Wulff Construction for Deformable Media

Joseph Rudnick and Robijn Bruinsma

Department of Physics, University of California, Los Angeles, California 90024

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Abstract

A domain in a Langmuir monolayer can be expected to have a shape that reflects the textural anisotropy of the material it contains. This paper explores the consequences of $XY$-like ordering. It is found that an extension of the Wulff construction allows for the calculation of two-dimensional domain shapes when each segment of the perimeter has an energy that depends both on its orientation and its location. This generalized Wulff construction and newly-derived exact expressions for the order parameter texture in a circular domain lead to results for the shape of large domains. The most striking result is that, under general conditions, such domains will inevitably develop a cusp. We show that the development of cusps is mathematically related to phase transitions. The present approach is equivalent to a Landau mean-field version of the theory.

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I. INTRODUCTION

The regularities in the shapes of crystalline materials have long been understood to be macroscopic expressions of the positional order of crystals at the atomic level. The angles between the faces of a crystal are, for instance, structural invariants dependent only on a certain set of integers characterizing the faces (Miller indices [1]). In a classic paper [2], Wulff developed a geometrical construction allowing for the determination of the shape of a crystal, provided one knows the values of the surface energy of the crystal as one varies the Miller indices. One “draws” planes with every possible set of Miller indices. The distance of each plane from a fixed point in space is proportional to the energy per unit area of a surface parallel to that plane. The inner envelope of the planes is then the equilibrium shape of a finite piece of crystal.

Key to the Wulff construction is the dependence of the interfacial energy on orientation. Anisotropic surface energies are, however, not restricted to the crystalline solids. A portion of the surface of a liquid-crystalline mesophase has, in general, a surface energy whose value depends on its orientation relative to the optical axis. The principal difference between this system and a crystal is that liquid crystals may have crystallographic directions that are easily deformable (e.g. smectics) or they may lack crystallographic order altogether—and only exhibit orientational order (e.g. nematics). It seems obvious that the internal softness of liquid crystals and like systems will suppress such characteristic surface features of solid crystals as facets and edges. In the case of an extremely soft system the optical axis ought to adjust itself so as to minimize the effective surface energy for all orientations. A sample is then expected to relax to a spherical shape to minimize its overall interfacial energy. According to this argument, one should expect to encounter edge-like features only in liquid-crystalline materials that are relatively rigid. As we will see in this paper, this last conclusion is, in fact, quite incorrect. Edges can be seen even in very soft liquid crystals.

The possibility of sharp edges, or cusps, in liquid crystalline materials was first suggested by Herring in the early 1950’s. He utilized the Wulff construction to demonstrate that liquid
crystals with rigid orientational order can have interfaces with sharp cusps, provided that the surface energy is sufficiently anisotropic. The resulting cusp angle are no longer geometrical invariants but instead depend on material parameters. It was also noted by Burton, Cabrera and Frank (BCF) in 1951 that the Wulff construction acquires important simplifications in two dimensions ($D = 2$) [4]. Its derivation becomes a simple exercise in the calculus of variations, in contrast to the situation in three dimensions, for which there is no entirely rigorous and general demonstration of the correctness of the Wulff construction [3]. To implement the Wulff construction in two dimensions, one solves a simple linear differential equation, while in three dimensions the only known method is the geometrical construction described above.

Anisotropic shapes of samples in thermal equilibrium are, indeed, encountered in experiments on $D = 2$ mesophases. The systems in question are Langmuir monolayers consisting of surfactant molecules at an air-water interface [11]. The phase diagram of such materials generally contain, in addition to the $D = 2$ analogue of the solid liquid and gaseous phases, the so-called liquid condensed (LC) phase, which is liquid-crystalline. The LC phases are two dimensional anisotropic liquids in which the direction of the tilted hydrophobic tails define an anisotropy axis, $\hat{c}$. Because of the anisotropy between the polar head groups and the non-polar tail there is no $\hat{c} \rightarrow -\hat{c}$ symmetry (as is the case for nematic liquid crystals).

At the phase boundary between the LC and isotropic liquid phases, stable coexistence droplets are observed with shapes that are, in general, non-circular. Recently, polarized fluorescence microscopy studies of coexistence droplets of pentadecanoic acid with a linear dimension in excess of 25 $\mu$m have reported that the boundaries of these droplets contain a cusp [12]. Such a cusp is illustrated in Fig. 1a. The interior angle of the cusp was found to increase with the size of the domain.

The existence of cusps on the boundary of these droplets would not seem to be too surprising, as droplets in surfactant systems have been found to contain topological defects in the pattern—or texture—of the anisotropy axis. A defect located at the boundary could well produce a cusp. However, Brewster angle microscopy studies—which allow for detailed
visualization of textures—on these materials have revealed defect-free textures of the “virtual boojum” type (see Fig. 1b) \[13\], with the cusp in the sample shape located opposite the focus of the boojum.

The determination of the shape of these systems demands a simultaneous minimization of the free energy with respect to the *shape* and the *internal structure* of the sample. In other words, we must find the analogue of the Wulff construction for deformable media. The question of finding such a generalized Wulff construction for Langmuir layers belongs to a wider class of shape minimization problems, as encountered, for instance, in ferrofluid droplets \[9\], where the shape energy depends on the internal structure of the sample far from the surface. Analytical treatment of such problems beyond perturbation theory has proven difficult because the coupling between different parts of the surface, as mediated by the deformable bulk structure, is highly non-local. As suggested by BCF \[7\], shape calculations are more easily carried out in \(D = 2\). We will demonstrate in this article that a generalized Wulff construction can be found in \(D = 2\) for the case when the internal structure of the sample is describable by an \(X − Y\) model. As discussed below, Langmuir monolayers in the LC have an order parameter which, under certain conditions, reduces to an \(X − Y\) model. We will show that cusp singularities ought to be generic features of \(2D\) drops with an \(X − Y\) order parameter.

We will start in Section II with a discussion of the free energy minimization for a fixed sample shape (a circle) and the resulting textures. In Section III we will keep the texture fixed and minimize the free energy with respect to sample shape, following the method of BCF \[7\]. Simultaneous minimization of the free energy with respect to both shape and sample texture can be done perturbatively, as discussed in Section IV. Our general method, based on complex function theory, is discussed in Section V. A brief summary of the method has been published elsewhere \[8\].
II. FREE ENERGY OF XY DROPLETS

In this Section we define the Hamiltonian and examine the order parameter textures. We will assume a rigid circular boundary, so free energy minimization simply involves finding the lowest energy texture consistent with the boundary energy. The order parameter is taken to be the unit vector \( \hat{c} = (\cos \Theta, \sin \Theta) \) with an associated effective Hamiltonian

\[
H[\Theta(x, y)] = \int_{\text{interior}} \frac{\kappa}{2} \left| \nabla \Theta \right|^2 \, dx \, dy + \int_{\text{boundary}} \sigma (\theta - \Theta) \, dS. \tag{2.1}
\]

The first term in Eq. (2.1) describes the free energy cost associated with a position dependence of the order parameter \( \hat{c}(x) \). The coefficient \( \kappa \) is, for the \( XY \) model, the so-called spin-wave stiffness. For Langmuir monolayers in the \( LC \) phase, \( \kappa \) corresponds to the Frank constant for the special case that the so-called “splay” and “bend” Frank constants are equal. The second term on the right hand side of Eq. (2.1) represents the “surface” energy of the domain. The variable \( \theta \) is the angle that the unit normal makes with respect to the axis to which the director angle is referred.

If the boundary has a fixed shape, minimization of the energy in Eq. (2.1) implies the following two extremum equations

\[
\nabla^2 \Theta(x, y) = 0, \tag{2.2}
\]

and

\[
\kappa \frac{\partial \Theta(x, y)}{\partial n} - \sigma'(\theta - \Theta) = 0. \tag{2.3}
\]

Eq. (2.2) applies in the bulk, and Eq. (2.3) at the surface of the domain. The derivative \( \partial \Theta/\partial n \) in Eq. (2.3) is along the surface normal, and \( \sigma'(x) = d\sigma(x)/dx \). The bulk extremum equation, Eq. (2.2), requires a \( \Theta(x, y) \) that is a harmonic function. The general solution of Eq. (2.2) in \( D = 2 \) can then be written, for the case at hand, as:

\[
\Theta(x, y) = \frac{1}{i} (f(x + iy) - f(x - iy)) , \tag{2.4}
\]
with \( f(z) \) an arbitrary analytic function of \( z = x + iy \). As an example of this method, expand \( f(z) \) in a Taylor series:

\[
f(z) = \sum_{n=1}^{\infty} \frac{\alpha_n}{2n} z^n \quad (2.5)
\]

Then, using Eq. (2.4), we find

\[
\Theta(x, y) = \alpha_1 y + \alpha_2 y x + \alpha_3 y (3x^2 - y^2) + \cdots
\]

\[
= \frac{1}{i} \left[ \sum_n \frac{\alpha_n}{2n} (x + iy)^n - \sum_n \frac{\alpha_n}{2n} (x - iy)^n \right]. \quad (2.6b)
\]

which is the most general analytic texture with \( \hat{c}(r = 0) = \hat{x} \) and \( c_y(x, y) = -c_y(x, -y) \).

The most general form for the surface energy is

\[
\sigma(\theta - \Theta) = \sum_{n=0}^{\infty} a_n \cos(n(\theta - \Theta)) \quad (2.7)
\]

Physically, the coefficient \( a_0 \) can be identified as the isotropic line tension. The coefficient \( a_1 \) measures the lowest order surface anisotropy. If \( a_1 < 0 \), then the associated surface energy favors a \( \hat{c} \)-vector along the outward boundary normal, while for \( a_1 > 0 \) it favors a \( \hat{c} \) lying along the inward normal. For Langmuir monolayers, \( a_1 \) is in general nonzero, but for \( D = 2 \) nematic liquid crystals \( a_1 = 0 \) by symmetry. In that case we must go to the next term \((n = 2)\). If \( a_2 < 0 \) then the surface energy favors a normal orientation for \( \hat{c} \) at the boundary without distinguishing whether it is outward or inward, while \( a_2 > 0 \) favors a parallel orientation for \( \hat{c} \).

Under the assumption of a circular domain, the boundary condition, Eq. (2.3), becomes

\[
\kappa \left[ e^{i\theta} f'(e^{i\theta}) - e^{-i\theta} f'(e^{-i\theta}) \right] + \frac{R_0}{2} \sum_{n=0}^{\infty} n a_n \left[ e^{in\theta} e^n (f(e^{i\theta}) + f(e^{-i\theta})) - e^{-in\theta} e^n (f(e^{i\theta}) - f(e^{-i\theta})) \right] = 0. \quad (2.8)
\]

Eq. (2.8) can be solved by iteration when \( a_n \ll \kappa/R_0 \). For instance, if only \( a_0 \) and \( a_1 \) are non-zero, then we find a Taylor series for \( f(z) \):

\[
f(z) = -\frac{a_1 R_0}{2\kappa} z - \frac{1}{2} \left( \frac{a_1 R_0}{2\kappa} z \right)^2 + O(a_1^3). \quad (2.9)
\]
The choice of the function $f(z)$ is thus imposed by the solution of Eq. (2.3). Comparing Eqs. (2.9) and (2.6) one can verify $\alpha_1 = -a_1 R_0 / 2 \kappa$ and $\alpha_2 = -(a_1 R_0 / 2 \kappa)^2$. The resulting texture is shown in Fig. 1b. It has a mathematical singularity outside the sample, which is called a “virtual” boojum. Textures of this type are, indeed, frequently encountered in both Langmuir monolayers and on the surface of smectic C* liquid crystals. The distance of this virtual singularity in the textural structure from the center of the domain, $R_B$, is obtained by extrapolating lines of constant $\Theta$ to their point of intersection. Inserting Eq. (2.9) into Eq. (2.4) and performing the required extrapolation, one obtains

$$ R_B = 2 \kappa / a_1 R_0. \quad (2.10) $$

Note that as $a_1 \to 0$, the boojum recedes to infinity and the texture becomes uniform.

For the case $n = 2$, the 2D nematic drop, we must set $a_1 = 0$. If only $a_2$ is non-zero, then iterative solution of Eq. (2.8) yields

$$ f(z) \approx -\frac{1}{2} \frac{a_2 z^2}{R_0 \kappa}, $$

so $\alpha_1 = 0$ and $\alpha_2 = -a_2 / R_0 \kappa$. The resulting texture now has two virtual singularities, but this time they are located along the $y$ axis.

The above result for $\alpha_1$ and $\alpha_2$, for the case $a_1 \neq 0$, in the perturbation region $a_1 \ll \kappa / R_0$ suggests a Taylor expansion of $f(z)$ with the coefficients $\alpha_n = \frac{1}{n} (a_1 R_0 / 2 \kappa)^n$. This is indeed an exact solution of Eq. (2.8). In fact, whenever the boundary energy has the special form $\sigma(\theta - \Theta) = a_n \cos n(\theta - \Theta)$, i.e. whenever only one $a_n$ is nonzero (besides $a_0$), an exact solution of Eq. (2.8) can be found for $f(z)$:

$$ f(z) = \frac{1}{n} \log \left(1 - \alpha_n z^n\right), \quad (2.11) $$

with

$$ \alpha_n R_0^n = \frac{n a_n R_0 / \kappa}{1 + \sqrt{1 + (n a_n R_0 / \kappa)^2}}. \quad (2.12) $$

A demonstration that Eqs. (2.11) and (2.12) indeed yield a solution to the boundary condition Eq. (2.8) is contained in Appendix A.
If \( n = 1 \), then the exact solution corresponds to a virtual boojum, lying a distance \( R_B \) away from the center of the domain, where

\[
R_B = R_0 \frac{1 + \sqrt{1 + (a_1 R_0 / \kappa)^2}}{a_1 R_0 / \kappa}.
\]  

(2.13)

As the ratio \( a_1 R_0 / \kappa \) goes to zero, the boojum again retreats to infinity. As \( a_1 R_0 / \kappa \) goes to infinity, corresponding to a very strong anisotropic surface energy, or a very large domain, \( R_B \to R_0 + \kappa/a_1 \). The boojum thus approaches the sample in this regime, but the spacing remains finite in the limit \( R_0 \to \infty \).

When \( n \) is greater than one, the exact solution for the texture is equivalent to the texture produced by \( n \) singularities lying outside of the domain (see Figs. 2b-d). The virtual singularities are no longer boojums. The singularities for \( n > 2 \) are “fractionally charged” in the sense that we do not recover the starting orientation of the director field if we perform a circuit around the singularity. For \( n > 2 \) the resulting singularity is equivalent to a nematic disclination. There are singular lines attached to the singularities where \( \Theta \) jumps by \( 2\pi(n-2)/n \), but these lines do not intersect the sample.

Textures corresponding to \( a_1, \ldots, a_4 \neq 0 \) are displayed in Fig. 2. For clarity of presentation, the singularities are placed on the boundary of the domains.

III. WULFF CONSTRUCTION IN TWO DIMENSIONS

We now turn to the second part of the problem: minimizing the free energy with respect to sample shape for a rigid texture. We will first review the analysis of BCF [7] of the \( D = 2 \) Wulff construction, and then we will use their method to see under what conditions we ought to expect to encounter sample shapes with cusps. The texture is assumed to be uniform in the analysis immediately following.

We start by introducing a parameterization of a two dimensional curve. This parameterization expresses the co-ordinates of a point on the curve in terms of the angle between the tangent to the curve and the x-axis. If this angle is \( \theta \) and the distance between the tangent line and the origin is \( R(\theta) \), then
\[ x(\theta) = R(\theta) \cos(\theta) - \frac{dR(\theta)}{d\theta} \sin(\theta) \quad (3.1a) \]
\[ y(\theta) = R(\theta) \sin(\theta) + \frac{dR(\theta)}{d\theta} \cos(\theta). \quad (3.1b) \]

The quantities \( \theta \) and \( R(\theta) \) are displayed in Fig. 3. It is relatively straightforward to express \( \theta \) and \( R(\theta) \) in terms of \( x \) and \( y \). One has

\[ \cot(\theta) = -\frac{dy}{dx} \]
\[ R(\theta) = \left| \frac{x \frac{dy}{dx} - y}{\sqrt{1 + (dy/dx)^2}} \right|. \quad (3.2) \]

The following relations follow immediately from Eqs. \((3.1)\).

\[ \frac{dx}{d\theta} = -\sin(\theta) \left[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} \right], \quad (3.3a) \]
\[ \frac{dy}{d\theta} = \cos(\theta) \left[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} \right], \quad (3.3b) \]

and

\[ \frac{dS}{d\theta} = \sqrt{\left( \frac{dx}{d\theta} \right)^2 + \left( \frac{dy}{d\theta} \right)^2} = \left| R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} \right|. \quad (3.4) \]

Furthermore, the area inside a closed curve is simply expressed as an integral over \( \theta \):

\[ A = \frac{1}{2} \int \left[ xdy - ydx \right] = \frac{1}{2} \int \left[ R(\theta) \left[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} \right] \right]. \quad (3.5) \]

The integral in Eq. \((3.5)\) is taken counterclockwise around the curve.

Suppose, now, that one wishes to minimize the boundary energy of a two dimensional domain having an anisotropic surface energy, \( \sigma(\theta) \). Here, the angle \( \theta \) is both the angle that the boundary’s unit normal makes with respect to the \( x \)-axis and the angle that parameterizes the bounding curve in the parameterization of Eq. \((3.1)\). This minimization is to be achieved subject to the constraint that the total enclosed area is a constant. Using Lagrange multipliers, we arrive at the following extremum equation:

\[ 0 = \frac{\delta}{\delta R(\theta)} \int \left[ \sigma(\theta') \left[ R(\theta') + \frac{d^2 R(\theta')}{d\theta'^2} \right] - \frac{\lambda}{2} R(\theta') \left[ R(\theta') + \frac{d^2 R(\theta')}{d\theta'^2} \right] \right] d\theta' \]
\[ = \sigma(\theta) + \frac{d^2 \sigma(\theta)}{d\theta^2} - \lambda \left[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} \right], \quad (3.6) \]
or,

\[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} = \frac{1}{\lambda} \left[ \sigma(\theta) + \frac{d^2 \sigma(\theta)}{d\theta^2} \right]. \] (3.7)

The solution of the above equation is

\[ R(\theta) = \frac{1}{\lambda} \sigma(\theta) + C_1 \cos(\theta) + C_2 \sin(\theta). \] (3.8)

According to Eq. (3.8), apart from the \( C_1 \) and \( C_2 \) terms, the minimum energy shape has a bounding curve such that \( R(\theta) \) is proportional to the anisotropic surface tension, \( \sigma(\theta) \). Since \( R(\theta) \) is the distance from the origin to the tangent of the bounding curve, we have recovered the Wulff construction precisely. It can be shown, by direct substitution into Eqs. (3.1), that the only effect of the additive sine and cosine terms is to translate the domain without changing its shape.

As a first example of the use of Eqs. (3.1) and (3.8), consider again the case in which only \( a_0 \) and \( a_1 \) are finite in the Fourier expansion, Eq. (2.7), of \( \sigma(\theta) \). Setting \( \Theta = 0 \) in Eq. (2.7) then gives

\[ \sigma(\theta) = a_0 + a_1 \cos(\theta). \] (3.9)

Inserting Eq. (3.9) into the right hand side of Eq. (3.7) we obtain

\[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} = \frac{1}{\lambda} \left[ a_0 + a_1 \cos \theta + \frac{d^2}{d\theta^2}(a_0 + a_1 \cos \theta) \right] = \frac{1}{\lambda} a_0. \] (3.10)

The solution of Eq. (3.10) is, then, identical to that for the case \( a_1 = 0 \), which is a circle. According to Eq. (3.10) a simple \( \cos \theta \) contribution to the anisotropic surface energy leads to no distortion of the shape of the domain. In fact, we show in Appendix B that in general a contribution to \( \sigma(\theta) \) that is proportional to \( \cos \theta \) cannot affect the sample shape for rigid textures and, in particular, cannot produce any cusps.

Next, consider a surface energy of the form:

\[ \sigma(\theta) = \sigma_0 e^{\beta \cos(\theta)}. \] (3.11)
Using Eq. (3.11) and inserting the result in Eq. (3.8) with \( C_1 = C_2 = 0 \) gives

\[
\begin{align*}
    x(\theta) &= \left[ \cos(\theta) + \beta \sin(\theta) \right]^2 e^{\beta \cos(\theta)}, \\
    y(\theta) &= [1 - \beta \cos(\theta)] \sin(\theta) e^{\beta \cos(\theta)}.
\end{align*}
\] (3.12a, 3.12b)

Fig. 4 displays the boundaries for \( \beta = 0.5, 1 \) and 1.5. For \( \beta = 1.5 \), the bounding curve has a “swallowtail” feature. According to the rule that one keeps only the inner envelope, the proper prescription is to amputate this feature and retain only the left-hand portion of the curve, which now has a cusp. The development of swallowtail singularities in a family of one-parameter curves is a familiar feature of the theory of catastrophes. It is, for instance, encountered in a set of curves evolving according to the Huyghens construction of physical optics, where swallowtail singularities are associated with the development of caustics. In our case, the curve parameter is \( \beta \), and this parameter must have a finite value for swallowtail singularities to develop. In Appendix C we prove that the swallowtail feature appears first at \( \beta = 1 \), so the sample boundary is smooth for \( \beta < 1 \).

The key difference between the two anisotropic boundary energies, Eq. (3.10) and Eq. (3.11), is that the latter boundary energy contains higher order harmonics. Indeed, if we include the higher harmonics of Eq. (2.7):

\[
\sigma(\theta) = \sum_{n=0}^{\infty} a_n \cos(n\theta).
\] (3.13)

and insert Eq. (3.13) into Eq. (3.7)

\[
R(\theta) + \frac{d^2R(\theta)}{d\theta^2} = \sum_{n=0}^{\infty} a_n \left(1 - n^2\right) \cos(n\theta).
\] (3.14)

then, as soon as Fourier components with \( n > 2 \) are included in Eq. (3.14) we find a distorted boundary, but as long as the \( a_n \) coefficients with \( n > 2 \) remain small compared to \( a_0 \), we find no cusp singularity. The swallowtail features cannot in general be obtained perturbatively. In other words, the anisotropic contribution to \( \sigma(\theta) \) must be comparable to the isotropic line energy \( a_0 \) before any singularities in the bounding shape can develop. This would suggest that the experimentally observed cusp feature can only be explained if one
assumes a highly anisotropic line tension. In the Section we will use perturbation theory to show why this conclusion is quite incorrect.

IV. CONNECTION WITH PHASE TRANSITIONS

The example discussed in the previous Section also serves to illustrate the mathematical connection between the onset of a cusp and a thermodynamic phase transition. This connection is more readily developed if one recasts the problem of calculating the minimum energy bounding surface into more conventional notation. In this notation the procedure giving rise to a cusp produces expressions identical to those encountered in the standard $\phi^4$ model of a symmetry-breaking phase transition.

We begin by writing the expression for the domain’s bounding curve in the form $x = f(y)$. This single-valued function describes the domain in the immediate vicinity of $y = 0$, where the cusp will occur in the case at hand. The orientation-dependent surface tension has the form

$$
\sigma(\theta) = e^{\beta \cos(\theta)}
$$

$$
= e^{\beta / \sqrt{1 + (dx/dy)^2}}
$$

$$
= e^{\beta / \sqrt{1 + f'(y)^2}}
$$

(4.1)

The surface tension of the portion of the boundary curve lying in the top half of the $x - y$ plane is

$$
\int \sigma(\theta) dS = \int e^{\beta / \sqrt{1 + f'(y)^2}} \sqrt{1 + f'(0)^2} dy
$$

(4.2)

Taking the functional derivative of the above expression with respect to $f(y)$, we obtain the following extremum equation, which applies at the end-point $y = 0$.

$$
0 = \frac{d}{df'(0)} \left[ e^{\beta \sqrt{1 + f'(0)^2}} \sqrt{1 + f'(0)^2} \right]
$$

(4.3a)

$$
= \frac{f'(0)}{1 + f'(0)^2} \left[ \sqrt{1 + f'(0)^2} - \beta \right]
$$

(4.3b)
When $\beta < 1$ the only solution to the above equation is $f'(0) = 0$, while when $\beta > 1$ there are the additional solutions corresponding to $\sqrt{1 + f'(0)^2} = \beta$, or, returning to angular variables, $\beta = 1/\cos(\theta_{\text{cusp}})$.

To gain further insight into the mathematical nature of the onset of the cusp, we expand the term in brackets on the right hand side of Eq. (4.3a). If $f'(0)$ is small and $\beta \approx 1$, then

$$F (f'(0)) \equiv \sqrt{1 + f'(0)^2} e^{\beta/\sqrt{1 + f'(0)^2}} = e^\beta \left[1 + (1 - \beta)f'(0)^2 + \frac{1}{8} f''(0)^4 + O \left(f'(0)^6, (\beta - 1)f''(0)^4\right)\right]. \quad (4.4)$$

The quantity $F (f'(0))$ is the surface energy per unit length along the $y$-axis, at the point the cusp develops. The right hand side of Eq. (4.4) has precisely the form of a Ginzburg-Landau-like mean field theory. The combination $1 - \beta$ plays the role of the reduced temperature and $f'(0)$ is the order parameter. The expression possesses a local minimum at $f'(0) = 0$ when $\beta < 1$, which becomes a local maximum as $\beta$ passes through one. The onset of the cusp corresponds to the system’s choosing on the the non-zero values of $f'(0)$ associated with the local minima at

$$f'(0) = \pm 2\sqrt{\beta - 1} \quad (4.5)$$

Only one of the solutions of Eq. (4.5) is physically relevant. According to the Wulff construction, the sign of $f'(0)$ must be the one associated with an outward-pointing cusp. This implies a small symmetry-breaking term in the theory, at this point unidentified in our analysis.

In general, if the surface tension $\sigma(\theta)$, has a maximum at $\theta = 0$, then Eq. (4.4) can be written as

$$F (f'(0)) = C_1 [\sigma(0) + \sigma''(0)] (f'(0))^2 + C_2 (f'(0))^4. \quad (4.6)$$

Cusps appear when $\sigma(0) + \sigma''(0)$ changes sign. This is consistent with the results of Appendix C, where it is demonstrated that cusps appear when $R(0) + R''(0)$ changes sign.
V. SOFT LIMIT: EFFECTIVE SURFACE TENSION

Before developing the general formalism, we will first consider the limiting case of very small $\kappa$, for which the problem simplifies significantly. In this limit we can define an effective surface tension which can be used in the two-dimensional Wulff construction, as applied to rigid materials. In other words, we include the deformability of the material by a re-definition of the surface energy.

In the soft limit the texture of the sample deforms itself to respond to the surface energy anisotropy. We start by setting $\kappa = 0$. The texture can then adjust itself freely to minimize the anisotropic line tension. Let $\sigma_0$ be this minimum value. Since the line tension is a constant, and since the textural energy is zero, the sample shape must be circular. The line tension is minimized when the director $\hat{c}$ lies along the outward-directed normal to the circle, so $\hat{c}$ is in the radial direction along the circle perimeter. The associated texture must be a solution of Eq. (2.2) obeying this boundary condition. In general, the solution will have one or more singularities. We will focus on the solution of Laplace’s equation with a singularity on the circle perimeter: the boojum texture:

$$\Theta_B(x, y) = 2 \arctan \left( \frac{y}{x + R} \right). \quad (5.1)$$

Now, let $\kappa$ be small but finite. Two things must happen: (i) the $\hat{c}$-director exerts a torque on the boundary which is then deformed away from a perfectly circular shape, and (ii) the $\hat{c}$-director is no longer perfectly along the boundary normal. We will first keep the texture fixed at the at Eq. (5.1), allowing the sample shape to relax, and then we will allow the texture to relax and reconsider the sample shape.

First, use Gauss’s law to rewrite the total energy as a line integral over the boundary assuming $\Theta$ to be a solution of Eq. (2.2):

$$F = \oint ds \left\{ \frac{\kappa}{2} \Theta(s) \frac{\partial \Theta(s)}{\partial n} + \sigma (\theta - \Theta) \right\}. \quad (5.2)$$

The quantity $\sigma_{\text{eff}}$ given by
\[ \sigma_{\text{eff}} = \frac{\kappa}{2} \Theta \frac{\partial \Theta}{\partial n} + \sigma (\theta - \Theta) \]  \hspace{1cm} (5.3)

then appears as an effective line tension. The function \( \Theta(s) \) is, however, a functional of the boundary shape so the right hand side of Eq. (5.3) is really a non-local expression and cannot be simply interpreted as a line tension. If, nevertheless, we use use Eq. (5.1) in Eq. (5.3) we find:

\[ \sigma_{\text{eff}} = \frac{\kappa}{2R} \frac{\sin \theta}{1 - \cos \theta} + \sigma_0. \]  \hspace{1cm} (5.4)

The resulting effective surface tension is an analytic, but aperiodic function of \( \theta \). The line tension anisotropy only depends on the dimensionless parameter \( \Gamma = \kappa / \sigma_0 R \), with \( R \) the sample radius. It can be inserted into the Wulff construction and leads to a cusp at \( \theta = 0 \), with a cusp angle proportional to \( \Gamma \).

We now redo this calculation while allowing for textural relaxation. First, assume a circular boundary. Allow \( \Theta \) to deviate from the boojum texture, and expand the line energy around its minimum \( \sigma_0 \):

\[ \Theta(x, y) = \Theta_B(x, y) + w(x, y) \] \hspace{1cm} (5.5)

\[ \sigma (\theta - \Theta) \approx \sigma_0 + \frac{1}{2} \sigma''_0 (\theta - \Theta)^2. \] \hspace{1cm} (5.6)

To find \( w \) we must solve \( \nabla^2 w = 0 \) subject to the boundary conditions Eq. (2.3). In terms of \( w \):

\[ \kappa \frac{\partial w}{\partial r} \bigg|_{r=R} + \sigma''(0) w(s) = -\kappa \frac{\partial \Theta_B}{\partial r} \bigg|_{r=R}. \] \hspace{1cm} (5.7)

The solution of this mixed boundary condition problem for \( w \) can be written as a Fourier expansion in \( \theta \):

\[ w(r, \theta) = \sum_{m=1}^{\infty} a_m r^m \sin m\theta \] \hspace{1cm} (5.8)

with coefficients:

\[ a_m = -\frac{\kappa}{\pi \sigma''(0) R_m \left( 1 + \frac{\kappa m}{\sigma''(0)} \right)} \int_{-\pi}^{\pi} d\theta' \frac{\partial \Theta_B(\theta')}{\partial r} \bigg|_{r=R}. \] \hspace{1cm} (5.9)
Inserting Eqs. (5.8) and (5.9) into Eq. (5.2) yields:

\[ F = R \int_{-\pi}^{\pi} d\theta \left\{ \sigma_0 - \frac{1}{2} \sigma''_0 w(r = R, \theta) + O(w^4) \right\}, \quad (5.10) \]

where we have used Eq. (5.7). We neglect the fourth and higher order terms in \( w \). Inserting the solution Eq. (5.8) into the line integral expression for \( F \) gives, as expected, a non-local expression:

\[ F = R \int_{-\pi}^{\pi} d\theta \left\{ \sigma_0 + \theta \int_{-\pi}^{\pi} d\theta' K(\theta, \theta') \frac{\partial \Theta_B(\theta')}{\partial r} \right\}, \quad (5.11) \]

with a kernel \( K(\theta, \theta') \):

\[ K(\theta, \theta') = \frac{\kappa}{2\pi} \sum_{m=1}^{\infty} \frac{\sin m\theta \sin m\theta'}{1 + \frac{m\kappa}{\sigma_0 R}}. \quad (5.12) \]

In the large \( R \) limit, this kernel reduces to two delta functions, at \( \theta = \pm \theta' \), while for finite \( R \), these two delta functions broaden by an amount \( \delta \theta \) of order \( \kappa/\sigma''_0 R \). To second order in \( \kappa/R \) we can neglect the spreading of the delta functions. In the large \( R \) limit, the non-local line energy thus becomes a local line tension. Using Eq. (5.12) in (5.11), one obtains:

\[ F = R \int_{-\pi}^{\pi} d\theta \left\{ \sigma_0 + \frac{\kappa}{2} \frac{\partial \Theta_B(\theta)}{\partial r} \right\} \bigg|_{r=R}. \quad (5.13) \]

As \( R \to \infty \), surprisingly, we recover the “naive” line tension of Eq. (5.4). If we now allow the shape to relax, we find the shape discussed earlier. This shape relaxation must then be used in a recalculation of \( w \), but in the large \( R \) limit such corrections are higher order in \( 1/R \). We conclude that in the limit of small \( \kappa \) and large \( R \) the sample shape is expected to have a cusp with an excluded angle proportional to \( \kappa/\sigma_0 R \).

**VI. GENERALIZATION OF THE WULFF CONSTRUCTION**

We now relax the condition of small \( \kappa \) and develop our method, which allows for a determination of the sample shape, even when the \( \sigma_{eff} \) of Eq. (5.3) is truly non-local. Our
method will be a generalization of the BCF procedure [7] and the results of Section [1]. We will assume that the texture always obeys Laplace’s equation, Eq. (2.2), with the director angle $\Theta$ specified by a complex function $f(z)$ through Eq. (2.4). The function $f(z)$ is, for a given sample shape, determined by Eq. (2.8). The remaining problem is now to minimize the sample free energy with respect to sample shape. We will use the BCF parameterization $R(\theta)$ for the sample shape. To find the optimal sample shape, we must compute the variational derivative of both surface and textural energy and equate it to the variational derivative of the sample area $A$ with respect to $R(\theta)$ times the Lagrange multiplier $\lambda$—in direct analogy with Eq. (3.6). We will, in the following, always assume near-circular shapes.

We start with the variational derivative of the textural energy. Imagine a two dimensional domain containing an order parameter described by the director angle $\Theta(x, y)$. If $\Theta(x, y)$ is given by Eq. (2.4) then

$$\left|\nabla \Theta\right|^2 = 4f'(x + iy)f'(x - iy), \quad (6.1)$$

and the bulk contribution to the energy in Eq. (2.1) is, then,

$$2\kappa \int F(x, y(x)) dx, \quad (6.2)$$

where $y(x)$ denotes the boundary line energy, and where

$$F(x, y) = \int y f'(x + iy') f'(x - iy') dy'. \quad (6.3)$$

The textural energy, Eq. (6.2) is explicitly dependent on the shape of the boundary, and, again, can be treated as a non-local contribution to the line tension. Using Eqs. (3.3) and (3.4) we rewrite the infinitesimal $dx$ as $-\sin \theta ds$, with $s(\theta)$ the arclength. The derivative with respect to $R(\theta)$ of the textural energy Eq. (6.2) is then

$$\frac{\delta}{\delta R(\theta)} 2\kappa \int F(x(\theta'), y(\theta')) \sin \theta' ds(\theta') = 2\kappa f'\left(x(\theta) + iy(\theta)\right) f'\left(x(\theta) - iy(\theta)\right). \quad (6.4)$$

We now turn to the variational derivative of the surface energy, Eq. (2.7). Using the Fourier expansion, Eq. (2.7), for $\sigma(\theta - \Theta)$ we find:
\[
\frac{\delta}{\delta R(\theta)} \int \sigma (\theta - \Theta) \, dS = \\
\text{Re} \left\{ \sum_n a_n e^{-in\theta} e^{nf(x+iy)-nf(x-iy)} \left[ n(n+1)(x+iy)f'(x+iy) + n(n-1)(x-iy)f'(x-iy) + 1 - n^2 \right] \right\}.
\]

(6.5)

The algebraic steps in the derivation of Eqs. (6.4) and (6.5) are outlined in Appendix D.

The two variational derivatives appear to be forbiddingly intricate. However, our complex function \( f(z) \) is not just any function; it must obey Eq. (2.8), and we use this to simplify Eqs. (6.4) and (6.5). First, we rescale lengths in the circular domain so that its radius is unity, as described in Section I. On the boundary of the domain, one can then replace \( x + iy \), respectively \( \exp(in\theta) \) by \( z \), respectively \( z^n \) (where \( |z| = 1 \)) and the quantities \( x-iy \), respectively \( \exp(-in\theta) \) by \( 1/z \), respectively \( 1/z^n \). Equation (2.8) which determines \( f(z) \) then simplifies to:

\[
\kappa \left[ zf'(z) - \frac{1}{z} f' \left( \frac{1}{z} \right) \right] + \frac{R_0}{2} \sum_n na_n \left[ n e^{-nf(z)+nf(1/z)} - z^{-n} e^{nf(z)-nf(1/z)} \right] = 0.
\]

(6.6)

Dividing both sides by \( z \) and integrating yields

\[
\kappa \int^z \left[ f'(x) - \frac{1}{x^2} f' \left( \frac{1}{x} \right) \right] \, dx = -\sum_n \frac{a_n}{2} \left[ n e^{-nf(z)+nf(1/z)} + z^{-n} e^{nf(z)-nf(1/z)} \right] + \kappa \int^z \left[ x f'(x) - \frac{1}{x} f' \left( \frac{1}{x} \right) \right] \left[ f'(x) + \frac{1}{x^2} f' \left( \frac{1}{x} \right) \right] \, dx
\]

(6.7)

Using Eqs. (6.3) and (6.7) in Eqs. (6.4) and (6.5) we find that the functional derivative with respect to \( R(\theta) \) of the energy of the domain, as given by the sum of the right hand sides of Eqs. (6.4) and (6.5), is equal to \( \mathcal{F}(z) \), with

\[
\mathcal{F}(z) = \\
z\kappa \frac{d}{dz} \left[ zf'(z) - \frac{1}{z} f' \left( \frac{1}{z} \right) \right] + \kappa \left[ zf'(z) \right]^2 + \kappa \left[ \frac{1}{z} f' \left( \frac{1}{z} \right) \right]^2 \\
-\kappa \left[ f(z) + f \left( \frac{1}{z} \right) \right] + \kappa \int^z \left[ w f'(w)^2 - \frac{1}{w^2} f' \left( \frac{1}{w} \right)^2 \right] \, dw,
\]

(6.8)
up to an unimportant constant.

The equation determining the optimal shape is now found by repeating the steps between Eqs. (3.5) and (3.6), with the result:

\[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} = \frac{1}{\lambda} [\sigma_0 R_0 + \mathcal{F}(\theta)], \tag{6.9} \]

where \( \sigma_0 \) is the isotropic contribution to the surface tension, and where \( \mathcal{F}(\theta) \) is given by Eq. (6.8) with \( z \) replaced by \( e^{i\theta} \).

Eqs. (6.8) and (6.9), which hold as long as the domain boundary is not too far deformed from a circular shape, form the basis of our method. The sample shape is determined in three steps: (i) solve Eq. (6.6) to obtain \( f(z) \) for a given anisotropic line tension \( \sigma(\theta - \Theta) \), (ii) compute \( \mathcal{F}(\theta) \) from Eq. (6.8) to obtain the effective line tension, and (iii) solve the BCF formula, Eq. (6.9) with \( \mathcal{F}(\theta) \) to find \( R(\theta) \). We will now consider some examples of the application of our method.

A. \( \sigma(\phi) = \sigma_0 + a_1 \cos \phi \)

Our first example is the case in which \( a_n = 0 \) for \( n > 2 \) in the Fourier expansion, Eq. (2.7). Recall that for an imposed, rigid, uniform texture the minimum energy shape was a perfect circle (Eq. (3.10)), and that for an imposed circular domain shape the minimum energy texture was the virtual boojum (Eq. (2.11) with \( n = 1 \)). To implement our recipe for finding the shape which minimizes the total free energy, we first note that the virtual boojum texture:

\[ f(z) = \log(1 - \alpha_1 z) \tag{6.10} \]

is an exact solution of Eq. (6.8), with \( \alpha_1 \) given by Eq. (2.12). If we then insert \( f(z) \) into \( \mathcal{F}(z) \) (Eq. (6.8)) we find \( \mathcal{F}(z) = \text{constant} \). The resulting shape equation

\[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} = \frac{1}{\lambda} [\sigma_0 R_0 + \text{const.}] \tag{6.11} \]
is the equation for a perfect circle. We conclude that the virtual boojum texture in a circular domain is a free energy minimum, both with respect to domain shape and domain texture. We have yet to find a simple physical argument that explains why the perfect circle remains a free energy minimum for this anisotropic form of the line tension.

**B.** \( \sigma(\phi) = \sigma_0 + a_n \cos n\phi \) \((n > 1)\)

Let us now try the same procedure for \( n > 1 \). First, assume a perfect circular sample. The associated texture then follows from \( f(z) = \frac{1}{n} \log(1 - \alpha_n z^n) \), which is a solution of Eq. (6.6). If we now compute \( \mathcal{F}(z) \) and insert the result in the shape equation we find

\[
R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} = R_0 + \kappa \left[ \frac{(n-1)^2}{n} \frac{1}{1 - \alpha_n e^{in\theta}} + \frac{1 - n}{(1 - \alpha_n e^{in\theta})^2} \right] \frac{\kappa}{\sigma_0} \left[ \frac{(n-1)^2}{n} \frac{1}{1 - \alpha_n e^{-in\theta}} + \frac{1 - n}{(1 - \alpha_n e^{-in\theta})^2} \right].
\]

(6.12)

The circular shape is no longer a free energy minimum. In the limit of very small domains, with \( \sigma_0 R_0 / \kappa \ll 1 \), Eq. (6.11) reduces to

\[
R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} \approx \frac{R_0}{\sigma_0} \left[ \sigma_0 + (1 - n^2) a_n \cos n\theta \right],
\]

(6.13)

with solution

\[
R(\theta) \approx R_0 \left( 1 + \frac{a_n}{\sigma_0} \cos n\theta \right).
\]

(6.14)

The domain shape has an \( n \)'th harmonic shape deformation on top of the circular shape. Note that the domain shape is independent of the Frank constant \( \kappa \). This result is, of course, not quite exact, since \( f(z) \) will, for a non-circular shape, no longer be given by Eq. (2.11), but the resulting corrections are higher order in \( a_n / \sigma_0 \) and \( \sigma_0 R_0 / \kappa \).

**C.** \( \sigma(\phi) = \sigma_0 + a_1 \cos \phi + a_2 \cos 2\phi \)

We have seen under A that for a pure \( \cos \phi \) line tension anisotropy we can find a free energy minimum in the perfectly circular shape. Since we have an exact solution, we can use
perturbation theory to assess the effect of higher order harmonics. We thus include one more term—\( n = 2 \), with \( a_2 \ll a_1 \)—and recompute the shape. This particular form of the surface term has been argued to be relevant for Langmuir films [16]. From our earlier results one would naively expect a nearly circular sample shape with a small \( n = 2 \) correction. However, things turn out a little differently.

If we take \( a_2 \ll a_1 \) then it will be possible to expand \( f(z) \) about its \( a_2 = 0 \) form. Writing

\[
f(z) = \log(1 - \alpha z) + f_1(z),
\]

with \( \alpha \equiv \alpha_1 R_0 \) given by Eq. (2.12), the boundary condition Eq. (6.6) becomes, to first order in \( a_2 \) and \( f_1 \),

\[
\frac{\kappa}{R_0} \left[ z f_1'(z) - \frac{1}{z} f_1' \left( \frac{1}{z} \right) \right] - \frac{a_1}{2} f_1(z) \left[ \frac{z - \alpha}{1 - \alpha z} + \frac{1 - \alpha z}{z - \alpha} \right] + \frac{a_1}{2} f_1 \left( \frac{1}{z} \right) \left[ \frac{z - \alpha}{1 - \alpha z} + \frac{1 - \alpha z}{z - \alpha} \right] + \frac{a_2}{2} \left[ \frac{z - \alpha}{1 - \alpha z} \right]^2 - \frac{(1 - \alpha z)^2}{1 - \alpha z} = 0.
\]

We separate Eq. (6.16) into two equations:

\[
\frac{a_1}{2} \left[ \frac{1}{\alpha} - \alpha \right] z f_1'(z) - \frac{a_1}{2} f_1(z) \left[ \frac{z - \alpha}{1 - \alpha z} + \frac{1 - \alpha z}{z - \alpha} \right] + \frac{a_2}{2} \left[ \frac{z - \alpha}{1 - \alpha z} \right]^2 = 0,
\]

and an identical equation with \( z \) replaced by \( 1/z \). Each of those equations is a simple linear first order differential equation, solvable by standard methods. One finds

\[
f_1(z) = -\frac{a_2}{a_1} \frac{\alpha}{1 - \alpha^2} \frac{z - \alpha}{1 - \alpha z} \int_1^z t^{2\alpha^2/(1-\alpha^2)} \frac{zt - \alpha}{1 - \alpha z} dt.
\]

Computing \( F(z) \) with the use of \( f(z) = \log(1 - \alpha z) + f_1(z) \) one finds the shape equation

\[
r(z) = \frac{1}{2} - \frac{\kappa}{\sigma_0 R_0} \left[ f_1(z) + 2\alpha (1 - \alpha z) \int_z^1 \frac{f_1(t)}{(1 - \alpha t)^2} dt \right],
\]

where \( R(z) = r(z) + 1/r(z) \). The final reduction of the result for \( R(\theta) \) consists of algebraic manipulations. First, we note that the quantity \( \alpha \equiv \alpha_1 R_0 \) as given by Eq. (2.12) approaches 1 as \( R_0 \to \infty \). This means that, in the limit that \( R_0 \) is large we can replace \( 1 - \alpha \) by \( \kappa/a_1 R_0 \). Furthermore, inspection reveals that in the limit \( \kappa/a_1 R_0 \ll 1 \) and \( a_2 \ll a_1 \) the first
order contribution to \( x(\theta), y(\theta) \) is negligible compared to the zeroth order one except in the immediate vicinity of \( \theta = 0 \). After a series of changes of variables that take this behavior into account we arrive at the following expression for \( R(\theta) \)

\[
R(\theta) = 1 + \frac{2\kappa}{\sigma_0 R_0 a_1} \text{Re} \left[ X \left( \frac{\theta R_0 a_1}{\kappa} \right) \right], \tag{6.20}
\]

where the dimensionless function \( X(\psi) \) is given by

\[
X(\psi) = \frac{1 + i\psi}{1 - i\psi} \int_0^\infty \frac{e^{-y}}{1 - iy + y} \, dy
\]

\[
-4(1 - i\psi) \int_0^\infty \frac{e^{-y}}{y^3} \left\{ \log(1 - iy + y) - \log(1 - iy) - \frac{y}{1 - iy} + \frac{y^2}{2(1 - iy)^2} \right\} \, dy
\]

\[
+ 2(1 - i\psi) \int_0^\infty \frac{e^{-y}}{y^2} \left\{ -\log(1 - iy + y) + \log(1 - iy) + \frac{y}{1 - iy} \right\} \, dy. \tag{6.21}
\]

A graph of the real part of the function \( X(\psi) \) is displayed in Fig. 5. The following properties of the function play an important role in the behavior of the boundary

1. \( \text{Re} [X(\psi)] \) is an even, nonsingular function of its argument, and can thus be expanded in a power series in \( \psi \).

2. \( \text{Re} [X(\psi)] \) has a negative second derivative at \( \psi = 0 \).

3. \( \text{Re} [X(\psi)] \) possesses a minimum at \( \psi \approx 2.74 \).

**1. Onset of a cusp**

As discussed in Section [IV] and Appendix C, the onset of a cusp is signaled by a change in sign of the function \( R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} \). From the previous arguments it follows that this is most likely to happen at \( \theta = 0 \). Making use of our result, Eq. (6.20), for \( R(\theta) \) we find

\[
R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} \bigg|_{\theta=0} = 1 + \frac{2\kappa}{\sigma_0 R_0 a_1} \text{Re}X(0) + \frac{2a_2 a_1 R_0}{\sigma_0 \kappa} \frac{X''(0)}{X''(0)}. \tag{6.22}
\]

In the limit of very small \( a_2 \) the expression on the right hand side will be positive unless the domain radius \( R_0 \) exceeds a threshold value, the leading contribution to which is given by
\begin{equation}
R_{\text{threshold}} = \frac{\sigma_0 \kappa}{2 a_1 a_2 |X'(0)|} = 0.356 \frac{\sigma_0 \kappa}{a_1 a_2},
\end{equation}

where the number in the last equality above follows from a numerical evaluation of the second derivative. When the sample radius is slightly in excess of \( R_{\text{threshold}} \) the excluded cusp angle, \( \psi \) (the difference between the cusp angle and \( 2\pi \)), obeys

\[ \psi \propto \sqrt{R - R_{\text{threshold}}}. \tag{6.24} \]

As in the case of the example discussed in Section \[ IV \], the behavior of the cusp angle at onset obeys a power law consistent with a \( \phi^4 \) mean field theory. A graph of the excluded angle of the cusp as a function of domain radius can be found in Fig. 6. The domain radius is expressed in units of \( \kappa/a_1 \). In that case, the only other adjustable parameter is the ratio \( a_2/\sigma_0 \). In the Figure, that ratio is equal to 0.05.

2. Large \( R \) limit

The behavior of the excluded angle when \( R_0 \) is very large can also be determined by inspection of Eq. \( (6.20) \). As the symmetry of the domain is the same in this case as in the illustrative case discussed in Section \[ III \] and in Appendix C, we locate a cusp by searching for a solution to the equation \( y(\theta) = 0 \), with \( \theta \) small but not equal to zero. Substituting the right hand side of Eq. \( (6.20) \) into Eq. \( (3.1b) \) we find that, for small \( \theta \) and large \( R_0 \), with \( \theta R_0 \) finite,

\begin{equation}
y(\theta) = \frac{2 a_1 a_2 R_0}{\sigma_0 \kappa} \theta \left\{ \frac{\text{Re} \left[ X'(\theta R_0 a_1/\kappa) \right]}{\theta R_0 a_1/\kappa} \right\}. \tag{6.25}
\end{equation}

Because of the properties of the function \( X(\psi) \) enumerated above, the ratio in curly brackets in Eq. \( (6.25) \) is well-behaved as a function of the variable \( \theta R_0 a_1/\kappa \). Neglected in Eq. \( (6.25) \) are terms of zeroth order in \( R_0 \).

According to Eq. \( (6.25) \), \( y(\theta) = 0 \) when either \( \theta = 0 \) or \( \text{Re} \left[ X'(\theta R_0 a_1/\kappa) \right] = 0 \). Finite cusp angles correspond to the second case. Because \( \text{Re} \left[ X(\psi) \right] \) when \( \psi = 2.74 \), we conclude
that $\theta = 2.74 (\kappa/R_0 a_1)$. The interior angle of the cusp is then equal to $\pi - 5.48\kappa/a_1 R_0$ (see Appendix C) and the excluded angle of the cusp, defined as $\pi$ minus the interior angle, is equal to $5.48\kappa/a_1 R_0$. The excluded angle decays as $1/R_0$ and is independent of $a_2$ when $R_0$ is sufficiently large.

Fig. 7 shows what the domain boundary looks like when a cusp is induced by the $a_2 \cos 2\phi$ term. The energy parameters have been set so that the inequalities relied upon in this Section are satisfied. In particular, $a_2/\sigma_0 = 0.25$ and $R_0 a_1/\kappa = 5$. Note that a swallowtail appears, just as in the illustrative example cited previously.

**VII. CONCLUSIONS AND COMPARISON WITH EXPERIMENT**

In summary, we have demonstrated that a two-dimensional domain containing a deformable medium describable by an $X-Y$ model has a purely circular boundary, as long as the surface anisotropy term is of the form $a_1 \cos \phi$ where $\phi$ is the angle between the $X-Y$ vector and the unit normal to the bounding curve. This remarkable result no longer holds if one introduces the small anisotropic surface energy $a_2 \cos 2\phi$. In certain regimes the surface deformation is singular; a cusp appears when the sample size exceeds a threshold determined by the coefficients of the anisotropic and the bulk Frank constant, $\kappa$. The cusp angle ultimately decays with increasing sample size as one over the domain radius. The threshold domain radius is proportional to $\sigma_0 \kappa/a_1 a_2$, where $\sigma_0$ is the isotropic boundary energy. Note that the more deformable the material in the domain is (i.e. the smaller the value of $\kappa$) the more likely it is to develop a cusp—which contradicts naive intuition based on the appearance of facets in crystalline materials.

How does our theory compare with the experimentally measured cusp angles? In Fig. 8 we show a set of cusp angles measured as a function of sample size by Schwartz, et al [12] for pentadecanoic acid. The data has been fitted to the curve displayed in Figure 6. The ratio $a_2/\sigma$ has been set equal to 0.05. No attempt was made to adjust that ratio so as to optimize the fit, but the quaitities $a_1$ and $\kappa$ were effectively varied by adjusting the vertical
and horizontal scales. Note that the measured cusp angles show no evidence of a sharp onset at a threshold radius.

An even more serious discrepancy between the data and our results lies in the fact that the best fit to the asymptotic power law decay of the measured cusp angle with domain size is $\theta_{\text{cusp}} \propto R_0^{-0.3}$. Our mean field theory gives a decay as $1/R_0$. One possible origin of the discrepancy is that we did not identify the correct operator as the one that “breaks” the degeneracy of the pure $a_1 \cos \psi$ boundary energy. Langmuir monolayers have Frank constants $\kappa_1$ and $\kappa_3$ for splay and bend that are not identical [16]. We have assumed in Eq. (2.1) that $\kappa_1 = \kappa_3$. The bulk equation satisfied by the director angle $\Theta$ is now nonlinear. Is the solution to this equation related in any way to the virtual boojum solution that plays such an important role in the determination of the domain’s shape? Preliminary work indicates that cusps also appear if we let $\kappa_1 \neq \kappa_3$. Another possibility is that thermal fluctuations lead to a renormalization of the effective anisotropic boundary energies [17]. This possibility is under current study.

The cusp singularities discussed in this paper should be generic features of boundary lines in Langmuir layers and two-dimensional liquid crystalline materials in general. Indeed, defect lines in hexatic Langmuir monolayers frequently exhibit a scalloped appearance [18], which may have the same origin as the cusps discussed here. The extension of the work reported here to more general sample shapes is not straightforward. With regard to the family of exact solutions for the texture we have found, an obvious question is whether some variation on a conformal transformation allows one to generate from it the texture appropriate to a non-circular domain. It is readily verified that a simple conformal transformation will not simultaneously deform the domain’s bounding curve and appropriately alter the texture. This is because of the nonlinear nature of the boundary conditions. However, given that we have obtained a set of exact solutions for the texture in the presence of realistic boundary conditions, an extension of the applicability of those solutions would be highly desirable.
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APPENDIX A: THE VIRTUAL BOOJUM SOLUTION

In this Appendix we show that Eqs. (2.11) and (2.12) represent exact solutions to the boundary value problem represented by Eq. (2.8), with one nonzero $a_n$. The demonstration is by direct substitution. We have

$$\frac{1}{2} a_n \left[ e^{in\theta} e^n (f(e^{i\theta})+f(e^{-i\theta})) - e^{-in\theta} e^n (f(e^{i\theta})-f(e^{-i\theta})) \right]$$

$$= \frac{1}{2} a_n \left[ \frac{e^{in\theta} - \alpha_n}{1 - \alpha_n e^{in\theta}} - \frac{e^{-in\theta} - \alpha_n}{1 - \alpha_n e^{-in\theta}} \right]$$

$$= \frac{1}{2} a_n \left[ \frac{1/\alpha_n - \alpha_n}{1 - \alpha_n e^{in\theta}} - \frac{1/\alpha_n - \alpha_n}{1 - \alpha_n e^{-in\theta}} \right] \quad (A1)$$

and

$$\frac{\kappa}{R_0} \left[ e^{i\theta} f'(e^{i\theta}) - e^{-i\theta} f'(e^{-i\theta}) \right] = \frac{\kappa}{R_0} \left[ \frac{\alpha_n e^{in\theta}}{1 - \alpha_n e^{in\theta}} + \frac{\alpha_n e^{-in\theta}}{1 - \alpha_n e^{-in\theta}} \right]$$

$$= \frac{\kappa}{R_0} \left[ \frac{1}{1 - \alpha_n e^{in\theta}} + \frac{1}{1 - \alpha_n e^{-in\theta}} \right] \quad (A2)$$

According to Eq. (2.8), the sum of the left hand sides of Eqs. (A1) and (A2) equals zero. The two right hand sides sum to zero if

$$\frac{1}{\alpha_n} - \alpha_n - \frac{2\kappa}{a_n R_0} = 0. \quad (A3)$$

The solution to this equation for the parameter $\alpha_n$ that has the proper limiting behavior is displayed in Eq. (2.12).
APPENDIX B: STABILITY OF THE BOUNDARY AGAINST $\sigma(\theta) \propto \cos(\theta)$

Consider an anisotropic surface tension having the form $\sigma(\theta) = A\cos(\theta)$. The total boundary energy of a closed boundary of arbitrary shape is

$$\oint \hat{c} \cdot \hat{n} ds. \quad (B1)$$

The quantity $\hat{c}$ in the above expression is a constant vector, $\hat{n}$ is the unit normal to the boundary and $ds$ is the infinitesimal element of length along the boundary. In two dimensions we can write

$$\hat{c} \cdot \hat{n} ds = \hat{z} \cdot (\hat{c} \times d\vec{s}), \quad (B2)$$

where $\hat{z}$ is the unit vector out of the plane and $d\vec{s}$ is the directed infinitesimal length element along the boundary. This means that the boundary energy is

$$\hat{z} \cdot \left[\left(\oint d\vec{s}\right) \times \hat{c}\right]. \quad (B3)$$

The closed integral on the right hand side of Eq. (B3) is always equal to zero. This means that a $\sigma(\theta) \propto \cos(\theta)$ has absolutely no effect on the shape of a two dimensional domain.

APPENDIX C: ON THE APPEARANCE OF CUSPS

To demonstrate exactly how the implementation of the Wulff construction in two dimensions leads to cusps on boundaries we consider the equation for the bounding curve generated by Eqs. (3.12)—that is, the boundary when the anisotropic surface tension is given by Eq. (3.11). Because of the symmetry of the domain, as illustrated in Figs 4, a cusp lying on the rightmost edge of the domain represents a solution to the equation $y(\theta) = 0$, subject to the additional condition $\theta \neq 0$. According to Eq. (3.12b), the above requirements are met when

$$\beta \cos \theta = 1. \quad (C1)$$

This equality can only be satisfied if $\beta > 1$. By simple geometry, we find that the interior angle of the cusp is equal to $\pi - 2\theta_c$, where $\theta_c = \arccos(1/\beta)$ is the angle satisfying Eq. (C1).
Fig. 4c depicts the boundary when $\beta = 1.5$, while Fig. 4b show how the domain looks when $\beta$ is equal to its critical value of 1.

Of interest is the “swallowtail” appendage attached to the cusp in the former case. The construction of the inner envelope corresponding to the equilibrium boundary shape is completed by the amputation of this appendage. Although the behavior of $x(\theta)$ and $y(\theta)$ in the tail is, thus, nominally irrelevant to the shape of the domain, a brief discussion of the properties of $x$ and $y$ in the tail region yields useful information regarding the mathematical signals that accompany the onset of a cusp. Consider, for instance, the cusps in the tail, at either end of the “trailing” edge. Using Eqs. (3.3), we find $dy/dx = -\cot(\theta)$. Thus, there will be no discontinuity in the slope of the curve given by Eqs. (3.1) as long as $\theta$ varies continuously. On the other hand, if the combination $R(\theta) + d^2R(\theta)/d\theta^2$ changes sign, then both $x(\theta)$ and $y(\theta)$ reverse directions with increasing $\theta$, leading to a cusp at which both segments of the curve meet tangentially. Such cusps represent the only type of discontinuity that can appear in the boundary generated by the construction outlined in Eqs. (3.1)—in the absence of an amputation at a point at which the boundary crosses itself. If we assume that any cusp generated by the Wulff construction will make its appearance accompanied by a swallowtail, then the onset of a cusp is signaled by a change in sign of $R(\theta) + d^2R(\theta)/d\theta^2$. This sign change first appears at the point on the boundary at which the cusp develops.

**APPENDIX D: ON VARIATIONAL DERIVATIVES**

In the implementation of the generalized version of the Wulff construction one is, characteristically, faced with the task of taking the variational derivative with respect to $R(\theta)$ of an integral of the form

$$
\int A(\sin \theta, \cos \theta) f(x(\theta), y(\theta)) \, dS,
$$

(D1)

where $A(\sin \theta, \cos \theta)$ is a polynomial in $\sin \theta$ and $\cos \theta$, $f(x(\theta), y(\theta))$ is a polynomial in $x(\theta)$ and $y(\theta)$ and $dS = [R(\theta) + d^2R(\theta)/d\theta^2] \, d\theta$ is the infinitesimal length element along the
boundary. While the relatively simple dependence of \( x \) and \( y \) on \( \theta \) allows the variational derivatives to be implemented in a straightforward manner, the complete and accurate determination of the derivative with respect to \( R(\theta) \) of an integral in which the functions \( f(x, y) \) and \( A(\sin \theta, \cos \theta) \) have any but the simplest form becomes extremely tedious, in the absence of a stratagem that allows for the evaluation of functional derivatives of non-trivial integrands. Fortunately, such a stratagem exists.

Consider the following version of the integral above:

\[
\int \sin \theta f(x, y) dS. \quad (D2)
\]

First, note that

\[
\sin \theta dS = \sin \theta \frac{dS}{d\theta} = \sin \theta \left[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} \right] = -\frac{dx(\theta)}{d\theta}. \quad (D3)
\]

The integral can thus be rewritten as

\[
-\int f(x(\theta), y(\theta)) \frac{dx}{d\theta} d\theta. \quad (D4)
\]

Now, we take the derivative \( \delta/\delta R(\theta) \) of the above integral:

\[
\frac{\delta}{\delta R(\theta)} \int f(x(\theta), y(\theta)) \frac{dx}{d\theta} d\theta = -\int \left\{ \frac{\partial f}{\partial x} \frac{\delta x}{\delta R} \frac{dx}{d\theta} + \frac{\partial f}{\partial y} \frac{\delta y}{\delta R} \frac{dx}{d\theta} + f(x, y) \frac{d}{d\theta} \frac{\delta}{\delta R} \right\} d\theta
\]

\[
= -\int \left\{ \frac{\partial f}{\partial x} \frac{dx}{d\theta} - \frac{\partial f}{\partial y} \frac{dy}{d\theta} \right\} d\theta - \int \left\{ \frac{\partial f}{\partial x} \frac{dx}{d\theta} \frac{dy}{d\theta} + \frac{\partial f}{\partial y} \frac{dy}{d\theta} \right\} d\theta
\]

\[
= \int \frac{\partial f}{\partial y} \left[ \frac{\delta x}{\delta R} \frac{dy}{d\theta} - \frac{\delta y}{\delta R} \frac{dx}{d\theta} \right] d\theta. \quad (D5)
\]

Now, given Eqs. (B.1), we have

\[
\frac{\delta x}{\delta R(\theta')} = \frac{\delta}{\delta R(\theta')} \left[ R(\theta) \cos \theta - \frac{dR(\theta)}{d\theta} \sin \theta \right]
\]

\[
= \delta(\theta - \theta') \cos \theta - \delta'(\theta - \theta') \sin \theta, \quad (D6)
\]
and

\[ \frac{\delta y}{\delta R(\theta')} = \delta(\theta - \theta') \sin \theta + \delta'(\theta - \theta') \cos \theta. \quad \text{(D7)} \]

With the use of the above two relations and Eqs. (D.1) the right hand side of Eq. (D5) becomes

\[ \int \frac{\partial f}{\partial y} \delta(\theta - \theta') \left[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} \right] d\theta \]

\[ = \frac{\partial f}{\partial y(\theta')} \left[ R(\theta') + \frac{d^2 R(\theta')}{d\theta'^2} \right]. \quad \text{(D8)} \]

Thus,

\[ \frac{\delta}{\delta R(\theta)} \int \sin \theta f(x, y) dS = \frac{\partial f}{\partial y} \left[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} \right]. \quad \text{(D9)} \]

A similar set of manipulations yields the result

\[ \frac{\delta}{\delta R(\theta)} \int \cos \theta f(x, y) dS = \frac{\partial f}{\partial x} \left[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} \right]. \quad \text{(D10)} \]

Note that the final results hold no matter what form is taken by the function \( f(x, y) \). The method described above can be fruitfully applied when the integrands are more complicated than the one above.

It is important to note that the steps leading to the final result, Eq. (D10), included integrations by parts, in which the “perfect derivative” terms were neglected. If the domain has a boundary that is free of singularities—especially cusps—one can easily justify this. However, when cusps are present, so that periodic boundary conditions on an integral around the circumference of a domain wall cannot be assumed, more attention to those terms is called for. The absence of a detailed analysis of the effects of a cusp in the boundary on the results of an integration by parts is a gap in the development in this work. Such an analysis is clearly called for.
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FIGURES

FIG. 1. A drawing of the kind of cusped domains seen in experiments. Such domains contain liquid condensed regions in an environment of the liquid expanded phase of a Langmuir monolayer. Figure 1a depicts the domain as it is seen in fluorescence microscopy. Figure 1b adds the “virtual boojum” texture that is conjectured to be responsible for the cusp.

FIG. 2. The various virtual singularity textures that emerge from exact solutions to Eqs. (2.2) and (2.3) when only one of the $a_n$’s in the surface energy in non-zero and the domain is circular. Figure 2a: $n = 1$, 2b: $n = 2$, 2c: $n = 3$, 2d: $n = 4$. The singularities sit outside the domain, except in the limit of infinite $\kappa$. For ease of depiction, they are shown on the domain boundary.

FIG. 3. The quantities $\theta$ and $R(\theta)$, as defined in Eqs. (3.1).

FIG. 4. The shape of a domain, when the surface tension has the anisotropic dependence on $\theta$, $e^{\beta \cos(\theta)}$, and $x(\theta)$ and $y(\theta)$ are given by Eqs. (3.12). As indicated in the Figure, the three cases depicted are $\beta = 0.5$, $\beta = 1$ and $\beta = 1.5$.

FIG. 5. The function $\text{Re}[X(\psi)]$, as defined in Eq.(6.21)

FIG. 6. A plot of the excluded angle $\Delta \psi = \pi - \psi_{\text{in}}$ versus the radius of the domain. The radius of the domain is expressed in units of $\kappa/a_1$. The ratio $a_2/\sigma_0$ has been set equal to 0.05. The quantities are defined in Section VI. The quantity $\psi_{\text{in}}$ is the interior angle of the cusp, and is shown in Figure 7

FIG. 7. The domain when $a_2/\sigma_0 = 0.25$ and $R_0a_1/\kappa = 5$. For definitions of the quantities, see Section VI. The interior angle, $\psi_{\text{in}}$, is indicated in the Figure.
FIG. 8. A comparison between the curve for the excluded cusp angle displayed in Figure 6 and data obtained by Schwartz, Tsao and Knobler (see ref. 12). The axes are both logarithmic and scales are adjusted to obtain a by-eye fit. No attempt was made to optimize agreement by adjusting energy parameters in the theoretical result.