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Approximate Kinetic Theory of Hard-Sphere Fluids Near Equilibrium: II. A Quasihydrodynamic Approximation for the Velocity Autocorrelation Function

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We apply the kinetic theory of hard spheres recently developed by Lebowitz and Résibois to the calculation of the velocity correlation function. To simplify the calculations, a hydrodynamic approximation is made on the non-Markovian kernel of this kinetic equation. The results are in qualitative agreement with computer experiments at all densities.

KEY WORDS: Velocity autocorrelation function; kinetic equation; hard sphere fluid; hydrodynamic modes; long time tails; Enskog theory.

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1. INTRODUCTION

In a recent paper[1] (hereafter referred to as I), Résibois and Lebowitz have proposed an approximate but explicit kinetic equation to describe the time evolution of the one-particle self-distribution function[2] $f_{s,1}(x_1; t)$ in a hard-sphere fluid close to equilibrium.

This equation reads

$$\partial_t f_{s,1}(x_1; t) = \tilde{C}^{E}_{s,1} f_{s,1}(t) + \int_0^t G_{s,1}(t') f_{s,1}(t - t')\, dt' \tag{1}$$

Here, $\tilde{C}^{E}_{s,1}$ is the linearized self-Enskog operator, defined in I [Eqs. (50) and (51)], and the non-Markovian kernel $G_{s,1}(t)$ takes the form

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

where $\tilde{C}_i{}^{E}$ is the linearized Enskog operator for an arbitrary fluid particle $i \neq 1$ [see I, Eqs. (57)–(59)],[3] while the operators $\mathscr{L}_{1,2}$ and $\mathscr{L}_{2,1}$ have been explicitly defined in Eqs. (45) and (48) of I, respectively.

The rationale underlying the approximate kinetic equation (1) has been discussed in detail in I and will not be repeated here. Let us simply recall a few exact properties which are satisfied by Eq. (1).

(i) At $t = 0$, it gives the exact two first derivatives of $f_{s,1}(x_1; t)$.

(ii) At low density, it correctly gives, beyond the Boltzmann contribution, those terms of the Choh–Uhlenbeck triple collision operator that describe one, two, and three binary collisions. These terms are known to be largely dominant in the calculation of transport coefficients.[2]

(iii) It also leads to the correct nonanalytic contribution ($\propto \rho \ln \rho$) to the density expansion of the self-diffusion coefficient.[3]

(iv) In the limit of long times, it leads to the expected $t^{-3/2}$ long-time tail for the velocity autocorrelation function,[4] except that the numerical coefficient of the law is exact at low densities only.

These properties make Eq. (1) a very appealing candidate for an approximate description of the dynamic properties of a hard-sphere fluid for all times and all densities.

However, Eq. (1), albeit explicit, is not easy to solve. The main difficulty is apparent in Eq. (2), which shows that the non-Markovian kernel $G_{s,1}(t)$ involves the Enskog operators in the argument of an exponential. An exact calculation of $G_{s,1}(t)$ thus requires in principle knowledge of the spectral properties of the Enskog operators, and these are presently not available; this

[2] We follow the notation of I.

[3] The operator $\tilde{C}_i{}^{E}$ here is the one that comes from the short-time expansion method[13] and is slightly different from the original Enskog operator. This difference is carefully discussed in Ref. 22.

is, however, not an insuperable difficulty if one notices the great similarity between the Enskog operators and the corresponding Boltzmann operators, $\tilde{C}^{B}$, to which they reduce in the dilute gas limit: Indeed, after the pioneering work of Gross and co-workers,[5] systematic methods have been developed to derive very precise representations (often called *kinetic models*) of the operator $\exp[\tilde{C}^{B}t]$ with the aim of calculating the Van Hove response function in the dilute gas.[6] An extension of these calculations to the Enskog operator has already appeared in the literature.[7]

Unfortunately, these calculations involve fairly heavy numerical work and their extension to our present problem is worsened by the fact that the exponential in (2) is bilinear in the Enskog operators. Hence, before jumping into such awkward kinetic model calculations, it is certainly worthwhile to investigate whether a rough approximation to (2) would not reproduce the main qualitative features of hard-sphere dynamics. The aim of this paper is to discuss such a simple model.

To be specific, we shall be concerned here with the calculation of the normalized velocity autocorrelation function

$$\Gamma(t) = m\langle v_{1x}(t)v_{1x}(0)\rangle/k_{B}T \tag{3}$$

which, as shown in I, can be written as

$$\Gamma(t) = \int dv_1\, v_{1x} f_{s,1}(\mathbf{v}_1; t) \tag{4}$$

where $f_{s,1}(\mathbf{v}_1; t)$ is the ($\mathbf{r}_1$-independent) one-particle self-distribution function subject to the initial condition

$$f_{s,1}(\mathbf{v}_1; 0) = mv_{1x}\varphi(v_1)/k_{B}T \tag{5}$$

Of course, in our approximation, $f_{s,1}(\mathbf{v}_1; t)$ has to be calculated from (1). We have choosen to study the velocity correlation function as a typical example of application of the theory because it is rather sensitive to the details of the dynamics; moreover, extensive computer data exist for $\Gamma(t)$: These will provide us with some hint as how to develop approximations and, at the same time, they will offer a serious check on the validity of the theory. On the contrary, the other physically observable self-correlation function, namely the Van Hove function, does not seem as interesting because the use of simple sum rules and of the conservation laws already allows us to get a very good fit of the experimental results: Such simple arguments are of little help in reproducing the features of $\Gamma(t)$.

In Section 2, we first approximately reduce Eq. (1), which is an operator equation in velocity space, to an integrodifferential equation in time only for the function $\Gamma(t)$:

$$\partial_t\Gamma(t) = -(2/3\tau_{E})\Gamma(t) + \int_0^t \tilde{G}(t')\Gamma(t - t')\, dt' \tag{6}$$

Here τ_E is the well-known relaxation time in the Enskog approximation:

$$1/\tau_E = 4\sqrt{\pi}\rho g_2(a_+)a^2(k_BT/m)^{1/2} \tag{7}$$

and $\tilde{G}(t)$ depends on time only; for $t > 0$, the expression for $\tilde{G}(t)$, which is displayed in (15), remains formal because it still involves the Enskog operators in an exponential, as in (2). After briefly discussing the errors involved in going from (1) to (6), we spend some time in discussing the zero-time kernel $\tilde{G}(0)$, which gives us information on the second derivative of $\Gamma(t)$:

$$\left.\frac{d^2\Gamma(t)}{dt^2}\right|_{t=0} = \frac{4}{9\tau_E^2} + \tilde{G}(0) \tag{8}$$

This quantity $\tilde{G}(0)$, which describes a *correlated* sequence of two hard-sphere collisions, has not, to the best of our knowledge, been calculated before for arbitrary density.

This short-time behavior is, however, of little help when looking at the evolution of the system for arbitrary times, and we need some further approximation which allows us to get $\tilde{G}(t)$ in compact form for $t > 0$. This approximation is suggested by the observation by Alder and co-workers[8] that the main deviations from Enskog behavior come from times which are fairly large on the time scale fixed by τ_E; for such times, we expect the dominant contributions to $\exp[(\tilde{C}_{s,1}^E + \tilde{C}_2^E)t]$ in (2) to come from the hydrodynamic modes and, *roughly speaking*, we expect the following replacement to be valid:

$$\exp[(\tilde{C}_{s,1}^E + \tilde{C}_2^E)t] \approx (1/8\pi^3)\int d\mathbf{k} \sum_{\alpha=1}^{5} \{|\Phi_\alpha^{\mathbf{k}}\rangle|\Phi_{s,1}^{-\mathbf{k}}\rangle \times \exp[(\Lambda_\alpha^k + \Lambda_{s,1}^k)t]\langle\bar{\Phi}_\alpha^{\mathbf{k}}|\langle\bar{\Phi}_{s,1}^{-\mathbf{k}}|\} \tag{9}$$

where $|\Phi_\alpha^{\mathbf{k}}\rangle$ (resp. $|\Phi_{s,1}^{\mathbf{k}}\rangle$) and Λ_α^k (resp. $\Lambda_{s,1}^k$), respectively, represent the hydrodynamic (resp. self-diffusion) eigenfunctions and eigenvalues with wave number $\mathbf{k}$ of the operator $\tilde{C}_2^E$ (resp. $\tilde{C}_{s,1}^E$). Yet, since we want an expression for $\tilde{G}(t)$ valid for all times, we have to suitably extrapolate (9) for all t and k values: this *quasihydrodynamic approximation* is discussed in Sections 3 and 4. Let us immediately stress that, in the present state of the theory, this approximation is largely ad hoc and is mostly justified by its success; we hope, however, that further work, based on the above-mentioned kinetic model methods, will provide stronger support for it.

This quasihydrodynamic approximation allows us to reduce the kernel $\tilde{G}(t)$ to a quadrature over wave numbers, which cannot be evaluated analytically. However, in Section 5, we show that this expression is very useful from two complementary viewpoints:

(i) It allows, for any density, a numerical solution of (6), leading to explicit values of $\Gamma(t)$ for all times, as well as to values for the diffusion coefficient D:

$$D = (k_B T/m) \int_0^\infty \Gamma(t)\, dt \tag{10}$$

(ii) It also permits, without any calculations, of a good understanding of the general features displayed by these numerical results. In particular, the importance of collisional transfer at high densities appears very clearly.

The comparison of these results with the computer data is very encouraging: The main features of Alder's calculations are qualitatively reproduced by the theory, including the remarkable change of sign of the deviations from Enskog theory when the highest densities are approached. Suggestions for further improvement and relation to other work are also presented in Section 5. Finally, some of the calculations are given in the appendices.

2. APPROXIMATE KINETIC EQUATION FOR $\Gamma(t)$ AND SHORT-TIME BEHAVIOR

A major simplification occurs in the calculation of the velocity autocorrelation function if we assume that, for all times, the self-distribution function $f_{s,1}(\mathbf{v}_1; t)$ keeps the same form it has at $t = 0$ [see (5)]:

$$f_{s,1}(\mathbf{v}_1; t) = c(t)(m/k_B T) v_{1x} \varphi(v_1) \tag{11}$$

Multiplying both sides of this equation by v_{1x} and integrating over $\mathbf{v}_1$, we readily see that the unknown coefficient $c(t)$ can be identified with $\Gamma(t)$ itself:

$$c(t) \equiv \Gamma(t) \tag{12}$$

and, performing the same operation on Eq. (1), we readily obtain a closed equation for $\Gamma(t)$:

$$\partial_t \Gamma(t) = -\nu_E \Gamma(t) + \int_0^t \tilde{G}(t - t')\Gamma(t')\, dt' \tag{13}$$

where the coefficient ν_E is given by

$$\nu_E = -(m/k_B T) \int d\mathbf{v}_1\, v_{1x} C_{s,1}^E v_{1x} \varphi(v_1) \tag{14}$$

while the function $\tilde{G}(t)$ is

$$\tilde{G}(t) = (m/k_B T) \int d\mathbf{v}_1\, v_{1x} G_{s,1}(t) v_{1x} \varphi(v_1) \tag{15}$$

In the present problem, we have no rigorous justification of this assumption; however, for the Enskog equation itself [i.e., when dropping the non-Markovian term in (1)], it is known[8,9,13] that this so-called zeroth-order Sonine polynomial approximation leads to only a few percent error in the computation of transport coefficients and of correlation functions; this is much less than the deviations from Enskog predictions which are observed in the computer experiments and which, hopefully, will be accounted for by the non-Markovian term in Eq. (1); moreover, it would be extremely surprising if the presence of this latter term would deeply alter the validity of (11). Hence, we shall adopt Eq. (14) with no further concern.

The calculation of the frequency ν_E is standard[8,9] and will not be repeated here; one finds

$$\nu_E = 2/3\tau_E \tag{16}$$

where the relaxation time τ_E, defined in (7), is the natural time scale of our problem. For this reason, it is convenient to work with the following dimensionless quantities:

$$\tau = t/\tau_E, \qquad \gamma(\tau) = \Gamma(\tau\tau_E), \qquad g(\tau) = \tau_E{}^2\tilde{G}(\tau\tau_E) \tag{17}$$

in which case Eq. (13) becomes

$$\partial_t\gamma(\tau) = -\tfrac{2}{3}\gamma(\tau) + \int_0^\tau g(\tau')\gamma(\tau - \tau')\,d\tau' \tag{18}$$

Notice that, in these units, the ratio of the diffusion coefficient D to its Enskog approximation D_E takes the simple form

$$D/D_E = 1/\left[1 - \tfrac{2}{3}\int_0^\infty g(\tau)\,d\tau\right] \tag{19}$$

Our main problem in this paper will be to obtain a compact expression for the kernel $g(\tau)$. It is convenient to decompose this function into two parts:

$$g(\tau) = g^{(1)}(\tau) + g^{(2)}(\tau) \tag{20}$$

where, in agreement with (2), (15), and (17) and I (45) and (48), we have

$$g^{(1)}(\tau) = (m\tau_E{}^2/k_BT)\int d\mathbf{v}_1\,dx_2\,v_{1x}K_{12}\exp[(\tilde{C}_{s,1}^E + \tilde{C}_2^E)\tau_E\tau]$$
$$\times\ \rho g_2(\mathbf{r}_1, \mathbf{r}_2)[K_{12}, v_{1x}]\varphi(v_1)\varphi(v_2) \tag{21}$$

and

$$g^{(2)}(\tau) = (m\tau^2{}_E/k_BT)\int d\mathbf{v}_1\,dx_2\,dx_3\,v_{1x}K_{12}\exp[(\tilde{C}_{s,1}^E + \tilde{C}_2^E)\tau_E\tau]$$
$$\times\ \rho^2\{g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g_2(\mathbf{r}_1, \mathbf{r}_2)g_2(\mathbf{r}_1, \mathbf{r}_3)\}[K_{13}, v_{1x}]$$
$$\times\ \varphi(v_1)\varphi(v_2)\varphi(v_3) \tag{21'}$$

We have already mentioned in I that some care has to be exercized when dealing with the singular operators K_{ij}. This is nicely illustrated in Eq. (21): Suppose that we replace there the "Enskog propagator" $\exp[(\tilde{C}_{s,1}^{E} + \tilde{C}_{2}^{E})\tau\tau_E]$ by the "free motion propagator" $\exp[-(\mathscr{L}_1^0 + \mathscr{L}_2^0)\tau\tau_E]$, where $\mathscr{L}_i^0$ is defined by

$$\mathscr{L}_i^0 = \mathbf{v}_i \cdot \partial/\partial \mathbf{r}_i \tag{22}$$

We then have

$$K_{12} \exp[-(\mathscr{L}_1^0 + \mathscr{L}_2^0)\tau_E\tau][K_{12}, v_{1x}] \equiv 0 \tag{23}$$

which expresses the geometric fact that two hard spheres cannot collide twice in succession.[10] In order to keep this property explicit in $g^{(1)}(\tau)$, it is convenient to use (22) in order to rewrite $g^{(1)}(\tau)$ as

$$\begin{aligned} g^{(1)}(\tau) = (m\tau_E^2/k_BT) \int d\mathbf{v}_1\, dx_2\, K_{12}\{&\exp[(\tilde{C}_{s,1}^{E} + \tilde{C}_{2}^{E})\tau_E\tau] \\ &- \exp[-(\mathscr{L}_1^0 + \mathscr{L}_2^0)\tau_E\tau]\}\rho g_2(\mathbf{r}_1, \mathbf{r}_2)[K_{12}, v_{1x}] \\ &\times \varphi(v_1)\varphi(v_2) \end{aligned} \tag{24}$$

We shall wait until the next section before discussing how to approximately calculate $g(\tau)$ for arbitrary τ. Here, we shall limit ourselves to looking at its zero-time value. From (24), we immediately see that $g^{(1)}(0) \equiv 0$ and thus we get from Eq. (19))

$$\left.\frac{\partial^2 \gamma(\tau)}{\partial \tau^2}\right|_{\tau=0} = \frac{4}{9} + g^{(2)}(0) \tag{25}$$

This equation has a very simple interpretation. Indeed, the second derivative of $\gamma(\tau)$ describes the effect of two successive collisions; the first term on the right-hand side of (25) represents the contribution due to an *uncorrelated* sequence of two such collisions (with a small error due to the use of the zeroth-order Sonine polynomial approximation) and the second term describes a correlated sequence of two collisions between three particles. In order to estimate the role of these correlations, we need to evaluate (21′) for $\tau = 0$. Although with the explicit form of K_{12} given in I (40), this expression looks quite involved, it can nevertheless be reduced to the following simple integral:

$$g^{(2)}(0) = \frac{\pi}{6} \int_{-1}^{+1} dx\, x\Phi(x)\left[\frac{g_3(-x)}{g_2(a_+)^2} - 1\right] \tag{26}$$

In this formula, we have used the abbreviation

$$g_3(x) = g_3(|r_{12}| = a, |r_{13}| = a, \mathbf{r}_{12}\cdot\mathbf{r}_{13} = a^2x) \tag{27}$$

to denote the triplet correlation function at contact; $\Phi(x)$ represents the function

$$\Phi(x) = \frac{1}{\pi}(4 - x^2)^{1/2}\left\{i_1\left(\frac{-x}{2}\right)\left[1 + \frac{x^2}{2}\right] + \frac{3x}{2}\right\} \tag{28}$$

with:

$$i_1(x) = \frac{2}{(1 - x^2)^{1/2}}\left(\tan^{-1}\frac{1 + x}{(1 - x^2)^{1/2}} - \tan^{-1}\frac{x}{(1 - x^2)^{1/2}}\right) \tag{29}$$

This function is plotted in Fig. 1. Though the proof of (26) involves no more than a succession of quadratures, this calculation is long enough to deserve some explanations; these are given in Appendix A.

Since (26) involves the triplet correlation function, it cannot be evaluated analytically. Worse than this, even at contact, very few data exist for g_3 and, in most cases, we have to resort to the superposition approximation; then (26) reduces to

$$g^{(2)}(0)|_{\text{superp}} = \tfrac{1}{6}\pi\int_{-1}^{+1} dx\, x\Phi(x)\{g_2([2a(x + 1)]^{1/2}) - 1\} \tag{30}$$

In (30), we may use the empirical receipe due to Verlet and Weiss[11] to obtain a fairly accurate representation of g_2. When the density increases, we may, however, expect the approximation (30) to be seriously in error.

In Table I, we present the numerical results based on (30) at a series of densities measured by the ratio V/V_0, where V is the volume per hard sphere and V_0 is this same volume at close packing. Moreover, we also compare this approximate value with the one based on (26) for two densities where a good Monte Carlo calculation of the triplet correlation function at contact has been made[12]: As can be seen, the discrepancy is rather severe.

We have few other comments to make on the results of this table; indeed, without a knowledge of the analyticity properties of $\gamma(\tau)$ near $\tau = 0$, not much use can be made of these numerical estimates for guessing the short (but finite) time behavior of $\gamma(\tau)$. At best, we can get some comfort in noticing that, compared to the uncorrelated term $\frac{4}{9} = 0.4444...$, the contribution from the correlated collisions is quite small for all densities (from 2% to 20%); this observation leads to one more argument in favor of the Enskog theory as a good first approximation.

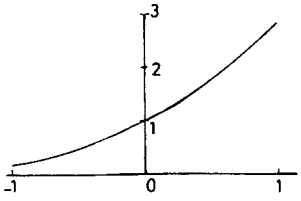

Fig. 1. The function $\Phi(x)$, Eq. (29).

Table I. Values of $g(0)$ at Various Densities

V/V_0	Superposition approximation [Eq. (30)]	Monte Carlo calculation of Ref. 12 [Eq. (26)]
20	0.075	—
10	0.069	—
7	0.062	—
5	0.052	—
4	0.041_5	—
3	0.025	—
2.5	0.014	—
2	0.009	—
1.83	0.012	0.041
1.69	0.021	0.026
1.6	0.031	—
1.5	0.046	—

Finally, prior to our discussion of Section 3, in order not to leave the reader with a deceptive impression, we immediately stress that our poor knowledge of $g(0)$ turns out to be of minor importance in determining the overall deviations of $\gamma(\tau)$, for all τ, from its Enskog value.

3. THE QUASIHYDRODYNAMIC APPROXIMATION

In order to get an approximate formula for $g(\tau)$ for $\tau > 0$, it is convenient to express Eqs. (20) and (21) in the Fourier variable $\mathbf{k}$ associated with $\mathbf{r}_2$ (or $\mathbf{r}_{12}$, by translation invariance). Consider, for example, $g^{(1)}(\tau)$; with Eq. (40) of I for the collision operator K_{12}, we have

$$g^{(1)}(\tau) = (m\tau_E{}^2 a^2/k_B T) \int d\mathbf{v}_1\, d\mathbf{v}_2 \int d^2\boldsymbol{\varkappa}\, v_{1x}(\boldsymbol{\varkappa}\cdot\mathbf{v}_{12})\theta(\boldsymbol{\varkappa}\cdot\mathbf{v}_{12}) \times [S^{(1)}(\mathbf{r}_1, \mathbf{v}_1'; \mathbf{r}_1 - a\boldsymbol{\varkappa}, \mathbf{v}_2'; \tau) - S^{(1)}(\mathbf{r}_1, \mathbf{v}_1; \mathbf{r}_1 + a\boldsymbol{\varkappa}, \mathbf{v}_2; \tau)] \tag{31}$$

where we have put

$$S^{(1)}(\mathbf{r}_1, \mathbf{v}_1; \mathbf{r}_2, \mathbf{v}_2; \tau) = \{\exp[(\tilde{C}_{s,1}^{E} + \tilde{C}_2{}^{E})\tau_E\tau] - \exp[-(\mathscr{L}_1{}^0 + \mathscr{L}_2{}^0)\tau_E\tau]\} S^{(1)}(\mathbf{r}_1, \mathbf{v}_1; \mathbf{r}_2, \mathbf{v}_2; 0) \tag{32}$$

with

$$S^{(1)}(\mathbf{r}_1, \mathbf{v}_1; \mathbf{r}_2, \mathbf{v}_2; 0) = \rho g_2(\mathbf{r}_1, \mathbf{r}_2)[K_{12}, \mathbf{v}_{1x}]\varphi(v_1)\varphi(v_2) \tag{33}$$

In the part of (31) corresponding to the first term in the bracket, we change the integration variables from $\mathbf{v}_1$, $\mathbf{v}_2$ to $\mathbf{v}_1'$, $\mathbf{v}_2'$ [see (A.3)] and we also use $-\boldsymbol{\varkappa}$ instead of $\boldsymbol{\varkappa}$ in the integral over the angles of collision. We obtain then

$$g^{(1)}(\tau) = -(m\tau_E{}^2 a^2/k_B T)\int d\mathbf{v}_1\, d\mathbf{v}_2 \int d^2\boldsymbol{\varkappa}\, \kappa_x(\boldsymbol{\varkappa}\cdot\mathbf{v}_{12})^2 \times \theta(\boldsymbol{\varkappa}\cdot\mathbf{v}_{12}) S^{(1)}(\mathbf{r}_1, \mathbf{v}_1; \mathbf{r}_1 + a\boldsymbol{\varkappa}, \mathbf{v}_2; \tau) \tag{34}$$

and, with the help of the Fourier transform,

$$S^{(1)}_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_1; \mathbf{v}_2; \tau) = (1/8\pi^3)\int d\mathbf{k}\, \exp[-i\mathbf{k}\cdot\mathbf{r}_{12}] S^{(1)}(\mathbf{r}_1, \mathbf{v}_1; \mathbf{r}_2, \mathbf{v}_2; \tau) \tag{35}$$

we arrive at

$$g^{(j)}(\tau) = -\frac{m\tau_E{}^2 a^2}{k_B T}\frac{1}{8\pi^3}\int d\mathbf{v}_1\, d\mathbf{v}_2 \int d\mathbf{k} \int d^2\boldsymbol{\varkappa} \times \exp[-ia\mathbf{k}\cdot\boldsymbol{\varkappa}]\kappa_x(\boldsymbol{\varkappa}\cdot\mathbf{v}_{12})^2\theta(\boldsymbol{\varkappa}\cdot\mathbf{v}_{12}) S^{(j)}_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_1; \mathbf{v}_2; \tau) \tag{36}$$

with $j = 1$. Here $S^{(1)}_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_1; \mathbf{v}_2; \tau)$ can be written as

$$S^{(1)}_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_1; \mathbf{v}_2; \tau) = \{\exp[(\tilde{C}^E_{s,1} + \tilde{C}_2{}^E)\tau_E\tau] - \exp[-i\mathbf{k}\cdot\mathbf{v}_{12}\tau\tau_E]\} S^{(1)}_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_1; \mathbf{v}_2; 0) \tag{37}$$

because the Enskog operators are diagonal in $\mathbf{k}$-space. Indeed, in (37), we have

$$\tilde{C}^E_{s,1} f_{\mathbf{k}}(\mathbf{v}_1) = (-i\mathbf{k}\cdot\mathbf{v}_1 + C^E_{s,1}) f_{\mathbf{k}}(\mathbf{v}_1) \tag{38}$$

where $C^E_{s,1}$ is $\mathbf{k}$ independent [see I (51)] and similarly, from I (57) we get

$$\tilde{C}_2{}^E f_{-\mathbf{k}}(\mathbf{v}_2) = (i\mathbf{k}\cdot\mathbf{v}_2 + C'^E_{-k}) f_{-\mathbf{k}}(\mathbf{v}_2) \tag{39}$$

where

$$C'^E_k f_k = -i\beta\rho V_k(\mathbf{k}\cdot\mathbf{v}_2)\varphi(\mathbf{v}_2)\int d\mathbf{v}_3 f_k(\mathbf{v}_3) + \rho a^2 g_2(a_+)\int d\mathbf{v}_3 \int d^2\boldsymbol{\varkappa}\, \theta(\boldsymbol{\varkappa}\cdot\mathbf{v}_{23})(\boldsymbol{\varkappa}\cdot\mathbf{v}_{23})[f_k(\mathbf{v}_2')\varphi(\mathbf{v}_3') + f_k(\mathbf{v}_3')\varphi(\mathbf{v}_2')\exp(-i\mathbf{k}\cdot\boldsymbol{\varkappa}a) - f_k(\mathbf{v}_2)\varphi(\mathbf{v}_3) - f_k(\mathbf{v}_3)\varphi(\mathbf{v}_2)\exp(i\mathbf{k}\cdot\boldsymbol{\varkappa}a)] \tag{40}$$

Here V_k is the Fourier transform of the "potential" $V(r)$ defined in I (59):

$$-\beta V_k = a^3\rho\tilde{C}(ka) + \tfrac{4}{3}\pi a^3\rho g_2(a_+)\tilde{\rho}(ka) \tag{41}$$

In this formula, $\tilde{C}(y)$ is the Fourier transform of the direct correlation function $C(r)$:

$$\tilde{C}(y) = \int d^3(\mathbf{r}/a)\exp[i\mathbf{y}\cdot\mathbf{r}/a]\, C(r) \tag{42}$$

and $\tilde{\rho}(y)$ is given by

$$\tilde{\rho}(y) = 3(\sin y - y\cos y)/y^3 \tag{43}$$

A simple calculation shows that Eq. (36) also holds for $g^{(2)}(\tau)$ provided we now put $j = 2$ and use the definitions [see also (A.2)]

$$S^{(2)}_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_1;\mathbf{v}_2;\tau) = \exp[(\tilde{C}^{\mathrm{E}}_{s,1} + \tilde{C}_2{}^{\mathrm{E}})\tau_{\mathrm{E}}\tau]S^{(2)}_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_1;\mathbf{v}_2;0) \tag{44}$$

and

$$\begin{aligned} S^{(2)}_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_1;\mathbf{v}_2;\tau) = \rho^2 a^2 \int d\mathbf{v}_3 \int d^2\boldsymbol{\kappa}'\, \kappa_x'(\boldsymbol{\kappa}'\cdot\mathbf{v}_{13})^2\theta(\boldsymbol{\kappa}'\cdot\mathbf{v}_{13}) \\ \times \int d\mathbf{r}_{12} \exp[-i\mathbf{k}\cdot\mathbf{r}_{12}]\{g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_1 - a\boldsymbol{\kappa}') \\ - g_2(\mathbf{r}_1,\mathbf{r}_2)g_2(a_+)\}\varphi(v_1)\varphi(v_2)\varphi(v_3) \end{aligned} \tag{45}$$

Since the spectrum of the Enskog operator is not known, it is clear that the calculation of (37) and (44) cannot be made exact. In order to proceed further, we shall limit ourselves here to a very rough approximation. This is easier to discuss if we first introduce some convenient notation: A function $f(\mathbf{v}_1)$ is considered as the velocity space representation of an abstract vector $|f_1\rangle$:

$$f(\mathbf{v}_1) = \langle \mathbf{v}_1 | f_1 \rangle \tag{46}$$

in a Hilbert space, where the scalar product is defined by

$$\langle g_1 | f_1 \rangle = \int d\mathbf{v}_1\, \varphi(v_1)^{-1} g^*(v_1) f(v_1) \tag{47}$$

Notice that we have put a subscript 1 in bras and kets in order to insist that they refer to particle 1. We also consider a complete basis $|n_1\rangle$ in this space (for example, the Sonine polynomials) which contains, in particular, the following five orthonormal vectors:

$$\begin{aligned} \langle \mathbf{v}_1 | 1_1 \rangle &= \varphi(v_1) \\ \langle \mathbf{v}_1 | i_1 \rangle &= \frac{v_{1,i}}{(k_{\mathrm{B}}T/m)^{1/2}}\varphi(v_1), \qquad i = x, y, z \equiv 2, 3, 4 \\ \langle \mathbf{v}_1 | 5_1 \rangle &= \left(\frac{2}{3}\right)^{1/2}\left(\frac{m v_1{}^2}{2k_{\mathrm{B}}T} - \frac{3}{2}\right)\varphi(v_1) \end{aligned} \tag{48}$$

These five vectors will be generically denoted by $|\alpha_1\rangle$ ($\alpha \in 1, 2, \ldots, 5$).

In order to treat (37), we use the identity

$$\begin{aligned} &\exp[(\tilde{C}^{\mathrm{E}}_{s,1} + \tilde{C}_2{}^{\mathrm{E}})\tau_{\mathrm{E}}\tau] \\ &= \sum_{\substack{n,m,\\ n',m'}} |n_1', m_2'\rangle\langle n_1', m_2'| \exp[(\tilde{C}_{s1}{}^{\mathrm{E}} + \tilde{C}_2{}^{\mathrm{E}})\tau\tau_{\mathrm{E}}]|n_1, m_2\rangle\langle n_1, m_2| \end{aligned} \tag{49}$$

where $|n_1, m_2\rangle = |n_1\rangle \otimes |m_2\rangle$, etc., and we use the *empirical* observation made by Alder and co-workers[8] that the main deviations from the Enskog

theory come for times τ which are long compared to the relaxation time ($\tau > 1$). For such times, we find that:

(i) If the wave number k [see, for example, (38)] is small, all contributions to (49) have decayed essentially to zero except those corresponding to $n_1, m_1' \equiv 1$ and to $m_2, m_2' \in (\alpha)$. The special property of these latter terms stems from the fact that they are exactly stationary when $\mathbf{k} = 0$, as a well-known consequence of the conservation properties of the Enskog operators.[9]

(ii) If the wave number $\mathbf{k}$ is large, then all contributions to (49) have decayed almost to zero, because of the free motion term $-i\mathbf{k}\cdot\mathbf{v}_{12}$ [see (38)].

These properties suggest strongly that we keep only the terms $n_1, n_1' \equiv 1$ *and* $m_1, m_1' \in (\alpha)$ *in* (49). Of course, a more fundamental analysis (based on kinetic models) is required to justify this assumption but we shall not do this here: We shall simply a posteriori verify that it leads to reasonable results.

Inserting this approximation into (37) leads to us:

$$S^{(1)}_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_1; \mathbf{v}_2; \tau) = \sum_{\alpha,\alpha'} \langle \mathbf{v}_1, \mathbf{v}_2 | 1_1, \alpha_2 \rangle [\mathscr{V}_{s;1,1}(\mathbf{k}a; \tau)\mathscr{V}_{\alpha,\alpha'}(-\mathbf{k}a; \tau) - \mathscr{V}^{(0)}_{s;1,1}(\mathbf{k}a; \tau)\mathscr{V}^{(0)}_{\alpha,\alpha'}(-\mathbf{k}a; \tau)] \langle 1_1, \alpha_2' | S^{(1)}_{\mathbf{k},-\mathbf{k}} \rangle \quad (50)$$

where

$$\mathscr{V}_{s;1,1}(\mathbf{k}a; \tau) = \langle 1_1 | \exp[\tilde{C}^{\mathrm{E}}_{s,1}\tau_{\mathrm{E}}\tau] | 1_1 \rangle \quad (51)$$

represents the "density–density" propagator of the tagged particle in the Enskog approximation; similarly,

$$\mathscr{V}_{\alpha,\alpha'}(-\mathbf{k}a; \tau) = \langle \alpha_2 | \exp[\tilde{C}_2{}^{\mathrm{E}}\tau_{\mathrm{E}}\tau] | \alpha_2' \rangle, \qquad \alpha, \alpha', \in 1, 2, \ldots, 5 \quad (52)$$

denotes the (α, α') component of the "propagator matrix" for a fluid particle; and

$$\mathscr{V}^{(0)}_{s;1,1}(\mathbf{k}a; \tau) = \langle 1_1 | \exp[-i\mathbf{k}\cdot\mathbf{v}_1\tau\tau_{\mathrm{E}}] | 1_1 \rangle \quad (53)$$

and

$$\mathscr{V}^{(0)}_{\alpha,\alpha'}(-\mathbf{k}a; \tau) = \langle \alpha_2 | \exp[i\mathbf{k}\cdot\mathbf{v}_2\tau\tau_{\mathrm{E}}] | \alpha_2' \rangle \quad (54)$$

describe the corresponding free-particle propagators. A similar approximate formula of course holds for $S^{(2)}_{\mathbf{k},-\mathbf{k}}$.

Inserting (50) into (36), we get an expression for $g^{(1)}(\tau)$ which, though suitable for numerical calculations, is too involved for good comprehension, because of the large number of terms. A further simplification can be achieved if we notice that, at $k = 0$, the fluid propagator matrix takes the simple form

$$\mathscr{V}_{\alpha,\beta}(0; \tau) = \delta^{\mathrm{Kr}}_{\alpha,\beta} \quad (55)$$

Thus, if the small $\mathbf{k}$ components dominate in (36), we expect that the approximation

$$\mathscr{V}_{\alpha,\beta}(\mathbf{k}a;\tau) \simeq \mathscr{V}_{\alpha\alpha}(\mathbf{k}a;\tau)\delta^{\mathrm{Kr}}_{\alpha,\beta} \tag{56}$$

will be satisfactory. In the same spirit, we decompose the velocity $\mathbf{v}_2$ into its transverse and longitudinal parts:

$$\mathbf{v}_2 = \mathbf{v}_{\parallel} + \mathbf{v}_{\perp} \tag{57}$$

with

$$\mathbf{v}_{\parallel} = (\mathbf{1}_{\mathbf{k}}\cdot\mathbf{v}_2)\mathbf{1}_{\mathbf{k}}, \qquad \mathbf{v}_{\perp} = \mathbf{v}_2 - \mathbf{v}_{\parallel} \tag{58}$$

where $\mathbf{1}_{\mathbf{k}}$ is the unit vector along $\mathbf{k}$, and we use the approximation

$$\begin{aligned}\mathscr{V}_{i,i}(-\mathbf{k}a;\tau) = {} & (1 - 1^2_{\mathbf{k},i})\mathscr{V}_{\perp,\perp}(a|\mathbf{k}|;\tau) \\ & + 1^2_{\mathbf{k},i}\mathscr{V}_{\parallel,\parallel}(a|\mathbf{k}|;\tau), \qquad i \equiv x, y, z \equiv 2, 3, 4\end{aligned} \tag{59}$$

where $\mathscr{V}_{\perp,\perp}$ and $\mathscr{V}_{\parallel,\parallel}$, respectively, denote the Enskog propagators for the transverse and longitudinal velocity fields:

$$\mathscr{V}_{\perp,\perp}(ak;\tau) = \langle \mathbf{v}_{\perp}| \exp[\tilde{C}_2{}^{\mathrm{E}}\tau_{\mathrm{E}}\tau]|\mathbf{v}_{\perp}\rangle/\langle \mathbf{v}_{\perp}|\mathbf{v}_{\perp}\rangle \tag{60}$$

$$\mathscr{V}_{\parallel,\parallel}(ak;\tau) = \langle \mathbf{v}_{\parallel}| \exp[\tilde{C}_2{}^{\mathrm{E}}\tau\tau_{\mathrm{E}}]|\mathbf{v}_{\parallel}\rangle/\langle \mathbf{v}_{\parallel}|\mathbf{v}_{\parallel}\rangle \tag{61}$$

Again, (59) becomes rigorous in the $k \to 0$ limit.

We get

$$\begin{aligned}S^{(1)}_{\mathbf{k},-\mathbf{k}}(\mathbf{v}_1;\mathbf{v}_2;\tau) = {} & \sum_{\alpha} \langle \mathbf{v}_1, \mathbf{v}_2|1_1, \alpha_2\rangle[\mathscr{V}_{s;1,1}(\mathbf{k}a;\tau) \\ & \times \mathscr{V}_{\alpha,\alpha}(-\mathbf{k}a;\tau) - \mathscr{V}^{(0)}_{s;1,1}(\mathbf{k}a;\tau)\mathscr{V}^{(0)}_{\alpha,\alpha}(-\mathbf{k}a;\tau)]^{\bullet}\end{aligned} \tag{62}$$

and a similar formula for $S^{(0)}_{\mathbf{k},-\mathbf{k}}$.

The replacement of (37) by (62) forms our *quasihydrodynamic approximation*; the term "hydrodynamic" tems from the fact that we have retained those contributions that become dominant for small k and large τ; however, since we do not want to introduce any artificial cutoff in the theory, we prefer to speak of *quasi*hydrodynamic approximation to stress the fact that (62) is used for *all* $\mathbf{k}$ and *all* τ, the rapid decay (to be verified later on) of this quantity for large $\mathbf{k}$ providing a natural cutoff.

To get an explicit expression for $g^{(i)}(\tau)$ is now straightforward: We introduce (62) into (36) and we use simple symmetry properties to eliminate most terms in the sum over α in (62). We arrive at

$$\begin{aligned}g^{(1)}_{qh}(\tau) = {} & \frac{m\rho a^4 g_2(a_+)\tau_{\mathrm{E}}{}^2}{k_{\mathrm{B}}T(8\pi^3)} \int d\mathbf{k}\, m_{xx}(\mathbf{k})^2 \\ & \times [\mathscr{V}_{s;1,1}(|\mathbf{k}|a;\tau)\mathscr{V}_{22}(-\mathbf{k}a;\tau) - \mathscr{V}^{(0)}_{s;1,1}(|\mathbf{k}|a;\tau)\mathscr{V}^{(0)}_{22}(-\mathbf{k}a;\tau)]\end{aligned} \tag{63}$$

and

$$g_{qh}^{(2)}(\tau) = \frac{m\rho^2 a^4 \tau_E^2}{k_B T(8\pi^3)} \int d\mathbf{k}\, n_x(k)\tilde{n}_x(k)\mathscr{V}_{s;1,1}(|\mathbf{k}|a;\tau)\mathscr{V}_{1,1}(|\mathbf{k}|a;\tau) \tag{64}$$

(the subscript qh is used for "quasihydrodynamic"), where we have introduced the following quantities:

$$m_{xx}(\mathbf{k}) = \int d\mathbf{v}_1\, d\mathbf{v}_2 \int d^2\boldsymbol{\varkappa}\, \exp[-ia\boldsymbol{\varkappa}\cdot\mathbf{k}]\kappa_x v_{2x}(\boldsymbol{\varkappa}\cdot\mathbf{v}_{12})^2\theta(\boldsymbol{\varkappa}\cdot\mathbf{v}_{12})\varphi(v_1)\varphi(v_2) \tag{65}$$

$$n_x(\mathbf{k}) = \int d\mathbf{v}_1\, d\mathbf{v}_2 \int d^2\boldsymbol{\varkappa}\, \exp[-ia\boldsymbol{\varkappa}\cdot\mathbf{k}]\kappa_x(\boldsymbol{\varkappa}\cdot\mathbf{v}_{12})^2\theta(\boldsymbol{\varkappa}\cdot\mathbf{v}_{12})\varphi(v_1)\varphi(v_2) \tag{66}$$

and

$$\tilde{n}_x(\mathbf{k}) = \int d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{v}_3 \int d^2\boldsymbol{\varkappa}\, \kappa_x(\boldsymbol{\varkappa}\cdot\mathbf{v}_{13})^2\theta(\boldsymbol{\varkappa}\cdot\mathbf{v}_{13})\varphi(v_1)\varphi(v_2)\varphi(v_3)$$
$$\times \int d\mathbf{r}_{12} \exp[-i\mathbf{k}\cdot\mathbf{r}_{12}]\{g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1 - a\boldsymbol{\varkappa}) - g_2(\mathbf{r}_1, \mathbf{r}_2)g_2(a_+)\} \tag{67}$$

The calculation of m_{xx} and n_x involves integrals well known in kinetic theory[9]; we merely quote the results in Appendix B. The evaluation of $\tilde{n}_x$ is more delicate because it involves the triplet correlation function g_3. However, in Appendix B, we show that $\tilde{n}_x$ can be exactly expressed in terms of the pair correlation function g_2 only.

Using these results as well as the decomposition (59), the angular integrations in (63) and (64) are easily performed, and, in terms of the reduced wave number $y = ka$, we finally arrive at the fairly compact expression

$$g_{qh}(\tau) = g_{qh}^{(1)}(\tau) + g_{qh}^{(2)}(\tau) \tag{68}$$

with

$$g_{qh}^{(1)}(\tau) = (16\Lambda/27\pi^{3/2}) \int_0^\infty y^2\, dy\, \{\varphi_\perp(y)[\mathscr{V}_{s;1,1}(y;\tau)$$
$$\times \mathscr{V}_{\perp,\perp}(y;\tau) - \mathscr{V}_{s;1,1}^{(0)}(y;\tau)\mathscr{V}_{\perp,\perp}^{(0)}(y;\tau)]$$
$$+ \tfrac{1}{2}\varphi_\parallel(y)[\mathscr{V}_{s;1,1}(y;\tau)\mathscr{V}_{\parallel,\parallel}(y;\tau) - \mathscr{V}_{s;1,1}^{(0)}(y;\tau)\mathscr{V}_{\parallel,\parallel}^{(0)}(y;\tau)]\} \tag{69}$$

and

$$g_{qh}^{(2)}(\tau) = (\Lambda/18\pi^{3/2}) \int_0^\infty y^4\, dy\, \psi(y)\tilde{\rho}(y)\mathscr{V}_{s;1,1}(y;\tau)\mathscr{V}_{1,1}(y;\tau) \tag{69'}$$

In these expressions, we have introduced the dimensionless mean free path,

$$\Lambda = 1/4\sqrt{\pi}(a^3\rho)g_2(a_+) \tag{70}$$

and the following dimensionless functions [see also (43)]:

$$\varphi_\perp(y) = 9(6i_2^2 + 5i_3^2 - 8i_2i_3)/35 \tag{71}$$

$$\varphi_\parallel(y) = 9(2i_2^2 + 11i_3^2 + 2i_2i_3)/35 \tag{72}$$

$$\Psi(y) = [\tilde{G}(y)/g_2(a_+)] + \tfrac{4}{3}\pi\tilde{\rho}(y) \tag{73}$$

where

$$i_2(y) = \sin y/y; \qquad i_3(y) = [2y\cos y - (y^2 - 2)\sin y]/y^3 \tag{74}$$

and $\tilde{G}(y)$ is the (dimensionless) Fourier transform of the equilibrium pair correlation function:

$$\tilde{G}(y) = \tilde{C}(y)/[1 - (a^3\rho)\tilde{C}(y)] \tag{75}$$

Notice that the functions $\varphi_\perp$, $\varphi_\parallel$, and $\tilde{\rho}$ tend to 1 when y goes to zero, while ψ tends to a finite constant; moreover, these functions tend to zero for $y \gg 1$. These two features call for the following remarks.

(i) For τ finite, we see that the integrand of $g_{qh}^{(1)}(\tau)$ at small wave number behaves like y^2 and is thus larger than the corresponding contribution to $g_{qh}^{(1)}(\tau)$ ($\propto y^4$). However, we see from (68) that $g_{qh}^{(1)}(\tau)$ starts as 0 at $\tau = 0$; moreover, the numerical factors weighting $g_{qh}^{(1)}$ and $g_{qh}^{(2)}$ are different. Hence, even though we are working in a quasihydrodynamic approximation, it is hard to tell which term will dominate in the intermediate time regime ($\tau \simeq 3$–10) and we have no good a priori reason to neglect $g_{qh}^{(2)}$ as compared to $g_{qh}^{(1)}$.

(ii) Similarly, we do not feel it legitimate to take the limiting values at $y = 0$ for the functions $\varphi_\perp$, $\varphi_\parallel$, $\tilde{\rho}$, and ψ in the integrands of (68) and (69), even though we expect the dominant contributions to come from "small" y. Indeed, we have to give up our naive ideas taken from the kinetic theory of dilute gases: There, hydrodynamic behavior is known to hold for $y\Lambda \leqslant 1$ and, because $\Lambda \gg 1$, this implies $y \ll 1$. However, in a dense fluid, the Enskog mean free path is exceedingly small (for example, $\Lambda \simeq \frac{1}{30}$ for $V/V_0 \simeq 1.6$) and hydrodynamic behavior may be expected to hold at least up to $y \simeq O(1)$, in which case the y dependence of the functions $\varphi_\perp$, $\varphi_\parallel$, ψ, and $\tilde{\rho}$ may not be neglected; this point is further discussed in Section 4.

Before closing this section, let us investigate the meaning of our quasihydrodynamic approximation at $t = 0$. Of course, this approximation was not devised to correctly describe this zero-time behavior, but it is nevertheless important to verify that, in this limit, it does not lead to absurd results.

With the property

$$\mathscr{V}_{\alpha,\alpha}(0) = \mathscr{V}^{(0)}_{\alpha,\alpha}(0) = 1 \tag{76}$$

we readily see that the exact property $g^{(1)}(0) = 0$ is maintained:

$$g^{(1)}_{qh}(0) = 0 \tag{77}$$

Moreover, tedious but straightforward manipulations lead to

$$g^{(2)}_{qh}(0) = -\frac{1}{12a^3\rho(g_2(a_+))^2}\left.\frac{\partial[g_2(r) - g_2(a_+)\theta(r-a)]}{\partial r}\right|_{r=a_+} \tag{78}$$

It is readily verified, with the help of the BBGKY hierarchy, that this same result would come out of the exact result (26) if we replace there the function $\Phi(x)$ by the approximation $\Phi_{qh}(x) = 1$. In other words, (78) can be rewritten formally as

$$g^{(2)}_{qh}(0) = \frac{\pi}{6}\int_{-1}^{+1} dx\, x\left[\frac{g_3(-x)}{g_2(a_+)^2} - 1\right] \tag{79}$$

Inspection of Fig. 1 indicates that, loosely speaking, $\Phi_{qh}(x) = 1$ is the most reasonable constant value to approximate the true $\Phi(x)$. Moreover, the x dependence of Φ expresses the angular dependence of the various correlated sequences of two collisions and we may expect that this angular dependence is rapidly damped after a few further collisions: Hence Eq. (79) appears as very reasonable.

In Table II, we give the values of $g^{(2)}_{qh}(0)$, on the basis of the Verlet–Weiss rule[11] (which is of course not very precise for the derivative of the pair correlation at contact), and of the Bellemans–Orban calculations,[19] at

Table II. Values of $g_{qh}(0)$ at Various Densities

V/V_0	Eq. (75) and Verlet–Weiss rule	Eq. (76) and Bellemans–Orban calculation
20	0.189	—
10	0.182	—
7	0.177	—
5	0.170	—
4	0.165	—
3	0.157	—
2.5	0.150	—
2	0.140	—
1.83	0.135	0.154
1.69	0.129	0.143
1.6	0.126	—
1.5	0.120	—

various densities. The characteristic feature of these data is that $g_{qh}^{(2)}(0)$ is much larger, at all densities, than the exact $g^{(2)}(0)$. Nevertheless, it is this value which governs the long-time value of $g^{(2)}(\tau)$, though it leads of course to an incorrect second derivative of γ at $\tau = 0$.

4. THE PROPAGATORS

In order to use the approximate kernels $g_{qh}^{(1)}(\tau)$ and $g_{qh}^{(2)}(\tau)$ for solving the kinetic equation (18) for $\gamma(\tau)$, we still need explicit expressions for the propagators $\mathscr{V}$ [see Eqs. (69) and (69′)]. Though this problem is simpler than the calculation of the full Enskog operator of motion (49), it cannot be solved exactly either: We only know explicitly a few asymptotic properties, which we shall use to guess reasonable interpolation formulas valid for all values of y and τ.

To illustrate the procedure, we consider in some detail the case of the transverse velocity propagator $\mathscr{V}_{\perp,\perp}(y;\tau)$. The calculations leading to the results presented below are often long and tedious; moreover, some of them are already available in the literature (see for example Refs. 7 and 13); we shall thus not display them here and we shall rather concentrate upon the method.

We start with a dimensional analysis of the problem; to do this, we use the decomposition (39) of the Enskog operator. The first term, $i\mathbf{k}\cdot\mathbf{v}_2$, represents free motion, or, in a language which is more appropriate to transport theory, it describes *kinetic transfer* of the molecular properties of the system. In dimensionless units, its matrix elements in our basis $|n_2\rangle$ [see (44)] can be estimated by

$$\langle n_2|i\mathbf{k}\cdot\mathbf{v}_2\tau_E|n_2'\rangle \sim ik(k_BT/m)^{1/2}\tau_E \sim i(y\Lambda), \qquad \text{all } n, n' \tag{80}$$

In general, the second term, $C_k'^E$, which represents the effect of the interactions, has the simple estimated value

$$\langle n_2|C_k'^E\tau_E|n_2'\rangle \sim 1 \tag{81}$$

where the right-hand side represents a function of y which is of order unity for all y. However, (81) only holds if n and n' are *not* any of the conserved states (α) [see (48)]; due to well-known conservation properties at $k = 0$,

$$\langle n_2|C_0'^E\tau_E|\alpha_2\rangle = \langle\alpha_2|C_0'^E\tau_E|n_2\rangle = \langle\alpha_2|C_0'^E\tau_E|\beta_2\rangle = 0 \tag{82}$$

$$\alpha, \beta \in (1,\ldots,5); \quad n \notin (1,\ldots,5)$$

this estimate has to be refined when conserved states are involved in the matrix element of $C_k'^E$. From simple symmetry arguments (see, for example, Ref. 7), one finds that some of the matrix elements analogous to (82) for y finite, start like y for small y while others start like y^2. Neglecting for simplicity these

latter terms, which do not affect our present qualitative argument, we have thus to keep in mind that some matrix elements of $C_k'^{\mathrm{E}}$, involving conserved states, have the following behavior:

$$\langle \alpha_2 | C_k'^{\mathrm{E}} \tau_{\mathrm{E}} | n_2 \rangle \simeq \langle n_2 | C_k'^{\mathrm{F}} \tau_{\mathrm{E}} | \alpha_2 \rangle \sim iy \qquad \text{if} \quad y \ll 1$$
$$\sim 0 \qquad \text{if} \quad y \gg 1 \tag{83}$$
$$\alpha \in (1,\ldots,5); \quad n \notin (1,\ldots,5)$$

These matrix elements describe *collisional transfer*.

Finally, we should remember that the dimensionless mean free path Λ measures the density of the system: In dilute system, we have $\Lambda \gg 1$, while dense systems correspond to $\Lambda \ll 1$.

With these preliminary remarks, we may distinguish the following regimes.

1. *Free motion regime*, $\Lambda y \gg 1$.

Comparing (80) with (81) and (83), we see that free flow dominates the effect of the interactions; for all times, the propagator is thus

$$\mathscr{V}_{\perp,\perp}(y;\tau) \simeq \langle 3_2 | \exp[ikv_{2x}\tau_{\mathrm{E}}\tau] | 3_2 \rangle \tag{84}$$

where, for simplicity, we have oriented the vector $\mathbf{k}$ along the x axis. A trivial integration over velocity leads to

$$\mathscr{V}_{\perp,\perp}(y;\tau) \simeq \exp[-(y\Lambda)^2\tau^2/2] = \mathscr{V}_{\perp,\perp}^{(0)}(y;\tau), \qquad y\Lambda \gg 1 \tag{85}$$

The last equality in (85), which fixes the unperturbed propagator, is of course valid for any $(y\Lambda)$.

Notice that, at low density, this regime covers a very wide range of y values ($y \gg 1/\Lambda \to 0$), while, at the highest densities, it is only applicable for fairly large wave numbers ($y \gg 1/\Lambda \gg 1$).

2. *Collision-dominated regime*, $\Lambda y \ll 1$.

Here, we have to separately consider two regions of time:

(a) *Large times* $\tau \gg 1$. Here, collisions dominate and continuously maintain the system in a state of local equilibrium, slightly perturbed by kinetic and collisional transfers; the relative importance of these two mechanisms depends of course of the density, as measured by Λ. Here is the region where hydrodynamics holds and we may use the well-known formula (the superscript h stands for "hydrodynamic")

$$\mathscr{V}_{\perp,\perp}^{h}(y;\tau) = \exp[-(y\Lambda)^2\tilde{\eta}_{\mathrm{E}}\tau] \tag{86}$$

where $\tilde{\eta}_{\mathrm{E}}$ denotes the dimensionless shear viscosity in the Enskog approximation:

$$\tilde{\eta}_{\mathrm{E}} = \eta_{\mathrm{E}}\tau_{\mathrm{E}}/\rho m a^2 \Lambda^2 \tag{87}$$

This result can be obtained by a straightforward application of the general theory of hydrodynamic modes previously developed by Résibois[14]: Starting from the Enskog operator (39) and expanding it in powers of k, one may easily compute the shear diffusion eigenvalue by a perturbation calculus in k.

However, for values of y which are not too small (as may occur at the highest densities), it is preferable to keep the full y dependence of the collisional transfer terms (83) and, proceeding in the same way as for the strict hydrodynamic regime, one arrives then at the following *generalized hydrodynamic formula*[4]:

$$\mathscr{V}_{\perp,\perp}^{gh}(y;\tau) = \exp[-(y\Lambda)^2\tilde{\eta}_{\mathrm{E}}(y)\tau] \tag{88}$$

where the dimensionless wavenumber-dependent viscosity is given by

$$\tilde{\eta}_{\mathrm{E}}(y) = \frac{5}{4}\left[1 + \frac{\sqrt{\pi}\lambda(y)}{15\Lambda}\right]^2 + \frac{\kappa(y)}{15\Lambda^2} \tag{89}$$

Here the dimensionless functions $\lambda(y)$ and $\kappa(y)$ are, respectively,

$$\lambda(y) = [(15/y^5)(3\sin y - 3y\cos y \dot{-} y^2\sin y)] \tag{90}$$

$$\kappa(y) = [(30/y^5)(-\sin y + y\cos y) + (10/y^2)] \tag{91}$$

Since we have $\kappa(0) = \lambda(0) = 1$, and, of course, $\tilde{\eta}_{\mathrm{E}} = \tilde{\eta}_{\mathrm{E}}(0)$, it is readily checked that, at $y = 0$, Eq. (89) agrees with the original Enskog results, provided it is taken in the zeroth-order Sonine polynomial approximation.

(b) *Small times*, $\tau \ll 1$. For such short times, the hydrodynamic regime is not yet reached but we may use the short-time expansion

$$\begin{aligned}\mathscr{V}_{\perp,\perp}(y;\tau) = 1 &+ \langle 3_2|(ikv_{2x} + C'^{\mathrm{E}}_{-k})|3_2\rangle\tau_{\mathrm{E}}\tau \\ &+ \langle 3_2|(ikv_{2x} + C'^{\mathrm{E}}_{-k})^2|3_2\rangle(\tau_{\mathrm{E}}\tau)^2/2! + \cdots\end{aligned} \tag{92}$$

Except for the amount of labor, there is no particular difficulty in evaluating the matrix elements involved in this formula, provided the second-order term is calculated again within the zeroth-order Sonine polynomial approximation; the result is

$$\mathscr{V}_{\perp,\perp}(y;\tau) = 1 - \frac{y^2\kappa(y)}{15}\tau - \left\{\left[1 + \frac{\sqrt{\pi}\lambda(y)}{15\Lambda}\right]^2 - \frac{y^2\kappa(y)^2}{225\Lambda^2}\right\}(y\Lambda)^2\frac{\tau^2}{2!} + \cdots \tag{93}$$

Though it is difficult to say anything rigorous about the convergence of this series, one sees that the terms of order τ [remember $\kappa(y) \to 0$ for $y \gg 1$] and τ^2 are small in the regime $\tau \ll 1$ and $(\Lambda y) \ll 1$, an indication that (93) can be safely used in this regime.

[4] A similar calculation of y-dependent transport coefficients was presented, in a very different context, in Ref. 15.

An important feature of this result is the presence of a term of order τ: It describes the well-known purely collisional transfer effect,[8,16] which, due to the instantaneous character of the collisions, starts right away at time $\tau = 0$. As shown by Wainwright,[16] this corresponds to a delta-function singularity in the Green–Kubo integrand associated with shear viscosity.

We now propose an interpolation formula which smoothly fits these various limiting regimes; we write, for all y and τ,

$$\mathscr{V}_{\perp,\perp}(y;\tau) = \{\exp[-(\alpha\tau)^2]\mathscr{V}^{s}_{\perp,\perp}(y;\tau) + \{1 - \exp[-(\alpha\tau)^2]\}\mathscr{V}^{gh}_{\perp,\perp}(y;\tau) \quad (94)$$

Here, $\mathscr{V}^{gh}_{\perp,\perp}$ has been defined in (88) and $\mathscr{V}^{s}_{\perp,\perp}$ is given by

$$\mathscr{V}^{s}_{\perp,\perp}(y;\tau) = \exp\left[-(y\Lambda)^2\left\{\frac{\kappa(y)\tau}{15\Lambda^2} + \left(1 + \frac{\sqrt{\pi}\lambda(y)}{15\Lambda}\right)^2\frac{\tau^2}{2}\right\}\right] \quad (95)$$

Moreover, α is a constant parameter, of order unity, which ensures the transition between the regions $\tau \gg 1$ and $\tau \ll 1$.

Notice that for $y\Lambda \gg 1$ and $\tau \gg 1$, Eq. (94) leads to

$$\mathscr{V}_{\perp,\perp}(y;\tau) \simeq \exp[-\tfrac{5}{4}(y\Lambda)^2\tau], \qquad y\Lambda \gg 1, \quad \tau \gg 1 \quad (96)$$

which is different from the exact result (85). However, since in this regime both formulas tell us that $\mathscr{V}_{\perp,\perp}(y;\tau) \simeq 0$, this difference is irrelevant.

The same method may be applied to the other propagators; in the example of self-diffusion, the situation is particularly simple because there is no collisional transfer (the particle number is conserved by $C^{E}_{s,1}$) and the three limiting cases are as follows.

1. $y\Lambda \gg 1$

$$\mathscr{V}_{s;1,1}(y;\tau) \simeq \exp[-(y\Lambda)^2\tau^2/2] = \mathscr{V}^{(0)}_{s;1,1}(y;\tau) \quad (97)$$

where, again, the last equality holds for arbitrary $(y\Lambda)$.

2a. $y\Lambda \ll 1$, $\tau \gg 1$:

$$\mathscr{V}^{gh}_{s;1,1}(y;\tau) \simeq \exp[-(y\Lambda)^2\tilde{D}_{E}\tau] \quad (98)$$

where the dimensionless diffusion coefficient is simply

$$\tilde{D}_{E} = D_{E}\tau_{E}/a^2\Lambda^2 = \tfrac{3}{2} \quad (99)$$

2b. $y\Lambda \ll 1$, $\tau \ll 1$:

$$\mathscr{V}_{s;1,1}(y;\tau) \simeq 1 - \tfrac{1}{2}(y\Lambda)^2\tau^2 + \cdots \quad (100)$$

From these results, we propose the interpolation formula

$$\mathscr{V}_{s;1,1}(y;\tau) = \{\exp[-(\alpha\tau)^2]\}\mathscr{V}^{(0)}_{s;1,1}(y;\tau) + \{1 - \exp[-(\alpha\tau)^2]\} \times \mathscr{V}^{gh}_{s;1,1}(y;\tau) \quad (101)$$

Similar equations have been obtained for the density and the longitudinal velocity propagators; since these formulas are rather elaborate but involve no new principle, we present them in Appendix C. We close this section with a few remarks.

(i) The extrapolation formulas we have proposed here are rather involved and, moreover, they are certainly not the only ones which have (or will be) suggested. In particular, for self-diffusion, it is common practice to use, instead of (101), the more compact expression based on the well-known Gaussian approximation[17]

$$\mathscr{V}_{s;1,1}(y;\tau) = \exp\left[-(y\Lambda)^2 \int_0^\tau (\tau - \tau') \exp(-2\tau'/3)\, d\tau'\right] \tag{102}$$

which also satisfies the asymptotic properties (97), (98), and (100). The undoubted superiority of (102) over (101) is that it involves no adjustable parameter. However, the generalization of a formula of the type (102) to the propagators $\mathscr{V}_{1,1}$ and $\mathscr{V}_{\parallel,\parallel}$ is very difficult: The complicated coupling of density, longitudinal velocity, and kinetic energy (which, in the long term, leads to the sound and entropy modes) makes it very hard to write down a compact formula which holds for times both short and long. On the contrary, our representation can easily be written down for these propagators also, as can be seen in Appendix C. Moreover, by choosing α once for all, independently of the density, we minimize the freedom it offers; we have adopted the value $\alpha = \frac{1}{3}$, but changing it by a factor of 2 does not affect qualitatively our results. This value of $\alpha = \frac{1}{3}$ is very reasonable in view of our above discussion.

(ii) Though our interpolation formulas are rather involved, they are very convenient in numerical calculations and moreover they become extremely simple in the two regions $\tau \gg 1$ and $\tau \ll 1$, where analytical calculations are feasible.

(iii) An important feature of $\mathscr{V}_{\perp,\perp}$, already noticed following (93) (and which also applies to $\mathscr{V}_{\parallel,\parallel}$), is the presence of collisional transfer terms, which lead to a rapid decay of this propagator for short times. To be more precise, consider first the self-diffusion propagator $\mathscr{V}_{s;1,1}$, where no collision transfer mechanism occurs; from (101) and (97), we readily verify that, for all y and τ,

$$\mathscr{V}_{s;1,1}(y;\tau) \geqslant \mathscr{V}_{s;1,1}^{(0)}(y;\tau) \tag{103}$$

This equation expresses the obvious fact that diffusion of a tagged particle is always slower in the presence of interactions than with free motion. The same is true for $\mathscr{V}_{\perp,\perp}$ *in the dilute gas limit*:

$$\mathscr{V}_{\perp,\perp}(y;\tau) \geqslant \mathscr{V}_{\perp,\perp}^{(0)}(y;\tau), \qquad \Lambda \to \infty \tag{104}$$

but, if we compare $\mathscr{V}_{\perp,\perp}$ and $\mathscr{V}^{(0)}_{\perp,\perp}$ in general, we find that for *short wave numbers* $y \lesssim 1$ *and for times* $\tau \lesssim 1/\Lambda$ (which may be quite long for high density systems), we have

$$\mathscr{V}_{\perp,\perp}(y;\tau) < \mathscr{V}^{(0)}_{\perp,\perp}(y;\tau), \qquad y \lesssim 1, \quad \tau \lesssim 1/\Lambda \tag{105}$$

Here, collision transfer is an extremely efficient mechanism to damp a velocity fluctuation: It is even more efficient than free motion! This point will be extremely important in interpreting the results of the next section; it was completely overlooked in the approximation for the propagators proposed by Mazenko[18] and is at the origin of the failure of his theory at high density.

5. RESULTS AND DISCUSSION

We have numerically computed our approximate kernel $g_{qh}(\tau)$ [see (68), (69), and (69′)] at various densities with the help of the formulas for the propagators given in Section 4 and in Appendix C. A further integration over time leads, then, with the help of (19), to the result displayed in Fig. 2 for the ratio D/D_E (solid curve). This curve is to be compared with the data of Alder and co-workers, extrapolated to an infinite number of particles (dashed curve).[8] We observe that, at low density ($V/V_0 \gtrsim 7$), the agreement is quite good: The discrepancy is of the order expected by the use of the zeroth-order Sonine approximation; at intermediate densities ($2 \lesssim V/V_0 \lesssim 7$) the theory is still qualitatively correct, although the enhancement of D is

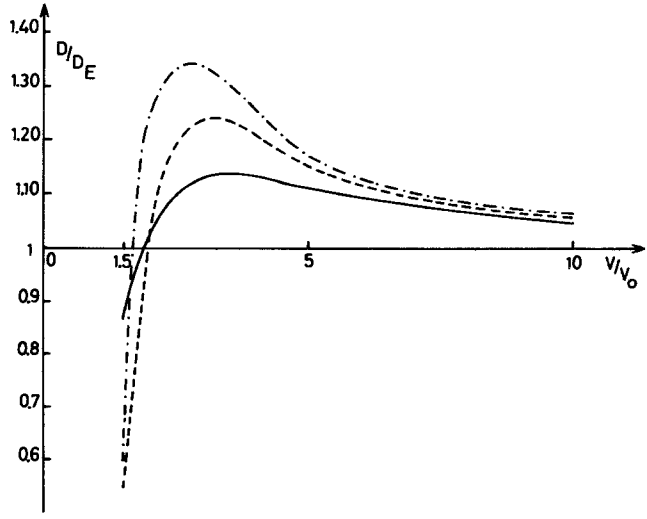

Fig. 2. The ratio D/D_E as a function of V/V_0. (——) Present theory; (–·–) Alder and co-workers (extrapolated); (– – –) Present theory corrected for long times [see (123)].

significantly too small; finally, at the highest densities ($1.5 \leqslant V/V_0 \leqslant 2$), we see that the ratio D/D_E becomes smaller than unity, a nontrivial feature which is clearly exhibited in the computer experiments. We shall come back to the interpretation of this result below.

A more severe test of the theory is provided by the analysis of the time-dependent correlation function $\gamma(\tau)$ itself. In order to do this, we have numerically solved the kinetic equation (18) and from this, we have computed the deviation from the Enskog theory:

$$\delta\gamma(\tau) = \gamma(\tau) - \gamma^E(\tau) \tag{106}$$

where $\gamma^E(\tau)$ is the exponential Enskog prediction, $\exp(-2\tau/3)$.

To illustrate these results, in Fig. 3 we have plotted $\delta\gamma(\tau)$ from the present theory (solid curve) together with the Alder results (dashed curves) at the two characteristic densities $V/V_0 = 5.0$ and $V/V_0 = 1.6$.

Although it is difficult to make a detailed comparison with the computer results, because these are rather sensitive to the total number N of particles taken in the calculation,[8,19] we see that the following qualitative features are well reproduced by the theory.

1. The deviation $\delta\gamma(\tau)$ is the largest for times larger than 1, and the position of this maximum is shifted toward larger times when the density is increased.

2. The value of $\delta\gamma(\tau)$ at this maximum is strongly density dependent; in particular, it becomes *negative* at the highest densities, a property which implies the negative deviation of the diffusion coefficient from its Enskog value already shown in Fig. 1.

Moreover, Fig. 2 shows that the theory is in default in two respects:

3. It leads to a too positive $\delta\gamma(\tau)$ at short times; in particular, the positive bump we obtain for $V/V_0 = 1.6$ is absent in the computer calculations.

4. It leads to a too rapid decay of $\delta\gamma(\tau)$ for large times.

Despite the fact that very little analytic information can be extracted from our expressions (69) and (69′), we shall see now that these four features can be understood, by a close inspection of these formulas, without any numerical calculation. Our discussion will also indicate the way to remedy the main defects of the present theory.

1. We first notice that the characteristic decay time of the kernel $g(\tau)$ [and thus also that of $\delta\gamma(\tau)$] is governed by the corresponding time for the propagators $\mathscr{V}_{\alpha,\alpha}(y;\tau)$ for some value y^* where the integrands $y^2\varphi_\parallel(y)$, $y^2\varphi_\perp(y)$, and $y^4\psi(y)\rho(y)$ [see (69) and (69′)] have their maxima. These quantities are only weakly density dependent and their maxima occur for a

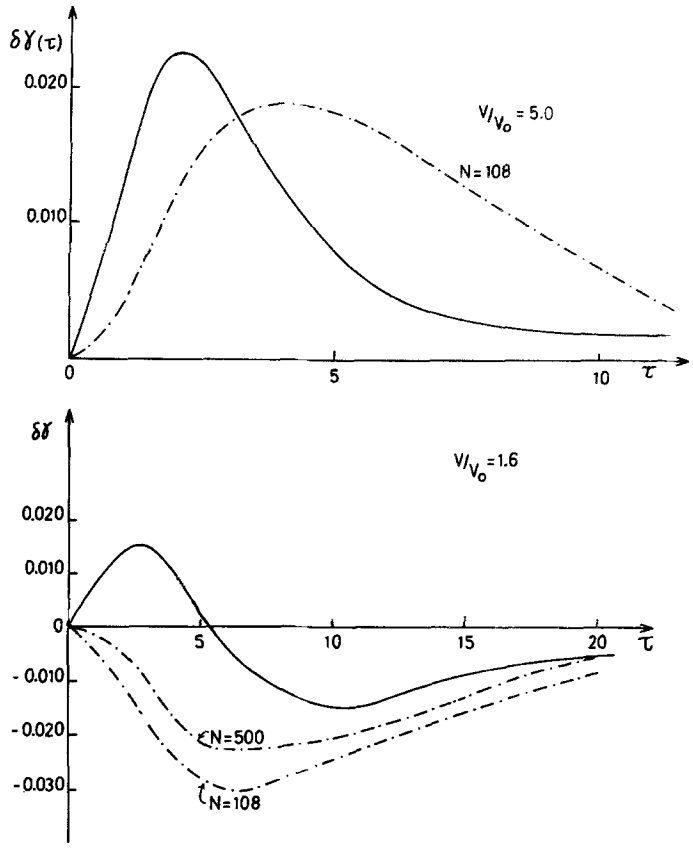

Fig. 3. The deviation of the velocity autocorrelation function from its Enskog value at the densities $V/V_0 = 5.0$ and $V/V_0 = 1.6$, respectively. (——) Present theory; (–·–) Alder and co-workers.

value $y^* \sim 1$. For such y^*, the propagators are characterized by a decay time τ_{rel} which we may estimate as [see, for example, (88)]

$$\begin{aligned} \tau_{\text{rel}} &\propto 1/\Lambda^2 \to 0 \qquad \text{for} \quad V/V_0 \to \infty \\ \tau_{\text{rel}} &\propto 1 \qquad\qquad\quad \text{for} \quad V/V_0 \sim 1 \end{aligned} \tag{107}$$

This shows that the maximum of $\delta\gamma(\tau)$ does indeed shift toward larger times as V/V_0 decreases. (We are of course unable to locate precisely this maximum.)

2. The low-density result [see (103) and (104)]

$$\mathscr{V}_{\perp,1}(y;\tau)\mathscr{V}_{s;1,1}(y;\tau) \geqslant \mathscr{V}^{(0)}_{\perp,1}(y;\tau)\mathscr{V}^{(0)}_{s;1,1}(y;\tau), \qquad V/V_0 \to \infty \tag{108}$$

indicates that all contributions to $g(\tau)$ are positive at low densities,[5] leading in turn to a positive $\delta\gamma(\tau)$. On the contrary, the mechanism discussed in (105) allows $g_{qh}^{(1)}(\tau)$ to become negative at the highest densities. Since this latter term itself dominates $g_{qh}^{(2)}(\tau)$ [see (109) and (110) below], we see that collisional transfer is responsible for the negative deviation $\delta\gamma(\tau)$ in this high-density region; this observation is confirmed by the fact that these negative contributions start to appear for $V/V_0 \lesssim 2.0$, where collisional transfer is well known to dominate transport phenomena.

As far as we know, this mechanism was not fully understood previously, except by the rather vague concept of "backward scattering,"[8] which was difficult to define because, as was lucidly pointed out by Alder and co-workers, it was describing a collective effect, which can now be pointed out precisely.

3. Though the present theory was initially devised to give a correct short-time behavior of the correlation function $\gamma(\tau)$, the fairly important discrepancy between our calculation and the computer results in this time regime is not really surprising. Indeed, this correct behavior was lost when we replaced our "exact" kernel $g(\tau)$ by its quasihydrodynamic approximation $g_{qh}(\tau)$. As was pointed out above, the difference $[g(0) - g_{qh}(0)]$ is fairly large and the same presumably remains true for $\tau \lesssim 1$: We can expect that this difference is at the origin of the difficulty. Yet, we have not found any simple convincing way to restore this short-time behavior; as a matter of fact, it is probably in this problem that the use of kinetic models will bring the most spectacular improvement over our rough theory, because it will automatically incorporate the correct short-time behavior. We shall not dwell upon this point any further here, except to note that rough estimates indicate that the results found above for the diffusion coefficient are only little affected by these short-time errors.

4. Let us now come to the long-time behavior predicted by this theory. For $\tau \to \infty$, it is readily seen from (69′) that the contribution $g_{qh}^{(2)}(\tau)$ takes the form

$$g_{qh}^{(2)}(\tau) \underset{\tau\to\infty}{\propto} \int_0^\infty y^4 dy \exp[-(y\Lambda)^2\alpha(\Lambda)\tau] \underset{\tau\to\infty}{\propto} 1/\tau^{5/2} \tag{109}$$

(the function $\alpha(\Lambda)$ need not be specified here); it is dominated by $g_{qh}^{(1)}(\tau)$, which takes the form

$$g_{qh}^{(1)}(\tau) \underset{\tau\to\infty}{\propto} \int_0^\infty y^2\, dy \exp[-(y\Lambda)^2\beta(\Lambda)\tau] \underset{\tau\to\infty}{\propto} 1/\tau^{3/2} \tag{110}$$

It is quite easy to get the precise asymptotic behavior of $g_{qh}^{(1)}(\tau)$; with the help of (88) and (98), we get indeed

$$g_{qh}^{(1)}(\tau) \underset{\tau\to\infty}{\simeq} \left(\frac{2}{3}\right)^2 \frac{1}{3\pi\Lambda^2} \left(\frac{1}{\beta(\Lambda)\tau}\right)^{3/2} \tag{111}$$

[5] We neglect here the oscillating contributions from the sound waves, which are rapidly damped anyway.

where the coefficient $\beta(\Lambda)$ is defined by

$$\beta(\Lambda) = \left[\frac{3}{2} + \frac{1}{15\Lambda^2} + \frac{5}{4}\left(1 + \frac{\sqrt{\pi}}{15\Lambda}\right)^2\right] \tag{112}$$

Thus, as already announced in I, the kernel of our non-Markovian kinetic equation finally decays to zero as a $\tau^{-3/2}$ power law, with a positive defined coefficient. Formula (111) does not tell us, however, how long we have to wait before it becomes valid; the numerical calculation of $g_{qh}(\tau)$ shows us, for example, that, for $V/V_0 = 5.0$, the asymptotic value (111) is reached within $1/10^4$ for times $\tau > 17$; yet, at the highest density ($V/V_0 = 1.6$), $g_{qh}(\tau)$ is still *negative* up to times $\tau > 80$, though we can check that it will finally end up with the correct asymptotic behavior (111)!

The asymptotic formula (111) generates a similar long-time tail for the velocity correlation function itself; the simplest procedure to get it is to define the Laplace transform of the kernel

$$\tilde{g}_{qh}(s) = \int_0^\infty e^{-st} g_{qh}(\tau)\, d\tau \tag{113}$$

and a similar expression for $\tilde{\gamma}(s)$. One gets then from (18)

$$\tilde{\gamma}(s) = 1/[s + \tfrac{3}{2} - \tilde{g}_{qh}(s)] \tag{114}$$

which, for small s, can be expanded as

$$\tilde{\gamma}(s) = \frac{1}{\frac{3}{2} - \tilde{g}_{qh}(0)} + \left(\frac{1}{\frac{3}{2} - \tilde{g}_{qh}(0)}\right)^2 [\tilde{g}_{qh}(s) - \tilde{g}_{qh}(0)] + O(s) \tag{115}$$

With the help of (19), we have then from known asymptotic theorems[20]

$$\delta\gamma(\tau) \underset{\tau\to\infty}{\simeq} \left(\frac{D}{D_E}\right)^2 \frac{1}{3\pi\Lambda^2} \frac{1}{[\beta(\Lambda)\tau]^{3/2}} \tag{116}$$

Incidentally, note that (116) can also be written formally as

$$\delta\gamma(\tau) \underset{\tau\to\infty}{\simeq} \int_0^\tau \int_0^{\tau'} d\tau'\, d\tau'' \{\exp[-D(\tau - \tau')]\} g_{qh}(\tau' - \tau'') \exp(-D\tau'') \tag{117}$$

which has a very intuitive meaning: The long-time decay of $\delta\gamma(\tau)$ can be described as the exponential decay of the initial perturbation with the *exact* transport coefficient D, perturbed by the small memory effect of the non-Markovian kernel.

Equation (116) has to be compared with what is believed to be the correct asymptotic behavior of the velocity correlation function[4]

$$\Gamma(t)|_{\text{exact}} \underset{t\to\infty}{\simeq} \frac{2}{3[4\pi(D + \eta/nm)t]^{3/2}} \tag{118}$$

If we insert in (118) the transport coefficients D and η in the Enskog approximation, we get the following approximate result:

$$\delta\gamma(\tau)|_{\text{Enskog}} \underset{\tau\to\infty}{\simeq} \frac{g_2(a_+)}{3\pi\Lambda^2} \frac{1}{[\beta(\Lambda)\tau]^{3/2}} \tag{119}$$

which is, in our reduced units, the result obtained by Dorfman and Cohen[21] by summing the ring graphs: It is known to fit quite well the computer data for $\tau \to \infty$.[19]

The difference between (116) and (119), which was already noticed by Mazenko,[18] can be interpreted as follows:

(i) The extra factor $(D/D_E)^2$ in (116) can be traced back in (117); indeed, this factor would *not* appear if we had written instead

$$\delta\gamma(\tau) \underset{\tau\to\infty}{\simeq} \int_0^\tau \int_0^{\tau'} d\tau'\, d\tau'' \{\exp[-D_E(\tau - \tau')]\} g_{qh}(\tau' - \tau'') \exp(-D_E\tau'') \tag{120}$$

with an "unperturbed" *Enskog* transport coefficient in the exponential decay.

Similarly, no such factor appears in the (formally) exact theory[23]; here one has

$$\delta\gamma(\tau) \underset{\tau\to\infty}{\simeq} \int_0^\tau \int_0^{\tau'} d\tau'\, d\tau'' \{\exp[-D(\tau - \tau')]\} g^{\text{ren}}(\tau' - \tau'') \exp(-D\tau'') \tag{121}$$

Here the "renormalized" kernel g^{ren} involves the full transport coefficient D:

$$g^{\text{ren}}(\tau) = (D_E/D)^2 g_{qh}(\tau) \tag{122}$$

Yet, in any perturbative kind of approach, it is difficult to write down a consistent approximation of the type sketched either in (120) or in (121): While the kernel $g_{qh}(\tau)$ modifies the transport coefficient from its Enskog value to its "correct" value D, it does not "renormalize itself" and leads thus to the unsymmetric expression (116). In their dense fluid calculation, Dorfman and Cohen[21] avoided this factor $(D/D_E)^2$ by using an approximation equivalent to (120).

(ii) The factor $g_2(a_+)$ missing in (116), as compared to (119), is numerically important at high density and, as we shall see later, it is presumably at the origin of our too small values for the ratio shown in Fig. 2. To understand why this factor is lacking, let us go back to our original expression (21) for the kernel $g^{(1)}(\tau)$: We see that one factor $g_2(\mathbf{r}_1, \mathbf{r}_2)$ appears at time $\tau = 0$, when particles 1 and 2 first interact, but, at later times, these two particles are

taken as completely uncorrelated.[6] As was shown in I (Appendix D), this is all right for *short times* (i.e., including three-body effects): Then, the single pair correlation function $g_2(\mathbf{r}_1, \mathbf{r}_2)$ does the job of preventing any unphysical recollision process between particles 1 and 2. However, if we consider a dynamical process where particles 1 and 2 first become greatly separated and then come back to collide with each other—to make up a so-called "ring" event—it is clear that the description offered by (21) is unsatisfactory: This recollision process does not take place in the vacuum but rather in a dense medium where all other particles are at equilibrium. Hence, arguing as Enskog originally did, we would expect that $g_{qh}(\tau)$ should be replaced by

$$g^{\text{corr}}(\tau) \underset{\tau \to \infty}{=} g_2(a_+) g_{qh}(\tau) \tag{123}$$

where this extra factor $g_2(a_+)$ precisely accounts for the geometrical effect due to the other particles in the medium.

As was already pointed out by Mazenko in a rather different formalism,[24] it is quite difficult to devise a reasonable theory which would give (31) for short times and would gradually lead to (123) when time increases: How to do this seems the most puzzling challenge in dense hard-sphere dynamics. Of course, if one is only interested in the long-time behavior of $\gamma(\tau)$, there is no special difficulty in picking up a special class of graphs leading to the asymptotic behavior (123), as was done by Dorfman and Cohen. It remains, however, an open problem to treat such a class of graphs consistently, and explicitly, for all times.

In order to check whether a modification of the type indicated in (123) could account for the high-density deviations between our theoretical value for D/D_E and those obtained by Alder and co-workers, we have computed this ratio from (28) by assuming (123) to be valid for *all* times. The hypothesis here is that the main contributions to D come from times large enough so that (123) is valid. The result is reported in Fig. 2 (dotted curve) and shows almost quantitative agreement with the computer data; the corresponding data for $\delta\gamma(\tau)$ are, however, very poor at short times, as could be expected, and will not be displayed here.

The main conclusions of this work can be summarized in three points: First, the quasihydrodynamic approximation to the kinetic equation of Résibois and Lebowitz, Eq. (1), gives the correct qualitative features of the velocity autocorrelation function in dense hard-sphere fluids; in particular, the collective nature of the dominant effects, first pointed out by Alder and co-workers, is nicely exhibited: *These dominant effects all appear as precursors,*

[6] As a matter of fact, our approximation is such that the time-dependent pair correlation $S^{(1)}(\mathbf{r}_1; \mathbf{v}_1; \mathbf{r}_2; \mathbf{v}_2; \tau)$ [see (32)] even generally does not vanish inside the unphysical region $|\mathbf{r}_1 - \mathbf{r}_2| < a$.

for shorter times, of the now well-established power-law long-time tails, including at the highest densities.

Second, this quasihydrodynamic approximation is rather unsuccessful for short times but this does not disprove the validity of the kinetic equation (1), which has been constructed in such a way that this regime is in principle exactly described: It rather indicates the need for a more sophisticated solution of this equation, in particular through the use of kinetic models.

Third, the theory seems basically incorrect for long times at the highest densities; the important unsolved problem remains to write down an explicit and manageable kinetic equation which would incorporate the modification suggested by (123) for long times, while reducing to the present approximation in the short-time limit. We hope to come back to this point in later work.

APPENDIX A. CALCULATION OF $\tilde{g}^{(2)}(0)$

With the explicit formula I (40) for K_{12}, we may rewrite Eq. (21) for $\tau = 0$ as

$$\tilde{g}^{(2)}(0) = (m\tau_E{}^2 a^2/k_B T) \int d\mathbf{v}_1 \int d\mathbf{v}_2 \int d^2\boldsymbol{\kappa}\, v_{1x}(\boldsymbol{\kappa}\cdot\mathbf{v}_{12})\theta(\boldsymbol{\kappa}\cdot\mathbf{v}_{12}) \times [S^{(2)}(\mathbf{r}_1, \mathbf{v}_1'; \mathbf{r}_1 - a\boldsymbol{\kappa}, \mathbf{v}_2'; 0) - S^{(2)}(\mathbf{r}_1, \mathbf{v}_1; \mathbf{r}_1 + a\boldsymbol{\kappa}, \mathbf{v}_2; 0)] \tag{A.1}$$

where

$$\begin{aligned} &S^{(2)}(\mathbf{r}_1, \mathbf{v}_1; \mathbf{r}_2, \mathbf{v}_2; 0) \\ &\quad = a^2\rho^2 \int d\mathbf{r}_3\, d\mathbf{v}_3 \int d^2\boldsymbol{\kappa}'\, (\boldsymbol{\kappa}'\cdot - \mathbf{v}_{13}) \\ &\qquad \times \theta(\boldsymbol{\kappa}'\cdot\mathbf{v}_{13})\, \delta(\mathbf{r}_{13} - a\boldsymbol{\kappa}')\{g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g_2(\mathbf{r}_1, \mathbf{r}_2)g_2(\mathbf{r}_1, \mathbf{r}_3)\} \\ &\qquad \times (v_{1x}' - v_{1x})\varphi(v_1)\varphi(v_2)\varphi(v_3) \end{aligned} \tag{A.2}$$

Let us recall that $\mathbf{v}_1'$ and $\mathbf{v}_2'$ denote the velocities after the collision:

$$\mathbf{v}_1' = \mathbf{v}_1 - (\boldsymbol{\kappa}\cdot\mathbf{v}_{12})\boldsymbol{\kappa}, \qquad \mathbf{v}_2' = \mathbf{v}_2 + (\boldsymbol{\kappa}\cdot\mathbf{v}_{12})\boldsymbol{\kappa} \tag{A.3}$$

In the term of (A.1) involving $S^{(2)}(\mathbf{r}_1, \mathbf{v}_1'; \mathbf{r}_1 - a\boldsymbol{\kappa}, \mathbf{v}_2')$, we use $\mathbf{v}_1'$ and $\mathbf{v}_2'$ as new integration variables and replace $\boldsymbol{\kappa}$ by $\boldsymbol{\kappa}'' = -\boldsymbol{\kappa}$. With the help of (A.3) and (7), we then readily get

$$\tilde{g}^{(2)}(0) = \frac{1}{48\pi} \int d^2\boldsymbol{\kappa}\, d^2\boldsymbol{\kappa}'\, (\boldsymbol{\kappa}\cdot\boldsymbol{\kappa}')\left\{\frac{g_3(-\boldsymbol{\kappa}\cdot\boldsymbol{\kappa}')}{g_2(a_+)^2} - 1\right\}\Phi(\boldsymbol{\kappa}, \boldsymbol{\kappa}') \tag{A.4}$$

where the function $\Phi(\boldsymbol{\kappa}, \boldsymbol{\kappa}')$ is defined by

$$\Phi(\boldsymbol{\kappa}, \boldsymbol{\kappa}') = (m/k_B T)^2 \int d\mathbf{v}_1\, d\mathbf{v}_2\, d\mathbf{v}_3\, (\boldsymbol{\kappa}\cdot\mathbf{v}_{12})^2\theta(\boldsymbol{\kappa}\cdot\mathbf{v}_{12}) \times (\boldsymbol{\kappa}'\cdot\mathbf{v}_{13})^2\theta(\boldsymbol{\kappa}'\cdot\mathbf{v}_{13})\varphi(v_1)\varphi(v_2)\varphi(v_3) \tag{A.5}$$

We then notice that Φ, being a scalar, can only depend on $\varkappa$ and $\varkappa'$ through their scalar product:

$$\Phi(\varkappa, \varkappa') \equiv \Phi(\varkappa \cdot \varkappa') \tag{A.6}$$

and this allows us to reduce (A.4) to (26) with $x = \varkappa \cdot \varkappa'$. We are thus left with the proof that (A.5) can be reduced to (28); the steps of this calculation are:

(i) Use $\mathbf{g}_2 = \mathbf{v}_2 - \mathbf{v}_1$ and $\mathbf{g}_3 = \mathbf{v}_3 - \mathbf{v}_1$ instead of $\mathbf{v}_2$ and $\mathbf{v}_3$ as integration variables and perform the $\mathbf{v}_1$ integral. The result is

$$\Phi(x) = \frac{(m/k_B T)^2}{(2\pi k_B T/m)^3 3^{3/2}} \int d\mathbf{g}_2\, d\mathbf{g}_3\, (\varkappa \cdot \mathbf{g}_2)^2 \theta(\varkappa \cdot \mathbf{g}_2) \times (\varkappa' \cdot \mathbf{g}_3)^2 \theta(\varkappa' \cdot \mathbf{g}_3) \exp\left[-\frac{m(g_2^2 + g_3^2 - \mathbf{g}_2 \cdot \mathbf{g}_3)}{3k_B T} \right] \tag{A.7}$$

(ii) Suppose $\varkappa \neq \pm \varkappa'$ (the case $\varkappa \equiv \pm \varkappa'$ follows by continuity); choose the z axis for $\mathbf{g}_2$ and $\mathbf{g}_3$ perpendicular to the $(\varkappa, \varkappa')$ plane: The g_{2z} and g_{3z} integrals are readily performed:

$$\Phi(x) = \frac{(m/k_B T)^2}{(2\pi k_B T/m)^{2/3}} \int d^2\mathbf{g}_{2\parallel}\, d^2\mathbf{g}_{3\parallel}\, (\varkappa \cdot \mathbf{g}_{2\parallel})^2 \theta(\varkappa \cdot \mathbf{g}_{2\parallel}) \times (\varkappa' \cdot \mathbf{g}_{3\parallel})^2 \theta(\varkappa' \cdot \mathbf{g}_{3\parallel}) \exp\left[-\frac{m(g_{2\parallel}^2 + g_{3\parallel}^2 - \mathbf{g}_{2\parallel} \cdot \mathbf{g}_{3\parallel})}{3k_B T} \right] \tag{A.8}$$

where $\mathbf{g}_{2\parallel}$ and $\mathbf{g}_{3\parallel}$ are two-dimensional vectors lying in the $(\varkappa, \varkappa')$ plane.

(iii) Decompose $\mathbf{g}_{i\parallel}$ $(i = 2, 3)$ according to

$$\mathbf{g}_{2\parallel} = u_2 \varkappa + w_2 \varkappa_\perp, \qquad \mathbf{g}_{3\parallel} = u_3 \varkappa' + w_3 \varkappa_\perp' \tag{A.9}$$

where $\varkappa_\perp$ and $\varkappa_\perp'$ are perpendicular to $\varkappa$ and $\varkappa'$, respectively. Again, the w_2 and w_3 integrals are easy to evaluate and we get

$$\Phi(x) = \frac{1}{2\pi} \frac{(m/k_B T)^3}{(4 - x^2)^{1/2}} \int_0^\infty du_2 \int_0^\infty du_3\, u_2^2 u_3^2 \times \exp\left[-\frac{m(u_2^2 + u_3^2 - x u_2 u_3)}{(4 - x^2) k_B T} \right]$$

$$= \frac{1}{2\pi} (4 - x^2)^{5/2} \int_0^\infty y^2 dy \int_0^\infty z^2 dz \exp[-(y^2 + z^2 - xyz)] \tag{A.10}$$

(iv) Use polar coordinates (r, θ) in the (y, z) plane and perform the r integral:

$$\Phi(x) = \frac{(4 - x^2)^{5/2}}{8\pi} \int_0^{\pi/2} \frac{d\Phi' \sin^2 \Phi'}{(1 - \frac{1}{2} x \sin \Phi')^3} \tag{A.11}$$

where $\Phi' = 2\theta$.

(v) Performing the remaining elementary integral over Φ', we arrive at Eq. (28).

APPENDIX B. CALCULATION OF $\tilde{n}_x(k)$, $n_x(k)$, $m_{xx}(k)$

We rewrite (67) as

$$\tilde{n}_x(k) = \int d\mathbf{r}_{12} \exp(-i\mathbf{k}\cdot\mathbf{r}_{12}) \int d^2\boldsymbol{\kappa}'\, \kappa_x'\{g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1 - a\boldsymbol{\kappa}) - g_2(\mathbf{r}_1, \mathbf{r}_2)g_2(a_+)\}f(\boldsymbol{\kappa}') \tag{B.1}$$

where

$$f(\boldsymbol{\kappa}') = \int d\mathbf{v}_1\, d\mathbf{v}_3\, (\boldsymbol{\kappa}'\cdot\mathbf{v}_{13})^2\theta(\boldsymbol{\kappa}'\cdot\mathbf{v}_{13})\varphi(\mathbf{v}_1)\varphi(\mathbf{v}_3) \tag{B.2}$$

The scalar $f(\boldsymbol{\kappa}')$ is readily evaluated[10] to be

$$f(\boldsymbol{\kappa}') = k_B T/m \tag{B.3}$$

Moreover, from the second BBGKY equilibrium hierarchy equation, we get

$$\int d^2\boldsymbol{\kappa}'\, \kappa_x'\{g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1 - a\boldsymbol{\kappa}') - g_2(\mathbf{r}_1, \mathbf{r}_2)g_2(a_+)\} = \frac{1}{a^3\rho}\, a\, \frac{\partial}{\partial r_{12,x}}\, [g_2(|\mathbf{r}|) - g_2(a_+)\theta(|\mathbf{r}| - a)] \tag{B.4}$$

We obtain

$$\tilde{n}_x(k) = \frac{i(ka)g_2(a_+)}{a^3\rho}\, \frac{k_B T}{m} \left[\frac{\tilde{G}(ka)}{g_2(a_+)} + \frac{4\pi}{3}\, \tilde{\rho}(ka)\right] 1_{\mathbf{k},x} \tag{B.5}$$

where $\tilde{G}(y)$ and $\tilde{\rho}(y)$ are respectively defined in (43) and (75).

Similarly, one finds

$$n_x(\mathbf{k}) = \frac{4\pi i(ak)}{3}\, \frac{k_B T}{m}\, \tilde{\rho}(ka) 1_{\mathbf{k},x} \tag{B.6}$$

and

$$m_{xx}(\mathbf{k}) = -\frac{k_B T}{m}\, \frac{8\sqrt{\pi}}{3} \left[\frac{i_2 - i_3}{3} + 1_{\mathbf{k},x}^2\, \frac{3i_3 - i_2}{2}\right] \tag{B.7}$$

where i_2 and i_3 are defined by (74).

APPENDIX C. DENSITY AND LONGITUDINAL VELOCITY PROPAGATORS

The results are as follows.

1. $\Lambda y \gg 1$:

$$\mathscr{V}_{1,1}(y;\tau) \simeq \exp[-(y\Lambda)^2\tau^2/2] = \mathscr{V}_{1,1}^{(0)}(y;\tau) \tag{C.1}$$

and

$$\mathscr{V}_{\parallel,\parallel}(y;\tau) \simeq [1 - (y\Lambda)^2\tau^2]\exp[-(y\Lambda)^2\tau^2/2] = \mathscr{V}^{(0)}_{\parallel,\parallel}(y;\tau) \tag{C.2}$$

2a. $\Lambda y \ll 1;\ \tau \gg 1$:

$$\mathscr{V}^{gh}_{1,1}(y;\tau) = \left\{\frac{C_v}{C_p(y)}\cos[c(y)\Lambda y\tau]\exp[-(y\Lambda)^2\tilde{\Gamma}_{\mathrm{E}}(y)\tau] + \left(1 - \frac{C_v}{C_p(y)}\right)\exp - \frac{(y\Lambda)^2\tau\tilde{\kappa}_{\mathrm{E}}(y)}{C_p(y)}\right\} \tag{C.3}$$

and

$$\mathscr{V}^{gh}_{\parallel,\parallel}(y;\tau) = \cos[c(y)\Lambda y\tau]\exp[-(y\Lambda)^2\tilde{\Gamma}_{\mathrm{E}}(y)\tau] \tag{C.4}$$

Here $C_p(y)$, $c(y)$, $\tilde{\Gamma}_{\mathrm{E}}(y)$, and $\tilde{\kappa}_{\mathrm{E}}(y)$ represent, respectively, generalized specific heat at constant pressure, sound velocity, sound damping coefficient, and thermal conductivity, all expressed in dimensionless units:

$$C_p(y) = \frac{3}{2} + \frac{[1 + \sqrt{\pi}\tilde{p}(y)/6\Lambda]^2}{1 - a^3\rho\tilde{C}(y)} \tag{C.5}$$

[see (42) and (43)]

$$c^2(y) = [1 - a^3\rho\tilde{C}(y)]C_p(y)/C_v \tag{C.6}$$

$$\tilde{\Gamma}_{\mathrm{E}}(y) = \left[\frac{5}{6}\left(1 + \frac{\sqrt{\pi}\tilde{\theta}(y)}{15\Lambda}\right)^2 + \frac{\mu(y)}{10\Lambda^2} + \frac{1}{2}\left(\frac{1}{C_v} - \frac{1}{C_p(y)}\right)\tilde{\kappa}_{\mathrm{E}}(y)\right] \tag{C.7}$$

$$\tilde{\kappa}_{\mathrm{E}}(y) = \frac{75}{16}\left(1 + \frac{\sqrt{\pi}\tilde{p}(y)}{10\Lambda}\right)^2 + \frac{\pi(y)}{6\Lambda^2} \tag{C.8}$$

Here the following functions have been introduced:

$$\tilde{\theta}(y) = (15/2y^2)(-y^3\cos y + 4y^2\sin y + 9y\cos y - 9\sin y) \tag{C.9}$$

$$\pi(y) = (6/y^2)[1 - (\sin y/y)] \tag{C.10}$$

$$\mu(y) = [(10/3y^2) - (10/y^5)(y^2\sin y + 2y\cos y - 2\sin y)] \tag{C.11}$$

Moreover, $C_v = \frac{3}{2}$.

Since $\tilde{\theta}(0) = \pi(0) = \mu(0) = 1$, it is readily verified that, at $y = 0$, Eqs. (C.3) and (C.4) are consistent with Enskog transport theory and with the thermodynamic requirements for a hard-sphere fluid.

2b. $y\Lambda \ll 1$, $\tau \ll 1$:

$$\mathscr{V}_{1,1}(y;\tau) = 1 - (y\Lambda)^2\tau^2/2 + \cdots \tag{C.12}$$

$$\mathscr{V}_{\parallel,\parallel}(y;\tau) = 1 - \frac{\mu(y)\tau}{5} - \left[3\bar{\Phi}(y) - \frac{y^2\mu(y)}{25\Lambda^2}\right]\frac{(y\Lambda\tau)^2}{2} + \cdots \tag{C.13}$$

where we have put

$$\bar{\Phi}(y) = \tfrac{1}{3}c^2(y) + \tfrac{4}{3}\{1 + [\sqrt{\pi}\tilde{\theta}(y)/15\Lambda]\}^2 \tag{C.14}$$

On the basis of these results, we propose the following extrapolation formulas:

$$\mathscr{V}_{1,1}(y;\tau) = \{\exp[-(\alpha\tau)^2]\}\mathscr{V}_{1,1}^{(0)}(y;\tau) + \{1 - \exp[-(\alpha\tau)^2]\}\mathscr{V}_{1,1}^{gh}(y;\tau) \tag{C.15}$$

and

$$\mathscr{V}_{\parallel,\parallel}(y;\tau) = \{\exp[-(\alpha\tau)^2]\}\mathscr{V}_{\parallel,\parallel}^{s}(y;\tau) + \{1 - \exp[-(\alpha\tau)^2]\}\mathscr{V}_{\parallel,\parallel}^{gh}(y;\tau) \tag{C.16}$$

where

$$\mathscr{V}_{\parallel,\parallel}^{s}(y;\tau) = [1 - (\Lambda y\tau)^2\bar{\Phi}(y)]\exp\left[-(y\Lambda)^2\left(\frac{\mu(y)\tau}{5\Lambda^2} + \frac{\bar{\Phi}(y)\tau^2}{2}\right)\right] \tag{C.17}$$

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