

Model for dynamics in supercooled water

C. Y. Liao,¹ F. Sciortino,² and S. H. Chen¹

¹*Department of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

²*Dipartimento di Fisica, Universita di Roma La Sapienza, Piazzale Aldo Moro 2, I-00185 Roma, Italy*

(Received 27 July 1999)

We propose a phenomenological model for the intermediate scattering function (ISF) associated with density fluctuation in low temperature water. The motivation is twofold: to extract various physical parameters associated with the ISF computed from extended simple-point-charge model water at supercooled temperatures, and to apply this model to analyze high resolution inelastic x -ray scattering data of water in the future. The ISF of the center of mass of low temperature water computed from 10 M -step molecular dynamics (MD) data shows clearly time-separated two-step relaxation with a well-defined plateau in-between. We interpret this result as due to the formation of a stable hydrogen-bonded, tetrahedrally coordinated cage around a typical molecule in low temperature water. We thus model the long-time cage relaxation by the well-known Kohlrausch form $\exp[-(t/\tau)^\beta]$ with an amplitude factor which is a k -dependent Debye-Waller factor $A(k)$, and treat the short-time relaxation as due to molecular collisional motions within the cage. The latter motions can be described by the generalized Enskog equation, taking into account the confinement effect of the cage. We shall show that the effect of the confinement changes the collisional dynamics by modifying certain input parameters in the kinetic theory by a factor $[1-A(k)]^{1/2}$. We solve the generalized Enskog equation approximately but analytically by a Q -dependent triple relaxation time kinetic model. This kinetic model was previously shown to account for the large k behavior of Rayleigh-Brillouin scattering from moderately dense, simple fluids. We find that our model fits well with the MD generated collective as well as single-particle ISFs. For the short-time collisional dynamics, we fix values of the hard sphere diameter σ and pair correlation function at contact $g(\sigma)$, without introducing any adjustable parameters. The calculated ISFs reproduce the correct Brillouin peak frequencies at low k values. From the long-time dynamics, we deduce values of the Debye-Waller factor $A(k)$, the Kohlrausch exponent $\beta(k)$, and the cage relaxation time $\tau(k)$. [S1063-651X(99)13412-3]

PACS number(s): 61.20.Ja, 64.70.Pf

I. BACKGROUND

The anomalous transport behavior of water upon supercooling [1,2] has attracted a great deal of attention among physical chemists and biophysicists. It has been found that the shear viscosity of supercooled water shows an apparent power law divergence on approaching a singular but experimentally inaccessible temperature of about $T_s = 227$ K at ambient pressure [3]. In a related fashion, the self-diffusion constant tends to zero at T_s also with a power law [4,5]. These experimental facts have stimulated some theoretical conjectures in an attempt to explain the origin of this singularity [2]. One of us [6] has recently noted that some dynamical properties of interfacial water measured by incoherent quasi-elastic neutron scattering show similarities 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 relevance to biotechnology, pharmaceutical, and the food industry.

Computer molecular dynamics (MD) has been used extensively in the past to explore the phase behavior of supercooled water, but few of them has been directed toward investigation of dynamics of water near T_s . The computation of the 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 some of us using the extended simple-point-charge (SPC/E) model wa-

ter [7–10]. One of the interesting findings of this series of MD simulations is an unambiguous identification of a structural arrest temperature at 50 K below the temperature of maximum density of SPC/E water (250 K). This implies that the mode coupling theory, which predicts on fairly general ground the existence of such a structural arrest temperature in sufficiently supercooled simple liquids, may also be applicable to describe long-time dynamics of the center of mass motion of a subtle molecular liquid such as water.

The objective of this article is to propose an analytical, physical model to analyze these numerically computed intermediate scattering functions (ISF's) by molecular dynamics both for the collective and single-particle data. This is motivated by a hope that the simple physical model we derived here can be used to analyze present and future high resolution quasielastic and inelastic neutron (or x -ray) scattering experiments on bulk supercooled and interfacial water.

II. COMMENTS ON THE USE OF MODE-COUPLING THEORY (MCT) AND KINETIC THEORY

MCT is a theory that focuses its attention on the cage effect in the liquid state which can be pictured as a temporal trapping of a molecule by its neighbors as a result of lowering the temperature or increasing the density [11,12]. Molecular scale density fluctuations of high temperature dense fluids usually relax rapidly in a time scale of few picoseconds. The MCT does not attempt to address the detailed molecular dynamics in this time regime. However, upon

lowering the temperature below the freezing point, 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 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 in the fluid. MCT predicts 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. The existence of the crossover temperature T_c from normal liquid behavior to a non-ergodic state is a major prediction of MCT and has been observed to exist in some experiments [12]. At T_c , the coupling of density fluctuation modes leads to a structural arrest, characterized by the emergence of a nondecaying plateau in ISF with a positive value of a non-ergodicity parameter. On approaching T_c from above, there will be an increasing separation between the time scales describing the rattling motion of a particle in the cage and the eventual structural relaxation time of the cage. The ISF decays from the well-defined plateau at the intermediate time to zero through an α relaxation that can be described approximately by a Kohlrausch formula $\exp[-(t/\tau)^\beta]$. This has been shown numerically for various model systems, such as a hard sphere system [13], a mixed Lennard-Jones system [14], and supercooled water [7]. The initial part of this long-time decay is a time fractal, called von Schweidler's law, which can be derived through asymptotic expansions of the MCT equation [15].

Although an asymptotic solution of the MCT equation near the T_c provides time fractals for approaching the α relaxation and for the β relaxation approaching the plateau, the initial decay of the ISF remains the region covered by conventional kinetic theory. Kinetic theory has been employed successfully in describing density fluctuations in dense gas [16] and normal liquid region [17]. The theory usually writes the collision kernel explicitly and uses some approximations to solve an integro-differential equation for the ISF. Due to complications, the collision kernel can be written explicitly only in a simple hard sphere case and only considering the uncorrelated binary collisions. This is called the generalized Enskog equation, which has been solved numerically by the method of kinetic model [18,19].

To have a complete description of the dynamics of supercooled liquids, one needs an appropriate collision kernels to account for the microscopic time scale relaxation and the mode-coupling term as well to account for the cooperative molecular movements. With a very tedious computation, these dynamic equations can be solved self-consistently and numerically [20]. In this paper we shall introduce an approximation to reduce the complete dynamic equation into one effective kinetic equation without the mode-coupling terms. The addition of the mode-coupling terms in the memory function only affects the kinetic equation by giving rise to a well-defined non-ergodicity factor (or the Debye-Waller factor) and eventually the α relaxation. We take this into account as a multiplicative factor. This drastic approximation seems applicable to supercooled water, as we shall demonstrate in the following analysis.

Application of the 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 hydrogen-bonded, tetrahedrally coordinated first- and second-neighbor shells 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 [21]. Thus the so-called cage in water has a qualitatively different property from the corresponding hard sphere or Lennard-Jones fluids. In the latter cases, 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 (a lower density structure) is an inherently more stable structure locally and has a longer lifetime.

III. A PHENOMENOLOGICAL THEORY FOR DYNAMICS IN SUPERCOOLED WATER

The ISF is defined as the time-dependent autocorrelation function of the k th Fourier component of the number density fluctuation. In this paper the ISF is normalized by its initial value which is the static structure factor $S(k)$ [for the self-part of ISF, $S(k)=1$] and therefore is unity at $t=0$. The ISF or its time-Fourier transform (the dynamic structure factor) is measurable by coherent inelastic neutron or x -ray scatterings. According to our MD simulation [10], the ISF of supercooled water initially decays within 1 ps to a plateau value determined by the Debye-Waller factor $A(k)$. Then it relaxes slowly, according to a stretched exponential time dependence, with a k -dependent relaxation time $\tau(k)$ and a stretch exponent $\beta(k)$. The evolution of the ISF can therefore be expressed as a product of two factors: the relaxation function representing motions within the cage and the k -dependent cage relaxation function. The in-cage relaxation function decays from an initial value of unity to the Debye-Waller factor in a short-time scale defined by the potential well of the confining cage. The cage relaxation or the local structural relaxation can be described by the Kohlrausch formula $\exp[-(t/\tau)^\beta]$.

To calculate the short-time relaxation, we adopt a Q -dependent triple relaxation time (QTRT) kinetic model of Furtado, Mazenko, and Yip [22] and Boon and Yip [23] which is an approximate solution of the generalized Enskog equation. The QTRT calculates the dynamic structure factor from a given $S(k)$. The dynamic structure factor gives the correct second moment $k^2 v_0^2/S(k)$ and third moment for the hard sphere system as well [24]. QTRT is known to describe the density fluctuation of moderately dense hard sphere fluids well [25,16] even at large k . The normalized ISF for the entire time range is therefore written as

$$F(k,t) = \{[1 - A(k)]\tilde{F}_{\text{QTRT}}(k,t) + A(k)\} \exp[-(t/\tau)^\beta], \quad (1)$$

where $\tilde{F}_{\text{QTRT}}(k,t)$ is the normalized ISF calculated by a modified QTRT model to be explained in Sec. IV. Equation (1) can also be written alternatively as

$$F(k,t)=[1-A(k)]\tilde{F}_{\text{QTRT}}(k,t)+A(k)\exp[-(t/\tau)^\beta]. \quad (1')$$

This latter form is plausible when the ISF shows a clear two-step relaxation with a widely separated time scale. This ISF satisfies the initial condition that at $t=0$, the normalized ISF is unity. Since the correct short-time behavior of the ISF requires that the second derivative of the total ISF at $t=0$ be $-k^2 v_0^2/S(k)$, the second derivative at $t=0$ of the $\tilde{F}_{\text{QTRT}}(k,t)$ should be $-k^2 v_0^2\{S(k)[1-A(k)]\}$. This amounts to modifying the thermal speed v_0 by a factor $1/[1-A(k)]^{1/2}$, an important point which is verified in our subsequent analysis of ISF obtained by MD.

We may digress here by commenting that the structure of the MCT equation also indicates that Eqs. (1) and (1') are plausible. The equation of the motion for the ISF in the schematic MCT is written as [15]

$$\begin{aligned} \partial_t^2 F(k,t) + \Omega^2(k)F(k,t) + \nu(k)\partial_t F(k,t) \\ + \Omega^2(k) \int_0^t m(k,t-t')\partial_{t'} F(k,t')dt' = 0, \end{aligned} \quad (2)$$

where the parameter $\Omega(k) = \sqrt{k^2 v_0^2/S(k)} > 0$ is the microscopic frequency defining the frequency or time scale of the model, $\nu(k) > 0$ the stochastic friction constant describing the binary collisions between particles, and $m(k,t)$ the mode-coupling relaxation kernel describing the cooperative molecular motions. At the point of the structural arrest, the total ISF $F(k,t)$ can be written as the sum of the Debye-Waller $A(k)$ and a short-time correlation function $[1-A(k)]\hat{F}(k,t)$ [15]

$$F(k,t) = A(k) + [1-A(k)]\hat{F}(k,t), \quad (3)$$

where the reduced short-time correlation function $\hat{F}(k,t)$ can be shown to satisfy the same equation of motion as Eq. (2), except that the microscopic frequency is modified to $\hat{\Omega}(k) = \Omega(k)/[1-A(k)]^{1/2}$ to give the correct second derivative of $F(k,t=0)$, and the mode-coupling kernel changes to another form $\hat{m}(k,t)$,

$$\begin{aligned} \partial_t^2 \hat{F}(k,t) + \hat{\Omega}^2(k)\hat{F}(k,t) + \nu(k)\partial_t \hat{F}(k,t) + \hat{\Omega}^2(k) \\ \times \int_0^t \hat{m}(k,t-t')\partial_{t'} \hat{F}(k,t')dt' = 0. \end{aligned} \quad (4)$$

For the short-time correlation function $\hat{F}(k,t)$, the mode-coupling term plays less important role and can be ignored. By ignoring in Eq. (4) the modified mode-coupling terms, the equation reduces schematically to a kinetic equation which has the same binary collision term $\nu(k)$ as the original equation [Eq. (2)]. The reduced kinetic equation can be written explicitly in the hard sphere case where the uncorrelated binary collision term is known, and QTRT provides an approximate solution of it. In the supercooled liquid regime above the structural arrest temperature, the long-time part of the ISF decays to zero eventually, approximatedly as $\exp[-(t/\tau)^\beta]$. Hence, one can multiply the stretched expo-

ponential decay to the right-hand side of Eq. (3) to describe the ISF in the supercooled liquid phase and obtain Eq. (1).

IV. QTRT KINETIC MODEL

Since the QTRT model is expected to find useful applications in analyses of data generated by the recently developed and rapidly growing inelastic x -ray scattering technique [26], we shall describe in detail a practical implementation of the theory in this section. It is well known that the Boltzmann equation can be used to describe the collective density fluctuation of fluids [23]. The linearized Boltzmann equation is valid in the case of thermal density fluctuations in dilute gases where the wavelength of the fluctuation is much larger than the molecular size and the frequency is smaller than the inverse of the molecular collision time. In the case of dense fluids where the intermolecular collision frequency is comparable to the inverse collision time between two molecules and the mean free path between two successive collisions not large compared to the molecular dimension, the Boltzmann equation description breaks down. Instead, the appropriate kinetic equation for calculation of transport coefficients in dense fluids is the Enskog model. Within the Enskog model, when the collision kernel is properly modified to take into account the mean field effect, the finite diameter of the particles, and the spatial correlation of the colliding pair of particles at contact, the so-called generalized Enskog equation is obtained which has been shown to provide an accurate means for calculating dynamic structure factor $S(k,\omega)$, of moderately dense hard sphere fluids [22,23,16,17]. For a hard sphere system, the generalized Enskog equation treats the particle collisions as binary but uncorrelated. It is therefore unable to describe the long-time structural relaxation phenomenon. This deficiency of the generalized Enskog equation can be improved by taking into account the so-called ring (or repeated, correlated) collision effects in the memory function [23]. This route leads to a greatly increased complexity in numerical computations and is not suited for a practical analysis of experimental data. Instead, it is more tractable to approximate the ring collision effects by using the mode-coupling theory. Even this latter approximation is much too complicated for the practical treatment of large k Rayleigh-Brillouin scattering encountered in the inelastic x -ray scattering (IXS) data. In this paper we find that the bulk of this ring collision effect can be incorporated into the QTRT framework by adding phenomenologically a term representing the α relaxation weighted by the Debye-Waller factor. This simplified treatment seems good enough for the analyses of our MD data in supercooled water.

The generalized Enskog equation deals with dynamical processes of a fluid system in the phase space. The basic dynamical variable in a kinetic theory description is the phase-space density defined as

$$\rho(\vec{r}\vec{p}t) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i(t))\delta(\vec{p} - \vec{p}_i(t)). \quad (5)$$

From the phase-space density, the number density at the position \vec{r} can be obtained by integrating the momentum vari-

able out, which gives $n(\vec{r}, t) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i(t))$. One then proceeds to construct the time-dependent phase-space density correlation function,

$$C(\vec{r} - \vec{r}', \vec{p}\vec{p}', t) = \langle \delta\rho(\vec{r}\vec{p}t) \delta\rho(\vec{r}'\vec{p}'0) \rangle, \quad (6)$$

where $\delta\rho$ is the deviation of phase-space density from the equilibrium value,

$$\delta\rho(\vec{r}\vec{p}t) = \rho(\vec{r}\vec{p}t) - \langle \rho(\vec{r}\vec{p}t) \rangle. \quad (7)$$

The \langle, \rangle denotes the N -particle equilibrium canonical ensemble average. In a homogeneous fluid, the correlation function depends only on the positional difference and the time difference. So it can be written simply as $C(\vec{r}, \vec{p}\vec{p}', t)$, taking the origin as a reference point.

From the time-dependent phase-space density correlation function, one can generate the van Hove space-time correlation function of interest by integrating out the momentum variables,

$$G(\vec{r}, t) = \frac{1}{n} \int d^3p \int d^3p' C(\vec{r}, \vec{p}\vec{p}', t), \quad (8)$$

where n is the average number density. The dynamical structure factor $S(k, \omega)$ is then defined as

$$S(k, \omega) = \frac{1}{2\pi} \int d^3r \int_{-\infty}^{\infty} e^{i(\vec{k} \cdot \vec{r} - \omega t)} G(\vec{r}, t) dt. \quad (9)$$

With the above definition, the generalized Enskog kinetic equation can be written in the following form:

$$\begin{aligned} \left(z - \frac{\vec{k} \cdot \vec{p}}{M} \right) C(\vec{k}\vec{p}\vec{p}'z) - \int d^3p'' \Phi(\vec{k}\vec{p}\vec{p}''z) C(\vec{k}\vec{p}''\vec{p}'z) \\ = -C(\vec{k}\vec{p}\vec{p}'), \end{aligned} \quad (10)$$

where a (\vec{k}, z) -dependent correlation function is obtained from the (\vec{r}, t) -dependent correlation function by

$$C(\vec{k}\vec{p}\vec{p}'z) = i \int d^3r \int_0^{\infty} dt e^{-i(\vec{k} \cdot \vec{r} - zt)} C(\vec{r}, \vec{p}\vec{p}', t), \quad (11)$$

and the initial condition in Eq. (10) is given by

$$\begin{aligned} C(\vec{k}\vec{p}\vec{p}') = \int d^3r e^{-i\vec{k} \cdot \vec{r}} C(\vec{r}, \vec{p}\vec{p}', t=0) = n f_0(p) \delta(\vec{p} - \vec{p}') \\ + n f_0(p) f_0(p') [S(k) - 1], \end{aligned} \quad (12)$$

where $f_0(p)$ is the normalized Maxwell-Boltzmann distribution.

The function $\Phi(\vec{k}\vec{p}\vec{p}'z)$ containing the mean field term and collision terms is called the phase-space collision memory function in this paper. Generally speaking, the collision memory function is a wave number and frequency dependent. In the case of hard spheres, collisions in the generalized Enskog theory are the binary collisions which are nonlocal in space but instantaneous in time. This implies that the memory function is independent of frequency. The generalized Enskog equation, Eq. (10), is an integro-differential

equation with a given initial condition, Eq. (12). Direct solution of the equation is very tedious [22]. Fortunately, it has been known that the Born-Green-Kirkwood (BGK) method [23,17] is an approximate but practical method for solving the above equation. It begins by regarding the above equation as a linear operator equation represented in the continuous momentum space. To see this, we rewrite the first term on the right-hand side (rhs) of Eq. (10) as

$$\begin{aligned} \left(k - \frac{\vec{k} \cdot \vec{p}}{M} \right) C(\vec{k}\vec{p}\vec{p}'z) = \int d^3p'' \left(z - \frac{\vec{k} \cdot \vec{p}}{M} \right) \\ \times \delta(\vec{p} - \vec{p}'') C(\vec{k}\vec{p}''\vec{p}'z). \end{aligned} \quad (13)$$

Then Eq. (13) can be written as a matrix equation,

$$[\hat{V}(kz) - \hat{\Phi}(kz)] \cdot \hat{C}(kz) = -\hat{C}(k), \quad (14)$$

where operators $\hat{V}(kz), \hat{\Phi}(kz), \hat{C}(kz), \hat{C}(k)$ are matrix representations of $V(\vec{k}\vec{p}\vec{p}'z), \Phi(\vec{k}\vec{p}\vec{p}'z), C(\vec{k}\vec{p}\vec{p}'z), C(\vec{k}\vec{p}\vec{p}')$ in the continuous momentum space, and $V(\vec{k}\vec{p}\vec{p}'z) = (z - \vec{k} \cdot \vec{p}/M) \delta(\vec{p} - \vec{p}')$. For example, one can explicitly write

$$\Phi(\vec{k}\vec{p}\vec{p}'z) = \langle \vec{p} | \hat{\Phi}(kz) | \vec{p}' \rangle, \quad (15)$$

where the set of bases $\{|\vec{p}\rangle\}$ span a complete linear vector space. In the momentum space, Eq. (14) is equivalent to an infinite number of linear algebraic equations. To solve Eq. (14) approximately, one would like to find a suitable discrete set of momentum eigenfunctions $\{|\alpha\rangle\}$, spanning a subspace in which the memory function operator $\hat{\Phi}(kz)$ can be well approximated by a sum of two operators: one can be represented as a finite, N th-order matrix and the other an infinite diagonal matrix. Thus in the N th order BGK method, the memory function operator becomes

$$\hat{\Phi}(k) = \hat{\Phi}_{N \times N}(k) - ia_N(k) \hat{I}, \quad (16)$$

where $\hat{\Phi}_{N \times N}(k)$ is the operator that is a $N \times N$ matrix in the new basis $\{|\alpha\rangle\}$, and

$$-ia_N(k) = \langle \alpha_{N+1} | \hat{\Phi} | \alpha_{N+1} \rangle. \quad (17)$$

The matrix elements of the operator in this approximation is therefore

$$\begin{aligned} \langle \alpha_i | \hat{\Phi}_{N \times N}(k) | \alpha_j \rangle = \langle \alpha_i | \hat{\Phi}(k) | \alpha_j \rangle + ia_N(k) \delta_{i,j} \\ \text{when } i, j < N. \end{aligned} \quad (18)$$

One can then apply Eq. (16) to Eq. (14) and get a matrix equation

$$[\hat{V}(kz) + ia_N(k) \hat{I}] \cdot \hat{C}(kz) = \hat{\Phi}_{N \times N}(k) \cdot \hat{C}(kz) - \hat{C}(k). \quad (19)$$

The matrix $\hat{C}(kz)$ can then be solved from Eq. (19) as

$$\hat{C}(kz) = -[\hat{I} - \hat{R}(kz) \hat{\Phi}_{N \times N}(k)]^{-1} \cdot \hat{R}(kz) \cdot \hat{C}(k), \quad (20)$$

where the $\hat{R}(kz)$ matrix is given by

$$\hat{R}(kz) = [\hat{V}(kz) + ia_N(k)\hat{I}]^{-1}. \quad (21)$$

In the bases $\{|\alpha\rangle\}$, the operator $\hat{\Phi}_{N \times N}(k)$ is a $N \times N$ matrix, and the infinite matrix of the operator $\hat{R}(kz)$ can be truncated to a $N \times N$ matrix directly. Thus, Eq. (20) is a $N \times N$ matrix equation.

QTRT (Q -dependent triple-relaxation-time kinetic model) is a seventh order BGK method. In the QTRT, the Hermite polynomials in the Cartesian coordinate are chosen to construct a complete set of orthonormal functions of momentum.

$$\Psi_\alpha(\vec{p}) = \frac{H_l(p_x/\sqrt{2})H_m(p_y/\sqrt{2})H_n(p_z/\sqrt{2})}{(l!m!n!)^{1/2}2^{(l+m+n)/2}}, \quad (22)$$

where $H_i(x)$ is the Hermite polynomial and α stands for the set of three indices (l, m, n) . The orthogonality condition is

$$\int d^3p_1 \Psi_\alpha(\vec{p})\Psi_\beta(\vec{p})f_0(p) = \delta_{\alpha\beta}. \quad (23)$$

It is useful to introduce the Dirac notation for the eigenket $|\alpha\rangle = |l, m, n\rangle$, which has a momentum representation given by

$$\langle \vec{p} | \alpha \rangle = \langle \vec{p} | l, m, n \rangle = \Psi_\alpha(\vec{p})[f_0(p)]^{1/2}. \quad (24)$$

The first five functions in this complete set of momentum basis functions are the five hydrodynamical momentum states, namely,

$$\begin{aligned} \Psi_{0,0,0}(\vec{\xi}) &= 1, \\ \Psi_{0,0,1}(\vec{\xi}) &= \xi_z, \\ |E\rangle &= 1/\sqrt{3}(|2,0,0\rangle + |0,2,0\rangle + |0,0,2\rangle), \\ \Psi_{1,0,0}(\vec{\xi}) &= \xi_x, \\ \Psi_{0,1,0}(\vec{\xi}) &= \xi_y, \end{aligned} \quad (25)$$

where $\vec{\xi} = \vec{p}/Mv_0$ is a dimensionless momentum. The first three momentum states are associated with longitudinal hydrodynamical modes (number density, longitudinal current, energy). The last two are associated with transverse currents. In addition, the states that correspond to the part of the stress tensor related to the shear viscosity and to the energy current are the sixth and seventh basis functions,

$$\begin{aligned} |\eta\rangle &= |0,1,1\rangle, \\ |k\rangle &= \frac{1}{\sqrt{5}}[|2,0,1\rangle + |0,2,1\rangle + \sqrt{3}|0,0,3\rangle]. \end{aligned} \quad (26)$$

Before applying the above complete set of momentum basis functions to obtain the matrix representation of the kinetic equation, one should rewrite Eq. (10) as

$$\begin{aligned} \left(z - \frac{\vec{k} \cdot \vec{p}}{M}\right) C'(\vec{k}\vec{p}\vec{p}'z) - \int d^3p'' \Phi'(\vec{k}\vec{p}\vec{p}''z) C'(\vec{k}\vec{p}''\vec{p}'z) \\ = -C'(\vec{k}\vec{p}\vec{p}'), \end{aligned} \quad (27)$$

where the primed quantities are defined in terms of unprimed ones by

$$\begin{aligned} C'(\vec{k}\vec{p}\vec{p}'z) &= \frac{C(\vec{k}\vec{p}\vec{p}'z)}{[f_0(p)f_0(p')]^{1/2}}, \\ \Phi'(\vec{k}\vec{p}\vec{p}'z) &= \frac{\Phi(\vec{k}\vec{p}\vec{p}'z)f_0(p')}{[f_0(p)f_0(p')]^{1/2}}, \\ C'(\vec{k}\vec{p}\vec{p}') &= \frac{C(\vec{k}\vec{p}\vec{p}')}{[f_0(p)f_0(p')]^{1/2}}. \end{aligned} \quad (28)$$

From Eq. (27) we see that the solution of Eq. (20) is still valid, if we only replace $\hat{C}(kz), \hat{C}(k), \hat{\Phi}(k)$ with $\hat{C}'(kz), \hat{C}'(k), \hat{\Phi}'(k)$. The matrix element of the memory function operator present in the generalized Enskog equation, Eq. (27), is defined as

$$\begin{aligned} \Phi_{\alpha,\beta}(k) &= \langle \alpha | \hat{\Phi}'(k) | \beta \rangle \\ &= \int d^3p \int d^3p' \Phi(\vec{k}\vec{p}\vec{p}') \Psi_\alpha(\vec{p}) \Psi_\beta(\vec{p}') f_0(p') \end{aligned} \quad (29)$$

and the matrix element of the \hat{R} operator in Eq. (21)

$$\begin{aligned} R_{\alpha,\beta}(kz) &= \langle \alpha | \hat{R}(k, z) | \beta \rangle = \int d^3p \frac{\Psi_\alpha(\vec{p})\Psi_\beta(\vec{p})f_0(p)}{z - \vec{k} \cdot \vec{p}/M + ia_N(k)} \\ &= \frac{1}{\sqrt{2}k v_0} \int d^3\xi \frac{\Psi_\alpha(\vec{\xi})\Psi_\beta(\vec{\xi})f_0(\xi)}{x + iy - \xi_z/\sqrt{2}}, \end{aligned} \quad (30)$$

where

$$\begin{aligned} x &= \frac{z}{\sqrt{2}k v_0}, \\ y &= \frac{a_N(k)}{\sqrt{2}k v_0}, \end{aligned}$$

$$a_N(k) = \sqrt{\pi n \sigma^2 v_0} g(\sigma) \left[\frac{62}{15} - \frac{2 \sin(k\sigma)}{k\sigma} \right]. \quad (31)$$

The matrix element for the initial correlation function $C(kpp')$ is

$$\begin{aligned} C_{\alpha,\beta}(k) &= \langle \alpha | \hat{C}'(k) | \beta \rangle \\ &= \int d^3p \int d^3p' C(\vec{k}\vec{p}\vec{p}') \Psi_\alpha(\vec{p}) \Psi_\beta(\vec{p}') \\ &= n[\delta_{\alpha,\beta} + (S(k) - 1)\delta_{\alpha 1}\delta_{\beta 1}]. \end{aligned} \quad (32)$$

The matrix element of the phase-space correlation function is

TABLE I. Memory elements of the generalized memory function for hard sphere $\Phi_{\alpha,\beta}[\sqrt{\pi n \sigma^2} v_0 g(\sigma)]^{-1}$. $Q = k\sigma$; $j_1(Q)$ is the spherical Bessel function of order 1; $S(k) = [1 - nC(k)]^{-1}$.

	$ 0,0,0\rangle$	$ 0,0,1\rangle$	$ E\rangle$	$ 0,1,0\rangle$	$ \eta\rangle = 0,1,1\rangle$	$ \kappa\rangle$
$ 0,0,0\rangle$	0	0	0	0	0	0
$ 0,0,1\rangle$	$-\frac{kC(k)}{\sqrt{\pi\sigma^2}g(\sigma)}$	$-8i\left[\frac{1}{3} + \frac{d^2}{dQ^2}j_0(Q)\right]$	$4\sqrt{\frac{\pi}{6}}j_1(Q)$	0	0	$-\frac{4i}{\sqrt{10}}\left[\frac{1}{3} + \frac{d^2}{dQ^2}j_0(Q)\right]$
$ E\rangle$	0	$4\sqrt{\frac{\pi}{6}}j_1(Q)$	$-\frac{8i}{3}[1-j_0(Q)]$	0	0	$6\sqrt{\frac{\pi}{15}}j_1(Q)$
$ 0,1,0\rangle$	0	0	0	$-4i\left[\frac{2}{3} - \left(1 + \frac{d^2}{dQ^2}\right)j_0(Q)\right]$	$-4\sqrt{\pi}\frac{d}{dQ}\left[\frac{1}{Q}j_1(Q)\right]$	0
$ \eta\rangle$	0	0	0	$-4\sqrt{\pi}\frac{d}{dQ}\left[\frac{1}{Q}j_1(Q)\right]$	$-16i\left[\frac{4}{15} + \frac{d^2}{dQ^2}\left(\frac{1}{Q}j_1(Q)\right)\right]$	0
$ \kappa\rangle$	0	$-\frac{4i}{\sqrt{10}}\left[\frac{1}{3} + \frac{d^2}{dQ^2}j_0(Q)\right]$	$6\sqrt{\frac{\pi}{15}}j_1(Q)$	0	0	$-\frac{i}{15}\left[59 + 81\frac{d^2}{dQ^2}j_0(Q)\right]$

TABLE II. Matrix elements of $D_{\alpha\beta}(x,y)$. $W(z)$ is the plasma dispersion function, $w'(z) = -2[1 + zw(z)]$, $z = x + iy$.

	$ 0,0,0\rangle$	$ 0,0,1\rangle$	$ E\rangle$	$ 0,1,0\rangle$	$ 0,1,1\rangle$	$ \kappa\rangle$
$ 0,0,0\rangle$	$-w(z)$	$\frac{\sqrt{2}}{2}w'(z)$	$\frac{1}{2}\sqrt{\frac{2}{3}}[w(z) + zw'(z)]$	0	0	$\frac{\sqrt{20}}{10}\left[1 + \left(\frac{3}{2} - z^2\right)w'(z)\right]$
$ 0,0,1\rangle$	$\frac{\sqrt{2}}{2}w'(z)$	$zw'(z)$	$\frac{1}{2}\sqrt{\frac{1}{3}}[(2z^2 - 1)w'(z) - 2]$	0	0	$-\frac{\sqrt{2}}{5}\left[2 + \left(\frac{3}{2}z - z^3\right)w'(z)\right]$
$ E\rangle$	$\frac{1}{2}\sqrt{\frac{2}{3}}[w(z) + zw'(z)]$	$\frac{1}{2}\sqrt{\frac{1}{3}}[(2z^2 - 1)w'(z) - 2]$	$\frac{1}{3}\left[(z^3 - z)w'(z) - z - \frac{5}{2}w(z)\right]$	0	0	$\frac{\sqrt{30}}{30}\left[1 - 2z^2 + \left(\frac{7}{2} - 4z^2 + 2z^4\right)w'(z)\right]$
$ 0,1,0\rangle$	0	0	0	$-w(z)$	$\frac{\sqrt{2}}{2}w'(z)$	0
$ 0,1,1\rangle$	0	0	0	$\frac{\sqrt{2}}{2}w'(z)$	$zw'(z)$	0
$ \kappa\rangle$	$-\frac{\sqrt{20}}{10}\left[1 + \left(\frac{3}{2} - z^2\right)w'(z)\right]$	$-\sqrt{\frac{2}{5}}\left[z + \left(\frac{3}{2}z - z^3\right)w'(z)\right]$	$\frac{\sqrt{30}}{30}\left[1 - 2z^2 + \left(\frac{7}{2} - 4z^2 + 2z^4\right)w'(z)\right]$	0	0	$\frac{2}{5}\left[\frac{3}{2}z - z^3 + \left(\frac{13}{4}z - 3z^3 + z^5\right)w'(z)\right]$

$$C_{\alpha,\beta}(kz) = \langle \alpha | \hat{C}'(kz) | \beta \rangle \\ = \int d^3p \int d^3p' C(\vec{k}\vec{p}\vec{p}'z) \Psi_\alpha(\vec{p}) \Psi_\beta(\vec{p}'). \quad (33)$$

Because the $\Psi_{\alpha=1}(\vec{p}) = \Psi_{0,0,0}(\vec{p}) = 1$, and by applying Eqs. (8), (9), (11), and (33), the dynamic structure factor can be calculated as

$$S(k, \omega) = \frac{1}{n\pi} \text{Im}[C_{1,1}(kz)]_{z=\omega+i0^+}. \quad (34)$$

If we combine Eqs. (30), (31), (32), (34), and (20), we finally get a closed-form matrix equation:

$$S(k, \omega) = -\frac{S(k)}{\pi\sqrt{2}k v_0} \\ \times \text{Im} \left[\left(\vec{I} - \frac{y}{ia_N(k)} \vec{D}(x, y) \cdot \vec{\Phi}_{N \times N} \right)^{-1} \right. \\ \left. \times \vec{D}(x, y) \right]_{(1,1), z=\omega+i0^+}, \quad (35)$$

where

$$D_{i,j}(x, y) = \int d^3\xi \frac{\Psi_i(\vec{\xi}) \Psi_j(\vec{\xi}) f_0(\vec{\xi})}{x + iy - \xi_z/\sqrt{2}} = \sqrt{2}k v_0 R_{i,j}(k, z). \quad (36)$$

One notes that $\sqrt{2}k v_0 S(k, \omega)/S(k)$ is a dimensionless quantity. The elements of the matrix $\vec{\Phi}_{N \times N}(k\sigma)$ and $\vec{D}(x, y)$ are given in Tables I and II, respectively. One can see that the matrix $\vec{\Phi}_{N \times N}(k\sigma)$ [including $ia_N(k)$] is a function of $k\sigma$ and $S(k)$. Thus if the thermodynamic state in terms of the number density and the thermal speed are specified for the system under study, three system parameters: the hard-sphere diameter σ , the pair correlation function at contact $g(\sigma)$, and the static structure factor $S(k)$, have to be given in order to calculate the dynamic structure factor $S(k, \omega)$.

We can summarize the merit of the QTRT as follows: it gives correct transport coefficients and thermodynamic properties of a hard sphere system; it gives correct short- and long-time properties of the intermediate scattering function, and it gives an analytical $S(k, \omega)$ accurate to within about 5% of the numerically converged solution of the generalized Enskog equation [25].

We need to comment here, in addition, on our application of a hard sphere kinetic theory to a system of molecules interacting with a hard core plus an attractive potential such as the SPC/E water and real water. In these systems the nature of the molecular collisions is obviously different from purely binary collisions of a hard sphere system. One can imagine that there will be ‘‘hard collisions’’ as well as ‘‘soft collisions’’ with systems having continuous potentials. Use of the hard sphere kinetic theory amounts to ignoring all the soft collisions and the possibility of formation of bound states in the latter systems. This could result in a serious deficiency of the model at very low temperatures. But the systems we are considering are at moderate temperatures so

that hopefully one can still use a concept of effective hard collisions. Looking at the experimental data, we see that the density fluctuation spectrum still qualitatively displays a triplet with Lorentzian line shapes at sufficiently low k and makes a transition to a Gaussian line shape at sufficiently high k , as predicted by the hard sphere kinetic theory. This means that the concept of the collision mean free path is still valid in the latter systems. The general structure of the hard sphere kinetic theory is probably still valid for the latter systems provided we introduce an appropriate ‘‘collision frequency,’’ $\sqrt{\pi n} \sigma^2 v_0 g(\sigma)$, which appears as a scaling factor in the collisional memory matrix given in Table I.

In order to apply the QTRT model in the framework of Eq. (1), we need to modify two input parameters v_0 and $g(\sigma)$ that enter into the calculation of the dynamic structure factor. First of all, in order to preserve the second moment, as we have already mentioned in Sec. III, the thermal speed v_0 has to be multiplied by a factor $1/[1-A(k)]^{1/2}$. Also for a hard sphere system, the third moment exists [24] and is proportional to $n\sigma^2 v_0 g(\sigma) (k v_0)^2$. In order to preserve the third moment as well, we need to multiply $g(\sigma)$ by a factor $[1-A(k)]^{1/2}$. This shows that the Debye-Waller factor, which is determined largely by the plateau value of the $F(k, t)$ at the intermediate time, also has a subtle effect on the short-time part of the ISF through its effects on the modification of v_0 and $g(\sigma)$. We note that these changes are equivalent mathematically to the multiplication of the frequency matrix (including free streaming and mean field terms) in the generalized Enskog equation by the factor $1/[1-A(k)]^{1/2}$, which is suggested by the modification of $\Omega(k)$ to $\hat{\Omega}(k)$ in MCT.

In order to calculate the self-part of ISF by QTRT, we can put the direct correlation function $C(k)=0$ in the collision memory function matrix (Table I) and take the large k limit of the matrix elements [18]. This means that we should put all the spherical Bessel functions and their derivatives to zero. In addition, to account for the cage confinement effect in supercooled water, one has to modify v_0 and $g(\sigma)$ by the same factors as the density fluctuation case.

V. DATA ANALYSIS

The ISFs are taken from MD simulation using a SPC/E model potential [8,10]. We analyzed both the collective and self-part of ISFs calculated at four temperatures. These temperatures are 238 K [−12 K below temperature of maximum density (TMD)], 225 K (−25 K below TMD), 215 K (−35 K below TMD), and 207 K (−43 K below TMD). At these temperatures, the ISF at each k shows clearly a time-separated two-step relaxation with a well-defined intermediate plateau that defines the value of the Debye-Waller factor. The long-time α relaxation can be well fitted by a stretched exponential for both the self-part and collective ISFs [27,7,8,9]. To use Eq. (1) to calculate the ISF, we take the center of mass structure factor $S(k)$ from the MD calculation. The hard sphere diameter σ is taken to be 0.275 nm which is the size of a water molecule, and the pair correlation function at contact $g(\sigma)$ to be 3.2, as calculated from the Carnahan-Stirling equation of state for hard spheres [28]. The three fitting parameters are the Debye-Waller factor

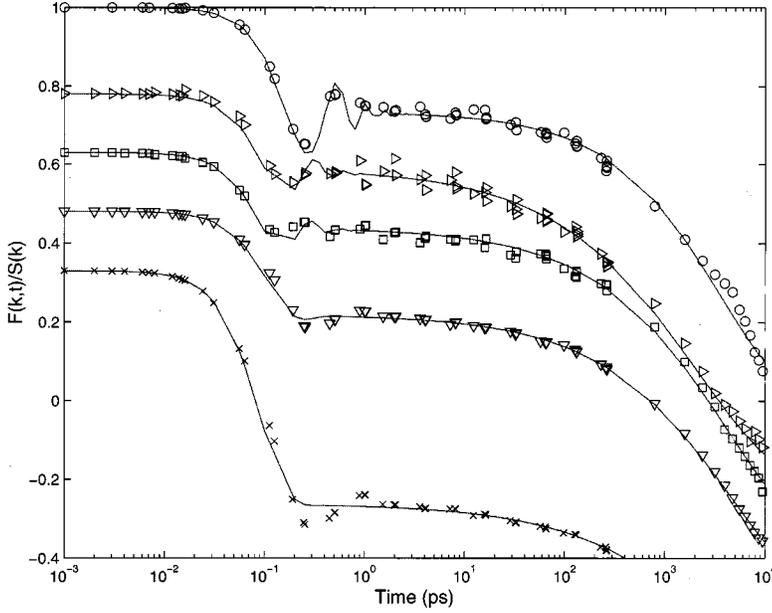


FIG. 1. Collective ISFs at $T=207$ K. The symbols denote the MD data (circle $k = 3.33 \text{ nm}^{-1}$, right triangle $k = 5.56 \text{ nm}^{-1}$, square $k = 6.67 \text{ nm}^{-1}$, down triangle 22.23 nm^{-1} , cross 44.46 nm^{-1}). The solid lines are the calculation of Eq. (1).

$A(k)$, the α relaxation time $\tau(k)$, and the stretched exponent $\beta(k)$. These three parameters are largely determined by the long-time part of the ISF, although $A(k)$ does come into calculation of the short-time part through the modification of v_0 and $g(\sigma)$. Our calculation shows that these modifications are absolutely essential in order to fit the short-time piece of ISF.

Figure 1 shows the comparison of the MD calculated collective ISFs (symbols) at five different k values and the theoretical fits (solid lines) by using Eq. (1) at $T=207$ K (-43 K below TMD). The fits are reasonable considering that there are no adjustable parameters for the short-time part (up to 1 ps). The oscillations around 0.6 ps occurring at the lowest curve is not reproduced in the fit. This curve corresponds to $k=44.46 \text{ nm}^{-1}$, too large to have a well-defined Brillouin peak. We think the oscillation is due to spurious effects in MD simulation as will be discussed later.

Equation (1) can fit the data with the collective ISFs in all four temperatures and the k values ranging from 3.33 to 100 nm^{-1} with only three parameters. The variations of the three parameters with temperatures and wave numbers shown in Fig. 2 confirm the results obtained in Ref. [10]. The three parameters oscillate with the same period as the $S(k)$. While one cannot see any significant variation of the Debye-Waller factor and $S(k)$ with the temperatures, the relaxation time and stretch exponent change drastically with the temperature. As water is supercooled, the relaxation time increases and the stretch exponent decreases.

Figure 3 is the short-time part of the collective ISF at $T=215$ K (-35 K below TMD). The oscillations at the time around $t=0.6$ ps are due to artifacts of MD simulation using a finite simulation size. This type of artifact has already been discussed in one of our previous publications [27]. In Fig. 3, one can see that there is another type of oscillation overlapping with this artifact, but showing a systematic change with k . We marked the peaks of these damped oscillations with arrows. The occurrence time of these oscillations becomes earlier when the k increases. As k becomes large enough, the oscillation becomes invisible. Through the QTRT calculation, we find that these oscillations correspond to side peaks

of $S(k, \omega)$ shown in Fig. 4. We denote also with arrows the positions of the corresponding frequencies where the damped oscillations marked in Fig. 3 occur. One can therefore see that these damped oscillations in the time domain are not due to the MD artifact but correspond to genuine Brillouin peaks

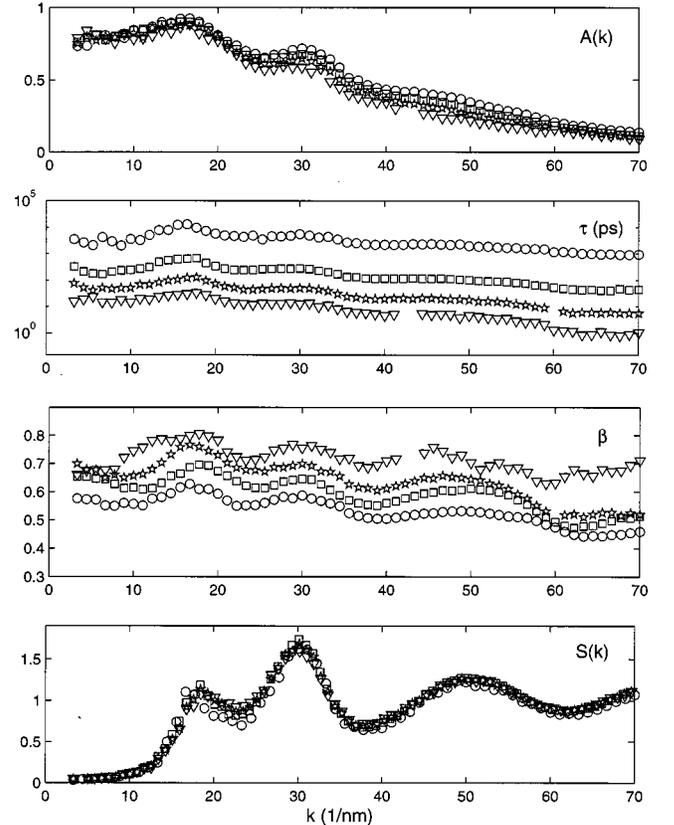


FIG. 2. Three fitting parameters for collective ISF: Debye-Waller factor $A(k)$, the stretch exponent β , the α relaxation time scale τ , are plotted together with the structure factor $S(k)$. The symbols denote different temperatures (circle $T = -43$ K below TMD, square $T = -35$ K below TMD, pentagon $T = -15$ K below TMD, triangle $T = -12$ K below TMD).

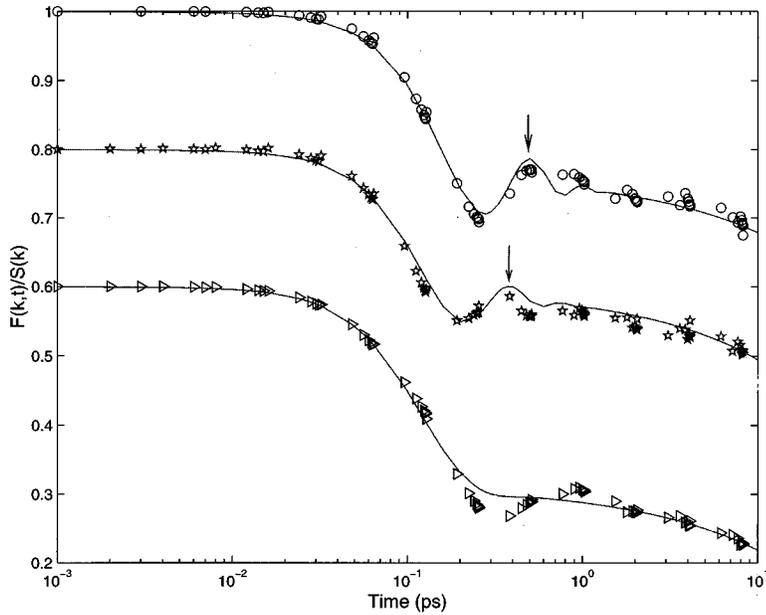


FIG. 3. Short-time part of collective ISF at $T=215$ K (-35 K below TMD). The symbols denote the MD data (circle $k=3.33$ nm $^{-1}$, pentagon $k=4.45$ nm $^{-1}$, triangle 22.23 nm $^{-1}$). Solid lines are the calculations of Eq. (1). The arrows mark the damped oscillation corresponding to Brillouin peaks in $S(k, \omega)$.

in the dynamic structure factor. It should be noted that since the stretched exponential part in the ISF has a much longer relaxation time, its contribution to $S(k, \omega)$ is limited to the very low frequency region and does not affect the position of the Brillouin peak calculated from QTRT. We therefore can extract the sound speed from the positions of these peaks in the dynamic structure factor. Figure 5 shows the Brillouin peak positions extracted from the QTRT calculations at different k values and temperatures. The apparent Brillouin peaks are only visible for k below 8 nm $^{-1}$. The uncertainty in determining the peak positions is indicated by the error bars. The sound speed above $k=3.3$ nm $^{-1}$ can be calculated from the slope of the peak position vs k curve. This gives $c=3600 \pm 300$ m/s. One can see that there is no significant difference in the Brillouin peak positions and the sound speed at different temperatures. The best experimental value for the high frequency sound speed in water at 5°C is 3200 m/s [26].

The self-ISF for the four different temperatures can also be well fitted using Eq. (1) with the three adjustable parameters. One such example at $T=238$ K (-12 K below TMD) is shown in Fig. 6. The agreement between the phenomenological theory [Eq. (1)] and the MD data is remarkable. Figure 7 shows the results of the three parameters extracted from the fittings. It is noted that the Debye-Waller factor can be fitted by the expression $\exp(-k^2 a^2/3)$ (solid lines), with a^2 denoting the mean square vibrational amplitude within the cage. a has a value of 0.047 nm at temperature -12 K below the TMD, decreasing slightly as the temperature is lowered. We check that the stretch exponent β approaches unity and the power law behavior of $1/\tau$ approaches the form k^2 as $k \rightarrow 0$ [27]. Thus, the diffusion limit is restored at low enough k .

Lastly, we come to discuss the possible source of the artifacts occurring around $t=0.6$ ps, shown in the lowest curve in Fig. 1. The origin of the oscillation can be attributed

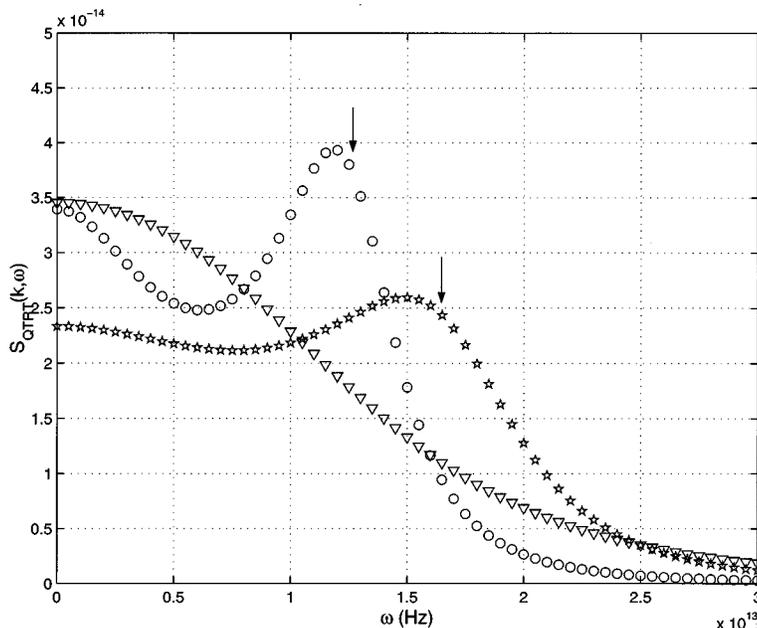


FIG. 4. $S(k, \omega)$ calculated by the QTRT kinetic theory at $T=215$ K (-35 below TMD). The symbols denote the different k values as in Fig. 3. The arrows mark the frequency position where the damped oscillations occur in Fig. 3.

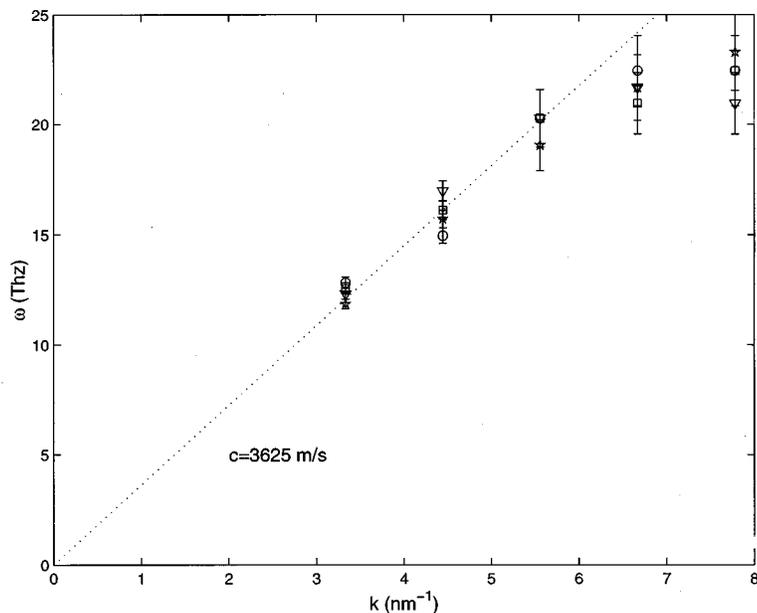


FIG. 5. Extracted Brillouin peak positions from the QTRT calculation. The symbols denote the different temperatures as in Fig. 2. The sound speed c is calculated to be 3600 ± 300 m/s. The dotted line indicates the dispersion relation $\omega = ck$.

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 the 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 $L = 18.65 \text{ \AA}$. The speed of high frequency sound known to propagate in the water is about $c = 3200$ m/s [26]. The time it takes for the disturbance to travel to the wall and come back to the same point is $L/c = 0.6$ ps. We have also tried to simulate a larger system (216×64 particles). The preliminary result shows that the spurious oscillation no longer occurs at 0.6 ps.

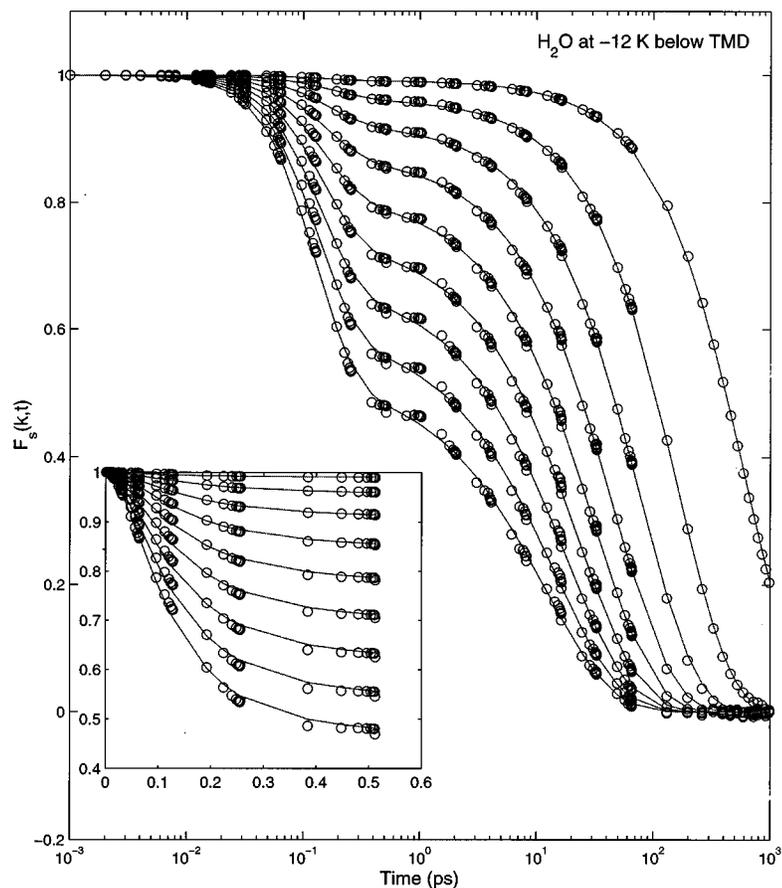


FIG. 6. Self-part ISFs at $T = 207$ K (-43 below TMD). The symbols denote the MD data, the solid lines are the theoretical calculations. k values are from 3.3 – 29.7 nm^{-1} from the top to the bottom. The inset figure shows the expanded curves focusing on the short-time part.

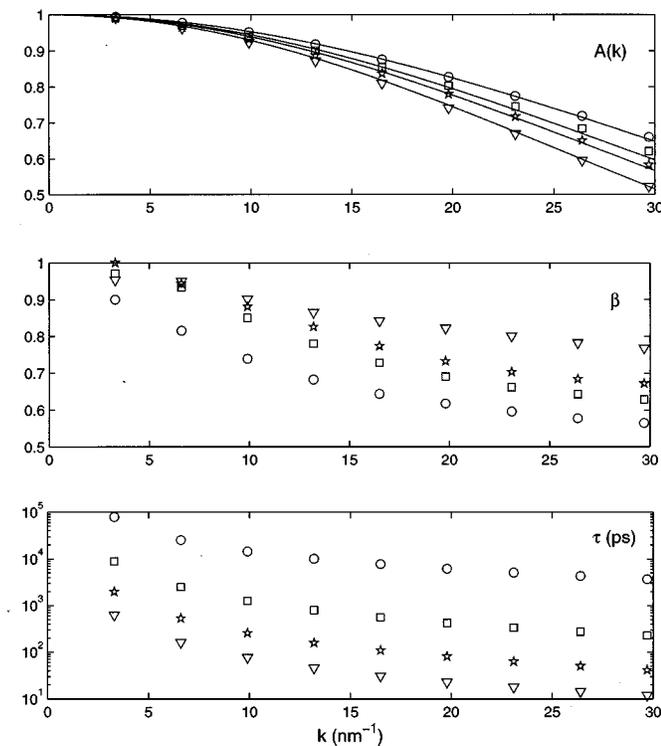


FIG. 7. Three parameters for the self-part ISF $A(k)$: Debye-Waller factor; β : the stretched exponent; τ : the α relaxation time. The symbols denote the different temperatures as in Fig. 2. The solid lines in the Debye-Waller factor curves are the fits to the point using the function of form $\exp(-k^2 a^2/3)$. $a = 0.038$ nm at $T = 207$ K, $a = 0.042$ nm at $T = 215$ K, $a = 0.043$ nm at $T = 225$ K, and $a = 0.047$ nm at $T = 238$ K.

VI. DISCUSSION AND CONCLUSION

We have shown by analyzing MD-generated ISFs of supercooled water that the incorporation of both the appropriate short-time collisional dynamics and a long-time structural relaxation represented by an α relaxation process is essential in the construction of an analytical model aiming at the analyses of coherent inelastic neutron [29] and x -ray scattering spectra of low temperature water. For both the INS and IXS spectra, the characteristic feature of the unusually strong central peak demands the presence of a component having the form of the α relaxation, besides the regular Rayleigh-Brillouin components provided by the kinetic theory description of high temperature density fluctuations in dense fluids. We stress here that in order to analyze experimental spectra, which are invariably measured in the frequency domain, we have to have a theory that covers the ISF in their entire time domain, both short time and long time. In this regard, the use of either the kinetic theory that correctly treats only the un-

correlated binary collisions or MCT with a schematic short-time behavior but deals correctly with the long-time structural relaxation, is insufficient for this purpose. One needs, in fact, both theories. Strictly speaking, it would be more consistent theoretically to incorporate the effects of the uncorrelated binary collisions and the cooperative mode coupling effects at the level of the memory function in the generalized kinetic equation description. Then at the level of intermediate scattering functions, the two effects will be coupled to a certain extent. Calculations of the ISF will then be very cumbersome numerically because one needs to solve two coupled nonlinear integro-differential equations [20]. Fortunately, in the supercooled liquid regime or in low temperature water, the time scales representing the two respective effects are widely separated that they are effectively decoupled and become additive even at the level of the ISF. In this sense, a description of the physical processes in supercooled liquids is simpler.

On the other hand, the generalized Enskog theory applied to the short-time part of the ISF in supercooled water must be modified to account for the cage effect. The modified kinetic theory has the same collision term as the original one, and the only modification is to multiply by a k -dependent factor to the QTRT input parameter v_0 to preserve the second moment and to $g(\sigma)$ to preserve the third moment of the dynamic structure factor for the hard sphere system. The modification factor is related to the Debye-Waller factor. The Debye-Waller factor gives the probability of the formation of the periodic cages with wave vector k . This makes the Debye-Waller factor an important parameter for describing the short-time dynamics by affecting the free streaming term and the mean field term in the kinetic theory. This results in the modification of v_0 and $g(\sigma)$ by a k -dependent factor. Without this modification to the kinetic theory, the fit to the short-time piece of the ISF would never be achieved.

We want to emphasize that the formalism described in details in this paper is analytical, practical, and straightforward to implement, admittedly phenomenological, when applied to the analysis of high resolution IXS spectra of low temperature water. We have made analyses of a series of IXS spectra of low temperature water with the present theory. The results are satisfactory and will be reported elsewhere.

ACKNOWLEDGMENTS

The part of this research done at MIT is supported by a grant from the Materials Research Division of US DOE. We acknowledge our collaboration with Professor P. Tartaglia and Dr. P. Gallo in generating the MD data of water we used in this analysis. We also appreciate frequent discussions of the QTRT formalism with Professor S. Yip during the course of this work.

- [1] C. A. Angell, *Annu. Rev. Phys. Chem.* **34**, 593 (1983).
- [2] C. A. Angell, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1981), Chap. 1.
- [3] P. G. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, 1998).
- [4] R. J. Speedy and C. A. Angell, *J. Chem. Phys.* **65**, 851 (1976).
- [5] F. X. Prielmeir, E. W. Lang, R. J. Speedy, and H. D. Ludeman,

- Phys. Rev. Lett.* **59**, 1128 (1987).
- [6] S. H. Chen, P. Gallo, and M. C. Bellissent-Funel, *Can. J. Phys.* **73**, 703 (1995).
- [7] P. Gallo, F. Sciortino, P. Tartaglia, and S. H. Chen, *Phys. Rev. Lett.* **76**, 2730 (1996).
- [8] F. Sciortino, P. Gallo, S. H. Chen, and P. Tartaglia, *Phys. Rev. E* **54**, 6331 (1996).

- [9] S. H. Chen, P. Gallo, F. Sciortino, and P. Tartaglia, *Phys. Rev. E* **56**, 4231 (1997).
- [10] F. Sciortino, L. Fabbian, S. H. Chen, and P. Tartaglia, *Phys. Rev. E* **56**, 5397 (1997).
- [11] E. Leuthesser, *Phys. Rev. A* **29**, 2765 (1984); U. Bengtzelius, W. Gotze, and A. Sjolander, *J. Phys. C* **17**, 5915 (1984).
- [12] W. Gotze and L. Sjogren, *Rep. Prog. Phys.* **55**, 241 (1992).
- [13] M. Fuchs, I. Hofacker, and L. Latz, *Phys. Rev. A* **45**, 898 (1992).
- [14] L. Bosio, S.-H. Chen, and J. Teixeira, *Phys. Rev. A* **27**, 1468 (1983).
- [15] W. Gotze, in *Liquids, Freezing, and Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier Science, Amsterdam, 1991).
- [16] K. Toukan, S. H. Chen, and S. Yip, *Mol. Phys.* **55**, 1421 (1985).
- [17] I. M. de Schepper and E. D. G. Cohen, *Phys. Rev. A* **22**, 287 (1980); *J. Stat. Phys.* **27**, 223 (1982); B. Kamgar-Parisi, E. D. G. Cohen, and I. M. de Schepper, *Phys. Rev. A* **35**, 4781 (1987); E. G. Cohen and I. M. De Schepper, *Nuovo Cimento Soc. Ital. Fis., B* **12**, 521 (1990); U. Bafle *et al.*, *Phys. Rev. Lett.* **65**, 2394 (1990).
- [18] G. F. Mazenko, T. Y. C. Wei, and S. Yip, *Phys. Rev. A* **6**, 1981 (1972).
- [19] I. M. de Schepper, E. G. D. Cohen, and B. Kamgar-Parsi, *J. Stat. Phys.* **54**, 273 (1989).
- [20] E. Leutheusser, *J. Phys. C* **15**, 2801 (1982); *Solid State Phys.* **15**, 2827 (1982).
- [21] F. Sciortino, A. Geiger, and H. E. Stanley, *J. Chem. Phys.* **96**, 3857 (1992); C. Masciovecchio, U. Bergmann, M. Krisch, G. Ruocco, F. Sette, and R. Verbeni, *Nucl. Instrum. Methods Phys. Res. B* **111**, 181 (1996).
- [22] P. M. Furtado, G. F. Mazenko, and S. Yip, *Phys. Rev. A* **13**, 1641 (1976).
- [23] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).
- [24] P. M. Furtado, Ph.D. thesis, Massachusetts Institute of Technology, 1976.
- [25] S. Yip, W. E. Alley, and B. J. Alder, *J. Stat. Phys.* **27**, 201 (1982).
- [26] F. Sette, G. Ruocco, M. Krisch, C. Masciovecchio, R. Verbeni, and U. Bergmann, *Phys. Rev. Lett.* **77**, 83 (1996).
- [27] S.-H. Chen, C. Liao, F. Sciortino, P. Gallo, and P. Tartaglia, *Phys. Rev. E* **59**, 6708 (1999).
- [28] N. F. Carnahan and K. E. Stirling, *J. Chem. Phys.* **51**, 635 (1969).
- [29] J. Teixeira, M. C. Bellissent-Funel, S. H. Chen, and B. Dorner, *Phys. Rev. Lett.* **54**, 2681 (1985).