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Refractive index of waterlike fluids

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The refractive index of a waterlike fluid is calculated from a frequency- and wave-vector-dependent dielectric function. This model for the dielectric function of waterlike fluids as symmetric rotors is formulated in terms of the self-part of the dipole-dipole correlation function and a static, wave-vector-dependent local-field factor. The dielectric response of the waterlike fluids has been generalized to take into account the vibrational degree of freedom of the atoms. We calculate the refractive index of waterlike fluids at the microwave-, infrared-, and optical-frequency region and compare it to the available experimental data.

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I. INTRODUCTION

Water is the most common liquid on Earth. Its properties are anomalous, including the index of refraction. The propagation, absorption, and reflection of light in water all pose scientific and practical problems, which require accurate knowledge of the refractive index for their solutions. The refractive index of liquid water [1–7] under atmospheric pressure has been measured by many researchers at room temperature repeatedly for well over a century. In spite of all of this study, problems and ambiguities remain. Among the information accumulated over the years on the wavelength-, temperature-, and pressure-dependence of the refractive index, we are interested in the frequency dependence, which is the least well understood property. The main structure of water-molecular fluids are dominated by the infrared- and lower-frequency range of refractive index.

Recently, we published a paper on the wave-vector- and frequency-dependent dielectric function of waterlike fluids [8], where we developed a theory of dynamical dielectric response. The dielectric function of waterlike fluids was expressed in terms of the self-part of the dipole-dipole correlation function and a static wave-vector-dependent local-field factor. The self-correlation function was calculated in a number-conserving relaxation-time approximation [8] which correctly interpolates between diffusive behavior at low frequency and free-particle behavior at high frequency. The local-field factor was obtained by matching the static limit of the dielectric function to the one obtained by a reference hypernetted-chain approximation in Ref. [9]. The resulting behavior of the dielectric function was compared with the ones obtained in previous theoretical calculations [10] and with available experimental data for water. The refractive index of the waterlike fluids at frequencies up to the microwave-frequency range was found to be dominated by diffusive behavior. The refractive index showed a single "free-rotation" peak because it was a symmetric rotor, and the longitudinal dielectric function exhibited a collective resonance.

In this Brief Report our previous theory for the dielectric response of the waterlike fluids is generalized to take into account the vibrational degree of freedom of the atoms which are experimentally measured. The effects of these corrections on the free rotor peak which was obtained in Ref. [8] is studied and the comparison of the refractive index of the waterlike fluids with experimental data is extended to higher frequencies. Then we interpret the refractive index of liquid water in terms of our waterlike fluid idealization.

The starting point is a collection of highly idealized molecules, here symmetric rotors with a number of electric multipoles built into them to produce their mutual pairwise interactions. Each molecule vibrates with small amplitude so it can be considered as almost rigid. Generally, the frequency- and wave-vector-dependent dielectric function has a tensor form, but we only consider the dipole interaction. Therefore the system interacts with each other via a permanent electric dipole moment μ parallel to the symmetry axis and a hard-core contact repulsion. The value of μ is taken to be equal to the dipole moment of an isolated water molecule. The values of the moments of inertia (parallel and perpendicular to the symmetry axis, respectively) are selected to approximate the behavior of a water molecule in Fig. 1. We consider only linear small oscillation between one oxygen atom and two hydrogen atoms, for simplicity. Three normal-mode frequencies were measured by Walrafen

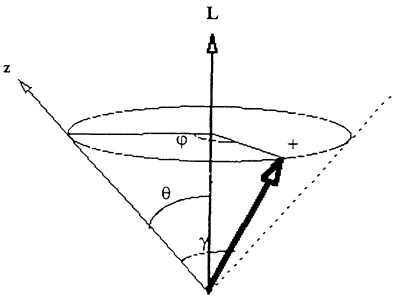

FIG. 1. A waterlike molecule. The torque-free symmetric rotor of the symmetric waterlike molecular has angular momentum **L**, and the rotor axis precesses around the **L** axis with uniform angular velocity L/I_1.

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[11] and we study the three frequencies for the symmetric waterlike molecule model.

II. THEORY

From the usual macroscopic electromagnetic equation [9] we obtain the dielectric function ϵ as a function of the dynamic electric susceptibility χ.

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

The real part of the refractive index is expressed as $n(\omega)\cong\mathrm{Re}\sqrt{\epsilon(\omega)}$ for a nonmagnetic material such as water. There are two components of the dielectric tensor; one parallel to the wave vector of the applied field $\mathbf{q}$, and the other perpendicular to the wave vector $\mathbf{q}$. In the $q\rightarrow 0$ limit the difference between parallel and perpendicular components vanishes.

A linear response in mean-field theory is obtained by assuming that the system responds as a collection of noninteracting particles to an effective potential which includes the effects of interactions of a molecule with all other molecules. Once the static properties are calculated, the dynamical correlation functions are constructed by means of the Kerr approximation [12]. Therefore in the linear response one assumes that

$$\chi(\omega)=\frac{\chi_S(\omega)}{1-\Psi\chi_S(\omega)} . \tag{2}$$

$\chi_s(\omega)$ is the self-part of the electric susceptibility $\chi(\omega)$, or single-dipole response. The local-field factor Ψ includes all the frequency-independent coherent effects of all of the other dipoles and it is determined from the static dielectric function $\epsilon(0)$ only. Notice that a more general mean-field ansatz consists in taking Ψ to be frequency dependent. In addition, Ψ includes the local-field correction to the average interaction

$$\chi_s(\omega)=\chi_s(0)\{1+i\omega G_s(\omega)\} , \tag{3}$$

where $\chi_s(0)$ is $\chi_s^0(0)$, the noninteracting self-response, because collisions do not affect the static response. The static mean field Ψ is completely determined by the static limit of the linear-response function.

$$\Psi=\{\chi_s(0)\}^{-1}-\{\chi(0)\}^{-1} , \tag{4}$$

where $\chi_s(0)=\rho\beta\mu^2/3$. ρ is the particle density and $\beta=1/k_BT$.

The self-correlation function χ_s is calculated in a number-conserving relaxation-time approximation [8] which correctly interpolates between diffusive behavior at low frequency and free-particle behavior at high frequency:

$$\chi_s(\omega)=\frac{\left[\omega+\frac{i}{\tau}\right]\chi_s^0\left[\omega+\frac{i}{\tau}\right]}{\omega+\frac{i}{\tau}\frac{\chi_s^0\left[\omega+\frac{i}{\tau}\right]}{\chi_s^0(0)}} . \tag{5}$$

If we use $\chi_s^0(\omega+i/\tau)$ instead of Eq. (5) for $\chi_s(\omega)$, it fails to conserve local particle number density. The result in Eq. (5) corresponds with that of the electron-gas model [13]. The evaluation of Eq. (5) requires only a knowledge of the noninteracting response function χ_s^0, which is obtained from the self-part of the Van Hove function G_s,

$$\chi_s^0(\omega)=\chi_s^0(0)\left[1+i\omega\int_0^\infty dt\, G_s(t)e^{i\omega t}\right] , \tag{6}$$

where $G(t)=\langle\mu(0)\mu(t)\rangle/\mu^2$, and $\langle\ \rangle$ is the statistical average in the absence of applied fields.

The Fourier transforms of the vibrational terms by three normal-mode frequencies are given by some simple shifts of the frequencies of the nonvibrational terms. They are added to Eq. (6) to give the complete form of $\chi_s^0(\omega+i/\tau)$ in Eq. (5) (see the Appendix and Ref. [8] for the details of the calculation).

III. INTERPRETATION

The refractive index of waterlike fluids is plotted and compared to the experimental data in Fig. 2. We reproduced the first drop A' of real water fluids due to diffusion effects in Fig. 2. A phenomenological description for A was given by Debye [14] early in this century. His theory described the microwave frequency falloff of the dielectric function, but was essentially frequency independent and was much too large at all higher frequencies. Thus in his theory water would appear as dark and cloudy to infrared and visible light.

Here again, our results B' show the free-particle peak at the characteristic precessional frequency of the waterlike symmetric rotor. We interpret this peak as a consequence of the renormalized free-rotor behavior among interacting water molecules. Then B_1 is a torque-free precession of a water molecule. This measurement has been carried out by Simpson, Bean, and Perkowitz [4] at the temperature 25 °C, which will be called a "precession" peak. But there should be another rotation peak B_2 coming from asymmetrical rotation effects of the real water molecule, called a "nutation" peak. In the asymmetric

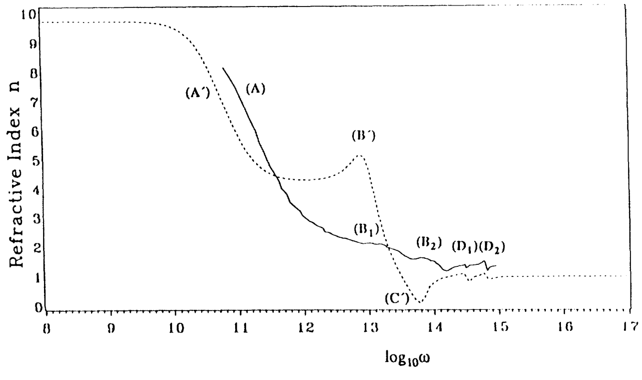

FIG. 2. The real parts of the refractive index of water and waterlike fluids. The solid line is the experimental results measured from liquid water. The dotted line is the results of the theoretical waterlike fluids from Ref. [8] and some additions of higher frequencies described here.

model now under study, we find that the single free rotor peak B' splits into two peaks B_1 and B_2.

At frequencies just above the free-particle peak, we observe a rapid drop in Fig. 2. The most interesting feature of these curves is the sharp resonance C that occurs at a single wave-vector-dependent value of the frequency $\Omega_q=(7-8)\times 10^{13}$ sec^{-1}. The physical meaning of this resonance is that the system supports a long-lived collective excitation at the frequency Ω_q in the longitudinal tensor component of $\epsilon(\mathbf{q},\omega)$. The present excitation is the exact analog of the plasmon in the charged one-component classical plasma. In the present case, we call it a "dipolaron," because it includes long-range oscillations of electric dipoles. These were first discussed by Lobo and co-workers [15] and the possibility of this collective excitation was first convincingly demonstrated by Pollock and Alder [16] in their molecular-dynamics study of the Stockmayer fluid. Our results show that this collective mode exists in symmetric rotor models. Such excitations are outside of the validity of the previous hydrodynamics-based theories [10,17]. We expect that in the asymmetric model the collective excitation may disappear or be strongly reduced. However, since the collective dipolaron depends on $\mathbf{q}$ dispersion, which cannot be measured through the traditional capacitance-bridge techniques used to measure $\epsilon(\omega)$, it follows that a new light- or neutron-scattering measurement will be required to test this feature of our theory.

The spectral line D_1 in Fig. 3(a) arises from a bending normal-mode oscillation which was measured independently, called a "bending" peak. The peak D_2 comes from a superposition of the two other normal-mode oscillations; asymmetric and symmetric stretching in Fig. 3(b), called a "stretching" peak. Actually, it is two peaks which are unresolved at this accuracy. These are simple harmonic oscillations originating from small-amplitude normal-mode oscillations.

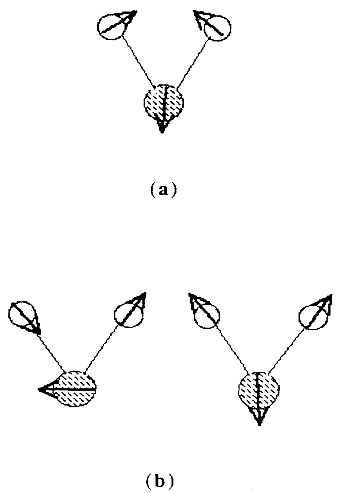

FIG. 3. The vibrational motion of the three normal-mode frequencies. At the high-infrared- and optical-frequency region, the structure of the refractive index contains peaks due to vibrations. These were measured independently in Ref. [11].

We have applied a simplified model to the calculation of the dielectric response of a waterlike fluid of symmetric rotors carrying a permanent electric dipole moment and vibrating with three normal-model frequencies. Although we studied the symmetric waterlike molecule, we could explain all of the major peaks and valleys in the data of the asymmetric water molecule successfully. Of course, the asymmetric calculation of the waterlike molecule is more realistic, but the calculation requires Jacobi elliptic functions which are much more complicated. In the future we will report on the refractive index of the more general asymmetric water model of liquid water.

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APPENDIX

The water molecule has mass $M\approx 18m_{\mathrm{H}}$ and three different moments of inertia, $J_1=0.6127m_{\mathrm{H}}\,\text{Å}^2$, $J_2=1.1477m_{\mathrm{H}}\,\text{Å}^2$, and $J_3=1.7160m_{\mathrm{H}}\,\text{Å}^2$ [18], where m_{H} is the hydrogen mass. Our model is a three-dimensional, almost rigid, symmetrical rotor with moments of inertia $I_3=J_2$ and $I_1=I_2=(J_1+J_3)/2$. We assume only one relaxation time τ as the measured relaxation time of water at 25° C, $\tau=8.46\times 10^{12}$ sec [19].

The motion of the single waterlike molecule in Fig. 1 is composed of a free precession at $\dot{\varphi}=L/I_1$, around the direction of the angular momentum $\mathbf{L}$, and a uniform translation of the center of mass $\dot{\mathbf{r}}=\mathbf{P}/M$. Assuming that, at time $t=0$, the molecule is at the origin with the 3-axis pointing up along the $\hat{\mathbf{z}}$ direction, the time evolution of the angle γ between the principal axis of the molecule and the $\hat{\mathbf{z}}$ axis is given by $\cos\gamma(t)=\cos^2\theta_L+\sin^2\theta_L\cos[\varphi(t)]$, where θ_L is the angle between the angular momentum axis and the $\hat{\mathbf{z}}$ axis, and the angle φ is defined in Fig. 1.

The thermal statistical average of the noninteracting Van Hove function without vibration is given by

$$\langle P_1(\cos[\gamma(t)])\rangle=H(t)\ , \tag{A1}$$

where $P_1(\cos[\gamma(t)])$ is the Legendre polynomial. This is calculated by integrating over all possible values of $\mathbf{L}$ at time $t=0$ with Boltzmann weight $e^{-\beta T}/Z$, where Z is the partition function. We use Eq. (6) to calculate G_s in the present work.

Let $\mu(t)=ez(t)\cos[\theta(t)]$ and $z_i(t)=z_0+\eta_i(t)$, where $z(t)$ is the distance between oxygen and hydrogen atoms. $\theta(0)=0$, $\theta(t)=\gamma(t)$, and $\mu_0=ez_0$. Therefore

$$\begin{aligned}G_s(t)&=\langle\mu(0)\mu(t)\rangle\\&=\langle\cos[\gamma(t)]\rangle\left[1+\tfrac{1}{3}\sum_{i=1}^{3}[\langle\eta_i(0)\rangle\cos(\omega_i t)]/z_0^2\right]\ .\end{aligned} \tag{A2}$$

The three normal-mode frequencies [11] are $\omega_1 = 6.50\times 10^{14}\ \text{sec}^{-1}$, $\omega_2 = 3.09\times 10^{14}\ \text{sec}^{-1}$, and $\omega_3 = 6.81\times 10^{14}\ \text{sec}^{-1}$. From the quantum-mechanical calculation of the small oscillation $\langle [\eta_i(0)]^2\rangle = \hbar/2m\omega_i$, where m is the reduced mass of the system, $16m_{\text{H}}/9$. The self-part of the Van Hove correlation function including the vibrational effect is

$$G_s(\omega+i/\tau) = H(\omega+i/\tau) + \left[\frac{1}{3z_0^2}\right]\sum_{i=1}^{3}\langle[\eta_i(0)]^2\rangle[H(\omega+\omega_i+i/\tau)+H(\omega-\omega_i+i/\tau)]/2 \ . \tag{A3}$$

The other calculations are identical with the steps shown in Ref. [8].

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