Long-range orientation correlation in dipolar liquids probed by hyper-Rayleigh scattering

David P. Shelton[a)]

Department of Physics and Astronomy, University of Nevada, Las Vegas, Nevada 89154-4002, USA

Hyper-Rayleigh scattering (HRS) is sensitive to long-range molecular orientation correlation in isotropic liquids composed of dipolar molecules. The correlation functions that appear in the calculation of HRS mediated by the vector part of the first hyperpolarizability β are the same as the correlation functions for the homogeneous isotropic random vector fields that appear in the description of fluid turbulence. Recent experiments measuring the angle and polarization dependence of HRS from water find a dominant transverse mode contribution with amplitude independent of the scattering wavevector, and this observation of transverse mode HRS strongly constrains the form of the orientation correlation function. Analysis of these HRS results for water determines that the long-range molecular orientation correlation function varies as $r^{-3\pm\varepsilon}$ with $|\varepsilon| < 0.03$ on spatial scales up to 2000 nm. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4931973]

I. INTRODUCTION

The defining structural feature of liquids is their lack of long-range positional order. Although it has long been understood that liquids exhibit local structure related to the shape of the molecules and short-range steric effects,[1–4] it is generally assumed that the intermolecular correlations in liquids extend at most a few molecular diameters, and that liquids are macroscopically homogeneous, isotropic, and random. However, evidence for molecular orientation correlations in water at spatial scales up to 2000 nm has been found in recent experiments measuring the angle and polarization dependence of second-harmonic or hyper-Rayleigh light scattering (HRS).[5] The work presented below explains the relationship between HRS and molecular orientation correlation in dipolar liquids and analyzes the HRS data for water to obtain information about the form of the long-range orientation correlation.

HRS mediated by the third-rank molecular hyperpolarizability β is light radiated at the second-harmonic frequency by the induced dipole[6,7]

$$\mu_i^{(2\omega)} = \frac{1}{2}\beta_{ijk}(-2\omega;\omega,\omega)E_j^{(\omega)}E_k^{(\omega)}. \quad (1)$$

HRS probes non-centrosymmetric fluctuations such as orientation fluctuations of polar molecules. The recent HRS measurements for water were made with linearly polarized light at scattering angles in the range from 0° to 180°, for configurations with incident and scattered light polarized either perpendicular or parallel to the horizontal scattering plane.[5] These configurations are denoted VV, HV, VH, and HH, where V denotes vertical polarization, H denotes horizontal polarization, and the first and second letters refer to the incident and scattered light, respectively. Long-range molecular correlations are revealed in these experiments by the observation $I_{HV} \neq I_{VH}$ for the HRS intensities. The intensities I_{HV} and I_{VH} are equal by symmetry for scattering from isotropic liquids when only short-range correlations exist between the molecules, but this symmetry can be broken when long-range correlations are present.

II. INCOHERENT HRS

The third rank Cartesian molecular hyperpolarizability tensor $\beta_{ijk}(-2\omega;\omega,\omega)$ for second-harmonic scattering is symmetric in the last two indices j and k since the corresponding applied optical fields are indistinguishable, and far from resonance β also has approximate permutation symmetry in all indices (Kleinman symmetry, which becomes exact in the limit $\omega \to 0$). An alternative expression for β is the direct sum of four irreducible spherical tensors,[6]

$$\beta = \beta^{[ss,1]} \oplus \beta^{[ms,1]} \oplus \beta^{[ms,2]} \oplus \beta^{[ss,3]}, \quad (2)$$

where $\beta_m^{[\nu,l]}$ is a spherical tensor of rank l with $2l+1$ components m, index ν labels the symmetry under permutation of the Cartesian tensor indices (ss is totally symmetric, while ms is non-symmetric for first index permutations), and the mixed symmetry ν = ms tensors vanish when Kleinman symmetry holds.

The HRS intensities for the four polarization configurations of interest, obtained as the incoherent sums for randomly oriented molecules, are[6]

$$I_{VV}/C = \frac{9}{45}\left|\beta^{[ss,1]}\right|^2 + \frac{6}{105}\left|\beta^{[ss,3]}\right|^2, \quad (3a)$$

$$I_{HV}/C = \frac{1}{45}\left|\beta^{[ss,1]}\right|^2 + \frac{2}{9\sqrt{5}}\text{Re}\left(\beta^{[ss,1]}\beta^{[ms,1]*}\right)$$
$$+ \frac{1}{9}\left|\beta^{[ms,1]}\right|^2 + \frac{1}{15}\left|\beta^{[ms,2]}\right|^2 + \frac{4}{105}\left|\beta^{[ss,3]}\right|^2, \quad (3b)$$

$$I_{VH} = I_{HV}, \quad (3c)$$

$$I_{HH} = I_{HV}\sin^2\theta_s + I_{VV}\cos^2\theta_s, \quad (3d)$$

a)shelton@physics.unlv.edu

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where $|\beta^{[v,l]}|^2 = \sum_m |\beta_m^{[v,l]}|^2$, θ_s is the scattering angle, and C includes all incident intensity, sample density, and geometric factors. It is convenient to consider together the β components with $l = 1$ that transform as vectors under rotations, and set $I_{VV}/I_{HV} = R^2$ as the HRS intensity ratio due to just these terms, and $I_{VV}/I_{HV} = P^2$ as the HRS intensity ratio due to just the terms with $l = 2$ and 3. When Kleinman symmetry holds $R^2 = 9$ and $P^2 = 3/2$. Kleinman symmetry breaking will result in a small decrease for P^2, while the change for R^2 will usually be much larger and can be either an increase or decrease depending on the sign of the cross term $\mathrm{Re}\left(\beta^{[ss,1]}\beta^{[ms,1]*}\right)$. The following work will consider orientation correlations which affect the $l = 1$ HRS contribution.

III. VECTOR HRS

The non-vanishing Cartesian components for the pure vector β ($l = 1$ only) are $\beta_{zzz} = \beta_0$, $u\beta_{zzz} = \beta_{zxx} = \beta_{zyy}$, and $v\beta_{zzz} = \beta_{xxz} = \beta_{xzx} = \beta_{yyz} = \beta_{yzy}$, with $u + 2v = 1$. In the case that Kleinman symmetry holds, $u = v = 1/3$. The second harmonic dipole $\vec{\mu}$ induced by the applied optical field $\vec{E}$ for this β tensor is[8]

$$\vec{\mu} = \frac{1}{2}\beta_0 E^2 \left[u\hat{n} + 2v(\hat{n} \cdot \hat{E})\hat{E}\right], \tag{4}$$

where $\hat{n}$ is the unit vector in the direction of the molecular z-axis. The laboratory Cartesian coordinate frame used to evaluate the second harmonic induced dipole components for HRS in the VV, HV, VH, and HH polarization configurations has Z perpendicular to the scattering plane, Y in the direction of the scattering vector $\vec{K} = 2\vec{k}_i - \vec{k}_s$ [with $K \approx 4k_i \sin(\theta_s/2)$], and with X perpendicular to Y and Z. The incident and scattered light directions in this frame are $\hat{k}_i = \cos(\theta_s/2)\hat{X} + \sin(\theta_s/2)\hat{Y}$ and $\hat{k}_s = \cos(\theta_s/2)\hat{X} - \sin(\theta_s/2)\hat{Y}$, respectively. With these coordinates, the unit vectors for the incident and scattered polarizations, and the scattering vector, are

$$\hat{V}_i = \hat{V}_s = \hat{Z}, \tag{5a}$$

$$\hat{H}_i = -\sin(\theta_s/2)\hat{X} + \cos(\theta_s/2)\hat{Y}, \tag{5b}$$

$$\hat{H}_s = \sin(\theta_s/2)\hat{X} + \cos(\theta_s/2)\hat{Y}, \tag{5c}$$

$$\hat{K} = \hat{Y}. \tag{5d}$$

For each incident polarization, projecting Eq. (4) onto the scattered polarization vector gives the relevant dipole component

$$\mu_{VV} = (\frac{1}{2}\beta_0 E^2)\left[u\hat{n} + 2v(\hat{n} \cdot \hat{V}_i)\hat{V}_i\right] \cdot \hat{V}_s$$
$$= (\frac{1}{2}\beta_0 E^2)(\hat{n} \cdot \hat{Z}), \tag{6a}$$

$$\mu_{HV} = (\frac{1}{2}\beta_0 E^2)\left[u\hat{n} + 2v(\hat{n} \cdot \hat{H}_i)\hat{H}_i\right] \cdot \hat{V}_s$$
$$= (\frac{1}{2}\beta_0 E^2)u(\hat{n} \cdot \hat{Z}), \tag{6b}$$

$$\mu_{VH} = (\frac{1}{2}\beta_0 E^2)\left[u\hat{n} + 2v(\hat{n} \cdot \hat{V}_i)\hat{V}_i\right] \cdot \hat{H}_s$$
$$= (\frac{1}{2}\beta_0 E^2)u\left[(\hat{n} \cdot \hat{X})\sin(\theta_s/2) + (\hat{n} \cdot \hat{Y})\cos(\theta_s/2)\right], \tag{6c}$$

$$\mu_{HH} = (\frac{1}{2}\beta_0 E^2)\left[u\hat{n} + 2v(\hat{n} \cdot \hat{H}_i)\hat{H}_i\right] \cdot \hat{H}_s$$
$$= (\frac{1}{2}\beta_0 E^2)u[(\hat{n} \cdot \hat{X})\{1 - (R - 1)\cos\theta_s\}\sin(\theta_s/2)$$
$$+ (\hat{n} \cdot \hat{Y})\{1 + (R - 1)\cos\theta_s\}\cos(\theta_s/2)], \tag{6d}$$

where $R = 1/u$. Summing the contributions from all N molecules a in the sample of number density ρ, the HRS intensities for a representative orientation distribution are

$$I_{VV} = \left|\sum_a \mu_{VV,a}\exp(i\vec{K} \cdot \vec{r}_a)\right|^2$$
$$= (\frac{1}{2}\beta_0 E^2)^2 N\rho \int d^3r \exp(i\vec{K} \cdot \vec{r})\langle n_Z(\vec{0})n_Z(\vec{r})\rangle, \tag{7a}$$

$$I_{HV} = u^2 I_{VV}, \tag{7b}$$

$$I_{VH} = (\frac{1}{2}\beta_0 E^2)^2 u^2 N\rho \int d^3r \exp(i\vec{K} \cdot \vec{r})$$
$$\times [\langle n_X(\vec{0})n_X(\vec{r})\rangle \sin^2(\theta_s/2)$$
$$+ \langle n_X(\vec{0})n_Y(\vec{r})\rangle \sin\theta_s$$
$$+ \langle n_Y(\vec{0})n_Y(\vec{r})\rangle \cos^2(\theta_s/2)], \tag{7c}$$

$$I_{HH} = (\frac{1}{2}\beta_0 E^2)^2 u^2 N\rho \int d^3r \exp(i\vec{K} \cdot \vec{r})$$
$$\times [\langle n_X(\vec{0})n_X(\vec{r})\rangle\{1 - (R - 1)\cos\theta_s\}^2\sin^2(\theta_s/2)$$
$$+ \langle n_X(\vec{0})n_Y(\vec{r})\rangle\{1 - (R - 1)^2\cos^2\theta_s\}\sin\theta_s$$
$$+ \langle n_Y(\vec{0})n_Y(\vec{r})\rangle\{1 + (R - 1)\cos\theta_s\}^2\cos^2(\theta_s/2)]. \tag{7d}$$

The HRS intensities are expressed in terms of correlation functions between molecular orientation vector components parallel (n_Y) and perpendicular (n_X, n_Z) to the scattering vector ($\hat{K} = \hat{Y}$), where, for example, $\langle n_Z(\vec{0})n_Z(\vec{r})\rangle$ is the correlation function for the Z component of the molecular orientation vector. For randomly oriented, uncorrelated molecules, the correlation functions are

$$\langle n_I(\vec{0})n_J(\vec{r})\rangle = \frac{1}{3}\delta_{IJ}\delta(\vec{r}) \tag{8}$$

so the corresponding HRS intensities are $I_{VV} = R^2 I_{HV}$, $I_{VH} = I_{HV}$, and $I_{HH} = I_{HV}\sin^2\theta_s + I_{VV}\cos^2\theta_s$, consistent with Eq. (3).

IV. HOMOGENEOUS ISOTROPIC RANDOM VECTOR FIELDS

The most general correlation function for a homogeneous, isotropic, random scalar field is a function of radial distance r only, but for a homogeneous, isotropic, random vector field $\vec{U}(\vec{r})$ the most general correlation function has the form[9,10]

$$B_{ij}(\vec{r}) = \langle U_i(\vec{0})U_j(\vec{r})\rangle$$
$$= B_T(r)[\delta_{ij} - r_i r_j/r^2] + B_L(r)r_i r_j/r^2, \tag{9}$$

where $r_i r_j/r^2$ is the longitudinal projection operator (onto $\vec{r}$), and where $B_T(0) = B_L(0)$. The tensor B_{ij} is diagonal when one coordinate axis is aligned along $\vec{r}$, with the transverse and longitudinal correlation functions B_T and B_L as the diagonal components. The corresponding spatial spectrum is

$$S_{ij}(\vec{K}) = \int d^3R B_{ij}(\vec{r})\exp(i\vec{K} \cdot \vec{r})$$
$$= S_T(K)[\delta_{ij} - K_i K_j/K^2] + S_L(K)K_i K_j/K^2. \tag{10}$$

The tensor S_{ij} is diagonal when one coordinate axis is aligned along $\vec{K}$, with the transverse and longitudinal spectra S_T and S_L as the diagonal components. For a function $B_{ij}(\vec{r})$ to be a correlation function, the corresponding spectra $S_T(K)$ and $S_L(K)$ must be real and non-negative for all K. The expressions for S_T and S_L obtained by substituting Eq. (9) for $B_{ij}(\vec{r})$ into the integral in Eq. (10), transforming to polar coordinates, and integrating, are

$$S_T(K) = 4\pi \int_0^\infty r^2 dr \left[\left\{ j_0(Kr) - \frac{j_1(Kr)}{Kr} \right\} B_T(R) + \frac{j_1(Kr)}{Kr} B_L(r) \right], \tag{11}$$

$$S_L(K) = 4\pi \int_0^\infty r^2 dr \left[2\frac{j_1(Kr)}{Kr} B_T(r) + \left\{ j_0(Kr) - 2\frac{j_1(Kr)}{Kr} \right\} B_L(r) \right], \tag{12}$$

where $j_n(x)$ are spherical Bessel functions.

An arbitrary isotropic random vector field can be represented as the sum of two uncorrelated isotropic vector fields, one of which is solenoidal (zero divergence) and one of which is potential (zero curl).[9] To obtain a solenoidal field, for which $S_L(K) = 0$, the condition on the correlation function is[9]

$$B_T(r) = B_L(r) + \frac{r}{2} \frac{d}{dr} B_L(r), \tag{13}$$

whereas to obtain a potential field, where $S_T(K) = 0$, the condition is

$$B_L(r) = B_T(r) + r \frac{d}{dr} B_T(r). \tag{14}$$

In the case that the transverse and longitudinal correlation functions are equal,

$$B_T(r) = B_L(r) = B(r), \tag{15}$$

the expression for the spatial spectrum is simply

$$S_T(K) = S_L(K) = S(K) = 4\pi \int_0^\infty r^2 dr\, j_0(Kr) B(r), \tag{16}$$

which is the same as for an isotropic random scalar field.

The spatial spectrum can be sensitive to the distinction between transverse and longitudinal correlations. For example, the short-range scalar correlation function

$$B(r) = \exp(-br) \tag{17}$$

has the spatial spectrum

$$S(K) = 8\pi b/(b^2 + K^2)^2, \tag{18}$$

which decreases as K^{-4} for large K, is nearly constant for small K, and has its maximum value at $K = 0$. The result is different for a solenoidal vector field with exponential short-range correlation. Although the spectrum of this solenoidal field also decreases as K^{-4} for large K, the spectrum varies as K^2 for small K, and vanishes at $K = 0$.

V. HRS FROM ISOTROPIC RANDOM VECTOR FIELDS

The general results for random vector fields can be applied to the molecular orientation correlation functions for vector HRS appearing in Eq. (7). In particular, the off-diagonal correlations vanish for the chosen coordinate system aligned with the scattering vector $\vec{K}$, and the remaining integrals are just the spectra $S_T(K)$ or $S_L(K)$. The vector correlations do not affect the octupolar HRS. The HRS intensities, including the HRS contributions from both the vector and octupolar parts of β, have the form

$$I_{VV} = P^2 A_0 S_0(K) + R^2 A_T S_T(K), \tag{19a}$$

$$I_{HV} = A_0 S_0(K) + A_T S_T(K), \tag{19b}$$

$$I_{VH} = A_0 S_0(K) + A_T S_T(K)\sin^2(\theta_s/2) + A_L S_L(K)\cos^2(\theta_s/2), \tag{19c}$$

$$\begin{aligned} I_{HH} &= A_0 S_0(K)[\sin^2\theta_s + P^2\cos^2\theta_s] \\ &+ A_T S_T(K)\{1 - (R-1)\cos\theta_s\}^2\sin^2(\theta_s/2) \\ &+ A_L S_L(K)\{1 + (R-1)\cos\theta_s\}^2\cos^2(\theta_s/2), \end{aligned} \tag{19d}$$

where A_0 is the octupolar HRS intensity coefficient and A_T, A_L are the vector HRS intensity coefficients. It is assumed that $P^2 = 3/2$ for the octupolar HRS contribution and that any correlations affecting octupolar HRS are short-range and that $S_0(K)$ is a constant function of K. Expressions with the form of Eq. (19) have been used previously in the analysis of HRS data,[5,11,12] but without attention to the spatial spectral functions $S_T(K)$ and $S_L(K)$.

VI. ANALYSIS OF HRS DATA

The recent HRS measurements for water at scattering angles in the range from 0° to 180° were analyzed to obtain results for $A_T S_T(K)$ and $A_L S_L(K)$.[5] Two main results of the experiment are that HRS for water is principally transverse, with $A_T S_T(K)/A_L S_L(K) = 12.0 \pm 0.6$, and the transverse contribution $A_T S_T(K)$ is nearly constant, increasing $3\% \pm 5\%$ over the range $0.1 < K/K_{max} < 1$, where $K_{max} = 0.031$ nm^{-1}. The HRS experimental results indicate that the molecular orientation distribution is a solenoidal isotropic random field with constant transverse spectrum $S_T(K)$ for small K. The transverse HRS spectrum for water is consistent with the correlation function

$$B_L(r) = a^3(a^2 + r^2)^{-3/2}, \tag{20a}$$

$$B_T(r) = a^3(a^2 + r^2)^{-3/2}[1 - (3/2)r^2/(a^2 + r^2)], \tag{20b}$$

which produces the transverse spatial spectrum

$$S_T(K) = 2\pi a^3 K a K_1(Ka), \tag{21a}$$
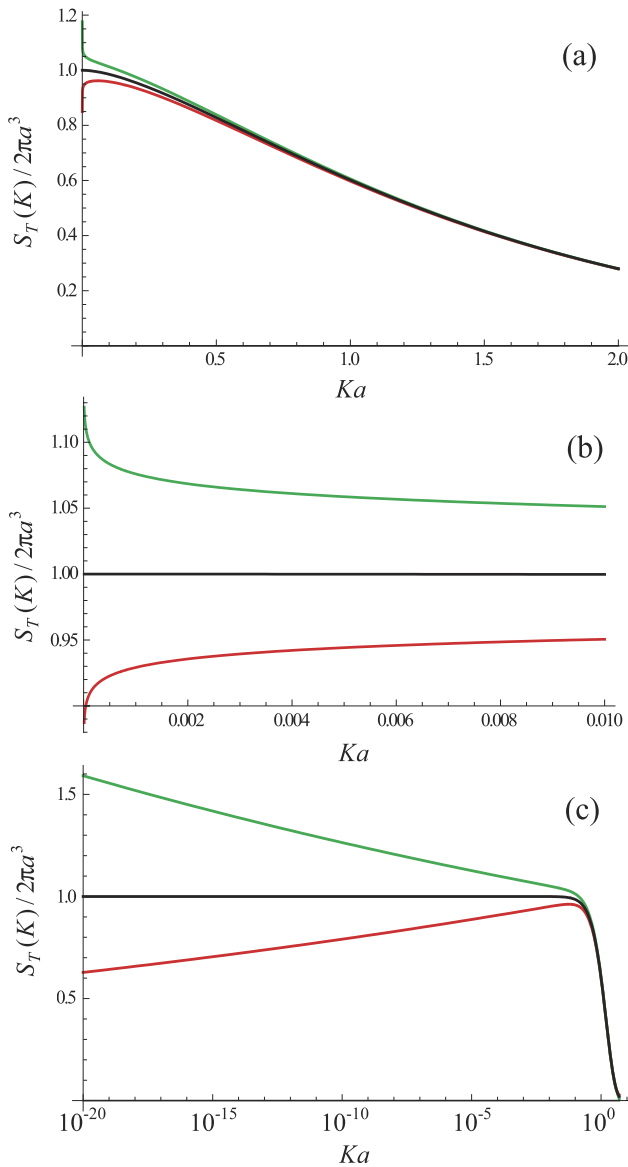
$$S_L(K) = 0, \tag{21b}$$

FIG. 1. Transverse spatial spectra $S_T(K)$ for solenoidal random fields with correlation function $B_L(r) = [1 + (r/a)^2]^{-(3+\varepsilon)/2}$, for $\varepsilon = -0.01$, 0, and $+0.01$ (top, middle, and bottom curves), are plotted (a) over a wide Ka range, (b) over the Ka range of the HRS experiment,[5] and (c) with a logarithmic scale to show the divergence as $Ka \to 0$. The function for $\varepsilon = 0$ is $S_T(K) = 2\pi a^3 Ka K_1(Ka)$.

where $K_n(x)$ is the modified Bessel function of the second kind, of order n. This spectrum S_T is plotted versus Ka in Figure 1. One expects that the correlation functions in Eq. (20) will be near their maximum value for nearest neighbour molecules, so a provisional estimate for the length parameter is $a = 0.28$ nm (the radius of the first peak of the radial pair distribution function for water).[4,13] Choosing this length parameter gives $0.001 < Ka < 0.009$ for the HRS experiment. The variation of $S_T(K)$ given by Eq. (21a) is <0.03% over this range, consistent with the experimental result.

The requirement that the spatial spectrum $S_T(K)$ is non-zero and flat for small K is very restrictive for solenoidal fields. Correlation functions which decrease more rapidly than r^{-3} as $r \to \infty$ give $S_T(K)$ which decreases logarithmically as $K \to 0$, reaching $S_T(K) = 0$ at $K = 0$, while correlation functions decreasing more slowly than r^{-3} as $R \to \infty$ give $S_T(K)$ which

diverges logarithmically as $K \to 0$. The behaviour of $S_T(K)$ is illustrated in Figure 1, which shows the transverse spectra $S_T(K)$ calculated for solenoidal vector fields with correlation functions $B_L(r) = [1 + (r/a)^2]^{-(3+\varepsilon)/2}$, for $\varepsilon = -0.01$, 0, and 0.01, for large and small values of Ka. Bounds on ε can be determined from the flatness of $S_T(K)$ at small Ka. The fractional change $\Delta S_T/S_T$ over the range $0.001 < Ka < 0.009$ (Ka assuming $a = 0.28$ nm) is proportional to ε, where $|\varepsilon| = 0.01$ results in $|\Delta S_T/S_T| = 0.02$ for this Ka range. For small Ka, the logarithmic divergence gives $\Delta S_T/S_T$ proportional to the ratio $(Ka)_{max}/(Ka)_{min}$, so the same fractional change for $S_T(K)$ is obtained using any estimate of the length parameter $a < 1.4$ nm. The structure of water has been studied by x-ray and neutron diffraction measurements[13] and molecular dynamics (MD) simulations,[14,15] and an upper bound $a = 0.24$ nm for the length parameter of the long-range correlation has been estimated from the results for one of the MD simulations for water.[15] Thus, from the HRS experimental result $|\Delta S_T/S_T| < 0.06$ over the observed range for water, one deduces that the orientation correlation function at long range varies as $r^{-3 \pm \varepsilon}$ with $|\varepsilon| < 0.03$.

The finite size of the molecules results in an excluded volume around each molecule, and it is also usual to separate the correlations between different molecules from the self-correlations. Starting with the correlation functions given by Eq. (20), the effect of an excluded volume is introduced by setting $B_L(r) = B_T(r) = 0$ for $0 < r < r_1$, and the self-correlation is accounted for by adding the delta function contribution given by Eq. (8). At $K = 0$, one has

$$S_T(0) = 2\pi \int_0^\infty r^2 dr [B_T(r) + B_L(r)], \qquad (22a)$$

$$S_L(0) = 4\pi \int_0^\infty r^2 dr\, B_T(r). \qquad (22b)$$

The volume integral of the delta function correlation in Eq. (8) is $(1/3)(4\pi r_0^3/3)$, where $4\pi r_0^3/3 = \rho^{-1}$ is the volume per molecule ($r_0 = 0.193$ nm for water). For this model, the values at $K = 0$ for the spatial spectra are

$$S_{T,1}(0) = 2\pi a^3 + \frac{4\pi}{9} r_0^3$$
$$- \pi a^3 \left[\sinh^{-1}(r_1/a) - \frac{a^2 r_1}{(a^2 + r_1^2)^{3/2}} \right], \qquad (23a)$$

$$S_{L,1}(0) = 0 + \frac{4\pi}{9} r_0^3$$
$$+ 2\pi a^3 \left[\sinh^{-1}(r_1/a) - \frac{a^2 r_1 + 2r_1^3}{(a^2 + r_1^2)^{3/2}} \right], \qquad (23b)$$

where the first terms in Eq. (23) are from Eq. (21), the second terms are the result of adding the self-correlation delta functions, and the third terms are the result of introducing the excluded volume. The short-range contributions added to the correlation functions result in a non-zero longitudinal spectrum, and the experimentally observed value $S_T(K)/S_L(K) = 12.0 \pm 0.6$ can be fit by adjusting the value of a in Eq. (23). The result with $r_0 = 0.193$ nm and $r_1 = 0.240$ nm is $a = 0.177$ nm, in agreement with $a \leq 0.24$ nm from a molecular dynamics simulation.[15] The vector VV HRS intensity S_T
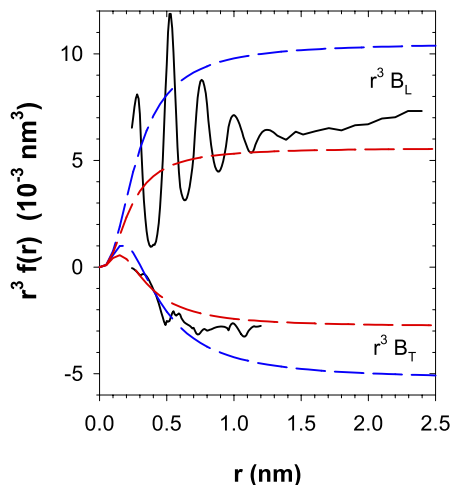
FIG. 2. Longitudinal and transverse orientation correlation functions for water are plotted. The solid curves are from a molecular dynamics simulation (Fig. 2 of Ref. 14), while the dashed curves are from Eqs. (20) for $a = 0.177$ nm (red middle curves) and $a = 0.219$ nm (blue outer curves).

estimated from Eq. (23a) is 3.05 times larger than the intensity $4\pi r_0^3/9$ for uncorrelated molecules.

Figure 2 shows orientation correlation functions obtained from the MD simulation for water in Ref. 14 (at $T = 300$ K, $r \geq 0.24$ nm, from Fig. 2, where $B_L(r) = L(r)$ and $B_T(r) = (1/2)[F(r) - L(r)]$). Correlation functions given by Eq. (20) with $a = 0.177$ nm are also shown in Fig. 2 and fall close to the MD curves, although $B_L(r)$ does not have the large oscillations seen for the MD result. A more realistic model inserts the short-range MD correlation functions for $0 < r < r_1$, between the central delta function and the outer long-range correlation function. For $r_1 = 1.2$ nm, the contributions added to Eq. (23) from the short-range MD correlation functions are $S_{T,2} = -S_{L,2} = 2\pi(0.182 \text{ nm})^3$, and a fit to $S_T/S_L = 12.0$ is obtained for $a = 0.219$ nm. The intensity enhancement is $S_T/(4\pi r_0^3/9) = 3.55$ compared to uncorrelated molecules, with the correlations for $r > 1.2$ nm contributing 52% of the total intensity. Using the MD orientation correlation functions weighted with the radial distribution function $g_{OO}(r)$ for D_2O (from Fig. 3(c) of Ref. 16) gives slightly larger values: $S_{T,2} = 2\pi(0.189 \text{ nm})^3$, $S_{L,2} = -2\pi(0.183 \text{ nm})^3$, $a = 0.226$ nm, and $S_T/(4\pi r_0^3/9) = 4.01$. The correlation functions given by Eq. (20) with $a = 0.219$ nm (or 0.226 nm) fall outside the MD curves shown in Fig. 2. The strength of the long-range correlation was increased to fit the observed S_T/S_L value, compensating for the reduction of S_L by the short-range MD contribution, but this compensation could also be obtained by a departure from pure solenoidal long-range correlations.

VII. RELATION TO MOLECULAR THEORY FOR POLAR LIQUIDS

The theoretical description of the structure of molecular liquids starts with the molecular pair distribution function including translational and orientational degrees of freedom, which may be expanded in terms of radial functions and Wigner rotation matrices, and the goal is to determine the fluid structure and properties from the intermolecular interaction

energy function. The correlation functions for polar fluids will have a long-range part decaying asymptotically as r^{-3} due to the dipole-dipole interaction between the molecules.[4,15] The long-range orientation correlations of the molecular dipoles are related to the dielectric response of polar fluids, with different longitudinal and transverse contributions.[4,17] The orientation correlations appearing in Eq. (7) for the HRS intensities are essentially the same as the correlations $\langle |M_i(\vec{K})|^2 \rangle$ for the dipole moment density $\vec{M}(K) = \mu \sum_a \hat{n}_a \exp(i\vec{K} \cdot \vec{r}_a)$ for a fluid of non-polarizable dipoles, where $\langle |M_i(\vec{K})|^2 \rangle = N\mu^2/3$ for N uncorrelated dipoles. It is argued that for such a fluid, with a large static dielectric constant $\varepsilon(0)$ and no short-range correlations, the transverse and longitudinal dipole correlations for $K \to 0$ are (p. 485 of Ref. 17)

$$\langle |M_T(\vec{K})|^2 \rangle = (3/2)N\mu^2/3, \tag{24a}$$

$$\langle |M_L(\vec{K})|^2 \rangle = \langle |M_T(\vec{K})|^2 \rangle / \varepsilon(0). \tag{24b}$$

These theoretical results for polar liquids are consistent with the HRS results for water. The long-range correlations required to explain the HRS measurements have the same r^{-3} asymptotic dependence as the correlations due to dipole-dipole interactions. The HRS intensity increase due to molecular correlations predicted by Eq. (24a) is a factor of 3/2, as compared to the factor about 3.5 estimated in Sec. VI. And Eq. (24b) predicts $S_T(K)/S_L(K) = 80$ as compared to 12.0 ± 0.6 observed, where the lower observed value can be accounted for by the additional short-range correlations. This qualitative agreement suggests that the orientation correlations explaining the HRS experimental observations are the result of dipole-dipole intermolecular interactions.

This work provides information about long-range orientation correlations that is complementary to the information from other techniques. Local structure and short-range correlations are measured in water using experimental techniques such as x-ray and neutron scattering,[13,16] but these probes are insensitive to long-range orientation correlations. Dipolar orientation correlations at the nm scale have also been found using density functional theory[18] and MD simulations[14,15,19,20] for water, but these simulations cannot directly address the length scale probed by the HRS experiment. Although both HRS and the dielectric response of polar liquids are sensitive to orientation correlations, the polarization and scattering vector dependence for HRS provide additional information not accessible with dielectric measurements.

In summary, the effect of molecular orientation correlation on the vector β contribution to HRS has been examined using the mathematics of homogeneous, isotropic, random vector fields which appears in the description of fluid turbulence. The observed polarization and angle dependence of HRS from dipolar molecular liquids are explained by a molecular orientation distribution with the form of a transverse random vector field, with orientation correlations that decay as r^{-3} at long range. This is the same form as the predominantly transverse vector field at small K due to dipole-dipole interactions in a polar liquid. The expressions developed here are used to analyze previous HRS measurements for water and determine the form for the long-range orientation correlation function.

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[1] D. Chandler, Acc. Chem. Res. **7**, 246 (1974).

[2] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, UK, 1995).

[3] J.-L. Barrat and J.-P. Hansen, *Basic Concepts for Simple and Complex Liquids* (Cambridge University Press, Cambridge, UK, 2003).

[4] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 4th ed. (Academic Press, Oxford, 2013).

[5] D. P. Shelton, J. Chem. Phys. **141**, 224506 (2014).

[6] P. D. Maker, Phys. Rev. A **1**, 923 (1970).

[7] R. Bersohn, Y. H. Pao, and H. L. Frisch, J. Chem. Phys. **45**, 3184 (1966).

[8] D. P. Shelton, J. Chem. Phys. **138**, 154502 (2013).

[9] A. S. Monin and A. M. Yaglom, in *Statistical Fluid Mechanics: Mechanics of Turbulence* (MIT Press, Cambridge, MA, 1975), Vol. 2, Chap. VI.

[10] A. Malyarenko and M. Ostoja-Starzewski, Math. Mech. Complex Syst. **2**, 209–231 (2014).

[11] D. P. Shelton, J. Chem. Phys. **138**, 054502 (2013).

[12] D. P. Shelton, J. Chem. Phys. **136**, 044503 (2012).

[13] G. N. I. Clark, C. D. Cappa, J. D. Smith, R. J. Saykally, and T. Head-Gordon, Mol. Phys. **108**, 1415 (2010).

[14] C. Zhang and G. Galli, J. Chem. Phys. **141**, 084504 (2014).

[15] G. Mathias and P. Tavan, J. Chem. Phys. **120**, 4393 (2004).

[16] A. K. Soper and C. J. Benmore, Phys. Rev. Lett. **101**, 065502 (2008).

[17] P. Madden and D. Kivelson, Adv. Chem. Phys. **56**, 467–566 (1984).

[18] Y. Liu and J. Wu, J. Chem. Phys. **139**, 041103 (2013).

[19] P. Kumar, G. Franzese, S. V. Buldyrev, and H. E. Stanley, Phys. Rev. E **73**, 041505 (2006).

[20] D. C. Elton and M.-V. Fernandez-Serra, J. Chem. Phys. **140**, 124504 (2014).