Band Structure of Orientational Modes in Quasiperiodic Mesoscale Liquid-Crystal–Polymer Dispersions

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The dispersion relation of the orientational fluctuations in a quasiperiodic holographic polymer-dispersed liquid-crystal structures with tenfold symmetry was studied by dynamic light scattering. At each scattering vector we observe two relaxation modes. The relaxation rate of the slow one goes to a very low value close to every Bragg reflection spot. We interpret our findings with a qualitative model in which quasiperiodically distributed regions of pure LC are separated by regions of high polymer content with high rotational viscosity. This gives rise to a sequence of dispersion branches of the orientational fluctuations, which is analogous to phonon bands in solid crystals. The main difference in our system is that the important periodicity is in the dissipation, not potential. The slow mode extends over many characteristic lengths of the structure, while the fast mode is localized to a single cell of the structure.

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Liquid crystals confined to polymer matrices of characteristic lengths on the scale of light wavelengths exhibit many interesting static and dynamic phenomena associated with the mesoscopic size, large surface to volume ratio, and strong elastic deformations imposed on the liquid crystal by the embedding matrix [1]. Structures ranging from submicrometer sized well-defined droplets of liquid crystal in polymer to loose strands of polymer in liquid crystal have all been studied. Most of the studies are focused on the structural properties and the effect of confinement on the phase transitions [2–7], but much less is known about the peculiarities of the interdroplet interaction. Over the past few years, much attention in the field of liquid-crystal–polymer composites has been focused on different periodic and quasiperiodic structures formed by holographic methods [8,9]. These materials, known as holographic polymer-dispersed liquid crystals (H-PDLCs), are promising for various applications due to their advanced electro-optic switching capability [2,10,11]. In principle, all 14 Bravais lattices can be created in H-PDLCs using a simultaneous multiple-beam holographic exposure process. Recently, it has also been demonstrated that 2D quasiperiodic structures with 10, 14 and 18-fold rotational symmetry can be created using the holographic method based on 5, 7, and 9 writing beams [12,13].

In a composite system, in which the individual liquid-crystal droplets are well separated by fully polymerized rigid walls, the orientational fluctuations in different droplets are decoupled and the orientational dynamics consists of intradroplet fluctuations only. This situation prevails in PDLC systems with relatively low liquid-crystal concentration. In the opposite case of low polymer concentration, i.e., in so-called volume stabilized LCs, liquid crystal permeates through the whole sample and the fluctuations are correlated over distances much larger than the typical size of the voids in the polymer matrix. In the intermediate case of varied morphology, droplets are in some way coupled through the polymer matrix, and one can expect to observe both: intradroplet fluctuation modes and interdroplet collective modes, extending over many droplets. In H-PDLCs, the density of the liquid-crystal droplets is periodically modulated, so such extended fluctuations must have the form of Bloch waves analogous to phonon dispersion in ordinary crystals. As a consequence, the wave vectors of the extended fluctuation modes that differ by a reciprocal-lattice vector are expected to be equivalent. In particular, if the collective fluctuations are very slow at $\mathbf{q} = \mathbf{0}$, they are expected to be slow also around any reciprocal-lattice vector, that is, around Bragg scattering directions.

In this Letter we report on the results of a dynamic light scattering (DLS) investigation of the orientational dynamics in a 2D quasicrystal H-PDLC in which we observed, in addition to local intradroplet fluctuation, the collective fluctuation mode, which shows a well-defined dispersion relation of the relaxation rate that goes to very small values around every Bragg diffraction peak.

Measurements were preformed on 15 μm thick H-PDLC samples with tenfold quasicrystal morphology. The material was sandwiched between two glass plates coated with indium-tin oxide electrodes. The samples were prepared by exposing a homogeneous liquid-crystal–polymer mixture of 43 wt.% aliphatic urethane resin oligomers, 35 wt.% nematic liquid crystal BL038, 12 wt.% photo initiator solution, and 10 wt.% surfactant to an interference field of five coherent laser beams (see Ref. [12]). The tenfold quasicrystal structure was confirmed through diffraction pattern analysis and by Fourier transformation of images made by polarizing optical microscopy, which both show the expected tenfold symmetry.

The system showed the transition from the nematic scattering state to the isotropic transparent state at 373 K. In the nematic state, the sample was still approximately transparent, so the amount of multiple scattering was small.

The light source used for DLS measurements was a He-Ne laser with a wavelength of 632.8 nm. The scattered light intensity correlation function $g^{(2)}(\tau) = \langle I(t)I(t+\tau)\rangle / \langle I(t)\rangle\langle I(t+\tau)\rangle$ was measured using an ALV-6010/160 correlator that enables the measurements over a correlation time range of 6.25×10^{-9}–5×10^{4} s. Measurements were performed at different scattering angles and temperatures, and also as a function of applied external electric ac field (50 kHz). The directions of the incoming and scattered light were chosen so that the scattering vector was in the plane of the sample, that is, perpendicular to the applied field. According to the selection rules, the scattering on the orientational fluctuations in the nematic LCs is strongest for the orthogonal polarizations of incident and scattered light; in our experiment, the incoming beam was polarized perpendicular to the scattering plane and the scattered light was polarized in the scattering plane.

The amplitude of the decaying part of $g^{(2)}(\tau)$ was around 0.002, which signifies our experiments were performed in the heterodyne regime, in which the statically scattered light acted as a local oscillator and consequently $g^{(2)}(\tau) = [I_{\mathrm{LO}}^2 + 2I_{\mathrm{LO}}I_D g^{(1)}(\tau)]/I_{\mathrm{LO}}^2 = 1 + 2g^{(1)}(\tau)I_D/I_{\mathrm{LO}}$, where I_{LO} and I_D are the intensities of the local oscillator and dynamically scattered light, respectively, and $g^{(1)}(\tau)$ the normalized field autocorrelation function of the scattered light. So $g^{(2)}(\tau)$ is proportional to $g^{(1)}(\tau)$. In the measured functions, $g^{(1)}(\tau)$, two relaxation processes are observed, a fast and a slow one. A double stretched exponential function fits well both relaxation processes of $g^{(1)}(\tau)$.

We attribute the fast mode to the intradroplet fluctuations and the slow one to the collective interdroplet mode. Let us first discuss the second one. The lower dispersion relation in Fig. 1 shows the dependence of the slow relaxation rate on the scattering vector. The dispersion relation shows pronounced minima at the wave vectors corresponding to the Bragg diffraction peaks, that is, to the reciprocal-lattice vectors. The successive reciprocal-lattice vectors that correspond to the position of the first, second, third, and fourth Bragg directions have magnitudes: $|\mathbf{G}_1| = 4.7 \times 10^6\ \mathrm{m}^{-1}$, $|\mathbf{G}_2| = 8.1 \times 10^6\ \mathrm{m}^{-1}$, $|\mathbf{G}_3| = 1.28 \times 10^7\ \mathrm{m}^{-1}$, and $|\mathbf{G}_4| = 2.09 \times 10^7\ \mathrm{m}^{-1}$, and these values form approximately a Fibonacci chain, as expected in a quasicrystal structure [14]. In the vicinity of the minima, the dispersion relation for the collective mode should be quadratic:

$$\frac{1}{\tau} = \frac{K(\mathbf{q})}{\eta(\mathbf{q})} \approx \frac{K_{\mathrm{eff}}}{\eta_{\mathrm{eff}}} |\mathbf{q} - \mathbf{G}_m|^2, \tag{1}$$

with the same value for the effective diffusion constant $K_{\mathrm{eff}}/\eta_{\mathrm{eff}}$. Indeed, the fit of Eq. (1) to the measured data around the successive minima gives: $K_{\mathrm{eff}}/\eta_{\mathrm{eff}} = (2.17 \pm 0.19, 2.32 \pm 0.23, 2.09 \pm 0.15, 2 \pm 0.14) \times 10^{-11}\ \mathrm{m}^2/\mathrm{s}$. These values of the effective diffusion constant are about 10 times smaller than in the bulk nematic phase of a pure LC compound [3].

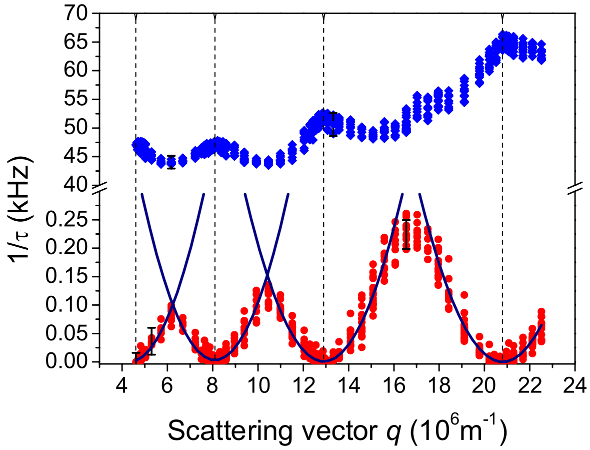

FIG. 1 (color online). Dependence of the relaxation rate of the slow interdroplet fluctuation mode (lower dispersion relation) and fast intradroplet fluctuation mode (upper dispersion relation) on the scattering vector q. The solid lines show fits to quadratic dispersion with the minimum at the position of the first $|\mathbf{G}_1| = 4.7 \times 10^6\ \mathrm{m}^{-1}$, second $|\mathbf{G}_2| = 8.1 \times 10^6\ \mathrm{m}^{-1}$, third $|\mathbf{G}_3| = 1.28 \times 10^7\ \mathrm{m}^{-1}$, and fourth $|\mathbf{G}_4| = 2.09 \times 10^7\ \mathrm{m}^{-1}$ Bragg peaks, respectively. Different data points at the same q correspond to measurements performed in different regions of the H-PDLC sample. Vertical dashed lines show the positions of the first, second, third, and fourth Bragg peaks. ($T = 295$ K.)

The slow mode relaxation rate at a given scattering vector is not sharply defined, but is relatively broadly distributed as evidenced by the fact that the measured correlation function is not a single exponential but rather a stretched exponential function with a stretching exponent in the interval 0.35–0.98. We attribute this effect to the inhomogeneity of the sample on the scale of about ten micrometers that can also be observed under polarizing microscope [15]. Some stretching of the exponent is probably also due to some multiple scattering which is present in the sample. In the following discussion, we will show that the slow mode relaxation rate is expected to strongly depend on the liquid-crystal–polymer ratio, which is probably the source of the inhomogeneity.

The fast mode relaxation rate that corresponds to the upper dispersion relation in Fig. 1 slightly oscillates around a constant value up to $q_0 \approx 12 \times 10^6\ \mathrm{m}^{-1}$ and then increases with increasing scattering vector. This is typical for fluctuations confined to a finite sized space, where the smallest wave number must be of the order of π/d, with d the size of the enclosure [16–19]. In our case $d \sim \pi/q_0$ is about 0.3 μm, which is about the size of the liquid-crystal rich region of our structure. The observed value of the fast relaxation rate for $q \rightarrow 0$ is also similar to the bulk nematic relaxation rate at $q > 10^7\ \mathrm{m}^{-1}$ [3]. So the fast relaxation rate can be attributed to the fluctuations within single liquid-crystal region.

The existence of the dispersion relation that goes to zero at $\mathbf{q} = \mathbf{G}_m$, similar to the dispersion of acoustic phonons in periodic crystals, is only possible if the fluctuations are extended over several periods of the structure. So our experimental results show that the orientational fluctuations in one LC-rich area must be coupled to the next one. The transmission of torque can be due to anchoring of the LC on the polymer and first order elasticity of the polymer and/or to the existence of some nematic ordering of the polymer, which can then transmit torque through orientational elasticity. In any case, the deformations in the polymer-rich regions are expected to be accompanied by considerable amount of dissipation, so that the effective rotational viscosity of the polymer-rich regions is high. The observed experimental results can now be understood with the help of a simple model, in which we assume that the sample consists of periodically distributed regions of low viscosity LC and high viscosity polymer-rich matrix, which also transmits torque and can be described with an effective orientational elastic constant, which for simplicity we take to be equal to the elastic constant of LC. Considering a different value for the elastic constant makes no qualitative difference in the results. The quasicrystal structure of the measured samples projected on a 1D subspace has a form which may be viewed as a regular periodic chain with an incommensurate modulation of the distances between successive liquid-crystal regions around its average value Λ [14,20]. According to Ref. [14], in quasicrystal both dispersion curves can be treated as belonging to a pseudo-Brillouin-zone corresponding to a lattice with an average spacing Λ. The size of the liquid-crystal regions is a. This one-dimensional model (Fig. 2) can be easily analyzed numerically. The fluctuation modes have the form of Bloch waves, so they are characterized by a wave number q. On the boundaries $\mathbf{n}_i(x)$ and $K_i \partial \mathbf{n}_i / \partial x$ are continuous, where the K_i are elastic constants for first and second region ($i = 1, 2$). Then, the secular equation of the linear system of the coupled fluctuation modes is solved numerically. The resulting dispersion of the modes is shown in Fig. 3. There is one branch of the fluctuation modes with zero relaxation rate at $q = 0$ and at all values of q equal to the reciprocal-lattice vector $|\mathbf{G}_m|$, which, in light scattering, correspond to Bragg reflections. This is analogous to the acoustic phonon branch in crystals in the extended zone representation and is a necessary consequence of the quasiperiodicity of the system. Around the minima, the dispersion relation is parabolic. The effective diffusion constant is determined by the ratio of the nematic elastic constant to the effective viscosity, which can be large due to contribution of the polymer walls in which the rotational viscosity can be several orders of magnitude larger than in pure liquid crystal. Qualitatively similar results as in our experiments are obtained for $a/\Lambda \approx 0.8$, $K_1 \approx K_2$, and with the ratio of rotational viscosities between two regions $\gamma_2/\gamma_1 \approx 400$.

The other branches of the fluctuation modes have nonzero relaxation rates for all values of q and show only little dispersion. These modes essentially represent orientational fluctuations of the liquid crystal within one cell of the system. They are analogous to optical phonon branches in crystals. The relaxation rates of these modes depend on elastic constants, viscosities, and polymer wall thickness. For very viscous polymer walls, the first optical mode is much faster than the acoustic mode at the first zone boundary, that is, at its maximum. This is exactly what we observe in our samples, in which, at a pseudozone boundary, the relaxation rate of the fast mode is 2 orders of magnitude larger then the relaxation rate of the slow mode.

That the effective viscosity of the polymer-rich regions must be high can be seen through the following argument. The polymer structure is to a certain degree rigid and pins the orientational fluctuations. This acts as an external field on the nematic director so that the dispersion relation should not go to zero at $q = 0$ and at $\mathbf{G}_m$. The experimental finding that the relaxation rate of the slow mode at $q = |\mathbf{G}_m|$ goes to very small values can only be

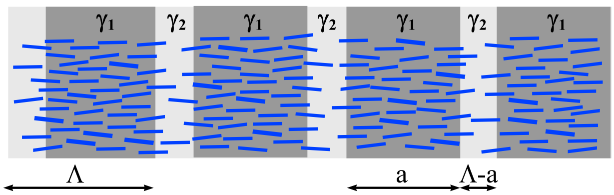

FIG. 2 (color online). Illustration of the one-dimensional model of orientational fluctuations in the system of periodically varying viscosity. The dark regions represent pure LC compound with parameters: a: length, γ_1: rotational viscosity, and bright regions: polymer walls with parameters $\Lambda - a$ and γ_2.

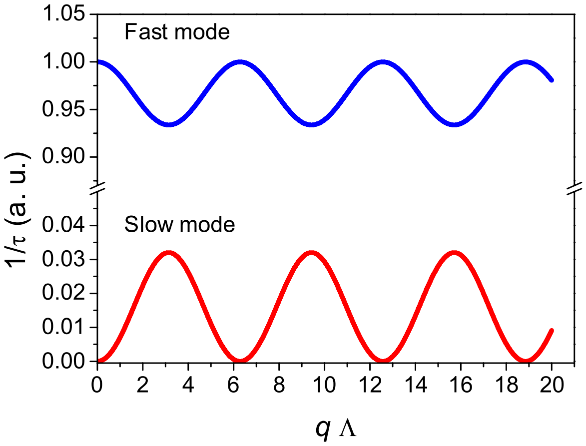

FIG. 3 (color online). The dispersion curves for the fast (upper curve) and the slow mode (lower curve) computed from the model of the visco-coupled fluctuation modes. Values of the parameters taken for the calculation are $a/\Lambda = 0.8$, $K_1 = K_2$, $\gamma_2 = 400\gamma_1$.

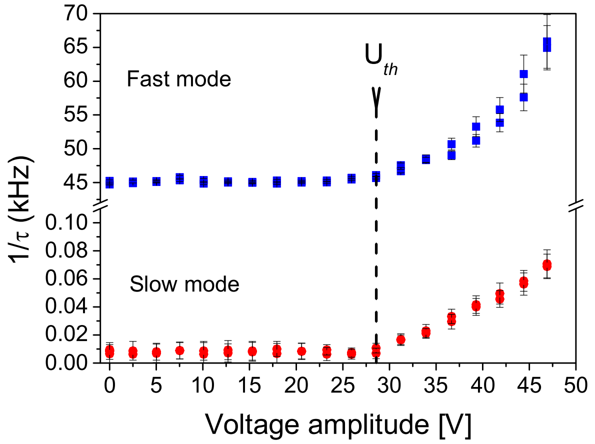

FIG. 4 (color online). Dependence of the relaxation rate of the slow interdroplet mode (upper curve) and fast intradroplet mode (lower curve) on applied voltage. The data were achieved by successively increasing and decreasing voltage. ($T = 298$ K, scattering vector $q = 8.86 \times 10^6$ m^{-1}.)

explained if the viscosity of the polymer-rich regions is taken to be high.

The proposed model is also supported by the observed behavior of both the fast and slow mode in an external electric field, which is presented in Fig. 4. The relaxation rates of both modes start to increase at approximately the same magnitude of the external field. This shows that the slow and the fast mode are not the result of some imperfections in the different regions of the sample having different local structure or properties, but are two modes of the same structure. In the opposite case, when the two modes come from different regions of LC, i.e., the slow from large and the fast from small LC-rich domains, both modes would not have the same threshold voltage U_{th} at which the corresponding relaxation rates start to increase. It also shows the slow mode cannot be slow due to some very small restoring elasticity. In that case the slow mode should be influenced by a correspondingly smaller external field.

In this Letter we have shown that the orientational fluctuation modes in quasicrystals or crystal H-PDLC structures have a number of properties analogous to phonon modes in crystals. The main difference is that the periodicity is in the dissipation, not potential, and this can cause a very large difference in the relaxation rate of the acoustic and optical branches at the Brillouin zone boundary. The existence of an acousticlike branch of fluctuations shows the torque is elastically transmitted over the polymer-rich regions, which must possess much higher orientational viscosity than the pure liquid crystal. The quasiperiodic nature of the system causes the acoustic branch relaxation rate to go to zero at all reciprocal-lattice points.

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