Supercooling and freezing processes in nanoconfined water by time-resolved optical Kerr effect spectroscopy

A Taschin¹, P Bartolini¹, A Marcelli¹, R Righini¹,² and R Torre¹,³

¹ European Laboratory for Non-Linear Spectroscopy (LENS), Università di Firenze, Via N. Carrara 1, I-50019 Sesto Fiorentino, Firenze, Italy
² Dipartimento di Chimica, Università di Firenze, via Della Lastruccia 13, I-50019 Sesto Fiorentino, Firenze, Italy
³ Dipartimento di Fisica e Astronomia, Università di Firenze, via Sansone 1, I-50019 Sesto Fiorentino, Firenze, Italy

E-mail: torre@lens.unifi.it

Received 31 July 2014, revised 10 October 2014
Accepted for publication 17 October 2014
Published 29 April 2015

Abstract
Using heterodyne-detected optical Kerr effect (HD-OKE) measurements, we investigate the vibrational dynamics and the structural relaxation of water nanoconfined in Vycor porous silica samples (pore size ≃ 4 nm) at different levels of hydration and temperatures. At low levels of hydration corresponding to two complete superficial water layers, no freezing occurs and the water remains mobile at all the investigated temperatures with dynamic features similar, but not equal to, the bulk water. The fully hydrated sample shows the formation of ice at about 248 K. This process does not involve all the contained water; a part of it remains in a supercooled phase. The structural relaxation times measured from the decay of the time-dependent HD-OKE signal shows the temperature dependence largely affected by the hydration level; the low frequency (ν < 500 cm⁻¹) vibrational spectra obtained by the Fourier transforms of the HD-OKE signal appear less affected by confinement.

Keywords: nanoconfined water, porous glass, optical Kerr effect

1. Introduction
The characterization and understanding of confined and interfacial water is relevant to many technological and natural processes that span from biological science to geological topics [1]. Despite much research and numerous investigations, several fundamental problems remain to be clarified. In fact, if liquid water interacts with a material surface, the water layers at the interface show structural and dynamic alterations that turn into non-trivial modifications of the water’s fundamental chemical-physical properties. These phenomena are particularly relevant when water is completely confined in a matrix at the nanometric scale.

Many recent physics research efforts have focused on the investigation and measurements of water confined in porous glasses that can be considered prototype materials for these studies [2–11].

Among them, Vycor glasses are perhaps the most utilized in the experimental investigations [12–17] and studied by numerical simulations [18–24].

These glass matrices are characterized by well-defined pore diameters of nanometric dimensions, providing a tight hydrophilic confinement. In a series of previous works, we studied liquid-filled Vycor samples by transient grating spectroscopy measuring the acoustic propagation [25–27], the liquid flow, and the thermal diffusion phenomena [28–30]. Recently, we investigated the optical Kerr effect (HD-OKE) of the water dynamics in Vycor at variable hydrations by heterodyne detection [31].

Several basic questions about the physics of water confined at the nanometric scale still remain open. Simply a physical intuition suggests that nanoconfined water can be divided into two types: The outer water (i.e. the water layers close to pore surface) and the inner water (i.e. the internal
water layers). The outer layers present a liquid structure and dynamics modified by the interactions with the pore surfaces; the inner water seems to have characteristics very similar to the bulk water.

The simulation studies from Gallo et al. [18–21] provided a numerical support to this scenario. Our recent study [31] gave some experimental evidence; the HD-OKE data at ambient temperature identify the outer water as the two water layers close to the pore surface, whereas the remaining internal 4–5 layers can be ascribed as the inner water. Here we extend the HD-OKE investigation to lower temperatures in order to study the variations induced by the temperature to the nanoconfined water dynamics.

2. Optical Kerr effect experiments

In the optical Kerr effect (OKE) experiments a linear-polarized short laser pulse (pump) induces a transient birefringence in an optically transparent medium [32, 33]. This impulsive excitation is followed by the dynamic phenomena that return the sample to the equilibrium state. Measuring the polarization modifications in a second laser pulse (the probe) the relaxation processes can be monitored. The pump and probe beams are spatially superimposed and the probe pulse is delayed with respect to the pump pulse by a controlled optical delay line. The OKE signal measures the time-derivative of the correlation function of the anisotropic liquid susceptibility and it contains the relaxation processes and the vibrational response of the sample. By employing femtosecond laser pulses, this experiment enables the measurement of the vibrations of relatively low frequencies and the relaxation phenomena.

Typically, the OKE investigations cover a large dynamic range from a few femtoseconds to many picosecond timescales. So it has been used for studying several liquid matter phases; from simple molecular liquids [34, 35] to liquid crystals [36, 37], from supercooled liquids [38–41] to glass-formers [42–46].

The OKE signal is defined by the convolution of the material response function with the instrumental function, $G(t)$ [33, 41]:

$$S(t) = \int \left[ k\delta(t - t') + R_p(t - t') \right] G(t')dt'. \quad (1)$$

The nuclear part of the response $R_n(t)$ is [47]:

$$R_n(t) \propto -\frac{\partial}{\partial t} \left( \chi_{xx}(t)\chi_{xy}(0) \right) \quad (2)$$

where $\chi_{xx}$ is the anisotropic component of the susceptibility tensor. The frequency-dependent response can be obtained by a Fourier transform of $R_p(t)$, and can be related to the signal measured in a depolarized light scattering experiment [33, 41].

Detailed information on the experimental apparatus can be found in reference [41]. In summary: The laser system is a self-mode-locked Ti:sapphire laser producing pulses of 20 fs duration and of 3 nJ energy; the heterodyne-detection follows the configuration introduced previously [41, 48, 49, 50], which is based on the differential acquisition of the two opposite-phase optical signals generated by the circular polarization of the probe and detected by a balanced double photodiode; the electronic signal is then processed by a lock-in amplifier.

The extraction of the OKE response from the measured signal requires the knowledge of the instrumental function $G(t)$; this is a difficult experimental problem that requires particular attention in the measurements of bulk water [40, 41] and confined water [31]. In order to measure the $G(t)$ we performed an OKE experiment on a CaF$_2$ sample. The CaF$_2$ plate is placed side by side with the Vycor sample. As already reported [40, 41], to measure the instrumental function correctly it is extremely important to preserve the experimental configuration during the two measurements (i.e. on the CaF$_2$ and the Vycor sample).

The Vycor samples produce a relatively high scattering of laser beams that generate some interference effects in the measured signal; we averaged them out by inserting a vibrating mirror in the pump optical path [31].

3. Sample

We nanoconfined water in Vycor porous glasses (code 7930 by Corning Company$^4$), a porous glass characterized by 4 nm pore diameters (other details are reported in the technical data sheet$^5$). We used Vycor slabs of $8 \times 8 \times 2$ mm$^3$, cleaned by immersion in 35% hydrogen peroxide solution at 90°C for 2 h. After repeated washing in distilled water, the samples were stored in P$_2$O$_5$ (phosphoric anhydride) until usage. We used a vapor phase exothermic transfer from the bulk to realize a controlled hydration procedure [16] of the Vycor, whereas heating the Vycor at 400°C for 10 h produced the dry samples. The water content of all the samples were checked by accurate weighing and by Fourier transform infra-red measurements [31].

The hydration level can be quantified by the ratio between the confined water weight and borosilicate glass weight, composing the Vycor matrix. This is the Filling Fraction parameter: $f = \text{H}_2\text{O} (\text{g})/\text{Vycor} (\text{g})$.

We performed the HD-OKE experiment on 3 samples; a ‘dry’ Vycor and two hydrated slabs. A sample is hydrated at $f = 11.6 \pm 0.5\%$, which corresponds to the presence of about ‘two water layers’ on the pore surfaces and 50% of permitted filling water; the other sample at $f = 24.3 \pm 0.9\%$, which corresponds to the ‘full hydration’ condition [16], i.e. 100% of filling water.

4. Results on bulk water

First of all, we measured the HD-OKE data of the bulk water (i.e. not confined in the Vycor) using the same experimental set-up and procedures. These data represent our benchmark of water dynamics that will enable us to perform a comparison with the HD-OKE data of nanoconfined water.

The HD-OKE data of the liquid and supercooled bulk water provide unique information on the vibrational dynamics and structural relaxation taking place in water. The theoretical interpretation and the importance of the HD-OKE data in the discussion of water anomalies has been reported in [39–41].

$^4$ www.corning.com/lightingmaterials/products/.

$^5$ www.corning.com/lightingmaterials/images/Vycor_7930.pdf.
In figure 1 we report the HD-OKE data measured in the bulk water in three different states, from the top: Crystal, supercooled, and liquid. In the left panel we report the data in the time-domain; in the right panel we show the OKE response function in the frequency-domain. The time-domain data of the liquid and supercooled phases clearly show the signature of fast oscillatory dynamics at short times, extending up to 1 ps, followed by a slower monotonic relaxation. The initial oscillatory component is due to the intermolecular vibrational dynamics and the slower decay to the structural relaxation dynamics [39–41]. The lower temperature data show only an under-damped oscillation without slower relaxation processes, which is the signature of ice crystal dynamics.

In order to get the spectra of the HD-OKE response function, we Fourier transform the measured data, deconvolute them from the instrumental response, and retain the imaginary part of it: $\text{Im}[\tilde{R}_n(\nu)] \propto \text{Im}[FT [S(t)] / FT [G(t)]]$, see also equation (1). The details about these procedures are reported in Taschin et al. [40, 41]. The $\text{Im}[\tilde{R}_n(\nu)]$ obtained from the HD-OKE data are reported in right panel of figure 1. As expected, the liquid and the supercooled data present very similar dynamic features characterized by a shoulder appearing at very low frequency, $\nu \lesssim 10 \text{ cm}^{-1}$, due to the relaxation processes and by the two intermolecular vibrational bands around 50 and 175 cm$^{-1}$, named the ‘bending’ and ‘stretching’ modes, respectively. The ice crystal phase, hexagonal ice, clearly shows different dynamics with arrested structural and low frequency dynamics; the vibrational spectrum for $\nu > 150 \text{ cm}^{-1}$ presents the typical spectrum of ice [51].

5. Results on nanoconfined water

We measured the HD-OKE response on the Vycor samples at different temperatures from ambient down to the occurrence of crystallization for three different hydrations: Dry, $f = 11.6\%$ (bilayer hydration) and 24.3\% (full hydration).

The experimental results with $f = 11.6\%$ hydration are collected in figure 2, those for the $f = 24.3\%$ sample in figure 3. The left panels show in a log-linear plot the data in the time; the results for the longer delay times are shown in the insets in a linear–linear plot. A relatively slow oscillation extending in the picosecond time-scale is present; see both insets of the left panels. This is likely due to an acoustic-like vibration localized on the pore surface [31,53]. In the hydrated Vycor, the presence of liquid water adds a monotonic decay that becomes the dominant feature at full hydration; this contribution is attributed to the relaxation processes of nanoconfined water. In the right panels the Fourier transforms of the HD-OKE responses are reported.

Just a simple look at these data reveals that there are no signatures of ice formation at any temperature for the sample with $f = 11.6\%$, whereas the presence of ice is clear in the $f = 24.3\%$ sample at 248 K, the lower temperature measured. In fact, this appears as a clear under-dumped oscillation (i.e. a sharp peak at about 215 cm$^{-1}$ in the frequency domain) easily detectable in both the time and frequency domain data. The supercooled nanoconfined water shows dynamics apparently similar to the bulk water; in fact it is characterized by a spectrum extending up to about 400 cm$^{-1}$ presenting two broad vibrational peaks very similar to the bending and stretching bands; see also figure 4. A closer view shows how the positions and relative amplitudes are modified both in the bilayer and fully hydrated samples. As we mentioned previously, the lower frequency range is characterized by a low peak attributed to an acoustic-like pore vibration and a shoulder that is related to the structural relaxation process. The slow dynamics, hardly visible in the frequency-domain, are better extracted from the time-domain data using a fitting procedure.
Figure 2. We report HD-OKE data of nanoconfined water at $f = 11.6\%$ corresponding to a bilayer water hydration at different temperatures together with the dry sample data. In the left panel the data are reported in a log-linear plot (Full circles: Experimental data; continuous line: Best fit results). In the inset, two signal decays (data on a dry sample and on a bilayer hydrated sample at 293 K) at longer times are shown in a linear-linear plot. The data have been vertically shifted to make all the kinetics clearly visible. In the right panel: Fourier transforms of the HD-OKE data, deconvoluted from the instrumental response according to the procedure described in [31, 41]. The data have been re-normalized on the high frequency peak, $\nu \approx 800\text{ cm}^{-1}$, corresponding to the transverse optical mode of the silica matrix [52].

Figure 3. HD-OKE data of nanoconfined water at full hydration $f = 24.3\%$ with the best fit results (continuous lines). In the left panel the data are reported in a log-linear plot, while the decays at longer times are shown in the inset. In the right panel we report the Fourier transforms of the HD-OKE data, deconvoluted from the instrumental response, on nanoconfined water at full hydration at different temperatures.

The rigorous definition of the OKE response function for water is a very complex issue [41], which becomes even more problematic for nanoconfined water. Here we decided to use a simple function in order to fit the data and provide an immediate comparison between the bulk and nanoconfined features. The response is taken as [31]:

$$R_n(t) = AR_{\text{dry}}(t) + B \frac{d}{dt} \exp \left[-\left(\frac{t}{\tau}\right)^\beta\right] + \sum_i C_i \exp \left(-\gamma_i^2 t^2\right) \sin(\omega_i t).$$  \hspace{1cm} (3)

Equation (1) describes the convolution of the response function $R_n(t)$ with the instrumental function $G(t)$, where the $\delta$-function reproduces the instantaneous electronic response. Equation (3) gives the response function simulating the material dynamics. The liquid water dynamics is described by the sum of the relaxation functions in the form of the time derivative of a stretched exponential [39], and of a few damped oscillators (DO). The main fitting parameters of the model are: The structural relaxation time $\tau$, the stretching factor $\beta$, the frequencies $\omega_i$, and the damping constants $\gamma_i$ of the DOs; the dry Vycor matrix response is taken into account.
adding a \( R_{\text{dry}}(t) \) function, which is simulated by a sum of a series of damped oscillators and exponential functions, whose characteristic parameters were determined by fitting the HD-OKE signal of the dry sample.

The equation (3) can be used to fit both the bulk (with \( A = 0 \)) and the nanoconfined water (with \( A \neq 0 \)) data; the results from the fits are reported as red continuous lines in the left panels of figures 2 and 3.

The fast part of the HD-OKE data has been fitted using a series of DOs (i.e. the last term in equation (3)) with the frequency and damping parameters showing a smooth temperature dependence. Without entering into a detailed analysis of the fitting parameters, the Fourier transform of the measured data enables a direct visualization of the frequency components present in the spectrum. We report in figure 4 the Fourier transforms of all the measured data after the spectrum of the dry sample has been subtracted; this would isolate the signal contributions coming from the nanoconfined water.

The spectrum of nanoconfined water in both samples for \( T > 248 \) K shows features similar to the bulk water; as expected, these similarities are greater in the full hydration water than in the bilayer water [31]. The stretching and bending vibrational bands are clearly present, and they show an increase in the intensity of the higher frequency component with respect to the lower frequency part with decreasing temperatures. At the lowest measured temperature, \( T = 248 \) K, the bilayer water does not crystallize, whereas the sample with full hydration does crystallize. The presence of ice inside the nanopores is proved by the evident and the relatively narrow peak appearing at the frequency of \( \nu \approx 215 \text{ cm}^{-1} \), typical of the external vibrations of ice crystals [51]. This spectrum features can certainly be assigned to ice, as proven by the measured data reported in figure 1. We cannot distinguish between the cubic or hexagonal ice, but according to the previous reported neutron scattering data [13–15], it is very likely cubic ice.

The spectrum of nanoconfined water at 248 K, reported in the right panel of figure 4, shows a broad band below the ice peaks not present in the bulk ice spectrum reported in the right panel of figure 1. This broad vibrational component, extending over the whole frequency window reported, is due to those parts of water that remain mobile, thus avoiding the freezing process. This water retains its vibrational dynamics and a finite structural relaxation time. A comparison of the reported experimental spectra suggests that the amount of water remaining in a supercooled state is a non-negligible part of the nanoconfined water. We estimated it from the spectrum area to be about 50% of the total amount of internal water. This is in fairly good agreement with the volumes occupied by the outer water (i.e. the two water layers at the pore surface) and the inner water (i.e. the remaining 4–5 layers of water filling the internal part of the pore).

The best fit procedure enables us to obtain the structural relaxation times of nanoconfined water, which are reported in figure 5. The stretched exponential provides good fits at all the investigated temperatures, but the fitting procedure does not enable the extraction of a reliable value for the stretching exponent; we fixed it to the value found for the bulk water. Moreover, the presence of the slow oscillating signal reduces the accuracy of the fitting parameters.

The results reported in figure 5 show that the structural relaxation time does vary appreciably from the bilayer hydration \( f = 11.6\% \), to full hydration \( f = 24.3\% \), both as value and temperature dependence.

The structural relaxation time of nanoconfined water at lower hydration, i.e. two water layers, experiences a temperature dependence that is reduced with respect to the bulk water that turns into an increase in the characteristic time scale of about a factor of 4 at higher temperatures. These dynamics are strongly affected by the interactions with the silica surfaces; this was proven by the previous HD-OKE measurements with increasing hydrations [31], and it is confirmed by the present
data of the structural dynamics, which show a surprisingly weak temperature dependence.

The structural relaxation times at full hydration and high temperatures are indeed intermediate between the bulk and bilayer water relaxation times. Moreover, they show a slowing down process approaching the lower temperatures stronger than that taking place in the bulk water; the data suggest that by reducing the temperature, the molecular network is more stabilized in fully hydrated pores than in a partially hydrated sample. At 248 K, when part of the water freezes, the HD-OKE still detects a very slow decay in the signal that suggests the presence of mobile water inside the pores.

The temperature dependence of the bulk water follows a power law dependence \( \tau \propto (T - T_c)^{-\gamma} \), with a critical exponent \( \gamma = 1.7 \) and a critical temperature \( T_c = 227 K \) [40]. In the right panel of figure 5 we report the relaxation times in a linearized plot in order to verify if this power law also applies to nanoconfined water. Even if the measured temperatures are the minimum to verify a linear dependence, we find that the hydration water possibly follows a power law with similar critical exponents, but with different critical temperatures; lower for the bilayer water and higher for the full hydration water.

Our experimental results on the structural dynamics of confined water in Vycor are in good agreement with those obtained from molecular dynamics simulations [18, 19]. In particular, both studies found similar values for the relaxation times, with a comparable difference between the partial and full hydration conditions. Moreover, both investigations limit the extension of the surface effects on water dynamics up to two molecular layers. Unfortunately, a detailed quantitative comparison between the numerical results and the experimental data cannot be fully realized because the measured and simulated physical observables are different.

6. Conclusion

These results, as in the previous studies, can be rationalized considering the presence of two water types inside the hydrophilic nanopores: the water close to pore surface, outer water, and the more internal part of the water, inner water. We must distinguish the outer water (i.e. water in contact with the pore surfaces at full hydration) from the multilayer water: Water in contact with the pore surfaces and water vapor at low hydration levels. Unfortunately, our experimental investigations cannot measure selectively the outer water dynamics, but only the multilayer water. In fact only the numerical simulation can probe the outer/inner water components. Nevertheless, the experimental data at different levels of hydration can provide meaningful indications [31].

According to our results, the water nanoconfined in 4 nm hydrophilic pores shows vibrational dynamics that have general features similar to bulk water even during the supercooled phase. This is basically true for both the partially hydrated (i.e. bilayer water) and for the fully hydrated samples (i.e. outer/inner water). At the lower temperature of 248 K, the vibrational dynamics of the fully hydrated samples are modified, reporting the contemporary presence of ice (the inner water that freezes) and the supercooled water (the outer water that remains mobile).

Instead, the structural dynamics of nanoconfined water shows several differences from bulk water, as well as the structural relaxation of the bilayer water from the full hydration water. The temperature dependence of the structural relaxation times of the various samples has a complex scenario that is not immediately understandable. The relaxation times in the bilayer water are slower than in the bulk water, and they show a weaker temperature dependence. This is certainly due to the interactions of water layers with the pore surfaces, which hinder the structural rearrangements and frustrate the nucleation processes. These effects are likely weakly dependent on the temperature. In the fully hydrated pores, by lowering the temperature the structural relaxation undergoes a slowing down phenomenon stronger than in the bulk water. This experimental evidence could suggest the following physical scenario; during the supercooled phase the water’s local structures are unstable and subject to two
opposite effects: The surface interactions and the nucleation processes taking place in the inner part of the pores. These instabilities would generate slow fluctuations affecting the structural relaxation times.

Acknowledgments

This work was supported by R Toscana, prog. POR-CRO-FSE-UNIFI-26, by E Cassa di Risparmio Firenze, prog. 2012-0584, and by MIUR, prog. PRIN-2010ERFKXL-004. We acknowledge M De Pas, A Montori, and M Giuntini for providing their continuous assistance in the electronic set-ups; and R Ballerini and A Hajeb for the mechanical realizations.

References

[1] Brovchenko I and Oleinikova A 2008 Interfacial and Confined Water (Amsterdam: Elsevier).
[2] Jähnert S, Vaca Chávez F, Schaumann G E, Schreiber A, Schönhoff M and Findenegg G H 2008 Phys. Chem. Chem. Phys. 10 6039.
[3] Gallo P, Rovere M and Chen S H 2010 J. Phys. Chem. Lett. 1 729.
[4] de la Llave E, Molinero V and Scherlis D A 2010 J. Chem. Phys. 133 034513.
[5] Ogumi M, Kanke Y, Nagoe A and Namba S 2011 J. Phys. Chem. B 115 14023.
[6] Caer S L, Pin S, Esnouf S, Raffy Q, Renault J P, Brubach J B, Creff G and Roy P 2011 Phys. Chem. Chem. Phys. 13 17658.
[7] Milischuk A a and Ladanyi B M 2011 J. Chem. Phys. 135 174709.
[8] Giovanbattista N, Rossky P and Debenedetti P 2012 Annu. Rev. Phys. Chem. 63 179.
[9] Limmer D T and Chandler D 2012 J. Chem. Phys. 137 044509.
[10] Milischuk A a, Krewald V and Ladanyi B M 2012 J. Chem. Phys. 136 224704.
[11] Bertrand C E, Zhang Y and Chen S H 2013 Phys. Chem. Chem. Phys. 15 721.
[12] Bruni F, Ricci M A and Soper A K 1998 J. Chem. Phys. 109 1478.
[13] Bellissent-Funel M 1998 J. Mol. Liq. 78 19.
[14] Dore J 2000 Chem. Phys. 258 327.
[15] Bellissent-Funel M C 2001 J. Chem. Phys. 115 9165.
[16] Tombri E, Salvetti G, Ferrari C and Johari G P 2005 Phys. Chem. Chem. Phys. 7 5407.
[17] Tombri E, Salvetti G, Ferrari C and Johari G P 2005 J. Chem. Phys. 122 104712.
[18] Gallo P, Rovere M and Spohr E 2000 J. Chem. Phys. 113 11324.
[19] Gallo P, Rovere M and Spohr E 2000 Phys. Rev. Lett. 85 4317.
[20] Gallo P, Ricci M and Rovere M 2002 J. Chem. Phys. 116 342.
[21] Rovere M and Gallo P 2003 Eur. Phys. J.: E Soft Matter 12 77.
[22] Puibasset J and Pelleng R J M 2003 Eur. Phys. J. E: Soft Matter 12 67.
[23] Puibasset J and Pelleng R J M 2004 J. Phys.: Condens. Matter 16 S5329.
[24] Puibasset J and Pelleng R J M 2005 J. Chem. Phys. 122 094704.
[25] Cucini R, Taschini A, Ziparo C, Bartolini P and Torre R 2007 Euro. Phys. J.: Spec. Top. 141 133.
[26] Taschini A, Cucini R, Ziparo C and Torre R 2007 Phil. Mag. 87 715.
[27] Taschini A, Cucini R, Bartolini P and Torre R 2008 Europhys. Lett. 81 58003.
[28] Cucini R, Taschini A, Bartolini P and Torre R 2010 J. Mech. Phys. Solids 58 1302.
[29] Cucini R, Taschini A, Bartolini P and Torre R 2010 J. Phys.: Conf. Ser. 214 012032.
[30] Taschini A, Cucini R, Bartolini P and Torre R 2010 Europhys. Lett. 92 26005.
[31] Taschini A, Bartolini P, Marcelli A, Righini R and Torre R 2013 Faraday Discuss. 167 293.
[32] Hunt N T, Jaye A A and Meech S R 2007 Phys. Chem. Chem. Phys. 9 2167.
[33] Bartolini P, Taschini A, Eramo R and Torre R 2008 Optical Kerr Effect Experiments on Complex Liquids, a Direct Access to Fast Dynamic Processes (New York: Springer) chapter 2, pp. 73–127.
[34] Ricci M, Torre R, Foggi P, Kamalov V and Righini R 1995 J. Chem. Phys. 102 9537.
[35] Bartolini P, Ricci M, Torre R, Righini R and Santta I 1999 J. Chem. Phys. 110 8653.
[36] Torre R, Ricci M, Saielli G, Bartolini P and Righini R 1995 Mol. Cryst. Liq. Cryst. 262 391.
[37] Torre R, Tempestini F, Bartolini P and Righini R 1998 Phil. Mag. B 77 645.
[38] Ricci M, Wiebel S, Bartolini P, Taschini A and Torre R 2004 Philos. Mag. 84 1491.
[39] Torre R, Bartolini P and Righini R 2004 Nature 428 296.
[40] Taschini A, Bartolini P, Eramo R, Righini R and Torre R 2013 Nat. Commun. 4 2401.
[41] Taschini A, Bartolini P, Eramo R, Righini R and Torre R 2014 J. Chem. Phys. 141 084507.
[42] Torre R, Bartolini P and Pick R 1998 Phys. Rev. E 57 1912.
[43] Torre R, Bartolini P, Ricci M and Pick R 2000 Europhys. Lett. 52 324.
[44] Ricci M, Bartolini P, Torre R 2002 Phil. Mag. B 82 541.
[45] Prevosto D, Bartolini P, Torre R, Ricci M, Taschini A, Capaccioli S, Lucchesi M and Rolla P 2002 Phys. Rev. E 66 11502.
[46] Pratesi G, Bartolini P, Senatra D, Ricci M, Barocchi F, Righini R and Torre R 2003 Phys. Rev. E 67 021505.
[47] Hellwarth R W 1970 J. Chem. Phys. 52 2128.
[48] Slepkov A D, Hegmann F A, Zhao Y, Tykwinski R R and Kamada K 2002 J. Chem. Phys. 116 3834.
[49] Giraud G, Gordon C, Dunkin I and Wynne K 2003 J. Chem. Phys. 119 464.
[50] Bartolini P, Taschini A, Eramo R, Righini R and Torre R 2009 J. Phys.: Conf. Ser. 177 012009.
[51] Kanno H, Tomikawa Y and Mishima O 1998 Chem. Phys. Lett. 293 412.
[52] Pilla O, Fontana A, Caponi S, Rossi F, Viliani G, Gonzalez M, Fabiani E and Varsamis C 2003 J. Non-Cryst. Solids 322 53.
[53] Wöignier T, Sauvajol J, Pelous J and Vacher R 1990 J. Non-Cryst. Solids 121 206.