PHYSICAL REVIEW A VOLUME 22, NUMBER 6 DECEMBER 1980

Kinetic theory of current fluctuations in simple classical liquids

L. Sjögren
Institute of Theoretical Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden
(Received 31 March 1980)

A theory for the memory function of the phase-space correlation function is presented, based on a general kinetic approach. The memory function is separated into an essentially binary-collision part and a more collective tail represented by a mode-mode coupling term, which includes recollisions to all orders. From the resulting expression for the memory function we obtain calculable expressions for the longitudinal and transverse current correlation functions.

I. INTRODUCTION

In a recent paper,[1] hereafter referred to as I, we presented a microscopic kinetic theory for the self-motion, represented by the velocity correlation function $\Phi(t)$, in classical liquids. We also presented rather extensive numerical results for $\Phi(t)$ and its corresponding memory function $\Gamma(t)$ in both liquid argon and rubidium,[2] and we found a very good agreement with existing molecular dynamics (MD) data.

The general idea adopted in I was to separate the memory function of the phase-space correlation function into one term describing single uncorrelated binary collisions between the self-particle and the surrounding medium, and a second term describing repeated correlated collisions, i.e., the so-called ring and repeated ring events. The first term has a rapid time dependence related to the duration of a binary collision, while the second term represents collective processes with a much slower time dependence. By summing repeated collisions to all orders we obtained an expression for $\Gamma(t)$ which gave the correct short- and long-time behavior.

The purpose of the present paper is to extend the formulation in I to the case of the current fluctuations in order to obtain a calculable expression for the dynamical structure factor $S(q\omega)$. Our earlier treatment of this problem[3-5] was rather incomplete in the sense that the binary-collision part of the relevant memory function was handled phenomenologically with two adjustable parameters, and also that the mode-mode coupling term only included coupling to the density fluctuations. This treatment gave also, in the case of rubidium, rather large discrepancies for intermediate and small wave vectors[4] when compared with MD results of Rahman.[6]

In the present formulation we still have to make a simple ansatz for the binary part, but the parameters can now be determined from a short-time expansion. In the repeated collision term we can, apart from the density fluctuations, also include certain couplings to the currents.

Extensive theoretical studies of $S(q\omega)$ have been performed in recent years based either on a direct microscopic approach,[7-9] or on more phenomenological lines.[10-14] The present formulation is based on the kinetic-theory approach developed by Mazenko[15] and others,[3,5,16-18] and is similar to that given in I. In Sec. II we introduce the general concepts and we also give our earlier expression for $S(q\omega)$ in terms of its self-part and a certain memory function. Section III is then devoted to finding an approximate expression for this memory function. We also give a brief discussion of the validity of our approximations in the small q and z limit in Sec. IV. Some rather technical points are given in two appendices.

II. BASIC DEFINITIONS AND GENERAL FORMULATION

We consider a classical fluid comprised of N particles in a volume V and in thermodynamic equilibrium at the inverse temperature $\beta = 1/k_B T$. The position of the ith particle in the six-dimensional phase space is denoted by $q_i(t) = (\vec{r}_i(t), \vec{p}_i(t))$, and the particles are assumed to interact through a pairwise additive potential. The thermal fluctuations in the system are described through the microscopic phase-space distribution functions

$$f_1(1t) = \sum_{i=1}^{N} \delta(1 - q_i(t)),$$
$$f_2(12t) = \sum_{i \neq j = 1}^{N} \delta(1 - q_i(t))\, \delta(2 - q_j(t)), \quad (2.1)$$

etc., where $1 = (\vec{r}_1, \vec{p}_1)$ denotes a fixed point in phase space, and the δ function is over the six-dimensional phase-space variables.

In the thermodynamic limit ($N \to \infty$, $V \to \infty$, N/V

= const), we have the equilibrium statistical averages

$$\langle f_1(1t)\rangle = n\Phi_M(\vec{p}_1)\ ,$$

$$\langle f_2(12t)\rangle = n^2\Phi_M(\vec{p}_1)\,\Phi_M(\vec{p}_2)\,g(\vec{r}_1-\vec{r}_2)\ , \tag{2.2}$$

where

$$\Phi_M(\vec{p}) = (\beta/2\pi m)^{3/2}\exp(-\beta p^2/2m) \tag{2.3}$$

is the Maxwellian distribution, n is the mean particle density, and $g(\vec{r}_1-\vec{r}_2)$ denotes the static pair distribution function.

In a dense system the local static structure in the fluid has a strong influence on the dynamics, and we introduce the relevant static correlation functions expressed in terms of the fluctuations $\delta f = f - \langle f\rangle$ of f_1, f_2, etc. We define

$$\tilde{C}(12) = \langle\,\delta f_1(1t)\delta f_1(2t)\rangle\ ,$$

$$\tilde{C}(12;3) = \langle\delta f_2(12t)\delta f_1(3t)\rangle\ , \tag{2.4}$$

$$\tilde{C}(12;34) = \langle\,\delta f_2(12t)\delta f_2(34t)\rangle\ ,$$

etc. These can also be expressed in terms of the Maxwellian distribution and static distribution functions as, for instance,

$$\tilde{C}(12) = n\Phi_M(\vec{p}_1)\delta(12) + n^2\Phi_M(\vec{p}_1)\Phi_M(\vec{p}_2)[\,g(\vec{r}_1-\vec{r}_2)-1]\ . \tag{2.5}$$

The corresponding inverse function $\tilde{C}^{-1}$ to (2.5) is defined through

$$\int d\bar{1}\,\tilde{C}(1\bar{1})\tilde{C}^{-1}(\bar{1}2) = \delta(12)\ , \tag{2.6}$$

where the integration runs over the entire six-dimensional phase space. It yields

$$\tilde{C}^{-1}(12) = \delta(12)/n\Phi_M(\vec{p}_1) - c(\vec{r}_1-\vec{r}_2)\ , \tag{2.7}$$

where $c(r)$ is the direct correlation function. For the higher-order correlation functions in (2.4) we will introduce corresponding cluster functions as, for instance,[15(b)]

$$\tilde{G}(12;34) = \tilde{C}(12;34) - \int d\bar{1}\,d\bar{2}\,\tilde{C}(12;\bar{1})\tilde{C}^{-1}(\bar{1}\bar{2})\tilde{C}(\bar{2};34) \tag{2.8}$$

to which corresponds an inverse function $\tilde{G}^{-1}$ defined through

$$\int d\bar{1}\ d\bar{2}\,\tilde{G}^{-1}(12;\bar{1}\bar{2})\tilde{G}^{-1}(\bar{1}\bar{2};34) = \tfrac{1}{2}[\,\delta(13)\delta(24)+\delta(14)\delta(23)]\ . \tag{2.9}$$

$\tilde{G}$ can be expressed similarly to (2.4) as[5,17(b)]

$$\tilde{G}(12;34) = \langle\,\delta\bar{f}_2(12t)\delta\bar{f}_2(34t)\rangle\ , \tag{2.10}$$

where

$$\delta\bar{f}_2(12t) = \delta f_2(12t) - \int d\bar{1}\,d\bar{2}\,\tilde{C}(12;\bar{1})\tilde{C}^{-1}(\bar{1}\bar{2})\delta f_1(\bar{2}t)\,. \tag{2.11}$$

The last term in (2.11) describes the situation where one of the two particles in $\delta f_2(12t)$ is then always in equilibrium with respect to the other particle or possibly a third particle. The deviation from this situation is represented by $\delta\bar{f}_2$, which describes the fluctuations of a two-particle cluster.

The time evolution of the system is conveniently expressed through generalization of (2.4) to two different times:

$$C(1t;2t') = \langle\,\delta f_1(1t)\delta f_1(2t')\rangle\ , \tag{2.12}$$

etc. We will mostly work with its Fourier-Laplace transform, which is defined by

$$C(\vec{q}z;\vec{p}_1\vec{p}_2) = \int d(\vec{r}_1-\vec{r}_2) \times\int_0^\infty d(t-t')\exp[-i\vec{q}\cdot(\vec{r}_1-\vec{r}_2)] \times\exp[-z(t-t')]C(1t;2t')\ . \tag{2.13}$$

It is well known that the phase-space correlation function in (2.12) can be expressed in terms of a corresponding memory function through the equation

$$zC(\vec{q}z;\vec{p}_1\vec{p}_2) - \int d\vec{p}_{\bar{1}}\,\Omega(\vec{q};\vec{p}_1\vec{p}_{\bar{1}})C(\vec{q}z;\vec{p}_{\bar{1}}\vec{p}_2) + \int d\vec{p}_{\bar{1}}\,\Gamma(\vec{q}z;\vec{p}_1\vec{p}_{\bar{1}})C(\vec{q}z;\vec{p}_{\bar{1}}\vec{p}_2) = \tilde{C}(\vec{q};\vec{p}_1\vec{p}_2)\ . \tag{2.14}$$

The static part of the memory function Ω is given by

$$\Omega(\vec{q};\vec{p}_1\vec{p}_2) = -(i\vec{q}\cdot\vec{p}_1/m)\delta(\vec{p}_1-\vec{p}_2) + n\Phi_M(\vec{p}_1)(i\vec{q}\cdot\vec{p}_1/m)c(\vec{q})\ , \tag{2.15}$$

which gives the free-particle streaming term and the mean-field term, where the direct correlation function enters as an effective pair potential. We can consider the functions in (2.14) as matrices in momentum space, and we expand in a complete set of orthonormal Hermite polynomials $H_\mu(\vec{p})$. Equation (2.14) then takes the following form:

$$zC_{\mu\nu}(\vec{q}z) - \Omega_{\mu\lambda}(\vec{q})C_{\lambda\nu}(\vec{q}z) + \Gamma_{\mu\lambda}(\vec{q}z)C_{\lambda\nu}(\vec{q}z) = \tilde{C}_{\mu\nu}(\vec{q}) \ , \tag{2.16}$$

where summation over repeated indices is implied. The matrix elements are defined as

$$C_{\mu\nu}(\vec{q}z) = \int d\vec{p}_1\, d\vec{p}_2\, H_\mu(\vec{p}_1) C(\vec{q}z; \vec{p}_1\vec{p}_2)\, H_\nu(\vec{p}_2) \tag{2.17}$$

and

$$\Omega_{\mu\lambda}(\vec{q}) = \int d\vec{p}_1\, d\vec{p}_2\, H_\mu(\vec{p}_1)\, \Omega(\vec{q}; \vec{p}_1\vec{p}_2) H_\lambda(\vec{p}_2) \Phi_M(\vec{p}_2) \tag{2.18}$$

and similarly for $\Gamma_{\mu\lambda}$. The Hermite polynomials which explicitly will be used in this paper are ($\mu = 0-8$),

$$H_\mu(\vec{p}) = \{1, p_z/p_0,\ p_x/p_0,\ p_y/p_0,\ (1/6^{1/2})(p^2/p_0^2 - 1),\ \tfrac{1}{2}3^{1/2}(p_z^2/p_0^2 - \tfrac{1}{3}p^2/p_0^2),\ p_xp_z/p_0^2,\ p_yp_z/p_0^2,\ p_xp_y/p_0^2\}, \tag{2.19}$$

where $p_0 = (m/\beta)^{1/2}$ and the z direction is along $\hat{q} = \vec{q}/q$.

The five first components in (2.19) are related to the conserved hydrodynamic variables density, longitudinal and transverse currents, and temperature, respectively. The other components which do not correspond to conserved variables, are related to the kinetic part of the stress tensor.

We are basically concerned with the dynamical structure factor $S(\vec{q}\omega)$, which is measured in neutron scattering experiments, and defined as

$$S(\vec{q}\omega) = \pi^{-1} \operatorname{Re} F(\vec{q}, z = -i\omega) \ , \tag{2.20}$$

where

$$nF(\vec{q}z) = \int d\vec{p}_1\, d\vec{p}_2\, C(\vec{q}z; \vec{p}_1\vec{p}_2) = C_{00}(\vec{q}z) \ . \tag{2.21}$$

In order to obtain an approximate expression for C_{00} from (2.16), we will first formally rewrite this equation by separating out the self-motion whereby we obtain[3,10,14]

$$\begin{aligned} C_{\mu\nu}(\vec{q}z) = {} & C^s_{\mu\lambda}(\vec{q}z)\tilde{C}_{\lambda\nu}(\vec{q}) \\ & + iq(\beta m)^{-1/2} nc(\vec{q}) C^s_{\mu 1}(\vec{q}z) C_{0\nu}(\vec{q}z) \\ & - C^s_{\mu\lambda}(\vec{q}z)\Gamma^d_{\lambda\eta}(\vec{q}z)\, C_{\eta\nu}(\vec{q}z) \, . \end{aligned} \tag{2.22}$$

Here,

$$\Gamma^d_{\lambda\eta}(\vec{q}z) = \Gamma_{\lambda\eta}(\vec{q}z) - \Gamma^s_{\lambda\eta}(\vec{q}z) \tag{2.23}$$

and C^s and Γ^s represent the self-parts of C and Γ, respectively. Equation (2.22) still represents an infinite matrix equation to be solved. However, since Γ^d contains no part of the self-motion and represents the collective backflow around any single atom,[3] we may assume that this function can be described in terms of the conserved hydrodynamic variables. Here, we will also neglect the coupling to temperature fluctuations, and from (2.22) we can then obtain the rather simple expressions for the current correlation functions

$$C_l(\vec{q}z) = \frac{C^s_l(\vec{q}z)}{1 - [(q^2/\beta m z) nc(\vec{q}) - \Gamma^d_{11}(\vec{q}z)]\, C^s_l(\vec{q}z)} \tag{2.24}$$

and

$$C_t(\vec{q}z) = \frac{C^s_t(\vec{q}z)}{1 + \Gamma^d_{22}(\vec{q}z) C^s_t(\vec{q}z)} \ , \tag{2.25}$$

where $C_l = C_{11}/n$ denotes the longitudinal current-correlation function and $C_t = C_{22}/n$ denotes the transverse correlation function. From (2.24) we obtain the density correlation function F and thereby $S(\vec{q}\omega)$ via the continuity equation, i.e.,

$$z[zF(\vec{q}z) - S(\vec{q})] = -(q^2/\beta m) C_l(\vec{q}z) \ . \tag{2.26}$$

Equations (2.24) and (2.25) give the correct short-time behavior to the t^2 term, i.e., the correct fourth moment of $S(\vec{q}\omega)$ is reproduced. For small-q values (2.24) is not valid since temperature fluctuations will be important. Including these we would obtain a 3×3 matrix instead of (2.24) and we could then proceed along the lines proposed by John and Forster[10] and Sjödin and Sjölander.[14] For intermediate wave vectors covered by neutron scattering experiments, we expect (2.24) to give reliable results, and the problem is then restricted to calculating the matrix element $\Gamma_{11}(qz)$ together with its corresponding self-part. Equation (2.25) is valid also for small-q values where it gives a diffusive behavior for C_t with an approximate expression for the shear viscosity.

III. CALCULATION OF THE MEMORY FUNCTION

The derivation of expressions for Γ_{11} and Γ_{22} is analogous to that presented for Γ_{11}^s in I, and we can therefore closely follow the general lines adopted in that paper.

A. General expression for the memory function

The formally exact expression for Γ is known[5, 15(b), 17(b)] and can be written in matrix form as

$$\Gamma_{\mu\lambda}(\vec{q}z) = -(1/nV)\int d1\cdots d4\exp(-i\vec{q}\cdot\vec{r}_1)H_\mu(\vec{p}_1)[\vec{\nabla}_{r_1}v(\vec{r}_1-\vec{r}_2)\cdot\vec{\nabla}_{p_1}]G(12;34z)[\vec{\nabla}_{r_3}v(\vec{r}_3-\vec{r}_4)\cdot\vec{\nabla}_{p_3}]$$
$$\times H_\lambda(\vec{p}_3)\exp(i\vec{q}\cdot\vec{r}_3)\ , \tag{3.1}$$

where v is the interaction potential. The four-point function $G(12t;34t')$ can be related to $C(12t;34t')$ and lower-order functions,[15(b), 19] and it describes the correlated motion of two disturbances in the medium. Two particles move from the positions $(\vec{r}_3,\vec{p}_3)$ and $(\vec{r}_4,\vec{p}_4)$ at time t' and the same or possibly other particles are found at $(\vec{r}_1,\vec{p}_1)$ and $(\vec{r}_2,\vec{p}_2)$ at time t. The initial value of $G(12t;34t')$ at $t=t'$ is just the function $\tilde{G}(12;34)$ introduced in (2.8). If the motion of the two disturbances are uncorrelated, we have

$$G(12t;34t') = G^D(12t;34t')$$
$$\equiv C(1t;3t')C(2t;4t')$$
$$+C(1t;4t')C(2t;3t')\ , \tag{3.2}$$

where the superscript "D" stands for disconnected. The two terms in (3.2) reflect the symmetry of the particles in 1 and 2.

We can write an exact equation for $G(12;34z)$ analogous to (2.14) [Refs. 5, 15(b) and 17(b)] and it has the form

$$zG(12;34z) - \int d\bar{1}\,d\bar{2}\,\Omega(12;\bar{1}\bar{2})G(\bar{1}\bar{2};34z)$$
$$+\int d\bar{1}\,d\bar{2}\,\Gamma(12;\bar{1}\bar{2}z)G(\bar{1}\bar{2};34z) = \tilde{G}(12;34)\ . \tag{3.3}$$

The static part Ω can formally be written as

$$\Omega(12;34) = \int d\bar{1}\,d\bar{2} \langle \delta\dot{\bar{f}}_2(12t)\delta\bar{f}_2(\bar{1}\bar{2}t)\rangle \tilde{G}^{-1}(\bar{1}\bar{2};34)\ , \tag{3.4}$$

where the dot over $\delta\bar{f}_2$ means time derivation. The memory function Γ in (3.3) contains explicitly the correlated motion of three particles[15(b)] (see also Appendix B).

To lowest order in the density we have

$$\Omega(12;34) = -[(1/m)\vec{p}_1\cdot\vec{\nabla}_{r_1} + (1/m)\vec{p}_2\cdot\vec{\nabla}_{r_2}$$
$$-\vec{\nabla}_{r_1}v(\vec{r}_1-\vec{r}_2)\cdot(\vec{\nabla}_{p_1}-\vec{\nabla}_{p_2})]$$
$$\times\tfrac{1}{2}[\delta(13)\delta(24)+\delta(14)\,\delta(23)]\ , \tag{3.5}$$

which contains the free-particle flow term for the two particles and the bare interaction between them. For higher densities the static correlations with other particles will introduce an effective potential $(-1/\beta)\ln g$ instead of the bare one, and among other terms also the ordinary mean-field terms for the two particles appear. If we ignore Γ in (3.3) the equation describes essentially a binary collision between two particles and each one is moving in the mean field of the surrounding medium. This approximation for G would be valid only for short times, and corresponds in appropriate limits to the Boltzmann-Enskog expression for Γ in (3.1). The full dynamics for intermediate and long times is a result of repeated correlated binary collisions, and such events are included through Γ in (3.3).

The formal solution of (3.3) can be written

$$G = R\tilde{G} \tag{3.6}$$

with the propagator

$$R = (z-\Omega+\Gamma)^{-1}\ . \tag{3.7}$$

From the full propagator R we will now separate out a part R^B which represents one single binary-collision process. Except for the static renormalizations contained in Ω, we expect that rapid rearrangements among the neighboring particles can affect the two-body dynamics appreciably. Such rapid renormalizations will be represented by a part of Γ denoted by Γ^B and we define R^B as

$$R^B = (z-\Omega+\Gamma^B)^{-1}\ . \tag{3.8}$$

The full R can be expressed as a sequence of such binary collisions

$$R = R^B - R^B\Gamma_1R^B + R^B\Gamma_1R^B\,\Gamma_1R^B + \cdots$$
$$= R^B - R^B\,\Gamma_1R\ , \tag{3.9}$$

where $\Gamma_1 = \Gamma - \Gamma^B$. From (3.7) and (3.8) we have

$$\Gamma_1 = (R)^{-1} - (R^B)^{-1}$$
$$= -(R^B)^{-1}(R-R^B)(R)^{-1}\ . \tag{3.10}$$

Within a binary-collision time we have that $R - R^B$ is essentially zero and that afterwards when the particles are separated $R \simeq R^D$ and $R^B \simeq R^{BD}$. According to (3.2) R^D contains, via C, the full motion of the disconnected particles, while R^{BD} is given in terms of a correlation function which will be denoted by C^B. If we neglect Γ^B in (3.8), then C^B is given by the mean-field expression for C. With these replacements in (3.10) we can write (3.9) as

$$R = R^B + R^B (R^{BD})^{-1} (R^D - R^{BD}) (R^D)^{-1} R \,. \tag{3.11}$$

The approximation in (3.11) implies that between two binary collisions the two particles move independent of each other. With the full R on the right-hand side we include repeated collisions to all orders.

To obtain G we multiply (3.11) with $\tilde{G}$ from the right, and to shield the bare interaction on the left in (3.1) we rewrite

$$\begin{aligned} R^B (R^{BD})^{-1} &= R^B \tilde{G} \tilde{G}^{-1} (R^{BD})^{-1} \\ &\simeq R^B \tilde{G} (\tilde{G}^D)^{-1} (R^{BD})^{-1} \\ &= \tilde{G} R^{B\dagger} [(R^{BD})^{-1}]^\dagger (\tilde{G}^D)^{-1} \,, \end{aligned} \tag{3.12}$$

where $R^{B\dagger}(12;34z) = -R^B(34;12-z)$ and similarly for $[(R^{BD})^{-1}]^\dagger$. Furthermore, we have

$$R^D - R^{BD} = (G^D - G^{BD}) (\tilde{G}^D)^{-1} \,. \tag{3.13}$$

The matrix element Γ_{11} can, after these transformations, be written as

$$\Gamma_{11}(\vec{q}z) = \Gamma^B_{11}(\vec{q}z) + \Gamma^R_{11}(\vec{q}z) \tag{3.14}$$

with

$$\Gamma^B_{11}(\vec{q}z) = (\beta/mnV) \int d1 \cdots d4 \exp(-i\vec{q}\cdot\vec{r}_1)[\hat{q}\cdot\vec{\nabla}_{r_1} v(\vec{r}_1 - \vec{r}_2)]\, G^B(12;34z) [\hat{q}\cdot\vec{\nabla}_{r_3} v(\vec{r}_3 - \vec{r}_4)] \exp(i\vec{q}\cdot\vec{r}_3) \,, \tag{3.15}$$

where $G^B = R^B \tilde{G}$, and

$$\Gamma^R_{11}(\vec{q}z) = \frac{1}{2n} \int \frac{d\vec{q}\,'}{(2\pi)^3} T^{B\dagger}_{1;\lambda\eta}(\vec{q}\vec{q}\,'z) \Delta_{\lambda\eta;\sigma\zeta}(\vec{q}\vec{q}\,'z) T_{\sigma\zeta;1}(\vec{q}\vec{q}\,'z) \,. \tag{3.16}$$

The matrices T and T^B contain information on which modes are excited in the fluid and also the strength of the coupling. Formally, we have

$$\begin{aligned} T_{\sigma\zeta;1}(\vec{q}\vec{q}\,'z) = \left(\frac{\beta}{m}\right)^{1/2} \frac{1}{V} \int d1 \cdots d4 \exp[-i(\vec{q}-\vec{q}\,')\cdot\vec{r}_1] \exp(-i\vec{q}\,'\cdot\vec{r}_2) H_\sigma(\vec{p}_1) H_\zeta(\vec{p}_2) [R^D(12;\overline{1}\overline{2}z)]^{-1} G(\overline{1}\overline{2};34z) \\ \times [\hat{q}\cdot\vec{\nabla}_{r_3} v(\vec{r}_3 - \vec{r}_4)] \exp(i\vec{q}\cdot\vec{r}_3) \end{aligned} \tag{3.17}$$

and similarly for T^B with G and $(R^D)^{-1}$ replaced by G^B and $(R^{BD})^{-1}$, respectively. The matrix $T^{B\dagger}$ is obtained from the relation

$$T^{B\dagger}_{1;\lambda\eta}(\vec{q}\vec{q}\,'z) = T^B_{\lambda\eta;1}(-\vec{q}, -\vec{q}\,', -z) \,. \tag{3.18}$$

The quantity Δ is defined by

$$\begin{aligned} \Delta_{\lambda\eta;\sigma\zeta}(\vec{q}\vec{q}\,'z) = \tilde{C}^{-1}_{\lambda\lambda}(\vec{q}-\vec{q}\,') \tilde{C}^{-1}_{\eta\eta}(\vec{q}\,') \int_0^\infty dt\, e^{-zt} [C_{\lambda\sigma}(\vec{q}-\vec{q}\,', t) C_{\eta\zeta}(\vec{q}\,'t) - C^B_{\lambda\sigma}(\vec{q}-\vec{q}\,', t) C^B_{\eta\zeta}(\vec{q}\,'t)] \\ \times C^{-1}_{\sigma\sigma}(\vec{q}-\vec{q}\,') C^{-1}_{\zeta\zeta}(\vec{q}\,'), \end{aligned} \tag{3.19}$$

where we have used the fact that $\tilde{C}^{-1}$, defined in (2.7), has only diagonal elements. The factor containing C^B comes from G^{BD} in (3.13). For Γ_{22} we have expressions similar to those in (3.15)–(3.17) but with $\hat{q} = \hat{z}$ replaced with $\hat{q}_\perp = \hat{x}$. The first term in (3.14) has a fast time dependence and decays within a binary-collision time. The initial value of this term can be calculated exactly and is related to the fourth moment of $S(q\omega)$. The second term representing repeated correlated collisions, starts as t^4, grows to a maximum, and then decays rather slowly, due to the slowly decaying collective motions in C.

In the recollision term in (3.16) the coupling between all kinds of modes enter in the integrand. We will here assume that the dominant coupling comes from the hydrodynamic modes, which can persist for a rather long time for small and intermediate wave vectors. As before we will also neglect the temperature fluctuations. Our experience from the self-motion treated in papers I and II, indicate that this coupling together with the nonhydrodynamic modes give a rather small contribution to Γ^R. This approximation implies that only the matrix elements $T_{00;1}$, $T_{0\alpha;1}$, $T_{\alpha0;1}$, and $T_{\alpha\beta;1}$, where α, $\beta = 1-3$, have to be considered, and some of their properties are analyzed in Appendix B. In particular, it is shown that $T_{\alpha\beta;1}(\vec{q}\vec{q}'z)$ for small q and q' is related to the matrix elements $\Gamma_{\lambda 1}(\vec{q}z)$ where $\lambda = 4-8$, and such elements have earlier been neglected. Consequently, to be consistent with our earlier approximation leading to (2.24) and (2.25), we should also neglect $T_{\alpha\beta;1}$ in (3.16). The coupling to $T_{\alpha\beta;1}$, like that to the temperature, will also give contributions to Γ^R, which starts as t^6, compared with t^4 for the other three elements above.

Our conclusions here concerning the relevant couplings are only valid for short and intermediate times, which are the most important for interpreting neutron scattering experiments. Considering the long-time tails or equivalently the nonanalytic dispersion relations for the hydrodynamic modes,[20] the situation changes and the small q, q' and z behavior of T is important. We will come back to this question in Sec. IV in connection with the shear viscosity.

B. The binary-collision term

The binary part Γ_{11}^B contains all the contributions to Γ_{11} to order t^2. Since we expect Γ_{11}^B to decay quite rapidly to zero we will make the ansatz

$$\Gamma_{11}^B(\vec{q}t) = \Gamma_{11}^B(\vec{q}, t=0)\exp[-t^2/\tau_l^2(\vec{q})], \qquad (3.20)$$

where the parameters can be determined from a short-time expansion of the formally exact expression (3.15). The details of this expansion is given in Appendix A, and yields for the initial value the well-known result

$$\Gamma_{11}^B(\vec{q}, t=0) = \omega_0^2 + \gamma_d^l(\vec{q}) + (q^2/\beta m) n c(\vec{q}) . \qquad (3.21)$$

For $\tau_l(q)$ we obtain, after making the superposition approximation for the static three-particle distribution function,

$$\begin{aligned}\Gamma_{11}^B(\vec{q}, t=0)/\tau_l^2(\vec{q}) = {} & (q^2/2\beta m)[\omega_0^2 - 2\gamma_d^l(\vec{q})] + (n/m^2)\int d\vec{r}\,[1-\exp(-i\vec{q}\cdot\vec{r})][\hat{q}^\alpha\nabla^\alpha\nabla^\gamma v(\vec{r})]\,g(\vec{r})[\hat{q}^\beta\nabla^\beta\nabla^\gamma v(\vec{r})] \\ & + (n/\beta m^2)\, iq\int d\vec{r}\exp(-i\vec{q}\cdot\vec{r})g(\vec{r})(\hat{q}\cdot\vec{\nabla})^3 v(\vec{r}) \\ & + \frac{1}{2n}\int\frac{d\vec{q}'}{(2\pi)^3}\,\hat{q}^\alpha\gamma_d^{\alpha\gamma}(\vec{q}')\{[S(\vec{q}')-1]+[S(\vec{q}-\vec{q}')-1]\}[\gamma_d^{\beta\gamma}(\vec{q}')-\gamma_d^{\beta\gamma}(\vec{q}-\vec{q}')]\hat{q}^\beta, \end{aligned} \qquad (3.22)$$

where summation over repeated indices is implied. Here,

$$\omega_0^2 = \frac{n}{3m}\int d\vec{r}\, g(\vec{r})\nabla^2 v(\vec{r}) \qquad (3.23)$$

and

$$\begin{aligned}\gamma_d^{\alpha\beta}(\vec{q}) &= -\frac{n}{m}\int d\vec{r}\exp(-i\vec{q}\cdot\vec{r})g(\vec{r})\nabla^\alpha\nabla^\beta v(\vec{r}) \\ &= \hat{q}^\alpha\hat{q}^\beta\gamma_d^l(\vec{q}) + [\delta_{\alpha\beta} - \hat{q}^\alpha\hat{q}^\beta]\gamma_d^t(\vec{q}) . \end{aligned} \qquad (3.24)$$

The validity of the superposition approximation in the context of the calculation of moments has been tested by Bansal and Bruns,[21] and they found it to be very accurate. We may therefore expect that (3.22) gives reliable values for $\tau_l^2(q)$. The Gaussian ansatz (3.20) may, however, introduce some discrepancies in a narrow time interval, similar to what was found in papers I and II. In the limit of large-q values (3.22) reduces to the corresponding result for the self-motion given in paper I (see I: A11). For Γ_{22}^B we have expressions similar to (3.21) and (3.22) (see Appendix A).

C. The T matrix

In this section we will summarize some results obtained in Appendix B for the matrix elements $T_{00;1}$ and $T_{0\alpha;1}$. We find

$$\begin{aligned}T_{00;1}(\vec{q}\vec{q}'z) = {} & in(\beta m)^{-1/2} \\ & \times\{\hat{q}\cdot\vec{q}'\; S(\vec{q}-\vec{q}')[S(\vec{q}')-1] \\ & + \hat{q}\cdot(\vec{q}-\vec{q}')S(\vec{q}')[S(\vec{q}-\vec{q}')-1]\} . \end{aligned} \qquad (3.25)$$

This result is independent of z and it gives an instantaneous coupling to the density fluctuations. The component $T_{0\alpha;1}$ has a certain time dependence which we cannot calculate exactly, as is obvious from the formal expression (3.17). However, we can find an expression for the initial value, given by

$$T_{0\alpha;1}(\vec{q}\vec{q}',t=0)=\hat{q}^{\beta}nS(\vec{q}-\vec{q}')[\gamma_d^{\alpha\beta}(\vec{q}-\vec{q}')+(q-q')^{\alpha}(q-q')^{\beta}(n/\beta m)c(\vec{q}-\vec{q}')-\gamma_d^{\alpha\beta}(\vec{q}')-q'^{\alpha}q'^{\beta}(n/\beta m)c(\vec{q}')]. \tag{3.26}$$

In arriving at (3.25) and (3.26) we have made certain approximations for the three-particle distribution function as explained in Appendix B. We can also calculate exactly the whole time dependence of $T_{0\alpha;1}$ for $q'=0$ and this gives

$$T_{0\alpha;1}(\vec{q},\vec{q}'=0,z)=nS(\vec{q})\Gamma_{11}(\vec{q}z)\hat{q}^{\alpha}. \tag{3.27}$$

This is an important result since the same memory function as we want to calculate appears in (3.27). We notice that the approximate expression (3.26) is consistent with (3.27) at $t=0$. Using (3.26) and (3.27) we will make the following ansatz:

$$T_{0\alpha;1}(\vec{q}\vec{q}'z)=T_{0\alpha;1}(\vec{q}\vec{q}',t=0)/\Gamma_{11}(\vec{q},t=0)\Gamma_{11}(\vec{q}z)=nS(\vec{q}-\vec{q}')\hat{q}^{\beta}t^{\alpha\beta}(\vec{q}\vec{q}')\Gamma_{11}(\vec{q}z), \tag{3.28}$$

where $t^{\alpha\beta}$ is obtained from (3.26) and (3.21) as

$$t^{\alpha\beta}(\vec{q}\vec{q}')=\frac{\gamma_d^{\alpha\beta}(\vec{q}-\vec{q}')+(q-q')^{\alpha}(q-q')^{\beta}(n/\beta m)c(\vec{q}-\vec{q}')-\gamma_d^{\alpha\beta}(\vec{q}')-q'^{\alpha}q'^{\beta}(n/\beta m)c(\vec{q}')}{\omega_0^2+\gamma_d^{l}(\vec{q})+q^2(n/\beta m)c(\vec{q})}. \tag{3.29}$$

For the binary part we have $T^{B}_{00;1}=T_{00;1}$ and also relations similar to (3.26) and (3.27). This gives

$$T^{B}_{0\alpha;1}(\vec{q}\vec{q}'z)=nS(\vec{q}-\vec{q}')\hat{q}^{\beta}t^{\alpha\beta}(\vec{q}\vec{q}')\Gamma^{B}_{11}(\vec{q}z). \tag{3.30}$$

From the defining expression (3.17) it is easy to prove that

$$T_{\alpha 0;1}(\vec{q}\vec{q}'z)=T_{0\alpha;1}(\vec{q},\vec{q}-\vec{q}',z) \tag{3.31}$$

and we also have from (3.18)

$$T^{B\dagger}_{1;0\alpha}(\vec{q}\vec{q}'z)=-T^{B}_{0\alpha;1}(\vec{q}\vec{q}'z). \tag{3.32}$$

The merit with our ansatz (3.28) is that the q' and z dependence factorizes, and this enables us to obtain a closed expression for Γ_{11}. The assumption that the q' dependence in T only enters in the initial value and not in the time dependence, was tested numerically in papers I and II for the case of self-motion, and it was found to be quite accurate.

D. Expression for Γ_{11}

Using the results of Sec. III C to calculate Γ^{R} in (3.16) we obtain for Γ_{11} in (3.14):

$$\Gamma_{11}(\vec{q}z)=\frac{\Gamma^{B}_{11}(\vec{q}z)+R^{l}_{00}(\vec{q}z)+\Gamma^{B}_{11}(\vec{q}z)R^{l}_{01}(\vec{q}z)}{1-R^{l}_{01}(\vec{q}z)-\Gamma^{B}_{11}(\vec{q}z)[R^{l}_{11}(\vec{q}z)+R^{l}_{22}(\vec{q}z)]}. \tag{3.33}$$

We see that Γ_{11} is completely determined by Γ^{B}_{11} and certain mode-mode integrals denoted by R. R^{l}_{00} contains the coupling to the density and is given by

$$R^{l}_{00}(\vec{q}t)=\frac{n}{\beta m}\int\frac{d\vec{q}'}{(2\pi)^3}\,\hat{q}\cdot\vec{q}'c(\vec{q}')[\hat{q}\cdot\vec{q}'c(\vec{q}')+\hat{q}\cdot(\vec{q}-\vec{q}')c(\vec{q}-\vec{q}')][F(\vec{q}-\vec{q}',t)F(\vec{q}'t)-F^{B}(\vec{q}-\vec{q}',t)F^{B}(\vec{q}'t)], \tag{3.34}$$

where F was defined in (2.21) and $F^{B}=C^{B}_{00}/n$. For R^{l}_{01} we have

$$R^{l}_{01}(\vec{q}t)=\int\frac{d\vec{q}'}{(2\pi)^3}\left(\frac{\hat{q}^{\beta}\hat{q}'^{\alpha}}{q'}\right)t^{\alpha\beta}(\vec{q}\vec{q}')[\hat{q}\cdot\vec{q}'c(\vec{q}')+\hat{q}\cdot(\vec{q}-\vec{q}')c(\vec{q}-\vec{q}')]\Big(F(\vec{q}-\vec{q}',t)\frac{\partial}{\partial t}F(\vec{q}'t)-F^{B}(\vec{q}-\vec{q}',t)\frac{\partial}{\partial t}F^{B}(\vec{q}'t)\Big). \tag{3.35}$$

R^{l}_{11} and R^{l}_{22} contain the coupling to the longitudinal and transverse currents, respectively, and are given by

$$R^{l}_{11}(\vec{q}t) = -\frac{1}{n}\int \frac{d\vec{q}'}{(2\pi)^3}\, \hat{q}^{\gamma}\hat{q}^{\delta}\, t^{\alpha\gamma}(\vec{q}\vec{q}')t^{\beta\delta}(\vec{q}\vec{q}')$$
$$\times\Big[\hat{q}'^{\alpha}\hat{q}'^{\beta}\,[F(\vec{q}-\vec{q}',t)C_l(\vec{q}'t) - F^B(\vec{q}-\vec{q}',t)C^B_l(\vec{q}'t)]$$
$$+\frac{\hat{q}'^{\alpha}(q-q')^{\beta}}{(\vec{q}-\vec{q}')^2 q'}\,\beta m\Big(\frac{\partial}{\partial t}F(\vec{q}-\vec{q}',t)\frac{\partial}{\partial t}F(\vec{q}'t) - \frac{\partial}{\partial t}F^B(\vec{q}-\vec{q}',t)\frac{\partial}{\partial t}F^B(\vec{q}'t)\Big)\Big] \qquad (3.36)$$

and

$$R^{l}_{22}(\vec{q}t) = -\frac{1}{n}\int \frac{d\vec{q}'}{(2\pi)^3}\, \hat{q}^{\gamma}\hat{q}^{\delta}(\delta_{\alpha\beta} - \hat{q}'^{\alpha}q'^{\beta})t^{\alpha\gamma}(\vec{q}\vec{q}')t^{\beta\delta}(\vec{q}\vec{q}')[F(\vec{q}-\vec{q}',t)C_t(\vec{q}'t) - F^B(\vec{q}-\vec{q}',t)C^B_t(\vec{q}'t)], \qquad (3.37)$$

where C_l and C_t denote the longitudinal and transverse current-current correlation functions, normalized to unity for $t=0$. The last term in (3.36) comes from cross terms like $T^B_{1;0\alpha}\Delta_{0\alpha;\beta 0}T_{\beta 0;1}$ in (3.16). In arriving at (3.35)–(3.37) we have used relation (3.31) together with the substitution $\vec{q}' \to \vec{q}-\vec{q}'$. For Γ_{22} we have a similar expression as (3.33) except that Γ^B_{11} is replaced by Γ^B_{22}, and $\hat{q}=\hat{z}$ in the mode-mode terms is replaced by $\hat{q}_\perp = \hat{x}$. In the coupling constant $t^{\alpha\beta}$ in (3.29) we should, of course, also replace $\Gamma_{11}(q, t=0)$ with $\Gamma_{22}(q, t=0)$.

We notice that no couplings like C_lC_l or C_tC_t enter in the mode-mode expressions, and this is a consequence of the fact that we have neglected $T_{\alpha\beta;1}$ in (3.16). The general structure of (3.33) is essentially the same as the corresponding result for the self-motion. The main difference is that in the latter case the correct asymptotic behavior for the corresponding generalized transport coefficient was obtained by a simple modification of the coefficient before the term corresponding to R^l_{22}. In the case of the density and current fluctuations considered here, the asymptotic behavior is more complicated, and can not be reproduced from our expression (3.33). We will consider this point more closely in Sec. IV. In order to obtain numerical results from (3.33)–(3.37) we have to specify the functions F^B, including its two first time derivatives, and C^B_t which appear in the mode-mode integrals. These functions are directly related to R^B in (3.8), which describes a single binary collision of two particles in the presence of a medium, which introduces static and dynamic renormalizations of the collision process. This means that R^B should contain all fast processes which decay within a binary-collision time. In particular, we argue that the nonhydrodynamic terms in the mode-mode integral (3.16) represent fast processes, and should therefore actually be included in R^B. Since C^B in (3.19) is the disconnected part of R^B this implies that these nonhydrodynamic couplings are also included in the time dependence of F^B and C^B_t. The difference between the full C and C^B appearing in (3.19) and (3.34)–(3.37) is then, according to this argument, due to slowly decaying hydrodynamic fluctuations. Our argument here is similar to that of Furtado *et al.*[22] and Mehaffey *et al.*[23] who used a simple relaxation time approach to incorporate the effects of all nonhydrodynamic couplings into C^B. However, we will proceed in a slightly different way.

In our earlier treatment of the self-motion we used the approximation $C^B = C$, and this gave very good numerical results for the recollision term for that case. Obviously we cannot use the same approximation here since the mode-mode integrals would vanish. We can separate C^B into its self and distinct parts as

$$C^B_{\mu\nu}(\vec{q}t) = C^{sB}_{\mu\nu}(\vec{q}t) + C^{dB}_{\mu\nu}(\vec{q}t), \qquad (3.38)$$

where C^{sB} describes the motion of the atom originally involved in the binary collision and C^{dB} describes the motion of the surrounding atoms. Obviously we have $C^{sB} = C^0$, where C^0 is the free-particle expression for C, while C^{dB} essentially describes the dynamics of a homogeneous $(N-1)$ particle system. Considering the transverse current we have

$$C_t(\vec{q}t) - C^B_t(\vec{q}t) = C^s_t(\vec{q}t) - C^0_t(\vec{q}t) + C^d_t(\vec{q}t) - C^{dB}_t(\vec{q}t). \qquad (3.39)$$

The two terms involving the self-motion have a rapid time dependence, since the current of a self-particle is not conserved. According to the discussion above, such rapid processes should be included in the binary part, and should not contribute to the difference between C_t and C^B_t. We will therefore neglect this difference arising from the self-motions, and this also implies that we neglect the difference between C^d_t and C^{dB}_t, since there is a rather strong correlation between the self and distinct parts. Consequently, we make the approximation $C^B_t = C_t$ in (3.37). With similar arguments for the longitudinal currents in (3.35) and (3.36) we will take $\partial F^B/\partial t = \partial F/\partial t$ and $C^B_l = C_l$.

The whole contribution to the mode-mode coupling terms in (3.34)–(3.37) will with these approximations be due to differences between F^B and F. Since F^B describes just one binary collision we expect that it should decay faster than F.

Neglecting Γ^B in (3.8) we obtain

$$F^B(\vec{q}t) = F^{mf}(\vec{q}t), \quad (3.40)$$

where F^{mf} is the mean-field expression obtained by Nelkin and Ranganathan.[24] This expression decays more rapidly than F for short times, but it has very sharp density oscillations which persist for long times. We expect that these density oscillations, which are contained in F^{dB} should be strongly damped due to collisions among the distinct particles. We will here assume that the time dependence of F^{dB} relative to F^d is the same as their respective self-parts, i.e., we make the ansatz

$$F^B(\vec{q}t) = [F^o(\vec{q}t)/F^s(\vec{q}t)]F(\vec{q}t). \quad (3.41)$$

With this approximation together with the results for the self-motion obtained in paper I, we can obtain numerical results for $S(q\omega)$. More details about this and results of numerical calculations will be presented in a forthcoming paper.

IV. SMALL-q AND -z BEHAVIOR OF $\Gamma_{\mu\nu}(qz)$

The expressions for the longitudinal and transverse current correlation functions in (2.24) and (2.25) together with their respective memory functions given in Sec. III D have been designed to give accurate results for intermediate and large-q values, which are the most relevant ones in neutron scattering experiments. A large part of the scattering amplitude is given by the self-part F^s (Ref. 25) and this is the motivation for extracting this part from Γ. For smaller wave vectors where the concept of self-motion is not well defined, we expect a generalized hydrodynamic description to be valid. It can be shown[3] that our expressions for C_l and C_t reduce to the hydrodynamic forms (with temperature fluctuations excluded), in the limit of small-q values, and we obtain approximate expressions for the transport coefficients. These can be compared with exact formal expressions for these coefficients, which can be obtained from Eq. (2.16) by introducing the hydrodynamic projection operator[26]

$$P = \sum_{\mu=0}^{4} |H_\mu(\vec{p})\rangle\langle H_\mu(\vec{p})| = 1 - Q. \quad (4.1)$$

Multiplying (2.16), written in operator form, with P and Q, respectively, we obtain two coupled equations for the hydrodynamic and nonhydrodynamic modes, respectively. Solving for the latter we obtain a 5×5 matrix equation for the hydrodynamic modes. Here we will restrict our attention to the transverse case, which is the simplest to analyze, and we obtain for C_t [Refs. 15(b) and 26]:

$$C_t(\vec{q}z) = 1/[z + D_t(\vec{q}z)], \quad (4.2)$$

where

$$D_t(\vec{q}z) = \langle 2|(-\Omega+\Gamma)|2\rangle - \langle 2|(-\Omega+\Gamma)Q[z - Q(\Omega-\Gamma)Q]^{-1}Q(-\Omega+\Gamma)|2\rangle \quad (4.3)$$

and $\langle 2|\Gamma|2\rangle = \Gamma_{22}$, etc. We should notice that $\Omega_{22} = 0$ and also that the mean-field term in Ω vanishes in the last term in (4.3). The two terms in (4.3) are often referred to as the direct and indirect terms, respectively. From our expression (2.25) we obtain an approximate expression for D_t which can be written as

$$D_t(\vec{q}z) = [C_t^s(\vec{q}z)]^{-1} - z + \Gamma_{22}^d(\vec{q}z). \quad (4.4)$$

Similarly to (4.2), we can express here, C_t^s in terms of a function D_t^s related to Γ^s through an expression similar to (4.3). Comparing (4.3) and (4.4) we then see that all contributions from Γ^d in the indirect term in (4.3) are neglected in (4.4). This assumes of course that C_t^s can be treated exactly, which in practice is not possible. The direct term Γ_{22} in (4.3) will vanish in a dilute gas compared with the indirect term, where only the kinetic contribution will remain. Our result (4.4) will therefore, at low densities, only include the contribution from the self-motion to the shear viscosity. Even when we go to higher densities the indirect term may give a large contribution to the shear viscosity compared with Γ_{22}.[8] Similar arguments as above also apply to the longitudinal case.

Another point of great principal interest concerns the nonanalytic behavior of the generalized transport coefficients extensively studied by Pomeau,[27] Ernst and Dorfman,[20] Ernst *et al.*[28] and De Schepper *et al.*[29] using either the phenomenological mode-mode coupling theory[30] or a kinetic-theory approach. The approximation (4.4) with an expression similar to (3.33) for Γ_{22} does not recover the correct nonanalytic behavior for D_t in the small-q and -z limits. In fact, not only the whole indirect term in (4.3), but also additional couplings via $T_{\alpha\beta;\nu}$ in (3.16), has to be included.

In the hydrodynamic region we have $\langle 2|(-\Omega^0+\Gamma)Q \propto q$, where Ω^0 denotes the free-particle term in Ω. In the denominator we also have that $(z - Q\Omega^0 Q) \propto q$ and to order q^3 we therefore have

$$D_t(\vec{q}z) = \langle 2|\Gamma|2\rangle - \langle 2|(-\Omega^0+\Gamma)Q(Q\Gamma Q)^{-1}Q(-\Omega^0+\Gamma)|2\rangle + O(q^3). \quad (4.5)$$

We now have to investigate the matrix elements $\langle 2|\Gamma|2\rangle$, $\langle 2|\Gamma Q$, and $Q\Gamma Q$ which appear in (4.5). We therefore start by considering the T matrix for small values of its arguments. From Appendix B we find

$$T_{00;2}(\vec{q}\vec{q}'z) = in(\beta m)^{-1/2}q_x'[S(\vec{q}-\vec{q}') - S(\vec{q}')] \quad (4.6)$$

and this is for small q and q' proportional to qq'^2. Similarly we have

$$T_{0\alpha;2}(\vec{q}\vec{q}'z) = T_{0\alpha;2}(\vec{q}\vec{q}', t=0)/\Gamma_{22}(\vec{q}, t=0)\Gamma_{22}(\vec{q}z) \propto qq' \quad (4.7)$$

and

$$T_{\alpha\beta;2}(\vec{q}\vec{q}'z) = T_{\alpha\beta;\lambda}(\vec{q}\vec{q}', t=0)/(2\omega_0^2)\Gamma_{\lambda 2}(\vec{q}z) \propto q \quad (4.8)$$

for small q and q'. Notice that $T_{0\alpha;2}(\vec{q}, \vec{q}'=0, z) \propto q^2$ and this gives terms of order q^3 in (4.5). Both $T_{00;2}$ and $T_{0\alpha;2}$ vanishes with q' and these couplings will therefore give less singular contributions to $\langle 2|\Gamma|2\rangle$ than $T_{\alpha\beta;2}$ which is finite in this limit.

To calculate $\langle 2|\Gamma Q$ and $Q\Gamma Q$ we also have to consider matrix elements $T_{00;\nu}$, $T_{0\alpha;\nu}$, and $T_{\alpha\beta;\nu}$, where ν is a nonhydrodynamic mode. Since we already have a factor q^2 in (4.5) coming from the coupling constants in (4.6)–(4.8) we can in this case take $q=0$. It is clear from Appendix B that $T_{00;\nu}=0$ if ν is a nonhydrodynamic mode and also $T_{0\alpha;\nu} \propto q'$ for $q=0$, while $T_{\alpha\beta;\nu}$ tends to a finite constant for certain values of $\nu > 4$. This means that in the transverse case, the most singular terms in Γ come from couplings via the matrix elements $T_{\alpha\beta;\nu}$ for all ν. When calculating the matrix elements of Γ in (4.5) we can therefore extract all other couplings in the mode-mode term, and incorporate these into a generalized coupling coefficient. This gives (cf. Sec. IV and Appendix C in I)

$$\Gamma_{\mu\nu}(\vec{q}z) = \Gamma^C_{\mu\nu}(\vec{q}z) + \frac{1}{2n}\int \frac{d\vec{q}'}{(2\pi)^3} T^C_{\mu;\alpha\beta}(\vec{q}\vec{q}'z)\Delta_{\alpha\beta;\gamma\delta}(\vec{q}\vec{q}'z) \times T_{\gamma\delta;\nu}(\vec{q}\vec{q}'z), \quad (4.9)$$

where $\alpha-\delta=1-3$. Here Γ^C and T^C generalizes Γ^B and T^B in (3.15) and (3.16) and the former functions include, except for the rapid binary part, all the mode couplings which decay faster than those kept in (4.9). On an asymptotic time scale only the modes coupling via $T_{\alpha\beta;\nu}$ will survive, while all the other modes build up the coupling constant T^C. From (B28) and (B29) and similar relations for T^C we obtain

$$\Gamma_{\mu\nu}(\vec{q}z) = \Gamma^C_{\mu\nu}(\vec{q}z) + \Gamma^C_{\mu\lambda}(\vec{q}z)R_{\lambda\eta}(\vec{q}z)\Gamma_{\eta\nu}(\vec{q}z), \quad (4.10)$$

which is a matrix equation for Γ. The mode-mode term R is given by

$$R_{\lambda\eta}(\vec{q}z) = -\frac{1}{2n}\int \frac{d\vec{q}'}{(2\pi)^3} \frac{T_{\lambda;\alpha\beta}(\vec{q}\vec{q}', t=0)}{2\omega_0^2} \times \Delta_{\alpha\beta;\gamma\delta}(\vec{q}\vec{q}'z) \times \frac{T_{\gamma\delta;\eta}(\vec{q}\vec{q}', t=0)}{2\omega_0^2}, \quad (4.11)$$

which according to Appendix B, is nonzero only for $\lambda, \eta = 4-8$. The terms in (4.10) with λ or $\eta=4$ couple to the matrix elements $\Gamma^C_{\mu 4}$ or $\Gamma_{4\nu}$. For these elements it can be shown that[15(b),26(b)]

$$\Gamma_{4\nu}(\vec{q}z) = zE_{4\nu}(\vec{q}z) + i\vec{q}\cdot\vec{J}^E_{4\nu}(\vec{q}z), \quad (4.12)$$

where the functions E and $\vec{J}^E$ have definite limits when $q, z\to 0$. This means that the terms with λ or $\eta=4$ in (4.10) give contributions of a least order q^3 when inserted in (4.5), and they can therefore be neglected. Of course, for the special case μ or $\nu=2$ in (4.10) we have $\Gamma^C_{24}=\Gamma_{42}\equiv 0$ by symmetry. The sum over λ and η in (4.10) runs then only over nonhydrodynamic states, i.e., we have

$$RQ = QR = R. \quad (4.13)$$

Formally, we can write (4.10) as

$$\Gamma = (1-\Gamma^C R)^{-1}\Gamma^C = [(\Gamma^C)^{-1} - R]^{-1}. \quad (4.14)$$

Using (4.13) and (4.14) we can now calculate the various matrix elements in (4.5) and we find

$$Q\Gamma Q = [(Q\Gamma^C Q)^{-1} - R]^{-1} \quad (4.15)$$

and

$$\langle 2|\Gamma Q = \langle 2|\Gamma^C Q(Q\Gamma^C Q)^{-1}Q\Gamma Q. \quad (4.16)$$

We also have

$$\langle 2|\Gamma|2\rangle = \langle 2|\Gamma^C|2\rangle - \langle 2|\Gamma^C Q(Q\Gamma^C Q)^{-1}Q\Gamma^C|2\rangle + \langle 2|\Gamma Q(Q\Gamma Q)^{-1}Q\Gamma|2\rangle. \quad (4.17)$$

Using (4.15)–(4.17) we can now write (4.5) as

$$D_t(\vec{q}z) = \langle 2|\Gamma^C|2\rangle - \langle 2|(-\Omega^0+\Gamma^C)Q(Q\Gamma^C Q)^{-1}Q(-\Omega^0+\Gamma^C)|2\rangle + \langle 2|\Omega^0 R\Omega^0|2\rangle + O(q^3). \quad (4.18)$$

We notice that the first term in (4.18) has exactly the same structure as (4.5) except that Γ is replaced with Γ^C. This term will, therefore, for instance, give the Boltzmann-Enskog contribution to D_t. For the mode-mode coupling term we have

$$\langle 2|\Omega^0 R\Omega^0|2\rangle = -(q^2/\beta m)R_{66}(\vec{q}z), \quad (4.19)$$

where we have inserted the explicit form for Ω^0. From (3.19), (4.11), and the result

$$T_{\alpha\beta;6}(\vec{q}=0, \vec{q}'=0, t=0)/\{2\omega_0^2\} = n(\delta_{\alpha z}\delta_{\beta x} + \delta_{\alpha x}\delta_{\beta z}) \quad (4.20)$$

it is easy to show that (4.19) is identical with the mode-mode coupling result of Ernst and Dorfman,[20] which is believed to be exact. Considering the longitudinal viscosity the situation is more complicated since the couplings are more involved. Not only $T_{\alpha\beta;\nu}$ but also the other current elements and the coupling to temperature will contribute. We also have to consider the couplings between Γ_{11}, Γ_{14}, and Γ_{44} which leads to a 3×3 matrix equation.

V. DISCUSSION

We have here presented a microscopic kinetic theory for the memory function of the phase-space correlation function. The results for the relevant matrix element Γ_{11} given in (3.33)–(3.37) can, together with the corresponding results for the self-part given in paper I, be used to obtain numerical results for $S(q\omega)$. We have calculated $S(q\omega)$ for liquid rubidium and find very good agreement with MD and experimental results. These calculations will be presented in a forthcoming paper.

As in the case of the self-motion we have separated the memory function into a binary part and a more collective tail. Actually, in a dense system the two-body collisions will be strongly influenced by the presence of other atoms, and the binary part therefore includes also all other rapid processes in the system. In particular we argue that the nonhydrodynamic couplings in the mode-mode term (3.16) represent such fast processes and should therefore be included into the binary part of the memory function. It is clear that our simple Gaussian ansatz for Γ_{11}^B may be a rather rough approximation for the time dependence. However, currently we do not see any possibility of improving this point. Fortunately, our calculations indicate that $S(q\omega)$ is not very sensitive to this point. In a hard-core system the binary part would be a δ function in time, and in such a system all interesting time dependence is therefore connected with the tail. Strictly speaking our derivation here is limited to continuous potentials, but we can always take the hard-core limit in our final expressions, i.e., using a potential $v(r)=\epsilon(\sigma/r)^n$ and let $n\to\infty$. Except for the binary part a hard-core potential will also modify the coupling constants, i.e., the T matrix. Due to (3.27), which will still be valid, the T matrix contains a δ function, and this implies that the initial value (3.26) diverges, i.e., the fourth moment $\gamma_d^{\alpha\beta}$ becomes infinitely large. However, it should be noted that the coupling constant $t^{\alpha\beta}$ in (3.29) still remains finite, and this as well as $c(q)$ therefore has a hard-core limit which can be used in the mode-mode integrals. The fourth moment $\gamma_d^{\alpha\beta}$ is very accurately given in terms of the Einstein frequency ω_0^2 and spherical Bessel functions.[31] In the hard-core limit ω_0^2 diverges, but when calculating $t^{\alpha\beta}$ it drops out, and this coupling constant is then expressed entirely in terms of spherical Bessel functions.

For the tail we have here made essentially the same approximations as in our earlier treatment of the self-motion, i.e., we have only considered mode-mode contributions coupling via the matrix elements $T_{00;1}$ and $T_{0\alpha;1}$. In particular, this implies that the correct asymptotic behavior of the memory function is violated as demonstrated in Sec. IV. However, including more matrix elements both in the solution of (2.22) and in the mode-mode integral (3.16), which would be necessary to recover the correct asymptotic behavior, rapidly increases the complexity of the theory. In contrast to the self-motion it does not, therefore, seem possible to obtain a theory which has both the correct short- and long-time behavior within the present kinetic approach. However, for ordinary dense liquids the long-time tails do not seem to play any significant quantitative role, but the situation would be different near the critical point and possibly also for gases and two-dimensional systems.

ACKNOWLEDGMENTS

The author would like to thank Professor Alf Sjölander for many helpful discussions during the development of this work, and for many valuable comments on the manuscript. This work has been supported by the Swedish Natural Science Research Council.

APPENDIX A: SHORT-TIME EXPANSION OF $\Gamma_{11}^B(qt)$ AND $\Gamma_{22}^B(qt)$

In this Appendix we discuss the short-time or large-z expansion of Γ_{11}^B and Γ_{22}^B given by (3.15). For convenience we consider the quantity $\Gamma_{\alpha\beta}^B$ with $\alpha,\beta=1-3$, from which we immediately obtain the other two functions, i.e., from (3.1) and (3.15):

$$\Gamma_{\alpha\beta}^B(\vec{q}z)=(\beta/mnV)\int d1\cdots d4\exp(-i\vec{q}\cdot\vec{r}_1)[\nabla_{r_1}^\alpha v(\vec{r}_1-\vec{r}_2)]G^B(12;34z)[\nabla_{r_3}^\beta v(\vec{r}_3-\vec{r}_4)]\exp(i\vec{q}\cdot\vec{r}_3). \quad \text{(A1)}$$

$G^B=R^B\tilde{G}$ is first expanded in powers of $1/z$ which according to (3.8) gives

$$G^B = (z - \Omega + \Gamma^B)^{-1}\tilde{G} = \left(\frac{1}{z} + \frac{1}{z^2}\,\Omega + \frac{1}{z^3}\,[\Omega\Omega - \Gamma^B(t=0)] + \cdots\right)\tilde{G}\,. \tag{A2}$$

Since G^B satisfies the continuity equation and the entire contribution to this comes from the free-particle flow term, we have

$$\int d\vec{p}_1\, d\vec{p}_2\, \Gamma^B(12;34z) = 0\,, \tag{A3}$$

and this implies that the contribution from $\Gamma^B(t=0)$ in (A2) vanishes when inserted into (A1): From the continuity equation we also have

$$\int d\vec{p}_1\, d\vec{p}_2\, \Omega(12;34) = -\int d\vec{p}_1\, d\vec{p}_2 \left(\frac{1}{m}\,\vec{p}_1\cdot\vec{\nabla}_{r_1} + \frac{1}{m}\,\vec{p}_2\cdot\vec{\nabla}_{r_2}\right)\tfrac{1}{2}\,[\delta(13)\delta(24) + \delta(14)\delta(23)]\,. \tag{A4}$$

From (A4) and the fact that the momentum dependence of $\tilde{G}$ is Maxwellian, it follows that the $1/z^2$ term in (A2) also vanishes when inserted in (A1), which reflects the fact that $\Gamma^B_{\alpha\beta}$ is even in time. Using also that $\Omega\Omega\tilde{G} = \Omega\tilde{G}\Omega^\dagger$, where

$$\Omega^\dagger(12;34) = -\Omega(34;12)\,, \tag{A5}$$

as is easily proved from (3.4), we obtain from (A2) and (A4)

$$\begin{aligned}\Gamma^B_{\alpha\beta}(\vec{q}z) = (\beta/mnV)\Bigg\{&\frac{1}{z}\int d1\cdots d4\,\exp(-i\vec{q}\cdot\vec{r}_1)[\nabla^\alpha_{r_1}v(\vec{r}_1-\vec{r}_2)]\,\tilde{G}(12;34)[\nabla^\beta_{r_3}v(\vec{r}_3-\vec{r}_4)]\exp(i\vec{q}\cdot\vec{r}_3)\\ &-\frac{1}{z^3}\int d1\cdots d4\left[\left(\frac{1}{m}\,\vec{p}_1\cdot\vec{\nabla}_{r_1} + \frac{1}{m}\,\vec{p}_2\cdot\vec{\nabla}_{r_2}\right)\exp(-i\vec{q}\cdot\vec{r}_1)\nabla^\alpha_{r_1}v(\vec{r}_1-\vec{r}_2)\right]\tilde{G}(12;34)\\ &\times\left[\left(\frac{1}{m}\,\vec{p}_3\cdot\vec{\nabla}_{r_3} + \frac{1}{m}\,\vec{p}_4\cdot\vec{\nabla}_{r_4}\right)\exp(i\vec{q}\cdot\vec{r}_3)\nabla^\beta_{r_3}v(\vec{r}_3-\vec{r}_4)\right] + \cdots\Bigg\}\,.\end{aligned} \tag{A6}$$

$\tilde{G}$ can be expressed in terms of static distribution functions from (2.8) and the evaluation of (A6) is then straightforward. We find

$$\begin{aligned}\Gamma^B_{\alpha\beta}(\vec{q}z) = &\frac{1}{z}\left[\omega_0^2\delta_{\alpha\beta} + \gamma_d^{\alpha\beta}(\vec{q}) + \left(\frac{q^\alpha q^\beta}{\beta m}\right)nc(\vec{q})\right]\\ &-\frac{1}{z^3}\Bigg[\left(\frac{q^2}{\beta m}\right)\omega_0^2\delta_{\alpha\beta} - \left(\frac{2q^\alpha q^\beta}{\beta m}\right)\gamma_d^l(\vec{q}) + \left(\frac{2n}{m^2}\right)\int d\vec{r}\,[1-\exp(-i\vec{q}\cdot\vec{r})][\nabla^\alpha\nabla^\gamma v(\vec{r})]g(\vec{r})[\nabla^\beta\nabla^\gamma v(\vec{r})]\\ &+\left(\frac{2n}{\beta m^2}\right)iq^\gamma\int d\vec{r}\,\exp(-i\vec{q}\cdot\vec{r})\,g(\vec{r})\,\nabla^\alpha\nabla^\beta\nabla^\gamma v(\vec{r})\\ &+\left(\frac{n^2}{m^2V}\right)\int d\vec{r}_1\,d\vec{r}_2\,d\vec{r}_3\{1-\exp[-i\vec{q}\cdot(\vec{r}_1-\vec{r}_3)] + \exp[-i\vec{q}\cdot(\vec{r}_2-\vec{r}_3)] - \exp[-i\vec{q}\cdot(\vec{r}_2-\vec{r}_1)]\}\\ &\times[\nabla^\alpha_{r_1}\nabla^\gamma_{r_1}v(\vec{r}_1-\vec{r}_2)][g_3(\vec{r}_1\vec{r}_2\vec{r}_3) - g(\vec{r}_1-\vec{r}_2)g(\vec{r}_1-\vec{r}_3)][\nabla^\beta_{r_1}\nabla^\gamma_{r_1}v(\vec{r}_1-\vec{r}_3)]\Bigg] + \cdots\,,\end{aligned} \tag{A7}$$

which should be compared with Eq. (A8) in I. In (A7) summation over repeated indices is implied. ω_0^2 is the Einstein frequency and $\gamma_d^{\alpha\beta}$ is given by

$$\gamma_d^{\alpha\beta}(\vec{q}) = -\frac{n}{m}\int d\vec{r}\,\exp(-i\vec{q}\cdot\vec{r})g(\vec{r})\nabla^\alpha\nabla^\beta v(\vec{r}) = \hat{q}^\alpha\hat{q}^\beta\gamma_d^l(\vec{q}) + [\delta_{\alpha\beta} - \hat{q}^\alpha\hat{q}^\beta]\gamma_d^t(\vec{q})\,. \tag{A8}$$

For the triplet distribution g_3, which enters in the last term in (A7) we will make the superposition approximation, and this gives

$$\Gamma^B_{\alpha\beta}(\vec{q}z)=\frac{1}{z}\left[\omega_0^2\delta_{\alpha\beta}+\gamma_d^{\alpha\beta}(\vec{q})+\left(\frac{q^\alpha q^\beta}{\beta m}\right)nc(\vec{q})\right]$$
$$-\frac{1}{z^3}\left[\left(\frac{q^2}{\beta m}\right)\omega_0^2\delta_{\alpha\beta}-\left(\frac{2q^\alpha q^\beta}{\beta m}\right)\gamma_d^l(\vec{q})+\left(\frac{2n}{m^2}\right)\int d\vec{r}[1-\exp(-i\vec{q}\cdot\vec{r})][\nabla^\alpha\nabla^\gamma v(\vec{r})]g(\vec{r})[\nabla^\beta\nabla^\gamma v(\vec{r})]\right.$$
$$+\left(\frac{2n}{\beta m^2}\right)iq^\gamma\int d\vec{r}\exp(-i\vec{q}\cdot\vec{r})g(\vec{r})\nabla^\alpha\nabla^\beta\nabla^\gamma v(\vec{r})$$
$$\left.+\frac{1}{n}\int\frac{d\vec{q}'}{(2\pi)^3}\gamma_d^{\alpha\gamma}(\vec{q}')\{[S(\vec{q}')-1]+[S(\vec{q}-\vec{q}')-1]\}[\gamma_d^{\beta\gamma}(\vec{q}')-\gamma_d^{\beta\gamma}(\vec{q}-\vec{q}')]\right]+\cdots. \quad (A9)$$

If we now approximate $\Gamma^B_{\alpha\beta}(qt)$ by a simple Gaussian as

$$\Gamma^B_{\alpha\beta}(\vec{q}t)=\hat{q}^\alpha\hat{q}^\beta\Gamma^B_{11}(\vec{q}t)+[\delta_{\alpha\beta}-\hat{q}^\alpha\hat{q}^\beta]\Gamma^B_{22}(\vec{q}t)$$
$$=\hat{q}^\alpha\hat{q}^\beta\Gamma^B_{11}(\vec{q},t=0)\exp[-t^2/\tau_l^2(\vec{q})]+(\delta_{\alpha\beta}-\hat{q}^\alpha\hat{q}^\beta)\Gamma^B_{22}(\vec{q},t=0)\exp[-t^2/\tau_t^2(\vec{q})], \quad (A10)$$

we find the large-z expansion

$$\Gamma^B_{\alpha\beta}(\vec{q}z)=z^{-1}[\hat{q}^\alpha\hat{q}^\beta\Gamma^B_{11}(\vec{q},t=0)+(\delta_{\alpha\beta}-\hat{q}^\alpha\hat{q}^\beta)\Gamma^B_{22}(\vec{q},t=0)]$$
$$-z^{-3}[\hat{q}^\alpha\hat{q}^\beta 2\Gamma^B_{11}(\vec{q},t=0)/\tau_l^2(\vec{q})+(\delta_{\alpha\beta}-\hat{q}^\alpha\hat{q}^\beta)2\Gamma^B_{22}(\vec{q},t=0)/\tau_t^2(\vec{q})], \quad (A11)$$

and comparing this with (A9) we get immediately the initial values and the relaxation times in (A10).

APPENDIX B: CALCULATION OF THE T MATRIX

Here, we consider the properties of the T matrix defined in (3.17), or rather the more general quantity

$$T_{\sigma\zeta;\nu}(\vec{q}\vec{q}'z)=\frac{1}{V}\int d1\cdots d\bar{4}\exp[-i(\vec{q}-\vec{q}')\cdot\vec{r}_1]\exp(-i\vec{q}'\cdot\vec{r}_2)H_\sigma(\vec{p}_1)H_\zeta(\vec{p}_2)$$
$$\times[R^D(12;\bar{1}\bar{2}z)]^{-1}R(\bar{1}\bar{2};34z)\tilde{G}(34;\bar{3}\bar{4})[\vec{\nabla}_{r_{\bar{3}}}v(\vec{r}_{\bar{3}}-\vec{r}_{\bar{4}})\cdot\vec{\nabla}_{p_{\bar{3}}}]H_\nu(\vec{p}_{\bar{3}})\exp(-i\vec{q}\cdot\vec{r}_{\bar{3}}), \quad (B1)$$

which for $\nu=1$ reduces to (3.17). An immediate consequence of (B1) is that

$$T_{\zeta\sigma;\nu}(\vec{q}\vec{q}'z)=T_{\sigma\zeta;\nu}(\vec{q},\vec{q}-\vec{q}',z). \quad (B2)$$

From (3.7) and the corresponding equation for the disconnected part of R we find that

$$(R^D)^{-1}R=1+(\Omega-\Omega^D-\Gamma+\Gamma^D)R \quad (B3)$$

and we insert this into (B1). From the term containing the identity operator in (B3) we obtain an instantaneous part of the T matrix given by

$$T^{(1)}_{\sigma\zeta;\nu}(\vec{q}\vec{q}'z)=\frac{1}{V}\int d1\cdots d4\exp[-i(\vec{q}-\vec{q}')\cdot\vec{r}_1]$$
$$\times\exp(-i\vec{q}'\cdot\vec{r}_2)H_\sigma(\vec{p}_1)H_\zeta(\vec{p}_2)$$
$$\times\tilde{G}(12;34)[\vec{\nabla}_{r_3}v(\vec{r}_3-\vec{r}_4)\cdot\vec{\nabla}_{p_3}]H_\nu(\vec{p}_3)$$
$$\times\exp(-i\vec{q}\cdot\vec{r}_3). \quad (B4)$$

This expression can be evaluated in terms of the two- and three-particle distribution functions. Since our knowledge of the latter function is limited we will use an approximation employed earlier by Sjögren and Sjölander[3] and Sjögren,[5] which can be written

$$\int d4\,\tilde{G}(12;34)\vec{\nabla}_{r_3}v(\vec{r}_3-\vec{r}_4)$$
$$\simeq-\frac{1}{\beta}\int d4\,\tilde{G}^D(12;34)\vec{\nabla}_{r_3}c(\vec{r}_3-\vec{r}_4). \quad (B5)$$

Inserting (B5) into (B4) we obtain

$$T^{(1)}_{\sigma\zeta;\nu}(\vec{q}\vec{q}'z)=\left(\frac{i}{\beta}\right)\{\tilde{C}_{\sigma\lambda}(\vec{q}-\vec{q}')q'^\alpha[S(\vec{q}')-1]\delta_{\zeta o}$$
$$+\tilde{C}_{\zeta\lambda}(\vec{q}')(q-q')^\alpha[S(\vec{q}-\vec{q}')-1]\delta_{\sigma o}\}$$
$$\times\int d\vec{p}\,\Phi_M(\vec{p})H_\lambda(\vec{p})\nabla^\alpha_p H_\nu(\vec{p}). \quad (B6)$$

For the special case $\nu=1$ we obtain

$$T^{(1)}_{\sigma\zeta;1}(\vec{q}\vec{q}'z)=in(\beta m)^{-1/2}$$
$$\times\{\hat{q}\cdot\vec{q}'S(\vec{q}-\vec{q}')[S(\vec{q}')-1]$$
$$+\hat{q}\cdot(\vec{q}-\vec{q}')S(\vec{q}')[S(\vec{q}-\vec{q}')-1]\}\delta_{\sigma o}\delta_{\zeta o}, \quad (B7)$$

and the instantaneous part couples then only to the density fluctuations. From the last term in (B3) we obtain

$$T^{(2)}_{\sigma\zeta;\nu}(\vec{q}\vec{q}'z)=\frac{1}{V}\int d1\cdots d\bar{4}\exp[-i(\vec{q}-\vec{q}')\cdot\vec{r}_1]\exp(-i\vec{q}'\cdot\vec{r}_2)H_\sigma(\vec{p}_1)H_\zeta(\vec{p}_2)$$
$$\times[\Omega(12;\overline{12})-\Omega^D(12;\overline{12})-\Gamma(12;\overline{12}z)+\Gamma^D(12;\overline{12}z)]R(\overline{12};34z)$$
$$\times\tilde{G}(34;\overline{34})[\vec{\nabla}_{r_{\bar{3}}}v(\vec{r}_{\bar{3}}-\vec{r}_{\bar{4}})\cdot\vec{\nabla}_{p_{\bar{3}}}]H_\nu(\vec{p}_{\bar{3}})\exp(i\vec{q}\cdot\vec{r}_{\bar{3}}), \tag{B8}$$

which is obviously a very complicated quantity. We notice that $T^{(2)}_{oo;\nu}=0$ due to particle conservation. The large-z expansion of (B8) gives the initial value of $T^{(2)}_{\sigma\zeta;\nu}$, and we obtain

$$T^{(2)}_{\sigma\zeta;\nu}(\vec{q}\vec{q}',t=0)=\frac{1}{V}\int d1\cdots d4\exp[-i(\vec{q}-\vec{q}')\cdot\vec{r}_1]\exp(-i\vec{q}'\cdot\vec{r}_2)H_\sigma(\vec{p}_1)H_\zeta(\vec{p}_2)$$
$$\times[\Omega 12;\overline{12})-\Omega^D(12;\overline{12})]\tilde{G}(\overline{12};34)[\vec{\nabla}_{r_3}v(\vec{r}_3-\vec{r}_4)\cdot\vec{\nabla}_{p_3}]H_\nu(\vec{p}_3)\exp(i\vec{q}\cdot\vec{r}_3). \tag{B9}$$

We now need more explicit expressions for Ω and Ω^D, where the former is defined in (3.4). Using the fluctuation-dissipation theorem we find (cf. Appendix B in I)

$$\langle\dot{\overline{\delta f}}_2(12t)\delta\bar{f}_2(34t)\rangle=\left[-\frac{1}{\beta}(1+P_{12})\vec{\nabla}_{r_1}\cdot\left(\vec{\nabla}_{p_1}+\frac{\beta}{m}\vec{p}_1\right)+\frac{1}{\beta}(1+P_{34})\vec{\nabla}_{r_3}\cdot\left(\vec{\nabla}_{p_3}+\frac{\beta}{m}\vec{p}_3\right)\right]\tilde{G}(12;34), \tag{B10}$$

where the operator P_{12} permutes 1 and 2. From (B10) and (3.4) together with corresponding results for Ω^D we can now write (B9) as

$$T^{(2)}_{\sigma\zeta;\nu}(\vec{q}\vec{q}',t=0)=\frac{1}{\beta V}\int d1\cdots d4\exp(-i(\vec{q}-\vec{q}')\cdot\vec{r}_1]\exp(-i\vec{q}'\cdot\vec{r}_2)H_\sigma(\vec{p}_1)$$
$$\times H_\zeta(\vec{p}_2)\left(\tilde{G}(12;34)\nabla^\alpha_{r_3}\nabla^\beta_{r_3}v(\vec{r}_3-\vec{r}_4)+\tilde{G}^D(12;34)\frac{1}{\beta}\nabla^\alpha_{r_3}\nabla^\beta_{r_3}c(\vec{r}_3-\vec{r}_4)\right)$$
$$\times\left[\left(\nabla^\alpha_{p_3}-\frac{\beta}{m}p_3^\alpha\right)-\left(\nabla^\alpha_{p_4}-\frac{\beta}{m}p_4^\alpha\right)\right]\nabla^\beta_{p_3}H_\nu(\vec{p}_3)\exp(i\vec{q}\cdot\vec{r}_3), \tag{B11}$$

where we have made some partial integrations, and also the approximation $\Omega^D\tilde{G}\nabla v\simeq-\Omega^D\tilde{G}^D\beta^{-1}\nabla c$. Inserting the explicit expressions for $\tilde{G}$ and $\tilde{G}^D$ in (B11) we obtain

$$T^{(2)}_{\sigma\zeta;\nu}(\vec{q}\vec{q}',t=0)=\left(\frac{mn}{\beta}\right)\left[\gamma_4^{\alpha\beta}(\vec{q}')+\left(\frac{q'^\alpha q'^\beta}{\beta m}\right)nc(\vec{q}')\right]\int d\vec{p}\,\Phi_M(\vec{p})\left[\nabla^\alpha_p H_\sigma(\vec{p})\delta_{\zeta o}-\left(\frac{\beta}{m}\right)^{1/2}H_\sigma(\vec{p})\delta_{\zeta\alpha}\right]\nabla^\beta_p H_\nu(\vec{p})$$
$$+\left(\frac{n^3}{\beta}\right)\int d1\,d2\left[\exp(-i\vec{q}'\cdot\vec{r}_1)\exp[-i(\vec{q}-\vec{q}')\cdot\vec{r}_2]\left(\frac{\beta}{m}\right)^{1/2}\delta_{\sigma o}\delta_{\zeta\alpha}\right.$$
$$\left.-\exp[i\vec{q}'\cdot(\vec{r}_1-\vec{r}_2)]\nabla^\alpha_{p_1}H_\sigma(\vec{p}_1)\delta_{\zeta o}\right]\left([g_3(\vec{r}_1\vec{r}_2)-g(\vec{r}_1-\vec{r}_2)g(\vec{r}_1)]\nabla^\alpha_{r_1}\nabla^\beta_{r_1}v(\vec{r}_1)\right.$$
$$\left.+[g(\vec{r}_2)-1]\frac{1}{\beta}\nabla^\alpha_{r_1}\nabla^\beta_{r_1}c(\vec{r}_1)\right)$$
$$\times\Phi_M(\vec{p}_1)\Phi_M(\vec{p}_2)\nabla^\beta_{p_1}H_\nu(\vec{p}_1)+[\sigma\rightleftarrows\zeta,\vec{q}'\to(\vec{q}-\vec{q}')], \tag{B12}$$

where the last term indicates that we should exchange σ, ζ, and q' with $(q-q')$. The three-particle distribution function enters again in (B12) and as in Appendix A, we make the superposition approximation for it. We also notice that the static correlation between r_1 and r_2 in (B12) represented by $g(\vec{r}_1-\vec{r}_2)$ is not combined with any potential interaction between these points, and it has therefore only the effect of excluding a small volume in the integration over r_1 and r_2. For this reason we will neglect this correlation and make the approximation

$$g_3(\vec{r}_1\vec{r}_2)-g(\vec{r}_1-\vec{r}_2)g(\vec{r}_1)\simeq[g(\vec{r}_2)-1]g(\vec{r}_1). \tag{B13}$$

We then obtain

$$T^{(2)}_{\sigma\zeta;\nu}(\vec{q}\vec{q}\,',t=0)=\left(\frac{mn}{\beta}\right)\left[\gamma_d^{\alpha\beta}(\vec{q}\,')+\left(\frac{q'^{\alpha}q'^{\beta}}{\beta m}\right)nc(\vec{q}\,')\right]$$
$$\times\int d\vec{p}\,\Phi_M(\vec{p})\left[S(\vec{q}\,')\nabla^{\alpha}_{p}H_{\sigma}(\vec{p})\delta_{\zeta o}-\left(\frac{\beta}{m}\right)^{1/2}H_{\sigma}(\vec{p})\delta_{\zeta\alpha}-[S(\vec{q}-\vec{q}\,')-1]\left(\frac{\beta}{m}\right)^{1/2}\delta_{\sigma o}\delta_{\zeta\alpha}\right]\nabla^{\beta}_{p}H_{\nu}(\vec{p})$$
$$+[\sigma\rightleftarrows\zeta,\vec{q}\,'\to(\vec{q}-\vec{q}\,')]\,. \tag{B14}$$

With $\nu=1$ this gives for $\sigma=0$ and $\zeta=\alpha=1-3$:

$$T^{(2)}_{o\alpha;1}(\vec{q}\vec{q}\,',t=0)=nS(\vec{q}-\vec{q}\,')\hat{q}^{\beta}\{\gamma_d^{\alpha\beta}(\vec{q}-\vec{q}\,')+[(q-q')^{\alpha}(q-q')^{\beta}/\beta m]nc(\vec{q}-\vec{q}\,')-\gamma_d^{\alpha\beta}(\vec{q}\,')-(q'^{\alpha}q'^{\beta}/\beta m)nc(\vec{q}\,')\}\,. \tag{B15}$$

We will now consider $T^{(2)}_{o\alpha;\nu}(q,q'=0,z)$, which from (B8), is given by

$$T^{(2)}_{o\alpha;\nu}(\vec{q},\vec{q}\,'=0,z)=\left(\frac{\beta}{m}\right)^{1/2}\left(\frac{1}{V}\right)\int d1\cdots d\bar{4}\exp(-i\vec{q}\cdot\vec{r}_1)p_2^{\alpha}[\Omega(12;\bar{1}\bar{2})-\Omega^{D}(12;\bar{1}\bar{2})-\Gamma(12;\bar{1}\bar{2}z)+\Gamma^{D}(12;\bar{1}\bar{2}z)]$$
$$\times R(\bar{1}\bar{2};34z)\tilde{G}(34;\bar{3}\bar{4})[\vec{\nabla}_{r_{\bar{3}}}v(\vec{r}_{\bar{3}}-\vec{r}_{\bar{4}})\cdot\vec{\nabla}_{p_{\bar{3}}}]H_{\nu}(\vec{p}_{\bar{3}})\exp(i\vec{q}\cdot\vec{r}_{\bar{3}})\,. \tag{B16}$$

The terms containing Γ and Γ^D vanish, and the proof of this is analogous to that presented in I. The conservation of the total momentum gives

$$\frac{d}{dt}\sum_{i=1}^{N}p_i^{\alpha}(t)=-\sum_{i\neq j=1}^{N}\nabla^{\alpha}_{r_i}v(\vec{r}_i(t)-\vec{r}_j(t))=-\sum_{i\neq j=1,1,j\neq k}^{N}\nabla^{\alpha}_{r_i}v(\vec{r}_i(t)-\vec{r}_j(t))=0 \tag{B17}$$

for any k. From this we find that

$$\int d1\,d2\,d3\,\exp(-i\vec{q}\cdot\vec{r}_1)H_{\sigma}(\vec{p}_1)\nabla^{\alpha}_{r_2}v(\vec{r}_2-\vec{r}_3)\delta f_3(123t)=0 \tag{B18}$$

holds for all times and hence

$$\int d1\,d2\,d3\,\exp(-i\vec{q}\cdot\vec{r}_1)H_{\sigma}(\vec{p}_1)p_2^{\alpha}[\vec{\nabla}_{r_2}v(\vec{r}_2-\vec{r}_3)\cdot\vec{\nabla}_{p_2}]\langle\delta f_3(123t)\delta f_n(\bar{1}\bar{2}\ldots\bar{n},0)\rangle=0\,. \tag{B19}$$

The formally exact expression for Γ is given by[15(b),19]

$$\Gamma(12;\bar{1}\bar{2}z)=-\int d3\ldots d6[\vec{\nabla}_{r_1}v(\vec{r}_1-\vec{r}_3)\cdot\vec{\nabla}_{p_1}+\vec{\nabla}_{r_2}v(\vec{r}_2-\vec{r}_3)\cdot\vec{\nabla}_{p_2}]G(123;456z)$$
$$\times[\vec{\nabla}_{r_4}v(\vec{r}_4-\vec{r}_6)\cdot\vec{\nabla}_{p_4}+\vec{\nabla}_{r_5}v(\vec{r}_5-\vec{r}_6)\cdot\vec{\nabla}_{p_5}]\tilde{G}^{-1}(45;\bar{1}\bar{2})\,, \tag{B20}$$

where $G(123;456z)$ can be written as a linear combination of $C(123;456z)$, $C(123;45z)$ and $C(123;4z)$. Using (B19) with $\sigma=0$ it then follows that

$$\int d1\,d2\,\exp(-i\vec{q}\cdot\vec{r}_1)p_2^{\alpha}\Gamma(12;\bar{1}\bar{2}z)=0\,, \tag{B21}$$

and we also have a similar relation for Γ^D since this conserves the total momentum for particle 2. The evaluation of the remaining part of (B16) is most easily done by using the explicit expressions[5,15(b)]

$$\Omega(12;\bar{1}\bar{2})=-\left(\frac{1}{m}\vec{p}_1\cdot\vec{\nabla}_{r_1}+\frac{1}{m}\vec{p}_2\cdot\vec{\nabla}_{r_2}-\vec{\nabla}_{r_1}v(\vec{r}_1-\vec{r}_2)\cdot(\vec{\nabla}_{p_1}-\vec{\nabla}_{p_2})\right)\tfrac{1}{2}[\delta(1\bar{1})\delta(2\bar{2})+\delta(1\bar{2})\delta(2\bar{1})]$$
$$+\int d3\,d4\,d5[\vec{\nabla}_{r_1}v(\vec{r}_1-\vec{r}_3)\cdot\vec{\nabla}_{p_1}+\vec{\nabla}_{p_2}v(\vec{r}_2-\vec{r}_3)\cdot\vec{\nabla}_{p_2}]\langle\delta f_3(123t)\delta\bar{f}_2(45t)\rangle\tilde{G}^{-1}(45;\bar{1}\bar{2})$$
$$-\int d3\,\tilde{C}(12;3)\,\tfrac{1}{2}[\tilde{C}^{-1}(3\bar{1})+\tilde{C}^{-1}(3\bar{2})]\vec{\nabla}_{r_{\bar{1}}}v(\vec{r}_{\bar{1}}-\vec{r}_{\bar{2}})\cdot(\vec{\nabla}_{p_{\bar{1}}}-\vec{\nabla}_{p_{\bar{2}}}) \tag{B22}$$

and

$$\Omega^{D}(12;\bar{1}\bar{2})=-(m^{-1}\vec{p}_1\cdot\vec{\nabla}_{r_1}+m^{-1}\vec{p}_2\cdot\vec{\nabla}_{r_2})\tfrac{1}{2}[\delta(1\bar{1})\delta(2\bar{2})+\delta(1\bar{2})\delta(2\bar{1})]$$
$$-(1+P_{12})\vec{\nabla}_{r_1}\cdot\vec{\nabla}_{p_1}n\Phi_M(\vec{p}_1)(\tfrac{1}{2}\beta)[c(\vec{r}_1-\vec{r}_{\bar{1}})\delta(2\bar{2})+c(\vec{r}_1-\vec{r}_{\bar{2}})\delta(2\bar{1})] \tag{B23}$$

The free-particle terms in (B22) and (B23) cancel each other. The second term in (B22) vanishes according to (B19), and the second term in (B23) also vanishes when inserted in (B16). Using the explicit expression for $\bar{C}(12;3)$ defined in (2.4) we find

$$T^{(2)}_{\sigma\alpha;\nu}(\vec{q},\vec{q}'=0,z)=\left(\frac{\beta}{m}\right)^{1/2}\left(\frac{1}{V}\right)\int d\bar{1}d1\cdots d4\exp(-i\vec{q}\cdot\vec{r}_{\bar{1}})[\delta(\bar{1}1)+n\Phi_M(\vec{p}_{\bar{1}})g(\vec{r}_{\bar{1}}-\vec{r}_1)][\nabla^{\alpha}_{r_1}v(\vec{r}_1-\vec{r}_2)]$$
$$\times G(12;34z)[\vec{\nabla}_{r_3}v(\vec{r}_3-\vec{r}_4)\cdot\vec{\nabla}_{p_3}]\times H_\nu(\vec{p}_3)\exp(i\vec{q}\cdot\vec{r}_3)=nS(\vec{q})\Gamma_{\alpha\nu}(\vec{q}z)\,, \tag{B24}$$

where we have used the fact that $\Gamma_{\alpha\nu}(q=0,z)=0$. The relation (B24) is an exact consequence of (B16). We notice that although the expression (B15) for the initial value was obtained via certain approximations it agrees with (B24) for $q'=0$, and this verifies our earlier approximations. For T^B we obtain the same relations for the instantaneous part in (B6) and for the initial value in (B14). We also obtain a relation like (B24) but with Γ replaced by Γ^B.

We will also consider the matrix elements $T_{\alpha\beta;\nu}$ since these appear in our analysis of the shear viscosity in Sec. IV. It is clear from (B6) that there is no instantaneous contribution in this case. Using (B19) with $q=0$ and taking σ to be a current element, we obtain

$$\int d1\,d2\,p_1^\alpha p_2^\beta\,\Gamma(12;\bar{1}\bar{2}z)=0\,. \tag{B25}$$

Together with a similar relation for Γ^D and (B22) and (B23) we obtain

$$T_{\alpha\beta;\nu}(\vec{q}=0,\vec{q}'=0,z)=-\left(\frac{\beta}{mV}\right)\int d1\cdots d4\,p_1^\alpha p_1^\beta[\vec{\nabla}_{r_1}v(\vec{r}_1-\vec{r}_2)\cdot\vec{\nabla}_{p_1}]G(12;34z)[\vec{\nabla}_{r_3}v(\vec{r}_3-\vec{r}_4)\cdot\vec{\nabla}_{p_3}]H_\nu(\vec{p}_3)\,. \tag{B26}$$

With $\alpha=\beta=1$ we have for instance

$$T_{11;\nu}(\vec{q}=0,\vec{q}'=0,z)=\frac{2}{\sqrt{3}}n\Gamma_{5\nu}(\vec{q}=0,z)+(\tfrac{2}{3})^{1/2}n\Gamma_{4\nu}(\vec{q}=0,z) \tag{B27}$$

and similar relations for other combinations of α and β. Again we find that our result (B14) is consistent with (B27) for $t=0$.

We now make the following ansatz:

$$T_{\alpha\beta;\nu}(\vec{q}\vec{q}'z)=a_{\alpha\beta;\lambda}(\vec{q}\vec{q}')\Gamma_{\lambda\nu}(\vec{q}z)\,, \tag{B28}$$

where summation over λ is implied, and we determine the coefficients $a_{\alpha\beta;\lambda}$ from a large-z expansion. This gives

$$a_{\alpha\beta;\lambda}(\vec{q}\vec{q}')=T_{\alpha\beta;\lambda}(\vec{q}\vec{q}',t=0)/2\omega_0^2\,, \tag{B29}$$

where only $\lambda=4-8$ gives a nonzero value as can be proved from (B14). We have also used the fact that

$$\Gamma_{\lambda\nu}(\vec{q},t=0)=2\omega_0^2\delta_{\lambda\nu} \tag{B30}$$

for $\lambda=4-8$.

[1]L. Sjögren and A. Sjölander, J. Phys. C 12, 4369 (1979).
[2]L. Sjögren, J. Phys. C 13, 705 (1980), referred to as II.
[3]L. Sjögren and A. Sjölander, Ann. Phys. (N.Y.) 110, 122 (1978).
[4]L. Sjögren, Ann. Phys. (N.Y.) 110, 122 (1978); 110, 173 (1978); L. Sjögren and A. Sjölander, *ibid.* 110, 421 (1978).
[5]L. Sjögren, Ann. Phys. (N.Y.) 113, 304 (1978).
[6]A. Rahman, Phys. Rev. Lett. 32, 52 (1974); Phys. Rev. A 9, 1667 (1974).
[7]W. Götze and M. Lücke, Phys. Rev. A 11, 2173 (1975); J. Bosse, W. Götze, and M. Lücke, *ibid.* 17, 434 (1978); 17, 447 (1978); 18, 1176 (1978).
[8]P. M. Furtado, G. F. Mazenko, and S. Yip, Phys. Rev. A 12, 1653 (1975).
[9]T. Munakata and A. Igarashi, Prog. Theor. Phys. 60, 45 (1978).
[10]M. S. Jhon and D. Forster, Phys. Rev. A 12, 254 (1975).
[11]F. Yoshida, Prog. Theor. Phys. 58, 1331 (1977); F. Yoshida and S. Takeno, *ibid.* 58, 15 (1978); J. Phys. C 11, 2895 (1978).
[12]A. Zippelius and W. Götze, Phys. Rev. A 17, 414 (1978).
[13]P. K. Kahol, R. Bansal, and K. N. Pathak, Phys. Rev. A 14, 408 (1976); P. K. Kahol and D. K. Chaturwedi,

ibid. 18, 2717 (1978).
[14]S. Sjödin and A. Sjölander, Phys. Rev. A 18, 1723 (1978).
[15](a) G. F. Mazenko, Phys. Rev. A 7, 209 (1973); (b) *ibid.* 9, 360 (1974); (c) G. F. Mazenko and S. Yip, in *Modern Theoretical Chemistry*, edited by B. J. Berne (Plenum, New York, 1977), Vol. 6.
[16]E. P. Gross, Ann. Phys. (N.Y.) 69, 42 (1972); J. Stat. Phys. 11, 503 (1974); 15, 181 (1976).
[17](a) C. D. Boley, Ann. Phys. (N.Y.) 86, 91 (1974); (b) Phys. Rev. A 11, 328 (1975).
[18]P. Resibois and J. L. Lebowitz, J. Stat. Phys. 12, 483 (1975).
[19]M. Lindenfeld, Phys. Rev. A 15, 1801 (1977).
[20]M. H. Ernst and J. R. Dorfman, Physica (Utrecht) 61, 157 (1972); J. Stat. Phys. 12, 311 (1975).
[21]R. Bansal and W. Bruns, Phys. Rev. A 18, 1637 (1978).
[22]P. M. Furtado, G. F. Mazenko, and S. Yip, Phys. Rev. A 14, 869 (1976).
[23]J. R. Mehaffey, R. C. Desai, and R. Kapral, J. Chem. Phys. 66, 1665 (1977).
[24]M. Nelkin and S. Ranganathan, Phys. Rev. 164, 222 (1967).
[25]K. E. Larsson, Phys. Chem. Liq. (in press).
[26](a) D. Forster and P. C. Martin, Phys. Rev. A 2, 1575 (1970); (b) D. Forster, Phys. Rev. A 9, 943 (1974).
[27]Y. Pomeau, Phys. Rev. A 5, 2569 (1972); 7, 1134 (1973).
[28]M. H. Ernst, E. H. Hauge, and J. M. J. Van Leeuwen, Phys. Rev. A 4, 2055 (1971); J. Stat. Phys. 15, 7 (1976).
[29]I. M. De Schepper, H. Van Beyren, and M. H. Ernst, Physica (Utrecht) 75, 1 (1974); I. M. De Schepper and M. H. Ernst, *ibid.* 98A, 189 (1979).
[30]L. P. Kadanoff and J. Swift, Phys. Rev. 166, 89 (1968); K. Kawasaki, Ann. Phys. (N.Y.) 69, 1 (1970); M. H. Ernst, E. H. Hauge, and J. M. J. Van Leeuwen, J. Stat. Phys. 15, 23 (1976).
[31]J. R. D. Copley and S. W. Lovesey, Rep. Prog. Phys. 38, 461 (1975).