Shape of domains in two-dimensional systems: virtual singularities and a generalized Wulff construction

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Abstract

We report on a generalized Wulff construction that allows for the calculation of the shape of two-dimensional materials with orientational order but no positional order. We demonstrate that for sufficiently large domain radii, the shape necessarily develops mathematical singularities, similar to those recently observed in Langmuir monolayers. The physical origin of the cusps is shown to be related to the softness of the material and is fundamentally different from that of the sharp angles seen in the shape of hard crystals.

61.30.Cz, 68.10.-m, 68.35.Md, 82.65.Dp
The singularities in the shape of crystalline materials have long been understood to be a macroscopic expression 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 (Miller indices [1]). In a classic paper [2], Wulff developed a geometrical construction that allows one to determine the equilibrium shape of a crystal, provided one knows the values of the surface energies for the various Miller indices. If, for every index, the corresponding surface is placed a distance from a fixed point proportional to the surface energy, then the inner envelope of the planes constitutes the minimum energy crystal shape.

Surprisingly, sharp edges in the shapes of samples are not just encountered for hard, crystalline materials. Using the Wulff construction, Herring argued that liquid crystals without positional order, but with orientational order could also display sharp angles, or cusps [3]. The cusps are no longer material invariants. Cusped domain shapes are, indeed, well-documented for three dimensional liquid crystals [4,5]. More recently, studies of the shapes of two dimensional materials without positional order have also revealed cusps and sharp angles [6]. These studies have also revealed that the internal structure of such “soft” materials is significantly deformed and dependent on the domain shape, while Herring assumed a rigid internal structure. Thus, the Wulff construction is not manifestly valid in this case.

In this paper we present a formalism which allows for the construction of domain shapes of soft two dimensional materials when the internal structure is described by a two dimensional XY model (e. g. hexatic or nematic liquid crystals). We will demonstrate that cusps are, indeed, not just possible, but that they ought to be a generic feature of such domain shapes. Moreover, the cusp angle provides important information on the elastic moduli and surface energy of the material.

We will model the internal structure of a domain by a unit vector \( \hat{c} = (\cos \Theta(\vec{r}), \sin \Theta(\vec{r})) \). The associated XY model free energy is

\[
H[\Theta(x, y)] = \int \frac{\kappa}{2} |\nabla \Theta|^2 \, dx \, dy + \int_{\text{boundary}} ds \, \sigma (\theta - \Theta) .
\]  

(1)

Here, \( \kappa \) is the stiffness (or Frank constant) of the order parameter field and \( \sigma \) is the
anisotropic surface energy, which depends on the relative angle, $\Theta - \theta$, between the order parameter and the outward normal $\hat{n} = (\cos \theta, \sin \theta)$ to the domain boundary. Note that $\sigma(\phi - 2\pi) = \sigma(\phi)$.

To find the optimal domain shape we must minimize $H[\Theta(x, y)]$ with respect to $\Theta(x, y)$ and the domain shape, while keeping the domain area, $A$, fixed. We start with the limiting case $\kappa = \infty$ when the texture is rigid so that $\Theta = 0$ and only the shape needs to be varied.

$$\kappa = \infty$$

The domain shape is a closed planar curve. We will express the co-ordinates $(x, y)$ of a point on the curve in terms of the angle $\theta$ of $\hat{n}$ and the minimum distance $R(\theta)$ between the tangent line through $(x, y)$ and the origin. In terms of $R(\theta)$:

$$x(\theta) = R(\theta) \cos(\theta) - \frac{dR(\theta)}{d\theta} \sin(\theta),$$

$$y(\theta) = R(\theta) \sin(\theta) + \frac{dR(\theta)}{d\theta} \cos(\theta).$$

The variational equation determining the domain shape is, then

$$\frac{\delta}{\delta R(\theta)} \oint \left[ \sigma(\theta') \left( R(\theta') + \frac{d^2 R(\theta')}{d\theta'^2} \right) - \lambda \frac{1}{2} R(\theta') \left( R(\theta') + \frac{d^2 R(\theta')}{d\theta'^2} \right) \right] d\theta' = 0. \quad (3)$$

The first term above is just the surface energy, with $(R(\theta) + d^2 R(\theta)/d\theta^2) \, d\theta$ a line element along the domain boundary. The second terms is $-\lambda A$, with $\lambda$ a Lagrange multiplier. The variational equation reduces to

$$R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} = \frac{1}{\lambda} \left[ \sigma(\theta) + \frac{d^2 \sigma(\theta)}{d\theta^2} \right], \quad (4)$$

with $R(\theta) = \sigma(\theta)/\lambda$ as the solution, modulo an overall translation of the domain. *The domain shape $R(\theta) = \sigma(\theta)/\lambda$ corresponds precisely to the Wulff construction.* The somewhat unusual parameterization of two dimensional curves thus allows for a straightforward and analytical determination of the domain shape.

The results above have been derived previously [7]. However, it has not, to our knowledge, been noted that variational derivatives with respect to $R(\theta)$ can be carried out when the
anisotropic surface energy of an element of boundary depends on the location of the element as well as its orientation. One simply replaces $\sigma(\theta)$ by $\sigma(x, y, \theta)$ and parameterizes $x$ and $y$ as in Eqs. (2). In the remainder of this Letter we describe the consequences of this strategy as applied to a two-dimensional domain.

\[ \kappa \text{ finite} \]

We now allow the internal structure of the domain to respond to changes in the domain shape. Minimizing $H[\Theta(x, y)]$ with respect to the angle $\Theta(x, y)$ leads to the requirement

\[ \nabla^2 \Theta(x, y) = 0 \quad (5a) \]

\[ \kappa \frac{\partial \Theta(x, y)}{\partial n} \bigg|_{\text{boundary}} - \sigma'(\theta - \Theta(x, y)) \bigg|_{\text{boundary}} = 0 \quad (5b) \]

In Eq. (5b) the $\partial/\partial n$ derivative is along the outward normal. With no loss of generality we can write the solution of Eq. (5a) as

\[ \Theta(x, y) = \frac{1}{i} (f(x + iy) - f(x - iy)) \quad (6) \]

with $f(z)$ an arbitrary analytic function. It is convenient to rescale $x$ and $y$ by the mean domain radius $R_0$. The domain boundary in the complex plane of a nearly circular domain is, then, the unit circle $z = e^{i\theta}$. Eq. (5b) then reduces to

\[ \frac{\kappa}{R_0} (zf'(z) - 1/zf'(1/z)) = i\sigma' \left( -i \log z + \frac{1}{i} (f(z) - f(1/z)) \right) \quad (7) \]

with $z$ on the unit circle.

If we now go through the same free energy minimization as for $\kappa = \infty$, we find instead of Eq. (4)

\[ R(\theta) + \frac{d^2 R(\theta)}{d\theta^2} = \sigma_0 + \mathcal{F}(\theta) \quad (8) \]

with $\sigma_0$ an isotropic surface tension and

\[ \mathcal{F}(\theta) = \frac{\kappa}{R_0} \left[ \frac{d}{dz} \left[ zf'(z) - \frac{1}{z} f'(1/z) \right] - [f(z) + f(1/z)] + (zf(z))^2 + \left( \frac{1}{z} f(1/z) \right)^2 + \int z^2 dw \left[ f'(w)^2 - \frac{1}{w^4} f'(1/w)^2 \right] \right]_{z = e^{i\theta}} \quad (9) \]
Equations (8) and (9), the latter relation holding if the domain is not too deformed from a perfect circle, are our key results. If we know the function $f(z)$ on the unit circle—through Eq. (8)—then we can reconstruct the domain shape with the use of Eqs. (8) and (9). Note from the discussion following Eq. (4) that we can interpret the solution $R(\theta)$ of Eq. (8) as being proportional to the effective surface tension, i.e. a surface tension that incorporates the interior softness of the domain.

Finding the complex function $f(z)$ looks like an intractable problem, as Eq. (7) is highly nonlinear. We will consider some physically relevant forms for $\sigma(\phi)$ to show how $f(z)$ and the domain shape may be found.

\[ \sigma(\phi) = \sigma_0 + a_n \cos n\phi \]

The case $n = 1$ corresponds to an anisotropic surface energy proportional to $\hat{c} \cdot \hat{n}$. The case $n = 2$ corresponds to the anisotropy energy of a two dimensional nematic.

It can be verified, by direct substitution, that

\[ f(z) = \frac{1}{n} \log (1 - \alpha_n z^n) \]

is a solution of Eq. (7), with

\[ \alpha_n R_0^n = \frac{n a_n R_0/\kappa}{1 + \sqrt{1 + (n a_n R_0/\kappa)^2}}. \]

When $n = 1$ the texture corresponds to the two-dimensional version of a “virtual boojum”—a singularity in the texture that lies outside of the domain. Imaging of domains of monolayer and near-monolayer films by Brewster angle microscopy reveals strong evidence for the existence of this structure. The distance of the boojum from the center of the domain, $R_B$, is given by

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

If the parameter $\Gamma \equiv \kappa/a_1 R_0$ is small compared to one, then $R_B$ approaches $R_0$, while in the limit $\Gamma = \infty$ the boojum retreats to infinity. The texture is, clearly, highly deformed when $\Gamma << 1$.
The domain shape is found by substituting from Eq. (10) into Eq. (9). Surprisingly, $\mathcal{F}(\theta) = 0$, so $R(\theta) = R_0$. The domain shape is thus a perfect circle for $n = 1$. For $n > 1$ the exact solution for the texture is equivalent to the texture produced by $n$ singularities lying outside of the domain. These singularities are no longer boojums in the accepted sense of the term [3,4]. The order parameter angle advances by $4\pi/n$ as one traces a path encircling one of the singularities; an advance of $4\pi$ characterizes the boojum. The singularities for $n > 2$ are “fractionally charged” in the topological sense. However, the fractional nature of these singularities appears to have no consequence for the textural structure of interest, as the singularities lie outside of the domain. Now $\mathcal{F}(\theta)$ is no longer equal to zero. The domain shape is deformed from perfect circularity.

$$\sigma(\phi) = \sigma_0 + a_1 \cos \phi + a_2 \cos 2\phi$$

This is the anisotropic boundary energy believed to be relevant to domains of liquid-condensed phase in Langmuir monolayers. It represents the lowest three terms in a systematic Fourier expansion of the anisotropic surface energy. For $a_2 \ll a_1$, the function $f(z)$ is given by

$$f(z) = \log (1 - \alpha z) \frac{a_2}{a_1} z \frac{1 - \alpha^2}{1 - \alpha z} \int_0^1 t^{2\alpha^2/(1 - \alpha^2)} \left[ \frac{zt - \alpha}{1 - \alpha z t} \right] dt + O \left( \left( \frac{a_2}{a_1} \right)^2 \right), \quad (13)$$

as can be checked by direct substitution. The small admixture of $a_2 \cos 2\phi$ in $\sigma(\phi)$ has dramatic effects on the shape. Using Eq. (13) in Eqs. (8) and (9), we find that

- For $R_0 < 0.356\sigma_0 \kappa/a_1 a_2$, the domain has a smooth, nearly circular, shape.
- For $R_0 > 0.356\sigma_0 \kappa/a_1 a_2$, the domain has a cusp singularity in its shape. For $R_0 \to \infty$, the cusp angle $\Delta \psi$—the difference between the inner angle of the cusp and $\pi$—obeys

$$\Delta \psi(R_0) = 5.48 \frac{\kappa}{a_1 R_0} + O \left( \frac{1}{R_0^2} \right). \quad (14)$$

Note that the asymptotic variation in the excluded angle is independent of the parameter $a_2$. The $a_2 \cos 2\phi$ term is thus a singular perturbation. The domain remains nearly circular outside of the immediate vicinity of the cusp.
Large domains will, thus, always have a cusped boundary. Figure 1 graphs the evolution of the excluded angle of the cusp as a function of the radius of a domain in which surface and bulk energy parameters have values that are consistent with the expansion described above. Figure 2 depicts a cusped domain as generated by the generalized Wulff construction for a specific domain radius. The inner angle of the cusp, $\psi_{\text{in}}$, is indicated in the Figure.

The measurement of cusp angle can be achieved by visual inspection of the domain. In light of the results reported above, a plot of $\Delta \psi$ versus $R_0$ should yield the parameter ratio $\kappa/a_1$, and also the combination $\sigma_0 \kappa/a_1 a_2$. A measurement of the cusp angle as a function of domain radius has, in fact, been carried out [13]. The results will be reported elsewhere.

In summary, we have found that deformable domains of materials with an $XY$-like order parameter may have shape singularities, even though their texture is perfectly analytic in the domain of definition. It is important to note that the material softness plays a key role. If we set the stiffness, $\kappa$, to infinity, then the boundary does not have a cusp. The physical origin of our cusp is thus strikingly different from that of hard crystalline materials. It would be interesting to know whether the results reported here extend to three dimensions.

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FIGURES

FIG. 1. The excluded angle, $\Delta \psi$, of the cusped domain, defined as the difference between $\psi_{in}$, the inner angle of the cusp (shown in Figure 2), and $\pi$. The plot is of the excluded angle versus domain radius when two of the parameters controlling surface and bulk energy satisfy $a_2/\sigma = 0.05$. The domain radius is in units of $\kappa/a_1$.

FIG. 2. The shape of a domain when the parameters controlling surface and bulk energy are such that the domain has a cusp. Note that the domain is nearly circular, except in the immediate vicinity of the cusp. Barely visible in the Figure is the “swallow tail” that appears as an appendage, attached to the domain at the cusp, when one implements the Wulff construction. This appendage is amputated to generate the true domain shape. The virtual boojum lies outside of the domain and near the cusp. In the Figure, $a_2/\sigma = 0.25$ and $R_0a_1/\kappa = 5$. 
