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Theory of the generalized dynamic structure factor of polyatomic molecular fluids measured by inelastic x-ray scattering

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We describe a theory for the calculation of the generalized dynamic structure factor $S(k,\omega)$ as measured by an inelastic x-ray scattering (IXS) experiment on single-component molecular or polyatomic molecular fluids. IXS spectrum of a simple fluid is proportional to the dynamic structure factor of a single species of atom. In the case of a molecular fluid, however, IXS spectrum is a weighted sum of partial dynamic structure factors of pairs of atomic species. The weighting factors are products of the atomic form factors of the pairs. We call this weighted average dynamic structure factor the generalized dynamic structure factor. We extend the formalism of a three effective eigenmode theory (TEE) developed previously for simple fluids to derive an approximate evolution equation for the generalized dynamic structure factor, which can be considered as a generalized hydrodynamic equation for molecular fluids. As examples, we first study the contributions of the partial dynamic structure factor to the generalized dynamic structure factor computed from molecular dynamics simulation of SPC/E model water. We found that the generalized dynamic structure factor of water measured by IXS can be well approximated by the center of mass or the oxygen atom dynamic structure factors. The generalized TEE model was then employed to analyze IXS spectra of nearly fully hydrated dilauroylphosphatidylcholine. The theory is able to fit all of the spectra in the k range from 5 to 32 nm^{-1} quantitatively and gives their deconvoluted generalized dynamic structure factors.

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I. INTRODUCTION

Collective density fluctuation of simple fluids has been studied extensively both experimantally and theoretically in the past two decades [1–3]. It is well known that, in Born approximation, the double differential cross sections of both inelastic photon and neutron scattering from simple fluids are proportinal to the dynamic structure factor $S(k,\omega)$ where k is the magnitude of the wave vector transfer and $\hbar\omega$ the energy transfer in the scattering experiment. Owing to the fluctuation-dissipation theorem, valid for an equilibrium system, $S(k,\omega)$ is also the spectral density of the equilibrium atomic density fluctuation in the fluid. This gives an incentive for formulating a dynamical theory of fluid that contains explicitly the dynamic structure factor. There are two known asymptotic forms of the dynamical structure factor: the short wavelength (large k) limit where the free streaming or the ideal gas limit can be taken and $S(k,\omega)$ is a single Gaussian peak centered around $\omega=0$ in the classical limit; the long wavelength (small k) limit where the macroscopic hydradynamic equations can be used to show that $S(k,\omega)$ consists of three Lorenzian peaks, one Rayleigh peak, centered around $\omega=0$, having a width Γ_h, and two symmetrically sifted Brillouin peaks, centered around $\pm\Omega_s$, having a width Γ_s. Ω_s and Γ_s are, respectively, the frequency and damping of the propagating ordinary sound. The so-called generalized hydrodynamics theory is intended to describe correlations between a set of quasiconserved slow dynamical quantities (modes). It extends the macroscopic hydrodynamic description to density fluctuations with wavelengths comparable to interparticle distances. On the other hand, the so-called generalized kinetic theory of liquids employs an idealized hard sphere potential to give evolution of the microscopic phase-space time correlation function. It has been shown that the mode description can be derived directly from the generalized kinetic theory by expanding the phase-space correlation function into a series of momentum dependent eigen functions [3,4]. While the generalized kinetic theory requires a knowledge of interparticle potential and also involves an extensive computation, the mode description is a more practical method and can be easily applied to interpret experimental measurements. Among various mode descriptions, the three effective eigenmode model (TEE) is a direct extension of the macroscopic hydrodynamic theory. It includes three k-dependent quasihydrodynamic modes, namely, the number density, the longitudinal current, and the energy density. The TEE model has been applied to analyze the dynamic structure factor at finite k values for a hard sphere system [5], a Lennard-Jones fluid [6], classical simple fluids like Ar [7], Ne, Kr, ^{4}He at high temperatures, super fluid ^{4}He [8], and bulk water [9].

The study of atomic collective dynamics at large wave vector transfers and energies is, traditionally, the domain of inelastic neutron scattering (INS) spectroscopy. Recently, a high-resolution inelastic x-ray scattering (IXS) technique has been developed at European Synchrotron Research Facility (ESRF), in Grenoble, France. As a complementary method to INS, the advantages of IXS can be summarized as follows: IXS can investigate a much larger frequency and wave vector transfer ranges at a constant scattering angle; IXS is able to maintain a constant k (magnitude of the wave vector trasfer) measurement at a constant scattering angle for the energy transfer up to the order of k_BT, which is impossible for INS; the absence of multiple scattering processes allows direct measurement of the dynamics structure factor without having to use sophisticated procedures for the reduction of raw data. To interpret IXS data, one may directly extend the method for the analysis of INS data. The analysis is straightforward if the scatterer consists of only a single species of atom, such as simple fluids. In this case, both INS and IXS measure the dynamic structure factor of the system. The only difference is that the prefactor is related to nuclear scattering length for INS and the atomic form factor for IXS . When the scatterer consists of multiple types of atoms, such as molecular fluids, the inelastic scattering spectra are not given by dynamic structure factor of any single atom, but by a generalized dynamic structure factor defined as weighted sum over partial dynamic structure factors of all pairs of atomic species. The weights are dependent on the scattering prefactor and number density of atoms. In the literature, the generalized dynamic structure factor has been shown to be the sum over partial dynamic structure factors by the authors dealing with binary mixtures in computer simulations [10]. However, the inclusion of the form factors into the generalized dynamic structure and its applications to analyze the IXS spectrum have, to the best of our knowledge, never been carried out until this paper. In this paper, we develop a generalized three effective eigenmode (GTEE) model to analyze IXS spectra of polyatomic molecular systems. We shall show that the TEE model for smple fluids can be extended to the case for polyatomic molecular fluids in a straight forward way. As examples, we present the GTEE analysis of computer generated dynamic structure factor of SPC/E model water and IXS spectra of fully hydrated dilauroylphosphatidylcholine (DLPC) bilayers.

II. GENERALIZED DYNAMIC STRUCTURE FACTOR

Consider an ensemble consisting of N particles (atoms), with the Liouville operator,

$$L=\sum_{i}^{N}\left\{\mathbf{v}_i\cdot\frac{\partial}{\partial\mathbf{r}_i}-\frac{1}{m_i}\sum_{j\neq i}^{N}\frac{\partial\phi_{ij}}{\partial\mathbf{r}_{ij}}\cdot\frac{\partial}{\partial\mathbf{v}_i}\right\},\tag{2.1}$$

where m_i is the mass of the particle i, ϕ_{ij} is the pair potential between particle i and j. The Liouville operator defined this way is an anti-Hermitian operator [3].

In a scattering experiment, each target particle converts the incident plane wave into a spherical scattered wave with a specific amplitude. The scattering amplitude of each scattering particle is generally k dependent. In the case of INS, the scattering amplitude is proportional to the scattering length of the nucleus, while in IXS the scattering amplitude of the particle (atom) is proprtional to $r_0 f_i(k)$, with r_0 denoting the classical radius of electron, and $f_i(k)$ the form factor of the scattering atom with index i. The form factor is normalized in such way that it is equal to the atomic number z when $k\rightarrow 0$. One can find the tabulated value of the form factors of different atoms in international tables for x-ray crystallography [11]. In this paper, we will take IXS as example but the result of this section can be easily extended to the case of INS. The double differential cross section for IXS from a sample containing N atoms is formally written as [12]

$$\begin{aligned}\frac{d^2\sigma}{d\Omega dE}&=Nr_0^2(\varepsilon_i\cdot\varepsilon_f)\frac{k_f}{k_i}\frac{1}{N}\\&\quad\times\sum_{F_n,I_n}P_{In}\left|\langle F_n|\sum_{j}^{N}f_j(k)e^{i\mathbf{k}\cdot\mathbf{r}_j}|I_n\rangle\right|^2\\&\quad\times\delta(E-E_f+E_i),\end{aligned}\tag{2.2}$$

where E denotes the energy transfer of an x-ray photon to the medium in the scattering process and ε the polarization of the x ray. The indices i,f denote the incident and scattered x rays, respectively. I_n, F_n are the initial state and final state of the system under study. P_{I_n} is the probability that the system is in the initial state I_n. One can define the generalized dynamic structure factor as

$$\begin{aligned}S(k,E)&=\frac{1}{N}\sum_{Fn,In}P_{In}\left|\langle F_n|\sum_{j}^{N}f_j(k)e^{i\mathbf{k}\cdot\mathbf{r}_j}|I_n\rangle\right|^2\\&\quad\times\delta(E-E_f+E_i)\end{aligned}\tag{2.3}$$

$$\begin{aligned}&=\frac{1}{2\pi\hbar}\frac{1}{N}\int dte^{iEt/\hbar}\sum_{j,l}^{N}\langle f_j(k)f_l(k)\\&\quad\times e^{i\mathbf{k}\cdot\mathbf{r}_l(t)}e^{-i\mathbf{k}\cdot\mathbf{r}_j(0)}\rangle.\end{aligned}\tag{2.4}$$

The double differential cross section can then be written as

$$\frac{d^2\sigma}{d\Omega dE}=Nr_0^2(\varepsilon_i\cdot\varepsilon_f)\frac{k_f}{k_i}S(k,E).\tag{2.5}$$

In the following we shall use the notation $S(k,\omega)=\hbar S(k,E)$. The generalized intermediate scattering function is the inverse Fouriour transform of the generalized dynamics structure factor $S(k,\omega)$,

$$F(k,t)=\frac{1}{N}\sum_{j,l}\langle f_j(k)f_l(k)e^{i\mathbf{k}\cdot\mathbf{r}_l(t)}e^{-i\mathbf{k}\cdot\mathbf{r}_j(0)}\rangle.\tag{2.6}$$

Define now the generalized density fluctuation $n(k,t)$ as

$$n(k,t)=\frac{1}{\sqrt{N}}\sum_{j}f_j(k)e^{-i\mathbf{k}\cdot\mathbf{r}_j(t)}\tag{2.7}$$

then we have $F(k,t)=\langle n^*(k,0)n(k,t)\rangle$.

The above defined generalized dynamic structure factor can be decomposed into the weighted average of partial dynamic structure factor. This is accomplished by splitting the generalized density fluctuation into the sum of the density fluctuation of each type of atom, which is

$$n(k,t)=\sum_{\alpha}f_\alpha(k)\omega_\alpha n_\alpha(k,t),\tag{2.8}$$

where α denotes the type of atom, $\omega_\alpha=\sqrt{N_\alpha/N}$ the square root of the number fraction of atomic type α over the total atomic number, and $n_\alpha(k,t)$ the density fluctuation of the atom type α.

$$n_\alpha(k,t)=\frac{1}{\sqrt{N_\alpha}}\sum_j^{N_\alpha}{}' \; e^{-i\mathbf{k}\cdot\mathbf{r}_j(t)}, \tag{2.9}$$

where the prime denotes the sum only over the different atoms within type α. By using $F(k,t)=\langle n^*(k,0)n(k,t)\rangle$, we have,

$$F(k,t)=\sum_{\alpha,\beta} f_\alpha(k)f_\beta(k)\omega_\alpha\omega_\beta F_{\alpha\beta}(k,t) \tag{2.10}$$

where the partial intermediate scattering function is defined as

$$F_{\alpha\beta}(k,t)=\langle n_\alpha^*(k,0)n_\beta(k,t)\rangle. \tag{2.11}$$

The Fouriour pair relationship between the dynamic structure factor and intermediate scattering function implies that the moments of the dynamic structure factor determine the short time behavior of $F(k,t)$. In particular, the zeroth order moment is the structure factor $S(k)$, which is initial value of $F(k,t)$. The generalized static structure factor $S(k)$ as measured by a diffraction experiments is

$$S(k)=\langle n^*(k)n(k)\rangle=\frac{1}{N}\sum_{j,l}\langle f_j(k)f_l(k)e^{i\mathbf{k}\cdot\mathbf{r}_l-i\mathbf{k}\cdot\mathbf{r}_j}\rangle \tag{2.12}$$

Insert Eq. (2.8) into the above equation, we have

$$S(k)=\sum_{\alpha\beta} f_\alpha(k)f_\beta(k)\omega_\alpha\omega_\beta S_{\alpha\beta}(k) \tag{2.13}$$

with the partial structure factor $S_{\alpha\beta}(k)=\langle n_\alpha^*(k)n_\beta(k)\rangle$. The partial static structure factor is also the initial value of the corresponding partial dynamic structure factor. We note that the generalized dynamic structure factor or the static stucture factor is a weighted sum over any partial dynamic structure factor or partial static structure factor, respectively, with the same weights determined by the number fraction and atomic form factor of the pair. Each type of atom contributes to the total spectra of IXS through the partial dyanmic structure factor with other types.

The second moment of $S(k,\omega)$ can be written as the initial value of the second order derivative of F(k,t): $\langle\omega^2\rangle=-d^2F(k,t)/dt^2|_{t=0}$, which can be calculated explicitly,

$$\frac{\partial^2F(k,t=0)}{\partial t^2}=\langle n(k,0)^*\ddot{n}(k,0)\rangle \tag{2.14}$$

$$=-\langle\dot{n}(k,0)^*\dot{n}(k,0)\rangle \tag{2.15}$$

$$=-\frac{1}{N}\sum_j^N\langle(\mathbf{k}\cdot\mathbf{v}_j)^2f_j^2(k)\rangle \tag{2.16}$$

$$=-k^2\langle v_{0,j}^2f_j^2(k)\rangle, \tag{2.17}$$

where the second equality follows from the anti-Hermitian of Liouvillian, and $v_{0,j}=\sqrt{k_BT/m_j}$, is a single cartesian component of the thermal velocity of the particle j. The average of the last equality is over different individual particles. One can calculate the average explicitly and define a generalized thermal velocity as the weighted average of thermal velocities of different types of atoms.

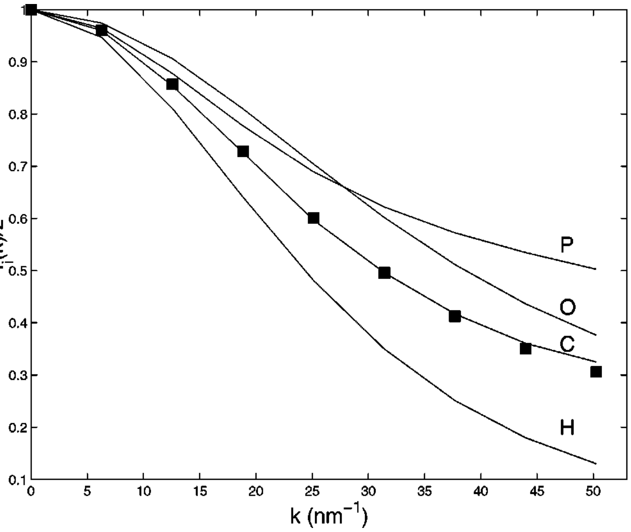

FIG. 1. The k dependence of generalized thermal velocity $v_0(k)$ of fully hydrated DLPC (symbol), plotted as $v_0(k)/v_0(k=0)$. The solid lines are the form factor of the atoms H,C,O,P divided by their atomic number z.

$$v_0^2(k)=\langle v_{0,j}^2f_j^2(k)\rangle=\sum_\alpha f_\alpha^2(k)\omega_\alpha^2v_{0\alpha}^2 \tag{2.18}$$

where the index j is for different individual atoms, index α for different types of atoms, $v_{0\alpha}$ the thermal velocity of the atom type α. Then the second moment of $S(k,\omega)$ can be written as $k^2v_0^2(k)$, a similar expression of the second moment of conventional $S(k,\omega)$.

We note that the generalized thermal velocity $v_0(k)$ varied with different k values. This k-dependence should be the same as that of atomic form factor if there is only one type of atoms. In multiatomic fluids, the k dependence of $v_0(k)$ is mainly contributed by the k dependence of the atomic form factor of atoms that have large atomic numbers and atomic number fractions in the fluid. Figure 1 shows the atomic form factor of H,O,C,P divided by their atomic number. In the same figure, the generalized thermal velocity of the hydrated DLPC is shown. We calculate this quantity by taking the weighted ratio of water in DLPC to be 20%. The k dependence of $v_0(k)$ of hydrated DLPC is almost the same as that of atomic form factor of Carbon.

III. GENERALIZED THREE EFFECTIVE EIGENMODE THEORY

A mode is a k and time dependent function, which is a sum over all particles and each sum component is a function of the phase-space coordinate $(\mathbf{r}^N,\mathbf{p}^N)$. Each mode describes one type of microscopic fluctuation at a specific time in the k space. The variations and interplays of these modes are described by their time-dependent correlation functions. The evolution of these correlation functions is governed by a set of coupled first order differential equations that have their roots on the evolutional equation of the phase-space coordinates. The mode correlation functions in the frequency domain are defined as

$$G_{\alpha\beta}(k,z)=\left\langle b_{\alpha}^{*}(k)\frac{1}{z-L}b_{\beta}(k)\right\rangle, \tag{3.1}$$

where $b_{\alpha}(k)$ are the microscopic fluctuations with the first three defined as

$$b_1(k)=\tilde{n}(k)=\frac{1}{\sqrt{NS(k)}}\sum_j f_j(k)e^{-i\mathbf{k}\cdot\mathbf{r}_j} \tag{3.2}$$

is the generalized microscopic density fluctuation.

$$b_2(k)=\tilde{j}_l(k)=\frac{1}{\sqrt{N}}\sum_j f_j(k)\frac{\mathbf{k}\cdot\mathbf{v}_j}{kv_0}e^{-i\mathbf{k}\cdot\mathbf{r}_j} \tag{3.3}$$

is the generalized microscopic longitudinal velocity fluctuation with the generalized thermal velocity v_0 defined in Eq. (2.18).

$$b_3(k)=\tilde{e}(k)=\frac{1}{\sqrt{N}}\sum_j \frac{3-m_j v_j^2/(k_BT)}{\sqrt{6}}e^{-i\mathbf{k}\cdot\mathbf{r}_j} \tag{3.4}$$

is the microscopic temperature fluctuation. The above modes are generalized three hydrodynamic quasiconserved modes defined in the way such that they are orthornomal. One can also generally define a set of microscopic dynamic quantities $b_{\alpha}(k)$ with $\alpha>3$, so that they are orthonormal $\langle b_{\alpha}^{*}(k)b_{\beta}(k)\rangle=\delta_{\alpha\beta}$ and complete $\Sigma_{\alpha}|b_{\alpha}(k)\rangle\langle b_{\alpha}(k)|=\mathbf{I}$.

We note that the first matrix element of the correlation matrix in Eq. (3.1) in the time domain is $G_{11}(k,t)=F(k,t)/S(k)$, with $F(k,t)$ given by Eq. (2.6). The Eq. (3.1) can be rewritten as $G_{\alpha\beta}(k,z)=\langle b_{\alpha}^{*}(k)b_{\beta}(k,z)\rangle$, with $b_{\beta}(k,z)=[1/(z-L)]b_{\beta}(k)$. We then have,

$$zb_{\beta}(k,z)=Lb_{\beta}(k,z)+b_{\beta}(k). \tag{3.5}$$

After multiplying $b_{\alpha}^{*}(k)$ to the above Eq. (3.5), and averaging over the ensemble, one gets

$$zG_{\alpha\beta}(k,z)=\sum_{\gamma} L_{\alpha\gamma}^{\infty}(k)G_{\gamma\beta}(k,z)+\delta_{\alpha\beta}, \tag{3.6}$$

where the element of the infinite symmetric matrix is $L_{\alpha\beta}^{\infty}(k)=\langle b_{\alpha}^{*}(k)Lb_{\beta}(k)\rangle$.

The above infinite matrix equation is an exact equation governing the evolution of the mode correlation functions. Because of the anti-Hermitian of Liouvillian, the eigenvalues are all imaginary, the general solution of this equation is a weighted sum over an infinite set of oscillations with different frequencies. The weight is related to the power spectrum density at each frequency (eigenvalue). After decomposing the infinite matrix into four blocks as

$$\mathbf{A}=\begin{bmatrix}\mathbf{A}_{33} & \mathbf{A}_{3M}\\ \mathbf{A}_{M3} & \mathbf{A}_{MM}\end{bmatrix}_{M->\infty}, \tag{3.7}$$

one can further decompose the infinite matrix equation 3.6 into four different matrix equations, their dimensions are $3\times3, 3\times M, M\times3, M\times M$, respectively. After a few algebra, one can get a 3×3 matrix equation [9]:

$$z\mathbf{G}_{33}(k,z)=\mathbf{H}_{33}(k,z)\mathbf{G}_{33}(k,z)+\mathbf{I}_{33} \tag{3.8}$$

with a z-dependent matrix

$$\mathbf{H}_{33}(k,z)=\mathbf{L}_{33}(k)+\mathbf{L}_{3M}(k)[z\mathbf{I}_{MM}-\mathbf{L}_{MM}(k)]^{-1}\mathbf{L}_{M3}(k). \tag{3.9}$$

We note that the first term of Eq. (3.9) corresponds to the frequency matrix, and the second term to the memory function in the generalized Zwanzig-Mori projector operator formalism [3]. By using the fact

$$Lb_1(k)=\frac{-ikv_0(k)}{\sqrt{S(k)}}b_2(k), \tag{3.10}$$

where $v_0(k)$ is the generalized thermal velocity, one finds from the above equation that the elements of the first column and the first row of the infinite Liouville matrix $\mathbf{L}$ are all zero, except the two elements

$$L_{21}(k)=L_{12}(k)=-if_{un}(k)=\frac{-ikv_0(k)}{\sqrt{S(k)}}. \tag{3.11}$$

This makes the second term (memory function) in Eq. (3.9) not contributing to the first column and first row of the matrix $\mathbf{H}_{33}$. The matrix $\mathbf{H}_{33}$ contains only three unknown z-dependent quantities: $H_{22}(k,z), H_{23}(k,z)$ $[=H_{32}(k,z)], H_{33}(k,z)$, which come from the memory function and are generally z dependent. The z dependence can be dropped by invoking the Markovian approximation when the decay times of the memory matrix are shorter than those of the correlation functions between hydrodynamic quantities. In the interpretation of experimental data, we treat the three unknown quantities as fitting parameters, which vary with k only. In the remaining part of the paper, we will omit the indices of matrix $\mathbf{H}_{33}$ and write it as $\mathbf{H}$. Using the symmetry properties of the modes and the Liouville operator, one finds out that the diagonal elements in matrix $\mathbf{H}$ are real for all k and the nondiagonal elements are imaginary. We finally rewrite $\mathbf{H}$ as

$$\mathbf{H}(k)=\begin{bmatrix}0 & if_{un}(k) & 0\\ if_{un}(k) & z_u(k) & if_{uT}(k)\\ 0 & if_{uT}(k) & z_T(k)\end{bmatrix} \tag{3.12}$$

with $f_{un}=kv_0(k)/\sqrt{S(k)}$. The eigenvalues of the matrix $\mathbf{H}$ consist of one real number z_h and a couple of conjugate complex numbers $\Gamma_s\pm i\omega_s$. We can therefore write the solution of the normalized dynamic structure factor in a hydrodynamiclike form [1,13],

$$S(k,\omega)/S(k)=\frac{1}{\pi}\left\{A_0\frac{z_h}{\omega^2+z_h^2}+A_s\frac{\Gamma_s+b(\omega+\omega_s)}{(\omega+\omega_s)^2+\Gamma_s^2}\right.$$
$$\left.+A_s\frac{\Gamma_s-b(\omega-\omega_s)}{(\omega-\omega_s)^2+\Gamma_s^2}\right\} \tag{3.13}$$

with $b=-\mathrm{Im}(A)/\mathrm{Re}(A), A_s=\mathrm{Re}(A)$, and

$$A_0=\frac{B(z_h)}{(\Gamma_s-z_h)^2+\omega^2}, \tag{3.14}$$

$$A=\frac{B(\Gamma_s-i\omega_s)}{2i\omega_s(z_h-(\Gamma_s-i\omega_s))} \tag{3.15}$$

$$B(x)=-x^2-(z_u+z_T)x+z_u z_T+f_{uT}^2. \tag{3.16}$$

Equation (3.13) has six parameters, but they are dependent only on four independent parameters in the matrix **H** in GTEE model. When the static structure factor is known, the number of free parameters can be further reduced to three. In the Rayleigh-Brillouin scattering, the width of the central peak is determined by the heat diffusion damping z_h. The density fluctuation associated with sound propagation is maniested as a pair of inelastic peaks, whose position and width are determined by ω_s and Γ_s, respectively.

IV. SPC/E WATER

We first take SPC/E model water as an example of application of GTEE model. In calculating molecular dynamics (MD) trajectories, we use 4096 water molecules interacting with SPC/E model potential [14,15] and enclosed in a cubic box with periodic boundary conditions. The density is $1\,\mathrm{g/cm}^3$ and the temperature is approximately 250 K, which is the temperature of maximum density for SPC/E water. The electrostatic long-range interactions are taken into account with the reaction field method described by Steinhauser [16]. The MD code used here to generate the trajectories is the same as that in Ref. [14]. A heat bath [17] has been used to allow for heat exchange. The time step for the integration of the molecular trajectories is 1 fs. We saved the trajectories of each atom every 10 fs up to 100 ps. Figure 2 shows the structure factor for O-O correlation, center of mass correlation and water molecule-molecule correlation, respectively. The curves are obtained by averaging different directions of k-vectors. The structure factor of O-O atom was calculated as $S_{oo}(k)=1/N_o\Sigma_{l,j}\exp[i\mathbf{k}\cdot(\mathbf{r}_{o,l}-\mathbf{r}_{o,j})]$, where $\mathbf{r}_{o,l},\mathbf{r}_{o,j}$ are the coordinates of oxygen atoms of different molecules, N_o is the number of oxygen atoms. The structure factor of center of mass was calculated by the same definition, except that the atomic coordinate was replaced by that of the center of mass of each molecule. The generalized structure factor defined in Eq. (2.12) shown in the inset is proportional to the structure factor measurable by an x-ray diffraction experiment. The distribution of electron density in a water molecule is very nearly spherical, and orientational correlation between molecules in the liquid is weak and cannot be seen in x-ray diffraction [18]. Therefore, the generalized dynamic structure factor can be decomposed into the multiplication of the molecular form factor and intermolecular structure factor. The derived intermolecular structure factor is very similar to the partial structure factor of O atom or center of mass.

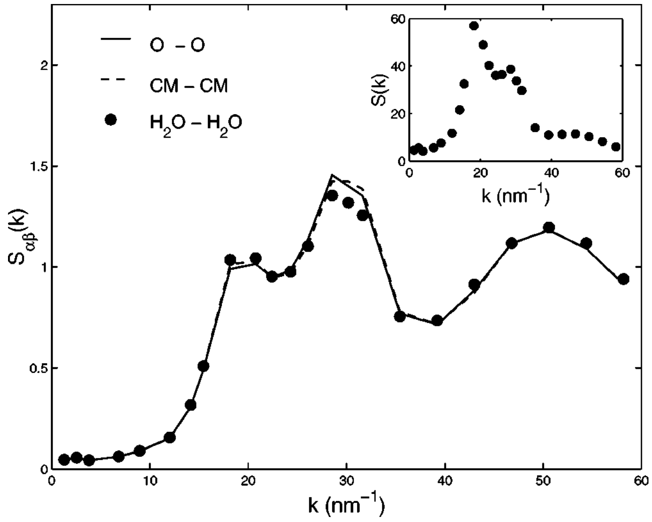

FIG. 2. The static structure factor of SPC/E water: O-O partial structure factor (full line), center mass structure factor (dash line), and intermolecular structure factor measurable by an x-ray diffraction (symbol). The intermolecular structure factor was calculated by dividing the generalized structure factor $S(k)$ [Eq. (2.12), shown in the inset] by the molecular form factor given by Ref. [18].

From the stored trajectories one can calculate the density fluctuations of O atom, center of mass, and also the atomic form factor weighted density fluctuation. From these, the respective intermediate scattering functions are generated [Eq. (2.7)]. These intermediate scattering functions are shown in Fig. 3. At small k values, the three normalized intermediate scattering functions are almost identical. As k increases, the

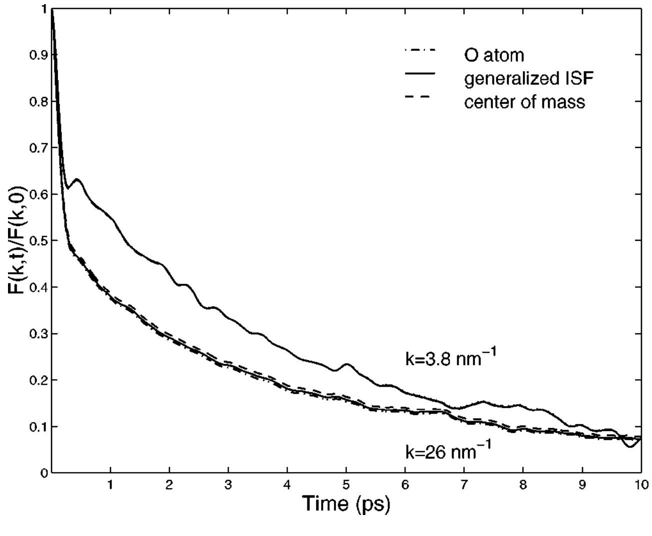

FIG. 3. The generalized density-density correlation function (intermediate scattering function ISF) of SPC/E water (full line) with partial ISFs of O atom (dash-dot line) and center of mass (dash line). The ISFs are normalized to have unity initial values and averaged over independent **k**-vector directions.

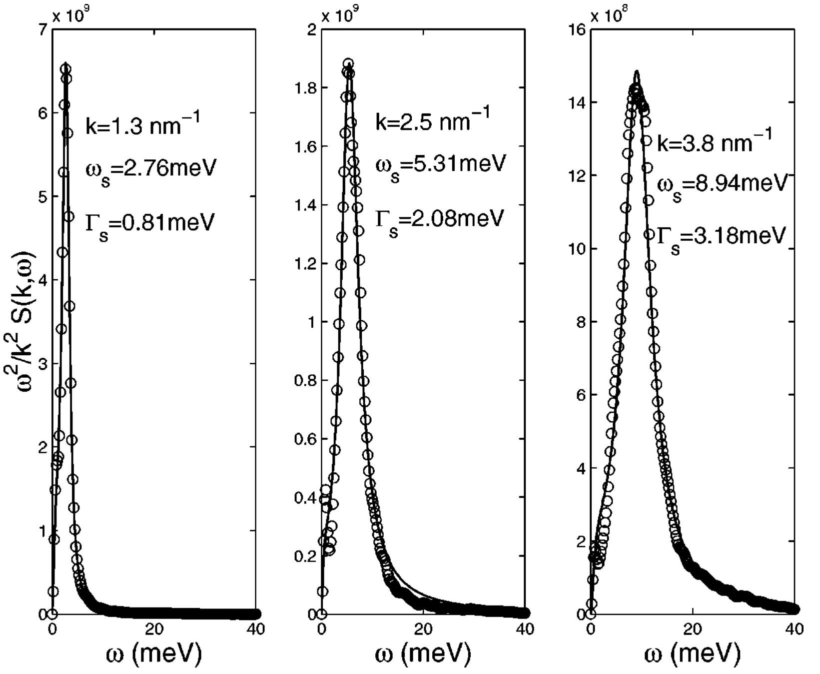

FIG. 4. Comparison of the dynamic structure factor of center of mass of SPC/E water (symbols) with TEE calculation of single atomic system (full line).

intermediate scattering functions exhibit small differences among each other. In the interested k range (<30 nm^{-1}) and energy range, one can introduce an approximation that a water molecule can be considered as a single particle (either oxygen atom or center of mass). This approximation is also verified by the similarity of static structures discussed at the last paragraph (see Fig. 2). The dynamic structure factors can be calculated from the power spectrum of density fluctuations. Figure 4 shows the longitudinal current correlation spectral density function $J(k,\omega)=(\omega^2/k^2)S(k,\omega)$ calculated from the density fluctuations of the center of mass. A Hanning window has been employed to reduce the noise. The $J(k,\omega)$ has been averaged over independent k directions. The full lines are the TEE model calculations with $f_{un}=kv_0(k)/\sqrt{S(k)}$. The eigenvalues of the best fitted matrix **H** are shown in the same figure. The eigenvalues of the propagating sound frequency show a sound speed of about 3300 m/s, which agrees with our previous model analysis of SPC/E supercooled bulk water [19].

V. FULLY HYDRATED DLPC BY IXS

Fully hydrated phospholipid bilayers have been employed as a model membrane in many biological studies to provide insights into the structure and function of biological membranes. The structures of phospholipid bilayers have been studied by a variety of methods such as x-ray and neutron diffraction [20–22], differential scanning calorimetry [23,24], ^{2}H nuclear magnitude resonance [23,25], and the diffusion and rotation of lipid molecules have been studied by incoherent quasielastic neutron scattering [26], nuclear magnetic resonance (NMR) relaxation [27], and Raman scattering [28]. Studies of collective dynamics of lipid bilayers are scarce so far. However, density fluctuations are essential for the functions of natural membranes. In particular, the in-plane collective density fluctuation provides possibility of the transmembrane transport of small molecules or ions, and formation of functional enzyme complexes. The collective out-of-plane excitation of bilayers contributes significantly to the intermembrane repulsion [26].

The IXS experiment was carried out at a very high-resolution IXS beamline (BL21-ID 16) at ESRF [29,30]. The undulator x-ray source was premonochromated by a Si(111) double crystal monochromator and then followed with a high energy resolution backscattering monochromator (temperature controlled and scanned), operating at the Si(11 11 11) Bragg reflection (x-ray energy 21.748 KeV). The scattered photons were collected by a grooved spherical silicon crystal

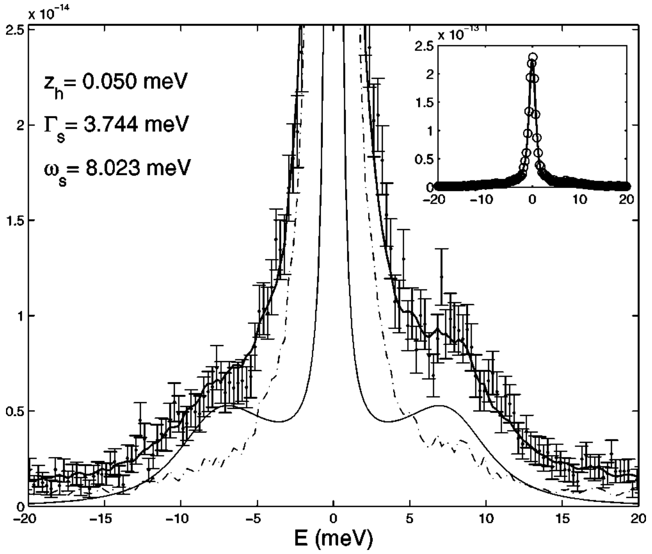

FIG. 5. The IXS spectra of fully hydrated DLPC and GTEE model fit at $k=5.0$ nm^{-1} and $T=269$ K. The thick and thin solid lines denote the GTEE model calculation after and before convolution with a resolution function. The dash-dot line is the resolution function. Inset figure shows the whole spectra and GTEE fit.

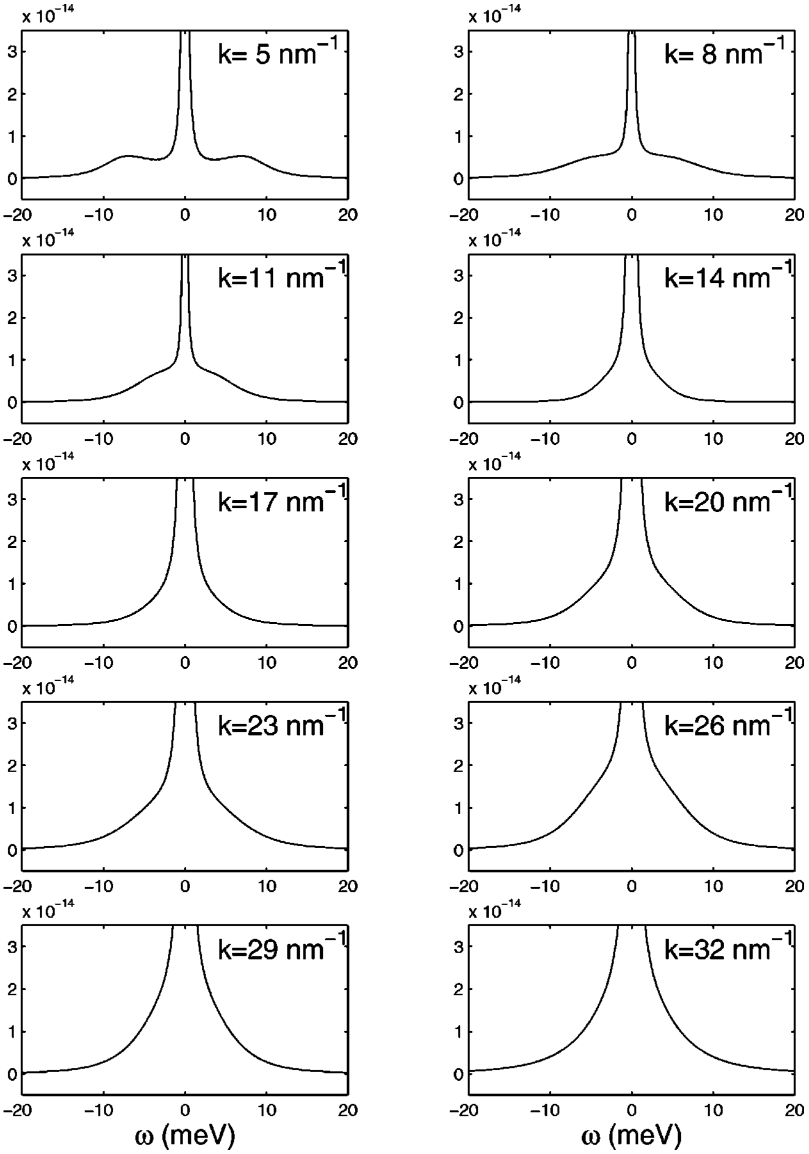

FIG. 6. $S(k,\omega)$ of GTEE model calculated with the best fitting parameters for the IXS spectra of $T=269$ K and different k values.

analyzer operating at the same Bragg back reflections, and in Rowland geometry. The net energy resolution was measured by an elastic scattering of a plastic sample at its maximum of structure factor. This gives an energy resolution of 1.5 meV full width at half maximum—(FWHM). The x-ray beam size at the sample was $0.15\ \mathrm{mm}\times 0.35$ mm. The fully hydrated DLPC sample was in a state of partially oriented multilamellar vesicles. The sample was measured at two temperatures: $T=269$ K and 294 K. Since the main transition temperature of hydrated DLPC is about 272 K [31], these two temperatures correspond to the gel phase ($L_{\beta'}$) and liquid crystal phase (L_{α}).

Since a DLPC molecule has a large polar head group and double hydrophobic chains, we do not expect that the measured dynamic structure factor could be approximated by the center of mass dynamic structure factor for DLPC. Therefore, we need to use the generalized TEE model to fit the data. There are four fitting parameters: $f_{un}(k)$, $z_u(k)$, $z_T(k)$, $f_{uT}(k)$. The calculated $S(k,\omega)/S(k)$ was multiplied by a detailed balance factor and convoluted with the resolution function before comparing with the IXS spectra that have been normalized to have unit area. Figure 5 is a typical fit of the IXS spectra at $T=269$ K, $k=5\ \mathrm{nm}^{-1}$. The fit gives the width of the central peak, 0.05 meV, much less than the width of the resolution function. The sound propagation frequency is about 8.0 meV, giving the sound propagating speed of 2440 m/s.

Figures 6 and 7 show $S(k,\omega)$ calculated by GTEE model with the best fit parameters to the IXS spectra at $T=269$ K and $T=294$ K, respectively. They are plotted without convolution with the resolution function. As k increases, the sound damping becomes larger and the central peak broader. The central peaks however become narrower at $k=14\ \mathrm{nm}^{-1}$ due to the deGennes narrowing at the peak of the structure factor. The discussions of the k dependent and temperature dependent variations of fitted parameters have been published [32]. One of the verifications of the GTEE analysis of the hydrated DLPC can be obtained by comparing the experimentally determined $S(k)$ with the calculated structure factor from fitting parameters. Figure 8 shows such a com-

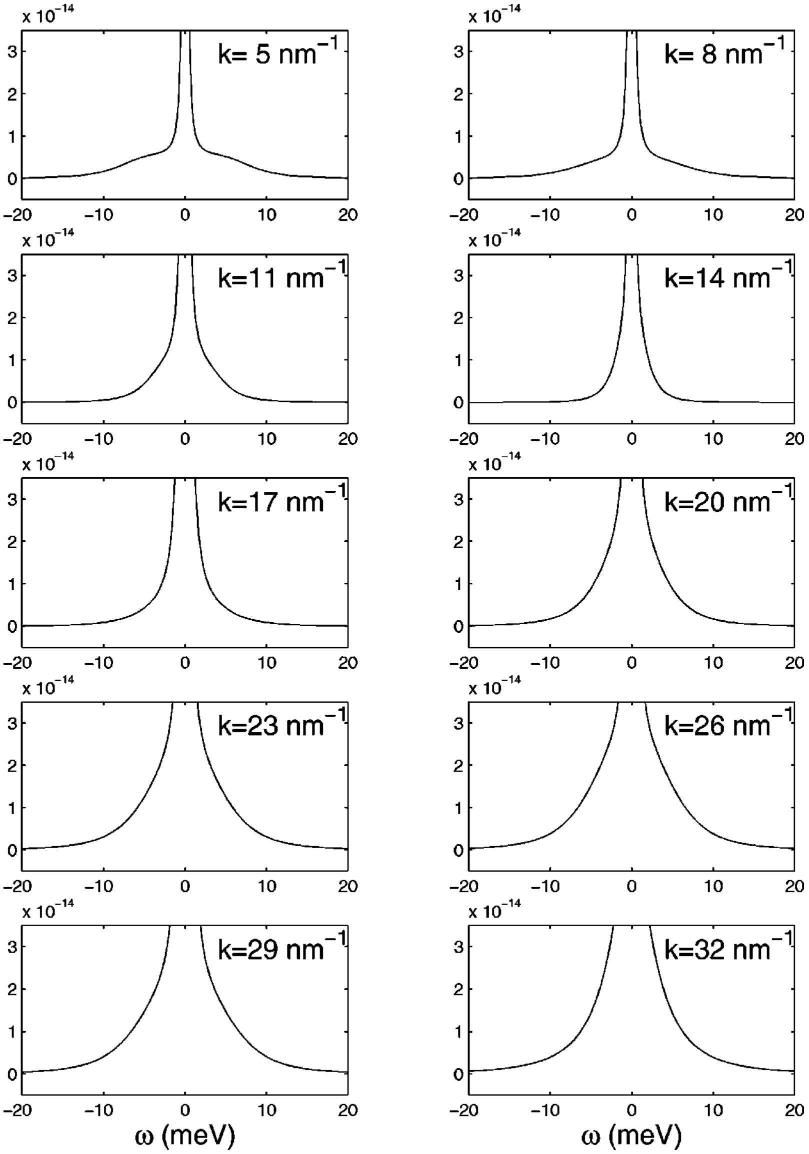

FIG. 7. $S(k,\omega)$ of GTEE model calculated with the best fitting parameters for the IXS spectra of $T=294$ K and different k values.

parison. The calculated $S(k)$ is obtained by the equation: $S(k)=[kv_0(k)/f_{un}(k)]^2$, where the generalized thermal velocity $v_0(k)$ is calculated by Eq. (2.18), and the experimental $S(k)$ is obtained from x-ray scattering without energy analysis at the same IXS spectrometer. In order to compare them at the same scale, the experimental $S(k)$ were multiplied by one appropriate constant factor. The two curves (lines and symbols) obtained through different methods show over all good agreement. In this figure, the structure factor of the $L_{\beta'}$ gel phase at $T=269$ shows a sharp peak at $k=15$ nm^{-1}, corresponding to the ordered structure formed by hydrocarbon chains in the bilayers [33,34,22]. Unfortunately, we did not measure the IXS spectrum at $k=15$ nm^{-1}.

VI. DISCUSSIONS AND CONCLUSIONS

High-resolution IXS spectroscopy is one of the most powerful experimental techniques developed for the study of molecular scale dynamics in soft matter in recent years. For the purpose of a quantitative analysis of IXS spectra of poly-

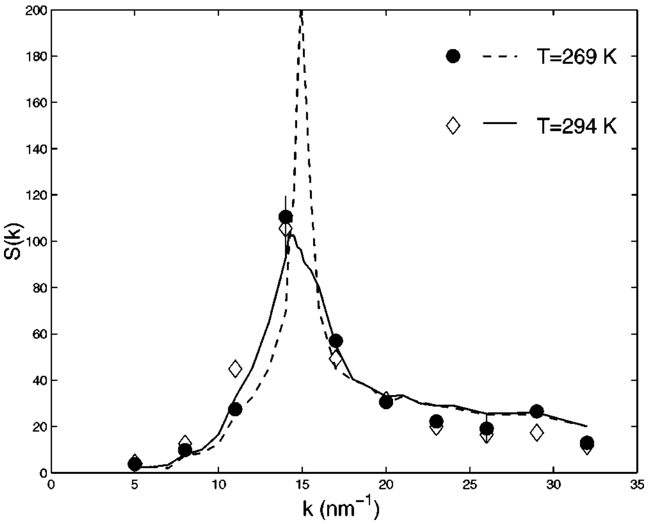

FIG. 8. The static structure factor $S(k)$ measured by x-ray scattering (lines) and calculated $S(k)$ (symbols) from the GTEE fitted parameter $f_{un}(k)$. The y axis is in arbitrary unit.

atomic molecular fluids, we have, in this paper, formulated a theory for the generalized dynamic structure factor obtainable directly from the double differential cross section of the IXS. The generalized dynamic structure factor is a weighted average of partial dynamic structure factors of pairs of atomic species in the system. The weighting factors are the products of the atomic form factors of the pairs. Evolution of the generalized dynamic structure factor is approximately given by a 3×3 matrix equation, which is an extension of the TEE model formulated for simple fluids. Through comparisons of the partial intermediate scattering function of the oxygen atom (or the center of mass) with the generalized intermediate scattering function calculated from MD of SPC/E water, we conclude that IXS spectra of water can be well approximated by the partial dynamics structure factor of the oxygen atom or the center of mass. That is because the oxygen atom has much larger atomic number than the hydrogen, and in the practical wave vector and energy transfer ranges of interest, the collective movements of O and H are not very different. In this case, the GTEE model is reduced to the TEE model. However, this single-atom approximation is in general not justified for IXS spectra of polyatomic molecular systems, where the GTEE model has to be used. In the case of hydrated DLPC, one could imagine that the IXS spectra are mainly contributed by the dynamics of O atom in the hydration water and C atom in the hydrocarbon chains of the lipids. However, from the structure factor measured by x-ray diffraction, one can see a diffraction peak due to two adjacent hydrocarbon segments located at about $14\ \mathrm{nm}^{-1}$ but one does not see the first diffraction peak of hydration water, which should be located at about $20\ \mathrm{nm}^{-1}$. This is perhaps because hydrated water molecules are in a state of less order than the hydrocarbon segments in DLPC molecules. This gives information about the relative importance of contributions of various partial dynamic structure factors in the generalized dynamic structure factor. Since a structure factor is the total spectral area in a dynamic structure factor, we conclude that the generalized dynamic structure factor of hydrated lipid bilayers is dominated by the partial dynamic structure factor of C-C, and the dynamic quantities extracted from analyzing measured IXS spectra of lipid bilayers are largely reflecting movements of the hydrocarbon segments of lipid molecules.

In conclusion, we would like to point out that, although the GTEE theory is a very versatile and robust method for fitting IXS spectra of supramoleculars liquid and for extracting experimental generalized dynamic structure factors from them, the model parameters so determined have not straightforward physical interpretations at this stage of development. Furthermore, the three effective eigenmodes we used in this paper may not be sufficiently ‘‘complete’’ to represent all the slow modes of the particular system studied. If this is the case, the generalized dynamic structure factors we extracted from the measured spectra may be of only limited accuracy. But in view of the fairly noisy data one is getting at present time with a limited integration time at a third generation synchrotron source, it is not wise to further increase the number of modes in the model and thus also increasing the corresponding number of fitting parameters. We are fortunate for the case of SPC/E water at its temperature of maximum density and for lipid bilayers at moderate temperatures that the three effective eigenmodes we used seems to be a sufficiently good approximation, judging from the results. The success of the GTEE as a useful IXS data analysis tool could not be fully assessed without applying it further to diverse variety of systems in the future and examining their results.

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