Mathematical Models of Liquid Crystals and Related Materials



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Abstract

In the broadest sense, the focus of this thesis concerns the role of entropy in macroscopic systems related to liquid crystals in equilibrium. We begin by defining a broad generalisation of the Ball-Majumdar potential, applicable to a wide variety of order parameter models relevant to liquid crystals. First we provide a geometric characterisation of the set of admissible order parameters for general systems. We demonstrate the key properties of convexity, regularity, and blow up at the boundary of the singular potential. This is then followed by a discussion of applications to Onsager type models and enforcing physicality constraints in Landau expansion-type models.

Next we consider the recently proposed Onsager-type model of Zheng, Taylor and Palffy-Muhoray. Unlike Onsager's free energy density, the non-trivial solutions to the new model all have non-trivial support, implying two-sided variations cannot find solutions. In order to overcome this issue, we apply similar heuristics to the previous chapter to split the minimisation into two steps, a strictly convex minimisation problem with linear constraints and a finite dimensional, C^1 minimisation problem, the latter of which provides an Euler-Lagrange-type equation satisfied by all L^p-local minimisers. We also perform a more direct analysis on the model to obtain the qualitative features of its phase behaviour.

Finally, we consider an extension of the Kuhn-Grün model of polymer elasticity, adapted for use in the modelling of main-chain nematic elastomers. This is a particular case of the generalised singular potential, where the anisotropy of the polymer network is included as a further parameter in the energy. This shows the expected energetic coupling between the anisotropy of the system and the extension of a single chain. Furthermore, the polymer chain is finitely extensible, with the energy blowing up as the chain reaches the taut-chain limit, and an implicit force/extension relationship is provided. We conclude with a discussion of network theo-

ries for describing macroscopic deformations, with particular focus on the rigidity properties that arise from the growth rate of the chain energy.

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Chapter 1

Introduction

1.1 Liquid crystals

The first discovery of liquid crystalline phases dates back to Reinitzer's work in 1888, discovering a fluid which appeared to have two melting points [43]. At the time there was a thoroughly believed trichotomy of only solid-liquid-gas phases, so the observed cloudy fluid phase was vexing. Further work by Lehmann, made possible by his then state-of-the-art polarising microscope, provided many of the early insights into the properties of these mesophases [31]. After much research between many groups, with debate on the exact nature and cause of these phases, Friedel published his famed manuscript suggesting that the phases were driven by underlying structure, and the early classification of liquid crystalline phases into the now commonly used nematic, smectic and cholesteric phases was proposed [23]. Over 100 years later we now understand liquid crystalline phases as intermediate phases between an isotropic liquid and crystalline solid, where asymmetric molecules adopt a kind of intermediate order that is far less rigid than for a classical crystal. Since their first discovery a rich plethora of such mesophases has been found, and much scientific work has been dedicated to understanding their origins, properties and applications. The prototypical molecules that can form liquid crystalline phases are rigid, extended, rod-like molecules. The commonly used molecule 5CB is sufficiently extended to form liquid crystalline phases, and in the modelling process we tend to idealise such molecules as ellipsoids or spherocylinders. Significantly, our models will often treat the molecule as having a distinguished axis, about which the molecule is both rotationally and head-to-tail symmetric. This allows us to describe the orientation of such molecules by a unit vector $p \in \mathbb{S}^2$ with the equivalence $p \sim -p$.

The prototypical phase that such molecules can form is the nematic phase, wherein

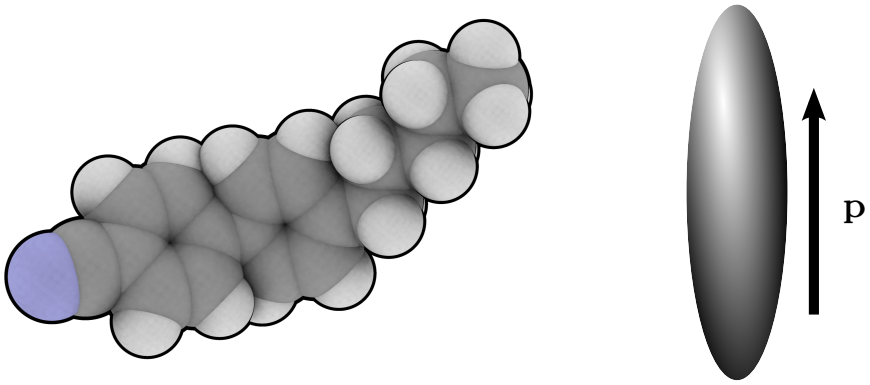


Figure 1.1: A 5CB molecule and its idealisation as an ellipsoid, demonstrating the orientation $p \in \mathbb{S}^2$.

molecules have local orientational order but little positional order. These are often found as uniaxial phases, where there is a distinguished direction $n \in \mathbb{S}^2$ such that molecules are generally well aligned with $p \approx n$, although n may vary on larger length scales throughout a sample, in particular near defects. Generally far more complex phases may exist, such as smectic phases which admit a 1-dimensional translational symmetry, cholesteric phases which produce chiral twisted structures, or blue phases which form 3-dimensional periodic structures.

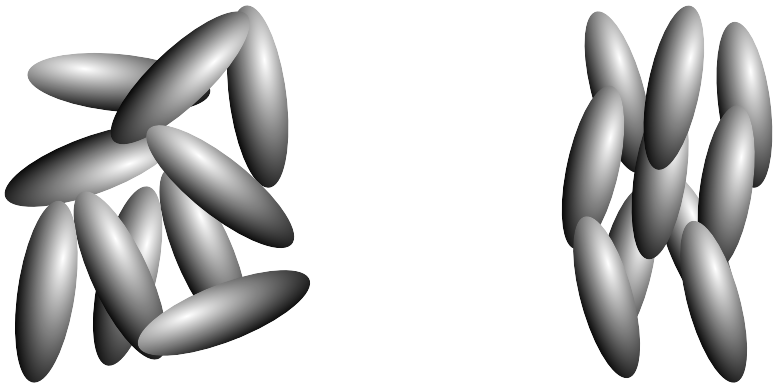


Figure 1.2: An idealisation of isotropic liquid (left) and nematic phase (right) of ellipsoidal molecules

Beyond classical liquid crystals themselves, there is also much scientific interest in more complex materials which take advantage of the properties offered by liquid crystalline systems. Examples include colloidal liquid crystals, where the liquid crystal interacts with nanoparticles and can produce a variety of behaviour such as disclination loops called Saturn rings [49], and liquid crystal elastomers, where polymer

based materials are infused with liquid crystal phase forming molecules, leading to the development of anisotropic rubber-like materials [58], the latter of which will be relevant to this work. The key feature of these liquid crystal elastomers is that strains which align with the orientation of the liquid crystalline phase are generally favoured, and this can produce a two-way coupling, whereby mechanical deformation induces a change in orientation, and altering the orientation by e.g. heating [48] or photonic effects [25] can induce spontaneous strains.

The interest in liquid crystal elastomers was heavily sparked by the observation of soft elastic modes, wherein large strains can be observed under very small stresses [57]. Furthermore, the development of microstructure such as the stripe domain instability identifies these materials as being distinct from classical isotropic rubbers [30]. In fact in both of these respects, the liquid crystalline material becomes analogous to shape-memory alloys, where microstructure is often unavoidable and its rearrangement can reduce stresses [11]. While these materials are somewhat recent in their development, their proposed future applications include a basis for active prosthesis [50], bifocal contact lenses [4] and a candidate for haptic displays [52].

1.2 Models describing liquid crystals and related materials

Just as there exists a wide family of liquid crystal phases, there are a large number of competing models to try and describe and predict their behaviour. Even for modelling a single material one may consider a variety of different models depending on the features and length scales one is interested in. These vary from the molecular dynamics systems where a smaller number of molecules can be simulated, even down to the scale of individual atoms to understand fine level structure [42], all the way to the macroscopic continuum descriptions such as Landau-de Gennes [18] and Oseen-Frank [41]. We now provide a brief overview of the models of interest to this thesis.

1.2.1 Onsager's model of phase transitions

Onsager's model is a mesoscale model, more coarse grained than molecular dynamics but still not a continuum model [40]. The primary aim of the Onsager model is to understand phase transitions, and is seldom used for understanding features such as defects. Each molecule is assumed to live in some state space X with measure μ, typically given as a subset of $\mathrm{SO}(3) \times \mathbb{R}^n$, describing the orientation and position of

the molecule. For the commonly considered case of spatially homogeneous phases only SO(3) is necessary, and if molecules admit axial symmetry then their orientation can be described by an element of $\mathbb{S}^2$, corresponding to the equivalence classes of SO(3) which leave the molecule invariant. The entire system is then described by a one-particle probability distribution f belonging to $\mathcal{P}(X)$, the space of probability distributions on X. The system is generally taken to be held at fixed concentration ρ_0. Equilibrium configurations of the sample are then described by local minimisers of the free energy

$$k_B T \int_X \rho_0 f(t) \ln \rho_0 f(t) \, d\mu(t) - \frac{\rho_0^2}{2} \int_X f(t) \left(\int_X K(t,s) f(s) \, d\mu(s) \right) d\mu(t), \tag{1.1}$$

where $T > 0$ is temperature, k_B the Boltzmann constant and $K : X^2 \to \mathbb{R}$ is a pairwise interaction potential. Onsager originally justified the model based on statistical mechanics by a non-rigorous argument via a mean-field approximation, although there have been more contemporary attempts to make the arguments rigorous [6]. Furthermore, the free energy's significance can also be seen as, at least in some cases, the Lyapunov functional of the Doi-Onsager equation for describing the evolution of a liquid crystal system [60]. Taking $X = \mathbb{S}^2$ for simplicity and the derivative operators to be those corresponding to functions on the sphere, the Doi-Onsager equation is given by

$$\frac{\partial f}{\partial t}(p,t) = \nabla \cdot \left(\nabla f(p,t) - \rho_0 f(p,t) \nabla U(p,t) \right), \tag{1.2}$$

with the potential U given by

$$U(p,t) = \int_{\mathbb{S}^2} f(q,t) K(p,q) \, dq. \tag{1.3}$$

1.2.2 The Landau-de Gennes Q-tensor model

The Landau-de Gennes model aims to describe liquid crystals on a larger macroscopic scale. It is a specific case of the Landau expansion, of which the central object is the order parameter [51]. Generally order parameters are macroscopic averages of microscopic quantities, which may vary across spatial regions. In the case of the liquid crystal systems treated in this work, we will consider Onsager-type models at the fine scale, so that at each point x in some spatial domain $\Omega \subset \mathbb{R}^n$ there exists some local ensemble of molecules described by a probability distribution on a state space, $f_x \in \mathcal{P}(X)$. The order parameters will then be described by averages of bounded functions from X to a finite-dimensional vector space V, $a \in L^\infty(X, V)$, meant to be

representative of the macroscopic behaviour of the system. Explicitly, we define the order parameter

$$b(x) = \int_X a(t) f_x(t)\, d\mu(t). \tag{1.4}$$

The convention is typically taken so a is renormalised to have $b(x) = 0$ at the ground state or high-temperature phase. The Landau expansion argues that the free energy should be of the form

$$\int_\Omega W(\nabla b(x), b(x))\, dx, \tag{1.5}$$

where W is an analytic function that respects the symmetry of the system. Due to these assumptions, at least for configurations near the high temperature state $b = 0$, we can approximate W by a low-order polynomial in b and its derivative that respects the symmetry of the system. In the Landau-de Gennes model $X = \mathbb{S}^2$, $V = \mathrm{Sym}_0(3)$, the space of traceless symmetric matrices, and $a(p) = p \otimes p - \frac{1}{3} I$. The order parameter is known as the Q-tensor, typically denoted Q, and a form of the free energy often considered is

$$\int_\Omega \frac{L}{2} |\nabla Q(x)|^2 + \frac{a(T - T_c)}{2} \mathrm{tr}(Q(x)^2) + \frac{b}{3} \mathrm{tr}(Q(x)^3) + \frac{c}{4} \mathrm{tr}(Q(x)^2)^2\, dx. \tag{1.6}$$

Such models can be derived on less phenomenological grounds by considering Onsager models in the small interaction distance limit [24].

However a truncated Taylor expansions of the free energy, such as that in (1.6) may be inaccurate away from the high temperature phase. In particular, in the Landau-de Gennes model there is a first order isotropic-nematic phase transition, so that near the transition temperature we expect that the truncated Taylor expansion may be inaccurate at the ground state. It is thus appropriate to question the validity of the Landau expansion. An example of such an issue is the so-called physicality condition. Recalling the definition of the Q-tensor, we see that a traceless symmetric matrix can be written as $\int_{\mathbb{S}^2} \left(p \otimes p - \frac{1}{3} I\right) f(p)\, dp$ if and only if its smallest eigenvalue is strictly larger than $-\frac{1}{3}$. The Landau-de Gennes free energy has no penalisation to enforce this constraint however, and cases have been noted where the constraint fails [35]. Tto overcome this Ball and Majumdar [8], building on previous work of Katriel *et. al.* [27], proposed replacing the quartic bulk potential by a singular potential that blows up as $\lambda_{\min}(Q) \to -\frac{1}{3}$, arguing on physical grounds that the entropic contribution to the energy of any probability distribution with such a Q-tensor must be extremely high [8]. In Chapter 2 we consider a broad generalisation of this singular potential.

1.2.3 The Kuhn-Grün model in isotropic elasticity and its derivatives

Before commenting on models for liquid crystal elastomers it is necessary to provide some historical remarks on isotropic elasticity. A wide range of models exist for describing the elastic behaviour of isotropic rubbers, with varying derivations and arguments, ranging from the phenomenological [39] to statistical mechanical viewpoints [28]. In this work we will be considering a particular class of models based on two key assumptions. Firstly, that there is a system of non-interacting polymer chains, which admit a spring-type chain deformation energy $w_c : \mathbb{R}^3 \to \mathbb{R} \cup \{+\infty\}$ that describes the elastic behaviour of a single chain, so if that the end points a polymer chain is spanned by a vector $R \in \mathbb{R}^3$, the elastic energy is $w_c(R)$. Secondly, that under a (local) macroscopic deformation $x \mapsto Fx + b$ for $F \in \mathbb{R}^{3\times 3}$ and $b \in \mathbb{R}^3$, the energy of deformation can be described as a sum of such chain energies with respect to a measure representing the configuration of chains in the reference configuration. Explicity, we assume the deformation energy $W_d : \mathbb{R}^{3\times 3} \to \mathbb{R} \cup \{+\infty\}$ is given by

$$W_d(F) = \int_{\mathbb{R}^3} w_c(FR)\, d\nu(R) \tag{1.7}$$

for an appropriate probability measure ν that may depend on the deformation gradient F itself. The assumption that the chains deform affinely with the macroscopic deformation is analogous to the Cauchy-Born rule in the solid mechanics of crystals [20]. The simplest of such chain energies is to take a quadratic chain function, $w_c(R) = \frac{c}{2}|R|^2$, based on a linear tension/displacement relationship with constant of proportionality c, also known as a Hookean spring. This can be justified as an entropic spring in a small strain regime [28]. Rubbers however are significant in that they can undergo very large deformations, and so there is interest in describing the chains under large extension. One such attempt to explain the behaviour of rubbers in the large-strain regime is the Kuhn-Grün chain energy [29]. Similarly to the Hookean spring, it treats the polymer chain as an entropic spring, however by not taking a small-strain assumption, an isotropic chain energy can be obtained which blows up as the chain reaches its taut limit. Explicitly, the energy can be given as (in non-dimensional form)

$$w_c(R) = \frac{|R|}{L}\beta + \ln\left(\frac{\beta}{\sinh(\beta)}\right), \tag{1.8}$$

where $L > 0$ is the length of a taut chain, and $\coth(\beta) - \frac{1}{\beta} = \frac{|R|}{L}$. Once the chain energy has been established, there are numerous ways of implanting these into macroscopic models of deformations of the form given above. Typically, these will assume that ν is supported on a discrete subset of $l\sqrt{N}\mathbb{S}^2$ where l is the length of a single monomer and N is the number of monomers in a chain. This corresponds to a root-mean-square assumption. The discrete set will also typically depend on the eigenbasis of F^TF to ensure isotropy. Examples are the 3-chain [56] and 8-chain models [5]. Both of these n-chain models considers the measure to be a sum of Dirac masses, given as

$$W_d(F) = \sum_{i=1}^{n} w_c(FR_i(F)) \tag{1.9}$$

for frame-indifferent maps R_i, depending on the principal axes of F. Explicitly, if $(e_i)_{i=1}^3$ denotes the eigenvectors of F^TF, then the various models take the supports of ν to be

- 3-chain: $(e_i)_{i=1}^3$.
- 8-chain: $\pm e_1 \pm e_2 \pm e_3$, with the three independent sign choices giving eight distinct vectors.

One significant model for this work is the full-network Wu-Van der Geissen model, which takes ν to be the 2-dimensional Hausdorff measure on $\ell\sqrt{N}\mathbb{S}^2$ [59], so that the deformation energy is given by

$$W_d(F) = \frac{1}{4\pi N^2 \ell} \int_{\sqrt{N}\ell\mathbb{S}^2} w_c\left(FR\right)\, dR. \tag{1.10}$$

Although this gives rise to a more complex deformation energy, it is advantageous over the other models in that we do not need to prescribe some frame indifferent probability measure depending on the deformation. That is, the distribution of chains in the reference configuration does not vary with F. In all of these models, the finite extensibility of the chain energy gives rise to finite extensibility effects in deformations. It should be noted that all such deformation energies require an additional volumetric term to avoid matter wishing to compress to a single point, and typically incompressibility ($\det(F) = 1$) is assumed, however for the sake of this work this will generally be unimportant.

1.2.4 Warner-Bladon-Terentjev's Neo-Hookean model

In nematic elastomers, nematic phase forming monomers are placed into a flexible polymer network. The elasticity of the network and the ordering of the nematic are intimately linked. The first theoretical attempt at describing this relationship was given by Warner, Bladon and Terentjev [57] and is based on a similar argument to that of the isotropic Hookean theory. The main divergence in their work however is that the distribution of chains is given by an anisotropic distribution, described in the reference configuration (deformed configuration, respectively) by a so-called anisotropic step tensor $L_0 \in \mathbb{R}^{3\times 3}$ ($L \in \mathbb{R}^{3\times 3}$, respectively). In the case of uniaxial nematics, we can take $L = I + \alpha n \otimes n$ and $L_0 = I + \alpha n_0 \otimes n_0$, where n, n_0 are the directors in the deformed and reference configuration, and $\alpha > -1$ represents the coupling of the anisotropy. In this case, their work gives that for small-strain deformations, the energy should be given as

$$W_D(F, L, L_0) = |L^{-\frac{1}{2}} F L_0^{\frac{1}{2}}|^2. \tag{1.11}$$

Within the class of incompressible deformations, the energy minimising deformations subject to given n, n_0 are then given as $L^{\frac{1}{2}}\mathrm{SO}(3)L_0^{-\frac{1}{2}}$, which can geometrically be viewed as undoing a spontaneous strain in the reference configuration, followed by a rigid motion and then a spontaneous strain in the deformed configuration. Generally the model has proved successful, explaining stripe domain instabilities and soft elastic modes as consequences of the non-quasiconvexity of the effective deformation energy [16], although similarly to the classical Hookean model, it is strictly only valid in the small-strain regime.

1.3 Outline of this thesis

1.3.1 Outline of Chapter 2 - The singular potential

The main aim of this section is to adapt the singular potential of Ball and Majumdar for Landau-de Gennes into a framework which can be applied to much more general models involving statistically defined order parameters. Before the singular potential can be defined the set of admissible moments, to be denoted $\mathcal{Q}$, must first be understood. This will form the bulk of Section 2.1. This is an example of the problem of moments [2], which in the general case is poorly understood. The classical problem considers $X = \mathbb{R}$, and functions $a_i(x) = x^i$, although others have considered the

more general setting. For example, Lewis has provided a characterisation of the set of moments that roughly corresponds to the existence of solutions to certain optimisation problems [33]. In Section 2.1 a more geometric description of the set $\mathcal{Q}$ will be useful, in which the set is described in terms of supporting hyperplanes (Proposition 2.1.9). Whilst this description of $\mathcal{Q}$ is abstract, and in general is unlikely to give an explicit expression for $\mathcal{Q}$, it is nonetheless appropriate for the analysis in this work. In particular, this characterisation is used in providing growth bounds on the singular potential (Theorem 2.2.4). Throughout both Sections 2.1 and 2.2 the assumption is made that the constraint functions $(a_i)_{i=1}^k$ and the constant function $a_0(t) = 1$ form a pseudo-Haar set of functions (Definition 2.1.1), a property first defined by Borwein and Lewis [12], which provides an elegant theory without being overly restrictive to applications in mean-field theory. A series of counterexamples are presented in Section 2.2.1 to illustrate how the results presented in this work can fail if the pseudo-Haar condition is not satisfied.

The singular potential is defined and analysed in Section 2.2. The singular potential corresponds to the greatest possible entropy of a probability distribution, subject to observed moments (Definition 2.2.2). This is an application of the principle of maximum entropy, pioneered in the seminal work of Jaynes [26], which has since been influential in a vast array of applications. Mathematically it can be phrased as a convex optimisation problem for the probability distribution subject to linear constraints. For the bulk of this work more general objective functions will be considered than the Shannon entropy, which is given by $\phi(x) = x \ln x$. The objective function will be required to share similar properties to the Shannon entropy (see Definition 2.2.1). One of these properties is that the objective function is not differentiable at 0, which combined with the non-negativity constraint $\rho \geq 0$ has a consequence of not permitting two-sided variations about the minimiser ρ^*, unless it is known beforehand that $\operatorname{ess\,inf}_{t \in X} \rho^*(t) > 0$. Borwein and Lewis [12] provide an ideal framework for this kind of problem, based on duality, that will be exploited in this work. The main results of this section are that, under appropriate conditions, the singular potential ψ_s is strictly convex (Proposition 2.2.3), has the same differentiability as the objective function (Corollary 2.2.9), and that $\psi_s(b)$ blows up to $+\infty$ uniformly as the distance from b to $\partial\mathcal{Q}$ approaches zero (Corollary 2.2.5).

In Section 2.3 the results from the earlier sections are used to demonstrate an equivalence between certain minimisation problems in $\mathcal{P}(X)$ and $\mathcal{Q}$, giving the possibility of using the singular potential to rephrase harder questions relating to functional analysis in terms of simpler questions of several variable calculus. Particular mention

is given to the Onsager model, where in the literature a rigorous treatment of the non-negativity constraint is often neglected, and the results presented here demonstrate that the solutions obtained using the first variation are correct. Furthermore the equivalence of local/global minimisers of the macroscopic and microscopic free energies has the implication that under the assumptions presented in this work, equilibria of mean-field free energies can be described using only macroscopic variables and the optimal entropy assumption. The methods also provide a further equivalent finite-dimensional minimisation problem in a variable that is dual to the order parameter. As noted by Decarreau *et. al* [19], the dual formulation of the optimisation problem, which rephrases the optimisation problem in terms of finitely many Lagrange multipliers, is the most desirable from the point of numerical analysis. The "moment-space" representation outlined in this work is loosely speaking equivalent, permits a simpler state space for analytical problems, and also allows the problem to be phrased directly in terms of order parameters. Also we provide a further equivalent finite dimensional problem in a naturally arising dual order parameters, which is removes some technicalities of the moment-space problem.

Expanding further on the work of Ball and Majumdar [7], in Section 2.4 models with spatial inhomogeneities will be considered. It is shown that for a particular class of free energy models, minimisers are strictly physical, in the sense that the minimiser is bounded away from $\partial\mathcal{Q}$. However the class of models in which this analysis works is rather limited so that it remains open if more general free energies have strictly physical minimisers. Even in 2-dimensional problems that give rise to a semilinear Euler-Lagrange equation, the answer appears to be far from trivial [9].

In Section 2.5 there is a discussion of issues surrounding the approximation of the singular potential by globally defined functions, in particular by polynomials. The Landau theory of phase transitions [51] states that since the free energy should be analytic in the order parameters, one can consider a Taylor expansion of the free energy to low (typically fourth) order and perform an energy minimisation over the approximation. It is shown that even within some simple one dimensional examples, the fourth order Taylor approximation to the singular potential in general fails to reproduce various desirable properties of the singular potential such as convexity, the existence of a single critical point and even a lower bound. Whilst it is possible to approximate the singular potential by convex polynomials due to a Weierstrass-type result, constructive methods appear to be out of reach. Similarly, due to the difficulty of establishing the convexity of fourth order polynomials in several variables, even providing conditions for the Taylor approximation to be convex appears to be

unobtainable. In response to this, the Yosida-Moreau approximation [38] is suggested as a globally defined approximation that preserves meaningful properties of the singular potential. The drawback however is that the Yosida-Moreau approximation is similarly defined through an optimisation procedure that, loosely speaking, is no less, although fortunately no more, difficult to solve than the optimisation problem that defines the singular potential itself.

To illustrate the framework in a concrete example, in Section 2.6 the McMillan model [37] for isotropic-nematic-smectic A phase transitions is used as a guiding example. The isotropic phase corresponds to a disordered liquid, the nematic phase corresponds to molecules having orientational, but no positional order, and the smectic A phase corresponds to molecules having orientational order, as well as positional order in one direction, parallel to the molecular orientation. This model is described by a mean field free energy, with state space $X = \mathbb{S}^2 \times [0,1]$, and two order parameters (S, σ) defined as

$$\begin{aligned} S =& \frac{1}{2}\int_0^1 \int_{\mathbb{S}^2} \rho(p,x)\left(3\cos^2(p\cdot e_1)-1\right)\, d\mathcal{H}^2(p)\, dx \\ \sigma =& \frac{1}{2}\int_0^1 \int_{\mathbb{S}^2} \rho(p,x)\left(3\cos^2(p\cdot e_1)-1\right)\cos(2\pi x)\, d\mathcal{H}^2(p)\, dx. \end{aligned} \tag{1.12}$$

Here e_1 is a unit vector. If $S = \sigma = 0$ then the system is in the isotropic phase, if $S \neq 0$ and $\sigma = 0$ then the system is in the nematic phase, and finally if $S \neq 0$ and $\sigma \neq 0$, the system is in the smectic A phase.

1.3.2 Outline of Chapter 3 - Density functional with logarithmic potential

Perhaps the simplest case of an Onsager model is the Maier-Saupe free-energy [34], where a spatially homogeneous system is identified with a probability distribution on the sphere, $f \in \mathcal{P}(\mathbb{S}^2)$, describing the orientations of axially symmetric molecules. At fixed temperature and concentration, we look for local minimisers of

$$\int_{\mathbb{S}^2} f(p)\ln f(p) - \frac{U_0\rho f(p)}{2T}\int_{\mathbb{S}^2} f(q)\left((p\cdot q)^2 - \frac{1}{3}\right)\, dq\, dp, \tag{1.13}$$

with $U_0 > 0$ a fixed constant, $T > 0$ the temperature and $\rho > 0$ the number density. While the model provides a qualitatively accurate description of the phase behaviour of nematic liquid crystals, there is no barrier to prevent arbitrarily high number

density, and as such the model is strictly only valid in low concentration regimes.

The recent work of Zheng, Taylor and Palffy-Muhoray [61] proposes a new free-energy functional that aims to demonstrate the consequences of a lack of available configuration space in high density regimes. At fixed concentration and in the absence of thermal, attractive interactions, this gives a non-dimensionalised free energy density of the form

$$\mathcal{F}(f,\eta) = \int_{\mathbb{S}^2} f(p)\ln f(p) - f(p)\ln\left(\int_{\mathbb{S}^2}\left((p\cdot q)^2 - \frac{1}{3}\right) f(q)\,dq - \eta\right)\,dp, \qquad (1.14)$$

where $\eta = \frac{\rho c - 1}{\rho d}$ is a dimensionless parameter, increasing in the number density ρ, and $c, d > 0$ are constants related to the dimensions of the molecule. For the majority of this work, η will be fixed and the explicit dependence of $\mathcal{F}$ on η will be supressed. The key feature of the model is that at higher densities, molecules must be more strongly aligned in order for the energy to be finite, and minimisers must in some cases be zero on some non-empty subset of $\mathbb{S}^2$, in stark contrast to the solutions of the Maier-Saupe model which are always bounded away from zero [21]. The interpretation of this is that at higher densities it becomes not just energetically unfavourable but geometrically impossible for molecules to align against the order. Furthermore there exists a saturation density at which there are no finite energy configurations.

The singularity of the free energy density means it is not immediately clear if minimisers will satisfy the Euler-Lagrange equation due to having non-trivial support, and the energy is not regular enough for standard applications of first order variational techniques to obtain all minimisers. In order to establish an Euler-Lagrange equation satisfied by minimisers we will instead split the problem into two more manageable steps using a similar method to Section 2.3. By restricting ourselves only to probability distributions f such that the Q-tensor

$$Q = \int_{\mathbb{S}^2}\left(p\otimes p - \frac{1}{3}I\right) f(p)\,dp \qquad (1.15)$$

is fixed, we see that the free energy becomes convex with linear constraints and can be tackled using the results of Borwein and Lewis [12]. Once this problem has been tackled, it remains only to minimise over the set of admissible Q-tensors. By considering this finite-dimensional problem, we can obtain the Euler-Lagrange equation, which is consistent with the non-rigorous results of Zheng, Taylor and Palffy-Muhoray [61], and prove that L^p-local minimisers satisfy it. This is then seen to be equivalent to considering a particular set of curves $f : (-\delta, \delta) \to \mathcal{P}(\mathbb{S}^2)$ and solving a vanishing

derivative condition $\frac{d}{dt}\mathcal{F}(f_t)\big|_{t=0} = 0$.

The structure of the chapter and key results are as follows. First in Section 3.1 we follow the spirit of Van Kampen [54] and provide a heuristic derivation of the free energy density. In Section 3.2 we will first prove that global minimisers of the free energy exist if and only if $\eta < \frac{2}{3}$, with no finite energy configurations otherwise (Proposition 3.2.5). We will also investigate local minimisers that are bounded away from zero and infinity by taking $L^\infty(\mathbb{S}^2)$ variations. It will be shown that such a method can produce certain trivial minimisers, but in general it does not produce satisfactory results, which is more precisely stated in Corollary 3.2.13. In particular, only the isotropic state when $\eta < 0$ and a continuum of solutions when $\eta = -\frac{2}{15}$ are found by this method. Section 3.3 will be concerned with reducing the global minimisation problem to a macroscopic minimisation problem over the set of Q-tensors. More precisely, if $A(Q) = \left\{ f \in \mathcal{P}(\mathbb{S}^2) : \int_{\mathbb{S}^2} f(p) \left(p \otimes p - \frac{1}{3} I \right) \, dp = Q \right\}$, then we split the minimisation problem as

$$\min_{f \in \mathcal{P}(\mathbb{S}^2)} \mathcal{F}(f) = \min_{Q \in \mathcal{Q}} \left(\min_{f \in A(Q)} \mathcal{F}(f) \right) = \min_{Q \in \mathcal{Q}} J(Q), \tag{1.16}$$

where the inner minimisation problem defining the macroscopic functional J is convex with continuous linear constraints, and as such can be tackled by the techniques in [12]. By showing that the macroscopic functional J is sufficiently regular (Proposition 3.3.18), we can obtain a critical point condition for global minimisers which acts as the Euler-Lagrange equation for the free energy $\mathcal{F}$. Theorem 3.3.19 is the main result of this section, showing the equivalence of the minimisation problems, an equivalent finite-dimensional saddle-point problem and the relationship between their solutions. Explicitly, global minimisers must be of the form

$$f(p) = \frac{1}{Z} \exp(\Lambda p \cdot p) \max(Qp \cdot p - \eta, 0), \tag{1.17}$$

where $\Lambda, Q \in \mathrm{Sym}_0(3)$ satisfy

$$\begin{aligned} Q &= \int_{\mathbb{S}^2} f(p) \left(p \otimes p - \frac{1}{3} I \right) \, dp, \\ \Lambda &= \int_{\mathbb{S}^2} \frac{f(p)}{Qp \cdot p - \eta} \left(p \otimes p - \frac{1}{3} I \right) \, dp, \end{aligned} \tag{1.18}$$

and also solve the saddle-point problem

$$\min_{Q_0 \in \mathcal{Q}} \max_{\lambda \in \mathrm{Sym}_0(3)} Q_0 \cdot \lambda - \ln \left(\int_{\mathbb{S}^2} \exp(\lambda p \cdot p) \max(Q_0 p \cdot p - \eta, 0)\, dp \right). \tag{1.19}$$

Furthermore, Q will also be a global minimiser of $J(Q)$.

In Section 3.4, we will consider L^p-local minimisers of $\mathcal{F}$. While the decomposition of the minimisation problem was effective for finding global minimisers, the $L^\infty(\mathbb{S}^2)$ continuity of the map from a given Q-tensor to its optimal energy probability distribution will also allow us to make similar claims for local minimisers. In particular, local minimisers of the macroscopic function J correspond to L^p-local minimisers of $\mathcal{F}$ in a statement analogous to that for global minimisers (Theorem 3.4.2). Furthermore the equivalence shows that local minimisers with respect to the topologies of L^p for $p \in [1, +\infty]$, $W^{1,p}$ for $p \in [1, \infty)$ and C^α for $\alpha < 1$ are all equivalent (Proposition 2.3.7).

Section 3.5 will be concerned with related models that can be tackled using previous results in this work. Section 3.5.1 will account for thermal, attractive interactions between molecules, represented by an adjusted free energy

$$\mathcal{F}_\tau(f) = \mathcal{F}(f) - \frac{1}{2\tau} \left| \int_{\mathbb{S}^2} f(p) \left(p \otimes p - \frac{1}{3} I \right) dp \right|^2, \tag{1.20}$$

where $\tau > 0$ is proportional to temperature. The results from previous sections can be extended in a straightforward manner to provide an Euler-Lagrange equation for the thermal model (Theorem 3.5.3). A local analysis around the isotropic state for $\eta < 0$ demonstrates the stability of the isotropic state for $\tau > \tau_c = \frac{15}{2} \left(\frac{15\eta}{2+15\eta} \right)^2$ and instability if $\tau < \tau_c$ (Proposition 3.5.2). In particular, this gives a re-emergence of local stability for the isotropic phase as concentration is increased at fixed temperature, in contrast to Maier-Saupe and Onsager, as well as a more exotic relationship between the transition temperature and concentration than the inversely proportional relationship given by Onsager. In Section 3.5.2 we consider uniaxial systems as a restricted class of admissible probability distributions that are rotationally invariant about some axis. Experimentally, one often observes such symmetry in nematic systems, and the theory is generally simpler due to having fewer degrees of freedom. In this subsection we rigorously obtain the Euler-Lagrange equation for local minimisers used in [61] (Proposition 3.5.6). Furthermore, the results in this subsection allow us to show the existence of certain uniaxial critical points to the unconstrained problem in higher density regimes. (Corollaries 3.5.9 and 3.5.10).

In Section 3.6 we present some numerical results to illustrate for uniaxially constrained systems the phase behaviour and energy landscape, an illustration of the pressure for the three locally stable branches, and an illustration of the saddle-point problem used to understand solutions.

1.3.3 Outline of Chapter 4 - Finite extensibility in liquid crystal elastomers

The purpose of this chapter is to generalise the model of Kuhn and Grün, for brevity denoted the KG-model, to permit anisotropic behaviour in the elasticity of a single polymer chain. In particular the free energy will be coupled to the orientation distribution function that describes the alignment of liquid crystal molecules within a main-chain liquid crystal elastomer. The derivation presented in this work mainly follows that of the KG-model, with the key difference that the *a priori* probability of finding a monomer with a particular orientation in a free system will no longer be assumed to be isotropic, and instead will be coupled with the nematic orientation distribution function. The derivation is then shown to be equivalent to a maximum relative entropy assumption on the end-to-end vectors of the chains, where the relative entropy is taken against a probability distribution that reflects the anisotropic nature of the elastomer. More precisely, the approach gives the chain energy as a case of the singular potential as given in Definition 2.2.2, where the measure one is concerned with is a further parameter in the model and controls the anisotropy.

In order to describe the energy of deformation for the material one must make assumptions on both the behaviour of the polymer network in the reference configuration, as well as the manner in which it deforms with the material. By considering a second order Taylor approximation of the chain energy and taking an affine displacement assumption on the chains, the deformation energy will reduce to the the Neo-Hookean formulation. Furthermore the fourth order Taylor expansion can be taken to produce a deformation energy that couples to the second and fourth order moments of the nematic distribution in the both reference and deformed configurations. This can be viewed as either a correction to the Neo-Hookean theory, or an approximation of a full-network theory.

There are symmetry considerations that do not permit simpler network theories such as that given by Arruda and Boyce [5], and instead one must consider full-network type models such as those given by Wu and Van der Geissen [59]. This particular kind of network, combined with the logarithmic growth rate of the chain

energy, gives rise to a phenomenon where certain strains at the limiting deformation have finite energy. That is to say, the set of finite energy strain is not an open set. This gives rise to some interesting rigidity properties of elasticity problems which are discussed in Section 4.2.1.

To conclude, in Section 4.3 we provide some numerically obtained results to illustrate the behaviour of the model, such as monomer orientation functions, energy landscapes and force/extension relationships for the polymer chains.

Chapter 2

The singular potential

2.1 The moment problem

The key condition required for the framework presented to be successful is the pseudo-Haar property of a finite set of functions.

Definition 2.1.1 (Pseudo-Haar functions, from [13])**.** Let (X, μ) be a finite measure space. Let $k \in \mathbb{N}$ and $f_i : X \to \mathbb{R}$, for $i = 1, ..., k$. The set $\{f_i : i = 1, ..., k\}$ is called pseudo-Haar if for every $Y \subset X$ with $\mu(Y) > 0$, the set $\{f_i|_Y : i = 1, ..., k\}$ is linearly independent.

Remark 2.1.2. If (X, μ) is a measure space with atoms, so that there exists some $t \in X$ with $\mu(\{t\}) > 0$, then any set of two or more functions on X cannot be pseudo-Haar, since restricted to the set $\{t\}$ one is simply a multiple of the other. In particular the theory presented here is not applicable to discrete state spaces, such as X a finite subset of $\mathbb{N}$.

Lewis [32] showed that for X a subset of $\mathbb{R}^n$, and $(f_i)_{i=1}^k$ analytic and linearly independent on a connected neighbourhood of X then the functions are pseudo-Haar with respect to the Lebesgue measure. This result can be slightly extended to manifolds, which has applications in liquid crystal theory, where in particular X is taken as $\mathbb{S}^2$ for axially symmetric molecules or SO(3) for molecules with lower symmetry. By phrasing the problem in local coordinates, the result of Lewis can be used to extend the result to when the domain is a Riemannian manifold, and the measure taken will be the one induced by the metric, to be denoted by μ_g. The result can trivially be extended for any other measure μ' such that for all $A \subset X$, $\mu'(A) = 0 \Rightarrow \mu_g(A) = 0$. For a relatively self contained introduction to the theory of

integration on manifolds, the reader is directed to [3]. Before attempting the proof, some preliminaries will be taken covered.

Definition 2.1.3. Let be X an analytic manifold with atlas $((U_\alpha, \phi_\alpha))_{\alpha \in J}$, where J is some index set. Say that $f : X \to \mathbb{R}$ is analytic if $f \circ \phi_\alpha^{-1} : \phi(U_\alpha) \to \mathbb{R}$ is analytic for all $\alpha \in J$.

Proposition 2.1.4 (Proposition 12.1.6 of [3])**.** Let (X, g) be an n-dimensional Riemannian manifold with induced measure μ_g. Then $\mu_g(A) = 0$ if and only if $\mathcal{L}^n(\phi(A \cap U)) = 0$ for all charts (U, ϕ) of X.

Proposition 2.1.5 (From [32])**.** Let $\Omega \subset \mathbb{R}^n$ be open and connected, and let $f : \Omega \to \mathbb{R}$ be analytic. Then if there exists some set $A \subset \Omega$ with $\mathcal{L}^n(A) > 0$ so that $f|_A = 0$, then $f = 0$.

Using these results it is now straightforward to obtain the required result.

Proposition 2.1.6. Let (X, g) be a connected, analytic, Riemannian manifold. Denote by μ the measure on X induced by the metric g. Let $f_i : X \to \mathbb{R}$ be analytic functions on X for $i = 1, .., k$ for some $k \in \mathbb{N}$. Then the set $\{f_i : i = 1, .., k\}$ is linearly independent if and only if it is pseudo-Haar.

Proof. If the functions are pseudo-Haar then linear independence is immediate. To show the converse, assume the result is false. This implies that there exists some $\xi \in \mathbb{R}^k$ with $\xi \neq 0$ and $A \subset X$ so that $\mu_g(A) > 0$ and $\sum_{i=1}^{k} \xi_i f_i(x) = 0$ for all $x \in A$. For simplicity denote $F = \sum_{i=1}^{k} \xi_i f_i$. Then it is clear that F is analytic, and $F|_A = 0$. Without loss of generality take all charts to be connected by splitting the charts into connected components where necessary. Using Proposition 2.1.4, there must exist some chart (U, ϕ) so that $\mathcal{L}^n(\phi(A \cap U)) > 0$. For brevity let $\tilde{U} = \phi(U)$ and $\tilde{A} = \phi(A \cap U)$. Also let $\tilde{F} = F \circ \phi^{-1} : \tilde{U} \to \mathbb{R}$. Since F is analytic, then $\tilde{F}$ is analytic. Therefore since $\tilde{F}|_{\tilde{A}} = 0$ with $\mu_g(\tilde{A}) > 0$, and $\tilde{F}$ analytic on the connected open set $\tilde{U}$, by Proposition 2.1.5 it must hold that $\tilde{F} = 0$ on $\tilde{U}$. Composing $\tilde{F}$ with ϕ gives that $F = 0$ on U, which is open. Therefore since X is connected and analytic, F is zero on all of X. Recalling the definition of F, this implies $\sum_{j=1}^{k} \xi_i f_i = 0$, contradicting the linear independence assumption and completing the proof. □

Definition 2.1.7 (The sets $\mathcal{P}(X)$ and $\mathcal{Q}$)**.** Let (X, μ) be a finite measure space. Consider finitely many constraint functions $a_i \in L^\infty(X)$ for $i = 1, ..., k$, such that the

set $\{t \mapsto 1\} \cup \{a_i : i = 1, .., k\}$ is pseudo-Haar. For ease of notation let $a = (a_i)_{i=1}^k \in L^\infty(X, \mathbb{R}^k)$. Define the sets

$$\begin{aligned} \mathcal{P}(X) &= \left\{ \rho \in L^1(X) : \rho \geq 0 \ \ \mu\text{-a.e.}, \int_X \rho \, d\mu = 1 \right\}, \\ \mathcal{Q} &= \left\{ \int_X a\rho \, d\mu : \rho \in \mathcal{P}(X) \right\} \subset \mathbb{R}^k. \end{aligned} \tag{2.1}$$

Furthermore, if $b \in \mathcal{Q}$, then b will be called physical, and if $b = \int_X \rho a \, d\mu$, then b is generated by ρ.

Definition 2.1.8. Let $u \in \mathbb{S}^{k-1}$. Given the constraint functions $(a_i)_{i=1}^k$ with $a_i \in L^\infty(X)$ for $i = 1, .., k$, define $S_u \in \mathbb{R}$ by

$$S_u = \operatorname*{ess\,sup}_{t \in X} u \cdot a(t). \tag{2.2}$$

Let $\epsilon > 0$. Define the set $E_\epsilon^u \subset X$ as

$$E_\epsilon^u = \{ t \in X : S_u < u \cdot a(t) + \epsilon \}. \tag{2.3}$$

Note that since $\mu(X) < \infty$, $L^\infty(X) \subset L^2(X)$, so that up to an invertible linear transformation, it can be assumed that the functions $(a_i)_{i=1}^k$ are $L^2(X)$ orthonormal functions, so that $\int_X a_i a_j \, d\mu = \delta_{ij}$, and orthogonal to any constant so that $\int_X a_i \, d\mu = 0$. For simplicity of calculation, this will be assumed unless stated otherwise, although it has little effect on the results since the non-normalised framework is equivalent up to an affine map on $\mathcal{Q}$. This has the consequence that the uniform distribution, $\rho_U(t) = \frac{1}{\mu(X)}$, satisfies $\int_X \rho_U(t) a(t) \, d\mu(t) = 0$. This is relevant in Landau theory where the order parameters are required to be zero in the high temperature uniform state. In order to establish a necessary and sufficient condition for $b \in \mathcal{Q}$, some properties of $\mathcal{Q}$ will be established. The method is to describe $\mathcal{Q}$ in terms of supporting hyperplanes.

Proposition 2.1.9. The set $\mathcal{Q}$ is convex, bounded and open.

Proof. Convexity is immediate from the convexity of $\mathcal{P}(X)$. To show boundedness, let $b \in \mathcal{Q}$, corresponding to some $\rho \in \mathcal{P}(X)$. Then

$$\begin{aligned} |b| &= \left| \int_X a(t) \rho(t) \, d\mu(t) \right| \\ &\leq \operatorname*{ess\,sup}_{t \in X} |a(t)| \end{aligned} \tag{2.4}$$

so that $\mathcal{Q}$ is bounded. To see that $\mathcal{Q}$ is open, consider some $b \in \mathcal{Q}$ and let $\xi \in \mathbb{R}^k$. Since the functions $t \mapsto 1$ and a_i are pseudo-Haar, by [12, Theorem 2.9] there exists some $\rho \in \mathcal{P}(X)$ that generates b and $\epsilon > 0$ such that $\rho(t) \geq \epsilon > 0$ almost everywhere. Define the function $\chi_\xi \in L^\infty(X)$ by

$$\chi_\xi(t) = \sum_{i=1}^{k} a_i(t)\xi_i. \tag{2.5}$$

Then $\int_X \chi_\xi \, d\mu = 0$ and $\int_X a(t)\chi_\xi(t) \, d\mu(t) = \xi$ due to the orthogonality of $(a_i)_{i=1}^k$ and the constant function. Note that $|\chi_\xi(t)| = |\xi \cdot a(t)| \leq |\xi| \operatorname*{ess\,sup}_{s \in X} |a(s)|$. Hence if

$$|\xi| < \frac{\epsilon}{\operatorname*{ess\,sup}_{s \in X} |a(s)|}, \tag{2.6}$$

then $\rho_\xi = \rho + \chi_\xi$ is non-negative almost everywhere. Combining the previous results, this gives that $\rho_\xi \in \mathcal{P}(X)$, and $\int_X a(t)\rho_\xi(t) \, d\mu(t) = b + \xi$, so that $\mathcal{Q}$ is open. □

Using these properties it is now possible to characterise $\mathcal{Q}$ in terms of its supporting hyperplanes, and this will provide the necessary and sufficient condition for $b \in \mathcal{Q}$.

Theorem 2.1.10. Let $b \in \mathbb{R}^k$. Then $b \in \mathcal{Q}$ if and only if

$$b \cdot u < \operatorname*{ess\,sup}_{t \in X} a(t) \cdot u = S_u \tag{2.7}$$

for all $u \in \mathbb{S}^{k-1}$.

Proof. By [44, Theorem 11.5] it is known that a closed convex set $K \subset \mathbb{R}^k$ can be written as the intersection of all closed half spaces containing K, so that $x \in K$ is equivalent to

$$x \cdot u \leq \sup_{z \in K} z \cdot u \tag{2.8}$$

for all $u \in \mathbb{S}^{k-1}$. If $\Omega \subset \mathbb{R}^k$ is a bounded open convex set, then by considering $K = \bar{\Omega}$ it is straightforward to deduce that $x \in \Omega$ is equivalent to

$$x \cdot u < \sup_{z \in K} z \cdot u = \sup_{z \in \Omega} z \cdot u \tag{2.9}$$

for all $u \in \mathbb{S}^{k-1}$, since a non-zero linear function cannot attain its maximum over a

set in the interior. By taking $\Omega = \mathcal{Q}$, the supremum can be computed as

$$\begin{aligned} \sup_{z \in \mathcal{Q}} z \cdot u &= \sup_{\rho \in \mathcal{P}(X)} \int_X u \cdot a(t) \rho(t) \, d\mu(t) \\ &= \operatorname*{ess\,sup}_{t \in X} u \cdot a(t) \\ &= S_u, \end{aligned} \tag{2.10}$$

by considering ρ uniform on the set $E_\epsilon^u = \{t \in X : \operatorname{ess\,sup} u \cdot a(s) < u \cdot a(t) + \epsilon\}$ and zero elsewhere, then taking $\epsilon \to 0$, which gives the necessary and sufficient condition. □

Using the necessary and sufficient condition given previously it is possible to formalise the intuition that if b is close to the boundary of $\mathcal{Q}$, any probability distribution ρ generating b must be concentrated on some subset of X with small measure. Firstly, it will be shown that if $b \in \mathcal{Q}$ is close to the boundary of $\mathcal{Q}$, then there is a certain set, depending on b, on which any $\rho \in \mathcal{P}(X)$ with $\int_X a\rho \, d\mu = b$ must have most of its mass. Then secondly, it will be shown that as b approaches the boundary of $\mathcal{Q}$, this set becomes arbitrarily small in measure. These results will also be important in providing a growth bound for the singular potential in the next section.

Lemma 2.1.11. Let $b \in \mathcal{Q}$, $b_0 \in \partial\mathcal{Q}$ with $|b_0 - b| = \min_{\tilde{b} \in \partial\mathcal{Q}} |\tilde{b} - b|$. Define $u \in \mathbb{S}^{k-1}$ to be the unit vector in the direction of $b_0 - b$. Then u is normal to a supporting hyperplane of $\mathcal{Q}$ at b_0, so that $b_0 \cdot u = S_u$, and $d(b, \partial\mathcal{Q}) = S_u - b \cdot u$. Furthermore, there is only one supporting hyperplane of $\mathcal{Q}$ at b_0, with outward-pointing unit normal vector given by u.

Proof. First it will be shown that u is normal to a supporting hyperplane at b_0. Assume otherwise for the sake of contradiction. Then there exists some $u' \in \mathbb{S}^2$, normal to a supporting hyperplane at b_0, which must satisfy $u \neq u'$. Let $x \in \mathbb{R}^k$ be the projection of b onto the hyperplane given by the set of all $\tilde{b} \in \mathbb{R}^k$ with $\tilde{b} \cdot u' = S_{u'}$, In particular, $x \notin \mathcal{Q}$. Furthermore, $|x - b| < |b_0 - b|$. By considering the straight line from b to x, there must be some $y \in \partial\mathcal{Q}$ such that $|y - b| \leq |x - b| < |b_0 - b|$, contradicting the assumption that $|b_0 - b| = \min_{\tilde{b} \in \partial\mathcal{Q}} |\tilde{b} - b|$. Then it holds that

$$\begin{aligned} S_u - b \cdot u &= (b_0 - b) \cdot u \\ &= \frac{1}{|b_0 - b|} (b_0 - b) \cdot (b_0 - b) \\ &= |b_0 - b| = d(b, \partial\mathcal{Q}). \end{aligned} \tag{2.11}$$

To show that this is the only such hyperplane, assume that $u_1 \in \mathbb{S}^{k-1}$, $u_1 \neq u$ and $u_1 \cdot b_0 = S_{u_1}$. By the same argument as before, by projecting b onto the supporting hyperplane with normal u_1, it contradicts that b_0 was a closest point on the boundary. □

Proposition 2.1.12. Let $b \in \mathcal{Q}$, $b_0 \in \partial\mathcal{Q}$ with

$$|b - b_0| = \min_{\tilde{b} \in \partial\mathcal{Q}} |b - \tilde{b}|, \tag{2.12}$$

define $u = \frac{1}{|b_0 - b|}(b_0 - b)$ and $\epsilon^2 = |b_0 - b|$. Let S_u, E_ϵ^u be as in Definition 2.1.8. Then $S_u - b \cdot u = \epsilon^2$ and

$$\int_{E_\epsilon^u} \rho(t)\, d\mu(t) \geq 1 - \epsilon \tag{2.13}$$

for all $\rho \in \mathcal{P}(X)$ generating b.

Proof. To see that $S_u - b \cdot u = \epsilon^2$ is a result of the previous lemma, and observing that $S_u - b \cdot u = (b_0 - b) \cdot u$. Letting $E = E_\epsilon^u$ for brevity, from the assumptions it can be seen that for any $\rho \in \mathcal{P}(\mathbb{S}^2)$ that generates b,

$$\begin{aligned} 0 &= u \cdot b - S_u + \epsilon^2 \\ &= \int_X \left(u \cdot a(t) - S_u + \epsilon^2\right) \rho(t)\, d\mu(t) \\ &= \int_E \left(u \cdot a(t) - S_u + \epsilon^2\right) \rho(t)\, d\mu(t) + \int_{X \setminus E} \left(u \cdot a(t) - S_u + \epsilon^2\right) \rho(t)\, d\mu(t) \\ &\leq \epsilon^2 \int_E \rho\, d\mu + (\epsilon^2 - \epsilon) \int_{X \setminus E} \rho\, d\mu, \end{aligned} \tag{2.14}$$

using that for $t \in X$, $u \cdot a(t) - S_u \leq 0$, and for $t \in X \setminus E$ that $S_u - u \cdot a(t) \geq \epsilon$. If $I = \int_E \rho\, d\mu$ for brevity, then this chain of inequalities gives that

$$0 \leq \epsilon^2 I + (\epsilon^2 - \epsilon)(1 - I) \tag{2.15}$$

so that dividing through by ϵ and rearranging gives the desired result. □

Proposition 2.1.13. For $u \in \mathbb{S}^{k-1}$ and $\epsilon > 0$, let $E_\epsilon^u \subset X$ be as in Definition 2.1.8. Then $\lim_{\epsilon \to 0} \mu(E_\epsilon^u) = 0$, where the convergence is uniform in u.

Proof. That $\lim_{\epsilon \to 0} \mu(E_\epsilon^u) = 0$ is a consequence of the pseudo-Haar property of the

constraint functions. Since $E^u_\epsilon = (S_u - a \cdot u)^{-1}((-\infty, \epsilon))$, it holds that

$$\begin{aligned} \lim_{\epsilon \to 0} \mu(E^u_\epsilon) &= \mu\left(\bigcap_{\epsilon > 0} E^u_\epsilon\right) \\ &= \mu\left(\{t \in X : S_u - u \cdot a(t) = 0\}\right) = 0 \end{aligned} \tag{2.16}$$

by the pseudo-Haar property.

To see that the convergence is uniform, assume otherwise so that there exists some $\gamma > 0$, and $(u_j)_{j \in \mathbb{N}}$, $(\alpha_j)_{j \in \mathbb{N}}$ so that the sets $E_j = E^{u_j}_{\alpha_j}$ satisfy $\mu(E_j) \geq \gamma$ for all j, and $\lim_{j \to \infty} \alpha_j = 0$. For brevity, denote the functions $f_j(t) = S_{u_j} - u_j \cdot a(t) - \alpha_j$. Up to a subsequence (not relabelled) it can be assumed that $u_j \to u^*$, and since the convergence of $u_j \cdot a(t) \to u^* \cdot a(t)$ is uniform, there is a corresponding $S^* = S_{u^*} = \lim_{j \to \infty} S_{u_j}$. Let $\epsilon > 0$. Let $f = \lim_{j \to \infty} f_j$. Then for sufficiently large j since $f_j \to f$ uniformly, it must hold that if $t \in E_j$ then $f(t) > -\epsilon$. This means that $E_j \subset E^{u^*}_\epsilon$ for sufficiently large j. Therefore for large j,

$$\begin{aligned} \mu(E_j) &\leq \mu(E^{u^*}_\epsilon) \\ \Rightarrow \limsup_{j \to \infty} \mu(E_j) &\leq \mu(E^{u^*}_\epsilon). \end{aligned} \tag{2.17}$$

Since ϵ was arbitrary and $\lim_{\epsilon \to 0}(E^{u^*}_\epsilon) = 0$, this leads to the conclusion that $0 < \gamma \leq \limsup_{j \to \infty} \mu(E_j) \leq 0$, a contradiction. □

2.2 The singular potential

In order to define the singular potential, there are certain constraints on the objective function ϕ that are necessary to ensure that the minimisation problem is well posed and the resulting singular potential has desirable properties. Motivated by the Shannon entropy, $\phi(x) = x \ln x$ as the prototypical example, any function satisfying these constraints will be called *entropy-like*.

Definition 2.2.1. Let $\phi : \mathbb{R} \to (-\infty, \infty]$. Define $\mathrm{dom}(\phi) = \{x \in \mathbb{R} : \phi(x) < +\infty\}$. Then ϕ is entropy-like if and only if $\mathrm{int}\ \mathrm{dom}(\phi) = (0, \infty)$, $\phi|_{(0,\infty)}$ is strictly convex, continuously differentiable, $\lim_{x \to \infty} \frac{\phi(x)}{x} = +\infty$ and $\lim_{x \to 0^+} \phi'(x) = -\infty$.

In particular any entropy-like function is of Legendre type, so that ϕ' is a continuous bijection between $(0, \infty)$ and $\mathbb{R}$ [44]. This definition does not place any restriction on the limiting value of ϕ at zero. It may hold that $\lim_{x \to 0^+} \phi(x)$ is bounded, such as in

the case of the Shannon entropy, or the limit may be infinite, such as for the example $\phi(x) = \frac{1}{x} + x^2$.

Definition 2.2.2. Let ϕ be an entropy-like function. Define the singular potential $\psi_s : \mathcal{Q} \to \mathbb{R}$ by

$$\psi_s(b) = \min_{\rho \in \mathcal{A}_b} \int_X \phi(\rho)\, d\mu \tag{2.18}$$

where the set $\mathcal{A}_b$ is defined as

$$\mathcal{A}_b = \left\{ \rho \in \mathcal{P}(X) : \int_X \rho(t) a(t)\, d\mu(t) = b \right\}. \tag{2.19}$$

Using the definition of the singular potential, the next results will be concerned with establishing some key properties of the function.

Proposition 2.2.3. Let $b \in \mathcal{Q}$. Then the singular potential, $\psi_s(b)$ is well defined in the sense that the minimisation problem admits solutions. Furthermore, the minimiser is unique, and ψ_s is a strictly convex function.

Proof. The minimisation problem is a convex minimisation problem subject to linear constraints, with constraint functions that are pseudo-Haar. Together with the growth conditions imposed on ϕ, this ensures the existence of a unique minimising ρ, with ρ bounded away from 0 and $+\infty$, so that $\psi_s(b) < +\infty$ [12, Theorem 4.8]. To see convexity, first since $\mathcal{Q}$ is convex there is no problem in taking convex combinations of elements of $\mathcal{Q}$. Let $b_1, b_2 \in \mathcal{Q}$, $\epsilon \in [0,1]$. If ρ_1, ρ_2 solve the minimisation problems corresponding to b_1, b_2 respectively, then $\epsilon\rho_1 + (1-\epsilon)\rho_2 \in \mathcal{A}_{\epsilon b_1 + (1-\epsilon)b_2}$. Hence

$$\begin{aligned}
\psi_s\left(\epsilon b_1 + (1-\epsilon)b_2\right) &= \min_{\rho \in \mathcal{A}_{\epsilon b_1 + (1-\epsilon)b_2}} \int_X \phi(\rho(t))\, d\mu(t) \\
&\leq \int_X \phi\left(\epsilon\rho_1(t) + (1-\epsilon)\rho_2(t)\right)\, d\mu(t) \\
&\leq \int_X \epsilon\phi(\rho_1(t)) + (1-\epsilon)\phi(\rho_2(t))\, d\mu(t) \\
&= \epsilon\psi_s(b_1) + (1-\epsilon)\psi_s(b_2).
\end{aligned} \tag{2.20}$$

Furthermore, note that the strict convexity of ϕ gives that for $b_1 \neq b_2$ and $\epsilon \in (0,1)$, $\rho_1 \neq \rho_2$ on a set of positive measure, giving that this inequality is strict. □

Theorem 2.2.4. There exists some $c > 0$ such that for all $b \in \mathcal{Q}$, $b_0 \in \partial\mathcal{Q}$ with

$\min_{\tilde{b}\in\partial\mathcal{Q}} |\tilde{b}-b| = |b_0-b| = \epsilon^2$ and $\epsilon < c$, the singular potential satisfies the inequality

$$\psi_s(b) \geq \mu(E_\epsilon^u)\phi\left(\frac{1-\epsilon}{\mu(E_\epsilon^u)}\right) + \mu(X\setminus E_\epsilon^u)\phi\left(\frac{\epsilon}{\mu(X\setminus E_\epsilon^u)}\right), \tag{2.21}$$

where E_ϵ^u is as defined in Definition 2.1.8 and $u = \frac{1}{|b_0-b|}(b_0-b)$.

Proof. Let $b \in \mathcal{Q}$, with corresponding b_0, ϵ, u. Let $E = E_\epsilon^u$ for brevity. From Proposition 2.1.12 it is known that $\int_E \rho\, d\mu > 1-\epsilon$ for all ρ with $\int_X \rho a\, d\mu = b$. In particular by taking $\rho \in \mathcal{A}_b$ to be the unique minimiser given in Proposition 2.2.3 so that $\psi_s(b) = \int_X \phi(\rho)\, d\mu$, then

$$\begin{aligned}\psi_s(b) &= \int_E \phi(\rho)\, d\mu + \int_{X\setminus E} \phi(\rho)\, d\mu \\ &\geq \mu(E)\phi\left(\frac{1}{\mu(E)}\int_E \rho\, d\mu\right) + \mu(X\setminus E)\phi\left(\frac{1}{\mu(X\setminus E)}\int_{X\setminus E}\rho\, d\mu\right)\end{aligned} \tag{2.22}$$

by applying Jensen's inequality. Since $\frac{1}{\mu(E)}\int_E \rho\, d\mu \geq \frac{1-\epsilon}{\mu(E)}$, using the uniform convergence of $\mu(E)\to 0$ in u from Proposition 2.1.13 and that ϕ is an increasing function for sufficiently large argument, it must hold that there exists some $c_1 > 0$ so that if $\epsilon < c_1$ then

$$\phi\left(\frac{1}{\mu(E)}\int_E \rho\, d\mu\right) \geq \phi\left(\frac{1-\epsilon}{\mu(E)}\right). \tag{2.23}$$

Similarly for $\epsilon < c_2$ since ϕ is decreasing for sufficiently small argument, it must hold that

$$\phi\left(\frac{1}{\mu(X\setminus E)}\int_{X\setminus E} \rho\, d\mu\right) \geq \phi\left(\frac{\epsilon}{\mu(X\setminus E)}\right). \tag{2.24}$$

Combining these inequalities gives the lower bound. □

Corollary 2.2.5. For $j \in \mathbb{N}$ let $b_j \in \mathcal{Q}$ with $\lim_{j\to\infty} \inf_{\tilde{b}\in\partial\mathcal{Q}} |\tilde{b}-b_j| = 0$. Then $\lim_{j\to\infty} \psi_s(b_j) = +\infty$. Furthermore the convergence is uniform in $\inf_{\tilde{b}\in\partial Q} |b-b_j|$, so that

$$\lim_{\epsilon\to 0} \left(\inf\left\{\psi_s(b) : d(b,\partial\mathcal{Q}) \leq \epsilon\right\}\right) = +\infty. \tag{2.25}$$

Proof. Let $b \in \mathcal{Q}$, and $E_\epsilon^u = E$ for brevity. Using the lower bound for ψ_s, and that ϕ is bounded below, for some real constant C, independent of b,

$$\psi_s(b) \geq \mu(E)\phi\left(\frac{1-\epsilon}{\mu(E)}\right) + C = (1-\epsilon)\frac{\phi(\xi)}{\xi} + C, \tag{2.26}$$

where $\xi = \frac{1-\epsilon}{\mu(E)}$. Using that $\mu(E) \to 0$ uniformly as $b \to \partial\mathcal{Q}$ and the superlinear growth of ϕ gives the required result. □

The precise form of the minimiser can be obtained by considering the dual optimisation problem. For a more thorough account of duality the reader is referred to [44], although for completeness a brief heuristic argument will be provided here.

Let X be some Banach space, $F : X \to \mathbb{R}$ be convex, and $T : X \to \mathbb{R}^k$ be continuous and linear. Let $b \in \mathbb{R}^k$ and consider the minimisation problem

$$\begin{aligned} &\min_{x \in X} F(x) \\ &\text{subject to } Tx = b. \end{aligned} \tag{2.27}$$

Trivially, if x does not satisfy $Tx = b$, then $\max_{\lambda \in \mathbb{R}^k} (-\lambda \cdot (Tx - b)) = +\infty$, and if $Tx = b$, then $(-\lambda \cdot (Tx - b)) = 0$ for all $\lambda \in \mathbb{R}^k$. Therefore the minimisation problem can be written as

$$\min_{x \in X} \max_{\lambda \in \mathbb{R}^k} F(x) - \lambda \cdot (Tx - b). \tag{2.28}$$

Let X^* be the dual space to X with duality pairing $\langle \cdot, \cdot \rangle$, $T^* : \mathbb{R}^k \to X^*$ be the adjoint of T, and $F^* : X^* \to \mathbb{R}$ be the convex conjugate of F defined by $F^*(x^*) = \sup_{x \in X} \langle x^*, x \rangle - F(x)$. Assuming that the minimum and maximum in (2.28) can be exchanged, this minimisation problem can be written as

$$\begin{aligned} \max_{\lambda \in \mathbb{R}^k} \min_{x \in X} F(x) - \lambda \cdot (Tx - b) &= \max_{\lambda \in \mathbb{R}^k} \lambda \cdot b - \left(\max_{x \in X} \langle T^* \lambda, x \rangle - F(x) \right) \\ &= \max_{\lambda \in \mathbb{R}^k} \lambda \cdot b - F^*(T^* \lambda). \end{aligned} \tag{2.29}$$

If the interchange of minimum and maximum is permitted, then the dual problem

$$\max_{\lambda \in \mathbb{R}^k} \lambda \cdot b - F^*(T^* \lambda) \tag{2.30}$$

can provide information about the original so-called primal problem. Furthermore, since the minimisation is over a finite dimensional set without constraints, it may be easier to approach. This is what is done in the work of Borwein and Lewis [12], and their results will be exploited for the sake of this work. In particular the minimiser of the primal problem can be described in terms of the maximiser of the dual problem.

Proposition 2.2.6. Let $\phi : \mathbb{R} \to (-\infty, \infty]$ be an entropy-like function. Then for

$b \in \mathcal{Q}$, the unique minimiser of

$$\min_{\rho \in \mathcal{A}_b} \int_X \phi(\rho)\, d\mu \tag{2.31}$$

is achieved by

$$\rho_b(t) = (\phi')^{-1}\left(\alpha + \lambda \cdot a(t)\right), \tag{2.32}$$

where $\alpha \in \mathbb{R}$, $\lambda \in \mathbb{R}^k$ are the unique maximisers of the dual optimisation problem,

$$\max_{\tilde{\alpha},\tilde{\lambda}} \tilde{\alpha} + \tilde{\lambda} \cdot b - \int_X \phi^*\left(\tilde{\alpha} + \tilde{\lambda} \cdot a(t)\right) d\mu. \tag{2.33}$$

Proof. This is a straightforward application of [12, Theorem 4.8]. □

The next stage is to establish smoothness properties of the singular potential. In order to show differentiability of ψ_s, the key point is to observe that the map from the Lagrange multipliers to the moments b is explicitly given and invertible. As such the differentiability of ψ_s is inherited from the explicit map from the Lagrange multipliers to $\mathcal{Q}$.

Proposition 2.2.7. Let $\phi : \mathbb{R} \to (-\infty, \infty]$ be entropy-like, C^m on $(0, \infty)$ for $m \geq 2$, with ϕ'' positive everywhere. Then the map $b \mapsto (\alpha, \lambda)$ is C^{m-1}, where α, λ solve the dual optimisation problem.

Proof. For $(\alpha, \lambda) \in \mathbb{R} \times \mathbb{R}^k$, consider the map

$$h : (\alpha, \lambda) \mapsto \int_X (1, a(t))\left(\phi'\right)^{-1}\left(\alpha + \lambda \cdot a(t)\right) d\mu(t) = (\beta, b). \tag{2.34}$$

Since ϕ'' is positive, the inverse function theorem can be applied to $(\phi')^{-1}$, and the differentiability of ϕ gives that $(\phi')^{-1}$ is C^{m-1} on $\mathbb{R}$. In particular, this implies that $h \in C^{m-1}\left(\mathbb{R}^{k+1}, \mathbb{R}^{k+1}\right)$. The Jacobian matrix of h is given by

$$\frac{\partial h(\alpha, \lambda)}{\partial(\alpha, \lambda)} = \int_X (1, a(t)) \otimes (1, a(t))\left(\phi'' \circ \left(\phi'\right)^{-1}\left(\alpha + \lambda \cdot a(t)\right)\right)^{-1} d\mu(t). \tag{2.35}$$

Here $\circ$ denotes function composition. If this Jacobian matrix failed to be invertible, there would exist some $\xi \in \mathbb{R}^{k+1}$ with $\xi \neq 0$ so that

$$0 = \int_X \left((1, a(t)) \cdot \xi\right)^2 \left(\phi'' \circ \left(\phi'\right)^{-1}\left(\alpha + \lambda \cdot a(t)\right)\right)^{-1} d\mu(t). \tag{2.36}$$

Since ϕ'' is positive everywhere, this implies that $(\xi \cdot (1, a(t)))^2 = 0$ almost everywhere in X; however by the pseudo-Haar property this cannot hold, a contradiction. By applying the inverse function theorem to h, this gives that the map

$$(\beta, b) \mapsto (\alpha, \lambda) \tag{2.37}$$

is C^{m-1} for $(\beta, b) \in h(\mathbb{R}^{k+1})$. In particular, $h^{-1}(1, b)$, which maps $b \in \mathcal{Q}$ to (α, λ) is also a C^{m-1} function. Global invertibility is not problematic, since the existence and uniqueness of solutions for dual problem ensures the existence and unique pair (α, λ) for each $b \in \mathcal{Q}$, and non-existence otherwise. □

Proposition 2.2.8. Let ϕ be a C^2 entropy-like function with ϕ'' positive. Then for $b \in \mathcal{Q}$, $\frac{\partial \psi_s}{\partial b}(b) = \lambda$, where λ solves the dual optimisation problem corresponding to b.

Proof. From [12] it is possible to write the singular potential in terms of the Lagrangian dual optimisation problem, so that for dual optimal α, λ, the singular potential can be written as

$$\psi_s(b) = \alpha + \lambda \cdot b - \int_X \phi^*(\alpha + \lambda \cdot a(t))\, d\mu(t) \tag{2.38}$$

Using from Proposition 2.2.7 that the map $b \mapsto (\alpha, \lambda)$ is at least C^1, differentiating through gives that

$$\begin{aligned} \frac{\partial \psi_s}{\partial b} &= \frac{\partial \alpha}{\partial b} + \frac{\partial \lambda}{\partial b} \cdot b + \lambda - \int_X (\phi')^{-1}(\alpha + \lambda \cdot a(t)) \left(\frac{\partial \alpha}{\partial b} + \frac{\partial \lambda}{\partial b} \cdot a(t) \right) d\mu(t) \\ &= \lambda + \frac{\partial \alpha}{\partial b} \left(1 - \int_X \rho_b(t)\, d\mu(t) \right) + \frac{\partial \lambda}{\partial b} \cdot \left(b - \int_X \rho_b(t) a(t)\, d\mu(t) \right) \\ &= \lambda. \end{aligned} \tag{2.39}$$

□

Corollary 2.2.9. If ϕ is entropy-like, C^m for $m \geq 2$ on $(0, \infty)$ and ϕ'' is positive, then $\psi_s \in C^m(\mathcal{Q}, \mathbb{R})$.

Proof. Combining the results of Proposition 2.2.7 and Proposition 2.2.8, it holds that

$$\frac{\partial \psi_s}{\partial b} = \lambda \in C^{m-1}(\mathcal{Q}; \mathbb{R}^k), \tag{2.40}$$

so that $\psi_s \in C^m(\mathcal{Q}, \mathbb{R})$. □

Proposition 2.2.10. Assume ϕ is entropy-like, C^m for $m \geq 2$ on the interior of its domain and that ϕ'' is positive. Let $b_0 \in \mathcal{Q}$, and denote $\rho = \rho_{b_0}$, $\sigma = \frac{1}{\phi''(\rho)}$, $Z = \int_X \sigma \, d\mu$. and $\tilde{\sigma} = \frac{1}{Z}\sigma$. Then

$$\frac{\partial \lambda}{\partial b}(b_0) = \frac{1}{Z}\left(\int_X a \otimes a\tilde{\sigma} \, d\mu - \int_X a\tilde{\sigma} \, d\mu \otimes \int_X a\tilde{\sigma} \, d\mu\right)^{-1}. \tag{2.41}$$

In particular, if ϕ is the Shannon entropy $\phi(x) = x \ln x$, then

$$\frac{\partial \lambda}{\partial b}(b_0) = \left(\int_X a \otimes a\rho \, d\mu - b_0 \otimes b_0\right)^{-1}. \tag{2.42}$$

Proof. Under the standing assumptions α, λ as functions of b are at least C^1. Following a similar argument to Proposition 2.2.7,

$$\begin{aligned} 1 &= \int_X (\phi')^{-1}(\alpha + \lambda \cdot a) \, d\mu \\ \Rightarrow 0 &= \int_X \left(\frac{\partial \alpha}{\partial b_i} + \frac{\partial \lambda}{\partial b_i} \cdot a\right) \sigma \, d\mu \\ &= Z\frac{\partial \alpha}{\partial b_i} + \int_X a\sigma \, d\mu \cdot \frac{\partial \lambda}{\partial b_i}. \end{aligned} \tag{2.43}$$

Similarly, considering the relation between α, λ and b gives

$$\begin{aligned} b_i &= \int_X a_i (\phi')^{-1}(\alpha + \lambda \cdot a) \, d\mu \\ \Rightarrow \delta_{ij} &= \int_X \left(a_i \frac{\partial \alpha}{\partial b_j} + a_i \frac{\partial \lambda}{\partial b_j} \cdot a\right) \sigma \, d\mu \\ &= -\frac{1}{Z}\int_X a_i\sigma \, d\mu \int_X a\sigma \, d\mu \cdot \frac{\partial \lambda}{\partial b_j} + \int_X a_i a\sigma \, d\mu \cdot \frac{\partial \lambda}{\partial b_j} \\ \Rightarrow I &= Z\left(\int_X a \otimes a\tilde{\sigma} \, d\mu - \int_X a\tilde{\sigma} \, d\mu \otimes \int_X a\tilde{\sigma} \, d\mu\right)\frac{\partial \lambda}{\partial b}. \end{aligned} \tag{2.44}$$

Since ϕ'', and therefore σ is positive, and $\tilde{\sigma} = \frac{1}{\int_X \sigma \, d\mu}\sigma$, this gives that $\tilde{\sigma} \in \mathcal{P}(X)$, and furthermore due to the bounds on ρ, $\tilde{\sigma}$ is bounded away from zero. Therefore by use of the pseudo-Haar condition analogously to in Proposition 2.2.7, the matrix

$$Z\left(\int_X a \otimes a\tilde{\sigma} \, d\mu - \int_X a\tilde{\sigma} \, d\mu \otimes \int_X a\tilde{\sigma} \, d\mu\right) \tag{2.45}$$

is invertible, so that taking its inverse gives the result. To prove the final part of the statement we take ϕ to be the Shannon entropy. The result then follows immediately

since $\phi''(x) = \frac{1}{x}$, which gives $\sigma = \rho$, so $Z = 1$ and $\tilde{\sigma} = \rho$. □

Proposition 2.2.11. Let $\phi : \mathbb{R} \to (-\infty, \infty]$ be an entropy-like function, C^2 with ϕ'' positive on $(0, \infty)$. Then the map $F : \mathcal{Q} \to \mathcal{P}(X)$ given by $F(b) = \rho_b$ is continuous with respect to the L^∞ topology on $\mathcal{P}(X)$.

Proof. From the argument in Proposition 2.2.7 it is sufficient to show that the map $G : (\alpha, \lambda) \mapsto (\phi')^{-1}(\alpha + \lambda \cdot a)$ is continuous as a function from $\mathbb{R}^{k+1}$ to L^∞. That $G(\alpha, \lambda) \in L^\infty$ is a consequence of $(\phi')^{-1}$ being continuous and the inequality $|\alpha + \lambda \cdot a(t)| < |\alpha| + |\lambda|\,||a||_\infty$. To show continuity, fix α_0, λ_0. Define $K = |\alpha_0| + |\lambda_0|\,||a||_\infty$. Consider α, λ with $|\alpha - \alpha_0| + |\lambda - \lambda_0|\,||a||_\infty < \epsilon$ for $\epsilon > 0$. Then

$$\begin{aligned} |\alpha + \lambda \cdot a(t)| &= |\alpha - \alpha_0 + (\lambda - \lambda_0) \cdot a(t) + \alpha_0 + \lambda_0 \cdot a(t)| \\ &\leq \epsilon + K. \end{aligned} \tag{2.46}$$

Since $(\phi')^{-1}$ is C^1 on $\mathbb{R}$, it is Lipschitz on $[-(K+\epsilon), K+\epsilon]$ with Lipschitz constant L, say. Hence

$$\begin{aligned} \left|(\phi')^{-1}(\alpha + \lambda \cdot a(t)) - (\phi')^{-1}(\alpha_0 + \lambda_0 \cdot (a(t))\right| &\leq L|\alpha - \alpha_0 + (\lambda - \lambda_0) \cdot a(t)| \\ &\leq L\left(|\alpha - \alpha_0| + |\lambda - \lambda_0|\,||a||_\infty\right) \\ &\leq L\epsilon. \end{aligned} \tag{2.47}$$

□

Proposition 2.2.12. Assume that X is a differentiable manifold, $\phi : \mathbb{R} \to (-\infty, \infty]$ is an entropy-like function, $m > 2$, C^{m+2} with ϕ'' positive on $(0, \infty)$, and a has finite $C^m(X)$ norm. Then the map $F : \mathcal{Q} \to \mathcal{P}(X)$ given by $F(b) = \rho_b$ is continuous with respect to the $C^m(X)$ topology on $\mathcal{P}(X)$.

Proof. Differentiating $\rho_b(t) = (\phi')^{-1}(\alpha + \lambda \cdot a(t))$ k times with respect to t simply gives a polynomial in α, λ, the first k derivatives of a with respect to t, the first $k+2$ derivatives of ϕ acting on $\alpha + \lambda \cdot a(t)$, and $\phi''\left((\phi')^{-1}(\alpha + \lambda \cdot a(t))\right)^{-1}$. By the same argument as before, this is then continuous in $L^\infty(X)$ as a function of α, λ, and thus is a continuous function of b. □

2.2.1 Counterexamples if the pseudo-Haar condition fails

Here some technicalities that arise when the constraint functions are no longer pseudo-Haar, in particular how they provide counterexamples to the theorems proven, will

be illustrated. One example will be able to highlight many of these issues, where the state space $X = \{(x, y) \in \mathbb{R}^2 : x^2 + y^2 = 1,\ y > 0\} \cup \big([-1, 1] \times \{0\}\big)$, with $\mu = \mathcal{H}^1 \llcorner X$ as the measure. Take two constraint functions, $a_1(x, y) = x$ and $a_2(x, y) = y$. In this case, it is seen that on the set $[-1, 1] \times \{0\}$ we have $a(x, y) \cdot (0, 1) = a_2(x, y) = 0$, so that the constraint functions and the constant function form a linearly independent, but not pseudo-Haar set.

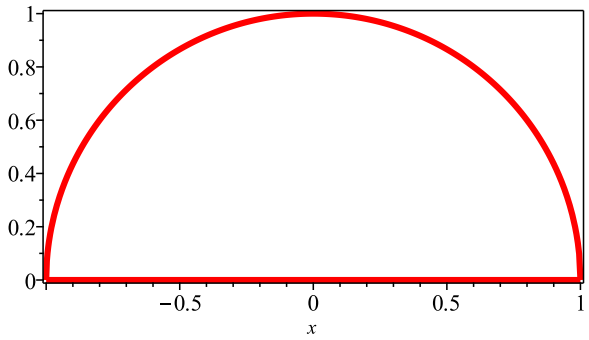


Figure 2.1: X as a subset of $\mathbb{R}^2$.

In this subsection we define the set of moments $\mathcal{Q}$ and singular potential $\psi_s : Q \to \mathbb{R}$ identically to the case when the constraint functions satisfy the pseudo-Haar condition, but with the constraint functions not necessarily satisfying the pseudo-Haar condition.

Proposition 2.2.13 (Counterexample to Proposition 2.1.9)**.** If the constraint functions do not satisfy the pseudo-Haar condition, $\mathcal{Q}$ is not necessarily open.

Proof. It suffices to find a single $b \in \mathcal{Q}$ so that all balls containing b have non-empty intersection with $\mathbb{R}^2 \setminus \mathcal{Q}$. First take $\rho = \frac{1}{2}$ on $[-1, 1] \times \{0\}$ and zero elsewhere. Then ρ has corresponding moment $(0, 0) \in \mathcal{Q}$. Since $y \geq 0$ for all $(x, y) \in X$, this implies that $b_2 \geq 0$ for all $b \in \mathcal{Q}$. Therefore $(0, -\epsilon) \notin \mathcal{Q}$ for all $\epsilon > 0$, completing the proof. □

Proposition 2.2.14 (Counterexample to Proposition 2.1.13)**.** If the constraint functions do not satisfy the pseudo-Haar condition, it is possible for there to exist $u \in \mathbb{S}^{k-1}$ so that $\mu(E^u_\epsilon)$ is bounded away from zero for all $\epsilon > 0$.

Proof. Take $u = (0, -1)$. Then $u \cdot a(x, y) = -y$, and $S_u = 0$. Then

$$E^\epsilon_u = \{(x, y) \in X : -y + \epsilon > S_u\} \supset [-1, 1] \times \{0\}, \tag{2.48}$$

so that $\mu(E^u_\epsilon) > 2$ for all $\epsilon > 0$. □

Proposition 2.2.15 (Counterexample to Corollary 2.2.5)**.** If the constraint functions do not satisfy the pseudo-Haar condition, the singular potential does not necessarily blow up as $b \to \partial\mathcal{Q}$.

Proof. Using the same example in Proposition 2.2.13, there exists $b = (0,0) \in \partial\mathcal{Q}$ so that $\psi_s(b) < +\infty$, taking any ϕ such that $\lim_{x\to 0^+} \phi(x) < +\infty$ by testing the ρ given. □

Proposition 2.2.16 (Counterexample I to Proposition 2.2.6)**.** If the constraint functions are not pseudo-Haar, the optimal entropy distribution for a given $b \in \mathcal{Q}$ is not necessarily bounded away from zero.

Proof. As before, take $b = (0,0) \in \mathcal{Q} \cap \partial\mathcal{Q}$. Take any $\rho \in \mathcal{A}_b$. Then $0 = \int_X a_2(x,y)\rho(x,y)\,d\mu(x,y) = \int_X y\rho(x,y)\,d\mu(x,y)$. Since the integrand is non-negative, it must hold that $y\rho(x,y) = 0$ for μ-a.e. $(x,y) \in X$. Therefore on the set $\{(x,y) \in X : y > 0\}$, which is of positive measure, $\rho(x,y) = 0$. Therefore $\operatorname{supp}(\rho) \subset [-1,1] \times \{0\}$ for all $\rho \in \mathcal{A}_b$, in particular for the optimal entropy distribution. □

Proposition 2.2.17 (Counterexample II to Proposition 2.2.6)**.** If the constraint functions are not pseudo-Haar, the dual maximisation problem

$$\max_{\alpha,\lambda} \alpha + \lambda \cdot b - \int_X \phi^*(\alpha + \lambda \cdot a(t))\,d\mu(t) \tag{2.49}$$

does not necessarily admit a solution.

Proof. Take $b = (0,0)$ again, $\phi(x) = x\ln x$ and consider only $\lambda_1 = 0$ and $\alpha = 1 - \ln\left(\int_X \exp(\lambda_2 x)\,d\mu(x,y)\right)\,dx$. By considering only $\lambda_2 < 0$, the dual functional evaluates as

$$\begin{aligned} -\ln\left(\int_X \exp(\lambda_2 y)\,d\mu(x,y)\right) &= -\ln\left(2\int_0^1 \exp(\lambda_2 y)\,dy\right) \\ &= -\ln\left(\frac{\exp(\lambda_2)-1}{2\lambda_2}\right) \\ &= -\ln\left(1-\exp(\lambda_2)\right) + \ln(-2\lambda_2). \end{aligned} \tag{2.50}$$

As $\lambda_2 \to -\infty$, the first term tends to $\ln(1) = 0$, while the second term tends to $+\infty$, so that the dual problem is unbounded from above and therefore does not admit a solution. □

In all of these counterexamples, it appears that the underlying thread is that probability distributions may no longer be bounded away from zero, in particular if

$\mathcal{Q} \cap \partial\mathcal{Q} \neq \emptyset$. In fact, if $\mathcal{Q}$ is open, then the singular potential must necessarily blow up.

Proposition 2.2.18. If $\mathcal{Q}$ is open, then $\lim_{b \to \partial\mathcal{Q}} \psi_s(b) = +\infty$.

Proof. Assume otherwise for the sake of contradiction. Then there exists $b_j \in \mathcal{Q}$ and $M \in \mathbb{R}$ so that $d(b_j, \partial\mathcal{Q}) \to 0$ and $\psi_s(b_j) < M$. Since $\mathcal{Q}$ must still be bounded and convex, $\partial\mathcal{Q}$ is compact, so up to a subsequence (not relabelled), $b_j \to b \in \partial\mathcal{Q}$. Let ρ_j be the maximum entropy distribution for b_j. Then $\int_X \phi(\rho_j)\, d\mu$ is bounded, so up to a subsequence (not relabelled), $\rho_j \rightharpoonup \rho$ in $L^1(X)$. Furthermore, $\int_X a\rho\, d\mu = b$. Therefore $b \in \mathcal{Q} \cap \partial\mathcal{Q}$, contradicting that $\mathcal{Q}$ was open. □

An example of a space X' and constraint functions so that $\mathcal{Q}$ is open but the pseudo-Haar condition is not satisfied is given by $X' = [0, 3]$ with $\mathcal{L}^1$ and a single constraint given by $a(x) = x$ for $x \in [0, 1)$, $a(x) = 1$ for $x \in [1, 2)$ and $a(x) = x - 1$ for $x \in [2, 3]$.

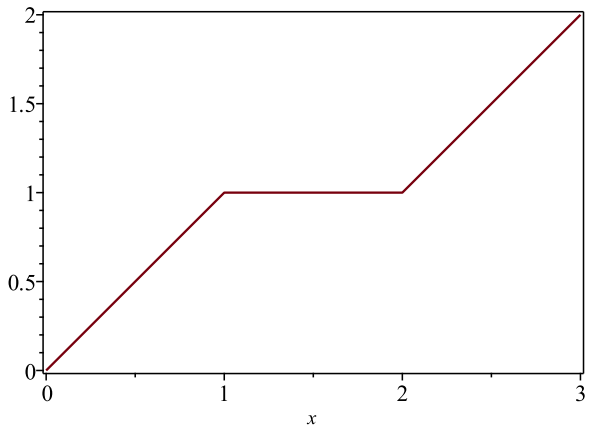


Figure 2.2: The constraint function a on X'

As a single constraint it is straightforward to see that $\mathcal{Q} = (0, 2)$, although $a(x) - 1 = 0$ on $[1, 2]$, which has measure 1. Heuristically, even though $\mathcal{Q}$ is not open, the important property that the sets E^u_ϵ become arbitrarily small still hold in this case, which appears to drive the entropy blow up. In fact if the result of Proposition 2.1.12 holds true, then the estimate in Theorem 2.2.4 will give the blow up criteria. This may suggest that by taking the result of Proposition 2.1.12 as an *assumption*, rather than a result, much of the machinery of the singular potential will still hold. This is equivalent to assuming that for all $u \in \mathbb{S}^{k-1}$, $\mu\left(\{t \in X : u \cdot a(t) = S_u\}\right) = 0$. This is aesthetically very similar to the pseudo-Haar condition itself, that $\mu(\{t \in X :$

$\xi \cdot a(t) = c\}) = 0$ for all $\xi \in \mathbb{R}^k$ and $c \in \mathbb{R}$. Taking this assumption will also give that $\mathcal{Q}$ is open, since otherwise there would be a supporting hyperplane with normal u, tangent to $\mathcal{Q}$ at $b \in \mathcal{Q} \cap \partial\mathcal{Q}$, so that $b \cdot u = \max_{b_0 \in \mathcal{Q}} u \cdot b_0$, where it is significant that the maximum is attained. In this case, we have $\rho \in \mathcal{A}_b$ so that $\int_X u \cdot a\rho \, d\mu = S_u$, therefore $\mathrm{supp}(\rho) \subset \{t \in X : u \cdot a(t) = S_u\}$, a set of measure zero giving a contradiction.

2.3 Mean field and nonlinear constraint models

The aim of this section is to establish some elementary results on minimisation problems for certain functionals on $\mathcal{P}(X)$ by reducing the problem to a finite dimensional problem via the machinery of the singular potential. The key point is to establish equivalence between global minima, local minima and critical points of functionals on $\mathcal{P}(X)$ and global minima, local minima and critical points (respectively) of functions on $\mathcal{Q}$. Once this has been shown it is possible to establish standard results such as existence of minimisers by using simple tools of real analysis rather than having to resort to more complicated arguments based on functional analysis. Critical points of the functionals on $\mathcal{P}(X)$ will be expressed as implicit relations on the dual variables. This loosely provides a framework for dealing with such minimisation problems, whereby the model is derived as a problem in $\mathcal{P}(X)$ by some physical argument, then the singular potential allows analytical questions to be asked in the simpler language of real analysis as a problem in $\mathcal{Q}$, and then finally the dual variables provide a framework that is attractive from the point of view of numerical analysis.

Let $\emptyset \neq A \subset \mathcal{Q}$ be relatively closed in $\mathcal{Q}$. Let $f : \mathcal{Q} \to \mathbb{R}$ be continuous on A and bounded from below, with $f|_{\mathcal{Q}\setminus A} = +\infty$. For a given $\rho \in \mathcal{P}(X)$ define

$$b_\rho = \int_X \rho(t) a(t) \, d\mu(t). \tag{2.51}$$

Define the functionals $\mathcal{I}_\mathcal{P} : \mathcal{P}(X) \to \mathbb{R} \cup \{+\infty\}$ and $\mathcal{I}_\mathcal{Q} : \mathcal{Q} \to \mathbb{R}$ by

$$\begin{aligned} \mathcal{I}_\mathcal{P}(\rho) &= \int_X \phi(\rho) \, d\mu + f(b_\rho), \\ \mathcal{I}_\mathcal{Q}(b) &= \psi_s(b) + f(b) = \mathcal{I}_\mathcal{P}(\rho_b). \end{aligned} \tag{2.52}$$

Consider the minimisation problems (P1) and (P2) given by

$$\begin{aligned} &\text{(P1)} \quad \min_{\rho\in\mathcal{P}(X)} \mathcal{I}_{\mathcal{P}}(\rho) \\ &\text{(P2)} \quad \min_{b\in\mathcal{Q}} \mathcal{I}_{\mathcal{Q}}(b). \end{aligned} \tag{2.53}$$

The aim of this section is to show equivalence of global minima, local minima and critical points for (P1) and (P2) and characterise such points. For applications (P1) will be obtained through a physical argument, and (P2) loosely speaking is a simpler, macroscopic, equivalent model. The motivation for the problem (P1) comes from two different areas. Firstly one can see maximum entropy methods subject to nonlinear constraints as an example. Let $g : \mathcal{Q} \to \mathbb{R}$ be a continuous function. Consider the minimisation problem

$$\begin{gathered} \min_{\rho\in\mathcal{P}(X)} \int_X \phi(\rho)\, d\mu \\ \text{subject to } g(b_\rho) = 0 \end{gathered} \tag{2.54}$$

Define $f(b) = 0$ if $g(b) = 0$ and $f(b) = +\infty$ if $g(b) \neq 0$ so that $A = \{b \in \mathcal{Q} : g(b) = 0\}$, which by the continuity of g is relatively closed. Then the minimisation problem

$$\min_{\rho\in\mathcal{P}(X)} \int_X \phi(\rho)\, d\mu + f(b_\rho) \tag{2.55}$$

is equivalent to the nonlinear constraint model. Examples from the literature of such models are seen in statistical models of isotropic elasticity [53], where $X = \mathbb{S}^2$, $a_i(p) = p_i$ (in Cartesian coordinates) for $p \in \mathbb{S}^2$ represents the orientation of molecules in a polymer chain and b corresponds to the end to end vector spanned by the entire chain. The constraint in this case is of the form $|b| = r$ for $r \in [0, 1)$. Maximum entropy methods with nonlinear constraints were also considered by Decarreau *et.al.* [19] as a method for dealing with the phase problem in crystallography. In diffraction experiments it is much simpler to observe the intensity of a wave than its phase, and mathematically this corresponds to having knowledge of the modulus of a Fourier coefficient representing the wave whilst its argument is unknown. For example, Decarreau *et al.* consider minimisation problems such as

$$\begin{cases} \min_{\rho\in\mathcal{P}(\Omega)} \int_\Omega \phi(\rho(x))\, dx, \\ \left(\int_\Omega \cos(n\cdot x)\rho(x)\, dx\right)^2 + \left(\int_\Omega \sin(n\cdot x)\rho(x)\, dx\right)^2 = m_n^2 \ \ \forall n \in N \end{cases} \tag{2.56}$$

where $\Omega = [0, 2\pi]$, N is some finite subset of $\mathbb{N}$ and m_n are given real numbers.

A second example of problems of the form (P1) are given by the mean field approximation. Given some state space X and constraint functions $(a_i)_{i=1}^k$, the free energy is typically of the form

$$T \int_X \phi(\rho)\, d\mu - \frac{1}{2} K b_\rho \cdot b_\rho - H \cdot b_\rho \tag{2.57}$$

where $T > 0$ represents temperature, K is a positive definite $k \times k$ matrix that represents some kind of interaction potential, and $H \in \mathbb{R}^k$ is representative of some kind of external influence such as magnetic/electric fields. In practice the Shannon entropy $\phi(x) = x \ln x$ is almost exclusively used, although for this analysis this is not necessary.

In the literature these minimisation problems often are not dealt with rigorously, and in particular the issue of non-differentiability of the objective function ϕ at 0 is often neglected, so that the given solution is obtained by considering only points where the first variation of the free energy is zero. The following results will aim to show that under rather non-restrictive assumptions the minimisation problems are well posed and the solutions behave as one would expect with a non-rigorous analysis. Through use of the singular potential the minimisation problem can be reduced to an analytically simpler but equivalent problem (P2) in finite dimensions, for which one can easily obtain the desired results.

Proposition 2.3.1. There exists global minimisers b^* and ρ^* of $\mathcal{I}_\mathcal{Q}$ and $\mathcal{I}_\mathcal{P}$ respectively, and all global minimisers of $\mathcal{I}_\mathcal{Q}$ are in one-to-one correspondence with global minimisers of $\mathcal{I}_\mathcal{P}$ via the map $b \mapsto \rho_b$. In particular, global minimisers of $\mathcal{I}_\mathcal{P}$ are bounded away from zero and infinity.

Proof. From the assumptions on ϕ, f, it is immediate that these functionals are bounded below. Furthermore, their infima coincide, since

$$\begin{aligned} \inf_{\rho \in \mathcal{P}(X)} \mathcal{I}_\mathcal{P}(\rho) &= \inf_{b \in \mathcal{Q}} \left(\inf_{\rho \in \mathcal{A}_b} \mathcal{I}_\mathcal{P}(\rho) \right) \\ &= \inf_{b \in \mathcal{Q}} \mathcal{I}_\mathcal{Q}(b). \end{aligned} \tag{2.58}$$

Since $\mathcal{Q}$ is a precompact set, $\mathcal{I}_\mathcal{Q}$ is continuous on the relatively closed set A, and $\lim_{b \to \partial\mathcal{Q}} \mathcal{I}_\mathcal{Q}(b) = +\infty$, it must hold that a minimum exists for $\mathcal{I}_\mathcal{Q}$, with corresponding minimiser b^*. Furthermore, since $\mathcal{I}_\mathcal{P}(\rho_{b^*}) = \mathcal{I}_\mathcal{Q}(b^*)$, the minimum of $\mathcal{I}_\mathcal{P}$ must be attained at ρ_{b^*}. Finally, if ρ^* is a global minimiser for $\mathcal{I}_\mathcal{P}$, then it must hold that

$\rho^* = \rho_{b^*}$ for $b^* = b_{\rho^*}$, since otherwise $\mathcal{I}_{\mathcal{P}}(\rho^*) > \mathcal{I}_{\mathcal{Q}}(b^*) = \mathcal{I}_{\mathcal{P}}(\rho_{b^*})$. □

By splitting the global minimisation into two manageable minimisation problems, it was possible to reduce the minimisation of $\mathcal{I}_{\mathcal{P}(X)}$ to a finite dimensional problem. The next natural question is if analogous results can be obtained for local minimisers. In the case of the infinite dimensional problem, in the general case one must take care as to with respect to which topology a local minimiser refers to. In the following, a general framework for establishing equivalence between local minimisers of analogous problems will be presented so that it may be adapted in later sections with ease.

Definition 2.3.2. Let $(V, ||\cdot||_V)$ be a Banach space, $U \subset V$, $T : V \to \mathbb{R}^k$ be a finite-rank continuous linear operator. Let $\mathcal{Q} = TU$, and $\mathcal{F} : U \to \mathbb{R} \cup \{+\infty\}$ admit a lower bound, be coercive and be lower semicontinuous with respect to the weak topology on V. Assume that if $f \in U$ and $\mathcal{F}(f) < +\infty$, then $\mathcal{F}$ is strictly convex on the set where $b = Tf$ is constant. Analogously to before, define $A(b) = \{f \in U : Tu = b\}$ and let $D = \{Tu : \mathcal{F}(f) < +\infty\}$. Define the right inverse $T^{-1} : D \to V$ by

$$T^{-1}(b) = \operatorname*{arg\,min}_{f \in A(b)} \mathcal{F}(f). \tag{2.59}$$

Define $U_{\mathcal{F}} = T^{-1}D$. In the following, assume $U_{\mathcal{F}} \subset X \subset V$, where $(X, ||\cdot||_X)$ is a Banach space with $||\cdot||_X$ inducing a topology at least as strong as that induced by $||\cdot||_V$ when restricted to X, and T^{-1} is continuous with respect to the topology induced by $||\cdot||_X$. Finally, define

$$J(b) = \min_{f \in A(b)} \mathcal{F}(b). \tag{2.60}$$

Remark 2.3.3. Note that T^{-1} is only a right inverse, since $TT^{-1} = \mathrm{Id}$, but $T^{-1}Tf = f$ if and only if $f \in \mathcal{P}_{\mathcal{F}}(\mathbb{S}^2)$. In this work, candidates for X will be the L^p spaces for $1 \leq p \leq \infty$ and C^k spaces, and the the standard topology on V will be the L^1 topology. Furthermore, the conditions on $\mathcal{F}$ ensure a unique solution $T^{-1}b$.

Proposition 2.3.4. Assume that $f^* \in U$ is an X-local minimiser. Then $f^* \in U_{\mathcal{F}}$.

Proof. For the sake of contradiction assume otherwise. Let $f = T^{-1}Tf^* \neq f^*$. Then $Tf = Tf^*$, and $\mathcal{F}(f^*) > \mathcal{F}(f)$. Furthermore, since $\mathcal{F}$ is strictly convex on $A(Tf)$, this means that for $1 > \gamma > 0$

$$\begin{aligned} \mathcal{F}(\gamma f + (1-\gamma)f^*) <& \gamma\mathcal{F}(f) + (1-\gamma)\mathcal{F}(f^*) \\ \leq& \gamma\mathcal{F}(f^*) + (1-\gamma)\mathcal{F}(f^*) = \mathcal{F}(f^*). \end{aligned} \tag{2.61}$$

However, $||(\gamma f + (1-\gamma)f^*) - f^*||_X = \gamma||f^*||_X$, so by taking $\gamma \to 0$, this contradicts that f^* is an X-local minimiser. □

Proposition 2.3.5. Assume that f^* is an X-local minimiser of $\mathcal{F}$. Then $b^* = Tf^*$ is a local minimiser of J.

Proof. Assume otherwise for the sake of contradiction. Then there exists $b_j \to b$ with $J(b_j) < J(b^*)$ for all j. Then, by the continuity assumption, $f_j = T^{-1}b_j \to f^* = T^{-1}b^*$ in X, where the final equality holds because $f \in U_{\mathcal{F}}$. Then

$$\mathcal{F}(f^*) = J(b^*) > J(b_j) = \mathcal{F}(f_j), \tag{2.62}$$

contradicting that f^* is an X-local minimiser of $\mathcal{F}$. □

Proposition 2.3.6. Assume b^* is a local minimiser for J. Then $T^{-1}b^* = f^*$ is an X-local minimiser for $\mathcal{F}$.

Proof. Assume otherwise for the sake of contradiction, so that there exists $f_j \to f$ in X with $\mathcal{F}(f_j) < \mathcal{F}(f^*)$ for all j. Let $b_j = Tf_j$. In particular, since $f_j \to f$, this implies $b_j \to b$. Furthermore

$$J(b^*) = \mathcal{F}(f^*) > \mathcal{F}(f_j) \geq J(b_j), \tag{2.63}$$

contradicting that b^* is a local minimiser of J. □

Proposition 2.3.7. Let X, X' be any two topologies satisfying the conditions in Definition 2.3.2. Then f^* is an X-local minimiser if and only if it is an X'-local minimiser

Proof. The proof is symmetric, so only one direction will be shown. Assume that f^* is an X-local minimiser. Then Tf^* is a local minimiser of J by Proposition 2.3.5. Therefore $T^{-1}Tf^*$ is an X'-local minimiser of $\mathcal{F}$ by Proposition 2.3.6. Finally, $T^{-1}Tf^* = f^*$ by Proposition 2.3.4. □

Corollary 2.3.8. There is a one-to-one correspondence between local minimisers of $\mathcal{I}_{\mathcal{Q}}$ and L^1-local minimisers of $\mathcal{I}_{\mathcal{P}}$, given by the map $b \mapsto \rho_b$, so that $\rho^* \in \mathcal{P}(X)$ is an L^1-local minimiser if and only if $b_{\rho^*} \in \mathcal{Q}$ is a local minimiser, and vice versa. In particular, all local minimisers of $\mathcal{I}_{\mathcal{P}}$ are bounded away from zero and infinity. The equivalence also holds for strict local minimisers.

Proof. This follows from Propositions 2.3.4 to 2.3.6 □

Corollary 2.3.9. If $\rho \in \mathcal{P}(X)$ is an L^p-local minimiser of $\mathcal{I}_{\mathcal{P}(X)}$ for some $p \in [1, \infty]$ if and only if ρ is an L^p-local minimiser of $\mathcal{I}_{\mathcal{P}(X)}$ for all $p \in [1, \infty]$.

Proof. By using the continuity result Proposition 2.2.11 and the equivalence result Proposition 2.3.7 it follows that ρ is an L^1-local minimiser if and only if ρ is an L^∞-local minimiser. Since $\mu(X) < +\infty$, the L^p topology is stronger than the $L^{p'}$ topology for $p > p'$, which then implies the result. □

Corollary 2.3.10. Assume that X is a differentiable manifold, $\phi : \mathbb{R} \to (-\infty, \infty]$ is an entropy-like function, $m > 2$, C^{m+2} with ϕ'' positive on $(0, \infty)$, and a has finite $C^m(X)$ norm. Then $\rho \in \mathcal{P}(X)$ is an L^1-local minimiser of $\mathcal{I}_{\mathcal{Q}}$ if and only if it is a C^k-local minimiser for $k \leq m$.

Proof. Again this follows from Propositions 2.2.12 and 2.3.7. □

For the following result, a critical point of a function $F : \mathcal{P}(X) \to \mathbb{R}$ is defined to be any ρ in $\mathcal{P}(X)$ that is bounded away from zero, such that for all $\xi \in L^\infty(X)$ with $\int_X \xi \, d\mu = 0$,

$$\frac{d}{d\tau} F(\rho + \tau\xi)\bigg|_{\tau=0} = 0. \tag{2.64}$$

This is to avoid issues with taking variations at the boundary of the domain. In particular, L^∞ variations must be taken since $\mathcal{P}(X)$ has empty interior in $L^1(X)$ with respect to the L^1-topology.

Proposition 2.3.11. Let $\text{int}(A) \neq \emptyset$ and let f be C^1 on $\text{int}(A)$. Then $b^* \in \text{int}(A)$ is a critical point of $\mathcal{I}_{\mathcal{Q}}$ if and only if $\rho^* = \rho_{b^*}$ is a critical point of $\mathcal{I}_{\mathcal{P}}$ in $\{\rho \in \mathcal{P}(X) : b_\rho \in \text{int}(A)\}$.

Proof. Since b^* is a critical point of the C^1 function $\mathcal{I}_{\mathcal{Q}}$, it holds that

$$\begin{aligned} 0 &= \nabla \mathcal{I}_{\mathcal{Q}}(b^*) \\ &= \lambda(b^*) + \nabla f(b^*). \end{aligned} \tag{2.65}$$

This implies that $\phi'(\rho^*) = \alpha - \nabla f(b^*) \cdot a$. Consider any $\xi \in L^\infty(X)$ with $\int_X \xi \, d\mu = 0$. This gives

$$\begin{aligned} \frac{d}{d\tau} \mathcal{I}_{\mathcal{P}}(\rho^* + \tau\xi)\bigg|_{\tau=0} &= \int_X (\phi'(\rho^*) - \nabla f(b^*) \cdot a) \, \xi \, d\mu \\ &= \alpha \int_X \xi \, d\mu \\ &= 0. \end{aligned} \tag{2.66}$$

The converse follows by the same argument. □

Remark 2.3.12. Whilst Corollary 2.3.8 shows that there is a one-to-one correspondence between local minima of $\mathcal{I}_{\mathcal{P}}$ and $\mathcal{I}_{\mathcal{Q}}$, an analogous result does not hold for local maxima. Let $b \in \mathcal{Q}$ be a local maximum for $\mathcal{I}_{\mathcal{Q}}$, and let $\xi \in L^\infty(X) \setminus \{0\}$ be such that $\int_X \xi \, d\mu = 0$ and $\int_X a\xi \, d\mu = 0$. Then $\rho_b + \tau\xi \in \mathcal{A}_b$ for $\tau \in \mathbb{R}$ sufficiently small to ensure the non-negativity constraint is satisfied, and hence

$$\begin{aligned} \mathcal{I}_{\mathcal{P}}(\rho_b + \tau\xi) &= \int_{\mathbb{S}^2} \phi(\rho_b + \tau\xi) + f(b) \\ &> \psi_s(b) + f(b) \\ &= \mathcal{I}_{\mathcal{Q}}(b) \\ &= \mathcal{I}_{\mathcal{P}}(\rho_b). \end{aligned} \tag{2.67}$$

By taking τ sufficiently small shows that ρ_b is not a local maximum, although if $f \in C^1$, ρ_b will be a critical point by Proposition 2.3.11.

Corollary 2.3.13. Consider the minimisation problem (P1). If $A = \mathcal{Q}$ and $f \in C^1(\overline{\mathcal{Q}}; \mathbb{R})$ then there exists a global minimum, and all L^1-local minima and critical points satisfy

$$\rho^*(t) = (\phi')^{-1} (\alpha - \nabla f(b_\rho) \cdot a(t)) \tag{2.68}$$

for some constant $\alpha \in \mathbb{R}$.

Proof. This is a straightforward application of Proposition 2.3.1, Corollary 2.3.8 and Proposition 2.3.11. □

Corollary 2.3.14. Consider the minimisation problem (P1). Let $g \in C^1(\mathcal{Q}, \mathbb{R})$ and $A = \{b \in \mathcal{Q} : g(b) = 0\} \neq \emptyset$. Then there exists a global minimum, and all L^1-local minima and critical points satisfy

$$\rho^*(t) = (\phi')^{-1} (\alpha + \eta \nabla g(b) \cdot a(t)) \tag{2.69}$$

for all $t \in X$ and some Lagrange multiplier $\eta \in \mathbb{R}$.

Proof. Again this is a straightforward application of Proposition 2.3.1, Corollary 2.3.8 and Proposition 2.3.11. □

Although the equivalent problem (P2) is simpler by virtue of being finite-dimensional, the non-explicit representation of the energy limits its usefulness. However, an order parameter that is in some sense dual to $b \in \mathcal{Q}$ can be considered, and reduces the dual

optimisation scheme needed at each point in the domain to a simple 1-dimensional problem. First, a lemma is required.

Lemma 2.3.15. Let $\lambda \in \mathbb{R}^k$. Then there exists a unique $\alpha_\lambda \in \mathbb{R}$ such that $\int_X (\phi')^{-1} (\alpha_\lambda + \lambda \cdot a(t))\, d\mu(t) = 1$, which can be found by solving

$$\max_{\alpha \in \mathbb{R}} \alpha - \int_X \phi^*(\alpha + \lambda \cdot a(t))\, d\mu(t). \tag{2.70}$$

Furthermore, if ϕ is C^m on its effective domain for $m \geq 2$ then α is a C^{m-1} function of λ.

Proof. Existence of such an α_λ can be seen by recalling that $(\phi')^{-1}$ is an increasing bijection between $\mathbb{R}$ and $(0, \infty)$ and the map $\alpha \mapsto \int_X (\phi')^{-1} (\alpha + \lambda \cdot a(t))\, d\mu(t)$ is a continuous function of α by applying the intermediate value theorem. Uniqueness follows from the strict monotonicity of $(\phi')^{-1}$. The regularity follows from the implicit function theorem, using an argument analogous to Proposition 2.2.7. The existence of a maximiser for the problem in (2.70) follows from the existence of a unique critical point and the strict concavity of the functional. □

Remark 2.3.16. In the case of the Shannon entropy, the additive property of the exponential greatly simplifies the previous lemma, since α_λ can explicitly be given as

$$\alpha_\lambda = 1 - \ln \left(\int_X \exp\left(\lambda \cdot a(t)\right)\, d\mu(t) \right). \tag{2.71}$$

We now define $\lambda \in \mathbb{R}^k$ to be the dual order parameter. It corresponds to the classical order parameter through the relationship

$$b = \int_X (\phi')^{-1} (\alpha_\lambda + \lambda \cdot a(t))\, a(t)\, d\mu(t). \tag{2.72}$$

If ϕ is C^m for $m \geq 2$, then it follows that the relationship between the dual and classical order parameters is a C^{m-1} bijection between $\mathbb{R}^k$ and $\mathcal{Q}$. Furthermore, if $b^\lambda \in \mathcal{Q}$ is the classical order parameter corresponding to a dual order parameter λ, then it is immediate that

$$\mathcal{I}_{\mathcal{Q}}(b^\lambda) = \alpha_\lambda + \lambda \cdot b^\lambda + f(b^\lambda) = \mathcal{I}_{\mathbb{R}^k}(\lambda) \tag{2.73}$$

The map $\lambda \mapsto b^\lambda$ is a continuous open map, which implies that local minimisers of $\mathcal{I}_{\mathbb{R}^k}$ and $\mathcal{I}_{\mathcal{Q}}$ are in one-to-one correspondence also. The advantage of considering $\mathcal{I}_{\mathbb{R}^k}$

is that the domain is no longer a constrained set, and at each point one must only solve a 1-dimensional optimisation problem rather than a $(k+1)$-dimensional one. In the case of the Shannon entropy, the explicit expression of α_λ as mentioned in Remark 2.3.16 requires no optimisation problem to be solved in order to evaluate the energy. In the case of the Onsager energy, the following proposition explicitly states these conclusions.

Proposition 2.3.17. Let $\lambda \in \mathbb{R}^k$. Define

$$\begin{aligned} Z_\lambda &= \int_X \exp(\lambda \cdot a(t))\, d\mu(t), \\ b^\lambda &= \frac{1}{Z_\lambda} \int_X \exp(\lambda \cdot a(t)) a(t)\, d\mu(t). \end{aligned} \tag{2.74}$$

Then all global minimisers, L^1-local minimisers and critical points (respectively) of Onsager's free energy

$$\mathcal{I}_{\mathcal{P}(X)}(\rho) = T \int_X \rho(t) \ln \rho(t)\, d\mu(t) - \frac{1}{2} K b_\rho \cdot b_\rho \tag{2.75}$$

are in one-to-one correspondence with global minimisers, local minimisers and critical points (respectively) of the function

$$T\left(\lambda \cdot b^\lambda - \ln(Z_\lambda)\right) - \frac{1}{2} K b^\lambda \cdot b^\lambda \tag{2.76}$$

by the relation

$$\rho = \frac{1}{Z_\lambda} \exp(\lambda \cdot a(t)). \tag{2.77}$$

Proof. This follows from the preceding discussion. □

Finally using the machinery of the singular potential it is possible to obtain some simple estimates on the stability of the isotropic phase $\rho(t) = \frac{1}{\mu(X)}$ in mean field free energy models. In the following ϕ will be taken as the Shannon entropy $\phi(x) = x \ln x$, and the constraint functions a_i are taken to be orthonormal in $L^2(X)$. Define the mean field free energy on $\mathcal{P}(X)$ for $T > 0$ and a positive definite $k \times k$ matrix K as

$$\mathcal{I}_{\mathcal{P}}(\rho) = T \int_X \rho \ln \rho\, d\mu - \frac{1}{2} K b \cdot b \tag{2.78}$$

Proposition 2.3.18. If $T > ||a||_\infty^2 \lambda_{\max}(K)$ then the isotropic state is globally stable and there are no other critical points of $\mathcal{I}_{\mathcal{P}}$. If $T > \frac{1}{\mu(X)} \lambda_{\max}(K)$ then the isotropic state is at least locally stable. If $T < \frac{1}{\mu(X)} \lambda_{\max}(K)$ then the isotropic state is unstable.

Proof. Consider the corresponding free energy functional $\mathcal{I}_{\mathcal{Q}} : \mathcal{Q} \to \mathbb{R}$ defined by

$$\mathcal{I}_{\mathcal{Q}}(b) = T\psi_s(b) - \frac{1}{2}Kb \cdot b \tag{2.79}$$

Note first that the isotropic state $b = 0$ is always a critical point for $\mathcal{I}_{\mathcal{Q}}$. The Hessian matrix of $\mathcal{I}_{\mathcal{Q}}$ at b is given by

$$H(b) = \frac{\partial^2 \mathcal{I}_{\mathcal{Q}}}{\partial b^2}(b) = T\left(\int_X a \otimes a\rho_b \, d\mu - b \otimes b\right)^{-1} - K. \tag{2.80}$$

The Hölder inequality and the fact that $b \otimes b$ is positive semi-definite give

$$\int_X a \otimes a\rho_b \, d\mu - b \otimes b \leq \int_X a \otimes a\rho_b \, d\mu \leq ||a||_\infty^2 I \tag{2.81}$$

so that $H(b) \geq \frac{T}{||a||_\infty^2} I - K$. This gives that for $T > ||a||_\infty^2 \lambda_{\max}(K)$ that $H(b)$ is positive definite for all $b \in \mathcal{Q}$ so that $\mathcal{I}_{\mathcal{Q}}$ is a strictly convex function on $\mathcal{Q}$, so that there exists at most one critical point. This implies that the isotropic state must be the global minimum and only critical point. Applying Proposition 2.3.1 gives the corresponding result for $\mathcal{I}_{\mathcal{P}}$. Due the the normalisation of the functions $(a_i)_{i=1}^k$ it holds that $H(0) = T\mu(X)I - K$. Consequently if $T > \frac{1}{\mu(X)}\lambda_{\max}(K)$ then $H(0)$ is positive definite so that $b = 0$ is a local minimum. Conversely, if $T < \frac{1}{\mu(X)}\lambda_{\max}(K)$ then $H(0)$ has a negative eigenvalue so that $b = 0$ is unstable. Applying Corollary 2.3.8 gives the desired result for the functional $\mathcal{I}_{\mathcal{P}}$. □

Remark 2.3.19. In the work of Vollmer [55] an analogous condition for global stability of the isotropic state is given for the case where $X = \mathbb{S}^2$ but the pairwise interaction term is given by a general continuous function We can compare Vollmer's result with the estimate from Proposition 2.3.18 by taking a single constraint with $k = 1$, which gives that K is a scalar. It should be stressed that this is not a direct like-for-like comparison, since the work of Vollmer can account for certain cases this work cannot, and conversely this work can account for state spaces that Vollmer's work does not. The single constraint case on the sphere however provides an simpler situation in which we can compare the two estimates. Following the proof in this work for the global stability condition, we can remove the condition that $\int_X a(t) \otimes a(t) \, d\mu(t) = I$, and instead choose a normalisation that simplifies the algebra, so that $||a||_\infty = 1$. In this case, the estimate given by Vollmer is that the isotropic state is globally stable if $8\pi \exp\left(\frac{16K}{T}\right) \leq \frac{T}{K}$, which numerically can be evaluated to $\frac{T}{K} > \tau^* \approx 38.205$. The estimate given in Proposition 2.3.18 gives that $\frac{T}{K} > 1$, providing in this case a significant

improvement by over an order of magnitude on the result of Vollmer. Furthermore, if the first and second derivatives of ψ_s are taken as a black box result, the proof presented in this work requires none of the infinite-dimensional variational techniques required for the result of Vollmer, in particular those with regards to correct function spaces.

Due to Ball and Majumdar [8], in the case when the single constraint corresponds to the uniaxial Maier-Saupe potential, we can compare these to the exact value at which the isotropic state ceases to be the unique critical point. In their work they show that the isotropic state is the unique critical point of the corresponding macroscopic functional analogous to (2.52) if and only if $\frac{2}{3}\frac{T}{K} > \frac{3}{20}$. By Proposition 2.3.11 this implies the isotropic state is the only critical point of the corresponding Onsager-type energy. This gives the exact bound as $\frac{T}{K} > \frac{9}{40} = 0.225$. This demonstrates that the estimate given in this work is also somewhat crude.

Remark 2.3.20. If L^∞-local minimisers are *a priori* known to be bounded away from zero and $+\infty$, then L^∞ variations can obtain a critical point condition for L^∞-local minimisers analogous to Corollary 2.3.13 and Corollary 2.3.14. Similarly, taking the second variation can provide estimates analogous to Proposition 2.3.18 to assess the stability under L^∞ perturbations. The advantages of the methods presented in this work are twofold; firstly that all statements are in reference to L^1-local minimisers, a stronger condition which could not be obtained by two-sided variations since $\mathcal{P}(X)$ has empty relative interior in $L^1(X)$, and secondly the technicality that local minimisers must be shown to be bounded away from zero and $+\infty$ is removed.

Remark 2.3.21. More general mean-field like free energies can be defined by

$$\mathcal{I}_{\mathcal{P}}(\rho) = \int_X \rho \ln \rho \, d\mu - \int_X \int_X K(t,s)\rho(t)\rho(s) \, d\mu(t) \, d\mu(s) \tag{2.82}$$

with $K \in L^\infty(X \times X)$ a symmetric kernel. If, for example, X is a connected, analytic, bounded, Riemannian manifold then the eigenvectors of the Laplace-Beltrami operator on X, denoted $(a_i)_{i=1}^\infty$, form a countable, dense, orthogonal basis for $L^2(X)$ with a_i analytic for $i \in \mathbb{N}$ [10]. By Proposition 2.1.6 they must therefore form a pseudo-Haar set. This allows the decomposition of K as

$$K(t,s) = \sum_{i,j=1}^{\infty} c_{ij} a_i(t) a_j(s), \tag{2.83}$$

so that by truncating this series to finitely many terms the kernel can be approxi-

mated, and the approximating model fits into the framework presented in this paper. In many models related to liquid crystals this decomposition would be superfluous, as the kernel is assumed to have a decomposition of the form in (2.83) with c_{ij} non-zero for only finitely many i, j. For example, if $V_\lambda(X)$ denotes the eigenspace of the Laplace-Beltrami operator on X with corresponding eigenvalue λ, then the constraint functions corresponding to the Maier-Saupe potential (dipolar potential, respectively) for nematic liquid crystals are in $V_{-6}(\mathbb{S}^2)$ ($V_{-2}(\mathbb{S}^2)$, respectively) [21], the McMillan model (see Section 2.6) has two constraint functions, one in $V_{-6}(\mathbb{S}^2 \times [0,1])$ and another in $V_{-2\pi}(\mathbb{S}^2 \times [0,1])$, and the Strayley model [47] uses elements of $V_{-6}(\mathrm{SO}(3))$.

Remark 2.3.22. Proposition 2.3.1, Corollary 2.3.8 and Proposition 2.3.11 presented together imply that globally stable, locally stable and unstable equilibrium points of the functionals on $\mathcal{P}(X)$ can be found by considering a macroscopic functional defined only on $\mathcal{Q}$, combined with the maximum entropy assumption.

2.4 Models with spatial inhomogeneities

If, as in the Q-tensor theory of liquid crystals, one wishes to consider models with inhomogeneities in a domain $\Omega \subset \mathbb{R}^n$, then one could appeal to the calculus of variations and consider functions $b : \Omega \to \overline{\mathcal{Q}}$ (note that the closure of $\mathcal{Q}$ is taken for compactness properties), and investigate minimisers of the functional

$$\mathcal{I}(b) = \int_\Omega W(\nabla b(x), b(x)) + F(b(x))\, dx \tag{2.84}$$

in some appropriate function space, where $W : \mathbb{R}^{k\times n} \times \mathcal{Q} \to \mathbb{R}$ represents the energy of distortions, and $F : \overline{\mathcal{Q}} \to \mathbb{R}$ represents the free energy of a homogeneous system. However, if F were to be bounded on $\partial\mathcal{Q}$, as is the case for a Landau expansion, then it is possible that minimisers could satisfy $b(x) \in \partial\mathcal{Q}$ for all x in some set of positive measure, providing unphysical solutions. Furthermore this is undesirable from a mathematical perspective since the minimiser would not satisfy the Euler-Lagrange equation. However, if one considers a functional $\mathcal{I}_s$, given by

$$\mathcal{I}_s(b) = \int_\Omega W(\nabla b(x), b(x)) + \psi_s(b(x)) + f(b(x))\, dx \tag{2.85}$$

for some f, W bounded away from $-\infty$, then provided finite energy configurations exist, it is immediate that minimisers satisfy $b(x) \in \mathcal{Q}$ for almost every $x \in \Omega$. Furthermore, in particular simple models it is possible to show strict physicality, in the

sense that there exists some compact set $K \subset \mathcal{Q}$ for which any global minimiser b satisfies $b \in K$ almost everywhere, which has the consequence that global minimisers satisfy the Euler-Lagrange equation allowing PDE methods to be applied to the problem. This is shown by a projection method based similar to that in [7].

Lemma 2.4.1. Let $g : \mathcal{Q} \to \mathbb{R}$ be Lipschitz continuous with Lipschitz constant L. Given $M \in \mathbb{R}$ define the set $K_M = \{b \in \mathcal{Q} : \psi_s(b) \leq M\}$, and the nearest point projection $P_M : \mathcal{Q} \to K_M$. Furthermore given $b \in \mathcal{Q}$ denote $b_M = P_M b$. Then there exists $M_0 \in \mathbb{R}$ so that for all $M > M_0$ and $b \in \mathcal{Q}$,

$$\psi_s(b) + g(b) \geq \psi_s(b_M) + g(b_M). \tag{2.86}$$

Proof. First note that the projection is well defined, since the convexity and continuity of ψ_s ensure that K_M is a compact, convex set. Suppose that the result is false. Then there must exist sequences $M^k \in \mathbb{R}$, $b_k \in \mathcal{Q}$ so that $\lim_{k\to\infty} M^k = +\infty$, and defining $c_k = P_{M^k} b_k$, for each k the inequality

$$\psi_s(c_k) + g(c_k) > \psi_s(b_k) + g(b_k) \tag{2.87}$$

is satisfied. By taking a subsequence if necessary (not relabelled), assume that $(M^k)_{k\in\mathbb{N}}$ is an increasing sequence. Using the fact that g is Lipschitz and elementary inequalities for convex functions, it holds that

$$\begin{aligned} L|c_k - b_k| &\geq g(c_k) - g(b_k) \\ &> \psi_s(b_k) - \psi_s(c_k) \\ &\geq \nabla\psi_s(c_k) \cdot (b_k - c_k). \end{aligned} \tag{2.88}$$

From the construction of K_M, ∂K_M is a level set of ψ_s, so that $\nabla\psi_s(c_k)$ is normal to the surface ∂K_{M^k} at c_k. Also from the properties of projections it holds that $b_k - c_k$ is normal to ∂K_{M^k} at c_k, with the same sign as $\nabla\psi_s(c_k)$ in the sense that $\nabla\psi_s(c_k) = s(b_k - c_k)$ for some $s > 0$. This implies $\nabla\psi_s(c_k) \cdot (b_k - c_k) = |\nabla\psi_s(c_k)|\,|b_k - c_k|$. Combining this with the previous chain of inequalities gives

$$\begin{aligned} L|c_k - b_k| &\geq |\nabla\psi_s(c_k)|\,|c_k - b_k| \\ \Rightarrow L &\geq |\nabla\psi_s(c_k)| \end{aligned} \tag{2.89}$$

for all k. However since $\mathcal{Q}$ is bounded, a subsequence (not relabelled) can be taken so that $c_k \to c^*$, and since $c_k \in \partial K_{M^k}$ for all k, this gives that $c^* \in \partial\mathcal{Q}$. Since

$\lim_{b\to\partial\mathcal{Q}} \psi_s(b) = +\infty$, and ψ_s is convex, this also implies that $\lim_{b\to\partial\mathcal{Q}} |\nabla\psi_s(b)| = +\infty$. Taking the limit as $k \to \infty$ of the inequality $L \geq |\nabla\psi_s(c_k)|$ gives a contradiction, completing the proof. □

Theorem 2.4.2. Let $\Omega \subset \mathbb{R}^n$ be an open bounded domain. Consider the minimisation problem

$$\min_{b\in\mathcal{A}} \int_\Omega |\nabla b(x)|^p + \psi_s(b(x)) + g(b(x))\,dx, \tag{2.90}$$

where $\mathcal{A} = \{b \in W^{1,p}(\Omega;\overline{\mathcal{Q}}) : b|_{\partial\Omega} = b_0\} \neq \emptyset$, $g : \overline{\mathcal{Q}} \to \mathbb{R}$ is Lipschitz continuous with Lipschitz constant L, $p > 1$ and there exists some compact $K \subset \mathcal{Q}$ such that $b_0(x) \in K$ for $\mathcal{H}^{n-1}$-almost every $x \in \partial\Omega$. Then there exists a global minimiser, and all global minimisers are strictly physical in the sense that $\psi_s(b) \in L^\infty(\Omega, \mathbb{R})$. In particular, any global minimiser $b^* : \Omega \to \overline{\mathcal{Q}}$ satisfies the Euler-Lagrange equation for the energy functional if $g \in C^1(\overline{\mathcal{Q}})$.

Proof. The existence of minimisers follows from a standard direct method argument [17]. To see that the global minimiser must be strictly physical, assume for the sake of contradiction that there exists a global minimiser $b \in \mathcal{A}$ such that $\psi_s(b)$ is unbounded on Ω. Let $M > M_0$ (as defined in Lemma 2.4.1) and b_M be the projection of b onto the set K_M as defined in Lemma 2.4.1. Take M sufficiently large so that $K \subset K_M$, so that b_M satisfies the same boundary conditions as b. Then $\psi_s(b_M) + g(b_M) \leq \psi_s(b) + g(b)$ almost everywhere in Ω by Lemma 2.4.1. Furthermore, since the term on the left is bounded, and by assumption the term on the right is unbounded this equality is strict on a set of positive measure. Finally since $|\nabla Pb| \leq |\nabla b|$ for any function in $W^{1,p}$ and projection P onto a convex set (see Lemma 10 in [7]), it holds that

$$\int_\Omega |\nabla b_M(x)|^p + \psi_s(b_M(x)) + g(b_M(x))\,dx < \int_\Omega |\nabla b(x)|^p + \psi_s(b(x)) + g(b(x))\,dx, \tag{2.91}$$

contradicting that b is a global minimiser. Since the minimiser is bounded away from $\partial\mathcal{Q}$ it is possible to take smooth variations so that the minimiser satisfies the Euler-Lagrange equation since the higher order terms in the weak formulation are integrable and the lower order terms are boounded. □

Corollary 2.4.3. Consider the minimisation problem given in Theorem 2.4.2. Then if b^* is an L^∞-local minimiser, b^* is strictly physical.

Proof. Let $\mathcal{F}(b) = \int_\Omega |\nabla b(x)|^p + \psi_s(b(x)) + g(b(x))\,dx$. The previous theorem was proven by assuming otherwise and constructing a sequence so that $\mathcal{F}(b_M) < \mathcal{F}(b^*)$ for sufficiently large M. To prove the analogous result for L^∞-local minimisers, by the

same argument it then suffices to show that this sequence satisfies $b_M \to b$ in $L^\infty(\Omega)$, which is equivalent to showing that $P_M \to \mathrm{Id}$ in $L^\infty(\overline{\mathcal{Q}})$. For the sake of contradiction assume otherwise, so that there exists $\epsilon > 0$ and $b_M \in \bar{\mathcal{Q}}$ with $\epsilon < \inf_{b_0 \in K_M} |b_0 - b_M|$. Then, without relabelling, take a subsequence so that $b_M \to b_\infty$, and

$$\begin{aligned} \epsilon <& \inf_{b_0 \in K_M} |b_0 - b_\infty| + |b_\infty - b_M| \\ =& d(b_\infty, K_M) + |b_\infty - b_M|. \end{aligned} \tag{2.92}$$

Since the sets K_M are nested, $d(b_\infty, K_M) \searrow d\left(b_\infty, \bigcup_{M>0} K_M\right) = d(b_\infty, \mathcal{Q}) = 0$ for all $b_\infty \in \overline{\mathcal{Q}}$. Also $|b_\infty - b_M| \to 0$ by construction, giving a contradiction and completing the proof. □

2.5 Approximation of the singular potential by everywhere defined functions

In some situations it may be preferable to approximate the singular potential by a globally defined function. In particular, as mentioned in Section 2.4, in models with inhomogeneities the blow up property can pose issues with minimisers satisfying the Euler-Lagrange equation. One tool kit for providing such an approximation is to use the Landau theory [51], which argues that the free energy of a system must be analytic in the order parameters, and therefore it is possible to replace the free energy with a polynomial in the order parameters that respects the symmetry of the system. Typically, this polynomial will be taken to fourth order. However, as will be shown in this section, the Landau expansion is not necessarily compatible with free energies of the form given in Section 2.3 , since the Taylor approximation does not necessarily preserve shape properties possessed by the singular potential. This section will only be concerned with the Shannon entropy, due to the relative simplicity of its Taylor approximation as well as its physical relevance.

2.5.1 One-Dimensional examples and counterexamples

The fourth order Taylor approximation about zero of the singular potential is derived in Appendix A. For simplicity consider only a single constraint function, and state space $X = [-1, 1]$. Define $m_i = \frac{1}{2}\int_X a(x)^i \, dx$. The fourth order Taylor approximation

$\psi_s^4 : \mathbb{R} \to \mathbb{R}$ is given by

$$\begin{aligned}\psi_s^4(b) =& \psi_s(0) + \sum_{j=2}^{4} \frac{d^j \psi_s}{db^j}(0) \frac{b^j}{j!} \\ =& \frac{1}{2m_2} b^2 - \frac{m_3}{6m_2^3} b^3 + \frac{3m_3^2 - m_2 m_4 + 3m_2^3}{24 m_2^5} b^4 + \psi_s(0).\end{aligned} \tag{2.93}$$

If the Taylor approximation is to represent a kind of macroscopic version of entropy, and approximate the singular potential, then at the very least it should be convex, posses a single local minimum, and be coercive so that the approximation blows up to $+\infty$ as $b \to \pm\infty$. Coercivity is perhaps the most important property, since if it fails then energy minimisation is not possible. The existence of a single critical point prevents the appearance of "phantom" minimisers for the entropy which should not exist. Finally convexity is a useful property in minimisation problems that one would want to inherit from the singular potential. In the one dimensional case presented, these three conditions have a chain of implication, so that convexity implies the existence of a single critical point, and a single critical point implies coercivity. Note that these implications rely on the fact that ψ_s^4 is convex in some neighbourhood of the origin, and that it is not linear. Similarly since ψ_s^4 is a polynomial that is not affine, convexity implies strict convexity.

Fortunately in the one dimensional case, verifying if these properties hold for a given example is relatively straightforward. In order to be coercive, the coefficient of b^4 must be positive, which gives the condition

$$d_1 = 3m_3^2 - m_2 m_4 - 3m_2^3 > 0. \tag{2.94}$$

If $b \neq 0$ is a critical point of ψ_s^4, this implies the existence of a non-zero real solution to

$$\frac{d\psi_s^4}{db}(b) = b\left(\frac{1}{m_2} - \frac{1}{2m_2^3} m_3 b + \frac{1}{6m_2^5}\left(3m_2^3 - m_2 m_4 + 3m_3^2\right) b^2\right) = 0. \tag{2.95}$$

By considering the discriminant of the quadratic, this means that ψ_s^4 possesses no non-trivial critical points if and only if

$$d_2 = 72m_2^3 - 24 m_2 m_4 + 63 m_3^2 > 0. \tag{2.96}$$

Finally for convexity, the second derivative of ψ_s^4 is a quadratic in b given by

$$\frac{d^2\psi_s^4}{db^2}(b) = \frac{1}{m_2} - \frac{m_3}{m_2^3}b + \frac{1}{2m_2^5}\left(3m_2^3 - m_2m_4 + 3m_3^2\right)b^2, \tag{2.97}$$

so by the same argument ψ_s^4 is strictly convex if and only if

$$d_3 = 6m_2^3 - 2m_2m_4 + 5m_3^2 > 0. \tag{2.98}$$

Within the chain of implication that

$$\text{Convexity} \Rightarrow \text{A single critical point} \Rightarrow \text{Coercivity},$$

none of the implications are equivalent for the singular potential. Using the domain $X = [-1, 1]$, there are four examples that produces all four possibilities, as seen in Figure 2.3.

$a(x) =$	x	$x^4-7x^3-2x^2+3x+\frac{7}{15}$	$7x^3 - x^2 + x + \frac{1}{3}$	x^3
$m_2 =$	$\frac{1}{3}$	$\frac{904}{525}$	$\frac{92}{9}$	$\frac{1}{7}$
$m_3 =$	0	$\frac{-6796096}{3378375}$	$\frac{-12112}{945}$	0
$m_4 =$	$\frac{1}{5}$	$\frac{4297061248}{287161875}$	$\frac{6938192}{19305}$	$\frac{1}{13}$
$d_1 =$	$\frac{2}{45}$	$\frac{765059068785152}{452732233078125}$	$\frac{998000512}{42567525}$	$\frac{-10}{4459}$
Coercive	Yes	Yes	Yes	No
$d_2 =$	$\frac{16}{15}$	$\frac{624228970176512}{150910744359375}$	$\frac{-618770176}{675675}$	$\frac{-240}{4459}$
Single Critical Point	Yes	Yes	No	No
$d_3 =$	$\frac{4}{45}$	$\frac{-905889167393792}{1358196699234375}$	$\frac{-2998034944}{25540515}$	$\frac{-20}{4459}$
Convex	Yes	No	No	No

Figure 2.3: Table of examples and discriminant values

As these simple examples show, the Taylor expansion approach to providing a polynomial approximation to the free energy will not necessarily work in general, and this is perhaps unsurprising given that the Taylor approximation is generally only a local approximation of a function. However, the following Weierstrass-type result

shows that convex polynomial approximation is possible.

Proposition 2.5.1 (From [45])**.** Let $M \subset \mathbb{R}^k$ be convex and compact, and $f : M \to \mathbb{R}$ be convex and continuous. Then for every $\epsilon > 0$ there exists some polynomial p_ϵ which is convex on $\mathbb{R}^k$ such that

$$\sup_{x \in M} |f(x) - p_\epsilon(x)| < \epsilon. \tag{2.99}$$

The main limitations of this result, however, are that the approximation can only be performed on compact subsets of $\mathcal{Q}$, and also, much like the classical Weierstrass result, the proof is non-constructive. It should also be noted that this result requires the function to be only continuous, rather than analytic, so that the Landau theory's assumption of an analytic free energy is unnecessary. One might hope that it is possible to establish a necessary and sufficient condition for the fourth order Taylor approximation to be convex, but in general the problem of establishing if a given polynomial is convex is an NP-hard problem [1]. Rather than pursuing a polynomial approximation, the Yosida-Moreau regularisation may be more appropriate, due to its shape preservation properties.

Definition 2.5.2. For $J > 0$, define the Yosida-Moreau regularisation of ψ_s, denoted ψ^J by

$$\psi^J(b) = \min_{\tilde{b} \in \mathcal{Q}} \psi_s(b) + \frac{J}{2}|\tilde{b} - b|^2. \tag{2.100}$$

The following proposition outlines several of the key properties which suggest that the Yosida-Moreau approximation is an appropriate approximation for the singular potential. The results presented are for the general entropy-like objective functions and pseudo-Haar constraint functions.

Proposition 2.5.3.

1. The Yosida-Moreau approximation preserves minima, in the sense that for all $J > 0$, $\min \psi^J = \psi^J(0) = \psi_s(0) = \min \psi_s$. For all $b \in \mathbb{R}^k$, $J > 0$, the minimisation problem defining ψ^J, as defined in Equation (2.100), admits a unique solution denoted $G_J(b)$.

2. For every $b \in \mathbb{R}^k$, $\psi^J(b) \nearrow \psi_s(b)$, where the limit is infinite for $b \notin \mathcal{Q}$.

3. For all $J > 0$, ψ^J is a convex, differentiable function. Furthermore, the gradient is Lipschitz with Lipschitz constant J. The derivative of ψ^J can be given in terms of $G_J(b)$ by

$$\frac{\partial \psi^J}{\partial b}(b) = J\left(b - G_J(b)\right) = \lambda\left((G_J(b)\right). \tag{2.101}$$

4. The Yosida-Moreau approximation can be evaluated numerically by the dual problem,

$$\psi^J(b) = \max_{\alpha\in\mathbb{R},\lambda\in\mathbb{R}^k} \alpha + \lambda\cdot b - \int_X \phi^*(\alpha+\lambda\cdot a)\,d\mu - \frac{1}{2J}|\lambda|^2. \tag{2.102}$$

Proof. The preservation of minima in statement 1 is immediate from the definition, by testing $\tilde{b}=0$. The existence and uniqueness of a minimiser follow from the coercivity and strict convexity of the objective function. Statement 2 can be found in [38]. Statement 3 can be found in [15]. Statement 4 is given in [19]. □

Remark 2.5.4. The previous proposition has several consequences. Firstly, statements 1 and 2 say that ψ^J approximates ψ_s, as well as preserving desirable shape properties. Statement 3 gives that ψ^J is sufficiently regular for first order methods to be used. Lastly, statement 4 shows that the dual optimisation problem defining ψ^J is, at face value, no harder to approach than the optimisation problem defining ψ_s.

2.6 An illustrative example: The McMillan model

As an illustrative and physically meaningful example consider the McMillan model for Isotropic-Nematic-Smectic-A phase transitions [37]. This is a mean field theory as described previously where the state space is $X=\mathbb{S}^2\times[0,1]$, and two constraint functions are given by

$$\begin{aligned} a_1(p,x) =& \frac{1}{2}\left(3(p\cdot e_1)^2-1\right), \\ a_2(p,x) =& \frac{1}{2}\left(3(p\cdot e_1)^2-1\right)\cos(2\pi x). \end{aligned} \tag{2.103}$$

Here e_1 is a unit vector, physically corresponding to the orientation of the material. Due to the rotational symmetry of the constraint functions, it is possible to consider only state variables $(\theta,x)\in[0,\pi]\times[0,1]$, where $\cos(\theta)=p\cdot e_1$. This approach views X as equivalent to a subset of $\mathbb{R}^2$ with measure $d\mu(\theta,x)=2\pi\sin(\theta)\,d\theta\,dx$. The constraint functions are analytic and linearly independent, and since the measure μ has the same null sets as the Lebesgue measure, the pseudo-Haar condition is satisfied.

These constraints give two order parameters, denoted

$$S = 2\pi \int_0^1 \int_{-\pi}^{\pi} a_1(\theta, x)\rho(\theta, x)\, d\theta\, dx$$
$$\sigma = 2\pi \int_0^1 \int_{-\pi}^{\pi} a_2(\theta, x)\rho(\theta, x)\, d\theta\, dx.$$

Loosely speaking S corresponds to the degree of orientational order of the molecules, and σ represents a coupling between the order of the molecules and the location of their centre of mass. If $S = \sigma = 0$, then the sample is in an isotropic phase. If $S \neq 0$ and $\sigma = 0$ then it is a nematic phase, and if $S \neq 0$ and $\sigma \neq 0$ then it is a smectic A phase. Before any analysis can be performed, the set of physical moments will be established.

Proposition 2.6.1. The set $\mathcal{Q}$ for the constraint functions of the McMillan model is given by

$$\mathcal{Q} = \left\{ (S, \sigma) \in \mathbb{R}^2 : S \in \left(-\frac{1}{2}, 1 \right), |\sigma| < \frac{S+2}{3} \right\}. \tag{2.104}$$

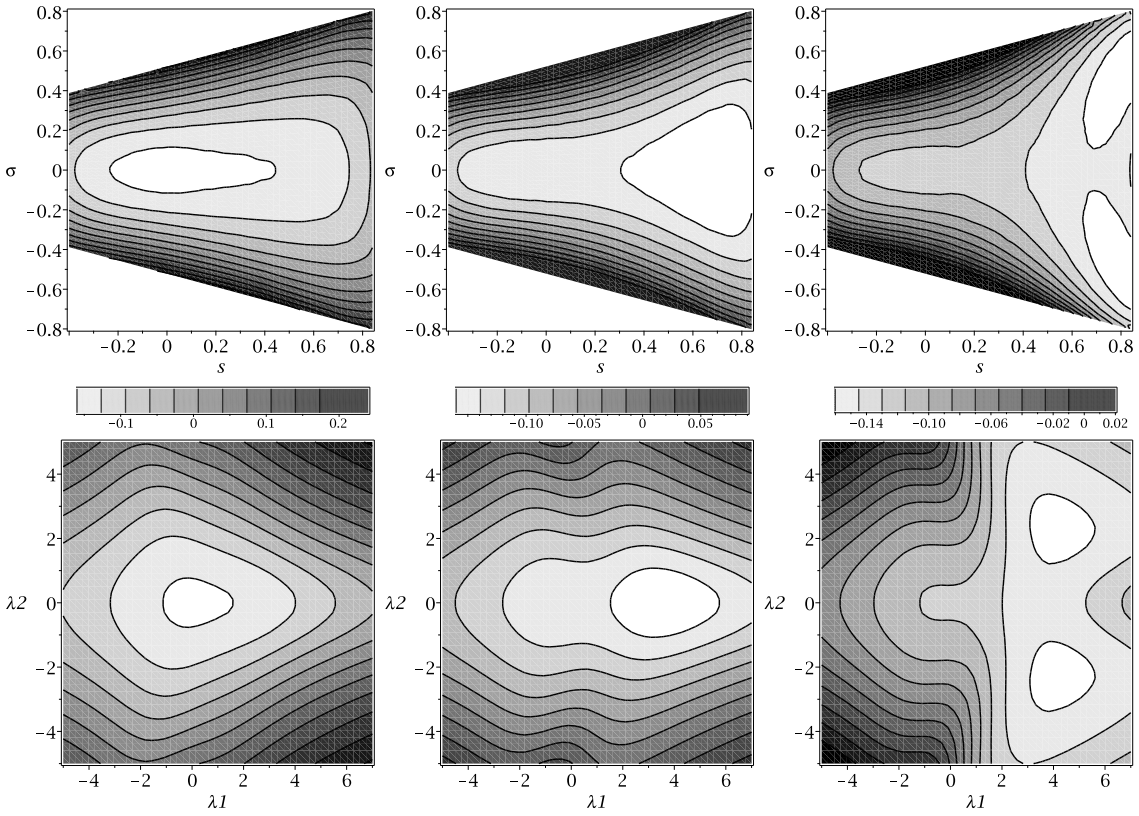
Proof. To see that the candidate set contains $\mathcal{Q}$, use Theorem 2.1.10 and test against $(\pm 1, 0)$ and $\left(-\frac{1}{3}, \pm 1\right)$. The maxima a_1 and $-a_1$ are 1 and $\frac{1}{2}$ respectively, which gives that $S \in \left(-\frac{1}{2}, 1\right)$. The maximum of $-\frac{1}{3}a_1(\theta, x) - a_2(\theta, x)$ can be found by noting that

$$\begin{aligned} -\frac{1}{3}a_1(\theta, x) - a_2(\theta, x) =& \frac{1}{2}\left(1 - 3\cos^2(\theta)\right)\left(\frac{1}{3} + \cos(2\pi x)\right) \\ \leq& \frac{1}{2} \cdot \frac{4}{3} = \frac{2}{3}, \end{aligned} \tag{2.105}$$

which is attained at $\theta = \pi$ and $x = 0$. For $u = \left(-\frac{1}{3}, 1\right)$ the same argument is used. To show that $\mathcal{Q}$ contains the candidate set is equivalent to showing that the closure of the candidate set is a subset of the closure of $\mathcal{Q}$ since the sets are convex. To prove this, it is then sufficient to show that the four vertices $((1, \pm 1), \left(-\frac{1}{2}, \pm\frac{1}{2}\right))$ are contained in the closure of $\mathcal{Q}$. This can be done constructively, and here only one vertex will be proven with the rest being shown by the same method. Let $0 < \epsilon < 1$, and define the set $A_\epsilon = \{(\theta, x) : \cos^2(\theta) > 1 - \epsilon, \cos(2\pi x) > 1 - \epsilon\}$. Define

$$\rho_\epsilon(\theta, x) = \left(2\pi \int_{A_\epsilon} \sin(\Theta)\, d\Theta \right)^{-1} 2\pi \sin(\theta)\chi_{A_\epsilon}(\theta, x). \tag{2.106}$$

This corresponds to a distribution uniform with respect to the measure on X on A_ϵ.



(a) $T = 0.23$, $\alpha = 0.3$, isotropic at the global equilibrium.

(b) $T = 0.19$, $\alpha = 0.3$, nematic at the global equilibrium

(c) $T = 0.19$, $\alpha = 0.8$, Smectic-A at the global equilibrium

Figure 2.4: Energy landscapes in the order parameter and dual variable space for various parameter values

Let the corresponding moments be denoted $S_\epsilon, \sigma_\epsilon$. Then it is immediate that

$$\begin{aligned} 1 > S_\epsilon &> \frac{1}{2}(3(1-\epsilon)-1) = 1 - \frac{3}{2}\epsilon \\ 1 > \sigma_\epsilon &> \frac{1}{2}(3(1-\epsilon)-1)(1-\epsilon) = 1 - \frac{5}{2}\epsilon + \frac{3}{2}\epsilon^2. \end{aligned} \tag{2.107}$$

Therefore $(S_\epsilon, \sigma_\epsilon) \in \mathcal{Q}$, and by taking ϵ to 0, $(1,1) \in \overline{\mathcal{Q}}$. □

Figure 2.4 shows plots of the macroscopic analogue of the Onsager energy, in both order parameter space (as defined to be $\mathcal{I}_\mathcal{Q}$ in (2.52)) and dual variables (as defined

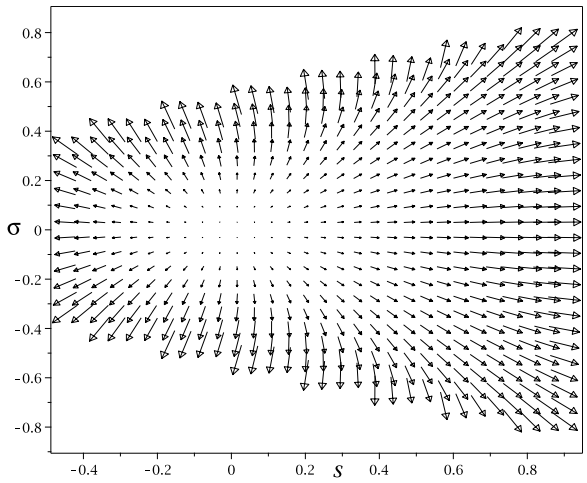


Figure 2.5: A field plot of the dual variables, (λ_1, λ_2) as a function of the order parameters S, σ

to be $\mathcal{I}_{\mathbb{R}^k}$ in (2.73)), given depending on parameters $T, \alpha > 0$ as

$$\begin{aligned}\mathcal{I}_{\mathcal{Q}}(S,\sigma) &= T\psi_s(S,\sigma) - \frac{1}{2}(S^2 + \alpha\sigma^2),\\ \mathcal{I}_{\mathbb{R}^k}(\lambda) &= T\left(\lambda_1 \cdot S^\lambda + \lambda_2\sigma^\lambda - \ln\int_0^1\int_{-\pi}^{\pi} \exp\left(\lambda \cdot a(\theta,x)\right)\, d\theta\, dx\right) - \frac{1}{2}\left((S^\lambda)^2 + \alpha(\sigma^\lambda)^2\right).\end{aligned} \tag{2.108}$$

Within this we can see the three regimes found numerically in [37], firstly where the global minimiser is isotropic, statisfying $(S^*, \sigma^*) = (\lambda_1^*, \lambda_2^*) = (0,0)$, then where the nematic state is the global minimiser, at $S^* \neq 0 \neq \lambda_1^*$ and $\sigma^* = \lambda_2^* = 0^*$, and finally where $S^* \neq 0 \neq \lambda_1^*$ and $\sigma^* \neq 0 \neq \lambda_2^*$. The singular potential was computed numerically via a gradient ascent on the dual optimisation scheme.

In Figure 2.5 the dual parameters are shown as a function of the order parameters, again computed via a gradient ascent on the dual optimisation problem. Due to the growth near the boundary the figures are only shown for order parameters a distance of 10^{-1} from the boundary.

2.6.1 Approximating by everywhere defined functions

Using the formula given in Appendix A, the exact symbolic integration package in Maple gives the fourth order Taylor approximation to the singular potential as

$$\psi_s^4(S,\sigma) = \frac{425}{196}S^4 + \frac{50}{49}\sigma^2 S^2 + \frac{825}{196}\sigma^4 - \frac{25}{21}S^3 - \frac{50}{7}\sigma^2 S + \frac{5}{2}S^2 + 5\sigma^2 + \psi_s(0,0). \quad (2.109)$$

Proposition 2.6.2. For the McMillan model, ψ_s^4 is coercive, so that

$$\lim_{|(S,\sigma)|\to+\infty} \psi_s^4(S,\sigma) = +\infty. \quad (2.110)$$

Proof. It is sufficient to show that the fourth order terms are coercive. This can be written as a bilinear form in S^2 and σ^2, since

$$\frac{425}{196}S^4 + \frac{50}{49}\sigma^2 S^2 + \frac{825}{196}\sigma^2 = \begin{bmatrix} S^2 \\ \sigma^2 \end{bmatrix} \cdot \begin{bmatrix} \frac{425}{196} & \frac{25}{49} \\ \frac{25}{49} & \frac{825}{196} \end{bmatrix} \begin{bmatrix} S^2 \\ \sigma^2 \end{bmatrix}.$$

The eigenvalues of the matrix are given by $\frac{625}{196} \pm \frac{25}{49}\sqrt{5}$, which are both positive (evaluating at approximately 2.04 and 4.33), so that the leading order terms are positive. □

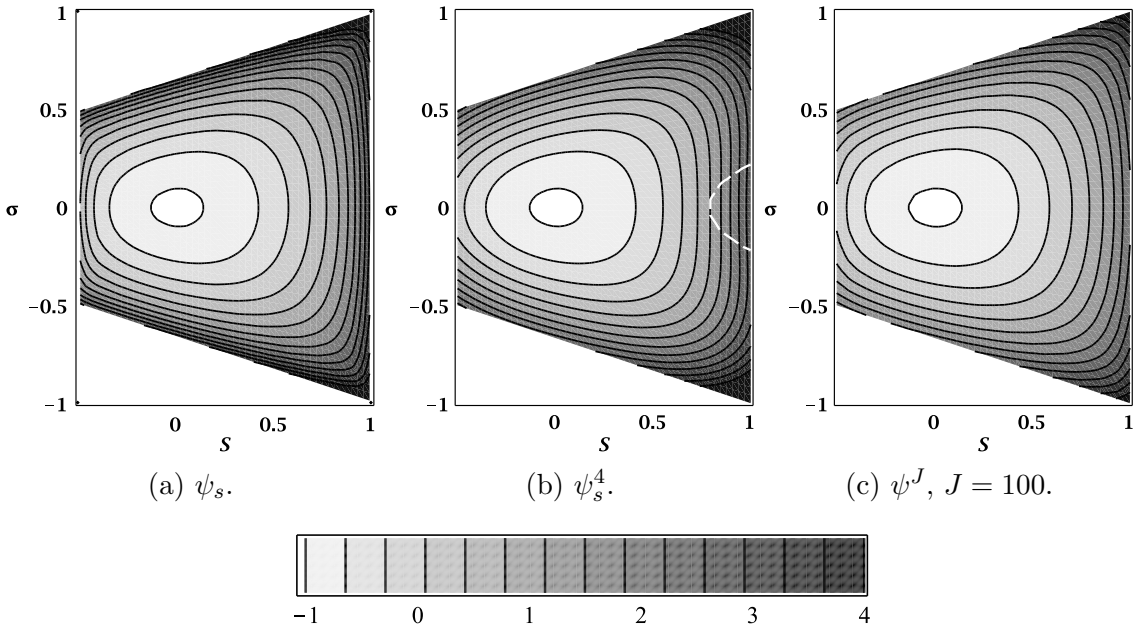
Proposition 2.6.3. In the McMillan model, ψ_s^4 is not a convex function of S, σ, even when restricted to $\mathcal{Q}$.

Proof. It is sufficient to show that the Hessian matrix of ψ_s^4 has a negative eigenvalue for some (S,σ). The Hessian matrix is readily computed as

$$\begin{aligned} H(S,\sigma) =& \frac{1}{49}\begin{bmatrix} 1275S^2 + 100\sigma^2 - 350S + 245 & 200S\sigma - 700\sigma \\ 200S\sigma - 700\sigma & 100S^2 + 2475\sigma^2 - 700S + 490 \end{bmatrix}, \\ \Rightarrow H(1,0) =& \frac{1}{49}\begin{bmatrix} 1275 - 350 + 245 & 0 \\ 0 & 100 - 700 + 490 \end{bmatrix} \\ =& \frac{1}{49}\begin{bmatrix} 1170 & 0 \\ 0 & -110 \end{bmatrix}. \end{aligned}$$

Therefore it has a negative eigenvalue, and ψ_s^4 is not convex in this case. In particular, it is not convex in a neighbourhood of $(1,0)$, since the Hessian is continuous. By noting that the intersection of any neighbourhood of $(1,0)$ with $\mathcal{Q}$ is non-empty since $(1,0) \in \partial\mathcal{Q}$, this implies that ψ_s^4 is not convex on $\mathcal{Q}$. □

To conclude, contour plots of of the singular potential and its approximations are given in Figure 2.6. The singular potential itself is given in Figure 2.6a. It should be noted that ψ_s is only given on $\{(S,\sigma) \in \mathcal{Q} : d((S,\sigma), \partial\mathcal{Q}) > 10^{-2}\}$ to avoid the difficulty in calculating the singular potential near $\partial\mathcal{Q}$. The fourth order Taylor approximation is given in Figure 2.6b. Also included on the plot is a white dashed line, which is the boundary of the set where the Hessian matrix has a negative eigenvalue. The Yosida-Moreau approximation for $J = 100$ is given in Figure 2.6c. The numerical values for ψ_s and ψ^J were obtained via a steepest descent algorithm on the dual optimisation problem.



(a) ψ_s. (b) ψ_s^4. (c) ψ^J, $J = 100$.

Figure 2.6: Contour plots of the singular potential and its approximations.

Chapter 3

Density functional with logarithmic potential

3.1 Derivation

Although a derivation of the free energy density is provided by Zheng, Taylor and Palffy-Muhoray [61], we include an alternative derivation following the reasoning of Van Kampen [54] to account for thermal interactions. Consider a system of N ellipsoidal molecules inside a volume $V > 0$, with $(N_i)_{i=1}^M$ occupying one of a discrete number of orientations $(p_i)_{i=1}^M \in \mathbb{S}^2$. We neglect information regarding the positions of the molecules, and consider only their orientations. We assume that the excluded volume of two molecules with orientations $p, q \in \mathbb{S}^2$ is given by $v_{ex}(p, q)$. The amount of volume, assuming only pairwise steric interactions, available to a molecule with orientation p_i is then given by $V - \sum_{j=1}^{M} N_i v_{ex}(p_i, p_j) + \epsilon_i$ where the final term $\epsilon_i = v_{ex}(p_i, p_i)$ accounts for double counting in the sum. Furthermore we assume an energetic pairwise interaction $\frac{1}{V}k_{i,j} = \frac{1}{V}k(p_i, p_j)$. We justify the inverse scaling of the interaction energy with respect to volume in Section 3.1.1.

Following the reasoning of Van Kampen, the canonical partition function is for $\beta = (kT)^{-1}$ given by

$$\frac{1}{N!} \sum_{\{N_i\}} \frac{N!}{\prod_{i=1}^{M} N_i!} \left(\prod_{i=1}^{M} \omega_i^{N_i} \right) \exp\left(-\frac{1}{2V} \sum_{i,j=1}^{M} \beta k_{i,j} N_i N_j \right) \tag{3.1}$$

and the energy to be minimised is

$$-kT\left(\sum_{i=1}^{M} N_i \ln \omega_i - \ln(N_i!) - \frac{1}{2V}\beta N_i \sum_{j=1}^{M} k_{i,j} N_j\right). \tag{3.2}$$

We will take (3.2) as a black box result, and taking a limit to obtain the free energy density for this work. Applying Stirling's approximation gives

$$\approx kT\left(\sum_{i=1}^{M} N_i \ln N_i - N_i - N_i \ln \omega_i + \frac{1}{2V}\beta N_i \sum_{j=1}^{M} k_{i,j} N_j\right). \tag{3.3}$$

Taking $\frac{N_i}{V} = \rho_i$ and $\frac{N}{V} = \rho_0$, this gives

$$\begin{aligned} \approx & kTV\left(\sum_{i=1}^{M} \rho_i \ln V\rho_i - \rho_i \ln \omega_i - \rho_i + \frac{1}{2}\beta\rho_i \sum_{j=1}^{M} k_{i,j}\rho_j\right) \\ = & kTV\left(\sum_{i=1}^{M} \rho_i \ln \rho_i - \rho_i \ln \frac{\omega_i}{V} - \rho_i + \frac{\beta}{2}\rho_i \sum_{j=1}^{M} k_{ij}\rho_j\right). \end{aligned} \tag{3.4}$$

Dividing through by V, and taking the limit as $V, M \to +\infty$ with ρ_0 fixed and assuming that $\rho_i \approx \rho(p)\Delta p$ for $\rho \in \mathcal{P}(\mathbb{S}^2)$ gives the free energy density per unit volume as

$$kT\int_{\mathbb{S}^2} \rho(p)\ln\rho(p) - \rho(p)\ln\left(1 - \int_{\mathbb{S}^2} \rho(q)v_{ex}(p,q)\,dq\right) - \frac{\beta}{2}\rho(p)\int_{\mathbb{S}^2} \rho(q)k(p,q)\,dq\,dp. \tag{3.5}$$

For the bulk of this work we will take the pairwise interaction term to be zero to give a purely entropy-type energy. In this case, we now define $f(p) = \frac{1}{\rho_0}\rho(p)$, which gives the free energy density at number density ρ_0 with orientational probability distribution f as

$$kT\left(\rho_0\int_{\mathbb{S}^2} f(p)\ln f(p) - f(p)\ln\left(1 - \rho_0\int_{\mathbb{S}^2} v_{ex}(p,q)f(q)\,dq\right)\,dp + \rho_0\ln\rho_0\right). \tag{3.6}$$

Furthermore, when unimportant we will take $kT = 1$ for simplicity.

As in [61], we consider the excluded volume term

$$v_{ex}(p,q) = c - \frac{3d}{2}\left(p\otimes p - \frac{1}{3}I\right)\cdot\left(q\otimes q - \frac{1}{3}I\right). \tag{3.7}$$

The constants $c, d > 0$ are given in terms of the length $L > 0$, width $W > 0$ with

$W \neq L$ and volume $v_0 = \frac{\pi}{6} LW^2$ of the ellipsoid as

$$\begin{aligned} c =& \frac{4v_0}{3}\left(\frac{L}{W} + \frac{W}{L} + 4\right), \\ d =& \frac{4v_0}{3}\left(\frac{L}{W} + \frac{W}{L} - 2\right). \end{aligned} \tag{3.8}$$

In this case, the excluded volume integral reduces to $c - \frac{3d}{2} Qp \cdot p$, with the Q-tensor

$$Q = \int_{\mathbb{S}^2} f(p)\left(p \otimes p - \frac{1}{3} I\right). \tag{3.9}$$

The energy can be written as $kT\left(\rho_0 \mathcal{F}(f,\eta) + \rho_0 \ln \frac{3d}{2}\right)$, where the dimensionless parameter

$$\eta = \frac{2(c\rho_0 - 1)}{3d\rho_0} \tag{3.10}$$

is the only influence on energy minimisation at fixed concentrations, and the non-dimensionalised energy is given by

$$\mathcal{F}(f,\eta) = \int_{\mathbb{S}^2} f(p) \ln f(p) - f(p) \ln(Qp \cdot p - \eta)\, dp. \tag{3.11}$$

Denoting $R = \frac{L}{W}$, we can obtain bounds for η, and see that for L, W fixed but ρ_0 variable,

$$\begin{aligned} \eta =& \frac{2c}{3d} - \frac{2}{3d\rho_0} \\ =& \frac{2(R + R^{-1})^2 + 12}{3(R + R^{-1})^2} - \frac{2}{3d\rho_0} \\ =& \frac{2}{3} + \frac{4}{(R + R^{-1})^2} - \frac{2}{3d\rho_0}. \end{aligned} \tag{3.12}$$

This demonstrates that η is increasing in ρ_0, and satisfies

$$\eta \in \left(-\infty, \frac{2}{3} + \frac{4}{(R + R^{-1})^2}\right) \supset \left(-\infty, \frac{2}{3}\right]. \tag{3.13}$$

3.1.1 Justification of scaling with volume

We now justify why the pairwise interaction energy varies inversely with volume, so that the total pairwise interaction energy is given as

$$\frac{1}{2}\sum_{ij=1}^{M}\frac{1}{V}N_iN_jk_{ij}. \tag{3.14}$$

Consider a configuration space $\Gamma = \Omega \times \mathbb{S}^2$, with $|\Omega| = V$. Similarly to before, consider a partition of the sphere $(U_i)_{i=1}^M$ with a discrete set of representatives $(p_i)_{i=1}^M$, and a partition of Ω, $(V_i)_{i=1}^M$ with representative elements $(x_i)_{i=1}^M$. Consider a pairwise interaction energy for molecules (x,p), (y,q) as $W(x,p,y,q) = g(x-y)k(p,q)$. We take g to integrate to one and have compact support for simplicity. Assume that the number of molecules occupying $V_i \times U_j$ is given by N_{ij}. We assume a spatially homogeneous system, so that $N_{ij} = \frac{|V_i|}{V}N_j$. The total interaction energy is then given by

$$\begin{aligned}
&\frac{1}{2}\sum_{ijkl=1}^{M} W(x_i,p_j,x_k,p_l)N_{ij}N_{kl}\\
=&\frac{1}{2}\sum_{ijkl=1}^{M} g(x_i-x_k)k(p_j,p_l)N_jN_l\frac{|V_i||V_k|}{V^2}N_jN_l\\
=&\frac{1}{2}\sum_{jl=1}^{M} N_jN_lk(p_j,p_l)\left(\sum_{ik=1}^{M}\frac{|V_i||V_k|}{V^2}g(x_i-x_k)\right).
\end{aligned}$$

Focusing on the inner sum, we approximate this by

$$\frac{1}{2}\sum_{ik=1}^{M}\frac{|V_i||V_k|}{V^2}g(x_i-x_k) \approx \frac{1}{2V^2}\int_\Omega\int_\Omega g(x-y)\,dx\,dy.$$

If we take Ω to be sufficiently large, then by Proposition 3.1.1, this simplifies as

$$\frac{1}{2}\sum_{ik=1}^{M}\frac{|V_i||V_k|}{V^2}g(x_i-x_k) \approx \frac{1}{2V}\int_{\mathbb{R}^d} g(x)\,dx = \frac{1}{2V},$$

recalling that g integrates to 1. Therefore the total interaction energy is then given approximately as

$$\frac{1}{2}\sum_{ij=1}^{M}\frac{1}{V}N_iN_jk(p_i,p_j).$$

We now conclude with the proof of Proposition 3.1.1.

Proposition 3.1.1. Let $g \in L^1(\mathbb{R}^d)$ have compact support. Then if B_r is the ball of radius r in $\mathbb{R}^d$ and $V_r = \mathcal{L}^d(B_r)$, then for r sufficiently large,

$$\frac{1}{V_r}\int_{B_r}\int_{B_r} g(x-y)\,dx\,dy = \int_{\mathbb{R}^d} g(x)\,dx. \tag{3.15}$$

Proof. Let $R > 0$ be such that $\operatorname{supp}(g) \subset B_R$. First we note that if $r > R$, then $\int_{B_r} g(x-y)\,dx = \int_{\mathbb{R}^d} g(x-y)\,dx$. Therefore we have that for $r > R$,

$$\begin{aligned}
\frac{1}{V_r}\int_{B_r}\int_{B_r} g(x-y)\,dx\,dy =& \frac{1}{V_r}\int_{\Omega}\int_{\mathbb{R}^d} g(x-y)\,dx\,dy \\
=& \int_{\mathbb{R}^d}\int_{B_r} \frac{1}{V_r} g(x-y)\,dy\,dx \\
=& \int_{\mathbb{R}^d}\int_{\mathbb{R}^d} g(x-y)\left(\frac{1}{V_r}\chi_{B_r}(y)\right)\,dy\,dx \\
=& \int_{\mathbb{R}^d}\left[g * \left(\frac{1}{V_r}\chi_{B_r}\right)\right](x)\,dx \\
=& \int_{\mathbb{R}^d} g(x)\,dx \int_{\mathbb{R}^d} \frac{1}{V_r}\chi_{B_r}(x)\,dx = \int_{\mathbb{R}^d} g(x)\,dx,
\end{aligned} \tag{3.16}$$

with χ_{B_r} denoting the indicator function for B_r and $*$ denoting convolution. □

3.2 Finding solutions by variations

Definition 3.2.1 (Notation and energy)**.** Let $\mathrm{Sym}_0(3) \subset \mathbb{R}^{3\times 3}$ denote the set of traceless, symmetric 3×3 matrices. Let $\mathcal{Q} = \{Q \in \mathrm{Sym}_0(3) : v_{\min}(Q) > -\frac{1}{3}\}$ be the set of physical Q-tensors. Let $\mathcal{P}(\mathbb{S}^2) = \left\{f \in L^1(\mathbb{S}^2) : f \geq 0 \text{ a.e. }, \int_{\mathbb{S}^2} f\,dp = 1\right\}$. All integrals $\int_{\mathbb{S}^2} g(p)\,dp$ use dp to denote the 2-dimensional Hausdorff measure on the sphere. Given the parameter $\eta \in \mathbb{R}$, define the energy functional $\mathcal{F} : \mathcal{P}(\mathbb{S}^2) \times \mathbb{R} \to \mathbb{R} \cup \{+\infty\}$ by

$$\mathcal{F}(f,\eta) = \int_{\mathbb{S}^2} f(p)\ln f(p) - f(p)\ln\left(\int_{\mathbb{S}^2}\left((p\cdot q)^2 - \frac{1}{3}\right) f(q)\,dq - \eta\right)\,dp. \tag{3.17}$$

$-\ln$ is extended by $+\infty$ for non-positive argument, and the convention $0 \times +\infty = 0$ is taken. When unambiguous, the dependence of $\mathcal{F}$ on η will be suppressed, so that

$\mathcal{F}(f,\eta) = \mathcal{F}(f)$. For brevity, given $f \in \mathcal{P}(\mathbb{S}^2)$, define

$$Q = \int_{\mathbb{S}^2} \left(p \otimes p - \frac{1}{3} I \right) f(p)\, dp \in \mathcal{Q}. \tag{3.18}$$

Before any analysis, of course one must ensure that minimisers of the energy actually exist. In the next lemma it will be shown that solutions exist if and only if $\eta < \frac{2}{3}$, although this is due to a lack of finite-energy configurations, rather than minimising sequences being lost due to a lack of lower semicontinuity or coercivity of the functional. The issue causing non-admissibility is considering the energetics, we immediately see that if $f \in \mathcal{P}(\mathbb{S}^2)$ has finite energy, then for almost every $p \in \mathbb{S}^2$ such that $Qp \cdot p < \eta$, $f(p) = 0$. In particular, since the eigenvalues of Q must be greater than $-\frac{1}{3}$, if $\eta \geq \frac{2}{3}$, then $Qp \cdot p - \eta < 0$ for all p and Q.

Lemma 3.2.2. There exists some $f \in \mathcal{P}(\mathbb{S}^2)$ with $\mathcal{F}(f) < +\infty$ if and only if $\eta < \frac{2}{3}$.

Proof. Assume that $\eta \geq \frac{2}{3}$. Then for any $f \in \mathcal{P}(\mathbb{S}^2)$, and corresponding Q-tensor $Q \in \mathcal{Q}$, it must hold that $Qp \cdot p - \eta \leq 0$ for all $p \in \operatorname{supp}(f) \subset \mathbb{S}^2$ due to the eigenvalue constraint on Q. In particular, $-\ln(Qp \cdot p - \eta) = +\infty$ for all $p \in \operatorname{supp}(f)$, and $\mathcal{F}(f) = +\infty$.

Assume $\eta < \frac{2}{3}$. In order to demonstrate that there exists some admissible f, in the sense that it has finite energy, it is sufficient, using that $-\ln(\cdot)$ is continuous on its domain, to show that there exists some f, so that $\operatorname{supp}(f) \subset \{\eta + \delta \leq Qp \cdot p < \frac{2}{3}\}$, and also having finite entropy. The upper bound is trivial, due to the eigenvalue constraint on the Q-tensor. Let $e \in \mathbb{S}^2$ be arbitrary, and $\epsilon > 0$. Define $f^\epsilon = \frac{1}{2\pi\epsilon} \chi_{\{p \cdot e > 1-\epsilon\}}$. A straightforward calculation gives that $f \in \mathcal{P}(\mathbb{S}^2)$, and $Q^\epsilon = \left(1 - \frac{3}{2}\epsilon + \frac{1}{2}\epsilon^2\right)\left(e \otimes e - \frac{1}{3} I\right)$. Therefore $Q^\epsilon p \cdot p = \left(1 - \frac{3}{2}\epsilon + \frac{1}{2}\epsilon^2\right)\left((p \cdot e)^2 - \frac{1}{3}\right)$. It suffices to show that, for some $\epsilon > 0$, $\{p \cdot e > 1 - \epsilon\} = \operatorname{supp}(f^\epsilon) \subset \{Q^\epsilon p \cdot p > \eta + \delta\} = \left\{(p \cdot e)^2 > \frac{2(\eta+\delta)}{2 - 3\epsilon + \epsilon^2} + \frac{1}{3}\right\}$. It then needs to be shown that there exists some $\epsilon > 0$ so that

$$(1-\epsilon)^2 - \frac{2(\eta+\delta)}{2 - 3\epsilon + \epsilon^2} - \frac{1}{3} > 0. \tag{3.19}$$

At $\epsilon = 0$, the left-hand side of this inequality is $\frac{2}{3} - (\eta + \delta)$ which by assumption is strictly positive for sufficiently small δ. Then, by continuity at $\epsilon = 0$ (the denominator of the rational function is zero only at $\epsilon = 1, 2$), this implies that for sufficiently small $\epsilon > 0$, the strict inequality holds also. Therefore $\mathcal{F}(f_\epsilon) < +\infty$ for sufficiently small ϵ. □

Remark 3.2.3. The previous proposition is a weaker form of Proposition 3.3.4, although it is included for its more straightforward proof. Furthermore, following the

argument leading to (3.13), this implies that for any ellipsoid dimensions L, W with $L \neq W$, there is always a finite saturation point at which no configurations have finite energy.

Lemma 3.2.4. Let $f_j \in \mathcal{P}(\mathbb{S}^2)$, with $f_j \rightharpoonup f$ in $L^1(\mathbb{S}^2)$. Then

$$\liminf_{j\to\infty} \mathcal{F}(f_j) \geq \mathcal{F}(f). \tag{3.20}$$

Proof. The Shannon entropy term is trivially lower semicontinuous. It suffices to show that

$$\liminf_{j\to\infty} -\int_{\mathbb{S}^2} f_j(p) \ln(Q_j p \cdot p - \eta)\, dp \geq -\int_{\mathbb{S}^2} f(p) \ln(Qp \cdot p - \eta)\, dp. \tag{3.21}$$

For $M \in \mathbb{R}$, let $\ln^M(x) = \max(\ln(x), -M)$. Then note since $Q_j \to Q$, $Q_j p \cdot p - \eta \to Qp \cdot p$ uniformly on $\mathbb{S}^2$, and $-\ln^M(Qp \cdot p - \eta) \to -\ln^M(Qp \cdot p - \eta)$ uniformly. This then implies that

$$\begin{aligned} &\liminf_{j\to\infty} -\int_{\mathbb{S}^2} f_j(p) \ln(Q_j p \cdot p - \eta)\, dp \\ \geq &\liminf_{j\to\infty} -\int_{\mathbb{S}^2} f_j(p) \ln^M(Q_j p \cdot p - \eta)\, dp \\ = &\int_{\mathbb{S}^2} -f(p) \ln^M(Qp \cdot p - \eta)\, dp \end{aligned} \tag{3.22}$$

We then apply the monotone convergence theorem by taking $M \to +\infty$ in the final integral to give

$$\liminf_{j\to\infty} -\int_{\mathbb{S}^2} f_j(p) \ln(Q_j p \cdot p - \eta)\, dp \geq \int_{\mathbb{S}^2} -f(p) \ln(Qp \cdot p - \eta)\, dp. \tag{3.23}$$

□

Proposition 3.2.5. There exists a minimiser of $\mathcal{F}$ if and only if $\eta < \frac{2}{3}$.

Proof. The proof will follow a standard direct method argument (e.g. [17]). The eigenvalue constraint on Q gives that $Qp \cdot p - \eta$ is bounded from above, so that $-\ln(Qp \cdot p - \eta)$ is bounded from below. Similarly, the Shannon entropy is bounded from below, so we have a minimising sequence $(f_j)_{j\in\mathbb{N}}$ provided $\mathrm{dom}(F) \neq \emptyset$, which is precisely when $\eta < \frac{2}{3}$ from Lemma 3.2.2. Since $\mathcal{F}(f_j)$ is bounded, this implies that $\int_{\mathbb{S}^2} f_j(p) \ln f_j(p)\, dp$ is bounded, so there exists a subsequence (not relabelled)

which converges weakly in L^1 to some $f^* \in \mathcal{P}(\mathbb{S}^2)$. Finally, $\mathcal{F}$ is $L^1(\mathbb{S}^2)$ weakly lower semicontinuous by Lemma 3.2.4, completing the proof. □

One might hope to find minimisers by taking smooth variations, although the first immediate issue is that if $f \in \mathcal{P}(\mathbb{S}^2)$ is not bounded away from zero, it cannot be guaranteed that an arbitrary variation of the form $f + \epsilon\varphi$ is in the domain of $\mathcal{F}$. Let $\mathcal{P}_+(\mathbb{S}^2) = \left\{ f \in \mathcal{P}(\mathbb{S}^2) : \exists M > 0,\ \frac{1}{M} \leq f(p) \leq M \text{ a.e.} \right\}$ denote the set of probability distributions bounded away from zero and infinity. Note that if $f \in \mathcal{P}_+(\mathbb{S}^2) \cap \mathrm{dom}(\mathcal{F})$, then $v_{\min}(Q) > \eta$, and in particular if $\mathrm{dom}(\mathcal{F}) \cap \mathcal{P}_+(\mathbb{S}^2) \neq \emptyset$, then $\eta < 0$. The converse also holds, since the isotropic state $f_U(p) = \frac{1}{4\pi}$ satisfies $\mathcal{F}(f_U) < +\infty$ if and only if $\eta < 0$. This set is significant because it contains all of the probability distributions where arbitrary variations of the form $f + \epsilon\varphi$ can be taken, with $\varphi \in L^\infty(\mathbb{S}^2)$, $\int_{\mathbb{S}^2} \varphi(p)\, dp = 0$. In particular, with respect to the L^∞ topology, $\mathcal{P}_+(\mathbb{S}^2) \cap \mathrm{dom}(\mathcal{F})$ is open in $\mathcal{P}(\mathbb{S}^2)$.

Proposition 3.2.6. Let $\eta < 0$. The first and second variations of $\mathcal{F}$ about $f \in \mathcal{P}_+ \cap \mathrm{dom}(\mathcal{F})$ are given by

$$\begin{aligned} \delta\mathcal{F}(f)[\phi] &= \int_{\mathbb{S}^2} \phi \ln(f) + \phi - \phi \ln\left(Qp \cdot p - \eta\right) - \frac{fAp \cdot p}{Qp \cdot p - \eta}\, dp, \\ \delta^2\mathcal{F}(f)[\phi, \phi] &= \int_{\mathbb{S}^2} \frac{1}{f} \left(\phi - \frac{fAp \cdot p}{Qp \cdot p - \eta} \right)^2 dp, \end{aligned} \tag{3.24}$$

where $\phi \in L^\infty(\mathbb{S}^2)$, $A = \int_{\mathbb{S}^2} \left(p \otimes p - \frac{1}{3} I \right) \phi(p)\, dp \in \mathrm{Sym}_0(3)$ and $\int_{\mathbb{S}^2} \phi(p)\, dp = 0$.

In particular, $\mathcal{F}$ is convex when restricted to $\mathcal{P}_+(\mathbb{S}^2) \cap \mathrm{dom}(\mathcal{F})$. Furthermore, the first variation of $\mathcal{F}$ vanishes at $f_U = \frac{1}{4\pi}$, and the second variation at f_U is strictly positive if $\eta \neq -\frac{2}{15}$

Proof. Let $\phi \in L^\infty(\mathbb{S}^2)$, with $\int_{\mathbb{S}^2} \phi(p)\, dp = 0$. Denote $A = \int_{\mathbb{S}^2} \phi(p) \left(p \otimes p - \frac{1}{3} I \right) dp$. For readability the p dependence of f, ϕ will be implicit. The variations are readily

calculated as

$$\begin{aligned}
\mathcal{F}(f+\epsilon\phi) &= \int_{\mathbb{S}^2} (f+\epsilon\phi)\ln\left(\frac{(f+\epsilon\phi)}{(Q+\epsilon A)p\cdot p-\eta}\right)\,dp,\\
\frac{d}{d\epsilon}\mathcal{F}(f+\epsilon\phi) &= \int_{\mathbb{S}^2} \phi\ln(f+\epsilon\phi)+\phi-\phi\ln\left((Q+\epsilon A)p\cdot p-\eta\right)\\
&\quad -\frac{(f+\epsilon\phi)Ap\cdot p}{(Q+\epsilon A)p\cdot p-\eta}\,dp,\\
\frac{d^2}{d\epsilon^2}\mathcal{F}(f+\epsilon\phi) &= \int_{\mathbb{S}^2} \frac{\phi^2}{f+\epsilon\phi}-2\frac{\phi Ap\cdot p}{(Q+\epsilon A)\cdot p-\eta}\\
&\quad +\frac{(f+\epsilon\phi)(Ap\cdot p)^2}{((Q+\epsilon A)p\cdot p-\eta)^2}\,dp,\\
\frac{d}{d\epsilon}\mathcal{F}(f+\epsilon\phi)\bigg|_{\epsilon=0} &= \int_{\mathbb{S}^2} \phi\ln(f)+\phi-\phi\ln\left(Qp\cdot p-\eta\right)\\
&\quad -\frac{fAp\cdot p}{Qp\cdot p-\eta}\,dp,\\
\frac{d^2}{d\epsilon^2}\mathcal{F}(f+\epsilon\phi)\bigg|_{\epsilon=0} &= \int_{\mathbb{S}^2} \frac{\phi^2}{f}-\frac{2\phi Ap\cdot p}{Qp\cdot p-\eta}+\frac{f(Ap\cdot p)^2}{(Qp\cdot p-\eta)^2}\,dp\\
&= \int_{\mathbb{S}^2} \frac{1}{f}\left(\phi-\frac{fAp\cdot p}{Qp\cdot p-\eta}\right)^2\,dp.
\end{aligned} \tag{3.25}$$

The convexity of $\mathcal{F}$ on the restricted set then follows since $\mathcal{P}_+(\mathbb{S}^2)$ is convex and open in $\mathrm{dom}(\mathcal{F})$ with respect to the strong $L^\infty(\mathbb{S}^2)$ topology, with positive second variation on its domain. Taking $f(p)=\frac{1}{4\pi}$ gives $Q=0$, and the first variation is

$$\int_{\mathbb{S}^2}\phi(p)\left(1-\ln(4\pi)-\ln(-\eta)\right)\,dp+\frac{1}{3\eta}I\cdot A=0. \tag{3.26}$$

The second variation at $f=f_U$ is then given as

$$4\pi\int_{\mathbb{S}^2}\left(\phi(p)+\frac{1}{4\pi\eta}Ap\cdot p\right)^2\,dp. \tag{3.27}$$

This is strictly positive unless

$$(-4\pi\eta)\phi(p)=Ap\cdot p=\int_{\mathbb{S}^2}\left((p\cdot q)^2-\frac{1}{3}\right)\phi(q)\,dq \tag{3.28}$$

almost everywhere. This eigenvalue problem is implicitly solved in [21], where they establish that the linear operator on the right is, when defined for L^2 complex valued functions, $\frac{8\pi}{15}$ multiplied by the projection onto the set of spherical harmonics of order

two. Hence the eigenvalue problem has only the trivial solution $-4\pi\eta = 0$, at which point f_U is inadmissible, and $-4\pi\eta = \frac{8\pi}{15} \Rightarrow \eta = -\frac{2}{15}$. Therefore the second variation of $\mathcal{F}$ at $f_U = \frac{1}{4\pi}$ is strictly positive unless $\eta = -\frac{2}{15}$ □

While for $\eta < 0$ $\mathcal{F}$ is convex on a subset of its domain, we now show that $\mathcal{F}$ is generally not convex.

Proposition 3.2.7. Let $0 \leq \eta < \frac{2}{3}$. Then the effective domain of $\mathcal{F}$ is not convex and in particular $\mathcal{F}$ itself is not convex.

Proof. Let $f_1 \in \mathcal{P}(\mathbb{S}^2) \cap \mathrm{dom}(\mathcal{F}) \neq \emptyset$. Without loss of generality take its Q-tensor, Q_1, to be diagonal with eigenvalues q_1, q_2, q_3 corresponding to basis vectors e_1, e_2, e_3 respectively. Let f_2, f_3 be defined by rotations acting on f_1, so that their corresponding Q-tensors Q_2 and Q_3 have the same eigenbasis but with permuted eigenvectors. Explicitly, $Q_2 e_i = q_{i+1} e_i$ and $Q_3 e_i = q_{i+2} e_i$, with indices taken modulo 3. In this case, $\frac{1}{3}(Q_1 + Q_2 + Q_3)e_i = \frac{1}{3}(q_1 + q_2 + q_3) = 0$. If the domain of $\mathcal{F}$ were convex, then $\frac{1}{3}(f_1 + f_2 + f_3)$ must have finite energy. However, since the Q-tensor of $\frac{1}{3}(f_1 + f_2 + f_3)$ is zero and $\eta \geq 0$, this implies that $\mathcal{F}\left(\frac{1}{3}(f_1 + f_2 + f_3)\right) = +\infty$, giving a contradiction. □

Proposition 3.2.8. For all $\eta < 0$, the isotropic state is a global minimiser on $\mathcal{P}_+(\mathbb{S}^2) \cap \mathrm{dom}(\mathcal{F})$, and the unique global minimiser on this set if $\eta \neq -\frac{2}{15}$.

Proof. Since $\mathcal{F}$ is convex on the restricted set, which is open in L^∞, and the first variation vanishes, f_U must be a global minimiser. Furthermore, since the second variation is strictly positive for $\eta \neq -\frac{2}{15}$, this implies it is a strict local minimiser, and therefore a unique global minimiser on the restricted set. □

Corollary 3.2.9. Unless $\eta = -\frac{2}{15}$, the only L^∞ local minimiser that can be found by solving

$$\frac{d}{dt}\mathcal{F}(f + t\phi)\bigg|_{t=0} = 0 \tag{3.29}$$

for all $\phi \in L^\infty(\mathbb{S}^2)$ with $\int_{\mathbb{S}^2} \phi(p)\, dp = 0$ is the isotropic state, and only when $\eta < 0$.

Remark 3.2.10. In Corollary 3.2.9 we have seen that support conditions raise difficulties in finding solutions by taking variations and solving

$$\frac{d}{d\epsilon}\mathcal{F}(f^* + \epsilon\phi)\bigg|_{\epsilon=0} = 0. \tag{3.30}$$

Furthermore, Proposition 3.2.7 also states that attempting variational inequalities and finding solutions by considering

$$\frac{d}{d\epsilon}\mathcal{F}((1-\epsilon)f^* + \epsilon f)\bigg|_{\epsilon=0} \geq 0 \tag{3.31}$$

is not generally possible either. Together, these results imply that non-standard techniques will be needed for finding local minimisers.

Proposition 3.2.11. Let $\eta = -\frac{2}{15}$, and V denote the subspace of real valued functions in the span of the second order spherical harmonics. Then if $f = \frac{1+u}{4\pi}$ for $u \in V$, $\inf_{p\in\mathbb{S}^2} u(p) > -1$. We then have $\mathcal{F}(f) = \mathcal{F}(f_u) = \ln\left(\frac{15}{8\pi}\right)$.

Proof. First, since since u integrates to zero and the lower bound, $f \in \mathcal{P}(\mathbb{S}^2)$ and is bounded away from zero. Let Q denote the corresponding Q tensor for f. Then

$$\begin{aligned} Qp\cdot p =& \int_{\mathbb{S}^2}\left((p\cdot q)^2 - \frac{1}{3}\right)\frac{1+u(q)}{4\pi}\,dq \\ =& \frac{1}{4\pi}\int_{\mathbb{S}^2}\left((p\cdot q)^2 - \frac{1}{3}\right)u(q)\,dq \\ =& \frac{2}{15}u(p). \end{aligned} \tag{3.32}$$

Therefore substituting this into the energy,

$$\begin{aligned} \mathcal{F}(f) &= \int_{\mathbb{S}^2} f(p)\ln f(p) - f(p)\ln\left(\frac{2}{15}u(p) + \frac{2}{15}\right)\,dp \\ &= \int_{\mathbb{S}^2} f(p)\ln f(p) - f(p)\ln\left(\frac{8\pi}{15}\frac{1+u(p)}{4\pi}\right)\,dp \\ &= \int_{\mathbb{S}^2} f(p)\ln f(p) - f(p)\ln\left(\frac{8\pi}{15}f(p)\right)\,dp \\ &= \int_{\mathbb{S}^2} f(p)\ln\left(\frac{15}{8\pi}\right)\,dp = \ln\left(\frac{15}{8\pi}\right). \end{aligned} \tag{3.33}$$

□

Remark 3.2.12. The numerical results of [61] suggest that these are not global minimisers of the energy at $\eta = -\frac{2}{15}$.

Corollary 3.2.13. When $\eta = -\frac{2}{15}$, the isotropic state is no longer a strict L^∞-local minimiser, but it is an L^∞- local minimiser.

Proof. From the previous results we have that the second variation is only degenerate for variations in V, which have the same energy as the isotropic state. □

Loosely speaking, the results in this section imply that taking variations to obtain the Euler-Lagrange equation can only find trivial solutions. In particular, when $\eta \in \left[0, \frac{2}{3}\right)$, it cannot provide any results even though minimisers exist. Rather than tackle the full minimisation problem, following the spirit of Section 2.3, the minimisation problem will instead be split into two manageable steps.

3.3 The auxiliary problem and the Euler-Lagrange equation for global minimisers

Given $Q \in \mathcal{Q}$, define

$$A(Q) = \left\{ f \in \mathcal{P}(\mathbb{S}^2) : \int_{\mathbb{S}^2} \left(p \otimes p - \frac{1}{3} I \right) f(p)\, dp = Q \right\} \tag{3.34}$$

to be the admissible set for Q. Then the minimisation problem can be split into

$$\min_{f \in \mathcal{P}(\mathbb{S}^2)} \mathcal{F}(f, \eta) = \min_{Q \in \mathcal{Q}} \left(\min_{f \in A(Q)} \mathcal{F}(f, \eta) \right). \tag{3.35}$$

The interior minimisation problem over $\mathcal{A}(Q)$ will be referred to as the auxiliary problem. Since $\mathcal{F}$ is strictly convex on $\mathcal{A}(Q)$, this problem is much more readily tackled, drawing mainly on results from Borwein and Lewis [12]. Once this simpler problem has been analysed, it remains to consider the finite-dimensional problem of minimising the macroscopic auxiliary function over admissible Q-tensors.

Definition 3.3.1. Define the auxiliary function $J : \mathcal{Q} \times \mathbb{R} \to \mathbb{R} \cup \{+\infty\}$ by

$$J(Q, \eta) = \inf_{f \in A(Q)} \mathcal{F}(f, \eta). \tag{3.36}$$

For fixed η, define the set

$$E_Q = \{ p \in \mathbb{S}^2 : Qp \cdot p > \eta \}. \tag{3.37}$$

Note that if $f \in \mathcal{P}(\mathbb{S}^2)$ with Q-tensor Q and $\mathcal{F}(f) < +\infty$, then $\operatorname{supp}(f) \subset E_Q$. As before, when the dependence of J on η is unambiguous, the dependence will be suppressed so that $J(Q, \eta) = J(Q)$.

Proposition 3.3.2. Let $Q \in \operatorname{dom}(J)$. Then there exists a unique solution to

$\min_{f \in A(Q)} \mathcal{F}(f)$, given by

$$f_Q(p) = \frac{1}{Z} \exp(\Lambda(Q)p \cdot p) \max(Qp \cdot p - \eta, 0) \tag{3.38}$$

for all $p \in \mathbb{S}^2$, where $Z > 0$ is a normalising constant depending on (Q, η), and $\Lambda(Q) \in \mathrm{Sym}_0(3)$ maximises the dual objective function $F : \mathrm{dom}(J) \times \mathrm{Sym}_0(3) \to \mathbb{R}$ given by

$$F(Q, \lambda) = \lambda \cdot Q - \ln \left(\int_{\mathbb{S}^2} \exp(\lambda p \cdot p) \max(Qp \cdot p - \eta, 0)\, dp \right). \tag{3.39}$$

In particular $J(Q) = F(Q, \Lambda(Q)) = \max_{\lambda \in \mathrm{Sym}_0(3)} F(Q, \lambda)$.

Proof. Existence follows by the same argument as Proposition 3.2.5, noting that $A(Q)$ is weakly closed, under the assumption that $Q \in \mathrm{dom}(J)$, which ensures the admissible set is non-empty. Uniqueness follows from the strict convexity of $\mathcal{F}$ when restricted to $A(Q)$. Recall that $\mathrm{supp}(f) \subset E_Q = \{p \in \mathbb{S}^2 : Qp \cdot p > \eta\}$, else the energy is infinite. The minimisation problem can then be written as

$$\begin{aligned} \text{minimise } & \int_{E_Q} f(p) \ln f(p) - f(p) \ln(Qp \cdot p - \eta)\, dp, \\ \text{subject to } 0 \leq & f(p) \text{ a.e.}, \\ 1 = & \int_{E_Q} f(p)\, dp, \\ Q = & \int_{E_Q} f(p) \left(p \otimes p - \frac{1}{3} I \right) dp. \end{aligned} \tag{3.40}$$

Define $\tilde{f}(p) = \frac{1}{Qp \cdot p - \eta} f(p)$ on E_Q. Define the measure μ_Q on E_Q as $d\mu_Q(p) = (Qp \cdot p - \eta) dp$. Then the minimisation problem is equivalent to

$$\begin{aligned} \text{minimise } & \int_{E_Q} \tilde{f}(p) \ln \tilde{f}(p)\, d\mu_Q(p), \\ \text{subject to } 0 \leq & \tilde{f}(p) \text{ a.e.}, \\ 1 = & \int_{E_Q} \tilde{f}(p)\, d\mu_Q(p), \\ Q = & \int_{E_Q} \tilde{f}(p) \left(p \otimes p - \frac{1}{3} I \right) d\mu_Q(p). \end{aligned} \tag{3.41}$$

This is a straightforward entropy minimisation subject to linear constraints, and [12]

can be applied. The only technicality that needs to be addressed for the results of Borwein and Lewis to be applied is that the *pseudo-Haar* condition is satisfied by the constraint functions. By Proposition 2.1.6, since the constraint functions are analytic on the sphere, and the non-null subsets of E_Q with respect to μ_Q are also non-null subsets with respect to $\mathcal{H}^2$, this is not problematic. The solution is then given by

$$\tilde{f}(p) = \exp(\Lambda(Q)p \cdot p + \alpha^* - 1) \tag{3.42}$$

on E_Q for $\Lambda(Q) \in \mathrm{Sym}_0(3)$ and $\alpha^* \in \mathbb{R}$ that maximise the dual objective function

$$(\lambda, \alpha) \mapsto \lambda \cdot Q + \alpha - \ln\left(\int_{E_Q} \exp(\alpha - 1 + \lambda p \cdot p)\mu_Q(p)\, dp\right). \tag{3.43}$$

Since the objective function is smooth and strictly concave in (λ, α), we can eliminate α by setting the derivative with respect to α to zero, which gives

$$\lambda \cdot Q - \ln\left(\int_{E_Q} \exp(\lambda p \cdot p)\, d\mu_Q(p)\, dp\right), \tag{3.44}$$

which the form given in the statement. Finally, f can be reclaimed from $\tilde{f}$ as

$$f(p) = (Qp \cdot p - \eta)\tilde{f}(p) = \frac{1}{Z}\exp(\Lambda(Q)p \cdot p)(Qp \cdot p - \eta), \tag{3.45}$$

on E_Q with $Z = \exp(1 - \alpha^*)$. Noting that f must be zero when $Qp \cdot p \leq \eta$ provides the form in the statement. □

In general the domain of J will depend on η. For example, it is immediate that $J(0) = +\infty$ if $\eta \geq 0$, but $J(0)$ is finite otherwise by taking the uniform distribution $p \mapsto \frac{1}{4\pi}$. The domain can fortunately be explicitly determined. The key step is to establish that $J(Q)$ is finite if and only if Q lives in a particular convex set depending on itself, which admits an explicit representation in terms of supporting hyperplanes. First we include a lemma necessary for the proof.

Lemma 3.3.3. Let $A \in \mathrm{Sym}_0(3) \cap \mathrm{Diag}(3)$, $R_{e_i}(\theta)$ denote the rotation about basis vector e_i by angle θ and $p_i \in \mathbb{S}^2$. Then j, k can be chosen so that $\{i, j, k\} = \{1, 2, 3\}$ and

$$\frac{d}{d\theta} AR_{e_i}(\theta)p \cdot R_{e_i}(\theta)p\Big|_{\theta=0} = (A_{kk} - A_{jj})p_k p_j, \tag{3.46}$$

Proof. First note that

$$\begin{aligned}\frac{d}{d\theta}AR_{e_i}(\theta)p\cdot R_{e_i}(\theta)p\Big|_{\theta=0} &= A\frac{dR_{e_i}(\theta)}{d\theta}p\cdot R_{e_i}(\theta)p + AR_{e_i}(\theta)p\cdot\frac{dR_{e_i}(\theta)}{d\theta}p\Big|_{\theta=0}\\ &= 2A\frac{dR_{e_i}(\theta)}{d\theta}p\cdot R_{e_i}(\theta)p\Big|_{\theta=0}\\ &= 2A\frac{dR_{e_i}(\theta)}{d\theta}p\cdot p\Big|_{\theta=0}\end{aligned} \tag{3.47}$$

Represent the rotation about e_i by angle θ as

$$R = e_i\otimes e_i + \cos(\theta)(e_j\otimes e_j + e_k\otimes e_k) + \sin(\theta)(e_j\otimes e_k - e_k\otimes e_j), \tag{3.48}$$

for $\{i,j,k\} = \{1,2,3\}$. Then

$$\begin{aligned}\frac{dR_{e_i}(\theta)}{d\theta} &= -\sin(\theta)(e_j\otimes e_j + e_k\otimes e_k) + \cos(\theta)(e_j\otimes e_k - e_k\otimes e_j)\\ \Rightarrow \frac{dR_{e_i}(\theta)}{d\theta}\Big|_{\theta=0} &= (e_j\otimes e_k - e_k\otimes e_j)\\ \Rightarrow \frac{dR_{e_i}(\theta)}{d\theta}\Big|_{\theta=0}p &= p_je_k - p_ke_j\\ \Rightarrow A\,\frac{dR_{e_i}(\theta)}{d\theta}\Big|_{\theta=0}p &= A_{kk}p_je_k - A_{jj}p_ke_j\\ \Rightarrow A\,\frac{dR_{e_i}(\theta)}{d\theta}\Big|_{\theta=0}p\cdot p &= A_{kk}p_jp_k - A_{jj}p_kp_j = (A_{kk}-A_{jj})p_kp_j\end{aligned} \tag{3.49}$$

□

Proposition 3.3.4. The domain of J is given by $\mathcal{Q}\cap\{Q\in\mathrm{Sym}_0(3) : |Q|^2 > \eta\}$. In particular, $\mathrm{dom}(J)$ is open.

Proof. Given $Q\in\mathcal{Q}$, taken without loss of generality to be in its diagonal frame, define

$$\mathcal{Q}_Q = \left\{\int_{E_Q}\left(p\otimes p - \frac{1}{3}I\right)f(p)\,d\mu_Q(p) : f\in\mathcal{P}(E_Q;\mu_Q)\right\}\cap\mathrm{Diag}(3), \tag{3.50}$$

where $\mathcal{P}(E_Q;\mu_Q)$ explicitly denotes that integration is with respect to μ_Q as given in Proposition 3.3.2. Using the results of Borwein and Lewis [12] and the equivalent minimisation problem given in (3.41), $J(Q) < +\infty$ if and only if $Q\in\mathcal{Q}_Q$. By

Theorem 2.1.10, $\mathcal{Q}_Q$ is an open, convex set and we have $Q_0 \in \mathrm{Sym}_0(3) \cap \mathrm{Diag}(3)$ with $Q_0 \in \mathcal{Q}_Q$ if and only if, for all $A \in \mathrm{Sym}_0(3) \cap \mathrm{Diag}(3) \setminus \{0\}$,

$$A \cdot Q_0 < \sup_{p \in E_Q} Ap \cdot p. \tag{3.51}$$

If $Q \in \mathrm{dom}(J)$ then $Q \in \mathcal{Q}$, so the eigenvalue constraint must be satisfied. By taking $A = -Q$ this implies that

$$(-Q) \cdot Q < \sup_{p \in E_Q} (-Q)p \cdot p = -\eta + \sup_{p \in E_Q} (\eta - Qp \cdot p)\, dp \leq -\eta, \tag{3.52}$$

so multiplying both sides by -1 gives that $|Q|^2 > \eta$.

Now assume that $|Q|^2 > \eta$ and $v_{\min}(Q) > -\frac{1}{3}$, and take $A \in \mathrm{Sym}_0(3) \cap \mathrm{Diag}(3) \setminus \{0\}$. Then the aim is to show that there exists $p \in E_Q$ so that $Q \cdot A < Ap \cdot p$. Rather than finding some p satisfying the strict inequality, some $p \in E_Q$ will be found so that equality holds, and then a perturbation argument will be used to show that such a p is not a maximiser of $Ap \cdot p$.

Take p^* to be given componentwise by $p_i^* = \sqrt{v_i(Q) + \frac{1}{3}}$, where $v_i(Q)$ is the eigenvalue of Q corresponding to e_i. Note that the eigenvalue constraint on Q gives that this is well defined, and the tracelessness condition gives that $|p^*|^2 = 1$. It remains to be verified that $p^* \in E_Q$, which holds since

$$Qp^* \cdot p^* = \sum_{i=1}^{3} v_i(Q) \sqrt{v_i(Q) + \frac{1}{3}}^2 = \sum_{i=1}^{3} v_i(Q)^2 + \frac{v_i(Q)}{3} = |Q|^2 > \eta. \tag{3.53}$$

Finally, the desired equality holds since

$$Q \cdot A = \sum_{l=1}^{3} Q_{ll} A_{ll} = \sum_{l=1}^{3} (p_l^*)^2 A_{ll} = Ap^* \cdot p^*. \tag{3.54}$$

If it can then be shown that p^* is not a maximum of $p \mapsto Ap \cdot p$ on E_Q, then the result is proven. Since p^* is in E_Q, which is open in $\mathbb{S}^2$, a perturbation argument can be used. As in Lemma 3.3.3, let $R_{e_i}(\theta)$ denote the rotation about basis vector e_i by angle θ. Since $R_{e_i}(\theta)$ is continuous in θ, this means that $R_{e_i}(\theta)p^* \to p^*$ as $\theta \to 0$. If p^* were a maximum of $p \to Ap \cdot p$ on the open set E_Q, for each choice of $\{i, j, k\} = \{1, 2, 3\}$ we would have

$$0 = \frac{d}{d\theta}\bigg|_{\theta=0} AR_{e_i}(\theta)p^* \cdot R_{e_i}(\theta)p^* = \sqrt{v_j(Q) + \frac{1}{3}} \sqrt{v_k(Q) + \frac{1}{3}} (A_{jj} - A_{kk}) \tag{3.55}$$

Since $p_i^* \neq 0$ for all i due to the eigenvalue constraint on Q, this implies that $A_{jj} - A_{kk} = 0$ for all $j \neq k$, which since A is traceless and diagonal implies that $A = 0$, a contradiction. □

Proposition 3.3.5. *J is convex on the set $\{Q \in \mathrm{dom}(J) : v_{\min}(Q) > \eta\}$.*

Proof. If $v_{\min}(Q) > \eta$, then $Qp \cdot p - \eta > 0$ for all $p \in \mathbb{S}^2$, and $E_Q = \mathbb{S}^2$. For such Q,

$$\begin{aligned} J(Q) &= \max_{\lambda \in \mathrm{Sym}_0(3)} \lambda \cdot Q - \ln\left(\int_{\mathbb{S}^2} \exp(\lambda p \cdot p)(Qp \cdot p - \eta)\, dp\right) \\ &= \max_{\lambda \in \mathrm{Sym}_0(3)} \lambda \cdot Q - \ln\left(Q \cdot \int_{\mathbb{S}^2} \exp(\lambda p \cdot p) p \otimes p\, dp - \eta \int_{\mathbb{S}^2} \exp(\lambda p \cdot p)\, dp\right). \end{aligned} \tag{3.56}$$

By writing it this way, it is clear that J can be written as the maximum of a set of convex functions, which follows immediately from the convexity of the negative logarithm. Therefore J is convex. □

Proposition 3.3.6 (Uniform blow up of J)**.** *For $Q \in \mathrm{dom}(J)$, $J(Q) \geq \psi_s(Q) - \ln(|Q|^2 - \eta)$, where ψ_s is the Ball-Majumdar singular potential [8] given by*

$$\psi_s(Q) = \min_{f \in \mathcal{A}(Q)} \int_{\mathbb{S}^2} f(p) \ln f(p)\, dp. \tag{3.57}$$

In particular, J blows up to $+\infty$ uniformly at the boundary of its domain.

Proof. Using Jensen's inequality,

$$\begin{aligned} \min_{f \in A(Q)} \mathcal{F}(f) &= \min_{f \in A(Q)} \int_{\mathbb{S}^2} f(p) \ln f(p) - f(p) \ln(Qp \cdot p - \eta)\, dp \\ &\geq \min_{f \in A(Q)} \int_{\mathbb{S}^2} f(p) \ln f(p) - f(p)\, dp - \ln\left(\int_{\mathbb{S}^2} (Qp \cdot p - \eta) f(p)\, dp\right) \\ &= \min_{f \in A(Q)} \int_{\mathbb{S}^2} f(p) \ln f(p)\, dp - \ln(|Q|^2 - \eta) \\ &= \psi_s(Q) - \ln(|Q|^2 - \eta). \end{aligned} \tag{3.58}$$

If $Q_j \to \partial\mathrm{dom}(J)$, then this means either $v_{\min}(Q) \to -\frac{1}{3}$, in which case $\psi_s(Q_j) \to +\infty$ [8], or $|Q_j|^2 \to \eta$, in which case the logarithmic term blows up. □

This blow up of J at the boundary of its domain serves to ensure that minimising sequences cannot be lost at the boundary. More precisely, if $J(Q_j) \to \min_{Q \in \mathcal{Q}} J(Q)$, then we must have some $\delta > 0$ so that $\mathrm{dist}(Q_j, \partial\mathrm{dom}(J)) > \delta$ for all j. Furthermore,

combining this with the continuity of J which will be given in Proposition 3.3.18, this gives that the sublevel sets $J^{-1}((-\infty, M])$ for $M \in \mathbb{R}$ are compact.

Proposition 3.3.7. Λ is a frame-indifferent function of Q, and if $e \in \mathbb{S}^2$ is an eigenvector of $Q \in \mathrm{dom}(J)$, then e is an eigenvector of the corresponding maximiser of the dual problem $\Lambda(Q)$, and the converse holds if $\Lambda(Q) \neq 0$.

Proof. By writing the dual objective function as

$$F(Q, \lambda) = \lambda \cdot Q - \ln\left(\int_{\mathbb{S}^2} \exp(\lambda p \cdot p) \max(Qp \cdot p - \eta, 0)\, dp\right), \tag{3.59}$$

it is immediate that F is frame indifferent, so that for all $R \in \mathrm{SO}(3)$, $F(RQR^T, R\lambda R^T) = F(Q, \lambda)$. In particular, combined with the uniqueness of maximisers, implies that $\Lambda(RQR^T) = R\Lambda(Q)R^T$. Since Λ is frame indifferent, it can be written as $\Lambda(Q) = \sum_{i=0}^{3} g_i(Q)Q^i$, with g_i scalar-valued frame-indifferent functions of Q, so that if e is an eigenvector of Q, e must be an eigenvector of $\Lambda(Q)$. since $\mathrm{Tr}(\Lambda(Q)) = 0$, this implies that the decomposition can be written as $\Lambda(Q) = g_2(Q)\left(Q^2 - \frac{|Q|^2}{3}I\right) + g_0(Q)Q$. Both terms in the sum have exactly the same eigenbasis as Q unless they are zero. □

Remark 3.3.8. The previous result leaves the possibility that $\Lambda(Q)$ may have eigenvectors that Q does not if $\Lambda(Q) = 0$. By considering the example when $\eta = -\frac{2}{15}$ in Proposition 3.2.11, there are constructed examples such that $Q \neq 0$, but $\Lambda(Q) = 0$ which demonstrate that $\Lambda(Q)$ can have eigenvectors that Q does not. However, if $\Lambda(Q)$ is uniaxial and non-zero, then Q must be uniaxial and non-zero also.

Corollary 3.3.9. If f_Q is the optimal energy distribution corresponding to Q, then for all $R \in \mathrm{SO}(3)$, $f_{RQR^T}(p) = f_Q(Rp)$. In particular, if $RQR^T = Q$, then $f_Q(Rp) = f_Q(p)$. Furthermore J is frame indifferent so that $J(RQR^T) = J(Q)$.

Proof. This follows immediately since f_Q can be written as

$$f_Q(p) = \frac{1}{Z}\exp(\Lambda(Q)p \cdot p)\max(Qp \cdot p - \eta, 0). \tag{3.60}$$

Frame indifference of J then follows since if $[Rf](p) = f(Rp)$, then $J(RQR^T) = \mathcal{F}(f_{RQR^T}) = \mathcal{F}([Rf_Q]) = \mathcal{F}(f_Q) = J(Q)$, using that $\mathcal{F}$ is frame indifferent. □

At face-value, the dual maximisation problem $\max_{\lambda \in \mathrm{Sym}_0(3)} F(Q, \lambda)$ is over a five-dimensional vector space. However by fixing Q in its diagonal frame and using the previous results, it is therefore possible to only consider λ in the same diagonal frame.

In particular, the maximisation is only over a two-dimensional vector space, which is advantageous if one wishes to calculate J numerically via the dual optimisation problem.

In order to establish smoothness properties of J, the first step will be to establish smoothness of the map $\Lambda : \mathrm{dom}(J) \to \mathrm{Sym}_0(3)$. This will be done using an implicit function theorem argument on the relation

$$0 = G(Q, \Lambda(Q)) = Q - \frac{\int_{E_Q} \exp(\Lambda(Q)p \cdot p)(Qp \cdot p - \eta)\left(p \otimes p - \frac{1}{3}I\right)\, dp}{\int_{E_Q} \exp(\Lambda(Q)p \cdot p)(Qp \cdot p - \eta)\, dp}. \tag{3.61}$$

Before the implicit function theorem can be used, it must first be established that G is C^1 on $\mathrm{dom}(J) \times \mathrm{Sym}_0(3)$. We can illustrate the techniques required in a simpler setting in order to establish stronger regularity results on the set $\{Q \in \mathcal{Q} : v_{\min}(Q) > \eta\}$. For the following, we take Λ, J to depend explicitly on η also.

Proposition 3.3.10. Λ and J are C^∞ on $\{(Q, \eta) \in \mathcal{Q} \times \mathbb{R} : |Q|^2 > \eta\,, Q \in \mathcal{Q} : v_{\min}(Q) > \eta\}$.

Proof. First note that that on $\mathrm{dom}(J) \cap \{Q \in \mathcal{Q} : v_{\min}(Q) > \eta\}$, $E_Q = \mathbb{S}^2$, and $Q, \Lambda(Q)$ are related by

$$0 = Q - \frac{1}{\int_{\mathbb{S}^2} \exp(\Lambda p \cdot p)(Qp \cdot p - \eta)\, dp} \int_{\mathbb{S}^2} \exp(\Lambda p \cdot p)(Qp \cdot p - \eta)\left(p \otimes p - \frac{1}{3}I\right) dp. \tag{3.62}$$

Since there is no issue with the domain of integration, and the integrand is C^∞, this then gives that G is C^∞ for $Q, \Lambda(Q)$ in the given subdomain. The derivative of G with respect to λ at $(Q, \Lambda(Q))$ is given by

$$\int_{\mathbb{S}^2} \left(p \otimes p - \frac{1}{3}I\right) \otimes \left(p \otimes p - \frac{1}{3}I\right) f_Q(p)\, dp - Q \otimes Q, \tag{3.63}$$

which is strictly positive definite by Cauchy-Schwarz and the fact that the linearly independent components of $p \otimes p - \frac{1}{3}$ and the constant function form a pseudo-Haar set. Therefore the implicit function theorem gives that Λ is a C^∞ function of Q. Using that $J(Q) = F(Q, \Lambda(Q))$, where F is also C^∞ on the given subdomain implies that J is a C^∞ function of Q too. □

Next we turn to the C^1 regularity of J on its entire domain. Similarly to before, the main ingredient will be the regularity of the function $G : \mathrm{dom}(J) \times \mathrm{Sym}_0(3) \times \mathbb{R} \to$

$\mathrm{Sym}_0(3)$ defined by

$$\begin{aligned} &G(Q,\lambda,\eta) \\ =&Q - \left(\int_{E_Q} \exp(\lambda p\cdot p)(Qp\cdot p-\eta)\,dp\right)^{-1} \int_{E_Q} \exp(\lambda p\cdot p)(Qp\cdot p-\eta)\left(p\otimes p-\frac{1}{3}I\right)\,dp. \end{aligned} \tag{3.64}$$

Due to the dependence of the domain of integration on Q, it is less clear how regular G is as a function of Q. Heuristically, the integrand vanishing on ∂E_Q avoids difficulties up to C^1 regularity. We proceed by showing that functions $g : \mathrm{dom}(J) \times \mathrm{Sym}_0(3) \times\mathbb{R} \to V$, where V is a real vector space, given by

$$g(Q,\lambda,\eta) = \int_{E_Q} h(Q,\lambda,p)(Qp\cdot p-\eta)\,dp, \tag{3.65}$$

are C^1 under appropriate assumptions on h. Rather than turn to a proof based in differential geometry, the method we will use to demonstrate this is to consider instead approximations

$$g_\epsilon(Q,\lambda) = \int_{\mathbb{S}^2} h(Q,\lambda,p)\varphi_\epsilon(Qp\cdot p-\eta)(Qp\cdot p-\eta)\,dp, \tag{3.66}$$

where $\varphi_\epsilon(x) \to \max(x,0)$, $\varphi_\epsilon'(x) \to \chi_{(0,+\infty)}(x)$ and $\varphi_\epsilon \in C^1(\mathbb{R},(0,+\infty))$. The challenge is that the convergence of φ_ϵ cannot be in C^1 norm. We will have to permit the convergence to be non-uniform at $x=0$, and then show that this is not problematic since the size of the set where $Qp\cdot p \approx \eta$ can be controlled in a uniform way. More precisely, it will be shown that for all compact $K \subset \{(Q,\eta)\in\mathcal{Q}\times\mathbb{R} : |Q|^2 > \eta\}$,

$$\limsup_{t\to 0^+} \sup_{(Q,\eta)\in K} \mathcal{H}^2(\{p\in\mathbb{S}^2 : |Qp\cdot p-\eta|<t\}) = 0, \tag{3.67}$$

and that this allows us to prove that g_ϵ has a limit with the C^1_{loc} topology. The limit is then shown to be g as expected, providing the necessary result.

Lemma 3.3.11. Let $K \subset \{(Q,\eta)\in\mathcal{Q}\times\mathbb{R} : |Q|^2>\eta\}$ be compact. Then

$$\limsup_{t\to 0^+} \sup_{(Q,\eta)\in K} \mathcal{H}^2(\{p\in\mathbb{S}^2 : |Qp\cdot p-\eta|<t\}) = 0. \tag{3.68}$$

Proof. Take $t_j \to 0$ and $(Q_j, \eta_j) \in K$ so that

$$\lim_{j\to\infty} \mathcal{H}^2(\{p \in \mathbb{S}^2 : |Q_j p \cdot p - \eta_j| < t_j\}) = \limsup_{t\to 0^+} \sup_{Q\in K} \mathcal{H}^2(\{p \in \mathbb{S}^2 : |Qp \cdot p - \eta| < t\}). \tag{3.69}$$

Take a subsequence, not relabelled, so that $t_j \searrow t$, $(Q_j, \eta_j) \to (Q, \eta) \in K$, and $\sup_{p\in\mathbb{S}^2} |(Q_j - Q)p \cdot p + \eta_j - \eta| \searrow 0$. Note that $(Q, \eta) \neq (0, 0)$ since K is compact. Let $p \in \{q \in \mathbb{S}^2 : |Q_j p \cdot p - \eta_j| < t_j\}$. Then

$$\begin{aligned} t_j >& |Q_j p \cdot p - \eta_j| \\ =& |Q_j p \cdot p - \eta + (Q - Q_j)p \cdot p + (\eta - \eta_j)| \\ \geq& \, ||Qp \cdot p - \eta| - |(Q - Q_j)p \cdot p + \eta - \eta_j|| \end{aligned} \tag{3.70}$$

so that $\delta_j = t_j + \sup_{q\in\mathbb{S}^2} |(Q_j - Q)q \cdot q + \eta_j - \eta| \geq |Qp \cdot p - \eta|$ and $\delta_j \searrow 0$. Therefore using that the sets $\{p \in \mathbb{S}^2 : |Qp \cdot p - \eta| < \delta_j\}$ are nested in j,

$$\begin{aligned} &\limsup_{t\to 0^+} \sup_{(Q,\eta)\in K} \mathcal{H}^2(\{p \in \mathbb{S}^2 : |Qp \cdot p - \eta| < t\}) \\ =& \lim_{j\to\infty} \mathcal{H}^2(\{p \in \mathbb{S}^2 : |Q_j p \cdot p - \eta_j| < t_j\}) \\ \leq& \lim_{j\to\infty} \mathcal{H}^2\left(\{p \in \mathbb{S}^2 : |Qp \cdot p - \eta| < \delta_j\}\right) \\ =& \mathcal{H}^2\left(\bigcap_{j=1}^{\infty} \{p \in \mathbb{S}^2 : |Qp \cdot p - \eta| < \delta_j\}\right) \\ =& \mathcal{H}^2\left(\{p \in \mathbb{S}^2 : Qp \cdot p = \eta\}\right) = 0, \end{aligned} \tag{3.71}$$

since $(Q, \eta) \neq (0, 0)$ using the pseudo-Haar condition. □

Let $\varphi_\epsilon : \mathbb{R} \to \mathbb{R}$ be so that $\varphi_\epsilon(x) \to \max(x, 0) = \varphi_0(x)$ in $L^\infty_{\text{loc}}(\mathbb{R})$, $\varphi'_\epsilon(x) \to \chi_{(0,\infty)}(x) = \varphi_0(x)$ in $L^\infty_{\text{loc}}(\mathbb{R} \setminus \{0\})$. and $||\varphi'_\epsilon||_{K',\infty}$ is bounded independently of $\epsilon > 0$ on compact subsets K' of $\mathbb{R}$. The example to have in mind is

$$\varphi_\epsilon(x) = \epsilon \int_{-\infty}^{\frac{x}{\epsilon}} \frac{\operatorname{erf}(x) + 1}{2}\, dx. \tag{3.72}$$

Let $\mathcal{A} = \{(Q, \lambda, \eta) \in \mathcal{Q} \times \operatorname{Sym}_0(3) \times \mathbb{R} : |Q|^2 > \eta\}$.

Proposition 3.3.12. Let $h : \mathcal{Q} \times \operatorname{Sym}_0(3) \times \mathbb{S}^2 \to \mathbb{R}^k$ be continuous. Then for all

$K \subset\subset \mathcal{A}$,

$$\int_{\mathbb{S}^2} h(Q,\lambda,p)\varphi_\epsilon(Qp\cdot p-\eta)\,dp \to \int_{E_Q} h(Q,\lambda,p)(Qp\cdot p-\eta)\,dp \tag{3.73}$$

uniformly on K.

Proof. The result is immediate using that h is continuous so can be bounded independently of Q,λ and p, and that $\varphi_\epsilon \to \varphi_0$ uniformly. □

Proposition 3.3.13. Let $h : \mathcal{Q}\times \mathrm{Sym}_0(3)\times\mathbb{S}^2 \to \mathbb{R}^k$. Then for all $K\subset\subset\mathcal{A}$,

$$\int_{\mathbb{S}^2} h(Q,\lambda,p)\varphi'_\epsilon(Qp\cdot p-\eta)\,dp \to \int_{E_Q} h(Q,\lambda,p)\,dp \tag{3.74}$$

uniformly on K.

Proof. Let $M^+_{Q,\eta,\delta} = \{p\in\mathbb{S}^2 : |Qp\cdot p-\eta|\geq\delta\}$ and $M^-_{Q,\eta,\delta}$ denote its complement. Then

$$\begin{aligned}
&\left|\int_{\mathbb{S}^2} h(Q,\lambda,p)\varphi'_\epsilon(Qp\cdot p-\eta)\,dp - \int_{E_Q} h(Q,\lambda,p)\,dp\right| \\
=&\left|\int_{\mathbb{S}^2} h(Q,\lambda,p)\varphi'_\epsilon(Qp\cdot p-\eta)\,dp - \varphi'_0(Qp\cdot p-\eta)h(Q,\lambda,p)\,dp\right| \\
\leq&\left|\int_{M^+_{Q,\eta,\delta}} h(Q,\lambda,p)(\varphi'_\epsilon(Qp\cdot p-\eta)-\varphi'_0(Qp\cdot p-\eta)\,dp\right| \\
&+\left|\int_{M^-_{Q,\eta,\delta}} h(Q,\lambda,p)(\varphi'_\epsilon(Qp\cdot p-\eta)-\varphi'_0(Qp\cdot p-\eta)\,dp\right|.
\end{aligned} \tag{3.75}$$

Since h is continuous and $(Q,\lambda,\eta)\in K$, the L^∞ norm, denoted $||h||_{K,\infty}$, can be pulled out, to give

$$\begin{aligned}
&\left|\int_{\mathbb{S}^2} h(Q,\lambda,p)\varphi'_\epsilon(Qp\cdot p-\eta)\,dp - \int_{E_Q} h(Q,\lambda,p)\,dp\right| \\
\leq&||h||_{K,\infty}\left(\int_{M^+_{Q,\eta,\delta}} |\varphi'_\epsilon(Qp\cdot p-\eta)-\varphi'_0(Qp\cdot p-\eta)|\,dp\right. \\
&\left.+\int_{M^-_{Q,\eta,\delta}} |\varphi'_\epsilon(Qp\cdot p-\eta)-\varphi'_0(Qp\cdot p-\eta)|\,dp\right) \\
\leq&||h||_{K,\infty}\left(4\pi||\varphi'_\epsilon-\varphi'_0||_{[-L,\delta]\cup[\delta,L],\infty}+\mathcal{H}^2(M^-_{Q,\eta,\delta})||\varphi'_\epsilon-\varphi'_0||_{(-\delta,\delta),\infty}\right)
\end{aligned} \tag{3.76}$$

for sufficiently large $L > 0$. Since $\varphi'_\epsilon \to \varphi'_0$ uniformly on compact sets not containing the origin by assumption, the left-hand term tends to zero. By Lemma 3.3.11 $\mathcal{H}^2(M^-_{Q,\eta,\delta})$ tends to zero and $||\varphi'_\epsilon - \varphi'_0||_{(-\delta,\delta),\infty}$ remains bounded, so the right-hand term tends to zero also. □

Proposition 3.3.14. Let $h : \mathcal{Q} \times \mathrm{Sym}_0(3) \times \mathbb{S}^2 \to \mathbb{R}^k$ be C^1 in its first two variables, with all derivatives continuous on the entire domain. Let $g_\epsilon : \mathcal{A} \to \mathbb{R}^k$ be given by

$$g_\epsilon(Q, \lambda, \eta) = \int_{\mathbb{S}^2} \varphi_\epsilon(Qp \cdot p - \eta) h(Q, \lambda, p)\, dp. \tag{3.77}$$

Then for all $K \subset\subset \mathcal{A}$,

$$\begin{aligned}
g_\epsilon(Q, \lambda, \eta) &\overset{\text{uni.}}{\to} \int_{E_Q} (Qp \cdot p - \eta) h(Q, \lambda, p)\, dp \\
\frac{\partial g_\epsilon}{\partial Q}(Q, \lambda, \eta) &\overset{\text{uni.}}{\to} \int_{E_Q} (Qp \cdot p - \eta) \frac{\partial h}{\partial Q}(Q, \lambda, p) + h(Q, \lambda, p) \left(p \otimes p - \frac{1}{3} I \right) dp \\
\frac{\partial g_\epsilon}{\partial \lambda}(Q, \lambda, \eta) &\overset{\text{uni.}}{\to} \int_{E_Q} (Qp \cdot p - \eta) \frac{\partial h}{\partial \lambda}(Q, \lambda, p) \\
\frac{\partial g_\epsilon}{\partial \eta}(Q, \lambda, \eta) &\overset{\text{uni.}}{\to} - \int_{E_Q} h(Q, \lambda, p)\, dp
\end{aligned} \tag{3.78}$$

Proof. Since φ_ϵ and h are C^1 we can exchange derivatives in g_ϵ with ease. We show only the result for $\frac{\partial g_\epsilon}{\partial Q}$ as an example, with the rest following by the same method.

$$\begin{aligned}
\frac{\partial g_\epsilon}{\partial Q}(Q, \lambda, \eta) =& \frac{\partial}{\partial Q} \int_{\mathbb{S}^2} h(Q, \lambda, p) \varphi_\epsilon(Qp \cdot p - \eta)\, dp \\
=& \int_{\mathbb{S}^2} \frac{\partial h}{\partial Q}(Q, \lambda, p) \varphi_\epsilon(Qp \cdot p - \eta) \\
&+ h(Q, \lambda, p) \varphi'_\epsilon(Qp \cdot p - \eta) \left(p \otimes p - \frac{1}{3} I \right) dp.
\end{aligned} \tag{3.79}$$

Using Proposition 3.3.12 for the left-hand term and Proposition 3.3.13 for the right-hand term, on K this converges uniformly to

$$\int_{E_Q} \frac{\partial h}{\partial Q}(Q, \lambda, p)(Qp \cdot p - \eta)\, dp + h(Q, \lambda, p) \left(p \otimes p - \frac{1}{3} I \right) dp. \tag{3.80}$$

□

Corollary 3.3.15. Let $h : \mathcal{Q} \times \mathrm{Sym}_0(3) \times \mathbb{S}^2 \to \mathbb{R}^k$, C^1 in its first two variables with

all derivatives continuous. Then $g : \mathcal{A} \to \mathbb{R}^k$ given by

$$g(Q, \lambda, \eta) = \int_{E_Q} (Qp \cdot p - \eta) h(Q, \lambda, p)\, dp \tag{3.81}$$

is C^1, with

$$\begin{aligned}
\frac{\partial g}{\partial Q}(Q, \lambda, \eta) &= \int_{E_Q} (Qp \cdot p - \eta) \frac{\partial h}{\partial Q}(Q, \lambda, p) + h(Q, \lambda, p) \left(p \otimes p - \frac{1}{3} I \right) dp \\
\frac{\partial g}{\partial \lambda}(Q, \lambda, \eta) &= \int_{E_Q} (Qp \cdot p - \eta) \frac{\partial h}{\partial \lambda}(Q, \lambda, p) \\
\frac{\partial g}{\partial \eta}(Q, \lambda, \eta) &= - \int_{E_Q} h(Q, \lambda, p)\, dp
\end{aligned} \tag{3.82}$$

Proof. Using Proposition 3.3.14, we have that on all compact subsets of $\mathcal{A}$, g_ϵ is a Cauchy sequence in C^1, and $g_\epsilon \to g$ in C^0_{loc}, therefore $g \in C^1$, and its derivatives are given by the locally uniform limits of the derivatives of g. □

Proposition 3.3.16. Λ is a C^1 function of (Q, η) on $\{(Q, \eta) \in \mathcal{Q} \times \mathbb{R} : |Q|^2 > \eta\}$.

Proof. For notational brevity, let $\Lambda = \Lambda(Q, \eta)$ when unambiguous. For each $Q \in \{(Q, \eta) \in \mathcal{Q} \times \mathbb{R} : |Q|^2 > \eta\}$, $\Lambda(Q, \eta)$ is uniquely determined, so being globally ill defined is not an issue. The argument will only be needed to show that the map is C^1. To see this, note that

$$\begin{aligned}
0 =& G(Q, \Lambda, \eta) \\
=& Q - \frac{1}{\int_{E_Q} \exp(\Lambda p \cdot p)(Qp \cdot p - \eta)\, dp} \int_{E_Q} \exp(\Lambda p \cdot p)(Qp \cdot p - \eta) \left(p \otimes p - \frac{1}{3} I \right) dp
\end{aligned} \tag{3.83}$$

for all $Q, \Lambda(Q, \eta), \eta$. In particular, note that both terms in the quotient are C^1 in (Q, Λ, η) by Corollary 3.3.15, so that G is C^1. The invertibility of $\frac{\partial G}{\partial \Lambda}$ comes from Equation (3.63) at (Q, Λ, η), with $f_Q(p) = \frac{1}{Z} \exp(\Lambda p \cdot p) \max(Qp \cdot p - \eta, 0)$ as before. If $A \in \text{Sym}_0(3)$ then

$$\frac{\partial G}{\partial \Lambda}(Q, \lambda) A \cdot A = \int_{\mathbb{S}^2} (Ap \cdot p)^2 f_Q(p)\, dp - \left(\int_{\mathbb{S}^2} Ap \cdot p f_Q(p)\, dp \right)^2, \tag{3.84}$$

which by Cauchy-Schwarz is positive unless $Ap \cdot p = 0$ on $\text{supp}(f)$, however this implies that $A = 0$ by the pseudo-Haar condition. Therefore Λ is a C^1 function of (Q, η). □

Corollary 3.3.17. The map from Q to its optimal energy distribution is continuous with respect to the $W^{1,q}(\mathbb{S}^2)$ topology for all $q \in [1, \infty)$, and by extension with respect to $C^\alpha(\mathbb{S}^2)$ for $\alpha < 1$ and $L^q(\mathbb{S}^2)$ for $q \in [1, \infty]$.

Proof. First we show the continuity in $W^{1,q}(\mathbb{S}^2)$, from which the other results will follow. Let $Q \in \mathcal{Q} \cap \mathrm{dom}(J)$. f_Q is C^1 everywhere except where $Qp \cdot p = \eta$, which is a set of zero measure, so it certainly admits a weak derivative. Then using $\nabla_{\mathbb{S}^2}$ to denote the (weak) gradient operator on $\mathbb{S}^2$,

$$\nabla_{\mathbb{S}^2} f_Q(p) = \frac{1}{Z} \exp(\Lambda p \cdot p) \left(\max(Qp \cdot p - \eta,))\Lambda_{\alpha\beta} + \chi_{(0,\infty)}(Qp \cdot p - \eta) Q_{\alpha\beta} \right) \nabla_{\mathbb{S}^2} p_\alpha p_\beta, \tag{3.85}$$

with summation over α, β. Now if $Q_i \to Q$, and $f_{Q_i}(p) = \frac{1}{Z_i} \exp(\Lambda_i p \cdot p) \max(Q_i p \cdot p - \eta, 0)$, then we see that all terms in Equation (3.85) converge uniformly, with the exception of $\chi_{(0,\infty)}(Q_i p \cdot p - \eta)$. It therefore suffices to show that if $Q_i \to Q$, then $\chi_{(0,\infty)}(Q_i p \cdot p - \eta)$ converges to $\chi_{(0,\infty)}(Qp \cdot p - \eta)$ in $L^q(\mathbb{S}^2)$. Since these functions only admit values $0, 1$ however, it suffices to show that the convergence holds in $L^1(\mathbb{S}^2)$. However by taking $h(Q, \lambda, p) = 1$ in Corollary 3.3.15, we see that this holds since the function

$$Q \mapsto \int_{E_Q} dp \tag{3.86}$$

is continuous. Therefore if $Q_i \to Q$, then $f_{Q_i} \to f_Q$ in $W^{1,q}(\mathbb{S}^2)$ for all $q \in [1, \infty)$, and in particular the convergence also holds in $C^\alpha(\mathbb{S}^2)$ for all $\alpha < 1$, and in $L^q(\mathbb{S}^2)$ for all $q \in [1, \infty]$. □

Proposition 3.3.18. J is C^1 on its domain, with its derivatives given by

$$\begin{aligned} \frac{\partial J}{\partial Q} &= \Lambda(Q, \eta) - \int_{E_Q} \frac{f_Q(p)}{Qp \cdot p - \eta} \left(p \otimes p - \frac{1}{3} I \right) dp, \\ \frac{\partial J}{\partial \eta} &= - \int_{E_Q} \frac{f_Q(p)}{Qp \cdot p - \eta} \, dp, \end{aligned} \tag{3.87}$$

where f_Q is the optimal energy distribution for Q.

Proof. Recalling that $J(Q, \eta) = F(Q, \Lambda(Q, \eta), \eta)$, with Λ a C^1 function by Proposition 3.3.16 and F C^1 from Corollary 3.3.15 gives that J is C^1. Since it is known that J and Λ are C^1 functions of Q, it is straightforward to differentiate the expression for J. For brevity denote

$$Z = \int_{E_Q} \exp(\Lambda(Q) p \cdot p)(Qp \cdot p - \eta) \, dp. \tag{3.88}$$

Then the derivatives of J can be found as

$$\begin{aligned}\frac{\partial J}{\partial Q} =&\frac{\partial}{\partial Q}\left(\Lambda\cdot Q-\ln\left(\int_{E_Q}\exp(\Lambda p\cdot p)(Qp\cdot p-\eta)\,dp\right)\right)\\ =&\Lambda-\frac{1}{Z}\int_{E_Q}\exp(\Lambda p\cdot p)\left(p\otimes p-\frac{1}{3}I\right)\,dp\\ &+\frac{\partial\Lambda}{\partial Q}\cdot\frac{\partial}{\partial\Lambda}\left(Q\cdot\Lambda-\int_{E_Q}\exp(\Lambda p\cdot p)(Qp\cdot p-\eta)\,dp\right)\\ =&\Lambda-\int_{E_Q}\frac{f_Q(p)}{Qp\cdot p-\eta}\left(p\otimes p-\frac{1}{3}I\right)\,dp.\end{aligned}\tag{3.89}$$

Note that the derivative with respect to Λ vanishes by the dual optimality condition. By the same argument,

$$\begin{aligned}\frac{\partial J}{\partial\eta} =&\frac{\partial\Lambda}{\partial\eta}\cdot\left(Q-\frac{1}{Z}\int_{E_Q}\exp(\Lambda p\cdot p-\eta)(Qp\cdot p-\eta)\left(p\otimes p-\frac{1}{3}I\right)\,dp\right)\\ &+\frac{1}{Z}\int_{E_Q}\exp(\Lambda p\cdot p)\,dp\\ =&\frac{\partial\Lambda}{\partial\eta}\left(Q-\int_{E_Q}f_Q(p)\left(p\otimes p-\frac{1}{3}I\right)\,dp\right)+\int_{E_Q}\frac{f_Q(p)}{Qp\cdot p-\eta}\,dp\\ =&\int_{E_Q}\frac{f_Q(p)}{Qp\cdot p-\eta}\,dp.\end{aligned}\tag{3.90}$$

□

Theorem 3.3.19. Let $f\in\mathcal{P}(\mathbb{S}^2)$ be a global minimiser for $\mathcal{F}$. Then f satisfies the Euler-Lagrange equation given by

$$\begin{aligned}f(p) =&\frac{1}{Z}\exp(\Lambda p\cdot p)\max(Qp\cdot p-\eta,0),\\ Q =&\int_{\mathbb{S}^2}f(p)\left(p\otimes p-\frac{1}{3}I\right)\,dp,\\ \Lambda =&\int_{\mathbb{S}^2}\frac{f(p)}{Qp\cdot p-\eta}\left(p\otimes p-\frac{1}{3}I\right)\,dp.\end{aligned}\tag{3.91}$$

Furthermore, Q,Λ solve the saddle point problem

$$\min_{Q_0\in\mathrm{dom}(J)}\max_{\lambda\in\mathrm{Sym}_0(3)}Q_0\cdot\lambda-\ln\left(\int_{\mathbb{S}^2}\exp(\lambda p\cdot p)\max(Q_0p\cdot p-\eta,0)\,dp\right),\tag{3.92}$$

and Q satisfies $J(Q)=\min_{Q_0\in\mathcal{Q}}J(Q_0)$.

Proof. From the minimisation decomposition, $\min_{f\in\mathcal{P}(\mathbb{S}^2)} \mathcal{F}(f) = \min_{Q\in\mathcal{Q}} \left(\min_{f\in A(Q)} \mathcal{F}(f) \right) = \min_{Q\in\mathcal{Q}} J(Q)$, first we minimise J. Since $\mathrm{dom}(J)$ is open, and J is C^1 on its domain, this implies that at the global minimiser, $\frac{\partial J}{\partial Q}(Q) = 0$. Therefore

$$\Lambda(Q) - \int_{\mathbb{S}^2} \frac{f_Q(p)}{Qp\cdot p - \eta} \left(p\otimes p - \frac{1}{3} I \right) dp \tag{3.93}$$

is the critical point condition for a global minimiser Q of J. If Q is a minimiser of J, then f_Q must also be a global minimiser of $\mathcal{F}$, and the unique minimiser with corresponding Q-tensor Q by uniqueness of solutions to the auxiliary problem. In particular, this means that f_Q can be written in the form given in the statement. The saddle-point representation is a direct consequence of Proposition 3.3.2. □

Remark 3.3.20. The saddle-point representation of the global minimisation problem is at face-value a 10-dimensional problem. However, from Proposition 3.3.7, it is known that all eigenvectors of the minimising Q are eigenvectors of $\Lambda(Q)$. Therefore using the frame indifference of the energy, it is possible to fix both into the same diagonal frame, leaving only two degrees of freedom each, so that the problem is only four dimensional. Furthermore, using a similar argument to Corollary 3.3.17, if $(Q_0, \lambda_0) \approx (Q^*, \Lambda(Q)^*))$, where Q^* is a true global minimiser of J, then $f_0(p) = \frac{1}{Z}\exp(\lambda_0 p\cdot p)\max(Q_0 p\cdot p - \eta, 0)$ is close in $L^\infty(\mathbb{S}^2)$ to a true global minimiser of $\mathcal{F}$, providing a degree of stability in the approximation. Finally it should be noted that the necessary condition for minimisers given in Theorem 3.3.19 differs only from the vanishing variation condition on $\mathcal{P}_+(\mathbb{S}^2)$ that can be obtained from Proposition 3.2.6 in as far as the support is unknown. This may suggest that the method presented in this work could be equivalent to considering more careful variations, such as solving $\frac{d}{dt}\mathcal{F}(f_t)\big|_{t=0} = 0$ for $f : (-\epsilon, \epsilon) \to \mathcal{P}(\mathbb{S}^2)$ smoothly varying in $\mathrm{dom}(\mathcal{F})$. This will be addressed more thoroughly in Proposition 3.4.7.

We can establish the behaviour of systems as they approach the saturated regime, proving that they achieve perfect order in the appropriate limit. The result requires two ingredients, firstly that we can bound the support of global minimisers onto some small set, and secondly that solutions have even symmetry. First we include a necessary lemma.

Lemma 3.3.21. Let $Q_j \in \mathcal{Q}$, $|Q_j|^2 \to \frac{2}{3}$. Then there exist rotations $R_j \in \mathrm{SO}(3)$ such that $R_j Q_j R_j^T \to \left(e\otimes e - \frac{1}{3}I\right)$ for some unit vector e. In particular, as $\eta \to \frac{2}{3}$

from below, the corresponding minimisers Q_j of J satisfy $Q_j \to e \otimes e - \frac{1}{3}I$ for some $e \in \mathbb{S}^2$ up to rotations.

Proof. First we show that $\frac{2}{3} = \max_{Q \in \overline{\mathcal{Q}}} |Q|^2$, and that if $|Q|^2 = \frac{2}{3}$ for $Q \in \overline{\mathcal{Q}}$, then $Q = e \otimes e - \frac{1}{3}$ for some $e \in \mathbb{S}^2$. Since $\mathcal{Q}$ is a bounded set, there exists at least one maximiser of $|Q|^2$ on $\overline{\mathcal{Q}}$. The maximum cannot be in the interior, since if $Q \in \mathcal{Q}$ then $(1+\epsilon)Q \in \mathcal{Q}$ for small $\epsilon > 0$. Since $Q \in \partial\mathcal{Q}$, at least one eigenvalue of Q must be $-\frac{1}{3}$. This means we can write Q as a diagonal matrix, $Q = D\left(-\frac{1}{3}, a, \frac{1}{3} - a\right)$ for some $a \in \left[-\frac{1}{3}, \frac{2}{3}\right]$. In this case, $|Q|^2 = 2a^2 - \frac{2a}{3} + \frac{1}{9}$. This is a positive quadratic and therefore the maximum must be on the boundary. Either choice $a = -\frac{1}{3}, \frac{2}{3}$ gives the same result up to permuting the eigenvectors that $Q = D\left(-\frac{1}{3}, -\frac{1}{3}, \frac{2}{3}\right)$, with $|Q|^2 = \frac{2}{3}$. Now take $|Q_j|^2 \to \frac{2}{3}$ with $Q_j \in \mathcal{Q}$. Take R_j to be any rotation such that $R_j Q_j R_j^T e = v_{\max}(Q_j)e$. If $R_j Q_j R_j^T$ did not have limit $\left(e \otimes e - \frac{1}{3}I\right)$, then there would be a subsequence (not relabelled) such that $\inf_{e \in \mathbb{S}^2} \left|R_j Q_j R_j^T - e \otimes e - \frac{1}{3}I\right|$ is bounded away from zero, and also $R_j Q_j R_j^T \to Q^*$, up to a subsequence, by compactness. It must then hold that $|Q^*|^2 = \frac{2}{3}$ and $Q^* \in \overline{\mathcal{Q}}$, so $Q^* = e \otimes e - \frac{1}{3}$ for some $e \in \mathbb{S}^2$, contradicting the assumptions. The conclusion that global minimisers must approach $e \otimes e - \frac{1}{3}$, modulo rotations, then holds since $\eta_j < |Q_j|^2 < \frac{2}{3}$. □

Proposition 3.3.22. Let $\eta_j \to \frac{2}{3}$ from below, and f_j be a corresponding global minimiser of $\mathcal{F}$. Given $R \in \mathrm{SO}(3)$ let $[Rf] \in \mathcal{P}(\mathbb{S}^2)$ be given by $[Rf](p) = f(Rp)$. Then there exists rotations R_j such that, $[R_j f_j] \overset{*}{\rightharpoonup} \frac{1}{2}\left(\delta_{e_1} + \delta_{-e_1}\right)$ in $C(\mathbb{S}^2)^*$.

Proof. Let Q_j denote the Q-tensor of f_j. By the Lemma 3.3.21, we take R_j so that $R_j Q_j R_j^T \to e \otimes e - \frac{1}{3}I = Q$ for a given $e \in \mathbb{S}^2$. Using that $R_j Q_j R_j^T p \cdot p - \eta_j$ converges uniformly on $\mathbb{S}^2$ to $Qp \cdot p - \frac{2}{3}$, we have that for a given $\epsilon > 0$ and sufficiently large j, $\mathrm{supp}([R_j f_j]) \subset \left\{p \in \mathbb{S}^2 : Qp \cdot p - \frac{2}{3} > -\epsilon\right\} = U_\epsilon$. Let $g \in C(\mathbb{S}^2)$. Then using that $f_j(p) = f_j(-p)$ for all $p \in \mathbb{S}^2$, this gives that for sufficiently large j,

$$\begin{aligned}\int_{\mathbb{S}^2} [R_j f_j](p) g(p)\, dp &= \frac{1}{2}\int_{\mathbb{S}^2} f_j(R_j p)\left(g(p) + g(-p)\right)\, dp \\ &= \int_{U_\epsilon} f_j(R_j p)\frac{g(p) + g(-p)}{2}\, dp \\ &\in \left[\min_{p \in U_\epsilon} \frac{g(p) + g(-p)}{2}, \max_{p \in U_\epsilon} \frac{g(p) + g(-p)}{2}\right].\end{aligned} \tag{3.94}$$

This implies that the limit inferior and limit superior of $\int_{\mathbb{S}^2} [R_j f_j](p) g(p)\, dp$ as $j \to +\infty$ must lie in this interval also. However, $\epsilon > 0$ was arbitrary. Using that g

is continuous and U_ϵ are nested, open neighbourhoods of $\{-e_1, e_1\}$ with $\bigcap_{\epsilon>0} U_\epsilon = \{-e_1, e_1\}$, it holds that

$$\min_{p\in U_\epsilon} \frac{g(p)+g(-p)}{2} \nearrow \min_{p\in\{-e_1,e_1\}} \frac{g(p)+g(-p)}{2} = \frac{g(e_1)+g(-e_1)}{2}. \tag{3.95}$$

The same argument gives that $\max_{p\in U_\epsilon} \frac{g(p)+g(-p)}{2} \searrow \frac{g(e_1)+g(-e_1)}{2}$. Therefore a squeezing argument gives that

$$\lim_{j\to\infty} \int_{\mathbb{S}^2} [R_j f_j](p) g(p)\, dp = \frac{g(e_1)+g(-e_1)}{2} \tag{3.96}$$

as required.

□

Proposition 3.3.23. If $\eta < -\frac{1}{3}$, then the isotropic state is the unique global minimiser of $\mathcal{F}$.

Proof. Assume $\eta < -\frac{1}{3}$. For $Q \in \mathcal{Q}$, we have that the optimal energy distribution for Q is given by $f_Q(p) = \frac{1}{Z}\exp(\Lambda(Q)p\cdot p)(Qp\cdot p - \eta)$, and in particular it is bounded away from zero and $+\infty$. Since all global minimisers of $\mathcal{F}$ must be the optimal energy distribution for their Q-tensor, all global minimisers are bounded away from zero and $+\infty$, and the global minimiser satisfies $f^* \in \mathcal{P}_+(\mathbb{S}^2)$. By Proposition 3.2.8, the isotropic state is the unique global minimiser of $\mathcal{P}_+(\mathbb{S}^2)$, so the isotropic state must be the unique global minimiser on $\mathcal{P}(\mathbb{S}^2)$. □

While obtaining the full phase diagram analytically appears to be out of reach, we can obtain some further qualitative results on the phase diagram. We will now show that for η sufficiently small, the isotropic state is not a global minimiser. The result holds trivially for $\eta \geq 0$ since the isotropic state has infinite energy.

Proposition 3.3.24. There exists some $\eta^* < 0$ so that for $\eta^* < \eta < 0$, the isotropic state is not a global minimiser of $\mathcal{F}$.

Proof. We will show this result using a perturbation argument. For clarity, we will recall the dependence of $\mathcal{F}$ explicitly on η. We know that for $|Q|^2 > \eta$, $\mathcal{F}$ is continuous. Take $Q^* \in \mathcal{Q}\setminus\{0\}$. Then $J(Q^*, 0) = M < +\infty$. Since J is continuous, this means that $J(Q^*, \eta) < 2M$ for all $|\eta|$ sufficiently small. Since J blows up uniformly at the boundary of its domain and $(0,0) \in \partial\mathrm{dom}(J)$, we know that there exists some ball $(0,0) \in B \subset \mathcal{Q}\times\mathbb{R}$ so that if $(Q,\eta) \in B$, then $J(Q,\eta) > 2M$. In particular, if

$\{\eta \in \mathbb{R} : \exists Q, (Q, \eta) \in B\} = B' \subset \mathbb{R}$, then $J(0, \eta) > 2M$ for all $\eta \in B'$. Therefore $J(Q^*, \eta) < 2M < J(0, \eta)$ for all $|\eta|$ sufficiently small. Therefore the isotropic state is not the global minimiser for sufficiently small $|\eta|$. □

Remark 3.3.25. It is possible to use this free energy density to provide an analogue of the Van der Waals equation of state for the system. Returning to original units, the free energy density is given by

$$\frac{1}{k_B T}\mathcal{F}(f, \rho) = \rho \ln \rho + \rho \int_{\mathbb{S}^2} f(p) \ln f(p) - f(p) \ln \left(1 - \rho \left(c - \frac{3}{2} dQp \cdot p\right)\right) dp. \quad (3.97)$$

This is related to the pressure P via

$$P = -\mathcal{F} + \rho \frac{\partial \mathcal{F}}{\partial \rho}. \quad (3.98)$$

There is an issue in that the derivative of the free energy cannot rigorously be taken with respect to number density at non-trivial minimisers due to the support condition. However, by reducing the energy to the macroscopic free-energy function J, the energy becomes sufficiently regular for the derivative with respect to number density to be taken (see Proposition 3.3.18) . First, we note that in original units, $J = J(Q, \eta)$ can be written as

$$\min_{f \in A(Q)} \mathcal{F}(f, \rho) = k_B T \left(\rho J \left(Q, \frac{2(\rho c - 1)}{3\rho d}\right) - \rho \ln d\right), \quad (3.99)$$

with k_B the Boltzmann constant, $T > 0$ temperature and $c, d > 0$ material constants. This then gives the pressure as

$$\begin{aligned}
\frac{1}{k_B T} P =& \rho \frac{\partial}{\partial \rho} \left(\rho J \left(Q, \frac{2(\rho c - 1)}{3\rho d}\right) - \rho \ln d\right) - \left(\rho J \left(Q, \frac{2(\rho c - 1)}{3\rho d}\right) - \rho \ln d\right) \\
=& \rho^2 \frac{\partial J}{\partial \eta} \left(Q, \frac{2(\rho c - 1)}{3\rho d}\right) \frac{\partial}{\partial \rho} \left(\frac{2(\rho c - 1)}{3\rho d}\right) \\
=& \frac{2}{3} \rho^2 \int_{E_Q} \frac{f_Q(p)}{Qp \cdot p - \frac{2(\rho c - 1)}{3\rho d}} dp \left(\frac{\rho c d - d(\rho c - 1)}{(\rho d)^2}\right) \\
=& \frac{1}{d} \int_{E_Q} \frac{f_Q(p)}{Qp \cdot p - \frac{2(\rho c - 1)}{3\rho d}} dp
\end{aligned} \quad (3.100)$$

This then gives the generalised Van der Waals equation of state,

$$P = k_B T \rho \int_{E_Q} \frac{f_Q(p)}{1 - \rho\left(c - \frac{3}{2} dQp \cdot p\right)}\, dp \tag{3.101}$$

This then allows us to demonstrate how the pressure blows up at the saturation limit, since returning to dimensionless units and using Jensen's inequality,

$$\begin{aligned}
\frac{2\rho d}{3k_B T} P =& \int_{E_Q} \frac{f_Q(p)}{Qp \cdot p - \eta}\, dp \\
\geq& \frac{1}{\int_{E_Q} (Qp \cdot p - \eta)\, f_Q(p)\, dp} \\
=& \frac{1}{|Q|^2 - \eta} \\
\geq& \frac{1}{\frac{2}{3} - \eta} \\
=& \frac{3\rho d}{3 - \rho(2d - 3c)} \\
=& \left(\frac{3\rho d}{3c - 2d}\right) \frac{1}{\rho - \frac{3}{2d - 3c}}
\end{aligned} \tag{3.102}$$

where the saturation limit $\eta \nearrow \frac{2}{3}$ corresponds to $\rho \nearrow \rho_s = \frac{1}{c-d}$. This gives a lower bound of the blow up rate of the pressure as $P \geq \frac{C}{\rho_s - \rho}$. In particular, we can consider a dimensionless analogue of pressure, $P^* = \frac{2\rho d}{3k_B T} P$, and see that we have

$$P^* \geq \frac{1}{|Q|^2 - \eta} \geq \frac{1}{\frac{2}{3} - \eta}. \tag{3.103}$$

3.4 Local minimisers of $\mathcal{F}$

We now turn to the question of understanding local minimisers of $\mathcal{F}$ via the finite dimensional minimisation problem. The style of the problem is similar to that seen in Section 2.3, and as such many results can be drawn immediately.

Theorem 3.4.1. If $f \in \mathcal{P}(\mathbb{S}^2)$ is a $W^{1,q}$-local minimiser for any $q \in [1, \infty)$, then f is an L^1-local minimiser. In particular, local minimisation with respect to L^q ($q \in [1, \infty]$), C^α ($\alpha < 1$) or $W^{1,q}$ ($q \in [1, \infty)$) are all equivalent.

Proof. This follows from Proposition 2.3.7 and Corollary 3.3.17. □

Theorem 3.4.2 (Euler-Lagrange equation for L^p local minimisers)**.** Assume that $f \in \mathcal{P}(\mathbb{S}^2)$ is an L^1-local minimiser of $\mathcal{F}$. Then f satisfies the Euler-Lagrange equation

$$\begin{aligned} f(p) =& \frac{1}{Z} \exp(\Lambda p \cdot p) \max(Qp \cdot p - \eta, 0), \\ Q =& \int_{\mathbb{S}^2} f(p) \left(p \otimes p - \frac{1}{3} I \right) \, dp, \\ \Lambda =& \int_{\mathbb{S}^2} \frac{f(p)}{Qp \cdot p - \eta} \left(p \otimes p - \frac{1}{3} I \right) \, dp. \end{aligned} \tag{3.104}$$

Furthermore, (Q, Λ) is a critical point of the dual function F.

Proof. This is a consequence of Proposition 2.3.6 by the same argument as Theorem 3.3.19. □

Corollary 3.4.3. The uniform state $f_U(p) = \frac{1}{4\pi}$ is an L^1-local minimiser for all $\eta < 0$.

Proof. In Proposition 3.2.6 and Corollary 3.2.13 it is shown that f_U is an L^∞ local minimiser if $\eta < 0$, so by Theorem 3.4.1 it is an L^1 local minimiser also. □

Corollary 3.4.4. For all $q \in [1, \infty]$, no L^q-local minimisers can be found by solving the equation

$$\frac{d}{dt} \mathcal{F}(f^* + t\phi) \bigg|_{t=0} = 0 \tag{3.105}$$

for all $\phi \in L^\infty(\operatorname{supp}(f))$ with $\int_{\operatorname{supp}(f)} \phi(p) \, dp = 0$, with the exception of the isotropic state when $\eta < 0$ and the set $\left\{ \frac{1+u}{4\pi} : u \in V \right\} \cap \mathcal{P}(\mathbb{S}^2)$ as given in Proposition 3.2.11

Proof. Let f^* be an L^q-local minimiser that is not one of the exceptions given. If Q^* is the corresponding Q-tensor of f^*, then $v_{\min}(Q) < \eta$ and $\{p \in \mathbb{S}^2 : Qp \cdot p - \eta > 0\}$ has positive measure. Take any $\phi \in L^\infty(\operatorname{supp}(f))$ with $\operatorname{supp} \phi$ compactly supported in $\operatorname{int} \operatorname{supp}(f^*)$, and also so that $A = \int_{\operatorname{supp}(f)} \left(p \otimes p - \frac{1}{3} I \right) \phi(p) \, dp \neq 0$. Take any $p_0 \in \mathbb{S}^2$ so that $Qp_0 \cdot p_0 - \eta = 0$ and $Ap_0 \cdot p_0 \neq 0$, without loss of generality taking $Ap \cdot p < 0$. Take $t > 0$. Then $Qp_0 \cdot p_0 + tAp_0 \cdot p_0 - \eta < Qp_0 \cdot p_0 - \eta = 0$, so there is a neighbourhood B_t of p_0 so that $Qp \cdot p + tAp \cdot p - \eta < 0$ for all $p \in B_t$. Since $p_0 \in \{p \in \mathbb{S}^2 : Qp \cdot p = \eta\} = \partial \operatorname{supp}(f^*)$, this means that $B_t \cap \operatorname{supp}(f^*)$ and $B_t \cap \operatorname{int} \operatorname{supp}(f)$ have positive measure for all t. Since ϕ is supported on the interior of $\operatorname{supp}(f^*)$, this implies that for t sufficiently small, $f^* + t\phi$ is positive on $\operatorname{int} \operatorname{supp}(f^*)$. Therefore the energy has a contribution

$$\mathcal{F}(f + t\phi) \geq c + \int_{B_t \cap \operatorname{int} \operatorname{supp}(f^*)} (f(t) + t\phi) \ln(Qp \cdot p + tAp \cdot p - \eta) \, dp = +\infty. \tag{3.106}$$

In particular, since $\mathcal{F}(f+t\phi) = +\infty$ for $t > 0$, the limit

$$\lim_{t\to 0} \frac{\mathcal{F}(f+t\phi) - \mathcal{F}(f)}{t} \tag{3.107}$$

can be at best infinite, and certainly non-zero □

One might ask the question of how to interpret a critical point of J in terms of the microscopic model. In particular, the numerical studies in [61] provide evidence for the existence of critical points of J that are not local minimisers. The inability to take arbitrary L^∞ variations about f_Q when Q is a non-trivial critical point of J means that one cannot easily say in what sense f_Q should be a critical point of $\mathcal{F}$. In particular, we aim to produce a result analogous to Proposition 2.3.11 for Onsager-type models. The next result shows that the critical points of J are in one-to-one correspondence with points f_0 where, for a certain family of curves f_t in $\mathrm{dom}(\mathcal{F})$,

$$\frac{d}{dt}\mathcal{F}(f_t)\bigg|_{t=0} = 0 \tag{3.108}$$

Without the toolkit developed in this work however it is unclear if all local minimisers of $\mathcal{F}$ can be found using such curves, but the results presented here answer the question in the affirmative. First, we will need a lemma concerning the differentiability of the map $Q \mapsto f_Q$.

Lemma 3.4.5. Let $Q \in \mathrm{dom}(J)$, $p \in \{q \in \mathbb{S}^2 : Qq\cdot q > \eta\}$. For a function $a : \mathbb{S}^2 \to \mathbb{R}$, and $f \in \mathcal{P}(\mathbb{S}^2)$, define $[a(p)]_f = a(p) - \int_{\mathbb{S}^2} a(q)f(q)\,dq$. Then

$$\frac{\partial f_Q(p)}{\partial Q} = f_Q(p)\left[\sum_{i,j=1}^{3} \frac{\partial \Lambda_{ij}}{\partial Q} p_i p_j + \frac{1}{Qp\cdot p - \eta}\left(p\otimes p - \frac{1}{3}I\right)\right]_{f_Q}. \tag{3.109}$$

In particular, the map $(Q,p) \mapsto \frac{\partial f_Q(p)}{\partial Q}$ is continuous for $\bigcup_{Q\in\mathrm{dom}(J)} \{Q\}\times E_Q$.

Proof. The result is found by directly differentiating the expression

$$f_Q(p) = \frac{1}{Z}\exp(\Lambda(Q)p\cdot p)(Qp\cdot p - \eta), \tag{3.110}$$

on the domain $Qp \cdot p > \eta$, noting that

$$\begin{aligned} Z &= \int_{E_Q} \exp(\Lambda(Q)p \cdot p)(Qp \cdot p - \eta)\, dp \\ \Rightarrow \frac{\partial Z}{\partial Q} &= \int_{E_Q} \frac{\partial}{\partial Q}(\exp(\Lambda(Q)p \cdot p)(Qp \cdot p - \eta))\, dp \\ \Rightarrow \frac{\partial f_Q(p)}{\partial Q} &= \frac{1}{Z}\frac{\partial}{\partial Q}\exp(\Lambda(Q)p \cdot p)(Qp \cdot p - \eta) \\ &\quad - \frac{1}{Z} f_Q(p) \int_{E_Q} \frac{\partial}{\partial Q}\exp(\Lambda(Q)p \cdot p)(Qp \cdot p - \eta)\, dp \\ &= f_Q(p)\left[\sum_{i,j=1}^{3} \frac{\partial \Lambda_{ij}}{\partial Q} p_i p_j + \frac{1}{Qp \cdot p - \eta}\left(p \otimes p - \frac{1}{3}I\right)\right]_{f_Q}. \end{aligned} \tag{3.111}$$

The continuity of this map follows from the explicit representation using that Λ is a C^1 function of Q and the map $Q \to f_Q$ is continuous with L^∞. □

Definition 3.4.6. Let

$$V = \left\{ u \in L^\infty(\mathbb{S}^2) : \int_{\mathbb{S}^2} \left(p \otimes p - \frac{1}{3}I\right) u(p)\, dp = 0\,, \int_{\mathbb{S}^2} u(p)\, dp = 0 \right\}. \tag{3.112}$$

We say that a map $f_t : (-\epsilon, \epsilon) \to L^1(\mathbb{S}^2)$ satisfies assumption (A1) if there exists $Q \in C^1(-\epsilon, \epsilon; \mathrm{dom}(J))$, $u, u_0 \in V$ so that

1. $f_t = f_{Q_t} + u_0 + tu$.
2. $\mathrm{supp}(u)$ and $\mathrm{supp}(u_0)$ are compactly supported in E_{Q_0}.
3. $f_t \in \mathrm{dom}(\mathcal{F})$ for all $-\epsilon < t < \epsilon$.

If (1) and (2) are satisfied, then by taking ϵ sufficiently small (3) is satisfied also.

Proposition 3.4.7. Let $f^* \in \mathrm{dom}(\mathcal{F})$. Then

$$\frac{d}{dt}\mathcal{F}(f_t)\bigg|_{t=0} = 0 \tag{3.113}$$

for all curves $t \mapsto f_t$ satisfying (A1) with $f_0 = f^*$ if and only if its Q-tensor, Q^* is a critical point of J, and $f^* = f_{Q^*}$.

Proof. First we split $\mathcal{F}(f_t)$ into parts so that its differentiability is clearer to see.

$$\begin{aligned}\mathcal{F}(f_t) =& J(Q_t) + \mathcal{F}(f_t) - \mathcal{F}(f_{Q_t}) \\ =& J(Q_t) + \left(\int_{\mathbb{S}^2} f_t(p)\ln f_t(p) - f_{Q_t}(p)\ln f_{Q_t}(p)\,dp\right) \\ &+ \int_{\mathbb{S}^2} u_t(p)\ln(Q_t p\cdot p - \eta)\,dp \\ =& J(Q_t) + \left(\int_{\mathrm{supp}(u_t)} f_t(p)\ln f_t(p) - f_{Q_t}(p)\ln f_{Q_t}(p)\,dp\right) \\ &+ \int_{\mathrm{supp}(u_t)} u_t(p)\ln(Q_t p\cdot p - \eta)\,dp\end{aligned} \tag{3.114}$$

Now the derivative of this expression can be taken, where the support condition on u_t removes any issues about non-differentiability of the terms involving logarithms at zero, and the sufficient differentiability of $f_{Q_t}(p)$ on its domain comes from Lemma 3.4.5.

$$\begin{aligned}&\frac{d}{dt}\mathcal{F}(f_t) \\ =&\frac{\partial J}{\partial Q}(Q_t)\cdot\frac{dQ_t}{dt} + \int_{\mathrm{supp}(u_t)} (\ln(f_t) - \ln(f_{Q_t}))\,\frac{\partial f_t(p)}{\partial Q}\frac{dQ_t}{dt}\,dp + \int_{\mathrm{supp}(u_t)} \ln(f_t(p))u(p)\,dp \\ &- \int_{\mathrm{supp}(u_t)} \frac{u_t(p)}{Q_t p\cdot p - \eta}\left(p\otimes p - \frac{1}{3}I\right) - u(p)\ln(Q_t p\cdot p - \eta)\,dp \\ =&\left(\frac{\partial J}{\partial Q}(Q_t) + \int_{\mathrm{supp}(u_t)} (\ln(f_t(p)) - \ln(f_{Q_t}(p)))\,\frac{\partial f_{Q_t}(p)}{\partial Q} - \frac{u_t(p)}{Q_t p\cdot p - \eta}\left(p\otimes p - \frac{1}{3}I\right)\,dp\right)\cdot\frac{dQ_t}{dt} \\ &+ \int_{\mathrm{supp}(u_t)} (\ln f_t(p) - \ln(Q_t p\cdot p - \eta))\,u(p)\,dp\end{aligned} \tag{3.115}$$

If the curve goes through f_{Q^*}, where Q^* is a critical point of J, then at $t = 0$ $u_0 = 0$, $\mathrm{supp}(u_0) = \emptyset$ and all terms vanish, so that $\frac{d}{dt}\mathcal{F}(f_t)\big|_{t=0} = 0$.

Conversely, assume that this vanishes at $t = 0$ for all such curves satisfying (A1). Considering Q constant in t, this implies

$$\int_{\mathrm{supp}(u_0)} \ln\frac{f^*(p)}{Q^* p\cdot p - \eta} u(p) = 0 \tag{3.116}$$

In particular, since $u \in V$,

$$\ln\left(\frac{f_0}{Q_0 p\cdot p - \eta}\right) = \alpha + \lambda p\cdot p \tag{3.117}$$

by Hahn-Banach, so that $f^*(p) = \frac{1}{z}\exp(\lambda p \cdot p)(Q^* p \cdot p - \eta)$ on $\operatorname{supp} f^* = E_{Q^*}$. By uniqueness of the solution to the dual problem, this implies that $\lambda = \Lambda(Q^*)$ and $z = Z$. In particular, $f^* = f_{Q^*}$, and $u_0 = 0$. Substituting this back into the expression for when Q is not constant in t gives that

$$\frac{\partial J}{\partial Q}(Q_0) \cdot \left.\frac{dQ_t}{dt}\right|_{t=0} = 0, \tag{3.118}$$

which then implies that $\frac{\partial J}{\partial Q}(Q_0) = 0$, so that Q_0 is a critical point of J.

□

In Onsager-type models we can avoid difficulties in differentiating logarithms at zero if we restrict ourselves only to probability distributions bounded away from zero. A heuristic interpretation of the previous result is that if we look at the restricted set of probability distributions $f \in \mathcal{P}(\mathbb{S}^2)$ with $\operatorname{supp}(f) \subset E_Q$ so that $f(p) = f_Q(p)$ for p near ∂E_Q, then we can avoid analogous differentiability issues in this model.

3.5 Related models

3.5.1 The inclusion of attractive, thermally dependent, interactions

Consider the temperature dependent free-energy density accounting for attractive interactions, from (3.5). We will take $k(p,q)$ to be affine in $(p \cdot q)^2$ for simplicitly, which gives the energy to be of the form

$$kT\rho_0 \int_{\mathbb{S}^2} f(p)\ln f(p) - f(p)\ln\left(1 - \rho_0\left(c - \frac{2}{3}dQp \cdot p\right)\right) dp - \rho_0^2 U(a + b|Q|^2). \tag{3.119}$$

Dividing through by $\rho_0 kT$, which leave the minimisation unchanged, this can be non-dimensionalised again as

$$\begin{aligned}&\int_{\mathbb{S}^2} f(p)\ln f(p) - f(p)\ln\left(Qp \cdot p - \frac{2(\rho_0 c - 1)}{3\rho_0 d}\right) - \frac{\rho_0}{k_B T}(bU)|Q|^2 + \frac{\rho_0 U a}{kT} - \ln(\rho_0 d)\\ &= \int_{\mathbb{S}^2} f(p)\ln f(p) - f(p)\ln\left(Qp \cdot p - \eta\right) - \frac{1}{2\tau}|Q|^2 + C_1\end{aligned} \tag{3.120}$$

where C_1 is irrelevant to the minimisation and $\tau = \frac{2k_B T}{\rho_0 bU} > 0$. Since this is a Q-dependent perturbation of the original minimisation problem, this can easily be

treated using the methodology given previously.

Proposition 3.5.1. All global and L^p-local minimisers of $\mathcal{F}_\tau$ are in one-to-one correspondence with global and local minimisers of J_τ, where $J_\tau : \mathrm{dom}(J) \to \mathbb{R}$ by

$$J_\tau(Q) = J(Q) - \frac{1}{2\tau}|Q|^2. \tag{3.121}$$

Proof. This follows from the results of Section 2.3, noting that

$$\min_{f \in A(Q)} \mathcal{F}_\tau(f) = \min_{f \in A(Q)} \mathcal{F}(f) - \frac{1}{2\tau}|Q|^2. \tag{3.122}$$

□

Proposition 3.5.2. Let $\eta < 0$. Then $Q = 0$ is a critical point of J_τ for all $\tau > 0$. Let $\tau_c = \frac{15}{2}\left(1 + \frac{2}{15\eta}\right)^{-2}$. Then if $\tau < \tau_c$, $Q = 0$ is a local minimum of J_τ, and if $\tau > \tau_c$ then Q is a local maximum of J_τ.

Proof. The first derivative of J_τ is easily given by

$$\frac{\partial J_\tau}{\partial Q}(0) = \frac{\partial J}{\partial Q}(0) - \frac{1}{\tau}0, \tag{3.123}$$

at which point the critical point condition is satisfied, since $Q = 0$ is always a local minimum of J. The second derivative at 0, using Proposition 3.A.2, is then given by

$$\frac{\partial^2 J_\tau}{\partial Q^2}(0) = \left(\frac{15}{2}\left(1 + \frac{2}{15\eta}\right)^2 - \frac{1}{\tau}\right)\mathrm{Id}. \tag{3.124}$$

Therefore the second derivative is positive if $\tau < \frac{15}{2}\left(1 + \frac{2}{15\eta}\right)^{-2}$, and is negative if $\tau > \frac{15}{2}\left(1 + \frac{2}{15\eta}\right)^{-2}$. □

All of the results in this subsection can be summarised in the following theorem.

Theorem 3.5.3. If $f^* \in \mathcal{P}(\mathbb{S}^2)$ is an L^p-local minimiser for any $p \in [1, \infty]$, then f^* is an L^q-local minimiser for all $q \in [1, \infty]$. All L^p-local minimisers f^* satisfy the

Euler-Lagrange equation

$$\begin{aligned} f^*(p) =& \frac{1}{Z}\exp(\lambda^* p\cdot p)\max(Q^* p\cdot p-\eta,0),\\ Q^* =& \int_{\mathbb{S}^2}\left(p\otimes p-\frac{1}{3}I\right)f^*(p)\,dp,\\ \lambda^* =& \int_{\mathbb{S}^2}\frac{f^*(p)}{Q^* p\cdot p-\eta}\left(p\otimes p-\frac{1}{3}I\right)\,dp+\frac{1}{\tau}Q^*. \end{aligned} \tag{3.125}$$

Q^*, λ^* are also saddle points of $F : \mathrm{dom}(J)\times \mathrm{Sym}_0(3)\to\mathbb{R}$ given by

$$F(Q,\lambda) = Q\cdot\lambda - \frac{1}{2\tau}|Q|^2 - \ln\left(\int_{\mathbb{S}^2}\exp(\lambda p\cdot p)\max(Qp\cdot p-\eta,0)\,dp\right). \tag{3.126}$$

Finally, for $\eta<0$, the isotropic state $f_u=\frac{1}{4\pi}$ is an L^p-local minimiser if $\tau<\tau_c=\frac{15}{2}\left(1+\frac{2}{15\eta}\right)^{-2}$, and is not a local minimiser if $\tau>\tau_c$.

It is also possible to produce a statement similar to Proposition 3.3.22 for the zero-temperature limit.

Proposition 3.5.4. Let $\eta<\frac{2}{3}$, $\tau_j\nearrow 0$, and let $f_j\in\mathcal{P}(\mathbb{S}^2)$ be corresponding minimisers of $\mathcal{F}_{\tau_j}$. Then up to rotations $f_j \overset{*}{\rightharpoonup} \frac{1}{2}\left(\delta_{e_1}+\delta_{-e_1}\right)$ in $C(\mathbb{S}^2)^*$.

Proof. Following the proof of Proposition 3.3.22, it suffices to show that the corresponding Q-tensors Q_j satisfy $|Q_j|^2\to\frac{2}{3}$. For the sake of contradiction assume otherwise, so that there exists some $0<R<\frac{2}{3}$ and a subsequence (not relabelled) so that $|Q_j|^2\le R$ for all j. Let $Q=\frac{3(R+\epsilon)}{2}\left(e\otimes e-\frac{1}{3}I\right)$ with $\epsilon>0$ sufficiently small so that $R+\epsilon<\frac{2}{3}$, and let $f=f_Q$. Then

$$\begin{aligned} \mathcal{F}_{\tau_j}(f_j)-\mathcal{F}_{\tau_j}(f) =& J_{\tau_j}(Q_j)-J_{\tau_j}(Q)\\ \ge& \left(J(0)-\frac{1}{\tau_j}R^2\right)-\left(J(Q)-\frac{1}{\tau_j}(R+\epsilon)^2\right)\\ =& \left(J(0)-J(Q)\right)+\frac{\epsilon R+\epsilon^2}{\tau_j}. \end{aligned} \tag{3.127}$$

Taking $j\to\infty$ gives $\tau_j\to 0$ and the right-hand side blows up to $+\infty$. Therefore for sufficiently large j, $\mathcal{F}_{\tau_j}(f_j)>\mathcal{F}_{\tau_j}(f)$, contradicting that f_j was a global minimiser. Therefore if f_j is the sequence of minimisers, $\frac{2}{3}\ge\limsup_{j\to\infty}|Q_j|^2\ge\liminf_{j\to\infty}|Q_j|^2>R$. Since $R<\frac{2}{3}$ was arbitrary, $\lim_{j\to\infty}|Q_j|^2=\frac{2}{3}$. □

One immediate difference compared to the Maier-Saupe model is that for fixed temperature, by increasing the concentration it is possible to undergo a local isotropic-

nematic-isotropic phase transition. In the original units, b, V, U, c, d will generally be fixed and taken to be independent of the temperature and concentration, so it is possible to produce a local stability phase portrait for the isotropic state, changing only temperature and concentration by fixing these values (see Figure 3.1). In particular, as $\rho_0 \to \frac{1}{c}$, the limiting concentration for the isotropic state to have finite energy, the transition temperature approaches zero. This can be seen since

$$\tau_c = \frac{15}{2}\left(1 + \frac{2}{15\eta}\right)^{-2} = \frac{15}{2}\left(\frac{15\eta}{15\eta + 2}\right)^2, \tag{3.128}$$

so as $\rho_0 \to \frac{1}{c}$, $\eta \to 0$, so $\tau_c \to 0$, and $T_c = \tau_c \frac{\rho_0 bU}{2} \to 0$. This analysis only accounts for local stability, and the numerical analysis in [61] would suggest that in all the region where $\eta > -\frac{2}{15}$, the isotropic state is globally unstable in the absence of attractive interactions, which since $J_\tau(0) = J(0)$ and $J_\tau(Q) < J(Q)$ for $Q \neq 0$, this then suggests that the isotropic state is globally unstable in this concentration regime when temperature effects are considered also. In particular, the concentration regime $-\frac{2}{15} < \eta < 0$ where the isotropic state regains local stability would be difficult to observe in reality if the model is truly accurate.

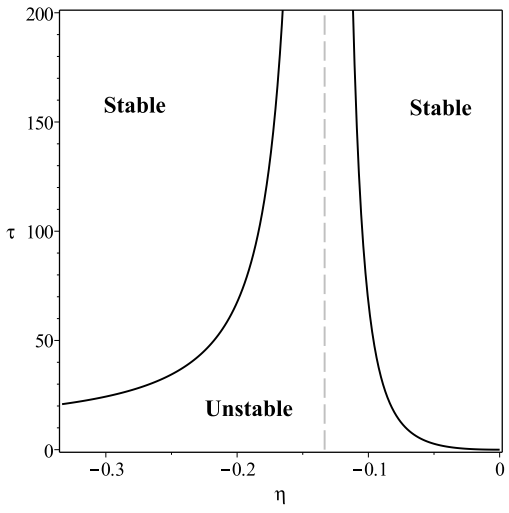


Figure 3.1: Local stability regions in terms of η, τ with the asymptote corresponding to $\eta = -\frac{2}{15}$

Remark 3.5.5. Similarly to Remark 3.3.25, we can obtain an equation of state with the inclusion of thermally attractive interactions. Returning to original units and

using the reduction to J again, we have

$$\begin{aligned}\frac{1}{k_BT}P =& \left(-1+\rho\frac{\partial}{\partial\rho}\right)\left(\rho J\left(Q,\frac{2(\rho_0 c-1)}{3\rho_0 d}\right)-\frac{\rho^2 U}{k_BT}(a+b|Q|^2)\right)\\ =&\rho\int_{\mathbb{S}^2}\frac{f_Q(p)}{1-\rho(c-\frac{3}{2}dQp\cdot p)}\,dp-\frac{\rho^2U}{k_BT}(a+b|Q|^2).\end{aligned} \tag{3.129}$$

This can then be rearranged to be given in a more classical form,

$$\left(P+\rho^2U\left(a+b|Q|^2\right)\right)\left(\rho\int_{\mathbb{S}^2}\frac{f_Q(p)}{1-\rho(c-dQp\cdot p)}\,dp\right)^{-1}=k_BT. \tag{3.130}$$

In this case the average excluded volume term is given in terms of the harmonic mean rather than the arithmetic mean, although in the sphere limit where $d=0$, the two means are equal.

3.5.2 Uniaxial systems

In order to reduce the complexity of the problem it is often assumed that nematic systems have axial symmetry about a fixed unit vector, removing a degree of freedom. Studies in Onsager models suggest that in certain situations at least it can be energetically favourable for nematic systems to form such uniaxial systems [21, 55]. As such it is frequently an assumption made in the modelling process, for example being a key assumption of the Oseen-Frank theory [22]. In particular, this gives corresponding Q-tensors of the form $Q=S\left(e_1\otimes e_1-\frac{1}{3}I\right)$ with $S\in\left(-\frac{1}{2},1\right)$. We say that Q is oblate if $S<0$ and prolate if $S>0$. The numerical studies in [61] invoke a uniaxial ansatz on solutions. It is possible to extend the previous results of this work to the case where systems are constrained to be uniaxial. Even if global/local minimisers of the full biaxial model are not uniaxial, the following results show the existence of prolate and oblate uniaxial critical points of the full biaxial problem in certain concentration regimes, with the precise statements given in Corollaries 3.5.9 and 3.5.10. First, we define the set of uniaxial probability distributions,

$$\mathcal{P}_U(\mathbb{S}^2)=\{f\in\mathcal{P}(\mathbb{S}^2):\exists\tilde{f}:[-1,1]\to\mathbb{R},e\in\mathbb{S}^2\text{ such that }f(p)=\tilde{f}(p\cdot e)\}, \tag{3.131}$$

and take the normalisation on the second Legendre polynomial

$$P_2(x)=\frac{1}{2}(3x^2-1). \tag{3.132}$$

With fixed eigenbasis, and $S \in \left(-\frac{1}{2}, 1\right)$ we take $Q_S = S\left(e_1 \otimes e_1 - \frac{1}{3}I\right)$.

Proposition 3.5.6. If $f \in \mathcal{P}_{\mathrm{U}}(\mathbb{S}^2)$ is an L^p-local minimiser of $\mathcal{F}|_{\mathcal{P}_{\mathrm{U}}(\mathbb{S}^2)}$, then there exists $\hat{f} \in \mathcal{P}([-1,1])$ and $n \in \mathbb{S}^2$ so that $\frac{1}{2\pi}\hat{f}(p \cdot n) = f(p)$ and

$$\begin{aligned} \hat{f}(x) =& \frac{1}{Z}\exp(lP_2(x))\max(SP_2(x) - \eta, 0), \\ S =& \int_{-1}^{1} P_2(x)\hat{f}(x)\,dx, \\ l =& \frac{2}{3}\int_{-1}^{1} P_2(x)\frac{\hat{f}(x)}{SP_2(x) - \eta}\,dx. \end{aligned} \tag{3.133}$$

Proof. If f is uniaxial about $n \in \mathbb{S}^2$, then its corresponding Q-tensor can be written as $Q = S\left(n \otimes n - \frac{1}{3}I\right)$, with $S = \int_{-1}^{1} P_2(x)\hat{f}(x)\,dx$. Therefore returning to the macroscopic function J, any local minimum of the uniaxially constrained Q-tensor problem can be described by its order parameter S, so by fixing the axis of symmetry,

$$\begin{aligned} 0 =& \frac{d}{dS}J\left(S\left(n \otimes n - \frac{1}{3}I\right)\right) \\ =& \frac{\partial J}{\partial Q}\left(S\left(n \otimes n - \frac{1}{3}I\right)\right) \cdot \frac{\partial}{\partial S}S\left(n \otimes n - \frac{1}{3}I\right) \\ =& \left(\Lambda(Q_S) - \frac{1}{Z}\int_{\mathbb{S}^2} \frac{\exp(\Lambda(Q_S)p \cdot p)}{SP_2(p \cdot n) - \eta}\left(p \otimes p - \frac{1}{3}I\right)\,dp\right) \cdot \left(n \otimes n - \frac{1}{3}I\right). \end{aligned} \tag{3.134}$$

Now recall from Proposition 3.3.7 that since $\Lambda(Q_S)$ shares an eigenbasis with Q_S, there exists a scalar l so that $\Lambda(Q_S) = l\left(n \otimes n - \frac{1}{3}I\right)$. Therefore this can be written as

$$\begin{aligned} 0 =& \frac{2l}{3} - \frac{1}{Z}\int_{\mathbb{S}^2} \frac{\exp(lP_2(p \cdot n))}{SP_2(p \cdot n) - \eta}P_2(p \cdot n)\,dp \\ =& \frac{2l}{3} - \int_{-1}^{1} \frac{\hat{f}(x)}{SP_2(x) - \eta}P_2(x)\,dx. \end{aligned} \tag{3.135}$$

The dual optimality condition is similarly rephrased in terms of $\hat{f}$ as

$$\begin{aligned} S =& \frac{1}{Z}\int_{\mathbb{S}^2} \exp(\Lambda(Q_S)p \cdot p)\max(SP_2(p \cdot n) - \eta, 0)f(p)\,dp \\ =& \int_{-1}^{1} \exp(lP_2(x))\max(SP_2(x) - \eta, 0)\hat{f}(x)\,dx. \end{aligned} \tag{3.136}$$

The equivalence of local minimisation comes from the argument in Section 2.3. □

Proposition 3.5.7. Assume that $\hat{f}$ satisfies the uniaxial Euler-Lagrange equation. Then given $n \in \mathbb{S}^2$, $f \in \mathcal{P}(\mathbb{S}^2)$ defined by $f(p) = \frac{1}{2\pi}\hat{f}(p \cdot n)$ satisfies the full biaxial Euler-Lagrange equation.

Proof. The dual optimality condition automatically holds by Proposition 3.3.7, so it only remains to show that the derivative of J is zero at the corresponding Q-tensor. By writing the derivative condition in the uniaxial case as

$$\frac{\partial J}{\partial Q}(Q) \cdot \left(n \otimes n - \frac{1}{3} I \right) = 0, \tag{3.137}$$

it suffices to show that $\frac{\partial J}{\partial Q}(Q)$ is parallel to $\left(n \otimes n - \frac{1}{3} I\right)$, or equivalently that $\frac{\partial J}{\partial Q}$ is uniaxial with distinguished direction n. Recalling that the derivative is given by

$$\frac{\partial J}{\partial Q}(Q) = \Lambda(Q) - \frac{1}{Z} \int_{E_Q} \exp(\Lambda(Q) p \cdot p) \left(p \otimes p - \frac{1}{3} I \right) \, dp, \tag{3.138}$$

and that if Q is uniaxial then so is $\Lambda(Q)$ with the same distinguished direction, the result immediately follows. □

Remark 3.5.8. This tells us that if Q is uniaxial and a critical point of the constrained problem, then Q is a critical point of the unconstrained problem. However, this does not say that uniaxially constrained (local) minimisers are necessarily unconstrained (local) minimisers. Nor does it imply that all critical points are uniaxial. We can however deduce the existence of certain uniaxial critical points of the biaxial system.

Corollary 3.5.9. For $0 \leq \eta < \frac{2}{3}$, there exists a prolate uniaxial critical point of J. Furthermore, there exists rotations $R_j \in \mathrm{SO}(3)$ so that as $\eta_j \to \frac{2}{3}$ from below, $[R_j f_j] \overset{*}{\rightharpoonup} \frac{1}{2}\left(\delta_{e_1} + \delta_{-e_1}\right)$ in $C(\mathbb{S}^2)^*$.

Proof. Consider the map $S \mapsto J\left(S\left(e_1 \otimes e_1 - \frac{1}{3} I\right)\right)$ for $S \in \left(\sqrt{\frac{3\eta}{2}}, 1\right)$. This is a continuous map on an open set, which blows up at the boundary by Proposition 3.3.6. Therefore it admits a local minimum, and the derivative must vanish there. Therefore the corresponding prolate uniaxial Q-tensor is a critical point of J. The convergence result follows by the same argument as Proposition 3.3.22 □

Corollary 3.5.10. If $0 \leq \eta < \frac{1}{6}$. There exists an oblate uniaxial critical point of J. Furthermore, there exists rotations $R_j \in \mathrm{SO}(3)$ so that as $\eta_j \to \frac{1}{6}$ from below, $[R_j f_j] \overset{*}{\rightharpoonup} \frac{1}{2\pi}\mathcal{H}^1 \llcorner \{p \in \mathbb{S}^2 : e \cdot p = 0\}$ in $C(\mathbb{S}^2)^*$.

Proof. The proof is similar to the previous result, by taking the map $S \mapsto J\left(S\left(e \otimes e - \frac{1}{3}I\right)\right)$ restricted to $S \in \left(-\frac{1}{2}, -\sqrt{\frac{3\eta}{2}}\right)$. By the same argument this produces an oblate uniaxial critical point of J, and the corresponding probability distribution satisfies the Euler-Lagrange equation.

Now let $\eta_j \to \frac{1}{6}$ from below, let S_j be the corresponding local minimiser and f_j be the probability distribution corresponding to the local minimiser $S_j\left(e_j \otimes e_j - \frac{1}{3}I\right)$ for some $e_j \in \mathbb{S}^2$. The proof follows a similar argument to Proposition 3.3.22. We first let R_j be any rotation such that $R_j^T e_j = e$. If $\hat{f}_j = [R_j f_j]$, then $\hat{f}_j$ has Q-tensor $S_j\left(e \otimes e - \frac{1}{3}I\right) \to -\frac{1}{2}\left(e \otimes e - \frac{1}{3}I\right)$. We have that $|Q_j|^2 \to \frac{1}{6}$, and in particular $S_j^2 \to \frac{1}{6}$. This implies that given $\epsilon > 0$, for sufficiently large j, supp(
$hat f_j) \subset \{p \in \mathbb{S}^2 : |e \cdot p| < \epsilon\} = U_\epsilon$. Let $g \in C(\mathbb{S}^2)$, and let $\tilde{g} : [0, \pi] \times [0, 2\pi]$ denote its representation in spherical coordinates, with $\theta = 0$ corresponding to e. Similarly, let $\tilde{f}_j : [0, \pi] \to \mathbb{R}$ be the representation of $\hat{f}_j$ in spherical coordinates, which by axial symmetry is independent of ϕ. We can then write

$$\begin{aligned}\int_{\mathbb{S}^2} \hat{f}_j(p) g(p)\, dp &= \int_0^\pi \int_0^{2\pi} \sin(\theta) \tilde{f}_j(\theta) \tilde{g}(\theta, \phi)\, d\phi\, d\theta \\ &= \int_0^\pi \sin(\theta) \tilde{f}_j(\theta) \left(\int_0^{2\pi} \tilde{g}(\theta, \phi)\, d\phi\right) d\theta \\ &= \int_{\mathbb{S}^2} \hat{f}_j(p) \frac{g_s(p)}{2\pi}\, dp,\end{aligned} \tag{3.139}$$

where $g_s(p)$ is the axially symmetric function defined in spherical coorindates by

$$\tilde{g_s}(\theta) = \int_0^{2\pi} \tilde{g}(\theta, \phi)\, d\phi. \tag{3.140}$$

Since g is continuous, this implies that g_s is continuous also. Furthermore, $\text{supp}(f_j) \subset U_\epsilon$ for all large j, and for each $\epsilon > 0$, U_ϵ is a neighbourhood of $U_0 = \{p \cdot e = 0\}$, and $\bigcap_{\epsilon > 0} U_\epsilon = U_0$. Therefore for large j,

$$\begin{aligned}\int_{\mathbb{S}^2} \hat{f}_j(p) g(p)\, dp &= \int_{\mathbb{S}^2} f_j(p) \frac{g_s(p)}{2\pi}\, dp \\ &= \int_{U_\epsilon} \hat{f}_j(p) \frac{g_s(p)}{2\pi}\, dp \\ &\in \left[\min_{p \in U_\epsilon} \frac{g_s(p)}{2\pi}, \max_{p \in U_\epsilon} \frac{g_s(p)}{2\pi}\right].\end{aligned} \tag{3.141}$$

As in Proposition 3.3.22, a squeeze argument then gives that

$$\lim_{j\to\infty}\int_{\mathbb{S}^2}\hat{f}_j(p)g(p)\,dp\in\left[\min_{p\in U_0}\frac{g_s(p)}{2\pi},\max_{p\in U_0}\frac{g_s(p)}{2\pi}\right]=\left\{\frac{1}{2\pi}g_s(e_2)\right\},\tag{3.142}$$

where e_2 can be any vector orthogonal to e, due to the axial symmetry of g_s. Substituting this back into the definition of g_s then gives that

$$\lim_{j\to+\infty}\int_{\mathbb{S}^2}[R_jf_j](p)g(p)\,dp=\frac{1}{2\pi}\tilde{g}_s(0)=\int_0^{2\pi}\tilde{g}(0,\phi)\,d\phi=\frac{1}{2\pi}\int_{\{p\cdot e_1=0\}}g(p)\,d\mathcal{H}^1(p).\tag{3.143}$$

□

Corollary 3.5.11. There exists $\eta_0<0$ so that for all $\eta_0<\eta<0$, there exists two uniaxial critical points of J, one oblate and one prolate, denoted Q_ϵ^+ and Q_ϵ^- respectively, such that $Q_\eta^\pm\to 0$ as $\eta\nearrow 0$. Furthermore, these are local maxima of the uniaxially constrained problem.

Proof. Only the existence of the prolate branch will be shown, with the oblate branch proof being identical. We first show that there exists a branch of local maximisers as stated, from which the result follows. Let $\eta_j\nearrow 0$ with $\eta_j>-\frac{2}{15}$ for all $j\in\mathbb{N}$. In particular, the isotropic state is a strict local minimiser for all η_j. Define $S_j=\inf\{S\in(0,1):J(S,\eta_j)<J(0,\eta_j)\}$. The infima may be over an empty set, but for j sufficiently large we can show this set is non-empty and that as $j\to+\infty$, $S_j\to 0$. Let $\epsilon>0$ be small. Since J is continuous, $J\left(\epsilon\frac{1}{2},\eta_j\right)-J(0,\eta_j)\to-\infty$. In particular, for large j, $J(\epsilon,\eta_j)<J(0,\eta_j)$, proving that the set is non-empty. Furthermore, since ϵ was arbitrary, $S_j\to 0$. Since the isotropic state is a strict local minimiser, and $J(S_j,\eta_j)=J(0,\eta_j)$, this implies that for large j, there exists a local maximum $S_{\eta_j}^+$ so that $0<S_{\eta_j}^+<S_j\to 0$. Since $S_{\eta_j}^+$ is a local maximum of a C^1 function it must be a critical point, and therefore there exists a corresponding critical point of the unconstrained biaxial problem. □

Remark 3.5.12. Recall from Remark 3.3.25 that the dimensionless pressure P^* can be given as

$$P^*=\int_{\mathbb{S}^2}\frac{f(p)}{Qp\cdot p-\eta}\,dp\geq\frac{1}{|Q|^2-\eta}.\tag{3.144}$$

From Corollary 3.5.9 we know that for $\eta>0$ we have a prolate local minimiser of the uniaxially constrained problem. For prolate uniaxial Q-tensors, $|Q|^2=\frac{2S^2}{3}<\frac{2}{3}$. We can then therefore estimate the blowup of the dimensionless pressure for prolate

uniaxial states as

$$P^* \geq \frac{1}{\frac{2S^2}{3} - \eta} \geq \frac{1}{\frac{2}{3} - \eta}. \tag{3.145}$$

Similarly, from Corollary 3.5.10 we know that for $\eta > 0$ there exists an oblate local minimiser of the uniaxially constrained problem. For an oblate uniaxial Q-tensor, $|Q|^2 = \frac{2S^2}{3} < \frac{1}{6}$. This gives us an analogous esimate for the dimensionless pressure for the oblate local minimiser,

$$P^* \geq \frac{1}{\frac{2S^2}{3} - \eta} \geq \frac{1}{\frac{1}{6} - \eta}. \tag{3.146}$$

In the case of the first estimate, this is beneficial since it requires no knowledge of the microscopic structure, only the equilibrium order parameter and η. The second estimate does not require any knowledge about the local minimiser other than whether it is prolate or oblate.

3.6 Numerical results

In Figure 3.2 we show plots of the dimensionless pressure $P^* = \int_{\mathbb{S}^2} \frac{f(p)}{Qp \cdot p - \eta}\, dp$ for the 3 numerically found locally stable branches of the uniaxially constrained problem. The solutions were obtained by a fixed point iteration on the equilibrium equations. For comparison, the estimates in Equations (3.145) and (3.146) are shown for the prolate and oblate uniaxial branches. In each case we see that the expected blow up of pressure in the isotropic state as $\eta \to 0$, the oblate state as $\eta \to \frac{1}{6}$, and the prolate state as $\eta \to \frac{2}{3}$.

In Figure 3.3 we see a phase diagram adapted from [61], with the equilibrium branches of the uniaxially constrained problem. We see an isotropic branch, globally stable for $\eta < \eta_{NI} \approx 0.149$, at which point it is locally stable until it is inadmisible at $\eta = 0$. Similarly to Maier-Saupe, we observe a saddle-node bifurcation in the prolate region, forming a locally unstable equilibrium with smaller distinguished eigenvalue and a locally stable equilibrium with larger eigenvalue, and the locally stable state becomes globally stable for η larger, approaching $S = \frac{2}{3}$ as $\eta \to \frac{2}{3}$. However, in contast to Maier-Saupe, the lower branch does not undergo a transcritical bifurcation, exchanging stability with the isotropic state. Instead the branch connects with the isotropic branch at $S = 0, \eta = 0$ as described in Corollary 3.5.11, at which the isotropic state becomes inadmissible. Furthemore, there is a second saddle-node bifurcation in the oblate region, which a similar unstable branch which crosses connects into

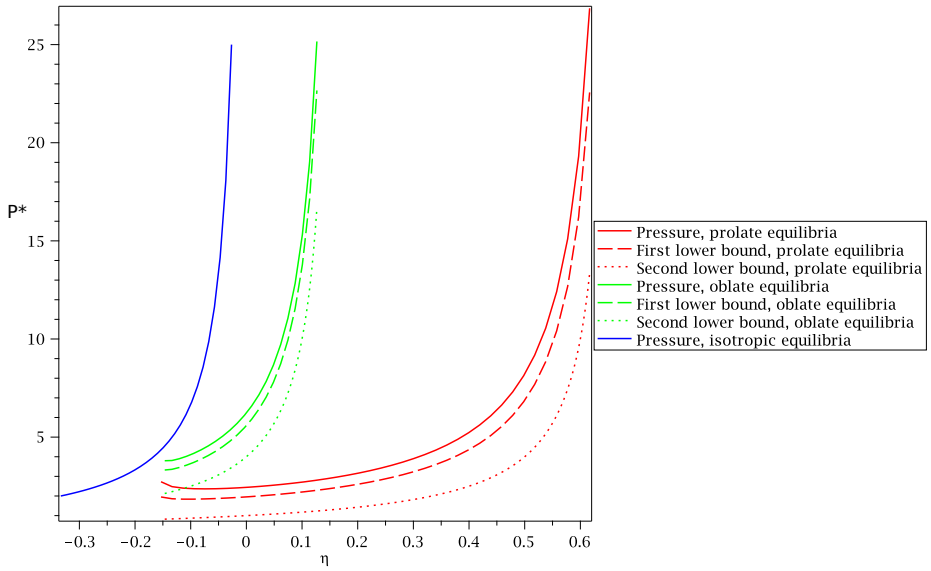


Figure 3.2: The dimensionless pressure and its approximations for the three locally stable uniaxial branches

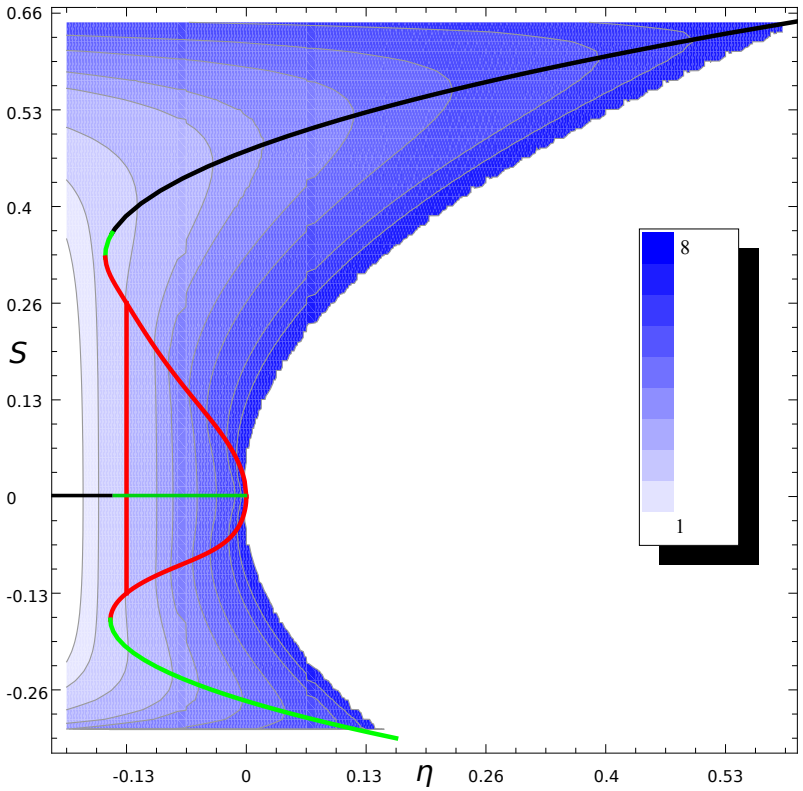


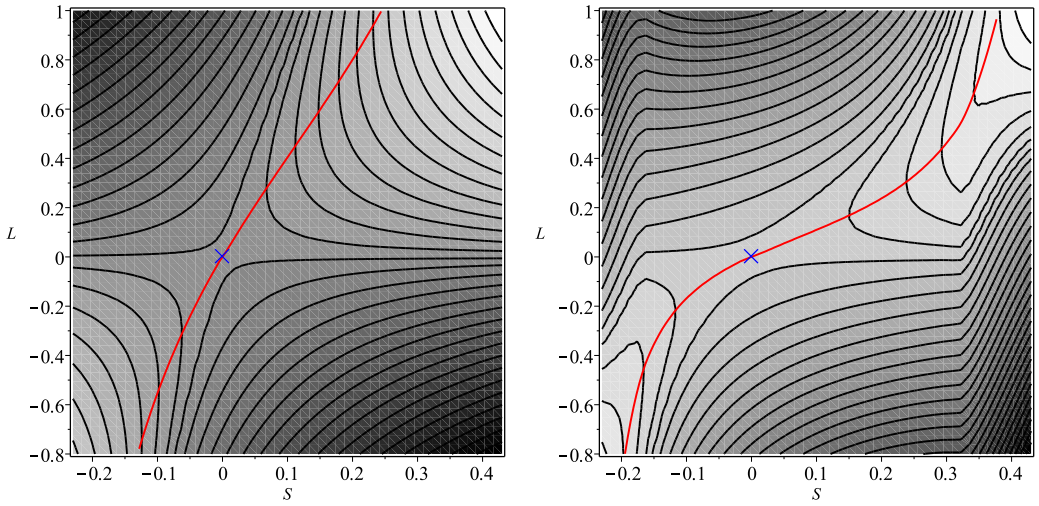
Figure 3.3: The stationary branches and energy landscape depending on η, adapted from [61]

$S = 0, \eta = 0$ and a locally stable branch which approaches $S = -\frac{1}{2}$ as $\eta \to \frac{1}{6}$. Finally at $\eta = -\frac{2}{15}$, we see the connected set of order parameters on which the energy is constant, which joins the two unstable branches.

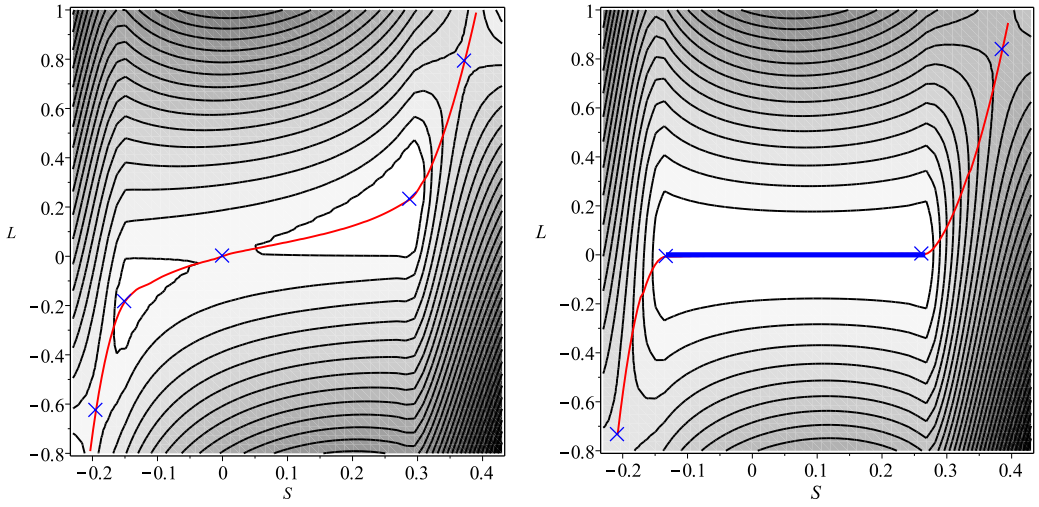
In Figure 3.4 we show contours plots of the uniaxially constrained saddle-point energy,

$$F_D(S, l) = Sl - \ln\left(\int_{-1}^{1} \exp(lP_2(x)(x)) \max(SP_2(x) - \eta, 0)\, dx\right). \tag{3.147}$$

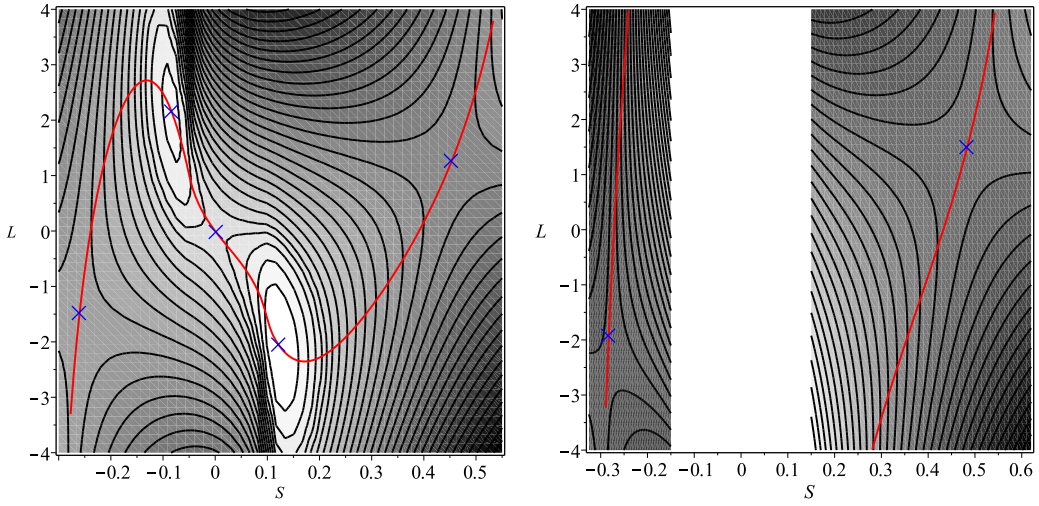
The solutions to $\max_{l \in \mathbb{R}} F_D(S, l)$ as a function of S are shown as a red curve, and critical points are shown as blue crosses. Recall that locally stable equilibria of the uniaxially constrained problem are described by saddle points of F_D. At $\eta = -\frac{2}{15}$ we see the connected set so that $L(S) = 0$, and the development of further equilibria between $\eta = -0.16$ and $\eta = -0.145$.



(a) $\eta = -0.3$ (b) $\eta = -0.16$



(c) $\eta = -0.145$ (d) $\eta = -0.133$



(e) $\eta = -0.05$ (f) $\eta = 0.01$

Figure 3.4: The saddle-point energy, dual solutions and critical points for representative values of η.

3.A The second derivative of J at 0

Proposition 3.A.1. Let M be the fourth-order tensor defined by

$$M = \frac{1}{4\pi} \int_{\mathbb{S}^2} p \otimes p \otimes p \otimes p \, dp. \tag{3.148}$$

Acting as a linear operator from $\mathrm{Sym}_0(3)$ to itself, given by

$$M(A)_{ij} = \sum_{\alpha,\beta=1}^{3} M_{\alpha\beta ij} A_{\alpha\beta}, \tag{3.149}$$

can be simplified as $M(A) = \frac{2}{15} A$.

Proof. If A is a symmetric matrix (not necessarily traceless) and $R \in \mathrm{SO}(3)$, then $M(RAR^T) = RM(A)R^T$, which is seen by using a change of variables $q = Rp$ in the integrand. By [46], this implies that there are continuous scalar functions g_0, g_1, g_2 so that $M(A) = \sum_{i=0}^{3} g_i(A) A^i$. Viewed only as a map from $\mathrm{Sym}_0(3)$ to itself, this simplifies as $M(A) = g_2(A) \left(A^2 - \frac{|A|^2}{3} I \right) + g_1(A)$. Since M is a linear map, we have that for any $r \in \mathbb{R} \setminus \{0\}$,

$$\begin{aligned} M(A) =& \frac{1}{r} M(rA) \\ =& \frac{1}{r} \left(r^2 g_2(rA) \left(A^2 - \frac{|A|^2}{3} I \right) + r g_1(rA) A \right) \\ =& r g_2(rA) \left(A^2 - \frac{|A|^2}{3} I \right) + g_1(rA) A \\ \Rightarrow M(A) =& \lim_{r \to 0} r g_2(rA) \left(A^2 - \frac{|A|^2}{3} I \right) + g_1(rA) A \\ =& g_1(0) A, \end{aligned} \tag{3.150}$$

using that g_1, g_2 are continuous. We have therefore established that M is simply a multiple of the identity. To establish this constant, let $A = \left(e \otimes e - \frac{1}{3} I \right)$ for some

$e \in \mathbb{S}^2$. Then the multiple can be established as

$$\begin{aligned} g_1(0) =& \frac{M(A) \cdot A}{A \cdot A} \\ =& \frac{3}{2}\frac{1}{4\pi}\int_{\mathbb{S}^2}\left((p \cdot e)^2 - \frac{1}{3}\right) dp \\ =& \frac{3}{2}\frac{1}{2}\int_{-1}^{1}\left(x^2 - \frac{1}{3}\right)^2 dx \\ =& \frac{3}{2}\frac{4}{45} = \frac{2}{15}. \end{aligned} \tag{3.151}$$

□

Proposition 3.A.2. The second derivative of J at $Q = 0$ is given by

$$\frac{\partial^2 J}{\partial Q^2}(0) = \frac{15}{2}\left(1 + \frac{2}{15\eta}\right)^2 \mathrm{Id}, \tag{3.152}$$

where Id is the identity operator on $\mathrm{Sym}_0(3)$.

Proof. First recall that J can be written as $J(Q) = \max_{\lambda \in \mathrm{Sym}_0(3)} F(Q, \lambda) = F(Q, \Lambda(Q))$ with

$$F(Q, \lambda) = Q \cdot \lambda - \ln\left(\int_{\mathbb{S}^2} \exp(\lambda p \cdot p)(Qp \cdot p - \eta)\, dp\right). \tag{3.153}$$

Thus the derivative of J can be written as

$$\begin{aligned} \frac{\partial J}{\partial Q_{ij}} =& \frac{\partial F}{\partial Q_{ij}} + \frac{\partial F}{\partial \lambda_{\alpha\beta}}\frac{\partial \Lambda_{\alpha\beta}}{\partial Q_{ij}} \\ =& \frac{\partial F}{\partial Q_{ij}} \end{aligned} \tag{3.154}$$

due to the optimality condition of $\Lambda(Q)$. Similarly the second derivative can be given as

$$\frac{\partial^2 F}{\partial Q_{ij}\partial Q_{kl}} = \frac{\partial^2 F}{\partial Q_{ij}\partial Q_{kl}} + \frac{\partial^2 F}{\partial \lambda_{\alpha\beta}\partial Q_{ij}}\frac{\partial \Lambda_{\alpha\beta}}{\partial Q_{kl}}. \tag{3.155}$$

Furthermore the derivative of Λ with respect to Q can be found as

$$\begin{aligned} 0 =& \frac{\partial F}{\partial \lambda_{ij}}(Q, \Lambda(Q)) \\ 0 =& \frac{\partial^2 F}{\partial \lambda_{ij} \partial Q_{kl}} + \frac{\partial^2 F}{\partial \lambda_{ij} \partial \lambda_{\alpha\beta}} \frac{\partial \Lambda_{\alpha\beta}}{\partial Q_{kl}} \\ -\left(\frac{\partial^2 F}{\partial \lambda^2} \right)^{-1}_{ij,\alpha\beta} \frac{\partial^2 F}{\partial \lambda_{\alpha\beta} \partial Q_{kl}} =& \frac{\partial \Lambda_{ij}}{\partial Q_{kl}}. \end{aligned} \tag{3.156}$$

By an argument similar to Proposition 2.2.10,

$$\frac{\partial^2 F}{\partial \lambda^2}(Q, \Lambda(Q)) = Q \otimes Q - \int_{\mathbb{S}^2} f_Q(p) \left(p \otimes p - \frac{1}{3} I \right)^{\otimes 2} \, dp. \tag{3.157}$$

At the isotropic state, this reduces to

$$\frac{\partial^2 F}{\partial \lambda^2}(0, 0) = -\frac{1}{4\pi} \int_{\mathbb{S}^2} \left(p \otimes p - \frac{1}{3} I \right)^{\otimes 2} \, dp. \tag{3.158}$$

Using Proposition 3.A.1, viewing this as a linear operator on $\mathrm{Sym}_0(3)$, and denoting $\mathrm{Id} : \mathrm{Sym}_0(3) \to \mathrm{Sym}_0(3)$ the identity operator, this identified with

$$\frac{\partial^2 F}{\partial \lambda^2}(0, 0) = -\frac{2}{15} \mathrm{Id}. \tag{3.159}$$

Next to find the mixed derivative

$$\begin{aligned} \frac{\partial^2 F}{\partial \lambda_{ij} \partial Q_{kl}} =& \frac{\partial}{\partial Q_{kl}} \left(Q_{ij} - \frac{1}{Z} \int_{\mathbb{S}^2} \exp(\lambda p \cdot p)(Qp \cdot p - \eta) \left(p_i p_j - \frac{1}{3} \delta_{ij} \right) \, dp \right) \\ =& \delta_{ik}\delta_{jl} - \frac{\int_{\mathbb{S}^2} \exp(\lambda p \cdot p) \left(p_i p_j - \frac{1}{3}\delta_{ij} \right) \left(p_k p_l - \frac{1}{3} \right) \, dp}{Z} \\ &+ \frac{\int_{\mathbb{S}^2} \exp(\lambda p \cdot p)(Qp \cdot p - \eta) \left(p_i p_j - \frac{1}{3}\delta_{ij} \right) \, dp}{Z^2} \\ &\times \int_{\mathbb{S}^2} \exp(\lambda p \cdot p)(Qp \cdot p - \eta) \left(p_k p_l - \frac{1}{3}\delta_{kl} \right) \, dp. \end{aligned} \tag{3.160}$$

Taking $Q = \lambda = 0$, then

$$\begin{aligned} \frac{\partial^2 F}{\partial \lambda_{ij} \partial Q_{kl}}(0, 0) =& \delta_{ik}\delta_{jl} + \frac{1}{4\pi\eta} \int_{\mathbb{S}^2} \left(p_i p_j - \frac{1}{3}\delta_{ij} \right) \left(p_k p_l - \frac{1}{3}\delta_{kl} \right) \, dp \\ =& \left(1 + \frac{2}{15\eta} \right) \mathrm{Id}_{ijkl}. \end{aligned} \tag{3.161}$$

Finally, for the second derivative with respect to Q,

$$\begin{aligned}\frac{\partial^2 F}{\partial Q_{ij}\partial Q_{kl}} =& \frac{\partial}{\partial Q_{kl}}\left(\lambda_{ij} - \frac{1}{Z}\int_{\mathbb{S}^2}\exp(\lambda p\cdot p)\left(p_i p_j - \frac{1}{3}\delta_{ij}\right)\,dp\right)\\ =& \frac{1}{Z^2}\int_{\mathbb{S}^2}\exp(\lambda p\cdot p)\left(p_i p_j - \frac{1}{3}\delta_{ij}\right)\,dp\int_{\mathbb{S}^2}\exp(\lambda p\cdot p)\left(p_k p_l - \frac{1}{3}\delta_{kl}\right)\,dp,\end{aligned} \tag{3.162}$$

therefore evaluating at $Q = \lambda = 0$ gives $\frac{\partial^2 F}{\partial Q^2}(0,0) = 0$. Now combining these results gives

$$\begin{aligned}\frac{\partial^2 J}{\partial Q_{ij}\partial Q_{kl}}(0) =& \frac{\partial^2 F}{\partial Q_{ij}\partial Q_{kl}}(0,0) + \frac{\partial^2 F}{\partial \lambda_{\alpha\beta}\partial Q_{ij}}(0,0)\frac{\partial \lambda_{\alpha\beta}}{\partial Q_{kl}}(0,0)\\ =& \left(1+\frac{2}{15\eta}\right)\mathrm{Id}_{\alpha\beta ij}\cdot\frac{15}{2}\mathrm{Id}_{\alpha\beta\gamma\delta}\left(1+\frac{2}{15}\eta\right)\mathrm{Id}_{\gamma\delta kl}\\ =& \frac{15}{2}\left(1+\frac{2}{15\eta}\right)^2\mathrm{Id}_{ijkl}.\end{aligned} \tag{3.163}$$

□

Chapter 4

Finite extensibility in liquid crystal elastomers

4.1 Derivation of the chain energy

Assumptions

Consider a chain in the crosslinked polymer network, with $R \in \mathbb{R}^3$ spanning the two points of cross-linking, the so-called end-to-end vector. As in [29], the methodology will be first to consider a discrete system, where the monomers can have one of finitely many orientations. Then the entropically optimal configuration for a given R will be found in this discrete case, and continuum limits of the solution will be taken.

Partition the surface of the unit sphere into M disjoint sections, $(U_j)_{j=1}^M$ so that $\bigcup_{j=1}^{M} U_j = \mathbb{S}^2$, and $U_i \cap U_j = \emptyset$ for $i \neq j$. Furthermore assume that the maximum diameter of $(U_j)_{j=1}^M$ tends to zero as $M \to \infty$. We assume that the admissible orientations p_j for $j = 1, ..., M$ satisfy $p_j \in U_j$. Let n_j denote the average number of monomers with orientation p_j. We make the following assumptions on the chain.

1. The total number of monomers is equal to N, that $\sum_{j=1}^{M} n_j = N$.

2. The length of each monomer in the chain is equal to $\ell > 0$, so that $\ell \sum_{j=1}^{M} n_j p_j = R$.

These two assumptions are common between this work and the work of Kuhn and Grün. The next assumption is to establish the description of the rod-like liquid crystal and flexible components of the polymer chain.

3. The monomers can be split into two classes, those in the flexible polymer backbone of number fraction $1-\gamma$, and the nematic mesogens of number fraction γ.

The next assumption is the key deviation from the Kuhn and Grün model, so that the entropy is taken with respect to an anisotropic distribution, which will drive the properties of our model. It makes an assumption on what Treloar referred to as the "*a priori*" probability of finding a monomer with a certain orientation [53], and can loosely be interpreted as the natural state of the monomers in the absence of the rest of the polymer network.

4. The *a priori* probability of finding a mesogenic monomer with a particular orientation is described by some given $\rho \in \mathcal{P}(\mathbb{S}^2)$, and the *a priori* probability of finding a backbone monomer with a given orientation is described by the uniform distribution $\frac{1}{4\pi}$.

The law of total probability then gives that the *a priori* probability of finding an arbitrary monomer with a particular orientation is ρ^t with superscript t to denote the total probability, explicitly given as

$$\rho^t = \frac{1-\gamma}{4\pi} + \gamma\rho. \tag{4.1}$$

There are generally a large number of chain configurations that could provide the observed end-to-end vector, so we need an assumption in order to determine what the most likely chain configuration is.

5. (Maximum entropy assumption) If the end-to-end vector R is observed, then the corresponding n_j are of maximum entropy, given the *a priori* distribution ρ^t.

In the absence of an internal energy term, which will be taken in most of this work, the free energy depends only on the entropy and temperature. In particular, maximising the entropy is equivalent to minimising the free energy, and the free energy can be thought of as being purely entropic.

Derivation

Let Δp_j denote the surface area of U_j. Define the probability of a monomer having orientation p_j to be $\rho^t(p_j)\Delta p_j$, corresponding to the approximation

$$\int_{U_j} \rho^t(p)\, dp \approx \int_{U_j} \rho^t(p_j)\, dp = \rho^t(p_j)\Delta p_j. \tag{4.2}$$

Treating the orientations of each monomer as independent and using the multinomial distribution, the probability of the observed chain R is given by

$$W = N! \left(\prod_{j=1}^{M} (n_j!) \right)^{-1} \prod_{j=1}^{M} (\rho^t(p_j)\Delta p_j)^{n_j} \tag{4.3}$$

It should be remarked that in the original derivation of Kuhn and Grün, they implicitly assumed an isotropic *a priori* distribution in the previous step, whereas we take Assumption (4) here. Much of the remainder of the derivation is common to their work. Taking negative logarithms (to give an entropic energy) and using Stirling's approximation ($\ln n! \approx n \ln n - n$), approximately it holds that

$$-\ln W \approx N - N \ln N + \sum_{j=1}^{M} (n_j \ln n_j - n_j) - \sum_{j=1}^{M} n_j \ln \left(\rho^t(p_j)\Delta p_j \right) \tag{4.4}$$

Using Assumption (5) so that (n_j) must be energetically optimal, and using Lagrange multipliers $\alpha \in \mathbb{R}$, $\beta \in \mathbb{R}^k$ to satisfy the constraints from Assumptions (1,2),

$$\begin{aligned} 0 =& \frac{\partial}{\partial n_j} \left(-\ln W - \alpha \left(\sum_{i=1}^{M} n_i - N \right) - \beta \cdot \left(\sum_{i=1}^{M} n_i p_i - \frac{1}{\ell} R \right) \right) \\ =& \ln n_j - \ln \left(\rho(p_j^T)\Delta p_j \right) - \alpha - \beta \cdot p_j. \end{aligned}$$

Rearranging then gives

$$n_j = \exp(\alpha + \beta \cdot p_j)\rho^t(p_j)\Delta p_j. \tag{4.5}$$

Substituting this back into the energy gives

$$\begin{aligned}
-\ln W =& N - N\ln N + \sum_{j=1}^{M} n_j \left(\alpha + \beta\cdot p_j - \ln\left(\rho^t(p_j)\Delta p_j\right)\right) - \sum_{j=1}^{M} n_j \ln\left(\rho^t(p_j)\Delta p_j\right)\\
=& N - N\ln N + N\alpha + \beta\cdot\frac{1}{\ell}R\\
=& N - N\ln N + N\left(\alpha + \beta\cdot\frac{1}{N\ell}R\right).
\end{aligned}$$

Taking the continuum limit as $M\to\infty$, a measure ξ is obtained (depending on R and ρ) of bond angles so that

$$d\xi(p) = \exp(\alpha+\beta\cdot p)\rho^t(p)dp \tag{4.6}$$

with the requirements that

$$\int_{\mathbb{S}^2} d\xi(p) = \int_{\mathbb{S}^2} \exp(\alpha+\beta\cdot p)\rho^t(p)\,dp = N,$$

$$\int_{\mathbb{S}^2} p\,d\xi(p) = \int_{\mathbb{S}^2} \exp(\alpha+\beta\cdot p)\rho^t(p)p\,dp = \frac{1}{\ell}R$$

The constant α can be eliminated to obtain an implicit representation of β by observing that

$$\frac{1}{N\ell}R = \frac{1}{\int_{\mathbb{S}^2}\exp(\beta\cdot p)\rho^t(p)\,dp}\int_{\mathbb{S}^2} p\exp(\beta\cdot p)\rho^t(p)\,dp. \tag{4.7}$$

In particular this gives $\frac{1}{N\ell}R$ as the first moment of a continuous probability distribution on the sphere. Therefore we must have that $|R| < N\ell$, or otherwise there cannot be solutions β.

Let $\sigma(p) = \frac{1}{Z}\exp(\beta\cdot p)\rho^t(p)$ be the minimising probability distribution, so $\int_{\mathbb{S}^2}\sigma(p)\,dp = 1$ and $\int_{\mathbb{S}^2} p\sigma(p)\,dp = \frac{1}{N\ell}R$. Then note that

$$\begin{aligned}
N - N\ln N + N\left(\alpha+\beta\cdot\frac{1}{N\ell}R\right) =& N - N\ln N + N\int_{\mathbb{S}^2}\sigma(p)\left(\alpha+\beta\cdot p\right)\,dp\\
=& N - N\ln N + N\int_{\mathbb{S}^2}\sigma(p)\ln\left(\frac{\sigma(p)}{\rho^t(p)}\right)\,dp,
\end{aligned}$$

so that the energy can be expressed in terms of the relative entropy of σ with respect

to ρ^t. If we consider the problem of minimising

$$\left(N - N\ln N + N\int_{\mathbb{S}^2}\tilde{\sigma}(p)\ln\frac{\tilde{\sigma}(p)}{\rho^t(p)}\,dp\right) \tag{4.8}$$

over all $\tilde{\sigma}\in\mathcal{P}(\mathbb{S}^2)$ such that

$$\begin{aligned}\int_{\mathbb{S}^2}\tilde{\sigma}(p)\,dp =& 1,\\ \int_{\mathbb{S}^2}p\tilde{\sigma}(p)\,dp =& \frac{1}{N\ell}R,\end{aligned}$$

we see that $\sigma(p)=\frac{1}{Z}\exp(\beta\cdot p)\rho^t(p)$ satisfies the Euler-Lagrange equation corresponding to the minimisation problem. This means that the derivation is equivalent to a maximum *relative* entropy assumption on the chain, whereas the classical Kuhn and Grün model can be viewed as a maximum classical entropy assumption. It is this representation of the chain energy that will be most useful for the analysis.

Basic properties

By fixing ρ, and using the substitution $\rho^t\sigma'=\tilde{\sigma}$, the minimisation problem is equivalent to

$$\min_{\sigma'\in\mathcal{B}(R,\rho^t)} k_BT\left(N\ln N + N\int_{\mathbb{S}^2}\sigma'(p)\ln\sigma'(p)\rho^t(p)\,dp\right), \tag{4.9}$$

where $\mathcal{B}(R,\rho^t)$ is the set of all $\sigma':\mathbb{S}^2\to[0,+\infty)$ which are measurable with respect to $\rho^t(p)\,dp$, satisfying the linear constraints

$$\begin{aligned}\int_{\mathbb{S}^2}\sigma'(p)\rho^t(p)\,dp =& 1,\\ \int_{\mathbb{S}^2}p\sigma'(p)\rho^t(p)\,dp =& \frac{1}{N\ell}R.\end{aligned}$$

This is advantageous since this can be viewed as a classical entropy maximisation, but with the usual surface area measure replaced by $\rho^t(p)$. In particular, methods from Chapter 2 can be applied to immediately provide some relevant results. Recalling from (4.1) that $\rho^t=\frac{1-\gamma}{4\pi}+\gamma\rho$, where γ is taken to be fixed, we note that the energy can be taken as dependent on ρ, the nematic orientation distribution function, rather than ρ^t. Define

$$W_c(R,\rho)=\min_{\sigma'\in\mathcal{B}(R,\rho^t)} k_BT\left(N\ln N + N\int_{\mathbb{S}^2}\sigma'(p)\ln\sigma'(p)\rho^t(p)\,dp\right). \tag{4.10}$$

Some key properties of W_c, which can be taken from results in Chapter 2, are that

1. $W_c(R,\rho)$ is a smooth convex function of R for $|R| < N\ell$ (Proposition 2.2.3 and Corollary 2.2.9.

2. For fixed ρ, β is a smooth bijection between all $R \in \mathbb{R}^3$ with $|R| < N\ell$ and $\mathbb{R}^3$ (From Proposition 2.2.7).

3. As $|R| \to N\ell$, $W_c(R, N\ell) \to +\infty$, so the energy blows up in the taut chain limit (Corollary 2.2.5).

4. The value of W_c can be found numerically by the dual problem

$$W_c(R,\rho) = k_BTN\ln N + k_BTN \max_{(\alpha,\lambda)\in\mathbb{R}^{1+3}} \alpha + \frac{1}{N\ell}R\cdot\lambda - \int_{\mathbb{S}^2} \exp(\alpha - 1 + \lambda\cdot p)\rho^t(p)\,dp. \tag{4.11}$$

   Furthermore the maximising pair (α,λ) has that $\lambda = \beta$ (Proposition 2.2.6).

Two important properties, relating to invariance, are as follows.

5. W_c is frame indifferent, so that if $S\rho$ is defined as $(S\rho)(p) = \rho(Sp)$ for a rotation S, then $W_c(SR, S\rho) = W_c(R,\rho)$. Similarly, $S\beta(SR, S\rho) = \beta(R,\rho)$.

6. If $W_c^{N,\ell}$ explicitly denotes W_c with given number of monomers N of length ℓ,

$$\frac{1}{k_BTN}\left(W_c^{N,\ell}(R,\rho) - k_BTN\ln N\right) = W_c^{1,1}\left(\frac{1}{N\ell}R,\rho\right). \tag{4.12}$$

   That is to say, up to an additive and multiplicative constant, W_c depends only on $\frac{1}{N\ell}R$ and ρ.

These two invariance properties are readily seen by noting that the Euler-Lagrange equation for the minimisation problem is invariant under these transformations also.

Property 3 demonstrates the finite extensibility of the chain. The blow up occurs because if $|R| \approx N\ell$, there is very little configuration space available. The more precise statement and argument can be found in Proposition 2.1.12, and loosely states that if $|R| \approx N\ell$ then any probability distribution $\sigma \in \mathcal{P}(\mathbb{S}^2)$ that has $\frac{1}{N\ell}R$ as its first moment must be concentrated on some set with small size. This then implies that the energy, defined in terms of the relative entropy, must be large. We can obtain more explicit bounds in the following.

Proposition 4.1.1. Let Let $\rho \in \mathbb{S}^2$. Then there exists constants $\delta > 0$, $c_1 > 0$ and $c_2 \in \mathbb{R}$ such that $W_c(R,\rho) > -c_1\ln(1-|R|)$ for $1 > |R| > 1-\delta$

Proof. Given $u \in \mathbb{S}^2, \epsilon > 0$ define the set $E^u_\epsilon = \{p \in \mathbb{S}^2 : p \cdot u > 1 - \epsilon\}$. Using Theorem 2.2.4, it is sufficient to find an upper bound for $\mu(E^u_\epsilon)$ to obtain the bound on W_c, where $\mu(X) = \int_X \rho^t(p)\, dp$. This is straightforward since $\mu(E^u_\epsilon) \leq ||\rho^t||_\infty \mathcal{H}^2(E^u_\epsilon)$. Then

$$\begin{aligned}
\mathcal{H}^2(E^u_\epsilon) &= \int_{\{p\cdot u > 1-\epsilon\}} d\mathcal{H}^2 \\
&= \int_0^{2\pi} \int_{\{\theta\in[0,\pi]:\cos(\theta)>1-\epsilon\}} \sin\theta \, d\theta d\phi \\
&= 2\pi \int_{1-\epsilon}^1 dx = 2\pi\epsilon.
\end{aligned}$$

Thus if $1 - |R| = \epsilon^2$ for sufficiently small ϵ, then $\mu(E^u_\epsilon) \leq 2\pi||\rho_T||_\infty \epsilon$, this gives that

$$\begin{aligned}
W_c(R,\rho) &\geq (1-\epsilon)\ln\left(\frac{1}{2\pi||\rho^t||_\infty \epsilon}\right) \\
&= -(1-\epsilon)\ln(\epsilon) - (1-\epsilon)\ln(2\pi||\rho^t||_\infty) \\
&= -(1-\epsilon)\ln\left(\sqrt{1-|R|}\right) - (1-\epsilon)\ln(2\pi||\rho^t||_\infty) \\
&= -\frac{1-\epsilon}{2}\ln(1-|R|) - (1-\epsilon)\ln(2\pi||\rho^t||_\infty) \\
&\geq -c_1 \ln(1-|R|) + c_2
\end{aligned}$$

for ϵ sufficiently small.

□

Proposition 4.1.2. For $c = \ln\frac{2\pi}{1-\gamma}$,

$$W_c(R,\rho) \leq c - \ln(1-|R|) \tag{4.13}$$

for all $R \in B(0,1)$.

Proof. As before, let $E^u_\epsilon = \{p \in \mathbb{S}^2 : u \cdot p > 1 - \epsilon\}$. Then $\mathcal{H}^2(E^u_\epsilon) = 2\pi\epsilon$. Let $\sigma_\epsilon(p) = \frac{1}{2\pi\epsilon}$, then by symmetry we see that $\int_{\mathbb{S}^2} \sigma_\epsilon(p) p\, dp \parallel u$, and by putting the integral into spherical coordinates,

$$\begin{aligned}
u \cdot \int_{\mathbb{S}^2} \sigma_\epsilon(p) p\, dp =& \frac{1}{2\pi\epsilon} \int_{\cos(\theta)>1-\epsilon} \int_0^{2\pi} \cos(\theta)\, d\theta\, d\phi \\
=& \frac{1}{\epsilon}\int_{1-\epsilon}^1 x\, dx \\
=& \frac{1}{2\epsilon}\left(1 - (1-\epsilon)^2\right) = 1 - \frac{\epsilon}{2}.
\end{aligned} \tag{4.14}$$

Therefore if $R = ru$ for $u \in \mathbb{S}^2$, then by taking $\epsilon = 2(1-r)$, $\sigma_\epsilon \in \mathcal{A}_R$. Then we can test the energy against σ_ϵ, giving that

$$\begin{aligned} W_c(R,\rho) &\leq \int_{\mathbb{S}^2} \ln\left(\frac{\sigma_\epsilon(p)}{\rho^t(p)}\right)\sigma_\epsilon(p)\,dp \\ &\leq \int_{\mathbb{S}^2} \ln\left(\frac{\sigma_\epsilon(p)}{\frac{1-\gamma}{4\pi}}\right)\sigma_\epsilon(p)\,dp \\ &= \ln\frac{4\pi}{2(1-\gamma)(1-r)} \\ &= c - \ln(1-|R|). \end{aligned}$$

□

Furthermore, we include a lower semicontinuity result that will be of use later.

Proposition 4.1.3. Let $R_j \to R$ and $\rho_j \rightharpoonup \rho$ in L^1. Then $\liminf_{j\to\infty} W_c(R_j,\rho_j) \geq W_c(R,\rho)$.

Proof. Let $F : \mathbb{R}^2_+ \to \mathbb{R}$ be defined by $F(x,y) = x\ln(x) - x\ln(a+\gamma y)$ for constants $a = \frac{1-\gamma}{4\pi}$. It is immediate that F is convex (although not strictly convex) by considering its Hessian matrix. Let $\rho_j \rightharpoonup \rho$, $R_j \to R$, and let σ_j, σ denote the corresponding minimisers. First note from the growth bound that if $W_c(R,\rho) = +\infty$, then $W_c(R_j,\rho_j) \to +\infty$. If $W_c(R,\rho) < +\infty$, then it suffices to only consider sequences with $W_c(R_j,\rho_j) < +\infty$ for all j. Denote $\rho^T = a + \gamma\rho$. Then almost everywhere in $\mathbb{S}^2$ (noting that σ and ρ^T are bounded from zero, and infinite only on a set of measure, so non-differentiability is not an issue), it must hold that

$$\begin{aligned} F(\sigma_j,\rho_j) &\geq F(\sigma,\rho) + F_x(\sigma,\rho)(\sigma_j-\sigma) + F_y(\sigma,\rho)(\rho_j-\rho) \\ &= F(\sigma,\rho) + (\ln(\sigma) + 1 - \ln(\rho^T))(\sigma_j-\sigma) - \frac{\gamma\sigma}{\rho^T}(\rho_j-\rho) \\ &= F(\sigma,\rho) + \left(\ln\left(\frac{\sigma}{\rho^T}\right)+1\right)(\sigma_j-\sigma) - \gamma\frac{\sigma}{\rho^T}(\rho_j-\rho) \\ &= F(\sigma,\rho) + (\beta\cdot p + 1 - \ln(Z))(\sigma_j-\sigma) - \gamma\frac{1}{Z}\exp(\beta\cdot p)(\rho_j-\rho) \\ \Rightarrow W_c(R_j,\rho_j) &\geq W_c(R,\rho) + \int_{\mathbb{S}^2}(\beta\cdot p + 1 - \ln(Z))(\sigma_j-\sigma) - \gamma\frac{1}{Z}\int_{\mathbb{S}^2}\exp(\beta\cdot p)(\rho_j-\rho) \\ &= W_c(R_j,\rho) + \beta\cdot(R_j-R) - \frac{\gamma}{Z}\int_{\mathbb{S}^2}\exp(\beta\cdot p)(\rho_j-\rho) \end{aligned}$$

using that σ_j, σ both integrate to 1, and both have first moments R_j, R. To complete

the proof, using that $\rho_j \rightharpoonup \rho$ gives

$$\begin{aligned}\liminf_{j\to\infty} W_c(R_j,\rho_j) &\geq W_c(R,\rho) + \liminf_{j\to\infty} \beta\cdot(R_j - R) - \frac{\gamma}{Z}\int_{\mathbb{S}^2}\exp(\beta\cdot p)(\rho_j-\rho)\\ &= W_c(R,\rho),\end{aligned}$$

giving lower semicontinuity. □

4.2 Networks and the quartic approximation

Take the head-to-tail symmetry assumption on ρ, so that $\rho(p) = \rho(-p)$ for all $p \in \mathbb{S}^2$. Using the formula from Appendix A, the fifth order Taylor approximation of $W_c(\cdot,\rho)$ is given, up to an additive constant, as

$$\frac{1}{Nk_BT}W_c^5(R,\rho) = \frac{1}{2(N\ell)^2}|V^{\frac{1}{2}}R|^2 + \frac{1}{24(N\ell)^4}\,(3L\otimes L - M) : (VR)^{\otimes 4}, \tag{4.15}$$

where $u^{\otimes i}$ denotes the tensor product of u with itself i times, and $A : B$ denotes $\sum_{ijkl} A_{ijkl}B_{ijkl}$ for fourth order tensors, L and M are the second and fourth moment of ρ^t respectively and $V = L^{-1}$. The form simplifies significantly from the general expression since all odd ordered moments of ρ vanish due to the head-to-tail symmetry condition, including the fifth-order term.

Consider a polymer network, with cross-linking points $(y_i)_{i\in I}$. Take an affine displacement assumption, so that if the continuum deforms by an affine map $x \mapsto Fx + x_0$ for some matrix F and vector x_0, then the cross-linking points also deform as $y_i \mapsto Fy_i + x_0$. This means that the end to end vectors $(R_{i,j})_{(i,j)\in I'}$, where I' is a subset of $I \times I$, can be written as $R_{ij} = y_i - y_j$ therefore deform as $R_{i,j} \mapsto FR_{i,j}$. The affine-displacement assumption is common in models of isotropic elasticity (see e.g. [14] or [53]). This assumption in particular treats the chains as phantom, neglecting the effects of entanglements and volumetric effects. For this reason only incompressible systems will be considered. Furthermore we assume that the energy of deformation is simply the sum of of the energies of the particular chains. If the distribution of end-to-end vectors in the reference configuration is taken to be some probability measure ν, and $n > 0$ is the number of chains per unit volume, then the energy per unit volume is therefore given as

$$W_D(F,\rho) = n\int_{\mathbb{R}^3} W_c(FR,\rho)\nu(R)\,dR. \tag{4.16}$$

At this point one could couple the energy of ρ in one of two ways. Firstly by adding an Onsager-type contribution to the energy, so that for example

$$W_{\text{total}}(F,\rho) = W_D(F,\rho) + c_1 \int_{\mathbb{S}^2} \rho(p)\ln\rho(p) - \rho(p)\int_{\mathbb{S}^2} K(p\cdot q)\rho(q)\,dq\,dp \tag{4.17}$$

for some appropriate constant c_1 and interaction kernel K. Alternatively, one could constrain ρ to be in the minimising set for an Onsager-type energy, which follows the argument that the nematic contribution to the energy is greater than the elastic energy, and therefore can be minimised independently. The latter approach is many respects simpler since the minimising set is often simply generated by rotations acting on a particular solution, giving finitely many degrees of freedom in one-to-one correspondence with a subset of SO(3). For the sake of this work though the contribution to the energy from the "free" nematic is generally unimportant as we will only be considering W_D.

Substituting the Taylor expansion of the chain energy into the deformation energy thus gives, up to an additive constant,

$$\frac{1}{k_BTNn}W_D^5(F,\rho) = \int_{\mathbb{R}^3}\left(\frac{1}{2(N\ell)^2}|V^{\frac{1}{2}}FR|^2 + \frac{1}{24(N\ell)^4}\left(3L\otimes L - M\right) : (VFR)^{\otimes 4}\right)d\nu(R).$$

Defining L_0 and M_0 to be the second and fourth order moments of ν respectively, and letting $\tilde{F} = VF$ for brevity, this integral can then be expanded as

$$\begin{aligned}&\frac{1}{2(N\ell)^2}|L^{\frac{1}{2}}\tilde{F}(L_0)^{\frac{1}{2}}|^2\\ &+\frac{1}{24(N\ell)^4}\left(3L_{i_1i_2}L_{i_3i_4} - M_{i_1i_2i_3i_4}\right)\tilde{F}_{i_1j_1}\tilde{F}_{i_2j_2}\tilde{F}_{i_3j_3}\tilde{F}_{i_4j_4}(M_0)_{j_1j_2j_3j_4},\end{aligned}$$

where the summation notation is used in the second line. This provides a quartic approximation, depending on the second and fourth moments of ρ^t and ν.

This is similar to the expression given by Mao [36], although in the work of Mao only a priori distributions $\rho^t(p) = \frac{1}{Z}\exp\left(\tilde{h}(p\cdot v)^2\right)$ for $n\in\mathbb{S}^2$ and $\tilde{h}\in\mathbb{R}$ are considered, which puts constraints on the relationships between L and M (the details of which are included in Appendix A of their work). The reader should take note of the difference in notation with the tensor L_0 in this work being proportional to $N\ell_0$ in the notation of Mao, so that the scaling with N is consistent between the two works.

Furthermore, by truncating this to only second order the approximation can be

written as

$$\frac{1}{2(N\ell)^2}|L^{-\frac{1}{2}}FL_0^{\frac{1}{2}}|^2. \tag{4.18}$$

We see that up to a multiplicative constant, this is equivalent to the Neo-Hookean energy for a freely jointed main chain nematic elastomer (see [58, Exercise 3.1]), with the step tensor L determined as the second moment of ρ^t. In particular this allows us to view the Neo-Hookean energy as a small-strain approximation to the energy presented in this work.

Network theories and symmetry

If the chain energy is not replaced with its Taylor approximation then the behaviour will be more dependent on the precise form of ν, rather than just some of its moments if we take deformation energies of the form (4.16). In the examples of isotropic elasticity there are a large number of competing theories (see e.g. [14] for a broad review) that correspond to using the KG energy with an affine displacement assumption, only varying the corresponding probability measure ν. The simplest of such models, such as the 3-chain and 8-chain models (see Section 1.2.3) take a finite number of representative chains, chosen to depend on the principle axes of the deformation gradient F. In the cases of isotropic elasticity, we have the symmetry condition $w_D(S_1FS_2) = w_D(F)$ for all $F \in \mathbb{M}^3$, $S_1, S_2 \in \mathrm{SO}(3)$, corresponding to invariance under rigid motions in the deformed and reference configuration. It is this symmetry condition that allows such simple models using finitely many representatives of the polymer network, whereby such chains are chosen to be functions of the principle stretches. In the case of a nematic elastomer however, anisotropy is the driving force behind interest in these materials, so such a simple argument cannot be used. In this case, we consider analogues of the Wu-Van der Geissen full-network model [59],

$$\frac{1}{4\pi N\ell^2}\int_{\ell\sqrt{N}\mathbb{S}^2} w_c\left(\frac{1}{N\ell}FR\right)\,dR. \tag{4.19}$$

The significant advantage this model provides is that the reference configuration of polymer chains is independent of the deformation gradient and does not rely on isotropy of the energy. Thus we propose a deformation energy given of the form

$$\int_{\ell\sqrt{N}\mathbb{S}^2} W_c\left(\frac{1}{N\ell}FR,\rho)\right)\frac{d\nu}{d\mathcal{H}^2}(R)\,d\mathcal{H}^2(R). \tag{4.20}$$

It is worth emphasising that candidate deformation energies defined in terms of

principle axes cannot be defined since $F \mapsto W_D(F, \rho)$ is not generally expected to be isotropic, however the energy should be frame indifferent as a function of both F and ρ, so that if $S[\rho](p) = \rho(Sp)$ for $S \in \mathrm{SO}(3)$, then we require that

$$W_D(SF, S[\rho]) = W_D(F, \rho), \tag{4.21}$$

corresponding to invariance under rigid deformations in the deformed configuration. The rotations $S \in \mathrm{SO}(3)$ such that $W_D(FS, \rho) = W_D(F, \rho)$ will correspond to the symmetries of the undeformed state.

We can illustrate the finitely extensible nature of the full network by considering a system isotropic at crosslinking, so that $d\nu(R) = \frac{1}{4\pi\ell^2 N} dR$, a straightforward extension of the Wu-Van der Geissen model. A simple change of variables then gives that $W_D(FS, \rho) = W_D(F, \rho)$ for all $S \in \mathrm{SO}(3)$. In this case, if the largest singular value of the deformation gradient F is larger than $\sqrt{N}$, then we have a set $A \subset \ell\sqrt{N}\mathbb{S}^2$ with $\nu(A) > 0$ and $\left|\frac{1}{N\ell} FR\right| > N\ell$ for all $R \in A$. This implies that $\int_{\ell\sqrt{N}\mathbb{S}^2} W_c\left(\frac{1}{N\ell} FR, \rho\right) d\nu(R) = +\infty$, so that the arbitrary deformations are not permitted. Conversely, if the largest singular value of F is strictly less than $\sqrt{N}$, then the energy is finite, so $\sqrt{N}$ as the extensibility limit just as in the Wu and Van der Geissen model from isotropic elasticity. If we take a Wu-Van der Geissen type model and the distribution of chains in the reference configuraiton is taken to be isotropic, the energy of deformation is given by

$$\begin{aligned} W_D(F, \rho) =& \frac{1}{4\pi\ell^2 N} \int_{\ell\sqrt{N}\mathbb{S}^2} W_c\left(FR, \rho\right) \, d\mathcal{H}^2(R) \\ =& \frac{1}{4\pi} \int_{\mathbb{S}^2} W_c\left(\frac{1}{\sqrt{N}} Fp, \rho\right) \, dp. \end{aligned} \tag{4.22}$$

Relevant to minimisation problems, then have the following result.

Proposition 4.2.1. W_D, as defined by (4.22), is lower semicontinuous, so that if $F_j \to F$ and $\rho_j \rightharpoonup \rho$ in L^1, then $\liminf_{j\to\infty} W_D(F_j, \rho_j) \geq W_D(F, \rho)$.

Proof. This is a simply application of Fatou's lemma, combined with the result of Proposition 4.1.3. □

Unsurprisingly, the lower semicontinuity result can then be applied to ensure solutions to minimisation problems.

Corollary 4.2.2. Let $\mathcal{F} : \mathcal{P}(\mathbb{S}^2) \to [0, \infty]$ be an energy function representing a free nematic, such as Onsager's free energy in (1.1), which is coercive and lower semicon-

tinuous with respect to the L^1 topology. Then the effective deformation energy,

$$W_{eff}(F) = \min_{\rho \in \mathcal{P}(\mathbb{S}^2)} W_D(F, \rho) + \mathcal{F}(\rho) \tag{4.23}$$

admits a minimiser ρ^*.

Proof. The result follows by a standard direct method argument. □

Corollary 4.2.3. Let $a \in L^\infty(\mathbb{S}^2, \mathbb{R}^k)$ satisfy the pseudo-Haar condition, $\mathcal{H}^2(\{p \in \mathbb{S}^2 : \xi \cdot a(p) = c\}) = 0$ for all $(\xi, c) \in \mathbb{R}^{k+1} \setminus \{(0,0)\}$. Let $\mathcal{Q}$ denote the set of moments and ρ_b the maximal entropy distribution for a given $b \in \mathcal{Q}$ as in Chapter 2. Let $W : \mathbb{R}^{k\times 3} \to [0, \infty]$ satisfy $c(|A|^p - 1) < W(A)$ for some $p \in (1, \infty)$ and $c > 0$, and $g \in C(\overline{\mathcal{Q}})$. Let $\Omega \subset \mathbb{R}^3$ be open and Lipschitz. Then provided admissible functions exist, there exists solutions to the minimisation problem

$$\min_{y \in W^{1,\infty}, b \in W^{1,p}} \int_\Omega W_D(\nabla y(x), \rho_{b(x)}) + \psi_s(b(x)) + g(b(x)) + W(\nabla b(x))\, dx, \tag{4.24}$$

subject to Dirichlet boundary conditions on b, y.

Proof. Again, the result follows by a direct method argument, noting that if $b_j \rightharpoonup b$ in $W^{1,p}$, then we can take a subsequence with $b_j \to b$ pointwise almost everywhere, so that $\rho_{b_j(x)} \to \rho_{b(x)}$ in L^∞ almost everywhere. □

4.2.1 Limiting strains and admissibility

Using the previously obtained estimates, we can obtain an interesting feature of the Wu-Van der Geissen model (both in the classical isotropic and nematic elastomer context) which puts it at a stark difference to models such as Arruda-Boyce. First we obtain bounds on the growth of the energy, and show that as long as one singular value remains bounded away from the limiting strain $\sqrt{N}$, the energy remains bounded.

Proposition 4.2.4. Let $\rho \in \mathcal{P}(\mathbb{S}^2)$. Let $F \in \mathbb{M}^3$ have singular values $\sqrt{N} \geq l_1 \geq l_2 \geq l_3$, with $l_3 < \sqrt{N}$. Then $W_D(F, \rho) < +\infty$. In particular, the energy can be bounded as

$$W_D(F, \rho) < c_4 - \ln\left(1 - \frac{l_3^2}{N}\right) \tag{4.25}$$

for a constant c_4 depending only on γ.

Proof. Take a basis corresponding to the eigenvectors of $F^T F$, and let $\alpha = \left(\frac{l_3}{\sqrt{N}}\right)^2 \in$

$(0,1)$. In this case, it is known that

$$\begin{aligned}
W_D(F,\rho_U) &\leq c_1 - \frac{1}{4\pi}\int_{\mathbb{S}^2} \ln\left(1-\frac{1}{\sqrt{N}}|Fp|\right)\,dp \\
&\leq c_2 - \frac{1}{4\pi}\int_{\mathbb{S}^2} \ln\left(1-\frac{1}{N}|Fp|^2\right)\,dp \\
&\leq c_2 - \frac{1}{4\pi}\int_{\mathbb{S}^2} \ln\left(1-\frac{l_1^2}{N}(p_1^2+p_2^2-\alpha p_3^2)\right)\,dp \\
&\leq c_2 - \frac{1}{4\pi}\int_{\mathbb{S}^2} \ln\left((1-\alpha)p_3^2\right)\,dp \\
&= c_2 - \frac{1}{2}\int_{-1}^{1} \ln\left((1-\alpha)x^2\right)\,dx \\
&= c_3 - 2\int_0^1 \ln(x)\,dx - \ln(1-\alpha) \\
&= c_4 - \ln(1-\alpha).
\end{aligned}$$

□

Proposition 4.2.5. As before let $F \in \mathbb{M}^3$ have singular values $\sqrt{N} \geq l_1 \geq l_2 \geq l_3$ with $l_3 < \sqrt{N}$. Then the deformation energy can be bounded from below as

$$W_D(F,\rho) \geq c_5 - 4\pi c_1 \ln\left(1-\frac{l_3^2}{N}\right), \tag{4.26}$$

with c_1 as in Proposition 4.1.1 and some $c_5 \in \mathbb{R}$.

Proof. We use the lower bound from the chain energy to give that

$$\begin{aligned}
W_D(F,\rho) \geq& 4\pi c_2 - c_1\int_{\mathbb{S}^2} \ln\left(1-\frac{1}{\sqrt{N}}|Fp|\right)\,dp \\
\geq& c_5 - c_1\int_{\mathbb{S}^2} \ln\left(1-\frac{1}{N}|Fp|^2\right)\,dp \\
\geq& c_5 - c_1\int_{\mathbb{S}^2} \ln\left(1-\frac{l_3^2}{N}\right)\,dp = c_5 - 4\pi c_1 \ln\left(1-\frac{l_3^2}{N}\right).
\end{aligned} \tag{4.27}$$

□

In the case of Arruda-Boyce type models that take a discrete distribution ν to describe chains in the reference configuration, it holds that $W_D(F) \to +\infty$ as F approaches the limiting strain. As the previous results have shown, however, in Wu-Van der Geissen models this is not necessarily the case, since we have finite energy deformations at the limiting strain $v_{\max}(F) = \sqrt{N}$. Importantly, the domain of the

deformation energy is not open. In the context of variational problems this can provide issues with taking variations. In particular, we can find boundary data that forces rigidity in the system so that no variations can be taken.

Let $\Omega \subset \mathbb{R}^3$ be bounded, open and convex. In the following, given $x \in \Omega$, let $t_2 = \inf\{t > 0 : x + te_1 \notin \Omega\}$, and $t_1 = \sup\{t < 0 : x + te_2 \notin \Omega\}$. Note that since Ω is bounded, these are well defined. Furthermore $x_i = x + t_i e_1 \in \partial\Omega$ since x_i can be approximated by elements in the closed set $\mathbb{R}^d \setminus \Omega$, and also that for $t \in (t_1, t_2)$ that $x + te_1 \in \Omega$ which follows from the definition.

Lemma 4.2.6. Let $e \in \mathbb{S}^{d-1}$ and $A \in \mathbb{R}^{d\times d}$. Let $|A|$ denote the operator norm, $\sup_{1\leq i\leq d} |v_i|$. Then $|Ae \cdot e| \leq |A|$ with equality if and only if $Ae = \pm|A|e$.

Proof. This follows immediately from Cauchy-Schwarz and its equality condition along with the definition of the operator norm. □

Lemma 4.2.7. Let $\Omega \subset \mathbb{R}^n$ be a bounded, strictly convex, open set. Let $F \in \mathbb{M}^3$ be positive definite, and choose a frame of reference so that $Fe_1 = v_1 e_1 = v_{\max}(F)e_1$. Let $y \in W^{1,\infty}(\Omega, \mathbb{R}^3)$, so that $v_{\max}(Dy) \leq v_{\max}(F) = v_1$ almost everywhere and $y|_{\partial\Omega} = F$. Then for almost every $x \in \Omega$, $Dy(x)e_1 = v_1 e_1$.

Proof. Assume that there exists some set of positive measure E so that $Dy(x)e_1 \notin \{v_1e_1, -v_1e_1\}$ for almost every $x \in E$. Let E_1 be the intersection of E with the set of lines parallel to e_1 on which y is absolutely continuous. Since $y \in W^{1,1}(\Omega, \mathbb{R}^3)$, E_1 has positive measure. For every $x_0 \in E_1$, we have that $|Dy(x_0)e_1 \cdot e_1| < v_1$. Let x_1, x_2, t_1, t_2 be as before. Then we have that

$$
\begin{aligned}
v_1 =& |Fe_1 \cdot e_1| \\
=& \left| \frac{1}{t_2 - t_1} \left(F(x_0 + t_2 e_1) - F(x_0 + t_1 e_1) \right) \cdot e_1 \right| \\
=& \left| \frac{1}{t_2 - t_1} \left(y(x_{t_2}) - y(x_{t_1}) \right) \cdot e_1 \right| \\
=& \left| \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} \frac{d}{dt} y(x_t)\, dt \cdot e_1 \right| \\
=& \left| \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} Dy(x_t) \dot{x}_t \cdot e_1\, dt \right| \\
=& \left| \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} Dy(x_t) e_1 \cdot e_1\, dt \right| \\
\leq& \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} |Dy(x_t) e_1 \cdot e_1|\, dt \\
<& \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} v_1\, dt \\
=& v_1,
\end{aligned}
$$

where the final inequality is strict due our assumptions, providing a contradiction. This then implies that for every $x \in E_1$, $Dy(x)e_1 \in \{v_1 e_1, -v_1 e_1\}$. Take any line L on which y is absolutely continuous, parallel to e_1, which makes up almost line parallel to e_1. We can write that $Dy(x) = \kappa(x) v_1 e_1$, where $\kappa(x) = \frac{1}{v_1} Dy(x)e_1 \cdot e_1 \in \{+1, -1\}$ everywhere. Let x_1, x_2 denote the upper and lower boundary points with respect to an interior point x. Integrating over L,

$$
\begin{aligned}
(t_2 - t_1) v_1 e_1 =& F(x_2 - x_1) \\
=& \int_{t_1}^{t_2} Dy(x + te_1)\, dx \\
=& v_1 e_1 \int_{t_1}^{t_2} \kappa(x)\, dx \\
\Rightarrow 1 =& \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} \kappa(x)\, dx.
\end{aligned}
$$

This then implies that $\kappa(x) = 1$ almost everywhere. Therefore, $Dy(x)e_1 = v_1 e_1$ for almost every $x \in \Omega$. □

Proposition 4.2.8. Let $\Omega \subset \mathbb{R}^3$ be a strictly convex, bounded and open set. If $y \in W^{1,1}(\Omega, \mathbb{R}^d)$, $y|_{\partial\Omega}(x) = Fx$ and $v_{\max}(Dy(x)) \leq v_{\max}(F)$ for almost every $x \in \Omega$,

then $y(x) = Fx$ for all $x \in \Omega$.

Proof. Let $x \in \Omega$. Let x_1 be the lower boundary point in direction e_1 and $x_1 + t_1 e_1 = x$ as before. Note that $Fe_1 = v_{\max}(F)e_1$. By the fundamental theorem of calculus along lines parallel to e_1 on which y is absolutely continuous, we have that

$$\begin{aligned} y(x) =& y(x_1) + \int_{t_1}^{0} Dy(x_1 + te_1)e_1 \, dt \\ =& Fx_1 + \int_{t_1}^{0} v_{\max}(F)e_1 \, dt \\ =& Fx_1 + t_1 v_{\max}(F)e_1 \\ =& Fx_1 + t_1 Fe_1 \\ =& F(x_1 + t_1 e_1) \\ =& Fx. \end{aligned}$$

□

Theorem 4.2.9. Let $\Omega \subset \mathbb{R}^3$ be a bounded, open, Lipschitz set. If $y \in W^{1,1}(\Omega, \mathbb{R}^3)$, $y|_{\partial\Omega}(x) = Fx$ and $v_{\max}(Dy(x)) \leq v_{\max}(F)$ for almost every $x \in \Omega$, then $y(x) = Fx$ for all $x \in \Omega$.

Proof. Since Ω is Lipschitz and $x \mapsto y(x) - Fx \in W_0^{1,1}(\Omega, \mathbb{R}^3)$, we can extend $\tilde{y}$ by Fx to an open ball B sufficiently large to contain Ω, so that $\tilde{y}|_{B\setminus\Omega}(x) = Fx$ and $\tilde{y} \in W^{1,1}(B, \mathbb{R}^3)$. At which point we apply the previous proposition to give that $\tilde{y}(x) = Fx$ for almost every $x \in B \supset \Omega$. □

Corollary 4.2.10. Let $W : \mathbb{M}^3 \to \mathbb{R}$ be the Wu/Van der Geissen elastic energy with chain length N. Let $\Omega \subset \mathbb{R}^3$ be Lipschitz and bounded. Then the minimisation problem

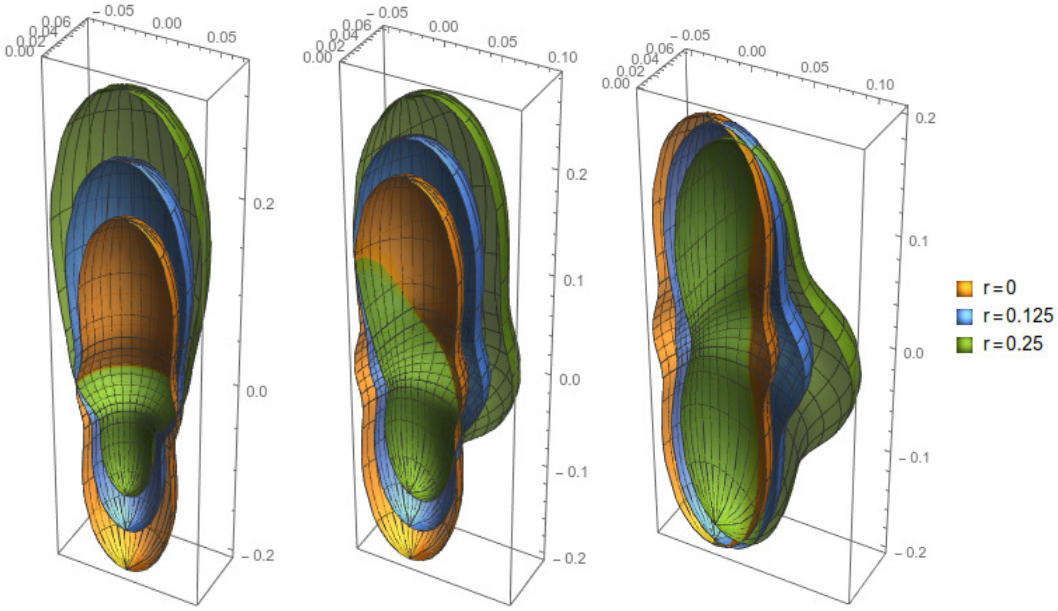
$$\min_{y \in W^{1,1}(\Omega, \mathbb{R}^3)} \int_\Omega W(Dy(x)) \, dx \tag{4.28}$$

subject to boundary condition $y|_{\partial\Omega} = \left(\sqrt{N} n \otimes n + \frac{1}{\sqrt[4]{N}} (I - n \otimes n)\right) x$ for $n \in \mathbb{S}^2$ has only one admissible deformation, given by the linear extension of the boundary data.

Remark 4.2.11. Note that we have neglected any volumetric effects. We can implement volumetric effects in the standard way by including a term in the energy in (4.28) such as $\int_\Omega h(\det(\nabla y(x))) \, dx$ for $h : \mathbb{R} \to [0, \infty]$ convex and lower semicontinuous such that $h(1) < +\infty$, and the result trivially remains true.

4.3 Illustrative figures

For simplicity, only probability distributions of the form $\rho(p) = \frac{1}{z}\exp\left(a(p\cdot u)^2\right)$, where $a \in \mathbb{R}$ and $u \in \mathbb{S}^2$ will be considered for the nematic orientation distribution function. Probability distributions of this form are taken since they correspond to equilibria for the Maier-Saupe free energy [21], with the constant a depending on the temperature. Furthermore due to the axial symmetry this allows simpler 2-dimensional graphics to be produced. In each case we take $N\ell = 1$ to provide a dimensionless version of the chain energy, and arbitrary units are taken. The relatively large number fraction $\gamma = 0.3$ will be taken so that the behaviour is clearly visible.



(a) $\theta = 0$ (b) $\theta = \frac{\pi}{4}$ (c) $\theta = \frac{\pi}{2}$

Figure 4.1: The optimal chain distribution σ for $\frac{1}{N\ell}R = r\left(\cos(\theta)u + \sin(\theta)u^{\perp}\right)$.

In Figure 4.1, we take $\rho(p) = \frac{1}{Z}\exp(5(p\cdot u)^2)$. The corresponding Q-tensor for ρ has distinguished eigenvalue of $\lambda \approx 0.431$. The unit vector $u^{\perp}$ is taken so that $u \cdot u^{\perp} = 0$. The figure demonstrates the optimal orientation distribution σ for various values of the nematic director and chain length. The three figures all show the expected symmetry, as well as elongation in the direction of R as $\frac{1}{N\ell}|R| = r$ increases.

In Figure 4.2 a plot in polar coordinates of $W_c\left(\frac{1}{2}e_\theta, \rho_\lambda\right)$ is shown, where $e_\theta = (\cos(\theta), \sin(\theta), 0)$, and ρ_λ is of the form given previously with its corresponding Q-tensor having distinguished eigenvalue λ, and corresponding eigenvector $n = e_0$. The coordinate direction e_0 is shown by the arrow on the figure. The figure illustrates that in a prolate nematic phase, stronger alignment of the nematic gives stronger preference

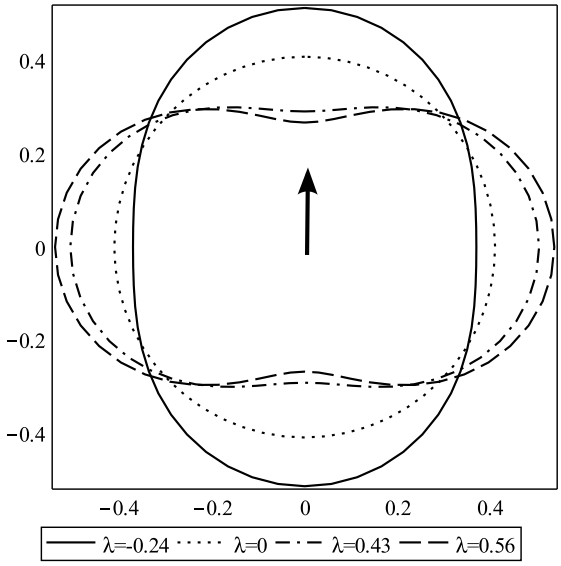
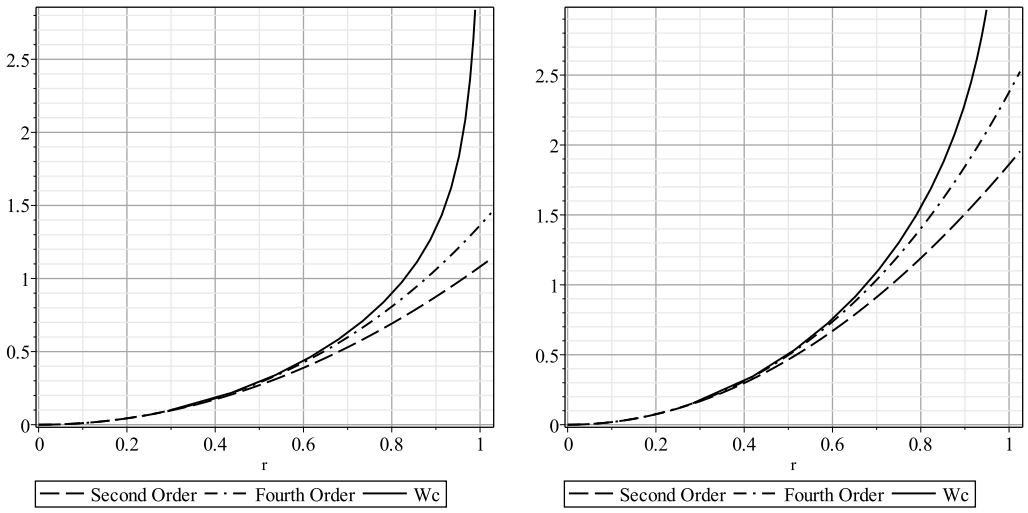


Figure 4.2: $W_c\left(\frac{1}{2}e_\theta, \rho_\lambda\right)$, for various values of λ.

to the chain aligning parallel to the director, and with oblate nematics there is an energetic preference for the chain to be perpendicular to the director. The heuristics to understand why this happens is that, particularly for larger $|R|$, any σ such that $\int_{\mathbb{S}^2} p\sigma(p)\,dp = \frac{1}{N\ell}R$ must be large in the region where $p \approx \frac{R}{|R|}$ (Proposition 2.1.12). In the KG-model this would give a high energy, however in the anisotropic model the energy can be lowered if $\rho^t(p)$ is also large in the same region. This suggests for R with fixed length but variable orientation, $W_c(R, \rho)$ will be lower in regions where $\rho^t\left(\frac{R}{|R|}\right)$ is larger.

In Figure 4.3 again $\rho(p) = \frac{1}{Z}\exp(5(p \cdot u)^2)$ is taken. The figure shows $r = |R|$ against the energy, with $\hat{R}$ either parallel or perpendicular to the nematic alignment. The asymptote at $|R| = 1$ is shown in dashed grey, and the second and fourth Taylor approximations are also included for comparison. Just as in the Neo-Hookean model, the true chain energy and its approximations show that the energetic preference is for the chain to be aligned with the nematic. Furthermore, similarly to the case in isotropic elasticity (see [53]) it can be seen that the second order approximation is accurate up to around a third of the maximum extension.

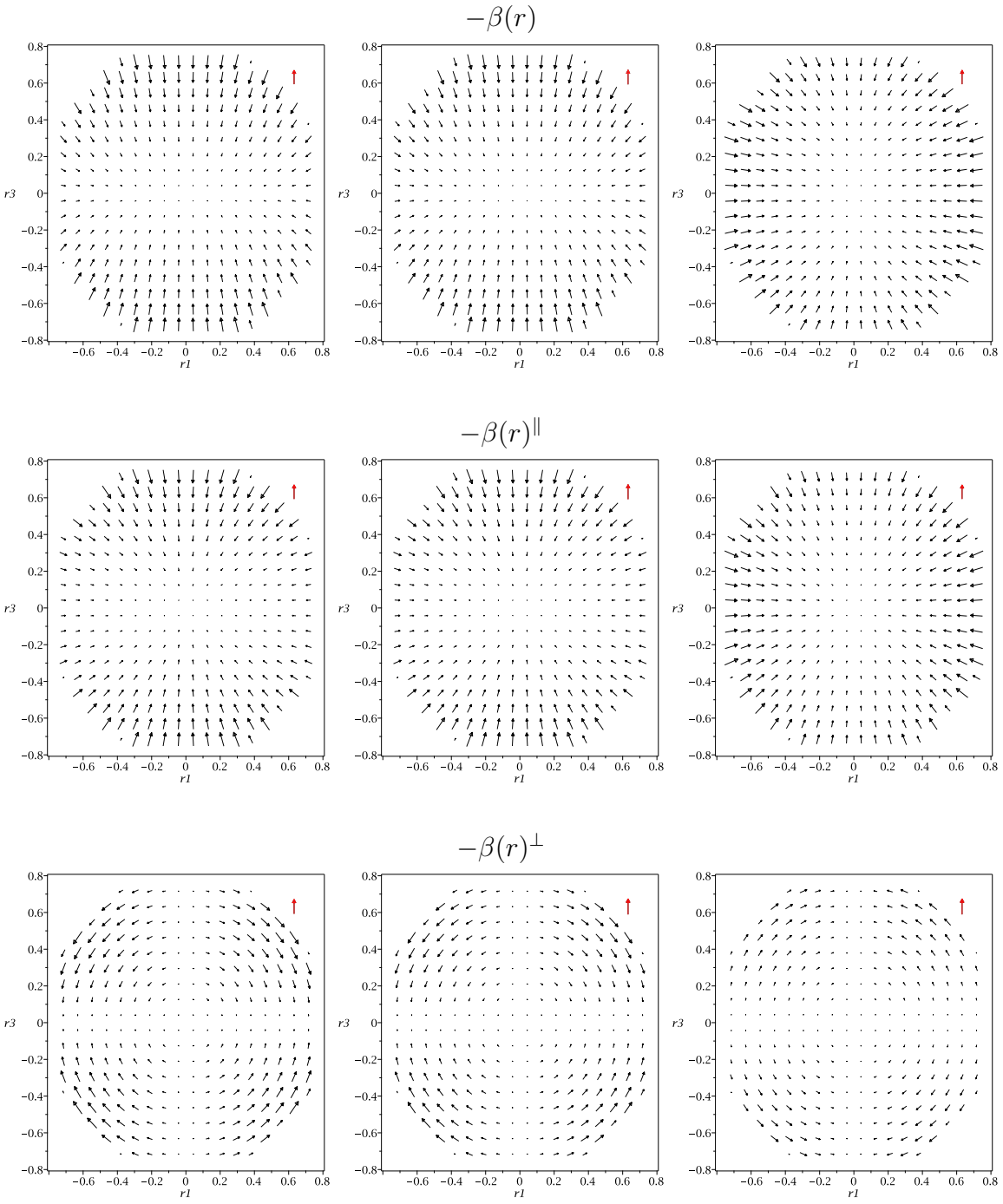
In Figure 4.4 the tension, represented by $-\beta(R)$, acting on chains with end-to-end vectors $R = r_1e_1 + r_3e_3$ are shown for various nematic orders, given by uniaxial distributions $\rho(p) = \frac{1}{Z}\exp\left(a(p \cdot e_1)^2\right)$ and concentration $\gamma = 0.3$. The different nematic orders are indexed by the distinct eigenvalue of their corresponding Q-tensor $\lambda(Q)$. In order to greater demonstrate the anisotropy of the stresses, further plots are shown



(a) Parallel alignment (b) Perpendicular alignment

Figure 4.3: The "full" finitely extensible chain energy and its approximations with parallel and perpendicular alignment.

with the radial components $-\beta^(R) \|= \frac{1}{|R|^2}(-\beta(R)\cdot R)R$ and tangential components $-\beta(R)^\perp = \left(\frac{1}{|R|^2}R\otimes R - I\right)\beta(R)$. For scale, red arrows are included representing $5e_3$ in the plots for $-\beta(R), -\beta(R)^\|$ and representing $\frac{3}{2}e_3$ in the plots for $-\beta(R)^\perp$. From these illustrations we see the tendency that the tension is generally lower in directions aligned with prolate nematic order and against oblate nematic order. The significance of $-\beta(R)^\perp$ is that it is a strong representative of the anisotropy of the system, since if β were isotropic the tension would act parallel to the end-to-end vector. In the plots for $\beta(R)^\perp$ we see that the anisotropic part of the tension has a clear desire to force the chain towards aligning with a prolate nematic ordering or against an oblate nematic ordering.



(a) $\lambda(Q) \approx 0.546$ (b) $\lambda(Q) \approx 0.431$ (c) $\lambda(Q) \approx -0.235$

Figure 4.4: The stresses $-\beta$, their radial and tangential components for varying degrees of nematic order

Appendix A

Fourth order Taylor approximation of the singular potential

For this section consider the pseudo-Haar constraint functions $(a_i)_{i=1}^k$ to be orthogonal to the constant function so that $\int_X a_i \, d\mu = 0$, but not necessarily orthogonal to each other. Furthermore the in this section the convention that Greek indices are summed over, whilst Latin indices are free, is used. Given $n \in \mathbb{N}$ and $\rho \in \mathcal{P}(X)$ define the tensor $M^n \in \mathbb{R}^{k^n}$ component-wise by

$$M^n_{i_1 i_2 \ldots i_n}(\rho) = \int_X a_{i_1} a_{i_2} \ldots a_{i_n} \rho \, d\mu. \tag{A.1}$$

for $i_j = 1, .., k$, $j = 1, ..n,$. Consider the function $b \mapsto M^n(\rho_b)$, which when unambiguous will simply be denoted M^n, with ρ_b maximal entropy under the Shannon entropy $\phi(x) = x \ln x$. This allows any maximal entropy $\rho \in \mathcal{P}(X)$ to be written as

$$\rho(t) = \frac{1}{Z} \exp\left(\lambda \cdot a(t)\right). \tag{A.2}$$

The map $b \mapsto M^n(\rho_b)$ is differentiable, so by applying the chain rule the derivative can be found as

$$\begin{aligned} \frac{\partial M^n_{i_1 i_2 \ldots i_n}}{\partial b_{i_{n+1}}} &= \frac{\partial M^n_{i_1 i_2 \ldots i_n}}{\partial \lambda_\alpha} \frac{\partial \lambda_\alpha}{\partial b_{i_{n+1}}} \\ &= \left(\int_X a_{i_1} a_{i_2} \ldots a_{i_n} a_\alpha \rho_b \, d\mu - \frac{1}{Z} M^n_{i_1 i_2 \ldots i_n} \frac{\partial Z}{\partial \lambda_\alpha} \right) \left((M^2 - b \otimes b)^{-1} \right)_{\alpha i_{n+1}} \\ &= \left(M^{n+1}_{i_1 i_2 \ldots i_n i_\alpha} - M^n_{i_1 i_2 \ldots i_n} b_\alpha \right) V_{\alpha i_{n+1}} \end{aligned} \tag{A.3}$$

where for brevity $V = (M^2 - b \otimes b)^{-1}$. That the derivatives can be seen to satisfy this by applying Propositions 2.2.7 and 2.2.8 with some elementary calculus. From here it is now possible to perform a Taylor expansion of ψ_s to low order. Immediately it holds that $\psi_s(0) = -\frac{1}{\mu(X)} \ln(\mu(X))$. For the first derivative it was shown in Proposition 2.2.8 that

$$\frac{\partial \psi_s}{\partial b_i}(b) = \lambda_i. \tag{A.4}$$

Using the strict convexity of ϕ, it is immediate that the uniform distribution is the global entropy minimiser of $\mathcal{P}(X)$, so that in particular $\frac{1}{\mu(X)} = \rho_b(t)$ for $b = 0$ and almost every $t \in X$. By rewriting the uniform distribution on X as $\frac{1}{\mu(X)} = (\phi')^{-1}(\alpha + \lambda \cdot a(t))$ for $\lambda = 0$ and $\alpha = (\phi')\,(\mu(X)^{-1})$ demonstrates that $\lambda(0) = 0$, so that

$$\frac{\partial \psi_s}{\partial b_i}(0) = 0.$$

Furthermore this gives that $b = 0$ is always a critical point for ψ_s and for any truncated Taylor expansion of ψ_s about $b = 0$ with order greater than or equal to 1. For the second derivative it has been seen in Prop. 2.2.10 that

$$\begin{aligned} \frac{\partial^2 \psi_s}{\partial b_{i_1} \partial b_{i_2}}(b) &= \left(\left(M^2(b) - b \otimes b \right)^{-1} \right)_{i_1 i_2} \\ \Rightarrow \frac{\partial^2 \psi_s}{\partial b_{i_1} \partial b_{i_2}}(0) &= \left(\left(M^2(0) \right)^{-1} \right)_{i_1 i_2}. \end{aligned} \tag{A.5}$$

As seen before, this is necessarily a positive definite matrix, and consequently $b = 0$ is always a local minimum for ψ_s and any Taylor expansion of order greater than or equal to 2. For the third derivative first note that the derivative of V will have to be taken and since this involves a matrix inverse a more complex expression appears,

$$\begin{aligned} \frac{\partial V_{i_1 i_2}}{\partial b_{i_3}} &= -V_{i_1 \alpha_1} V_{i_2 \alpha_2} \frac{\partial M^2_{\alpha_1 \alpha_2} - b_{\alpha_1} b_{\alpha_2}}{\partial b_{i_3}} \\ &= -V_{\alpha_1 i_1} V_{\alpha_2 i_2} V_{\alpha_3 i_3} \left(M^3_{\alpha_1 \alpha_2 \alpha_3} - b_{\alpha_1} M^2_{\alpha_2 \alpha_3} - b_{\alpha_2} M^2_{\alpha_1 \alpha_3} - b_{\alpha_3} M^2_{\alpha_1 \alpha_2} \right). \end{aligned} \tag{A.6}$$

This gives that the third derivative at $b = 0$ can be given by

$$\frac{\partial^3 \psi_s}{\partial b_{i_1} \partial b_{i_2} \partial b_{i_3}}(0) = -V_{i_1 \alpha_1}(0) V_{i_2 \alpha_2}(0) V_{i_3 \alpha_3}(0) M^3_{\alpha_1 \alpha_2 \alpha_3}(0). \tag{A.7}$$

Since the Taylor expansion will only be taken to fourth order, and the expansion is to be performed around $b = 0$, all terms with factors of b will be denoted as Ab, which can later be neglected in calculating the fourth derivative of ψ_s at $b = 0$. It can be

given as

$$\begin{aligned}\frac{\partial^4 \psi_s}{\partial b_{i_1} \partial b_{i_2} \partial b_{i_3} \partial b_{i_4}} &= V_{i_1\beta_1} V_{i_2\alpha_2} V_{i_3\alpha_3} V_{i_4\beta_3} V_{\alpha_1\beta_2} M^3_{\alpha_1\alpha_2\alpha_3} M^3_{\beta_1\beta_2\beta_3} \\ &+ V_{i_1\alpha_1} V_{i_2\beta_1} V_{i_3\alpha_3} V_{i_4\beta_3} V_{\alpha_2\beta_2} M^3_{\alpha_1\alpha_2\alpha_3} M^3_{\beta_1\beta_2\beta_3} \\ &+ V_{i_1\alpha_1} V_{i_2\alpha_2} V_{i_3\beta_1} V_{i_4\beta_3} V_{\alpha_3\beta_2} M^3_{\alpha_1\alpha_2\alpha_3} M^3_{\beta_1\beta_2\beta_3} \\ &- (V_{i_1\alpha_1} V_{i_2\alpha_2} V_{i_3\alpha_3} V_{i_4\alpha_4}) \\ &\times \left(M^4_{\alpha_1\alpha_2\alpha_3\alpha_4} - M^2_{\alpha_1\alpha_2} M^2_{\alpha_3\alpha_4} - M^2_{\alpha_1\alpha_3} M^2_{\alpha_2\alpha_4} - M^2_{\alpha_1\alpha_4} M^2_{\alpha_2\alpha_3} \right) \\ &+ Ab. \end{aligned} \tag{A.8}$$

At the isotropic state it must hold that $Ab = 0$, so that the fourth derivative at $b = 0$ is given by the remaining terms.

Appendix B

Codes Used

The following codes were all written and executed in Maple 17 for producing the illustrative figures within this work.

McMillan Numerics

Order parameters and energy.

Our constraint functions

> $a := (x, z) \to \left[\frac{1}{2} \cdot \left(3\,x^2 - 1\right),\ \frac{1}{2} \cdot \left(3\,x^2 - 1\right) \cdot \cos(2 \cdot \mathrm{Pi} \cdot z) \right]$:

Defining the order parameters as functions of the dual variables.

> $Z := (l1, l2) \to evalf\left(Int\left(\exp(l1 \cdot a(x, z)[1] + l2 \cdot a(x, z)[2]), x = -1..1, z = 0..1\right)\right)$:

> $S := (l1, l2, zed) \to \frac{1}{zed} \cdot evalf\left(Int\left(\exp(l1 \cdot a(x, z)[1] + l2 \cdot a(x, z)[2]\right) \cdot a(x, z)[1], x = -1..1, z = 0..1\right)\right)$:

> $\mathrm{Sigma} := (l1, l2, zed) \to \frac{1}{zed} \cdot evalf\left(Int\left(\exp(l1 \cdot a(x, z)[1] + l2 \cdot a(x, z)[2]\right) \cdot a(x, z)[2], x = -1..1, z = 0..1\right)\right)$:

The energy as a function of the dual variables.

```
> F := proc(l1, l2, T, alpha)
    local s, sigma, zed;
    zed := Z(l1, l2);
    s := S(l1, l2, zed);
    sigma := Sigma(l1, l2, zed);
    return( [s, sigma, T·(s·l1 + sigma·l2 − ln(zed)) − 1/2·(s^2 + alpha·σ^2)] );
    end proc:
```

Produce an array of the energy as a function of the dual variables.

```
> dualEnergy := proc(l1low, l1high, l2low, l2high, steps, T, alpha)
    local X1, X2, Y;
    X1 := [seq(l1low + (i·(l1high − l1low))/(steps − 1), i = 0..steps − 1)];
    X2 := [seq(l2low + (i·(l2high − l1low))/(steps − 1), i = 0..steps − 1)];
    Y := [seq([seq(F(l1low + (i·(l1high − l1low))/(steps − 1), l2low + (j·(l2high − l2low))/(steps − 1), T,
      alpha)[3], i = 0..steps − 1)], j = 0..steps − 1)];
    return( [X1, X2, Y] );
    end proc:
```

A single step of the gradient ascent iteration for finding the dual variables corresponding to a given order parameter.

```
> findL1step := proc(s, sigma, l10, l20, delta)
    local l1, l2, zed;
    zed := Z(l10, l20);
```

```
    l1 := l10 + delta·(s − S(l10, l20, zed));
    l2 := l20 + delta·(sigma − Sigma(l10, l20, zed));
    return([l1, l2]);
    end proc:
```

The repeated gradient ascent iteration for finding the dual variables. Terminates when first order conditions are zero to within a tolerance of 10^-4.

```
> findL := proc(s, sigma, delta)
    local test, l1, l2, X;
    l1 := s;
    l2 := sigma;
    test := 1;
    while test > 10^-4 do;
    X := findL1step(s, sigma, l1, l2, delta);
    test := sqrt((l1 − X[1])^2 + (l2 − X[2])^2);
    l1 := X[1];
    l2 := X[2];
    end do;
    return([l1, l2]);
    end proc:
```

Proceedure for producing an array of dual variables corresponding to order parameters, with tolerance so we do not compute too close to the boundary where the numerics become less stable.

```
> manyL := proc(steps, delta)
    local i, j, s, sigma, X, Y, t;
    X := [ ];
    for i from 0 to steps − 1 do;
    print(i);
    s := -0.45 + (i·(0.9 + 0.45))/(steps − 1);
    Y := [findL(s, 0, delta)];
    for j from 1 to floor(steps/2) do;
    sigma := (j·0.9)/floor(steps/2);
    if |sigma| < (s + 2)/3 − 0.075 then;
    t := findL(s, sigma, delta);
    Y := [t, op(Y), t];
    else;
    Y := [op(Y), [0, 0]];
    end if;
    end do;
    X := [op(X), Y];
    end do;
    return(X);
    end proc:
```

Numerically approximating the singular potential

```
> psiS := proc(s, sigma)
  local X, l1, l2;
  X := findL(s, sigma, 0.5);
  l1 := X[1];
  l2 := X[2];
  return(s·l1 + sigma·l2 − ln(Z(l1, l2)));
  end proc:
```

Proceedure for generating an array of values of the singular potential.

```
> manypsiS := proc(steps)
  local i, j, s, sigma, X, Y, t;
  X := [ ];
  for i from 0 to steps − 1 do;
  print(i);
  s := -0.4 + i·(0.85 + 0.4) / (steps − 1);
  Y := [psiS(s, 0)];
  for j from 1 to floor(steps / 2) do;
  sigma := j·0.85 / floor(steps / 2);
  if |sigma| < (s + 2) / 3 − 0.1 then;
  t := psiS(s, sigma, delta);
  Y := [t, op(Y), t];
  else;
  Y := [0, op(Y), 0];
  end if;
  end do;
  X := [op(X), Y];
  end do;
  return(X);
  end proc:
```

A single iteration for the gradient ascent for the Yosida-Moreau approximation

```
> findL1stepYM := proc(s, sigma, a0, l10, l20, delta, J)
  local a, l1, l2;
  l1 := l10 + delta·(s − S(l10, l20, exp(1 − a0)) − (1/J)·l10);
  l2 := l20 + delta·(sigma − Sigma(l10, l20, exp(1 − a0)) − (1/J)·l20);
  a := a0 + delta·(1 − exp(a − 1)·evalf(Int(exp(l1·a(x, z)[1] + l2·a(x, z)[2]), x = -1
       ..1, z = -1 ..1)));
  return([a, l1, l2]);
  end proc:
```

Repeating the iteration until the first order condition is within a tolerance of 10^-4

```
> findLYM := proc(s, sigma, delta, J)
```

```
local test, a, l1, l2, X;
a := 1;
l1 := s;
l2 := sigma;
test := 1;
while test > 10^-4 do;
 X := findL1step(s, sigma, l1, l2, delta, J);
test := sqrt( (a - X[1])^2 + (l1 - X[2])^2 + (l2 - X[3])^2);
a := X[1];
l1 := X[2];
l2 := X[3];
end do;
return([al1, l2]);
end proc:
```

Evaluating the Yosida-Moreau regularisation

```
> psiYM := proc(s, sigma, J)
  local X, l1, l2, a;
  X := findLYM(s, sigma, 0.5, J);
  a := X[1];
  l1 := X[2];
  l2 := X[3];
  return( a + l1·s + l2·sigma - evalf(Int(exp(a - 1 + l1·a(x, z)[1] + l2·a(x, z)[2]), x =
      -1..1, z = 0..1)) - 1/(2 J) · (l1^2 + l2^2) );
  end proc:
```

Taylor expansion for McMillan

Defining the moment tensors at the uniform state, necessary for the expansion.

```
> Emptytensor := proc(n)
  local A, i, B;
  A := [];
  for i from 1 to 2 do;
  A := [op(A), 0];
  end do;
  for i from 1 to n - 1 do;
  A := [A, A];
  end do;
  return(A);
  end proc:
```

Start with the second order tensor and its inverse, to make the second order coefficients v2.

```
> M2 := (i, j) → int(a(x, z)[i]·a(x, z)[j], x = -1..1, z = 0..1) / 2 :
```

```
> with(LinearAlgebra) :
> m2 := Matrix([[M2(1, 1), M2(2, 1)], [M2(1, 2), M2(2, 2)]]) :
> V2 := MatrixInverse(m2) :
```

```
> v2 := V2 :
```

Then the third order tensor, which is then used to form the third order coefficients v3.

```
> M3 := (i, j, k) → int(a(x, z)[i]·a(x, z)[j]·a(x, z)[k], x = -1..1, z = 0..1) / 2 :
> makem3 := proc(dummy)
  local A, i, j, k;
  A := Emptytensor(3);
  for i from 1 to 2 do;
  for j from 1 to 2 do;
  for k from 1 to 2 do;
  A[i, j, k] := M3(i, j, k);
  end do;
  end do;
  end do;
  return(A);
  end proc:
> m3 := makem3(dummy) :
> V3 := (i, j, k) → -add(add(add(v2[i, a1]·v2[j, a2]·v2[k, a3]·m3[a1, a2, a3], a1 = 1
      ..2), a2 = 1..2), a3 = 1..2) :
> makev3 := proc(dsa)
  local A, i, j, k;
  A := Emptytensor(3);
  for i from 1 to 2 do;
  for j from 1 to 2 do;
  for k from 1 to 2 do;
  A[i, j, k] := V3(i, j, k);
  end do;
  end do;
  end do;
  return(A);
  end proc:
> v3 := makev3(dummy) :
```

The fourth moment tensor is made, and used to make the fourth order coefficients v4.

```
> M4 := (i, j, k, l)
      → int(a(x, z)[i]·a(x, z)[j]·a(x, z)[k]·a(x, z)[l], x = -1..1, z = 0..1) / 2 :
> makem4 := proc(dummy)
  local A, i, j, k, l;
  A := Emptytensor(4);
  for i from 1 to 2 do;
  for j from 1 to 2 do;
  for k from 1 to 2 do;
  for l from 1 to 2 do;
  A[i, j, k, l] := M4(i, j, k, l);
  end do;
  end do;
  end do;
  end do;
```

```
    return(A);
    end proc:
> m4 := makem4(dummy) :
> V4 := (i,j,k,l)→add(add(add(add(add(add((v2[i,b1]·v2[j,a2]·v2[k,a3]·v2[l,
      b3]·v2[a1,b2]+v2[i,a1]·v2[j,b1]·v2[k,a3]·v2[l,b3]·v2[a2,b2]+v2[i,a1]
      ·v2[j,a2]·v2[k,b1]·v2[l,b3]·v2[a3,b2])·m3[a1,a2,a3]·m3[b1,b2,b3],a1=1
      ..2),a2=1..2),a3=1..2),b1=1..2),b2=1..2),b3=1..2)
      -add(add(add(add(v2[i,a1]·v2[j,a2]·v2[k,a3]·v2[l,a4]·(m4[a1,a2,a3,a4]
      -m2[a1,a4]·m2[a2,a3]-m2[a1,a2]·m2[a3,a4]-m2[a1,a3]·m2[a2,a4]),
      a1=1..2),a2=1..2),a3=1..2),a4=1..2) :
> makev4 :=proc(dummy)
    local A,i,j,k,l;
    A := Emptytensor(4);
    for i from 1 to 2 do;
    for j from 1 to 2 do;
    for k from 1 to 2 do;
    for l from 1 to 2 do;
    A[i,j,k,l] := V4(i,j,k,l);
    end do;
    end do;
    end do;
    end do;
    return(A);
    end proc:
> v4 := makev4(dummy) :

Now the fourth order approximation can be produced by combining the coefficients.

> psi4 := X→1/4! add(add(add(add(v4[i,j,k,l]·X[i]·X[j]·X[k]·X[l],i=1..2),j=1
      ..2),k=1..2),l=1..2)+1/3! add(add(add(v3[i,j,k]·X[i]·X[j]·X[k],i=1
      ..2),j=1..2),k=1..2)+1/2! add(add(v2[i,j]·X[i]·X[j],i=1..2),j=1..2) :

> psi4([s,sigma])
      425/196 s^4+50/49 σ^2 s^2+825/196 σ^4-25/21 s^3-50/7 σ^2 s+5/2 s^2+5 σ^2      (1.1.1.1)
```

Pressure plots

```
> a := x -> 1/2 * (3*x^2 - 1) :
> m := x -> piecewise(x > 0, 1) :
> ch := x -> x*m(x) :
>
```

A single step of the fixed point iteration on the equilibrium equation.

```
> oneStep := proc(s, l, eta)
    local S, L, Z;
    Z := evalf(Int(exp(3/2 * l*a(x)) * ch(s*a(x) - eta), x = -1..1, digits = 6));
    S := 1/Z * evalf(Int(a(x)*exp(l*a(x))*ch(s*a(x) - eta), x = -1..1, digits = 6));
    L := 1/Z * evalf(Int(a(x)*exp(l*a(x))*m(s*a(x) - eta), x = -1..1, digits = 6));
    return(S, L);
    end proc:
>
```

The full fixed point iteration subject to given initial condition, until the equilibrium equation is satisfied to a given tolerance.

```
> iterStep := proc(s0, l0, eta)
    local X, i, err, s, l;
    s := s0;
    l := l0;
    err := 1;
    while err > 10^(-3) do;
    X := oneStep(s, l, eta);
    err := sqrt((s - X[1])^2 + (l - X[2])^2);
    s := X[1];
    l := X[2];
    end do;
    return([s, l]);
    end proc:
>
```

The dimensionless pressure for a given solution.

```
> VdW := (s, l, eta) -> 1/evalf(Int(exp(l*a(x))*ch(s*a(x) - eta), x = -1..1)) *
      evalf(Int(exp(l*a(x))*m(s*a(x) - eta), x = -1..1)) :
>
```

A proceedure for generating the locally stable prolate branch of the phase diagram.

```
> ManyIterationsHigh := proc(etalow, etahigh, etasteps)
    local Pressures, s, l, eta, OPs, Ss, Ls;
    OPs := [seq([2/3 * (etalow + i*(etahigh - etalow)/(etasteps - 1))],
      op(iterStep(0.95, 0.5, etalow + i*(etahigh - etalow)/(etasteps - 1))),
      i = 0..etasteps - 1)];
```

$$Ss := [seq([OPs[i,1], OPs[i,2]], i = 1..etasteps)];$$
$$Ls := [seq([OPs[i,1], OPs[i,3]], i = 1..etasteps)];$$
$$Pressures := \left[seq\left(\left[OPs[i,1], VdW\left(OPs[i,2], OPs[i,3], \frac{3}{2}\, OPs[i,1]\right)\right], i = 1..nops(OPs)\right)\right];$$

return([*OPs*, *Pressures*, *Ss*, *Ls*]);
end proc:

A proceedure for generating the locally stable oblate branch of the phase diagram

> *ManyIterationsLow* := **proc**(*etalow*, *etahigh*, *etasteps*)
local *Pressures*, *s*, *l*, eta, *OPs*, *Ss*, *Ls*;

$$OPs := \left[seq\left(\left[\frac{2}{3}\left(etalow + \frac{i\cdot(etahigh - etalow)}{etasteps - 1}\right), op\left(iterStep\left(-0.45, -0.5, etalow + \frac{i\cdot(etahigh - etalow)}{etasteps - 1}\right)\right)\right], i = 0..etasteps - 1\right)\right];$$

$$Ss := [seq([OPs[i,1], OPs[i,2]], i = 1..etasteps)];$$
$$Ls := [seq([OPs[i,1], OPs[i,3]], i = 1..etasteps)];$$
$$Pressures := \left[seq\left(\left[OPs[i,1], VdW\left(OPs[i,2], OPs[i,3], \frac{3}{2}\, OPs[i,1]\right)\right], i = 1..nops(OPs)\right)\right];$$

return([*OPs*, *Pressures*, *Ss*, *Ls*]);
end proc:

Generating the solutions on the three stable branches

> $SolutionsProlate := ManyIterationsHigh(-0.23, 0.925, 40):$

> $$SolutionsIsotropic := \left[seq\left(\left[\frac{2}{3}\cdot\left(-0.5 + \frac{i\cdot(0.5 - 0.04)}{30}\right), VdW\left(0, 0, -0.5 + \frac{i\cdot(0.5 - 0.04)}{30}\right)\right], i = 0..30\right)\right]:$$

> $SolutionsOblate := ManyIterationsLow(-0.22, 0.19, 22):$

Obtaining the first estimate given the equilibrium order parameter

> $$FirstEstimateProlate := \left[seq\left(\left[SolutionsProlate[3,i,1], \frac{1}{(SolutionsProlate[3,i,2])^2 - \frac{3}{2}\, SolutionsProlate[3,i,1]}\right], i = 1..nops(X[3])\right)\right]:$$

> $$FirstEstimateOblate := \left[seq\left(\left[SolutionsOblate[3,i,1], \frac{1}{(SolutionsOblate[3,i,2])^2 - \frac{3}{2}\, SolutionsOblate[3,i,1]}\right], i = 1..nops(Z[3])\right)\right]:$$

Finite Extensibility Numerics

The Energy and Dual Variables

Defining the concentration and basic functions.

```
> c := 0.3 :
> Z := (b1, b2) → evalf(Int(exp(b1·cos(t)^2 + b2·sin(t)^2·sin(p)^2)·sin(t), t = 0..Pi, p = 0..2·Pi)) :
> rho := (t, p, b1, b2, z) → 1/z·exp(b1·cos(t)^2 + b2·sin(t)^2·sin(p)^2) :
> with(LinearAlgebra) :
>
```

Unit vectors in spherical coordinates and inner products.

```
> u := (t, p) → Matrix([[cos(t)], [sin(t)·sin(p)], [sin(t)·cos(p)]]) :
> d := (u, v) → (Transpose(u).v)[1, 1] :
>
```

One step of the gradient ascent iteration.

```
> dual1step := proc(r, l0, a0, b1, b2, z)
  local l, a;
  l := evalf(l0 + 1·(r − evalf(map(Int, u(t, p)·exp(a0 − 1 + d(l0, u(t, p)))·sin(t)
      ·((1 − c)/(4·Pi) + c·rho(t, p, b1, b2, z)), t = 0..Pi, p = 0..2·Pi, digits = 6)))));
  a := evalf(a0 + 1·(1 − evalf(Int(exp(a0 − 1 + d(l0, u(t, p)))·sin(t)·((1 − c)/(4·Pi) + c
      ·rho(t, p, b1, b2, z)), t = 0..Pi, p = 0..2·Pi, digits = 6)))));
  return([l, a]);
  end proc:
>
```

Iterating the gradient ascent to within a tolerance of 10^-2

```
> dualnstep := proc(r, b1, b2, z)
  local i, l, a, X, l0, test, a0;
  l := r;
  a := 1;
  l0 := r;
  a0 := a;
  test := 1;
  while test > 10^-2 do
  X := dual1step(r, l, a, b1, b2, z);
  l := X[1];
  a := X[2];
  test := evalf(sqrt(d(l − l0, l − l0) + (a − a0)^2));
  l0 := l;
  a0 := a;
  end do;
  return([l, a]);
```

```
end proc:
>
```

Evaluating the chain energy

```
> Wc := proc(r, b1, b2, z)
  local l, a, X;
  X := dualnstep(r, b1, b2, z);
  l := X[1];
  a := X[2];
  return(evalf(d(l, r) + a - evalf(Int(exp(a - 1 + d(l, u(t, p)))·sin(t)·((1 - c)/(4 Pi)
      + c·rho(t, p, b1, b2, z)), t = 0..Pi, p = 0..2·Pi))));
  end proc:
>
```

Taylor Expansion

Numerically evaluating the coefficients for the Taylor approximation.

```
> makeL := (b1, b2, z) → evalf(map(Int, u(t, p).Transpose(u(t, p))·((1 - c)/(4 Pi) + c
      ·rho(t, p, b1, b2, z))·sin(t), t = 0..Pi, p = 0..2·Pi, digits = 8))
> makeM := proc(b1, b2, z)
  local A, i, j, k, l;
  A := [0, 0, 0];
  for i from 1 to 3 do;
  A := [A, A, A];
  end do;
  for i from 1 to 3 do;
  for j from 1 to 3 do;
  for k from 1 to 3 do;
  for l from 1 to 3 do;
  A[i, j, k, l] := evalf(Int((u(t, p)[i, 1])·(u(t, p)[j, 1])·(u(t, p)[k, 1])·(u(t, p)[l, 1])
      ·((1 - c)/(4 Pi) + c·rho(t, p, b1, b2, z))·sin(t), t = 0..Pi, p = 0..2·Pi, digits = 8));
  end do;
  end do;
  end do;
  end do;
  return(A);
  end proc:
> Wc4ish := (R, V, L, M) → (1/24)·add(add(add(add((3 L[i, j]·L[k, l] - M[i, j, k, l])·((V
      .R)[i, 1])·((V.R)[j, 1])·((V.R)[k, 1])·((V.R)[l, 1]), i = 1..3), j = 1..3), k = 1..3)
      , l = 1..3):
> Wc2 := (R, V) → (1/2)·d(V.R, R):
>
```

Comparison of Approximations

Evaluating the second and fourth order approximations along fixed directions. By splitting into homogeneous parts the calculation is simplified.

```
> makeWc2 := proc(b1, b2, T, P, steps, Rhigh)
   local K, V, z, X, U, i, r, Thing;
   z := Z(b1, b2);
   U := u(T, P);
   V := MatrixInverse(makeL(b1, b2, z));
   X := [ ];
   Thing := Wc2(U, V);
  return(Thing)
   end proc:
```

```
> makeWc4 := proc(b1, b2, T, P, steps, Rhigh)
   local K, V, z, X, U, i, r, L, M, Thing;
   z := Z(b1, b2);
   U := u(T, P);
   L := makeL(b1, b2, z);
   V := MatrixInverse(L);
   M := makeM(b1, b2, z);
  return([Wc2(U, V), Wc4ish(U, V, L, M)])
   end proc:
```

```
> spacing := x -> sqrt(2·(1.1)^-1·(x + 0.05) - (1.1)^-2·(x + 0.05)^2) :
```

Generates a comparison of the second order, fourth order and true energy in a prescribed direction subject to given anisotropy.

```
> makeComparisonFixedUnit := proc(b1, b2, steps, T, P, Rhigh, Title)
   local z, X, Coeffs, U, r, i;
   Coeffs := makeWc4(b1, b2, T, P, steps, Rhigh);
   z := Z(b1, b2);
   X := [ ];
   U := u(T, P);
   for i from 0 to steps - 1 do;
   r := Rhigh·spacing(i/(steps - 1));
   X := [op(X), [r, Wc(r.U, b1, b2, z)]];
   end do;
   return(display(plot([R^2·Coeffs[1], R^2·Coeffs[1] + R^4·Coeffs[2]], R = 0..1.025, color
       = [black, black], linestyle = [dash, dashdot], legend = ["Second Order",
      "Fourth Order"], gridlines, labels = ["r", ""]), pointplot(X, connect = true, axes
       = boxed, legend = "Wc")));
   end proc:
```

Optimal Chain Distribution

Generates the optimal chain distribution given the a priori distribution and end-to-end vector.

```
> sigma := (t, p, b1, b2, z, a, l) -> exp(a - 1 + d(l, u(t, p)))·((1 - c)/(4 Pi) + c·rho(t, p, b1, b2,
      z)) :
```

```
> makeSigma := proc(b1, b2, R)
  local z, X;
  z := Z(b1, b2);
  X := dualnstep(R, b1, b2, z);
  return(sigma(t, p, b1, b2, z, X[2], X[1]));
  end proc:
```

Radial Comparison

Generates a plot at fixed end-to-end vector length but varying orientation with prescribed a priori distribution.

```
> Radplot := proc(b1, steps)
  local z, X, i, t;
  X := [ ];
  z := Z(b1, 0);
  for i from 0 to steps do;
  t := 2·Pi·i / steps;
  X := [op(X), [Wc((1/2)·u(t, 0), b1, 0, Z(b1, 0)), t + Pi/2]];
  end do;
  return(X);
  end proc:
```

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