

Phase transitions of nematic rubbers

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Abstract. – Single-crystal nematic elastomers undergo a transition from a strongly ordered phase N to an “isotropic” phase I . We show that: a) samples produced under tension by the Finkelmann procedure are intrinsically anisotropic and should show a small (temperature-dependent) birefringence in the high-temperature I phase; b) for the $I \rightarrow N$ transition via cooling there is a spinodal limit but for the $N \rightarrow I$ transition via heating there is no soft mode at the standard spinodal temperature; c) the $N \rightarrow I$ transition is reminiscent of a *martensitic transformation*: nucleation of the I phase should occur in the form of platelets, making a well-defined angle with the director.

Introduction. – Nematic rubbers were first constructed in a single domain form by Finkelmann and coworkers [1]. They show a spectacular change in shape when they are switched from low temperatures ($T < T_c$) to high temperatures ($T > T_c$). Many properties resulting from the coupling between nematic order and elastic deformations [2] have been analyzed by Warner, Terentjev and coworkers [3]. We are concerned here mainly by the transition from the nematic phase N to the high-temperature phase I .

Two striking facts should be mentioned here: a) the transition is expected to be first order, but the plots of birefringence *vs.* temperature T are continuous [4]; b) the transition is very slow (minutes) [5].

Our aim here is to discuss some effects of the nematic/elastic coupling on the phase transition. First, we discuss the anisotropy induced by the preparation method. We show that this preparation imposes a fixed *external field* coupled to the order parameter: under this field the plots of order *vs.* temperature are expected to be continuous. Second, we analyze T -jumps: for a cooling jump we find a traditional spinodal transition. But for a heating jump we show that the elastic couplings tend to suppress the spinodal instability. Finally, we discuss the nucleation of an I phase inside a nematic single crystal, and show that it should take place in the form of platelets, with well-defined geometrical conditions.

Anisotropy effects. – In the Finkelmann scheme, a very weak network is prepared first, and is put under a prescribed deformation ε_{zz}^0 along one axis [1]. Then a second reaction is started and the final nematic rubber is generated. The basic energy for this situation is of the form

$$F = F_0(Q_{\alpha\beta}) - \Lambda Q_{\alpha\beta} \varepsilon_{\beta\alpha} + \mu (\varepsilon_{\alpha\beta} - \varepsilon_{\alpha\beta}^0) (\varepsilon_{\beta\alpha} - \varepsilon_{\beta\alpha}^0), \quad (1)$$

where summation over the repeated indices is implied. For simplicity, we restrict our attention to small deformations $\varepsilon_{\alpha\beta}$. F_0 is the standard Landau free energy of the nematic order, Λ describes the coupling between deformation and order, and the last term is the shear elastic energy (we consider only incompressible systems: $Q_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$ are *symmetric traceless tensors*). The crucial point in eq. (1) is that the elastic energy (with a strong coefficient μ) is minimal *in the original state* ($\varepsilon = \varepsilon^0$). We can shift the definition of deformations, writing

$$\varepsilon = \varepsilon^0 + e, \quad (2)$$

where e measures actual deformations from the high-temperature I phase. Then the energy is (in contracted notation)

$$F = F_0 - \Lambda Q \varepsilon_0 - \Lambda Q e + \mu e^2. \quad (3)$$

There is a *constant field* $\sigma_0 = \Lambda \varepsilon_0$ acting on the order parameter. This linear term in Q implies that, in the nominally isotropic I phase, we have a non-zero order Q .

Writing explicitly for small Q

$$F = A_0(T) Q_{\alpha\beta} Q_{\beta\alpha} - \sigma_{\alpha\beta}^0 Q_{\beta\alpha} - \Lambda Q_{\alpha\beta} e_{\beta\alpha} + \mu e_{\alpha\beta} e_{\beta\alpha} \quad (4)$$

via minimization in terms of $e_{\alpha\beta}$:

$$e_{\alpha\beta} = \frac{\Lambda}{2\mu} Q_{\alpha\beta}, \quad (5)$$

we first arrive at the classical renormalization of $A_0(T) \simeq a_0(T - T_0)$:

$$F = a(T) Q_{\alpha\beta} Q_{\beta\alpha} - \sigma_{\alpha\beta}^0 Q_{\beta\alpha}, \quad (6)$$

where

$$a(T) = A_0(T) - \frac{\Lambda^2}{4\mu} \equiv A_0(T) - a_0 \Delta T_c. \quad (7)$$

This minimized energy gives a finite high-temperature order:

$$Q_{\alpha\beta}^I = \frac{\sigma_{\alpha\beta}^0}{2a(T)}. \quad (8)$$

This describes a birefringence which is high near the transition point (where a is small) very much like the Kerr effect in standard nematics. This may be an explanation for the results of ref. [4].

In the following, we employ a Landau expansion in terms of $Q \rightarrow Q - Q^I$, and set the free energy to be zero at this “isotropic” phase, which now corresponds to $Q = 0$.

Absence of spinodal instabilities. – Can we achieve the transition by soft phonon modes? Since our materials are essentially incompressible, we must investigate the transverse phonons. We assume rapid equilibration for the elastic degrees of freedom: we always use eq. (5).

For a transverse phonon of wave vector \mathbf{q} and displacement field \mathbf{u} (with $\mathbf{q} \cdot \mathbf{u} = 0$) the deformation is

$$e_{\alpha\beta} = \frac{1}{2} (q_\alpha u_\beta + q_\beta u_\alpha). \quad (9)$$

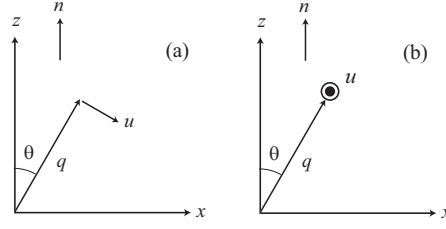


Fig. 1 – (a) First transverse mode $\mathbf{u} = (u \cos \theta, 0, -u \sin \theta)$. (b) Second transverse mode $\mathbf{u} = (0, u, 0)$. Note the difference from fig. 2: the director vector is parallel to the z-axis.

a) Consider first the instability of the disordered phase upon *cooling* ($I \rightarrow N$ transition). Here the Landau free energy in eq. (6) for small but nonzero amplitudes reduces to

$$F = a(T)Q_{\alpha\beta}Q_{\beta\alpha} \quad (10)$$

and at the spinodal temperature T^{**} the coefficient $a(T^{**})$ vanishes. Note again that, in this expansion, Q is actually the difference from Q^I .

Amplitudes of our transverse phonons are proportional to $Q_{\alpha\beta}$ (eq. (5)) and the energy required for the phonon generation vanishes at $T = T^{**}$: the phonons are soft at this temperature.

b) The situation is different for the $N \rightarrow I$ transition upon *heating*. Here we start with a uniaxial nematic phase with nonzero components $(Q_{xx}, Q_{yy}, Q_{zz}) = (-S/2, -S/2, S)$; we can find a candidate for the spinodal temperature T^* for a special value $S = S^*$, satisfying the conditions

$$\frac{\partial F}{\partial S} = \frac{\partial^2 F}{\partial S^2} = 0 \quad (\text{at } S = S^* \quad \text{and} \quad T = T^*). \quad (11)$$

We employ the Landau expansion (which is already minimized for the elasticity)

$$F - F_0 = aQ_{\alpha\beta}Q_{\beta\alpha} - bQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + c(Q_{\alpha\beta}Q_{\beta\alpha})(Q_{\gamma\delta}Q_{\delta\gamma}), \quad (12)$$

where b and c are positive (see Chapt. 2 of ref. [6]).

We expand the free energy to second order around the spinodal point. At this point the coefficient $\partial^2 F / \partial Q_{zz}^2 = 0$ but the other curvature coefficients do not vanish. We find

$$F(Q) - F(Q^*) = \frac{9b^2}{64c} [(Q_{xx} - Q_{yy})^2 + 4Q_{xy}^2]. \quad (13)$$

The linear term in $\Delta Q_{\alpha\beta} \equiv Q_{\alpha\beta} - Q_{\alpha\beta}^*$ and the ΔQ_{zz}^2 term vanish as expected from eq. (11). In addition, there is no term proportional to Q_{zz}^2 and Q_{zy}^2 : they are ruled out by the rotational invariance around the director axis z .

We can now investigate the transverse phonon modes (fig. 1).

The first mode, with \mathbf{q} and \mathbf{u} in the x - z plane (fig. 1a), induces a component proportional to Q_{xx} ($\simeq q_x u_x = \varepsilon \sin \theta \cos \theta$ with $\varepsilon \equiv qu$), but not to Q_{yy} . Thus, it contributes to the $(Q_{xx} - Q_{yy})^2$ term in the free energy, which is positive ($\simeq \mu \varepsilon_{xy}^2 \sim (\varepsilon \sin \theta)^2$). A finite $Q_{xx} - Q_{yy}$ implies a biaxial nematic, and this costs energy.

The second mode, with \mathbf{u} normal to both \mathbf{q} and director vector, induces an amplitude of Q_{xy} ($\simeq q_x u_y = \varepsilon \sin \theta$): again this induces biaxiality and requires a finite energy ($\simeq \mu \varepsilon_{xy}^2 \sim (\varepsilon \sin \theta)^2$).

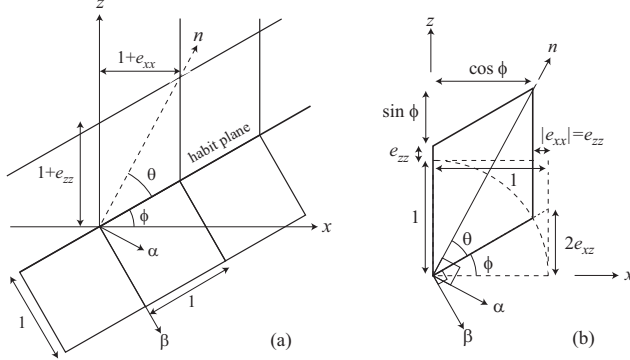


Fig. 2

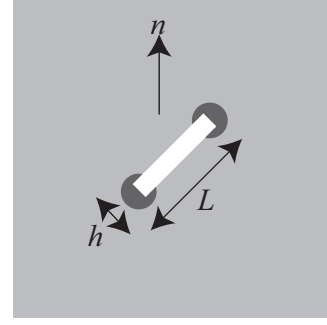


Fig. 3

Fig. 2 – (a) Habit plane separating nematic and isotropic regions. In two dimensions the “isotropic” network is represented by a square array, while the nematic network is represented by parallelograms. Along the habit plane the two networks match. (b) Detailed definitions of angles and axes.

Fig. 3 – Platelet nucleus in the nematic phase accompanied by a large strain around the periphery.

We conclude that both transverse modes are not soft for all nonzero angles ($\theta \neq 0$) at $T = T^*$. The $\theta = 0$ mode is soft at all temperatures, if $F(Q)$ has full rotational invariance. But this mode cannot cause a change in the magnitude of the order parameter and does not catalyze the transition.

Nucleation of a high-temperature I phase. – We consider now a T -jump from a temperature just below the thermodynamic transition point T_c towards a higher temperature T , in the region where spinodal instabilities are ruled out.

A) Choice of a habit plane

We now investigate a possible plane boundary (*habit plane*) between I and N phase.

A.1) The two-dimensional case (plane strain)

This two-dimensional example (in the x - z plane) is shown in fig. 2, where we impose compatibility between an I phase (represented symbolically by a square unit cell) and a uniaxial N phase (represented by parallelograms). The squares have been rotated by an angle ϕ from the x -axis. The N phase has an elongation e_{zz} along the z -axis, which will be determined below. Note here that the director is *not* parallel to the z -axis; the parallelograms are sheared with a strain

$$e_{xz} = \frac{1}{2}(\partial_x u_z + \partial_z u_x) = \frac{1}{2} \tan \phi. \quad (14)$$

Here and hereafter displacement fields are defined in the x - z frame shown in fig. 2b. There is also a deformation $e_{xx} = -e_{zz}$ in the N phase (we assume incompressibility) and matching imposes $1 + e_{xx} = \cos \phi$. The two-dimensional deformation matrix is written as

$$\hat{e} \equiv \begin{pmatrix} e_{xx} & e_{xz} \\ e_{xz} & e_{zz} \end{pmatrix} = \begin{pmatrix} \cos \phi - 1 & \frac{1}{2} \tan \phi \\ \frac{1}{2} \tan \phi & 1 - \cos \phi \end{pmatrix}. \quad (15)$$

Thus from fig. 2b the angle θ between the director axis and the habit plane is given by

$$\tan(\theta + \phi) = \frac{1 + e_{zz} + \sin \phi}{\cos \phi} = \frac{2 - \cos \phi + \sin \phi}{\cos \phi}. \quad (16)$$

Note that, for small ϕ , the parallelogram is a lozenge, and the director is parallel to the long axis of the lozenge — at $\pi/4$ from the habit plane (fig. 3 corresponds to this limit).

The magnitude of ϕ is fixed by the condition that the elastic energy of N state be equal to the equilibrium value $f(T_i)$ in the initial nematic phase. Under the incompressibility condition, we have $f(T_i) = \mu(e_{xx}^2 + e_{zz}^2 + 2e_{xz}^2) = 2\mu(e_{xx}^2 + e_{xz}^2)$. Thus, ϕ is determined by

$$f(T_i)/(2\mu) = (1 - \cos \phi)^2 + \frac{1}{4}(\tan \phi)^2. \quad (17)$$

For this two-dimensional case, we achieve a perfectly isotropic state I on one side and the standard N state of the other side. However, as we shall see, this perfect matching is not possible in 3D (exactly as in similar martensitic transformations [7]).

A.2) The three-dimensional case

We can try a similar construction for the three-dimensional case (see fig. 2 again). We take the habit plane perpendicular to the x - z plane (the director axis stays in the x - z plane). In the rectangular coordinate composed of the director axis (n), y -axis, and α -axis (perpendicular to the others, see fig. 2), the nonzero strain components are $e_n(T_i) \equiv e_i \neq 0$ (in the director axis), and $e_{\alpha\alpha} = e_{yy} = -e_i/2$. The elastic energy associated with this is given by $f_i = \frac{3}{2}\mu e_i^2$. In the (x, y, z) coordinate the strain tensor is given as

$$\hat{e} \equiv \begin{pmatrix} e_{xx} & e_{xy} & e_{xz} \\ e_{yx} & e_{yy} & e_{yz} \\ e_{zx} & e_{zy} & e_{zz} \end{pmatrix} = \begin{pmatrix} \cos \phi - 1 & 0 & \frac{1}{2} \tan \phi \\ 0 & -e_i/2 & 0 \\ \frac{1}{2} \tan \phi & 0 & 1 - \cos \phi + e_i/2 \end{pmatrix} \quad (18)$$

and the elastic energy is given by $f_i/\mu = e_{xx}^2 + e_{yy}^2 + e_{zz}^2 + 2e_{zx}^2$. Thus, we can fix ϕ by requiring that the energy is the same in the (n, y, α) and (x, y, z) coordinates:

$$\frac{5}{4}e_i^2 = (\cos \phi - 1)^2 + (1 - \cos \phi + e_i/2)^2 + \frac{1}{2}(\tan \phi)^2. \quad (19)$$

In addition, we have

$$\tan(\theta + \phi) = \frac{2 - \cos \phi + e_i/2 + \sin \phi}{\cos \phi}. \quad (20)$$

We note that eqs. (19) and (20) predict that the habit angle approaches $\pi/4$ again in the small deformation limit ($e_i, \phi \rightarrow 0$).

In this three-dimensional case, the N phase has a third component of strain $e_{yy} = -e_i/2$ and this cannot be eliminated in the I phase. From the incompressibility condition in the I phase, we must also have a strain $e_{\beta\beta} = -e_{yy}$; inside the nucleus, there must be nonzero strain components $(e_{yy}, e_{\beta\beta}) = (-e_i/2, e_i/2)$, which results in a residual elastic energy (per unit volume)

$$E_I = \mu e_i^2/2. \quad (21)$$

Thus we reach a state which is not totally isotropic.

B) Homogeneous nucleation

Again, we think of a T -jump from an initial temperature T_i just below T_c (we take $T_i = T_c$ in practice for simplicity) up to a final temperature T lying about 10 degrees above T_c . Our assumed shape for the nucleus is a platelet corresponding to the habit plane orientation, with a thickness h and dimension L (fig. 3). From now on we construct only crude estimates, ignoring all numerical coefficients: for instance, the platelet volume is taken to be $L^2 h$.

The platelet energy is of the form

$$f = -L^2 h \cdot \Delta + E_I L^2 h + \gamma L^2 + E_p. \quad (22)$$

Here Δ is the gain in free energy (per unit volume) obtained by switching from N to I at the temperature T . Thermodynamics imposes

$$\Delta = (T - T_c)\Delta S, \quad (23)$$

where $\Delta S \simeq a_0 Q^2$ is the entropy jump at the transition temperature T_c .

The second term E_I in eq. (22) is due to the residual stress in the I phase (the principal axes of the deformation here are the y and β axes and another axes normal to them, *i.e.* the nonzero elements of the diagonalized deformation matrix are $(e_{yy}, e_{\beta\beta}) = (-e_i/2, e_i/2)$) and is only a fraction of the initial elastic energy. The original elastic energy is $\frac{3}{2}\mu e_i^2$, while we have here $\mu(e_{yy}^2 + e_{\beta\beta}^2) = \frac{1}{2}\mu e_i^2$.

Thus we lump the elastic correction into Δ , writing

$$\tilde{\Delta} = \Delta - \frac{1}{2}\mu e_i^2 \equiv (T - T_m)\Delta S, \quad (24)$$

where we have introduced T_m in analogy with eq. (23). T_m is the minimal final temperature for nucleation. From a scaling point of view, we should have

$$\frac{\tilde{\Delta}}{\mu e_i^2} \simeq \frac{T - T_m}{\Delta T_c}, \quad (25)$$

where ΔT_c corresponds to an increase in the N - I transition temperature due to the coupling (see eq. (7)). This can be explicitly shown by using the relation $\mu e_i^2 \simeq \Lambda^2 Q^2 / \mu$ and $\Delta S \simeq a_0 Q^2$. We assume from now on that $\tilde{\Delta}$ is positive but small.

The third term in eq. (22) is a surface term, with a certain interfacial energy γ , which might be estimated by a Ginzburg-Landau-type free energy (including the spatial dependence of the order parameter) plus elastic tensors. Because of these latter terms γ is positive even when $T > T^*$ as indicated by the previous arguments on the absence of the spinodal instability.

The last term in eq. (22) is another elastic term, due to distortions at the *periphery* of our platelet. Here, there is no matching at all (the matching was achieved only at the habit plane boundary), we have *large deformations* taking place in a toroidal region near the periphery (fig. 3). The length scale relevant for this extra peripheral deformation and the size of deformation are both around h and, because the deformation fields always satisfy the Laplace equation, this deformation dies out only at a distance $\simeq h$ from the torus: the strain e_p (at least of the order of e_i) is stored around the periphery of the volume $\simeq Lh^2$ (fig. 3):

$$E_p \simeq Lh^2 \Delta_p \quad (26)$$

with

$$\Delta_p = \mu e_p^2. \quad (27)$$

We now write eq. (22) in the following form:

$$F = -\tilde{\Delta} L^2 h + \gamma L^2 + Lh^2 \Delta_p. \quad (28)$$

By minimizing the above energy with respect to h , we have

$$h_0 = \frac{\tilde{\Delta}}{2\Delta_p} L, \quad (29)$$

$$F_0 = -\frac{\tilde{\Delta}}{4\Delta_p} \tilde{\Delta} L^3 + \gamma L^2. \quad (30)$$

Thus, the assumption $L \gg h$ corresponds to $\tilde{\Delta} \ll \Delta_p$: if the peripheral energy Δ_p is large compared with the bulk gain $\tilde{\Delta}$, the platelet tends to become thin.

The energy expression in eq. (30) is in contrast with the classical case of a spherical nucleus without any elastic contribution: $F = -\Delta \cdot L^3 + \gamma L^2$. For $\Delta_p > \tilde{\Delta}$, the bulk term for the disk droplet is quite small compared with the surface term. If we look for the maximum of eq. (30) with respect to L , we find an energy barrier $U = F_0(L^*)$ for the formation of a critical droplet:

$$L^* = \frac{\gamma}{\tilde{\Delta}} \cdot \frac{8\Delta_p}{3\tilde{\Delta}}, \quad (31)$$

$$U = \frac{2}{3} \left(\frac{8\Delta_p \Delta}{3\tilde{\Delta}^2} \right)^2 U_c, \quad (32)$$

where $U_c \simeq \gamma^3/\Delta^2$ is the standard barrier. In our regime, $U \gg U_c$, the nucleation rate can be thus dramatically suppressed.

Conclusions. – 1) Equation (32) shows clearly that homogeneous nucleation is prohibited in nematic rubbers —just as it is in martensites. Clearly, we need heterogeneities to nucleate, and we do expect them in networks. 2) Even when dealing with heterogeneous nucleation, it is reasonable to think that platelets (or needles) close to the habit angle will be preferentially generated. This would possibly be observed by electron microscopy or by force microscopy on the outer surface. 3) From a practical point of view, it should be beneficial to accelerate the commutation process —we can think of at least two ways: a) adding colloidal platelets (clay?) at the correct angle (possibly orienting them by fields during the synthesis); b) shearing the sample with a shear plane near the habit angle.

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