

Determination of the anisotropic part of the surface thermodynamic potential of a nematic liquid crystal

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A method is proposed for determining the anisotropic surface thermodynamic potential W of a nematic liquid crystal, which depends on the polar angle θ . A $W(\theta)$ curve has been found experimentally for the nematic liquid crystal 5CB. The results are compared with a Rapini potential.

Nematic liquid crystals have no preferential spatial configuration and instead adopt the shape of the closed volume that they occupy. On the other hand, they do have an orientational elasticity. Their orientational configuration (the director field) is determined unambiguously by the elastic moduli K_{11} and K_{33} and by the boundary conditions, which depend on the anisotropic part of the surface thermodynamic potential W (Ref. 1; it is assumed here that there are no defects). The potential W is thus an important characteristic of the interaction of the liquid crystal with the solid boundaries. The precise value of this potential is of considerable interest for the molecular-statistics theory of the interaction of nematic liquid crystals with solid boundaries.

Most of the studies of the binding energy between nematic liquid crystals and substrates have postulated the analytic form of the surface potential. In most cases, this potential has been postulated in the form proposed by Rapini: $W = [W_0 \sin^2(\theta_0 - \theta)]/2$, where the constant W_0 characterizes the strength of the binding with the surface. It is the second derivative of the Rapini potential with respect to the disorientation angle in the equilibrium position. This constant is referred to as the "binding energy."

The Rapini potential, however, is only an approximation of the actual situation. It does not describe all the known experimental facts.³ We know of only a single attempt⁴ to determine an accurate value for W . We should point out that the method which was proposed in that study for determining $W(\theta)$ requires a substantial computational effort, is poorly reproducible, and is unstable with respect to variations in the parameters of the liquid crystal. For example, a variation of only 0.5% in the parameter $\gamma = \epsilon_{\parallel}/\epsilon_{\perp}$ (ϵ_{\parallel} and ϵ_{\perp} are the dielectric constants of the liquid crystal respectively parallel and perpendicular to the director) results in a catastrophic change in W .

The idea underlying our own method for determining W follows from the assertion above that the director field of the liquid crystal is determined unambiguously by W , K_{11} , K_{33} , and the geometry of the surface.

We consider a plane-parallel cell with a hybrid orientation: with a "strong" planar binding ($W_p \rightarrow \infty$) and a "weak" homeotropic binding ($W_h \neq \infty$) (see the inset in Fig. 1).

With decreasing thickness of the liquid-crystal layer, the polar angle at the homeotropic boundary, θ_h , increases from $\approx 0^\circ$ (at large thicknesses) to $\approx 90^\circ$ (at small thicknesses). We write the boundary condition at a homeotropic surface:⁵

$$(\partial W / \partial \theta)_{\theta = \theta_h} = (K_{11} \sin^2 \theta_h + K_{33} \cos^2 \theta_h) (\partial \theta / \partial z)_{\theta = \theta_h}. \quad (1)$$

Since the distribution of the director field in the volume is determined by the angles of the director at the boundary, it is simple to express $(\partial \theta / \partial z)_{\theta = \theta_h}$ in terms of the edge angle. Following Ref. 6, we write

$$(\partial \theta / \partial z)_{\theta = \theta_h} = (f(\pi/2 - \theta_h)L)^{-1} \int_0^{\pi/2 - \theta_h} f(x) dx, \quad (2)$$

where $f(x) = \sqrt{(K_{11}/K_{33} - I) \cos^2 x + I}$. As the thickness of the liquid-crystal layer is varied, we thus find the values of the derivative $(\partial W / \partial \theta)_{\theta = \theta_h}$ from expressions (1) and (2). Integrating $(\partial W / \partial \theta)$ over the angle θ , and using the fact $W_h(0) = 0$, we find the angular dependence $W_h(\theta)$. If the dependence $\theta_h(L)$ in the homeotropic layers of the liquid crystal is known, we can thus reconstruct $W(\theta)$ by the procedure outlined above.

In the experiments, homeoplanar cells with 5CB of various thicknesses, were studied. The planar orientation with strong binding was produced by treating the surface with polyvinylketal, and an orientation with weak homeotropic binding was

achieved by treating the surface with a material equivalent to Chromolan. The director angle near the surface, θ_h , was measured in two ways: by modulation ellipsometry [the light was incident on the interface of the liquid crystal and glass ($N = 1.806$) at angles above the angle of total internal reflection]⁷ and by a pyroelectric method.⁸

Figure 1 shows a curve of θ_h as a function of the layer thickness L . The first two points here were obtained by modulation ellipsometry and correspond to large thicknesses and therefore small angles. (The method of modulation ellipsometry is more sensitive than the pyroelectric method. In addition, the calculation procedure is simpler than that of the pyroelectric method specifically at small angular deviations of the director from the normal to the layer.) All the other points on this curve were obtained by the pyroelectric method. (The data are from Ref. 8.) Figure 2 shows the experimental results on the derivative $\partial W/\partial\theta$ and a least-squares polynomial fit of these results. This polynomial is $\partial W/\partial\theta = 1.63 \times 10^{-2}\theta - 5.8 \times 10^{-2}\theta^3 + 7.5 \times 10^{-2}\theta^5$. In the limit of small angles θ the Rapini potential and the measured surface potential should agree, so we find $W_0 = 1.6 \times 10^{-2}$ erg/cm². Such a value of W_0 agrees well with data in the literature.⁹ Shown for comparison in Fig. 3 are two curves, an experimental $W_h(\theta)$ curve and a Rapini curve $W_h = (W_0 \sin^2\theta)/2$. The real surface treated with the material equivalent to Chromolan turns out to be "softer" than predicted by the classical Rapini potential.

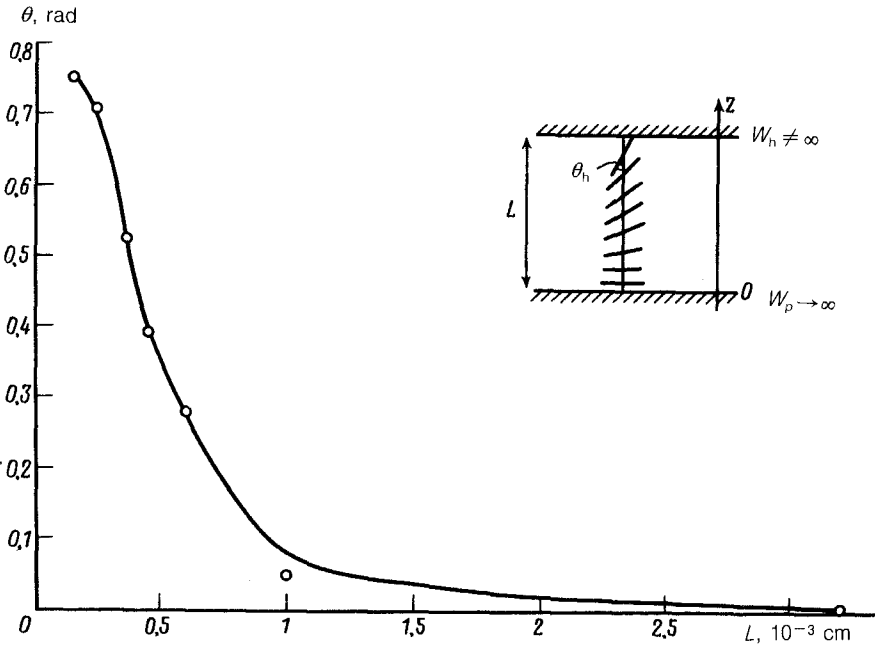


FIG. 1. Inclination angle of the director at a homeotropic boundary versus the cell thickness. The inset shows a plane-parallel cell with a hybrid orientation.

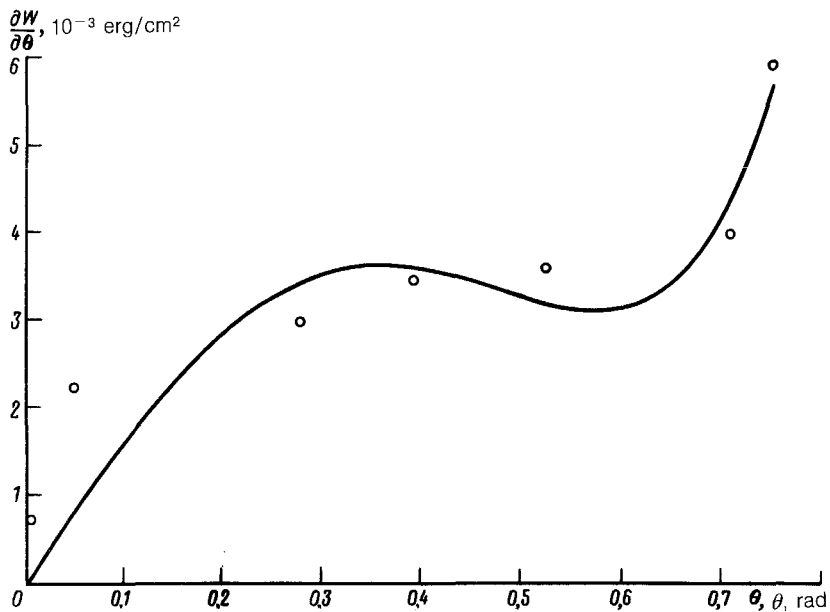


FIG. 2. Experimental θ dependence of $(\partial W/\partial \theta)_{\theta=\theta_n}$ (points) and a corresponding polynomial fit.

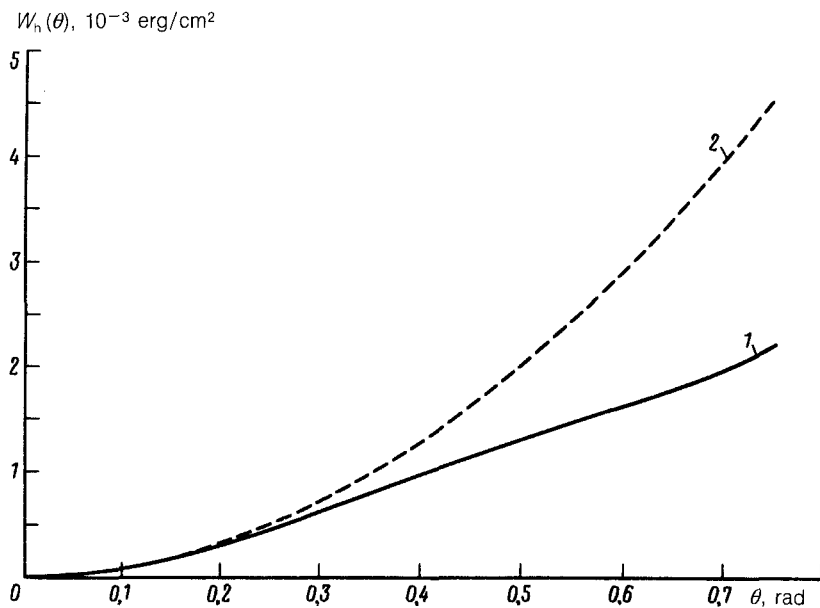


FIG. 3. 1—Experimental results on the anisotropic thermodynamic potential versus the angle θ ; 2—Rapini approximation.

CONCLUSION

The principle of a minimum of the free energy thus dictates a certain angle at a boundary with a "weak" binding energy in homeoplanar layers of a nematic liquid crystal. Measurements of this angle as a function of the thickness yielded an accurate value of the anisotropic surface potential $W_h(\theta)$. Our estimates show that this potential amounts to less than 1% of the total Oseen-Frank elastic energy [$L = 10 \mu\text{m}$, $K = 1.33 \times 10^{-6} \text{ erg/cm}$, $\theta \approx 1/30$, $W_0 \theta^2 / 2 \approx 10^{-5} \text{ erg/cm}^2$, $F_0 = 1/2 \int_L^0 K (d\theta/dz)^2 dz = K\pi^2/8L \approx 1.6 \times 10^{-3} \text{ erg/cm}^2$]. Specifically, because $W_h(\theta)$ is small in comparison with $F_0(\theta)$, we feel that in measurements of the surface potential one should give preference to methods that probe the layer of the nematic liquid crystal in direct contact with the solid boundary and that do not involve the interior of the liquid crystal.

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