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Velocity-Correlation Functions in Two and Three Dimensions: Low Density

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The long-time behavior of velocity-correlation functions $\rho^{(d)}(t)$ characteristic for self-diffusion, viscosity, and heat conductivity is calculated for a gas of hard disks or hard spheres on the basis of the kinetic theory of dense gases. In d dimensions one finds that $\rho^{(d)}(t)$, after an initial exponential decay for a few mean free times t_0, exhibits for times up to at least $\sim 40t_0$ a decay $\sim \alpha^{(d)}(\rho)(t_0/t)^{d/2}$, where $\alpha^{(d)}$ is of the order of ρ^{d-1}, $\rho = na^d$ with n the number density, and a the hard-disk or hard-sphere diameter. The $\alpha^{(d)}(\rho)$ are determined by the same dynamical events that are responsible for the divergences in the virial expansion of the transport coefficients. In this paper the $\alpha^{(d)}(\rho)$ are calculated to lowest order in ρ. In this order, they are identical to the low-density limit of the $\alpha^{(d)}(\rho)$ that have been obtained by other authors on the basis of hydrodynamical considerations.

I. INTRODUCTION

Recently Alder and Wainwright[1,2] computed the velocity-autocorrelation function $\rho_D^{(2)}(t)$ for a system of 500 hard-disk particles using computer-simulated molecular dynamics. The particles were studied for about 30 mean free times t_0 for a range of densities from 0.2 to 0.5 of the density at close packing. Although for a few mean free times Alder and Wainwright found the exponential decay that would be predicted on the basis of the Boltzmann or Enskog equation, they noted that for times t in the range $10t_0 < t \leqq 30t_0$, $\rho_D^{(2)}(t)$ showed a nonexponential slowly decaying behavior. Similar results over a comparable range of densities and times were obtained later for the velocity-correlation functions $\rho_\eta^{(2)}(t)$ and $\rho_\lambda^{(2)}(t)$, characteristic for viscosity and heat conductivity.[3]

Although they reported only one result in three dimensions for the velocity-autocorrelation function $\rho_D^{(3)}(t)$, there seems to be little doubt that both the two-dimensional and the three-dimensional results can be represented for $10t_0 < t \leqq 30t_0$ by

$$\rho_D^{(d)}(t) \equiv \frac{\langle \vec{v}(0)\cdot\vec{v}(t)\rangle}{\langle v^2(0)\rangle} \sim \alpha_D^{(d)}(\rho)\left(\frac{t_0}{t}\right)^{d/2} . \qquad (1.1)$$

Here $\vec{v}(t)$ is the velocity at time t of a chosen particle in the fluid, whose initial velocity is $\vec{v}(0)$, and d is the dimension of space, $\rho = na^d$, where n is the number density and a the diameter of the hard disks or hard spheres. The brackets denote a molecular dynamic time average over all particles in the system.[4]

For $d=2$, (1.1) describes $\rho_D^{(2)}(t)$ over the entire reported range of densities and time within the "experimental error" which is estimated to be on the order of 10%.

For $d=2$ and 3, (1.1) also agrees with a hydrodynamical theory of $\rho_D^{(d)}(t)$. A hydrodynamical description of their results for $\rho_D^{(d)}(t)$ was presented by Alder and Wainwright, based on a numerical solution of the Navier-Stokes equations, which was in good agreement with the molecular dynamics calculations.[1,2] In fact, the molecular dynamics calculation for $d=2$ exhibited a vortex type of velocity correlation between a chosen molecule and the surrounding molecules, which is very similar to the hydrodynamical flow field surrounding a moving volume element in a fluid which is initially at rest. Furthermore, using hydrodynamical arguments based on an analytic solution of the linearized Navier-Stokes equations, Alder and Wainwright,[1,2,4] and Ernst, Hauge, and van Leeuwen[5] were able to derive theoretical expressions for the asymptotic time behavior of $\rho_D^{(d)}(t)$ as well as of $\rho_\eta^{(d)}(t)$ and $\rho_\lambda^{(d)}(t)$ which are in agreement with Eq. (1.1) and lead to expressions for $\alpha_D^{(d)}(\rho)$, $\alpha_\eta^{(d)}(\rho)$, and $\alpha_\lambda^{(d)}(\rho)$ that are numerically consistent with the available computer calculations. The same results for $\rho^{(d)}(t)$ have been obtained by Kawasaki[6] and by Ernst,[7] using the hydrodynamical mode-mode coupling theory.

The purpose of this paper is to elaborate on a discussion of the Alder and Wainwright results using the methods of the kinetic theory of gases and an analysis originated by Pomeau.[8] A preliminary version of this work has been reported elsewhere.[9]

We shall illustrate our calculations of the long-time behavior of $\rho_D^{(d)}(t)$ in detail, while we only sketch the very similar calculations for $\rho_\eta^{(d)}(t)$ and $\rho_\lambda^{(d)}(t)$.

Our starting point is the definition of $\rho_D^{(d)}(t)$ given by Eq. (1.1), where the average is now interpreted as that over a canonical ensemble in the thermodynamical limit. Such an average is assumed to be identical with the average used in the computer calculations, if the number of particles used in these calculations is sufficiently large. In this paper we will only consider the low-density limit of $\alpha^{(d)}(\rho)$; in a subsequent paper, the extension of the present calculations to higher densities will be given.[10] We shall formulate the theory for a general short-ranged intermolecular potential. The formulas will be applied, however, to hard disks and hard spheres only.

In Sec. II we outline the cluster expansion on which our discussion of $\rho_D^{(d)}(t)$ is based. In Sec. III we discuss a rearrangement of this cluster expansion which is necessary if one wants to find the long-time behavior of $\rho_D^{(d)}(t)$. In Sec. IV the hydrodynamical modes of the linearized Lorentz-Boltzmann equation and the Boltzmann equation, which are needed to find the long-time behavior of $\rho_D^{(d)}(t)$, are summarized. In Sec. V the $t^{-d/2}$ time dependence and the coefficient $\alpha_D^{(d)}(\rho)$ are obtained for hard disks and hard spheres in lowest order of the density. In Sec. VI the corresponding expressions for the long-time behavior of $\rho_\eta^{(d)}(t)$ and $\rho_\lambda^{(d)}(t)$ are given. The calculation leading to these expressions is outlined in the Appendix. In Sec. VII some aspects of the results obtained in this paper are discussed.

II. CLUSTER EXPANSION FOR $\rho_D^{(d)}(t)$

We consider N particles in a volume V at temperature $T=(\beta k_B)^{-1}$, where k_B is Boltzmann's constant. The definition of $\rho_D^{(d)}(t)$ is[11]

$$\rho_D^{(d)}(t)=\frac{\langle v_{1x}v_{1x}(-t)\rangle}{\langle v_{1x}^2\rangle}$$

$$=\lim_{\substack{N,V\to\infty\\ N/V=n}}\langle v_{1x}^2\rangle^{-1}\int dx^N v_{1x}S_{-t}(x^N)\rho(x^N)v_{1x}$$

$$=\int d\vec{v}_1\, v_{1x}\Phi_D^{(d)}(\vec{v}_1,t)\,, \tag{2.1}$$

where

$$\Phi_D^{(d)}(\vec{v}_1,t)=\lim_{\substack{N,V\to\infty\\ N/V=n}} m^d\langle v_{1x}^2\rangle^{-1}V \times\int dx^{N-1}\,S_{-t}(x^N)\rho(x^N)v_{1x}\,. \tag{2.2}$$

Here $x^N=x_1x_2\cdots x_N$ stands for the phases $x_i=\vec{r}_i,\vec{p}_i$ of the N particles $1,\ldots N$; and m is the mass of a particle. The N-particle streaming operator $S_{-t}(x^N)$, when acting on a function $f(x^N)$ of the phases of the N particles, transforms this function into

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

where $x^N(-t)=x_1(-t)\cdots x_N(-t)$ are the initial phases of the particles $1,\ldots,N$ which lead to the phases x^N after a time t. They can be obtained from x^N by solving the equations of motion of the N-particle system with the Hamilton function

$$H(x^N)=\sum_{i=1}^N\frac{p_i^2}{2m}+\sum_{i<j=1}^N\phi(r_{ij})\,, \tag{2.3}$$

where the interparticle potential $\phi(r_{ij})$ is short ranged and depends only on the distance $r_{ij}=|\vec{r}_i-\vec{r}_j|$ between the two particles i and j. For hard disks and hard spheres of diameter a, one has

$$\phi(r)=\begin{cases}\infty, & r\leq a\\ 0, & r>a\,.\end{cases} \tag{2.4}$$

The operator $S_{-t}(x^N)$ can be formally written

$$S_{-t}(x^N)=\exp[-t\mathcal{H}(x^N)]\,, \tag{2.5}$$

where

$$\mathcal{H}(x^N)=\{\;,H(x^N)\}=\mathcal{H}_0(x^N)-\sum_{i<j}\theta_{ij}\,. \tag{2.6}$$

Here we have

$$\mathcal{H}_0(x^N)=\sum_{i=1}^N\frac{\vec{p}_i}{m}\cdot\nabla_{r_i} \tag{2.7a}$$

and

$$\theta_{ij}=\frac{\partial\phi(r_{ij})}{\partial\vec{r}_i}\cdot\frac{\partial}{\partial\vec{p}_i}+\frac{\partial\phi(r_{ij})}{\partial\vec{r}_j}\cdot\frac{\partial}{\partial\vec{p}_j}\,, \tag{2.7b}$$

where the curly brackets $\{\;,H(x^N)\}$ denote the Poisson brackets with the Hamiltonian function $H(x^N)$. For hard disks and hard spheres, the operator θ_{ij} and consequently $\mathcal{H}(x^N)$ are singular. However, in this case it is still possible to obtain a suitable representation of the streaming operator $S_{-t}(x^N)$. Since we do not need this representation in this paper, we shall not give it here but refer to it in the literature.[12]

$\rho(x^N)$ is the probability density in the canonical ensemble

$$\rho(x^N)=Z^{-1}e^{-\beta H(x^N)}\,,$$

where

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

Finally v_{1x} is the component of the velocity of the chosen particle 1. We note that because of the time translational invariance of the equilibrium average, we have $\rho_D^{(d)}(t)=\rho_D^{(d)}(-t)$ [cf. Eq. (1.1)].

In order to avoid the necessity of solving the N-body problem in the computation of $\rho_D^{(d)}(t)$, one expands $\rho_D^{(d)}(t)$ in a systematic way in terms of the solution of the 2-, 3-, 4-, ... body problem. This can be achieved by generalizing the cluster expansions used in equilibrium statistical mechanics[13] to obtain virial expansions of thermodynamic quantities and reduced distribution functions to the case of nonequilibrium statistical mechanics.[14]

A cluster expansion of $\rho_D^{(d)}(t)$ can be obtained in a variety of ways. Our starting point will be the following cluster expansion of the N-particle streaming operator $S_{-t}(x^N)$ in terms of 1-, 2-, 3-,... particle streaming operators[14]:

$$S_{-t}(x^N)=\mathfrak{U}(x_1,t)S_{-t}(x^{N-1})+\sum_{i=2}^{N}\mathfrak{U}(x_1,x_i,t)S_{-t}(x^{N-2})$$
$$+\sum_{2\leq i<j\leq N}\mathfrak{U}(x_1,x_i,x_j,t)S_{-t}(x^{N-3})+\cdots, \quad (2.8)$$

where the operators $\mathfrak{U}(x_1,t), \mathfrak{U}(x_1,x_i,t)\cdots$ can be obtained successively from Eq. (2.8) by writing out the equation for $N=1, 2, \ldots,$ respectively.

By substituting the cluster expansion Eq. (2.8) into the right-hand side of Eq. (2.2), and by using Liouville's theorem, i.e.,

$$\int dx^{N-l}\,S_{-t}(x^{N-l})\,f(x^N)=\int dx^{N-l}f(x^N),$$

and spatial homogeneity, i.e., $\Phi_D^{(d)}$ does not depend on $\vec{r}_1$, one obtains the following cluster expansion for $\Phi_D^{(d)}(\vec{v}_1,t)$:

$$\Phi_D^{(d)}(\vec{v}_1,t)=\beta m[1+n\int d2\,\mathfrak{U}(x_1,x_2,t)g(\vec{r}_1,\vec{r}_2)\varphi_0(v_2)$$
$$+\tfrac{1}{2}n^2\int d2\int d3\,\mathfrak{U}(x_1,x_2,x_3,t)$$
$$\times g(\vec{r}_1,\vec{r}_2,\vec{r}_3)\varphi_0(v_2)\varphi_0(v_3)+\cdots]\varphi_0(v_1)v_{1x}, \quad (2.9)$$

where we have used that $\langle v_{1x}^2\rangle^{-1}=\beta m$ and written $d\vec{r}_2 d\vec{v}_2=d2$, etc. Here the s-particle equilibrium distribution functions $g(\vec{r},\vec{r}_2,\ldots,\vec{r}_s)$ possess well-defined density expansions[13,15]

$$g(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_s)=\sum_{l=0}^{\infty}n^l g_l(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_s), \quad (2.10)$$

with

$$g_l(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_s)=\int d\vec{r}_{s+1}\cdots\int d\vec{r}_{s+l}\,g_l(\vec{r}_1,\ldots,\vec{r}_s|\vec{r}_{s+1},\ldots,\vec{r}_{s+l}), \quad (2.11)$$

where we refer to the literature for the $g_l(\vec{r}_1,\cdots,\vec{r}_s|\vec{r}_{s+1},\cdots,\vec{r}_{s+l})$. In particular we have

$$g_0(\vec{r}_1,\ldots,\vec{r}_s)=\exp\Big(-\beta\sum_{i<j}^{s}\phi(r_{ij})\Big). \quad (2.12)$$

Finally, we have

$$\varphi_0(v)=(\beta m/2\pi)^{d/2}\exp(-\tfrac{1}{2}\beta m v^2). \quad (2.13)$$

The computation of $\rho_D^{(d)}(t)$ for $t\gg t_0$ is considerably simplified, in particular in connection with the resummations to be carried out later, if we first compute the Laplace transform of $\rho_D^{(d)}(t)$, which we denote by $\rho_D^{(d)}(\epsilon)$, and is defined by

$$\rho_D^{(d)}(\epsilon)\equiv\int_0^\infty dt\,e^{-\epsilon t}\rho_D^{(d)}(t)=\int d\vec{v}_1\,v_{1x}\Phi_D^{(d)}(\vec{v}_1,\epsilon), \quad (2.14)$$

where

$$\Phi_D^{(d)}(\vec{v}_1,\epsilon)=\lim_{\substack{N,V\to\infty\\ N/V=n}}\beta(m)^{d+1}V\times\int dx^{N-1}G(x^N,\epsilon)\rho(x^N)v_{1x} \quad (2.15)$$

and the operator

$$G(x^N,\epsilon)\equiv[\epsilon+\mathcal{H}(x^N)]^{-1}=\int_0^\infty dt\exp(-\epsilon t)\exp[-t\mathcal{H}(x^N)] \quad (2.16)$$

is the Laplace transform of the streaming operator $S_{-t}(x^N)$. The operator $G(x^N,\epsilon)$ should always be interpreted as given by the right-hand side of the Eq. (2.16).

If we take the Laplace transform of Eq. (2.9), we can obtain a cluster expansion of $\Phi_D^{(d)}(\vec{v}_1,\epsilon)$ similar to that for $\Phi_D^{(d)}(\vec{v}_1,t)$. In so doing we will encounter the Laplace transform of the cluster operator $\mathfrak{U}(x_1,\ldots,x_s,t)$, which we denote by $\mathfrak{U}(x_1,\cdots,x_s,\epsilon)$. We show elsewhere[11,16] that from the application of Liouville's theorem, spatial homogeneity and repeated use of identities like

$$[\epsilon+\mathcal{H}(x_1,x_2,x_3)]^{-1}=[\epsilon+\mathcal{H}(x_1,x_2)+\mathcal{H}(x_3)]^{-1}$$
$$+[\epsilon+\mathcal{H}(x_1,x_2)+\mathcal{H}(x_3)]^{-1}(\theta_{13}+\theta_{23})\times[\epsilon+\mathcal{H}(x_1x_2x_3)]^{-1},$$

we obtain the following equality:

$$\frac{1}{(s-1)!}\int d2\cdots\int ds\,\mathfrak{U}(x_1,x_2,\cdots,x_s)\times g(\vec{r}_1,\ldots,\vec{r}_s)\prod_{i=1}^{s}\varphi_0(v_i)$$
$$=\frac{1}{\epsilon}\int d2\cdots\int ds\,\mathfrak{A}(x_1,x_2,\ldots,x_s)\times g(\vec{r}_1,\ldots,\vec{r}_s)\prod_{i=1}^{s}\varphi_0(v_i), \quad (2.17)$$

where the left- and right-hand side of Eq. (2.7) are operators which act only on functions of $\vec{v}_1$ but not $\vec{r}_1$, and where

$$\mathfrak{A}(x_1,x_2,\epsilon)=\theta_{12}G(x_1,x_2,\epsilon),$$
$$\mathfrak{A}(x_1,x_2,x_3,\epsilon)=\theta_{12}G(x_1,x_2,\epsilon)(\theta_{13}+\theta_{23})G(x_1,x_2,x_3,\epsilon),$$
$$\mathfrak{A}(x_1,x_2,\ldots,x_s,\epsilon)=\theta_{12}G(x_1,x_2,\epsilon)\times(\theta_{13}+\theta_{23})G(x_1,x_2,x_3,\epsilon)\cdots$$
$$\times(\theta_{1s}+\theta_{2s}+\cdots+\theta_{s-1,s})G(x_1,x_2,\ldots,x_s,\epsilon). \quad (2.18)$$

We remark that for hard-disk and hard-sphere particles, it is possible to give a representation of these $\mathcal{A}$ operators in terms of binary collision operators which avoids the use of θ_{ij}.[16,17] As a result of Eq. (2.17) we obtain the following cluster expansion for $\Phi_D^{(d)}(\vec{v}_1, \epsilon)$:

$$\Phi_D^{(d)}(\vec{v}_1,\epsilon)=(\beta m/\epsilon)\Big[1+n\int d2\;\mathcal{A}(x_1,x_2,\epsilon)g(\vec{r}_1,\vec{r}_2)\varphi_0(v_2)+n^2\int d2\int d3\,\mathcal{A}(x_1,x_2,x_3,\epsilon)g(\vec{r}_1,\vec{r}_2,\vec{r}_3)\varphi_0(v_2)\varphi_0(v_3)+\cdots+n^l\int d2\cdots\int dl\;\mathcal{A}(x_1,x_2,\ldots,x_l,\epsilon)g(\vec{r}_1,\ldots,\vec{r}_l)\prod_{i=2}^{l}\varphi_0(v_i)+\cdots\Big]\varphi_0(v_1)v_{1x}\;. \quad (2.19)$$

If we further expand the $g(\vec{r}_1,\ldots,\vec{r}_s)$ in powers of n, using (2.10), the following formal density expansion for $\Phi_D^{(d)}(\vec{v}_1,\epsilon)$ results:

$$\Phi_D^{(d)}(\vec{v}_1,\epsilon)=(\beta m/\epsilon)\Big[1+\sum_{l=1}^{\infty}n^l\mathcal{A}_{l+1}^D(\vec{v}_1,\epsilon)\Big]\varphi_0(v_1)v_{1x}\;, \quad (2.20)$$

where

$$\mathcal{A}_2^D(\vec{v}_1,\epsilon)=\int d2\;\mathcal{A}(x_1,x_2,\epsilon)g_0(\vec{r}_1,\vec{r}_2)\varphi_0(v_2)\;,$$

$$\vdots \qquad\qquad \vdots$$

$$\mathcal{A}_l^D(\vec{v}_1,\epsilon)=\int d2\cdots\int dl\,\Big[\mathcal{A}(x_1,\ldots,x_l,\epsilon)g_0(\vec{r}_1,\ldots,\vec{r}_l)+\mathcal{A}(x_1,\ldots,x_{l-1},\epsilon)g_1(\vec{r}_1,\ldots,\vec{r}_{l-1}|\vec{r}_l)+\cdots+\mathcal{A}(x_1,x_2,\epsilon)g_{l-2}(\vec{r}_1,\vec{r}_2|\vec{r}_3\cdots\vec{r}_l)\Big]\prod_{i=2}^{l}\varphi_0(v_i)\;. \quad (2.21)$$

The cluster expansions (2.9) or (2.20) cannot be used to determine the behavior of $\Phi_D^{(d)}(\vec{v}_1,t)$ for times $t\geq t_0$; or equivalently, to determine the small-ϵ behavior of $\Phi_D^{(d)}(\vec{v}_1,\epsilon)$. For in addition to the factor $1/\epsilon$ on the right-hand side of Eq. (2.19), a dynamical analysis of $\mathcal{A}_l^D(\vec{v}_1,\epsilon)$ with $l\geq 2$ reveals that each term diverges as $\epsilon\to 0$, and that the most divergent contribution to each $\mathcal{A}_l^D$ comes from sequences of $(l-1)$ uncorrelated binary collisions[18,19] among l particles, leading to an $\epsilon^{-(l-1)}$ divergence of $\mathcal{A}_l^D$.

An improved expression which eliminates the above-mentioned divergences can be obtained by regarding $\Phi_D^{(d)}(\vec{v}_1,\epsilon)$, to be determined by the equation[20]

$$\epsilon\Big[1+\sum_{l=1}^{\infty}n^l\mathcal{A}_{l+1}^D(\vec{v}_1,\epsilon)\Big]^{-1}\Phi_D^{(d)}(\vec{v}_1,\epsilon)=\beta m\,\varphi_0(v_1)v_{1x}\;, \quad (2.22)$$

rather than by Eq. (2.20). We may define a new set of operators $\mathcal{B}_l^D(\vec{v}_1,\epsilon)$ by means of the density expansion of the inverse operator appearing on the left-hand side of (2.22), i.e., by[21]

$$\Big[1+\sum_{l=1}^{\infty}n^l\mathcal{A}_{l+1}^D(\vec{v}_1,\epsilon)\Big]^{-1}=1-\sum_{l=1}^{\infty}n^l\mathcal{B}_{l+1}^D(\vec{v}_1,\epsilon)\;, \quad (2.23)$$

which yields

$$\mathcal{B}_{l+1}^D(\vec{v}_1,\epsilon)=\sum_{j=1}^{l}(-1)^{j+1}\sum_{\substack{j\{a_i\}\\ \Sigma_{i=1}^{j}a_i=l}}\mathcal{A}_{a_1+1}^D\cdot\mathcal{A}_{a_2+1}^D\cdots\mathcal{A}_{a_j+1}^D\;. \quad (2.24)$$

This leads to the following equation for $\Phi_D^{(d)}(\vec{v}_1,\epsilon)$:

$$\Phi_D^{(d)}(\vec{v}_1,\epsilon)=\beta m\Big(\epsilon-\sum_{l=1}^{\infty}n^l\epsilon\,\mathcal{B}_{l+1}^D(\vec{v}_1,\epsilon)\Big)^{-1}\varphi_0(v_1)v_{1x}\;. \quad (2.25)$$

The operators $\mathcal{B}_l^D(\vec{v}_1,\epsilon)$ may easily be obtained successively from Eq. (2.24) as

$$\mathcal{B}_2^D(\vec{v}_1,\epsilon)=\mathcal{A}_2^D(\vec{v}_1,\epsilon)=\int d2\,\theta_{12}G(x_1,x_2,\epsilon)g_0(\vec{r}_1,\vec{r}_2)\varphi_0(v_2), \quad (2.26a)$$

$$\mathcal{B}_3^D(\vec{v}_1,\epsilon)=\mathcal{A}_3^D(\vec{v}_1,\epsilon)-[\mathcal{A}_2^D(\vec{v}_1,\epsilon)]^2=\int d2\int d3\,\theta_{12}G(x_1,x_2,\epsilon)\big[(\theta_{13}+\theta_{23})G(x_1,x_2,x_3,\epsilon)g_0(\vec{r}_1,\vec{r}_2,\vec{r}_3)-g_0(\vec{r}_1,\vec{r}_2)\theta_{13}G(x_1,x_3,\epsilon)g_0(\vec{r}_1,\vec{r}_3)+g_1(\vec{r}_1,\vec{r}_2|\vec{r}_3)\big]\varphi_0(v_2)\varphi_0(v_3), \quad (2.26b)$$

and so on.

Although in three dimensions there are phase-space arguments, based on the dynamics of 2 and 3 particles, which indicate that $\epsilon\mathcal{B}_2^D$ and $\epsilon\mathcal{B}_3^D$ exist in the $\lim \epsilon \to 0$; these same dynamical phase-space arguments suggest that for $l \geqq 4$ the $\epsilon\mathcal{B}_l^D$ diverges as $\epsilon \to 0$ when acting on a general function of $\vec{v}_1$.[19,22] In fact these phase-space arguments suggest that for $\epsilon \to 0$, $\epsilon\mathcal{B}_4^D \sim \ln\epsilon$, while $\epsilon\mathcal{B}_l^D \sim \epsilon^{-(l-4)}$ for $l > 4$, for particles interacting with a short-range repulsive potential. Similarly for $d=2$, although $\epsilon\mathcal{B}_2^D$ exists, phase-space arguments give that for $\epsilon \to 0$, $\epsilon\mathcal{B}_3^D \sim \ln\epsilon$, while $\epsilon\mathcal{B}_l^D \sim \epsilon^{-(l-3)}$ for $l > 3$. For a gas of hard disks, the phase-space arguments for the divergence $\epsilon\mathcal{B}_3^D$ have been substantiated by Sengers[23] and others,[24] and similar results have been obtained for a variety of Lorentz models.[25,26] Thus, although the introduction of the operators $\mathcal{B}_l^D$ removes the most divergent contributions for $\epsilon \to 0$ in each order of n in the density expansion (2.20) of $\Phi_D^{(d)}(\vec{v}_1, \epsilon)$, there still remain divergent contributions in the $\mathcal{B}_l^D$ operators if $\epsilon \to 0$. A further rearrangement of the expansion (2.25) is therefore necessary.

Since no rigorous proof of these divergences in the $\epsilon\mathcal{B}_l^D$ has been given, other than for $\epsilon\mathcal{B}_3^D$ for hard disks, we will carry out a rearrangement of the expansion (2.25) in the following section based on the assumptions: (a) the qualitative behavior of $\epsilon\mathcal{B}_l^D$ for small ϵ *is* the one quoted above, and (b) this behavior is due to the dynamical events discussed in Sec. III.

III. BINARY COLLISION EXPANSION OF $\mathcal{B}_l^D(\vec{v}_1, \epsilon)$; RESUMMATION

It is generally assumed, although not proven, that for a short-ranged repulsive potential, such as that given by Eq. (2.4), sequences of l binary collisions are responsible for the most divergent contributions to the operators $\mathcal{B}_l^D(\vec{v}_1, \epsilon)$ in the $\lim \epsilon \to 0$. In order to isolate these most divergent contributions in each $\mathcal{B}_l^D$ and then to sum them up into a well-behaved operator, we introduce in this section an expansion of $\mathcal{B}_l^D(\vec{v}_1, \epsilon)$ in terms of sequences of binary collisions: the binary-collisions expansion of the $\mathcal{B}_l^D(\vec{v}_1, \epsilon)$.

The basic binary-collision expansion which we use reads for a general potential[12,16,20]

$$\theta_\alpha G(x_1, \ldots, x_s, \epsilon) = C_s(\alpha, \epsilon)\Big[1 + \sum_{\beta\neq\alpha} C_s(\beta, \epsilon) + \sum_{\beta\neq\alpha,\gamma\neq\beta} C_s(\beta, \epsilon) C_s(\gamma, \epsilon) + \cdots\Big] \quad . \quad (3.1)$$

Here $\alpha, \beta, \gamma, \cdots$ denote pairs of particles chosen from the particles $(1, 2, \ldots, s)$, and the operator $C_s(\alpha, \epsilon)$ is defined by

$$C_s(\alpha, \epsilon) = \theta_\alpha G_s(\alpha, \epsilon) \quad , \quad (3.2\text{a})$$

where

$$G_s(\alpha, \epsilon) = [\epsilon + \mathcal{H}_0(x^s) - \theta_\alpha]^{-1} \quad . \quad (3.2\text{b})$$

In deriving the expansion (3.1), repeated use has been made of identities similar to that preceding Eq. (2.17). We further define a binary collision operator $\overline{T}_s(\alpha, \epsilon)$ in terms of $C_s(\alpha, \epsilon)$ by

$$C_s(\alpha, \epsilon) = \overline{T}_s(\alpha, \epsilon) G_0(x^s) \quad , \quad (3.3)$$

with

$$G_0(x^s) = [\epsilon + \mathcal{H}_0(x_1, x_2, \ldots, x_s)]^{-1} \quad . \quad (3.4)$$

The following developments are all based on the binary-collision expansion (3.1), using the binary-collision operator $\overline{T}_s(\alpha, \epsilon)$ given by (3.3). The operator defined in (3.3) is denoted by $\overline{T}_s(\alpha, \epsilon)$, in order to conform with the literature where a representation of this operator is discussed for hard disks and hard spheres.[12]

An analysis of $\epsilon\mathcal{B}_3^D, \epsilon\mathcal{B}_4^D, \ldots$ on the basis of the binary-collision expansion leads to expressions for these operators as[22,27] [(LDT) stands for less-divergent terms]

$$\epsilon\mathcal{B}_2^D(\vec{v}_1, \epsilon) = \epsilon \int d2\, C_2(x_1, x_2, \epsilon)\, g_0(\vec{r}_1, \vec{r}_2)\, \varphi_0(v_2) \,, \quad (3.5\text{a})$$

$$\epsilon\mathcal{B}_3^D(\vec{v}_1, \epsilon) = \epsilon \int d2 \int d3\, C_2(x_1, x_2, \epsilon)\, \Lambda_3^D(x_1, x_2 | x_3; \epsilon) \times C_2(x_1, x_2, \epsilon)\, \varphi_0(v_2)\, \varphi_0(v_3) + (\text{LDT}) \,, \quad (3.5\text{b})$$

$$\epsilon\mathcal{B}_4^D(\vec{v}_1, \epsilon) = \epsilon \int d2 \int d3 \int d4\; C_2(x_1, x_2, \epsilon) \times \Lambda_3^D(x_1, x_2 | x_3; \epsilon) \Lambda_3^D(x_1, x_2 | x_4; \epsilon) \times C_2(x_1, x_2, \epsilon) \prod_{i=2}^{4} \varphi_0(v_i) + (\text{LDT}) \;, \quad (3.5\text{c})$$

and so on, where

$$\Lambda_3^D(x_1 x_2 | x_j; \epsilon) = C_3(x_1, x_j, \epsilon) + C_3(x_2, x_j \epsilon)(1 + P_{2j}) \quad , \quad (3.6)$$

with P_{ij} the permutation operator which exchanges particle indices i and j. In obtaining Eq. (3.5b), etc., one uses, apart from Liouville's theorem, that when acting on a function of velocities of the particles 1, 2, 3, $\cdots$ the operator $C_s(x_1, x_2, \epsilon)$ can be replaced by the operator $C_2(x_1, x_2, \epsilon)$, and that a sequence such as

$$C_2(x_1, x_2, \epsilon) C_3(x_1, x_3, \epsilon)\, C_2(x_2, x_3, \epsilon)$$

which ends in a C operator that does not contain particle 1 in the interacting pair is not a most divergent contribution to $\epsilon\mathcal{B}_l^D$. The terms which we have explicitly written out in Eq. (3.5b) contain the contributions from those sequences of l binary collisions among l particles that we assume to be the most divergent in each $\mathcal{B}_l^D$ in the limit $\epsilon \to 0$.[19] Due to the graphical representation of these terms given by Kawasaki and Oppenheim,[22] these terms are generally referred to as the "ring events." The remaining parts of $\epsilon\mathcal{B}_l^D$ are indicated by LDT and contain (a) sequences of more than l binary collisions among l particles, which are all less divergent or convergent, (b) terms that contain equilibrium cluster functions $[(g_0(\vec{r}_1, \ldots, \vec{r}_l) - 1, g_1(\vec{r}_1, \ldots, \vec{r}_l)$, etc.], and (c) terms where more than two particles are within a distance of the $O(a)$ at the same time. These latter terms may involve genuine n-tuple collisions for $n > 2$, or a number of binary collisions which take place within a few collision times t_c. For a further discussion of these points we refer to the literature.[16,19]

Although in three dimensions $\epsilon\mathcal{B}_3^D$ is finite as $\epsilon \to 0$, it will be convenient for the determination of the long-time behavior of $\rho_D^{(d)}(t)$ to include this term, as given in Eq. (3.5b), in the resummation to be performed below.

We are now in a position to consider the summation of the most divergent terms or ring events in the $\mathcal{B}^D$ series appearing in Eq. (2.25). We write

$$\epsilon - \sum n^l \epsilon\, \mathcal{B}_{l+1}^D = \epsilon - n\epsilon\mathcal{B}_2^D - n\epsilon\mathcal{R}^D(\vec{v}_1, \epsilon) + (\mathrm{LDT}) \ , \tag{3.7}$$

with

$$\epsilon\mathcal{R}^D(\vec{v}_1, \epsilon) = \epsilon \int d2\, C_2(x_1, x_2, \epsilon)[1 - n\int d3\, \Lambda_3^D(x_1, x_2 | x_3;\, \epsilon)\varphi_0(v_3)]^{-1} C_2(x_1, x_2, \epsilon)\varphi_0(v_2) \ . \tag{3.8}$$

To obtain (3.8) we have added and subtracted a finite term

$$\epsilon n \int d2\, C_2(x_1 x_2, \epsilon) C_2(x_1, x_2, \epsilon)\varphi_0(v_2)$$

to the geometric series used to obtain $\mathcal{R}^D(\vec{v}_1, \epsilon)$. The subtracted term together with all the LDT (and finite terms) of order n^2 and higher, which have not been included in $\mathcal{R}^D(\vec{v}_1, \epsilon)$, are collected in the term which we denote by LDT in Eq. (3.7).

The expression for $\epsilon\mathcal{R}^D(\vec{v}_1, \epsilon)$ may be further simplified by using the relation between C and $\overline{T}$ operator given by Eq. (3.3) and by using the fact that $\epsilon\mathcal{R}^D$ acts only on functions of the velocity of particle 1. Thus we may write[27]

$$\epsilon\mathcal{R}^D(\vec{v}_1, \epsilon) = \int d2\, \overline{T}_2(x_1, x_2, \epsilon)[\epsilon + \mathcal{H}_0(x_1, x_2) - n\int d3\, \lambda_3^D(x_1, x_2 | x_3;\, \epsilon)\varphi_0(v_3)]^{-1} \times \overline{T}_2(x_1, x_2, \epsilon)\varphi_0(v_2) \ , \tag{3.9}$$

where

$$\lambda_3^D(x_1, x_2 | x_3;\, \epsilon) = \overline{T}_3(x_1, x_3, \epsilon) + \overline{T}_3(x_2, x_3, \epsilon)(1 + P_{23}) \ . \tag{3.10}$$

The determination of the long-time behavior of $\rho_D^{(d)}(t)$ to be carried out later will be greatly facilitated, if we go over to a Fourier representation of $\epsilon\mathcal{R}^D(\vec{v}_1, \epsilon)$. To do this we use the fact that $\epsilon\mathcal{R}^D(\vec{v}_1, \epsilon)$ does not depend on $\vec{r}_1$ and write

$$\epsilon\mathcal{R}^D(\vec{v}_1, \epsilon) = \int d\vec{v}_2 \int d\vec{r}_1 \int d\vec{r}_2\, \delta(\vec{r}_1)\, \overline{T}_2(x_1, x_2, \epsilon)[\epsilon + \mathcal{H}_0(x_1, x_2) - n\int d\vec{r}_3 \int d\vec{v}_3\, \lambda_3^D(x_1, x_2 | x_3;\, \epsilon)\varphi_0(v_3)]^{-1}\, \overline{T}_2(x_1, x_2, \epsilon)\varphi_0(v_2) \ . \tag{3.11}$$

Then by inserting δ functions, using their Fourier representation, and that[20]

$$\int d\vec{r}_1 \cdots \int d\vec{r}_l \exp\Big(-i\sum_{j=1}^{l} \vec{k}_j \cdot \vec{r}_j\Big)\, \overline{T}_l(x_1, x_2, \epsilon) \exp\Big(+i\sum_{j=1}^{l} \vec{k}_j' \cdot \vec{r}_j\Big) = (2\pi)^{d(l-1)}\, \delta(\vec{k}_1 + \vec{k}_2 - \vec{k}_1' - \vec{k}_2') \prod_{j=3}^{l} \delta(\vec{k}_j - \vec{k}_j') \langle \vec{k}_1, \vec{k}_2, \ldots, \vec{k}_l | \overline{T}_l(x_1, x_2, \epsilon) | \vec{k}_1', \vec{k}_2' \cdots \vec{k}_l' \rangle \ , \tag{3.12}$$

one finds[28]

$$\epsilon\mathcal{R}^D(\vec{v}_1, \epsilon) = \int \frac{d\vec{k}}{(2\pi)^d} \int d\vec{v}_2 \langle 0, 0 | \overline{T}_2(x_1, x_2, \epsilon) | \vec{k}, -\vec{k}\rangle \times [\epsilon + i\vec{k}\cdot\vec{v}_{12} - n\lambda_{\vec{k}}^D(\vec{v}_1, \epsilon) - n\lambda_{-\vec{k}}(\vec{v}_2, \epsilon)]^{-1} \langle \vec{k}, -\vec{k} | \overline{T}_2(x_1, x_2, \epsilon) | 0, 0\rangle\, \varphi_0(v_2) \ , \tag{3.13}$$

where

$$\lambda_{\vec{k}}^D(\vec{v}_1, \epsilon) = \int d\vec{v}_3 \langle \vec{k}, -\vec{k}, 0 | \overline{T}_3(x_1, x_3, \epsilon) | \vec{k}, -\vec{k}, 0\rangle\, \varphi_0(v_3) \ , \tag{3.14a}$$

$$\lambda_{\vec{k}}(\vec{v}_2, \epsilon) = \int d\vec{v}_3 \langle \vec{k}, -\vec{k}, 0 | \overline{T}_3(x_2, x_3, \epsilon)(1 + P_{23}) | \vec{k}, -\vec{k}, 0\rangle\, \varphi_0(v_3) \ , \tag{3.14b}$$

and

$$\vec{v}_{12} = \vec{v}_1 - \vec{v}_2 \ .$$

Although the procedure leading to expression (3.13) for the sum of the most divergent terms in the $\mathcal{B}_l^D$ expansion has been carried out for a general potential we will in the remainder of the paper restrict our attention to the special case of hard-disk and hard-sphere molecules. For this case one can show that the binary-collision operators $\overline{T}_s(\alpha, \epsilon)$ are independent of ϵ as well as of the phases of all the particles except those of the interacting pair α.[12,16] Moreover, for this case one can show that $\lambda_{\vec{k}}^D(\vec{v}_1, \epsilon)$ is independent of $\vec{k}$ and ϵ and can therefore be denoted by $\lambda_0^D(\vec{v}_1)$, while $\epsilon\mathcal{B}_2^D$ is independent of ϵ and equals $\lambda_0^D(\vec{v}_1)$ the Lorentz-Boltzmann collision operator given by[29]

$$\lambda_0^D(\vec{v}_1)\varphi_0(v_1)f(\vec{v}_1) = \int d\vec{v}_3 \int d\vec{b}\,|\vec{v}_{13}| \times [f(\vec{v}_1') - f(\vec{v}_1)]\varphi_0(v_1)\varphi_0(v_3) \ , \quad (3.15)$$

with

$$|\vec{v}_{13}| = |\vec{v}_1 - \vec{v}_3|$$

and

$$d\vec{b} = \begin{cases} b\,db\,d\psi & (0 \leq b \leq a,\ 0 \leq \psi \leq 2\pi), \quad d = 3 \\ db & (-a \leq b \leq a), \quad d = 2 \end{cases} \quad (3.16)$$

where $f(\vec{v}_1)$ is an arbitrary function of $\vec{v}_1$, and the primed velocities are the restituting velocities.

In the following we will also replace $\lambda_{-\vec{k}}(\vec{v}_2)$ by

$$\lambda_0(\vec{v}_2) = \lim_{\vec{k}\to 0} \lambda_{-\vec{k}}(\vec{v}_2) \ ,$$

where $\lambda_0(\vec{v})$ is the linearized Boltzmann collision operator which is for hard spheres or hard disks given by[29]

$$\lambda_0(\vec{v}_1)\varphi_0(\vec{v}_1)f(\vec{v}_1) = \int d\vec{v}_3 \int d\vec{b}\,|\vec{v}_{13}| \times [f(\vec{v}_1') + f(\vec{v}_3') - f(\vec{v}_1) - f(\vec{v}_3)]\varphi_0(v_1)\varphi_0(v_3) \ . \quad (3.17)$$

It will be shown in a subsequent paper that this replacement leads to an error of higher order in the density, than considered here.

On the basis of these considerations, it follows that for hard-disk and hard-sphere particles at low density, we may write Eq. (2.25) for $\Phi_D^{(d)}(\vec{v}_1, \epsilon)$ in the form

$$\Phi_D^{(d)}(\vec{v}_1, \epsilon) = \beta m[\epsilon - n\lambda_0^D(\vec{v}_1) - n\epsilon\mathcal{R}_0^D(\vec{v}_1, \epsilon) - (\text{LDT})]^{-1}\varphi_0(v_1)v_{1x} \ , \quad (3.18)$$

where $\epsilon\mathcal{R}_0^D(\vec{v}_1, \epsilon)$ is given by Eq. (3.13) with $\lambda_{\vec{k}}^D$ and $\lambda_{\vec{k}}$ replaced by λ_0^D and λ_0, respectively, and $\epsilon\mathcal{B}_2^D$ has been set equal to λ_0^D.

IV. HYDRODYNAMIC MODES

In Sec. V we shall argue that the dominant contributions to $\epsilon\mathcal{R}_0^D(\vec{v}, \epsilon)$ for small ϵ come from the small-k region of the $\vec{k}$ integration, i.e., from $k = |\vec{k}| < l^{-1}$, where l is of the order of a mean free path. It will be convenient to have a representation of the operator $[\epsilon + i\vec{k}\cdot\vec{v}_{12} - n\lambda_0^D(\vec{v}_1) - n\lambda_0(\vec{v}_2)]^{-1}$ expressed in terms of the eigenfunctions and eigenvalues of the operators $i\vec{k}\cdot\vec{v} - n\lambda_0^D(\vec{v})$ and $i\vec{k}\cdot\vec{v} - n\lambda_0(\vec{v})$. In the region where $k < l^{-1}$, these may be found from the eigenvalues and eigenfunctions of $n\lambda_0^D(\vec{v})$ and $n\lambda_0(\vec{v})$, respectively, by means of perturbation theory regarding the operator $i\vec{k}\cdot\vec{v}$ as a perturbation.[30,31]

Following Pomeau,[8] we notice that among the eigenvalues of the operators $i\vec{k}\cdot\vec{v}_1 - n\lambda_0^D(\vec{v}_1)$ and $i\vec{k}\cdot\vec{v}_2 - n\lambda_0(\vec{v}_2)$, there are those which go to zero as $k\to 0$. These eigenvalues and the corresponding eigenfunctions will be shown in Sec. V to give the leading contribution to $\rho_D^{(d)}(\epsilon)$ as $\epsilon\to 0$ or to $\rho_D^{(d)}(t)$ for long times. The eigenfunctions of $i\vec{k}\cdot\vec{v} - n\lambda_0^D(\vec{v})$ and $i\vec{k}\cdot\vec{v} - n\lambda_0(\vec{v})$ with eigenvalues going to zero as $k\to 0$ are called hydrodynamic modes, and they arise from the eigenfunctions of λ_0^D and λ_0 belonging to the eigenvalues zero, respectively, under the perturbation $i\vec{k}\cdot\vec{v}$ for small k. We now determine these hydrodynamic modes.

The eigenfunctions and eigenvalues of the operators $i\vec{k}\cdot\vec{v} - n\lambda_0^D(\vec{v})$ and $i\vec{k}\cdot\vec{v} - n\lambda_0(\vec{v})$ will be given by the solution of the equations

$$[i\vec{k}\cdot\vec{v} - n\lambda_0^D(\vec{v})]\,\chi^{(\omega)}(\vec{k},\vec{v})\,\varphi_0(v) = \omega(k)\,\chi^{(\omega)}(\vec{k},\vec{v})\,\varphi_0(v) \quad (4.1a)$$

and

$$[i\vec{k}\cdot\vec{v} - n\lambda_0(\vec{v})]\,\Theta^{(\omega)}(\vec{k},\vec{v})\,\varphi_0(v) = \Omega(k)\,\Theta^{(\omega)}(\vec{k},\vec{v})\,\varphi_0(v) \ , \quad (4.1b)$$

respectively. We impose the condition that $\chi^{(\omega)}(\vec{k},\vec{v})$ and $\Theta^{(\omega)}(\vec{k},\vec{v})$ are normalized according to

$$\int d\vec{v}\,[\chi^{(\omega)}(\vec{k},\vec{v})]^2\,\varphi_0(v) = 1 \quad (4.2a)$$

and

$$\int d\vec{v}\,[\Theta^{(\Omega)}(\vec{k},\vec{v})]^2\,\varphi_0(v) = 1 \ , \quad (4.2b)$$

respectively, and we require that different eigenfunctions are orthogonal, according to the relations

$$\int d\vec{v}\ \chi^{(\omega')}(\vec{k},\vec{v})\chi^{(\omega)}(\vec{k},\vec{v})\,\varphi_0(v) = 0 \quad (4.2c)$$

and

$$\int d\vec{v}\ \Theta^{(\Omega')}(\vec{k},\vec{v})\,\Theta^{(\Omega)}(\vec{k},\vec{v})\,\varphi_0(v) = 0 \ . \quad (4.2d)$$

These points will be further discussed elsewhere.[16]

The hydrodynamic eigenfunctions and eigenvalues which are of interest here may be obtained by assuming that $\chi^{(\omega)}(\vec{k},\vec{v})$ and $\Theta^{(\Omega)}(\vec{k},\vec{v})$, and $\omega(k)$ and $\Omega(k)$ have expansions in powers of k for small k, and by requiring that for $k\to 0$, $\omega(k=0) = 0$ and $\Omega(k=0) = 0$.

Using the fact that $\lambda_0^D(\vec{v}_1)$ has only one zero eigenvalue, one can write

$$\omega(k)=\omega_0+\omega_1 k+\omega_2 k^2+\cdots , \tag{4.3a}$$

$$\chi^{(\omega)}(\vec{k},\vec{v})=\chi_0^{(\omega)}(\vec{v})+k\chi_1^{(\omega)}(\vec{v})+\cdots , \tag{4.3b}$$

and that the one hydrodynamic mode of the operator $i\vec{k}\cdot\vec{v}-n\lambda_0^D(\vec{v})$ is a diffusive mode which is to $O(k^2)$ given by

$$\omega_0=\omega_1=0 , \tag{4.4a}$$

$$\omega_2=D_0 , \tag{4.4b}$$

and

$$\chi_0^{(\omega)}=1 , \tag{4.5}$$

where D_0 is the value for the self-diffusion coefficient obtained on the basis of the Boltzmann equation. Similarly, using the fact that $\lambda_0(\vec{v})$ has $(d+2)$ zero eigenvalues and writing

$$\Omega(k)=\Omega_0+k\Omega_1+k^2\Omega_2+\cdots \tag{4.6}$$

and

$$\Theta^{(\Omega)}(\vec{k},\vec{v})=\Theta_0^{(\Omega)}(\vec{v})+k\,\Theta_1^{(\Omega)}(\vec{v})+\cdots , \tag{4.7}$$

we find that to $O(k^2)$ the eigenvalues are given by

$$\Omega_0=\Omega_1^{(V_i)}=\Omega_1^{(H)}=0 , \quad i=(1,\ldots,d-1) \tag{4.8a}$$

$$\Omega_1^{(\pm)}=\pm ic_0 , \tag{4.8b}$$

$$\Omega_2^{(V_i)}\equiv\nu_0=\eta_0/nm , \tag{4.8c}$$

$$\Omega_2^{(H)}\equiv D_{T_0}=\lambda_0/nC_{p0} , \tag{4.8d}$$

and

$$\Omega_2^{(\pm)}\equiv\tfrac{1}{2}\Gamma_{S0}=\tfrac{1}{2}\left(\frac{2(d-1)}{d}\,\nu_0+(\gamma_0-1)D_{T_0}\right) . \tag{4.8e}$$

Here H denotes a heat mode V_i, $i=1,\ldots,d-1$, the $(d-1)$ the shear (or viscous) modes, and $(\pm)$ denotes the two sound modes. Furthermore, $c_0=[(d+2)/(\beta md)]^{1/2}$ is the ideal-gas sound velocity in d dimensions $\gamma_0=C_{p0}/C_{v0}=(d+2)/d$, where C_{p0} and C_{v0} are the ideal-gas specific heats per particle at constant pressure and volume, respectively, and η_0 and λ_0 are the values for the coefficients of viscosity and thermal conductivity, respectively, obtained from the Boltzmann equation. We note that the bulk viscosity vanishes in the low-density limit. The subscript 0 denotes that the low-density limit has been taken. The corresponding eigenfunctions to $O(k)$ are

$$\Theta_0^{(V_i)}(\vec{k},\vec{v})=(\beta m)^{1/2}(\hat{k}_\perp^{(i)}\cdot\vec{v}), \tag{4.9a}$$

$$\Theta_0^{(H)}(\vec{k},\vec{v})=(\tfrac{1}{2})^{1/2}(\tfrac{1}{2}\beta m v^2-2), \qquad d=2 \tag{4.9b}$$

$$\Theta_0^{(H)}(\vec{k},\vec{v})=(\tfrac{2}{5})^{1/2}(\tfrac{1}{2}\beta m v^2-\tfrac{5}{2}), \qquad d=3 \tag{4.9c}$$

$$\Theta_0^{(\pm)}(\vec{k},\vec{v})=\tfrac{1}{2}[\tfrac{1}{2}\beta m v^2\pm\beta m c_0(\hat{k}\cdot\vec{v})], \quad d=2 \tag{4.9d}$$

and

$$\Theta_0^{(\pm)}(\vec{k},\vec{v})=(\tfrac{3}{10})^{1/2}[\tfrac{1}{3}\beta m v^2\pm\beta m c_0(\hat{k}\cdot\vec{v})], \quad d=3 . \tag{4.9e}$$

Here $\hat{k},\hat{k}_\perp^{(1)},\ldots,\hat{k}_\perp^{(d-1)}$ form a Cartesian set of mutually orthogonal unit vectors.

We use the hydrodynamic modes to express the operator $[\epsilon+i\vec{k}\cdot\vec{v}_{12}-n\lambda_0{}^D(\vec{v}_1)-n\lambda_0(\vec{v}_2)]^{-1}$ for small k when acting on a function of the form $f(\vec{v}_1,\vec{v}_2)\times\varphi_0(v_1)\varphi_0(v_2)$ as

$$[\epsilon+i\vec{k}\cdot\vec{v}_{12}-n\lambda_0{}^D(\vec{v}_1)-n\lambda_0(\vec{v}_2)]^{-1}f(\vec{v}_1,\vec{v}_2)\varphi_0(v_1)\varphi_0(v_2)$$
$$=S^D{}_H\; f(\vec{v}_1,\vec{v}_2)\varphi_0(v_1)\varphi_0(v_2)+S^D{}_\perp\times f(\vec{v}_1,\vec{v}_2)\varphi_0(v_1)\varphi_0(v_2) , \tag{4.10a}$$

where

$$S^D{}_H f(\vec{v}_1,\vec{v}_2)\varphi_0(v_1)\varphi_0(v_2)=\sum_{\omega,\Omega}{}'\,[\epsilon+\omega(k)+\Omega(k)]^{-1}\chi^{(\omega)}(\vec{k},\vec{v}_1)\;\Theta^{(\Omega)}(-\vec{k},\vec{v}_2)\times\varphi_0(v_1)\varphi_0(v_2)\int d\vec{v}_1\int d\vec{v}_2\,\chi^{(\omega)}(\vec{k},\vec{v}_1)\times\Theta^{(\Omega)}(-\vec{k},\vec{v}_2)\;f(\vec{v}_1,\vec{v}_2)\varphi_0(v_1)\varphi_0(v_2) . \tag{4.10b}$$

Here the prime on the summation symbol indicates that only the hydrodynamic modes $\chi^{(\omega)}$ and $\Theta^{(\Omega)}$ are to be included in the sum. The other operator $S_\perp^D$ contains the contribution from nonhydrodynamic eigenfunctions, i.e., from perturbed eigenfunctions obtained from nonzero eigenvalues of χ_0^D and λ_0.

V. BEHAVIOR OF $\rho_D^{(d)}(t)$ IN TIME: $t^{d/2}$ DEPENDENCE

In this section we shall compute the behavior of $\rho_D^{(d)}(t)$ in time for hard disks and hard spheres by iterating the operator on the right-hand side of Eq. (3.18) about $[\epsilon-n\lambda^D{}_0(\vec{v}_1)]^{-1}$. In this way we shall obtain an initial exponential decay, which in the low-density limit can be derived from the Boltzmann equation, as well as a long-time behavior $\sim t^{-d/2}$.

Using the Eqs. (3.18) and (3.13) we have then

$$\rho_D^{(d)}(\epsilon)=\rho_{D,0}^{(d)}(\epsilon)+\rho_{D,1}^{(d)}(\epsilon)+\cdots , \tag{5.1}$$

with

$$\rho_{D,0}^{(d)}(\epsilon)=\beta m\int d\vec{v}_1\,v_{1x}[\epsilon-n\lambda^D{}_0(\vec{v}_1)]^{-1}v_{1x}\varphi_0(v_1) \tag{5.2}$$

and

$$\rho^{(d)}{}_{D,1}(\epsilon)=\beta mn\int d\vec{v}_1\,v_{1x}[\epsilon-n\lambda^D{}_0(\vec{v}_1)]^{-1}\times\epsilon\,\mathcal{R}_0^D(\vec{v}_1,\epsilon)\cdot[\epsilon-n\lambda^D{}_0(\vec{v}_1)]^{-1}v_{1x}\varphi_0(v_1). \tag{5.3}$$

Here we have assumed that one can drop the LDT's in Eq. (3.18) for the computation of the long-time behavior of $\rho_D^{(d)}(t)$ for hard disks and hard spheres at low density. An indication for the correctness of this assumption can be found in a subsequent paper.[10] Since we shall only calculate the first two iterates, the time interval over which our results are valid may be restricted. This point will be further discussed in Sec. VII.

The Laplace inversion of $\rho_{D,0}^{(d)}(\epsilon)$ leads to an expression for $\rho_{D,0}^{(d)}(t)$ for all t of the form

$$\rho_{D,0}^{(d)}(t)=\beta m\int d\vec{v}_1\, v_{1x}\, e^{n\lambda_0^D(\vec{v}_1)t}\, v_{1x}\,\varphi_0(v_1)\,. \quad (5.4)$$

Although the expression may be evaluated in terms of the eigenvalues and eigenfunctions of the operator $n\lambda^D{}_0(\vec{v})$ as a sum of exponentials, it is a sufficiently good approximation to replace (5.4) by

$$\rho_{D,0}^{(d)}(t)\cong e^{-t(\beta m D_{00})^{-1}}\,, \quad (5.5)$$

where D_{00} is the self-diffusion coefficient obtained from the Lorentz-Boltzmann equation in first Enskog approximation.[32] Since $\beta m D_{00}$ is proportional to the mean free time t_0, $\rho_{D,0}^{(d)}(t)$ decays over a few mean free times.[33]

We now evaluate $\rho_{D,1}^{(d)}(t)$ [Eq. (5.3)] and divide the $\vec{k}$ integral appearing in this expression into two pieces for which $0\leqq k\leqq k_0$ and $k_0\leqq k\leqq\infty$, respectively, where k_0^{-1} is on the order of a mean free path. The contribution to $\rho_{D,1}^{(d)}(\epsilon)$ coming from $k>k_0$ will be neglected, for we assume that this part of the $\vec{k}$ integration incorporates the effects of collisions which take place on a small space scale compared to a mean free path, in which we are not interested here. The region for which $k<k_0$, is the region where the perturbation theory outlined in the previous section is valid. Using Eqs. (4.10a) and (4.10b), we may express this part of $\rho_{D,1}^{(d)}(\epsilon)$ as

$$\rho_{D,1}^{(d)}(\epsilon)\sim n\beta m\int_{k<k_0}\frac{d\vec{k}}{(2\pi)^d}\sum_{\omega,\Omega}{}'[\epsilon+\omega(k)+\Omega(k)]^{-1}\int d\vec{v}_1\int d\vec{v}_2\, v_{1x}[\epsilon-n\lambda^D{}_0(\vec{v}_1)]^{-1}$$
$$\times\langle 0,0\,|\,\overline{T}_2(x_1,x_2)\,|\,\vec{k},-\vec{k}\rangle\chi^{(\omega)}(\vec{k},\vec{v}_1)\,\Theta^{(\Omega)}(-\vec{k},\vec{v}_2)\,\varphi_0(v_1)\varphi_0(v_2)$$
$$\times\int d\vec{v}_1\int d\vec{v}_2\,\chi^{(\omega)}(\vec{k},\vec{v}_1)\Theta^{(\Omega)}(-\vec{k},\vec{v}_2)\langle\vec{k},-\vec{k}\,|\,\overline{T}_2(x_1,x_2)\,|\,0,0\rangle[\epsilon-n\lambda^D{}_0(\vec{v}_1)]^{-1}v_{1x}\,\varphi_0(v_1)\varphi_0(v_2)\,. \quad (5.6)$$

Here we have assumed that the contributions from nonhydrodynamic modes can be neglected for the discussion of the long-time behavior of $\rho_{D,1}^{(d)}$, since we expect that they will lead to contributions decaying exponentially over a few mean free times.

In evaluating (5.6), we can make a k expansion of the numerator on the right-hand side of the equation and keep only the lowest-order terms in k. That is, we can replace $\langle 0,0\,|\,\overline{T}_2(x_1,x_2)\,|\,\vec{k},-\vec{k}\rangle$ and $\langle\vec{k},-\vec{k}\,|\,\overline{T}_2(x_1,x_2)\,|\,0,0\rangle$ by $\overline{T}_{00}(x_1,x_2)$, where

$$\overline{T}_{00}(x_1,x_2)=\lim_{k\to0}\langle 0,0\,|\,\overline{T}_2(x_1,x_2)\,|\,\vec{k},-\vec{k}\rangle$$
$$=\lim_{k\to0}\langle\vec{k},-\vec{k}\,|\,\overline{T}_2(x_1,x_2)\,|\,0,0\rangle\,. \quad (5.7)$$

Furthermore, we can replace $\chi^{(\omega)}(\vec{k},\vec{v}_1)$ and $\Theta^{(\Omega)}(-\vec{k},\vec{v}_2)$ by $\chi_0^{(\omega)}(\vec{k},\vec{v}_1)=1$ [cf., Eq. (4.5)] and by $\Theta_0^{(\Omega)}(-\vec{k},\vec{v}_2)$ [Eqs. (4.9a)–(4.9e)], respectively. The terms involving higher powers of k can easily be seen to lead to a more rapid decay of $\rho_{D,1}^{(d)}$, than the terms retained. Thus we write

$$\rho_{D,1}^{(d)}(\epsilon)\sim n\beta m\sum_{\Omega}{}'\int_{k<k_0}\frac{d\vec{k}}{(2\pi)^d}[\epsilon+\omega(k)+\Omega(k)]^{-1}\int d\vec{v}_1\int d\vec{v}_2\, v_{1x}$$
$$\times[\epsilon-n\lambda^D{}_0(\vec{v}_1)]^{-1}\;\overline{T}_{00}(x_1x_2)\Theta_0^{(\Omega)}(-\vec{k},\vec{v}_2)\;\varphi_0(v_1)\varphi_0(v_2)\int d\vec{v}_1\int d\vec{v}_2\Theta_0{}^{(\Omega)}(-k,\vec{v}_2)$$
$$\times\overline{T}_{00}(x_1,x_2)\;[\epsilon-n\lambda^D{}_0(\vec{v}_1)]^{-1}v_{1x}\,\varphi_0(v_1)\varphi_0(v_2)\,. \quad (5.8)$$

The expression for $\rho_{D,1}^{(d)}(\epsilon)$ given by Eq. (5.8) can be simplified by using the symmetry of the operators λ_0^D and λ_0, that

$$\lambda_0^D(\vec{v}_1)=\int d\vec{v}_2\,\overline{T}_{00}(x_1,x_2)\,\varphi_0(v_2)\,,$$

and that the $\Theta_0{}^{(\Omega)}$ are linear combinations of summational invariants in a binary collision,[29] so that

$$\int d\vec{v}_1\int d\vec{v}_2\, v_{1x}[\epsilon-n\lambda_0^D(\vec{v}_1)]^{-1}$$
$$\times\overline{T}_{00}(x_1,x_2)\Theta_0^{(\Omega)}(-\vec{k},\vec{v}_2)\,\varphi_0(v_1)\varphi_0(v_2)$$
$$=-\int d\vec{v}_1\, v_{1x}[\epsilon-n\lambda_0^D(\vec{v}_1)]^{-1}$$
$$\times\lambda^D{}_0(\vec{v}_1)\;\Theta_0^{(\Omega)}(-\vec{k},\vec{v}_1)\,\varphi_2(v_1)$$

and

$$\int d\vec{v}_1 \int d\vec{v}_2 \Theta_0^{(\Omega)}(-\vec{k},\vec{v}_2) \times \overline{T}_{00}(x_1,x_2)\,[\epsilon - n\lambda_0^D(\vec{v}_1)]^{-1} v_{1x}\varphi_0(v_1)\varphi_0(v_2)$$
$$= -\int d\vec{v}_1 \Theta_0^{(\Omega)}(-\vec{k},\vec{v}_1)\ \lambda_0^D(\vec{v}_1) \times [\epsilon - n\lambda_0^D(\vec{v}_1)]^{-1} v_{1x}\varphi_0(v_1)\ ,$$

which leads to the following expression for $\rho_{D,1}^{(d)}(\epsilon)$:

$$\rho_{D,1}^{(d)}(\epsilon) \sim n\beta m \sum_{\Omega}{}' \int_{k<k_0} \frac{d\vec{k}}{(2\pi)^d}\,[\epsilon + \omega(k) + \Omega(k)]^{-1} \times \left\{ \int d\vec{v}_1 v_{1x}\ \lambda_0^D(\vec{v}_1)\ [\epsilon - n\lambda_0^D(\vec{v}_1)]^{-1} \times \Theta_0^{(\Omega)}(-\vec{k},\vec{v}_1)\varphi_0(v_1) \right\}^2 . \quad (5.9)$$

Inverting the Laplace transform, we find that for $t > t_0$, $\rho_{D,1}^{(d)}(t)$ can be expressed as

$$\rho_{D,1}^{(d)}(t) \sim \frac{\beta m}{n} \sum_{\Omega}{}' \int \frac{d\vec{k}}{(2\pi)^d} \exp[-(\Omega(k)+\omega(k))t] \times \left[\int d\vec{v}_1 v_{1x}\Theta_0^{(\Omega)}(-\vec{k},\vec{v}_1)\varphi_0(v_1)\right]^2 . \quad (5.10)$$

Considering the tensorial character of the hydrodynamical modes $\Theta_0^{(\Omega)}(\vec{k},\vec{v}_1)$, we see that only the sound and shear modes give a contribution to Eq. (5.10). Of these modes, the shear modes give the dominant contribution to $\rho_{D,1}^{(d)}(t)$, since the presence of the $\pm ikc_0$ in the sound-mode eigenvalues can be shown to result in a faster time decay than that given by the shear modes.[16] We therefore obtain

$$\rho_{D,1}^{(d)}(t) \sim \frac{\beta m}{n} \sum_{i=1}^{d-1} \int_{k<k_0} \frac{d\vec{k}}{(2\pi)^d} \exp[-tk^2(D_0+\nu_0)] \times \left[\int d\vec{v}_1 v_{1x}\Theta_0^{(V_i)}(-\vec{k},\vec{v}_1)\varphi_0(v_1)\right]^2 . \quad (5.11)$$

Using the fact that for $d=2$, $\hat{k}_\perp = (1/k)(k_y, -k_x)$, we obtain, with (4.9), for $d=2$,

$$\rho_{D,1}^{(2)}(t) \sim [8\pi n(D_0+\nu_0)t]^{-1}\{1-\exp[-(D_0+\nu_0)k_0^2 t]\}\ , \quad (5.12)$$

or for $t \gg t_0$,

$$\rho_{D,1}^{(2)}(t) \sim [8\pi n(D_0+\nu_0)t_0]^{-1}(t_0/t)\ . \quad (5.13)$$

For hard disks of diameter a, t_0 is in the low-density limit given by

$$t_0 = \frac{(\beta m/\pi)^{1/2}}{2na}\ , \quad (5.14)$$

while D_0 and ν_0 are in first Enskog approximation[34]

$$D_0 = [2na(\beta m\pi)^{1/2}]^{-1}\ , \quad (5.15a)$$
$$\nu_0 = [2na(\beta m\pi)^{1/2}]^{-1}\ , \quad (5.15b)$$

so that for such particles

$$\rho_{D,1}^{(2)}(t) \sim \tfrac{1}{4}na^2(t_0/t)\ . \quad (5.16)$$

Similarly, for $d=3$, $\rho_{D,1}^{(3)}(t)$ becomes

$$\rho_{D,1}^{(3)}(t) \sim \frac{\beta m}{n}\sum_{i=1}^{2}\int_{k<k_0}\frac{d\vec{k}}{(2\pi)^3}\exp[-k^2 t(D_0+\nu_0)] \times \left[\int d\vec{v}_1 v_{1x}\Theta_0^{(V_i)}(-\vec{k},\vec{v})\varphi_0(v_1)\right]^2$$
$$= \frac{1}{8\pi^3 n}\int d\hat{k}(\hat{k}_{1x}^{(1)2}+\hat{k}_{1x}^{(2)2}) \times \int_0^{k_0} dk\,k^2\exp[-k^2 t(D_0+\nu_0)]\ , \quad (5.17)$$

where $\hat{k}_{1x}^{(1)}$ and $\hat{k}_{1x}^{(2)}$ are the x components of the two mutually orthogonal unit vectors which together with $\hat{k}$ form a Cartesian set. The $\hat{k}$ integral may be shown to be equal to $\frac{8}{3}\pi$ so that

$$\rho_{D,1}^{(3)}(t) \sim \frac{1}{3\pi^2 n}\int_0^{k_0} dk\,k^2\exp[-k^2 t(D_0+\nu_0)]$$
$$\sim \frac{1}{12n}\,[\pi(D_0+\nu_0)t_0]^{-3/2}\left(\frac{t_0}{t}\right)^{3/2} \quad (5.18)$$

for $t \gg t_0$. For hard spheres of diameter a, t_0 is for low densities given by[29]

$$t_0 = \frac{(\beta m/\pi)^{1/2}}{4na^2}\ , \quad (5.19)$$

and using the values of D_0 and ν_0 in the first Enskog approximation[29]

$$D_0 = (3/8na^2)(\beta m\pi)^{-1/2}\ ,$$
$$\nu_0 = (5/16na^2)(\beta m\pi)^{-1/2}\ ,$$

we obtain[35]

$$\rho_{D,1}^{(3)}(t) \cong \tfrac{1}{12}(\tfrac{64}{11})^{3/2}(na^3)^2(t_0/t)^{3/2}$$
$$\cong 1.17\,(na^3)^2(t_0/t)^{3/2}\ . \quad (5.20)$$

Equations (5.16) and (5.20) exhibit the $t^{-d/2}$ behavior found by Alder and Wainwright and are consistent with the computer results extrapolated to low density.

VI. BEHAVIOR OF $\rho_\eta^{(d)}(t)$ AND $\rho_\lambda^{(d)}(t)$ IN TIME

Using similar procedures as those for $\rho_D^{(d)}(t)$, the behavior of other velocity-correlation functions with time can be determined. In this section we discuss those velocity-correlation functions that give the kinetic contributions to the coefficients of shear viscosity and thermal conductivity. In particular we shall consider functions of the form[36]

$$\rho_J^{(d)}(t) = \left\langle \sum_{i=1}^{N} J(\vec{v}_i(0)) \sum_{i=1}^{N} J(\vec{v}_i(-t)) \right\rangle \Big/ \left\langle \left[\sum_{i=1}^{N} J(\vec{v}_i)\right]^2 \right\rangle\ , \quad (6.1)$$

where for the viscosity η

$$J_\eta(\vec{v}_i) = v_{ix} v_{iy} , \qquad (6.2a)$$

and for the thermal conductivity λ

$$J_\lambda(\vec{v}_i) = v_{ix}\left[\tfrac{1}{2}\beta m v_i^2 - \tfrac{1}{2}(d+2)\right] . \qquad (6.2b)$$

Here again the angular brackets denote an average over a canonical ensemble in the thermodynamic limit.

Expression (6.1) can be written in the form

$$\rho_J^{(d)}(t) = \int d\vec{v}_1 J(\vec{v}_1) \; \Phi_J^{(d)}(\vec{v}_1, t) , \qquad (6.3a)$$

where using the identity of all N particles, one has

$$\Phi_J^{(d)}(\vec{v}_1, t) = \lim_{\substack{N, V\to\infty \\ N/V=n}} \langle J^2(\vec{v}_1)\rangle^{-1} m^d V \times \int dx^{N-1} S_{-t}(x^N)\rho(x^N) \sum_{i=1}^{N} J(\vec{v}_1). \quad (6.3b)$$

In view of the great similarity of the Eqs. (6.1) and (6.3) to (2.1) and (2.2), it will be clear that the time behavior of $\rho_J^{(d)}(t)$ can be determined in a manner similar to that used for $\rho_D^{(d)}(t)$. We will briefly outline this procedure in the Appendix and only give the main results here.

Corresponding to Eq. (5.2), we may expand $\rho_J^{(d)}(\epsilon)$ as

$$\rho_J^{(d)}(\epsilon) = \rho_{J,0}^{(d)}(\epsilon) + \rho_{J,1}^{(d)}(\epsilon) + \cdots . \qquad (6.4)$$

The Laplace inversion of $\rho_{J,0}^{(d)}(\epsilon)$ leads to an exponentially decaying function similar to that given by Eq. (5.4) for $\rho_{D,0}^{(d)}(t)$. Thus we write

$$\rho_{J,0}^{(d)}(t) = \langle J^2(\vec{v}_1)\rangle^{-1} \int d\vec{v}_1 J(\vec{v}_1) \times e^{n\lambda_0(\vec{v}_1)t} \; J(\vec{v}_1)\varphi_0(v_1) \quad (6.5)$$

for all t. In the first Enskog approximation

$$\rho_{\eta,0}^{(d)}(t) \cong \exp[-t(\beta m \nu_{00})^{-1}] \qquad (6.6a)$$

and

$$\rho_{\lambda,0}^{(d)}(t) \cong \exp[-t(\beta m D_{T_{00}})^{-1}] , \qquad (6.6b)$$

where ν_{00} and $D_{T_{00}}$ are the first Enskog approximations to ν_0 and D_{T_0}, that have been defined in the Eqs. (4.8c) and (4.8d), respectively.

We remark that $\rho_{J,0}^{(d)}(t)$ decays over a period of a few mean free times.

A treatment of $\rho_{J,1}^{(d)}(t)$ similar to that given for $\rho_{D,1}^{(d)}(t)$ shows that for long times, the dominant behavior is contained in the expression

$$\rho_{J,1}^{(d)}(t) \sim \frac{\langle J^2(\vec{v}_1)\rangle^{-1}}{2n} \times {\sum_{\Omega,\Omega'}}' \int_{k<k_0} \frac{d\vec{k}}{(2\pi)^d} \exp[-t(\Omega(k)+\Omega'(k))] \times\left(\int d\vec{v}_1 J(\vec{v}_1)\Theta_0^{(\Omega)}(\vec{k},\vec{v}_1) \times \Theta_0^{(\Omega')}(-\vec{k},\vec{v}_1)\varphi_0(v_1)\right)^2 , \quad (6.7)$$

where the prime on the summation sign means that only the hydrodynamic eigenfunctions $\Theta^{(\Omega)}$ and $\Theta^{(\Omega')}$ are to be included, and the subscript zero on the eigenfunctions refers to them in the approximation given by Eq. (4.9). Of all the hydrodynamic modes in the summation in Eq. (6.7) the dominant contribution to $\rho_{J,1}^{(d)}(t)$ comes from those combinations of Ω and Ω' which are such that the sum $\Omega(k)+\Omega'(k)$ is $\sim k^2$. These combinations are easily seen to arise from (a) two shear modes, (b) two heat modes, (c) a heat and a shear mode, and (d) two sound modes such that one has eigenvalue $ikc_0 + \frac{1}{2}\Gamma_{s0}k^2$ and the other $-ikc_0 + \frac{1}{2} \times \Gamma_{s0}k^2$.

Inserting the expressions for $\Omega(k)$ given by Eq. (4.8) and for $\Theta_0^{(\Omega)}$ given by (4.9), we find that only combinations of two shear modes or two "opposite" sound modes contribute to $\rho_{\eta,1}^{(d)}(t)$, while combinations of one shear mode and one heat mode, or two "opposite" sound modes contribute to $\rho_{\lambda,1}^{(d)}(t)$, because of the tensorial character of the functions $J_\eta(\vec{v}_1)$ and $J_\lambda(\vec{v}_1)$, respectively.

For $d=2$, the long-time behavior of $\rho_{\eta,1}^{(2)}(t)$ is given by

$$\rho_{\eta,1}^{(d)}(t) \sim \frac{1}{n}\int_{k<k_0} \frac{d\vec{k}}{(2\pi)^2} \frac{k_x^2 k_y^2}{k^4} \left(2e^{-2\nu_0 t k^2} + e^{-\Gamma_{s0}k^2 t}\right) , \qquad (6.8)$$

where the first term in the parentheses incorporates the contributions of the shear modes, while the second term contains the sound-mode contribution.

Carrying out the k integrals, we obtain for $t \gg t_0$

$$\rho_{\eta,1}^{(2)}(t) \sim (32\pi n t_0)^{-1}\left[\nu_0^{-1} + \left(\nu_0 + \frac{\lambda_0}{2nk_B}\right)^{-1}\right]\left(\frac{t_0}{t}\right) \qquad (6.9a)$$

or

$$\rho_{\eta,1}^{(2)}(t) \sim \tfrac{1}{6}(na^2)(t_0/t) , \qquad (6.9b)$$

where we have used that $\langle v_x^2 v_y^2\rangle = (\beta m)^{-2}$ and the values for λ_0 and η_0 for hard disks of diameter a in the first Enskog approximation.

Similarly, we have

$$\rho_{\lambda,1}^{(2)}(t) \sim \frac{1}{2n}\int_{k<k_0} \frac{d\vec{k}}{(2\pi)^2}\left\{\frac{2k_y^2}{k^2}\exp\left[-k^2 t\left(\nu_0 + \frac{\lambda_0}{2nk_B}\right)\right] + \frac{2k_x^2}{k^2}\exp[-\Gamma_{s0}k^2 t]\right\} , \quad (6.10)$$

where the first term in the curly brackets incorporates the contributions from combinations of shear and heat modes, while the second term contains the sound-mode contribution. Thus, we write

$$\rho_{\lambda,1}^{(2)}(t) \sim (4\pi n t_0)^{-1}\left(\nu_0 + \frac{\lambda_0}{2nk_B}\right)^{-1}\left(\frac{t_0}{t}\right) \tag{6.11a}$$

or

$$\rho_{\lambda,1}^{(2)}(t) \sim \tfrac{1}{3}(na^2)(t_0/t) \ , \tag{6.11b}$$

where the values for η_0 and λ_0 in first approximation have been used. For $d=3$, we find that[35]

$$\rho_{\eta,1}^{(3)}(t) \sim (120 n\pi^{3/2})^{-1}\left[7(2\nu_0 t_0)^{-3/2} + \left(\frac{4\lambda_0 t_0}{15nk_B} + \frac{4\nu_0 t_0}{3}\right)^{-3/2}\right]\left(\frac{t_0}{t}\right)^{3/2}, \tag{6.12a}$$

or using the values for λ_0 and η_0 for hard spheres of diameter a in first Enskog approximation[29]

$$\rho_{\eta,1}^{(3)}(t) \sim 1.05(na^3)^2(t_0/t)^{3/2} \ , \tag{6.12b}$$

while for $\rho_{\lambda,1}^{(3)}(t)$ we find that[35]

$$\rho_{\lambda,1}^{(3)}(t) \sim (12n\pi^{3/2})^{-1}\left[\left(\nu_0 t_0 + \frac{2\lambda_0 t_0}{5nk_B}\right)^{-3/2} + \frac{1}{3}\left(\frac{4\lambda_0 t_0}{15nk_B} + \frac{4}{3}\nu_0 t_0\right)^{-3/2}\right]\left(\frac{t_0}{t}\right)^{-3/2} \tag{6.13a}$$

or

$$\rho_{\lambda,1}^{(3)}(t) \sim 1.32(na^3)^2(t_0/t)^{3/2} \ , \tag{6.13b}$$

if the Enskog approximation to η_0 and λ_0 for hard spheres is used.

Equations (6.9), (6.11)–(6.13) are consistent with the computer results of Alder and Wainwright, extrapolated to low densities.

VII. DISCUSSION

A number of remarks can be made in connection with the results presented here.

(i) The expressions given by the Eqs. (5.13), (5.18), (6.9a), (6.11a), (6.12a), and (6.13a) are identical with those derived by Alder and Wainwright,[1,2,4] Ernst, Hauge, and van Leeuwen,[5] and Kawasaki[6] for $\rho_D^{(d)}(t)$, $\rho_\eta^{(d)}(t)$, and $\rho_\lambda^{(d)}(t)$ on the basis of hydrodynamical considerations, if one replaces the transport coefficients in the expressions given by the above-mentioned authors by their low-density values.

(ii) The results of Secs. V and VI for the long-time behavior of $\rho^{(d)}(t)$ seem also to apply to a general class of systems with short-range interparticle forces. This obtains in spite of the $\vec{k}$ and ϵ dependence of the Fourier representation of the $\overline{T}$, λ^D, and λ operators in this case. For this $\vec{k}$ and ϵ dependence seems to incorporate effects on the scale of the range of the interparticle forces and of the duration of a collision, which both should lead to corrections of $O(n)$ compared to the effects on the scale of the mean free path and mean free time, considered here. This expectation seems to be borne out by machine calculations of $\rho_D^{(3)}(t)$ by Verlet and Levesque for systems of particles interacting with a 12–6 Lennard-Jones potential.[37]

(iii) As remarked before, the results obtained here are consistent with the machine calculations of Alder and Wainwright[1,2,4] extrapolated to low density.

In this connection it is interesting to note that in two dimensions a $(1/t)$ time dependence is obtained for $\rho^{(2)}(t)$, *without* carrying out the rearrangement discussed in Sec. III. This is due to the $\ln\epsilon$ behavior of $\epsilon\mathcal{B}_3^D$ and $\epsilon\mathcal{B}_3$, which is defined in the Appendix, for small ϵ. Using the results of Sengers[23] for the coefficients of the $\ln\epsilon$ terms in $\epsilon\mathcal{B}_3^D$ and $\epsilon\mathcal{B}_3$, we have computed the coefficient of (t_0/t), which would be obtained from $\epsilon\mathcal{B}_3^D$ and $\epsilon\mathcal{B}_3$. A comparison of the results for the coefficients of the (t_0/t) term in $\rho^{(2)}(t)$ before and after resummation is presented in Table I. It is clear that the unresummed coefficient is *inconsistent* with the machine calculations of Alder and Wainwright, having the opposite sign in two cases, and being between 5 and 20 times smaller than the coefficient obtained in the resummed theory. Thus the agreement with the Alder and Wainwright machine computations can be taken as an *a posteriori* justification for the rearrangement carried out in Sec. III and as consistent with the existence of the divergences in $\epsilon\mathcal{B}_l^D$ as $\epsilon\to 0$, which necessitate such an arrangement. In fact, the same dynamical events responsible for the most divergent contributions to the $\epsilon\mathcal{B}_l^D$ and $\epsilon\mathcal{B}_l$ are after resummation responsible for the $(t_0/t)^{d/2}$ tails in the velocity-correlation functions $\rho_D^{(d)}(t)$, $\rho_\eta^{(d)}(t)$, and $\rho_\lambda^{(d)}(t)$.

(iv) We have considered here only the first two terms in the iteration method to determine $\rho^{(d)}(t)$. This may set an upper limit for the time interval over which the results obtained here are valid. The higher iterates involve more complicated dy-

TABLE I. Comparison of the coefficients of t_0/t as obtained (a) from the divergence of the three-body collision term $\epsilon\mathcal{B}_3^D$ or $\epsilon\mathcal{B}_3$ (Refs. 23 and 34) for hard disks, and (b) from the method outlined in this paper, after a resummation of the $\mathcal{B}_l^D$ and $\mathcal{B}_l$ series has been carried out.

	Before resummation	After resummation
$\rho_D^{(2)}(t)$	$-0.06\ \frac{na^2}{4}\frac{t_0}{t}$	$\frac{na^2}{4}\frac{t_0}{t}$
$\rho_\eta^{(2)}(t)$	$-0.22\ \frac{na^2}{6}\frac{t_0}{t}$	$\frac{na^2}{6}\frac{t_0}{t}$
$\rho_\lambda^{(2)}(t)$	$+0.18\ \frac{na^2}{3}\frac{t_0}{t}$	$\frac{na^2}{3}\frac{t_0}{t}$

namical events than considered here. A rough estimate of the terms we have neglected suggests that they may make themselves felt for times longer than about $40t_0$. This would imply that the $(t_0/t)^{d/2}$ terms should be dominant in $\rho^{(d)}(t)$ for the times relevant in the Alder and Wainwright machine computations.

(v) Physically the long-time tails of the correlation functions are caused in our calculation by the slowly decaying hydrodynamic modes. Kinetically this is due, among others, to the possibility of recollisions, i.e., collisions between two particles that have collided before. They lead to a much slower decay of the initial state of a particle than if they are excluded, since they can still "remind" the particle of its initial state after many collisions have taken place.

(vi) Since the transport coefficients are related to time integrals of the time correlation functions $\rho^{(d)}(t)$, the results (5.13), (6.9a), and (6.11a), if valid for *all* $t \gg t_0$, would imply that the time-correlation-function expressions for the Navier-Stokes transport coefficients do not exist in two dimensions. Similarly, the results (5.18), (6.12a), and (6.13a) would imply that the time-correlation-function expressions for the Burnett transport coefficients do not exist in three dimensions, since integrals of the form[5,38]

$$\int_0^\infty dt\, t\,\rho^{(d)}(t)$$

occur. However, we stress that in view of the fact that the results obtained here may only hold over a restricted time interval, the existence or nonexistence of these transport coefficients is an open question.

(vii) In view of the long tail of the time correlation functions $\rho^{(t)}(t)$, a sharp separation of kinetic and hydrodynamic time scales is not possible. Therefore the precise range of validity of even the Navier-Stokes equations is not clear, since in their derivation it is tacitly assumed that the transport coefficients attain their full value on a kinetic time scale which is much shorter than the hydrodynamical time scales to which the equations apply. In particular, it is not clear to what extent these equations can be used for phenomena which are not infinitely slowly varying in space and time.

In a subsequent paper we shall discuss how the present considerations can be generalized to higher densities. We will obtain there, in a similar fashion as in this paper, an initial exponential decay followed by a decay proportional to $(t_0/t)^{d/2}$ with coefficients that reduce to those obtained here in the low-density limit and which can also be compared with the results of the hydrodynamical theories. These results will also allow a comparison with the computer data of Alder and Wainwright over the whole range of densities for which they are available.

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APPENDIX

Here we outline the method which leads to Eqs. (6.9a), (6.10), (6.12a), and (6.13a) for $\rho_{\eta,1}^{(d)}(t)$ and $\rho_{\lambda,1}^{(d)}(t)$. Since the method closely parallels that used to obtain $\rho_{D,1}^{(d)}(t)$, we will only indicate the essential modifications.

By taking the Laplace transform of Eqs. (6.3a) and (6.3b), one can write

$$\rho_J{}^{(d)}(\epsilon) = \int d\vec{v}_1\, J(\vec{v}_1)\, \Phi_J^{(d)}(\vec{v}_1, \epsilon), \tag{A1}$$

with

$$\Phi_J^{(d)}(\vec{v}_1, \epsilon) = \lim_{\substack{N,V\to\infty \\ N/V=n}} V m^d \langle J^2(\vec{v}_1)\rangle^{-1} \times \int dx^{N-1}\, G(x^N, \epsilon)\, \rho(x^N) \sum_{i=1}^{N} J(\vec{v}_i). \tag{A2}$$

Using the method outlined in Sec. II, one obtains for $\Phi_J^{(d)}(\vec{v}_1, \epsilon)$ [see, Eq. (2.20)]

$$\Phi_J^{(d)}(\vec{v}_1, \epsilon) = (1/\epsilon)\left[1 + \sum n^l \mathcal{A}_{l+1}(\vec{v}_1, \epsilon)\right] \times \varphi_0(v_1)\; J(\vec{v}_1)\cdot \langle J^2(\vec{v}_1)\rangle^{-1}, \tag{A3}$$

where $\mathcal{A}_l(\vec{v}_1 \epsilon)$ are given by the Eqs. (2.21), provided that in the operators $\mathcal{A}_l^D(\vec{v}_1, \epsilon)$ the product $\prod_{i=2}\varphi_0(v_i)$ is replaced by

$$\prod_{i=1}^{l} \varphi_0(v_i) \sum_{i=1}^{l} P_{1i} [\varphi_0(v_1)]^{-1}.$$

Defining the operator $\mathcal{B}_l(\vec{v}, \epsilon)$ by an identity similar to (2.23) and using $\mathcal{A}_l$ instead of $\mathcal{A}_l^D$, one can give an expression for $\Phi_J^{(d)}(\vec{v}_1, \epsilon)$ in a form similar to Eq. (2.25) for $\Phi_D^{(d)}(\vec{v}_1, \epsilon)$:

$$\Phi_J^{(d)}(\vec{v}_1, \epsilon) = \langle J^2(\vec{v}_1)\rangle^{-1} \left[\epsilon - \sum_{l=1}^{\infty} n^l \epsilon \mathcal{B}_{l+1}(\vec{v}_1, \epsilon)\right]^{-1} \times \varphi_0(v_1) J(\vec{v}_1). \tag{A4}$$

Here the $\mathcal{B}_l$ bear the same relation to the $\mathcal{A}_l$ as the $\mathcal{B}_l^D$ do to the $\mathcal{A}_l^D$, of Eq. (2.26). For hard disks and spheres, the operator $\epsilon\mathcal{B}_2(\vec{v}_1, \epsilon)$ is the linearized Boltzmann collision operator $\lambda_0(\vec{v}_1)$ given by Eq. (3.17).

Using the binary-collision expansion, one can sum the most divergent terms in the B expansion with the result

$$\sum_{l=2} n^l \epsilon \mathcal{B}_{l+1}(\vec{v}_1, \epsilon) = n\epsilon \mathcal{R}(\vec{v}_1, \epsilon) + (\text{LDT}) , \qquad \text{(A5a)}$$

with

$$\epsilon\mathcal{R}(\vec{v}_1, \epsilon) = \int \frac{d\vec{k}}{(2\pi)^d} \int d\vec{v}_2 \langle 0, 0, |\overline{T}_2(x_1, x_2)|\vec{k}, -\vec{k}\rangle$$
$$\times [\epsilon + i\vec{k}\cdot\vec{v}_{12} - n\lambda_{\vec{k}}(\vec{v}_1) - n\lambda_{-\vec{k}}(\vec{v}_2)]^{-1}$$
$$\times \langle\vec{k}, -\vec{k}|\overline{T}_2(x_1, x_2)(1+P_{12})|0, 0,\rangle\varphi_0(v_2). \qquad \text{(A5b)}$$

For reasons identical to those given in Sec. III, we replace in (A5b) the operator

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

by the operator

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

to obtain $\epsilon\mathcal{R}_0(\vec{v}_1, \epsilon)$.

Equations (6.4) and (6.5) for $\rho_J^{(d)}(\epsilon)$ and $\rho_{J,0}^{(d)}(\epsilon)$, respectively, are obtained by writing

$$\Phi_J^{(d)}(\vec{v}_1, \epsilon) = \langle J^2(\vec{v}_1)\rangle^{-1} [\epsilon - n\lambda_0(\vec{v}_1) - n\epsilon\mathcal{R}_0(\vec{v}_1, \epsilon)]^{-1} \times J(\vec{v}_1)\varphi_0(v_1), \qquad \text{(A6)}$$

by iterating about the operator $[\epsilon - n\lambda_0(\vec{v}_1)]^{-1}$, and then by using (A1). $\rho_{J,1}^{(d)}(\epsilon)$ is obtained from Eq. (A6) as

$$\rho_{J,1}^{(d)}(\epsilon) = n\langle J^2(\vec{v}_1)\rangle^{-1} \int d\vec{v}_1 J(\vec{v}_1) [\epsilon - n\lambda_0(\vec{v}_1)]^{-1} \times \epsilon\mathcal{R}_0(\vec{v}_1, \epsilon)[\epsilon - n\lambda_0(\vec{v}_1)]^{-1} J(\vec{v}_1)\varphi_0(v_1). \qquad \text{(A7)}$$

Proceeding as in Sec. V and using identities similar to those employed in the transition from Eq. (5.8) to (5.9), the following expression for $\rho_{J,1}^{(d)}(\epsilon)$ is obtained[16,39] [cf., Eq. (5.9)]:

$$\rho_{J,1}^{(d)}(\epsilon) \sim \tfrac{1}{2} n\langle J^2(\vec{v}_1)\rangle^{-1} \sum_{\Omega,\Omega'}{}' \int_{k<k_0} \frac{d\vec{k}}{(2\pi)^d} [\epsilon + \Omega(k) + \Omega'(k)]^{-1}$$
$$\times \left(\int d\vec{v}_1 J(\vec{v}_1) \lambda_0(\vec{v}_1)[\epsilon - n\lambda_0(\vec{v}_1)]^{-1} \times \Theta_0^{(\Omega)}(\vec{k}, \vec{v}_1) \Theta_0^{(\Omega')}(-\vec{k}, \vec{v}_1)\varphi_0(v_1) \right)^2. \qquad \text{(A8)}$$

Laplace inversion of (A8) leads for $t > t_0$ to the Eq. (6.7), from which all further results of Sec. VI can be derived.

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[32]That is, we treat v_{1x} as an approximate eigenfunction of $n\lambda_0^D(\vec{v}_1)$ with approximate eigenvalue $(\beta m D_{00})^{-1}$. See also Ref. 29.

[33]One can show that the initial slope of $\rho_D^{(d)}(t)$ for hard disks and hard spheres is given by (Ref. 16)

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

where χ is the equilibrium radial distribution function evaluated at an interparticle distance equal to their diameter (Ref. 29). We are indebted to Dr. E. H. Hauge and Dr. W. W. Wood for this remark.

[34]Cf. J. V. Sengers, Ref. 23; and in *Lectures in Theoretical Physics* (*Boulder*), edited by W. E. Brittin (Gordon and Breach, New York, 1967), Vol. 9c, p. 335.

[35]Equation (5.18) for $\rho_D^{(3)}(t)$ has been obtained by Dufty on the basis of a procedure which does not involve the iteration method used in this section, but other approximations. He determines the approximate eigenvalues of the operator $(\epsilon-n\lambda_0^D-n\epsilon\mathcal{R}_0^D)^{-1}$. He also obtains by his method Eq. (6.12a) for $\rho_\eta^{(3)}(t)$ [J. Dufty, Phys. Rev. A 5, 2247 (1972)].

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Non-Ohmic Electron Transport on Liquid Helium

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The transport coefficients in high electric fields are obtained for electrons bound in image-potential-induced surface states on a dielectric liquid surface. A two-dimensional Boltzmann equation is solved in the diffusion approximation, assuming the principle electron scatterers are gas atoms and surface waves. At high temperatures, where gas-atom scattering dominates both energy and momentum relaxation, the transport coefficients are field independent even though the average electron energy is much higher than the product of Boltzmann's constant and the liquid temperature. At low temperatures, where surface-wave scattering dominates the momentum relaxation, the conductivity and Hall mobility increase rapidly with increasing electric field. For ^{4}He this non-Ohmic transport should occur below 1 K at fields below 0.1 V/cm.

I. INTRODUCTION

Cole and Cohen[1] and later Shikin[2] predicted that electrons should form surface states outside liquid He, H_2, D_2, and Ne. The idea is that an electron can be drawn to and localized outside the liquid surface because of the dielectric image force. Because of the short-range repulsive interaction between the electron and the liquid, the electron is not drawn into the liquid. This one-dimensional attractive image potential gives rise to electronic states that are nearly hydrogenic in their motion perpendicular to the liquid surface. However, the motion parallel to the liquid surface is assumed to be free-electron-like. A surface state was detected on liquid ^{4}He by Williams, Crandall, and Willis[3] and by Crandall and Williams.[4] They measured the lifetime of electrons in this surface state. However, they were unable to explain the magnitude of the lifetime in terms of the above image-potential model.[4,5] The experimental values of the lifetime were much longer than the theoretical values. Cole[6] calculated the mobility of electrons parallel to the liquid surface and predicted that above about 1 K electrons would be scattered mainly by ^{4}He atoms in the vapor phase, whereas below this temperature the mobility would be determined by surface wave scattering. Crandall and Williams[7] suggested that electron motion parallel to the liquid surface may not be free-electron-like but rather that electrons are arranged in a crystalline array. Sommer and Tanner[8] recently