Theory and simulation of the nematic anchoring coefficient

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Abstract

Combining molecular simulation, Onsager theory and the elastic description of nematic liquid crystals, we study the dependence of the nematic liquid crystal elastic constants and the zenithal surface anchoring coefficient on the value of the bulk order parameter.

Introduction

The anchoring phenomenon is the tendency of a liquid crystal to orient in a particular direction when in contact with the container walls. The equilibrium director orientation set by the interaction of the liquid crystal with the aligning surface is called an **easy orientation axis**. The simplest, strong anchoring, assumption is that the director has a fixed orientation at the boundaries along the easy orientation axis. However, it has been discovered that the coupling of the director with the orienting surface can be rather weak. This results in deviation of the surface director from the easy axis in response to small perturbations.

On a phenomenological level, weak anchoring can be described by adding an appropriate **surface potential** to the free energy of the system. The simplest form of the surface potential has been proposed by Rapini and Papoular [1]

$$f_s = -\frac{1}{2}W(\mathbf{n}\cdot\mathbf{e})^2, \tag{1}$$

where the parameter, W, is termed an anchoring energy.
There have been several attempts to estimate the anchoring coefficient theoretically [2] and by combining molecular simulation with a local density functional approach [3]. The main difficulty here is that one needs to know the direct pair correlation function of the nematic state, which is usually unknown, and must hence be estimated with some uncontrolled approximations or assumptions.

The present work attempts to remedy the situation by combining the elastic description with Onsager theory and Monte Carlo simulation results. We study the dependence of the elastic (K_{33}) and surface anchoring (W) coefficients on the liquid crystal state point, which is defined by the bulk value of the order parameter Q.

Methods

Elastic description

The easiest way to obtain the surface anchoring coefficient W is to create a director deformation far from the surface. Then, measuring the response of the director near the cell surface, or fitting the director profile with a theoretically predicted profile, yields an estimate of the anchoring extrapolation length and ratios of the elastic constants.

Indeed, consider one of the possible geometries suitable for the measurement of the zenithal anchoring strength. Let the director have fixed orientation at the boundary $z = L$. The surface at $z = 0$ is assumed to provide homeotropic anchoring of strength W. In the elastic description, deformations of the director field $\mathbf{n}$ are

$$E(\theta,\delta) = E(\theta_L,\delta)\frac{z+\lambda}{L+\lambda}. \tag{2}$$

Note, that for small angles θ_L and, correspondingly, for small θ, $E(\theta,\delta) = \theta$ and we have linear dependence of the director angle on the z coordinate

$$\delta n_x(z) \approx \theta(z) = \theta_L\frac{z+\lambda}{L+\lambda}. \tag{3}$$

Using eqn (2), one can fit the director profiles $\theta(z)$ with $\lambda = K_{33}/W$ and $\delta = (K_{33}-K_{11})/K_{33}$ as adjustable parameters. To simplify the procedure, it is more appropriate to fit $z(\theta)$ rather than $\theta(z)$.

Onsager approach

The Helmholtz free energy in the Onsager approach is expressed in terms of the single-particle density, $\rho(\mathbf{1})$, where $(\mathbf{1}) = (\mathbf{r}_1,\mathbf{\Omega}_1)$ represents both position $\mathbf{r}_1$ and orientation $\mathbf{\Omega}_1$. It has the following form [4]

$$\beta\mathcal{F}[\rho] = \int\rho(\mathbf{1})\left\{\ln\rho(\mathbf{1})\Lambda^3 - 1 - \beta\mu + \beta U(\mathbf{1})\right\}d(\mathbf{1}) - \frac{1}{2}\int f(\mathbf{1},\mathbf{2})\rho(\mathbf{1})\rho(\mathbf{2})d(\mathbf{1})d(\mathbf{2}). \tag{4}$$

Here $\beta = 1/k_BT$, Λ is the de Broglie wavelength, μ is the chemical potential, U is the external potential energy (including the surface potential), and $f(\mathbf{1},\mathbf{2})$ is the Mayer f-function.

The equilibrium single-particle density that minimizes the free energy (4) is a solution of the following Euler-Lagrange equation

$$\ln\rho(\mathbf{1})\Lambda^3 - \beta\mu + \beta U(\mathbf{1}) - \int f(\mathbf{1},\mathbf{2})\rho(\mathbf{2})d(\mathbf{2}) = 0, \tag{5}$$

which can be obtained from the variation of the functional (4).

Molecular model and simulation methods

We performed Monte Carlo (MC) simulation of a liquid crystal confined between parallel walls, with finite homeotropic anchoring at the walls. The molecules in this study were modeled as hard ellipsoids of revolution of elongation $e = a/b = 15$.

The slab geometry is defined by two hard parallel confining walls, which cannot be penetrated by the **centers** of the ellipsoidal molecules.

A sequence of runs was carried out for systems of $N = 2000$ particles using the constant-NVT ensemble, allowing typically 10^5 MC sweeps for equilibration and 4×10^7 sweeps for accumulation of averages. The wall separation was fixed and equal to $L_z \approx 4.93a$.
The same molecular model and interaction of the molecules with the walls was adopted for the Onsager calculations.

Results

Anchoring energy

To obtain the microscopic expression for the extrapolation length λ, we start from the equation for the single-particle density (5). Assume that the solution for a ground state, i.e. for homeotropically aligned liquid crystal in slab geometry, is given by the single-particle density ρ_0. Consider a small perturbation around the ground state, $\rho = \rho_0 + \delta\rho$. To first order in $\delta\rho$, eqn (5) can be written as

$$\frac{\delta\rho(\mathbf{1})}{\rho_0(\mathbf{1})} = \int f(\mathbf{1},\mathbf{2})\delta\rho(\mathbf{2})d(\mathbf{2}). \tag{6}$$

In the case of slowly-varying director fields we assume that the free energy functional is locally in equilibrium. This is equivalent to the mathematical simplification [5]

$$\rho(\mathbf{r},\mathbf{\Omega}) = \rho_0\left(\mathbf{r},\mathbf{n}(\mathbf{r})\cdot\mathbf{\Omega}\right). \tag{7}$$

In slab geometry, with the z axis normal to the surfaces, the single particle density ρ_0 depends on the z coordinate only and can be expanded in spherical harmonics. Conducting angular integrations in eqn (6)

$$c_{\ell_1}(z_1)\delta n_x(z_1) = 4\pi\sum_{\ell_2=2}^{\text{even}}\sqrt{\frac{\ell_2(\ell_2+1)}{\ell_1(\ell_1+1)}}\times \int_0^\infty A_{\ell_1,\ell_2,1}(z_2-z_1)\rho_{\ell_2}(z_2)\delta n_x(z_2)dz_2. \tag{8}$$

Equation (8) allows one to calculate the director profile (for small director deviations from the ground state) once the single-particle density ρ_0 of the ground state is known.
In the ideal case, often considered in phenomenological approaches [6], the density and order parameter are assumed to be constant in the cell. The anchoring appears only due to the presence of the interface, which breaks translational symmetry. Then the anchoring coefficient is proportional to the first moment of the excluded area coefficient $A_{2,2,1}(z)$

$$\lambda = -\frac{8\pi}{V_{22}}\int_0^\infty zA_{2,2,1}(z)dz, \tag{9}$$

and does not depend on the value of density or order parameter, since excluded area, as well as excluded volume, are completely defined by the geometry of the overlapping molecules. This means that in the ideal case of a uniform nematic, the anchoring coefficient $W = K_{33}/\lambda$ has the same dependence on the order parameter as the elastic constant K_{33}.

Onsager theory

Minimization of the grand potential was carried out for the system with an external field applied near the right wall. Profiles of director angle $\theta(z)$ are compared with elastic theory (eqn (2)) in Fig. 1.

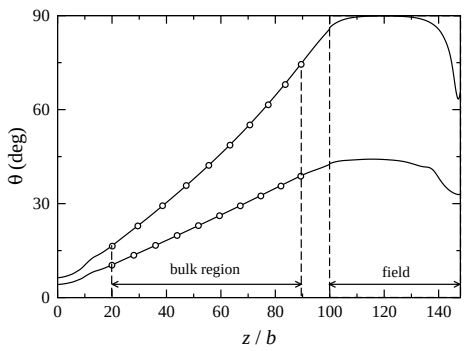

Figure 1 Typical profiles of director angle $\theta(z)$ in the slab geometry. Orienting fields are applied in the region $100 < z/b < 148$ near the right wall, favouring director angles of $\pi/4$ and $\pi/2$ relative to the surface normal. The left wall is unperturbed. Solids lines: Onsager theory. Circles: results of fitting the profiles in the bulk region with the prediction of elastic theory.

The elastic theory has been fitted to the director angle profiles predicted by the Onsager theory using two adjustable parameters,
The dependence of the extrapolation length, λ, on the order parameter Q is shown in Fig 2.
We have also carried out minimization of the grand potential for the system without an external field. As a result, we obtained the single-particle density with a homeotropic distribution of the director in the cell. The dependence of the extrapolation length on the order parameter was then calculated using eqn (8) and is also shown in Fig 2. The results qualitatively agree with the results of fitting obtained by combining Onsager theory and elastic theory. The extrapolation length tends to grow with increase in the order parameter and has the same order of magnitude.

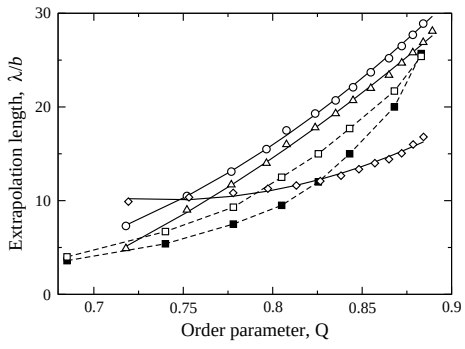

Figure 2 Extrapolation length λ as a function of the order parameter. Circles: Onsager theory in slab geometry, director profiles fitted with elastic theory, for anchoring field with $\alpha = \pi/4$. Triangles: the same, but for $\alpha = \pi/2$. Diamonds: Onsager theory in slab geometry, with no field, extrapolation length calculated using equation (8). Filled squares: Monte Carlo results obtained by measuring director fluctuations. Open squares: Monte Carlo results, with applied field near the right-hand wall.

MC simulation

Simulations were carried out in slab geometry for several values of the number density.
The order tensor fluctuations in reciprocal space were calculated and fitted to the simulation results.
Typical order fluctuation amplitudes together with the corresponding fitting curves are plotted in Fig 3.

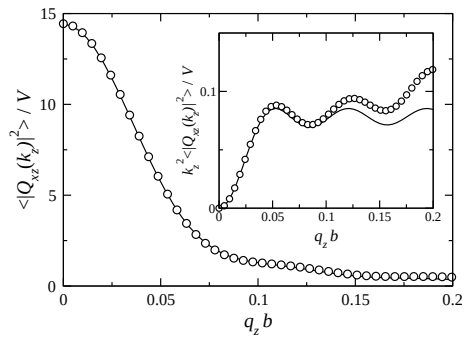

Figure 3 Fluctuations of the director (arbitrary units) as a function of wave-vector (normalized by the molecular minor axis length b). Symbols: Monte Carlo results. Solid lines: elastic theory, fitted to parameters discussed in the text. Inset: fluctuations multiplied by $(k_z b)^2$ to emphasize structure at higher wave numbers.

The dependence of the extrapolation length, λ, on the order parameter Q is shown in Fig 2, together with the results from the Onsager theory. It should be noted that combining the elastic approach with the Onsager calculations does not allow one to determine, separately, L_w and λ. Therefore, the results of the Onsager theory in Fig 2 really represents $\lambda + L_w$, which is one of the possible origins of the systematic difference between the two approaches.

To double check the results obtained by examining the director fluctuation amplitudes, we performed the same type of experiments as in the Onsager slab system. Within a range $7.5b$ of the right-hand wall, a strong coupling field was applied to molecular orientations, $V^{\text{ext}} \sim (\mathbf{u}_i\cdot\mathbf{e}_z)^2$, aligning the molecules near the right wall parallel to it. After the system was equilibrated, the director profile was fitted to the result of the elastic theory, eqn (2). The dependence of the extrapolation length λ on the order parameter Q is also shown in Fig 2. One can see that the agreement between the two methods is quite good.

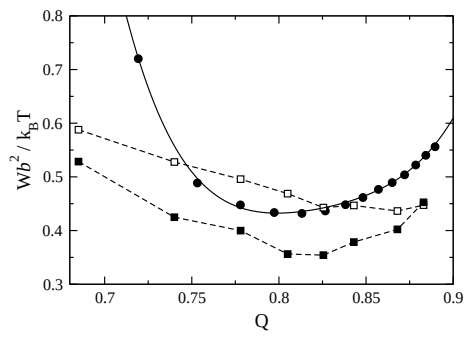

Figure 4 Anchoring energy W as a function of the order parameter. Circles: Onsager theory (with a smooth curve to guide the eye). Open squares: MC results obtained by measuring director fluctuations. Filled squares: MC results, field near the right-hand wall.

Finally, we plot the dependence of the anchoring energy coefficient, $W = K_{33}/\lambda$, which is an intrinsic charachteristic of the interface region, in Fig. 4. For Onsager theory, $\lambda(Q)$ is given by the results in slab geometry fitted with the elastic theory (Fig. 2), $K_{33}(Q)$ - by the Poniewierski - Stecki expressions. For MC simulations, we used the elastic constant obtained from the analysis of the director fluctuation amplitudes. All methods predict that the anchoring coefficient is a non-monotonic function of the order parameter, even though the actual variation is small.

Conclusions

We have studied the dependence of the zenithal surface anchoring coefficient on the order parameter of a lyotropic nematic liquid crystal modeled by hard ellipsoids. Several techniques have been used: Onsager theory combined with elastic theory; Monte Carlo simulations fitted to elastic theory; analysis of the director fluctuation amplitudes obtained from Monte Carlo simulations.

A microscopic semi-qualitative expression for the extrapolation length allowed us to conclude that subsurface variations of the single-particle density, mainly defined by the nematic order parameter and density variation, contribute substantially to the anchoring phenomenon. We showed that for an ideal system, in which the single-particle density in the cell is assumed to be uniform, the extrapolation length does not depend on the nematic order parameter. This dependence is therefore associated with the subsurface variations of the single-particle density.

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