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Model for single-particle dynamics in supercooled water

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We analyze a set of 10 M-step molecular dynamics (MD) data of low-temperature SPC/E model water with a phenomenological analytical model. The motivation is twofold: to extract various *k*-dependent physical parameters associated with the single-particle or the self-intermediate scattering functions (SISFs) of water at a deeply supercooled temperature and to apply this analytical model to analyses of new high resolution quasielastic neutron scattering data presented elsewhere. The SISF of the center of mass computed from the MD data show clearly time-separated two-step relaxations with a well defined plateau in between. We model the short time relaxation of the test particle as a particle trapped in a harmonical potential well with the vibrational frequency distribution function having a two-peak structure known from previous inelastic neutron scattering experiments. For the long time part of the relaxation, we take the α relaxation suggested by mode-coupling theory. The model fits the low-temperature SISF over the entire time range from 1 fs to 10 ns, allowing us to extract peak positions of the vibrational density of states, the structural relaxation rate $1/\tau$ of the cage (the potential well) and the stretch exponent β. The structural relaxation rate has a power law dependence on the magnitude of the wave vector transfer k and the stretch exponent varies from 0.55 at large k to unity at small k. [S1063-651X(99)04406-2]

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I. BACKGROUND

The behavior of water upon supercooling has been of great interest to the scientific community that concerns itself with this ubiquitous liquid on earth [1–3]. It has been found that there are anomalous increases of thermodynamic quantities and apparent divergences of dynamic properties on approaching a singular but experimentally inaccessible temperature of about 227 K, at ambient pressure [4,5]. The discovery has stimulated a considerable amount of experimental, theoretical, and computational work in an attempt to clarify the origin fo this singularity [3]. We have recently noted [6] that some dynamical properties of interfacial water show similarity to that of bulk supercooled water at a lower temperature. In this context, investigation of dynamical properties of bulk supercooled water may lead to a better understanding of the corresponding properties of interfacial water which are of paramount importance to biology and industry.

While the phase behavior of supercooled water has been extensively explored in the molecular dynamics (MD) literature, few studies have been directed toward the investigation of dynamics near the apparent singular temperature T_s. A computation of long-time behavior of correlation functions, both single-particle and collective, needs to be made for any meaningful studies of dynamical properties of water near T_s. Very recently one such attempt has been made by us using a SPC/E model water [7–10]. One of the interesting findings of this series of MD simulations is an unbiguous identification of a structural arrest temperature at 50 K below the temperature of maximum density of SPC/E water (250 K). Thus we can infer T_s as the temperature at which the self-diffusion constant D of water goes to zero. This is not unexpected since the mode coupling theory predicts on a fairly general ground the existence of such a structural arrest temperature in sufficiently supercooled dense liquids.

The objective of this article is to propose a simple analytical physical model for analyses of these numerically computed self-intermediate scattering functions (SISFs) by MD. This is motivated by a hope that the simple physical model we derive here can be used to analyze present and future high resolution quasi-elastic and inelastic neutron scattering experiments on bulk supercooled and interfacial water.

A. Computer molecular dynamic (MD) simulations

We made MD simulations in a NVE ensemble with 216 molecules contained in a cubic box of an edge 18.65 Å. The effective potential used is the extended simple point charge model SPC/E [11]. This potential treats a single water molecule as a rigid set of point masses with an OH distance of 0.1 nm and an HOH angle equal to the tetrahedral angle 109.47°. The point charges are placed on the atoms and their magnitudes are $q_H = 0.4238e$ and $q_0 = -2q_H = -0.8476e$. Only the oxygen atoms interact among themselves via a Lennard-Jones potential, with the parameters $\sigma = 0.31656$ nm and $\epsilon = 0.64857$ kJ/Mol. The interaction between pairs of molecules is calculated explicitly when their separation is less than a cutoff distance r_c of 2.5σ. The contribution due to Coulomb interactions beyond r_c is calculated using the reaction-field method, as described by Steinhauser [12]. Also, the contribution of Lennard-Jones interactions between pairs separated more than r_c is included in the evaluation of thermodynamic properties by assuming a uniform density beyond r_c. The MD code used here to calculate the SPC/E trajectories is the same as that used in Ref. [13]. A heat bath [14] has been used to allow for heat exchange. In our simulation, periodic boundary conditions are used. The time step

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for the integration of the molecular trajectories is 1 fs. Simulations at low T were started from equilibrated configurations at higher T. Equilibration was monitored via the time dependence of the potential energy. In all cases the equilibration time t_{eq} was longer than the time needed to enter the diffusive regime.

The SPC/E potential has been explicitly parametrized to reproduce the experimental value of the self-diffusion constant at ambient temperature and density of 1 $\mathrm{g/cm^3}$ and it has been widely studied over the last few years [15,16]. Moreover, this potential is able to reproduce a pressure-dependent temperature of maximum density (TMD) [13,16]. As was shown in Ref. [16], the SPC/E 1 bar isobar is characterized by a TMD of about 235 K and a corresponding density of 1.026 $\mathrm{g/cm^3}$. The -40 MPa isobar is instead characterized by a TMD of about 250 K and a corresponding density of 1.000 $\mathrm{g/cm^3}$ [13], in agreement with the experimental pressure dependence of the TMD line. We have studied the -80 MPa isobar. Seven simulations have been performed at the states ranging from 35° above the TMD to 45° below, thus covering both the normal and supercooled states of water, for time periods ranging from a few hundredth of a ps at high T, to 200 ns at the lowest T.

B. Mode-coupling theory

In the following formulation of the model we shall use an idea borrowed from mode coupling theory (MCT) of supercooled liquids. MCT is a theory that focuses its attention on the cage effect in the liquid state which can be pictured as a transient trapping of molecules as a result of lowering the temperature or on increasing the density [17,18]. Microscopic density fluctuations of disordered high temperature and low density fluids usually relax rapidly in a time scale of a few picoseconds. The MCT does not attempt to address the detailed system specific dynamics in this time regime. However, upon lowering the temperature below the freezing point or increasing the density of the liquid by applying a pressure, there is a rapid increase in the local order surrounding a particle (called a cage), leading to a substantial increase of the local structural relaxation time. In the supercooled or dense liquid regime, a trapped particle in a cage can migrate only through rearrangement of a large number of particles surrounding it. There is thus a strong coupling between the single particle motion and the density fluctuations of the fluid. MCT addresses primarily physical processes in this time regime. According to MCT, the equilibrium structure factor $S(k)$ of the liquid completely determines the long time cage structural relaxation behavior. It predicts that on approaching T_s from above, there is a further and further separation between the time scales describing the rattling motion of a particle in the cage and the eventual structural relaxation time of the cage. At T_s the structural relaxation time becomes infinity and the supercooled liquid shows a phenomenon of structural arrest. It has been shown numerically for various model systems, such as a hard sphere system [19] or a mixed Lennard-Jones system [20], that the time evolution of the structural relaxation (called the α relaxation) is well approximated by a stretched exponential decay with a system dependent stretch exponent.

Application of the above concept derived from MCT to supercooled water represents an interesting special case. It is well known that upon supercooling, water undergoes an expansion or lowering of density. At the molecular level this can be traced to a tendency for water to form a hydrogen-bonded, tetrahedrally coordinated first and second neighbor shell around a given molecule, on lowering the temperature below the freezing point. This configuration is a more open structure as compared to five or six neighbor configurations which are known to be present with higher probability at higher temperatures. Thus the so-called cage in water has a qualitatively different property from the hard sphere or Lennard-Jones fluids. In the latter case, density of the liquid actually increases upon cooling. The structural relaxation time of water increases rapidly upon supercooling because the tetrahedrally coordinated hydrogen-bonded structure as depicted in Fig. 1 is an inherently more stable structure locally and has a longer lifetime.

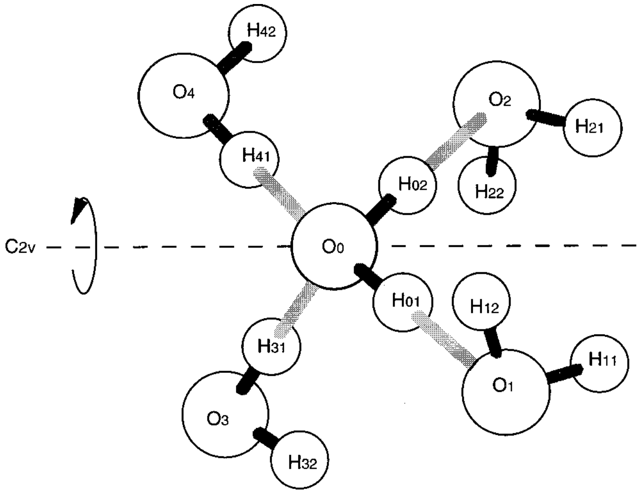

FIG. 1. A schematic diagram for the hydrogen-bonded, tetrahedrally coordinated nearest neighbor cage in supercooled water.

II. RELAXING CAGE MODEL FOR THE SELF-INTERMEDIATE SCATTERING FUNCTION

It is obvious by a careful inspection of the SISF of the oxygen atom calculated in the long-time MD simulation of supercooled SPC/E water that the center of mass motion of a water molecule in supercooled states can be considered as a compounded motion of a short-time in-cage vibrations and a long-time cage relaxation, having two widely separated time scales. According to this picture, the SISF is a product of contributions from these two types of motions. The SISF is the two-time autocorrelation function of fluctuation of Fourier component of the test particle density and is defined as

$$F_s(k,t)=\langle \exp[-i\mathbf{k}\cdot\mathbf{r}(0)]\exp(\mathbf{k}\cdot\mathbf{r}(t))\rangle. \tag{1}$$

The in-cage librations and vibrations of a water molecule can be treated approximately as motions of the center of mass in an isotropic harmonic potential well provided by the mean field of its neighbors. Thus the Hamiltonian of a typical particle with mass M is assumed to be

$$H=\frac{P^2}{2M}+\frac{M\omega^2 r^2}{2}, \tag{2}$$

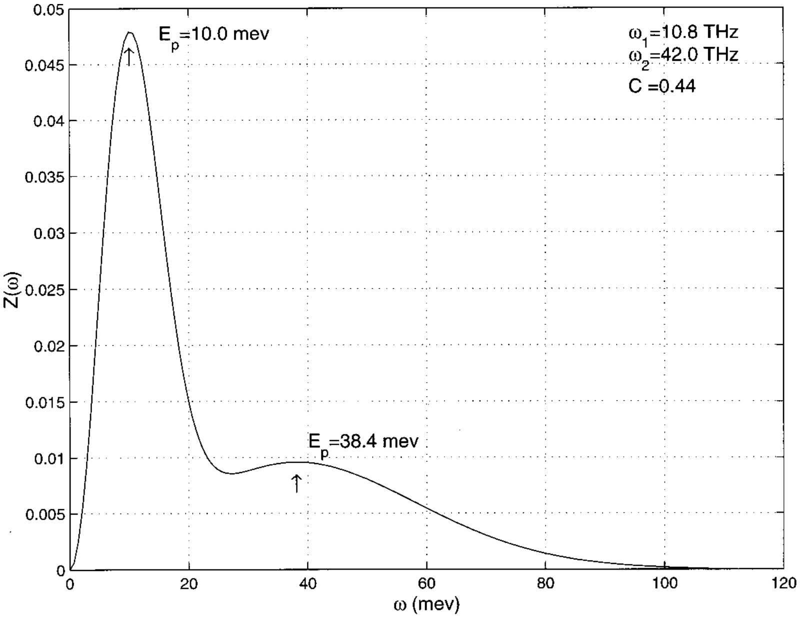

FIG. 2. The two-peak structure of the vibrational density of states of supercooled water at 47° below the temperature of density maximum. Notice that the first prominent peak occurs at about 10 meV and the second low-lying peak at about 38 meV.

where ω is the characteristic vibrational frequency which we shall take to be a variable different for individual water molecules situated in different spatial locations. Since in liquids the test particle motion is isotropic, the SISF depends only on magnitude of the wave vector transfer k. Under this circumstance, we can arbitrarily choose the direction of the k vector to be in the x direction. Hence for a system obeying classical mechanics, we can write the vibrational part of the SISF as

$$\begin{aligned} F_v(K,t) &= \langle \exp\{ik[x(t)-x(0)]\}\rangle \\ &= \exp\left[-\frac{1}{2}k^2\langle [x(t)-x(0)]^2\rangle\right], \end{aligned} \tag{3}$$

where the second equality is established by using the so-called Bloch identity valid for a system with a simple harmonic oscillator Hamiltonian [21]. With this observation, one can calculate the SISF for particles in an ensemble of harmonic potential wells as

$$\begin{aligned} F_v(k,t) &= \exp\left[-\frac{1}{2}k^2\left\langle\left(\int_0^t v_x(t')dt'\right)^2\right\rangle\right] \\ &= \exp\left[-k^2\left(\int_0^t (t-\tau)\langle v_x(0)v_x(\tau)\rangle d\tau\right)\right], \end{aligned} \tag{4}$$

where the second equality follows from the stationary property of a time-correlation function. We next introduce the normalized velocity autocorrelation function $\psi(\tau)$, and its Fourier transfer $Z(\omega)$ as follows:

$$\psi(\tau) = \langle \mathbf{v}(0)\cdot\mathbf{v}(\tau)\rangle/\langle v^2\rangle, \quad v_0^2 = \langle v_x^2\rangle = k_B T/M,$$

$$Z(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\psi(t)dt. \tag{5}$$

$Z(\psi)$ is also called the generalized frequency distribution of the translational motions. In terms of these functions, the vibrational SISF can now be transformed into the form

$$\begin{aligned} F_v(k,t) &= \exp\left[-k^2 v_0^2 \int_0^t (t-\tau)\psi(\tau)d\tau\right] \\ &= \exp\left[-2k^2 v_0^2 \int_0^\infty d\omega Z(\omega)\frac{1-\cos\omega t}{\omega^2}\right]. \end{aligned} \tag{6}$$

For water we take the frequency distribution function of the following form:

$$\begin{aligned} Z(\omega) &= (1-C)\frac{\omega^2}{\omega_1^2\sqrt{2\pi\omega_1^2}}\exp\left(-\frac{\omega^2}{2\omega_1^2}\right) \\ &\quad + C\frac{\omega^2}{\omega_2^2\sqrt{2\pi\omega_2^2}}\exp\left(-\frac{\omega^2}{2\omega_2^2}\right), \end{aligned} \tag{7}$$

where we redefine $Z(\omega)$ by normalizing it to unity over the whole range of frequencies. This form of the distribution function has a two peak structure as illustrated by Fig. 2. The introduction of this form is suggested by the low-frequency proton density of states of water measured by a previous incoherent inelastic neutron scattering experiment [22]. Using Eq. (7), the integration in the exponent of Eq. (6) can then be performed analytically to obtain the result

$$\begin{aligned} F_v(k,t) = \exp\Bigg\{-k^2 v_0^2\Bigg[&\frac{1-C}{\omega_1^2}(1-e^{-\omega_1^2 t^2/2}) \\ &+ \frac{C}{\omega_2^2}(1-e^{-\omega_2^2 t^2/2})\Bigg]\Bigg\}. \end{aligned} \tag{8}$$

This is the short-time behavior of the SISF of the test particle. It starts from unity at $t=0$ and decays rapidly to a flat plateau determined by an incoherent Debye-Waller factor $A(k)$ given by

$$A(k) = \exp\left\{-k^2 v_0^2\left(\frac{1-C}{\omega_1^2}+\frac{C}{\omega_2^2}\right)\right\}, \tag{9}$$

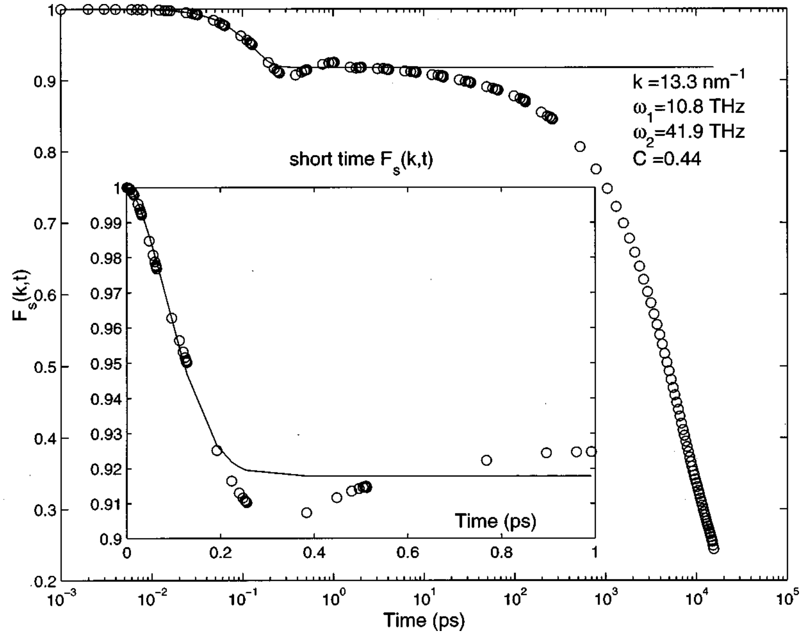

FIG. 3. Illustration of the short-time dynamics of SISF as described by vibrations in a harmonic potential well with the characteristic frequencies having a two-peak distribution. Notice since the motions are confined, at long time, the SISF tends to a constant level given by a Debye-Waller factor (solid line). In the inset, we show the short time decay of SISF in a linear scale. The oscillation of the MD data around 0.6 ps is an artifact due to the finite size of the simulation box.

which has a Gaussian form in k. The decay rate of the short time part is seen to be controlled by three parameters ω_1, ω_2, and C. A plot of $F_v(k,t)$ vs t according to the Eq. (8) is given in Fig. 3.

The cage relaxation at long time can be described by the standard alpha relaxation model [18]:

$$F_\alpha(k,t)=\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \qquad (10)$$

with a structural relaxation time τ and a stretch exponent β. From Eqs. (8) and (10), the SISF, valid for the entire time range can be constructed as

$$\begin{aligned} F_s(k,t)&=F_v(k,t)F_\alpha(k,t)\\ &=\exp\left\{-k^2v_0^2\left[\frac{1-C}{\omega_1^2}(1-e^{-\omega_1^2t^2/2})\right.\right.\\ &\quad\left.\left.+\frac{C}{\omega_2^2}(1-e^{-\omega_2^2t^2/2})\right]\right\}\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]. \qquad (11)\end{aligned}$$

This form of SISF satisfies the two general boundary conditions $F_3(k,t=0)=1$ and $F_s(k=0,t)=1$, provided that $1/\tau$ has a power-law dependence on k with a positive power which was shown to be true experimentally [23,24].

III. DATA ANALYSIS

We use the relaxing cage model to analyze a series of SISFs for water at 207 K generated by MD with the SPC/E potential [8]. The time range of SISF is from 1 fs to 10 ns for each scattering wave number k. The range of k covered is from 3.3 to 29.7 nm^{-1}. The data set includes SISFs for 9 different k values in an interval of 3.3 nm^{-1}. The fitting uses the model given in Eq. (11) with five fitting parameters: C, ω_1, ω_2, τ, and β. The results of the fits are shown in Fig. 4, where k increases from top to bottom. The inset shows in an expanded scale the fits to the short time part of SISF up to 0.5 ps. The decay of SISF can be divided into two well separated stages: the short time relaxation due to movements of particles in the harmonic potential wells having different characteristic frequencies and the long time, alpha relaxation due to the structural relaxation of the cages.

We find that the fitted parameters C, ω_1, ω_2 vary only slightly for different values of k. Figure 5 shows nine superposed curves of the vibrational density of states $Z(\omega)$ generated by the nine sets of parameters C, ω_1, ω_2. This figure shows a nearly k independence of $Z(\omega)$, which implies that the short time dynamics of supercooled water is, to a good approximation, harmonic. This is in agreement with the finding of Sciortino and Tartaglia [25] who demonstrated this point by carrying out an instantaneous normal mode analysis of the MD data. The k independence of $Z(\omega)$ also guarantees the Gaussian shape of the Debye-Waller factor as a function of k according to Eq. (9). We can write the Debye-Waller factor as $A(k)=\exp[-k^2a^2/3]$, where a is the root mean square vibrational amplitude of water molecules in the cage in which the particle is constrained during its short time movements. If we take the mean values from the fits $C=0.44$, $\omega_1=10.8$ THz, $\omega_2=42.0$ THz, it leads to a value $a=0.38$ A.

The best fitted parameters for the alpha relaxation, β and τ, are clearly k dependent. It is seen from Fig. 6(a) that as k increases, the long time decay of SISF deviates more and more from an exponential form. The stretch exponent β increases smoothly from 0.57 at $k=30$ nm^{-1} to 0.9 at $k=3.3$ nm^{-1}, showing a tendency of approaching unity at $k=0$. The relaxation rate $1/\tau$ vs k in a log-log plot gives approximately a straight line, which indicates that variation of τ obeys the power law $1/\tau\propto k^{\gamma}$ with slightly k-dependent γ [Fig. 6(b)]. The inset of Fig. 6(b) shows that the exponent γ remains constant at 1.2 down to $k=1$ nm^{-1}, swings up thereafter and shows a tendency of approaching 2 at $k=0$. There is thus a clear indication that at a sufficiently small k, the normal diffusion process is restored in such a way that $F_s(k,t)=\exp(-Dk^2t)$.

Finally, let us point out a spurious oscillation in SISF due to finite size of the MD simulation box. Careful examination

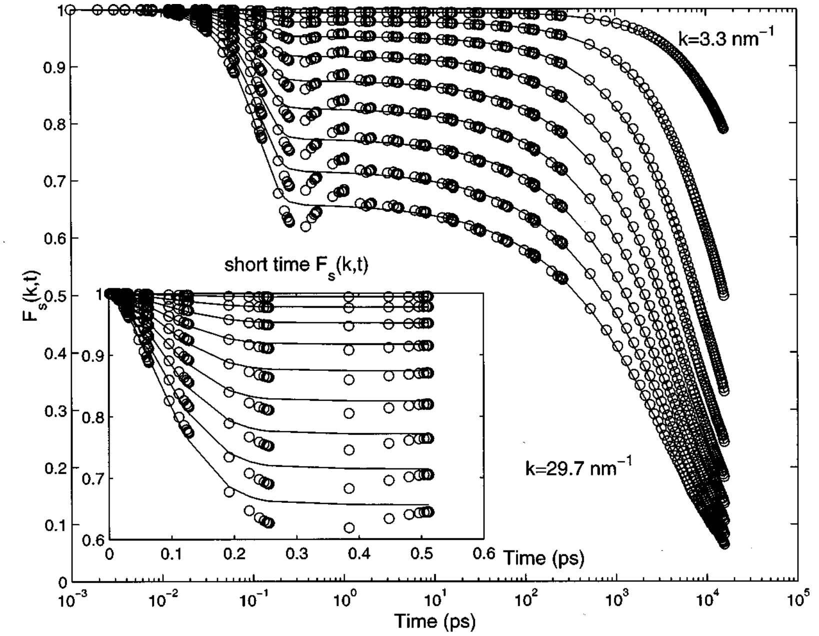

FIG. 4. MD generated SISFs at nine k values for SPC/E water at 207 K and their analyses. Solid lines are the model analyses, circles are the MD data. The k values increase from top to bottom with equal intervals. The inset shows the expanded short time parts of the MD SISFs and their model fits.

of Fig. 4 shows that there exists an oscillation in SISF which our model does not reproduce. Inspection of the oscillations in SISF for different k values reveals that these oscillations occur at the same average time of around 0.6 ps (position of the mode) and may be attributed to an artifact of the simulation. This statement is further strengthened if we examine both coherent $F(k,t)$ and $F_s(k,t)$ together in the same time scale (Fig. 7) The existence of a well-defined Brillouin peak in coherent dynamic structure factor $S(k,\omega)$ corresponds to a damped oscillation in the coherent $F(k,t)$. This can be seen in that function at low k values (the top three curves of the lower group of curves). For larger k, the coherent $F(k,t)$ should exhibit no damped oscillation because there is no long-range order in liquids. Hence there is no well-defined Brillouin peak. But the MD data of the coherent $F(k,t)$ still shows an oscillation at the same time (0.6 ps). Combining the observation that the same oscillation exists in both the coherent $F(k,t)$ at high k and $F_s(k,t)$ at all k values, we may conclude that this oscillation at around 0.6 ps is an artifact of the simulation. The origin of the oscillation can be attributed to reflection of a propagating density disturbance at a point within the box by the walls of the simulation box due to the imposition of the periodic boundary conditions. For example, a disturbance propagating along positive x direction when it reaches the boundary of the simulation will be brought back to the opposite boundary by the periodic boundary condition. Then it continues to propagate in the x direction and comes back to the point where it started after it travels exactly a distance L The edge of the cubic simulation box is $L=18.65$ Å. The speed of high frequency sound known to propagate in water is $v=3000$ m/s [26]. The time it takes for the disturbance to travel to the wall and come back to the same point is exactly $L/v=0.622$ ps (private communication with the late Dr. Aneesur Rahman [27]). We have also tried to simu-

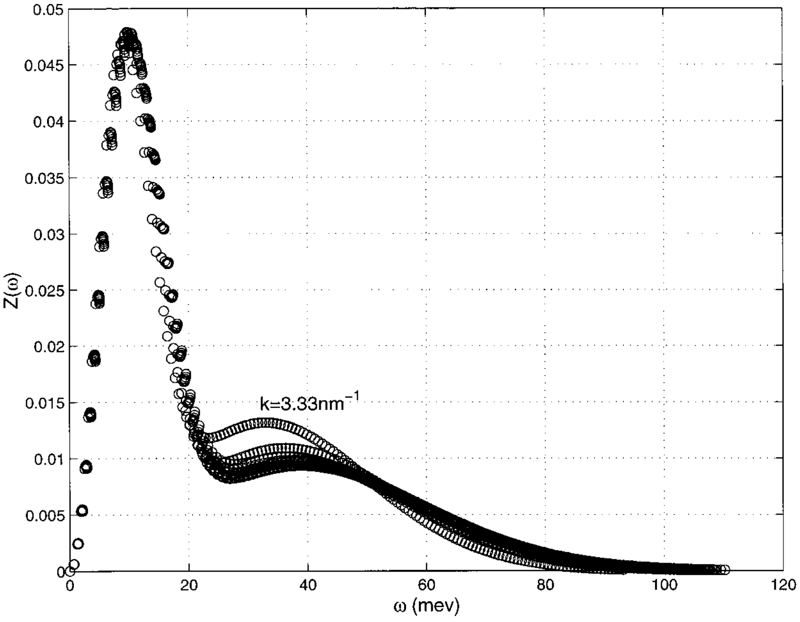

FIG. 5. The nine distribution functions $Z(\omega)$ calculated from the best fitting parameters C, ω_1, ω_2 to the MD generated SISFs at different k values. Notice all the distributions superposed on top of one another except for the lowest k case.

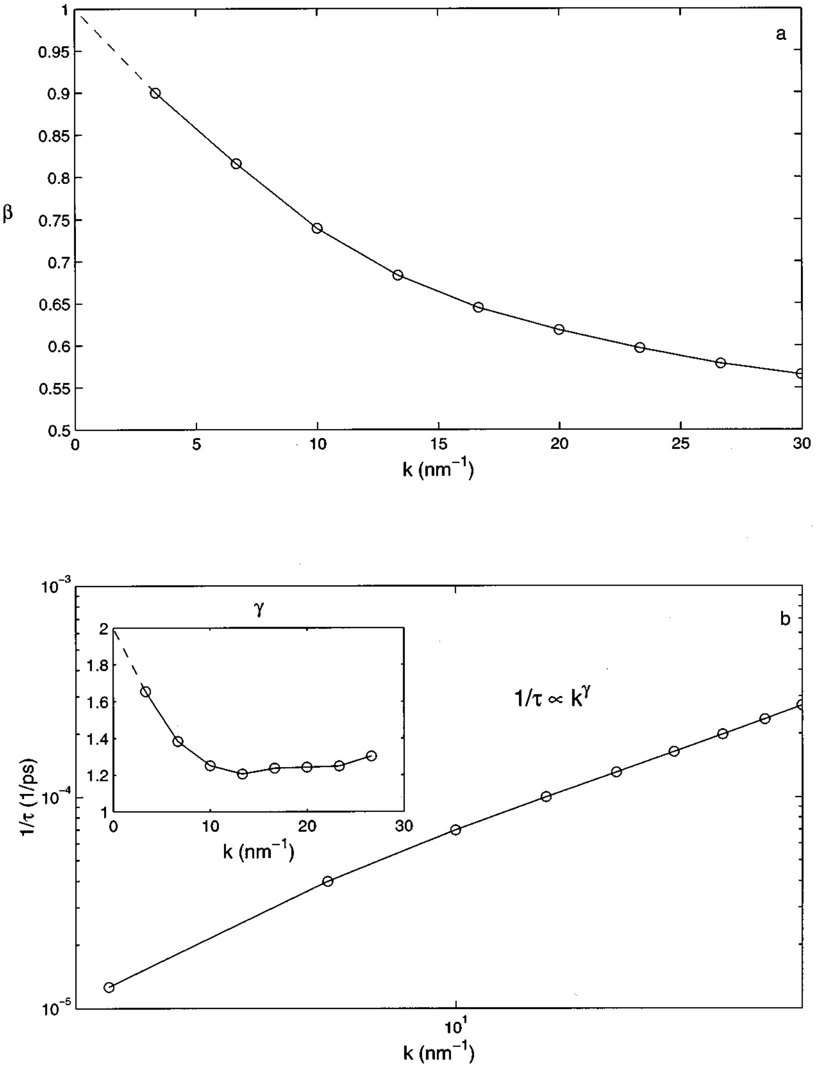

FIG. 6. k dependence of the best fit parameters β (a) and $1/\tau$ (b). Solid lines are lines connecting the nine data points. Notice that the $1/\tau$ vs k in a log-log plot follows approximately a straight line. The inset show the dependence of the slope of the straight line on k.

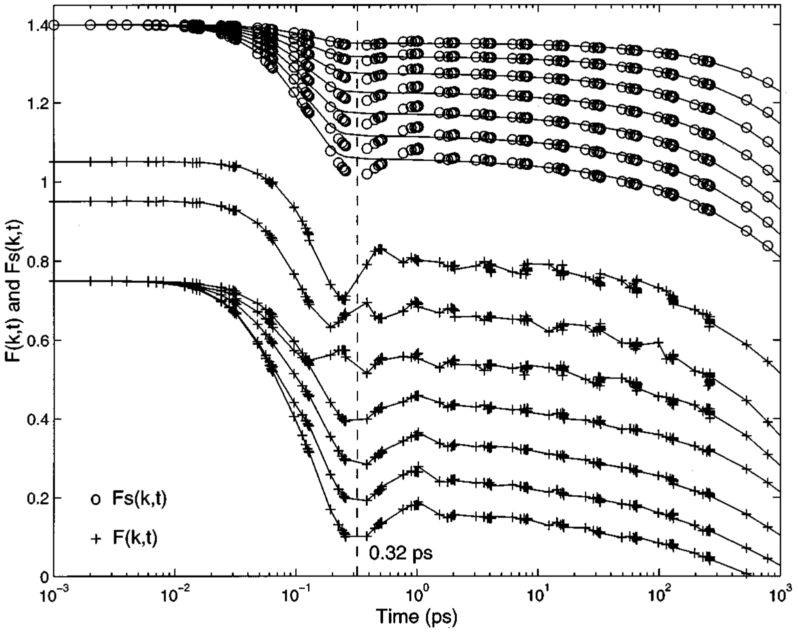

FIG. 7. Plausible evidence of a spurious oscillation in $F_s(k,t)$ and $F(k,t)$ caused by the finite size of the simulation box. The upper seven curves of circles are $F_s(k,t)$ of different k values with k increasing from the top to bottom. The lower seven curves of pulses are $F(k,t)$ of different k values with k increasing from the top to bottom. The damped oscillation at around 0.6 ps, existing in all curves (indicated by a dash line), must be due to an artifact induced by the periodic boundary condition imposed in the simulation.

late a much larger system (216×64 particles). The preliminary result shows that the spurious oscillation no longer occurs at 0.6 ps (Sciortino).

IV. DISCUSSION AND CONCLUSION

We have shown, by analyzing MD generated SISFs of supercooled water, that incorporation of both an appropriate short-time in-cage dynamics and a long-time cage relaxation represented by an α relaxation process is essential in construction of an analytical model for analyses of high resolution incoherent quasielastic spectra. We found that the short-time dynamics can be well approximated by harmonic vibrations of a molecule in a cage with a frequency distribution function which has a two-peak structure known from an analysis of MD data [25] and a previous inelastic incoherent neutron scattering [22] experiment. In a high resolution quasielastic neutron scattering (QENS) spectrum, the line shape having a sharp central component and an extended slowly decaying wing is a clear frequency-domain manifestation of a stretched exponential relaxation. We stress that in order to analyze an experimentally measured spectrum which covers an extensive frequency range, we need a theory which covers the SISF for their entire time domain, both short time and long time. In this regard, the use of only the alpha relaxation is not enough for this purpose.

We would like to emphasize that the formalism described in this paper is straightforward, analytical and practical when applied to analyses of high resolution QENS data. Previously a QENS experiment of supercooled water was performed with a moderate resolution and analyzed with a conventional theory [28,29] in which the α relaxation contribution was not included. We have recently analyzed a new high resolution QENS experiment of supercooled water contained in a porous glass specifically to test the theory of incoherent scattering described here [30]. The analysis demonstrated that the present theory describes the QENS line shape quite well in a k range from 0.1 to 1.0 Å^{-1}, and we are able to extract the average α relaxation time which shows a power-law dependence on the magnitude of wave vector transfer k.

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