Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Elasticity of a Nematic Polymer in the Infinite Molecular Chain Limit

Victor G. Taratuta[a]; Robert B. Meyer[a]
[a] Martin Fisher School of Physics, Brandeis University, Waltham, Massachusetts, USA

To cite this Article Taratuta, Victor G. and Meyer, Robert B.(1987) 'Elasticity of a Nematic Polymer in the Infinite Molecular Chain Limit', Liquid Crystals, 2: 3, 373 — 379
To link to this Article: DOI: 10.1080/02678298708086682
URL: http://dx.doi.org/10.1080/02678298708086682

LIQUID CRYSTALS, 1987, VOL. 2, NO. 3, 373–379

Elasticity of a nematic polymer in the infinite molecular chain limit

by VICTOR G. TARATUTA† and ROBERT B. MEYER
Martin Fisher School of Physics, Brandeis University, Waltham,
Massachusetts 02254, U.S.A.

(*Received 25 September 1986; accepted 12 December 1986*)

Some of the consequences of constructing a nematic phase out of infinitely long non-rigid molecules are discussed. The basic idea consists in the fact that splay deformation is difficult in a nematic composed of long molecules and becomes strictly impossible in the infinite molecular chain limit. Some of the implications of this effect for low energy elastic deformations in a polymer nematic liquid crystal are explored. A practically important example of the interaction of a long molecular chain nematic with an undulating surface is worked out.

1. Introduction

In order to understand the possible differences between a low molecular weight nematic and a polymer nematic liquid crystal, we consider a limit of infinitely long molecular chains. It was first pointed out by de Gennes [1] that in polymer nematics the splay deformation imposes local changes in the density and thus requires large energy. To achieve splay at constant density requires that the gaps opened up between the molecules be filled by the ends of neighbouring molecules [2, Chap. 6]. As the molecules become long, there are fewer ends available to fill the gaps, making splay difficult. In the limit of infinitely long chains, with no chain ends available and for chains that are not kinked, we can write down a static analogue of a continuity equation for a nematic director

$$\nabla \cdot (\varrho \mathbf{n}) = 0, \tag{1}$$

where ϱ is the number density of chains in a plane normal to the nematic director $\mathbf{n}$. The coupling between splay and density gradients then becomes exact

$$\nabla \cdot \mathbf{n} = -\mathbf{n}\frac{\nabla\varrho}{\varrho}, \tag{2}$$

and there can be no splay deformation if the density of the system is to stay constant. In polymer nematics, once this idea was realized, it served as a clue to understanding various structural phenomena. In the static limit of a splay Fredericks transition for example, a nematic sample of poly-γ-benzyl glutamate (PBG) exhibits a spatially periodic, rather than uniform [3], response to an applied magnetic field. This phenomenon was explained to be caused by the large anisotropy between the splay and the twist elastic constant ($K_1/K_2 > 3{\cdot}3$ is the condition for this effect to occur) and is not observed in low molecular weight nematics.

---

† Present address: Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A.

Bend and twist deformations are not constrained by the increased molecular length. A non-rigid molecule will bend to follow the local director pattern. For flexible enough molecules, the bend elastic constant will be independent of their length. For any real 'rigid' molecule, there must exist a crossover regime at a length beyond which it bends to follow the local curvature.

Twist deformation for highly ordered states of a nematic should likewise not be inhibited as there is no interference between successive layers of molecules, no matter how long they are. In the case of imperfect order (order parameter $S < 1$), the molecules will have a component of their orientation parallel to the twist axis, thus entering regions in which they are misaligned. This effect becomes more significant as the molecular length increases. However, non-rigid molecules will bend to follow the local director, thus keeping the twist elastic constant finite as the chain length grows.

One interesting aspect of splay deformation in long-chain nematics has been pointed out by Meyer [2, pp. 147–150]. If there are chain ends available, splay deformation at constant density can be achieved by arranging the ends of molecules to fit between one another. However, this process leads to the segregation of 'bottom' ends of the molecules from their 'top' ends in the region of splay. This single particle entropy effect exists for rigid rods or flexible molecules and results in a contribution to the splay elastic constant which scales linearly with the chain length.

To summarize, in a very long chain limit, in which all real molecules must be thought of as flexibile, the twist and the bend elastic constants will remain finite and only the splay elastic constant will diverge with the length of the molecule.

In continuum elasticity the fundamental deformations of a system consist of displacements of small volume elements from their undistorted positions. The elastic free energy density of a single crystal of an infinite chain polymer nematic will depend on the gradients of displacements of the molecular chains. We are interested in those deformations that result in the rotations of the director. Gradients in the displacements parallel to the director correspond to stretching or compressing the chains, a rather different elastic process, much like a bulk compressibility. It can be taken into account by a first order elasticity term in the expression for the free energy density given below. Therefore, a complete description of the curvature elasticity of an infinite chain nematic can be made using only the displacements transverse to the director. The two components of these displacements are $u(r)$, in the x direction and $v(r)$ in the y direction, as shown in figure 1. For small displacements it directly follows from (2) that the components of the director are given by

$$n_x = \frac{\partial u}{\partial z}, \quad n_y = \frac{\partial v}{\partial z}. \tag{3}$$

In an ordinary nematic director rotations are not coupled to any macroscopic displacements of volume elements and, therefore, these displacements cannot be used to describe the elastic processes. In an infinite chain nematic, however, all long wavelength rotations of the director are described by the gradients of displacements. In terms of these displacements the elastic free energy density has the form (a subscript indicates a partial derivative)

$$\begin{aligned} f = {} & \tfrac{1}{2}E(u_x + v_y)^2 + \tfrac{1}{2}K_1(u_{xz} + v_{yz})^2 + \tfrac{1}{2}K_2(u_{yz} - v_{xz})^2 + \tfrac{1}{2}K_3(u_{zz}^2 + v_{zz}^2) \\ & - (K_2 + K_{24})(u_{xz}v_{yz} - u_{yz}v_{xz}). \end{aligned} \tag{4}$$

The first term describes the elastic compressibility effects, due to the changes in the lateral packing density of the molecular chains. For less than perfect order of a

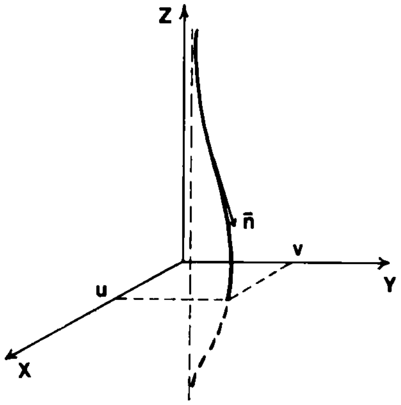

Figure 1. Average director is parallel to the z axis. The gradients of the displacements u and v describe the director **n** at any point.

nematic, the stretching of the chains leads to a decrease in the cross-sectional area of the corresponding volume element. This process involves almost no bulk compression. The compressibility E^{-1} for a solution, therefore, can be much larger than a typical compressibility for a neat liquid. For a polymer solution [4], we estimate it to be equal to $10^7\,\mathrm{erg/cm^3}$.

K_1, K_2, and K_3 are the usual Frank elastic terms. The last term, involving K_{24}, must be considered in certain surface interaction problems. We will discuss a case later in which this term plays an important role.

Equation (4) implies that for long wavelength distortions in the z direction the splay energy can be neglected compared to the compressibility term. The splay term becomes comparable to the E term for wavelengths shorter than

$$\lambda_s = 2\pi(K_1/E)^{1/2}, \tag{5}$$

which is of the order of 100 Å, based on the recent measurements of elastic constants in PBLG [5].

To construct the equilibrium equations for the solution of boundary value problems, we minimized the elastic free energy f with respect to both transverse components of the displacement. The calculus of variations yields, for u and v

$$\left.\begin{aligned} -E(u_{xx} + v_{yx}) + K_1(u_{xxzz} + v_{xyzz}) + K_2(u_{yyzz} - v_{xyzz}) + K_3 u_{zzzz} &= 0,\\ -E(u_{xy} + v_{yy}) + K_1(u_{xyzz} + v_{yyzz}) - K_2(u_{xyzz} - v_{xxzz}) + K_3 v_{zzzz} &= 0.\end{aligned}\right\} \quad (6)$$

2. Interaction with a grooved surface

To illustrate some of the implications of the infinite chain limit, we consider static distortions of a polymer nematic liquid crystal produced by an inhomogeneous surface. For the sake of simplicity, we treat the interaction of a semi-infinite slab of a nematic with a grooved surface, as shown in figure 2. Such a surface can be produced, for example, by rubbing a substrate, by oblique evaporation of thin films [6], or by microlithography techniques [7]. The aligning effects of a grooved surface in low molecular weight nematics [6] as well as in nematic solutions of PBG [8] have been discussed in the literature. Here we consider a somewhat idealized case of a 'slippery' boundary condition at the surface; the nematic director can rotate freely

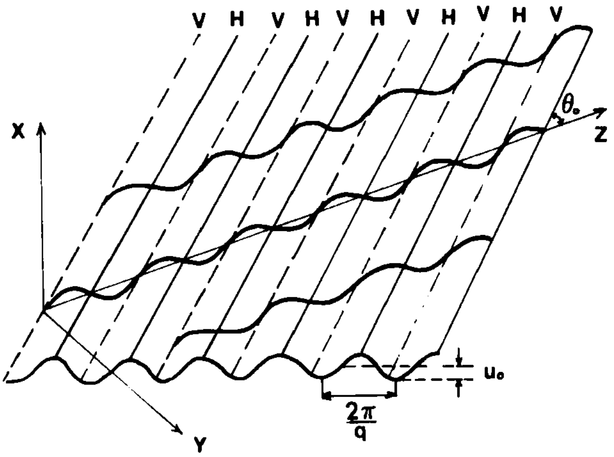

Figure 2. Response of a nematic to a grooved surface, the mean director is at an angle θ_0 to the grooves. The undulations of the director are shown relative to the hills (H) and valleys (V).

around the surface normal. An analogous problem for ordinary nematics has been treated previously [9]. Possible differences of the aligning effect of grooves in ordinary nematics and in long-chain polymer nematics have been pointed out in an earlier work of Meyer [2, Chap. 6] which treated a special case of a director perpendicular to the grooves. Here we extend the previous analysis to include a general case of a mean director orientation oblique to the grooves, which illustrates an essential part of the actual response to the undulating surface in the infinite chain limit.

The amplitude of the grooves u_0 must be small compared to their wavelength $\lambda = 2\pi/q$, $u_0 q \ll 1$. The problem possesses an obvious symmetry; nothing changes along the direction of the grooves. The 'slippery' boundary condition requires that the vertical component of the surface torque vanish

$$\left[\frac{\partial f}{\partial v_{xz}}\right]_{x=0} = [K_2 v_{xz} - K_{24} u_{yz}]_{x=0} = 0. \tag{7}$$

The remaining boundary conditions are introduced by assuming that the director is parallel to the surface and becomes constant far from the surface

$$u(x=0,z) = u_0 \sin(\mathbf{q}\cdot\mathbf{r}), \quad u(x=\infty,z) = v(x=\infty,z) = 0, \tag{8}$$

where $\mathbf{q}\cdot\mathbf{r} = q_1 z + q_2 y$ with $q_1 = q\sin\theta_0$ and $q_2 = -q\cos\theta_0$, and θ_0 is the angle between the mean director and the direction of the grooves.

If the director is exactly normal to the grooves, then $\partial/\partial y = 0$, $v = 0$, and the twist distortion disappears. The elastic free energy density is then reduced to

$$f = Eu_x^2 + K_1 u_{xz}^2 + K_3 u_{zz}^2, \tag{9}$$

and the equilibrium equations for u and v to

$$-Eu_{xx} + K_1 u_{xxzz} + K_3 u_{zzzz} = 0. \tag{10}$$

The solution of equation (10) with the boundary conditions (8) becomes

$$u(x,z) = u_0 \sin(qz) \exp\left[-x\left[\frac{K_3 q^4}{E + K_1 q^2}\right]^{1/2}\right] \tag{11}$$

and the elastic energy per unit area of surface due to the undulations is

$$F = \tfrac{1}{4}u_0^2 q^2[K_3(E + K_1 q^2)]^{1/2}. \tag{12}$$

For example, if the groove spacing is ten microns, $K_1 q^2 \sim 10\,\mathrm{erg/cm^3}$ and can be ignored compared to E. The undulations of the director at the surface then relax in the bulk with a characteristic length

$$x^0 = (q^2\lambda_b)^{-1}, \quad \lambda_b = (K_3/E)^{1/2}. \tag{13}$$

We observe here a smectic-like response of the liquid crystal to an undulating surface. The characteristic relaxation length x^0 is quadratic in the width of the grooves. Note that x^0 is much larger than the groove spacing $2\pi/q$. For ten-micron grooves, $2\pi/q = 10\,\mu\mathrm{m}$, and $\lambda_b = 20\,\text{Å}$, then $x^0 \sim 1{\cdot}5\,\mathrm{mm}$.

In a low molecular weight nematic ($E = 0$), however, this problem has a solution for the director

$$n_x = \frac{\partial u}{\partial z} = u_0 \cos(qz) \exp[-qx(K_3/K_1)^{1/2}], \tag{14}$$

and the free energy becomes

$$F = \tfrac{1}{4}u_0^2 q^3 (K_1 K_3)^{1/2}. \tag{15}$$

In this case the relaxation length is linear in the width of the grooves, $x^0 = [q(K_3/K_1)^{1/2}]^{-1}$. If $K_1 \simeq K_3$, then $x^0 = 1/q$, i.e. of the order of the groove spacing. Thus, for the director normal to the grooves, a static distortion produced by surface undulations relaxes much more slowly in a nematic of long chains than in a low molecular weight nematic. The ratio of the surface energies for the two cases considered is

$$\frac{F^{(\mathrm{lmw})}}{F^{(\mathrm{inf})}} = \lambda_s q \ll 1. \tag{16}$$

This result can be understood by observing that in order to relax the bend imposed by the undulating surface, one must introduce a splay deformation with a wavevector along the surface normal. In the infinite chain limit the splay costs a lot of energy and the bend distortion has to relax slowly, propagating a long distance into the bulk, resulting in a higher elastic energy.

The case of a director perpendicular to the grooves points out a possibility of unusual elastic behaviour of a polymer nematic liquid crystal, rather different from that found in an ordinary nematic. However, it corresponds to an artificial physical situation, difficult to achieve experimentally. To complete the above picture of the aligning effect of grooves, one must consider a general case of a mean director oblique to the grooves. In that case the boundary condition (12) requires that $v \neq 0$, i.e. undulations of the director in the plane of the surface appear. Each component of the displacement then (u–vertical and v–horizontal) gives rise to a splay–bend and twist–bend elastic distortions. These distortions relax in the bulk each with its own characteristic length, $\lambda_1 = 2\pi/k_1$ for the splay–bend, and $\lambda_2 = 2\pi/k_2$ for the twist-bend. The solution of the equilibrium equations (3) consistent with the boundary conditions (12) and (13) then becomes in the infinite chain limit

$$\left.\begin{aligned} u &= \frac{u_0}{K_3 q_1^2}\big[[K_3 q_1^2 + q_2^2(K_2 + K_{24})]\exp(-k_1 x) \\ &\quad - q_2^2(K_2 + K_{24})\exp(-k_2 x)\big]\sin(\mathbf{q}\cdot\mathbf{r}), \\ v &= \frac{u_0 q^2}{K_3 q_1^2}\bigg[-\frac{1}{k_2}[K_3 q_1^2 + q_2^2(K_2 + K_{24})]\exp(-k_1 x) \\ &\quad + k_1(K_2 + K_{24})\exp(-k_2 x)\bigg]\cos(\mathbf{q}\cdot\mathbf{r}), \end{aligned}\right\} \tag{17}$$

where

$$k_1^2 = q_2^2 + q_1^4\frac{K_3}{E + K_1 q_1^2}, \quad k_2^2 = q_2^2 + q_1^2\frac{K_3}{K_2}. \tag{18}$$

The energy of deformation per unit area of the undulating surface is computed by substituting the solution for u and v into the general free energy (1).

$$F = \tfrac{1}{4}u_0^2 q^3\left[\frac{1}{K_3}\frac{[K_3 s^2 + (K_2 + K_{24})c^2]^2}{[c^2 + q^2 s^4(K_3/(E + K_1 q^2 s^2))]^{1/2}} - \frac{(K_2 + K_{24})^2}{K_3}c^2\left[c^2 + s^2\frac{K_3}{K_2}\right]^{1/2}\right], \tag{19}$$

with $s = \sin\theta_0$, $c = \cos\theta_0$. For an ordinary nematic we simply put $E = 0$.

We see from equations (17) and (18) that for any finite θ_0 the characteristic relaxation lengths for splay–bend (x_1^0) and twist–bend (x_2^0) distortions now have the form ($\theta_0 = \pi/4$)

$$x_1^0 = \frac{1}{(q/\sqrt{2})[1 + (q^2/2)\lambda_b^2]^{1/2}}, \quad x_2^0 = \frac{1}{(q/\sqrt{2})[1 + (K_3/K_2)]^{1/2}}. \tag{20}$$

Here the elastic relaxation again exhibits a nematic-like rather than the smectic-like behaviour. Both relaxation lengths are linear in the groove spacing. What is remarkable, however, is that both splay–bend and twist–bend deformations relax into the bulk with characteristic lengths of comparable magnitude, which is of the order of the groove spacing. Taking again ten micron grooves as an example, we find $x_1^0 \sim 1\ \mu$m, instead of 1·5 mm for the director perpendicular to the grooves. Assuming $K_3/K_2 = 8$, for example, we find for the ratio $x_1^0/x_2^0 = 3$. At the first sight, this is a surprising result. One would have expected a larger number for this ratio since splay is strongly inhibited in the infinite chain limit, while twist remains easy. However, one realizes that there is now an in-plane component of splay, opposite to the out-of-plane component, needed to relax the bend imposed by the undulating surface. The two components of splay tend to cancel each other, which results in a lower splay energy. This effect exists in low molecular weight nematics, but is not important energetically. In polymer nematics, however, it is crucial. The infinite chain nematic behaves again like an ordinary nematic rather than like a smectic.

If the director is parallel to the grooves, then $F = 0$. For small deviations of the mean director from the direction of the grooves, one can define an elastic anchoring coefficient A by expanding a free energy to second order in θ_0

$$F = A\theta_0^2 + O(\theta_0^4). \tag{21}$$

Using equation (19) we obtain

$$A^{(\mathrm{inf})} = \tfrac{1}{8}u_0^2q^3(K_2 + K_{24})\left[4 - (K_2 + K_{24})\left[\frac{1}{K_2}\right]\right], \tag{22}$$

in the infinite chain limit and

$$A^{(\mathrm{lmw})} = \tfrac{1}{8}u_0^2q^3(K_2 + K_{24})\left[4 - (K_2 + K_{24})\left[\frac{1}{K_2} + \frac{1}{K_1}\right]\right], \tag{23}$$

for a low molecular weight nematic. We see here again that the elastic anchoring at an undulating surface is not significantly different in an ordinary nematic, where $K_1 \simeq K_2$, and in an infinite chain nematic, where splay deformation is impossible.

This example illustrates that the splay–avoidance effects are an essential part of the response of the infinite chain nematic to an undulating surface. They are also very important to understanding the nature of other types of static elastic deformations in a polymer nematic liquid crystal.

This research was supported in part by the National Science Foundation through Grant No. DMR–8210477, and by the Martin Fisher School of Physics, Brandeis University.

References

[1] DE GENNES, P. G., 1977, *Molec. Crystals liq. Crystals Lett.*, **34**, 177.

[2] MEYER, R. B., 1982, *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Krigbaum and R. B. Meyer (Academic), Chap. 6.

[3] LONBERG, F., and MEYER, R. B., 1985, *Phys. Rev. Lett.*, **55**, 718.

[4] See, for example, FLORY, P. J., 1983, *Principles of Polymer Chemistry* (Cornell University), Chap. VII.

[5] TARATUTA, V., HURD, A., and MEYER, R., 1985, *Phys. Rev. Lett.*, **55**, 246.

[6] BERREMAN, D., 1972, *Phys. Rev. Lett.*, **28**, 1683.

[7] KANEL, H. V., LITSTER, J. D., MELNGAILIS, J., and SMITH, H. I., 1981, *Phys. Rev.* A, **24**, 2713.

[8] TARATUTA, V., SRAJER, G., and MEYER, R. B., 1985, *Molec. Crystals liq. Crystals*, **116**, 245.

[9] WOLFF, U., GRUEBEL, W., and KRUGER, H., 1973, *Molec. Crystals liq. Crystals*, **23**, 187.