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Wetting of ring-shaped surface domains

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Abstract. – Wetting of ring-shaped surface domains is studied both theoretically and experimentally. The liquid channels covering these domains exhibit a volume-induced morphological transition from a homogeneous to a bulge state. The continuous symmetry of the low-volume channels is spontaneously broken by the transition to the high-volume regime. Therefore, an angular displacement of the bulge does not cost any (free) energy and the corresponding interface deformation represents a "Goldstone boson" which should be observable for domains in the micrometer regime.

Modern experimental methods make it possible to laterally structure a substrate in a controlled way, *i.e.* to endow a given substrate with a pattern of distinct surface domains, see, *e.g.*, refs. [1–6]. If such a structured surface is in contact with a liquid, the 2-dimensional pattern within the substrate leads to boundary conditions for the liquid which determine its 3-dimensional morphology.

These wetting systems are interesting both as templates for technologically relevant microscale structures, as, *e.g.*, microfluidic devices [7], and as models for fundamental research with unique geometric and topological properties. The interplay between the pattern of surface domains and the wetting layer morphology leads to a variety of new wetting phenomena such as i) non-spherical droplet shapes; ii) novel transitions of liquid channels [8]; and iii) morphological wetting transitions between different droplet patterns [9].

The channels studied in [8] were located on long striped surface domains which had a width of about 30 micrometers. These channels were found to undergo a transition from a homogeneous state with constant cross-section to an inhomogeneous state with a single bulge. For a stripe domain with a finite length, the bulge state has lowest free energy if the bulge sits in the middle between the two ends of the stripe. From the theoretical point of view, it would be appealing to have a stripe with periodic boundary conditions. In this latter case, the appearance of the bulge would break the translational symmetry in the direction parallel to the stripe, and the bulge state would be degenerate since its displacement along the stripe would not cost any energy.

In real systems, such periodic boundary conditions can be realized by ring-shaped surface domains consisting of an annulus with a constant width. This is the geometry which will be

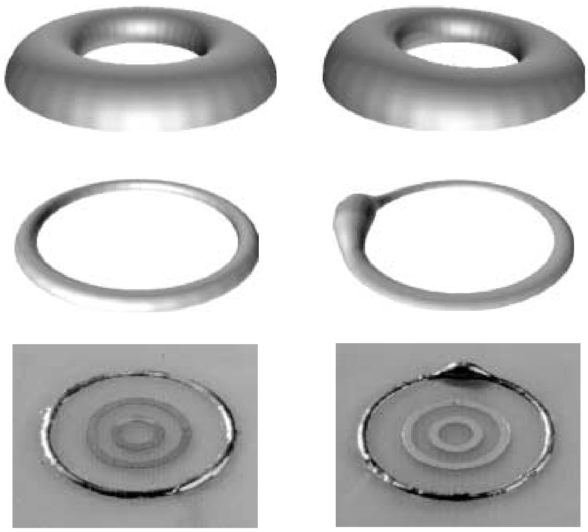

Fig. 1 – Morphological transition of wetting channels on a ring-shaped surface domain which is bounded by two concentric circles with diameters a_γ and $a_\delta < a_\gamma$. The channels displayed on the left have a relatively small volume and are axially symmetric; the channels on the right have a somewhat larger volume and exhibit a single bulge which breaks the axial symmetry. The shapes in the two upper rows have been calculated by numerical minimization; the shapes in the bottom row represent experimental observations on the millimeter scale. The shape of the bulge-state depends on the lyophilic area fraction $X \equiv (a_\gamma/a_\delta)^2$. The top, middle and bottom row correspond to $X = 4$, $X = 1.44$, and $X = 1.21$, respectively.

studied in this article. First, we calculate the corresponding shapes of the wetting channels i) by using analytical results for special constant-mean-curvature surfaces, so-called nodoids, and ii) by minimizing the interfacial free energies by numerical methods. These calculations predict a morphological transition from a nodoid channel to a ring channel with a single bulge. We also report experimental observations which confirm these theoretical predictions.

In fig. 1, we display examples of the calculated and observed shapes. The left and the right column in fig. 1 corresponds to shapes for relatively small and relatively large liquid volume, respectively. Inspection of these figures clearly shows that channels on ring-shaped surface domains undergo a volume-induced morphological transition from a state with constant cross-section, which is axially symmetric, to a bulge state for which this continuous symmetry is spontaneously broken. Note that, after the transition, both the theoretical and the real channels exhibit only a *single* bulge.

The experiments shown in the bottom row of fig. 1 were performed with channels of molten tin-lead alloys on ring-shaped domains of copper with a width of 1 mm. Thus, our study also shows that the morphological transitions which have been previously observed in the micrometer regime are also present on much larger scales. In fact, there are several well-established technologies, such as, *e.g.*, flatbed printing and soldering processes, which use wetting and dewetting of laterally structured surfaces in the millimeter regime. It seems likely that a systematic understanding of the morphological wetting transitions discussed here will find some applications in these technologies.

The channel shape. – To proceed, denote the vapor and the liquid phase by (α) and (β), and the hydrophilic (or lyophilic) and hydrophobic (or lyophobic) surface domains by (γ) and

(δ), respectively. The interfacial region between phase (i) and phase (j) has surface area A_{ij} and interfacial tension Σ_{ij}. The two surface regions are characterized by two contact angles θ_γ and θ_δ which are related to the interfacial tensions via the usual Young relations. We generally assume $0 \leq \theta_\gamma < \pi/2 < \theta_\delta \leq \pi$. In the following, we will concentrate on relatively large domains with a size which exceeds a few μm. Then, the equilibrium state of the wetting layer with prescribed volume V corresponds to the global minimum of the total interfacial free energy as given by [9]

$$F = \Sigma_{\alpha\beta} A_{\alpha\beta} + A_{\alpha w}(\Sigma_{\beta w} - \Sigma_{\alpha w}) + \Delta P(V_\beta - V), \tag{1}$$

with $w = \gamma$ or $w = \delta$. Since we work in an ensemble of constant volume, the pressure difference $\Delta P = (P_\alpha - P_\beta)$ represents a Lagrange multiplier which guarantees the volume constraint.

We neglect the effects of gravity since it should only have a small influence on the channel shapes but can lead to symmetry-breaking contributions which cannot be handled analytically, cf., *e.g.*, [10]. In the absence of gravity, the ($\alpha\beta$) interface is a *surface of constant mean curvature* M which satisfies the Laplace equation $2M\Sigma_{\alpha\beta} = P_\beta - P_\alpha$.

Next, we introduce a coordinate system with its origin at the center of (γ) and its z-axis perpendicular to the substrate surface. The domain then lies in the xy-plane and its boundary is given by two concentric circles with diameters a_γ and $a_\delta < a_\gamma$. The substrate is thus hydrophobic for $0 \leq r < a_\delta/2$ and $r > a_\gamma/2$ and hydrophilic for $a_\delta/2 < r < a_\gamma/2$.

It is now possible to calculate analytically the axisymmetric channel shapes which cover the hydrophilic ring completely. In three spatial dimensions, any surface which has both constant mean curvature and axial symmetry must be a plane, sphere, cylinder, catenoid, unduloid or nodoid as first shown by Delaunay [11]. For a ring-shaped surface domain, the channel shape must correspond to a certain segment of a nodoid since the remaining surfaces cannot fulfill the boundary conditions.

In order to calculate the channel shape explicitly, we will now proceed in three steps: i) First, we choose a parameterization for the nodoids; ii) we derive the conditions, which determine the nodoid segment representing the channel shape for $\theta_\gamma = 0$ and $\theta_\delta = \pi$; and iii) we generalize this analysis to $\theta_\gamma > 0$ and $\theta_\delta < \pi$.

The vector $R(z_N, \varphi) = (r(z_N)\cos\varphi, r(z_N)\sin\varphi, z_N)$ parameterizes the contour of the nodoid, with [12]

$$z_N(r|r_0, r_1) \equiv -r_0 \mathrm{F}(\kappa, p) - r_1 \mathrm{E}(\kappa, p) + \frac{1}{r}\sqrt{(r_1^2 - r^2)(r^2 - r_0^2)}. \tag{2}$$

Here, $\sin^2\kappa \equiv r_1^2(r^2 - r_0^2)/r^2(r_1^2 - r_0^2)$, $p^2 \equiv (r_1^2 - r_0^2)/r_1^2$ and F and E denote elliptic integrals of the first and second kind [13], respectively. Equation (2) generates the parameterization of the contour of a nodoid or more precisely of a whole sequence of nodoids. This sequence has two free parameters $r_0 < 0$ and $r_1 > 0$, where $|r_0|$ represents the minimal distance of the contour from the axis of rotation and r_1 its maximal distance. Thus, one has $|r_0| \leq r(z_N) \leq r_1$ in (2). By periodic continuation of $z_N(r|r_0, r_1)$, one obtains a surface which is defined for all values of z [14]. An example of such a nodoid contour is displayed in fig. 2(a). In this figure, the bold segment corresponds to the analytical expression (2), and its periodic continuation leads to the full contour of the axisymmetric shape (which is, in general, self-intersecting).

Now, the values of r_0 and r_1 have to be chosen in such a way that the boundary conditions at the contact lines are fulfilled. First, consider the special case $\theta_\gamma = 0$ and $\theta_\delta = \pi$. Then, the channel covers the whole domain and, for a given ring geometry, one has to choose a nodoid which satisfies

$$z_N(r = a_\gamma/2|r_0, r_1) = z_N(r = a_\delta/2|r_0, r_1). \tag{3}$$

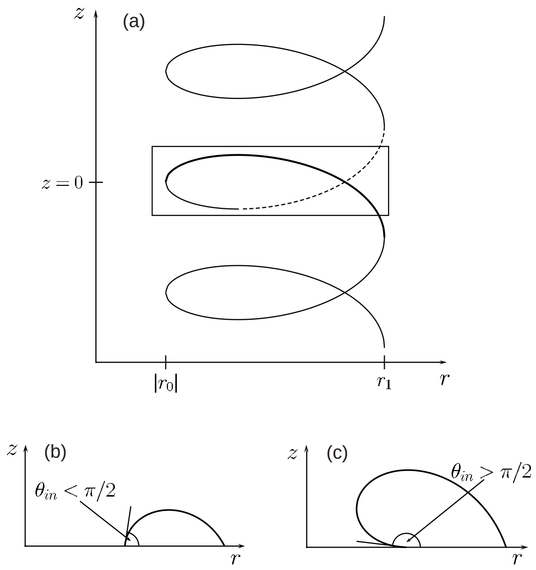

Fig. 2 – Construction of axially symmetric nodoid channels: (a) Contour of the nodoid in the (r, z)-plane. The segment representing the channel shape is obtained by cutting the nodoid perpendicular to the z-axis. For intermediate volumes V the channel covers the whole domain and one has to choose a segment whose boundaries lie on the domain boundaries and which fulfills the volume constraint $V_d = V$. These conditions can be satisfied by adjusting the free parameters r_0 and r_1. Depending on V one then obtains channels with interior contact angle (b) $\theta_{\rm in} < \pi/2$ or (c) $\theta_{\rm in} > \pi/2$. Both channel shapes correspond to a segment of the nodoid which is drawn as solid line in the box of panel (a).

This represents an implicit equation for $r_1 = r_1(r_0)$. The remaining parameter r_0 has to be adjusted in such a way that the volume $V_d = V_d(r_0, r_1)$ of the ring channel satisfies $V_d = V$. Finally, denote by $\theta_{\rm in}$ the interior contact angle at $r = a_\delta/2$ and by $\theta_{\rm out}$ the outer contact angle at $r = a_\gamma/2$. Then, one has $0 \leq \theta_{\rm in}, \theta_{\rm out} \leq \pi$ with values which depend only on the volume $V_d = V$.

In this way, one may calculate the functional dependence $r_1 = r_1(r_0)$ [12]. An analysis of this dependence shows that r_1 diverges in the limit of small $|r_0|$. This implies that such a solution exists for all ring geometries with $0 < a_\delta < a_\gamma$. In all cases, one has $\theta_{\rm out} < \pi/2$ provided $|r_0| > 0$.

For the general case $\theta_\gamma > 0$ and $\theta_\delta < \pi$, the values of $\theta_{\rm in}$ and $\theta_{\rm out}$ must satisfy $\theta_\gamma \leq \theta_{\rm in}, \theta_{\rm out} \leq \theta_\delta$. Thus, the outer contact line detaches from the domain boundary at $r = a_\gamma/2$ below a critical volume $V < V^{(1)} = V^{(1)}(\theta_\gamma)$. Likewise, the interior contact line retracts from the domain boundary at $r = a_\delta/2$ above a critical volume $V > V^{(2)} = V^{(2)}(\theta_\delta)$. In this case, the above analysis applies to $V^{(1)} < V < V^{(2)}$.

From the explicit solution for the channel shape, the mean curvature M can be calculated. Again, by first concentrating on $\theta_\gamma = 0$ and $\theta_\delta = \pi$, the divergence theorem implies

$$M = \frac{2}{a_\gamma^2 - a_\delta^2} \left(a_\gamma \sin\theta_{\rm out} + a_\delta \sin\theta_{\rm in} \right). \tag{4}$$

For a given channel volume $V_d = V$, the contact angles $\theta_{\rm out}$ and $\theta_{\rm in}$ are not independent. Thus, $\theta_{\rm in}$ can be chosen as an *order parameter* characterizing the channel shape. As shown in fig. 3, the mean curvature M has a maximal value $M = M_{\rm max}$ at $\theta_{\rm in} = \theta_{\rm in}^{\rm max}$, with $\pi/2 < \theta_{\rm in}^{\rm max} < \pi$.

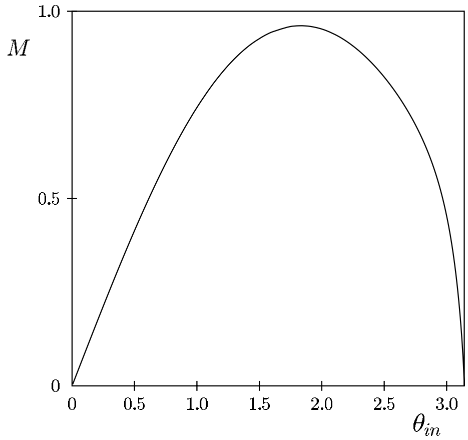

Fig. 3 – Mean curvature M of nodoid channel as a function of the interior contact angle $\theta_{\rm in}$ for ring-shaped surface domains with $a_\gamma/a_\delta = 2$.

The location of this maximum depends on the geometry, which can be characterized by the area fraction of the hydrophilic domains $X \equiv a_\gamma^2/a_\delta^2$. Thus, contrary to the case of circular or stripe domains [9], $\theta_{\rm in}^{\rm max}$ has no universal value here.

Since $\mathrm{d}^2M/\mathrm{d}\theta_{\rm in}^2 < 0$ and $M(0) = M(\pi) = 0$ one has a "thin" and a "fat" homogeneous channel for each value of $M < M_{\rm max}$. This already indicates the possibility of channel states with position-dependent order parameter, *i.e.*, with an interior contact angle $\theta_{\rm in} = \theta_{\rm in}(x)$. As shown in fig. 1 and described in the next section, we find indeed ring channels with a single bulge. These latter channels are built up from "thin" and "fat" channel segments with the same mean curvature [15].

Morphological transition. – The ring channels with a bulge are found for sufficiently small a_γ/a_δ and sufficiently large volumes using an extension of the numerical algorithm developed in [8]. Thus, our system undergoes a volume-induced morphological phase transition between an axisymmetric and a non-axisymmetric channel state. This transition corresponds to an exact symmetry breaking. Figure 1 shows the transition in two special geometries, for $a_\gamma/a_\delta = 2$ and $a_\gamma/a_\delta = 1.2$. In the first geometry the critical volume [16] is $V^*/((a_\gamma - a_\delta)/2)^3 \approx 3.9$, whereas in the second one $V^*/((a_\gamma - a_\delta)/2)^3 \approx 13.63$. In both geometries, the bulge state attains its largest contact angle along the interior domain boundary at $r = a_\delta/2$. For $a_\gamma/a_\delta = 2$ and 1.2, the largest contact angle is given by $\theta_{\rm in} \equiv \theta_> = 2.2$ and 2.65, respectively.

These results can be easily generalized to $\theta_\delta < \pi$. At the interior domain boundary, the maximum contact angle fulfills $\theta_> < \pi$ at the critical volume. Thus, if θ_δ is sufficiently large, one has $\theta_> < \theta_\delta$ and the contact line cannot detach from the domain boundary. Such a detachment is possible for small $\theta_\delta < \theta_>$; since the interior contact angle is larger than the outer one, the contact line detaches only from the interior boundary. Similar arguments apply to $\theta_\gamma > 0$.

Shape diffusion. – Since a displacement of the bulge along the ring does not change its interfacial free energy, the bulge state of the channel should undergo thermally excited shape diffusion. To be specific, let us assume that (α) is a vapor phase. The main source of dissipation for a moving bulge should then arise from the viscous flows within the bulge. If $L_{\rm b}$ and $v_{\rm b}$ are the linear dimension and the velocity of the bulge, the dissipated energy per unit time should be proportional to $\eta(v_b/L_b)^2L_b^3 = \eta L_b v_b^2$ as follows from the standard theory of hydrodynamics [17]. This implies a friction coefficient $f_b \sim \eta L_b$ and a diffusion coefficient

$$D_b = T/f_b \simeq T/\eta L_b. \tag{5}$$

For water at room temperature, one has $\eta \simeq 0.9 \times 10^{-3}$ kg/ms and $T \simeq 4 \times 10^{-21}$ J, which implies $D_b \simeq 5(\mu m/L_b)\mu m^2/s$. Thus, for ring-shaped domains in the micrometer range, it should take of the order of seconds for the bulge to diffuse around the domain. In practice, this diffusion process may be blocked by energy barriers arising, *e.g.*, from inhomogeneities in the domain thickness $a_\gamma - a_\delta$ or from pinning centers such as dust particles.

Experimental observations. – We have also performed a relatively simple experimental study of the wetting behavior on ring-shaped surface domains. Thus, we have produced a lyophilic ring with a width of 1 mm on a planar, lyophobic substrate using standard printed circuit board technology. Thus, the (δ)-regions are given by an epoxy-glass laminate and the (γ)-regions by copper. The wetting liquid consists of a metallic tin-lead alloy as used for soldering in electronics. The contact angles as determined by direct inspection are approximately $\theta_\gamma \simeq 0$ deg and $\theta_\delta \simeq 120$ deg. The alloy was heated above the melt-point and brought onto the substrate; when subsequently cooled down to room temperature, it solidified.

The experimental observations confirm our theory. Depending on the amount of molten metallic alloy, *i.e.* depending on the volume of liquid, the wetting layer morphology was either given by a homogeneous channel or a channel with a single bulge. One example for these experimentally observed transitions is shown in fig. 1. Inspection of this figure shows that the theoretical and experimental channel shapes are in good agreement. The only difference arises from the fact that gravity cannot be completely neglected on the millimeter scale, and the experimentally observed shapes are slightly flattened. Due to the large value of θ_δ, the contact line does *not* detach from the domain boundary at the critical volume. Since the channel and the bulge had a size in the millimeter range, the thermally excited shape diffusion was not accessible in these experiments.

In summary, we have studied the wetting of ring-shaped surface domains both theoretically and experimentally. The wetting layers covering these domains display a volume-induced shape transition from a homogeneous channel state with constant cross-section to an inhomogeneous channel with a single bulge. At this transition, the rotational symmetry is spontaneously broken. Because of this broken symmetry, there is no restoring force for an angular displacement of the bulge, and, for surface domains in the micrometer domain, this bulge should undergo thermally excited diffusion along the ring.

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[14] Unfortunately, derivations of this parameterization and in particular of eq. (2) are difficult to find in standard references. However, eq. (2) can be interpreted geometrically. If a hyperbola is rolled along a line, its focus describes a curve given by $z_N(r)$. The parameters r_0 and r_1 are then related to the semimajor axis $a = (r_1 + r_0)/2$ and $b = \sqrt{r_1 r_0}$ of the hyperbola.
[15] On substrates with many domains the order parameter also becomes position-dependent at the transition, but this dependence is only discrete.
[16] On stripes with length $L = 2\pi(a_\gamma + a_\delta)/4$ channels with a contact angle of $\theta = \pi/2$ have the volume $V/((a_\gamma - a_\delta)/2)^3 \approx 3.7$ for $a_\gamma/a_\delta = 2$ and $V/((a_\gamma - a_\delta)/2)^3 \approx 13.57$ for $a_\gamma/a_\delta = 1.2$.
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