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Optical and statistical anisotropy in nematics

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Fisica matematica. — *Optical and statistical anisotropy in nematics.* Nota di PAOLO BISCARI e GIANFRANCO CAPRIZ, presentata (*) dal Corrisp. G. Capriz.

ABSTRACT. — Two parameters seem to be of the essence for the description of the distribution of molecular directions in a nematic: the degrees of prolation and of triaxiality. Fundamental mechanical and optic properties can be expressed in terms of the two parameters.

KEY WORDS: Nematic liquid crystals; Anisotropy; Biaxiality.

RIASSUNTO. — *Anisotropia ottica e statistica nei nematici.* Si introducono due parametri essenziali nella descrizione della distribuzione delle direzioni molecolari in un cristallo liquido nematico: i gradi di prolazione e di triassialità. In termini di quei parametri si discutono alcune proprietà meccaniche e ottiche fondamentali.

1. INTRODUCTION

In the continuum theory of liquid crystals, when one wishes to go beyond the bare indication of the field of preferred directions $\boldsymbol{n}$, one may involve the field of the second-order tensors $\boldsymbol{M}$ representing locally the second order moment of the distribution of molecular orientations. $\boldsymbol{M}$ is symmetric, non-negative and with unit trace; it is reputed to coincide (a factor apart) with the dielectric tensor, which is experimentally accessible through optic observations. The importance of these observations is such that one often speaks of biaxiality in liquid crystals because the optic axes are distinct, though really $\boldsymbol{M}$ is triaxial. The matter is not only of terminology: optic uniaxiality and geometric triaxiality of $\boldsymbol{M}$ may even coexist, albeit only in degenerate cases. Furthermore some mechanical properties (the elastic potential of orientation, for instance) depend only on the invariants of $\boldsymbol{M}$, *i.e.* they are symmetric functions of the eigenvalues λ_i of $\boldsymbol{M}$, whereas the optic properties involve the eigenvectors in an appropriate order.

Here we show how two invariant measures, of triaxiality β and of prolation s, are related to the second and third principal invariants of $\boldsymbol{M}$. We recall the usual formula for the angle between optic axes that requires an ordering of eigenvalues; such ordering, though convenient, is not essential in principle, so that it is possible to express that angle in terms of s and β only. We give the elastic potential of orientation for uniform states also in terms of β, s only and remark on some immediate consequences.

2. DEGREE OF PROLATION AND OF TRIAXIALITY

We have already introduced in [1] the two parameters, β and s, which are symmetric

(*) Nella seduta del 18 giugno 1993.

functions of the eigenvalues of $\boldsymbol{M}$.

$$\beta = \left(6\sqrt{3}\left|\prod_{i=1}^{3}(\lambda_i - \lambda_{i+1})\right|\right)^{1/3}, \qquad s = \left(\frac{1}{2}\prod_{i=1}^{3}(3\lambda_i - 1)\right)^{1/3}; \tag{2.1}$$

in the first formula the indices of eigenvalues are understood to be modulo 3; factors are there to make β vary in $[0, 1]$ and s in $[-1/2, 1]$.

In [1] we have used the name degree of orientation for s, because s reduces to the parameter of that name [2] when two eigenvalues coincide: precisely, if the three eigenvalues are $\lambda, (1-\lambda)/2$, and $(1-\lambda)/2$, then $s = (3\lambda - 1)/2$. However, the name is not totally appropriate; true, the ellipsoid $\mathcal{E}_M$ associated with $\boldsymbol{M}$ is prolate when s is positive, degenerating into a segment when $s = 1$. But, when $s = 0$, $\mathcal{E}_M$ is not necessarily a sphere; besides, s may take on also negative values; then, the ellipsoid $\mathcal{E}_M$ is oblate and reduces to a disc when $s = -1/2$. Thus a name as «degree of prolation» is perhaps more appropriate for s (if musicologist allow us to borrow the term).

Certainly the name used in [1] for β (*i.e.* degree of biaxiality) is inappropriate: the qualifier biaxial is adopted rather loosely in papers on liquid crystals, but refers properly to the optic response, which depends on the angle between the circular sections of $\mathcal{E}_M$. Having in mind that ellipsoid, β could be better called degree of triaxiality: when $\beta = 0$, $\mathcal{E}_M$ is axially symmetric; when $\beta \neq 0$, $\mathcal{E}_M$ is triaxial and when β is maximal, $\mathcal{E}_M$ degenerates into an elliptic disc, for which the ratio of the axes is $(1+\sqrt{3})/(1-\sqrt{3})$. If

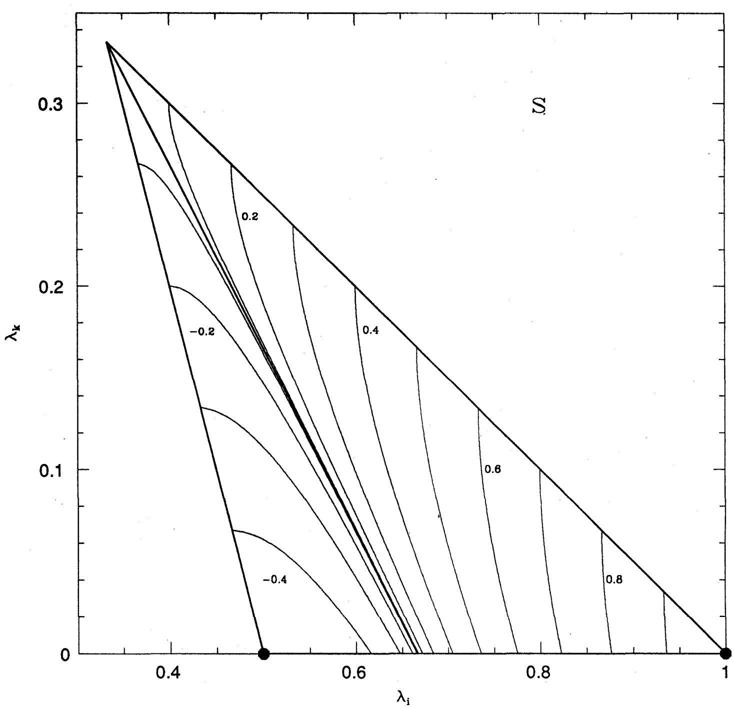

Fig. 1.

and only if β and s vanish together, $\mathcal{E}_M$ reduces to a sphere (*i.e.*, the distribution of molecular directions is isotropic).

Whereas s may happen to take any value in $[-1/2,\ 1]$, and similarly β in $[0, 1]$, not all couples of values (s, β) in the rectangle $[-1/2,\ 1] \times [0,\ 1]$ are accessible, as a consequence of the properties of $\boldsymbol{M}$. If we call $\mathcal{D}$ the accessible domain in the plane (s, β), then there is a one-to-one mapping of $\mathcal{D}$ into the rectangle $[0,\ 1/3] \times [0,\ 1/27]$ of the plane $(\mathrm{II}, \mathrm{III})$, where II and III are the second and third principal invariants of $\boldsymbol{M}$. The mapping is as follows:

$$\text{(2.2)}\quad \mathrm{II} = [1 - (s^6 + \beta^6/16)^{1/3}]/3\,, \qquad \mathrm{III} = [1 + 2s^3 - 3(s^6 + \beta^6/16)^{1/3}]/27\,,$$

and

$$\text{(2.3)}\qquad \begin{cases} s = 3\left(\dfrac{1}{2}\ \mathrm{III} - \dfrac{1}{6}\ \mathrm{II} + \dfrac{1}{27}\right)^{1/3}, \\ \beta = 3^{1/2}\, 2^{1/3}\,(-27\ \mathrm{III}^2 + 18\ \mathrm{III}\ \mathrm{II} - 4\ \mathrm{III} - 4\ \mathrm{II}^3 + \mathrm{II}^2)^{1/6}\,. \end{cases}$$

$\mathcal{D}$ is the domain where both II and III are non-negative, *i.e.* where the following inequalities are satisfied

$$\text{(2.4)}\qquad \max\,((2/3)s^3,\ 0) \leqslant (s^6 + \beta^6/16)^{1/3} \leqslant (2/3)s^3 + 1/3\,.$$

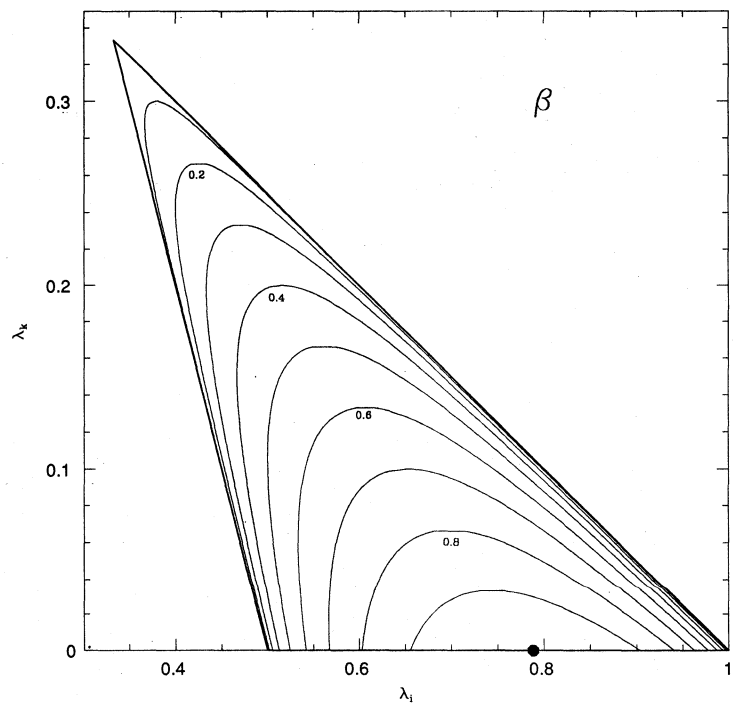

Fig. 2.

Actually the left-hand inequality is not restrictive. The right-hand one can be written equivalently

$$\beta^6 \leqslant (16/27)(s^3 - 1)^2(8s^3 + 1)\,, \tag{2.5}$$

and is easily taken care of: the right-hand member is positive in the open interval $(-1/2,\ 1)$ and vanishes at the ends; it is less than one, except at $s = 2^{-2/3}$ where it reaches its maximum.

For convenience, we show in figs. 1, 2 level lines of s and β as functions of two distinct eigenvalues of $\boldsymbol{M}$, say λ_i and λ_k. The domain of definition is the triangle $\mathcal{T}$, in the non-negative quadrant of the (λ_i, λ_k)-plane, where $1 - \lambda_i - \lambda_k$ is positive $(i \neq k)$. The numbering of eigenvalues is irrelevant, of course; thus, the triangle $\mathcal{T}$ can be subdivided in six subtriangles in one of which λ_i is the largest and λ_k is the smallest eigenvalue; in the other five all other possible permutations occur. Only the first subtriangle (where $\lambda_i \geqslant \lambda_j \geqslant \lambda_k$, $\lambda_j = 1 - \lambda_i - \lambda_k$) is shown in the figures.

Remark that, in the subtriangle, s and β could be taken as curvilinear coordinates in lieu of λ_i, λ_k.

3. Optical properties

The optic axes are two stright lines normal to the circular sections of $\mathcal{E}_M$; those sections contain the principal axis of $\mathcal{E}_M$ relative to the intermediate eigenvalue λ_j. Hence the position of the axes depends on the ordering of eigenvalues, whereas the angle α between them is an objective quantity and can be expressed in terms of s and β. The well-known formula for $\cos\alpha$ (see, *e.g.*, [3, p. 70])

$$\cos\alpha = (2\lambda_i^2\,\lambda_k^2 - \lambda_i^2\,\lambda_j^2 - \lambda_j^2\,\lambda_k^2)/(\lambda_j^2(\lambda_i^2 - \lambda_k^2))\,, \tag{3.1}$$

applies if $\lambda_i \geqslant \lambda_j \geqslant \lambda_k$, *i.e.* it is valid in the subtriangle; however, α is an objective quantity. Figure 3 gives level values of α as a function of s and β. It is interesting to remark

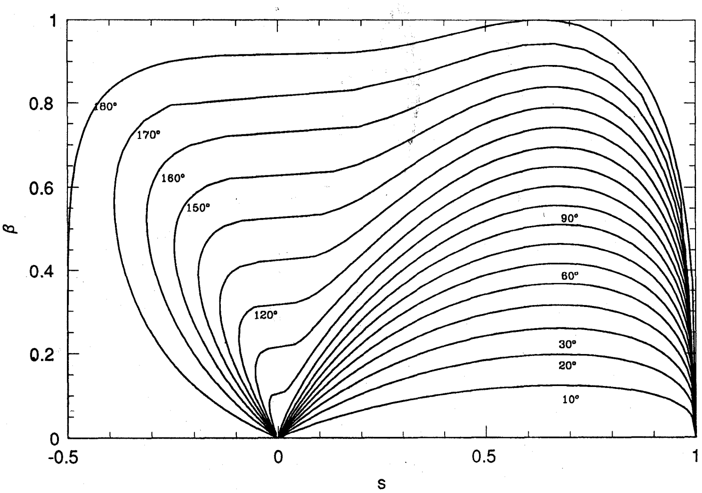

Fig. 3.

that the states on the whole boundary of the domain $\mathcal{D}$ (and only these states) are optically uniaxial, even where β is positive.

During any process, α may change drastically from point to point and with time. The crystal class depends also generally on place and time; boundary conditions and external fields are deciding factors. One could possibly identify classes of solutions; for instance, the special family considered in [4] could be classed as monoclinic.

4. Elastic potential of orientation

The free energy density for (biaxial) nematics normally used for the study of special problems is a low-order polynomial scalar function of $\boldsymbol{Q} = \boldsymbol{M} - (1/3)\boldsymbol{I}$. The simplest example is

$$\sigma = \kappa(\nabla \boldsymbol{Q})^2 + a \operatorname{tr} \boldsymbol{Q}^2 - b \operatorname{tr} \boldsymbol{Q}^3 + c \operatorname{tr} \boldsymbol{Q}^4 , \tag{4.1}$$

where a, b and c are appropriate constants. We study here σ only under homogeneous conditions; then σ reduces to $\bar{\sigma}$, the sum of the last three addenda. Elementary calculations allow us to express $\bar{\sigma}$ in terms of β and s only

$$\bar{\sigma} = \frac{2a}{3}\gamma^2 - \frac{2b}{9}s^3 + \frac{2c}{9}\gamma^4 , \qquad \gamma = \left(s^6 + \frac{\beta^6}{16}\right)^{1/6} ; \tag{4.2}$$

reference to (2.2) evidences the fact that the sum is a linear combination of II, II^2, and III.

The minima of $\bar{\sigma}$ determine the «natural» states of the liquid crystal; we discuss them below under the assumption that c be positive.

(*i*) If $a \geqslant 0$ and $b^2 \leqslant (32/3)ac$, the isotropic state ($s = 0$, $\beta = 0$) is the only stationary point for $\bar{\sigma}$; it is actually its absolute minimum.

(*ii*) If $a \geqslant 0$ and $(32/3)ac < b^2 \leqslant 12ac$, the isotropic state is still the absolute minimum for $\bar{\sigma}$, but two other stationary points emerge if $b \neq 0$: a relative minimum at

$$s = s_+ = \frac{3b}{8c}\left(1 + \sqrt{1 - \frac{32\,ac}{3b^2}}\right), \qquad \beta = 0 , \tag{4.3}$$

and a saddle point at

$$s = s_- = \frac{3b}{8c}\left(1 - \sqrt{1 - \frac{32\,ac}{3b^2}}\right), \qquad \beta = 0 . \tag{4.4}$$

(*iii*) If $a \geqslant 0$ and $b^2 > 12\,ac$, the point $(s_+ , 0)$ becomes the absolute minimum (the stable state is uniaxial rather than isotropic).

(*iv*) When $a < 0$ and $b \neq 0$, there is a fourth stationary point at

$$s = 0 , \qquad \beta = \bar{\beta} = 2^{1/6}\sqrt{-3a/c} , \tag{4.5}$$

a triaxial state; however, this point is neither a relative minimum nor a saddle point; it is a «side-saddle»: the absolute minimum is still at $(s_+, 0)$.

(v) When $a < 0$ and $b = 0$, a degenerate case appears: $\bar{\sigma}$ attains its minimum along a whole curve

$$s = 2^{-2/3}\bar{\beta}\cos^{1/3}\varphi, \qquad \beta = \bar{\beta}\sin^{1/3}\varphi, \qquad \forall\varphi \in [0, \pi]. \tag{4.6}$$

More specifically, in cases (ii), (iii), and (iv), $\bar{\sigma}$ behaves, in the neighbourhood of the relative minimum, as follows:

$$\begin{aligned}\bar{\sigma}(s,\beta) = \bar{\sigma}(s_+, 0) + \frac{bs_+}{3}\sqrt{1-\frac{32\,ac}{3b^2}}\,(s-s_+)^2 + \\ + \frac{b}{9}\left(1 + 3\sqrt{1-\frac{32\,ac}{3b^2}}\right)(s-s_+)^3 + \frac{2c}{9}(s-s_+)^4 + \frac{b}{144\,s_+^3}\beta^6 + \\ + o[((s-s_+)^2+\beta^2)^3].\end{aligned} \tag{4.7}$$

In case (iv) the development of $\bar{\sigma}$ in the neighbourhood of $(0, \bar{\beta})$ is

$$\begin{aligned}\bar{\sigma}(s,\beta) = \bar{\sigma}(0,\bar{\beta}) + \bar{\beta}^2(\beta-\bar{\beta})^2 + 2^{4/3}\bar{\beta}(\beta-\bar{\beta})^3 + \\ + 2^{2/3}(\beta-\bar{\beta})^4 - \frac{b}{c}s^3 + o[(s^2+(\beta-\bar{\beta})^2)^3].\end{aligned} \tag{4.8}$$

The two developments justify the assertions made above.

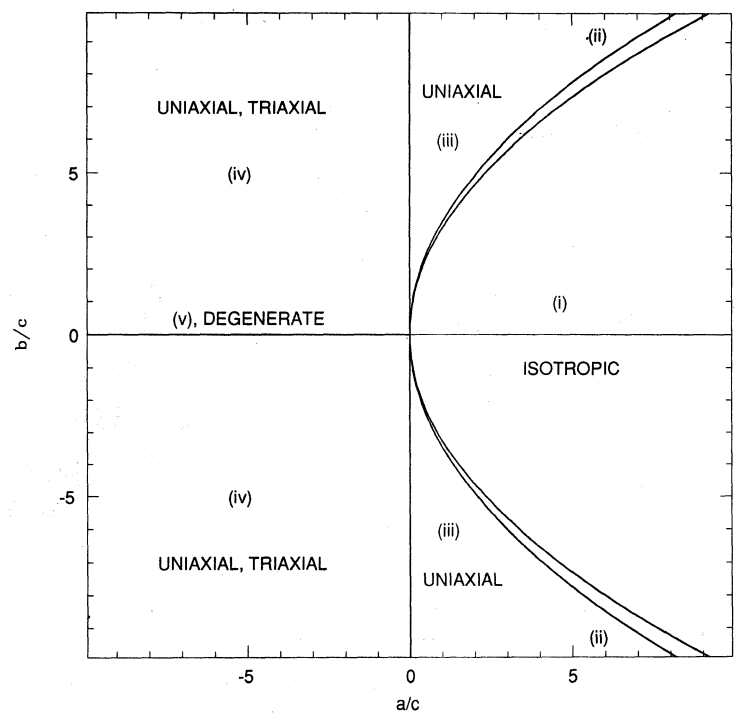

Fig. 4.

On the whole it appears from the remarks above that triaxial states are never preferred, though a degenerate case may happen. The general situation is summarized in fig. 4: if $a \geqslant 0$ larger absolute values of b are in favour of uniaxial nematic states; more complex behaviour may be expected if a is negative.

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