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Liquid crystal anchoring transitions induced by thermal motion

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The thermal motion of a substrate is shown to have strong effects on the orientation of liquid crystal molecules in contact with it. Using an inverted-pendulum model, we find that the orientation of the liquid crystal molecules can have a sequence of transitions between planar and homeotropic orientations. Analytical expressions for stability conditions for the homeotropic orientations are found for both monochromatic and some multiple-mode thermal motions, and in both homeotropic and planar anchoring cases. Numerical simulations confirm the analytical model calculations and show that strong interactions between molecules favour processes of dynamic stabilization and destabilization of the homeotropic orientation.

1. Introduction

The orientation, or anchoring, of liquid crystal molecules on a solid substrate is determined by a number of factors, including the type of liquid crystal and substrate in question, the surface condition, and the temperature [1, 2]. Consequently, transitions in anchoring direction are expected as those factors are varied. Anchoring transitions attributed to several origins have been reported in experiments [3–11]: changes in interfacial surfactants, substrate structure and temperature all appear capable of inducing anchoring transitions [1, 2]. In systems of liquid crystals on substrates coated with amphiphilic compounds, anchoring transitions from tilted to homeotropic (i.e., vertical) alignments have been reported when the temperature is increased [7–9]. A sequence of transitions from a tilted to a homeotropic then back to the tilted alignment have been observed in systems of MBBA on glass substrates coated with emissions from charred paper, and of cyanobiphenyl materials on substrates coated with fluorocarbon polymer [5, 6].

There have been several theoretical papers [12–15] discussing the surface free energy and anchoring energy. However, there appears to be little discussion in the literature of the microscopic mechanism of the temperature-driven anchoring transition which is the topic of this paper. We will consider the effects of thermal motion of the substrate on anchoring changes of liquid crystal molecules. By using an inverted-pendulum model with a vibrating point of support, we will show that in either planar or homeotropic alignment the thermal motion can stabilize or destabilize the homeotropic alignment and be a driving force for anchoring transitions [16].

2. The model

We consider a uniform rigid rod of length l and mass m attached to a pivot point which vibrates vertically (i.e. perpendicular to the surface) as shown in figure 1. A potential $\omega(\theta)$, which can favour either a horizontal or vertical orientation, acts on the

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rod. This inverted-pendulum model is employed as a simple model for a rod-shaped nematic liquid crystal molecule in interaction with a substrate. The classical Lagrangian \mathcal{L} for the displacement θ of the molecule from the z direction is given by

$$\mathcal{L} = \frac{1}{6}ml^2 \left(\frac{d\theta}{dt}\right)^2 + \frac{1}{2}m \left(\frac{dz}{dt}\right)^2 - \frac{1}{2}ml \sin \theta \left(\frac{d\theta}{dt}\right) \left(\frac{dz}{dt}\right) - \omega(\theta). \quad (1)$$

Here $z(t)$ is the vertical position of the vibrating substrate and the potential $\omega(\theta)$ determines the preferred alignment of the liquid crystal molecule in the absence of dynamic effects. We write this molecular anchoring energy function $\omega(\theta)$, which includes the effects of all static interactions between a single molecule and a substrate surface, as

$$\omega(\theta) = \frac{1}{2}\omega_0 \sin^2(\gamma\theta), \quad (2)$$

where ω_0 is the molecular anchoring energy (positive for homeotropic and negative for planar anchoring), and $\gamma = (1 - 2\phi_0/\pi)^{-1}$, with ϕ_0 being the small angle between the in-plane and easy directions when $\omega_0 < 0$. Forms similar to expression (2) have been derived for dispersion and polar interactions between liquid crystal and substrate molecules based on van der Waals forces. Expression (2) is also similar in form to the Rapini–Papoular expression [17] for anchoring energy.

The equation of motion derived from the lagrangian (1) is then

$$\frac{d^2\theta}{dt^2} = -\frac{3}{ml^2} \frac{d\omega(\theta)}{d\theta} + \frac{3}{2l} \left(\frac{d^2z}{dt^2}\right) \sin \theta. \quad (3)$$

The two terms on the right-hand side of this equation have different origins. The torque $d\omega(\theta)/d\theta$ caused by the anchoring energy favours a planar or homeotropic alignment depending on the sign of ω_0 , while the surface vibration, d^2z/dt^2 , gives rise to an effective force of dynamic origin, and can stabilize or destabilize the homeotropic alignment depending on the magnitude of the vibration.

If the substrate vibration z is taken to be a simple harmonic oscillator, we can write

$$z(t) = a \cos(\Omega t + \eta), \quad (4)$$

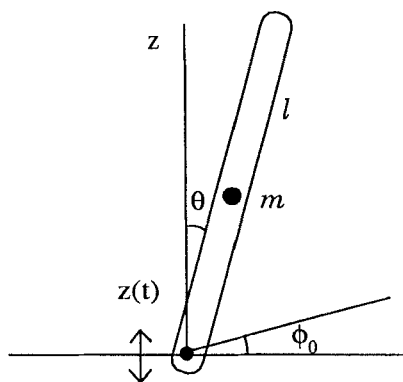


Figure 1. An inverted-pendulum model for a nematic liquid crystal molecule on a substrate.

with Ω a typical phonon frequency and η an arbitrary phase. Then the general equation of motion (3) is written as

$$\frac{d^2\theta}{dt^2} = -\frac{3}{ml^2} \frac{d\omega(\theta)}{d\theta} - \frac{3}{2}\Omega^2 \left(\frac{a}{l}\right) \cos(\Omega t + \eta) \sin \theta. \tag{5}$$

3. Homeotropic anchoring energy

For a homeotropic anchoring energy, the γ factor in equation (2) is unity and

$$\omega(\theta) = \frac{1}{2}\omega_0 \sin^2 \theta \tag{6}$$

with $\omega_0 > 0$, reflecting the fact that the minimum energy occurs when the liquid crystal molecule is oriented vertically. The corresponding equation of motion is

$$\frac{d^2\theta}{dt^2} + \frac{3\omega_0}{2ml^2} \sin 2\theta - \frac{3}{2}\left(\frac{a}{l}\right)\Omega^2 \cos \Omega t \sin \theta = 0, \tag{7}$$

where η in equation (4) has been taken to be π . Making a small-angle approximation for θ gives

$$\frac{d^2\theta}{dt^2} + \left[\frac{3\omega_0}{ml^2} - \frac{3}{2}\left(\frac{a}{l}\right)\Omega^2 \cos \Omega t \right] \theta = 0. \tag{8}$$

This is a Mathieu equation [18] and is homologous to the Schrödinger equation for an electron moving in a cosinusoidal potential in one dimension. Its solutions are Mathieu functions, and can be written in the general form

$$\theta(t) = Au(\xi, t) \exp(i\xi t) + Bu(\xi, -t) \exp(-i\xi t), \tag{9}$$

where $u(\xi, t)$ is a periodic function of time with period $2\pi/\Omega$ and A and B are constants. Only when ξ is real can the solution for $\theta(t)$ remain small, corresponding to a homeotropic alignment of the molecule. Real ξ values exist over certain ranges of ω_0 , Ω and a . Figure 2 shows the form of ξ as a function of the amplitude a of vibration for fixed ω_0 and Ω , and shows the existence of a range of a over which no real ξ exists.

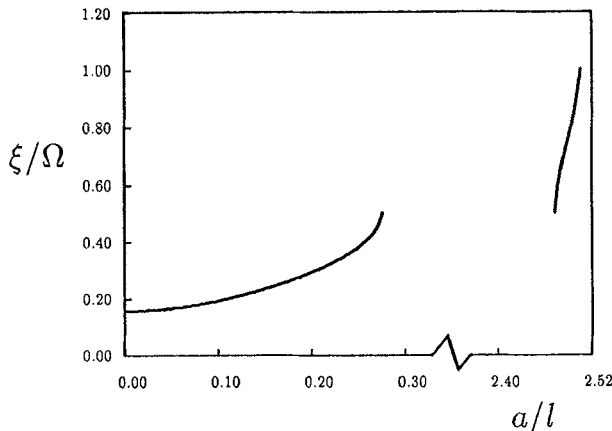


Figure 2. A typical band structure of the frequency ξ in a homeotropic-anchoring system. For the example shown, $3\omega_0/(ml^2\Omega^2) = 0.025$. The system is in a homeotropic alignment when $(a/l) = 0$.

When the amplitude a and frequency Ω of the oscillation in equation (4), are small, one expects that the motion of the molecule will be stable around $\theta=0$, and the observed director will remain homeotropic. However, as a becomes larger, the vibration starts to destabilize the homeotropic orientation. The threshold values of ω_0 , Ω and a where ξ becomes complex mark the transition to a planar alignment, homeotropic alignment becoming unstable, and can be approximately related by the equation

$$\frac{12\omega_0}{ml^2\Omega^2} = 1 - 3\left(\frac{a}{l}\right), \quad (10)$$

for the frequency range $\Omega^2 \geq (12\omega_0/ml^2)$, which is the typical frequency range of the maximum phonon-mode frequency. Figure 3 shows two numerically-calculated stability regions (phase diagram) for homeotropic and planar alignments in (ω_0, a) space. Since a typical physical system corresponds to the area around the origin in the phase diagram, the region marked *I* is the prime homeotropic region. The negative- ω_0 portion of the diagram corresponds to planar anchoring, and will be discussed in the following section. An anchoring transition from a homeotropic to a planar alignment occurs as the amplitude a exceeds the threshold value determined by equation (10). If we consider our model to represent a liquid crystal molecule vibrating in a monochromatic mode that contains thermal energy $k_B T$, which is of the order of $ma^2\Omega^2$, the condition for destabilization of the homeotropic phase becomes

$$3\sqrt{\left(\frac{k_B T}{ml^2\Omega^2}\right) + \frac{12\omega_0}{ml^2\Omega^2}} \geq 1.$$

After the transition, the system will stay in the planar phase for a certain range of a , depending on the values of ω_0 and Ω . As a is further increased, the system will in principle enter the second homeotropic region marked *II* in figure 3; this however, is not physically realizable since as we shall see, the typical value of $\omega_0/(ml^2\Omega^2)$ is around

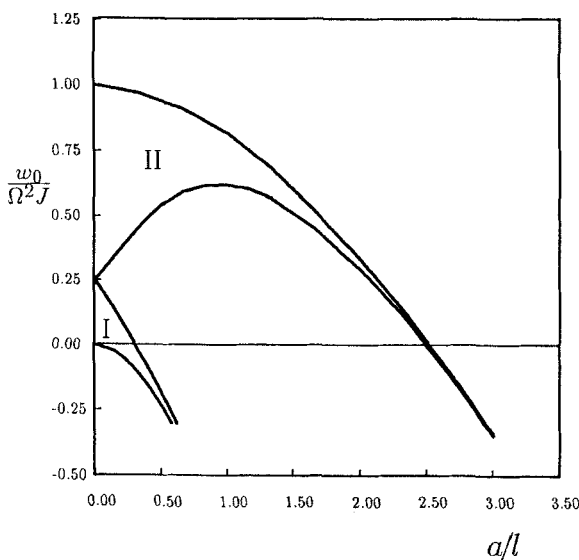


Figure 3. Phase diagram of homeotropic (regions *I* and *II*) and planar alignments. Here $J = \frac{1}{3}ml^2$.

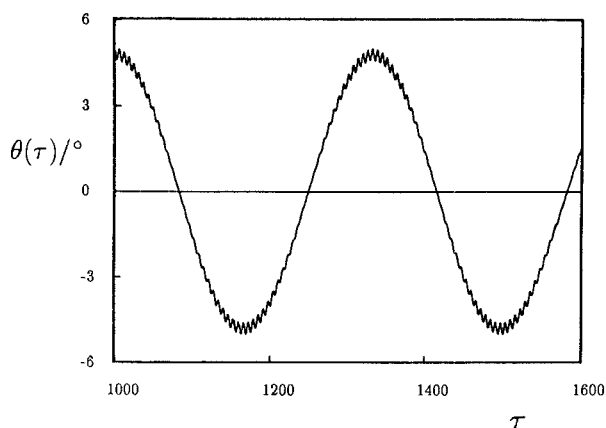


Figure 4. Stable motion of a liquid crystal molecule in the homeotropic alignment, as obtained from numerical calculations. Here $\tau = \Omega t$.

10^{-2} . Figure 3 accordingly shows that the amplitude a would have to be several times the molecular length for this condition to be satisfied.

It is worthwhile noting that the discussion in this section has focused on the stability of the homeotropic alignment ($\theta \approx 0$) for initially homeotropic anchoring. The condition (equation (10)) for the anchoring transition from homeotropic to planar alignment is the condition under which the homeotropic anchoring loses its stability. That is, the solutions described in equation (9) cease to be oscillatory and become exponentially increasing with time. This takes θ out of the small-angle regime of the linearized equation and sends the molecule into the region of near-planar alignment. The reverse transition occurs when θ can again take on small, oscillating values.

Within a homeotropic region, the form of $\theta(t)$ is like that shown in figure 4. The molecule's orientation displays a rapid component, having angular frequency Ω , superimposed on a slower oscillation of angular frequency ξ .

4. Planar anchoring energy

When the anchoring energy favours a planar orientation, $\omega(\theta)$, still written as a function of θ measured from the z axis, has the form

$$\omega(\theta) = \frac{1}{2} \omega_0 \sin^2(\gamma\theta), \quad (11)$$

with ω_0 negative, and where $\gamma > 1$ represents a near-planar tilted anchoring and $\gamma = 1$ corresponds to a planar anchoring. We will use the term 'planar' to refer to both the planar and the tilted anchorings. As in the case of homeotropic anchoring, imposition of a vertical harmonic oscillation of the substrate, given by equation (4) with $\eta = 0$ and with the anchoring energy as in equation (11), leads to the equation of motion

$$\frac{d^2\theta}{dt^2} + \frac{3\gamma\omega_0}{2ml^2} \sin(2\gamma\theta) - \frac{3}{2} \left(\frac{a}{l}\right) \Omega^2 \cos \Omega t \sin \theta = 0. \quad (12)$$

Now although the planar orientation corresponds to $\theta \sim \pi/2$, we are seeking the possibility that the thermal motion of the substrate destabilizes this orientation, and

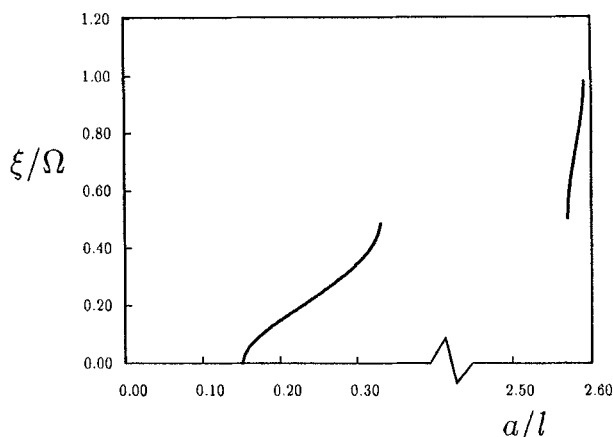


Figure 5. A typical band structure of the frequency ξ in a planar-anchoring system. The parameter $3\omega_0/(ml^2\Omega^2) = -0.025$. In this case the system is not in a homeotropic alignment when $(a/l) = 0$.

causes a transition to the homeotropic alignment. We accordingly look for solutions of equation (12) corresponding to small θ . The linearized form of equation (12) is then

$$\frac{d^2\theta}{dt^2} + \left[\frac{3\gamma^2\omega_0}{ml^2} - \frac{3}{2} \left(\frac{a}{l} \right) \Omega^2 \cos \Omega t \right] \theta = 0. \quad (13)$$

This again is a Mathieu equation, but now with a negative constant coefficient. General solutions to equation (13) are still described by equation (9) and real values of the frequency ξ are found for certain ranges of a as shown in figure 5. The lower half-space of the phase diagram in figure 3 represents this situation for the case when $\gamma = 1$. In contrast to the homeotropic anchoring case, a small vibration amplitude a now allows the liquid crystal molecule to be in a planar orientation. Only as a exceeds a threshold value, which depends on ω_0 and Ω , can the liquid crystal molecule be stabilized in the homeotropic orientation. If the amplitude a is small compared to the molecular length l , an analytical approximation can be found for the condition that the molecule be stabilized in the homeotropic orientation. We have

$$-\gamma^2\omega_0 = \frac{3}{4} \left(\frac{1}{2} ma^2\Omega^2 \right). \quad (14)$$

These threshold values of a and Ω indicate that thermal energies need to be comparable to the anchoring potential for the liquid crystal molecule to be in the homeotropic orientation. As the amplitude a is further increased, the system will remain in the homeotropic alignment until a exceeds another threshold value, a point on the right-hand boundary of region I in figure 3. Then we expect a second anchoring transition at which the system reverts to a planar alignment. As this anchoring transition occurs at a large vibration amplitude, a simple analytic expression for threshold values of a and Ω cannot be obtained, and numerical calculations must be made to determine them. Equation (10), however, continues to give results that are correct to within a few percent for realistic values of ω_0 .

Planar-homeotropic-planar transition sequences have been experimentally observed, and were reported in [5] and [6]. In some other experiments [7-9], only the transitions of planar to homeotropic anchoring were observed as the temperature was

increased, probably due to the fact that the clearing temperature was reached before the system moved into the re-entrant planar phase.

The preceding analysis has shown that there are conditions under which a homeotropic orientation can become dynamically stabilized in a system in which the anchoring potential alone favours a planar alignment. However, we have not yet discussed any mechanism by means of which the planar to homeotropic transition can be activated. Our assumption is that thermal fluctuations will be sufficient to induce temporary regions of near-homeotropic orientation, and that this region will nucleate the transition in the system as a whole. This supposition has been confirmed by numerical simulations of a more complex multilayer model.

5. Effects of phonon dispersion

The model equations (8) and (13) were obtained by assuming that the pivot displacement $z(t)$ was a simple sinusoid, and is equivalent to adopting an Einstein model for the lattice vibrations. In reality the solid substrate will exhibit a spectrum of phonon frequencies. In this section, we consider the effects of phonon dispersion on anchoring transitions and on the stability of the homeotropic phase, and compare the results with the results for the monochromatic model.

For a liquid crystal molecule oscillating with the bulk phonon spectrum of the substrate, $z(t)$ can be written as

$$z(t) = N^{-1/2} \sum_{q,s} z_{q,s} \exp [i(\Omega_{q,s}t + \eta_{q,s})], \quad (15)$$

where N is the number of substrate atoms, $z_{q,s}$ the real amplitude of the mode of wave number q and polarization s , and $\eta_{q,s}$ a random phase. To simplify the mathematical treatment, we consider a model with only one atom of mass M per unit cell, and for which the phonon spectrum is one-dimensional. We also assume temperatures well above the Debye temperature. We then write the pivot acceleration in the form

$$\frac{d^2z}{dt^2} = - \sum_q a_q \Omega_q^2 \cos(\Omega_q t + \eta_q), \quad (16)$$

where $a_q = (2k_B T / MN \Omega_q^2)^{1/2}$, and is an appropriately averaged thermal vibration amplitude for mode q . The equation of motion can be obtained from equation (3) with d^2z/dt^2 as given in equation (16).

The qualitative nature of the solutions to this problem can be found by returning to our analogy with the Schrödinger equation for an electron in one dimension. It is known that in most circumstances the eigenfunctions of the Schrödinger equation are localized for a disordered potential in one dimension [19]. This at first sight would seem to imply that the stabilized vertical states of the liquid crystal molecule will not exist when a stochastic sum of normal modes provides the driving force of the pivot point. In physical terms, the phases of the various modes will occasionally tend to cancel, and then the molecule falls down.

This analogy, however, is somewhat oversimplified, as there is a constraint on d^2z/dt^2 that cannot be ignored. In the case of a random alloy, the electron states of the lowest energy are localized in regions where there is a large statistical fluctuation in the concentration of the component with the strongest attractive potential. There is no theoretical limit on the number of consecutive atoms of this one species that can occur sequentially. In the inverted pendulum problem, on the other hand, the integral of

d^2z/dt^2 over a time interval represents the velocity change of the pivot point, and the integral of this represents its displacement, which is limited by anharmonic forces.

These considerations suggest that perturbation-theoretic approaches to finding the form of $\theta(t)$ may be unreliable, and numerical simulation should instead be employed. For small vibration amplitudes, however, we can still derive analytic expressions similar to equations (10) and (14) for threshold values of the liquid crystal system's first anchoring transition. Let us first consider the case of planar anchoring energy. Equations (3), (11) and (16) give the equation of motion

$$\frac{d^2\theta}{dt^2} + \left[\frac{3\omega_0\gamma}{ml^2} - \frac{3}{2} \sum_n \frac{a_n}{l} \Omega_n^2 \cos \Omega_n t \right] \theta = 0. \quad (17)$$

We now assume a frequency of the Debye form, so that $\Omega_n = n\Omega$ with n integral, and rewrite equation (17) as

$$\frac{d^2\theta}{d\tau^2} + \left[p - 2g \sum_n A_n \cos(2n\tau) \right] \theta = 0, \quad (18)$$

where $\tau = \frac{1}{2}\Omega t$, $p = 12\omega_0\gamma^2 ml^2 \Omega$, and $g = 3(\bar{a}/l)$ with \bar{a} being the average amplitude, and $A_n = (a_n/\bar{a})n^2$. When the average amplitude is small compared to the molecular length, then $g \ll 1$, and we have

$$\theta = C_0 + gC_1(\tau) + g^2C_2(\tau) + g^3C_3(\tau) + \dots; \quad (19)$$

$$p = \alpha_1 g + \alpha_2 g^2 + \alpha_3 g^3 + \dots. \quad (20)$$

Substituting equations (19) and (20) into equation (18) gives an equation in powers of g of the form

$$\begin{aligned} g \left[C_1'' + \alpha_1 C_0 - 2 \sum_n C_0 A_n \cos(2n\tau) \right] + g^2 \left[C_2'' + \alpha_2 C_0 + \alpha_1 C_1 - 2C_1 \sum_n A_n \cos(2n\tau) \right] \\ + g^3 \left[C_3'' + \alpha_3 C_0 + \alpha_2 C_1 + \alpha_1 C_2 - 2C_2 \sum_n A_n \cos(2n\tau) \right] + \dots = 0, \end{aligned} \quad (21)$$

from which each power of g gives an independent equation. The g^1 equation yields

$$\alpha_1 = 0, \quad (22)$$

$$C_1 = -2 \sum_n \frac{C_0 A_n}{(2n)^2} \cos(2n\tau). \quad (23)$$

Using this α_1 and C_1 in the g^2 equation

$$C_2'' + \alpha_2 C_0 + \alpha_1 C_1 - 2C_1 \sum_n A_n \cos(2n\tau) = 0 \quad (24)$$

we find

$$\begin{aligned} C_2'' + \alpha_2 C_0 + 2 \sum_n \frac{C_0 A_n^2}{(2n)^2} [1 + \cos(4n\tau)] \\ + 2 \sum_{n \neq n'} \frac{C_0 A_n A_{n'}}{(2n)^2} \{ \cos[2(n-n')\tau] + \cos[2(n+n')\tau] \} = 0, \end{aligned} \quad (25)$$

from which

$$\alpha_2 = -2 \sum_n \frac{A_n^2}{(2n)^2}. \quad (26)$$

The critical condition for a molecule initially in a planar orientation (i.e. with $\omega_0 < 0$) to make a transition to the homeotropic orientation is now

$$p = \alpha_2 g^2, \quad (27 a)$$

when terms only of order g^2 are retained. That is,

$$\gamma^2 \omega_0 = -\frac{3}{4} \sum_n \frac{1}{2} m a_n^2 \Omega_n^2. \quad (27 b)$$

This is similar to the critical condition (14) for the single-frequency model. It shows that the total energy of a substrate atom should be at least of the order of the planar anchoring energy in order to stabilize the molecule in the homeotropic orientation.

Numerical calculations, in which equation (17) was solved directly by the standard Runge–Kutta method, have confirmed expression (27). Our calculations also indicate that the commensuration of frequencies is not necessary as long as the vibration amplitudes are small and the frequencies high.

For the homeotropic anchoring energy (i.e. $\omega_0 > 0$), the effects of phonon dispersion on the dynamics of the molecule are much greater. In fact, the transition from homeotropic to planar alignment predicted by equation (10) is in general eliminated. The reason for this lies in the nature of the motion of the molecule in the single-frequency model. At the critical amplitude for instability, the orientation of the molecule is oscillating with a dominant frequency component equal to half the driving frequency of the substrate. That is to say, the instability occurs as the result of a resonance phenomenon. The presence of phonon dispersion reduces the Q -factor of this resonance to the point where the instability no longer occurs. In the analogy with the Schrödinger equation for a disordered solid, one could say that the forbidden band of energies between valence and conduction bands is now filled with impurity states.

The homeotropic to planar transition may thus be eliminated by phonon dispersion. The planar to homeotropic transition, on the other hand, is retained, and the similarity in the form of the critical condition for this anchoring transition in the multi-frequency and the single-frequency cases suggests that the single-frequency model may be an adequate approximation if an appropriate frequency is chosen.

6. Collective effects

In the preceding sections we have studied the dynamic effects of thermal motion on the orientation of an isolated molecule. The most important characteristic, however, of a liquid crystal is the influence of intermolecular interactions on the orientation of individual molecules. We accordingly now enlarge our study to include the collective motion of an assembly of liquid crystal molecules.

We consider a line of liquid crystal molecules on a substrate. Each molecule has a vibrating pivot and each interacts with its nearest neighbours through an interaction potential $p(\theta_i, \theta_j)$ which is taken to be of the simple form

$$p(\theta_i, \theta_j) = K'(\theta_i - \theta_j)^2, \quad (28)$$

with θ_i and θ_j the orientation of two neighbouring molecules and K' a constant. The motion is thus assumed confined to a plane, and motion out of the plane is ignored. This

reflects the characteristic property of nematic liquid crystal molecules of tending to align parallel to each other's long axis. The torque Γ_i on a molecule is then a sum of the form

$$\Gamma_i = -\sum_j K'(\theta_i - \theta_j), \quad (29)$$

with j summed over nearest neighbours of i .

The small-angle approximation to a more accurate expression proportional to $\sin 2(\theta_1 - \theta_j)$ will be valid at temperatures well below the clearing point. Because the multi-frequency analysis of the planar to homeotropic anchoring transition conditions gave qualitatively the same results as that of the single-frequency model, we will use the single-frequency model here, but assume that the phase η_i of vibration for each molecule is random. In reality there will be correlations between the phases of the motion of neighbouring atoms, but we ignore this correlation in order to err on the side of underestimating the magnitude of the effect of the substrate motion.

The equation of motion is now a set of coupled differential equations. In the case of planar anchoring energy, the equations of motion have the form

$$\left. \begin{aligned} \frac{d^2\theta_1}{dt^2} &= \left[\frac{3\omega_0\gamma^2}{ml^2} - \frac{3}{2} \left(\frac{a_1}{l} \right) \Omega^2 \cos(\Omega t + \eta_1) \right] \theta_1 - K(\theta_1 - \theta_2), \\ \frac{d^2\theta_i}{dt^2} &= \left[\frac{3\omega_0\gamma^2}{ml^2} - \frac{3}{2} \left(\frac{a_i}{l} \right) \Omega^2 \cos(\Omega t + \eta_i) \right] \theta_i + K(\theta_{i-1} - \theta_i) - K(\theta_i - \theta_{i+1}), \\ \frac{d^2\theta_N}{dt^2} &= \left[\frac{3\omega_0\gamma^2}{ml^2} - \frac{3}{2} \left(\frac{a_N}{l} \right) \Omega^2 \cos(\Omega t + \eta_N) \right] \theta_N + K(\theta_{N-1} - \theta_N), \end{aligned} \right\} \quad (30)$$

$i = 2, 3, \dots, N-1,$

where the interaction constant $K = 3\gamma^2 K'/ml^2$, and the η_i are random phases. The motions of an array of 50 interacting molecules, the equations of motion of which are given by equation (30), were computed numerically. The initial configurations for the equations were always a homeotropic alignment for each amplitude \bar{a} used. The calculations thus tested the ability of the substrate thermal motion to maintain a homeotropic alignment rather than their ability to induce it in an initially planar system. We rely on the results of simulations of larger, multilayer systems to assure us that the assembly will eventually make a transition from any starting orientation to the homeotropic orientation when that orientation is dynamically stabilized.

The anchoring-transition pattern for the planar-anchoring system shown in figure 6 is the same as that predicted in the independent-molecule model. The director direction $\langle \bar{\theta} \rangle$ in figure 6 is defined as the time and ensemble average of molecular axial angles θ_i . As the average amplitude \bar{a} (proportional to $T^{1/2}$) is increased, the first anchoring transition from a planar to a homeotropic alignment occurs, and the system stays in the homeotropic alignment as the amplitude is further increased until at very high temperatures it goes beyond the homeotropic region boundary, at which the system enters a planar phase.

Although the strength of the intermolecular interaction does not change the pattern of anchoring transitions, it affects the temperature ranges of planar and homeotropic alignments. As shown in figure 6, the range of homeotropic alignment decreases as the interaction constant K increases.

As mentioned in the paragraph preceding equation (30), the assumption was made that the phase η_i of the vibrations of each anchoring site were uncorrelated. In reality,

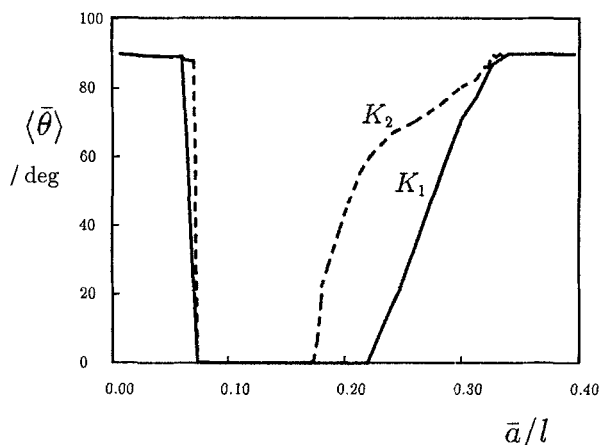


Figure 6. Numerical simulation gives these results for anchoring transitions in a line of 50 interacting molecules. The larger interaction constant K_2 leads to a smaller range of homeotropic-anchoring stability than the case for the smaller value K_1 .

there will be some coherence in the motions of neighbouring substrate sites. In order to test the importance of this effect, some sample calculations were performed in which equation (30) was solved with all phases equal by setting $\eta_i = 0$ for all i . The transition behaviour shown in figure 6 was not significantly altered, although the amplitudes \bar{a} for both planar to homeotropic and homeotropic to planar transitions were decreased slightly.

7. Discussion

The formal analysis of the effect of substrate vibration on the preferred orientation of a surface layer of liquid crystal molecules has led to a number of conclusions:

- (i) As the temperature, and hence the amplitude of monochromatic vibration of the substrate is increased beyond a certain critical value, a single planar-anchored molecule makes a transition to the homeotropic orientation.
- (ii) As the temperature is further increased to a considerably higher value, the system re-enters the planar phase. At a comparable temperature a homeotropically anchored system can make a transition to a planar orientation.
- (iii) Inclusion of the effects of phonon dispersion does not significantly alter the prediction for the transition from planar to homeotropic. These effects may, however, weaken or eliminate the transition from homeotropic to planar.
- (iv) Collective effects, of the type that give rise to nematic or smectic phases, do not appreciably alter the predicted transition temperatures.

It now only remains to offer some semi-quantitative estimates of the temperatures at which these transitions are predicted to occur. As an example we consider the liquid crystal MBBA [20] of which the molecular mass, m , is around 4×10^{-25} kg and the molecular length is about 1 nm. The macroscopic surface anchoring is about $-10^{-4} \text{ J m}^{-2}$, so that for a surface number density of 10^{17} – 10^{18} m^{-2} the anchoring energy per molecule is $\omega_0 \approx -10^{-21} \text{ J}$ or -10^{-22} J . For a typical substrate phonon angular frequency Ω of around 10^{12} s^{-1} the thermal vibration amplitude a is of the

order of 0.1 nm. As a result the dimensionless combination $\omega_0/ml^2\Omega^2$ lies between -10^{-2} and -10^{-3} , while (a/l) is about 10^{-1} . On the basis of the analysis given in this paper, we would conclude that the only transition likely to be physically realizable in this material is the initial transition from planar to homeotropic, which is predicted to occur at a temperature of a few hundred Kelvin. Succeeding transitions caused by substrate vibration would not be easily realizable, as the predicted transition temperatures lie above the clearing point. The observed second transition reported in MBBA [5] would thus seem likely to have a different origin.

In our model we have assumed that the anchoring strength (strength of attachment) of molecules ω_0 does not change with temperature. This may appear to be in conflict with many experimental measurements [8, 21, 22] that have shown the anchoring strength ω_0 to be temperature-decreasing. We suggest that the effect of substrate thermal vibrations may just be a microscopic contribution to the apparent temperature dependence of ω_0 ; the destruction of stability is equivalent to the weakening of anchoring strength. However, we do recognize that substrate thermal vibrations are not the only contributor to the temperature dependence of the anchoring strength, given that this behaviour has also been observed in the free surface of liquid crystals [23].

Finally, we note that no damping terms were included in the equations of motion of the models presented here for either the individual or collective behaviour. The reason for this omission lies in the microscopic character of the model, in which the randomness of the phases of the vibrations plays a role equivalent to thermal dissipation. However, we have run simulations of systems in which damping terms were included. The effects of including dissipation in this way were found to be insignificant; only very small changes in the anchoring transition temperatures were observed.

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