Liquid crystal director fluctuations and surface anchoring by molecular simulation

Denis Andrienko¹, Guido Germano¹,², and Michael P. Allen¹

¹ H. H. Wills Physics Laboratory, University of Bristol
Royal Fort, Tyndall Avenue, Bristol BS8 1TL, United Kingdom
² Fakultät für Physik, Universität Bielefeld, 33501 Bielefeld, Germany

We propose a simple and reliable method to measure the liquid crystal surface anchoring strength by molecular simulation. The method is based on the measurement of the long-range fluctuation modes of the director in confined geometry. 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. By studying different slab thicknesses, we are able to calculate separately the position of the elastic boundary condition, and the extrapolation length.

PACS numbers: PACS: 61.30.Cz,61.20.Ja,07.05.Tp,68.45.-v

I. INTRODUCTION

Liquid crystal anchoring effects have been intensively studied both experimentally and theoretically during the past decades [1, 2]. Such an interest is well understood since most liquid crystal devices are cells comprising orienting surfaces with a liquid crystal in between. Typically, aligning surfaces provide a uniform orientation of the liquid crystal director in the cell interior. On the phenomenological level, liquid crystal anchoring can be described by two basic parameters: the easy axis direction, ε, and the anchoring coefficient W. These two parameters are critical design parameters for every liquid crystal device [3]. A variety of experimental methods have been proposed to measure anchoring parameters, in particular the anchoring coefficient W [4, 5]. Most of them measure surface director deviations in an external field and involve rather complicated optical setups.

In spite of the practical importance, the mechanism of the director alignment is still not well understood. Experimental techniques always involve optical measurements. They 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 [3, 4].

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 [3, 4], the surface anchoring strength [12], and structures of disclination cores [13, 14]. 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 [15, 16, 17, 18]. However, most of them do not characterize aligning surfaces using well established parameters. Questions about the formation of a solid interface layer, values of the easy axis angle and anchoring coefficient are still open. The reason for this is probably a lack of reliable methods to measure these parameters by computer simulation.

In this paper, 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. A similar approach has already been used for the experimental characterization of the interface [19] and is based on measuring the light scattering caused by the director fluctuations. In computer simulation, the director fluctuations can be studied directly, using ensemble averages of functions of the second-rank order tensor components. A fit to the fluctuation amplitudes with equations predicted by elasticity theory then allows determination of the surface anchoring strength.

II. THEORY

Large length- and time-scale fluctuations of the director n(r) can be described in the continuum model of liquid crystals, based on the phenomenological elastic constants. In this approach, the hydrodynamic equations for the director and the boundary conditions can be obtained by minimization of the cell free energy [20]:

\[ F = F_b + F_v, \]

where \( F_b = \frac{1}{2} \gamma (\partial n / \partial t)^2 \) is a hydrodynamic term with an effective viscosity coefficient \( \gamma \), \( F_b \) is the Frank elastic free energy, and \( F_v \) is the surface anchoring energy.

In what follows we use the one-elastic-constant approximation, i.e. \( K_{11} = K_{22} = K_{33} = K \). Then the Frank free energy can be brought into the form:

\[ F_b = \frac{1}{2} K \int_V \left( (\nabla \cdot n)^2 + (\nabla \times n)^2 \right) dV. \]

The liquid crystal cell is bounded by surfaces \( z = 0, L \) which provide some kind of anchoring condition [1]. Below we consider homeotropic anchoring, that is, normal
to the surface. Planar anchoring can be treated in the same way. We assume that the interaction of the director with the cell surfaces has the Rapini-Papoular form [2]:

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

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 $\mathbf{r}_\perp = (x, y)$.

Equations for the director and boundary conditions can be obtained by minimization of the cell free energy eqn (4). In the case of homeotropic anchoring on both surfaces the stationary director distribution in the cell is homeotropic, i.e. $\mathbf{n}_0 = \mathbf{e}_z$. Therefore, we have to investigate small perturbations of the director around the distribution:

$$\mathbf{n}(\mathbf{r}) = \mathbf{n}_0 + \delta \mathbf{n}(\mathbf{r}) .$$  \hspace{1cm} (2)

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

$$\gamma \frac{\partial}{\partial t} \delta \mathbf{n} = K \nabla^2 \delta \mathbf{n} ,$$  \hspace{1cm} (3)

and boundary conditions

$$W \delta \mathbf{n} \pm K \frac{\partial}{\partial z} \delta \mathbf{n} \Bigg|_{z=L,0} = 0 .$$  \hspace{1cm} (4)

for the fluctuations. Taking into account eqn. (2), the expression for the free energy fluctuations can be rewritten in the form of the average of the self-conjugate (Hermitian) operator $-\frac{1}{2} K \nabla^2$:

$$\delta F_b = -\frac{1}{2} K \int_V \delta \mathbf{n}(\mathbf{r}) \nabla^2 \delta \mathbf{n}(\mathbf{r}) \, d\mathbf{r} .$$  \hspace{1cm} (5)

The eigenfunctions of the operator $-\frac{1}{2} K \nabla^2$, which satisfy boundary conditions (4), form a complete set of orthogonal functions characterized by wave vector $\mathbf{q}$. Therefore, $\delta \mathbf{n}(\mathbf{r})$ can be expanded in a series of these orthogonal functions:

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

where $\mathbf{q}_\perp = (q_x, q_y)$, and

$$\delta \mathbf{n}^{(-)} = \frac{i \xi - \xi}{i \xi + \xi} \delta \mathbf{n}^{(+)} .$$  \hspace{1cm} (7)

Here we have introduced the dimensionless wave vector $\chi = q_z L$ and anchoring parameter

$$\xi = \frac{WL}{K} = \frac{L}{\chi} ,$$  \hspace{1cm} (8)

where $\lambda$ is the extrapolation length [20]. The wave vectors $\mathbf{q}_z$ form a discrete spectrum because of confinement in the $z$ direction which depends on the anchoring energy $W$ (see Appendix for details). The explicit form of the $q_z$ spectrum is given by the secular equation:

$$(\xi^2 - \chi^2) \sin \chi + 2 \chi \chi \cos \chi = 0 .$$  \hspace{1cm} (9)

Each individual mode can now be seen from eqn (3) to relax exponentially with a relaxation time given by

$$\tau = \frac{\gamma}{K} (q_z^2 + q_z^2) .$$  \hspace{1cm} (10)

Substituting expansion (5) into the free energy (5), and performing the integration over the cell volume we obtain:

$$\delta F_b = \frac{K}{V} \sum_{\mathbf{q}_\perp, q_z} q_z^2 (2 \xi + \chi^2 + \xi^2) \times \delta \mathbf{n}^{(+)}(\mathbf{q}_\perp, q_z) \delta \mathbf{n}^{(+)}(-\mathbf{q}_\perp, q_z) .$$  \hspace{1cm} (11)

Integrating, we took into account the orthogonality of the eigenfunctions in the expansion (5) with different eigenvectors $\mathbf{q}$, which allowed us to reduce the summations over $\mathbf{q}$, $\mathbf{q}'$ to a single sum over $\mathbf{q}$.

Application of the equipartition theorem of classical statistical mechanics, just as for elastic fluctuations in bulk liquid crystals [22], gives the fluctuation amplitudes:

$$\left\langle \delta \mathbf{n}^{(+)}(\mathbf{q}_\perp, q_z) \delta \mathbf{n}^{(+)}(-\mathbf{q}_\perp, q_z) \right\rangle = \frac{k_B TV (i \chi + \xi)^2}{2 K q_z^2 (2 i \chi^2 + \xi^2)} ,$$  \hspace{1cm} (12)

where $\langle \ldots \rangle$ denotes an ensemble average.

In molecular simulations, rather than measuring director fluctuations, it is more convenient to measure fluctuations of the second-rank order tensor components (following Forster [24]). We define the real-space order tensor density

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

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

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

$$Q_{\alpha\beta}(\mathbf{r}) = \frac{3}{2} Q n_\alpha(\mathbf{r}) n_\beta(\mathbf{r}) - \frac{1}{2} Q \delta_{\alpha\beta} ,$$

where $Q$ is the order parameter, i.e. the largest eigenvalue of $Q_{\alpha\beta}(\mathbf{r})$. If the director $\mathbf{n}_0$ is taken to lie along the $z$ axis throughout the sample, the off-diagonal components $Q_{\alpha z}(\mathbf{r})$, $\alpha = x, y$, are proportional to the fluctuations of the corresponding director components

$$Q_{\alpha z}(\mathbf{r}) = \frac{3}{2} Q \delta n_\alpha(\mathbf{r}) .$$
This is the situation for homeotropic anchoring at both surfaces. For planar anchoring, with the director along \( x \) and the surface normal along \( z \), the components \( Q_{xy} \), \( Q_{zz} \) are important (and non-equivalent).

Measurements are performed directly in reciprocal space. The Fourier transform of the real-space order tensor is

\[
Q_{\alpha\beta}(k) = \int_V Q_{\alpha\beta}(r)e^{ik\cdot r}dr = \frac{V}{N} \sum_i Q_{\alpha\beta}^i e^{i\mathbf{k}\cdot \mathbf{r}_i}.
\]

Then the fluctuations \( \langle |Q_{\alpha\beta}(k)|^2 \rangle \) can be easily measured from simulations:

\[
|Q_{\alpha\beta}(k)|^2 = \frac{V^2}{N^2} \left[ \left( \sum_i Q_{\alpha\beta}^i \cos(\mathbf{k} \cdot \mathbf{r}_i) \right)^2 + \left( \sum_i Q_{\alpha\beta}^i \sin(\mathbf{k} \cdot \mathbf{r}_i) \right)^2 \right]. \tag{13}
\]

We explicitly relate simulation-measured fluctuation modes with theoretically predicted amplitudes of the director fluctuations for \( q_z = 0 \)

\[
Q_{\alpha z}(k_z) = \frac{3}{21} \sum_{q_z} \delta \mathbf{n}(+)(0, q_z) \left[ \frac{\epsilon^{i(\kappa+\chi)} - 1}{\kappa + \chi} + \frac{i \chi - \xi}{i \chi + \xi} \frac{\epsilon^{i(\kappa-\chi)} - 1}{\kappa - \chi} \right].
\]

where \( \kappa = k_z L \). Note that the \( q_z \) take discrete (but not equally spaced) values as discussed earlier, while the \( k_z \) values are unrestricted.

Since \( \delta \mathbf{n}(r) \) is real, using eqn (13) we have

\[
\left[ \delta \mathbf{n}(+)(q_z, q_z) \right]^* = -\frac{\xi^2 + \chi^2}{(\xi + i \chi)^2} \delta \mathbf{n}(+)(-q_z, q_z^*).
\]

Taking this equation into account, and the fact that fluctuations with different wavevectors are independent, i.e. \( \langle \delta \mathbf{n}(+)(q_z, q_z) \delta \mathbf{n}(+)(-q_z, q_z) \rangle = 0 \) if \( q_z \neq q_z^* \), the corresponding ensemble average of the squared order parameter can be rewritten as

\[
\langle |Q_{\alpha z}(k_z)|^2 \rangle = \frac{9}{8} k_B T \frac{Q^2 V}{K} \sum_{q_z} \frac{\chi^2}{q_z^2 (2\xi + \chi^2 + \xi^2)} \left[ \frac{\epsilon^{i(\kappa+\chi)} - 1}{\kappa + \chi} + \frac{i \chi - \xi}{i \chi + \xi} \frac{\epsilon^{i(\kappa-\chi)} - 1}{\kappa - \chi} \right]^2. \tag{14}
\]

We measure \( Q \) and \( \langle |Q_{\alpha z}(k_z)|^2 \rangle \) from simulations, eqn (13), and then compare with the theoretical prediction, eqn (14), which is parametrized by \( L, \lambda \) and \( K \). Both the permitted \( q_z \) spectrum, and the variation of \( \langle |Q_{\alpha z}(k_z)|^2 \rangle \) with \( k_z \) are sensitive to the anchoring strength parameter \( \xi = L/\lambda \).

Fluctuation amplitudes given by eq. (14) have features that simplify the fitting procedure. First, terms with small \( q_z \) values dominate because of the \( q_z^2 \) in the denominator of eq (14). Therefore, it is always possible to truncate this sum and use only the first values of the \( q_z \) spectrum. Then, for large \( k_z \) or for \( \kappa >> \chi \), eq. (14) can be simplified so that the dependence on \( k_z \) is explicit:

\[
\langle |Q_{\alpha z}(k_z)|^2 \rangle = \frac{9}{2} k_B T \frac{Q^2 V}{K} \left[ \sin(\kappa/2) \right]^2 \sum_{q_z} \frac{\chi^2}{q_z^2 (2\xi + \chi^2 + \xi^2)}. \tag{15}
\]

Therefore, for large \( k_z \), the fluctuation amplitude \( \langle |Q_{\alpha z}(k_z)|^2 \rangle \) has a characteristic oscillation with the period given by \( \kappa = k_z L = 2\pi \). This means that we can adjust the cell thickness \( L \) independently of parameters \( \lambda \) and \( K \) by examining characteristic wavelength of the fluctuation amplitude \( \langle |Q_{\alpha z}(k_z)|^2 \rangle \).

III. MOLECULAR MODEL AND SIMULATION METHODS

To test the technique proposed, we simulated a liquid crystal confined between parallel walls (slab geometry),
We performed Monte Carlo (MC) simulation of the liquid crystal system. We used a molecular model which has been studied earlier in this geometry \cite{10}. The molecules in this study were modelled as hard ellipsoids of revolution of elongation $e = a/b = 15$, where $a$ is the length of the semi-major axis and $b$ the length of the two equal semi-minor axes. The phase diagram and properties of this family of models are well studied \cite{23, 24, 25, 26, 27}. It is useful to express the density as a fraction of the close-packed density $\rho_{cp}$ of perfectly aligned hard ellipsoids, assuming an affinely-transformed face-centred cubic or hexagonal close packed lattice. In this case, the isotropic-nematic phase transition occurs at quite a low density, $\rho/\rho_{cp} \approx 0.2$, and the simulations are performed at a state point corresponding to $\rho/\rho_{cp} \approx 0.28$, for which the nematic order parameter is $Q \approx 0.85$. For this model, temperature is not a significant thermodynamic quantity, so it is possible to choose $k_B T = 1$ throughout.

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. Surface anchoring in this system has been studied recently \cite{10} for a system with wall separation $L_z = 125 b = 8.33a$, by applying an orienting perturbation at one of the walls and observing the response at the other. This yielded an estimate of the extrapolation length $\lambda \approx 35b \approx 2.33a$. In the current work, simulations were carried out for systems of $N = 2000$ particles with wall separations $L_z = 6.58a, 8.22a, 9.86a$, which (from the above estimate of $\lambda$) would correspond to surface anchoring parameters in the range $2.8 \leq \xi \leq 4.2$.

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 (one sweep is one attempted move per particle).

### IV. SIMULATION RESULTS AND DISCUSSION

The simulation results were analysed to give a density profile, and an order tensor profile, which are shown in Figs 1, 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 \cite{13}. 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 former is a physical quantity, which, in statistical mechanics, is determined by the positions at which the liquid number density becomes identically zero. The latter appears in the elastic theory: it is determined by the positions at which the orientational elastic boundary conditions are applied. Physically, 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 $L_w$ (which may be positive or negative) 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 ra-
tios $\langle |Q_{\alpha z}(k_z, L_1)|^2 \rangle / \langle |Q_{\alpha z}(k_z, L_2)|^2 \rangle$ for different $L_{1,2}$ since they reveal more structure for large $k_z$. Plotting the results in this way removes the overall scaling of the amplitudes of fluctuations, which are sensitive to changes in $\lambda$, while the shapes of the curves, and the characteristic oscillation wavelengths, are sensitive to the choice of $L_w$. These ratios with $L_1 = 6.58a$, $8.22a$, $L_2 = 9.86a$ and corresponding fitting curves are plotted in Fig. 3. The best fits were obtained with $L_w/a = 0.59$. In this figure we also plot theoretical curves with $L_w = 0$: the clear discrepancy with the simulation results indicates that the simulation box size $L_z$ is indeed significantly different from the actual cell thickness.

Following the determination of $L_w$, we adjusted the extrapolation length $\lambda$ 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. The best fits were obtained with a bulk elastic constant $K a/k_B T \approx 66$ 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 $k_z$.

Finally, we note that the extrapolation distance relative to the simulation wall position is $L_w + \lambda \approx 2.89a$, which compares moderately well with the value $\lambda \approx 2.33a$ obtained in the previous study of this system. It should be noted that the director configuration of that work does not allow one to determine, separately, $L_w$ and $\lambda$, so the quoted value of $\lambda$ really represents $\lambda + L_w$.

We have to point out some possible limitations of the method. The first one is computational time. The effect of the surfaces is to dampen the amplitude of long-wavelength modes; these have the longest relaxation times, according to eqn (10), and so it is essential to carry out very long runs to adequately sample them. We have paid some attention to estimating the error bars on the measured values of $|Q_{\alpha z}(k_z)|^2$, as indicated in Fig. 4: the larger values at low $k_z$ follow directly from this effect. We shall return to examine the time-dependence of fluctuations in a future publication. The second limitation is the actual sensitivity of the measured averages to the variation in the anchoring strength and cell thickness. One might expect that in practice it is not possible to measure large values of the anchoring parameter $\xi = L_z/\lambda$, so we need reasonably thin cells. As the cell thickness $L_z$ becomes large, the fluctuation spectrum becomes insensitive to $L_w$. However, it is important that the walls do not become too close: the bulk region should be sufficiently large compared to the interfacial region. Only in this case can we assume that the scalar order parameter $Q$ in the liquid crystal bulk is constant for large scale fluctuation modes.

To summarize, analysis of the director fluctuations in nematic liquid crystal slabs allowed us to measure the surface anchoring strength parameter. The method has been tested for a system of hard ellipsoids of revolution of elongation $e = 15$ confined between hard walls with homeotropic anchoring. Careful analysis of fluctuations in slabs of different thickness has allowed us to resolve, for the first time, the position of the elastic boundary condi-
tion relative to the simulation wall, as well as measuring the extrapolation length. The elastic theory gives a good description at low wavenumbers, but is less accurate at higher wavenumbers.

Acknowledgments

This research was supported by EPSRC. D.A. acknowledges support through grant ORS/99007015 of the Overseas Research Students Award; G.G. acknowledges the support of a British Council Grant; M.P.A. is grateful to the Alexander von Humboldt foundation. Some of this work was carried out while visiting the Max Planck Institute for Polymer Research, Mainz, and the Institute of Physics, University of Mainz; the authors are grateful to Kurt Kremer and Kurt Binder for their hospitality, and conversations with F. Schmid and H. Lange are gratefully acknowledged.

Fluctuation spectrum

To obtain the spectrum of the \( q_z \) modes of the fluctuations we need to select from the eigenfunctions of the operator \(-\frac{1}{2}K\nabla^2 \) those which satisfy the boundary conditions \( \delta \). Substituting eqn (16) into the boundary conditions \( \delta \), we obtain a set of linear equations

\[
(\xi + i\chi)e^{i\xi\delta n^{(+)}(\pi)} + (\xi - i\chi)e^{-i\xi\delta n^{(-)}(\pi)} = 0,
\]

\[
(\xi - i\chi)\delta n^{(+)}(\pi) + (\xi + i\chi)\delta n^{(-)}(\pi) = 0.
\]

This set of linear homogeneous equations for \( \delta n^{(\pm)} \) has a nontrivial solution if its determinant equals zero. This condition leads to the secular equation for the \( q_z \) vector \( \Phi \) and relation (16).

In the case of strong anchoring, \( \xi \rightarrow \infty \), the q spectrum is equidistant: \( q_zL = \pi n \), where \( n \) is a positive integer. For finite anchoring coefficient \( \xi \), we have a shift in this spectrum. The magnitude of the shift depends on the anchoring parameter \( \xi \). Indeed, for sufficiently strong anchoring parameters, \( \xi >> 1 \), asymptotically:

\[
q_zL = \pi n - \frac{2\pi n}{\xi}, \quad n = 1, 2, ..., \ n/\xi << 1,
\]

which is equivalent to replacing \( L \) by \((L + 2\lambda)\), \( \lambda \) being the extrapolation length.

For weak anchoring, \( \xi << 1 \):

\[
q_zL = \pi n + \frac{2\pi}{\pi n}, \quad n = 1, 2, ..., \qquad q_zL = \xi^{1/2}, \quad n = 0.
\]

The spectrum of the \( q_z, q_y \) wavevectors depends on the system geometry. Again, if we have periodic boundary conditions in \( x \) and \( y \) directions, the \( q_x \) and \( q_y \) have a discrete spectrum, on a finite grid \( q_xL = 2\pi n_{\alpha}, \ (n_{\alpha} = 0, 1, 2, ...), \) otherwise \( q_x = (q_x, q_y) \) are unrestricted.

It is also easy to show that the eigenfunctions which correspond to different eigenvalues \( q_z \) and \( q_z' \) are orthogonal. Indeed, using eqn (16) we can rewrite

\[
\Phi(q_{\perp}, q_z) = \delta n^{(+)}(q_{\perp}, q_z)e^{i\pi n_{\perp}r_{\perp}} + \delta n^{(-)}(q_{\perp}, q_z)e^{-i\pi n_{\perp}r_{\perp}} = \frac{2i}{\chi \xi + \chi} \left[ \chi \cos(q_zz) + \xi \sin(q_zz) \right] \delta n^{(+)}(q_{\perp}, q_z).
\]

It is easy to check using the secular equation \( \delta \) that functions \( \phi(q_z) = \chi \cos(q_zz) + \xi \sin(q_zz) \) are orthogonal, i.e.

\[
\int_0^L \phi(q_z)\phi(q_z')dz = \frac{1}{2} L (2\xi + \chi^2 + \xi^2) \delta_{q_z, q_z'}, \quad (16)
\]

where \( \delta_{q_z, q_z'} \) is the Kronecker delta. Therefore, the eigenfunctions \( \Phi(q_{\perp}, q_z) \) are orthogonal and can be normalized using eqn (16).

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