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Hydrodynamic Correlation Functions of Hard-Sphere Fluids at Short Times

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The short-time behavior of the coherent intermediate scattering function for a fluid of hard-sphere particles is calculated exactly through order t^4, and the other hydrodynamic correlation functions are calculated exactly through order t^2. It is shown that for all of the correlation functions considered the Enskog theory gives a fair approximation. Also, the initial time behavior of various Green–Kubo integrands is studied. For the shear-viscosity integrand it is found that at density $n\sigma^3 = 0.837$ the prediction of the Enskog theory is 32% too low. The initial value of the bulk viscosity integrand is nonzero, in contrast to the Enskog result. The initial value of the thermal conductivity integrand at high densities is predicted well by Enskog theory.

KEY WORDS: Neutron scattering function; shear viscosity; bulk viscosity; thermal conductivity; Green–Kubo integrand; hard-sphere fluid; short-time expansion.

1. INTRODUCTION

Several kinetic theories can be based on short-time properties of correlation functions. Notably, linearized revised Enskog theory (RET)[(1)] may be obtained by extending the short-time decay of the one-particle distribution function to arbitrary times.[(2–4)] The same applies to the linearized version[(5)] of the square-well kinetic equations derived recently by Karkheck *et al.*[(6)]

Apart from this, exact short-time expansions of correlation functions are of importance as a reference point for checking more general, but necessarily approximate theories. Short-time estimates of Green–Kubo integrands may be helpful in the calculation of transport coefficients; in most cases the dominant contributions to Green–Kubo integrals come from a short-time interval.

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The pioneering work in this field was done by de Schepper and Cohen,[7] who calculated the velocity autocorrelation function of a hard-sphere fluid exactly through order t^2, thereby correcting a preceding calculation by Résibois.[8] A more detailed derivation was given by de Schepper *et al.*, (SEC)[9] who, moreover, extended this work to a calculation of the incoherent scattering function through order t^4.

Here we generalize the results of SEC so as to treat wavelength-dependent hydrodynamic correlation functions, such as the coherent intermediate scattering function. Comparing to RET, we find that the latter describes the wavelength dependence of the initial decay reasonably well. The limit of long wavelengths yields the initial values of the Green–Kubo integrands. Comparing again, we find RET to give good predictions for the initial values of the thermal conductivity integrand, but not so for the integrands of shear and bulk viscosity.

The plan of the paper is as follows: In Section 2 we introduce hydrodynamic time correlation functions, in Section 3 we identify several contributions to their short-time behavior and work out explicit expressions for these. In Section 4 we compute numerical results for a few densities and compare these to the predictions of Enskog theory. Concluding remarks are made in Section 5.

2. TIME CORRELATION FUNCTIONS

Consider a fluid of N classical hard-sphere particles of mass m and diameter σ at a temperature T confined in a volume V, so the density is $n = N/V$. Here we consider time correlation functions of the hydrodynamic densities, which can be distinguished into longitudinal and transverse ones. Transverse velocity correlations will be treated in Section 3.5.

Microscopic definitions of the longitudinal hydrodynamic densities are: the particle number density

$$\overline{n_k} = a_1 = \frac{1}{[NS(k)]^{1/2}} \sum_j \exp(i\mathbf{k}\mathbf{r}_j) \tag{2.1}$$

where $S(k) - 1$ is the Fourier transform of the pair correlation function; the longitudinal velocity and the microscopic temperature

$$v_k^l = a_2, \qquad T_k = a_3 \tag{2.2}$$

where

$$a_i = \frac{1}{\sqrt{N}} \sum_j [\exp(i\mathbf{k}\mathbf{r}_j)]\, \phi_i(\mathbf{v}_j), \qquad i \geqslant 2 \tag{2.3}$$

and

$$\phi_2(\mathbf{v}_j) = (\beta m)^{1/2}\,(\mathbf{v}_j \cdot \hat{\mathbf{k}}) \tag{2.4}$$

$$\phi_3(\mathbf{v}_j) = \frac{1}{\sqrt{6}}\,(\beta m \mathbf{v}_j^2 - 3) \tag{2.5}$$

where $\hat{\mathbf{k}} = \mathbf{k}/k$. We will also need $\phi_1(\mathbf{v}) = [S(k)]^{-1/2}$.

The longitudinal correlations can be arranged into the matrix $F_{ij}(k, t)$ correlating particle density, longitudinal velocity, and temperature to themselves and to each other

$$\begin{aligned} F_{ij}(k, t) &= \langle a_i \mid a_j(t) \rangle \equiv \langle a_i^* a_j(t) \rangle \\ &= \langle a_i^* e^{L^+ t} a_j \rangle \qquad (i, j = 1, 2, 3) \end{aligned} \tag{2.6}$$

Here $\langle \cdots \rangle$ denotes an average over the canonical ensemble ρ_N,

$$\langle \cdots \rangle = \int d\Gamma \rho_{N,\mathrm{eq}} \cdots \tag{2.7}$$

and L^+ is the forward streaming pseudo-Liouville operator[10] for hard spheres. The pseudo-Liouville operator consists of two terms

$$L^{\pm} = L_0 \pm L_c^{\pm} \tag{2.8}$$

Here

$$L_0 = \sum_i \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} \tag{2.9}$$

is the free streaming operator, which describes free particle motion, and

$$L_c^{\pm} = \sum_{i<j} T_{ij}^{\pm} \tag{2.10}$$

where

$$T_{ij}^{\pm} = \exp(L_0 0^{\pm})\,\delta(r_{ij} - \sigma)\,|\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}|\,\theta(\mp \mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij})(B_{ij} - 1) \tag{2.11}$$

is the collision operator. The operator $\exp(L_0 0^{\pm})$ is needed to define the behavior at discontinuities. The operator B_{ij} acts on functions of the velocities $\mathbf{v}_i$ and $\mathbf{v}_j$ by replacing their precollisional values by the postcollisional ones,

$$B_{ij} f(\mathbf{v}_i, \mathbf{v}_j) = f(\mathbf{v}_i', \mathbf{v}_j') \tag{2.12}$$

with

$$\mathbf{v}_i' = \mathbf{v}_i - \hat{\mathbf{r}}_{ij}(\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}) \tag{2.13a}$$

$$\mathbf{v}_j' = \mathbf{v}_j + \hat{\mathbf{r}}_{ij}(\mathbf{v}_{ij} \cdot \hat{\mathbf{r}}_{ij}) \tag{2.13b}$$

The function θ in (2.11) is the unit step function defined as $\theta(x) = 0$ if $x < 0$, and $\theta(x) = 1$ for $x \geqslant 0$.

The microscopic densities a_i are normalized in the sense that

$$F_{ij}(k, t=0) = \delta_{ij} \tag{2.14}$$

Between a_1 and a_2 we have the relation

$$\partial_t a_1 = L^+ a_1 = \frac{ik}{[\beta m S(k)]^{1/2}} a_2 \tag{2.15}$$

This implies that F_{i1} and F_{1i} can be found by taking the time integral of F_{i2} and F_{2i}, respectively. For this reason we will restrict ourselves to $i, j = 2, 3$ till the end of section 3.2.

Invariance of the equations of motion under time inversion yields the symmetry relation

$$F_{ij}(k, t) = \varepsilon_i \varepsilon_j F_{ji}^*(k, t) = F_{ji}(k, t) \tag{2.16}$$

where ε_i denotes the parity of a_i in velocity space. For the second equality to hold it is essential that F_{ij} is a complex matrix.

3. SHORT-TIME BEHAVIOR

This section closely follows the treatment of SEC.[9] Using the definition (2.6), we readily obtain

$$\partial_t F_{ij}(k, t)|_{t=0^+} = \langle a_i^*(L_0 + L_c) a_j \rangle \tag{3.1}$$

The right-hand side of this equation defines another matrix, consisting of matrix elements of L_0 and L_c, given explicitly in Eqs. (3.6) and (3.7). The second time derivatives at $t = 0^+$ are more delicate. To be careful, we consider the limit $t \to 0^+$ and obtain

$$\begin{aligned} \partial_t^2 F_{ij}(k, t)|_{t=0^+} &= \lim_{t \to 0^+} \langle a_i^* L^+ e^{L^+ t} L^+ a_j \rangle \\ &= -\langle (L_0 a_i^*)(L_0 a_j) \rangle \\ &\quad - \langle (L_0 a_i^*)(L_c^+ a_j) \rangle + \langle (L_c^- a_i^*)(L_0 a_j) \rangle \\ &\quad + \lim_{t \to 0^+} \langle (L_c^- a_i^*) e^{L^+ t} (L_c^+ a_j) \rangle \end{aligned} \tag{3.2}$$

Here we have used the Hermitean conjugates $L_0^\dagger = -L_0$, $(L_c^+)^\dagger = \bar{L}_c^-$, and the relation[10]

$$\bar{L}^- \rho_{N,\mathrm{eq}} = \rho_{N,\mathrm{eq}} L^- \tag{3.3}$$

Equation (3.2) consists of three physically different terms: one with L_0^2, called the kinetic–kinetic or simply kinetic term; one with $(L_0 L_c + L_c L_0)$, called the kinetic–potential or cross term; and the last one contains $L_c L_c$, and is called the potential–potential or simply potential term. The relative importance of these contributions depends both on density and wavenumber. For long wavelengths it is determined by the ratio of the mean free time t_e and the hard-sphere diameter traversal time $t_\sigma = \sigma(\beta m)^{1/2}$. For high densities $(n\sigma^3 > 0.3)$ the potential term is found to be largest. For shorter wavelengths, the potential and kinetic terms at high densities are of the same order when $kl_e \simeq 1$, where $l_e = [2^{1/2}\pi n\sigma^2 g(\sigma)]^{-1}$ is the mean free path.

For the first time derivatives of F_{ij} we need to know the matrix elements of the operators L_0 and L_c^+ on the basis (a_1, a_2, a_3). For the kinetic and cross term in (3.2) it is useful also to consider the matrix elements of L_0 and L_c^+ for the so-called kinetic currents, for if one knows these, the kinetic and cross terms can be obtained from a matrix multiplication. For the potential term this approach does not work out, as will become apparent further on. The kinetic currents can be obtained by letting L_0 act upon a_2 and a_3, projecting the resulting functions orthogonal to a_1, a_2, and a_3, and normalizing. One obtains the longitudinal part of the kinetic stress tensor a_4, defined through (2.3), with

$$\phi_4(\mathbf{v}) = \frac{\beta m}{\sqrt{12}} [3(\mathbf{v}\cdot\hat{\mathbf{k}})^2 - \mathbf{v}^2] \tag{3.4}$$

and the kinetic part of the heat current a_5, defined through

$$\phi_5(\mathbf{v}) = \left(\frac{\beta m}{10}\right)^{1/2} (\mathbf{v}\cdot\hat{\mathbf{k}})(\beta m \mathbf{v}^2 - 5) \tag{3.5}$$

The matrix elements of L_0 and L_c^+ on the basis $(a_1, a_2, a_3, a_4, a_5)$ follow from a lengthy, but straightforward calculation. They are given in the matrices

$$L_0 = \frac{ik}{(\beta m)^{1/2}} \begin{pmatrix} 0 & [S(k)]^{1/2} & 0 & 0 & 0 \\ 1/[S(k)]^{1/2} & 0 & \sqrt{\frac{2}{3}} & \frac{2}{\sqrt{3}} & 0 \\ 0 & \sqrt{\frac{2}{3}} & 0 & 0 & \sqrt{\frac{5}{3}} \\ 0 & \frac{2}{\sqrt{3}} & 0 & 0 & \sqrt{\frac{8}{15}} \\ 0 & 0 & \sqrt{\frac{5}{3}} & \sqrt{\frac{8}{15}} & 0 \end{pmatrix} \tag{3.6}$$

and

$$L_c^+ = \frac{1}{t_e}\begin{pmatrix} 0 & \dfrac{ikt_e}{(\beta m)^{1/2}}\dfrac{1-S(k)}{[S(k)]^{1/2}} & 0 & 0 & 0 \\ 0 & -\dfrac{2}{3}(1-j_0+2j_2) & i\left(\dfrac{\pi}{6}\right)^{1/2} j_1 & \dfrac{i}{5}\left(\dfrac{\pi}{3}\right)^{1/2}(2j_1-3j_3) & \dfrac{-1}{3\sqrt{10}}(1-j_0+2j_2) \\ 0 & i\left(\dfrac{\pi}{6}\right)^{1/2} j_1 & -\dfrac{2}{3}(1-j_0) & -\dfrac{2}{3}\cdot 2^{1/2} j_2 & \dfrac{i}{2}\left(\dfrac{3\pi}{5}\right)^{1/2} j_1 \\ 0 & \dfrac{i}{5}\left(\dfrac{\pi}{3}\right)^{1/2}(2j_1-3j_3) & -\dfrac{2}{3}\cdot 2^{1/2} j_2 & -\dfrac{16}{15}+\dfrac{4}{15}j_0-\dfrac{8}{21}j_2+\dfrac{24}{35}j_4 & \dfrac{i}{5}\left(\dfrac{3\pi}{10}\right)^{1/2}(2j_1-3j_3) \\ 0 & \dfrac{-1}{3\sqrt{10}}(1-j_0+2j_2) & \dfrac{i}{2}\left(\dfrac{3\pi}{5}\right)^{1/2} j_1 & \dfrac{i}{5}\left(\dfrac{3\pi}{10}\right)^{1/2}(2j_1-3j_3) & -\dfrac{59}{60}+\dfrac{27}{60}(j_0-2j_2) \end{pmatrix} \tag{3.7}$$

Here $j_n \equiv j_n(k\sigma)$ is a spherical Bessel function of the argument $k\sigma$, and t_e is the (Enskog) mean free time between two subsequent collisions,

$$t_e = \left(\frac{\beta m}{\pi}\right)^{1/2} \frac{1}{4n\sigma^2 g(\sigma)} \tag{3.8}$$

Here $n = N/V$, and $g(\sigma)$ is the pair correlation function at contact. Notice that, even though L_0 and L_c are not symmetric, their sum is symmetric, in agreement with (2.16). The matrix elements L_{44}, L_{45}, and L_{55} do not occur in the expressions for the second derivatives at $t = 0^+$, but we have given them for completeness.

There remains the potential part

$$F_{ij}^p = \lim_{t \to 0^+} \langle (L_c^- a_i^*)\, e^{L^+ t}(L_c^+ a_j) \rangle \tag{3.9}$$

This term is considerably more difficult than the kinetic or the cross term, due to the contributions from correlated collision sequences. The same difficulty was encountered and resolved by de Schepper and Cohen[7] in their calculation of the t^2 term in the expansion of the velocity autocorrelation. A more detailed treatment has been given by SEC. Here we extend their calculations, considering all wavelength-dependent hydrodynamic correlation functions.

Using the definitions of a_i and L_c, we find

$$F_{ij}^{p} = \lim_{t \to 0^+} \left\langle (N-1)\left(\sum_{a<b} T_{ab}^{-}\{[\exp(-i\mathbf{k}\cdot\mathbf{r}_a)]\,\phi_i(\mathbf{v}_a) + [\exp(-i\mathbf{k}\cdot\mathbf{r}_b)]\,\phi_i(\mathbf{v}_b)\}\right) \times [\exp(L^+ t)]\{T_{12}^{+}[\exp(i\mathbf{k}\cdot\mathbf{r}_1)]\,\phi_j(\mathbf{v}_1)\} \right\rangle \tag{3.10}$$

where we have used that $T_{12}\phi(\mathbf{v}_3)=0$. We split F_{ij}^{p} into three terms, one where $(a, b)=(1, 2)$ and one where a equals either 1 or 2 and b is larger than 2, and a term where both a and b are larger than 2. So

$$F_{ij}^{p} = F_{ij}^{(2)} + F_{ij}^{(3)} + F_{ij}^{(4)} \tag{3.11}$$

For the three-particle term we may take $b=3$ in (3.10). The limit $t \to 0^+$ can be taken without complications and we find

$$F_{ij}^{(3)} = \langle (N-1)(N-2)(T_{13}^{-}\{\phi_i(\mathbf{v}_1) + [\exp(i\mathbf{k}\cdot\mathbf{r}_{13})]\,\phi_i(\mathbf{v}_3)\} + T_{23}^{-}\{\phi_i(\mathbf{v}_2)\exp(i\mathbf{k}\cdot\mathbf{r}_{12}) + \phi_i(\mathbf{v}_3)\exp(i\mathbf{k}\cdot\mathbf{r}_{13})\})[T_{12}^{+}\phi_j(\mathbf{v}_1)]\rangle \tag{3.12}$$

The four-particle contribution is given by

$$F_{ij}^{(4)} = \langle (N-1)(N-2)(N-3)(T_{34}^{-}\{[\exp(-i\mathbf{k}\cdot\mathbf{r}_3)]\,\phi_i(\mathbf{v}_3)\}) \times \{T_{12}^{+}[\exp(i\mathbf{k}\cdot\mathbf{r}_1)]\,\phi_j(\mathbf{v}_1)\}\rangle \tag{3.13}$$

and the two-particle contribution is

$$F_{ij}^{(2)} = \lim_{t \to 0^+} \langle (N-1)(T_{12}^{-}\{[\exp(-i\mathbf{k}\cdot\mathbf{r}_1)]\,\phi_i(\mathbf{v}_1) + [\exp(-i\mathbf{k}\cdot\mathbf{r}_2)]\,\phi_i(\mathbf{v}_2)\}) \times [\exp(L^+ t)]\{T_{12}^{+}[\exp(i\mathbf{k}\cdot\mathbf{r}_1)]\,\phi_j(\mathbf{v}_1)\}\rangle \tag{3.14}$$

For the two-particle contribution we must leave the limit $t \to 0^+$. The three contributions defined in the last equations will be treated separately in the next subsections.

3.1. The Three-Particle Contribution

In order to evaluate (3.12), we first notice that ϕ_2 and ϕ_3 are collision invariants, i.e.,

$$T^{+}_{12}[\phi_j(\mathbf{v}_1)+\phi_j(\mathbf{v}_2)]=0, \qquad j=2, 3 \tag{3.15}$$

Exchanging the dummy indices 1 and 2 in the T_{23} term of (3.12) and repeatedly using (3.15), we find

$$\begin{aligned} F^{(3)}_{ij} &= \langle (N-1)(N-2)(T^{-}_{13}\{\phi_i(\mathbf{v}_1)[1-\exp(-i\mathbf{k}\cdot\mathbf{r}_{12})] \\ &\quad +\phi_i(\mathbf{v}_3)[\exp(i\mathbf{k}\cdot\mathbf{r}_{13})-\exp(i\mathbf{k}\cdot\mathbf{r}_{23})]\})[T^{+}_{12}\phi_j(\mathbf{v}_1)]\rangle \\ &= \langle (N-1)(N-2)[T^{-}_{13}\phi_i(\mathbf{v}_1)][T^{+}_{12}\phi_j(\mathbf{v}_1)] \\ &\quad \times[1-\exp(-i\mathbf{k}\cdot\mathbf{r}_{12})-\exp(i\mathbf{k}\cdot\mathbf{r}_{13})+\exp(i\mathbf{k}\cdot\mathbf{r}_{23})]\rangle \end{aligned} \tag{3.16}$$

If for $F^{(3)}_{22}$ we take the limit $k\to\infty$, we recover a result of Resibois[8] and SEC.

The collision operator T acts on ϕ_2 and ϕ_3 as

$$\begin{aligned} T^{\pm}_{12}(\hat{\mathbf{k}}\cdot\mathbf{v}_1) &= -\delta(r_{12}-\sigma)\,|\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}|\,\theta(\mp\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}) \\ &\quad \times(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{12})(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}) \end{aligned} \tag{3.17}$$

and

$$\begin{aligned} T^{\pm}_{12}(\mathbf{v}_1^2) &= -\delta(r_{12}-\sigma)\,|\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}|\,\theta(\mp\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}) \\ &\quad \times[(\mathbf{v}_1+\mathbf{v}_2)\cdot\hat{\mathbf{r}}_{12}](\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}) \end{aligned} \tag{3.18}$$

Using (3.17), we find

$$\begin{aligned} F^{(3)}_{22} &= \beta m\langle (N-1)(N-2)\,\delta(r_{13}-\sigma)\,|\mathbf{v}_{13}\cdot\hat{\mathbf{r}}_{13}|\,\theta(\mathbf{v}_{13}\cdot\hat{\mathbf{r}}_{13}) \\ &\quad \times(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{13})(\mathbf{v}_{13}\cdot\hat{\mathbf{r}}_{13})\,\delta(r_{12}-\sigma)\,|\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}|\,\theta(-\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}) \\ &\quad \times(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{12})(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})[1-\exp(-i\mathbf{k}\cdot\mathbf{r}_{12}) \\ &\quad -\exp(i\mathbf{k}\cdot\mathbf{r}_{13})+\exp(i\mathbf{k}\cdot\mathbf{r}_{23})]\rangle \\ &= \frac{-1}{\beta m}\langle (N-1)(N-2)\,\delta(r_{13}-\sigma)(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{13})\,\delta(r_{12}-\sigma)(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{12}) \\ &\quad \times V_1(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13})[1-\exp(-i\mathbf{k}\cdot\mathbf{r}_{12})-\exp(i\mathbf{k}\cdot\mathbf{r}_{13})+\exp(i\mathbf{k}\cdot\mathbf{r}_{23})]\rangle \end{aligned} \tag{3.19}$$

where V_1 is defined as the velocity average

$$V_1(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13})=(\beta m)^2\int d\mathbf{v}_1\int d\mathbf{v}_2\int d\mathbf{v}_3 f_m(v_1)\, f_m(v_2)\, f_m(v_3) \times(\mathbf{v}_{13}\cdot\hat{\mathbf{r}}_{13})^2\,\theta(\mathbf{v}_{13}\cdot\hat{\mathbf{r}}_{13})(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})^2\,\theta(-\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}) \quad (3.20)$$

Here f_m is the Maxwell–Boltzmann velocity distribution. The ensemble average in (3.19) yields a three-particle equilibrium correlation function, and we obtain

$$F_{22}^{(3)}=\frac{-n^2}{\beta m}\int d\mathbf{r}_{12}\int d\mathbf{r}_{13}\,\delta(r_{12}-\sigma) \times\delta(r_{13}-\sigma)\, V_1(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13})\, g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{13})(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{12}) \times[1-\exp(-i\mathbf{k}\cdot\mathbf{r}_{12})-\exp(i\mathbf{k}\cdot\mathbf{r}_{13})+\exp(i\mathbf{k}\cdot\mathbf{r}_{23})] \quad (3.21)$$

It is more convenient to use the dimensionless quantity $t_e^2 F_{22}^{(3)}$, which can be written as

$$t_e^2 F_{22}^{(3)}=\frac{-1}{16\pi}\int_{-1}^{1} dz\, V_1(z)\, g_3(z)\, F_1(k, z) \quad (3.22)$$

where $z=\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13}$, the function $g_3(z)$ is the reduced three-particle correlation function

$$g_3(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13})=[g(\sigma)]^{-2}\, g_3(\mathbf{r}_1, \mathbf{r}_1-\sigma\hat{\mathbf{r}}_{12}, \mathbf{r}_1-\sigma\hat{\mathbf{r}}_{13}) \quad (3.23)$$

and $F_1(k, z)$ is given as

$$F_1(k, z)=\int d\hat{\mathbf{r}}_{12}\int d\hat{\mathbf{r}}_{13}\,\delta(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13}-z)(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{12})(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{13}) \times[1-\exp(-i\mathbf{k}\cdot\mathbf{r}_{12})-\exp(i\mathbf{k}\cdot\mathbf{r}_{13})+\exp(i\mathbf{k}\cdot\mathbf{r}_{23})] \quad (3.24)$$

In a similar manner we arrive at expressions for the other correlation functions. We find

$$t_e^2 F_{23}^{(3)}=\frac{-1}{16\pi}\int_{-1}^{1} dz\, V_2(z)\, g_3(z)\, F_2(k, z) \quad (3.25)$$

with

$$V_2(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13})=\frac{(\beta m)^{5/2}}{\sqrt{6}}\int d\mathbf{v}_1\int d\mathbf{v}_2\int d\mathbf{v}_3 f_m(v_1)\, f_m(v_2)\, f_m(v_3)(\mathbf{v}_{13}\cdot\hat{\mathbf{r}}_{13})^2 \times\theta(\mathbf{v}_{13}\cdot\hat{\mathbf{r}}_{13})(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})^2[(\mathbf{v}_1+\mathbf{v}_2)\cdot\hat{\mathbf{r}}_{12}]\,\theta(-\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}) \quad (3.26)$$

and

$$F_2(k, z)=\int d\hat{\mathbf{r}}_{12}\int d\hat{\mathbf{r}}_{13}\,\delta(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13}-z)(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{13}) \times[1-\exp(-i\mathbf{k}\cdot\mathbf{r}_{12})-\exp(i\mathbf{k}\cdot\mathbf{r}_{13})+\exp(i\mathbf{k}\cdot\mathbf{r}_{23})] \quad (3.27)$$

Also,

$$t_e^2 F_{33}^{(3)} = \frac{-1}{16\pi} \int_{-1}^{1} dz\, V_3(z)\, g_3(z)\, F_3(k, z) \tag{3.28}$$

now with

$$\begin{aligned} V_3(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{13}) = \frac{(\beta m)^3}{6} \int d\mathbf{v}_1 \int d\mathbf{v}_2 \int d\mathbf{v}_3 \\ \times f_m(v_1)\, f_m(v_2)\, f_m(v_3)(\mathbf{v}_{13} \cdot \hat{\mathbf{r}}_{13})^2 \\ \times [(\mathbf{v}_1 + \mathbf{v}_3) \cdot \hat{\mathbf{r}}_{13}]\, \theta(\mathbf{v}_{13} \cdot \hat{\mathbf{r}}_{13})(\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12})^2 \\ \times [(\mathbf{v}_1 + \mathbf{v}_2) \cdot \hat{\mathbf{r}}_{12}]\, \theta(-\mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}) \end{aligned} \tag{3.29}$$

and

$$\begin{aligned} F_3(k, z) = \int d\hat{\mathbf{r}}_{12} \int d\hat{\mathbf{r}}_{13}\, \delta(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{13} - z) \\ \times [1 - \exp(-i\mathbf{k} \cdot \mathbf{r}_{12}) - \exp(i\mathbf{k} \cdot \mathbf{r}_{13}) + \exp(i\mathbf{k} \cdot \mathbf{r}_{23})] \end{aligned} \tag{3.30}$$

Calculation of the functions V_i is straightforward, but not trivial. Details are given in Appendix A. The functions F_i are calculated in Appendix B. The explicit results read

$$V_1(z) = \frac{2}{\pi} \left[\left(1 + \frac{z^2}{2}\right) \arccos \frac{z}{2} - \frac{3}{2} z \left(1 - \frac{z^2}{4}\right)^{1/2} \right] \tag{3.31a}$$

$$V_2(z) = \frac{2}{(6\pi)^{1/2}}\, z \left(1 - \frac{z}{2}\right)^2 \tag{3.31b}$$

$$V_3(z) = \frac{1}{\pi} \left[z \left(\frac{z^2}{2} + \frac{1}{3}\right) \arccos \frac{z}{2} - \frac{7}{6} z^2 \left(1 - \frac{z^2}{4}\right)^{1/2} \right] \tag{3.31c}$$

and

$$\begin{aligned} F_1(k, z) = 8\pi^2 \left\{ \frac{z}{3} - \frac{2z}{3} [j_0(k\sigma) - 2j_2(k\sigma)] + \frac{z}{3} j_0(k\tau) \right. \\ \left. + \left(\frac{1}{2} - \frac{z}{6}\right) j_2(k\tau) \right\} \end{aligned} \tag{3.32a}$$

$$F_2(k, z) = i8\pi^2 \left[(z-1)\, j_1(k\sigma) + \left(\frac{1-z}{2}\right)^{1/2} j_1(k\tau) \right] \tag{3.32b}$$

$$F_3(k, z) = 8\pi^2 [1 - 2j_0(k\sigma) + j_0(k\tau)] \tag{3.32c}$$

where $\tau = \sigma(2-2z)^{1/2}$. For computing the $F_{ij}^{(3)}$, only $g_3(z)$ is needed in addition. In Section 4 we will present numerical estimates, based on simulation results and low-density approximations for g_3.

3.2. The Four-Particle Contribution

From (3.17) and (3.18) it follows that the four-particle contribution vanishes unless $i=j=2$. For $i=j=2$ the velocity integrals are trivial and we obtain

$$F_{22}^{(4)} = -\frac{1}{\beta m}\langle (N-1)(N-2)(N-3) \times \delta(r_{12}-\sigma)(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{12})\,\delta(r_{34}-\sigma)(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{34})\exp(i\mathbf{k}\cdot\mathbf{r}_{13})\rangle \tag{3.33}$$

The expression (3.33) involves a four-particle correlation function. This expression can be simplified by using the third equation of the BBGKY hierarchy to

$$\begin{aligned} F_{22}^{(4)} = \frac{-n^2}{\beta m V}\int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 (\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{12}) \\ \times \delta(r_{12}-\sigma)\exp(i\mathbf{k}\cdot\mathbf{r}_{13}) \\ + \left[\hat{\mathbf{k}}\cdot\frac{\partial}{\partial \mathbf{r}_3} - \delta(r_{13}-\sigma)(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{31}) \right. \\ \left. - \delta(r_{23}-\sigma)(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{32})\right] g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \end{aligned} \tag{3.34}$$

Using the second equation of the BBGKY hierarchy, this can be simplified to

$$\begin{aligned} F_{22}^{(4)} &= \frac{-ikn}{\beta m V}\int d\mathbf{r}_1 \int d\mathbf{r}_3 [\exp(i\mathbf{k}\cdot\mathbf{r}_{13})] \\ &\quad \times \left[\hat{\mathbf{k}}\cdot\frac{\partial}{\partial \mathbf{r}_1} - \delta(r_{13}-\sigma)(\hat{\mathbf{k}}\cdot\mathbf{r}_{13})\right] g_2(\mathbf{r}_1, \mathbf{r}_3) \\ &\quad + \frac{n^2\sigma^4}{\beta m}\int d\hat{\mathbf{r}}_{12}\int d\hat{\mathbf{r}}_{13}(\hat{\mathbf{k}}\cdot\mathbf{r}_{12})(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{13}) \\ &\quad \times [\exp(i\mathbf{k}\cdot\mathbf{r}_{23}) - \exp(i\mathbf{k}\cdot\mathbf{r}_{13})]\, g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ &= \frac{-k^2}{\beta m}[S(k)-1] - \frac{kn\sigma^2}{\beta m} 4\pi g(\sigma)\, j_1(k\sigma) \\ &\quad + \frac{n^2\sigma^4}{\beta m}[g(\sigma)]^2 \int_{-1}^{1} dz\, g_3(z)\,\tilde{F}(k,z) \end{aligned} \tag{3.35}$$

For the function $\tilde{F}$ we have

$$\tilde{F}(k, z) = \int d\hat{\mathbf{r}}_{12} \int d\hat{\mathbf{r}}_{13}\, \delta(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{13} - z) \times (\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_{12})(\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_{13})[\exp(i\mathbf{k} \cdot \mathbf{r}_{23}) - \exp(i\mathbf{k} \cdot \mathbf{r}_{13})]$$
$$= 8\pi^2 \left\{ -\frac{z}{3} [j_0(k\sigma) - 2j_2(k\sigma)] + \frac{z}{3} j_0(k\tau) + \left(\frac{1}{2} - \frac{z}{6}\right) j_2(k\tau) \right\} \tag{3.36}$$

In obtaining (3.36), we have used results from Appendix B.

3.3. The Two-Particle Contribution

From the arguments presented in ref. 9, it follows that besides the three- and four-particle contributions, the two-particle contribution defined in (3.14) is also nonvanishing. At first glance this may seem surprising as $T_{12}^- e^{L_0 t} T_{12}^+$ vanishes (the same two particles cannot collide twice without the intervention of a third particle). So one needs an intermediate collision, and seemingly (3.14) is proportional to t and would vanish in the limit $t \to 0^+$. This is not the case, however, because of the large probability that, if an intermediate collision occurs in a certain short time interval, particles 1 and 2 will recollide in the same time interval. Details are described in SEC. In the cases considered by de Schepper and Cohen and by SEC the numerical importance turned out to be small. As the two-particle contribution comes from recollisions, $F_{ij}^{(2)}$ is also called the recollision contribution.

Here we closely follow the treatment by SEC and just sketch the details of our calculation. Using that ϕ_2 and ϕ_3 are collision invariants, we find that

$$F_{ij}^{(2)} = \lim_{t \to 0^+} \langle (N-1)(1 - \exp(i\mathbf{k} \cdot \mathbf{r}_{12}))[T_{12}^- \phi_i(\mathbf{v}_1)] \times e^{L^+ t}[T_{12}^+ \phi_j(\mathbf{v}_1)] \rangle \tag{3.37}$$

Using the binary collision expansion, SEC showed that the relevant contribution to the second derivative at $t = 0^+$ is

$$F_{ij}^{(2)} = \lim_{t \to 0^+} \int_0^t dt_1 \langle (N-1)(N-2)[1 - \exp(i\mathbf{k} \cdot \mathbf{r}_{12})][T_{12}^- \phi_i(\mathbf{v}_1)] \times \{\exp[L_0(t - t_1)]\}(T_{13}^+ + T_{23}^+)[\exp(L_0 t_1)][T_{12}^+ \phi_j(\mathbf{v}_1)] \rangle$$

$$
\begin{aligned}
&= 2 \Big\langle (N-1)(N-2)[1-\exp(i\mathbf{k}\cdot\mathbf{r}_{12})] \\
&\quad \times \delta(r_{12}-\sigma)\,\delta(r_{13}-\sigma)\,\frac{\theta(-\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13})}{|\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13}|} \\
&\quad \times \theta(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\,|\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}|\,[(B_{12}-1) \\
&\quad \times \phi_i(\mathbf{v}_1)]\,B_{13}^{+}[\theta(-\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}) \\
&\quad \times |\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}|\,[(B_{12}-1)\,\phi_j(\mathbf{v}_1)]\Big\rangle
\end{aligned}
\tag{3.38}
$$

The velocity integrals in (3.38) are independent of both $\hat{\mathbf{k}}$ and $\hat{\mathbf{r}}_{12}$. Replacing the integral over $\hat{\mathbf{r}}_{12}$ by one over $\hat{\mathbf{k}}$ and performing this integral yields the wavelength dependence of $F_{ij}^{(2)}$. In a manner similar to that used in Section 3.1, the ensemble average can be taken. The velocity integrals are treated in Appendix A. The final results of these steps are

$$
t_e^2 F_{22}^{(2)} = -\frac{\pi}{3}\,[1-j_0(k\sigma)+2j_2(k\sigma)]\int_{-1}^{0} dz\, W_1(z)\, g_3(z) \tag{3.39a}
$$

$$
t_e^2 F_{23}^{(2)} = i\pi j_1(k\sigma)\int_{-1}^{0} dz\, W_2(z)\, g_3(z) \tag{3.39b}
$$

$$
t_e^2 F_{33}^{(2)} = -\pi[1-j_0(k\sigma)]\int_{-1}^{0} dz\, W_3(z)\, g_3(z) \tag{3.39c}
$$

where

$$
W_1(z) = \frac{2}{\pi z}\,(6-4z^2+z^4)\arcsin\frac{z}{2} - \frac{3}{\pi}\,(2-z^2)\left(1-\frac{z^2}{4}\right)^{1/2} \tag{3.40a}
$$

$$
W_2(z) = -\frac{z^5}{2(6\pi)^{1/2}} \tag{3.40b}
$$

An expression for $W_3(z)$ is given in (A.19c).

The results for the correlation functions $F_{ij}(k, t)$, with $t \geqslant 0$, obtained so far can be summarized as

$$
F_{22}(k, t) = 1 - \frac{2}{3}\,[1-j_0(k\sigma)+2j_2(k\sigma)]\,\frac{t}{t_e} + C(k\sigma)\,\frac{t^2}{2} + O(t^3) \tag{3.41}
$$

$$
\begin{aligned}
C(k\sigma) = &-\frac{k^2}{\beta m}\,[4-S(k)] \\
&-\frac{2k\sqrt{\pi}}{5t_e(\beta m)^{1/2}}\,[3j_1(k\sigma)-2j_3(k\sigma)] + F_{22}^{p}(k\sigma)
\end{aligned}
\tag{3.42}
$$

$$F_{23}(k,t)=i\left[\frac{k}{(\beta m)^{1/2}}\left(\frac{2}{3}\right)^{1/2}+\left(\frac{\pi}{6}\right)^{1/2}\frac{j_1(k\sigma)}{t_e}\right]t$$
$$+\left\{\frac{-ik}{t_e(\beta m)^{1/2}}\left(\frac{3}{2}\right)^{1/2}[1-j_0(k\sigma)+2j_2(k\sigma)]\right.$$
$$\left.+F^p_{23}(k\sigma)\right\}\frac{t^2}{2}+O(t^3) \tag{3.43}$$

$$F_{33}(k,t)=1-\frac{2[1-j_0(k\sigma)]}{3}\frac{t}{t_e}$$
$$+\left(\frac{-7k^2}{3\beta m}-\frac{5k\sqrt{\pi}}{3t_e(\beta m)^{1/2}}j_1(k\sigma)+F^p_{33}(k\sigma)\right)\frac{t^2}{2}+O(t^3) \tag{3.44}$$

with $F^p_{ij}=F^{(2)}_{ij}+F^{(3)}_{ij}+\delta_{i2}\,\delta_{j2}F^{(4)}_{22}$; and $F^{(2)}_{ij}$, $F^{(3)}_{ij}$, and $F^{(4)}_{22}$ are given in (3.39), in (3.22), (3.25), (3.28), and in (3.34), respectively. By time integration of (3.41) and using the initial conditions for $F_{11}(k,t)$, we arrive at the following result for the normalized coherent intermediate scattering function:

$$F_{11}(k,t)=1-\frac{k^2}{\beta m S(k)}\frac{t^2}{2}+\frac{2}{3}[1-j_0(k\sigma)+2j_2(k\sigma)]\frac{k^2}{\beta m S(k)}\frac{t^3}{6t_e}$$
$$-C(k\sigma)\frac{k^2}{\beta m S(k)}\frac{t^4}{24}+O(t^5) \tag{3.45}$$

3.4. Enskog Theory

The linearized wavelength-dependent Enskog operator[1] acts on functions in one-particle velocity space. For forward streaming the Enskog operator is given by

$$L^{(E)}=L^{(E)}_0+L^{(E)}_c \tag{3.46}$$

where the free streaming term is

$$L^{(E)}_0=i\mathbf{k}\cdot\mathbf{v} \tag{3.47}$$

and the Enskog collision operator acts on a given function $h(\mathbf{v})$ as

$$L^{(E)}_c h(\mathbf{v}_1)=n\sigma^2 g(\sigma)\int d\hat{\mathbf{r}}_{12}\int d\mathbf{v}_2 f_m(v_2)\,\theta(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\,|\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}|$$
$$\times(B_{12}-1)\{h(\mathbf{v}_1)+[\exp(ik\sigma\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{12})]\,h(\mathbf{v}_2)\}$$
$$-i\left(1-\frac{1}{S(k)}-4\pi g(\sigma)\,n\sigma^3\frac{j_1(k\sigma)}{k\sigma}\right)$$
$$\times\int d\mathbf{v}_2 f_m(v_2)(\mathbf{k}\cdot\mathbf{v}_2)\,h(\mathbf{v}_2) \tag{3.48}$$

The first term is the collision term, the second term the mean field term. We have chosen to absorb the mean field term in the collision operator in order to keep the nomenclature consistent with the previous sections. We define an inner product in one-particle space through equilibrium correlation functions in N-particle space[5,11]: Define

$$\Phi(h(\mathbf{v})) = (N)^{-1/2} \sum_{i=1}^{N} [\exp(i\mathbf{k}\cdot\mathbf{r}_i)]\, h(\mathbf{v}_i) \tag{3.49}$$

Then our inner product is given by

$$(a(\mathbf{v})\,|\,b(\mathbf{v})) = \langle \Phi(a(\mathbf{v}))\,|\,\Phi(b(\mathbf{v}))\rangle = \langle \Phi(a(\mathbf{v}))^*\, \Phi(b(\mathbf{v}))\rangle \tag{3.50}$$

In the context of equilibrium time correlation functions, this is a very natural definition of an inner product, for instance the *full* Enskog operator is symmetric under this inner product, but not the free streaming and collision parts separately. The Hermitean adjoint of the Enskog operator (3.46) can now be found, and is given by[2]

$$(L^{(\mathrm{E})})^\dagger = (L_0^{(\mathrm{E})})^\dagger + (L_c^{(\mathrm{E})})^\dagger \tag{3.51}$$

with the adjoint of the Enskog collision operator being given by

$$\begin{aligned}(L_c^{(\mathrm{E})})^\dagger h(\mathbf{v}_1) = {}& n\sigma^2 g(\sigma) \int d\hat{\mathbf{r}}_{12} \int d\mathbf{v}_2\, \theta(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\, |\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12}| \\ &\times (B_{12}-1)\{h(\mathbf{v}_1) + [\exp(-ik\sigma\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{12})\, h(\mathbf{v}_2)\} \\ &- i4\pi g(\sigma)\, n\sigma^3 \frac{j_1(k\sigma)}{k\sigma} \int d\mathbf{v}_2 f_m(v_2)(\mathbf{k}\cdot\mathbf{v}_2)\, h(\mathbf{v}_2) \\ &+ i\mathbf{k}\cdot\mathbf{v}_1[S(k)-1] \int d\mathbf{v}_2 f_m(v_2)\, h(\mathbf{v}_2)\end{aligned} \tag{3.52}$$

The adjoint of the (Enskog) free streaming operator is

$$\begin{aligned}(L_0^{(\mathrm{E})})^\dagger h(\mathbf{v}_1) = {}& -i(\mathbf{k}\cdot\mathbf{v}_1)\, h(\mathbf{v}_1) \\ &- i\int d\mathbf{v}_2 f_m(v_2) \Big\{ [S(k)-1](\mathbf{k}\cdot\mathbf{v}_1) \\ &+ \left(\frac{1}{S(k)}-1\right)(\mathbf{k}\cdot\mathbf{v}_2)\Big\}\, h(\mathbf{v}_2)\end{aligned} \tag{3.53}$$

[2] The operator $(L^{(\mathrm{E})})^\dagger$ is identical to the operator $\Lambda_{E,s}$ of Cohen and de Schepper,[12] but our separation into a free streaming term and a collision part is slightly different. This is connected to the definition (3.47) of the Enskog free streaming operator and our choice of the inner product (3.50).

Within the framework of RET, the hydrodynamic correlation functions can be expressed as

$$F_{ij}^{(\mathrm{E})}(k, t) = (\phi_i \,|\, e^{L^{(\mathrm{E})}t}\phi_j) \tag{3.54}$$

which is an approximation of the exact expression (2.6). The RET approximation of the first time derivatives

$$\partial_t F_{ij}^{(\mathrm{E})}(k, t) = (\phi_i \,|\, L^{(\mathrm{E})}\phi_j) \tag{3.55}$$

is easily shown to be exact, i.e., identical to (3.1).[2-4]

The second time derivative can be expressed as

$$\partial_t^2 F_{ij}^{(\mathrm{E})} = ((L^{(\mathrm{E})})^\dagger \, \phi_i(\mathbf{v}) \,|\, L^{(\mathrm{E})} \, \phi_j(\mathbf{v})) \tag{3.56}$$

As before, we can identify three different contributions. As the kinetic currents are one-particle densities, the kinetic and the cross terms as given by RET are identical to the exact results. The potential term is approximated. Using (3.48) and (3.52), we find that within RET the potential term is given by (3.22), (3.25), and (3.28) if we set $g_3(z) = 1$. There is also a contribution $F_{ij}^{(\mathrm{E,mf})}$ due to the mean field term. This contribution is only nonzero if $i = j = 2$, and is given by

$$F_{ij}^{(\mathrm{E,mf})} = -\delta_{i2}\,\delta_{j2} \left\{ \frac{k^2}{\beta m} \left[S(k) - 2 + \frac{1}{S(k)} \right] + \frac{\pi}{t_e^2} \left[j_1(k\sigma) \right]^2 \right\} \tag{3.57}$$

The recollision, or two-particle, term is absent in RET.

A different expression for the Enskog value of the potential term of the second derivative at $t = 0^+$ can be obtained from (3.56) as the expansion

$$\begin{aligned} F_{ij}^{\mathrm{e}} &= ((L_c^{(\mathrm{E})})^\dagger \, \phi_i(\mathbf{v}) \,|\, L_c^{(\mathrm{E})}\phi_j(\mathbf{v})) \\ &= \sum_n \, (\phi_i(\mathbf{v}) \,|\, L_c^{(E)\dagger}\phi_n(\mathbf{v}))(\phi_n(\mathbf{v}) \,|\, L_c^{(E)}\phi_j(\mathbf{v})) \\ &= \sum_n \, \langle a_i^* L_c^- \, a_n \rangle \langle a_n^* L_c^+ \, a_j \rangle \end{aligned} \tag{3.58}$$

where the functions ϕ_n are a complete set of orthonormal functions on the one-particle velocity space, under the inner product generated by (3.50). We can approximate the infinite sum in (3.58) by only taking the five polynomials ϕ_i, $i = 1,\ldots, 5$. This can be expected to be a very good approximation, as (1) the five-polynomial approximation yields the same initial value for all Green–Kubo integrands we consider in this paper as the full Enskog theory (see Section 3.6); and (2) the limit $k \to \infty$ for the second time derivative of the longitudinal velocity correlation function $F_{22}(k, t)$ in the Enskog theory is known to be 0.4556592 (in reduced units).[9] In the five-polynomial approximation it is $41/90 = 0.45555$.

We found that the five-polynomial approximation is accurate within 1% for all wavelengths for F_{22} and F_{23}. For F_{33} the five-polynomial approximation is only accurate within 5%.

3.5. The Transverse Velocity Correlation Function

An entirely analogous analysis can be made of the transverse velocity correlation function. Define a_6 through (2.3), with

$$\phi_6(\mathbf{v}) = (\beta m)^{1/2} (\hat{\mathbf{k}}^{\perp} \cdot \mathbf{v}) \tag{3.59}$$

The transverse velocity correlation function is then given as $F_{66}(k, t)$, defined through (2.6). In (3.59), $\hat{\mathbf{k}}^{\perp}$ is an arbitrary unit vector perpendicular to $\hat{\mathbf{k}}$. For the kinetic and cross parts of the second time derivative we also need the kinetic part of the transverse stress tensor a_7, defined through (2.3) and

$$\phi_7(\mathbf{v}) = \beta m(\hat{\mathbf{k}} \cdot \mathbf{v})(\hat{\mathbf{k}}^{\perp} \cdot \mathbf{v}) \tag{3.60}$$

The first time derivative of $F_{66}(k, t)$ at $t = 0^+$ again can be represented by matrix elements of L_0 and L_c. On the basis (a_6, a_7) we have

$$L_0 = \frac{ik}{(\beta m)^{1/2}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{3.61}$$

and

$$L_c = \frac{1}{t_e} \begin{pmatrix} -\frac{2}{3}(1 - j_0 - j_2) & \frac{i\sqrt{\pi}}{5}(j_1 + j_3) \\ \frac{i\sqrt{\pi}}{5}(j_1 + j_3) & -\frac{16}{15} + \frac{4}{15} j_0 - \frac{4}{21} j_2 - \frac{16}{35} j_4 \end{pmatrix} \tag{3.62}$$

As to the second derivative at $t = 0^+$, the kinetic and cross parts follow again from a matrix multiplication of the matrices just presented. The potential part follows in an analogous manner as in Sections 3.1–3.3. For $F_{66}^{(3)}$ only the angular average is slightly different and is described in Appendix B. We obtain

$$t_e^2 F_{66}^{(3)} = \frac{-1}{16\pi} \int_{-1}^{1} dz\, V_1(z)\, g_3(z)\, F_4(k, z) \tag{3.63}$$

with

$$F_4(k, z) = \frac{8\pi^2}{3}\left[z - 2zj_0(k\sigma) - 2zj_2(k\sigma) + zj_0(k\tau) - \left(\frac{3}{4} - \frac{z}{4}\right) j_2(k\tau)\right] \tag{3.64}$$

The four-particle contribution is given as

$$F_{66}^{(4)} = \frac{1}{16\pi}\int_{-1}^{1} dz\, g_3(z)\, \hat{F}(k, z) \tag{3.65}$$

with

$$\hat{F}(k, z) = \frac{8\pi^2}{3}\left\{-z[j_0(k\sigma) + j_2(k\sigma)] + zj_0(k\tau) + \frac{z-3}{4} j_2(k\tau)\right\} \tag{3.66}$$

and for the recollision term we find

$$t_e^2 F_{66}^{(2)} = -\frac{\pi}{3}[1 - j_0(k\sigma) - j_2(k\sigma)] \int_{-1}^{0} dz W_1(z)\, g_3(z) \tag{3.67}$$

Now we turn to the hydrodynamic limit.

3.6. Hydrodynamic Limit and Green–Kubo Integrands

In the long-wavelength limit we obtain an exact result for the Green–Kubo integrands that determine the transport coefficients. For the shear viscosity the Green–Kubo expression is[13]

$$\eta = mn \int_0^\infty dt \langle J_{xy} | J_{xy}(t) \rangle \tag{3.68}$$

with J_{xy}, the current associated with the shear viscosity, the transverse part of the stress tensor. This current is defined as

$$J_{xy} = \lim_{k \to 0} \frac{1}{ik} \partial_t a_6 = \lim_{k \to 0} \frac{1}{ik} L^+ a_6 \tag{3.69}$$

(Our choice of the normalization of J_{xy} is somewhat unconventional.) For the current correlation function, (3.69) leads to

$$\langle J_{xy} | J_{xy}(t) \rangle = \lim_{k \to 0} \frac{-1}{k^2} \partial_t^2 F_{66}(k, t) \tag{3.70}$$

For hard spheres already the first time derivative at $t = 0^+$ is nonzero, although F_{66} is an even function of time. This property leads to the presence of a delta function in the current correlation function. Using the results of Section 3.5, we find for short times

$$\langle J_{xy} | J_{xy} \rangle = \frac{\sigma^2}{15t_e} 2\delta(t) + \frac{1}{\beta m} + \frac{2\sigma}{15t_e}\left(\frac{\pi}{\beta m}\right)^{1/2} + \frac{\sigma^2}{t_e^2}(S_\eta + R_\eta + P_\eta) + O(t) \tag{3.71}$$

where S_η is given by

$$S_\eta = \frac{\pi}{2}\int_{-1}^{1} dz\, g_3(z)\, V_1(z)\frac{3z^2-1}{30} \tag{3.72}$$

the four-particle contribution gives

$$P_\eta = \frac{\pi}{2}\int_{-1}^{1} dz\, g_3(z)\frac{-3z^2+z+1}{30} \tag{3.73}$$

and the recollision contribution is

$$R_\eta = \frac{\pi}{30}\int_{-1}^{0} dz\, W_1(z)\, g_3(z) \tag{3.74}$$

The delta function in (3.71) is understood to be $2\delta(t) = \delta(t-0^+) + \delta(t-0^-)$.

The Enskog theory[3] reproduces the $\delta(t)$ term exactly as well as the kinetic and cross terms, represented by the second and third terms on the right-hand side of (3.71). The four-particle and recollision contributions are absent, and S_η is approximated by

$$S_\eta^{(E)} = \frac{\pi}{2}\int_{-1}^{1} dz\, V_1(z)\frac{3z^2-1}{30} = \frac{\pi}{225} \tag{3.75}$$

where we have used (3.31a). Numerical comparisons are made in Section 4.

The other Green–Kubo integrands are slightly harder to obtain. This is due to the fact that the current defined as in (3.68) contains conserved parts which have to be subtracted. To be more precise, define

$$\hat{J}_{xx} = \lim_{k \to 0} \frac{1}{ik} L^+ a_2 \tag{3.76}$$

[3] In the hydrodynamic limit the standard Enskog theory[14] and RET for a one-component system yield identical results.

Then it follows from (3.6) and (3.7) that both $|n\rangle\langle n\hat{J}_{xx}\rangle$ and $|T\rangle\langle T\hat{J}_{xx}\rangle$ are nonzero and conserved. It is well known[13] that these terms have to be subtracted to obtain the correct Green–Kubo integrand for the bulk viscosity. Define

$$J_{xx} = \hat{J}_{xx} - n\langle n|\hat{J}_{xx}\rangle - T\langle T|\hat{J}_{xx}\rangle \tag{3.77}$$

The Green–Kubo expression for the longitudinal viscosity is then given as

$$\eta_l = \frac{4}{3}\eta + \kappa = mn\int_0^\infty dt\langle J_{xx}J_{xx}(t)\rangle \tag{3.78}$$

Here κ is the bulk viscosity. The exact short-time result for the current correlation function is

$$\langle J_{xx}J_{xx}(t)\rangle = \frac{\sigma^2}{5t_e}2\delta(t) + \frac{4}{3\beta m} + \frac{8\sigma}{45t_e}\left(\frac{\pi}{\beta m}\right)^{1/2} + \frac{\sigma^2}{t_e^2}(S_l + R_l + P_l) + O(t) \tag{3.79}$$

with

$$S_l = \frac{\pi}{2}\int_{-1}^{1} dz\, g_3(z)\, V_1(z)\frac{1+2z^2}{15} - \frac{7\pi}{54} \tag{3.80}$$

$$R_l = \frac{\pi}{10}\int_{-1}^{0} dz\, W_1(z)\, g_3(z) \tag{3.81}$$

and the four-particle contribution is

$$P_l = \frac{t_e^2}{\beta m\sigma^2}\left[\frac{4\pi}{3}n\sigma^3 g(\sigma) + 1 - \frac{1}{S(k=0)}\right] - \frac{\pi}{2}\int_{-1}^{1} dz\, g_3(z)\left(\frac{1}{15} - \frac{z}{10} + \frac{2z^2}{15}\right) + \frac{\pi}{9} \tag{3.82}$$

A Green–Kubo expression for the bulk viscosity can be found by combination of (3.68) and (3.78),

$$\kappa = mn\int_0^\infty dt J_\kappa(t) \tag{3.83}$$

with the current correlation function $J_\kappa(t)$ defined as

$$J_\kappa(t) = \langle J_{xx}|J_{xx}(t)\rangle - \tfrac{4}{3}\langle J_{xy}|J_{xy}(t)\rangle \tag{3.84}$$

The exact short-time result for the current correlation function J_κ is

$$J_\kappa(t)=\frac{\sigma^2}{9t_e}\,2\delta(t)+\frac{\sigma^2}{t_e^2}\,(S_\kappa+R_\kappa+P_\kappa) \tag{3.85}$$

with

$$S_\kappa=\frac{\pi}{18}\int_{-1}^{1}dz\,g_3(z)\,V_1(z)-\frac{7\pi}{54} \tag{3.86}$$

$$P_\kappa=\frac{t_e^2}{\beta m\sigma^2}\left[\frac{4\pi}{3}n\sigma^3g(\sigma)+1-\frac{1}{S(k=0)}\right]$$
$$+\frac{\pi}{9}+\frac{\pi}{36}\int_{-1}^{1}dz\,g_3(z)(z-2) \tag{3.87}$$

and

$$R_\kappa=\frac{\pi}{18}\int_{-1}^{0}dz\,W_1(z)\,g_3(z) \tag{3.88}$$

The Enskog theory gives $S_\kappa^{\mathrm{E}}=0$.

The definition of the current correlation function occurring in the Green–Kubo integral for the thermal conductivity λ again is complicated by the fact that a term has to be subtracted. Define

$$\hat{J}_Q=\lim_{k\to 0}\frac{1}{ik}\,L^+a_3 \tag{3.89}$$

The current to be used then is[13]

$$J_Q=\hat{J}_Q-v_l\langle v_l\,|\,\hat{J}_Q\rangle \tag{3.90}$$

and the thermal conductivity is given as

$$\lambda=\frac{3}{2}nk_{\mathrm{B}}\int_0^\infty dt\langle J_Q\,|\,J_Q(t)\rangle \tag{3.91}$$

where k_{B} is the Boltzmann constant. The exact short-time result for the heat current correlation function is

$$\langle J_Q\,|\,J_Q(t)\rangle=\frac{\sigma^2}{9t_e}\,2\delta(t)+\frac{5}{3\beta m}+\frac{\sigma}{3t_e}\left(\frac{\pi}{\beta m}\right)^{1/2}$$
$$+\frac{\sigma^2}{t_e^2}\,(S_\lambda+R_\lambda)+O(t) \tag{3.92}$$

with

$$S_\lambda = \frac{\pi}{2}\int_{-1}^{1} dz\, g_3(z)\, V_3(z)\frac{z}{3} - \frac{\pi}{54} \tag{3.93}$$

and

$$R_\lambda = \frac{\pi}{6}\int_{-1}^{0} dz\, W_3(z)\, g_3(z) \tag{3.94}$$

The Enskog theory gives no recollision contribution, and S_λ^E is given by

$$S_\lambda^{\mathrm{E}} = \frac{\pi}{2}\int_{-1}^{1} dz\, V_3(z)\frac{z}{3} - \frac{\pi}{54} = \frac{\pi}{60} \tag{3.95}$$

where we have used (3.31c).

4. NUMERICAL RESULTS

Explicit evaluation of $F_{ij}(k, t)$ requires knowledge of the three-particle correlation functions. To lowest order in the density ($n\sigma^3 = 0$) we have

$$\begin{aligned} g_3(z) &= 0 \qquad \text{if} \quad z > 1/2 \\ &= 1 \qquad \text{if} \quad z \leqslant 1/2 \end{aligned} \tag{4.1}$$

The three-particle correlation function has been studied in the literature for intermediate densities ($n\sigma^3 = 0.421$)[15] and liquid densities ($n\sigma^3 = 0.837$).[16] These three-particle correlation functions have been used in obtaining the results of this section. The three-particle correlation function is close to unity for $z = -1$; even at $n\sigma^3 = 0.837$, important deviations occur only near $z = 1/2$.

In Fig. 1, $t_e^2 F_{66}^p(k)$ is plotted at the three densities mentioned. There is a noticeable density dependence of about 10%. The density dependence of F_{23}^p and F_{33}^p is of the order of 5%. In Figs. 2 and 3 we compare our exact results for $t_e^2 F_{22}^p$ with RET at two densities. For $S(k)$ we have used the Percus–Yevick approximation with the Verlet–Weis correction (see e.g., ref. 17). At the intermediate density RET performs very well and the deviations of the sum of the three- and four-particle contributions and RET are largely compensated for by the recollision term. This no longer holds at high densities, but RET is still a good approximation. The recollision term is small.

In Fig. 4 we present $t_e^2 F_{23}^p$, and in Fig. 5, $t_e^2 F_{33}^p$. In the latter RET gives too high a value; for large wavenumbers the deviations are of the

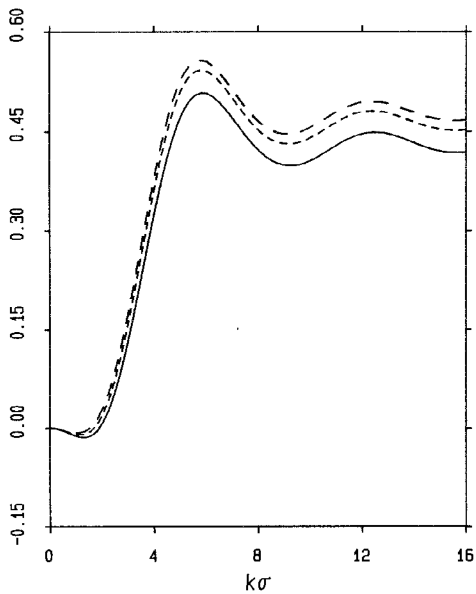

Fig. 1. The potential part of the second time derivative at $t=0^+$ of the transverse velocity correlation function $F_{66}(k, t)$ multiplied by t_e^2, at three different densities. Solid line: $n\sigma^3 = 0.837$; dashed line: $n\sigma^3 = 0.421$; long-dashed line: $n\sigma^3 = 0$.

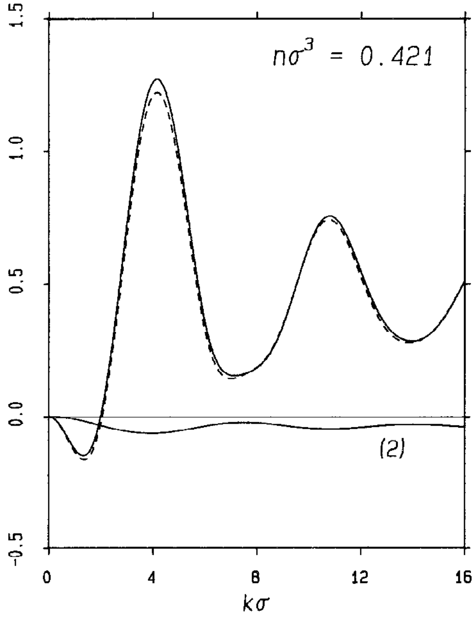

Fig. 2. The potential part of the second time derivative at $t=0^+$ of the longitudinal velocity correlation function $F_{22}(k, t)$ multiplied by t_e^2 at an intermediate density. The solid line is the exact result, the RET approximation is given as the dashed line. The recollision contribution is also plotted separately, and is indicated by (2).

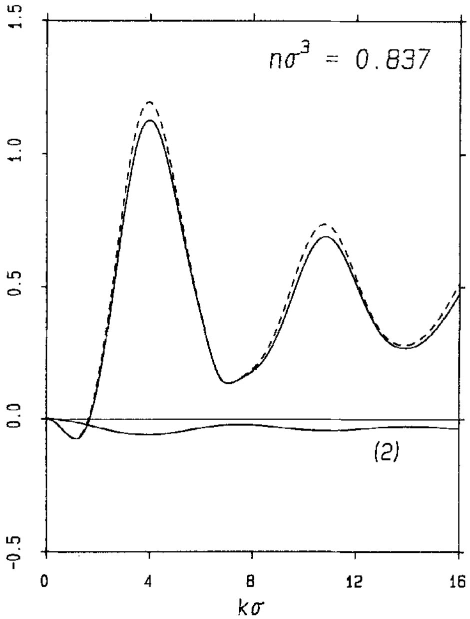

Fig. 3. As in Fig. 2, at a high density.

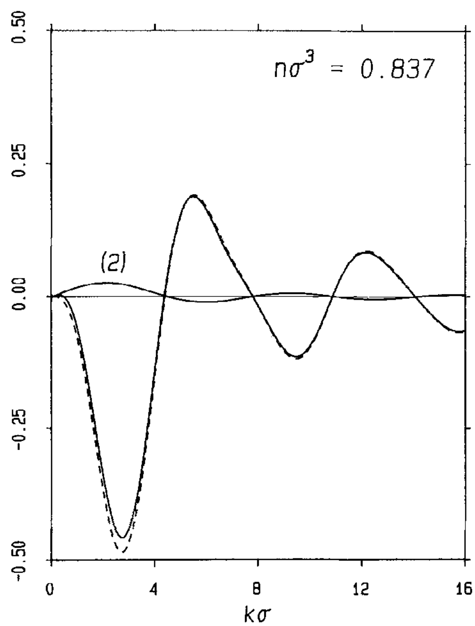

Fig. 4. The potential part of the second time derivative at $t = 0^+$ of the correlation function $-iF_{23}(k, t)$ multiplied by t_e^2 at high density. The solid line is the exact result, the RET approximation is given as the dashed line. The recollision contribution is also given separately, and is indicated by (2).

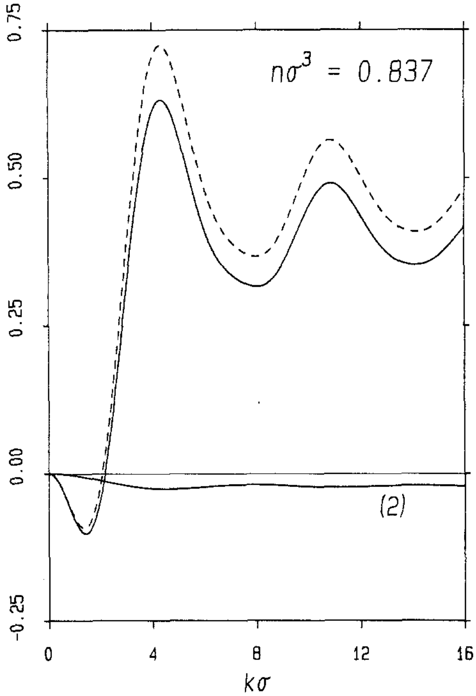

Fig. 5. As in Fig. 4, for the correlation function $F_{33}(k, t)$.

order of 10%. At lower densities RET performs better, but the deviations are still of the order of 5%. In Fig. 6 we present $t_e^2 F_{66}^p$.

For long wavelengths the second time derivative tends to zero as k^2. In order to obtain information for long wavelengths, we present $t_e^2 F_{66}^p(k)/(k\sigma)^2$ in Fig. 7, as well as its various contributions. The striking feature is the relative importance of both the recollision and four-particle contributions. For wavenumbers larger than $k\sigma = 5$ these contributions are no longer numerically important.

Initial values for the Green–Kubo integrands excluding the delta contribution are given in Tables I–III. The recollision term is only weakly dependent on density for all transport coefficients. The four-particle contribution is both strongly density dependent and large. This density dependence is only partly compensated by the three-particle term. At high densities the Green–Kubo integrand of the shear viscosity is significantly larger than the Enskog value. A surprising result is that the bulk viscosity integrand is negative at short times. Due to the presence of the delta term, this does not lead to inconsistencies like negative transport coefficients.

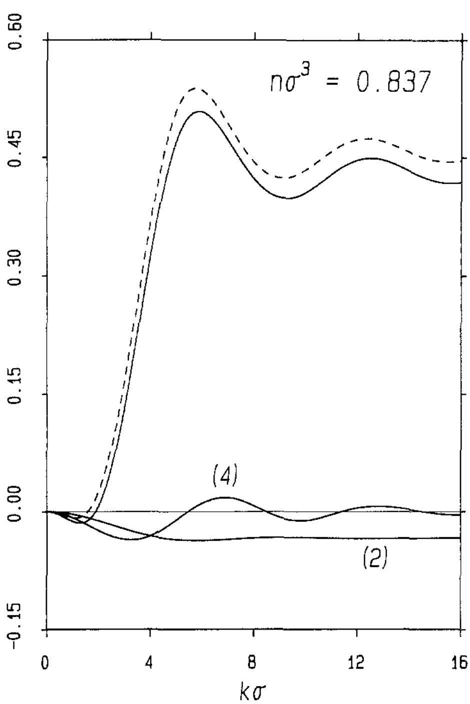

Fig. 6. The potential part of the second time derivative at $t=0^+$ of the transverse velocity correlation function $F_{66}(k, t)$ multiplied by t_e^2 at high density. The exact result (solid line) is compared with the Enskog theory result (dashed line). The recollision contribution is indicated by (2), and the four-particle contribution is indicated by (4).

The initial value of the Green–Kubo integrand for thermal conductivity is 15% larger than the Enskog value at low densities. However, at these densities the most important contributions come from the kinetic and cross terms, which are given correctly by the Enskog theory.

The only computer simulations for the initial-time Green–Kubo integrands of which we are aware are those of Alder *et al.*[18] For shear viscosity at low and intermediate densities their results are consistent with ours. Both at $n\sigma^3 = 0.786$ and $n\sigma^3 = 0.884$ they found $S_\eta + R_\eta + P_\eta = 2.30 \times 10^{-2}$, a value that is significantly different from our exact result. For thermal conductivity their results agree with ours, but their low-density value is almost equal to the Enskog value, and different from the exact value.

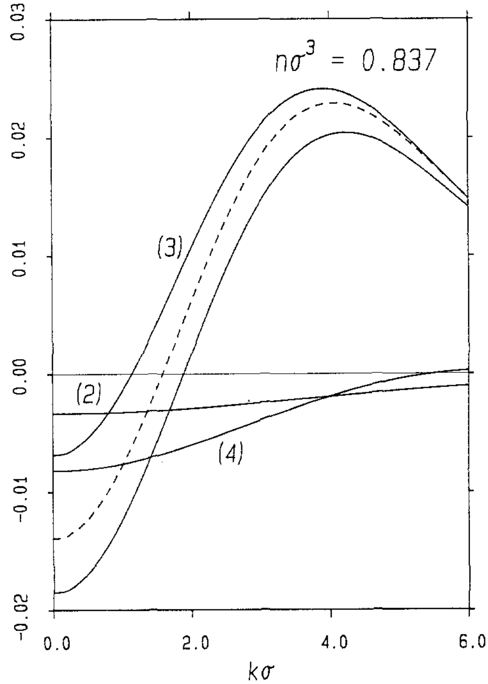

Fig. 7. The potential part of the second time derivative at $t=0^+$ of the transverse velocity correlation function $F_{66}(k, t)$ at high density, but now multiplied by $t_e^2/(k\sigma)^2$. The exact result (solid line) is compared with the Enskog theory result (dashed line). The recollision contribution is indicated by (2), the three-particle contribution is indicated by (3), and the four-particle contribution is indicated by (4).

Table I. Initial Value of Potential Term of the Shear Viscosity Integrand Excluding the Delta Term

$n\sigma^3$	$S_\eta + R_\eta + P_\eta$	S_η	R_η	P_η
0.	12.95×10^{-3}	9.34×10^{-3}	3.60×10^{-3}	0
0.421	15.79×10^{-3}	8.15×10^{-3}	3.58×10^{-3}	4.06×10^{-3}
0.837	18.53×10^{-3}	6.90×10^{-3}	3.38×10^{-3}	8.24×10^{-3}
(Enskog)	13.96×10^{-3}			

Table II. Initial Value of Potential Term of the Bulk Viscosity Integrand Excluding the Delta Term

$n\sigma^3$	$S_\kappa + R_\kappa + P_\kappa$	S_κ	R_κ	P_κ
0.	-2.12×10^{-2}	-2.72×10^{-2}	0.60×10^{-2}	0
0.421	-0.87×10^{-2}	-2.27×10^{-2}	0.60×10^{-2}	0.80×10^{-2}
0.837	-0.32×10^{-2}	-2.97×10^{-2}	0.56×10^{-2}	2.09×10^{-2}
(Enskog)	0			

5. DISCUSSION

We have calculated exact results for the short-time behavior of the hydrodynamic correlation functions. We found that for the potential part there are three contributions which at high densities and long wavelengths are of the same order of magnitude. The revised Enskog theory yields the first time derivative exactly, as well as the kinetic and cross parts of the second time derivative. RET yields the potential part as a certain approximation of only the three-particle term. Nevertheless, RET gives a fair approximation to the potential term of the second time derivative. Based on this, one may hope that RET will give a reasonable approximation of equilibrium time correlation functions not only for short times, but also for longer times, a hope that is supported by results of computer simulations of the hard-sphere system at not too high densities ($n\sigma^3 < 0.5$).[19] At high densities there are large discrepancies, most noticeably at long times. These can probably be attributed to mode coupling effects.[20–22] For the Green–Kubo integrand of shear viscosity we have shown that already at $t = 0^+$ there is a significant contribution from recollisions.

In principle, the short-time expansions of the hydrodynamic correlation functions could be extended by including higher powers of t. However,

Table III. Initial Value of the Potential Term of the Thermal Conductivity Integrand Excluding the Delta Term

$n\sigma^3$	$S_\lambda + R_\lambda$	S_λ	R_λ
0.	6.05×10^{-2}	5.67×10^{-2}	0.38×10^{-2}
0.421	5.99×10^{-2}	5.61×10^{-2}	0.38×10^{-2}
0.837	5.47×10^{-2}	5.11×10^{-2}	0.36×10^{-2}
(Enskog)	5.24×10^{-2}		

the dynamical processes involved rapidly become more and more complex and in addition one requires equilibrium correlation functions of increasingly higher orders, about which little is known.

Another possible extension which could certainly be made is to systems of particles interacting through a square-well or square-shoulder potential. However, here, too, the calculational work involved rapidly increases because of the four different types of collisions that are possible.[6]

APPENDIX A. CALCULATION OF THE VELOCITY INTEGRALS

Here we calculate the functions V_i which are defined in (3.20), (3.26), and (3.29). The method used is straightforward, but somewhat laborious. We transform as many integrals as possible to Gaussian ones using the substitutions given below. The velocity integrals can be restricted to the two-dimensional plane spanned by $\hat{\mathbf{r}}_{12}$ and $\hat{\mathbf{r}}_{13}$, as the integrals over the other direction are trivial. We have

$$\Phi = \mathbf{v}_1^2 + \mathbf{v}_2^2 + \mathbf{v}_3^2 = 3\mathbf{v}_T^2 + \tfrac{2}{3}(\mathbf{v}_{12}^2 + \mathbf{v}_{13}^2 - \mathbf{v}_{12} \cdot \mathbf{v}_{13}) \tag{A.1}$$

with $\mathbf{v}_T = (\mathbf{v}_1 + \mathbf{v}_2 + \mathbf{v}_3)/3$. Write

$$\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{13} = \cos\phi \tag{A.2a}$$

$$\hat{\mathbf{r}}_{12}^{\perp} \cdot \hat{\mathbf{r}}_{13} = \sin\phi \tag{A.2b}$$

and

$$\begin{aligned} a &= \mathbf{v}_T \cdot \hat{\mathbf{r}}_{12}, \qquad & s &= \mathbf{v}_{13} \cdot \hat{\mathbf{r}}_{13}, \qquad & x &= \mathbf{v}_{13} \cdot \hat{\mathbf{r}}_{13}^{\perp} \\ b &= \mathbf{v}_T \cdot \hat{\mathbf{r}}_{12}^{\perp}, \qquad & t &= \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}, \qquad & y &= \mathbf{v}_{12} \cdot \hat{\mathbf{r}}_{12}^{\perp} \end{aligned} \tag{A.3}$$

We now have

$$\begin{aligned} \Phi &= 3(a^2 + b^2) + \tfrac{2}{3}[t^2 + y^2 + s^2 + x^2 - \cos\phi(ts + xy) - \sin\phi(sy - tx)] \\ &= 3(a^2 + b^2) + \frac{2}{3}\left[\tilde{y}^2 + \lambda\tilde{x}^2 + \frac{3}{4\lambda}(t^2 + s^2 - ts\cos\phi)\right] \end{aligned} \tag{A.4}$$

with

$$\lambda = 1 - \frac{\cos^2\phi}{4} \tag{A.5}$$

and

$$\tilde{y} = y - \frac{\sin\phi}{2}s - \frac{\cos\phi}{2}x \tag{A.6a}$$

$$\tilde{x} = x - \frac{s}{4\lambda}\sin\phi\cos\phi + \frac{t}{2\lambda}\sin\phi \tag{A.6b}$$

The integrals to be calculated are

$$V_1(\cos\phi) = (\beta m)^2 \int d^2\mathbf{v}_1 \int d^2\mathbf{v}_2 \int d^2\mathbf{v}_3 \left(\frac{\beta m}{2\pi}\right)^3 \times \exp\left(-\frac{\beta m}{2}\Phi\right) s^2\theta(s)\, t^2\theta(-t) \tag{A.7a}$$

$$V_2(\cos\phi) = \frac{(\beta m)^{5/2}}{\sqrt{6}} \int d^2\mathbf{v}_1 \int d^2\mathbf{v}_2 \int d^2\mathbf{v}_3 \left(\frac{\beta m}{2\pi}\right)^3 \times \exp\left(-\frac{\beta m}{2}\Phi\right) s^2\theta(s)\, t^2\theta(-t)[(\mathbf{v}_1+\mathbf{v}_2)\cdot\hat{\mathbf{r}}_{12}] \tag{A.7b}$$

$$V_3(\cos\phi) = \frac{(\beta m)^3}{6} \int d^2\mathbf{v}_1 \int d^2\mathbf{v}_2 \int d^2\mathbf{v}_3 \left(\frac{\beta m}{2\pi}\right)^3 \times \exp\left(-\frac{\beta m}{2}\Phi\right) s^2\theta(s)\, t^2\theta(-t) \times [(\mathbf{v}_1+\mathbf{v}_2)\cdot\hat{\mathbf{r}}_{12}][(\mathbf{v}_1+\mathbf{v}_3)\cdot\hat{\mathbf{r}}_{13}] \tag{A.7c}$$

Now the integrals over a, b, $\tilde{x}$, and $\tilde{y}$ are Gaussian, and the transformation $(\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3) \to (a, b, s, t, \tilde{x}, \tilde{y})$ has Jacobian one. Calculating the integrals over a, b, $\tilde{x}$, and $\tilde{y}$ and substituting

$$\tilde{s} = s\left(\frac{\beta m}{4\lambda}\right)^{1/2} \tag{A.8a}$$

$$\tilde{t} = -t\left(\frac{\beta m}{4\lambda}\right)^{1/2} \tag{A.8b}$$

we arrive at

$$V_1(\cos\phi) = 16\lambda^{5/2} I_{22}(\cos\phi) \tag{A.9a}$$

$$V_2(\cos\phi) = \frac{8}{\sqrt{6}}\lambda^2(2\cos\phi + \cos^2\phi)\, I_{23}(\cos\phi) \tag{A.9b}$$

$$V_3(\cos\phi) = \tfrac{2}{3}\lambda^{3/2}[4\cos\phi I_{22}(\cos\phi) - 4\cos^3\phi I_{24}(\cos\phi) - (\cos^4\phi + 4\cos^2\phi)\, I_{33}(\cos\phi)] \tag{A.9c}$$

with

$$I_{nm}(z) = \frac{1}{\pi}\int ds \int dt (s^n)(t^m)\, \theta(s) \times \theta(t) \exp(-t^2 - s^2 - tsz) \tag{A.10}$$

The function I_{22} can be calculated by changing to polar coordinates, and is given by

$$I_{22}(z)=\frac{1}{8\pi}\left(1-\frac{z^2}{4}\right)^{-5/2}\times\left[\left(1+\frac{z^2}{2}\right)\arccos\frac{z}{2}-\frac{3}{2}z\left(1-\frac{z^2}{4}\right)^{1/2}\right] \tag{A.11}$$

Furthermore, we have

$$I_{33}(z)=-\frac{d}{dz}I_{22}(z) \tag{A.12}$$

and

$$I_{24}(z)=\frac{3}{2}I_{22}(z)-\frac{z}{2}I_{33}(z) \tag{A.13}$$

The function I_{23} can be found by considering its symmetric and antisymmetric parts. We have

$$I_{23}(z)=\frac{1}{\pi^{1/2}(2+z)^3} \tag{A.14}$$

Combination of the expressions (A.9) and (A.11)–(A.13) yields the results given in (3.31),

$$V_1(z)=\frac{2}{\pi}\left[\left(1+\frac{z^2}{2}\right)\arccos\frac{z}{2}-\frac{3}{2}z\left(1-\frac{z^2}{4}\right)^{1/2}\right] \tag{A.15a}$$

$$V_2(z)=\frac{2}{(6\pi)^{1/2}}z\left(1-\frac{z}{2}\right)^2 \tag{A.15b}$$

$$V_3(z)=\frac{1}{\pi}\left[z\left(\frac{z^2}{2}+\frac{1}{3}\right)\arccos\frac{z}{2}-\frac{7}{6}z^2\left(1-\frac{z^2}{4}\right)^{1/2}\right] \tag{A.15c}$$

The velocity integrals occurring in the recollision term $F_{ij}^{(2)}$ are only needed for $\cos\phi<0$. They are

$$\begin{aligned}W_1(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13})=\frac{(\beta m)^2}{|\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13}|}&\int d^2\mathbf{v}_1\int d^2\mathbf{v}_2\int d^2\mathbf{v}_3\\&\times f_m(v_1)\,f_m(v_2)\,f_m(v_3)\\&\times(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})^2\,\theta(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})\\&\times(\mathbf{v}_{1'2}\cdot\hat{\mathbf{r}}_{12})^2\,\theta(-\mathbf{v}_{1'2}\cdot\hat{\mathbf{r}}_{12})\end{aligned} \tag{A.16}$$

where $\mathbf{v}_{1'}=\mathbf{v}_1-\hat{\mathbf{r}}_{13}(\mathbf{v}_{13}\cdot\hat{\mathbf{r}}_{13})$ and $\mathbf{v}_{1'2}=\mathbf{v}_{1'}-\mathbf{v}_2$. Also,

$$W_2(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13})=\frac{(\beta m)^{5/2}}{\sqrt{6}\,|\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13}|}\int d^2\mathbf{v}_1\int d^2\mathbf{v}_2\int d^2\mathbf{v}_3$$
$$\times f_m(v_1)\,f_m(v_2)\,f_m(v_3)(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})^2$$
$$\times\,\theta(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})(\mathbf{v}_{1'2}\cdot\hat{\mathbf{r}}_{12})^2$$
$$\times\,[(\mathbf{v}_{1'}+\mathbf{v}_2)\cdot\hat{\mathbf{r}}_{12}]\,\theta(-\mathbf{v}_{1'2}\cdot\hat{\mathbf{r}}_{12}) \tag{A.17}$$

and

$$W_3(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13})=\frac{(\beta m)^{3}}{6\,|\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13}|}\int d^2\mathbf{v}_1\int d^2\mathbf{v}_2\int d^2\mathbf{v}_3$$
$$\times f_m(v_1)\,f_m(v_2)\,f_m(v_3)(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})^2$$
$$\times\,[(\mathbf{v}_1+\mathbf{v}_2)\cdot\hat{\mathbf{r}}_{12}]\,\theta(\mathbf{v}_{12}\cdot\hat{\mathbf{r}}_{12})(\mathbf{v}_{1'2}\cdot\hat{\mathbf{r}}_{12})^2$$
$$\times\,[(\mathbf{v}_{1'}+\mathbf{v}_2)\cdot\hat{\mathbf{r}}_{12}]\,\theta(-\mathbf{v}_{1'2}\cdot\hat{\mathbf{r}}_{12}) \tag{A.18}$$

These integrals can be treated in an entirely similar manner, now using $\mathbf{v}_{1'2}\cdot\hat{\mathbf{r}}_{12}$ instead of $\mathbf{v}_{13}\cdot\hat{\mathbf{r}}_{13}$. We find

$$W_1(z)=16z^4\left(1-\frac{z^2}{4}\right)^{5/2} I_{22}(2-z^2) \tag{A.19a}$$

$$W_2(z)=-\frac{32}{\sqrt{6}}z^5\left(1-\frac{z^2}{4}\right)^{3} I_{23}(2-z^2) \tag{A.19b}$$

$$W_3(z)=\frac{8}{3}\left(\frac{1-z^2}{4}\right)^{3/2} z^4\Bigg[(2-z^2)\,I_{22}(2-z^2)$$
$$-(2z^2-z^4)\,I_{24}(2-z^2)$$
$$+\left(-2z^2+z^4-\frac{z^6}{4}\right)I_{33}(2-z^2)\Bigg] \tag{A.19c}$$

From (A.19a) and (A.19b) the results presented in (3.40) can be obtained.

APPENDIX B. THE ANGULAR AVERAGE

The functions $F_i(k, z)$ are defined as

$$F_i(k,z)=\int d\hat{\mathbf{r}}_{12}\int d\hat{\mathbf{r}}_{13}\,\delta(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13}-z)$$
$$\times(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{12})^{n_i}(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{13})^{n_i'}$$
$$\times\{1-\exp(-ik\sigma\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{12})-\exp(ik\sigma\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}_{13})+\exp[ik\sigma\hat{\mathbf{k}}\cdot(\hat{\mathbf{r}}_{13}-\hat{\mathbf{r}}_{12})]\} \tag{B.1}$$

with $n_1 = n_1' = 1$, $n_2 = 0$, $n_2' = 1$, and $n_3 = n_3' = 0$. We write (B.1) as

$$F_i(k, z) = G_i(0, 0, z) - G_i(0, k\sigma, z) - G_i(-k\sigma, 0, z) + G_i(-k\sigma, k\sigma, z) \tag{B.2}$$

where

$$G_i(\lambda, \mu, z) = (-i)^{n_i + n_i'} \left(\frac{\partial}{\partial\lambda}\right)^{n_i} \left(\frac{\partial}{\partial\mu}\right)^{n_i'} H(\lambda, \mu, z) \tag{B.3}$$

In (B.3) we have introduced

$$H(\lambda, \mu, z) = \int d\hat{\mathbf{r}}_{12} \int d\hat{\mathbf{r}}_{13}\, \delta(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{13} - z) \times \exp[i\lambda(\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_{12})] \exp[i\mu(\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_{13})] \tag{B.4}$$

The function H does not depend on $\hat{\mathbf{k}}$, so instead of integrating over $\hat{\mathbf{r}}_{12}$, we can also integrate over $\hat{\mathbf{k}}$. The function H can be calculated exactly. Write

$$\hat{\mathbf{r}}_{12} = \hat{z}, \tag{B.5a}$$

$$\hat{\mathbf{k}} = \cos\theta\hat{z} + \sin\theta(\cos\phi\hat{x} + \sin\phi\hat{y}) \tag{B.5b}$$

$$\hat{\mathbf{r}}_{13} = \cos\alpha\hat{z} + \sin\alpha(\cos\beta\hat{x} + \sin\beta\hat{y}) \tag{B.5c}$$

We have

$$H(\lambda, \mu, z) = \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\phi \int_{-1}^{1} d\cos\alpha \times \int_0^{2\pi} d\beta\, \delta(\cos\alpha - z) \exp(i\lambda\cos\theta) \times \exp\{i\mu[\cos\alpha\cos\theta + \sin\alpha\sin\theta\cos(\phi - \beta)]\} \tag{B.6a}$$

$$= 4\pi \int_{-1}^{1} d\cos\theta \int_0^{\pi} d\phi \{\exp[i(\lambda + \mu z)\cos\theta]\} \times \cos[\mu(1 - z^2)^{1/2} \sin\theta\cos\phi] \tag{B.6b}$$

$$= 8\pi^2 \int_0^1 dx \cos[(\lambda + \mu z)x] \times J_0(\mu(1 - z^2)^{1/2} (1 - x^2)^{1/2}) \tag{B.6c}$$

$$= 8\pi^2 j_0(\kappa) \tag{B.6d}$$

with $\kappa^2 = \lambda^2 + 2\lambda\mu z + \mu^2$. The derivation of (B.6b) is trivial, and in obtaining (B.6c) and (B.6d) we have made use of standard integrals.[23] The results given in (3.32) follow by differentiation of H.

For the transverse velocity correlation function it is necessary to calculate the function $F_4(k, z)$, which is defined as

$$F_4(k, z) = \int d\hat{\mathbf{r}}_{12} \int d\hat{\mathbf{r}}_{13}\, \delta(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{13} - z) \times (\hat{\mathbf{k}}^{\perp} \cdot \hat{\mathbf{r}}_{12})(\hat{\mathbf{k}}^{\perp} \cdot \hat{\mathbf{r}}_{13})\{1 - \exp(-ik\sigma\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_{12}) - \exp(ik\sigma\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_{13}) + \exp[ik\sigma\hat{\mathbf{k}} \cdot (\hat{\mathbf{r}}_{13} - \hat{\mathbf{r}}_{12})]\} \tag{B.7}$$

This integral does not depend on the choice of either $\hat{\mathbf{k}}$ or $\hat{\mathbf{k}}^{\perp}$, so we add integrations over these vectors. As before, we write F_4 as a sum of four terms

$$F_4(k, z) = \hat{H}(0, 0, z) - \hat{H}(0, k\sigma, z) - \hat{H}(-k\sigma, 0, z) + \hat{H}(-k\sigma, k\sigma, z) \tag{B.8}$$

and because of the preceding remark, $\hat{H}$ can be given as

$$\hat{H}(\lambda, \mu, z) = \frac{1}{2\pi} \int d\hat{\mathbf{k}} \int d\hat{\mathbf{k}}^{\perp} \int d\hat{\mathbf{r}}_{13} \times \delta(\hat{\mathbf{k}} \cdot \hat{\mathbf{k}}^{\perp})\, \delta(\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{13} - z)(\hat{\mathbf{k}}^{\perp} \cdot \hat{\mathbf{r}}_{12})(\hat{\mathbf{k}}^{\perp} \cdot \hat{\mathbf{r}}_{13}) \times \exp[i\lambda(\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_{12})]\, \exp[i\mu(\hat{\mathbf{k}} \cdot \hat{\mathbf{r}}_{13})] \tag{B.9}$$

Using the same standard integrals, we now obtain

$$\hat{H}(\lambda, \mu, z) = 4\pi^2 \left(z + \frac{\partial^2}{\partial\lambda\, \partial\mu} \right) j_0(\kappa) \tag{B.10}$$

This yields the result given in (3.64).

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