

Ultrafast optical Kerr effect spectroscopy of water confined in nanopores of the gelatin gel

B. Ratajska-Gadomska^{a)}

Laboratory of Physicochemistry of Dielectrics and Magnetics, Department of Chemistry, Warsaw University, ul. Zwirki i Wigury 101, 02-089 Warsaw, Poland

B. Bialkowski

Institute of Physical Chemistry, Polish Academy of Science, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland

W. Gadomski

Laboratory of Physicochemistry of Dielectrics and Magnetics, Department of Chemistry, Warsaw University, ul. Zwirki i Wigury 101, 02-089 Warsaw, Poland

Cz. Radzewicz

Physics Department, Warsaw University, ul. Hoża 69, 00-681 Warsaw, Poland

(Received 28 November 2006; accepted 20 March 2007; published online 14 May 2007)

We report on the investigation of a short-time collective dynamics of water confined in the pores of the gelatin gel, using the femtosecond optical Kerr effect spectroscopy. The ultrafast responses of water molecules obtained in bulk liquid and in three concentrations of gelatin gels are explained theoretically, both in a long time and in a short time regime, taking into account all molecular motions. We prove that the contribution of molecules involved in tetrahedral, strongly H-bonded structures stabilizing the gel network increases with the gel concentration. On the other hand the long-time relaxation of water molecules is significantly slowed down in the gel pores. © 2007 American Institute of Physics. [DOI: [10.1063/1.2730506](https://doi.org/10.1063/1.2730506)]

I. INTRODUCTION

Confined liquids are present in many technological and biological processes. Investigation of the influence of confinement on the structure and properties of fluids is the subject of interest of many scientific groups.^{1–22} In particular, water deserves a special attention due to a crucial role that it plays in our everyday life. There is a number of experimental^{1–3,16–18,23} and theoretical^{19–25} papers treating water near interfaces and in small nanopores, mainly in vycor glass^{1,2} and other porous silicas,^{6,7,11} but also in vicinity of proteins,^{3,16,17} in biological cells,^{9,10} and quite recently in carbon nanotubes.¹³ They all have shown that the dynamics of water is significantly perturbed by the interaction with hydrophilic or hydrophobic substrates at various levels of hydration. In biological systems hydration is one of the most important processes, maintaining the three dimensional structure and functions of proteins. It has been shown recently in experimental^{13,9,10,15,16,23} and theoretical studies^{17,22,24,25} that the short time dynamics of water molecules close to the protein surface is slowed down and their residence time is significantly longer²³ in comparison with that of bulk water. It is connected with the structural changes in the momentary short-range order of water molecules. Optical Kerr effect (OKE) spectroscopy is a powerful tool for investigating the intermolecular dynamics of the short-living molecular structures.^{4–6,9,26–31} Herewith we are using this technique to study the dynamics of water molecules imprisoned within the pores of the gelatin gel. Gelatin is the protein

obtained from collagen by the denaturing process. In aqueous solution, called the sol state, the gelatin molecules are the separate, randomly oriented coils. Below the temperature $T=35$ °C, the polymer chains undergo the conformation change during the process of the sol-gel transition. They rebuild the hydrogen junctions, broken by the denaturation process, and, in an attempt to renature themselves back to the helix form, they construct the network of the chains.³² Such a self-assembled system is called the gel. Water molecules are imprisoned within irregular pores of the gelatin gel.³³ Studying the structural changes and, thus, the macroscopic properties of this confined water is of great importance to food and cosmetic industries, and to understanding of many biological processes. In particular, water in the gelatin gel has a direct correspondence to water in biological cells of living organisms. In this paper we present the results of our OKE experiments performed for three concentrations of the aqueous gelatin solutions, what yields different sizes of the gel pores.³³ In the theoretical interpretation of the experimental data we apply the model developed in our previous paper for bulk water.³¹ The model is based on the concept that a femtosecond pulse sees the liquid as a collection of instantaneous locally ordered molecular clusters, which maintain the quasicrystalline structure for a finite although very short time. Following Walrafen *et al.*,^{34,35} we consider the simplified picture of water as composed of two species; the hydrogen bonded (H-bonded) icelike structures of the tetrahedral symmetry and nonhydrogen bonded (non-H-bonded) molecules interacting with their neighbors via dipole-dipole interactions. The low frequency Raman spectra, observed and calculated in liquid water^{29,34–37} are

^{a)}Electronic mail: gado@chem.uw.edu.pl; Fax: 048 (22) 822 5695.

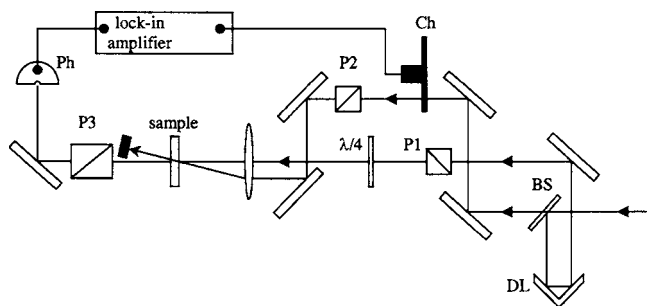


FIG. 1. The experimental setup. BS is a 1 mm thick beamsplitter with dielectric coatings, P1 and P2 are, respectively, the polarizer and analyzer placed in the probe beam path, P3 is the pump beam polarizer rotated by 45° with respect to P1, $\lambda/4$ is a quarter wave plate. Ch is a mechanical chopper modulating the pump beam, Ph is a photodiode, and DL is an optical delay line.

usually assigned to normal vibrations of the tetrahedral structures.³⁶ Such an assumption is justified due to the correspondence of the frequencies observed in liquid water to the appropriate low frequency vibrations in ice.^{34,35} In our model the fast part of the signal is due to the coherent vibrational response of the local H-bonded structures, whereas the slow, “diffusionlike” part of the signal results from, both, the rotational diffusion of single molecules and the overdamped translational vibrations of H-bonded molecular clusters.^{39,40} We have found the lifetime of the coherence to be very short, of the order of 120 fs, which is in agreement with the recent reports of Cowan *et al.*⁴¹ and Fecko *et al.*⁴² The long-time relaxation term in the diffusionlike response, determined in our model, is of the order of the longer diffusion lifetime found by other authors.^{36,29,43,44} The interpretation of this term as due to single molecule rotational relaxation is in agreement with the arguments given by Winkler *et al.*⁴⁴ Although the process of a single molecule rotational diffusion in water involves the breakage and formation of hydrogen bonds, it can be well described by the classical Stokes-Einstein-Debye theory of the molecular reorientation in viscous liquids.⁴⁴ The inhomogeneous broadening of the corresponding spectral lines in the short-time response is assumed to be caused by certain distribution of the cluster normal mode frequencies, which, in turn, is the direct result of the distribution of the cluster parameters.³¹ In our model we can directly differentiate the part of the OKE response connected with the tetrahedrally ordered molecules and the part connected with the single molecule response. Thus, applying this model for interpretation of the OKE response of water imprisoned in the pores of the gelatin gel, we can directly estimate how the contribution of H-bonded molecules has changed upon confinement. We have to stress that in our model we do not differentiate bulk water molecules and polymer-bound molecules. Both groups of molecules take part both in the short-time and in the long-time response.

II. EXPERIMENT

The experimental setup is shown in Fig. 1. A 100 MHz train of femtosecond pulses was generated by a homemade Ti:sapphire oscillator pumped by the Verdi V5 (Coherent, Inc.) laser operating at 532 nm. The oscillator delivered 30 fs

pulses with the average power of 380 mW and the central wavelength of 775 nm. To minimize group velocity dispersion introduced by the optical elements in the setup the output of the oscillator was first directed into a SK4 glass prism dispersion line for precompression. The precompressed beam was divided with a beamsplitter (BS) (see Fig. 1) into pump and probe beams with 70/30 ratio. In order to control the delay between pulses a stepper motor driven delay line was placed in probe beam path. We used three Glan-Thomson crystalline polarizers. Two of them (P1 and P2) were placed in the probe beam path and crossed providing a measured extinction ratio as high as 10^6 . The third one was placed in the pump beam and rotated by 45° with respect to the probe beam polarization. It was identical to the P1 polarizer which caused the group velocity dispersion experienced by both beams to be almost identical. Because of that the precompression enabled us to obtain both pulses close to their Fourier limit at the entrance of the sample.

The beams were focused with $f=150$ mm lens and crossed in the sample at an angle of approximately 4° . The static birefringence of the lens caused by mechanical stress can significantly increase the leakage through crossed polarizers and decrease the setup sensitivity. To avoid this the lens was mounted in a rotational holder and its orientation carefully adjusted prior to measurement. We used a heterodyne scheme⁴⁵ which enables one to measure the Kerr response of the medium directly. This was achieved by placing a zero-order quarter wave plate in the probe beam just after the first polarizer (P1) and rotating its axis slightly (approximately 2°) with respect to the axis of this polarizer. The signal was registered by a Si photodiode and a lock-in amplifier (SRS-830) which was referenced to a mechanical chopper modulating the pump beam at 2 kHz. To reduce the scattered light, the pump beam was blocked immediately after the sample and the photodiode placed far away from the sample. Our sample holder was made of a 2 mm thick gold plated brass spacer and two microscope cover glass plates which served as thin windows with low birefringence. The position of the sample cell mounted on an X-Y translation stage was carefully adjusted to minimize both the birefringence and scattering. We have found that mechanical impurities in sample liquids pose a serious problem. Any particle floating freely in the focal area in the sample strongly scatters the pump beam, which makes the data completely useless. To get rid of those impurities—present even in chemically clean samples—we purified the liquids using 0.4 μm millipore syringe filters. All measurements were performed under normal conditions.

The experimental setup was controlled by a computer. To achieve a good signal-to-noise ratio, which is crucial for Kerr measurement in water it is necessary to average the signal for extended periods of time. A drift in the laser power during this time would lead to signal distortion which is difficult to distinguish from real Kerr dynamics. This has been avoided by performing several scans of a shorter duration. Each scan lasted about 5 min (the delay range of 4000 fs) providing data with signal-to-noise ratio of approximately 100. All data presented in this paper are the average of 20 subsequent scans and allow us to observe signals spanning four decades.

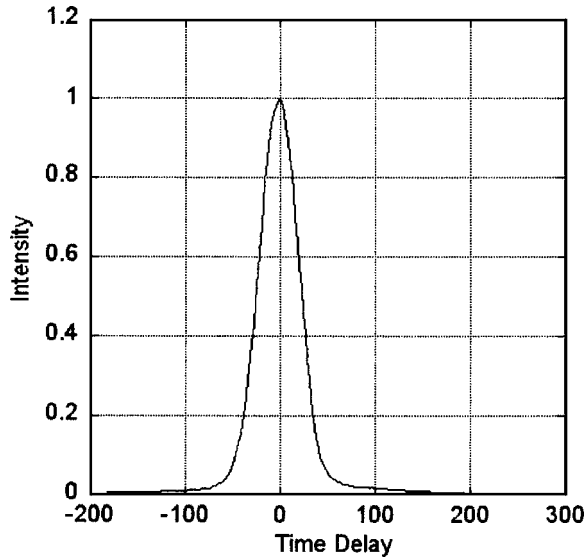


FIG. 2. Kerr response of a 1 mm thick quartz plate.

To estimate the time resolution in our experiment we have measured the Kerr signal of a 1 mm thick quartz plate placed in the position of the sample. The results shown in Fig. 2 indicate that the instrumental function width (about 30 fs) is consistent with the laser pulse duration determined in an independent measurement.

III. THEORY

The optically induced birefringence of the medium, measured by the heterodyne detected OKE signal, is expressed directly by the average nonlinear polarizability of the medium,

$$\Delta n(t) = \frac{2\pi}{n_0} (\langle P_{\parallel}^{\text{NL}}(t) \rangle - \langle P_{\perp}^{\text{NL}}(t) \rangle), \quad (1)$$

where $P_{\parallel}^{\text{NL}}$ and P_{\perp}^{NL} denote the diagonal components of the polarizability tensor, parallel and perpendicular to the incident optical field direction, respectively. The averaging is performed according to the Maxwell-Boltzmann distribution with the unperturbed Hamiltonian. The third order medium polarizability consists of two separable parts: the first one which is due to the electronic hyperpolarizability of molecules, $\chi_{ijkl}^{(3)}$, and the second nuclear one, $P_{ij}^{\text{nuclear}}(t)$, which is connected with the internal and external vibrations of the whole molecules^{40,30} and includes the dependence on the nuclear coordinates,

$$P_{ii}^{\text{NL}}(t) = 6 \frac{N}{V} \chi_{iikk} |F_k(t)|^2 + P_{ii}^{\text{nuclear}}(t), \quad (2)$$

where $F_k(t) = (\epsilon_k + 2/3) E_k^{\text{pump}}(t)$ is the local optical field, $E_k^{\text{pump}}(t)$ is the incident optical field, and N and V denote the number of molecules and the volume of a liquid, respectively.

In order to describe the nuclear OKE response of water confined in the gel we adopt the model of bulk water proposed by Walrafen^{34,35} and already used by us in our previous papers.^{14,15,31} It assumes that, for the incident femtosecond pulse, water can be treated as a composition of

momentary strongly H-bonded tetrahedrally ordered molecular clusters and single non-H-bonded molecules. The lifetime of molecular clusters is very short, but still within this time they undergo translational and rotational normal vibrations. A distribution of cluster sizes results in inhomogeneous broadening of vibrational spectral lines corresponding to cluster normal modes. Here we assume the “modified Gaussian distribution”³⁹ of normal mode frequencies $g(\omega_{\alpha}) = \omega_{\alpha} \exp[-(\omega_{\alpha 0} - \omega_{\alpha})^2 / 2(\Delta\omega_{\alpha})^2] / \Delta\omega_{\alpha} \sqrt{2\pi}$, with the width of spectral line $\Delta\omega_{\alpha}$, treated as a fit parameter. In the present approach we do not introduce any new species for water in the gel. Water molecules, which create the H bonds with the gelatin chains, are included into the group of ordered structures. Thus, the increased variety of those structures in the gel, in comparison to that in bulk water, leads to the enlarged inhomogeneous broadening of the spectral line $\Delta\omega_{\alpha}$ corresponding to a given normal vibration. The polarizability of a cluster is expressed as the sum of effective polarizabilities of molecules, modified by induced dipole-induced dipole interaction with their surrounding,^{40,30}

$$P_{\mu\nu}^k = \sum_n \alpha_{\mu\nu}^{\text{eff}}(n) = \sum_{n\gamma} \alpha_{\mu\gamma}(n) T_{\gamma\nu}(n), \quad (3)$$

where $T_{\gamma\nu}(n) = \sum_{n'} (I-A)_{\gamma\nu}^{-1}(n, n')$ is the tensor expressed in the local frame of reference connected with the cluster and the summation is taken over the nearest neighbors n' of the n th molecule.

$$A_{\gamma\nu}(n, n') = \sum_{\rho} \frac{\alpha_{\rho\nu}}{r^3(n, n')} \left| \frac{r_{\rho}(n, n') r_{\gamma}(n, n')}{r^2(n, n')} - \delta_{\rho\gamma} \right| \quad (4)$$

is a $3N_k$ rank tensor (N_k ; number of molecules in a cluster) of dipole-dipole interactions between the n th and n' th molecules.

Thus, the momentary polarizability, being the sum of the mean polarizabilities of the clusters, can be expressed as the power series of small normal mode amplitudes $Q_{\alpha}(t)$.^{40,30} We assume that the clusters are randomly oriented with respect to the electric field of the incident light wave, and, for simplicity, they perform the same normal vibrations.

We assume that the total OKE response of the medium can be composed of two contributions; the short-time response due to collective vibrations of H-bonded ordered clusters and the long-time response due to rotational diffusion of single molecules. In the short-time region H-bonded and non-H-bonded molecules of water can be differentiated. For times longer than the correlation time of the hydrogen bond, which is estimated to be of order of 500 fs,⁴⁷ molecules from both groups behave individually and take part in the orientational relaxation related to H-bond breaking and making.^{47,48} It has been shown by Winkler *et al.*,⁴⁷ that despite the complicated nature of the relaxation process, it can be well described by the Stokes-Einstein-Debye theory of single molecule rotating in a viscous liquid. Thus, the total nuclear part of the nonlinear polarizability of the system consists of two parts,^{40,30} the first one connected with the vibrations of H-bonded molecules and the second one connected with the rotational diffusion of single molecules,

$$P_{ij}^{\text{nuclear}}(t) = \frac{N_C}{V} \left\langle \left(\sum_{\alpha} \int_0^{\infty} g(\omega_{\alpha}) [P_{rs}^{(1)}(\alpha) \langle Q_{\alpha}(t) \rangle_k + \frac{1}{2} P_{rs}^{(2)}(\alpha, \alpha) \langle |Q_{\alpha}(t)|^2 \rangle_k] d\omega_{\alpha} \right) e_{ir} e_{js} \right\rangle_{\Omega} + \frac{\bar{N}}{V} \langle d_{ij}(t) \rangle, \quad (5)$$

where

$$\langle d_{ij} \rangle = \frac{1}{2kT} \sum_{\mu, \nu} \alpha_{\mu} \alpha_{\nu} \langle e_{\mu i} e_{\nu j} e_{\mu z} e_{\nu z} \rangle_{\Omega} \times \int_{-\infty}^t \exp\left(-\frac{t-t'}{T_2}\right) |F_z(t')|^2 dt'$$

denotes the mean nonlinear polarizability of an isolated molecule, of polarizabilities α_{μ} and α_{ν} with respect to molecular axes, knocked out from its momentary position by the pulsed electric field and relaxing to the state of thermal equilibrium with the diffusion lifetime T_2 ; N_C is the number of clusters, n is the number of molecules in a cluster, the symbol $\langle \rangle_k$ denotes averaging within the cluster with the Maxwell-Boltzmann distribution, and $\langle \rangle_{\Omega}$ denotes the averaging over all orientations of cluster axes (or molecular axes) with respect to the laboratory frame of reference, whereas $e_{ri} e_{sj}$ are the respective direction cosines, and k and T denote the Boltzmann constant and temperature, respectively; \bar{N} is the mean number of molecules, which contribute in the long-time diffusion process.

The first term in Eq. (5) describes the coherent response of all momentary clusters in a liquid. This term vanishes when the set of clusters loses its coherence due to mutual interactions. Thus, we treat the cluster dephasing time as the lifetime T_1 of the normal modes $Q_{\alpha}(t)$, the same for all modes. The optical field of the pump has been assumed to be a plain wave with Gaussian envelope,

$$E_z(t) = E_{0z} \exp\left(-\frac{t^2}{(\Delta t)^2} + i\omega t\right), \quad (6)$$

where Δt is the pulse width, ω is the central frequency, and the incident optical field is directed along the z axis.

The mean normal coordinate $\langle Q_{\alpha}(t) \rangle_k$ and mean square normal coordinate $\langle |Q_{\alpha}(t)|^2 \rangle$ for each H-bonded tetrahedral structure can be found as the solutions of the following dynamic equations, obtained from Hamilton equations:^{40,50}

$$\frac{dx}{d\tau} = 2z,$$

$$\frac{dy}{d\tau} = -2z\left[1 - \xi(t)\right] - 4\Gamma\left(y - \frac{1}{1 - \xi(t)}\right)\left[1 - \xi(t)\right] - \beta p x + h(t)p, \quad (7)$$

$$\frac{dz}{d\tau} = y - x\left[1 - \xi(t)\right] - 2\Gamma z\left[1 - \xi(t)\right] - \beta q x + h(t)q,$$

$$\frac{dq}{d\tau} = p,$$

$$\frac{dp}{d\tau} = -q\left[1 - \xi(t)\right] - 2\Gamma p\left[1 - \xi(t)\right] - \beta x - h(t),$$

where we have introduced dimensionless variables,

$$x = \frac{\langle |Q_{\alpha}|^2 \rangle_k}{\langle |Q_{\alpha 0}|^2 \rangle_k}, \quad y = \frac{\langle |P_{\alpha}|^2 \rangle_k}{\omega_{\alpha}^2 \langle |Q_{\alpha 0}|^2 \rangle_k}, \quad z = \frac{\langle Q_{\alpha}^* P_{\alpha} + Q_{\alpha} P_{\alpha}^* \rangle_k}{2\omega_{\alpha} \langle |Q_{\alpha 0}|^2 \rangle_k},$$

$$q = \frac{\langle Q_{\alpha} + Q_{\alpha}^* \rangle_k}{2\sqrt{\langle |Q_{\alpha 0}|^2 \rangle_k}}, \quad p = \frac{\langle P_{\alpha} + P_{\alpha}^* \rangle_k}{2\omega_{\alpha} \sqrt{\langle |Q_{\alpha 0}|^2 \rangle_k}}, \quad \tau = t\omega_{\alpha},$$

normalized by the initial mean square amplitudes $\langle |Q_{\alpha 0}|^2 \rangle_k$ calculated for the system in thermal equilibrium. β is the intensity dependent third-order nonlinearity coefficient; $\Gamma = T_1^{-1}$, whereas T_1^{-1} is the inverse coherence time of the clusters; $\xi(t) = H_{Irs}^{(2)}(\alpha) F_r F_s(t) / \omega_{\alpha}^2$ is the time dependent coefficient of modulation and $h(t) = H_{Irs}^{(1)}(\alpha) F_r(t) \times F_s(t) / (\omega_{\alpha}^2 \sqrt{\langle |Q_{\alpha 0}|^2 \rangle_k})$, whereas $H_{Irs}^{(1)}(\alpha) F_r(t) F_s(t)$ and $H_{Irs}^{(2)}(\alpha) F_r(t) F_s(t)$ denote the first and second derivatives of the interaction Hamiltonian for a given cluster k ,

$$H_{lk} = -\frac{1}{2} \sum_{\substack{n \in k \\ ijprst}} \alpha_{ij}(n) T_{ip}(n) T_{jt}(n) e_{pr} e_{ts} F_r(t) F_s(t),$$

with respect to the mode α . We can see that optical field dependence in Eqs. (7) is included not only in the term of inhomogeneity, but also in the term modulating the normal mode frequencies. It means that the optical field changes the intermolecular forces binding molecules in the momentary clusters. For the general case Eqs. (7) have to be solved numerically. Anyway, in harmonic approximation, $\beta=0$, and for low intensity of the external electric field, Eqs. (7) for $\langle Q_{\alpha}(t) \rangle$ and $\langle |Q_{\alpha}|^2 \rangle(t)$ can be solved analytically. Then, the nuclear part of the optically induced birefringence of the medium can be expressed in the form

$$(n_{zz}^{\text{nuclear}} - n_{xx}^{\text{nuclear}})(t) = \frac{1}{\Delta t} \int_{-\infty}^t R^{(3)}(t-t') |E_z|^2(t') dt', \quad (8)$$

where

$$R^{(3)}(t) = \sum_{\alpha} \left[\int_{1/T_1}^{\infty} g(\omega_{\alpha}) \left(C_{\alpha}^I \exp\left(-\frac{t}{T_1}\right) \sin(\tilde{\omega}_{\alpha} t) + C_{\alpha}^{II} \exp\left(-\frac{2t}{T_1}\right) \sin^2(\tilde{\omega}_{\alpha} t) \right) d\omega_{\alpha} \right] + \sum_{\alpha} \left[\int_0^{1/T_1} g(\omega_{\alpha}) \left(\tilde{C}_{\alpha}^I \exp\left(-\frac{t}{T_1} \left(1 - T_1 \sqrt{\frac{1}{T_1^2} - \omega_{\alpha}^2}\right)\right) + \tilde{C}_{\alpha}^{II} \exp\left(-\frac{2t}{T_1} \left(1 - T_1 \sqrt{\frac{1}{T_1^2} - \omega_{\alpha}^2}\right)\right) \right) d\omega_{\alpha} \right] + D \exp\left(-\frac{t}{T_2}\right), \quad (8a)$$

where $\tilde{\omega}_\alpha = \sqrt{\omega_\alpha^2 - 1/T_1^2}$ is the frequency of the damped oscillator.

The dimensionless coefficients in Eq. (8a), normalized with respect to the electronic hyperpolarizability shift,

$$\frac{N}{V}\Delta\chi = \frac{N}{V}\left(\frac{\varepsilon_z + 2}{3}\right)^2 \times \left[6 \sum_{rstv} \chi_{rstv} \langle e_{rz} e_{sz} e_{tz} e_{vz} - e_{rx} e_{sx} e_{tx} e_{vx} \rangle \Omega \right],$$

have the following forms:

- (i) The linear term coefficient,^{40,30}

$$C_\alpha^I = \frac{\Delta t N_C}{N \Delta \chi \tilde{\omega}_\alpha} \left(\frac{\varepsilon_z + 2}{3} \right)^2 \times \sum_{rstv} P_{rs}^{(1)} H_{1tv}^{(1)} \langle e_{rz} e_{sz} e_{tz} e_{vz} - e_{rx} e_{sx} e_{tx} e_{vx} \rangle \Omega.$$

- (ii) The quadratic term coefficient,^{40,30}

$$C_\alpha^{II} = \frac{\Delta t N_C \langle |Q_{\alpha 0}|^2 \rangle}{4 N \Delta \chi \tilde{\omega}_\alpha} \left(\frac{\varepsilon_z + 2}{3} \right)^2 \times \sum_{rstv} P_{rs}^{(2)} H_{1tv}^{(2)} \langle e_{rz} e_{sz} e_{tz} e_{vz} - e_{rx} e_{sx} e_{tx} e_{vx} \rangle \Omega$$

(in expressions for \hat{C}_α^I and \hat{C}_α^{II} the symbol $\hat{\omega}_\alpha$ should be substituted by $\sqrt{1/T_1^2 - \omega_\alpha^2}$).

- (iii) The diffusion coefficient,

$$D = \frac{\bar{N}}{N} \frac{\Delta t}{30 \Delta \chi k T} \left(\frac{\varepsilon_z + 2}{3} \right)^2 \times [(\alpha_1 - \alpha_2)^2 + (\alpha_1 - \alpha_3)^2 + (\alpha_3 - \alpha_2)^2].$$

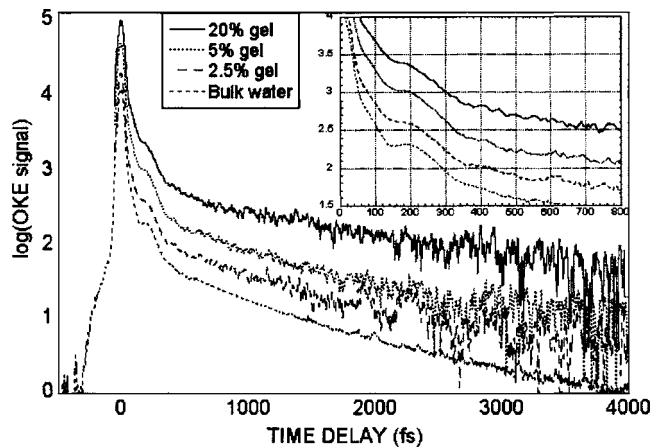


FIG. 3. Comparison of experimental OKE signals for bulk water and for water in 2.5%, 5%, and 20% gels. Vertical axis is in logarithmic scale. The plots are displaced from one another for clarity.

The integral over frequencies in Eq. (8a) has been divided into two terms.^{39,40} The first oscillating term for frequencies $\omega_\alpha > 1/T_1$, and the second one for frequencies $\omega_\alpha \leq 1/T_1$, decaying with the time $T'_1 = T_1 / (1 - \sqrt{1 - \omega_\alpha^2 T_1^2}) > T_1$, resulting from cluster vibrations that are overdamped (those decaying with the time $T'_1 = T_1 / (1 + \sqrt{1 - \omega_\alpha^2 T_1^2}) < T_1$ have been omitted). We have shown in our previous paper³¹ that this term is responsible for the diffusionlike intermediate OKE response in water.

IV. RESULTS AND DISCUSSION

The experimental OKE signals for bulk water and for water in gelatin gels for three weight concentrations of gela-

TABLE I. Values of parameters in Eq. (8a). Parameters $C_{\alpha 0}^I$ and $C_{\alpha 0}^{II}$ correspond to the frequency $\omega_{\alpha 0}$.

	$\omega_{\alpha 0}$ (cm ⁻¹)	$\Delta \omega_\alpha$ (cm ⁻¹)	$C_{\alpha 0}^I$	$C_{\alpha 0}^{II}$	C_{60}^I / C_{170}^I	D	D	T_1 (fs)	T_2 (fs)
H ₂ O	60	23	0.033 46	0.000 12					
	170	38	0.036 67	0.000 12					
	420	191	0.033 95	0.000 37	0.91	0.000 86		116	1333
	530	223	0.053 46	0.000 77					
	720	223	0.000 12	0.000 01					
2.5% gel	60	24	0.041 50	0.000 14					
	170	41	0.038 70	0.000 13					
	420	143	0.035 40	0.000 35	1.07	0.000 77		116	1493
	530	149	0.066 80	0.000 95					
	720	160	0.000 01	9×10^{-9}					
5% gel	60	25	0.046 07	0.000 15					
	170	44	0.044 63	0.000 14					
	420	143	0.032 69	0.000 33	1.03	0.000 62		116	1666
	530	149	0.057 90	0.000 95					
	720	160	0.000 01	9×10^{-9}					
20% gel	60	28	0.058 30	0.000 18					
	170	43	0.048 40	0.000 16					
	420	180	0.032 60	0.000 35	1.20	0.000 51		116	3030
	530	190	0.057 90	0.001 20					
	720	200	0.000 01	9×10^{-9}					

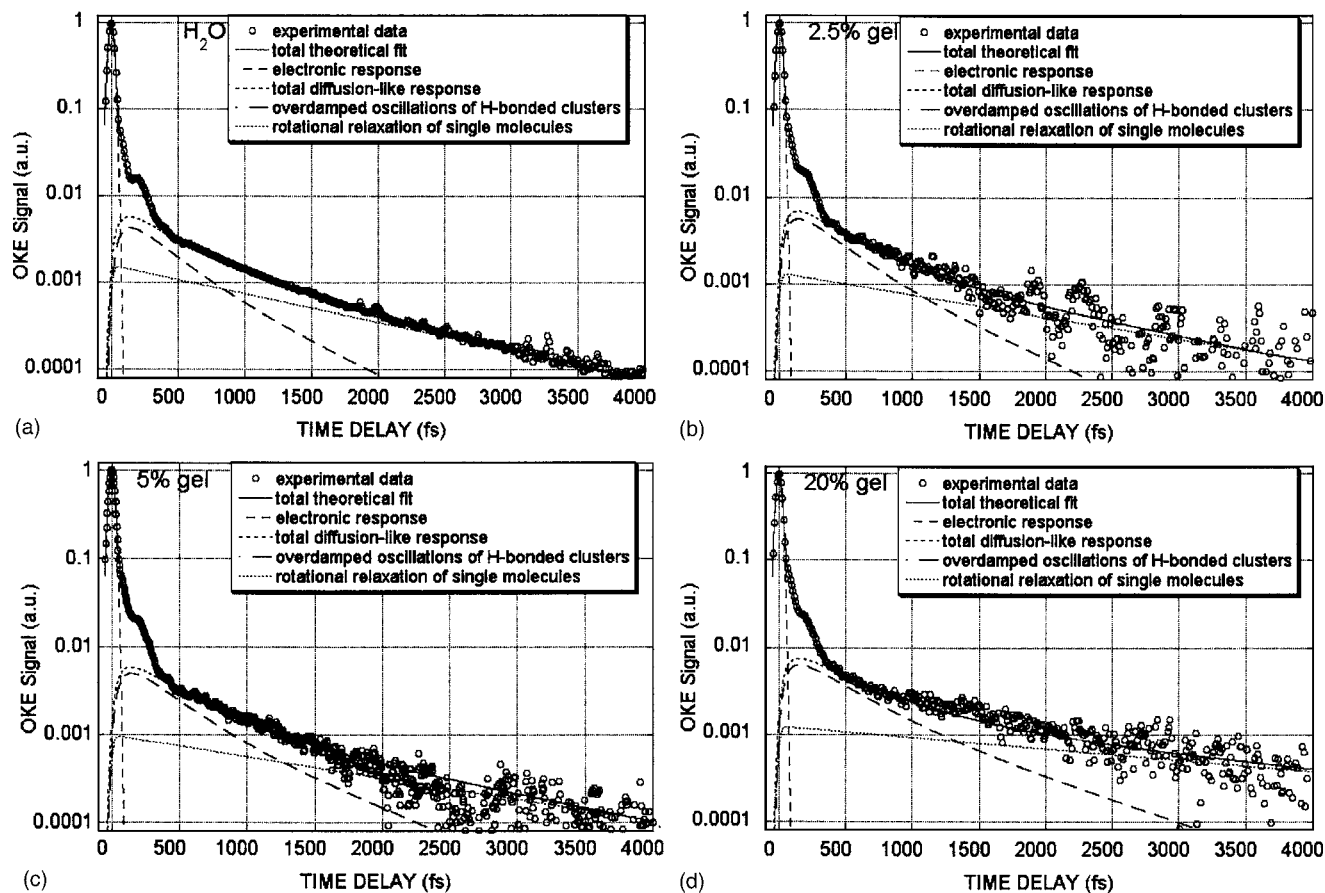


FIG. 4. Total experimental OKE signals and theoretical fits, of total signal, electronic, and both diffusive contributions, for (a) bulk water, (b) 2.5% gel, (c) 5% gel, and (d) 20% gel. Vertical axis is in logarithmic scale.

tin, 2.5%, 5%, and 20%, are shown in Fig. 3. All signals are normalized with respect to the electronic signal. For clarity of the picture the plots have been displaced from one another. At first glance it can be seen that the slope of the long time tails of the plots decreases with the increase of the gelatin concentration, which is equivalent to the decrease of the average pore size in the gel network.³³ Such a result is similar to the one observed by Scodinu and Fourkas⁶ for water confined in the nanopores of the silica sol-gel glass. The short time part of signals is enlarged in the inset in Fig. 3. It can be noticed that the small peak around 200 fs preceded by the small dip, characteristic for the water OKE signal,^{31,29,44,28} is present in all plots at the same delay time. This observation justifies our assumptions that we do not register any contribution from the low frequency vibrations of the gelatin molecules, which must be suppressed in the gel network. OKE signals of aqueous solutions of some proteins give radically different picture in comparison with that of bulk water.⁴⁶ We attribute flattening of the dip in OKE signals of water in the gels to the growing contribution of particular vibrations of tetrahedral structures. Following the procedure described in our previous paper for bulk water,³¹ we have first fitted the long time tails of the signals using only the diffusive part of Eq. (5), relevant to single molecules. The lifetimes T_2 and coefficients D used in the fits for bulk water and three gels are presented in Table I. Since the diffusion process of a single molecule proceeds as the train of

succeeding acts of breakage and formation of H bonds with neighboring molecules,^{47,48} the lifetime T_2 carries information about the H-bond network rearrangements. It can be seen that the diffusion lifetime of single water molecules becomes longer when water is confined in the gelatin gel and increases with gelatin concentration. In 20% gel it is more than twice longer than that in the bulk. Such a lowering of the mobility of water molecules has been observed in vicinity of proteins^{1-3,23} and in intracellular water.⁹ Thus, we attribute the increase of the diffusion lifetime T_2 to the growing hydration shell of water molecules H bonded to the gelatin molecules, when the concentration of the gelatin increases.⁴⁹ The effect is equivalent to the enhancement of the medium viscosity, which results in a longer single molecule Stokes-Debye diffusion time, in agreement with the arguments given by Winkler *et al.*⁴⁴ On the other hand we can observe (see Table I) that the single molecule contribution in OKE signal drops with the decrease of the size of the gelatin gel pores. This fact can be related to the growing number of molecules involved in tetrahedral structures, including also water molecules bound with polymer through H bonds. In order to calculate the OKE response due to ordered H-bonded molecules we have subtracted the electronic response and the diffusive response of single molecules from the total experimental signal. It has been shown for bulk water^{31,47} that this part of the signal can be perfectly fitted by the composition of vibrational contributions of normal

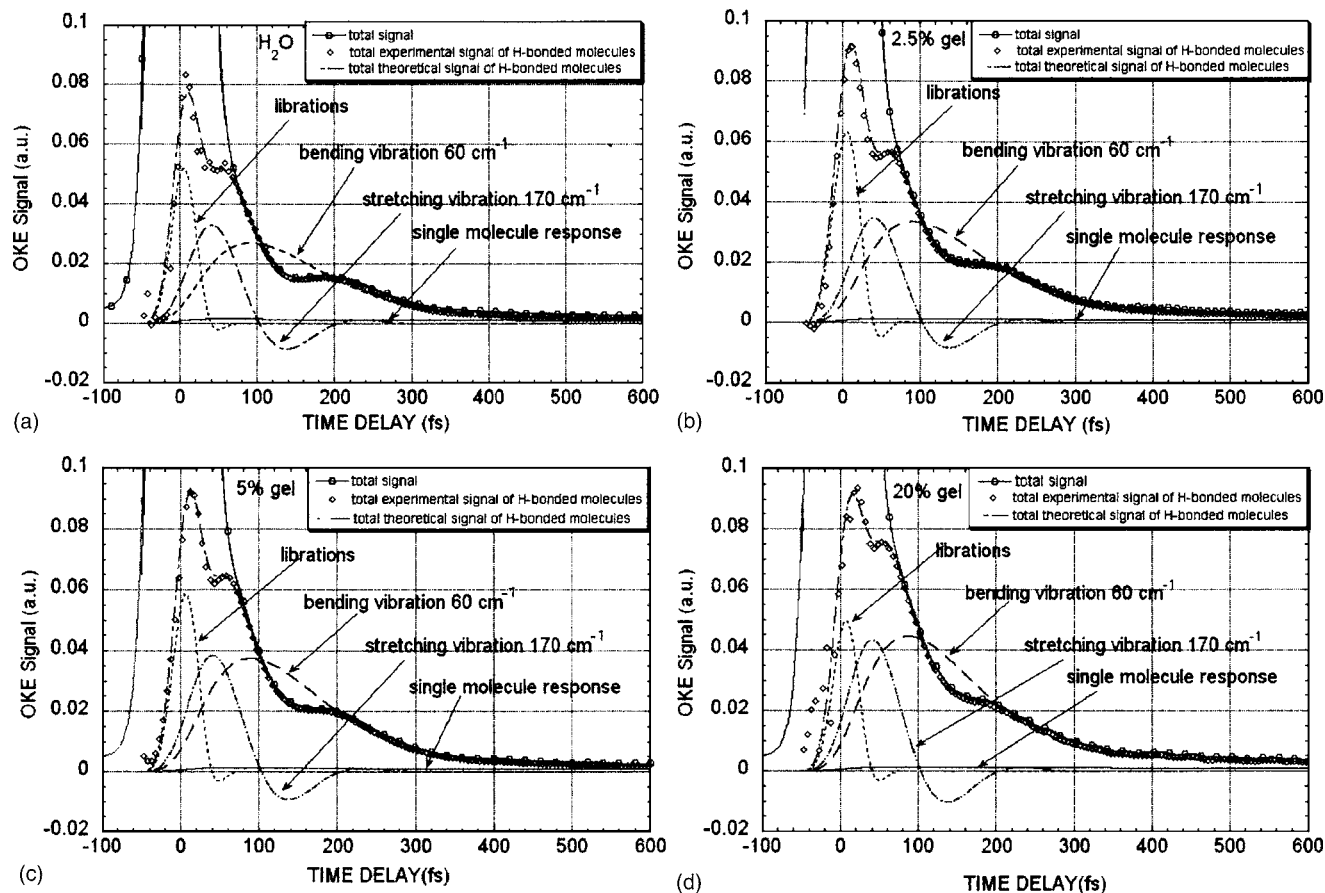


FIG. 5. Short time part of experimental OKE signals and theoretical fits for (a) bulk water, (b) 2.5% gel, (c) 5% gel, and (d) 20% gel. Vertical axis is in linear scale.

modes of the tetrahedral structure.³⁸ These are vibrations observed in Raman spectra of bulk water,^{34,35} i.e., a triply degenerate asymmetric H-bond stretching vibration of frequency 170 cm^{-1} , a triply degenerate H-bond bending vibration of frequency 60 cm^{-1} , and three rotational vibrations around molecular axes of symmetry of frequencies 420 , 530 , and 720 cm^{-1} . Due to the similarity of the appropriate frequencies observed in the low frequency spectrum of crystalline ice,^{34,35} both translational vibrations, 60 and 170 cm^{-1} , are treated as the proof of existence of tetrahedral icelike structures in liquid water. Using the same vibrations to fit OKE signals for water confined in three gels we have got an excellent accuracy. The coefficients C_{α}^I and C_{α}^{II} , the lifetime T_1 , and the inhomogeneous line widths $\Delta\omega_{\alpha}$ found in the fits, are given in Table I. The fits of OKE signals for water in bulk and in three gels, together with marked diffusion responses, are given in Fig. 4. The diffusionlike responses of the overdamped oscillations of H-bonded clusters, expressed by the second integral in Eq. (8a), have been separated in order to show their role in the intermediate-time part of the response. In the case of water the condition $\omega_{\alpha} \leq 1/T_1$ concerns only the bending mode of frequency 60 cm^{-1} . The corresponding fits of the short time part of the signal, together with contributions of particular vibrations are given in Fig. 5. It can be seen in Fig. 5 and in Table I that the contributions of both translational vibrations, 60 and 170 cm^{-1} , is higher in water confined in the gel than in bulk

water. Moreover this contribution grows with the gelatin concentration. It means that the amount of the structured H-bonded water is enhanced by the presence of the gelatin gel. On the other side the inhomogeneous broadening of spectral lines also increases, what can be assigned to the growing variety of tetrahedral structures. We relate this fact to the structures created by water molecules H bonded to the polymers. Such a picture is in agreement with the results of recent Raman studies of water in gelatin gels.^{31,50} The slightly changed ratio of the bending vibration 60 cm^{-1} contribution to the stretching vibration 170 cm^{-1} contribution (see C_{60}^I/C_{170}^I in Table I) in comparison to that in bulk water might also suggest that some tetrahedral structures of water molecules in the gel have different parameters than in the bulk. This difference can be attributed to the interstitial water molecules, which are built into triple helices being the nodes in the gel network. These molecules are known to be tetrahedrally ordered²³ and to perform translational vibrations of frequency around 60 cm^{-1} .⁵¹ Since the number of helices in the gel increases with the gelatin concentration,³² it involves the growing contribution from low-density strongly bound water.

In summary, we have presented the results of the femtosecond optical Kerr effect spectroscopy investigations of water confined in the gelatin gels. We conclude that the number of H-bonded ordered structures increases in the gel, whereas it concerns both the bulk water and the polymer-bound water.

The mobility of single water molecules, responsible for long time OKE response, is lower within gel pores than in the bulk.

ACKNOWLEDGMENT

The paper has been supported by Grant No. N202 115 31/1463 of Polish Ministry of Science and Higher Education.

- ¹M. C. Bellissent-Funel, J. Lai, and L. Bosio, *J. Chem. Phys.* **98**, 4246 (1993).
- ²J. M. Zanotti, M. C. Bellissent-Funel, and S. H. Chen, *Phys. Rev. E* **59**, 3084 (1999).
- ³M. C. Bellissent-Funel, J. Teixeira, K. F. Bradley, S. H. Chen, and H. L. Crespi, *Physica B* **180**, 740 (1992).
- ⁴B. Loughnane, R. A. Farrer, A. Scodinu, and J. T. Fourkas, *J. Chem. Phys.* **111**, 5116 (1999).
- ⁵B. Loughnane, A. Scodinu, and J. T. Fourkas, *Chem. Phys.* **253**, 323 (2000).
- ⁶A. Scodinu and J. T. Fourkas, *J. Phys. Chem. B* **106**, 10292 (2002).
- ⁷V. Crupi, S. Magazu, D. Majolino, G. Maisano, and P. Migliardo, *J. Mol. Liq.* **80**, 133 (1999).
- ⁸R. Bergman and J. Swenson, *Nature (London)* **403**, 2 (2000).
- ⁹E. O. Potma, W. P. de Boeij, and D. A. Wiersma, *Biophys. J.* **80**, 3019 (2001).
- ¹⁰C. Czeslik and R. Winter, *J. Mol. Liq.* **98**, 283 (2002).
- ¹¹V. Crupi, D. Majolino, P. Migliardo, and V. Venutti, *J. Mol. Liq.* **117**, 165 (2005).
- ¹²J. Marti, G. Nagy, M. C. Gordillo, and E. Guardia, *J. Chem. Phys.* **124**, 094703 (2006).
- ¹³A. Kolesnikov, J. M. Zanotti, C. K. Loong, P. Thiyagarajan, A. Moravsky, R. O. Loufty, and C. J. Burnham, *Phys. Rev. Lett.* **93**, 035503 (2004).
- ¹⁴B. Ratajska-Gadomska and W. Gadomski, *J. Chem. Phys.* **121**, 12583 (2004).
- ¹⁵W. Gadomski and B. Ratajska-Gadomska, *Chem. Phys. Lett.* **399**, 471 (2004).
- ¹⁶B. Bagchi, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **99**, 127 (2003).
- ¹⁷S. Pal, S. Balasubramanian, and B. Bagchi, *J. Chem. Phys.* **120**, 1912 (2004).
- ¹⁸F. Mallamace, J. C. Earnshaw, N. Micalli, S. Trusso, and C. Vasi, *Physica A* **231**, 207 (1996).
- ¹⁹P. Gallo, M. Rovere, M. A. Ricci, C. Hartnig, and E. Spohr, *Europhys. Lett.* **49**, 183 (2000).
- ²⁰I. Brovchenko, D. Paschek, and A. Geiger, *J. Chem. Phys.* **113**, 5026 (2000).
- ²¹P. Jedlovsky and M. Mezei, *J. Phys. Chem. B* **105**, 3614 (2001).
- ²²S. H. Lee and P. J. Rossky, *J. Chem. Phys.* **100**, 3334 (1994).
- ²³M. C. Bellissent-Funel, *J. Mol. Liq.* **84**, 39 (2000).
- ²⁴Y. C. Liu, Q. Wang, and L. H. Lu, *Chem. Phys. Lett.* **381**, 210 (2003).
- ²⁵M. Tarek and D. J. Tobias, *Phys. Rev. Lett.* **89**, 275501 (2002).
- ²⁶D. McMorro and W. T. Lotshaw, *Chem. Phys. Lett.* **178**, 69 (1991).
- ²⁷D. McMorro and W. T. Lotshaw, *Chem. Phys. Lett.* **201**, 369 (1993).
- ²⁸Y. J. Chang and E. W. Castner, *J. Chem. Phys.* **99**, 7289 (1993).
- ²⁹S. Palese, S. Mukamel, R. J. D. Miller, and W. T. Lotshaw, *J. Chem. Phys.* **100**, 10380 (1996).
- ³⁰B. Ratajska-Gadomska, W. Gadomski, P. Wiewór, and Cz. Radzewicz, *J. Chem. Phys.* **108**, 8489 (1998).
- ³¹B. Ratajska-Gadomska, B. Bialkowski, W. Gadomski, and Cz. Radzewicz, *Chem. Phys. Lett.* **429**, 575 (2006).
- ³²M. Djabourov, J. Leblond, and P. Papon, *J. Phys. (France)* **49**, 319 (1988).
- ³³M. Djabourov, N. Bonnet, H. Kaplan, N. Favard, P. Favard, J. P. Lechaire, and M. Maillard, *J. Phys. II* **3**, 611 (1993).
- ³⁴F. Franks, in *The Physics and Physical Chemistry of Water*, Water, A Comprehensive Treatise V. I (Plenum, New York, 1972).
- ³⁵G. E. Walrafen, M. R. Fisher, M. S. Hokmabadi, and W. H. Yang, *J. Chem. Phys.* **85**, 6970 (1986).
- ³⁶E. W. Castner, Jr., Y. J. Chang, Y. C. Chu, and G. E. Walrafen, *J. Chem. Phys.* **102**, 653 (1995).
- ³⁷W. B. Bosma, L. E. Fried, and S. Mukamel, *J. Chem. Phys.* **98**, 4413 (1993).
- ³⁸N. Agmon, *J. Chem. Phys.* **100**, 1072 (1996).
- ³⁹D. McMorro, N. Thantu, V. Kleinman, J. S. Mellinger, and W. T. Lotshaw, *J. Phys. Chem. A* **105**, 7960 (2001).
- ⁴⁰B. Ratajska-Gadomska, *J. Chem. Phys.* **116**, 4563 (2002).
- ⁴¹M. L. Cowan, B. D. Bruner, N. Huse, J. R. Dwyer, B. Chugh, E. T. Nibbering, T. Elsaesser, and R. J. D. Miller, *Nature (London)* **434**, 199 (2005).
- ⁴²J. Fecko, J. J. Loparo, S. T. Roberts, and A. Tokmanoff, *J. Chem. Phys.* **122**, 054506 (2005).
- ⁴³S. Saito and I. Ohime, *J. Chem. Phys.* **106**, 4890 (1997).
- ⁴⁴K. Winkler, J. Lindner, H. Bursing, and P. Vohringer, *J. Chem. Phys.* **113**, 4674 (2000).
- ⁴⁵G. L. Eesley, M. D. Levenson, and W. M. Tolles, *IEEE J. Quantum Electron.* **QE-14**, 45 (1978).
- ⁴⁶G. Giraud, J. Karolin, and K. Wynne, *Biophys. J.* **85**, 1903 (2003).
- ⁴⁷K. Winkler, J. Lindner, and P. Vohringer, *Phys. Chem. Chem. Phys.* **4**, 2144 (2002).
- ⁴⁸D. Laage and J. T. Hynes, *Science* **311**, 832 (2006).
- ⁴⁹M. C. Bellissent-Funel, J. Teixeira, K. F. Bradley, S. H. Chen, and H. L. Crespi, *Physica B* **180-181**, 740 (1992).
- ⁵⁰N. Tsukida, Y. Maeda, and H. Kitano, *Macromol. Chem. Phys.* **197**, 1681 (1996).
- ⁵¹H. D. Middendorf, R. L. Hayward, S. F. Parker, J. Bradshaw, and A. Miller, *Biophys. J.* **69**, 660 (1995).