

Semiclassical mode-coupling factorizations of coherent nonlinear optical response

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The identification of relevant collective coordinates is crucial for the interpretation of coherent nonlinear spectroscopies of complex molecules and liquids. Using an \hbar expansion of Liouville space generating functions, we show how to factorize multitime nonlinear response functions into products of lower-order correlation functions of collective coordinates, and derive closed expressions for linear, second- and third-order response functions. In addition to providing systematic quantum corrections, \hbar offers a convenient bookkeeping device even for the purely classical response, since including quantum fluctuations allows to circumvent the expensive computation of stability matrices which is a major bottleneck in molecular dynamics simulations. The existing classical simulation strategies, including mode coupling in \mathbf{k} space and in real space, Langevin equations, and instantaneous normal modes are compared from a unified viewpoint. © 2003 American Institute of Physics. [DOI: 10.1063/1.1610437]

I. INTRODUCTION

In 1993 Tanimura and Mukamel had proposed the fifth-order Raman response¹ as a multidimensional spectroscopic technique especially suitable for investigating the structure and dynamics of molecular liquids by revealing detailed information unavailable from linear spectroscopies. That article had triggered an intense experimental investigations mainly on liquid CS₂.^{2–16} Earlier experimental investigations were haunted by competing, sequential, low order (cascading) processes. Separating the direct and sequential contributions had drawn considerable attention.^{8,15,17,18}

Several theoretical techniques have been employed to predict the fifth-order response from molecular dynamics simulations of liquids. Two methods obtain the response directly without further approximations, other than that the response is classical. The first, based on calculating time correlation functions, relies on propagation of the full stability matrix [Eq. (25)].^{19–21} Since the stability matrix depends on the number of phase space coordinates squared, it is very time consuming and was only implemented for small systems.^{22–25} The other, finite field, method is based on propagating only one column of the stability matrix, giving rise to a particular response function of interest, significantly reducing the computational effort. This method is a direct simulation of the experiment, where forces originating from interactions between the electric fields and the molecules are incorporated in the simulation on the fly.^{26–28} One drawback of computing the actual non equilibrium response rather than response functions is that the entire simulation needs to be repeated for each choice of time intervals and pulse configurations. Both of these methods are therefore computationally very demanding. Developing alternative numerically more affordable approaches, which could also provide physical insight will therefore be highly desirable.

Some discrepancies currently exist between various real-space simulations performed under slightly different simula-

tion conditions on liquid CS₂.^{24,29} These differences are most pronounced along the second time axis (τ_{32}), where both a ridge^{29,30} and nodes^{24,25} have been reported. A fundamental understanding of the underlying physical processes should help resolve the questions about the origin of the nodes and the ridges.

The first approximate scheme employed to analyze the fifth order Raman response was based on the instantaneous normal modes (INM).^{20,22,31–37} This method uses snapshots of the liquid “normal modes” assuming that they are harmonic and do not change over the time scale of the experiment. However, in general the normal modes do change on the time scale of their own periods³⁸ and recent studies have shown that the INM gives rather poor results for the fifth-order response of liquid xenon.^{23,34}

A more attractive procedure is to identify some relevant *collective coordinates* and adopt a reduced description for the response. Unlike microscopic INM where a harmonic model for molecular liquids may not be justified, collective coordinates can have Gaussian statistics by virtue of the central limit theorem. A simple and tractable physical picture for the origin of the response is then, in principle, possible. The multimode Brownian oscillator model has been successfully employed in the analysis of solvation dynamics in electronic spectroscopy,^{21,39–41} where the response may be expressed using a few (overdamped or underdamped) collective coordinates. This model has been used to simulate the fifth-order response of liquid water,^{42,43} but identifying the microscopic origin of these modes still remains an open challenge.⁴⁴ Non-linear hydrodynamics and mode coupling theories successfully use collective variables in momentum (\mathbf{k}) space to describe slow, long-wavelength, variables and their fluctuations. Mode-coupling (MC) theory^{45–51} has been applied to relate the fifth-order Raman response^{52–56} to fluctuations of density modes in \mathbf{k} space. Another related approach is based on the generalized Langevin equations (GLE).^{57,58}

Classical mode-coupling theory contains some ambiguities regarding the proper factorization of high-order response functions, and Schofield⁵⁹ and Keyes⁵⁷ and collaborators have discussed possible simulation strategies based on Langevin equations.

In this paper we apply a unifying superoperator picture of quantum field and mode-coupling Green function theories developed recently^{41,60,61} to derive expressions for the first-, second-, and third-order response functions. The technique provides an unambiguous, unique, factorization scheme of multitime correlation functions and allows the perturbative incorporation of anharmonicities as well as quantum corrections through an \hbar expansion. Applications are made to the fifth-order Raman response and compared with other approximate methods. In Sec. II we present the superoperator formalism. In Sec. III we describe how third- and fifth-order Raman response can be obtained from the general first- and second-order response functions. We discuss the connections, similarities and differences of the present formulation with other approaches. Conclusions are given in Sec. IV.

II. LIOUVILLE SPACE FORMULATION OF RESPONSE FUNCTIONS

The present approach is based on superoperators (A_+ and A_-) corresponding to an ordinary Hilbert space operator A , defined by their action on some Hilbert space operator Ω .³⁹

$$\begin{aligned} A_+ \Omega &\equiv \frac{1}{2}(A\Omega + \Omega A), \\ A_- \Omega &\equiv A\Omega - \Omega A. \end{aligned} \quad (1)$$

Using this notation, a compact expression for the n -dimensional (n D) quantum mechanical response functions can be written in terms of the dipole superoperators (μ_+ and μ_-),⁶⁰⁻⁶²

$$R^{(nD)} = \left(\frac{i}{\hbar}\right)^n \langle \mu_+(\tau_{n+1}) \mu_-(\tau_n) \cdots \mu_-(\tau_1) \rangle. \quad (2)$$

The superscript of $R^{(nD)}$ indicates that it depends on the n time intervals between successive times $\tau_1 \cdots \tau_{n+1}$ and thus constitutes an n -dimensional technique. The average $\langle A \rangle \equiv \text{Tr}[A \rho_{\text{eq}}]$ denotes the trace with respect to the equilibrium density matrix of the system ρ_{eq} .

The Hamiltonian will be partitioned into a Harmonic, quadratic, part (H_0) and an anharmonic (V) part

$$H = H_0 + V, \quad (3)$$

and the response function of a weakly anharmonic system will be expanded perturbatively in V ,⁶⁰

$$\begin{aligned} R^{(nD)} &= \sum_{m=0}^{\infty} \left(\frac{i}{\hbar}\right)^{m+n} (-1)^m \int_{-\infty}^{\tau_{n+1}} d\tau'_1 \cdots \int_{-\infty}^{\tau_{n+1}} d\tau'_m \\ &\quad \times \langle T \tilde{\mu}_+(\tau_{n+1}) \tilde{\mu}_-(\tau_n) \cdots \tilde{\mu}_-(\tau_1) \\ &\quad \times \tilde{V}_-(\tau'_m) \cdots \tilde{V}_-(\tau'_1) \rangle_0. \end{aligned} \quad (4)$$

Here \tilde{V}_v and $\tilde{\mu}_v$ are the superoperators associated with the anharmonic part of the potential and with the interaction dipole, respectively, in the interaction picture with respect to H_0 , i.e.,

$$\tilde{A}_v(\tau) \equiv \exp\left(\frac{i}{\hbar} L_0 \tau\right) A_v \exp\left(-\frac{i}{\hbar} L_0 \tau\right). \quad (5)$$

Here

$$L_0 \Omega = [H_0, \Omega] \equiv (H_0)_- \Omega, \quad (6)$$

is the Liouville operator corresponding to H_0 . The average $\langle A \rangle_0 \equiv \text{Tr}[A \rho_0]$ is defined as the trace with respect to the equilibrium density operator for the harmonic system ρ_0 . T is the time ordering operator in Liouville space which arranges all superoperators so that their time arguments decrease from left to right.⁶⁰

We shall represent H_0 in terms a few primary (collective) coordinates Q_j (Refs. 41, 62, and 63) described by the Hamiltonian

$$H_m = \sum_j \left(\frac{P_j^2}{2M_j} + \frac{M_j \Omega_j^2 Q_j^2}{2} \right) + V(\mathbf{Q}), \quad (7)$$

where $P_j(Q_j)$ is the momentum (coordinate) operator of the j th primary mode, Ω_j and M_j are its frequency and reduced mass, respectively. The anharmonic potential V , is

$$V(\mathbf{Q}) = \sum_{N=3}^{\infty} \frac{1}{N!} V_{j_1 \cdots j_N}^{(N)} Q_{j_1} \cdots Q_{j_N}. \quad (8)$$

We assume that the dipole operator μ only depends on the primary coordinates and expand it as

$$\mu = \sum_{N=1}^{\infty} \frac{1}{N!} \mu_{j_1 \cdots j_N}^{(N)} Q_{j_1} \cdots Q_{j_N}. \quad (9)$$

The primary modes further interact with a large number of low-frequency harmonic (bath) coordinates which induce relaxation and dephasing. These bath degrees of freedom \mathbf{q} and their linear coupling to the primary modes are described by the Hamiltonian H_B ,

$$H_B = \sum_{j\alpha} \left[\frac{p_{j\alpha}^2}{2m_{j\alpha}} + \frac{m_{j\alpha} \omega_{j\alpha}^2}{2} \left(q_{j\alpha} - \frac{c_{j\alpha}}{m_{j\alpha} \omega_{j\alpha}^2} Q_j \right)^2 \right], \quad (10)$$

and $p_{j\alpha}(q_{j\alpha})$ are momentum (coordinate) operators of bath oscillators. $c_{j\alpha}$ are the coupling constants between the primary and bath coordinates. The total harmonic Hamiltonian is given by⁴⁰

$$H_0 = H_m(\mathbf{Q}) + H_B(\mathbf{Q}, \mathbf{q}). \quad (11)$$

Applying the algebraic rules for superoperators given in Appendix A⁶⁰, the Taylor expansions of $\mu_+(\tau)$, $\mu_-(\tau)$, and $V_-(\tau)$ can be expressed in terms of the elementary superoperators Q_{j+} and Q_{j-} . Using these expansions, we can convert the time-ordered product of superoperators into a time ordered product of primary superoperators. This transforms the computation of response functions [Eq. (4)] to the evaluation of products of the form

$$W\{j_m \nu_m \tau_m\} \equiv \langle Q_{j_1 \nu_1}(\tau_1) \cdots Q_{j_N \nu_N}(\tau_N) \rangle_0, \quad (12)$$

where $\nu_1, \dots, \nu_N = \pm$, and j_m runs over the collective coordinates. Note that the number N of operators in the product needed to compute $R^{(nD)}$ is generally greater than $n, N \geq n$. The reasons are (i) μ_ν may be nonlinear in the elementary operators. (ii) The expansion in V_- adds more operators to the product. Generally some of the τ_j in Eq. (12) will be the same since $R^{(nD)}$ only depends on $n+m+1$ times, which is smaller than or equal to N .

We next introduce the *superoperator generating functional*⁶⁰

$$S(\{J(t)\}) \equiv \left\langle T \exp \left[\sum_{j\nu} \int J_{j\nu}(\tau) Q_{j\nu}(\tau) d\tau \right] \right\rangle_0. \quad (13)$$

Since the Hamiltonian H_0 is quadratic, the generating functional may be computed exactly using the second-order cumulant expansion. This gives

$$S(\{J(t)\}) = \exp \left\{ \sum_{j,k} \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \times [-i\hbar J_{j+}(\tau_2) J_{k-}(\tau_1) G_{jk}^{+-}(\tau_{21}) + J_{j+}(\tau_2) J_{k+}(\tau_1) G_{jk}^{++}(\tau_{21})] \right\}. \quad (14)$$

We have introduced the notation $\tau_{ij} \equiv \tau_i - \tau_j$ and the two basic Liouville space Green functions,

$$G_{ij}^{+-}(\tau_{21}) \equiv \frac{i}{\hbar} \langle T Q_+^i(\tau_2) Q_-^j(\tau_1) \rangle_0, \quad (15)$$

$$G_{ij}^{++}(\tau_{21}) \equiv \langle T Q_+^i(\tau_2) Q_+^j(\tau_1) \rangle_0. \quad (16)$$

Using Eq. (1), Eqs. (15) and (16) can be recast as combinations of ordinary (Hilbert space) correlation functions

$$G_{ij}^{+-}(\tau_{21}) = \theta(\tau_{21}) \frac{i}{\hbar} (\langle Q^i(\tau_2) Q^j(\tau_1) \rangle_0 - \langle Q^j(\tau_1) Q^i(\tau_2) \rangle_0), \quad (17)$$

$$G_{ij}^{++}(\tau_{21}) = \frac{1}{2} (\langle Q^i(\tau_2) Q^j(\tau_1) \rangle_0 + \langle Q^j(\tau_1) Q^i(\tau_2) \rangle_0). \quad (18)$$

G^{++} and G^{+-} may also be expressed in terms of the spectral densities $C_{ij}(\omega)$,

$$G_{ij}^{+-}(\tau) = 2\theta(\tau) \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} C_{ij}(\omega) \sin(\omega\tau), \quad (19)$$

$$G_{ij}^{++}(\tau) = \hbar \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} C_{ij}(\omega) \cos(\omega\tau) \coth\left(\frac{\hbar\omega}{2k_B T}\right). \quad (20)$$

Equation (19) is the definition of the spectral density, where $\theta(\tau)$ is the Heaviside step function (equal to zero for $\tau < 0$ and equal to one for $\tau \geq 0$). In the classical, high temperature, limit $\coth(\hbar\omega/2k_B T) \approx 2k_B T/\hbar\omega$, and both G^{+-} and G^{++} become independent of \hbar . In that case the two are related by the classical fluctuation-dissipation relation

$$G_{ij}^{+-}(\tau) = -\frac{1}{k_B T} \theta(\tau) \frac{d}{d\tau} G_{ij}^{++}(\tau). \quad (21)$$

Semiclassical approximations to the response may be developed by expanding G^{++} in powers of \hbar .

Time-ordered correlation functions of superoperators may be obtained from the generating functional by functional derivatives⁶⁰

$$W\{j_m \nu_m \tau_m\} = \frac{\partial}{\partial J_{j_1 \nu_1}(\tau_1)} \cdots \frac{\partial}{\partial J_{j_N \nu_N}(\tau_N)} S\{J(\tau)\} \Big|_{J=0}. \quad (22)$$

In order to compute the response function (which gives the response to very short pulses) to a given order in the field, the generating functional can be simplified since only a limited number of times will contribute, and the primary operators connected with the last time will have to be + operators since $\langle A_-(\tau_1) B_\nu(\tau_2) \rangle$ vanishes for $\tau_1 \geq \tau_2$.⁶⁰ The generating functional for two time quantities $\langle A_\nu(\tau_1) B_{\nu'}(\tau_2) \rangle$ thus reads

$$S^{(1)}(\{J(\tau)\}) = \exp \left\{ \sum_{j,k} -i\hbar J_{j+}(\tau_2) J_{k-}(\tau_1) G_{jk}^{+-}(\tau_{21}) + J_{j+}(\tau_2) J_{k+}(\tau_1) G_{jk}^{++}(\tau_{21}) + J_{j+}(\tau_2) J_{k+}(\tau_2) G_{jk}^{++}(0) + J_{j+}(\tau_1) J_{k+}(\tau_1) G_{jk}^{++}(0) \right\}. \quad (23)$$

Here we assumed Gaussian statistics of Q_j so that the exact generating functional is given by the second-order cumulant expansion. The generating functional provides a compact form for Wick's theorem. Generating functionals for multi-time quantities may be written in a similar way.

Using the general expression for the n 'th-order response function given in Appendix A, we can expand $R^{(nD)}$ to any desired order in the primary operators. Since the J 's always come in pairs in the generating functional, the derivatives will vanish for all terms with an odd number of elementary operators, once the $J=0$ limit is taken.

Note the delicate interplay of the \hbar factors in Eq. (A6). Keeping \hbar alive even in the classical limit, is what allows us to avoid the computation of stability matrices. \hbar retains information about quantum fluctuations which are differences between "left" and "right" trajectories:^{19,21,39} The stability matrices are the corresponding derivatives as \hbar tends to zero. In the classical evaluation of Eq. (A6) we keep terms in the generating function to order (\hbar^{n+m}) . \hbar then cancels out by the prefactor in Eq. (4) and the result is independent of \hbar , as it should be.³⁹ Higher order terms in \hbar provide quantum corrections to the response. We further note that the response function, which is a particular combination of correlation functions, has a well-defined classical limit. Individual correlation functions in Hilbert space generally do not have an obvious physical meaning and consequently their $\hbar \rightarrow 0$ limit is ill defined. \hbar therefore cancels only once these combinations are evaluated to yield an observable.

As an example, the one-dimensional (1D) response function expanded to fourth order in the elementary operators is given by

$$\begin{aligned}
 R^{(1D)} = & \sum_{ij} \mu_i^{(1)} \mu_j^{(1)} G_{ij}^{+-}(\tau_{21}) \\
 & + \sum_{ijkl} \mu_{ij}^{(2)} \mu_{kl}^{(2)} G_{ik}^{+-}(\tau_{21}) G_{jl}^{++}(\tau_{21}) \\
 & + \sum_{ijk} \mu_{ijk}^{(3)} \mu_i^{(1)} G_{il}^{+-}(\tau_{21}) G_{jk}^{++}(0). \quad (24)
 \end{aligned}$$

These two lowest-orders in the expansion are independent of the anharmonicity, and the 1D response can be expected to be dominated by the harmonic part of the potential. Closed expressions for the two-dimensional (2D) and three-dimensional (3D) response functions expanded to sixth order in the primary coordinates are given in Appendix B.

III. COMPARISON OF SIMULATION STRATEGIES FOR 2D FIFTH-ORDER RAMAN RESPONSE

In off-resonant Raman spectroscopy, the field-matter interaction comes through the dipole moment induced by an electric field instead of the permanent dipole moment. The Raman response can therefore be obtained by simply substituting the dipole operators in the expressions in Eq. (24) and Appendix B with the operator for the induced dipole, which in turn is given by the product of the polarizability and the inducing field. μ is therefore simply replaced by $\alpha \cdot E$. This substitution leads to a higher-order dependence on the electric field: The nD response is n th order in the field for dipole (e.g., infrared) response but $(2n+1)$ th order for Raman. The Raman response that is third order in the electric fields is therefore described by the 1D response function. The fifth-order Raman response is given by the 2D response function and so forth.

The various approaches used for the simulation of fifth-order Raman signals differ not only by the simulation technique, but also by the model used, which complicates their direct comparison. The expressions derived in this paper allow a critical comparison of the various simulations. This will be done next.

Classical MD simulations in real space: The real-space simulations by Saito *et al.*,²⁴ Ma *et al.*,^{22,23} and Jansen *et al.*^{26,27} use the nuclear coordinates as basis and the response is calculated without invoking Wick's theorem. The calculated classical response functions therefore formally include all orders anharmonicities of the expansion derived here. The price is the need to compute stability matrices. The nuclear coordinates might not be the best choice of basis for the expansion derived in the preceding section and analyzing the response in this basis might be inconvenient. The real-space simulations give the full response including all anharmonicities and nonlinearities of the polarizability. Analyzing the response calculated with these methods is a daunting task, since all terms which depend on different modes and nonlinearities are added. This makes it difficult to establish the connection between the spectral features and the underlying dynamics.

The stability matrix ($M(\tau_2, \tau_1)$) is a $N \times N$ matrix, where N is the number of phase space coordinates.^{19,20,23,64}

Each matrix element is given by the derivative of a phase space coordinate x_k at time τ_1 with respect to a phase space coordinate x_j at another time, τ_2 ,

$$M_{jk}(\tau_2, \tau_1) = \left\{ \frac{\partial x_k(\tau_1)}{\partial x_j(\tau_2)} \right\}. \quad (25)$$

Schemes for obtaining the stability matrix using the Hessian matrix have been described in the literature.^{19,20,23,25,64–66}

Equilibrium simulations^{19,20,22–25} are based on propagating the full stability matrix¹⁹ in order to evaluate the Poisson bracket arising in the time correlation function expression for the fifth-order response. The major bottleneck in the equilibrium method is the propagation of the $N \times N$ stability matrix.^{19,20} In contrast, in the nonequilibrium, finite field, approach,^{26,27,64} propagation of the full stability matrix is avoided and only a few vectors of dimension N corresponding to the response function are propagated. In this approach the evaluation of the first-order derivatives of the polarizability, needed in order to calculate the forces exerted by the electric fields, is the most time consuming part of the simulation.²⁷

Instantaneous normal modes: For a collection of oscillators with frequencies ω_i we have¹

$$\begin{aligned}
 G_{ij}^{+-}(\tau) &= \theta(\tau) \frac{1}{M_i \omega_i} \sin(\omega_i \tau) \delta_{ij}, \\
 G_{ij}^{++}(\tau) &= \hbar \frac{1}{2M_i \omega_i} \cos(\omega_i \tau) \coth\left(\frac{\hbar \omega_i}{2k_b T}\right) \delta_{ij}. \quad (26)
 \end{aligned}$$

INM simulations combine these expressions with MD simulations of real liquids. The system is assumed to evolve independently in the different normal modes giving rise to the Kronecker deltas in Eq. (26). INM simulations have most often been applied in the classical, high temperature limit, where only the first term in the expansion of \coth is retained [$\coth(x) \approx 1/x$]. Equations (B1)–(B6) reduce to the INM expressions if the INM coordinates are used as the primary operators and the anharmonicities are neglected. In this paper we use a different bookkeeping: terms have been kept to a certain order in the primary operators, whereas the INM expressions traditionally have been truncated by neglecting terms containing third- and higher-order nonlinearities of the polarizability,^{20,22,36,37} retaining only Eqs. (B2) and (B3). Our formulation suggests that terms which include second-order derivatives should be considered on an equal footing with all other terms including a total of six derivatives, since they depend on the same number of fundamental quantum Green functions G^{++} and G^{+-} .

In a recent INM simulation of Ma and Stratt³⁴ the lowest-order anharmonic contribution corresponding to Eq. (B6) was found to give a significant contribution to the total response of liquid xenon. The fifth-order Raman response computed with this model did, however, still deviate significantly from that calculated using time correlation functions.^{23,34}

Both the diagonalization of the Hessian needed to obtain the normal modes and the evaluation of the derivatives of the polarizability are time consuming processes. Which of these is the slowest depend on the model used to describe the

polarizability. For the first-order dipole induced dipole model the derivatives can be evaluated very effectively analytically. This simple model is, however, known to fail for systems with large polarizability⁶⁷ and in atomic liquids it gives an isotropic polarizability that is coordinate independent.

In liquids, the basic assumption in the INM theory that motion can be described in static normal modes is not generally justified. In a liquid the molecules rotate and diffuse around changing the normal modes on the time scale that is studied in femtosecond and picosecond experiments. Instead of using a static set of coordinates one can use a dynamic basis set. Ma and Stratt used a basis of normal modes that was allowed to change with time.³⁴ They obtained the Green's function describing the time evolution in one mode by applying WKB theory.^{34,68} In our notation, this result reads

$$G_{ij}^{+-}(\tau) = \theta(\tau) \frac{\sin(\int_0^\tau \omega_i(\tau') d\tau')}{M_i \sqrt{\omega_i(\tau)\omega_i(0)}} \delta_{ij}. \quad (27)$$

The time evolution depends on the time dependent frequency $\omega_i(\tau)$ or each normal mode. In this picture not only the frequencies are time dependent, but the polarizability derivatives and anharmonicities also change as the basis set changes. Computationally it is expensive to repeatedly diagonalize the Hessian at short intervals to obtain the dynamic normal mode basis set and the method was not yet tested.

Mode coupling in k space: Reichman⁵²⁻⁵⁴ and Cao^{55,56} adopted mode-coupling theory of nonlinear hydrodynamics in \mathbf{k} space. Translational invariance then greatly simplifies the final expressions and the time dependence is accounted for through the dynamical structure factor $F(\mathbf{k}, t)$. They employed the atomic first-order dipole induced dipole model for the polarizability. The resulting classical expression is^{52,53}

$$R^{(2D)}(\tau_{32}, \tau_{21}) = \sum_{\mathbf{k}} \left(\frac{V(\mathbf{k})}{S(\mathbf{k})^2} \right)^3 \frac{1}{k_b T} \frac{dF(\mathbf{k}, \tau_{32})}{d\tau_{32}} \times \left[\frac{1}{k_b T} \frac{dF(\mathbf{k}, \tau_{32} + \tau_{21})}{d\tau_{21}} F(\mathbf{k}, \tau_{21}) + \frac{1}{k_b T} \frac{dF(\mathbf{k}, \tau_{21})}{d\tau_{21}} F(\mathbf{k}, \tau_{31}) \right]. \quad (28)$$

This expression does not contain the leading (fourth-order) term [Eq. (B2)] and only retains one of the sixth-order terms [Eq. (B3)]. The time derivative of the dynamical structure factor is proportional to the Fourier transform of G^{+-} , while the dynamical structure factor itself is proportional to the Fourier transform of G^{++} . The $V(\mathbf{k})/S(\mathbf{k})^2$ factors correspond to polarizability derivatives in \mathbf{k} space.^{52,53}

The quantum mechanical response function contains information about the local response assuming that the relevant coherence size is much smaller than the wavelength of the light. This is obviously the case for the response of many polyatomic molecules and aggregates. However, it usually holds for molecular liquids as well, where the coherence size underlying the response is small due to local disorder. It fails near critical points where the coherence lengths become very large.^{51,69-71} Since the response is local, this expansion should be made in real space and not in \mathbf{k} space. The simu-

lation should provide a localized response since all six dipoles contributing to $R^{(2D)}$ should act within a small region [of order of the first solvation shell in (CS₂)] in order to generate the local response. Of course, the signal should eventually be calculated in \mathbf{k} space. This can be done purely macroscopically by solving Maxwell's equations within the local field approximation as described in Chap. 16 of Ref. 39. The only microscopic information that enters the signal is the effective local response, which can be obtained from simulations performed on the entire liquid.

Mode coupling in real space; Langevin equations: Using the Hamiltonian [Eqs. (7)–(10)] the Brownian oscillator motion is described by the following generalized Langevin equation:⁴⁰

$$M_j \ddot{Q}_j(t) + M_j \Omega_j Q_j(t) + M_j \sum_i \times \int_{-\infty}^t d\tau [\gamma_{ji}(t-\tau) + i \Sigma_{ji}(t-\tau)] \dot{Q}_i(\tau) = f_j(t) + F_j(t). \quad (29)$$

γ_{ij} (Σ_{ij}) is the imaginary (real) parts of a self-energy operator representing relaxation (level shift). f_j is a Gaussian stochastic random force representing the bath degrees of freedom on the coordinate j and F_j is an external driving force,

$$\gamma_{ij}(\omega) = \frac{\pi}{M_i} \sum_{\alpha} \frac{c_{j\alpha} c_{i\alpha}}{2m_{\alpha} \omega_{\alpha}^2} [\delta(\omega - \omega_{\alpha}) + \delta(\omega + \omega_{\alpha})], \quad (30)$$

Σ is related to γ by the Kramers–Kronig relation,

$$\Sigma_{ij}(\omega) = -\frac{1}{\pi} \text{Re} \int_{-\infty}^{\infty} d\omega' \frac{\gamma_{ij}(\omega')}{\omega' - \omega}. \quad (31)$$

In Appendix C the matrix of spectral densities is derived by solving Eq. (29),^{60,63}

$$C''(\omega) = \text{Im} \left(\frac{1}{M(\Omega^2 + \omega \Sigma(\omega) - I\omega^2 + i\omega \gamma(\omega))} \right). \quad (32)$$

M , Ω , and I are all diagonal matrices with matrix elements are given as follows $M_{ij} = \delta_{ij} M_j$, $\Omega_{ij} = \delta_{ij} \Omega_j$, and $I_{ij} = \delta_{ij}$. $C''(\omega)$ is the odd part of the spectral density, which is related to the even part $C'(\omega)$ by the fluctuation–dissipation theorem.³⁹ The matrix of spectral densities is given by $C(\omega) = [1 + \coth(\beta \hbar \omega / 2)] C''(\omega)$, where

$$C''(\omega) = \frac{\omega}{\gamma(\Omega^2 - \omega^2 I + \Sigma \omega) \gamma^{-1}(\Omega^2 - \omega^2 I + \Sigma \omega) + \gamma^2 \omega^2} \times \gamma M^{-1}. \quad (33)$$

Ordinary Langevin equations are obtained by first neglecting the frequency dependence of γ_{ij} , setting $\gamma_{ij}(\omega) = \gamma_{ij}$ and $\Sigma_{ij}(\omega) = 0$. We then take the overdamped limit $\gamma_{ij} \gg \Omega_{ij}$ of Eq. (32) where the matrix of spectral densities assumes the form⁶²

$$C''(\omega) = \frac{\omega}{\omega^2 + \Lambda^2} \Lambda \lambda, \quad (34)$$

with the $N \times N$ matrices Λ and Ω are $\Lambda = \gamma^{-1} \Omega^2$ and $\lambda = M^{-1}(\Omega^{-1})^2$,^{40,62} N being the number of Brownian oscil-

lator modes. The nonlinear response of systems described by Langevin equations can be obtained by using Eq. (34) for the matrix of spectral densities. Upon the substitution of Eq. (34) in Eq. (19) we get for the superoperator Greens functions in matrix notation

$$G^{+-}(\tau) = 2\theta(\tau)\exp(-\Lambda\tau)\Lambda\lambda, \quad (35)$$

$$G^{++}(\tau) = \hbar \exp(-\Lambda\tau)\Lambda\lambda \coth(\beta\hbar\Lambda) + \frac{4}{\beta} \sum_{n=1}^{\infty} \frac{\nu_n \exp(-\nu_n\tau)}{\nu_n^2 - \Lambda^2} \Lambda\lambda, \quad (36)$$

where $\nu_n = 2\pi n/\hbar\beta$ are the Matsubara frequencies.⁷² In the high temperature ($\beta\hbar\Lambda \ll 1$) limit the second sum in Eq. (36) decays rapidly and may be neglected and the $\coth(\beta\hbar\Lambda)$ factor can be approximated by $1/\beta\hbar\Lambda$ in the first term, yielding

$$G^{++}(\tau) = \beta^{-1} \exp(-\Lambda\tau)\Lambda\lambda\Lambda^{-1}. \quad (37)$$

In the generalized Langevin equation approach of Kim and Keyes⁵⁷ the response function is factorized using the scheme suggested by van Zon and Schofield⁵⁹ which assumes fast decay of the fluctuating forces. This factorization results in the first-order term for the 2D response proportional to $G^{+-}(\tau_{32})G^{+-}(\tau_{21})$ [the second term in Eq. (B2)], whereas the first term $G^{+-}(\tau_{32})G^{+-}(\tau_{31})$ is neglected. The systematic mode-coupling factorization of the present paper is unambiguous and require no further assumptions about the behavior of the correlation functions.

Adiabatic simulations: In systems with large scale variation of structure such as proteins and liquids it can be useful to employ a dynamic basis set instead of a static one. The natural starting point for such a description is to employ the adiabatic basis.⁷³⁻⁷⁵ A quantum description is obtained when one uses the eigenstates of the vibrational Hamiltonian as a dynamic basis. Using this basis we can derive an adiabatic theory for the response functions. When this basis changes slowly, the adiabatic approximation can be employed, considerably simplifying the calculation of the time evolution, since the system remains in the same adiabatic state at all times.

There are two independent Liouville space pathways contributing to the 2D response,⁴⁰

$$R^{(2D)}(\tau_{32}, \tau_{21}) = R_1(\tau_{32}, \tau_{21}) + R_2(\tau_{32}, \tau_{21}) + \text{c.c.} \quad (38)$$

In the adiabatic approximation these are given by

$$R_1(\tau_{32}, \tau_{21}) = \left(\frac{i}{\hbar}\right)^2 \sum_{abc} \mu_{ca}(\tau_3) I_{ca}(\tau_{32}) \mu_{cb}(\tau_2) \times I_{ba}(\tau_{21}) \mu_{ba}(\tau_1) P(a), \quad (39)$$

$$R_2(\tau_{32}, \tau_{21}) = \left(\frac{i}{\hbar}\right)^2 \sum_{abc} \mu_{cb}(\tau_3) I_{bc}(\tau_{32}) \mu_{ca}(\tau_2) \times I_{ba}(\tau_{21}) \mu_{ba}(\tau_1) P(a),$$

where

$$I_{ab}(\tau_{21}) = \exp\left[-\int_{\tau_1}^{\tau_2} i\epsilon_a(\tau)d\tau\right] \exp\left[\int_{\tau_1}^{\tau_2} i\epsilon_b(\tau)d\tau\right]. \quad (40)$$

$\epsilon_a(\tau)$ and $\epsilon_b(\tau)$ are the eigenvalues of the Hamiltonian at time τ . $\mu_{ab}(\tau)$ are the transition dipoles in the adiabatic basis. $P(a)$ is the equilibrium population of state a . When the energies change rapidly, the adiabatic approximation breaks down and nonadiabatic transitions need to be taken into account.

In order to simulate the time evolution of the system one would have to diagonalize the vibrational Hamiltonian at short intervals. Such a treatment is therefore only feasible when the number of states is sufficiently small to allow repeated diagonalizations. This may be the case if a subset of vibrational coordinates are of interest and the rest are treated as bath coordinates. It should be noted that treating the vibrational states of the system explicitly only makes sense for high frequency modes, where the excited vibrational states have a low thermal population and only few states need to be considered.

For all methods based on an expansion of the response function in the coordinates, evaluating the contributing terms gets increasingly more expensive with the order of the expansion. While the first and the second-order derivatives of the polarizability needed to evaluate the lowest order terms can be handled rather easily, higher order derivatives get increasingly more difficult to evaluate. Unless the coordinates can be chosen such that the expansion may be truncated at some low order, it will be harder to simulate the classical response functions using the expansion, compared with real-space simulation methods.

IV. CONCLUSIONS

We have developed a systematic perturbative approach for computing response functions using an expansion in the nonlinearities, the effective dipoles, and the anharmonicities. Closed form expressions for the lower order terms have been derived for the first-, second-, and third-order response functions, and applications were made to the 1D and 2D response corresponding to third- and fifth-order Raman techniques, respectively.

The mode-coupling factorizations presented in this paper provide a unified framework for deriving all the approximate methods used so far in the simulations of the fifth-order Raman. Our expressions reduce to the instantaneous normal mode as well as the mode-coupling expressions by making additional approximations. This description allows a direct comparison of the various methods and can be used to develop semiclassical expansions. All existing simulations were compared and connected to the mode-coupling factorization presented in Sec. II.

The present Green function formalism allows the explicit incorporation of anharmonicities and gives a rigorous algorithm for truncating the expansion of the response functions, depending on the number of derivatives involved. At the same time, quantum corrections to the response functions may be computed as well. Mode-coupling theories in \mathbf{k} space⁵²⁻⁵⁶ utilize a nonlocal polarizability in order to de-

scribe response functions that are local in nature. This leads to the neglect of the leading order term in both the third- and fifth-order Raman response functions; contributions of all terms involving the first-order derivative of the polarizability are missed.

Collective coordinates are likely to have Gaussian statistics. Identifying a set of collective coordinates that should allow a relatively simple interpretation of the response is the key open challenge in the simulation of nonlinear response in the condensed phase.

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APPENDIX A: SUPEROPERATOR ALGEBRA

The following relations for the superoperators Q_- and Q_+ that follow directly from the definitions of the superoperators [Eq. (1)] can be used in expand the nonlinear response in terms of these superoperators,

$$(Q^j Q^i)_+ = (Q_+^j Q_+^i + \frac{1}{4} Q_-^j Q_-^i), \tag{A1}$$

$$(Q^j Q^i)_- = (Q_+^j Q_-^i + Q_-^j Q_+^i), \tag{A2}$$

$$(Q^k Q^j Q^i)_+ = \frac{1}{4} (4 Q_+^k Q_+^j Q_+^i + Q_+^k Q_-^j Q_-^i + Q_-^k Q_+^j Q_-^i + Q_-^k Q_-^j Q_+^i), \tag{A3}$$

$$(Q^k Q^j Q^i)_- = (Q_+^k Q_+^j Q_-^i + Q_+^k Q_-^j Q_+^i + Q_-^k Q_+^j Q_+^i + \frac{1}{4} Q_-^k Q_-^j Q_-^i), \tag{A4}$$

and so forth. Using these rules we can express the superoperator corresponding to an arbitrary product of ordinary operators as a product of superoperators,

$$(Q^{i_n} \dots Q^{i_1})_- = \sum_{\nu_1 \dots \nu_n} f_{\nu_1 \dots \nu_n}^- Q_{\nu_n}^{i_n} \dots Q_{\nu_1}^{i_1}, \tag{A5}$$

$$(Q^{i_n} \dots Q^{i_1})_+ = \sum_{\nu_1 \dots \nu_n} f_{\nu_1 \dots \nu_n}^+ Q_{\nu_n}^{i_n} \dots Q_{\nu_1}^{i_1},$$

where the coefficients f^+ and f^- are determined by application of the rules [Eqs. (A1)–(A3)] and the ν 's denote either + or -.

For a given set of expansion coefficients the n -dimensional response can be expressed in terms of derivatives of the generating functional,⁶⁰

$$\begin{aligned} R_{m:n_1 \dots n_{n+1}}^{(nD)}(\tau_{n+1}, \dots, \tau_1, \tau'_m, \dots, \tau'_1) &= \frac{1 + \delta_{m0}}{(m+2)! n_1! \dots n_{n+1}!} \left(\frac{i}{\hbar}\right)^{m+n} (-1)^m \sum_{j^1 \dots j^{n+1} k^1 \dots k^m} \int_{-\infty}^{\tau_{n+1}} d\tau'_1 \dots \int_{-\infty}^{\tau_1} d\tau'_m \\ &\times \mu_{j^1 \dots j^1}^{(n_1)} \dots \mu_{j^{n+1} \dots j^{n+1}}^{(n_{n+1})} V_{k^1 \dots k^1}^{m_1} \dots V_{k^m \dots k^m}^{m_m} \\ &\times \sum_{\nu^1 \dots \nu^n} f_{\nu^1 \dots \nu^1}^- \dots f_{\nu^n \dots \nu^n}^- \left(\frac{\partial}{\partial J_{j^1}^{n_1}(\tau_n)} \dots \frac{\partial}{\partial J_{j^n}^{n_n}(\tau_{n+1})} \right) \\ &\times \left(\frac{\partial}{\partial J_{j^1 \nu^1}(\tau_1)} \dots \frac{\partial}{\partial J_{j^{n_1} \nu^1}(\tau_1)} \right) \dots \left(\frac{\partial}{\partial J_{j^{n_n} \nu^n}(\tau_n)} \dots \frac{\partial}{\partial J_{j^{n_n} \nu^n}(\tau_n)} \right) \\ &\times \sum_{\xi^1 \dots \xi^m} \left(\frac{\partial}{\partial J_{k^1 \xi^1}(\tau'_1)} \dots \frac{\partial}{\partial J_{k^m \xi^1}(\tau'_1)} \right) \dots \left(\frac{\partial}{\partial J_{k^m \xi^m}(\tau'_m)} \dots \frac{\partial}{\partial J_{k^m \xi^m}(\tau'_m)} \right) \\ &\times f_{\xi^1 \dots \xi^1}^- \dots f_{\xi^m \dots \xi^m}^- S\{J(t)\}_{J=0}. \end{aligned} \tag{A6}$$

APPENDIX B: 2D AND 3D RESPONSE TO SIXTH ORDER IN THE PRIMARY COORDINATES

The 2D and 3D response functions are derived in the same way as the 1D response function that was given in Eq. (24). The 2D response function expanded to sixth order in the primary coordinates is given by

$$R^{(2D)} = R_{211}^{(2D)} + R_{222}^{(2D)} + R_{321}^{(2D)} + R_{411}^{(2D)} + R_{3:111}^{(2D)} + \dots, \tag{B1}$$

where the first term is fourth order in the coordinates

$$R_{211}^{(2D)} = \sum_{ijkl} \mu_{ij}^{(2)} \mu_k^{(1)} \mu_l^{(1)} G_{ik}^{+-}(\tau_{32})(G_{jl}^{+-}(\tau_{31}) + G_{jl}^{+-}(\tau_{21})). \tag{B2}$$

The remaining contributions are sixth order in the coordinates

$$\begin{aligned} R_{222}^{(2D)} &= \sum_{ijklmn} \mu_{ij}^{(2)} \mu_{kl}^{(2)} \mu_{mn}^{(2)} G_{ik}^{+-}(\tau_{32})(G_{jn}^{+-}(\tau_{31})G_{lm}^{++}(\tau_{21}) \\ &+ G_{ln}^{+-}(\tau_{21})G_{jm}^{++}(\tau_{31})), \end{aligned} \tag{B3}$$

$$\begin{aligned}
R_{321}^{(2D)} = & \frac{1}{2} \sum_{ijklmn} \mu_{ijk}^{(3)} \mu_{lm}^{(2)} \mu_n^{(1)} G_{ij}^{++}(0) (G_{ln}^{+-}(\tau_{21}) G_{km}^{+-}(\tau_{32}) + G_{mk}^{+-}(\tau_{21}) G_{nl}^{+-}(\tau_{32})) + \frac{1}{2} \sum_{ijklmn} \mu_{ijk}^{(3)} \mu_{lm}^{(2)} \mu_n^{(1)} G_{ij}^{++}(0) \\
& \times (G_{ln}^{+-}(\tau_{31}) G_{mk}^{+-}(\tau_{32}) + G_{mk}^{+-}(\tau_{31}) G_{ln}^{+-}(\tau_{32})) + \sum_{ijklmn} \mu_{ijk}^{(3)} \mu_{lm}^{(2)} \mu_n^{(1)} (G_{il}^{++}(\tau_{32}) G_{kn}^{+-}(\tau_{31}) G_{jm}^{+-}(\tau_{32}) \\
& + G_{il}^{++}(\tau_{31}) G_{km}^{+-}(\tau_{31}) G_{jn}^{+-}(\tau_{32})) + \sum_{ijklmn} \mu_{ijk}^{(3)} \mu_{lm}^{(2)} \mu_n^{(1)} (G_{li}^{++}(\tau_{32}) G_{kn}^{+-}(\tau_{21}) G_{mj}^{+-}(\tau_{32}) \\
& + G_{il}^{++}(\tau_{21}) G_{nk}^{+-}(\tau_{32}) G_{jm}^{+-}(\tau_{21})), \tag{B4}
\end{aligned}$$

$$R_{411}^{(2D)} = \frac{1}{2} \sum_{ijklmn} \mu_{ijkl}^{(4)} \mu_m^{(1)} \mu_n^{(1)} G_{ij}^{++}(0) (G_{ln}^{+-}(\tau_{31}) G_{km}^{+-}(\tau_{32}) + G_{ln}^{+-}(\tau_{21}) G_{mk}^{+-}(\tau_{32})), \tag{B5}$$

$$R_{3:111}^{(2D)} = - \sum_{ijklmn} \mu_i^{(1)} \mu_j^{(1)} \mu_k^{(1)} V_{lmn}^{(3)} \int_{-\infty}^{\tau_3} d\tau_1' G_{il}^{+-}(\tau_{31}') G_{jm}^{+-}(\tau_{1'1}) G_{kn}^{+-}(\tau_{1'2}). \tag{B6}$$

The two lowest-order terms contain numerous contributions. As noted earlier¹ all terms in the 2D response contain nonlinearities either in form of anharmonicities or higher-order derivatives of the dipole operator.

The 3D response function expanded to sixth order in the coordinates is

$$\begin{aligned}
R^{(3D)} = & \sum_{ijklmn} \mu_{ij}^{(2)} \mu_{kl}^{(2)} \mu_m^{(1)} \mu_n^{(1)} [G_{ik}^{+-}(\tau_{43}) (G_{jm}^{+-}(\tau_{42}) \\
& \times G_{ln}^{+-}(\tau_{31}) + G_{jn}^{+-}(\tau_{41}) G_{lm}^{+-}(\tau_{32})) + G_{ik}^{+-}(\tau_{42}) \\
& \times G_{jm}^{+-}(\tau_{43}) G_{ln}^{+-}(\tau_{21}) + G_{ik}^{+-}(\tau_{32}) G_{jn}^{+-}(\tau_{21}) \\
& \times G_{ml}^{+-}(\tau_{43})] + \sum_{ijklmn} \mu_{ijk}^{(3)} \mu_l^{(1)} \mu_m^{(1)} \mu_n^{(1)} \\
& \times G_{im}^{+-}(\tau_{43}) G_{jn}^{+-}(\tau_{42}) G_{kl}^{+-}(\tau_{41}). \tag{B7}
\end{aligned}$$

Numerous eighth-order terms exist including an anharmonic term. They can be readily obtained using the rules outlined earlier and will not be given here.

APPENDIX C: THE MATRIX OF SPECTRAL DENSITIES

The matrix of spectral densities for a system described by the Hamiltonian defined in Eqs. (7), (10), and (11) can be determined by solving the generalized Langevin equation (29).^{39,40,63} The generalized Langevin equation can also be written in the form

$$\begin{aligned}
M_j \ddot{Q}_j(t) + M_j \Omega_j^2 Q_j(t) \\
+ \sum_i \int_{-\infty}^t d\tau \frac{\langle \delta f_j(t-\tau) \delta f_i(0) \rangle}{k_B T} \dot{Q}_i(\tau) \\
= f_j(t) + F_j(t), \tag{C1}
\end{aligned}$$

with the external driving force $F_j(t)$ and the rapidly fluctuating force of the bath on the primary coordinate j $f_j(t)$. This force is determined from the system-bath Hamiltonian [Eq. (10)],

$$f_j = \frac{dH_B}{dQ_j} = - \sum_{\alpha} (c_{j\alpha} q_{\alpha}) + \sum_{i,\alpha} 2 \frac{c_{j\alpha} c_{i\alpha}}{2m_{\alpha} \omega_{\alpha}^2} Q_i, \tag{C2}$$

where the second term is independent of the bath coordinates.

Comparing Eqs. (29) and (C1) allows us to identify γ and Σ as the real and imaginary part of the correlations function of the fluctuating forces $f_j(t)$,

$$\gamma_{ji}(t-\tau) + i\Sigma_{ji}(t-\tau) \equiv \frac{\langle \delta f_j(t-\tau) \delta f_i(0) \rangle}{M_j k_B T}. \tag{C3}$$

Averaging over the bath coordinates and taking the Fourier transform of the generalized Langevin equation [Eq. (C1)] gives

$$\begin{aligned}
- M_j \langle \tilde{Q}_j(\omega) \rangle \omega^2 + M_j \Omega_j^2 \langle \tilde{Q}_j(\omega) \rangle \\
+ M_j \sum_i (-i\tilde{\gamma}_{ji}(\omega) + i^2 \tilde{\Sigma}_{ji}(\omega)) \omega \langle \tilde{Q}_i(\omega) \rangle = \tilde{F}_j(\omega). \tag{C4}
\end{aligned}$$

In matrix form this gives

$$M(\Omega^2 - \omega^2 I + \Sigma \omega - i\gamma \omega) \langle \tilde{Q}(\omega) \rangle = \tilde{F}(\omega). \tag{C5}$$

The matrices M , Ω , and I are all diagonal with matrix elements $M_{ij} = \delta_{ij} M_j$, $\Omega_{ij} = \delta_{ij} \Omega_j$, and $I_{ij} = \delta_{ij}$. Q and F are vectors.

The change in the coordinates induced by an external driving force is

$$\begin{aligned}
\langle \tilde{Q}(\omega) \rangle = \alpha(\omega) \tilde{F}(\omega) \\
= \frac{1}{M(\Omega^2 - \omega^2 I + \Sigma \omega - i\gamma \omega)} \tilde{F}(\omega), \tag{C6}
\end{aligned}$$

which define the susceptibility $\alpha(\omega)$.

The odd part of the spectral density matrix is the imaginary part of the susceptibility,

$$C''(\omega) = \text{Im} \left(\frac{1}{M(\Omega^2 + \omega \Sigma(\omega) - I\omega^2 + i\omega \gamma(\omega))} \right), \tag{C7}$$

where the imaginary part of a matrix is $\text{Im} A = (A - A^\dagger)/2i$.

The even part of the spectral density is related to the odd part by the fluctuation–dissipation theorem. γ and Σ are determined by the correlation function of the fluctuating forces. The fluctuating force was determined by the derivative of the Hamiltonian,

$$\langle \delta f_j(t) \delta f_i(0) \rangle = \sum_{\alpha\beta} c_{j\alpha} c_{i\beta} \langle \dot{q}_\alpha(t) \dot{q}_\beta(0) \rangle. \quad (\text{C8})$$

The part of the fluctuating force that does not depend on the bath coordinates vanishes, when averaged over the bath coordinates.

γ is determined by the real part of the time correlation function of the bath coordinates

$$\gamma_{ij}(t) = \sum_{\alpha\beta} \frac{c_{i\alpha} c_{j\beta}}{M_j k_B T} \text{Re} \langle \dot{q}_\alpha(t) \dot{q}_\beta(0) \rangle \quad (\text{C9})$$

$$= \sum_{\alpha\beta} \frac{1}{2M_j} \frac{c_{i\alpha} c_{j\beta}}{m_\alpha \omega_\alpha^2} \delta_{\alpha\beta} \cos(\omega_\alpha t), \quad (\text{C10})$$

$\gamma_{ij}(\omega)$ is the Fourier transform of $\gamma_{ij}(t)$ and is given in Eq. (30).

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