

# Stress-Driven Surface Instabilities in Ionic Solids Containing Charged Point Defects

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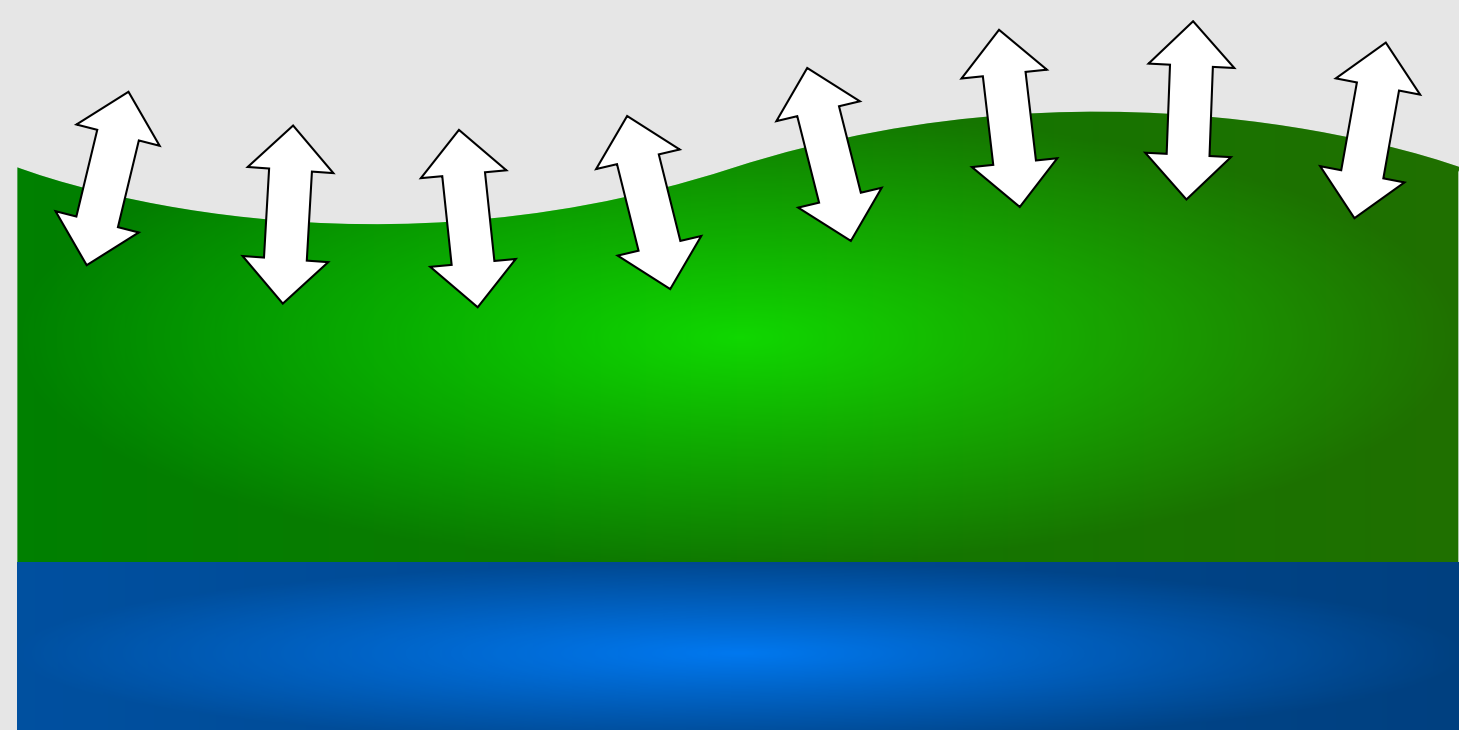
## 1. Introduction

Oxides exhibit a wide range of functional characteristics that make them suitable for numerous technological applications. In many of these applications, the oxides form epitaxial systems with the underlying support structure, giving rise to internal stresses that affect both surface mass rearrangement and bulk point defect distributions. In oxides, however, point defects can be charged, and their concentrations are also influenced by space charge formation and the associated internal electric fields. We present a continuum model for ionic solids containing charged point defects coupled with elasticity and electrostatics. Using a 3D finite element scheme, we demonstrate the effects of these defects on the film's morphological stability and characterize incipient instabilities in terms of model parameters.

## 2. Theory

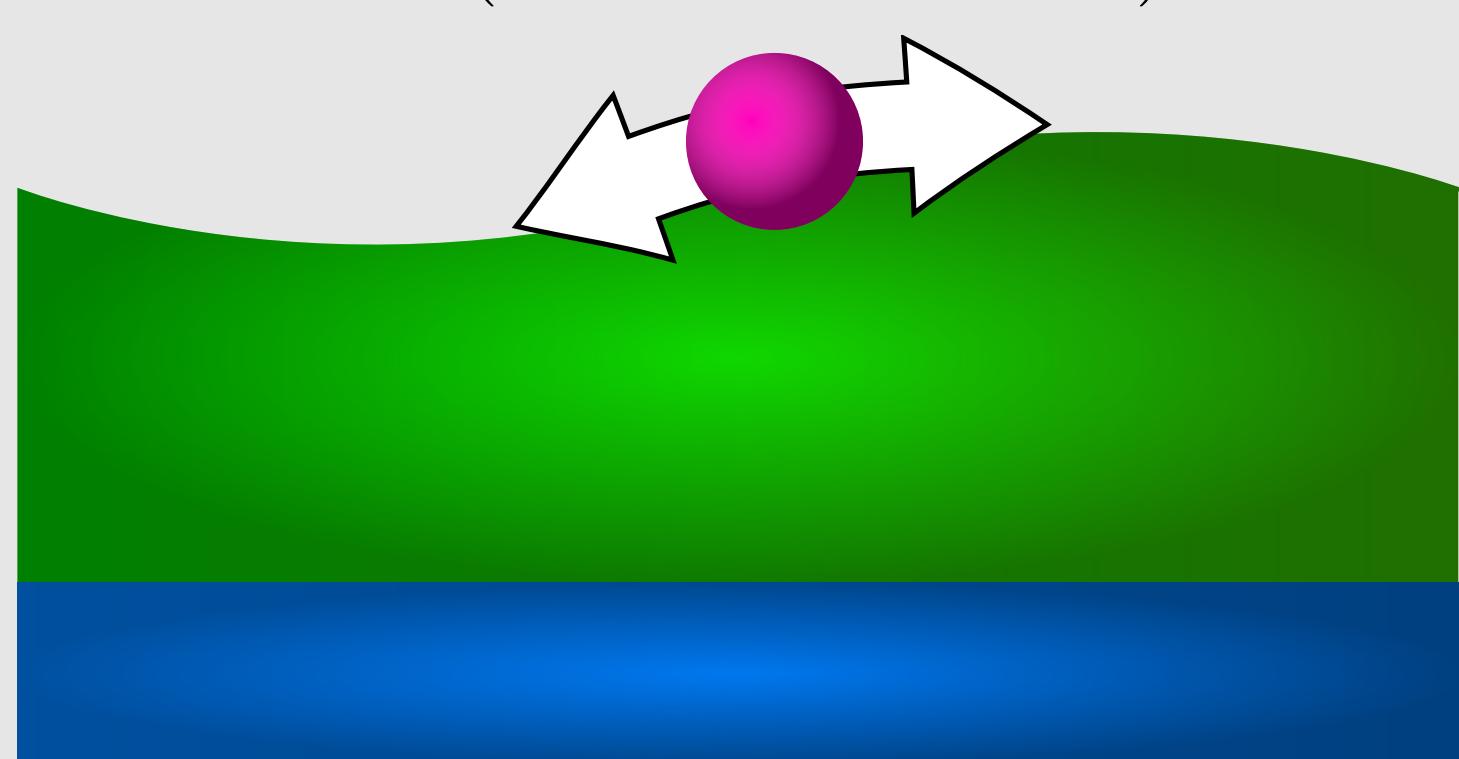
Here, we present a thermodynamically-consistent set of equations to describe the free surface evolution of an oxide system containing mobile charged point defects. Our model includes the elastic effects of the film-substrate misfit strain, electrostatic space charge to account for the presence of charged point defects and interfaces, and a dynamic surface update procedure to evolve the film-vapor interface. The equation governing the evolution of the film's free surface is a statement of mass conservation.

$$v_{(n)} = -\Omega (j_{\alpha}^{\alpha} + J_i n^i) \quad (1)$$



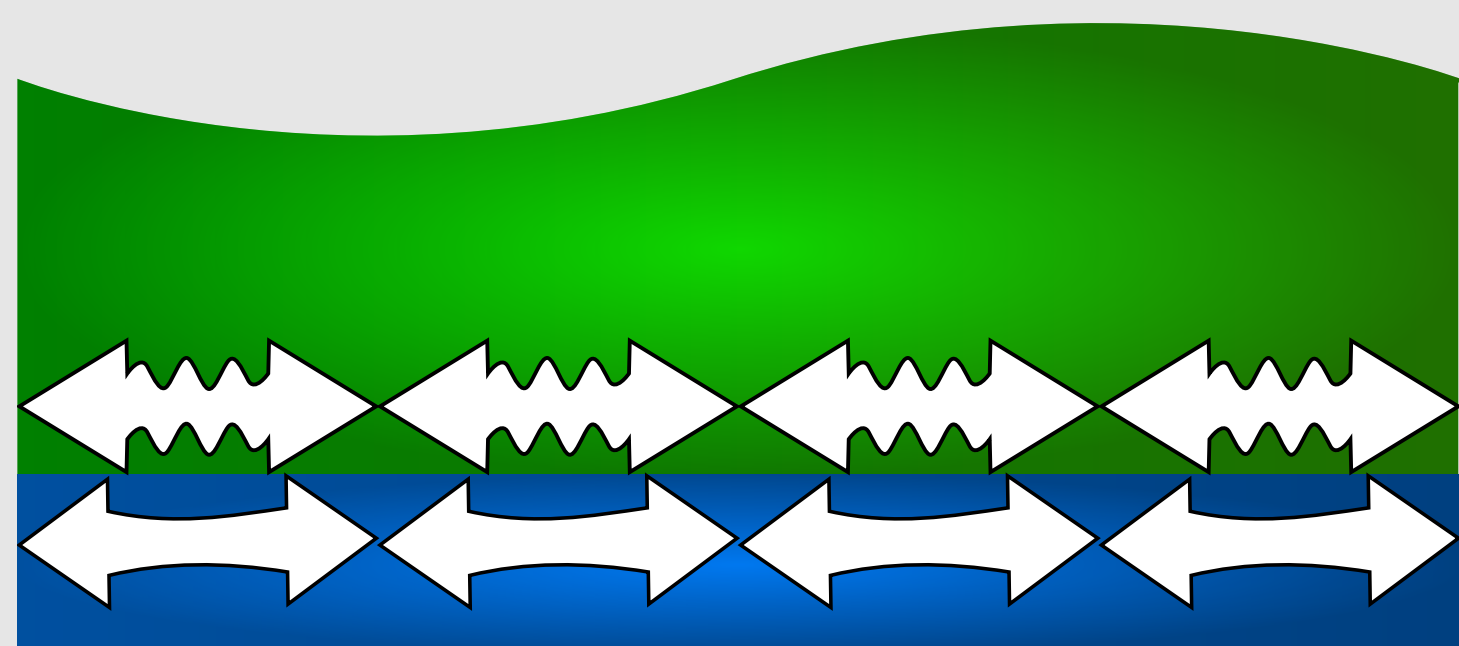
In the above equation,  $\Omega$  is the atomic volume of the defect species, and the speed at which the interface propagates along its normal direction  $v_{(n)}$  includes contributions from the atomic surface diffusive flux  $j_{\alpha}$  and the evaporative flux  $J_i$ , which expels mass along the outward unit normal  $n_i$ . The surface diffusive flux is proportional to the gradient of a surface diffusion potential that includes elastic, electric, defect, and surface energies.

$$j_{\alpha} = -M_{\alpha\beta}\Omega \left( \frac{1}{2}\sigma_{ij}\epsilon^{ij} + \frac{1}{2}D_i E^i + N\mathcal{G} - \gamma\kappa \right)^{\beta} \quad (2)$$



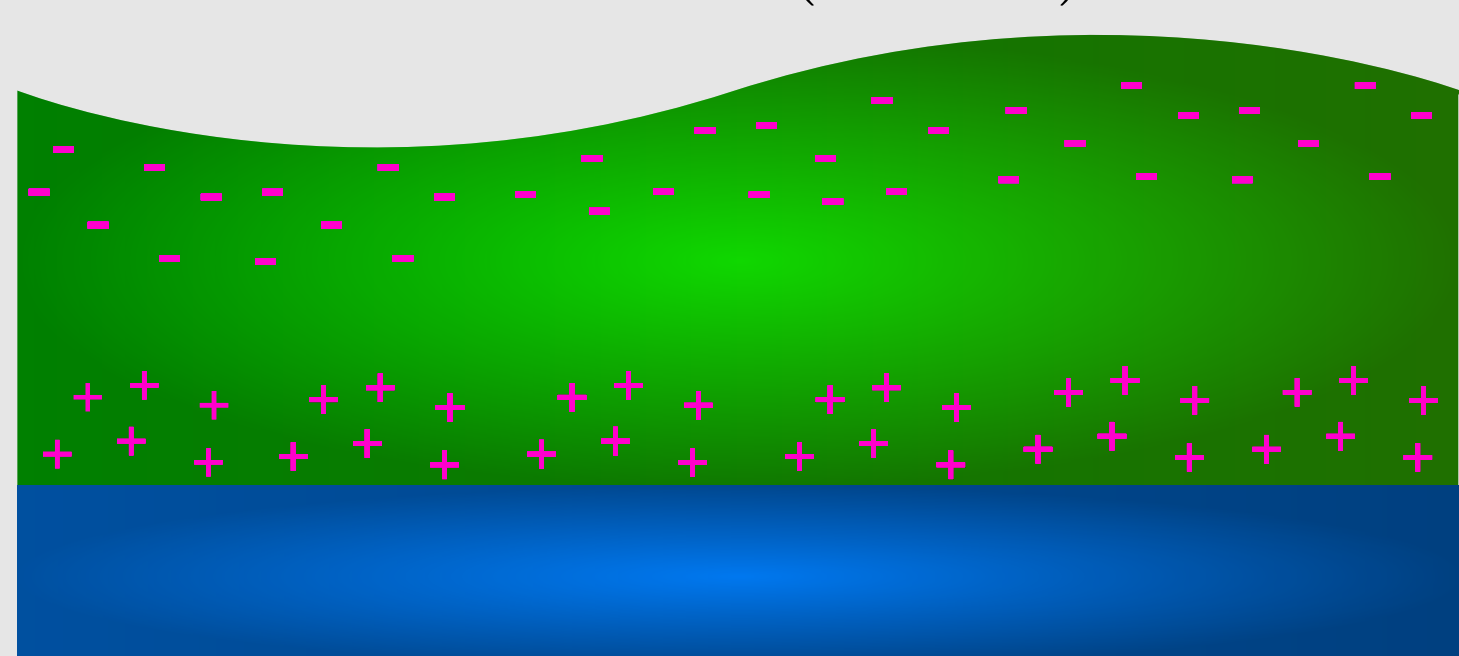
Here,  $M_{\alpha\beta}$  are the surface mobility coefficients,  $\sigma_{ij}$  and  $\epsilon_{ij}$  are the elastic stress and strain,  $D_i$  and  $E_i$  are the electric displacement and field,  $N$  is the number of defects per volume,  $\mathcal{G}$  is the free energy of defects,  $\gamma$  is the surface energy, and  $\kappa$  is twice the mean surface curvature. Since solid oxides are often brittle, we assume that the system is well-represented using small-strain elasticity.

$$\{C_{ijkl} [\epsilon - \epsilon^{okl}]\}^{ij} = 0 \quad (3)$$



In this equation, we introduce the elastic coefficients  $C_{ijkl}$ , mechanical displacements  $u_i$ , strain  $\epsilon_{ij} \equiv \frac{1}{2}(u_{i,j} + u_{j,i})$ , and eigenstrain  $\epsilon^{okl}$ . Assuming that point defects achieve their thermal equilibrium distribution much faster than the interface propagates, their concentrations and electrostatic effects can be determined using the non-linear Maxwell-Boltzmann equation.

$$(-\hat{\epsilon}_{ij}\phi^j)^i = ezN^{\circ}\exp\left(-\frac{\mathcal{F} + ez\phi}{kT}\right) \quad (4)$$



This includes the electrostatic potential  $\phi$ , permittivity  $\hat{\epsilon}_{ij}$ , elementary charge  $e$ , valency  $z$ , reference concentration  $N^{\circ}$ , formation energy  $\mathcal{F}$ , Boltzmann constant  $k$ , and absolute temperature  $T$ .

## 3. Non-Dimensionalization

We assume isotropic material parameters

$$M_{\alpha\beta} = M_{\alpha\alpha\beta}$$

$$\hat{\epsilon}_{ij} = \hat{\epsilon}g_{ij}$$

$$C_{ijkl} = \left(\frac{2G\nu}{1-2\nu}\right)g_{ij}g_{kl} + G(g_{ik}g_{jl} + g_{il}g_{jk})$$

and perform a change of variables so that every length is normalized by  $\ell$ , time by  $\tau$ , energy by  $\mathcal{W}$ , evaporation flux by  $\mathcal{J}$ , surface diffusive flux by  $j$ , and electrostatic potential by  $\mathcal{V}$ . We choose these scaling factors to remove as many material properties as possible from the equations, which simultaneously simplifies the equations and suggests natural quantities-of-interest for further analysis.

$$\text{Time: } \tau = \frac{\ell}{\Omega\mathcal{J}} \quad \text{Thermal Voltage: } \mathcal{V} = \frac{kT}{e}$$

$$\text{Length: } \ell = \frac{\gamma}{\mathcal{W}} \quad \text{Debye Length: } \hat{\ell} = \frac{e\ell}{\sqrt{2zN^{\circ}}}$$

$$\text{Evap. Flux: } \mathcal{J} = \frac{j}{\ell} \quad \text{Diffusive Flux: } j = \frac{j}{\ell}$$

The energy length scale is arbitrary and we choose to follow [2] and scale energies by the strain energy density of the flat, defect-free film.

$$\text{Energy: } \mathcal{W} = 2G(\epsilon^{\circ})^2 \left(\frac{1+\nu}{1-\nu}\right)$$

With all quantities understood to be non-dimensionalized, we can rewrite our governing equations in the following form.

$$v_{(n)} = - (j_{\alpha}^{\alpha} + J_i n^i) \quad (5)$$

$$j_{\alpha} = - \left( \frac{\hat{\lambda}}{2}\epsilon_i^i \epsilon_j^j + \hat{G}\epsilon_{ij}\epsilon^{ij} + \frac{1}{2}\frac{N^{\circ}kT\hat{\ell}^2}{\mathcal{W}}\phi_{,i}\phi^{,i} + \frac{N\mathcal{G}}{\mathcal{W}} - \kappa \right)_{,\alpha} \quad (6)$$

$$\hat{\lambda}\epsilon_k^k g_{ij} + 2\hat{G}\epsilon_{ij} = 0 \quad (7)$$

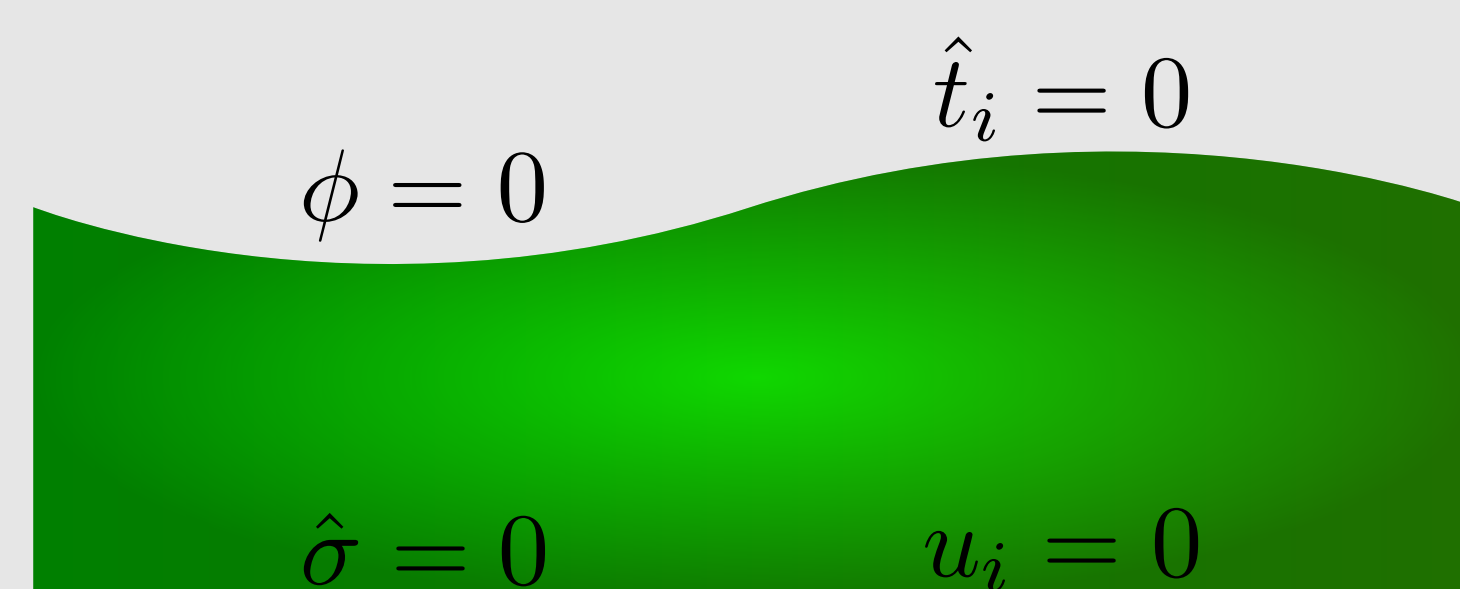
$$-\hat{\epsilon}(\phi_{,i})^{,i} = \exp(-\phi) \quad (8)$$

In these equations, we have defined an electrostatic parameter and the rescaled elastic coefficients now depend entirely on geometric quantities.

$$\hat{\epsilon} = \frac{\hat{\ell}^2}{\ell^2} \exp(\mathcal{F}) \quad \hat{\lambda} = \frac{2\hat{G}\nu}{1-2\nu} \quad \hat{G} = \frac{1-\nu}{2(\epsilon^{\circ})^2(1+\nu)}$$

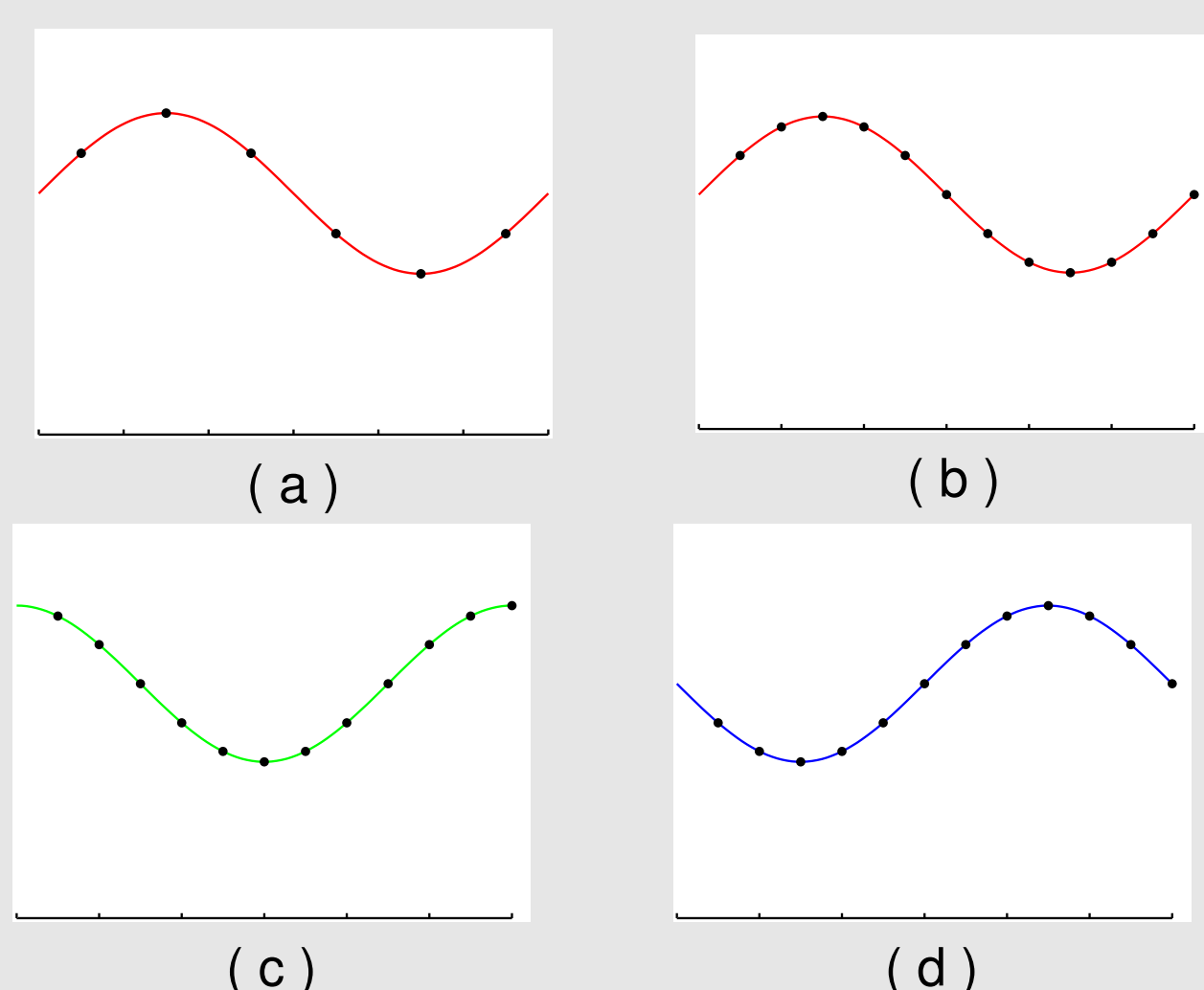
## 4. Solution Method

The governing equations are non-dimensionalized and a three-dimensional finite element method is used to solve the elasticity and electrostatics equations in the bulk of the thin film. The nonlinearity in the Poisson-Boltzmann equation is handled using a fixed-point iteration. Finite element methods require a discretization of the spatial domain, for which we choose isoparametric quadratic elements. This particular choice enables computation of the geometrical quantities necessary for evolving the interface.



**Figure 5:** The thin film is assumed to be in epitaxy with a rigid substrate, so any misfit is incorporated as an eigenstrain in the film and we can fix null displacements at the film-substrate interface. Space charge theory treats the film as one half of an electric dipole, so we electrically ground the film's free surface and there will be no surface charge at the base of the film. Through these choices, we have incorporated the effects of the surroundings as boundary conditions and the computational domain consists solely of the thin film region.

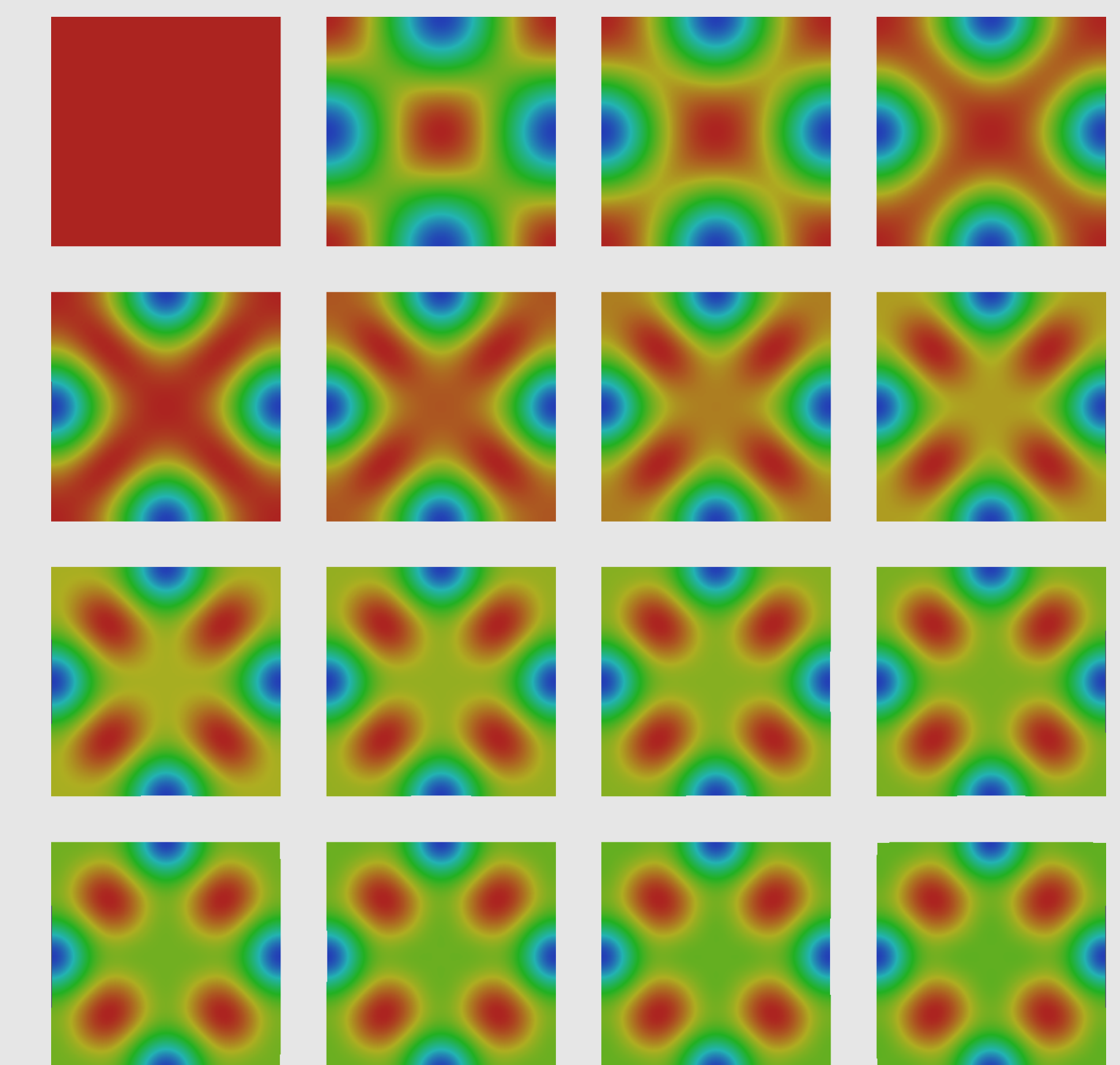
Since we have exhausted the continuity of the finite element mesh in computing the surface diffusion potential (which is now piecewise determined on element faces), we resort to Fourier approximation to compute the remaining surface derivatives. Fourier methods are particularly well-suited to this application because they exhibit rapid convergence and naturally account for periodic boundary conditions. Since the surface geometry is generally curvilinear, we must map the physical surface to a flat, uniform space where these quantities can be computed.



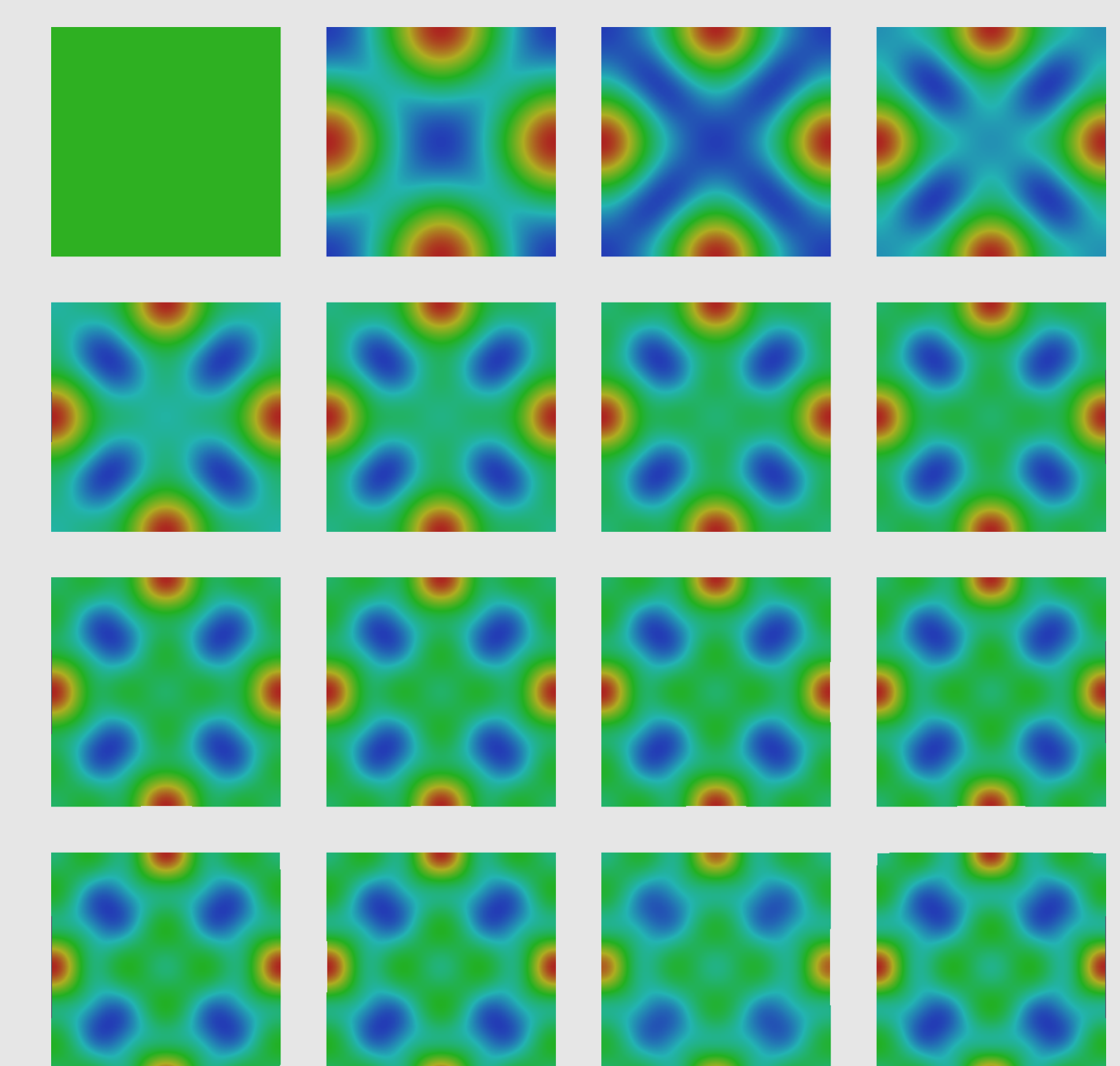
**Figure 6:** The finite elements chosen allow computation of the chemical potential on element faces (a). The discrete Fourier transform (DFT) is then used to smoothly interpolate nodal values (b) and, when combined with surface geometrical information, facilitates high accuracy approximations of the surface diffusive flux (c) and normal velocity (d).

## 5. Results

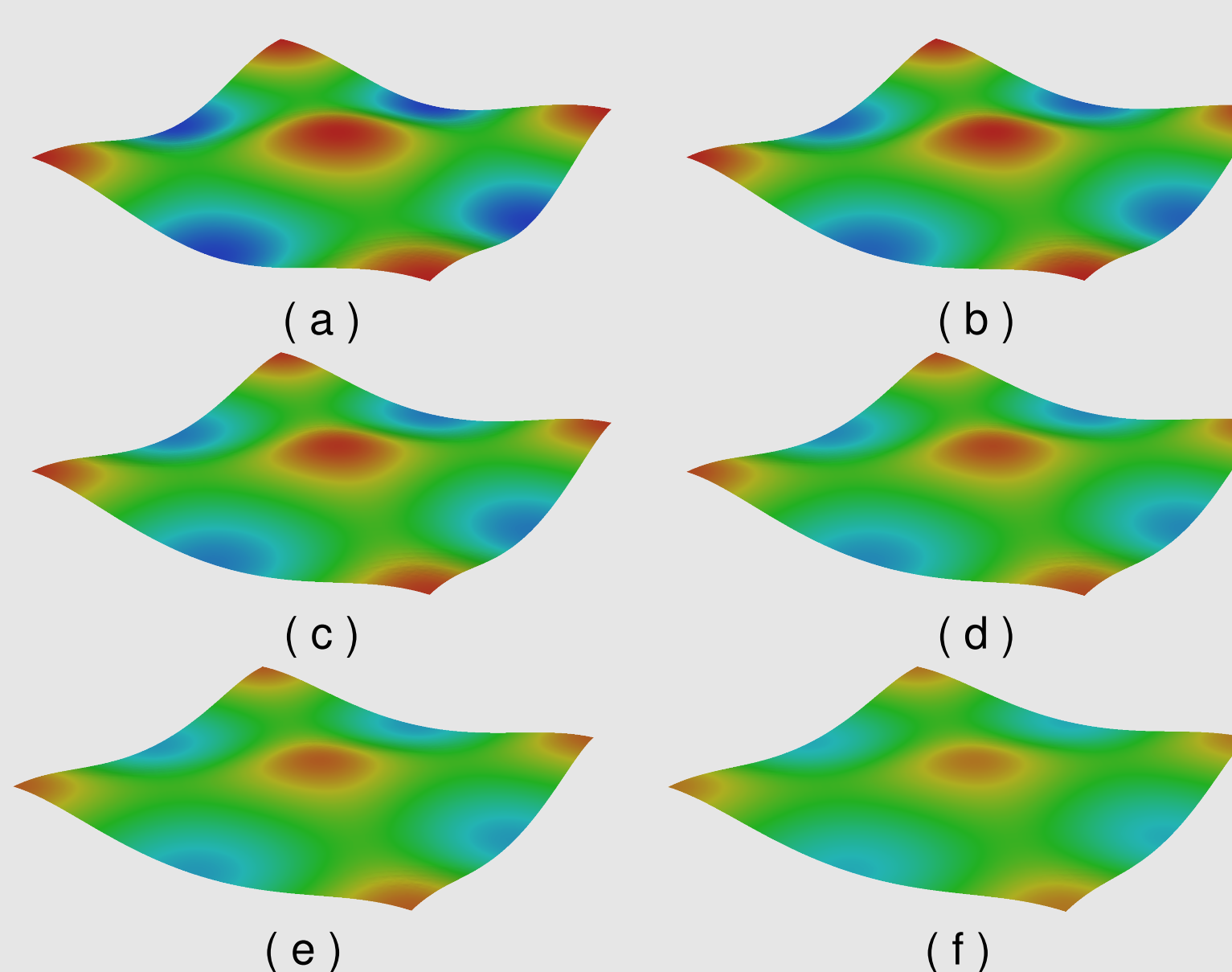
Here, we demonstrate our model and solution scheme for the case of an initial sinusoidal perturbation in both the  $x_1$  and  $x_2$  directions. Material properties are chosen to roughly reflect those of  $\text{TiO}_2$ . In addition to sinusoidal perturbations, we are currently exploring the behavior of dot and pit morphologies (modeled as Gaussians) which are readily observed in thin film systems, but require a more complex analysis.



**Figure 7:** Patterns in the surface diffusion potential as a function of wave amplitude for a double-sinusoidal perturbation. The upper-left image corresponds to an unperturbed surface, and the amplitude increases left-to-right, top-to-bottom by 0.01 in the non-dimensional length scale.



**Figure 8:** Through taking surface derivatives of the above diffusion potentials, we obtain the surface normal velocity, the speed at which the free interface propagates in the direction of its normal vector.



**Figure 9:** A surface perturbed by a double sinusoid with amplitude 0.01 is evolved using an explicit time marching scheme. The time increment between frames is  $10^{-5}$  on the non-dimensional time scale. This sequence demonstrates an instability that suppresses the perturbation and returns the film to a flat morphology. By appropriate choice of the initial film geometry, it is also possible to achieve a roughening instability where mass rearrangement is driven to enhance surface features.

## References

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