Spontaneous buckling of compressible droplet chains in free standing smectic-*C* films

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Isotropic spheres or droplets dispersed in a smectic freely suspended film can self-organize in chains that interact with the *c*-director field of the embedding smectic material. Spontaneous buckling of such chains has been reported when the chains grow under geometrical restrictions, by incorporation of additional droplets. We refine the original model for incompressible chains by taking into account a finite energy associated with the variation of the intrachain droplet-droplet-distance. In addition to the wavelength selection described already by the inelastic chain model, the refined model yields a critical threshold for spontaneous buckling, in agreement with experimental observations.

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I. INTRODUCTION

An interesting phenomenon observed in suspensions of isotropic droplets in liquid crystalline phases is their interaction and self-organization via the orientational elasticity of the anisotropic matrix. In nematic phases, the interactions of oil or water droplets have been studied extensively [1–5]. In free standing smectic-*C* and C^* films, chaining of isotropic or cholesteric droplets has been described (e.g., [6–10]). Qualitatively, one can consider this as an analogy to chaining in electrorheological fluids [11].

In the investigated material, each droplet carries a pair of half-integer defects of the *c*-director field (local orientation of the smectic-*C* film) at its boundary [9,10], and the droplet itself can be described qualitatively by a virtual defect of strength $S=1$. Droplets and their attached defects impose distortions in the *c*-director field of the surrounding film and form topological dipoles, which interact by orientational elastic forces in the smectic film and lead to the spontaneous chaining of the droplets.

The equilibrium configuration of such droplet chains is straight, with regular equilibrium droplet distances within the chains [6,7] depending on the droplet diameters and the anchoring conditions of the *c*-director at the droplet border. The *c*-director is aligned to the chain direction and antiparallel on both sides of the chain.

Recently, the observation of an instability in such chain structures (Figs. 1 and 2) has been reported, which occurs in films where droplet chains are regularly arranged in a circular pattern (target pattern) of the *c*-director [10]. The films have lateral dimensions of 1 mm and above, with uniform film thicknesses below 1 μm (in the order of 100 smectic layers). Droplet sizes are in the micrometer range. Details of the experiment, the preparation of the target pattern, and control of droplet density are described elsewhere [10]. Figures 1 and 2 show reflection microscopy images of free standing smectic-*C* films, observed with crossed polarizers (horizontal and vertical). In dark domains, the *c*-director is parallel to one of the polarizers, in bright regions it is diagonal.

The droplet density can be controlled by the illumination of the photosensitive mesogenic film material (*cis-trans*-isomerization of the azoxy-derivative). With increasing light intensity, the *cis*-isomer concentration rises and smectic material may melt locally into the isotropic phase. New droplets appear in the film, they are incorporated into existing chains so that the chains grow in length. Short chain segments (Fig. 3), arranged tangentially in the target pattern, grow until they completely fill circular rings. Closed rings can grow further only by developing characteristic undulations. At some threshold droplet density, the chains are subject to a spontaneous buckling with rather well-defined periodicity (Fig. 2). The amplitude of the undulations increases with increasing droplet density, while the wavelength is almost insensitive to the experimental conditions. There is a striking analogy to biological growth processes and Euler buckling observed in a variety of physical and biological systems [12–15].

The density of droplets increases towards the inner chains, which collect most of the droplets that form in the film middle ("hurricanes eye"). Buckling starts with the innermost chains when a certain "supersaturation" is reached. Below that critical value, completely filled chains remain circular (Fig. 1) and may be compressed, i.e., the internal

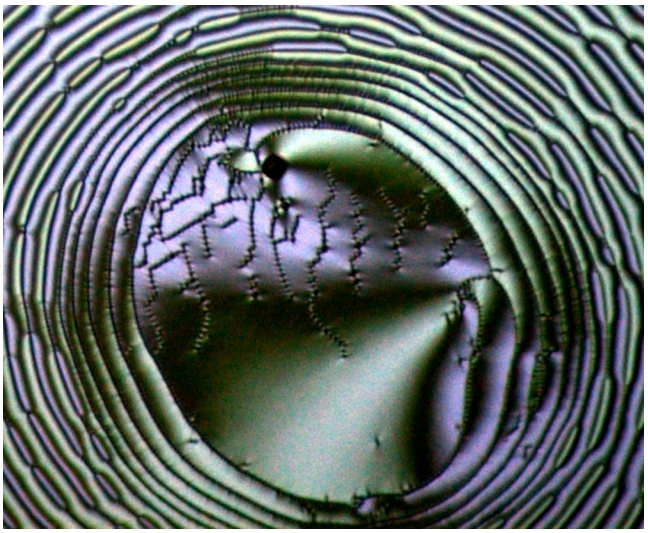

FIG. 1. (Color online) Droplet chains in a target pattern of the *c*-director field. The droplets consist of molten, isotropic film material. Individual droplets are not resolved in the picture [cf. Fig. 3(a)], the droplet chains are seen as dark lines. The image shows completely filled (supersaturated) chain rings before the onset of buckling, the image width is 0.4 mm.

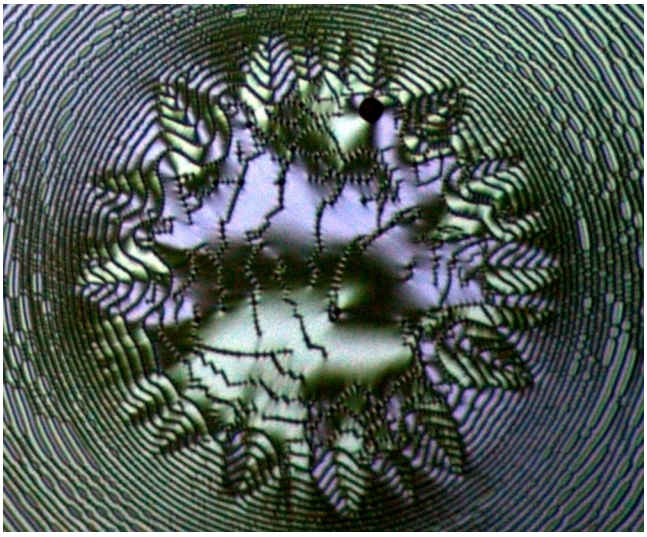

FIG. 2. (Color online) Buckling of droplet chains after increasing the droplet density, image width ≈0.4 mm, geometry and polarizers as in Fig. 1.

droplet distance becomes smaller than the equilibrium value. Figure 3(b) compares a chain from an outer, incompletely filled ring (left) with a segment of a closed ring that is not buckled yet (right). Its compression reaches about 10%. While the wavelength selection has been predicted already with a simple model for incompressible chains [10], the existence of a critical droplet density for buckling is not obtained within that model. In the extension presented here, we allow for a compressibility of the chains and obtain an expression for a critical droplet density leading to the onset of the undulation.

We treat the chains as elastic strings characterized by a certain bending rigidity, a longitudinal compressibility and an interaction with their neighbors, mediated by the *c*-director field. A spatial restriction is imposed by the circumference of a given circular chain. In the model, we make

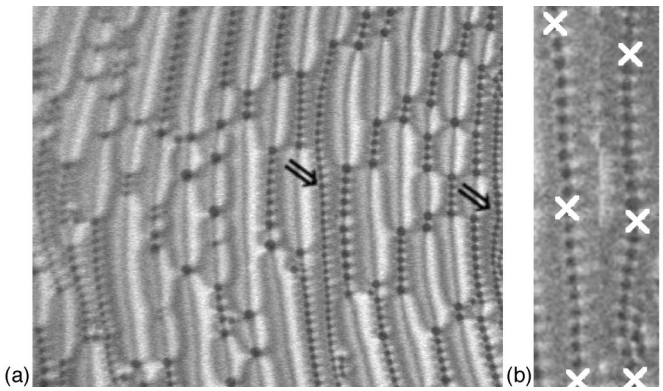

FIG. 3. (a) Enlarged detail of a target pattern with individual droplets in the chains resolved. The chains prefer bend regions of the *c*-director and contract these regions to slightly more than the droplet diameter. Arrows mark the two chains compared in (b). (b) Comparison of a free chain (left) with a compressed, but still almost straight chain (right), for better comparison every 10th droplet is marked with a white cross. The chain is compressed by approximately 10%.

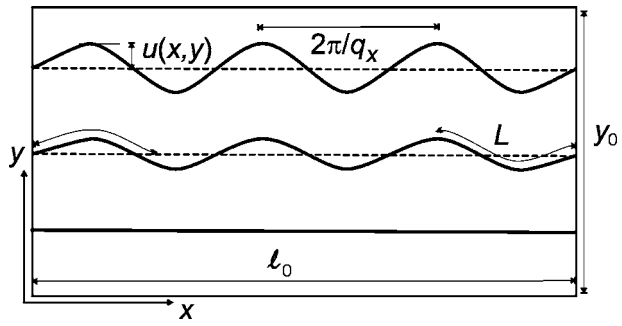

FIG. 4. Model geometry of the chain deformation and wavelength selection (see text).

the following three assumptions: (1) Droplets in the chains have an equilibrium distance, and a force is necessary to elongate or compress the chains. (2) The chains prefer a straight shape, any chain deflection costs energy. This energy is associated with the curvature of the *c*-director field between neighboring chains, and with a chain bending rigidity. The latter is related to elastic forces of the *c*-director field surrounding each droplet. (3) The chains prefer an equilibrium distance between each other. There is no straightforward way to measure this force, but its presence is suggested by the experimental observations (see Fig. 1). A direct quantitative relation between the *c*-director field distortions and the interchain potential cannot be given until a rigorous calculation of the director configuration has been achieved. Some additional assumptions are made to keep the model simple, they will not influence the qualitative predictions.

II. MODEL AND DISCUSSION

Figure 4 sketches the simplified model geometry. The circular chains in the cylindrical arrangement have been "unwrapped" to Cartesian coordinates. The box dimensions are ℓ_0 and y_0. In the actual experimental geometry, ℓ_0 corresponds to the circumference of a closed ring, and y_0 to the radial range completely filled with droplet rings. The undulations are described by an ansatz $u(x,y) = u_0 \sin(q_y y)\cos(q_x x)$.

A parameter $\sigma(y)$ describes the excess droplet density, it defines the theoretical length $\ell = [1+\sigma(y)]\ell_0$ of a force-free chain at position y, given by the number of droplets and the equilibrium droplet distance in the chain. The expression $\sigma+1 = N/N_0$ gives the ratio of the actual number N of droplets in the chain and the number N_0 of droplets in a relaxed straight chain of length ℓ_0 (in the experiment, the number of droplets that fill a closed chain with a given radius). We assume that $\sigma(y)$ is a monotonically increasing function of y with the value S in the innermost ring. We may use an ansatz $\sigma = S \sin(q_y y)$ with $q_y = \pi/(2y_0)$, but the choice of this function is not crucial. With other functions, one obtains somewhat different quantitative results for thresholds, but the same critical wavelengths, as shown below.

The energy necessary to reduce or increase the droplet-droplet distance in a single chain is described with the ansatz (Hooke's law) $W_{L1} = \gamma_1[\ell(y) - L(y)]^2/2$, where

$$L(y) = \int_0^{\ell_0} u(x,y)dx \approx \left(1 + \frac{1}{4}q_x^2 u_0^2 \sin^2(q_y y)\right)\ell_0$$

is the actual chain length, which differs from ℓ when the chain is stretched or compressed. A specific energy W_L (per film area) is obtained after division of W_{L1} by the effective area per single chain, $\ell_0 d_C$, d_C being the equilibrium interchain distance. One obtains

$$W_L = (\gamma/2)[\ell(y) - L(y)]^2 = (\gamma/2)\left[S\sin(q_y y) - \tfrac{1}{4}q_x^2 u_0^2 \sin^2(q_y y)\right]^2 \quad (1)$$

with the compression modulus $\gamma = \gamma_1/(d_C \ell_0)$.

The second specific energy contribution is related to the curvature of the chains and to the bend of the director field in the interchain gaps, it provides an effective chain bending rigidity

$$W_K = \tfrac{1}{2}K\left(\partial^2 u/\partial x^2\right)^2 = \tfrac{1}{2}Kq_x^4 u_0^2 \sin^2(q_y y)\cos^2(q_x x). \quad (2)$$

K is expected to be linearly related to the coefficients K_{splay}, K_{bend} describing elastic deformations of the c-director in the smectic layers. The third energy density term accounts for the interchain potential, approximated by

$$W_B = \tfrac{1}{2}B\left(\partial u/\partial y\right)^2 = \tfrac{1}{2}Bq_y^2 u_0^2 \cos^2(q_y y)\cos^2(q_x x). \quad (3)$$

We average these contributions over the (x,y)-plane, using $\overline{\cos^2(q_x x)} = \overline{\cos^2(q_y y)} = \overline{\sin^2(q_y y)} = \tfrac{1}{2}$, $\overline{\sin^3(q_y y)} = 4/3\pi$, $\overline{\sin^4(q_y y)} = \tfrac{3}{8}$. The averaged specific energy is

$$w = \frac{1}{8}Kq_x^4 u_0^2 + \frac{1}{8}Bq_y^2 u_0^2 + \frac{3\gamma}{256}q_x^4 u_0^4 - \frac{\gamma}{3\pi}Sq_x^2 u_0^2 + \left(\frac{\gamma}{4}S^2\right). \quad (4)$$

All coefficients of this equation except one control parameter s can be set to unity by introducing the dimensionless quantities

$$Q^4 = \left(K/Bq_y^2\right)q_x^4, \quad U^2 = \left(3\gamma/32K\right)u_0^2,$$

$$W = \left(3\gamma/4BKq_y^2\right)w, \quad \text{and } s = \left(8\gamma/3\pi\sqrt{BK}q_y\right)S.$$

One arrives at the equation

$$W = Q^4U^4 + Q^4U^2 + U^2 - sQ^2U^2 \quad (5)$$

where a constant (proportional to S^2) has been dropped. Figure 5 shows the energy profiles for three selected values of s. The extrema of W are found from $dW/dU = 4Q^4U^3 + 2Q^4U + 2U^2 - 2sQ^2U = 0$, and $dW/dQ = 4Q^3U^4 + 4Q^3U^2 - 2sQU^2 = 0$. These equations are satisfied by the trivial solution $U=0$ (chain compression, no buckling). In addition, there are the nontrivial solutions $Q = \pm 1$, $U = \pm\sqrt{(s-2)/2}$ for $s > 2$. The interpretation is as follows: The wave number of the equilibrium deformation is $|Q| = 1$, independent of the excess saturation s. Expressed in actual spatial coordinates,

$$q_x^2 = \sqrt{\frac{B}{K}}\left(\pi/2y_0\right). \quad (6)$$

This result had already been found in a simplified model, valid in the limit of very large γ [10], i.e., for incompressible chains. The amplitude of the deflection is zero when the supersaturation s is below the critical value $s_c = 2$. At subcritical s, the nontrivial energy minima do not exist. This result confirms the experimental data [Figs. 3(b) and 1] which indicate that a slight supersaturation s leaves the droplet chains circular. At $s = s_c$, buckling sets in with an amplitude u_0 that increases with $(s - s_c)^{1/2}$.

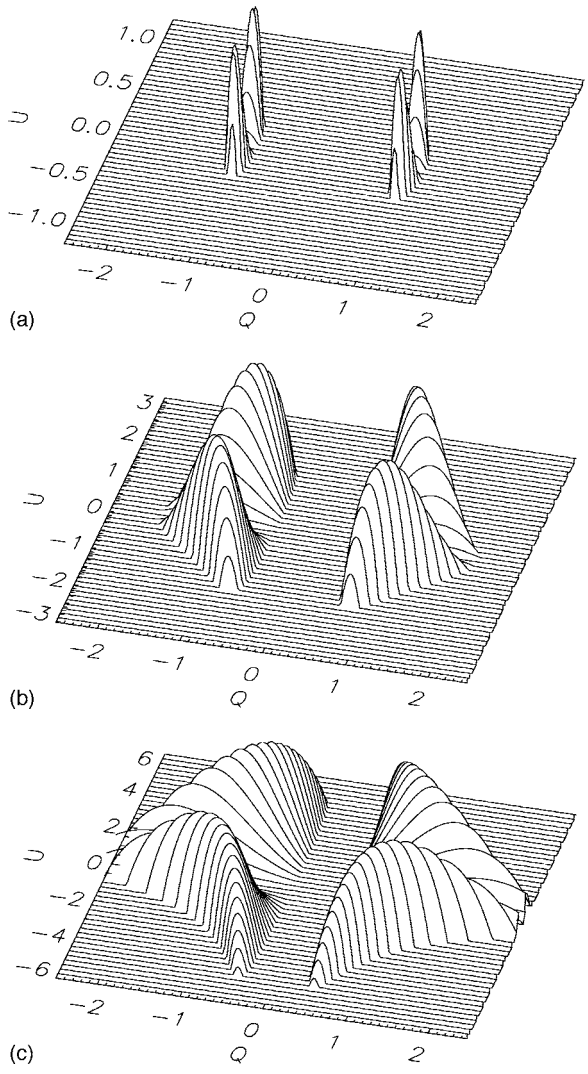

FIG. 5. Energy profiles $-W(Q,U)$ for $s = 2.1$, 4.0, 10, respectively. (left to right). Positive values of W have been clipped.

The assumption of a sine quarterwave in the $\sigma(y)$-dependence has been quite arbitrary in this model, but it is very difficult to access these characteristics experimentally. Thus we have chosen the simplest ansatz. Any other smooth, monotonic function $\sigma(y)$ that starts from zero at $y=0$ and reaches its maximum at y_0 can be employed as well. This will yield a certain different threshold s_c, but the qualitative picture remains valid.

Now we can discuss the experimental accessibility of these model parameters. There is a good chance to access K from the simulation of the director field with numerical or analytical methods, since K can be completely reduced to an elastic energy computation for straight and bent chains. The interaction potential between the chains is also based entirely on elastic interactions by the c-director field. Probably, it can

also be derived from numerical director field calculations and a relation to the elastic constants can be found. The same applies to the chain compressibility. Once the droplet interaction potential has been obtained, one can easily derive the force constant. We note that all the discussed forces and energies scale linearly with the film thickness, so that the structures should not show any film thickness dependence.

Finally, we try a very crude estimation: K is simply set equal to the averaged elastic constant $(K_{\mathrm{splay}}+K_{\mathrm{bend}})/2$, and we approximate B with $K(\pi/d_{\mathrm{C}})^2$. Further we assume that we have approximately $n=10$ filled chains (as in Fig. 2), i.e., $y_0 \approx 10 d_{\mathrm{C}}$. Then we find from Eq. (6) the undulation wavelength

$$\lambda = \frac{2\pi}{q_x} = 2\pi\left(\sqrt{\frac{K}{B}}\frac{2y_0}{\pi}\right)^{1/2} \approx 2\pi\sqrt{\frac{y_0}{n\pi}\frac{2y_0}{\pi}} = \sqrt{\frac{8}{n}}y_0.$$

The wavelength is of a comparable length as y_0, which is satisfactorily confirmed by the experiment in Fig. 2. We can also try to estimate at least the order of magnitude of the force constant γ when we consider that the critical value S_c is of the order of probably 20% [Fig. 3(b)]. Then,

$$2 = s_{\mathrm{c}} = \frac{8\gamma}{3\pi\sqrt{BK}q_y}S_{\mathrm{c}} \approx \frac{8\gamma}{3\pi}\frac{\pi}{Bd_{\mathrm{C}}}\frac{2y_0}{\pi} \times 0.2, \quad \gamma \approx 1.2B,$$

the chain compression coefficient γ is of the same order of magnitude as B. Even though our estimation is rather crude, the result is quite reasonable. Both quantities originate from the same physical effect, the distortion of the c-director field, and the relative droplet displacement in the chains is smaller but of the same order of magnitude as the interchain distances.

III. SUMMARY

Our model of the energetic conditions in elastic chains of isotropic droplets in smectic-C films predicts, in qualitative accordance with the experiment, the selection of a preferred undulation wavelength independent of the excess droplet density. In addition, a critical supersaturation

$$S_{\mathrm{c}} = \left(3\pi^2/8\right)\left(\sqrt{BK}/\gamma y_0\right)$$

is found for the onset of spontaneous buckling. For subcritical S, the chains are slightly compressed but remain straight. In the target patterns, they form circular, undeformed rings.

We have derived this result by making the simple assumption here that the y-dependence of the droplet density is proportional to $\sin(q_y y)$. Actually, this assumption is quite arbitrary, and one may ask how other model functions influence the general results of the calculation. If one starts with $\sigma = S\sin^2(q_y y)$, and $q_y = \pi/y_0$ instead, the droplet density of the first and last chain are the same as in the previous calculation (however, the average excess $\bar{\sigma}=\int \sigma dy$ decreases from $S\times 2/\pi$ to $S/2$), but Eq. (1) changes to $W_L = \gamma/2(S - q_x^2 u_0^2/4)^2 \sin^4(q_y y)$ and Eq. (4) is modified in the last two terms to

$$w = \frac{1}{8}Kq_x^4u_0^2 + \frac{1}{8}Bq_y^2u_0^2 + \frac{3\gamma}{256}q_x^4u_0^4 - \frac{3\gamma}{32}Sq_x^2u_0^2 + \left(\frac{3\gamma}{16}S^2\right), \tag{7}$$

and one has to redefine the dimensionless control parameter by $s=[3\gamma/(4\sqrt{BK}q_y)]S$, which does not influence the wavelength selection but changes the critical value

$$S_{\mathrm{c}} = \left(8\pi/3\right)\left(\sqrt{BK}/\gamma y_0\right),$$

i.e., the numerical prefactor changes from 3.70 to 8.37, with all qualitative conclusions of the model remaining valid. A change of this numerical factor is reasonable, it was noted above that the total amount of excess chain material $(\bar{\sigma})$ for the same parameter S is lower in the latter situation.

Although the model is applied here only to a very special situation, its application is by far not restricted to this situation. With proper translation of the involved energy terms, it has the potential to describe buckling phenomena of coupled elastic chain or string arrays in different physical or biological systems.

ACKNOWLEDGMENT

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