# LIQUID CRYSTALS

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### Summary

Since the beginning of the 1970's the term *soft matter* has been established to describe the complex behavior of a large variety of materials that share some common features, mainly related to the nontrivial interaction between the micro- and the macroscopic degrees of freedom. Liquid crystals, colloids, polymers, granular materials and biological tissues are only a few among the many soft materials that challenge today's research.

It is the aim of the present chapter to review in some detail the properties of two soft materials of keen technological importance: nematic liquid crystals and nematic elastomers.

# 1. The Liquid Crystalline Phase

Liquid crystals are aggregates of molecules which interact to build up an ordered phase whose physical properties are intermediate between those of fluids and solids. In the liquid-crystalline phase, the molecules possess orientational order, though they do not exhibit complete positional order. In this chapter we will review the mathematical definition of such a phase, and the order parameters that characterize its physical properties. We will further present the variational theories that govern the equilibrium properties as hyperelastic continua. A section is devoted to the constitutive equations that portray liquid crystals as anisotropic viscoelastic continua. Finally, we analyze in some detail the equilibrium properties of nematic elastomers, and show how the soft elasticity modes arise as their mechanical fingerprints.

### Director

Many different chemical substances possess a liquid-crystalline phase. Their molecules may be quite different in shape, size, and composition, but they share the common property that their central ellipsoid of inertia is (sufficiently close to be) a spheroid, either sharply prolate (rod-like or *calamitic* liquid crystals), or sharply oblate (disk-like or *discotic* liquid crystals). In both cases, we may identify the molecular orientation by means of a unit vector  $\mathbf{n}$ , called the *director*, parallel to the axis of rotational symmetry of the spheroid.

In addition, most liquid crystal molecules possess an extra head-and-tail symmetry. This means that their physical properties are not altered if we perform a reflection with respect to the plane orthogonal to the director. The directors **n** and  $-\mathbf{n}$  describe thus one and the same physical state. The reflection symmetry may be taken into account by assuming that the director **n** is not an element of the unit sphere  $\mathbb{S}^2 = \{\mathbf{v} \in \mathbb{R}^3 : \mathbf{v} \cdot \mathbf{v} = 1\}$ , but rather an element of the real projective plane  $\mathbb{RP}^2 = \mathbb{S}^2/\sim$ . The equivalence relation defining the above quotient labels as equivalent any two parallel unit vectors (*i.e.*, given  $\mathbf{n}, \mathbf{m} \in \mathbb{S}^2$ , we say that  $\mathbf{n} \sim \mathbf{m}$  whenever  $\mathbf{n} \wedge \mathbf{m} = 0$ ). An alternative way to characterize the real projective plane is provided by its representation as a compact submanifold of the set of symmetric linear tensors  $\operatorname{Lin}(\mathbb{R}^3)$ :

$$\mathbb{RP}^2 \cong \{\mathbf{n} \otimes \mathbf{n}, \text{with } \mathbf{n} \in \mathbb{S}^2\} \subset \{L \in \operatorname{Lin}(\mathbb{R}^3) : L = L^{\mathrm{T}}, \operatorname{tr} L = 1, L \ge 0\}.$$
(1)

To better understand the above definition we recall that the tensor product  $\mathbf{a} \otimes \mathbf{b}$  represents the tensor that operates on a vector  $\mathbf{u}$  as follows

$$(\mathbf{a} \otimes \mathbf{b})\mathbf{u} = (\mathbf{b} \cdot \mathbf{u})\mathbf{a} \quad \text{with } \mathbf{a}, \mathbf{b}, \mathbf{u} \in \mathbb{R}^3.$$
 (2)

Moreover, we remind when a symmetric linear tensor L is labeled as positive semidefinite:

$$L \ge 0 \quad \Leftrightarrow \quad L\mathbf{u} \cdot \mathbf{u} \ge 0 \quad \forall \, \mathbf{u} \in \mathbb{R}^3.$$

Thus  $\mathbf{n} \otimes \mathbf{n} \ge 0$ , since its spectrum is given by  $\operatorname{sp}(\mathbf{n} \otimes \mathbf{n}) = \{0,1\}$ . The representation given in (1) will be useful in constructing the order tensor theory below (see §5).

If we let  $\mathcal{B}$  be the region occupied by the material, we will often nevertheless identify liquid crystal configurations through applications  $\mathbf{n}: \mathcal{B} \to \mathbb{S}^2$ . When necessary, the equivalence relation above will help us in reproducing the (physically correct) application which takes values in the real projective plane.

### **Steric and Atomic Interactions**

The tendency of a liquid crystal to exhibit orientational order is a macroscopic outcome of the microscopic interaction between nearby molecules. The first rigorous proof of the onset of a liquid-crystalline phase in a system of rod-like molecules was derived by Lars Onsager in 1949. He considered a system of rigid, rod-like molecules of length  $\ell$  and diameter d, exhibiting only steric, excluded-volume interactions. Under suitable assumptions on the aspect ratio  $\ell/d$ , the entropic effects manage to induce a low-temperature ordered phase.

The orientational organization of the liquid crystal molecules is also fostered by Van der Waals' inter-atomic forces, which penalize any lack of parallelism between nearby molecules. The mean field theory which derives the continuum theories we will study below from the microscopic interactions was put forward by Wilhelm Maier and Alfred Saupe in 1958.

### Nematic and Smectic Liquid Crystals

In the liquid-crystalline phase the molecular directors are coherently aligned, which is a typical crystalline property. What distinguishes liquid crystals from other solids is that they do not exhibit complete positional order.

In a *nematic* liquid crystal the molecular centers of mass are disordered, and flow as fluid elements. A *smectic* liquid crystal is more structured. In it, the molecular centers of mass are not randomly dispersed throughout the region  $\mathcal{B}$ . Indeed, it is possible to identify within  $\mathcal{B}$  a family of surfaces  $\{\Sigma_n\}$  (called *layers*) to which the molecules' centers are mostly confined. Within each layer, the smectic molecules are free to behave as a two-dimensional fluid, while the molecular migration from one layer to another is energetically hindered.

The segregation of the smectic molecules in layers establishes the need of a further order parameter that fixes the layers' position. We thus introduce the *smectic phase*  $\omega: \mathcal{B} \to \mathbb{R}$ , a real function whose level surfaces (at fixed values) provide the layers

$$\Sigma_n = \{ \mathbf{x} \in \mathcal{B} : \boldsymbol{\omega}(\mathbf{x}) = n \}.$$

Whenever  $\omega$  is a differentiable function, and away from the (possible) singular points where its gradient vanishes, the *layer normal* v is given by

$$\nu = \frac{\nabla \omega}{|\nabla \omega|}.$$

The relative orientation of the layer normal and the director allows us to define two smectic sub-phases. A smectic-A is a smectic in which the director is parallel to the layer normal, whereas a smectic-C is a smectic in which the two directions above do not coincide.

We restrict our treatment of smectic liquid crystals to these simple kinematic considerations, and focus attention on nematic liquid crystals throughout the rest of this chapter. However, before proceeding further, we want to stress that the above phase classification, while captures the essence of the most common liquid crystal phases, is definitely not complete. In fact, there are a number of liquid crystal systems whose physical properties require the introduction of new order parameters. Chiral

(cholesteric) liquid crystals and further smectic phases (smectic-F, smectic-G, and the newly identified B-phases) are just some examples of a theory whose complete treatment goes far beyond the objectives of the present text. We refer to the bibliographic section below to address the interested reader to more complete introductions to liquid crystal phases.

### **Optic Axis**

The molecular orientation determines the optical properties of a liquid crystal. In fact, it is this very property that has determined the massive technological importance of liquid crystals. Without entering in much detail, we simply recall that the key link between the director orientation and liquid crystal optics is the fact that the Fresnel ellipsoid of the liquid crystal is a spheroid, symmetric about the director axis, which is then also the optic axis of the material. In few words, light propagates at different speeds depending on whether it is polarized parallel or orthogonal to the director. Thus, an incident ray spontaneously splits into two waves: the one with polarization orthogonal to the director is labeled as *ordinary*, whereas the parallel one is called *extraordinary*. A simple experimental setup can then select one wave or another, thus delivering a *display*, which becomes transparent or opaque depending on how the molecular orientation complies with the light polarization. Last but not least key to liquid crystals' success is the fact that very low energies and short time intervals are required to switch the molecular orientations, so that liquid crystal displays turn out to be both fast and cheap instruments.

### 2. Frank Director Theory

This section is devoted to the analysis of the classical variational theory that captures most of the equilibrium properties of nematic liquid crystals. In statics, liquid crystals may be successfully modeled as hyperelastic materials, whose stable equilibrium configurations are relative minimizers of a suitable energy potential. In experimental conditions, the temperature of the system can easily be fixed and kept constant from the outside. Thus, we can assume that the system is in contact with a temperature *reservoir*, and the potential to be introduced next provides the Helmholtz free-energy functional of the system.

The free-energy functional we analyze in this section was first derived by Sir Charles Frank in 1958, though it is possible to catch anticipations of the same functional in previous works by Hans Zocher (1928) and Carl Wilhelm Oseen (1933). The key mathematical requirements for the functional to be derived are the following.

1. The free energy can be expressed by means of a functional depending on the director field and its first gradient:

$$\mathcal{F}_{\mathrm{Fr}}[\mathbf{n}] = \int_{\mathcal{B}} \sigma_{\mathrm{Fr}}(\mathbf{n}, \nabla \mathbf{n}) dv.$$
(3)

We remark that the definition (3) automatically complies with the Principle of local action, which states that the stresses at any given point  $\mathbf{x}$  must not depend on the state of material points at finite distances from  $\mathbf{x}$ . Moreover,  $F_{\rm Fr}$  characterizes a

*homogeneous* material, since no explicit dependence on **x** is allowed in  $\sigma_{\rm Fr}$ .

2. The potential  $\sigma_{Fr}$  must be *frame-indifferent*. In other words, it must be invariant when any rigid displacement is imposed on any given configuration

$$\sigma_{\mathrm{Fr}}(R\mathbf{n}, R\nabla \mathbf{n}R^{\mathrm{T}}) = \sigma_{\mathrm{Fr}}(\mathbf{n}, \nabla \mathbf{n}) \quad \text{for any} \quad R \in \mathcal{O}(\mathbb{R}^3)$$

where  $\mathcal{O}(\mathbb{R}^3) = \{ R \in \operatorname{Lin}(\mathbb{R}^3) : R\mathbf{u} \cdot R\mathbf{v} = \mathbf{u} \cdot \mathbf{v}, \forall \mathbf{u}, \mathbf{v} \in \mathbb{R}^3 \}$  denotes the set of orthogonal tensors acting on  $\mathbb{R}^3$ .

tensors acting on  $\mathbb{R}^{\circ}$ .

3. The potential  $\sigma_{\rm Fr}$  complies with the head-and-tail symmetry of the nematic molecules:

$$\sigma_{\mathrm{Fr}}(-\mathbf{n},-\nabla\mathbf{n})=\sigma_{\mathrm{Fr}}(\mathbf{n},\nabla\mathbf{n}).$$

4. We require  $\sigma_{Fr}$  to reflect the molecular tendency to become parallel. In terms of the free energy, this is tantamount to assume that the potential is minimized in the ground state where the field  $\mathbf{n}(x)$  is constant:

$$\sigma_{\mathrm{Fr}}(\mathbf{n}, \nabla \mathbf{n}) \ge \sigma_{\mathrm{Fr}}(\mathbf{n}_0, 0) \quad \forall \mathbf{n}_0 \in \mathbb{S}^2$$
(4)

We remark that the frame indifference requirement (ii) implies that the minimum value of  $\sigma_{\rm Fr}$  cannot depend on the particular direction  $\mathbf{n}_0$ , provided it is constant throughout the system. Thus, and without any lack of generality, we may assume that the groundstate value, attained by  $\sigma_{\rm Fr}$  in any uniform field, is null:  $\sigma_{\rm Fr}(\mathbf{n}_0, 0) = 0$ . Finally, we further reinforce (8) by assuming that  $\sigma_{\rm Fr}(\mathbf{n}, \nabla \mathbf{n}) > 0$   $\sigma_{\rm Fr(\mathbf{n}, \nabla \mathbf{n}) > 0}$  whenever  $\nabla \mathbf{n} \neq 0$ .

5. By the requirement above, the gradient of the director is expected to be as small as the external conditions will allow it to be. Consequently, and having in mind a sort of a Taylor expansion for the free-energy potential, we assume that  $\sigma_{\rm Fr}$  is a polynomial in  $\nabla \mathbf{n}$ . Since a linear polynomial would clearly violate condition (8), we truncate the expansion at the first non-trivial order and assume that  $\sigma_{\rm Fr}$  is a *quadratic* polynomial in  $\nabla \mathbf{n}$ .

The following theorem provides the *Frank formula* for the free-energy potential of a nematic liquid crystal.

**Theorem.** The most general free-energy functional displaying the properties (i)-(v) is given by (3), with

$$\sigma_{\mathrm{Fr}}(\mathbf{n}, \nabla \mathbf{n}) = K_1 (\operatorname{div} \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \operatorname{curl} \mathbf{n})^2 + K_3 |\mathbf{n} \wedge \operatorname{curl} \mathbf{n}|^2 + (K_2 + K_4) (\operatorname{tr} (\nabla \mathbf{n})^2 - (\operatorname{div} \mathbf{n})^2)$$
(5)

The parameters  $\{K_1, ..., K_4\}$  are respectively known as splay, bend, twist, and saddle-

splay Frank elastic constants. The potential (5) obeys the positivity requirement (4) whenever they fulfil the following conditions:

$$K_1 \ge \frac{1}{2}(K_2 + K_4), \quad K_2 \ge |K_4|, \quad K_3 \ge 0.$$
 (6)

The proof of the above Theorem is beyond is scope of the present treatment. (See Bibliography below for references.) We remark that, in particular, conditions (6) require that  $K_1$ ,  $K_2$ ,  $K_3$ , and  $K_2 + K_4$  must be non-negative. A quite common approximation to the exact expression (5) is obtained by setting  $K_1 = K_2 = K_3 = K > 0$ , and  $K_4 = 0$ . In such a case it is possible to show that (5) yields

$$\sigma_{\mathrm{Fr},1} = K |\nabla \mathbf{n}|^2,$$

an expression which is known as *one-constant approximation* to  $\sigma_{\rm Fr}$ .

### **Boundary Conditions**

In view of the ground state identification (iv), one may wonder why the search of an equilibrium configuration of a nematic liquid crystal is not a trivial exercise, since all we have to do is to minimize a functional whose absolute minimizer is explicitly identified in (8). To this aim, there are two important facts that we have to keep in mind. First, external fields (either electric or magnetic) may interact with the nematic molecules, and in that case we need to add some extra contributions to the free-energy functional (see below).

In addition, it is always possible to treat the external boundary of the region occupied by the liquid crystal in order to induce some preferred orientation on it. This prescription provides a set of Dirichlet boundary conditions for the free-energy minimizers. The more common surface treatments fix the director to be either parallel or orthogonal to the external boundary. The former (called *planar anchoring*) is obtained by physically scratching the external surface along particular directions. The outmost molecules are thus induced to lie within the grooves, which determine a boundary condition everywhere tangent to the surface itself. On the contrary, a treatment of the boundary with suitable surfactants induces the latter, *homeotropic*, anchoring. In this case, the director is forced to be everywhere parallel to the external normal.

Once the boundary conditions are prescribed it is possible to show that the last term in (5) may be neglected. Indeed, simple calculations allow us to show that

$$\operatorname{tr}(\nabla \mathbf{n})^{2} - (\operatorname{div} \mathbf{n})^{2} = \operatorname{div}((\nabla \mathbf{n})\mathbf{n} - (\operatorname{div} \mathbf{n})\mathbf{n}).$$

Moreover, if we denote by  $\nu$  the normal to a smooth surface  $\partial \mathcal{B}$ , it turns out that

 $((\nabla \mathbf{n})\mathbf{n} - (\operatorname{div}\mathbf{n})\mathbf{n}) \cdot \mathbf{v} = ((\nabla_{s}\mathbf{n})\mathbf{n} - (\operatorname{div}_{s}\mathbf{n})\mathbf{n}) \cdot \mathbf{v},$ 

where  $\nabla_s$  and  $div_s$  respectively denote the surface gradient and the surface divergence on  $\partial B$ . By making use of both identities we thus obtain

$$\int_{\mathcal{B}} (\operatorname{tr}(\nabla \mathbf{n})^2 - (\operatorname{div} \mathbf{n})^2) dv = \int_{\partial \mathcal{B}} ((\nabla \mathbf{n}) \mathbf{n} - (\operatorname{div} \mathbf{n}) \mathbf{n}) \cdot v \, da$$
$$= \int_{\partial \mathcal{B}} ((\nabla_{\mathrm{s}} \mathbf{n}) \mathbf{n} - (\operatorname{div}_{\mathrm{s}} \mathbf{n}) \mathbf{n}) \cdot v \, da.$$

The contribution of the  $(K_2 + K_4)$ -term depends then only on the values that the director attains on the boundary. Once these values are fixed by the boundary conditions, such contribution yields simply a constant that may be neglected in the minimization process.

### **Electric and Magnetic Fields**

The director orientation breaks the material isotropy, as we have already remarked. In particular, when we apply an electric or a magnetic field, the electric displacement D and the magnetization vector M will in general not be parallel to the inducing fields E, H:

$$\mathbf{D} = \epsilon \mathbf{E} = \epsilon_{\perp} \mathbf{E} + \epsilon_{a} (\mathbf{E} \cdot \mathbf{n}) \mathbf{n}, \qquad \mathbf{M} = \chi \mathbf{H} = \chi_{\perp} \mathbf{H} + \chi_{a} (\mathbf{H} \cdot \mathbf{n}) \mathbf{n}.$$
(7)

In (7),  $\varepsilon$  and  $\chi$  are respectively the *dielectric* and *susceptibility* tensors,  $\epsilon_{\perp}$  and  $\chi_{\perp}$  are the transverse dielectric and diamagnetic susceptibilities (they characterize the response of the liquid crystal to fields orthogonal to the director), and  $\epsilon_a$  and  $\chi_a$  are the dielectric and diamagnetic anisotropies, which provide the extra response of the liquid crystal when the fields are parallel to the director.

The anisotropy effects in a nematic liquid crystal have quite different orders of magnitude depending on whether the material is subject to an electric or a magnetic field. This depends on the fact that, while  $\varepsilon_a$  may be almost of the same order of magnitude of  $\varepsilon_{\perp}$ , its magnetic counterpart is typically much smaller:  $\chi_a \ll \chi_{\perp}$ . A direct consequence of this simple estimate is that, when we apply an external magnetic field **H**, we may often neglect the perturbations that the liquid crystal induces on **H**. On the contrary, in the case of an applied electric field, **E** itself will in general depend on the director distribution **n**.

In all cases, in the presence of external fields, the complete free-energy functional will be given by  $\mathcal{F} = \mathcal{F}_{Fr} + \mathcal{F}_{em}$ , with (in c.g.s. electromagnetic units)

$$\mathcal{F}_{\rm em} = -\frac{1}{8\pi} \int_{\mathcal{B}} \mathbf{D} \cdot \mathbf{E} \, dv - \frac{1}{2} \int_{\mathcal{B}} \mathbf{M} \cdot \mathbf{H} \, dv.$$
(8)

### 3. Nematic Displays: Freedericksz Transition

As soon as an external field induces a preferred director orientation which is not in agreement with the boundary prescriptions the problem of minimizing the complete free-energy functional is far from being trivial. In this section we study the so-called Freedericksz transition, a bifurcation instability that governs the on-and-off mechanism of most liquid crystal displays.

Before entering the physical problem, we first study in some detail a toy variational model which clarifies the mathematical origin of the bifurcation phenomenon we describe below.

### 3.1. The Variational Origin of Freedericksz' Threshold

Let us consider the functional

$$\mathcal{F}_{\epsilon}[u] \int_{a}^{b} \left( f(u) u'^{2} + \epsilon g(u) \right) dx,$$

with  $\epsilon \ge 0$ , and  $f, g \in C^1(\mathbb{R})$  such that  $f(t) \ge f_0 > 0$  for all  $t \in \mathbb{R}$ , while g is bounded from below, with g(0) = 0, and

(9)

$$g(t) = -\alpha t^{\beta} + o(t^{\beta})$$
 when  $t \to 0$ , for some  $\beta \ge 1$ . (10)

We consider the problem of finding  $u_{\varepsilon}$ , the minimizer of  $\mathcal{F}_{\epsilon}$  in the Sobolev space  $H_0^1(a,b) = \{u \in H^1(a,b) : u(a) = u(b) = 0\}$ .

The Euler-Lagrange equation relative to the functional (9) is given by

$$2f(u_{\epsilon})u_{\epsilon}'' + f'(u_{\epsilon})u_{\epsilon}'^2 - \epsilon g'(u_{\epsilon}) = 0.$$
<sup>(11)</sup>

When  $\varepsilon = 0$ , the trivial solution  $u_0(x) \equiv 0$  satisfies both the differential equation (11) and the boundary conditions. Moreover, in view of the positivity of f, it is indeed the absolute minimizer of  $\mathcal{F}_0$ . More in general, the trivial null solution is a stationarity point of the functional for any  $\varepsilon$  whenever  $\beta > 1$  in (10) (and, thus, g'(0) = 0). Same conclusions apply if g is non-negative, since moving u away from its null boundary values has a positive cost in the first term of (9). Such cost has to be balanced by a gain in the second term for nontrivial minimizers to arise. For this reason we will assume  $\alpha > 0$  in (10).

When the lower bound of g is negative, but  $\varepsilon$  is small, the minimizer is small as well. Let  $\inf g = -g_0 < 0$ . Then  $\mathcal{F}_{\epsilon}[u] \ge f_0 ||u'||_2^2 - \epsilon g_0(b-a)$ , where  $||\cdot||_2$  denotes the  $L^2(a,b)$ -norm. Any nontrivial minimizer must then satisfy

$$\|u'\|_{2}^{2} \leq \frac{\epsilon g_{0}(b-a)}{f_{0}}$$

if it aims at being preferred to the trivial solution. As a consequence,

$$\|u\|_{2}^{2} \leq \frac{(b-a)^{2}}{\pi^{2}} \|u'\|_{2}^{2} \leq \frac{\epsilon g_{0}(b-a)^{3}}{f_{0}\pi^{2}}$$

A more intriguing property is that when  $\epsilon$  is sufficiently small, the potential g is not able to induce any modification of the minimizer if  $\beta \ge 2$  in (10). To better understand this feature, we assume  $u_{\epsilon}(x) = \epsilon^{\gamma} u_{\gamma}(x) + o(\epsilon^{\gamma})$ , with  $\gamma$  a positive exponent to be determined. The leading order of the differential equation (11) yields

$$2f(0)\epsilon^{\gamma}u_{\gamma}'' + \alpha\beta\epsilon^{\gamma(\beta-1)+1}u_{\gamma}^{\beta-1} + o(\epsilon^{\gamma}) + o(\epsilon^{\beta-1}) = 0.$$
(12)

For any  $\beta \ge 2$ ,  $\gamma(\beta - 1) + 1 > \gamma$  and the second term in equation (21) can be neglected with respect to the first. The leading order of (21) is thus  $u_{\gamma}'' = 0$  that, together with the boundary conditions, yields  $u_{\gamma} \equiv 0$ .

As an exercise, the reader may show that if  $\beta = 1$  the minimizer is given by

$$u_{\epsilon}(x) = \frac{\epsilon \alpha (a-x)(x-b)}{4f(0)} + o(\epsilon), \quad \text{when} \quad \epsilon \to 0.$$

Moreover, if  $1 \le \beta < 2$  the minimizer is  $u_{\epsilon}(x) = O(\epsilon^{1/(2-\beta)})$  when  $\epsilon \to 0$ .

When  $\beta \ge 2$ , we can complete our analysis by searching for possible bifurcations from the trivial minimizer that may arise at finite values of  $\epsilon$ , say  $\epsilon_{\rm cr}$ . Let then  $\delta = \epsilon - \epsilon_{\rm cr}$ , and let  $u_{\epsilon}(x) = \delta^{\gamma} u_{\gamma}(x) + o(\delta^{\gamma})$ , with  $\gamma$  a positive exponent to be again determined. The Euler-Lagrange equation (11) yields now

$$2f(0)\delta^{\gamma}u_{\gamma}'' + \epsilon_{\rm cr}\alpha\beta\delta^{\gamma(\beta-1)}u_{\gamma}^{\beta-1} + o\left(\delta^{\gamma}\right) + o\left(\delta^{\gamma(\beta-1)}\right) = 0$$
<sup>(13)</sup>

If  $\beta > 2$ , equation (13) does never admit nontrivial solutions, since the second term is infinitesimal with respect to the first, and the limit equation is still  $u_{\gamma}'' = 0$ .

The critical case  $\beta = 2$  is peculiar: in such a case, the limit equation becomes

$$u_{\gamma}'' + \omega^2 u_{\gamma} = 0, \quad \text{with} \quad \omega := \sqrt{\frac{\epsilon_{\text{cr}} \alpha}{f(0)}},$$

which admits the nontrivial solution  $u_{\gamma}(x) = A \sin \omega(x-a)$  provided

 $u_{\nu}(b) = A \sin \omega (b-a) = 0$ . Thus, we must have

$$\omega(b-a) = n\pi \quad \Rightarrow \quad \epsilon_{\rm cr} = \frac{n^2 \pi^2 f(0)}{\alpha (b-a)^2}.$$
(14)

Equation (14) provides a discrete set of values of critical values at which nontrivial solutions bifurcate from the null solution.

In summary, we have unveiled the following picture. If the potential g behaves as  $g(u) \sim u^{\beta}$  when u is small, the exponent  $\beta$  governs the stability of the null minimizer.

- If g is non-negative, the minimizer does never abandon its null value.
- If  $\beta \in [1,2)$  the minimizer leaves the null value as soon as the potential is switched on.
- If  $\beta = 2$  a bifurcation from the null solution appears at a finite value of the potential intensity: we may be in the presence of a second-order phase transition.
- If  $\beta > 2$  no bifurcation arises. The null solution is abandoned at a finite value of the potential intensity through a discontinuous, first-order phase transition.

As a further exercise the reader may prove the following properties.

Assume that  $\mathcal{F}_{\overline{\epsilon}}[\overline{u}] \leq \mathcal{F}_{\overline{\epsilon}}[u_0]$  for some  $\overline{\epsilon} > 0$  and some  $\|\overline{u}\|_2 > 0$  that complies with the prescribed null boundary conditions. Show that  $\mathcal{F}_{\epsilon}[\overline{u}] < \mathcal{F}_{\epsilon}[u_0]$  for any  $\epsilon > \overline{\epsilon}$ . (As a consequence, the trivial solution  $u_0$  is a minimizer only in an interval of values of  $\epsilon$ .)

Let inf g < 0. Show that the trivial solution  $u_0$  is a minimizer only in a finite interval  $\epsilon \in [0, \tilde{\epsilon}]$ . [Hint: Let  $u_1$  such that  $g(u_1) < 0$ . Construct explicitly a function  $\overline{u}(x)$  that attains the value  $u_1$  in  $[a + \epsilon^{\gamma}, b - \epsilon^{\gamma}]$ . Show, by suitably choosing  $\gamma$ , that it exists an  $\varepsilon$  above which  $\overline{u}$  is preferred to the trivial solution.]

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#### **Bibliographical Sketch**

**Paolo Biscari**, born 1964 in Madrid, Spain. He earned his Physics and PhD degrees at the Scuola Normale Superiore in Pisa. At present, he is Full Professor in Mathematical Physics at the Mathematics Department of the Politecnico di Milano, and Head of the PhD program *Mathematical Models and Methods in Engineering*. His research is focused in the soft matter area, and more specifically in liquid crystals and continuum biomechanics. He has been Invited Professor at the Universities of Southampton and Cambridge (UK), and at the Institute of Mathematics and its Applications, of the University of Minnesota (US). He has published approx. 50 research papers in internationally refereed journals, two books, and has contributed to approx. 40 international congresses as Invited Speaker. In 2004, he earned the *Bruno Finzi* Prize, awarded by the *Istituto Lombardo, Accademia di Scienze e Lettere* for his research in applied mechanics.