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Hidden solidlike properties in the isotropic phase of the 8CB liquid crystal

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Novel dynamic experiments have enabled the identification of a macroscopic solidlike response in the isotropic phase of a low molecular weight liquid crystal, 4,4'-*n*-octylcyanobiphenyl (8CB). This unknown property indicates that the low frequency shear elasticity identified in the isotropic phase of liquid crystal polymers is not reminiscent from the glass transition but reveals likely a generic property of the liquid state. The comparison to high molecular weight liquid crystals indicates, however, that the shear modulus is much enhanced when the liquid crystal moieties are attached to a polymer chain. The macroscopic length scales probed (0.050–0.100 mm) exclude wall-induced effects.

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The knowledge of the timescales involved in liquid crystalline systems is of outmost importance to understand, control, and improve their characteristics. The submillimeter scales properties attract a tremendous research interest [1–4]. However, few studies concern the isotropic phase away from pretransitional effects. Assimilated to ordinary viscous liquids, the isotropic phase is not supposed to exhibit solidlike properties, or at very high frequency only (mega- or gigahertz) as ordinary liquids. For this reason, the low frequency behavior of the isotropic phase remains mistakenly unexplored.

Experimentally, the viscous or solidlike nature of a material is deduced from its response to a low frequency mechanical solicitation. A couple of years ago, careful dynamic experiments carried out in the isotropic phase of high molecular weight liquid crystals [side-chain liquid crystalline polymers (SCLCPs)] have revealed an as-yet unknown property: the isotropic melt does not flow but exhibits a finite shear elasticity of about several thousand Pascals at low frequency (0.1–10 Hz) [5–9]. The identification of low frequency shear elasticity in the isotropic phase of SCLCPs away from the isotropic-nematic transition opens numerous questions on the origin of this new property. It neither seems to result from the contribution of the liquid crystal moieties nor from surface anchoring effects, but likely from a generic property of the liquid state. Measurable in SCLCPs at macroscopic length scales as far as 100° away from the glass transition temperature [5,7,9], the shear elasticity of SCLCPs still raises the debated question of reminiscent glass transition effects.

In this Rapid Communication, we probe the dynamic properties of the low molecular counterpart: the 4,4'-*n*-octylcyanobiphenyl (8CB). The widely studied molecule can be considered as a representative liquid crystal molecule. 8CB exhibits a crystalline phase at low temperatures that enables one to rule on the question of pretransitional glass transition effects. We reveal a low frequency, solidlike response at several tens of micrometers sample thickness in the isotropic phase of 8CB, meaning that long range correlations are preserved when the orientational order is lost. This shear elasticity is detectable if special attention is paid to boundary conditions between the substrate and the sample. Under these conditions, the shear stress is optimally transmitted between the sample and the substrate. The optimization of the boundary conditions is here achieved by improving the total wetting of the liquid to the substrate and by probing small gaps. Length scales up to 0.200 mm are probed, showing that the low frequency shear elasticity measured in the isotropic phase cannot be interpreted as a surface-induced effect but might indicate a bulk property.

Mechanical oscillatory shear is used in solid mechanics as well as in fluids to probe their dynamic properties at low frequency. This method gives access to long relaxation times. It consists in applying an as weak as possible oscillatory strain to the sample to probe equilibrium properties (at rest). The equilibrium state properties are described as a function of the frequency (ω), typically from 0.1 to 100 rad s^{-1}. The transfer of the motion to the liquid is here achieved by ensuring total wetting boundary conditions between the liquid and the substrate (alumina plates of 40 mm diameter) and by probing small gaps. The oscillatory motion and the shear stress measurement are provided using a dynamic force apparatus (ARES2). A seven-digit voltmeter (Keitley, rate 300 data/s) measures the voltage of the motor imposing the oscillation (input wave), while another seven-digit voltmeter measures the voltage associated to the sensor (output wave). This setup enables simultaneous access to the strain/stress signals and to the dynamic profile versus frequency and versus strain amplitude. The analysis of the signals defines the strain range for which the conventional formalism in terms of elastic G' and viscous G'' moduli can be applied, i.e., as long as the stress wave keeps the shape of the imposed strain wave (sinusoidal-like). Under these conditions, the shear stress and the shear strain are related by $\sigma(\omega) = G_0\gamma_0 \sin(\omega t + \Delta\phi)$, with G_0 the viscoelastic modulus, t the time, ω the frequency and $\Delta\phi$ the phase shift between the input and the output waves, or in terms of shear elastic (G') and viscous (G'') moduli: $\sigma(\omega) = \gamma_0[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)]$, with G' the component in phase with the strain, and G'' the out-of-phase component.

A liquidlike character is identifiable by a vanishing response at long time scale, whereas a solidlike behavior (elastic) exhibits a finite response independent of the frequency (Fig. 1, right). A perfect solidlike response exhibits no phase shift. Experimentally, solidlike materials always exhibit a short delay due to internal freedom degrees and thus exhibit a nonzero G''. When the phase shift is lower than $\Delta\phi < \pi/4$, the elastic component G' dominates the viscous component G'' (Fig. 1, right). If the output response of the material presents

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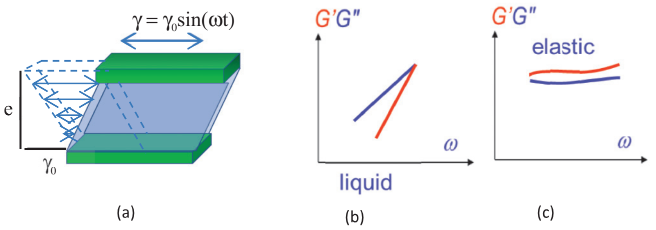
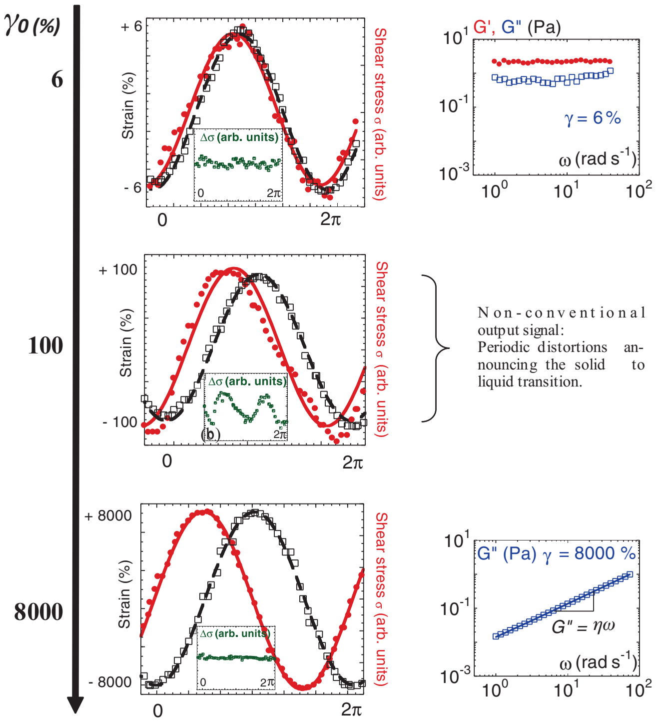


FIG. 1. (Color online) Scheme of an oscillatory shear (a) and of typical dynamic relaxation spectra. (b) Flow behavior ($G' < G''$, with G' and G'' vanishing with the frequency). (c) Solidlike behavior ($G' > G''$, with G' and G'' weakly dependent on the frequency).



Non-conventional output signal: Periodic distortions announcing the solid to liquid transition.

FIG. 2. (Color online) Input shear strain sine wave (open black squares, ☐) and output shear stress wave (red circles, ●) of 8CB in the isotropic phase at 0.050 mm gap thickness for low [$\gamma_0 = 6$ %, (a)], intermediate [$\gamma_0 = 100$ %, (b)], and high [$\gamma_0 = 8000$ %, (c)] strain amplitudes. The black and red lines correspond to a sine modeling of the input (– –) and the output waves (—) of the data points. Insets: Data resulting from the subtraction of the model sine function from the data points ($\sigma_{\text{experimental}} - \sigma_0 = \Delta\sigma$, green squares, ■). Dynamic relaxation spectra (G': red circles, ●; G'' open blue squares, ☐) are shown for (a) and (c).

a phase shift larger than $\pi/4$, then the viscous component G'' dominates the elastic component G' (Fig. 1, left). The sample behaves liquidlike. If the phase shift reaches $\pi/2$ (G' vanishes), the sample is defined as purely viscous. A (Maxwell) liquidlike behavior typically displays a vanishing response characterized by a ω scaling of the viscous modulus and a ω^2 scaling dependence of the elastic modulus.

8CB (4,4'-*n*-octylcyanobiphenyl) was purchased from Aldrich and used as received. It shows crystalline ($T < 21\,^\circ$C), smectic A ($T < 33\,^\circ$C), nematic ($T < 40.5\,^\circ$C), and isotropic phases. The phases and the transition temperatures were verified optically using a polarization microscope in accordance with the literature data [10,11].

Figure 2 illustrates the input sinusoidal strain wave and the output shear stress wave transmitted by a layer of 0.050 mm in the isotropic phase of 8CB for low, intermediate, and large strain amplitudes. The liquid crystal is solicited at $T = 42.5\,^\circ$C ($\pm 0.05\,^\circ$C), i.e., at $T = T_{NI} + 2\,^\circ$C above the *N-I* transition temperature (*in situ* optically verified).

At low strain amplitude [$\gamma_0 = 6\%$, (a)] the input and output waves show almost superposition with a phase shift $\Delta\varphi$ of 12°. This indicates a nearly instantaneous sample response, i.e., a solidlike response. A similar in-phase signal is observed for a wide range of frequencies from 1 up to 40 rad s^{-1}. Since the low frequency output shear stress is sinusoidal (linear regime), it can be described in terms of elastic G' and viscous G'' moduli. On the right side of Fig. 2(a) the evolution of G' and G'' is presented as a function of the frequency at low strain amplitude. Being at least three times as large as G'', the elastic shear modulus G' dominates the viscous contribution. The elastic modulus G' shows no apparent dependencies on the frequency. The viscous modulus G'' is also nearly constant at low frequency and does not obey a ω scale, as it would be expected for liquid behavior. Therefore both moduli indicate a nonflowing state.

For intermediate strain amplitudes [$\gamma_0 = 100\%$, Fig. 2(b)], the output signal becomes slightly distorted and its phase is shifted with respect to the input signal. The insets in the strain-stress diagrams in Fig. 2 show the discrepancy ($\Delta\sigma$) between the sine function model and the experimental points. For small ($\gamma_0 = 6\%$) and for large ($\gamma_0 = 8000\%$) deformations a straight line is obtained, indicating a convenient fit, while for intermediate ($\gamma_0 = 100\%$) strain amplitude $\Delta\sigma$ yields a pronounced periodical deviation. The latter displays two harmonics over one period. The appearance of these harmonics can be interpreted as the entrance into the nonlinear regime, where the moduli G' and G'' become strongly strain and frequency dependent. A modeling of the signals in terms of G' and G'' is questionable. The occurrence of a slip mechanism might be addressed to illustrate the sin wave distortion in this regime.

At large strain amplitudes [Fig. 2(c)] i.e., away from equilibrium conditions, the distorsion is no more visible and the output wave recovers a sinusoidal shape, enabling a modeling in terms of G'' and G'. The phase shift is nearly $\pi/2$, in agreement with a viscous behavior. The corresponding dynamic relaxation spectrum displayed on the right side of Fig. 2(c) confirms the liquidlike response; G'' obeys a ω scaling with a slope of 14 mPa s, yielding a dynamic viscosity according to the literature data [12].

We have seen that the in-phase (solidlike) response is easily lost upon increasing the perturbation of the sample, being progressively replaced by a completely out-of-phase (viscous) response.

Figure 3 presents the evolution of the dynamic moduli in the isotropic phase on increasing the strain amplitude from 0.3% up to 10^4%. The experiment was carried out at a given frequency of $\omega = 5$ rad s^{-1} and a gap thickness of 0.050 mm.

At low strain amplitude, the elastic modulus G' dominates the viscous modulus G'', which contributes in average only about 4% of the total modulus [$G = \sqrt{(G'^2 + G''^2)}$].

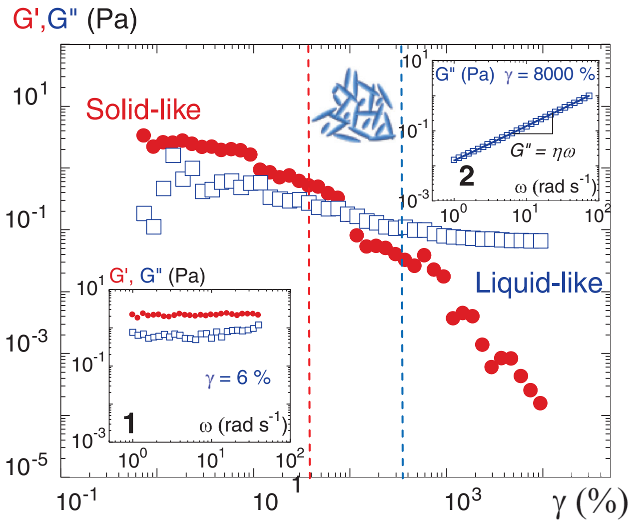
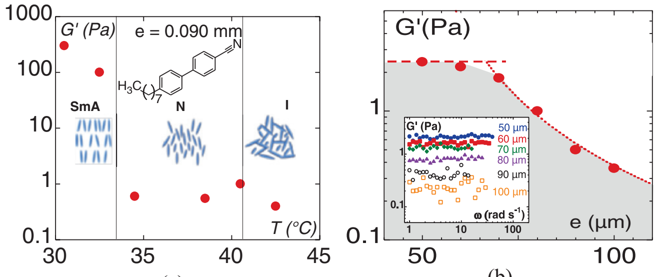


FIG. 3. (Color online) Strain dependence of the viscoelastic moduli (G': red circles, ●; G'' open blue squares, ☐) of 8CB in the isotropic phase ($T = 42.5\,^\circ$C) at 0.050 mm gap thickness at a frequency of $\omega = 5$ rad s^{-1} (γ_0 evolves from 2.8 up to 10^4%). The vertical dashed bars delimit the zone where the output signal exhibits periodic distortions. Insets: Details of the frequency dependence at weak (1) and at large (2) strain amplitudes ($\gamma_0 = 6\%$ and at $\gamma_0 = 8000\%$, respectively). The straight blue line in (2) shows the ω scale of G'', indicating a dynamic viscosity, in agreement with conventional experiments [12].

Upon increasing the strain amplitude, both the elastic and viscous moduli decrease with a more pronounced fall of G', leading to a transition from solidlike to liquidlike behavior. At high strain amplitude, the viscous modulus dominates the elastic modulus, the latter becoming negligible with respect to the total modulus (less than 1%).

The usual and generally expected viscous behavior of the liquid crystal in the isotropic phase is recovered by applying high strain amplitudes, thus away from mechanical equilibrium conditions. As a major result, a linear solidlike regime is found to precede the conventional flow regime. The solidlike response collapses upon entering the viscous regime.



(a) (b)

FIG. 4. (Color online) (a) Shear modulus G' (logarithmic scale) of 8CB versus temperature at 0.090-mm gap thickness. The vertical lines indicate the transition temperatures of the smectic (SmA)-nematic transition (N) and the nematic-isotropic (I) transition. (b) Shear modulus G' (logarithmic scale) of 8CB versus gap thickness at T (42.5 °C) $> T_{NI}$. Above 70 μm, the values lower rapidly following an exponential decrease (small dashed points). The inset displays the shear modulus from 1 up to 40 rad s^{-1} at different gap thicknesses.

For a better understanding of the origin of the elastic response, the experiments were also carried out for $T < T_{NI}$ in the nematic and smectic phases. Figure 4(a) shows the values of the shear elasticity measured at low thickness versus temperature. Both nematic and isotropic phases exhibit values of G' of around 0.8–1 Pa with no significant temperature dependency upon crossing the N-I transition temperature. This result indicates that neither pretransitional dynamics nor the nematic phase have an influence on the elastic response. Similar observations were reported for liquid crystal polymers [5,7]. The situation is different regarding below the SmA-N transition. Due to the positional order of the smectic phase, the values of the shear elasticity obtained in this phase exceed at least by 2 decades the ones found for the nematic and isotropic phases.

The thickness of the sample has also a significant influence on the elastic response. Figure 4(b) presents the evolution of the elastic modulus of 8CB in the isotropic phase as a function of the gap thickness. The average values of G' increase upon decreasing the gap thickness from 0.100 to 0.050 mm following an exponential law:

$$G' = (G'_0 - G'_\infty)\exp -\left(\frac{e - e_{\text{crossover}}}{e_0}\right)^{\frac{1}{2}} + G'_\infty,$$

up to around $e_{\text{crossover}} = 70\ \mu$m, the thickness value at the onset of the saturation, with $G'_0 = 1.7$ Pa the saturated shear modulus, $e_0 = 7.3\ \mu$m a constant length scale, and $G'_\infty = 0.12$ Pa the shear modulus at infinite thickness, which is negligible. The rapid lowering of the shear modulus might result from multiple effects such as increased voids, degree of freedom, loss of the shear stress transmission from and to the surfaces or dimensional character of the elastic property. In contrast, wall or capillary effects cannot explain the reinforcement of the moduli at low thickness. The probed gap distances far exceed coherence lengths that lie in the order of several nanometers by at least a factor of 1000 [13–16]. An interpretation in terms of surface effects or in terms of Frank's elasticity [13] might be an explanation for the viscoelastic properties found in the nematic phase [17,18], but this would be irrelevant in the present case since the elasticity is transmitted in the isotropic phase. The nematic and isotropic phases yield similar shear moduli, indicating that neither pretransitional dynamics nor the symmetry of the phase have an influence on the elastic response.

Shear elasticity was found but of stronger moduli for a series of liquid crystal polymers in the isotropic phase. To our knowledge, the low frequency elastic response of a liquid crystal polymer was firstly identified at low thickness by Gallani *et al.* [5] using a piezoelectric rheometer. Their interpretation was based on pretransitional dynamics related to the glass transition. In comparison to the low molecular weight liquid crystal 8CB, the presence of polymeric chains yields 10^3–10^4 times higher values for the elastic modulus, i.e., elastic moduli of the order of 10^3–10^4 Pa in the isotropic phase [8]. Also, a similar dependence of the elastic modulus on the gap thickness is observed [5,7]. The identification of finite macroscopic, low frequency shear elasticity in both small molecular weight and high molecular weight liquid crystals indicates that it originates neither from polymer chains, mesomorphic properties, nor pretransitional effects. Similarly, glass transition effects previously discussed to explain the low frequency elasticity of liquid crystal polymers are excluded.

We interpret the results in favor of long range intermolecular effects leading to the conclusion that the isotropic phase is a fragile, long range, elastically correlated "self-assembly." The strength of the solidlike response depends on the architecture of the molecule (polymer or not) and likely on the nature of the intermolecular interactions (van der Waals, H-bond, polar), in agreement with results obtained on other materials [19,20].

In conclusion, careful dynamic relaxation measurements have revealed a delicate solidlike response at macroscopic scale in the isotropic phase of 8CB, i.e., the liquid does not flow below a shear elastic threshold. This finite, low frequency shear elasticity is accessible by applying a weak mechanical stress to a submillimeter thickness sample. The solidlike character is established by the nearly instantaneous (in-phase) response to the input shear strain. The conversion of these mechanical waves in conventional terms of elastic G' (in phase) and viscous moduli G'' (out of phase) indicates that G' dominates G'' with no apparent (G') or very weak (G'') dependence on the frequency, indicating a major solidlike response over a wide frequency range (10^{-1} to 10^{2} rad s^{-1}).

An indispensable condition for measuring this low frequency shear elasticity is a strong anchoring of the liquid crystal on the substrate, i.e., total wetting conditions. This solidlike regime is found for small strains prior to the usual viscous regime which is in apparence recovered at high strain amplitudes. These two linear regimes (solidlike and viscouslike regimes) are however not equivalent. Since the weaker strain amplitudes guarantee a weaker perturbation of the material, the elastic response needs to be considered as the fundamental response of the sample (at equilibrium). The usual viscous behavior (which is generally obtained when no special attention is paid to the wetting properties) corresponds to a second linear domain occuring as a highly perturbative state with respect to the solidlike regime.

The comparison to results obtained for high molecular weight liquid crystal polymers shows that the shear elasticity is neither related to pretransitional effects, mesomorphic properties, glass transition, the contribution of polymeric chains, nor anchoring effects, as predicted in recent theoretical works pointing out a significant enhancement of the shear modulus in the nematic phase of SCLCPs [21]. Figure 5 compares the shear moduli displayed in the liquid phase, by a low molecular weight liquid crystal (8CB), a side-chain liquid crystal polyacrylate, and a low molecular weight polybutylacrylate chain. It shows that the regular grafting of liquid crystal moieties on a polymer chain reinforces strongly the elastic character with respect to the low molecular weight liquid crystal but also with respect to the chain alone, pointing out the key role of the intermolecular interactions.

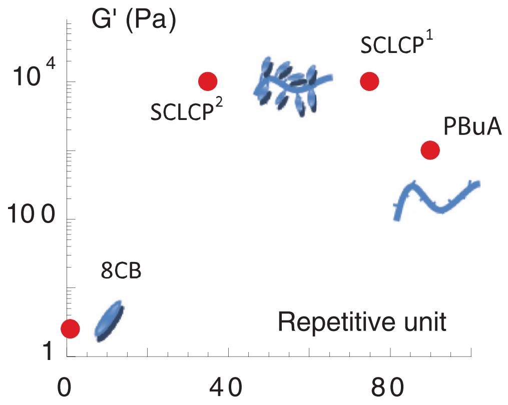


FIG. 5. (Color online) Comparison of the shear moduli G' measured in the liquid phase classified versus degree of polymerization (repetitive unit): 8CB, a polybutylacrylate chain (PBuA), a liquid crystal polyacrylate with a phenyl benzoate moiety (SCLCP^1), and another liquid crystal polymer with a cyanobiphenyl moiety (SCLCP^2). The three polymers are described in Ref. [7] and Eur. Phys. J. E **19**, 87 (2006).

This analysis and the fact that for other liquids, a low frequency shear elasticity was detected [19,20], support the assumption that we deal with a generic property of the liquid state. We therefore interpret the low frequency shear elasticity as a measurement of the strength of long range intermolecular interactions. To our knowledge, very few theoretical developments set the role of the latter as crucial. In molecular liquids, noteworthy approaches consider a solidlike continuum [22] and even predict a low frequency shear elasticity, the strength of which depends on the network size [23]. Long range elastic correlations could be the origin of the shear-induced birefringence observed in the isotropic phase of high birefringence liquid crystals [24], of high molecular weight liquid crystals [25], or wormlike micellar solutions [26,27]. Predicted to result from a coupling with the lifetime of the pretransitional orientational fluctuations [28–30], these shear-induced behaviors are in fact observed for very much longer time scales.

[1] J. G. Cuennet, A. E. Vasdekis, L. De Sio, and D. Psaltis, Nat. Photonics **5**, 234 (2011).

[2] J.-C. Géminard, R. Hołyst, and P. Oswald, Phys. Rev. Lett. **78**, 1924 (1997).

[3] M. Vilfan, T. Apih, A. Gregorovic, B. Zalar, G. Lahajnar, S. Zumer, G. Hinze, R. Böhmer, and G. Althoff, Magn. Reson. Imaging **19**, 433 (2001).

[4] D. Porter, J. R. Savage, I. Cohen, P. Spicer, and M. Caggioni, Phys. Rev. E **85**, 041701 (2012).

[5] J. L. Gallani, L. Hilliou, P. Martinoty, and P. Keller, Phys. Rev. Lett. **72**, 2109 (1994).

[6] P. Martinoty, L. Hilliou, M. Mauzac, L. Benguigui, and D. Collin, Macromolecules **32**, 1746 (1999).

[7] H. Mendil, P. Baroni, and L. Noirez, Eur. Phys. J. E **19**, 77 (2006).

[8] H. Mendil, P. Baroni, and L. Noirez, Europhys. Lett. **72**, 983 (2005).

[9] L. Noirez, Phys. Rev. E **72**, 051701 (2005).

[10] B. Struth, K. Hyun, E. Kats, T. Meins, M. Walther, M. Wilhelm, and G. Grübel, Langmuir **27**, 2880 (2011).

[11] G. S. Iannacchione and D. Finotello, Phys. Rev. Lett. **69**, 2094 (1992).

[12] J. Jadzyn, R. Dabrwoski, T. Lech, and G. Czechowski, J. Chem. Eng. Data **46**, 110 (2001).

[13] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Oxford University Press, Oxford, UK, 1993).

[14] B. Chu, C. S. Bak, and F. L. Lin, Phys. Rev. Lett. **28**, 1111 (1972).

[15] P. Sheng, Phys. Rev. A **26**, 1610 (1982).

[16] B. Jerôme, A. Bosseboeuf, and P. Pieranski, Phys. Rev. A **42**, 6032 (1990).

[17] W. R. Burghardt, J. Rheol. **35**, 49 (1991).

[18] P. Oswald and A. Dequidt, Europhys. Lett. **103**, 26002 (2013).

[19] L. Noirez, P. Baroni, and H. Cao, J. Mol. Liq. **176**, 71 (2012).

[20] L. Noirez and P. Baroni, J. Phys.: Condens. Matter **24**, 372101 (2012).

[21] E. P. Choate, M. G. Forest, and L. Ju, Rheol. Acta **49**, 335 (2010).

[22] A. V. Granato, Mater. Sci. Eng. A **521-522**, 6 (2009).

[23] F. Volino, Annales de Physique **22**, 142 (1997).

[24] C. Bailey, K. Fodor-Csorba, R. Verduzco, J. T. Gleeson, S. Sprunt, and A. Jákli, Phys. Rev. Lett. **103**, 237803 (2009).

[25] C. Pujolle-Robic, and L. Noirez, Nature (London) **409**, 167 (2001).

[26] F. Lequeux, V. Schmitt, A. Pousse, and D. Roux, Langmuir **10**, 955 (1994).

[27] D. C. Roux, J. F. Berret, G. Porte, and P. Lindner, Europhys. Lett. **25**, 521 (1994).

[28] P. D. Olmsted and P. Goldbart, Phys. Rev. A **46**, 4966 (1992).

[29] S. Hess, Z. Naturforsch. **31a**, 1507 (1976).

[30] S. Hess and P. Ilg, Rheol. Acta **44**, 465 (2005).