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Approximate Kinetic Theory of Hard-Sphere Fluids Near Equilibrium. I. Formal Theory

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We propose a kinetic theory of hard-sphere fluids which systematically generalizes the Enskog equation by taking successively into account binary, ternary,... dynamic correlations in a system close to equilibrium. The first approximation, beyond Enskog, is displayed explicitly; it reproduces most of the results previously established in limiting cases (short- and long-time behavior, low-density expansions) and appears to give a good description of hard-sphere dynamics for all times and all densities. This explicit study will be presented in another publication.

KEY WORDS: Kinetic theory; hard-sphere fluids; time-dependent correlation functions; short- and long-time behavior.

1. INTRODUCTION

"Time-dependent correlation functions" play an important role in nonequilibrium statistical mechanics. While most of the experimental observations on nonequilibrium systems (including the very important "computer experiments") can be interpreted in terms of such correlation functions,[3] they nevertheless present a well-posed problem which is considerably

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[3] For a general review see, e.g., Ref. 1.

simpler, in principle at least, than the general problem of nonequilibrium processes.

Of course, knowing what should be computed does not necessarily help in carrying out explicit calculations, and so far the precise evaluation of these time-dependent correlation functions has been confined either to unrealistic but exactly soluble models (like the one-dimensional hard-rod system(2)) or to systems which are realistic but of limited applicability (like the dilute gas system). Most of the time, one has to rely on some kind of semiphenomenological approach,[4] particularly when one wants to treat dense systems. In the development of such an approach, the information that can be gained from computer experiments(4–6) is most valuable and, from this viewpoint, the spirit of the present paper will be very similar to that of the work cited above. In particular, we shall rely upon the fact that realistic dense systems seem to present the same qualitative features as hard-sphere systems.(4–6) Since the dynamics of these latter systems, being of a purely geometric nature, is much simpler, we shall limit ourselves here to hard-sphere systems, which already pose the most challenging questions. Once this system has been properly understood, it seems likely that the effect of the soft attractive potential of real molecules will be amenable to treatment by some kind of a perturbative method. Indeed, in the limiting case of very long-range forces, such a perturbation calculation has already been carried out.(8)

In order to make this paper as simple as possible, we shall limit ourselves to the so-called kinetic self-correlation functions, in which one particle of the system, the "labeled" particle, plays a special role. They are of the form

$$\Gamma_s(t) = \lim_{\Omega} \langle \Phi_1(t) \Psi_1(0) \rangle_\Omega \tag{1}$$

where the brackets denote the average,

$$\langle \cdots \rangle_\Omega = \int dx_1 \cdots dx_N \cdots \mu_0 \tag{2}$$

over the canonical ensemble density μ_0 of a system containing N particles in a box of volume Ω and $x_i = (r_i, v_i)$ stands for the position and velocity of the ith particle[5]; the symbol $\lim_\Omega$ indicates the well-known thermodynamic limit[6]

$$N \to \infty, \quad \Omega \to \infty, \quad N/\Omega = \rho \quad \text{finite} \tag{3}$$

$\Phi_1(t)$ denotes the value of the dynamical function Φ_1 at time t:

$$\Phi_1(t) = \exp[-iL_N t]\Phi_1 \tag{4}$$

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[4] See Refs. 3 and 4 for various approaches.

[5] We do not write the vector symbols explicitly, except when there might be some ambiguity otherwise.

[6] The existence of this limit follows from the recent work on the time evolution of infinite systems by Landford and others.(10)

(L_N is the Liouville operator), and Ψ_1 and Φ_1 are functions which depend only on the phase space coordinates of the labeled particle 1,[7]

$$\Psi_1 = \Psi_1(x_1), \qquad \Phi_1 = \Phi_1(x_1) \tag{5}$$

The theory to be developed below can be extended with little difficulty to the so-called "total" case where the dynamical functions would depend symmetrically on all particles in the system as a sum of single or pairs of phase space variables, but we shall not do this here.⁽⁹⁾

Typical examples of (1) correspond to the choices

$$\Psi_1 = \delta(r' - r_1), \qquad \Phi_1 = \delta(r - r_1) \tag{6}$$

Γ_s being then the Van Hove self-correlation function, and

$$\Psi_1 = \Phi_1 = v_1 \tag{7}$$

which defines Γ_s as the velocity autocorrelation function, for which very extensive data are available in the case of hard spheres.(4)

It is well known that the calculation of (1) can be reduced to the solution of a linearized kinetic equation for a one-body self-distribution function $f_{s,1}(x_1; t)$,

$$f_{s,1}(x_1; t) = \lim_{\Omega} \int dx_2 \cdots dx_N \, \mu(x_1, ..., x_N; t) \tag{8}$$

where $\mu(x_1, ..., x_N; t)$ is the ensemble density at time t obtained as the solution of the Liouville equation with the initial condition[8]

$$\mu(x_1, ..., x_N, 0) = \Psi_1(x_1)\mu_0 \tag{9}$$

We get from (1)

$$G_s = \int dx_1 \, \Phi_1(x_1) f_{s,1}(x_1; t) \tag{10}$$

and hence knowledge of $f_{s,1}(x_1; t)$ suffices for the calculation of G_s. Moreover, the kinetic equation obeyed by $f_{s,1}$ has to be linear in view of the linear nature of the deviation from equilibrium (9).

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[7] Formally we have a composite system consisting of a fluid of $n - 1$ identical particles in a volume Ω with $N \to \infty$, $\Omega \to \infty$, $N/\Omega \to \rho$ in the thermodynamic limit and a "one-particle system" which "happens" to be confined to the same volume Ω and is otherwise similar to the other fluid particles.

[8] In the case of the velocity autocorrelation function (7), $\mu(x_1, ..., x_N; t)$ is normalized to zero and $f_{s,1}(x_1; t)$ is not really a "distribution function" in the usual sense. Formally, however, this makes no difference and we will continue to talk of a self-distribution function that is normalized to unity. Indeed, because of linearity, *all* the results can be expressed in terms of the Green's function $f_{s,1}(x_1; t/x_1')$ corresponding to $\psi_1(x_1) = \delta(r_1 - r_1')\,\delta(v_1 - v_1')$.

In this paper, we want to exploit two observations to develop an approximate kinetic theory for $f_{s,1}$. The first one is of an "experimental" character and results from the interesting computer calculations of Alder *et al.*(4): Even at fairly high densities, the Enskog theory provides a very good "first approximation" to the behavior of hard-sphere systems. The second is of a theoretical nature: It was remarked by Lebowitz *et al.*(3b) that the Enskog theory also yields the *exact* value of the first derivative of $f_{s,1}$ at $t = 0$. This property is a consequence of the fact that, at $t = 0$, *the distribution function* μ, Eq. (9), *only involves a one-body deviation from equilibrium.* Thus, at $t = 0$, all correlations in the system are purely *static* and this is sufficient to make the Enskog equation exact. Indeed, as will be seen later, all that is required is that the two-particle distribution have the form

$$f_{s,2}(x_1, x_2; t) = \rho g_2(r_1, r_2) f_{s,1}(x_1; t)\varphi(v_2) \tag{11}$$

when particles are *entering* a collision. Here $g_n(r_1, ..., r_n)$ is the equilibrium n-particle correlation function and $\varphi(v)$ denotes the Maxwellian distribution function.

Of course, such a property is *not* satisfied for $t > 0$ and correlations of *dynamical* origin, involving successively two, three,... particles, build up in the system and the Enskog theory is no longer exact. Yet the empirical success of the Enskog theory suggests that the effect of such dynamical correlations on the development of Γ_s remain small; hence the idea of a systematic scheme which would take into account such binary, ternary,... dynamical correlations.

The formal realization of such a scheme, oriented toward applications, motivates this paper. In Section 2 we give a precise definition of the n-body dynamical correlations and we study their formal exact time evolution. This analysis rapidly becomes very awkward with increasing n; moreover, very little results beyond $n = 2$ are required for applications. Hence we have not found it useful to explicitly write down here the full development of the theory for dynamical correlations of order higher than two: The relevant general results will merely be stated and the proofs will be presented elsewhere.(9)

In Section 3 the basic hypothesis of our work is stated and used. Loosely speaking we assume that, as a zeroth approximation, the n particles involved in an n-body dynamical correlation evolve as if they were independent of each other, each moving in an equilibrium fluid. Deviations from this "*independent particle approximation*" are supposed to be small and are measured by a formal smallness parameter ϵ. They are treated by a systematic perturbation scheme in powers of ϵ. At the formal level, this assumption has the following attractive consequences.

1. To order ϵ^0, we get a most natural extension of the Enskog assumption (11) to the n-body distribution function; namely we have

$$f_{s,n}^{(0)}(x_1,\ldots, x_n; t) = \rho^{n-1} g_n(r_1,\ldots, r_n) f_{s,1}(x_1; t) \prod_{i=2}^{n} \varphi(v_i) \tag{12}$$

2. To order ϵ^n $(n > 0)$, $f_{s,1}(x_1; t)$ has its first $2n$ time derivatives exact at $t = 0$ (for $n = 0$, we still have *one* correct derivative); from this point of view, the present work generalizes the short-time kinetic equation approach of Lebowitz *et al.*[(3b)]

3. It can be argued that the $f_{s,n}$ will approach their correct equilibrium value as $t \to \infty$ to every order in ϵ.

Of course, explicit calculations cannot be pursued to arbitrary order, and in Section 3 we limit ourselves to the first-order correction in ϵ. Already to this order, the kinetic equation we derive has many virtues:

1. As already stated, the first two time derivatives of $f_{s,1}$ are exact at $t = 0$.

2. At low density, we obtain correctly, beyond the Boltzmann contribution, the terms of the Choh–Uhlenbeck triple collision operator which describe one, two, and three dynamic binary collisions.[(11)] These terms are known to give the dominant effects.[(12)]

3. The solution of this equation also leads to what is believed to be the correct nonanalytic contribution ($\alpha \rho \ln \rho$) to the density expansion of the self-diffusion coefficient.[(13)]

4. In the limit of long times, it leads to the $t^{-3/2}$ long-time tail for the velocity autocorrelation function,[(14)] though the numerical coefficients are only correct in the low density limit.[(15)],[9]

These properties (which incorporate almost all that is safely known in the kinetic theory of fluids) make this first-order kinetic equation very appealing; moreover, its form for all times and all densities is sufficiently simple that one can find its explicit solution, at least approximately. However, we shall leave this last point for another paper of this series.[(16)]

While our interest lies entirely in the time evolution of the $f_{s,n}(x_1,\ldots, x_n; t)$ (particularly for $n = 1$) in the thermodynamic limit and our final equations deal exclusively with these functions, the analysis which motivates and gives a rationale to our later approximations has to be formulated in terms of finite, albeit arbitrarily large, systems. This leads to a certain awkwardness in that our intermediate formulas contain expressions that become infinite or meaningless, e.g., $\mu(x_1,\ldots, x_N; t)$, in this thermodynamic limit. We discuss this further in Section 5.

Some calculations are relegated to appendices.

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[9] Technically, 3 and 4 are consequences of the fact that our kinetic equation includes, among others, the so-called "Enskog ring terms."

2. THE HIERARCHY OF n-BODY DYNAMICAL CORRELATIONS

Let us suppose that we know the ensemble density μ at time t. We formally expand it in the following way[10]:

$$\mu = \mu^{(1)} + \mu^{(2)} + \mu^{(3)} + \cdots \tag{13}$$

where[11]

$$\mu^{(1)} = \Omega\mu_0 \frac{W_1(x_1; t)}{\varphi(v_1)} \tag{14}$$

$$\mu^{(2)} = \Omega\mu_0 \left(\sum_{j \neq 1} \frac{W_2(x_1, x_j; t)}{\varphi(v_1)\varphi(v_j)} + \frac{W_2^{(1)}(x_1; t)}{\varphi(v_1)} \right) \tag{15}$$

$$\mu^{(3)} = \Omega\mu_0 \left(\sum_{1 \neq j < k} \frac{W_3(x_1, x_j, x_k; t)}{\varphi(v_1)\varphi(v_j)\varphi(v_k)} + \sum_{1 \neq j} \frac{W_3^{(2)}(x_1, x_j; t)}{\varphi(v_1)\varphi(v_j)} \right.$$
$$\left. + \frac{W_3^{(1)}(x_1; t)}{\varphi(v_1)} \right) \tag{16}$$

The higher order terms, which are written in Appendix A, similarly correspond to contributions involving successively groups of four, five,... molecules, always including the tagged particle 1; the functions $W_m^{(n)}$ can be taken as symmetric in their $n - 1$ variables different from x_1 [see footnote to Eq. (5)].

Of course, the single condition (13) leaves us with an enormous arbitrariness in the choice of the functions W. We now specify them in the following way: For W_1, we impose that $\mu^{(1)}$ alone leads to the correct one-body distribution $f_{s,1}(x_1; t)$. Hence we require

$$f_{s,1}(x_1; t) = \lim_{\Omega} \int dx_2 \cdots dx_N \, \Omega\mu_0 \frac{W_1(x_1; t)}{\varphi(v_1)} \tag{17}$$

which tells us, using the usual definitions of the equilibrium distribution functions (cf. Ref. 3b), that

$$W_1(x_1; t) = f_{s,1}(x_1; t) \tag{18}$$

Comparing (17) with the definition (8), we get an extra condition on $\mu^{(2)}, \mu^{(3)}, \ldots$:

$$\lim_{\Omega} \int dx_2 \cdots dx_N \, [\mu^{(2)} + \mu^{(3)} + \cdots] = 0 \tag{19}$$

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[10] A similar expansion, with a rather different aim, can be found in Ref. 17.

[11] The Ω appearing in these equations properly belongs in the denominator, $\varphi(v_1)/\Omega$ being the equilibrium distribution of the labeled particles in a uniform system.

We further impose that this condition is *separately* satisfied for each $\mu^{(i)}$ $(i \geqslant 2)$:

$$\lim_{\Omega} \int dx_2 \cdots dx_N \, \mu^{(i)} = 0, \qquad i \geqslant 2 \tag{20}$$

For example, in the case $i = 2$, Eqs. (15) and (20) immediately lead to:

$$\lim_{\Omega} \left[\rho \int dx_2 \, g_2(r_1, r_2) W_2(x_1, x_2; t) + W_2^{(1)}(x_1; t) \right] = 0 \tag{21}$$

a relation which determines $W_2^{(1)}$ in terms of W_2,[12]

$$W_2^{(1)}(x_1; t) = -\rho \int dx_2 \, g_2(r_1, r_2) W_2(x_1, x_2; t) \tag{22}$$

Similarly, we determine W_2 by imposing that the two first terms of the expansion (13) lead to the correct two-body d.f. $f_{s,2}(x_1, x_2; t)$, which is defined by

$$f_{s,2}(x_1, x_2; t) = \lim_{\Omega} N \int dx_3 \cdots dx_N \, \mu(x_1, \ldots, x_N; t) \tag{23}$$

Hence we require

$$f_{s,2}(x_1, x_2; t) = \lim_{\Omega} N \int dx_3 \cdots dx_N \, [\mu^{(1)} + \mu^{(2)}] \tag{24}$$

With the help of (22), we thus have

$$f_{s,2}(x_1, x_2; t) = \rho g_2(r_1, r_2) f_{s,1}(x_1; t) \varphi(v_2) + \delta f_{s,2}(x_1, x_2; t) \tag{25}$$

where

$$\begin{aligned} &\delta f_{s,2}(x_1, x_2; t) \\ &\quad = \rho W_2(x_1, x_2; t) g_2(r_1, r_2) + \rho^2 \varphi(v_2) \\ &\qquad \times \int dx_2' \, [g_3(r_1, r_2, r_2') - g_2(r_1, r_2) g_2(r_1, r_2')] W_2(x_1, x_2'; t) \end{aligned} \tag{26}$$

These equations provide us with a *definition* of W_2 in terms of $f_{s,2}$. As a consequence of the equality between (23) and (24), we have

$$\lim_{\Omega} N \int dx_3 \cdots dx_N \, [\mu^{(3)} + \cdots] = 0 \tag{27}$$

and, in analogy with (20), we impose separately

$$\lim_{\Omega} N \int dx_3 \cdots dx_N \, \mu^{(i)} = 0, \qquad i \geqslant 3 \tag{28}$$

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[12] The existence of the integral on the right-hand side of (22) in the large-volume limit requires that W_2 vanishes for large separation between 1 and 2; this implies, of course, that our nonequilibrium ensemble μ describes a local perturbation around the tagged particle.

In the case $i = 3$, Eqs. (20) and (28) provide us with two linear relations between W_3, $W_3^{(2)}$, and $W_3^{(1)}$; this in principle leaves us with the only unknown W_3.

As shown in Appendix A, the pedestrian procedure followed here for W_1 and W_2 can be formalized for arbitrary W_n, although the explicit expressions rapidly become complicated. Let us briefly summarize the main results: The functions $W_n^{(i)}$ $(i = 1,..., n - 1)$ can all be determined in terms of W_n with the help of conditions analogous to (20) and (28) and the W_n themselves are defined in general through the set of equations

$$f_{s,n} = \sum_{m \leqslant n} A_{n,m} W_m \tag{29}$$

The $A_{n,m}$ are *linear integral operators*:

$$A_{n,m} W_m \equiv \int dx_1' \cdots dx_m' \, \mathscr{A}_{n,m}(x_1 \cdots x_n | x_1' \cdots x_m') W_m(x_1',..., x_m'; t) \tag{30}$$

entirely determined in terms of purely equilibrium quantities. For example, we see from (18), (25), and (26) that

$$\begin{aligned} \mathscr{A}_{1,1} &= \delta(x_1 - x_1'), \qquad \mathscr{A}_{2,1} = \rho g_2(r_1, r_2)\varphi(v_2)\delta(x_1 - x_1') \\ \mathscr{A}_{2,2} &= \{\rho g_2(r_1, r_2)\, \delta(x_2 - x_2') + \rho^2 \varphi(v_2)[g_3(r_1, r_2, r_2') \\ &\quad - g_2(r_1, r_2) g_2(r_1, r_2')]\}\, \delta(x_1 - x_1') \end{aligned} \tag{31}$$

If we assume that Eq. (29) can be inverted, we get

$$W_m = \sum_{n \leqslant m} B_{m,n} f_{s,n} \tag{32}$$

where, with the same formal matrix notation as in (29),

$$B_{n,m} = (A^{-1})_{n,m} \tag{33}$$

The explicit construction of $B_{n,m}$ is in general very difficult (in Appendix B, we show how this can be done for $B_{2,2}$); yet it is remarkable that no such *explicit* construction is required for the further development of the theory. The important point is that Eq. (32) provides us in principle with a complete characterization of the set of functions W_m that are equivalent to the original distribution functions $f_{s,m}$. For m given, they are entirely determined by the distribution functions of order $n \leqslant m$, through linear integral operators which depend only on the equilibrium properties of the system. Moreover, once the linear operators $A_{n,m}$ have been defined, all reference to the N-body distribution μ can be forgotten: All calculations are done in the thermodynamic limit; see Section 5 for further discussion of this point. As a last formal point, let us notice that it is generally convenient to use the function $\delta f_{s,m}$ defined by

$$\delta f_{s,m} = A_{m,m} W_m, \qquad m > 1 \tag{34}$$

instead of W_m; this notation is consistent with (26) and (31).

Let us now pause and investigate the physical meaning of the functions $\delta f_{s,m}$ (or W_m). First let us remark that if we truncate Eq. (29) at any order m, we generate a well-defined but approximate n-body reduced distribution function $f_{s,n}$ for *all n*. For example, if we only retain W_1, we get precisely Eq. (12), which corresponds to

$$\mathscr{A}_{n,1} = \rho^{n-1} g_n(r_1, \dots, r_n)\, \delta(x_1 - x_1') \prod_{i=2}^{N} \varphi(v_i) \tag{35}$$

To this order, the only nonequilibrium effects that we retain are of the one-body type: All n-particle correlations are purely static.

As discussed in Ref. 3b, this corresponds to a description where one supposes that the higher order distribution functions accommodate instantaneously to the one-particle distribution, which is not at equilibrium, in a state of conditional equilibrium relative to this particle; i.e., the ratio

$$f_{s,n}(x_1, \dots, x_n; t)/f_{s,1}(x_1; t)$$

is equal to its equilibrium value even though $f_{s,1}$ changes with time. When we now retain W_2 (or $\delta f_{s,2}$), we get an extra contribution to $f_{s,n}$ which we denote $f_{s,n}^{(2)}$. Let us limit ourselves to $n \leqslant 3$. We have

$$f_{s,1}^{(2)}(x_1; t) = 0 \tag{36}$$

which is obvious because, by definition, $f_{s,1}$ was already correctly described in the first approximation:

$$f_{s,2}^{(2)}(x_1, x_2; t) = \delta f_{s,2}(x_1, x_2; t) \tag{37}$$

which guarantees that, to this "order," $f_{s,2}$ is also correctly described.

From (15) and (22) we get also

$$\begin{aligned} f_{s,3}^{(2)}(x_1, x_2, x_3; t) &= A_{3,2} W_2 \\ &\equiv \rho^2 g_3(r_1, r_2, r_3)[W_2(x_1, x_2; t)\varphi(v_3) \\ &\quad + W_2(x_1, x_3; t)\varphi(v_2)] \\ &\quad + \rho^3 \varphi(v_2)\varphi(v_3) \int dx_2' \, [g_4(r_1, r_2, r_3, r_2') \\ &\quad - g_3(r_1, r_2, r_3) g_2(r_1, r_2)] W_2(x_1, x_2'; t) \end{aligned} \tag{38}$$

which together with (26) leads to $f_{s,3}$ being a linear functional of $f_{s,1}$ and $\delta f_{s,2}(x_1, x_2; t)$. Comparing (35) and (37) to (12), we see that we have improved the description of our system by including *two-body dynamical correlations* in the system, measured by $\delta f_{s,2}$, to which all higher order distributions now adjust in a nontrivial manner. Clearly, the "higher order" contributions $\delta f_{s,n}$ ($n = 3, \dots$) similarly describe the effect of triple,... dynamical correlations in the system.

We see thus that the relation (29) provides a systematic procedure to construct the higher order distribution functions once the lower order ones are given; it furnishes a most natural generalization of the conditional static equilibrium formula (12).

Until now, we have considered our system at one instant of time only. As we shall see in the next section, the relations (29) and (34) are most useful in deriving (in principle systematically) approximate kinetic equations for $f_{s,1}$, when it is used in connection with the BBGKY hierarchy. This hierarchy can be written (see, e.g., Ref. 18)

$$\begin{aligned}\partial_t f_{s,n} + \sum_{i=1}^{n} v_i \frac{\partial f_{s,n}}{\partial r_i} - \sum_{i>j=1}^{n} K_{ij} f_{s,n} \\ = \sum_{i=1}^{n} \int dx_{n+1}\, K_{i,n+1} f_{s,n+1}(x_1, x_2, \ldots x_{n+1}; t)\end{aligned} \tag{39}$$

While our previous treatment was valid for arbitrary forces, we shall now specify, for reasons explained below, that we consider a hard-sphere system. In this case the operator K_{ij} is[13]

$$\begin{aligned}K_{ij} = a^2 \int d\boldsymbol{\varkappa}\, (\boldsymbol{\varkappa}\cdot\mathbf{v}_{ij})\theta(\boldsymbol{\varkappa}\cdot\mathbf{v}_{ij})\, [\delta^{(3)}(\mathbf{r}_{ij} - a\boldsymbol{\varkappa}) b_{\varkappa}(\mathbf{v}_i, \mathbf{v}_j) \\ - \delta^{(3)}(\mathbf{r}_{ij} + a\boldsymbol{\varkappa})]\end{aligned} \tag{40}$$

Here a denotes the hard-sphere diameter; $\mathbf{v}_{ij}$ is $\mathbf{v}_i - \mathbf{v}_j$; $\mathbf{r}_{ij}$ is $\mathbf{r}_i - \mathbf{r}_j$; $\boldsymbol{\varkappa}$ is a unit vector; and $\theta(x)$ is the Heaviside function [$\theta(x) = 0$ for $x < 0$; $\theta(x) = 1$ for $x > 0$]; finally $b_{\varkappa}(\mathbf{v}_i, \mathbf{v}_j)$ is a displacement operator in the velocity space of particles i and j:

$$b\boldsymbol{\varkappa}(\mathbf{v}_i, \mathbf{v}_j) = \exp\left[-(\boldsymbol{\varkappa}\cdot\mathbf{v}_{ij})\boldsymbol{\varkappa}\cdot\left(\frac{\partial}{\partial \mathbf{v}_i} - \frac{\partial}{\partial \mathbf{v}_j}\right)\right] \tag{41}$$

which turns the velocities $\mathbf{v}_i$ and $\mathbf{v}_j$ prior to collision into the velocities $\mathbf{v}_i'$ and $\mathbf{v}_j'$ after the collision, e.g.,

$$\mathbf{v}_1' = \mathbf{v}_1 - (\boldsymbol{\varkappa}\cdot\mathbf{v}_{12})\boldsymbol{\varkappa}, \qquad \mathbf{v}_2' = \mathbf{v}_2 + (\boldsymbol{\varkappa}\cdot\mathbf{v}_{12})\boldsymbol{\varkappa} \tag{42}$$

Using (29), (32), and (34), one can write down from (39) an analogous hierarchy in terms of $f_{s,1}$ and $\delta f_{s,n}$ ($n > 1$). Although we have done this in general,[(9)] we shall limit ourselves here to the cases $n = 1$ and 2. From the first BBGKY hierarchy, we immediately obtain

$$\partial_t f_{s,1} = \mathscr{L}_{1,1} f_{s,1} + \mathscr{L}_{1,2}\, \delta f_{s,2} \tag{43}$$

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[13] To avoid a complicated notation, we slightly oversimplify the expression for K_{ij} here; indeed, in case K_{ij} acts on a function which itself is singular at hard core contact, one should use a limiting procedure to define K_{ij}. Although this point should be kept in mind for some later explicit calculation, we shall ignore it here and refer the reader to the literature, in particular the excellent discussion of Ref. 19. See also Ref. 10.

where the operators $\mathscr{L}_{1,1}$ and $\mathscr{L}_{1,2}$ are defined by

$$\mathscr{L}_{1,1} f_{s,1} = \left[-v_1 \frac{\partial}{\partial r_1} + \int dx_2\, K_{12} g_2(r_1, r_2) \varphi(v_2) \right] f_{s,1}(x_1; t) \tag{44}$$

and

$$\mathscr{L}_{1,2}\, \delta f_{s,2} = \int dx_2\, K_{12}\, \delta f_{s,2}(x_1, x_2; t) \tag{45}$$

The case $n = 2$ is still easy, albeit tedious. We write

$$\partial_t\, \delta f_{s,2} = \partial_t f_{s,2} - \rho(\partial_t f_{s,1}) g_2(r_1, r_2) \varphi(v_2) \tag{46}$$

and we use the first and second BBGKY equations to transform the right-hand side. Finally, we express $f_{s,2}$ and $f_{s,3}$ back in terms of $f_{s,1}$, $\delta f_{s,2}$, and $\delta f_{s,3}$ with the help of (29) and (34) [see also (31), (35), and (38)]. We find, then,

$$\partial_t\, \delta f_{s,2} = \mathscr{L}_{2,1} f_{s,1} + \mathscr{L}_{2,2}\, \delta f_{s,2} + \mathscr{L}_{2,3}\, \delta f_{s,3} \tag{47}$$

The operator $\mathscr{L}_{2,1}$ which results from this straightforward calculation is given in Appendix C, together with $\mathscr{L}_{2,2}$ and $\mathscr{L}_{2,3}$. After some manipulations sketched in Appendix C, we get the compact expression[14]

$$\begin{aligned} \mathscr{L}_{2,1} f_{s,1} &= \rho g_2(r_1, r_2) [K_{12}, f_{s,1}(x_1, t)/\varphi(v_1)] \varphi(v_1) \varphi(v_2) \\ &\quad + \rho^2 \int dx_2'\, [g_3(r_1, r_2, r_2') - g_2(r_1, r_2') g_2(r_1, r_2)] \\ &\quad \times [K_{12'}, f_{s,1}(x_1; t)/\varphi(v_1)] \varphi(v_1) \varphi(v_2) \varphi(v_2') && \text{(48a)} \\ &\equiv A_{2,2} [K_{12}, f_{s,1}(x_1, t)/\varphi(v_1)] \varphi(v_1) \varphi(v_2) && \text{(48b)} \end{aligned}$$

Here [..., ...] denotes the usual commutator. We shall not need the formulas for $\mathscr{L}_{2,2}$ and $\mathscr{L}_{2,3}$, except in the appendices.

The formal extension of (47) to $\partial_t\, \delta f_{s,n}$ ($n > 2$) will not be presented here; we merely quote one property which we shall need later. One finds in general that

$$\partial_t\, \delta f_{s,n} = \mathscr{L}_{n,n-1}\, \delta f_{s,n-1} + \mathscr{L}_{n,n}\, \delta f_{s,n} + \mathscr{L}_{n,n+1}\, \delta f_{s,n+1} \tag{49}$$

i.e., $\delta f_{s,n}$ only couples to correlations of order $n \pm 1$, while a naive glance at (29), (32), (35), and (39) would lead one to believe that it also couples to $\delta f_{s,m}$, $1 \leqslant m \leqslant n - 1$. The proof of (49) is not trivial (see Ref. 9) and rests

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[14] In Eq. (48a), we find a combination of the operator $K_{12'}$, which is singular for $|\mathbf{r}_{12'}| = a$, with the correlation functions $g_3(r_1, r_2, r_2')$ and $g_2(r_1, r_2')$, which are discontinuous on the same surface. However, because in our starting equation (39) these correlation functions are on the right of the operator, the rules of Ref. 19 unambiguously tell us that they should be taken at $|\mathbf{r}_{12'}| = a_+$.

upon the explicit form of the coefficients $A_{n,m}$ in Eq. (29). Yet this result is physically very reasonable, because, if our interpretation of $\delta f_{s,n}$ as a *dynamical* n-body correlation is correct, the only way it can be created through a single collision process from a lower order dynamical correlation is by having one dynamically uncorrelated particle interacting with a "cluster" of $n - 1$ already dynamically correlated particles.

Notice that with the notation $\delta f_{s,1} \equiv f_{s,1}$ and $\delta f_{s,0} \equiv 0$, Eq. (49) also applies for $n = 1$: It then reduces to (43).

3. INDEPENDENT PARTICLE APPROXIMATION

The formalism introduced in Section 2 is exact, but to make use of it, we need some kind of approximation scheme.

In order to get a hint, let us reconsider the operator $\mathscr{L}_{1,1}$ [Eq. (43)]. With the help of (40), it can be rewritten

$$\mathscr{L}_{1,1} = [-v_1\,(\partial/\partial r_1) + C^{\mathrm{E}}_{s,1}] \equiv \tilde{C}^{\mathrm{E}}_{s,1} \tag{50}$$

where $C^{\mathrm{E}}_{s,1}$ is the self-Enskog linearized collision operator:

$$\begin{aligned} C^{\mathrm{E}}_{s,1} f_{s,1}(t) = {}& a^2 \rho g_2(a_+) \int d\mathbf{v}_2 \int d\boldsymbol{\varkappa}\,(\boldsymbol{\varkappa}\cdot\mathbf{v}_{12})\theta(\boldsymbol{\varkappa}\cdot\mathbf{v}_{12}) \\ & \times [f_{s,1}(\mathbf{r}_1, \mathbf{v}_1'; t)\varphi(\mathbf{v}_2') - f_{s,1}(r_1, \mathbf{v}_1; t)\varphi(\mathbf{v}_2)] \end{aligned} \tag{51}$$

Hence, if we completely neglect $\delta f_{s,2}$, we obtain the Enskog equation for $f_{s,1}$. This latter equation has two important virtues:

1. For any initial condition of the type (9), it is exact at $t = 0$. This was shown explicitly in Ref. 3b and appears here as a consequence of the fact that

$$\delta f_{s,n}(0) = 0, \qquad n > 1 \tag{52}$$

for such an initial condition.

2. As can be observed from the experimental data of Alder *et al.*,$^{(4)}$ the Enskog equation gives a good approximate description of the time-dependent correlation functions at all times. From this point of view, the equation corresponding to (50) with soft potentials is much less interesting because it merely describes the free motion of the tagged particle.$^{(3b)}$ This is why we limit ourselves here to hard-sphere interactions.

Since the Enskog equation already gives good results, it is tempting to systematically improve it by taking into account the dynamical correlations due to two, three,... particles. The simplest procedure which comes to mind is of course truncation of our hierarchy for $\delta f_{s,n}$ at an order $n > 1$: For example, we could argue that since $\delta f_{s,2}$ is small (at least at contact)—as is testified by the success of the Enskog equation—$\delta f_{s,3}$ should be even smaller. Setting $\delta f_{s,3} = 0$ in Eq. (49) would give a closed system of equations for

$f_{s,1}$ and $\delta f_{s,2}$, from which a non-Markovian kinetic equation for $f_{s,1}$ would emerge. Although physically attractive, this procedure presents a number of difficulties, i.e., the complicated nature of the operator $\mathscr{L}_{2,2}$ [see Eqs. (C.2)–(C.4)] makes the resulting kinetic equation mathematically untractable.

We propose now an alternative approximation scheme, which is more useful. Suppose we have, at time t, an n-body dynamical correlation $\delta f_{s,n}(x_1, x_2, \ldots, x_n; t)$ and consider a configuration of the n particles such that all distances $|\mathbf{r}_{ij}|$ $(i, j \in \{1, \ldots, n\})$ are much larger than the range of molecular *equilibrium* correlations;[15] then these n particles have no way to influence each other and the evolution of $\delta f_{s,n}$ is given by the independent evolution of each of the n particles surrounded by a locally equilibrium fluid. We then assume that, at *all* distances $|\mathbf{r}_{ij}|$, this independent particle picture still furnishes a good zeroth-order approximation to the exact motion of $\delta f_{s,n}$. In order to put this verbal statement in a mathematical frame, let us remark that the operators $\mathscr{L}_{n,n-1}$, $\mathscr{L}_{n,n}$, and $\mathscr{L}_{n,n+1}$ depend on the spatial coordinates $r_1, \ldots, r_n$, e.g.,

$$\mathscr{L}_{n,n} f_{s,n} = \int \mathscr{L}_{n,n}(r_1, v_1, \ldots, r_n, v_n | x_1', \ldots, x_n') f_{s,n}(x_1', \ldots, x_n')\, dx_1' \cdots dx_n'$$

in a much more complicated way (involving the equilibrium correlations) than do the K_{ij} and $K_{i,n+1}$ defined in (39) and (40). We consider now the following limit:

$$\underset{(\infty)}{\mathscr{L}_{n,m}} \equiv \lim_{\substack{|r_{ij}| \to \infty \\ \forall ij \in \{1, \ldots, n\}}} \mathscr{L}_{n,m}, \qquad m = n - 1, n, n + 1 \tag{53}$$

Of course, $\mathscr{L}_{n,m}$ still depends on $x_1, \ldots, x_n$; as a matter of fact we shall see soon that it is of the form

$$\mathscr{L}_{n,m} = \sum_{i=1}^{n} l_{n,m}^{(i)}(x_i) \tag{54}$$

where $l_{n,m}^{(i)}$ only depends on the coordinate x_i.

The independent particle approximation amounts to assuming that $\mathscr{L}_{n,m}$ is a good zeroth-order approximation to the exact $\mathscr{L}_{n,m}$ for all distances. We thus write (49) as

$$\begin{aligned} \partial_t \delta f_{s,n} &- \big(\underset{\infty}{\mathscr{L}_{n,n-1}}\, \delta f_{s,n-1} + \underset{\infty}{\mathscr{L}_{n,m}}\, \delta f_{s,n} + \underset{\infty}{\mathscr{L}_{n,n+1}}\, \delta f_{s,n+1}\big) \\ &= \big(\mathscr{L}_{n,n-1} - \underset{\infty}{\mathscr{L}_{n,n-1}}\big)\, \delta f_{s,n-1} + \big(\mathscr{L}_{n,n} - \underset{\infty}{\mathscr{L}_{n,n}}\big)\, \delta f_{s,n} \\ &\quad + \big(\mathscr{L}_{n,n+1} - \underset{\infty}{\mathscr{L}_{n,n+1}}\big)\, \delta f_{s,n+1} \end{aligned} \tag{55}$$

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[15] Thinking in particular about the long-range hydrodynamic correlations which play such an important role in mode–mode coupling theories,(14) it is clear that dynamical correlations can persist over distances much larger than the range of the equilibrium correlations.

and we assume that the operators on the right-hand side of this equation can be formally treated as small quantities.

One nice feature of this formulation is that the operators $\underset{\infty}{\mathscr{L}}_{n,m}$ can be determined explicitly and turn out to be particularly simple. One finds

$$\underset{\infty}{\mathscr{L}}_{n,n-1} = 0 \tag{56a}$$

$$\underset{\infty}{\mathscr{L}}_{n,n} = \tilde{C}^{\mathrm{E}}_{s,1} + \sum_{i=2}^{n} \tilde{C}_i^{\mathrm{E}} \tag{56b}$$

$$\underset{\infty}{\mathscr{L}}_{n,n+1} = \mathscr{L}_{n,n+1} \tag{56c}$$

where $\tilde{C}^{\mathrm{E}}_{s,1}$ is the Enskog operator (50) corresponding to the labeled particle 1 and $\tilde{C}_i^{\mathrm{E}}$ is the corresponding operator for an arbitrary fluid particle $i \neq 1$; acting on a function $f(x_i; t)$, it gives[(3b)]

$$\begin{aligned} \tilde{C}_i^{\mathrm{E}} f(\ ,t) = \Big[& -\mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} - \beta\rho\varphi(v_i)\mathbf{v}_i \\ & \times \frac{\partial}{\partial r_i} \int dx_i' \, V(|\mathbf{r}_i - \mathbf{r}_i'|) f(x_i'; t) + C_i^{\mathrm{E}} f(\ ,t) \Big] \end{aligned} \tag{57}$$

where

$$\begin{aligned} C_i^{\mathrm{E}} f(\ ,t) = a^2 \rho g_2(a_+) \int d\mathbf{v}_j \int d\boldsymbol{\varkappa}\, (\boldsymbol{\varkappa}\cdot\mathbf{v}_{ij})\theta(\boldsymbol{\varkappa}\cdot\mathbf{v}_i) & \\ \times \Big[f(\mathbf{r}_i, \mathbf{v}_i'; t)\varphi(\mathbf{v}_j') + \varphi(\mathbf{v}_i') & \\ \times \int (\mathbf{r}_i - a\boldsymbol{\varkappa}, \mathbf{v}_j'; t) - f(r_i, \mathbf{v}_i; t)\varphi(\mathbf{v}_1) & \\ - \varphi(\mathbf{v}_i) f(\mathbf{r}_i + a\boldsymbol{\varkappa}, \mathbf{v}_j; t) \Big] & \end{aligned} \tag{58}$$

and

$$-\beta V(|\mathbf{r}_i - \mathbf{r}_i'|) = c(|\mathbf{r}_i - \mathbf{r}_i'|) + g(a_+)\theta(a - |\mathbf{r}_i - \mathbf{r}_i'|) \tag{59}$$

where $c(r)$ is the direct correlation function.

The proof of (56) for general n is far from trivial and will be reported elsewhere[(9)]; nevertheless, the simplest nontrivial example, $n = 2$, already nicely illustrates the general result, and this case is treated in detail in Appendix C.

With the help of (56), we now rewrite (55) as

$$\begin{aligned} \partial_t \delta f_{s,n} - \Big(\tilde{C}^{\mathrm{E}}_{s,1} + \sum_{i=2}^{n} \tilde{C}_i^{\mathrm{E}} \Big) \delta f_{s,n} - \mathscr{L}_{n,n+1}\, \delta f_{s,n+1} & \\ = \Big\{ \epsilon \mathscr{L}_{n,n-1}\, \delta f_{s,n-1} + \Big[\mathscr{L}_{n,n} - \Big(\tilde{C}^{\mathrm{E}}_{s,1} + \sum_{i=2}^{n} \tilde{C}_i^{\mathrm{E}} \Big) \Big] \delta f_{s,n} \Big\} & \end{aligned} \tag{60}$$

where we have introduced a dimensionless parameter ϵ ($\epsilon = 1$!), which we formally consider as small.

Let us examine a few formal properties of this hierarchy:

1. To order ϵ^0, we may neglect the right-hand side of Eq. (60) and, with the help of the initial condition (52), we find immediately

$$\delta f^{(0)}_{s,n}(t) = 0, \qquad n > 1 \tag{61}$$

Using (29) and (32), we recover (12). Hence, neglecting all deviations from the independent particle picture leads to a very natural generalization of the Enskog assumption (11) to the higher order distribution functions.

2. For ϵ small, a simple dimensional analysis of Eq. (60) tells us that, for fixed t,

$$\delta f_{s,n_1} \sim O(\epsilon^{n_1-1}) \tag{62}$$

Hence, if we want a theory correct to order ϵ^{n_1}, we may truncate the hierarchy at $n = n_1 + 1$ and the $(n_1 + 1)$th equation may be replaced by

$$\partial_t \delta f_{s,n_1+1} - \left(\tilde{C}^{\mathrm{E}}_{s,1} + \sum_{i=2}^{n_1+1} \tilde{C}_i^{\mathrm{E}}\right) \partial f_{s,n_1+1} = \epsilon \mathscr{L}_{n_1+1,n_1}\, \delta f_{s,n_1} + O(\epsilon^{n_1+1}) \tag{63}$$

We then get a closed system of equations for $f_{s,1}$, $\delta f_{s,2} \ldots \delta f_{s,n_1+1}$, whose solution for $\delta f_{s,2} \ldots \delta f_{s,n_1+1}$ leaves us in principle with a closed kinetic equation for $f_{s,1}$. This point will be illustrated in the next section for $n_1 = 1$.

3. We can also check that, to order ϵ^{n_1}, the first $2n_1$ time derivatives of $f_{s,1}$ at time $t = 0$ are given correctly. The only exceptional case is $n_1 = 0$, where the first time derivative is still given correctly. In order to show this, we notice that, in the short-time limit, we have

$$\delta f_{s,n} \propto t^{n-1} \tag{64}$$

as a consequence of the structure of the exact hierarchy (49) and of the initial condition (52). But the substitution of (63) in place of the exact corresponding equation (60) amounts to neglecting terms of the type

$$\epsilon\, \delta f_{s,n_1+1}, \quad \epsilon\, \delta f_{s,n_1+2} \tag{65}$$

From (64), neglecting such terms is rigorous when calculating the first n_1 derivatives of $\delta f_{s,n_1+1}$ at $t = 0$. It is easy to verify that the first $n_1 + 1$ derivatives of $\delta f_{s,n_1}$,..., first $2n$ derivatives of $f_{s,1}$ are then also reproduced correctly. The exceptional character of the case $n_1 = 0$ stems from the fact that, to order ϵ^0, no term of the type $\epsilon f_{s,1}$ is neglected in the first hierarchy equation.

4. Although no rigor can be claimed for the following remark, we have an argument which indicates that, to any order in ϵ, the distribution functions

$f_{s,n}$ tend, for long times, toward their equilibrium value. A convincing argument on this point would be very encouraging: It is known that very often no order-by-order perturbation expansion is possible because of secular effects; this is the case, for example, with a straightforward expansion in power of the coupling strength for smooth potentials (see, e.g., Ref. 20). Our argument is presented in Appendix E.

4. THE FIRST APPROXIMATION

Although the formalism introduced in the preceding section shows interesting formal properties, it remains to demonstrate that it is useful for explicit calculations. Of course, expansion to arbitrary order in ϵ is hopeless and we shall henceforth limit ourselves to the first nontrivial order ϵ^1. Moreover, we shall postpone for separate publication$^{(16)}$ the detailed study of this first-order kinetic equation; we shall content ourselves here with presenting those general properties of this equation that can be inferred very simply from previous work on hard-sphere dynamics.

We thus take Eq. (63), with $n_1 = 1$, and formally solve it for $\delta f_{s,2}$ in terms of $\delta f_{s,1} \equiv f_{s,1}$, with the help of initial condition (52):

$$\delta f_{s,2}(t) = \epsilon \int_0^t d\tau \, \{\exp[(\tilde{C}^{\mathrm{E}}_{s,1} + \tilde{C}_2{}^{\mathrm{E}})\tau]\} \mathscr{L}_{2,1} f_{s,1}(t-\tau) \tag{66}$$

Let us stress that, in contrast with (62), we do not expand $\delta f_{s,2}$ itself in powers of ϵ; we shall discuss this procedure later.

Putting (66) into (43), we arrive at a closed kinetic equation for $f_{s,1}$ [see also (50)]:

$$\partial_t f_{s,1}(x_1; t) = \tilde{C}^{\mathrm{E}}_{s,1} f_{s,1}(t) + \epsilon \int_0^t G_{s,1}(\tau) f_{s,1}(t-\tau)\, d\tau \tag{67}$$

where the non-Markovian kernel $G_{s,1}(\tau)$ is defined by

$$G_{s,1}(\tau) f_{s,1}(t-\tau) = \mathscr{L}_{1,2}\{\exp[(\tilde{C}^{\mathrm{E}}_{s,1} + \tilde{C}_2{}^{\mathrm{E}})\tau]\} \mathscr{L}_{2,1} f_{s,1}(t-\tau) \tag{68}$$

We see here that the approximation (66) amounts to replacing the kernel $\mathscr{G}_{s,1}(\tau)$ of the exact formal kinetic equation for $f_{s,1}$,

$$\partial_t f_{s,1}(x_1; t) = \int_0^t g_{s,1}(\tau) f_{s,1}(t-\tau)\, d\tau \tag{69}$$

by the first two terms,

$$\mathscr{G}_{s,1}(\tau) = \tilde{C}^{\mathrm{E}}_{s,1}\, \delta(\tau) + \epsilon G_{s,1}(\tau) + O(\epsilon^2) \tag{70}$$

in its ϵ expansion. Although this procedure is, strictly speaking, not completely consistent (one should expand the *solution* of the kinetic equation around its zeroth-order approximation, and not the non-Markovian kernel of this equation), similar expansions are often made in the literature (see Ref. 22 for the example of the density expansion); they can be developed quite systematically. Here, to order ϵ^1, there is of course no need for such a systematic procedure, and the simple equation (50) suffices. Although the only exact property of (51) is that it leads to the correct first ϵ^1 correction for its solution $f_{s,1}$, it is hoped that it also retains some relevant part of the higher order terms.

From the explicit definition (68) of the kernel $G_{s,1}(\tau)$, we now want to verify the properties of the kinetic equation (67) which were described in the introduction. We first remark that, at $t = 0$, the exact first two derivatives of $f_{s,1}$ are obtained exactly from (51):

$$\partial_t f_{s,1}\big|_{t=0}^{\text{exact}} = \tilde{C}_{s,1}^{\mathrm{E}} f_{s,1}(0) \tag{71}$$

$$\partial_t^2 f_{s,1}\big|_{t=0}^{\text{exact}} = (\tilde{C}_{s,1}^{\mathrm{E}})^2 f_{s,1}(0) + G_{s,1}(0) f_{s,1}(0) \tag{72}$$

This is an immediate consequence of a general property established in Section 3.

Second, in the low-density limit, we can show that Eq. (67) correctly reproduces, beyond the trivial Boltzmann term, those terms in the linearized Choh–Uhlenbeck triple collision operator that describe one, two, and three dynamic binary collisions, weighted by the correct excluded volume factors(12,23); quadruple collisions terms are completely absent but they are known to be extremely small [$\sim O(10^{-6})$]. We have not been able to find any deep justification for this result, which we prove, in Appendix D, by a pedestrian comparison with previous calculations.

Third, the calculation of the density expansion of the self-diffusion coefficient with this equation leads to nonanalytic contributions(13):

$$D = (1/\rho)D^{(0)} + D^{(1)} + (\rho \ln \rho)D^{(2)} + \cdots \tag{73}$$

where $D^{(2)}$ agrees with other work.

Fourth, the velocity correlation function calculated with the same equation leads to a long-time tail of the form

$$\langle \mathbf{v}(t)\mathbf{v}(0)\rangle \underset{t\to\infty}{=} \alpha / t^{3/2} \tag{74}$$

However, the proportionality coefficient α does not take the value which is believed now to be correct (i.e., $\alpha = k_B T/\{12[\pi(\eta/nm + D)]^{3/2}\}$, where η and D, respectively, are the exact viscosity and diffusion coefficients), except in the dilute gas limit.

The two properties (73) and (74) are closely connected. Indeed, they both are known to be consequences of the dominant role played by the so-called "ring diagrams" in these problems. But we can readily verify that the kernel $G_{s,1}(\tau)$ [Eq. (68)] does contain, among other things, these "ring" contributions. Indeed, if we retain only the first term on the right-hand side of (48a) for $\mathscr{L}_{2,1}$, we generate a corresponding expression for the kernel:

$$G_{s,1}(\tau)|_{\text{ring}} = \rho \int dx_2\, K_{12}\, \{\exp[(\tilde{C}^{\mathrm{E}}_{s,1} + C_2{}^{\mathrm{E}})\tau]\} g_2(r_1, r_2) \times [K_{12}, f_{s,1}(t)/\varphi(v_1)]\varphi(v_1)\varphi(v_2) \tag{75}$$

By direct comparison with previous works,(13,15) this expression can be identified with the "ring" terms, evaluated in the Enskog approximation.[16] Hence, (73) and (74) will be immediate consequences of our theory if we can show that the second term of (48a) does not spoil these asymptotic formulas. This can be done with little difficulty, but, since a similar problem will be tackled explicitly in the second paper of this series,(16) we shall not do this here.

These very attractive features make our first-order kinetic equation (51) an excellent candidate for approximately describing the dynamic properties of a hard-sphere fluid for all times and all densities. We shall, however, leave such an analysis for a further publication.(16) The extension of the theory to the "total" case, where all the particles play a symmetric role, and to an interaction involving a small attractive part superimposed on the hard core, is straightforward and will be reported elsewhere.(9)

5. DISCUSSION

In this section we summarize the formalism developed in this paper. By eliminating all computational details, the structure, including all the weak links, is exposed.

Let $f_{s,n}(x_1, \ldots, x_n; t)$, $n = 1, 2, \ldots$, be the thermodynamic (infinite-volume) limit of the time-dependent self-distribution of a fluid. These functions are the solution of the infinite BBGKY hierarchy, which may be written in the form(11)

$$\partial f_{s,n}/\partial t = H_{n,n} f_{s,n} + H_{n,n+1} f_{s,n+1} \tag{76}$$

with specified initial conditions:

$$\begin{aligned} f_{s,1}(x_1; 0) &= W_1(x_1) \\ f_{s,l}(x_1, \ldots, x_l; 0) &= \left[\prod_{j=2}^{l} \varphi(v_j)\right] \rho^{l-1} g_l(r_1, \ldots, r_l) W_1(x_1), \qquad l > 1 \end{aligned} \tag{77}$$

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[16] Professor E. G. D. Cohen has informed us that D. Lieberworth is also analyzing the role of the finite time contributions of these "ring terms."

Before discussing our approximation scheme we make several remarks on these equations:

1. The operators $H_{n,n}$ and $H_{n,n+1}$ are "well-defined" for hard-sphere systems. Indeed, since $H_{n,n+1}$ is an integral (not a differential–integral) operator for hard spheres, Eq. (76), which can be written concisely as

$$\partial \mathbf{f}_s/\partial t = H\mathbf{f}_s, \qquad \mathbf{f}_s = (f_{s,1}, f_{s,2}, \ldots) \tag{78}$$

has solutions which are in some ways better behaved for hard spheres than for systems with soft forces.(24)

2. It follows from recent results on the time evolution of infinite systems(24,25) that (76) with the initial conditions (77) will have a well-defined solution for all fixed time t. Whether the solution has a limit as $t \to \infty$ and whether that limit corresponds to an approach to equilibrium depends on the ergodic properties of infinite systems, about which very little is known at the present time(26) [For finite systems of hard spheres, it follows from Sinai's results (unpublished but see Ref. 26) that the $f_{s,n}$ do approach their equilibrium values as $t \to \infty$).

3. Since the operators $H_{n,n}$ and $H_{n,n+1}$ and the equilibrium correlations $g_n(r_1,\ldots, r_n)$ are symmetric in $x_1,\ldots x_n$, it follows from (77) that $f_{s,n}(x_1,\ldots x_n; t)$ will be symmetric in $x_2,\ldots, x_n$ but not in x_1 *unless* $W_1(x_1) = \text{const} \times \varphi(v_1)$, which corresponds to the $f_{s,n}(x_1,\ldots, x_n; 0)$ being equal (or proportional) to their equilibrium values. For such initial conditions we would of course have $\partial f_{s,n}/\partial t = 0$.

There is clearly no hope of ever obtaining an exact solution of (76) for any system more complicated than a one-dimensional system of hard rods.(2) We are therefore forced to look for approximation schemes. Desirable criteria for good approximation schemes include: (1) physical reasonableness, (2) mathematical tractability, and (3) a systematic procedure for improving the approximation; in principle at least, this would give a sequence of approximate $f_{s,n}$ that converge to the exact solution. We are actually interested primarily in $f_{s,1}$; or even more restrictively, just in certain moments of $f_{s,1}$, such as the velocity autocorrelation function or the incoherent neutron scattering function.

The approximation scheme developed in this paper is, to our mind, the natural generalization of the (unsystematic) first approximation for hard spheres given by Lebowitz *et al.*,(3b) which leads to the Enskog equation for $f_{s,1}$. Our method utilizes a specific nontrivial representation of the $f_{s,n}$. We write

$$f_{s,n}(x_1,\ldots, x_n; t) = \sum_{j=1}^{n} D_{n,j}\, \delta f_{s,j} \tag{79}$$

where the $D_{n,j}$ are time-independent linear operators,

$$D_{n,j}\,\delta f_{s,j} = \int \cdots \int dx_1' \cdots dx_j'\, \mathscr{D}_{n,j}(x_1 \cdots x_n | x_1' \cdots x_j') \times \delta f_{s,j}(x_1',..., x_j'; t) \tag{80}$$

which depend only on the equilibrium correlations g_l, $l \leqslant n + j$; they are symmetric in $\{x_2,..., x_n\}$ and in $\{x_2',..., x_j'\}$, with

$$\mathscr{D}_{n,n} = \prod_{i=1}^{n} \delta(x_i - x_i'), \qquad \delta f_1 \equiv f_1 \tag{81}$$

Using the same notation as in (78), we may write (79) in the form

$$\mathbf{f}_s = D\,\boldsymbol{\delta}\mathbf{f}_s \tag{82}$$

Taken by themselves, Eqs. (79)–(81) do not in any way define the $D_{n,j}$ for $j < n$. (In particular we could set them equal to zero and have trivially $f_{s,n} = \delta f_{s,n}$.) What we are interested in, however, is to choose the $D_{n,j}$ in such a way that if we set $\delta f_{s,j} = 0$ for $j > k$ we would have, for our problem, a good (hopefully the best) approximate description of the $f_{s,n}$ for $n > k$ in terms of the first k distributions.

Our physical intuition then leads us (cf. Refs. 3b and 17) to define the $D_{n,j}$ through the W's introduced in Section 2. This, we believe, makes the $D_{n,j}$, for $j \leqslant k$, describe the effects of the j-particle dynamical correlations in $f_{s,n}$.

Our belief is strengthened by the form which the BBGKY equations take on in terms of the $\delta f_{s,n}$. Combining (82) with (78) gives

$$\partial \boldsymbol{\delta}\mathbf{f}_s/\partial t = (D^{-1}HD)\,\boldsymbol{\delta}\mathbf{f}_s = \mathscr{L}\,\boldsymbol{\delta}\mathbf{f}_s \tag{83}$$

The interesting fact is now that $\mathscr{L}$ is just a tridigonal operator matrix, which shows that the dependence of $\delta f_{s,n}$ on $\delta f_{s,k}$, $k < n$, changes in time only through collisions of a dynamically correlated group of $n - 1$ particles with an uncorrelated particle.

Equation (83) is formally equivalent to (76) or (78) and the initial conditions (77) correspond now to

$$\delta f_{s,1}(x_1; 0) = W_1(x_1), \qquad \delta f_{s,j}(x_1,..., x_j; 0) = 0, \quad j \geqslant 2 \tag{84}$$

All we have gained by transforming (76) and (77) into (83) and (84) is a form suitable for our approximation scheme. Setting $\delta f_{s,j} = 0$ for $j \geqslant 2$ leads to a non-Markovian equation for $f_{s,1}$ which contains, we believe, all the essential physics of the problem, e.g., the long-time tails in the velocity autocorrelation function. This is, however, only a belief since the resulting equation for $f_{s,1}$ is hardly mathematically tractable. We therefore chose, in

Section 3, an alternative scheme which we believe is physically reasonable. We write formally

$$\mathscr{L} = \underset{\infty}{\mathscr{L}} + \epsilon\left[\mathscr{L} - \underset{\infty}{\mathscr{L}}\right] \tag{85}$$

and then argue that, with our initial conditions (84), $\delta f_{s,n} \propto O(\epsilon^{n-1})$ for any fixed time t. Therefore to zeroth order in ϵ we again obtain the Enskog equation, while to first order in ϵ we still obtain a closed set of equations for $f_{s,1}$ and $\delta f_{s,2}$ which now leads to a more tractable non-Markovian equation for f. This equation is solved approximately in Ref. 16 and the good results obtained from it are described in Section 4.

We should mention here that while it would be very desirable to express the $D_{n,j}$ directly in terms of the infinite-volume equilibrium correlations, without going through the awkward use of the W's for finite systems, we have so far not found a simple, general way for doing this.

APPENDIX A. CONSTRUCTION OF THE $A_{n,m}$

Consider first the quantity

$$I_n = \lim_{\Omega} N^{n-1} \int dx_{n+1} \cdots dx_n\, \Omega\mu_0 \sum_{1<j_2<j_3\cdots<j_m} \frac{f_m(x_1, x_{j_2},\ldots, x_{j_m}; t)}{\varphi(v_1)\varphi(v_{j_2}) \cdots \varphi(v_{j_m})} \tag{A.1}$$

defined for any function f_m, symmetric in its $m-1$ variables different from x_1, which goes to zero at large distances; I_n is a linear functional of f_m and can be written formally as

$$\begin{aligned} I_n \equiv \int dx_2' \cdots dx_m'\, \mathscr{E}_{n,m}(x_1, x_2,\ldots, x_n | x_1, x_2',\ldots, x_m') \\ \times f_m(x_1, x_2',\ldots, x_m'; t) \end{aligned} \tag{A.2}$$

where $\mathscr{E}_{n,m}$ depends on the equilibrium correlation functions $g_{n+m}, g_{n+m-1},\ldots, g_u$, with $u = \text{Max}\,(m, n)$. Its explicit form can be written in general but we shall not need this here. For example, we have

$$\begin{aligned} \mathscr{E}_{3,2}(x_1, x_2, x_3 | x_1, x_2') = \rho^2 g_3(r_1, r_2, r_3)\,[\delta(x_1 - x_2')\varphi(v_3) \\ + \delta(x_3 - x_2')\varphi(v_2)] \\ + \rho^3 g_4(r_1, r_2, r_3, r_2')\varphi(v_2)\varphi(v_3) \end{aligned} \tag{A.3}$$

We shall generally abbreviate (A.2) by writing

$$I_n = E_{n,m} f_m \tag{A.4}$$

Take now the mth term in the expansion (13):

$$\mu^{(m)} = \Omega\mu_0\Bigg[\sum_{1<j_2\cdots<j_m} \frac{W_m(x_1, x_{j_2},\ldots, x_{j_m}; t)}{\varphi(v_1)\cdots\varphi(v_{j_m})} + \sum_{1<j_2\cdots<j_{m-1}} \frac{W_m^{(m-1)}(x_1, x_{j_2},\ldots, x_{j_{m-1}}; t)}{\varphi(v_1)\cdots\varphi(v_{j_{m-1}})} + \cdots + \frac{W_m^{(1)}(x_1; t)}{\varphi(v_1)}\Bigg] \tag{A.5}$$

The conditions that generalize (20) and (28) impose

$$\lim_{\Omega} N^{n-1}\int dx_{n+1}\cdots dx_N\,\mu^{(m)} = 0, \qquad n = 1, 2,\ldots, m-1 \tag{A.6}$$

With the help of the notation (A.4), this leads to a system of $m - 1$ linear equations:

$$E_{n,m}W_m + E_{n,m-1}W_m^{(m-1)} + \cdots + E_{n,1}W_m^{(1)} = 0, \qquad n = 1, 2,\ldots, m-1 \tag{A.7}$$

which, in principle, can be solved for $W_m^{(m-1)},\ldots, W_m^{(1)}$ in terms of W_m. We write this solution as

$$W_m^{(m-i)} = \Gamma_{m-i,m}W_m, \qquad i = 1, 2,\ldots, m-1 \tag{A.8}$$

where the $\Gamma_{m',m}$ $(m' < m)$ are linear functionals of the same type as the $E_{n,m}$. Of course, their explicit form is in general very complicated, but it can be found in simple cases (see Appendix B).

For $n \geqslant m$, the contribution of $\mu^{(m)}$ to $f_{s,m}$ is given by

$$\begin{aligned} f_{s,n} &= \lim_{\Omega} N^{n-1}\int dx_{n+1}\cdots dx_N\,\mu^{(m)} \\ &= E_{n,m}W_m + \sum_{i=1}^{m-1} E_{n,i}W_m^{(m-i)} \end{aligned} \tag{A.9}$$

and, from (A.8), this can be rewritten as

$$f_{s,n} = A_{n,m}W_m \tag{A.10}$$

where

$$A_{n,m} = \sum_{m'\leqslant m} E_{n,m}\Gamma_{m',m} \tag{A.11}$$

with $\Gamma_{m,m} \equiv 1$. Summing (A.10) over all $m \leqslant n$, we recover Eq. (29) of the text.

APPENDIX B. CALCULATION OF $B_{2,2}$

Because of the condition $m \leqslant n$ on the summation in Eq. (29), the inversion of the matrix A [see (33)] can be done step by step. For example, from $f_{s,1} = W_1$ and [see (31)]

$$f_{s,2} = A_{2,1}W_1 + A_{2,2}W_2 \tag{B.1}$$

we get readily

$$W_2 = (A_{2,2})^{-1}[f_{s,2}(x_1, x_2; t) - \rho g_2(r_1, r_2)f_{s,1}(x_1; t)\varphi(v_2)] \tag{B.2}$$

Thus

$$B_{2,2} = (A_{2,2})^{-1} \tag{B.3}$$

Nevertheless, because $A_{2,2}$ is a linear functional [see (31)], the calculation of $(A_{2,2})^{-1}$ is not trivial. To see how this can be done, at least in principle, let us introduce the following three-body conditional correlation function:

$$G_3(r_1; r_2, r_3) = \left[\frac{g_3(r_1, r_2, r_3)}{g_2(r_1, r_2)g_2(r_1, r_3)} - 1\right] \tag{B.4}$$

and let us define a three-body direct correlation function $d(r_1; r_2, r_3)$ by the formula

$$G_3(r_1; r_2, r_3) = d(r_1; r_2, r_3) + \rho \int dr_1\, d(r_1; r_2, r_4)g_2(r_1, r_4) \times G_3(r_1; r_4, r_3) \tag{B.5}$$

In order to see more clearly the physical meaning of this quantity d_3, let us notice that the tagged particle 1 plays a special role in the above equations; hence, it is rather natural to consider this particle 1 as the source of an external field which acts on the other molecules in the system; with this interpretation, we identify

$$\rho g_2(r_1, r_2) \equiv \tilde{\rho}_1(r_2), \qquad \rho g_3(r_1, r_2, r_3) \equiv \tilde{\rho}_2(r_2, r_3) \tag{B.6}$$

where the $\tilde{\rho}_n(r_2, \ldots, r_{n+1})$ denote the fluid distribution functions in this external field. Letting $\tilde{d}(r_2, r_3) = d(r_1; r_2, r_3)$, we see that (B.5) can be written as

$$\tilde{G}_2(r_2, r_3) = \tilde{d}(r_2, r_3) + \int dr_4\, \tilde{d}(r_2, r_4)\tilde{\rho}_1(r_4)\tilde{G}_2(r_4, r_3) \tag{B.7}$$

with an obvious definition for the pair correlation function $\tilde{G}_2$. We see that $\tilde{d}$ is nothing else than the usual Ornstein–Zernicke direct correlation function in the external field created by particle 1. With the definition (B.5), it is a simple matter to formally invert $A_{2,2}$, given by (31) (see Ref. 3b for a similar calculation). If we define the quantity $\mathscr{F}(x_1, x_2, x_3)$ by

$$\mathscr{F}(x_1; x_2, x_3) = \delta(x_2 - x_3) - \rho\varphi(v_2)g_2(r_1, r_2)d(r_1; r_2, r_3) \tag{B.8}$$

it is easily shown that

$$W_2(x_1, x_2; t) = \frac{1}{\rho g_2(r_1, r_2)} \int dx_3 \, \mathscr{F}(x_1; x_2, x_3)[f_{s,2}(x_1, x_3; t) - \rho g_2(r_1, r_3) f_{s,1}(x_1; t)\varphi(v_3)], \qquad |r_{12}| > a \tag{B.8$'$}$$

which is the explicit representation of (B.2).

For later use, let us point out an interesting property of the function d. Consider Eq. (26) in the limit where the distance between particles 1 and 2 becomes much larger than the range of interaction (mathematically, we take $|r_{12}| \to \infty$). With the abbreviation

$$k(r_1, r_2, r_2') \equiv [g_3(r_1, r_2, r_2') - g_2(r_1, r_2) g_2(r_1, r_2')\} \tag{B.9}$$

we decompose in this limit the integral on the right-hand side of (26) into three parts:

1. $|r_{2'1}|$ *finite* (hence $|r_{2'2}| \to \infty$).

$$\lim k(r_1, r_2, r_2') = 0, \qquad |r_{2'1}| \text{ finite}, \quad |r_{2'2}| \to \infty \tag{B.10}$$

2. $|r_{2'2}|$ *finite* (hence $|r_{1'1}| \to \infty$):

$$\lim k(r_1, r_2, r_2') = [g_2(r_2, r_2') - 1], \qquad |r_{2'2}| \text{ finite}, \quad |r_{2'1}| \to \infty \tag{B.10$'$}$$

3. $|r_{2'1}|$ *and* $|r_{2'2}|$ *both large*:

$$\lim k(r_1, r_2, r_2') = 0, \qquad |r_{2'2}| \to \infty, \quad |r_{2'1}| \to \infty \tag{B.10$''$}$$

In this limit, Eq. (26) thus becomes

$$\delta f_{s,2}(x_1, x_2; t) \underset{|r_{12}| \to \infty}{=} \rho W_2(x_1, x_2; t) + \rho\varphi(v_2) \int dx_2' \times [g_2(r_2, r_2') - 1] W_2(x_1, x_2'; t) \tag{B.11}$$

The inversion of this formula can be done immediately with the help of the usual (Ornstein–Zernicke) direct correlation function $c(|r_1 - r_2|)$,(3b)

$$W_2(x_1, x_2; t) \underset{|r_{12}| \to \infty}{=} (1/\rho) \int dx_3 \, \tilde{C}(x_2, x_3) \, \delta f_{s,2}(x_1, x_3; t) \tag{B.12}$$

where

$$\tilde{C}(x_2, x_3) = \delta(x_2 - x_3) - \rho\varphi(v_2) c(|r_2 - r_3|) \tag{B.13}$$

Comparing this limiting result (B.11) and (B.12) with the exact equations (B.8) and (B.9), we infer that

$$\lim d(r_1; r_2, r_3) \underset{|r_{12}| \to \infty}{=} c(r_2, r_3) \tag{B.14}$$

APPENDIX C. PROPERTIES OF $\mathscr{L}_{2,m}$ $(m = 1, 2, 3)$

Direct computation along the lines indicated in the text, after Eq. (46), leads to Eq. (47), with the following expressions for $\mathscr{L}_{2,1}$, $\mathscr{L}_{2,2}$, $\mathscr{L}_{2,3}$. We have

$$\begin{aligned}\mathscr{L}_{2,1}f_{s,1}(t) = {} & \rho\left[\left(-v_1\frac{\partial}{\partial r_1} - v_2\frac{\partial}{\partial r_2}\right)g_2(r_1, r_2)\right]f_{s,1}(x_1; t)\varphi(v_i) \\ & + \rho K_{12}f_{s,1}(x_1; t)\varphi(v_2)g_2(r_1, r_2) \\ & + \rho^2\int dx_3\, K_{13}[g_3(r_1, r_2, r_3) - g_2(r_1, r_2)g_2(r_1, r_3)] \\ & \times f_{s,1}(x_1; t)\varphi(v_2)\varphi(v_3) \\ & + \rho^2\int dx_3\, K_{23}g_3(r_1, r_2, r_3)f_{s,1}(x_1; t)\varphi(v_2)\varphi(v_3) \qquad \text{(C.1)}\end{aligned}$$

and

$$\mathscr{L}_{2,2} = -v_1\frac{\partial}{\partial r_1} - v_2\frac{\partial}{\partial r_2} + \mathscr{L}'_{2,2} + \mathscr{L}''_{2,2} + K_{12} \qquad \text{(C.2)}$$

where

$$\begin{aligned}&\mathscr{L}'_{2,2}\,\delta f_{s,2}(t) \\ &\quad = \int dx_3\, K_{13}\Big\{\rho^2 g_3(r_1, r_2, r_3)W_2(x_1, x_2; t)\varphi(v_3) \\ &\quad + \rho^2[g_3(r_1, r_2, r_3) - g_2(r_1, r_2)g_2(r_1, r_3)] \\ &\quad \times W_2(x_1, x_3; t)\varphi(v_2) \\ &\quad + \rho^3\int dx_4[g_4(r_1, r_2, r_3, r_4) - g_3(r_1, r_2, r_3)g_2(r_1, r_4) \\ &\quad - g_3(r_1, r_3, r_4)g_2(r_1, r_2) + g_2(r_1, r_3)g_2(r_1, r_4)g_2(r_1, r_3)] \\ &\quad \times W_2(x_1, x_4; t)\varphi(v_2)\varphi(v_3)\Big\} \qquad \text{(C.3)}\end{aligned}$$

and

$$\begin{aligned}&\mathscr{L}''_{2,2}\,\delta f_{s,2}(t) \\ &\quad = \int dx_3\, K_{23}\Big\{\rho^2 g_3(r_1, r_2, r_3)[W_2(x_1, x_2; t)\varphi(v_3) \\ &\quad + W_2(x_1, x_3; t)\varphi(v_2)] \\ &\quad + \rho^3\int dx_4[g_4(r_1, r_2, r_3, r_4) - g_3(r_1, r_2, r_3) \\ &\quad \times g_2(r_1, r_4)]W_2(x_1, x_4; t)\varphi(v_2)\varphi(v_3)\Big\} \qquad \text{(C.4)}\end{aligned}$$

Here W_2 is itself linearly related to $\delta f_{s,2}$ by (26). Finally, we get

$$\mathscr{L}_{2,3}\,\delta f_{s,3}(t) = \int dx_3\,(K_{13} + K_{23})\,\delta f_{s,3}(x_1, x_2, x_3; t) \qquad \text{(C.5)}$$

In order to transform $\mathscr{L}_{2,1}$ into the compact form of Eq. (48) of the text, we merely have to use the second BBGKY equation at equilibrium:

$$\left(v_1 \frac{\partial}{\partial r_1} + v_2 \frac{\partial}{\partial r_2} - K_{12}\right) g_2(r_1, r_2)\varphi(v_1)\varphi(v_2)$$

$$= \rho \int dx_3\,[K_{13} + K_{23}] g_3(r_1, r_2, r_3)\varphi(v_1)\varphi(v_2)\varphi(v_3) \qquad \text{(C.6)}$$

in order to rewrite the first and last terms in the right-hand side of (C.1).

We now want to establish the asymptotic properties (56a)–(56c) for the case $n = 2$. Equation (56a), which becomes here

$$\lim_{|r_{12}|\to\infty} \mathscr{L}_{2,1} = 0 \qquad \text{(C.7)}$$

is quite trivial to prove; indeed, the first term in (48a) vanishes in the limit $|r_{12}| \to \infty$ because we have [see (40)]

$$\lim_{|r_{12}|\to\infty} K_{12} \propto \lim_{|r_{12}|\to\infty} \delta(|r_{12}| - a) = 0 \qquad \text{(C.8)}$$

and, with the help of (B.10), a similar property is readily established for the second term.

Equation (56b), namely

$$\lim_{|r_{12}|\to\infty} \mathscr{L}_{2,2} = \tilde{C}^{\mathrm{E}}_{s,1} + \tilde{C}_2^{\mathrm{E}} \qquad \text{(C.9)}$$

is trickier to prove. Consider, for example, in this limit $\mathscr{L}''_{2,2}$ given by Eq. (C.4). Because of (C.8), we know that in the integral over r_3 in (C.4), the only region that contributes is such that r_3 is close to r_2, and thus far from r_1 in the limit $|r_{12}| \to \infty$. In analogy with (B.9) and (B.10), we put

$$l(r_1, r_2, r_3, r_4) \equiv [g_4(r_1, r_2, r_3, r_4) - g_3(r_1, r_2, r_3) g_2(r_1, r_4)] \qquad \text{(C.10)}$$

and we consider three regions in the limit $|r_{12}| \to \infty$:

1. $|r_{41}|$ *finite* (thus $|r_{34}|$ and $|r_{24}| \to \infty$):

$$\lim l(r_1, r_2, r_3, r_4) = 0 \qquad \text{(C.11a)}$$

$|r_{41}|$ finite, $|r_{23}|$ finite, $|r_{12}| \to \infty$

2. $|r_{42}|$ *and* $|r_{43}|$ *finite* (hence $|r_{14}| \to \infty$):

$$\lim l(r_1, r_2, r_3, r_4) = (g_3(r_2, r_3, r_4) - g_2(r_2, r_3)) \qquad \text{(C.11b)}$$

$|r_{12}| \to \infty$, $|r_{23}|$, $|r_{24}|$ finite

3. $|r_{43}|$ *and* $|r_{42}| \to \infty$ (and $|r_{41}| \to \infty$):

$$\lim l(r_1, r_2, r_3, r_4) = 0 \tag{C.11c}$$

$|r_{12}| \to \infty, \qquad |r_{14}| \to \infty, \qquad |r_{23}|$ finite

Since the only nonvanishing term, (C.11a), goes to zero for $|r_{24}| \to \infty$, we may thus write from (C.3)

$$\begin{aligned}\lim_{|r_{12}|\to\infty} \mathscr{L}''_{2,2}\, \delta f_{s,2} = \lim_{|r_{12}|\to\infty} \rho \int dx_3\, K_{23} \Big\{ & g_2(r_2, r_3)[\rho W_2(x_1, x_2; t) \\ & \times \varphi(v_3) + \rho W_2(x_1, x_3; t)\varphi(v_2)] \\ & + \rho^2 \int dx_4\, [g_3(r_2, r_3, r_4) - g_2(r_2, r_3)] \\ & \times W_2(x_1, x_4; t)\varphi(v_2)\varphi(v_3) \Big\}\end{aligned} \tag{C.12}$$

where the x_4 integral extends over the whole phase space of particle 4. We now use (B.11) in order to transform the first two terms of (C.12). With the help of the identity

$$\int dx_3\, K_{23} g_2(r_2, r_3)\varphi(v_2)\varphi(v_3)\Phi(x_1, x_2) = 0 \tag{C.13}$$

valid for any function $\Phi(x_1, x_2)$ (as can be immediately verified by using as integration variable $r_{32} = r_3 - r_2$), we then cast (C.12) into the following form:

$$\lim_{|r_{12}|\to\infty} \mathscr{L}''_{2,2}\, \delta f_{s,2} = C_2{}^{\mathrm{E}}\, \delta f_{s,2} + \delta\mathscr{L}''_{2,2}\, \delta f_{s,2} \tag{C.14}$$

where $C_2{}^{\mathrm{E}}$ is given by Eq. (59), while we have

$$\begin{aligned}\delta\mathscr{L}''_{2,2}\, \delta f_{s,2} = \lim_{|r_{12}|\to\infty} \rho \int dx_3\, K_{23} \Big\{ & -\rho^2 g_2(r_2, r_3) \\ & \times \varphi(v_2)\varphi(v_3) \int dx_4\, [g_2(r_3, r_4) - 1] W_2(x_1, x_4; t) \\ & + \rho^2 \int dx_4\, g_3(r_2, r_3, r_4) W_2(x_1, x_4; t) \Big\}\end{aligned} \tag{C.15}$$

The term of (C.15) involving g_3 is simplified with the help of the second BBGKY equilibrium hierarchy (C.6). After some rearrangement of dummy variables, we arrive at

$$\begin{aligned}\delta\mathscr{L}''_{2,2}\, \delta f_{s,2} = \lim_{|r_{12}|\to\infty} \Big\{ & -\rho^2 \int dx_4\, [W_2(x_1, x_4; t) + \rho\varphi(v_4) \\ & \times \int dx_4{}'\, g_2(r_4, r_4{}') W_2(x_1, x_4{}'; t)] \\ & \times K_{24} g_2(r_2, r_4)\varphi(v_2)\varphi(v_4) \\ & + \rho^2 v_2 \frac{\partial}{\partial r_2} \int dx_4\, [g_2(r_2, r_4) - 1] W_2(x_1, x_4; t) \Big\}\end{aligned} \tag{C.16}$$

Because the distance $|r_{14}|$ goes to infinity with $|r_{12}|$, we may use Eq. (B.10) to simplify the first term of (C.16); in the second term, we use similarly (B.11) together with the definition

$$[g_2(r_2, r_4) - 1] = c(|r_2 - r_4|) + \rho \int dr_4'\, c(|r_2 - r_4'|) g_2(r_4', r_4) \tag{C.17}$$

of the direct correlation function $c(|r_1 - r_2|)$. We obtain then

$$\delta \mathscr{L}''_{2,2}\, \delta f_{s,2} = -\beta \rho \varphi(v_2) v_2 \frac{\partial}{\partial r_2} \int dx_2'\, V(r_2 - r_2')\, \delta f_{s,2}(x_1, x_2'; t) \tag{C.18}$$

in agreement with Eqs. (57) and (59). A similar but simpler proof holds for $\mathscr{L}'_{2,2}$ but we shall not reproduce it here. We are then immediately led to (C.10). The demonstration for arbitrary n runs along similar lines, though it is technically much more involved.$^{(10)}$

APPENDIX D. LOW-DENSITY LIMIT[17]

The detailed analysis of hard-sphere three-body collisions is a technically complicated problem, and has been discussed mostly by Sengers and co-workers (see, e.g., Refs. 21 and 23). In order to compare their results with the low-density limit of the present theory, we shall rely heavily upon Refs. 12 and 23, which will be denoted as S I and S II, respectively. Whenever possible, we use the notation of these papers, with no explicit redefinition.

It is shown in S I that the three-body collision operator that determines transport coefficients can be written [S I (A.7)]

$$K(fff) = \tfrac{1}{2} \sum_{\mu=1}^{4} \int dx_2\, dx_3\, T_\mu(123) f(x_1; t) f(x_2; t) f(x_3; t) \tag{D.1}$$

where the operator T_μ will be defined below. In the linearized approximation, and taking into account that in self-diffusion only particle 1 is out of equilibrium, we get:

$$K_s f_{s,1} \equiv \tfrac{1}{2}\rho^2 \sum_{\mu=1}^{4} \int dx_2\, dx_3\, T_\mu(123) f_{3,1}(x_1; t) \varphi(v_2) \varphi(v_3) \tag{D.2}$$

The operators T_μ, which physically describe μ successive binary collisions, are defined by

$$T_1(123) = 2 f_{13} f_{23} \bar{T}_{12} \tag{D.3}$$

$$T_2(123) = -2[\bar{T}_{12} f_{23} S^0 f_{23} T_{12} + \bar{T}_{12} f_{23} S^0 \bar{T}^n_{23} S^0 T_{13} + \bar{T}^{12} S^0 T^n_{23} S^0 f_{23} T_{13}] \tag{D.4}$$

$$\begin{aligned} T_3(123) = 2[&\bar{T}_{12} S^0 T^i_{23} S^0 T_{12} + \bar{T}_{12} S^0 T^i_{13} S^0 T_{12} \\ &+ \bar{T}_{12} S^0 T^i_{23} S^0 T_{13} - \bar{T}_{12} S^0 T^n_{23} S^0 \bar{T}^n_{23} S^0 T_{13}] \end{aligned} \tag{D.5}$$

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[17] The reader of this appendix is assumed to be familiar with Refs. 12 and 23.

where we have taken into account the symmetry of particles 2 and 3. A similar expression exists for $T_4(123)$; we shall not need it here, although it is worthwhile to recall that it contributes extremely little [$\sim O(10^{-6})$] to the transport coefficients.

To compare these results with the present theory, we transform T_2 and T_3 with the help of a series of identities summarized in S II. Using S II (1.5) and S II (1.6), we get from (D.4) and (D.5)

$$\begin{aligned} T_2 + T_3 = {} & 2\bar{T}_{12}[S^0\bar{T}^n_{23}S^0 + S^0 f_{23} + S^0 T^i_{23} S^0]T_{13} \\ & + 2\bar{T}_{12}[S^0(T^i_{23} + T^i_{13})S^0]T_{12} \end{aligned} \tag{D.6}$$

Using then S II (2.12) and S II (II.1), we arrive at the following compact expression:

$$T_2 + T_3 = 2\bar{T}_{12}(S^0 f_{23} + S^0\bar{T}_{23}S^0)T_{13} + 2\bar{T}_{12}S^0(\bar{T}_{23} + \bar{T}_{13})S^0 T_{12} \tag{D.7}$$

Consider now the collision term in Eq. (67); expand it to second order in the density and take its Laplace transform; denote the result by $\bar{K}_s$. We write it

$$\bar{K}_3 f_{s,1} = \bar{K}_s' f_{s,1} + \bar{K}_s'' f_{s,1} \tag{D.8}$$

We have

$$\bar{K}_s' f_{s,1} \equiv \rho^2 \int dx_2\, g^{(1)}(r_1, r_2) K_{12} f_{s,1} \varphi(v_2) \tag{D.9}$$

Here $g^{(1)}(r_1, r_2)$ represents the first density correction to the pair correlation function; outside the core, we have

$$g^{(1)}(r_1, r_2) = \int dr_3\, f_{13} f_{23} \tag{D.10}$$

and we get thus, comparing with (D.2) and (D.3),

$$\bar{K}_s' f_{s,1} = \tfrac{1}{2}\rho^2 \int dx_2\, dx_3\, T_1(123) f_{s,1}(x_1, t)\varphi(v_2)\varphi(v_3) \tag{D.11}$$

Similarly, $\bar{K}_s''$ is defined by

$$\begin{aligned} \bar{K}_s'' f_{s,1} \equiv \rho^2 \int dx_2\, dx_3\, \{ & K_{12} S^0 \llbracket (g_3{}^0(r_1, r_2, r_3) - g_2{}^0(r_1, r_2) \\ & \times g_2{}^0(r_1, r_3))[K_{13}, f_{s,1}(x_1, t)/\varphi(v_1)] \\ & + (K_{13} + K_{23}) S^0 g_2{}^0(r_1, r_2) \\ & \times [K_{12}, f_{s,1}(x_1; t)/\varphi(v_1)] \\ & + K_{23} S^0 g_2{}^0(r_1, r_3)[K_{13}, f_{s,1}(x_1, t)/\varphi(v_1)] \rrbracket \\ & \times \varphi(v_1)\varphi(v_2)\varphi(v_3)\} \end{aligned} \tag{D.12}$$

where $g_n{}^0$ similarly represents the correlation function g_n to zeroth order in the density:

$$\begin{aligned} g_2{}^0(r_1, r_2) &= 1 + f_{12} \\ g_3{}^0(r_1, r_2, r_3) &= (1 + f_{12})(1 + f_{23})(1 + f_{13}) \end{aligned} \tag{D.13}$$

We can now transform (D.12) with the help of[18]

$$f_{13}[K_{13}, f_{s,1}/\varphi(v_1)] = 0 \tag{D.14}$$

$$K_{12}S^0 f_{12} = 0 \tag{D.15}$$

which are obvious consequences of the geometry of a binary collision (see also S II); we get

$$\begin{aligned} \bar{K}_2{}'' f_{s,1} = \rho^2 \int dx_2\, dx_3\, \{K_{12} \llbracket (S^0 f_{23} &+ S^0 K_{23} S^0) \\ &\times [K_{13}, f_{s,1}(x_1; t)/\varphi(v_1)] \\ &+ S^0(K_{13} + K_{23}) S^0 [K_{12}, f_{s,1}(x_1; t)/\varphi(v_1)] \rrbracket \\ &\times \varphi(v_1)\varphi(v_2)\varphi(v_3)\} \end{aligned} \tag{D.16}$$

If we notice that the definitions of the present paper and of S I and S II imply

$$K_{12} \equiv \bar{T}_{12} \tag{D.17}$$

$$[K_{12}, f_{s,1}(x_1; t)/\varphi(v_1)]\varphi(v_1)\varphi(v_2) \equiv T_{12} f_{s,1}(x_1; t)\varphi(v_2) \tag{D.18}$$

the comparison between (D.16) and (D.7) leads to:

$$\begin{aligned} \bar{K}_s{}'' f_{s,1} = \tfrac{1}{2}\rho^2 \int dx_2\, dx_3\, &[T_2(123) + T_3(123)] \\ &\times f_{s,1}(x_1; t)\varphi(v_2)\varphi(v_3) \end{aligned} \tag{D.19}$$

Together with (D.9), this last formula implies the statement made in the text.

APPENDIX E. THE APPROACH TO EQUILIBRIUM

From Eqs. (12), (29), and (34), the $f_{s,n}$ will reach their equilibrium value for long times if

$$f_{s,1}(x_1; t) \equiv \delta f_{s,1}(x_1; t) \to 0 \tag{E.1a}$$

$$\delta f_{s,n}(x_1, \ldots, x_n; t) \to 0 \qquad n > 1 \tag{E.1b}$$

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[18] We use here the remark in footnote 13.

In order to prove (E.1a) and (E.1b) order by order in an ϵ expansion, we formally expand

$$\delta f_{s,n} = \sum_{m=0}^{\infty} \epsilon^m \, \delta f_{s,n}^{(m)} \tag{E.2}$$

Conditions (E.1a) and (E.1b) are the consequences, in the infinite-volume limit, of the fact that we have taken only one tagged particle, which diffuses away in the whole system. However, we expect our description for one tagged particle to remain valid when we have N_1 of them, provided that the density $\rho_1 = N_1/\Omega \ll \rho$; in this case, we expect that the corresponding one-particle d.f., denoted $f'_{s,1}$, tends to

$$f'_{s,1}(x_1; t) \xrightarrow[t\to\infty]{} \rho_1 \varphi^{\mathrm{eq}}(v_1) \tag{E.3}$$

which is stronger than (E.1a). In order to prove (E.1a) and (E.2) we shall formally work here in a finite, albeit large, system and we shall show that, to leading order in Ω, the distribution $f_{s,1}$ (normalized to unity in Ω) satisfies

$$f_{s,1}(x_1; t) \xrightarrow[t\to\infty]{} (1/\Omega)\varphi^{\mathrm{eq}}(v_2) \tag{E.4}$$

When $\Omega \to \infty$, this reduces of course to (E.1a), but it also implies (E.3) when N_1 particles are considered at density $\rho_1 \ll \rho$. From (60), we obtain the time evolution of $\delta f_{s,n}^{(n)}$ as

$$\begin{aligned}\delta f_{s,n}^{(m)}(t) = \int_0^t \exp\left\{\left[\tilde{C}_{s,1}^{\mathrm{E}} + \sum_{i=2}^{n} \tilde{C}_i^{\mathrm{E}}\right](t-t')\right\} \\ \times \Bigg[\mathscr{L}_{n,n+1}\, \delta f_{s,n+1}^{(m)}(t') + \left(\mathscr{L}_{n,n} - \tilde{C}_{s,1}^{\mathrm{E}} - \sum_{i=2}^{n} \tilde{C}_i^{\mathrm{E}}\right) \delta f_{s,n}^{(m-1)}(t') \\ + \mathscr{L}_{n,n-1}\, \delta f_{s,n-1}^{(m-1)}(t')\Bigg], \qquad m > 0\end{aligned} \tag{E.5}$$

The argument runs by recurrence. Suppose that

$$\delta f_{s,n'}^{(m-1)}(t) \xrightarrow[t\to\infty]{} 0 \qquad \text{all } n' \tag{E.6}$$

$$\delta f_{s,n+1}^{(m)}(t) \xrightarrow[t\to\infty]{} 0 \tag{E.7}$$

Thus the bracket in (E.5) vanishes for large t'.

Moreover, we know that in the limit where $t - t'$ is large the effect of the operator $\exp\,[\tilde{C}_{s,1}^{\mathrm{E}}(t-t')]$ is to bring any function $f(x_1; t')$ to the spatially uniform equilibrium state[19]

$$\{\exp[\tilde{C}_{s,1}^{\mathrm{E}}(t-t')]\} f(x_1; t') \xrightarrow[t-t'\to\infty]{} \frac{1}{\Omega}\, \varphi(v_1) \int dx_1\, f(x_1; t') \tag{E.8}$$

[19] Of course, due to hydrodynamic effects, the Enskog operator $\tilde{C}_{s,1}^{\mathrm{E}}$ (and $\tilde{C}_i^{\mathrm{E}}$) has eigenvalues which are as small as we wish in the long-wavelength limit. Thus the approach to (E.8) can be very slow. This feature makes it very difficult to make the present argument rigorous and is of course related to the "long-time tails" already mentioned.$^{(14,15)}$

Similarly the operator $\tilde{C}_i^{\rm E}$ projects the function $f(x_i; t')$ onto the conserved part of its zero-wavenumber Fourier component:

$$\{\exp[\tilde{C}_i^{\rm E}(t - t')]\}f(x_i; t') \xrightarrow[t-t'\to\infty]{} \frac{1}{\Omega} \sum_{\alpha=1}^{5} \varphi_\alpha(v_i) \int dv_i\, \varphi(v_i)^{-1} \times \varphi_\alpha(v_i) \int dr_i\, f(r_i, v_i; t) \qquad \text{(E.9)}$$

where the $\varphi_\alpha(v_i)$, $\alpha = 1,\ldots, 5$, denote the five well-known orthogonal conserved states⁽²¹⁾; we shall not need their explicit form here.[20]

From (E.5), (E.8), and (E.9) we get thus for $n > 1$

$$\exp\left[\left(\tilde{C}^{\rm E}_{s,1} + \sum_{i=2}^{n} \tilde{C}_i^{\rm E}\right)(t - t')\right]\{\mathscr{L}_{n,n+1}\, \delta f^{(m')}_{s,n+1}(t') + \cdots\} \to \cdots \frac{1}{\Omega^n} \int dr_1 \cdots dr_n\, \{\mathscr{L}_{n,n+1}\, \delta f^{(m')}_{s,n+1}(t') + \cdots\} \qquad \text{(E.10)}$$

where we have found no need to write down explicitly the (obvious) velocity factors coming from (E.8) and (E.9). One can easily check that the bracket in (E.10) is a function of $r_1,\ldots, r_n$ and is localized in space, and the right-hand side of (E.10) is thus of order Ω^{-n}; for $n > 1$, it becomes negligible compared to (E.4) in the large-volume limit.

For $n = 1$, we write more explicitly

$$\{\exp[\tilde{C}^{\rm E}_{s,1}(t - t')]\}\mathscr{L}_{1,2}\, \delta f^{(m)}_{s,2}(t') \xrightarrow[t-t'\to\infty]{} \frac{1}{\Omega}\, \varphi(v_1) \int dx_1\, \mathscr{L}_{1,2}\, \delta f^{(m)}_{s,2}(t') \qquad \text{(E.11)}$$

and we use the easily checked property [see (45)]

$$\int dx_1\, \mathscr{L}_{1,2} \cdots = 0 \qquad \text{(E.12)}$$

to prove that the right-hand side of (E.11) is zero.

Therefore, for $t \to \infty$, the integrand of (E.5) vanishes for all t' and we get

$$\delta f^{(m)}_{s,n}(t) \xrightarrow[t\to\infty]{} 0 \qquad \text{(E.13)}$$

We have now to reexamine the basis of our recurrence argument, Eqs. (E.6)–(E.7). In order to assert (E.7), for given m and n, it is sufficient to notice that, from (62) and (E.2), we have identically

$$\delta f^{(m)}_{s,m+1+i}(t) = 0, \qquad i > 0, \qquad \text{all } t \qquad \text{(E.14)}$$

---

[20] In (E.8) and (E.9) we have used the usual scalar product in velocity space⁽²¹⁾: $\langle f | g \rangle = \int dv\, \varphi(v)^{-1} f^*(v) g(v)$.

Then (E.9) guarantees that the same result holds for $m, m-1, \ldots, 1$. Similarly, the validity of (E.6) will be asserted if we can show that

$$\delta f_{s,1}^{(0)}(t) \underset{t\to\infty}{=} 0 \qquad \text{all } n' \tag{E.15}$$

For $n' > 1$, this is trivially true in view of (61).

For $n' = 1$, $m = 0$, on the other hand, the Enskog equation tells us that

$$\delta f_{s,1}^{(0)}(x_1; t) \equiv f_{s,1}^{(0)}(x_1; t) \to (1/\Omega)\varphi(v_1) \tag{E.16}$$

which contradicts (E.6). This exceptional case is, however, completely harmless because $\delta f_{s,1}^{(0)}$ only enters (E.5) in the combination

$$\begin{aligned} \mathscr{L}_{2,1}\, \delta f_{s,1}^{(0)}(t) &\xrightarrow[t\to\infty]{} (1/\Omega)\, \mathscr{L}_{2,1}\varphi(v_1) \\ &= 0 \text{ as } t \to \infty \end{aligned} \tag{E.17}$$

Hence, even in this case, the argument leading to (E.13) remains valid.

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