

## Diffusive and Collective Motion in Classical Fluids

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A "perturbation" technique previously developed is used to generate a systematic sequence of approximate relations between the coherent and incoherent scattering functions of classical fluids measured by inelastic neutron scattering. This sequence, recently obtained independently by Kim and Nelkin, has as its first member the Vineyard convolution approximation, while the second member is Kerr's generalization of this result. We show that the third member leads to a relationship between diffusion and viscosity coefficients of a form previously obtained by very different theories.

## I. INTRODUCTION

The van Hove<sup>1</sup> density autocorrelation function,

$$G(\mathbf{r}, t) = G^s(\mathbf{r}, t) + G^d(\mathbf{r}, t), \quad (1)$$

can be decomposed into a contribution  $G^s(\mathbf{r}, t)$  associated with single-particle, or diffusive, motion and a contribution  $G^d(\mathbf{r}, t)$  associated with multiparticle, or collective, motion. Of the two, the "self" term  $G^s(\mathbf{r}, t)$  is the easier to compute from more-or-less basic principles. This fact provides one motivation for seeking to express the "distinct" term  $G^d(\mathbf{r}, t)$ , or equivalently  $G(\mathbf{r}, t)$ , in terms of just the diffusive contribution  $G^s(\mathbf{r}, t)$ . Indeed, one of the earliest attempts to calculate the density autocorrelation function, that of Vineyard,<sup>2</sup> involved such an assumed relationship between the diffusive and collective motions. Since the two contributions can be separately measured by means of incoherent and coherent inelastic scattering of neutrons,<sup>1</sup> such relationships are of more than academic interest. More complete data yet, in this respect, are provided by the numerical "experiments" of molecular dynamics.<sup>3,4</sup>

In this paper, we deal with two aspects of this topic. First, we present in Sec. II a systematic method of generating approximate relations between  $G(\mathbf{r}, t)$  and  $G^s(\mathbf{r}, t)$ . The lowest-order member of this sequence of approximations is the Vineyard convolution equation<sup>2</sup> and the next is an equation derived by Kerr<sup>5</sup> by means of a quite different analysis. The general sequence<sup>6</sup> is obtained as another instance of a "perturbation" calculation employed previously by Lado,<sup>7</sup> though the presentation given here is formally simpler. This same chain of approximations has also been recently obtained independently by Kim and Nelkin,<sup>8</sup> using Mori's<sup>9</sup> memory function formalism. The derivation given here is somewhat different from theirs.

Second, we examine in Sec. III the implications of an assumed relationship between coherent and incoherent scattering functions with respect to the transport coefficients these determine, namely viscosity and diffusion, respectively. In particular, we show that the third member of this sequence leads to the equation

$$\frac{4}{3}\eta + \zeta = k_B T / a_0 D, \quad (2)$$

where  $\eta$  and  $\zeta$  are the shear and bulk viscosities,  $D$  is the diffusion coefficient, and  $a_0$  is a length defined in terms of the pair correlation function and the intermolecular potential. The two lower-order members of the sequence do not contain this result.<sup>10</sup>

## II. SEQUENCE OF APPROXIMATIONS

Consider a classical system of  $N$  identical molecules of mass  $m$  in thermal equilibrium at the temperature  $T = (k_B \beta)^{-1}$  and contained in the volume  $V$ . We write, for the intermediate scattering function of coherent scattering,

$$nG_{\mathbf{k}}(t) = N^{-1} \langle R_{-\mathbf{k}}(0) R_{\mathbf{k}}(t) \rangle, \quad (3)$$

with

$$R_{\mathbf{k}}(t) = \sum_{j=1}^N \exp[i\mathbf{k} \cdot \mathbf{r}_j(t)] - N\delta_{\mathbf{k},0}, \quad (4)$$

so that, as in I,  $G(\mathbf{r}, t)$  is a dimensionless function normalized to zero at large  $r$ . Here,  $\mathbf{r}_j(t)$  is the position of the  $j$ th molecule at time  $t$ ,  $n$  is the mean number density  $N/V$ , and the angular brackets denote a canonical ensemble average over the initial state at  $t=0$ . Similarly, for incoherent scattering, we write

$$nG_{\mathbf{k}}^s(t) = \langle R_{-\mathbf{k}}^s(0) R_{\mathbf{k}}^s(t) \rangle, \quad (5)$$

$$R_{\mathbf{k}}^s(t) = \exp[i\mathbf{k} \cdot \mathbf{r}_1(t)], \quad (6)$$

which makes  $G^s(\mathbf{r}, t)$  also dimensionless.

The principal result we need from I is that it is possible to write the Laplace transform,

$$\hat{G}_{\mathbf{k}}(z) = \int_0^{\infty} dt e^{-zt} G_{\mathbf{k}}(t), \quad (7)$$

in the form of a ratio of two infinite tridiagonal determinants,

$$\hat{G}_{\mathbf{k}}(z) = G_{\mathbf{k}}(0) i\mathcal{D}_1(z) / \mathcal{D}_0(z), \quad (8a)$$

$$\mathcal{D}_j(z) = \begin{vmatrix} iz & \nu_j & 0 & \cdots \\ 1 & iz & \nu_{j+1} & \cdots \\ 0 & 1 & iz & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix}, \quad (9)$$

a result that is equivalent to Mori's<sup>11</sup> continued fraction representation. The coefficients  $\nu_j$  in (9) are  $k$ -dependent quantities that depend only on the equilibrium correlations present in the system at time  $t=0$ . More specifically, a given  $\nu_j$  depends on the first  $2j+2$  moments of the dynamic scattering function,

$$S(\mathbf{k}, \omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt e^{-i\omega t} nG_{\mathbf{k}}(t) \quad (10)$$

$$= (n/\pi) \lim_{\epsilon \rightarrow 0^+} \text{Re} \hat{G}_{\mathbf{k}}(\epsilon + i\omega). \quad (11)$$

We shall return to these coefficients below, since it is clear from (8a) and (9) that they constitute the heart of the problem. Here we wish to note finally that the determinants  $\mathcal{D}_j(z)$  satisfy the recurrence relation

$$\mathcal{D}_j(z) = iz\mathcal{D}_{j+1}(z) - \nu_j \mathcal{D}_{j+2}(z), \quad (12)$$

easily obtained from Eq. (9) by expansion in minors of the first row or column. This relation, used on  $\mathcal{D}_0(z)$  in (8a), leads to the memory function expression

$$\hat{G}_{\mathbf{k}}(z) = \frac{G_{\mathbf{k}}(0)}{z + \nu_0 i \mathcal{D}_2(z) / \mathcal{D}_1(z)}. \quad (8b)$$

The feature we wish to emphasize, however, is that neither  $\mathcal{D}_1(z)$  nor  $\mathcal{D}_2(z)$  contain  $\nu_0$ , so that the dependence of  $\hat{G}_{\mathbf{k}}(z)$  on this quantity appears explicitly in (8b). Similarly, another application of (12) brings out all of the dependence on both  $\nu_0$  and  $\nu_1$ ,

$$\hat{G}_{\mathbf{k}}(z) = G_{\mathbf{k}}(0) / \left( z + \frac{\nu_0}{z + \nu_1 i \mathcal{D}_3(z) [\mathcal{D}_2(z)]^{-1}} \right). \quad (8c)$$

As noted in I, indefinite continuation of this process leads to the continued fraction expression of Mori.<sup>11</sup>

The same analysis can be applied to Eq. (5) for the single-particle motion, with the analogous results

$$\hat{G}_{\mathbf{k}}^s(z) = G_{\mathbf{k}}^s(0) i \mathcal{D}_1^s(z) / \mathcal{D}_0^s(z) \quad (13a)$$

$$= \frac{G_{\mathbf{k}}^s(0)}{z + \nu_0^s i \mathcal{D}_2^s(z) / \mathcal{D}_1^s(z)} \quad (13b)$$

$$= G_{\mathbf{k}}^s(0) / \left( z + \frac{\nu_0^s}{z + \nu_1^s i \mathcal{D}_3^s(z) [\mathcal{D}_2^s(z)]^{-1}} \right), \quad (13c)$$

etc.

Here,  $\mathcal{D}_j^s(z)$  is defined as in Eq. (9), but with the corresponding "self"-coefficients  $\nu_j^s$  replacing the  $\nu_j$ . These in turn are similarly determined by the moments of the incoherent scattering function,

$$S^s(\mathbf{k}, \omega) = (n/\pi) \lim_{\epsilon \rightarrow 0^+} \text{Re} \hat{G}_{\mathbf{k}}^s(\epsilon + i\omega). \quad (14)$$

The method of systematically generating approximations for  $\hat{G}_{\mathbf{k}}(z)$  may now be briefly stated. If we assume that the coefficients  $\nu_j$  for  $j > n$  are equal to the corresponding  $\nu_j^s$ , then the ratio  $\mathcal{D}_{n+2}(z) / \mathcal{D}_{n+1}(z)$  becomes equal to the corresponding ratio of the "self"-quantities. This latter ratio can be expressed in terms of  $\hat{G}_{\mathbf{k}}^s(z)$  and  $\nu_0^s, \nu_1^s, \dots, \nu_n^s$  using Eqs. (13) and substituted into the appropriate one of Eqs. (8), yielding then an approximate equation for  $\hat{G}_{\mathbf{k}}(z)$  in terms of  $\hat{G}_{\mathbf{k}}^s(z)$  and the first  $n$  of the  $\nu_j, \nu_j^s$ . For  $n=0-2$ , for example, we get in this way, after some rearrangement,

$$\hat{G}_{\mathbf{k}}^{(0)}(z) = G_{\mathbf{k}}(0) [\hat{G}_{\mathbf{k}}^s(z) / G_{\mathbf{k}}^s(0)], \quad (15a)$$

$$\hat{G}_{\mathbf{k}}^{(1)}(z) = G_{\mathbf{k}}(0) \{ \nu_0 \hat{G}_{\mathbf{k}}^s(z) / [\nu_0 G_{\mathbf{k}}^s(0) - (\nu_0 - \nu_0^s) z \hat{G}_{\mathbf{k}}^s(z)] \}, \quad (15b)$$

$$\hat{G}_{\mathbf{k}}^{(2)}(z) = G_{\mathbf{k}}(0) \frac{[\nu_0^s \nu_1 + (\nu_1 - \nu_1^s) z^2] \hat{G}_{\mathbf{k}}^s(z) - (\nu_1 - \nu_1^s) z G_{\mathbf{k}}^s(0)}{[\nu_0^s \nu_1 - \nu_0 \nu_1^s + (\nu_1 - \nu_1^s) z^2] z \hat{G}_{\mathbf{k}}^s(z) + [\nu_0 \nu_1^s - (\nu_1 - \nu_1^s) z^2] G_{\mathbf{k}}^s(0)}, \quad (15c)$$

where the suffix on  $\hat{G}_{\mathbf{k}}(z)$  identifies the level of the approximation. Other sequences<sup>7,12</sup> can be obtained in the same way by a different choice of the approximating coefficients here taken to be the "self"-quantities  $\nu_j^s$ .

The first member of the sequence (15) is the well-known convolution approximation,<sup>2</sup> while the second was first obtained by Kerr,<sup>5</sup> using more physically motivated arguments. The third and fourth members of this sequence have recently been studied numerically by Kurkijärvi<sup>13</sup> and by Kim and Nelkin,<sup>8</sup> respectively.

As noted above, the coefficients  $\nu_j$ , which encapsulate the properties of the autocorrelation function, are functions of the moments

$$m_j = \int_{-\infty}^{\infty} d\omega \omega^j \frac{S(\mathbf{k}, \omega)}{S(\mathbf{k})}, \quad (16)$$

where

$$S(\mathbf{k}) = nG_{\mathbf{k}}(0) \quad (17)$$

is the liquid structure factor. Explicitly, they are given by<sup>14,15</sup>

$$\nu_j = D_{j+1} D_{j-1} / D_j^2, \quad (18)$$

$$D_j \equiv \begin{vmatrix} 1 & m_1 & \cdots & m_j \\ m_1 & m_2 & \cdots & m_{j+1} \\ \cdots & \cdots & \cdots & \cdots \\ m_j & m_{j+1} & \cdots & m_{2j} \end{vmatrix}. \quad (19)$$

Since the odd moments vanish, we have in particular

$$\nu_0 = m_2, \quad (20)$$

$$\nu_1 = (m_4 - m_2^2) / m_2. \quad (21)$$

The moments  $m_2$  and  $m_4$  have been evaluated by de Gennes<sup>16</sup> and can be computed from a knowledge of the intermolecular potential  $\phi(r)$  and the pair correlation function  $g(r)$ . These expressions yield for the first two  $\nu_j$  coefficients

$$\nu_0 = k^2/\beta m S(k), \tag{22}$$

$$\nu_1 = 3k^2/\beta m - k^2/\beta m S(\mathbf{k}) + (n/m) \int d\mathbf{r} g(\mathbf{r}) (1 - \cos \mathbf{k} \cdot \mathbf{r}) (\hat{k} \cdot \nabla)^2 \phi(\mathbf{r}), \tag{23}$$

where  $\hat{k}$  is a unit vector in the direction of  $\mathbf{k}$ . In the same manner, the corresponding coefficients for the "self"-motion are found to be

$$\nu_0^s = k^2/\beta m, \tag{24}$$

$$\nu_1^s = 2k^2/\beta m + (n/m) \int d\mathbf{r} g(\mathbf{r}) (\hat{k} \cdot \nabla)^2 \phi(\mathbf{r}). \tag{25}$$

For large  $k$ , the interference terms cancel and we have, in this limit,

$$\nu_j \rightarrow \nu_j^s, \tag{26}$$

thus making the replacements in Eqs. (8) discussed above appropriate at large  $k$ . What makes the resulting sequence [Eqs. (15)] more interesting, however, is the reasonable conjecture that the value of  $k$  at which the replacement becomes valid grows smaller as the index  $j$  increases; that is, that (26) represents an asymptotic relation in  $j$  for a given  $k$ . This appears so because the integrands of higher moments will involve higher derivatives of  $\phi(r)$  or multiparticle correlation functions or both, leading to weaker, longer-ranged integrands for the interference terms and hence shorter-ranged Fourier transforms. Such behavior is verified by numerical calculation in the case of  $\nu_0 - \nu_0^s$  and  $\nu_1 - \nu_1^s$ .<sup>6</sup> Furthermore, each successive member of the sequence evidently incorporates correctly one more even moment of  $S(\mathbf{k}, \omega)$ . These considerations then ensure that Eqs. (15) are an *improving* sequence of approximations.

### III. RELATION BETWEEN TRANSPORT COEFFICIENTS

Following Gyorffy and March,<sup>10</sup> we note that an assumed relation between scattering functions  $S(\mathbf{k}, \omega)$  and  $S^s(\mathbf{k}, \omega)$  may imply, through the Kubo relations,

$$D = \pi \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \omega^2 S^s(\mathbf{k}, \omega) / k^2, \tag{27}$$

$$\Gamma = \pi \beta m^2 n \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \omega^4 S(\mathbf{k}, \omega) / k^4, \tag{28}$$

a relation between the diffusion constant  $D$  and the longitudinal viscosity coefficient,

$$\Gamma = \frac{4}{3} \eta + \zeta, \tag{29}$$

where  $\eta$  and  $\zeta$  are the shear and bulk viscosities, respectively. In this section, we examine in particular the implication of the third approximation, Eq. (15c),

in this respect. Since we deal only with  $\hat{G}_k^{(2)}(z)$ , we shall omit the superscript.

Using Eq. (11), we obtain from the third approximation a relation between coherent and incoherent scattering functions,

$$S(\mathbf{k}, \omega) = \frac{n G_k(0)}{\pi} \times \frac{\nu_0 \nu_0^s \nu_1 \nu_1^s G_k^s(0) G_k^{s'}(\omega)}{[A_k(\omega) G_k^s(0) - \omega B_k(\omega) G_k^{s''}(\omega)]^2 + [\omega B_k(\omega) G_k^{s'}(\omega)]^2}, \tag{30}$$

where

$$A_k(\omega) = \nu_0 \nu_1^s + (\nu_1 - \nu_1^s) \omega^2, \tag{31}$$

$$B_k(\omega) = \nu_0^s \nu_1 - A_k(\omega), \tag{32}$$

and where we have put

$$\hat{G}_k^s(i\omega) = G_k^s(\omega) + i G_k^{s''}(\omega). \tag{33}$$

The real part  $G_k^s(\omega)$  is of course just  $\pi S^s(\mathbf{k}, \omega) / n$ .

We now proceed to obtain the  $k \rightarrow 0$  limit of  $S(\mathbf{k}, \omega) / k^4$ . To do so, it is convenient to first rewrite Eq. (30) in terms of

$$F_k(t) = -\beta m n \ddot{G}_k^s(t), \tag{34}$$

for which the Laplace transform is

$$\hat{F}_k(z) = \beta m n [z G_k^s(0) - z^2 \hat{G}_k^s(z)]. \tag{35}$$

It follows therefore that the real and imaginary parts of  $\hat{F}_k(i\omega)$  are related to those of  $\hat{G}_k^s(i\omega)$  by

$$F_k'(\omega) = \beta m n \omega^2 G_k^{s'}(\omega), \tag{36}$$

$$F_k''(\omega) = \beta m n [\omega^2 G_k^{s''}(\omega) + \omega G_k^s(0)]. \tag{37}$$

These relations are now used to eliminate  $G_k^{s'}(\omega)$  and  $G_k^{s''}(\omega)$  in (30). The result is

$$\frac{\omega^4}{k^4} S(\mathbf{k}, \omega) = \frac{\omega^4}{\pi \beta m} \times \frac{k^{-2} \nu_1 \nu_1^s k^{-2} F_k'(\omega)}{[\nu_1 \omega - B_k(\omega) k^{-2} F_k''(\omega)]^2 + [B_k(\omega) k^{-2} F_k'(\omega)]^2}, \tag{38}$$

where we have used (17), (22), (24), and  $G_k^s(0) = n^{-1}$  to further simplify this expression. The following limits for vanishing  $k$  are easily demonstrated:

$$\lim_{k \rightarrow 0} (\nu_1 \nu_1^s / k^2) = n I_0 I_1 / (\beta m)^2, \tag{39}$$

$$\lim_{k \rightarrow 0} \nu_1 = 0, \tag{40}$$

$$\lim_{k \rightarrow 0} B_k(\omega) = n \omega^2 I_0 / \beta m, \tag{41}$$

$$\lim_{k \rightarrow 0} F_k'(\omega) / k^2 = \psi'(\omega) = \pi \tilde{\psi}(\omega), \tag{42}$$

$$\lim_{k \rightarrow 0} \frac{F_k''(\omega)}{k^2} = \psi''(\omega) = \mathcal{P} \int_{-\infty}^{\infty} \frac{\tilde{\psi}(\omega')}{\omega' - \omega} d\omega', \tag{43}$$

where

$$I_0 \equiv \int d\mathbf{r} g(\mathbf{r}) \partial^2 \beta \phi(\mathbf{r}) / \partial z^2, \quad (44)$$

$$I_1 \equiv 2 + nC_0 + \frac{1}{2} n \int d\mathbf{r} g(\mathbf{r}) z^2 \partial^2 \beta \phi(\mathbf{r}) / \partial z^2, \quad (45)$$

$$\tilde{\psi}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \psi(t), \quad (46)$$

and where

$$\psi(t) = \beta m \langle v_1^z(0) v_1^z(t) \rangle \quad (47)$$

is the normalized velocity autocorrelation function. As usual,  $\psi'(\omega)$  and  $\psi''(\omega)$  are the real and imaginary parts of the Laplace transform  $\hat{\psi}(i\omega)$ ; the last equality in (43) follows from the Kramers-Kronig relation between these parts. The quantity  $C_0$  in (45) is the vanishing  $k$  limit of the Fourier transform  $C_k$  of the direct correlation function. In these expressions, we have taken the direction of  $\mathbf{k}$  as defining the  $z$  axis.

With these results, it is evident that

$$\lim_{k \rightarrow 0} \frac{\omega^4}{k^4} S(\mathbf{k}, \omega) = \frac{I_1}{\pi^2 \beta m n I_0} \times \tilde{\psi}(\omega) / \left[ \left( \pi^{-1} \mathcal{P} \int_{-\infty}^{\infty} \frac{\tilde{\psi}(\omega')}{\omega' - \omega} d\omega' \right)^2 + [\tilde{\psi}(\omega)]^2 \right] = \tilde{Q}(\omega) / m^2 n. \quad (48)$$

The second equality in (48) introduces the time Fourier transform of the longitudinal stress correlation function<sup>17</sup>

$$Q(t) = V^{-1} \langle \sigma'^{zz}(0) \sigma'^{zz}(t) \rangle, \quad (49)$$

where  $\sigma'^{\alpha\beta}$  is the fluctuating part of

$$\sigma^{\alpha\beta} = m \sum v_j^\alpha v_j^\beta - \frac{1}{2} \sum_{i,j}' (r_{ij}^\alpha r_{ij}^\beta / r_{ij}) \phi'(r_{ij}). \quad (50)$$

Thus we have, in passing, found a relationship between this function and the velocity autocorrelation function, namely,

$$\tilde{Q}(\omega) = \frac{m I_1}{\pi^2 \beta I_0} \times \tilde{\psi}(\omega) / \left[ \left( \pi^{-1} \mathcal{P} \int_{-\infty}^{\infty} \frac{\tilde{\psi}(\omega')}{\omega' - \omega} d\omega' \right)^2 + [\tilde{\psi}(\omega)]^2 \right], \quad (51)$$

which is implied by the approximation for  $\hat{G}_k^{(2)}(z)$ .

Finally, the transport coefficients  $D$  and  $\Gamma$  are now obtained in the vanishing  $\omega$  limit as

$$D = (\pi / \beta m) \lim_{\omega \rightarrow 0} \tilde{\psi}(\omega), \quad (52)$$

$$\Gamma = \pi \beta \lim_{\omega \rightarrow 0} \tilde{Q}(\omega). \quad (53)$$

Since the imaginary part  $\psi''(\omega)$  vanishes at  $\omega=0$ , we get finally from (51)

$$\Gamma = I_1 / \beta I_0 D = k_B T / a_0 D, \quad (54)$$

where

$$a_0 \equiv I_0 / I_1 \quad (55)$$

is a density and temperature dependent length.

Equation (54) is the relationship between transport coefficients  $\Gamma$  and  $D$  implied by Eq. (15c). It resembles equations derived elsewhere<sup>18-20</sup> by quite different methods, in that the two coefficients are inversely proportional with a proportionality constant essentially linear in temperature, though it must be pointed out that previous theories relate the diffusion constant to the shear viscosity  $\eta$  alone. (An exception<sup>10</sup> to this is the Hubbard-Beeby theory.<sup>21</sup>) Nevertheless, this feature does not seem to be a serious limitation to any testing of (54), in that experimental results have recently been obtained relating the shear and bulk viscosities for certain liquids and temperatures.<sup>22-24</sup> With such a relationship and experimental data relating  $D$  and  $\eta$ , quantitative tests of Eq. (54) could be performed.

In conclusion, we have found that the third member [Eq. (15c)] of the approximation sequence obtained in Sec. II yields a qualitatively correct relation between transport coefficients, as well as an untested relation between the autocorrelation functions of velocity and longitudinal stress. This was not the case for the two lower-order approximations.<sup>10</sup> In this sense, the third member can be said to constitute a significant improvement over the two previous ones.

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