

Gaussian factorization of hydrodynamic correlation functions and mode-coupling memory kernels

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A simple method to determine mode-coupling memory functions in generalized Langevin equations is obtained by explicitly expressing the random force of the slow hydrodynamic modes in terms of pair interactions in liquids and by Gaussian factoring the resulting multiple-point time correlation functions into products of linear correlation functions. The approach is used to derive the mode-coupling memory kernels for the velocity autocorrelation function, four-point bilinear density correlation function, and density correlation function of linear molecular liquids. These generalized Langevin equations and their associated memory kernels are useful for calculating relaxation processes and spectroscopic measurements in liquids and solvents. As a central result of our analysis, the non-Gaussian behavior of the bilinear density correlation function is quantitatively related to the nonexponential nature of linear hydrodynamic modes. This relation aids in the understanding of recent simulation results of non-Gaussian indicators in supercooled liquids.

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I. INTRODUCTION: GENERALIZED LANGEVIN EQUATION, GAUSSIAN FACTORIZATION, AND MODE-COUPLING THEORY

The time correlation functions of hydrodynamic modes are essential for studying liquids and solvents. These hydrodynamic modes are a set of slowly varying stochastic dynamical variables whose relaxation can be described by the generalized Langevin equation (GLE). The time-dependent memory kernel describes the memory effect on the relaxation of the system. The usual hydrodynamics limit assumes the Markovian approximation, where the GLE reduces to the Langevin equation and the hydrodynamic mode decays exponentially. However, deviations from the hydrodynamic behavior have been observed on the experimental time scale, especially in heterogeneous systems such as low-temperature glass-forming liquids. In these systems, linear hydrodynamic modes are coupled to nonlinear modes, which slow down the relaxation dramatically. These mode-coupling effects were first used to calculate transport coefficients near the critical point [1–3]. Later, the mode-coupling concept was shown to be crucial in the interpretation of the hydrodynamic long-time tail. Götze derived mode-coupling equations to explain the α and β relaxation processes of the glass transition [4]. Other approaches include extended hydrodynamics and the field theoretical formalism of nonlinear hydrodynamic coupling [5]. A recent review by Bagchi and Bhattacharyya provides a comprehensive account of various approaches in mode-coupling theory [6]. Although successful, the standard mode-coupling approximation has not been obtained in a systematic and straightforward fashion. A simple understanding of mode-coupling effects and their validity for describing low-temperature dynamics is still lacking [7]. In this paper, we explore an alternative route to obtaining ideal mode-coupling equations via the direct Gaussian factorization of the multiple-point correlation function in the memory kernel. Within this approximation, we examine the underlying rela-

tion between the non-Gaussian behavior of nonlinear hydrodynamic modes and the nonexponential behavior of linear hydrodynamic modes.

The general goal of molecule hydrodynamic analysis is to predict time correlation over the complete time domain from equilibrium distributions and other measurements. One way to establish such a relationship is the simple Gaussian approximation, which treats density fluctuations in liquids as Gaussian variables and decomposes a nonlinear time correlation function into products of linear correlation functions. The simple factorization scheme destroys the initial and final equilibrium distributions and leads to unphysical results of overlapping particles. To avoid this, thermal equilibrium is imposed at the initial and final times. Formally, we represent the Gaussian factorization approximation as

$$G(\Gamma, \Gamma', t) = \langle \Gamma' | e^{iLt} | \Gamma \rangle \approx g(\Gamma) g(\Gamma') \prod_{i \in \Gamma, j \in \Gamma'} G(i, j, t), \quad (1)$$

where Γ is a set of phase space points at the initial time, Γ' is a set of phase space points at the final time, and $G(\Gamma, \Gamma', t)$ is the multipoint time correlation function. As a result of the decomposition, $g(\Gamma)$ and $g(\Gamma')$ are the equilibrium distribution functions for the initial and final phase space points, and $G(i, j, t)$ is the linear time correlation function with i in the initial configuration and j in the final configuration. Equation (1) recovers the long-time equilibrium limit but is not correct in the short time. As an alternative, we impose the correct initial distribution by writing $G(\Gamma, \Gamma', t) \approx g(\Gamma) \prod_{i,j} G(i, j, t) / G(i, j, 0)$ where the linear time correlation function is normalized. To bridge the two limiting cases, we can further improve the approximation by combining the above two expressions as

$$G(\Gamma, \Gamma', t) \approx g(\Gamma) g(\Gamma') [\prod_{i,j} G(i, j, t) - \prod_{i,j} G_s(i, j, t)] + g(\Gamma) \prod_{i,j} G_s(i, j, t) / G(i, j, 0),$$

where $G_s(t)$ is the short-time part of the time correlation function. Although there are various versions of Gaussian

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factorization, the key element of dynamics decomposition remains the same. Equation (1) will be used in this paper because we are mainly concerned with the long-time behavior.

A rigorous formulation for calculating dynamic correlation functions is the generalized Langevin equation derived with the projection operator technique [8,9]. Instead of decomposing the correlation function directly, we now apply the approximation to the memory kernel, yielding

$$M(\Gamma, \Gamma', t) \propto \langle \Gamma' | e^{iQLt} | \Gamma \rangle \approx g(\Gamma)g(\Gamma') \prod_{i \in \Gamma, j \in \Gamma'} G(i, j, t), \quad (2)$$

where $Q = 1 - P$ is orthogonal to the projector P , and all other notation follows the definition in Eq. (1). Combined with the random phase approximation for the direct correlation function $c(r) \approx -\beta U(r)g(r)$, this approach leads to the standard mode-coupling approximation for the memory kernel [10]. This approach is better justified in an elegant derivation by Zaccarelli *et al.*, which exploits the self-consistency of the fluctuation-dissipation relationship [11]. Because the memory kernel propagates in phase space orthogonally to the slow variable, dynamic decomposition of the memory kernel is more reasonable than direct decomposition. Thus, the mode-coupling approximation is believed to be more reliable than the direct factorization expression. It then follows that we can apply the factorization scheme to higher-order memory kernels as represented in the form of continued fractions. In this sense, the GLE provides a compact formalism to construct dynamic correlation with initial moments and nonlinear memory kernels in the most economical way, whereas Gaussian factorization simply provides a closure to the hierarchy. Higher-order memory kernels and other forms of closure may lead to alternatives to the standard mode-coupling expressions. In the following sections, we apply the Gaussian decomposition approach and, equivalently, the self-consistent derivation by Zaccarelli *et al.* to obtain mode-coupling kernels for the velocity autocorrelation function, bilinear density correlation function, and density fluctuations in linear molecular liquids.

The Gaussian approximation is valid for long-time and large displacements, which according to the central limit theorem can be treated as random Gaussian fluctuations. Away from the hydrodynamic limit, the relaxation process is not Markovian and the fluctuation is not Gaussian. The dynamic decomposition scheme has to be modified to incorporate nonhydrodynamic effects observed on the experimental time scale. This indeed is the case for low-temperature systems with dynamic clustering effects. Recently, the validity of Gaussian factorization in low-temperature liquids was examined and non-Gaussian effects were investigated. For example, the difference between

$$\langle \rho(\vec{r}_1, t) \rho(\vec{r}_1, 0) \rho(\vec{r}_2, t) \rho(\vec{r}_2, 0) \rangle$$

and

$$\langle \rho(\vec{r}_1, t) \rho(\vec{r}_1, 0) \rangle \langle \rho(\vec{r}_2, t) \rho(\vec{r}_2, 0) \rangle$$

was studied by Glozter and co-workers in glassy systems using numerical simulation [12,13]. Their results show that the Gaussian factorization scheme fits the short-time limit when the equilibrium effects dominate. The error introduced by the Gaussian approximation increases to a maximum value before decaying to zero. The peak value of the non-Gaussian indicator and the corresponding time increase strongly as the temperature decreases. These non-Gaussian effects have also been observed in recent experiments by Angell, Weeks *et al.*, and Cui and Rice and are correlated with the behavior of low-temperature liquids near the glass transition temperature [14–16]. These measurements supplement traditional scattering measurements, which often reveal highly nonexponential decay in complex systems. An important result of the paper is the relation between the non-Gaussian behavior of the nonlinear density correlation function and the nonexponential decay of the linear hydrodynamics mode. This relation is developed in Sec. IV B.

II. DERIVATION OF IDEAL MODE-COUPLING THEORY EQUATION FOR THE INTERMEDIATE SCATTERING FUNCTION

We begin with the GLE and the standard projection operator formalism. The notation here follows a review article by Berne [9]. The projection operator P is defined as $P = \langle \dots, A^\dagger \rangle \langle A, A^\dagger \rangle^{-1}$, where $\langle A, B^\dagger \rangle$ is the average over the equilibrium canonical ensemble: $\langle A, B^\dagger \rangle = \int d\Gamma \rho_0(\Gamma) A(\Gamma) B^\dagger(\Gamma)$. The GLE is written as $\dot{A}(t) = i\Omega A(t) - \int K(t-\tau) A(\tau) d\tau + f(t)$, where Ω is the projection of the eigenfrequency matrix onto the slow variable space, defined as $i\Omega = \langle iLA, A^\dagger \rangle \langle A, A^\dagger \rangle^{-1}$, $iL = \{ \dots, H \}$ is the Liouville operator, and H is the Hamiltonian. The random force $f(t)$ represents the fast decay of the system, defined as $f(t) = \exp\{iQLt\} QiLA$, with the projector $Q = 1 - P$. The memory kernel is related to the reduced correlation function of the random force by the fluctuation-dissipation relation $K(t) = \langle f(t), f^\dagger \rangle \langle A, A^\dagger \rangle^{-1}$. One widely used approach for evaluating the memory kernel is to project the random force to a bilinear operator and factor the resulting kernel onto the product of correlation functions of linear modes [17]. The difficulty with this approach is that the choice of the bilinear variable is ambiguous and is difficult to justify rigorously. Also, the random force in the fast space, $f(t) = \exp\{iQLt\} QiLA$, is approximated by the evolution of the random force in the full space, $f(t) = \exp\{iLt\} QiLA$. In a more rigorous approach developed by Oppenheim and co-workers [18–20], all the possible combinations of the slow modes, such as AA, AAA, \dots , are included in the construction of the slow space. It is shown that in evaluating the GLE a relatively few additional nonlinear variables are involved.

In a recent paper [10], we employed a simple approach to obtain the mode-coupling memory kernel for $F(\vec{k}, t)$. The intermediate scattering function is defined as $F_{\vec{k}}(\vec{k}, t) = \langle \rho(\vec{k}, t) \rho(-\vec{k}) \rangle$, where $\rho(\vec{k}, t) = \sum_{n=1}^N \exp\{i\vec{k} \cdot \vec{r}_n(t)\}$ is the collective density and N is the total number of particles in the system [21]. Our approach is motivated by the observation that the random force on the slow mode involves the inter-

action potential and its derivatives, which can be written as Fourier integrals of the bilinear density mode. This bilinear density mode provides a natural choice for the projection and decomposition used in the mode-coupling approximation. Our derivation of the ideal mode-coupling equation involves Gaussian factorization and the random phase approximation (RPA). The GLE for $A = \{\rho(\vec{k}, t), \dot{\rho}(\vec{k}, t)\}$ is

$$\frac{d}{dt} \begin{pmatrix} \rho(\vec{k}, t) \\ \dot{\rho}(\vec{k}, t) \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -\omega_k^2 & 0 \end{pmatrix} \begin{pmatrix} \rho(\vec{k}, t) \\ \dot{\rho}(\vec{k}, t) \end{pmatrix} - \int_0^t \begin{pmatrix} 0 & 0 \\ 0 & K_{22}(t-\tau) \end{pmatrix} \times \begin{pmatrix} \rho(k, \tau) \\ \dot{\rho}(k, \tau) \end{pmatrix} d\tau + \begin{pmatrix} 0 \\ f_2(t) \end{pmatrix}, \quad (3)$$

where $\omega_k^2 = k^2 / (S_k m \beta)$ and S_k is the structure factor. By virtue of the fluctuation-dissipation relation, the nonzero element $K_{22}(t)$ of the memory kernel matrix is given by

$$K_{22}(t) = \frac{m\beta \langle \ddot{\rho} + \omega_k^2 \rho | e^{iQLt} | \ddot{\rho} + \omega_k^2 \rho \rangle}{Nk^2}, \quad (4)$$

where the random force $f_2(t) = \exp\{iQLt\} \langle \ddot{\rho} + \omega_k^2 \rho \rangle$. The second-order time derivative of the collective density in Fourier space is

$$\ddot{\rho}(\vec{k}, t) = - \sum_q \frac{kq_z}{mV} U_q \rho(\vec{k}-\vec{q}, t) \rho(\vec{q}, t) - k^2 \sum_{n=1}^N v_{nz}^2(t) e^{i\vec{k} \cdot \vec{r}_n(t)}, \quad (5)$$

where $U_{\vec{q}}$ is the Fourier transform of the pair interaction potential. The second term in the above equation is neglected because the first term is larger in the small k limit. The Gaussian factorization approximation of the relevant part of the memory kernel leads to

$$\begin{aligned} \langle \ddot{\rho} | e^{iQLt} | \ddot{\rho} \rangle &= \frac{k^2}{m^2 V^2} \sum_{\vec{q}, \vec{q}'} q_z q'_z U_{\vec{q}} U_{\vec{q}'} \\ &\times \langle \rho(\vec{k}-\vec{q}) \rho(\vec{q}) | e^{iQLt} | \rho(\vec{k}-\vec{q}') \rho(\vec{q}') \rangle \\ &\approx \sum_{\vec{q}} \frac{N^2 k^2}{m^2 V^2} [q_z^2 U_{\vec{q}}^2 + q_z(k-q_z) U_q U_{k-\vec{q}}] \\ &\times F_{k-\vec{q}}^-(t) F_{\vec{q}}^-(t), \end{aligned} \quad (6)$$

where $\exp\{iQLt\}$ is approximated by $\exp\{iLt\}$ for the fast random force and the wave vector \vec{k} is directed along the z axis. Using the random phase approximation, $U_{\vec{k}}$ is proportional to the direct correlation function, $c_{\vec{k}}^- = -\beta U_{\vec{k}}$, which allows us to rewrite the above equation as the well-known mode-coupling memory kernel for the intermediate scattering function $F_{\vec{k}}^-(t)$ [21]:

$$\begin{aligned} K_{22}(t) &= \frac{n}{m\beta} \frac{1}{(2\pi)^3} \int d\vec{q} [q_z^2 c_{\vec{q}}^2 + q_z(k-q_z) c_q c_{k-\vec{q}}] \\ &\times F_{k-\vec{q}}^-(t) F_{\vec{q}}^-(t), \end{aligned} \quad (7)$$

where $n = \langle \rho \rangle$ is the number density. In this approach, the introduction of the extra bilinear mode projection operator is avoided, and the nonlinear coupling term comes from the Fourier expansion of the random force on the density. The Gaussian factorization and the mean-field approximation (i.e., RPA) lead to a self-consistent mode-coupling memory kernel. Similar approximations have been used recently for computing linear and nonlinear Raman line shapes [10].

In our derivation, $\exp\{iQLt\}$ is approximated as $\exp\{iLt\}$ and higher-order \vec{k} terms are ignored. These difficulties are resolved in a recent paper by Zaccarelli *et al.* [11]. In their paper, a self-consistent approach is introduced to derive an exact formal expression for the random force. The explicit operator expression of the random force, $f(t) = \exp\{iQLt\}$, is not used, because the projection operator Q is difficult to evaluate. Instead, they derived the expression for the random force by applying the GLE directly:

$$f_2(t) = \ddot{\rho}(\vec{k}, t) + \omega_k^2 \rho(\vec{k}, t) + \int_0^t K_{22}(t-\tau) \dot{\rho}(\vec{k}, t) d\tau. \quad (8)$$

The fluctuation-dissipation relationship is used to evaluate the memory kernel. Gaussian factorization of the memory kernel leads to

$$\begin{aligned} \langle f_2(t) f_2^*(t) \rangle &= \sum_{\vec{q} \neq \vec{k}} \frac{N^2 k^2}{m^2 V^2} [q_z^2 U_{\vec{q}}^2 + q_z(k-q_z) U_q U_{k-\vec{q}}] \\ &\times F_{k-\vec{q}}^-(t) F_{\vec{q}}^-(t) \\ &+ \frac{k^4 N}{m^2 \beta^2} (1 + \beta n U_{\vec{k}}^- S_k^{-1})^2 F_{\vec{k}}^-(t) \\ &+ \frac{k^2 N}{m\beta} (1 + \beta n U_{\vec{k}}^- S_k^{-1}) \\ &\times \int_0^t K_{22}(t-\tau) \frac{\partial}{\partial t} F_{\vec{k}}^-(\tau) d\tau. \end{aligned} \quad (9)$$

The direct correlation function c_k is related to the structure factor S_k by $c_k = (1 - S_k^{-1})/n$, so that $1 + \beta n U_{\vec{k}}^- S_k^{-1} \approx c_k + \beta U_{\vec{k}} \approx 0$. By virtue of the RPA, the additional terms cancel, leading to the lowest-order mode-coupling memory kernel.

Based on the above description, a simple procedure to derive the mode-coupling memory kernels follows. The GLE for a set of slow variables A defines an expression for the random force $f(t) = \dot{A} - i\Omega A - K * A$. The fluctuation-dissipation relation $K(t) = \langle f(t) f(0) \rangle$ determines a self-consistent equation for the memory kernel. The first term in the equation, $\langle \dot{A} \dot{A} \rangle$, is rewritten in terms of the interaction potential and the bilinear density mode, and is then decomposed into products of linear hydrodynamic correlation functions. Several other terms, including the self-consistent terms, are removed under the random phase approximation or mean-field approximations of a similar nature. Although we use this procedure in our derivation, we can obtain exactly the same mode-coupling expression from the simpler scheme introduced in Ref. [10] and in Eqs. (6) and (7). In fact, the removal of the self-consistent terms of the memory kernel in Eq. (9) justifies the direct evaluation of the memory

kernel [10]. The random force can be written as $f=(1-Q)iLA\approx\int d\vec{k}U(\vec{k})A_2(\vec{k},t)$, where A_2 is the correlation function of bilinear modes. Then Gaussian factorization leads to $K(t)=\langle f(t)f(0)\rangle\approx A(\vec{k},t)A(\vec{k},t)$, which recovers the mode-coupling memory kernel.

III. VELOCITY AUTOCORRELATION FUNCTION

The velocity autocorrelation function of one tagged particle in liquids has a long-time tail, which decays as $t^{-3/2}$ [22]. Mode-coupling theory successfully explains this long-time tail. We apply the approach outlined earlier to derive the same mode-coupling effects predicted by other methods [17,23,24]. We first use a basis set with a single element $A=v_{1t}(t)$. Using the projection operator method, we write the random force as $f(t)=\dot{A}(t)+\int_0^t K(t-\tau)A(\tau)d\tau$, where the kernel is given by the fluctuation-dissipation theorem,

$$K(t)=m\beta\langle f(t)f^*\rangle =m\beta\left\langle\left[\dot{A}(t)+\int_0^t K(t-\tau)\dot{A}(\tau)d\tau\right]A^*\right\rangle. \quad (10)$$

Expressing $\dot{A}(t)$ in Fourier space,

$$\dot{A}(t)=\sum_{\vec{q}\neq 0}\frac{iq_x}{m_1V}U_{1q}\rho_1(-\vec{q},t)[\rho(\vec{q},t)-\rho_1(\vec{q},t)], \quad (11)$$

the correlation function of the random force becomes

$$\begin{aligned} \langle f(t)f^*\rangle &= \sum_{\vec{q},\vec{q}'}\frac{q_xq'_x}{m_1^2V^2}U_{1\vec{q}}U_{1\vec{q}'}\langle\{\rho_1(-\vec{q},t)[\rho(\vec{q},t) \\ &\quad -\rho_1(\vec{q},t)]\}\{\rho_1(-\vec{q}',t)[\rho(\vec{q}',t)-\rho_1(\vec{q}',t)]\}\rangle^* \\ &\quad +\int_0^t K(t-\tau)\langle A(\tau)A^*\rangle, \end{aligned} \quad (12)$$

where the density of the tagged particle is $\rho_1(\vec{k},t)=\exp[i\vec{k}\cdot\vec{r}_1(t)]$. With Gaussian factorization and the RPA (i.e., $c_{1\vec{k}}\approx-\beta U_{1\vec{k}}$), the mode-coupling memory kernel becomes

$$K(t)=\frac{n}{V}\sum_{\vec{q}}q_x^2c_{1\vec{q}}^2F_{\vec{q}}^s(t)F_{\vec{q}}(t), \quad (13)$$

where the self-intermediate scattering function is defined as $F_{\vec{k}}^s(t)=\langle\rho_1(\vec{k},t)\rho_1(-\vec{k})\rangle$. This result can also be obtained by inserting the projection operator of the bilinear mode $\rho_{1\vec{k}}\rho_{\vec{k}}^*$ into $K(t)$. Clearly, this bilinear mode arises from the expansion of $\dot{v}_{1t}(t)$ in Fourier space.

Next we study the time evolution of the longitudinal current and the density of the tagged particle. Unlike the basis set for the collective density, this basis set includes the double time derivative of the tagged particle density because the single longitudinal current is not a conserved quantity

even for zero wave vector. Using the projection operator method, the GLE for the three-basis-set elements is written as

$$\begin{aligned} \frac{d}{dt}\begin{pmatrix} \rho_1(\vec{k},t) \\ \dot{\rho}_1(\vec{k},t) \\ \ddot{\rho}_1(\vec{k},t) \end{pmatrix} &= \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & -(3\omega_0^2+\Omega_0^2) & 0 \end{pmatrix} \begin{pmatrix} \rho_1(\vec{k},t) \\ \dot{\rho}_1(\vec{k},t) \\ \ddot{\rho}_1(\vec{k},t) \end{pmatrix} \\ &\quad + \begin{pmatrix} 0 \\ 0 \\ f_3(t) \end{pmatrix} - \int_0^t \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ K_{31}(\tau) & 0 & K_{33}(\tau) \end{pmatrix} \\ &\quad \times \begin{pmatrix} \rho_1(\vec{k},t-\tau) \\ \dot{\rho}_1(\vec{k},t-\tau) \\ \ddot{\rho}_1(\vec{k},t-\tau) \end{pmatrix} d\tau, \end{aligned} \quad (14)$$

where the random force is given by

$$\begin{aligned} f_3(t) &= \frac{d}{dt}\dot{\rho}_1(\vec{k},t)+(3\omega_0^2+\Omega_0^2)\dot{\rho}_1(\vec{k},t) \\ &\quad +\int_0^t K_{31}(t-\tau)\rho_1(\vec{k},\tau)d\tau \\ &\quad +\int_0^t K_{33}(t-\tau)\ddot{\rho}_1(\vec{k},\tau)d\tau. \end{aligned} \quad (15)$$

$\omega_0^2=k^2/(m\beta)$ and Ω_0 is the Einstein frequency, $\Omega_0^2=\langle\Delta^2U(r)\rangle/3m$. Then, $d\dot{\rho}_1(\vec{k},t)/dt$ is explicitly expanded as

$$\begin{aligned} \frac{d}{dt}\dot{\rho}_1(\vec{k},t) &= -ik^3v_{1z}^3(t)e^{i\vec{k}\cdot\vec{r}_1(t)} \\ &\quad -3ik^2\sum_{\vec{q}}\frac{q_z}{m_1V}U_{1\vec{q}}j_{1z}(\vec{k}-\vec{q},t)\rho(\vec{q},t) \\ &\quad +i\sum_{\vec{q}}\frac{kq_z}{m_1V}U_{1\vec{q}}[q_\alpha j_{1\alpha}(\vec{k}-\vec{q},t)]\rho(\vec{q},t) \\ &\quad -i\sum_{\vec{q}}\frac{kq_z}{m_1V}U_{1\vec{q}}[q_\alpha j_\alpha(\vec{q},t)]\rho_1(\vec{k}-\vec{q},t), \end{aligned} \quad (16)$$

where $j_\alpha(\vec{k},t)$ is the collective current density function along the α axis, $j_\alpha(\vec{k},t)=\sum_{n=1}^Nv_\alpha(t)\exp[i\vec{k}\cdot\vec{r}_n(t)]$, $j_{1\alpha}(\vec{k},t)$ is the single current density function along the α axis, $j_\alpha(\vec{k},t)=v_{1\alpha}(t)\exp[i\vec{k}\cdot\vec{r}_1(t)]$, and the repeated α indicates the sum over the three Cartesian axes. By substituting Eq. (15) into the expression for the random force, the memory kernel matrix is calculated from the fluctuation-dissipation relationships, using the approximations $\Omega_0=0$, $F_{\vec{k}}(t)=S_kF_{\vec{k}}^s(t)$, and $c_{1\vec{k}}=-\beta U_{1\vec{k}}$, and applying the Gaussian factorization procedure. The correlation function of the random force simplifies to

$$\langle f_3(t)f_3^* \rangle = \sum_q \frac{2Nk^2 q_z^2 U_1^2 \bar{q}}{m_1^2 V^2} [C_{k-\bar{q},x}^s(t) F_{\bar{q}}(t) + F_{k-\bar{q}}^s(t) C_{\bar{q},x}(t)]. \quad (17)$$

In the above equation, we ignore the longitudinal current correlation functions, which decay faster than the transverse current correlation functions. Equation (17) gives the same result as the mode-coupling theory (MCT) expression obtained by inserting the bilinear mode $\rho_{1,k-\bar{q}} \bar{q}_z$ [21].

IV. BILINEAR DENSITY MODES

A. GLE

In this section, we study the time evolution of the bilinear collective density mode used in calculating Raman spectra of liquids. The bilinear modes $\rho(\vec{k},t)\rho(-\vec{k},t)$ do not follow simple hydrodynamic equations. Calculations of the bilinear density correlation function have been carried out, particularly, in the context of Raman spectra [10,25,26,27]. A simple approach to evaluating the bilinear correlation function is to decompose the four-point correlation function into the product of two linear density correlation functions [10]. Here we apply the proposed scheme to obtain the time evolution of the bilinear density with the mode-coupling memory kernel and, in the next subsection, we compare the

MCT result with simple Gaussian factorization to establish the validity of the Gaussian factorization scheme.

A three-element basis set of bilinear modes is constructed,

$$A(t) = \begin{pmatrix} A_1(t) \\ A_2(t) \\ A_3(t) \end{pmatrix} = \begin{pmatrix} \rho(\vec{k},t)\rho(-\vec{k},t) \\ \rho(\vec{k},t)P(-\vec{k},t) + \rho(-\vec{k},t)P(\vec{k},t) \\ P(\vec{k},t)P(-\vec{k},t) \end{pmatrix}, \quad (18)$$

where $P(\vec{k},t)$ is the momentum density function, $P(\vec{k},t) = \sum_{n=1}^N P_{nz} \exp\{i\vec{k} \cdot \vec{r}_n(t)\}$, and P_{nz} is the longitudinal momentum of the n th particle. A similar basis set was used by Madden for analyzing a depolarized Raman spectrum [25]. As an approximation, we neglect temperature fluctuations because the effects of the temperature fluctuations are smaller than the coupling between the density and momentum fluctuations [28].

We derive the GLE for this basis set with the projection operator approach. A complete description of the projection operator includes the projection onto different wave vectors. However, according to Madden and to Keyes and Oppenheim, the dominant contribution arises from the diagonal elements with the same wave vectors, which allows us to ignore the mixing effects of different wave vectors in our derivation [25,29]. The susceptibility matrix of this basis set is

$$(A, A^\dagger) = \begin{pmatrix} N^2 S_k^{(4)} & 0 & -N^2 m \beta^{-1} S_k \\ 0 & 2Nm\beta^{-1} [NS_k - \text{Re}(S_{k,k,-2k}^{(3)})] & 0 \\ -N^2 m \beta^{-1} S_k & 0 & Nm^4 \langle v_z^4 \rangle + Nm^2 \beta^{-2} (2N + S_{2k} - 3) \end{pmatrix}. \quad (19)$$

In Eq. (19), $S_k^{(4)}$ is the four-point equilibrium distribution correlation function, defined as $\langle \rho_{\vec{k}} \rho_{\vec{k}} \rho_{-\vec{k}} \rho_{-\vec{k}} \rangle / N^2$, which reduces to $2S_k^2$ for a Gaussian system; $S_{k,k,-2k}^{(3)}$ is the three-point equilibrium distribution correlation function, defined as $\langle \rho_{\vec{k}} \rho_{\vec{k}} \rho_{-2\vec{k}} \rangle / N$, which has the same N order as S_k . The GLE is explicitly given as

$$\begin{pmatrix} \dot{A}_1(t) \\ \dot{A}_2(t) \\ \dot{A}_3(t) \end{pmatrix} = i \begin{pmatrix} 0 & \Omega_{12} & 0 \\ \Omega_{21} & 0 & \Omega_{23} \\ 0 & \Omega_{32} & 0 \end{pmatrix} \begin{pmatrix} A_1(t) \\ A_2(t) \\ A_3(t) \end{pmatrix} - \begin{pmatrix} K_{11} & K_{12} & K_{13} \\ K_{21} & K_{22} & K_{23} \\ K_{31} & K_{32} & K_{33} \end{pmatrix} * \begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix} + \begin{pmatrix} f_1(t) \\ f_2(t) \\ f_3(t) \end{pmatrix}, \quad (20)$$

where the eigenfrequencies are

$$\begin{aligned} \Omega_{12} &= \frac{k}{m}, \\ \Omega_{21} &= \frac{k}{m} \frac{2m[3NS_k + 2S_k S_{2k} - 2S_k^2 - 2\text{Re}(S_{k,k,-2k}^{(3)}) - S_{2k} \text{Re}(S_{k,k,-2k}^{(3)})/N]}{\beta[N(2S_k^{(4)} - S_k^2) + S_{2k} S_k^{(4)}]}, \\ \Omega_{23} &= \frac{k}{m} \frac{2[N(S_k^{(4)} + S_k^2) + S_{2k} S_k^{(4)} - 2S_k S_k^{(4)} - S_k \text{Re}(S_{k,k,-2k}^{(3)})]}{N(2S_k^{(4)} - S_k^2) + S_{2k} S_k^{(4)}}, \\ \Omega_{32} &= \frac{k}{m} \frac{m(N + S_{2k} - 2S_k)}{NS_k - \text{Re}(S_{k,k,-2k}^{(3)})}, \end{aligned} \quad (21)$$

with $*$ representing a convolution, $A*B = \int_0^t A(t-\tau)B(\tau)d\tau$. When the equilibrium system is Gaussian, the eigenfrequencies simplify to

$$\Omega_{12} \approx \frac{k}{m}, \quad \Omega_{21} \approx \frac{2k}{\beta S_k}, \quad \Omega_{23} \approx \frac{2k}{m}, \quad \Omega_{32} \approx \frac{k}{\beta S_k}, \quad (22)$$

which is accurate to the order of N^{-1} . The random forces are given as

$$f_1(t) = 0,$$

$$f_2(t) = \dot{A}_2(t) - i\Omega_{21}A_1(t) - i\Omega_{23}A_3(t) + K_{21}*A_1 + K_{22}*A_2 + K_{23}*A_3,$$

$$f_3(t) = \dot{A}_3(t) - i\Omega_{32}A_2(t) + K_{31}*A_1 + K_{32}*A_2 + K_{33}*A_3, \quad (23)$$

with $\dot{A}_2(t)$ and $\dot{A}_3(t)$ explicitly expressed as

$$\dot{A}_2(t) = i \frac{k}{m} [2A_3(t) + E(\vec{k}, t)\rho^*(\vec{k}, t) + E^*(\vec{k}, t)\rho(\vec{k}, t)], \quad (24)$$

$$\dot{A}_3(t) = i \frac{k}{m} [E(\vec{k}, t)P(-\vec{k}, t) + E^*(\vec{k}, t)P(\vec{k}, t)], \quad (25)$$

and $E(\vec{k}, t)$ defined as

$$E(\vec{k}, t) = \sum_{n=1}^N P_{nz}^2 e^{i\vec{k} \cdot \vec{r}_n(t)} + \frac{m}{V} \sum_q \frac{U_q q_z}{k} \rho(\vec{k} - \vec{q}, t) \rho(\vec{q}, t). \quad (26)$$

Within the proposed scheme, we assume that the equilibrium system is close to Gaussian, which allows us to use the eigenfrequencies in Eq. (22) instead of Eq. (21). The multipoint correlation functions, e.g., $\langle \rho(\vec{k} - \vec{q}, t) \rho(\vec{q}, t) \rho(-\vec{k}, t) \rho^*(\vec{k} - \vec{q}', t) \rho^*(\vec{q}', t) \rho(\vec{k}, t) \rangle$, are factored as $N^3 F_{\vec{k}}(t) F_{\vec{k}-\vec{q}}(t) F_{\vec{q}}(t)$. In addition, the RPA relation $c_{\vec{k}} = -\beta U_{\vec{k}}$ removes the linear terms in the memory kernel matrix. A complicated random phase approximation to the three- and four-body interactions is required here. Since we assume that the equilibrium system is Gaussian, the additional many-body terms reduce to pair interaction terms. Using these approximations, the three nonzero elements of the memory kernel matrix are

$$K_{22}(t) \approx \frac{n}{mk^2 \beta V S_k} \sum_{q \neq k} C(k, q) F_{\vec{k}-\vec{q}}(t) F_{\vec{q}}(t) F_{\vec{k}}(t),$$

$$K_{31}(t) \approx \frac{2n}{3S_k k^2 \beta^2 V} \sum_{q \neq k} C(k, q) F_{\vec{k}-\vec{q}}(t) F_{\vec{q}}(t) \Phi_{PP, \vec{k}}(t),$$

$$K_{33}(t) \approx \frac{4n}{3mk^2 \beta V} \sum_{q \neq k} C(k, q) F_{\vec{k}-\vec{q}}(t) F_{\vec{q}}(t) \Phi_{PP, \vec{k}}(t), \quad (27)$$

where

$$C(k, q) = c_q^2 (\vec{k} \cdot \vec{q})^2 + c_q c_{|\vec{k}-\vec{q}|} [\vec{k} \cdot (\vec{k} - \vec{q})],$$

$$\Phi_{PP, \vec{k}}(t) = \frac{\beta \langle P_{\vec{k}}(t) P_{\vec{k}}^*(0) \rangle}{Nm}. \quad (28)$$

Equations (20) and (27) relate the bilinear density correlation function to the linear density correlation function and give the explicit mode-coupling memory kernel matrix for evaluating the bilinear density correlation function. In principle, once fast-decay memory kernels are incorporated, we can explicitly evaluate the relaxation of the bilinear collective density over the complete time scale and predict the non-Gaussian effects of the bilinear density correlation function. In this paper, we do not make this explicit calculation; instead, we examine the long-time behavior of the bilinear density correlation function and the nature of Gaussian factorization in the next section.

B. Non-Gaussian effects

In the hydrodynamic limit, we can apply the Gaussian factorization directly to the four-point density correlation function to yield the product of two linear density correlation functions. In the previous section, the mode-coupling equation for the bilinear mode is derived using the Gaussian approximation. As stated earlier, the GLE describes the true dynamics, which is neither linear nor Gaussian, whereas the Gaussian approximation introduces a closure to the hierarchical equation. In a sense, the Gaussian approximation is not compatible with the nonlinear nature of the GLE. Thus, we can explore this inconsistency by calculating the error introduced by non-Gaussian effects. In this section, we examine the nature of non-Gaussian effects within the framework of the mode-coupling equation for the bilinear mode and demonstrate that the non-Gaussian effects can be quantified by the nonexponential decay of the linear hydrodynamic mode.

In Sec. IV A, we use the GLE to describe the time evolution of the bilinear collective density and explicitly derive eigenfrequencies and mode-coupling memory kernels. The expressions thus obtained are

$$\dot{A}_1(t) = i \frac{k}{m} A_2(t),$$

$$\dot{A}_2(t) = i \frac{2k}{\beta S_k} A_1(t) + i \frac{2k}{m} A_3(t) - K_{22}*A_2 + f_2(t),$$

$$\dot{A}_3(t) = i \frac{2k}{\beta S_k} A_2(t) - K_{31}*A_1 - K_{33}*A_3 + f_3(t), \quad (29)$$

where the equilibrium system is assumed to be Gaussian, and the memory kernels are from Eq. (20). Since the above memory kernels do not include the fast-decay friction in the short time, we focus on the long-time behavior of the system. As stated in the Introduction, we can either apply the Gaussian factorization directly to the bilinear correlation function

and obtain a simple Gaussian expression, or apply the Gaussian factorization to the memory kernel to obtain a mode-coupling expression. These two procedures leads to inconsistency between the nonlinear memory kernel and the linear Gaussian factorization. Therefore, we can evaluate the non-Gaussian behavior by comparing the results obtained from direct factorization and from factoring the mode-coupling memory kernel.

Direct Gaussian factorization of $\langle A_1(t)A_1 \rangle$ yields $\langle A_1(t)A_1 \rangle_G = N^2 F_k^2(t)$. From Eq. (29) the first-order time derivative of $\langle A_1(t)A_1^* \rangle$ is

$$\langle \dot{A}_1(t)A_1^* \rangle = i \frac{k}{m} \langle A_2(t)A_1^* \rangle, \quad (30)$$

which, after Gaussian factorization, becomes

$$\langle \dot{A}_1(t)A_1^* \rangle_G = 2N^2 F_k^{\dot{}}(t) \dot{F}_k^{\dot{}}(t). \quad (31)$$

The first-order time derivative of $N^2 F_k^2(t)$ gives the same result, i.e., $\langle \dot{A}_1(t)A_1^* \rangle_G = d/dt[\langle A_1(t)A_1^* \rangle_G]$, which demonstrates that the Gaussian factorization scheme of MCT is consistent for the first-order time derivative.

The second-order time derivative of $\langle A_1(t)A_1^* \rangle$ is

$$\begin{aligned} \left\langle \frac{d^2}{dt^2} A_1(t)A_1^* \right\rangle &= -2 \frac{k^2}{m\beta S_k} \langle A_1(t)A_1^* \rangle - 2 \frac{k^2}{m^2} \langle A_3(t)A_1^* \rangle \\ &\quad - \int_0^t K_{22}(t-\tau) \langle \dot{A}_1(\tau)A_1^* \rangle d\tau, \end{aligned} \quad (32)$$

which, after Gaussian factorization, becomes

$$\begin{aligned} \left\langle \frac{d^2}{dt^2} A_1(t)A_1^* \right\rangle_G &= -2 \omega_k^2 N^2 F_k^2(t) - 2N^2 \dot{F}_k^2(t) \\ &\quad - \frac{2nN^2}{mk^2\beta V S_k} \sum_{q \neq k} C(k,q) \\ &\quad \times \int_0^t F_{k-\vec{q}}^{\dot{}}(t-\tau) F_{\vec{q}}^{\dot{}}(t-\tau) F_k^{\dot{}}(t-\tau) \\ &\quad \times F_k^{\dot{}}(\tau) \dot{F}_k^{\dot{}}(\tau) d\tau. \end{aligned} \quad (33)$$

To simplify the above equation, we notice that $F_k^{\dot{}}(t-\tau) \dot{F}_k^{\dot{}}(\tau)$ reduces to $F_k^{\dot{}}(t) S_k$ when $\tau \rightarrow 0$ or t . This equivalence holds for the exponential expression, which corresponds to the hydrodynamic limit. Therefore, we introduce a difference function defined by $F_k^{\dot{}}(t-\tau) \dot{F}_k^{\dot{}}(\tau) = F_k^{\dot{}}(t) S_k + \Delta(t,\tau)$. To be consistent, the mode-coupling equation of the intermediate scattering function $F_k^{\dot{}}(t)$ is used for its second-order derivative, giving

$$\begin{aligned} \dot{F}_k^{\dot{}}(t) &= -\omega_k^2 F_k^{\dot{}}(t) - \sum_{\vec{q} \neq k} \frac{n}{mk^2\beta V} C(\vec{k},\vec{q}) \\ &\quad \times \int_0^t F_{k-\vec{q}}^{\dot{}}(t-\tau) F_{\vec{q}}^{\dot{}}(t-\tau) \dot{F}_k^{\dot{}}(\tau) d\tau. \end{aligned} \quad (34)$$

Substituting the above equation into Eq. (33), the final result simplifies to

$$\begin{aligned} \left\langle \frac{d^2}{dt^2} A_1(t)A_1^* \right\rangle_G &= 2N^2 \dot{F}_k^{\dot{}}(t) F_k^{\dot{}}(t) + 2N^2 \dot{F}_k^2(t) \\ &\quad - \frac{2nN^2}{mk^2\beta V S_k} \sum_{q \neq k} C(k,q) \\ &\quad \times \int_0^t \Delta(t,\tau) F_{k-\vec{q}}^{\dot{}}(t-\tau) F_{\vec{q}}^{\dot{}}(t-\tau) \\ &\quad \times \dot{F}_k^{\dot{}}(\tau) d\tau. \end{aligned} \quad (35)$$

Then, the difference between the two Gaussian factorization schemes, i.e., the non-Gaussian deviation, is

$$\begin{aligned} \left\langle \frac{d^2}{dt^2} A_1(t)A_1^* \right\rangle - \frac{d^2}{dt^2} \langle A_1(t)A_1^* \rangle_G &= -\frac{2nN^2}{mk^2\beta V S_k} \sum_{q \neq k} C(k,q) \int_0^t \Delta(t,\tau) F_{k-\vec{q}}^{\dot{}}(t-\tau) \\ &\quad \times F_{\vec{q}}^{\dot{}}(t-\tau) \dot{F}_k^{\dot{}}(\tau) d\tau, \end{aligned} \quad (36)$$

which depends on the difference function $\Delta(t,\tau)$.

Equation (36) relates the non-Gaussian behavior of the bilinear correlation function to the non-Markovian nature of the correlation functions. The difference function $\Delta(t,\tau)$ starts from zero and reaches a maximum at an intermediate time, and then decays to zero in the hydrodynamics limit. Therefore, the difference function explains the non-Gaussian behavior observed numerically [12,13]. If the system is in the hydrodynamic limit, the bilinear time correlation function is Gaussian in the second-order time derivative. In this limit, the mode-coupling equation for the bilinear density is consistent with the mode-coupling equation for the linear density up to the second-order time derivative. Thus, up to second order, Gaussian factorization is a good approximation for normal liquids in the long-time limit because $\Delta(t,\tau)$ is small compared to $F_k^{\dot{}}(t) S_k$. The relaxation in glasses strongly deviates from exponential decay, making the nonexponential factor $\Delta(t,\tau)$ important in determining the non-Gaussian behavior of the glass system.

As the last step, we calculate the third-order time derivative of $\langle A_1(t)A_1^* \rangle$. The higher-order time derivatives are unnecessary because the original equations for this basis set are only exact at the third order, and the higher-order time derivatives repeat the results of these three lower-order derivatives. From Eq. (29), the third-order time derivative of $\langle A_1(t)A_1^* \rangle$ is written as

$$\begin{aligned} \left\langle \frac{d^3}{dt^3} A_1(t)A_1^* \right\rangle &= -2 \frac{k^2}{m\beta S_k} \langle \dot{A}_1(t)A_1^* \rangle - 2 \frac{k^2}{m^2} \langle \dot{A}_3(t)A_1^* \rangle \\ &\quad - \frac{d}{dt} \int_0^t K_{22}(t-\tau) \langle \dot{A}_1(\tau)A_1^* \rangle d\tau. \end{aligned} \quad (37)$$

Similarly to the second-order calculations, we rewrite the equation as

$$\begin{aligned}
 F_{\vec{k}}^-(t-\tau)\langle\ddot{A}_1(\tau)A_1^*\rangle_G &= N^2 S_k [2\dot{F}_{\vec{k}}^-(t)\dot{F}_{\vec{k}}^-(\tau) + \ddot{F}_{\vec{k}}^-(t)F_{\vec{k}}^-(\tau) \\
 &\quad + \ddot{F}_{\vec{k}}^-(\tau)F_{\vec{k}}^-(t)] + \Delta_1(t, \tau), \\
 \Phi_{PP, \vec{k}}(t-\tau)\langle A_1(\tau)A_1^*\rangle_G &= \frac{N^2 S_k m \beta}{k^2} \ddot{F}_{\vec{k}}^-(t)F_{\vec{k}}^-(\tau) + \Delta_2(t, \tau), \\
 \Phi_{PP, \vec{k}}(t-\tau)\langle A_3(\tau)A_1^*\rangle_G &= \frac{N^2 m^2}{k^2} \dot{F}_{\vec{k}}^-(t)\dot{F}_{\vec{k}}^-(\tau) + \Delta_3(t, \tau).
 \end{aligned} \tag{38}$$

$\Delta_i(t, \tau)$ are quantities similar to $\Delta(t, \tau)$ used in the second-order time derivative and also vanish in the hydrodynamic limit. The factored result for the third-order time derivative of $\langle A_1(t)A_1^* \rangle$ is

$$\begin{aligned}
 \left\langle \frac{d^3}{dt^3} A_1(t)A_1^* \right\rangle_G &= \frac{d^3}{dt^3} \langle A_1(t)A_1^* \rangle_G \\
 &\quad + \frac{n^2 \beta N}{mk^2} \sum_{\vec{q} \neq \vec{k}} C(\vec{k}, \vec{q}) \int_0^t d\tau F_{\vec{k}-\vec{q}}^-(t-\tau) \\
 &\quad \times F_{\vec{q}}^-(t-\tau) \Delta \mathcal{F}(t, \tau),
 \end{aligned} \tag{39}$$

with

$$\begin{aligned}
 \Delta \mathcal{F}(t, \tau) &= \frac{7}{3} \ddot{F}_{\vec{k}}^-(t)F_{\vec{k}}^-(\tau) - F_{\vec{k}}^-(t)\ddot{F}_{\vec{k}}^-(\tau) \\
 &\quad - \frac{4}{3} \dot{F}_{\vec{k}}^-(t)\dot{F}_{\vec{k}}^-(\tau) + \sum_{i=1}^3 \Delta_i(t, \tau),
 \end{aligned} \tag{40}$$

which vanishes in the hydrodynamic limit. Thus, in agreement with the second-derivative result, $\langle (d^3/dt^3)A_1(t)A_1^* \rangle_G$ and $(d^3/dt^3)\langle A_1(t)A_1^* \rangle_G$ are the same in the hydrodynamic limit.

Our results demonstrate the strong correlation between the non-Gaussian behavior of the bilinear correlation function and the nonexponential decay of linear hydrodynamic modes. For simple liquids close to the hydrodynamic limit, Gaussian factorization is a good approximation to the bilinear correlation function because $\Delta \mathcal{F}(t, \tau)$ is a small quantity. For complex liquid systems, $\Delta \mathcal{F}(t, \tau)$ is significant and the non-Gaussian behavior becomes more prominent. For glassy systems, the regime of nonhydrodynamic relaxation and the peak value of the non-Gaussian behavior increase with decreasing temperature. These conclusions are consistent with experiments and simulations.

V. LINEAR MOLECULAR LIQUIDS

In this section, we derive MCT for liquid systems consisting of linear molecules such as CS_2 . Linear molecular liquids are a bridge between atomic liquids that have no rotation and vibration degrees of freedom and nonlinear molecule liquids that have more complicated coupling

among the rotational, translational, and vibrational degrees of freedom. For the linear molecule liquid, we study the coupling among different degrees of freedom, which provides guidance for understanding more complicated liquids [30,31]. The coupling between rotation and translation is more important than couplings involving vibrations since these two degrees of freedom have similar relaxation time scales. In our derivation, we focus on the rotation-translational couplings and consider the molecule as a rigid rotor without vibrations. In this section, we use our simplified scheme to explore the hydrodynamic equations of motion in linear molecular liquids. The resulting MCT equations are essentially equivalent to those based on angular expansion [32,33] but are different in format from those based on the interaction-site picture [34].

Because of the coupling between translation and rotation, the collective density of linear molecular liquids is expanded both in the wave vector space and in the spherical harmonic space, resulting in the expression $\rho_\lambda(\vec{k}, t) = \sum_{n=1}^N \exp\{i\vec{k} \cdot \vec{r}_n(t)\} Y_\lambda(\Omega_n(t))$. In this definition, the basis-set function of the rotational space is $Y_\lambda(\Omega_n(t))$, where λ is a set of eigenvalues representing the spherical harmonic function, $\lambda = \{l, m\}$. Unlike the atomic liquid, where the basis set for the GLE is the collective density and the longitudinal translational current, the basis set of hydrodynamic modes for the linear molecular liquid is $A = \{\rho_\lambda(\vec{k}, t), j_{\lambda, z}^T(\vec{k}, t), j_{\lambda}^R(\vec{k}, t)\}$, which includes both translational and rotational currents. In this basis set, the longitudinal current is $j_{\lambda, z}^T(\vec{k}, t) = \sum_n v_{n, z}(t) \exp\{i\vec{k} \cdot \vec{r}_n(t)\} Y_\lambda(\Omega_n(t))$, and the rotational current is $j_{\lambda, \gamma}^R(\vec{k}, t) = \sum_n \omega_{n, \gamma}(t) \exp\{i\vec{k} \cdot \vec{r}_n(t)\} Y_\lambda(\Omega_n(t))$, where $\gamma = x, y, z$ represents the Cartesian coordinates. For this basis set, the non-zero elements of the susceptibility matrix are

$$\langle \rho_\lambda(\vec{k}) \rho_{\lambda'}^*(\vec{k}) \rangle = N S_{\lambda\lambda'}(k),$$

$$\langle j_{\lambda, \gamma}^\alpha(\vec{k}) j_{\lambda', \gamma'}^{*\alpha'}(\vec{k}) \rangle = \frac{N}{I_\alpha \beta} \delta_{\alpha\alpha'} \delta_{\gamma\gamma'} \delta_{\lambda\lambda'}, \tag{41}$$

with

$$I_\alpha = \begin{cases} M, & \alpha = T, \\ I, & \alpha = R. \end{cases} \tag{42}$$

In the above equation, M is the mass of the linear molecule and I is its inertial moment tensor. To construct the GLE, we calculate the first-order time derivative of the collective density,

$$\begin{aligned}
 \frac{d}{dt} \rho_\lambda(\vec{k}, t) &= \sum_{n=1}^N i k v_{nz} e^{i\vec{k} \cdot \vec{r}_n(t)} Y_\lambda(\Omega_n(t)) \\
 &\quad + \sum_{n=1}^N e^{i\vec{k} \cdot \vec{r}_n(t)} i [\vec{L} Y_\lambda(\Omega_n(t))] \vec{\omega}_n(t),
 \end{aligned} \tag{43}$$

where \vec{L} is the angular momentum operator. This equation simplifies to

$$\begin{aligned} \frac{d}{dt} \rho_{\lambda}(\vec{k}, t) &= ik j_{\lambda, z}^T(\vec{k}, t) + \frac{im^+}{2} j_{\lambda^+, x}^R(\vec{k}, t) + \frac{im^-}{2} j_{\lambda^-, x}^R(\vec{k}, t) \\ &+ \frac{m^+}{2} j_{\lambda^+, y}^R(\vec{k}, t) - \frac{m^-}{2} j_{\lambda^-, y}^R(\vec{k}, t) + im j_{\lambda, z}^R(\vec{k}, t), \end{aligned} \quad (44)$$

with

$$\begin{aligned} m^+ &= \sqrt{l(l+1) - m(m+1)}, \quad m^- = \sqrt{l(l+1) - m(m-1)}, \\ \lambda^+ &= \{l, m+1\}, \quad \lambda^- = \{l, m-1\}. \end{aligned} \quad (45)$$

Using these equations, we derive the first-order time derivative of the longitudinal translational current. Since there is no equilibrium coupling between the first-order moments of the current, the only nonzero eigenfrequencies come from the coupling between the longitudinal-translational current and the collective density. The first-order time derivative of the longitudinal-translational current is

$$\frac{d}{dt} j_{\lambda, z}^T(\vec{k}, t) = i \Omega_{\lambda\lambda}^{T, z} \rho_{\lambda'}(k, t) + K_{\lambda z, \lambda' \gamma}^{T, \alpha} j_{\lambda' \gamma}^{\alpha} + f_{\lambda, z}^T(\vec{k}, t), \quad (46)$$

where $K_{\lambda z, \lambda' \gamma}^{T, \alpha}$ represents the memory kernels between the longitudinal-translational currents and all the other possible currents. The repeated symbols indicate summation over all modes. The resulting eigenfrequencies are

$$i \Omega_{\lambda, \lambda'}^{T, z} = (j_{\lambda, z}^T(\vec{k}), \rho_{\lambda'}^*(\vec{k})) (\rho_{\lambda''}(\vec{k}) \rho_{\lambda'}^*(\vec{k}))^{-1} = \frac{ik}{M\beta} (S^{-1})_{\lambda, \lambda'}, \quad (47)$$

and the random forces for the longitudinal-translational currents are

$$\begin{aligned} f_{\lambda, z}^T(\vec{k}, t) &= \frac{d}{dt} j_{\lambda, z}^T(\vec{k}, t) - \frac{ik}{M\beta} (S^{-1})_{\lambda, \lambda'} \rho_{\lambda'}(\vec{k}, t) \\ &- K_{\lambda z, \lambda' \gamma}^{T, \alpha} j_{\lambda' \gamma}^{\alpha}. \end{aligned} \quad (48)$$

If the potential of the system is dominated by the two-body interaction, the first-order time derivative of $j_{\lambda, z}^T(\vec{k}, t)$ can be expanded in the wave vector space and the spherical harmonic space. From the previous sections, the mode-coupling memory kernels arise from the bilinear-bilinear terms and the other terms vanish in the mean-field approximation. As a result, only the bilinear-bilinear terms remain in the first-order time derivative for the longitudinal-translational current, giving

$$\begin{aligned} \frac{d}{dt} j_{\lambda, z}^T(\vec{k}, t) &\simeq \sum_{q, \lambda_1, \lambda_2, \lambda_3} \frac{iq_z}{MV} U(\lambda_1, \lambda_2, \vec{q}) \\ &\times D(\lambda, \lambda_1, \{\lambda_3\}) \rho_{\lambda_3}(\vec{k} - \vec{q}, t) \rho_{\lambda_2}(\vec{q}, t), \end{aligned} \quad (49)$$

where $U(\lambda_1, \lambda_2, \vec{q})$ is the two-body interaction term expanded in the wave vector and spherical harmonic spaces. The constant $D(\lambda, \lambda_1, \lambda_3)$ is

$$\begin{aligned} D(\lambda_1, \lambda_2, \lambda_3) &= \left[\frac{(2l_1+1)(2l_2+1)}{2l_3+1} \right]^{1/2} C(l_1 l_2 l_3; 000) \\ &\times C(l_1 l_2 l_3; m_1 m_2 m_3), \end{aligned} \quad (50)$$

where $C(l_1 l_2 l_3; m_1 m_2 m_3)$ are the Clebsch-Gordan coefficients. The mode-coupling memory kernels between the different longitudinal-translational currents are

$$\langle f_{\lambda, z}^T(\vec{k}, t) f_{\lambda', z}^{T, *}(\vec{k}) \rangle = \sum_{\vec{q}, \{\lambda\}, \{\lambda'\}} \frac{n^2 q_z U_1 D_1 D_2}{M^2} \mathcal{K}(t), \quad (51)$$

where

$$\begin{aligned} \mathcal{K}(t) &= q_z U_2 F_{\lambda_3, \lambda_3'}(\vec{k} - \vec{q}, t) F_{\lambda_2, \lambda_2'}(\vec{q}, t) \\ &+ (k - q_z) U_2' F_{\lambda_3, \lambda_2'}(\vec{k} - \vec{q}, t) F_{\lambda_2, \lambda_3'}(\vec{q}, t), \\ U_1 &= U(\lambda_1, \lambda_2, \vec{q}), \quad U_2 = U(\lambda_1', \lambda_2', \vec{q}), \\ U_2' &= U(\lambda_1', \lambda_2', \vec{k} - \vec{q}), \\ D_1 &= D(\lambda, \lambda_1, \lambda_3), \quad D_2 = D(\lambda', \lambda_1', \lambda_3'). \end{aligned} \quad (52)$$

The same approach can be used to derive the nonlinear terms of the first-order time derivatives of the other currents. As a result, we obtain all possible mode-coupling memory kernels from these nonlinear terms:

$$\langle f_{\lambda, z}^R(\vec{k}, t) f_{\lambda', z}^{T, *}(\vec{k}) \rangle = - \sum_{\vec{q}, \{\lambda\}, \{\lambda'\}} \frac{n^2 m_1 U_1 D_1 D_2}{MI} \mathcal{K}(t), \quad (53)$$

$$\begin{aligned} \langle f_{\lambda, x}^R(\vec{k}, t) f_{\lambda', z}^{T, *}(\vec{k}) \rangle \\ = - \sum_{\vec{q}, \{\lambda\}, \{\lambda'\}} \frac{n^2 (m_1^+ D_1^+ + m_1^- D_1^-) U_1 D_2}{2MI} \mathcal{K}(t), \end{aligned} \quad (54)$$

$$\begin{aligned} \langle f_{\lambda, y}^R(\vec{k}, t) f_{\lambda', y}^{T, *}(\vec{k}) \rangle \\ = \sum_{\vec{q}, \{\lambda\}, \{\lambda'\}} i \frac{n^2 (m_1^+ D_1^+ - m_1^- D_1^-) U_1 D_2}{2MI} \mathcal{K}(t), \end{aligned} \quad (55)$$

$$\langle f_{\lambda, z}^R(\vec{k}, t) f_{\lambda', z}^{R, *}(\vec{k}) \rangle = \sum_{\vec{q}, \{\lambda\}, \{\lambda'\}} \frac{n^2 m_1 m_1' U_1 D_1 D_2}{I^2} \mathcal{K}_1(t), \quad (56)$$

$$\begin{aligned} & \langle f_{\lambda,x}^R(\vec{k},t) f_{\lambda',z}^{R,*}(\vec{k}) \rangle \\ &= \sum_{\vec{q},\{\lambda\},\{\lambda'\}} \frac{n^2(m_1^+ D_1^+ + m_1^- D_1^-) m_1' U_1 D_2}{2I^2} \mathcal{K}_1(t), \end{aligned} \quad (57)$$

$$\begin{aligned} \langle f_{\lambda,x}^R(\vec{k},t) f_{\lambda',x}^{R,*}(\vec{k}) \rangle &= \sum_{\vec{q},\{\lambda\},\{\lambda'\}} \frac{n^2 U_1}{4I^2} (m_1^+ m_1'^+ D_1^+ D_2^+ \\ &+ m_1^- m_1'^- D_1^- D_2^- + m_1^+ m_1'^- D_1^+ D_2^- \\ &+ m_1^- m_1'^+ D_1^- D_2^+) \mathcal{K}_1(t), \end{aligned} \quad (58)$$

$$\begin{aligned} & \langle f_{\lambda,y}^R(\vec{k},t) f_{\lambda',z}^{R,*}(\vec{k}) \rangle \\ &= \sum_{\vec{q},\{\lambda\},\{\lambda'\}} \frac{in^2(m_1^- D_1^- - m_1^+ D_1^+) m_1' U_1 D_2}{2I^2} \mathcal{K}_1(t), \end{aligned} \quad (59)$$

$$\begin{aligned} \langle f_{\lambda,y}^R(\vec{k},t) f_{\lambda',x}^{R,*}(\vec{k}) \rangle &= \sum_{\vec{q},\{\lambda\},\{\lambda'\}} \frac{n^2 U_1}{4I^2} (m_1^- m_1'^+ D_1^- D_2^+ \\ &+ m_1^- m_1'^- D_1^- D_2^- - m_1^+ m_1'^- D_1^+ D_2^- \\ &- m_1^+ m_1'^+ D_1^+ D_2^+) \mathcal{K}_1(t), \end{aligned} \quad (60)$$

$$\begin{aligned} \langle f_{\lambda,y}^R(\vec{k},t) f_{\lambda',x}^{R,*}(\vec{k}) \rangle &= \sum_{\vec{q},\{\lambda\},\{\lambda'\}} \frac{in^2 U_1}{4I^2} (m_1^- m_1'^+ D_1^- D_2^+ \\ &+ m_1^- m_1'^- D_1^- D_2^- - m_1^+ m_1'^- D_1^+ D_2^- \\ &- m_1^+ m_1'^+ D_1^+ D_2^+) \mathcal{K}_1(t), \end{aligned} \quad (61)$$

$$\begin{aligned} \langle f_{\lambda,y}^R(\vec{k},t) f_{\lambda',y}^{R,*}(\vec{k}) \rangle &= \sum_{\vec{q},\{\lambda\},\{\lambda'\}} \frac{n^2 U_1}{4I^2} (m_1^+ m_1'^+ D_1^+ D_2^+ \\ &+ m_1^- m_1'^- D_1^- D_2^- - m_1^+ m_1'^- D_1^+ D_2^- \\ &- m_1^- m_1'^+ D_1^- D_2^+) \mathcal{K}_1(t), \end{aligned} \quad (62)$$

where

$$\begin{aligned} \mathcal{K}_1(t) &= U_2 F_{\lambda_3, \lambda_3'}(\vec{k} - \vec{q}, t) F_{\lambda_2, \lambda_2'}(\vec{q}, t) \\ &+ U_2' F_{\lambda_3, \lambda_2'}(\vec{k} - \vec{q}, t) F_{\lambda_2, \lambda_3'}(\vec{q}, t), \\ D_1^+ &= D(\lambda^+, \lambda_1, \lambda_3), \quad D_1^- = D(\lambda^-, \lambda_1, \lambda_3), \\ D_2^+ &= D(\lambda'^+, \lambda_1', \lambda_3'), \quad D_2^- = D(\lambda'^-, \lambda_1', \lambda_3'). \end{aligned} \quad (63)$$

For $\lambda=0$, the linear molecular liquid becomes an atomic molecular liquid, and the above expressions vanish except for the correlation function for the longitudinal-translational currents. For Eq. (51), all harmonic eigenvalues are zero, and we have

$$\begin{aligned} \langle f_{0,z}^T(\vec{k},t) f_{0,z}^{T,*}(\vec{k}) \rangle &= \sum_{\vec{q}} \frac{n^2 D_1 D_2}{M^2} [q_z^2 U_q^2 + q_z (k \\ &- q_z) U_q U_{|\vec{k}-\vec{q}|}] F(\vec{k} - \vec{q}, t) F(\vec{q}, t), \end{aligned} \quad (64)$$

which reduces to the mode-coupling kernel for the atomic liquid.

VI. CONCLUDING REMARKS

The goals of this paper are to apply the Gaussian factorization approximation to derive ideal mode-coupling memory kernels for linear and nonlinear hydrodynamic modes and to examine the non-Gaussian behavior of the bilinear density correlation function [10]. Based on the observation that the random force $f=QILA$ is related to pair interactions in liquids, mode-coupling memory kernels can be expressed in terms of bilinear hydrodynamic modes. Then direct Gaussian factorization of the memory kernels and the random phase approximation for the direct pair distribution function lead to standard mode-coupling expressions. In this paper, we adopt a more rigorous approach introduced by Zaccarelli *et al.* [11] to derive essentially the same results. In this approach, a self-consistent equation for the random force arises directly from the fluctuation-dissipation relation and the pair interaction term of the force on the slow variables. The mode-coupling memory kernel is obtained by removing the self-consistent coupling terms with the mean-field approximation and factoring multiple-point time correlation functions. Thus, the random phase approximation, or other approximations of mean-field nature, is necessary for removing the coupling terms that are difficult to evaluate in the self-consistent expression of the memory kernel. Effectively, this derivation justifies the simpler scheme of applying factorization directly to the bilinear term in the memory kernel.

Within the Gaussian factorization scheme, we derived mode-coupling memory kernels for the velocity autocorrelation function (VAF) in Sec. III, the bilinear density mode in Sec. IV A, and the density fluctuation of linear molecular liquids in Sec. V. In Sec. III, we used the random phase approximation for the direct pair correlation function between the tagged particle and the solvent to obtain the standard mode-coupling expression for the VAF. In Sec. V A, we applied Gaussian factorization to the six-point correlation function and used the RPA to recast the three- and four-body distribution functions. The resulting equation takes into account the initial distribution as well as mode-coupling effects. The four-point correlation function can be useful for calculating third-order Raman spectra and for further examination of non-Gaussian effects. In Sec. V, we expanded the collective density of a linear molecule liquid in terms of spherical harmonics and derived mode-coupling expressions in the spherical harmonic function space. The zero component of the spherical harmonic function recovers the limit of atomic liquids. These results for linear molecular liquids are useful for analyzing rotational spectra and Raman spectra in molecular liquids and solvents.

A key result of this paper is the investigation of non-

Gaussian effects in bilinear (four-point) density correlation functions in Sec. IV B. In the hydrodynamic limit, we can directly factor the four-point correlation function into the product of two pairs of density correlation functions. In principle, the same Gaussian factorization can also be applied to the GLE of the four-point density correlation function. In order to examine the consistency of direct factorization and mode-coupling equations, we compare the difference between applying factorization before and after taking the time derivatives of the GLE for the four-point correlation function. The two procedures are identical for the first-order time derivative, but different for the second- and third-order time derivatives. The differences depend on $\Delta = F_{\vec{k}}(t-\tau)F_{\vec{k}}(\tau) - F_{\vec{k}}(t)S_{\vec{k}}$, the deviation from exponential behavior of the linear density mode predicted from hydrodynamics. This difference function starts small initially and then approaches zero in the long-time hydrodynamic limit. It then follows that the non-Gaussian indicator has a maximum at an intermediate time. The amplitude of the maximum depends on the strength of the non-Markovian behavior in the liquid. For liquids close to the hydrodynamic limit, the nonexponential deviation of the linear mode is small and direct Gaussian factorization is a good approximation for the four-point correlation function in the long-time limit. In contrast, low-temperature systems exhibit strong nonhydrodynamic behavior in density fluctuations so that the non-Gaussian behavior becomes significant. Since the nonhydrodynamic behavior increases with decreasing temperature, the non-Gaussian behavior shows a similar trend. These observations agree with

the results from several numerical simulations [12,13]. Our analysis confirms and quantifies the correlation between the non-Gaussian behavior in multiple-point correlation functions and the nonhydrodynamic behavior of linear modes.

The key relation established in Sec. IV B is also relevant to experimental measurements. Scattering experiments have been carried out to quantify the nonexponential relaxation in density fluctuations [35–38]. Recent nonlinear experiments are designed to investigate non-Gaussian behavior and dynamic heterogeneities [15,16,39]. Equations (36) and (40) demonstrate that the information content from these two kinds of experiments can be correlated within the mode-coupling formalism. In other words, if the system is not far from the hydrodynamic regime, the two aspects of nonhydrodynamic deviation, i.e., the nonexponential decay and non-Gaussian fluctuations, are related quantitatively. The validity of this quantitative relation becomes questionable when the system is far away from the hydrodynamic limit and is dynamically heterogeneous. To interpret measurements in these systems, we should introduce non-Gaussian coupling explicitly, as in stochastic diffusion/hopping models [40–42] and dynamic frustration models [43–45].

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