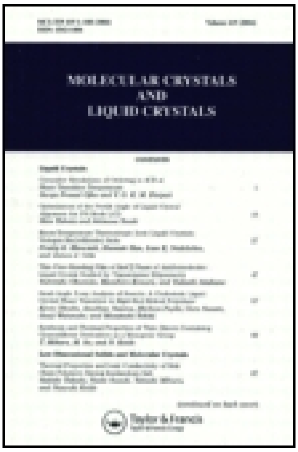

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Analysis of Liquid Crystalline Fiber Coatings

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Analysis of Liquid Crystalline Fiber Coatings

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A phenomenological model for the spreading of nematic liquid crystals on fibers of circular cross section is presented. The model is used to calculate the wetting thresholds of nematics on fibers for three chracteristic director orientations: axial (undistorted), radial (splay), and azimuthal (bend); the wetting thresholds are given in terms of critical film thickness h_c and critical spreading parameter S_c. When the spreading parameter S is greater than the critical value S_c, nematic liquid crystal fiber wetting is similar to that of viscous fluids when director distortions are absent. In other cases when nematic liquid crystals spread on fibers the distortion due to the cylindrical geometry gives rise to Frank elasticity. For symmetric director boundary conditions the characteristic modes of splay and bend increase the magnitude of critical spreading parameter S_c. It is found that when spreading occurs ($S > S_c$) the equilibrium film thickness decreases with increasing elastic storage. The film thickness for rod-like and disc-like nematics differs because the splay-bend elastic anisotropy is reversed.

Keywords: fiber wetting; spreading of nematic liquid crystals; Frank elasticity; film thickness

1. INTRODUCTION

Fiber wetting is an important process in the fabrication of composites , textiles, and in the cosmetics industries [1]. Fiber wetting by viscous coating fluids is curently well understood and characterized [2–4]. The use of nematic liquid crystals as coating materials is less well known, but potential applications such as mesophase carbon coatings and nematic polymer composites may require a better understanding of fiber wetting phenomena involving liquid crystals.

The statics and dynamics of wetting phenomena of nematic liquid crystals in planar surfaces has been described by several groups [5–7]. It is found that the

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wetting behaviour of nematic drops on solid planar substrates is similar to that of isotropic fluids. The main diffrences arise due to the presence of Frank elasticity when the director surface orientation at the solid substrate is different than at the free surface. The presence of asymmetric boundary conditions leads to the storage of Frank elasticity through director gradients which can not be eliminated during the film formation. For low molar mass nematics the equilibrium film thickness on planar solid substrates is of the order of 10^{-5} cm to 10^{-6} cm [5].

Fiber wetting by viscous fluids differs from that of planar substrates [3,4,8]. The fiber curvature adds the capillary pressure to the usual spreading and disjoining pressure mechanisms operating in planar substrates. An important consequence is that fiber wetting only occurs when the spreading parameters S is greater than a critical value S_c, while wetting of planar substrates occurs when the spreading parameter is positive. In addition, under the same conditions the film thickness is greater for fibers than for planar substrates [4].

The presence of fiber curvature leads to new phenomena for nematic liquid crystals because unless the director is along the fiber axis, the director will splay and/or bend. Thus fiber wetting by nematics involves the determination of director orientation in annular spaces, a problem that has been solved under general boundary conditions [9]. It is important to note in the context of wetting that planar substrates lead to director distortions only for asymmetric boundary conditions [6], but curved substrates lead to director distortions even with symmetric boundary conditions.

The objective of the paper is to extend the fiber wetting analysis for viscous fluids to nematic liquid crystals. The analysis is for the statics of ultrathin films and the effect of Frank elasticity is determined for circular fibers in the presence of 2-D director fields, that is, the more complex twist distortions are not included in the present paper. Section 2 presents the basic equations used in the analysis, including the new nematic contribution for fibers of circular cross section. Section 3 presents the main results including the film thickness and wetting criteria, and effect of elastic moduli on wetting behaviour. Section 4 presents the conclusions.

2. FIBER WETTING WITH NEMATIC LIQUID CRYSTALS

We start by presenting the well known wetting principles for isotropic viscous fluids [3,4]. The wettability of a dry ideal solid by a liquid is determined by the spreading coefficient S:

$$S = \gamma_S - \gamma_{S\ell} - \gamma \tag{1}$$

which is the difference between the interfacial energy γ_s for an ideal dry solid surface and the interfacial energy for a completed wetted surface, $\gamma_{s\ell} + \gamma$; $\gamma_{s\ell}$ is the solid-liquid surface tension and γ is the liquid-vapor surface tension. When S > 0 a fluid drop will spread spontaneously on a planar surface because the wetted surface has a lower free energy than the dry surface, an instance known as total wetting. When S < 0 the fluid partially wets the surface, such that

$$S = \gamma(-1 + \cos\alpha) \tag{2}$$

where α is the contact angle.

When a liquid spreads into a thin film on a surface long range interactions become significant. The free energy per unit area Φ due to nonretarded London-van der Waals long range interactions in a film of thickness h is:

$$\Phi(h) = \frac{A}{12\pi h^2} \tag{3}$$

where A is the Hamaker constant, whose typical value is of the order of 10^{-20} J. The disjoining pressure associated with the long range interactions Π is given by:

$$\Pi(h) = -\frac{d\Phi}{dh} = \frac{2\Phi}{h} \tag{4a, b}$$

and when A > 0 the effect of this pressure is to thicken the film.

When considering a wetting film on a fiber of cylindrical cross section an additional free energy contribution arising from the changes in curvature at the solid substrate and at the free surface must be taken into account. For a liquid film of thickness h on a fiber of radius b (Figure 1), the free energy contribution from the curvature of the liquid-vapor interface, on a volume basis, is [4] :

$$F_\gamma = \frac{\gamma}{b + h} \tag{5}$$

For nematic liquid crystals the Frank elasticity due to orientational gradients must be taken into account [10]. The elastic free energy density F_e for uniaxial nematics is:

$$2Fe = K_{11}(\nabla \cdot n)^2 + K_{22}(\mathbf{n} \cdot \text{curl } \mathbf{n})^2 + K_{33}\left|\mathbf{n} \times \text{curl } \mathbf{n}\right|^2 \tag{6}$$

where $\{K_{ii}\}$; ii =11,22,33, are the temperature dependent elastic moduli (energy per unit length) for spaly, twist and bend, and where **n** is the director orientation (**n.n**=1) For planar orientation modes no twist deformation arises. Figure 2 shows schematics of the three representative director field considered in this paper, corresponding to axial (undistorted), azimuthal (bend), and radial (splay) orientation. In all cases the director boundary conditions are the same at both surfaces. Other more complex cases arising from asymetric boundary conditions are not treated here. It is interesteting to note that even in planar orientation (i.e., no

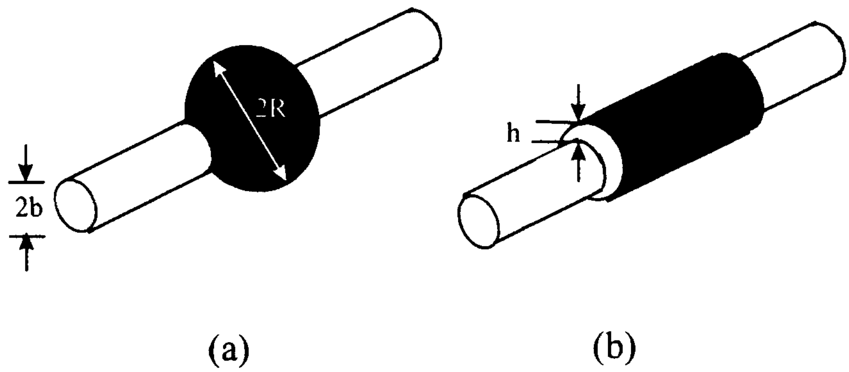


FIGURE 1 Schematics of the wetting geometries and conditions studied in this paper. (a) Droplet of nematic liquid crystal of radius R placed on a fiber of radius b. In this paper R>>b. (b) When the spreading coefficient S is larger than the critical value S_c the droplet spreads and forms an annular sheath of thickness h on the fiber. The critical spreading coefficient is a function of the director orientation (see equations 10,12, 14)

twist) with symmetric boundary conditions complex director profiles can be expected due to spaly-bend anisotropies. In such cases wetting transitions are likely to occur. For a sheat of thickness h and inner radius b the elastic free energies densities for the axial (F_e^u), azimuthal (F_e^b), and radial (F_e^s) orientation are :

$$F_e^u = 0; \quad F_e^b = \frac{K_{33}}{2bh} \ln\left(1 + \frac{h}{b}\right); \quad F_e^s = \frac{K_{11}}{2bh} \ln\left(1 + \frac{h}{b}\right) \quad (7a, b, c)$$

For the case studies in this paper b>>h and the elastic energy per unit volume of the sheat scales with b^2.

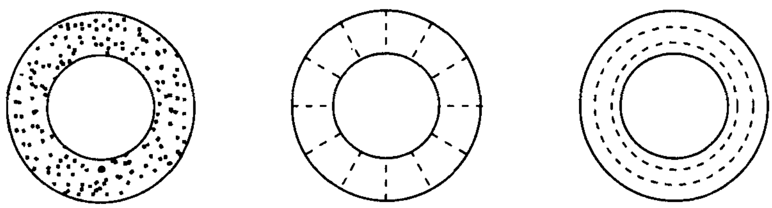
Collecting results, the total free energy F_f for a nematic film of thickness h and volume V on a fiber of radius b is given by:

$$F_f = (-S + \Phi)\frac{V}{h} + \frac{\gamma}{b + h} V + \int_v F_e dV \quad (8)$$

In this paper we analyze the conditions under which a nematic droplet of radius R deposited on a fiber of radius b spreads into a sheat of thickness h, as indicated in figure 1. In this paper we consider large droplets (R >> b) so that its free energy can be neglected when compared to a thin film. Thus the critical condition or threshold for the spreading of a droplet into sheat is found when F_f=0 and $\partial F_f/\partial h$=0. The threshold conditions are given as the critical thickness h_c and the critical spreading coefficient S_c. For nematic films it will be shown that S_c is a function of the characteristic Frank elasticity constant. When S > Sc spreading occurs and the resulting sheat thickness h that minimizes the free energy is found from $\partial F_f/\partial h=0$.

3. RESULS AND DISCUSSION

In this section we present the results that describe the fiber wetting with large nematic droplets , including the threshold conditions (h_c, S_c) and the resulting sheath thickness h when S > Sc, for the three representative geometries shown in Figure 2.



(a) (b) (c)

FIGURE 2 Schematics of the three representative director orientations in the nematic annular sheath. Cylindrical coordinates (r, θ, z) are used. (a) In the axial orientation the director orients along the fiber axis, $\mathbf{n} = (0, 0, 1)$, and there are no director gradients. Fiber wetting phenbomena is described by viscous isotropic fluid models. (b) In the radial orientation the director field is $\mathbf{n} = (1, 0, 0)$, and bending deformations (K_{33}) occur. The film thickness h decreases with increasing K_{33} . (c) In the azimuthal orientation the director field is $\mathbf{n} = (0, 1, 0)$, and spaly deformations (K_{11}) occur. The film thickness h decreases with increasing K_{11}

3.1 Wetting Thresholds

a. Axial orientation-undistorted mode

A nematic sheath with axial director orientation does not store Frank energy because the director is spatially homogeneous ; see Fig 2a. Thus the wetting threshold (h_c^u, S_c^u) is the same as that obtained for isotropic fluids [4]:

$$h_c^u = \left(\frac{Ab}{6\pi\gamma}\right)^{1/3} \tag{9}$$

$$S_c^u = \frac{3}{2}\gamma\frac{h_c}{b} = \frac{3}{2}\left(\frac{A\gamma^2}{6\pi b^2}\right)^{1/3} \tag{10}$$

b. Radial orientation-splay mode

A nematic sheath with azimuthal director orientation stores bend elasticity; see Figure 2b. In this case the wetting threshold (h_c^s, S_c^s) is given by the following function of the splay energy:

$$h_c^s = \left(\frac{Ab}{6\pi\gamma\left(1 + \frac{K_{11}}{2\gamma b}\right)} \right)^{1/3} \tag{11}$$

$$S_c^s = \frac{3}{2} \left(\frac{A\gamma^2 \left(1 + \frac{K_{11}}{2\gamma b}\right)^2}{6\pi b^2} \right)^{1/3} \tag{12}$$

By setting $K_{11}=0$ we recover the classical result for isotropic fluids [4]. Splay energy increases the critical spreading parameter and reduces the critical film thickness relative to the isotropic fluid.

c. Azimuthal orientation-bend mode

A nematic sheath with azimuthal director orientation stores bend elasticity, see Figure 2c. In this case the wetting threshold (h_c^b, S_c^b) is given by the following function of the bend energy:

$$h_c^b = \left(\frac{Ab}{6\pi\gamma\left(1 + \frac{K_{33}}{2\gamma b}\right)} \right)^{1/3} \tag{13}$$

$$S_c^b = \frac{3}{2} \left(\frac{A\gamma^2 \left(1 + \frac{K_{33}}{2\gamma b}\right)^2}{6\pi b^2} \right)^{1/3} \tag{14}$$

By setting $K_{33}=0$ we recover the classical result for isotropic fluids [4]. Bend energy increases the critical spreading parameter and reduces the critical film thickness relative to the isotropic fluid.

For low molar mass rodlike nematics the elastic constant ordering is $K_{33}>K_{11}$ and the threshold ordering for a given fiber is:

$$h_c^u > h_c^s > h_c^b \quad ; \quad S_c^b > S_c^s > S_c^u \tag{16a, b}$$

On the other hand for low molar mass disclike nematics and for nematic polymers the elastic constant ordering is $K_{11}>K_{33}$ and the threshold ordering for a given fiber is:

$$h_c^u > h_c^b > h_c^s \quad ; \quad S_c^s > S_c^b > S_c^u \tag{17a,b}$$

3.2 Film Thickness

When $S > S_c$ the droplet spreads into a sheath and the selected equilibrium film thickness h is the one that minimizes the free energy. The presence of Frank elasticity affects h as follows:

$$h^i = \left[\frac{Sb^2}{2\gamma^i}\left(1-\sqrt{1-\frac{A\gamma^i}{S^2b^2\pi}}\right)\right]^{1/2} \quad ; \quad i = u,\ s,\ b \tag{18a,b}$$

$$\gamma^u = \gamma \quad ; \quad \gamma^s = \gamma\left(1-\frac{K_{11}}{4b}\right) \quad ; \quad \gamma^b = \gamma\left(1-\frac{K_{33}}{4b}\right) \tag{19a,b,c}$$

In the absence of Frank elasticity all results coincide with the isotropic viscous fluid case. Frank elasticity decreases the film thickness relative to the isotropic fluid.

For low molar mass rodlike nematics the film thickness ordering for a given fiber is:

$$h^u > h^s > h^b \tag{19}$$

On the other hand for low molar mass disclike nematics and nematic polymers the film thickness ordering is :

$$h^u > h^b > h^s \tag{20}$$

In all the above results the magnitude of the Frank elasticity effect depends on the dimensionless number

$$P = \frac{K_{ii}}{\gamma b} \quad ; \quad ii = 11, 33 \tag{21}$$

For typical low molar mass nematics and for a fiber of radius 0.1 μm, P is of the order of 10^{-3}. For high molecular weight nematic polymers we expect the splay constant to be high and for low-molar mass nematics sufficiently close to nematic-smectic A transition we expect the splay Frank constant to be high and hence in these cases P is expected to be significantly higher. In this two cases it is possible that orientation transitions, such as those described in [9] for annular spaces set in, but that problem is outside the scope of this paper.

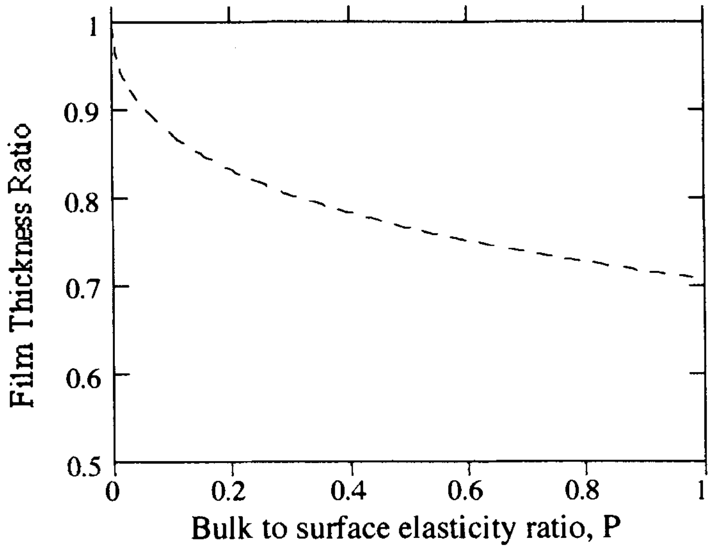


FIGURE 3 Ratio of film thickness with either splay (h^s) or bend (h^b) distortions to the film thickness for the undistorted case (h^u) as a function of the ratio of bulk to surface elasticity (P), for S^2 b^2 π /A γ = 1. The figure shows that when P increases the film thickness ratio (h^i/h^u; i = s, b) decreases and thus the maximum effect is observed when P is equal to one

In addition for the model to describe nematic fiber wetting, equations (18a,b) show that the physical limits of P are :

$$1 - \frac{S^2 b^2 \pi}{A\gamma} < P < 1 \tag{22}$$

Figure 3 shows the ratio of film thickness with either splay (h^s) or bend (h^b) to the film thickness for the undistorted case (h^u) as a function of the ratio of bulk to surface elasticity (P), for S^2 b^2 π /A γ = 1. The figure shows that when P increases the film thickness ratio (h^i/h^u; i = s, b) decreases and thus the maximum effect is observed when P is equal to one. In addition the maximum value of this ratio is:

$$\max\ (h^i/h^u) = \sqrt{1/2} \quad ; \quad i = s, b \tag{23}$$

4. CONCLUSIONS

The spreading of nematic liquid crystals on fibers is similar to that of viscous fluids when director distortions are absent. This is only possible when the director aligns along the fiber axis. Besides this special case, when nematic liquid crystals spread on fibers the distortion due to the cylindrical geometry gives rise to Frank elasticity. For symmetric director boundary conditions the characteristic modes of splay and bend increase the magnitude of critical spreading parameter S_c. It is found the when spreading occurs ($S > S_c$) the equilibrium film thickness decreases with increasing elastic storage. The film thickness for rod-like and disc-like nematics differs because the elastic anisotropy between splay and bend elasticity is reversed.

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