From the above considerations, we have in the small-ϵ limit

$$S_1^{RR} \simeq S_2^{RR} \simeq S_3^{RR}, \quad S_4^{RR} \simeq S_5^{RR} \simeq S_6^{RR},$$

$$S_1^{RV} \simeq S_2^{RV}, \quad S_2^{VR} \simeq S_3^{RV},$$

$$S_4^{RV} \simeq S_5^{RV}, \quad S_5^{VR} \simeq S_6^{RV},$$

and

$$K_2(\epsilon) \underset{\epsilon \to 0}{\simeq} \frac{2m^2 \tau K_0^2}{75(k\tau)^5} [(2S_2^{VV} + S_3^{VV} + 2S_5^{VV} + S_6^{VV}) - 4(S_2^{RV} + S_2^{VR} + S_5^{RV} + S_5^{VR}) + 4(S_1^{RR} + S_4^{RR})] .$$

We still remain with ten diverging terms. They are schematized in Fig. 3, and the problem is now to compute them explicitly. A first step consists in exhibiting the dominant contribution when $\epsilon \to 0$. This part of our program is already achieved, and we have recovered in any case the predicted $\ln \epsilon$ behavior. The methods we have used are generalizations of those in Sec. III and Refs. 7 and 8. We shall detail them in a forthcoming paper.

The second step consists in computing the numerical value of the coefficient of $\ln \epsilon$ which is still a complicated sum of numbers given by multidimensional integrals. In many cases, the reduction of these integrals to low-dimensional integrals or to elementary quantities is a very difficult, if not impossible, task. In some cases, the calculations can be completely carried out. We describe in Sec. III two of these contributions: S_2^{VV} and S_5^{VV}.

Before ending this section, let us point out that all the above arguments hold without any change for the second-order diverging correction to the shear viscosity $\eta_2(\epsilon)$. This reads

$$\eta_2(\epsilon) \underset{\epsilon \to 0}{\simeq} \frac{1}{20}\left(\frac{1}{k\tau}\right)^3 \eta_0^2 [2R_2^{VV} + R_3^{VV} + 2R_5^{VV} + R_6^{VV} - 4(R_2^{RV} + R_2^{VR} + R_5^{VR} + R_5^{RV}) + 4(R_1^{RR} + R_4^{RR})] ,$$

where

$$\eta_0 = \frac{5}{16} \frac{m}{a^2} \left(\frac{k\tau}{\pi m}\right)^{1/2}$$

is the first Enskog value of the viscosity at the Boltzmann order, and where the quantities R are deduced from the quantities S with the same indices by replacing the heat current $\vec{j}_i$ by the traceless tensor

$$\overleftrightarrow{t}_i = m(\vec{v}_i \vec{v}_i - \tfrac{1}{3} v_i^2 \overleftrightarrow{1}) .$$

Some modifications occur when we deal with the self-diffusion coefficient: we have to point out one of the particle, say 1, and so, for obvious reasons, the sequence s_3 does not contribute, whereas sequences s_1, s_2, s_4, and s_5 must be reckoned twice owing to straightforward symmetries. Thus, the divergent second-order contribution to D is the sum of nine contributions:

$$D_2(\epsilon) \underset{\epsilon \to 0}{\simeq} \frac{D_0^2}{3}\left(\frac{m}{k\tau}\right)^2 [2\Delta_2^{VV} + 2\Delta_5^{VV} + \Delta_6^{VV} - 6\Delta_2^{RV} - 2\Delta_2^{VR} - 6\Delta_5^{RV} - 4\Delta_5^{VR} + 4\Delta_1^{RR} + 5\Delta_4^{RR}] ,$$

with

$$D_0 = \frac{3}{8a^2}\left(\frac{k\tau}{\pi m}\right)^{1/2} ,$$

and where the Δ's are deduced from the S's by replacing $\vec{j}_1$ by $\vec{v}_1$ and $\vec{j}_{2-4}$ by 0.

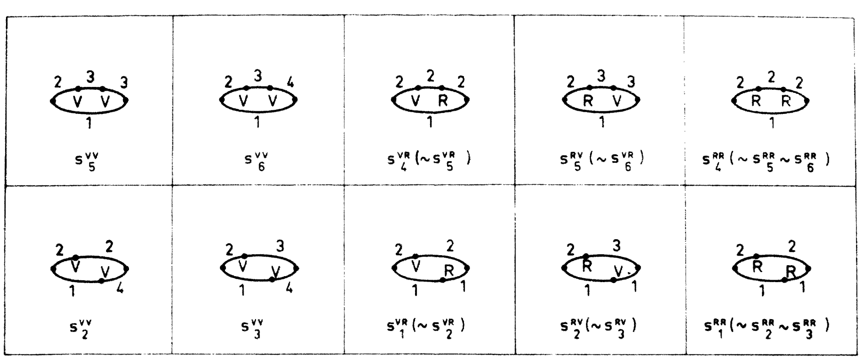

FIG. 3. Diagrams of the ten distinct contributions to the divergent part of $K_2(\epsilon)$ [or $\eta_2(\epsilon)$]; the nature of the intermediate collision (real or virtual) is precised with label R or V.

III. COMPUTATION OF S_2^{VV} AND S_5^{VV}

We are interested in the following collision sequences:

(i) (12) (23)^V (14)^V (13). Note that both the intermediate collisions (23) and (14) are virtual. The corresponding contribution to K_2 is called S_2^{VV}. It will be simpler to consider it together with the time-reversed sequence (12) (14)^V (23)^V (13) of contribution $S_2'^{VV} = S_2^{VV}$ and to deal with $\frac{1}{2}(S_2'^{VV} + S_2^{VV})$ instead of S_2^{VV} itself.

(ii) (12) (23)^V (34)^V (13). This contribution, where the intermediate collisions are again virtual, is called S_5^{VV}.

From Eqs. (3), (7), and (9)

$$S_2^{VV} = \pi a^2 \int \prod_{i=1}^{4} \Phi(\vec{v}_i)\, d\vec{v}_i \int \frac{d\vec{q}}{(2\pi)^3} \int d\vec{b}\, d\vec{b}'\, d\vec{b}''' \exp\{i\vec{q}\cdot[\vec{\rho}(\vec{b},\vec{v}_{12}) + \vec{\rho}(\vec{b}',\vec{v}_{23}) - \vec{\rho}(\vec{b}''',\vec{v}_{13})]\}$$

$$\times \frac{v_{12} v_{23} v_{14} v_{13} \Delta\vec{J}(\vec{b};\vec{v}_1,\vec{v}_2)\cdot\Delta\vec{J}(\vec{b}''';\vec{v}_1,\vec{v}_3)}{(\epsilon - i\vec{q}\cdot\vec{v}_{12})(\epsilon - i\vec{q}\cdot\vec{v}_{13})^2}. \tag{12a}$$

We get $S_2'^{VV}$ by commuting on the right-hand side of (12a) indices 2 and 3. The impact parameters $\vec{b}$, $\vec{b}'$, $\vec{b}'''$ move in circles of radius a in planes perpendicular to $\vec{v}_{12}$, $\vec{v}_{23}$, $\vec{v}_{13}$, respectively. The integration over the parameter $\vec{b}''$ of the virtual collision (24) has been performed and yields a factor πa^2.

In a similar manner, we get for S_5^{VV}

$$S_5^{VV} = \pi a^2 \int \prod_{i=1}^{4} \Phi(\vec{v}_i)\, d\vec{v}_i \int \frac{d\vec{q}}{(2\pi)^3} \int d\vec{b}\, d\vec{b}'\, d\vec{b}''' \times \exp\{i\vec{q}\cdot[\vec{\rho}(\vec{b},\vec{v}_{12}) + \vec{\rho}(\vec{b}',\vec{v}_{23}) - \vec{\rho}(\vec{b}''',\vec{v}_{13})]\}$$

$$\times \frac{v_{12} v_{23} v_{34} \Delta\vec{J}(\vec{b};\vec{v}_1,\vec{v}_2)\cdot\Delta\vec{J}(\vec{b}''';\vec{v}_1,\vec{v}_3)}{(\epsilon - i\vec{q}\cdot\vec{v}_{12})(\epsilon - i\vec{q}\cdot\vec{v}_{13})^2}. \tag{12b}$$

Formulas (12) look very much the same and the similarity will hold throughout all the calculation, although the integrand in S_5^{VV} will appear less symmetrical than S_2^{VV} and thus yields slightly more complicated computations. We shall detail the calculation of the "symmetrical" term S_2^{VV} only and give at each step the corresponding result for S_5^{VV}. We shall proceed in the following way: (i) choose the integration variables, (ii) integrate over $\vec{q}$ and express the divergence near $\epsilon = 0$, (iii) integrate over the impact parameters $\vec{b}$, $\vec{b}'$, $\vec{b}'''$, (iv) integrate over the remaining variables.

A. Choice of the integration variables

The integrand in Eq. (12a) depends mostly on the relative velocities, and particle 1 plays a special role. So we choose as new variables the velocity of the center of mass

$$\vec{V}_g = \tfrac{1}{4}(\vec{v}_1 + \vec{v}_2 + \vec{v}_3 + \vec{v}_4)$$

and the three relative velocities

$$\vec{v}_{12} = \vec{v}_1 - \vec{v}_2,\quad \vec{v}_{13} = \vec{v}_1 - \vec{v}_3,\quad \vec{v}_{14} = \vec{v}_1 - \vec{v}_4 .$$

The Jacobian of the transformation is equal to 1 and

$$\sum_{i=1}^{4} v_i^2 = 4V_g^2 + B_r$$

with

$$B_r = \tfrac{3}{4}(v_{12}^2 + v_{13}^2 + v_{14}^2) - \tfrac{1}{2}(\vec{v}_{12}\cdot\vec{v}_{13} + \vec{v}_{13}\cdot\vec{v}_{14} + \vec{v}_{14}\cdot\vec{v}_{12}) . \tag{13}$$

Moreover, the orientation in space of the trihedral $\vec{v}_{12}$, $\vec{v}_{13}$, $\vec{v}_{14}$ plays no role in the integrand of the right-hand side of (12a). Thus, we may fix the direction of the vector $\vec{v}_{12}$, which amounts to an integration over a solid angle and provides a 4π factor, and choose as reference plane, the plane of the vectors $\vec{v}_{12}$, $\vec{v}_{13}$ (whence a 2π factor). Once this frame is fixed, the trihedral $\vec{v}_{12}$, $\vec{v}_{13}$, $\vec{v}_{14}$ is completely determined by the lengths v_{12}, v_{13}, v_{14} and the three angles

$$\theta = (\vec{v}_{12}, \vec{v}_{13}),\quad 0 \le \theta \le \pi$$

$$\theta' = (\vec{v}_{12}, \vec{v}_{14}),\quad 0 \le \theta' \le \pi$$

φ' = angle between planes

$$(\vec{v}_{12}, \vec{v}_{13}) \text{ and } (\vec{v}_{12}, \vec{v}_{14}),\quad 0 \le \varphi' \le 2\pi.$$

With these variables S_2^{VV} reads

$$S_2^{VV}=\left(\frac{m}{2\pi kT}\right)^6(\pi a^2)(8\pi^2)\int d\vec{V}_g\, e^{-(2m/kT)\vec{V}_g^2}\int_0^\infty\int_0^\infty\int_0^\infty v_{12}^3 v_{13}^3 v_{14}^3 v_{23}\, dv_{12}\, dv_{13}\, dv_{14}$$

$$\times\int_0^\pi \sin\theta\, d\theta\int_0^\pi \sin\theta'\, d\theta'\int_0^{2\pi} d\varphi'\, e^{-(m/2kT)B_r}$$

$$\times\int\int\int d\vec{b}\, d\vec{b}'\, d\vec{b}'''\ \Delta\vec{J}_{12}(\vec{b})\cdot\Delta\vec{J}_{13}(\vec{b}''')\int\frac{d\vec{q}}{(2\pi)^3}\,\frac{\exp\{i\vec{q}\cdot[\vec{\rho}_{12}(\vec{b})+\vec{\rho}_{23}(\vec{b}')-\vec{\rho}_{13}(\vec{b}''')]\}}{(\epsilon-i\vec{q}\cdot\vec{v}_{12})(\epsilon-i\vec{q}\cdot\vec{v}_{13})^2}, \tag{14}$$

where we have adopted the shortened notations $\Delta\vec{J}_{12}(\vec{b})$ and $\vec{\rho}_{12}(\vec{b})$ for $\Delta\vec{J}(\vec{b};\vec{v}_1,\vec{v}_2)$ and $\vec{\rho}(\vec{b},\vec{v}_{12})$.

B. The logarithmic singularity

The $\vec{q}$ integration is carried out by using

$$E=\int\frac{d\vec{q}}{(2\pi)^3}\,\frac{e^{-i\vec{q}\cdot\vec{A}}}{(\epsilon-i\vec{q}\cdot\vec{B})(\epsilon-i\vec{q}\cdot\vec{C})^2}$$

$$=\delta(A_z)\Theta\left(\frac{A_y}{C_y}\right)\Theta\left(\frac{A_xC_y-A_yC_x}{B_xC_y}\right)\frac{A_y}{C_y}$$

$$\times\frac{1}{|C_y||B_x|}\exp\left[-\epsilon\left(\frac{A_y}{C_y}+\frac{A_xC_y-A_yC_x}{B_xC_y}\right)\right],$$

where the trihedral $0xyz$ has been chosen in such a way that $\vec{B}$ is parallel to $0x$ (and $B_x>0$) and $\vec{C}$ lies in the $x0y$ plane; $\Theta(x)$ is the Heaveside step function

$$\Theta(x)=1\quad\text{when } x>0$$
$$=0\quad\text{otherwise.}$$

When the quantities A_x, A_y, C_y, ... are in turn variables in further integration, a singularity may occur near $\epsilon=0$ arising from the part of the domain of integration where C_y is very small. Near $C_y=0$,

$$E\simeq\delta(A_z)\Theta(A_y/C_y)\Theta(-C_x/B_x)\frac{A_y}{C_y|C_y||B_x|}$$
$$\times\exp[-\epsilon(A_y/C_y)(1-C_x/B_x)].$$

By inspection of Eq. (14), we shall choose

$$\vec{B}\equiv\vec{v}_{12},\quad \vec{C}\equiv\vec{v}_{13},$$

and

$$\vec{A}=-\vec{\rho}_{12}(\vec{b})-\vec{\rho}_{23}(\vec{b}')+\vec{\rho}_{13}(\vec{b}''');$$

as the singularity occurs when $C_y\equiv v_{13}\sin\theta$ is small, it corresponds either to $\theta\simeq0$ or $\theta\simeq\pi$. From the Heaveside function $\Theta(-C_x/B_x)$, one must have $-(v_{13}/v_{12})\cos\theta>0$ which eliminates $\theta\simeq0$. Then the dominant contribution to S_2^{VV} arises from a configuration where $\vec{v}_{12}$ and $\vec{v}_{13}$ are almost antiparallel; the impact parameters $\vec{b}$, $\vec{b}'$, $\vec{b}'''$ move inside the circle of radius a of the $y0z$ plane [Fig. 4(b)]. This corresponds to an unbounded recollision time for particles 1 and 3 [Fig. 4(b)] and one can wonder if this infinite time has a physical meaning or is actually bounded by the mean free flight time.

Near $\epsilon\to0$, one may replace

$$\int\frac{d\vec{q}}{(2\pi)^3}\,\frac{\exp\{i\vec{q}\cdot[\vec{\rho}_{12}(\vec{b})+\vec{\rho}_{23}(\vec{b}')-\vec{\rho}_{13}(\vec{b}''')]\}}{(\epsilon-i\vec{q}\cdot\vec{v}_{12})(\epsilon-i\vec{q}\cdot\vec{v}_{13})^2}$$

by

$$\frac{\delta(b_z+b_z'-b_z''')\Theta(b_y+b_y'-b_y''')(b_y+b_y'-b_y''')}{v_{12}v_{13}^2\sin^2\theta}\exp\left(-\frac{\epsilon}{\sin\theta}\,\frac{(b_y+b_y'-b_y''')(v_{12}+v_{13})}{v_{12}v_{13}}\right)$$

In order to exhibit the divergence, we shall perform the θ integration near $\theta=\pi$. The Boltzmann factor B_r and the scalar product remain finite at $\theta=\pi$ and take a simplified form that we shall explicate later on. In the $\epsilon\to0$ limit they are to be multiplied by

$$\int_0^\pi\frac{d\theta}{\sin\theta}\Theta(-\cos\theta)\exp\left(-\frac{\epsilon(b_y+b_y'-b_y''')}{v_{12}v_{13}\sin\theta}(v_{12}+v_{13})\right)\underset{\epsilon\to0}{\simeq}-\ln\epsilon,$$

where the dependence on the impact parameters has disappeared. Gathering all these results, we obtain the dominant contribution to S_2^{VV} in the symmetrical form:

$$2S_2^{VV}=S_2^{VV}+S_2'^{VV}\underset{\epsilon\to 0}{\simeq}-8\pi^2\left(\frac{m}{2\pi kT}\right)^6(\pi a^2)\ln\epsilon\left(\frac{kT}{m}\right)^{19/2}\int d\vec{V}_g\,e^{-2V_g^2}\int_0^\infty dv_{12}\int_0^\infty dv_{13}$$
$$\times\int_0^\infty dv_{14}\,v_{12}v_{13}v_{14}^3(v_{12}+v_{13})^2\int_0^\pi d\theta'\sin\theta'\int_0^{2\pi}d\varphi'\,e^{-B_0/2}\int d\vec{b}\int d\vec{b}'$$
$$\times\int d\vec{b}'''\;\delta(b_z+b_z'-b_z''')\,(b_y+b_y'-b_y''')\Theta(b_y+b_y'-b_y''')\Delta\vec{J}_{12}(\vec{b})\cdot\Delta\vec{J}_{13}(\vec{b}''')\Big|_{\theta=\pi}. \tag{15a}$$

The integrand has been written in a dimensionless form and

$$B_0\equiv B_r\,|_{\theta=\pi}=\tfrac{3}{4}(v_{12}^2+v_{13}^2+v_{14}^2)+\tfrac{1}{2}v_{12}v_{13}-\tfrac{1}{2}v_{14}\cos\theta'(v_{12}-v_{13}). \tag{15b}$$

The corresponding result for S_5^{VV} reads

$$2S_5^{VV}\underset{\epsilon\to 0^+}{\simeq}-\left(\frac{m}{2\pi kT}\right)^6(2\pi a^2)\,8\pi^2\left(\frac{kT}{m}\right)^{19/2}\ln\epsilon\int d\vec{V}_g\,e^{-2\vec{V}_g^2}\int_0^\infty dv_{12}\int_0^\infty dv_{13}$$
$$\times\int_0^\infty dv_{34}\,v_{12}^2(v_{12}+v_{13})v_{13}v_{34}^3\int_0^\pi d\theta'\sin\theta'\int_0^{2\pi}d\varphi'\,e^{-B_0'/2}\int d\vec{b}\int d\vec{b}'$$
$$\times\int d\vec{b}'''\;\delta(b_z+b_z'-b_z''')\,(b_y+b_y'-b_y''')\,\Theta(b_y+b_y'-b_y''')\Delta\vec{J}_{12}(\vec{b})\cdot\Delta\vec{J}_{14}(\vec{b}''')\,|_{\theta=\pi}, \tag{16a}$$

with

$$B_0'=\tfrac{5}{4}v_{12}^2+v_{13}^2+\tfrac{3}{4}v_{34}^2+v_{12}v_{13}-\tfrac{1}{2}(v_{12}+2v_{13})\,v_{34}\cos\theta'. \tag{16b}$$

C. Integration over the impact parameters

It becomes necessary to give explicitly $\Delta\vec{J}_{12}(\vec{b})\cdot\Delta\vec{J}_{13}(\vec{b}''')\,|_{\theta=\pi}$. In the reference frame of Sec. III B, this quantity can be put into the form

$$\Delta\vec{J}_{12}(\vec{b})\,\Delta\vec{J}_{13}(\vec{b}''')\,|_{\theta=\pi}=\frac{m^2v_{12}^2v_{13}^2}{4}\sum_{\lambda,\mu=x,y,z}U_{\lambda\mu}(\vec{b},\vec{b}''')V_\lambda W_\mu\,,$$

where $U_{\lambda\mu}$'s are functions of the impact parameters only, and where the cartesian coordinates V_λ and W_μ of

$$\vec{V}\equiv\tfrac{1}{2}(\vec{v}_1+\vec{v}_2)\quad\text{and}\quad\vec{W}\equiv\tfrac{1}{2}(\vec{v}_1+\vec{v}_3)$$

read

$$V_x=V_{gx}-\tfrac{1}{4}(v_{12}+v_{13})+\tfrac{1}{4}v_{14}\cos\theta'\,,$$
$$W_x=V_{gx}+\tfrac{1}{4}(v_{12}+v_{13})+\tfrac{1}{4}v_{14}\cos\theta'\,,$$
$$V_y=W_y=V_{gy}+\tfrac{1}{4}v_{14}\sin\theta'\cos\varphi'\,,$$
$$V_z=W_z=V_{gz}+\tfrac{1}{4}v_{14}\sin\theta'\sin\varphi'\,.$$

After integration over $\vec{V}_g$ and φ', the crossed terms like V_xW_y, $V_xW_z,\ldots$, yield vanishing contributions, whereas the contributions of V_yW_y and V_zW_z are equal. Thus we need only the values of U_{xx} and $U_{yy}+U_{zz}$. From the definition of $\Delta\vec{J}$ given in Eq. (10)

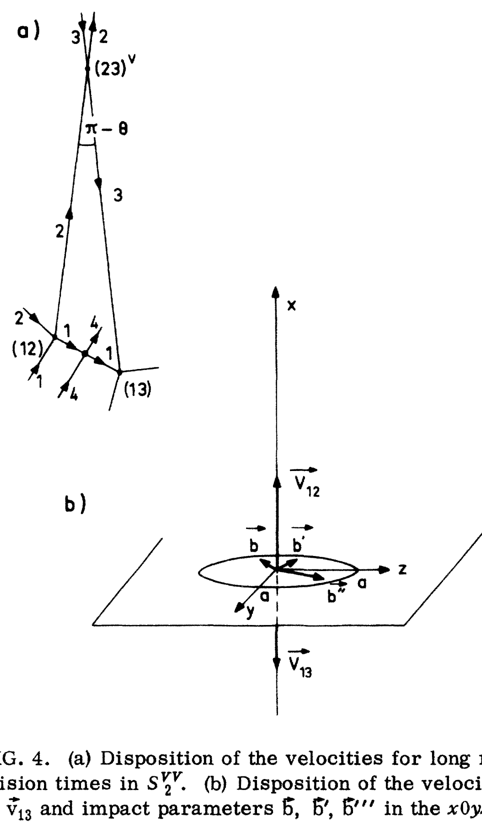

FIG. 4. (a) Disposition of the velocities for long recollision times in S_2^{VV}. (b) Disposition of the velocities $\vec{v}_{12}$, $\vec{v}_{13}$ and impact parameters $\vec{b}$, $\vec{b}'$, $\vec{b}'''$ in the $x0yz$ reference frame.

$$U_{xx}=(16/a^8)b^2b'''^2(a^2-b^2)(a^2-b'''^2)-(4/a^8)(2b^2-a^2)\times(2b'''^2-a^2)\vec{b}\cdot\vec{b}'''[(a^2-b^2)(a^2-b'''^2)]^{1/2} \quad (17a)$$

$$U_{yy}+U_{zz}=(16/a^8)(a^2-b^2)(a^2-b'''^2)(\vec{b}\cdot\vec{b}''')^2-(4/a^8)(2b^2-a^2)(2b'''^2-a^2)\vec{b}\cdot\vec{b}'''\times[(a^2-b^2)(a^2-b'''^2)]^{1/2}, \quad (17b)$$

and the right-hand sides of Eqs. (17a) and (17b) are functions of the length and of the scalar product of $\vec{b}$ and $\vec{b}'''$. The problem of the integration of this kind of quantity over the impact parameters $\vec{b}$ and $\vec{b}'''$ is solved in Appendix C, and we get from (C2)

$$\int\int\int d\vec{b}\,d\vec{b}'\,d\vec{b}'''U_{xx}\,\Theta(b_y+b'_y-b'''_y)(b_y+b'_y-b'''_y)\times\delta(b_z+b'_z-b'''_z)=\tfrac{2}{9}\pi^2a^6,$$

$$\int\int\int d\vec{b}\,d\vec{b}'\,d\vec{b}'''(U_{yy}+U_{zz})(b_y+b'_y-b'''_y)\times\Theta(b_y+b'_y-b'''_y)\,\delta(b_z+b'_z-b'''_z)=\tfrac{1}{9}\pi^2a^6,$$

and after integration over $\vec{V}_g$ and φ' we may write $S_2^{VV}+S_2'^{VV}$ as

$$S_2^{VV}+S_2'^{VV}\underset{\epsilon\to0}{\simeq}-\frac{m^2a^8\pi\sqrt{\pi}}{288\sqrt{2}}\left(\frac{kT}{m}\right)^{7/2}\ln\epsilon\left(\frac{3}{4}I_1-\frac{I_2}{8}+\frac{I_3}{8}+\frac{I_4}{32}\right), \quad (18a)$$

with

$$I_1=\int_0^\infty dv_{12}\int_0^\infty dv_{13}\,v_{12}^3v_{13}^3(v_{12}+v_{13})^2\times\int_0^\infty dv_{14}\,v_{14}^3\int_0^\pi d\theta'\sin\theta'\,e^{-B_0/2},$$

$$I_2=\int_0^\infty dv_{12}\int_0^\infty dv_{13}\,v_{12}^3v_{13}^3(v_{12}+v_{13})^4\times\int_0^\infty dv_{14}v_{14}^3\int_0^\pi d\theta'\sin\theta'\,e^{-B_0/2},$$

$$I_3=\int_0^\infty dv_{12}\int_0^\infty dv_{13}\,v_{12}^3v_{13}^3(v_{12}+v_{13})^2\int_0^\infty dv_{14}\,v_{14}^5\times\int_0^\pi d\theta'\sin\theta'\cos^2\theta'\,e^{-B_0/2},$$

$$I_4=\int_0^\infty dv_{12}\int_0^\infty dv_{13}\,v_{12}^3v_{13}^3(v_{12}+v_{13})^2\int_0^\infty dv_{14}\,v_{14}^5\times\int_0^\pi d\theta'\sin^3\theta'\,e^{-B_0/2}.$$

For the "unsymmetrical" term, we get

$$2S_5^{VV}\underset{\epsilon\to0}{\simeq}-\frac{m^2a^8\pi\sqrt{\pi}}{144\sqrt{2}}\left(\frac{kT}{m}\right)^{7/2}\times\ln\epsilon\left(\frac{3}{4}I'_1-\frac{I'_2}{8}+\frac{I'_3}{8}+\frac{I'_4}{32}-\frac{I'_5}{4}\right) \quad (18b)$$

with

$$I'_1=\int_0^\infty\int_0^\infty v_{12}^4v_{13}^3(v_{12}+v_{13})\,dv_{12}\,dv_{13}\int_0^\infty v_{34}^3\,dv_{34}\times\int_0^\pi\sin\theta'\,d\theta'\,e^{-B'_0/2},$$

$$I'_2=\int_0^\infty\int_0^\infty v_{12}^5v_{13}^3(v_{12}+v_{13})(v_{12}+2v_{13})\,dv_{12}\,dv_{13}\times\int_0^\infty v_{34}^3\,dv_{34}\int_0^\pi\sin\theta'\,d\theta'\,e^{-B'_0/2},$$

$$I'_3=\int_0^\infty\int_0^\infty v_{12}^4v_{13}^3(v_{12}+v_{13})\,dv_{12}\,dv_{13}\int_0^\infty v_{34}^3\,dv_{34}\times\int_0^\pi\sin\theta'\cos^2\theta'\,d\theta'\,e^{-B'_0/2},$$

$$I'_4=\int_0^\infty\int_0^\infty v_{12}^4v_{13}^3(v_{12}+v_{13})\,dv_{12}\,dv_{13}\int_0^\infty v_{34}^5\,dv_{34}\times\int_0^\pi\sin^3\theta'\,d\theta'\,e^{-B'_0/2},$$

$$I'_5=\int_0^\infty\int_0^\infty v_{12}^4v_{13}^4(v_{12}+v_{13})\,dv_{12}\,dv_{13}\int_0^\infty v_{34}^4\,dv_{34}\times\int_0^\pi\sin\theta'\cos\theta'\,d\theta'\,e^{-B'_0/2},$$

B'_0 being given in (16b).

D. Final results

We look for the diagonalization of the quadratic forms which define B_0 and B'_0. In the first case, the symmetric role of v_{12} and v_{13} suggests that we take as new integration variables

$$x=\tfrac{1}{2}(v_{12}+v_{13}),\quad y=\tfrac{1}{2}(v_{12}-v_{13}),\quad z=\tfrac{1}{2}v_{14},$$

and so the I_α's take the simplified form

$$I_1=2^8\int_0^\infty x^2e^{-x^2}dx\int_0^x(x^2-y^2)^3e^{-y^2/2}\Phi(y)\,dy,$$

$$I_2=2^{10}\int_0^\infty x^4e^{-x^2}dx\int_0^x(x^2-y^2)^3e^{-y^2/2}\Phi(y)\,dy,$$

$$I_3=2^{10}\int_0^\infty x^2e^{-x^2}dx\int_0^x(x^2-y^2)^3e^{-y^2/2}\frac{d^2\Phi(y)}{dy^2}\,dy,$$

$$I_4 = 2^{11}\int_0^\infty x^2 e^{-x^2}dx\int_0^x (x^2-y^2)^3\frac{e^{-y^2/2}}{y}\frac{d\Phi(y)}{dy}dy\,,$$

where

$$\Phi(y)=\int_0^\infty z^3 e^{-3z^2/2}dz\int_0^\pi e^{yz\cos\theta'}\sin\theta'\,d\theta'$$

$$=\frac{2}{9}+\frac{2}{27}\frac{e^{y^2/6}}{y}(y^2+3)\int_0^y e^{-t^2/6}dt\,.$$

The I_α ($\alpha=1,\ldots,4$) can then be expressed as linear combinations of

$$A_n^m=\int_0^\infty x^{2m}e^{-x^2}dx\int_0^x y^{2n+1}e^{-y^2/3}dy\int_0^y e^{-t^2/6}dt$$

(m, n integers; $n\geq -1$, $m\geq 0$),

$$C_n^m=\int_0^\infty x^{2m}e^{-x^2}dx\int_0^x e^{-y^2/2}y^{2n}dy\quad (m,\ n\geq 0)\,,$$

and

$$b_m=\int_0^\infty x^{2m}e^{-4x^2/3}dx\int_0^x e^{-t^2/6}dt\quad (m\geq 0)\,,$$

which may be computed by means of the recurrence relations:

$$A_n^m=\tfrac{1}{2}(2m-1)A_n^{m-1}+\tfrac{1}{2}b_{m+n}\,,$$
$$A_n^m=3nA_{n-1}^m+\tfrac{3}{2}C_n^m-\tfrac{3}{2}b_{m+n}\,,$$
$$C_0^m=\tfrac{1}{2}(2m-1)C_0^{m-1}+\tfrac{1}{4}(m-1)!\,(\tfrac{2}{3})^m\,,$$
$$C_n^m=(2n-1)C_{n-1}^m-\tfrac{1}{2}(m+n-1)!\,(\tfrac{2}{3})^{m+n}\,,$$
$$b_m=\tfrac{3}{8}(2m-1)b_{m-1}+\tfrac{3}{16}(\tfrac{2}{3})^m(m-1)!\,.$$

So we can calculate the A_n^m's, C_n^m's, and b_m's as linear functions of $b_0=(3/\sqrt{8})\arctan(1/\sqrt{8})$, $C_0^0=(1/\sqrt{2})\arctan(1/\sqrt{2})$, and

$$A_{-1}^0\equiv\int_0^\infty dx\,e^{-x^2}\int_0^x\frac{dy}{y}e^{-y^2/3}\int_0^y dt\,e^{-t^2/6}$$

$$=\frac{1}{2}\int_0^1 dt\left(\frac{6}{2+t^2}\right)^{1/2}\arctan\left(\frac{2+t^2}{6}\right)^{1/2}$$

$$\simeq 0.447\,193\,51\ldots\,.$$

Using the REDUCE[9] program, we have obtained the following expression for the last factor on the right-hand side of (18a):

$$\tfrac{3}{4}I_1-\tfrac{1}{8}I_2+\tfrac{1}{8}I_3+\tfrac{1}{32}I_4=\tfrac{1}{288}(-1200384C_0^0+491451b_0-257280A_{-1}^0+261785)\,.$$

In a similar manner, the change of variables $x=\frac{1}{2}v_{12}$, $y=\frac{1}{2}(v_{12}+2v_{13})$, and $z=\frac{1}{2}v_{34}$ makes possible a separation of the exponent B_0' into a sum of functions of x and of y. Using again the REDUCE[9] program, we have found

$$\tfrac{3}{4}I_1'-\tfrac{1}{8}I_2'+\tfrac{1}{8}I_3'+\tfrac{1}{32}I_4'-\tfrac{1}{4}I_5'=\tfrac{1}{72}(73728C_0^0-73152D_0^0-232533b_0+107520B_{-1}^0-17623)$$

with

$$D_0^0\equiv\int_0^\infty dx\,e^{-x^2}\int_0^\infty dy\,e^{-y^2/2}=\tfrac{1}{4}\pi\sqrt{2}-C_0^0\,,$$

and

$$B_{-1}^0\equiv\int_0^\infty dx\,e^{-x^2}\int_x^\infty\frac{dy\,e^{-y^2/3}}{y}\int_0^y dt\,e^{-t^2/6}$$

$$=\tfrac{1}{4}\pi\sqrt{6}\,\mathrm{arcsinh}(1/\sqrt{2})-A_{-1}^0\,.$$

Replacing all the constants by their numerical values, we obtain the contribution to $n^2K_2(\epsilon)$ from the two sequences studied in this section

$$+0.3714K_0(na^3)^2\ln\epsilon\,.$$

In a similar manner, we get the corresponding expressions for shear viscosity and self-diffusion coefficients. We have

$$R_2^{VV}+R_2'^{VV}\underset{\epsilon\to 0}{\simeq}-\frac{m^2a^8}{3\pi}\left(\frac{2\pi kT}{m}\right)^{5/2}\ln\epsilon\times(10A_{-1}^0+39C_0^0-10b_0-3)\tfrac{1}{24}\,,$$

$$2R_5^{VV}\underset{\epsilon\to 0}{\simeq}-\frac{4m^2a^8}{3\pi}\left(\frac{2\pi kT}{m}\right)^{5/2}\ln\epsilon\times\left(C_0^0+\tfrac{25}{16}D_0^0+\tfrac{97}{48}b_0-\tfrac{35}{24}B_{-1}^0-\tfrac{1}{4}\right)\,,$$

$$\Delta_2^{VV}+\Delta_2'^{VV}\underset{\epsilon\to 0}{\simeq}+\left(\frac{2\pi kT}{m}\right)^{3/2}a^8\ln\epsilon\times\left(\tfrac{13}{8}C_0^0+\tfrac{5}{12}A_{-1}^0-\tfrac{640}{1536}b_0-\tfrac{1}{8}\right)\,,$$

$$2\Delta_5^{VV}\underset{\epsilon\to 0}{\simeq}+\left(\frac{2\pi kT}{m}\right)^{3/2}a^8\ln\epsilon\times(6C_0^0+10B_{-1}^0-3D_0^0-13b_0+6)\tfrac{1}{12}\,,$$

where the R_i^{VV} and Δ_i^{VV} have been defined in Sec. IIC. The corresponding second-order corrections for viscosity and self-diffusion are then

$$-0.349\,\eta_0(na^3)^2\ln\epsilon$$

and

$$+1.6212D_0(na^3)^2\ln\epsilon\,,$$

respectively.

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APPENDIX A

In this Appendix we consider those contributions to K_2 which have been neglected in the bulk of this paper. The main result is that none of these contributions involve the super-Choh-Uhlenbeck operator and that they cannot yield the related divergences. We shall sketch a proof of this assumption, but no detailed calculations will be done, as they are not particularly illuminating and involve a lot of formalism. We are not interested in the numerical value but only in the convergence properties of the various contributions. We shall consider successively the so-called potential-potential K^{VV}, potential-kinetic K^{VK}, and kinetic-kinetic terms K^{KK}.

We shall show first that the potential-potential contribution to K, K^{VV} in the usual terminology, is of order n^3 in the low-density limit, that it does not diverge, and so does not contribute to K_2. The potential part of the fluctuating heat current is a sum of two particle contributions which, for hard spheres, are in fact "pseudocurrents",[10] but this does not change essentially reasoning. Let

$$\mathcal{J}^U = \sum_{i<j} \vec{y}_{ij}$$

be this potential heat flux. Neglecting any effect from the equilibrium correlations, we have

$$K^{VV}(\epsilon) = \frac{1}{3kT^2 V} \langle \vec{\mathcal{J}}^U \cdot (\epsilon - iL)^{-1} \vec{\mathcal{J}}^U \rangle$$

$$\underset{n\to 0}{\simeq} \frac{n^2}{3kT^2} \left\langle V \vec{y}_{12} \cdot (\epsilon - iL)^{-1} \sum_{l<m} \vec{y}_{lm} \right\rangle,$$

where the last average is carried out over the equilibrium ensemble of a perfect gas. Again we shall derive the low-density value of K^{VV} from the binary-collision expansion of $(\epsilon - iL)^{-1}$. The renormalization leading to the inverse sum of linearized collision operators, as in Eq. (3), is no longer needed here: as $(\epsilon - iL)^{-1}$ acts on nonconstant functions of the positions, G_0 is never equal to ϵ^{-1}, as it can be in the case of the kinetic-kinetic part of K, but to $(\epsilon - i\vec{q}\cdot\vec{v}_{ij})^{-1}$ in Fourier transform, with $q \neq 0$, and this suppresses the divergences of the "naive" density expansion of the Green-Kubo average.

The first term in the binary-collision expansion of $(\epsilon - iL)^{-1}$ leads to a contribution proportional to

$$\sum_{l<m} \langle \vec{y}_{12} \cdot (\epsilon - iL_0)^{-1} \vec{y}_{lm} \rangle .$$

If the pair of particles (12) and (lm) are not the same, this vanishes owing to the property

$$\int d\vec{v}_i \, \Phi(\vec{v}_i) \vec{y}_{ij} = 0 ,$$

although, if the pairs (12) and (lm) are identical, this contribution vanishes for hard spheres, as $\vec{y}_{ij}$ involves collision operator and two isolated hard spheres cannot collide twice.

Accordingly, the first term in the density expansion of $K^{VV}(\epsilon)$ involves at least one collision with a particle which is not in the argument of the potential currents on the left and right of the Green-Kubo average. This binary-collision expansion does not end after this single collision with an external particle, since, at the same order in the density (i.e., without adding another external particle), one has to consider the complete dynamics of the system of particles, where the number of collisions is not limited to three [= (one intermediate collision) + (one collision in each of the currents $\vec{y}_{12}$ and $\vec{y}_{lm}$)]. However we shall write the first term of this binary collision expansion. For that purpose we define $\vec{y}_{ij}(\vec{q})$ as the Fourier transform of $\vec{y}_{ij}$ in the variable $\vec{r}_{ij}$, this is a function of $\vec{v}_i$, $\vec{v}_j$, and $\vec{q}$. The first contribution to $K^{VV}(\epsilon)$ is, for hard spheres,

$$K^{VV}(\epsilon) \underset{n\to 0}{\simeq} \frac{n^3}{3kT^2} \int \frac{d\vec{q}}{(2\pi)^3} \int \prod_{i=1}^{3} d\vec{v}_i \, \Phi(\vec{v}_i) \vec{y}_{12}(-\vec{q}) \cdot (\epsilon - i\vec{q}\cdot\vec{v}_{12})^{-1} [\langle \vec{q}, 0 | T_{13} | \vec{q}, 0 \rangle (\epsilon - i\vec{q}\cdot\vec{v}_{12})^{-1} \vec{y}_{12}(\vec{q})$$
$$+ \langle \vec{q}, 0 | T_{13} | 0, \vec{q} \rangle (\epsilon - i\vec{q}\cdot\vec{v}_{13})^{-1} \vec{y}_{13}(\vec{q})] . \qquad \text{(A1)}$$

This contribution makes a three-particle "ring event" appear and is of order n^3, as announced. It involves *two* propagators $(\epsilon - i\vec{q}\cdot\vec{v})^{-1}$ only, and so does *not* present the type of divergence studied in the bulk of this paper that was crucially related to integrals over $\vec{q}$ of products of three propagators $(\epsilon - i\vec{q}\cdot\vec{v})^{-1}$. At higher order in the binary-collision expansion, more complicated events appear in this contribution to K^{VV} and yield an expansion very similar to the one of the Choh-Uhlenbeck collision operator, as it depends on the dynamics of three isolated particles. Thus in the low-density limit no divergence appears in K^{VV} at the ring order and $K^{VV}(\epsilon)$ contributes first to K_3 in the virial expansion of K.

Consider now the kinetic-potential part of the heat conductivity. As shown by Sengers *et al.*,[10] it contributes to the heat conductivity at the order n at least. The first virial correction to this term involves again a number of effects: one has to keep the next order term in the virial expansion of the intermediate collision operator and to account for the next term in the virial expansion of the equilibrium weight. We shall consider these two corrections successively.

Let us consider the potential-kinetic term with an intermediate Choh-Uhlenbeck collision operator and without equilibrium correlations. This contribution may be reduced to the following form:

$$K^{VK}_{2,\mathrm{CU}}(\epsilon) = -\frac{n^2}{3kT^2}\int \prod_{i=1}^{2} d\vec{v}_i\,\Phi(\vec{v}_i)\int_{r_{12}\geq a} d\vec{r}_{12}\,\vec{y}_{12}\cdot$$

$$\times\{(\epsilon+n\Lambda_B)^{-1}n^2\Lambda_{\mathrm{CU}}(\epsilon+n\Lambda_B)^{-1}\}_{\vec{v}_1}\vec{j}(\vec{v}),$$

where the notation $\{\ldots\}_{\vec{v}_1}$ means that the product of operators $(\epsilon+n\Lambda_B)^{-1}n^2\Lambda_{\mathrm{CU}}(\epsilon+n\Lambda_B)^{-1}$ acting on some function of the velocity, like $\vec{j}(\vec{v})$, yields a function of the velocity $\vec{v}_1$. As[10]

$$\int d\vec{v}_2\,\Phi(\vec{v}_2)\int_{r_{12}\geq a} d\vec{r}_{12}\,\vec{y}_{12} = \tfrac{4}{5}\pi a^3\vec{j}_1,$$

the above-defined contribution to K_2^{VK} is found by multiplying by the factor $\frac{4}{5}\pi n a^3$ that part of K_1 wherein the linearized Choh-Uhlenbeck operator appears. Let $K_{1,\mathrm{CU}}$ be this part of K_1. As $K_{1,\mathrm{CU}}$ exists, this contribution to K_2 is convergent.

Consider now the correction to K_2 arising from the virial expansion of the equilibrium weight. The effects of the equilibrium correlations appear as follows. The binary-collision expansion of $(\epsilon - iL)^{-1}$ yields series of products

$$\sum_{\alpha_i\neq\alpha_{i+1}} G_0 T_{\alpha_1} G_0\cdots T_{\alpha_n}.$$

When the equilibrium correlations are neglected, each particle of the pairs $\{\alpha_i\}$ has $(1/V)\Phi(\vec{v})$ as the statistical weight, and the first correction to this approximation will appear by accounting for equilibrium correlations between particles of the same, or of different, pairs.[11] One of these corrections to K_2^{VK} takes the following form:

$$\frac{n^4}{3kT^2}\int\prod_{i=1}^{4} d\vec{v}_i\,\Phi(\vec{v}_i)\int d\vec{r}_{14}\,\vec{y}_{14}\{(\epsilon+n\Lambda_B)^{-1}\}_{\vec{v}_1}$$

$$\times\int d\vec{r}_{23}\,T_{12}G_0T_{13}\,g(2,3)\{(\epsilon+n\Lambda_B)^{-1}\}_{\vec{v}_1}\vec{j}(\vec{v}),$$

where $g(2,3)$ is the equilibrium pair correlation function. From

$$\int d\vec{v}_4\,\Phi(\vec{v}_4)\int d\vec{r}_{14}\,\vec{y}_{14} = \tfrac{4}{5}\pi a^3\vec{J}_1,$$

the above contribution is again equal to $\frac{4}{5}\pi n a^3$ times some of the first virial corrections to the kinetic-kinetic part of K. Similar considerations could be applied to most of the contributions to K_2^{VK} due to the equilibrium correlations. However there is an effect on K^{VK} due to these correlations which does not appear in the case of K^{KK}. As the potential pseudocurrent $\vec{y}_{ij}$ depends on the relative position of the two particles at $r_{ij}=a$, it has to be multiplied by the equilibrium two-body pair-distribution function. This yields well-defined corrections to K^{VK} proportional to the terms of the virial expansion of the equilibrium pair-distribution function at $r_{ij}=a$.

We have considered in the bulk of this paper that kinetic-kinetic contribution to K_2 which involves the super-Choh-Uhlenbeck collision operator. There are in fact many more kinetic-kinetic contributions to K_2. Only one of them (the super-Choh-Uhlenbeck contribution being excluded) does not involve the equilibrium correlations. In fact, part of the virial expansion of transport coefficients is derived from the power expansion of the intermediate inverse linearized collision operator $[\epsilon+n\Lambda_B+n^2\Lambda_{\mathrm{CU}}-n^3\Lambda_{\mathrm{SCU}}+O(n^4)]^{-1}$, $(\epsilon+n\Lambda_B)$ being kept constant. Including up to the second order, this expansion reads

$$[\epsilon+n\Lambda_B+n^2\Lambda_{\mathrm{CU}}-n^3\Lambda_{\mathrm{SCU}}+O(n^4)]^{-1}$$

$$=(\epsilon+n\Lambda_B)^{-1}-(\epsilon+n\Lambda_B)^{-1}n^2\Lambda_{\mathrm{CU}}(\epsilon+n\Lambda_B)^{-1}$$

$$+(\epsilon+n\Lambda_B)^{-1}[n^2\Lambda_{\mathrm{CU}}(\epsilon+n\Lambda_B)^{-1}n^2\Lambda_{\mathrm{CU}}+n^3\Lambda_{\mathrm{SCU}}]$$

$$\times(\epsilon+n\Lambda_B)^{-1}+\cdots.$$

At the third order, two terms appear in this expansion: the one depending on Λ_{SCU} is studied in the bulk of this paper, the other one is formally quadratic in Λ_{CU}. In the first Enskog approximation, the contribution to K_2 of this last term is simply equal to $-(K_{1,\mathrm{CU}})^2/K_0$. There remains to study the kinetic-kinetic contribution to K_2 involving the equilibrium correlations.

As already pointed out, these corrections arise when one accounts for the correlations between particles in the index of the T operators in the expansion of $(\epsilon-iL)^{-1}$. These equilibrium correlations are to be considered together with the dynamical correlations due to the recollisions. The simplest corrections are obtained by multiplying the Boltzmann collision operator by the equilibrium pair-distribution function of two hard spheres at $r_{12}=a$. This yields part of the well-known Enskog formula for the transport coefficients, which is analytical at any order in the density.

Another class of correction is due to the "mixing" of the Choh-Uhlenbeck collision operator with the equilibrium correlations. This linearized Choh-Uhlenbeck collision operator acting on some function $\psi(\vec{v})$ may be written as

$$\Phi(\vec{v}_1)\int\prod_{i=2}^{3} d\vec{x}_i\, d\vec{v}_i\,\Phi(\vec{v}_i)T_{123}W(1,2,3)\sum_{j=1}^{3}\psi(\vec{v}_j)\,,$$

where $W(1,2,3)$ is equal to zero, if any one of the r_{ij} $(i,j=1,2,3)$ is smaller than a, and equal to 1 otherwise, and where T_{123} is a ternary collision operator. [Note that in the case of the super-Choh-Uhlenbeck operator one should introduce also a function $W(1,2,3,4)$ accounting for the condition of absence of overlapping at the beginning of the collision event; however, this is of no importance for the large cycles]. The equilibrium correlations cause $W(1,2,3)$ to be replaced by the exact triplet distribution function. But, although in the Boltzmann case the equilibrium correlations introduced a simple multiplicative factor, the substitution of the triplet distribution function in place of $W(1,2,3)$ yields more drastic changes in the Choh-Uhlenbeck collision operator. A quantitative discussion of this point should lead to complicated formulas, even more intricate than the ones found[10,11] for the Choh-Uhlenbeck operator with the simple $W(1,2,3)$ function. Also, we shall explain only qualitatively why these triplet correlations do not yield "ring" divergences at the Choh-Uhlenbeck order.

Consider a ring event between particles 1, 2, and 3 which starts with a collision 1-2. If the event has a long duration, particle 3 is very far from particles (12) at the instant of this first collision, and the triplet distribution, which is a weighting factor for the initial conditions, is approximately equal to the pair-distribution function of particles 1-2 at $r_{12}=a$ times a constant. Thus, for the ring events with a long duration, the introduction of the equilibrium correlations makes a multiplicative factor appear, that is analytical in the density and so does not yield any new divergence.

The last type of corrections we have to consider have an origin similar to that of the "EVD" (excluded volume dynamical) terms of Henline and Condiff.[11] They can be understood as follows. In the Boltzmann theory, the motion of a particle, say particle 1, is described by a set of collisions with uncorrelated particles, say particles 2, 3,. . . . A first type of correction to the Boltzmann theory (that is accounted for by the Choh-Uhlenbeck collision operator) arises from the correlations created by an intermediate collision (23). Another type of correlation between 2 and 3 exists, that is due to the equilibrium effects which, for hard spheres, account for the absence of overlapping. As shown by Henline and Condiff,[11] this EVD contribution to K_1 is proportional to an integral like

$$\int d\vec{r}_3\int d\vec{v}_2\int d\vec{v}_3\,\Phi(\vec{v}_2)\Phi(\vec{v}_3)\int_0^{\tau_m} d\tau\,,$$

where the time τ_m is defined as follows. It is assumed that, when particle 1 hits particle 2 at time zero, 2 and 3 overlap; the time τ_m is the positive time after which particles 1 and 3 cannot collide, $\vec{r}_{13}$, $\vec{r}_{12}$, and the velocities being given at $\tau=0$. In a theory starting from the binary-collision expansion of the evolution operator, as sketched at the beginning of this paper, the role of this time integration is played by a factor G_0. Let us study the convergence of the τ integral at large times. For that purpose, one starts from the formula

$$\int d\vec{r}_3\int d\vec{v}_2\int d\vec{v}_3\,\Phi(\vec{v}_2)\Phi(\vec{v}_3)\int_0^{\tau_m} d\tau$$
$$=\int_0^{\infty} d\tau\int_{\tau_m\geq\tau} d\vec{r}_3\, d\vec{v}_2\, d\vec{v}_3\,\Phi(\vec{v}_2)\Phi(\vec{v}_3)\,,$$

where $\int_{\tau_m\geq\tau}\cdots$ means that the initial conditions (i.e., $\vec{r}_2$, $\vec{r}_3$, $\vec{v}_2$, $\vec{v}_3$, . . .) are limited by the condition that collision (23) occurs after a time τ. At time 0 the three particles are at a distance of order a, and τ_m is of the order of an inverse velocity. At large values of τ_m, this range of variation of the relative velocity is limited to the inside of a small sphere of radius τ^{-1}. As the integration over velocities yields a result roughly proportional to the volume of this small sphere, the integrand, as a function of τ, decreases like τ^{-3} and no trouble appears originating from the collision sequences with a long duration.

Consider now the EVD contributions to K_2. Again, as the order in the density increases, the number of contributions increases too. The EVD part of K_1 is obtained by looking at initial situations where particles 2 and 3 overlap (but do not interact!). Actually this overlapping accounts for the presence of a weight $W(2,3)-1$ for the initial conditions [$W(i,j)=0$ if $r_{ij}<a$ and 1 otherwise]. This weight is the first term in the virial expansion of the pair correlation function, and, at the next order in the density, $W(2,3)$ must be replaced by the first virial correction to the equilibrium pair correlation function. This correlation function has a finite range in space, and so, the previous reasoning may be applied to this EVD contribution to K_2. Another EVD contribution to K_2

is obtained by replacing in the previous collision sequence the first collision (12) (or the last collision 13) by a three-body event. Consider a sequence of collision 12-23-13-14, with the condition that, at the instant of the collision (12), particles 2 and 3 or 4 and 2 overlap. Again, the corresponding EVD contribution to K_2 is roughly proportional to

$$\int_0^\infty d\tau \int_{\tau_m > \tau} d\vec{r}_3 d\vec{r}_4 \int \prod_{i=2}^{4} d\vec{v}_i \; \Phi(\vec{v}_i),$$

where τ_m is the time interval between collisions (12) and (14).

In order to study the long-time behavior of this integral, we consider first the events for which the size of the triangle drawn by the collision sequence 12-23-13 is limited by a maximum length, say 10a. Thus the previous reasoning about the convergence of the EVD contribution to K_1 remains valid as particle 4 has only to run over a finite distance before hitting particle 1. Consider now the case where the size of the triangle (12)(23)(13) may become arbitrarily large. It is of the order of the thermal velocity times the time elapsed between collisions (12) and (14). It is known[4] that for large times the volume of phase space of particle 3 for which a recollision (13) is allowed after the time τ after the sequence 12-23 is of order τ^{-2} at large τ. Moreover the relative velocity $\vec{v}_{14}$ is included into a solid angle of aperture τ^{-2} in order to allow the recollision (14) after the same time τ. Thus, at large τ, the integrand decreases like τ^{-4} and again there is no trouble due to long cycles of collisions.

The last type of EVD corrections we have to consider originate from the equilibrium three-body correlations. As in the case of the EVD contribution to K_1, one considers a situation where 2 particles, say 1 and 2, collide at $\tau = 0$, although a third particle, say 3, overlaps particle 2, but, at the same time a fourth particle, say 4, overlaps both 2 and 3. Again the corresponding contribution to K_2 is obtained by some time integration, but now there is double time integral (corresponding to *two* G_0 factors in the binary-collision expansion): one of the integrations is limited up to the instant of the collision (13) and the second up to the collision (14). A simple extension of the previous reasonings show that, at large times, both integrals converge like $\int^\infty d\tau/\tau^3$. This completes our study of the convergence of the contributions to K_2 which do not depend on the super-Choh-Uhlenbeck collision operator.

APPENDIX B

In this Appendix, we prove the invariance of some diverging contributions to $K_2(\epsilon \to 0)$ under the substitution (real intermediate collision with transfer) $\to$ (real intermediate collision without transfer). The class of sequences under consideration may be defined as follows: an intermediate collision being real, the other one must be either *real* or virtual *with transfer*; this rejects the contribution to S_i where two intermediate Green's functions G_0 are equal.

Consider a collision event where the first intermediate collision, between particles 2 and 3 for instance, is real. When no transfer of correlation takes place at this collision, the corresponding contribution to $K_2(\epsilon)$ is proportional to an integral of the type

$$\Lambda_1 = \int \frac{d\vec{q}}{(2\pi)^3} \int d\vec{b}' \exp[i\vec{q}\cdot\vec{\rho}(\vec{b},\vec{v}_{12})] \frac{1}{\epsilon - i\vec{q}\cdot\vec{v}_{12}} v_{23} \frac{1}{\epsilon - i\vec{q}\cdot\vec{v}'_{12}} \exp[-i\vec{q}\cdot\vec{R}(\vec{v}_1,\vec{v}'_2,\vec{v}_4)] \times \frac{1}{\epsilon - i\vec{q}\cdot\vec{V}(\vec{v}_1,\vec{v}'_2,\vec{v}_4)} \Delta\vec{J}(\vec{v}_1,\vec{v}_2;\vec{b})\cdot\Delta\vec{K}(\vec{v}_1,\vec{v}'_2,\vec{v}_4)\ , \tag{B1}$$

where $\Delta\vec{J}$ could be any vector function of $\vec{v}_1$, $\vec{v}_2$, and $\vec{b}$, nonsingular for any finite value of its arguments, where $\Delta\vec{K}$, $\vec{V}$ and $\vec{R}$ depend on the velocities $\vec{v}_1, \ldots, \vec{v}_4$ and on the impact parameters $\vec{b}''$ and $\vec{b}'''$ of the collisions not considered explicitly in (A1) (note that we do not consider the case where $\vec{V}$ is equal to $\vec{v}_{12}$ or $\vec{v}'_{12}$) and where $\vec{v}'_{12} = \vec{v}_1 - \vec{v}'_2$ with

$$\vec{v}'_2 = \tfrac{1}{2}(\vec{v}_2 + \vec{v}_3) + \tfrac{1}{2}\vec{w}_{23}(\vec{b}';\vec{v}_{23})\ , \tag{B2a}$$

$$\vec{v}'_3 = \tfrac{1}{2}(\vec{v}_2 + \vec{v}_3) - \tfrac{1}{2}\vec{w}_{23}(\vec{b}';\vec{v}_{23})\ , \tag{B2b}$$

$\vec{b}'$ being the impact parameter of collision (23), perpendicular to $\vec{v}_{23}$.

Consider now the contribution deduced from the preceding one by writing that a *transfer* of correlation occurs at the collision (23), i.e., by replacing 2 by 3 on the right of $T_{23}{}^R$. The transform of Λ_1 reads

$$\Lambda_2=\int\frac{d\vec{q}}{(2\pi)^3}\int d\vec{b}'\exp[i\vec{q}\cdot\vec{\rho}(\vec{b},\vec{v}_{12})]\frac{1}{\epsilon-i\vec{q}\cdot\vec{v}_{12}}$$
$$\times v_{23}\frac{\exp[-i\vec{q}\cdot\vec{\rho}(\vec{b}',\vec{v}_{23})]}{\epsilon-i\vec{q}\cdot\vec{v}_{13}}\frac{\exp[-i\vec{q}\cdot\vec{R}(\vec{v}_1,\vec{v}_3',\vec{v}_4)]}{\epsilon-i\vec{q}\cdot\vec{V}(\vec{v}_1,\vec{v}_3',\vec{v}_4)}$$
$$\times\Delta\vec{J}(\vec{v}_1,\vec{v}_2;\vec{b})\cdot\Delta\vec{K}(\vec{v}_1,\vec{v}_3',\vec{v}_4)\,. \qquad \text{(B3)}$$

This quantity differs from Λ_1 by the exchange of the velocities $\vec{v}_2'$ and $\vec{v}_3'$ and the factor $\exp[-i\vec{q}\cdot\vec{\rho}(\vec{b}',\vec{v}_{23})]$, that comes out from the distance between particles 2 and 3 at the instant of the collision (23). In order to prove $\Lambda_2\simeq\Lambda_1$ near $\epsilon=0$, we shall proceed in two steps: (i) Prove $\Lambda_2=\Lambda_1'$ with

$$\Lambda_1'=\int\frac{d\vec{q}}{(2\pi)^3}\int d\vec{b}'\exp[i\vec{q}\cdot\vec{\rho}(\vec{b},\vec{v}_{12})]\frac{1}{\epsilon-i\vec{q}\cdot\vec{v}_{12}}\,v_{23}\,\frac{1}{\epsilon-i\vec{q}\cdot\vec{v}_{12}'}\exp\{-i\vec{q}\cdot[\vec{\rho}(-\vec{b}',\vec{v}_{23})+\vec{R}(\vec{v}_1,\vec{v}_2',\vec{v}_4)]\}$$
$$\times\frac{1}{\epsilon-i\vec{q}\cdot\vec{V}(\vec{v}_1,\vec{v}_2',\vec{v}_4)}\Delta\vec{J}(\vec{v}_1,\vec{v}_2;\vec{b})\cdot\Delta\vec{K}(\vec{v}_1,\vec{v}_2',\vec{v}_4)\,; \qquad \text{(B4)}$$

(ii) prove $\Lambda_1'\simeq\Lambda_1$ where $\epsilon\to 0$.

1. Proof of $\Lambda_2=\Lambda_1'$

This proof uses the isotropy of the classical scattering cross section between two hard spheres. Let $F(\vec{v}_2',\vec{v}_3')$ be some function of $\vec{v}_2'$ and $\vec{v}_3'$ [i.e., of $\vec{v}_2$, $\vec{v}_3$, and $\vec{b}'$ from (B2)]. Let $d\Omega_{\vec{u}}$ be the surface element on the unit sphere on which moves the vector

$$\vec{u}=-\vec{w}_{23}(\vec{b}',\vec{v}_{23})/v_{23}\,;$$

then

$$\int d\vec{b}'\,F(\vec{v}_2',\vec{v}_3')=\frac{a^2}{4}\int d^2\Omega_{\vec{u}}\,F\left(\frac{\vec{v}_2+\vec{v}_3}{2}-\frac{v_{23}}{2}\vec{u},\ \frac{\vec{v}_2+\vec{v}_3}{2}+\frac{v_{23}}{2}\vec{u}\right).$$

Making the substitution $\vec{u}\leftrightarrow-\vec{u}$ into this last formula and taking

$$F(\vec{v}_2',\vec{v}_3')=\frac{1}{\epsilon-i\vec{q}\cdot\vec{v}_{13}'}\times\frac{\exp\{-i\vec{q}\cdot[\vec{\rho}(\vec{b}',\vec{v}_{23})+\vec{R}(\vec{v}_1,\vec{v}_3',\vec{v}_4)]\}}{\epsilon-i\vec{q}\cdot\vec{V}(\vec{v}_1,\vec{v}_3',\vec{v}_4)}\times\Delta\vec{J}(\vec{v}_1,\vec{v}_2;\vec{b})\cdot\Delta\vec{K}(\vec{v}_1,\vec{v}_2',\vec{v}_4)\,,$$

one readily finds $\Lambda_2=\Lambda_1'$.

2. Proof of $\Lambda_1'\simeq\Lambda_1$ where $\epsilon\to 0$

In order to carry out the $\vec{q}$ integration on the right-hand side of (A1) we use the identity

$$\int\frac{d\vec{q}}{(2\pi)^3}\frac{1}{\epsilon-i\vec{q}\cdot\vec{A}}\frac{1}{\epsilon-i\vec{q}\cdot\vec{B}}\frac{1}{\epsilon-i\vec{q}\cdot\vec{C}}e^{-i\vec{q}\cdot\vec{D}}\equiv\Theta\left(\frac{(\vec{D},\vec{B},\vec{C})}{(\vec{A},\vec{B},\vec{C})}\right)\Theta\left(\frac{(\vec{A},\vec{D},\vec{C})}{(\vec{A},\vec{B},\vec{C})}\right)\Theta\left(\frac{(\vec{A},\vec{B},\vec{D})}{(\vec{A},\vec{B},\vec{C})}\right)$$
$$\times\frac{1}{|(\vec{A},\vec{B},\vec{C})|}\exp\left(-\frac{\epsilon}{(\vec{A},\vec{B},\vec{C})}[(\vec{D},\vec{B},\vec{C})+(\vec{A},\vec{D},\vec{C})+(\vec{A},\vec{B},\vec{D})]\right), \qquad \text{(B5)}$$

where Θ still denotes the step function and $(\vec{A},\vec{B},\vec{C})$ the determinant of the three vectors $\vec{A}$, $\vec{B}$, and $\vec{C}$. Both for Λ_1 and Λ_1', we shall take $\vec{A}=\vec{V}(\vec{v}_1,\vec{v}_2',\vec{v}_4)$, $\vec{B}=\vec{v}_{12}$, and $\vec{C}=\vec{v}_{12}'$ although in Λ_1, $\vec{D}=-\vec{\rho}(\vec{b},\vec{v}_{12})+\vec{R}$ and in Λ_1', $\vec{D}$ will be equal to $-\vec{\rho}(\vec{b},\vec{v}_{12})+\vec{R}+\vec{\rho}(\vec{b}',\vec{v}_{23})$.

We shall explain now why the divergence appearing near $\epsilon=0$, when Λ_1 or Λ_1' are integrated again over velocities and impact parameters, does not depend on this value of $\vec{D}$, making Λ_1 different from Λ_1'. In fact, this divergence will appear for the small values of $(\vec{A},\vec{B},\vec{C})$, i.e., when the three vectors are almost coplanar and in this range of values, the right-hand side of (A5) is approximately equal to

$$\frac{\Theta(\gamma/\nu)\Theta(-\lambda)\Theta(-\mu)}{|\nu|\,|\vec{B}\times\vec{C}|^2}\exp\left(-\frac{\epsilon\gamma}{\nu}(1-\lambda-\mu)\right)$$

where the numbers $\lambda,\mu,\nu,\alpha,\beta,\gamma$ are defined by

$$\vec{A}=\lambda\vec{B}+\mu\vec{C}+\nu\vec{B}\times\vec{C}\,,$$
$$\vec{D}=\alpha\vec{B}+\beta\vec{C}+\gamma\vec{B}\times\vec{C}\,,$$

and so the right-hand side of (B5) depends on $\vec{D}$ through $\gamma=(\vec{D},\vec{B},\vec{C})/|\vec{B}\times\vec{C}|^2$ only.

In any case, it can be shown that ν is either directly an integration variable or depends continuously on some integration variable, say x, with $\partial x/\partial\nu|_{\nu=0}\neq 0$. Accordingly, the divergence which appears in the contribution to $K_2(\epsilon\to 0)$ coming from Λ_1 or Λ_1' is found by carrying out an integral of the form

$$\int_{\nu\simeq 0} d\nu\left(\frac{\partial x}{\partial\nu}\right)_{\nu=0}\Theta\left(\frac{\gamma}{\nu}\right)\frac{1}{|\nu|}e^{-(\epsilon\gamma/\nu)(1-\lambda-\mu)} \simeq \frac{\partial x}{\partial\nu}\bigg|_{\nu=0}\int_0 \frac{1}{\nu}e^{-\epsilon\gamma/\nu}\,d\nu \simeq -\frac{\partial x}{\partial\nu}\bigg|_{\nu=0}\ln\epsilon\,, \qquad \text{(B6)}$$

where any term not explicitly written down remains finite near $\epsilon=0$ as can be verified in any case. This proves $\Lambda_1\simeq\Lambda_1'$ where $\epsilon\to 0$, as the variable γ, that was a function of $\vec{D}$, has completely disappeared in the final result.

Let us end with three remarks:

(i) In some of the ring contributions to $K_2(\epsilon)$, two among the three vectors $\vec{A},\vec{B},\vec{C}$ in the Green's functions $(\epsilon+i\vec{q}\cdot\vec{A})^{-1}\ldots$ are the same: That is, the case for instance, for the pairs of sequences (s_2^{VR}, s_1^{VR}) and (s_5^{VR}, s_4^{VR}). For these situations, the above proof is no longer valid, as (B5) does not hold anymore. However, the invariance of the diverging contribution to $K_2(\epsilon\to 0)$ under the transformation (transfer)$\leftrightarrow$(no transfer) still remains true, and can be readily proved by using results quoted in Appendix C.

(ii) The assumption that the intermediate collision with or without transfer is real, is a crucial one; the invariance under the transformation (transfer)$\leftrightarrow$(no transfer) is not true in general for *virtual* collision; for example $S_1^{VV}=0$, although the transformed sequences do not yield vanishing contribution to $K_2(\epsilon)$ in general.

(iii) The above proof still holds when the kinetic heat current is replaced, for instance, by the traceless part of the kinetic pressure tensor and so these results can be used for any transport coefficients.

APPENDIX C

In this Appendix we shall calculate quantities of the general form:

$$F_n=\int\int\int_{b,b',b'''<a} d\vec{b}\,d\vec{b}'\,d\vec{b}'''(\vec{b}\cdot\vec{b}''')^n \times f(b)g(b')h(b''')\delta(b_z+b_z'-b_z'') \times(b_y+b_y'-b_y'')\Theta(b_y+b_y'-b_y''), \qquad \text{(C1)}$$

n being a positive integer, and f,g,h some functions of the length of the impact parameters $\vec{b},\vec{b}',\vec{b}'''$ which lie the $y0z$ plane.

Rewrite the singular functions δ and Θ in terms of their Fourier transform. From

$$\delta(b_z+b_z'-b_z''')=\frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ik_z(b_z+b_z'-b_z''')}\,dk_z$$

and

$$\Theta(b_y+b_y'-b_y''')(b_y+b_y'-b_y''') = -\frac{1}{2\pi}\lim_{\eta\to 0^+}\int_{-\infty}^{+\infty}\frac{dk_y}{k_y-i\eta}\frac{d}{dk_y}\exp[ik_y(b_y+b_y'-b_y''')],$$

one obtains

$$F_n=-\int\frac{d\vec{k}}{(2\pi)^2}\lim_{\eta\to 0}\frac{1}{k_y-i\eta}\frac{d}{dk_y}\int_{b,b'''<a}e^{i\vec{k}\cdot\vec{b}} \times f(b)\,d\vec{b}\,e^{-i\vec{k}\cdot\vec{b}'''}h(b''')\,d\vec{b}'''(\vec{b}\cdot\vec{b}''')^n \times\int_{b'<a}e^{i\vec{k}\cdot\vec{b}'}g(b')\,d\vec{b}',$$

where k_z and k_y are the components of the two-dimensional vector $\vec{k}$.

The result of the integration over the impact parameters $\vec{b}$, $\vec{b}'$, and $\vec{b}'''$ is a function of $k\equiv|\vec{k}|$ only, as the scalar product $(\vec{b}\cdot\vec{b}''')$ does not depend on the choice of the reference frame. Then

$$F_n=-\int\frac{d\vec{k}}{(2\pi)^2}\lim_{\eta\to 0}\frac{1}{k_y-i\eta}\frac{d}{dk_y}\Phi_n(k),$$

where Φ_n is some function of the length of $\vec{k}$. Thus,

$$F_n=-\int\frac{d\vec{k}}{(2\pi)^2}\lim_{\eta\to 0}\frac{1}{k_y-i\eta}\frac{k_y}{k}\frac{d}{dk}\Phi_n(k) = -\frac{1}{2\pi}\int_0^\infty dk\frac{d}{dk}\Phi_n(k)=\frac{\Phi_n(0)}{2\pi}$$

as $\Phi_n(\infty)=0$ (the functions f,g,h being of bounded variation and vanishing outside the interval $0,a$). Whence

$$F_n=\frac{1}{2\pi}\int_{b,b'''<a}f(b)h(b''')(\vec{b}\cdot\vec{b}''')^n\,d\vec{b}\,d\vec{b}''' \times\int_{b'<a}g(b')\,d\vec{b}', \qquad \text{(C2)}$$

which vanishes for odd n.

By using result (C2) with

$$n=0,\quad g=1,\quad f=h,\quad f(b)=(4b^2/a^4)(a^2-b^2)$$

or

$$n=1,\quad g=1,\quad f=h,$$

$$f(b)=(2/a^4)(2b^2-a^2)(a^2-b^2)^{1/2}$$

and

$$n=2,\quad g=1,\quad f=h,\quad f(b)=(4/a^4)(a^2-b^2)$$

one gets Eq. (16).

When $g=1$, the integration over the impact parameter $\vec{b}'$ yields a factor πa^2; this is very similar to the factor found in a virtual collision *without* transfer, but this must be thought as a coincidence and we cannot conclude that virtual collisions with or without transfer yield the same final contribution. When the intermediate collision is real, using (C2) and computational methods of Sec. III B, we can show that, when two intermediate Green's function G_0 are equal, real collisions with or without transfer give the same contribution near $\epsilon=0$; an explanation of this fact has been sketched in Sec. II C.

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