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Nematic liquid crystals : from Maier-Saupe to a continuum theory

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Abstract

We define a continuum energy functional in terms of the mean-field Maier-Saupe free energy, that describes both spatially homogeneous and inhomogeneous systems. The Maier-Saupe theory defines the main macroscopic variable, the \mathbf{Q} -tensor order parameter, in terms of the second moment of a probability distribution function. This definition requires the eigenvalues of \mathbf{Q} to be bounded both from below and above. We define a thermotropic bulk potential which blows up whenever the eigenvalues tend to these lower and upper bounds. This is in contrast to the Landau-de Gennes theory which has no such penalization. We study the asymptotics of this bulk potential in different regimes and discuss phase transitions predicted by this model.

1 Introduction

There are two commonly used approaches to the mathematical modelling of nematic liquid crystals. The first is the mean-field approach [9, 4]. In

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the mean-field framework, the state of alignment of the nematic molecules is described by a probability distribution function ρ on the unit sphere. The main macroscopic variable, the \mathbf{Q} -tensor order parameter, is defined in terms of the second moment of ρ as shown below [4, 11]

$$\mathbf{Q} = \int_{S^2} \left(\mathbf{p} \otimes \mathbf{p} - \frac{1}{3} \mathbf{I} \right) \rho(\mathbf{p}) d\mathbf{p} \quad (1)$$

and this definition immediately requires the \mathbf{Q} -tensor to be a symmetric, traceless 3×3 matrix whose eigenvalues $\{\lambda_i(\mathbf{Q})\}$ are constrained by the following inequalities [7, 10]

$$-\frac{1}{3} \leq \lambda_i(\mathbf{Q}) \leq \frac{2}{3} \quad i = 1, 2, 3; \quad \sum_{i=1}^3 \lambda_i(\mathbf{Q}) = 0. \quad (2)$$

In the rest of the paper we refer to (2) as physical constraints and to the range $\lambda_i \in \left(-\frac{1}{3}, \frac{2}{3}\right)$ as the physical regime.

The second approach is the phenomenological Landau-de Gennes theory [4, 11]. The Landau-de Gennes theory also describes the state of a nematic liquid crystal by the macroscopic \mathbf{Q} -tensor order parameter. Within the Landau-de Gennes theory, the \mathbf{Q} -tensor order parameter is a symmetric, traceless 3×3 matrix with no *a priori* bounds on the eigenvalues and is often defined in terms of anisotropic macroscopic quantities such as the magnetic susceptibility. In the absence of surface energies and external fields, the Landau-de Gennes energy functional is given by

$$I_{LG}[\mathbf{Q}] = \int f_B(\mathbf{Q}) + w(\mathbf{Q}, \nabla \mathbf{Q}) dV. \quad (3)$$

Here f_B is a thermotropic bulk potential that governs the preferred phase of the nematic liquid crystal - isotropic, uniaxial or biaxial - as function of the

temperature and w is an elastic energy density that penalizes spatial inhomogeneities. The function f_B is a polynomial in the scalar invariants of the \mathbf{Q} -tensor with material-dependent and temperature-dependent coefficients [4, 11, 10]

$$f_B(\mathbf{Q}) = \frac{1}{2}a(T) \text{tr} \mathbf{Q}^2 + \frac{1}{3}b \text{tr} \mathbf{Q}^3 + \frac{1}{4}c (\text{tr} \mathbf{Q}^2)^2 + \dots \quad (4)$$

and has no term that enforces the physical constraints on the eigenvalues in (2). The equilibrium (physically observable) configurations correspond either to global or local minimizers of the Landau-de Gennes energy subject to the imposed boundary conditions. We can make quantitative predictions about the order parameters (eigenvalues) of equilibrium configurations in both the spatially homogeneous and spatially inhomogeneous cases and these explicit estimates show that, since the Landau-de Gennes energy density has no forcing term to penalize configurations outside the physical regime, the equilibrium order parameters can take values outside the range (2) even for temperatures quite close to the nematic-isotropic transition temperature [10].

In this paper, we define a continuum energy functional in terms of the mean-field Maier-Saupe energy. Our approach is very similar to that in the paper by Katriel *et.al* [8] but we present our results in the continuum framework as opposed to the statistical mechanics framework. We account for both uniaxial and biaxial phases and include spatial inhomogeneities in the model. The key step is to define a new bulk potential ψ_B that blows up whenever the eigenvalues approach the limiting values of either $-\frac{1}{3}$ or $\frac{2}{3}$ in (2) i.e. ψ_B acts as an infinitely steep well that enforces the equilibrium order parameters to be physically realistic in both the spatially homogeneous and inhomogeneous cases. We show that ψ_B exhibits a logarithmic divergence

as the eigenvalues approach either $-\frac{1}{3}$ or $\frac{2}{3}$. We also study phase transitions within this framework and show that ψ_B predicts a first-order nematic-isotropic phase transition. Finally, we also consider an elastic energy density $w(\mathbf{Q}, \nabla \mathbf{Q})$ with four elastic constants. In this case the Landau-de Gennes energy I_{LG} is in general unbounded from below, so that there is no global energy minimizer. However, this unphysical behaviour disappears if we use our bulk potential ψ_B instead of the Landau-de Gennes bulk potential f_B .

2 The Model

For a spatially homogeneous system, the mean-field Maier-Saupe free energy is given by [9, 8, 6] -

$$I_{MS}[\rho] = T \int_{S^2} \rho(\mathbf{p}) \ln \rho(\mathbf{p}) \, d\mathbf{p} - \kappa |\mathbf{Q}|^2 \quad (5)$$

where ρ is the probability distribution function for molecular orientations, T is the absolute temperature, κ is a constant related to the strength of the intermolecular interactions and \mathbf{Q} is the normalized second moment of ρ as in (1). We refer to the first integral term in (5) as the entropy term and to the second term as the intermolecular interaction term.

We define a bulk potential $\psi_B = \psi_B(\mathbf{Q})$ as follows:

$$\psi_B(\mathbf{Q}) = T \inf_{\rho \in \mathcal{A}_{\mathbf{Q}}} \int_{S^2} \rho(\mathbf{p}) \ln \rho(\mathbf{p}) \, d\mathbf{p} - \kappa |\mathbf{Q}|^2 \quad (6)$$

where

$$\mathcal{A}_{\mathbf{Q}} = \left\{ \rho : S^2 \rightarrow \mathbb{R}, \rho \geq 0, \int_{S^2} \rho(\mathbf{p}) \, d\mathbf{p} = 1; \mathbf{Q} = \int_{S^2} \left(\mathbf{p} \otimes \mathbf{p} - \frac{1}{3} \mathbf{I} \right) \rho(\mathbf{p}) \, d\mathbf{p} \right\}. \quad (7)$$

Thus, for a given \mathbf{Q} , we minimize the entropy term over all probability dis-

tributions ρ that have a fixed normalized second moment \mathbf{Q} . Consequently, ψ_B is a function of \mathbf{Q} and not of ρ (see Katriel *et.al* for a similar definition) and can describe both equilibrium and non-equilibrium liquid crystal configurations.

3 The Bulk Potential

Let

$$f(\mathbf{Q}) = \begin{cases} \inf_{\rho \in \mathcal{A}_{\mathbf{Q}}} \int_{S^2} \rho(\mathbf{p}) \ln \rho(\mathbf{p}) \, d\mathbf{p}, & \text{if } \lambda_i(\mathbf{Q}) \in \left(-\frac{1}{3}, \frac{2}{3}\right), \\ +\infty, & \text{otherwise} \end{cases} \quad (8)$$

i.e. the minimization over $\mathcal{A}_{\mathbf{Q}}$ is only defined for those \mathbf{Q} -tensors which can be expressed as the normalized second moment of a probability distribution function ρ and whose eigenvalues obey the physical constraints (2). We define $f(\mathbf{Q})$ to be unbounded (to be $+\infty$) for those \mathbf{Q} -tensors which are outside this physical regime. Then

$$\psi_B(\mathbf{Q}) = T f(\mathbf{Q}) - \kappa |\mathbf{Q}|^2 \quad (9)$$

and the main aim of this analysis is to study the properties of the function $f(\mathbf{Q})$. We first present some preliminary facts about $f(\mathbf{Q})$ below.

Proposition 1. *For a given \mathbf{Q} with eigenvalues $\lambda_i(\mathbf{Q}) \in \left(-\frac{1}{3}, \frac{2}{3}\right)$, the minimization problem*

$$f(\mathbf{Q}) = \inf_{\rho \in \mathcal{A}_{\mathbf{Q}}} \int_{S^2} \rho(\mathbf{p}) \ln \rho(\mathbf{p}) \, d\mathbf{p} \quad (10)$$

has a unique minimizer ρ^* in the class $\mathcal{A}_{\mathbf{Q}}$, where ρ^* is given by

$$\rho^*(\mathbf{p}) = \frac{\exp\left(\sum_{i=1}^3 \mu_i p_i^2\right)}{Z(\mu_1, \mu_2, \mu_3)}, \quad (11)$$

where $\mathbf{p} = (p_1, p_2, p_3) \in S^2$, $\{\mu_1, \mu_2, \mu_3\}$ are Lagrange multipliers (unique up to the addition of an arbitrary constant) associated with the constraint

$\mathbf{Q} = \int_{S^2} (\mathbf{p} \otimes \mathbf{p} - \frac{1}{3}\mathbf{I}) \rho(\mathbf{p}) d\mathbf{p}$ (see the definition of $\mathcal{A}_{\mathbf{Q}}$ in (7)), $Z(\mu_1, \mu_2, \mu_3)$ is the partition function defined by

$$Z(\mu_1, \mu_2, \mu_3) = \int_{S^2} \exp\left(\sum_{i=1}^3 \mu_i p_i^2\right) d\mathbf{p} \quad (12)$$

and

$$\begin{aligned} \frac{1}{Z} \frac{\partial Z}{\partial \mu_1} &= \lambda_1 + \frac{1}{3} \\ \frac{1}{Z} \frac{\partial Z}{\partial \mu_2} &= \lambda_2 + \frac{1}{3} \\ \frac{1}{Z} \frac{\partial Z}{\partial \mu_3} &= \lambda_3 + \frac{1}{3}. \end{aligned} \quad (13)$$

Proof. The proof of this proposition is quite technical. The key steps are to show that (i) $\mathcal{A}_{\mathbf{Q}}$ is nonempty for any \mathbf{Q} whose eigenvalues obey the physical constraints (2), (ii) $f(\mathbf{Q})$ is a strictly convex function of the \mathbf{Q} -tensor and (iii) the Euler-Lagrange equations hold for the minimization problem (10). We point out that the relations (13) implicitly define the Lagrange multipliers μ_i as functions of \mathbf{Q} up to the addition of an arbitrary constant to each μ_i , i.e. the differences $\mu_i - \mu_j$ are unique. The proof is similar in spirit to the methods in [8, 6] and we omit the details here for brevity. \square

Proposition 2. *The function $f(\mathbf{Q}) \rightarrow +\infty$ whenever one of the eigenvalues approaches the lower limiting value of $-\frac{1}{3}$ in (2) i.e. when $\lambda_i(\mathbf{Q}) \rightarrow -\frac{1}{3}^+$*

for some $i = 1, 2, 3$.

Proof. For definiteness, let us assume that $\lambda_1(\mathbf{Q}) \rightarrow -\frac{1}{3}^+$. We recall that this lower bound describes a liquid crystal configuration where the nematic molecules are everywhere perpendicular to the corresponding eigenvector [7, 10]. In this limit, the probability distribution function ρ is necessarily singular in the sense that it is supported on the unit circle perpendicular to this eigenvector. Therefore, $\ln \rho$ diverges and consequently, $f(\mathbf{Q}) \rightarrow \infty$ or $f(\mathbf{Q})$ becomes unbounded. Analogous remarks apply if $\lambda_i(\mathbf{Q}) \rightarrow \frac{2}{3}$ for some $i = 1, 2, 3$ as this describes the physically unrealistic state of perfect alignment along the corresponding eigenvector. For technical details, see [2]. \square

Given the minimizing ρ^* in (11), we have from (9) and (12) that

$$\psi_B(\mathbf{Q}) = T \sum_{i=1}^3 \mu_i \left(\lambda_i(\mathbf{Q}) + \frac{1}{3} \right) - T \ln Z(\mu_1, \mu_2, \mu_3) - \kappa |\mathbf{Q}|^2 \quad (14)$$

$$= T(\mu_1 - \mu_3) \left(\lambda_1 + \frac{1}{3} \right) + T(\mu_2 - \mu_3) \left(\lambda_2 + \frac{1}{3} \right) - \kappa |\mathbf{Q}|^2 - T \ln \left[\int_{S^2} \exp((\mu_1 - \mu_3) p_1^2 + (\mu_2 - \mu_3) p_2^2) d\mathbf{p} \right]. \quad (15)$$

In (15), we have used the explicit form of the partition function Z in (12). From the definition of ψ_B in (9), it is evident that $\psi_B(\mathbf{Q}) \rightarrow +\infty$ if and only if $f(\mathbf{Q}) \rightarrow \infty$ and from the semi-explicit expression in (15), $\psi_B \rightarrow +\infty$ if and only if either $\mu_1 - \mu_3 \rightarrow \pm\infty$ or $\mu_2 - \mu_3 \rightarrow \pm\infty$ or both. Since the function $f(\mathbf{Q})$ diverges whenever $\lambda_i(\mathbf{Q}) \rightarrow -\frac{1}{3}^+$ for some $i = 1 \dots 3$, we deduce that

Corollary 1. *The limits $\mu_1 - \mu_3 \rightarrow \pm\infty$ or $\mu_2 - \mu_3 \rightarrow \pm\infty$ correspond to one or more of the eigenvalues approaching the lower bound in (2) i.e. they describe physically unrealistic configurations.*

As an illustrative example, let us consider the arbitrary uniaxial state $(\lambda_1, \lambda_2, \lambda_3) = (\lambda, \lambda, -2\lambda)$ where λ is the non-zero degenerate eigenvalue. From (11), the minimizing ρ^* is given by

$$\rho^*(\theta, \phi) = \frac{\exp(\mu_1 \sin^2 \theta + \mu_3 \cos^2 \theta)}{Z(\mu_1, \mu_3)}, \quad (16)$$

where (θ, ϕ) are spherical polar coordinates on the unit sphere, $Z(\mu_1, \mu_3) = 2\pi \exp(\mu_3) \int_{-1}^1 \exp((\mu_1 - \mu_3)(1 - \nu^2)) d\nu$ is the partition function and

$$\frac{1}{Z} \frac{\partial Z}{\partial \mu_3} = \frac{1}{2(\mu_1 - \mu_3)} - \frac{2\pi \exp(\mu_3)}{\mu_1 - \mu_3} \frac{1}{Z(\mu_1, \mu_3)} = -2\lambda + \frac{1}{3}. \quad (17)$$

(We note that (16)-(17) is the same as the uniaxial formulation in Kartiel *et.al* [8] and that $Z(\mu_1, \mu_3)$ can be explicitly expressed in terms of the Dawson's integral although we will not need the explicit expression for this discussion.)

The question of interest is - what do the limits $\mu_1 - \mu_3 \rightarrow \pm\infty$ correspond to in terms of the eigenvalue λ ? It is straightforward to verify from (17) that if $\mu_1 - \mu_3 \rightarrow +\infty$, then

$$\lambda = \frac{1}{6} - \frac{1}{4(\mu_1 - \mu_3)} + o\left(\frac{1}{\mu_1 - \mu_3}\right) \quad (18)$$

($o\left(\frac{1}{\mu_1 - \mu_3}\right)$ includes terms which are much smaller than $\frac{1}{\mu_1 - \mu_3}$ in this limit) and

$$\psi_B(\mathbf{Q}) = TC_1 \ln(\mu_1 - \mu_3) - \frac{\kappa}{6} + TC_2 + \frac{\kappa}{2(\mu_1 - \mu_3)} + o\left(\frac{1}{\mu_1 - \mu_3}\right) \quad (19)$$

where C_1 and C_2 are positive constants independent of μ_1, μ_3 and κ . Thus, the limit $\mu_1 - \mu_3 \rightarrow +\infty$ corresponds to the oblate uniaxial state $(\lambda_1, \lambda_2, \lambda_3) = (\frac{1}{6}, \frac{1}{6}, -\frac{1}{3})$ and the bulk potential ψ_B exhibits a logarithmic divergence in

this limit.

Similarly, if $\mu_1 - \mu_3 \rightarrow -\infty$, then we can carry out standard asymptotic estimates using Laplace's method [3] to show that

$$\lambda = -\frac{1}{3} + \frac{1}{4|\mu_1 - \mu_3|} + o\left(\frac{1}{|\mu_1 - \mu_3|}\right) \quad (20)$$

in this limit and

$$\psi_B(\mathbf{Q}) = TB_1 \ln |\mu_1 - \mu_3| - \frac{2\kappa}{3} + TB_2 + \frac{\kappa}{|\mu_1 - \mu_3|} + o\left(\frac{1}{|\mu_1 - \mu_3|}\right) \quad (21)$$

as $\mu_1 - \mu_3 \rightarrow -\infty$, where B_1, B_2 are positive constants independent of μ_1, μ_3 and κ . Therefore, the limit $\mu_1 - \mu_3 \rightarrow -\infty$ corresponds to the prolate uniaxial state $(\lambda_1, \lambda_2, \lambda_3) = (-\frac{1}{3}, -\frac{1}{3}, \frac{2}{3})$ and ψ_B exhibits a logarithmic divergence in this case too.

These calculations can be generalized to the biaxial case where $Z(\mu_1, \mu_2, \mu_3)$ is given by (12) and we are interested in the limits $\mu_1 - \mu_3 \rightarrow \pm\infty$ and $\mu_2 - \mu_3 \rightarrow \pm\infty$. The main results are:

1. $\mu_1 - \mu_3, \mu_2 - \mu_3 \rightarrow +\infty$ corresponds to a \mathbf{Q} -tensor with

$$\lambda_3 + \frac{1}{3} = C \left\{ \frac{1}{\mu_1 - \mu_3} + \frac{1}{\mu_2 - \mu_3} \right\} + o\left(\frac{1}{\mu_1 - \mu_3} + \frac{1}{\mu_2 - \mu_3}\right) \quad (22)$$

where C is a positive constant.

2. $\mu_1 - \mu_3 \rightarrow +\infty, \mu_2 - \mu_3 \rightarrow -\infty$ corresponds to a prolate uniaxial state $(\lambda_1, \lambda_2, \lambda_3) = (\frac{2}{3}, -\frac{1}{3}, -\frac{1}{3})$
3. $\mu_1 - \mu_3 \rightarrow -\infty, \mu_2 - \mu_3 \rightarrow +\infty$ corresponds to the prolate uniaxial state $(\lambda_1, \lambda_2, \lambda_3) = (-\frac{1}{3}, \frac{2}{3}, -\frac{1}{3})$
4. $\mu_1 - \mu_3, \mu_2 - \mu_3 \rightarrow -\infty$ corresponds to the prolate uniaxial state

$$(\lambda_1, \lambda_2, \lambda_3) = \left(-\frac{1}{3}, -\frac{1}{3}, \frac{2}{3}\right).$$

Cases with $\mu_1 - \mu_3 \rightarrow \pm\infty$ and $\mu_2 - \mu_3 = O(1)$ or $\mu_1 - \mu_3 = O(1)$ and $\mu_2 - \mu_3 \rightarrow \pm\infty$ can be treated in an analogous manner and, in all cases, the bulk potential ψ_B exhibits a logarithmic divergence. We can summarize these computations as follows.

Corollary 2. *Let $\mu_i - \mu_j \rightarrow \pm\infty$ in the definition of $Z(\mu_1, \mu_2, \mu_3)$ in (12), for a pair of Lagrange multipliers μ_i and μ_j . Then one or more of the eigenvalues approach the lower bound of $-\frac{1}{3}$ in (2) and the leading order asymptotics of ψ_B is given by*

$$\psi_B \sim TC \ln |\mu_i - \mu_j| \quad (23)$$

where C is a positive constant.

4 Nematic-Isotropic Phase Transition

In this section, we show that the bulk potential ψ_B predicts a first-order nematic-isotropic phase transition as in the Landau-de Gennes theory. Our first result concerns the nature of stationary points of ψ_B .

Proposition 3. *Every stationary point of the bulk potential*

$$\begin{aligned} \psi_B(\mathbf{Q}) &= T f(\mathbf{Q}) - \kappa |\mathbf{Q}|^2 \\ &= T \sum_{i=1}^3 \mu_i(\mathbf{Q}) \left(\lambda_i(\mathbf{Q}) + \frac{1}{3} \right) - T \ln Z(\mu_1, \mu_2, \mu_3) - \kappa |\mathbf{Q}|^2 \end{aligned} \quad (24)$$

must have at least two equal eigenvalues.

This implies that every stationary point of ψ_B must be either uniaxial or isotropic. The proof is very similar to the methods in [6] and we omit the

details here for brevity.

Let $(\lambda_1, \lambda_2, \lambda_3) = (\lambda, \lambda, -2\lambda)$ be a uniaxial stationary point of ψ_B in (9).

The corresponding \mathbf{Q} -tensor is

$$\mathbf{Q}_u = S \left(\mathbf{e}_3 \otimes \mathbf{e}_3 - \frac{1}{3} \mathbf{I} \right) \quad (25)$$

where $S = -3\lambda$ and \mathbf{e}_3 is the distinguished eigenvector (with eigenvalue -2λ). Then the stationarity condition $d\psi_B/d\lambda = 0$ coupled with the relations (17) necessarily implies that

$$\mu_1 - \mu_3 = 6\kappa\lambda. \quad (26)$$

Without going into technical details, (26) enables us to obtain an explicit expression for $\psi_B(\mathbf{Q}_u)$, where \mathbf{Q}_u is a stationary point by assumption, and explicitly compute the stationary values of λ (or equivalently the stationary values of the uniaxial order parameter S) within this framework. There are precisely three stationary values of λ :

$$\begin{aligned} \lambda &= 0 \\ \lambda_{\pm}(T) &= \frac{-1 \pm \sqrt{9 - \frac{30T}{\kappa}}}{12} \end{aligned} \quad (27)$$

where $\lambda_{\pm}(T)$ correspond to the ordered nematic phases and $\lambda_-(T)$ is the stable nematic stationary point. As $T \rightarrow 0$, $\lambda_-(T) \rightarrow -\frac{1}{3}$ and the corresponding value of $S = -3\lambda_-(T) \rightarrow 1$ in this limit. Similarly, $\lim_{T \rightarrow 0} \lambda_+(T) \rightarrow \frac{1}{6}$ and therefore $S = -3\lambda_+(T) \rightarrow -\frac{1}{2}$ in this limit.

As in the Landau-de Gennes theory, there are precisely three character-

istic values of T , $T_1 < T_2 < T_3$ within this model -

$$\begin{aligned}
T_1 &= \frac{3\kappa}{10}, \text{ above which nematic states are not defined} \\
T_2 &: \psi_B(0) = \psi_B(\lambda_-(T_2)) \\
T_3 &= \frac{4\kappa}{15}, \text{ below which the isotropic state } \lambda = 0 \text{ loses its stability.}
\end{aligned} \tag{28}$$

We note that T_2 is the analogue of the nematic-isotropic transition temperature and that the equilibrium uniaxial order parameter at the transition point $S_{NI} = -3\lambda_-(T_2)$ lies in the range $\frac{1}{4} < S_{NI} < \frac{1}{2}$. Thus, this model predicts a first-order nematic-isotropic phase transition whilst respecting the physical constraints (2).

5 Spatial Inhomogeneities

Having studied the bulk potential ψ_B in some detail, we next include spatial inhomogeneities into the model. We work within the one-constant approximation for the elastic energy density. Then the corresponding energy functional is

$$E[\mathbf{Q}] = \int_{\Omega} \psi_B(\mathbf{Q}) + L|\nabla \mathbf{Q}|^2 dV \tag{29}$$

where $\mathbf{Q} = \mathbf{Q}(\mathbf{x})$, Ω is a smooth, simply-connected domain in three-dimensional space and L is an elastic constant. The equilibrium (physically observable) configurations are given either by global or local minimizers of this energy subject to the imposed boundary conditions.

Theorem 1. *Let \mathbf{Q}^* be a global minimizer of $E[\mathbf{Q}]$ subject to the fixed boundary condition (strong anchoring), $\mathbf{Q} = \mathbf{Q}_b$ on $\partial\Omega$. We take the boundary condition \mathbf{Q}_b to be physically realistic in the sense $-\frac{1}{3} + \epsilon_0 < \lambda_i(\mathbf{Q}_b) < \frac{2}{3} - \epsilon_0$ for $i = 1, 2, 3$, for some $\epsilon_0 > 0$, or equivalently $\psi_B(\mathbf{Q}_b)$ is bounded. Then*

the eigenvalues, $\lambda_i(\mathbf{Q}^*)$, of \mathbf{Q}^* are constrained by the inequalities

$$-\frac{1}{3} + \epsilon < \lambda_i(\mathbf{Q}^*) < \frac{2}{3} - \epsilon \quad i = 1, 2, 3 \quad (30)$$

for some $\epsilon > 0$ i.e. the eigenvalues of \mathbf{Q}^* obey the physical constraints in (2).

Remark: Since ψ_B blows up whenever the physical constraints (2) are violated, it is evident that a global energy minimizer \mathbf{Q}^* must obey $-\frac{1}{3} < \lambda_i(\mathbf{Q}^*) < \frac{2}{3}$ almost everywhere on Ω , except possibly for a set of zero volume. The force of the above Theorem lies in the fact that $\lambda_i(\mathbf{Q}^*)$ remain bounded away from the limiting values, $-\frac{1}{3}$ or $\frac{2}{3}$, everywhere in Ω i.e. they cannot approach the limiting values arbitrarily closely. While this is plausible, there are well-known examples in the calculus of variations in which minimizers have defects where the energy density (the analogue of ψ_B in our case) blows up.

Proof. The proof of this theorem follows from a maximum principle approach [5] and the details are omitted here for brevity. \square

6 Example with Four Elastic Constants

We have considered the one-constant approximation for the elastic energy density $w(\mathbf{Q}, \nabla \mathbf{Q})$ in Section 5. There are more general forms of the elastic energy density such as [11]

$$w(\mathbf{Q}, \nabla \mathbf{Q}) = L_1 |\nabla \mathbf{Q}|^2 + L_2 Q_{ik,j} Q_{ij,k} + L_3 Q_{ij,j} Q_{ik,k} + L_4 Q_{lk} Q_{ij,k} Q_{ij,l} \quad (31)$$

where $\mathbf{Q} = (Q_{ij})$, $Q_{ij,k} = \frac{\partial Q_{ij}}{\partial x_k}$ and L_1, \dots, L_4 are material-dependent elastic constants. We present an example with four elastic constants in the Landau-

de Gennes framework and show that if $L_4 \neq 0$, then the energy is unbounded from below.

Proposition 4. *For any boundary conditions, if $L_4 \neq 0$, then the Landau-de Gennes energy*

$$I_{LG}[\mathbf{Q}] = \int_{\Omega} f_B(\mathbf{Q}) + w(\mathbf{Q}, \nabla \mathbf{Q}) \, dV \quad (32)$$

where $f_B(\mathbf{Q})$ is as in (4) and $w(\mathbf{Q}, \nabla \mathbf{Q})$ is as in (31), is unbounded from below (that is, there exists a \mathbf{Q} such that $I_{LG}[\mathbf{Q}] \rightarrow -\infty$).

Proof. Choose any \mathbf{Q} satisfying the boundary conditions and redefine it by multiplying it by a smooth function ϕ , which equals one in a neighbourhood of the domain boundary and is zero in some ball $B \subset \Omega$, which we can take to be the unit ball $B(0, 1)$. Thus \mathbf{Q} vanishes on B and we are free to alter \mathbf{Q} in B subject to $\mathbf{Q}|_{\partial B} = 0$. We alter \mathbf{Q} in B so that $I_{LG}[\mathbf{Q}]$ is arbitrarily large and negative. We set

$$\mathbf{Q}(\mathbf{x}) = \eta(|\mathbf{x}|) \left[\frac{\mathbf{x}}{|\mathbf{x}|} \otimes \frac{\mathbf{x}}{|\mathbf{x}|} - \frac{1}{3} \mathbf{I} \right], \quad \eta(1) = 0. \quad (33)$$

Then

$$|\nabla \mathbf{Q}|^2 = Q_{ij,k} Q_{ij,k} = \frac{2}{3} \eta'^2 + \frac{4}{|\mathbf{x}|^2} \eta^2$$

and

$$Q_{lk} Q_{ij,k} Q_{ij,l} = \frac{4}{9} \eta \left(\eta'^2 - \frac{3}{|\mathbf{x}|^2} \eta^2 \right).$$

Therefore, since $|Q_{ik,j} Q_{ij,k}|$ and $|Q_{ij,j} Q_{ik,k}|$ are bounded by $\text{const.} \times |\nabla \mathbf{Q}|^2$,

$$\begin{aligned} I_{LG}[\mathbf{Q}] &\leq 4\pi C \int_0^1 r^2 \left[f_B(\mathbf{Q}) + \frac{2}{3} \eta'^2 + \frac{4}{|\mathbf{x}|^2} \eta^2 \right] dr \\ &+ 4\pi \int_0^1 \frac{4L_4}{9} \eta \left(\eta'^2 - \frac{3}{|\mathbf{x}|^2} \eta^2 \right) r^2 dr + \int_{\Omega \setminus B} f_B(\mathbf{Q}) + w(\mathbf{Q}, \nabla \mathbf{Q}) \, dV \end{aligned} \quad (34)$$

where $r = |\mathbf{x}|$ and C is a positive constant. We define

$$\eta(r) = \begin{cases} \eta_0 (2 + \sin kr), & 0 < r < \frac{1}{2}, \\ 2\eta_0 (2 + \sin \frac{k}{2}) (1 - r), & \frac{1}{2} < r < 1. \end{cases} \quad (35)$$

Explicit computations now show that by choosing η_0 to be sufficiently negative ($\eta_0 < 0$, $|\eta_0| \gg 1$) and k to be sufficiently large and positive, $I_{LG}[\mathbf{Q}]$ can be made arbitrarily large and negative. \square

The above proposition implies in particular that there is no global minimizer for the Landau-de Gennes energy in the presence of the given cubic term in the elastic energy density. On the other hand, for our modified energy functional

$$E[\mathbf{Q}] = \int_{\Omega} \psi_B(\mathbf{Q}) + w(\mathbf{Q}, \nabla \mathbf{Q}) \, dV \quad (36)$$

it is possible to prove the existence of global minimizers when $L_4 \neq 0$, under suitable hypotheses on the elastic constants L_i . This is because the eigenvalue constraints (2) allow one to estimate the cubic term in terms of the quadratic ones (see [2]) and consequently, $E[\mathbf{Q}]$ remains bounded from below.

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