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Simultaneous Characterization of Optical Turbidity, Specific Heat and Latent Heat of Liquid Crystals Nanocolloids

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We report on calorimetric measurements carried out in an upgraded Photopyroelectric set up enabling a frequency dependence detection of the specific heat and of the latent heat exchanged over first order transitions as well as the simultaneously determined optical turbidity obtained from light scattering measurements. It has been applied to the Nematic-Isotropic transition of 8CB liquid crystal confined in a silica nanoparticle network, where the specific heat shows a double peak structure. The larger strain involved with the nematic phase nucleating over the low temperature peak, due to the interaction of the liquid crystal molecules with the network, induces a considerable lower latent heat than the one involved with the quasi bulk like nematic material nucleating over the higher temperature peak. Moreover, the frequency dependent measurements have shown a substantially different dynamics of the nematic nucleating over each of the peaks. The determined nematic correlation length, obtained from turbidity measurements, showed the characteristic two step-like nematic nucleation process previously reported only for the specific heat.

Keywords Liquid crystal nanocolloids; thermal and optical parameters

Introduction

Thermal and optical characterizations are often used in nanostructured material investigations. In particular they are used, for example, in physical gels for the study of the thermodynamics of the sol-gel transition and of the modification of the optical

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properties induced by the gel formation. Examples are the liquid crystal (LC) gels obtained using low molecular mass organogelators [1] and nanocolloidal dispersions of particles in an anisotropic host [2], which have proved to be very interesting both as model systems and for applications.

Strong temperature dependence of the optical and thermal parameters may be expected in the vicinity of the transition temperature when probing phase transitions of the hosted medium confined in a network. High temperature resolution measuring configurations are then required. Moreover, the experimental conditions in the different measuring systems, in terms of temperature resolution and also of sample composition, should be as similar as possible for a homogeneous comparison of the different characterizations. For example, the Nematic – Isotropic (NI) transition in silica nanoparticles (aerosil) dispersed LC [2–5], where the LC molecules are aligned homeotropically at the particle surface, has attracted considerable interest because of the double peak feature shown by the specific heat over the two-phase coexistence region. This indicated that the transition occurred in two steps: when cooling the sample, bulk-like nematic material nucleates first over the high temperature peak (HTP) while more strained nematic, lying close to the particle surfaces, nucleates over the low temperature peak (LTP). In addition, recent results showed a different vs. frequency behaviour observed at each peak [6]. The determination of the frequency dependence of also the exchanged latent heat, associated with the known phase inter-conversion characteristic time [2], could also be useful to possibly explain the observed results. Finally, high temperature resolution polarization microscopy images [3], obtained simultaneously with calorimetric measurements performed in a photopyroelectric (PPE) setup [4], showed a non monotonic evolution of the nematic texture when cooling the sample from the isotropic phase, correlating well with the double peak feature observed in the specific heat. The nematic domains were found to initially grow over the HTP region until they touched each other, and to break into smaller ones over the LTP region. The corresponding LC texture evolved from a coarse grain to a fine grain structure, implying a change in the nematic correlation length when crossing to the LTP region. This seemed in contradiction with the measured values of the nematic length, ξ, obtained by scattering measurements carried out on a sample that had showed the double peak feature in the specific heat [5], and it was concluded that the double peaked feature on the specific heat was basically due to a change in the rate of the nucleation of nematic material with respect to temperature, in the two-phase coexistence region. It was associated to a crossover of the effect of disorder on the LC, from random dilution to random field regimes, with no change in the domain size.

In an effort to try and provide an overall picture of the processes occurring over the two peak region of the NI transition of the LC nanocolloid, we report on: 1) a procedure enabling to obtain an indirect determination of the frequency dependence of the latent heat exchanged over each of the previously mentioned two peaks, as well as that of the specific heat; 2) scattering measurements, performed simultaneously with those of high temperature resolution calorimetry, to achieve highly temperature resolved characterizations of the optical as well as the thermal properties, and an accurate correlation of the different measured quantities at the various temperatures. The sample texture inspection [4] was also carried out during the experiment.

Experimental and Results

Photopyroelectric calorimetry (PPE) is a high resolution a.c. technique which has been proved to be very useful in the study of phase transitions in LC [7]. It enables frequency dependent measurements of the thermal parameters and the correlation of the thermal characterization with measurements of optical properties of the material. This is due to the optical access to the sample granted by such technique, which has already been exploited to perform additional polarization microscopy observations of the investigated material [8] and can be further used also for simultaneous scattering measurements.

For the latent heat detection performed as a function of frequency and aerosil concentration the sample was contained in a 100 μm thick cell covered by a 300 μm thick $LiTaO_3$ pyroelectric transducer. When also scattering measurements were performed, a 30 μm cell was used, covered by the pyroelectric transducer with transparent ITO electrodes. In the latter case, only half of the cell surface in contact with the sample is coated with a Ti thin layer to ensure light absorption. The cell is illuminated by two distinct He-Ne laser beams, 3 mm apart, whose intensities are modulated at different frequencies in order to avoid any interference in the signals they give rise to. The first beam (30 Hz) provided the heating necessary for the PPE signal generation while the second (1.5 kHz), incident on the transparent side of the cell, probed the sample optical turbidity [10]. The cells were contained in an oven where the sample is heated at a rate typically of 1 mK/min.

Latent Heat Detection

Figure 1 helps illustrating the principle according to which latent heat was detected. It shows the results for the amplitude, A, and the phase, ϕ, of the PPE signal, obtained for a particle concentration (mass of particles/volume of LC) of 0.02 gm/cm^3 at a frequency of 2 Hz, over the first order NI transition region. The inset reports the

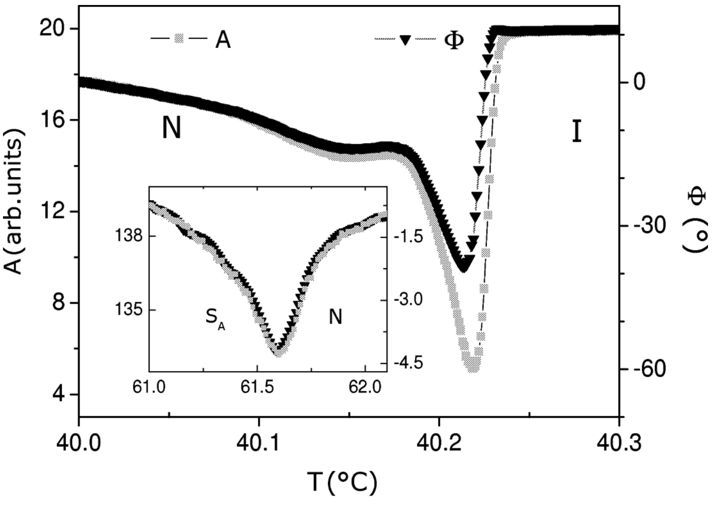

Figure 1. PPE signal amplitude (A) and phase (ϕ) over NI coexistence region of 8CB LC nanocolloid with 0.02 gm/cm^3 particle concentration. Inset: A and ϕ over S_A-N transition in $\bar{8}S5$ LC.

A and ϕ data obtained over the second order Smectic-A–Nematic phase transition in pure $\bar{8}S5$ where no latent heat is involved. For both transitions, only the specific heat is known to show critical behaviour, while the thermal conductivity is known to remain smooth [7]. For the second order transition, A and ϕ show, qualitatively, very similar changes over the transition region reflecting the specific heat change likewise affecting the two profiles. On the contrary, over the NI transition of the LC nanocolloid, A and ϕ show different profiles over the transition. Such difference can only be ascribed to latent heat exchange in the present case and, in general, also to other kind of enthalpy exchange, as previously reported [9]. So we tried to single out the relative profile of the latent heat exchange over the two peaks, as well as that of the effective specific heat, by processing the amplitude and phase data in terms of an expression for the complex PPE signal which included effects of latent heat exchanges as described in detail in ref. [10]. Figure 2 shows the profiles of effective specific heat, $c_{eff}(T)$, and of the latent heat term, $I_L(T)$, obtained according to such an approach. The double peak featured is evident for both quantities. It can be observed that the peak position for $c_{eff}(T)$ and $I_L(T)$ are not coincident. The temperature relative to the peak in I_L correspond to the flexing point of the steep part of $c_{eff}(T)$, that is where the nematic nucleation rate with respect to temperature is largest. Moreover the presence of the LTP in c_{eff}, indicates that a relevant fraction of nematic material has nucleated over that temperature region. In spite of this, the latent heat involved over the LTP is considerably smaller than that involved over the HTP.

The temperature range of non zero I_L values corresponds to the NI two-phase coexistence region where the relative qualitative profiles of $A(T)$ and $\phi(T)$ are different. The range where this occurs can also be considered as a marker of the coexistence region and well agrees with the one determined by the simultaneously performed polarizing microscopy observation (not shown). The determination of I_L, though not providing absolute values of the latent heat, gives relative estimates of the latent heat exchanged, for example, in samples with different particle concentration and, in particular, at different frequencies to study the dynamics, as

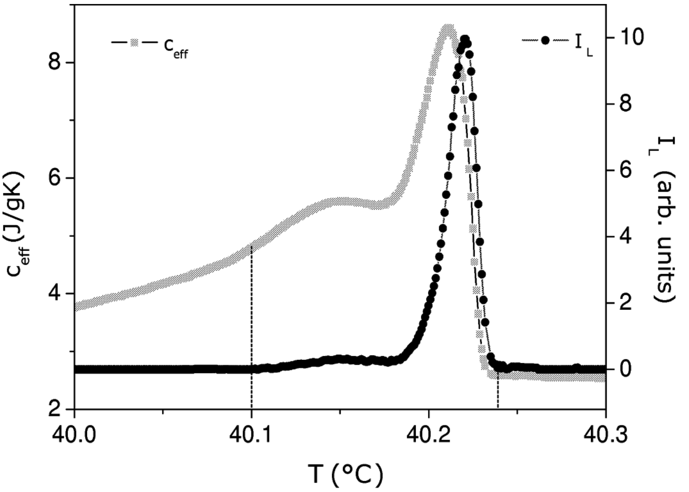

Figure 2. c_{eff} and I_L (see text) profiles over NI coexistence region of 8CB LC nanocolloid with 0.02 gm/cm^3 particle concentration. Coexistence region within vertical lines.

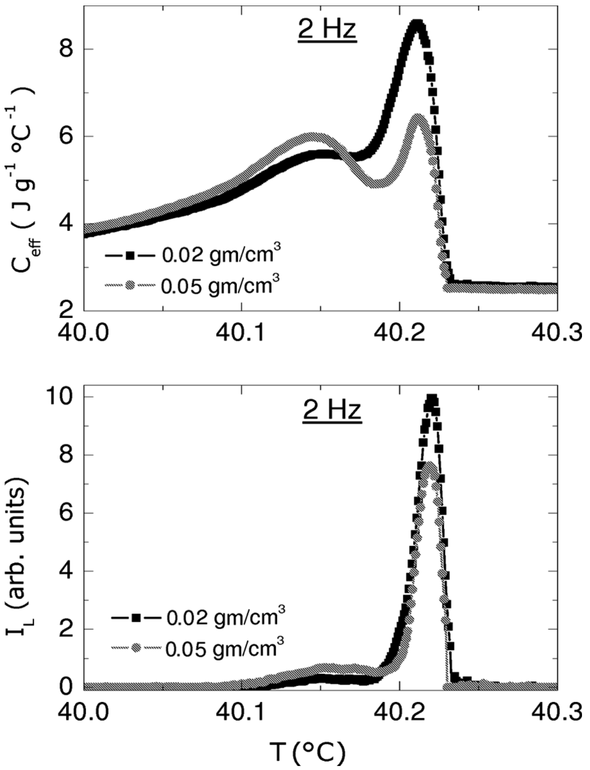

Figure 3. c_{eff} and I_L (see text) profiles over NI coexistence region of 8CB LC nanocolloid at 2 Hz with 0.02 and 0.05 gm/cm^3 particle concentration.

shown in Figures 3 and 4. Figure 3 reports the I_L and c_{eff} profiles obtained for samples with particle concentrations of 0.02 gm/cm^3 and 0.05 gm/cm^3, at 2 Hz. The larger particle concentration leads to a decrease and an increase, respectively, of the peak values of c_{eff} over the HTP and LTP, this indicating an increased fraction of nematic material nucleating over the LTP due to the reduction of the mean pore size in the silica particle network [2]. The latent heat peaks show similar corresponding changes over the two regions, the one corresponding to the HTP still remaining substantially larger than the one obtained at the LTP. Concerning the lower values of I_L over the LTP for both concentrations, it has been reported that, in such a system, the detected latent heat averaged over both peaks decreases over the NI transition with increasing particle concentration and, therefore, average strain in the nucleated material [2,11]. Such an aspect has been also predicted theoretically [12,13]. The nematic material nucleating over the LTP is affected by considerably larger strain than that at the HTP. In fact, when the sheath of material close to the particles turns nematic over the LTP, with the molecular director constrained normal to the particle surface, the large strain involved induces fragmentation of the domains and affects the nature of the transition. It is therefore not surprising to find considerable lower latent heat involved over the LTP with respect to the HTP. It is worthwhile pointing out that the application of the present method has provided the possibility and the resolution to monitor the relative latent heat involved over each of the peaks, unlike previous reports where the measured latent heat corresponded to

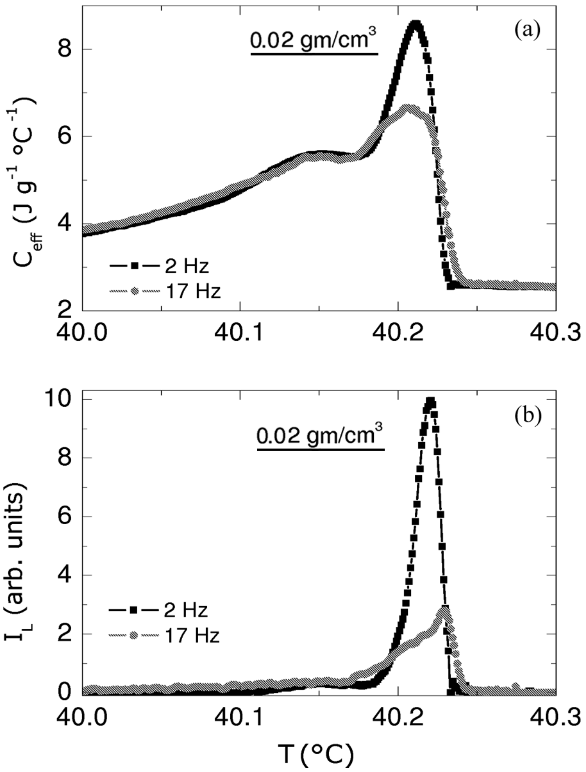

Figure 4. c_{eff} and I_L (see text) profiles over NI coexistence region of 8CB LC nanocolloid with $0.02\,\mathrm{gm/cm^3}$ particle concentration at 2 and 19 Hz.

the one averaged over both peaks [2,11]. This capability is important also for the results shown in Figure 4 where a comparison of what obtained at different frequencies (2 and 17 Hz) for the sample with particle concentration of $0.02\,\mathrm{gm/cm^3}$ is reported. As previously mentioned, in a.c. measurements the detected values of both I_L and c_{eff} may be frequency dependent over a first order transition because of the characteristic time involved in the phase inter-conversion [2]. A substantial decrease with frequency occurs for both such quantities over the HTP while negligible effects are observed over the LTP in the present frequency range. So while the inter-conversion dynamical effect clearly affects the HTP feature, no effect is detectable over the LTP. This can imply that either the phase inter-conversion characteristic time has substantially been changed by the considerable strain over the LTP or that the heat exchange giving rise to I_L over such a peak could be caused also by a mechanism different from latent heat, such as, for example, enthalpy exchange associated with relaxing strain as observed over the Hexatic-B–Smectic-A transition in pure 65OBC [9]. These results agree with the previously reported ones indicating different dynamics of the processes occurring over the two peaks [6].

Scattering Measurements

Figure 5 shows the simultaneously detected probe beam transmission I_T/I_0 and PPE signal amplitude A obtained when cooling the sample over the N-I transition.

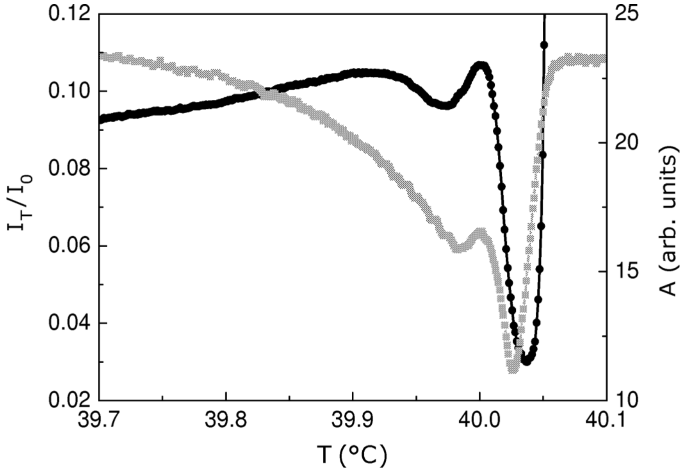

Figure 5. Transmission (I_T/ I_0, black symbols) and PPE signal amplitude (A, grey symbols) vs. temperature, simultaneously measured on a sample a concentration of 0.02 g/cm^3.

The double step feature, corresponding to the double peak in the specific heat, is evident in both the detected quantities. Figure 6a shows the $c_{eff}(T)$ and $I_L(T)$ profiles while Figure 6b shows the ones relative to the optical turbidity τ and nematic

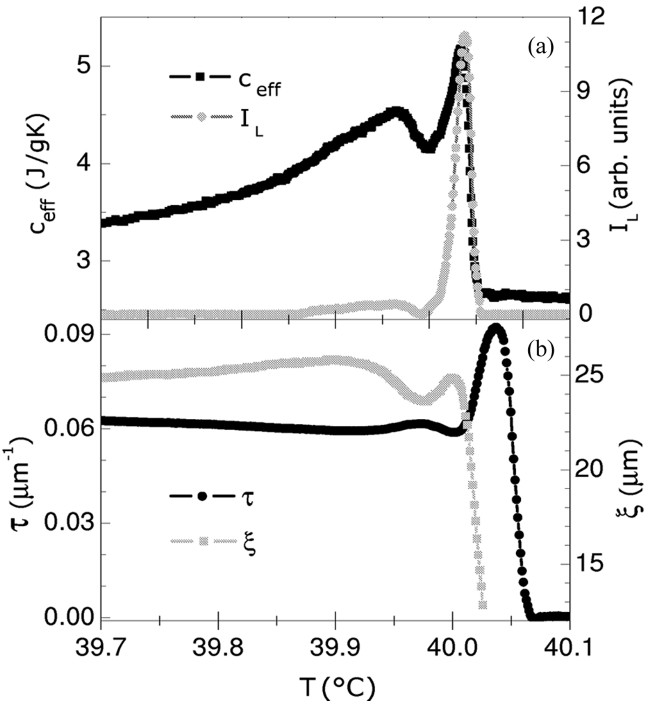

Figure 6. c_{eff} and I_L (see text) (a) and optical turbidity τ and nematic correlation length χ (b), vs. temperature, obtained from the data reported in Figure 5.

correlation length ξ. A double step-like feature is clearly shown in the turbidity profile, similar to the one observed in the specific heat. We have limited the evaluation of ξ only in the temperature region where the sample texture images (not shown) showed that the available volume for free growth of the nematic domains almost saturated. We could thus adopt a uniform profile for the nucleated nematic volume fraction Φ. In fact, in such a range, the residual latent heat value is small and only minor changes in the $\Phi(T)$ profile should therefore be expected upon further cooling. Details of the model adopted for the evaluation of ξ are reported in refs. [14,15]. The two-step process appearing in the thermal parameters and turbidity profiles, in the present case is also evident in the calculated profile of the correlation length. Outside the coexistence region, the obtained saturation value, $\xi \approx 25\,\mu\text{m}$ in the nematic phase is very close to the one reported for 6CB LC with very similar concentration of aerosil particles [15]. We have also calculated $\xi(T)$ adopting a non uniform $\Phi(T)$, obtained by integrating the latent heat relative profile shown in Figure 3a, similarly to the procedure adopted in ref. [5]. Though with different absolute values in the vicinity of the double step feature, $\xi(T)$ (not shown) qualitatively maintained a two-step like profile, despite a variation in the rate of change of $\Phi(T)$ with temperature (not shown) observed over the LTP region, similar to that reported in ref. [5]. We therefore believe that the $\Phi(T)$ behaviour alone cannot account for the two-step like profile observed in the specific heat, as suggested in ref. [5], nor in that observed in the optical turbidity τ in the present work.

We have obtained the same two-step like behaviours in ξ also for larger particle concentrations, with the saturation values in the nematic phases also approaching the corresponding ones reported in ref. [15].

If the profiles of the various quantities reported in Figures 6a and 6b are compared, the following scenario occurring over NI transition can be proposed. When cooling from the isotropic phase, the system enters the two phase coexistence region where the bulk-like nematic domains nucleate and expand while their number rapidly increases giving rise to the fast increase of both I_L and τ, the latter reaching a maximum value where the expanding single domains tend to saturate the available volume for their free growth. Correspondingly, c_{eff} is also found to grow rapidly with the steep part of its profile corresponding to the maximum of I_L where the release of latent heat is largest. Upon further cooling, the nucleated nematic domains start to coalesce thus leading to a local maximum of ξ, or equivalently to a local minimum of τ, due to the increased optical homogeneity of the sample. At lower temperature, also the LC close to the particle surface, which has a lower transition temperature because of its disorder, starts nucleating in strained nematic domains, as confirmed by the renewed increase of I_L and c_{eff}, which then break into smaller ones relieving the strain and giving rise to the observed fine-grained texture [3]. Over such temperature range, I_L and c_{eff} approach the low temperature maximum value while ξ reaches the local minimum. At still lower temperatures the nematic correlation length tends towards the saturation value in the N phase, compatible with the given concentration of aerosil particles. It is also interesting to point out that the low temperature peaks of I_L and c_{eff} are broader towards the lower temperature region with respect to τ. In our opinion, as the temperature is lowered beyond the LTP, the average nematic domain size nucleating in the vicinity of the particle surface cannot substantially change, since it is strongly limited by the LC molecules pinning on the particle surface. The turbidity is therefore not significantly affected by the nucleation of the new nematic volumes, a process which, on the contrary, still significantly affects both c_{eff} and I_L.

Conclusions

In conclusion, thanks to an upgraded version of our PPE calorimeter, we have presented the simultaneous, high temperature resolution characterization of the optical turbidity, specific heat and latent heat of a LC nanocolloid sample. The detection of the frequency dependence of the specific heat and of the latent heat have shown a substantially different dynamics of the nematic nucleating over each of the peaks. The obtained scattering results allowed to correlate the two-step nematic nucleation process, previously observed in the specific heat over the NI coexistence region, to the one we have also observed in the nematic correlation length.

References

[1] He, J., Yan, B., Yu, B., Bao, R., Wang, X., & Wang, Y. (2007). *Journal of Colloid and Interface Science*, *316*, 825.

[2] Iannachione, G. S., Garland, C. W., Mang, J. T., & Rieker, T. P. (1998). *Phys. Rev. E*, *58*, 5966 and references therein.

[3] Mercuri, F., Paoloni, S., Zammit, U., & Marinelli, M. (2005). *Phys. Rev. Lett.*, *94*, 247801.

[4] Mercuri, F., Pizzoferrato, R., Zammit, U., & Marinelli, M. (2002). *Appl. Phys. Lett.*, *81*, 4148.

[5] Caggioni, M., Roshi, A., Barjami, S., Mantegazza, F., Iannacchione, G. S., & Bellini, T. (2004). *Phys. Rev. Lett.*, *93*, 127801.

[6] Marinelli, M., Mercuri, F., Paoloni, S., & Zammit, U. (2005). *Phys. Rev. Lett.*, *95*, 237801.

[7] Marinelli, M., Mercuri, F., Zammit, U., & Scudieri, F. (1996). *Phys. Rev. E*, *53*, 701; (b) Mercuri, F., Zammit, U., & Marinelli, M. (1998). *Phys. Rev. E*, *57*, 596.

[8] Mercuri, F., Pizzoferrato, R., Zammit, U., & Marinelli, M. (2002). *J. Appl. Phys.*, *81*, 4148.

[9] Mercuri, F., Paoloni, S., Zammit, U., Scudieri, F., & Marinelli, M. (2006). *Phys. Rev. E*, *74*, 041707.

[10] Mercuri, F., Marinelli, M., Paoloni, S., Zammit, U., & Scudieri, F. (2008). *Appl. Phys. Lett.*, *92*, 251911.

[11] Jemée, P., Pitsi, G., & Thoen, J. (2002). *Phys. Rev. E*, *66*, 021707.

[12] Zakharov, A. V. & Thoen, J. (2004). *Phys. Rev. E*, *69*, 011704.

[13] Imry, Y. & Wortis, M. (1979). *Phys. Rev. B*, *19*, 3580.

[14] Mercuri, F., Paoloni, S., Zammit, U., Marinelli, M., Neamtu, C., & Dadarlat, D. *Phys. Rev. E*, to be published.

[15] Bellini, T., Clark, N. A., Degiorgio, V., Mantegazza, F., & Natale, G. (1998). *Phys. Rev. E*, *57*, 2996.