

Ageing of the nonlinear optical susceptibility in soft matter

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 205129

(<http://iopscience.iop.org/0953-8984/19/20/205129>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 18:48

Please note that [terms and conditions apply](#).

Ageing of the nonlinear optical susceptibility in soft matter

N Ghofraniha¹, C Conti^{2,3}, R Di Leonardo^{3,4}, B Ruzicka^{3,4} and G Ruocco^{3,4}

¹ SMC-INFM-CNR, c/o Università di Roma 'La Sapienza', Piazzale Aldo Moro 2, 00185, Roma, Italy

² Research Centre 'Enrico Fermi', Via Panisperna 89/A, 00184 Rome, Italy

³ SOFT-INFM-CNR, c/o Università di Roma 'La Sapienza', Piazzale Aldo Moro 2, 00185, Roma, Italy

⁴ Dipartimento di Fisica, Università di Roma 'La Sapienza', Piazzale Aldo Moro 2, 00185, Roma, Italy

E-mail: neda.ghofraniha@roma1.infn.it

Received 28 December 2006, in final form 4 February 2007

Published 25 April 2007

Online at stacks.iop.org/JPhysCM/19/205129

Abstract

We investigate the nonlinear optics response of a colloidal dispersion undergoing dynamics slowing down with age, by using Z -scan and dynamic light scattering measurements. We study the high optical nonlinearity of an organic dye (rhodamine B) dispersed in a water–clay (Iaponite) suspension. We consider different clay concentrations (2.0–2.6 wt%) experiencing dynamics arrest. We find that (i) the concentration dependent exponential growth of both *mean relaxation time* and *nonlinear absorption coefficient* can be individually scaled to a master curve and (ii) the scaling times are the same for the two physical quantities. These findings indicate that the optical nonlinear susceptibility exhibits the same ageing universal scaling behaviour, typical of disordered out of equilibrium systems.

1. Introduction

Complex systems undergoing glass/gel transition (including soft materials) are characterized by an exponentially large number of metastable states [1], while staying out of equilibrium and taking a huge amount of time to reach a stable state (depending on the initial conditions in which the sample is prepared). This very slow relaxation is called *ageing*: the older systems relax in a slower manner than the younger ones. The glass properties are therefore strongly related to the age or *waiting time* t_w . During ageing, the fluctuation-dissipation theory (FDT) does not strictly hold, but a generalization has been recently proposed [2] and numerically tested [3, 4]. According to this generalization the temperature, appearing in the FDT as a proportionality factor, between response and correlation function, is substituted by an effective temperature, higher than the thermal bath one. In ageing systems, which are subject to fluctuations larger

than the corresponding equilibrium ones, also nonlinear effects are expected to be strongly sensitive to the presence of dynamics slowing down with age.

In this respect, nonlinear optics experiments in complex systems can be considered as a promising tool for studying these out of equilibrium dynamics. However, while on one hand the time dependent behaviour of the nonlinear optical coefficients has been considered since the beginning of nonlinear optics [5] and various authors have recently reported detailed investigations and new models for the time dynamics of specific nonlinear optical effects (like modulational instability or soliton formation, [6–9]), on the other, no studies have been reported for the ageing behaviour of the nonlinear optical coefficients of colloids.

With the aim of studying these effects it is hence useful to consider a complex material undergoing structural arrest with nonlinear optical response strongly affected by this aggregation process. We report on an experimental investigation of a laponite clay powder dispersed in the dye rhodamine B aqueous solution, displaying both high thermal nonlinear optical response and dynamics arrest characteristic of the clay suspension. Clear experimental evidence and quantitative assessment of ageing of the nonlinear susceptibility are reported.

2. Sample preparation

Rhodamine B (RhB) solution in deionized water ($\text{pH} = 7$) was prepared at 0.6 mM concentration. Laponite powder, supplied by Laporte Ltd, was then dispersed in RhB solution, stirred vigorously until the suspensions were cleared and filtered through 0.22 μm pore size Millipore filters. We consider the starting ageing time ($t_w = 0$) as the time when the suspension was filtered. We prepared four different samples at 2.0, 2.2, 2.4 and 2.6 wt% clay concentrations and on each of them we performed contemporaneously the two different experiments (dynamic light scattering and Z-scan) described below.

Rhodamine molecule adsorption on clay discs is well known [17] and, indeed, for our samples we estimated about 60 RhB molecules for each laponite platelet, far fewer than the maximum allowed adsorption sites (about 500 sites as provided by the Laporte Ltd data sheet); consequently all dye particles in solution can be considered as attached to the colloids. Moreover the presence of rhodamine molecules in the sample increases the ionic force causing faster colloid aggregation.

3. Evidence of ageing

We utilized homodyne–dynamic light scattering (DLS) measurements, in order to provide clear evidence of the nonstationary dynamics in our samples, and for their quantitative characterization. We used a standard optical set-up based on a He–Ne ($\lambda = 632.8$ nm) 10 mW laser, a monomode optical fibre and a photomultiplier detector in combination with a homemade correlator [10]. We observed directly the normalized intensity $I(q, t)$ correlation function $g_2(q, t) = \langle I(q, t)I(q, 0) \rangle / \langle I(q, 0) \rangle^2$, with q the modulus of the scattering wavevector defined as $q = (4\pi n/\lambda) \sin(\theta/2)$, the scattering angle being $\theta = 90^\circ$ in our experiment. Homodyne–DLS data were fitted assuming a correlation function made from the square of the sum of an exponential function with relaxation time τ_1 and a stretched exponential function with relaxation time τ_2 and stretching coefficient β , as reported in [11] and commonly used in photocorrelation measurements analysis for liquid-like (ergodic) samples.

Examples of homodyne–DLS data, together with their best fits, are shown in figure 1 as symbols and full lines at the indicated waiting times. The mean relaxation time τ_m ,

$$\tau_m = \tau_2 \beta^{-1} \Gamma(\beta^{-1}), \quad (1)$$

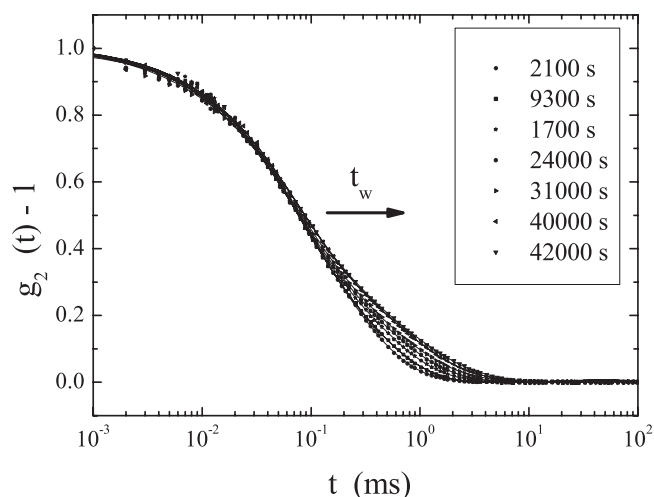


Figure 1. DLS–homodyne correlation function data for laponite 2.2 wt% dispersion in RhB 0.6 mM water solution for different waiting times t_w and corresponding fits (full lines); see the text.

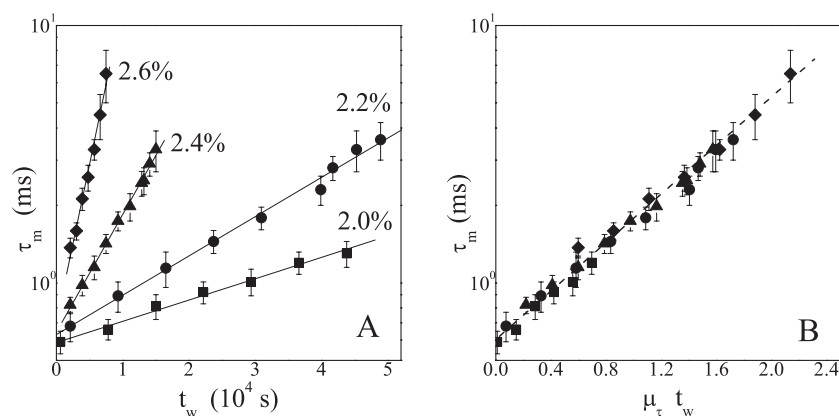


Figure 2. Mean relaxation time τ_m versus waiting time t_w (A) and versus the scaled variable $\mu_\tau t_w$ (B) on a log–linear scale at various clay concentrations; continuous lines in (A) are the fitted curves.

with $\Gamma(x)$ the usual Euler gamma function, can be taken as a parameter representing the slow dynamics behaviour of the correlation function, while the fast dynamics correlation time τ_1 turns out to be quite constant for our clay concentrations during the gelation process, as described elsewhere [12]. In figure 2(A) the τ_m versus t_w data on a log–linear scale exhibit the common exponential growth behaviour—valid for samples far from dynamics arrest— $\tau_m(t_w) = \tau_0 \exp(\mu_\tau t_w)$ (full line through the data) of the mean relaxation time for different laponite concentrations. These results reflect clearly the ageing behaviour of the material, that corresponds to t_w dependent relaxation times. The specific t_w dependence of $\tau_m(t_w)$ leads us to consider a scaling law, that makes all data collapse onto a single master curve. This curve is reported in figure 2(B) where the DLS derived $\tau_m(t_w)$ data are shown as a function of $\mu_\tau t_w$.

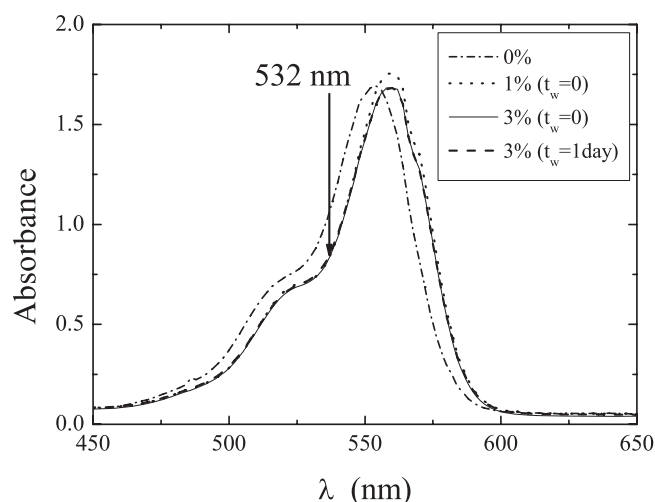


Figure 3. Absorption spectra of RhB 2.4×10^{-5} M water solution (0%) and laponite dispersions in RhB 2.4×10^{-5} M solution at different clay concentrations and waiting times.

4. Linear absorption measurements

In order to show that ageing has no role in the *linear* optical response of our system, we measured the linear absorption spectra with a UV–visible spectrometer. In figure 3 we report representative absorption spectra of RhB 2.4×10^{-5} M water solution at 0, 1 and 3 wt% clay concentrations, showing that the linear absorption of RhB changes in the presence of laponite and it can be considered independent of the colloid concentration and the waiting time. These samples were prepared following the same procedure as described above, using a lower concentration RhB solution to avoid saturation in absorbance spectra. The linear absorbance coefficient α_0 for the 0.6 mM RhB solution was also found to be $\alpha_0 \simeq 6.2 \text{ mm}^{-1}$ and $\alpha_0 \simeq 4.8 \text{ mm}^{-1}$ for all our RhB–laponite dispersions, by measuring the sample transmission at $\lambda = 532 \text{ nm}$, confirming the absence of ageing in the linear optical absorption.

5. Ageing of the nonlinear susceptibility

By using the Z-scan technique [13] we measured both nonlinear absorption and refraction: the sample was moved along the z -axis through the focal point of the input Gaussian beam, and the transmitted power was measured, as a function of z in the far field using a photodiode behind a small calibrated pinhole. In our experiments we used a CW pumped diode laser operating at power $P = 10 \text{ mW}$ and wavelength $\lambda = 532 \text{ nm}$. The beam was focused by means of a 75 mm focal length lens giving a $20 \mu\text{m}$ beam waist radius w_0 and a $I_0 = 8 \times 10^6 \text{ W m}^{-2}$ beam central intensity at the focus ($z = 0$). A photodetector, at distance 310 mm from the lens focus, was used to probe the light power behind a 2 mm aperture and the sample, in 1 mm thick cell, was scanned across the focus with a 5 cm translation stage.

In figure 4 we show as an example the Z-scan curves of RhB–2.2 wt% clay dispersion for increasing t_w correspondingly to the DLS correlation functions (shown in figure 1). The dynamics slowing down for the system clearly affects the nonlinear response. In figure 4 we also report the 0.6 mM RhB solution (without clay) transmittance curve (open symbols). Similarly to the linear absorption shown in figure 3, the nonlinear optical response is influenced

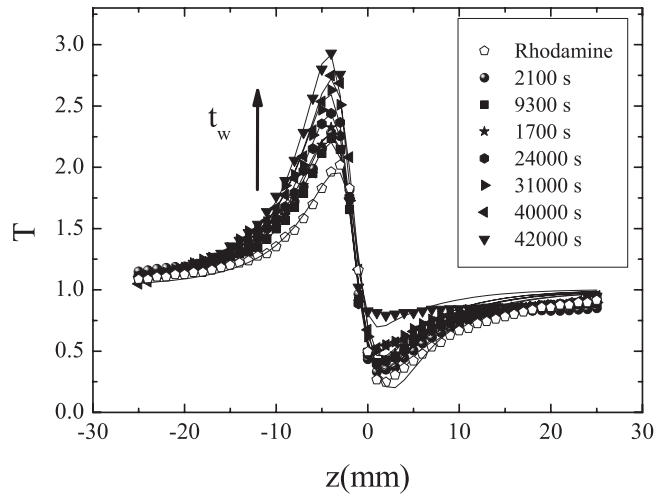


Figure 4. Z-scan curves of laponite 2.2 wt% dispersion in RhB 0.6 mM water solution for different waiting times t_w (symbols) and corresponding fits (full lines); see the text. We also report the RhB 0.6 mM scan (open symbols).

by the presence of laponite platelets, while, more interestingly, contrarily to the linear absorbance, the nonlinear susceptibility does actually vary, undergoing dynamics slowing down.

The transmittance curve shape in figure 4 corresponds to a defocusing nonlinear system due to thermal lens-like behaviour, well known in dye solutions. In fact temperature variation in presence of light absorption [14] causes a local refractive index gradient due to local solvent density change. To fit the experimental data we used the analytical description of the Z-scan method reported in [15], based on the Fresnel–Huygens principle, here enriched by including sample nonlinear absorbance effects on transmittance, not considered previously.

The following equations govern laser beam phase $\Phi(\zeta)$ and intensity $I(\zeta)$ variations inside a nonlinear sample:

$$\frac{dI(\zeta)}{d\zeta} = -\alpha(I_0)I(\zeta) \tag{2}$$

$$\frac{d\Phi(\zeta)}{d\zeta} = kn(I(\zeta)) \tag{3}$$

where $\alpha(I_0) = \alpha_0 + \alpha_2 I_0$, with α_0 the linear absorption coefficient, and α_2 the nonlinear coefficient, $n(I(\zeta)) = n_0 + n_2 I(\zeta)$, with n_0 , the linear refractive index, and n_2 the Kerr coefficient. In (2) and (3) ζ is the coordinate inside the sample along the z -direction and k the wavenumber. We used the expression for the transmittance reported in [15] and by solving equations (2) and (3) for a TEM₀₀ electric incident field intensity distribution and by determining the electric far field E_C , the transmittance results as

$$T = \frac{|E_C(z, \Phi_0(z))|^2}{|E_C(z, 0)|^2} = \left| \frac{\xi(z)\Gamma(\xi(z), i\Phi_0(z))}{[i\Phi_0(z)]^{\xi(z)}} \right|^2. \tag{4}$$

In equation (4) $\Gamma(x, y)$ is the lower incomplete gamma function,

$$\xi(z) = \frac{1}{2} \left[\frac{i}{z_0} \left(z + \frac{z^2 + z_0^2}{d - z} \right) + 1 \right], \tag{5}$$

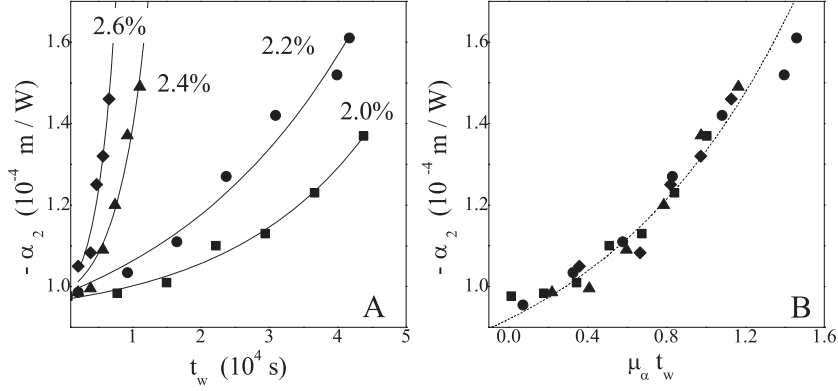


Figure 5. Nonlinear absorption coefficient α_2 versus waiting time t_w (A) and versus the scaled variable $\mu_\alpha t_w$ (B) at various clay concentrations; continuous lines in (A) are the fitted curves.

Table 1. Timescaling parameters: μ_τ from DLS data and μ_α from Z-scan data.

Clay (wt%)	μ_τ	μ_α
2.0	$(1.9 \pm 0.2) \times 10^{-5}$	$(2.3 \pm 0.2) \times 10^{-5}$
2.2	$(3.5 \pm 0.1) \times 10^{-5}$	$(3.3 \pm 0.2) \times 10^{-5}$
2.4	$(10.5 \pm 0.2) \times 10^{-5}$	$(10.9 \pm 0.5) \times 10^{-5}$
2.6	$(28 \pm 1) \times 10^{-5}$	$(17 \pm 1) \times 10^{-5}$

$$\Phi_0(z) = \frac{kn_2 \Lambda I_0}{1 + z^2/z_0^2}, \quad (6)$$

where $z_0 = 2kw_0^2$, d is the distance between the observation point and the beam waist and Λ is the effective sample thickness

$$\Lambda = \frac{1 - \exp[-\alpha(I_0)L]}{\alpha(I_0)}, \quad (7)$$

with L the actual sample thickness. We used (4) as the fitting expression for estimating both n_2 and α_2 ; the latter is shown in figure 5(A) versus t_w for different clay concentrations, while from our analysis n_2 values (not reported) are practically unchanged during the ageing time. Indeed, the nonlinear refractive index coefficient n_2 is less sensitive to matter structural changes, as explained below.

On the other hand, it is evident from figure 5(A) that the nonlinear absorption (α_2) is clearly influenced by the clay structural evolution.

According to the *theoretical analysis* reported below, we fitted the Z-scan curves using the function $\alpha_2 = a + b \exp(\mu_\alpha t_w)$, with a , b and μ_α as free parameters. The fitting curves are reported in figure 5(A) as full lines. In figure 5(B) the same data collapsed onto a single master curve are reported as a function of the scaled time $\mu_\alpha t_w$. The timescaling parameters, μ_τ and μ_α , obtained respectively from DLS and Z-scan data, are shown in table 1. It can be noticed that μ_τ and μ_α values are comparable except for the highest concentration, most likely due to the different durations of the experiments (i.e. 5 min for photocorrelation and about 15 min for Z-scan single measurement), which are not negligible in the presence of a fast arrest process.

6. Theoretical analysis

At microscopic level, the observed data can be interpreted by taking into account the so called Ludwig–Soret effect [16], i.e. the laponite platelet concentration (Δc) gradient induced by the presence of a temperature gradient. Specifically, as the value of ∇c depends—at fixed ∇T —on the mass self-diffusion coefficient, in turn strongly related to the ageing time, we expect a waiting time dependence of $\nabla(\Delta c)$. This mass diffusion process strongly affects the rhodamine molecule concentration due to the adsorption on clay discs, as reported in *sample preparation*. Indeed, clay–dye concentration variation causes the evident absorption coefficient change during the dynamics arrest process, whereas particle diffusion does not influence refractive index (n) change due to the slight difference between laponite and water indices of refraction.

The previous argument can be put on a quantitative basis by considering the absorption as due to $N(t_w, I_0)$ dye particles varying in time due to matter and thermal diffusion processes and yielding an overall absorption coefficient

$$\bar{\alpha}(t_w, I_0) = N(t_w, I_0)\alpha(I_0). \quad (8)$$

Since $\alpha = \alpha_0 + \alpha_2 I_0$, expanding $N(t_w, I_0)$ at first order in I_0 , and retaining only the terms linear in I_0 , equation (8) reads

$$\bar{\alpha}(t_w, I_0) = N_0\alpha_0 + \left[N_0\alpha_2 + \alpha_0 \left(\frac{\partial N}{\partial I_0} \right) \right] I_0, \quad (9)$$

From equation (9), the time dependent nonlinear absorption coefficient is then written as

$$\bar{\alpha}_2(t_w) = N_0\alpha_2 + \alpha_0(\partial N/\partial I_0) \quad (10)$$

which undergoes ageing because of the t_w dependence of $(\partial N/\partial I_0)$, i.e. because of the variation of the particle number due to diffusive effects. To determine the waiting time dependence of $\partial N/\partial I_0$ in (10), we rely on the stationary solutions of both the heat equation and the mass flow continuity equation reported in [16], which give the following radial profile for the concentration variation $\Delta c(r, t_w)$ ($\propto N(r, t_w)$):

$$\nabla^2(\Delta c(r, t_w)) = \frac{2\alpha_0 I_0}{\kappa} \frac{D_T}{D(t_w)} \bar{c}(1 - \bar{c}) e^{-2r^2/w_0^2} \quad (11)$$

where κ is the thermal conductivity, $2\alpha_0 I_0 \exp(-2r^2/w_0^2)$ the Gaussian beam source term, \bar{c} the average colloid concentration, $D(t_w)$ the mass diffusion coefficient and D_T the thermal diffusion coefficient. In writing equation (11) we assume that the concentration gradient time dependence is contained uniquely in the mass diffusion coefficient, while D_T is assumed to be unchanged, and all other terms are constant. Solution of equation (11) yields the following difference of concentration variation from the beam centre:

$$\Delta c(r, t_w) - \Delta c(0, t_w) = c_0 \left[E_i \left(\frac{-2r^2}{w_0^2} \right) - \ln \left(\frac{-2r^2}{w_0^2} \right) - \gamma \right] \quad (12)$$

where

$$c_0 = \frac{D_T \alpha_0 I_0 w_0^2 \bar{c}(1 - \bar{c})}{2\kappa D(t_w)}, \quad (13)$$

$E_i(x)$ denotes the exponential integral function and γ the Euler constant. The maximum difference in concentration within the sample in a confined geometry of height H —given by (12)—is

$$c(t_w) = \Delta c(H, t_w) - \Delta c(0, t_w) = c_0 \left[E_i \left(\frac{-2H^2}{w_0^2} \right) - \ln \left(\frac{-2H^2}{w_0^2} \right) - \gamma \right]. \quad (14)$$

Finally, from equations (14) and (10),

$$\bar{\alpha}_2(t_w) = N_0\alpha_2 - C \frac{\alpha_0}{D(t_w)} \quad (15)$$

where the constant C contains all time independent terms in (14) and it also accounts for the proportionality relation $c(t_w) \propto N(t_w)$. Expression (15), considering that $D \propto \tau_m^{-1}$ with τ_m the relaxation time previously introduced, provides the t_w dependent behaviour of $\bar{\alpha}_2$ as a sum of a constant and an exponentially growing term, justifying the fitting expression previously utilized.

In conclusion, we studied the ageing of the nonlinear optical susceptibility in a water–RhB–clay solution. The dye molecules are adsorbed on the clay surface, creating a complex medium with a high optical nonlinearity capable of performing a liquid–gel transition on a timescale μ_τ^{-1} , dependent on the clay concentration. To analyse the waiting time dependence of the Z-scan curves, we derived equations (4)–(6), which generalize the result obtained in [15] to the case where photon absorption is present. We showed that, at variance with the linear optical properties, which are not affected by ageing, (i) the nonlinear optical susceptibility actually ages, (ii) its t_w dependence is only a function of a concentration dependent timescale μ_α^{-1} , (iii) this timescale is the same as that for the waiting time dependence of the relaxation time measured using DLS, and (iv) the waiting time dependence can be microscopically explained assuming a thermodiffusive behaviour of the clay platelets (Soret effect).

Acknowledgments

We thank A Martinelli for the UV–visible absorption spectra, E Del Re, R Piazza, F Sciortino, S Trillo and L Zulian for interesting discussions and useful suggestions.

References

- [1] Mézard M, Parisi G and Virasoro M A 1987 *Spin Glass Theory and Beyond* (Singapore: World Scientific)
- [2] Cugliandolo L F and Kurchan J 1993 *Phys. Rev. Lett.* **71** 173
- [3] Cugliandolo L F and Kurchan J 1975 *J. Phys. A: Math. Gen.* **27** 5749
- [4] Di Leonardo R, Angelani L, Parisi G and Ruocco G 2000 *Phys. Rev. Lett.* **84** 6054
- [5] Shen Y R 1984 *Principle of Nonlinear Optics* (New York: Wiley–Interscience)
- [6] Wright E M, Mansuripur M, Liberman V and Bates K 1999 *Appl. Opt.* **38** 5785
- [7] Conti C, Trillo S and Ruocco G 2005 *Phys. Rev. Lett.* **95** 183902
- [8] Streppel U, Michaelis D, Kowarschik R and Bräuer A 2005 *Phys. Rev. Lett.* **95** 073901
- [9] Del Re E and Palange E 2006 *J. Opt. Soc. Am. B* **23** 2323
- [10] Ianni F, Di Leonardo R, Gentilini S and Ruocco G 2006 *Phys. Rev. E* **75** 011408
- [11] Ruzicka B, Zulian L and Ruocco G 2004 *Phys. Rev. Lett.* **93** 258301
- [12] Ruzicka B, Zulian L and Ruocco G 2004 *J. Phys.: Condens. Matter* **16** S4993
- [13] Bahae M S, Said A A, Wei Y H, Hagan D J and van Stryland E W 1999 *IEEE J. Quantum Electron.* **26** 760
- [14] Sinha S, Ray A and Dasgupta K 2000 *J. Appl. Phys.* **87** 3222
- [15] Samad R E and Viera N D 1998 *J. Opt. Soc. Am. B* **15** 2742
- [16] Rusconi R, Isa L and Piazza R 2004 *J. Opt. Soc. Am. B* **21** 605
- [17] Arbeloa F L, Martinez J M H, Arbeloa T L and Arbeloa I L 1998 *Langmuir* **14** 4566