

## Dynamic dielectric response function of liquid water

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Our previous theory for the dielectric response of waterlike fluids [Phys. Rev. A **46**, 7548 (1992); Phys. Rev. E **48**, 3172 (1993)] is generalized to take into account the asymmetrical inertia tensor of the water molecules around the dipolar axis. The frequency dependent dielectric function and the refractive index are calculated. The resulting behavior of the refractive index is compared with available experimental data for water. The refractive index, as a function of frequency, shows a slightly better agreement with experimental data than the previous symmetric molecule model. The “free rotation” peak is reduced in area and a new structure is obtained.

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### I. INTRODUCTION

Water is the most abundant compound on the surface of the earth and it is the principal constituent of all living organisms. Its dielectric properties are of special interest because they control both the electrostatic forces and the propagation of electromagnetic waves in biological media. Nevertheless, a full theoretical understanding of these properties from classical statistical mechanics has not yet been accomplished, despite the excellence of some work [1–14]. The reason is that the dielectric response involves very different physics at different frequency scales, so it is very difficult to devise a model that is sufficiently simple to be calculable, yet accurate enough to capture all the different aspects of the physics.

In two recent papers [15] we attempted to model the frequency dependent dielectric function of water. In the first paper [15(a)] we introduced a formalism to calculate the frequency and wave-vector dependent dielectric function of a classical fluid, given a knowledge of the *static* dielectric function and one phenomenological relaxation time. The individual water molecule was treated as a rigid symmetric top with an intrinsic electric dipole moment along the symmetry axis. The molecules interacted via the dipole field and via a contact repulsion. Our approach was similar to the integral equation approach of Wei and Patey [12] and is therefore *complementary* to the molecular dynamics studies in Refs. [6,9,13,14]. Our self-dielectric response was generalized to one which is correct both in the hydrodynamic regime of small wave vector  $\mathbf{q}$  and frequency  $\omega$ , as was theirs, and in the collisionless regime of large  $\mathbf{q}$  and  $\omega$ . Also, the inertia was treated in more detail. Specifically, the self-part of the dynamical von Hove correlation function [11,12,15] was calculated by solving the Boltzmann transport equation for the one-particle distribution function in phase space, in the presence of a time dependent potential (treated in the linear response approximation). Collisions with other

molecules were treated in a number-conserving relaxation-time approximation [15(a)], which guaranteed the occurrence of the diffusion regime at small  $\mathbf{q}$  and  $\omega$ . The full dielectric function was then approximately constructed by combining the dynamical self-part of the van Hove correlation function with static structural information from the reference hypernetted chain (RHNC) approximation calculations by Wei and Patey [11,12]. The Kerr approximation [16] corresponds to the frequency independence of the local field factor  $\psi(\mathbf{q})$ . In Fig. 4 of Ref. [15(a)] the index of refraction was compared to the integral equation approach of Wei and Patey [12] and the Stockmayer fluids (point molecule) molecular dynamics simulation of Pollock and Alder [6]. The Kerr approximation was found to be very reliable in both cases. The resulting dielectric function was compared with those obtained in previous theoretical calculations and with available experimental data for water. Overall, the approximation overestimated the refractive index in the infrared frequency regime. Two striking features of the result were (i) the peak in the refractive index at the characteristic frequency of free rotation of symmetric molecules and (ii) the high frequency zero in the longitudinal dielectric function indicating a collective excitation of the dipolar type. The peak predicted in (i) was actually observed in recent experimental measurements [17,18], but our theory gave a peak that is much too large.

In the second paper [15(b)] the rigid symmetric model was generalized to take into account the vibrational degrees of freedom of a water molecule. The refractive index of water was satisfactorily reproduced in the optical frequency range by combining the symmetric model of the previous paper [15(a)] with the main vibrational modes of a water molecule. We could then explain the major structures in the data over 15 decades of frequency range.

In the present paper, our calculation of the dynamic dielectric response function is generalized to take into account the true asymmetric tensor of inertia of water molecules. The water molecule is treated as a rigid triangular structure with one oxygen and two hydrogen atoms at the corners. The moments of inertia are calculated from the known masses of the constituent atoms and from

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molecular geometry. The electric dipole moment is oriented along the intermediate principal axis. We apply our computational approach to an ensemble of such molecules assuming that, for simplicity, the static structural properties remain the same as calculated in Ref. [15]. Thus the asymmetric inertia enters only the calculation of the self-part of the dynamical van Hove correlation function. The analytical solution of the classical equation of motion is complicated by the fact that the dipole moment of inertia is along an axis of unstable rotation. This circumstance precludes the possibility of any continuous limit existing between symmetric and asymmetric models. The dynamics is strongly nonlinear and the trigonometric functions of the symmetric model are replaced by the more complicated Jacobi elliptic functions. The main results of our calculations are the following: (i) a small reduction in the value of the refractive index at intermediate frequency, which improves the agreement with experimental data; (ii) a partial suppression of the free rotation peak of the symmetric model, which also improves the agreement of the model with experiment; and (iii) a hint of a structure in the intermediate frequency regime. The results are largely unchanged at low and high frequencies.

This paper is organized as follows. In Sec. II, we briefly review the fundamental theory introduced in the previous papers. The general ideas of this model were presented at some length in our first article [15(a)]. In Sec. III, we describe in detail the calculation for the asymmetric rigid water molecule. In Sec. IV, a summary and discussion of our results are presented.

## II. THEORY

The formalism introduced in our previous paper [15] was applied to a collection of rigid molecules. The position and orientation of a molecule are defined by the center of mass coordinated ( $\mathbf{r}$ ) and Euler angles ( $\theta, \varphi, \psi$ ) of the inertia tensor relative to a fixed frame of reference. The molecules interact with each other via the electric dipole moment  $\mu$  which is oriented along the  $x_3$  axis as shown in Fig. 1. There is also a hard core contact repulsion whose effects are incorporated in the RHNC calculation [11] of the static correlation function.

Since the liquid is homogeneous and isotropic, the dielectric tensor has two components: longitudinal and transverse with respect to the direction of the wave vector  $\mathbf{q}$  of the applied electric field

$$\epsilon_{\alpha\beta}(\mathbf{q}, \omega) = \epsilon_{\parallel}(\mathbf{q}, \omega) q_{\alpha} q_{\beta} / q^2 + \epsilon_{\perp}(\mathbf{q}, \omega) \{ \delta_{\alpha\beta} - q_{\alpha} q_{\beta} / q^2 \}. \quad (2.1)$$

In the  $q \rightarrow 0$  limit the difference between the two components vanishes. From the usual macroscopic electromagnetic equations, the dielectric tensor can also be expressed in terms of the dielectric polarizability  $\chi$  [11]

$$\epsilon(\mathbf{q}, \omega) = 1 + \frac{4\pi\chi(\mathbf{q}, \omega)}{1 - 4\pi(\mathbf{q}\mathbf{q}/q^2)\chi(\mathbf{q}, \omega)}. \quad (2.2)$$

The longitudinal and transverse components of  $\chi$  are the special cases of the generalized response

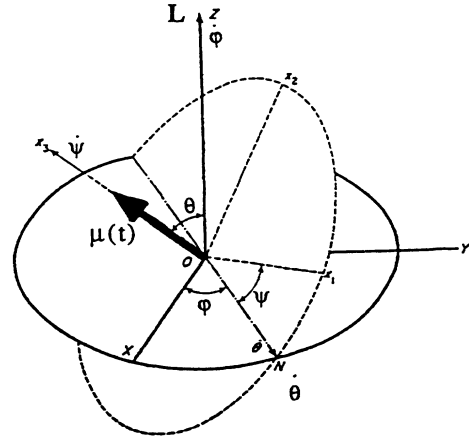


FIG. 1. The motion of the water dipole in the Euler angle coordinates. The angular velocities  $\dot{\theta}$ ,  $\dot{\varphi}$ , and  $\dot{\psi}$  are time derivatives of the Euler angles.

function  $\chi_{(L,M,N;L',M',N')}$ , which describes the linear response of the  $LMN$  component of the particle distribution function in Euler angles [ $f_{LMN} = \int d\Omega f(\theta, \varphi, \psi) P_L(\cos\theta) e^{iM\varphi} e^{iN\psi}$ ] to an external potential that couples linearly to the  $L'M'N'$  component of this distribution. Specifically, the longitudinal and transverse components correspond to diagonal elements of  $\chi$  with  $L=1, M=N=0$  and  $L=1, M=\pm 1, N=0$ , respectively.

The polarizability tensor in Eq. (2.2) is expressed in terms of its self-part  $\chi_s$ , and the static local field factor  $\Psi(\mathbf{q})$  as follows [15(a)]:

$$\chi(\mathbf{q}, \omega) = \chi_s(\mathbf{q}, \omega) [1 - \Psi(\mathbf{q})\chi_s(\mathbf{q}, \omega)]^{-1}. \quad (2.3)$$

The self-part of the electric polarizability describes the polarization response of a single molecule embedded in a viscous medium. The local field factor  $\Psi(\mathbf{q})$  includes the coherent effects of all the other molecules in modifying the effective field experienced by any given molecule. A fundamental assumption in Eq. (2.3) is that the local field factor depend only on wave vector, but not on frequency. In other words, the local field factor  $\Psi(\mathbf{q})$  has been assumed to be, like  $\chi_s$ , diagonal in the  $LMN$  indices. From all the above we see that the static local field factor  $\Psi(\mathbf{q})$  is completely determined by the static polarizability tensor  $\chi(\mathbf{q}, 0)$  and the static dielectric function, provided the self-polarizability function is known, i.e.,

$$\Psi(\mathbf{q}) = [\chi_s(\mathbf{q}, 0)]^{-1} - [\chi(\mathbf{q}, 0)]^{-1}. \quad (2.4)$$

The main effort in our approach goes into the determination of this function.

The number-conserving relaxation-time approximation for the self-correlation function  $\chi_s$  has been derived and discussed in detail in Refs. [15(a)] and [19], so we simply give the result

$$\chi_s(\mathbf{q}, \omega) = \frac{(\omega + i/\tau)\chi_s^0(\mathbf{q}, \omega + i/\tau)}{\omega + \frac{i}{\tau} \frac{\chi_s^0(\mathbf{q}, \omega + i/\tau)}{\chi_s^0(\mathbf{q}, 0)}}. \quad (2.5)$$

Here  $\chi_s^0$  is the polarizability function of a single molecule *in the absence of the viscous medium*. The effects of the latter are described by the phenomenological relaxation time  $\tau$ . The appearance of a single relaxation time is a consequence of the original relaxation time assumptions on the dynamics of the one-particle distribution function in phase space and also of the neglect of coupling between different angular momentum channels. From Eq. (2.5) we see that the function  $\chi_s^0$  needs to be known for complex values of the frequency  $\omega + i/\tau$ .

The calculation of  $\chi_s^0$  starts from the Kubo fluctuation-dissipation theorem [20], which relates  $\chi_s^0(\mathbf{q}, \omega)$  to the Fourier Laplace transformation of the self-part of the van Hove correlation function  $G_s(\theta\varphi\psi r; \theta'\varphi'\psi'r', t)$ , the latter being defined as the probability density of finding a molecule with coordinates  $\{q'_\alpha\}$  at time  $t$ , given that it had coordinates  $\{q_\alpha\}$  at time 0. The relation between them is

$$\chi_s^0(\mathbf{q}, \omega) = \chi_s^0(\mathbf{q}, 0) [1 + i\omega G_s(\mathbf{q}, \omega)] , \quad (2.6)$$

where  $\chi_s^0(\mathbf{q}, 0)$  coincides with  $\chi_s(\mathbf{q}, 0)$  because collisions do not affect the static response.  $G_s(\mathbf{q}, \omega)$  is the diagonal (100) component of the full correlation matrix  $G_s$ , which is given by

$$\begin{aligned} G_{s, LMN, L'M'N'}(\mathbf{q}, \omega) \\ = \delta_{LL'} \delta_{MM'} \delta_{NN'} \int_0^\infty dt e^{i\omega t} \langle e^{-i\mathbf{q}\cdot\mathbf{r}(t)} P_L[\cos\gamma(t)] \rangle , \end{aligned} \quad (2.7)$$

where  $\mathbf{r}$  is the position of the center of mass of the water molecule and  $P_L[\cos\gamma(t)]$  is a Legendre polynomial. The angle  $\gamma$  is the angle between the directions of the dipole at time 0 and at time  $t$ . Observe that  $G_s$  is diagonal in the angular indices because the electric quadrupole tensor of the water molecule is neglected. This correction will be added in future work in the form

$$\mu^2 \cos\gamma(t) \Rightarrow \mu^2 [\cos\gamma_1(t) + \mu^2 \cos\gamma_2(t)] . \quad (2.8)$$

Here we focus on the  $L=1$  component, which is necessary to calculate the dielectric function in our simplified model where the quadrupole moments were neglected. The statistical mechanical average  $\langle e^{-i\mathbf{q}\cdot\mathbf{r}(t)} P_{L=1}[\cos\gamma(t)] \rangle$  is calculated by integrating over all possible values of  $\mathbf{p}$  and angular momentum  $\mathbf{L}$  at the initial time with Boltzmann weight  $e^{-\beta E}/Z$ , where  $E$  is the kinetic energy and  $Z$  is the partition function:

$$G_s(\mathbf{q}, \omega) = \int_0^\infty dt e^{i\omega t} \langle e^{-i\mathbf{q}\cdot\mathbf{r}(t)} \cos\gamma(t) \rangle . \quad (2.9)$$

In the next section we will discuss the calculation of  $\cos\gamma(t)$  from the classical equation of motion of the molecule and the evaluation of  $G_s$  from Eq. (2.9) with the neglect of the quadrupole moment.

### III. CALCULATION OF THE FREE van HOVE CORRELATION FUNCTION FOR WATER MOLECULES

Consider a rigid triangular molecule with one oxygen and two hydrogen atoms at its corners as shown in Fig. 2.

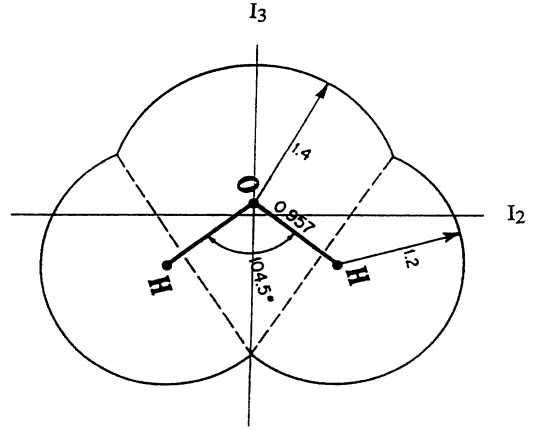


FIG. 2. The geometry of a water molecule [3]. The two perpendicular axes are centered at the center of mass.  $I_1 = I_2 + I_3$ .

The bond lengths are each 0.967 Å and the angle between the two bonds is 104.5° [1–3]. The principal axes are shown in Figs. 1 and 2. The moments of inertia are  $I_1 = 1.7605 \text{ m}\text{\AA}^2$  ( $=I_2 + I_3$ ),  $I_2 = 0.6127 \text{ m}\text{\AA}^2$ , and  $I_3 = 1.1477 \text{ m}\text{\AA}^2$ , where  $m$  is the hydrogen mass. The electric dipole moment is parallel to the  $x_3$  axis and its static value is  $\mu = 1.855 \times 10^{-18} \text{ esu cm}$  [8]. We will assume a single relaxation time  $\tau$ , which is of the order of Debye relaxation time [1], and choose  $\tau$  from the comparison with the reliable experimental data. In this paper we chose  $\tau = 2.8 \times 10^{-12} \text{ sec}$  at room temperature. More generally, it could be a function of the applied frequency, but that possibility will not be investigated here.

The  $\cos\gamma(t)$  in Eq. (2.9) can be expressed as

$$\begin{aligned} \cos\gamma(t) &= \mu(0) \cdot \mu(t) / \mu^2 \\ &= \cos\theta_0 \cos\theta(t) \\ &\quad + \sin\theta_0 \sin\theta(t) \cos\{\varphi_0 - \varphi(t)\} , \end{aligned} \quad (3.1)$$

where  $\theta_0$  and  $\theta(t)$  are the values of the angle  $\theta$  at times 0 and  $t$ , respectively, and the quadrupole tensor has been neglected. The  $\cos\gamma(t)$  is invariant under an arbitrary rotation of the molecule about the axis of the constant angular momentum, which we assume to coincide with the  $z$  axis in Fig. 1. This circumstance has allowed us to assume  $\varphi_0 = 0$  with generality. On the other hand, the initial angles  $\theta_0$  and  $\psi_0$  can assume any value between 0 and  $\pi$  and between 0 and  $2\pi$ , respectively. We only evaluate Eq. (2.9) in the  $q \rightarrow 0$  limit, which is relevant to the calculation of the refractive index in the suboptical frequency region.

We start from the observation that

$$\cos\theta(t) = I_3 \Omega(t) / L , \quad (3.2)$$

where  $\Omega_3$  is the component of the angular velocity along the water dipole axis and  $L$  is the magnitude of the angular momentum. The other angles are also expressed by means of the angular velocity components [21,22]

$$\tan\psi(t) = I_1 \Omega_1(t) / I_2 \Omega_2(t) , \quad (3.3)$$

$$\begin{aligned} d\varphi/dt &= (\Omega_1 \sin\varphi + \Omega_2 \cos\varphi) / \sin\theta \\ &= L(I_1 \Omega_1^2 + I_2 \Omega_2^2) / (I_1^2 \Omega_1^2 + I_2^2 \Omega_2^2). \end{aligned} \quad (3.4)$$

We can express  $\Omega_1$  and  $\Omega_2$  in terms of  $\Omega_3$  as

$$\begin{aligned} \Omega_1^2 &= \{L^2 - 2EI_2 - I_3(I_3 - I_2)\Omega_3^2\} / I_1(I_1 - I_2), \\ \Omega_2^2 &= \{2EI_1 - L^2 - I_3(I_1 - I_3)\Omega_3^2\} / I_2(I_1 - I_2). \end{aligned} \quad (3.5)$$

The rotational kinetic energy  $E$  can be expressed in the simple form

$$E = (L^2/2I_3)f(\theta_0, \psi_0). \quad (3.6)$$

$f(\theta, \psi)$  is a dimensionless function of the initial angles which is defined by

$$\begin{aligned} f(\theta_0, \psi_0) &= (I_3/I_1)\sin^2\theta_0\sin^2\psi_0 \\ &\quad + (I_3/I_2)\sin^2\theta_0\cos^2\psi_0 + \cos^2\theta_0, \end{aligned} \quad (3.7)$$

where  $0 \leq \theta_0 \leq \pi$  and  $0 \leq \psi_0 \leq 2\pi$ .

Now, we can calculate the angular velocity component  $\Omega_3$  from the torque free Euler equation of motion [21,22], that is,  $d\Omega_3/dt = \Omega_1\Omega_2(I_1 - I_2)/I_3$ . Introducing dimensionless variables for time and angular velocity components as

$$\begin{aligned} u &= (L/I_3)t, \quad v_i = (I_3/L)\Omega_i, \\ \alpha &= I_2/I_3 \quad (I_1/I_3 = 1 + \alpha), \end{aligned} \quad (3.8)$$

then Eq. (3.5) becomes

$$\begin{aligned} v_1^2 &= \{1 - \alpha f - (1 - \alpha)v_3^2\} / (1 + \alpha), \\ v_2^2 &= \{(1 + \alpha)f - 1 - \alpha v_3^2\} / \alpha. \end{aligned} \quad (3.9)$$

Depending on the initial conditions, Euler's equation of motion of  $\Omega_3(t)$  in dimensionless variables  $dv_3/du = v_1(u)v_2(u)$  becomes the following elliptic integral: (i) when  $f(\theta_0, \psi_0) \geq 1$ ,

$$\frac{d}{du} \left[ \frac{v_3}{A_3} \right] = b \left[ 1 - \left[ \frac{v_3}{A_3} \right]^2 \right]^{1/2} \left[ 1 - m \left[ \frac{v_3}{A_3} \right]^2 \right]^{1/2}, \quad (3.10)$$

where  $A_3$  and  $m$  ( $0 \leq m \leq 1$ ) are the amplitude and modulus of the above Jacobi elliptic functions [22] given by

$$\begin{aligned} A_3 &= [(1 - \alpha f) / (1 - \alpha)]^{1/2}, \\ m(\theta_0, \psi_0) &= \alpha(1 - \alpha f) / [(1 - \alpha)\{(1 + \alpha)f - 1\}]. \end{aligned} \quad (3.11a)$$

$b$  is a constant and related to the periodicity of the  $v_i$  given by

$$b(\theta_0, \psi_0) = [(1 - \alpha)\{(1 + \alpha)f - 1\} / \{\alpha(1 + \alpha)\}]^{1/2}. \quad (3.11b)$$

Then, from the solution of Eq. (3.10),

$$v_3(u) = A_3 \operatorname{sn}(bu + C, m), \quad (3.12a)$$

where the constants appearing in this expression are determined by initial conditions as follows:  $\operatorname{sn}(C, m) = \cos\theta_0/A_3$ . With the help of Eq. (3.9) we obtain the other two angular velocities in the following form: (ii) when  $f(\theta_0, \psi_0) < 1$ ,

$$\begin{aligned} v_1(u) &= A_1 \operatorname{cn}(bu + C, m), \\ \text{where } A_1 &= [(1 - \alpha f) / (1 + \alpha)]^{1/2}, \end{aligned} \quad (3.12b)$$

$$\begin{aligned} v_2(u) &= A_2 \operatorname{dn}(bu + C, m), \\ \text{where } A_2 &= [\{(1 + \alpha)f - 1\} / \alpha]^{1/2}. \end{aligned}$$

Define  $m'$  and  $b'$  such as

$$m'(\theta_0, \psi_0) = 1/m(\theta_0, \psi_0), \quad (3.13a)$$

$$b'(\theta_0, \psi_0) = [(1 - \alpha f) / (1 + \alpha)]^{1/2}. \quad (3.13b)$$

By the same procedure we calculate the other case of the solution. Then the three components of the angular velocities are

$$\begin{aligned} v_1(u) &= A_1 \operatorname{dn}(b'u + C', m'), \\ v_2(u) &= A_2 \operatorname{cn}(b'u + C', m'), \\ v_3(u) &= A_2 \operatorname{sn}(b'u + C', m'), \end{aligned} \quad (3.14)$$

with  $\operatorname{sn}(C', m) = \cos\theta_0/A_2$ .

The angular velocity components  $v_i(u)$  are periodic functions of dimensionless time  $u$  and the period is given by  $4K(m)/b$  [22], where  $K(m)$  is a complete elliptic integral of the first kind [23]. Similarly,  $\varphi(u)$  in Eq. (3.4) is obtained as an integral form

$$\varphi(u) = \int_0^u dx \frac{(1 + \alpha)v_1(x)^2 + \alpha v_2(x)^2}{(1 + \alpha)^2 v_1(x)^2 + \alpha^2 v_2(x)^2}. \quad (3.15)$$

We now have all the elements to calculate  $\cos\gamma(t)$  in Eq. (3.1) and obtain the self-part of the van Hove function  $G_s(\omega)$  in Eq. (2.9), the self-electric susceptibility  $\chi_s(\omega)$  in Eqs. (2.5) and (2.6), and the dielectric function of water  $\epsilon(\omega)$  from Eq. (2.2). From Eq. (2.9) the self-part of the van Hove function is directly related to the Laplace transform of the time correlation function of the dipoles, i.e.,

$$G_s(\omega + i/\tau) = \frac{I_3}{Z} \int_0^\infty du \exp \left\{ i(\omega + i/\tau) \frac{I_3 u}{L} \right\} \int_0^\pi d\theta_0 \sin\theta_0 \int_0^{2\pi} d\psi_0 \int_0^\infty dL L \exp \left[ \frac{-\beta f L^2}{2I_3} \right] \cos\gamma(u), \quad (3.16)$$

where  $t$  has been replaced by the dimensionless variable  $u$ . The partition function of the system  $Z$  is easily calculated and equals  $Z = (2\pi I_3/\beta)^{3/2} \{\alpha(1+\alpha)\}^{1/2}$ . Unfortunately, an analytic form of the Laplace transforms of the Jacobi elliptic functions does not exist [24]. Therefore, we proceed in the following manner. First, we define a complex function  $\Phi(z)$

$$\begin{aligned} \Phi(z) &= \int_0^\infty dx x \exp\left[-x^2 - \frac{z}{x}\right] \\ &= \int_0^\infty dy y^{-3} \exp\left[-\frac{1}{y^2} - zy\right]. \end{aligned} \quad (3.17)$$

This function is defined for a complex variable  $z$  satisfying the condition  $z = z' - iz''$ , where  $z' \geq 0$  and  $z'' \geq 0$ . The real and imaginary parts of this formula for the special case  $z = re^{-i\theta}$  with  $\theta = \pi/4$  and  $\pi/2$  are plotted versus  $r$  in Fig. 3. Then the result of the integration over  $L$  in Eq. (3.16) can be expressed as

$$\int_0^\infty dL L \exp\left\{\frac{-\beta f L^2}{2I_3} - (1/\tau - i\omega) \frac{I_3 u}{L}\right\} = \frac{2I_3}{\beta f} \Phi(z), \quad (3.18)$$

where  $z = (f/2)(u/\bar{\tau} - i\bar{\omega}u)$ ,  $\bar{\tau} = \tau/(\beta I_3)^{1/2}$ , and  $\bar{\omega} = (\beta I_3)^{1/2}\omega$ .  $f$  was defined in Eq. (3.7).

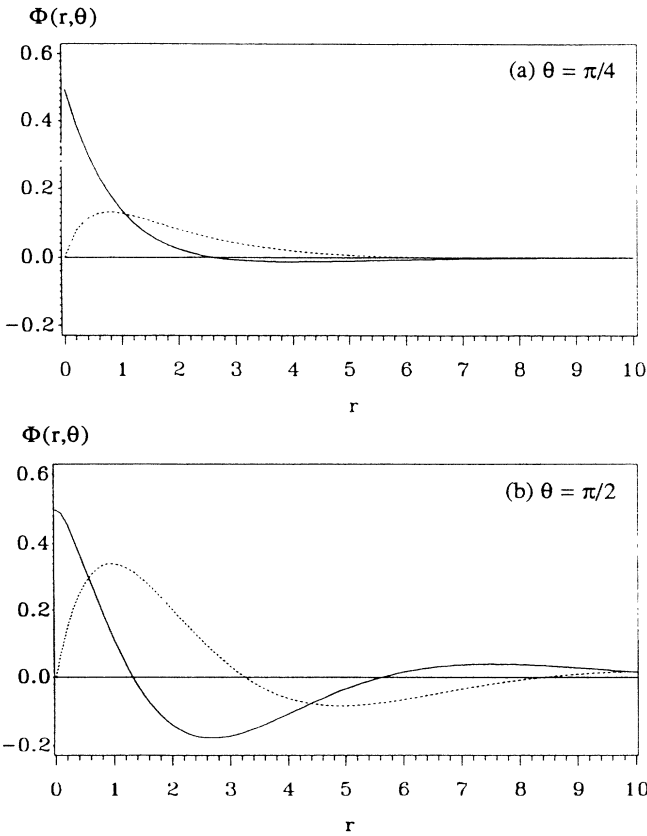


FIG. 3. The real and imaginary parts of the special function  $\Phi(z) = \Phi(r, \theta)$ ,  $z = re^{-i\theta}$ , as a function of  $r$  for (a)  $\theta = \pi/4$  and (b)  $\theta = \pi/2$ .

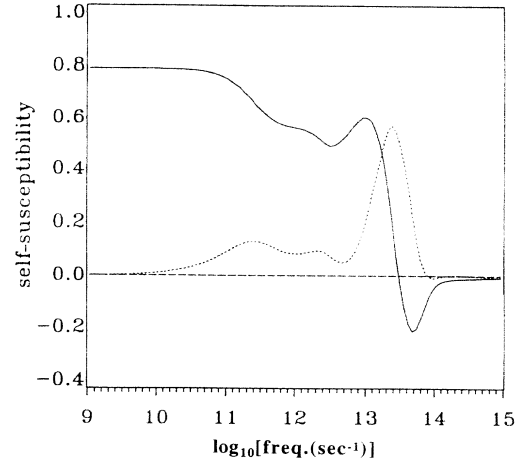


FIG. 4. The real and imaginary parts of the self-electric susceptibility  $\chi_s(\omega)$  in Eq. (2.5) are plotted at the wave vector  $\mathbf{q} \rightarrow \mathbf{0}$ . The solid line is the real part and the dotted line is the imaginary part of  $\chi_s(\omega)$ .

Finally, the self-part of the van Hove function in Eq. (3.16) takes the dimensionless form

$$\begin{aligned} \frac{G_s(\omega + i/\tau)}{\sqrt{\beta I_3}} &= \frac{2}{\bar{Z}} \int_0^\pi d\theta_0 \sin\theta_0 \int_0^{2\pi} d\psi_0 \frac{1}{f(\theta_0, \psi_0)} \\ &\quad \times \int_0^\infty du \cos\gamma(u) \Phi(z), \end{aligned} \quad (3.19)$$

where  $\bar{Z} = Z/(I_3/\beta)^{3/2}$ . The remaining three-dimensional integral is done numerically. We first do the time integral ( $u$  integral) for different values of the angular initial conditions. Then we average over the angular initial conditions. The whole procedure is rather time consuming.

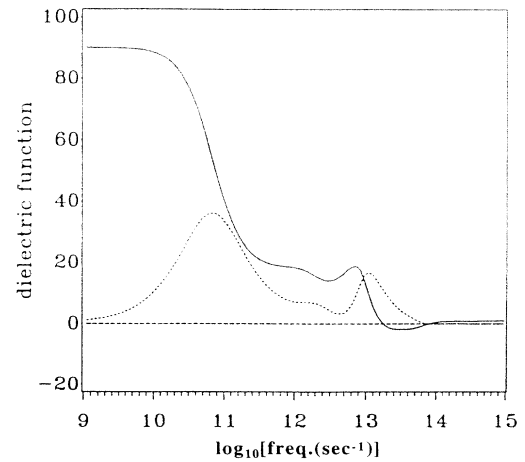


FIG. 5. The plot of the frequency dependent dielectric function at the wave vector  $\mathbf{q} \rightarrow \mathbf{0}$  is shown. The solid line is the real part and the dotted line is the imaginary part.

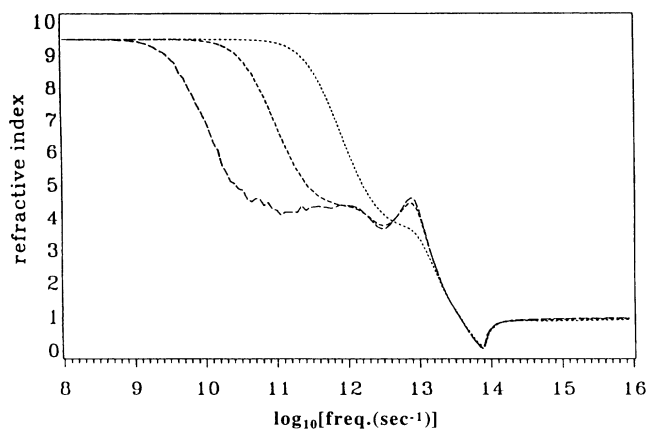


FIG. 6. The refractive index of water with three different values of the relaxation times. From left to right, the relaxation times are  $10\tau$  (some computational noise is shown in the low frequency region),  $\tau$ , and  $1/10\tau$ .

#### IV. RESULTS AND DISCUSSION

The real and imaginary parts of the self-electric susceptibility  $\chi_s(\omega)$  in Eq. (2.5) are plotted in Fig. 4. At lower frequencies the diffusion dominates and at higher frequencies the sign of the response changes. We identify a small peak between these two regions. This is a new structure which was not present in our previous calculations with symmetric molecules. A plot of the frequency dependent dielectric function is shown in Fig. 5. We see that the imaginary part of the dielectric function  $\epsilon(\omega)$  has two well resolved peaks in the low and the high frequency region and one small peak in the intermediate frequency region. The low frequency peak is the diffusion peak found in Debye theory [1] and the high frequency peak is the free-rotor peak also found in our previous paper [15(a)]. The high frequency peak is located at the characteristic precessional frequency of the free molecules in thermal equilibrium  $\langle d\phi/dt \rangle$ . The intermediate peak is an interesting feature of the present theory and is entirely due to the asymmetry of the inertia tensor.

The refractive index of water is obtained from the dielectric function by  $n(\omega) \approx \{\epsilon(\omega)\}^{1/2}$ . We show the dependence of our result on different values of the single parameter appearing in our theory, the relaxation time  $\tau$ . Figure 6 shows the refractive index of water for three different values of the relaxation times. In Fig. 7 we compared our refractive index with available experimental

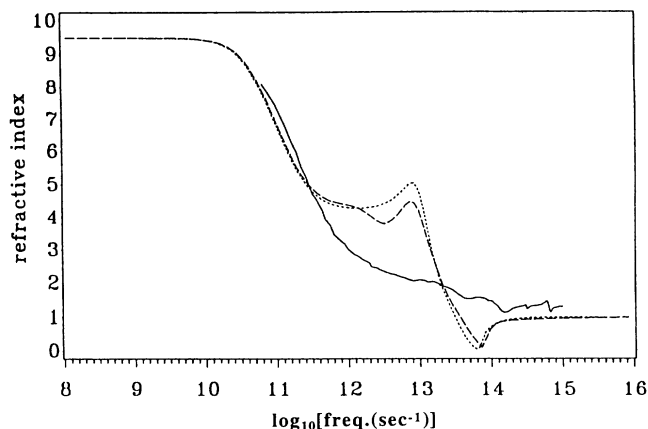


FIG. 7. Comparison of the refractive index of water with that of the symmetric and asymmetric models. The solid line is the experimental data measured from liquid water, the short dashed line is the results of the previous symmetric model, and the long dashed line is the results of the present asymmetric model.

data of water [17,18] and previous results of the symmetric model. The free-rotor peak in the infrared frequency region is lowered and the collective excitation slightly weakened. Therefore, the refractive index of water is in slightly better agreement with experiment. Again, we find an additional structure of the dielectric function. Neither the intermediate frequency peak nor the collective dipolaron mode has yet been experimentally observed. This may be due to the scarcity of experiments in the correct frequency regions, but it could arise from missing infrared physics in this model. It is true that 0.1–1 mm wavelengths are a particularly difficult part of the electromagnetic spectrum to measure, but the importance of understanding the structure of water should justify these additional efforts. There may also be some short range order in the liquid which complicates or even invalidates the local field factor. The fact that water has an intrinsic rotational instability, which should produce chaotic motions, merits additional study and more research is required to determine these issues and to obtain improved agreement with experiment.

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$$K(m) = \int_0^1 ds / \sqrt{(1-s^2)\sqrt{(1-ms^2)}} \\ = \int_0^{\pi/2} du / \sqrt{(1-m \sin^2 u)} .$$
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