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Solid-state dewetting and island morphologies in strongly anisotropic materials

Wei Jiang [a,b,*], Yan Wang [c], Quan Zhao [c], David J. Srolovitz [d,e], Weizhu Bao [c]

[a] School of Mathematics and Statistics, Wuhan University, Wuhan 430072, China
[b] Computational Science Hubei Key Laboratory, Wuhan University, Wuhan 430072, China
[c] Department of Mathematics, National University of Singapore, 119076, Singapore
[d] Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA
[e] Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA 19104, USA

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ABSTRACT

We propose a sharp-interface continuum model based on a thermodynamic variational approach to investigate the strong anisotropic effect on solid-state dewetting including contact line dynamics. For sufficiently strong surface energy anisotropy, we show that multiple equilibrium shapes may appear that cannot be described by the widely employed Winterbottom construction, i.e., the modified Wulff construction for an island on a substrate. We repair the Winterbottom construction to include multiple equilibrium shapes and employ our evolution model to demonstrate that all such shapes are dynamically accessible.

Solid-state dewetting is a ubiquitous phenomenon in thin film technology [1–5] which can either be deleterious, destabilizing a thin film structure, or advantageous, leading to the controlled formation of an array of nanoscale particles, e.g., used in sensor devices [6] and as catalysts for the growth of carbon or semiconductor nanowires [7,8]. Recently, solid-state dewetting has been attracting increased attention both because of interest in the underlying pattern formation physics and its potential application as an economical approach to obtain nanostructured surfaces and nanodevices [9–18].

The dewetting of thin solid films deposited on substrates is similar to the dewetting of liquid films [19,20]. However, mass transport during solid-state dewetting is usually dominated by surface diffusion rather than fluid dynamics. Solid-state dewetting can be modeled as interface-tracking problem where morphology evolution is governed by surface diffusion and contact line migration [17,18]. In early studies, a number of simplifying assumptions were made in order to keep the analysis tractable. For example, under the assumption that all interface energies are isotropic, Srolovitz and Safran [9] proposed a sharp-interface model to analyze hole growth; based on the above model. Wong et al. [10,11] designed a "marker particle" numerical scheme to study the two-dimensional retraction of an island and a perturbed cylindrical wire on a substrate. Recently, Jiang et al. [17] solved a similar problem using a phase field approach that naturally captures the topological events that occur during evolution and is applicable in any number of dimensions.

However, many experiments have demonstrated that the morphology evolution that occurs during thin solid film dewetting is strongly affected by crystalline anisotropy [3]. Recent approaches that incorporate crystalline anisotropy have included a discrete model [12], a kinetic Monte Carlo method [13,14] and the crystalline method [15,16]. The main drawback of these approaches is that the evolution does not account for the full anisotropic free energy of the system or do not represent a completely mathematical description. To overcome these shortcomings, we [18] proposed a continuum model for simulating morphology evolution during solid-state dewetting for weakly anisotropic surface energies. But it is not straightforward to extend this approach to the strongly anisotropic case, and the major difficulty comes from how to understand the thermodynamic variation including contact line migration. In this letter, we extend this dynamical evolution continuum model to include the common case where the anisotropy is strong and its influence on solid-state dewetting morphologies is pronounced.

We note at the outset, that although we apply this dynamical evolution model to the simulation of morphology evolution during the solid-state dewetting of thin films, it also naturally provides a much more general solution to the problem of how to determine the equilibrium shape of a crystalline island on a substrate than is currently available. This is a problem of long-standing in the materials science and applied mathematics communities; receiving important attentions from many

* Corresponding author at: School of Mathematics and Statistics, Wuhan University, Wuhan 430072, China.
E-mail addresses: jiangwei1007@whu.edu.cn (W. Jiang), matbaowz@nus.edu.sg (W. Bao).

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researchers over more than one hundred years [21–27]. This problem can be stated as follows: determine the island shape that minimizes the total interface energy,

$$\min_{\Omega} \; W_1 = \int_{\Gamma} \gamma(\theta)\; d\Gamma + \underbrace{(\gamma_{FS}-\gamma_{VS})\left(x_c^r - x_c^l\right)}_{\text{Substrate Energy}}, \tag{1}$$

where Ω denotes the region occupied by the island, the volume of the island is conserved, i.e., $|\Omega|$ = constant, Γ represents the film (or island)/vapor interface, and the right and left contact points are x_c^r and x_c^l (these are points/lines where the vapor, film and substrate coexist), and γ_{FV}, γ_{FS} and γ_{VS} are, respectively, the surface energy densities of the film/vapor, film/substrate and vapor/substrate interfaces. We assume that the film/vapor interface energy (density) γ_{FV} is a function only of the interface normal, i.e., $\gamma_{FV}=\gamma(\theta)$, $\theta\in[-\pi,\pi]$ represents the local orientation of the outer normal to the film/vapor interface, and γ_{FS} and γ_{VS} are independent constants. The solution to problem (1) yields an equilibrium shape with minimal interface/surface energy of prescribed area (or volume).

As is well known, if the island is free-standing (i.e., not in contact with the substrate), the equilibrium shape is given by the classical Wulff construction [21–24]. If, on the other hand, the island is in contact with a flat, rigid substrate, the equilibrium shape is classically described using the Winterbottom construction [25,26]. However, when the surface energy anisotropy is strong, the Wulff envelope may include "ears"; cutting off the "ears" gives the equilibrium shape [23,28]. In the case of an island on a substrate, however, the existence of "ears" in the Wulff envelope can give rise to multiple stable (or metastable) shapes. As we demonstrate below, the existence of such additional states has a profound effect on morphology evolution; giving rise to stable morphologies never seen on the basis of the widely accepted and applied Winterbottom construction. Incorporation of such non-Winterbottom effects is essential in describing observed island morphologies that arise during kinetic phenomena such as the solid-state dewetting process discussed here.

We first derive the dynamical evolution model directly from the free energy, including the effect of strong interface energy anisotropy. The total free energy of the system for solid-state dewetting problems under strongly anisotropic conditions can be written in two parts: $W=W_1+W_2$, where the first term W_1 was defined in Eq. (1) (also see Ref. [18]). When the surface energy anisotropy is sufficiently large, the surface diffusion evolution equations become ill-posed. To address this issue, we add a regularization term W_2 (i.e., a Willmore energy regularization) into the system [29–32]:

$$W_2 = \frac{\varepsilon^2}{2}\int_{\Gamma} \kappa^2\; d\Gamma, \tag{2}$$

where ε is a small regularization parameter and κ denotes the curvature of the film/vapor interface, Γ.

We calculate the first variation of the energy functional W with respect to the interface shape Γ and the left and right moving contact points, x_c^l and x_c^r [33]. Then, following a procedure similar to that in the weakly anisotropic case [18], we find that the two-dimensional solid-state dewetting of a thin film with strongly anisotropic surface energies on a flat solid substrate can be described in the following dimensionless form in a sharp-interface model (see Supplemental Material for more details):

$$\frac{\partial \mathbf{X}}{\partial t} = V_n\mathbf{n} = \frac{\partial^2 \mu}{\partial s^2}\mathbf{n}, \tag{3}$$

$$\mu = (\gamma(\theta)+\gamma''(\theta))\kappa - \varepsilon^2\left(\frac{\partial^2\kappa}{\partial s^2}+\frac{\kappa^3}{2}\right), \tag{4}$$

where $\Gamma=\mathbf{X}(s,t)=(x(s,t),y(s,t))$ represents the moving film/vapor interface, s is the arc length or distance along the interface and t is the time, V_n is the velocity of the interface in the direction of its outward normal, $\mathbf{n}$ is the interface outer unit normal direction and μ denotes the chemical potential. Note that all lengths and interface energies are scaled by two constants R_0 and γ_0, chosen as described below. The governing Eqs. (3)–(4) are subject to the following dimensionless boundary conditions:

(I) Contact point condition (BC1)

$$y(0,t)=0, \quad y(L,t)=0, \tag{5}$$

where $L=L(t)$ denotes the total length of the interface at time t, and therefore we can use $s=0$ and $s=L$ to represent the left and right contact points (x_c^l and x_c^r).

(II) Relaxed contact angle condition (BC2)

$$\frac{dx_c^l}{dt} = \eta f_{\varepsilon}\left(\theta_d^l\right), \quad \frac{dx_c^r}{dt} = -\eta f_{\varepsilon}(\theta_d^r), \tag{6}$$

where θ_d^l (or θ_d^r) is the (dynamical) contact angle at the left (or right) contact point, η represents the contact line mobility, $f_{\varepsilon}(\theta)=\gamma(\theta)\cos\theta-\gamma'(\theta)\sin\theta-\sigma-\varepsilon^2\frac{\partial\kappa}{\partial s}\sin\theta$, and the material parameter $\sigma=(\gamma_{VS}-\gamma_{FS})/\gamma_0$.

(III) Zero-mass flux condition (BC3)

$$\frac{\partial\mu}{\partial s}(0,t)=0, \quad \frac{\partial\mu}{\partial s}(L,t)=0. \tag{7}$$

(IV) Zero-curvature condition (BC4)

$$\kappa(0,t)=0, \quad \kappa(L,t)=0. \tag{8}$$

Because these dynamical evolution PDEs are sixth-order (fourth-order for weak anisotropy [18]), to make the system well-posed, we introduced an additional boundary condition (BC4), which rigorously comes from the variation of the total energy functional [34]. The total free energy of the system described in Eqs. (3)–(8) can be shown to decrease monotonically at all times and that the total mass of the solid film on top of the substrate is conserved during the evolution.

We solve the governing Eqs. (3)–(8) by using a parametric semi-implicit mixed finite element scheme [35]. Compared to traditional explicit finite difference approaches (e.g., marker particle methods), the proposed finite element method allows for larger time steps while satisfying numerical stability requirements [36]. We set the initial film thickness to unity (i.e., we choose R_0 as the initial film thickness) and assume a dimensionless anisotropic surface energy of the form:

$$\gamma(\theta) = 1+\beta\cos[m(\theta+\phi)], \tag{9}$$

where β controls the magnitude of the anisotropy, m is the rotational symmetry order and ϕ represents a phase shift angle describing a rotation of the crystallographic axes of the island with respect to the substrate plane (ϕ is set to zero except where noted). It should be pointed out that although we assume that the surface energy is smooth, for the non-smooth or "cusped" surface energy, we can deal with the problem by smoothing the surface energy with small parameters.

We now turn to the issue: how does strong anisotropy affect solid film dewetting morphologies — especially, the stable island shapes produced by dewetting? In the proposed model, we find that if the small