



Measurement of the phenomenological parameters of the nematic-wall interface by molecular simulation

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Abstract

We propose a simple and reliable method to measure the liquid crystal surface anchoring strength by molecular simulation. The method is based on sampling the long-range fluctuation modes of the director in confined geometry using ensemble averages of functions of the second-rank order tensor components. As an example, molecular simulations of a liquid crystal in slab geometry between parallel walls with homeotropic anchoring have been carried out using the Monte Carlo technique. A fit to the fluctuation amplitudes with equations predicted by elastic theory then allows to determine the surface anchoring strength. By studying different slab thicknesses, we are able to calculate separately the position of the elastic boundary condition and the extrapolation length.

1 Introduction

On the phenomenological level, liquid crystal anchoring can be described by two basic parameters: the easy axis direction, \mathbf{e} , and the anchoring coefficient W . These two parameters are critical design parameters for every liquid crystal device. In spite of the practical importance, the mechanism of the director alignment is still not well understood. Experimental techniques test the entire liquid crystal cell and therefore cannot provide a satisfactory description of the thin interface region. Theoretical investigations of anchoring are also quite controversial. For example, the usual continuous phenomenological theory has divergent surface terms in the elastic free energy expansion.

One of the approaches for the systematic investigation of anchoring phenomena is computer simulation of liquid crystals in confined geometries. Indeed, computer simulation is a well established method to treat bulk elastic coefficients [1], the surface anchoring strength [2], and structures of disclination cores [3, 4]. This means that computer simulation allows investigation of details of the liquid crystalline structure which cannot be resolved experimentally.

Several papers have already been published trying to search for reasonable surface potentials to use in simulations [5, 6, 7, 8, 9, 10]. However, most of them do not characterize aligning surfaces using well established parameters. The reason for this is probably a lack of reliable methods to measure these parameters by computer simulation. In this work, we propose a technique to measure the surface anchoring strength W by computer simulation. The method itself is based on the study of the *director fluctuations* in the liquid crystal cell.

2 Theory

Large length- and time-scale fluctuations of the director $\mathbf{n}(\mathbf{r})$ can be described in the continuum model of liquid crystals, based on the phenomenological elastic constants.

In this approach, the equations for the director and the boundary conditions can be obtained by minimization of the cell free energy [11]:

$$F = F_b + F_s, \quad (1)$$

where F_b is the Frank elastic free energy, and F_s is the surface anchoring energy. Below we consider *homeotropic* anchoring. We assume that the interaction of the director with the cell surfaces has the Rapini-Papoular form [12]:

$$F_s = -\frac{1}{2}W \int_{S_0, S_L} (\mathbf{n} \cdot \mathbf{e}_{0,L})^2 d\mathbf{r}_\perp, \quad (2)$$

where unit vectors $\mathbf{e}_{0,L}$ define directions of the easy axes at $z = 0, L$: $\mathbf{e}_0 = \mathbf{e}_z, \mathbf{e}_L = -\mathbf{e}_z$; W is the anchoring energy, and $\mathbf{r}_\perp = (x, y)$. We have to investigate small perturbations of the director around the distribution:

$$\mathbf{n}(\mathbf{r}) = \mathbf{n}_0 + \delta\mathbf{n}(\mathbf{r}). \quad (3)$$

Minimizing the total free energy (1) and linearizing the equations for the director and boundary conditions with respect to $\delta\mathbf{n}$, we obtain equations

$$\gamma \delta \dot{\mathbf{n}} = K \nabla^2 \delta \mathbf{n}, \quad (4)$$

and boundary conditions

$$W \delta \mathbf{n} \pm K \frac{\partial}{\partial z} \delta \mathbf{n} \Big|_{z=L,0} = 0. \quad (5)$$

for the fluctuations.

Fluctuation amplitudes can be expanded in a series of the orthogonal functions:

$$\delta \mathbf{n}(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{q}_\perp, q_z} e^{i\mathbf{q}_\perp \cdot \mathbf{r}_\perp} \left[\delta \mathbf{n}^{(+)}(\mathbf{q}_\perp, q_z) e^{iq_z r_z} + \delta \mathbf{n}^{(-)}(\mathbf{q}_\perp, q_z) e^{-iq_z r_z} \right], \quad (6)$$

where $\mathbf{q}_\perp = (q_x, q_y)$, $\delta \mathbf{n}^{(-)} = \frac{i\chi - \xi}{i\chi + \xi} \delta \mathbf{n}^{(+)}$, $\chi = q_z L$, $\xi = \frac{WL}{K} = \frac{L}{\lambda}$, λ is the extrapolation length [11]. The wave vectors q_z form a discrete spectrum because of confinement in the z direction which depends on the anchoring energy W .

In molecular simulations, rather than measuring director fluctuations, it is more convenient to measure fluctuations of the second-rank order tensor components. We define the real-space order tensor density

$$Q_{\alpha\beta}(\mathbf{r}) = \frac{V}{N} \sum_i \delta(\mathbf{r} - \mathbf{r}_i) Q_{\alpha\beta}^i, \quad (7)$$

$$Q_{\alpha\beta}^i = \frac{3}{2} \left(u_{i\alpha} u_{i\beta} - \frac{1}{3} \delta_{\alpha\beta} \right),$$

where $\alpha, \beta = x, y, z$, in terms of the orientation vectors \mathbf{u}_i of each molecule i . If we assume that there is no variation in the *degree* of ordering, we may write

$$Q_{\alpha\beta}(\mathbf{r}) = \frac{3}{2} Q \delta n_\alpha(\mathbf{r}). \quad (7)$$

The Fourier transform of the real-space order tensor is $Q_{\alpha\beta}(\mathbf{k}) = \int_V Q_{\alpha\beta}(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} d\mathbf{r} = \frac{V}{N} \sum_i Q_{\alpha\beta}^i e^{i\mathbf{k} \cdot \mathbf{r}_i}$. Then the fluctuations $\langle |Q_{\alpha\beta}(\mathbf{k})|^2 \rangle$ can be easily measured from simulations:

$$\langle |Q_{\alpha\beta}(\mathbf{k})|^2 \rangle = \frac{V^2}{N^2} \left[\left(\sum_i Q_{\alpha\beta}^i \cos(\mathbf{k} \cdot \mathbf{r}_i) \right)^2 + \left(\sum_i Q_{\alpha\beta}^i \sin(\mathbf{k} \cdot \mathbf{r}_i) \right)^2 \right]. \quad (8)$$

Using the equipartition theorem and eq.(7), the corresponding ensemble average of the squared order parameter can be rewritten as

$$\langle |Q_{\alpha\beta}(k_z)|^2 \rangle = \frac{9}{8} k_B T \frac{Q^2 V}{K} \sum_{q_z} \frac{\chi^2 + \xi^2}{q_z^2 (2\xi + \chi^2 + \xi^2)} \times \left| \frac{e^{i(\kappa + \chi)} - 1}{\kappa + \chi} + \left(\frac{i\chi - \xi}{i\chi + \xi} \right) \frac{e^{i(\kappa - \chi)} - 1}{\kappa - \chi} \right|^2. \quad (9)$$

We measure Q and $\langle |Q_{\alpha\beta}(k_z)|^2 \rangle$ from simulations, eqn (8), and then compare with the theoretical prediction, eqn (10), which is parametrized by L , λ and K .

3 Molecular model and simulation methods

To test the technique proposed, we simulated a liquid crystal confined between parallel walls (slab geometry), with finite homeotropic anchoring at the walls. The director fluctuations occur around the preferred, *uniform*, alignment perpendicular to the walls.

We performed Monte Carlo (MC) simulations of the liquid crystal system. The molecules were modelled 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 *centres* of the ellipsoidal molecules. Packing considerations generate homeotropic ordering at the surface.

Simulations were carried out for systems of $N = 2000$ particles with wall separations $L_z = 6.58a, 8.22a, 9.86a$.

To be sure that we have the same state point for each simulation, we adjusted the density to have the same P_{zz} component of the pressure tensor for all systems. Then a sequence of runs was carried out using the constant- NVT ensemble, allowing typically 10^5 MC sweeps for equilibration and 10^7 sweeps for accumulation of averages.

4 Simulation results

The simulation results were analysed to give a density profile, and an order tensor profile, which are shown in Figs (1,2).

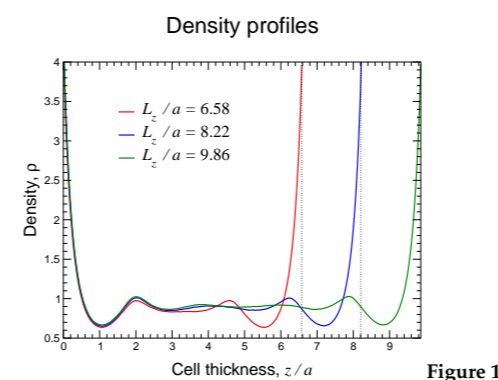


Figure 1

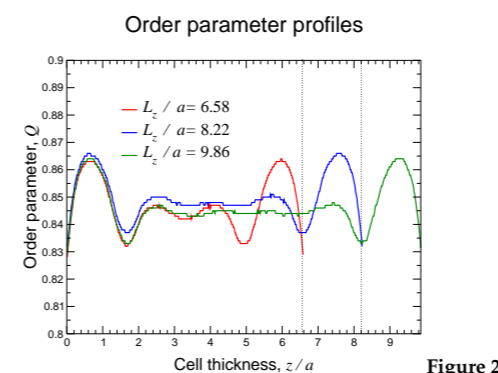


Figure 2

From these profiles we can see that the walls are sufficiently well separated, and the variation of the order parameter across the slab is small, even in spite of the large change in local density near the walls.

The order tensor fluctuations in reciprocal space were calculated using expression (8). To fit the simulation results with the elastic theory we have to remember that the size of the simulation box L_z is not necessarily equal to the liquid crystal cell thickness L appearing in the elastic theory. The difference may be ascribed to partial penetration of the walls by the liquid crystal molecules, formation of an ordered (or solid) layer near the walls, or other molecular-scale features. We assume that we may write $L = L_z + 2L_w$, where the value L_w is characteristic of the wall, independent of L_z , and may be determined in our fitting process. The best estimate of the wall-induced separation distance L_w was obtained examining the ratios $\langle |Q_{\alpha\beta}(L_1)|^2 \rangle / \langle |Q_{\alpha\beta}(L_2)|^2 \rangle$ (Fig.3).

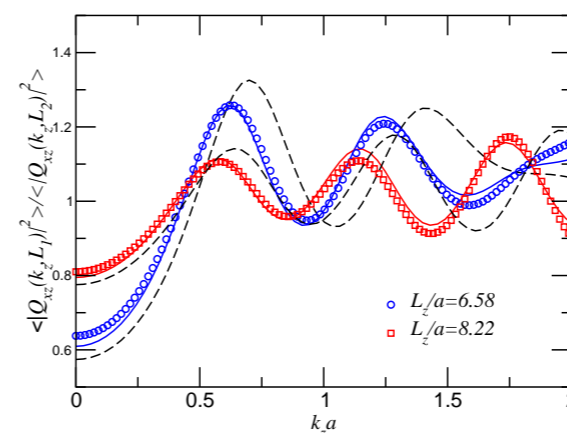


Figure 3 Ratio of the director fluctuations as function of wavevector for different wall separations. Symbols: Monte Carlo results; solid lines: elastic theory; dashed lines: elastic theory, without correction for the difference between the elastic-theory cell thickness L and the simulation box size L_z . The best fits were obtained with $L_w/a = 0.59$.

Following the determination of L_w , we adjusted the extrapolation length λ to obtain the best fit to the fluctuation data: the fluctuation amplitudes with small k_z are most sensitive to this quantity. Together with the corresponding fitting curves for the different slab thicknesses, our results are plotted in Fig. 4.

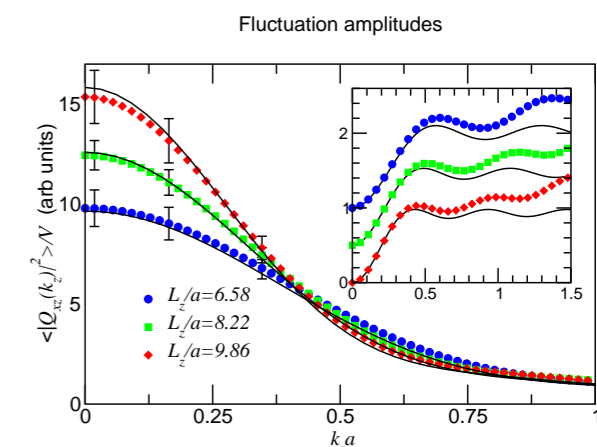


Figure 4 Director fluctuations (arbitrary units) as function of wavevector (normalized by the molecular semi-axis length a) for different wall separations. Symbols: Monte Carlo results; error estimates are indicated at some representative points, at higher wave-vectors the errors are smaller than the plotting symbols. Solid lines: elastic theory, fitted to parameters discussed in the text. Inset: fluctuations multiplied by $(k_z a)^2$ to emphasize structure at higher wavenumbers. Successive curves are offset by 0.5 for clarity.

The best fits were obtained with a bulk elastic constant $Ka/k_B T \approx 66$ and an extrapolation length $\lambda/a \approx 2.3$. The theoretical fitting curves agree well with the simulation results, for small values of k_z , as one would expect for a theory valid for long wavelength fluctuations. At higher k_z , the structure (emphasized in the inset of Fig. 4 by a multiplying factor k_z^2) is not perfectly reproduced, but the agreement is satisfactory. This is not surprising, since we expect the elastic theory to become less accurate at higher k_z .

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