

## Mode-coupling theory for molecular liquids based on the interaction-site model

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We develop a microscopic theory for dynamics of molecular liquids that is based on the interaction-site model for polyatomic fluids, the projection-operator formalism of Zwanzig and Mori, and the mode-coupling theory. Closed nonlinear equations are derived for a self-consistent treatment of density propagation in a classical polyatomic liquid, which enable one to calculate dynamic structure factors provided the equilibrium structure functions of liquids are known. [S1063-651X(98)04911-3]

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### I. INTRODUCTION

In a recent paper [1], hereafter referred to as paper I, we presented a microscopic theory for dynamics of polyatomic fluids based on the projection-operator formalism of Zwanzig and Mori [2–4] and on the interaction-site model for molecular liquids [5,6]. An approximation scheme is developed for memory functions appearing in the generalized Langevin equation by assuming an exponential form for memory kernels and by extending the method of Lovesey for monatomic liquids [7,8] to polyatomic fluids. Numerical results were obtained for collective and single-particle site-site density correlation functions and longitudinal current spectra of a model diatomic liquid. We also discussed how the longitudinal current spectra, the wave-vector-dependent density of states of the system, can be interpreted in terms of collective excitations that originate from the translational and rotational motions of constituent molecules.

Although a number of essential features concerning dynamics of molecular liquids can be well captured by our theory of paper I, an intense investigation through experimental, theoretical, and molecular-dynamics simulation studies for simple liquids has revealed that the microscopic processes underlying various time-dependent phenomena cannot be fully accounted for by a simplified memory-function approach [9–11]. In particular, the assumption that the decay of memory kernels is ruled by a simple exponential-type relaxation must be significantly revised in view of the results of the kinetic framework developed for dense liquids [12–20]. This motivated us to further improve the theory for dynamics of polyatomic fluids presented in paper I.

In the kinetic framework based on the phase-space description, it has been shown that memory functions generally consist of their fast and slow portions: the fast portion is due to the rapidly decaying “binary collision” contributions, whereas the slow portion stems from correlated collisional effects. The “slowness” of the latter is based on the notion that any correlation effect between collisions, which is expected to appear at high-density liquids, requires some finite time to build up. Since a proper treatment of correlated col-

lisional effects is important in describing the dense-liquid dynamics, the primary interest in this framework is put on the slow portion of memory functions.

In the formulation of the slow portion of memory kernels, the concept of “couplings to relevant decay channels” has played a major role [19,20]. Typically, the relevant decay channels are provided by a bilinear mode combination of quasiconserved (or hydrodynamic) variables, and memory kernels are expressed as a superposition of nonlinear mode contributions. Another important feature in this context is that the memory functions for some dynamical quantities that we wish to determine depend on the same dynamical quantities: the overall framework has the structure of a self-consistent approach, and it enables one to calculate time-correlation functions provided the equilibrium structure functions of liquids are known.

It is well established that the functional form for the slow portion of memory functions can be obtained also by a direct mode-coupling approach [9–11]. In view of this, we develop in the present paper a mode-coupling theory for molecular liquids based on the interaction-site model so that an important contribution from the slow portion of memory kernels can be incorporated in describing the dynamics of polyatomic fluids. However, since we do not attempt to make the full phase-space description based on the phase-space density, and since memory kernels obtained from the direct mode-coupling approach are valid only in the long-time region, we have to separately treat the fast portion of memory kernels so that the short-time regime can also be adequately described. This will be done by exploiting the “frequency sum rules,” and the fast and slow portions of memory kernels will be connected according to the prescription by Sjögren [19,20].

The rest of the paper is organized as follows. In the following section, after giving basic definitions, the generalized Langevin equations for collective and single-particle site-site density correlation functions are presented based on the projection-operator formalism of Zwanzig and Mori and on the interaction-site model for molecular liquids. A formal definition of memory kernels is given in terms of projected random forces. In Sec. III, we develop an approximation scheme for memory kernels of molecular liquids based on the frequency sum rules and on the mode-coupling approach. This provides closed nonlinear equations for a self-consistent

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treatment of density propagation in polyatomic fluids. Section IV concludes the paper. Some rather technical details in evaluating memory kernels under the mode-coupling approach are given in Appendixes A and B.

## II. GENERALIZED LANGEVIN EQUATIONS

In this section, generalized Langevin equations (GLE's) for density-correlation functions are presented based on the interaction-site representation of a molecular liquid. Throughout the paper, we consider a homogeneous and isotropic fluid comprised of  $N$  molecules in a volume  $V$  at the inverse temperature  $\beta=1/k_B T$ , and the thermodynamic limit with density  $\rho=N/V$  is implied.

### A. Basic definitions

We begin with the definition of two basic dynamical variables  $\delta\rho$  and  $\mathbf{j}$ .  $\delta\rho$  is a row vector whose component is a local density of atom (site)  $\alpha$  at time  $t$  in Fourier  $k$  space,

$$\delta\rho_\alpha(\mathbf{k},t) \equiv \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i^\alpha(t)}, \quad (1)$$

where  $\mathbf{r}_i^\alpha(t)$  specifies the location of  $\alpha$  atom in the  $i$ th molecule at time  $t$ . Hereafter, the Greek subscripts and superscripts refer to the interaction sites of a molecule and the roman letters label the molecules unless specified otherwise.  $\mathbf{j}$  is a row vector of which each component is a longitudinal current density,

$$j_\alpha(\mathbf{k},t) \equiv \sum_i v_{i,z}^\alpha(t) e^{i\mathbf{k}\cdot\mathbf{r}_i^\alpha(t)}, \quad (2)$$

where the wave vector  $\mathbf{k}$  is chosen such that it is along the  $z$  axis of the space-fixed laboratory frame, and  $v_{i,z}^\alpha(t)$  denotes  $z$  component of the velocity of  $\alpha$  atom in the  $i$ th molecule at time  $t$ . These two vectors satisfy the following continuity equation:

$$\delta\dot{\rho}(\mathbf{k},t) = ik\mathbf{j}(\mathbf{k},t), \quad (3)$$

where the dot denotes the time derivative.

The site-site intermediate scattering function matrix is defined in terms of  $\delta\rho$  as

$$\mathbf{F}(k,t) \equiv (\delta\rho(\mathbf{k}), \delta\rho(\mathbf{k},t)). \quad (4)$$

(The absence of any indication for time  $t$  in a dynamical variable means that the latter is evaluated at  $t=0$ .) Here the inner product of two row vectors  $\mathbf{A}_1$  and  $\mathbf{A}_2$  is defined as the canonical ensemble average,

$$(\mathbf{A}_1, \mathbf{A}_2) \equiv \frac{1}{N} \langle \mathbf{A}_1^\dagger \mathbf{A}_2 \rangle, \quad (5)$$

where  $\mathbf{A}_1^\dagger$  denotes a column vector adjoint to  $\mathbf{A}_1$ , and the factor  $1/N$  is a matter of convention. Similarly, we define the matrix of the site-site longitudinal current correlation functions by

$$\mathbf{J}(k,t) = (\mathbf{j}(\mathbf{k}), \mathbf{j}(\mathbf{k},t)). \quad (6)$$

The matrices of the site-site dynamic structure factors and the longitudinal current spectra are respectively defined as the time Fourier transforms of the corresponding time-correlation functions:

$$\mathbf{S}(k,\omega) \equiv \int_{-\infty}^{\infty} dt e^{i\omega t} \mathbf{F}(k,t), \quad (7)$$

$$\mathbf{C}_L(k,\omega) \equiv \int_{-\infty}^{\infty} dt e^{i\omega t} \mathbf{J}(k,t). \quad (8)$$

The continuity equation, Eq. (3), implies that these two matrices are connected through the relation

$$\mathbf{C}_L(k,\omega) = \frac{\omega^2}{k^2} \mathbf{S}(k,\omega). \quad (9)$$

The initial value of  $\mathbf{F}(k,t)$  is the matrix of the site-site static structure factors

$$\mathbf{F}(k,0) \equiv \boldsymbol{\chi}(k) = \mathbf{w}(k) + \rho\mathbf{h}(k), \quad (10)$$

where  $\mathbf{w}(k)$  and  $\mathbf{h}(k)$  are the intramolecular and intermolecular total correlation function matrices defined by

$$w_{\alpha\beta}(k) \equiv \frac{1}{N} \left\langle \sum_i e^{-i\mathbf{k}\cdot\mathbf{r}_i^\alpha} e^{i\mathbf{k}\cdot\mathbf{r}_i^\beta} \right\rangle, \quad (11)$$

$$\rho h_{\alpha\beta}(k) \equiv \frac{1}{N} \left\langle \sum_i \sum_{j \neq i} e^{-i\mathbf{k}\cdot\mathbf{r}_i^\alpha} e^{i\mathbf{k}\cdot\mathbf{r}_j^\beta} \right\rangle. \quad (12)$$

Equation (11) can be further decomposed into

$$w_{\alpha\beta}(k) = \delta_{\alpha\beta} + (1 - \delta_{\alpha\beta}) s_{\alpha\beta}(k), \quad (13)$$

and for a rigid molecule,  $s_{\alpha\beta}(k)$  takes the form

$$s_{\alpha\beta}(k) = j_0(kl_{\alpha\beta}), \quad (14)$$

where  $j_0(x)$  is the zeroth-order spherical Bessel function and  $l_{\alpha\beta}$  denotes the ‘‘bond’’ length between  $\alpha$  and  $\beta$  sites. The inverse of the matrix  $\boldsymbol{\chi}(k)$ , which is required later, can be related to the matrix of the site-site direct correlation functions  $\mathbf{c}(k)$ , based on the reference interaction-site model (RISM) equation (often referred to as the site-site Ornstein-Zernike equation) [5,6],

$$\mathbf{h}(k) = \mathbf{w}(k)\mathbf{c}(k)\mathbf{w}(k) + \mathbf{w}(k)\mathbf{c}(k)\rho\mathbf{h}(k), \quad (15)$$

and is given by

$$\boldsymbol{\chi}^{-1}(k) = \mathbf{w}^{-1}(k) - \rho\mathbf{c}(k). \quad (16)$$

The initial value of  $\mathbf{J}(k,t)$  can be discussed as follows. Having assumed the molecule to be rigid, the velocity of  $\alpha$  atom consists of translational and rotational contributions:

$$v_{i,z}^\alpha = v_{i,z}^C + [\boldsymbol{\omega}_i \times \delta\mathbf{r}_i^{C\alpha}]_z, \quad (17)$$

where  $v_{i,z}^C$  represents  $z$  component of the center-of-mass velocity of the  $i$ th molecule,  $\boldsymbol{\omega}_i$  its angular velocity, and  $\delta\mathbf{r}_i^{C\alpha}$  the vector joining the center-of-mass and  $\alpha$  atom. Due to the

statistical independence of translational and rotational velocities at the same time, the initial value of  $\mathbf{J}(k, t)$  has a generic form [1,21,22]

$$\mathbf{J}(k, 0) \equiv \mathbf{J}(k) = \mathbf{J}^{\text{trans}}(k) + \mathbf{J}^{\text{rot}}(k). \quad (18)$$

It is readily accomplished to evaluate elements of  $\mathbf{J}^{\text{trans}}(k)$ , due to the statistical independence of the translational velocities and coordinates:

$$J_{\alpha\beta}^{\text{trans}}(k) = \frac{k_B T}{M} w_{\alpha\beta}(k), \quad (19)$$

where  $M$  denotes the total mass of the molecule and we have used Eq. (11). Elements of  $\mathbf{J}^{\text{rot}}(k)$ , on the other hand, depend on the molecular model. It is rather straightforward to obtain elements of  $\mathbf{J}^{\text{rot}}(k)$  having a definite molecular model, and those for a water molecule [21,22] and a diatomic molecule [1] have been presented elsewhere.

### B. GLE for collective density correlation function

Combining our primary dynamical variables  $\delta\rho$  and  $\mathbf{j}$  to form a new row vector

$$\mathbf{C}(\mathbf{k}, t) \equiv (\delta\rho(\mathbf{k}, t) \quad \mathbf{j}(\mathbf{k}, t)), \quad (20)$$

we introduce the following projection operator  $\mathcal{P}$ , which acts on a row vector  $\mathbf{X}$ :

$$\mathcal{P}\mathbf{X} \equiv \mathbf{C}(\mathbf{C}, \mathbf{C})^{-1}(\mathbf{C}, \mathbf{X}). \quad (21)$$

The standard procedure of the Zwanzig-Mori formalism leads to the following GLE in the time domain [9–11,23]:

$$\ddot{\mathbf{F}}(\mathbf{k}, t) + \langle \omega_k^2 \rangle \mathbf{F}(\mathbf{k}, t) + \int_0^t d\tau \mathbf{K}(\mathbf{k}, t - \tau) \dot{\mathbf{F}}(\mathbf{k}, \tau) = \mathbf{0}, \quad (22)$$

where  $\langle \omega_k^2 \rangle$  denotes the normalized second frequency moment matrix of  $\mathbf{S}(k, \omega)$  and is given by [1]

$$\langle \omega_k^2 \rangle = k^2 \mathbf{J}(k) \boldsymbol{\chi}^{-1}(k). \quad (23)$$

For later convenience, we introduce  $\langle \omega_k^n \rangle$ , the normalized  $n$ th frequency moment matrix of  $\mathbf{S}(k, \omega)$ , defined through the following relations:

$$\overline{\omega_k^n} \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \omega^n \mathbf{S}(k, \omega) = (-1)^{n/2} \left[ \frac{d^n}{dt^n} \mathbf{F}(k, t) \right]_{t=0'} \quad (24)$$

$$\langle \omega_k^n \rangle \equiv \overline{\omega_k^n} \left[ \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \mathbf{S}(k, \omega) \right]^{-1} = \overline{\omega_k^n} \boldsymbol{\chi}^{-1}(k), \quad (25)$$

where we have used the inverse relation of Eq. (7) and the definition of  $\boldsymbol{\chi}(k)$ , Eq. (10).  $\mathbf{K}(k, t)$  in Eq. (22) is the memory-function matrix (or simply called the memory kernel) whose formal expression reads

$$\mathbf{K}(k, t) \equiv (\mathbf{R}(k), \exp(i\mathcal{Q}Lt) \mathbf{R}(k)) \mathbf{J}^{-1}(k), \quad (26)$$

where  $\mathcal{Q} \equiv 1 - \mathcal{P}$ , and  $\mathbf{R}(k)$  is the fluctuating random force vector defined by

$$\mathbf{R}(k) \equiv \mathbf{j}(k) - ik \delta\rho(k) \boldsymbol{\chi}^{-1}(k) \mathbf{J}(k). \quad (27)$$

### C. GLE for single-particle density-correlation function

We next consider single-particle counterparts. The term ‘‘particle’’ in this paper refers to one molecule as a whole, and not to an individual atom that constitutes the molecule. Our basic dynamical variables in this case are density and longitudinal current density of an arbitrarily chosen tagged particle,  $\delta\rho^s$  and  $\mathbf{j}^s$ , whose components are respectively given by

$$\delta\rho_\alpha^s(\mathbf{k}, t) = e^{i\mathbf{k} \cdot \mathbf{r}_1^\alpha(t)}, \quad (28)$$

$$j_\alpha^s(\mathbf{k}, t) = v_{1,z}^\alpha(t) e^{i\mathbf{k} \cdot \mathbf{r}_1^\alpha(t)}. \quad (29)$$

The self-part of the site-site intermediate scattering function matrix is defined by

$$\mathbf{F}^s(k, t) \equiv (\delta\rho^s(\mathbf{k}), \delta\rho^s(\mathbf{k}, t))_s, \quad (30)$$

where the inner product in the single-particle variable case is given by

$$(\mathbf{A}_1^s, \mathbf{A}_2^s)_s \equiv \langle \mathbf{A}_1^{s\dagger} \mathbf{A}_2^s \rangle. \quad (31)$$

Note the absence of the factor of  $1/N$  compared to Eq. (5). The initial value of  $\mathbf{F}^s(k, t)$  reads [see Eq. (11)]

$$\mathbf{F}^s(k, 0) = \mathbf{w}(k). \quad (32)$$

The self-part of the site-site dynamic structure factors, also called the incoherent dynamic structure factors,  $S_{\alpha\beta}^s(k, \omega)$ , are defined as the time Fourier transform of  $F_{\alpha\beta}^s(k, t)$  as in Eq. (7). The unnormalized and normalized frequency moment matrices of  $\mathbf{S}^s(k, \omega)$  are also defined as in Eqs. (24) and (25):

$$\overline{\omega_{k,s}^n} \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \omega^n \mathbf{S}^s(k, \omega) = (-1)^{n/2} \left[ \frac{d^n}{dt^n} \mathbf{F}^s(k, t) \right]_{t=0'} \quad (33)$$

$$\langle \omega_{k,s}^n \rangle \equiv \overline{\omega_{k,s}^n} \left[ \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \mathbf{S}^s(k, \omega) \right]^{-1} = \overline{\omega_{k,s}^n} \mathbf{w}^{-1}(k). \quad (34)$$

Finally, GLE for  $\mathbf{F}^s(k, t)$  reads

$$\ddot{\mathbf{F}}^s(k, t) + \langle \omega_{k,s}^2 \rangle \mathbf{F}^s(k, t) + \int_0^t d\tau \mathbf{K}^s(k, t - \tau) \dot{\mathbf{F}}^s(k, \tau) = \mathbf{0}, \quad (35)$$

in which

$$\langle \omega_{k,s}^2 \rangle = k^2 \mathbf{J}(k) \mathbf{w}^{-1}(k), \quad (36)$$

$$\mathbf{K}^s(k, t) = (\mathbf{R}^s(k), \exp(i\mathcal{Q}Lt) \mathbf{R}^s(k))_s \mathbf{J}^{-1}(k), \quad (37)$$

$$\mathbf{R}^s(k) = \mathbf{j}^s(k) - ik \delta\rho^s(k) \mathbf{w}^{-1}(k) \mathbf{J}(k). \quad (38)$$

The appearance of  $\mathbf{J}(k)$ , which is common to the collective variable case, is due to the fact that  $\mathbf{J}(k)$  is essentially a

single-particle quantity since the velocities of different molecules at the same time are statistically independent.

### III. MODE-COUPPLING THEORY

The Zwanzig-Mori formalism that leads to GLE's presented in the last section is, in a sense, merely a formal rephrasing of the equation of motion (Liouville equation) for a dynamical variable, say  $\mathbf{C}(t)$ ,

$$\frac{\partial}{\partial t} \mathbf{C}(t) = i\mathcal{L}\mathbf{C}(t), \quad (39)$$

in a different language, shifting the difficulty in solving dynamical problems to that in evaluating the memory kernel, so the merits of the new formulation may not be apparent at this stage. However, the establishment of the alternative framework is strongly biased by a number of physical arguments, allowing the practical approximation schemes for the memory kernel to solve dynamical problems. The bases of such approximation schemes, which are capable of treating even high-density liquids, were set during the 1970s and the early 1980s by several researchers [12–20], and our argument here is an extension of their work to molecular fluids.

A starting point of our argument is that the memory kernel  $\mathbf{K}(k, t)$  consists of its fast and slow portions:

$$\mathbf{K}(k, t) = \mathbf{K}_{\text{fast}}(k, t) + \mathbf{K}_{\text{slow}}(k, t). \quad (40)$$

The fast portion is due to the rapidly decaying binary collision contributions (associated with fast collisional events), and the slow one stems from correlated collisional effects. We discuss the fast and slow portions of the memory kernel separately in the following. For the treatment of the latter, we employ the mode-coupling approach.

#### A. Fast portion of the memory kernel

It is reasonable to expect that the initial decay of the full memory kernel is dominated by its fast portion. Indeed, it has been shown that at sufficiently short times the effects of nonbinary (slow) contributions are at least of the order  $t^4$  [19,20]. As a result, up to the order of  $t^2$  in the short-time regime, the full and the fast portion of the memory kernel coincide, and the initial decay of the fast portion can be deduced by analyzing the short-time behavior of the full memory kernel.

At sufficiently short times, the full memory kernel  $\mathbf{K}(k, t)$  can be expanded as

$$\begin{aligned} \mathbf{K}(k, t) &= \mathbf{K}(k, 0) + \frac{t^2}{2!} \left[ \frac{d^2}{dt^2} \mathbf{K}(k, t) \right]_{t=0} + \dots \\ &= [\mathbf{I} - t^2 \boldsymbol{\tau}^{-2}(k) + \dots] \mathbf{K}(k, 0), \end{aligned} \quad (41)$$

where only even powers of time appear due to the even character of  $\mathbf{K}(k, t)$ , and we have defined a matrix,

$$\boldsymbol{\tau}^{-2}(k) \equiv -\frac{1}{2} \ddot{\mathbf{K}}(k, 0) \mathbf{K}^{-1}(k, 0). \quad (42)$$

By differentiating Eq. (22) with respect to  $t$  repeatedly and setting  $t=0$ , it follows

$$\mathbf{K}(k, 0) = \langle \boldsymbol{\omega}_k^4 \rangle \langle \boldsymbol{\omega}_k^2 \rangle^{-1} - \langle \boldsymbol{\omega}_k^2 \rangle, \quad (43)$$

$$-\ddot{\mathbf{K}}(k, 0) = \langle \boldsymbol{\omega}_k^6 \rangle \langle \boldsymbol{\omega}_k^2 \rangle^{-1} - (\langle \boldsymbol{\omega}_k^4 \rangle \langle \boldsymbol{\omega}_k^2 \rangle^{-1})^2, \quad (44)$$

in terms of normalized frequency moment matrices defined in Eq. (25).

As mentioned above, up to the order of  $t^2$  in the short-time regime, the full and the fast portion of the memory kernel coincide. This fact is conveniently exploited by assuming that the overall time dependence of the fast portion can be written in terms of the shape function  $g(x)$  that decays rapidly and satisfies  $g(x) \approx 1 - x^2$  for small  $x$ . Often adopted are  $g(x) = \exp(-x^2)$  and  $g(x) = \text{sech}^2(x)$ . Thus, we approximate the fast portion of the memory kernel  $\mathbf{K}(k, t)$  as

$$\mathbf{K}_{\text{fast}}(k, t) \approx g[t\boldsymbol{\tau}^{-1}(k)] \mathbf{K}(k, 0), \quad (45)$$

where the function  $g$  of a matrix is defined in terms of its Taylor-series expansion. If  $\mathbf{U}(k)$  is a matrix that diagonalizes  $\boldsymbol{\tau}^{-2}(k)$ , it follows

$$\mathbf{U}^{-1}(k) \boldsymbol{\tau}^{-2}(k) \mathbf{U}(k) = \text{diag}(\tau_\alpha^{-2}(k)), \quad (46)$$

where  $\tau_\alpha^{-2}(k)$ 's denote the eigenvalues of the matrix  $\boldsymbol{\tau}^{-2}(k)$ , and  $\text{diag}()$  represents a diagonal matrix. Then the fast portion of the memory kernel can be written as

$$\mathbf{K}_{\text{fast}}(k, t) = \mathbf{U}(k) [\text{diag}(g(t/\tau_\alpha(k)))] \mathbf{U}^{-1}(k) \mathbf{K}(k, 0). \quad (47)$$

#### B. Slow portion of the memory kernel

We next investigate the long-lasting tails of the memory kernel exploiting the mode-coupling approach. The basic idea behind the mode-coupling theory is that the fluctuation of a given dynamical variable decays, at intermediate and long times, predominantly into pairs of hydrodynamic modes associated with quasiconserved dynamical variables. The possible ‘‘decay channels’’ of a fluctuation are determined by ‘‘selection rules’’ based, for example, on time-reversal symmetry or on physical considerations.

It is reasonable to expect that the decay of the memory kernel at intermediate and long times is dominated by those mode correlations that have the longest relaxation times. The sluggishness of the structural relaxation processes typical of dense liquids suggests that the slow decay of the memory kernel at long times is basically due to couplings to wave-vector-dependent density modes of the form

$$A_{\lambda\mu}(\mathbf{q}, \mathbf{p}) \equiv \delta\rho_\lambda(\mathbf{q}) \delta\rho_\mu(\mathbf{p}). \quad (48)$$

Then, the slow portion of the memory kernel can be expressed as a sum of products of the wave-vector-dependent density modes provided a decoupling (or factorization) approximation is made (see below).

The simplest way to extract the dominant slow portion of the memory kernel is to introduce another projection operator  $\mathcal{P}_2$  that projects any variable onto the subspace spanned by  $A_{\lambda\mu}(\mathbf{q}, \mathbf{p})$ . Translational invariance of the system implies that the only  $A_{\lambda\mu}(\mathbf{q}, \mathbf{p})$ , whose inner products with a dynamical variable  $X(\mathbf{k})$  are nonzero, are of the form

$$A_{\lambda\mu}(\mathbf{q}, \mathbf{k} - \mathbf{q}) = \delta\rho_\lambda(\mathbf{q}) \delta\rho_\mu(\mathbf{k} - \mathbf{q}), \quad (49)$$

for various  $\mathbf{q}$ 's, and we define the second projection operator  $\mathcal{P}_2$  in terms of  $A_{\lambda\mu}$  as follows:

$$\mathcal{P}_2 X(\mathbf{k}) \equiv \frac{1}{2} \sum_{\mathbf{q}} \sum_{\lambda, \mu, \lambda', \mu'} A_{\lambda\mu} (A_{\lambda\mu}, A_{\lambda'\mu'})^{-1} (A_{\lambda'\mu'}, X(\mathbf{k})), \quad (50)$$

where the factor of  $\frac{1}{2}$  is to avoid the double counting. From here on, in order to simplify the notation,  $A_{\lambda\mu}(\mathbf{q}, \mathbf{k} - \mathbf{q})$  will be simply denoted as  $A_{\lambda\mu}$ , and we shall often adopt the convention of writing the wave vectors as if they were discrete. Conversion prescription to the continuous wave vectors is as follows:

$$\delta_{\mathbf{k}, \mathbf{k}'} \rightarrow \frac{(2\pi)^3}{V} \delta(\mathbf{k} - \mathbf{k}'), \quad (51)$$

$$\sum_{\mathbf{k}} \rightarrow \frac{V}{(2\pi)^3} \int d\mathbf{k}. \quad (52)$$

In Eq. (50), the inverse is defined by

$$\sum_{\lambda', \mu'} (A_{\lambda\mu}, A_{\lambda'\mu'}) (A_{\lambda'\mu'}, A_{\lambda''\mu''})^{-1} = \delta_{\lambda\lambda''} \delta_{\mu\mu''}. \quad (53)$$

It is readily verified that  $\mathcal{P}_2$  defined above is idempotent and Hermitian.

The first approximation of the mode-coupling treatment corresponds to replacing the time-evolution operator  $\exp(iQLt)$  by its projection on the subspace spanned by  $A_{\lambda\mu}$ :

$$\exp(iQLt) \approx \mathcal{P}_2 \exp(iQLt) \mathcal{P}_2. \quad (54)$$

At the same time, the anomalous time-propagator  $\exp(iQLt)$  in the right-hand side is replaced by the conventional one, the final expression being

$$\exp(iQLt) \approx \mathcal{P}_2 \exp(iLt) \mathcal{P}_2. \quad (55)$$

Under these approximations, the memory kernel in Eq. (26) reads

$$\mathbf{K}_{MCT}(k, t) = (\mathcal{P}_2 \mathbf{R}(\mathbf{k}), \exp(iLt) \mathcal{P}_2 \mathbf{R}(\mathbf{k})) \mathbf{J}^{-1}(k). \quad (56)$$

The second approximation usually made in the mode-coupling approach is to assume that the four-variable correlation functions are factorized into products of two-variable correlation functions. For example, the denominator of Eq. (50) reads

$$\begin{aligned} (A_{\lambda\mu}, A_{\lambda'\mu'}) &= \frac{1}{N} \langle \delta\rho_{\lambda}^*(\mathbf{q}) \delta\rho_{\mu}^*(\mathbf{k} - \mathbf{q}) \delta\rho_{\lambda'}(\mathbf{q}) \delta\rho_{\mu'}(\mathbf{k} - \mathbf{q}) \rangle \\ &\approx \frac{1}{N} \langle \delta\rho_{\lambda}^*(\mathbf{q}) \delta\rho_{\lambda'}(\mathbf{q}) \rangle \\ &\quad \times \langle \delta\rho_{\mu}^*(\mathbf{k} - \mathbf{q}) \delta\rho_{\mu'}(\mathbf{k} - \mathbf{q}) \rangle \\ &= N \chi_{\lambda\lambda'}(q) \chi_{\mu\mu'}(k - q), \end{aligned} \quad (57)$$

and it follows from Eq. (53) that

$$(A_{\lambda\mu}, A_{\lambda'\mu'})^{-1} = \frac{1}{N} [\chi^{-1}(q)]_{\lambda\lambda'} [\chi^{-1}(k - q)]_{\mu\mu'}. \quad (58)$$

Now let us evaluate the elements of the memory kernel, Eq. (56). To this end, the explicit expression for the elements of the projected random force,

$$\mathcal{P}_2(\mathbf{R}(\mathbf{k}))_{\alpha} = \mathcal{P}_2(\mathbf{j}(\mathbf{k}))_{\alpha} - ik \mathcal{P}_2(\delta\rho(\mathbf{k}) \chi^{-1}(k) \mathbf{J}(k))_{\alpha}, \quad (59)$$

is required. Evaluation of each term in the above equation is somewhat involved, and it is presented in Appendix B. From the result of Appendix B, it follows [see Eq. (B12)]

$$\begin{aligned} \mathcal{P}_2(\mathbf{R}(\mathbf{k}))_{\alpha} &= -\frac{i\rho}{N} \sum_{\mathbf{q}} \sum_{\lambda, \mu} q_z [wc(q)]_{\mu\lambda} J_{\alpha\mu}(k) \delta\rho_{\lambda}(\mathbf{q}) \delta\rho_{\mu}(\mathbf{k} - \mathbf{q}), \end{aligned} \quad (60)$$

where we have introduced

$$[wc(q)]_{\lambda\mu} \equiv \sum_{\sigma} w_{\lambda\sigma}(q) c_{\sigma\mu}(q). \quad (61)$$

By substituting Eq. (60) into Eq. (56) and noting that

$$\begin{aligned} \langle \delta\rho_{\lambda}^*(\mathbf{q}) \delta\rho_{\mu}^*(\mathbf{k} - \mathbf{q}) \delta\rho_{\lambda'}(\mathbf{q}', t) \delta\rho_{\mu'}(\mathbf{k} - \mathbf{q}', t) \rangle \\ \approx N^2 F_{\lambda\lambda'}(q, t) F_{\mu\mu'}(k - q, t) \delta_{\mathbf{q}, \mathbf{q}'} \\ + N^2 F_{\lambda\mu'}(q, t) F_{\mu\lambda'}(k - q, t) \delta_{\mathbf{q}, \mathbf{k} - \mathbf{q}'}, \end{aligned} \quad (62)$$

under the factorization approximation, one obtains the following memory kernel:

$$\begin{aligned} [K_{MCT}(k, t)]_{\alpha\beta} &= \frac{\rho}{(2\pi)^3} \sum_{\lambda, \mu, \nu} \int d\mathbf{q} \{ q_z^2 [wc(q)]_{\lambda\mu} [wc(q)]_{\beta\nu} \\ &\quad \times F_{\mu\nu}(q, t) F_{\lambda\beta}(k - q, t) + q_z(k - q_z) \\ &\quad \times [wc(q)]_{\lambda\mu} [wc(k - q)]_{\beta\nu} F_{\mu\beta}(q, t) \\ &\quad \times F_{\lambda\nu}(k - q, t) \} J_{\alpha\lambda}(k), \end{aligned} \quad (63)$$

where we have renamed dummy indices for convenience. In an appropriate limit, this expression for molecular liquids reduces to that for mixtures of simple liquids [24–26].

At this point, it may be tempting to identify the mode-coupling contribution given by Eq. (63) with the slow portion of the full memory kernel. However, as mentioned earlier, the slow portion should evolve at the order of  $t^4$  in the short-time regime, and we have to manipulate Eq. (63) in order to guarantee this feature: this is exactly the extra price we should pay due to the abandonment of the full phase-space description. Following the work of Sjögren [19,20], we introduce the following auxiliary function:

$$f_{\alpha\beta}(k, t) \equiv \frac{F_{\alpha\beta}^0(k, t)}{F_{\alpha\beta}^s(k, t)}, \quad (64)$$

where  $F_{\alpha\beta}^0(k,t)$  denotes an element of the following intermediate scattering function matrix:

$$\mathbf{F}^0(k,t) \equiv \exp[-\frac{1}{2}\langle \omega_{k,s}^2 \rangle t^2] \mathbf{w}(k). \quad (65)$$

This intermediate scattering function matrix is essentially that of a noninteracting molecule. It is readily verified that  $F^0(k,t)$  and  $\mathbf{F}^s(k,t)$  coincide up to the order of  $t^2$  in the short-time regime by construction. It is also obvious that the former decays more rapidly than the latter, which has the long-lasting portion (see below). Thus, the auxiliary function defined in Eq. (64) satisfies the following relations:

$$f_{\alpha\beta}(k,t) = 1 \quad (\text{up to the order of } t^2 \text{ for } t \ll 1), \quad (66)$$

$$\lim_{t \rightarrow \infty} f_{\alpha\beta}(k,t) = 0. \quad (67)$$

It should be also noticed that  $f_{\alpha\beta}(k,t)$  is symmetric since  $F_{\alpha\beta}^0(k,t)$  and  $F_{\alpha\beta}^s(k,t)$  are symmetric matrices. By inserting this auxiliary function into Eq. (63) according to Sjögren's prescription, we eventually obtain the slow portion of the memory kernel that evolves at the order of  $t^4$  in the short-time regime:

$$\begin{aligned} & [K_{\text{slow}}(k,t)]_{\alpha\beta} \\ &= \frac{\rho}{(2\pi)^3} \sum_{\lambda,\mu,\nu} \int d\mathbf{q} \{ q_z^2 [wc(q)]_{\lambda\mu} [wc(q)]_{\beta\nu} \\ & \quad \times [1 - f_{\mu\nu}(q,t) f_{\lambda\beta}(k-q,t)] F_{\mu\nu}(q,t) F_{\lambda\beta}(k-q,t) \\ & \quad + q_z(k-q_z) [wc(q)]_{\lambda\mu} [wc(k-q)]_{\beta\nu} \\ & \quad \times [1 - f_{\mu\beta}(q,t) f_{\lambda\nu}(k-q,t)] \\ & \quad \times F_{\mu\beta}(q,t) F_{\lambda\nu}(k-q,t) \} J_{\alpha\lambda}(k). \end{aligned} \quad (68)$$

Numerical results for  $\mathbf{F}(k,t)$  can be obtained self-consistently by solving Eqs. (22), (40), (47), and (68), provided the equilibrium structure functions of liquids are known.

### C. Single-particle variable case

The single-particle counterpart can be obtained by a similar procedure. The fast portion of the memory kernel  $\mathbf{K}^s(k,t)$  reads

$$\mathbf{K}_{\text{fast}}^s(k,t) = \mathbf{U}_s(k) [\text{diag}(g(t/\tau_{s,\alpha}(k)))] \mathbf{U}_s^{-1}(k) \mathbf{K}^s(k,0). \quad (69)$$

In the above equation,  $\tau_{s,\alpha}^{-2}(k)$ 's are the eigenvalues of the matrix  $\boldsymbol{\tau}_s^{-2}(k)$  defined by

$$\boldsymbol{\tau}_s^{-2}(k) \equiv -\frac{1}{2} \ddot{\mathbf{K}}^s(k,0) [\mathbf{K}^s(k,0)]^{-1}, \quad (70)$$

and  $\mathbf{U}_s(k)$  is a matrix that diagonalizes  $\boldsymbol{\tau}_s^{-2}(k)$ . The matrices appearing in the right-hand side of Eq. (70) can be expressed, as in Eqs. (43) and (44), as

$$\mathbf{K}^s(k,0) = \langle \omega_{k,s}^4 \rangle \langle \omega_{k,s}^2 \rangle^{-1} - \langle \omega_{k,s}^2 \rangle, \quad (71)$$

$$-\ddot{\mathbf{K}}^s(k,0) = \langle \omega_{k,s}^6 \rangle \langle \omega_{k,s}^2 \rangle^{-1} - (\langle \omega_{k,s}^4 \rangle \langle \omega_{k,s}^2 \rangle^{-1})^2, \quad (72)$$

in terms of the normalized frequency moment matrices of  $\mathbf{S}^s(k,w)$  defined in Eq. (34).

To obtain the slow portion of  $\mathbf{K}^s(k,t)$ , we introduce the following second projection operator for the single-particle variable case:

$$\mathcal{P}_2^s X(\mathbf{k}) \equiv \sum_{\mathbf{q}} \sum_{\lambda,\mu,\lambda',\mu'} A_{\lambda\mu}^s (A_{\lambda\mu}^s, A_{\lambda'\mu'}^s)_s^{-1} (A_{\lambda'\mu'}^s, X(\mathbf{k}))_s, \quad (73)$$

where  $A_{\lambda\mu}^s$  is defined by

$$A_{\lambda\mu}^s \equiv \delta\rho_\lambda^s(\mathbf{q}) \delta\rho_\mu^s(\mathbf{k}-\mathbf{q}). \quad (74)$$

Note the absence of the factor  $\frac{1}{2}$  in the above equation compared to Eq. (50). The inverse  $(A_{\lambda\mu}^s, A_{\lambda'\mu'}^s)_s^{-1}$  is defined similarly to Eq. (53), and in the present case, it follows under the factorization approximation that

$$(A_{\lambda\mu}^s, A_{\lambda'\mu'}^s)_s^{-1} = \frac{1}{N} [w^{-1}(q)]_{\lambda\lambda'} [\chi^{-1}(k-q)]_{\mu\mu'}. \quad (75)$$

Using the projection operator  $\mathcal{P}_2^s$ , the memory kernel reads, as in Eq. (56),

$$\mathbf{K}_{MCT}^s(k,t) = (\mathcal{P}_2^s \mathbf{R}^s(\mathbf{k}), \exp(i\mathcal{L}t) \mathcal{P}_2^s \mathbf{R}^s(\mathbf{k}))_s \mathbf{J}^{-1}(k). \quad (76)$$

The evaluation of the elements of the projected random force  $\mathcal{P}_2^s(\mathbf{R}^s(k))_\alpha$  can be performed by a similar procedure to that employed in Appendix B, the final result being

$$\begin{aligned} \mathcal{P}_2^s(\mathbf{R}^s(\mathbf{k}))_\alpha &= -\frac{i\rho}{N} \sum_{\mathbf{q}} \sum_{\lambda,\mu} (k-q_z) [wc(k-q)]_{\lambda\mu} \\ & \quad \times J_{\alpha\lambda}(k) \delta\rho_\lambda^s(\mathbf{q}) \delta\rho_\mu^s(\mathbf{k}-\mathbf{q}). \end{aligned} \quad (77)$$

By substituting this equation into Eq. (76) and adopting the factorization approximation for four-variable correlation functions, one obtains the following memory kernel under the mode-coupling approach:

$$\begin{aligned} [K_{MCT}^s(k,t)]_{\alpha\beta} &= \frac{\rho}{(2\pi)^3} \sum_{\lambda,\mu,\nu} \int d\mathbf{q} (k-q_z)^2 [wc(k-q)]_{\lambda\mu} \\ & \quad \times [wc(k-q)]_{\beta\nu} F_{\lambda\beta}^s(q,t) \\ & \quad \times F_{\mu\nu}(k-q,t) J_{\alpha\lambda}(k). \end{aligned} \quad (78)$$

In order to obtain the slow portion of the memory kernel, which evolves at the order of  $t^4$  in the short-time regime, we manipulate this expression as in Eq. (68) using the same auxiliary function defined by Eq. (64):

$$\begin{aligned} & [K_{\text{slow}}^s(k,t)]_{\alpha\beta} \\ &= \frac{\rho}{(2\pi)^3} \sum_{\lambda,\mu,\nu} \int d\mathbf{q} (k-q_z)^2 [wc(k-q)]_{\lambda\mu} \\ & \quad \times [wc(k-q)]_{\beta\nu} [1 - f_{\lambda\beta}(q,t) f_{\mu\nu}(k-q,t)] F_{\lambda\beta}^s(q,t) \\ & \quad \times F_{\mu\nu}(k-q,t) J_{\alpha\lambda}(k). \end{aligned} \quad (79)$$

Numerical results for the single-particle  $\mathbf{F}^s(k, t)$  can be obtained self-consistently by solving Eqs. (35), (40), (69), and (79).

#### IV. CONCLUDING REMARKS

In this paper, we derived closed nonlinear equations for a self-consistent treatment of density propagation in a classical polyatomic liquid based on the projection-operator formalism of Zwanzig and Mori and on the mode-coupling theory. A distinctive feature of our formulation is that it is based on the interaction-site model for molecular liquids, and is capable of treating the general class of polyatomic fluids without too much difficulty. This is in contrast to other theories for dynamics of molecular liquids based on the rotational-invariant expansions [27,28], in which theories become much more complicated when there is no symmetry in a molecule.

Numerical results for  $\mathbf{F}(k, t)$  can be obtained by solving Eqs. (22), (40), (47), and (68), and corresponding results for the self part can be evaluated similarly. We have calculated site-site intermediate scattering functions, longitudinal current spectra, velocity autocorrelation functions and their spectra for model diatomic liquid based on the present formulation, and found fairly good agreement with molecular-dynamics simulation results. These calculations will be reported in a forthcoming paper.

Although our primary aim in the present paper is to develop a molecular theory for dynamics of the ordinary liquid state, our formalism based on the mode-coupling theory can also be used to investigate the nature of the supercooled state and the glass transition of molecular liquids. The research for this direction is one of our concerns in the future study.

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#### APPENDIX A: APPROXIMATIONS FOR TRIPLET CORRELATIONS

In this appendix, we develop approximation schemes for triplet correlations that are required in evaluating the memory kernel under the mode-coupling approach. It should be remembered that, in the present paper, the greek subscripts and superscripts refer to the interaction sites of a molecule, and the roman letters label the molecules. It is assumed in the following that  $q \neq 0$ ,  $k - q \neq 0$ , and  $k \neq 0$ , and the thermodynamic limit is also anticipated.

##### 1. Convolution approximation

We investigate here how to approximate triplet (three-site) correlations,

$$\begin{aligned} & (\delta\rho_\lambda(\mathbf{q}) \delta\rho_\mu(\mathbf{k}-\mathbf{q}), \delta\rho_\nu(\mathbf{k})) \\ &= \frac{1}{N} \langle \delta\rho_\lambda^*(\mathbf{q}) \delta\rho_\mu^*(\mathbf{k}-\mathbf{q}) \delta\rho_\nu(\mathbf{k}) \rangle, \end{aligned} \quad (\text{A1})$$

in terms of two-site correlation functions  $w_{\lambda\mu}(k)$  and  $h_{\lambda\mu}(k)$ . To this end, we generalize the convolution approximation, employed in mode-coupling approaches for simple liquids [29] and mixtures of simple liquids [24], to polyatomic liquids. We first note that the right-hand side of Eq. (A1) can be rearranged into

$$\begin{aligned} & \langle \delta\rho_\lambda^*(\mathbf{q}) \delta\rho_\mu^*(\mathbf{k}-\mathbf{q}) \delta\rho_\nu(\mathbf{k}) \rangle \\ &= \left\langle \sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i^\lambda} \sum_j e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_j^\mu} \sum_l e^{i\mathbf{k}\cdot\mathbf{r}_l^\nu} \right\rangle \quad (\text{A2}) \\ &= (i=j=l) + (i=j \neq l) + (j=l \neq i) \\ &\quad + (l=i \neq j) + (i \neq j \neq l). \end{aligned} \quad (\text{A3})$$

The term  $(i=j=l)$  symbolically denotes the case where  $i=j=l$  in Eq. (A2), and others have similar meanings except for  $(i \neq j \neq l)$ , which summarizes the case where  $i \neq j$ ,  $j \neq l$ , and  $l \neq i$ .

The term  $(i=j=l)$  may be called intramolecular triplet correlation function since only one molecule is involved. The terms  $(i=j \neq l)$ ,  $(j=l \neq i)$ , and  $(l=i \neq j)$  will be referred to as intracoupled intermolecular triplet correlation functions where two different molecules are concerned, one of which offers two sites. We call the final term  $(i \neq j \neq l)$  intermolecular triplet correlation function to which three different molecules contribute. An approximation scheme for each class of triplet correlation functions is separately investigated in the following.

##### a. $(i=j=l)$ term in Eq. (A2)

We first consider the  $(i=j=l)$  term in Eq. (A2), which can be further decomposed into

$$\begin{aligned} & \left\langle \sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i^\lambda} e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_i^\mu} e^{i\mathbf{k}\cdot\mathbf{r}_i^\nu} \right\rangle \\ &= N \langle e^{-i\mathbf{q}\cdot\mathbf{r}_1^\lambda} e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_1^\mu} e^{i\mathbf{k}\cdot\mathbf{r}_1^\nu} \rangle \\ &= N [(\lambda = \mu = \nu) + (\lambda = \mu \neq \nu) + (\mu = \nu \neq \lambda) \\ &\quad + (\nu = \lambda \neq \mu) + (\lambda \neq \mu \neq \nu)]. \end{aligned} \quad (\text{A4})$$

The first four terms are readily evaluated in terms of site-site correlation functions, the results being

$$(\lambda = \mu = \nu) = \delta_{\lambda\mu} \delta_{\mu\nu}, \quad (\text{A5})$$

$$(\lambda = \mu \neq \nu) = \delta_{\lambda\mu} \tilde{s}_{\mu\nu}(k), \quad (\text{A6})$$

where we have defined [see also Eq. (13)]

$$\tilde{s}_{\lambda\mu}(k) \equiv (1 - \delta_{\lambda\mu}) s_{\lambda\mu}(k). \quad (\text{A7})$$

The terms  $(\mu = \nu \neq \lambda)$  and  $(\nu = \lambda \neq \mu)$  have expressions similar to Eq. (A6). The last term in Eq. (A4) is a triplet correlation. Defining

$$\begin{aligned} \tilde{s}_{\lambda\mu\nu}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') &\equiv (1 - \delta_{\lambda\mu})(1 - \delta_{\mu\nu})(1 - \delta_{\lambda\nu}) \langle \delta(\mathbf{r} - \mathbf{r}'_1) \\ &\quad \times \delta(\mathbf{r}' - \mathbf{r}'_1) \delta(\mathbf{r}'' - \mathbf{r}'_1) \rangle, \end{aligned} \quad (\text{A8})$$

the last term in Eq. (A4) can be expressed as

$$\begin{aligned} (\lambda \neq \mu \neq \nu) &= \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \int d\mathbf{r}' e^{-i\mathbf{q} \cdot \mathbf{r}'} \\ &\quad \times \int d\mathbf{r}'' \tilde{s}_{\nu\lambda\mu}^{(3)}(\mathbf{r} + \mathbf{r}'', \mathbf{r}' + \mathbf{r}'', \mathbf{r}'') \\ &= V \int d\mathbf{r} \int d\mathbf{r}' e^{i\mathbf{k} \cdot \mathbf{r}} e^{-i\mathbf{q} \cdot \mathbf{r}'} \tilde{s}_{\nu\lambda\mu}^{(3)}(\mathbf{r}, \mathbf{r}'), \end{aligned} \quad (\text{A9})$$

where we have noticed the translational invariance of the system.

To approximate this in terms of two-site correlation functions, we introduce the following convolution approximation:

$$\begin{aligned} \tilde{s}_{\nu\lambda\mu}^{(3)}(\mathbf{r}, \mathbf{r}') &\approx \tilde{s}_{\nu\mu}(r) \tilde{s}_{\lambda\mu}(r') \tilde{s}_{\nu\lambda}(|\mathbf{r} - \mathbf{r}'|) \\ &\quad - \tilde{t}_{\nu\mu}(r) \tilde{t}_{\lambda\mu}(r') \tilde{t}_{\nu\lambda}(|\mathbf{r} - \mathbf{r}'|) \\ &\quad + \sum_{\sigma} \frac{1}{V} \int d\mathbf{r}'' \tilde{t}_{\mu\sigma}(r'') \tilde{t}_{\lambda\sigma}(|\mathbf{r}' - \mathbf{r}''|) \\ &\quad \times \tilde{t}_{\nu\sigma}(|\mathbf{r} - \mathbf{r}''|), \end{aligned} \quad (\text{A10})$$

where we have defined

$$\tilde{t}_{\lambda\mu}(r) \equiv \tilde{s}_{\lambda\mu}(r) - \frac{1}{V}. \quad (\text{A11})$$

Note that the triplet correlation function under this approximation satisfies the relation

$$\tilde{s}_{\lambda\mu}(|\mathbf{r} - \mathbf{r}'|) = V \int d\mathbf{r}'' \tilde{s}_{\lambda\mu\nu}^{(3)}(\mathbf{r}, \mathbf{r}'', \mathbf{r}''), \quad (\text{A12})$$

and similar relations with subscripts or variables of integration appropriately interchanged. Then, it follows from Eqs. (A9) and (A10) that

$$\begin{aligned} (\lambda \neq \mu \neq \nu) &= \tilde{t}_{\lambda\mu}(q) \tilde{t}_{\nu\mu}(k) + \tilde{t}_{\nu\lambda}(q) \tilde{t}_{\nu\mu}(k - q) \\ &\quad + \tilde{t}_{\lambda\mu}(k - q) \tilde{t}_{\nu\lambda}(k) \\ &\quad + \sum_{\sigma} \tilde{t}_{\lambda\sigma}(q) \tilde{t}_{\mu\sigma}(k - q) \tilde{t}_{\nu\sigma}(k). \end{aligned} \quad (\text{A13})$$

By noting that

$$\tilde{t}_{\lambda\mu}(k) = \tilde{s}_{\lambda\mu}(k), \quad (\text{A14})$$

in  $k$  space when  $k \neq 0$ , substituting Eqs. (A5), (A6), and (A13) into Eq. (A4) yields

$$\begin{aligned} (i = j = l) &= \left\langle \sum_i e^{-i\mathbf{q} \cdot \mathbf{r}'_i} e^{-i(\mathbf{k} - \mathbf{q}) \cdot \mathbf{r}'_i} e^{i\mathbf{k} \cdot \mathbf{r}'_i} \right\rangle \\ &\approx N \sum_{\sigma} w_{\lambda\sigma}(q) w_{\mu\sigma}(k - q) w_{\nu\sigma}(k), \end{aligned} \quad (\text{A15})$$

where we have used Eq. (13).

### b. ( $i = j \neq l$ ) term in Eq. (A2)

We next consider the ( $i = j \neq l$ ) term in Eq. (A2). The terms represented by ( $j = l \neq i$ ) and ( $l = i \neq j$ ) can be treated in a similar manner. The ( $i = j \neq l$ ) term can be further decomposed into

$$\begin{aligned} &\left\langle \sum_i e^{-i\mathbf{q} \cdot \mathbf{r}'_i} e^{-i(\mathbf{k} - \mathbf{q}) \cdot \mathbf{r}'_i} \sum_{l \neq i} e^{i\mathbf{k} \cdot \mathbf{r}'_l} \right\rangle \\ &= \delta_{\lambda\mu} \left\langle \sum_i \sum_{l \neq i} e^{-i\mathbf{k} \cdot \mathbf{r}'_i} e^{i\mathbf{k} \cdot \mathbf{r}'_l} \right\rangle + (1 - \delta_{\lambda\mu}) \\ &\quad \times \left\langle \sum_i e^{-i\mathbf{q} \cdot \mathbf{r}'_i} e^{-i(\mathbf{k} - \mathbf{q}) \cdot \mathbf{r}'_i} \sum_{l \neq i} e^{i\mathbf{k} \cdot \mathbf{r}'_l} \right\rangle \\ &= (\lambda = \mu) + (\lambda \neq \mu). \end{aligned} \quad (\text{A16})$$

The term ( $\lambda = \mu$ ) is easily evaluated using Eq. (12):

$$(\lambda = \mu) = N \delta_{\lambda\mu} \rho h_{\lambda\nu}(k). \quad (\text{A17})$$

To evaluate the term ( $\lambda \neq \mu$ ), let us define the following triplet correlation function:

$$\begin{aligned} \rho^2 \underline{g}'_{\lambda\mu\nu}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') &\equiv (1 - \delta_{\mu\nu}) \\ &\quad \times \left\langle \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}'_i) \delta(\mathbf{r}' - \mathbf{r}'_j) \delta(\mathbf{r}'' - \mathbf{r}'_j) \right\rangle. \end{aligned} \quad (\text{A18})$$

The underline ( $\mu\nu$ ) emphasizes that these two sites are within the same molecule, and the factor  $\rho^2$  indicates that two different molecules are involved here. Then, the second term in Eq. (A16) can be written, as in Eq. (A9), as

$$(\lambda \neq \mu) = N \rho \int d\mathbf{r} \int d\mathbf{r}' e^{i\mathbf{k} \cdot \mathbf{r}} e^{-i\mathbf{q} \cdot \mathbf{r}'} \underline{g}'_{\nu\lambda\mu}(\mathbf{r}, \mathbf{r}'). \quad (\text{A19})$$

An approximation of Eq. (A19) in terms of site-site correlation functions can be achieved by introducing the following convolution approximation:

$$\begin{aligned} \underline{g}'_{\nu\lambda\mu}(\mathbf{r}, \mathbf{r}') &\approx g_{\nu\mu}(r) \tilde{s}_{\lambda\mu}(r') g_{\nu\lambda}(|\mathbf{r} - \mathbf{r}'|) \\ &\quad - h_{\nu\mu}(r) \tilde{t}_{\lambda\mu}(r') h_{\nu\lambda}(|\mathbf{r} - \mathbf{r}'|) \\ &\quad + \sum_{\sigma} \int d\mathbf{r}'' \tilde{t}_{\mu\sigma}(r'') \tilde{t}_{\lambda\sigma}(|\mathbf{r}' - \mathbf{r}''|) h_{\nu\sigma}(|\mathbf{r} - \mathbf{r}''|). \end{aligned} \quad (\text{A20})$$

It is readily verified that the triplet correlation function under this approximation satisfies the sequential conditions



$$g_{\nu\lambda}(|\mathbf{r}-\mathbf{r}'|) = \int d\mathbf{r}'' g'_{\nu\lambda\mu}{}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}''), \quad (\text{A21})$$

$$\tilde{s}_{\lambda\mu}(|\mathbf{r}'-\mathbf{r}''|) = \frac{\rho}{N-1} \int d\mathbf{r} g'_{\nu\lambda\mu}{}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}''). \quad (\text{A22})$$

Then, from Eqs. (A19) and (A20), it is straightforward to derive

$$\begin{aligned} (\lambda \neq \mu) = & N \left[ \tilde{t}_{\lambda\mu}(k-q) \rho h_{\nu\lambda}(k) + \tilde{t}_{\lambda\mu}(q) \rho h_{\nu\mu}(k) \right. \\ & + \frac{\rho}{V} h_{\nu\lambda}(q) h_{\nu\mu}(k-q) \\ & \left. + \sum_{\sigma} \tilde{t}_{\lambda\sigma}(q) \tilde{t}_{\mu\sigma}(k-q) \rho h_{\nu\sigma}(k) \right]. \quad (\text{A23}) \end{aligned}$$

Substituting Eqs. (A17) and (A23) into Eq. (A16) finally gives

$$\begin{aligned} (i \neq j \neq l) = & \left\langle \sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i^\lambda} e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_i^\mu} \sum_{l \neq i} e^{i\mathbf{k}\cdot\mathbf{r}_l^\nu} \right\rangle \\ \approx & N \sum_{\sigma} w_{\lambda\sigma}(q) w_{\mu\sigma}(k-q) \rho h_{\nu\sigma}(k), \quad (\text{A24}) \end{aligned}$$

where we have used Eqs. (13) and (A14).

### c. ( $i \neq j \neq l$ ) term in Eq. (A2)

Finally, an approximation for ( $i \neq j \neq l$ ) term in Eq. (A2) is investigated here. For this purpose, the following triplet correlation function is defined:

$$\begin{aligned} \rho^3 g_{\lambda\mu\nu}{}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') = & \left\langle \sum_i \sum_{j \neq i} \sum_{l \neq i \neq j} \delta(\mathbf{r}-\mathbf{r}_i^\lambda) \delta(\mathbf{r}'-\mathbf{r}_j^\mu) \right. \\ & \left. \times \delta(\mathbf{r}''-\mathbf{r}_l^\nu) \right\rangle, \quad (\text{A25}) \end{aligned}$$

where the factor  $\rho^3$  indicates that three different molecules are involved. Then, ( $i \neq j \neq l$ ) term in Eq. (A2) can be expressed, as in Eqs. (A9) and (A19), as

$$\begin{aligned} & \left\langle \sum_{i \neq j \neq l} e^{-i\mathbf{q}\cdot\mathbf{r}_i^\lambda} e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_j^\mu} e^{i\mathbf{k}\cdot\mathbf{r}_l^\nu} \right\rangle \\ & = N \rho^2 \int d\mathbf{r} \int d\mathbf{r}' e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\mathbf{q}\cdot\mathbf{r}'} g_{\nu\lambda\mu}{}^{(3)}(\mathbf{r}, \mathbf{r}'). \quad (\text{A26}) \end{aligned}$$

We introduce the following convolution approximation for  $g_{\nu\lambda\mu}{}^{(3)}(\mathbf{r}, \mathbf{r}')$ :

$$\begin{aligned} & g_{\nu\lambda\mu}{}^{(3)}(\mathbf{r}, \mathbf{r}') \\ & \approx g_{\nu\mu}(r) g_{\lambda\mu}(r') g_{\nu\lambda}(|\mathbf{r}-\mathbf{r}'|) - h_{\nu\mu}(r) h_{\lambda\mu}(r') \\ & \times h_{\nu\lambda}(|\mathbf{r}-\mathbf{r}'|) + \rho \sum_{\sigma} \int d\mathbf{r}'' h_{\mu\sigma}(r'') h_{\lambda\sigma}(|\mathbf{r}'-\mathbf{r}''|) \\ & \times h_{\nu\sigma}(|\mathbf{r}-\mathbf{r}''|) + \sum_{\sigma} \int d\mathbf{r}'' \tilde{s}_{\mu\sigma}(r'') h_{\lambda\sigma}(|\mathbf{r}'-\mathbf{r}''|) \\ & \times h_{\nu\sigma}(|\mathbf{r}-\mathbf{r}''|) + \sum_{\sigma} \int d\mathbf{r}'' h_{\mu\sigma}(r'') \tilde{s}_{\lambda\sigma}(|\mathbf{r}'-\mathbf{r}''|) \\ & \times h_{\nu\sigma}(|\mathbf{r}-\mathbf{r}''|) + \sum_{\sigma} \int d\mathbf{r}'' h_{\mu\sigma}(r'') h_{\lambda\sigma}(|\mathbf{r}'-\mathbf{r}''|) \\ & \times \tilde{s}_{\nu\sigma}(|\mathbf{r}-\mathbf{r}''|). \quad (\text{A27}) \end{aligned}$$

Notice that the triplet correlation function under this approximation satisfies the sequential condition

$$g_{\lambda\mu}(|\mathbf{r}-\mathbf{r}'|) = \frac{\rho}{N-2} \int d\mathbf{r}'' g_{\lambda\mu\nu}{}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}''). \quad (\text{A28})$$

Then, from Eqs. (A26) and (A27), one obtains

$$\begin{aligned} (i \neq j \neq l) = & \left\langle \sum_{i \neq j \neq l} e^{-i\mathbf{q}\cdot\mathbf{r}_i^\lambda} e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_j^\mu} e^{i\mathbf{k}\cdot\mathbf{r}_l^\nu} \right\rangle \\ \approx & N \sum_{\sigma} [w_{\lambda\sigma}(q) \rho h_{\mu\sigma}(k-q) \rho h_{\nu\sigma}(k) + \rho h_{\lambda\sigma}(q) \\ & \times w_{\mu\sigma}(k-q) \rho h_{\nu\sigma}(k) + \rho h_{\lambda\sigma}(q) \rho h_{\mu\sigma}(k-q) \\ & \times w_{\nu\sigma}(k) + \rho h_{\lambda\sigma}(q) \rho h_{\mu\sigma}(k-q) \rho h_{\nu\sigma}(k)], \quad (\text{A29}) \end{aligned}$$

where Eq. (13) has been used.

### d. Summary of Eq. (A2)

Under the convolution approximations discussed in the previous parts, it eventually follows from Eqs. (A3), (A15), (A24), and (A29) that

$$\begin{aligned} & (\delta\rho_\lambda(\mathbf{q}) \delta\rho_\mu(\mathbf{k}-\mathbf{q}), \delta\rho_\nu(\mathbf{k})) \\ & = \frac{1}{N} \langle \delta\rho_\lambda^*(\mathbf{q}) \delta\rho_\mu^*(\mathbf{k}-\mathbf{q}) \delta\rho_\nu(\mathbf{k}) \rangle \\ & \approx \sum_{\sigma} \chi_{\lambda\sigma}(q) \chi_{\mu\sigma}(k-q) \chi_{\nu\sigma}(k), \quad (\text{A30}) \end{aligned}$$

where we have used Eq. (10).

## 2. Triplet correlations involving velocity fields

This subsection deals with the triplet correlations involving one density and two velocity fields. We first consider the following triplet correlation:

$$\langle \delta\rho_\lambda^*(\mathbf{q}) j_\mu^*(\mathbf{k}-\mathbf{q}) j_\nu(\mathbf{k}) \rangle. \quad (\text{A31})$$

Due to the statistical independence of the translational and rotational velocities, by employing the notation in Eq. (17), it follows that

$$\begin{aligned}
& \langle \delta\rho_\lambda^*(\mathbf{q})j_\mu^*(\mathbf{k}-\mathbf{q})j_\nu(\mathbf{k}) \rangle \\
&= \left\langle \sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i^\lambda} \sum_j (v_{j,z}^C)^2 e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_j^\mu} e^{i\mathbf{k}\cdot\mathbf{r}_j^\nu} \right\rangle \\
&+ \left\langle \sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i^\lambda} \sum_j [\boldsymbol{\omega}_j \times \delta\mathbf{r}_j^{C\mu}]_z \right. \\
&\quad \left. \times [\boldsymbol{\omega}_j \times \delta\mathbf{r}_j^{C\nu}]_z e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_j^\mu} e^{i\mathbf{k}\cdot\mathbf{r}_j^\nu} \right\rangle. \quad (\text{A32})
\end{aligned}$$

The first term is readily evaluated, using the results of the convolution approximation, Eqs. (A15) and (A24), and noting the statistical independence of the translational velocities and coordinates, as follows:

$$\begin{aligned}
& \left\langle \sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i^\lambda} \sum_j (v_{j,z}^C)^2 e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_j^\mu} e^{i\mathbf{k}\cdot\mathbf{r}_j^\nu} \right\rangle \\
&\approx N \sum_\sigma \chi_{\lambda\sigma}(q) w_{\mu\sigma}(k-q) J_{\nu\sigma}^{\text{trans}}(k), \quad (\text{A33})
\end{aligned}$$

where  $J_{\alpha\beta}^{\text{trans}}(k)$  is defined in Eq. (19).

The evaluation of the second term in Eq. (A32) is a non-trivial problem, and we assume it to have the same functional form as Eq. (A33). Then, one has

$$\langle \delta\rho_\lambda^*(\mathbf{q})j_\mu^*(\mathbf{k}-\mathbf{q})j_\nu(\mathbf{k}) \rangle \approx N \sum_\sigma \chi_{\lambda\sigma}(q) w_{\mu\sigma}(k-q) J_{\nu\sigma}(k). \quad (\text{A34})$$

Expressions for two other similar triplet correlation functions are required in the main text. These correlation functions can be approximated within the same spirit as above, the final results being

$$\langle \delta\rho_\lambda^*(\mathbf{q})j_\mu^{s*}(\mathbf{k}-\mathbf{q})j_\nu^s(\mathbf{k}) \rangle \approx \sum_\sigma \chi_{\lambda\sigma}(q) w_{\mu\sigma}(k-q) J_{\nu\sigma}(k), \quad (\text{A35})$$

$$\langle \delta\rho_\lambda^{s*}(\mathbf{q})j_\mu^*(\mathbf{k}-\mathbf{q})j_\nu^s(\mathbf{k}) \rangle \approx \sum_\sigma w_{\lambda\sigma}(q) w_{\mu\sigma}(k-q) J_{\nu\sigma}(k). \quad (\text{A36})$$

## APPENDIX B: EVALUATION OF THE PROJECTED RANDOM FORCE

In this appendix, we briefly outline the derivation of the expression for the projected random force for the collective variable case: the single-particle counterpart can be derived by a similar procedure. For simplicity, we shall often adopt in the following the notation of  $A_{\lambda\mu}$  defined by Eq. (49). (Note that  $A_{\lambda\mu}$  is not symmetric with respect to the interchange of subscripts. However, when the wave vectors  $\mathbf{q}$  and  $\mathbf{k}-\mathbf{q}$  are interchanged, so are the subscripts.) Also, we may rearrange or rename dummy indices arbitrarily without any indication.

Let us evaluate the first term in the right-hand side of Eq. (59):

$$\mathcal{P}_2 \dot{j}_\alpha(\mathbf{k}) = \frac{1}{2} \sum_{\mathbf{q}} \sum_{\lambda,\mu,\lambda',\mu'} A_{\lambda\mu} (A_{\lambda\mu}, A_{\lambda'\mu'})^{-1} (A_{\lambda'\mu'}, \dot{j}_\alpha(\mathbf{k})). \quad (\text{B1})$$

The numerator can be expressed as

$$\begin{aligned}
& (\delta\rho_\lambda(\mathbf{q}) \delta\rho_\mu(\mathbf{k}-\mathbf{q}), \dot{j}_\alpha(\mathbf{k})) \\
&= -\frac{1}{N} \langle \delta\rho_\lambda^*(\mathbf{q}) \delta\rho_\mu^*(\mathbf{k}-\mathbf{q}) j_\alpha(\mathbf{k}) \rangle \\
&\quad -\frac{1}{N} \langle \delta\rho_\lambda^*(\mathbf{q}) \delta\rho_\mu^*(\mathbf{k}-\mathbf{q}) j_\alpha(\mathbf{k}) \rangle \\
&= iq_z \frac{1}{N} \langle \delta\rho_\mu^*(\mathbf{k}-\mathbf{q}) j_\lambda^*(\mathbf{q}) j_\alpha(\mathbf{k}) \rangle \\
&\quad + i(k-q_z) \frac{1}{N} \langle \delta\rho_\lambda^*(\mathbf{q}) j_\mu^*(\mathbf{k}-\mathbf{q}) j_\alpha(\mathbf{k}) \rangle, \quad (\text{B2})
\end{aligned}$$

where we have used the well-known relation  $\langle A\dot{B} \rangle = -\langle \dot{A}B \rangle$ , and the continuity equation Eq. (3). The evaluation of the above equation requires the knowledge of the triplet correlation functions involving one density and two longitudinal velocity fields, an approximation for which is presented in the Appendix A. Using Eq. (A34), it follows that

$$\begin{aligned}
& (\delta\rho_\lambda(\mathbf{q}) \delta\rho_\mu(\mathbf{k}-\mathbf{q}), \dot{j}_\alpha(\mathbf{k})) \\
&\approx iq_z \sum_\sigma \chi_{\mu\sigma}(k-q) w_{\lambda\sigma}(q) J_{\alpha\sigma}(k) \\
&\quad + i(k-q_z) \sum_\sigma \chi_{\lambda\sigma}(q) w_{\mu\sigma}(k-q) J_{\alpha\sigma}(k). \quad (\text{B3})
\end{aligned}$$

By substituting this into Eq. (B1) and using Eq. (58), one obtains

$$\begin{aligned}
\mathcal{P}_2 \dot{j}_\alpha(\mathbf{k}) &= \frac{i}{2N} \sum_{\mathbf{q}} \sum_{\lambda,\mu,\sigma} \{ q_z A_{\lambda\mu} [\chi^{-1}(q)]_{\lambda\sigma} w_{\sigma\mu}(q) J_{\alpha\mu}(k) \\
&\quad + (k-q_z) A_{\lambda\mu} [\chi^{-1}(k-q)]_{\mu\sigma} \\
&\quad \times w_{\sigma\lambda}(k-q) J_{\alpha\lambda}(k) \}. \quad (\text{B4})
\end{aligned}$$

It can be easily shown that the first and second term in the above equation are equal to each other, and it follows that

$$\mathcal{P}_2 \dot{j}_\alpha(\mathbf{k}) = \frac{i}{N} \sum_{\mathbf{q}} \sum_{\lambda,\mu,\sigma} q_z A_{\lambda\mu} [\chi^{-1}(q)]_{\lambda\sigma} w_{\sigma\mu}(q) J_{\alpha\mu}(k). \quad (\text{B5})$$

We next evaluate the second term in the right-hand side of Eq. (59) under the convolution approximation developed in the Appendix A:

$$\begin{aligned}
& \mathcal{P}_2 (\boldsymbol{\delta\rho}(\mathbf{k}) \boldsymbol{\chi}^{-1}(k) \mathbf{J}(k))_\alpha \\
&= \sum_{\gamma,\delta} (\mathcal{P}_2 \delta\rho_\gamma(\mathbf{k})) [\chi^{-1}(k)]_{\gamma\delta} J_{\delta\alpha}(k). \quad (\text{B6})
\end{aligned}$$

It follows from Eqs. (58) and (A30) that

$$\begin{aligned}
\mathcal{P}_2 \delta \rho_\gamma(\mathbf{k}) &= \frac{1}{2} \sum_{\mathbf{q}} \sum_{\lambda, \mu, \lambda', \mu'} A_{\lambda\mu}(A_{\lambda\mu}, A_{\lambda'\mu'})^{-1} \\
&\quad \times (\delta \rho_{\lambda'}(\mathbf{q}) \delta \rho_{\mu'}(\mathbf{k}-\mathbf{q}), \delta \rho_\gamma(\mathbf{k})) \\
&= \frac{1}{2N} \sum_{\mathbf{q}} \sum_{\lambda} A_{\lambda\lambda} \chi_{\gamma\lambda}(k). \quad (\text{B7})
\end{aligned}$$

Substituting this into Eq. (B6) yields

$$\mathcal{P}_2(\delta \rho(\mathbf{k}) \chi^{-1}(k) \mathbf{J}(k))_\alpha = \frac{1}{2N} \sum_{\mathbf{q}} \sum_{\lambda} A_{\lambda\lambda} J_{\alpha\lambda}(k). \quad (\text{B8})$$

It is more convenient to rewrite this equation in the following form:

$$\begin{aligned}
ik \mathcal{P}_2(\delta \rho(\mathbf{k}) \chi^{-1}(k) \mathbf{J}(k))_\alpha \\
&= \frac{i}{2N} \sum_{\mathbf{q}} \sum_{\lambda} \{q_z + (k - q_z)\} A_{\lambda\lambda} J_{\alpha\lambda}(k) \\
&= \frac{i}{N} \sum_{\mathbf{q}} \sum_{\lambda} q_z A_{\lambda\lambda} J_{\alpha\lambda}(k) \\
&= \frac{i}{N} \sum_{\mathbf{q}} \sum_{\lambda, \mu} q_z A_{\lambda\mu} J_{\alpha\mu}(k) \delta_{\lambda\mu}. \quad (\text{B9})
\end{aligned}$$

Finally, we combine Eqs. (B5) and (B9) to obtain the expression for  $\mathcal{P}_2(\mathbf{R}(\mathbf{k}))_\alpha$ :

$$\begin{aligned}
\mathcal{P}_2(\mathbf{R}(\mathbf{k}))_\alpha &= \frac{i}{N} \sum_{\mathbf{q}} \sum_{\lambda, \mu} q_z A_{\lambda\mu} J_{\alpha\mu}(k) \\
&\quad \times \left( \sum_{\sigma} [\chi^{-1}(q)]_{\lambda\sigma} w_{\sigma\mu}(q) - \delta_{\lambda\mu} \right). \quad (\text{B10})
\end{aligned}$$

The quantities in the parentheses read, using Eq. (16),

$$\sum_{\sigma} [\chi^{-1}(q)]_{\lambda\sigma} w_{\sigma\mu}(q) - \delta_{\lambda\mu} = -\rho [wc(q)]_{\mu\lambda}, \quad (\text{B11})$$

where the matrix element  $[wc(k)]_{\lambda\mu}$  is defined in Eq. (61). Substituting this into Eq. (B10) eventually gives

$$\begin{aligned}
\mathcal{P}_2(\mathbf{R}(\mathbf{k}))_\alpha &= -\frac{i\rho}{N} \sum_{\mathbf{q}} \sum_{\lambda, \mu} q_z [wc(q)]_{\mu\lambda} \\
&\quad \times J_{\alpha\mu}(k) \delta \rho_\lambda(\mathbf{q}) \delta \rho_\mu(\mathbf{k}-\mathbf{q}). \quad (\text{B12})
\end{aligned}$$

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- [1] S.-H. Chong and F. Hirata, Phys. Rev. E **57**, 1691 (1998).  
[2] R. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Britton, B. W. Downs, and J. Downs (Wiley Interscience, New York, 1961), Vol. III, p. 135.  
[3] H. Mori, Prog. Theor. Phys. **33**, 423 (1965).  
[4] H. Mori, Prog. Theor. Phys. **34**, 399 (1965).  
[5] D. Chandler and H. C. Andersen, J. Chem. Phys. **57**, 1930 (1972).  
[6] D. Chandler, in *The Liquid State of Matter*, edited by E. Montroll and J. L. Lebowitz (City, North-Holland, 1982).  
[7] S. W. Lovesey, J. Phys. C **4**, 3057 (1971).  
[8] J. R. D. Copley and S. W. Lovesey, Rep. Prog. Phys. **38**, 461 (1975).  
[9] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).  
[10] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1990).  
[11] U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Oxford University Press, New York, 1994).  
[12] G. F. Mazenko, Phys. Rev. A **7**, 209 (1973).  
[13] G. F. Mazenko, Phys. Rev. A **9**, 360 (1974).  
[14] W. Götze and M. Lücke, Phys. Rev. A **11**, 2173 (1975).  
[15] T. Munakata and A. Igarashi, Prog. Theor. Phys. **58**, 1345 (1977).  
[16] T. Munakata and A. Igarashi, Prog. Theor. Phys. **60**, 45 (1978).  
[17] J. Bosse, W. Götze, and M. Lücke, Phys. Rev. A **17**, 434 (1978).  
[18] J. Bosse, W. Götze, and M. Lücke, Phys. Rev. A **17**, 447 (1978).  
[19] L. Sjögren, Phys. Rev. A **22**, 2866 (1980).  
[20] L. Sjögren, Phys. Rev. A **22**, 2883 (1980).  
[21] M. A. Ricci, D. Rocca, G. Ruocco, and R. Vallauri, Phys. Rev. A **40**, 7226 (1989).  
[22] H. Resat, F. O. Raineri, and H. L. Friedman, J. Chem. Phys. **97**, 2618 (1992).  
[23] B. J. Berne and G. D. Harp, Adv. Chem. Phys. **17**, 63 (1970).  
[24] J. Bosse and M. Henel, Ber. Bunsenges. Phys. Chem. **95**, 1007 (1991).  
[25] J. S. Thakur and J. Bosse, Phys. Rev. A **43**, 4378 (1991).  
[26] J. Bosse and Y. Kaneko, Phys. Rev. Lett. **74**, 4023 (1995).  
[27] D. Wei and G. N. Patey, J. Chem. Phys. **91**, 7113 (1989).  
[28] D. Wei and G. N. Patey, J. Chem. Phys. **93**, 1399 (1990).  
[29] H. W. Jackson and E. Feenberg, Rev. Mod. Phys. **34**, 686 (1962).