Velocity-correlation functions in two and three dimensions. II. Higher density

J. R. Dorfman*
University of Maryland, College Park, Maryland 20742

E. G. D. Cohen
The Rockefeller University, New York, New York 10021
(Received 18 February 1975)

The short- and long-time behavior of the velocity-correlation functions characteristic for the coefficient of self-diffusion, and the kinetic parts of the coefficient of viscosity, and thermal conductivity, respectively, are computed approximately as a function of the density for a gas of hard disks or hard spheres on the basis of kinetic theory. The results obtained here are a generalization to higher densities of those obtained in an earlier paper, and reduce to them in the low-density limit. The density dependence is obtained by taking into account a larger number of dynamical events than previously considered. It is found that for short times the correlation functions decay exponentially, but that for longer times t, the correlation functions decay $\sim \alpha^{(d)}(n)(t/t_0)^{d/2}$ where n is the density, t_0 the mean free time between collisions, and d is the number of dimensions. The coefficient $\alpha^{(d)}(n)$ is determined by the transport coefficients of the Enskog theory for a dense gas of hard disks or hard spheres and is in very good agreement with existing computer experiments.

I. INTRODUCTION

In a previous Letter[1] results were given for the short- and long-time behavior of certain velocity autocorrelation functions. In a previous paper[2] (henceforth indicated by I) these results were derived to lowest order in the density on the basis of kinetic theory. In fact, we found that for hard disks or hard spheres of diameter a, the velocity correlation functions $\rho^{(d)}(t)$ were given in d dimensions, for long times t by the relation: $\rho^{(d)}(t) \sim \alpha^{(d)}(\rho)(t_0/t)^{d/2}$. Here the coefficient $\alpha^{(d)}(\rho)$ was determined to $O(\rho^{d-1})$, $\rho = na^d$, and t_0 is the mean free time. In the present paper these results will be generalized to higher densities and the full results quoted in the letter will be derived. In I the kinetic theory was presented for systems consisting of particles interacting with an additive, spherically symmetric (continuous) potential. However, the resulting expression [I Eq. (3.13)] was applied to hard spheres and to hard disks in spite of the fact that the binary collision operators appearing in this expression contained the derivative of the intermolecular potential, which is not well defined for such particles. It was argued that this was not serious, since for the final results the explicit forms of the binary collision operators occurring in these expressions were never needed. The results in the present paper, however, cannot be obtained without use of the special form that the binary collision operators take for hard-disk or hard-sphere potentials. Therefore in this paper we set up the kinetic theory, from the beginning, exclusively for such potentials, and also our final results are only meaningful for such potentials. Since these final results reduce, in lowest order of the density, to those obtained in I, they also present an *a posteriori* justification for them.

We consider a system consisting of N identical particles in a volume V, at temperature $T = (k_B\beta)^{-1}$, where k_B is Boltzmann's constant. We are interested in velocity autocorrelation functions that occur in the time-correlation-function expressions for the transport coefficients. We shall treat in detail the velocity autocorrelation function relevant for the self-diffusion coefficient D, which is the simplest. In d dimensions ($d=2, 3$) this correlation function is defined by

$$\rho_D^{(d)}(t) = \frac{\langle v_{1x} v_{1x}(-t)\rangle}{\langle v_{1x}^2\rangle} = \int d\vec{v}_1\, v_{1x} \Phi_D^{(d)}(\vec{v}_1; t)\,, \tag{1.1}$$

where

$$\Phi_D^{(d)}(\vec{v}_1; t) = \lim_{\substack{N, V\to\infty \\ N/V = n}} m^d \langle v_{1x}^2\rangle^{-1} V \int dx^{N-1}\, S_{-t}(x^N)\rho(x^N) v_{1x}\,. \tag{1.2}$$

Here $v_{1x}(t)$ is the x component of the velocity of particle 1, (mass m) at time t, $v_{1x}(0) = v_{1x}$. The angular brackets denote an average over a canonical ensemble, characterized by the probability density $\rho(x^N)$, where $x^N \equiv x_1, x_2, \ldots, x_N$ stands for the phases $x_i \equiv \vec{r}_i\vec{p}_i$ of the N particles $1, \ldots, N$. $S_{-t}(x^N)$ is the N-particle streaming operator which, when acting on a function $f(x^N)$ of the phases of the N particles, transforms this function as

$$S_{-t}(x^N) f(x^N) = f(x^N(-t))\,, \tag{1.3}$$

where $x^N(-t) \equiv x_1(-t), x_2(-t), \ldots, x_N(-t)$ are the (initial) phases of the particles $1, \ldots, N$ that lead to the phase x^N at time t, when they move according to their Hamilton function:

$$H(x^N)=\sum_{i=1}^{N}\frac{\vec{p}_i^{\,2}}{2m}+\sum_{\substack{i<j\\1}}^{N}\phi(r_{ij})\,. \tag{1.4}$$

Here the interparticle potential $\phi(r_{ij})$ depends only on the distance $r_{ij}=|\vec{r}_i-\vec{r}_j|$ of the particles i and j and is given by

$$\begin{aligned}\phi(r_{ij})&=\infty \quad \text{if } r_{ij}<a\\ &=0 \quad \text{if } r_{ij}\geq a\,,\end{aligned} \tag{1.5}$$

where a is the diameter of the hard disks or hard spheres. The canonical probability density $\rho(x^N)$ is given by

$$\begin{aligned}\rho(x^N)&=Z^{-1}\exp[-\beta H(x^N)]\\ &=Z^{-1}W(r^N)\exp\left(-\beta\sum_{i=1}^{N}\frac{\vec{p}_i^{\,2}}{2m}\right),\end{aligned} \tag{1.6}$$

where

$$W(r^N)=\exp\left(-\beta\sum_{\substack{i<j\\1}}^{N}\phi(r_{ij})\right)$$

is proportional to the configurational probability density to find the particles in the configuration $r^N\equiv\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N$ and Z is given by

$$Z=\int dx^N e^{-\beta H(x^N)}. \tag{1.7}$$

For the (hard core) potential (1.5), $W(r^N)=0$ when any pair of particles overlap, i.e. are separated by a distance smaller than a. The number density of the system is given by $n=N/V$.

In I an explicit representation of $S_{-t}(x^N)$ was given, but since it contained derivatives of the interparticle potential $\phi(r)$, this expression is not meaningful for hard-core potentials. In this paper two explicit representations[3a] of $S_{-t}(x^N)$, *in combination* with $W(r^N)$, will be used, which are such that the following two conditions are fulfilled: (1) The probability density for any configuration, in which two or more particles overlap, is zero; (2) when acting on a function $f(x^N)$, it gives $f(x^N(-t))$.

The representations are given in terms of operators $T(i,j)$ or $\overline{T}(i,j)$, depending on whether $W(r^N)$ precedes or follows $S_{-t}(x^N)$, respectively:

$$W(r^N)S_{-t}(x^N)=W(r^N)\exp\left[-t\left(\mathcal{H}_0(x^N)-\sum_{\substack{i<j\\1}}^{N}T(i,j)\right)\right] \tag{1.8}$$

and

$$S_{-t}(x^N)W(r^N)=\exp\left[-t\left(\mathcal{H}_0(x^N)-\sum_{\substack{i<j\\1}}^{N}\overline{T}(i,j)\right)\right]\,. \tag{1.9}$$

Upon comparing these expressions with the corresponding ones in I [Eqs. (2.5)–(2.7)], one sees that the T or $\overline{T}$ operators formally replace the θ operators in I.

In (1.8) and (1.9),

$$\mathcal{H}_0(x^N)=\sum_{i=j}^{N}\frac{\vec{p}_i}{m}\cdot\nabla_{\vec{r}_i}\,, \tag{1.10}$$

$$\begin{aligned}T(i,j)=a^{d-1}\int_{\vec{v}_{ij}\cdot\hat{\sigma}>0}d\hat{\sigma}\,|\vec{v}_{ij}\cdot\hat{\sigma}|\,\delta(\vec{r}_{ij}-a\hat{\sigma})\\ \times[R_\sigma(i,j)-1]\,,\end{aligned} \tag{1.11}$$

while

$$\begin{aligned}\overline{T}(i,j)=a^{d-1}\int_{\vec{v}_{ij}\cdot\hat{\sigma}>0}d\hat{\sigma}\,|\vec{v}_{ij}\cdot\hat{\sigma}|\,[\delta(\vec{r}_{ij}-a\hat{\sigma})R_\sigma(i,j)\\ -\delta(\vec{r}_{ij}+a\hat{\sigma})]\,.\end{aligned} \tag{1.12}$$

Here[3b] $\vec{v}_{ij}=\vec{v}_i-\vec{v}_j$; $\hat{\sigma}$ is a d-dimensional unit vector that characterizes the point of contact of the binary collision between the particles i and j in the relative coordinate system moving with particle j, with j as origin and $\vec{v}_{ij}$ as z axis. The operator $R_\sigma(i,j)$, when acting on functions of the velocities $\vec{v}_i$ and $\vec{v}_j$, replaces these by the velocities $\vec{v}_1'$ and $\vec{v}_j'$ of the restituting collision, which are given by

$$\vec{v}_i'=\vec{v}_i-(\vec{v}_{ij}\cdot\hat{\sigma})\hat{\sigma},\quad \vec{v}_j'=\vec{v}_j+(\vec{v}_{ij}\cdot\hat{\sigma})\hat{\sigma}\,. \tag{1.13}$$

For further details concerning these representations, we refer the reader to the literature. In Appendix A some properties of the T and $\overline{T}$ operators relevant for this paper are summarized. We note that because of the separate conservation of kinetic and potential energy in hard-disk and hard-sphere systems,

$$W(r^N)S_{-t}(x^N)=S_{-t}(x^N)W(r^N)\,. \tag{1.14}$$

In following sections $\rho_D^{(d)}(t)$ from (1.1) will be computed approximately for short as well as for long times. In Sec. II cluster expansions will be introduced that form the starting point of our calculations.[4]

In Sec. III the short-time behavior ($t\lesssim 3t_0$) of $\rho_D^{(d)}(t)$ will be derived. In Sec. IV the classes of dynamical events that are considered here in the calculation of the long-time behavior of $\rho_D^{(d)}(t)$ are given. In Sec. V the hydrodynamical modes that determine the long-time behavior of $\rho_D^{(d)}(t)$ are determined. In Sec. VI the long-time behavior of $\rho_D^{(d)}(t)$ and in Sec. VII that of $\rho_\eta^{(d)}(t)$ and $\rho_\lambda^{(d)}$ are obtained. This will allow us to make a comparison of the theoretical results derived here with the computer results obtained by Alder and Wainwright[5] and by Wood and Erpenbeck[6] for the long-time behavior of $\rho_D^{(d)}(t)$ over the full range of densities for which these results are available. A few comments on the results, supplementing those given in I, are given in Sec. VIII.

II. CLUSTER EXPANSIONS

Our starting point for the calculation of $\rho_D^{(d)}(\vec{v}_1;t)$ will be an expression for $\partial\Phi_D^{(d)}(\vec{v}_1;t)/\partial t$ that can be derived directly from Eq. (1.2):

$$\frac{\partial\Phi_D^{(d)}(\vec{v}_1,t)}{\partial t}=\beta m^{d+1}\lim_{\substack{N,V\to\infty\\ N/V=n}}\frac{V}{Z}\int dx^{N-1}\sum_{j=2}^{N}\overline{T}(1,j)S_{-t}(x^N)W(r^N)\exp\left(-\beta\sum_{j=1}^{N}\frac{\vec{p}_j^2}{2m}\right)v_{1x}. \tag{2.1}$$

Here we have used that $\langle v_{ix}^2\rangle^{-1}=\beta m$, the property (A7j) of $\overline{T}(i,j)$, spatial homogeneity of the system, and that $\rho(x^N)$ is assumed to vanish at the walls of the system.[7]

We consider $\partial\Phi_D/\partial t$ rather than $\Phi_D^{(d)}(t)$ as a starting point for the cluster expansion to be carried out below. The purpose of this is to use Eq. (2.1) together with Eq. (1.14), so that both T and $\overline{T}$ operators will appear in the cluster expansion. We will then see that the form obtained is especially convenient for the extraction of the Enskog theory results.[8]

We now introduce two cluster expansions, that lead to a formal density expansion of the right-hand side of Eq. (2.1).

(1) We invert, using Eq. (1.14), the order of $S_{-t}(x^N)$ and $W(r^N)$ in the integrand of Eq. (2.1). Then it is appropriate to use the representation of $S_{-t}(x^N)$ in terms of T operators as given by Eq. (1.8). We then expand $S_{-t}(x^N)$ for use in Eq. (2.1) as follows[9]

$$\begin{aligned}S_{-t}(x^N)&=\exp\left[-t\left(\mathcal{H}_0(x^N)-\sum_{\substack{i<j\\1}}^{N}T(i,j)\right)\right]\\&=\mathcal{U}(x_1,x_2;t)S_{-t}(x^{N-2})+\sum_{i=3}^{N}\mathcal{U}(x_1,x_2|x_i;t)S_{-t}(x^{N-3})+\sum_{3\le i<j\le N}\mathcal{U}(x_1,x_2|x_i,x_j;t)S_{-t}(x^{N-4})+\cdots.\end{aligned} \tag{2.2}$$

The operators $\mathcal{U}(x_1,x_2|x_3,\ldots,x_l;t)$ can be obtained successively from Eq. (2.2) by writing them out for $N=2,3,\ldots,N$. Thus one finds

$$\mathcal{U}(x_1,x_2;t)=S_{-t}(x_1,x_2)=\exp\{-t[\mathcal{H}_0(x_1,x_2)-T(1,2)]\}, \tag{2.3a}$$

$$\begin{aligned}\mathcal{U}(x_1,x_2|x_3;t)&=S_{-t}(x_1,x_2,x_3)-S_{-t}(x_1,x_2)S_{-t}(x_3)\\&=\exp\left[-t\left(\mathcal{H}_0(x_1,x_2,x_3)-\sum_{1\le i<j\le 3}T(i,j)\right)\right]-\exp\{-t[\mathcal{H}_0(x_1,x_2,x_3)-T(1,2)]\},\end{aligned} \tag{2.3b}$$

$$\begin{aligned}\mathcal{U}(x_1,x_2|x_3,x_4;t)&=S_{-t}(x_1,x_2,x_3,x_4)-S_{-t}(x_1,x_2,x_3)S_{-t}(x_4)-S_{-t}(x_1x_2x_4)S_{-t}(x_3)-S_{-t}(x_1,x_2)S_{-t}(x_3,x_4)\\&\quad+2S_{-t}(x_1,x_2)S_{-t}(x_3)S_{-t}(x_4),\end{aligned} \tag{2.3c}$$

etc.

Inserting cluster expansion (2.2) into the right-hand side of Eq. (2.1), using the identity of the particles and that the kinetic energy is a conserved quantity in a system of hard disks or hard spheres, so that

$$W(r^s)S_{-t}(x^s)\exp\left(-\frac{\beta m}{2}\sum_{i=1}^{s}\vec{v}_i^2\right)=W(r^s)\exp\left(-\frac{\beta m}{2}\sum_{i=1}^{s}\vec{v}_i^2\right)S_{-t}(x^s), \tag{2.4}$$

an expansion for $\partial\Phi_D^{(d)}/\partial t$ is obtained that contains the reduced equilibrium distribution functions of the system defined by

$$g(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_s)=\lim_{\substack{N,V\to\infty\\ N/V=n}}\frac{V^s}{Q}\int dr^{N-s}\,W(r^N) \tag{2.5a}$$

for $s=1,2,\ldots,$ where

$$Q=\int dr^N\,W(r^N). \tag{2.5b}$$

(2) In order to obtain an expansion in powers of the density n, one also has to make a cluster expansion of the $g(\vec{r}_1,\ldots,\vec{r}_s)$, which leads to the well-known density or virial expansion of the $g(\vec{r}_1,\ldots,\vec{r}_s)$[10]:

$$g(\vec{r}_1,\ldots,\vec{r}_s)=\sum_{l=0}^{\infty}g_l(\vec{r}_1,\ldots,\vec{r}_s)n^l \tag{2.6}$$

with

$$g_l(\vec{r}_1,\ldots,\vec{r}_s)=\int d\vec{r}_{s+1}\cdots\int d\vec{r}_{s+l}\times g_l(\vec{r}_1,\ldots,\vec{r}_s|\vec{r}_{s+1},\ldots,\vec{r}_{s+l}) \tag{2.7}$$

and in particular

$$g_0(\vec{r}_1,\ldots,\vec{r}_s)=\exp\left(-\beta\sum_{\substack{i<j\\1}}^{s}\phi(r_{ij})\right) \tag{2.8}$$

and

$$g_1(\vec{r}_1,\ldots,\vec{r}_s|\vec{r}_{s+1})=\exp\left(-\beta\sum_{\substack{i<j\\1}}^{s}\phi(r_{ij})\right)\times\sum_{j=2}^{s}\sum_{\substack{i_1<i_2<\cdots<i_j\\1}}^{s}f_{i_1,s+1}f_{i_2,s+1}\cdots\times f_{i_j,s+1}\,. \tag{2.9}$$

Here $f(r_{ij})\equiv f_{ij}$ are the Mayer f functions defined by

$$f(r_{ij})=e^{[-\beta\phi(r_{ij})]}-1\,. \tag{2.10}$$

For our hard-core potential, one finds, using Eq. (1.5), a unit step function for $f(r_{ij})$, viz.,

$$f(r_{ij})=-1 \quad \text{if } r_{ij}<a$$
$$=0 \quad \text{if } r_{ij}\geq a\,. \tag{2.11}$$

These two cluster expansions then lead to the following formal density expansion of $\partial\Phi_D^{(d)}/\partial t$:

$$\frac{\partial\Phi_D^{(d)}}{\partial t}=\beta m\sum_{l=1}^{\infty}n^l\,\mathcal{A}_{l+1}^D(\vec{v}_1;t)v_{1x}\varphi_0(v_1)\,, \tag{2.12}$$

where

$$\mathcal{A}_2^D(\vec{v}_1;t)=\int d2\,\overline{T}(1,2)g_0(\vec{r}_1,\vec{r}_2)\mathcal{U}(x_1x_2;t)\varphi_0(v_2)\,, \tag{2.13a}$$

$$\mathcal{A}_3^D(\vec{v}_1;t)=\int d2\int d3\,\overline{T}(1,2)[g_0(\vec{r}_1,\vec{r}_2,\vec{r}_3)\mathcal{U}(x_1x_2|x_3;t)+g_1(\vec{r}_1,\vec{r}_2|\vec{r}_3)\mathcal{U}(x_1x_2;t)]\varphi_0(v_2)\varphi_0(v_3)\,, \tag{2.13b}$$

$$\mathcal{A}_4^D(\vec{v}_1;t)=\tfrac{1}{2}\int d2\int d3\int d4\,\overline{T}(1,2)[g_0(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)\mathcal{U}(x_1x_2|x_3x_4;t)+g_1(\vec{r}_1,\vec{r}_2,\vec{r}_3|\vec{r}_4)\mathcal{U}(x_1x_2|x_3;t)$$
$$+g_1(\vec{r}_1,\vec{r}_2,\vec{r}_4|\vec{r}_3)\mathcal{U}(x_1x_2|x_4;t)+2g_2(\vec{r}_1,\vec{r}_2|\vec{r}_3,\vec{r}_4)\mathcal{U}(x_1x_2;t)]\varphi_0(v_2)\varphi_0(v_3)\varphi_0(v_4)\,,$$

$$\vdots \tag{2.13c}$$

$$\mathcal{A}_l^D(\vec{v}_1;t)=\frac{1}{(l-2)!}\int d2\cdots\int dl\,\overline{T}(1,2)\Big[g_0(\vec{r}_1,\ldots,\vec{r}_l)\mathcal{U}(x_1x_2|x_3\cdots x_l;t)$$
$$+\frac{(l-2)!}{(l-3)!}g_1(\vec{r}_1,\ldots,\vec{r}_{l-1}|\vec{r}_l)\,\mathcal{U}(x_1x_2|x_3\cdots x_{l-1};t)$$
$$+\frac{(l-2)!}{(l-4)!}g_2(\vec{r}_1,\ldots,\vec{r}_{l-2}|\vec{r}_{l-1},\vec{r}_l)\,\mathcal{U}(x_1x_2|x_3\cdots x_{l-2};t)+\cdots$$
$$+(l-2)!\,g_{l-2}(\vec{r}_1,\vec{r}_2|\vec{r}_3,\ldots,\vec{r}_l)\mathcal{U}(x_1x_2;t)\Big]\prod_{i=2}^{l}\varphi_0(v_i)\,. \tag{2.13d}$$

Here 1 stands for $\vec{r}_1,\vec{v}_1$, etc., $d2=d\vec{r}_2\,d\vec{v}_2$, etc., while $\varphi_0(v)$ is the Maxwell velocity distribution function:

$$\varphi_0(v)=(\beta m/2\pi)^{d/2}\exp(-\tfrac{1}{2}\beta m v^2)\,. \tag{2.14}$$

The $\mathcal{A}_l^D(\vec{v}_1;t)$, if Laplace transformed, formally reduce to those in I, when these are specialized to the case of hard-core systems.

The cluster expansion (2.12) for $\partial\Phi_D^{(d)}/\partial t$ can only be used to compute $\partial\Phi_D^{(d)}/\partial t$ for times of the order of $t_c=a/\langle v\rangle$, where $\langle v\rangle$ is an average velocity of the particles and t_c a time much smaller than the mean free time t_0. For a dynamical analysis of the $\mathcal{A}_l^D(\vec{v}_1;t)$ in terms of the collision sequences between the particles that contribute to the integrals reveals that they grow with time $\sim(t/t_c)^{l-2}$ as a result of sequences of $(l-1)$ binary collisions among the l particles.[9,11] An improved expression for $\partial\Phi_D^{(d)}/\partial t$, where these collision sequences have been eliminated, can be obtained by using the inversion procedure described in I. For that purpose it is convenient to consider the Laplace transform of Eq. (2.12), which is, using $\Phi_D^{(d)}(\vec{v}_1;t=0)=\beta m v_{1x}\varphi_0(v_1)$,

$$\epsilon\Phi_D^{(d)}(\vec{v}_1;\epsilon)=\beta m\left(1+\sum_{l=1}^{\infty}n^l\,\mathcal{A}_{l+1}^D(\vec{v}_1;\epsilon)\right)v_{1x}\varphi_0(v_1)\,, \tag{2.15a}$$

where

$$\Phi_D^{(d)}(\vec{v}_1;\epsilon)=\int_0^\infty dt\,e^{-\epsilon t}\Phi_D^{(d)}(\vec{v}_1;t) \tag{2.15b}$$

and

$$\mathcal{A}_{l+1}^D(\vec{v}_1;\epsilon)=\int_0^\infty dt\,e^{-\epsilon t}\mathcal{A}_{l+1}^D(\vec{v}_1;t)\,. \tag{2.15c}$$

We now define a new set of operators $\mathcal{B}_l^D(\vec{v}_1;\epsilon)$ by means of the identity[9,12]

$$1+\sum_{l=1}^{\infty}n^l\,\mathcal{A}_{l+1}^D(\vec{v}_1;\epsilon)=\left(1-\sum_{l=1}^{\infty}n^l\mathcal{B}_{l+1}^D(\vec{v}_1;\epsilon)\right)^{-1} \tag{2.16}$$

which yields

$$\mathcal{B}^D_{l+1}(\vec{v}_1;\epsilon)=\sum_{j=1}^{l}(-1)^{j+1}\sum_{\substack{\{a_i\}\\ \Sigma_{i=1}^{j}a_i=l}}\mathcal{A}^D_{a_1+1}\mathcal{A}^D_{a_2+1}\cdots\mathcal{A}^D_{a_j+1} \tag{2.17}$$

so that

$$\mathcal{B}^D_2(\vec{v}_1;\epsilon)=\mathcal{A}^D_2(\vec{v}_1;\epsilon)=\int d2\,\overline{T}(1,2)g_0(\vec{r}_1,\vec{r}_2)\mathcal{U}(x_1x_2;\epsilon)\varphi_0(v_2)\,, \tag{2.18a}$$

$$\begin{aligned}\mathcal{B}^D_3(\vec{v}_1;\epsilon)&=\mathcal{A}^D_3(\vec{v}_1;\epsilon)-[\mathcal{A}^D_2(\vec{v}_1;\epsilon)]^2\\&=\int d2\int d3\,\overline{T}(1,2)[g_0(\vec{r}_1,\vec{r}_2,\vec{r}_3)\mathcal{U}(x,x_2|x_3;\epsilon)+g_1(\vec{r}_1,\vec{r}_2|\vec{r}_3)\mathcal{U}(x_1x_2;\epsilon)\\&\qquad-g_0(\vec{r}_1,\vec{r}_2)\mathcal{U}(x_1x_2;\epsilon)\overline{T}(1,3)g_0(\vec{r}_1,\vec{r}_3)\mathcal{U}(x_1x_3;\epsilon)]\varphi_0(v_2)\varphi_0(v_3)\,,\end{aligned} \tag{2.18b}$$

$$\begin{aligned}\mathcal{B}^D_4(\vec{v}_1;\epsilon)&=\mathcal{A}^D_4(\vec{v}_1;\epsilon)-\mathcal{A}^D_3(\vec{v}_1;\epsilon)\mathcal{A}^D_2(\vec{v}_1;\epsilon)-\mathcal{A}^D_2(\vec{v}_1;\epsilon)\mathcal{A}^D_3(\vec{v}_1;\epsilon)+[\mathcal{A}^D_2(\vec{v}_1;\epsilon)]^3\\&=\tfrac{1}{2}\int d2\int d3\int d4\,\overline{T}(1,2)\{[g_0(\vec{r}_1,\vec{r}_2,\vec{r}_3,\vec{r}_4)\mathcal{U}(x_1x_2|x_3x_4;\epsilon)\\&\qquad+2g_1(\vec{r}_1,\vec{r}_2,\vec{r}_3|\vec{r}_4)\,\mathcal{U}(x_1x_2|x_3;\epsilon)+2g_2(\vec{r}_1,\vec{r}_2|\vec{r}_3,\vec{r}_4)\mathcal{U}(x_1x_2;\epsilon)]\\&\qquad-2[g_0(\vec{r}_1,\vec{r}_2,\vec{r}_3)\mathcal{U}(x_1x_2|x_3;\epsilon)+g_1(\vec{r}_1,\vec{r}_2|\vec{r}_3)\,\mathcal{U}(x_1x_2;\epsilon)]\overline{T}(1,4)g_0(\vec{r}_1,\vec{r}_4)\mathcal{U}(x_1x_4;\epsilon)\\&\qquad-2g_0(\vec{r}_1,\vec{r}_2)\mathcal{U}(x_1x_2;\epsilon)\overline{T}(1,3)[g_0(\vec{r}_1,\vec{r}_3,\vec{r}_4)\,\mathcal{U}(x_1x_3|x_4;\epsilon)+g_1(\vec{r}_1,\vec{r}_3|\vec{r}_4)\mathcal{U}(x_1x_3;\epsilon)]\\&\qquad+2g_0(\vec{r}_1,\vec{r}_2)\mathcal{U}(x_1x_2;\epsilon)\overline{T}(1,3)g_0(\vec{r}_1,\vec{r}_2)\mathcal{U}(x_1x_3;\epsilon)\,\overline{T}(1,4)g_0\,(\vec{r}_1,\vec{r}_4)\,\mathcal{U}(x_1x_4;\epsilon)]\}\\&\qquad\times\varphi_0(v_2)\varphi_0(v_3)\varphi_0(v_4)\,,\end{aligned} \tag{2.18c}$$

where $\mathcal{U}(x_1,x_2;\epsilon)$, $\mathcal{U}(x_1,x_2|x_3,\ldots;\epsilon)$ are the Laplace transforms of $\mathcal{U}(x_1,x_2;t)$, $\mathcal{U}(x_1,x_2|x_3,\ldots;t)$ defined by Eqs. (2.3a)–(2.3c).

One can show, by using Eq. (1.14) for $N=2,3,\ldots,$ that these expressions for $\mathcal{B}^D_{l+1}(\vec{v}_1,\epsilon)$ are identical with those given in I, if one replaces the θ_{ij} operator in I, by $\overline{T}(i,j)$.

Using (2.16) in (2.15a), we obtain

$$\Phi^{(d)}_D(\vec{v}_1;\epsilon)=\beta m\left(\epsilon-\sum_{l=1}^{\infty}n^l\epsilon\mathcal{B}^D_{l+1}(\vec{v}_1;\epsilon)\right)^{-1}v_{1x}\varphi_0(v_1)\,. \tag{2.19}$$

Although the collision sequences which lead to the secular growth of $\mathcal{A}^D_l(\vec{v}_1,t)$ do not contribute to the $\mathcal{B}^D_l$, and for hard spheres (i.e., $d=3$) indeed $\epsilon\mathcal{B}^D_2$ and $\epsilon\mathcal{B}^D_3$ exist in the limit $\epsilon\to0$, the higher $\epsilon\mathcal{B}^D_l$ do not, since $\epsilon\mathcal{B}^D_4\sim\log\epsilon$ and in general $\epsilon\mathcal{B}^D_l\sim\epsilon^{-(l-4)}$ for $l>4$.[13,14] Similarly for hard disks (i.e., $d=2$), $\epsilon\mathcal{B}^D_2$ exists as $\epsilon\to0$, but $\epsilon\mathcal{B}^D_3\sim\log\epsilon$, while in general $\epsilon\mathcal{B}^D_l\sim\epsilon^{-(l-3)}$ for $l>3$ as $\epsilon\to0$.[15,16]

Therefore also the expression (2.19) for $\Phi^{(d)}_D$ cannot be used to obtain the behavior of $\Phi^{(d)}_D(\epsilon)$ for $\epsilon\to0$ or of $\Phi^{(d)}_D(t)$ for large t. In I we showed that a rearrangement of the $\mathcal{B}^D_l$ series can be made, by summing the most divergent contributions to the $\mathcal{B}^D_l$ as $\epsilon\to0$ over all l. We obtained an expression for $\Phi^{(d)}_D(\vec{v}_1;\epsilon)$ that leads to an exponential-like behavior for short times and a behavior $(t/t_0)^{-d/2}$ for long times, but the coefficients occurring in both could only be determined to lowest order in the density.

In Secs. III and IV we will sketch a more extended rearrangement, in which not only the most divergent but also what we consider to be the most important less divergent contributions to the $\epsilon\mathcal{B}^D_l$ as $\epsilon\to0$, are summed. We will obtain an expression for $\Phi^{(d)}_D(t)$ that can be used to obtain the short- and the long-time behavior of $\Phi^{(d)}_D(t)$ and $\rho^{(d)}_D(t)$ valid for higher densities than the corresponding expressions in I.

III. SHORT-TIME BEHAVIOR OF $\rho^{(d)}_D(t)$: THE ENSKOG THEORY

The extended resummation of the $\mathcal{B}^D_l$ series mentioned in Sec. II requires a detailed study of the sequences of binary collisions that contribute to the $\mathcal{B}^D_l$. However, there is a simple and easily identifiable class of collision events, that determines the initial slope of $\rho^{(d)}_D(t)$ exactly and its short-time behavior to a good approximation. Before going into a more detailed analysis of the $\mathcal{B}^D_l$ in Sec. IV, we discuss in this section this above-mentioned class of events and the short-time behavior of $\rho^{(d)}_D(t)$.

The initial value of $\rho^{(d)}_D(t)$ follows directly from the definition (1.1): $\rho_D^{(d)}(0)=1$. The initial slope can also be found directly from (1.1), using (2.1), (2.5), and that $g(\vec{r}_1,\vec{r}_2)$ is only a function of $r_{12}=|\vec{r}_1-\vec{r}_2|$. One obtains

$$\left(\frac{d\rho_D^{(d)}(t)}{dt}\right)_{t=0}=n\beta m\chi(a)\int d\vec{v}_1 v_{1x}\,\lambda_0^D(\vec{v}_1)v_{1x}\,\varphi_0(v_1)$$

$$=-\chi(a)/\beta m D_{0,0} \qquad (3.1)$$

where $D_{0,0}$, the first Enskog approximation to the Lorentz-Boltzmann-equation value for the self-diffusion coefficient, is given by[17,18]

$$D_{0,0}=[2na(\beta\pi m)^{1/2}]^{-1} \quad \text{if } d=2$$
$$=3[8na^2(\beta\pi m)^{1/2}]^{-1} \quad \text{if } d=3\ . \qquad (3.2)$$

Here $\chi(a)\equiv g(r_{12}=a)$ occurs, because the δ functions in $\overline{T}(1,2)$ require that $r_{12}=a$. $\lambda_0^d(\vec{v}_1)$ is the Lorentz-Boltzmann operator defined by

$$\lambda_0^d(\vec{v}_1)=\int d\vec{v}_2\int d\vec{r}_2\,\overline{T}(1,2)\varphi_0(v_2)$$
$$=a^{d-1}\int d\vec{v}_2\int_{\vec{v}_{12}\cdot\hat{\sigma}>0}d\hat{\sigma}\,|\vec{v}_{12}\cdot\hat{\sigma}|$$
$$\times[R_\sigma(1,2)-1]\varphi_0(v_2)\ . \qquad (3.3)$$

Using Eqs. (2.6)–(2.9), one has for $\chi(a)$

$$\chi(a)=1+\sum_{l=1}^{\infty}n^l\chi_l(a)\ , \qquad (3.4)$$

where

$$\chi_l(a)=\int d\vec{r}_3\cdots\int d\vec{r}_{l+2}\,g_l(\vec{r}_1,\vec{r}_2|\vec{r}_3,\ldots,\vec{r}_{l+2})|_{r_{12}=a} \qquad (3.5)$$

and in particular[17,18]

$$\chi_0(a)=1\ , \qquad (3.6a)$$

$$\chi_1(a)=\int d\vec{r}_3 f_{13}f_{23}|_{r_{12}=a}$$
$$=\begin{cases}\frac{1}{2}(\frac{4}{3}-\sqrt{3}/\pi)\pi a^2 & \text{if } d=2\\ \frac{5}{12}\pi a^3 & \text{if } d=3\ .\end{cases} \qquad (3.6b)$$

The $\chi_l(a)$ ($l\geq 1$) take into account excluded volume corrections to the low-density result $\chi_0(a)=1$. Thus $\chi_1(a)$ corrects for the fact that the two particles 1 and 2 can only touch at $r_{12}=a$, if no third particle is in the way. In fact, the Mayer f functions occurring in (3.6b) require, for a nonvanishing contribution to the integral, that particle 3 overlaps simultaneously with the particles 1 and 2, so that $r_{13}<a$ and $r_{23}<a$.

Note that $\chi(a)\lambda_0^D(\vec{v}_1)$ is just the multiple collision correction of the Lorentz-Boltzmann equation according to the Enskog theory for a dense gas of hard spheres. One can therefore also say that the initial slope of $\rho_D^{(d)}(t)$ is given correctly by the Enskog dense-gas theory.[19]

For short times (i.e., time $t\lesssim 3t_0$) one could hope that the same excluded volume effects would give the leading contribution to $\rho_D^{(d)}(t)$. The $\overline{T}$ and $\mathfrak{U}(x_1,x_2|x_3,\ldots,x_s;\epsilon)$ operators and the functions $g_l(\vec{r}_1,\vec{r}_2|\vec{r}_3,\ldots,\vec{r}_{l+2})$ occurring in the integrand of the $\mathfrak{B}_l^D$ operators, Eq. (2.18), appear in such a way that those parts of the $\mathfrak{B}_l^D$ which lead to the Enskog theory can be immediately identified. These terms are those that take into account only the excluded-volume corrections to the binary collision between particles 1 and 2, and thus have the structure $\overline{T}(12)g_l(\vec{r}_1,\vec{r}_2|\vec{r}_3,\ldots,\vec{r}_{l+2})\mathfrak{U}(x_1,x_2;\epsilon)$ in the integrand, since the factor $g_l(\vec{r}_1,\vec{r}_2|\vec{r}_3,\ldots,\vec{r}_{l+2})$ incorporates l-particle excluded-volume corrections to the (1, 2)-binary collision event described by $\overline{T}(1,2)$.

Thus, approximating $\mathfrak{B}_l^D$ by this one term [cf. Eqs. (2.17) and (2.18)]:

$$\mathfrak{B}_{l,E}^D=\int d2\cdots\int dl\,\overline{T}(1,2)g_{l-2}(\vec{r}_1,\vec{r}_2|\vec{r}_3,\ldots,\vec{r}_l)$$
$$\times\,\mathfrak{U}(x_1x_2;\epsilon)\prod_{j=2}^{l}\varphi_0(v_j)$$
$$=\chi_{l-2}(a)\int d2\,\overline{T}(1,2)\mathfrak{U}(x_1x_2;\epsilon)\varphi_0(v_2)$$
$$=(1/\epsilon)\chi_{l-2}(a)\lambda_0^D(\vec{v}_1) \qquad (3.7)$$

leads to an expression for $\Phi_D^{(d)}(\vec{v}_1;\epsilon)$ of the form

$$\Phi_{D,E}^{(d)}(\vec{v}_1;\epsilon)=\left(\epsilon-\sum_{l=1}^{\infty}n^l\chi_{l-1}(a)\lambda_0^D(\vec{v}_1)\right)^{-1}v_{1x}\,\varphi_0(v_1)$$
$$=[\epsilon-n\chi(a)\lambda_0^D(\vec{v}_1)]^{-1}v_{1x}\,\varphi_0(v_1). \qquad (3.8)$$

The subscript E indicates that $\Phi_{D,E}^{(d)}(\vec{v}_1;\epsilon)$, when used to compute the coefficient of self-diffusion D, leads to a value given by the Enskog theory of hard-core particles. In arriving at Eq. (3.8), we used that the operator $\mathfrak{U}(x_1x_2;\epsilon)$, when acting on a function of $\vec{v}_1$, alone, can be replaced by $1/\epsilon$, on the basis of the Eqs. (2.3a) and (A7c).

Inversion of the Laplace transform leads to

$$\Phi_{D,E}^{(d)}(\vec{v}_1;t)=\exp[tn\chi(a)\lambda_0^D(\vec{v}_1)]v_{1x}\,\varphi_0(v_1)\ , \qquad (3.9)$$

so that, with Eq. (1.1), the corresponding expression for $\rho_D^{(d)}$ is given by

$$\rho_{D,E}^{(d)}(t)=\beta m\int d\vec{v}_1\,v_{1x}\exp[tn\chi(a)\lambda_0^D(\vec{v}_1)]v_{1x}\,\varphi_0(v_1)\ . \qquad (3.10)$$

The initial slope of $\rho_{D,E}^{(d)}(t)$ equals that of $\rho_D^{(d)}(t)$. A good approximation to $\rho_{D,E}^{(d)}(t)$ is given by[20]

$$\rho_{D,E}^{(d)}(t) \cong \exp(-t/\beta m D_{E,0}) , \qquad (3.11)$$

where $D_{E,0}$ is the first Enskog approximation to the coefficient of self-diffusion according to the Enskog dense-gas theory, given by[18]

$$D_{E,0} = D_{0,0}/\chi(a) , \qquad (3.12)$$

where $D_{0,0}$ is given in Eq. (3.2) for $d=2, 3$. Since $\beta m D_{E,0}$ is proportional to the mean free time t_0, $\rho_{D,E}^{(d)}(t)$ decays in a few mean free times. Equations (3.10)–(3.12) are a good approximation to the short-time behavior (i.e., for times $t \lesssim 3t_0$) of $\rho_D^{(d)}(t)$, and they agree well with the computer results over this period of time.[5,6]

In the next section a more complete resummation of the $\mathcal{B}_l^D$ series will be made.

IV. CLASSIFICATION OF DYNAMICAL EVENTS: RESUMMATION

In this section we consider the dynamical events that appear to determine the behavior of the velocity autocorrelation function for long times, in addition to those we considered in the previous section that dominate the short-time behavior.

In I it was shown that the resummation of the most divergent terms in the series

$$\sum_{l=1}^{\infty} \epsilon n^l \mathcal{B}_{l+1}^D$$

leads to the result that

$$\rho_D^{(d)}(t) \sim \alpha_D^{(d)} (t_0/t)^{d/2} ,$$

where the coefficient $\alpha_D^{(d)}$ is determined to $O(n^{d-1})$. In this section we will also take into account in the resummation several classes of less divergent dynamical events, which we believe on physical grounds, to give the dominant contribution to the long-time behavior for higher densities. The consequences of this resummation will be discussed in Sec. VI.

To carry out this resummation, one has to make a dynamical analysis of each operator $\epsilon\mathcal{B}_l^D$ as to the collision sequences that contribute to it; then one has to determine the long-time (or small ϵ) behavior of the $\mathcal{B}_l^D$ for these collision sequences and finally one has to sum the divergent contributions of all l in the series. We have only been able to carry this out for a restricted class of collisional events. We shall sketch the procedure followed on $\epsilon\mathcal{B}_3^D$ and $\epsilon\mathcal{B}_4^D$ and refer the reader to Appendix B for more details.

(a) $\epsilon\mathcal{B}_3^D$ is given by Eq. (2.18b). Using the Eqs. (3.6) and (3.7), we can rewrite $\epsilon\mathcal{B}_3^D$, using Eqs. (A7c) and (A7e), as follows:

$$\epsilon\mathcal{B}_3^D(\vec{v}_1;\epsilon) = \chi_1(a)\lambda_0^D(\vec{v}_1) + \epsilon\int d2\int d3\, \overline{T}(1,2)[g_0(\vec{r}_1,\vec{r}_2,\vec{r}_3)\,\mathcal{U}(x_1x_2|x_3;\epsilon) - g_0(\vec{r}_1,\vec{r}_2)G_0(x_1,x_2)\overline{T}(1,3)\,G_0(x_1,x_3)]\,\varphi_0(v_2)\varphi_0(v_3) , \qquad (4.1a)$$

where

$$G_0(x_1,x_2,\ldots,x_s) = [\epsilon + \mathcal{H}_0(x_1,x_2,\ldots,x_s)]^{-1} . \qquad (4.1b)$$

The dynamical analysis of $\epsilon\mathcal{B}_3^D$, and in fact of all $\epsilon\mathcal{B}_l^D$, is facilitated if one uses the binary-collision expansion of the operators $\mathcal{U}(x_1,x_2|x_3,\ldots,x_l;\epsilon)$ $(l=3,\ldots)$ in terms of the T operators as well as the cluster expansions of the equilibrium correlation functions $g_0(\vec{r}_1,\vec{r}_2)$, $g_1(\vec{r}_1,\vec{r}_2|\vec{r}_3)$ in terms of the Mayer f functions. Thus expanding the operator $\mathcal{U}(x_1,x_2|x_3;\epsilon)$ in terms of the operators $T(i,j)$ one finds, using the Eqs. (2.3b), (2.8), (2.10) and (A7a), (A7c), (A7f), and (A7i),

$$\epsilon\mathcal{B}_3^D(\vec{v}_1;\epsilon) = \chi_1(a)\lambda_0^D(\vec{v}_1) + \int d2\int d3\,\overline{T}(1,2)\,f(2,3)G_0(x_1,x_2,x_3)T(1,3)\varphi_0(v_2)\varphi_0(v_3) + \int d2\int d3\,\overline{T}(1,2)G_0(x_1,x_2)\lambda^D(12|3)G_0(x_1,x_2)T(1,2)\varphi_0(v_2) + \cdots \qquad (4.2)$$

with

$$\lambda^D(12|3) = [T(1,3) + T(2,3)(1+P_{23})]\,\varphi_0(v_3) , \qquad (4.3)$$

where P_{23} is a permutation operator that exchanges the indices of the particles 2 and 3. In (4.2) we have not written down the terms involving four or more collision operators or terms involving three or more collision operators combined with one or more Mayer f functions. A complete discussion of $\epsilon\mathcal{B}_3^D$ has been given by Sengers *et al.*,[21] and we shall mention only those points relevant for our discussion. The first term on the right-hand side of Eq. (4.2) represents the first density correction to $\lambda_0^D(\vec{v}_1)$, which was already discussed in the previous section. The short-time behavior of the second term on the right-hand side of Eq. (4.2) can be neglected compared to the first term.[22] In Appendix C, we take the long-time behavior of this term into account and show that it does not contribute to the $t^{-d/2}$ behavior of $\rho_D^{(d)}(t)$. The third term is the three-body ring term, already discussed in I. This term diverges ~lnϵ in $d=2$ and is finite in $d=3$ as $\epsilon \to 0$. It should be noted, that although this term differs from that in I, in that there only $\overline{T}$ operators occurred, the dominant behavior of both forms of the three-body ring term as $\epsilon \to 0$ is the same, since the difference between the expression in I in terms of $\overline{T}$ operators and the expression here is terms of $\overline{T}$ and T operators is determined by collision sequences with overlapping configurations of the particles. Such configurations do not contribute to the dominant behavior of $\epsilon\mathfrak{B}_3^D(\vec{v}_1;\epsilon)$ as $\epsilon \to 0$.[23] We remark that although the three-body ring events also contribute to the short-time behavior of $\rho_D^{(d)}(t)$, their contribution can be expected to be small in this case compared to the excluded-volume corrections contained in the first term in Eq. (4.2).[22]

(b) $\epsilon\mathfrak{B}_4^D$ is given by Eq. (2.18c). We expand $\mathfrak{U}(x_1,x_2\,|\,x_3;\epsilon)$, $\mathfrak{U}(x_1,x_2\,|\,x_4;\epsilon)$, etc. in terms of T operators and the equilibrium correlation functions in terms of Mayer f functions. Many of the resulting terms can then be shown to cancel or to vanish with the help of the Eqs. (A7a)–(A7g) and (A7i). Of the remaining terms, we shall restrict our attention to (i) the excluded-volume correction $\chi_2(a)\lambda_0^D$ to λ_0^D, already discussed in Sec. III; (ii) the four-body ring events that give the leading divergent contribution as $\epsilon \to 0$ and were already discussed in I; (iii) a certain class of excluded-volume corrections to the three-body ring term, that would appear to incorporate the leading density corrections to the long-time behavior of $\rho_D^{(d)}(t)$ obtained in I. We then obtain the following expression for $\epsilon\mathfrak{B}_4^D$:

$$\begin{aligned}\epsilon\mathfrak{B}_4^D(\vec{v}_1;\epsilon) = {} & \chi_2(a)\lambda_0^D(\vec{v}_1)\\ & + \int d2\int d3\int d4\,\overline{T}(1,2)\big[G_0\lambda^D(12\,|\,3)G_0\lambda^D(12\,|\,4)G_0T(1,2)\varphi_0(v_2)+f_{14}f_{24}G_0\lambda^D(12\,|\,3)G_0T(1,2)\varphi_0(v_2)\varphi_0(v_4)\\ & \qquad + f_{23}G_0\lambda^D(13\,|\,4)G_0T(1,3)\varphi_0(v_2)\varphi_0(v_3)+f_{13}f_{23}G_0\lambda^D(13\,|\,4)G_0T(1,3)\varphi_0(v_2)\varphi_0(v_3)\big]\\ & + \epsilon\tilde{\mathfrak{B}}_4^D + \text{LDT}\,, \end{aligned} \tag{4.4}$$

where G_0 in (4.4) is $G_0(x_1,x_2,x_3,x_4)$ defined in Eq. (4.1b). The first term on the right-hand side of Eq. (4.4) represents the second density correction to $\lambda_0^D(\vec{v}_1)$, which was already discussed in the previous section. The second term is the four-body ring term, the most divergent term in $\epsilon\mathfrak{B}_4^D$ as $\epsilon \to 0$ (~ϵ^{-1} in $d=2$ and ~lnϵ in $d=3$), which was already discussed in I (the difference between $\overline{T}$ and T operators for the dominant behavior as $\epsilon \to 0$ can be ignored again[23]). The third term represents an excluded-volume correction to the three-body ring term. That is, the particles 1, 2, and 3 perform the same sequence of binary collisions as in the three-body ring term, but in addition particle 4 overlaps with both particles 1 and 2 at the moment of the (1, 2) collision described by the operator $\overline{T}(1,2)$. These dynamical events are sketched schematically in Fig. 1(a). We shall refer to a configuration of three particles, where two are colliding while the third overlaps both, as a double overlapping configuration. Dynamical events that contribute to the fourth and fifth terms on the right-hand side of Eq. (4.4) are sketched schematically in Figs. 1(b) and 1(c). We remark that the third, fourth, and fifth term have the *same* ϵ dependence, for $\epsilon \to 0$, as the three-body ring term. The term $\epsilon\tilde{\mathfrak{B}}_4^D$ contains the contributions of products of five T operators, which also contain excluded-volume corrections to the three-body ring term and will be discussed below. The last term, indicated by LDT (less divergent terms) contains the contributions of all neglected terms. Since these contributions are less divergent in two and three dimensions as $\epsilon \to 0$ than those taken into account in the previous terms, they will not be considered here for the long-time behavior of $\Phi_D^{(d)}(t)$.

We remark that although $\epsilon\tilde{\mathfrak{B}}_4^D$ is finite in three dimensions as $\epsilon \to 0$, it is convenient to include it in the resummation of the divergent terms.

Of all the contributions contained in $\epsilon\tilde{\mathfrak{B}}_4^D$, we have examined in detail those that consist of a sequence of three binary collisions with an excluded-volume correction due to a double overlapping configuration at one of the collisions in the sequence (cf. Fig. 2). All these terms incorporate excluded-volume corrections to the three-body ring term. They subdivide into two classes: (i) simple excluded-volume corrections, where the "double overlapping" particle is not involved in any other collision in the sequence; (ii) connected excluded-volume corrections, where the "double overlapping" particle *also* participates in one or

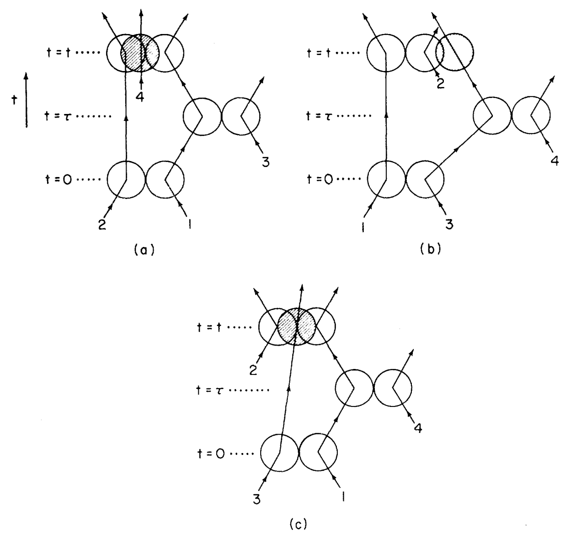

FIG. 1. Schematic illustration of some of the dynamical events which contribute to (a) the third term, (b) the fourth term, and (c) the fifth term on the right-hand side of Eq. (4.4). In these diagrams we consider the inverse Laplace transform of the right-hand side of (4.4). The vertical direction indicates the direction of increasing time. We have arranged the events such that the (1,2) collision described by the $\overline{T}(1,2)$ operator takes place at time t, the middle collision, which illustrates one of the collisions included in the λ^D operators, takes place at time $\tau (\tau < t)$ and the collision described by the T operator on the extreme right, takes place at time $t=0$, with $(t > \tau > 0)$. The shaded particle indicates the overlapping configuration in each figure.

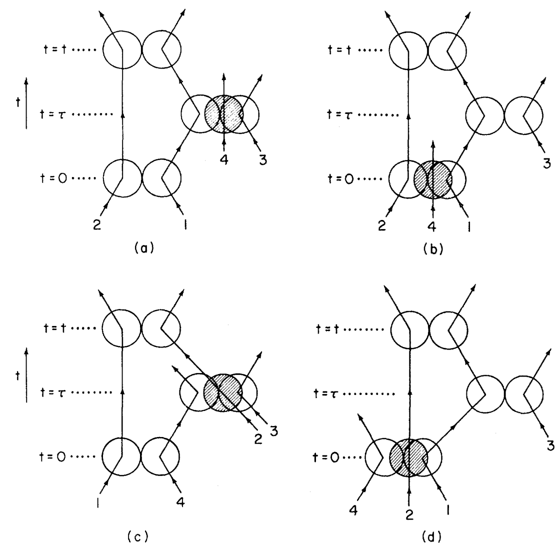

FIG. 2. Schematic illustration of some of the excluded volume corrections in $\epsilon\tilde{\mathfrak{B}}_4^D$ which are retained in our analysis. The times of the dynamical events are arranged as in Fig. 1. Shown here are (a) a simple excluded-volume correction to the middle collision in a three-body ring event; (b) a simple excluded-volume correction to the collision at $t=0$; (c) a connected excluded-volume correction to the middle collision; and (d) a connected excluded-volume correction to the collision at $t=0$. The shaded particle indicates the overlapping configuration.

both of the other two collisions that occur in the sequence [cf. Fig. 1(c), 2(c), and 2(d)]. We have assumed here that over the time scale relevant for comparison with the computer calculations, the excluded-volume corrections to the most divergent terms give the dominant density corrections to these terms. For this reason we consider in $\epsilon\mathfrak{B}_4^D$ only the Enskog term, the ring term, and the excluded-volume corrections to $\epsilon\mathfrak{B}_3^D$ contained in $\epsilon\mathfrak{B}_4^D$.

One might have thought that the only terms of the above type would be those written out explicitly on the right-hand side of Eq. (4.4). However, the $\epsilon\tilde{\mathfrak{B}}_4^D$ *also* contains terms of this type which are hidden in certain products of three T operators. For, one has the following relation:

$$[G_0(x_i, x_j, x_k, \ldots)T(i,j)G_0(x_i, x_j, x_k, \ldots)T(j,k)G_0(x_i, x_j, x_k, \ldots) + G_0(x_i, x_j, x_k, \ldots)T(j,k)G_0(x_i, x_j, x_k, \ldots)T(i,j)G_0(x_i, x_j, x_k, \ldots)]\,T(i,k)$$
$$= G_0(x_i, x_j, x_k, \ldots)f_{ij}f_{jk}\,T(i,k) + f_{ij}f_{jk}G_0(x_i, x_j, x_k, \ldots)T(i,k) - f_{ij}G_0(x_i, x_j, x_k, \ldots)f_{jk}T(i,k) - f_{jk}G_0(x_i, x_j, x_k, \ldots)f_{ij}T(i,k) + \cdots \tag{4.5}$$

where the dots at the end indicate contributions from non-double overlapping configurations. For an outline of a proof and further details, we refer to Appendix B. Using (4.5), one can extract the double overlapping contributions. A brief indication of how this is done is also given in Appendix B. Then one finds for the contribution, $\epsilon\tilde{\mathfrak{B}}_{4,i}^D$, of the simple excluded-volume corrections of class (i) to $\epsilon\tilde{\mathfrak{B}}_4^D$ $[G_0 = G_0(x_1, x_2, x_3, x_4)]$:

$$\epsilon\tilde{\mathfrak{B}}_{4,\mathrm{i}}^D = \int d2 \int d3 \int d4\; \overline{T}(1,2)G_0\{[f_{14}f_{34}T(1,3) + f_{24}f_{34}T(2,3)(1+P_{23})]\,G_0T(1,2)\varphi_0(v_3) + \lambda^D(12|3)G_0f_{14}f_{24}T(1,2)\} \times\varphi_0(v_2)\varphi_0(v_4) \tag{4.6}$$

while the contribution, $\epsilon\tilde{\mathfrak{B}}^D_{4,\text{ii}}$, of connected excluded-volume corrections of class (ii) to $\epsilon\tilde{\mathfrak{B}}_4^D$ is

$$\epsilon\tilde{\mathfrak{B}}^D_{4,\text{ii}} = \int d2 \int d3 \int d4\, \overline{T}(1,2)[G_0 f_{23} f_{24} T(3,4)\, G_0 T(1,4)\varphi_0(v_3) + G_0 \lambda^D(12|3)\, G_0\, f_{12} f_{24} T(1,4)]\, \varphi_0(v_2)\varphi_0(v_4)\,. \tag{4.7}$$

In (4.7) the first term on the right side gives the contribution of those sequences of three successive binary collisions, where the double overlapping configuration occurs in the middle of the three collisions [cf. Fig. 2(c)], while in the second term this configuration occurs at the bottom collision, i.e. the one taking place at $t=0$ [cf. Fig. 2(d)]. The restriction to double overlapping excluded-volume corrections to the three-body ring term in $\epsilon\mathfrak{B}_4^D$ is supported by Sengers'[21] calculations of $\epsilon\mathfrak{B}_3^D$, where the double overlap terms gave the overwhelmingly dominant contribution to $\epsilon\mathfrak{B}_3^D$. In addition, Alder, Gass, and Wainwright's computer calculation[5] of D for a gas of hard spheres over a very wide range of densities showed at most 30–40% deviations from D_E, given by the Enskog theory. Since the Enskog theory *only* takes double overlap corrections to the Boltzmann equation into account, these corrections appear to give the dominant corrections to the Boltzmann result, even for dense hard-sphere gases.

Combining Eqs. (4.4), (4.6), and (4.7), we can write $\epsilon\mathfrak{B}_4^D$ in the form

$$\epsilon\mathfrak{B}_4^D = \chi_2(a)\,\lambda_0^D + \epsilon\mathfrak{B}^D_{4,R} + \epsilon\mathfrak{B}^D_{4,Ex} + \epsilon\mathfrak{B}^D_{4,F} + \text{LDT}\,, \tag{4.8}$$

where

$$\epsilon\mathfrak{B}^D_{4,R} = \int d2 \int d3 \int d4\, \overline{T}(1,2) G_0(x_1,x_2)\, \lambda^D(12|3) G_0(x_1,x_2) \lambda^D(12|4) G_0(x_1,x_2) T(1,2)\varphi_0(v_2) \tag{4.9a}$$

is the four-body ring term;

$$\begin{aligned}\epsilon\mathfrak{B}^D_{4,Ex} = \int d2 \int d3 \int d4\, \overline{T}(1,2)[& f_{14} f_{24} G_0(x_1,x_2)\ \lambda^D(12|3) G_0(x_1,x_2) T(1,2)\\ &+ G_0(x_1,x_2)\ [T(1,3) f_{14} f_{34} + (1+P_{23}+P_{24}) f_{24} f_{34} T(2,3)]\, G_0(x_1,x_2) T(1,2)\varphi_0(v_3)\\ &+ G_0(x_1,x_2)\ \lambda^D(12|3) G_0(x_1,x_2) f_{14} f_{24} T(1,2)]\ \varphi_0(v_2)\varphi_0(v_4)\end{aligned} \tag{4.9b}$$

represents the contributions from the excluded-volume corrections of class (i) to the three-body ring term, as given by the third term on the right-hand side of Eq. (4.4) and by Eq. (4.6), as well as the contribution from the connected excluded-volume correction of class (ii) to the middle of the three collisions occurring in the three-body ring term from Eq. (4.7). Here we have rewritten this term as given in Eq. (4.7), with the help of the permutation operator P_{24} and Liouville's theorem. Finally,

$$\begin{aligned}\epsilon\mathfrak{B}^D_{4,F} = \int d2 \int d3 \int d4\, \overline{T}(1,2)[& f_{23}(1+f_{13}) G_0(x_1,x_3,x_4)\ \lambda^D(13|4) G_0(x_1,x_3) T(1,3)\varphi_0(v_3)\\ &+ G_0(x_1,x_2,x_4)\ \lambda^D(12|3) G_0(x_1,x_2,x_4) f_{12} f_{24} T(1,4)\varphi_0(v_4)]\ \varphi_0(v_2)\end{aligned} \tag{4.10}$$

represents the contribution from connected excluded-volume corrections of class (ii) to the first and the last of the three collisions occurring in the three-body ring term, as well as from the fourth term on the right-hand side of Eq. (4.4). All other contributions to $\epsilon\mathfrak{B}_4^D$ are denoted by LDT and are neglected.

(c) An analysis of $\epsilon\mathfrak{B}_5^D, \epsilon\mathfrak{B}_6^D, \ldots$ can be made, similar to that of $\epsilon\mathfrak{B}_4^D$ sketched in (b). The enormous number of terms that appear, especially after the binary collision expansion and the Mayer f expansion have been made, has prevented us from a systematic analysis.[24a] One can convince oneself, however, that the same types of terms that have been considered in $\epsilon\mathfrak{B}_4^D$ are also present in $\epsilon\mathfrak{B}_5^D$, $\epsilon\mathfrak{B}_6^D$, etc. In particular, they contain contributions $\chi_3(a)\,\lambda_0^D$, $\chi_4(a)\,\lambda_0^D$, etc. respectively. These contributions, together with λ_0^D and $\chi_1(a)\,\lambda_0^D$ from $\epsilon\mathfrak{B}_2^D$ and $\epsilon\mathfrak{B}_3^D$, respectively, yield upon summation the operator $\chi(a)\,\lambda_0^D$ considered already in the previous section. In addition, the operators $\epsilon\mathfrak{B}_5^D$, $\epsilon\mathfrak{B}_6^D, \ldots$ contain the five-, six-, ... particle ring terms of the form:

$$\int d2\, \overline{T}(1,2) G_0(x_1,x_2)\left(\int d3\, \lambda^D(12|3) G_0(x_1,x_2)\right)^{l-2} \times T(1,2)\varphi_0(v_2)$$

for $l=5, 6, \ldots$. Finally $\epsilon\mathfrak{B}_l^D$ will also contain the excluded-volume corrections of class (i) and (ii) to the ring operators in $\epsilon\mathfrak{B}_k^D$ with $k \leq l-1$.

(d) Before proceeding with the resummation of the above-mentioned operators from which we will obtain the $t^{-d/2}$ behavior of $\rho_D^{(d)}(t)$ for long times, we remark that $\epsilon\mathfrak{B}^D_{4,F}$ will not contribute to this behavior. For, by a partial resummation of terms of this type in the $\mathfrak{B}_l^D$ series, we show in Appendix C that the resummed expression will not contribute to the coefficient of $t^{-d/2}$. Therefore the following types of dynamical events will be included in the resummation to be carried out below: (1) All ring operator terms. This will lead to a resummation of the most divergent contributions in each order of the density and has already been carried out in I; (2) all simple excluded-volume corrections to the ring operator; (3) all connected excluded-volume corrections to the intermediate collisions in the sequence of collisions that occur in the ring operators, i.e., to all but the first and the last collisions in the sequence. These events are, for $\epsilon\mathfrak{B}_4^D$, contained in $\epsilon\mathfrak{B}_{4,R}^D$, and $\epsilon\mathfrak{B}_{4,Ex}^D$.

We carry out the resummation in a sequence of steps:

(i) We combine the three-body ring operator with all the simple and connected excluded-volume corrections to it, that are contained in $\epsilon\mathfrak{B}_4$, $\epsilon\mathfrak{B}_5,\ldots$ in order to obtain a "modified" three-body ring operator.

(ii) By including in a similar fashion simple and connected excluded-volume corrections to the l-body ring operators, we then construct modified l-body ring operators.

(iii) Finally all the modified l-body ring operators for $l=3,4,\ldots$ are summed to give the resummed ring operator.

To show how this is done, we first rewrite $\epsilon\mathfrak{B}_{4,Ex}^D$ in a different form. The simple excluded-volume corrections to the three-body ring operator contained in it can be rewritten in the suggestive form:

$$\int d2\int d3\,\overline{T}(1,2)[\chi_1(a)G_0(x_1,x_2)\lambda^D(12|3)G_0(x_1,x_2)+G_0(x_1,x_2)\chi_1(a)\lambda^D(12|3)G_0(x_1,x_2)+G_0(x_1,x_2)\lambda^D(12|3)G_0(x_1,x_2)\chi_1(a)]\times T(1,2)\varphi_0(v_2)\,. \tag{4.11}$$

Here we have used Eqs. (3.6) and (4.9b). Furthermore, the remaining term in $\epsilon\mathfrak{B}_{4,Ex}^D$, i.e., the connected excluded-volume correction to the three-body ring operator, can be rewritten in the form

$$\int d2\int d3\int d4\,\overline{T}(1,2)G_0(x_1,x_2)P_{24}g_1(\vec{r}_2,\vec{r}_3|\vec{r}_4)\times T(2,3)G_0(x_1,x_2)T(1,2)\varphi_0(v_2)\varphi_0(v_3)\varphi_0(v_4)\,. \tag{4.12}$$

Hence, resummation of all the simple excluded-volume corrections to the three-body ring operator, and all the connected excluded-volume corrections to the middle collision in $\epsilon\mathfrak{B}_3^D$ contained in the $\mathfrak{B}_l^D$ series will lead to a modified three-body ring operator $\epsilon\tilde{\mathfrak{B}}_3^D$ of the form

$$\epsilon\hat{\mathfrak{B}}_3^D=\int d2\int d3\,\chi(a)\overline{T}(1,2)G_0(x_1,x_2)\times[\chi(a)T(1,3)+\chi(a)T(2,3)(1+P_{23})+\Gamma(2|3)T(2,3)]\varphi_0(v_3)G_0(x_1,x_2)\chi(a)\times T(1,2)\varphi_0(v_2)\,, \tag{4.13}$$

where

$$\Gamma(2|3)=\sum_{l=1}^{\infty}n^l\int d4\cdots\times\int d(l+3)\,[P_{24}+P_{25}+\cdots+P_{2,l+3}]\times g_l(\vec{r}_2,\vec{r}_3|\vec{r}_4,\ldots,\vec{r}_{l+3}). \tag{4.14}$$

Note that the contributions of this type must be symmetric in the particles $4,5\ldots,l+3$ and that any one of these particles can participate in the "bottom" collision, i.e., the collision described by the T operator on the extreme right of Eq. (4.13).

We have now obtained the modified three-body ring operator. In a similar fashion one can construct a modified l-body ring operator given by

$$\epsilon\hat{\mathfrak{B}}_l^D(\vec{v}_1;\epsilon)=\int d2\,\chi(a)\overline{T}(1,2)G_0(x_1,x_2)\left\{\int d3\,[\chi(a)T(1,3)\varphi_0(v_3)+\chi(a)T(2,3)(1+P_{23})\varphi_0(v_3)+\Gamma(2|3)T(2,3)\varphi_0(v_3)]\right\}^{l-2}\times G_0(x_1,x_2)\chi(a)T(1,2)\varphi_0(v_2),\quad l=3,4,\ldots. \tag{4.15}$$

Summing these operators over all l, one obtains an approximate expression for the $\mathfrak{B}_l^D$ series which takes into account the above mentioned three classes of dynamical events. This expression reads

$$\sum_{l=1}^{\infty}n^l\epsilon\mathfrak{B}_{l+1}^D(\vec{v}_1;\epsilon)\cong n\chi(a)\lambda_0^D(\vec{v}_1)+n\epsilon\mathfrak{R}_E^D(\vec{v}_1;\epsilon) \tag{4.16}$$

with

$$n\epsilon\mathfrak{R}_E^D(\vec{v}_1;\epsilon)=\sum_{l=2}^{\infty}n^l\epsilon\hat{\mathfrak{B}}_{l+1}^D(\vec{v}_1;\epsilon)=n\int d2\,\overline{T}(1,2)\chi(a)\left[\epsilon+\mathcal{H}_0(x_1,x_2)-n\chi(a)\int d3\,\lambda^D(12|3)\varphi_0(v_3)-n\int d3\,\Gamma(2|3)T(2,3)\varphi_0(v_3)\right]^{-1}\times\chi(a)T(1,2)\varphi_0(v_2)\,, \tag{4.17}$$

where we have included a term $n\int d2\,\overline{T}(1,2)\chi(a)G_0(x_1,x_2)\chi(a)T(1,2)$, which is identically zero.

Thus $\Phi_D^{(d)}(\vec{v}_1;\epsilon)$ from Eq. (2.19) is now given by the equation

$$\Phi_D^{(d)}(\vec{v}_1;\epsilon)=\beta m[\epsilon-n\chi(a)\lambda_0^D(\vec{v}_1)-n\epsilon\mathcal{R}_E^D(\vec{v}_1;\epsilon)]^{-1}v_{1x}\varphi_0(v_1)\,. \tag{4.18}$$

It is convenient for a discussion of the long-time behavior of $\rho_D^{(d)}(t)$ to use a Fourier representation of $\epsilon\mathcal{R}_E^D(\vec{v}_1;\epsilon)$. Using that $\epsilon\mathcal{R}_E^D(\vec{v}_1;\epsilon)$ does not depend on $\vec{r}_1$ and by inserting δ functions on the right-hand side of Eq. (4.17) and using their Fourier representation, one can write $\epsilon\mathcal{R}_E^D(\vec{v}_1;\epsilon)$ in the form:

$$\epsilon\mathcal{R}_E^D(\vec{v}_1;\epsilon)=\int d\vec{v}_2\int\frac{d\vec{k}}{(2\pi)^d}\,\overline{T}_{-\vec{k}}(1,2)\chi(a)\,[\epsilon+i\vec{k}\cdot\vec{v}_{12}-n\chi(a)\lambda_0^D(\vec{v}_1)-n\chi(a)\lambda_{-\vec{k}}(\vec{v}_2)-nA_{-\vec{k}}(\vec{v}_2)]^{-1}\chi(a)T_{\vec{k}}(1,2)\,\varphi_0(v_2)\,. \tag{4.19}$$

Here

$$\overline{T}_{-\vec{k}}(1,2)=\int d\vec{r}_{12}\,e^{i\vec{k}\cdot\vec{r}_{12}}\overline{T}(1,2)\,, \tag{4.20a}$$

$$T_{\vec{k}}(1,2)=\int d\vec{r}_{12}\,e^{-i\vec{k}\cdot\vec{r}_{12}}T(1,2)\,, \tag{4.20b}$$

$$\lambda_{-\vec{k}}(\vec{v}_2)=\int d\vec{v}_3\,[T_0(2,3)+T_{-\vec{k}}(2,3)P_{23}]\,\varphi_0(v_3)\,. \tag{4.21}$$

and

$$A_{-\vec{k}}(\vec{v}_2)=\sum_{l=1}^{\infty}n^l\int d\vec{v}_3\cdots\int d\vec{v}_{l+3}\int d\vec{r}_{23}\cdots\int d\vec{r}_{2,l+3}\times e^{i\vec{k}\cdot\vec{r}_2}\sum_{i=4}^{l+3}P_{2i}\,g_l(\vec{r}_2,\vec{r}_3\,|\,\vec{r}_4,\ldots,\vec{r}_{l+3})T(2,3)\prod_{i=3}^{l+3}\varphi_0(v_i)e^{-i\vec{k}\cdot\vec{r}_2}\,. \tag{4.22}$$

The operator $A_{-\vec{k}}(v_2)$ when acting on a function of the form $\varphi_0(v_2)g(\vec{v}_2)$ can be further simplified and expressed as[24b]

$$A_{-\vec{k}}(\vec{v}_2)\varphi_0(v_2)g(\vec{v}_2)=-i\vec{k}[C(k)-\chi(a)f(k)]\cdot\int d\vec{v}_4\,\varphi_0(v_4)g(\vec{v}_4)\,\vec{v}_4\,, \tag{4.23}$$

where $C(k)$ is the Fourier transform of the direct correlation function and $f(k)$ is the Fourier transform of the Mayer f function [cf. Eq. (2.10)]

$$C(k)=\int d\vec{r}\,e^{-i\vec{k}\cdot\vec{r}}C(r)\,, \tag{4.24a}$$

$$f(k)=\int d\vec{r}\,e^{-i\vec{k}\cdot\vec{r}}f(r)\,, \tag{4.24b}$$

where $C(r)$ is the direct correlation function. A derivation of Eq. (4.23) is given in Appendix D.

In the next section we will consider the eigenvalues and the eigenfunctions of the operators $i\vec{k}\cdot\vec{v}_1-n\chi(a)\lambda_0^D(\vec{v}_1)$ and $-i\vec{k}\cdot\vec{v}_2-n\chi(a)\lambda_{-\vec{k}}(\vec{v}_2)-nA_{-\vec{k}}(\vec{v}_2)$ which appear in the $\epsilon\mathcal{R}_E^D$ operator, so as to make a spectral decomposition of this operator.

V. HYDRODYNAMIC MODES

We are interested in the long-time behavior of $\rho_D^{(d)}(t)$ or in the small-ϵ behavior of $\rho_D^{(d)}(\epsilon)$. Therefore we study $\epsilon\mathcal{R}_E^D(\vec{v}_1;\epsilon)$ only for small ϵ. For such values of ϵ the dominant contributions come from small $k=|\vec{k}|$ values or that region of the $\vec{k}$ integration in Eq. (4.19) where $k\leq l^{-1}$ say, where l is the mean free path. In this region the leading contributions to the integrand come from the hydrodynamic modes of the operators $i\vec{k}\cdot\vec{v}_1-n\chi(a)\lambda_0^D(\vec{v}_1)$ and $-i\vec{k}\cdot\vec{v}_2-n\chi(a)\lambda_{-\vec{k}}(\vec{v}_2)-nA_{-\vec{k}}(\vec{v}_2)$. These hydrodynamic modes are obtained from the zero-eigenvalue eigenfunctions of the operators $-n\chi(a)\lambda_0^D(\vec{v}_1)$ and $-n\chi(a)\lambda_0(\vec{v}_2)$ respectively, by using $i\vec{k}\cdot\vec{v}_1$ and $-i\vec{k}\cdot\vec{v}_2-n\chi(a)[\lambda_{-\vec{k}}(\vec{v}_2)-\lambda_0(\vec{v}_2)]-nA_{-\vec{k}}(\vec{v}_2)$, respectively, as a perturbation for small k. They lead to perturbed zero eigenvalues of the form c_1k^2, where c_1 is a constant independent of k. For small ϵ and k these contributions then give the dominant contributions to the integrand of $\mathcal{R}_E^D(\vec{v}_1;\epsilon)$, since they lead to integrals of the form $\int_{k<k_0}d\vec{k}\times(\epsilon+\alpha k^2)^{-1}$.

The hydrodynamic mode of the operator $i\vec{k}\cdot\vec{v}_1-n\lambda_0^D(\vec{v}_1)$ has been derived and discussed in I. The result obtained there can be used here if one replaces n by $n\chi(a)$. Thus the hydrodynamic mode solution of the eigenvalue equation

$$[i\vec{k}\cdot\vec{v}_1-n\chi(a)\lambda_0^D(\vec{v}_1)]\chi^{(\omega)}(\vec{k},\vec{v}_1)\varphi_0(v_1)=\omega(k)\chi^{(\omega)}(\vec{k},\vec{v}_1)\varphi_0(v_1) \tag{5.1}$$

can easily be shown to be[25]

$$\omega(k) = \omega_0 + \omega_2 k^2 + \omega_4 k^4 + \cdots , \tag{5.2}$$

with

$$\omega_0 = 0 , \tag{5.3a}$$

$$\omega_2 = D_E = D_0/\chi(a) , \tag{5.3b}$$

for the perturbed zero eigenvalue and

$$\chi^{(\omega)}(\vec{k}, \vec{v}_1) = \chi_0^{(\omega)}(\vec{v}_1) + k\chi^{(\omega)}(\hat{k}, \vec{v}_1) + \cdots \tag{5.4}$$

with

$$\chi_0^{(\omega)}(\vec{v}_1) \equiv 1 \tag{5.5}$$

for the eigenfunction.

The hydrodynamic modes of the operator $i\vec{k}\cdot\vec{v}_1 - n\chi(a)\lambda_{\vec{k}}(\vec{v}_1) - nA_{\vec{k}}(\vec{v}_1)$—we replaced $-\vec{k}$ by $+\vec{k}$—cannot be determined in the same way as was done in I for the operator $i\vec{k}\cdot\vec{v}_1 - n\lambda_0(\vec{v}_1)$ since, unlike this operator, the present operator is *not* symmetric.[26] Consequently, we will also consider the hydrodynamic modes of the adjoint operator: $i\vec{k}\cdot\vec{v}_1 - n\chi(a)\lambda_{\vec{k}}^T(\vec{v}_1) - nA_{\vec{k}}^T(\vec{v}_1)$ where the adjoint $\Gamma^T(\vec{v}_1)$ of an operator $\Gamma(\vec{v}_1)$ is defined by

$$\int d\vec{v}_1\, f(\vec{v}_1)\Gamma(\vec{v}_1)g(\vec{v}_1)\varphi_0(v_1)\, d\vec{v}_1 = \int d\vec{v}_1\, g(\vec{v}_1)\Gamma^T(\vec{v}_1)f(\vec{v}_1)\varphi_0(v_1) \tag{5.6}$$

for functions $f(\vec{v}_1)$ and $g(\vec{v}_1)$ of $\vec{v}_1$.

Therefore we have to distinguish between right and left eigenfunctions of the operator $i\vec{k}\cdot\vec{v}_1 - n\chi(a)\lambda_{\vec{k}}(\vec{v}_1) - nA_{\vec{k}}(\vec{v}_1)$. The right eigenfunctions $\Theta_R^{(\Omega)}(\vec{k}, \vec{v}_1)$ are defined by

$$[i\vec{k}\cdot\vec{v}_1 - n\chi(a)\lambda_{\vec{k}}(\vec{v}_1) - nA_{\vec{k}}(\vec{v}_1)]\Theta_R^{(\Omega)}(\vec{k}, \vec{v}_1)\varphi_0(v_1) = \Omega(k)\Theta_R^{(\Omega)}(\vec{k}, \vec{v}_1)\varphi_0(v_1) , \tag{5.7}$$

while the left eigenfunctions are defined by

$$[i\vec{k}\cdot\vec{v}_1 - n\chi(a)\lambda_{\vec{k}}^T(\vec{v}_1) - nA_{\vec{k}}^T(\vec{v}_1)]\Theta_L^{(\Omega)}(\vec{k}, \vec{v}_1)\varphi_0(v_1) = \Omega(k)\Theta_L^{(\Omega)}(\vec{k}, \vec{v}_1)\varphi_0(v_1) . \tag{5.8}$$

Using (5.7) and (5.8), one can easily show that right and left eigenfunctions corresponding to different eigenvalues are orthogonal, i.e.,

$$\int d\vec{v}_1\, \Theta_L^{(\Omega')}(\vec{k}, \vec{v}_1)\Theta_R^{(\Omega)}(\vec{k}, \vec{v}_1)\varphi_0(v_1) = 0 \quad \text{if } \Omega(k) \neq \Omega'(k) \tag{5.9a}$$

and conversely, if

$$\int d\vec{v}_1\, \Theta_L^{(\Omega')}(\vec{k}, \vec{v}_1)\Theta_R^{(\Omega)}(\vec{k}, \vec{v}_1)\varphi_0(v_1) \neq 0$$

then

$$\Omega(k) = \Omega'(k) . \tag{5.9b}$$

Therefore for every nondegenerate eigenvalue Ω, there is a right eigenfunction $\Theta_R^{(\Omega)}(\vec{k}, \vec{v})$ and a left eigenfunction $\Theta_L^{(\Omega)}(\vec{k}, \vec{v})$; and for every degenerate eigenvalue Ω, there is a set of right eigenfunctions $\Theta_{R,i}^{(\Omega)}(\vec{k}, \vec{v})$, $i = 1, \ldots, g$, and a set of left eigenvalues $\Theta_{L,i}^{(\Omega)}(\vec{k}, \vec{v})$, $i = 1, \ldots, g$, where g is the order of the degeneracy of the eigenvalue. These eigenfunctions can be taken to satisfy the orthonormality relation

$$\int d\vec{v}\, \Theta_{L,i}^{(\Omega')}(\vec{k}, \vec{v})\Theta_{R,i}^{(\Omega)}(\vec{k}, \vec{v})\varphi_0(v) = \delta_{\Omega',\Omega}\delta_{i,j} , \tag{5.10}$$

where δ is the Kronecker delta.

In order to find the hydrodynamic eigenfunctions and eigenvalues, we expand all k-dependent quantities in the Eqs. (5.7) and (5.8) in a power series in k. Using that $\lambda_0^T(\vec{v}_1) = \lambda_0(\vec{v}_1)$, we obtain

$$\Omega(k) = \Omega_0 + k\Omega_1 + k^2\Omega_2 + \cdots , \tag{5.11a}$$

$$\Theta_R^{(\Omega)}(\vec{k}, \vec{v}_1) = \Theta_{R,0}^{(\Omega)}(\hat{k}, \vec{v}_1) + k\Theta_{R,1}^{(\Omega)}(\hat{k}, \vec{v}_1) + \cdots , \tag{5.11b}$$

$$\Theta_L^{(\Omega)}(\vec{k}, \vec{v}_1) = \Theta_{L,0}^{(\Omega)}(\hat{k}, \vec{v}_1) + k\Theta_{L,1}^{(\Omega)}(\hat{k}, \vec{v}_1) + \cdots , \tag{5.11c}$$

$$\lambda_{\vec{k}}(\vec{v}_1) = \lambda_0(\vec{v}_1) + k\lambda_1(\vec{v}_1) + k^2\lambda_2(\vec{v}_1) + \cdots , \tag{5.11d}$$

$$\lambda_{\vec{k}}^T(\vec{v}_1) = \lambda_0(\vec{v}_1) + k\lambda_1^T(\vec{v}_1) + k^2\lambda_2^T(\vec{v}_1) + \cdots , \tag{5.11e}$$

$$A_{\vec{k}}(\vec{v}_1) = A_0(\vec{v}_1) + kA_1(\vec{v}_1) + k^2A_2(\vec{v}_1) + \cdots , \tag{5.11f}$$

$$A_{\vec{k}}^T(\vec{v}_1) = A_0(\vec{v}_1) + kA_1^T(\vec{v}_1) + k^2A_2^T(\vec{v}_1) + \cdots . \tag{5.11g}$$

Here we have not indicated explicitly the possible $\hat{k}$ dependence of the expansion coefficients λ_i, λ_i^T, A_i, and A_i^T ($i \geq 1$). Furthermore, from Eq. (4.22) by expanding the exponents in powers of k, one has that

$$A_0(\vec{v}_1) = A_2(\vec{v}_1) = A_2^T(\vec{v}_1) = 0 \tag{5.12}$$

while for functions $f(\vec{v}_1)$ we show in Appendix D that

$$kA_1(\vec{v}_1)f(\vec{v}_1)\varphi_0(v_1) = -in\pi a^d\left(\frac{d\chi(a)}{dn}\right) \times \left(\frac{d-1}{d}\right)\varphi_0(v_1) \times \int d\vec{v}_3(\vec{k}\cdot\vec{v}_3)f(\vec{v}_3)\varphi_0(v_3) . \tag{5.13}$$

Similarly, expressions for $\lambda_1(\vec{v}_1)$ and $\lambda_2(\vec{v}_1)$ can be found from the Eq. (4.21) (replacing $\vec{k}$ by $-\vec{k}$) and by expanding the exponent in powers of k and using Eqs. (4.20b) and (1.11). From $A_1(\vec{v}_1)$, $\lambda_1(\vec{v}_1)$, and $\lambda_2(\vec{v}_1)$ their adjoints $A_1^T(\vec{v}_1)$, $\lambda_1^T(\vec{v}_1)$, and $\lambda_2^T(\vec{v}_1)$ can be found using their definitions with Eq. (5.6).

The hydrodynamic eigenfunctions and eigenvalues can now be obtained by substituting the expansions (5.11) into the eigenvalue equations (5.7) and (5.8), equating the coefficients of equal powers of k on both sides of these equations for $\Omega_0=0$, and using the orthonormality relations (5.9) and (5.10).

Then the following results for the (hydrodynamic) eigenvalues are obtained[26b]:

$$\Omega_0=0\ , \tag{5.14a}$$

$$\Omega_1^{(V_i)}=\Omega^{(H)}=0\ ,\quad i=1,\ldots,d-1 \tag{5.14b}$$

$$\Omega_1^{(\pm)}=\pm ic\ , \tag{5.14c}$$

$$\Omega_2^{(V_i)}=\nu_E=\eta_E/nm\ ;\quad i=1,\ldots,d-1 \tag{5.14d}$$

$$\Omega_2^{(H)}=D_{T,E}=\lambda_E/nc_p\ , \tag{5.14e}$$

$$\Omega_2^{(\pm)}=\tfrac{1}{2}\Gamma_{S,E}=\tfrac{1}{2}\left\{\frac{\lambda_E}{nc_p}(\gamma-1)+\frac{1}{nm}\left[\zeta_E+2\left(\frac{d-1}{d}\right)\eta_E\right]\right\}. \tag{5.14f}$$

Here the V_i indicate the $(d-1)$ shear modes, H the heat mode and $\pm$ the two sound modes;

$$c=\left[\frac{\gamma}{m}\left(\frac{\partial p}{\partial n}\right)_T\right]^{1/2}$$

is the adiabatic sound velocity in the gas, where $\gamma=c_p/c_v$ is the ratio of the specific heat at constant pressure p and at constant volume, respectively, and p is given by the equation of state $\beta p=n[1+nb_2^{(d)}\chi(a)]$, with $b_2^{(2)}=\pi a^2/2$ for $d=2$ and $b_2^{(3)}=2\pi a^3/3$ for $d=3$. $\nu_E=\eta_E/nm$, λ_E and ζ_E are the values for the kinematic viscosity, heat conductivity, and bulk viscosity, respectively, according to the Enskog theory of dense gases.[27] $D_{T,E}$ and $\Gamma_{S,E}$ denote the thermal diffusivity and the sound absorption coefficient in the Enskog theory. It should be noted that the factor $\chi(a)$ as well as the $\vec{k}$ dependence in the operator $\chi(a)\lambda_{\vec{k}}(\vec{v}_1)$ are together responsible for the appearance of the complete Enskog-theory transport coefficient in the expression for the eigenvalues given by (5.14). In particular, the $\vec{k}$ dependence of the operator $\lambda_{\vec{k}}$ incorporates the collisional transfer effects, while the $\chi(a)$ take into account the density dependence of the collision frequency.

For the (hydrodynamic) eigenfunctions one finds the following. For the shear modes,

$$\Theta_{R,0}^{(V_i)}(\hat{k},\vec{v}_1)=\Theta_{L,0}^{(V_i)}(\hat{k},\vec{v}_1)=(\beta m)^{1/2}\vec{v}_1\cdot\hat{k}_\perp^{(i)};\quad i=1,\ldots,d-1; \tag{5.15a}$$

for the heat modes,

$$\Theta_{R,0}^{(H)}(\vec{v}_1)=\frac{b}{(B+b^2)^{1/2}}\left[\frac{1}{b}\left(\frac{2}{d}\right)^{1/2}\left(\frac{\beta m}{2}v_1^2-\frac{d}{2}\right)-1\right], \tag{5.15b}$$

$$\Theta_{L,0}^{(H)}(\vec{v}_1)=\frac{b}{(B+b^2)^{1/2}}\left[\frac{B}{b}\left(\frac{2}{d}\right)^{1/2}\left(\frac{\beta m}{2}v_1^2-\frac{d}{2}\right)-1\right]; \tag{5.15c}$$

for the sound modes,

$$\Theta_{R,0}^{(\pm)}(\hat{k},\vec{v}_1)=\frac{b}{c(2\beta m)^{1/2}}\left[\left(\frac{2}{d}\right)^{1/2}\left(\frac{\beta m}{2}v_1^2-\frac{d}{2}\right)+\frac{B}{b}\pm\frac{c\beta m}{b}(\hat{k}\cdot\vec{v}_1)\right], \tag{5.15d}$$

$$\Theta_{L,0}^{(\pm)}(\hat{k},\vec{v}_1)=\frac{b}{c(2\beta m)^{1/2}}\left[\left(\frac{2}{d}\right)^{1/2}\left(\frac{\beta m}{2}v_1^2-\frac{d}{2}\right)+\frac{1}{b}\pm\frac{c\beta m}{b}(\hat{k}\cdot\vec{v}_1)\right]. \tag{5.15e}$$

Here B and b are defined in $d=2,3$ by

$$B=\left(\frac{\partial(\beta p)}{\partial n}\right)_T \tag{5.16}$$

and

$$b=\left(\frac{2}{d}\right)^{1/2}\frac{\beta p}{n} \tag{5.17}$$

and $\hat{k},\hat{k}_\perp^{(1)},\ldots,\hat{k}_\perp^{(d-1)}$ form a set of mutually orthogonal unit vectors. In the low-density limit these eigenfunctions and eigenvalues reduce to those given in I.

We can now give a spectral decomposition of the operator

$$[\epsilon+i\vec{k}\cdot\vec{v}_{12}-n\chi(a)\lambda_0^D(\vec{v}_1)-n\chi(a)\lambda_{-\vec{k}}(\vec{v}_2)-nA_{-\vec{k}}(\vec{v}_2)]^{-1}$$

in the form

$$[\epsilon+i\vec{k}\cdot\vec{v}_{12}-n\chi(a)\lambda_0^D(\vec{v}_1)-n\chi(a)\lambda_{-\vec{k}}(\vec{v}_2)-nA_{-\vec{k}}(\vec{v}_2)]^{-1}f(\vec{v}_1,\vec{v}_2)\varphi_0(v_1)\varphi_0(v_2)=S_H^Df(\vec{v}_1,\vec{v}_2)\varphi_0(v_1)\varphi_0(v_2)+S_I^Df(\vec{v}_1,\vec{v}_2)\varphi_0(v_1)\varphi_0(v_2) \tag{5.18}$$

with

$$S_H^Df(\vec{v}_1,\vec{v}_2)\varphi_0(v_1)\varphi_0(v_2)=\sum_{\omega,\Omega}{}'[\epsilon+\omega(k)+\Omega(k)]^{-1}\chi^{(\omega)}(\vec{k},\vec{v}_1)\Theta_R^{(\Omega)}(-\vec{k},\vec{v}_1)\varphi_0(v_1)\varphi_0(v_2)\times\int d\vec{v}_1\int d\vec{v}_2\chi^{(\omega)}(\vec{k},\vec{v}_1)\Theta_L^{(\Omega)}(-\vec{k},\vec{v}_1)\,f(\vec{v}_1,\vec{v}_2)\varphi_0(v_1)\varphi_0(v_2)\ , \tag{5.19}$$

where the prime on the summation symbol indicates that only hydrodynamic modes are to be included in the sum and where $f(\vec{v}_1, \vec{v}_2)$ is a function of $\vec{v}_1$ and $\vec{v}_2$. The second term on the right-hand side of Eq. (5.18), with $S^D_\perp$, contains the contributions involving all other eigenfunctions, i.e. where at least one eigenfunction is not a hydrodynamic eigenfunction. These nonhydrodynamic modes are obtained, for small k, by perturbing the nonzero eigenvalues of λ^D_0 and λ_0 and appear to lead to contributions to $\rho^{(d)}_D(t)$ which decay exponentially over a few mean free times.

In the next section we shall use the representation (5.18), (5.19) of the operator $[\epsilon + i\vec{k}\cdot\vec{v}_{12} - n\chi(a)\lambda^D_0(\vec{v}_1) - n\chi(a)\lambda_{-\vec{k}}(\vec{v}_2) - nA_{-\vec{k}}(\vec{v}_2)]^{-1}$ to obtain the long-time behavior of $\rho^{(d)}_D(t)$.

VI. LONG-TIME BEHAVIOR OF $\rho^{(d)}_D(t)$

The long-time behavior of $\rho^{(d)}_D(t)$ can be obtained, in our approximation, from the small-ϵ behavior of

$$\rho^{(d)}_D(\epsilon) = \int_0^\infty dt\, e^{-\epsilon t}\rho^{(d)}_D(t) = \int d\vec{v}_1 v_{1x}\Phi^{(d)}_D(\vec{v}_1;\epsilon)$$

$$\cong \beta m \int d\vec{v}_1 v_{1x}[\epsilon - n\chi(a)\lambda^D_0(\vec{v}_1) - n\epsilon\mathcal{R}^D_E(\vec{v}_1;\epsilon)]^{-1} \times v_{1x}\varphi_0(v_1)\ . \quad (6.1)$$

The operator $n\epsilon\mathcal{R}^D_E(v_1;\epsilon)$ can, on the basis of the discussion in the previous section, be divided into two parts: a hydrodynamic part $n\epsilon\mathcal{R}^D_{E,H}$ and a nonhydrodynamic part $n\epsilon\mathcal{R}^D_{E,\perp}$ defined by

$$n\epsilon\mathcal{R}^D_{E,H} = n\int_{k<k_0}\frac{d\vec{k}}{(2\pi)^d}\int d\vec{v}_2\chi(a)\overline{T}_{-\vec{k}}(1,2)S^D_H \times\chi(a)T_{\vec{k}}(1,2)\varphi_0(v_2) \quad (6.2)$$

and

$$n\epsilon\mathcal{R}^D_{E,\perp} = n\epsilon\mathcal{R}^D_E - n\epsilon\mathcal{R}^D_{E,H}$$
$$= n\int_{k>k_0}\frac{d\vec{k}}{(2\pi)^d}\int d\vec{v}_2\chi(a)\overline{T}_{-\vec{k}}(1,2)[\epsilon + i\vec{k}\cdot\vec{v}_{12} - n\chi(a)\lambda^D_0(\vec{v}_1) - n\chi(a)\lambda_{-\vec{k}}(\vec{v}_2) - nA_{-\vec{k}}(\vec{v}_2)]^{-1}$$
$$+ n\int_{k<k_0}\frac{d\vec{k}}{(2\pi)^d}\int d\vec{v}_2\chi(a)\overline{T}_{-\vec{k}}(1,2)S^D_\perp\chi(a)T_{\vec{k}}(1,2)\varphi_0(v_2)\ . \quad (6.3)$$

The first term on the right-hand side of Eq. (6.3) includes contributions of collisions that take place on a space scale small compared to the mean free path l and which should not be relevant for the long-time behavior of $\rho^{(d)}_D(t)$. The second term includes contributions of nonhydrodynamic modes, which will decay exponentially in a few mean free times. We shall therefore neglect $n\epsilon\mathcal{R}^D_{E,\perp}$ in obtaining the long-time behavior of $\rho^{(d)}_D(t)$.

Using then $n\epsilon\mathcal{R}^D_{E,H}$ from Eq. (6.2) for $n\epsilon\mathcal{R}^D_E$ in Eq. (6.1), we obtain

$$\rho^{(d)}_D(\epsilon) \cong \beta m\int d\vec{v}_1\, v_{1x}[\epsilon - n\chi(a)\lambda^D_0(\vec{v}_1) - n\epsilon\mathcal{R}^D_{E,H}]^{-1} \times v_{1x}\varphi_0(v_1)\ . \quad (6.4)$$

We proceed by iterating the operator $[\cdots]^{-1}$ on the right-hand side of Eq. (6.4) about $[\epsilon - n\chi(a)\times\lambda^D_0(\vec{v}_1)]^{-1}$. We will restrict our discussion to the first two iterates, which are given by the Eqs. (6.6a) and (6.6b). This restriction is necessary, because we have neglected dynamical events which give contributions to $\rho^{(d)}_D$ that are of the same order in the density as those of the third and higher iterates in Eq. (6.5). This, in turn, may limit the time range over which our results are valid. We will discuss this point further in Sec. VIII.

Thus

$$\rho^{(d)}_D(\epsilon) = \rho^{(d)}_{D,0}(\epsilon) + \rho^{(d)}_{D,1}(\epsilon) + \cdots\ , \quad (6.5)$$

where

$$\rho^{(d)}_{D,0}(\epsilon) = \beta m\int d\vec{v}_1\, v_{1x}[\epsilon - n\chi(a)\lambda^D_0(\vec{v}_1)]^{-1}v_{1x}\varphi_0(v_1) \quad (6.6a)$$

and

$$\rho^{(d)}_{D,1}(\epsilon) = \beta m\int d\vec{v}_1\, v_{1x}[\epsilon - n\chi(a)\lambda^D_0(\vec{v}_1)]^{-1}n\epsilon\mathcal{R}^D_{E,H}[\epsilon - n\chi(a)\lambda^D_0(\vec{v}_1)]^{-1}v_{1x}\varphi_0(v_1)$$
$$= \beta nm\int d\vec{v}_1\int d\vec{v}_2\int_{k<k_0}\frac{dk}{(2\pi)^d}v_{1x}[\epsilon - n\chi(a)\lambda^D_0(\vec{v}_1)]^{-1}\chi(a)\overline{T}_{-\vec{k}}(1,2)S^D_H\chi(a)T_{\vec{k}}(1,2)[\epsilon - n\chi(a)\lambda^D_0(\vec{v}_1)]^{-1}$$
$$\times v_{1x}\varphi_0(v_1)\varphi_0(v_2)\ . \quad (6.6b)$$

Laplace inversion of $\rho^{(d)}_{D,0}(\epsilon)$ given by Eq. (6.6a) yields exactly the exponential decay of $\rho^{(d)}_D(t)$ discussed in Sec. III, Eq. (3.10).

Using Eq. (5.19) and taking into account that the summation in this equation involves only combinations of one diffusive mode $\chi^{(\omega)}(\vec{k},\vec{v}_1)$ and the $d+2$ hydrodynamic modes $\Theta^{(\Omega)}(-\vec{k},\vec{v}_2)$, one obtains for $\rho^{(d)}_{D,1}(\epsilon)$

$$\rho^{(d)}_{D,1}(\epsilon)\cong\beta nm\int d\vec{v}_1\int d\vec{v}_2\int_{k<k_0}\frac{d\vec{k}}{(2\pi)^d}\sum_{\Omega} v_{1x}[\epsilon-n\chi(a)\lambda_0^D(\vec{v}_1)]^{-1}\chi(a)\overline{T}_{-\vec{k}}(1,2)\,\chi^{(\omega)}(\vec{k},\vec{v}_1)\Theta^{(\Omega)}_R(-\vec{k},\vec{v}_2)\varphi_0(v_1)\varphi_0(v_2)$$
$$\times\int d\vec{v}_1\int d\vec{v}_2\,\chi^{(\omega)}(\vec{k},\vec{v}_1)\Theta^{(\Omega)}_L(-\vec{k},\vec{v}_2)\,\chi(a)T_{\vec{k}}(1,2)[\epsilon-n\chi(a)\lambda_0^D(\vec{v}_1)]^{-1}$$
$$\times v_{1x}\varphi_0(v_1)\varphi_0(v_2)[\epsilon+\omega(k)+\Omega(k)]^{-1}\,. \qquad (6.7)$$

To obtain the dominant behavior of $\rho^{(d)}_D(t)$ for long times or the dominant behavior of $\rho^{(d)}_{D,1}(\epsilon)$ for small ϵ, one can expand in k the operators $\overline{T}_{-\vec{k}}(1,2)$, $T_{\vec{k}}(1,2)$ as well as the functions $\Theta^{(\Omega)}_{L,R}(-\vec{k},\vec{v}_2)$ and keep only the lowest order terms in k, since the neglected terms lead to a faster decay with time than those kept.[28] In addition, since we will be interested in times $t\gg t_0$, one can neglect the terms of order ϵ in the operator $[\epsilon-n\chi(a)\lambda_0^D]^{-1}$. Then we obtain

$$\rho^{(d)}_{D,1}(\epsilon)\cong\frac{\beta m}{n}\sum_{\Omega}\int d\vec{v}_1\int d\vec{v}_2\int_{k<k_0}\frac{d\vec{k}}{(2\pi)^d}[\epsilon+\omega(k)+\Omega(k)]^{-1}v_{1x}(\lambda_0^D(\vec{v}_1))^{-1}\,T_{00}(1,2)\Theta^{(\Omega)}_{R,0}(-\hat{k},\vec{v}_2)\varphi_0(v_1)\varphi_0(v_2)$$
$$\times\int d\vec{v}_1\int d\vec{v}_2\Theta^{(\Omega)}_{L,0}(-\hat{k},\vec{v}_2)T_{00}(1,2)[\lambda_0^D(\vec{v}_1)]^{-1}\,v_{1x}\varphi_0(v_1)\varphi_0(v_2)\,. \qquad (6.8)$$

Here we have used Eq. (5.5) for $\chi_0^{(\omega)}(\vec{k},\vec{v}_1)$, replaced the operators $\overline{T}_{-\vec{k}}$ and $T_{\vec{k}}$ by their common value at $k=0$, which we have denoted by T_{00} in I and replaced $\Theta^{(\Omega)}_{R,L}$ by $\Theta^{(\Omega)}_{R,L,0}$.

The expression (6.8) for $\rho^{(d)}_{D,1}(\epsilon)$ can be analyzed further in exactly the same fashion as was the corresponding expression (5.8) in I, by using the fact that the $\Theta^{(\Omega)}_{R,L,0}$ are linear combinations of summational invariants in a binary collision. We only quote the results:

$$\rho^{(d)}_{D,1}(t)\cong\frac{\beta m}{n}\sum_{\Omega}\int_{k<k_0}\frac{d\vec{k}}{(2\pi)^d}e^{-t[\omega(k)+\Omega(k)]}$$
$$\times\left[\int d\vec{v}_1\,v_{1x}\Theta^{(\Omega)}_{R,0}(-\hat{k},\vec{v}_1)\varphi_0(v_1)\right]$$
$$\times\left[\int d\vec{v}_1\,v_{1x}\Theta^{(\Omega)}_{L,0}(-\hat{k},\vec{v}_1)\varphi_0(v_1)\right]\,. \qquad (6.9)$$

In two dimensions one finds that for $t\gg t_0$

$$\rho^{(2)}_D(t)\cong\rho^{(2)}_{D,1}(t)\cong\alpha^{(2)}_{D,E}(\rho)(t_0/t)\,, \qquad (6.10)$$

where

$$\alpha^{(2)}_{D,E}(\rho)=[8\pi n(D_E+\nu_E)t_0]^{-1} \qquad (6.11)$$

with the mean free time t_0 given by

$$t_0=\frac{(\beta m/\pi)^{1/2}}{2na\chi(a)}\,. \qquad (6.12)$$

The expression (6.11) for $\alpha^{(2)}_{D,E}$ is plotted as a function of $\rho=na^2$ in Fig. 3. The theory seems to be in very good agreement with the computer results of Alder and Wainwright[5] and of Wood and Erpenbeck[6,29] over the entire range of densities, for which these are available.

In three dimensions one finds that for $t\gg t_0$

$$\rho^{(3)}_D(t)\cong\rho^{(3)}_{D,1}(t)\cong\alpha^{(3)}_{D,E}(\rho)(t_0/t)^{3/2}\,, \qquad (6.13)$$

where

$$\alpha^{(3)}_{D,E}(\rho)=(1/12n)[\pi(D_E+\nu_E)t_0]^{-3/2} \qquad (6.14)$$

with

$$t_0=\frac{(\beta m/\pi)^{1/2}}{4na^2\chi(a)}\,. \qquad (6.15)$$

The expression (6.14) for $\alpha^{(3)}_{D,E}$ is also plotted as a function of $\rho=na^3$ in Fig. 3 and is consistent with the computer data of Wood and Erpenbeck.[6,29]

VII. BEHAVIOR OF $\rho^{(d)}_\eta(t)$ AND $\rho^{(d)}_\lambda(t)$ IN TIME

The short- and long-time behavior of the velocity correlation functions $\rho^{(d)}_\eta(t)$ and $\rho^{(d)}_\lambda(t)$ that determine the kinetic parts of the time-correlation function expressions for the viscosity and heat-conductivity coefficients, respectively, can be found in a similar fashion as for $\rho^{(d)}_D(t)$. We only give a brief outline of the procedure before we quote the results.

The correlation functions $\rho^{(d)}_\eta(t)$ and $\rho^{(d)}_\lambda(t)$ are given by

$$\rho^{(d)}_J(t)=\frac{\langle\sum_{i=1}^N J(\vec{v}_i(0))\sum_{j=1}^N J(\vec{v}_j(t))\rangle}{\langle[\sum_{i=1}^N J(\vec{v}_i(0))]^2\rangle}\,, \qquad (7.1)$$

where for the shear viscosity η

$$J(\vec{v}_i)=v_{ix}v_{iy} \qquad (7.2)$$

while for the heat conductivity λ

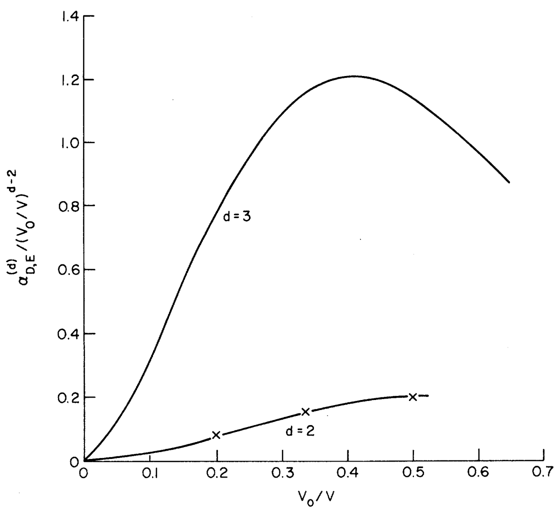

FIG. 3. $\alpha^{(d)}_{D,E}/(V_0/V)^{d-2}$ plotted as a function of the reduced volume V_0/V, where V_0 is the volume at close packing, for $d=2$ and $d=3$. The crosses indicate the computer results of Alder and Wainwright for $d=2$, Ref. 5.

$$J(\vec{v}_i)=v_{ix}\left(\frac{\beta m}{2}v_i^2-\frac{d+2}{d}\right). \tag{7.3}$$

One can write $\rho^{(d)}_J(t)$ in the form

$$\rho^{(d)}_J(t)=\int d\vec{v}_1 J(\vec{v}_1)\Phi^{(d)}_J(\vec{v}_1;t)\ , \tag{7.4}$$

where

$$\Phi^{(d)}_J(t)=\lim_{\substack{N,\,V\to\infty\\ N/V=n}}\langle J^2(\vec{v}_1)\rangle^{-1}m^d\frac{V}{Z}$$
$$\times\int dx^{N-1}\,S_{-t}(x^N)\,e^{-\beta H(x^N)}\sum_{i=1}^{N}J(\vec{v}_i) \tag{7.5}$$

since $\int d\vec{v}_1 J(\vec{v}_1)\varphi_0(v_1)=0$.

Proceeding as in Sec. II, one obtains for the Laplace transform $\Phi^{(d)}_J(\vec{v}_1;\epsilon)$ of $\Phi^{(d)}_J(\vec{v}_1;t)$ the equation

$$\Phi^{(d)}_J(\vec{v}_1;\epsilon)=\frac{\langle J^2(\vec{v}_1)\rangle^{-1}}{\epsilon}\left(1+\sum_{l=1}^{\infty}n^l\,\mathfrak{A}_l(\vec{v}_1;\epsilon)\right)$$
$$\times J(\vec{v}_1)\varphi_0(v_1)$$
$$=\langle J^2(\vec{v}_1)\rangle^{-1}\left(\epsilon-\sum_{l=1}^{\infty}n^l\epsilon\mathfrak{B}_{l+1}(\vec{v}_1;\epsilon)\right)^{-1}$$
$$\times J(\vec{v}_1)\varphi_0(v_1)\ . \tag{7.6}$$

Here the $\mathfrak{A}_l(\vec{v}_1;\epsilon)$ can be obtained from the expressions for $\mathfrak{A}^D_l(\vec{v}_1;\epsilon)$ given by Eq. (2.13), by replacing

$$\prod_{i=2}^{l}\varphi_0(v_1)$$

there by

$$\prod_{j=1}^{l}\varphi_0(v_j)\sum_{i=1}^{l}P_{1i}[\varphi_0(v_1)]^{-1}\ ,$$

while the $\mathfrak{B}_l$ are related to the $\mathfrak{A}_l$ in the same way as the $\mathfrak{B}^D_l$ are related to the $\mathfrak{A}^D_l$ [cf. Eq. (2.17)].

To compute the short- and the long-time behavior of $\Phi^{(d)}_J(t)$, only certain classes of dynamical events are taken into account in the sum

$$\sum_{l=1}^{\infty}n^l\epsilon\mathfrak{B}_{l+1}(\vec{v}_1,\epsilon)$$

on the right-hand side of Eq. (7.6). After making a binary collision expansion as well as a Mayer f expansion of the integrand of the operator $\epsilon\mathfrak{B}_{l+1}(\vec{v}_1,\epsilon)$, one keeps (a) the Enskog correction $\chi_{l-1}(a)\lambda_0(\vec{v}_1)$, to the linearized Boltzmann collision operator $\epsilon\mathfrak{B}_2(\vec{v}_1,\epsilon)=\lambda_0(\vec{v}_1)$; (b) the most divergent terms, in the limit $\epsilon\to 0$, in each order in the density, i.e., the ring terms; (c) the simple excluded-volume correction to the ring term; and (d) the connected excluded-volume corrections to all but the first and last binary collision operator in the ring terms.

Thus we use the approximation

$$\sum_{l=1}^{\infty}n^l\epsilon\mathfrak{B}_{l+1}(\vec{v}_1;\epsilon)\cong n\chi(a)\lambda_0(\vec{v}_1)+n\epsilon\mathfrak{R}_E(\vec{v}_1;\epsilon), \tag{7.7}$$

where

$$\epsilon\mathfrak{R}_E(\vec{v}_1;\epsilon)=\int d\vec{v}_2\int\frac{d\vec{k}}{(2\pi)^d}\chi(a)\overline{T}_{-\vec{k}}(1,2)\,[\epsilon+i\vec{k}\cdot\vec{v}_{12}-n\chi(a)\lambda_{\vec{k}}(\vec{v}_1)-nA_{\vec{k}}(\vec{v}_1)-n\chi(a)\lambda_{-\vec{k}}(\vec{v}_2)-nA_{-\vec{k}}(\vec{v}_2)]^{-1}$$
$$\times\chi(a)T_{\vec{k}}(1,2)(1+P_{12})\varphi_0(v_2)\ . \tag{7.8}$$

Comparing with Eq. (4.19) for $\epsilon\mathfrak{R}^D_E(\vec{v}_1;\epsilon)$, we see that this expression for $\epsilon\mathfrak{R}_E(\vec{v}_1;\epsilon)$ is of the same form, except that $\lambda^D_0(\vec{v}_1)$ in Eq. (4.19) has been replaced by $\lambda_{\vec{k}}(\vec{v}_1)$ and that additional operators $-nA_{\vec{k}}(\vec{v}_1)$ and $(1+P_{12})$ appear in Eq. (7.8).

Separating the $\vec{k}$ integral in Eq. (7.8) into regions where $k\le k_0$ and where[28] $k>k_0$ ($k_0\approx l^{-1}$) and analyzing the operator $[\cdots]^{-1}$ on the right-hand side of Eq. (7.8) for $\mathcal{R}_E(\vec{v}_1;\epsilon)$ into hydrodynamic and nonhydrodynamic modes, and taking into account only hydrodynamic modes, one obtains, in a similar fashion as in Sec. VI, by iteration the following expression for $\rho_J^{(d)}(t)$:

$$\rho_J^{(d)}(t)=\rho_{J,0}^{(d)}(t)+\rho_{J,1}^{(d)}(t)+\cdots, \tag{7.9}$$

where the short-time behavior is given by

$$\rho_{J,E}^{(d)}(t)=\langle J^2(\vec{v}_1)\rangle^{-1}\int d\vec{v}_1\, J(\vec{v}_1)\, e^{tn\chi(a)\lambda_0(\vec{v}_1)} \times J(\vec{v}_1)\varphi_0(v_1)\,. \tag{7.10}$$

Using the method outlined in Sec. III, one can easily show that the initial slope of $\rho_J^{(d)}(t)$ is given *exactly* by the initial slope of $\rho_{J,0}^{(d)}(t)$.

In first Enskog approximation,

$$\rho_{\eta,E}^{(d)}(t)=e^{-t\chi(a)/\beta m\nu_{0,0}} \tag{7.11}$$

and

$$\rho_{\lambda,E}^{(d)}(t)=e^{-t\chi(a)/\beta m D_{T_{0,0}}}, \tag{7.12}$$

where $\nu_{0,0}$ and $D_{T_{0,0}}$ are the kinematic viscosity ν and the thermal diffusivity D_T [cf. Eq. (5.14e)] computed on the basis of the Boltzmann equation in first Enskog approximation.[20] We expect that, like Eqs. (3.11) and (3.12) for $\rho_D^{(d)}(t)$, Eqs. (7.11) and (7.12) are good approximations to the short-time behavior of $\rho_\eta^{(d)}(t)$ and $\rho_\lambda^{(d)}(t)$.

The long-time behavior is given by

$$\rho_J^{(d)}(t)\cong\rho_{J,1}^{(d)}(t)\cong\frac{\langle J^2(\vec{v}_1)\rangle^{-1}}{2n}\sum_{\Omega,\Omega'}{}'\int_{k<k_0}\frac{d\vec{k}}{(2\pi)^d}\, e^{-t[\Omega(k)+\Omega(k')]}\left(\int d\vec{v}_1\, J(\vec{v}_1)\Theta_{R,0}^{(\Omega)}(\hat{k},\vec{v}_1)\Theta_{R,0}^{(\Omega')}(-\hat{k},\vec{v}_1)\varphi_0(v_1)\right) \times\left(\int d\vec{v}_1\, J(\vec{v}_1)\Theta_{L,0}^{(\Omega)}(\hat{k},\vec{v}_1)\Theta_{L,0}^{(\Omega')}(-\hat{k},\vec{v}_1)\varphi_0(v_1)\right), \tag{7.13}$$

where the prime on the summation symbol indicates that only hydrodynamic modes are to be included. Thus one finds for the long-time behavior of $\rho_J^{(d)}(t)$

$$\rho_\eta^{(d)}(t)\cong\rho_{\eta,1}^{(d)}(t)\cong\frac{1}{nd(d+2)}\left(\frac{d^2-2}{(8\pi\nu_E t_0)^{d/2}}+\frac{1}{(4\pi\Gamma_{S,E}t_0)^{d/2}}\right)\left(\frac{t_0}{t}\right)^{d/2} \tag{7.14}$$

and

$$\rho_\lambda^{(d)}(t)\cong\rho_{\lambda,1}^{(d)}(t)\cong\frac{(d+2)k_B}{2ndc_p}\left(\frac{d-1}{[4\pi(\nu_E+D_{T,E})t_0]^{d/2}}+\frac{\gamma-1}{(4\pi\Gamma_{S,E}t_0)^{d/2}}\right)\left(\frac{t_0}{t}\right)^{d/2}, \tag{7.15}$$

where $\Gamma_{S,E}$ has been defined in Eq. (5.14f).

VIII. DISCUSSION

The comments made in I concerning the long-time behavior of the $\rho^{(d)}(t)$ at low densities are equally valid for the results for $\rho^{(d)}(t)$ obtained here and we will not repeat them. A few remarks can be added, however.

(i) In view of the neglect of many dynamical events as well as of the limited number of iterations used, it is not possible to make any statement about the "true" asymptotic behavior of the $\rho^{(d)}(t)$ for the systems considered. However, in so far as the computer results are not for "true" asymptotic behavior either, it is not *a priori* clear which of the theoretical formulas—those derived here or those derived on the basis of quasihydrodynamical considerations[30]—will best describe the computer results for $\rho_D^{(d)}(t)$ for the time interval of $10t_0<t<50t_0$ over which they have been obtained. In two dimensions, of course, no theoretical quasihydrodynamical results are available since they lead to an inconsistency,[31] and only the results derived here are available. In three dimensions the quasihydrodynamical results[30] for the long-time behavior of $\rho^{(d)}(t)$ are given by Eqs. (6.13), (6.14), (7.14), and (7.15), except that the full transport coefficients D, η, λ, and ζ occur where in our case their Enskog values D_E, η_E, λ_E, and ζ_E appear. Over the range of densities studied so far on the computer, the difference between the two formulas is too small to be noticeable with the present computer accuracy.

We remark that very recently expressions for $\rho^{(3)}(t)$, containing the full transport coefficients have been obtained on the basis of kinetic theory by Pomeau and Résibois[32] and van Beijeren and Ernst.[33]

(ii) An essential feature of the analysis presented here is the appearance of the two factors $\chi(a)$ in the numerators of the resummed operators

$n\epsilon\mathcal{R}_E^D(\vec{v}_1,\epsilon)$ and $n\epsilon\mathcal{R}_E(\vec{v}_1,\epsilon)$ each, as given by Eqs. (4.17) and (7.8), respectively. These factors have their origin in the fact that we have taken into account excluded-volume corrections to each of the collisions in the ring events considered in I. A derivation of the $t^{-3/2}$ term in $\rho_D^{(d)}(t)$ for a gas of hard spheres, in which one of the $\chi(a)$ factors seems not accounted for, has recently been given by Mazenko.[34] Using a method based on the BBGKY hierarchy equations he arrives at an expression for $\alpha_D^{(3)}(\rho)$ that differs from ours given by Eq. (6.14), by a factor $\chi(a)^{-1}(D/D_E)^2$, where D is the full self-diffusion coefficient. The precise origin for this discrepancy is not clear at this moment.[34, 35]

(iii) Although the computer results of Alder and Wainwright,[5] and of Wood and Erpenbeck,[6] as well as the results obtained here apply only to hard-disk and hard-sphere systems, it was suggested in I that the $t^{-d/2}$ decay should hold for a larger class of intermolecular potentials. This has been confirmed recently by a computer calculation of Levesque and Ashurst,[36] who found a $t^{-3/2}$ behavior of $\rho_D^{(3)}(t)$ for a system of particles that interact with the repulsive part of a 12–6 Lennard-Jones potential.

(iv) We have considered here only the ring events, their excluded-volume corrections and the first two iterates in Eq. (6.5). It would be inconsistent to consider the contribution of higher iterates to Eq. (6.5), without taking into account also contributions from other dynamical events in the lower iterates.[37] This restriction makes it difficult to determine the precise interval of time over which the results obtained here are valid. In three dimensions the work of Pomeau and Résibois[32] and of van Beijeren and Ernst[33] indicates that the $t^{-3/2}$ behavior persists for asymptotically long times. For two dimensions, it is not yet clear what the true asymptotic behavior of $\rho^{(2)}(t)$ is.

(v) Very recently a beginning has been made of the computation of the behavior of $\rho_D^{(d)}(t)$ for intermediate times, i.e., for times of the order of $3t_0$ to $10t_0$, so that the full time behavior of $\rho_D^{(d)}(t)$ is obtained. Such an analysis has been undertaken by Resibois and Lebowitz,[38] using hierarchy equation methods and Lieberworth and Cohen,[39] using the Eq. (6.1) for $\rho_D^{(d)}(t)$ as a starting point. This may well lead to a microscopic explanation of the negative part of $\rho_D^{(d)}(t)$ for times $t \gtrsim 5t_0$, which have been observed in computer calculations.[5]

ACKNOWLEDGMENTS

The authors gratefully acknowledge stimulating discussions with Dr. J. V. Sengers, Dr. M. H. Ernst, Dr. H. van Beijeren, Dr. W. W. Wood, Dr. J. J. Erpenbeck, Dr. J. W. Dufty, Dr. B. J. Alder and Dr. Y. H. Kan.

APPENDIX A: BINARY COLLISION OPERATORS FOR HARD-CORE SYSTEMS

(a) For systems of hard disks or hard spheres the streaming operator $S_{-t}(x^N)$ is not defined, whenever any two particles, say i and j, are within each others' interaction sphere. To avoid having to deal with such configurations, one considers the operator $S_{-t}(x^N)$ combined with the function

$$W(r^N) = \exp\left(-\beta \sum_{\substack{i<j \\ 1}}^{N} \phi(r_{ij})\right),$$

where $\phi(r_{ij})$ is the pair potential for a hard-disk or a hard-sphere system.

For simplicity we consider first a system consisting of two particles moving in infinite space, i.e., the case that $N=2$. Then the operator $W(\vec{r}_1,\vec{r}_2)S_{-t}(x_1,x_2)$ is defined for all phases of the particles 1 and 2, and for all time t. The binary collision operator $T(1,2)$ is defined by the relation

$$W(\vec{r}_1,\vec{r}_2)S_{-t}(x_1,x_2) = W(\vec{r}_1,\vec{r}_2)S^0_{-t}(x_1,x_2) + W(\vec{r}_1,\vec{r}_2)\int_0^t d\tau\, S^0_{-\tau}(x_1,x_2)T(1,2) \times S^0_{-(t-\tau)}(x_1,x_2), \quad \text{(A1)}$$

where $S^0_{-t}(x_1,x_2)$ is the free-particle streaming operator

$$S^0_{-t}(x_1,x_2) = \exp[-t\mathcal{H}_0(x_1,x_2)]. \quad \text{(A2)}$$

Since the left-hand side of Eq. (A1) is well defined for all phases of the two particles, it is possible to calculate the result of $W(\vec{r}_1,\vec{r}_2)S_{-t}(x_1,x_2)f(x_1,x_2)$ for any function $f(x_1,x_2)$ and for every phase point (x_1,x_2). By using the fact that two particles moving in infinte space may collide at most once, one obtains an expression for the operator $W(\vec{r}_1,\vec{r}_2) \times S_{-t}(x_1,x_2)$ which has the structure of the right-hand side of Eq. (A1) with $T(1,2)$ as given by Eq. (1.11).

A formally simpler and more convenient expression for $W(\vec{r}_1,\vec{r}_2)S_{-t}(x_1,x_2)$ can be obtained from Eq. (A1), if we use the fact that $T(1,2)$ can be shown to satisfy the relation[40]

$$T(1,2)S^0_{-t}(x_1,x_2)T(1,2) = 0 \quad \text{(A3)}$$

for any time t, which expresses the fact that the two particles cannot collide more than once. Equation (A1), when combined with Eq. (A3), is equivalent to

$$W(\vec{r}_1,\vec{r}_2)\,S_{-t}(x_1,x_2) = W(\vec{r}_1,\vec{r}_2)\exp\{-t[\mathcal{H}_0(x_1,x_2)-T(1,2)]\} \tag{A4}$$

which is a special case ($N=2$) of Eq. (1.8).

In order to prove Eq. (1.8) for arbitrary N, one makes a formal expansion of the right-hand side of Eq. (1.8) in powers of the T operators. Then, using the explicit representation of the $T(i,j)$ operators, given by Eq. (1.11), and Eq. (A3), one shows that when the right-hand side of Eq. (1.8) acts on a function $f(x^N)$, it correctly determines $f(x^N(-t))$ for all x^N.[3]

In a similar fashion, using Eqs. (1.9) and (1.14) for $N=2$, one can define a $\overline{T}$ operator:

$$S_{-t}(x_1,x_2)W(\vec{r}_1,\vec{r}_2) = S^0_{-t}(x_1,x_2)W(\vec{r}_1,\vec{r}_2) + \int_0^t d\tau S^0_{-(t-\tau)}(x_1,x_2)\overline{T}(1,2) \times S^0_{-\tau}(x_1,x_2)W(\vec{r}_1,\vec{r}_2)\,. \tag{A5}$$

Using that Eq. (A3) holds for $\overline{T}$ as well as T operators, one can write Eq. (A5) in the form

$$S_{-t}(x_1,x_2)W(\vec{r}_1,\vec{r}_2) = \exp\{-t[\mathcal{H}_0(x_1,x_2)-\overline{T}(1,2)]\} \times W(\vec{r}_1,\vec{r}_2)\,, \tag{A6}$$

which is a special case of Eq. (1.9) for $N=2$. The generalization to arbitrary N can be performed in a similar fashion as for the T operators by making a formal expansion of the right-hand side of Eq. (1.9) in powers of the $\overline{T}$ operators. We remark that this expansion is equivalent to the inverse Laplace transform of the binary collision expansion given in I [Eq. (3.1)], if the θ operators there are replaced by $\overline{T}$ operators. One can show that the right-hand side of Eq. (1.9) is equal to the right-hand side of Eq. (1.8).[41] From this it follows that the right-hand side of Eq. (1.9) correctly generates $f(x^N(-t))$, when acting on $f(x^N)$, and that Eq. (1.14) is satisfied by this representation. The derivation of the explicit expressions (1.11) and (1.12) of the T and $\overline{T}$ operators given in the text is straightforward but rather lengthy. For this we refer the reader to the literature.[3]

(b) We now give a number of relations, which are satisfied by the binary collision operators $T(1,2)$ and $\overline{T}(1,2)$ and the Mayer f function and that are used in the text. They can be proved, using the explicit representations of the binary collision operators Eqs. (1.11) and 1.12).[3,40] They are

$$T(1,2)G_0(x_1,x_2)T(1,2)=0\,, \tag{A7a}$$

$$\overline{T}(1,2)G_0(x_1,x_2)\overline{T}(1,2)=0\,, \tag{A7b}$$

$$\overline{T}(1,2)G_0(x_1,x_2)T(1,2)=0\,, \tag{A7c}$$

$$f(r_{12})T(1,2)=0\,, \tag{A7d}$$

$$\overline{T}(1,2)f(r_{12})=0\,, \tag{A7e}$$

$$f(r_{12})G_0(x_1,x_2)T(1,2)=0\,, \tag{A7f}$$

$$\overline{T}(1,2)G_0(x_1,x_2)f(r_{12})=0\,, \tag{A7g}$$

$$f(r_{12})G_0(x_1,x_2)+G_0(x_1,x_2)T(1,2)G_0(x_1,x_2) = G_0(x_1,x_2)f(r_{12})+G_0(x_1,x_2)\overline{T}(1,2)G_0(x_1,x_2)\,, \tag{A7h}$$

$$T(1,2)\begin{Bmatrix}1\\ \vec{v}_1+\vec{v}_2\\ v_1^2+v_2^2\end{Bmatrix}=0\,, \tag{A7i}$$

$$\int d\vec{v}_1\int d\vec{v}_2\begin{Bmatrix}1\\ \vec{v}_1+\vec{v}_2\\ v_1^2+v_2^2\end{Bmatrix}\overline{T}(1,2)s(x_1,x_2)=0\,, \tag{A7j}$$

and

$$\int d\vec{r}_{12}T(1,2)h(\vec{v}_1,\vec{v}_2)=\int d\vec{r}_{12}\overline{T}(1,2)h(\vec{v}_1,\vec{v}_2)\,, \tag{A7k}$$

where $s(x_1,x_2)$ and $h(\vec{v}_1,\vec{v}_2)$ are functions of the phases x_1,x_2 and of the velocities $\vec{v}_1,\vec{v}_2$, respectively.

APPENDIX B: EXTRACTION OF DOUBLE OVERLAPPING TERMS IN $\epsilon\tilde{\mathfrak{B}}_4^D$

In this appendix we briefly outline the method we use to extract those contributions to $\epsilon\tilde{\mathfrak{B}}_4^D$ coming from sequences of three binary collisions, with an excluded-volume correction from a double overlapping configuration at one of the collisions in the sequence. The ϵ dependence of the contributions to $\epsilon\tilde{\mathfrak{B}}_4^D$ from these events is the same as the ϵ dependence of the contribution to $\epsilon\mathfrak{B}_3^D$ from the three-body ring events. Therefore the contributions from the events considered here represent excluded-volume corrections to the three-body ring contribution.

The above-mentioned contributions are contained in products of five binary collision operators in $\epsilon\tilde{\mathfrak{B}}_4^D$. Our analysis of these terms is based on the fact that many of them contain products of the form $T(i,j)G_0T(i,k)G_0T(j,k)$ or $T(i,k)G_0T(i,j)G_0T(j,k)$ where i,j,k are any three particles in the set $(1,2,3,4)$ and $G_0=G_0(x_1,x_2,x_3,x_4)$. These products contain nonvanishing contributions from configurations of the three particles (i,j,k) where particle i is simultaneously overlapping both particles j and k at the time of the (j,k) collision. Consequently, $\epsilon\tilde{\mathfrak{B}}_4^D$ contains many contributions from double overlapping configurations, that are hidden in the products of collision operators of the type given above. We will proceed by first showing that products of three T operators, as given above, do contain double overlapping contributions. Then we will discuss which products of five binary collision operators occur in $\epsilon\tilde{\mathfrak{B}}_4^D$ and in particular, which of those contain the relevant products of three T operators. Finally, we will briefly outline the method by which Eqs. (4.6) and (4.7) are obtained.

We begin by considering the products $T(1,2)G_0T(1,3)G_0T(2,3)$ and $T(1,3)G_0T(1,2)G_0T(2,3)$. To see that these terms contain a double overlapping configuration at the instant of the (2,3) collision, we first consider the geometry of the binary collision described by the operator $T(1,2)$, and for later convenience also of $\overline{T}(1,2)$.

The operators $T(1,2)$ and $\overline{T}(1,2)$, defined in (1.11) and (1.12) can be written as a sum of two parts: an interacting part, containing the operator $R_\sigma(1,2)$ and a noninteracting part: $T(1,2)=T^i(1,2)+T^n(1,2)$ and $\overline{T}(1,2)=T^i(1,2)+\overline{T}^n(1,2)$ where T^i, T^n, and $\overline{T}^n$ follow from the Eqs. (1.11) and (1.12). Of these three operators, only T^n leads to the overlapping configurations in which we are interested here. To see this we have to discuss the three operators in some detail. This is done in Fig. 4. Here we fix the relative velocity $\vec{v}_{12}$ of particle 1 with respect to particle 2, which is placed at the origin. The points on the action sphere, i.e. the sphere of radius a about the center of particle 2, where the δ functions occurring in the T operators are evaluated are indicated in Fig. 4 for the three cases. Since the binary collision operators in $\epsilon\tilde{\mathfrak{B}}_4^D$ appear in combination with $G_0(x_1,x_2,x_3;x_4)$, we are really interested in the operators $T^i(1,2)S^0_{-t}(x_1,x_2)$, $T^n(1,2)S^0_{-t}(x_1,x_2)$,

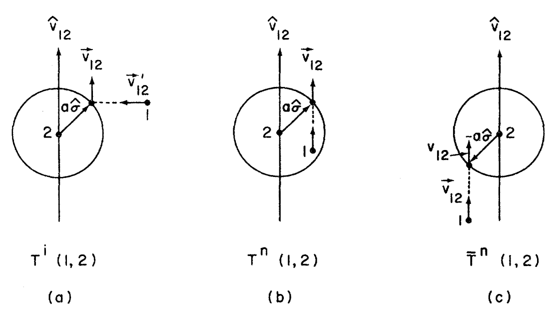

FIG. 4. Schematic illustration of the action of the operators: (a) $T^i(1,2)S^0_{-t}(x_1,x_2)$; (b) $T^{(n)}(1,2)S^0_{-t}(x_1,x_2)$; (c) $\overline{T}^n(1,2)S^0_{-t}(x_1,x_2)$ in the relative coordinate system of particles 1 and 2. The relative motion of particle 1 with respect to particle 2 is traced back in time in Figs. 4(a)–4(c), starting from a point on the action sphere, where the relative velocity of particle 1 is $\vec{v}_{12}$ and $\vec{r}_{12}=a\hat{\sigma}, a\hat{\sigma}, -a\hat{\sigma}$, respectively, to a point $\vec{r}_{12}(-t)=a\hat{\sigma}-\vec{v}_{12}'t$, $a\hat{\sigma}-\vec{v}_{12}t$, $-a\hat{\sigma}-\vec{v}_{12}t$ where the relative velocity is $\vec{v}_{12}'$, $\vec{v}_{12}, \vec{v}_{12}$, respectively. $\hat{v}_{12}$ is the unit vector in the direction $\vec{v}_{12}$.

$\overline{T}^n(1,2)S^0_{-t}(x_1,x_2)$, if we invert the Laplace transform and ignore the irrelevant particles 3 and 4. For the effect of these three operators we refer to Fig. 4. We remark that for $T^n(1,2)S^0_{-t}(x_1,x_2)$ particle 1 penetrates the action sphere, so that for a range of values of t the particles 1 and 2 are *within* their action sphere.

Using these geometrical properties of the T operators, we now show that the product $T(1,2)G_0(x_1,x_2,x_3,x_4)T(1,3)G_0(x_1,x_2,x_3,x_4)T(2,3)$ contains nonvanishing contributions from collision sequences where particle 1 is overlapping with both particles 2 and 3 at the time of the (2,3) collision. To see this we consider the inverse Laplace transform:

$$\int_0^t d\tau T(1,2)S^0_{-\tau}(x_1,x_2,x_3)T(1,3) \times S^0_{-(t-\tau)}(x_1,x_2,x_3)T(2,3)\,, \tag{B1}$$

where we have ignored the irrelevant particle 4 (cf. Fig. 5). We have arranged the time such that the (1,2) collision occurs at time $t=0$, the (1,3) collision at time $-\tau$, and (2,3) collision at time $-t$ with $t>\tau>0$. Writing in (B1) each T operator as the sum of a T^i and a T^n operator, we see that only the combination of the T^n parts of the (1,2)- and

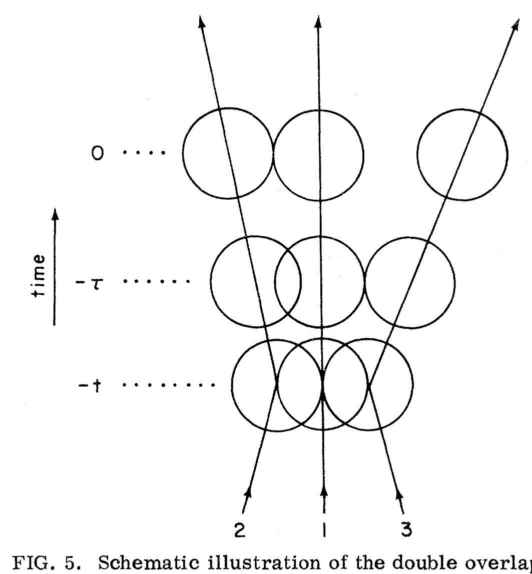

FIG. 5. Schematic illustration of the double overlapping configuration contained in $T^n(1,2)S^0_{-\tau}(x_1,x_2,x_3) \times T^n(1,3)S^0_{-(t-\tau)}(x_1,x_2,x_3)T^i(2,3)$. The vertical direction indicates the direction of increasing time. We have arranged the time such that time $t=0$, the $T(1,2)$ operator requires that particles 1 and 2 are separated by a molecular diameter. At time $-\tau$, the particles 1 and 2 are within each others interaction sphere, and the particles 1 and 3 are separated by a molecular diameter. At time $-t$, the particles 2 and 3 collide, while particle 1 overlaps both of them. In the figure only the result of the T^i part of the $T(2,3)$ operator is indicated.

(1,3)-collision operators with $T(2,3)$ leads to a configuration, where particle 1 is overlapping with both 2 and 3 at time $-t$, when the (2,3) collision takes place.

A similar dynamical analysis shows that also the product $T(1,3)G_0T(1,2)G_0T(2,3)$ contains nonvanishing contributions from configurations where particle 1 is overlapping with the particles 2 and 3 at the time of the (2,3) collision. One can convince oneself that, apart from permutations of the indices, these are the only products of three binary collision operators occurring in $\epsilon\tilde{\mathfrak{G}}_4^D$ that lead to double overlapping configurations.

We will now consider the products of five binary collision operators occurring in $\epsilon\tilde{\mathfrak{G}}_4^D$. Since a complete analysis is too lengthy to give here because it involves the consideration of several hundred terms, we will only give a brief discussion here. The operator $\epsilon\tilde{\mathfrak{G}}_4^D$ contains all products of five binary collision operators of the form

$$\overline{T}(1,2)G_0T(\alpha)G_0T(\beta)G_0T(\gamma)G_0T(\delta)G_0 \qquad \text{(B2)}$$

where $\alpha,\beta,\gamma,\delta$ represent pairs of particles chosen from the particles (1,2,3,4), such that (a) $\alpha\neq(1,2)$ by virtue of Eq. (A7c); (b) the T operator on the extreme right, $T(\delta)$, must contain particle 1 as a member of the pair δ, by virtue of Eq. (A7i); (c) all four particles must be contained in the pairs $(1,2),\alpha,\beta,\gamma$, since the product is canceled otherwise; and (d) all four particles must be contained in the pairs α, β, γ, δ, for the same reason as in (c).

(a) We first look for all products of five binary collision operators which lead to a sequence of three binary collisions with a double overlapping contribution at the collision described by the $T(\delta)$ operator. Using the geometrical arguments made earlier in this section, we see that the products

$$\overline{T}(1,2)G_0\,T(\alpha)G_0T(i,1)G_0T(i,k)G_0T(1,k)G_0 \qquad \text{(B3a)}$$

and

$$\overline{T}(1,2)G_0T(\alpha)G_0T(i,k)G_0T(i,1)G_0T(1,k)G_0 \qquad \text{(B3b)}$$

contain such contributions, where particle i is overlapping with both 1 and k at the instant of the $(1,k)$ collision. It should also be noted that while a product like $\overline{T}(1,2)G_0T(i,1)G_0T(\alpha)G_0T(i,k)\times G_0T(1,k)G_0$ also contains a double overlapping configuration at the $(1,k)$ collision, its contribution to $\epsilon\tilde{\mathfrak{G}}_4^D$ is less singular, for small ϵ, than the contribution from (B3a) and (B3b), and will therefore be disregarded. For, by inverting the Laplace transform, we see that for all such double overlapping configurations, the ordering of the T operators requires that the $T(\alpha)$ collision takes place at the same time that particle i overlaps with particle 1. Furthermore, the particles 1, i, k, and the pair α must contain all four particles, 1, 2, 3, 4, due to condition (c) above. Thus it follows that for the product of T operators we are considering, the double overlapping configuration is part of a configuration where all four particles are within a molecular diameter of each other. This condition imposes a dynamical restriction on this collision sequence. On the other hand, inspection of the inverse Laplace transform of (B3a) and (B3b) shows that there is no such restriction on the double overlapping configuration at the $(1,k)$ collision. Consequently, we retain in our analysis the contributions from the double overlapping events in these products only.

To extract, finally in an explicit form, the double overlapping contribution to the two products (B3a) and (B3b), we consider their sum

$$\overline{T}(1,2)G_0T(\alpha)\{[G_0T(i,1)G_0T(i,k)G_0 + G_0T(i,k)G_0T(i,1)G_0]T(1,k)G_0\} \qquad \text{(B4a)}$$

and examine the terms in the curly bracket, S:

$$S=[G_0T(i,1)G_0T(i,k)G_0 + G_0T(i,k)G_0T(i,1)G_0]T(1,k)G_0\,.$$

To extract the double overlapping contributions to S, we use (A7h) and $G_0fTG_0=G_0fG_0^{-1}G_0TG_0$ to write S in the form

$$S=S_1+S_2$$

with

$$S_1=G_0f(i,1)f(i,k)T(1,k)G_0+f(i,1)f(i,k)G_0T(1,k)G_0-f(i,1)G_0f(i,k)T(1,k)G_0-f(i,k)G_0f(i,1)T(1,k)G_0\,, \qquad \text{(B5a)}$$

$$S_2=[G_0\overline{T}(i,1)G_0T(i,k)G_0+G_0\overline{T}(i,k)G_0T(i,1)G_0+G_0\overline{T}(i,1)f(i,k)G_0+G_0\overline{T}(i,k)f(i,1)G_0-f(i,1)G_0\overline{T}(i,k)G_0 -f(i,k)G_0\overline{T}(i,1)G_0]T(1,k)G_0\,. \qquad \text{(B5b)}$$

A dynamical analysis of S_1 and S_2 shows that only S_1 can contain contributions from double overlapping configurations at the instant of the $(1,k)$ collision. For, the $\overline{T}$ operators occurring on the right-hand side of Eq. (B5b) always lead to configurations where particles i and 1 or i and k are not overlapping at the time of the $(1,k)$ collision described by the $T(1,k)$ on the extreme right.

Moreover, only the first term on the right-hand side of Eq. (B5a) for S_1 leads to a double overlapping configuration contribution to (B4a) that we retain, since the events that contribute to the other three terms are dynamically more restricted. To see this, one considers the inverse Laplace transform of Eq. (B4a) with S_1 replacing S. Then one notes that if there is a double overlapping configuration at the $(1,k)$ collision, the structure of all terms but the first requires that the α collision takes place while particle i is overlapping particles 1 and k. Since α contains at least one of the particles $1,\ i,k$, it follows that the last three terms on the right-hand side of Eq. (B5a) have additional restrictions placed on them for a nonvanishing contribution to (B4a), when compared to the first term. Therefore the last three terms can be neglected for the long-time behavior of $\rho_D^{(d)}(t)$ and the only contribution to $\epsilon\tilde{\mathcal{B}}_4^D$ retained from (B4a) is

$$\overline{T}(1,2)G_0T(\alpha)G_0f(1,i)f(k,i)T(1,k)G_0\,. \tag{B6}$$

When this analysis is applied to all terms of the form of (B3a) and (B3b) in $\epsilon\tilde{\mathcal{B}}_4^D$, the last terms on the right-hand sides of Eqs. (4.6) and (4.7) for $\epsilon\tilde{\mathcal{B}}_{4,\,\mathrm{i}}^D$ and $\epsilon\tilde{\mathcal{B}}_{4,\,\mathrm{ii}}^D$, respectively, are obtained.

(b) A similar discussion can be given for all terms in $\epsilon\tilde{\mathcal{B}}_4^D$ of the form

$$\overline{T}(1,2)G_0[T(i,j)G_0T(i,k)G_0 + T(i,k)G_0T(i,j)G_0]T(j,k)G_0T(\delta)G_0\,. \tag{B7}$$

These terms lead to double overlapping contributions of the type

$$\overline{T}(1,2)G_0f(i,j)f(i,k)T(j,k)G_0T(\delta)G_0 \tag{B8}$$

and give the remaining terms on the right-hand side of Eqs. (4.6) and (4.7) for $\epsilon\tilde{\mathcal{B}}_{4,\,\mathrm{i}}^D$ and $\epsilon\tilde{\mathcal{B}}_{4,\,\mathrm{ii}}^D$, respectively.

Terms of the form given by (B6) and (B8) are the only terms in $\epsilon\tilde{\mathcal{B}}_4^D$ which we retain.

APPENDIX C: THE REMOVAL OF $\epsilon\mathcal{B}_{4,F}^D$—EQ. (4.10)

In this appendix we sketch how, after a resummation, the term $\epsilon\mathcal{B}_{4,F}^D$, as given by Eq. (4.10), does not contribute to the $t^{-d/2}$ behavior of $\rho_D^{(d)}(t)$. To do this we consider $\mathcal{B}_{4,F}^D$ to be the first term in an (infinite) series of terms from $\epsilon\mathcal{B}_5^D$, $\epsilon\mathcal{B}_6^D, \ldots$ in which all powers of the ring operators $G_0(x_1,x_3) \times \int d4\,\lambda^D(13\,|\,4)$ and $G_0(x_1,x_2)\int d3\,\lambda^D(12\,|\,3)$ successively appear. Then $n^3\epsilon\mathcal{B}_{4,F}^D$ can be incorporated in a resummation which leads to $n^2\epsilon\mathcal{R}_F^D$ given by

$$n^2\epsilon\mathcal{R}_F^D = n^2\int d2\int d3\Big\{\overline{T}(1,2)f(2,3)[1+f(1,3)]\Big[\epsilon+\mathcal{H}_0(x_1,x_2)-n\int d4\,\lambda^D(13\,|\,4)\Big]^{-1}T(1,3)\varphi_0(v_3)$$
$$+\overline{T}(1,2)\Big[\epsilon+\mathcal{H}_0(x_1,x_2)-n\int d4\,\lambda^D(12\,|\,4)\Big]^{-1}f(1,2)f(2,3)T(1,3)\varphi_0(v_3)\Big\}\varphi_0(v_2)\,. \tag{C1}$$

Here we have added a finite term $n^2\int d2\int d3\times\overline{T}(1,2)f(2,3)G_0(x_1,x_3)T(1,3)\varphi_0(v_2)\varphi_0(v_3)$ from $\epsilon\mathcal{B}_3^D$ as well as a term

$$\int d2\int d3\,\overline{T}(1,2)[f(1,3)f(2,3)G_0(x_1,x_3)+G_0(x_1,x_2)f(1,2)f(2,3)]T(1,3)\varphi_0(v_2)\varphi_0(v_3) \tag{C2}$$

that, with the Eqs. (A7f) and (A7g), can be shown to vanish. For simplicity, we have not included in this resummation the various excluded-volume corrections, but as will be argued below, to do so would not change our conclusions. In order to extract the long-time behavior of $n^2\epsilon\mathcal{R}_F^D$, we can proceed in a similar way as with $n\epsilon\mathcal{R}_E^D(\vec{v}_1,\epsilon)$. Thus (a) expressing $n^2\epsilon\mathcal{R}_F^D$ in Fourier representation; (b) applying a spectral decomposition to $n^2\epsilon\mathcal{R}_F^D$; (c) setting $k=0$ everywhere except in the denominators of the form $[\epsilon+\omega(k)+\Omega(k)]^{-1}$; (d) using that

$$\int d\vec{r}_2\int d\vec{r}_3 f(2,3)[1+f(1,3)]\overline{T}(1,2) = \int d\vec{r}_3 f(2,3)[1+f(1,3)]\big|_{r_{12}=a}\int d\vec{r}_2\overline{T}(1,2) = [\chi_1(a)-2b_2^{(d)}]T_{00}(1,2)\,. \tag{C3}$$

and that

$$\int d\vec{r}_2\int d\vec{r}_3 f(1,2)f(2,3)T(1,3) = \int d\vec{r}_2 f(1,2)f(2,3)\big|_{r_{13}=a}\int d\vec{r}_3 T(1,3) = \chi_1(a)T_{00}(1,3); \tag{C4}$$

(e) neglecting the nonhydrodynamic parts of $n^2\epsilon\mathcal{R}_F^D$, one is lead to an expression for $n^2\epsilon\mathcal{R}_F^D$ that contains the operator

$$\int d\vec{v}_1\int d\vec{v}_3 x_0^{(\omega)}(\hat{k},\vec{v}_1)T_{00}(1,3)\varphi_0(v_1)\varphi_0(v_3)$$

acting on a function of $\vec{v}_1$ (and ϵ) and

$$\int d\vec{v}_2 T_{00}(1,2)\chi_0^{(\omega)}(\hat{k},\vec{v}_1)\varphi_0(v_1)\varphi_0(v_2)$$

which, using Eq. (5.5), can both be shown to vanish due to conservation of particle numbers in a binary collision. Consequently, unlike from $n\epsilon\mathcal{R}_E^D$, there is no long-time contribution $\sim t^{-d/2}$ from $n^2\epsilon\mathcal{R}_F^D$ to $\rho_D^{(d)}(t)$. The inclusion of excluded-volume corrections does not alter this conclusion because it does not affect the conservation of particle numbers in a binary collision.

APPENDIX D: DERIVATION OF (4.23)

We consider here the operator $nA_{\vec{k}}(\vec{v}_1)$ acting on a function $\varphi_0(v_1)g(\vec{v}_1)$, which according to Eq. (4.22) with $\vec{k}\to-\vec{k}$, and a relabeling of the particles is given by

$$nA_{\vec{k}}(\vec{v}_1)\varphi_0(v_1)g(\vec{v}_1)=\sum_{l=1}^{\infty}n^{l+1}l\int d2\cdots\int d(l+2)e^{-i\vec{k}\cdot\vec{r}_{12}}g_l(\vec{r}_2,\vec{r}_3\,|\,\vec{r}_1,\vec{r}_4,\ldots,\vec{r}_{l+2})T(2,3)\prod_{i=1}^{l+2}\varphi_0(v_i)g(\vec{v}_2). \tag{D1}$$

If we now use the explicit form of the $T(2,3)$ operator as given by Eq. (1.11), and carry out the integration over $\vec{v}_3,\ldots,\vec{v}_{l+2}$, in (D1), we obtain

$$nA_{\vec{k}}(\vec{v}_1)\varphi_0(v_1)g(\vec{v}_1)=-\sum_{l=1}^{\infty}n^{l+1}la^{d-1}\int d\vec{v}_2\int d\vec{r}_2\cdots\int d\vec{r}_{l+2}e^{i\vec{k}\cdot\vec{r}_{21}}\int d\hat{\sigma}\,\delta(\vec{r}_{23}-a\hat{\sigma})$$
$$\times g_l(\vec{r}_2,\vec{r}_3\,|\,\vec{r}_1,\vec{r}_4,\ldots,\vec{r}_{l+2})(\hat{\sigma}\cdot\vec{v}_2)\varphi_0(v_2)g(\vec{v}_2). \tag{D2}$$

Then using the following identity, derived by van Beijeren and Ernst[24]:

$$\frac{\partial}{\partial\vec{r}_2}[C(r_{12})-\chi(a)f(r_{12})]=\sum_{l=1}^{\infty}n^{l+1}la^{d-1}\int d\hat{\sigma}\int d\vec{r}_3\cdots\int d\vec{r}_{l+2}\,\hat{\sigma}\delta(\vec{r}_{23}-a\hat{\sigma})g_l(\vec{r}_2,\vec{r}_3\,|\,\vec{r}_1,\vec{r}_4,\ldots,\vec{r}_{l+2}) \tag{D3}$$

where $C(r_{12})$ is the direct correlation function, we obtain from Eq. (D2) the result that

$$nA_{\vec{k}}(\vec{v}_1)\varphi_0(v_1)g(\vec{v}_1)=i\vec{k}n[C(k)-\chi(a)f(k)]\cdot\int d\vec{v}_2\vec{v}_2\varphi_0(v_2)g(\vec{v}_2)\,. \tag{D4}$$

For Eq. (5.13) we need the k expansion of $A_{\vec{k}}(\vec{v}_1)$.[26] Using that

$$\lim_{k\to 0}nC(k)=1-\beta\left(\frac{\partial p}{\partial n}\right)_{\beta} \tag{D5}$$

and

$$\beta p=n[1+nb_2^{(d)}\chi(a)] \tag{D6}$$

with

$$b_2^{(d)}=-\tfrac{1}{2}\lim_{k\to 0}f(k)\,, \tag{D7}$$

Eq. (5.13) is recovered.

---

*Work supported in part by the National Science Foundation under grants No. NSF-GP-29385 and GP 38965 X.

[1]J. R. Dorfman and E. G. D. Cohen, Phys. Rev. Lett. 25, 1257 (1970).

[2]J. R. Dorfman and E. G. D. Cohen, Phys. Rev. A 6, 776 (1972).

[3](a) M. H. Ernst, J. R. Dorfman, W. R. Hoegy, J. M. J. van Leeuwen, Physica 45, 127 (1969). (b) We are using here a mixed notation, where the S operators are written in terms of the canonical variables $x=\vec{r},\vec{p}$, while the T operators, which are related to the Boltzmann operators [cf. Eq. (3.3)], are expressed in their natural variables $\vec{r},\vec{v}=\vec{p}/m$ in μ space. Although it is possible to adopt a uniform notation, in view of the later sections, it is not convenient to do so.

[4]It is also possible to compute $\rho_D^{(d)}(t)$ by finding approximate solutions to the BBGKY hierarchy equations satisfied by $\Phi_D^{(d)}(\vec{v},t)$. While elegant, this method has the disadvantage that the resulting expressions for $\Phi_D^{(d)}(t)$ must be carefully examined as to whether they are consistent in the density. Cf. J. R. Dorfman, in *Fundamental Problems in Statistical Mechanics*, edited by E. G. D. Cohen (North-Holland, Amsterdam, 1975), Vol. III, and references contained therein.

[5]B. J. Alder and T. E. Wainwright, Phys. Rev. A 1, 18 (1970); B. J. Alder, D. M. Gass and T. E. Wainwright, J. Chem. Phys. 53, 3813 (1970); Phys. Rev. A 4, 233 (1971).

[6]W. W. Wood and J. J. Erpenbeck (unpublished); see also W. W. Wood, in *The Boltzmann Equation*, edited by E. G. D. Cohen and W. Thirring (Springer, Vienna, 1973), p. 451; and in *Fundamental Problems in Statistical Mechanics*, edited by E. G. D. Cohen (North-Holland, Amsterdam, 1975), Vol. III.

[7]We tacitly assume that there is a wall potential. Alternatively, we can assume that the system has periodic boundary conditions.

[8]Although it is convenient to introduce a mixed T and $\overline{T}$ expression at this point, it is not necessary. One could follow the method used in I to obtain an expression where only $\overline{T}$ operators appear. This would make the analysis given in Sec. III and in Sec. IV, more compli-

cated however, since the extraction of the Enskog χ factor would be considerably more difficult.

[9]Note that the cluster expansion in Eq. (2.2) is based on fixing two particles 1 and 2, in contrast to that in Eq. (2.8) in I, where there is only one fixed particle. In fact, the cluster operators $\mathfrak{U}(x_1x_2|x_3,\ldots x_l;t)$ become identical with $\mathfrak{U}(x_1|x_3,\ldots,x_l;t)$ if the particles 1 and 2 are replaced by particle 1. A similar cluster expansion, but for the case of continuous potentials has been given by M. H. Ernst, L. K. Haines, and J. R. Dorfman, Rev. Mod. Phys. 41, 296 (1969). For a further discussion of cluster expansions in nonequilibrium statistical mechanics, see E. G. D. Cohen in *Fundamental Problems in Statistical Mechanics*, edited by E. G. D. Cohen (North-Holland, Amsterdam, 1968), Vol. II, p. 228 and references contained therein.

[10]Cf. J. DeBoer, Rep. Prog. Phys. 12, 305, (1949); G. E. Uhlenbeck and G. W. Ford, *Studies in Statistical Mechanics*, edited by G. E. Uhlenbeck and J. DeBoer (North-Holland, Amsterdam, 1961), Vol. I, p. 123.

[11]N. N. Bogoliubov, in *Studies in Statistical Mechanics* (North-Holland, Amsterdam, 1961), Vol. I, p. 1.

[12]R. Zwanzig, Phys. Rev. 129, 486 (1963).

[13]J. R. Dorfman and E. G. D. Cohen, J. Math. Phys. 8, 282 (1967).

[14]See Ref. 9 for a bibliography on the divergences. For a more recent discussion cf. Y. Pomeau and A. Gervois, Phys. Rev. A 9, 2196 (1974).

[15]J. V. Sengers, Phys. Fluids 9, 1685 (1966).

[16]L. K. Haines, J. R. Dorfman, and M. H. Ernst, Phys. Rev. 144, 207 (1966).

[17]J. V. Sengers, in *Lectures in Theoretical Physics*, edited by W. E. Brittin (Gordon and Breach, New York, 1967), Vol. 9c, p. 335.

[18]S. Chapman and T. G. Cowling, *The Mathematical Theory of Non Uniform Gases*, 3rd ed. (Cambridge U. P., London, 1970).

[19]This was first noticed by J. Lebowitz, J. Percus, and J. Sykes, Phys. Rev. 188, 487 (1969).

[20]Strictly speaking the right-hand side of Eq. (3.11) should be replaced by a sum of exponentials. A similar remark holds for Eqs. (7.11) and (7.12).

[21]W. R. Hoegy and J. V. Sengers, Phys. Rev. A 2, 2461 (1970); J. V. Sengers, M. H. Ernst, and D. T. Gillespie, J. Chem. Phys. 56, 5583 (1972); and J. V. Sengers, in *The Boltzmann Equation*, edited by E. G. D. Cohen and W. Thirring (Springer, Vienna, 1973), p. 177.

[22]In this connection it is relevant that for short times the Enskog-theory value for $\rho_D^{(d)}(t)$ is in good agreement with the computer results (Refs. 5, 6) and that for three dimensions the total contribution of this term to $\epsilon\mathcal{B}_3^D$ is a few percent of the contribution from the first term (Ref. 21) alone. A similar remark holds for the short-time contribution of the three-body ring terms to $\rho_D^{(d)}(t)$.

[23]Y. H. Kan, Ph.D. dissertation (Department of Physics and Astronomy, University of Maryland) (unpublished).

[24](a) For a more systematic analysis see H. van Beijeren, thesis (University of Nijmegen, 1974) (unpublished); and H. van Beijeren and M. H. Ernst (unpublished). (b) H. van Beijeren and M. H. Ernst, Physica 68, 437 (1973).

[25]This can be verified by direct computation. A discussion of the coefficient ω_4 has been given by W. W. Wood, J. J. Erpenbeck, and J. R. Dorfman (unpublished).

[26](a) This operator appears also in the theory of the short-time behavior of a class of functions called "memory" functions. Cf. Ref. 24 and references therein; J. Sykes, J. Stat. Phys. 8, 279 (1973); and K. Mo and J. Dufty, Physica 77, 777 (1974). (b) H. H. U. Konijnendijk and J. M. J. van Leeuwen, Physica 64, 342 (1973).

[27]See S. Chapman and T. G. Cowling, Ref. 18 for the Enskog theory transport coefficients for three dimensions. For two dimensions see D. M. Gass, J. Chem. Phys. 54, 1898 (1971).

[28]The neglect of the k dependence of the $\overline{T}_{\vec{k}}, T_{-\vec{k}}$ operators imposes the restriction that $k < a^{-1}$. For high densities, it is this restriction which determines the upper limit on the $\vec{k}$ integral, in Eq. (6.8), rather than $k < k_0 \approx 1/l = 1/\langle v\rangle t_0$, since for high densities $l < a$.

[29]In fact, Wood and Erpenbeck (last reference of Ref. 6) have shown that the computer data are in excellent agreement with the full result, Eq. (6.9), when account is taken of the fact that for a finite system the $\vec{k}$ integral should be replaced by a sum.

[30]Cf. M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen, Phys. Rev. Lett. 25, 1254 (1970); Phys. Rev. A 4, 2055 (1971).

[31]That is, if one assumes that the linearized Navier-Stokes equations are valid in two dimensions, one is lead to the conclusion that the transport coefficients appearing in them are infinite (cf. Ref. 30).

[32]Y. Pomeau and P. Résibois, Phys. Lett. 44A, 97 (1973), Physica 72, 493 (1974); P. Résibois, Physica 70, 413 (1973).

[33]M. H. Ernst and H. van Beijeren (unpublished).

[34]C. F. Mazenko, Phys. Rev. A 7, 209, 222 (1973).

[35]C. F. Mazenko, Phys. Rev. A 9, 360 (1974); and C. Boley, Ann. Phys. (N. Y.) 86, 91 (1974).

[36]D. Levesque and W. T. Ashurst, Phys. Rev. Lett. 33, 277 (1974).

[37]It is worth mentioning that the dominant long-time behavior of the higher iterates of the ring events are exactly cancelled by the long-time contributions from what have been called repeated ring events (H. van Beijeren, private communication). See M. H. Ernst and J. R. Dorfman, Physica 61, 157 (1972) and J. R. Dorfman, Ref. 4 for a discussion of the repeated ring events.

[38]P. Résibois and J. Lebowitz (unpublished).

[39]D. Lieberworth and E. G. D. Cohen (unpublished).

[40]For $t=0$, the left-hand side of Eq. (A3) is not well defined since squares of Dirac δ functions occur. To avoid this difficulty and to ensure that Eq. (A3) is satisfied for $t=0$, it is necessary to incorporate infinitesimal free streaming operators $\lim_{\eta\to 0} S^0_{-\eta}(x_1, x_2)$ into the definitions of $T(i,j)$ and $\overline{T}(i,j)$ as given by Eqs. (1.11) and (1.12), respectively. These infinitesimal streaming operators serve to define the binary collision operators when they act on functions, like the Mayer f functions, which are discontinuous at the surface of the action sphere $r_{ij}=a$. In addition they are necessary to ensure that Eqs. (A7a)–(A7g) are satisfied. For details see Ref. 3(a). For the analysis of this paper, the extended definition is not used: the identities (A7a)–(A7g) are used instead.

[41]To show this is tedious and involved for large N. In Ref. 3(a) an alternate and shorter presentation is given, which uses that $S_{-t}(x^N)W(r^N)$ can also be defined as the adjoint of the operator $W(r^N)S_{+t}(x^N)$.