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Molecular simulation and theory of liquid crystals: chiral parameters, flexoelectric coefficients, and elastic constants†

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We present an overview of the simulation methods available to calculate the phenomenological coefficients which appear in the Frank free energy of nematic liquid crystals: the elastic constants, helicity parameter, and flexoelectric coefficients. We concentrate on approaches which are based on measuring and correlating molecular orientational stresses, as these have not received much attention previously, and their statistical mechanical basis seems not to be widely understood. We relate methods which rely on applying external fields or distortions to methods which rely on static equilibrium correlations, highlighting some of the unresolved problems, and presenting some new results and perspectives.

I Introduction

The purpose of this article is to review some of the statistical mechanical expressions for calculating properties of nematic liquid crystals, from a knowledge of molecular properties, in computer simulations. We shall focus on the terms which appear in the Oseen–Frank free energy:[1–3] the flexoelectric coefficients, and the helicity parameter, which accompany linear terms in the director gradients; and the Frank elastic constants which appear with squared gradient terms. These properties, along with surface anchoring coefficients (which we shall not discuss here) are amongst the most fundamental in liquid crystal device design: there is a clear need to relate them to molecular shape, and the details of molecular interactions, and simulation provides a natural tool for this purpose. As part of this review, we present new methods for estimating flexoelectric coefficients and elastic constants, which may be worth testing in simulations, and a recently-tested method for calculating the helicity parameter, and hence the helical pitch.

A key element in this process is the identification of microscopic variables which correspond to macroscopic (orientational) stresses and strains, a situation which has been explored quite thoroughly in the analogous situation of computing solid-state elastic moduli. A one-dimensional example illustrates, schematically, the main points. Thermodynamic fluctuation theory[4,5] may allow one to write the free energy of a condensed-phase system in the form of an expansion in the gradient $\varphi' = \partial\varphi/\partial x$ of some order parameter $\varphi(x)$ which is assumed to vary smoothly in space

$$\begin{aligned}\mathscr{F}[\varphi(x)] &= \mathscr{F}_0 + \int_V \mathrm{d}x \frac{1}{2} K\varphi'(x)^2 \\ &= \mathscr{F}_0 + \frac{1}{V}\sum_k \frac{1}{2} Kk^2 |\tilde{\varphi}(k)|^2;\end{aligned} \tag{1}$$

$\tilde{\varphi}(k)$ denotes the Fourier transform of $\varphi(r)$ (see Appendix A). This expansion should hold at long wavelength or small wavenumber k, and a large-k cutoff is implicit in defining the scale of coarse-graining: the precise choice of cutoff should not be significant. Often one includes a term $\frac{1}{2}C\varphi(x)^2$ in the above equation, which would lead to the definition of a correlation length $\xi = \sqrt{(K/C)}$; omitting this implies that correlations are long-ranged (typically decaying algebraically rather than exponentially).

Suitable stress, $\sigma(x)$, and strain, $\varphi'(x)$, variables are defined through a fundamental thermodynamic relation such as

$$\begin{aligned}\mathrm{d}U &= T\mathrm{d}S + \int_V \mathrm{d}x\sigma(x)\mathrm{d}\varphi'(x) \\ &= T\mathrm{d}S + \frac{1}{V}\sum_k \tilde{\sigma}(-k)\mathrm{i}k\mathrm{d}\tilde{\varphi}(k),\end{aligned} \tag{2}$$

with an associated thermodynamic derivative, namely an elastic modulus K, which is assumed to depend at worst only weakly on k:

$$K = \frac{\partial\sigma}{\partial\varphi'} \Leftrightarrow \sigma(x) = K\varphi'(x) \Leftrightarrow \tilde{\sigma}(k) = \mathrm{i}kK\tilde{\varphi}(k). \tag{3}$$

Then it may be shown that the Helmholtz free energy $F = U - TS$, obtained from eqn. (2), satisfies

$$\left.\frac{\partial^2 F}{\partial\tilde{\varphi}(k)\partial\tilde{\varphi}(k')}\right|_T = k^2 K\delta_{-k',k}.$$

This provides the necessary link $F \leftrightarrow \mathscr{F}$.

One way to proceed is to recognize that the probability distribution function for fluctuations of φ will take a Gaussian form dictated by

$$\mathscr{P}[\varphi(x)] \propto \mathrm{e}^{-\beta\mathscr{F}[\varphi(x)]}, \quad \beta = 1/k_\mathrm{B}T.$$

An advantage of this approach lies in the relative ease of identifying a microscopic variable corresponding to φ. This leads to several variants of the ‘strain fluctuation’ method. In the context of crystal elastic constants, one may study strains defined through Fourier components of atomic displacements[6] giving a relation of the type

$$\langle\tilde{\varphi}(k)\tilde{\varphi}(-k)\rangle = \frac{Vk_\mathrm{B}T}{Kk^2}. \tag{4}$$

A similar equation based on molecular orientations, which

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define director fluctuations, may be derived for nematic liquid crystals.[7,8] In this context, 'strain' means a gradient of the director $\hat{\boldsymbol{n}}$: splay, twist or bend. This has been the standard approach to the determination of Frank elastic constants by simulation for many years.[9–13] It is well tailored to the periodic boundary conditions commonly used in simulation. On the other hand, an extrapolation to low-k is necessary (with an associated increase in the timescales of the most important, longest-wavelength, fluctuations); it is not possible simply to take the limit $k=0$ in eqn. (4). Moreover, for realistic, three-dimensional, systems, K is replaced by a tensor $\boldsymbol{K}$, and some kind of matrix inverse must be taken in eqn. (4), which complicates the analysis somewhat. A related approach (for crystals) is to perform a finite system-size analysis on the strain fluctuations in real space;[14] in a conventional periodic system one also needs to apply a constraint (in the analysis) to reflect the fact that the simulation box has fixed size and shape. Finally, one may modify the simulation to allow the system to change its shape and size, and hence (in principle) measure $\boldsymbol{K}$ from the overall strain fluctuations;[15,16] however, this approach seems to give poor convergence.[17,18] No similar approaches have been applied to liquid crystals, and we do not discuss them further here.

A second possible approach is to use the definition eqn. (3) directly: to carry out a simulation of a strained system, ideally one in which the strain is uniform, and measure the induced stress. This requires the derivation of a microscopic expression for the stress; for atomic crystals, the stress tensor may be defined in terms of intermolecular forces, while the analogous quantity for liquid crystals involves intermolecular torques. This approach is not widespread; to our knowledge, we carried out the only determination of a liquid crystal twist elastic constant in this way some years ago.[19] The geometry of periodic boundaries does not permit one to apply uniform splay or bend deformations, so this approach is limited. If one wishes to measure all the elastic constants in this way, it is necessary to perturb the system with some nonzero-k field, which induces a k-dependent orientational strain compatible with the boundaries. However, there are many possible perturbing fields, and the stress response may, in general, depend on which field is applied; part of this article is devoted to discussing this point. The situation is simpler if one wishes to measure terms in the free energy which are linear in the orientational strains. For chiral molecules, and for molecules exhibiting flexoelectric behaviour in the presence of a uniform electric field, the undistorted liquid crystal is already in a state of nonzero, uniform stress: this provides a practical route to the helicity parameter[20–23] and the flexoelectric coefficients. We describe this proposed method below.

A third approach combines equations like (3), (4) to give

$$\langle\tilde{\sigma}(k)\tilde{\sigma}(-k)\rangle = Vk_BTK \tag{5}$$

that is, one should be able to measure K through stress fluctuations. A key point of this equation is that the quantity on the left is expected to be well behaved when one takes the limit[24] $k\rightarrow 0$, so there is no longer any need to perform an extrapolation: one may simply study fluctuations of the extensive quantity $\sigma\equiv\lim_{k\rightarrow 0}\sigma(k)$. This makes it potentially very attractive from the viewpoint of simulations. However, this equation is misleading. When the conventional microscopic expression for the stress tensor is adopted, eqn. (5) gives an infinite frequency elastic modulus, defined as the ratio of the time derivative of the stress to the rate of strain. For example, in a simple liquid, the isothermal shear elastic constant is zero, while the infinite frequency shear elastic modulus is given by an equation like (5).[24] For crystals, the necessary expressions for isothermal elastic constants are quite well known.[16,18,25–27] For liquid crystals, corresponding derivations have appeared,[28–30] albeit in rather brief form. Our experience is that there is still considerable confusion about the statistical mechanical background to these equations, particularly in the context of periodic systems used in simulations; because of this, we devote a large part of the current article to them.

Yet a fourth approach exists. The squared-gradient form of eqn. (1) may be derived in a density functional formalism: in fact it arises directly from a low-k expansion of the direct correlation function $c(\mathbf{1},\mathbf{2})$, where $\mathbf{1}$ and $\mathbf{2}$ represent the positions $\boldsymbol{r}$ and orientations $\boldsymbol{\Omega}$ of two molecules. Accordingly, terms like the elastic constants, helicity coefficient, and flexoelectric coefficients, may be expressed as integrals over $c(\mathbf{1},\mathbf{2})$.[31–39] This has led to some determinations of these properties by simulation[40–45] in a two-stage process: (i) invert the pair correlation function $h(\mathbf{1},\mathbf{2})$ of a uniform liquid crystal, using the Ornstein–Zernike equation, to give $c(\mathbf{1},\mathbf{2})$; (ii) compute the various integrals over $c(\mathbf{1},\mathbf{2})$ to give properties of interest. This article will not focus on this approach, but we just make a few comments. Firstly, the inversion procedure $h(\mathbf{1},\mathbf{2})\rightarrow c(\mathbf{1},\mathbf{2})$ involves some of the same difficulties as the direct analysis of low-k 'strain' fluctuations: for example the asymptotic behaviour $\langle\tilde{\varphi}(k)\tilde{\varphi}(-k)\rangle\sim k^{-2}$ implies long-ranged correlations of some components of $h(\mathbf{1},\mathbf{2})\sim r^{-1}$ in three dimensions, which must be handled carefully. Secondly, care must be taken to formulate the distortion of the single-particle density, $\rho(\mathbf{1})\equiv(\boldsymbol{r},\boldsymbol{\Omega})$, which underpins the direct correlation function expressions, in a sufficiently general way. The simplest ansatz, used in deriving expressions for the Frank elastic constants, is to simply rotate the orientational distribution function so as to follow the director distortion: this, however, does not allow the kind of dipolar relaxation which gives rise to the flexoelectric effect, and this same relaxation produces corrections to the elastic constants which will be nonzero for unsymmetrical molecules.[38,39] The third point is that, to our knowledge, only in one case[45] has $c(\mathbf{1},\mathbf{2})$ been determined without making significant approximations in the inversion process, and only in this case has satisfactory agreement with elastic constants obtained by other methods been demonstrated. Although this approach is promising, it needs further testing and study.

The current paper is organized as follows. In section II we set out the macroscopic equations arising from the Frank free energy, and emphasize the way in which they suggest simulation 'experiments' to determine the coefficients appearing in them. In section III we set out the microscopic approach to determining these coefficients, concentrating on expressions involving 'orientational stresses', and making contact with statistical mechanical perturbation theory. Finally, in section IV, we summarize and draw some conclusions. Some of the definitions, derivations, and comparisons with other notation, are placed in appendices.

II. Macroscopic description

A. Real-space form

Begin with the notation established by Frank,[2] Meyer,[46] and Helfrich.[47] If we take the unperturbed director $\boldsymbol{n}=\boldsymbol{z}$, and consider only small deformations $\delta\hat{n}_x$, $\delta\hat{n}_y$, then there are six nonzero gradients[60]

$$\text{Splays:}\quad s_1=\partial_x\hat{n}_x \qquad s_2=\partial_y\hat{n}_y \tag{6a}$$

$$\text{Twists:}\quad t_1=\partial_y\hat{n}_x \qquad t_2=\partial_x\hat{n}_y \tag{6b}$$

$$\text{Bends:}\quad b_1=\partial_z\hat{n}_x \qquad b_2=\partial_z\hat{n}_y \tag{6c}$$

with $\partial_\alpha\equiv\partial/\partial r_\alpha$. The gradient tensor of $\hat{\boldsymbol{n}}$, defined by $(\nabla\hat{\boldsymbol{n}})_{\alpha\beta}=\partial_\alpha\hat{n}_\beta$, may be expressed

$$\boldsymbol{\nabla}\hat{\boldsymbol{n}}=\begin{pmatrix} s_1 & t_2 & 0 \\ t_1 & s_2 & 0 \\ b_1 & b_2 & 0 \end{pmatrix}.$$

It is sometimes convenient to define splay and bend vectors and a twist scalar, bearing in mind that all gradients of $\hat{n}_z$ are zero to first order:

$$\boldsymbol{s}=s_1\hat{\boldsymbol{z}}+s_2\hat{\boldsymbol{z}}=\hat{\boldsymbol{n}}(\nabla\cdot\hat{\boldsymbol{n}}) \tag{7a}$$

$$t=(t_1-t_2)=\hat{\boldsymbol{n}}\cdot\nabla\wedge\hat{\boldsymbol{n}} \tag{7b}$$

$$\boldsymbol{b}=b_1\hat{\boldsymbol{x}}+b_2\hat{\boldsymbol{y}}=(\hat{\boldsymbol{n}}\cdot\nabla)\hat{\boldsymbol{n}}=-\hat{\boldsymbol{n}}\wedge(\nabla\wedge\hat{\boldsymbol{n}}). \tag{7c}$$

This last equation follows from

$$\begin{aligned}-\left(\hat{\boldsymbol{n}}\wedge(\nabla\wedge\hat{\boldsymbol{n}})\right)_\alpha &= -\epsilon_{\alpha\beta\gamma}\hat{n}_\beta\epsilon_{\gamma\mu\nu}\partial_\mu\hat{n}_\nu \\ &= -\left(\delta_{\alpha\mu}\delta_{\beta\nu}-\delta_{\alpha\nu}\delta_{\beta\mu}\right)\hat{n}_\beta\partial_\mu\hat{n}_\nu \\ &= \hat{n}_\beta\partial_\beta\hat{n}_\alpha-\hat{n}_\beta\partial_\alpha\hat{n}_\beta \\ &= (\hat{\boldsymbol{n}}\cdot\nabla)\hat{n}_\alpha-\frac{1}{2}\partial_\alpha|\hat{\boldsymbol{n}}|^2\end{aligned}$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi–Civita tensor. Here and henceforth we sum over repeated Greek indices; the last term vanishes because $\hat{\boldsymbol{n}}$ is a unit vector. These definitions allow the Frank free energy density to be written in a manner independent of the choice of axes

$$\mathscr{F}=\int \mathrm{d}\boldsymbol{r}\mathscr{f}(\boldsymbol{r}) \tag{8a}$$

$$\mathscr{f}(\boldsymbol{r})=\frac{1}{2}\left[K_1|\boldsymbol{s}|^2+K_2t^2+K_3|\boldsymbol{b}|^2\right]+ht. \tag{8b}$$

K_1, K_2 and K_3 are respectively the splay, twist and bend elastic constants; for chiral phases, the helicity parameter determines the equilibrium pitch P, and corresponding wavenumber $k_0=2\pi/P$, through $h=K_2k_0$.

The flexoelectric effect arises from the coupling between polarization and director distortion. In the presence of an 'electric' field $\boldsymbol{E}(\boldsymbol{r})$ which couples to a macroscopic polarization density $\mathscr{p}(r)$, the free energy density becomes

$$\mathscr{g}(\boldsymbol{r})=\mathscr{f}(\boldsymbol{r})-\mathscr{p}(\boldsymbol{r})\cdot\boldsymbol{E}(\boldsymbol{r}).$$

The polarization density will take the form $\mathscr{p}(\boldsymbol{r})=\mathscr{p}^{\mathrm{el}}(\boldsymbol{r})+\mathscr{p}^{\mathrm{d}}(\boldsymbol{r})$ containing a part $\mathscr{p}^{\mathrm{el}}(\boldsymbol{r})$ proportional to the applied field and a part $\mathscr{p}^{\mathrm{d}}(\boldsymbol{r})$ proportional to the director distortion, each with corresponding phenomenological coefficients. Note that, in writing this, we simply acknowledge that a non-zero polarization may be induced by either of these physical mechanisms operating in isolation; this does not imply that we can write down a microscopic definition of $\mathscr{p}$ in which $\mathscr{p}^{\mathrm{el}}$ and $\mathscr{p}^{\mathrm{d}}$ appear separately. Symmetry considerations dictate[61]

$$\begin{aligned}\mathscr{p}^{\mathrm{el}}(\boldsymbol{r}) &= \varepsilon_\perp\hat{\boldsymbol{n}}\wedge\boldsymbol{E}(\boldsymbol{r})\wedge\hat{\boldsymbol{n}}+\varepsilon_\parallel(\boldsymbol{E}(\boldsymbol{r})\cdot\hat{\boldsymbol{n}})\hat{\boldsymbol{n}} \\ &\equiv \varepsilon_\perp\boldsymbol{E}_\perp(\boldsymbol{r})+\varepsilon_\parallel\boldsymbol{E}_\parallel(\boldsymbol{r})\end{aligned} \tag{9a}$$

$$\begin{aligned}\mathscr{p}^{d}(\boldsymbol{r}) &= e_1\hat{\boldsymbol{n}}(\boldsymbol{\nabla}\cdot\hat{\boldsymbol{n}}(\boldsymbol{r}))+e_3(\hat{\boldsymbol{n}}\cdot\boldsymbol{\nabla})\hat{\boldsymbol{n}}(\boldsymbol{r}) \\ &= e_1\hat{\boldsymbol{n}}(\boldsymbol{\nabla}\cdot\hat{\boldsymbol{n}}(\boldsymbol{r}))-e_3\hat{\boldsymbol{n}}\wedge(\boldsymbol{\nabla}\wedge\hat{\boldsymbol{n}}(\boldsymbol{r})) \\ &= e_1\boldsymbol{s}(\boldsymbol{r})+e_3\boldsymbol{b}(\boldsymbol{r}).\end{aligned} \tag{9b}$$

The field has been resolved into components

$$\boldsymbol{E}_\parallel(\boldsymbol{r})=(\boldsymbol{E}(\boldsymbol{r})\cdot\hat{\boldsymbol{n}})\hat{\boldsymbol{n}}\quad \boldsymbol{E}_\perp(\boldsymbol{r})=\hat{\boldsymbol{n}}\wedge\boldsymbol{E}(\boldsymbol{r})\wedge\hat{\boldsymbol{n}}=\boldsymbol{E}(\boldsymbol{r})-(\boldsymbol{E}(\boldsymbol{r})\cdot\hat{\boldsymbol{n}})\hat{\boldsymbol{n}}.$$

The dielectric tensor is assumed to be diagonal in the director frame, with components $\varepsilon_\parallel$ and $\varepsilon_\perp$, respectively, along and perpendicular to the director: these components dictate the response of the polarization to an applied field, even in the absence of coupling to nematic degrees of freedom. The flexoelectric coefficients e_1, e_3, reflect the fact that polarization can be induced by deforming the director, without applying a field $\boldsymbol{E}(\boldsymbol{r})$. The free energy density takes the following form[3]

$$\mathscr{G}=\mathscr{F}-\int \mathrm{d}\boldsymbol{r}\mathscr{p}(r)\cdot\boldsymbol{E}(\boldsymbol{r})=\int \mathrm{d}\boldsymbol{r}\mathscr{g}(\boldsymbol{r}) \tag{10a}$$

$$\begin{aligned}\mathscr{g}(\boldsymbol{r}) &= \frac{1}{2}[K_1|\boldsymbol{s}(\boldsymbol{r})|^2+K_2t(\boldsymbol{r})^2+K_3|\boldsymbol{b}(\boldsymbol{r})|^2] \\ &\quad +ht(\boldsymbol{r})-e_1\boldsymbol{E}(\boldsymbol{r})\cdot\boldsymbol{s}(\boldsymbol{r})-e_3\boldsymbol{E}(\boldsymbol{r})\cdot\boldsymbol{b}(\boldsymbol{r}) \\ &\quad -\frac{1}{2}[\varepsilon_\perp|\boldsymbol{E}_\perp(\boldsymbol{r})|^2+\varepsilon_\parallel|\boldsymbol{E}_\parallel(\boldsymbol{r})|^2].\end{aligned} \tag{10b}$$

It is convenient to describe small deformations of the director $\delta\hat{\boldsymbol{n}}$ in terms of a vector $\boldsymbol{\delta\theta}=\delta\theta\hat{\boldsymbol{\theta}}$, which represents a rotation through angle $\delta\theta$ about an axis $\hat{\boldsymbol{\theta}}$:

$$\boldsymbol{\delta\theta}=\hat{\boldsymbol{n}}\wedge\delta\hat{\boldsymbol{n}}\qquad \delta\theta_\alpha=\epsilon_{\alpha\beta\gamma}\hat{n}_\beta\delta\hat{n}_\gamma$$

$$\delta\hat{\boldsymbol{n}}=-\hat{\boldsymbol{n}}\wedge\boldsymbol{\delta\theta}=\boldsymbol{\delta\theta}\wedge\hat{\boldsymbol{n}}\qquad \delta n_\alpha=\epsilon_{\alpha\beta\gamma}\delta\theta_\beta\hat{n}_\gamma.$$

The gradient tensor of $\boldsymbol{\theta}$, $(\nabla\boldsymbol{\theta})_{\alpha\beta}=\partial_\alpha\theta_\beta\equiv\gamma_{\alpha\beta}$ is related to $\nabla\hat{\boldsymbol{n}}$ by

$$\nabla\theta=-(\nabla\hat{\boldsymbol{n}})\wedge\hat{\boldsymbol{n}}\qquad \partial_\alpha\theta_\delta=-(\partial_\alpha\hat{n}_\beta)\hat{n}_\gamma\epsilon_{\beta\gamma\delta}$$

$$\nabla\hat{\boldsymbol{n}}=(\nabla\theta)\wedge\hat{\boldsymbol{n}}\qquad \partial_\alpha\hat{n}_\delta=(\partial_\alpha\theta_\beta)\hat{n}_\gamma\epsilon_{\beta\gamma\delta}.$$

In terms of the deformations of eqn. (6), defined with respect to $\hat{\boldsymbol{n}}=\hat{\boldsymbol{z}}$:

$$\boldsymbol{\nabla\theta}=\begin{pmatrix} -t_2 & s_1 & 0 \\ -s_2 & t_1 & 0 \\ -b_2 & b_1 & 0 \end{pmatrix}.$$

Thermodynamic (functional) derivatives of eqn. (10) may be written

$$\boldsymbol{\pi}_{\mathrm{splay}}(\boldsymbol{r})\equiv\frac{\delta\mathscr{G}}{\delta\boldsymbol{s}(\boldsymbol{r})}=K_1\boldsymbol{s}(\boldsymbol{r})-e_1\boldsymbol{E}(\boldsymbol{r}) \tag{11a}$$

$$\pi_{\mathrm{twist}}(\boldsymbol{r})\equiv\frac{\delta\mathscr{G}}{\delta t(\boldsymbol{r})}=K_2t(\boldsymbol{r})+h \tag{11b}$$

$$\boldsymbol{\pi}_{\mathrm{bend}}(\boldsymbol{r})\equiv\frac{\delta\mathscr{G}}{\delta\boldsymbol{b}(\boldsymbol{r})}=K_3\boldsymbol{b}(\boldsymbol{r})-e_3\boldsymbol{E}(\boldsymbol{r}) \tag{11c}$$

$$\mathscr{p}(\boldsymbol{r})\equiv-\frac{\delta\mathscr{G}}{\delta\boldsymbol{E}(\boldsymbol{r})}=e_1\boldsymbol{s}(\boldsymbol{r})+e_3\boldsymbol{b}(\boldsymbol{r})+\varepsilon_\perp\boldsymbol{E}_\perp(\boldsymbol{r})+\varepsilon_\parallel\boldsymbol{E}_\parallel(\boldsymbol{r}). \tag{11d}$$

The quantities on the left of eqns. (11a)–(11c) are torques per unit area (see later), and they will vanish in the unstrained system. In all of these equations it is assumed that the variation of fields and responses is sufficiently smooth that the undistorted director orientation may be taken as a reference direction. If the gradients and fields are constants, $\boldsymbol{s}(\boldsymbol{r})=\boldsymbol{s}$, $\boldsymbol{E}(\boldsymbol{r})=\boldsymbol{E}$ *etc.* everywhere, the functional derivatives on the left of these equations become simple derivatives of the free energy density, and the dependence on $\boldsymbol{r}$ may be dropped:

$$\boldsymbol{\pi}_{\mathrm{splay}}=\frac{\boldsymbol{\Pi}_{\mathrm{splay}}}{V}\equiv\frac{\partial\mathscr{g}}{\partial\boldsymbol{s}}=K_1\boldsymbol{s}-e_1\boldsymbol{E} \tag{12a}$$

$$\pi_{\mathrm{twist}}=\frac{\Pi_{\mathrm{twist}}}{V}\equiv\frac{\partial\mathscr{g}}{\partial t}=K_2t+h \tag{12b}$$

$$\boldsymbol{\pi}_{\mathrm{bend}}=\frac{\boldsymbol{\Pi}_{\mathrm{bend}}}{V}\equiv\frac{\partial\mathscr{g}}{\partial\boldsymbol{b}}=K_3\boldsymbol{b}-e_3\boldsymbol{E} \tag{12c}$$

$$\mathscr{p}=\frac{\mathscr{P}}{V}\equiv-\frac{\partial\mathscr{g}}{\partial\boldsymbol{E}}=e_1\boldsymbol{s}+e_3\boldsymbol{b}+\varepsilon_\perp\boldsymbol{E}_\perp+\varepsilon_\parallel\boldsymbol{E}_\parallel. \tag{12d}$$

Note that, in contrast to the notation for the fields and gradients, we adopt a notation which distinguishes extensive variables $\boldsymbol{\Pi}=\int\mathrm{d}\boldsymbol{r}\;\boldsymbol{\pi}(\boldsymbol{r})$, $\mathscr{P}=\int\mathrm{d}\boldsymbol{r}\mathscr{p}(\boldsymbol{r})$ and intensive variables $\boldsymbol{\pi}=\boldsymbol{\Pi}/V$, $\mathscr{p}=\mathscr{P}/V$ *etc.*

Consider now the case where the undistorted director is $\hat{\boldsymbol{n}}=\hat{\boldsymbol{z}}$, $\hat{\boldsymbol{\theta}}=\hat{\boldsymbol{y}}$, director deformations are parametrized by the angle $\delta\theta_y$ such that $\delta\hat{\boldsymbol{n}}=\delta\theta_y\hat{\boldsymbol{x}}$, $\delta\boldsymbol{\theta}=\delta\theta_y\hat{\boldsymbol{y}}$, and we apply either a field $\boldsymbol{E}_\parallel=\boldsymbol{E}_z(x)\;\hat{\boldsymbol{z}}$ or $\boldsymbol{E}_\perp=\boldsymbol{E}_x(z)\hat{\boldsymbol{x}}$. Then we need only consider separate cases of pure splay, pure twist, or pure bend, generated by the three choices of gradient direction as defined in Table 1. The free energy per unit area takes the same form in each case:

$$\begin{aligned}\mathscr{G}/\mathscr{A} &= \int \mathrm{d}\zeta \frac{1}{2} K\theta'(\zeta)^2 - eE(\zeta)\theta'(\zeta) - \frac{1}{2}\varepsilon E(\zeta)^2 \\ &\equiv \int \mathrm{d}\zeta \mathscr{g}(\zeta)\end{aligned}$$

with the variables defined in Table 2, writing $\delta\theta_y = \theta$ for compactness. The calculus of variations is straightforwardly applied to this equation. Firstly, we may identify π with the torque. Add boundary terms of the form $\mathscr{G}_1(\theta_1)$ and $\mathscr{G}_2(\theta_2)$ where $\theta_1 = \theta(\zeta_1)$, $\theta_2 = \theta(\zeta_2)$. Minimize $\mathscr{G} + \mathscr{G}_1 + \mathscr{G}_2$, with respect to variations of $\theta(\zeta)$, for specified $E(\zeta)$. The term in ε is independent of θ and therefore does not affect the profile. The integrand depends on $\theta' = \mathrm{d}\theta/\mathrm{d}\zeta$, not on $\theta(\zeta)$ explicitly, so we may write the Euler–Lagrange equation

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\zeta}\frac{\partial \mathscr{g}}{\partial \theta'(\zeta)} &= \frac{\mathrm{d}}{\mathrm{d}\zeta}(K\theta'(\zeta) - eE(\zeta)) \\ &= \frac{\mathrm{d}\pi(\zeta)}{\mathrm{d}\zeta} = 0 \Rightarrow \pi(\zeta) = \pi = \text{constant.}\end{aligned} \tag{13}$$

At the boundaries we have

$$\left.\begin{aligned}\frac{\partial \mathscr{g}}{\partial \theta'}\Big|_{\zeta=\zeta_1} - \frac{\mathrm{d}\mathscr{G}_1/\mathscr{A}}{\mathrm{d}\theta_1} = 0 \\ \frac{\partial \mathscr{g}}{\partial \theta'}\Big|_{\zeta=\zeta_2} + \frac{\mathrm{d}\mathscr{G}_2/\mathscr{A}}{\mathrm{d}\theta_2} = 0\end{aligned}\right\} \Rightarrow -\pi = -\frac{\mathrm{d}\mathscr{G}_1/\mathscr{A}}{\mathrm{d}\theta_1} = \frac{\mathrm{d}\mathscr{G}_2/\mathscr{A}}{\mathrm{d}\theta_2}.$$

From this we see that $-\pi$ is the torque per unit area exerted by boundary 1 on the sample, and by the sample on boundary 2. Note carefully that periodic boundary conditions used in simulations do not imply that the torque is zero; they may, however, impose a constraint on the director gradient. The appropriate component of π for each symmetry case is given in Table 2. The profile will satisfy

$$\pi(\zeta) = \frac{\delta \mathscr{G}/\mathscr{A}}{\delta \theta'(\zeta)} = K\theta'(\zeta) - eE(\zeta) = \text{constant} \tag{14}$$

and the polarization will satisfy

$$\mathscr{p}(\zeta) = -\frac{\delta \mathscr{G}/\mathscr{A}}{\delta E(\zeta)} = e\theta'(\zeta) + \varepsilon E(\zeta). \tag{15}$$

These macroscopic equations suggest some ways of measuring the coefficients of interest, both in real experiments and in simulations. If $E(\zeta) = E$ is uniform, the gradient $\theta'(\zeta)$ will be constant; the typical periodic boundary conditions used in a simulation will make θ' zero or (in the case of twist) some other fixed value commensurate with the box length. In these situations, measurement of π will give K and e.

Table 1 Definitions of pure splay, twist and bend deformations for $\hat{\boldsymbol{n}} = \hat{\boldsymbol{z}}$ and $\delta\hat{\boldsymbol{n}}$ in the $\hat{\boldsymbol{x}}$ direction

	Gradient	$\delta\hat{\boldsymbol{n}}(\boldsymbol{r})$	$\delta\boldsymbol{\theta}(\boldsymbol{r})$	Real space	Fourier space
Splay	$\hat{\boldsymbol{x}}$	$\gamma x\hat{\boldsymbol{x}}$	$\gamma x\hat{\boldsymbol{y}}$	$\boldsymbol{s}(\boldsymbol{r}) = \partial_x\theta_y\hat{\boldsymbol{z}} = \gamma_{xy}\hat{\boldsymbol{z}} \equiv \gamma\hat{\boldsymbol{z}}$	$\tilde{\boldsymbol{s}}(\boldsymbol{k}) = \mathrm{i}k_x\tilde{\theta}_y(\boldsymbol{k})\hat{\boldsymbol{z}}$
Twist	$\hat{\boldsymbol{y}}$	$\gamma y\hat{\boldsymbol{x}}$	$\gamma y\hat{\boldsymbol{y}}$	$t(\boldsymbol{r}) = \partial_y\theta_y = \gamma_{yy} \equiv \gamma$	$\tilde{t}(\boldsymbol{k}) = \mathrm{i}k_y\tilde{\theta}_y(\boldsymbol{k})$
Bend	$\hat{\boldsymbol{z}}$	$\gamma z\hat{\boldsymbol{x}}$	$\gamma z\hat{\boldsymbol{y}}$	$\boldsymbol{b}(\boldsymbol{r}) = \partial_z\theta_y\hat{\boldsymbol{x}} = \gamma_{zy}\hat{\boldsymbol{x}} \equiv \gamma\hat{\boldsymbol{x}}$	$\tilde{\boldsymbol{b}}(\boldsymbol{k}) = \mathrm{i}k_z\tilde{\theta}_y(\boldsymbol{k})\hat{\boldsymbol{x}}$

Table 2 Correspondence of variables for pure splay, twist and bend deformations for $\hat{\boldsymbol{n}} = \hat{\boldsymbol{z}}$ and $\delta\hat{\boldsymbol{n}}$ in the $\hat{\boldsymbol{x}}$ direction

	Direction ζ, k	Elastic K	Flexoelectric e	Dielectric ε	Field E	Torque π
Splay	x, k_x	K_1	e_1	$\varepsilon_\parallel$	E_z	π_{xy}
Twist	y, k_y	K_2	$-h$	0	1	π_{yy}
Bend	z, k_z	K_3	e_3	$\varepsilon_\perp$	E_x	π_{zy}

B. Fourier-space form

Computer simulations are usually conducted in periodic boundaries, in which uniform gradients may not be conveniently applied. Hence, some of the above relations may be usefully expressed in Fourier space, with definitions given in Appendix A. We may then, in suitable circumstances, take the limit $k \longrightarrow 0$ to recover bulk expressions. Using eqn. (A2d), the free energy may be written

$$\begin{aligned}\mathscr{G} = \frac{1}{V}\sum_{\boldsymbol{k}} \frac{1}{2}&[K_1|\tilde{\boldsymbol{s}}(\boldsymbol{k})|^2 + K_2|\tilde{t}(\boldsymbol{k})|^2 + K_3|\tilde{\boldsymbol{b}}(\boldsymbol{k})|^2] \\ &+ h\tilde{t}(\boldsymbol{k}) - e_1\tilde{\boldsymbol{E}}(-\boldsymbol{k})\cdot\tilde{\boldsymbol{s}}(\boldsymbol{k}) - e_3\tilde{\boldsymbol{E}}(-\boldsymbol{k})\cdot\tilde{\boldsymbol{b}}(\boldsymbol{k}) \\ &- \frac{1}{2}[\varepsilon_\perp|\tilde{\boldsymbol{E}}_\perp(\boldsymbol{k})|^2 + \varepsilon_\parallel|\tilde{\boldsymbol{E}}_\parallel(\boldsymbol{k})|^2].\end{aligned}$$

We choose $\hat{\boldsymbol{n}} = \hat{\boldsymbol{z}}$ and $\delta\hat{\boldsymbol{n}} = \delta\theta_y\hat{\boldsymbol{x}}$ as before. Then, pure splay, twist and bend deformations are related to Fourier components of $\tilde{\theta}_y$ in the Cartesian directions as given in Table 1. Hence the free energy may be written

$$\begin{aligned}\mathscr{G} = \frac{1}{V}\sum_{\boldsymbol{k}} \frac{1}{2}&[K_1k_x^2 + K_2k_y^2 + K_3k_z^2]|\tilde{\theta}(\boldsymbol{k})|^2 \\ &+ \mathrm{i}k_yh\tilde{\theta}(\boldsymbol{k}) - \mathrm{i}k_xe_1\tilde{E}_z(-\boldsymbol{k})\tilde{\theta}(\boldsymbol{k}) \\ &- \mathrm{i}k_ze_3\tilde{E}_x(-\boldsymbol{k})\tilde{\theta}(\boldsymbol{k}) - \frac{1}{2}[\varepsilon_\perp|\tilde{E}_x(\boldsymbol{k})|^2 \\ &+ \varepsilon_\parallel|\tilde{E}_z(\boldsymbol{k})|^2],\end{aligned}$$

where again we abbreviate $\delta\tilde{\theta}_y = \tilde{\theta}$. We restrict our interest to one or another of these pure deformations as before. Then only one Cartesian component of $\boldsymbol{k}$ is relevant; coefficients $\tilde{\theta}(\boldsymbol{k})$ with nonzero values of the other components will be zero, and we may write

$$\begin{aligned}\mathscr{G} = \frac{1}{V}\sum_{k} \frac{1}{2}&Kk^2|\tilde{\theta}(k)|^2 - \mathrm{i}ke\tilde{E}(-k)\tilde{\theta}(k) \\ &- \frac{1}{2}\varepsilon|\tilde{E}(k)|^2\end{aligned} \tag{16}$$

where, once more, the variables appropriate to each case are identified in Table 2. Differentiating with respect to $\tilde{\theta}$ gives

$$\frac{1}{-\mathrm{i}k}\frac{\partial \mathscr{G}}{\partial \tilde{\theta}(-k)} = \frac{\mathrm{i}kK\tilde{\theta}(k) - e\tilde{E}(k)}{V} = \frac{\tilde{\Pi}(k)}{V}. \tag{17}$$

This equation exactly corresponds to eqn. (14). Differentiating the free energy with respect to $\tilde{E}$ gives

$$-\frac{\partial \mathscr{G}}{\partial \tilde{E}(-k)} = \frac{\mathrm{i}ke\tilde{\theta}(k) + \varepsilon\tilde{E}(k)}{V} = \frac{\tilde{\mathscr{P}}(k)}{V}. \tag{18}$$

This equation exactly corresponds to eqn. (15).

How do these equations suggest ways of measuring the desired coefficients in a simulation? In principle, in the absence of an electric field, or chirality, the elastic constant is determined from the relation between torque per unit area and orientational strain, through

$$K = \tilde{\Pi}(k)/\mathrm{i}k\tilde{\theta}(k) \tag{19}$$

while the flexoelectric coefficient is similarly determined through the polarization response

$$e = \tilde{\mathscr{P}}(k)/\mathrm{i}k\tilde{\theta}(k). \tag{20}$$

However, except for $k = 0$, where the periodic boundary conditions may constrain the corresponding director field component, $\mathscr{G}$ should be minimized with respect to arbitrary variations of $\tilde{\theta}(k)$. This means that $\tilde{\Pi}(k)$ as defined by eqn. (17) will be zero, so eqn. (19) cannot be used to estimate K directly. Also, if $\tilde{E}(k) = 0$, we deduce that $\mathrm{i}k\tilde{\theta}(k) = 0$, so eqn. (20) cannot be used to estimate e directly. We have

$$\mathrm{i}k\tilde{\theta}(k)=\frac{e}{K}\tilde{E}(k),$$

an equation which is only useful if both sides are nonzero. If this is the case, then the ratio e/K may be estimated from $\mathrm{i}k\tilde{\theta}(k)/\tilde{E}(k)$ (director response to spatially varying applied field), while eqn. (18) leads to

$$\tilde{\mathscr{P}}(k)=\mathrm{i}ke\tilde{\theta}(k)+\varepsilon\tilde{E}(k)=(\frac{e^2}{K}+\varepsilon)\tilde{E}(k)$$

(polarization response to applied field) which replaces eqn. (20). This is not very useful, as the ε term is likely to dominate in cases of practical interest. Notwithstanding this, the flexoelectric coefficient may be determined by applying an electric field, or equivalently the chiral parameter may be determined, by making a torque measurement and allowing $k \longrightarrow 0$:

$$\lim_{k\rightarrow 0}\tilde{\Pi}(k)=-e\tilde{E}(k)\Rightarrow\frac{\Pi}{V}-eE.$$

Note once more that $\Pi=\lim_{k\longrightarrow 0}\Pi(k)$ (an extensive dynamical variable), but that $E=\lim_{k\longrightarrow 0}\tilde{E}(k)/V$ where E represents the constant ('average') field.

Something more is necessary to generate a nonzero torque in the general case. Consider adding an extra term, of chosen wavenumber κ, to the free energy, of the form

$$\mathscr{G}_\lambda=\mathscr{G}_0+\lambda\tilde{\theta}(-\kappa)$$

where now $\mathscr{G}_0$ is the original free energy, eqn. (16); λ plays the role of a Lagrange multiplier, which will be chosen to generate a desired orientation profile. Minimizing $\mathscr{G}_\lambda$ with respect to variations of $\tilde{\theta}$ gives explicitly

$$\frac{1}{-\mathrm{i}\kappa}\frac{\partial\mathscr{G}_\lambda}{\partial\tilde{\theta}(-\kappa)}=\frac{\mathrm{i}\kappa K\tilde{\theta}(\kappa)-e\tilde{E}(\kappa)+\lambda V/(-\mathrm{i}\kappa)}{V}$$
$$=\frac{\tilde{\Pi}(\kappa)+\lambda V/(-\mathrm{i}\kappa)}{V}=0.$$

This gives the responses in the three variables of interest

$$\tilde{\Pi}(\kappa)=\lambda V/\mathrm{i}\kappa\Rightarrow\tilde{\tau}(\kappa)\equiv\mathrm{i}\kappa\tilde{\Pi}(\kappa)=\lambda V \tag{21a}$$

$$\tilde{\theta}(\kappa)=\frac{\lambda V}{\kappa^2 K}+\frac{e}{K}\frac{\tilde{E}(\kappa)}{\mathrm{i}\kappa}\Rightarrow\mathrm{i}\kappa\tilde{\theta}(\kappa)=\frac{\lambda V}{\mathrm{i}\kappa K}+\frac{e}{K}\tilde{E}(\kappa) \tag{21b}$$

$$\tilde{\mathscr{P}}(\kappa)=\frac{e}{K}\frac{\lambda V}{\mathrm{i}\kappa}+(\frac{e^2}{K}+\varepsilon)\tilde{E}(\kappa) \tag{21c}$$

where we have defined a macroscopic variable $\tilde{\tau}$ to satisfy $\tilde{\tau}(\kappa)=\mathrm{i}\kappa\tilde{\Pi}(\kappa)$. Under conditions of zero field, $\tilde{E}(\kappa)=0$ these satisfy eqns. (19,20). Note that, for the angle θ describing the distorted director profile to be small in the limit of low κ, it is necessary for the parameter λ to be of $\mathscr{O}(\kappa^2)$. Another interesting (and 'conjugate') modified free energy is

$$\mathscr{G}_\lambda-\mathscr{G}_0=\lambda\tilde{\tau}(-\kappa)=-\lambda\mathrm{i}\kappa\tilde{\Pi}(-\kappa)$$
$$=\lambda\mathrm{i}\kappa(-\mathrm{i}\kappa K\tilde{\theta}(-\kappa)-e\tilde{E}(-\kappa)).$$

Minimizing $\mathscr{G}_\lambda$ with respect to variations of $\tilde{\theta}$ gives

$$\frac{1}{-\mathrm{i}\kappa}\frac{\partial\mathscr{G}_\lambda}{\partial\tilde{\theta}(-\kappa)}=\frac{\tilde{\Pi}(\kappa)-\lambda V\mathrm{i}\kappa K}{V}=0$$

Hence the responses

$$\tilde{\Pi}(\kappa)=\mathrm{i}\kappa\lambda VK\Rightarrow\tilde{\tau}(\kappa)=\mathrm{i}\kappa\tilde{\Pi}(\kappa)=-\lambda V\kappa^2 K \tag{22a}$$

$$\tilde{\theta}(\kappa)=\lambda V+\frac{e}{K}\frac{\tilde{E}(\kappa)}{\mathrm{i}\kappa}\Rightarrow\mathrm{i}\kappa\tilde{\theta}(\kappa)=\mathrm{i}\kappa\lambda V+\frac{e}{K}\tilde{E}(\kappa) \tag{22b}$$

$$\tilde{\mathscr{P}}(\kappa)=\mathrm{i}\kappa\lambda Ve+(\frac{e^2}{K}+\varepsilon)\tilde{E}(\kappa) \tag{22c}$$

and these also satisfy eqns. (19,20). Note that, for the angle θ describing the distorted director profile to be small in the limit of low κ, it is necessary for the perturbation parameter λ to be of $\mathscr{O}(1)$. In the following section we address the question of whether these macroscopic results can be translated into microscopic perturbation-response expressions for the elastic and flexoelectric coefficients.

III. Microscopic description

It is not difficult to write down microscopic expressions for the polarization and the director variation. The polarization density is defined on the basis of a vector $\boldsymbol{\mathscr{p}}_i$ fixed in the frame of each molecule i, whose position vector is $\boldsymbol{r}_i$:

$$\boldsymbol{\mathscr{p}}(\boldsymbol{r})=\sum_i\boldsymbol{\mathscr{p}}_i\delta(\boldsymbol{r}-\boldsymbol{r}_i)\quad\tilde{\boldsymbol{\mathscr{P}}}(\boldsymbol{k})=\sum_i\boldsymbol{\mathscr{p}}_i\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}.$$

The choice of $\boldsymbol{\mathscr{p}}_i$ will affect the values of flexoelectric coefficients, but not the essential physics; for molecules possessing a degree of symmetry, a natural choice of $\boldsymbol{\mathscr{p}}_i$ may present itself; for realistic models, $\boldsymbol{\mathscr{p}}_i$ will be determined by the physical interaction of electrostatic multipole moments with applied electric fields.

The definition of director fluctuations was addressed by Forster.[48,49] Assume that, even if our molecules are not symmetrical, we may identify a unique axis unit vector $\hat{\boldsymbol{u}}_i$ whose collective alignment defines the director. Then we define a single-molecule second-rank orientation tensor $\boldsymbol{q}_i$

$$\boldsymbol{q}_i=\hat{\boldsymbol{u}}_i\hat{\boldsymbol{u}}_i-\frac{1}{3}\mathbf{1}\quad\boldsymbol{q}_{i\alpha\beta}=\hat{u}_{i\alpha}\hat{u}_{i\beta}-\frac{1}{3}\delta_{\alpha\beta}.$$

and the collective $\boldsymbol{q}$-tensor density

$$\boldsymbol{q}(\boldsymbol{r})=\sum_{i=1}^{N}\boldsymbol{q}_i\delta(\boldsymbol{r}-\boldsymbol{r}_i)\quad\tilde{\boldsymbol{Q}}(\boldsymbol{k})=\sum_{i=1}^{N}\boldsymbol{q}_\mathrm{i}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_\mathrm{i}}.$$

In an undistorted liquid crystal

$$\langle\boldsymbol{q}_i\rangle=S(\hat{\boldsymbol{n}}\hat{\boldsymbol{n}}-\frac{1}{3}\mathbf{1})\Rightarrow$$
$$\langle\boldsymbol{q}(\boldsymbol{r})\rangle=\frac{N}{V}\langle\boldsymbol{q}_i\rangle$$
$$=\rho S(\hat{\boldsymbol{n}}\hat{\boldsymbol{n}}-\frac{1}{3}\mathbf{1})\quad\text{everywhere}$$

where $\rho=N/V$ is the molecular number density and S is the order parameter. Small spatial director variations are then expected to appear in $\boldsymbol{q}$ as follows:

$$\boldsymbol{q}(\boldsymbol{r})=\rho S(\hat{\boldsymbol{n}}\hat{\boldsymbol{n}}+\delta\hat{\boldsymbol{n}}(\boldsymbol{r})\hat{\boldsymbol{n}}+\hat{\boldsymbol{n}}\delta\hat{\boldsymbol{n}}(\boldsymbol{r})-\frac{1}{3}\mathbf{1})$$

where $\delta\hat{\boldsymbol{n}}(\boldsymbol{r})\cdot\hat{\boldsymbol{n}}=0$. We may obtain $\delta\hat{\boldsymbol{n}}(\boldsymbol{r})$ from $\boldsymbol{q}(\boldsymbol{r})$ by contracting on one side with $\hat{\boldsymbol{n}}$ and on the other with $\mathbf{1}-\hat{\boldsymbol{n}}\hat{\boldsymbol{n}}$[48,49]

$$\delta\hat{\boldsymbol{n}}(\boldsymbol{r})=[1-\hat{\boldsymbol{n}}\hat{\boldsymbol{n}}]\cdot\frac{\boldsymbol{q}(\boldsymbol{r})}{\rho S}\cdot\hat{\boldsymbol{n}}=\hat{\boldsymbol{n}}\cdot\frac{\boldsymbol{q}(\boldsymbol{r})}{\rho S}\cdot[\mathbf{1}-\hat{\boldsymbol{n}}\hat{\boldsymbol{n}}].$$

In the coordinate system with $\boldsymbol{n}=\hat{\boldsymbol{z}}$, this equation is

$$\boldsymbol{q}(\boldsymbol{r})=\rho S\begin{pmatrix}-\frac{1}{3} & 0 & \delta\hat{n}_x(\boldsymbol{r})\\ 0 & -\frac{1}{3} & \delta\hat{n}_y(\boldsymbol{r})\\ \delta\hat{n}_x(\boldsymbol{r}) & \delta\hat{n}_y(\boldsymbol{r}) & \frac{2}{3}\end{pmatrix}.$$

$\boldsymbol{k}$-dependent fluctuations of the director may then be defined[48,49]

$$\tilde{n}_x(\boldsymbol{k})=\tilde{Q}_{xz}(\boldsymbol{k})/\rho S$$
$$\tilde{n}_y(\boldsymbol{k})=\tilde{Q}_{yz}(\boldsymbol{k})/\rho S$$
$$\tilde{n}_z(\boldsymbol{k})=0$$

where we abbreviate $\delta\tilde{\hat{\boldsymbol{n}}}=\tilde{\boldsymbol{n}}$ for clarity.

The considerations of the previous section suggest that the microscopic $\boldsymbol{k}$-dependent torque density

$$\tilde{\boldsymbol{\tau}}(\boldsymbol{k})=\sum_{i\neq j}(\boldsymbol{\tau}_{ij}+\frac{1}{2}\boldsymbol{r}_{ij}\wedge\boldsymbol{f}_{ij})e^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i} \tag{23}$$

may correspond to the variable $\tilde{\boldsymbol{\tau}}(\boldsymbol{k})$ defined in eqn. (21a). Here, $\boldsymbol{f}_{ij}$ is the force, and $\boldsymbol{\tau}_{ij}$ the torque, exerted on molecule i by molecule j; the separation vector is defined $\boldsymbol{r}_{ij}=\boldsymbol{r}_i-\boldsymbol{r}_j$. The laws of conservation of linear momentum and angular momentum give, respectively,

$$\boldsymbol{f}_{ij}+\boldsymbol{f}_{ji}=0 \quad \text{and} \quad \boldsymbol{\tau}_{ij}+\boldsymbol{\tau}_{ji}+\boldsymbol{r}_{ij}\wedge\boldsymbol{f}_{ij}=0.$$

Applying this last equation to eqn. (23) and exploiting symmetry under relabelling of indices $i\leftrightarrow j$, it follows that $\lim_{k\longrightarrow 0}\tilde{\boldsymbol{\tau}}(\boldsymbol{k})=0$. Therefore this quantity has a low-k expansion[50]

$$\begin{aligned}\tilde{\boldsymbol{\tau}}(\boldsymbol{k})&=\frac{1}{2}\sum_{i\neq j}(\boldsymbol{\tau}_{ij}+\frac{1}{2}\boldsymbol{r}_{ij}\wedge\boldsymbol{f}_{ij})(\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}-\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j})\\&=\frac{1}{2}\sum_{i\neq j}(\boldsymbol{\tau}_{ij}+\frac{1}{2}\boldsymbol{r}_{ij}\wedge\boldsymbol{f}_{ij})(1-\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{ij}})\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}\\&=\mathrm{i}\boldsymbol{k}\cdot[-\frac{1}{2}\sum_{i\neq j}\boldsymbol{r}_{ij}(\boldsymbol{\tau}_{ij}+\frac{1}{2}\boldsymbol{r}_{ij}\wedge\boldsymbol{f}_{ij})(\frac{\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{ij}}-1}{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{ij}})\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}]\\&=\mathrm{i}\boldsymbol{k}\cdot\tilde{\boldsymbol{\Pi}}(\boldsymbol{k}).\end{aligned} \tag{24}$$

This suggests that the microscopic (tensor) analogue of the variable $\tilde{\Pi}(\boldsymbol{k})$ appearing in the previous section is

$$\tilde{\boldsymbol{\Pi}}(\boldsymbol{k})=-\frac{1}{2}\sum_{i\neq j}\boldsymbol{r}_{ij}(\boldsymbol{\tau}_{ij}+\frac{1}{2}\boldsymbol{r}_{ij}\wedge\boldsymbol{f}_{ij})(\frac{\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{ij}}-1}{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_{ij}})\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}.$$

In the limit $k\longrightarrow 0$ this reduces to

$$\boldsymbol{\Pi}=\lim_{k\to 0}\tilde{\boldsymbol{\Pi}}(\boldsymbol{k})=-\frac{1}{2}\sum_{i\neq j}\boldsymbol{r}_{ij}\boldsymbol{\tau}_{ij} \tag{25}$$

where we use the identity

$$\sum_{i\neq j}r_{ij\alpha}(r_{ij}\wedge\boldsymbol{f}_{ij})_\beta=\sum_{i\neq j}r_{ji\alpha}(\boldsymbol{r}_{ji}\wedge\boldsymbol{f}_{ji})_\beta=-\sum_{i\neq j}r_{ij\alpha}(\boldsymbol{r}_{ij}\wedge\boldsymbol{f}_{ij})_\beta=0.$$

The tensor defined by eqn. (25) is the same as the one used elsewhere;[20–22,30] its derivation, both in Fourier space and directly in the $k=0$ limit has been given before,[19] and it is further discussed in Appendix B. Some justification for our definition of $\tilde{\boldsymbol{\tau}}(\boldsymbol{k})$ comes from the microscopic interpretation of $\boldsymbol{\Pi}$ as the transmitted torque per unit area. The argument follows the discussion of the virial expression for the pressure by Haile,[51] but it applies to any molecular pair property. Consider a plane in the liquid crystal, passing through the origin, perpendicular to the x direction. Suppose also that the molecular indices i, j, are chosen in order of increasing x coordinate. The total torque per unit area exerted by molecules lying on one side of the plane on molecules lying on the other side may be written

$$\text{Torque/area}=\frac{1}{\mathscr{A}}\sum_i{}^{\langle 0}\sum_j{}^{\rangle 0}\boldsymbol{\tau}_{ij}$$

where the notation indicates that each sum is restricted to molecules lying on the appropriate side of the plane. (For the case of interest to us, we may drop terms in $\boldsymbol{r}_{ij}\wedge\boldsymbol{f}_{ij}$, as they would correspond to a sustained antisymmetric component of the stress). Averaging this over a slab of liquid of width ℓ gives

$$\text{Average torque/area}=\frac{1}{\mathscr{A}}\frac{1}{\ell}\int_0^\ell\sum_i{}^{\langle x}\sum_j{}^{\rangle x}\boldsymbol{\tau}_{ij}\mathrm{d}x.$$

Now the integral is evaluated using the sequence of (uneven, but very small) intervals $\delta x_k=x_{k+1}-x_k=x_{k+1,k}$. The integral becomes a sum over all particles k lying in the interval $0\leqslant x_k\leqslant\ell$ and the resulting triple summation may be rearranged:

$$\begin{aligned}\text{Average torque/area}&=\frac{1}{V}\sum_k\sum_{i\leq k}\sum_{j>k}\boldsymbol{\tau}_{ij}\delta x_k\\&=\frac{1}{V}\sum_i\sum_{j>i}\boldsymbol{\tau}_{ij}\sum_{k=i}^{j-1}(x_{k+1}-x_k)\\&=-\frac{1}{V}\sum_i\sum_{j>i}\boldsymbol{\tau}_{ij}x_{ij}\\&=-\frac{1}{2V}\sum_i\sum_{j\neq i}\boldsymbol{\tau}_{ij}x_{ij}.\end{aligned}$$

This corresponds to the appropriate component of $\boldsymbol{\Pi}$, as defined by eqn. (25). Consideration of a narrow slab, $\ell\longrightarrow 0$, allows one to generalize to a spatially varying density $\boldsymbol{\Pi}(\boldsymbol{r})$ which behaves in the correct way, and whose Fourier transform is $\tilde{\boldsymbol{\Pi}}(\boldsymbol{k})$.

Notwithstanding the fact that $\tilde{\boldsymbol{\tau}}$ vanishes at low k, the correlation with director fluctuations remains non-zero in this limit. Take once more $\hat{\boldsymbol{n}}=\hat{\boldsymbol{z}}$ and examine fluctuations $\delta\hat{n}_x=\theta_y$. Masters[50] has shown that

$$\begin{aligned}\langle\tilde{n}_x(\boldsymbol{k})\tilde{\tau}_y(-\boldsymbol{k})\rangle&=\langle\tilde{\theta}_y(\boldsymbol{k})\tilde{\tau}_y(-\boldsymbol{k})\rangle\\&=\frac{\langle\tilde{Q}_{xz}(\boldsymbol{k})\tilde{\tau}_y(-\boldsymbol{k})\rangle}{\rho S}\\&=-Vk_BT\quad\text{as } k\to 0\end{aligned} \tag{26}$$

This result reflects the ‘softness’ of the liquid crystal response to a long-wavelength perturbation. If a term $\lambda H'$ with $H'=\tilde{\tau}_y(-\boldsymbol{k})$ is added to the hamiltonian, the response in the director field, given by conventional linear response theory (eqn. (B4)) would be

$$\langle\tilde{n}_x(\boldsymbol{k})|f_\lambda\rangle=-\beta\lambda\langle\tilde{n}_x(\boldsymbol{k})\tilde{\tau}_y(-\boldsymbol{k})\rangle=\lambda V \tag{27a}$$

$$\Rightarrow\langle\delta\tilde{n}_x(\boldsymbol{r})|f_\lambda\rangle=\lambda\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \tag{27b}$$

with appropriate superpositions giving real (sine or cosine) responses to real perturbations. Comparing this with eqn. (22b) supports the above identification of $\boldsymbol{\tau}$.

A. Twist deformations

In this and the following sections, we assume that the gradient is chosen along one of the coordinate axes, to generate a pure splay, twist, or bend deformation, with the definitions of Tables 1 and 2. We consider a twist first, in the absence of any fields, so the free energy $\mathscr{G}$ reduces to the standard Frank free energy $\mathscr{F}$. For a uniform twist of this kind, taking eqn. (8) and integrating over the volume V, we get

$$\text{Free energy: } \mathscr{F}/V=\frac{1}{2}K_2\gamma^2-h\gamma. \tag{28}$$

$$\text{Torque/area: } \frac{\langle\boldsymbol{\Pi}_{yy}\rangle_\gamma}{V}=\frac{\partial\mathscr{F}/V}{\partial\gamma}=K_2\gamma-h. \tag{29}$$

The reference state of minimum free energy has $\gamma=h/K_2$; nematics are called chiral if $h\neq 0$ and twisted if $\gamma\neq h/K_2$. Uniform twists with $\gamma\neq h/K_2$ are due, typically, to boundary conditions produced by the interaction with surfaces. In computer simulations a uniform twist can be conveniently introduced in a bulk cell of fluid using normal, or twisted, periodic boundary conditions.[19] If a fluid of achiral molecules, for which $h=0$ (and hence $\langle\Pi_{yy}\rangle_0=0$ when $\gamma=0$), is maintained in a state of uniform twist, $\gamma\neq 0$, then eqn. (29) may be used to determine K_2.[19] For a fluid of chiral molecules, for which $h\neq 0$ (and so $\langle\Pi_{yy}\rangle_0\neq 0$ when in the untwisted state $\gamma=0$), if the untwisted state is maintained by the boundary conditions, then eqn. (29) may be used to determine the chiral parameter h.[20–22] It has been found useful[23] to combine the equations with $\gamma=0$ and with $\gamma\neq 0$ to give

$$\frac{\langle \Pi_{yy}\rangle_0}{V}=-h \tag{30a}$$

$$\frac{\langle \Pi_{yy}\rangle_\gamma}{V}=K_2\gamma-h \tag{30b}$$

and hence

$$K_2=\frac{\langle \Pi_{yy}\rangle_\gamma-\langle \Pi_{yy}\rangle_0}{V\gamma} \tag{31a}$$

$$h=-\frac{\langle \Pi_{yy}\rangle_0}{V}. \tag{31b}$$

Thus, two simulations with different values of γ are sufficient to determine K_2 and k_0 separately. The same formulae hold equally well for pure phases, where every molecule is chiral, and solutions, where chiral and achiral molecules are mixed. It would be nice to determine K_2 from ensemble averages calculated in the untwisted state. Referring to Appendix B, it should be possible to rewrite eqn. (31a) in the form

$$\begin{aligned}K_2&=\frac{1}{V}\frac{\partial\langle \Pi_{yy}\rangle_\gamma}{\partial\gamma}\bigg|_{\gamma=0}\\&=\frac{\langle \Xi_{yyyy}\rangle-\beta(\langle \Pi_{yy}^2\rangle-\langle \Pi_{yy}\rangle^2)}{V}.\end{aligned} \tag{32}$$

This appears to be a new expression, untested in simulations. It is potentially more convenient than measuring fluctuations and extrapolating to low wavenumber, or applying a twist deformation and measuring the derivative numerically. Unfortunately (see Appendix B) the derivation of a microscopic expression for Ξ_{yyyy} seems to be nontrivial; although a suggestion has been given in the literature[29] that it is possible, no explicit expressions have been given.

One might hope that the Fourier space variables defined earlier in this section would resolve the issue. Suppose we apply a perturbation term of the form $\lambda H'$ with $H'=\tilde{\tau}_y(-\boldsymbol{k})$, choosing $\boldsymbol{k}=k\hat{\boldsymbol{y}}$ to generate twist. Then, referring to eqn. (27a), we expect to see the following responses:

$$\langle \tilde{n}_x(k)|f_\lambda\rangle=\lambda V \tag{33a}$$

$$\begin{aligned}\langle \tilde{\tau}_y(k)|f_\lambda\rangle&=-\beta\lambda\langle \tilde{\tau}_y(k)\tilde{\tau}_y(-k)\rangle\\&=-k^2\beta\lambda\langle \tilde{\Pi}_{yy}(k)\tilde{\Pi}_{yy}(-k)\rangle\end{aligned} \tag{33b}$$

$$\begin{aligned}\langle \tilde{\Pi}_{yy}(k)|f_\lambda\rangle&=-\beta\lambda\langle \tilde{\Pi}_{yy}(k)\tilde{\tau}_y(-k)\rangle\\&=\mathrm{i}k\beta\lambda\langle \tilde{\Pi}_{yy}(k)\tilde{\Pi}_{yy}(-k)\rangle.\end{aligned} \tag{33c}$$

Taking ratios, and allowing $k\longrightarrow 0$, would suggest

$$K_2=\lim_{k\to 0}(\mathrm{i}k)^{-1}\frac{\langle \tilde{\Pi}_{yy}(k)|f_\lambda\rangle}{\langle \tilde{n}_x(k)|f_\lambda\rangle}=\beta\frac{\langle \Pi_{yy}\Pi_{yy}\rangle}{V}.$$

Unfortunately, this is incorrect: it would imply a non-zero elastic constant even in an isotropic liquid. Thus, after all, a 'thought experiment' based on the microscopic torque density does not appear to be a suitable way to generate the desired deformation. Another way of putting this[24] is that $\tilde{\boldsymbol{\tau}}(k)$ is not a suitable variable onto which to 'project' microscopic variables in order to derive thermodynamic fluctuations.

B. Splay deformations

Consider now a splay deformation, once more in the absence of fields, so the free energy $\mathscr{G}$ again becomes $\mathscr{F}$. For a uniform splay, integrating eqn. (8) over volume gives

$$\text{Free energy: } \mathscr{F}/V=\frac{1}{2}K_1\gamma^2 \tag{34}$$

$$\text{Torque/area: } \frac{\langle \Pi_{xy}\rangle_\gamma}{V}=\frac{\partial\mathscr{F}/V}{\partial\gamma}=K_1\gamma. \tag{35}$$

The flexoelectric coefficient associated with splay, e_1, is defined as the response of the z-component of the polarization vector of molecules to the applied director deformation (see section IIA). Noting that there is no applied field coupling directly to $\mathscr{P}$, the coefficient satisfies

$$e_1\gamma=\frac{\langle \mathscr{P}_z\rangle_\gamma}{V}. \tag{36}$$

The above expressions involve measuring the torque density or polarization in a uniformly splayed system: this is not as convenient as imposing constant twist. However, it is also possible to convert them into equations which apply to the undistorted system.[30] Referring to Appendix B, and making the approximation that $\mathscr{P}_z$ does not depend explicitly on γ, gives

$$e_1=V^{-1}\frac{\partial\langle \mathscr{P}_z\rangle_\gamma}{\partial\gamma}\bigg|_{\gamma=0}=\frac{-\beta\langle \mathscr{P}_z\Pi_{xy}\rangle}{V} \tag{37}$$

This matches exactly the expression of Nemtsov and Osipov[30] (see Appendix C); this approach has been attempted in simulation by Billeter and Pelcovits.[52] The corresponding expression for the torque should be directly analogous to eqn. (32):

$$K_1=\frac{1}{V}\frac{\partial\langle \Pi_{xy}\rangle_\gamma}{\partial\gamma}\bigg|_{\gamma=0}=\frac{\langle \Xi_{xyxy}\rangle-\beta(\langle \Pi_{xy}^2\rangle-\langle \Pi_{xy}\rangle^2)}{V} \tag{38}$$

but again, its implementation relies on a suitable microscopic definition of Ξ_{xyxy}.

The flexoelectric coefficient may also be determined by measuring the torque per unit area in an undistorted system (*i.e.* splay $\boldsymbol{s}=\boldsymbol{0}$), in the presence of a uniform polarizing field $\boldsymbol{E}$. Add a coupling term $\lambda H'$ to the hamiltonian with $\lambda=E_z$, $H'=-\mathscr{P}_z$, and consider measuring a variable $A=\Pi_{xy}/V$. Instead of measuring this in a perturbed ensemble f_{Ez}, we may relate it to an average taken in the zero-field ensemble, using eqn. (B4). The free energy (see section IIA) takes the form

$$\text{Free energy: } \mathscr{G}/V=\frac{1}{2}K_1\gamma^2-e_1E_z\gamma-\frac{1}{2}\varepsilon_\parallel E_z^2$$

and in the limit $\gamma\longrightarrow 0$

$$\text{Torque/area: } -e_1E_z=\frac{\partial\mathscr{G}/V}{\partial\gamma}\bigg|_{\gamma=0}=\frac{\langle \Pi_{xy}|f_{Ez}\rangle}{V}$$

to give once more (see Appendix B)

$$e_1=-V^{-1}\frac{\partial\langle \Pi_{xy}|f_{E_z}\rangle}{\partial E_z}\bigg|_{E_z=0}=-\beta\frac{\langle \mathscr{P}_z\Pi_{xy}\rangle}{V}$$

in agreement with eqn. (37). Notice that the measurement of the polarization itself in the presence of the external field is not a useful route to the flexoelectric coefficient: $\mathscr{P}$ cannot be separated microscopically into a part due to distortion and a part due to the field, unless one or the other of them is zero. In this case, the polarization response is (see section IIA)

$$\frac{\langle \mathscr{P}_z|f_{E_z}\rangle}{V}=e_1\gamma+\varepsilon_\parallel E_z=\varepsilon_\parallel E_z\qquad\text{if }\gamma=0.$$

$$\varepsilon_\parallel=V^{-1}\frac{\partial\langle \mathscr{P}_z|f_{E_z}\rangle}{\partial E_z}\bigg|_{E_z=0}=\beta\frac{\langle \mathscr{P}_z^2\rangle}{V}.$$

Once more, one might hope that a Fourier-space perturbation would be suitable for simulation experiments; add a term $\lambda H'$

with $H' = \tilde{\tau}_y(-\boldsymbol{k})$ and select $\boldsymbol{k} = k\hat{\boldsymbol{x}}$ to generate splay:

$$\langle \tilde{n}_x(k) | f_\lambda \rangle = \lambda V \tag{39a}$$

$$\begin{aligned} \langle \tilde{\tau}_y(k) | f_\lambda \rangle &= -\beta\lambda \langle \tilde{\tau}_y(k) \tilde{\tau}_y(-k) \rangle \\ &= -k^2 \beta\lambda \langle \tilde{\Pi}_{xy}(k) \tilde{\Pi}_{xy}(-k) \rangle \end{aligned} \tag{39b}$$

$$\begin{aligned} \langle \tilde{\Pi}_{xy}(k) | f_\lambda \rangle &= -\beta\lambda \langle \tilde{\Pi}_{xy}(k) \tilde{\tau}_y(-k) \rangle \\ &= \mathrm{i}k\beta\lambda \langle \tilde{\Pi}_{xy}(k) \tilde{\Pi}_{xy}(-k) \rangle \end{aligned} \tag{39c}$$

$$\begin{aligned} \langle \mathscr{P}_z(k) | f_\lambda \rangle &= -\beta\lambda \langle \mathscr{P}_z(k) \tilde{\tau}_y(-k) \rangle \\ &= \mathrm{i}k\beta\lambda \langle \mathscr{P}_z(k) \tilde{\Pi}_{xy}(-k) \rangle. \end{aligned} \tag{39d}$$

Taking the limit $k \longrightarrow 0$, gives

$$K_1 = \lim_{k \to 0} (\mathrm{i}k)^{-1} \frac{\langle \tilde{\Pi}_{xy}(k) | f_\lambda \rangle}{\tilde{n}_x(k) | f_\lambda \rangle} = \beta \frac{\langle \Pi_{xy} \Pi_{xy} \rangle}{V}$$

$$e_1 = \lim_{k \to 0} (\mathrm{i}k)^{-1} \frac{\langle \tilde{\mathscr{P}}_z(k) | f_\lambda \rangle}{\langle \tilde{n}_x(k) | f_\lambda \rangle} = \beta \frac{\langle \mathscr{P}_z \Pi_{xy} \rangle}{V}$$

Again, these are clearly wrong: K_1 would be nonzero even in an isotropic liquid, while the expression for e_1 has the wrong sign.

C. Bend deformations

Consider finally a bend deformation, once more in the absence of fields, so the free energy is $\mathscr{F}$ once more. The derivation follows closely that of sections III B, III C. Integrating eqn. (8) gives

$$\text{Free energy: } \mathscr{F}/V = \frac{1}{2} K_3 \gamma^2 \tag{40}$$

$$\text{Torque/area: } \frac{\langle \Pi_{zy} \rangle_\gamma}{V} = \frac{\partial \mathscr{F}/V}{\partial \gamma} = K_3 \gamma. \tag{41}$$

The corresponding flexoelectric coefficient, e_3, is measured through the response in the x-component of polarization

$$e_3 \gamma = \frac{\langle \mathscr{P}_x \rangle_\gamma}{V}. \tag{42}$$

Rather than attempt to measure these quantities in a distorted system, they may be converted to averages in the uniform system:

$$e_3 = V^{-1} \frac{\partial \langle \mathscr{P}_x \rangle_\gamma}{\partial \gamma} \bigg|_{\gamma=0} = -\frac{\beta \langle \mathscr{P}_x \Pi_{zy} \rangle}{V}. \tag{43}$$

Again, the identical expression was obtained by Nemtsov and Osipov[30] (see Appendix C). The corresponding elastic constant expression should take the form

$$K_3 = \frac{1}{V} \frac{\partial \langle \Pi_{zy} \rangle_\gamma}{\partial \gamma} \bigg|_{\gamma=0} = \frac{\langle \Xi_{zyzy} \rangle - \beta(\langle \Pi_{zy}^2 \rangle - \langle \Pi_{zy} \rangle^2)}{V} \tag{44}$$

subject to a proper definition of Ξ_{zyzy}.

As before, it is illuminating to consider measuring the torque density in an undistorted system (*i.e.* bend $\boldsymbol{b} = \boldsymbol{0}$), in the presence of a uniform polarizing field. Add a term $\lambda H'$ to the hamiltonian with $\lambda = E_x$, $H' = -\mathscr{P}_x$, and measure $A = \Pi_{zy}/V$. We aim to compare with

$$\text{Free energy: } \mathscr{G}/V = \frac{1}{2} K_3 \gamma^2 - e_3 E_x \gamma - \frac{1}{2} \varepsilon_\perp E_x^2$$

and in the limit $\gamma \longrightarrow 0$

$$\text{Torque/area: } -e_3 E_x = \frac{\partial \mathscr{G}/V}{\partial \gamma} \bigg|_{\gamma=0} = \frac{\langle \Pi_{zy} | f_{E_x} \rangle}{V}$$

to give, from Appendix B

$$e_3 = -V^{-1} \frac{\partial \langle \Pi_{zy} | f_{E_x} \rangle}{\partial E_x} \bigg|_{E_x=0} = -\beta \frac{\langle \mathscr{P}_x \Pi_{zy} \rangle}{V}$$

in agreement with eqn. (43). If the bend is zero, the polarization response is (section IIA)

$$\frac{\langle \mathscr{P}_x | f_{E_x} \rangle}{V} = e_3 \gamma + \varepsilon_\perp E_x = \varepsilon_\perp E_x \qquad \text{if } \gamma = 0.$$

$$\varepsilon_\perp = V^{-1} \frac{\partial \langle \mathscr{P}_x | f_{E_x} \rangle}{\partial E_x} \bigg|_{E_x=0} = \beta \frac{\langle \mathscr{P}_x^2 \rangle}{V}.$$

The derivation in Fourier space goes through as before. Add a term $\lambda H'$ with $H' = \tilde{\tau}_y(-\boldsymbol{k})$ and select $\boldsymbol{k} = k\hat{\boldsymbol{z}}$ to generate bend. This gives

$$K_3 = \lim_{k \to 0} (\mathrm{i}k)^{-1} \frac{\langle \tilde{\Pi}_{zy}(k) | f_\lambda \rangle}{\langle \tilde{n}_x(k) | f_\lambda \rangle} = \beta \frac{\langle \Pi_{zy} \Pi_{zy} \rangle}{V}$$

$$e_3 = \lim_{k \to 0} (\mathrm{i}k)^{-1} \frac{\langle \tilde{\mathscr{P}}_x(k) | f_\lambda \rangle}{\langle \tilde{n}_x(k) | f_\lambda \rangle} = \beta \frac{\langle \mathscr{P}_x \Pi_{zy} \rangle}{V}$$

and these are, once more, incorrect.

IV. Conclusions

In this article, we have tried to make clear which expressions may be used to measure properties of interest in simulations of liquid crystals, and in which areas problems remain. Zero-wavevector expressions exist for flexoelectric coefficients, in terms of a microscopically-defined orientational stress. This can be thought of as measuring the response of the polarization to a uniform director gradient, or as measuring the field-induced stress, in a liquid crystal which is constrained to have a uniform director. A similar expression exists for the helicity parameter, which may be determined from the orientational stress in an untwisted liquid crystal composed of chiral molecules. The elastic constants may be determined in terms of the orientational stress in a liquid crystal with uniform director gradient; unfortunately, it is only convenient to do this for the twist elastic constant in a simulation employing periodic boundaries. In principle, zero-wavevector stress fluctuation expressions could provide an alternative route to the elastic constants, but the details have yet to be determined. A possible route *via* reciprocal-space perturbations and responses has been investigated, but has been found to give incorrect results.

One of the advantages of the stress–response equations presented here is that they enable one to look at the origin of the coefficients within the forces and torques between molecules. For example, the helicity parameter for a dilute solution of chiral dopants (*i.e.* the helical twisting power) can be resolved into primary terms arising directly from the solute–solvent interactions, and the secondary effects in the solvation shells around the dopant.

This article presents unfinished work: it is hoped that it will provoke some discussion and debate, which will hopefully lead to a resolution of the remaining difficulties. One possible approach will be to consider carefully the order of magnitude of perturbations and responses in Fourier space, *i.e.* to explicitly retain terms of a consistent order in k. It is also possible to examine the effects of more general canonical transformations than the simple one presented in Appendix B. Another avenue is to link, more directly, the stress response formulae to the direct correlation function which appears in density functional theory. Meanwhile, those expressions which are known to be correct are being usefully employed in simulations, aimed at understanding the link between molecular shapes, attractive forces, and phenomenological constants. Those results will be reported elsewhere.

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Appendix A: Fourier transform definitions

Assuming periodic boundaries, for which, in the limit of large volume,

$$\sum_{\boldsymbol{k}} \leftrightarrow \frac{V}{(2\pi)^3}\int \mathrm{d}\boldsymbol{k}$$

and for real fields $a(\boldsymbol{r})$, define

$$\tilde{A}(\boldsymbol{k}) = \int_V \mathrm{d}\boldsymbol{r}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}a(\boldsymbol{r}) = \tilde{A}(-\boldsymbol{k})^* \tag{A1a}$$

$$a(\boldsymbol{r}) = \frac{1}{V}\sum_{\boldsymbol{k}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\tilde{A}(\boldsymbol{k}) = \frac{1}{V}\sum_{\boldsymbol{k}} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\tilde{A}(-\boldsymbol{k}) \tag{A1b}$$

and note the standard relations

$$\text{Orthogonality: } \int_V \mathrm{d}\boldsymbol{r}\mathrm{e}^{\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}} = V\delta_{\boldsymbol{k},\boldsymbol{k}'} \tag{A2a}$$

$$\text{Completeness: } \sum_{\boldsymbol{k}} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')} = V\delta(\boldsymbol{r}-\boldsymbol{r}') \tag{A2b}$$

$$\text{Derivatives: } \widetilde{\nabla A}(\boldsymbol{k}) = \mathrm{i}\boldsymbol{k}\tilde{A}(\boldsymbol{k}) \tag{A2c}$$

$$\begin{aligned}\text{Parseval: } \int \mathrm{d}\boldsymbol{r}a(\boldsymbol{r})b(\boldsymbol{r}) &= \frac{1}{V}\sum_{\boldsymbol{k}} \tilde{A}(\boldsymbol{k})\tilde{B}(-\boldsymbol{k}) \\ &= \frac{1}{V}\sum_{\boldsymbol{k}} \tilde{A}(-\boldsymbol{k})\tilde{B}(\boldsymbol{k}).\end{aligned} \tag{A2d}$$

For properties which may be expressed as sums localized around individual molecules, we define a density

$$a(\boldsymbol{r}) = \sum_{i=1}^{N} a_i\delta(\boldsymbol{r}-\boldsymbol{r}_i) \qquad \tilde{A}(\boldsymbol{k}) = \sum_{i=1}^{N} a_i\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}.$$

For a dynamical variable A, we use the notation A without an argument to mean the extensive, zero-k, value:

$$A = \lim_{k\to 0}\tilde{A}(k) = \int_V \mathrm{d}\boldsymbol{r}a(r) = \sum_{i=1}^{N} a_i$$

whereas, for the fields and gradients, we mean the intensive quantities

$$\boldsymbol{E} = \lim_{k\to 0}\frac{\tilde{\boldsymbol{E}}(\boldsymbol{k})}{V} = \frac{1}{V}\int_V \mathrm{d}\boldsymbol{r}\boldsymbol{E}(\boldsymbol{r}), \quad \boldsymbol{s} = \lim_{k\to 0}\frac{\tilde{\boldsymbol{s}}(\boldsymbol{k})}{V} = \frac{1}{V}\int_V \mathrm{d}\boldsymbol{r}\,\boldsymbol{s}(\boldsymbol{r}), \text{ etc.}$$

Appendix B: Thermodynamic perturbation theory

Standard thermodynamic perturbation theory (see, for example, Gray and Gubbins,[53] or Hansen and McDonald,[54] p. 148) begins with the assumption that the hamiltonian $\mathscr{H}_\lambda$, and hence the ensemble distribution function

$$f_\lambda \propto \mathrm{e}^{-\beta\mathscr{H}_\lambda}$$

depend on a parameter λ which takes a value $\lambda = 0$ in the reference state. The free energy may then be written

$$\frac{\partial\mathscr{F}_\lambda}{\partial\lambda} = \left\langle\frac{\partial\mathscr{H}_\lambda}{\partial\lambda}\middle| f_\lambda\right\rangle. \tag{B1}$$

where we adopt the shorthand

$$\langle A|f_\lambda\rangle = \iint \mathrm{d}\boldsymbol{q}\mathrm{d}\boldsymbol{p}A(\boldsymbol{q},\boldsymbol{p})f_\lambda(\boldsymbol{q},\boldsymbol{p}) = \frac{\iint \mathrm{d}\boldsymbol{q}\mathrm{d}\boldsymbol{p}A\mathrm{e}^{-\beta\mathscr{H}_\lambda}}{\iint \mathrm{d}\boldsymbol{q}\mathrm{d}\boldsymbol{p}\mathrm{e}^{-\beta\mathscr{H}_\lambda}}$$

using generalized coordinates $\boldsymbol{q}$ and conjugate momenta $\boldsymbol{p}$ which are abbreviations for the full set q_μ, p_ν. Defining

$$\mathscr{H}'_\lambda = \frac{\partial\mathscr{H}_\lambda}{\partial\lambda}, \quad \mathscr{H}''_\lambda = \frac{\partial\mathscr{H}'_\lambda}{\partial\lambda} = \frac{\partial^2\mathscr{H}'_\lambda}{\partial\lambda^2}, \tag{B2}$$

the free energy of the perturbed system then becomes

$$\begin{aligned}\mathscr{F}_\lambda = \mathscr{F}_0 + \lambda\langle\mathscr{H}'\rangle + \frac{1}{2}\lambda^2[\langle\mathscr{H}''\rangle \\ -\beta(\langle\mathscr{H}'^2\rangle - \langle\mathscr{H}'\rangle^2)] + \mathscr{O}(\lambda^3),\end{aligned} \tag{B3}$$

where we abbreviate $\langle\mathscr{H}_0|f_0\rangle = \langle\mathscr{H}\rangle$. The average of some property A_λ in the perturbed ensemble may be written

$$\begin{aligned}\langle A\rangle_\lambda \equiv \langle A_\lambda|f_\lambda\rangle = \langle A\rangle + \lambda\langle A'\rangle \\ -\beta\lambda(\langle A\mathscr{H}'\rangle - \langle A\rangle\langle\mathscr{H}'\rangle) + \mathscr{O}(\lambda^2),\end{aligned} \tag{B4}$$

where we allow for the possibility that A also depends on λ, and so include a term in

$$A'_\lambda = \frac{\partial A}{\partial\lambda}. \tag{B5}$$

For our purposes, however, it is not obvious how to connect the response of variables to a distortion of the system with *mechanical* perturbations described through the hamiltonian, as above. Nonetheless, such a connection can be made; here we follow closely the discussion of elastic constants and viscoelasticity by Squire *et al.*,[25] Lutsko,[26] Hess *et al.*,[27] Bavaud *et al.*,[55] Bavaud[56,57] and the work of Nemtsov *et al.*[28] and Nemtsov.[29] Write the hamiltonian as:

$$\mathscr{H}_\lambda(\boldsymbol{q},\boldsymbol{p},t) = H(\boldsymbol{q},\boldsymbol{p}) + U_\lambda(\boldsymbol{q}).$$

H is the internal hamiltonian with (pair) potential and kinetic energy terms. U_λ is an external potential: initially it will be convenient to regard U_λ as a wall potential confining the system coordinates to a corresponding region D_λ. Deformations of the system (strains) enter through the effect of λ (which may, in principle, vary with time, although we shall not make this explicit) on the distortion of the domain D_λ and hence on the wall potential; we do not regard λ as appearing explicitly in U_λ in any other way. Consider now a canonical transformation of coordinates and momenta, generating the distorted system coordinates from those of an undistorted reference system: $(\boldsymbol{q},\boldsymbol{p})\leftarrow(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}})$. In fact, we shall consider an infinitesimal point transformation defined by the F_2-type generating function of Goldstein[58]

$$F_2(\mathring{\boldsymbol{q}},\boldsymbol{p}) = \mathring{\boldsymbol{q}}\cdot(\boldsymbol{1}+\lambda\boldsymbol{G})\cdot\boldsymbol{p}$$

where λ is a small parameter, and $\boldsymbol{G}$ is a matrix which does not depend explicitly on coordinates or momenta. In terms of this function

$$\frac{\partial F_2}{\partial\boldsymbol{p}} = \boldsymbol{q} = \mathring{\boldsymbol{q}}\cdot(\boldsymbol{1}+\lambda\boldsymbol{G}) \Rightarrow \mathring{\boldsymbol{q}} = \boldsymbol{q}\cdot(\boldsymbol{1}-\lambda\boldsymbol{G})$$

$$\boldsymbol{p} = (\boldsymbol{1}-\lambda\boldsymbol{G})\cdot\mathring{\boldsymbol{p}} \Leftarrow \frac{\partial F_2}{\partial\mathring{\boldsymbol{q}}} = \mathring{\boldsymbol{p}} = (\boldsymbol{1}+\lambda\boldsymbol{G})\cdot\boldsymbol{p}.$$

In inverting $(\boldsymbol{1}+\lambda\boldsymbol{G})^{-1} = \boldsymbol{1}-\lambda\boldsymbol{G}$ above, we drop terms $\mathscr{O}(\lambda^2)$. Conservation of phase-space volume under a canonical transformation allows us to relate the N-particle distribution functions

$$\mathring{f}_\lambda(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}}) \equiv f_\lambda(\mathring{q}+\lambda\mathring{q}\cdot\boldsymbol{G},\mathring{\boldsymbol{p}}-\lambda\boldsymbol{G}\cdot\mathring{\boldsymbol{p}}) = f_\lambda(\boldsymbol{q},\boldsymbol{p}).$$

The point of the transformation is that the domain D_λ is transformed along with the coordinates, so we can write

$$U_\lambda(\boldsymbol{q}) = U_\lambda(\mathring{\boldsymbol{q}} + \lambda\mathring{\boldsymbol{q}}\cdot\boldsymbol{G}) = U_0(\mathring{\boldsymbol{q}})$$

where U_0 represents the external potential in the undeformed domain D_0. The internal part of the hamiltonian transforms to give

$$\begin{aligned} H(\boldsymbol{q},\boldsymbol{p}) &= H(\mathring{\boldsymbol{q}} + \lambda\mathring{\boldsymbol{q}}\cdot\boldsymbol{G},\mathring{\boldsymbol{p}} - \lambda\boldsymbol{G}\cdot\mathring{\boldsymbol{p}}) \\ &= H(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}}) + \lambda H'(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}}) + \mathcal{O}(\lambda^2) \end{aligned}$$

where

$$H' = \boldsymbol{G}^{\mathrm{T}} : \boldsymbol{H} = G_{\mu\nu}H_{\mu\nu}, \quad H_{\mu\nu}(\boldsymbol{q},\boldsymbol{p}) = q_\mu \frac{\partial H}{\partial q_\nu} - \frac{\partial H}{\partial p_\mu}p_\nu. \tag{B6}$$

All the derivatives are defined at $\lambda = 0$ and we have dropped terms $\mathcal{O}(\lambda^2)$. The original system has now been mapped onto a system with no dynamical deformation, specified by the hamiltonian $H(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}}) + U_0(\mathring{\boldsymbol{q}})$, plus a small mechanical perturbation term $\lambda H'(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}})$.

Static ensemble averages in the perturbed reference system follow in a completely conventional way[53,54] (and time-dependent properties follow from a consideration of the Liouville equation,[28,29,57] but this does not concern us here). We set

$$\mathring{f}_\lambda(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}}) = f_0(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}})\mathrm{e}^{-\beta\lambda G_{\mu\nu}H_{\mu\nu}} = f_0(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}})\mathrm{e}^{-\beta\lambda H'}$$

and expand to first order in λ, to give the average of a property in the perturbed ensemble

$$\langle A|\mathring{f}_\lambda\rangle = \langle A\rangle - \beta\lambda[\langle AH'\rangle - \langle A\rangle\langle H'\rangle]. \tag{B7}$$

This is not the final expression, however. The connection with averages in the real, distorted, system is obtained by using the invariance of phase space elements under canonical transformations:

$$\begin{aligned} \langle A\rangle_\lambda \equiv \langle A|f_\lambda\rangle &= \iint \mathrm{d}\boldsymbol{q}\mathrm{d}\boldsymbol{p} f_\lambda(\boldsymbol{q},\boldsymbol{p})A(\boldsymbol{q},\boldsymbol{p}) \\ &= \iint \mathrm{d}\mathring{\boldsymbol{q}}\mathrm{d}\mathring{\boldsymbol{p}}\mathring{f}_\lambda(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}})A(\mathring{\boldsymbol{q}} + \lambda\mathring{\boldsymbol{q}}\cdot\boldsymbol{G},\mathring{\boldsymbol{p}} - \lambda\boldsymbol{G}\cdot\mathring{\boldsymbol{p}}) \\ &= \langle A|\mathring{f}_\lambda\rangle + \lambda G_{\mu\nu}\langle A_{\mu\nu}|\mathring{f}_\lambda\rangle \\ &= \langle A|\mathring{f}_\lambda\rangle + \lambda\langle A'|\mathring{f}_\lambda\rangle \end{aligned} \tag{B8}$$

where we expanded the dynamical variable

$$A(\mathring{\boldsymbol{q}} + \lambda\mathring{\boldsymbol{q}}\cdot\boldsymbol{G},\mathring{\boldsymbol{p}} - \lambda\boldsymbol{G}\cdot\mathring{\boldsymbol{p}}) = A(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}}) + \lambda A'(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}}) + \mathcal{O}(\lambda^2)$$

and

$$A' = \boldsymbol{G}^{\mathrm{T}} : \boldsymbol{A} = G_{\mu\nu}A_{\mu\nu}, \quad A_{\mu\nu}(\boldsymbol{q},\boldsymbol{p}) = q_\mu \frac{\partial A}{\partial q_\nu} - \frac{\partial A}{\partial p_\mu}p_\nu. \tag{B9}$$

Combining eqns. (B7) and (B8) gives the final result

$$\begin{aligned} \langle A\rangle_\lambda = \langle A\rangle + \lambda\langle A'\rangle - \beta\lambda[\langle AH'\rangle \\ - \langle A\rangle\langle H'\rangle] + \mathcal{O}(\lambda^2). \end{aligned} \tag{B10}$$

This has exactly the same form as eqn. (B4), but the derivatives H' and A' are defined by eqns. (B6) and (B9) instead of eqns. (B2) and (B5): neither H nor A depend mechanically on λ. Note that, once the result has been cast in the form of eqn. (B10), we no longer need to distinguish between the two sets of coordinates $\{\boldsymbol{q},\boldsymbol{p}\}$ and $\{\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}}\}$: they differ only infinitesimally from each other and they are, in any case, integrated over in performing ensemble averages.

The above derivation may seem mysterious. We seem to have got something out of nothing (a transformation of variables); only the boundary term $U_\lambda(\boldsymbol{q})$ transformed differently from the rest of the hamiltonian, and it does not feature prominently in the final result. Nonetheless, it is easy to see that, if $U_\lambda(\boldsymbol{q}) = 0$, and hence $H_\lambda = H$, the result is trivial. For then, Hamilton's equations

$$\dot{q}_\mu = \frac{\partial H}{\partial p_\mu} \quad \dot{p}_\mu = -\frac{\partial H}{\partial q_\mu}$$

and the hypervirial relations[53]

$$\langle\frac{\partial A}{\partial q_\mu}\rangle = \beta\langle A\frac{\partial H}{\partial q_\mu}\rangle \quad \langle\frac{\partial A}{\partial p_\mu}\rangle = \beta\langle A\frac{\partial H}{\partial p_\mu}\rangle$$

allow us to deduce from eqns. (B6) and (B9)

$$\begin{aligned} &H_{\mu\nu} = -\frac{\mathrm{d}}{\mathrm{d}t}(q_\mu p_\nu) \Rightarrow \langle H'\rangle = 0 \\ &\text{and } \langle A_{\mu\nu}\rangle = \beta\langle AH_{\mu\nu}\rangle \Rightarrow \langle A'\rangle = \beta\langle AH'\rangle \end{aligned}$$

making the right hand side of eqn. (B10) vanish. To put this in a familiar context, consider the response of the system to a homogeneous deformation of centre-of-mass positions. In this case, $\boldsymbol{G}$ may be condensed to a 3 × 3 strain matrix which applies to all molecules

$$q_\mu \rightarrow r_{i\alpha} \quad \lambda G_{\mu\nu} \rightarrow \lambda G_{i\alpha j\beta} = \delta_{ij}\varepsilon_{\alpha\beta}$$

where the small parameter λ has now been absorbed into the gradient tensor $\boldsymbol{\varepsilon}$. This means that positions and linear momenta transform as

$$r_{i\beta} = \mathring{r}_{i\beta} + \mathring{r}_{i\alpha}\varepsilon_{\alpha\beta} \qquad p_{i\alpha} = \mathring{p}_{i\alpha} - \varepsilon_{\alpha\beta}\mathring{p}_{i\beta} \quad \forall i$$

while it is understood that all orientational variables are left unchanged. Correspondingly, $H_{\mu\nu}$ reduces to the 3 × 3 stress tensor

$$S_{\alpha\beta} = \sum_i r_{i\alpha}\frac{\partial H}{\partial r_{i\beta}} - \frac{\partial H}{\partial p_{i\alpha}}p_{i\beta} = -\sum_i (r_{i\alpha}f_{i\beta} + m_i^{-1}p_{i\alpha}p_{i\beta})$$

and the internal part of the hamiltonian transforms as

$$H(\boldsymbol{q},\boldsymbol{p}) = H(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}}) + \varepsilon_{\alpha\beta}S_{\alpha\beta}(\mathring{\boldsymbol{q}},\mathring{\boldsymbol{p}})$$

Setting $A = S_{\alpha\beta}$ in eqn. (B10) gives a stress–strain relation

$$\begin{aligned} \langle S_{\alpha\beta}\rangle_\varepsilon = \langle S_{\alpha\beta}\rangle + \varepsilon_{\gamma\delta}\langle T_{\alpha\beta\gamma\delta}\rangle \\ - \beta\varepsilon_{\gamma\delta}\left[\langle S_{\alpha\beta}S_{\gamma\delta}\rangle - \langle S_{\alpha\beta}\rangle\langle S_{\gamma\delta}\rangle\right] \end{aligned} \tag{B11}$$

with

$$\begin{aligned} T_{\alpha\beta\gamma\delta} &= \sum_j r_{j\gamma}\frac{\partial S_{\alpha\beta}}{\partial r_{j\delta}} - \frac{\partial S_{\alpha\beta}}{\partial p_{j\gamma}}p_{j\delta} \\ &= \sum_{ij} r_{i\alpha}r_{j\gamma}\frac{\partial^2 H}{\partial r_{i\beta}\partial r_{j\delta}} - \frac{\partial^2 H}{\partial p_{i\alpha}\partial p_{j\gamma}}p_{i\beta}p_{j\delta} \end{aligned} \tag{B12}$$

from which the elastic constants (and, if the time dependence is analyzed, viscosity coefficients) may be obtained.[25,27,55,57] Using the fact that the equilibrium canonical distribution function factorizes into independent configurational and momentum-space parts, it is easy to see that the static cross-correlations are zero. The momentum-space part is relatively easy to evaluate. The configurational part of $\langle T_{\alpha\beta\gamma\delta}\rangle$ in eqn. (B12) is the so-called 'Born term', which dominates at low temperature; the 'fluctuation term' $-\beta[\langle S_{\alpha\beta}S_{\gamma\delta}\rangle - \langle S_{\alpha\beta}\rangle\langle S_{\gamma\delta}\rangle]$ may be significant at higher temperatures; in the fluid state, for shear strains, these terms exactly cancel.[27]

In the case of interest to us, the nonzero elements of $\boldsymbol{G}$ generate gradients of molecular orientation. Provided the deformations are small, the angles $\boldsymbol{\theta}_i$ may be treated as generalized coordinates, and the conjugate momenta are the corresponding Cartesian components of intrinsic angular momentum $\boldsymbol{s}_i$. The coordinates become $q_\mu \rightarrow \{r_{i\alpha}, \theta_{i\alpha}\}$, and $\lambda \boldsymbol{G}$ may be contracted to the following transformation

$$\theta_{i\beta} = \mathring{\theta}_{i\beta} + \mathring{r}_{i\alpha}\gamma_{\alpha\beta}$$

$$s_{i\alpha} = \mathring{s}_{i\alpha} - \gamma_{\alpha\beta}\mathring{p}_{i\beta} \quad \forall i$$

where it is understood that the positional coordinates and momenta are not transformed, and we once more absorb the small parameter λ into the definition of $\gamma_{\alpha\beta}$. The corresponding 'stress' is

$$\Pi_{\alpha\beta} = \sum_i r_{i\alpha}\frac{\partial H}{\partial \theta_{i\beta}} - \frac{\partial H}{\partial s_{i\alpha}} p_{i\beta},$$

in terms of which the internal hamiltonian transforms as

$$H(\boldsymbol{r},\boldsymbol{\theta},\boldsymbol{p},\boldsymbol{s}) = H(\mathring{\boldsymbol{r}},\mathring{\boldsymbol{\theta}},\mathring{\boldsymbol{p}},\mathring{\boldsymbol{s}}) + \gamma_{\alpha\beta}\Pi_{\alpha\beta}(\mathring{\boldsymbol{r}},\boldsymbol{\theta},\mathring{\boldsymbol{p}},\mathring{\boldsymbol{s}})$$

Once more, one may separate momentum-space and configuration-space terms, and in this case it is possible to show that the former do not contribute to the final result. The matrix $\boldsymbol{\Pi}$ takes the form

$$\Pi_{\alpha\beta} = \sum_i r_{i\alpha}\frac{\partial \mathscr{V}}{\partial \theta_{i\beta}}. \tag{B13}$$

The orientational stress-strain relation is

$$\begin{aligned} \langle \Pi_{\alpha\beta}\rangle_\gamma = \langle \Pi_{\alpha\beta}\rangle + \gamma_{\gamma\delta}\langle \Xi_{\alpha\beta\gamma\delta}\rangle - \beta\gamma_{\gamma\delta}[\langle \Pi_{\alpha\beta}\Pi_{\gamma\delta}\rangle \\ - \langle \Pi_{\alpha\beta}\rangle\langle \Pi_{\gamma\delta}\rangle] \end{aligned} \tag{B14}$$

consisting, as in the solid-state elastic constant case, of a Born term with a variable formally defined by

$$\Xi_{\alpha\beta\gamma\delta} = \sum_i \sum_j r_{i\alpha} r_{j\gamma}\frac{\partial^2 \mathscr{V}}{\partial \theta_{i\beta}\partial \theta_{j\delta}} \tag{B15}$$

and a fluctuation term; these two terms should cancel exactly in the disordered, isotropic, fluid. Convenient expressions for $\Pi_{\alpha\beta}$ have been obtained by several authors.[19–22,30] We proceed by re-writing $\Pi_{\alpha\beta}$ as follows:

$$\begin{aligned} \Pi_{\alpha\beta} &= \sum_i r_{i\alpha}\frac{\partial \mathscr{V}}{\partial \theta_{i\beta}} = -\sum_i r_{i\alpha}\tau_{i\beta} = -\sum_{i \neq j} r_{i\alpha}\tau_{ij\beta} \\ &= -\frac{1}{2}\sum_{i \neq j} r_{i\alpha}\tau_{ij\beta} + r_{j\alpha}\tau_{ji\beta}. \end{aligned}$$

Here we have assumed that the total torques on the respective molecules i, j can be decomposed into pairwise contributions $\boldsymbol{\tau}_i = \Sigma_j \boldsymbol{\tau}_{ij}$, $\boldsymbol{\tau}_j = \Sigma_i \boldsymbol{\tau}_{ji}$, and finally we have symmetrized the double sum with respect to i and j. Now set

$$\boldsymbol{r}_i = \boldsymbol{r}_{ij} + \boldsymbol{r}_j$$

to give

$$\Pi_{\alpha\beta} = -\frac{1}{2}\sum_{i \neq j} r_{ij\alpha}\tau_{ij\beta} + r_{j\alpha}(\tau_{ij\beta} + \tau_{ji\beta}).$$

Invariance of the pair potential energy to rotation of all the vectors *together* (*i.e.* angular momentum conservation) guarantees that

$$\boldsymbol{\tau}_{ij} + \boldsymbol{\tau}_{ji} + \boldsymbol{r}_{ij} \wedge \boldsymbol{f}_{ij} = 0.$$

This leads us to drop the second term: it is proportional to the vector dual of the antisymmetric stress, which vanishes in a fluid. (This remark holds true, strictly speaking, only after ensemble averaging). Thus, our final result is

$$\Pi_{\alpha\beta} = -\frac{1}{2}\sum_{i \neq j} r_{ij\alpha}\tau_{ij\beta} \tag{B16}$$

This expression is origin-independent, which is a requirement in periodic boundaries. A somewhat more satisfactory Fourier-space derivation of this result, taken from Allen and Masters,[19] was given in the main text, leading to eqn. (25). No corresponding derivation of $\Xi_{\alpha\beta\gamma\delta}$ in origin-independent form, starting from eqn. (B15), has appeared in the literature to date, and this is a significant obstacle to testing stress-formulae for liquid crystal elastic constants.

Appendix C: Comparison with Nemtsov–Osipov expressions

Note that Nemtsov and Osipov[30] adopt transposed definitions which we will write

$$\gamma^\dagger_{\alpha\beta} = \partial_\beta \theta_\alpha \qquad \text{so our gradient } \gamma_{\alpha\beta} = \gamma^\dagger_{\beta\alpha}$$

$$\Pi^\dagger_{\alpha\beta} = -\frac{1}{2}\sum_{i \neq j} \tau_{ij\alpha} r_{ij\beta} \qquad \text{so our tensor } \Pi_{\alpha\beta} = \Pi^\dagger_{\beta\alpha}.$$

Billeter and Pelcovits[52] seem to define $\Pi^\dagger_{\beta\alpha}$ with the opposite sign; however, this discrepancy may be cancelled by ambiguity in the sign convention for the centre-centre vector $\boldsymbol{r}_{ij}$. Nemtsov and Osipov[30] then define

$$E_{\alpha\beta\gamma} = -\frac{\beta\langle \mathscr{P}_\alpha \Pi^\dagger_{\beta\gamma}\rangle}{V}$$

so that

$$\frac{\langle \mathscr{P}_\alpha\rangle}{V} = E_{\alpha\beta\gamma}\gamma^\dagger_{\beta\gamma} = E_{\alpha\beta\gamma}\epsilon_{\beta\mu\nu}\hat{n}_\mu \partial_\gamma \hat{n}_\nu$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi–Civita tensor. Then they express

$$\begin{aligned} E_{\alpha\beta\gamma} &= E_1\epsilon_{\alpha\beta\gamma} + E_2\hat{n}_\gamma\hat{n}_\mu\epsilon_{\mu\alpha\beta} + E_3\hat{n}_\alpha\hat{n}_\mu\epsilon_{\mu\gamma\beta} + E_4\hat{n}_\beta\hat{n}_\mu\epsilon_{\mu\alpha\gamma} \\ &= E_1\epsilon_{\alpha\beta\gamma} + E_2\delta_{\gamma z}\epsilon_{z\alpha\beta} + E_3\delta_{\alpha z}\epsilon_{z\gamma\beta} + E_4\delta_{\beta z}\epsilon_{z\alpha\gamma} \end{aligned} \tag{C1}$$

with our chosen axes.

For the splay deformation of section III B, our interest lies in $\mathscr{P}_z$, for which only two components of $\boldsymbol{E}$ contribute

$$E_{z\beta\gamma} = E_1\epsilon_{z\beta\gamma} + E_3\epsilon_{z\gamma\beta} = (E_3 - E_1)\epsilon_{z\gamma\beta} \equiv e_1\epsilon_{z\gamma\beta}$$

$$\Rightarrow e_1 = E_{zyx} = -\frac{\beta\langle \mathscr{P}_z\Pi^\dagger_{yx}\rangle}{V} = -\frac{\beta\langle \mathscr{P}_z\Pi_{xy}\rangle}{V}$$

$$= -E_{zxy} = \frac{\beta\langle \mathscr{P}_z\Pi^\dagger_{xy}\rangle}{V} = \frac{\beta\langle \mathscr{P}_z\Pi_{yx}\rangle}{V}.$$

Nemtsov and Osipov[30] write this as (converting to our axes)

$$\begin{aligned} e_1 &= -\frac{1}{2}E_{\alpha\beta\gamma}\epsilon_{\mu\beta\gamma}\hat{n}_\alpha\hat{n}_\mu = -\frac{1}{2}E_{z\beta\gamma}\epsilon_{z\beta\gamma} \\ &= -\frac{1}{2}(E_{zyx} - E_{zxy}). \end{aligned}$$

These results agree with our eqn. (37).

For the bend flexoelectric coefficient, return to eqn. (C1); our interest lies in

$$E_{x\beta\gamma} = E_1\epsilon_{x\beta\gamma} + E_2\delta_{\gamma z}\epsilon_{zx\beta} + E_4\delta_{\beta z}\epsilon_{zxy} \Rightarrow$$

$$E_{xyz} = E_1 + E_2 \equiv e_3$$

$$E_{y\beta\gamma} = E_1\epsilon_{y\beta\gamma} + E_2\delta_{\gamma z}\epsilon_{zy\beta} \Rightarrow E_{yxz} = -E_1 - E_2 = -e_3$$

So

$$e_3 = E_{xyz} = -\frac{\beta\langle \mathscr{P}_x\Pi^\dagger_{yz}\rangle}{V} = -\frac{\beta\langle \mathscr{P}_x\Pi_{zy}\rangle}{V}$$

$$= -E_{yxz} = \frac{\beta\langle \mathscr{P}_y\Pi^\dagger_{xz}\rangle}{V} = \frac{\beta\langle \mathscr{P}_y\Pi_{zx}\rangle}{V}.$$

Nemtsov and Osipov[30] write this as (converting to our axes)

$$e_3 = \frac{1}{2}E_{\alpha\beta\gamma}\epsilon_{\alpha\beta\mu}\hat{n}_\gamma\hat{n}_\mu = \frac{1}{2}E_{\alpha\beta z}\epsilon_{\alpha\beta z} = \frac{1}{2}(E_{xyz} - E_{yxz}).$$

These results agree with eqn. (43) of the main text.

References

1. C. Oseen, *Trans. Faraday Soc.*, 1933, **29**, 883.
2. F. C. Frank, *Discuss. Faraday Soc.*, 1958, **25**, 19.
3. P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 1995, second, paperback edn.
4. L. D. Landau and E. M. Lifshitz, *Statistical physics. Course of Theoretical Physics, 5* , Pergamon Press, Oxford, 1980 (3rd revised edn., ed. E. M. Lifshitz and L. P. Pitaevskii).
5. P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics*, Cambridge University Press, Cambridge, 1995.
6. L. R. Pratt, *J. Chem. Phys.*, 1987, **87**, 1245.
7. D. Forster, T. C. Lubensky, P. C. Martin, J. Swift and P. S. Pershan, *Phys. Rev. Lett.*, 1971, **26**, 1016.
8. P. C. Martin, O. Parodi and P. S. Pershan, *Phys. Rev. A*, 1972, **6**, 2401.
9. M. P. Allen and D. Frenkel, *Phys. Rev. A*, 1988, **37**, 1813.
10. M. P. Allen and D. Frenkel, *Phys. Rev. A*, 1990, **42**, 3641, erratum.
11. D. J. Cleaver and M. P. Allen, *Phys. Rev. A*, 1991, **43**, 1918.
12. B. Tjipto-Margo, G. T. Evans, M. P. Allen and D. Frenkel, *J. Phys. Chem.*, 1992, **96**, 3942.
13. M. P. Allen, M. A. Warren, M. R. Wilson, A. Sauron and W. Smith, *J. Chem. Phys.*, 1996, **105**, 2850.
14. S. Sengupta, P. Nielaba, M. Rao and K. Binder, *Phys. Rev. E*, 2000, **61**, 1072.
15. M. Parrinello and A. Rahamn, *Phys. Rev. Lett.*, 1980, **45**, 1196.
16. J. R. Ray and A. Rahman, *J. Chem. Phys.*, 1984, **80**, 4423.
17. M. Sprik, R. W. Impey and M. L. Klein, *Phys. Rev. B*, 1984, **29**, 4368.
18. J. R. Ray, M. C. Moody and A. Rahman, *Phys. Rev. B*, 1985, **32**, 733.
19. M. P. Allen and A. J. Masters, *Mol. Phys.*, 1993, **79**, 277.
20. A. B. Harris, R. D. Kamien and T. C. Lubensky, *Phys. Rev. Lett.*, 1997, **78**, 1476.
21. A. B. Harris, R. D. Kamien and T. C. Lubensky, *Phys. Rev. Lett.*, 1997, **78**, 2867.
22. A. B. Harris, R. D. Kamien and T. C. Lubensky, *Phys. Rev. Lett.*, 1999, **71**, 1745.
23. G. Germano and M. P. Allen, *Simultaneous calculation of the helical pitch and the twist elastic constant in chiral liquid crystals by molecular simulation*, 2001, in preparation.
24. P. Schofield, *Proc. Phys. Soc.*, 1966, **88**, 149.
25. D. R. Squire, A. C. Holt and W. G. Hoover, *Physica*, 1969, **42**, 388.
26. J. F. Lutsko, *J. Appl. Phys.*, 1989, **65**, 2991.
27. S. Hess, M. Kroger and W. G. Hoover, *Physica A*, 1997, **239**, 449.
28. V. B. Nemtsov, V. S. Vikhrenko, E. T. Brook-Levinson and L. A. Rott, *Phys. Lett. A*, 1971, **34**, 105.
29. V. B. Nemtsov, *Physica A*, 1977, **86**, 513.
30. V. B. Nemtsov and M. A. Osipov, *Sov. Phys. Crystallogr.*, 1986, **31**, 125.
31. A. Poniewierski and J. Stecki, *Mol. Phys.*, 1979, **38**, 1931.
32. J. Stecki and A. Poniewierski, *Mol. Phys.*, 1980, **41**, 1451.
33. A. Poniewierski and J. Stecki, *Phys. Rev. A*, 1982, **25**, 2368.
34. Y. Singh, *Phys. Rev. A*, 1984, **30**, 583.
35. M. D. Lipkin, S. A. Rice and U. Mohanty, *J. Chem. Phys.*, 1985, **82**, 472.
36. M. A. Osipov, *Sov. Phys. Crystallogr.*, 1988, **33**, 482.
37. Y. Singh and U. P. Singh, *Phys. Rev. A*, 1989, **39**, 4254.
38. A. M. Somoza and P. Tarazona, *Mol. Phys.*, 1991, **72**, 911.
39. H. Yokoyama, *Phys. Rev. E*, 1997, **55**, 2938.
40. J. Stelzer, L. Longa and H. R. Trebin, *J. Chem. Phys.*, 1995, **103**, 3098.
41. J. Stelzer, L. Longa and H. R. Trebin, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A*, 1995, **262**, 455.
42. J. Stelzer, H.-R. Trebin and L. Longa, *J. Chem. Phys.*, 1997, **107**, 1295, erratum.
43. J. Stelzer, M. A. Bates, L. Longa and G. R. Luckhurst, *J. Chem. Phys.*, 1997, **107**, 7483.
44. J. Stelzer, R. Berardi and C. Zannoni, *Chem. Phys. Lett.*, 1999, **299**, 9.
45. N. H. Phuong, G. Germano and F. Schmid, *Elastic constants from direct correlation functions in nematic liquid crystals: A computer simulation study* (2001), *J. Chem. Phys.*, in press.
46. R. B. Meyer, *Phys. Rev. Lett.*, 1969, **22**, 918.
47. W. Helfrich, *Z. Naturforsch., Teil A*, 1971, **26**, 833.
48. D. Forster, *Ann. Phys.*, 1974, **85**, 505.
49. D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions*, vol. 47 of *Frontiers in Physics*, Benjamin, Reading, MA, 1975.
50. A. J. Masters, *Mol. Phys.*, 1985, **56**, 887.
51. J. M. Haile, *Molecular dynamics simulation: elementary methods*, Wiley, New York, 1992.
52. J. L. Billeter and R. A. Pelcovits, *Liq. Cryst.*, 2000, **27**, 1151.
53. C. G. Gray and K. E. Gubbins, *Theory of molecular fluids. 1. Fundamentals*, Clarendon Press, Oxford, 1984.
54. J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, Academic Press, London, , 2nd edn, 1986.
55. F. Bavaud, P. Choquard and J.-R. Fontaine, *J. Stat. Phys.*, 1986, **42**, 621.
56. F. Bavaud, *J. Stat. Phys.*, 1986, **45**, 171.
57. F. Bavaud, *J. Stat. Phys.*, 1987, **46**, 753.
58. H. Goldstein, *Classical Mechanics*, Addison Wesley, Reading, MA, 1980, 2nd edn.
59. P. Rudquist and S. T. Lagerwall, *Liq. Cryst.*, 1997, **23**, 503.
60. Elsewhere[2,47] the definitions of t_1 and t_2 are inconsequentially different.
61. The sign of e_3 has caused historical confusion as documented by Rudquist and Lagerwall.[59] The sign convention adopted here is the one first used by Nemtsov and Osipov,[30] Singh and Singh,[37] Meyer[46] and featuring in the book of de Gennes and Prost,[3] while the opposite one is the starting point for Stelzer *et al.*,[44] Billeter and Pelcovits,[52] which has recently been proposed as the standard by Rudquist and Lagerwall[59].