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The Incoherent Scattering Function and Related Correlation Functions in Hard Sphere Fluids at Short Times

I. M. de Schepper,[1] M. H. Ernst,[1] and E. G. D. Cohen[2]

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For a classical fluid of hard spheres and hard disks exact expressions for all densities and wave vectors are derived for the coefficients of t^n in the short-time expansion of the incoherent intermediate scattering function ($n = 0, 1, \ldots, 4$) and the velocity correlation function ($n = 0, 1, 2$). Similarly, we obtain the coefficient of the leading term in the short-time behavior of the cumulants of the displacements. Furthermore, $S(k, \omega)$ has a high-frequency tail $\sim\omega^{-4}$, characteristic for the hard-sphere fluid, which leads to a modification of the standard sum rules. We present estimates for the frequency range, in which this tail may be observed in neutron scattering off noble gases. The results are also compared with Enskog's theory and molecular dynamics calculations.

KEY WORDS: Incoherent scattering function; velocity correlation function; cumulants of displacement; hard-sphere fluid; short-time expansions.

1. INTRODUCTION

The short-time behavior of scattering functions is one of the few dynamical properties of classical systems in equilibrium which can be calculated exactly. This behavior has been studied extensively for particles interacting through a Lennard-Jones type of potential.[1-4] The theoretical results agree with experiments[5-8] and are frequently used to fit parameters in phenomenological theories that want to describe the scattering functions for all times.[3]

[1] Institute for Theoretical Physics, University of Utrecht, 3508 TA Utrecht, The Netherlands.
[2] The Rockefeller University, New York, New York 10021.
[3] See, e.g., Ref. 9.

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The methods employed to determine this short-time behavior cannot be applied straightforwardly to systems interacting through hard core potentials.[10–21]

The aim of this paper is to find the behavior of several types of correlation functions in hard-sphere systems at short times. A partial summary of the results has been published before.[22,23]

We consider N hard spheres in equilibrium contained in a volume V and obeying the laws of classical mechanics. The temperature $T = 1/k_B\beta$, where k_B is Boltzmann's constant, m is the mass of a particle, and σ its diameter, the density $n = N/V$, and d denotes the dimensionality of the system ($d \geqslant 2$).

The subject of interest is, more specifically, the short-time behavior of the incoherent intermediate scattering function $F(k,t)$, of the velocity correlation function $C(t)$, and of the cumulants $\gamma_n(t)$ of the displacement of a tagged hard sphere. Furthermore, we consider the large ω behavior of the incoherent scattering function $S(k,\omega)$.

The incoherent intermediate scattering function is defined as

$$F(k,t) = \langle \exp[i\mathbf{k}\cdot\mathbf{r}_1(0)]\exp[-i\mathbf{k}\cdot\mathbf{r}_1(t)]\rangle_0 = \langle \exp[-ik\Delta_x(t)]\rangle_0 \tag{1.1}$$

and $\Delta_x(t)$ is the x component of the displacement of particle 1,

$$\Delta_x(t) = x_1(t) - x_1(0) = \int_0^t d\tau\, v_{1x}(\tau) \tag{1.2}$$

where we have taken the $\hat{x}$ axis parallel to the vector $\mathbf{k}$. The velocity correlation function is defined as

$$C(t) = \langle v_{1x} v_{1x}(t)\rangle_0 \tag{1.3}$$

In these definitions the phase $(\mathbf{r}_i(t), \mathbf{v}_i(t))$ denotes the position and velocity of the ith particle at time t, when $(\mathbf{r}_i, \mathbf{v}_i)$ is the initial value at $t = 0$. The wave number $\mathbf{k}$ determines the scattering angle. The equilibrium average $\langle \cdots \rangle_0 = \int d\Gamma\, D_0(\Gamma) \ldots$ is taken with the distribution function $D_0(\Gamma)$ of the canonical ensemble, where $\Gamma = (\mathbf{r}_1\mathbf{v}_1\mathbf{r}_2\mathbf{v}_2 \ldots \mathbf{r}_N\mathbf{v}_N)$, and the bulk limit is understood to be taken.

The incoherent scattering function is defined as the Fourier transform of $F(k,t)$, i.e.,

$$S(k,\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{-i\omega t} F(k,t) = \frac{1}{\pi}\int_0^{\infty} dt \cos\omega t\, F(k,t) \tag{1.4}$$

where we have used that $F(k,t)$ is an even function of t, both for smooth as well as for hard-core interparticle potentials. For the latter case this will be shown in Section 2.2. As a result $S(k,\omega)$ is even in ω. The inverse relation therefore reads

$$F(k,t) = \int_{-\infty}^{+\infty} d\omega \cos \omega t \, S(k,\omega) \tag{1.5}$$

An equilibrium time correlation function for a system in which the particles $(i, j = 1, 2, \ldots, N)$ are interacting through a smooth potential $V(\mathbf{r}_{ij})$ with $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ can be written as

$$C_{ab}(t) = \langle a(0) b(t) \rangle_0 = \langle a e^{tL} b \rangle_0 \tag{1.6}$$

where a and b are dynamical variables, and L is the Liouville operator,

$$L = L_0 - \sum_{i<j}\sum \theta(ij) \tag{1.7}$$

with

$$L_0 = \sum_i v_i \cdot \frac{\partial}{\partial \mathbf{r}_i} \tag{1.8a}$$

$$\theta(ij) = \frac{1}{m} \frac{\partial V(r_{ij})}{\partial \mathbf{r}_{ij}} \cdot \left(\frac{\partial}{\partial \mathbf{v}_i} - \frac{\partial}{\partial \mathbf{v}_j} \right) \tag{1.8b}$$

The streaming operator e^{tL} generates the trajectories in Γ space.

For the special case of hard spheres the time evolution of a dynamical variable $a(t)$ can be represented by pseudo streaming operators, which generate the trajectories of the phase point in Γ space. They are defined for forward and backward streaming in time as[24,25]

$$a(t) = \begin{cases} \exp(tL_+)a, & t > 0 \\ \exp(tL_-)a, & t < 0 \end{cases} \tag{1.9}$$

The pseudo-Liouville operators $L_\pm$ are given by

$$L_\pm = L_0 \pm \sum_{i<j}\sum T_\pm(ij) \tag{1.10}$$

with binary collision operators

$$T_\pm(ij) = \sigma^{d-1} \int d\hat{\sigma} \, |\mathbf{v}_{ij} \cdot \hat{\sigma}| \theta(\mp \mathbf{v}_{ij} \cdot \hat{\sigma}) \delta(\mathbf{r}_{ij} - \sigma\hat{\sigma}) \left[b_{\hat{\sigma}}(ij) - 1 \right] \tag{1.11}$$

Here $\theta(x)$ is a unit step function; $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, and $\hat{a} = \mathbf{a}/|\mathbf{a}|$ is a unit vector. The substitution operator $b_{\hat{\sigma}}(ij)$ acts only on the velocities $\mathbf{v}_i$ and $\mathbf{v}_j$, and replaces them by the velocities $\mathbf{v}_i'$, $\mathbf{v}_j'$ after the binary collision,

$$\begin{aligned} b_{\hat{\sigma}}(ij)\mathbf{v}_i &= \mathbf{v}_i' = \mathbf{v}_i - \hat{\sigma}(\hat{\sigma} \cdot \mathbf{v}_{ij}) \\ b_{\hat{\sigma}}(ij)\mathbf{v}_j &= \mathbf{v}_j' = \mathbf{v}_j + \hat{\sigma}(\hat{\sigma} \cdot \mathbf{v}_{ij}) \end{aligned} \tag{1.12}$$

The operators $\exp(tL_\pm)$ generate the physical trajectories in Γ space either in forward ($t > 0$) or backward ($t < 0$) direction, starting from physical initial positions, in which hard spheres are not overlapping. These streaming operators also generate unphysical trajectories for unphysical, i.e., overlapping, initial conditions. However, Eq. (1.9) is only needed inside the averages (1.6). In fact, the correlation functions of interest are

$$\begin{aligned} F(k,t) &= \int d\Gamma\, D_0(\Gamma)\exp(i\mathbf{k}\cdot\mathbf{r}_1)\exp(tL_\pm)\exp(-i\mathbf{k}\cdot\mathbf{r}_1) \\ &\equiv \langle \exp(i\mathbf{k}\cdot\mathbf{r}_1)\exp(tL_\pm)\exp(-i\mathbf{k}\cdot\mathbf{r}_1)\rangle_0 \\ C(t) &= \int d\Gamma\, D_0(\Gamma) v_{1x}\exp(tL_\pm)v_{1x} \equiv \langle v_{1x}\exp(tL_\pm)v_{1x}\rangle_0 \end{aligned} \tag{1.13}$$

in which the unphysical overlapping initial configurations have a vanishing weight $D_0(\Gamma)$ so that only physical trajectories contribute to the averages. In averages $\langle \cdots \rangle_0$ containing the operators $L_\pm$, as in Eq. (1.13), the weight function D_0 is always understood to be to the left of all $L_\pm$ operators.

After the introduction of the relevant quantities we give the plan of this paper. Our method for short-time expansions is described in Section 2, and we rederive from our method the known results for $F(k,t)$ and $C(t)$, which involve one binary collision. In Section 3 we consider the next-order correction terms in the short-time expansions. They involve either two uncorrelated binary collisions, or three correlated binary collisions (recollision sequence). In order to determine which dynamical events are involved in the coefficient of t^n, we discuss in Section 4 short-time estimates for general collision sequences. In Section 5 we discuss the high-frequency tail of the incoherent scattering function $S(k,\omega)$, characteristic for a hard-sphere fluid, and its implication for the sum rules. In that section we further consider the transition from smooth to hard-sphere potentials, which yields some conditions on the applicability of hard-sphere models to real fluids.

In Section 6 we obtain the short-time behavior of the cumulants $\gamma_n(t)$ of the displacement of a tagged hard sphere. In Section 7 the exact results for $F(k,t)$, $C(t)$, and $\gamma_n(t)$ are compared with the Enskog theory for a hard-sphere fluid, and with available molecular dynamics data. We conclude with a discussion in Section 8.

All considerations in this paper refer to hard-sphere interactions, and whenever we refer to smooth interactions we state it explicitly.

2. METHOD AND KNOWN RESULTS

2.1. Description of the Method

The short-time expansion of correlation functions for a system with smooth interactions follows directly from Eq. (1.6) by writing e^{tL} as a

Taylor series,

$$C_{ab}(t) = \langle ab \rangle_0 + t\langle aLb \rangle_0 + (1/2)t^2\langle aL^2b \rangle_0 + \cdots \tag{2.1}$$

where the coefficient $\langle aL^n b \rangle_0$ is the nth derivative of $C_{ab}(t)$ at $t = 0$.

Our method for obtaining short-time expansions in hard-sphere systems resembles very closely the above method for smooth potentials, when the usual Liouville operator (1.7) is replaced by the pseudo Liouville operator (1.10), i.e., we calculate derivatives of $C_{ab}(t)$ at $t = 0$, and obtain the short-time behavior of $C_{ab}(t)$ as a Taylor series,

$$C_{ab}(t) = \sum_{k=0}^{n-1} \frac{t^k}{k!} C_{ab}^{(k)}(0) + R_n(t) \tag{2.2}$$

with a remainder

$$R_n(t) = \frac{1}{(n-1)!} \int_0^t d\tau (t-\tau)^{n-1} C_{ab}^{(n)}(\tau) \tag{2.3}$$

and $C_{ab}^{(n)}$ denotes the nth derivative. We continue this procedure till we encounter a derivative, say, $C_{ab}^{(n)}(t)$, which is not well defined at $t = 0$, but is still well defined for $t > 0$ or $t < 0$; then we determine the short-time behavior of $C_{ab}^{(n)}(t)$ ($t > 0$, or $t < 0$), from which we deduce $R_n(t)$ at short times using (2.3) by taking the limit $t \to 0+$ or $0-$. It depends on the functions considered which derivatives become ill defined at $t = 0$. For $F(k,t)$ it is the fourth derivative and for $C(t)$ the second one. These derivatives will be considered in the next section.

Our method differs from the approach of Sears[13] and Kleban[16] in which first the short-time expansion (2.1) is considered for smooth potentials and next the hard-sphere limit is taken. In our approach the order of these two limiting operations is reversed. Essentially the same procedure is followed in Refs. 11, 14, 15, and 18.

2.2. Useful Properties of $F(k,t)$ and $C(t)$

In order to obtain the short-time expansions of $F(k,t)$ and $C(t)$ for hard spheres we discuss three relations, which will simplify our considerations:

(i) F and C are *even* functions of time, i.e.,

$$\begin{aligned} F(k,t) &= F(k,-t) = F(k,|t|) \\ C(t) &= C(-t) = C(|t|) \end{aligned} \tag{2.4}$$

This can be seen from Eq. (1.13) by changing the variables $\mathbf{v}_i$ into $-\mathbf{v}_i$ for all $i = 1, 2, \ldots, N$, so that for $t < 0$ the operator $e^{tL_-} = e^{-|t|L_-}$ changes under this substitution into $e^{|t|L_+}$, whereas the remaining parts of the integrands are left unchanged. Hence, we restrict ourselves to $t > 0$.

(ii) For any pair of dynamical variables a and b the Hermitian adjoint of L_+ with respect to the inner product $(a,b) = \langle ab \rangle_0$ is given by

$$\langle aL_+ b\rangle_0 = -\langle bL_- a\rangle_0 \tag{2.5}$$

where the weight function $D_0(\Gamma)$ is to the left of all operators inside the brackets. For a proof of (2.5) we need two properties of pseudo Liouville operators, derived in Ref. 24, i.e.,

$$\int d\Gamma\, D_0 a\, e^{tL_+} b = \int d\Gamma\, b\, e^{-t\bar{L}_-} a D_0 = \int d\Gamma\, D_0 b\, e^{-tL_-} a \tag{2.6}$$

In the first equality we used that the Hermitian adjoint of L_+ with respect to the inner product $(a,b) = \int d\Gamma\, ab$ is $(-\bar{L}_-)$, of which the explicit form is not needed here. In the second equality we used the commutation relation $\exp(-t\bar{L}_-)D_0 = D_0 \exp(-tL_-)$. The time derivative of (2.6) at $t=0$ yields (2.5).

(iii) The functions $F(k,t)$ and $C(t)$ in (1.13) are related by

$$C(t) = -\lim_{k\to 0} F''(k,t)/k^2 \tag{2.7}$$

since we have from (1.10) and (2.5)

$$\begin{aligned} F''(k,t) &= -\left\langle \left[L_- \exp(i\mathbf{k}\cdot\mathbf{r}_1)\right] \exp(tL_+) L_+ \exp(-i\mathbf{k}\cdot\mathbf{r}_1)\right\rangle_0 \\ &= -k^2\left\langle \mathbf{v}_1\cdot\hat{k}\exp(i\mathbf{k}\cdot\mathbf{r}_1)\exp(tL_+)\mathbf{v}_1\cdot\hat{k}\exp(-i\mathbf{k}\cdot\mathbf{r}_1)\right\rangle_0 \end{aligned} \tag{2.8}$$

where the primes indicate partial derivatives with respect to t and $\hat{k} = \mathbf{k}/k$.

2.3. Contributions from at Most One Collision

In the remaining part of this section we rederive from our method the coefficients in the short-time expansion of $F(k,t)$ and $C(t)$, which have been obtained in the literature.[10-21] We start with $F(k,t)$ in (1.13) where

$$F(k,0) = 1 \tag{2.9}$$

$$F'(k,0) = \left\langle \exp(i\mathbf{k}\cdot\mathbf{r}_1) L_+ \exp(-i\mathbf{k}\cdot\mathbf{r}_1)\right\rangle_0 = 0 \tag{2.10}$$

$$F''(k,0) = -k^2\left\langle (\mathbf{v}_1\cdot\hat{k})^2\right\rangle_0 = -k^2/(\beta m) \tag{2.11}$$

$$\begin{aligned} F'''(k,0) &= -k^2\left\langle \mathbf{v}_1\cdot\hat{k}\exp(i\mathbf{k}\cdot\mathbf{r}_1) L_+ \mathbf{v}_1\cdot\hat{k}\exp(-i\mathbf{k}\cdot\mathbf{r}_1)\right\rangle_0 \\ &= -k^2(N-1)\left\langle \mathbf{v}_1\cdot\hat{k} T_+(12)\mathbf{v}_1\cdot\hat{k}\right\rangle_0 \end{aligned} \tag{2.12}$$

The first three expressions do not depend on the interparticle potential and, therefore, hold for smooth potentials as well. In order to derive these results Eq. (1.10) is needed; for the last two we have also used Eq. (2.8). The N-particle average in (2.12) is taken over a function of two particles only. Therefore, it can be expressed in terms of the static pair correlation function. In general, the static correlation functions are defined as

$$n^2 g(\mathbf{r}_{12}) = N(N-1)\int \cdots \int d\mathbf{r}_3 \ldots d\mathbf{r}_N \, d\mathbf{v}_1 \ldots d\mathbf{v}_N \, D_0(\Gamma)$$
$$n^3 g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = N(N-1)(N-2)\int \cdots \int d\mathbf{r}_4 \ldots d\mathbf{r}_N \, d\mathbf{v}_1 \ldots d\mathbf{v}_N \, D_0(\Gamma) \tag{2.13}$$

In fact, in this and all subsequent expressions the thermodynamic limit is understood. On account of these definitions Eq. (2.12) becomes

$$F'''(\mathbf{k},0) = -k^2 n \int d\mathbf{r}_{12}\, g(r_{12}) \langle\langle v_{1x} T_+ (12) v_{1x} \rangle\rangle \tag{2.14}$$

Since the right-hand side of (2.12) does not depend on the direction of the unit vector $\hat{k}$, it may be averaged over all directions of $\hat{k}$, using $\int d\hat{k}\, \hat{k}_\alpha \hat{k}_\beta = \Omega_d \delta_{\alpha\beta}/d$, where $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$ is the surface area of a d-dimensional unit sphere. Each pair of brackets $\langle \cdots \rangle$ in (2.14) stands for a one-particle velocity average, i.e.,

$$\langle \cdots \rangle = \int d\mathbf{v}_1 \, \phi_0(v_1) \ldots \tag{2.15}$$

with a Maxwellian weight, i.e.,

$$\phi_0(v) = \left(\frac{\beta m}{2\pi} \right)^{d/2} \exp\left[-(1/2)\beta m v^2 \right] \tag{2.16}$$

Introducing $\chi = g(\sigma)$, which is the static correlation function of two hard spheres at contact, and using (1.10) and (1.11), we reduce Eq. (2.14) further to

$$\begin{aligned} F'''(k,0) &= -\frac{k^2 n \sigma^{d-1} \chi}{d} \int d\hat{\sigma} \left\langle \left\langle \theta(-\mathbf{v}_{12}\cdot\hat{\sigma})(\mathbf{v}_{12}\cdot\hat{\sigma})^2 \mathbf{v}_1 \cdot \hat{\sigma} \right\rangle \right\rangle \\ &= 2k^2/(d\beta m t_E) \end{aligned} \tag{2.17}$$

In evaluating the integral in (2.17) it is convenient to introduce center-of-mass and relative velocity variables.

We have further introduced the Enskog mean free time between collisions t_E and the mean collision frequency t_0^{-1} at low density as

$$\begin{aligned} t_E &= t_0/\chi \\ t_0^{-1} &= n\sigma^{d-1} \int d\hat{\sigma} \langle\langle \mathbf{v}_{12} \cdot \hat{\sigma}\theta(\mathbf{v}_{12}\cdot\hat{\sigma}) \rangle\rangle = \frac{n\sigma^{d-1}\Omega_d}{(\pi\beta m)^{1/2}} \end{aligned} \tag{2.18}$$

Collecting results from (2.9)–(2.12) and (2.17), the Taylor series (2.2) yields for the incoherent scattering function at short times ($t > 0$)

$$F(k,t) = 1 - \frac{k^2 t^2}{2\beta m} + \frac{k^2 t^3}{3\, d\beta m t_E} + O(t^4) \tag{2.19}$$

and by virtue of Eq. (2.7) for the velocity correlation function

$$C(t) = \frac{1}{\beta m}\left[1 - \frac{2t}{dt_E} + O(t^2)\right] \tag{2.20}$$

In the following section these results will be extended to the next order in time.

3. CONTRIBUTIONS INVOLVING MORE COLLISIONS

3.1. Correlation Functions for the Fourth Derivative of $F(k,t)$

In this section we calculate the next approximation to $F(k,t)$ and $C(t)$, which will involve the static triplet correlation function. We start by considering the fourth derivative $F''''(k,t)$ for $t > 0$, which reads

$$F''''(\mathbf{k},t) = k^2\left\langle\left[L_-\mathbf{v}_1\cdot\hat{k}\exp(i\mathbf{k}\cdot\mathbf{r}_1)\right]\exp(tL_+)L_+\mathbf{v}_1\cdot\hat{k}\exp(-i\mathbf{k}\cdot\mathbf{r}_1)\right\rangle_0 \tag{3.1}$$

as follows from Eq. (2.8) and (2.5). It does not exist for $t = 0$, since it will contain terms of the form $\langle(T_-(12)\mathbf{v}_1\cdot\hat{k})(T_+(12)\mathbf{v}_1\cdot\hat{k})\rangle_0$ where each T operator, defined in Eq. (1.11), contains a factor $\delta(|\mathbf{r}_{12}| - \sigma)$. However, with any finite streaming e^{tL_+} between the two T operators, the expression is well defined and approaches a *finite limiting value* for $t \to 0+$, as will be shown in this section. The limiting behavior $F''''(\mathbf{k}, 0+)$ is all that is required to calculate the remainder $R_4(t)$ in (2.3) for small times up to $O(t^4)$ included.

In view of the fact that both L_+ and L_- in Eq. (1.10) consist of two terms, we divide $F''''(\mathbf{k},t)$ into

$$F''''(\mathbf{k},t) = A(t) + B(t) + \Gamma(t) + \Delta(t) \tag{3.2}$$

with

$$A(t) = k^4\left\langle(\mathbf{v}_1\cdot\hat{k})^2\exp(i\mathbf{k}\cdot\mathbf{r}_1)\exp(tL_+)(\mathbf{v}_1\cdot\hat{k})^2\exp(-i\mathbf{k}\cdot\mathbf{r}_1)\right\rangle_0 \tag{3.3}$$

$$B(t) = ik^3\left\langle(\mathbf{v}_1\cdot\hat{k})^2\exp(i\mathbf{k}\cdot\mathbf{r}_1)\exp(tL_+)\sum_j T_+(1j)\mathbf{v}_1\cdot\hat{k}\exp(-i\mathbf{k}\cdot\mathbf{r}_1)\right\rangle_0 \tag{3.4}$$

$$\Gamma(t) = ik^3\left\langle\left[\sum_j T_-(1j)\mathbf{v}_1\cdot\hat{k}\exp(i\mathbf{k}\cdot\mathbf{r}_1)\right]\exp(tL_+)(\mathbf{v}_1\cdot\hat{k})^2\exp(-i\mathbf{k}\cdot\mathbf{r}_1)\right\rangle_0 \tag{3.5}$$

$$\Delta(t) = -k^2\left\langle\left[\sum_j T_-(1j)\mathbf{v}_1\cdot\hat{k}\exp(i\mathbf{k}\cdot\mathbf{r}_1)\right]\right.$$
$$\left.\times\exp(tL_+)\sum_l T_+(1l)\mathbf{v}_1\cdot\hat{k}\exp(-i\mathbf{k}\cdot\mathbf{r}_1)\right\rangle_0 \tag{3.6}$$

As is clear upon comparison of (3.3)–(3.5) with (3.1) the derivatives $A''(t)$, $B'(t)$, and $\Gamma'(t)$ have the same structure as $\Delta(t)$, which, as will be shown below, will approach a finite value for $t \to 0+$. Hence $A(t) = A(0) + O(t)$, and similarly for $B(t)$ and $\Gamma(t)$, since the first derivative of these quantities exists at $t = 0$. Now, Eq. (3.3) yields

$$A(0) = k^4 \langle (\mathbf{v}_1 \cdot \hat{k})^4 \rangle_0 = \frac{3k^4}{(\beta m)^2} \tag{3.7}$$

Next, choosing $\hat{k}$ parallel to the x axis, we find

$$B(0) = ik^3 \left\langle v_{1x}^2 \sum_j T_+ (1j) v_{1x} \right\rangle_0 \tag{3.8}$$

Inserting the definition of the T operator yields

$$B(0) = ik^3 n\chi \int d\hat{\sigma}\, \hat{\sigma}_x \left\langle \left\langle v_{1x}^2 (\mathbf{v}_{12} \cdot \hat{\sigma})^2 \theta(-\mathbf{v}_{12} \cdot \hat{\sigma}) \right\rangle \right\rangle \tag{3.9}$$

The velocity average $\ll \cdots \gg$ in (3.9) has the structure $(a\hat{\sigma}^2 + b)$, so that $B(0)$ vanishes after averaging over all $\hat{\sigma}$. Hence for small times

$$B(t) = \Gamma(t) = O(t) \tag{3.10}$$

The arguments leading to Eq. (3.10) for $\Gamma(t)$ are completely analogous to those above.

3.2. Two-Collision Contribution $\Delta_d(t)$

Next we consider $\Delta(t)$ in (3.6), which we divide into the contributions from equal pairs, $\Delta_e(t)$, and from different pairs, $\Delta_d(t)$, i.e.,

$$\Delta(t) = \Delta_d(t) + \Delta_e(t) \tag{3.11}$$

with

$$\begin{aligned} \Delta_d(t) = & -k^2(N-1)(N-2)\langle (T_-(12)\mathbf{v}_1 \cdot \hat{k} \exp(i\mathbf{k} \cdot \mathbf{r}_1)) \\ & \times \exp(tL_+) T_+(13)\mathbf{v}_1 \cdot \hat{k} \exp(-i\mathbf{k} \cdot \mathbf{r}_1) \rangle_0 \end{aligned} \tag{3.12a}$$

$$\begin{aligned} \Delta_e(t) = & -k^2(N-1)\langle [T_-(12)\mathbf{v}_1 \cdot \hat{k} \exp(i\mathbf{k} \cdot \mathbf{r}_1)] \\ & \times \exp(tL_+) T_+(12)\mathbf{v}_1 \cdot \hat{k} \exp(-i\mathbf{k} \cdot \mathbf{r}_1) \rangle_0 \end{aligned} \tag{3.12b}$$

Δ_d will be considered in this section and Δ_e in the next one.

We first observe that $\Delta_d(0)$ exists. In the next section we will show that higher-order contributions are at least of $O(t)$ for small t. Hence, using Eq. (2.13) and (1.11) we obtain

$$\begin{aligned} \Delta_d(0) &= -k^2 n^2 \int d\mathbf{r}_{12} \int d\mathbf{r}_{13}\, g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \langle \langle \langle (T_-(12)\mathbf{v}_1 \cdot \hat{k}) T_+(13)\mathbf{v}_1 \cdot \hat{k} \rangle \rangle \rangle \\ &= \frac{k^2 n^2 \sigma^{2d-3}}{(\beta m)^2} \int d\hat{\sigma}_1 \int d\hat{\sigma}_2\, g_3(\hat{\sigma}_1 \cdot \hat{\sigma}_2)(\hat{\sigma}_1 \cdot \hat{k})(\hat{\sigma}_2 \cdot \hat{k}) V_1(\hat{\sigma}_1 \cdot \hat{\sigma}_2) \end{aligned} \tag{3.13}$$

where we have introduced the static triplet function for three spheres in contact

$$g_3(\hat{\sigma}_1 \cdot \hat{\sigma}_2) = g(\mathbf{r}, \mathbf{r} - \sigma\hat{\sigma}_1, \mathbf{r} - \sigma\hat{\sigma}_2) \tag{3.14}$$

It depends only on $\hat{\sigma}_1 \cdot \hat{\sigma}_2 = \cos\theta = x$ due to spatial isotropy of the equilibrium state, and $g_3(x)$ vanishes for overlapping configurations where $1/2 < x < 1$. In addition we have defined

$$V_1(\hat{\sigma}_1 \cdot \hat{\sigma}_2) = (\beta m)^2 \langle\langle \langle \theta(\mathbf{v}_{12} \cdot \hat{\sigma}_1)\theta(\mathbf{v}_{31} \cdot \hat{\sigma}_2)(\mathbf{v}_{12} \cdot \hat{\sigma}_1)^2(\mathbf{v}_{31} \cdot \hat{\sigma}_2)^2 \rangle\rangle\rangle \tag{3.15}$$

All velocity components orthogonal to the plane of $\hat{\sigma}_1$ and $\hat{\sigma}_2$ integrate trivially to unity. Hence, we can treat the velocity variables in (3.15) as two-dimensional vectors and the result, which does not depend on dimensionality, reads

$$\begin{aligned} V_1(x) &= \frac{1}{\pi}(2 + x^2)\cos^{-1}\frac{x}{2} - \frac{3x}{\pi}\left(1 - \frac{1}{4}x^2\right)^{1/2} \\ &= 1 + \frac{1}{2}x^2 - \frac{4x}{\pi}\,{}_2F_1\left(-\frac{1}{2}, -\frac{1}{2}; \frac{3}{2}; \frac{x^2}{4}\right) \end{aligned} \tag{3.16}$$

as is calculated explicitly in Appendix A, where also the Gaussian hypergeometric function ${}_2F_1(a, b; c; x)$ is defined. We can further evaluate Eq. (3.13) by averaging over all $\hat{k}$, which allows us to replace $(\hat{\sigma}_1 \cdot \hat{k})(\hat{\sigma}_2 \cdot \hat{k})$ by $(\hat{\sigma}_1 \cdot \hat{\sigma}_2)/d$. The integrand in (3.13) depends then only on $\hat{\sigma}_1 \cdot \hat{\sigma}_2$ so that the $\hat{\sigma}_1$ integration may be carried out, resulting in

$$\Delta_d(0) = \frac{\pi k^2}{d\beta m(t_E\chi)^2}\langle x V_1(x) g_3(x)\rangle_{\text{ang}} \tag{3.17}$$

where t_E was defined in Eq. (2.18) and $\langle \cdots \rangle_{\text{ang}}$ is an average over a d-dimensional solid angle, defined for an arbitrary function $h(x)$ with $x = \hat{\sigma}_1 \cdot \hat{\sigma}_2$ as

$$\langle h(x)\rangle_{\text{ang}} = \frac{1}{\Omega_d}\int d\hat{\sigma}_2\, h(\hat{\sigma}_1 \cdot \hat{\sigma}_2) \tag{3.18}$$

The contribution (3.17) has been calculated previously by Resibois,[19] and will be discussed in Section 8.

3.3. Recollision Contribution $\Delta_e(t)$

Next, we consider $\Delta_e(t)$ which does not exist for $t = 0$, as explained in the beginning of this section. In order to evaluate it for short positive times

t we use the binary collision expansion (BCE), as given in Refs. 24 and 25:

$$e^{tL_+} = e^{tL_0} + \sum_{\alpha} \int_0^t dt_1\, e^{(t-t_1)L_0} T_+(\alpha) e^{t_1 L_0}$$
$$+ \sum_{\alpha} \sum_{\beta} \int_0^t dt_1 \int_0^{t_1} dt_2\, e^{(t-t_1)L_0} T_+(\alpha) e^{(t_1-t_2)L_0} T_+(\beta) e^{t_2 L_0} + \cdots \tag{3.19}$$

where α, β ... run over all pairs of particles. We may restrict ourselves to $\alpha \neq \beta$, due to the impossibility of two consecutive binary collisions between the same pair, i.e.,[24,25]

$$T_+(\alpha) e^{tL_0} T_+(\alpha) = 0 \tag{3.20}$$

For the same reason the first term in the BCE, i.e., the free streaming term, e^{tL_0}, gives a vanishing contribution to $\Delta_e(t)$ in (3.12). For, $[T_-(12)v_{1x}]$ $e^{tL_0}[T_+(12)v_{1x}]$ vanishes, because the expression contains $\delta(\sigma\hat{\sigma}_1 + \mathbf{v}_{12}t - \sigma\hat{\sigma}_2)$ with $\mathbf{v}_{12} \cdot \hat{\sigma}_2 < 0$ and $\mathbf{v}_{12} \cdot \hat{\sigma}_1 > 0$, so that $|\sigma\hat{\sigma}_1 + \mathbf{v}_{12}t - \sigma\hat{\sigma}_2| > 0$. Therefore the first nonvanishing contribution to $\Delta_e(t)$ comes from the second term in the BCE. Here $T_+(\alpha) e^{tL_0} T_+(12) v_1 \cdot \hat{k} \exp(-i\mathbf{k} \cdot \mathbf{r}_1) \neq 0$, provided the pair (α) contains either particle 1 or 2, since $T(ij) f(\mathbf{r}_k, \mathbf{v}_k) = 0$ if $k \neq i$ or j and we obtain the so-called recollision term,

$$\Delta_e(t) = -k^2 n^2 \int d\mathbf{r}_{12} \int d\mathbf{r}_{13}\, g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \int_0^t dt_1 \Big\langle\Big\langle\Big\langle \big[T_-(12)\mathbf{v}_1 \cdot \hat{k} \exp(i\mathbf{k} \cdot \mathbf{r}_1)\big]$$
$$\times \exp\big[(t - t_1)L_0\big]\big[T_+(13) + T_+(23)\big]$$
$$\times \exp(t_1 L_0) T_+(12)\mathbf{v}_1 \cdot \hat{k} \exp(-i\mathbf{k} \cdot \mathbf{r}_1)\Big\rangle\Big\rangle\Big\rangle + O(t) \tag{3.21}$$

A recollision event is defined by a collision sequence $(ij)(ik)(ij)$ where $k \neq j$ and where (ij) denotes a binary collision between the particles i and j. The higher-order terms in the BCE contribute at most terms of $O(t)$ for small t, as will be shown in the next section. Although the integral (3.21) looks formally of $O(t)$ due to the appearance of one time integral, it will appear that the integrand contains a factor $\delta(t_1 - at)$ with $0 < a < 1$, so that the t_1 integration yields a finite contribution as $t \to 0+$.

In order to evaluate (3.21) we use the relation

$$\int_0^t dt_1 \big[T_-(12)\alpha(\mathbf{v}_1)\exp(i\mathbf{k} \cdot \mathbf{r}_1)\big] \exp\big[(t - t_1)L_0\big] T_+(13)$$
$$\times \exp(t_1 L_0) T_+(12)\, \beta(\mathbf{v}_1) \exp(i\mathbf{k} \cdot \mathbf{r}_1)$$
$$= \sigma^{2d-2} \int d\hat{\sigma}_1 \int d\hat{\sigma}_2\, \delta(\mathbf{r}_{12} - \sigma\hat{\sigma}_1)\delta(\mathbf{r}_{13} - \sigma\hat{\sigma}_2) \frac{\theta(-\hat{\sigma}_1 \cdot \hat{\sigma}_2)}{|\hat{\sigma}_1 \cdot \hat{\sigma}_2|} \theta(\mathbf{v}_{12} \cdot \hat{\sigma}_1)\mathbf{v}_{12} \cdot \hat{\sigma}_1$$
$$\times \big[(b_{\hat{\sigma}_1}(12) - 1)\alpha(\mathbf{v}_1)\big] b_{\hat{\sigma}_2}(13)\theta(-\mathbf{v}_{12} \cdot \hat{\sigma}_1)|\mathbf{v}_{12} \cdot \hat{\sigma}_1|$$
$$\times \big[(b_{\hat{\sigma}_1}(12) - 1)\beta(\mathbf{v}_1)\big] + O(t) \tag{3.22}$$

which is valid for arbitrary functions $\alpha(\mathbf{v}_1)$ and $\beta(\mathbf{v}_1)$ as derived in Appendix B. Then, with the help of (3.14) and the equation $[b_{\hat{\sigma}_1}(12)-1]\mathbf{v}_1\cdot\hat{k}=-(\hat{\sigma}_1\cdot\hat{k})(\mathbf{v}_{12}\cdot\hat{\sigma}_1)$ we obtain

$$\Delta_e(0+)=\frac{2k^2n^2\sigma^{2d-2}}{(\beta m)^2}\int d\hat{\sigma}_1\int d\hat{\sigma}_2\, g_3(\hat{\sigma}_1\cdot\hat{\sigma}_2)(\hat{\sigma}_1\cdot\hat{k})^2 \times\frac{\theta(-\hat{\sigma}_1\cdot\hat{\sigma}_2)}{|\hat{\sigma}_1\cdot\hat{\sigma}_2|}V_2(\hat{\sigma}_1\cdot\hat{\sigma}_2) \tag{3.23}$$

Here we have introduced

$$V_2(\hat{\sigma}_1\cdot\hat{\sigma}_2)=(\beta m)^2\Big\langle\Big\langle\Big\langle\theta(\mathbf{v}_{12}\cdot\hat{\sigma}_1)\theta(-\mathbf{v}_{1'2}\cdot\hat{\sigma}_1)(\mathbf{v}_{12}\cdot\hat{\sigma}_1)^2(\mathbf{v}_{1'2}\cdot\hat{\sigma}_1)^2\Big\rangle\Big\rangle\Big\rangle \tag{3.24}$$

where

$$\mathbf{v}_{1'2}=b_{\hat{\sigma}_2}(13)\mathbf{v}_{12}=\mathbf{v}_{12}-\hat{\sigma}_2(\hat{\sigma}_2\cdot\mathbf{v}_{13}) \tag{3.25}$$

and for $x<0$

$$\begin{aligned}V_2(x)&=V_1(2-x^2)\\&=-\frac{2}{\pi}(6-4x^2+x^4)\sin^{-1}\frac{x}{2}+\frac{3x}{2}(2-x^2)\Big(1-\frac{1}{4}x^2\Big)^{1/2}\\&=-\frac{8}{15\pi}x^5{}_2F_1\Big(\frac{1}{2},\frac{1}{2};\frac{7}{2};\frac{x^2}{4}\Big)\end{aligned} \tag{3.26}$$

as shown in Appendix A.

A factor 2 appears in front of (3.23), since the terms containing $T_+(13)$ and $T_+(23)$ in Eq. (3.21) are equal in the short-time limit. This can be seen by interchanging the labels of particles 1 and 2, using $T(12)(\mathbf{v}_1+\mathbf{v}_2)=0$, and observing that $\exp(\pm i\mathbf{k}\cdot\mathbf{r}_1)$ does not contribute to Eq. (3.22). By averaging Eq. (3.23) over all $\hat{k}$ we may replace $(\hat{\sigma}_1\cdot\hat{k})^2$ by $1/d$. Since the integrand depends only on $\hat{\sigma}_1\cdot\hat{\sigma}_2$, one can carry out the $\hat{\sigma}_1$ integration with the result

$$\Delta_e(0+)=\frac{-2\pi k^2}{d\beta m(t_E\chi)^2}\left\langle\frac{\theta(-x)}{x}V_2(x)g_3(x)\right\rangle_{\text{ang}} \tag{3.27}$$

where $x=\hat{\sigma}_1\cdot\hat{\sigma}_2$ and t_E is given in Eq. (2.18).

3.4. Results for $F(k,t)$ and $C(t)$

From the previous results follows that $F''''(k,t)=A(0)+\Delta(0+)+0(t)$, so that the remainder (2.3) in the Taylor series (2.2) for $F(k,t)$ at small positive t is given by

$$R_4(t)=\frac{t^4}{4!}\big[A(0)+\Delta(0+)\big]+O(t^5) \tag{3.28}$$

The results for $\Delta_d(0+)$, $\Delta_e(0+)$ and $\Delta(0+) = \Delta_d(0+) + \Delta_e(0+)$ follow from (3.11), (3.17), and (3.27) and may be summarized by the equations

$$t_E^2 \begin{bmatrix} \Delta_d(0+) \\ \Delta_e(0+) \\ \Delta(0+) \end{bmatrix} = -\frac{k^2}{\beta m}\frac{4\pi}{d}\left\langle \begin{bmatrix} W_E(x) \\ W_R(x) \\ W(x) \end{bmatrix} \frac{g_3(x)}{\chi^2} \right\rangle_{\text{ang}} \tag{3.29}$$

The average over the d-dimensional solid angle is defined in (3.18), the triplet correlation function for three spheres at contact $g_3(x)$ in (3.14), and the Enskog mean free time t_E in (2.18). The function $W(x)$ does not depend on dimensionality and is defined as

$$W(x) = W_E(x) + W_R(x) \tag{3.30}$$

with

$$\begin{aligned} W_E(x) &= -\tfrac{1}{4}xV_1(x) = \frac{3x^2}{4\pi}\left(1-\tfrac{1}{4}x^2\right)^{1/2} - \frac{x}{4\pi}(2+x^2)\cos^{-1}\frac{x}{2} \\ &= -\tfrac{1}{8}x(2+x^2) + \frac{x^2}{\pi}\,{}_2F_1\left(-\tfrac{1}{2}, -\tfrac{1}{2}; \tfrac{3}{2}; \tfrac{x^2}{4}\right) \end{aligned} \tag{3.31}$$

and

$$\begin{aligned} W_R(x) &= \frac{\theta(-x)}{2x}V_2(x) \\ &= \frac{3}{2\pi}(2-x^2)\left(1-\tfrac{1}{4}x^2\right)^{1/2} - \frac{1}{\pi}(6-4x^2+x^4)\frac{1}{x}\sin^{-1}\frac{x}{2} \\ &= -\frac{4}{15\pi}x^4\,{}_2F_1\left(\tfrac{1}{2}, \tfrac{1}{2}; \tfrac{7}{2}; \tfrac{x^2}{4}\right) \end{aligned} \tag{3.32}$$

Our final result for the short-time behavior of the incoherent scattering function $F(k,t)$ follows from (2.19) and (3.28) to be

$$F(k,t) = 1 - \frac{k^2t^2}{2\beta m} + \frac{k^2|t|^3}{3d\beta m t_E} + \frac{k^4t^4}{8(\beta m)^2} - \frac{\pi k^2 t^4}{6d\beta m t_E^2}\left\langle \frac{W(x)g_3(x)}{\chi^2}\right\rangle_{\text{ang}} + O(t^5) \tag{3.33}$$

The velocity correlation function $C(t)$ can be deduced from (3.33) by means of (2.7),

$$\beta m\, C(t) = 1 - \frac{2|t|}{dt_E} + \frac{2\pi t^2}{dt_E^2}\left\langle \frac{W(x)g_3(x)}{\chi^2}\right\rangle_{\text{ang}} + O(t^3) \tag{3.34}$$

We note that terms containing odd powers of $|t|$ appear in the expansions (3.33) and (3.34) for $F(k,t)$ and $C(t)$. Such terms are absent for systems interacting through a smooth potential.

4. ESTIMATES FOR GENERAL COLLISION SEQUENCES

4.1. General Rule

In the previous section we have calculated the function $\Delta_e(t)$ in (3.12b) for small times by using the binary collision expansion (3.19). We showed by explicit calculation that terms in the BCE which look *formally* of order t may contribute to order t^0. The question therefore is: which terms in the BCE or equivalently, the dynamics of how many particles, will be involved in determining the coefficient of t^k in the short-time expansion of a general correlation function $C_{ab}(t)$ of the form (1.6)?

From the work of Lanford,[26] specialized to the velocity correlation function as in Ref. 27, follows that the coefficient of t^k involves at most the dynamics of $(k+1)$ particles. On the basis of qualitative arguments we want to extend Lanford's results to more general correlation functions, and make it more precise by specifying the dominant $(k+1)$-particle collision sequences. In doing so we are able to argue that we have included in the previous sections all relevant contributions of $O(t^4)$ and $O(t^2)$ to $F(k,t)$ and $C(t)$, respectively. We restrict ourselves to equilibrium time correlation functions of the form

$$C_{ab}(t) = \langle a e^{tL_+} b \rangle_0 \tag{4.1}$$

where a and b are (sums of) functions of the velocities and positions of a few particles, such as Eqs. (3.3)–(3.6). Each function a and b may contain at most one operator $T_\pm(\alpha)$ with pair label α_a or α_b, respectively. The total number of $T_\pm$ operators in a and b is m_{ab}, so that $m_{ab} = 0$, 1, or 2. Estimates for the relevant contributions to $F(k,t)$ are obtained below, using Eq. (3.2) and using estimates for the functions (3.3)–(3.6) which are of the form (4.1).

Substitution of the binary collision expansion (3.19) in Eq. (4.1) yields an infinite set of cluster functions

$$C_{ab}(t) = \sum_{m=0}^{\infty} \sum_{\alpha_1 \ldots \alpha_m}' C_{ab}(\alpha_1\alpha_2 \ldots \alpha_m; t) \tag{4.2}$$

where the cluster functions represent the contribution from a collision sequence in T_+ operators with pair labels $\alpha_1\alpha_2 \ldots \alpha_m$. In the summation over the ordered set $\{\alpha_1\alpha_2 \ldots \alpha_m\}$ the pair label α_i runs over all pairs in the system with the restrictions, that consecutive pairs $\alpha_i\alpha_{i+1}$ are *different* [see Eq. (3.20)], and that the ordered set of T operators $\{\alpha_1\alpha_2 \ldots \alpha_m\}$ is *connected*, i.e., each pair α_i $(i = 1, 2, \ldots, m)$ contains at least one particle, which occurs already among the pairs $(\alpha_{i+1}, \ldots, \alpha_m)$ to its right or as argument of α_b in Eq. (4.1). The connectedness is a direct consequence of the form (1.11) for the T operators, which makes $T(ij)f(\mathbf{r}_k, \mathbf{v}_k) = 0$ for $k \neq i$ or j.

For short times each contribution $C_{ab}(\alpha_1\alpha_2 \ldots \alpha_m; t)$ obeys the following rule:

$$C_{ab}(\alpha_1\alpha_2 \ldots \alpha_m, t) = \gamma t^{m^* - m_{ab}}[1 + O(t)] \tag{4.3}$$

The coefficient γ depends on a and b, and the collision sequence $\{\alpha_1\alpha_2 \ldots \alpha_m\}$; m_{ab} is the total number of T operators in a and b, and m^* the total number of *different pairs* in the sequence $\{\alpha_a\alpha_1\alpha_2 \ldots \alpha_m\alpha_b\}$, including the pair labels possibly present in a and b; m is the total number of T operators and also the number of ordered time integrals involved in $C_{ab}(\alpha_1 \ldots \alpha_m; t)$.

4.2. Implications

Before discussing the justification of (4.3) we make a number of comments.

(i) m^* satisfies the inequalities

$$m_p - 1 \leqslant m^* \leqslant m + m_{ab} \tag{4.4}$$

where m_p is the number of *different particles* involved in the sequence $\{\alpha_a\alpha_1\alpha_2 \ldots \alpha_m\alpha_b\}$; the lower bound represents the minimum number of connected pairs which can be constructed for m_p particles; the upper bound is implied by the definition of m^*.

(ii) An exponent $m^* - m_{ab} = -1$ in (4.3) can only occur for $m_{ab} = 2$ and $m^* = 1$, i.e., for the collision sequence $(\alpha_a)(\alpha_b) = (12)(12)$. It gives a vanishing contribution according to Eq. (3.20). Hence

$$m^* - m_{ab} \geqslant 0 \tag{4.5}$$

(iii) According to Eq. (4.4) the dominant short-time contribution of a cluster function with m_p particles is $O(t^{m_p - m_{ab} - 1})$. Therefore, in order to determine $\Delta_d(t)$ and $\Delta_e(t)$ in Eqs. (3.12) with $m_{ab} = 2$ correctly to $O(t^0)$ one needs at most three particles, and the collision sequences $(12)(\alpha_1) \ldots (\alpha_m)(13)$ and $(12)(\alpha_1) \ldots (\alpha_m)(12)$, respectively, with $m^* = m_{ab} = 2$ different pairs. Since consecutive pairs must be different, only the sequences (12)(13), (12)(13)(12)(13), (12)(13)(12)(13)(12)(13), etc. are allowed in $\Delta_d(t)$, of which the second and higher ones are dynamically impossible, as shown in the literature.[28] The first one, (12)(13), has been calculated in (3.13). On the basis of similar arguments one finds that only the collision sequences (12)(13)(12) and (12)(23)(12) contribute to $\Delta_e(0+)$, as calculated in Eqs. (3.21)–(3.23). In order to determine the remaining terms (3.3)–(3.5) correctly to $O(t^0)$ the rule (4.3) yields for $A(t)$ the values $m_{ab} = 0$ and $m^* = 0$, and for $B(t)$ and $\Gamma(t)$ the values $m_{ab} = 1$ and $m^* = 1$, as calculated in Eqs. (3.7)–(3.9).

(iv) The rigorous bounds for the velocity correlation function $C(t)$ given in Refs. 26 and 27 are consistent with the general rule (4.3). For $C(t)$ the quantities a and b in (4.1) are equal to v_{1x} so that $m_{ab} = 0$ and therefore the exponent $m^* - m_{ab}$ in (4.3) equals m^*. In Lanford's rigorous estimates m^* is replaced by the *lower bound* $m_p - 1$ in (4.4), so that the rule (4.3) gives estimates that are *sharper* than Lanford's. However, we will not give a rigorous derivation of (4.3) but present only some qualitative arguments in the next section.

4.3. Outline of a Proof of Rule (4.3)

We first consider the arguments which lead to the rule (4.3) for the case $m_{ab} = 0$, i.e., when a and b are smooth functions of the phases [unlike the T operators in Eqs. (3.4)–(3.6)]. An estimate for $C_{ab}(\alpha_1 \ldots \alpha_m, t)$ can be obtained if one first performs all time integrals involved, and estimates the spatial configurations for which the integrand is nonvanishing. To find a nonvanishing contribution from a single collision ($m = m^* = 1$), say, a (12) collision, the center of particle 2 has to be in a spherical shell around the center of particle 1 with diameter σ and width proportional to the small time t. Hence $C_{ab}(12, t) \sim t$.

Next we compare the collision sequences (12)(13)(12) (with $m = 3$, $m^* = 2$) and (12)(13)(23) (with $m = m^* = 3$). The center of particle 2 has to be in a spherical shell around the center of particle 1 with diameter σ and width t for the first (12) collision to occur in the small time t. Similarly, for a subsequent (13) collision, the center of particle 3 has to be in a shell around the center of particle 1 with diameter σ and width t if a (13) collision is to occur in the small time t. Thus the volume of the combined phase spaces of the particles 2 and 3 for a (12)(13) sequence of collisions to occur in a small time t will be $\sim t^2$. If the third collision that is to occur between the three particles 1, 2, 3 is again a (12) collision, *no* new condition is introduced because 2 has to be in the same shell around 1 for this to occur as before (cf. Fig. 1a). If, however, the third collision were to occur between a different pair of particles [for instance (23)], then an extra condition is introduced since now 3 has to be in a shell not only around 1 but also around 2, so that the volume of the combined phase spaces for a (23)(13)(12) sequence of collisions will be $\sim t^3$ for small t (cf. Fig. 1b). The generalization of these phase space arguments to larger collision sequences $(\alpha_1) \cdots (\alpha_m)$ leads to the rule (4.3) in case $m_{ab} = 0$.

We next consider the case where $m_{ab} = 1$, i.e., either a or b in Eq. (4.1) contains a T operator. The corresponding cluster functions in Eq. (4.2) can

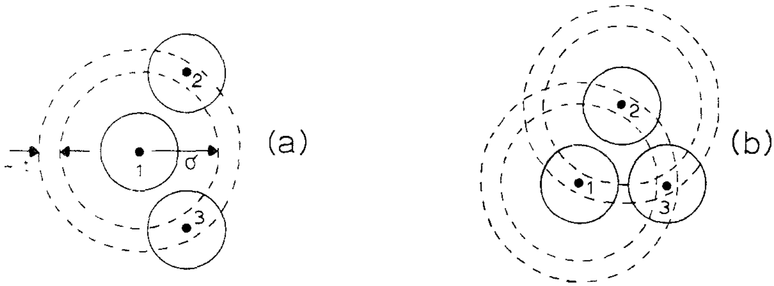

Fig. 1. Phase space estimates of two collision sequences for small times t. (a) For a sequence (12)(13)(12) to occur the particles 2 and 3 need to be in a shell around particle 1 with diameter σ and thickness $\sim t$. (b) For a sequence (12)(13)(23) to occur particle 3 must be in addition located in a shell around particle 2.

be obtained by differentiating $C_{ab}(\alpha_1\alpha_2 \ldots \alpha_m; t)$ with $m_{ab} = 0$ once with respect to time. The dominant short-time behavior of the *derivative* has only $(m-1)$ time convolutions, and is therefore equal to the dominant contribution of $C_{ab}(\alpha_2 \ldots \alpha_m; t)$ with $m_{ab} = 1$ and $\alpha_a = \alpha_1$, or to $C_{ab}(\alpha_1\alpha_2 \ldots \alpha_{m-1}; t)$ with $m_{ab} = 1$ and $\alpha_b = \alpha_m$. It behaves therefore as t^{m^*-1}, as follows from Eq. (4.4). By taking a second derivative one shows that $C''_{ab}(\alpha_1 \ldots \alpha_m; t) \sim t^{m^*-2}$ behaves dominantly as $C_{ab}(\alpha_2 \ldots \alpha_{m-1}; t)$ with $m_{ab} = 2$ and $\alpha_a = \alpha_1$ and $\alpha_b = \alpha_m$. This demonstrates our rule (4.4).[4]

5. INCOHERENT SCATTERING FUNCTION

5.1. High-Frequency Tail of $S(k, \omega)$

The essential difference in the short-time behavior of $F(k, t)$ for smooth and hard-core potentials manifests itself in an interesting fashion in the behavior of $S(k, \omega)$. Since $F(k, t)$ for a hard-sphere fluid is a nonanalytic function of t around the origin—i.e., $F''(k, t)$ has a cusp at $t = 0$—we expect a tail, i.e., a nonexponential behavior in the high-frequency behavior of $S(k, \omega)$, characteristic for a hard-sphere fluid. This point has been noticed in Refs. 12–14. In Refs. 12 and 13 it is implied that $S(k, \omega) \sim 1/\omega^4$ at large ω, although it is not stated explicitly. Sears[(13)] remarks that $S(k, \omega) \sim 1/\omega^\alpha$ as $\omega \to \infty$ with $3 < \alpha < 5$, and that the fourth and higher frequency moments of the scattering function are infinite.

The high-frequency behavior of $S(k, \omega)$ can be obtained from Eq. (1.4) by successive partial integrations. In view of the sum rules, to be discussed

[4]The extensions of Lanford's bounds to the correlation functions of interest here, were obtained in close cooperation with Dr. H. van Beijeren.

below, we first perform two partial integrations in Eq. (1.4), where we write $\cos\omega t = -\omega^{-2}(d^2\cos\omega t/dt^2)$. The result is

$$S(k,\omega) = -\int_0^\infty dt\,\frac{\cos\omega t}{\pi\omega^2}\,F''(k,t) \tag{5.1}$$

where we have used in addition that $F(k,t)$ vanishes for large t. Two more partial integrations yield

$$S(k,\omega) = \frac{F'''(k,0+)}{\pi\omega^4} + \int_0^\infty dt\,\frac{\cos\omega t}{\pi\omega^4}\,F''''(k,t) \tag{5.2}$$

By continuing this procedure we obtain, using Eq. (3.33)

$$S(k,\omega) = \frac{2k^2}{\pi\,d\beta\,mt_E}\,\frac{1}{\omega^4} + O\left(\frac{1}{\omega^6}\right) \tag{5.3}$$

This implies that odd powers t^{2m-1} in the *short time* behavior of $F(k,t)$ manifest themselves as even powers $1/\omega^{2m}$ in the *high-frequency* behavior of $S(k,\omega)$. No such power law decay of $S(k,\omega)$ is found for smooth potentials, since $F(k,t)$ is then an analytic function of t around $t=0$, in which only even powers of t occur.

5.2. Adjusted Sum Rules

The frequency moments of the scattering function for *smooth* potentials can be expressed in terms of static quantities

$$\int_{-\infty}^{+\infty} d\omega\,\omega^{2n}S(k,\omega) = (-)^n F^{(2n)}(k,0) \tag{5.4}$$

where $F^{(n)}(k,t)$ denotes the nth derivative of $F(k,t)$ with respect to t. Since all frequency moments can therefore be expressed as equilibrium averages, they are expected to exist.

For the *hard-sphere* fluid, however, only the zeroth and second moment exist on account of the high-frequency tail (5.3). By multiplying Eqs. (1.4) and (5.1) with $\omega^0 = 1$ and ω^2, respectively, integrating over ω, and using $\int_{-\infty}^{\infty} d\omega\,e^{i\omega t} = 2\pi\delta(t)$, we obtain

$$\int_{-\infty}^{+\infty} d\omega\,S(k,\omega) = F(k,0) = 1$$

$$\int_{-\infty}^{+\infty} d\omega\,\omega^2 S(k,0) = -F''(k,0) = \frac{k^2}{\beta m} \tag{5.5}$$

which are the standard sum rules for smooth and hard-core potentials. However, multiplying Eq. (5.2) with ω^4, and performing the ω integration yields

$$\int_{-\infty}^{+\infty} d\omega\left[\omega^4 S(k,\omega) - \frac{1}{\pi}F'''(k,0+)\right] = F''''(k,0+) \tag{5.6}$$

where the right derivatives $F'''(k,0+)$ and $F''''(k,0+)$ can be read off from (3.33). Therefore, the short-time coefficient $F''''(k,0)$ of a hard-sphere fluid can still be extracted from $S(k,\omega)$ by means of an adjusted sum rule.

5.3. Transition from Smooth to Hard-Core Potentials

According to Eq. (5.3) the quantity $\omega^4 S(k,\omega)$ approaches in a hard-sphere fluid a constant for high frequencies. We will now investigate to what extent this prediction of a hard-sphere fluid is applicable to a real fluid.

The hard-sphere model is only a meaningful approximation for times t and frequencies ω with

$$t > t_s = \omega_s^{-1} \quad \text{or} \quad \omega < \omega_s \tag{5.7}$$

where t_s is the average time a particle needs to transverse the steep part of the potential. An estimate for t_s can be obtained from the short-time expansion of the velocity correlation function for smooth potentials,[13] i.e.

$$\beta m C(t) = 1 - \alpha_1 \frac{t^2}{\beta m} + \alpha_2 \frac{t^4}{(\beta m)^2} + \cdots \tag{5.8}$$

where

$$\begin{aligned} \alpha_1 &= \frac{2}{3}\pi n \beta \int_0^\infty dr\, g(r)\left[r^2 V''(r) + 2rV'(r)\right] \\ \alpha_2 &= \frac{1}{9}\pi n \beta^2 \int_0^\infty dr\, g(r)\left\{r^2\left[V''(r)\right]^2 + 2\left[V'(r)\right]^2\right\} + n^2 M_1 \end{aligned} \tag{5.9}$$

M_1 is a term involving the static triplet distribution function. If the pair potential has a steep repulsive part with a range λ_s, then Sears[13] has shown that $\alpha_1 \sim \lambda_s^{-1}$ and $\alpha_2 \sim \lambda_s^{-3}$ for small λ_s, and that M_1 in α_2 does not contribute to the coefficient of the leading term, λ_s^{-3}. Since the expansion (5.8) is only meaningful when successive terms are small, we obtain the following estimate by comparing the second and third term in (5.8), i.e.,

$$\beta m t_s^2 = \frac{\alpha_1}{\alpha_2} \tag{5.10}$$

An approximate evaluation of α_1 and α_2 (M_1 is neglected) for the repulsive part of a Lennard-Jones potential $V(r) = \epsilon(\sigma/r)^\nu$ with $\nu \simeq 12$, using $g(r) \simeq \chi \exp[-\beta V(r)]$, yields

$$\frac{\beta m t_s^2}{\sigma^2} = \frac{6\Gamma(2 - 1/\nu)(\beta\epsilon)^{2/\nu}}{(\nu^2 + 2\nu + 3)\Gamma(2 + 1/\nu)} \tag{5.11}$$

With $\nu = 12$ and $T^* = k_B T/\epsilon$ we have

$$\frac{t_s}{\sigma(\beta m)^{1/2}} = \frac{0.18}{(T^*)^{1/12}} \tag{5.12}$$

For the mean free time t_E in the hard-sphere fluid we have

$$\frac{t_E}{\sigma(\beta m)^{1/2}} = \frac{1}{4\sqrt{\pi}\, n^* \chi} \simeq \frac{1.4}{n^* \chi} \tag{5.13}$$

so that

$$\frac{t_s}{t_E} \simeq \frac{1.3 n^* \chi}{(T^*)^{1/12}} \tag{5.14}$$

For the Lennard-Jones fluid at $n^* = n\sigma^3 = 0.85$ and $T^* = 0.72$ as in Ref. 6 and with $\chi \simeq 4.5$,[29] we find $t_s = 5t_E$. Since at the liquid densities considered, $\omega_E \simeq 5\omega_s$, and since Eq. (3.33) for $F(k,t)$ and Eq. (5.3) for $S(k,\omega)$ are only valid for $t < t_E = \omega_E^{-1}$ and $\omega > \omega_E$, respectively, we conclude from (5.7) that the hard-sphere high-frequency tail $S(k,\omega) \sim 1/\omega^4$ cannot be observed in a Lennard-Jones-like liquid.

However, at gas densities $n^* \simeq 0.1$ (where $\chi \simeq 1$) and at normal temperatures, t_E becomes large, so that $t_s \simeq 0.1 t_E$. Hence, there exists then a region, where both conditions, $\omega_E < \omega < \omega_s \simeq 10\omega_E$ can be met, and where a high-frequency tail in $S(k,\omega)$ might in principle be observed.

6. CUMULANTS AT SHORT TIMES

6.1. Moments and Cumulants

The cumulant expansion of the incoherent scattering function $F(k,t)$ is defined through[2,13]

$$\log F(k,t) = \sum_{n=1}^{\infty} (-)^n k^{2n} \gamma_n(t) \tag{6.1}$$

and the cumulants $\gamma_n(t)$ can be expressed directly in the moments of the displacement $\langle \Delta_x^n \rangle_0$, generated by the expansion

$$\begin{aligned} F(k,t) &= \langle e^{-ik\Delta_x(t)} \rangle_0 = \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \left\langle [\Delta_x(t)]^n \right\rangle_0 \\ &= \sum_{n=0}^{\infty} (-ik)^n \int_{0<\tau_1<\tau_2<\cdots<\tau_n<t} \cdots \int d\tau_1\, d\tau_2 \ldots d\tau_n \\ &\quad \times \langle v_{1x}(\tau_1) v_{1x}(\tau_2) \ldots v_{1x}(\tau_n) \rangle_0 \end{aligned} \tag{6.2}$$

where we have used Eq. (1.2) and ordered the time integrals. From a comparison of Eqs. (6.1) and (6.2) one obtains the cumulants in terms of the moments, e.g.,

$$\gamma_1(t) = \frac{1}{2!}\left\langle\left[\Delta_x(t)\right]^2\right\rangle_0$$

$$\gamma_2(t) = \frac{1}{4!}\left\{\langle\left[\Delta_x(t)\right]^4\rangle_0 - 3\langle\left[\Delta_x(t)\right]^2\rangle_0\right\} \tag{6.3}$$

Sears has discussed the short-time behavior of the cumulants both for smooth potentials and for hard-sphere systems.(13) For *smooth* potentials his results are

$$\gamma_1(t) = \frac{1}{2\beta m}t^2 + a_1 t^4 + b_1 t^6 + O(t^8)$$

$$\gamma_2(t) = a_2 t^8 + O(t^{10}) \tag{6.4}$$

$$\gamma_3(t) = O(t^{12})$$

with *explicit* expressions for a_1, a_2, and b_1, which involve both triplet (b_1 and a_2) and pair distribution functions. For *hard spheres* he gives

$$\gamma_1(t) = \frac{1}{2\beta m}t^2 - \frac{|t|^3}{3d\beta m t_E} + O(t^4)$$

$$\gamma_2(t) = \xi_2|t|^5/5! + \cdots \tag{6.5}$$

$$\gamma_3(t) = \xi_3|t|^7/7! + \cdots$$

From the results of section 3 the $O(t^4)$ term in $\gamma_1(t)$ may also be written down directly using Eq. (3.34) and the relation $\gamma_1''(t) = C(t)$. However, Sears' results for γ_2 and γ_3 are only qualitative, since his series for ξ_2 and ξ_3 are formally given by an infinite sum of divergent integrals, of which only the first few terms are obtained. Here we will calculate exactly the coefficients of the leading terms in the short time expansion of all cumulants γ_n. We start from the nth moment for hard spheres with $t > 0$,

$$\begin{aligned}\langle\Delta_x^n\rangle_0 = n! \int_{0<\tau_1<\tau_2<\cdots<\tau_n<t}\cdots\int d\tau_1\, d\tau_2 \\ \times \ldots d\tau_n\left\langle\exp(\tau_1 L_+)v_{1x}\exp\left[(\tau_2-\tau_1)L_+\right]v_{1x}\ldots v_{1x}\right. \\ \left.\times\exp\left[(\tau_n-\tau_{n-1})L_+\right]v_{1x}\right\rangle_0\end{aligned} \tag{6.6}$$

In these multitime correlation functions we have introduced pseudo Liouville operators, which are all L_+ operators, since all time differences $(\tau_l - \tau_{l-1})$ are positive.(24,30)

6.2. One-Collision Contributions

In order to evaluate the cumulants, we start by calculating the moment-generating function $F(k,t)$ in (6.2), since its logarithm (6.1) is the generating function for the cumulants. For short times $\exp(\tau L_+) = 1 + \tau L_+ + \cdots$, and by keeping only the two most dominant terms in (6.6), we obtain

$$\langle \Delta_x^n \rangle_0 = t^n \langle v_{1x}^n \rangle_0 + \frac{t^{n+1}}{n+1} \sum_{l=0}^{n} \langle v_{1x}^l L_+ v_{1x}^{n-l} \rangle + O(t^{n+2}) \tag{6.7a}$$

$$= t^n \int \frac{d\hat{\sigma}}{\Omega_d} \left\{ \langle v_{1x}^n \rangle + \frac{\alpha t}{n+1} \sum_{l=0}^{n} \left\langle \left\langle |\mathbf{v}_{12} \cdot \hat{\sigma}| v_{1x}^l [b_{\hat{\sigma}}(12) - 1] \right.\right.\right.$$

$$\left.\left.\left. \cdot v_{1x}^{n-l} \right\rangle \right\rangle + O(t^2) \right\} \tag{6.7b}$$

To obtain the last equality we have used steps similar to those leading from (2.12) to (2.17) via (2.14) and introduced

$$\alpha = (1/2) n \chi \sigma^{d-1} \Omega_d = (1/2)(\pi \beta m)^{1/2} / t_E \tag{6.8}$$

In addition we used that the $\hat{\sigma}$ integrand is even, so that $\theta(-\mathbf{v}_{12} \cdot \hat{\sigma})$ in the $T_+(12)$ operator may be replaced by $1/2$. The term $\sim \alpha t \sim t/t_E$ represents the *linear* term in an expansion of $\langle \Delta_x^n \rangle_0$ in powers of t/t_E. In order to evaluate the generating function $F(k,t)$ correct to linear order in αt, we insert (6.7b) into (6.2), and call $kt = q$, which leads to the result

$$F\left(\frac{q}{t}, t \right) = \int \frac{d\hat{\sigma}}{\Omega_d} \left\langle \left\langle \exp\{ -i\mathbf{q} \cdot \mathbf{v}_1 + \alpha t |\mathbf{v}_{12} \cdot \hat{\sigma}| [b_{\hat{\sigma}}(12) - 1] \} \right\rangle \right\rangle + O(t^2). \tag{6.9}$$

To verify Eq. (6.9) expand the exponential function, and keep only terms linear in αt (at fixed q), from which one recovers Eq. (6.7).

In the further evaluation of Eq. (6.9) we change to a center of mass $[\mathbf{V} = (1/2)(\mathbf{v}_1 + \mathbf{v}_2)]$ and a relative velocity $\mathbf{v} = \mathbf{v}_1 - \mathbf{v}_2$, which is further decomposed into Cartesian components $(v_a, v_b, \mathbf{v}_\perp)$, i.e.,

$$\mathbf{v} = v_a \hat{e}_a + v_b \hat{e}_b + \mathbf{v}_\perp \tag{6.10}$$

with orthonormal unit vectors ($\hat{q} = \mathbf{q}/|\mathbf{q}|$)

$$\hat{e}_a = \hat{\sigma}; \qquad \hat{e}_b = [\hat{q} - \hat{\sigma}(\hat{\sigma} \cdot \hat{q})] [1 - (\hat{q} \cdot \hat{\sigma})^2]^{-1/2} \tag{6.11}$$

The first term in the exponent of (6.9) becomes

$$\mathbf{q} \cdot \mathbf{v}_1 = \mathbf{q} \cdot \mathbf{V} + (1/2)\mathbf{q} \cdot \hat{\sigma} v_a + (1/2) q v_b [1 - (\hat{q} \cdot \hat{\sigma})^2]^{1/2} \tag{6.12}$$

We observe that $b_{\hat{\sigma}}$ in (6.9) acts only on v_a, with $b_{\hat{\sigma}} v_a = -v_a$. Hence, we can carry out the integrations over $\mathbf{V}$, v_b, and $\mathbf{v}_\perp$, using

$$\langle \exp(-i\mathbf{q}\cdot\mathbf{V})\rangle = \exp\left[-(1/2)q^2\langle V_x^2\rangle\right] = \exp(-q^2/4\beta m)$$
$$\left\langle \exp\left\{-(1/2)iqv_b\left[1-(\hat{q}\cdot\hat{\sigma})^2\right]^{1/2}\right\}\right\rangle = \exp\left\{-q^2\left[1-(\hat{q}\cdot\hat{\sigma})^2\right]/4\beta m\right\} \tag{6.13}$$

This yields

$$\begin{aligned}\exp(q^2/2\beta m)F(q/t,t) = \int (d\hat{\sigma}/\Omega_d)\exp\left[(\mathbf{q}\cdot\hat{\sigma})^2/4\beta m\right]\\ \cdot\left\langle \exp\left\{-(i/2)(\mathbf{q}\cdot\hat{\sigma})v_a + \alpha t|v_a|\left[b_{\hat{\sigma}}-1\right]\right\}\right\rangle_r\\ +O(t^2)\end{aligned} \tag{6.14}$$

where the brackets denote the one-dimensional velocity average

$$\langle\cdots\rangle_r = \left(\frac{\beta\mu}{2\pi}\right)^{1/2}\int_{-\infty}^{+\infty} dv_a \exp\left[-(1/2)\beta\mu v_a^2\right]\cdots \qquad \left[\mu = (1/2)m\right] \tag{6.15}$$

By expanding the exponential function inside the average in (6.14) we find

$$\begin{aligned}\exp(q^2/2\beta m)F\left(\frac{q}{t},t\right) = \int \frac{d\hat{\sigma}}{\Omega_d}\exp\left[(\mathbf{q}\cdot\hat{\sigma})^2/4\beta m\right]\\ \cdot\left\{\sum_{n=0}^{\infty}\frac{\left\langle\left[(-i/2)(\mathbf{q}\cdot\hat{\sigma})v_a\right]^n\right\rangle_r}{n!}\right.\\ \left. +t\sum_{n=0}^{\infty}c_n\left(\frac{-i}{2}\mathbf{q}\cdot\hat{\sigma}\right)^n + O(t^2)\right\}\end{aligned} \tag{6.16}$$

where

$$c_n = \frac{\alpha}{(n+1)!}\sum_{l=0}^{n}\left\langle |v_a|v_a^{n-l}(b_{\hat{\sigma}}-1)v_a^l\right\rangle_r \tag{6.17}$$

Clearly $c_0 = 0$, and since $b_{\hat{\sigma}}v_a^l = (-v_a)^l$ the label l in (6.17) must be odd, so that the label n must be even. Using (6.8) we obtain

$$\begin{aligned}c_{2n} &= -\frac{2\alpha n}{(2n+1)!}\left\langle |v_a|^{2n+1}\right\rangle_r = \frac{-1}{t_E(\beta m)^n}\,\frac{n\sqrt{\pi}}{\Gamma(n+3/2)}\\ &= -\frac{4}{3t_E(\beta m)^n}\,\frac{(2)_{n-1}}{(5/2)_{n-1}(n-1)!}\end{aligned} \tag{6.18}$$

For later convenience we have introduced the Pochhammer symbol

$$(a)_n = \frac{\Gamma(a+n)}{\Gamma(a)} = a(a+1)(a+2)\cdots(a+n-1) \tag{6.19}$$

The first sum in (6.16) equals $\exp[-(\mathbf{q}\cdot\hat{\sigma})^2/4\beta m]$, and with the notation $z = (\mathbf{q}\cdot\hat{\sigma})^2/4\beta m$ we obtain

$$\exp(q^2/2\beta m)F\left(\frac{q}{t}, t\right) = 1 + t\int \frac{d\hat{\sigma}}{\Omega_d}\exp(z)\sum_{n=1}^{\infty} c_n(-\beta m z)^n + O(t^2)$$

$$= 1 + \frac{4t}{3t_E}\int \frac{d\hat{\sigma}}{\Omega_d} z\, {}_1F_1\left(\frac{1}{2}; \frac{5}{2}; z\right) + O(t^2) \tag{6.20}$$

where we have used Eq. (6.18), and the confluent hypergeometric function[31]

$${}_1F_1(a; b; z) = \exp(z)\, {}_1F_1(b-a; b; -z) = \sum_{n=0}^{\infty} \frac{(a)_n}{(b)_n}\frac{z^n}{n!} \tag{6.21}$$

Integrating the hypergeometric series term by term, using

$$\int \frac{d\hat{\sigma}}{\Omega_d} z^{n+1} = \frac{1}{d}\frac{(3/2)_n}{[(d+2)/2]_n}\frac{q^2}{4\beta m} \tag{6.22}$$

we find

$$\exp(q^2/2\beta m)F\left(\frac{q}{t}, t\right) = 1 + \frac{q^2 t}{3d\beta m t_E} \times {}_2F_2\left(\frac{1}{2}, \frac{3}{2}; \frac{5}{2}, \frac{d+2}{2}; \frac{q^2}{4\beta m}\right) + O(t^2) \tag{6.23}$$

where ${}_2F_2$ is a hypergeometric series[32]

$${}_2F_2(a, b; c, d; z) = \sum_{n=0}^{\infty} \frac{(a)_n (b)_n}{(c)_n (d)_n}\frac{z^n}{n!} \tag{6.24}$$

The generating function for the cumulants is according to (6.1)

$$\log F\left(\frac{q}{t}, t\right) = \frac{-q^2}{2\beta m} + \frac{q^2 t}{3d\beta m t_E}\, {}_2F_2\left(\frac{1}{2}, \frac{3}{2}; \frac{5}{2}, \frac{d+2}{2}; \frac{q^2}{4\beta m}\right) + O(t^2) \tag{6.25}$$

By replacing $q = kt$ and identifying coefficients we find for $\gamma_1(t)$ the result in Eq. (6.5) and for $\gamma_n(t)$ with $n \geqslant 2$

$$\gamma_n(t) = \frac{(-)^n t^{2n+1}(1/2)_{n-1}(3/2)_{n-1}}{3d(5/2)_{n-1}((d+2)/2)_{n-1}(n-1)!2^{2n-1}} \frac{1}{t_E(\beta m)^n}\left[1 + O(t)\right] \tag{6.26a}$$

or

$$\gamma_n(t) = \frac{(-)^n t^{2n+1} n(1/2)_{n-1}(3/2)_{n-1}}{(2n+1)!(d/2)_{n-1}} \frac{1}{t_E(\beta m)^n}\left[1 + O(t)\right] \tag{6.26b}$$

This is our final result for the dominant term in the short-time expansion of the cumulant $\gamma_n(t)$. For $n = 2$ and $n = 3$ the coefficients ξ_2 and ξ_3 in Eq. (6.5) follow from (6.26). From the generating function (6.23) we can in principle also obtain the moments $\langle \Delta_x^{2n}(t) \rangle_0$, correct up to linear terms in t/t_E. The result is a linear combination of γ_k's with $k = 1, 2, \ldots, n$, which does not simplify any further and will not be written down explicitly.

6.3. Contributions from More Than One Collision

The calculation of the first correction to the leading term (6.26), which is of relative order t, is much more laborious. We will only outline the procedure of how to evaluate this correction in principle. The contributions are similar to $\Delta_d(t)$ and $\Delta_e(t)$ in Section 3, and involve the triplet correlation function and two or three T operators.

Let us illustrate this for the $O(t^6)$ term in $\gamma_2(t)$, i.e.,

$$\gamma_2(t) = \frac{1}{4!}\langle \Delta_x^4 \rangle_0 - \frac{1}{2}\gamma_1^2(t) = \frac{\xi_2 t^5}{5!} + O(t^6) \tag{6.27}$$

with $t > 0$. We follow the Taylor expansion method of Section 2 and have to calculate the sixth derivative of $\gamma_2(t)$. As $\gamma_1(t)$ is already known to the desired accuracy, we calculate the sixth derivative of $\langle \Delta_x^4 \rangle_0 / 4!$, as given in (6.6), and obtain after some calculation the result

$$\begin{aligned}\left(\frac{d}{dt}\right)^6 \frac{1}{4!}\langle \Delta_x^4 \rangle_0 = {} & \langle v_x L_+ e^{tL_+} L_+ v_x^3 \rangle_0 + \langle v_x^2 L_+ e^{tL_+} L_+ v_x^2 \rangle_0 \\ & + \langle v_x^3 L_+ e^{tL_+} L_+ v_x \rangle_0 + \langle v_x L_+ v_x^2 e^{tL_+} L_+ v_x \rangle_0 \\ & + \langle v_x L_+ v_x^2 e^{tL_+} L_+ v_x \rangle_0 + \langle v_x^2 L_+ v_x^2 e^{tL_+} L_+ v_x \rangle_0 \\ & + O(t)\end{aligned} \tag{6.28}$$

where v_x is the $\hat{x}$ component of the velocity of particle 1. At $t = 0$ none of these terms exist. However, they approach a finite limit as $t \to 0+$. Their explicit evaluation is rather similar to that of $\langle v_x L_+ e^{tL_+} v_x \rangle_0$, treated in Section 3, but will not be carried out here.

7. COMPARISON WITH ENSKOG'S THEORY AND MOLECULAR DYNAMICS

7.1. Enskog's One-Collision Contributions

The functions $F(k,t)$ and $C(t)$, as well as the cumulants $\gamma_n(t)$ may also be calculated by means of the Enskog theory which approximately describes a hard-sphere fluid. We want to compare the exact results found here with the predictions of Enskog's theory. If we restrict ourselves to $t > 0$ [see Eq. (1.9)], then the Enskog theory is obtained if the N-particle operator L_+ in the correlation functions (1.13) is replaced by the one-particle operator L_E, acting on functions of $(\mathbf{v}_1, \mathbf{r}_1)$,[11,25] i.e.,

$$L_E = \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + \Lambda_E^s \tag{7.1}$$

$$\Lambda_E^s = \chi \Lambda_B^s = \chi n \sigma^{d-1} \int d\mathbf{v}_2 \phi_0(v_2) \int_{\mathbf{v}_{12} \cdot \hat{\sigma} < 0} d\hat{\sigma} |\mathbf{v}_{12} \cdot \hat{\sigma}| \left[b_{\hat{\sigma}}(12) - 1 \right] \tag{7.2a}$$

$$= n \int d\mathbf{v}_2 \int d\mathbf{r}_2 \phi_0(v_2) g(r_{12}) T_+(12) \tag{7.2b}$$

and the N-particle average $\langle \cdots \rangle_0$ is replaced by the velocity average $\langle \cdots \rangle$, defined in (2.15). This yields for the intermediate scattering function $F(k,t)$ and the velocity correlation function $C(t)$,

$$F_E(k,t) = \langle \exp(i\mathbf{k} \cdot \mathbf{r}_1) \exp(tL_E) \exp(-i\mathbf{k} \cdot \mathbf{r}_1) \rangle \tag{7.3}$$

$$C_E(t) = \langle v_{1x} \exp(tL_E) v_{1x} \rangle = \langle v_{1x} \exp(t\Lambda_E^s) v_{1x} \rangle \tag{7.4}$$

and an analogous expression for $\langle \Delta_x^n \rangle_0$ of (6.6) with the same replacements.

One verifies directly that the exact results (2.9–2.12) for $F(k,t)$, yielding Eq. (2.19) up to $O(t^3)$ included, coincide with the Enskog prediction. This is true since $F'''_E(k,0) = -k^2 \langle v_{1x} \Lambda_E^s v_{1x} \rangle$, which in turn is identical to Eq. (2.14) on account of (7.2b). For the velocity correlation function one finds from (2.7), that the short-time prediction of Enskog's theory is exact to $O(t)$ included. Similarly, the dominant term (6.26) for the cumulant $\gamma_n(t)$ at short times is correctly given by Enskog's theory, since by replacing $\langle v_{1x}^l L_+ v_{1x}^{n-l} \rangle_0$ by $\langle v_{1x}^l L_E v_{1x}^{n-l} \rangle$ in Eq. (6.7a), one obtains also (6.7b). We may state the general conclusion that the Enskog theory for short times gives exact values for the first correction terms (proportional to t_E^{-1}) to the ideal gas behavior, for all quantities considered here.

7.2. Enskog's Coefficient of t^2 in $C(t)$

For a comparison of the contributions of more than one collision we consider only the velocity correlation function, which covers also $F(k,t)$ [cf. (3.33) and (3.34)].

The exact result (3.34) reads

$$\beta m C(t) = 1 - \frac{2|t|}{dt_E} + c\left(\frac{t}{t_E}\right)^2 + O(t^3) \tag{7.5}$$

with

$$c = \frac{2\pi}{d}\left\langle W(x) g_3(x)/\chi^2\right\rangle_{\text{ang}} \tag{7.6}$$

Enskog's prediction c_E for the coefficient c in (7.5) follows directly from (7.4) and (7.2b), i.e.,

$$\begin{aligned} c_E &= (1/2)t_E^2 \beta m\left\langle v_{1x}(\Lambda_E^s)^2 v_{1x}\right\rangle \\ &= (1/2)t_E^2\beta m n\int d\mathbf{r}_{12}\int d\mathbf{r}_{13} \\ &\quad\cdot g(r_{12})\, g(r_{13})\left\langle\left\langle\left\langle\left[T_-(12)\mathbf{v}_1\cdot\hat{k}\right]T_+(13)\mathbf{v}_1\cdot\hat{k}\right\rangle\right\rangle\right\rangle \end{aligned} \tag{7.7}$$

In order to evaluate this expression we compare (7.7) with (3.13) and observe that $-\Delta_d(0)/k^2$ is transformed into $2c_E/\beta m t_E^2$ upon the replacement of $g_3(x)$ by χ^2. Therefore Eq. (3.29) yields

$$c_E = \frac{2\pi}{d}\left\langle W_E(x)\right\rangle_{\text{ang}} \tag{7.8}$$

It may be evaluated explicitly, using (3.18) and (3.31) to yield

$$\begin{aligned} c_E &= \frac{2\pi}{d}\int_0^\pi d\theta(\sin\theta)^{d-2} W_E(\cos\theta)\Big/\int_0^\pi d\theta(\sin\theta)^{d-2} \\ &= \frac{4\Gamma(d/2)}{d\sqrt{\pi}\,\Gamma((d-1)/2)}\int_0^1 dx(1-x^2)^{(d-3)/2}x^2\,{}_2F_1\left(-\frac{1}{2},-\frac{1}{2};\frac{3}{2};\frac{x^2}{4}\right) \end{aligned} \tag{7.9}$$

After the substitution $x^2 = y$ the last integral can be obtained from Ref. 32, and gives

$$c_E = \frac{2}{d^2}\,{}_2F_1\left(-\frac{1}{2},-\frac{1}{2};\frac{d+2}{2};\frac{1}{4}\right) \tag{7.10}$$

We remark that ${}_2F_1$ is close to 1 (within 4%) for all values of d. Equation (7.10) reduces for $d=3$ to

$$c_E = \frac{\pi}{48} + \frac{3\sqrt{3}}{32} = 0.227\,829\,6 \qquad (d=3) \tag{7.11}$$

This result is obtained by evaluating (7.8) directly for $d=3$ in terms of elementary functions. Although one can express (7.10) for $d=2$ in terms of complete elliptic integrals, we may also compute c_E directly from the first few terms of the fast converging hypergeometric series (7.10) to yield

$$c_E = 0.515\,796\,0 \qquad (d=2) \tag{7.12}$$

7.3. Single Overlap and Recollision Contributions

By comparing (7.6) and (7.8) we see that the exact coefficient c contains c_E plus two additional contributions, i.e.,

$$c = c_E + c_S + c_R \tag{7.13}$$

with

$$c_S = \frac{2\pi}{d}\left\langle W_E(x)\left[\frac{g_3(x)}{\chi^2} - 1\right]\right\rangle_{\text{ang}} \tag{7.14}$$

$$c_R = \frac{2\pi}{d}\left\langle W_R(x)\frac{g_3(x)}{\chi^2}\right\rangle_{\text{ang}} \tag{7.15}$$

We refer to c_S as the *single overlap* contribution, since (for low densities) $[g_3(x)/\chi^2 - 1]$ is nonvanishing (and equal to -1) only for $1/2 < x < 1$ or $0 < \theta < \pi/3$ with $x = \cos\theta$ [see (3.14)], i.e., for configurations in which one pair of spheres is overlapping. The coefficient c_R is the *recollision* contribution, the integrand of which is only nonvanishing for $-1 < x < 0$ or $(1/2)\pi < \theta < \pi$, due to the presence of $\theta(-x)$ in (3.32). We want to assess the relative importance of the terms in (7.13). Consider first *low densities*. The recollision term can be obtained directly from (7.15) and (3.22), and yields[32]

$$\begin{aligned} c_R &= \frac{-8\Gamma(d/2)}{15\sqrt{\pi}\, d\Gamma((d-1)/2)}\int_0^1 dx\,(1-x^2)^{(d-3)/2} x^4\, {}_2F_1\!\left(\frac{1}{2},\frac{1}{2};\frac{7}{2};\frac{x^2}{2}\right) \\ &= -\frac{4}{5d^2(d+2)}\, {}_3F_2\!\left(\frac{1}{2},\frac{1}{2},\frac{5}{2};\frac{7}{2},\frac{d+4}{2};\frac{1}{4}\right) \end{aligned} \tag{7.16}$$

The hypergeometric function is again close to 1 (within 2%) for all values of d, and we find

$$\begin{aligned} c_R &= -0.018\ 02 \qquad (d=3) \\ &= -0.050\ 79 \qquad (d=2) \end{aligned} \tag{7.17}$$

At low densities the single overlap term (7.14) reduces to

$$c_S = \frac{-2\sqrt{\pi}\,\Gamma(d/2)}{d\Gamma((d-1)/2)}\int_{1/2}^1 dx\,(1-x^2)^{(d-3)/2} W_E(x) \tag{7.18}$$

We have not been able to evaluate (7.18) any further for general d, but for $d = 3$ it can be evaluated analytically in terms of elementary functions, and for $d = 2$ in terms of incomplete elliptic integrals. The numerical values are

$$\begin{aligned} c_S &= 0.028\,91\,5 \qquad (d = 3) \\ &= 0.054\,31 \qquad (d = 2) \end{aligned} \tag{7.19}$$

which can be obtained most easily by integration of the first few terms of the fast converging hypergeometric series. We have also obtained the first density corrections to the previous result using the density expansion[33] of $g_3(x)$ and χ with the result

$$\begin{aligned} c &= 0.238\,729 - 0.010\,60\frac{V_0}{V} + O(n^2) \quad (d = 3) \\ c &= 0.519\,315 - 0.005\,858\frac{V_0}{V} + O(n^2) \quad (d = 2) \end{aligned} \tag{7.20}$$

where V_0 is the close-packed volume, and

$$\frac{V_0}{V} = \begin{cases} (1/2)\sqrt{2}\,n\sigma^3 & (d = 3) \\ (1/2)\sqrt{3}\,n\sigma^2 & (d = 2) \end{cases} \tag{7.21}$$

The results (7.20) indicate that c depends weakly on the density and is dominated by the Enskog contribution given in (7.11) and (7.12).

7.4. Molecular Dynamics Result

For three dimensions and high fluid densities the triplet correlation function $g_3(x)$ with $x = \cos\theta$ has been studied in the literature.[34–36] For angles θ with $2\pi/3 \leqslant \theta \lesssim \pi$ one finds $g_3(x) \simeq \chi^2$, while for angles close to $\theta = \pi/3$ the result is $g_3(x) \simeq \chi^3$. The factor χ varies monotonically from $\chi = 1$ to $\chi \simeq 5$ for the typical liquid density $V_0/V = 0.625$.

Owing to this behavior of $g_3(x)$ and owing to the form of $W_R(x)$, as given in Fig. 2, we find c_R in (7.13) to be almost independent of the density. Therefore the ring correction c_R is small compared to c_E for *all* densities.

We find a somewhat stronger density dependence for c_S. This is due to the form of $W_E(x)$ (cf. Fig. 2) and the fact that $g_3(x) = \chi^3$ for $\theta \simeq \pi/3$.

In Fig. 3 $\Delta c = c - c_E$ is given as function of the density for $d = 3$. The result shows that the correction terms in (7.13) are small compared to c_E for *all* densities.

The theoretical prediction agrees reasonably well with experimental values for Δc, obtained from molecular dynamics experiments for $C(t)$ by Wood and Erpenbeck.[37]

It follows furthermore from Fig. 3 that for short times and low and intermediate densities the function $C(t) - C_E(t)$ will be positive while at

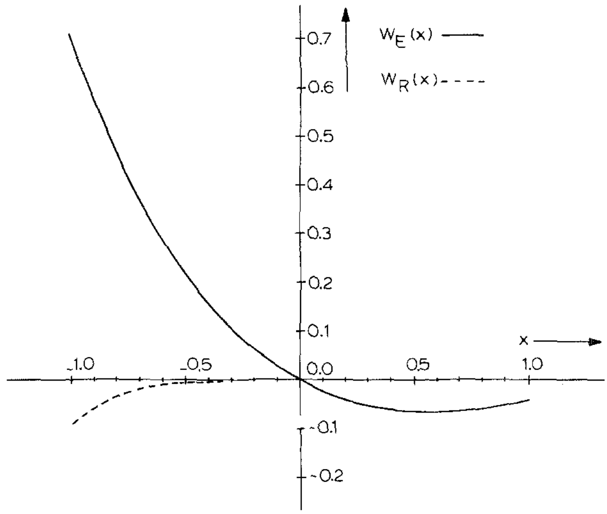

Fig. 2. The weight functions $W_E(x)$ and $W_R(x)$ as functions of $x = \cos\theta$. $W_E(x)$ appears in Eq. (7.14) and $W_R(x)$ in Eq. (7.15).

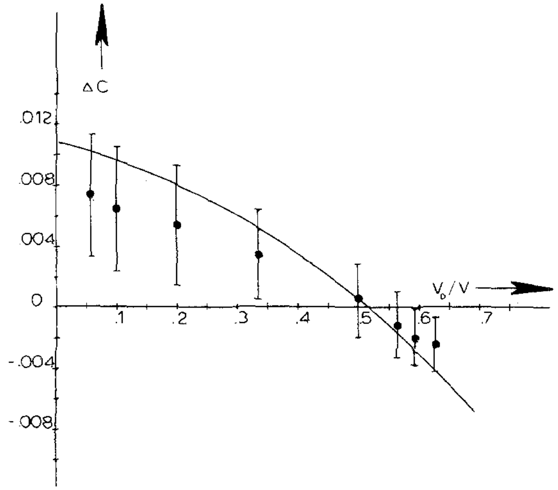

Fig. 3. The deviation $\Delta c = c - c_E$ of the exact coefficient c appearing in Eq. (7.5) from its corresponding Enskog value $c_E = 0.2278$ as a function of reduced density for a three-dimensional fluid of hard spheres. V_0 is the close-packed volume and $V_0/V = n\sigma^3/\sqrt{2}$. The curve represents the result of Eq. (7.6). The black circles are extracted from molecular dynamics data for $C(t)$ by Wood and Erpenbeck.[37]

high densities it will be negative. This effect has been observed in molecular dynamics experiments by Alder *et al.*[38] and might be related to the so-called "cage" effect, i.e., the occurrence of negative values of $C(t)$ at high densities and $t \simeq t_E$.

8. DISCUSSION

1. The results for the short-time expansion obtained in this paper apply to hard-sphere fluids and are valid for all densities, all values of k, and dimensionalities $d \geqslant 2$. We have calculated explicitly the coefficients of t^n in the short-time expansion of the incoherent scattering function $F(k,t)$ $(n = 0, 1, 2, 3, 4)$, the closely related coefficients [see Eq. (2.7)] for the velocity correlation function $C(t)$ $(n = 0, 1, 2)$, where the last coefficient in each case is a new result, as well as the explicit form of the dominant short-time behavior of all cumulants $\gamma_n(t)$ of the displacement of a tagged hard sphere.

(a) The coefficients (3.33) for $F(k,t)$ up to $|t|^3$, and the corresponding coefficients (3.34) for $C(t)$ up to $|t|$ agree with results given in the literature.[10, 11, 14, 15] The coefficient of t^2 in the expansion (3.34) for $C(t)$ differs from an early result derived by Résibois and Lebowitz in Refs. 18 and 19, where the ring events were overlooked (see 1d). In a later publication[21] these authors agree with the expression (3.34) for $C(t)$ which has been published before in Ref. 22.

(b) The most conspicuous difference in the short-time expansions of $F(k,t)$, $C(t)$, and $\gamma_n(t)$ between hard-core and smooth interaction potentials is the appearance of odd powers of t for hard-sphere fluids, while for soft potentials only even powers of t are present. Thus for hard spheres $\beta m C(t) = 1 - 2|t|/dt_E + c(t/t_E)^2 + \cdots$ in (7.5), while for smooth potentials $\beta m C(t) = 1 - \alpha_1 t^2/\beta m + \alpha_2 t^4/(\beta m)^2 + \cdots$ in (5.8). The coefficient c [Eqs. (7.8), (7.13–7.15)] involves the static triplet distribution function of three spheres in contact, $g_3(x)$, and the dynamical weight functions $W_E(x)$ and $W_R(x)$. The coefficient α_1 for smooth potentials contains the static pair distribution function and derivatives of the pair potential, and α_2 contains in addition the triplet function. Both coefficients diverge if the smooth potential approaches the hard-core potential (see Refs. 12 and 13 and Section 5.3). The hard-sphere results can be considered as a resummation of the most divergent terms in the hard-core limit of the corresponding expansions for smooth potentials, and Sears[13] has given the first few (most divergent) terms which have to be resummed. A similar comparison can be made for the hard-sphere expansion (3.33) for $F(k,t)$ with the corresponding one for smooth potentials.[13]

(c) Apart from the first cumulant or mean square displacement $\gamma_1(t)$

$= (1/2)\langle\Delta_x^2\rangle_0 = \int_0^t dt' \int_0^{t'} dt''\, C(t'')$, which is covered by the previous discussion, the higher cumulants $\gamma_n(t)$ $(n \geqslant 2)$ for *smooth* potentials are $\gamma_n(t) = \eta_n t^{4n}[1 + O(t^2)]$, where η_2 has been calculated by Sears.[13] For a *hard-sphere* fluid the dominant short-time behavior is $\gamma_n(t) = \xi_n |t|^{2n+1}/(2n+1)!$, with ξ_n given in (6.26).

(d) Our method for obtaining these expansions resembles closely those for smooth potentials [see Eq. (2.1)]. However, for hard spheres the matrix elements $\langle aL_+^n\, b\rangle_0$ do not exist in general, e.g., if a and b both depend on positions and velocities of the N particles, $\langle aL_+\, b\rangle_0$ exists, but $\langle aL_+^2\, b\rangle_0$ does not. The reason is that L_+^2 contains terms of the form $T_+(12)T_+(12)$, which contains products of δ functions with the same argument $(\mathbf{r}_{12} - \sigma\hat{\sigma})$. However, $d^2C_{ab}(t)/dt^2 = \langle aL_+\, e^{tL_+} L_+\, b\rangle_0$ does exist, and has a finite limit for $t \to 0+$. In particular, we find the unexpected result that the so-called recollision contribution, i.e., $\langle aT_+(12)\int_0^t d\tau\, e^{\tau L_0} T_+(13)\, e^{(t-\tau)L_0} T_+(12) b\rangle_0$, which looks formally of $O(t)$, has a finite *nonvanishing* limit as $t \to 0+$, as is shown in Appendix B. For general collision sequences we have given estimates of the short-time behavior in Section 4.

2(a) In order to discuss the region of times for which the short-time expansions are meaningful, we consider the time scales t_E, t_σ, and t_k: $t_E = t_0/\chi$ is the mean free time, and t_0, given in (2.18), is its low-density Boltzmann limit; $t_\sigma = \sigma(\beta m)^{1/2}$ and $t_k = (\beta m)^{1/2}/k$ are the average times needed to traverse the diameter σ and the inverse wave vector k^{-1}, respectively. Next, we write (3.33) as

$$F(k,t) = 1 - \frac{1}{2}\left(\frac{t}{t_k}\right)^2 + \frac{1}{3d}\left(\frac{t}{t_k}\right)^2 \frac{|t|}{t_E} + \frac{1}{8}\left(\frac{t}{t_k}\right)^4 - \frac{c}{12}\left(\frac{t}{t_k}\right)^2\left(\frac{t}{t_E}\right)^2 + O(t^5) \tag{8.1}$$

where c is given in (7.6). It is clear that the short-time expansion (8.1) is only valid for times t, such that

$$\begin{aligned} |t| &\lesssim t_E \\ |t| &\lesssim t_k \end{aligned} \tag{8.2}$$

However, there is an additional restriction, used in the derivation of c [see Appendix B, discussion preceding Eq. (B4)], i.e., $\langle v\rangle t$ must be small compared to the range σ of the static triplet distribution function, or

$$|t| \lesssim t_\sigma \tag{8.3}$$

For low densities $t_\sigma \ll t_E \simeq t_0$, while for liquid densities $t_E \ll t_\sigma$. For typical neutron-scattering experiments $(1/20)t_\sigma \lesssim t_k \lesssim t_\sigma$. The time scale t_k is absent in the expansions of $C(t)$ and $\gamma_n(t)$, since $k = 0$, so that $t_k \to \infty$. (Compare also the discussion in Section 5.3, on the average time t_s needed to traverse the steep part of a strongly repulsive potential.)

(b) We note that the restriction $t \lesssim t_k$ on (8.1) can be overcome by summing all terms in (8.1) of the form $(t/t_k)^n(t/t_E)^m$ over n, for given (fixed) values of m. In fact this was done in Section 6.2 for $m = 0$ and $m = 1$, where the result (6.23) can be written as (with $kt = (\beta m)^{1/2}t/t_k$)

$$F(k,t) = \exp\left[-\frac{1}{2}\left(\frac{t}{t_k}\right)^2\right]\left[1 + \frac{|t|}{t_E}h\left(\frac{t}{t_k}\right) + O\left(\left(\frac{t}{t_E}\right)^2\right)\right] \tag{8.4}$$

The leading term represents the ideal gas contribution, while $h(s)$ arises from one-collision events and is for all $s = t/t_k$ given by

$$h(s) = \frac{1}{3d}s^2\,{}_2F_2\left(\frac{1}{2},\frac{3}{2};\frac{5}{2},\frac{d+2}{2};\frac{s^2}{4}\right) \tag{8.5}$$

Hence (8.4) holds for all $t \lesssim t_E$ and $t \lesssim t_\sigma$.

(c) The restriction (8.3) on (8.1) has a curious consequence on the short-time expansions in the so-called Grad limit (i.e., $\sigma \to 0$, $n \to \infty$, such that t_0 or $n\sigma^{d-1}$ are finite); namely, taking the Grad limit and short-time limit in different orders yields different results. Van Beijeren *et al.*[27] have shown rigorously that $C(t)$ approaches in the Grad limit the prediction $C_B(t)$ from the Boltzmann equation, with $\beta m C_B(t) = \langle v_x e^{\Lambda_B^s t} v_x\rangle$ and Λ_B^s defined by (7.2a) (and $\chi = 1$.).

By performing now a short time expansion, one finds $\beta m C_B(t) = 1 - (2/3)(|t|/t_0) + c_E(t/t_0)^2$, where the results of Section 7.2 have been used.

However, taking the Grad limit after the short-time expansion has been performed [see (7.5)], one obtains a *different* result, namely, c_E replaced by $c_E + \Delta c$, where $\Delta c = c_S + c_R$ is given in the Grad limit by the low-density results (7.16) and (7.18). The reason for this difference is, of course, that the short-time expansion (7.5) is not valid in the Grad limit, since $t_\sigma \to 0$.

3. Interesting results are also the high-frequency tail $\sim 1/\omega^4$ in Eq. (5.3) of the incoherent scattering function $S(k,\omega)$ for the hard-sphere fluid in Section 5, and the adjusted sum rule (5.6) for the fourth frequency moment of $S(k,\omega)$. In Section 5.3 an estimate of the frequency range is given where the hard-sphere tail $\sim 1/\omega^4$ might be expected in noble gases. It is argued that this frequency tail is *not* expected in noble gases at *liquid densities*, but only at *lower* densities.

4. In Section 7 we have compared the exact results with their analogues in Enskog's theory of a hard-sphere fluid. We found that the predictions from Enskog's theory for $F(k,t)$, $C(t)$, and all $\gamma_n(t)$ give the first correction (proportional to t_E^{-1}) to the ideal gas behavior exactly. A comparison of the next correction term (proportional to t_E^{-2}) for $C(t)$ in three dimensions revealed that the Enskog prediction is amazingly close to the exact result for this term for all densities (cf. Fig. 3).

5. The methods used in this paper can be applied straightforwardly to

the calculations of other time correlation functions for the hard-sphere fluid, such as the coherent scattering function and the current–current correlation functions entering in the Green–Kubo formulas.

APPENDIX A: CALCULATION OF $V_1(x)$ AND $V_2(x)$

In Eq. (3.16) we introduced

$$V_1(\hat{\sigma}_1\cdot\hat{\sigma}_2)=(\beta m)^2\Big\langle\Big\langle\Big\langle\theta(\mathbf{v}_{12}\cdot\hat{\sigma}_1)\theta(\mathbf{v}_{31}\cdot\hat{\sigma}_2)(\mathbf{v}_{12}\cdot\hat{\sigma}_1)^2(\mathbf{v}_{31}\cdot\hat{\sigma}_2)^2\Big\rangle\Big\rangle\Big\rangle \tag{A1}$$

which should be evaluated for two-dimensional velocity vectors $\mathbf{v}_i$ ($i=1,2,3$), as explained below Eq. (3.15). The velocity averages $\langle\langle\langle\cdots\rangle\rangle\rangle$ are defined in (2.15). We further change to dimensionless variables $[(1/2)\beta m]^{1/2}\mathbf{v}_i\to\mathbf{v}_i$, and introduce new integration variables

$$\begin{aligned}\mathbf{V}&=(1/3)(\mathbf{v}_1+\mathbf{v}_2+\mathbf{v}_3)\\ \mathbf{u}&=\mathbf{v}_{12}=\mathbf{v}_1-\mathbf{v}_2\\ \mathbf{w}&=\mathbf{v}_{31}=\mathbf{v}_3-\mathbf{v}_1\end{aligned} \tag{A2}$$

for which the Jacobian equals 1. Since $\mathbf{v}_1^2+\mathbf{v}_2^2+\mathbf{v}_3^2=3\mathbf{V}^2+(2/3)(\mathbf{u}^2+\mathbf{w}^2+\mathbf{u}\cdot\mathbf{w})$ we can write (A1) as

$$\begin{aligned}V_1(\hat{\sigma}_1\cdot\hat{\sigma}_2)&=\frac{4}{3\pi^2}\int d\mathbf{u}\int d\mathbf{w}\exp\left[-(2/3)(\mathbf{u}^2+\mathbf{w}^2+\mathbf{u}\cdot\mathbf{w})\right]\\ &\quad\times\theta(\mathbf{u}\cdot\hat{\sigma}_1)\theta(\mathbf{w}\cdot\hat{\sigma}_2)(\mathbf{u}\cdot\hat{\sigma}_1)^2(\mathbf{w}\cdot\hat{\sigma}_2)^2\\ &=\frac{27}{4\pi^2}\int_0^\infty du_1\int_0^\infty dw_1\int_{-\infty}^{+\infty}du_2\int_{-\infty}^{+\infty}dw_2\,u_1^2w_1^2e^{-\Phi_1}\end{aligned} \tag{A3}$$

where we have performed the $\mathbf{V}$ integration. The vectors $\mathbf{u}$ and $\mathbf{w}$ are rescaled such that the factor $2/3$ in the exponent is replaced by 1; and $(u_1,u_2)=\mathbf{u}$ and $(w_1,w_2)=\mathbf{w}$ are Cartesian components along the axes $(\hat{\sigma}_1,\hat{\sigma}_{1\perp})$ and $(\hat{\sigma}_2,\hat{\sigma}_{2\perp})$, respectively, where $\hat{\sigma}_{i\perp}$ is a unit vector orthogonal to $\hat{\sigma}_i$, $\hat{\sigma}_1\cdot\hat{\sigma}_2=\cos\theta$, and the exponent Φ_1 has the form

$$\begin{aligned}\Phi_1&=\mathbf{u}^2+\mathbf{w}^2+\mathbf{u}\cdot\mathbf{w}\\ &=u_1^2+w_1^2+u_2^2+w_2^2+(u_1w_1+u_2w_2)\cos\theta+(w_2u_1-u_2w_1)\sin\theta\end{aligned} \tag{A4}$$

The integrations over u_2 and w_2 are Gaussian integrals which can be calculated most conveniently from the formula

$$\begin{aligned}&\int_{-\infty}^{+\infty}dx_1\cdots\int_{-\infty}^{+\infty}dx_n\exp\left(-\sum_{i,j=1}^{n}A_{ij}x_ix_j+\sum_{l=1}^{n}a_lx_l\right)\\ &\quad=\frac{\pi^{n/2}}{(\det A)^{1/2}}\exp\left(\frac{1}{4}\sum_{i,j=1}^{n}A_{ij}^{-1}a_ia_j\right)\end{aligned} \tag{A5}$$

Here $A = \{A_{ij}\}$ is a positive definite matrix; $A^{-1} = \{A_{ij}^{-1}\}$ is the inverse matrix, and $\det A$ its determinant. It can be derived easily by a transformation to principal axes. The resulting form for (A3) is

$$V_1(\cos\theta) = (16/\pi)\left[1 - (1/4)\cos^2\theta\right]^{5/2} S(\cos\theta) \tag{A6}$$

with

$$S(x) = \int_0^{\infty} du \int_0^{\infty} dw\, u^2 w^2 e^{-u^2 - w^2 - xuw} \tag{A7}$$

In going from (A3) to (A6–A7) the variables $u = \alpha u_1$, and $w = \alpha w_1$ are rescaled with

$$\alpha^2 = \frac{3}{4\det A} = \frac{3}{4}\left(1 - \frac{1}{4}\cos^2\theta\right)^{-1} \tag{A8}$$

Finally, the integral in (A7) can be performed by changing to polar coordinates, and we find

$$S(x) = \frac{1}{8}\left(1 - \frac{1}{4}x^2\right)^{-5/2}\left[\left(1 + \frac{1}{2}x^2\right)\cos^{-1}\frac{x}{2} - \frac{3}{2}x\left(1 - \frac{1}{4}x^2\right)^{1/2}\right] \tag{A9}$$

Combination of (A9) and (A6) yields expression (3.16) for $V_1(x)$, i.e.,

$$V_1(x) = \frac{2}{\pi}\left[\left(1 + \frac{1}{2}x^2\right)\cos^{-1}\frac{x}{2} - \frac{3}{2}x\left(1 - \frac{1}{4}x^2\right)^{1/2}\right] \tag{A10a}$$

$$= 1 + \frac{1}{2}x^2 - \frac{4x}{\pi}\,{}_2F_1\left(-\frac{1}{2}, -\frac{1}{2}; \frac{3}{2}; \frac{x^2}{4}\right) \tag{A10b}$$

as given in the body of the paper. Here ${}_2F_1$ is Gauss hypergeometric function[31] defined as

$${}_2F_1(a, b; c; x) = \sum_{n=0}^{\infty} \frac{(a)_n (b)_n}{(c)_n} \frac{x^n}{n!} \tag{A11}$$

and $(a)_n = a(a+1)\cdots(a+n-1)$ is a Pochhammer symbol. The expression (A10b) in terms of the Gauss hypergeometric function is very helpful in performing later integrations over x. It can be derived most conveniently by dividing $S(x)$ in (A7) into an even part $S_e(x)$ and an odd part $S_0(x)$ in x. The even part of (A7) yields directly $[1 + (1/2)x^2]$ in (A10b). In $S_0(x)$ we expand the odd part of e^{-uwx} in powers of x. A term by term integration yields

$$\begin{aligned} S_0(x) &= -\frac{x}{4}\,{}_2F_1\left(2, 2; \frac{3}{2}; \frac{x^2}{4}\right) \\ &= -\frac{x}{4}\left(1 - \frac{x^2}{4}\right)^{-5/2} {}_2F_1\left(-\frac{1}{2}, -\frac{1}{2}; \frac{3}{2}; \frac{x^2}{4}\right) \end{aligned} \tag{A12}$$

where the last equality is a linear transformation formula for ${}_2F_1$.[31]

Next, we consider $V_2(x)$, defined in (3.24):

$$V_2(\hat{\sigma}_1 \cdot \hat{\sigma}_2) = (\beta m)^2 \left\langle \left\langle \left\langle \theta(\mathbf{v}_{12} \cdot \hat{\sigma}_1)\theta(-\mathbf{v}_{1'2} \cdot \hat{\sigma}_1)(\mathbf{v}_{12} \cdot \hat{\sigma}_1)^2(\mathbf{v}_{1'2} \cdot \hat{\sigma}_1)^2 \right\rangle \right\rangle \right\rangle \tag{A13}$$

with $\mathbf{v}_{1'2} = \mathbf{v}_{12} + \hat{\sigma}_2(\hat{\sigma}_2 \cdot \mathbf{v}_{31}) \equiv \mathbf{u}'$. It is only needed for $\hat{\sigma}_1 \cdot \hat{\sigma}_2 < 0$. The calculation closely parallels that of (A1). We introduce again $(u_1, u_2) = \mathbf{u}$ as below (A3), but (w_1, w_2) are defined differently, i.e.,

$$\begin{aligned} w_1 &= -\mathbf{u}' \cdot \hat{\sigma}_1 = \mathbf{u} \cdot \hat{\sigma}_1 - (\hat{\sigma}_1 \cdot \hat{\sigma}_2)(\hat{\sigma}_2 \cdot \mathbf{w}) \\ w_2 &= \mathbf{w} \cdot \hat{\sigma}_{2\perp} \end{aligned} \tag{A14}$$

so that $d\mathbf{w} = dw_1\, dw_2 / |\hat{\sigma}_1 \cdot \hat{\sigma}_2|$. Hence (A12) becomes

$$V_2(\hat{\sigma}_1 \cdot \hat{\sigma}_2) = \frac{27}{4\pi^2 |\hat{\sigma}_1 \cdot \hat{\sigma}_2|} \int_0^\infty du_1 \int_0^\infty dw_1 \int_{-\infty}^\infty du_2 \int_{-\infty}^\infty dw_2\, u_1^2 w_1^2 e^{-\Phi_2} \tag{A15}$$

where

$$\begin{aligned} \Phi_2 &= \mathbf{u}^2 + \mathbf{w}^2 + \mathbf{u} \cdot \mathbf{w} = u_2^2 + w_2^2 + u_2 w_2 \cos\theta \\ &\quad + \frac{(w_1 + u_1)^2}{\cos^2\theta} - u_1 w_1 + u_2(w_1 + u_1)\tan\theta - u_1 w_1 \sin\theta \end{aligned} \tag{A16}$$

In deriving the last expression we need the inverse transformation of (A14). The $(u_2 w_2)$ integrations are again Gaussian, which may be performed using (A5), and the result is

$$V_2(\cos\theta) = (16/\pi)|\cos\theta|^5 \left[1 - (1/4)\cos^2\theta\right]^{5/2} S(2 - \cos^2\theta) \tag{A17}$$

where $S(x)$ is defined in (A7). Finally, we arrive at Eq. (3.26) in the body of the paper, which is only needed for $x < 0$,

$$\begin{aligned} V_2(x) &= V_1(2 - x^2) \\ &= -\frac{2}{\pi}(6 - 4x^2 + x^4)\sin^{-1}\frac{x}{2} + \frac{3x}{\pi}(2 - x^2)\left(1 - \frac{x^2}{4}\right)^{1/2} && \text{(A18a)} \\ &= -\frac{8}{15\pi} x^5 {}_2F_1\left(\frac{1}{2}, \frac{1}{2}; \frac{7}{2}; \frac{x^2}{4}\right) && \text{(A18b)} \end{aligned}$$

where we have used

$$\frac{\cos^{-1}\left[1 - (1/2)x^2\right]}{2|x|} = \frac{\sin^{-1}(x/2)}{x} \tag{A19}$$

Expression (A18b) can be derived from (A10b) by using linear and quadratic transformation formulas for ${}_2F_1$.[31]

APPENDIX B: RECOLLISION DYNAMICS

Consider the recollision operator, occurring in Eq. (3.21) for short times ($t > 0$), i.e.,

$$R(t) = \int_0^t dt_1 \left[T_-(12)\alpha(\mathbf{v}_1)\exp(i\mathbf{k}\cdot\mathbf{r}_1) \right] \exp\left[(t-t_1)L_0 \right] T_+(13)$$
$$\times \exp(t_1 L_0) T_+(12)\, \beta(\mathbf{v}_1)\exp(-i\mathbf{k}\cdot\mathbf{r}_1) \tag{B1}$$

where $\alpha(\mathbf{v})$ and $\beta(\mathbf{v})$ are arbitrary functions of the velocities. The operator $T_+(13)$ contains the factor $[b_{\hat{\sigma}_2}(13) - 1]$, the first term of which changes the directions of the vectors $\mathbf{v}_1$, $\mathbf{v}_3$, the second term leaves the directions unchanged and vanishes on account of Eq. (3.20). Hence, we find from (1.11)

$$R(t) = \sigma^{3d-3} \int_0^t dt_1 \int d\hat{\sigma}_1 \int d\hat{\sigma}_2 \int d\hat{\sigma}_3 \delta(\mathbf{r}_{12} - \sigma\hat{\sigma}_1)\delta(\mathbf{r}_{13} + \mathbf{v}_{13}(t-t_1) - \sigma\hat{\sigma}_2)$$
$$\cdot \delta(\mathbf{r}_{12} + \mathbf{v}_{1'2}t_1 + \mathbf{v}_{12}(t-t_1) - \sigma\hat{\sigma}_3)\theta(\mathbf{v}_{12}\cdot\hat{\sigma}_1)\mathbf{v}_{12}\cdot\hat{\sigma}_1$$
$$\cdot \Delta_\alpha(\hat{\sigma}_1, \mathbf{v}_1)\theta(-\mathbf{v}_{13}\cdot\hat{\sigma}_2)|\mathbf{v}_{13}\cdot\hat{\sigma}_2|\theta(-\mathbf{v}_{1'2}\cdot\hat{\sigma}_3)|\mathbf{v}_{1'2}\cdot\hat{\sigma}_3|\Delta_\beta(\hat{\sigma}_3, \mathbf{v}_1)$$
$$\cdot \exp\left[-i\mathbf{k}\cdot\mathbf{v}_{1'}t - i\mathbf{k}\cdot\mathbf{v}_1(t-t_1) \right] \tag{B2}$$

where we have used the relation $e^{tL_0}\mathbf{r}_i = \mathbf{r}_i + \mathbf{v}_i t$, and introduced

$$\mathbf{v}_{1'2} = \mathbf{v}_{1'} - \mathbf{v}_2$$
$$\mathbf{v}_{1'} = b_{\hat{\sigma}_2}(13)\mathbf{v}_1 = \mathbf{v}_1 + \hat{\sigma}_2(\hat{\sigma}_2\cdot\mathbf{v}_{31}) \tag{B3}$$
$$\Delta_\alpha(\hat{\sigma}_1, \mathbf{v}_1) = \left[b_{\hat{\sigma}_1}(12) - 1 \right]\alpha(\mathbf{v}_1)$$

and similarly for Δ_β. Notice that the first and third θ functions in (B2) automatically guarantee that $\theta(-\mathbf{v}_{13}\cdot\hat{\sigma}_2) = 1$. The first two delta functions in (B2) require that the triplet function in (3.21), i.e.,

$$g(\mathbf{r}_1, \mathbf{r}_1 - \mathbf{r}_{12}, \mathbf{r}_1 - \mathbf{r}_{13}) = g(\mathbf{r}_1, \mathbf{r}_1 - \sigma\hat{\sigma}_1, \mathbf{r}_1 - \sigma\hat{\sigma}_2 + \mathbf{v}_{13}(t-t_1))$$

is only needed for configurations $|\mathbf{r}_{13}| = |\sigma\hat{\sigma}_2 - \mathbf{v}_{13}(t-t_1)| > \sigma$, where it is a *smooth* function of the argument $\mathbf{r}_{13}$. Hence, for short times t ($t > t_1 > 0$) we may drop $\mathbf{v}_{13}(t-t_1)$ in the argument of the triplet function as well as in the argument of the second δ function in (B2). This implies the neglect of terms $O(t)$, and so does the replacement $\exp(i\mathbf{k}\cdot\mathbf{v}_{1'}t - i\mathbf{k}\cdot\mathbf{v}_1(t-t_1))$ by 1. Owing to these replacements the short-time expansion is valid only for $t < t_\sigma$ and $t < t_k$ where $t_\sigma = (\beta m)^{1/2}\sigma$ and $t_k = (\beta m)^{1/2}/k$ are the average times needed to traverse the diameter σ and the inverse wave vector k, respectively. Our next step is to perform the integrations over t_1 and $\hat{\sigma}_3$, i.e., we have to calculate an integral of the type

$$I = \sigma^{d-1} \int_0^t dt_1 \int d\hat{\sigma}_3\, \delta\left[\sigma\rho(t_1) - \sigma\hat{\sigma}_3 \right] f(\hat{\sigma}_3) \tag{B4}$$

with

$$\rho(t_1) = \hat{\sigma}_1 + \mathbf{v}_{1'2}t_1/\sigma + \mathbf{v}_{12}(t - t_1)/\sigma \tag{B5}$$

The d-dimensional delta function $\delta^{(d)}$ can be written as

$$\delta^{(d)}[\rho(t_1) - \hat{\sigma}_3] = \delta^{(1)}(|\rho(t_1)| - 1)\delta^{(d-1)}[\hat{\sigma}_3 - \hat{\rho}(t_1)] \tag{B6}$$

where $\delta^{(1)}$ ensures that $\hat{\rho}(t_1)$ is a unit vector. For small t ($t > t_1$) the argument of $\delta^{(1)}$ becomes

$$|\rho(t_1)| - 1 = \frac{1}{\sigma}[\hat{\sigma}_1 \cdot \mathbf{v}_{1'2}t_1 + \hat{\sigma}_1 \cdot \mathbf{v}_{12}(t - t_1)] + O(t^2) \tag{B7}$$

By virtue of (B3) and (B5) we have to dominant order for small t

$$\delta^{(1)}(|\rho(t_1)| - 1) = \frac{\sigma}{|(\hat{\sigma}_1 \cdot \hat{\sigma}_2)(\hat{\sigma}_2 \cdot \mathbf{v}_{13})|}\delta^{(1)}\left[t_1 - \frac{\hat{\sigma}_1 \cdot \mathbf{v}_{12}t}{(\hat{\sigma}_1 \cdot \hat{\sigma}_2)(\hat{\sigma}_2 \cdot \mathbf{v}_{13})}\right]$$

$$\delta^{(d-1)}[\hat{\sigma}_3 - \hat{\rho}(t_1)] = \delta^{(d-1)}(\hat{\sigma}_3 - \hat{\sigma}_1) \tag{B8}$$

so that (B4) becomes

$$I = \frac{1}{|\hat{\sigma}_1 \cdot \hat{\sigma}_2|\,|\hat{\sigma}_2 \cdot \mathbf{v}_{13}|}\theta\left[\frac{\hat{\sigma}_1 \cdot \mathbf{v}_{12}}{(\hat{\sigma}_1 \cdot \hat{\sigma}_2)(\hat{\sigma}_2 \cdot \mathbf{v}_{13})}\right]\theta\left[\frac{-\hat{\sigma}_1 \cdot \mathbf{v}_{1'2}}{(\hat{\sigma}_1 \cdot \hat{\sigma}_2)(\hat{\sigma}_2 \cdot \mathbf{v}_{13})}\right]f(\hat{\sigma}_1) \tag{B9}$$

The two θ functions come from the t_1 integration, where it is required that $0 < t_1 = at < t$ and where we have used (B3). Since (B9) has to be used inside (B2), the conditions $\mathbf{v}_{12} \cdot \hat{\sigma}_1 > 0$ and $\mathbf{v}_{1'2} \cdot \hat{\sigma}_1 < 0$ guarantee that (B9) reduces to

$$I = \frac{\theta(-\hat{\sigma}_1 \cdot \hat{\sigma}_2)}{|\hat{\sigma}_1 \cdot \hat{\sigma}_2|\,|\hat{\sigma}_2 \cdot \mathbf{v}_{13}|}f(\hat{\sigma}_1) \tag{B10}$$

Using all the above information in (B2) we find for the recollision operator

$$\begin{aligned} R(t) = {} & \sigma^{2d-2}\int d\hat{\sigma}_1 \int d\hat{\sigma}_2 \delta(\mathbf{r}_{12} - \sigma\hat{\sigma}_1)\delta(\mathbf{r}_{13} - \sigma\hat{\sigma}_2)\frac{\theta(-\hat{\sigma}_1 \cdot \hat{\sigma}_2)}{|\hat{\sigma}_1 \cdot \hat{\sigma}_2|} \\ & \cdot \theta(\mathbf{v}_{12} \cdot \hat{\sigma}_1)\mathbf{v}_{12} \cdot \hat{\sigma}_1 \Delta_\alpha(\hat{\sigma}_1, \mathbf{v}_1)\theta(-\mathbf{v}_{1'2} \cdot \hat{\sigma}_1)|\mathbf{v}_{1'2} \cdot \hat{\sigma}_1|\Delta_\beta(\hat{\sigma}_1, \mathbf{v}_1) \\ & + O(t) \end{aligned} \tag{B11}$$

or, by using (B3), we find the result given in Eq. (3.22), i.e.,

$$\begin{aligned} R(t) = {} & \sigma^{2d-2}\int d\hat{\sigma}_1 \int d\hat{\sigma}_2 \delta(\mathbf{r}_{12} - \sigma\hat{\sigma}_1)\delta(\mathbf{r}_{13} - \sigma\hat{\sigma}_2)\frac{\theta(-\hat{\sigma}_1 \cdot \hat{\sigma}_2)}{|\hat{\sigma}_1 \cdot \hat{\sigma}_2|} \\ & \cdot \theta(\mathbf{v}_{12} \cdot \hat{\sigma}_1)\mathbf{v}_{12} \cdot \hat{\sigma}_1\{[b_{\hat{\sigma}_1}(12) - 1]\alpha(\mathbf{v}_1)\}b_{\hat{\sigma}_2}(13)\theta(-\mathbf{v}_{12} \cdot \hat{\sigma}_1)|\mathbf{v}_{12} \cdot \hat{\sigma}_1| \\ & \cdot \{[b_{\hat{\sigma}_1}(12) - 1]\beta(\mathbf{v}_1)\} + O(t) \end{aligned} \tag{B12}$$

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