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On stability of self-assembled nanoscale patterns

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Abstract

We conduct linear and nonlinear stability analyses on a paradigmatic model of nanostructure self-assembly. We focus on the spatio-temporal dynamics of the concentration field of deposition on a substrate. The physical parameter of interest is the mean concentration C_0 of the monolayer. Linear stability analysis of the system shows that a homogeneous monolayer is unstable when C_0 lies within a band symmetric about $C_0 = \frac{1}{2}$. On increasing C_0 from zero, the homogeneous solution destabilizes to a hexagonal array, which then transitions to stripes. Transitions to and from the hexagonal state are subcritical. Square patterns are unstable for all values of C_0 transitioning either to hexagons or stripes. Further, we present stability maps for striped arrays by considering possible instabilities. The analytical results are confirmed by numerical integrations of the Suo–Lu model. Our formalism provides a theoretical framework to understand guided self-assembly of nanostructures.

Keywords: Self-assembly; Stability analysis; Nanostructures

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1. Introduction

Self-assembly, i.e., the spontaneous formation of patterns (Whitesides and Grzybowski, 2002), is emerging as a promising technique for epitaxial growth of regular nanoscale arrays on a substrate. For example, Pohl et al. (1999) observed that when a monolayer of silver deposited on a ruthenium (0 0 1) surface is exposed to sulfur, a regular array of 3.4 nm diameter (sulfur) disks is formed; Wahlström et al. (1999) showed that the deposition of sulfur on Cu (1 1 1) substrate at low temperature leads to the formation of honeycomb-like structures with a length scale of 1.67 nm; Umezawa et al. (2001) reported the growth of a network of equilateral triangles of side 3 nm when a Ag monolayer of fractional coverage 0.8 is deposited on Cu (1 1 1) substrate at room temperature.

At the scale of interest, each of the above experimental systems is (nearly) isotropic and homogeneous and the epitaxial deposition is spatially homogeneous except for stochastic effects. The destabilization of the homogeneous monolayer is caused by spontaneous symmetry breaking giving energetically favorable patterned structures (Cross and Hohenberg, 1993). Although detailed microscopic theories are needed to predict quantitative features of surface structures for a given experimental configuration, general characteristics of self-assembly can be studied using phenomenological field theoretic models. Factors that need to be included in such models are: (i) a double-welled free energy function of the epilayer to ensure phase separation; (ii) an interfacial energy between distinct monolayer phases; and (iii) an elastic energy due to non-uniformity of the surface stress (Ng and Vanderbilt, 1995; Glas, 1997; Guyer and Voorhees, 1998; Suo and Lu, 2000). The competition between (ii) and (iii) is responsible for size selection of self-assembled domains. The relative simplicity of the phenomenological models allows one to conduct a comprehensive theoretical analysis of self-assembled states, their stability domains, and how they destabilize.

Our studies are conducted on a Cahn–Hilliard type model of self-assembly due to Suo and Lu (2000) which is introduced briefly in Section 2. The physical variable of interest is the mean fractional coverage C_0 of the monolayer and the remaining parameters, such as the elastic mismatch and temperature, are kept fixed. Stability boundaries for the homogeneous solution are evaluated in Section 3 using linear stability analysis. Consistent with previous variational calculations, the homogeneous solution is unstable for an interval I symmetric about $C_0 = \frac{1}{2}$. Section 4 shows examples of hexagonal, striped and labyrinthine structures generated in numerical integrations of the model system while their stability maps are calculated using nonlinear stability analysis in Section 5. In Sections 6–8, we present the major new contributions of our work, namely *nonlinear* stability analyses of striped, square and hexagonal arrays using multiple scales analysis (Newell and Whitehead, 1969; Segel, 1969; Cross and Hohenberg, 1993). In particular, we show in Section 7 that square arrays are never stable, and in Sections 6 and 8 calculate stability boundaries for striped and hexagonal arrays. Theoretical results for striped arrays are shown to agree very well with those from numerical integrations of the Suo–Lu model. Agreement for the hexagonal case, although close, is imperfect. We argue that this disagreement is due to the finite amplitude of the hexagonal structures for parameter values considered in the paper. Section 9 discusses the merit of our work in providing a theoretical framework for guiding self-assembly of nanostructures.

Linear and nonlinear stability analysis have several advantages over techniques based on calculating the energy of a given collection of solutions. It does not require the underlying