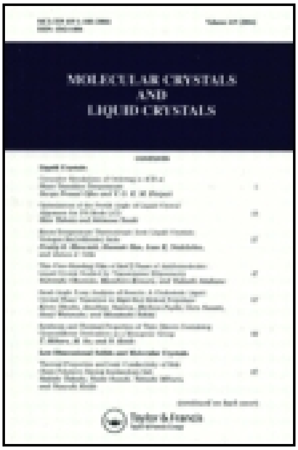

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The Influence of Van der Waals Forces on the Alignment of Nematic Liquid Crystals in Magnetic Fields

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The Influence of Van der Waals Forces on the Alignment of Nematic Liquid Crystals in Magnetic Fields

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We calculate the van der Waals free energy for a nematic liquid crystal confined between two parallel dielectric half spaces. We consider two configurations: (i) director (direction of anisotropic axis) perpendicular to the interface, (ii) director parallel to the interface. Assuming these energies dominate, their differences are compared for two configurations in the presence of a uniform magnetic field parallel to the interface. For a given specimen thickness ℓ a magnetic field H_c is found such that for $H < H_c$ the liquid crystal will be perpendicularly aligned and for $H > H_c$ parallel alignment will occur. The dependence of H_c on thickness ℓ is calculated and the experimental evidence is discussed. When *one* of the dielectric half spaces is replaced by a metal half space, we predict that no critical magnetic field will exist.

INTRODUCTION

It is well known that magnetic fields can affect the orientation of nematic liquid crystals.[1-5]

This arises because the molecules have an anisotropic magnetic susceptibility and the magnetic field can then exert a torque on the molecules which tends to orient them parallel to the field. Nematic liquid crystals have low viscosity

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(compared to the smectic phase) and can be completely aligned by uniform magnetic fields. Indeed, this is a well known method for obtaining large "monocrystalline" nematic layers.

The effect of surfaces on the orientation of the molecules is also well known (see Ref. 25–30 in the review by Chistyakov.[3] When a glass surface is polished in a particular direction and placed in contact with the liquid crystal, the molecules tend to line up parallel to the scratches on the glass surface. However, for a completely smooth surface the molecules tend to orient perpendicular to the surface. Frediriks[4,5] has studied the combined effects of surface and magnetic fields on the ordering of the liquid crystal molecules. The experiment is described by Chistyakov.[3] Briefly he placed a watchglass on a nematic liquid crystal which was on a plane glass surface (Figure 1). A magnetic field was then applied parallel to the lower slab surface. For each value of the field strength H there was found to be a critical film thickness z_c such that for $z < z_c$ the molecules were aligned perpendicular to the field and for $z > z_c$ the molecules align parallel to the field. Fredericks deduced the empirical relation

$$Hz_c = K$$

where K is a constant independent of the type of glass used.

The aim of this paper is to study this orientational effect from a theoretical viewpoint based on the hypothesis that interaction between the liquid crystal and the glass walls are dominated by dispersion energies. We calculate the van der Waals and magnetic free energies for the two different configurations. The

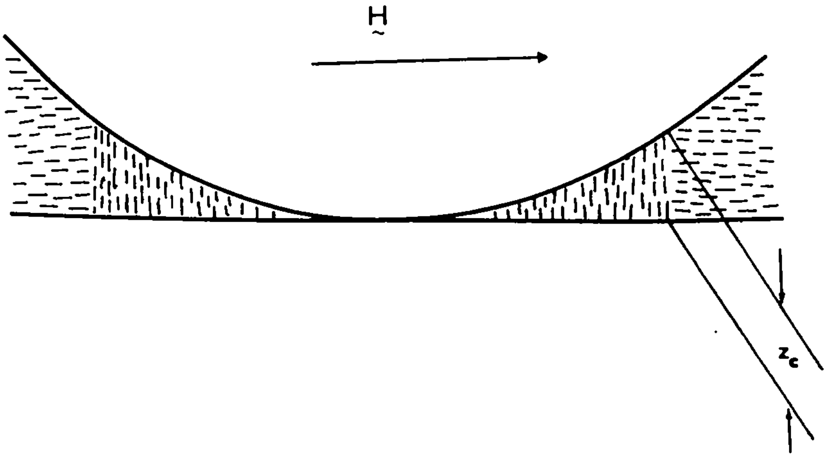

FIGURE 1 The experiment of Frederiks[4,5] (after Chistyakov[3]) showing the regions of distinct orientation in the nematic liquid crystal.

configuration of lowest free energy for a given field H and thickness ℓ is then the preferred state. The liquid crystal film thicknesses studied by Frediriks were $10^2 - 10^5$ A° and it is necessary when calculating the van der Waals forces to include retardation effects. This can be done most readily by the method of surface modes[6,7] The paper is set out as follows. In Sec. 2 we use the surface mode procedure to obtain the van der Waals free energy for the two configurations. In Sec. 3 we consider the magnetic free energy and show the existence of a critical field H_c and discuss qualitatively its dependence on film thickness ℓ. The results of precise numerical calculation are given in Sec. 4 along with a discussion of other contributions to the free energy. Finally in Sec. 5 we summarize our conclusions and suggest possible experiments which may be done with modern techniques.

VAN DER WAALS FREE ENERGY

As mentioned above, we shall compute the van der Waals free energy using the method of surface modes. The procedure uses dielectric permeabilities and is a macroscopic approach. Now we suppose the liquid crystal film is "monocrystalline" and the director $\underset{\sim}{\hat{n}}$ (the direction of the long axis of the molecules) is not position dependent. If $\underset{\sim}{\hat{\ell}}$ and $\underset{\sim}{\hat{m}}$ are two orthogonal unit vectors in the plane perpendicular to $\underset{\sim}{\hat{n}}$ and forming a right-handed coordinate system, the dielectric tensor is given by

$$\epsilon = \epsilon_\perp \underset{\sim}{\hat{\ell}}\underset{\sim}{\hat{\ell}} + \epsilon_\perp \underset{\sim}{\hat{m}}\underset{\sim}{\hat{m}} + \epsilon_\parallel \underset{\sim}{\hat{n}}\underset{\sim}{\hat{n}} \tag{2.1}$$

If we define

$$\lambda = (\epsilon_\parallel - \epsilon_\perp)/\epsilon_\perp, \; \epsilon = \epsilon_\perp \tag{2.2}$$

the expression (2.1) becomes

$$\epsilon = \epsilon(I + \lambda \underset{\sim}{\hat{n}}\underset{\sim}{\hat{n}}) \tag{2.3}$$

where I is the unit dyadic.

In our system the liquid crystal forms a planar slab of thickness ℓ sandwiched between two isotropic dielectric half spaces of dielectric permeabilities ϵ_1 and ϵ_3. The z axis is perpendicular to the planar interfaces which lie parallel to the x,y plane. The static magnetic field will later be assumed to be parallel to the x axis. We now obtain the surface modes for the two configurations: $\underset{\sim}{\hat{n}} \parallel \underset{\sim}{\hat{z}}$ (z anisotropy) and $\underset{\sim}{\hat{n}} \parallel \underset{\sim}{\hat{x}}$ (x anisotropy). The surface modes are in each case determined by solving the revelant Maxwell's equations

$$\nabla \times \underset{\sim}{E} = i\omega \underset{\sim}{B} \tag{2.4}$$

$$\nabla . \epsilon . \underset{\sim}{E} = 0 \tag{2.5}$$

as per

$$\nabla(\nabla . \underset{\sim}{E}) - \nabla^2 \underset{\sim}{E} = \frac{\omega^2}{c^2} \epsilon . \underset{\sim}{E} \tag{2.6}$$

subject to the usual boundary conditions. Although the magnetic permeability is not zero for static fields, it relaxes rapidly and does not affect the van der Waals energies which arise from fluctuations.[8] We consider each configuration separately.

z Anisotropy

The director is now parallel to the z axis. Fourier transforming Eq. (2.6) with respect to x and y we obtain

$$\frac{d^2 E_i}{dz^2} - q_1^2 E_i = 0 \quad \text{for } z < 0 \quad (i = x,y,z) \tag{2.7}$$

$$\frac{d^2 E_x}{dz^2} - q^2 E_x = -i\lambda u \frac{dE_z}{dz} \quad \text{for } 0 < z < \ell \tag{2.8}$$

$$\frac{d^2 E_y}{dz^2} - q^2 E_y = -i\lambda v \frac{dE_z}{dz} \quad \text{for } 0 < z < \ell \tag{2.9}$$

$$\frac{d^2 E_z}{dz^2} - p^2 E_z = 0 \quad \text{for } 0 < z < \ell \tag{2.10}$$

and

$$\frac{d^2 E_i}{dz^2} - q_3^2 E_i = 0 \quad \text{for } z > \ell \quad (i = x,y,z) \tag{2.11}$$

where

$$q^2 = u^2 + v^2 - \omega^2 \epsilon / c^2 \tag{2.12}$$

$$q_j^2 = u^2 + v^2 - \omega^2 \epsilon_j / c^2 \quad (j = 1,3) \tag{2.13}$$

$$p^2 = (u^2 + v^2) \; / \; (1 + \lambda) - \omega^2 \epsilon / c^2 \tag{2.14}$$

and (u,v) is a vector which lies in the x,y plane. The solutions to Eq. (2.7–2.14) which yield the surface modes can be readily obtained. Imposing the constraint (2.5) and using (2.4) to obtain the magnetic fields we have:

for $z < 0$

$$E_x = E \, e^{q_1 z} \tag{2.15}$$

$$E_y = F \, e^{q_1 z} \tag{2.16}$$

$$E_z = \frac{-i}{q_1} (uE + vF) \, e^{q_1 z} \tag{2.17}$$

$$i\omega(uB_x + vB_y) = q_1\ (vE - uF)\ e^{q_1 z} \tag{2.18}$$

for $0 < z < \ell$

$$E_x = \frac{-v}{u}\ (C\ e^{-qz} + D\ e^{qz}) + \frac{i\ (1+\lambda)u}{u^2 + v^2}\ \frac{dE_z}{dz} \tag{2.19}$$

$$E_y = C\ e^{-qz} + D\ e^{qz} + \frac{i\,(1+\lambda)\,v}{u^2 + v^2}\ \frac{dE_z}{dz} \tag{2.20}$$

$$E_z = A\ e^{-pz} + B\ e^{pz} \tag{2.21}$$

$$i\omega\,(uB_x + vB_y) = \frac{q\,(u^2 + v^2)}{u}\ (C\,e^{-qz} - D\ e^{qz}) \tag{2.22}$$

and for $z > \ell$

$$E_x = G\ e^{-q_3 z} \tag{2.23}$$

$$E_y = H\ e^{-q_3 z} \tag{2.24}$$

$$E_z = \frac{i}{q_3}\ (uG + vH)\ e^{-q_3 z} \tag{2.25}$$

$$i\omega(uB_x + vB_y) = q_3\ (uH - vG)\ e^{-q_3 z} \tag{2.26}$$

Applying continuity of D_z, E_x, E_y, B_x and B_y at the interface $z = 0$ we obtain after some algebra

$$C = \left(\frac{q-q_1}{q+q_1}\right) D \tag{2.27}$$

$$A = \left(\frac{\epsilon_1 p - \epsilon q_1}{\epsilon_1 p + \epsilon q_1}\right) B \tag{2.28}$$

Similarly at $z = \ell$

$$D = C\ \left(\frac{q-q_3}{q+q_3}\right)\ e^{-2q\ell} \tag{2.29}$$

$$B = A\ \left(\frac{\epsilon_3 p - \epsilon q_3}{\epsilon_3 p + \epsilon q_3}\right)\ e^{-2p\ell} \tag{2.30}$$

For non trivial solutions we now obtain the dispersion relations

$$D_1\ (k,\omega) = 1 - \left(\frac{q-q_1}{q+q_1}\right)\left(\frac{q-q_3}{q+q_3}\right)\ e^{-2q\ell} \tag{2.31}$$

$$D_2\ (k,\omega) = 1 - \left(\frac{\epsilon_1 p-\epsilon q_1}{\epsilon_1 p+\epsilon q_1}\right)\left(\frac{\epsilon_3 p-\epsilon q_3}{\epsilon_3 p+\epsilon q_3}\right)\ e^{-2p\ell} \tag{2.32}$$

where

$$k^2 = u^2 + v^2 .$$

In the non retaded limit ($c \to \infty$) these dispersion relations reduce to a form obtained by Parsegian and Weiss.[14] These may be combined to give the dispersion relation for z anisotropy

$$D_z(k,\omega) = D_1(k,\omega)\, D_2(k,\omega) \tag{2.33}$$

The van der Waals free energy per unit area is now given by the relation,[6]

$$F_z(\ell) = \frac{1}{2\pi\beta} \sum_{n=0}^{\infty}{}' \int_0^\infty \mathrm{d}k\, k \ln D_z(k,i\xi_n) \tag{2.34}$$

where $\xi_n = 2n\pi/\beta h$. The prime on the summation means the term for integer $n = 0$ is to have weight ½. Note that the dispersion relation is normalized so that $F_z(\infty) = 0$.

x Anisotropy

The differential equations and their solutions in regions 1 and 3 remain unchanged. In the region $0 < z < \ell$ we have

$$\frac{\mathrm{d}^2 E_x}{\mathrm{d}z^2} - r^2 E_x = 0 \tag{2.35}$$

$$\frac{\mathrm{d}^2 E_y}{\mathrm{d}z^2} - q^2 E_y = \lambda u v E_x \tag{2.36}$$

$$\frac{\mathrm{d}^2 E_z}{\mathrm{d}z^2} - q^2 E_z = -i\lambda u \frac{\mathrm{d}E_x}{\mathrm{d}z} \tag{2.37}$$

where

$$r^2 = u^2(1+\lambda) + v^2 - \omega^2 \epsilon (1+\lambda)/c^2 \tag{2.38}$$

Solving these equations with the constriant (2.5) and using (2.4) to obtain the magnetic fields we obtain

$$E_x = A\, \mathrm{e}^{-rz} + B\, \mathrm{e}^{rz} \tag{2.39}$$

$$E_y = C\, \mathrm{e}^{-qz} + D\, \mathrm{e}^{qz} + \left(\frac{uv}{q^2 - v^2}\right) E_x \tag{2.40}$$

$$E_z = \frac{iv}{q}\left(C\, \mathrm{e}^{-qz} - D\, \mathrm{e}^{qz}\right) - \left(\frac{iu}{q^2 - v^2}\right)\frac{\mathrm{d}E_x}{\mathrm{d}z} \tag{2.41}$$

$$i\omega\,(uB_x + vB_y) = uq\,(C\,\mathrm{e}^{-qz} - D\,\mathrm{e}^{qz}) - \left(\frac{v\omega^2\epsilon/c^2}{q^2 - v^2}\right)\frac{\mathrm{d}E_x}{\mathrm{d}z} \qquad (2.42)$$

Straightforward application of the boundary conditions yields a set of four homogeneous simultaneaous equations for A,B,C,D. Unfortunately these do not simplify as in the previous case. A method for obtaining the correctly normalized dispersion relation is outlined below. Briefly the response of a boundary to an incoming wave is determined and a dispersion relation obtained by identifying the incoming wave as the response of the other boundary.

We associate the coefficients of the exponentially decreasing and increasing solutions as column vectors

$$A = \binom{A}{C} \qquad B = \binom{B}{D} \qquad (2.43)$$

At $z = 0$ the boundary conditions enable us to eliminate the coefficients in region 1 and obtain two equations for A,B,C,D. These may be written in the form

$$A = \mathbf{M}(q_1, \epsilon_1)B \qquad (2.44)$$

where $\mathbf{M}\,(q_1, \epsilon_1)$ is the response matrix associated with the $z = 0$ boundary. Explicitly

$$M_{11} = [\alpha\,(1 + \frac{q_1}{q})\,(\frac{rq_1\epsilon}{q^2\epsilon_1} - 1) - \beta\,(\frac{r}{q} - \frac{q_1}{q})(\frac{\epsilon q_1}{\epsilon_1 q} + 1)]\,/\,\delta \qquad (2.45)$$

$$M_{12} = [\,(1 + \frac{q_1}{q})\,(\frac{\epsilon q_1}{\epsilon_1 q} - 1) - (1 - \frac{q_1}{q})\,(\frac{\epsilon q_1}{\epsilon_1 q} + 1)]/\,\delta \qquad (2.46)$$

$$M_{21} = \alpha\beta\,[\,(\frac{r}{q} - \frac{q_1}{q})\,(\frac{rq_1\epsilon}{q^2\epsilon_1} + 1) - (\frac{r}{q} + \frac{q_1}{q})\,(\frac{rq_1\epsilon}{q^2\epsilon_1} - 1)\,]\,/\,\delta \qquad (2.47)$$

$$M_{22} = [\alpha(1 - \frac{q_1}{q})(\frac{rq_1\epsilon}{q^2\epsilon_1} + 1) - \beta\,(\frac{r}{q} + \frac{q_1}{q})\,(\frac{\epsilon q_1}{\epsilon_1 q} - 1)]/\delta \qquad (2.48)$$

where

$$\delta = \alpha(\frac{rq_1\epsilon}{q^2\epsilon_1} + 1)\,(1 + \frac{q_1}{q}) - \beta\,(\frac{\epsilon q_1}{\epsilon_1 q} + 1)\,(\frac{r}{q} + \frac{q_1}{q}) \qquad (2.49)$$

$$\alpha = (\frac{u}{v})\,\frac{q^2}{q^2 - v^2} \qquad (2.50)$$

$$\beta = (\frac{v}{u})\,\frac{\omega^2\epsilon/c^2}{q^2 - v^2} \qquad (2.51)$$

At the $z = \ell$ boundary we define

$$\mathbf{A}' = \begin{pmatrix} Ae^{-r\ell} \\ Ce^{-q\ell} \end{pmatrix} = \begin{pmatrix} e^{-r\ell} & 0 \\ 0 & e^{-q\ell} \end{pmatrix} \begin{pmatrix} A \\ C \end{pmatrix} \tag{2.52}$$

$$\mathbf{B}' = \begin{pmatrix} Be^{r\ell} \\ Ce^{q\ell} \end{pmatrix} = \begin{pmatrix} e^{r\ell} & 0 \\ 0 & e^{q\ell} \end{pmatrix} \begin{pmatrix} B \\ D \end{pmatrix} \tag{2.53}$$

Using the boundary conditions as before we obtain

$$B' = \mathbf{M}'(q_3, \epsilon_3) A' \tag{2.54}$$

where $\mathbf{M}'(q_3, \epsilon_3)$ is the response matrix associated with the $z = \ell$ boundary. It is easily seen that

$$\mathbf{M}'(q_3, \epsilon_3) = \mathbf{M}(q_1 \rightarrow q_3, \epsilon_1 \rightarrow \epsilon_3) \tag{2.55}$$

either by appealing to the symmetry of the problem or by direct inspection of the simultaneous equations themselves. Thus from (2.54)

$$B = \mathbf{N}(q_3, \epsilon_3, \ell) A \tag{2.56}$$

where

$$\mathbf{N}(q_3 \epsilon_3, \ell) = \begin{pmatrix} e^{-r\ell} & 0 \\ 0 & e^{-q\ell} \end{pmatrix} \mathbf{M}(1 \rightarrow 3) \begin{pmatrix} e^{-r\ell} & 0 \\ 0 & e^{-q\ell} \end{pmatrix} \tag{2.57}$$

Equations (2.44) and (2.57) provide the dispersion relation correctly normalized

$$D_x(u, v, \omega) = |\mathbf{I} - \mathbf{MN}| = 0 \tag{2.58}$$

The van der Waals free energy per unit area is now given by

$$F_x(\ell) = \frac{1}{4\pi^2 \beta} \sum_{n=0}^{\infty}{}' \int_0^{\infty} k\, dk \int_0^{2\pi} d\phi\, \ln D_x(\underset{\sim}{k}, i\xi_n) \tag{2.59}$$

where $\underset{\sim}{k} = (u, v) = k(\cos\phi, \sin\phi)$.
Again $\tilde{F}_x(\infty) = 0$ from (2.57).

THE CRITICAL FIELD STRENGTH H_c

The free energy change per unit volume in the liquid crystal when the magnetic field is turned on is given by

$$F_V^{\mathrm{mag}} = -\frac{1}{8\pi} \underset{\sim}{\mathrm{H}} \cdot \chi \cdot \underset{\sim}{\mathrm{H}} \tag{3.1}$$

where

$$\chi = \chi_\perp \underset{\sim\sim}{\hat{\ell}\hat{\ell}} + \chi_\perp \underset{\sim\sim}{\hat{m}\hat{m}} + \chi_\parallel \underset{\sim\sim}{\hat{n}\hat{n}} \tag{3.2}$$

The free energy per unit area of the slab is then

$$F^{\mathrm{mag}} = \ell F_V^{\mathrm{mag}} = -\frac{1}{8\pi}\ell \underset{\sim}{H} \cdot \chi \cdot \underset{\sim}{H} \tag{3.3}$$

For the two configurations considered

$$F_z^{\mathrm{mag}} = -\frac{1}{8\pi}\chi_{\perp}\ell H^2 \tag{3.4}$$

$$F_x^{\mathrm{mag}} = -\frac{1}{8\pi}\chi_{\parallel}\ell H^2 \tag{3.5}$$

The total free energy per unit area of the slab is then

$$F_{x,z}^{\mathrm{tot}}(\ell,H) = F_{x,z}^{VdW}(\ell) + F_{x,z}^{\mathrm{mag}}(\ell,H) + F_{x,z}^{s} \tag{3.6}$$

where the van der Waals free energies are given by (2.34) and (2.59). The third term on the RHS of Eq. (3.6) is the contribution to the free energy from surface interactions. This is a constant independent of ℓ and H. At a certain value of the field H_c we have

$$F_x^{\mathrm{tot}}(\ell,H_c) = F_z^{\mathrm{tot}}(\ell,H_c) \tag{3.7}$$

Using (3.4) and (3.5) we obtain

$$H_c^2 = \left(\frac{8\pi}{\Delta\chi}\right)\frac{\Delta F(\ell)}{\ell} \tag{3.8}$$

where

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp} \tag{3.9}$$

$$\Delta F = \Delta F^{VdW} + \Delta F^{s} = (F_x^{VdW} - F_z^{VdW}) + (F_x^{s} - F_z^{s}) \tag{3.10}$$

While leaving precise numerical calculation until the next section we may make here some general remarks concerning the theoretical dependence of H_c on ℓ.

If for the moment we neglect the surface energy ΔF^s then in the non retarded region ($\ell < 10^2$ A°) van der Waals free energies for slab geometry have inverse square dependence on the separation ℓ and inverse third power in the retarded region ($\ell > 10^2$ A°). We would therefore expect from (3.8)

$$H_c \propto \ell^{-3/2} \tag{3.11}$$

in the non retarded region and

$$H_c \propto \ell^{-2} \tag{3.12}$$

in the retarded region. However as ℓ becomes large it is evident that the surface energy can dominate. In the regime then we would expect

$$H_c \propto \ell^{-1/2} \tag{3.13}$$

Our theory therefore indicates that Fredericks' empirical first power Law ($H_c \propto \ell^{-1}$) is only valid over a limited thickness regime. We shall illustrate more graphically this changing power Law dependence in a later section.

NUMERICAL RESULTS

The calculation of van der Waals free energies from equations (2.34) and (2.59) requires a knowledge of $\epsilon\ (i\xi)$, the dielectric constant evaluated on the imaginary frequency axis, for each substance. A representation of $\epsilon\ (i\xi)$ can be constructed from experimental data in the form[9]

$$\epsilon(i\xi) = 1 + \sum_m \frac{B_m}{1 + \xi/\omega_m} + \sum_e \frac{C_e}{1 + (\xi/\omega_e)^2} \tag{4.1}$$

where the ω_m are the microwave relaxation frequencies of the substance and the ω_e are the IR and UV absorption frequencies. The B_m and C_e are the changes in the real part of the dielectric constant across the absorption frequencies ω_m and ω_e. The absorption peaks are assumed to have negligible width. For $\xi >> $ UV frequencies the dielectric constant is given by

$$\epsilon(i\xi) \angle 1 + \omega_p^2/\xi^2 \tag{4.2}$$

An interpolation procedure is used to match the representations (4.1) and (4.2) and has been discussed by Richmond and Ninham.[10]

In our numerical calculations we use the avialable dielectric data for *p*-azoxyanisole at 125°C,[11,12,13] shown in Table 1. To test the sensitivity of the results to the dielectric constant of the half spaces, two crude models of the dielectric properties of glasses were used as shown in Table 2. We also examined the case when one of the dielectric half spaces is replaced by a metal for which we assume Eq. (2.4) is valid over all frequencies.

TABLE 1

Dielectric Data for *p*-azoxyanisole[11–13] at 125°C

$\epsilon_\parallel$ Relaxation frequency (rad/sec)	$B_m \cdot C_e$	$\epsilon_\perp$ Relaxation frequency (rad/sec)	$B_m \cdot C_e$
3.78×10^8	$B_1 = 0.93$	5.65×10^{10}	$B_1 = 3.08$
5.65×10^{10}	$B_2 = 1.23$	1.88×10^{14}	$C_1 = 0.38$
1.88×10^{14}	$C_1 = 0.16$	6.28×10^{15}	$C_2 = 1.40$
6.28×10^{15}	$C_2 = 2.31$		
$\omega_p = 3.42 \times 10^6$ rad/sec		$\omega_p = 3.42 \times 10^6$ rad/sec	

TABLE II

Dielectric Data for Model Glasses

Glass A		Glass B	
Relaxation frequency (rad/sec)	C_e	Relaxation frequency (rad/sec)	C_e
1.0×10^{14}	$C_1 = 1.56$	1.0×10^{14}	$C_1 = 3.28$
1.0×10^{16}	$C_2 = 1.25$	1.0×10^{16}	$C_2 = 1.72$

The difference in free energies in the two configurations, ΔF^{VdW}, is calculated numerically from Eq. (2.34) and (2.59) as a function of slab thickness ℓ for the cases (i) glass A in both half spaces, (ii) glass B in both half spaces, (iii) glass A in region 1 and metal ($\omega_p = 2 \times 10^6$ rad/sec) in region 3. Neglecting ΔF^S, the critical field strength H_c is calculated for each ℓ from Eq. (3.8) using the magnetic susceptibilities of *p*-azoxyanisole quoted by Tsvetkov[1,2] i.e.

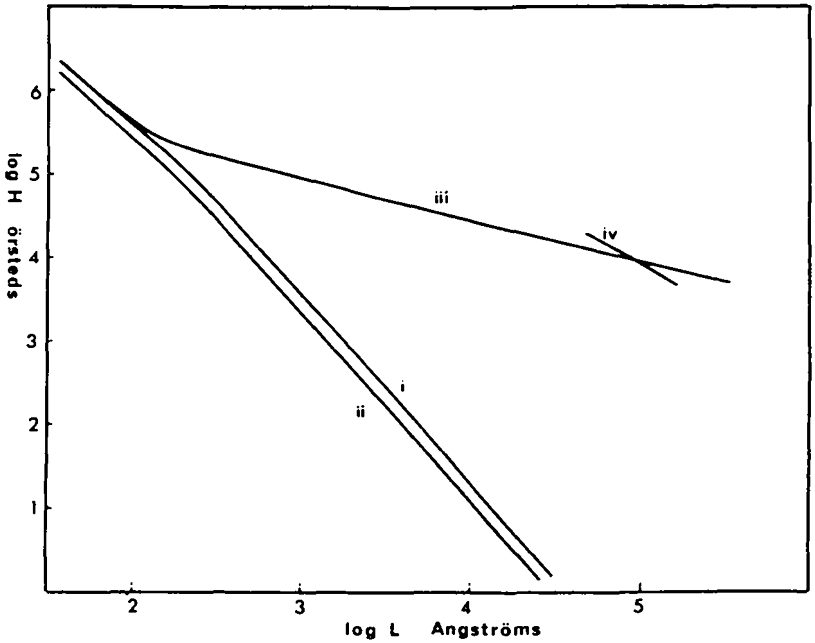

FIGURE 2 The dependence of critical fiel strength H_c (oersteds) on slab thickness ℓ (angströms) for the cases (i) glass A in regions 1 and 3 neglecting surface contribution, (ii) glass B in regions 1 and 3 neglecting surface contributions, (iii) glass A in regions 1 and 3 plus a fitted surface energy term, (iv) experiment results of Frederiks *et al.*

$\chi_{\parallel} = -4.7 \times 10^{-7}$, $\chi_{\perp} = -5.8 \times 10^{-7}$ at 125°C. H_c is plotted as a function of ℓ in Figure 2 for the cases (i) and (ii) above. The graph (iv) corresponds to the data of Fredericks.

We suppose now that the discrepancy is due to our neglect of the surface energy term. By using the complete expression and fitting to this data we deduce that $\Delta F^S \sim 10^{-4}$erg/cm^2. Experimental measurements of surface energies are not available and present theoretical methods[15-17] for calculation of surface energies will not yield the desired accuracy. However, we believe that 10^{-4}erg/cm is quite within the realm of possibilities.

In Figure 3 we plot the power law dependence as a function of ℓ assuming that $\Delta F^S = 3.46 \times 10^{-4}$ erg/cm^2. In the Frederiks' region our results indicate a power law of −0.5.

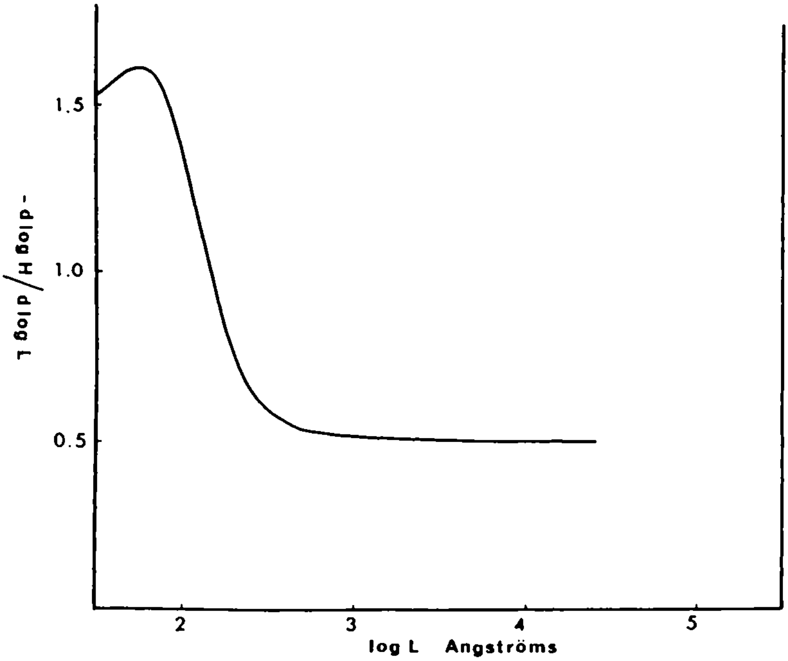

FIGURE 3 The slope−d log$H$/d logℓ showing the power law dependence of H on ℓ over a wide thickness regime.

DISCUSSION

From the result of Sec. 4 we see that a reasonable theoretical interpretation can be made of Fredriks' experiment in terms of molecular forces. The major discrepancy being the precise power law dependence of H_c ν ℓ. Now it is known that macroscopic van der Waals forces across curved surfaces differ in their distance dependence from those across parallel plates and this may modify the power law relation. But for watch glasses with a sufficiently large radius of curvature it is likely that these deviations are small. A complete theoretical analysis of Frederiks' experiment should also include stress effects which may be present in the region where the configuration of the liquid crystal changes. This region would introduce uncertainties in the measurement of ℓ by the Newton ring method.

Recently a number of new sophisticated techniques have been used to measure van der Waals forces.[18,19] Theoretical calculations[10] agree well with this data. We suggest that similar modern experimental methods may well be profitably applied to these liquid crystal systems. In particular it should be possible to do measurements for a planar system (thus minimizing stress regions) in the small ℓ region ($50\text{Å} \lesssim \ell \lesssim 1000\text{Å}$) where van der Waals energies of interaction may dominate surface energies.

The general conclusion of Fredericks that the result is independent of the type of glass used is to some extent verified by our work. Certainly when the surface energy can be neglected we see from Figure 2 that for the two glasses studied here, the curves agree to within 5%. We anticipate the surface energy is also insensitive to the nature of the glass. However, Chistyakov reports that Frederiks also performed the experiment with a thin metal film coated on the glass surfaces and observed no significant change. We have performed calculations again neglecting surface energy terms for the case where one glass half space is replaced by a metal and the results show that in this case the liquid crystal prefers the $\underset{\sim}{\hat{n}}\perp\underset{\sim}{\hat{z}}$ configuration. Therefore no critical field exists. Thus we expect this for experiments done in the small ℓ regime with metallic coated glass plates, the critical field H_c would decrease as the coating thickness increases. Beyond a critical coating thickness, no critical field H_c would exist. To our knowledge, this type of experiment has not yet been performed. Finally we note that theories based on internal elastic strains have been used to explain this phenomenon.[20] It may be that both explanations are appropriate according to the type of material used in the system.

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