PHYSICAL REVIEW E VOLUME 57, NUMBER 2 FEBRUARY 1998

Interaction-site-model description of collective excitations in classical molecular fluids

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(Received 10 September 1997)

We describe a molecular theory for liquid dynamics that provides a method for calculating dynamical correlation functions of classical molecular fluids. The theory is based on the generalized Langevin equation and on the interaction-site model for molecular liquids. A simple model for memory functions is developed by generalizing the conventional one that has been successfully applied to monatomic systems. The theory is applied to the calculation of longitudinal current spectra of a model diatomic liquid and collective excitations in this solvent are investigated. We also clarify how these excitations originate from the translational and rotational motions of molecules. [S1063-651X(98)06202-3]

PACS number(s): 61.20.Lc, 61.25.Em

I. INTRODUCTION

The study of the propagation of collective excitations of finite wave vectors in molecular fluids has been a subject of intense investigation through experiments [1–3], molecular-dynamics (MD) simulations [4–9], and dielectric theories [10,11] in the past decade. In their MD simulation studies, Ricci *et al.* [5] observed two different excitation modes in water: an expected one associated with the sound propagation (an acoustic mode) and a newly found high-frequency optical mode. Since the former is related to the center-of-mass motions of molecules [8] and the latter is known to stem from rotational motion [5,7], these two different excitations are expected to occur generally in molecular liquids.

In this paper we develop a molecular theory to study such collective excitations in polyatomic fluids. Two elements in the statistical mechanics are required to build such a theory, which have been developed relatively independently: the equilibrium statistical mechanics of static structure factors of molecular liquids and the general formalism describing the time evolution of relevant dynamical variables.

A traditional model for describing the equilibrium structure of a polyatomic fluid is the use of the rotational invariants to represent the orientational dependence of the intermolecular interactions and the static correlation functions [12]. However, methods based on this model become increasingly cumbersome as asphericity of a molecule gets larger, since the convergence of the invariant expansion is slow. In the equilibrium theory of molecular liquids, this problem has been successfully bypassed by using the interaction-site model [13,14], in which a molecule is seen as consisting of interaction sites most commonly located at the center of constituting atoms. In this model, given the intramolecular correlations (‘‘bonds’’) between atoms, the orientational correlation between a pair of molecules is represented by a density correlation function matrix whose components are center-to-center (i.e., radial) correlations between sites of the molecules. The method based on this model, referred to as the reference interaction-site method (RISM) [13,14], and its extended version [15,16], which is capable of treating polar fluids, has been successful in describing a large variety of equilibrium phenomena in the physical chemistry of liquids and solutions.

In the theoretical development of the calculation of time-correlation functions of liquids at wavelengths and frequencies of a molecular scale, memory functions, formalized through the use of the projection-operator methods [17–19], have played a key role. Since, in general, the memory functions cannot be evaluated exactly, several approximate models have been developed and successfully applied to the dynamical problems of monatomic fluids [20–22]. By generalizing this rather successful framework to polyatomic fluids based on the interaction-site representation of a molecule, it is possible to develop theories for dynamical correlation functions of molecular liquids and solutions. Along this line, Hirata and co-workers have proposed a theory for solvent dynamics, the site-site Smoluchowski-Vlasov (SSSV) theory [23], and a molecular theory for solvation dynamics [24]. Since the SSSV theory in its current form is valid only in the diffusion regime, in the present study we extend this theory incorporating the non-Markovian effects through the use of a simple model for memory functions.

An advantage of our theoretical approach is that, although both experiments and MD simulations have difficulty in obtaining the information in the important range of small wave vectors, it overcomes this limitation by construction and more insight into the nature of excitations in molecular fluids can be gained.

The paper is organized as follows. In the following section we develop an interaction-site representation for solvent dynamics based on the generalized Langevin equation (GLE). A simple model for memory functions appearing in the GLE is developed by generalizing a procedure that has been successfully applied to monatomic systems. The potential applicability of our theory is demonstrated in Sec. III by applying it to the study of collective excitations in molecular liquids. Section IV concludes the paper. The Appendix is devoted to the evaluation of elements of the frequency moment matrices (to be defined below) that are required in our theoretical calculations.

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II. THEORY

In this section we develop an interaction-site representation for solvent dynamics based on the GLE. In contrast to the monatomic solvent case, all functions appearing in the GLE for a molecular liquid take matrix forms. Throughout the paper, the fluid is assumed to be homogeneous and isotropic.

A. Generalized Langevin equation

We begin with the definition of the site-site intermediate scattering function matrix whose components are given by

$$F_{\alpha\beta}(k,t)\equiv\frac{1}{N}\langle\delta\rho_{\alpha}(\mathbf{k},0)^{*}\delta\rho_{\beta}(\mathbf{k},t)\rangle, \tag{1}$$

in which $\delta\rho_{\alpha}(\mathbf{k},t)$ denotes a local density of atom (site) α at time t in Fourier k space,

$$\delta\rho_{\alpha}(\mathbf{k},t)\equiv\sum_{i}e^{i\mathbf{k}\cdot\mathbf{r}_{i}^{\alpha}(t)}, \tag{2}$$

and N is the total number of the molecules in the system. $\mathbf{r}_{i}^{\alpha}$ specifies the location of α atom in the ith molecule. Hereafter, greek subscripts and superscripts refer to the interaction sites of a molecule and roman letters label the molecules unless specified otherwise. The initial value of $\mathbf{F}(k,t)$ is the matrix of the site-site static structure factors

$$\mathbf{F}(k,0)\equiv\boldsymbol{\chi}(k)=\mathbf{w}(k)+\rho\mathbf{h}(k), \tag{3}$$

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

$$w_{\alpha\beta}(k)\equiv\frac{1}{N}\left\langle\sum_{i}e^{-i\mathbf{k}\cdot\mathbf{r}_{i}^{\alpha}}e^{i\mathbf{k}\cdot\mathbf{r}_{i}^{\beta}}\right\rangle, \tag{4}$$

$$\rho h_{\alpha\beta}(k)\equiv\frac{1}{N}\left\langle\sum_{i}\sum_{j\neq i}e^{-i\mathbf{k}\cdot\mathbf{r}_{i}^{\alpha}}e^{i\mathbf{k}\cdot\mathbf{r}_{j}^{\beta}}\right\rangle \tag{5}$$

and ρ is the average density of the solvent. Having assumed the molecule to be rigid, $w_{\alpha\beta}(k)$ takes the form

$$w_{\alpha\beta}(k)=j_{0}(kl_{\alpha\beta}), \tag{6}$$

where $j_{0}(x)$ is the zeroth-order spherical Bessel function and $l_{\alpha\beta}$ denotes the "bond" length between α and β sites.

We choose the external wave vector $\mathbf{k}$ such that it is along the z axis of the space-fixed laboratory frame. With this choice, the continuity equation reads

$$\delta\dot{\rho}_{\alpha}(\mathbf{k},t)=ik\sum_{i}v_{i,z}^{\alpha}(t)e^{i\mathbf{k}\cdot\mathbf{r}_{i}^{\alpha}(t)}\equiv ikj_{\alpha}(\mathbf{k},t), \tag{7}$$

where $v_{i,z}^{\alpha}$ denotes the z component of the velocity of α atom in the ith molecule. The final equality defines the longitudinal current density in k space, the time-correlation function of which is the site-site longitudinal current correlation function

$$J_{\alpha\beta}(k,t)=\frac{1}{N}\langle j_{\alpha}(\mathbf{k},0)^{*}j_{\beta}(\mathbf{k},t)\rangle. \tag{8}$$

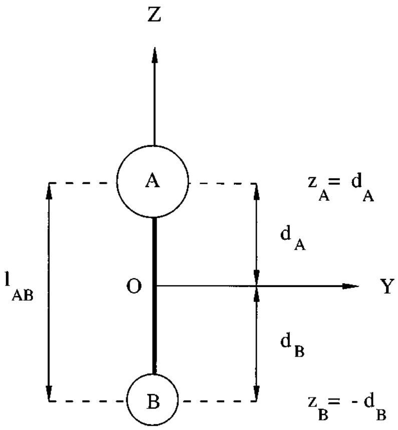

FIG. 1. Schematic representation of a diatomic molecule, consisting of atoms A and B, in the body-fixed molecular frame where the origin is taken to be the center of mass and the z axis is along the principal axis of the molecule. z_A and z_B denote the z coordinates of atoms A and B, respectively, and l_{AB} is the bond length of the molecule.

The matrices of the site-site dynamic structure factors and the longitudinal current spectra are respectively defined by

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

$$\mathbf{C}_{L}(k,\omega)\equiv\int_{-\infty}^{\infty}dt\ e^{i\omega t}\mathbf{J}(k,t). \tag{9}$$

The continuity equation (7) implies that these two matrices are connected through the relation

$$\mathbf{C}_{L}(k,\omega)=\frac{\omega^{2}}{k^{2}}\mathbf{S}(k,\omega). \tag{10}$$

The standard procedure of the projection operator formalism leads to the following GLE in the time domain [25]:

$$\ddot{\mathbf{F}}(k,t)+\langle\boldsymbol{\omega}_{k}^{2}\rangle\mathbf{F}(k,t)+\int_{0}^{t}d\tau\ \mathbf{K}_{L}(k,t-\tau)\dot{\mathbf{F}}(k,\tau)=\mathbf{0}. \tag{11}$$

In this equation, $\langle\boldsymbol{\omega}_{k}^{n}\rangle$ denotes the normalized nth frequency moment matrix of $\mathbf{S}(k,\omega)$ defined through the relations

$$\overline{\boldsymbol{\omega}_{k}^{n}}\equiv\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\ \omega^{n}\mathbf{S}(k,\omega)=(-1)^{n/2}\left[\frac{d^{n}}{dt^{n}}\mathbf{F}(k,t)\right]_{t=0}, \tag{12}$$

$$\langle\boldsymbol{\omega}_{k}^{n}\rangle\equiv\overline{\boldsymbol{\omega}_{k}^{n}}\left[\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\ \mathbf{S}(k,\omega)\right]^{-1}=\overline{\boldsymbol{\omega}_{k}^{n}}\boldsymbol{\chi}^{-1}(k), \tag{13}$$

where we have used the inverse relation of Eq. (9) and the definition of $\boldsymbol{\chi}(k)$ [see Eq. (3)]. Explicit expressions of elements of the frequency moment matrices depend on molecular models, and those of the second and fourth orders for diatomic molecule depicted in Fig. 1, which we consider throughout the paper, are reported in the Appendix.

$\mathbf{K}_L(k,t)$ in Eq. (11) is the memory function matrix, a model for which will be investigated below. The initial value of $\mathbf{K}_L(k,t)$ can be expressed in terms of the normalized frequency matrices as [22,25]

$$\mathbf{K}_L(k,0)=\langle\boldsymbol{\omega}_{k,L}^2\rangle-\langle\boldsymbol{\omega}_k^2\rangle\equiv\boldsymbol{\Delta}(k) \quad \text{with}$$

$$\langle\boldsymbol{\omega}_{k,L}^2\rangle\equiv\langle\boldsymbol{\omega}_k^4\rangle\langle\boldsymbol{\omega}_k^2\rangle^{-1}. \tag{14}$$

To obtain the GLE in the frequency domain, let us define the Laplace transform as

$$\tilde{\mathbf{F}}(k,z)\equiv i\int_0^\infty dt\; e^{izt}\mathbf{F}(k,t) \quad (\operatorname{Im} z>0). \tag{15}$$

Equation (11) then takes the form

$$\tilde{\mathbf{F}}(k,z)=-\{z\mathbf{I}-[z\mathbf{I}+\tilde{\mathbf{K}}_L(k,z)]^{-1}\langle\boldsymbol{\omega}_k^2\rangle\}^{-1}\boldsymbol{\chi}(k), \tag{16}$$

where we notice Eq. (3). It follows directly from Eq. (15) that

$$\lim_{\epsilon\to 0}\tilde{\mathbf{F}}(k,\omega+i\epsilon)=\mathbf{F}'(k,\omega)/2+i\mathbf{F}''(k,\omega)/2, \tag{17}$$

with the quantities on the right-hand side defined by

$$\mathbf{F}''(k,\omega)\equiv\int_{-\infty}^\infty dt\; e^{i\omega t}\mathbf{F}(k,t), \tag{18}$$

$$\mathbf{F}'(k,\omega)\equiv\frac{1}{\pi}\,\mathrm{P}\int_{-\infty}^\infty d\omega'\mathbf{F}''(k,\omega')/(\omega'-\omega), \tag{19}$$

where P denotes the principal integral. Applying these relations to Eq. (16), one obtains the GLE in the frequency domain

$$\mathbf{S}(k,\omega)=\left(\mathbf{Y}(k,\omega)[\mathbf{K}_L''(k,\omega)]^{-1}\mathbf{Y}(k,\omega)+\frac{\omega^2}{4}\mathbf{K}_L''(k,\omega)\right)^{-1}\langle\boldsymbol{\omega}_k^2\rangle\boldsymbol{\chi}(k), \tag{20}$$

in which $\mathbf{Y}(k,\omega)$ is defined by ($\mathbf{I}$ being the unit matrix)

$$\mathbf{Y}(k,\omega)\equiv\omega^2\mathbf{I}-\langle\boldsymbol{\omega}_k^2\rangle+\frac{\omega}{2}\mathbf{K}_L'(k,\omega). \tag{21}$$

We next consider single-particle counterparts. The self-part of the site-site intermediate scattering function matrix is defined by

$$F_{\alpha\beta}^s(k,t)\equiv\langle\delta\rho_\alpha^s(\mathbf{k},0)^*\delta\rho_\beta^s(\mathbf{k},t)\rangle, \tag{22}$$

where $\rho_\alpha^s(\mathbf{k},t)$ denotes a local density of α atom in an arbitrarily chosen tagged molecule

$$\delta\rho_\alpha^s(\mathbf{k},t)\equiv e^{i\mathbf{k}\cdot\mathbf{r}_1^\alpha(t)}. \tag{23}$$

The initial value of $\mathbf{F}^s(k,t)$ is

$$\mathbf{F}^s(k,0)=\mathbf{w}(k). \tag{24}$$

The self-part of the site-site dynamic structure factors, also called the incoherent dynamic structure factors $S_{\alpha\beta}^s(k,\omega)$, are defined as the time Fourier transform of $F_{\alpha\beta}^s(k,t)$. The unnormalized and normalized frequency moment matrices of $\mathbf{S}^s(k,\omega)$ are defined as in Eqs. (12) and (13):

$$\overline{\boldsymbol{\omega}_{k,s}^n}\equiv\frac{1}{2\pi}\int_{-\infty}^\infty d\omega\;\omega^n\mathbf{S}^s(k,\omega)=(-1)^{n/2}\left[\frac{d^n}{dt^n}\mathbf{F}^s(k,t)\right]_{t=0}, \tag{25}$$

$$\langle\boldsymbol{\omega}_{k,s}^n\rangle\equiv\overline{\boldsymbol{\omega}_k^n}\left[\frac{1}{2\pi}\int_{-\infty}^\infty d\omega\;\mathbf{S}^s(k,\omega)\right]^{-1}=\overline{\boldsymbol{\omega}_{k,s}^n}\mathbf{w}^{-1}(k). \tag{26}$$

The GLE in the frequency domain can be derived in a similar manner, the result being

$$\mathbf{S}^s(k,\omega)=\left(\mathbf{Y}^s(k,\omega)[\mathbf{K}_L^{s''}(k,\omega)]^{-1}\mathbf{Y}^s(k,\omega)+\frac{\omega^2}{4}\mathbf{K}_L^{s''}(k,\omega)\right)^{-1}\langle\boldsymbol{\omega}_{k,s}^2\rangle\mathbf{w}(k), \tag{27}$$

where $\mathbf{K}_L^s$ denotes the memory function matrix for the single-particle case and we have defined

$$\mathbf{Y}^s(k,\omega)\equiv\omega^2\mathbf{I}-\langle\boldsymbol{\omega}_{k,s}^2\rangle+\frac{\omega}{2}\mathbf{K}_L^{s'}(k,\omega). \tag{28}$$

B. Simple exponential model for $\mathbf{K}_L(k,t)$ and $\mathbf{K}_L^s(k,t)$

For a molecular liquid represented by the interaction-site model, Hirata has employed an overdamped description for the memory kernel [23] and Friedman and co-workers have proposed the reference memory function approximation [26,27]. However, both of the approximations require dynamical information as inputs (e.g., knowledge of diffusion constants is prerequisite in the former, while the latter utilizes a known time-correlation function of some reference dynamical variable) and do not offer a self-contained framework for solving dynamical problems. To overcome this limitation, we propose a simple model for the memory function matrix that is a direct generalization of the one developed by Lovesey [28,29] for treating monatomic liquids.

We write $\mathbf{K}_L(k,t)$ in Eq. (11) as

$$\mathbf{K}_L(k,t)=\exp[-t\boldsymbol{\tau}^{-1}(k)]\boldsymbol{\Delta}(k), \tag{29}$$

where we notice Eq. (14) and $\boldsymbol{\tau}(k)$ is a time-constant matrix to be specified below. It should be noted that this form of $\mathbf{K}_L(k,t)$ guarantees that the first three nonzero moment matrices of $\mathbf{S}(k,\omega)$ are correct regardless of the model for $\boldsymbol{\tau}(k)$. Defining $\mathbf{U}_\tau(k)$, which diagonalizes $\boldsymbol{\tau}^{-1}(k)$, one has

$$\mathbf{U}_\tau^{-1}(k)\boldsymbol{\tau}^{-1}(k)\mathbf{U}_\tau(k)=\operatorname{diag}[\tau_\lambda^{-1}(k)], \tag{30}$$

where $\tau_\lambda^{-1}(k)$'s denote eigenvalues of the matrix $\boldsymbol{\tau}^{-1}(k)$ and diag( ) represents a diagonal matrix. Then the memory function matrix can be written as

$$\mathbf{K}_L(k,t)=\mathbf{U}_\tau(k)[\operatorname{diag}(e^{-t/\tau_\lambda(k)})]\mathbf{U}_\tau^{-1}(k)\boldsymbol{\Delta}(k) \tag{31}$$

and in the frequency domain it follows from Eq. (17) that

$$\mathbf{K}'_L(k,\omega)=-2\mathbf{U}_\tau(k)\left[\mathrm{diag}\left(\frac{\omega}{\omega^2+[1/\tau_\lambda(k)]^2}\right)\right]\mathbf{U}_\tau^{-1}(k)\mathbf{\Delta}(k), \tag{32}$$

$$\mathbf{K}''_L(k,\omega)=2\mathbf{U}_\tau(k)\left[\mathrm{diag}\left(\frac{1/\tau_\lambda(k)}{\omega^2+[1/\tau_\lambda(k)]^2}\right)\right]\mathbf{U}_\tau^{-1}(k)\mathbf{\Delta}(k). \tag{33}$$

Now we specify $1/\tau_\lambda(k)$ by generalizing the procedure of Lovesey [28,29]. We first introduce a matrix $\mathbf{U}_\Delta(k)$ that diagonalizes $\mathbf{\Delta}(k)$:

$$\mathbf{U}_\Delta^{-1}(k)\mathbf{\Delta}(k)\mathbf{U}_\Delta(k)=\mathrm{diag}[\Delta_\lambda(k)], \tag{34}$$

where $\Delta_\lambda(k)$'s denote eigenvalues of the matrix $\mathbf{\Delta}(k)$. With the matrix $\mathbf{U}_\Delta(k)$, the square root of the matrix $\mathbf{\Delta}(k)$ can be defined

$$\mathbf{\Delta}^{1/2}(k)\equiv\mathbf{U}_\Delta(k)\{\mathrm{diag}[\sqrt{\Delta_\lambda(k)}]\}\mathbf{U}_\Delta^{-1}(k). \tag{35}$$

Then, generalizing the procedure of Lovesey, we write $\tau_\lambda^{-1}(k)$ in the form

$$\tau_\lambda^{-1}(k)=\xi_\lambda\sqrt{\Delta_\lambda(k)}. \tag{36}$$

The constant ξ_λ is determined by requiring that the resultant $\mathbf{S}(k,\omega=0)$ coincide with $\mathbf{S}^G(k,\omega=0)$ in the $k\to\infty$ limit, where $\mathbf{S}^G(k,\omega)$ is defined as the time Fourier transform of the Gaussian-approximated self-part of the intermediate scattering function matrix

$$\mathbf{F}^G(k,t)=\exp[-\tfrac{1}{2}\langle\boldsymbol{\omega}_{k,s}^2\rangle t^2]\mathbf{w}(k). \tag{37}$$

Since elements of the frequency moment matrices depend on molecular models, so do ξ_λ's.

As an example, using the results of the Appendix, the expression of ξ_λ for the diatomic molecule in Fig. 1 is found to be

$$\xi_\lambda=\sqrt{\frac{2}{\pi}\left(\frac{C}{D^2}-1\right)}, \tag{38}$$

in which the constants C and D are respectively given by

$$C\equiv3\left(\frac{k_BT}{M}\right)^2+4\frac{(k_BT)^2}{MI}z_\lambda^2+\frac{8}{5}\left(\frac{k_BT}{I}\right)^2z_\lambda^4,$$

$$D\equiv\frac{k_BT}{M}+\frac{2k_BT}{3I}z_\lambda^2. \tag{39}$$

Here M and I denote the total mass and the principal moment of inertia of the diatomic molecule, respectively, and z_λ is specified in Fig. 1.

For any model for diatomic molecule, it is found that all ξ_λ's are close to each other (and they are approximately equal to 1). In view of this, we approximate

$$\mathbf{U}_\tau(k)\approx\mathbf{U}_\Delta(k). \tag{40}$$

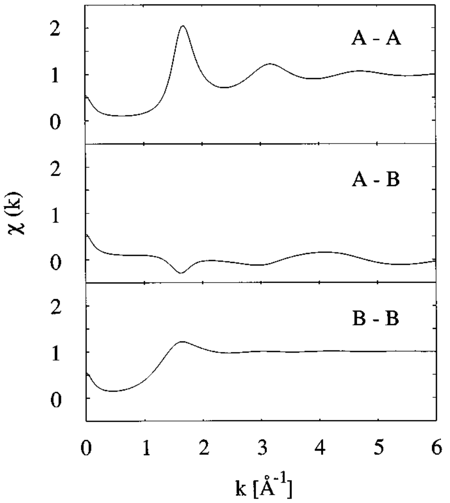

FIG. 2. Site-site static structure factors of the diatomic molecule, defined in Eq. (3), calculated by the extended version of the RISM.

Now all the quantities appearing in the right-hand side of Eq. (31) are specified. A similar model can be constructed for the single-particle counterpart $\mathbf{K}_L^s(k,t)$, starting from

$$\mathbf{K}_L^s(k,t)=\exp[-t\boldsymbol{\tau}_s^{-1}(k)]\mathbf{\Delta}_s(k)\quad\text{with}$$

$$\mathbf{\Delta}_s\equiv\langle\boldsymbol{\omega}_{k,s}^4\rangle\langle\boldsymbol{\omega}_{k,s}^2\rangle^{-1}-\langle\boldsymbol{\omega}_{k,s}^2\rangle, \tag{41}$$

and generalizing the procedure of Lovesey, as we have done above.

III. RESULTS AND DISCUSSION

A. System description

Throughout the paper we consider a solvent consisting of rigid diatomic molecules depicted in Fig. 1 with constituent atoms A and B of masses $m_A=36\ \mathrm{g\,mol}^{-1}$ and $m_B=4\ \mathrm{g\,mol}^{-1}$ separated from each other by a fixed distance of $l_{AB}=2.0$ Å. Atoms A and B carry partial charges $q_A=-0.25e$ and $q_B=+0.25e$, respectively, and the resultant dipole moment is 2.4 D. The Lennard-Jones parameters are $\sigma_A=4.0$ Å and $\epsilon_A/k_B=200$ K for atom A and $\sigma_B=2.0$ Å and $\epsilon_B/k_B=100$ K for atom B. The number density is 0.012 molecules Å^{-3} and the temperature is 250 K.

Figure 2 gives the site-site static structure factors (3) calculated by the extended version of RISM [15,16]. The peak positions are $k_{\max}=1.69$ Å^{-1} and $k_{\max}=1.65$ Å^{-1} for A-A and B-B pairs, respectively. Note that in the $k\to0$ limit, all the site-site structure factors coincide [12] and we define

$$\chi(0)\equiv\chi_{AA}(0)=\chi_{AB}(0)=\chi_{BB}(0). \tag{42}$$

We also define the following quantity for later convenience:

$$\chi''(0)=\chi''_{AA}(0)+\chi''_{BB}(0)-2\chi''_{AB}(0)\quad\text{with}$$

$$\chi''_{\alpha\beta}(0)=\lim_{k\to0}d^2\chi_{\alpha\beta}(k)/dk^2. \tag{43}$$

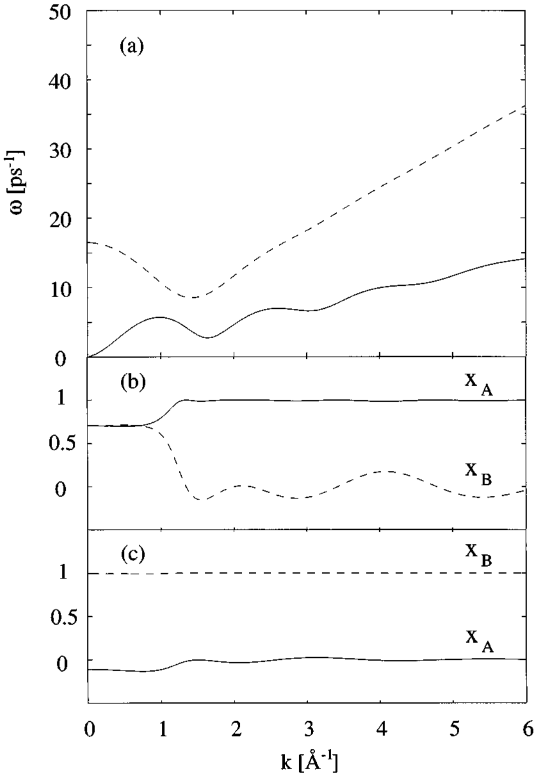

FIG. 3. (a) Eigenfrequencies as evaluated by diagonalizing $\langle \omega_k^2 \rangle$. Solid and dashed lines give the eigenfrequencies of the acoustic and optical modes, respectively. (b) x_A (solid line) and x_B (dashed line) defined in the text corresponding to the acoustic mode. (c) x_A (solid line) and x_B (dashed line) corresponding to the optical mode. x_A and x_B are normalized such that $x_A^2 + x_B^2 = 1$.

B. Eigenmodes of the system

In this subsection we investigate eigenmodes of the system and how each atom in the molecule contributes to the modes. To find the eigenmodes of $\mathbf{F}(k,t)$, we neglect the damping term (represented by the memory function matrix) in Eq. (11) and obtain

$$\ddot{\mathbf{F}}(k,0) = -\langle \boldsymbol{\omega}_k^2 \rangle \mathbf{F}(k,0). \tag{44}$$

Elements of $\langle \boldsymbol{\omega}_k^2 \rangle$ for the diatomic molecule can be calculated using Eqs. (13), (A1), and (A18) and the eigenmodes can be obtained by diagonalizing this matrix. The fact that $\langle \boldsymbol{\omega}_k^2 \rangle$ for the diatomic molecule is 2×2 matrix naturally leads to the possible existence of two modes, which turn out to be acoustic and optical ones, as is explained below.

In Fig. 3 we report the results of the diagonalization of $\langle \boldsymbol{\omega}_k^2 \rangle$. The solid line in Fig. 3(a) represents the dispersion curve corresponding to the acoustic branch. It is seen that the dispersion behavior of the acoustic mode is very similar to that of a monatomic system. The $k \to 0$ limit of the eigenfrequency of this mode is given by [5]

$$\omega_{\mathrm{acou}}^2(k \to 0) = \frac{k_B T}{M \chi(0)} k^2, \tag{45}$$

i.e., that of the ordinary sound mode that propagates with the isothermal sound velocity, consistent with the fact that energy fluctuations are not explicit dynamical variables in our theory.

The contributions from each atom to the acoustic mode can be extracted in the following way. Diagonalizing the matrix $\langle \boldsymbol{\omega}_k^2 \rangle$ corresponds to turning the description of the system in terms of the densities of each atom $\delta\rho_A(\mathbf{k})$ and $\delta\rho_B(\mathbf{k})$ to that in terms of their linear combination:

$$x_A(k)\,\delta\rho_A(\mathbf{k}) + x_B(k)\,\delta\rho_B(\mathbf{k}), \tag{46}$$

where $x_A(k)$ and $x_B(k)$ are the components of the eigenvector corresponding to the mode. It can be readily found for the acoustic mode that

$$\lim_{k \to 0} [x_A(k), x_B(k)] \propto [1,1]. \tag{47}$$

This is consistent with the fact that the sound mode stems from the center-of-mass (translational) motion of the molecules, i.e., each atom in the molecule equally contributes to this mode.

Figure 3(b) summarizes $x_A(k)$ and $x_B(k)$ of the acoustic branch at various wave vectors, normalized such that $x_A^2(k) + x_B^2(k) = 1$. It is seen from the figure that $x_A(k) \approx x_B(k)$ holds well in the small-k (up to ≈ 1.0 Å^{-1}) region. In the large-k (i.e., $k \gg k_{\mathrm{max}}$) region, however, it is found that $x_A(k) \approx 1$ with $x_B(k) \approx 0$, i.e., the dispersion curve of the acoustical branch in this region reflects the self-motion (the single-particle motion) of the heavier atom A. (The collective and single-particle nature of the modes will be discussed in Sec. III C.) In the intermediate-k (i.e., $k \approx k_{\mathrm{max}}$) region, $x_A(k) \approx x_B(k)$ does not hold and $x_B(k)$ becomes even negative [see Fig. 3(b)]. As will be clarified below, this fact reveals that the rotational motion is also involved in this k region.

We next turn our attention to the dispersion relation of the optical branch of $\langle \boldsymbol{\omega}_k^2 \rangle$, presented as a dashed line in Fig. 3(a). The optical branch is well separated from the acoustic one at all wave vectors (due to the large difference in the masses of constituent atoms) and it is apparent from the figure that this mode does not vanish in the $k \to 0$ limit. (The term ''optical'' comes from this fact.) The eigenfrequency in this limit is given by [5]

$$\omega_{\mathrm{opti}}^2(k \to 0) = \frac{4 k_B T}{3 I \chi''(0)} l_{AB}^2 \tag{48}$$

and the corresponding eigenvector, using the notation in Eq. (46), turns out to be

$$\lim_{k \to 0} [x_A(k), x_B(k)] \propto [z_A, z_B]. \tag{49}$$

Note from Fig. 1 that z_A and z_B are opposite in sign (the solvent model used here gives $\lim_{k \to 0}[x_A(k), x_B(k)] = [-0.11, 0.99]$ when the norm of the eigenvector is normalized to unity), thus A and B atoms contribute to this mode with the out-of-phase fashion in terms of Eq. (46). Since the magnitude of z_α gauges the efficiency of atom α for participating in the orientational motion, the optical mode is evidently related to the rotational motion of the molecules.

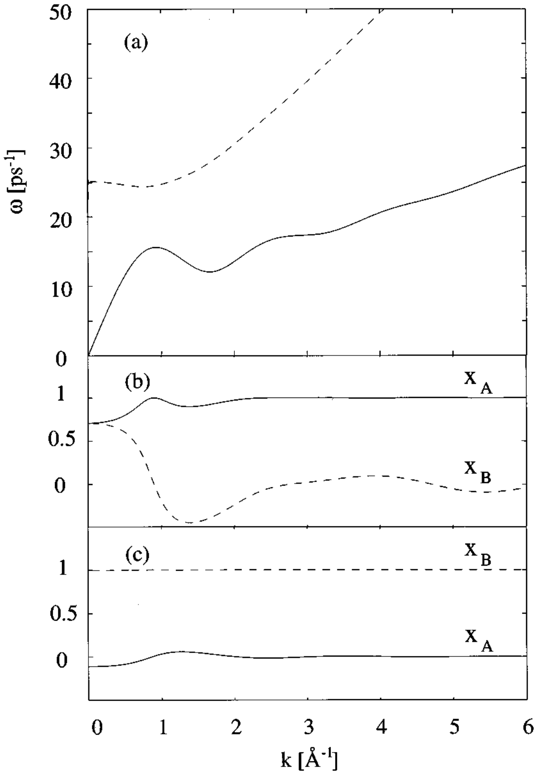

FIG. 4. Eigenfrequencies and the components of the eigenvectors for $\langle \omega_{k,L}^2 \rangle$ defined in Eq. (14). The notation is the same as in Fig. 3.

[This is also obvious by noting that Eq. (48) depends on the moment of inertia of the molecule.]

Figure 3(c) presents $x_A(k)$ and $x_B(k)$ corresponding to the optical mode at various wave vectors. (Note that since generally $\langle \boldsymbol{\omega}_k^2 \rangle$ is not a symmetrical matrix, the eigenvectors corresponding to the acoustic and optical modes are not orthogonal to each other.) It is seen that $[x_A(k),x_B(k)] \propto [z_A,z_B]$ is well satisfied in the small-k (up to approximately 1.0 Å^{-1}) region. In the larger-k region, it is found that the dispersion curve is dominated by the single-particle contribution from the lighter atom B, i.e., $x_B(k) \approx 1$ with $x_A(k) \approx 0$.

So far we discussed the eigenmodes of $\mathbf{F}(k,t)$, but a similar analysis can be applied to those of the longitudinal current correlation function $\mathbf{J}(k,t)$. The eigenmodes of $\mathbf{J}(k,t)$ can be obtained by the same manner from the GLE for $\mathbf{J}(k,t)$ which takes a form similar to Eq. (11), and it follows after the nondamping approximation

$$\ddot{\mathbf{J}}(k,0) = -\langle \boldsymbol{\omega}_{k,L}^2 \rangle \mathbf{J}(k,0), \tag{50}$$

which clarifies the physical meaning of $\langle \boldsymbol{\omega}_{k,L}^2 \rangle$ defined in Eq. (14). Elements of $\langle \boldsymbol{\omega}_{k,L}^2 \rangle$ for the diatomic molecule can be calculated using Eqs. (13), (A20), and (A22) and the eigenfrequencies and eigenvectors can be found by diagonalizing this matrix, the results of which are presented in Fig. 4.

C. Longitudinal current spectra

In the preceding subsection we discussed the eigenmodes of the system within the nondamping approximation. Here we analyze the collective excitations in our model liquid by solving the full GLE that incorporates the damping effect represented by the memory function matrix $\mathbf{K}_L(k,t)$.

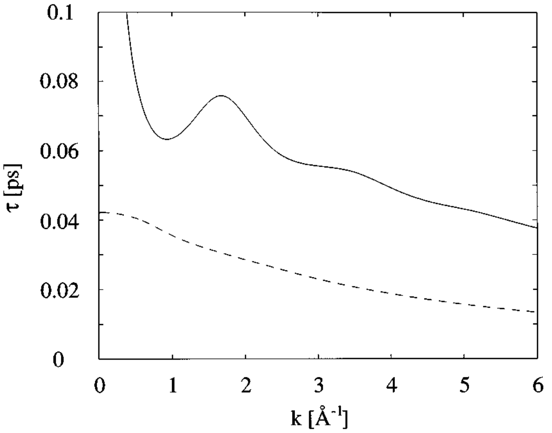

FIG. 5. Eigenvalues of the relaxation-time matrix as defined in Eq. (29). The solid line gives the relaxation times corresponding to the acoustic mode and the dashed line the optical mode.

As in other studies [5–7,9–11], we consider the longitudinal current spectra, rather than the dynamic structure factors, in investigating the collective excitations in the liquid since the former always exhibits a peaked structure even when the inelastic peaks in the latter are not well defined [20]. The physical information contained in these two quantities, however, is basically the same due to Eq. (10).

Before embarking on the analysis of the longitudinal current spectra, we briefly comment on the relaxation times for the memory functions defined through Eq. (29). In Fig. 5 we report the wave-vector dependence of the relaxation times calculated from Eqs. (36) and (38): The solid line gives those corresponding to the acoustic mode and the dashed line the optical mode. It is seen from the figure that the component of the optical mode relaxes faster than that of the acoustic mode at all wave vectors. It is worthwhile to note at this point that our prescription, Eq. (36), implies an infinite relaxation time for the acoustic mode in the $k \rightarrow 0$ limit since $\Delta_\lambda(k)$ corresponding to the mode vanishes as k^2 in the small-k region, which is inconsistent with the prediction of the hydrodynamic theory [22]. The inconsistency also occurs in the original theory of Lovesey [28,29]. It is known, however, in the monatomic liquid case that, although the simple exponential model for memory functions (often referred to as the viscoelastic model) is only expected to be reliable for wave vectors outside the strict hydrodynamic regime, the consequences of the above inconsistency are likely to be not so serious in practice [22]. Anticipating this to be valid also in the case of molecular fluids, we believe the essential features of the results to be presented below will not be altered significantly even after the inconsistency is removed in some way. This defect in the present theory, caused by the incorrect relaxation times in the small-k regime, may be remedied by improving the approximation scheme for memory functions, and such a study, exploiting the mode-coupling approximation, is currently under way in our group.

The longitudinal current spectra at various wave vectors are calculated using Eqs. (10) and (20) with the simple exponential model for $\mathbf{K}_L(k,t)$ of the form given by Eq. (29)

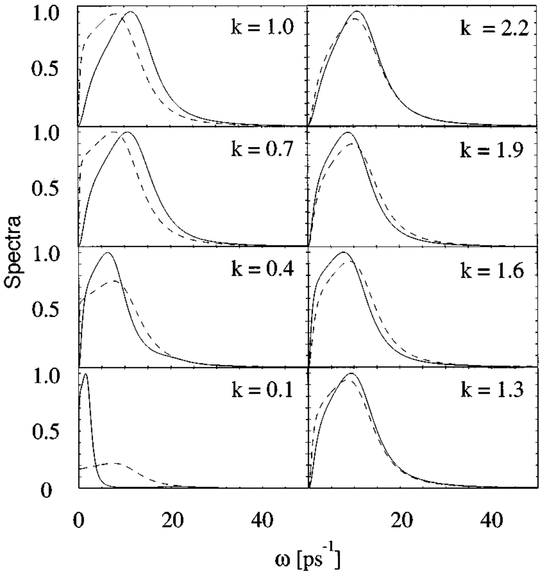

FIG. 6. Solid lines, the longitudinal current spectra of the A-A pair $C_{L,AA}(k,\omega)$ as a function of ω at the indicated k (in Å^{-1}) values, in arbitrary units; dashed lines, the single-particle contributions.

and the results for A-A and B-B pairs are presented as solid lines in Figs. 6 and 7, respectively. (Remember that atom A is much heavier than atom B.) Also added in these figures are the single-particle contributions (i.e., contributions from the self-motions), calculated using Eqs. (27) and (41), with the aim of elucidating the collective nature of the excitations in the small-k region.

A number of observations can be made concerning the theoretical results given in Figs. 6 and 7. We first note that two peaks are observable in both of the spectra at $k = 0.1$ Å^{-1}. However, $C_{L,AA}$ is dominated by the contribution from the lower-frequency acoustic mode and the higher-frequency peak (approximately 20 ps^{-1}) is only barely seen. The lower-frequency peak also appears in $C_{L,BB}$ because both atoms A and B participate in the center-of-mass density fluctuations as discussed above. The higher-frequency peak corresponding to the optical mode is exaggerated in $C_{L,BB}$ since the lighter atom B is much more responsible for the orientational motion of the molecule. The collective nature of these two excitations in the small-k region is apparent by comparing solid lines with dashed ones in Figs. 6 and 7. In the large-k region, however, the spectra are almost identical to those from the single-particle contributions: $C_{L,AA}$ is dominated by the contribution from the self-motion of atom A, while that of atom B determines the overall shape of $C_{L,BB}$.

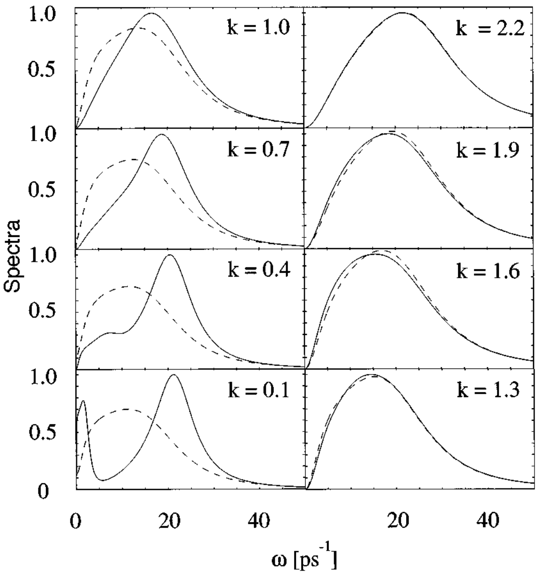

FIG. 7. Solid lines, the longitudinal current spectra of the B-B pair $C_{L,BB}(k,\omega)$ as a function of ω at the indicated k (in Å^{-1}) values, in arbitrary units; dashed lines, the single-particle contributions.

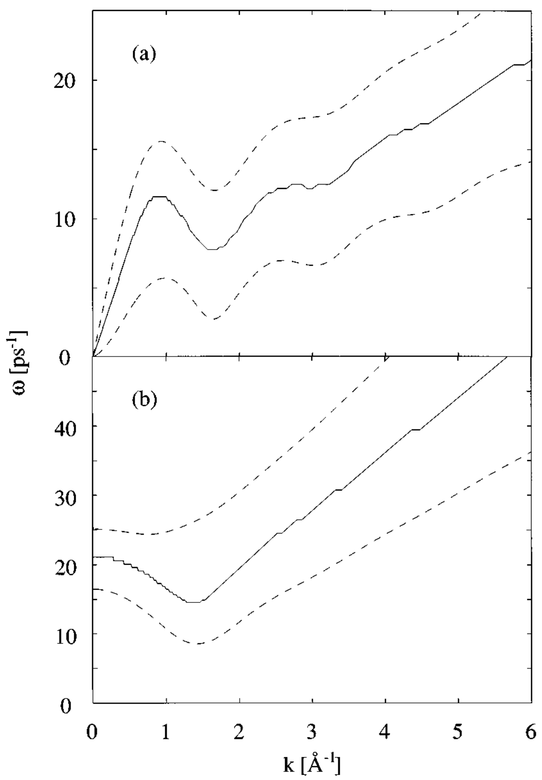

FIG. 8. Dispersion relation of the (a) acoustic and (b) optical modes as evaluated from the peak positions in the longitudinal current spectra (solid lines), by diagonalizing $\langle \omega_k^2 \rangle$ (lower dashed lines) and by $\langle \omega_{k,L}^2 \rangle$ (upper dashed lines).

The resultant low and high peak frequencies (dispersion relations) of the longitudinal current spectra are shown as solid lines in Figs. 8(a) and 8(b), respectively. It is seen from Fig. 8(a) that the dispersion curve of the low-frequency acoustic mode is very similar to that of monatomic fluids and the positive dispersion is apparent from the figure. The dispersion behavior of the optical mode presented in Fig. 8(b) is qualitatively in accord with that of water reported by Resat, Raineri, and Friedman [10], who calculated it based on a dielectric theory that takes into account the rotational motion of water.

The reasons for this qualitative correspondence of the dispersion behavior of the optical mode between our results and those of Resat, Raineri, and Friedman [10] (but for water) are twofold: similarities in the solvent models and in the descriptions of the mode. First, although our diatomic solvent model seems to be very different from water, they have a similarity other than being molecular liquids in that both of them have quite heterogeneous mass distributions of constituent atoms: The translational motion is almost carried by atom A in our model and by an oxygen atom in water, while the rotational motion is dominated by that of B and hydrogen atoms. Second, we have found in Sec. III B (but within the nondamping approximation) that the optical mode in the small-k region (this is the most interesting region) can be described in terms of the linear combination

$$z_A \delta\rho_A(\mathbf{k}) + z_B \delta\rho_B(\mathbf{k}). \tag{51}$$

This is ''nearly'' the same combination as that of the basic dynamical variable (the local charge density) in the dielectric theory of Resat, Raineri, and Friedman [10],

$$q_A \delta\rho_A(\mathbf{k}) + q_B \delta\rho_B(\mathbf{k}), \tag{52}$$

in terms of phase since z_A and z_B are opposite in sign and so are q_A and q_B (only the relative sign has importance). That the descriptions of the optical mode in terms of Eqs. (51) and (52) are nearly the same can also be understood by noting that the rotational motion gives rise to the local charge-density fluctuations, while the center-of-mass motion does not due to the charge neutrality of the solvent molecule; it is the former (the rotational motion) that is responsible for the optical mode.

In this connection, it is also instructive to note that the following linear combination, which is found to describe the acoustic mode in the small-k region:

$$\delta\rho_A(\mathbf{k}) + \delta\rho_B(\mathbf{k}), \tag{53}$$

is again nearly the same combination as that of the local mass-density fluctuations of the system

$$m_A \delta\rho_A(\mathbf{k}) + m_B \delta\rho_B(\mathbf{k}) \tag{54}$$

in terms of phase since masses are always positive. In fact, both of the above combinations can give the same description as far as the dynamics of the acoustic mode in the small-k region is concerned [9].

IV. CONCLUDING REMARKS

In the present paper we described a molecular theory for liquid dynamics that provides a method for calculating dynamical correlation functions of polyatomic fluids. The theory is based on the generalized Langevin equation and on the interaction-site model of molecular liquids and is capable of treating the general class of molecular fluids. Another distinctive feature of our theory is that it offers a self-contained framework for solving dynamical problems without making reference to any dynamical information from outside, i.e., it requires only the knowledge of parameters for potential functions and molecular geometry (such as bond lengths) as in simulation studies. As an application of the theory, we calculated longitudinal current spectra of a diatomic dipolar liquid, discussed the collective excitations in this solvent, and clarified how these excitations arise from the translational and rotational motions of the molecules.

The theory presented here can be applied to the description of time-dependent phenomena in polar fluids: solvation dynamics and dynamical solvent effect on charge transfer reactions will be among the most interesting applications. The research for this direction is currently under way in our group and we plan to report the results in subsequent papers.

In order to refine our theory further, several extensions are conceivable by developing approximation schemes for memory functions. The most promising extension will be adopting the mode-coupling approximation, in view of the success of the mode-coupling theory in describing time-correlation functions of simple liquids [22]. The research for this direction is also one of our concerns in the future study.

ACKNOWLEDGMENTS

The authors are grateful to Professor Munakata for fruitful discussions. We thank Dr. Raineri for private communication of Ref. [30]. S.-H.C. gratefully acknowledges financial support from the Japan Society for the Promotion of Science for Young Scientists. This work was supported by the Joint Studies Program of the Institute for Molecular Science.

APPENDIX

In this Appendix we present an evaluation of elements of the second and fourth frequency moment matrices, as defined in Eqs. (12) and (25). Since the final outcome depends on the molecular model, only the expressions for the diatomic molecule depicted in Fig. 1 are reported.

1. Second moment matrix

The outline of the calculation of the second moment matrix is given in the paper of Ricci *et al.* [5] and the results for various molecular fluids are presented by Raineri [30]. Since one requires similar manipulation repeatedly in obtaining elements of the fourth moment matrix, we evaluate those of the second moment matrix in some detail. Our treatment here follows closely that of Raineri [30].

We first note from Eqs. (7), (12), and (25) that

$$\begin{aligned}[\overline{\boldsymbol{\omega}_k^2}]_{\alpha\beta} &= k^2 \frac{1}{N} \sum_{i,j} \langle v_{i,z}^{\alpha} v_{j,z}^{\beta} e^{-i\mathbf{k}\cdot(\mathbf{r}_i^{\alpha}-\mathbf{r}_j^{\beta})} \rangle \\ &= k^2 \langle v_{1,z}^{\alpha} v_{1,z}^{\beta} e^{-i\mathbf{k}\cdot(\mathbf{r}_1^{\alpha}-\mathbf{r}_1^{\beta})} \rangle = [\overline{\boldsymbol{\omega}_{k,s}^2}]_{\alpha\beta} \equiv k^2 J_{\alpha\beta}(k).\end{aligned} \tag{A1}$$

The second equality is due to the statistical independence of the velocities of different molecules at the same time. In view of this relation, it suffices to evaluate $J_{\alpha\beta}(k)$ to obtain both $[\overline{\boldsymbol{\omega}_k^2}]_{\alpha\beta}$ and $[\overline{\boldsymbol{\omega}_{k,s}^2}]_{\alpha\beta}$.

Having assumed the molecule to be rigid, one has

$$\mathbf{v}_i^{\alpha} = \mathbf{v}_i^{C} + \mathbf{w}_i \times \delta\mathbf{r}_i^{C\alpha}, \tag{A2}$$

$$\mathbf{a}_i^{\alpha} = \mathbf{a}_i^{C} + \dot{\mathbf{w}}_i \times \delta\mathbf{r}_i^{C\alpha} + \mathbf{w}_i \times (\mathbf{w}_i \times \delta\mathbf{r}_i^{C\alpha}), \tag{A3}$$

where $\mathbf{v}_i^{\alpha}$ and $\mathbf{a}_i^{\alpha}$ denote the velocity and the acceleration of α atom in the ith molecule, respectively, $\mathbf{v}_i^{C}$ and $\mathbf{a}_i^{C}$ represent the velocity and the acceleration of the center of mass of the

ith molecule, respectively, $\mathbf{w}_i$ is its angular velocity, and $\delta\mathbf{r}_i^{C\alpha}$ is the vector joining the center of mass and atom α.

Due to the statistical independence of translational and rotational velocities, substituting Eq. (A2) into Eq. (A1) gives

$$\begin{aligned} J_{\alpha\beta}(k) &= \langle (v_{1,z}^{C})^2 e^{-i\mathbf{k}\cdot(\mathbf{r}_1^{\alpha}-\mathbf{r}_1^{\beta})}\rangle \\ &\quad + \langle [\mathbf{w}_1\times\delta\mathbf{r}_1^{C\alpha}]_z[\mathbf{w}_1\times\delta\mathbf{r}_1^{C\beta}]_z e^{-i\mathbf{k}\cdot(\mathbf{r}_1^{\alpha}-\mathbf{r}_1^{\beta})}\rangle \\ &\equiv J_{\alpha\beta}^{\mathrm{trans}}(k)+J_{\alpha\beta}^{\mathrm{rot}}(k). \end{aligned} \tag{A4}$$

The first term can be easily evaluated, due to the statistical independence of the translational velocities and coordinates, as

$$\begin{aligned} J_{\alpha\beta}^{\mathrm{trans}}(k) &= \langle (v_{1,z}^{C})^2\rangle\langle e^{-i\mathbf{k}\cdot(\mathbf{r}_1^{\alpha}-\mathbf{r}_1^{\beta})}\rangle = \frac{k_BT}{M}\,w_{\alpha\beta}(k) \\ &= \frac{k_BT}{M}\,j_0(kl_{\alpha\beta}), \end{aligned} \tag{A5}$$

where we notice Eqs. (4) and (6).

The evaluation of the rotational part $J_{\alpha\beta}^{\mathrm{rot}}(k)$ is somewhat involved. To this end, we note that $J_{\alpha\beta}^{\mathrm{rot}}(k)$ can be written in terms of a zeroth component of a spherical tensor of rank 1 defined by [12]

$$T_{10}^{\alpha} = \frac{i}{\sqrt{2}}\,[\mathbf{w}_1\times\delta\mathbf{r}_1^{C\alpha}]_z\,. \tag{A6}$$

Then $J_{\alpha\beta}^{\mathrm{rot}}(k)$ can be written as

$$J_{\alpha\beta}^{\mathrm{rot}}(k) = -2\langle T_{10}^{\alpha}T_{10}^{\beta}e^{-i\mathbf{k}\cdot\delta\mathbf{r}_{\alpha\beta}}\rangle, \tag{A7}$$

where $\delta\mathbf{r}_{\alpha\beta}\equiv\mathbf{r}_1^{\alpha}-\mathbf{r}_1^{\beta}$. Hereafter in this appendix, the label specifying the molecule 1 will be dropped. A Rayleigh expansion [12] of the exponential gives

$$e^{-i\mathbf{k}\cdot\delta\mathbf{r}_{\alpha\beta}} = \sum_{l,m}(-i)^l(2l+1)j_l(kl_{\alpha\beta})C_{lm}(\mathbf{e}_k^{(s)})C_{lm}^{*}(\mathbf{e}_{\alpha\beta}^{(s)}), \tag{A8}$$

in which $l_{\alpha\beta}\equiv|\delta\mathbf{r}_{\alpha\beta}|$, $\mathbf{e}_k^{(s)}$ and $\mathbf{e}_{\alpha\beta}^{(s)}$ denote unit vectors along $\mathbf{k}$ and $\delta\mathbf{r}_{\alpha\beta}$, respectively, $j_l(x)$ is the lth-order spherical Bessel function, and C_{lm} is the Racah spherical harmonics. The quantities with the superscript (s) refer to the space-fixed laboratory frame, which we abbreviate as the s frame from here on. (Do not confuse it with the subscript and superscript s indicating single-particle quantities.) Note that $C_{lm}(\mathbf{e}_k^{(s)})=\delta_{m,0}$ since we have chosen $\mathbf{k}$ to be along the z axis in the s frame, and Eq. (A7) becomes

$$\begin{aligned} J_{\alpha\beta}^{\mathrm{rot}}(k) &= -2\sum_{l}(-i)^l(2l+1)j_l(kl_{\alpha\beta}) \\ &\quad\times\langle T_{10}^{\alpha(s)}T_{10}^{\beta(s)}C_{l0}^{*}(\mathbf{e}_{\alpha\beta}^{(s)})\rangle. \end{aligned} \tag{A9}$$

It is more convenient to evaluate the ensemble averages in the body-fixed molecular frame (b frame), which we choose to be coincident with the inertial principal one. The transformation law to the b frame is [12]

$$T_{10}^{(s)} = \sum_{n}D_{0n}^{1*}(\Omega)T_{1n}^{(b)}, \quad C_{l0}^{(s)} = \sum_{n}D_{0n}^{l*}(\Omega)C_{ln}^{(b)}, \tag{A10}$$

where the quantities with the superscript (b) refer to the b frame and $D(\Omega)$ is the Wigner function (rotation matrix) in terms of the Eular angle Ω, which describes the orientation of the molecule with respect to the s frame. Substituting Eq. (A10) into Eq. (A9) and using the properties of the Wigner functions [12], one has

$$\begin{aligned} J_{\alpha\beta}^{\mathrm{rot}}(k) &= -\frac{2}{3}\sum_{l}(-i)^l(2l+1)j_l(kl_{\alpha\beta})\sum_{n_1,n_2}(-1)^{n_1} \\ &\quad\times C(l11;000)C(l11;n_1+n_2,\underline{n_2},n_1) \\ &\quad\times\langle T_{1n_1}^{\alpha(b)}T_{1n_2}^{\beta(b)}\rangle C_{l\underline{n_1+n_2}}(\mathbf{e}_{\alpha\beta}^{(b)}), \end{aligned} \tag{A11}$$

where $C(l_1l_2l;m_1m_2m)$ is the Clebsch-Gordan (CG) coefficient and $\underline{n}=-n$. Due to the properties of CG coefficients [12], only $l=0$ and 2 terms in the above equation can give a nonzero contribution and one obtains

$$J_{\alpha\beta}^{\mathrm{rot}}(k) = -\tfrac{2}{3}j_0(kl_{\alpha\beta})\sum_{n}(-1)^n\langle T_{1n}^{\alpha(b)}T_{1\underline{n}}^{\beta(b)}\rangle \tag{A12}$$

$$\begin{aligned} &-\tfrac{2}{3}\sqrt{10}j_2(kl_{\alpha\beta})\sum_{n_1,n_2}(-1)^{n_1} \\ &\times C(211;n_1+n_2,\underline{n_2},n_1) \\ &\times\langle T_{1n_1}^{\alpha(b)}T_{1n_2}^{\beta(b)}C_{2\underline{n_1+n_2}}(\mathbf{e}_{\alpha\beta}^{(b)})\rangle. \end{aligned} \tag{A13}$$

Averages of the form $\langle TT\rangle$ and $\langle TTC\rangle$ can be evaluated using the product rule for spherical tensors [12]:

$$T_{1n}^{\alpha(b)} = \sum_{m}C(111;m,n-m,n)w_m^{(b)}r_{n-m}^{\alpha(b)}, \tag{A14}$$

where $w_n^{(b)}$ and $r_n^{\alpha(b)}$ denote the spherical components of $\mathbf{w}^{(b)}$ and $\delta\mathbf{r}^{C\alpha(b)}$, respectively.

Finally, let us evaluate the elements of $J_{\alpha\beta}^{\mathrm{rot}}(k)$ for the diatomic molecule depicted in Fig. 1. In terms of the quantities in the b frame (which is specified in Fig. 1), one has

$$\langle T_{1n}^{\alpha(b)}T_{1\underline{n}}^{\beta(b)}\rangle = -\frac{n^2}{2}\,z_{\alpha}z_{\beta}\langle w_n^{(b)}w_{\underline{n}}^{(b)}\rangle, \tag{A15}$$

$$\langle T_{1n_1}^{\alpha(b)}T_{1n_2}^{\beta(b)}C_{2\underline{n_1+n_2}}(\mathbf{e}_{\alpha\beta}^{(b)})\rangle = -\frac{n^2}{2}\,z_{\alpha}z_{\beta}\langle w_n^{(b)}w_{\underline{n}}^{(b)}\rangle, \tag{A16}$$

where we notice $C_{2n}(\mathbf{e}_{\alpha\beta}^{(b)})=\delta_{n,0}$ for the diatomic molecule. Substituting these into Eq. (A13) and noting $\langle w_x^{(b)}w_x^{(b)}\rangle=\langle w_y^{(b)}w_y^{(b)}\rangle=k_BT/I$ for the diatomic molecule, one obtains

$$J_{\alpha\beta}^{\mathrm{rot}}(k) = \frac{2}{3}\,\frac{k_BT}{I}\,z_{\alpha}z_{\beta}[j_0(kl_{\alpha\beta})+j_2(kl_{\alpha\beta})]. \tag{A17}$$

The total $J_{\alpha\beta}(k)$ for the diatomic molecule is a sum of Eqs. (A5) and (A17), the final result being

$$J_{\alpha\beta}(k)=\frac{k_BT}{M}\,j_0(kl_{\alpha\beta})+\frac{2}{3}\,\frac{k_BT}{I}\,z_\alpha z_\beta[j_0(kl_{\alpha\beta})+j_2(kl_{\alpha\beta})]. \tag{A18}$$

2. Fourth moment matrix

We next consider the fourth moment matrix $[\overline{\boldsymbol{\omega}_k^4}]_{\alpha\beta}$. From Eqs. (1), (2), and (12), one has (defining $\mathbf{r}_{ij}^{\alpha\beta}\equiv\mathbf{r}_i^\alpha-\mathbf{r}_j^\beta$)

$$\begin{aligned}
[\overline{\boldsymbol{\omega}_k^4}]_{\alpha\beta}&=\frac{1}{N}\,\langle\delta\ddot{\rho}_\alpha(\mathbf{k},0)^*\,\delta\ddot{\rho}_\beta(\mathbf{k},0)\rangle\\
&=k^2\,\frac{1}{N}\sum_{i,j}\,\langle a_{i,z}^\alpha a_{j,z}^\beta e^{-i\mathbf{k}\cdot\mathbf{r}_{ij}^{\alpha\beta}}\rangle\\
&\quad+ik^3\,\frac{1}{N}\sum_{i,j}\,\langle[a_{i,z}^\alpha(v_{j,z}^\beta)^2-(v_{i,z}^\alpha)^2a_{j,z}^\beta]e^{-i\mathbf{k}\cdot\mathbf{r}_{ij}^{\alpha\beta}}\rangle\\
&\quad+k^4\,\frac{1}{N}\sum_{i,j}\,\langle(v_{i,z}^\alpha)^2(v_{j,z}^\beta)^2e^{-i\mathbf{k}\cdot\mathbf{r}_{ij}^{\alpha\beta}}\rangle\\
&\equiv[\overline{\boldsymbol{\omega}_{k,s}^4}]_{\alpha\beta}+[\overline{\boldsymbol{\omega}_{k,d}^4}]_{\alpha\beta},
\end{aligned} \tag{A19}$$

where $[\overline{\boldsymbol{\omega}_{k,s}^4}]_{\alpha\beta}$ denotes the self $(i=j)$ part and $[\overline{\boldsymbol{\omega}_{k,d}^4}]_{\alpha\beta}$ the distinct $(i\neq j)$ part.

Substituting Eqs. (A2) and (A3) into Eq. (A19) gives many terms and each term can be evaluated as we have done in deriving Eq. (A18). After straightforward but lengthy calculations, one has for the self-part of the diatomic molecule

$$\begin{aligned}
[\overline{\boldsymbol{\omega}_{k,s}^4}]_{\alpha\beta}&=k^2\left(\frac{k_BT}{M}\right)^2j_0\left\{3k^2+\sum_{\gamma,\delta}\,\Omega_{\gamma\delta}^2(0)\right\}\\
&\quad+k^2\,\frac{(k_BT)^2}{MI}\,(j_0+j_2)\left\{4z_\alpha z_\beta k^2\right.\\
&\quad\left.+\tfrac{2}{3}(z_\alpha+z_\beta)\sum_{\gamma,\delta}\,z_\gamma\Omega_{\gamma\delta}^2(0)\right\}\\
&\quad+k^2\left(\frac{k_BT}{I}\right)^2z_\alpha z_\beta\left\{z_\alpha z_\beta(\tfrac{8}{5}j_0+\tfrac{16}{7}j_2+\tfrac{24}{35}j_4)k^2\right.\\
&\quad\left.+\tfrac{8}{3}(j_0+j_2)+\tfrac{2}{3}(j_0+j_2)\sum_{\gamma,\delta}\,z_\gamma^2\Omega_{\gamma\delta}^2(0)\right\}.
\end{aligned} \tag{A20}$$

Here we have used the abbreviation $j_m\equiv j_m(kl_{\alpha\beta})$ and $\Omega_{\gamma\delta}^2(k)$ is defined by

$$\begin{aligned}
\Omega_{\gamma\delta}^2(k)&\equiv\frac{\rho}{k_BT}\int d\mathbf{r}\;e^{-i\mathbf{k}\cdot\mathbf{r}}g_{\gamma\delta}(r)\,\frac{\partial^2\phi_{\gamma\delta}(r)}{\partial z^2}\\
&=\frac{\rho}{3k_BT}\int d\mathbf{r}\,g_{\gamma\delta}(r)\left\{\phi_{\gamma\delta}''(r)[j_0(kr)-2j_2(kr)]\right.\\
&\quad\left.+\frac{2\phi_{\gamma\delta}'(r)}{r}\,[j_0(kr)+j_2(kr)]\right\}.
\end{aligned} \tag{A21}$$

In this equation, $\phi_{\gamma\delta}(r)$, $\phi_{\gamma\delta}'(r)$, and $\phi_{\gamma\delta}''(r)$ denote the site-site interaction potential and its first and second derivatives with respect to r, respectively.

The elements of the distinct part can be evaluated in a similar manner. It turns out that all the kinetic terms cancel out in the distinct part and one is left with the interaction terms, which can be summarized as

$$[\overline{\boldsymbol{\omega}_{k,d}^4}]_{\alpha\beta}=-k^2\sum_{\gamma,\delta}\,J_{\alpha\gamma}(k)\Omega_{\gamma\delta}^2(k)J_{\delta\beta}(k), \tag{A22}$$

where $J_{\alpha\beta}(k)$ in the case of the diatomic molecule is given by Eq. (A18).

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