A New Method for Simulating Strongly Anisotropic Cahn-Hilliard Equations

S. Torabi , S. Wise , J. Lowengrub
University of California, Irvine, California, USA

A. Rätz, A. Voigt
Institute für Wissenschaftliches Rechnen, Technische Universität Dresden, Dresden,Germany

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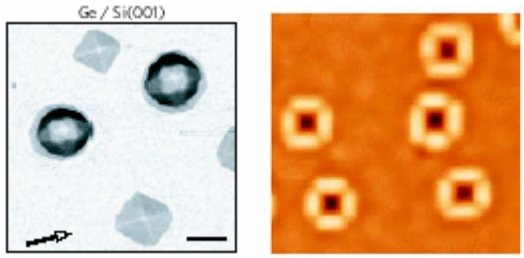
Abstract

We present a new approach for modeling strongly anisotropic crystal and epitaxial growth using regularized, anisotropic Cahn-Hilliard-type equations. Such problems arise during the growth and coarsening of thin films. When the surface anisotropy is sufficiently strong, sharp corners form and unregularized anisotropic Cahn-Hilliard equations become ill-posed. Our models contain a high order Willmore regularization to remove the ill-posedness. A key feature of our approach is the development of a new formulation in which the interface thickness is independent of crystallographic orientation. We present 2D numerical results using an adaptive, nonlinear multigrid finite-difference method. In particular, we find excellent agreement between the computed equilibrium shapes using the Cahn-Hilliard approach, with a finite but small Willmore regularization, and an analytical sharp-interface theory recently developed by Spencer [1].

Introduction

In order to overcome the fundamental limits that will prevent continued shrinking of microelectronics, revolutionary new quantum computing schemes will be needed within the next two decades. However, if we are to realize the extraordinary information processing potential offered by quantum logic, control at near-atomic length scales is required to build devices based on ordered assemblies of nanoscale quantum dots. While such structures are well beyond the capabilities of standard lithographic techniques, directed self-assembly approaches are already demonstrating how complex 3D nanostructures can be constructed via manipulation of the natural processes associated with their growth [4].

Self-organized semiconductor nanostructures are a promising inexpensive and effective approach to manufacture novel electronic and magnetic devices. Quantum dots (pyramids/domes) and other nanostructures such as quantum dot molecules (pits surrounded by four islands) (see Figure 1), for example, have a sharper density of states than higher-dimensional structures and may be used in diode lasers, amplifiers, biological sensors and data storage devices.



(a) (b)

Fig. 1 (a) Quantum dot pyramids (light) and domes (dark) [3]; (b) Quantum dot molecules [5]

The production of quantum-dot-based devices is still challenging. A fundamental understanding of the self-organization process (nucleation, growth and coarsening) during epitaxial growth is necessary to achieve controlled quantum scale structures. The influence of strain, surface energies and kinetics on the surface evolution have to be considered and may play a significant role in the evolution and equilibria. These effects can be analyzed by modeling and numerical studies that complement experimental investigations. The long-term goal is the production of large numbers of controlled self-assembly and spatially ordered nanostructures with narrow size distribution.

In many technologically important materials (e.g. Si-based materials for electronic devices and Fe-based materials for magnetic devices), the surface energy is strongly anisotropic and there are missing orientations. This poses a problem for standard sharp-interface or Cahn-Hilliard type models as the equations become ill-posed (e.g. see [12,13] and the references therein). In this work, we present a new approach for modeling strongly anisotropic crystal and epitaxial growth using regularized, anisotropic Cahn-Hilliard-type equations. Our models contain a high order Willmore regularization [2] to remove the ill-posedness. A key feature of our approach is the development of a new formulation in which the interface thickness is independent of crystallographic orientation. We present 2D numerical results using an adaptive, nonlinear multigrid finite-difference method. In particular, we find excellent agreement between the computed equilibrium shapes using the Cahn-Hilliard approach, with a finite but small Willmore regularization, and an analytical sharp-interface theory recently developed by Spencer [1].

Background

The interfacial energy γ can be a function of the crystallographic orientation of the interface, Figure 2. In 2D, the parametric form of the surface or interfacial energy can be

$$\gamma(\theta) = 1 + \varepsilon_m \cos(m\theta) \tag{1}$$

where γ is the interfacial energy density, ε_m is the anisotropy parameter, m is number of fold symmetry, θ is the crystallographic orientation (e.g. the angle the normal vector makes with a coordinate axis). In 2D, total energy for the sharp interface model is

$$E_s = \int \gamma(\theta)\ ds \tag{2}$$

where s is the interface arc length.

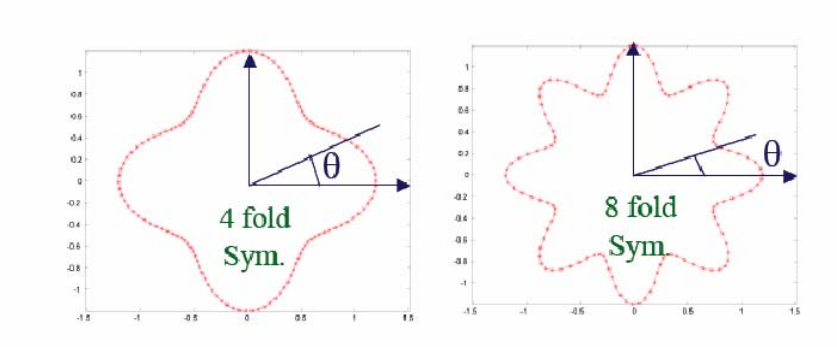


Figure 2 The interfacial energy is function of the crystallographic orientation

The equilibrium shape minimizes the total interfacial energy. The classical Equilibrium shape (sharp interface model) is the Wulff shape. In parametric form, the Wulff shape can be constructed by the following equations [7]:

$$x = \gamma(\theta)\cos\theta - \gamma'(\theta)\sin\theta \qquad (3\ a\&b)$$
$$y = \gamma(\theta)\sin\theta + \gamma'(\theta)\cos\theta$$

When surface stiffness is negative, $\gamma+\gamma''<0$, sharp corners and edges will be developed therefore certain orientations are missing from the equilibrium shape surface. In the four fold case (Figure 3), this occurs when $\varepsilon_4 > 1/15$.

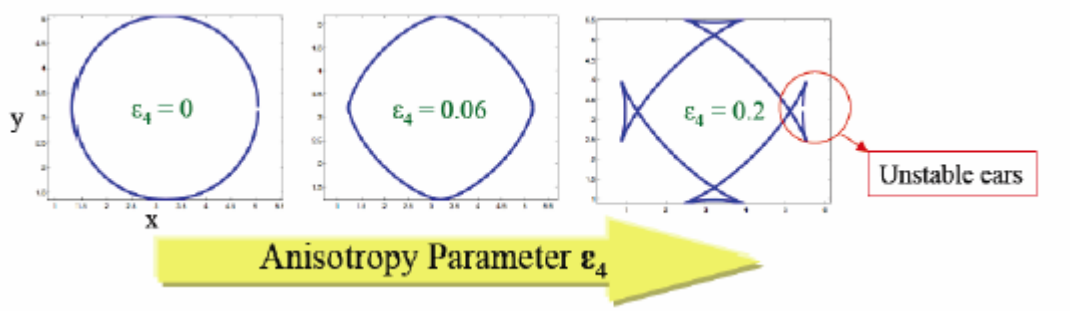


Figure 3 Wulff shapes at different ε values

Development of Equations

There are two kinds of interfaces, sharp and diffuse, as depicted in the Figure 4. For the sharp interface model, denote the interface by Σ, then the equations are given as follows:

- Free Energy

$$E = \int_{\Sigma} \gamma(\theta) ds \qquad (4)$$

- Chemical Potential

$$\mu = \frac{\delta E}{\delta \Sigma} = (\gamma(\theta) + \gamma_{\theta\theta}(\theta))\kappa \tag{5}$$

where κ is the curvature and $\delta E / \delta \Sigma$ is the variational derivative of the energy with respect to the interface Σ.

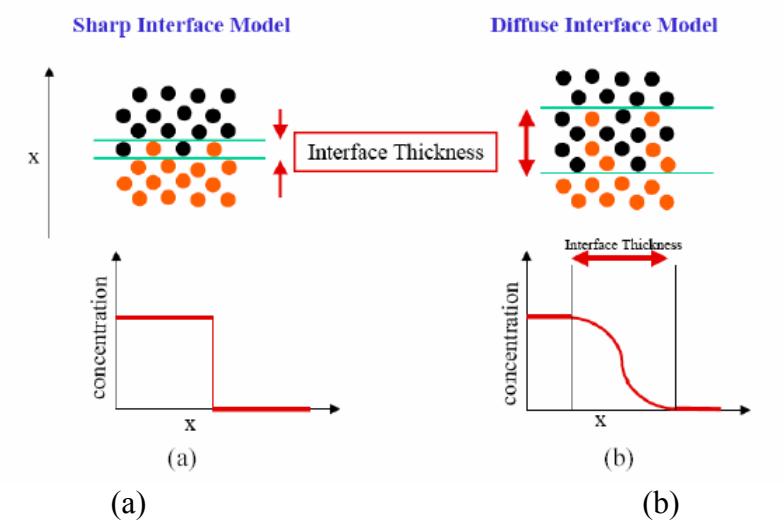


Figure 4 (a) Sharp and (b) Diffuse interface schematic

- Surface Diffusion (the interface is assumed to move by surface diffusion)

$$v = \partial_s(M \partial_s \mu) \tag{6}$$

where M is the mobility and v is the normal velocity of evolving surface.

As stated previously, the equilibrium shape for the sharp interface model is the Wulff shape and when the surface stiffness is negative, sharp corners will cause the equations to be ill-posed. In order to regularize the equation, a high order regularization term E_W may be added to the free energy:

$$E_W = \int \frac{\delta^2}{2} \kappa^2 ds \tag{7}$$

where δ is the regularization parameter. This is known as the Willmore or corner energy regularization [1, 2, 6, 9, 10]. Note that the effect of the regularization is highly localized at near corners in the interface and tends to smooth the corners. For the new energy (summation of energies in Eqs. (4) and (7) , the chemical potential becomes:

$$\mu = (\gamma(\theta) + \gamma_{\theta\theta}(\theta))k - \delta^2(\partial_{ss}k + k^3) \tag{8}$$

B. Spencer [1] has provided an asymptotic solution for the equilibrium shape (i.e. when μ is constant) near corners for the regularized sharp interface model. His solution has round corners where the degree of rounding depends on δ.

In the diffuse interface approach, sharp interfaces are replaced by narrow transition layers and an order parameter, φ that denotes the phases in a multiphase system, is introduced. The order parameter is constant (0 or 1) in each phase and the interface (transition layer) between phases corresponds to the region where φ varies from 0 to 1, see Figure 5. An advantage of using this method is that the explicit tracking of the interface is unnecessary as the evolution of the interface is captured by the evolution of level sets of φ.

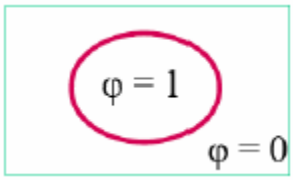


Figure 5 Phase field model schematic

The classical formulation of the diffuse interface equations for anisotropic systems dates to Kobayashi [11]. The energy and chemical potential in this formulation are given by

- Free Energy and Chemical potential

$$E = \int \frac{1}{\varepsilon}\left(f(\varphi) + \frac{\varepsilon^2}{2}\left|\gamma(\mathbf{n})\nabla\varphi\right|^2\right)dx \ , \tag{9}$$

$$\mu = \frac{\delta E}{\delta \varphi} = f' - \varepsilon^2 \nabla.\mathbf{m} \, , \tag{10}$$

where ε is a small parameter that is a measure of the interface transition layer thickness, f is a double-well free energy, i.e.,

$$f(\varphi) = \frac{A}{4}\varphi^2(1-\varphi)^2 , \tag{11}$$

where A provides a magnitude, $\mathbf{m}$ is the anisotropic gradient

$$\mathbf{m} = \gamma^2 \mathbf{p} + \gamma \ \left|\mathbf{p}\right| \ \mathbf{P}\nabla_{\mathbf{n}}\gamma \quad , \tag{12}$$

where we have defined $\mathbf{p}$ to be the gradient of φ, $\mathbf{n}$ to be the normal vector and P to be the tangential projection matrix:

$$\mathbf{p} = \nabla\varphi \quad , \ \mathbf{n} = \mathbf{p}/|\mathbf{p}| \text{ and} \tag{13}$$

$$\mathbf{P} = \left|\nabla\varphi\right| \ \frac{\partial \mathbf{n}}{\partial \mathbf{p}} \quad . \tag{14}$$

In the remainder of the paper, we will assume that the surface energy γ takes the form

$$\gamma(\mathbf{n}) = 1 + a \ \Gamma(\mathbf{n}) \quad . \tag{15}$$

Note that this formulation holds in both 2D and 3D. In 2D, this is equivalent to assuming γ depends on the normal angle θ as described above for sharp interfaces.

The evolution is assumed to decrease the total energy so $dE/dt \le 0$. Assuming a conservative evolution, this leads to Cahn-Hilliard type equation:

$$\frac{\partial \varphi}{\partial t} = \nabla.(M \nabla \mu), \tag{16}$$

where M is the mobility. If we consider evolution by surface diffusion, then M is localized near the interface, i.e.

$$M = \bar{M} \varphi \ (1-\varphi), \tag{17}$$

where $\bar{M} \approx \varepsilon^{-2}$ is a constant scale factor.

As in the sharp interface case, when the surface energy is strongly anisotropic, the Cahn-Hilliard system is ill-posed [12, 13]. To overcome the ill-posedness, regularizations are introduced. In one approach [14], the surface energy is convexified. However, convexification prevents the nucleation of new facets in the system [15]. As an alternative, high order derivative regularizations have been used [16, 17]. One approach that was proposed in [12] is to add a diffuse-interface analogue of the Willmore regularization described previously.

In recent work, Du et al. [18] developed a diffuse interface analogue of the Willmore regularization energy in the context of *isotropic* surface energies. This formulation requires that the interface thickness be uniform regardless of the crystallographic directions. Unfortunately, the formulation of anisotropic surface energies given above has the intrinsic property that the interface thickness varies with orientation. To overcome this difficulty, we have developed a new formulation of anisotropic systems.

Instead of using the energy E given in Eq. (9), we introduce the alternative energy and chemical potential:

$$E = \int \frac{1}{\varepsilon} \gamma(\mathbf{n}) \left(f(\varphi) + \frac{\varepsilon^2}{2} |\nabla \varphi|^2 \right) dx, \tag{18}$$

$$\mu = \gamma(\mathbf{n}) f' - \varepsilon^2 \nabla.\mathbf{m} \quad . \tag{19}$$

Note that now the anisotropic surface energy multiplies both the bulk and gradient terms. This is a natural formulation if we interpret the term $\left(f(\varphi) + \varepsilon^2 |\nabla \varphi|^2 / 2\right) / \varepsilon$ as approximating the surface delta function. It can be shown that this results in the development of interfaces whose thickness is independent of orientation [19]. As before, we take the anisotropic gradient to be **m**,

$$\mathbf{m} = \gamma(\mathbf{n}) \ \mathbf{p} + |\mathbf{p}| \ \mathbf{P} \ \nabla_{\mathbf{n}} \gamma \ . \tag{20}$$

where **p** and **P** are also the same as before.

Because the interface thickness is now uniform, we may take the diffuse interface form of the Willmore regularization [18]:

$$E_W = \frac{\varepsilon\delta^2}{2}\int(-\Delta\varphi + \frac{f'(\varphi)}{\varepsilon^2})^2\,dx \tag{21}$$

where δ is the regularization parameter. Taking the energy to be $E + E_W$, the chemical potential now becomes:

$$\mu = \gamma(\mathbf{n})f' - \varepsilon^2\nabla.\mathbf{m} + \frac{\varepsilon\delta^2}{2}(\nabla^3\mathbf{p} - \frac{f''\,\nabla\mathbf{p}}{\varepsilon^2}) \tag{22}$$

where **m** is given in Eq. (20). Finally, the evolution of φ is given as in Eqs. (16) and (17) but with the new definition of μ from Eq. (21). Note that this system is 6th order in space. We should point out that this evolution does not strictly guarantee that $dE/dt \le 0$ because of our choice of anisotropy gradient **m**. The **m** we use in Eq. (22) relies on the asymptotic result $\varepsilon^2|\mathbf{p}|^2/2 \approx f(\varphi)$ to replace the term $|\mathbf{p}|/2 + f(\varphi)/(\varepsilon^2|\mathbf{p}|)$, which arises from the variational derivative of the total energy $E + E_W$ with respect to φ, with $|\mathbf{p}|$. If we did not replace this term, the energy would be nonincreasing. However, the term $f(\varphi)/|p|$ can be problematic when ε is not sufficiently small since in principle $|p|$ could vanish in regions where f does not. Based on this assumption, we have also assumed that asymptotically $\varepsilon^2\nabla\mathbf{p}/2 \approx f'(\varphi)$ in Eq. (22). In a subsequent work [19], we demonstrate using matched asymptotic expansions that the new system converges to the classical sharp interface model as the interface thickness ε tends to 0.

Numerical Methods

To solve the 6th order system numerically, we adapt the numerical scheme we recently developed in [13] to this case. In this algorithm, an implicit time discretization is used to remove the high-order time step stability constraints. The equations are written as a system of three second order equations and are discretized using 2nd order accurate centered finite differences. One of the keys to the success of the method is the treatment of the anisotropic gradient. This term is discretized in conservation form in space and is lagged in time. Non-conservative treatments of the anisotropic term lead to numerical instability [13].

Other key components of the algorithm are the use of dynamic, block-structured Cartesian mesh refinement (e.g., [20, 21]), see Figure 6, and the use of an adaptive nonlinear multigrid method to solve the equations at the implicit time level. Locally refined block structured Cartesian meshes strike a balance between grid structure and efficiency and are very natural to use together with multilevel, multigrid methods. We note that other multilevel multigrid algorithms have been developed as part of the CHOMBO [22, 23] and the BEARCLAW [24] software packages. The Full Approximation Scheme (FAS) multigrid methodology presented in Kim et al. [25] for the isotropic Cahn-Hilliard equation, is used with appropriate modification so as to fit within the framework of the block-structured Multi-Level Adaptive Technique (MLAT) developed by Brandt [26]. See Trottenberg et al. [27, Ch.9].

We note there are adaptive mesh refinement schemes for the Cahn-Hilliard equation in the finite element framework. See [25] for the cases of weak surface energy anisotropy and strong kinetic anisotropy and the works of Garcke et al. [28] and Kay and Welford [29] for isotropic surface energies.

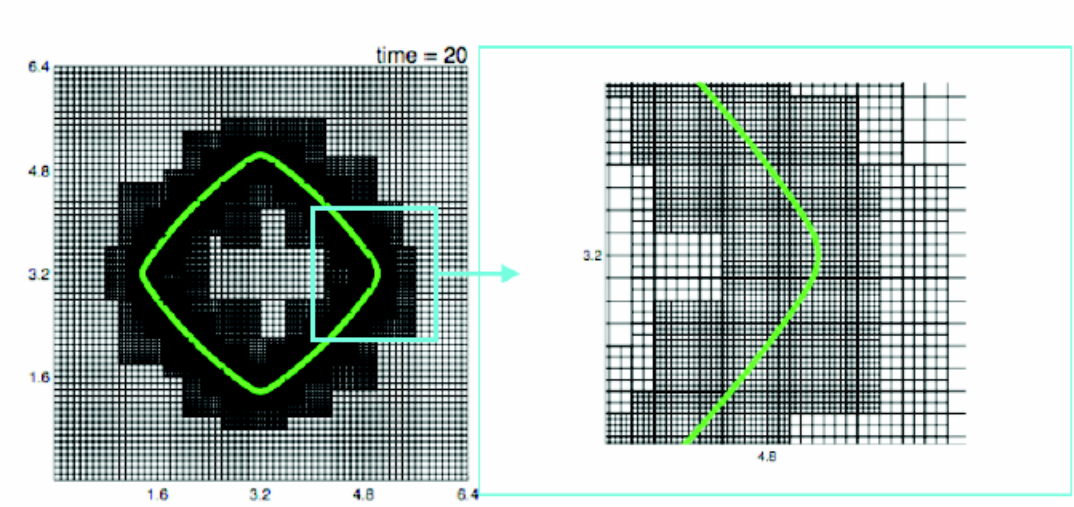


Figure 6 Adaptive mesh, showing finer mesh along the interface

Results

We begin by comparing the near equilibrium shapes we have obtained by solving the dynamical equations for long times with analytical results. We then investigate the dependence of the equilibrium shapes on the anisotropy and Willmore regularization parameters. We also simulate different surface energy anisotropies and initial conditions.

We first compare the result of the strongly anisotropic Cahn-Hilliard model and the classical sharp interface Wulff shape in Figure 7. Here we have plotted the $\varphi = 0.5$ level sets. Away from the corners, there is very good agreement between the numerical and analytical results. Near the corners, in contrast to the Wulff shape, the Cahn-Hilliard model yields interfaces with smoothed corners.

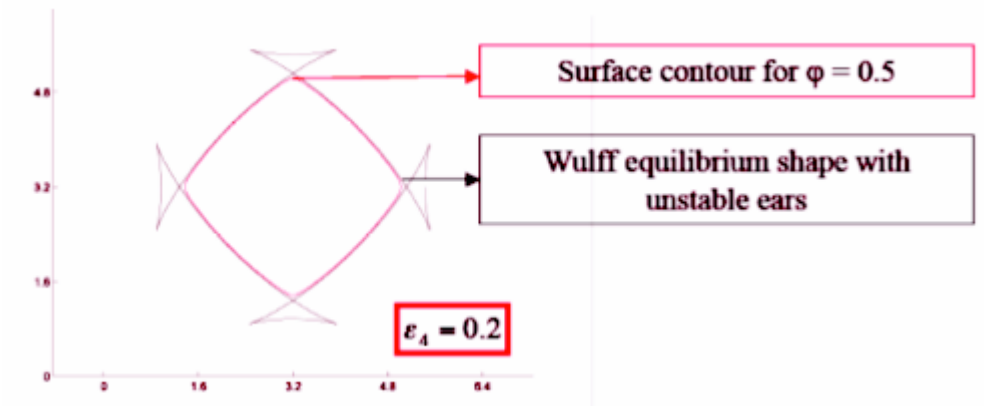


Figure 7 Comparisons between the Wulff shape and the Numerical Results

To investigate the Cahn-Hilliard model near corners, we next compare our model with Spencer's sharp interface asymptotic results that take into account the Willmore regularization term [1]. This is the first time we are aware of that such a comparison has been performed. In the Spencer approach, the equilibrium shape near a corner is parameterized as

$$x = \frac{\delta}{\varepsilon}\int (\cos(\theta)/\kappa)\ d\theta,$$
$$y = \frac{-\delta}{\varepsilon}\int (\sin(\theta)/\kappa)\ d\theta, \qquad \text{(23 a\&b)}$$

where κ is the curvature and can be approximated by

$$\kappa = \pm\sqrt{2(\gamma(\theta) + \overline{A}\cos(\theta) + B\sin(\theta))}\ , \qquad (24)$$

and $\overline{A}$ can be calculated via

$$\overline{A} = -\gamma(\theta_\infty)\cos(\theta_\infty) + \gamma'(\theta_\infty)\sin(\theta_\infty)\,, \qquad (25)$$

where θ_∞ satisfies

$$\gamma(\theta_\infty)\sin(\theta_\infty) + \gamma'(\theta_\infty)\cos(\theta_\infty) = 0\,. \qquad (26)$$

One can see from Figure 8, that the results of the Cahn-Hillard model completely match Spencer's asymptotic results near the rounded corners of the interface.

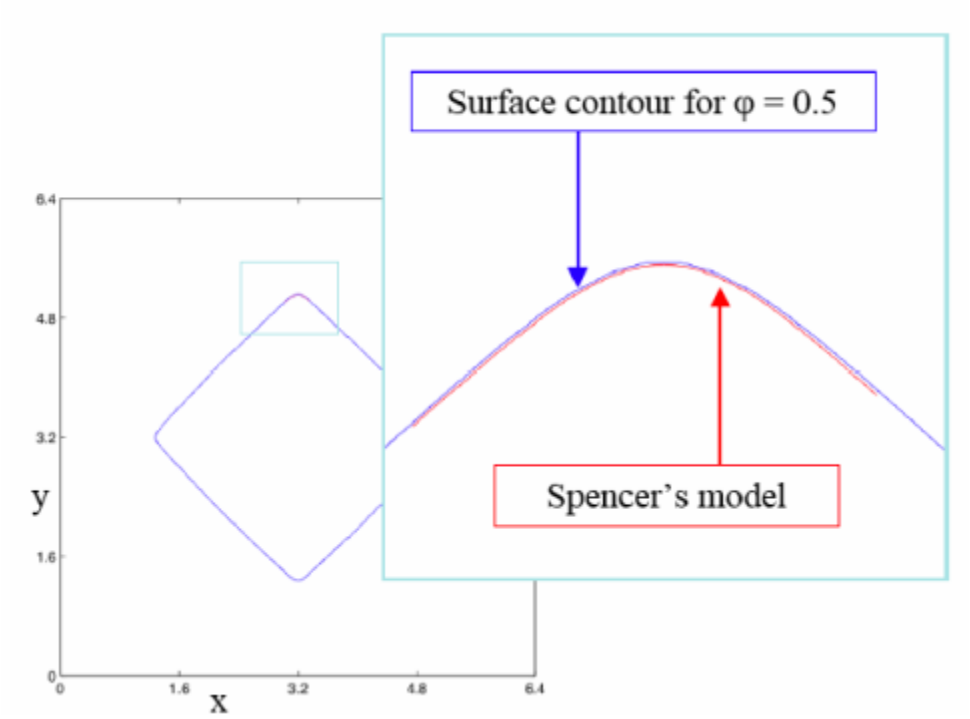


Figure 8 Comparisons between Spencer's equilibrium shape [1] and the Numerical Results

In Figure 9, we investigate the effect of varying the anisotropy parameter ε_4 and the regularization parameter δ. As ε_4 increases and as δ decreases, sharper corners form in the equilibrium interface morphologies and the sides are less curved.

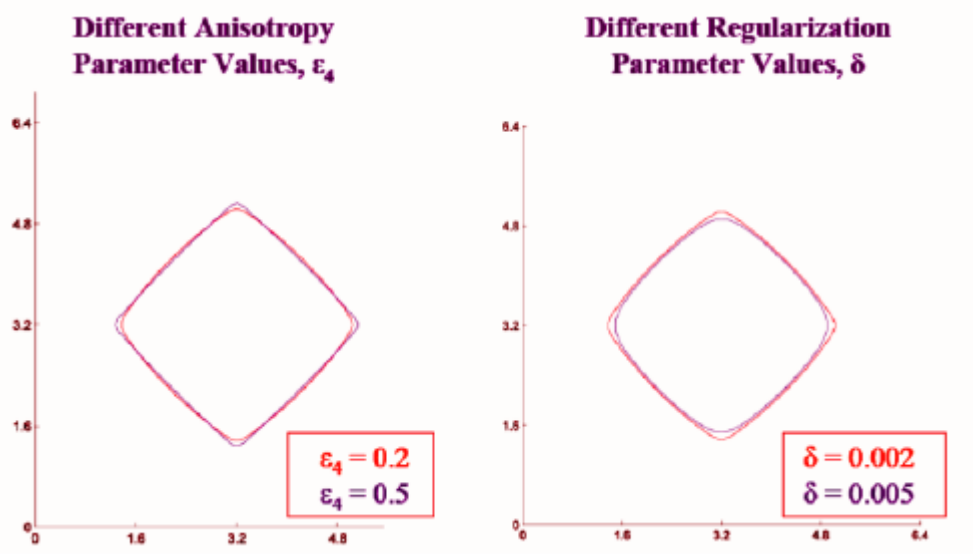


Figure 9 Numerical result for different values of the anisotropy parameter, ε_4, and the regularization parameter, δ

Next, in Figure 10, we demonstrate that the interface thickness is not a function of crystallographic direction using the new free energy model.

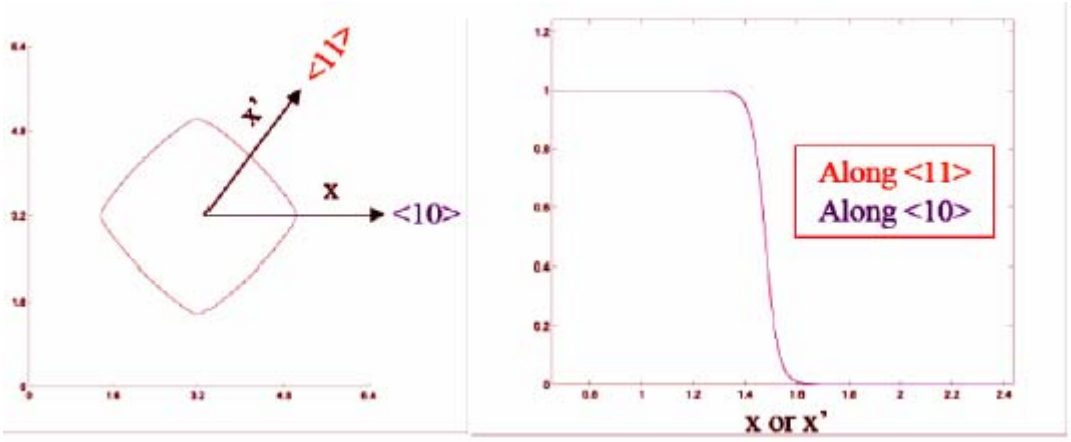


Figure 10 The interface thickness in the new model is not function of crystallographic direction

Finally, in Figure 11, we indicate the evolution towards equilibrium using the Cahn-Hilliard model and examine the effects of different anisotropies and initial interface shapes. For a closed interface, the difference between 4-fold and 8-fold surface energy anisotropies is quite significant while for open, periodic interfaces the differences are more subtle between the two anisotropies because the evolution is more highly constrained by the periodicity.

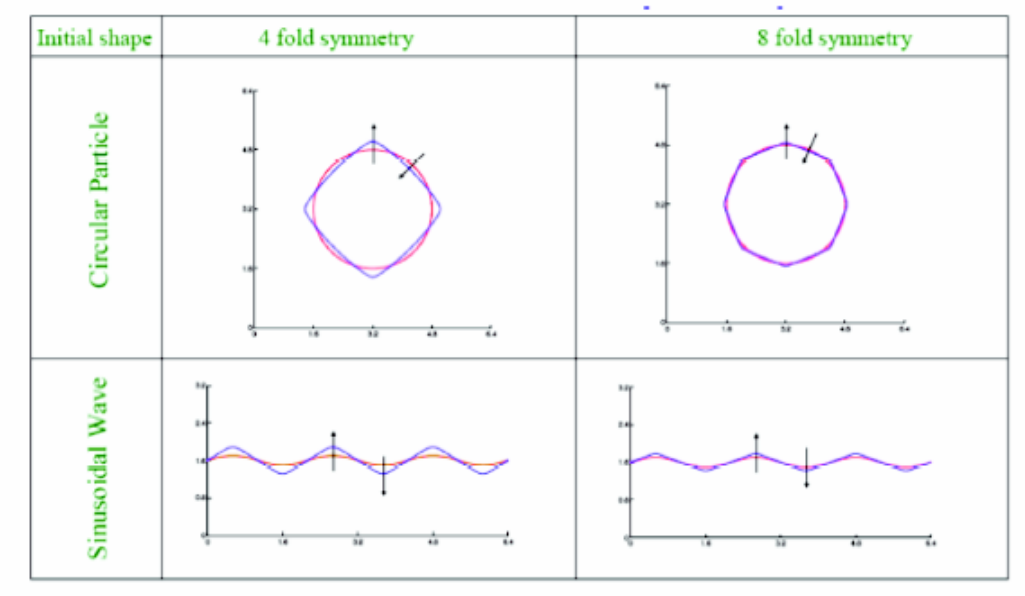


Figure 11 The surface contour for $\varphi = 0.5$, ε_4 & $\varepsilon_8 = 0.2$. The arrows denote the motion of the interface. Initial shape is in Red line and Equilibrium shape is in Blue line.

Conclusion

A new approach for modeling strongly anisotropic crystal and epitaxial growth has been proposed. In this new model, the interface thickness is independent of the crystallographic direction. When the surface anisotropy is sufficiently strong, sharp corners form and unregularized anisotropic Cahn-Hilliard equations become ill-posed. Our models contain high order diffuse Willmore regularization to remove the ill-posedness. We presented 2D numerical results using an adaptive, nonlinear multigrid finite-difference method. In particular, we found excellent agreement between the computed equilibrium shapes using the Cahn-Hilliard approach, with a finite but small Willmore regularization, and an analytical sharp-interface theory recently developed by Spencer [1]. We investigated the effects of anisotropy strength, the Willmore regularization, different anisotropies and initial conditions. In future work, we shall extend the computational model to 3D and we will incorporate elastic stress in the model and examine its effects on the results.

Acknowledgment

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