

## Soft-stiff regime crossover for an aerosil network dispersed in liquid crystals

George Cordoyiannis,<sup>1</sup> Samo Kralj,<sup>2,3</sup> George Nounesis,<sup>1,\*</sup> Slobodan Žumer,<sup>4,3</sup> and Zdravko Kutnjak<sup>3</sup>

<sup>1</sup>National Centre for Scientific Research "Demokritos," 153 10 Aghia Paraskevi, Greece

<sup>2</sup>Laboratory of Physics of Complex Systems, Faculty of Education, University of Maribor, Koroška 160, 2000 Maribor, Slovenia

<sup>3</sup>Jožef Stefan Institute, P.O. Box 3000, 1001 Ljubljana, Slovenia

<sup>4</sup>Department of Physics, Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia

(Received 31 October 2005; published 29 March 2006)

Hydrophilic and hydrophobic aerosil particles immersed in S-(+)-[4-(2-methylbutyl) phenyl 4-*n*-octylbiphenyl-4-carboxylate] or [*p*-(*n*-decyloxy) benzylidene-*p*-amino-(2-methylbutyl) cinnamate] compound have been studied by employing x-ray diffraction. The aerosil-induced relative layer compression  $\Delta d$  has been measured in the smectic *A* phase as a function of aerosil concentration  $x$ .  $\Delta d(x)$  is shown to sensitively monitor the *intermediate-rigid* transition of the adaptive aerosil network. The dominant mechanism leading to the  $\Delta d(x)$  profiles is the global establishment of the aerosil-induced molecular tilt in the smectic *A* phase.

DOI: 10.1103/PhysRevE.73.031707

PACS number(s): 61.30.-v, 61.10.-i, 64.70.Md

### I. INTRODUCTION

Intense interest has been shown in recent years in understanding the physics of adaptive randomly connected networks [1] encountered in a wide variety of complex systems including condensed matter, biological, and social [1–3]. Their essential property is the ability to continuously alter their organization and structure leading to an overall reduction of the stress imposed by the surrounding environment. Such networks exhibit universal properties with similar mathematical description [2,3].

Recent studies show [2] that at least three different network structural phases are expected if either the degree of connectivity or the concentration of constituent units forming the network are varied. The qualitative structural features depend on the relative number of degrees of freedom  $N_f$  and the number of constraints  $N_c$  imposed by forming network bonds within the system. For  $N_f \gg N_c$  the so called *floppy* phase is established characterized by zero probability  $p$  for a percolating cluster, spanning the entire system. The moieties, that can potentially form the network, are essentially independent of each other. The *intermediate* network phase is realized for  $N_f \sim N_c$ , with enhanced adaptive properties, giving rise to various structural and thermodynamic memory effects. It has been shown that in the *intermediate* phase long-range correlations play an important role [2]. From the percolation point of view this phase is characterized by  $0 < p < 1$ . The existence of a regime, where the *intermediate* phase is realized, has been reported only recently in chalcogenide glasses [4,5]. Finally, for  $N_f \ll N_c$  the *rigid* phase is encountered, in which  $p=1$  and the structure of the network can only be altered after being exposed to strong stresses.

A characteristic paradigm of an adaptive randomly connected network is that of aerosil particles with hydrophilic/hydrophobic treated surfaces dispersed in liquid crystals (LC) [6]. Aerosil-containing LCs have in the past few years been the targets of research efforts focusing primarily on

phase characterization as well as the study of phase transitions and critical phenomena [7,8]. So far, most studies concern the isotropic-nematic (*I-N*), nematic-smectic-*A* (*N-SmA*) [6,9–12] and smectic-*A*–smectic *C* (*SmA-SmC*) phase transitions [10,13–16]. By increasing the concentration  $x = m_a / (m_a + m_{LC})$  of aerosils a qualitatively different degree of disorder is imposed upon the hosting LC phase [6,17]. Here  $m_a$  and  $m_{LC}$  stand for the total mass of aerosil particles and LC molecules, respectively. For  $x < x_c^{(1)} \sim 0.01$  the aerosil particles, sole, or in small aggregates, form a colloidal state in which the aerosil network is in the *floppy* phase. In the so called *soft* regime of the LC-aerosil system [6], ranging between  $x \equiv x_c^{(1)}$  and  $x \equiv x_c^{(2)} \sim 0.1$ , a responsive aerosil network is formed corresponding to the *intermediate* [2] network phase. Finally, by further increasing  $x$  to  $x > x_c^{(2)}$ , the aerosil network enters the *rigid* phase [2] and the LC-aerosil dispersion the *stiff* regime.

So far, there exist only few experimental indications of the *soft-stiff* regime crossover in LC-aerosil dispersions. These include the *I-N*, *N-SmA*, and *SmA-SmC* phase transition temperature shifts as  $x$  is varied [6,9,10]. However, there are several dominant, but noncritical mechanisms influencing phase transition temperature shifts. The relative importance of these mechanisms depends on  $x$  in a rather complex way. Thus, the characterization of the *soft-stiff* regime transition based on the transition temperature shifts is difficult and in many cases impossible. In this contribution we study the LC phase behavior as a function of temperature and concentration  $x$  in the *SmA* phase by means of x-ray diffraction. Two chiral liquid crystals are used containing aerosil particles, with either hydrophilic or hydrophobic surface treatment, at various concentrations. We show, that the smectic-layer-spacing measurements in the *SmA* phase can be used as a sensible probe of the *intermediate-rigid* structural transition of the adaptive aerosil network. Possible origins of the observed phenomena are proposed and a qualitative agreement with the experimental results is obtained.

### II. EXPERIMENTAL PROCEDURES AND RESULTS

For all the experiments reported in this work, the LC compound S-(+)-[4-(2-methylbutyl) phenyl

\*E-mail address: nounesis@rrp.demokritos.gr

4-*n*-octylbiphenyl-4-carboxylate] (CE8) was supplied by Merck and was used without any additional treatment. The compound [*p*-(*n*-decyloxy) benzylidene-*p*-amino-(2-methylbutyl) cinnamate] (DOBAMBC) was synthesized at Jožef Stefan Institute. Hydrophilic aerosils 300 and hydrophobic R812 (spherical SiO<sub>2</sub> particles with diameter  $2R_a \sim 7$  nm, and active surface  $a=300$  and  $260$  m<sup>2</sup> g<sup>-1</sup>, respectively) were manufactured by Degussa. Preparation and mixing procedures as well as the details of the x-ray scattering technique have been described elsewhere [15]. The density of aerosil particles is given by  $\rho_a = m_a/V_{LC} \sim x\rho_{LC}$ . Here  $V_{LC}$  is the volume occupied by the LC phase and the mass density  $\rho_{LC}$  of LC molecules typically equals  $\rho_{LC} \sim 1$  g/cm<sup>3</sup>. The spherular aerosil particles have mass density  $\rho_s \sim 2.2$  g/cm<sup>3</sup>. These particles often assemble in larger aggregates with an average radius  $R = n_a R_a$ , where  $n_a$  typically ranges between 1 and 3 [6]. An important length characterizing the LC-aerosil mixture is the main aerosil network void size  $l_0 \sim 2/(a\rho_a)$  [6].

The smectic layer thickness  $d(x, T)$  was directly extracted from the x-ray scattering profiles. The relevant quantity of the relative layer compression  $\Delta d(x) = [d_0 - d(x)]/d_0$  was calculated far above the SmA-SmC\* transition temperature. Here  $d_0$  represents the equilibrium smectic A layer thickness observed in the bulk aerosil-free sample. The experimental results of  $\Delta d(x)$  for CE8 and DOBAMBC are presented in Fig. 1.

It is evident from the data presented in Fig. 1 that the anomalous change in  $\Delta d(x)$  observed for all the samples is indicative of a crossover behavior. For low  $x$ ,  $\Delta d(x)$  rises steeply while it approaches a plateau value at high  $x$ . This characteristic ‘‘crossover’’ behavior is peaked at  $x_t \sim 0.11 \pm 0.01$  for CE8. The effect of hydrophobic versus hydrophilic treatment of the aerosil surfaces is mild,  $x_t \sim 0.10$  vs  $x_t \sim 0.12$ . For DOBAMBC a similar trend is observed, although the plateau value for  $\Delta d$  is at a considerably lower value than for CE8. While there is a definite dependence of  $x_t$  upon the various samples, it is noteworthy that the experimental results roughly coincide with the previously reported threshold value  $x_t \sim 0.1$  for the *soft-stiff* regime structural transition [6] of aerosil containing LC dispersions.

### III. THEORY AND DISCUSSION

To discuss the obtained experimental results we estimate the aerosil-imposed contributions to  $\Delta d(x)$  arising from the recently observed pretilt in the SmA phase [15], by volume depletion, and by interparticle long-range interactions. The Landau-de Gennes-Ginzburg phenomenological approach [18] is introduced to describe the LC ordering in the SmA phase. In terms of the nematic director field  $\vec{n}$  and the complex smectic order parameter  $\psi = \eta e^{i\phi}$ , the elastic free energy density  $f_e$  in the SmA phase can be expressed as [18,19]

$$f_e = \frac{K}{2} |\nabla \vec{n}|^2 + C_{\parallel} |(\vec{n} \cdot \nabla - iq_0)\psi|^2 + C_{\perp} |(\vec{n} \times \nabla)\psi|^2. \quad (1)$$

The effective nematic elastic constant  $K$  describes the average resistance of LC ordering to orientational elastic dis-

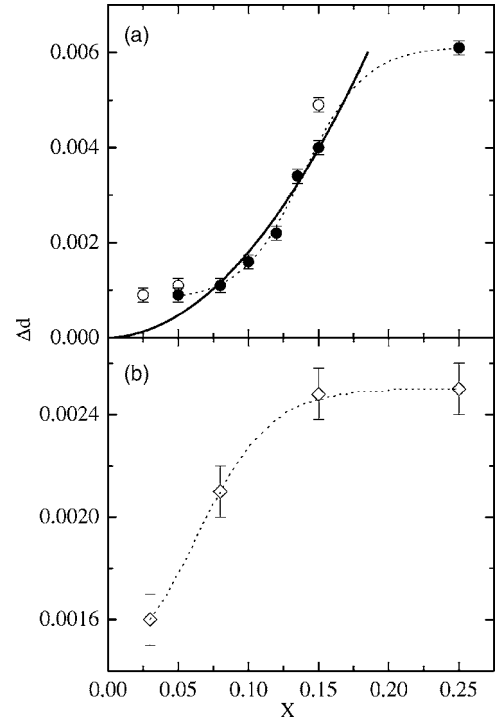


FIG. 1. (a) Relative layer compression  $\Delta d(x)$  for CE8 containing hydrophilic (solid circles) and hydrophobic aerosils (open circles). Solid line represents a calculation of  $\Delta d(x)$  for the hydrophilic sample by taking into account pretilt and volume depletion contributions in the vicinity of the *intermediate* phase nearing the *intermediate-rigid* transition (see text). The calculation clearly deviates from the experimental data obtained in the *floppy* and *rigid* phases. (b) Relative layer compression  $\Delta d(x)$  for DOBAMBC containing hydrophobic aerosils. The dotted lines are guides to the eye.

tortions. The smectic elasticity is represented by the smectic compressibility and the smectic bend term. In Eq. (1) they are weighted by positive compressibility ( $C_{\parallel}$ ) and bend ( $C_{\perp}$ ) smectic elastic constant respectively. In an elastically unconstrained configuration the smectic order parameter can be expressed as  $\psi = \eta_b e^{iq_0 \vec{n} \cdot \vec{r}}$ , where the equilibrium value  $\eta_b$  is spatially independent. Below the SmA-SmC phase transition temperature  $T_{AC}$  the elastic constant  $C_{\perp} \sim C_{\perp}^{(0)}(T/T_{AC} - 1)$  becomes negative. This triggers the tilt  $\theta = \arccos(\vec{n} \cdot \vec{v})$  of LC molecules with respect to  $\vec{v}$  (where  $\vec{v} = \nabla \phi / |\nabla \phi|$  defines the layer normal). Assuming that in the SmC phase the layer periodicity adopts the equilibrium value  $q = q_0 / \cos \theta$ , then for the spatially homogeneous case and  $\theta \ll 1$ , Eq. (1) takes the form  $f_e \sim \alpha_0 (T/T_{AC} - 1) \theta^2 + \beta \theta^4 / 2$ . Here  $\alpha_0 = C_{\perp}^{(0)} \eta_b^2 q^2$  and  $\beta$  is representative of higher order terms [not shown in Eq. (1)] needed to stabilize  $\theta$  at a finite value.

The orientational anchoring density term  $f_i$  is described at the aerosil-LC interface using the Rapini-Papoular [18] approach:  $f_i = \frac{W}{2} [1 - (\vec{e}_s \cdot \vec{n})^2]$ . Here  $W > 0$  is the surface anchoring strength and  $\vec{e}_s$  defines the surface easy axis. In all the samples studied here the aerosils enforce homeotropic anchoring, tending to align LC molecules along the LC-aerosil interface normal. The following characteristic lengths [18] are thus introduced: the orientational anchoring extrapolation length  $d_e = K/W$ , the smectic penetration lengths  $\lambda_i$

$= \sqrt{K/(\eta^2 C_i q_0^2)}$ , and the smectic order parameter correlation lengths  $\xi_i = C_i / \left| \frac{\alpha_0(T-T_{AC})}{T_{AC}} \right|$ , where the subscript  $i$  stands either for  $i=\parallel$  or  $i=\perp$ . Neglecting the anisotropy in the smectic elastic constants we set  $C \equiv C_{\parallel} \sim C_{\perp}$ , thus  $\lambda \equiv \lambda_{\parallel} - \lambda_{\perp}$  and  $\xi \equiv \xi_{\parallel} \sim \xi_{\perp}$ . For  $R/d_e > 1$  the aerosil particles enforce homeotropic anchoring. In the SmA phase, in the case that the director field is aligned along the aerosil strands, the latter become the pinning nuclei for the phase of smectic ordering. In general, near aerosils  $\vec{n}$  is tilted with respect to the layer normal, inducing layer compression.

The conditions are next analyzed, in which a pretilt of  $\vec{n}$  globally established in the entire sample can be expected due to the presence of aerosil particles. For this purpose we begin by comparing the free energies with homogeneous and distorted ordering in the nematic phase. In the first case we assume that the system orientational ordering is negligibly influenced by aerosil particles. The resulting free energy is then approximately  $F_{\text{hom}} \sim A_i W$ . In this case all significant free energy costs arise from the misalignment at the LC-aerosil interface. The subscript hom labels homogeneous structure with negligible pretilt and  $A_i \sim N_a 4\pi R^2$  is an estimate of the LC-aerosil interface area. Here  $N_a$  counts the number of aerosil particles or aerosil-particles aggregates. In the competing distorted configuration the conditions at the aerosil-LC interface are strictly obeyed (i.e., the anchoring contribution is now negligible). However, this triggers elastic distortions in the remaining volume occupied by LC molecules. In a volume  $l_0^3$  the elastic free energy density penalty is roughly given by  $K/l_0^2$ , yielding  $F_{\text{pre}} \sim N_a K l_0$ . The subscript pre now labels the distorted structure, i.e., the structure where a global pretilt  $\theta$  can be expected in the SmA phase.

The trade-off between these two estimates defines the threshold condition separating regimes with negligible and finite pretilt value. The configuration with significant ‘‘global’’ pretilt is expected when  $F_{\text{non}}/F_{\text{pre}} \sim \frac{4\pi R^2 W}{K l_0} = \frac{4\pi R^2}{d_e l_0} > 1$ . Taking into account  $l_0 \sim 2/(\rho_a a) \sim 2/(x \rho_{LC} a)$ , it follows:

$$x > x_t \equiv \frac{K}{2\pi R^2 W a \rho_{LC}}. \quad (2)$$

Setting  $K \sim 5 \times 10^{-12}$  J/m,  $a \sim 300$  g/m<sup>2</sup>,  $R = n_a \times 3.5$  nm,  $n_a \sim 3$ ,  $W \sim 10^{-4}$  J/m<sup>2</sup>,  $\rho_{LC} \sim 1$  g/cm<sup>3</sup> a rough estimate of the threshold condition  $x_t \sim 0.1$  is obtained.

In order to estimate the layer compression due to the pretilt an ‘‘inherent’’ as well as an ‘‘external’’ contribution in  $F$  must be considered

$$F \sim [\alpha_0(T/T_{AC} - 1)\theta^2 + \beta\theta^4/2]V_{LC} + A_i W(\theta_t - \theta)^2/2. \quad (3)$$

The inherent contribution, weighted with  $V_{LC}$ , tends to impose the elastically favored ordering [i.e.,  $\theta(T > T_{AC}) = 0$ ,  $\theta(T < T_{AC}) = \sqrt{\alpha_0(1 - T/T_{AC})/\beta}$ ]. On the other hand, the external field (i.e., the LC-aerosil interface) enforces  $\theta = \theta_t$ . In the SmA phase the two contributions result in the establishment of a global finite pretilt. From  $\frac{\partial F}{\partial \theta} = 0$  we get  $\theta \sim \frac{W\theta_t A_i}{2\alpha_{\text{eff}} V_{LC}} \sim \frac{3\theta_t W \rho_a}{2\alpha_{\text{eff}} \rho_s}$ , where the effective constant  $\alpha_{\text{eff}} > 0$  represents all the terms that are quadratic in  $\theta$ . Deep in the SmA phase one expects  $\lambda \sim d_0$ . Imposing a simple linear

$A_i = A_i(x)$  dependence:  $A_i \sim N_a 4\pi R^2 \sim V_{LC} 3\rho_{LC} x / (\rho_s R)$  yields  $\theta/\theta_t \sim 6\pi\eta^2 \frac{\rho_{LC}}{\rho_s} \frac{\xi^2}{R d_e} x$ . For  $d = d_0 \cos \theta \sim d_0(1 - \theta^2/2)$  it follows:

$$\Delta d \sim \frac{\theta_t^2 x^2}{2} \left( 6\pi\eta^2 \frac{\rho_{LC}}{\rho_s} \frac{\xi^2}{R d_e} \right)^2. \quad (4)$$

Based on the result of Eq. (3) the observed anomaly in the  $\Delta d(x)$  profile can be understood in the following way: With increasing  $x$  the tendency for pretilt increases. In the *soft* regime the aerosil network can partially relax the imposed strain, leading to a relatively weak compression of the smectic layers. However, in the neighborhood of the *intermediate-rigid* transition (i.e.,  $x \sim x_c^{(2)}$ ) the network’s ability to adapt diminishes and global tilt is imposed. In this regime the above derivation is sensible, suggesting  $\Delta d \propto x^2$ . In the regime  $x > x_c^{(2)}$  the pretilt tendency of the network is fully realized, leading  $\Delta d(x)$  to asymptotically approach a constant plateau value.

Aerosil-induced layer compression may also arise from the reduction of the volume available to LC molecules. We further estimate the contribution to  $\Delta d(x)$  assuming that the system volume  $V = L_x L_y L_z = L^3$  is constant, containing undistorted SmA layers stacked along the  $z$  axis. Then  $L_z = N_d d_0$ , where  $N_d$  stands for the number of smectic layers. When aerosil particles are added, the volume available to LC molecules equals  $V_{LC} = L^3 - N_a v_a$ . Here  $N_a = m_a / M_a$  equals the number of aerosil particles each occupying a volume  $v_a$ ,  $m_a$  is the total mass of aerosils in  $V$  and  $M_a$  is the mass of an individual aerosil particle. Taking into account the relations  $m_a = \rho_a V_{LC}$  and  $M_a = \rho_s v_a$ , one gets  $V_{LC} = L^3(1 - \rho_a/\rho_s) = L^2 N_d$ . If the number of smectic layers is conserved then  $V_{LC}/V = d/d_0$ , leading to

$$\Delta d \sim \frac{\rho_a}{\rho_s} \sim \frac{\rho_{LC}}{\rho_s} x. \quad (5)$$

This expression yields the upper limit of the compression of smectic layers due to the reduced volume, because a constant pressure condition is imposed upon all our samples. In Fig. 1(a) the solid line represents a calculation best matching the data in the intermediate range of concentrations for CE8 containing hydrophilic treated aerosils, by taking into account both pretilt and volume depletion contributions. It is clear that the quadratic term related to the pretilt is the dominant contribution. It must be noted that our argumentation is valid only for the intermediate range of concentrations near  $x_t \sim 0.1$ . Deviations at small concentrations on approaching the limit between the *intermediate* network phase and the *floppy* phase indicate the lower limit above which our model is realistic. Namely, there might be an additional qualitative change in behavior at low concentrations on crossing from the floppy to the intermediate network phase [6].

A third possible origin for layer compression may be the long range interactions between the aerosil particles. The compression mechanism is only sensible in the *intermediate* phase, in which the average interaerosil distance is within the range of the interaction. The interaction is of topological origin mediated by an intervening nematic director field. For strong enough anchoring (i.e., for  $R/d_e > 1$ ), a pair of aerosil

particles is equivalent to a pair of radial hedgehog defects separated by a few smectic layers. Consequently, a topological dipole is formed, which in the nematic phase is surrounded by a director field analogous to the electric field produced by an electric dipole [20,21].

The dipole-dipole interaction in the SmA phase leads to layer compression. The interaction energy  $U_{dip}$  between two topological dipoles, separated by  $r$  and aligned along the same direction, can be roughly expressed as [21]  $U_{dip} \sim 8\alpha\pi KR_a^4/r^3$ ,  $\alpha \sim 1$ . To estimate the smectic compression free energy density penalty  $f_{com}$  we set  $\vec{n}=(0,0,1)$  and  $\psi=\eta_b e^{iqz}$  in Eq. (1). It follows that  $f_{com} \sim C_{\parallel}\eta_b^2(q-q_0)^2 \sim C_{\parallel}\eta_b^2q_0^2(\Delta d)^2$ . We further assume that there is on average one dipole per volume  $V \sim l_0^3$ . By putting  $f_{com}l_0^3 \sim U_{dip}$  and  $r \sim l_0$  one gets the estimate

$$\Delta d \sim \sqrt{8\alpha\pi} \frac{\lambda R_a^2}{l_0^3}. \quad (6)$$

Deep in the SmA phase  $\lambda$  is comparable to a typical molecular size. Setting  $\lambda=d_0$  one gets

$$\Delta d \sim \sqrt{8\alpha\pi} d_0 R_a^2 / l_0^3 \sim \sqrt{\frac{\alpha\pi}{8}} d_0 R_a^2 a^3 \rho_{LC} x^3. \quad (7)$$

In the SmA phase, however, the strong influence of the smectic layers upon the director field screens the dipole-dipole interaction reducing the magnitude of layer compression due to long-range aerosil interactions. The influence of smectic layers on the director  $\vec{n}$  must also be considered. Simple analysis in which we consider a planar system with either an external homogeneous electric field or smectic layers shows that the free energy of these systems has similar structure for small deviation from the homogeneous director field structure. It follows that the smectic ordering has similar influence on  $\vec{n}$  as an external field, the strength of which

is given by  $\xi_f \sim \lambda_{\perp}$ . Here  $\xi_f$  stands for the field coherence length [18]. Deep in the SmA phase  $\lambda_{\perp} \sim \text{nm} < l_0$ , which corresponds to a relatively strong external field. Note that a strong external field for positive LC field anisotropy aligns  $\vec{n}$  along its direction. Consequently it screens the influence of a source enforcing inhomogeneous ordering in  $\vec{n}$ .

#### IV. CONCLUSIONS

To conclude, we have studied the *soft-stiff* regime crossover (i.e., *intermediate-rigid network transition*) in various LC-aerosil dispersions. Our x-ray scattering results reveal universal  $\Delta d(x)$  profiles exhibiting an anomalous change at the *soft-stiff* structural transition. We find that for all the studied samples  $x_t$  is material dependent. By exploring various scenarios for aerosil-induced smectic layer shrinkage it is shown that a dominant mechanism is the aerosil enforced pretilt upon the enclosing SmA phase. This pretilt can be globally established on approaching the *intermediate-rigid* phase transition. Above this transition the aerosil network can no longer adapt to the imposed strain originating from the elastically distorted LC phase. Consequently, the aerosil network structural transition is accompanied by the regime crossover in the LC ordering. It is known that in the *soft* (i.e., *intermediate*) regime potential interparticle long-range forces could play an important role. We show, that these forces could arise in ordered LC phases due to topological reasons if  $RW/K > 1$ . However, the presence of smectic layers strongly weakens their magnitude.

#### ACKNOWLEDGMENTS

This research was supported by the Slovene-Greek Scientific and Technological Cooperation under Project No. GR 16/2004 and Slovenian Office of Science program under Program No. P1-0125 and Project No. J1-6593-0106-04.

- 
- [1] A.-L. Barabási and E. Bonabeau, *Sci. Am.* **288**, 50 (2003).  
 [2] J. Barre, A. R. Bishop, T. Lookman, and A. Saxena, *Phys. Rev. Lett.* **94**, 208701 (2005).  
 [3] J. F. F. Mendes and N. S. Dorogovtsev, *Evolution of networks: From Biological Nets to the Internet and WWW* (Oxford University Press, Oxford, 2003).  
 [4] M. F. Thorpe, D. J. Jacobs, M. C. Chubinsky, and J. C. Phillips, *J. Non-Cryst. Solids* **266**, 859 (2000).  
 [5] X. Feng, W. J. Bresser, and P. Boolchand, *Phys. Rev. Lett.* **78**, 4422 (1997).  
 [6] G. S. Iannacchione, C. W. Garland, J. T. Mang, and T. P. Rieker, *Phys. Rev. E* **58**, 5966 (1998).  
 [7] D. E. Feldman and R. A. Pelcovits, *Phys. Rev. E* **70**, 040702(R) (2004).  
 [8] S. Kralj and V. Popa-Nita, *Eur. Phys. J. E* **14**, 115 (2004).  
 [9] A. Roshi, G. S. Iannacchione, P. S. Clegg, and R. J. Birgeneau, *Phys. Rev. E* **69**, 031703 (2004).  
 [10] P. S. Clegg, R. J. Birgeneau, S. Park, C. W. Garland, G. S. Iannacchione, R. L. Leheny, and M. E. Neubert, *Phys. Rev. E* **68**, 031706 (2003).  
 [11] R. L. Leheny, S. Park, R. J. Birgeneau, J.-L. Gallani, C. W. Garland, and G. S. Iannacchione, *Phys. Rev. E* **67**, 011708 (2003).  
 [12] G. S. Iannacchione, S. Park, C. W. Garland, R. J. Birgeneau, and R. L. Leheny, *Phys. Rev. E* **67**, 011709 (2003).  
 [13] Z. Kutnjak, S. Kralj, and S. Žumer, *Phys. Rev. E* **66**, 041702 (2002).  
 [14] Z. Kutnjak, G. Cordoyiannis, and G. Nounesis, *Ferroelectrics* **294**, 105 (2003).  
 [15] G. Cordoyiannis, G. Nounesis, V. Bobnar, S. Kralj, and Z. Kutnjak, *Phys. Rev. Lett.* **94**, 027801 (2005).  
 [16] S. A. Rozanski and J. Thoen, *Liq. Cryst.* **32**, 1013 (2005).  
 [17] T. Jin and D. Finotello, *Phys. Rev. E* **69**, 041704 (2004).  
 [18] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford University Press, Oxford, 1993).  
 [19] J. C. Loudet and P. Poulin, *Phys. Rev. Lett.* **87**, 165503 (2001).  
 [20] J. I. Fukuda and H. Yokoyama, *Phys. Rev. Lett.* **94**, 148301 (2005).  
 [21] P. Poulin and D. A. Weitz, *Phys. Rev. E* **57**, 626 (1998), and references therein.