

Graphene Formation using the PFC Model with a Vapor Phase

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*I dedicate this dissertation to the students, who, through learning,
endeavor to make the world a better and kinder place.*

Acknowledgments

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“Of making many books there is no end, and much study wearies the body.”

– Ecclesiastes 12:12b, NIV

Abstract

Graphene is a one-atom-thick allotrope, or form, of carbon. Within graphene, each carbon atom bonds with three neighboring carbon atoms. Hence, the crystal lattice geometry is honeycomb, where the atoms form the vertices of regular hexagons. Perhaps the strongest material on earth, graphene has very high electrical and thermal conductivity. Although the production of graphene is costly, it has many uses, including solar panels, semiconductors, and body armor. The benefits of graphene, along with its virtual two-dimensional nature, motivate our study. We use the phase field crystal (PFC) model to simulate graphene. The PFC model yields a probabilistic atomic density field and, thus, crystal geometry. Traditionally, the PFC model includes solid and liquid phases and one spatial frequency mode for the crystal structure. This single mode model results in triangular geometry. We use three modes to achieve the honeycomb geometry of graphene. Since graphene is typically manufactured using chemical vapor deposition (CVD), we also add a vapor phase field to the model. Using frequency domain analysis, we develop a new, more accurate approach for building the crystal honeycomb geometry. This provides greater stability and enables us to produce solid island growth. We study the surface energy resulting from the solid-vapor phase interface, and we provide new insight into the effects of the surface energy on nanocrystal (solid crystal region) formation. Finally, we present an original model for dual-layer graphene with a vapor phase.

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Chapter 1

Introduction

The goals of this study are to simulate the formation of graphene using the phase field crystal (PFC) model, to examine characteristics of the model, and to develop new adaptations and extensions to the model. The unique qualities of graphene, including excellent electrical and thermal conductivity, motivate this application of the PFC model. To understand the model, we begin with the classical density functional theory (CDFT). We then adapt the CDFT to the standard, single-mode PFC model, which produces a triangular crystal lattice in two dimensions. Next, we expand the PFC to the multimode PFC model with three modes to simulate the graphene honeycomb lattice. Since graphene is often generated using chemical vapor deposition (CVD) in the absence of a liquid phase, we add a vapor phase field to the model.

1.1 Graphene

Physicists Andre Geim and Konstantin Novoselov discovered graphene at the University of Manchester, in 2004. In 2010, Geim and Novoselov won the Nobel Prize in physics for their discovery [8]. Graphene can be obtained by isolating and flattening a layer of graphite. In fact, Geim and Novoselov used a piece of adhesive tape to obtain graphene from a piece of graphite.

Graphene is an allotrope, or form, of carbon that consists of a single layer of atoms (one-atom-thick). Within graphene, each carbon atom bonds with three neighboring carbon

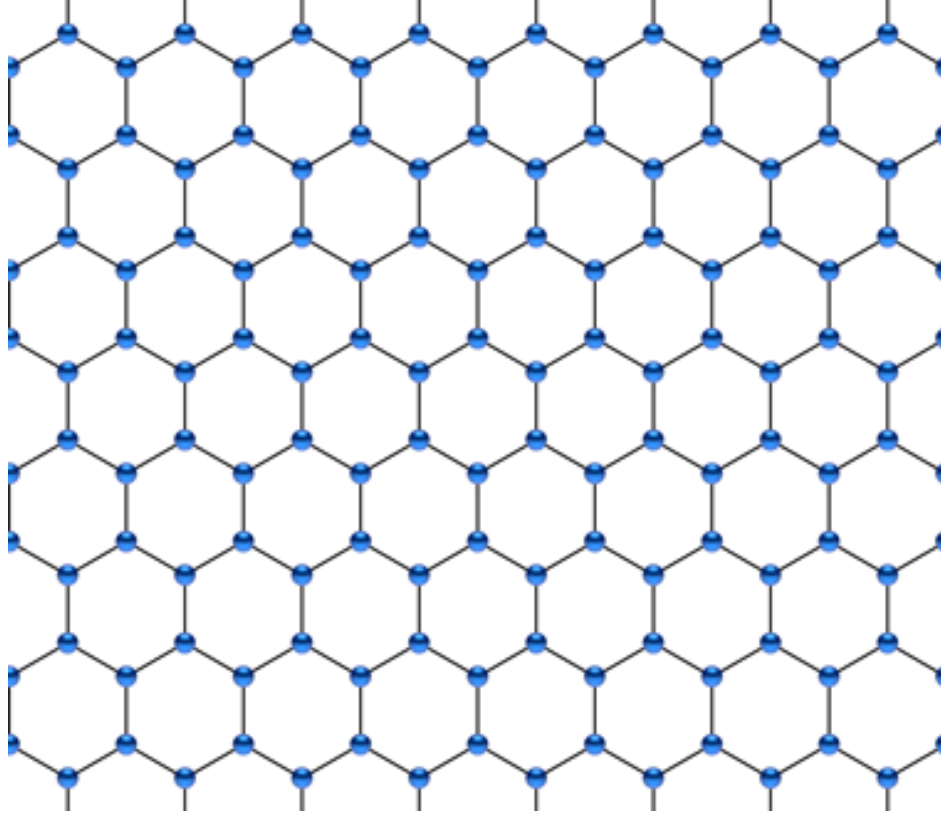


Figure 1.1: Graphene

atoms. Hence, the carbon atoms of graphene form the vertices of hexagons, yielding a honeycomb crystal lattice. Figure 1.1 exhibits this honeycomb geometry. The blue spheres represent carbon atoms, and the lines represent carbon-carbon bonds.

Graphene has high electrical and thermal conductivity, and it is stronger than steel. However, if the graphene is not pure, or if it possesses crystal misalignments, it may fracture. Twisted bilayer graphene can be used to manufacture superconductors [3]. Graphene oxide is used to build solar panels [28]. Bilayer graphene is suitable for field-effect transistors [21]. Finally, due to its strength and light weight, multilayer graphene can be used for bullet-proof vests [12]. Figure 1.2 shows a strip of single layer graphene in the middle and bilayer graphene on the right.

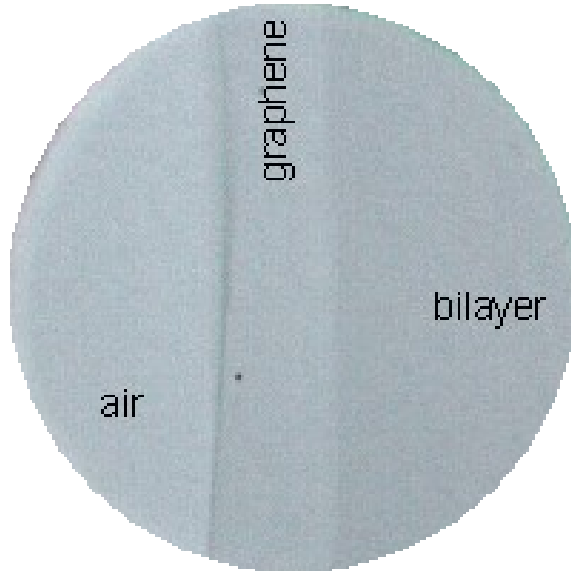


Figure 1.2: Graphene Strip

1.2 Phase Field Crystal (PFC) Model

We employ the *phase field crystal (PFC) model* to simulate graphene. The PFC model provides a probabilistic atomic density representation for crystal geometry at a constant, uniform temperature near the freezing point. The PFC model can be derived from classical density functional theory (CDFT) [20], which models the mass density for the solid and liquid phases. For constant temperature, the CDFT Helmholtz free energy functional can be expressed in two parts. The homogeneous part comes from the properties for an ideal gas:

$$\mathcal{F}_{cdft,homog,s}(\psi) := \int [(\psi + 1) \ln(\psi + 1) - \psi] d\mathbf{x}. \quad (1.1)$$

Here, ψ is a scaled and offset version of the mass density field. The homogeneous energy, which dominates in liquid regions, facilitates the diffusion of mass to establish an equilibrium. The gradient part uses correlation functions and convolutions to establish crystal geometry.

A version of this gradient energy, which includes only a second order correlation C_2 , is

$$\mathcal{F}_{cft,grad}(\psi) := \int \frac{1}{2} \psi (C_2 * \psi) d\mathbf{x}. \quad (1.2)$$

For the PFC model, we approximate the natural log expression of the CDFT homogeneous free energy density with a polynomial [18]. In addition, we replace the correlation function and convolution of the gradient energy density with a linear differential operator. The result is the standard PFC free energy functional

$$\mathcal{F}_{pfc,raw}(\psi) := \int \left\{ \frac{\psi^4}{12} - \frac{\psi^3}{6} + \frac{\psi^2}{2} + \frac{1}{2} \psi (2\Delta + \Delta^2) \psi \right\} d\mathbf{x}. \quad (1.3)$$

This functional results in triangular crystal geometry. Figure 1.3a shows a mass density field for the PFC model. Since graphene has honeycomb geometry, we expand this model to three modes [19]. We refer to this enhanced model as the multimode PFC model. Figure 1.3b provides a mass density field for the multimode PFC model with honeycomb geometry. We also add a vapor phase field. The resulting model is often referred to as the National Institute of Standards and Technology (NIST) model. The augmented free energy density includes the Allen-Cahn terms [10], which are the primary contributors to the surface free energy. We describe the model in detail in Chapter 2.

1.3 Goals

The purpose of this written work and the corresponding research is to enhance academic and industrial fields that involve one-atom-thick materials, such as graphene. In fact, we endeavor to progress the general studies of phase fields and crystal formation. We outline our goals as follows:

1. Provide researchers with a thorough understanding of and intuition for the PFC model by describing its development and mathematical equations and by providing simulations and observations thereof.

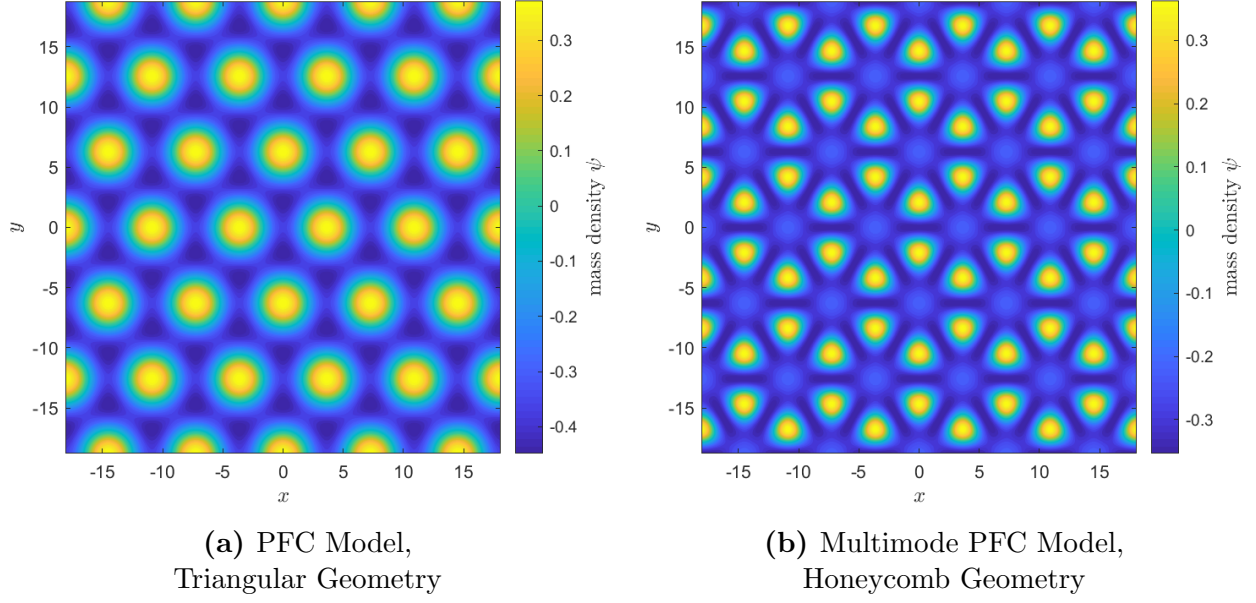


Figure 1.3: Basic Mass Density Fields

2. Modify and augment the PFC model to provide further computational stability and to describe additional natural phenomena.
3. Model physical phenomena for materials that are one-atom-thick, including:
 - (a) freezing
 - (b) melting
 - (c) sublimation
 - (d) deposition
 - (e) crystal formation, geometry, and facets
 - (f) nanocrystal shapes and isotropic energies
 - (g) phase interface thicknesses
 - (h) surface energies
 - (i) crystal alignment with substrates and between the layers of bilayer formations
4. Analyze the effects of the model designs and parameter values on the simulations of these phenomena.

5. Improve industry by providing new and more in-depth data for the behavior and formation of one-atom-thick solids, primarily graphene, to yield economical production methods.
6. Provide additional insight, tools, and models for physicists and mathematicians for their research and innovations in the areas of phase fields and crystal formation.

1.4 Summary of Chapters

Chapter 2 describes the evolution of the multimode phase field crystal (PFC) model with vapor field. A new design for the linear differential operator is defined. Common parameter values are established for this study. Chapter 2 also examines the phase equilibrium diagram for the model. We define a radial distribution function and, finally, add substrate and vapor deposition functionality. Next, Chapter 3 describes a Gaussian correlation function, which is an alternative to the differential operator. We study closely the surface energy for solid-vapor phase interfaces in Chapter 4. This chapter includes most of the simulations found in this study. Chapter 5 describes the binary phase field crystal model for honeycomb geometry and introduces a new vapor phase field extension. Finally, Chapter 6 presents a new design for the modeling of bilayer graphene. We refer to this as the dual-layer multimode PFC model. A vapor phase is included.

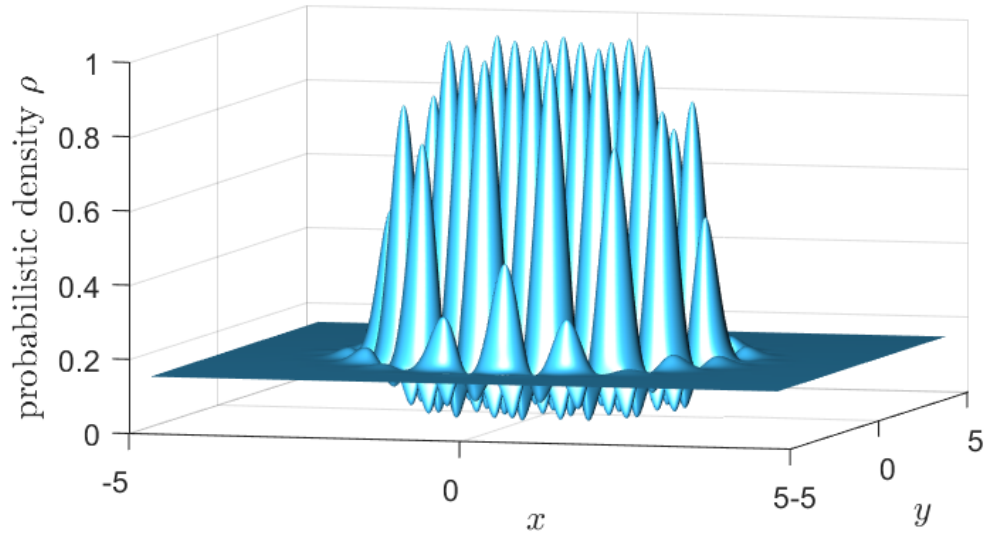
Chapter 2

The Model

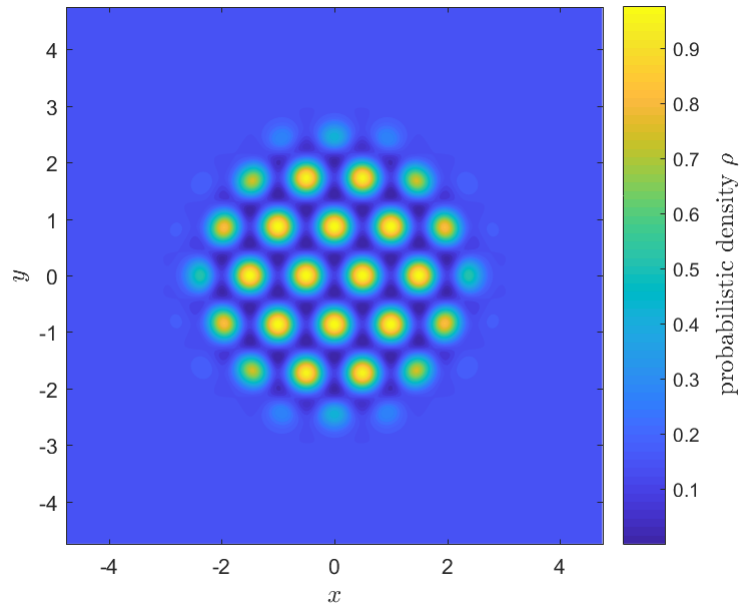
The phase field crystal (PFC) model was introduced by K. R. Elder, Mark Katakowski, Mikko Haataja, and Martin Grant, in 2002 [5]. The model effectually combines the phase field model, which includes only phase boundaries, with crystal geometry at the atomic length scale. Hence, crystal structures are apparent. Like the common phase field model, the PFC model includes solid and liquid phases, and it operates at a diffusive time scale to facilitate freezing and melting. Unlike models that use discreet atomic locations, the PFC model employs smooth atomic “probability” densities; that is, the mass density fields have peaks at the most probable locations for atoms in a crystal. Valleys identify the least likely positions. Furthermore, flat regions indicate the liquid phase. Note that the basic PFC model produces triangular geometry. Figure 2.1a provides a side view of a mass density field with both solid and liquid phases. Figure 2.1b views the same field from the top with a different color scheme. The yellow areas are the peaks - the atom locations, while the dark blue regions are the valleys. Figure 2.2 provides a cross-sectional view. Note that Figure 2.2 has more peaks and valleys than the fields of Figure 2.1.

The resulting mass density fields are infinitely differentiable over space. Hence, we can use a linear differential operator to design the crystal geometry. In fact, we can achieve various crystal structures by modifying this operator [17].

In the PFC model, the Helmholtz free energy is nonincreasing, and, typically, the free energy decreases toward an equilibrium over time. As the free energy decreases, the entropy increases. The partial differential equation (PDE) that interconnects the spatial



(a) Side View



(b) Top View

Figure 2.1: PFC Model, Mass Density Field, Triangular Geometry

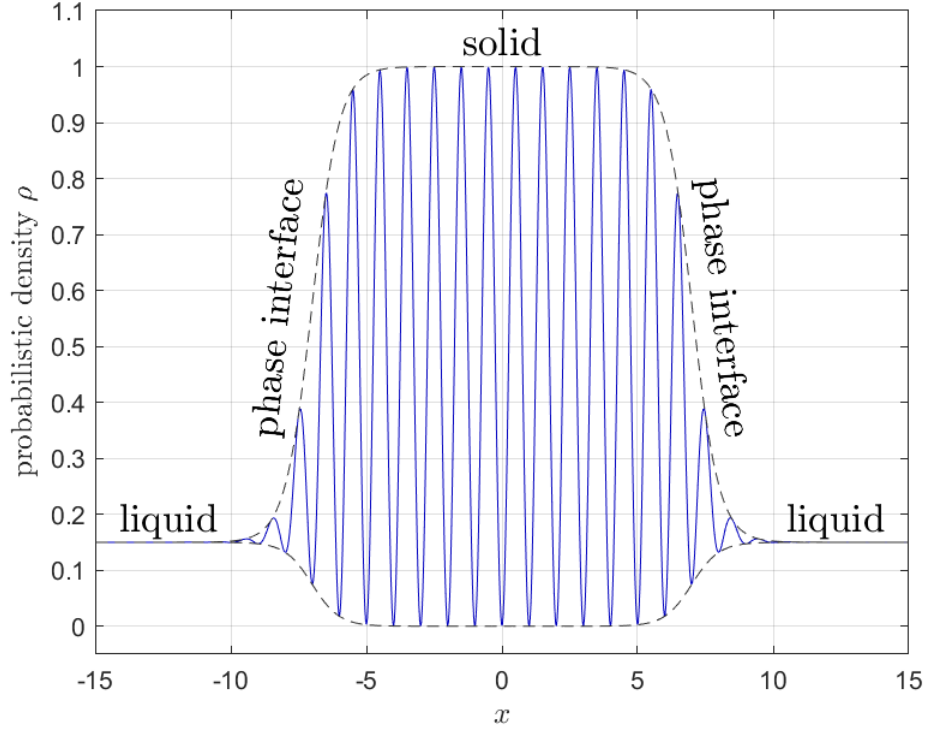


Figure 2.2: PFC Model, Mass Density Field, Triangular Geometry, Cross-Sectional View

and temporal changes in the mass density field yields nonincreasing total free energy. Hence, the mass density field of the PFC model evolves over time by driving toward a minimum, or equilibrium, energy. The key to the design of the free energy density (the free energy functional integrand) is to assign large energy values to undesirable mass density arrangements. Primarily, differences in density levels over the field result in high free energy values. However, each of the solid and liquid phases has a mass density that achieves a free energy minimum. In addition, mass density field arrangements that possess desired crystal geometry also reduce the overall free energy.

The model conserves mass, or, rather, total mass density. Another advantage of the PFC model is its rotational invariance [19]. The orientation of the crystal geometry is independent of the orientation of the computational box. Finally, at least to date, the model operates at a constant, uniform temperature. The model is configured for a temperature near the freezing point.

Since we are working with two-dimensional geometries, the fields in this study are defined on $\mathbb{R}^2$. Now, t is the time, and $\mathbf{x} = (x, y)$ is the position in $\mathbb{R}^2$. The scaled and shifted mass density field is $\psi(t, \mathbf{x})$. For models with a vapor phase, the vapor phase field is given by $\eta(t, \mathbf{x})$. The vapor phase field η takes values between 0 and 1, where 0 indicates the solid phase, and 1 designates the vapor phase. Spatially, we focus on a rectangular region, or computational box, Ω , which tiles $\mathbb{R}^2$. The fields are Ω -periodic; that is, the fields are identical on each Ω tile. We use the trapezoidal rule and periodicity to calculate the mean mass density per unit area and the free energy per unit area.

After discretizing the model, we apply the pseudo-spectral method [26] for differentiation in space. Since the mass density fields of the PFC models are often composed of sine functions, the pseudo-spectral method is ideal. In addition, we employ an implicit-explicit (IMEX) time scheme. The linear terms of the PDE's are handled implicitly, while the nonlinear terms are processed explicitly. To find the mean mass density per unit area for the discrete model, we sum the elements of the mass density field matrix and divide by the number of elements. Similarly, for the free energy per unit area, we plug the mass density and vapor phase matrices into the free energy functional, take the sum of the resulting elements, and divide by the number of elements. It can be shown that, barring machine roundoff errors and insufficient resolution, mass density is conserved and the free energy is nonincreasing in the discrete model.

We employ MATLAB for the numerical simulations. Each simulation involves three major function code files, `problem.m`, `psmultipliers.m`, and `pssolver.m`, along with a parameter text file. The `problem.m` function is the center of the operation. This function reads the parameters from the parameter file and establishes the initial field grid matrices. Next, `problem.m` calls the function `psmultipliers.m` to create the pseudo-spectral multiplier matrices and other constant multipliers that are used repeatedly during the simulation. These matrices also incorporate the implicit-explicit time scheme. The time increment for loop lies at the core of `problem.m`. At each time interval, `problem.m` calls `pssolver.m`. This function applies the discretized PDE's to the field matrices using the constant matrices and multipliers from `psmultipliers.m`. Finally, `problem.m` outputs periodic mass and energy updates and field data and image files. Some simulations take a

few hours to run, and others require days. The runtime is affected most by the number of fields and the number of grid points in each field. A typical field matrix is 768×768 , and the average number of time steps required for a system to reach a numerical free energy equilibrium is about 500,000. Including all stages of development and model simulations, this study employs 336, original MATLAB function files, including approximately 30,000 total lines of code. Note that we also use Mathematica for analyses involving continuous, or “nondiscrete”, functions.

The majority of this chapter details the construction of the multimode PFC model for honeycomb geometry with a vapor phase field. In Section 2.1, we investigate the classical density functional theory (CDFT). Next, in Section 2.2, we adapt the CDFT model to the standard, single-mode PFC model, which produces a triangular crystal lattice in two dimensions. We expand this PFC model to the multimode PFC (MMPFC) model in Section 2.3. The multimode PFC model has three modes to simulate the graphene honeycomb lattice. We add the vapor phase to the model in Section 2.4. We include Section 2.5 to describe the phase equilibrium mass densities and free energies for the multimode PFC model with vapor. In this section, we analyze the common tangent line for the solid and vapor equilibrium curves to prepare for the surface energy formula of Chapter 4. Section 2.6 introduces a method for finding the radial distribution function for the continuous mass density fields of the PFC models. Finally, in Section 2.7, we add a substrate and vapor deposition to the multimode PFC model with vapor. The goal of this last section is to model the common method for the formation of graphene. This production technique involves a copper substrate and chemical vapor deposition (CVD).

2.1 Classical Density Functional Theory (CDFT)

T. V. Ramakrishnan and M. Yussouff developed the classical density functional theory for freezing and published the results in 1979 [20]. Yashwant Singh produced additional in-depth work on this subject in 1991 [23]. We rely on the work of K. R. Elder, Nikolas Provatas, et al. [6], [19], who built the foundation for the transition from classical functional density theory

to the phase field crystal model. We also incorporate the CDFT to PFC model transitional steps from the work of Nirand Pisutha-Arnond, et al. [18].

The goal of this section is to develop a free energy functional for the PFC model by adapting a free energy functional derived from classical density functional theory. We first define the constant ρ_ℓ to be the liquid density, which is the number of particles per unit area for the liquid phase. Next, t is the time, and $\mathbf{x}$ is the two-dimensional position vector. We introduce two fields. The first is the particle density $\rho(t; \mathbf{x})$. In effect, this field represents a particle count. The second field is a related density field $\psi(t; \mathbf{x})$. Here, ψ is a conveniently scaled and shifted version of ρ . For clarity, we often refer to ψ as the mass density field. In addition, within the free energy functional integrand, we typically omit the input variables t and $\mathbf{x}$ from $\rho(t; \mathbf{x})$ and $\psi(t; \mathbf{x})$.

We can express the CDFT *Helmholtz free energy functional* as

$$\mathcal{F}_{\text{cdft}}(\rho) := \mathcal{F}_{\text{cdft,homog}}(\rho) + \mathcal{F}_{\text{cdft,grad}}(\rho), \quad (2.1)$$

where $\mathcal{F}_{\text{cdft,homog}}(\rho)$ is the ideal gas, or *homogeneous, free energy*, and $\mathcal{F}_{\text{cdft,grad}}(\rho)$ is the excess, or *gradient, free energy*. Now, the homogeneous free energy $\mathcal{F}_{\text{cdft,homog}}(\rho)$ is the diffusive energy, and, thus, its purpose is to “flatten out” the density field. The gradient free energy $\mathcal{F}_{\text{cdft,grad}}(\rho)$ works in opposition to establish the crystal lattice.

The homogeneous free energy for an ideal gas is

$$\mathcal{F}_{\text{cdft,homog,id}}(\rho) := \rho_\ell k_B T \int \left[\frac{\rho}{\rho_\ell} \ln \left(\frac{\rho}{\rho_\ell} \right) - \frac{\rho - \rho_\ell}{\rho_\ell} \right] d\mathbf{x}, \quad (2.2)$$

where k_B is the Boltzmann constant, and T is the temperature. Dropping these constants, we have a simpler homogeneous energy form

$$\mathcal{F}_{\text{cdft,homog,s}}(\rho) := \int \left[\frac{\rho}{\rho_\ell} \ln \left(\frac{\rho}{\rho_\ell} \right) - \frac{\rho - \rho_\ell}{\rho_\ell} \right] d\mathbf{x}. \quad (2.3)$$

Using ρ_ℓ , we scale and offset the density ρ to define a density-related field for all $t, \mathbf{x}$:

$$\psi(t; \mathbf{x}) := \frac{\rho(t; \mathbf{x}) - \rho_\ell}{\rho_\ell}. \quad (2.4)$$

This density field ψ is used throughout the chapters of this study. Note that

$$\frac{\rho(t; \mathbf{x})}{\rho_\ell} = \psi(t; \mathbf{x}) + 1, \quad (2.5)$$

and, so, the simplified CDFT homogeneous free energy becomes

$$\mathcal{F}_{cft,homog,s}(\psi) = \int [(\psi + 1) \ln(\psi + 1) - \psi] d\mathbf{x}. \quad (2.6)$$

Next, we require the simplicity of a polynomial integrand. Hence, we consider the Taylor series expansion of $(\psi + 1) \ln(\psi + 1)$ about $\psi_0 = 0$:

$$(\psi + 1) \ln(\psi + 1) = 0 + \psi + \frac{\psi^2}{2} - \frac{\psi^3}{6} + \frac{\psi^4}{12} - \frac{\psi^5}{20} + \cdots + \frac{(-1)^n \psi^n}{(n-1)n} + \cdots, \quad (2.7)$$

and, so, the simplified CDFT homogeneous free energy density (integrand) is

$$(\psi + 1) \ln(\psi + 1) - \psi = \frac{\psi^2}{2} - \frac{\psi^3}{6} + \frac{\psi^4}{12} - \frac{\psi^5}{20} + \cdots + \frac{(-1)^n \psi^n}{(n-1)n} + \cdots. \quad (2.8)$$

Finally, truncating to degree four yields the final form of the **homogeneous free energy**

$$\mathcal{F}_{cft,homog}(\psi) := \int \left[\frac{\psi^4}{12} - \frac{\psi^3}{6} + \frac{\psi^2}{2} \right] d\mathbf{x}. \quad (2.9)$$

This is, of course, an approximation of the ideal gas form of (2.2). Figure 2.3 provides a comparison between the logarithmic and truncated, fourth degree polynomial free energy densities. The mean mass densities of this study typically range from -0.23 to -0.16. Hence, Figure 2.3 indicates that the truncated polynomial approximation is sensible.

Next, the gradient free energy determines the crystal geometry. It realizes the interaction between every pair, every triplet, every quartet, etc., of atoms, or, in our case, high mass density regions. Hence, the gradient free energy density includes a correlation function, $C_n(\mathbf{x}_1, \dots, \mathbf{x}_n)$, for each point count $n \geq 2$. The CDFT gradient free energy (less constant

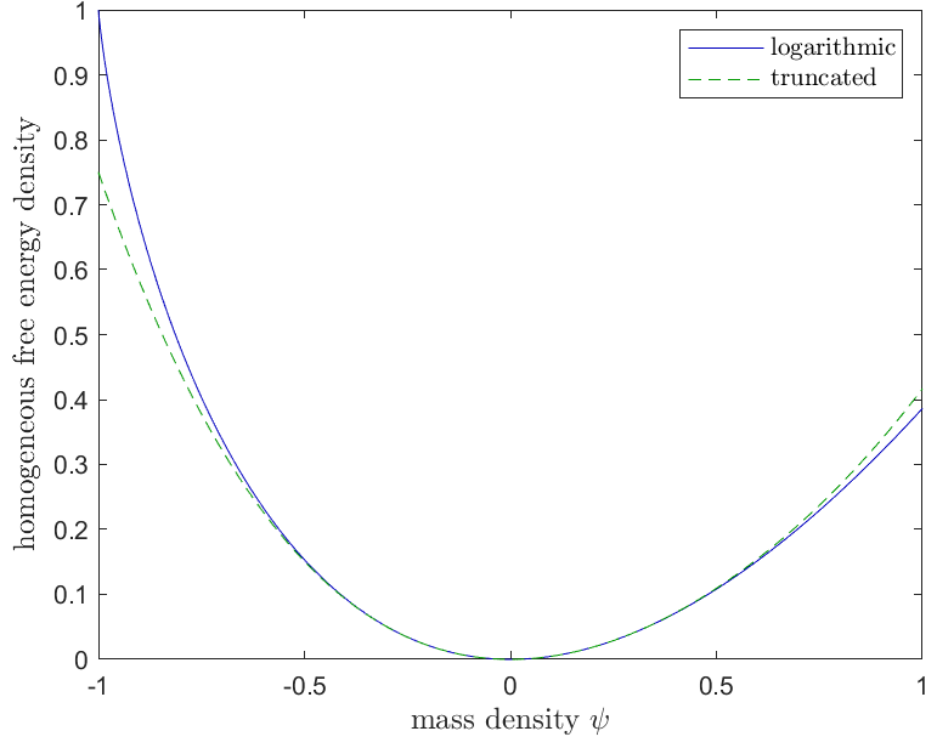


Figure 2.3: CDFT Homogeneous Free Energy Density, Logarithmic vs. Truncated

multipliers) is

$$\mathcal{F}_{\text{cdft,grad},n}(\psi) := \sum_{n \geq 2} \int \cdots \int \frac{1}{n!} C_n(\mathbf{x}_1, \dots, \mathbf{x}_n) \psi(\mathbf{x}_1) \cdots \psi(\mathbf{x}_n) d\mathbf{x}_n \cdots d\mathbf{x}_1. \quad (2.10)$$

We approximate the CDFT gradient free energy with only the two-point, or *pair, correlation*:

$$\mathcal{F}_{\text{cdft,grad},2}(\psi) := \int \int \frac{1}{2} C_2(\mathbf{x}, \mathbf{y}) \psi(\mathbf{x}) \psi(\mathbf{y}) d\mathbf{y} d\mathbf{x}. \quad (2.11)$$

Since only the distance between $\mathbf{x}$ and $\mathbf{y}$ is relevant, we redefine C_2 to yield:

$$\mathcal{F}_{\text{cdft,grad}}(\psi) := \int \int \frac{1}{2} C_2(\mathbf{x} - \mathbf{y}) \psi(\mathbf{x}) \psi(\mathbf{y}) d\mathbf{y} d\mathbf{x}. \quad (2.12)$$

Next, we rearrange the integrand to isolate the $\mathbf{y}$ terms

$$\mathcal{F}_{cdf,t,grad}(\psi) = \int \frac{1}{2} \psi(\mathbf{x}) \left[\int C_2(\mathbf{x} - \mathbf{y}) \psi(\mathbf{y}) d\mathbf{y} \right] d\mathbf{x}. \quad (2.13)$$

Indeed, the inner integral is a convolution, and, so, we have the final form for the **gradient free energy**:

$$\mathcal{F}_{cdf,t,grad}(\psi) = \int \frac{1}{2} \psi (C_2 * \psi) d\mathbf{x}. \quad (2.14)$$

Finally, we combine the homogeneous (2.9) and gradient (2.14) free energies to obtain the **CDFT free energy functional**

$$\mathcal{F}_{cdf,t}(\psi) = \int \left\{ \frac{\psi^4}{12} - \frac{\psi^3}{6} + \frac{\psi^2}{2} + \frac{1}{2} \psi (C_2 * \psi) \right\} d\mathbf{x}. \quad (2.15)$$

One might say that, in approximating the homogeneous free energy density logarithm with a polynomial and limiting the gradient free energy density to the pair correlation function, we have taken the first steps in transitioning from the CDFT form to the PFC model.

2.2 Phase Field Crystal (PFC) Model

The phase field crystal (PFC) model was introduced by K. R. Elder, Mark Katakowski, et al. in 2002 [5]. The PFC model inherits the homogeneous free energy of the classical functional density theory (CDFT). However, the PFC model replaces the nonlocal convolution of the CDFT gradient free energy with a linear differential operator. The result is a free energy density that involves local differentiation instead of nonlocal convolutions. Numerically, the PFC model is much more efficient.

Note that the standard PFC model has one mode. Each mode corresponds to a particular spatial frequency, or, in two dimensions, a spatial frequency magnitude, or radius. The radius is the square root of the sum of the squares of the x and y frequency components. A single mode yields triangular crystal geometry. Furthermore, for clarity, we use spatial angular frequencies, or angular wave numbers. For brevity, we often refer to a spatial angular frequency radius as an “angular frequency”. For simplicity, throughout this study, we use

Table 2.1: PFC Parameters**(a)** Solid/Liquid Phase Parameters

Parameter/Value	Description
$\epsilon = -0.15$	Temperature (scaled and shifted)

(b) Mass Density Field Initialization Parameters

Parameter/Value	Description
$amp = 0.3688$	Initial solid density amplitude
$cell_x = 7.255197457$	Initial unit cell width
$cell_y = 12.5663706144685$	Initial unit cell height
$thickness = 2.756975$	Initial phase interface thickness
$\mu_s = -0.171$	Initial solid mean density
$\mu_l = -0.228$	Initial liquid density

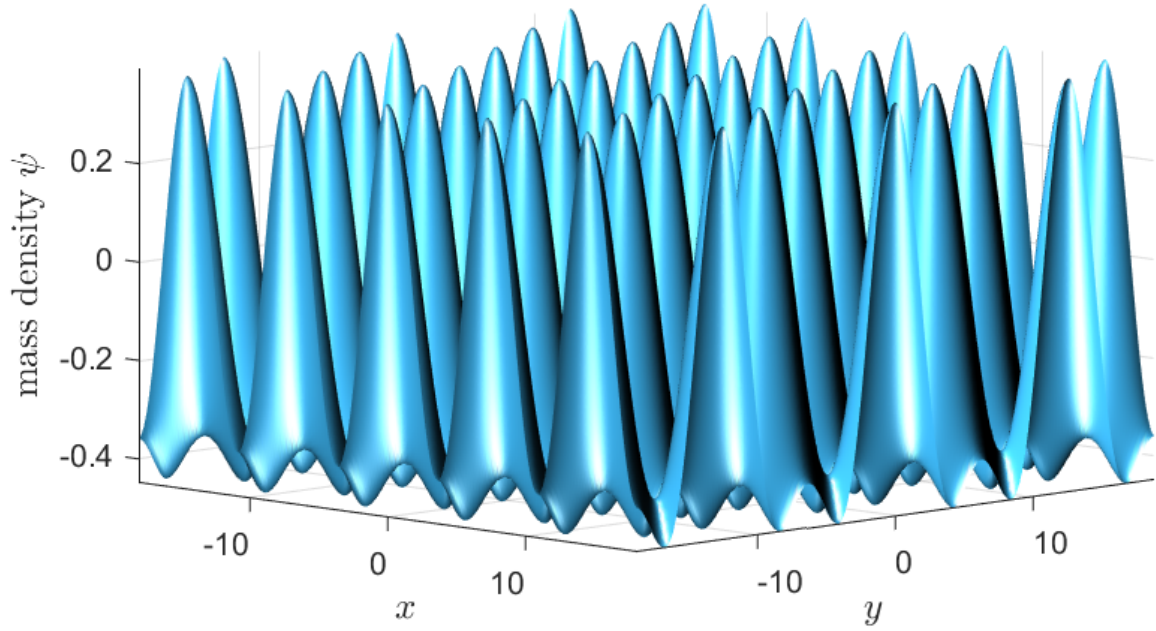
(c) Discretization Parameters

Parameter/Value	Description
$dt = 0.1$	Time increment
$h_x \approx 0.45$	x -granularity
$h_y \approx 0.45$	y -granularity

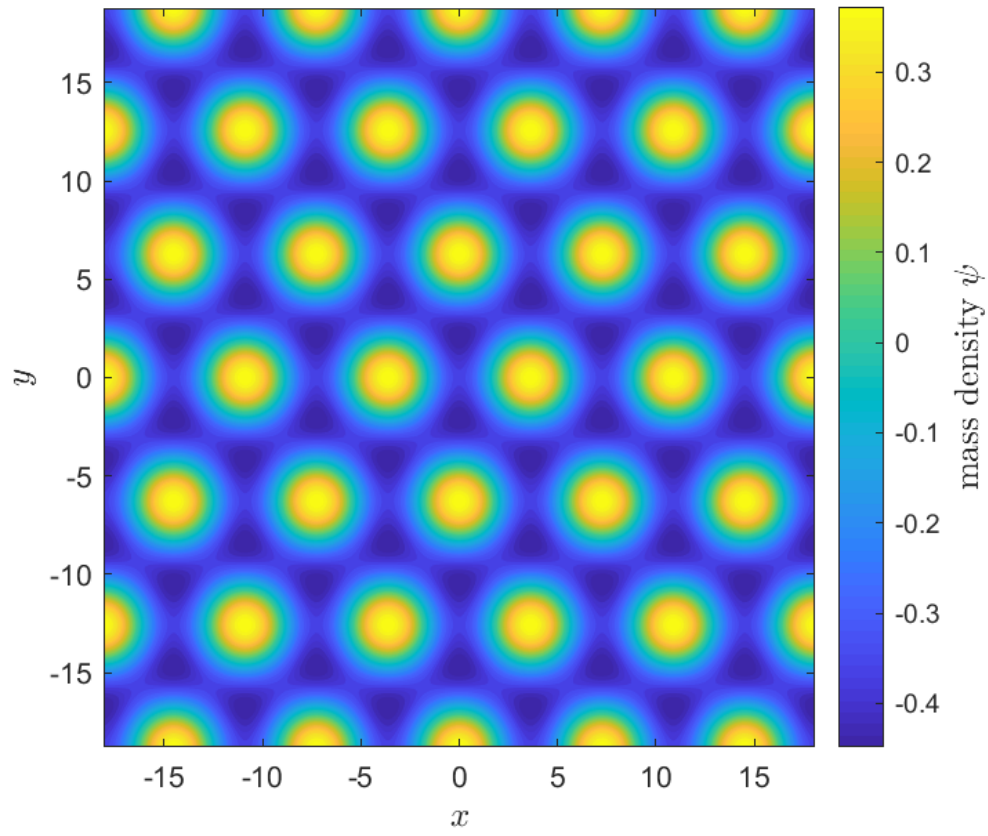
the angular frequency of 1 for our basis mode. Figure 2.4a provides a three-dimensional view of the triangular geometry of the standard PFC model, and Figure 2.4b shows the same field from the top with a different color mapping.

2.2.1 PFC Model Parameters

We now introduce the parameters for the PFC model. The multimode PFC model shares these parameters. However, some of the values vary. The PFC model has one structural parameter, ϵ , as listed in Table 2.1a. The parameter ϵ is a scaled and shifted temperature. Table 2.1b holds the parameters used to initialize the mass density field. Note that the initial solid mass density μ_s is the mean density across the initial solid region. Finally, Table 2.1c provides the discretization parameters.



(a) Side View



(b) Top View

Figure 2.4: PFC Model, Triangular Geometry

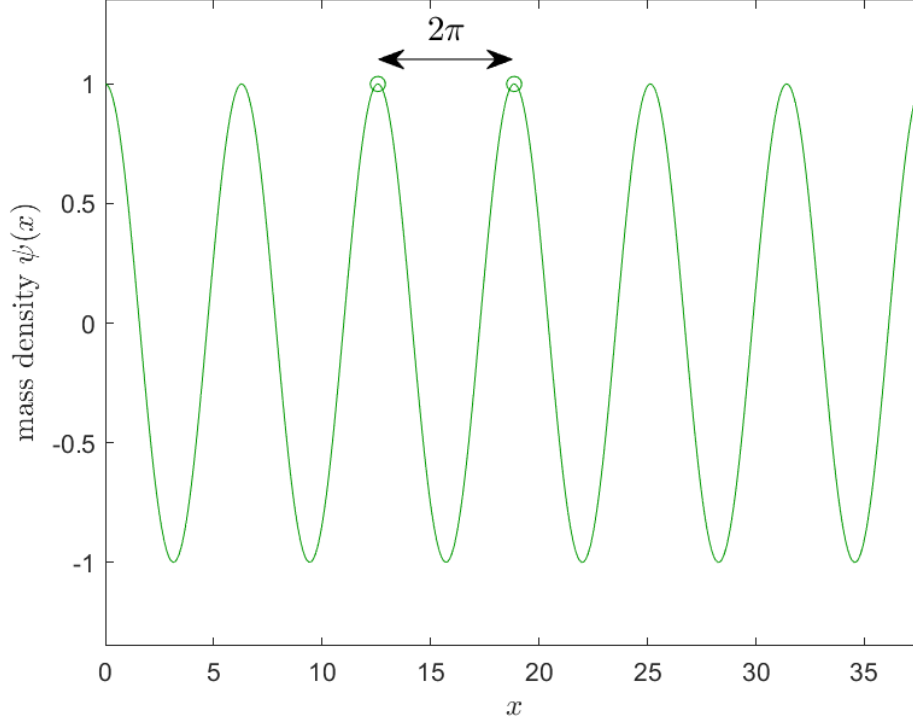


Figure 2.5: One-Dimensional Mass Density Field, Single Mode

2.2.2 PFC Model Equations

We begin the final transition from the CDFT to the PFC model by explaining the switch from the CDFT convolution to the PFC linear differential operator. First, note that convolution in real space is multiplication in Fourier, or k -, space. For the convolution, in Fourier space, the Fourier transform of the correlation function is multiplied by the Fourier transform of the mass density field. Indeed, differential operators also result in multiplication in Fourier space.

We first approximate the CDFT pair correlation function C_2 in one dimension. Now, a sine wave is the one-dimensional analogue of the two-dimensional triangular lattice. In addition, the spatial angular frequency of 1 has a wavelength of 2π . The corresponding one-dimensional mass density field, with an amplitude of 1, is given in Figure 2.5.

The models of our study result in nonincreasing total free energy. The free energy always “seeks” a minimum over time. Hence, mass density configurations with high free energies

diminish over time, while low energy arrangements endure. Therefore, we want mass density peaks that are 2π apart to result in low gradient free energy. We design our pair correlation function so that the gradient energy is least when the distance is $x - y = 2\pi$. We pick

$$C_{2,1D}(x - y) := -\frac{\exp\left(-\frac{(x-y)^2}{64}\right) \cos(x - y)}{2\sqrt{2}}, \quad (2.16)$$

for which the Fourier transform is

$$\widehat{C_{2,1D}}(\omega) := -\exp(-16(\omega + 1)^2) - \exp(-16(\omega - 1)^2), \quad (2.17)$$

where ω is the angular frequency. Figure 2.6a displays the real space function $C_{2,1D}$, while Figure 2.6b provides the corresponding Fourier transform $\widehat{C_{2,1D}}(\omega)$. Note that $\widehat{C_{2,1D}}(\omega)$ is the negative of the sum of two Gaussian functions and that $\widehat{C_{2,1D}}(\omega)$ is an even function. In addition, $\widehat{C_{2,1D}}(\omega)$ has local minima at angular frequencies extremely close to ± 1 . Therefore, spatial angular frequencies of ± 1 have the lowest free energy, and, as desired, crystal geometries with angular frequency radii of 1 endure.

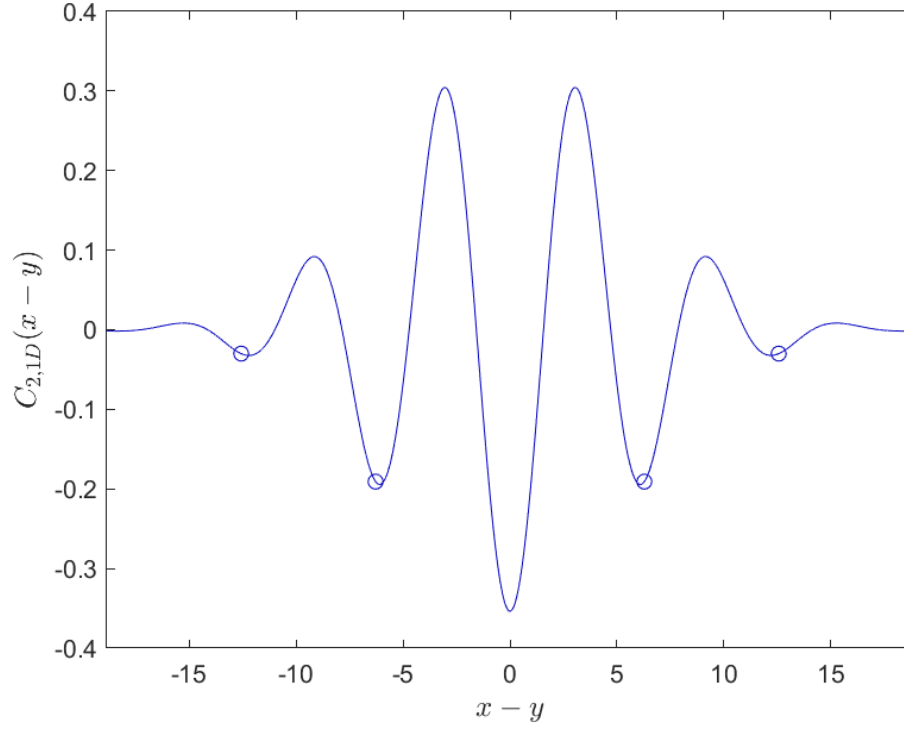
For one dimension, we define a linear differential operator C_{1D} such that the corresponding Fourier space multiplier $\widetilde{C_{1D}}$ approximates $\widehat{C_{2,1D}}$:

$$\widetilde{C_{1D}}(\omega) := -2\omega^2 + \omega^4. \quad (2.18)$$

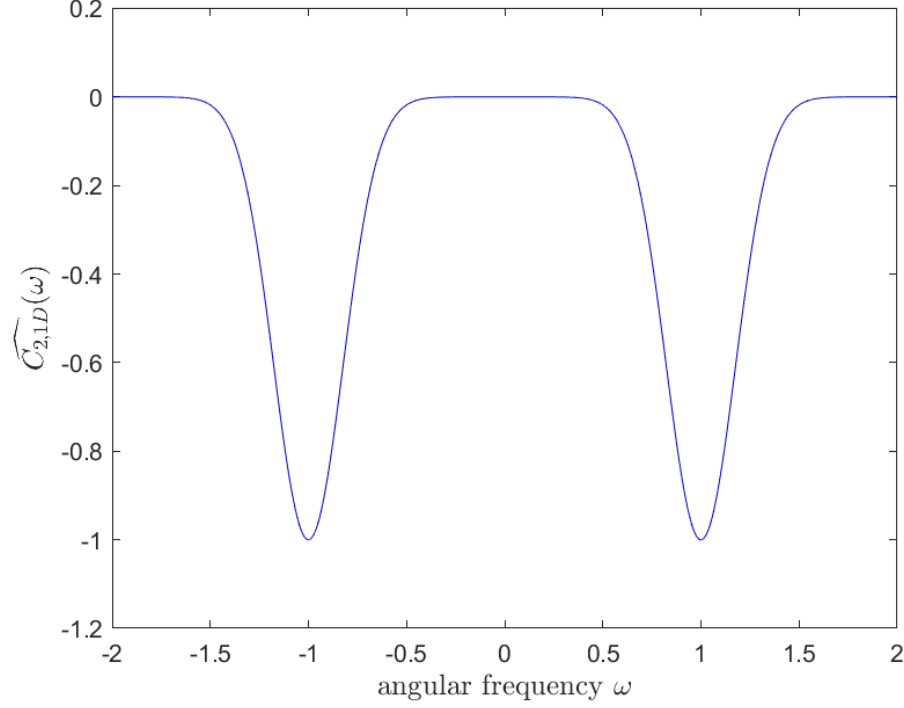
Figure 2.7 compares the one-dimensional correlation function Fourier transform to the Fourier space linear differential operator. In real space, the corresponding linear differential operator is

$$C_{1D} := 2\frac{\partial^2}{\partial x^2} + \frac{\partial^4}{\partial x^4}. \quad (2.19)$$

We establish the connection between the linear differential operator and its Fourier space multiplier for the two-dimensional case via Theorem D.2.



(a) $C_{2,1D}(x-y) = -\frac{1}{2\sqrt{2}} \exp\left(-\frac{(x-y)^2}{64}\right) \cos(x-y)$



(b) $\widehat{C_{2,1D}}(\omega) = -\exp(-16(\omega+1)^2) - \exp(-16(\omega-1)^2)$

Figure 2.6: One-Dimensional Correlation Function, Single Mode

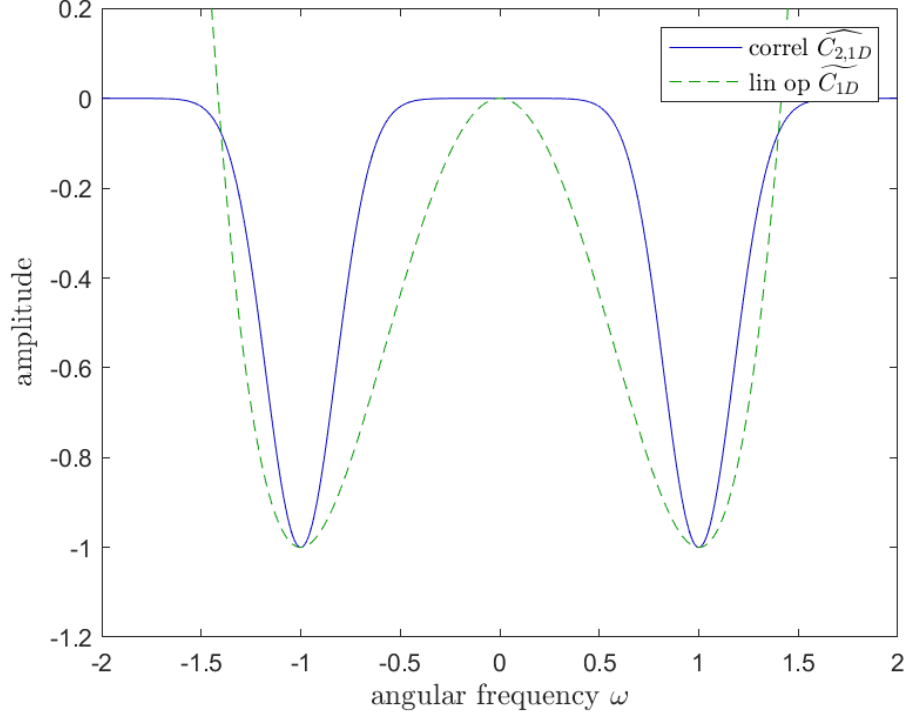


Figure 2.7: $\widehat{C_{2,1D}}(\omega) = -\exp(-16(\omega + 1)^2) - \exp(-16(\omega - 1)^2)$
vs. $\widetilde{C_{1D}}(\omega) = -2\omega^2 + \omega^4$

In two dimensions, we name the x and y angular frequency components ω_x and ω_y , respectively. We refer to the spatial angular frequency as a vector

$$\boldsymbol{\omega} := (\omega_x, \omega_y), \quad (2.20)$$

and we name its magnitude, or radius,

$$\omega := \sqrt{\omega_x^2 + \omega_y^2}. \quad (2.21)$$

Now, in two dimensions, (2.19) becomes the single-mode, raw PFC linear operator

$$C_{pfc,raw} := 2\Delta + \Delta^2, \quad (2.22)$$

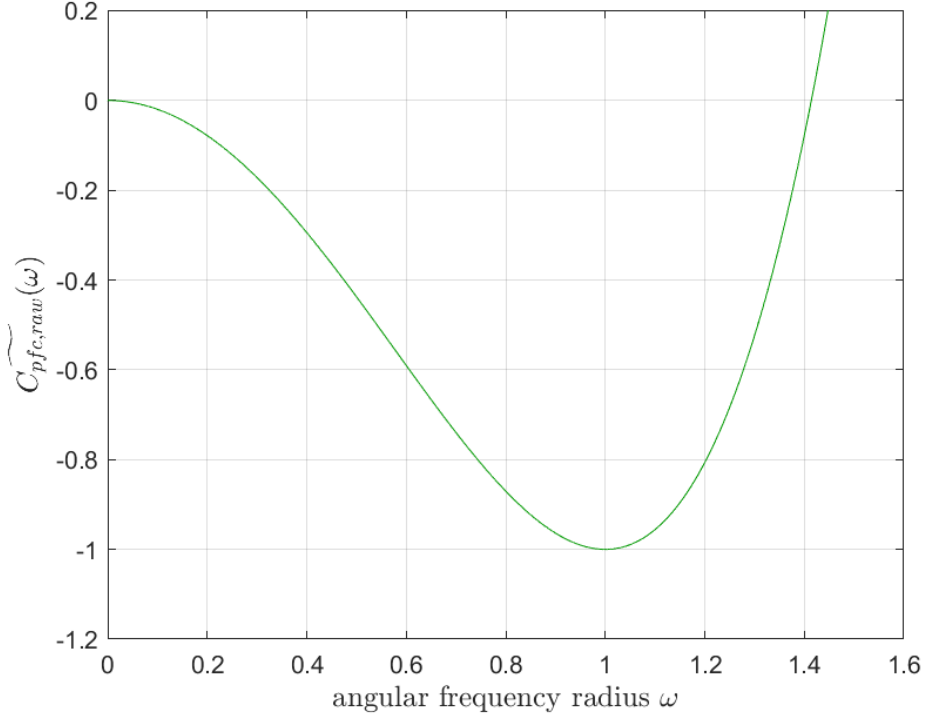


Figure 2.8: $\widetilde{C}_{pfc,raw}(\omega) = -2\omega^2 + \omega^4$

where Δ is the Laplacian, as defined in Appendix A. By Theorem D.2, the corresponding Fourier multiplier is

$$\widetilde{C}_{pfc,raw}(\omega) := -2\omega^2 + \omega^4. \quad (2.23)$$

Figure 2.8 provides the graph for $\widetilde{C}_{pfc,raw}(\omega)$. Note that $\widetilde{C}_{1D}$ and $\widetilde{C}_{pfc,raw}$ have the same polynomial shape. However, for the two-dimensional case, as a magnitude, ω only takes nonnegative values.

We recall that the CDFT gradient free energy from (2.14)

$$\mathcal{F}_{cft,grad}(\psi) = \int \frac{1}{2} \psi (C_2 * \psi) d\mathbf{x}. \quad (2.24)$$

Replacing the pair correlation convolution with the linear differential operator yields the raw form of the PFC gradient energy functional:

$$\mathcal{F}_{pfc,raw,grad}(\psi) := \int \frac{1}{2} \psi C_{pfc,raw} \psi d\mathbf{x} = \int \frac{1}{2} \psi (2\Delta + \Delta^2) \psi d\mathbf{x}. \quad (2.25)$$

Importantly, the action of the linear differential operator in (2.25) approximates the action of the convolution in (2.24) to produce triangular geometry. This gradient energy has a single mode, which corresponds to the spatial angular frequency radius of 1.

We combine the CDFT homogeneous (2.9) and raw PFC gradient (2.25) free energies to obtain the PFC free energy functional in its raw form

$$\mathcal{F}_{pfc,raw}(\psi) := \int \left\{ \frac{\psi^4}{12} - \frac{\psi^3}{6} + \frac{\psi^2}{2} + \frac{1}{2}\psi (2\Delta + \Delta^2) \psi \right\} d\mathbf{x}. \quad (2.26)$$

To arrive at the form most commonly referred to as the “PFC free energy functional” [5][19], we perform the following modifications to the free energy density (integral) in (2.26):

- replace the quartic term coefficient $\frac{1}{12}$ with $\frac{1}{4}$.
- remove the cubic term $-\frac{\psi^3}{6}$.
- “absorb” the quadratic term $\frac{\psi^2}{2}$ into the gradient free energy density.
- add a new quadratic term $\frac{\epsilon}{2}\psi^2$, where ϵ is a temperature-related parameter.

The result is

$$\begin{aligned} \mathcal{F}_{pfc,com}(\psi) &:= \int \left\{ \frac{1}{4}\psi^4 + \frac{\epsilon}{2}\psi^2 + \frac{1}{2}\psi (1 + 2\Delta + \Delta^2) \psi \right\} d\mathbf{x} \\ &= \int \left\{ \frac{1}{4}\psi^4 + \frac{\epsilon}{2}\psi^2 + \frac{1}{2}\psi(1 + \Delta)^2\psi \right\} d\mathbf{x}. \end{aligned} \quad (2.27)$$

The form for this gradient free energy density $\frac{1}{2}\psi(1 + \Delta)^2\psi$ is inspired by the work of Swift and Hohenberg [24] from 1977. The Swift-Hohenberg equation includes the linear differential operator $(1 + \Delta)^2$, which results in triangular crystal geometry. The connection was introduced by Elder, et al. [5] in their creation of the PFC model.

We define the final linear differential operator for the PFC model as

$$C_{pfc} := (1 + \Delta)^2 = 1 + 2\Delta + \Delta^2 = \Delta^0 + 2\Delta + \Delta^2. \quad (2.28)$$

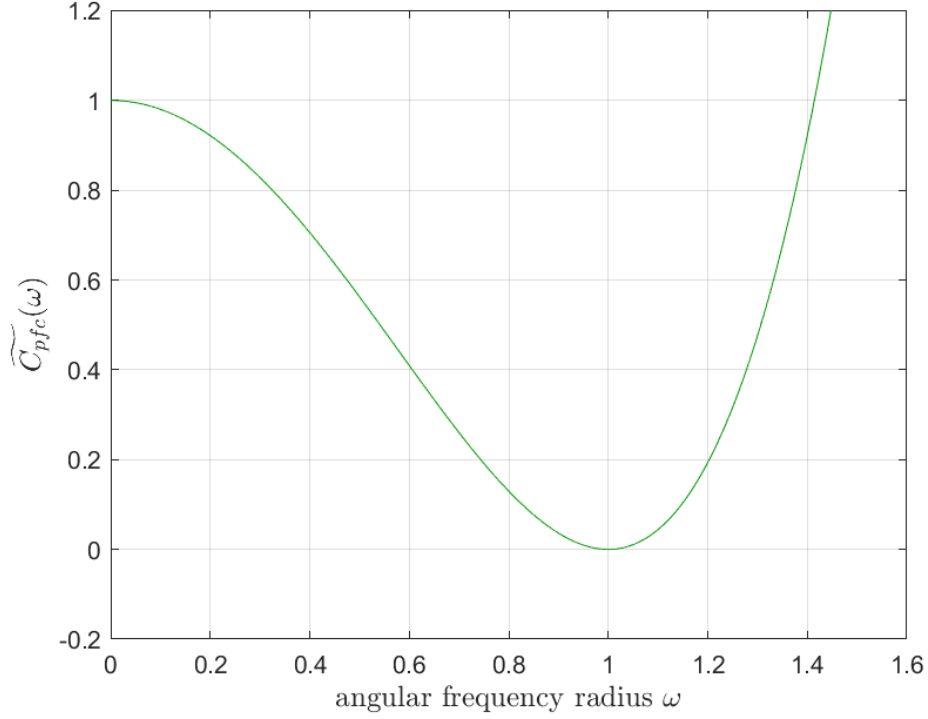


Figure 2.9: $\widetilde{C}_{pfc}(\omega) = -2\omega^2 + \omega^4$

This is a 4th order operator. By Theorem D.2, the corresponding Fourier space multiplier is

$$\widetilde{C}_{pfc}(\omega) := 1 - 2\omega^2 + \omega^4, \quad (2.29)$$

which is an even, 4th degree polynomial. Figure 2.9 shows the graph for $\widetilde{C}_{pfc}(\omega)$. Note that the shapes of the curves for $\widetilde{C}_{pfc,raw}(\omega)$ and for $\widetilde{C}_{pfc}(\omega)$ are identical, as seen in Figures 2.8 and 2.9, respectively. The curve for $\widetilde{C}_{pfc}(\omega)$ is simply shifted up by 1. The minimum occurs at $\omega = 1$ for both $\widetilde{C}_{pfc,raw}(\omega)$ and $\widetilde{C}_{pfc}(\omega)$.

For our studies, we limit the focus of our functional to the rectangular region Ω . At all times, the mass density field ψ is Ω -periodic; that is, the mass density field within the region

Ω tiles $\mathbb{R}^2$. Finally, adding time $t \in \mathbb{R}^+$, we have the **PFC free energy functional**

$$\begin{aligned}\mathcal{F}_{pfc}(t; \psi) &:= \int_{\Omega} \left\{ \frac{1}{4}\psi^4 + \frac{\epsilon}{2}\psi^2 + \frac{1}{2}\psi C_{pfc}\psi \right\} d\mathbf{x} \\ &= \int_{\Omega} \left\{ \frac{1}{4}\psi^4 + \frac{\epsilon}{2}\psi^2 + \frac{1}{2}\psi(1 + \Delta)^2\psi \right\} d\mathbf{x}.\end{aligned}\tag{2.30}$$

Therefore, the PFC homogeneous free energy is

$$\mathcal{F}_{pfc,homog}(t; \psi) := \int_{\Omega} \left\{ \frac{1}{4}\psi^4 + \frac{\epsilon}{2}\psi^2 \right\} d\mathbf{x},\tag{2.31}$$

and the gradient free energy is

$$\begin{aligned}\mathcal{F}_{pfc,grad}(t; \psi) &:= \int_{\Omega} \frac{1}{2}\psi C_{pfc}\psi d\mathbf{x} \\ &= \int_{\Omega} \frac{1}{2}\psi(1 + \Delta)^2\psi d\mathbf{x}.\end{aligned}\tag{2.32}$$

The PFC free energy density is the integrand of (2.30):

$$f_{pfc}(\psi, \Delta\psi, \Delta^2\psi) := \frac{1}{4}\psi^4 + \frac{\epsilon}{2}\psi^2 + \frac{1}{2}\psi C_{pfc}\psi = \frac{1}{4}\psi^4 + \frac{\epsilon}{2}\psi^2 + \frac{1}{2}\psi(1 + \Delta)^2\psi.\tag{2.33}$$

We use the variational derivative of $\mathcal{F}_{pfc}$ to define the partial differential equation (PDE) for the PFC model. The variational derivative of the Helmholtz free energy functional $\mathcal{F}_{pfc}$ is the chemical potential for the mass density field ψ . By Corollary E.3, the variational derivative, or chemical potential, is

$$\frac{\delta\mathcal{F}_{pfc}}{\delta\psi} = \psi^3 + \epsilon\psi + C_{pfc}\psi = \psi^3 + \epsilon\psi + (1 + \Delta)^2\psi.\tag{2.34}$$

To conserve mass density, we set the time derivative of the mass density to the Laplacian of the chemical potential:

$$\dot{\psi} := \Delta \frac{\delta\mathcal{F}_{pfc}}{\delta\psi}.\tag{2.35}$$

Finally, the **PFC partial differential equation (PDE)** is

$$\dot{\psi} = \Delta (\psi^3 + \epsilon\psi + (1 + \Delta)^2\psi), \quad (2.36)$$

which is sixth order.

In summary, the **phase field crystal (PFC) equations** are

$$\mathcal{F}_{pfc}(t; \psi) = \int_{\Omega} \left\{ \frac{1}{4}\psi^4 + \frac{\epsilon}{2}\psi^2 + \frac{1}{2}\psi(1 + \Delta)^2\psi \right\} d\mathbf{x} \quad (2.37)$$

and

$$\dot{\psi} = \Delta (\psi^3 + \epsilon\psi + (1 + \Delta)^2\psi). \quad (2.38)$$

2.2.3 PFC Model Mass Conservation and Nonincreasing Energy

We first prove that mass density is indeed conserved. Note that mass density is conserved if, and only, if

$$\frac{d}{dt} \int_{\Omega} \psi d\mathbf{x} = 0 \quad (2.39)$$

for all $t \in \mathbb{R}^+$. By Leibniz's rule, we have

$$\frac{d}{dt} \int_{\Omega} \psi d\mathbf{x} = \int_{\Omega} \dot{\psi} d\mathbf{x}. \quad (2.40)$$

Next, by (2.35),

$$\frac{d}{dt} \int_{\Omega} \psi d\mathbf{x} = \int_{\Omega} \Delta \frac{\delta \mathcal{F}_{pfc}}{\delta \psi} d\mathbf{x} = \int_{\Omega} 1 \cdot \Delta \frac{\delta \mathcal{F}_{pfc}}{\delta \psi} d\mathbf{x}. \quad (2.41)$$

By Green's first identity for periodic functions (C.4),

$$\frac{d}{dt} \int_{\Omega} \psi d\mathbf{x} = - \int_{\Omega} \nabla 1 \cdot \nabla \frac{\delta \mathcal{F}_{pfc}}{\delta \psi} d\mathbf{x}. \quad (2.42)$$

Since $\nabla 1 = \mathbf{0}$,

$$\frac{d}{dt} \int_{\Omega} \psi d\mathbf{x} = 0 \quad (2.43)$$

for all $t \in \mathbb{R}^+$, and, so, mass density is conserved.

Next, we prove that the free energy is nonincreasing over time. For this, it is necessary and sufficient to prove that

$$\frac{d\mathcal{F}_{pfc}}{dt} \leq 0. \quad (2.44)$$

By Theorem E.5, which provides the relationship between the variational derivative and the time derivative,

$$\frac{d\mathcal{F}_{pfc}}{dt} = \int_{\Omega} \frac{\delta\mathcal{F}_{pfc}}{\delta\psi} \dot{\psi} d\mathbf{x}. \quad (2.45)$$

Next, by (2.35),

$$\frac{d\mathcal{F}_{pfc}}{dt} = \int_{\Omega} \frac{\delta\mathcal{F}_{pfc}}{\delta\psi} \Delta \frac{\delta\mathcal{F}_{pfc}}{\delta\psi} d\mathbf{x}. \quad (2.46)$$

By Green's first identity for periodic functions (C.4),

$$\frac{d\mathcal{F}_{pfc}}{dt} = - \int_{\Omega} \nabla \frac{\delta\mathcal{F}_{pfc}}{\delta\psi} \cdot \nabla \frac{\delta\mathcal{F}_{pfc}}{\delta\psi} d\mathbf{x} = - \int_{\Omega} \left| \nabla \frac{\delta\mathcal{F}_{pfc}}{\delta\psi} \right|^2 d\mathbf{x}. \quad (2.47)$$

Since

$$\left| \nabla \frac{\delta\mathcal{F}_{pfc}}{\delta\psi} \right|^2 \geq 0$$

for all $t \in \mathbb{R}^+$ and all $\mathbf{x} \in \mathbb{R}^2$,

$$\frac{d\mathcal{F}_{pfc}}{dt} \leq 0 \quad (2.48)$$

for all t . Therefore, the free energy is nonincreasing.

2.2.4 PFC Model Frequency Analysis

Recall that the PFC linear operator is given by

$$C_{pfc} = (1 + \Delta)^2. \quad (2.49)$$

In addition, by Theorem D.2, the corresponding Fourier space multiplier is

$$\widetilde{C_{pfc}}(\omega) = 1 - 2\omega^2 + \omega^4, \quad (2.50)$$

where $\omega = \sqrt{\omega_x^2 + \omega_y^2}$ is the angular frequency radius. As we can see by the single minimum in Figure 2.9, we have one frequency mode. Therefore, mass density arrangements with angular frequency radii near 1 result in low free energies. This means that such arrangements persist over time. Arrangements with other angular frequency radii result in higher free energies and deteriorate over time.

This singular angular frequency mode results in mass densities with triangular geometry. To achieve this geometry, we add three spatial field components. Each component corresponds to a different angular frequency vector:

$$\boldsymbol{\omega}_{pfc,a} := \left(\frac{\sqrt{3}}{2}, \frac{1}{2} \right), \quad (2.51)$$

$$\boldsymbol{\omega}_{pfc,b} := \left(-\frac{\sqrt{3}}{2}, \frac{1}{2} \right), \quad (2.52)$$

and

$$\boldsymbol{\omega}_{pfc,c} := (0, 1). \quad (2.53)$$

The corresponding field components are given by

$$\psi_{pfc,a}(x, y) := -\cos\left(\frac{\sqrt{3}}{2}x + \frac{1}{2}y\right), \quad (2.54)$$

$$\psi_{pfc,b}(x, y) := -\cos\left(-\frac{\sqrt{3}}{2}x + \frac{1}{2}y\right), \quad (2.55)$$

and

$$\psi_{pfc,c}(x, y) := \cos(y), \quad (2.56)$$

respectively. We define $\psi_{pfc}(x, y)$ to be the sum of all three fields:

$$\begin{aligned} \psi_{pfc}(x, y) &:= \psi_{pfc,a}(x, y) + \psi_{pfc,b}(x, y) + \psi_{pfc,c}(x, y) \\ &= -\cos\left(\frac{\sqrt{3}}{2}x + \frac{1}{2}y\right) - \cos\left(-\frac{\sqrt{3}}{2}x + \frac{1}{2}y\right) + \cos(y). \end{aligned} \quad (2.57)$$

Field $\psi_{pfc}(x, y)$ is the triangular geometry that evolves over time as a result of the PFC linear operator C_{pfc} (2.49). Note that identical rotations of each of these three fields result in a sum that has the same triangular geometry. Indeed, the angles of the angular frequency vectors $\omega_{pfc,a}$, $\omega_{pfc,b}$, and $\omega_{pfc,c}$ differ by multiples of 60° . Field components for angular frequencies with angular spacings other than multiples of 60° produce angular frequencies other than 1.

Figures 2.10a, 2.10b, and 2.10e show fields $\psi_{pfc,a}$, $\psi_{pfc,b}$, and $\psi_{pfc,c}$, respectively. Figures 2.10c and 2.10d both display the sum $\psi_{pfc,a} + \psi_{pfc,b}$ to provide a visual connection and intermediary step in the summation of the three fields. Finally, Figure 2.10f reveals the sum of all three fields, $\psi_{pfc} = \psi_{pfc,a} + \psi_{pfc,b} + \psi_{pfc,c}$, the final PFC triangular geometry. Note that each graph in Figure 2.10 displays exactly one PFC unit cell.

We calculate the PFC unit cell width by multiplying the reciprocal of the x -component of $\omega_{pfc,a}$ by 2π radians. We have

$$p_{pfc,x} := \frac{2}{\sqrt{3}}2\pi = \frac{4\pi}{\sqrt{3}} \approx 7.255. \quad (2.58)$$

For the PFC unit cell height, we multiply twice the reciprocal of the y -component of $\psi_{pfc,c}$ by 2π . The result is

$$p_{pfc,y} := 2 \cdot 1 \cdot 2\pi = 4\pi \approx 12.566. \quad (2.59)$$

Finally, Figure 2.11 yields the Fourier space spectrum for the PFC geometry. Since two-dimensional Fourier space spectrums possess 180° rotational symmetry about the origin, only the top two quadrants are shown. For clarity, the constant component of the spectrum is omitted. The white boxes contain the phase angles for the corresponding angular frequency components. Since $\psi_{pfc,a}$ and $\psi_{pfc,b}$ have negative amplitudes, the corresponding phase angles are π .

2.2.5 PFC Model Simulations

We provide three simulations for the PFC model. As the free energy is nonincreasing, it decreases or remains constant over time. We run each simulation until the free energy per

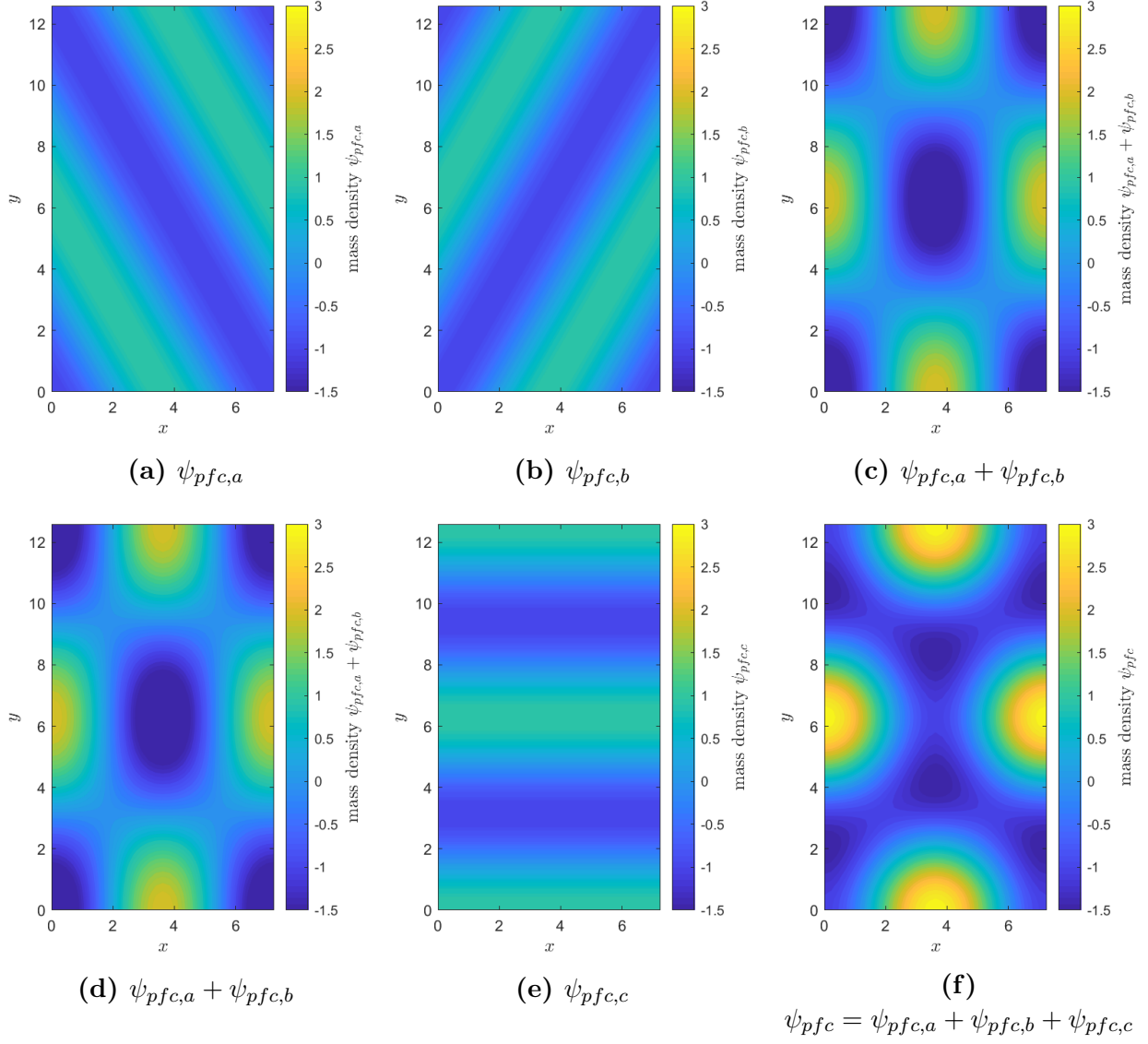


Figure 2.10: PFC Model, Field Components for Triangular Geometry

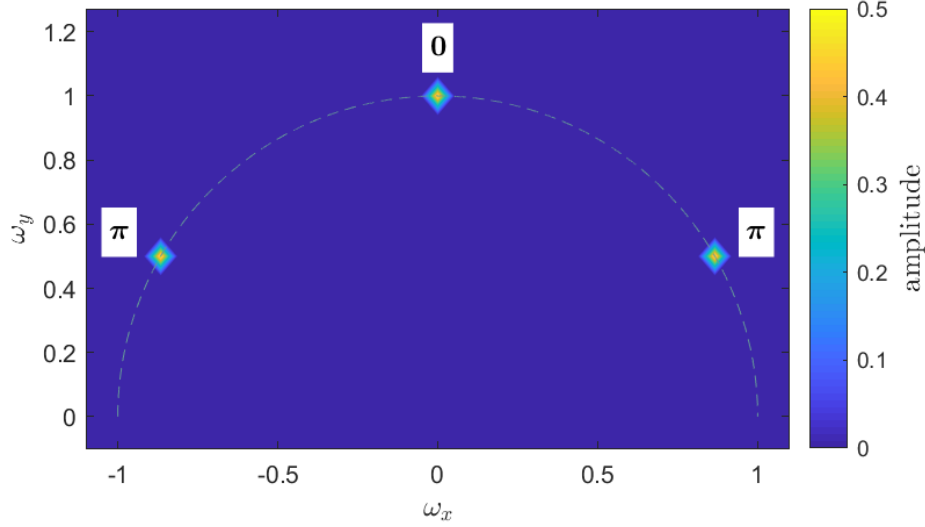


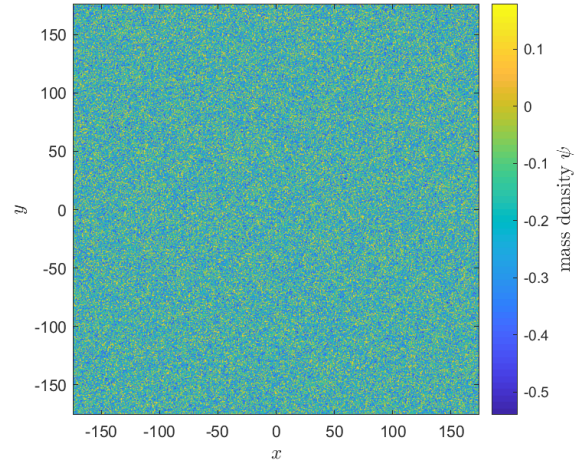
Figure 2.11: PFC Model, Fourier Space Spectrum

unit area descends to a minimum value and stabilizes. We call this state the *equilibrium state* of the system. Note that, since the numerical precision of computers is limited, this equilibrium occurs in a finite amount of time.

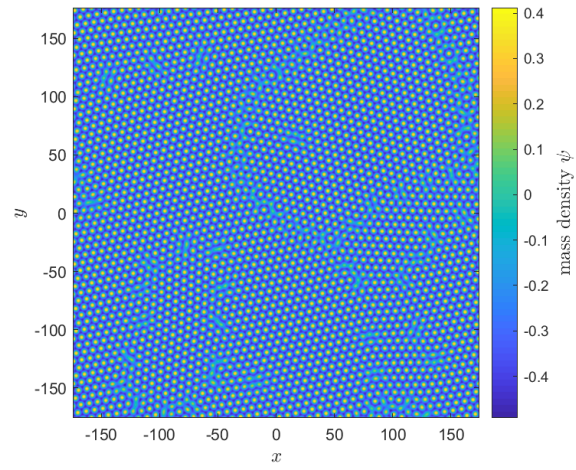
2.2.5.1 Uniformly Random

The first simulation begins with a uniformly random mass density field. Figure 2.12a displays this initial field. The triangular geometry forms relatively quickly, as shown in Figure 2.12b for time 1,000. In Figure 2.12b, we see irregularities where regions of triangular geometry with different orientations meet. These interfaces are called *grain boundaries*. The system reaches an equilibrium point at time 31,000. Finally, Figure 2.12c reveals the mass density field at the time of equilibrium. The misalignments are resolved, and, thus, no grain boundaries remain. Note that the triangular geometry is not aligned to the sides of the computational box. This evidences the rotational invariance of the PFC model.

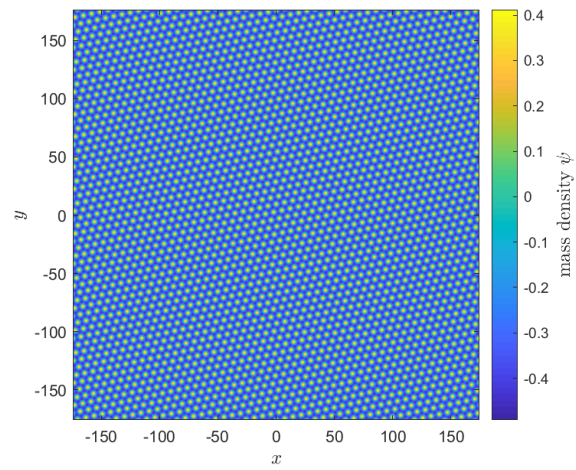
Figures 2.13a, 2.13b, and 2.13c provide the Fourier space spectrums for the times 0, 1,000, and 31,000, respectively. Figure 2.13a confirms that the Fourier space spectrum is also random at the start. Figure 2.13b indicates that, by the time 1,000, the surviving angular frequency components are already very close to 1. Because of the misalignments of



(a) Initial, Time = 0



(b) Time = 1,000



(c) Equilibrium, Time = 31,000

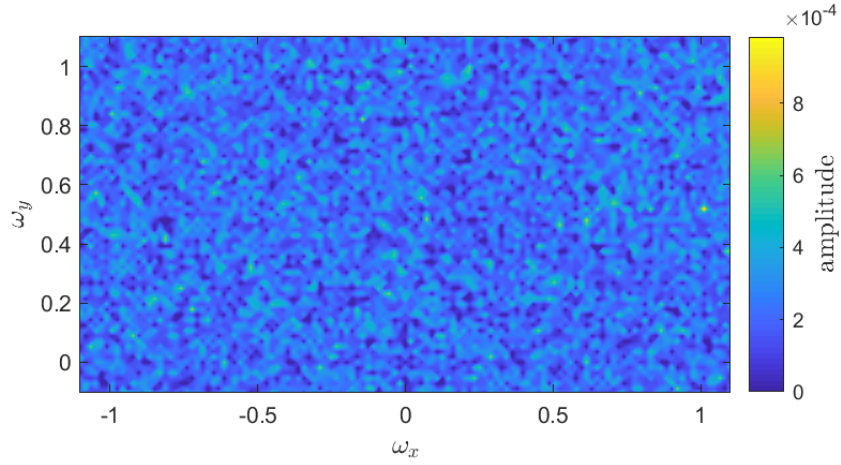
Figure 2.12: PFC Model, Uniformly Random Initial State, Mass Density Fields

the different triangular geometry regions, we do not have three sharp points, as in Figure 2.11. Finally, at the equilibrium point, Figure 2.13c reveals that only three angular frequency signals remain. Note that the angles for the corresponding angular frequency vectors differ by multiples of 60° . The spectrums of Figure 2.13c and Figure 2.11 both indicate three frequency components. However, the points in Figure 2.13c have a different orientation. This coincides with the difference in the orientations of the mass density field geometries of Figure 2.12c and Figure 2.10f.

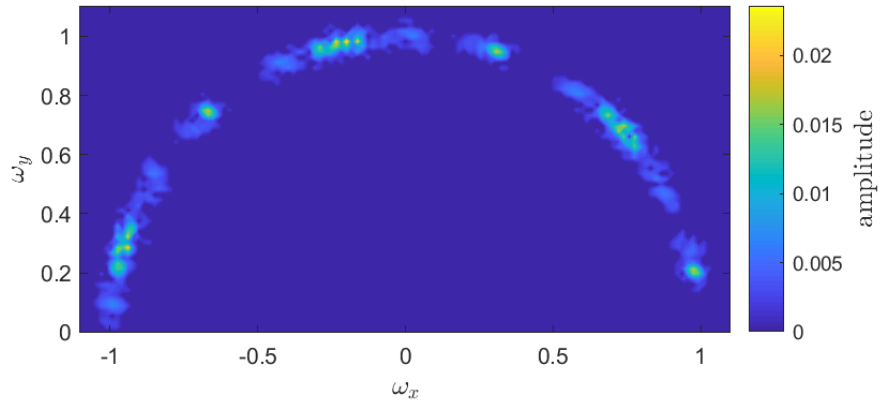
2.2.5.2 Disk Seed

Next, we begin with a solid disk region, or *seed*, in the center of the computational box. The mass density of this initial seed has triangular geometry. We call this solid region a *nanocrystal*. The rest of the box is filled with liquid. The mass density is flat in the liquid area. We choose a relatively high initial mass density for the liquid. By the design of the homogeneous part of the free energy, for the liquid phase, a minimum free energy is achieved at a particular mass density. There is also a minimum free energy for a particular mean mass density for the solid phase. Note that these phase equilibrium characteristics are examined in Section 2.5 for the multimode PFC model with the vapor phase field. Over time, the mass density of the liquid drops to reduce the overall free energy. At the solid-liquid phase interface, the mass density that is lost from the liquid results in an increase in the higher density solid area. Figure 2.14a presents the initial mass density field, while Figure 2.14b displays the mass density at time 500. The solid region, or nanocrystal, is larger at time 500. In addition, the phase interface has become wider. There is a minimum free energy associated with a particular phase interface thickness, as well. The equilibrium mass density field is shown in Figure 2.14c. The nanocrystal area is greatest when the system is at equilibrium.

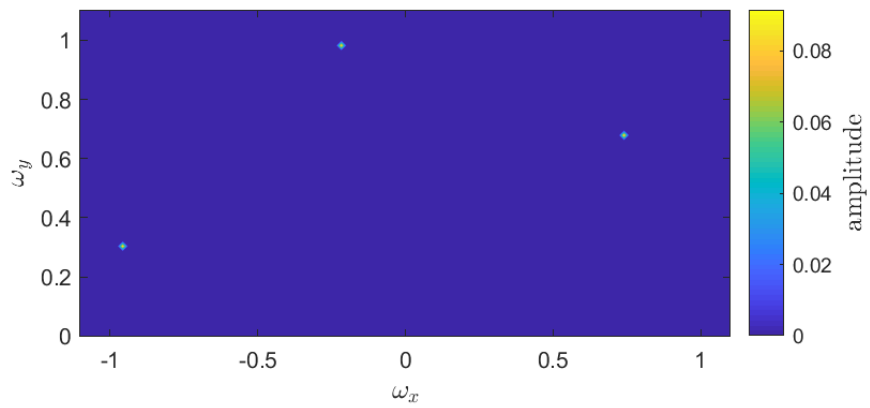
Next, Figures 2.15a, 2.15b, and 2.15c display the Fourier space spectrums for the times 0, 500, and 25,000, respectively. In Figure 2.15a, we see “halos” around the points for the three angular frequency components. These halos are the result of the solid-liquid phase interface. The interface results in small frequency component variations from the three prominent components for the PFC model. Since the initial phase interface is narrower than the subsequent phase interfaces, the corresponding frequency variations are, initially, relatively



(a) Initial, Time = 0

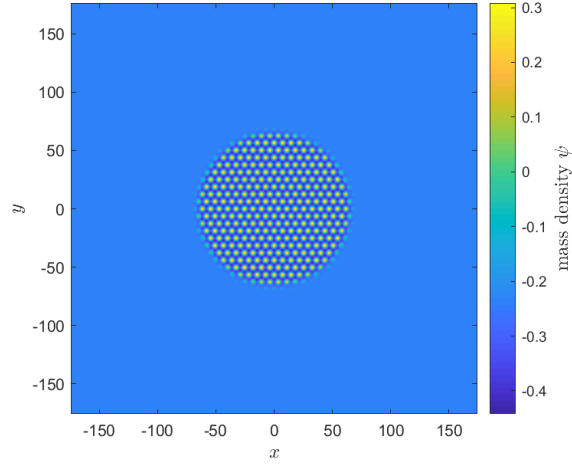


(b) Time = 1,000

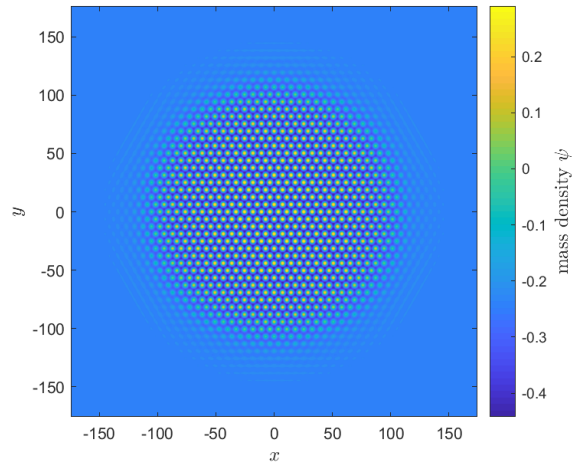


(c) Equilibrium, Time = 31,000

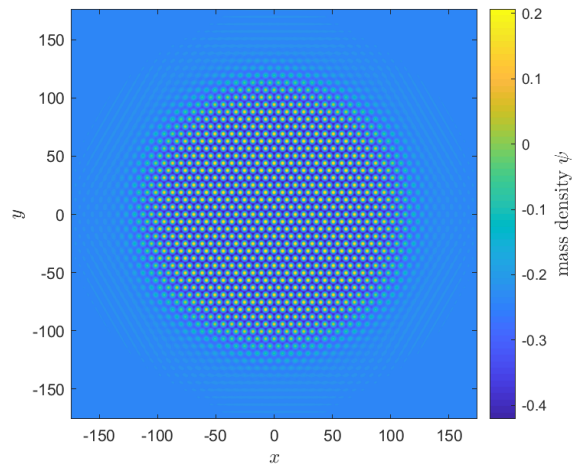
Figure 2.13: PFC Model, Uniformly Random Initial State, Fourier Space Spectrums



(a) Initial, Time = 0



(b) Time = 500



(c) Equilibrium, Time = 25,000

Figure 2.14: PFC Model, Triangular Geometry Disk Seed, Mass Density Fields

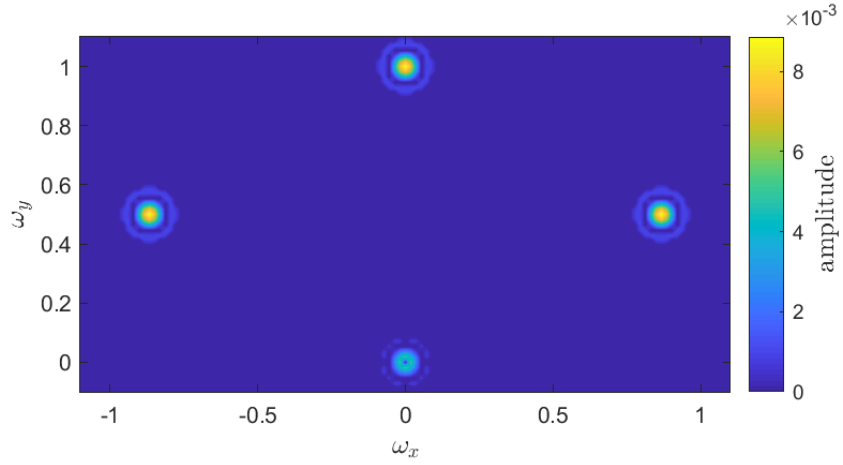
large. Figure 2.15b indicates that, as the phase interface widens, the angular frequency variations decrease. Figure 2.15c provides the spectrum for the system at equilibrium.

2.2.5.3 Random Disk Seed

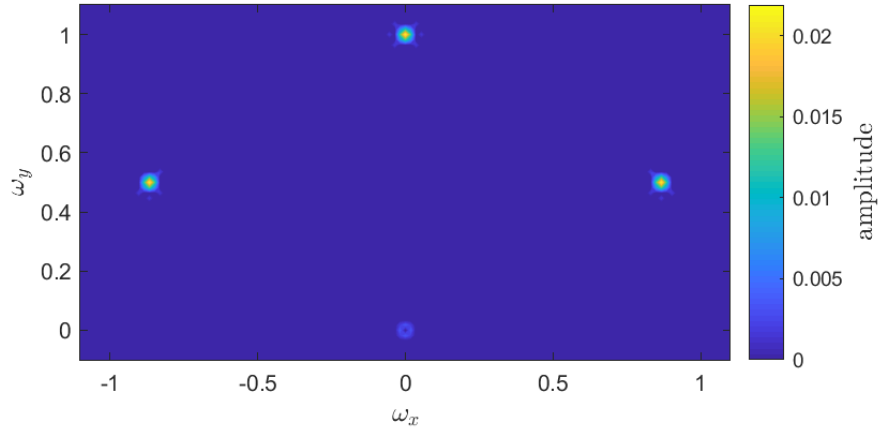
For the final PFC model simulation, we begin with a uniformly random disk seed surrounded by liquid. We set the initial liquid mass density to the elevated value from the triangular geometry seed simulation of Figures 2.14 and 2.15. Figure 2.16a displays the initial mass density field. Figure 2.16b reveals that, by time 1,000, the solid is divided into an upper region and a lower region. The upper region has a concave phase interface at its top, and the lower region contains two irregularities near its vertical center. Figure 2.16c provides the mass density field for time 2,000. By this time, the upper solid region has decreased in area, while becoming circular. By time 3,000, Figure 2.16d indicates that the upper solid region has been “absorbed” by the lower. The mass density field for time 11,000 is given by Figure 2.16e. The solid region has become circular, and no irregularities remain. Finally, Figure 2.16f shows the mass density field at equilibrium at time 43,000. Note that the size of the nanocrystal in Figure 2.16f matches that of the nanocrystal in Figure 2.14c.

We can see in the fields of Figure 2.16 that the solid region grows over time. In addition, we discover in the surface energy study of Chapter 4 that longer phase interfaces result in greater free energy. Note that, given a fixed total solid area, the shortest phase interface is achieved by a single solid disk. Hence, the system drives the solid regions into a single disk over time. This also is evidenced in the mass density fields of Figure 2.16.

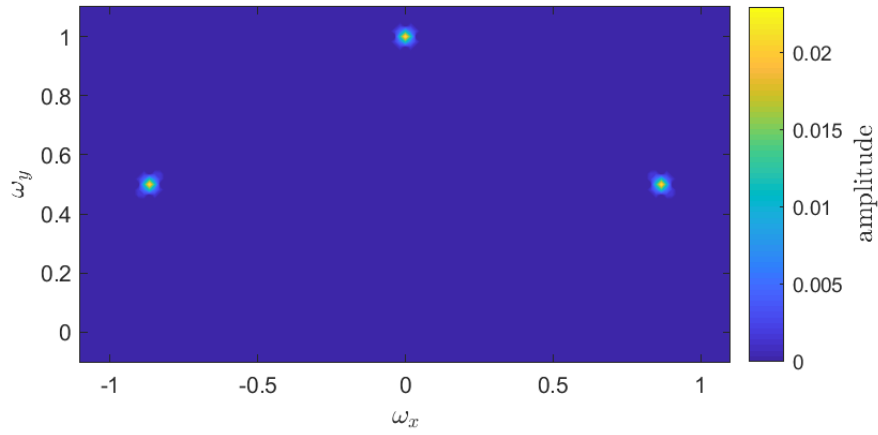
Figures 2.17a, 2.17b, and 2.17c provide the Fourier space spectrums for the times 0, 3,000, and 43,000, respectively. Initially, the liquid region has a mass density that is constant over space. The sole angular frequency component for a spatially constant field is 0. Many additional angular frequency components are present as a result of the random mass density of the solid disk. However, these additional components have negligible amplitudes when compared to that of the 0 component. In the initial Fourier space spectrum of Figure 2.17a, we find that the phase interface results in frequency component variations from the dominant 0 angular frequency. This is similar to the effects of the phase interface for the triangular geometry seed of Figures 2.14 and 2.15.



(a) Initial, Time = 0

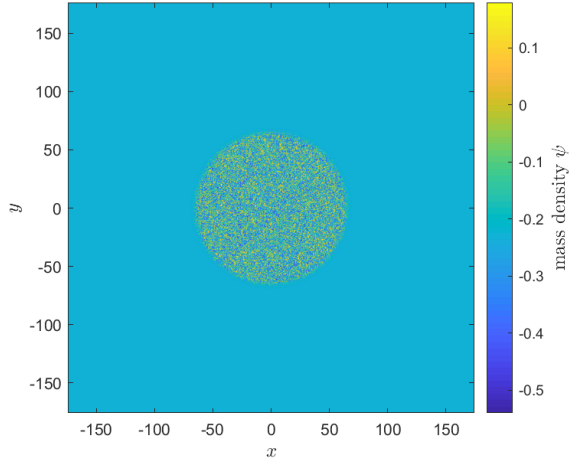


(b) Time = 500

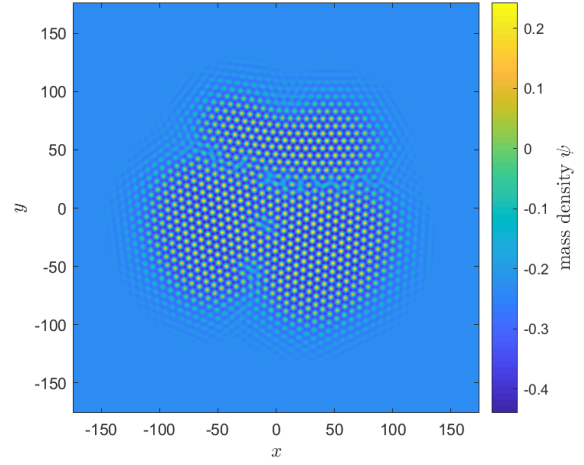


(c) Equilibrium, Time = 25,000

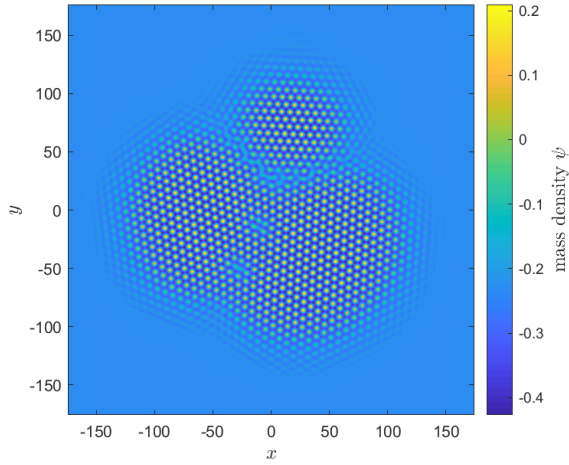
Figure 2.15: PFC Model, Triangular Geometry Disk Seed, Fourier Space Spectrums



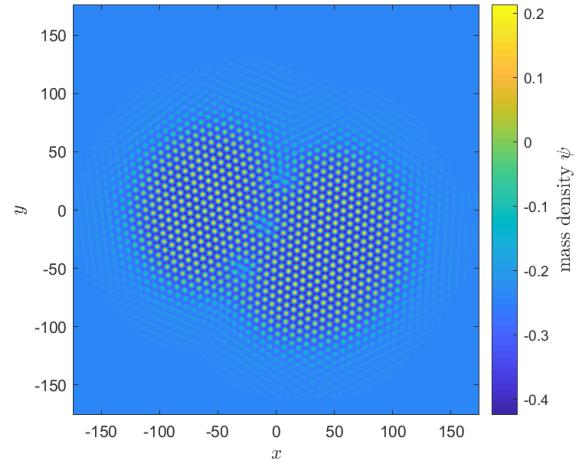
(a) Initial, Time = 0



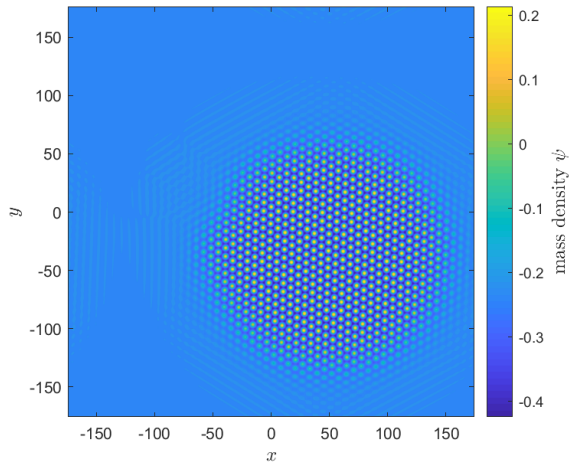
(b) Time = 1,000



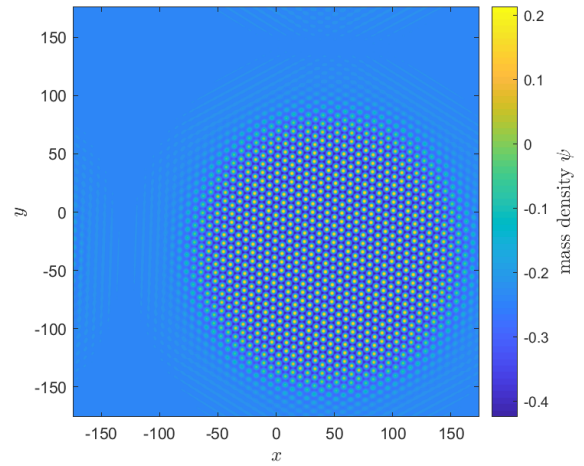
(c) Time = 2,000



(d) Time = 3,000



(e) Time = 11,000



(f) Equilibrium, Time = 43,000

Figure 2.16: PFC Model, Random Disk Seed, Mass Density Fields

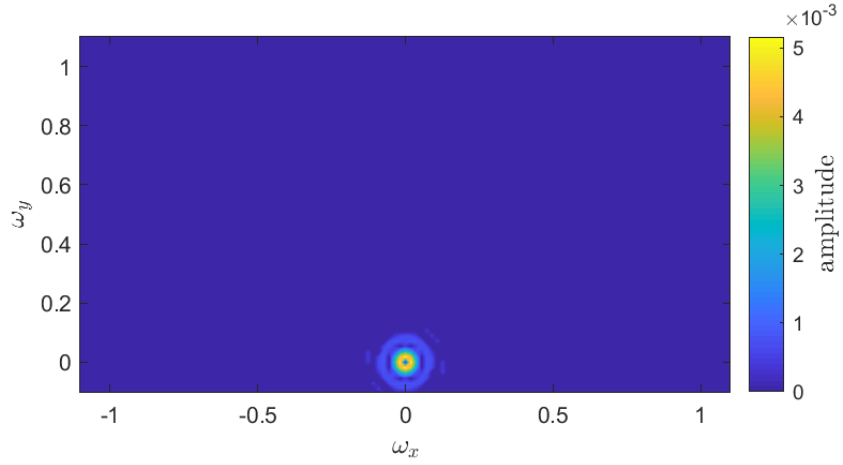
Now, at time 3,000, there are two triangular geometry orientations in the mass density field in Figure 2.16d. Hence, in the corresponding Fourier space spectrum of Figure 2.17b, we see two triplets of angular frequency components. Note that, because of the 180° rotational symmetry of Fourier space spectrums, the points beneath the ω_x -axis are redundant. We do not include them in our analysis. Finally, at the time of equilibrium, Figure 2.16f reveals that all of the triangular geometry shares the same orientation. Indeed, the corresponding Fourier space spectrum of Figure 2.17c displays a single triplet of frequency components. The halos around the dominant frequency components in Figure 2.17c are again a result of the phase interface.

2.3 Multimode Phase Field Crystal (MMPFC) Model

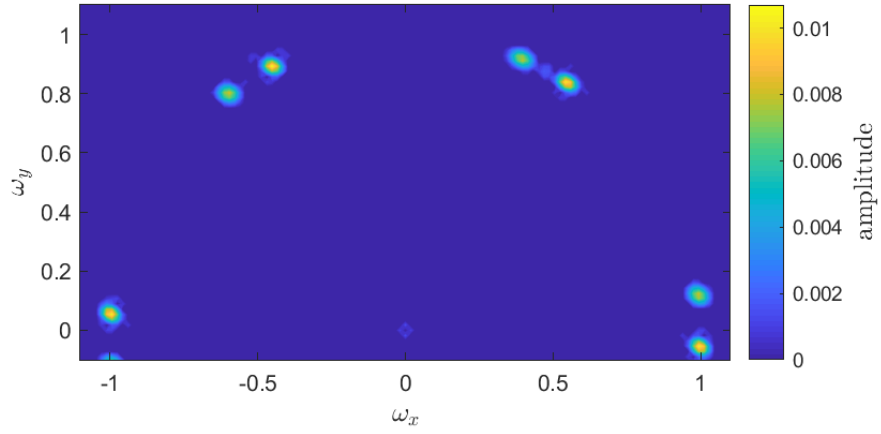
To achieve the honeycomb geometry of graphene, we add additional modes, or dominant angular frequencies, to the gradient portion of the PFC model free energy. In addition, we restore the cubic term to the homogeneous portion and add coefficient parameters for the quartic and cubic terms. We call this enhanced PFC model the *multiphase PFC model*. By design, the liquid phase of the multimode PFC model is energetically unfavorable and, thus, transient. The phase equilibrium study of Section 2.5 elaborates on this characteristic. Hence, outside of Section 2.5, the liquid phase is absent from our multimode PFC model studies. Since graphene is commonly produced by chemical vapor deposition (CVD) in the absence of the liquid phase, this multimode PFC model is apt.

Many different crystal geometries can be achieved by adding additional modes to the model and by adjusting the amplitudes of the corresponding amplitudes. In addition to honeycomb, the multimode model can produce square, rectangular, dimer, kagome, and intermediate geometries [17]. According to our interests, we use the term “multimode PFC model” to designate the model with a gradient free energy that produces honeycomb geometry. Recall that, for the honeycomb geometry, the mass density peaks mark the vertices of hexagons. For graphene, these vertices correspond to the positions of the carbon atoms.

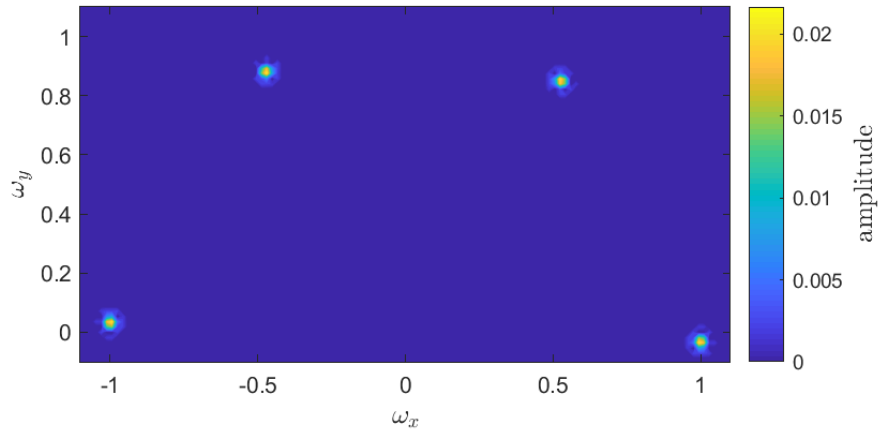
Now, the honeycomb geometry requires three spatial angular frequencies with the ratios $1:\sqrt{3}:2$. Indeed, since our base angular frequency is 1, we use 1, $\sqrt{3}$, and 2. However,



(a) Initial, Time = 0



(b) Time = 3,000



(c) Equilibrium, Time = 43,000

Figure 2.17: PFC Model, Random Disk Seed, Fourier Space Spectrums

designing a linear differential operator to produce these three frequency components is insufficient. The amplitudes of the components must also share a specific relationship. We discuss this further in Subsection 2.3.4. The three-dimensional honeycomb geometry of the multimode PFC model appears in Figure 2.18a. Figure 2.18b shows the same field from the top.

Furthermore, we introduce a new gradient energy linear differential operator in this chapter. The highest degree for the Laplace operators in common multimode models is 6. For our new multimode model, the highest Laplacian degree is 8. The additional, higher degree Laplace operators allow us to better fine tune the linear operator Fourier space multiplier. Through this tuning, we can make the honeycomb geometry sharper and achieve more stable nanocrystal growth.

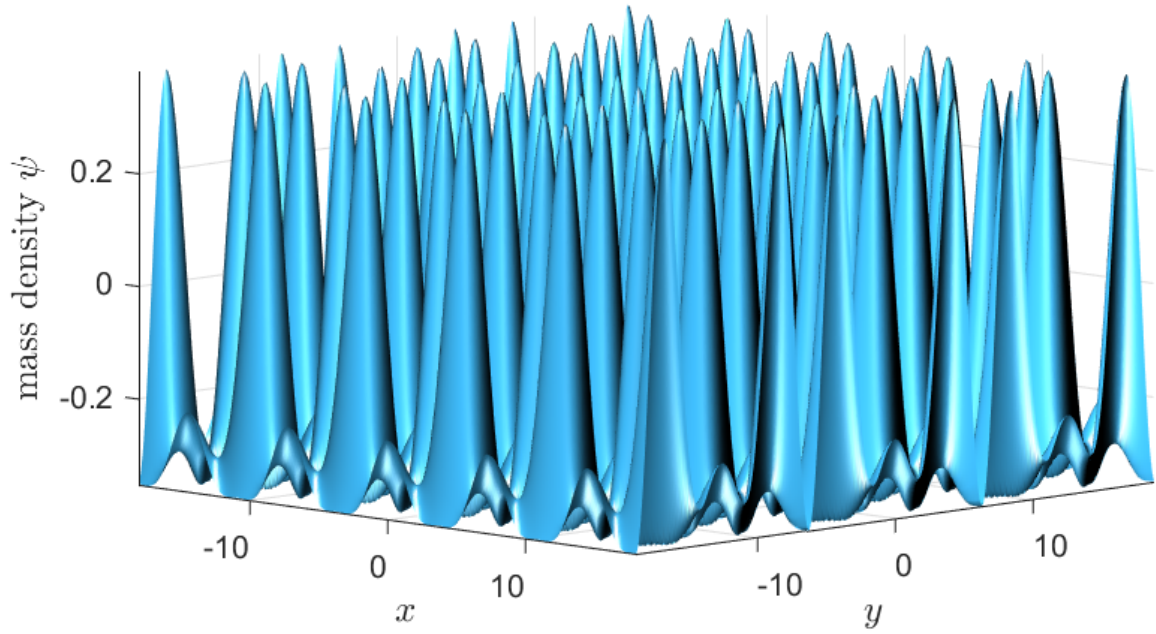
2.3.1 Multimode PFC Parameters

The parameters for the multimode PFC model appear in Table 2.2. The $c_0, c_1, \dots, c_8$ coefficients of Table 2.2a determine the crystal geometry of the solid phase. For all $i = 0, 1, \dots, 8$, c_i is the coefficient for the Laplacian of degree i . Note that Δ^0 is the identity operator. The coefficient λ is applied to the entire gradient energy density. Now, χ_4 and χ_3 are the homogeneous energy quartic and cubic term coefficients, respectively. As in the single-mode PFC model, ϵ is a scaled and shifted temperature. Table 2.2b provides the mass density field initialization parameters. No initial liquid density is provided, because the liquid phase does not endure in the multimode model. The discretization parameters are found in Table 2.2c.

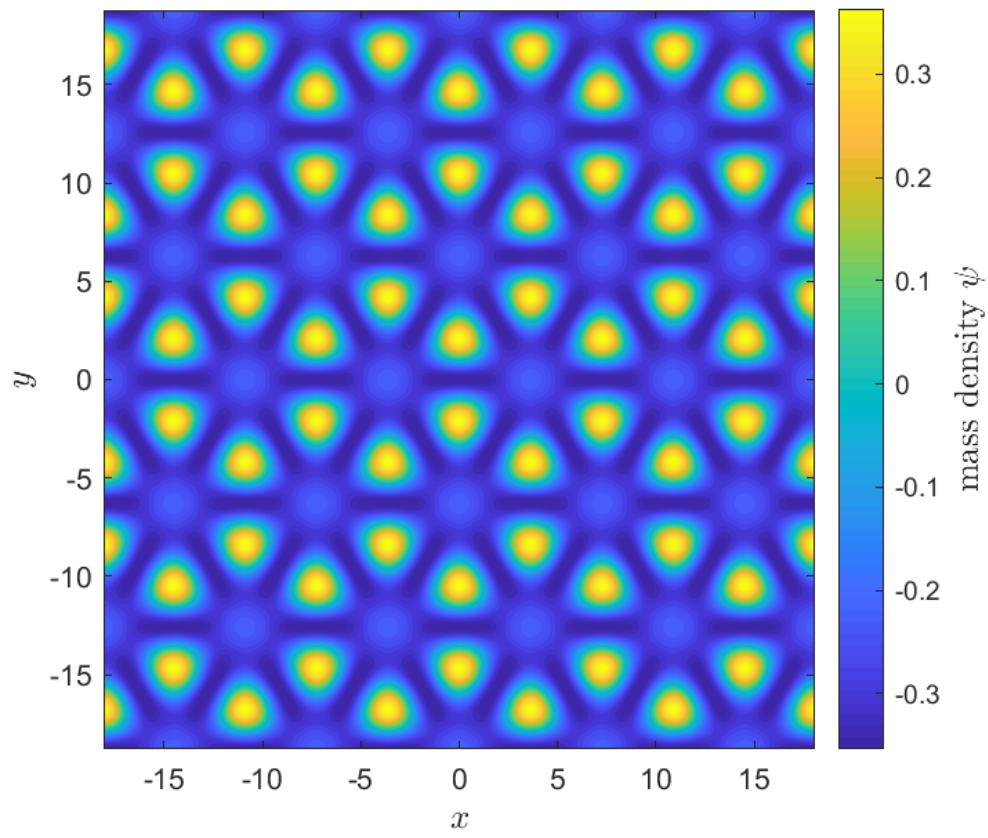
2.3.2 Multimode PFC Equations

The common multimode PFC free energy functional has the form

$$\begin{aligned} \mathcal{F}_{mmpfc,com}(t; \psi) := & \int_{\Omega} \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 \right. \\ & \left. + \frac{\lambda}{2} \psi \left[b_0 + (Q_0^2 + \Delta)^2 \right] \left[(b_1 + (Q_1^2 + \Delta)^2) \left[b_2 + (Q_2^2 + \Delta)^2 \right] \right] \psi \right\} d\mathbf{x}. \end{aligned} \quad (2.60)$$



(a) Side View



(b) Top View

Figure 2.18: Multimode PFC Model, Honeycomb Geometry

Table 2.2: Multimode PFC Parameters**(a)** Solid Phase Parameters

Parameter/Value	Description
$c_0 = 142.56$	Gradient coefficient 0
$c_1 = 562.422857143$	Gradient coefficient 1
$c_2 = 977.567142857$	Gradient coefficient 2
$c_3 = 986.032301587$	Gradient coefficient 3
$c_4 = 631.595396825$	Gradient coefficient 4
$c_5 = 257.264444444$	Gradient coefficient 5
$c_6 = 63.643968254$	Gradient coefficient 6
$c_7 = 8.637539683$	Gradient coefficient 7
$c_8 = 0.490634921$	Gradient coefficient 8
$\epsilon = -0.15$	Temperature (scaled and shifted)
$\lambda = 0.02$	Multimodal strength
$\chi_3 = -0.02$	Cubic term coefficient
$\chi_4 = 1.6$	Quartic term coefficient

(b) Mass Density Field Initialization Parameters

Parameter/Value	Description
$amp = 0.3688$	Initial solid density amplitude
$cell_x = 7.255197457$	Initial unit cell width
$cell_y = 12.5663706144685$	Initial unit cell height
$\mu_s = -0.171$	Initial solid mean density

(c) Discretization Parameters

Parameter/Value	Description
$dt = 0.1$	Time increment
$h_x \approx 0.45$	x -granularity
$h_y \approx 0.45$	y -granularity

Here, $Q_0 := 1$, $Q_1 := \sqrt{3}$, and $Q_2 := 2$ approximate the three resulting dominant angular frequencies, and b_0 , b_1 , and b_2 establish the amplitudes of these frequency components [17]. Therefore, the corresponding linear operator is given by

$$C_{com} := \left[b_0 + (Q_0^2 + \Delta)^2 \right] \left[(b_1 + (Q_1^2 + \Delta)^2) \left[b_2 + (Q_2^2 + \Delta)^2 \right] \right]. \quad (2.61)$$

The form of this linear differential operator is an enhancement of the single-mode PFC model operator $C_{pfc} := (1 + \Delta)^2$ from (2.28). The form of (2.61) is again inspired by the Swift-Hohenberg equation [15], [27]. Note that C_{com} is a 12th order differential operator. In addition, because of the factored form of (2.61), the three dominant angular frequencies produced by the linear operator are slightly different than the values of $Q_0 = 1$, $Q_1 = \sqrt{3}$, and $Q_2 = 2$.

To design our new linear operator, we start by expressing the common linear operator as a polynomial in ascending order:

$$C_{com} = \sum_{i=0}^6 c_i \Delta^i. \quad (2.62)$$

Selecting the appropriate values for $c_0, c_1, \dots, c_6$ in (2.62) yields an equivalence with (2.61). To establish the final linear differential operator for our multimode PFC model, we expand the linear operator to include 7th and 8th degree Laplacians

$$C := \sum_{i=0}^8 c_i \Delta^i. \quad (2.63)$$

This is a 16th order operator. By Theorem D.2, the corresponding Fourier space multiplier is

$$\tilde{C}(\omega) := \sum_{i=0}^8 c_i (-\omega^2)^i, \quad (2.64)$$

where $\omega = \sqrt{\omega_x^2 + \omega_y^2}$ is the angular frequency radius. Note that $\tilde{C}(\omega)$ is an even, 16th degree polynomial.

In this form, we can use linear algebra to pick the values for $c_0, c_1, \dots, c_8$ so that the three dominant angular frequencies are exactly 1, $\sqrt{3}$, and 2. In addition, we can indirectly control the amplitudes of these frequency components. We establish a system of nine linear

equations with the unknowns $c_0, c_1, \dots, c_8$. The first equation assigns a value to $\tilde{C}(0)$. Three equations assign values to $\tilde{C}(1)$, $\tilde{C}(\sqrt{3})$, and $\tilde{C}(2)$, respectively. Two more equations assign values for two intermediate angular frequencies, $\omega = \sqrt{2}$ and $\omega = \sqrt{\frac{7}{2}}$. Finally, to establish the local minima, the last three equations assign 0 to the derivative of $\tilde{C}(\omega)$ evaluated at 1, $\sqrt{3}$, and 2. We store the coefficients of the nine equations in a matrix A . We assign the corresponding constants to a column vector b . Finally, we solve $Ax = b$ to find the appropriate values for $c_0, c_1, \dots, c_8$ in the column vector x . These values are shown Table 2.2a.

Figure 2.19a provides the curve for $\tilde{C}(\omega)$. Next, Figure 2.19b shows $\lambda\tilde{C}(\omega)$. Multiplying $\tilde{C}(\omega)$ by $\lambda = 0.02$ results in a scaling equivalent to that of the single-mode PFC model linear multiplier. The PFC model multiplier appears in Figure 2.9.

Applying the new linear differential operator gives us the final **multimode PFC free energy functional**

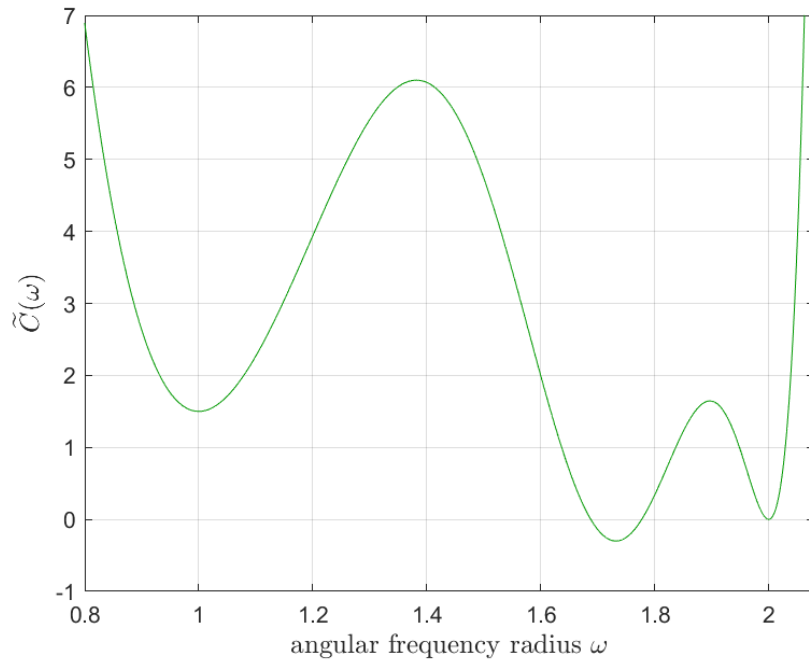
$$\begin{aligned}\mathcal{F}_{mmpfc}(t; \psi) &:= \int_{\Omega} \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi C \psi \right\} d\mathbf{x} \\ &= \int_{\Omega} \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi \left(\sum_{i=0}^8 c_i \Delta^i \right) \psi \right\} d\mathbf{x}.\end{aligned}\tag{2.65}$$

Hence, the multimode PFC homogeneous free energy is

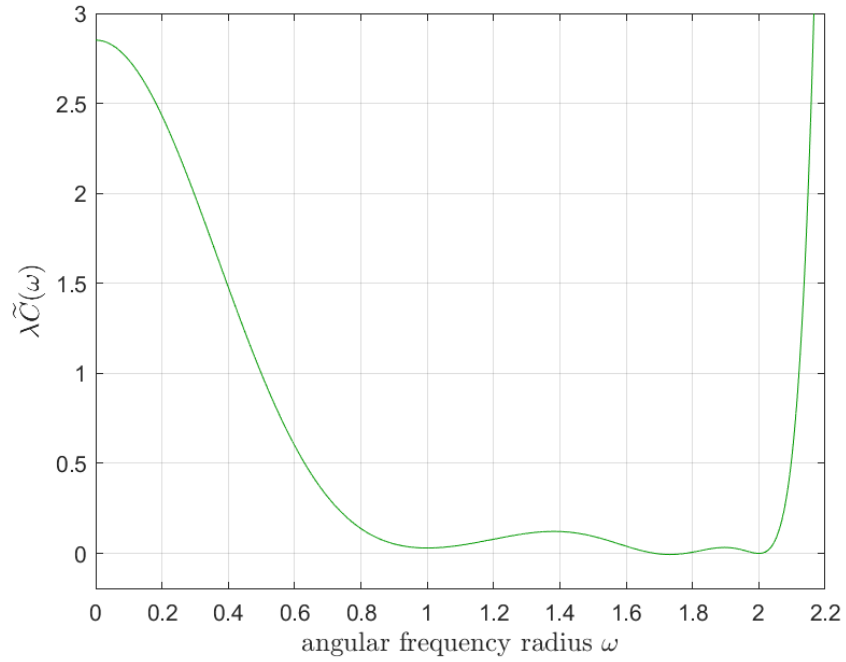
$$\mathcal{F}_{mmpfc, homog}(t; \psi) := \int_{\Omega} \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 \right\} d\mathbf{x},\tag{2.66}$$

and the gradient free energy is

$$\begin{aligned}\mathcal{F}_{mmpfc, grad}(t; \psi) &:= \int_{\Omega} \frac{\lambda}{2} \psi C \psi d\mathbf{x} \\ &= \int_{\Omega} \frac{\lambda}{2} \psi \left(\sum_{i=0}^8 c_i \Delta^i \right) \psi d\mathbf{x}.\end{aligned}\tag{2.67}$$



(a)
$$\tilde{C}(\omega) = \sum_{i=0}^8 c_i (-\omega^2)^i$$



(b)
$$\lambda \tilde{C}(\omega) = \lambda \sum_{i=0}^8 c_i (-\omega^2)^i$$

Figure 2.19: Multimode PFC Model, Linear Operator, Fourier Space Multiplier

The multimode PFC free energy density is the integrand of (2.65):

$$\begin{aligned} f_{mmpfc}(\psi, \Delta\psi, \dots, \Delta^8\psi) &:= \frac{\chi_4}{4}\psi^4 + \frac{\chi_3}{3}\psi^3 + \frac{\epsilon}{2}\psi^2 + \frac{\lambda}{2}\psi C\psi \\ &= \frac{\chi_4}{4}\psi^4 + \frac{\chi_3}{3}\psi^3 + \frac{\epsilon}{2}\psi^2 + \frac{\lambda}{2}\psi \left(\sum_{i=0}^8 c_i \Delta^i \right) \psi. \end{aligned} \quad (2.68)$$

As with the PFC model, we employ the variational derivative of $\mathcal{F}_{mmpfc}$ to construct the multimode model PDE. By Corollary E.3, the variational derivative, or chemical potential, is

$$\frac{\delta \mathcal{F}_{mmpfc}}{\delta \psi} = \chi_4 \psi^3 + \chi_3 \psi^2 + \epsilon \psi + \lambda C\psi = \chi_4 \psi^3 + \chi_3 \psi^2 + \epsilon \psi + \lambda \left(\sum_{i=0}^8 c_i \Delta^i \right) \psi. \quad (2.69)$$

To conserve mass density, we set the time derivative of the mass density to the Laplacian of the chemical potential:

$$\dot{\psi} := \Delta \frac{\delta \mathcal{F}_{mmpfc}}{\delta \psi}. \quad (2.70)$$

Finally, the **multimode PFC partial differential equation (PDE)** is

$$\dot{\psi} = \Delta \left(\chi_4 \psi^3 + \chi_3 \psi^2 + \epsilon \psi + \lambda \left(\sum_{i=0}^8 c_i \Delta^i \right) \psi \right), \quad (2.71)$$

which is of the 18th order.

To summarize, the **multimode phase field crystal (PFC) equations** are

$$\mathcal{F}_{mmpfc}(t; \psi) = \int_{\Omega} \left\{ \frac{\chi_4}{4}\psi^4 + \frac{\chi_3}{3}\psi^3 + \frac{\epsilon}{2}\psi^2 + \frac{\lambda}{2}\psi \left(\sum_{i=0}^8 c_i \Delta^i \right) \psi \right\} d\mathbf{x} \quad (2.72)$$

and

$$\dot{\psi} = \Delta \left(\chi_4 \psi^3 + \chi_3 \psi^2 + \epsilon \psi + \lambda \left(\sum_{i=0}^8 c_i \Delta^i \right) \psi \right). \quad (2.73)$$

2.3.3 Multimode PFC Mass Conservation and Nonincreasing Energy

The proofs for mass density conservation and nonincreasing energy follow directly from the work for the PFC model in Subsection 2.2.3. To prove mass density conservation, we first apply Leibniz's rule:

$$\frac{d}{dt} \int_{\Omega} \psi \, d\mathbf{x} = \int_{\Omega} \dot{\psi} \, d\mathbf{x}. \quad (2.74)$$

Then, by (2.70),

$$\frac{d}{dt} \int_{\Omega} \psi \, d\mathbf{x} = \int_{\Omega} \Delta \frac{\delta \mathcal{F}_{mmpfc}}{\delta \psi} \, d\mathbf{x} = \int_{\Omega} 1 \cdot \Delta \frac{\delta \mathcal{F}_{mmpfc}}{\delta \psi} \, d\mathbf{x}. \quad (2.75)$$

Green's first identity for periodic functions (C.4) yields

$$\frac{d}{dt} \int_{\Omega} \psi \, d\mathbf{x} = - \int_{\Omega} \nabla 1 \cdot \nabla \frac{\delta \mathcal{F}_{mmpfc}}{\delta \psi} \, d\mathbf{x}. \quad (2.76)$$

Since $\nabla 1 = \mathbf{0}$,

$$\frac{d}{dt} \int_{\Omega} \psi \, d\mathbf{x} = 0 \quad (2.77)$$

for all $t \in \mathbb{R}^+$.

For nonincreasing free energy, we apply Theorem E.5 to find

$$\frac{d\mathcal{F}_{mmpfc}}{dt} = \int_{\Omega} \frac{\delta \mathcal{F}_{mmpfc}}{\delta \psi} \dot{\psi} \, d\mathbf{x}. \quad (2.78)$$

By (2.70),

$$\frac{d\mathcal{F}_{mmpfc}}{dt} = \int_{\Omega} \frac{\delta \mathcal{F}_{mmpfc}}{\delta \psi} \Delta \frac{\delta \mathcal{F}_{mmpfc}}{\delta \psi} \, d\mathbf{x}. \quad (2.79)$$

Next, by Green's first identity for periodic functions (C.4),

$$\frac{d\mathcal{F}_{mmpfc}}{dt} = - \int_{\Omega} \nabla \frac{\delta \mathcal{F}_{mmpfc}}{\delta \psi} \cdot \nabla \frac{\delta \mathcal{F}_{mmpfc}}{\delta \psi} \, d\mathbf{x} = - \int_{\Omega} \left| \nabla \frac{\delta \mathcal{F}_{mmpfc}}{\delta \psi} \right|^2 \, d\mathbf{x}. \quad (2.80)$$

Since

$$\left| \nabla \frac{\delta \mathcal{F}_{mmpfc}}{\delta \psi} \right|^2 \geq 0$$

for all $t \in \mathbb{R}^+$ and all $\mathbf{x} \in \mathbb{R}^2$,

$$\frac{d\mathcal{F}_{mmpfc}}{dt} \leq 0 \quad (2.81)$$

for all t .

2.3.4 Multimode PFC Frequency Analysis

First, the multimode PFC linear operator is given by

$$C = \sum_{i=0}^8 c_i \Delta^i, \quad (2.82)$$

and, by Theorem [D.2](#), the corresponding Fourier space multiplier is

$$\tilde{C}(\omega) = \sum_{i=0}^8 c_i (-\omega^2)^i. \quad (2.83)$$

Through our selections for the values of $c_0, c_1, \dots, c_8$, the multimode PFC model has three modes, or prominent angular frequency radii. They are

$$\omega_1 := 1, \quad (2.84)$$

$$\omega_{\sqrt{3}} := \sqrt{3}, \quad (2.85)$$

and

$$\omega_2 := 2. \quad (2.86)$$

These angular frequency radii mark the locations of the local minima in Figure [2.19a](#). Mass density configurations with angular frequency radii near 1, $\sqrt{3}$, and 2 result in low free energies and persist over time. Furthermore, the values for $c_0, c_1, \dots, c_8$ drive the system to a point where the amplitudes of these frequency components have a particular relationship. Most importantly, the frequency components with radius 2 have relatively low amplitudes,

or strengths. In addition, the amplitudes of the 1 and $\sqrt{3}$ radius components are similar to each other. The relationship of the amplitudes of the angular frequency radii components is similar to the relationship of the depths of the corresponding wells in Figure 2.19a.

To build the resulting honeycomb geometry, we add nine spatial field components. There are three field components for each of the three angular frequency radii 1, $\sqrt{3}$, 2. Each of the triplets forms triangular geometry, as demonstrated in Subsection 2.2.4. The corresponding fields are

$$\psi_1(x, y) := \frac{81}{180} \left[\cos \left(\frac{\sqrt{3}}{2}x + \frac{1}{2}y \right) + \cos \left(-\frac{\sqrt{3}}{2}x + \frac{1}{2}y \right) - \cos(y) \right], \quad (2.87)$$

$$\psi_{\sqrt{3}}(x, y) := \frac{116}{180} \left[-\cos \left(\frac{\sqrt{3}}{2}x + \frac{3}{2}y \right) - \cos \left(-\frac{\sqrt{3}}{2}x + \frac{3}{2}y \right) + \cos(\sqrt{3}x) \right], \quad (2.88)$$

and

$$\psi_2(x, y) := \frac{48}{180} \left[-\cos(\sqrt{3}x + y) - \cos(-\sqrt{3}x + y) - \cos(2y) \right], \quad (2.89)$$

respectively. We define $\psi_{mmpfc}(x, y)$ as the sum of the three fields:

$$\psi_{mmpfc}(x, y) := \psi_1(x, y) + \psi_{\sqrt{3}}(x, y) + \psi_2(x, y). \quad (2.90)$$

As with the triangular geometry of the PFC model, sums of identical rotations of these fields also yield honeycomb geometry.

Figures 2.20a, 2.20b, and 2.20e display fields ψ_1 , $\psi_{\sqrt{3}}$, and ψ_2 , respectively. Figures 2.20c and 2.20d both show the sum $\psi_1 + \psi_{\sqrt{3}}$ to connect the field summation steps. Figure 2.20f is the sum of the three fields, $\psi_{mmpfc} = \psi_1 + \psi_{\sqrt{3}} + \psi_2$, and the final multimode PFC honeycomb geometry. Each graph in Figure 2.20 holds exactly one multimode PFC unit cell.

As in the angular frequency composition for the PFC model in Subsection 2.2.4, we see in (2.87) that $\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)$ is one of the three angular frequency components for $\omega_1 = 1$. We use the method from Subsection 2.2.4 to find the multimode PFC unit cell dimensions. The width and height are

$$p_x := \frac{2}{\sqrt{3}}2\pi = \frac{4\pi}{\sqrt{3}} \approx 7.255, \quad (2.91)$$

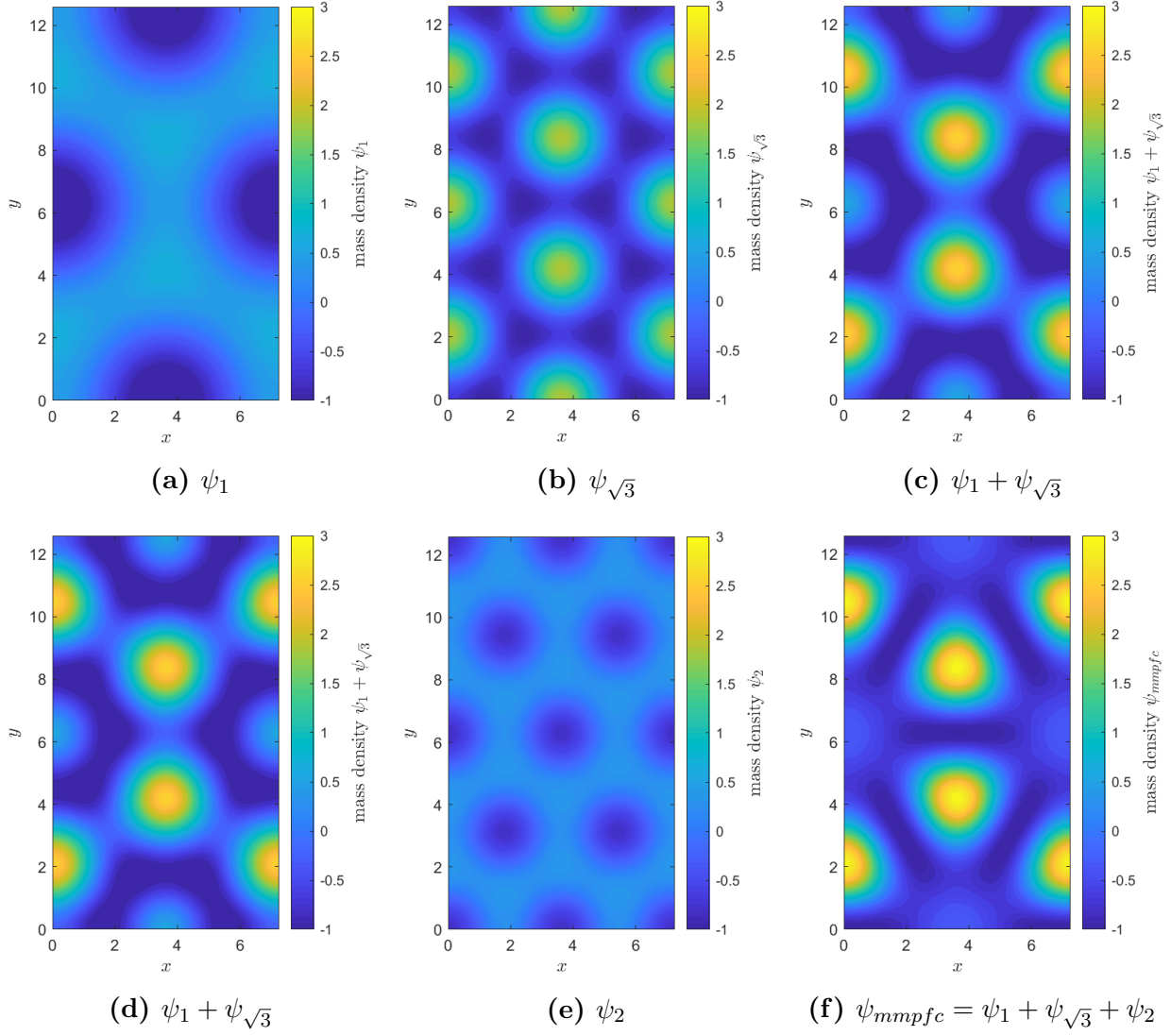


Figure 2.20: Multimode PFC Model, Field Components for Honeycomb Geometry

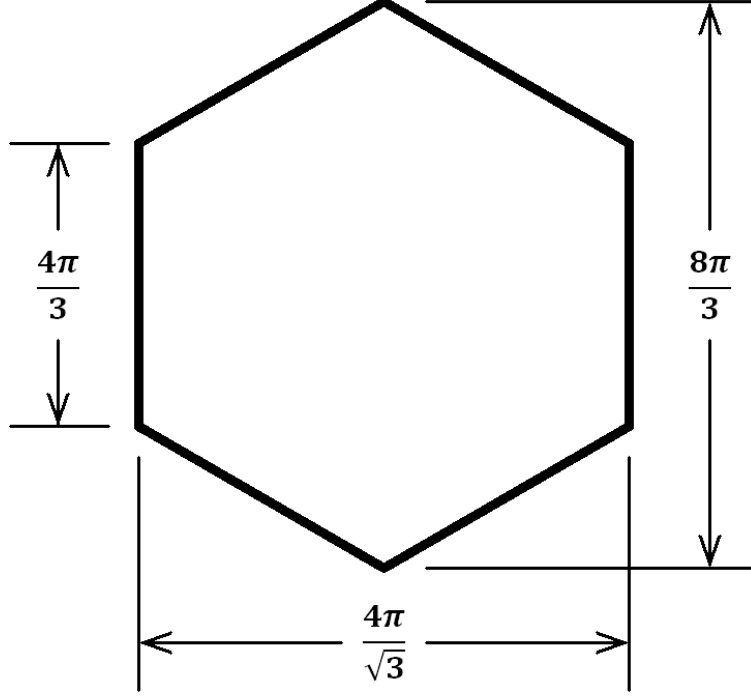


Figure 2.21: Honeycomb Geometry, Hexagon Dimensions

and

$$p_y := 2 \cdot 1 \cdot 2\pi = 4\pi \approx 12.566, \quad (2.92)$$

respectively. These dimensions are the same as those of the triangular geometry of the single-mode PFC model. The dimensions for each hexagon of the honeycomb geometry are given in Figure 2.21.

At last, Figure 2.22 provides the Fourier space spectrum for the multimode PFC honeycomb geometry. The constant component of the spectrum is omitted. The phase angle for each of the nine angular frequency components appears in a white box near the corresponding point. Note that the frequency components form vertical pairings. For $\omega_{\sqrt{3}} = \sqrt{3}$, due to the 180° rotational symmetry of the spectrum, the frequency components $(-\sqrt{3}, 0)$ and $(\sqrt{3}, 0)$ are equivalent.

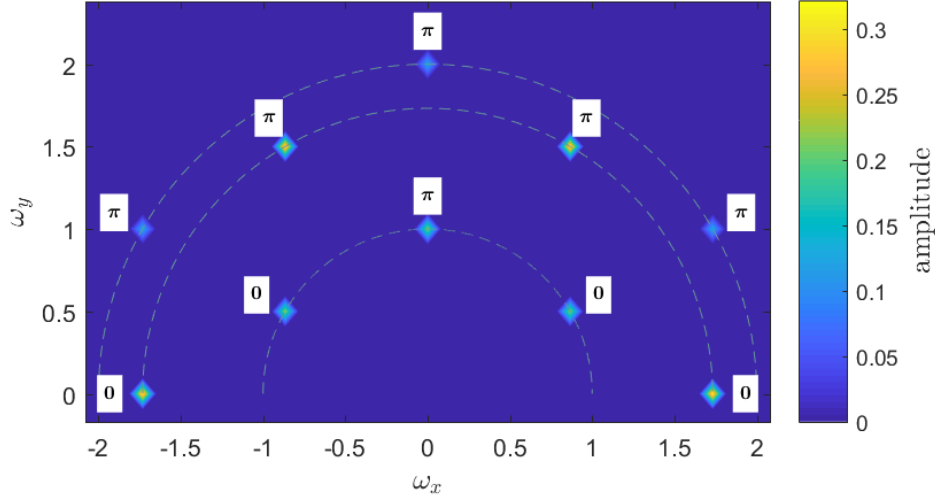
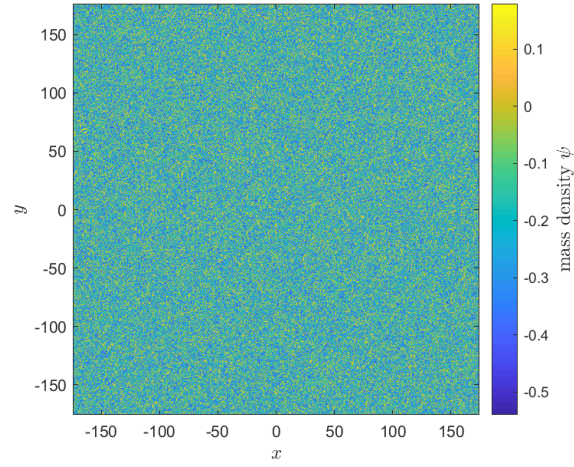


Figure 2.22: Multimode PFC Model, Fourier Space Spectrum

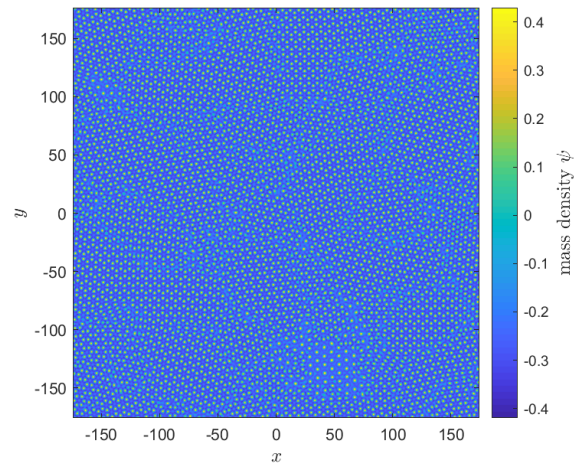
2.3.5 Multimode PFC Simulation

For the multimode PFC model simulation, we begin with a uniformly random mass density field. This initial field appears in Figure 2.23a. Figure 2.23b displays the mass density field for time 1,000. There are many patches of honeycomb geometry with different orientations. The patches form grain boundaries where they meet. The system reaches equilibrium by time 38,000. Figure 2.23c holds the equilibrium mass density field. Over time, a number of patches align with neighboring regions, and, thus, some of the grain boundaries are shortened or eliminated. However, even at the equilibrium, irregularities remain.

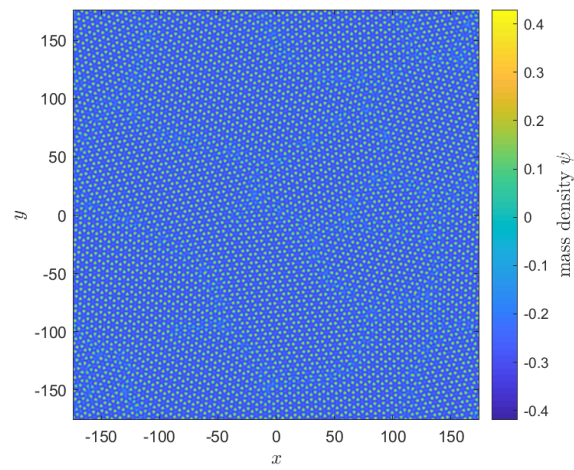
Figures 2.24a, 2.24b, and 2.24c yield the Fourier space spectrums for times 0, 1,000, and 38,000, respectively. At time 0, Figure 2.24a shows a random Fourier space spectrum. We see in Figure 2.24b that, by time 1,000, the frequency components have formed arcs with angular frequency radii of 1, $\sqrt{3}$, and 2. However, the arcs are indistinct, and, for each of the radii, there are many frequency components. This is a result of the many different honeycomb geometry orientations in the mass density field of Figure 2.23b. The grain boundaries result in angular frequency components with radii slightly different than 1, $\sqrt{3}$, and 2. The arcs are sharper at the system equilibrium, as evidenced in Figure 2.24c. If we look closely at the arc for a given angular frequency radius, we can see that patterns emerge with 60° cycles.



(a) Initial, Time = 0

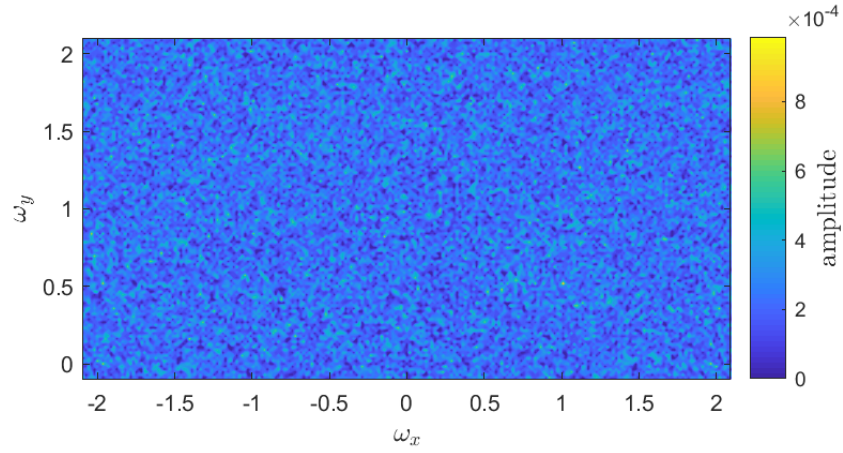


(b) Time = 1,000

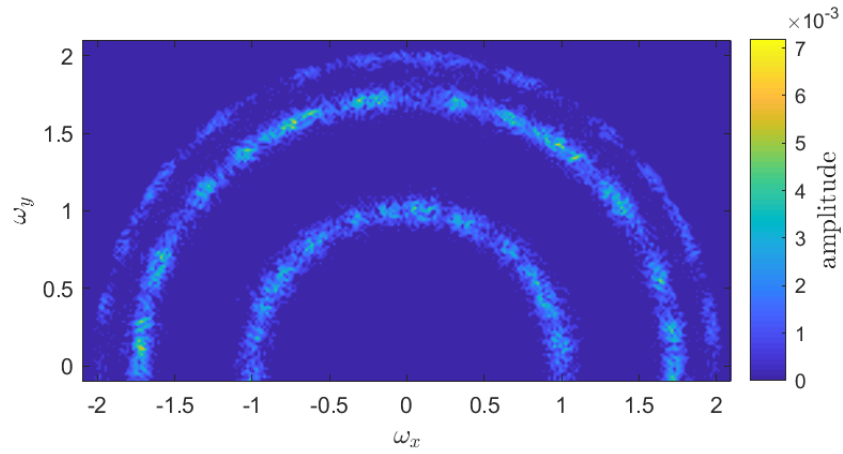


(c) Equilibrium, Time = 38,000

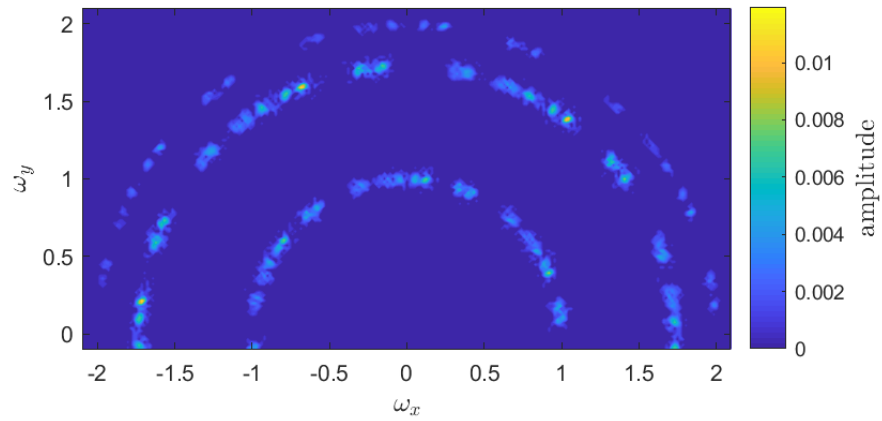
Figure 2.23: Multimode PFC, Uniformly Random Initial State, Mass Density Fields



(a) Initial, Time = 0



(b) Time = 1,000



(c) Equilibrium, Time = 38,000

Figure 2.24: Multimode PFC, Uniformly Random Initial State, Fourier Space Spectrums

2.4 Multimode Phase Field Crystal (MMPFC) Model with Vapor

To complete our model, we add a vapor phase field named $\eta(t; \mathbf{x})$. The vapor phase field η outputs values between 0 and 1. Here, 0 represents the solid phase, and 1 indicates the vapor phase. At the solid-vapor interface, the values of η transition smoothly from 0 to 1. This model is referred to as the National Institute of Standards and Technology, or NIST, model, and it was introduced by Schwalbach, Warren, Wu, and Voorhees in 2013 [22].

2.4.1 Multimode PFC with Vapor Parameters

Here, we introduce the parameters for the multimode PFC model with the vapor phase. Many of the parameter values are adapted from the work of Gu, Wang, Wang, et al. [9]. The structural parameters and values inherited from the multimode PFC model appear in Table 2.3a. Table 2.3b holds the vapor phase field parameters. Note that the phase interface energy coefficients W_v and κ_v vary throughout the study. Common values are $W_v = 0.1$ and $\kappa_v = 0.4455$. Table 2.3c provides the mass density field initialization parameters. For an angle of 0, the honeycomb geometry cell width is $\frac{4\pi}{\sqrt{3}} \approx 7.255197457$ and the cell height is $4\pi \approx 12.5663706144685$. An angle of $\frac{\pi}{2} \approx 1.57079632679490$ indicates a counterclockwise geometry rotation of 90° . Hence, for this angle, the honeycomb geometry cell width is $4\pi \approx 12.5663706144685$ and the cell height is $\frac{4\pi}{\sqrt{3}} \approx 7.255197457$. We vary the initial vapor and solid mean mass densities as well. However, common initial densities are $\mu_v = -0.219$ and $\mu_s = -0.171$, respectively. Finally, Table 2.3d provides the discretization parameters. These discretization parameter values are identical to those of the single-mode and multimode models.

2.4.2 Multimode PFC with Vapor Equations

For the multimode PFC model with the vapor phase, we build the Helmholtz free energy functional and partial differential equations (PDE's) by combining three free energies. These energies are the regular multimode PFC free energy, the vapor phase free energy, and the

Table 2.3: Multimode PFC Model with Vapor Parameters**(a)** Solid Phase Parameters

Parameter/Value	Description
$c_0 = 142.56$	Gradient coefficient 0
$c_1 = 562.422857143$	Gradient coefficient 1
$c_2 = 977.567142857$	Gradient coefficient 2
$c_3 = 986.032301587$	Gradient coefficient 3
$c_4 = 631.595396825$	Gradient coefficient 4
$c_5 = 257.264444444$	Gradient coefficient 5
$c_6 = 63.643968254$	Gradient coefficient 6
$c_7 = 8.637539683$	Gradient coefficient 7
$c_8 = 0.490634921$	Gradient coefficient 8
$\epsilon = -0.15$	Temperature (scaled and shifted)
$\lambda = 0.02$	Multimodal strength
$\chi_3 = -0.02$	Cubic term coefficient
$\chi_4 = 1.6$	Quartic term coefficient

(b) Vapor Phase Field Parameters

Parameter/Value	Description
$b_v = 4$	Vapor free energy scalar
$M_v = 1$	Vapor phase field mobility
W_v (varies)	Resistance to coexistence of phases
$\Delta_v = 0.0387683$	Vapor free energy differential
κ_v (varies)	Phase interface derivative strength
$\psi_v = -0.11$	Vapor equilibrium density

(c) Mass Density Field Initialization Parameters

Parameter/Value	Description
$amp = 0.3688$	Initial solid density amplitude
$angle = 0$ or 1.57079632679490	Initial angle of honeycomb geometry
$cell_x = 7.255197457$ or 12.5663706144685	Initial unit cell width
$cell_y = 12.5663706144685$ or 7.255197457	Initial unit cell height
$thickness = 2.756975$	Initial phase interface thickness
μ_s (varies)	Initial solid mean density
μ_v (varies)	Initial vapor density

(d) Discretization Parameters

Parameter/Value	Description
$dt = 0.1$	Time increment
$h_x \approx 0.45$	x -granularity
$h_y \approx 0.45$	y -granularity

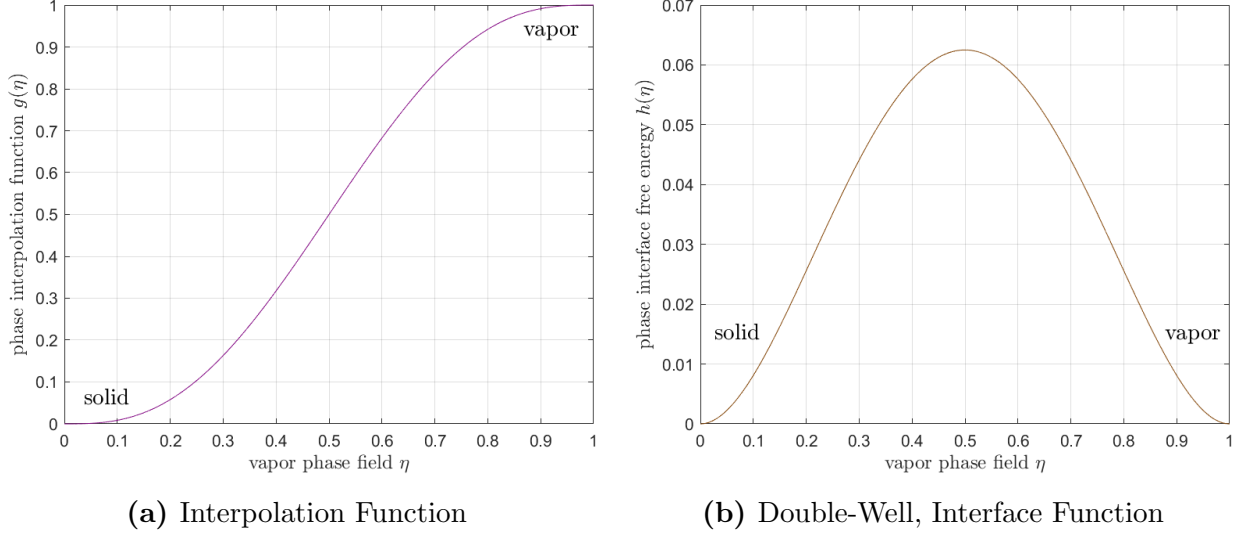


Figure 2.25: Phase Interpolation and Interface Functions

phase interface free energy. First, we introduce two functions that act on the vapor phase field η [2]. The phase interpolation function g is given by

$$g(\eta) := \eta^3 (6\eta^2 - 15\eta + 10), \quad (2.93)$$

and it appears in Figure 2.25a. For solid regions, $\eta = 0$, and, likewise, $g = 0$. For vapor regions, $\eta = 1$, and, so, $g = 1$. The phase interpolation function g acts like a switch to apply the energy density for the solid phase in the solid areas and the energy density for the vapor phase in vapor areas. In the phase interface region, g provides a smooth transition between these two energies. In fact, $g'(0) = g'(1) = 0$. Note also that g is nonnegative on the closed interval $[0, 1]$. We next define a nonnegative phase interface free energy function

$$h(\eta) := \eta^2 (\eta - 1)^2 = \eta^4 - 2\eta^3 + \eta^2. \quad (2.94)$$

This double-well function is shown in Figure 2.25b. Note that $h = 0$ for both the solid phase and for the vapor phase. In addition, h has a local maximum at $\eta = \frac{1}{2}$, and $h'(0) = h'(\frac{1}{2}) = h'(1) = 0$.

Now, we recall the multimode PFC free energy density from (2.68):

$$\begin{aligned} f_{mmpfc}(\psi, \Delta\psi, \dots, \Delta^8\psi) &:= \frac{\chi_4}{4}\psi^4 + \frac{\chi_3}{3}\psi^3 + \frac{\epsilon}{2}\psi^2 + \frac{\lambda}{2}\psi C\psi \\ &= \frac{\chi_4}{4}\psi^4 + \frac{\chi_3}{3}\psi^3 + \frac{\epsilon}{2}\psi^2 + \frac{\lambda}{2}\psi \left(\sum_{i=0}^8 c_i \Delta^i \right) \psi. \end{aligned} \quad (2.95)$$

This energy density corresponds to the solid phase. We next define the vapor phase free energy density to be [22]

$$f_{vap}(\psi) := \frac{b_v}{2}(\psi - \psi_v)^2 + \Delta_v. \quad (2.96)$$

Hence, this vapor phase energy density is parabolic with an absolute minimum at the parameter ψ_v . The vapor phase equilibrium free energy is Δ_v . Finally, the parameter b_v controls the width of the vapor phase free energy density parabola. Note that this vapor phase free energy density yields a homogeneous free energy. The mass density field is constant throughout a given vapor region.

The third free energy density is that of the phase interface [22]:

$$f_{int}(\eta) := W_v h(\eta) + \frac{\kappa_v}{2} |\nabla \eta|^2. \quad (2.97)$$

The first term, $W_v h(\eta)$, is greatest when $\eta = \frac{1}{2}$. Indeed, due to this term, greater phase interface widths result in higher free energies. Since the system strives for low free energy, the term $W_v h(\eta)$ causes the phase interface to be narrow. Now, the second term, $\frac{\kappa_v}{2} |\nabla \eta|^2$ does the opposite. Because of this second term, the free energy is greatest when the gradient of the vapor phase field η is greatest. Hence, the $\frac{\kappa_v}{2} |\nabla \eta|^2$ term acts to widen the phase interface. The two terms of $f_{int}(\eta)$ work against each other to establish the phase interface width and shape with the lowest free energy. Of course, this phase interface free energy also battles against the solid and vapor phase free energies of (2.95) and (2.96), respectively.

We now add the three free energy functionals, while employing the phase interpolation function g , to complete the **multimode PFC with vapor phase field free energy**

functional:

$$\begin{aligned} \mathcal{F}(t; \psi, \eta) := & \int_{\Omega} \left[g(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v \right\} \right. \\ & + (1 - g(\eta)) \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi C \psi \right\} \\ & \left. + W_v h(\eta) + \frac{\kappa_v}{2} |\nabla \eta|^2 \right] d\mathbf{x}. \end{aligned} \quad (2.98)$$

Note that the solid-vapor explicit phase interface free energy functional is

$$\mathcal{F}_{int}(t; \eta) := \int_{\Omega} \left\{ W_v h(\eta) + \frac{\kappa_v}{2} |\nabla \eta|^2 \right\} d\mathbf{x}. \quad (2.99)$$

We prepare to find the variational derivatives $\frac{\delta \mathcal{F}}{\delta \psi}$ and $\frac{\delta \mathcal{F}}{\delta \eta}$ to define the PDE's. Note that

$$\frac{\kappa_v}{2} |\nabla \eta|^2 = \frac{\kappa_v}{2} \nabla \eta \cdot \nabla \eta. \quad (2.100)$$

Then, by Green's first identity for periodic functions (C.4),

$$\int_{\Omega} \frac{\kappa_v}{2} |\nabla \eta|^2 d\mathbf{x} = \int_{\Omega} -\frac{\kappa_v}{2} \eta \Delta \eta d\mathbf{x}. \quad (2.101)$$

Hence, (2.98) is equivalent to

$$\begin{aligned} \mathcal{F}(t; \psi, \eta) := & \int_{\Omega} \left[g(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v \right\} \right. \\ & + (1 - g(\eta)) \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi C \psi \right\} \\ & \left. + W_v h(\eta) - \frac{\kappa_v}{2} \eta \Delta \eta \right] d\mathbf{x}. \end{aligned} \quad (2.102)$$

We define the multimode PFC with vapor phase free energy density to be

$$\begin{aligned}
f(\psi, \Delta\psi, \dots, \Delta^8\psi, \eta, \Delta\eta) &:= g(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v \right\} \\
&+ (1 - g(\eta)) \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi C \psi \right\} \\
&+ W_v h(\eta) - \frac{\kappa_v}{2} \eta \Delta\eta, \quad (2.103)
\end{aligned}$$

or, equivalently,

$$\begin{aligned}
f(\psi, \Delta\psi, \dots, \Delta^8\psi, \eta, \Delta\eta) &:= g(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v \right\} \\
&+ (1 - g(\eta)) \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi \left(\sum_{i=0}^8 c_i \Delta^i \right) \psi \right\} \\
&+ W_v h(\eta) - \frac{\kappa_v}{2} \eta \Delta\eta. \quad (2.104)
\end{aligned}$$

By Corollary E.4, we have a raw form of the variational derivative of the functional $\mathcal{F}$ with respect to the mass density field ψ :

$$\begin{aligned}
\frac{\delta \mathcal{F}}{\delta \psi} &= g(\eta) \{b_v (\psi - \psi_v)\} \\
&+ (1 - g(\eta)) \{ \chi_4 \psi^3 + \chi_3 \psi^2 + \epsilon \psi \} \\
&+ \sum_{i=1}^8 \left\{ (\Delta^i \psi) \left(\frac{\lambda}{2} c_i (1 - g(\eta)) \right) + \Delta^i \left[\frac{\lambda}{2} c_i (1 - g(\eta)) \psi \right] \right\}. \quad (2.105)
\end{aligned}$$

Next, we reestablish the C linear differential operator. We have

$$\begin{aligned}
\frac{\delta \mathcal{F}}{\delta \psi} &= g(\eta) \{b_v (\psi - \psi_v)\} \\
&+ (1 - g(\eta)) \{ \chi_4 \psi^3 + \chi_3 \psi^2 + \epsilon \psi \} \\
&+ \frac{\lambda}{2} \left\{ (1 - g(\eta)) \sum_{i=1}^8 c_i \Delta^i \psi + \sum_{i=1}^8 c_i \Delta^i [(1 - g(\eta)) \psi] \right\}, \quad (2.106)
\end{aligned}$$

and, so,

$$\begin{aligned}
\frac{\delta \mathcal{F}}{\delta \psi} &= g(\eta) \{b_v (\psi - \psi_v)\} \\
&\quad + (1 - g(\eta)) \{ \chi_4 \psi^3 + \chi_3 \psi^2 + \epsilon \psi \} \\
&\quad + \frac{\lambda}{2} \{ (1 - g(\eta)) C \psi + C [(1 - g(\eta)) \psi] \}. \quad (2.107)
\end{aligned}$$

We collect the terms with the linear operator C to arrive at

$$\begin{aligned}
\frac{\delta \mathcal{F}}{\delta \psi} &= g(\eta) \{b_v (\psi - \psi_v)\} \\
&\quad + (1 - g(\eta)) \{ \chi_4 \psi^3 + \chi_3 \psi^2 + \epsilon \psi \} \\
&\quad + \lambda C \psi - \frac{\lambda}{2} \{ g(\eta) C \psi + C [g(\eta) \psi] \}. \quad (2.108)
\end{aligned}$$

We gather the terms based on the $g(\eta)$ multiplier to find the final form for the variational derivative of the functional $\mathcal{F}$ with respect to the mass density field ψ :

$$\begin{aligned}
\frac{\delta \mathcal{F}}{\delta \psi} &= \chi_4 \psi^3 + \chi_3 \psi^2 + \epsilon \psi + \lambda C \psi \\
&\quad + g(\eta) \left\{ b_v (\psi - \psi_v) - \chi_4 \psi^3 - \chi_3 \psi^2 - \epsilon \psi - \frac{\lambda}{2} C \psi \right\} \\
&\quad - \frac{\lambda}{2} C [g(\eta) \psi]. \quad (2.109)
\end{aligned}$$

We assign the time derivative of the mass density to the Laplacian of this variational derivative to conserve mass density:

$$\dot{\psi} := \Delta \frac{\delta \mathcal{F}}{\delta \psi}. \quad (2.110)$$

Therefore, the **multimode PFC with vapor partial differential equation (PDE) for the mass density field** is

$$\begin{aligned} \dot{\psi} = \Delta \Bigg[& \chi_4 \psi^3 + \chi_3 \psi^2 + \epsilon \psi + \lambda C \psi \\ & + g(\eta) \left\{ b_v (\psi - \psi_v) - \chi_4 \psi^3 - \chi_3 \psi^2 - \epsilon \psi - \frac{\lambda}{2} C \psi \right\} \\ & - \frac{\lambda}{2} C [g(\eta) \psi] \Bigg]. \quad (2.111) \end{aligned}$$

which is an 18th order PDE.

We now find the variational derivative of $\mathcal{F}$ with respect to the vapor phase field η . We again employ Corollary E.4 to find that

$$\begin{aligned} \frac{\delta \mathcal{F}}{\delta \eta} = & \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v \right\} g'(\eta) \\ & + \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi C \psi \right\} (-g'(\eta)) \\ & + W_v h'(\eta) - \frac{\kappa_v}{2} \Delta \eta - \frac{\kappa_v}{2} \Delta \eta. \quad (2.112) \end{aligned}$$

Collecting the terms by the multiple $g'(\eta)$ gives us the final form:

$$\begin{aligned} \frac{\delta \mathcal{F}}{\delta \eta} = g'(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v - \frac{\chi_4}{4} \psi^4 - \frac{\chi_3}{3} \psi^3 - \frac{\epsilon}{2} \psi^2 - \frac{\lambda}{2} \psi C \psi \right\} \\ + W_v h'(\eta) - \kappa_v \Delta \eta. \quad (2.113) \end{aligned}$$

To guarantee nonincreasing free energy, we define the time derivative of the vapor phase field as the negative of the variational derivative for the vapor phase field. We also multiply the variational derivative by the mobility constant M_v . The result is

$$\dot{\eta} := -M_v \frac{\delta \mathcal{F}}{\delta \eta}. \quad (2.114)$$

Note that the vapor phase field is not conserved. Hence, the **multimode PFC with vapor partial differential equation (PDE) for the vapor phase field** is

$$\dot{\eta} = -M_v \left[g'(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v - \frac{\chi_4}{4} \psi^4 - \frac{\chi_3}{3} \psi^3 - \frac{\epsilon}{2} \psi^2 - \frac{\lambda}{2} \psi C \psi \right\} + W_v h'(\eta) - \kappa_v \Delta \eta \right]. \quad (2.115)$$

which is a 16th order PDE.

In summary, the **multimode phase field crystal (PFC) with vapor equations** are

$$\begin{aligned} \mathcal{F}(t; \psi, \eta) := & \int_{\Omega} \left[g(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v \right\} \right. \\ & + (1 - g(\eta)) \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi C \psi \right\} \\ & \left. + W_v h(\eta) + \frac{\kappa_v}{2} |\nabla \eta|^2 \right] d\mathbf{x}, \quad (2.116) \end{aligned}$$

$$\begin{aligned} \dot{\psi} = \Delta \left[& \chi_4 \psi^3 + \chi_3 \psi^2 + \epsilon \psi + \lambda C \psi \right. \\ & + g(\eta) \left\{ b_v (\psi - \psi_v) - \chi_4 \psi^3 - \chi_3 \psi^2 - \epsilon \psi - \frac{\lambda}{2} C \psi \right\} \\ & \left. - \frac{\lambda}{2} C [g(\eta) \psi] \right], \quad (2.117) \end{aligned}$$

and

$$\begin{aligned} \dot{\eta} = -M_v \left[& g'(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v - \frac{\chi_4}{4} \psi^4 - \frac{\chi_3}{3} \psi^3 - \frac{\epsilon}{2} \psi^2 - \frac{\lambda}{2} \psi C \psi \right\} \right. \\ & \left. + W_v h'(\eta) - \kappa_v \Delta \eta \right]. \quad (2.118) \end{aligned}$$

2.4.3 MMPFC with Vapor Mass Conservation and Nonincreasing Energy

We repeat the proof for the mass density conservation of the multimode PFC model of Subsection 2.3.3 for the multimode PFC with vapor model. However, the vapor phase field is not conserved. We also prove that the free energy is nonincreasing.

By Leibniz's rule and (2.110), we have

$$\frac{d}{dt} \int_{\Omega} \psi \, d\mathbf{x} = \int_{\Omega} \dot{\psi} \, d\mathbf{x} \quad (2.119)$$

and

$$\frac{d}{dt} \int_{\Omega} \psi \, d\mathbf{x} = \int_{\Omega} \Delta \frac{\delta \mathcal{F}}{\delta \psi} \, d\mathbf{x} = \int_{\Omega} 1 \cdot \Delta \frac{\delta \mathcal{F}}{\delta \psi} \, d\mathbf{x}, \quad (2.120)$$

respectively. By Green's first identity for periodic functions (C.4),

$$\frac{d}{dt} \int_{\Omega} \psi \, d\mathbf{x} = - \int_{\Omega} \nabla 1 \cdot \nabla \frac{\delta \mathcal{F}}{\delta \psi} \, d\mathbf{x}. \quad (2.121)$$

Because $\nabla 1 = \mathbf{0}$,

$$\frac{d}{dt} \int_{\Omega} \psi \, d\mathbf{x} = 0 \quad (2.122)$$

for all $t \in \mathbb{R}^+$.

To prove that the free energy is nonincreasing, we first use Corollary E.6 and the linearity of integration to find that

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \frac{\delta \mathcal{F}}{\delta \psi} \dot{\psi} + \frac{\delta \mathcal{F}}{\delta \eta} \dot{\eta} \right\} \, d\mathbf{x} = \int_{\Omega} \frac{\delta \mathcal{F}}{\delta \psi} \dot{\psi} \, d\mathbf{x} + \int_{\Omega} \frac{\delta \mathcal{F}}{\delta \eta} \dot{\eta} \, d\mathbf{x}. \quad (2.123)$$

By (2.110) and (2.114), we have

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \frac{\delta \mathcal{F}}{\delta \psi} \Delta \frac{\delta \mathcal{F}}{\delta \psi} \, d\mathbf{x} + \int_{\Omega} \frac{\delta \mathcal{F}}{\delta \eta} \left(-M_v \frac{\delta \mathcal{F}}{\delta \eta} \right) \, d\mathbf{x}. \quad (2.124)$$

Applying Green's first identity for periodic functions (C.4) to the first integral and rearranging the second yields

$$\frac{d\mathcal{F}}{dt} = - \int_{\Omega} \nabla \frac{\delta\mathcal{F}}{\delta\psi} \cdot \nabla \frac{\delta\mathcal{F}}{\delta\psi} d\mathbf{x} - M_v \int_{\Omega} \left(\frac{\delta\mathcal{F}}{\delta\eta} \right)^2 d\mathbf{x}, \quad (2.125)$$

and, so,

$$\frac{d\mathcal{F}}{dt} = - \int_{\Omega} \left| \nabla \frac{\delta\mathcal{F}}{\delta\psi} \right|^2 d\mathbf{x} - M_v \int_{\Omega} \left(\frac{\delta\mathcal{F}}{\delta\eta} \right)^2 d\mathbf{x}. \quad (2.126)$$

Since

$$\left| \nabla \frac{\delta\mathcal{F}}{\delta\psi} \right|^2 \geq 0,$$

and

$$\left(\frac{\delta\mathcal{F}}{\delta\eta} \right)^2 \geq 0$$

for all $t \in \mathbb{R}^+$ and all $\mathbf{x} \in \mathbb{R}^2$,

$$\frac{d\mathcal{F}}{dt} \leq 0 \quad (2.127)$$

for all t .

2.4.4 Multimode PFC with Vapor Simulations

We present two simulations for the multimode PFC with vapor model. For each simulation, we begin with a solid disk in the center of the computational box. The remainder of the box contains vapor. Note that the mass density is initially constant in the vapor region. For both simulations, the initial solid mean mass density is $\mu_s = -0.171$, and the initial vapor mass density is $\mu_v = -0.215$. The initial solid mean mass density is similar to the solid equilibrium mean mass density of $\mu_{seq} := -0.16894892$ from Section 2.5. However, the initial vapor mass density is notably higher than the vapor equilibrium mass density of $\mu_{veq} := -0.22990548$ from the same section. During each simulation, as the free energy decreases, the mass densities of both phases approach their respective equilibria. Since mass is conserved, the solid region must increase in area; that is, the nanocrystal grows over time.

We use the phase interface parameter values $W_v = 0.1$ and $\kappa = 0.4455$ for both simulations. We study the effect of these parameters on the size and shape of nanocrystals

in Chapter 4. In addition, this chapter discusses the nanocrystal facets that form for the multimode PFC model honeycomb geometry.

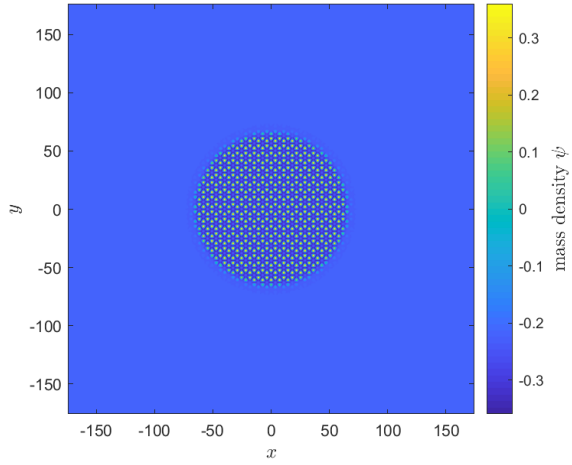
2.4.4.1 Disk Seed

For this first simulation, the mass density of the initial disk seed forms honeycomb geometry. Figure 2.26a provides the initial mass density field, while Figure 2.26c presents the mass density at time 1,000. We can see that the nanocrystal is larger at time 1,000. In addition, the sides of the nanocrystal are flatter. More clearly defined facets are forming over time. In our computations, the system reaches an equilibrium at time 23,000. Figure 2.26e yields the mass density field at the equilibrium point and reveals that the nanocrystal is significantly larger at the end of the simulation. The nanocrystal forms a dodecagon with relatively flat sides. In addition, Figures 2.26b, 2.26d, and 2.26f provide the vapor phase fields for times 0, 1,000, and 23,000, respectively. The solid region appears in blue and the vapor is in yellow.

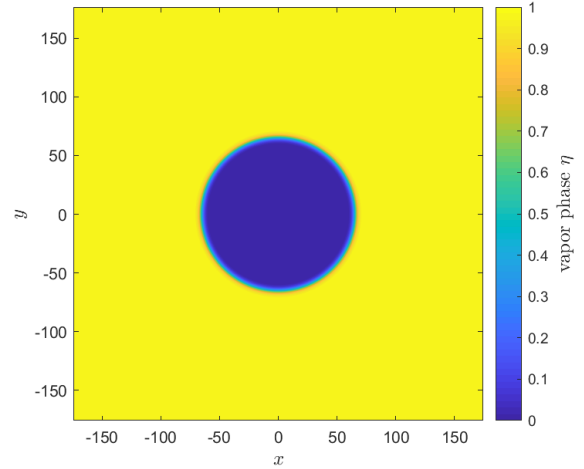
Finally, Figures 2.27a, 2.27b, and 2.27c display the Fourier space spectrums for the times 0, 1,000, and 23,000, respectively. The changes in the spectrum are subtle. First, in each spectrum, we find the same nine dominant angular frequencies that we detail in Subsection 2.3.4. However, there are halos around the corresponding points. These variations in the dominant angular frequencies are a result of the phase interface. Now, as the nanocrystal grows, the corresponding wavelengths increase. Hence, the variations in angular frequencies decrease. Indeed, we see that the variations in the angular frequencies in Figure 2.27c are lesser than those in Figures 2.27a and 2.27b.

2.4.4.2 Random Disk Seed

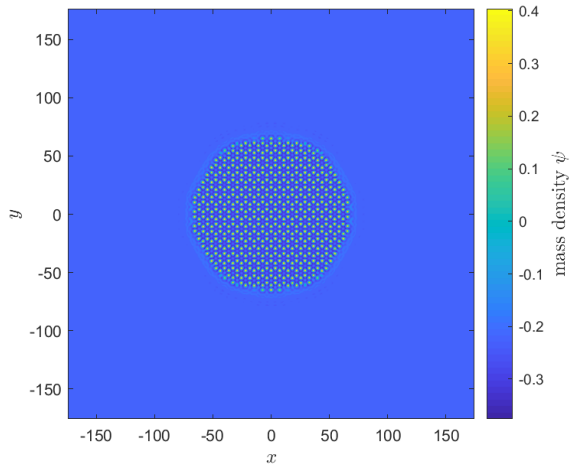
Next, we begin with a uniformly random disk seed. Figures 2.28a provides the initial mass density field, while Figure 2.28c reveals the mass density at time 1,000. By time 1,000, the honeycomb geometry prevails, but a number of irregularities remain. The system reaches its equilibrium by time 150,000. The corresponding mass density field appears in Figure 2.28e. There is one grain boundary, which runs horizontally across the nanocrystal. The orientation of the honeycomb geometry of the top of the nanocrystal is different from that of the bottom. Note that these top and bottom halves each form parts of a dodecagon. Again,



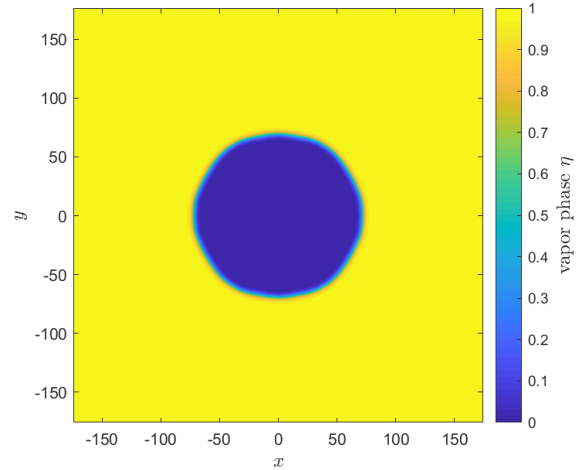
(a) Mass Density, Initial, Time = 0



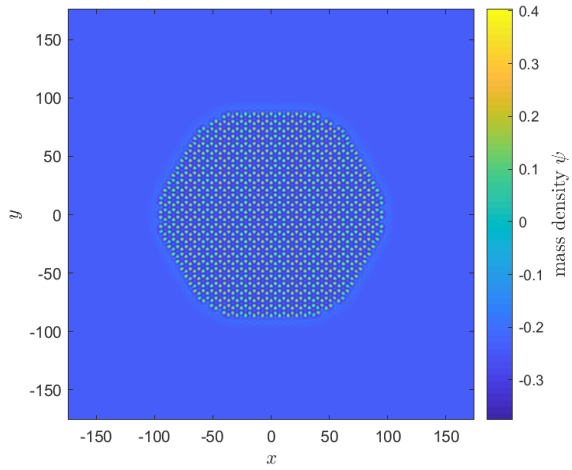
(b) Vapor Phase, Initial, Time = 0



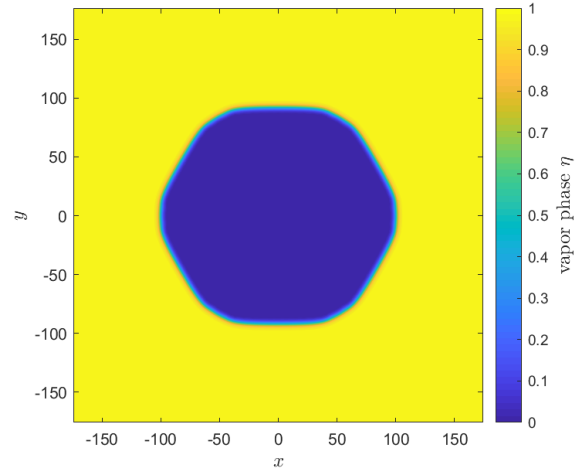
(c) Mass Density, Time = 1,000



(d) Vapor Phase, Time = 1,000

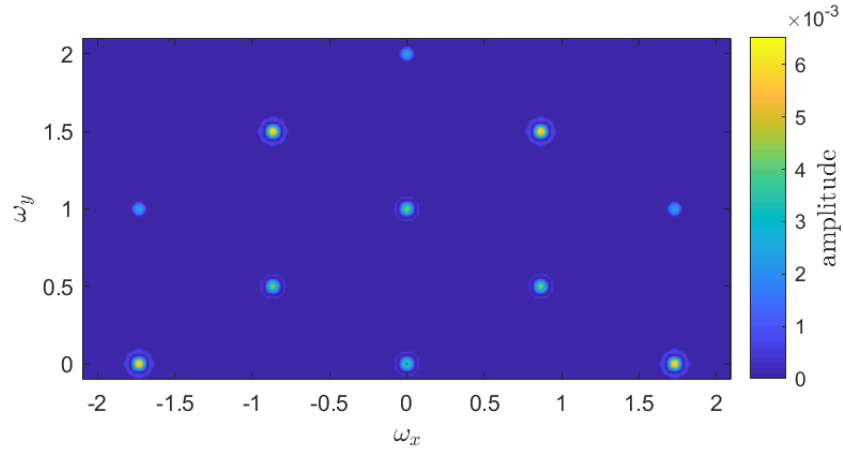


(e) Mass Density, Equil., Time = 23,000

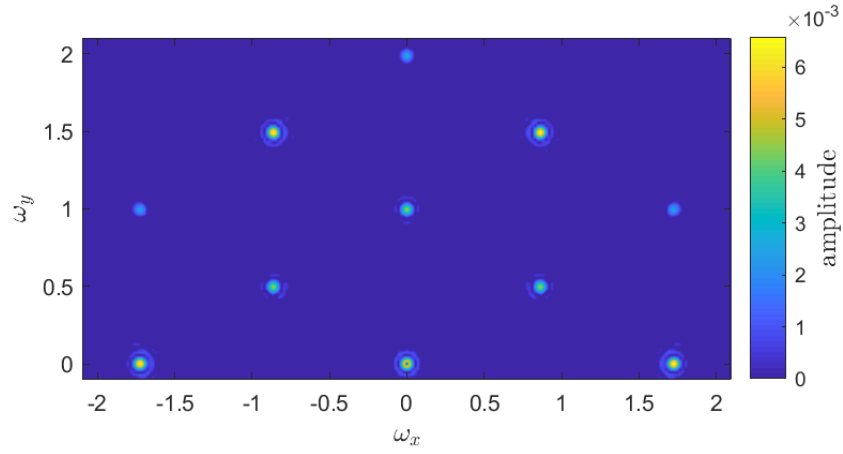


(f) Vapor Phase, Equil., Time = 23,000

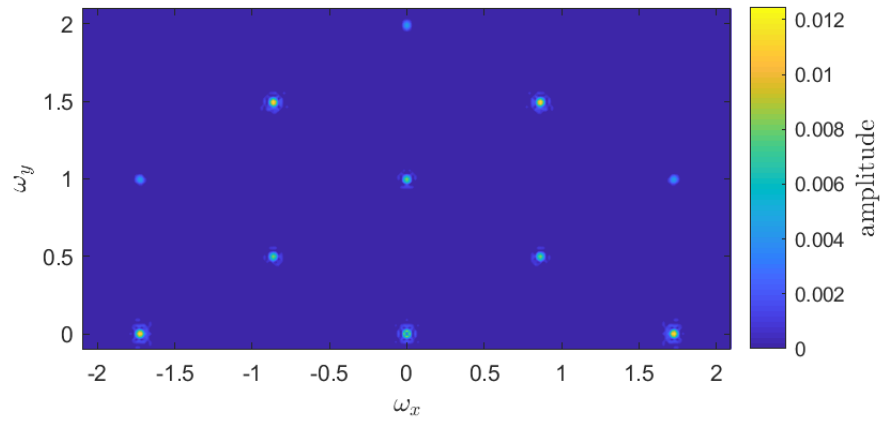
Figure 2.26: Multimode PFC, Vapor, Honeycomb Disk, Mass Density and Phase Fields



(a) Initial, Time = 0



(b) Time = 1000



(c) Equilibrium, Time = 23,000

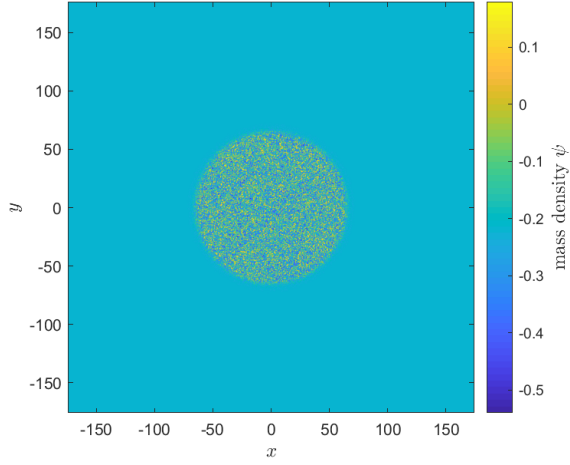
Figure 2.27: Multimode PFC, Vapor, Honeycomb Disk, Fourier Space Spectrums

we see that the nanocrystal grows over time. Note the similarity between the nanocrystal areas in Figures 2.26e and 2.28e. For reference, Figures 2.28b, 2.28d, and 2.28f reveal the vapor phase fields for times 0, 1,000, and 150,000, respectively.

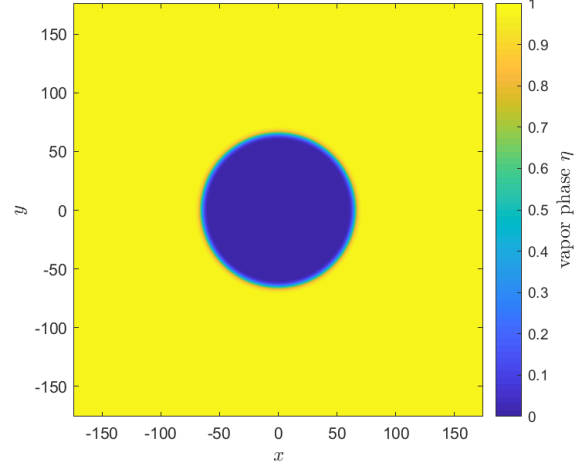
Finally, Figures 2.29a, 2.29b, and 2.29c offer the Fourier space spectrums for the times 0, 1,000, and 150,000, respectively. The vapor region has a constant mass density. This constant portion of the mass density field results in an angular frequency component of 0. The random disk seed produces many angular frequency components, but they are of lesser amplitude. The overall result is the angular frequency variations around 0 in Figure 2.29a. At time 1,000, Figure 2.29b indicates that the angular frequency components form arcs with angular frequency radii of 1, $\sqrt{3}$, and 2. The pattern for each arc repeats every 60° degrees. In fact, we can see three dominant triplets for each of the radii 1 and $\sqrt{3}$. Examining the nanocrystal of Figure 2.28c, we find that there are indeed three honeycomb geometry orientations. The orientation of the top half of the nanocrystal covers the greatest area. The orientation of the bottom middle and the orientation of the bottom right each cover areas of similar size. Finally, Figure 2.29c shows the Fourier space spectrum for the equilibrium point. Now, Figure 2.28e exhibits two honeycomb geometry orientations within the nanocrystal. Congruently, Figure 2.29c indicates that, for each of the radii 1, $\sqrt{3}$, and 2, there are two sets of triplets. Comparing the spectrums of Figures 2.29b and 2.29c, we find that the dominant frequency components form sharper points at the system equilibrium. At this time, there are fewer irregularities in the geometry, and the larger nanocrystal area results in smaller frequency variations.

2.5 Phase Equilibrium Free Energies

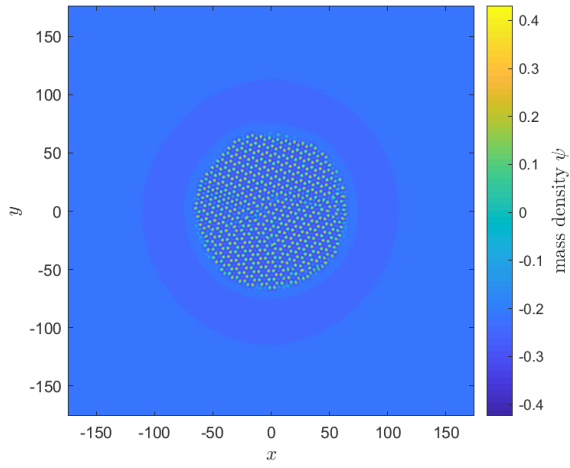
The diagrams in Figures 2.30a and 2.30b indicate the phase equilibrium energies for the multimode PFC with vapor model. The x -axis represents the mean mass density, while the y -axis is the equilibrium mean free energy. Hence, the units are mass density per unit area and free energy per unit area, respectively. Given a particular mean mass density and a particular phase, the corresponding phase equilibrium free energy is the mean free energy of the system after an infinite amount of time has passed.



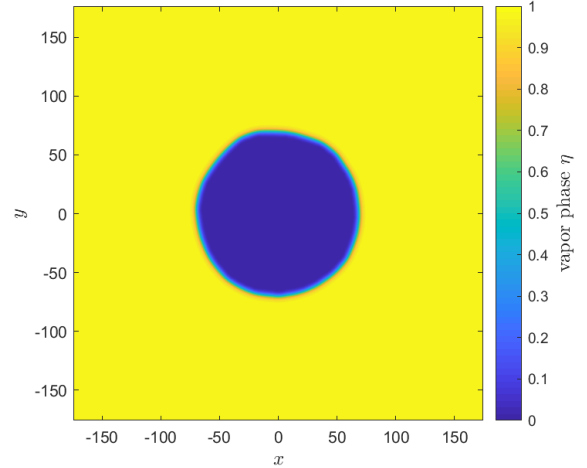
(a) Mass Density, Initial, Time = 0



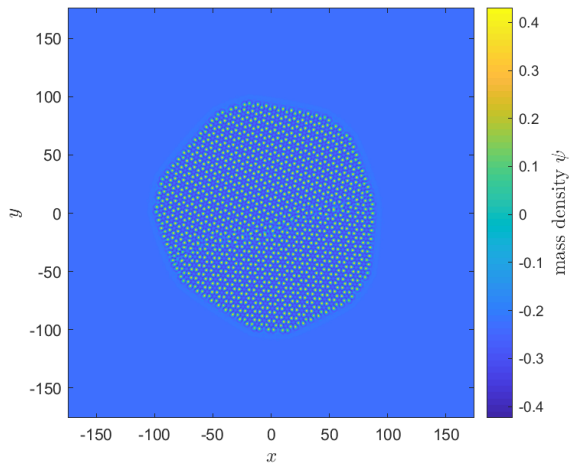
(b) Vapor Phase, Initial, Time = 0



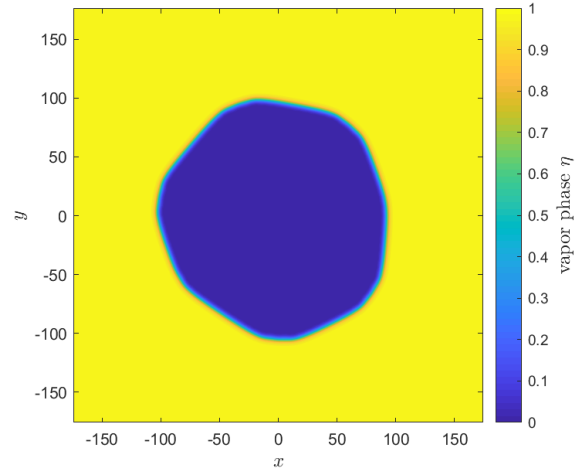
(c) Mass Density, Time = 1,000



(d) Vapor Phase, Time = 1,000

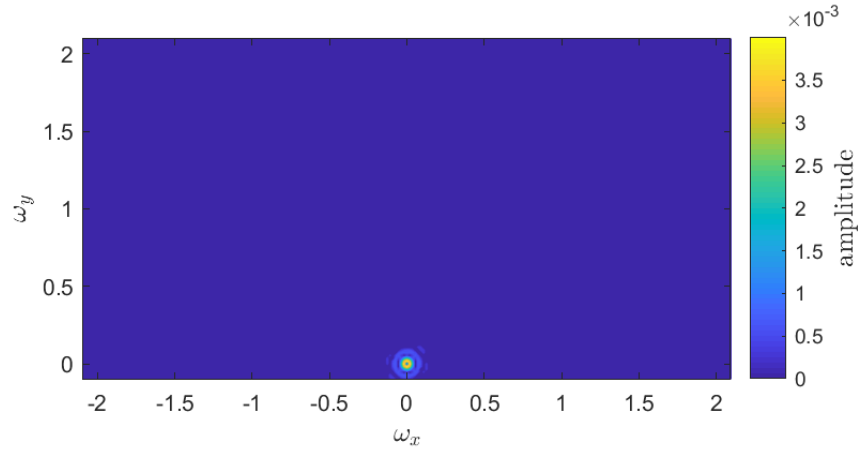


(e) Mass Density, Equil., Time = 150,000

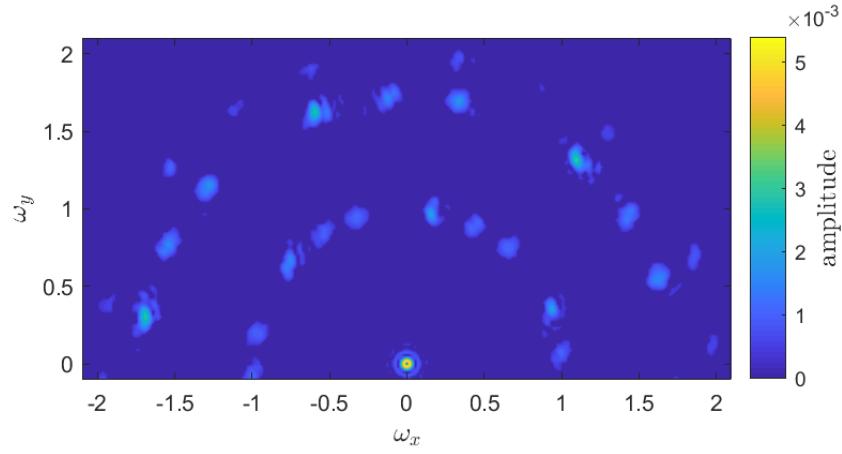


(f) Vapor Phase, Equil., Time = 150,000

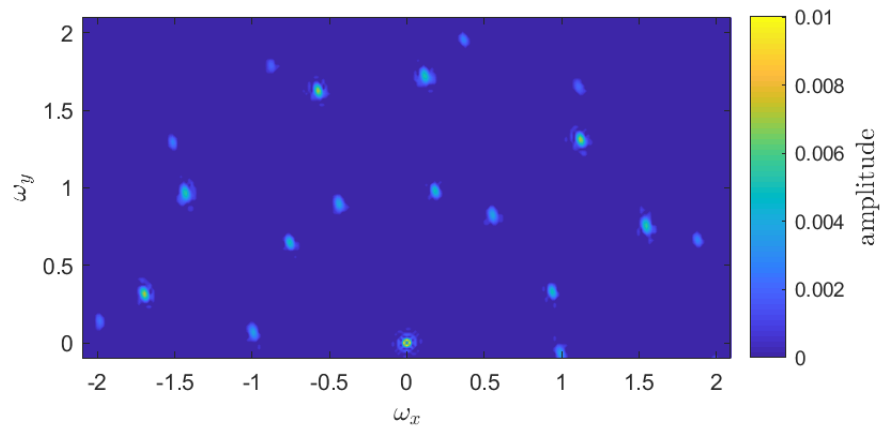
Figure 2.28: Multimode PFC, Vapor, Random Disk, Mass Density and Phase Fields



(a) Initial, Time = 0

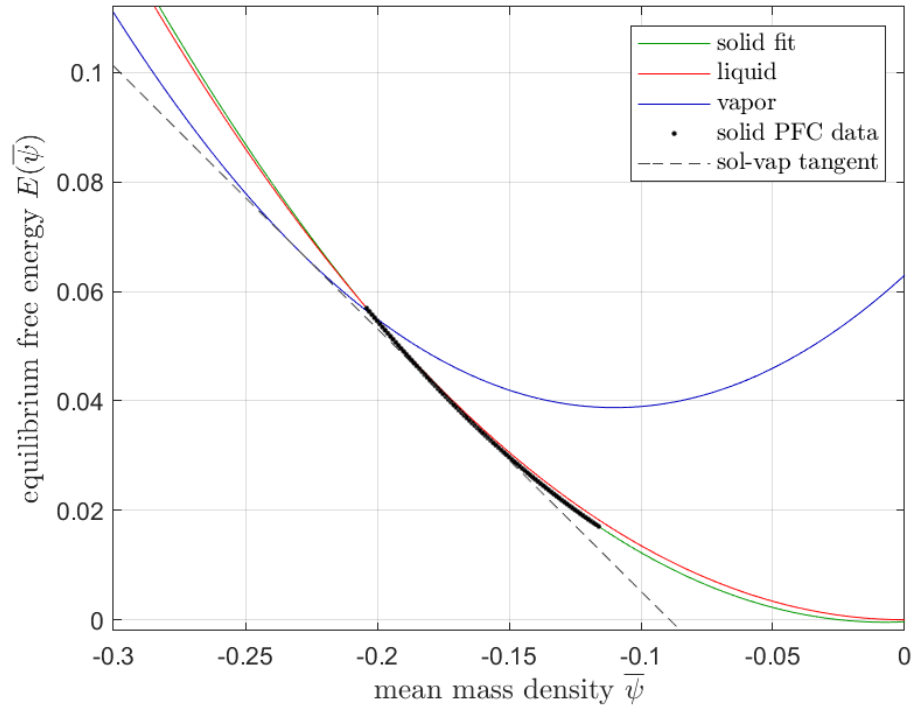


(b) Time = 1,000

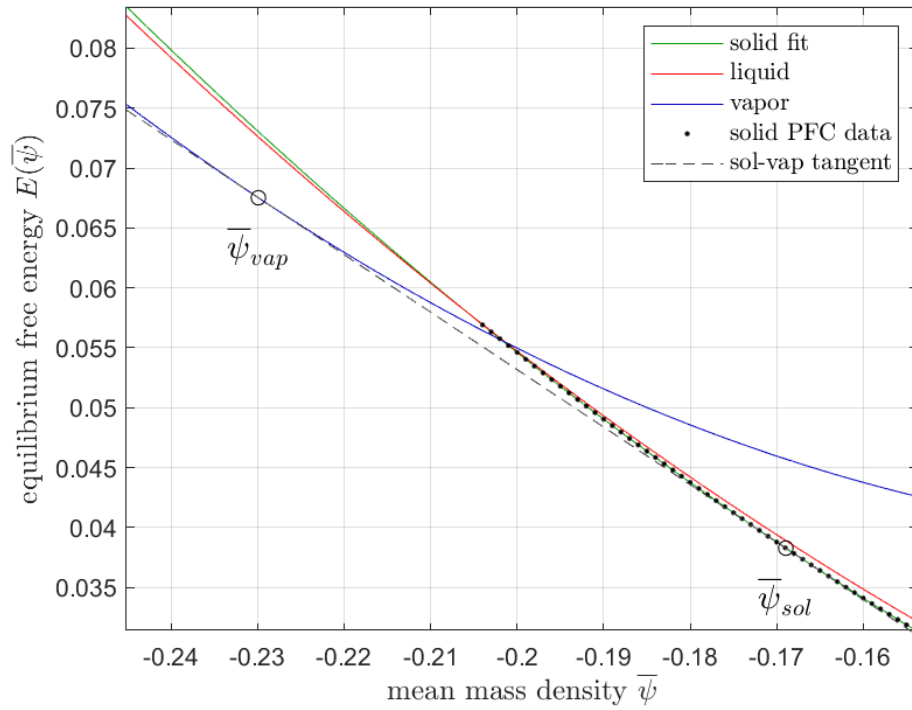


(c) Equilibrium, Time = 150,000

Figure 2.29: Multimode PFC, Vapor, Random Disk, Fourier Space Spectrums



(a) Full View



(b) Detailed View of Common Tangent Line

Figure 2.30: Phase Equilibrium Free Energies with Solid-Vapor Common Tangent Line

The blue vapor phase curve is given by the quadratic vapor energy density

$$f_{vap}(\psi) := \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v. \quad (2.128)$$

The red liquid phase curve is found by inserting a spatially constant mass density field into the expression

$$f_{sol.liq}(\psi) = \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi(C\psi). \quad (2.129)$$

The Laplacian terms vanish resulting in the quartic polynomial

$$f_{liq}(\psi) = \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon + \lambda c_0}{2} \psi^2. \quad (2.130)$$

Note from Figure 2.30b that the liquid phase is not energetically stable.

There is no straightforward way to find an explicit expression for the solid equilibrium free energy curve. Therefore, simulations are performed for crystal mass density fields with different mean mass densities. Each simulation is run until the system reaches a minimum free energy state. The dots in Figures 2.30a and 2.30b represent the simulation results. The green curve is a quadratic curve fit for the simulation data:

$$f_{sol}(\bar{\psi}) \approx 1.48468022876 \bar{\psi}^2 + 0.0220483276544 \bar{\psi} - 0.000366434921169. \quad (2.131)$$

However, the honeycomb geometry becomes unstable outside the mean densities of the dotted data.

We express points in the diagrams of Figures 2.30a and 2.30b as ordered pairs. The form is $(\bar{\psi}, E)$, where $\bar{\psi}$ is the mean mass density and E is the corresponding equilibrium mean free energy. For reference, the vapor equilibrium mass density and free energy is given by the parameters ψ_v and Δ_v to be $(-0.11, 0.0387683)$. For the liquid phase, the equilibrium occurs at $(0, 0)$. We extrapolate to find an equilibrium mean mass density and the corresponding mean free energy for the solid phase. The result is

$$(-0.00742527826104, -0.000448292405181).$$

The dashed line is the common tangent line for the solid and vapor phases. This line provides the equilibrium mean free energy for cases where both solid and vapor are present. The solid-vapor common tangent line touches the vapor energy curve at

$$(-0.229905476582, 0.0675229466288)$$

and the solid curve at

$$(-0.168948917169, 0.0382868454).$$

Hence, the equilibrium mass density for the vapor phase is

$$\mu_{veq} := -0.22990548, \tag{2.132}$$

and the equilibrium mean mass density for the solid phase is

$$\mu_{seq} := -0.16894892. \tag{2.133}$$

It follows that the equation for the solid-vapor tangent line is

$$E = -0.479621906329\bar{\psi} - 0.0427447563249. \tag{2.134}$$

Subsequently, we define the “phase equilibrium free energy” per unit area, E_{equil} , to be

$$E_{equil} := -0.479621906329\bar{\psi} - 0.0427447563249. \tag{2.135}$$

This equilibrium energy is the basis for the surface energy formula of Section 4.4.

Note that the diagrams and formulations in this section do not account for the explicit phase interface free energy of (2.99). Neither do they account for metastable equilibrium states caused by this energy. In these metastable cases, the mean mass densities of the solid and/or vapor regions may never reach their equilibria.

2.6 Radial Distribution Function

For a given field ψ on $\mathbb{R}^2$, point $\mathbf{x}_0 = (x_0, y_0) \in \mathbb{R}^2$, and radius $r \in \mathbb{R}^+$, we define the **radial distribution function (RDF)** to be a real-valued function $g(\psi, \mathbf{x}_0; r)$ that is the integral of the field ψ along the circumference of a circle of radius r centered at $\mathbf{x}_0 = (x_0, y_0)$. We begin with the raw form

$$g_{raw}(\psi, \mathbf{x}_0; r) := \frac{1}{2\pi} \int_0^{2\pi} \psi(x_0 + r \cos(\theta), y_0 + r \sin(\theta)) d\theta. \quad (2.136)$$

The traditional radial distribution function is based on a system containing a finite number of atoms and a mathematical model that tracks the positions of these atoms. Upon choosing one, particular atom, the traditional RDF yields the probability of finding another atom at a distance of r [16]. Our definition (2.136) is an analogue for the probabilistic density fields of the PFC model.

In our studies of purely solid phase fields, the triangular and honeycomb geometries are uniform throughout space. Hence, all atom positions, or density field peak locations, are equivalent. We add the requirement that the density field ψ is positioned so that the origin of the xy -plane is located at the position of an atom. Hence, (2.136) becomes

$$g(r) := \frac{1}{2\pi} \int_0^{2\pi} \psi(r \cos(\theta), r \sin(\theta)) d\theta. \quad (2.137)$$

Since the mass density fields for the PFC model are composed of trigonometric functions, the corresponding radial distribution functions consist of Bessel functions of the first kind with integration orders of 0. In addition, we investigate the Fourier transforms for the RDF's. The Fourier transforms of these Bessel functions produce, in part, the integral of the inverse sine.

2.6.1 Tools for Finding Radial Distribution Functions

Here, we present some important tools for computing radial distribution functions. Firstly, we recall some pertinent trigonometric identities. We have

$$\frac{1}{2} \cos(\theta) + \frac{\sqrt{3}}{2} \sin(\theta) = \sin\left(\frac{\pi}{6}\right) \cos(\theta) + \cos\left(\frac{\pi}{6}\right) \sin(\theta) = \sin\left(\theta + \frac{\pi}{6}\right), \quad (2.138)$$

$$\frac{\sqrt{3}}{2} \cos(\theta) + \frac{1}{2} \sin(\theta) = \sin\left(\frac{\pi}{3}\right) \cos(\theta) + \cos\left(\frac{\pi}{3}\right) \sin(\theta) = \sin\left(\theta + \frac{\pi}{3}\right), \quad (2.139)$$

$$\frac{\sqrt{3}}{2} \cos(\theta) - \frac{1}{2} \sin(\theta) = \sin\left(\frac{2\pi}{3}\right) \cos(\theta) + \cos\left(\frac{2\pi}{3}\right) \sin(\theta) = \sin\left(\theta + \frac{2\pi}{3}\right), \quad (2.140)$$

$$\frac{1}{2} \cos(\theta) - \frac{\sqrt{3}}{2} \sin(\theta) = \sin\left(\frac{5\pi}{6}\right) \cos(\theta) + \cos\left(\frac{5\pi}{6}\right) \sin(\theta) = \sin\left(\theta + \frac{5\pi}{6}\right), \quad (2.141)$$

and

$$\cos(\theta) = \sin\left(\theta + \frac{\pi}{2}\right). \quad (2.142)$$

Next, the Bessel function of the first kind with order 0 is defined by

$$J_0(r) := \frac{1}{2\pi} \int_0^{2\pi} \cos(r \sin(\theta)) d\theta. \quad (2.143)$$

In addition, for all $\phi \in \mathbb{R}$ with $\phi \neq (n + \frac{1}{2})\pi$ for all $n \in \mathbb{Z}$,

$$\cos(\phi) J_0(r) := \frac{1}{2\pi} \int_0^{2\pi} \cos(r \sin(\theta) + \phi) d\theta. \quad (2.144)$$

Lastly, the Fourier transform of the Bessel function of the first kind with order 0 is

$$\hat{J}_0(\omega) := \begin{cases} \frac{2}{\sqrt{1-\omega^2}} & \text{if } 0 \leq \omega < 1 \\ 0 & \text{if } \omega > 1 \end{cases}. \quad (2.145)$$

Furthermore, for all $c > 0$, by the properties of the Fourier transform, we have

$$\mathcal{F}[J_0(cr)](\omega) = \begin{cases} \frac{2}{c\sqrt{1 - \left(\frac{\omega}{c}\right)^2}} & \text{if } 0 \leq \frac{\omega}{c} < 1 \\ 0 & \text{if } \frac{\omega}{c} > 1 \end{cases}, \quad (2.146)$$

or, more simply,

$$\mathcal{F}[J_0(cr)](\omega) = \begin{cases} \frac{2}{\sqrt{c^2 - \omega^2}} & \text{if } 0 \leq \omega < c \\ 0 & \text{if } \omega > c \end{cases}. \quad (2.147)$$

2.6.2 PFC Model Radial Distribution Function

We now find the radial distribution function for the triangular geometry of the single-mode PFC model. The mass density field

$$\psi_{pfc,ans}(x, y) = \cos\left(\frac{\sqrt{3}}{2}x + \frac{1}{2}y\right) + \cos\left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right) + \cos(y) \quad (2.148)$$

is an ansatz, or solution, for the PFC model PDE (2.36). This field appears in Figure 2.31. Note that (2.148) is the same as the field (2.57) from Subsection 2.2.4, except that (2.148) is shifted so that there is a mass density peak at the origin.

The initial form of the PFC model radial distribution function is

$$g_{pfc}(r) := \frac{1}{2\pi} \int_0^{2\pi} \psi_{pfc,ans}(r \cos(\theta), r \sin(\theta)) d\theta. \quad (2.149)$$

Then, by the linearity of integration,

$$\begin{aligned} g_{pfc}(r) = \frac{1}{2\pi} \int_0^{2\pi} \cos\left(\frac{\sqrt{3}}{2}r \cos(\theta) + \frac{1}{2}r \sin(\theta)\right) d\theta \\ + \frac{1}{2\pi} \int_0^{2\pi} \cos\left(\frac{\sqrt{3}}{2}r \cos(\theta) - \frac{1}{2}r \sin(\theta)\right) d\theta \\ + \frac{1}{2\pi} \int_0^{2\pi} \cos(r \sin(\theta)) d\theta. \end{aligned} \quad (2.150)$$

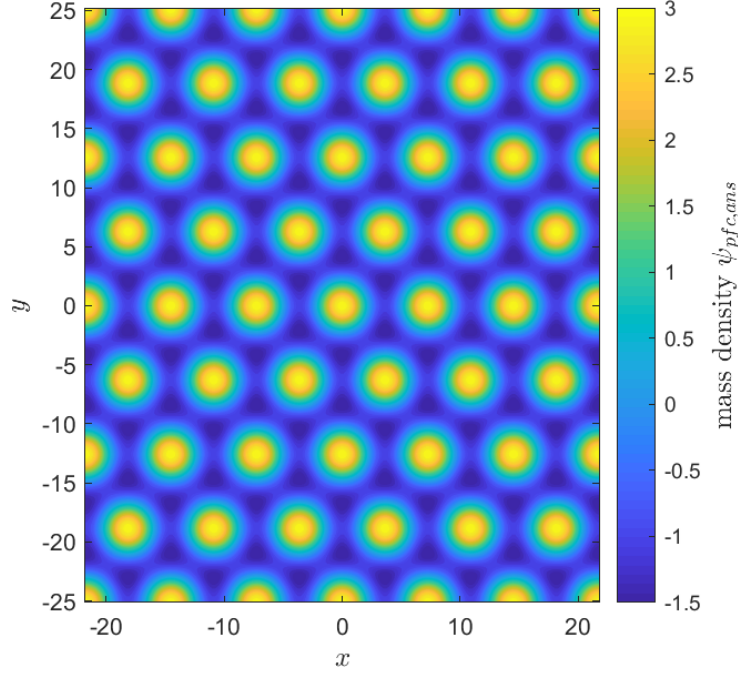


Figure 2.31: PFC Model, Ansatz, Mass Density Field

Factoring out the r within the first two integrals yields

$$\begin{aligned}
 g_{pfc}(r) = & \frac{1}{2\pi} \int_0^{2\pi} \cos \left(r \left[\frac{\sqrt{3}}{2} \cos(\theta) + \frac{1}{2} \sin(\theta) \right] \right) d\theta \\
 & + \frac{1}{2\pi} \int_0^{2\pi} \cos \left(r \left[\frac{\sqrt{3}}{2} \cos(\theta) - \frac{1}{2} \sin(\theta) \right] \right) d\theta \\
 & + \frac{1}{2\pi} \int_0^{2\pi} \cos(r \sin(\theta)) d\theta. \quad (2.151)
 \end{aligned}$$

Applying (2.139) and (2.140), respectively, we have

$$\begin{aligned}
 g_{pfc}(r) = & \frac{1}{2\pi} \int_0^{2\pi} \cos \left(r \sin \left(\theta + \frac{\pi}{3} \right) \right) d\theta \\
 & + \frac{1}{2\pi} \int_0^{2\pi} \cos \left(r \sin \left(\theta + \frac{2\pi}{3} \right) \right) d\theta \\
 & + \frac{1}{2\pi} \int_0^{2\pi} \cos(r \sin(\theta)) d\theta. \quad (2.152)
 \end{aligned}$$

Due to the periodicity of the sine function,

$$\begin{aligned}
g_{pfc}(r) = \frac{1}{2\pi} \int_0^{2\pi} \cos(r \sin(\theta)) d\theta \\
+ \frac{1}{2\pi} \int_0^{2\pi} \cos(r \sin(\theta)) d\theta \\
+ \frac{1}{2\pi} \int_0^{2\pi} \cos(r \sin(\theta)) d\theta. \quad (2.153)
\end{aligned}$$

Therefore, the final form for the **PFC model radial distribution function** is

$$g_{pfc}(r) = \frac{3}{2\pi} \int_0^{2\pi} \cos(r \sin(\theta)) d\theta. \quad (2.154)$$

The value of the scalar multiplier, which is 3 here, is insignificant. Note also that the field $\psi_{pfc,ans}$ is not unique to this radial distribution function. Now, by (2.143),

$$g_{pfc}(r) = 3J_0(r) \quad (2.155)$$

for all $r \in \mathbb{R}^+$. By (2.145), the Fourier transform of g_{pfc} is

$$\widehat{g_{pfc}}(\omega) := \begin{cases} \frac{6}{\sqrt{1-\omega^2}} & \text{if } 0 \leq \omega < 1 \\ 0 & \text{if } \omega > 1 \end{cases}. \quad (2.156)$$

Figure 2.32a displays the radial distribution function for the PFC model. We use the atom, or mass density peak, at the origin in Figure 2.31 as the center point for our analysis. The nearest six atoms form a hexagon, where each atom is a distance of $\frac{4\pi}{\sqrt{3}} \approx 7.255$ from the origin. As we expect, the first peak for the radial distribution function in Figure 2.32a occurs near $r = 7$. Moving outward from the origin, the atoms are arranged in hexagons of increasing size. However, as we increase the RDF input radius r to align with peaks of larger hexagons, high density regions from adjacent polygonal layers have a greater effect on the radial distribution. Indeed, as r increases, the distance between adjacent peaks in the radial distribution function decreases and approaches $2\pi \approx 6.283$. Finally, Figure 2.32b provides

the Fourier transform of the radial distribution function. There is a vertical asymptote at the PFC model dominant angular frequency of 1.

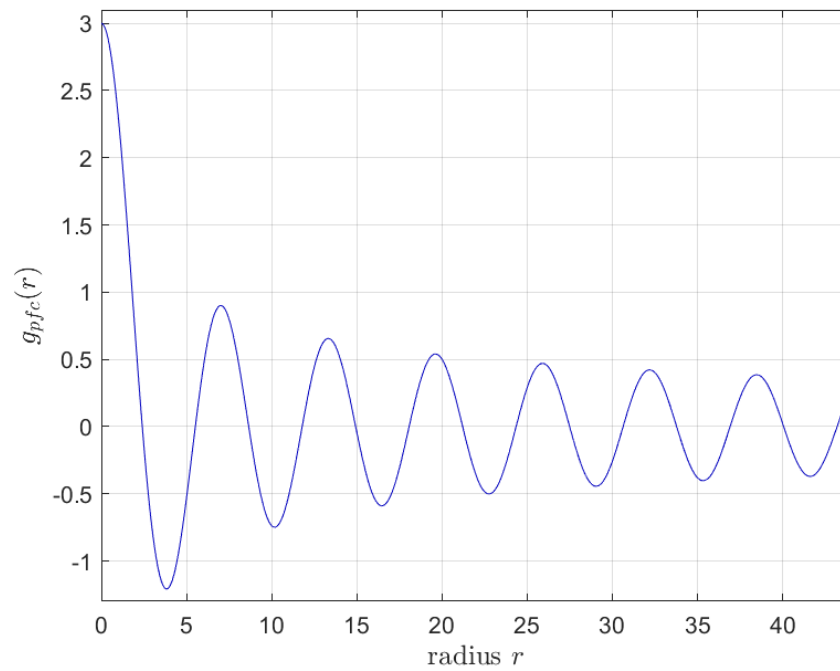
2.6.3 Multimode PFC Radial Distribution Function

We next determine the radial distribution function for the honeycomb geometry of the multimode PFC model. In the frequency analysis of Subsection 2.3.4, we design three component mass density fields, whose sum is the field for the honeycomb geometry of the multimode PFC model. The component fields correspond to the three dominant angular frequencies 1, $\sqrt{3}$, and 2, respectively. Each component field that we define here is the same as the corresponding component field of Subsection 2.3.4, except that, here, each component field is shifted in the same manner so that a mass density peak occurs at the origin of the xy -plane. Due to the complexity of the multimode model, the resulting mass density field given here is actually an approximation of an ansatz for the PDE of (2.71). Regardless, the result here is extremely close to a true ansatz, and, indeed, we refer to this result as such.

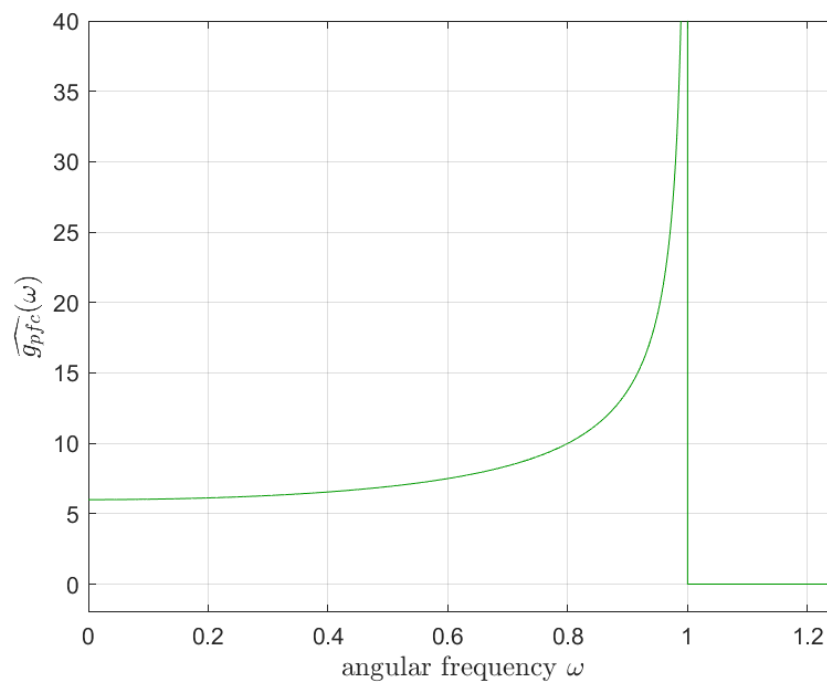
The ansatz component mass density fields for the dominant angular frequencies $\omega_1 = 1$, $\omega_{\sqrt{3}} = \sqrt{3}$, and $\omega_2 = 2$ are

$$\begin{aligned} \psi_{ans,1}(x, y) := \frac{9}{20} \left[\cos \left(\frac{\sqrt{3}}{2}x + \frac{1}{2}y + \frac{\pi}{3} \right) \right. \\ \left. + \cos \left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y + \frac{5\pi}{3} \right) \right. \\ \left. + \cos \left(y + \frac{5\pi}{3} \right) \right], \quad (2.157) \end{aligned}$$

$$\begin{aligned} \psi_{ans,\sqrt{3}}(x, y) := \frac{29}{45} \left[\cos \left(\frac{\sqrt{3}}{2}x + \frac{3}{2}y \right) \right. \\ \left. + \cos \left(\frac{\sqrt{3}}{2}x - \frac{3}{2}y \right) \right. \\ \left. + \cos \left(\sqrt{3}x \right) \right], \quad (2.158) \end{aligned}$$



(a) Radial Distribution Function



(b) Fourier Transform of the Radial Distribution Function

Figure 2.32: PFC Model, Radial Distribution Function and Fourier Transform

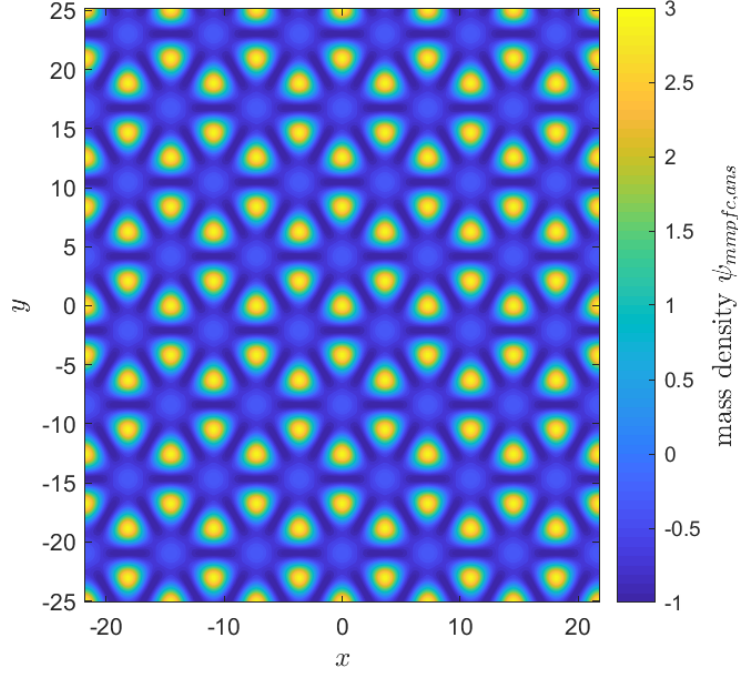


Figure 2.33: Multimode PFC Model, Ansatz, Mass Density Field

and

$$\begin{aligned} \psi_{ans,2}(x, y) := \frac{4}{15} \left[\cos \left(\sqrt{3}x + y + \frac{5\pi}{3} \right) \right. \\ \left. + \cos \left(\sqrt{3}x - y + \frac{\pi}{3} \right) \right. \\ \left. + \cos \left(2y + \frac{\pi}{3} \right) \right], \end{aligned} \quad (2.159)$$

respectively. Hence, the ansatz for the multimode PFC model is

$$\psi_{mmpfc,ans}(x, y) := \psi_{ans,1}(x, y) + \psi_{ans,\sqrt{3}}(x, y) + \psi_{ans,2}(x, y). \quad (2.160)$$

Figure 2.33 displays the ansatz mass density field $\psi_{mmpfc,ans}$.

Now, the initial form for the multimode PFC model radial distribution function is

$$g_{mmpfc}(r) := \frac{1}{2\pi} \int_0^{2\pi} \psi_{mmpfc,ans}(r \cos(\theta), r \sin(\theta)) d\theta. \quad (2.161)$$

By the linearity of integration, we have

$$\begin{aligned}
g_{mmpfc}(r) = & \frac{1}{2\pi} \int_0^{2\pi} \psi_{ans,1}(r \cos(\theta), r \sin(\theta)) d\theta \\
& + \frac{1}{2\pi} \int_0^{2\pi} \psi_{ans,\sqrt{3}}(r \cos(\theta), r \sin(\theta)) d\theta \\
& + \frac{1}{2\pi} \int_0^{2\pi} \psi_{ans,2}(r \cos(\theta), r \sin(\theta)) d\theta. \quad (2.162)
\end{aligned}$$

We define the following component radial distribution functions:

$$g_1(r) := \frac{1}{2\pi} \int_0^{2\pi} \psi_{ans,1}(r \cos(\theta), r \sin(\theta)) d\theta, \quad (2.163)$$

$$g_{\sqrt{3}}(r) := \frac{1}{2\pi} \int_0^{2\pi} \psi_{ans,\sqrt{3}}(r \cos(\theta), r \sin(\theta)) d\theta, \quad (2.164)$$

and

$$g_2(r) := \frac{1}{2\pi} \int_0^{2\pi} \psi_{ans,2}(r \cos(\theta), r \sin(\theta)) d\theta. \quad (2.165)$$

Therefore,

$$g_{mmpfc}(r) = g_1(r) + g_{\sqrt{3}}(r) + g_2(r). \quad (2.166)$$

Next, we determine the expressions for the component RDF's $g_1(r)$, $g_{\sqrt{3}}(r)$, and $g_2(r)$. By the linearity of integration, the radial distribution function for the $\omega_1 = 1$ ansatz field component is

$$\begin{aligned}
g_1(r) := & \frac{9}{40\pi} \int_0^{2\pi} \cos \left(\frac{\sqrt{3}}{2} r \cos(\theta) + \frac{1}{2} r \sin(\theta) + \frac{\pi}{3} \right) d\theta \\
& + \frac{9}{40\pi} \int_0^{2\pi} \cos \left(\frac{\sqrt{3}}{2} r \cos(\theta) - \frac{1}{2} r \sin(\theta) + \frac{5\pi}{3} \right) d\theta \\
& + \frac{9}{40\pi} \int_0^{2\pi} \cos \left(r \sin(\theta) + \frac{5\pi}{3} \right) d\theta. \quad (2.167)
\end{aligned}$$

Factoring out the radius r within the first and second integrands yields

$$\begin{aligned}
g_1(r) := & \frac{9}{40\pi} \int_0^{2\pi} \cos \left(r \left(\frac{\sqrt{3}}{2} \cos(\theta) + \frac{1}{2} \sin(\theta) \right) + \frac{\pi}{3} \right) d\theta \\
& + \frac{9}{40\pi} \int_0^{2\pi} \cos \left(r \left(\frac{\sqrt{3}}{2} \cos(\theta) - \frac{1}{2} \sin(\theta) \right) + \frac{5\pi}{3} \right) d\theta \\
& + \frac{9}{40\pi} \int_0^{2\pi} \cos \left(r \sin(\theta) + \frac{5\pi}{3} \right) d\theta. \quad (2.168)
\end{aligned}$$

Applying (2.139) and (2.140), respectively, to the first two integrals gives us

$$\begin{aligned}
g_1(r) = & \frac{9}{40\pi} \int_0^{2\pi} \cos \left(r \sin \left(\theta + \frac{\pi}{3} \right) + \frac{\pi}{3} \right) d\theta \\
& + \frac{9}{40\pi} \int_0^{2\pi} \cos \left(r \sin \left(\theta + \frac{2\pi}{3} \right) + \frac{5\pi}{3} \right) d\theta \\
& + \frac{9}{40\pi} \int_0^{2\pi} \cos \left(r \sin(\theta) + \frac{5\pi}{3} \right) d\theta. \quad (2.169)
\end{aligned}$$

By the periodicity of the sine function, we have

$$\begin{aligned}
g_1(r) = & \frac{9}{40\pi} \int_0^{2\pi} \cos \left(r \sin(\theta) + \frac{\pi}{3} \right) d\theta \\
& + \frac{9}{40\pi} \int_0^{2\pi} \cos \left(r \sin(\theta) + \frac{5\pi}{3} \right) d\theta \\
& + \frac{9}{40\pi} \int_0^{2\pi} \cos \left(r \sin(\theta) + \frac{5\pi}{3} \right) d\theta. \quad (2.170)
\end{aligned}$$

Applying (2.144) to each integral yields

$$g_1(r) = \frac{9}{40} J_0(r) + \frac{9}{40} J_0(r) + \frac{9}{40} J_0(r) = \frac{27}{40} J_0(r). \quad (2.171)$$

By (2.143), we have the final form for the RDF for the component field $\psi_{ans,1}$:

$$g_1(r) = \frac{27}{80\pi} \int_0^{2\pi} \cos(r \sin(\theta)) d\theta. \quad (2.172)$$

Now, by the linearity of integration, the radial distribution function for the $\omega_{\sqrt{3}} = \sqrt{3}$ component is

$$\begin{aligned}
g_{\sqrt{3}}(r) := & \frac{29}{90\pi} \int_0^{2\pi} \cos \left(\frac{\sqrt{3}}{2} r \cos(\theta) + \frac{3}{2} r \sin(\theta) \right) d\theta \\
& + \frac{29}{90\pi} \int_0^{2\pi} \cos \left(\frac{\sqrt{3}}{2} r \cos(\theta) - \frac{3}{2} r \sin(\theta) \right) d\theta \\
& + \frac{29}{90\pi} \int_0^{2\pi} \cos \left(\sqrt{3} r \cos(\theta) \right) d\theta. \quad (2.173)
\end{aligned}$$

Factoring out $\sqrt{3}r$ yields

$$\begin{aligned}
g_{\sqrt{3}}(r) = & \frac{29}{90\pi} \int_0^{2\pi} \cos \left(\left(\sqrt{3}r \right) \left(\frac{1}{2} \cos(\theta) + \frac{\sqrt{3}}{2} \sin(\theta) \right) \right) d\theta \\
& + \frac{29}{90\pi} \int_0^{2\pi} \cos \left(\left(\sqrt{3}r \right) \left(\frac{1}{2} \cos(\theta) - \frac{\sqrt{3}}{2} \sin(\theta) \right) \right) d\theta \\
& + \frac{29}{90\pi} \int_0^{2\pi} \cos \left(\left(\sqrt{3}r \right) \cos(\theta) \right) d\theta. \quad (2.174)
\end{aligned}$$

Next, applying (2.138), (2.141), and (2.142) to the first, second, and third integrals, respectively, we have

$$\begin{aligned}
g_{\sqrt{3}}(r) = & \frac{29}{90\pi} \int_0^{2\pi} \cos \left(\left(\sqrt{3}r \right) \sin \left(\theta + \frac{\pi}{6} \right) \right) d\theta \\
& + \frac{29}{90\pi} \int_0^{2\pi} \cos \left(\left(\sqrt{3}r \right) \sin \left(\theta + \frac{5\pi}{6} \right) \right) d\theta \\
& + \frac{29}{90\pi} \int_0^{2\pi} \cos \left(\left(\sqrt{3}r \right) \sin \left(\theta + \frac{\pi}{2} \right) \right) d\theta. \quad (2.175)
\end{aligned}$$

The periodicity of the sine function gives us

$$\begin{aligned}
g_{\sqrt{3}}(r) = & \frac{29}{90\pi} \int_0^{2\pi} \cos\left(\left(\sqrt{3}r\right) \sin(\theta)\right) d\theta \\
& + \frac{29}{90\pi} \int_0^{2\pi} \cos\left(\left(\sqrt{3}r\right) \sin(\theta)\right) d\theta \\
& + \frac{29}{90\pi} \int_0^{2\pi} \cos\left(\left(\sqrt{3}r\right) \sin(\theta)\right) d\theta. \quad (2.176)
\end{aligned}$$

The final form of the RDF for the component field $\psi_{ans,\sqrt{3}}$ is

$$g_{\sqrt{3}}(r) = \frac{29}{30\pi} \int_0^{2\pi} \cos\left(\left(\sqrt{3}r\right) \sin(\theta)\right) d\theta. \quad (2.177)$$

In addition, by (2.143),

$$g_{\sqrt{3}}(r) = \frac{29}{15} J_0\left(\sqrt{3}r\right). \quad (2.178)$$

Using the linearity of integration, the radial distribution function for the $\omega_2 = 2$ ansatz component is

$$\begin{aligned}
g_2(r) := & \frac{2}{15\pi} \int_0^{2\pi} \cos\left(\sqrt{3}r \cos(\theta) + r \sin(\theta) + \frac{5\pi}{3}\right) d\theta \\
& + \frac{2}{15\pi} \int_0^{2\pi} \cos\left(\sqrt{3}r \cos(\theta) - r \sin(\theta) + \frac{\pi}{3}\right) d\theta \\
& + \frac{2}{15\pi} \int_0^{2\pi} \cos\left(2r \sin(\theta) + \frac{\pi}{3}\right) d\theta. \quad (2.179)
\end{aligned}$$

We factor out $2r$ within the integrands to arrive at

$$\begin{aligned}
g_2(r) := & \frac{2}{15\pi} \int_0^{2\pi} \cos\left((2r) \left(\frac{\sqrt{3}}{2} \cos(\theta) + \frac{1}{2} \sin(\theta)\right) + \frac{5\pi}{3}\right) d\theta \\
& + \frac{2}{15\pi} \int_0^{2\pi} \cos\left((2r) \left(\frac{\sqrt{3}}{2} \cos(\theta) - \frac{1}{2} \sin(\theta)\right) + \frac{\pi}{3}\right) d\theta \\
& + \frac{2}{15\pi} \int_0^{2\pi} \cos\left((2r) \sin(\theta) + \frac{\pi}{3}\right) d\theta. \quad (2.180)
\end{aligned}$$

We next apply (2.139) and (2.140), respectively, to the first two integrals:

$$\begin{aligned}
g_2(r) = & \frac{2}{15\pi} \int_0^{2\pi} \cos \left((2r) \sin \left(\theta + \frac{\pi}{3} \right) + \frac{5\pi}{3} \right) d\theta \\
& + \frac{2}{15\pi} \int_0^{2\pi} \cos \left((2r) \sin \left(\theta + \frac{2\pi}{3} \right) + \frac{\pi}{3} \right) d\theta \\
& + \frac{2}{15\pi} \int_0^{2\pi} \cos \left((2r) \sin(\theta) + \frac{\pi}{3} \right) d\theta. \quad (2.181)
\end{aligned}$$

By the periodicity of the sine function,

$$\begin{aligned}
g_2(r) = & \frac{2}{15\pi} \int_0^{2\pi} \cos \left((2r) \sin(\theta) + \frac{5\pi}{3} \right) d\theta \\
& + \frac{2}{15\pi} \int_0^{2\pi} \cos \left((2r) \sin(\theta) + \frac{\pi}{3} \right) d\theta \\
& + \frac{2}{15\pi} \int_0^{2\pi} \cos \left((2r) \sin(\theta) + \frac{\pi}{3} \right) d\theta. \quad (2.182)
\end{aligned}$$

Applying (2.144) to each integral yields

$$g_2(r) = \frac{2}{15} J_0(2r) + \frac{2}{15} J_0(2r) + \frac{2}{15} J_0(2r) = \frac{2}{5} J_0(2r). \quad (2.183)$$

The definition (2.143) gives us the final form for the RDF for the component field $\psi_{ans,2}$:

$$g_2(r) = \frac{1}{5\pi} \int_0^{2\pi} \cos((2r) \sin(\theta)) d\theta. \quad (2.184)$$

Substituting (2.172), (2.177), and (2.184) into (2.166) gives us the final form for the **multimode PFC model radial distribution function**:

$$\begin{aligned}
g_{mmpfc}(r) = & \frac{27}{80\pi} \int_0^{2\pi} \cos(r \sin(\theta)) d\theta \\
& + \frac{29}{30\pi} \int_0^{2\pi} \cos \left(\left(\sqrt{3}r \right) \sin(\theta) \right) d\theta \\
& + \frac{1}{5\pi} \int_0^{2\pi} \cos((2r) \sin(\theta)) d\theta. \quad (2.185)
\end{aligned}$$

Collecting (2.171), (2.178), and (2.183) yields the radial distribution function in terms of Bessel functions of the first kind with order 0:

$$g_{mmpfc}(r) = \frac{27}{40}J_0(r) + \frac{29}{15}J_0(\sqrt{3}r) + \frac{2}{5}J_0(2r) \quad (2.186)$$

for all $r \in \mathbb{R}^+$. To find the Fourier transform of g_{mmpfc} , we utilize the linearity of the transform. In addition, we apply (2.145) to the first Bessel function in (2.186), and we apply (2.147) to the second and third. The initial result is the sum of three piecewise functions:

$$\begin{aligned} \widehat{g_{mmpfc}}(\omega) := & \begin{cases} \frac{27}{20\sqrt{1-\omega^2}} & \text{if } 0 \leq \omega < 1 \\ 0 & \text{if } \omega > 1 \end{cases} \\ & + \begin{cases} \frac{58}{15\sqrt{3-\omega^2}} & \text{if } 0 \leq \omega < \sqrt{3} \\ 0 & \text{if } \omega > \sqrt{3} \end{cases} \\ & + \begin{cases} \frac{4}{5\sqrt{4-\omega^2}} & \text{if } 0 \leq \omega < 2 \\ 0 & \text{if } \omega > 2 \end{cases}. \end{aligned} \quad (2.187)$$

The final form for the Fourier transform of g_{mmpfc} is

$$\widehat{g_{mmpfc}}(\omega) = \begin{cases} \frac{27}{20\sqrt{1-\omega^2}} + \frac{58}{15\sqrt{3-\omega^2}} + \frac{4}{5\sqrt{4-\omega^2}} & \text{if } 0 \leq \omega < 1 \\ \frac{58}{15\sqrt{3-\omega^2}} + \frac{4}{5\sqrt{4-\omega^2}} & \text{if } 1 < \omega < \sqrt{3} \\ \frac{4}{5\sqrt{4-\omega^2}} & \text{if } \sqrt{3} < \omega < 2 \\ 0 & \text{if } \omega > 2 \end{cases}. \quad (2.188)$$

The radial distribution function for the multimode PFC model appears in Figure 2.34a. Now, we focus on the atom, or mass density peak, at the origin in Figure 2.33. To find the distances between atoms near the origin, we reference the hexagonal dimensions of Figure 2.21 in Subsection 2.3.4. The three atoms that are closest to the origin form the vertices of a triangle. The distance between the origin and each of these three atoms is $\frac{4\pi}{3} \approx 4.189$.

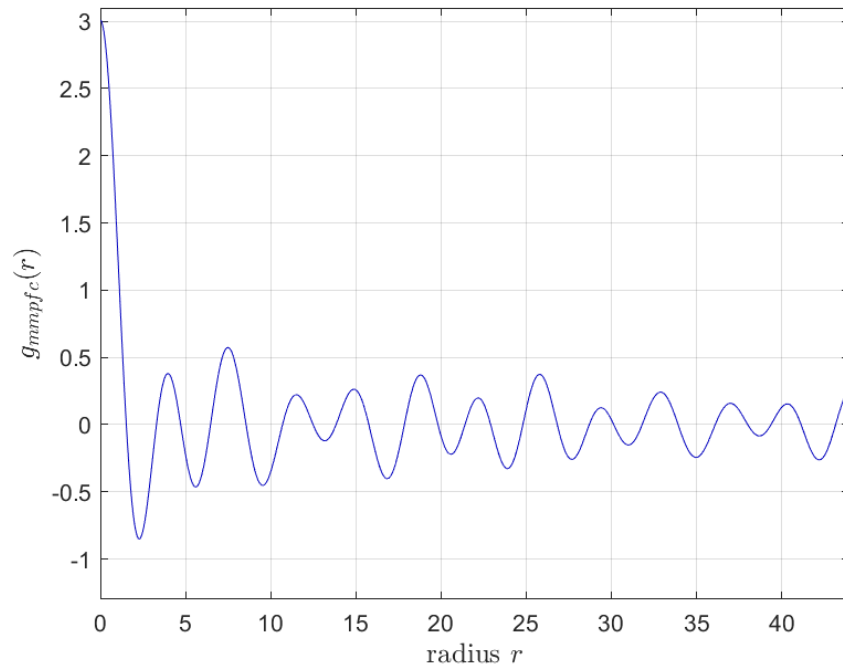
Indeed, the first peak in Figure 2.34a occurs near $r = 4$. The second “layer” of atoms forms a hexagon centered at the origin. The distance between each of the corresponding six atoms and the origin is $\frac{4\pi}{\sqrt{3}} \approx 7.255$. The third layer of atoms forms the vertices of a second triangle. The distance between the origin and each of these atoms is $\frac{8\pi}{3} \approx 8.378$. The distances for the second and third atom layers are so close that only one peak appears in the RDF of Figure 2.34a. This peak is near $r = 7.5$. Since there is a total of nine atoms in the second and third layers combined, the peak near $r = 7.5$ is higher than the peak near $r = 4$. Due to the relative complexity of the honeycomb geometry, the radial distribution function for the multimode PFC model is irregular. However, as the radius r increases, the distance between adjacent peaks approaches $\frac{2\pi}{\sqrt{3}} \approx 3.628$. Lastly, Figure 2.34b displays the Fourier transform of the radial distribution function. Note that there is a vertical asymptote at each of the multimode PFC dominant angular frequencies $\omega_1 = 1$, $\omega_{\sqrt{3}} = \sqrt{3}$, and $\omega_2 = 2$.

2.7 Graphene Growth on a Copper Substrate

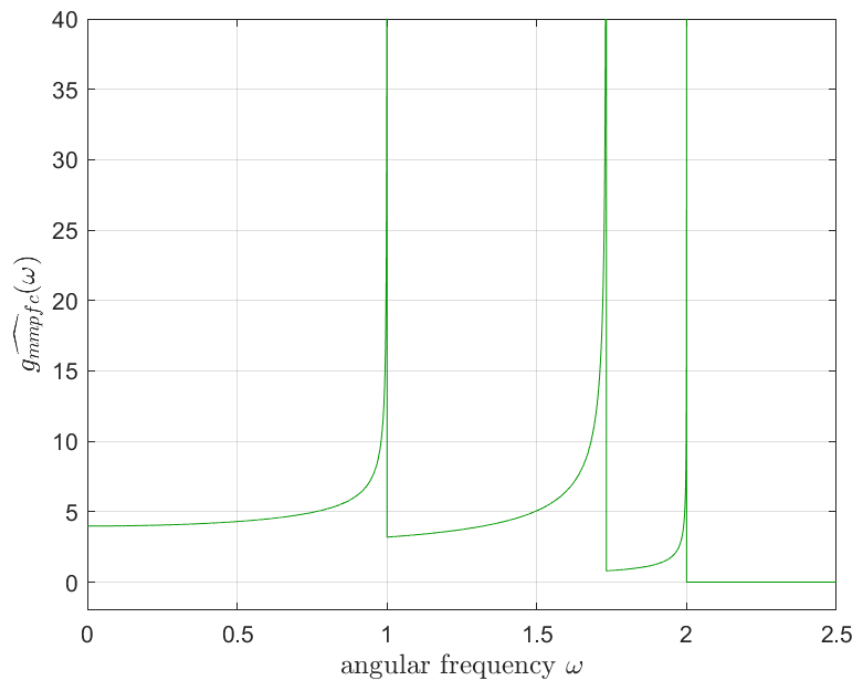
Graphene is typically grown on a copper substrate using chemical vapor deposition (CVD) [13]. A mixture of methane and hydrogen [13] is added to the tank at a rate proportional to the area of the substrate that has no graphene. Now, the crystal structure of copper is face-centered cubic (FCC). In the formation of graphene, the copper (111) facet is used for the substrate surface. The atoms at the surface of the copper (111) facet form a triangular lattice. Figure 2.35a details the copper crystal structure and the copper (111) facet. The dots are the copper atoms and the copper (111) facet appears in blue.

The graphene atoms tend to deposit at the centroids of the copper (111) triangles. Indeed, the triangular (or hexagonal) lattice is the dual of the honeycomb lattice. However, there is a slight misalignment between the copper and graphene. We first compute the distance d between the centroids of adjacent copper (111) triangles, as labeled in Figure 2.35b. In Figure 2.35a, the copper lattice constant along the $\frac{\pi}{2}$ angles is $\ell \approx 361.5$ pm. In Figures 2.35a and 2.35b, a is the length of each side of each copper (111) triangle. Referencing Figure 2.35a, we see that

$$a = \frac{\ell}{2 \cos\left(\frac{\pi}{4}\right)} = \frac{\ell}{\sqrt{2}} \approx 255.6 \text{ pm.} \quad (2.189)$$

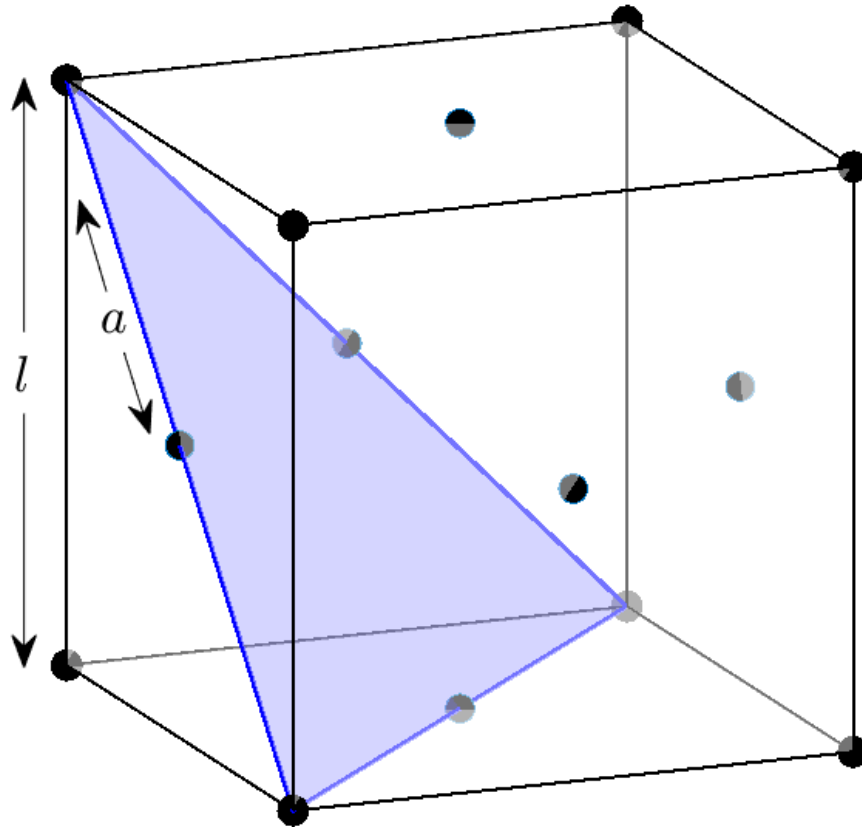


(a) Radial Distribution Function

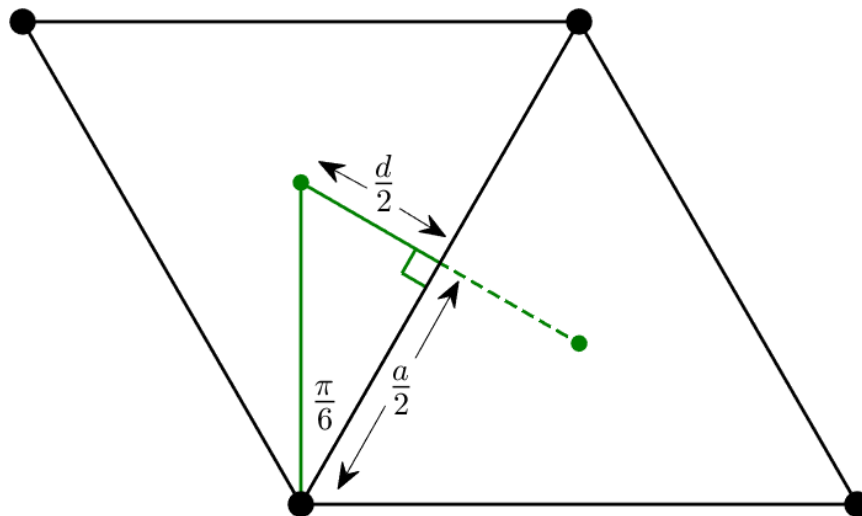


(b) Fourier Transform of the Radial Distribution Function

Figure 2.34: Multimode PFC Model, Radial Distribution Function and Fourier Transform



(a) Copper Crystal (FCC) with (111) Facet in Blue



(b) Copper (111) Facet, Adjacent Centroid Distance

Figure 2.35: Copper Crystal and (111) Facet Geometry

Finally, Figure 2.35b gives us the distance between adjacent copper (111) triangle centroids:

$$d = a \tan\left(\frac{\pi}{6}\right) = \frac{a}{\sqrt{3}} \approx \mathbf{147.6 \text{ pm.}} \quad (2.190)$$

In contrast, the distance between adjacent graphene atoms is $b \approx \mathbf{142 \text{ pm}}$. Hence, the ratio of the distance between copper (111) triangle centroids to the distance between graphene atoms is

$$\frac{d}{b} \approx \frac{147.6}{142} \approx \mathbf{1.039.} \quad (2.191)$$

Figure 2.36 demonstrates the misalignment between the triangle centroids of the copper (111) facet and the carbon atoms of graphene. This figure employs the honeycomb lattice of the multimode PFC model mass density field. The white circles represent the copper substrate atoms. This copper-graphene misalignment causes the graphene to delaminate, or lift and separate, from the copper substrate. Wrinkles form in the graphene [13]. Since our model is strictly two-dimensional, we see geometric irregularities where wrinkles might occur.

For the model, we name the substrate field ϕ . This field is constant and Ω -periodic. Now, ϕ is formed using the triangular geometry of the single-mode PFC model. Based on the unit cell width of the multimode PFC honeycomb geometry (2.91) and the copper-to-graphene ratio (2.191), the unit cell width for the substrate field ϕ is

$$1.039 \frac{4\pi}{\sqrt{3}} \approx 7.538. \quad (2.192)$$

Using the honeycomb unit cell height (2.92), the substrate unit cell height is

$$1.039 \cdot 4\pi \approx 13.056. \quad (2.193)$$

We use the amplitude of the substrate field to control the strength of the alignment between the substrate field ϕ and the mass density field ψ . For the vapor deposition, we add a parameter α_v to determine the rate at which the mass density of the vapor phase region increases. First, we add the coupling term $\phi\psi$ to the second line of the multimode PFC

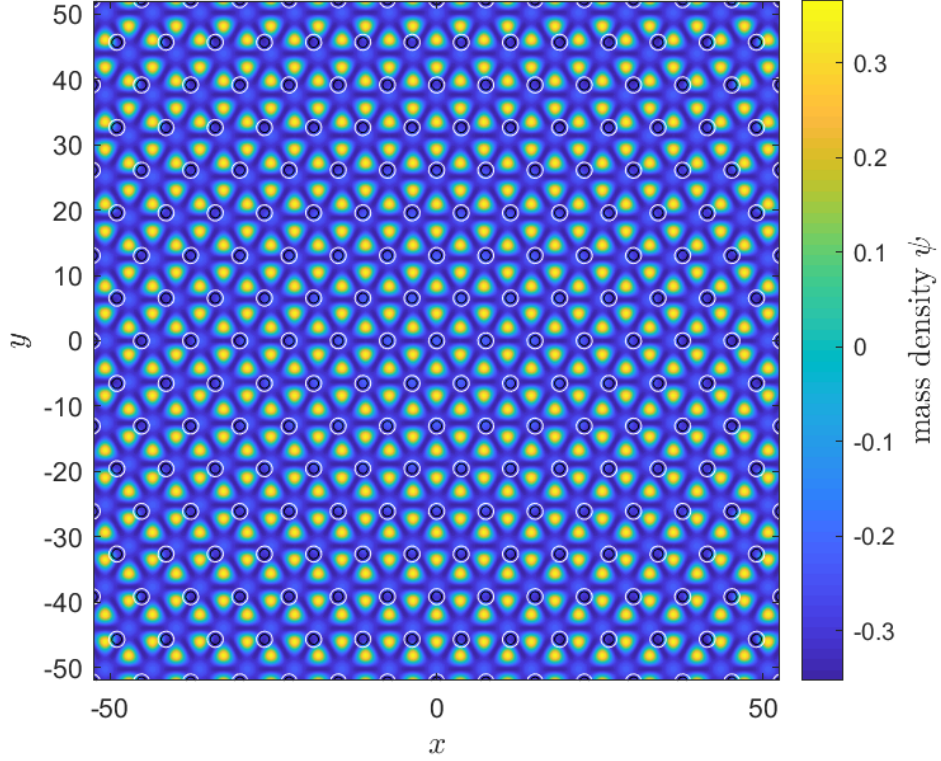


Figure 2.36: Honeycomb Graphene on Triangular Copper

model with vapor free energy equation (2.102) to arrive at

$$\begin{aligned}
 \mathcal{F}_{sub,cvd}(t; \psi, \eta) := & \int_{\Omega} \left[g(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v \right\} \right. \\
 & + (1 - g(\eta)) \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi C \psi + \phi \psi \right\} \\
 & \left. + W_v h(\eta) - \frac{\kappa_v}{2} \eta \Delta \eta \right] d\mathbf{x}. \quad (2.194)
 \end{aligned}$$

Next, we recall the time derivative of the mass density field from (2.110)

$$\dot{\psi} = \Delta \frac{\delta \mathcal{F}}{\delta \psi}. \quad (2.195)$$

We prove in Subsection 2.4.3 that this formulation results in the conservation of mass density. However, chemical vapor deposition causes the mass density of the system to increase. Therefore, the deposition term must be excluded from the free energy functional.

We implement the deposition as follows:

$$\dot{\psi} := \Delta \frac{\delta \mathcal{F}_{sub,cvd}}{\delta \psi} + \alpha_v \eta. \quad (2.196)$$

Recall that $\eta = 1$ everywhere there is vapor. Hence, the mass density increases uniformly across the vapor region. We adapt the multimode PFC with vapor partial differential equation (PDE) from (2.111) to define the PDE for this substrate with vapor deposition model:

$$\begin{aligned} \dot{\psi} = \Delta \Bigg[& \chi_4 \psi^3 + \chi_3 \psi^2 + \epsilon \psi + \lambda C \psi + \phi \\ & + g(\eta) \left\{ b_v (\psi - \psi_v) - \chi_4 \psi^3 - \chi_3 \psi^2 - \epsilon \psi - \frac{\lambda}{2} C \psi - \phi \right\} \\ & - \frac{\lambda}{2} C [g(\eta) \psi] \Bigg] + \alpha_v \eta. \end{aligned} \quad (2.197)$$

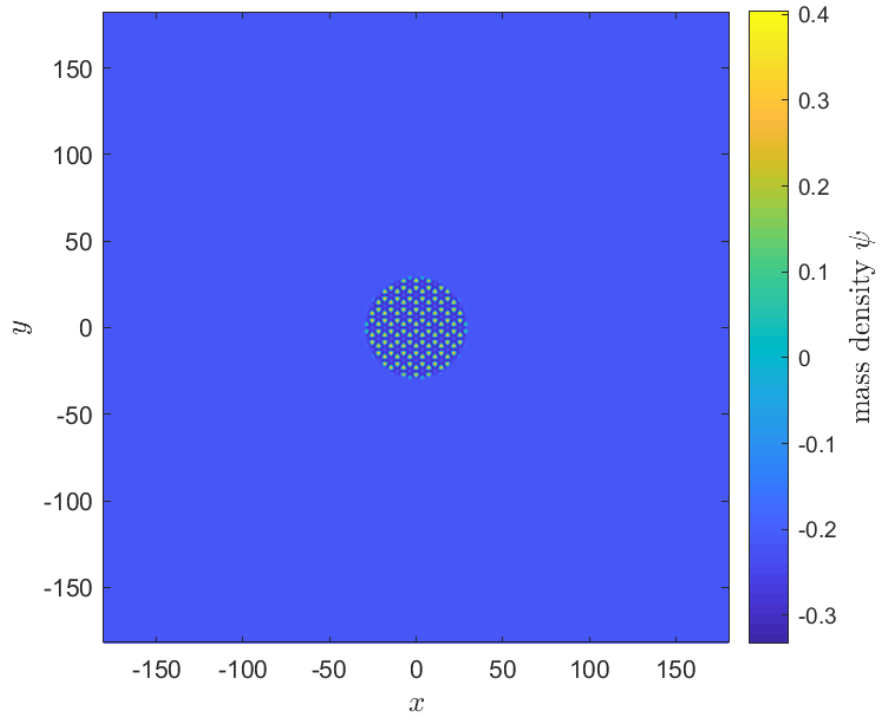
Finally, we modify the vapor phase field PDE from (2.115) to find that

$$\begin{aligned} \dot{\eta} = -M_v \Bigg[& g'(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v - \frac{\chi_4}{4} \psi^4 - \frac{\chi_3}{3} \psi^3 - \frac{\epsilon}{2} \psi^2 - \frac{\lambda}{2} \psi C \psi - \phi \psi \right\} \\ & + W_v h'(\eta) - \kappa_v \Delta \eta \Bigg]. \end{aligned} \quad (2.198)$$

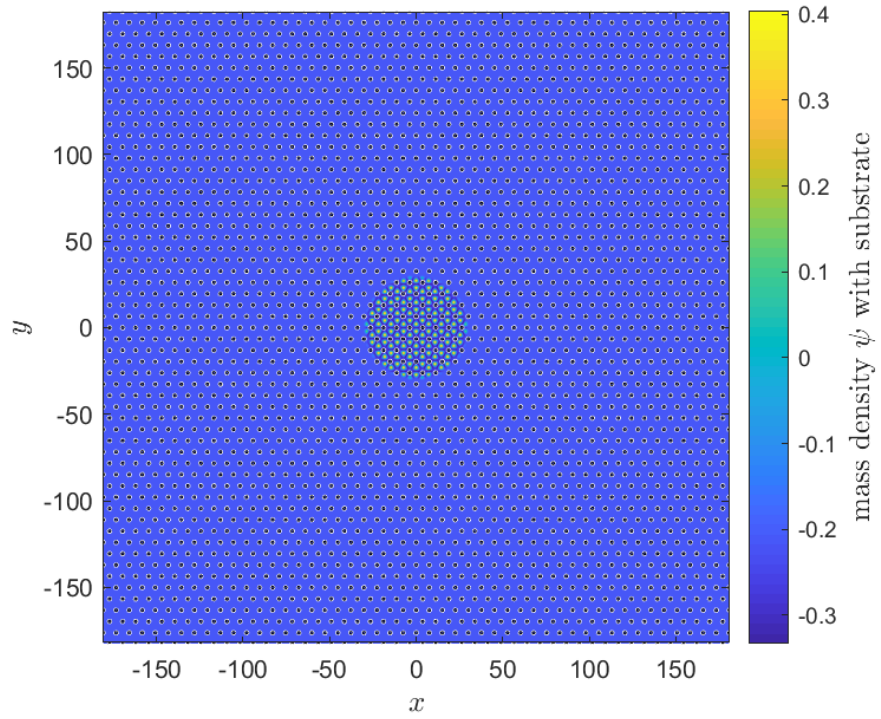
We now describe a simulation that models graphene growth on a copper substrate with chemical vapor deposition. We begin with a relatively small disk seed of honeycomb geometry at the center of the computational box. The center of this initial honeycomb geometry is aligned with the triangular geometry of the substrate. Figure 2.37a shows the initial mass density field, and Figure 2.37b provides this field with white circles marking the positions of the peaks of the substrate field. These circles represent the locations of copper atoms. The vapor deposition process causes the vapor mass density to increase. As the mass density of the vapor region decreases toward its equilibrium, the excess mass density collects at the phase interface, and the nanocrystal grows. Indeed, Figures 2.38a and 2.38b indicate that the nanocrystal is much larger at time 3,000. However, there are irregularities in the honeycomb geometry. At the center of the nanocrystal, we find the star-shaped kagome geometry. At

the phase interface, the peaks that make up each of the pairs that are normal to the interface are packed closely together.

The system achieves an equilibrium state at time 26,000. Figures 2.39a and 2.39b detail the final mass density field. As no vapor remains, the mass density of the system is constant. At this equilibrium state, honeycomb geometry is prevalent, but there appear to be four vertical zigzagging strips of rectangular geometry. A type of moiré pattern is evident. These irregular regions may correspond to locations of delamination in actual graphene formation. Recalling that the mass density field is Ω -periodic, we discover that there are actually only two distinct strips of irregular geometry. The middle strip is indeed one distinct region. We trace the second strip by starting at $(100, 100)$ and working down to the bottom of the box. This same strip continues at the top of the box near $x = 100$, where it moves to the right edge and coincides periodically with the left edge. This strip continues to zigzag down the left and right edges until it moves to the right to touch the bottom of the box near $x = -100$. The strip then continues at the top of box and moves downward to end near $(-100, -100)$. For a closer look at the geometry, Figures 2.40a and 2.40b display the top right quadrant of the equilibrium mass density field.

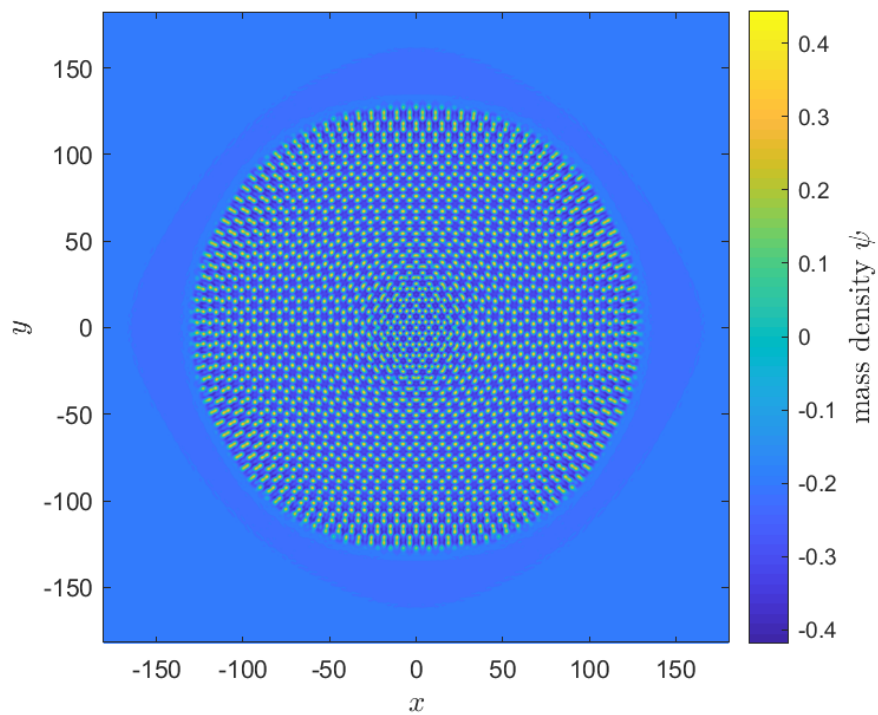


(a) Mass Density

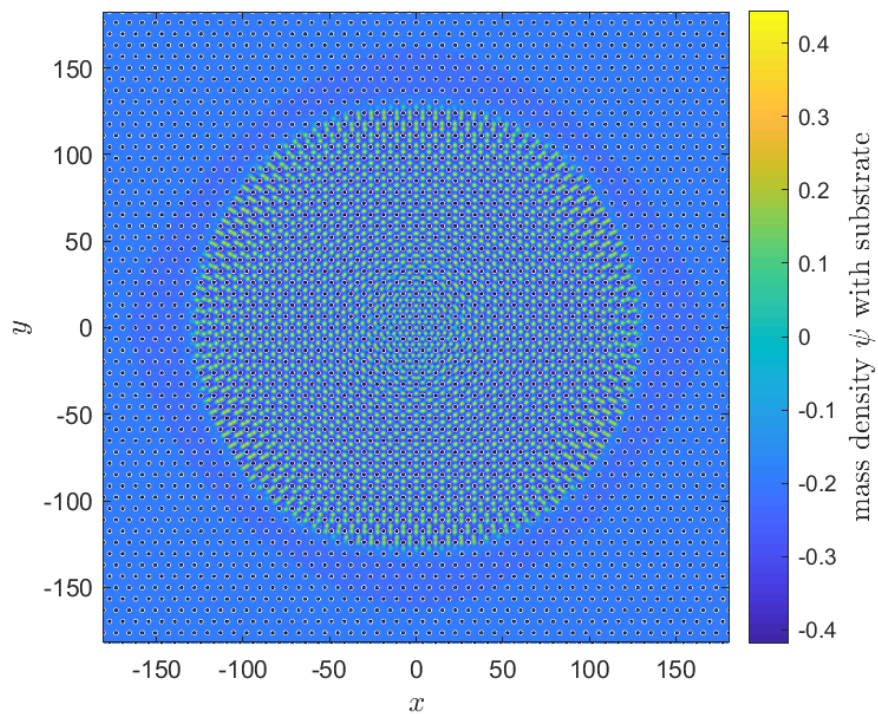


(b) Mass Density with Substrate

Figure 2.37: MMPFC with Substrate and CVD, Disk Seed, Time = 0

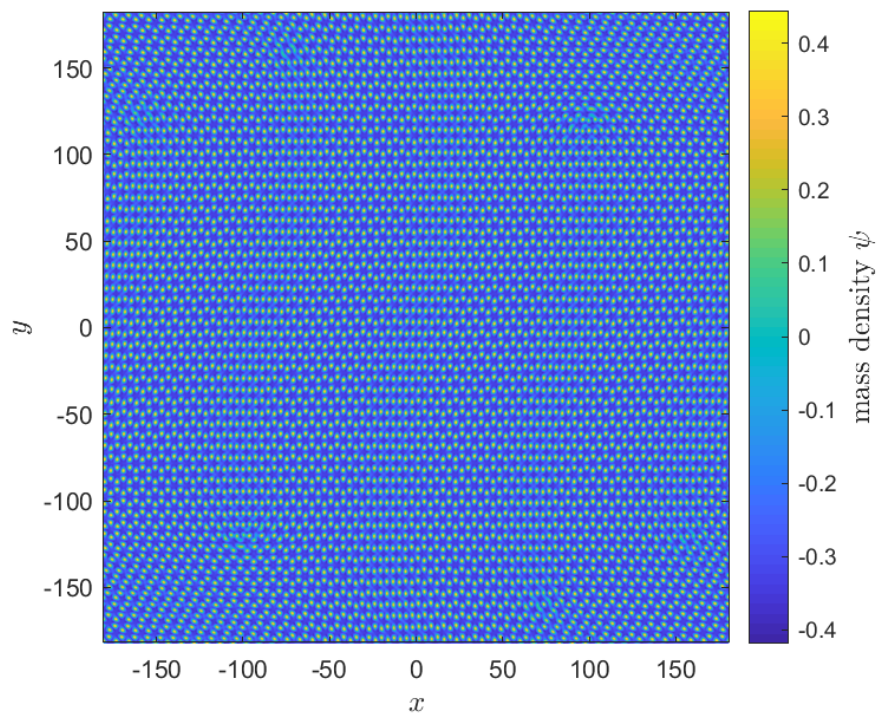


(a) Mass Density

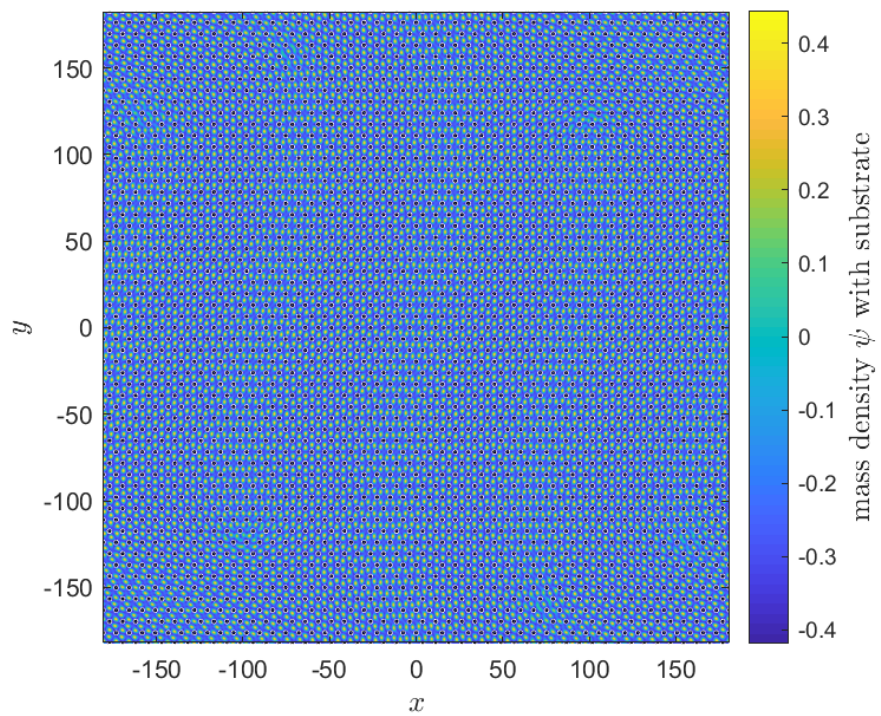


(b) Mass Density with Substrate

Figure 2.38: MMPFC with Substrate and CVD, Disk Seed, Time = 3,000

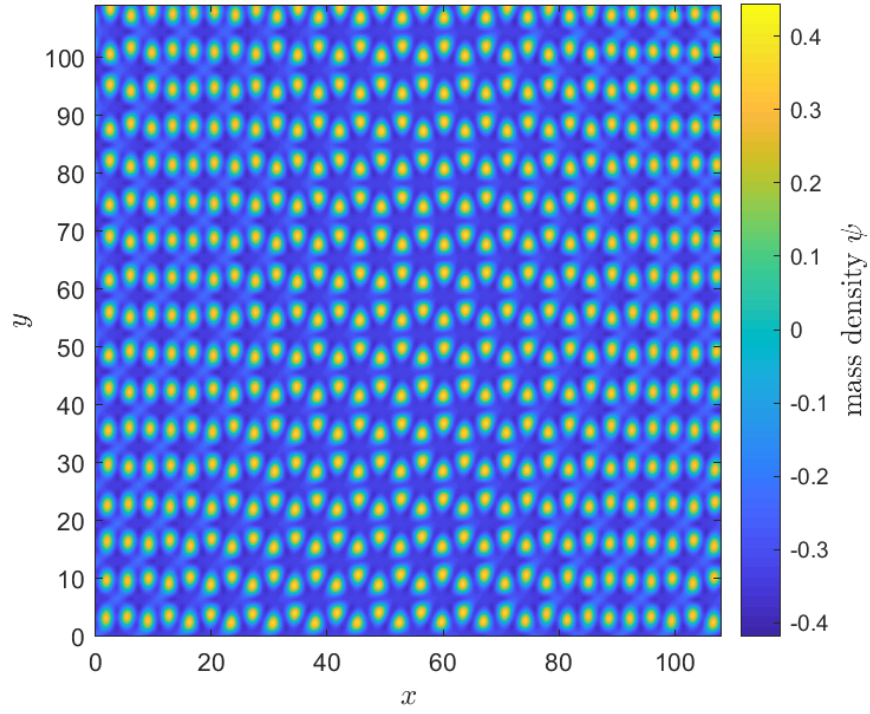


(a) Mass Density

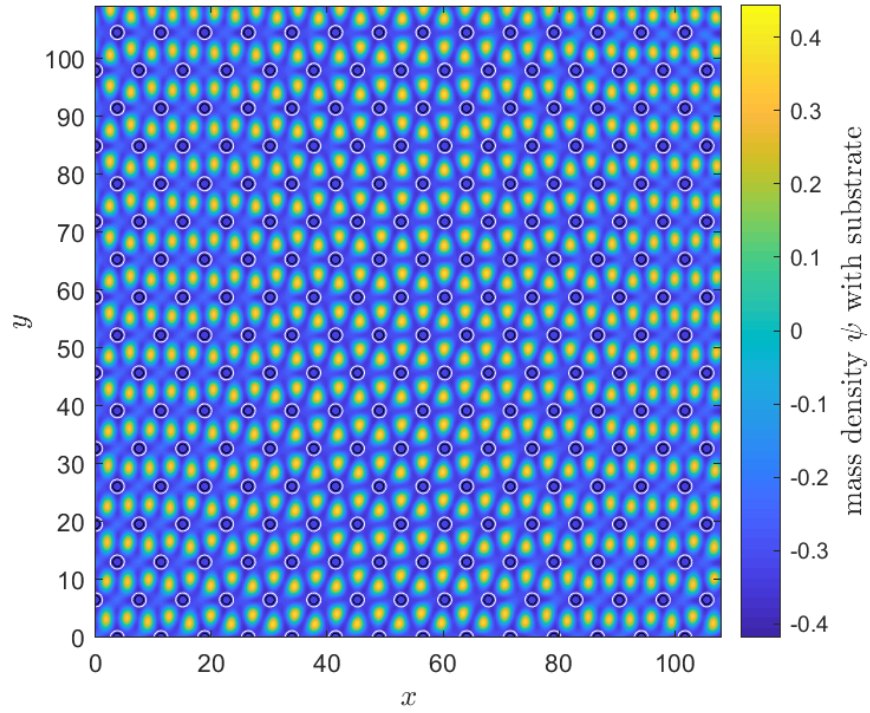


(b) Mass Density with Substrate

Figure 2.39: MMPFC with Substrate and CVD, Disk Seed, Time = 26,000



(a) Mass Density



(b) Mass Density with Substrate

Figure 2.40: MMPFC with Substrate and CVD, Top Right, Time = 26,000

Chapter 3

Gaussian Correlation Function

In Subsection 2.3.2, we introduce a 16th order linear differential operator (2.63), consisting of Laplacians, to establish the crystal honeycomb geometry for the multimode PFC model. We repeat the definition for the operator C here:

$$C := \sum_{i=0}^8 c_i \Delta^i. \quad (3.1)$$

In truth, we can replace this linear differentiation operation with a convolution that includes a two-point, or pair, correlation function. We call this modified multimode PFC model the *Gaussian multimode PFC model*. The “Gaussian” qualifier refers to the form of the Fourier transform of the correlation function. We design this Fourier transform by summing together different Gaussian functions. The goal is to produce local minima at the desired dominant angular frequencies. In fact, when we derive the single-mode PFC model from classical functional density theory (CDFT) in Subsection 2.2.2, we present such a correlation function (2.16) and its Fourier transform (2.17). We repeat them here respectively:

$$C_{2,1D}(x-y) := -\frac{\exp\left(-\frac{(x-y)^2}{64}\right) \cos(x-y)}{2\sqrt{2}} \quad (3.2)$$

and

$$\widehat{C_{2,1D}}(\omega) := -\exp(-16(\omega+1)^2) - \exp(-16(\omega-1)^2). \quad (3.3)$$

Now, the honeycomb geometry entails three dominant angular frequencies: $\omega_1 = 1$, $\omega_{\sqrt{3}} = \sqrt{3}$, and $\omega_2 = 2$. As with the Fourier space multiplier for the multimode PFC linear differential operator, the Fourier transform of the correlation function is expressed in terms of the angular frequency radius, or magnitude, $\omega := \sqrt{\omega_x^2 + \omega_y^2}$. In addition, the inverse Fourier transform of an odd function is imaginary, and, thus, the Gaussian functions must be added in pairs, where each pair results in an even function. Hence, we require three pairs of Gaussian functions - one pair for each dominant angular frequency.

3.1 Gaussian Multimode PFC Parameters

Table 3.1 provides the parameters for the Gaussian multimode PFC model. For $i = 0, 1, 2$, the a_i , b_i , and q_i parameters in Table 3.1a regulate the crystal geometry of the solid phase. These parameters are explained in Section 3.2. As with the standard multimode PFC model, ϵ is the shifted and offset temperature. Recall that, for the standard multimode PFC model, $\epsilon = -0.15$. Here, instead of adding a c_0 parameter as a constant offset for the Fourier space function, we add an offset of 20 to ϵ to arrive at $\epsilon = -0.15 + 20 = 19.85$. Collectively, the amplitude parameters a_0 , a_1 , and a_2 determine the magnitude, or strength, of the gradient portion of the free energy. Therefore, we have $\lambda = 1$. The values of parameters χ_3 and χ_4 match exactly those of the standard multimode PFC model from Table 2.2a. Tables 3.1b and 3.1c list the mass density field initialization and discretization parameters, respectively. These parameters and values are identical to those of Tables 2.2b and 2.2c, respectively, for the standard multimode PFC model.

3.2 Gaussian Multimode PFC Equations

We construct the equations for the Gaussian multimode PFC model using the standard multimode PFC equations as a reference. First, the homogeneous free energy of the Gaussian model is identical in form to that of the standard multimode PFC model (2.66). We have

$$\mathcal{F}_{g,homog}(t; \psi) := \int_{\Omega} \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 \right\} d\mathbf{x}. \quad (3.4)$$

Table 3.1: Gaussian Multimode PFC Parameters**(a)** Solid Phase Parameters

Parameter/Value	Description
$a_0 = -26.92214598944005$	Amplitude (negative), mode 0
$a_1 = -37.35554280420075$	Amplitude (negative), mode 1
$a_2 = -1.120959115923572$	Amplitude (negative), mode 2
$b_0 = 0.5948512639735250$	Gaussian width, mode 0
$b_1 = 0.8103244499046540$	Gaussian width, mode 1
$b_2 = 0.1005975805894645$	Gaussian width, mode 2
$q_0 = 0.6274789995603853$	Adjusted angular frequency, mode 0
$q_1 = 2.011623352347177$	Adjusted angular frequency, mode 1
$q_2 = 2.087639869653354$	Adjusted angular frequency, mode 2
$\epsilon = 19.85$	Temperature (scaled and shifted)
$\lambda = 1$	Multimodal strength
$\chi_3 = -0.02$	Cubic term coefficient
$\chi_4 = 1.6$	Quartic term coefficient

(b) Density Field Initialization Parameters

Parameter/Value	Description
$amp = 0.3688$	Initial solid density amplitude
$cell_x = 7.255197457$	Initial unit cell width
$cell_y = 12.5663706144685$	Initial unit cell height
$\mu_s = -0.171$	Initial solid mean density

(c) Discretization Parameters

Parameter/Value	Description
$dt = 0.1$	Time increment
$h_x \approx 0.45$	x -granularity
$h_y \approx 0.45$	y -granularity

To build the gradient free energy, we first give the name C_g to the two-point correlation function. Note that C_g is a function on $\mathbb{R}^2$. We name the corresponding Fourier transform $\widehat{C_g}$. Next, the gradient free energy for the Gaussian multimode PFC model is

$$\mathcal{F}_{g,grad}(t; \psi) := \int_{\Omega} \frac{\lambda}{2} \psi(C_g * \psi) d\mathbf{x}. \quad (3.5)$$

Numerically, we require that the grid function matrix for the convolution C_g is the same size as the grid matrix for the mass density field ψ . Since Ω is a rectangular region of $\mathbb{R}^2$, there exist $x_0, y_0 \in \mathbb{R}^2$ and $a, b \in \mathbb{R}^+$ such that

$$\Omega := [x_0, x_0 + a] \times [y_0, y_0 + b]. \quad (3.6)$$

Next, we define the rectangle

$$\Psi := \left[-\frac{a}{2}, \frac{a}{2}\right] \times \left[-\frac{b}{2}, \frac{b}{2}\right]. \quad (3.7)$$

Now, Ψ has the same dimensions as Ω , and Ψ is centered at the origin. Therefore, we define the grid function for C_g on Ψ so that the matrix for C_g has the same size as that of ψ . In addition, we require that the values of C_g approach 0 very quickly near the boundary of Ψ , so that C_g is, for the purposes of our numerical computations, compactly supported on the interior of Ψ . By Corollary F.2, we may express the gradient free energy as

$$\begin{aligned} \mathcal{F}_{g,grad}(t; \psi) \approx & \int_{\Omega} \frac{\lambda}{2} \psi(\mathbf{x}) \\ & \left(\int_{\Omega} \left[C_g(\mathbf{x} - \mathbf{y} + [-a, -b]^T) + C_g(\mathbf{x} - \mathbf{y} + [-a, 0]^T) + C_g(\mathbf{x} - \mathbf{y} + [-a, b]^T) \right. \right. \\ & \quad + C_g(\mathbf{x} - \mathbf{y} + [0, -b]^T) + C_g(\mathbf{x} - \mathbf{y}) + C_g(\mathbf{x} - \mathbf{y} + [0, b]^T) \\ & \quad \left. \left. + C_g(\mathbf{x} - \mathbf{y} + [a, -b]^T) + C_g(\mathbf{x} - \mathbf{y} + [a, 0]^T) + C_g(\mathbf{x} - \mathbf{y} + [a, b]^T) \right] \psi(\mathbf{y}) d\mathbf{y} \right) \\ & d\mathbf{x}, \end{aligned} \quad (3.8)$$

where both integrals are taken over the region Ω . Finally, combining (3.4) and (3.5), we have the **Gaussian multimode PFC free energy functional**:

$$\mathcal{F}_g(t; \psi) := \int_{\Omega} \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi (C_g * \psi) \right\} d\mathbf{x}. \quad (3.9)$$

Hence, the Gaussian multimode PFC free energy density is:

$$f_g(\psi) := \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi (C_g * \psi). \quad (3.10)$$

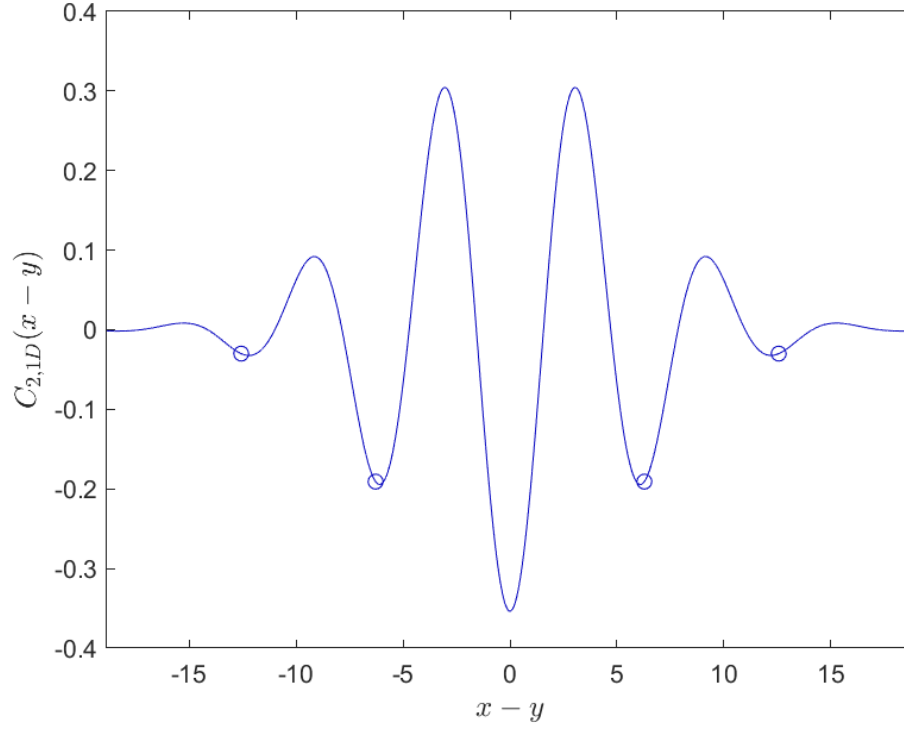
We proceed to build the Fourier transform, $\widehat{C}_g$, of the correlation function, C_g . Note that, due to the rotational invariance of our models, the angles of the vectors sent to C_g are irrelevant; only the magnitudes of the vectors matter. For the purpose of the construction of $\widehat{C}_g$, we treat C_g as function on $\mathbb{R}^+$. For two vectors $\mathbf{x}$ and $\mathbf{y}$ in $\mathbb{R}^2$, we define $r := \|\mathbf{x} - \mathbf{y}\|$, the Euclidean norm of the difference of the two vectors. Then, $C_g(r)$ is well-defined. Similarly, in Fourier space, we treat $\widehat{C}_g$ as a function on $\mathbb{R}^+$. Here, the angular frequency radius, or magnitude, is $\omega := \sqrt{\omega_x^2 + \omega_y^2}$, and, accordingly, $\widehat{C}_g(\omega)$ is well-defined.

Now, we consider the inverse Fourier transform of an even function that is the sum of two Gaussian functions. In one-dimensional spaces, the inverse Fourier transform is the product of a Gaussian function centered at 0 and the cosine. We see this in the correlation function (3.2) and its Fourier transform (3.3). Figures 3.1a and 3.1b recall the one-dimensional correlation function and its Fourier transform from Figures 2.6a and 2.6b, respectively. However, in two dimensions, the inverse Fourier transform for a such a Gaussian pair is more complicated. Nevertheless, in two dimensions, the shape of the inverse Fourier transform is similar to that of (3.2).

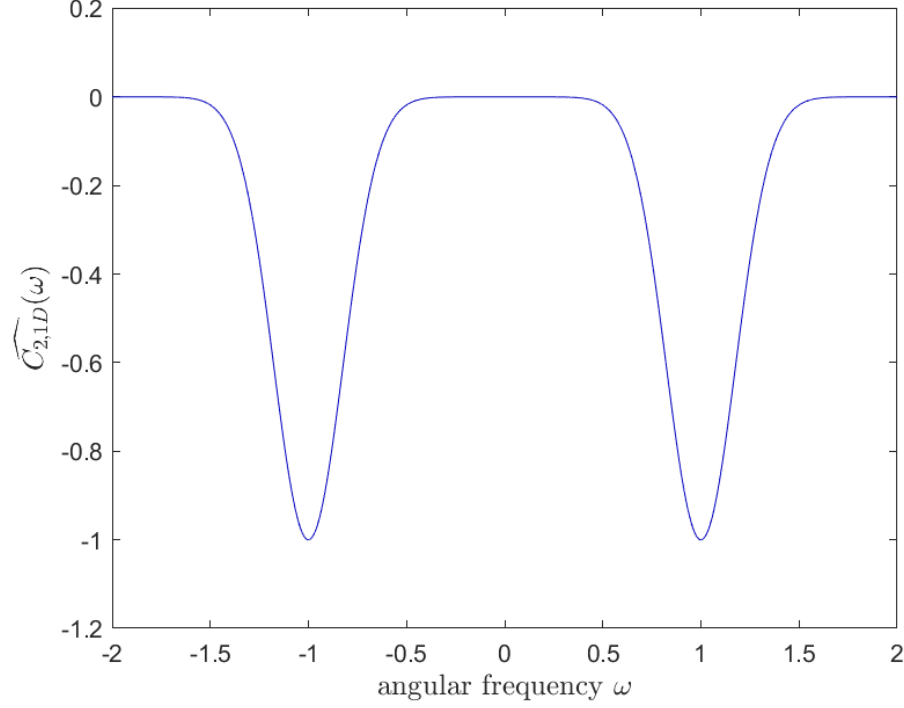
Now, the three Fourier space Gaussian pairs are defined by

$$\widehat{C}_{g,0}(\omega) := \frac{a_0}{2} \left(\exp \left(-\frac{(\omega + q_0)^2}{2b_0^2} \right) + \exp \left(-\frac{(\omega - q_0)^2}{2b_0^2} \right) \right), \quad (3.11)$$

$$\widehat{C}_{g,1}(\omega) := \frac{a_1}{2} \left(\exp \left(-\frac{(\omega + q_1)^2}{2b_1^2} \right) + \exp \left(-\frac{(\omega - q_1)^2}{2b_1^2} \right) \right), \quad (3.12)$$



(a) $C_{2,1D}(x-y) = -\frac{1}{2\sqrt{2}} \exp\left(-\frac{(x-y)^2}{64}\right) \cos(x-y)$



(b) $\widehat{C}_{2,1D}(\omega) = -\exp(-16(\omega+1)^2) - \exp(-16(\omega-1)^2)$

Figure 3.1: One-Dimensional Correlation Function, Single Mode

and

$$\widehat{C}_{g,2}(\omega) := \frac{a_2}{2} \left(\exp \left(-\frac{(\omega + q_2)^2}{2b_2^2} \right) + \exp \left(-\frac{(\omega - q_2)^2}{2b_2^2} \right) \right). \quad (3.13)$$

By linearity, the Fourier transform of the correlation function is

$$\widehat{C}_g(\omega) := \widehat{C}_{g,0}(\omega) + \widehat{C}_{g,1}(\omega) + \widehat{C}_{g,2}(\omega). \quad (3.14)$$

Note that $\widehat{C}_{g,0}$, $\widehat{C}_{g,1}$, and $\widehat{C}_{g,2}$ are even functions, and, therefore, their sum $\widehat{C}_g$ is even. For $i = 0, 1, 2$, we refer to a_i as the amplitude. We call b_i the width, or standard deviation, of each of the corresponding Gaussian functions. Finally, we refer to q_i as the adjusted angular frequency. Indeed, for each $i = 0, 1, 2$, $-q_i$ and q_i are the mean angular frequencies and centers for the corresponding individual Gaussian functions.

The selection of the values for the parameters a_i , b_i , and q_i , for $i = 0, 1, 2$, is a complicated task. All six of the Gaussian functions interfere with each other. We use the phrase “adjusted angular frequency” for each q_i , because, in the sum $\widehat{C}_g$, the center of each Gaussian curve is shifted by the other five. Therefore, we cannot use the dominant frequencies $\omega_1 = 1$, $\omega_{\sqrt{3}} = \sqrt{3}$, and $\omega_2 = 2$ for the adjusted angular frequencies q_0 , q_1 , and q_2 , respectively. However, these dominant frequencies are useful starting values.

We begin in a fashion similar to that of Subsection 2.3.2 to find the nine gradient coefficients $c_0, c_1, \dots, c_8$ for the standard multimode PFC model. We build a system of nine equations with unknowns a_i , b_i , and q_i for $i = 0, 1, 2$. The first equation sets a value for $\widehat{C}_g(0)$. Three equations assign values to $\widehat{C}_g(1)$, $\widehat{C}_g(\sqrt{3})$, and $\widehat{C}_g(2)$, respectively. Two more equations establish the $\widehat{C}_g$ values for two intermediate angular frequencies, $\omega = \sqrt{2}$ and $\omega = \sqrt{\frac{7}{2}}$. We select the constants for these first six equations to produce a Fourier space curve similar in shape to that of the linear differential operator Fourier multiplier for the multimode model. However, for the Gaussian model, we seek an average minimum of approximately -20 , instead of 0 . This offset of 20 is added back as part of the modified $\epsilon = -0.15 + 20 = 19.85$ value. Hence, the Gaussian model Fourier space multiplier has an effective supremum of 19.85 , which provides good numerical stability. Finally, to ensure that there is a local minimum at each of the dominant angular frequencies, we set the derivative of $\widehat{C}_g$ to 0 for each of $\omega_1 = 1$, $\omega_{\sqrt{3}} = \sqrt{3}$, and $\omega_2 = 2$.

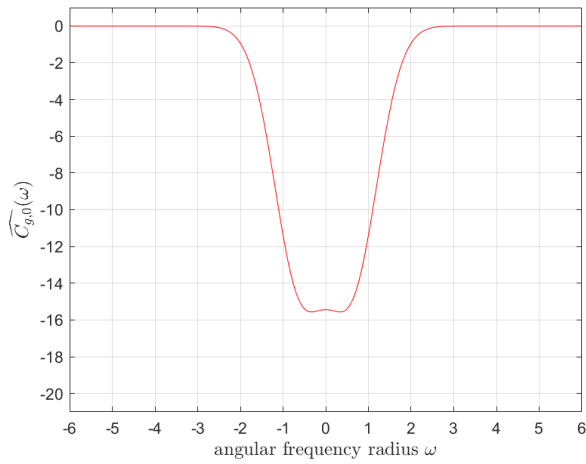
Unlike the standard multimode PFC model, these nine equations are nonlinear in terms of the nine parameters. Hence, we cannot use matrices to find the parameter values. First, many educated guesses are applied. The Hamiltonian Monte Carlo method is also used. When the initial guesses for the nine parameter values are close enough to the actual solution, we turn to the `FindRoot` function of Mathematica. Finally, Table 3.1a lists the proper values for a_i , b_i , and q_i , $i = 0, 1, 2$.

Now, the graphs for the individual Gaussian pairs for modes 0, 1, and 2 appear in Figures 3.2a, 3.2b, and 3.2c, respectively. Figure 3.2d provides the final form for the Fourier transform of the correlation function. To underscore the fact that the functions are even, we include function values for negative values of ω .

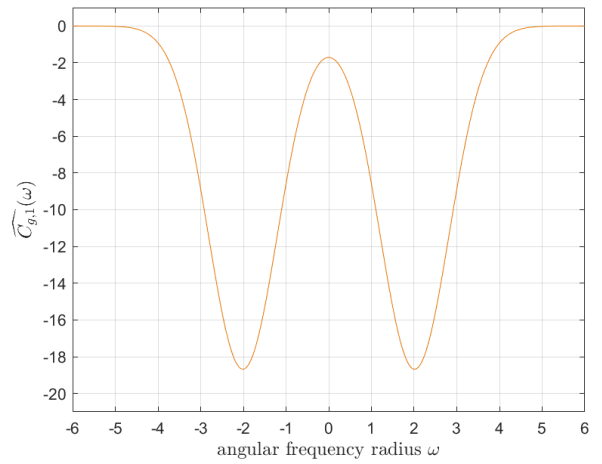
Next, Figures 3.3a, 3.3b, and 3.3c provide comparisons between the Fourier transform for the correlation function and the linear operator Fourier space multiplier for the standard multimode model. For a meaningful comparison, we multiply each Fourier space function by its corresponding λ value. In addition, we add the appropriate ϵ value. Since both Fourier space functions are even, the figures only include the function values for nonnegative ω . In Figure 3.3a, we see that the Gaussian model function approaches a supremum of 19.85 as ω grows larger. However, as a polynomial, the linear operator Fourier multiplier quickly climbs towards positive infinity. Computationally, this is a disadvantage of the standard multimode PFC model, because these large Fourier multiplier amplitudes can result in machine roundoff errors. Figure 3.3b reveals that the two Fourier functions have similar shapes and that the functions are equal at $\omega = 0$. Finally, Figure 3.3c focuses on the dominant angular frequencies. Note that, by design, the two Fourier space functions share the same values at the dominant angular frequencies $\omega_1 = 1$, $\omega_{\sqrt{3}} = \sqrt{3}$, and $\omega_2 = 2$ and at the intermediate angular frequency of $\omega = \sqrt{\frac{7}{2}} \approx 1.871$. The functions differ slightly at the intermediate angular frequency of $\omega = \sqrt{2} \approx 1.414$.

As with the standard multimode PFC model, the PDE for the Gaussian multimode PFC model is defined by

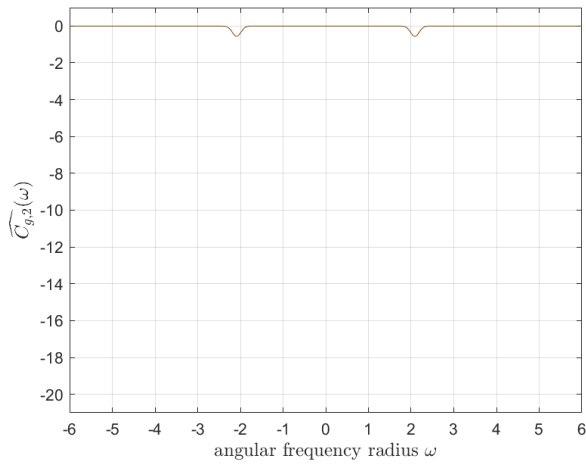
$$\dot{\psi} := \Delta \frac{\delta \mathcal{F}_g}{\delta \psi}. \quad (3.15)$$



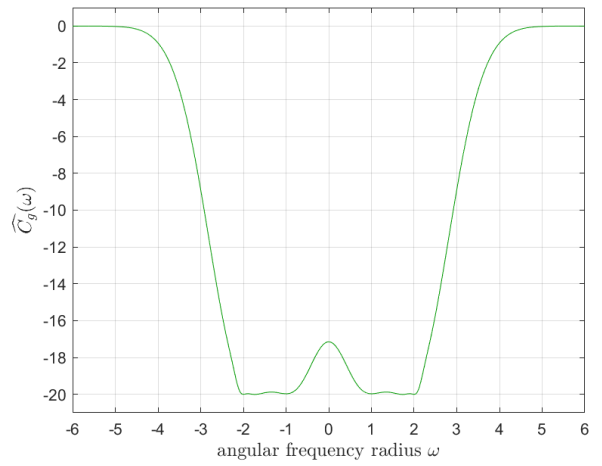
(a) $\widehat{C}_{g,0}(\omega)$



(b) $\widehat{C}_{g,1}(\omega)$

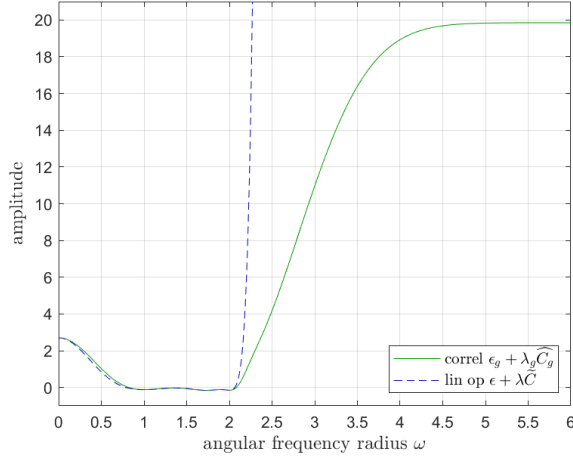


(c) $\widehat{C}_{g,2}(\omega)$

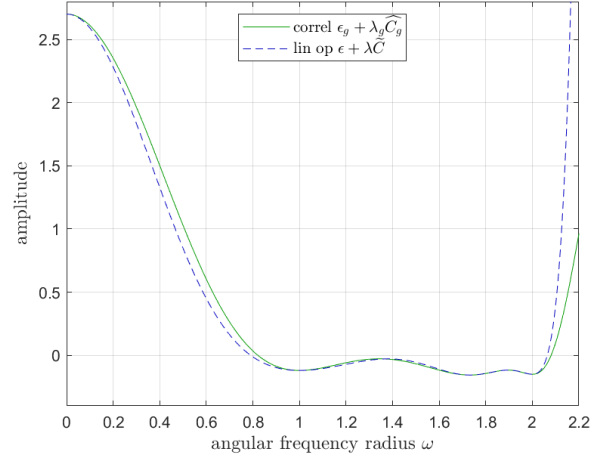


(d) $\widehat{C}_g(\omega)$

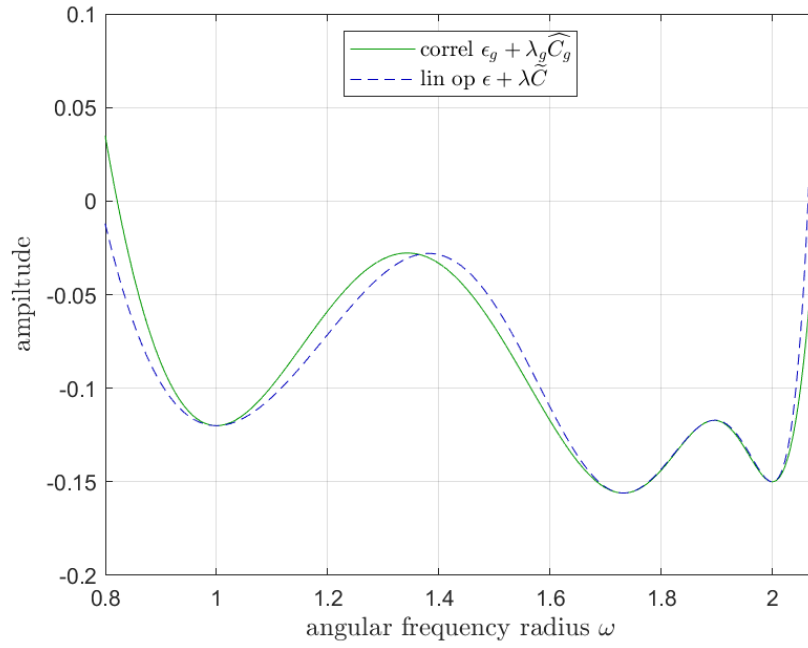
Figure 3.2: Correlation Function Fourier Transform Parts and Sum



(a) $\widehat{C}_g(\omega)$ vs. $\widetilde{C}(\omega)$, Wide View



(b) $\widehat{C}_g(\omega)$ vs. $\widetilde{C}(\omega)$, Middle View



(c) $\widehat{C}_g(\omega)$ vs. $\widetilde{C}(\omega)$, Narrow View

Figure 3.3: $\widehat{C}_g(\omega)$ vs. $\widetilde{C}(\omega)$

In addition, the vapor phase field is added to this Gaussian model in the same manner that it is added to the standard multimode PFC model. The same vapor phase parameter values are applied.

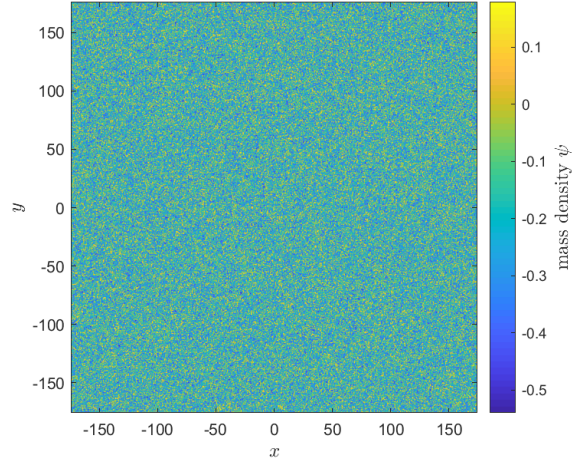
3.3 Gaussian Multimode PFC Simulation

We supply one simulation for the Gaussian multimode PFC model. Like the standard multimode PFC model simulation of Subsection 2.3.5, we start with a uniformly random mass density field. Figure 3.4a displays this initial field, while Figure 3.4b provides the mass density field at time 1,000. We see in Figure 3.4b various honeycomb geometry orientations and grain boundaries. The system is at its equilibrium at time 57,000. Figure 3.4c reveals the mass density field at this time. During the time span, some of the neighboring regions align and merge. However, many different orientations remain at the equilibrium state.

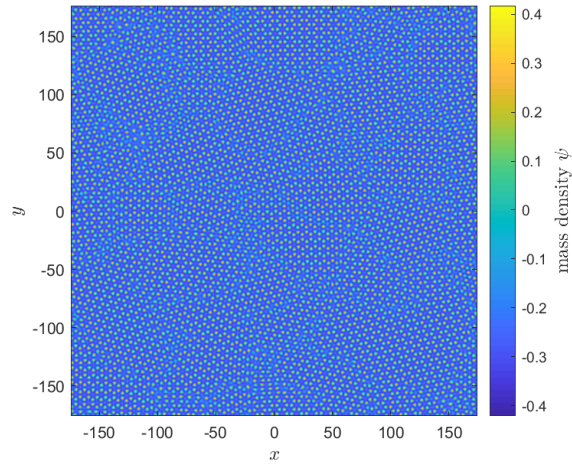
Figures 3.5a, 3.5b, and 3.5c provide the Fourier space spectrums for times 0, 1,000, and 57,000, respectively. For time 1,000, Figure 3.5b indicates that the frequency components are arranged in indistinct arcs with angular frequency radii near $\omega_1 = 1$, $\omega_{\sqrt{3}} = \sqrt{3}$, and $\omega_2 = 2$. At time 57,000, the arcs in Figure 3.5c are more tightly focused around those dominant angular frequency radii. However, due to the remaining variations in honeycomb geometry orientations in Figure 3.4c, we do not see a distinct triplet of frequency components for any of the dominant radii.

3.4 Gaussian Multimode PFC Model Summary

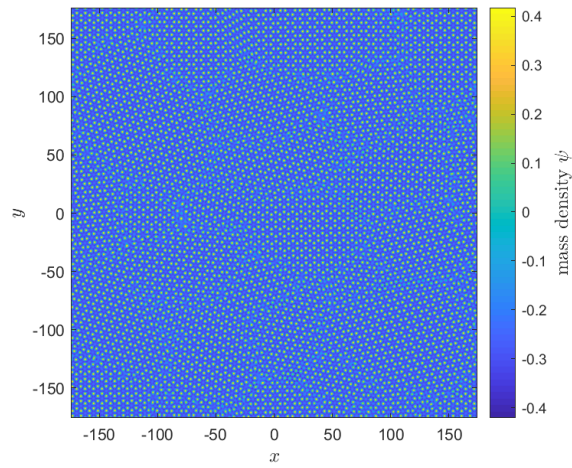
Overall, we find that the Gaussian multimode PFC model behaves very much like the standard multimode model. The Gaussian model has the advantage of a “natural” limit for the Fourier transform, where the standard model results in very large Fourier space amplitudes for large angular frequencies. However, for the Gaussian model, the process for finding useful values for the gradient free energy parameters is laborious. In addition, in two dimensions, there appears to be no explicit form for the real-space correlation function.



(a) Initial, Time = 0

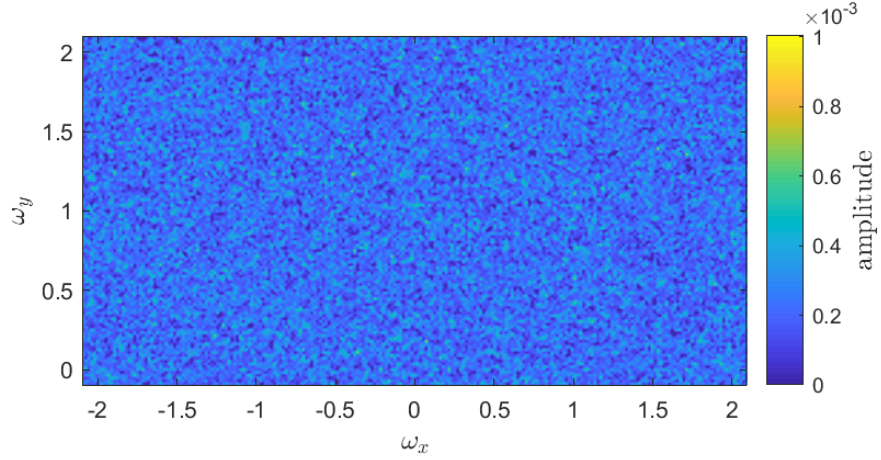


(b) Time = 1,000

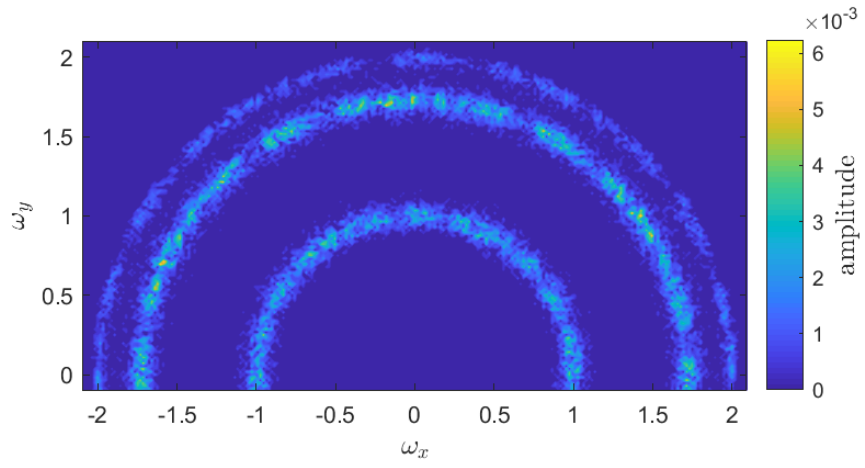


(c) Equilibrium, Time = 57,000

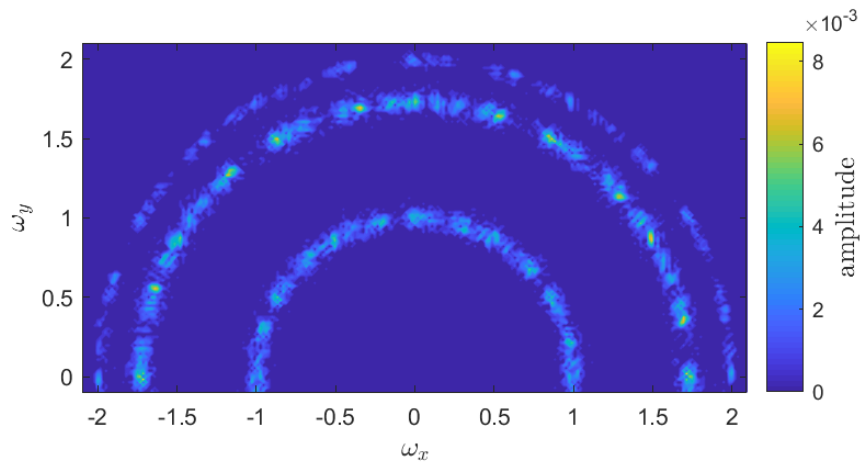
Figure 3.4: Gaussian Multimode PFC, Random Initial State, Mass Density Fields



(a) Initial, Time = 0



(b) Time = 1,000



(c) Equilibrium, Time = 57,000

Figure 3.5: Gaussian Multimode PFC, Random Initial State, Fourier Space Spectrums

Chapter 4

Surface Energy

The surface energy of a multiphase, homogeneous substance is the free energy generated by the interaction of different phases at their interfaces. Surface energy affects the size and shape of the solid regions of a substance. We refer to these solid regions as nanocrystals. First, we recall the explicit phase interface free energy functional for the multimode PFC model with vapor from (2.99) of Subsection 2.4.2:

$$\mathcal{F}_{int}(t; \eta) := \int_{\Omega} \left[W_v h(\eta) + \frac{\kappa_v}{2} |\nabla \eta|^2 \right] d\mathbf{x}. \quad (4.1)$$

The corresponding interface free energy density, as given in (2.97), is

$$f_{int}(\eta) := W_v h(\eta) + \frac{\kappa_v}{2} |\nabla \eta|^2. \quad (4.2)$$

Note that this free energy is isotropic. It is independent of the direction of crystal growth. We use the descriptor “explicit” to emphasize that the surface energy includes free energy from additional sources. Regardless, the two terms of the phase interface free energy density (4.2) are the primary contributors to the surface free energy.

Now, Section 4.1 illustrates common facets for honeycomb crystal geometry. These include the common armchair and zigzag facets, along with the alternative “top-to-top” and “left-to-right” facets. In Section 4.2, we describe the crystal seeds, or initial solid regions, that we use throughout this study, while viewing sample simulation field plots. In Section

4.3, we investigate a phase field minimizer for the phase interface free energy. Next, we use the solid-vapor common tangent line equation from Section 2.5 to develop an intuitive and meaningful formula for the calculation of the surface energy in Section 4.4.

In Section 4.5, we analyze the periodicity of the surface energies for initial vertical band seeds of increasing widths. We apply the armchair and zigzag facets and find that the surface energies are cyclical in space with periods proportional to the corresponding unit cell sizes. Section 4.6 compares the surface energies for the armchair and zigzag facets for two different phase interface energy levels. In Section 4.7, we consider the surface energies for the top-to-top and left-to-right facets. Section 4.8 explores the minimum and maximum surface energies for the armchair and zigzag facets. Overall, we find that the zigzag facet is more energetically stable than the armchair facet. Note that initial band seeds are employed for all of the simulations in Sections 4.5, 4.6, 4.7, and 4.8.

In Section 4.9, we investigate simulations where the initial seeds are disks. We vary the phase interface energy coefficients, W_v and κ_v , to analyze their effects on the nanocrystal sizes and shapes over time. In addition, we compare the varying levels of isotropy, which is influenced by the honeycomb geometry. Finally, Section 4.10 explores simulations where the initial seeds are vertical with sinusoidal phase interfaces on the left and right. We compare these results to those of the disk seeds from Section 4.9. Sections 4.9 and 4.10 serve to corroborate the facet observations of Sections 4.6 and 4.7.

The work in this chapter is based upon and is an extension of the honeycomb PFC surface energy work done by Dr. Ken R. Elder [4].

4.1 Facets and Unit Cells

The most common honeycomb facets, or faces “seen from the vapor region”, are the armchair and zigzag facets. We also investigate two additional facets: “top-to-top” and “left-to-right”. These titles are explained later. For each facet, we designate a unit cell, which fulfills the following requirements:

1. The unit cell is rectangular.

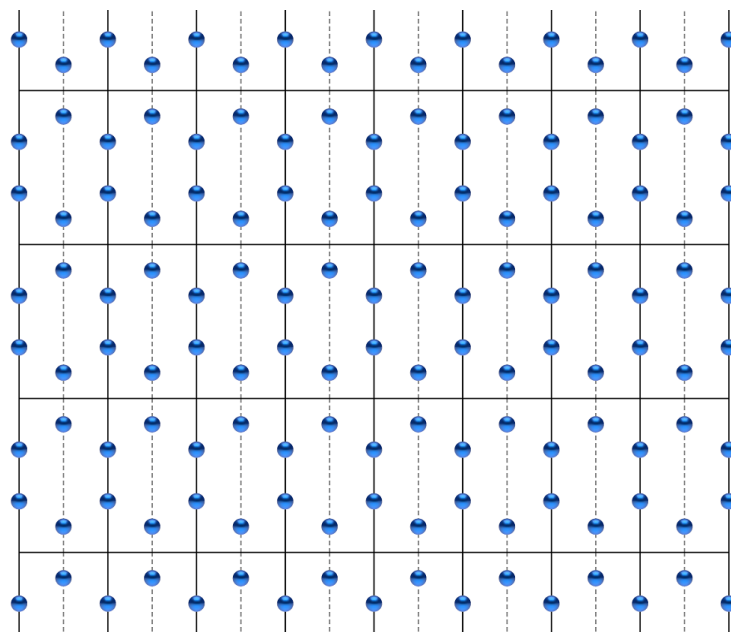


Figure 4.1: Armchair Facet with Delineated Unit Cells

2. The left and right boundaries of the unit cell are parallel to the facet.
3. The unit cell is of a minimal size, such that the cells can be tiled to create a perfect honeycomb geometry.

For each facet, there are uncountably many unit cells that satisfy these three requirements. We choose ones that provide straightforward visual interpretations.

The blue spheres in the facet figures represent atoms. In each of the facet diagrams, there is a vertical facet on the left and on the right. A vapor region borders the crystal on these two sides. The unit cells are delineated by solid lines. The vertical solid and dashed lines designate the geometric periodicity; that is, facets lying along the vertical lines are equivalent. This equivalency can be demonstrated by superimposing two copies of the geometry and sliding one of them up or down to align the copies.

Figure 4.1 illustrates the armchair facet. The name “armchair” is applied, because the facet appears to be a sequence of seats, each with individual arm rests. Note that, if growth occurs, each atom along the facet forms one bond with one “new” atom. Each atom in the new layer is bonded to one other new atom.

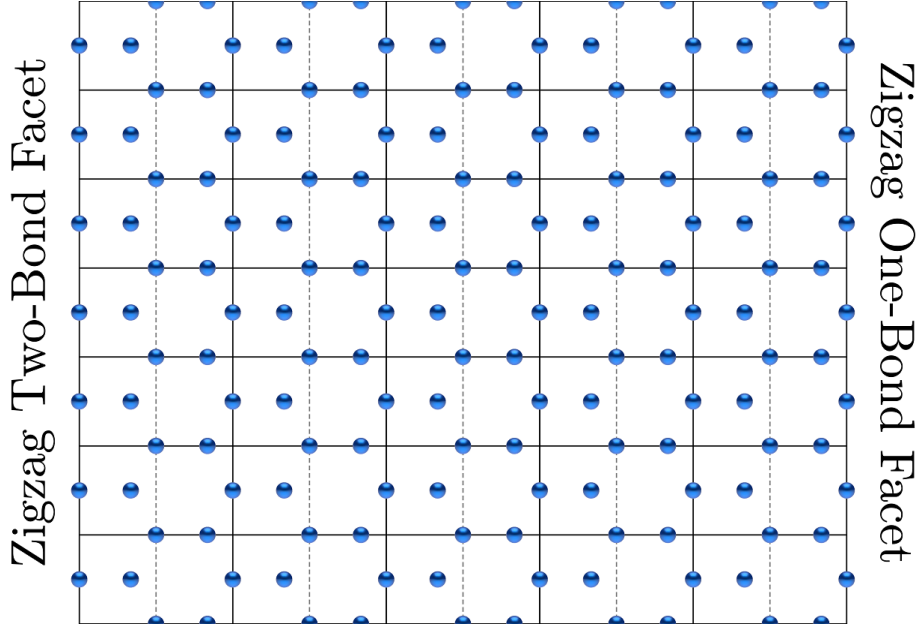


Figure 4.2: Zigzag Facet with Delineated Unit Cells

Next, Figure 4.2 reveals the zigzag facet. There are two stages for the zigzag facet. The facet on the right demonstrates the one-bond stage. During growth, each atom along this facet forms one bond with one new atom. The new atoms are not bonded directly to each other. The facet on the left represents the two-bond stage. When a new layer forms, each atom along this facet bonds to two new atoms. Therefore, each facet atom forms two bonds. Each new atom bonds to two facet atoms. Again, the atoms of the new layer do not bond directly to each other.

The zigzag facet may be obtained by rotating the line for the armchair facet clockwise or counterclockwise by $\frac{\pi}{6}$ radians, or 30° . The same holds for transitioning from the zigzag to the armchair facet. This angle arises from the geometry of a regular hexagon.

The top-to-top facet appears in Figure 4.3. To obtain this facet graphically, we begin with the crystal orientation for the armchair facet in Figure 4.1. One method is to rotate this crystal clockwise by $\tan^{-1}\left(\frac{\sqrt{3}}{9}\right)$ radians. (Note that $\tan^{-1}\left(\frac{\sqrt{3}}{9}\right) \approx \frac{2}{33}\pi \approx 10.9^\circ$.) Then, the facet is formed by drawing a vertical line. For the second method, we start by picking an adjacent pair of vertical atoms in Figure 4.1. Next, we draw a line segment from the top

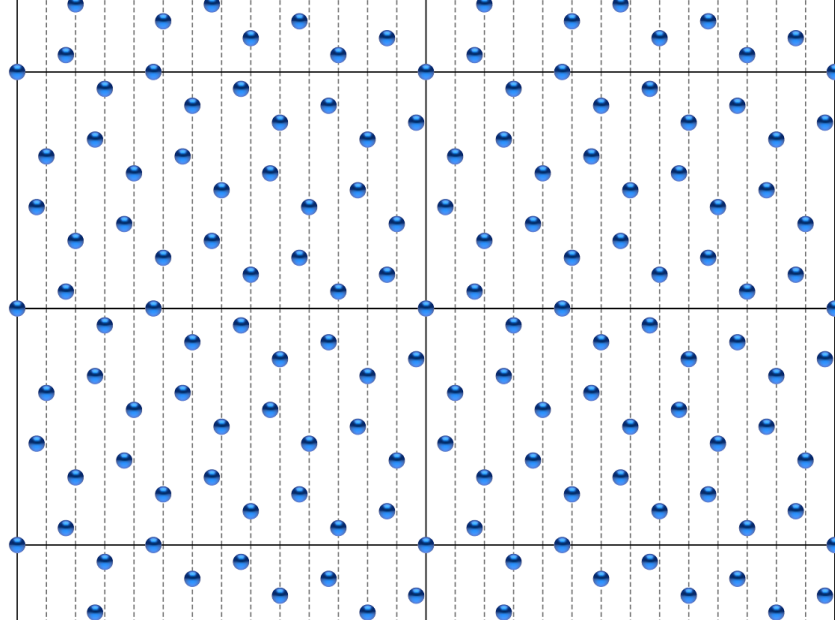


Figure 4.3: Top-to-Top Facet with Delineated Unit Cells

atom of the pair to the top atom of the vertically adjacent pair that is one half of a cell to the left and two pairs up. This gives us the facet name “top-to-top”.

Figure 4.4 displays the left-to-right facet. To produce this facet, we begin with the crystal orientation for the zigzag facet in Figure 4.2. For the first method, we rotate this crystal clockwise by $\tan^{-1}\left(\frac{\sqrt{3}}{9}\right)$ radians and draw a vertical line to form the left-to-right facet. Alternatively, we pick an adjacent pair of horizontal atoms in Figure 4.2. We then draw a line segment from the left atom of the pair to the right atom of the horizontally adjacent pair that is one and a half cells up and immediately to the left. This gives us the facet name “left-to-right”.

Note that the left-to-right facet may be generated by rotating the line for the top-to-top facet clockwise or counterclockwise by $\frac{\pi}{6}$ radians, or 30° . We may obtain the top-to-top facet by rotating the left-to-right facet line in the same way.

For the armchair facet simulations, the honeycomb geometry unit cell width is $\frac{4\pi}{\sqrt{3}}$ and the height is 4π . This is determined by the $c_0, c_1, \dots, c_8$ coefficients of the gradient portion of the free energy density. These coefficient values appear in Table 2.2a of Subsection 2.3.1. The armchair unit cell dimensions are switched for the unit cell of the zigzag facet simulations.

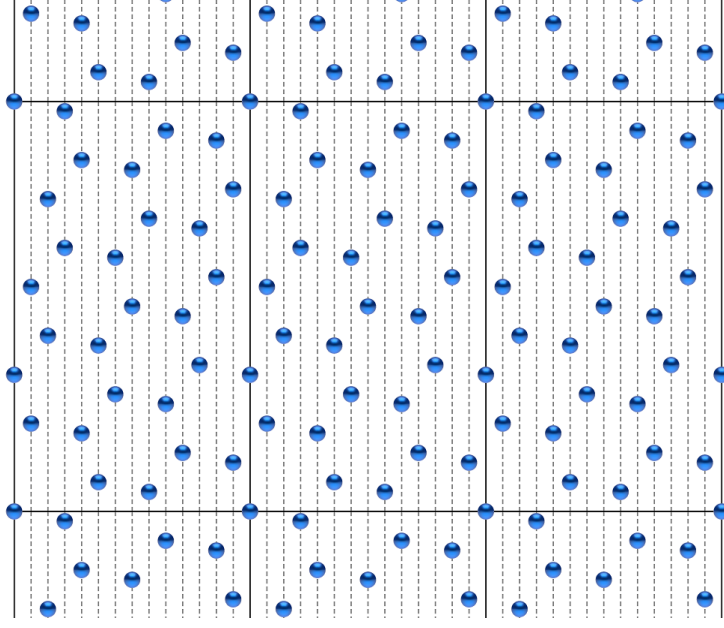


Figure 4.4: Left-to-Right Facet with Delineated Unit Cells

The unit cell for the top-to-top facet has a width of $4\pi\sqrt{7}$ and a height of $4\pi\sqrt{\frac{7}{3}}$. Swapping the dimensions for the top-to-top unit cell yields the dimensions for the left-to-right unit cell. Note that, for each facet, the width and height differ by a factor of $\sqrt{3}$.

4.2 The Simulations

In this surface energy study, we run each simulation until the free energy decreases and levels out; that is, we allow the system to reach its free energy equilibrium point - a minimum energy state. Unless it is otherwise noted, all of the field plots in this chapter represent the corresponding systems at equilibrium.

At time $t = 0$, the initial crystal, or solid, region is called the seed. Most of our simulations begin with a central band of crystal solid running from the top to the bottom of the computational box. The left and right sides are vapor. Figure 4.5 is an example of the initial mass density field for a band seed with armchair facets. We also examine simulations where the seed is a disk or the seed has sinusoidal phase interfaces. The hyperbolic tangent function is used to achieve initial smoothness at phase interfaces.

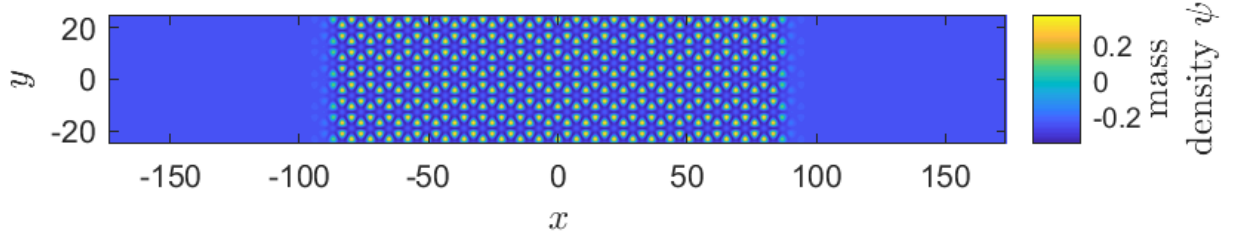


Figure 4.5: Band, Armchair, Initial Mass Density Field, Seed Multiple = 12.082461

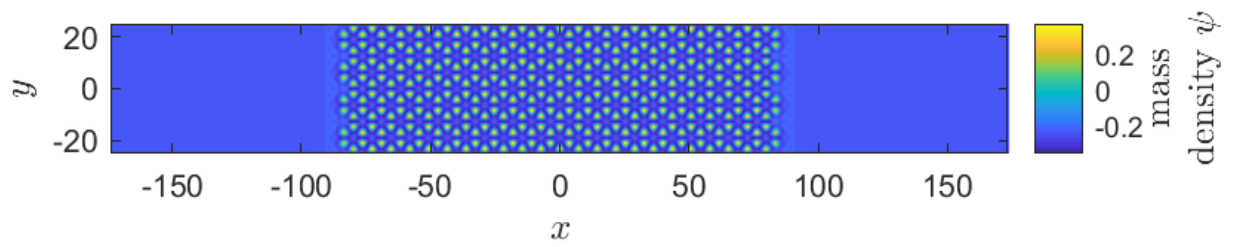
For the armchair and zigzag “band” simulations, the computational box is 48 unit cells wide and, with the exception of the examples in this section, one unit cell in height. For the armchair facet simulations, this gives us box dimensions of $l_x = 48 \frac{4\pi}{\sqrt{3}} \approx 348.249$ and $l_y = 4\pi \approx 12.566$. For the zigzag simulations, we have $l_x = 48 \cdot 4\pi \approx 603.186$ and $l_y = \frac{4\pi}{\sqrt{3}} \approx 7.255$. As the unit cells for the top-to-top and left-to-right facets are much wider, we select computational boxes that are only 20 unit cells in width. For the top-to-top band simulations, the box dimensions are $l_x = 20 \cdot 4\pi\sqrt{7} \approx 664.950$ and $l_y = 4\pi\sqrt{\frac{7}{3}} \approx 19.195$. For the left-to-right facet, the dimensions are $l_x = 20 \cdot 4\pi\sqrt{\frac{7}{3}} \approx 383.909$ and $l_y = 4\pi\sqrt{7} \approx 33.247$.

Initially, the number of unit cells between the y -axis and the left facet and the number between the y -axis and the right facet is exactly the same. We refer to this initial horizontal-center-to-facet cell count as the “seed multiple”. We identify each simulation by its initial *seed multiple* value. The word “initial” is often omitted for brevity.

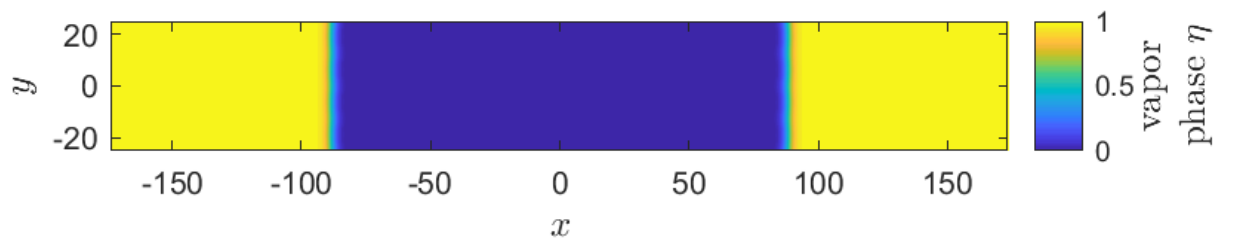
For the simulation sample results in this section, we use the phase interface coefficient values $W_v = 0.1$ and $\kappa_v = 0.4455$. For the band seed examples here, the computational box is more than one unit cell in height to provide more detail.

In Figure 4.6, we find the three fields for a band seed, armchair facet simulation at equilibrium. The first field is the mass density, the second is the vapor phase, and last field is the free energy density field. These plots correspond to the initial mass density field of Figure 4.5, where the initial seed multiple is 12.082461. Recall that the phase field η is 0 in solid regions and 1 in vapor regions.

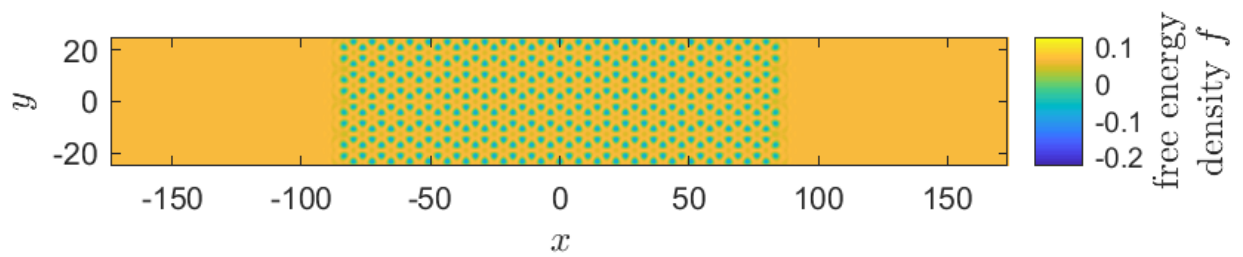
Figure 4.7a provides the mass density field for a zigzag facet, one-bond stage simulation at equilibrium, where the seed multiple is 12.174697. Figure 4.7b represents the same field



(a) Mass Density Field

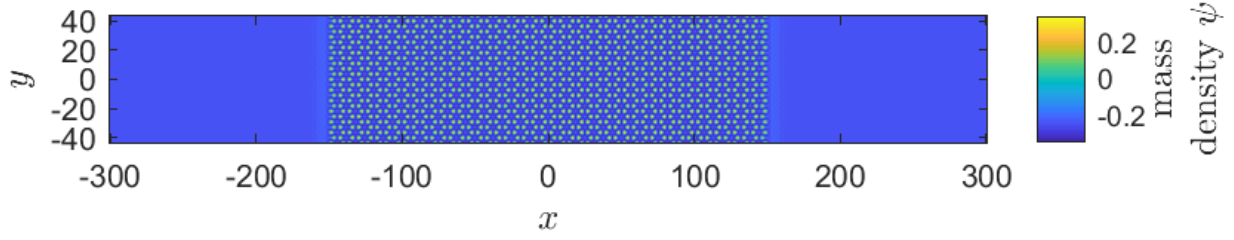


(b) Vapor Phase Field

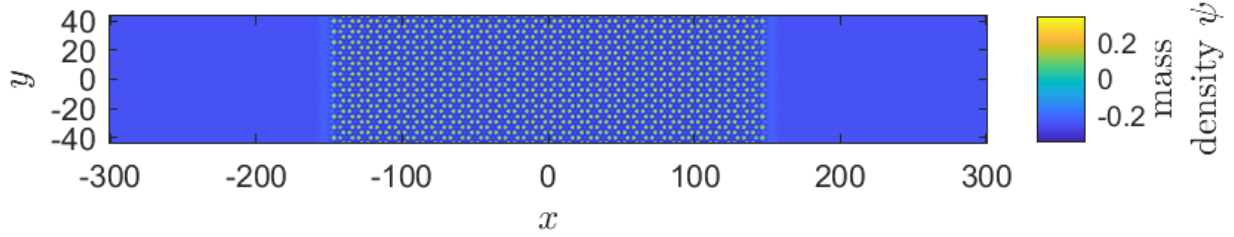


(c) Free Energy Density Field

Figure 4.6: Band Seed, Armchair Facet Fields, Seed Multiple = 12.082461



(a) One-Bond Stage, Seed Multiple = 12.174697



(b) Two-Bond Stage, Seed Multiple = 12.060525

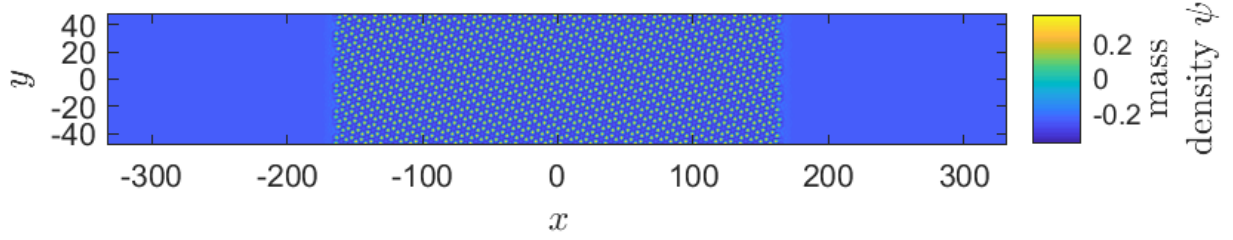
Figure 4.7: Band Seed, Zigzag Facets, Mass Density Fields

for the zigzag, two-bond facet with seed multiple 12.060525. The vapor phase and free energy density fields are omitted for these facets. However, they are analogous to the phase and free energy fields of Figure 4.6.

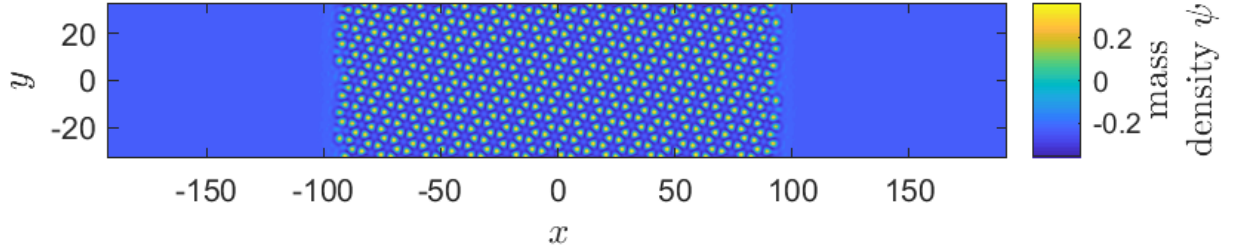
Figure 4.8a is the mass density field for the top-to-top facet with seed multiple 5.0420255, and Figure 4.8b provides the mass density field for the left-to-right facet with a seed multiple of 5.0320470.

Although using initial seed multiples to differentiate between similar simulations may seem somewhat arbitrary, it is a consistent and useful way to compare the surface energies for different facets. Furthermore, for many of the simulations, the initial solid mean density and the initial vapor density are at their respective free energy equilibrium points. For such simulations, the number of unit cells between the y -axis and either facet changes little. Note that the significance of the particular band seed multiples of this section are discussed in subsequent sections.

We also include simulations for disk seeds. Figure 4.9 shows the initial and equilibrium mass density fields for such a simulation. For all disk seed simulations, the facet along



(a) Top-to-Top Facet, Seed Multiple = 5.0420255



(b) Left-to-Right Facet, Seed Multiple = 5.0320470

Figure 4.8: Band Seed, Alternative Facets, Mass Density Fields

each vertical line is the armchair facet. Using the unit cell width for the armchair facet, we say that the initial radius seed multiple or, simply, seed multiple, for the simulation of Figure 4.9 is 16. Hence, the term “seed multiple” shares the same meaning for both band and disk simulations. For all disk seed simulations, the computational box dimensions are $l_x = 64 \frac{4\pi}{\sqrt{3}} \approx 464.333$ and $l_y = 37 \cdot 4\pi \approx 464.956$.

Finally, we incorporate simulations for sinusoidal front seeds. For half of the simulations, the mass density fields are symmetric about the y -axis, and, within the computational box, the nanocrystals are concave on the left and right sides. Figures 4.10a and 4.10b display the initial and equilibrium mass fields, respectively, for such a simulation. In this example, the armchair facet happens to lie along each vertical line. For the other half of the sinusoidal front simulations, the mass densities are asymmetric about the y -axis, and the nanocrystals are convex on the left and concave on the right. Figures 4.10c and 4.10d display initial and equilibrium mass fields, respectively, for an asymmetric simulation. Here, the zigzag facet lies along the vertical.

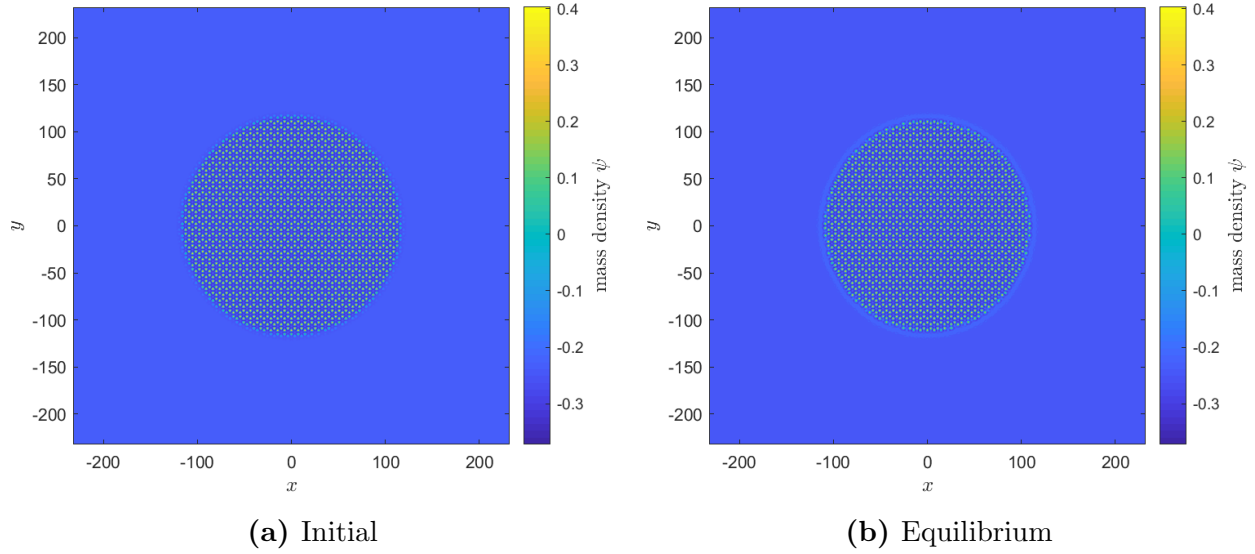
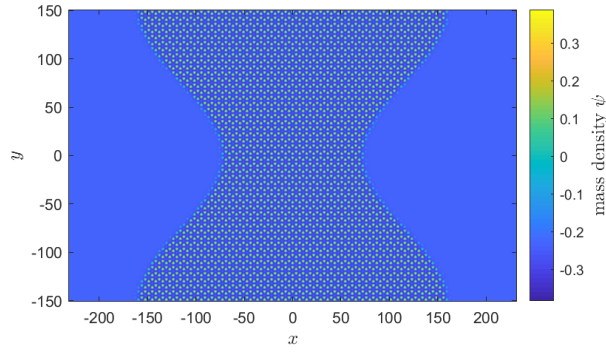
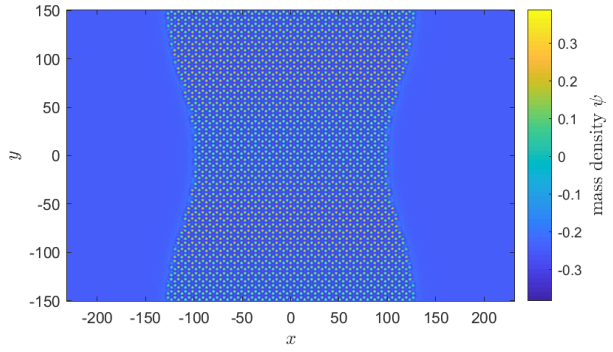


Figure 4.9: Disk Seed, Mass Density Fields, Seed Multiple = 16

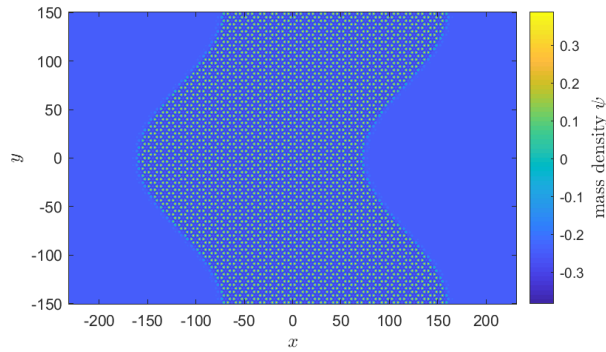
To find the initial seed multiple for each sinusoidal simulation, we begin with the average horizontal distance between the horizontal center and the phase interface. For simulations where the armchair facet lies along the vertical, we divide this average distance by the armchair facet unit cell width to find the seed multiple. When the zigzag facet lies on the vertical, we divide the average horizontal distance by the zigzag facet unit cell width. This approach is similar to the method for finding the seed multiple for standard band seeds, except that, since the phase interface is curved, we use the average horizontal distance between the horizontal center and the interface. Therefore, the usage of the term “seed multiple” is consistent for band, disk, and sinusoidal seeds. Note that the initial seed multiple is 16 for both of the simulations given in Figure 4.10. For sinusoidal simulations where the armchair facet lies along the vertical, the computational box dimensions are $l_x = 64 \frac{4\pi}{\sqrt{3}} \approx 464.333$ and $l_y = 24 \cdot 4\pi \approx 301.593$. The box dimensions are the same when the zigzag facet aligns with the vertical. However, for the zigzag case, the lengths are calculated differently. We have $l_x = \frac{64}{\sqrt{3}} 4\pi \approx 464.333$ and $l_y = 24\sqrt{3} \frac{4\pi}{\sqrt{3}} \approx 301.593$.



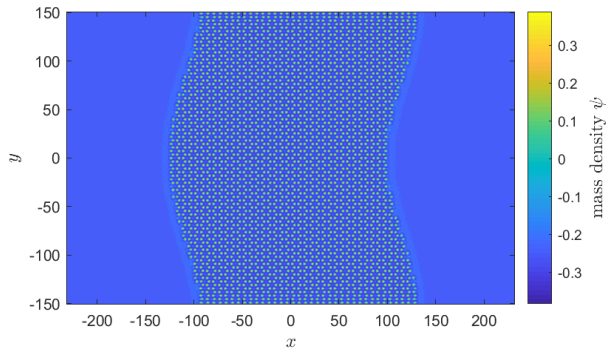
(a) Symmetric Armchair, Initial



(b) Symmetric Armchair, Equilibrium



(c) Asymmetric Zigzag, Initial



(d) Asymmetric Zigzag, Equilibrium

Figure 4.10: Sinusoidal Front Seeds, Mass Density Fields, Seed Multiple = 16

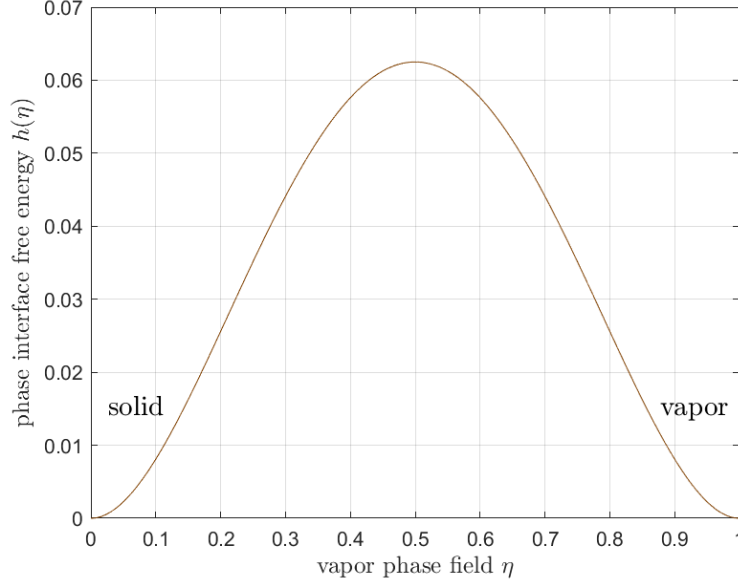


Figure 4.11: Double-Well, Phase Interface Function

4.3 Phase Interface Energy Minimization

In this section, we seek a minimizing vapor phase field for the explicit phase interface free energy from the multimode PFC model with vapor phase. This work was prompted by the minimizer found by Li, Choi, and Kim [14].

Let η be the vapor phase field, where $\eta = 0$ indicates the solid phase, and $\eta = 1$ indicates the vapor phase. Let W_v be a positive parameter that determines the level of resistance to the coexistence of phases, and let κ_v be a positive parameter that governs the resistance to sharp changes in η across space.

Let the double-well, phase interface free energy function be

$$h(\eta) := \eta^2 (\eta - 1)^2 = \eta^4 - 2\eta^3 + \eta^2. \quad (4.3)$$

This double-well function is shown in Figure 4.11.

Now, the explicit phase interface free energy for the PFC model with vapor (NIST model) is

$$\mathcal{F}_{int}(\eta) := \int_{\mathbb{R}^2} \left[W_v h(\eta) + \frac{\kappa_v}{2} |\nabla \eta|^2 \right] d\mathbf{x}. \quad (4.4)$$

We refer to this phase interface energy as explicit, because the total surface free energy, or the total free energy resulting from the presence of phase interfaces, manifests itself in additional ways. These include metastable equilibrium states and nanocrystal shapes that do not minimize the surface area.

4.3.1 One-Dimensional Case

We first focus on the one-dimensional case, where

$$\mathcal{F}_{int}(\eta) = \int_{-\infty}^{\infty} \left[W_v h(\eta) + \frac{\kappa_v}{2} \left(\frac{\partial \eta}{\partial x} \right)^2 \right] dx. \quad (4.5)$$

Since both $W_v h(\eta)$ and $\frac{\kappa_v}{2} \left(\frac{\partial \eta}{\partial x} \right)^2$ are nonnegative, $\mathcal{F}_{int}(\eta)$ is nonnegative. Due to the $W_v h(\eta)$ term, we expect that minimizers should consist of regions where η is close to 0 or to 1. To minimize $\frac{\kappa_v}{2} \left(\frac{\partial \eta}{\partial x} \right)^2$, phase transitions should be infrequent and should not be sharp. For cases where regions of both vapor and solid exist, these two free energy density terms work at cross purposes, and a balance must be found.

The trivial minimizers are given by the constant fields $\eta = 0$, where the entire field is solid, and $\eta = 1$, where the entire field is vapor. For both of these cases, the free energy is 0. No other field η produces 0 free energy.

4.3.1.1 Single Phase Interface Minimizer

Our primary goal is to prove that nonconstant phase fields of the form

$$\eta_1(x) := \frac{1}{2} \left(1 \pm \tanh \left(\sqrt{\frac{W_v}{2\kappa_v}} (x - c) \right) \right) \quad (4.6)$$

minimize $\mathcal{F}_{int}(\eta)$. For fields of this form, there is exactly one phase interface. Here, the real number c is the center point of the phase interface. Figure 4.12 shows the fields of η_1 for $W_v = \kappa_v = 1$ and $c = 0$.

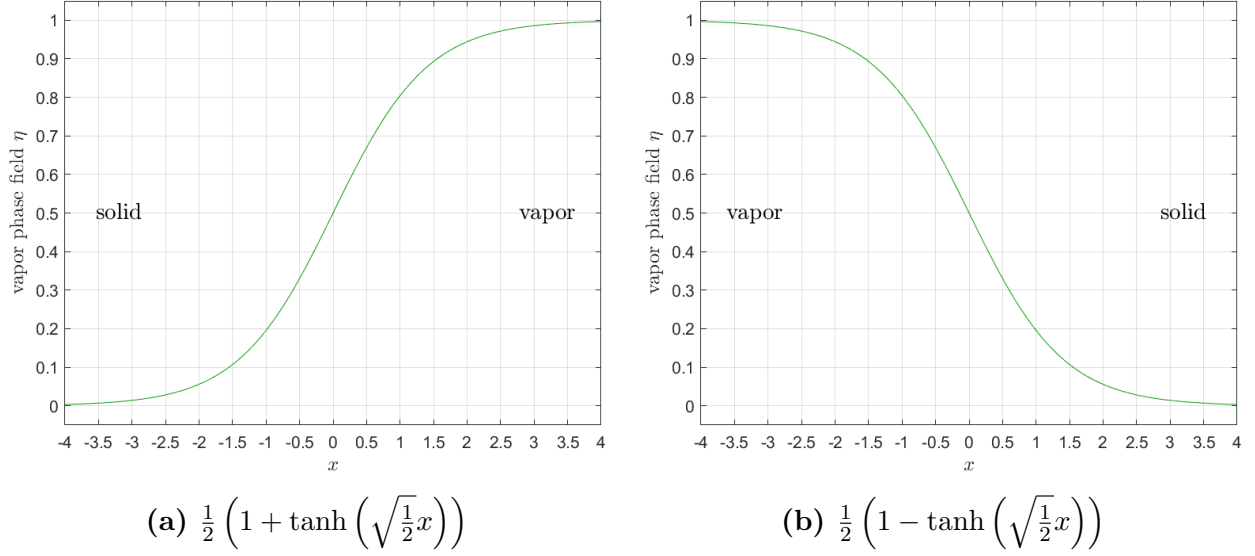


Figure 4.12: Hyperbolic Tangent, Vapor Phase η_1 Fields

By the properties of functional derivatives, (4.5) gives us

$$\frac{\delta \mathcal{F}_{int}}{\delta \eta} = W_v h'(\eta) - \kappa_v \frac{d^2 \eta}{dx^2}, \quad (4.7)$$

where $h'(\eta) = 4\eta^3 - 6\eta^2 + 2\eta$. Hence, the minimizing function must satisfy the equation

$$W_v h'(\eta) - \kappa_v \frac{d^2 \eta}{dx^2} = 0. \quad (4.8)$$

Applying (4.6) and using the identities of hyperbolic functions, we have

$$W_v h'(\eta_1(x)) = \pm \frac{W_v}{2} \text{sech}^2 \left(\sqrt{\frac{W_v}{2\kappa_v}} (x - c) \right) \tanh \left(\sqrt{\frac{W_v}{2\kappa_v}} (x - c) \right). \quad (4.9)$$

Now,

$$\frac{d\eta_1}{dx}(x) = \pm \frac{1}{2} \sqrt{\frac{W_v}{2\kappa_v}} \text{sech}^2 \left(\sqrt{\frac{W_v}{2\kappa_v}} (x - c) \right), \quad (4.10)$$

and, so,

$$\frac{d^2 \eta_1}{dx^2}(x) = \pm \frac{W_v}{2\kappa_v} \text{sech}^2 \left(\sqrt{\frac{W_v}{2\kappa_v}} (x - c) \right) \tanh \left(\sqrt{\frac{W_v}{2\kappa_v}} (x - c) \right). \quad (4.11)$$

Hence,

$$\kappa_v \frac{d^2 \eta}{dx^2}(x) = \pm \frac{W_v}{2} \operatorname{sech}^2 \left(\sqrt{\frac{W_v}{2\kappa_v}}(x - c) \right) \tanh \left(\sqrt{\frac{W_v}{2\kappa_v}}(x - c) \right). \quad (4.12)$$

Since (4.9) and (4.12) are identical, we have

$$W_v h'(\eta_1) - \kappa_v \frac{d^2 \eta_1}{dx^2} = 0. \quad (4.13)$$

Therefore, functions that match the form η_1 are minimizers for the case where there is exactly one phase interface.

4.3.1.2 Minimum Explicit Phase Interface Free Energy

We now find the minimum phase interface free energy for (4.6).

Inserting (4.6) into the first term of the energy density (integrand) of (4.5) and applying hyperbolic function identities gives us

$$W_v h(\eta_1(x)) = \frac{W_v}{16} \operatorname{sech}^4 \left(\sqrt{\frac{W_v}{2\kappa_v}}(x - c) \right). \quad (4.14)$$

Squaring (4.10), we discover that the second term of the energy density yields the same function:

$$\frac{\kappa_v}{2} \left(\frac{d\eta_1}{dx}(x) \right)^2 = \frac{W_v}{16} \operatorname{sech}^4 \left(\sqrt{\frac{W_v}{2\kappa_v}}(x - c) \right). \quad (4.15)$$

Hence,

$$\mathcal{F}_{int}(\eta_1) = \int_{-\infty}^{\infty} \frac{W_v}{8} \operatorname{sech}^4 \left(\sqrt{\frac{W_v}{2\kappa_v}}(x - c) \right) dx. \quad (4.16)$$

Now, for all $a \neq 0$,

$$\int_{-\infty}^{\infty} \operatorname{sech}^4(a(x - c)) dx = \frac{4}{3a}, \quad (4.17)$$

and, so,

$$\mathcal{F}_{int}(\eta_1) = \frac{\sqrt{2W_v\kappa_v}}{6}. \quad (4.18)$$

Therefore, the minimum explicit phase interface free energy is directly proportional to $\sqrt{W_v}$ and to $\sqrt{\kappa_v}$.

Note that, for the special case where $W_v\kappa_v = 18$, this minimum energy is 1.

4.3.1.3 Minimizer Phase Interface Thickness

Since (4.6) never reaches its horizontal asymptotes 0 (solid) or 1 (vapor), the phase interface thickness for this field is not well-defined. However, the reciprocal of the magnitude of the slope at $x = c$ can be used as a benchmark.

Since $\text{sech}(0) = 1$, replacing x by c in (4.10) gives us the slope

$$\frac{d\eta_1}{dx}(c) = \pm \frac{1}{2} \sqrt{\frac{W_v}{2\kappa_v}}. \quad (4.19)$$

We define the minimizer phase interface thickness to be the reciprocal of the magnitude of this slope:

$$\delta_{int} := 2 \sqrt{\frac{2\kappa_v}{W_v}}. \quad (4.20)$$

By (4.6), for all positive W_v and κ_v ,

$$\eta_1\left(c + \frac{\delta_{int}}{2}\right) = \frac{1}{2} (1 \pm \tanh(1)), \quad (4.21)$$

and

$$\eta_1\left(c - \frac{\delta_{int}}{2}\right) = \frac{1}{2} (1 \pm \tanh(-1)) = \frac{1}{2} (1 \mp \tanh(1)). \quad (4.22)$$

The corresponding η_1 values are approximately 0.88079708 and $0.11920292 = 1 - 0.88079708$. Note, also, that $\frac{1}{2}(1 - \tanh(1))$ and $\frac{1}{2}(1 + \tanh(1))$ are equidistant from $\frac{1}{2}$. We adopt these values as convenient thresholds for the calculation of the phase interface thickness. Hence, for all positive W_v and κ_v , δ_{int} is the distance between the x -values, for which $\eta_1 = \frac{1}{2}(1 - \tanh(1))$ and $\eta_1 = \frac{1}{2}(1 + \tanh(1))$. Figure 4.13 labels the thickness for $W_v = \kappa_v = 1$ and $c = 0$.

Regardless of our threshold selections for η_1 , we see that the minimizer phase interface thickness is directly proportional to $\sqrt{\kappa_v}$ and inversely proportional to $\sqrt{W_v}$.

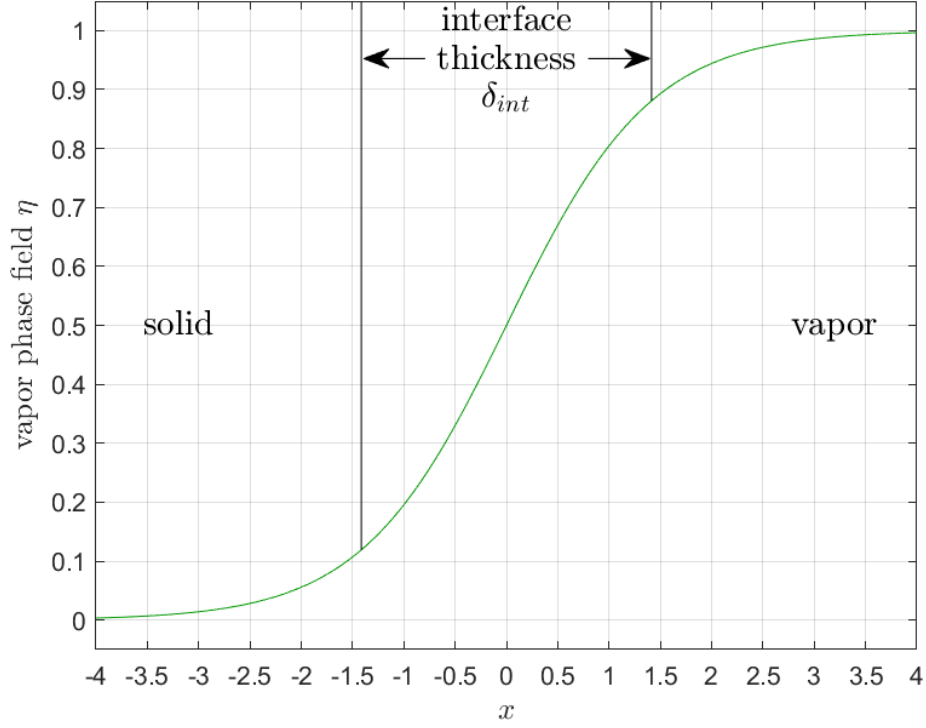


Figure 4.13: Minimizer Phase Interface Thickness, δ_{int}

4.3.1.4 Comparison of the Minimizer to Similar Field Forms

We consider two other phase fields that are similar in shape to (4.6). Both are piecewise functions that are differential everywhere. WLOG, we center the interface at $x = 0$ and consider only nondecreasing function forms. First, the minimizer becomes

$$\eta_{\tanh}(x) := \frac{1}{2} \left(1 + \tanh \left(\sqrt{\frac{W_v}{2\kappa_v}} x \right) \right) \quad \text{for all } x \in \mathbb{R}. \quad (4.23)$$

We next define a sinusoidal piecewise field:

$$\eta_{sine}(x) := \begin{cases} 0 & x < -\sqrt{\frac{2\kappa_v}{3W_v}} \pi \\ \frac{1}{2} \left(1 + \sin \left(\sqrt{\frac{3W_v}{8\kappa_v}} x \right) \right) & -\sqrt{\frac{2\kappa_v}{3W_v}} \pi \leq x \leq \sqrt{\frac{2\kappa_v}{3W_v}} \pi \\ 1 & x > \sqrt{\frac{2\kappa_v}{3W_v}} \pi \end{cases} \quad (4.24)$$

The coefficients and piecewise intervals in (4.24) minimize uniquely the explicit phase interface free energy for this sinusoidal form. Thirdly, we define a third-degree polynomial field:

$$\eta_{poly}(x) := \begin{cases} 0 & x < -\sqrt{\frac{1001\kappa_v}{162W_v}} \\ \frac{1}{2} \left(1 + \frac{3}{2} \sqrt{\frac{162W_v}{1001\kappa_v}} x - \frac{1}{2} \left(\sqrt{\frac{162W_v}{1001\kappa_v}} x \right)^3 \right) & -\sqrt{\frac{1001\kappa_v}{162W_v}} \leq x \leq \sqrt{\frac{1001\kappa_v}{162W_v}} \\ 1 & x > \sqrt{\frac{1001\kappa_v}{162W_v}} \end{cases} \quad (4.25)$$

Again, the coefficients and intervals of (4.25) minimize the free energy for this polynomial form. Note that neither (4.24) nor (4.25) satisfies the requirement of (4.8). Figure 4.14 displays the three fields for $W_v = \kappa_v = 1$.

From (4.18), we know that the explicit phase interface free energy for the hyperbolic tangent form is

$$\mathcal{F}_{tanh} := \frac{\sqrt{2}}{6} \sqrt{W_v \kappa_v}. \quad (4.26)$$

By similar means, we find the energies for the sinusoidal form and the polynomial form to be

$$\mathcal{F}_{sine} := \frac{\pi\sqrt{6}}{32} \sqrt{W_v \kappa_v} \quad (4.27)$$

and

$$\mathcal{F}_{poly} := \frac{27\sqrt{2002}}{5005} \sqrt{W_v \kappa_v}, \quad (4.28)$$

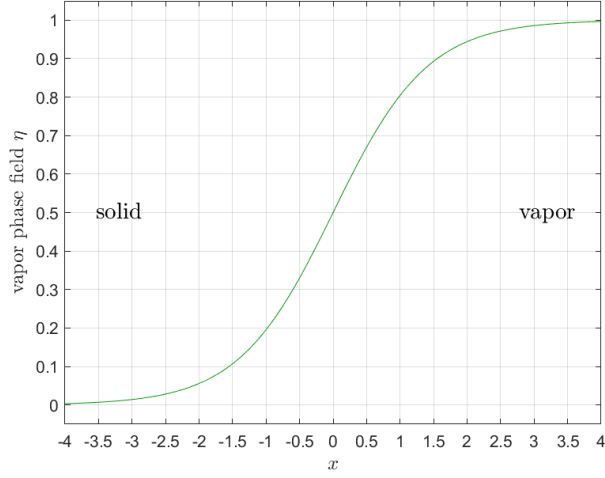
respectively. Setting $W_v = \kappa_v = 1$, we have the energies

$$\mathcal{F}_{tanh} = \frac{\sqrt{2}}{6} \approx 0.23570226, \quad (4.29)$$

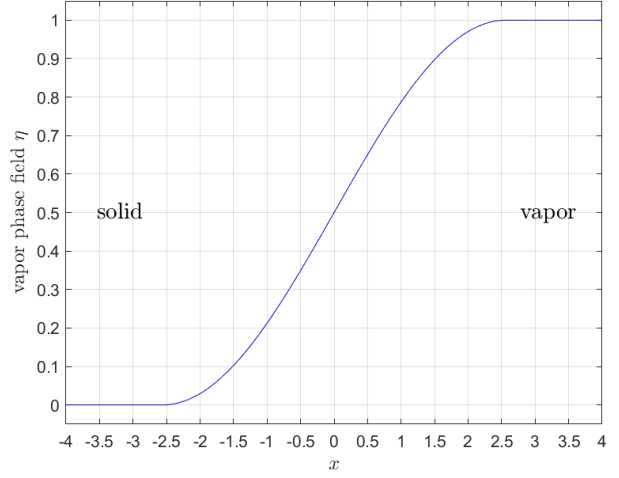
$$\mathcal{F}_{sine} = \frac{\pi\sqrt{6}}{32} \approx 0.24047809, \quad (4.30)$$

and

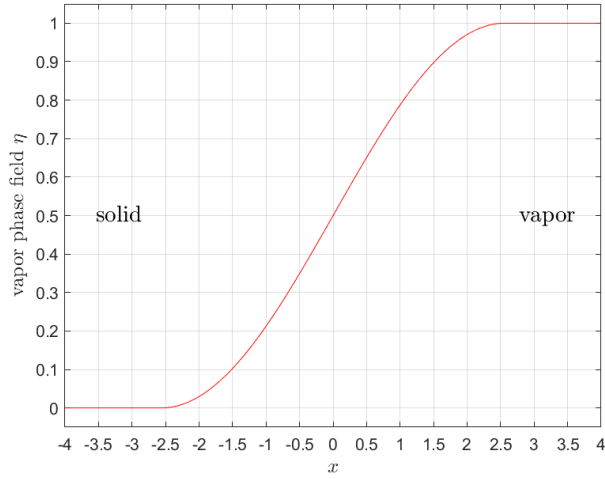
$$\mathcal{F}_{poly} = \frac{27\sqrt{2002}}{5005} \approx 0.24137468, \quad (4.31)$$



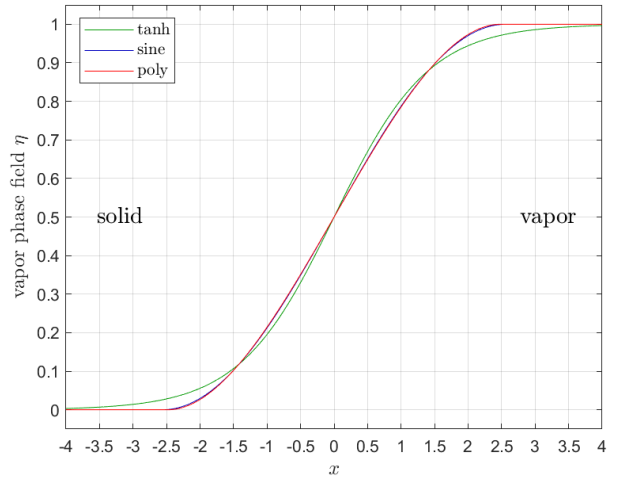
(a) $\frac{1}{2} \left(1 + \tanh \left(\sqrt{\frac{1}{2}} x \right) \right)$



(b) $\frac{1}{2} \left(1 + \sin \left(\sqrt{\frac{3}{8}} x \right) \right)$



(c) $\frac{1}{2} \left(1 + \frac{3}{2} \sqrt{\frac{162}{1001}} x - \frac{1}{2} \left(\sqrt{\frac{162}{1001}} x \right)^3 \right)$



(d) All Three Fields

Figure 4.14: Comparison of Vapor Phase Field Forms at the Phase Interface

respectively. This supports the claim that the hyperbolic tangent form is the unique minimizer for the case of exactly one phase interface.

To aid in the comparison of the curve shapes, the magnitudes of the slopes at the phase interface center $x = 0$ are given by

$$m_{tanh} := \frac{\sqrt{2}}{4} \sqrt{\frac{W_v}{\kappa_v}}, \quad (4.32)$$

$$m_{sine} := \frac{\sqrt{6}}{8} \sqrt{\frac{W_v}{\kappa_v}}, \quad (4.33)$$

and

$$m_{poly} := \frac{27\sqrt{2002}}{4004} \sqrt{\frac{W_v}{\kappa_v}}, \quad (4.34)$$

respectively. A comparison of the slopes at $x = 0$ with $W_v = \kappa_v = 1$ yields

$$m_{tanh} = \frac{\sqrt{2}}{4} \approx 0.35355339, \quad (4.35)$$

$$m_{sine} = \frac{\sqrt{6}}{8} \approx 0.30618622, \quad (4.36)$$

and

$$m_{poly} = \frac{27\sqrt{2002}}{4004} \approx 0.30171836, \quad (4.37)$$

respectively.

4.3.2 Two-Dimensional Case

We extend our one-dimensional minimizer result to two-dimensions. The trivial minimizers are again given by the constant fields $\eta = 0$ (all solid) and $\eta = 1$ (all vapor). These are the only fields that yield a free energy of 0.

If the vapor phase field η is not constant, we have at least one region of solid and at least one region of vapor. First, we limit our focus to one small phase interface region, where the explicit phase interface free energy is at or near a minimum. We then take a cross section of the phase field along the normal line. From the one-dimensional results, we expect that this cross-sectional phase field would take the hyperbolic tangent form of (4.6).

Next, given a fixed total solid area, it follows that the minimum surface energy would be obtained by a configuration that yields the minimum phase interface length, or the minimum one-dimensional surface area. This is achieved by a single solid disk.

In two-dimensions, we measure the overall surface free energy in units of free energy per unit length. For the two-dimensional case, we use (4.18) to define the minimum phase interface free energy per unit length as

$$\mathcal{E}_{int} := \frac{\sqrt{2W_v\kappa_v}}{6}. \quad (4.38)$$

Similarly, applying (4.20), we define the minimizer phase interface thickness for two dimensions to be

$$\delta_{int} := 2\sqrt{\frac{2\kappa_v}{W_v}}. \quad (4.39)$$

This thickness is the width of the phase interface along the line normal to the interface.

Note that this explicit interface energy does not account for all of the surface energy. The free energy of the multimode PFC model is strongly affected by the crystal geometry. This gradient free energy vies with the explicit phase interface energy. For example, at equilibrium, a single, bounded solid region is not perfectly round. For the case of honeycomb geometry, the solid region tends to take the shape of an irregular dodecagon. In addition, there are metastable equilibrium states, where the mass density in regions distant from phase interfaces does not reach the corresponding homogeneous equilibrium energy for the corresponding phase.

4.4 Surface Energy Formula

The surface energy formula was originally developed by Dr. Ken R. Elder [4]. We first present an analytical derivation of this formula. Then, we use a graphical method to arrive at the same result. Note that the units for the surface energy are “energy per unit length”.

4.4.1 Analytical Derivation

We use three steps to derive the surface energy formula. In step one, we use the phase equilibrium free energy (2.135) from Section 2.5:

$$E_{equil} := -0.479621906329\overline{\psi} - 0.0427447563249. \quad (4.40)$$

First, we calculate the mean mass density (per unit area), $\overline{\psi}$, within the computational box Ω . Next, we use (4.40) to calculate the corresponding phase equilibrium free energy (per unit area) E_{equil} for Ω . Therefore, this free energy result is based purely on mass density. It includes neither the explicit phase interface energy of (4.1) nor the additional free energy that may be “trapped” in other regions as a result of the interface. Hence, the phase equilibrium free energy “assumes” that the presence of a phase interface has no effect on the free energy of the system. Since mass is conserved in our model, $\overline{\psi}$ and, thus, E_{equil} are constant over time.

For step two, we employ the free energy functional (2.102) from Subsection 2.4.2. We repeat the free energy functional here for reference:

$$\begin{aligned} \mathcal{F}(\psi, \eta) := \int_{\Omega} & \left[g(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v \right\} \right. \\ & + (1 - g(\eta)) \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi C \psi \right\} \\ & \left. + W_v h(\eta) - \frac{\kappa_v}{2} \eta \Delta \eta \right] d\mathbf{x}. \quad (4.41) \end{aligned}$$

Now, we calculate the actual free energy per unit area of the system by dividing the free energy of (4.41) by the area of Ω . This actual, or total, free energy per unit area is given by

$$E_{total} := \frac{\mathcal{F}(\psi, \eta)}{l_x l_y}. \quad (4.42)$$

Hence, this actual free energy includes the explicit phase interface energy, in addition to the free energy trapped in other regions. We refer to E_{total} as, simply, the “free energy” of the system. Note that E_{total} typically decreases over time.

For the final step, we find the **surface energy per unit length** by multiplying the difference between the actual free energy (4.42) and the phase equilibrium free energy (4.40) by the area of Ω and dividing by the length of the phase interface l_{int} :

$$\mathcal{E}_{surf} := \frac{l_x l_y (E_{total} - E_{equil})}{l_{int}}. \quad (4.43)$$

Note that l_{int} is the total combined length of the phase interfaces within Ω . In this study, we only calculate surface energy for band seed simulations. For the band simulations, there are two phase interfaces - the left and the right. Hence, the total length of the phase interfaces within the computational box is $2l_y$. We have

$$\mathcal{E}_{surf} = \frac{l_x l_y (E_{total} - E_{equil})}{2l_y} = \frac{l_x}{2} (E_{total} - E_{equil}). \quad (4.44)$$

Inserting the expression for E_{equil} from (4.40), we have the form that we use in the software:

$$\mathcal{E}_{surf} = \frac{l_x}{2} (E_{total} - (-0.479621906329\bar{\psi} - 0.0427447563249)). \quad (4.45)$$

Note that (4.44) and (4.45) apply only to vertical band simulations.

4.4.2 Graphical Derivation

An equivalent approach to finding the surface energy involves areas under free energy density curves. Instead of free energies per unit area, we begin with free energy densities. We define the phase equilibrium free energy density as

$$f_{equil} := -0.479621906329\psi - 0.0427447563249. \quad (4.46)$$

This is an analogue of (4.40). The phase equilibrium free energy per unit area E_{equil} is replaced by the phase equilibrium free energy density f_{equil} , and the mean mass density $\bar{\psi}$ is replaced by the mass density field ψ . This energy density is based solely on the solid-vapor common tangent line, and it does not include phase interface energy. Next, we recall the

free energy density, or free energy functional integrand, from (2.103) of Subsection 2.4.2:

$$\begin{aligned}
f(\psi, \Delta\psi, \dots, \Delta^8\psi, \eta) := & g(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v \right\} \\
& + (1 - g(\eta)) \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi C \psi \right\} \\
& + W_v h(\eta) - \frac{\kappa_v}{2} \eta \Delta\eta. \quad (4.47)
\end{aligned}$$

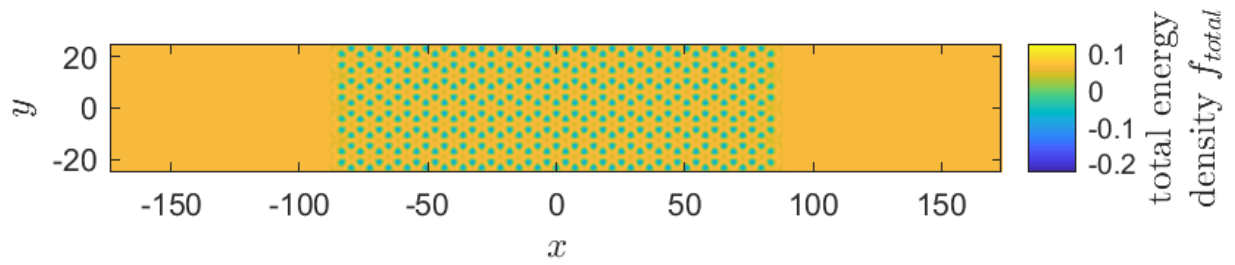
For clarity, we refer to this total free energy density as f_{total} . Finally, we define the surface energy free energy density to be the difference

$$f_{surf} := f_{total} - f_{equil}. \quad (4.48)$$

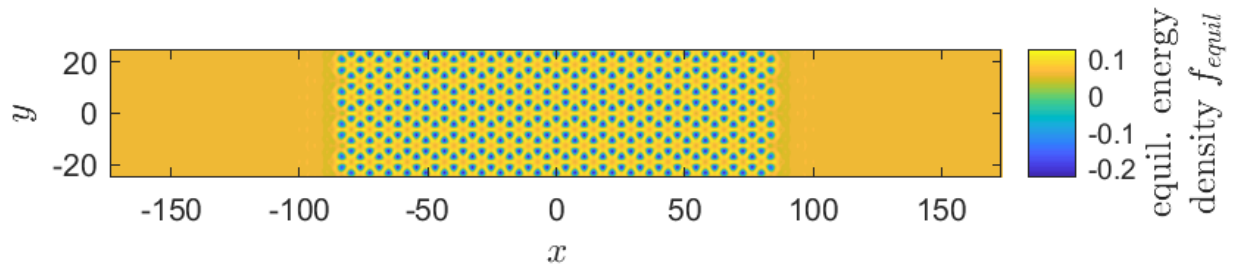
We refer to the armchair facet simulation of Section 4.2, Figure 4.6 for an example. Again, $W_v = 0.1$ and $\kappa_v = 0.4455$, while the seed multiple is 12.082461. In Figure 4.15a, we recall the total free energy density f_{total} from Figure 4.6c. Figure 4.15b shows the equilibrium free energy density f_{equil} resulting from (4.46). Finally, Figure 4.15c is the difference between the two density fields, the surface free energy density f_{surf} .

Since the mass density in the vapor region is near its equilibrium, there is little difference between the total energy and the equilibrium energy in these areas. Hence, as Figure 4.15c indicates, the surface energy density is approximately zero. Of great significance are the phase interface regions in the graphs. In Figure 4.15c, we can see that the surface energy density is greater at the phase interfaces. This is due primarily to the “explicit” phase interface free energy density $f_{int}(\eta)$ as defined in (4.2). Since the phase equilibrium energy diagram of Section 2.5 is based on mean mass densities, it follows that the crystal region of Figure 4.15b reflects the pattern of the mass density itself. Hence, the crystal regions in the graphs in Figure 4.15 are misleading. We are interested in the mean free energies and, so, we introduce smoothing in the next step.

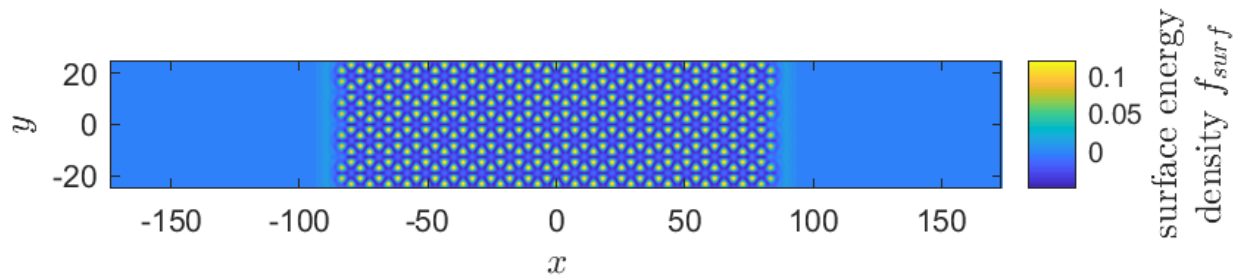
Next, for each energy density type, we generate a sort of horizontal “cross section”. For each x -coordinate, we find the mean free energy over all y -coordinates. In addition, for Figure 4.16a, we smooth the resulting free energy density curves, while maintaining the



(a) Total Free Energy Density Field



(b) Equilibrium Free Energy Density Field



(c) Surface Free Energy Density Field

Figure 4.15: Band Seed, Armchair Facet, Energy Fields, Seed Multiple = 12.082461

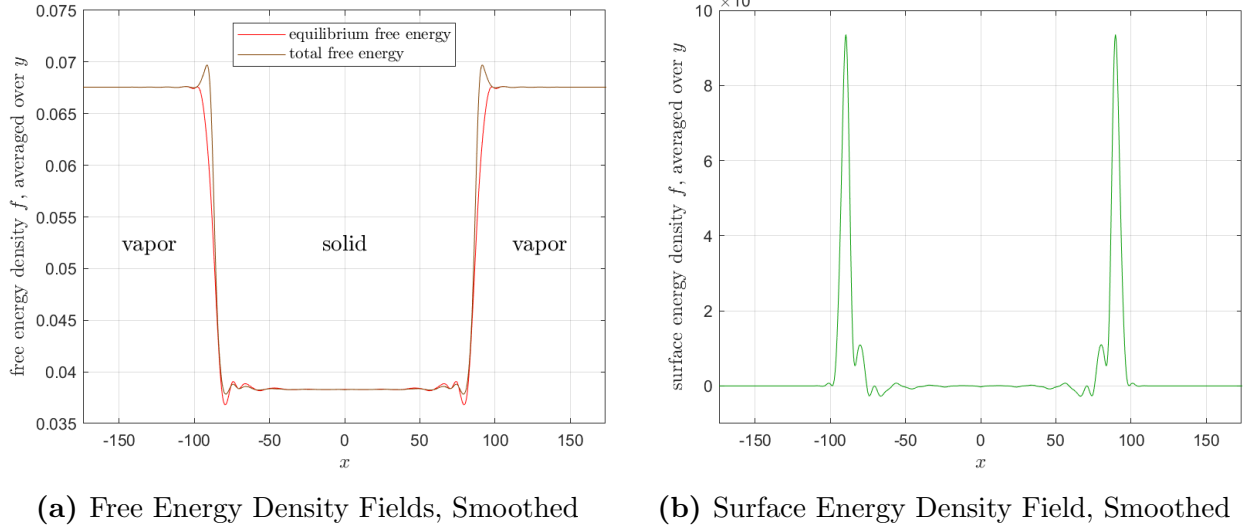


Figure 4.16: Band Seed, Armchair Facet, Energy Field Cross Sections

same area beneath each. This smoothing gives us a better idea of the mean density in the solid region. In Figure 4.16a, we see that the total free energy density is greater than the phase equilibrium energy at the phase interfaces. Figure 4.16b shows the difference between the smoothed and y -averaged total and phase equilibrium free densities.

The difference between the areas under the two curves in Figure 4.16a is proportional to the surface free energy. Since there are two interfaces, to find the surface energy per unit length $\mathcal{E}_{surf}$, we divide the difference in areas by 2.

For this armchair example, the area under the total free energy curve is approximately 18.51754006. The area under the phase equilibrium free energy curve is about 18.38863575. Hence, the surface energy per unit length is approximately

$$\mathcal{E}_{surf} \approx \frac{18.51754006 - 18.38863575}{2} \approx 0.06445216. \quad (4.49)$$

We compare this to the result found by using formula (4.45). The mass density field gives us an approximate mean mass density per unit area of $\bar{\psi} \approx -0.1992148573$. Applying ψ and η to (4.41), we find that the total free energy per unit area is approximately $E_{total} \approx$

0.05317320265. Recall also that $l_x \approx 348.2494779$. Then, (4.45) yields

$$\begin{aligned} \mathcal{E}_{surf} &\approx \frac{348.2494779}{2} (0.05317320265 - ((-0.4796219063) \cdot (-0.1992148573) - 0.0427447563)) \\ &\approx 0.06445216. \end{aligned} \quad (4.50)$$

We repeat this process for the zigzag, one-bond facet represented in Figure 4.7a of Section 4.2. The energy graphs are given in Figure 4.17. We find the mean energies over all y -values and smooth the resulting curves to arrive at Figure 4.18a. Figure 4.18b is the difference between the curves.

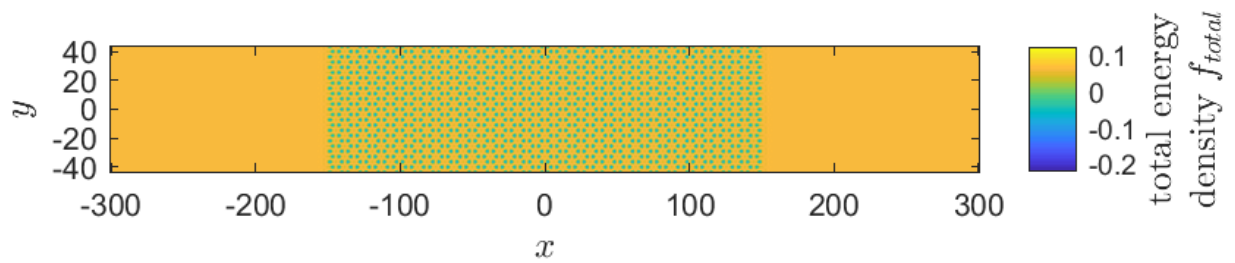
The area under the total free energy curve is approximately 31.91798353, and the area under the equilibrium curve is roughly 31.79065667. Then, the surface energy per unit length is approximately

$$\mathcal{E}_{surf} \approx \frac{31.91798353 - 31.79065667}{2} \approx 0.06366343. \quad (4.51)$$

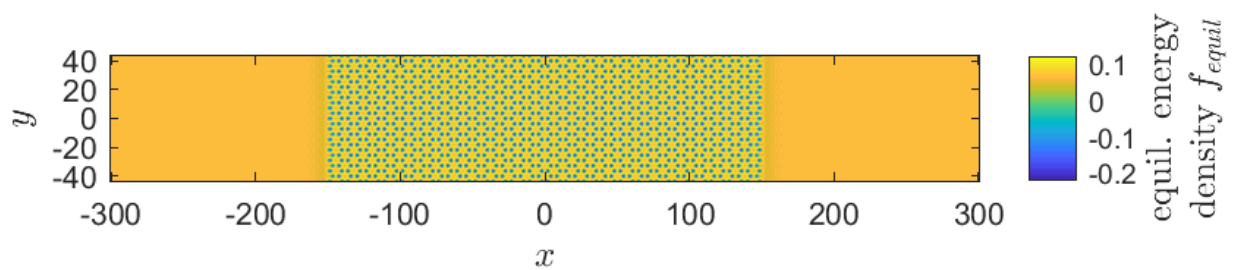
For this zigzag, one-bond simulation, we have $\bar{\psi} \approx -0.1990095531$, $E_{total} \approx 0.05291567554$, and $l_x \approx 603.1857895$. Using (4.45), we arrive at

$$\begin{aligned} \mathcal{E}_{surf} &\approx \frac{603.1857895}{2} (0.05291567554 - ((-0.4796219063) \cdot (-0.1990095531) - 0.0427447563)) \\ &\approx 0.06366343. \end{aligned} \quad (4.52)$$

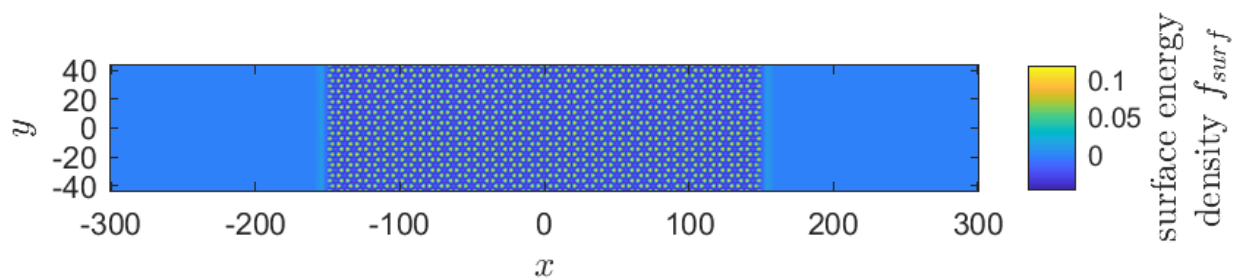
It is important to note that the phase interfaces affect the entire computational box. It is difficult to see in Figures 4.16 and 4.18, but the total and phase equilibrium free energy densities differ slightly in the “pure” vapor regions. The same is true for the mean energies of the solid region. Recall that the system is periodic in the horizontal direction. In the xy -plane, the solid region repeats. We conjecture that, if the model included semi-infinite



(a) Total Free Energy Density Field



(b) Equilibrium Free Energy Density Field



(c) Surface Free Energy Density Field

Figure 4.17: Band, Zigzag One-Bond Facet, Energy Fields, Seed Multiple = 12.174697

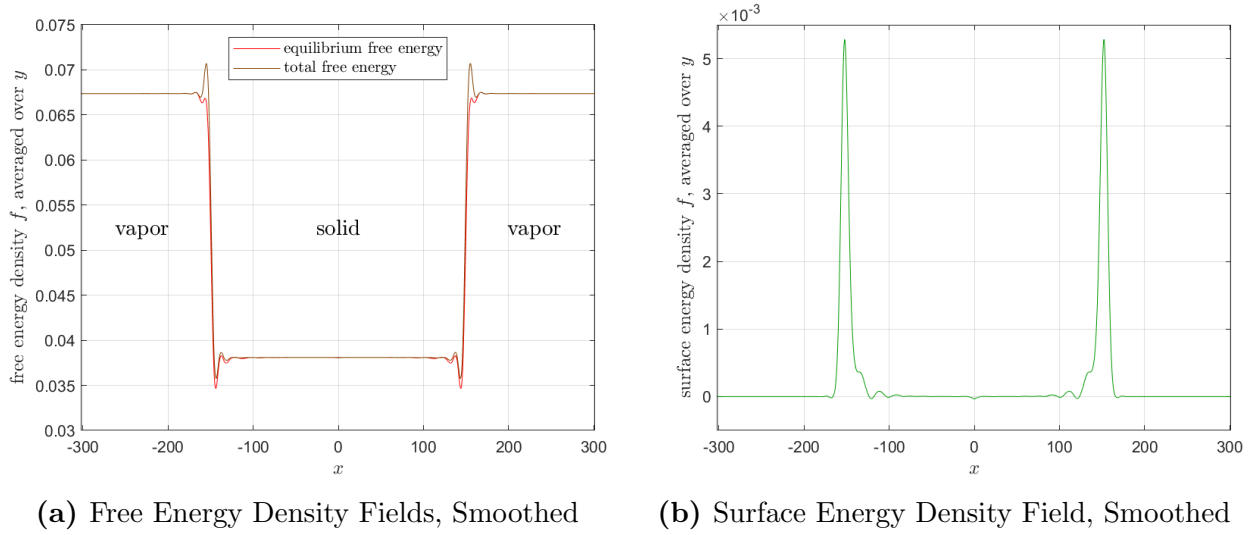


Figure 4.18: Band Seed, Zigzag One-Bond Facet, Energy Field Cross Sections

regions of vapor on both the left and right, the effect of the phase interface free energy would be more closely bound to the phase interface itself.

4.5 Surface Energy Periodicity

In this section, we study the periodicity of the surface energies for the armchair and zigzag facets. For the simulations, we set $W_v = 0.1$ and $\kappa_v = 0.4455$. Figure 4.19a displays the surface energy per unit length for the armchair facet. The seed multiple varies from 0 to 24. A seed multiple of 0 represents no solid region. Since the computational box is 48 unit cells in width, a seed multiple of 24 indicates that there is no vapor region. We can see that the surface energy is periodic, and its period is about one half of the unit cell width.

Figure 4.19b reinforces this observation by mapping the distances between consecutive surface energy maxima. Within each half unit cell width, we run simulations to find the seed multiple that produces the maximum surface energy. Then, we find and plot the difference between consecutive maximizing seed multiples. For instance, for the base seed multiple 12, we find the seed multiple between 12 and 12.5 that maximizes the surface energy. Likewise, for the base multiple 12.5, we determine the maximizing seed multiple between 12.5 and 13. We assign the difference between these two maximizing seed multiples to the base seed

multiple 12. Hence, according to Figures 4.19a and 4.19b, the surface energy period for the armchair facet is $\frac{1}{2} \frac{4\pi}{\sqrt{3}} = \frac{2\pi}{\sqrt{3}} \approx 3.62760$.

Figure 4.20a shows the surface energy per unit length for the zigzag facet. Again, the period is approximately one half of the zigzag unit cell width. Figure 4.20b displays the distances between consecutive surface energy maxima. The surface energy period for the zigzag facet is $\frac{1}{2} 4\pi = 2\pi \approx 6.28319$.

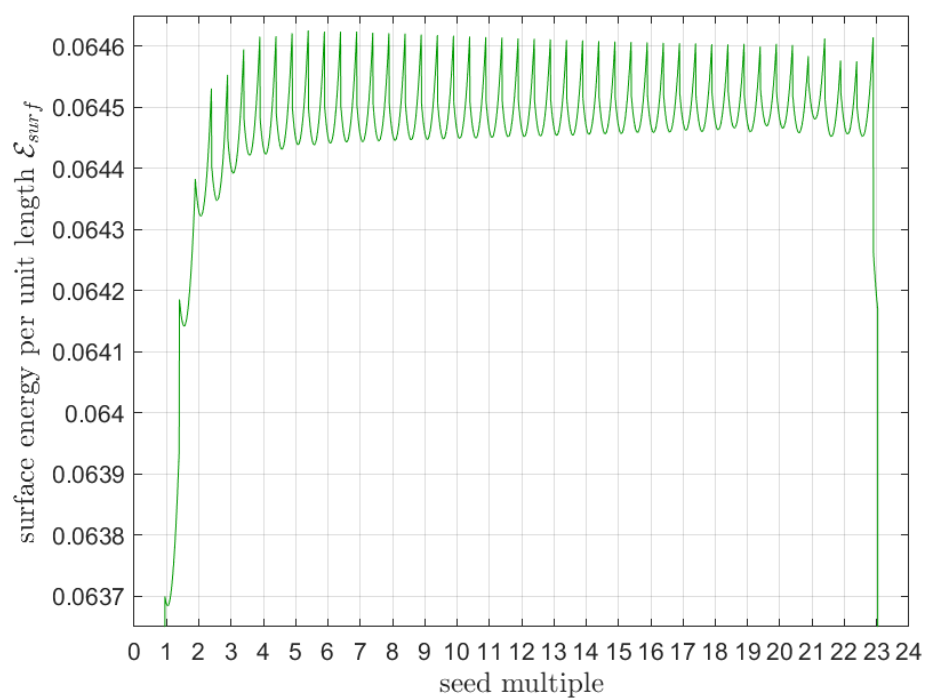
We now refer to Figure 4.1 of Section 4.1. We shift the right phase interface to the left by one half a of unit cell width - to the first dashed vertical line. We find that we end up with the same face, shifted vertically by one half of a unit cell height. Note that shifting the left interface to the right yields the same result. No smaller phase interface shift results in the same face. Hence, the period of one half of a unit cell width is to be expected in our simulations.

Next, we return to Figure 4.2. On the right we have the zigzag one-bond facet. Shifting the phase interface one half of a unit cell width to the left results in the same one-bond face, shifted vertically by one half of a unit cell height. Shifting the left interface to the right by one half cell width yields the same two-bond face. This gives us a period of one half of a unit cell width, which concurs with the simulation results.

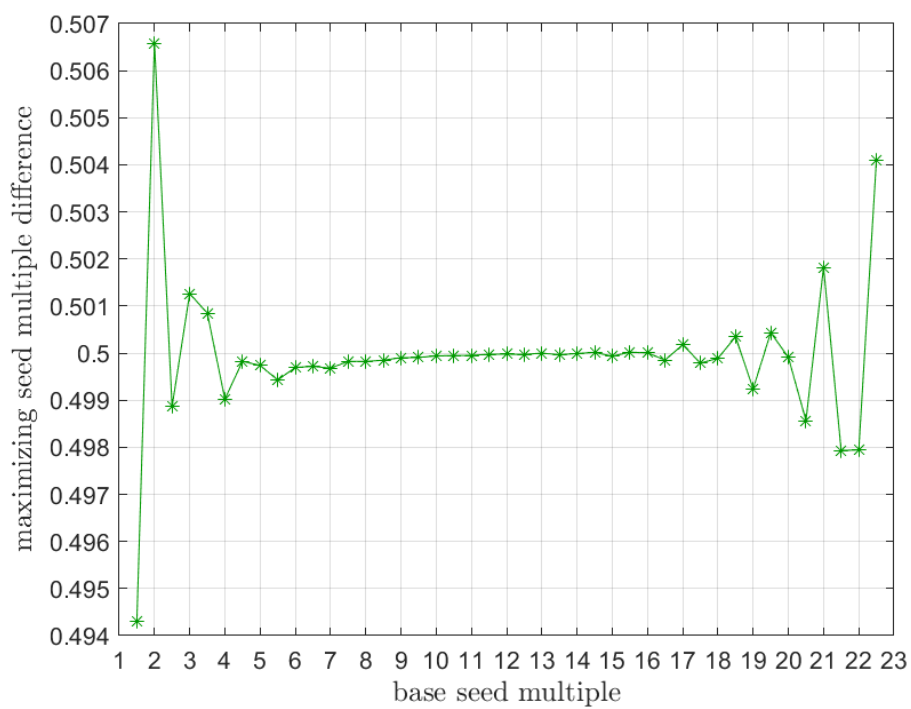
We can predict the periodicity for the top-to-top facet by reviewing Figure 4.3. We can see that moving the right phase interface to the left by one fourteenth of a unit cell width produces an identical face, shifted up by five fourteenths of a unit cell height. Shifting the left phase interface produces a similar result. Then, the periodicity for the top-to-top facet is one fourteenth of the unit cell width.

For the left-to-right facet, we turn to Figure 4.4. Again, we move the right phase interface to the left by one fourteenth of a unit cell width. We find an identical face, shifted down by three fourteenths of a unit cell height. Moving the left interface yields an analogous effect. Therefore, the periodicity for the left-to-right facet is also one fourteenth of the corresponding unit cell width.

The top-to-top and left-to-right facet simulations in Section 4.7 support these conclusions.

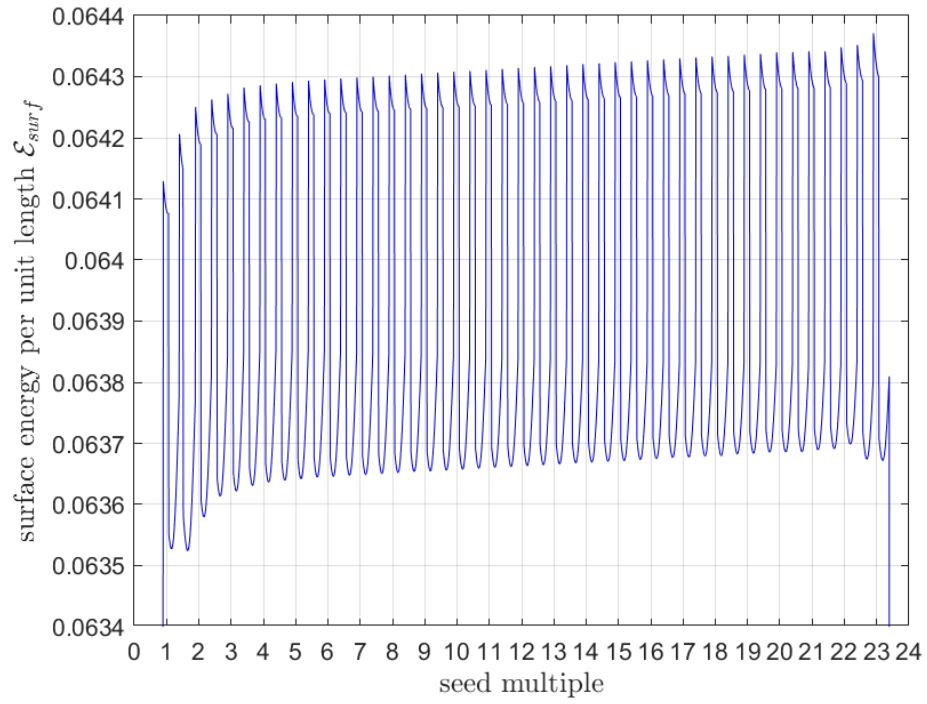


(a) All Seed Multiples

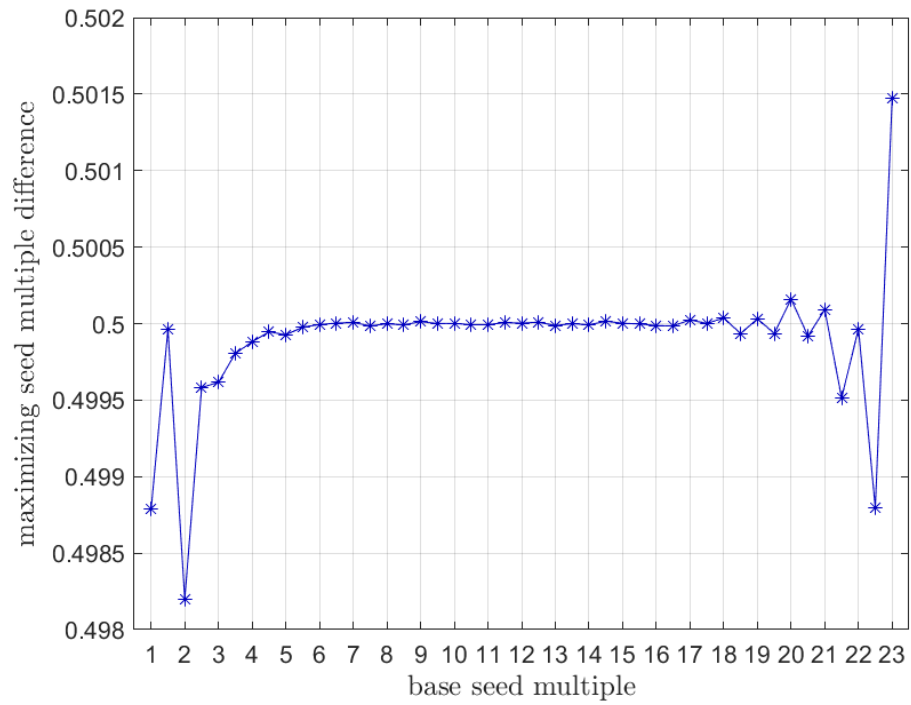


(b) Periods

Figure 4.19: Armchair Facet Surface Energies



(a) All Seed Multiples



(b) Periods

Figure 4.20: Zigzag Facet Surface Energies

4.6 Surface Energy and Phase Interface Free Energy

In this section, we study the surface energies for the armchair and zigzag facets. We graph surface energies as functions of initial seed multiples. In addition, we analyze the effects of the phase interface free energy on the surface energies, and we determine the phase interface thicknesses.

Recall that the phase interface free energy functional is

$$\mathcal{F}_{int}(\eta) := \int_{\Omega} \left[W_v h(\eta) + \frac{\kappa_v}{2} |\nabla \eta|^2 \right] d\mathbf{x}. \quad (4.53)$$

Hence, the parameters W_v and κ_v determine the magnitude of the interface energy. We first consider the pairing $W_v = 0.1$ and $\kappa_v = 0.4455$. We refer to this combination as the “full” interface free energy case. Second, we investigate $W_v = 0.05$ with $\kappa_v = 0.22275$, which produces “half” of the phase interface free energy. From (4.38) and (4.39) of Section 4.3, we know that the minimizing vapor phase field produces a minimum interface energy per unit length of

$$\mathcal{E}_{int} := \frac{\sqrt{2W_v\kappa_v}}{6}, \quad (4.54)$$

and a phase interface thickness of

$$\delta_{int} := 2\sqrt{\frac{2\kappa_v}{W_v}}. \quad (4.55)$$

We refer to these formulas in the following investigations.

All of the simulations in this section, both armchair and zigzag, involve an initial vertical band seed, centered horizontally within the computational box. In addition, the crystal geometry is symmetric about the y -axis. Hence, the left facet is identical to the right throughout each simulation. This can be seen in Figures 4.5, 4.6, and 4.7 of Section 4.2. In particular, for zigzag facet simulations, if there is a one-bond stage facet on the left, there is also a one-bond facet on the right. The same holds for the zigzag two-bond stage. Therefore, it is sufficient for us to focus on the phase interface at the right side of the band. Note that, for the armchair facet simulations, the computational box is $l_x = 48\frac{4\pi}{\sqrt{3}} \approx 348.249$ in width

and $l_y = 4\pi \approx 12.566$ in height. For the zigzag simulations, we have $l_x = 48 \cdot 4\pi \approx 603.186$ and $l_y = \frac{4\pi}{\sqrt{3}} \approx 7.255$.

For each simulation, we set the initial vapor phase mass density to $\mu_v = -0.22990548$ and the initial solid mean mass density to $\mu_s = -0.16894892$. These are the equilibrium densities of (2.132) and (2.133), respectively, from Section 2.5. This brings our initial mass density fields as close as possible to a final equilibrium state.

This section includes mass density fields for simulations where the seed multiples produce minimum and maximum surface energies. We also investigate the relationship between the surface energy and an additional layer of atoms. It is important to note that, when we speak about increasing the seed multiple, we are not referring to crystal growth over time. Instead, we refer to an increase in the initial width of the solid band. Although an increase in the seed multiple results in a greater mean mass density, the mean mass density is constant throughout a given simulation.

4.6.1 Full Phase Interface Energy

For this full interface energy case, we use $W_v = 0.1$ and $\kappa_v = 0.4455$. Plugging these values into (4.54), we find that the minimum phase interface energy per unit length is

$$\mathcal{E}_{full} := \frac{\sqrt{2 \cdot 0.1 \cdot 0.4455}}{6} \approx 0.049749372. \quad (4.56)$$

We expect the surface energy to be greater than this phase interface energy. Using (4.55), we calculate the corresponding phase interface thickness to be

$$\delta_{full} := 2\sqrt{\frac{2 \cdot 0.4455}{0.1}} \approx 5.9699246. \quad (4.57)$$

4.6.1.1 Armchair Facet

Figure 4.21 shows the surface energy per unit length for the armchair facet over seed multiples 12 through 13. The results are derived from simulations where the system has reached a minimum free energy, or equilibrium, state. Note that the surface energy average over this seed multiple range is 0.064494221. This is somewhat larger than the minimum phase

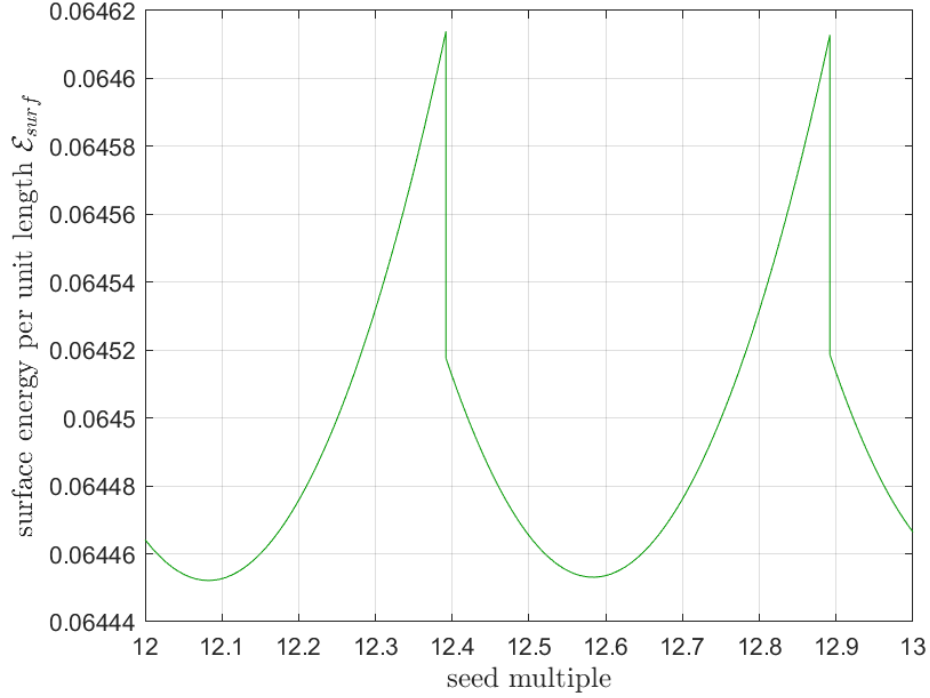


Figure 4.21: Armchair Facet Surface Energies for Full Interface Energy

interface energy of 0.049749372 calculated in (4.56). Per our discussions in Sections 4.3 and 4.4, the phase interface does not account for all of the surface energy. Systems find metastable states, where energy is trapped in the solid or vapor regions, away from the phase interfaces. In addition, a semi-infinite region of vapor to the left and to the right might bring the surface energy closer to the phase interface energy.

Between the seed multiples of 12 and 12.5, a minimum surface energy of 0.064452159 is achieved at a seed multiple of approximately 12.082461. Figure 4.22a displays the corresponding mass density field at the right phase interface. Note that this simulation data corresponds to the fields of Figures 4.5 and 4.6 in Section 4.2.

As the seed multiple increases beyond this minimum point, the surface energy also increases. Thus, the corresponding systems become less stable. As we can see in Figure 4.21, we confront a jump discontinuity at seed multiple 12.391795. To the left of the discontinuity, the surface energy reaches a maximum of about 0.064613848. The mass density for this maximum energy appears in Figure 4.22b. The system for this seed multiple has the least stability. Directly to the right of the discontinuity, there is an additional layer of atoms, and

the surface energy drops sharply to 0.064517582. The mass density field with this additional layer appears in Figure 4.22c. Due to the periodicity of the surface energy (Section 4.5), this process repeats itself between seed multiples 12.5 and 13.

We check the solid-vapor phase interface thickness for the minimizing seed multiple 12.082461. The vapor phase field is shown in Figure 4.23. Using this phase field, we find the phase interface to be about 5.5123793. This is close to the minimizer thickness of 5.9699246 calculated in (4.57). The difference could be attributed to the same reasons cited for the discrepancy between the phase interface and surface free energies.

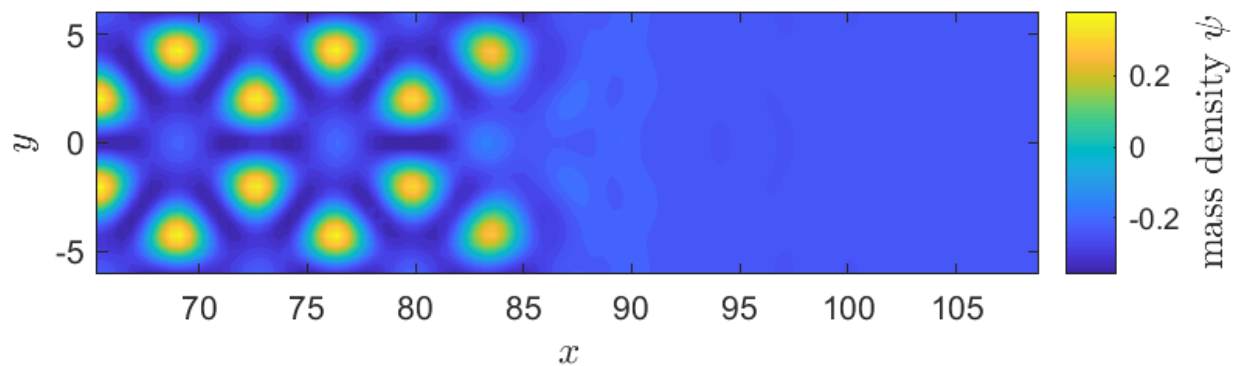
4.6.1.2 Zigzag Facet

Figure 4.24a shows the surface energy per unit length for the zigzag facet over seed multiples 12 through 13. In Figure 4.24a, we see that the one-bond stage has significantly lower energy than the two-bond stage. Hence, the one-bond stage is more stable and, thus, more prevalent in simulations. The average surface energy is 0.063910075, which is again greater than the minimum phase interface free energy of 0.049749372 from (4.56).

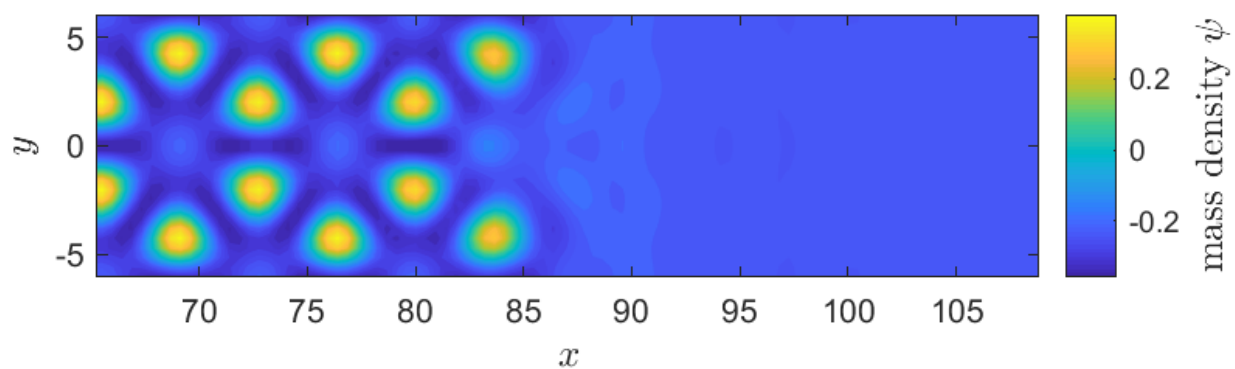
At the seed multiple of 12, the zigzag facet is in the two-bond stage. As the band seed widens, the surface energy decreases, and, so, the corresponding systems become more stable. Although it is difficult to see in Figure 4.24a, there is a surface energy well to the left of the discontinuity. Figure 4.24b provides a close-up view of this region. A minimum for this two-bond stage occurs near the seed multiple 12.060525, where the surface energy is about 0.064257077. Figure 4.25a displays the corresponding mass density field. Note that this system corresponds to Figure 4.7b in Section 4.2.

Next, as the seed multiple increases, the surface energy increases, and, eventually, we meet a discontinuity at multiple 12.068246. Immediately to the left of the discontinuity, we have a surface energy of roughly 0.064257195. The corresponding mass density field appears in Figure 4.25b. To the right of this first discontinuity, a new layer of atoms appear. We now have the one-bond stage, as shown in Figure 4.25c. The surface energy drops to 0.063698472, and the system is more stable.

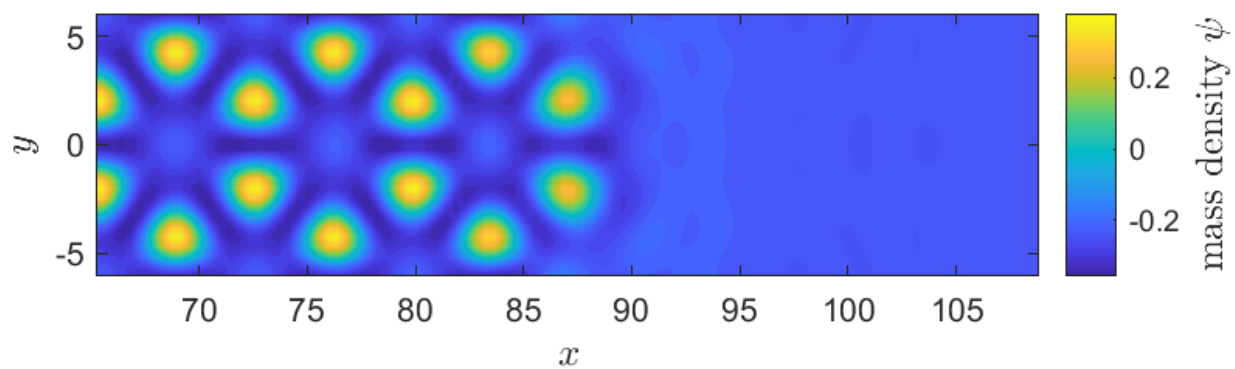
As the seed multiple continues to increase, the surface energy decreases to a one-bond stage minimum. This occurs around 12.174697, where the surface energy is near 0.063663464.



(a) Minimum, Seed Multiple = 12.082461



(b) Maximum, Seed Multiple = 12.391795



(c) New Atom Layer, Seed Multiple = 12.391795

Figure 4.22: Full Interface Energy, Armchair Facet, Mass Density Fields

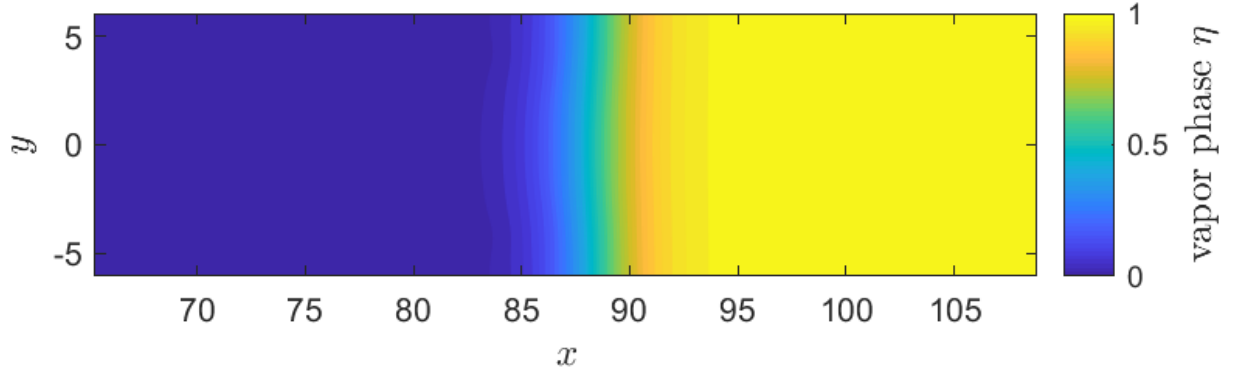
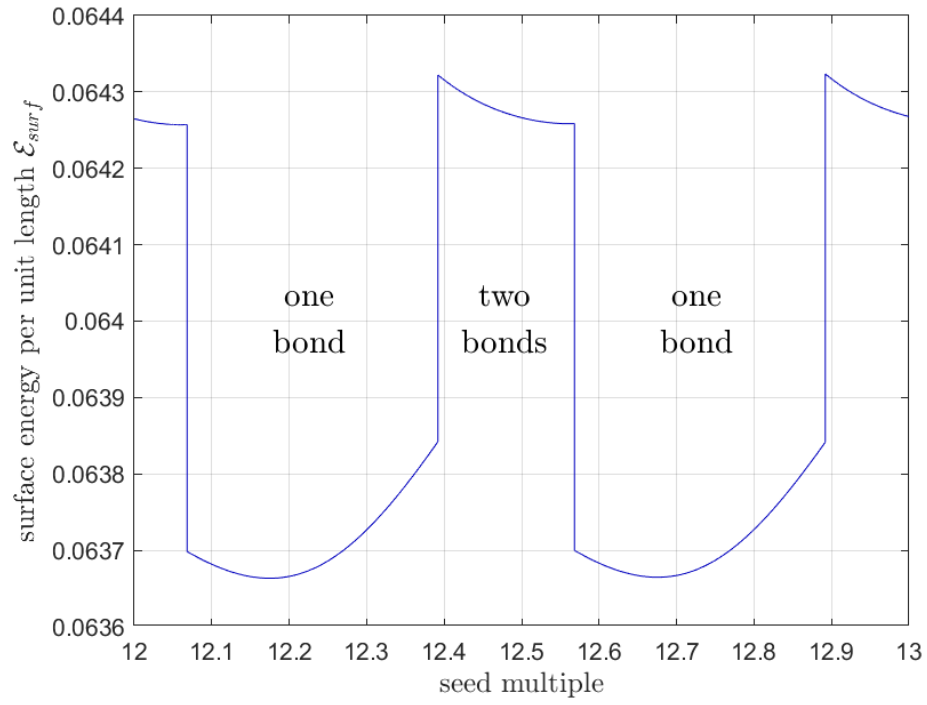


Figure 4.23: Full, Armchair, Minimum, Vapor Phase Field, Seed Multiple = 12.082461

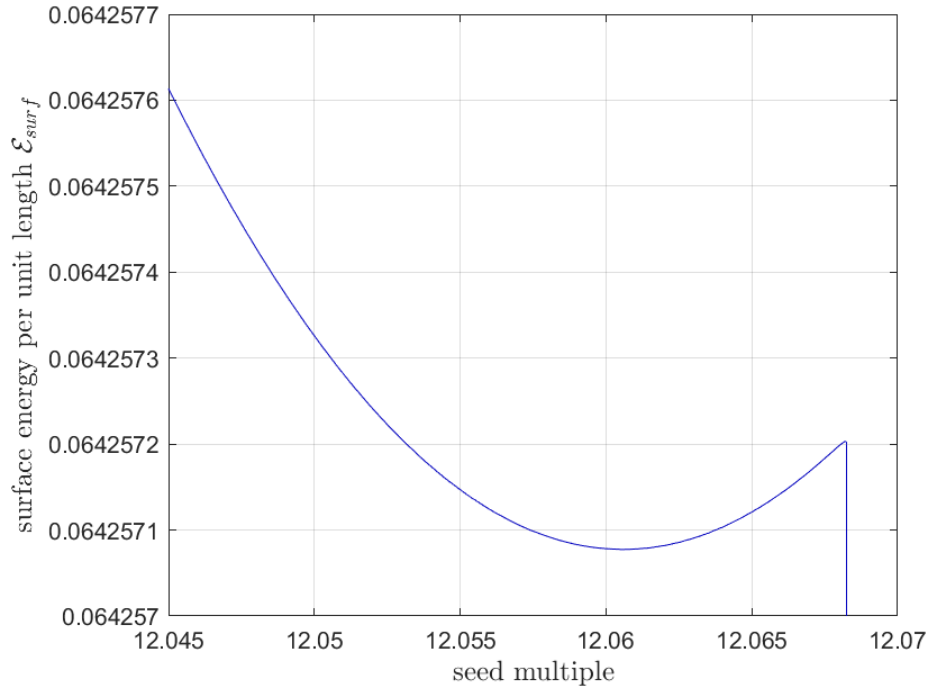
In fact, this is the overall minimum for the zigzag facet between seed multiples 12 and 12.5. Figure 4.26a provides the mass density field. This scenario corresponds to Figure 4.7a in Section 4.2.

As we further increase the seed multiple, the surface energy rises. A second discontinuity arises at seed multiple 12.391926. On the left, we reach the zigzag one-bond surface energy maximum of 0.063842236. Figure 4.26b describes the mass density field. Immediately to the right of the jump, a new layer of atoms emerges. This may be observed in the mass density of Figure 4.26c. Note, however, the instability has increased, as the surface energy peaks at 0.064322240. As we can see in Figure 4.24a, this seed multiple produces the maximum surface energy for not only the two-bond stage but also the entire seed multiple range of 12 to 12.5. After this point, the surface energy decreases until it reaches a second, two-bond stage minimum. The cycle repeats.

The vapor phase field for the one-bond, minimizing seed multiple 12.174697 appears in Figure 4.27a, and the phase field for the two-bond, minimizing seed multiple 12.060525 is given by Figure 4.27b. The phase interface thicknesses are 5.4588377 and 5.5448959, respectively. These thicknesses are similar to that of the armchair facet and less than the expected value of 5.9699246 from (4.57).

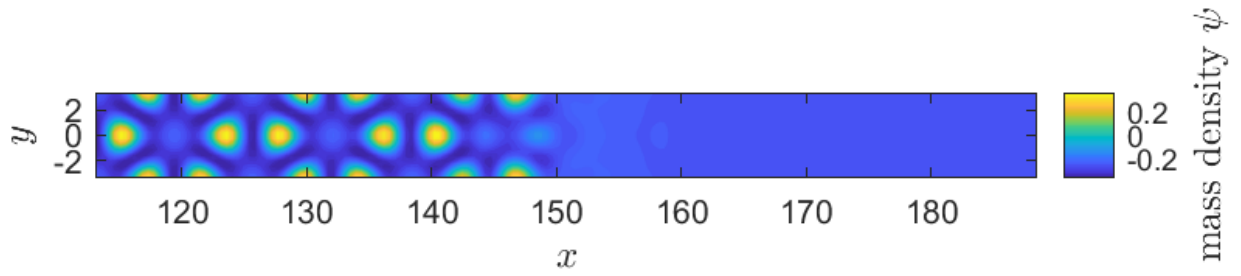


(a) Full View

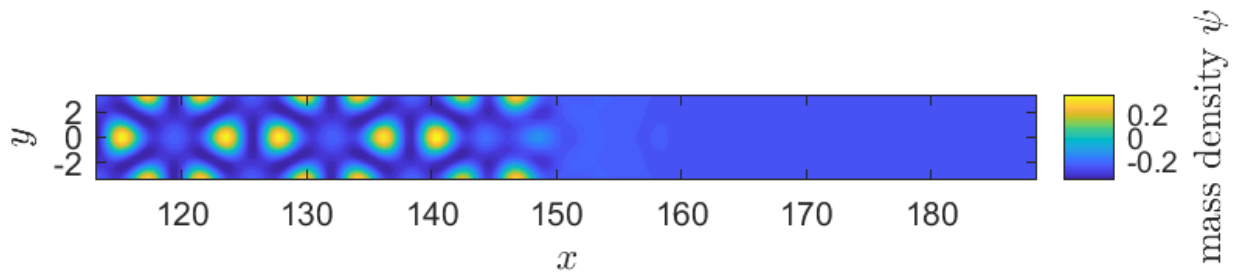


(b) Two-Bond Stage Surface Energy Well

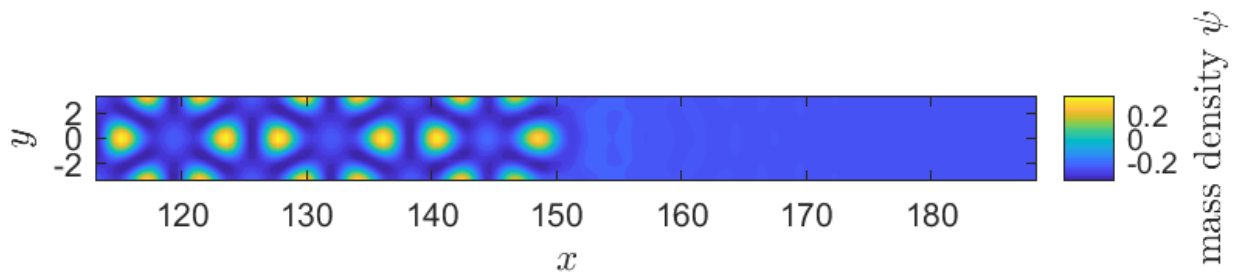
Figure 4.24: Zigzag Facet Surface Energies for Full Interface Energy



(a) Two-Bond Stage, Minimum, Seed Multiple = 12.060525

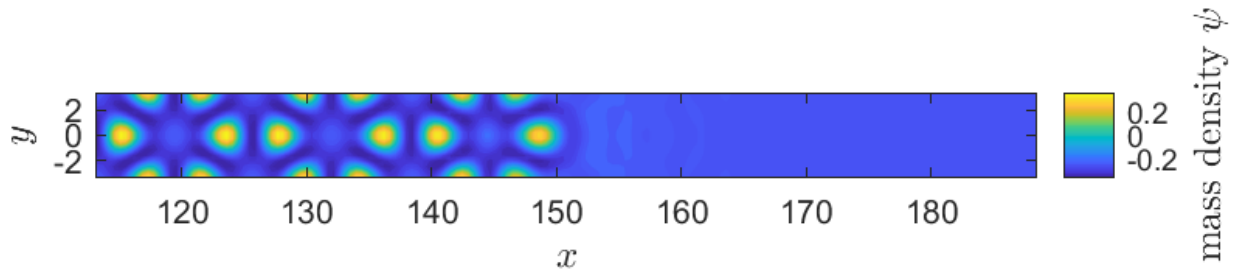


(b) Two-Bond Stage, Discontinuity Left, Seed Multiple = 12.068246

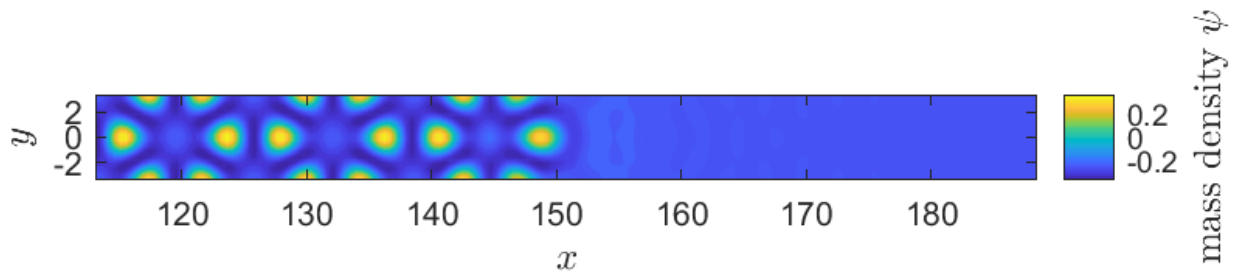


(c) One-Bond Stage, Discontinuity Right, Seed Multiple = 12.068246

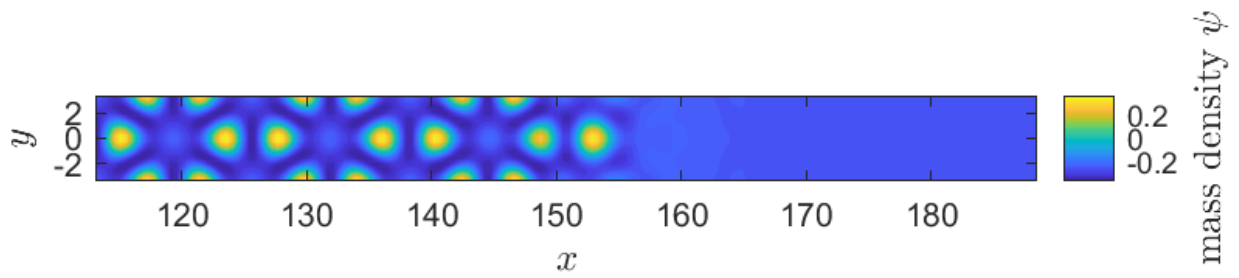
Figure 4.25: Full Interface Energy, Zigzag Facet, Mass Density Fields, Part A



(a) One-Bond Stage, Minimum, Seed Multiple = 12.174697

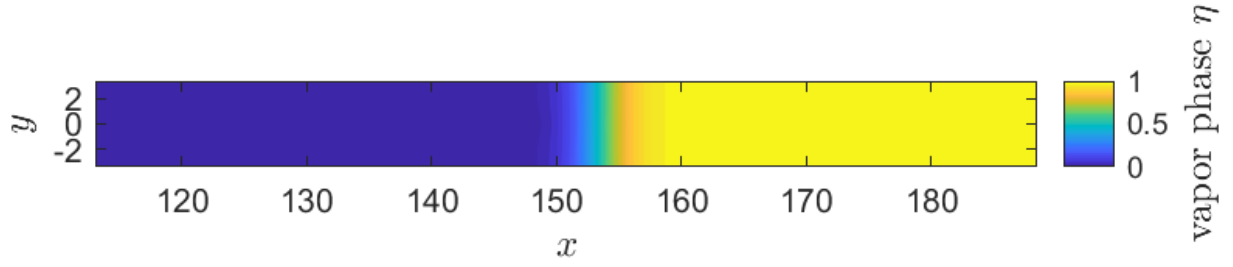


(b) One-Bond Stage, Maximum, Seed Multiple = 12.391926

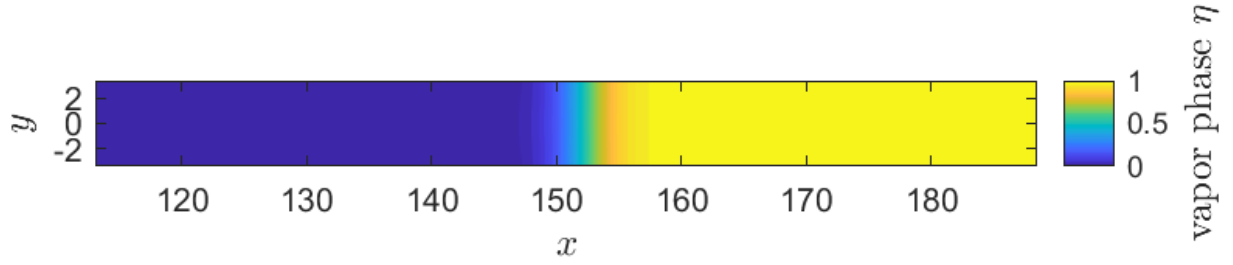


(c) Two-Bond Stage, Maximum, Seed Multiple = 12.391926

Figure 4.26: Full Interface Energy, Zigzag Facet, Mass Density Fields, Part B



(a) One-Bond Stage, Minimum, Seed Multiple = 12.174697



(b) Two-Bond Stage, Minimum, Seed Multiple = 12.060525

Figure 4.27: Full Interface Energy, Zigzag Facet, Vapor Phase Fields

4.6.1.3 Armchair and Zigzag Facet Comparison

Figure 4.28 combines the armchair and zigzag facet surface energy curves. The armchair facet surface energy is significantly higher than that of the zigzag facet. This indicates that the armchair facet is less stable than the zigzag facet. We expect the zigzag facet to be more prevalent at the solid-vapor phase interface.

Since the one-bond stage of the zigzag facet has the lowest energy, it should be the most dominant. We expect to see very little of the zigzag two-bond stage in the energy equilibrium states of our simulations. In Section 4.9, we introduce disk seed simulations that support this conjecture. Subsection 4.9.2 addresses directly the work of this section.

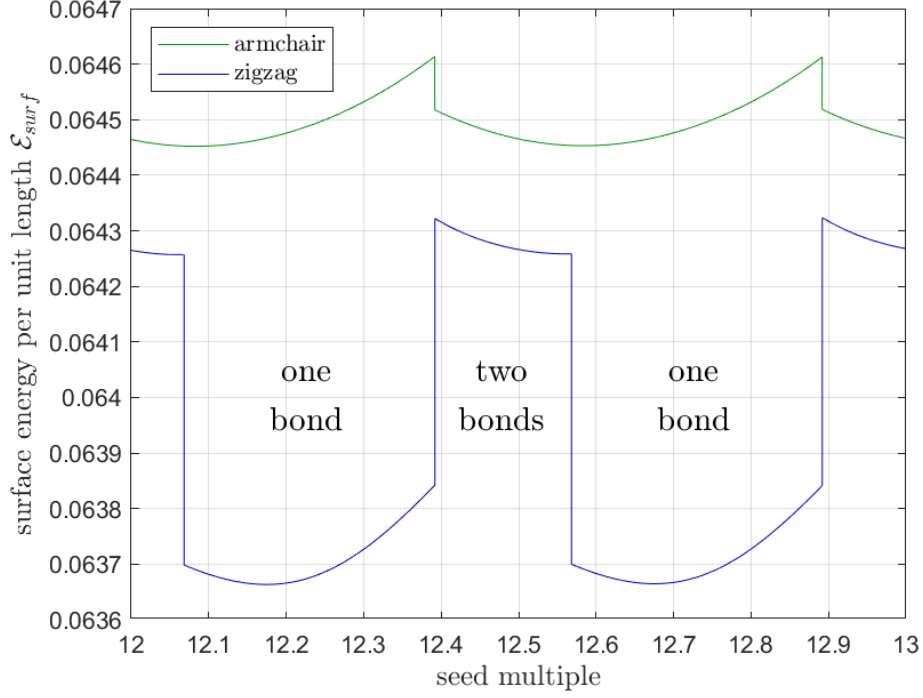


Figure 4.28: Armchair and Zigzag Facet Surface Energies for Full Interface Energy

4.6.2 Half Phase Interface Energy

Here, we use $W_v = 0.05$ and $\kappa_v = 0.22275$. Using (4.54), we calculate the minimum phase interface energy per unit length to be

$$\mathcal{E}_{half} := \frac{\sqrt{2 \cdot 0.05 \cdot 0.22275}}{6} \approx 0.024874686. \quad (4.58)$$

This is half of the minimum phase interface energy from the full interface energy study.

Applying (4.55) yields the minimizer phase interface thickness

$$\delta_{int} := 2\sqrt{\frac{2 \cdot 0.22275}{0.05}} \approx 5.9699246, \quad (4.59)$$

which is identical to the minimizer thickness for the full interface energy. Therefore, we expect the phase interface thicknesses of this subsection to be similar to those of the full energy subsection.

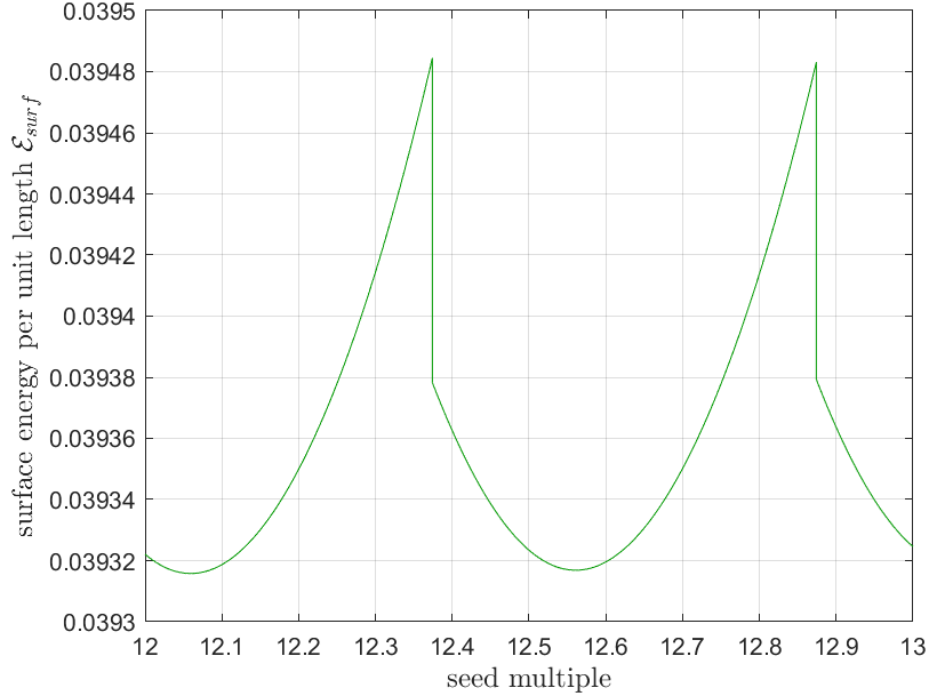
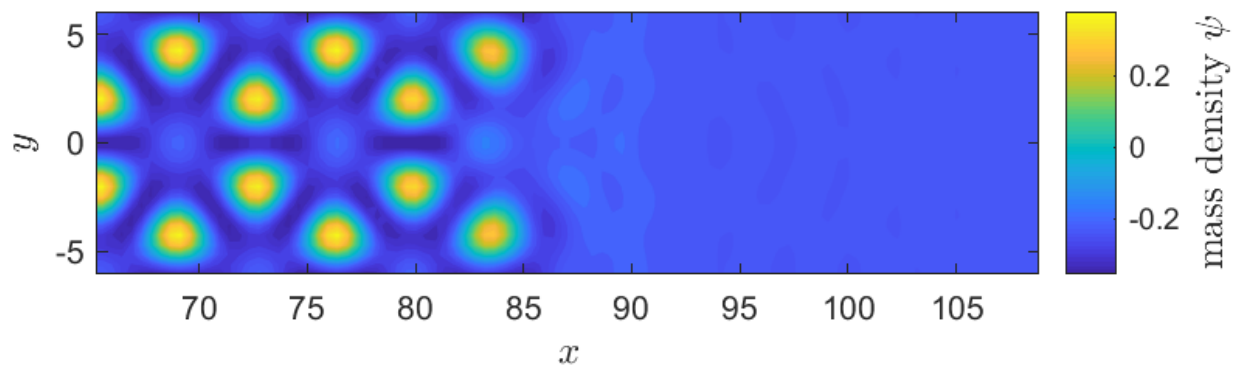


Figure 4.29: Armchair Facet Surface Energies for Half Interface Energy

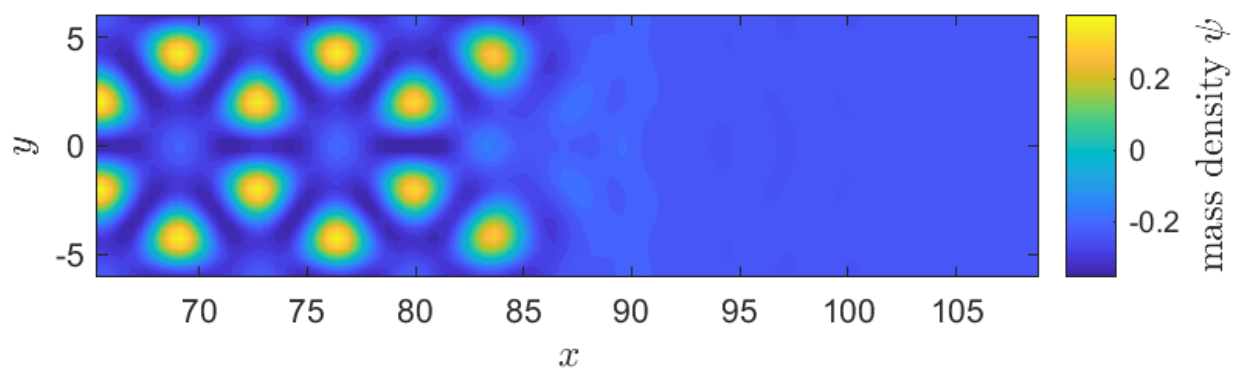
4.6.2.1 Armchair Facet

Figure 4.29 displays the surface energy per unit length for the armchair facet. The mean surface energy over seed multiples 12 to 13 is 0.039359456, which is considerably more than the minimum phase interface energy of 0.024874686 from (4.58). Again, we suspect that the simulations are reaching metastable states.

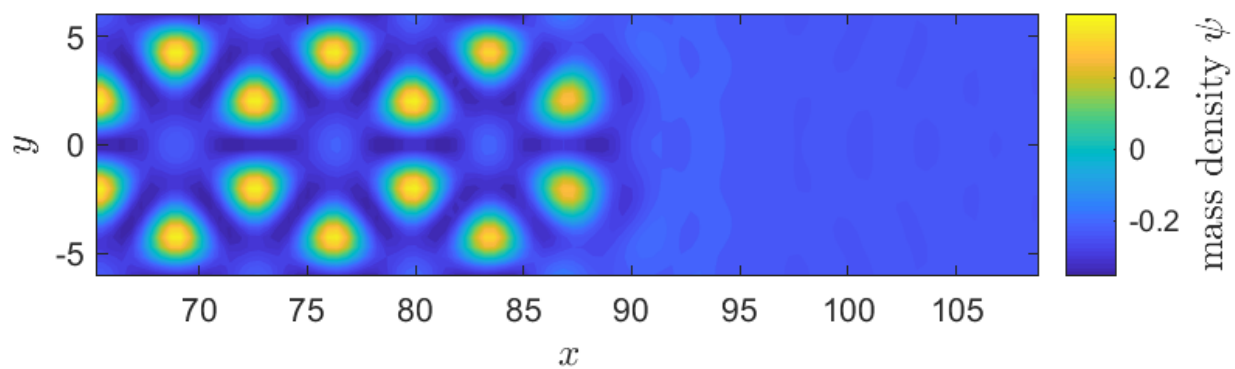
For the 12 to 12.5 seed multiple range, the minimum surface energy of 0.039315784 occurs near the seed multiple of 12.059419. The mass density field appears in Figure 4.30a. As the seed multiple increases, we reach a discontinuity near multiple 12.374136. At the left of the discontinuity, the surface energy obtains a maximum of approximately 0.039484457. This is the maximum surface energy for the first cycle. Figure 4.30b displays the corresponding mass density. An additional layer of atoms appears to the right of the jump discontinuity, and the surface energy drops to 0.039378212. This mass density field is given in Figure 4.30c. The periodic surface energy repeats its cycle as the seed multiple increases.



(a) Minimum, Seed Multiple = 12.059419



(b) Maximum, Seed Multiple = 12.374136



(c) New Layer, Seed Multiple = 12.374136

Figure 4.30: Half Interface Energy, Armchair Facet, Mass Density Fields

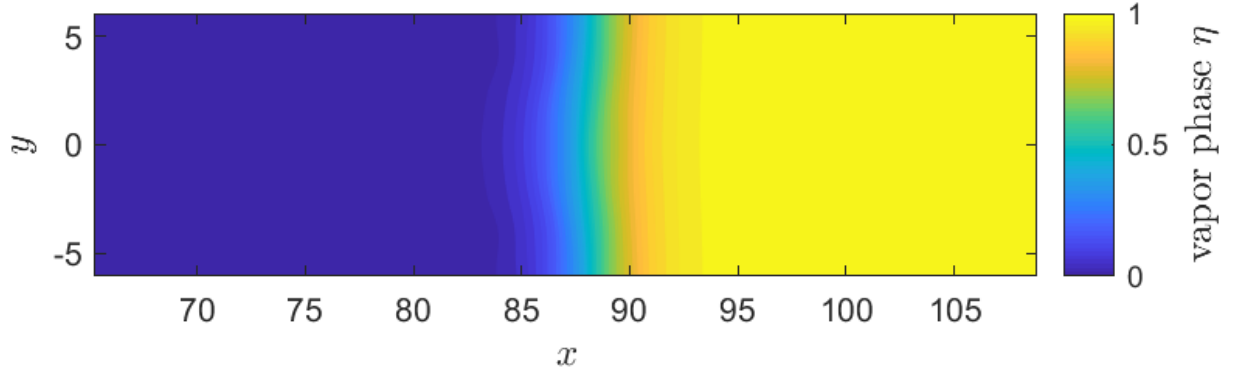


Figure 4.31: Half, Armchair, Minimum, Vapor Phase Field, Seed Multiple = 12.059419

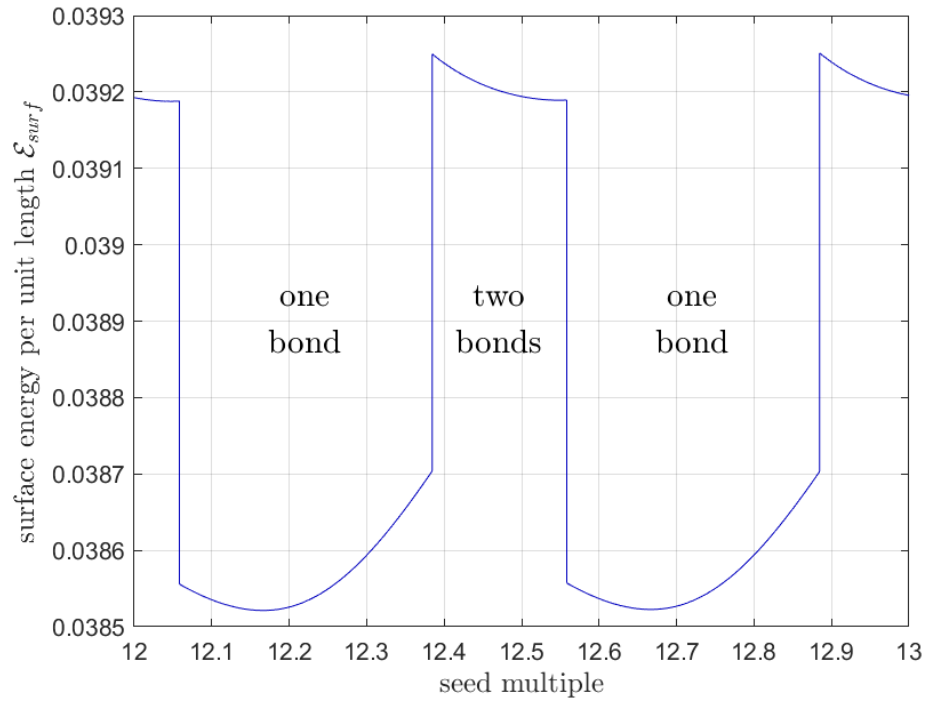
We use the minimizing seed multiple 12.059419 to find a phase interface thickness. Figure 4.31 displays the corresponding vapor phase field. This phase field reveals an approximate phase interface thickness of 5.1271168, which is comparable to, but somewhat less than, the minimizer thickness of 5.9699246 calculated in (4.59).

4.6.2.2 Zigzag Facet

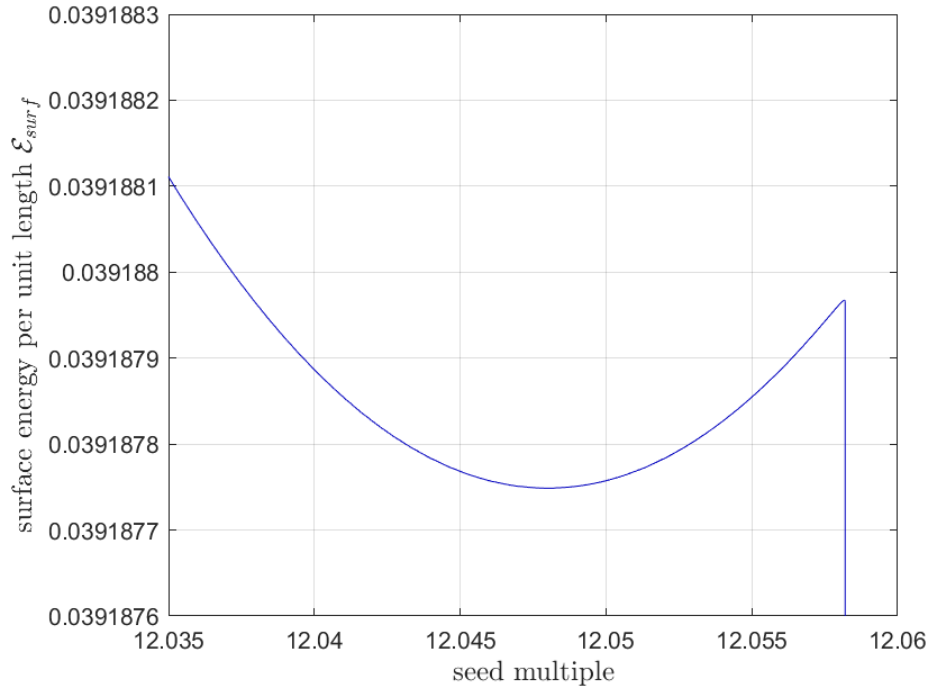
The surface energy per unit length for the zigzag facet over seed multiples 12 through 13 appears in Figure 4.32a. As with the full interface energy, the one-bond stage has lower energy than the two-bond stage. Here, the mean surface energy is 0.038789992, which is greater than the minimum interface energy of 0.024874686 from (4.58).

At the left of Figure 4.32a, we are in the zigzag two-bond stage. As shown in Figure 4.32b, a surface energy well lies to the left of the first discontinuity. The corresponding two-bond surface energy minimum of 0.039187749 occurs near the multiple 12.048142. Figure 4.33a shows the resultant mass density field. At the first discontinuity, the seed multiple is about 12.058198. Directly to the left, the surface energy is around 0.039187959, while to the right the surface energy drops immediately to 0.038555834. The lower energy is the result of the greater stability obtained by the new layer of atoms. Figures 4.33b and 4.33c provide the mass density fields immediately before and after this first discontinuity, respectively.

As we further increase the seed multiple, we arrive at the zigzag one-bond stage surface energy minimum. This minimum surface energy occurs near seed multiple 12.165943 and

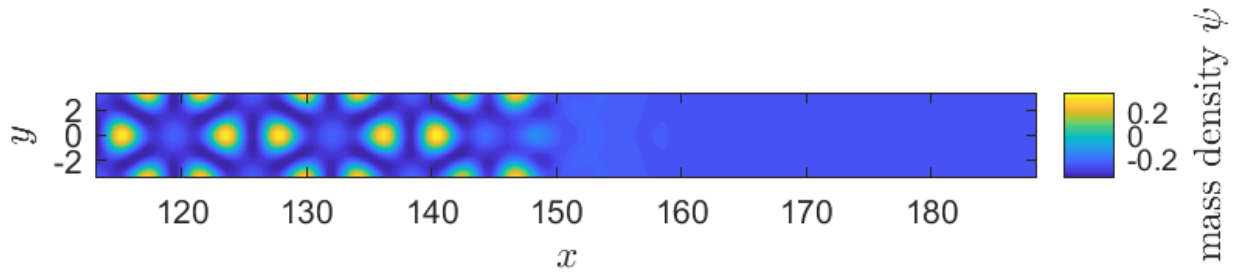


(a) Full View

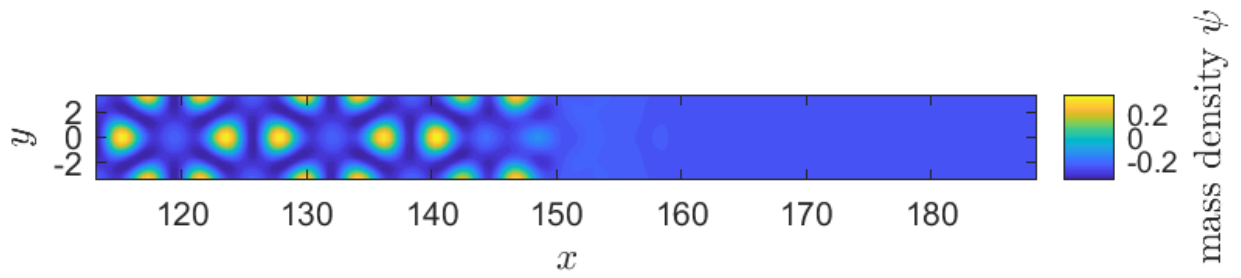


(b) Two-Bond Stage Surface Energy Well

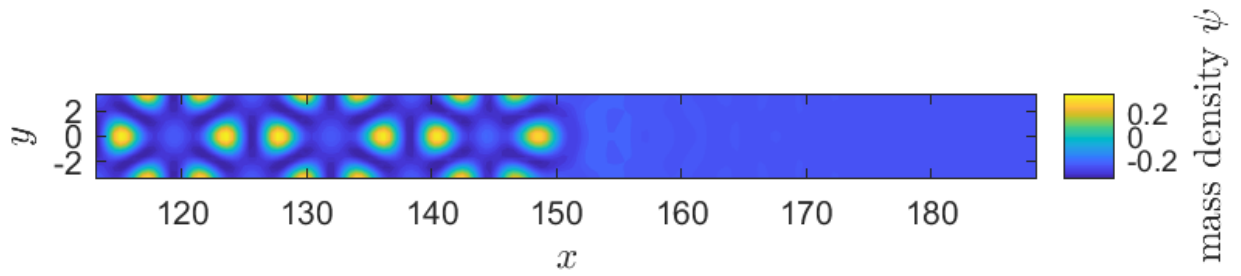
Figure 4.32: Zigzag Facet Surface Energies for Half Interface Energy



(a) Two-Bond Stage, Minimum, Seed Multiple = 12.048142



(b) Two-Bond Stage, Discontinuity Left, Seed Multiple = 12.058198



(c) One-Bond Stage, Discontinuity Right, Seed Multiple = 12.058198

Figure 4.33: Half Interface Energy, Zigzag Facet, Mass Density Fields, Part A

has a value of approximately 0.038521278. Figure 4.34a shows the mass density field. Note that this is the minimum surface energy for the entire 12 to 12.5 multiple cycle. Moving to greater seed multiples, we encounter the second surface energy discontinuity at seed multiple 12.384550. On the left of this discontinuity, the surface energy reaches the one-bond maximum of about 0.038703825. To the right, the surface energy spikes to around 0.039249666, which is the maximum surface energy for the two-bond stage and for the first cycle. An additional layer of atoms appears to the right of the second discontinuity, but the new layer does not result in additional stability. Figure 4.34b details the mass density for the left of the discontinuity, and Figure 4.34c provides the density for the right. As before, the cycle repeats.

Figure 4.35a shows the vapor phase field for the one-bond, minimizing seed multiple 12.165943, where the phase interface thickness is 5.0447798. Figure 4.35b presents the phase field for the two-bond minimizing multiple 12.048142. This phase interface thickness is 5.1757340. Similar to previous results, these thicknesses are close to the armchair facet thickness and less than the value of 5.9699246 calculated in (4.59).

4.6.2.3 Armchair and Zigzag Facet Comparison

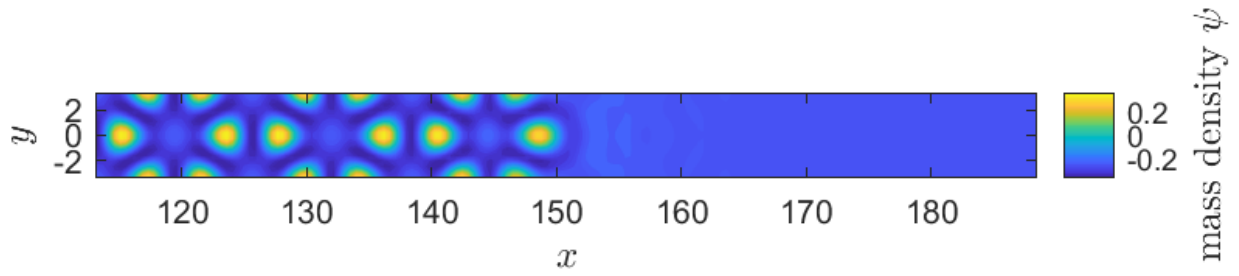
In Figure 4.36, we compare the armchair and zigzag facet surface energies.

As we saw with the full interface energy, the armchair facet surface energy is greater than that of the zigzag facet. Hence, we reaffirm the assumption that the zigzag one-bond stage facet is more common in simulations. Section 4.9 expands on this theory, while Subsection 4.9.2 references the results of this section.

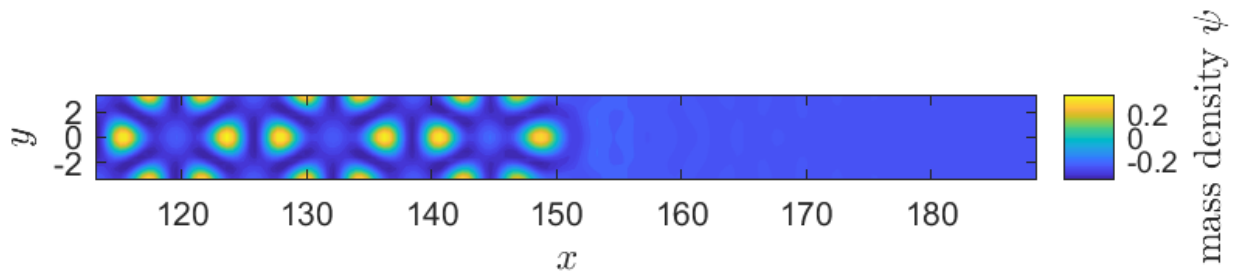
4.6.3 Full and Half Phase Interface Energy Comparison

We now compare the full and half phase interface free energy results. We review the surface energy plots, Figures 4.37a and 4.37b, for the two interface energies.

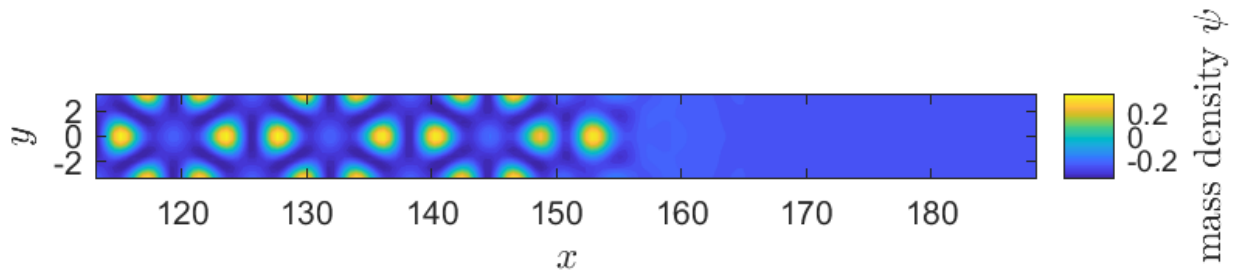
The calculations of (4.56) and (4.58) provide the minimum phase interface free energies for the full and half energy cases, respectively. The full minimum interface energy is 0.049749372, and the half minimum interface energy is half of this, or 0.024874686. Hence, the difference



(a) One-Bond Stage, Minimum, Seed Multiple = 12.165943

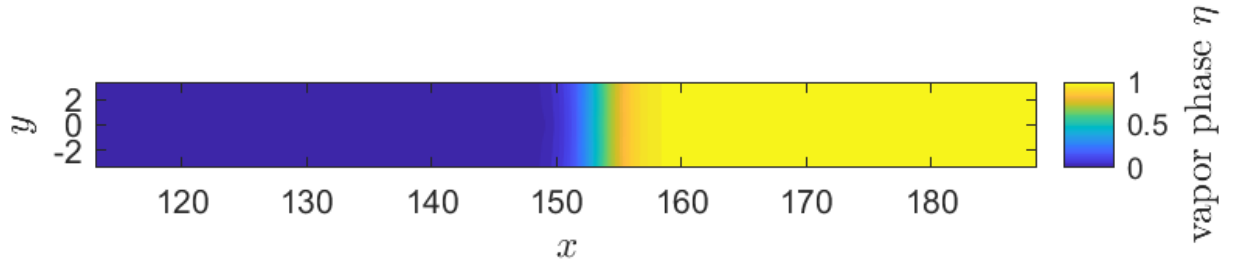


(b) One-Bond Stage, Maximum, Seed Multiple = 12.384550

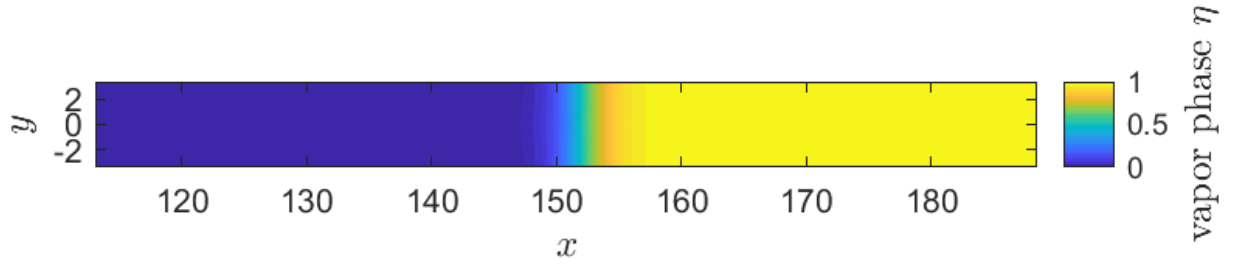


(c) Two-Bond Stage, Maximum, Seed Multiple = 12.384550

Figure 4.34: Half Interface Energy, Zigzag Facet, Mass Density Fields, Part B



(a) One-Bond Stage, Minimum, Seed Multiple = 12.165943



(b) Two-Bond Stage, Minimum, Seed Multiple = 12.048142

Figure 4.35: Half Interface Energy, Zigzag Facet, Vapor Phase Fields

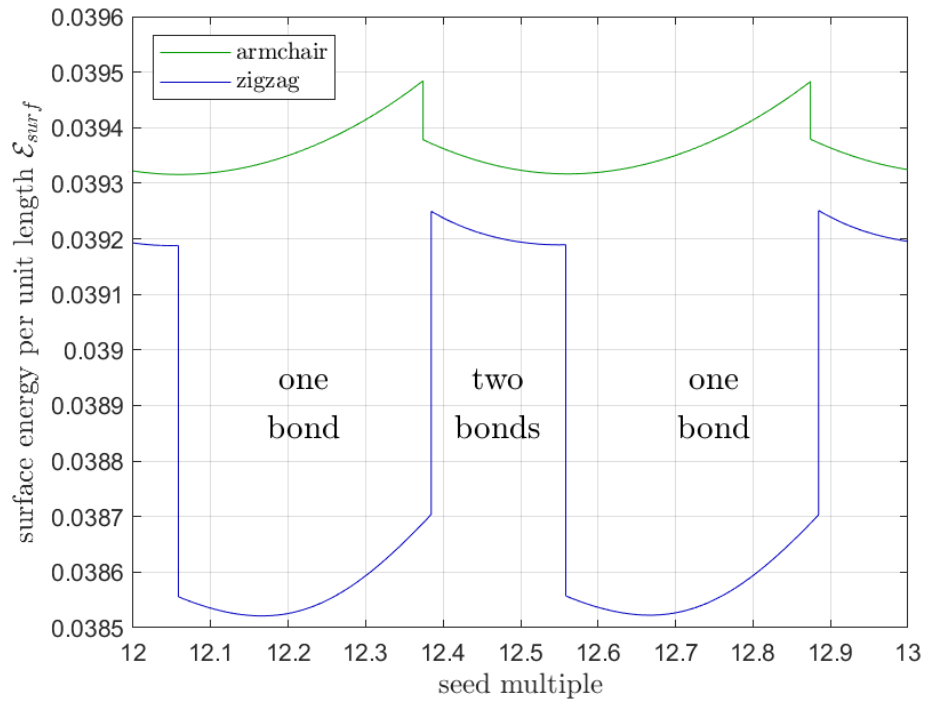
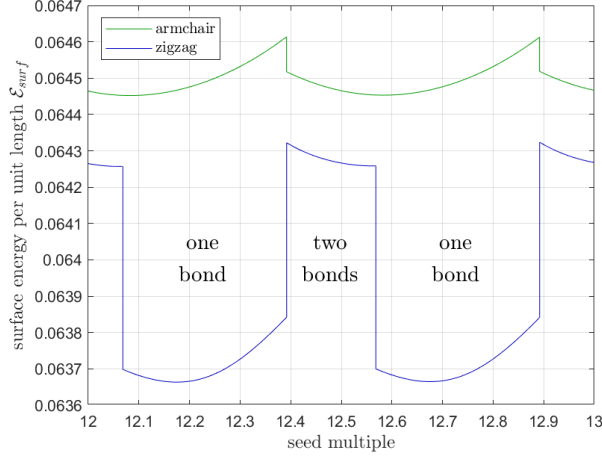
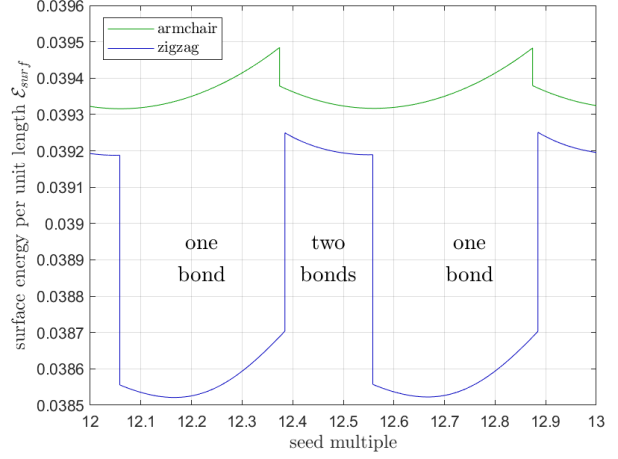


Figure 4.36: Armchair and Zigzag Facet Surface Energies for Half Interface Energy



(a) Full Interface Energy



(b) Half Interface Energy

Figure 4.37: Surface Energies for Full and Half Interface Energies

is 0.024874686. Therefore, we expect the difference between the minimum surface energies for the two cases to be at least 0.024874686. Indeed, the difference between the two armchair minimum surface energies is

$$0.064452159 - 0.039315784 = 0.025136375 > 0.024874686, \quad (4.60)$$

the difference between the zigzag one-bond minima is

$$0.063663464 - 0.038521278 = 0.025142186 > 0.024874686, \quad (4.61)$$

and the difference between the zigzag two-bond minima is

$$0.064257077 - 0.039187749 = 0.025069328 > 0.024874686. \quad (4.62)$$

The average surface energies over the seed multiple range 12 to 13 also meet this criterion. The differences between the armchair average surface energies and the zigzag averages are

$$0.064494221 - 0.039359456 = 0.025134765 > 0.024874686 \quad (4.63)$$

and

$$0.063910075 - 0.038789992 = 0.025120083 > 0.024874686, \quad (4.64)$$

respectively. We might expect that the surface energies themselves would be cut in half, but we can see that this is not the case. The differences of (4.60), (4.61), (4.62), (4.63), and (4.64) are all approximately 0.0251. Furthermore, the listed differences are all relatively close to the phase interface difference of 0.024874686. This tells us that the discrepancy between the surface energy and the minimum phase interface energy has very little to do with the magnitude of this minimum energy. The differences between the listed surface energies and their corresponding minimum phase interface energies range from about 0.0136 to 0.0147. We must attribute these differences to other factors. One such factor is the battle between the homogeneous and gradient portions of the overall free energy functional. We propose that these clashes result in metastable minimum energy states with surface energies that are greater than expected.

As (4.57) and (4.59) indicate, the minimizer phase interface thicknesses are identical for the full and half free energy scenarios. This common phase thickness is 5.9699246. The phase interface thicknesses for the surface energy minimums of our work are consistently less than but still close to 5.9699246. For the full interface energy simulations, these phase thicknesses are near 5.5. For the half energy simulations, they average about 5.1. It seems that the phase interface thickness is affected in a minor way by the magnitude of the phase interface free energy. Perhaps, for lower phase interface energies, the free energies for areas away from the interface are more dominant, forcing the phase interface to shrink.

We make additional observances regarding the relation between the armchair, zigzag one-bond, and zigzag two-bond surface energies. Firstly, for the full interface energy case, the difference between the zigzag facet two- and one-bond minimum surface energies is approximately 0.00059. The difference for the half interface energy is 0.00067. However, since the average zigzag surface energy for the half interface energy is considerably less than that of the full, the difference of 0.00067 is more pronounced for the half energy case. Therefore, we expect the zigzag two-bond stage to be less stable and, thus, less prevalent for the half interface energy simulations.

Finally, the difference between the armchair and zigzag one-bond minimum energies is the about 0.00079 for both interface energy cases. Again, since the average surface energy for the half phase interface energy case is less, this shared difference is more significant for the half energy case. Hence, we expect that the armchair facet would be even more unstable and uncommon for the half interface energy.

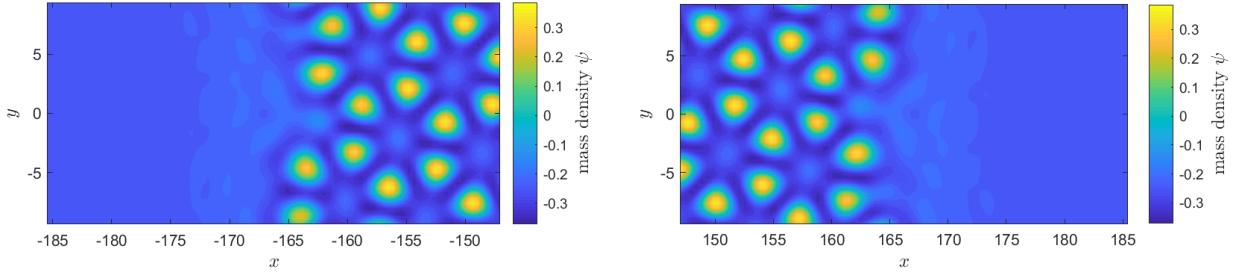
As we see in Section 4.9, lower phase interface energy parameters cause initial disk seeds to develop corners and become more polygonal in shape. This is caused by the dominance of the zigzag one-bond facet. For more rounded nanocrystals, armchair facets must be present to interconnect the different zigzag facets.

4.7 Surface Energy for Alternative Facets

In this section, we analyze the surface energies for the top-to-top and left-to-right facets. As in Section 4.6, each simulation begins with a vertical band seed and vapor and solid mean densities of $\mu_v = -0.22990548$ and $\mu_s = -0.16894892$, respectively. Throughout this section, $W_v = 0.1$ and $\kappa_v = 0.4455$, matching those of the full phase interface energy case of Subsection 4.6.1. For the top-to-top facet simulations, the computational box has a width of $l_x = 20 \cdot 4\pi\sqrt{7} \approx 664.950$ and a height of $l_y = 4\pi\sqrt{\frac{7}{3}} \approx 19.195$. For the left-to-right simulations, the box dimensions are $l_x = 20 \cdot 4\pi\sqrt{\frac{7}{3}} \approx 383.909$ and $l_y = 4\pi\sqrt{7} \approx 33.247$.

Unlike the bands for the armchair and zigzag simulations, the crystal geometry is not symmetric about the y -axis for the top-to-top and left-to-right facets. However, as demonstrated in Figures 4.38 and 4.39, rotating the right phase interface by 180° yields the left phase interface. Hence, for a given facet type, each of the left and right phase interfaces contributes equally to the surface energy.

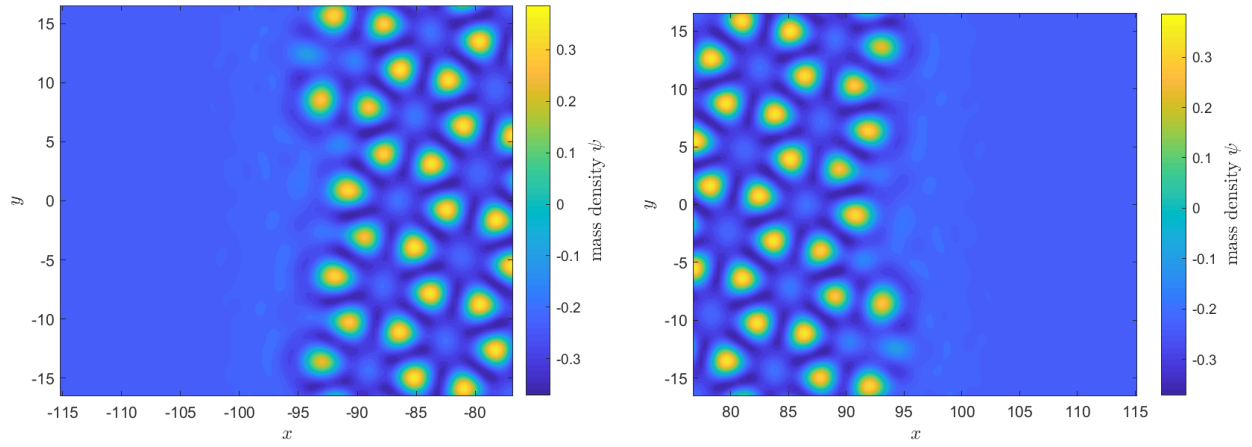
Since the unit cell widths for these facets are much larger than those of the armchair and zigzag, we use a base seed multiple of 5 instead of 12. This gives us band widths similar to those used for the armchair and zigzag facet bands. In addition, we plot one seventh of a seed multiple (or unit cell width), instead of a full seed multiple. As per Section 4.5, the period for both the top-to-top and left-to-right facet orientations is one fourteenth of the corresponding unit cell width. Hence, a range of one seventh provides two full cycles.



(a) Left Interface

(b) Right Interface

Figure 4.38: Top-to-Top Facet, Mass Density Fields, Left and Right Phase Interfaces



(a) Left Phase Interface

(b) Right Phase Interface

Figure 4.39: Left-to-Right Facet, Mass Density Fields, Left and Right Phase Interfaces

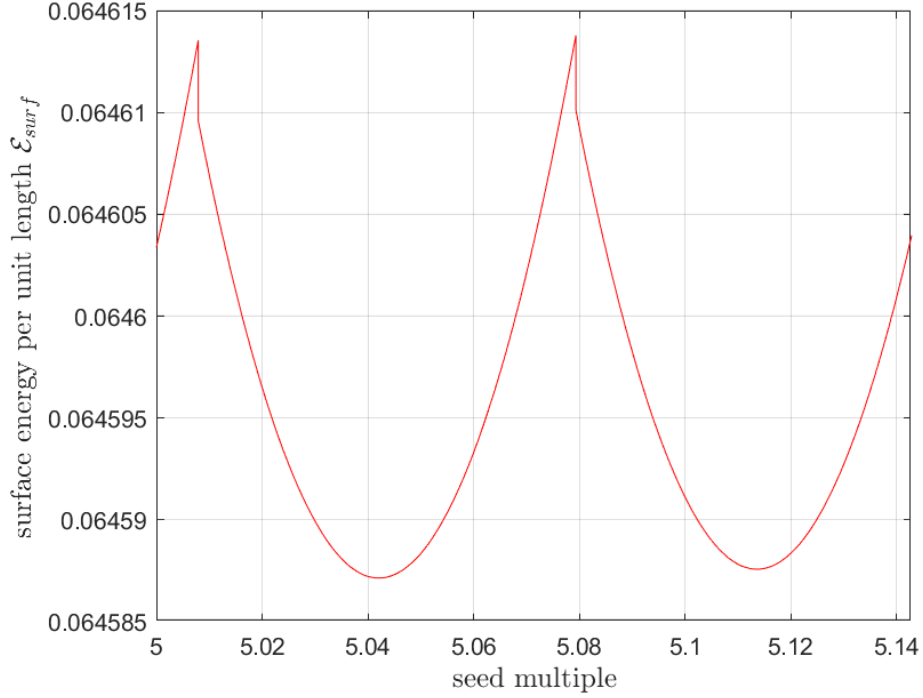
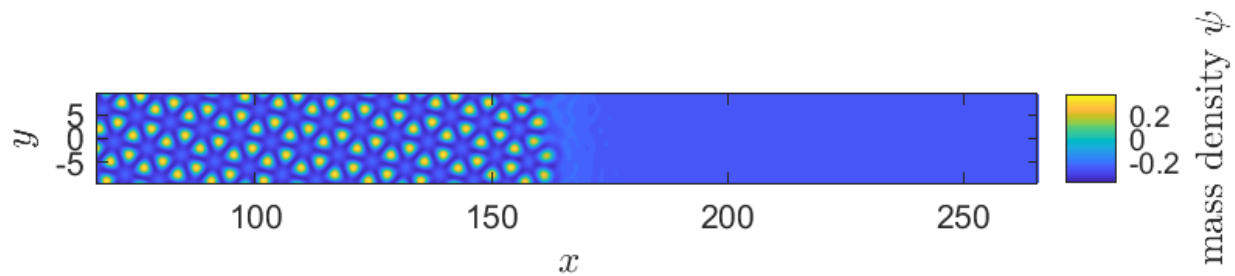


Figure 4.40: Top-to-Top Facet Surface Energies

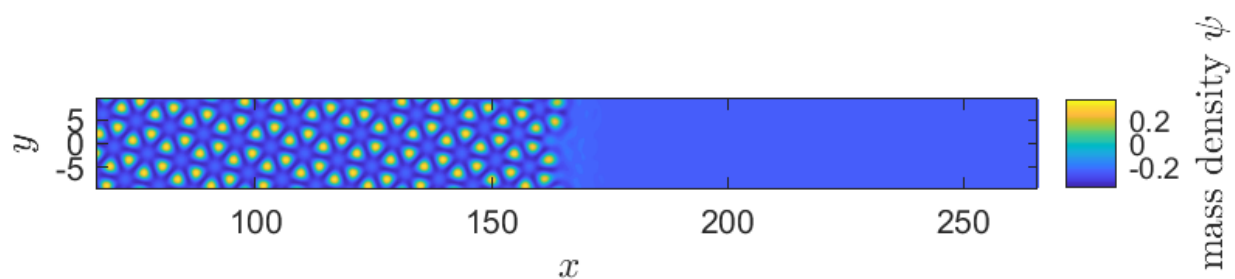
4.7.1 Top-to-Top Facet

Figure 4.40 displays the surface energy per unit length for the top-to-top facet. The surface energy average over this seed multiple range is 0.064595523.

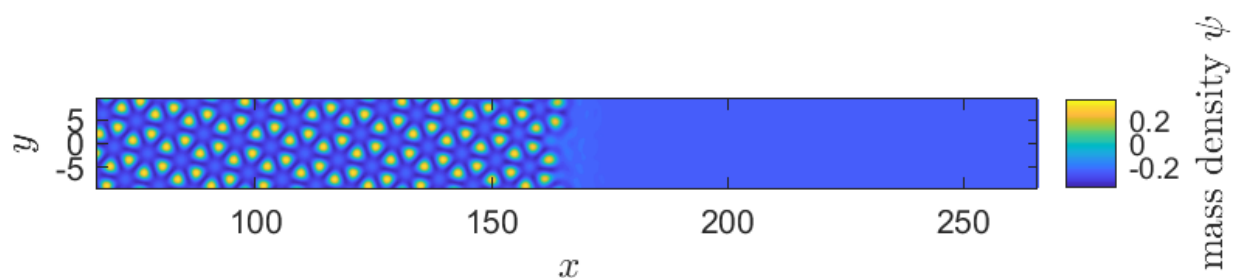
A slight discontinuity occurs at seed multiple 5.0079090. To the left of the discontinuity, the surface energy is at a maximum of approximately 0.06461353280. The corresponding mass density field is given in Figure 4.41a. Figure 4.41b indicates that an additional layer of atoms occurs directly to the right of the discontinuity, where the surface energy is 0.064609593. If we examine Figure 4.41b, we see that the two new atoms are not vertically aligned. We have a situation similar to the two stages of the zigzag facet. However, we are unable to produce a simulation where the left new atom of Figure 4.41b exists without the right. The surface energy is at a minimum of 0.064587136 near the seed multiple 5.0420255. This mass density field appears in Figure 4.41c. Due to periodicity, the energy cycle repeats itself in the right half of Figure 4.40.



(a) Maximum, Seed Multiple = 5.0079090



(b) New Atom Layer, Seed Multiple = 5.0079090



(c) Minimum, Seed Multiple = 5.0420255

Figure 4.41: Top-to-Top Facet, Mass Density Fields

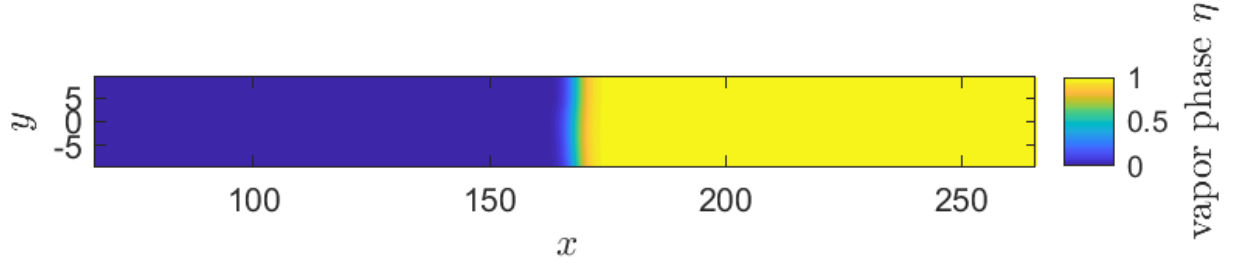


Figure 4.42: Top-to-Top Facet, Minimum, Vapor Phase Field, Seed Multiple = 5.0079090

Figure 4.42 provides the solid-vapor phase interface for the minimum surface energy case. The phase interface thickness is around 5.5298365.

4.7.2 Left-to-Right Facet

The surface energy per unit length for the left-to-right facet appears in Figure 4.43. Here, the surface energy average is 0.064525100. The shape of the curve is similar to that of the armchair facet as seen in Figures 4.21 and 4.29 in Section 4.6.

Moving left to right in Figure 4.43, we encounter a discontinuity at seed multiple 5.0122896. Figure 4.44a provides the mass density field for the left of the discontinuity, and Figure 4.44b shows the mass density for the right. The maximum surface energy of 0.064545548 occurs immediately to the left of the jump. As we can see in Figure 4.44b, a new atom layer emerges directly to the right of the jump, where the surface energy is around 0.064521671. The surface energy minimum for the first cycle occurs near seed multiple 5.0320470. This minimum energy is approximately 0.064517519. Figure 4.44c provides the mass density field for this minimum surface energy. Figure 4.43 shows that the cycle repeats.

The vapor phase field for the minimum surface energy simulation is given in Figure 4.45, where the phase interface thickness is around 5.5184026.

4.7.3 Summary

The minimum surface energies for the top-to-top and left-to-right facets are approximately 0.064587136 and 0.064517519, respectively. Both are greater than the minimum armchair

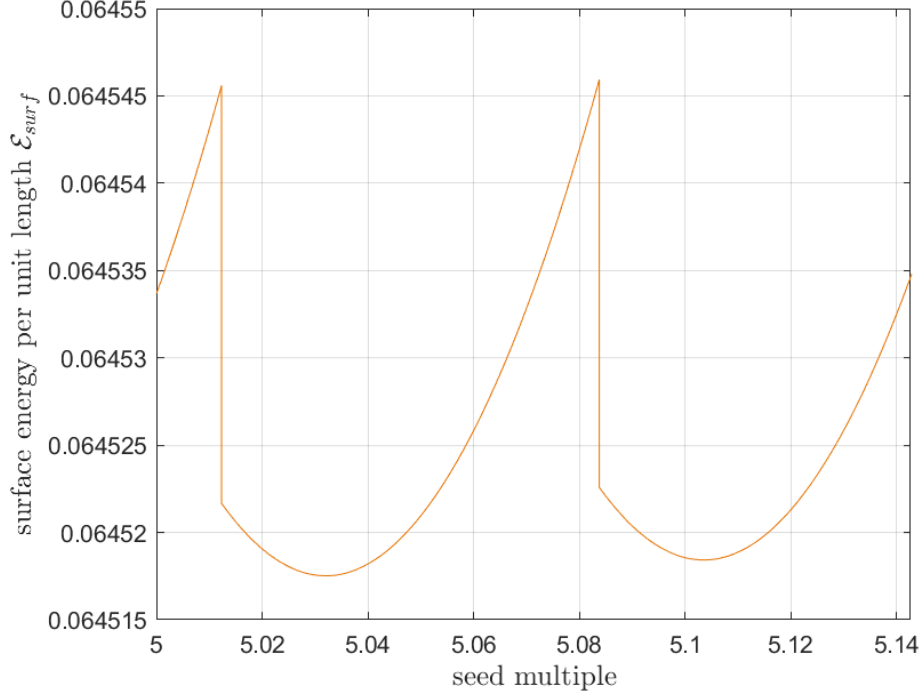
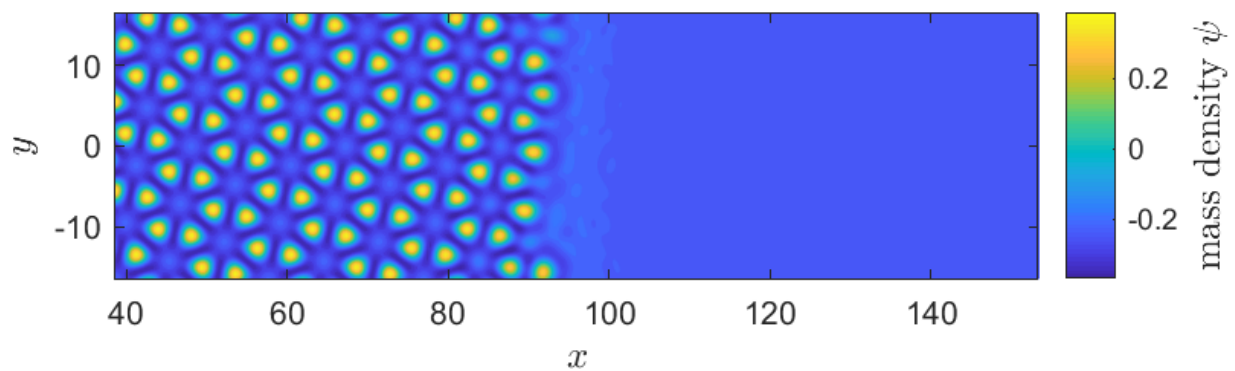


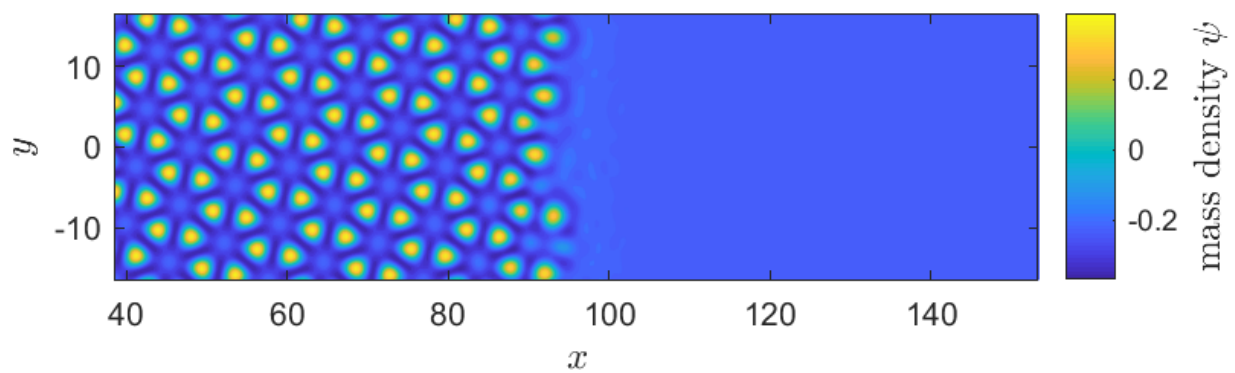
Figure 4.43: Left-to-Right Facet Surface Energies

surface energy of 0.064452159 from the full interface energy simulations of Subsection 4.6.1. This subsection also indicates that the zigzag one-bond and two-bond minimum surface energies are 0.063663464 and 0.064257077, respectively. These are both lower than the armchair minimum. Hence, we hypothesize that top-to-top and left-to-right facets are even less common than the armchair facet in simulations. We might expect to see these facets in the intermediary stages of simulations, before the systems reach equilibrium.

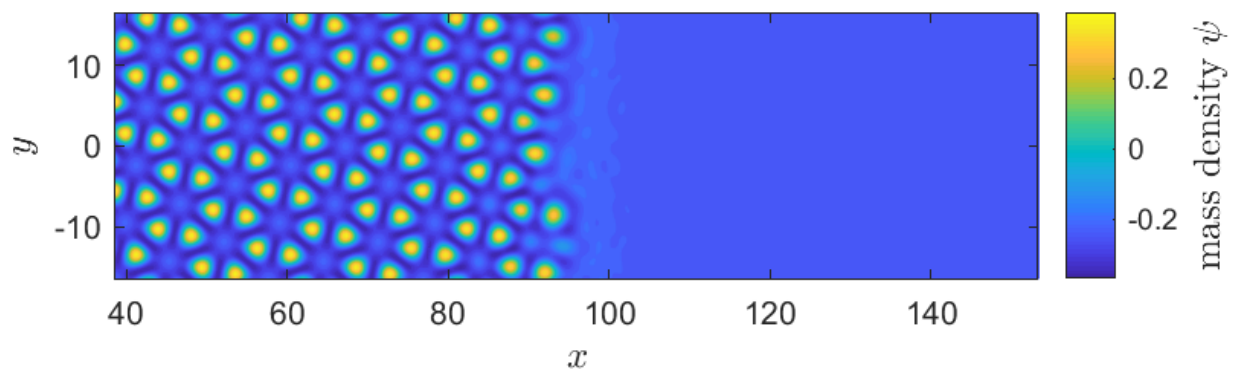
Finally, the phase interface thicknesses at the minimizing seed multiples for the top-to-top and left-to-right facets are 5.5298365 and 5.5184026, respectively. These are comparable to the full interface energy results from Subsection 4.6.1. At the minimizing seed multiples, the armchair facet interface thickness is about 5.5123793, and the corresponding thicknesses for the zigzag one-bond and two-bond stages are 5.4588377 and 5.5448959, respectively. We deduce that, although the phase interface thickness may be affected by the phase interface energy, the thickness is not significantly affected by the facet type.



(a) Maximum, Seed Multiple = 5.0122896



(b) New Atom Layer, Seed Multiple = 5.0122896



(c) Minimum, Seed Multiple = 5.0320470

Figure 4.44: Left-to-Right Facet, Mass Density Fields

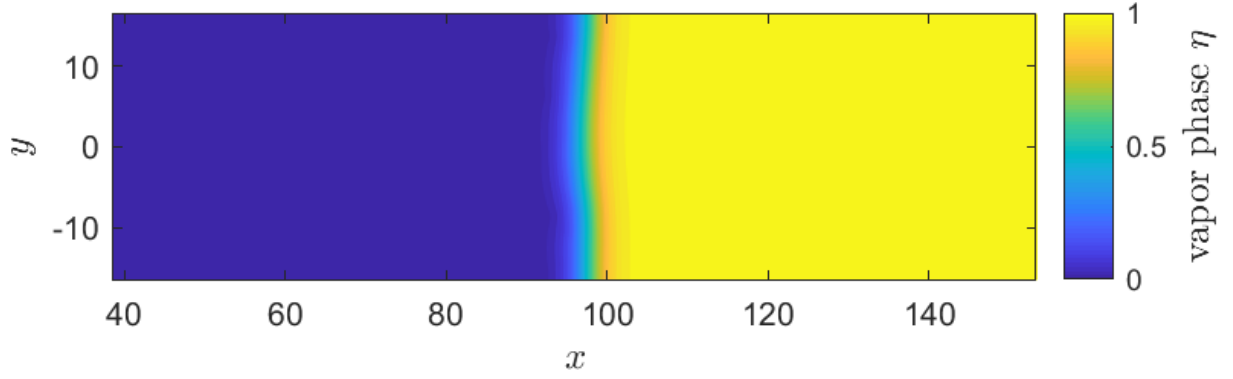


Figure 4.45: Left-to-Right Facet, Minimum, Vapor Phase Field, Seed Mult. = 5.0320470

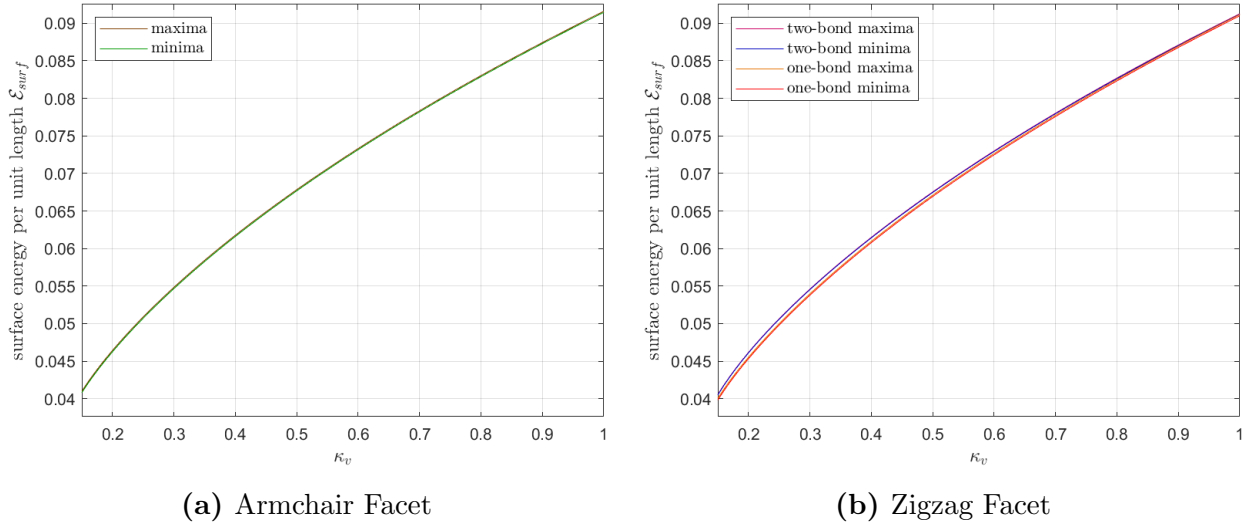


Figure 4.46: Minimum and Maximum Surface Energies

4.8 Maximum and Minimum Surface Energies

In this section, we examine the maximum and minimum surface energies for the armchair facet and zigzag facet one- and two-bond stages for values of κ_v ranging from 0.15 to 1.0 with $W_v = 0.1$. Figure 4.46 shows the maximum and minimum surface energies for the armchair and zigzag facets, respectively. Figure 4.47 combines the minimum and maximum energies of both facets.

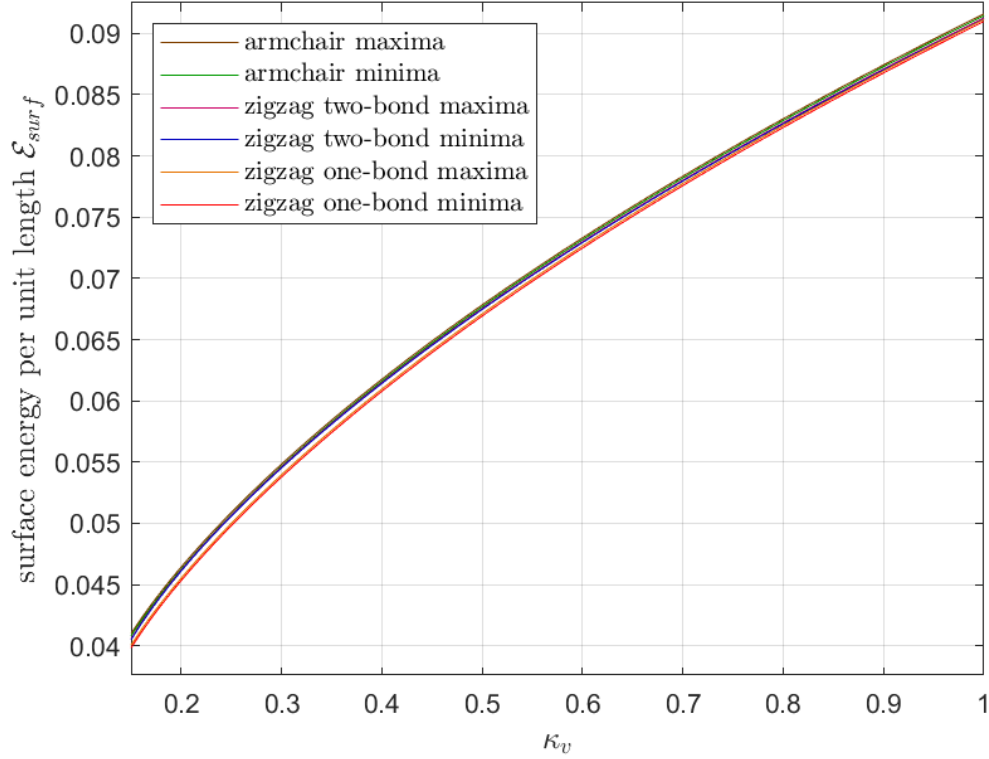
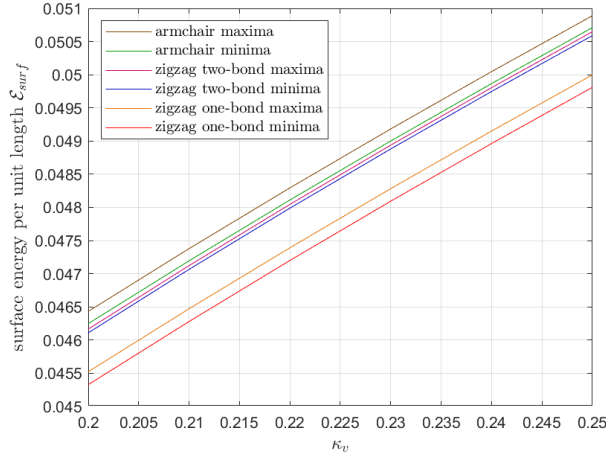


Figure 4.47: Armchair and Zigzag Facets, Minimum and Maximum Surface Energies

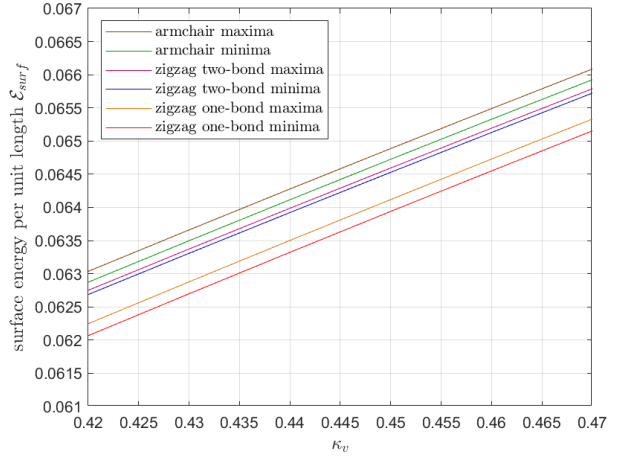
In Figures 4.46 and 4.47, the differences between the energies is almost indiscernible. Therefore, we zoom in on three different areas in Figure 4.48. Figure 4.48a holds the surface energies for $\kappa_v = 0.22275$, Figure 4.48b includes the energies for $\kappa_v = 0.4455$, and Figure 4.48c provides the energies for $\kappa_v = 0.891$. These are the values for κ_v that are used in the various simulations in this surface energy study.

Figures 4.46, 4.47, and 4.48 indicate that all of the surface energies increase as κ_v increases. From Figure 4.48, we see that, as κ_v increases, the differences between the maximum and minimum surface energies decrease. The decrease is much greater for the zigzag facet.

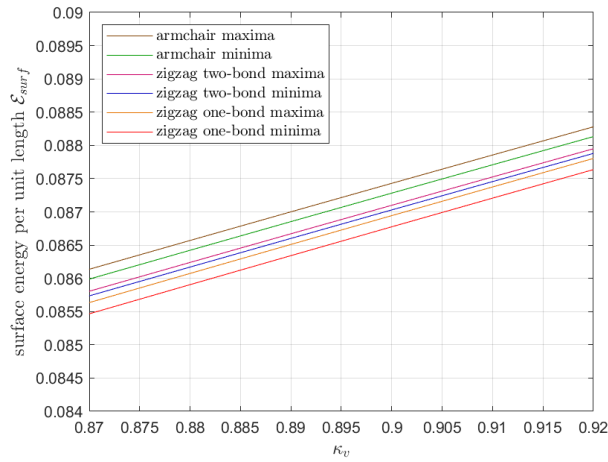
Figure 4.49a displays the difference between the minimum surface energies for the armchair facet and the zigzag one-bond stage. As κ_v increases this energy difference decreases. Therefore, we expect the armchair facet to become more common as κ_v increases. Next, Figure 4.49b presents the difference between the minimum surface energies of the zigzag two-bond and one-bond stages. After an increase in this energy difference for low values of



(a) $\kappa_v = 0.2$ to 0.25



(b) $\kappa_v = 0.42$ to 0.47



(c) $\kappa_v = 0.87$ to 0.92

Figure 4.48: Armchair and Zigzag, Minimum and Maximum Surface Energies, Zooms

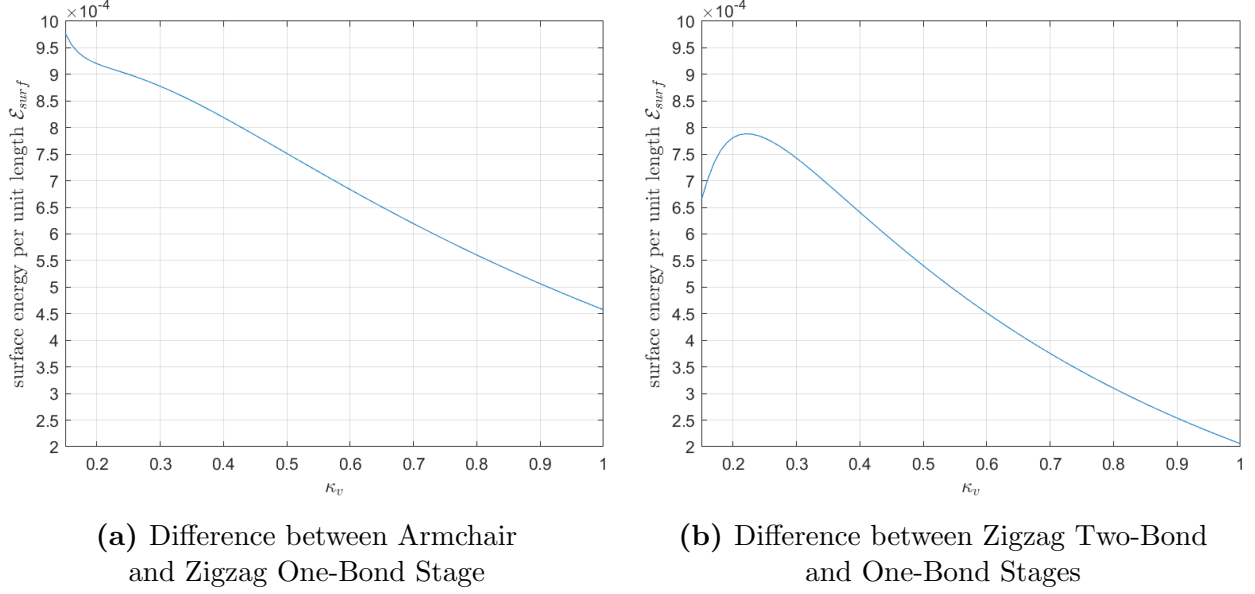


Figure 4.49: Minimum Surface Energy Differences

κ_v , the difference decreases as κ_v continues to increase. This indicates that the zigzag two-bond stage becomes more stable as κ_v increases. Both of these trends are intensified by the fact that the surface energies themselves are increasing. The conjectures here are supported by the disk seed simulations in Section 4.9. In particular, Subsection 4.9.3 refers to the results from this section.

Now, the band seed results from Section 4.6 and, in particular, from Subsection 4.6.3 indicate that the difference between the surface energy and the minimum phase interface energy is largely independent of the magnitude of this interface energy. We restate the equation for the minimum phase interface energy from Section 4.3:

$$\mathcal{E}_{int} := \frac{\sqrt{2W_v\kappa_v}}{6}. \quad (4.65)$$

For $W_v = 0.1$, (4.65) becomes

$$\mathcal{E}_{int} = \frac{\sqrt{5\kappa_v}}{30}, \quad (4.66)$$

and, so, the minimum interface energy is directly proportional to the square root of κ_v . Figure 4.50 combines the curves for the armchair facet minimum surface energies and the

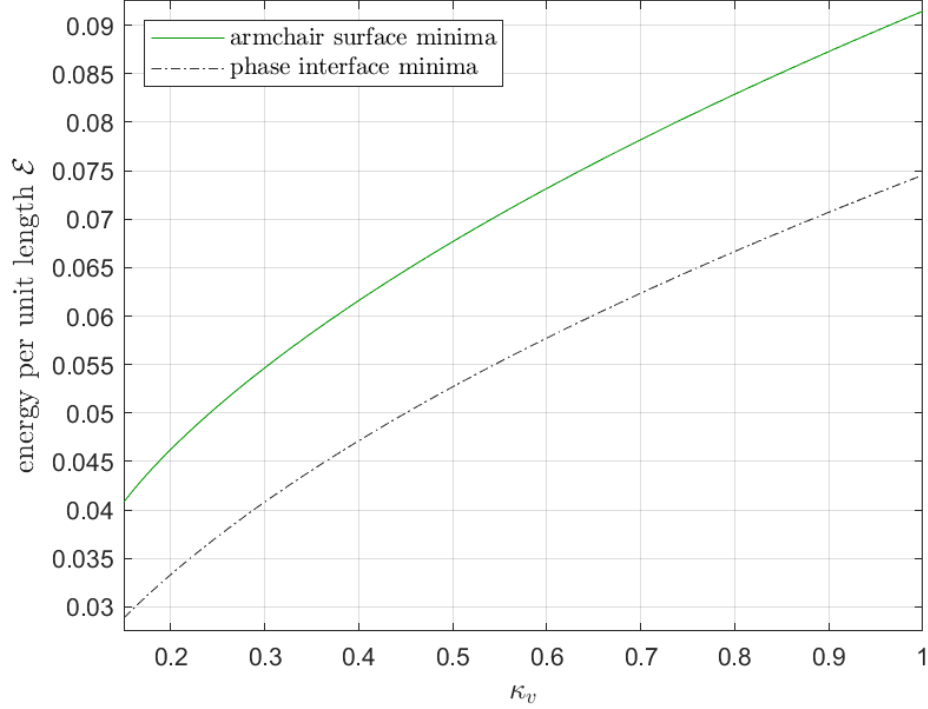


Figure 4.50: Armchair Minimum Surface Energy and Minimum Phase Interface Energy

minimum phase interface energies from (4.66). As a reference point, we consider the case for $\kappa_v = 0.4455$, which corresponds to the full phase interface energy study of Subsection 4.6.1. For this case, the armchair facet minimum surface energy is approximately 0.064452159, and, from (4.66), the minimum phase interface energy is 0.049749372. This gives us an energy difference of 0.014702787. If we consider similar energy differences in Figure 4.50, we confirm that the difference between the surface energy and minimum phase interface energy varies little over the wide range of κ_v values. This supports our conjecture that the magnitude of the minimum phase interface energy has little effect on the difference between the surface energy and the interface energy.

Note: To confirm the accuracy of the results in this section, we ran simulations for $0.15 \leq \kappa_v \leq 0.2$ with a smaller grid spacing ($h_x \approx h_y \approx 0.225$) and a smaller time increment ($dt = 0.02$). The differences between the surface energies for these high resolution simulations and those of our typical resolutions ($h_x \approx h_y \approx 0.45$ and $dt = 0.1$) were negligible.

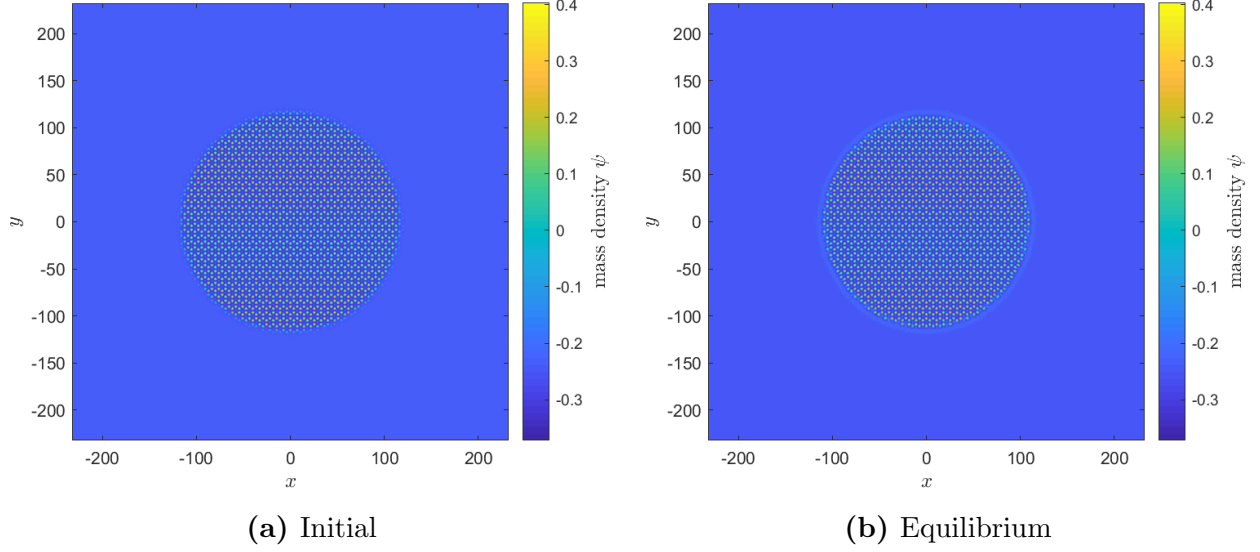


Figure 4.51: Disk Seed, Mass Density Fields, Seed Multiple = 16

4.9 Disk Seed Simulations

To test our dominant facet hypotheses, we run simulations that begin with an initial solid disk seed, which is centered at coordinates $(0,0)$. We consider different pairs of values for the phase interface energy parameters W_v and κ_v . For disk seed simulations, a seed multiple of 1 corresponds to the armchair facet unit cell width of $\frac{4\pi}{\sqrt{3}}$. The seed multiple corresponds to the number of unit cell widths between the initial disk center and circumference. For all disk seed simulations, the computational box is $l_x = 64\frac{4\pi}{\sqrt{3}} \approx 464.333$ in width and $l_y = 37 \cdot 4\pi \approx 464.956$ in height. In addition, note that all minimum phase interface and surface energies in this section are per unit length.

We first consider the case where the initial disk seed radius is 16. We set the initial vapor phase mass density to $\mu_v = -0.22990548$ and the initial solid mean mass density to $\mu_s = -0.16894892$, which are the equilibrium densities of (2.132) and (2.133), respectively, from Section 2.5. The phase interface parameters are set to $W_v = 0.10$ and $\kappa_v = 0.44550$, which correspond to the “full” phase interface energy studies of Sections 4.6 and 4.7. Overall, this configuration corresponds to Figures 4.9a and 4.9b of Section 4.2. For reference, these figures are repeated in Figures 4.51a and 4.51b, respectively.

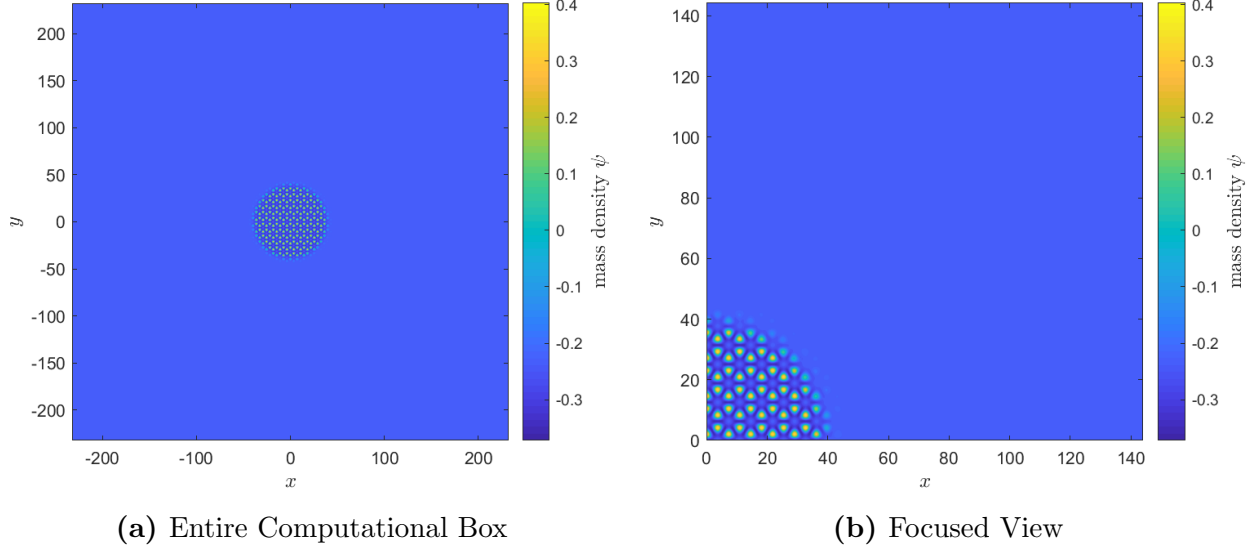


Figure 4.52: Disk Seed, Initial Mass Density Field, Seed Multiple = 5.3441259

An examination of Figures 4.51a and 4.51b indicates that there is little difference between the initial and equilibrium mass density fields. Starting at the phase equilibrium solid and vapor densities results in sort of stagnation of the nanocrystal shape. To better analyze nanocrystal formation, we use initial mass density fields that result in nanocrystal growth or shrinkage. To achieve this end, we use the method of supersaturation; that is, we set the initial vapor phase mass density to a level that is higher than its phase equilibrium. For the remaining nine simulations in this section, we choose the initial vapor phase mass density of $\mu_v = -0.219$, which is greater than the equilibrium of $\mu_{veq} = -0.22990548$. In addition, we choose the initial solid mean density of $\mu_s = -0.171$ and initial seed multiple of 5.3441259. Note that this corresponds to an initial seed diameter of approximately 77.5. For these three parameter values, the resultant overall mean mass density is equal to the mean density for the seed multiple of 16 with initial equilibrium mass densities μ_{veq} and μ_{seq} . This provides us with a standard comparison for the nine simulations. The initial mass density field for all remaining disk simulations is given in Figures 4.52a and 4.52b. Note that the nanocrystal area for this initial state is 4721.2796.

Now, Figure 4.52b displays only a portion of Quadrant I of the computational box. The bottom-left corner is positioned at the center of the box and of the solid disk itself. Since

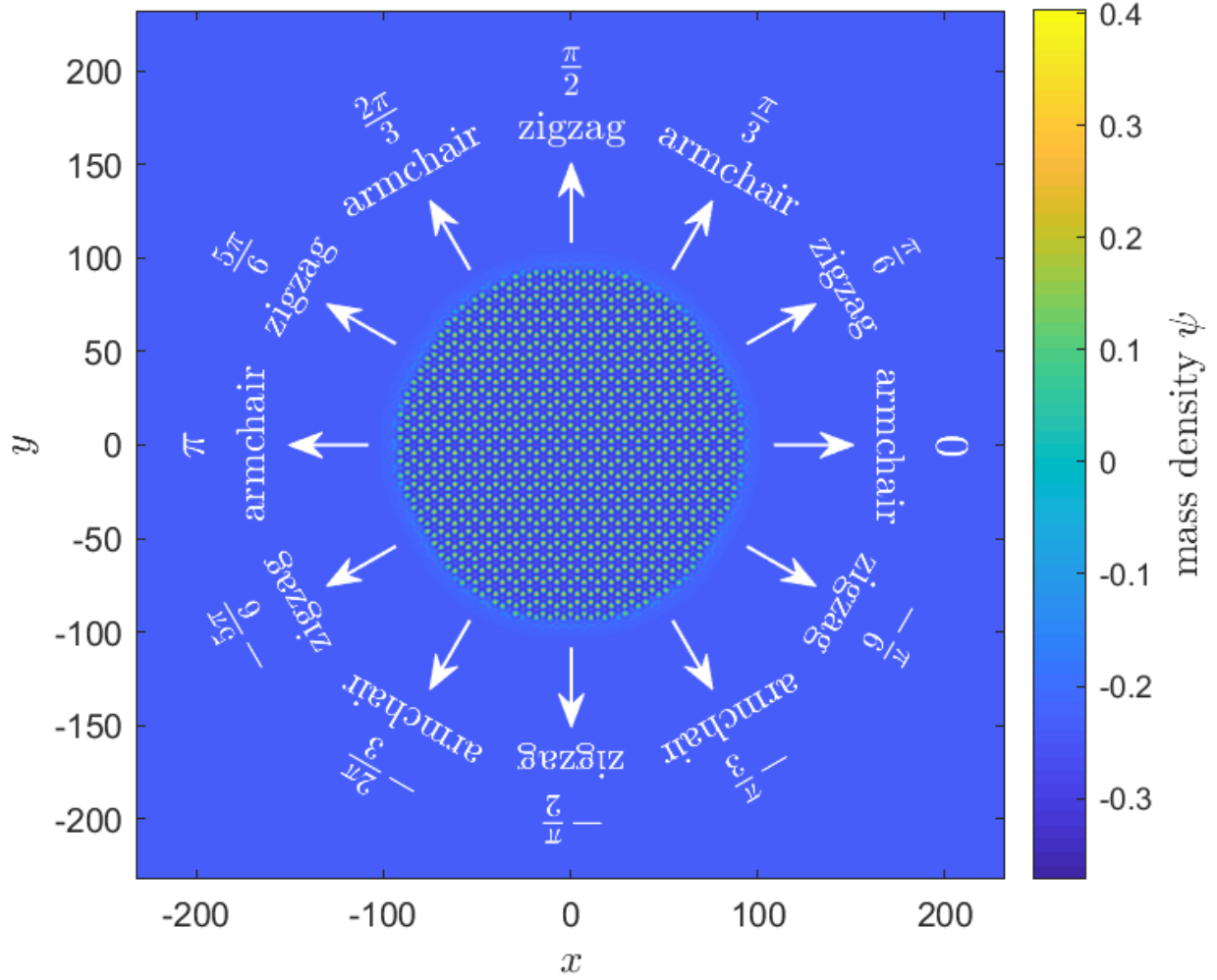


Figure 4.53: Disk Seed, Mass Density Field, $W_v = 0.05$, $\kappa_v = 0.89100$

the mass density field is symmetric about both the x -axis and the y -axis, this view provides all of the information that we require.

Next, we discuss the nanocrystal geometry that typically emerges as an initial disk seed system approaches equilibrium. Figure 4.53 shows the equilibrium mass density field for $W_v = 0.05$ and $\kappa_v = 0.89100$. The nanocrystal has the approximate shape of a 12-sided polygon, or dodecagon. Traveling around the perimeter of the nanocrystal, we see that the facets alternate between the armchair and zigzag facets every $\frac{\pi}{6}$ radians, or 30° .

Figure 4.54 is the focal point of this section. This figure provides the mass density fields for systems at equilibrium (after a long time has passed) for the nine possible

combinations of the phase interface energy parameter values $W_v = 0.05, 0.10, 0.20$ and $\kappa_v = 0.22275, 0.44550, 0.89100$. Again, for each simulation, the initial densities are $\mu_v = -0.219$ and $\mu_s = -0.171$, and the initial seed multiple is 5.3441259.

If the vapor and solid mean mass densities reached their equilibria ($\mu_{veq} = -0.22990548$ and $\mu_{seq} = -0.16894892$), then the nanocrystal “radii” for these simulations would be approximately 16 seed multiples, or 116.08316. However, the nanocrystal radii of Figure 4.54 are noticeably smaller. Hence, these systems achieve equilibrium at metastable states.

The mass density fields of Figure 4.54 also indicate that the zigzag facets, particularly the zigzag one-bond stage, are longer and, therefore, more prevalent than the armchair facets. We discuss this further in Subsection 4.9.2.

The minimum phase interface energy per unit length (4.38) and minimizer phase interface thickness (4.39) of Section 4.3 are

$$\mathcal{E}_{int} := \frac{\sqrt{2W_v\kappa_v}}{6}, \quad (4.67)$$

and

$$\delta_{int} := 2\sqrt{\frac{2\kappa_v}{W_v}}, \quad (4.68)$$

respectively. We use (4.67) to compute the minimum phase interface energies per unit length in Table 4.1a. Employing (4.68) gives us the minimizer phase interface thicknesses of Table 4.1b. Finally, Table 4.1c shows the areas of the nanocrystals for the nine systems at equilibrium. As a point of reference, the initial solid area for the nine simulations is 4721.2796. All three tables share the layout of Figure 4.54.

4.9.1 Constant Minimum Phase Interface Energy

As we move diagonally, up and to the right, in Tables 4.1a, 4.1b, and 4.1c, we find that the minimum phase interface energy remains constant, the minimizer interface thickness doubles, and the solid area increases. Correspondingly, the mass density fields of Figure 4.54 reveal that the nanocrystals become rounder.

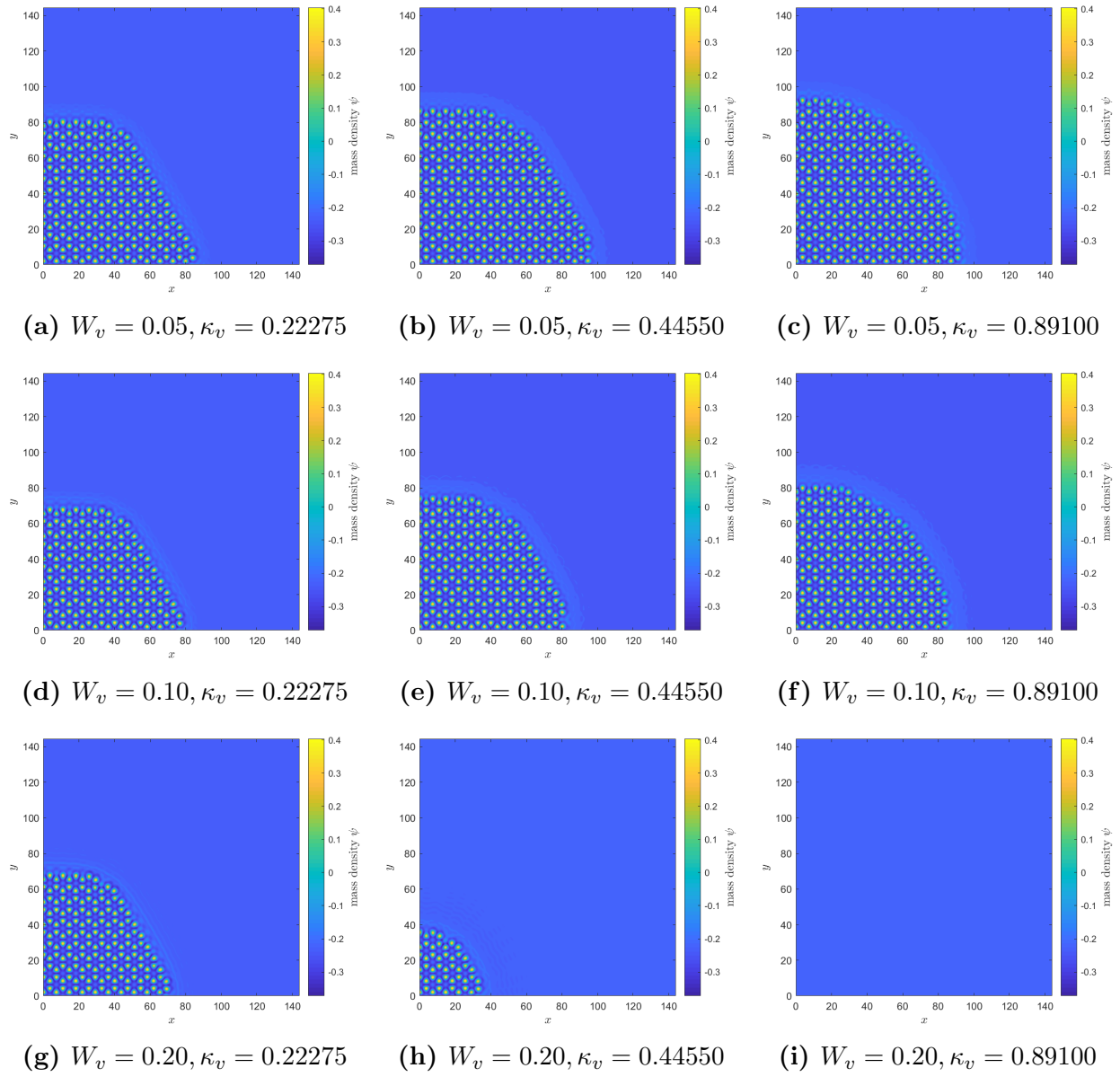


Figure 4.54: Disk Seed, Mass Density Fields, Seed Multiple = 5.3441259

Table 4.1: Disk Seed, Equilibrium State Characteristics, Seed Multiple = 5.3441259**(a)** Minimum Phase Interface Energies per Unit Length

	$\kappa_v = 0.22275$	$\kappa_v = 0.44550$	$\kappa_v = 0.89100$
$W_v = 0.05$	0.024874686	0.035178118	0.049749372
$W_v = 0.10$	0.035178118	0.049749372	0.070356236
$W_v = 0.20$	0.049749372	0.070356236	0.099498744

(b) Minimizer Phase Interface Thicknesses

	$\kappa_v = 0.22275$	$\kappa_v = 0.44550$	$\kappa_v = 0.89100$
$W_v = 0.05$	5.9699246	8.4427484	11.939849
$W_v = 0.10$	4.2213742	5.9699246	8.4427484
$W_v = 0.20$	2.9849623	4.2213742	5.9699246

(c) Solid Nanocrystal Areas

	$\kappa_v = 0.22275$	$\kappa_v = 0.44550$	$\kappa_v = 0.89100$
$W_v = 0.05$	23676.072	29550.340	30564.284
$W_v = 0.10$	19009.678	21882.521	24818.581
$W_v = 0.20$	16835.568	4799.0826	0

We surmise that wider phase interface regions produce a greater variety of potential mass density distributions within the interface. The results are twofold. First, the additional possibilities for interface density arrangements enable more mass density to transfer from the supersaturated vapor region into the solid region over time. This increases the area of the solid. Second, the wider variety of density distributions facilitates a smoother nanocrystal shape. We note here that greater nanocrystal circularity coincides with armchair facets that are closer in length to zigzag facets. Hence, at a constant minimum interface energy, increases in the minimizer interface thickness result in longer armchair facets. In addition, greater nanocrystal circularity indicates greater isotropy; that is, the nanocrystal grows more evenly in all radial directions. We can assume that increases in the minimizer interface thickness result in higher isotropic energies.

4.9.2 Constant Minimizer Phase Interface Thickness

Moving diagonally, down and to the right, in Tables 4.1a, 4.1b, and 4.1c, we discover that the minimum phase interface energy doubles, the minimizer interface thickness remains constant, and the solid area decreases. Following the same diagonal pattern across the fields of Figure 4.54 reveals a rounding of the nanocrystals. We expect that increases in the minimum phase interface energy result in increases in surface energy. Recall that both are per-unit-length energies. It follows that greater surface energies push for smaller nanocrystal perimeters. Hence, the solid region itself tends to be smaller for higher minimum interface energies. Furthermore, recall that, for a constant area, the smallest perimeter is obtained by a single disk shape. Hence, for these higher energies, the nanocrystal is more circular, and, thus, the armchair facets are longer. Therefore, greater surface energy per unit length results in greater isotropic energy.

Here, we discuss the full and half phase interface energy simulations of Section 4.6. The simulations of Section 4.6 employ initial band seeds and mean mass densities of $\mu_{veq} = -0.22990548$ and $\mu_{seq} = -0.16894892$. The full interface energy simulations of that section correspond to $W_v = 0.10$ and $\kappa_v = 0.44550$, while the half interface energy simulations match $W_v = 0.05$ and $\kappa_v = 0.22275$. Both the full and half interface energy studies of Section 4.6 share the same minimizer interface thickness. The mass density fields for the corresponding disk seed simulations are found in Figures 4.54e and 4.54a, respectively. We repeat them in Figures 4.55a and 4.55b.

Firstly, the results of Section 4.6 show that, for both the full and half interface energies, the surface energies for the armchair facet are greater than the corresponding surface energies for both the zigzag one-bond facet and the zigzag two-bond facet. For the disk seed simulations, we might expect the lower-energy zigzag facets to be longer than those of the armchair. The mass density fields of Figures 4.54a, 4.54b, 4.54c, 4.54d, 4.54e, 4.54f, 4.54g, and 4.54h fulfill our expectations. The zigzag facet is more prevalent.

Secondly, the summaries of Section 4.6 indicate that, on a relative scale, the surface energies of the armchair facet are closer to those of the zigzag facet for the full interface energy case. Therefore, we expect the armchair facet to be more prevalent for the full

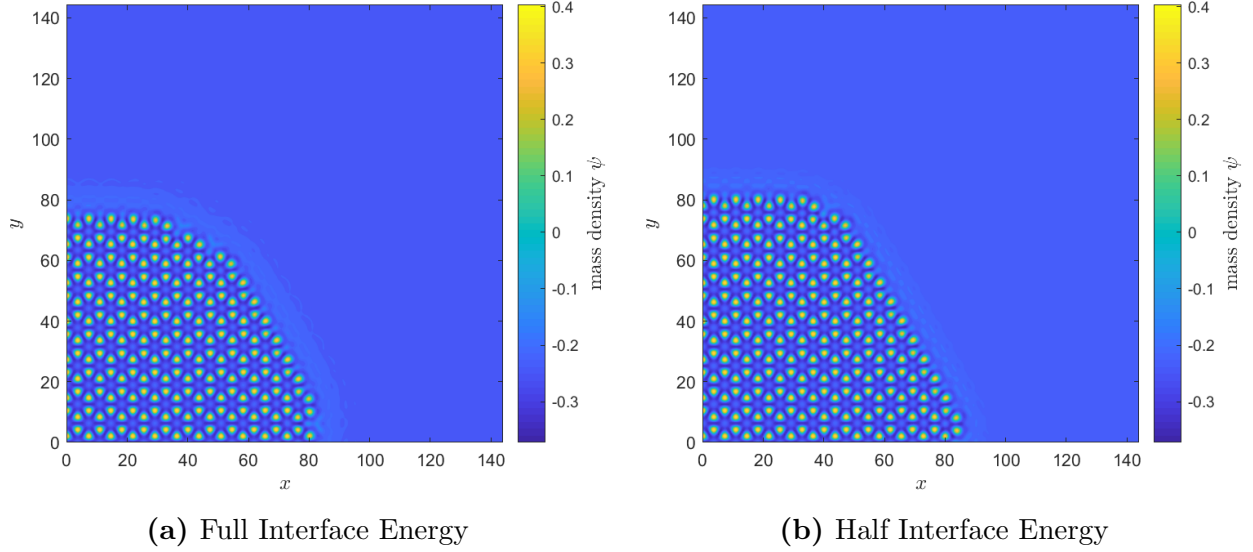


Figure 4.55: Disk Seed, Mass Density Fields, Seed Multiple = 5.3441259

interface energy case of Figure 4.55a than for the half interface energy case of Figure 4.55b. Indeed, we see that each armchair facet in Figure 4.55a is two unit cells in length, while each armchair facet in Figure 4.55b is one unit cell in length.

Thirdly, Section 4.6 suggests that the zigzag two-bond stage is relatively unstable. In fact, of all of the fields of Figure 4.54, the zigzag two-bond stage only appears in the equilibrium mass density fields of Figures 4.54c and 4.54f. In both cases, the zigzag two-bond stage only occurs as a single atom at each meeting of the armchair facet and the zigzag one-bond facet.

Therefore, the conjectures of Section 4.6 are supported by the results of this section. We have a correlation between band seeds with equilibrium initial mean mass densities and disk seeds with nonequilibrium initial mean densities.

4.9.3 Constant W_v

Traveling right across a given row in Tables 4.1a and 4.1b increases both the minimum phase interface energy and the minimizer interface thickness by a factor of $\sqrt{2}$. In Table 4.1c, we find that, moving to the right, the area increases for both $W_v = 0.05$ and $W_v = 0.10$. It seems that, for these W_v values, the increase in area caused by the increase in interface thickness overcomes the decrease in area caused by the increase in minimum interface energy. However,

for $W_v = 0.20$, the area decreases as we move to the right across Table 4.1c. For $W_v = 0.20$, the decrease in area from the increase of minimum interface energy is the dominant force.

Referencing Table 4.1c for $W_v = 0.20$ with $\kappa_v = 0.44550$ provides the equilibrium nanocrystal area of 4799.0826. This nanocrystal area is very close to the initial area of 4721.2796. Virtually, no nanocrystal growth takes place during this simulation.

However, for $W_v = 0.20$ with $\kappa_v = 0.89100$, no solid region remains. The nanocrystal shrinks over time as sublimation takes place. We conjecture that the surface energy is so great for this configuration that there can be no phase interface at all. Over time, the vapor mass density increases from the initial $\mu_v = -0.219$ to -0.217945137 . The level of supersaturation increases. This high level of vapor density causes the vapor free energy contribution of (2.96) to be relatively large. However, the presence of a phase interface and the corresponding surface free energy is larger still. Note that, if the entire region was solid, there would also be no phase interface. The resulting solid would have the relatively low mean density of $\mu_s = -0.217945137$. We may assume that, for $W_v = 0.20$ with $\kappa_v = 0.89100$, the total free energy for universal solid is greater than the total energy for universal vapor.

Regardless of the value of W_v , Figure 4.54 indicates an increase in the nanocrystal circularity as κ_v increases. Hence, larger values of κ_v result in greater isotropy.

Now, we apply the minimum surface energy results from Section 4.8. The many simulations of Section 4.8 involve initial band seeds and mean mass densities of $\mu_{veq} = -0.22990548$ and $\mu_{seq} = -0.16894892$. In addition, across all simulations, $W_v = 0.10$ is constant. Figures 4.54d, 4.54e, and 4.54f are the mass density fields for the disk seed simulations with $W_v = 0.10$. These fields are repeated in Figure 4.56.

Figure 4.48 provides close-ups of the minimum and maximum surface energy curves for the armchair and zigzag facets from Section 4.8. They are repeated in Figure 4.57. The surface energies for $\kappa_v = 0.22275$, $\kappa_v = 0.44550$, and $\kappa_v = 0.89100$ are found in Figures 4.57a, 4.57b, and 4.57c, respectively.

Table 4.2a lists the differences between the minimum surface energies of the armchair facet and the zigzag one-bond stage for the κ_v values of this section. Table 4.2b catalogs the differences between the minimum surface energies for the zigzag one-bond and two-bond stages. Again, this data corresponds to the simulations of Section 4.8.

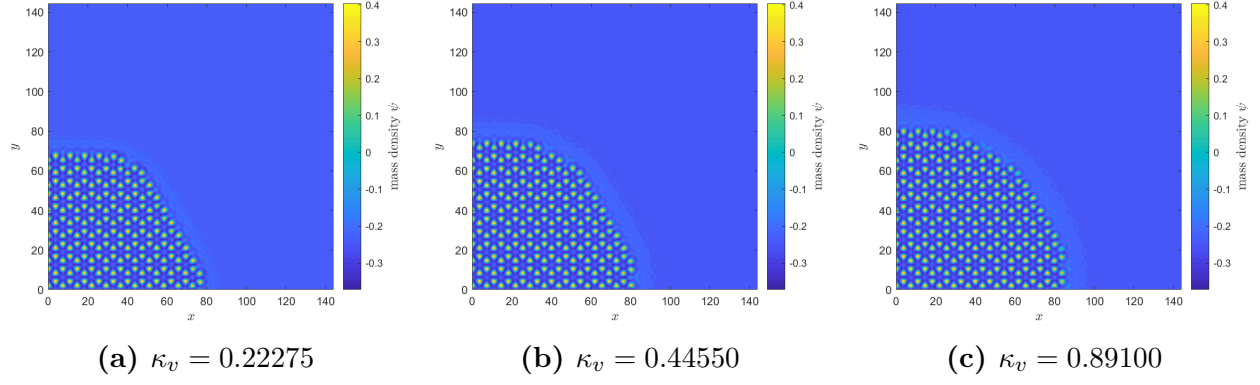


Figure 4.56: Disk Seed, Mass Density Fields, Seed Multiple = 5.3441259, $W_v = 0.10$

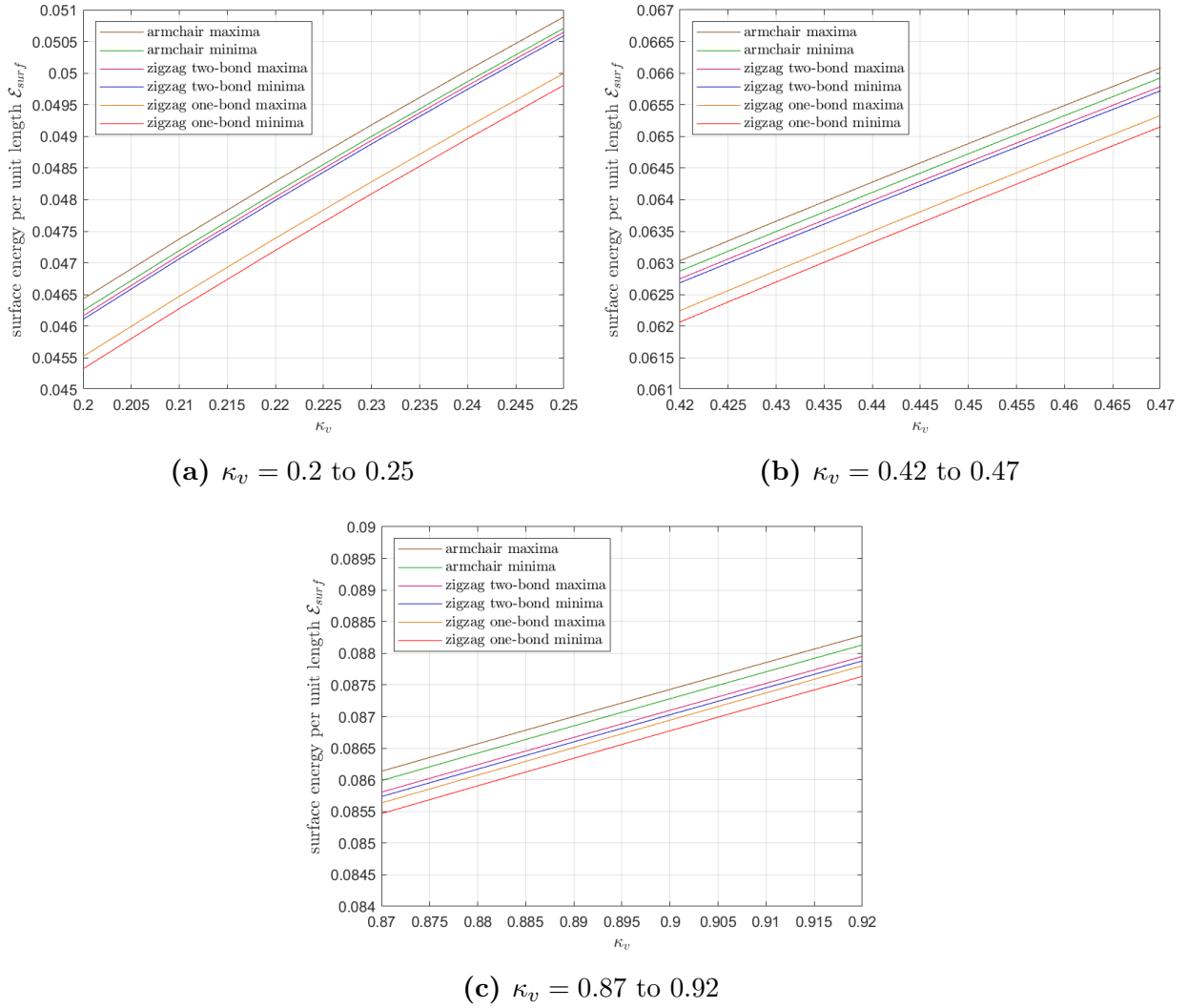


Figure 4.57: Armchair and Zigzag, Minimum and Maximum Surface Energies, Zooms

Table 4.2: Minimum Surface Energy Differences, $W_v = 0.10$ **(a)** Differences between the Armchair Facet and Zigzag One-Bond Stage

κ_v	energy difference
0.22275	0.0009106
0.44550	0.0007887
0.89100	0.0005113

(b) Differences between the Zigzag Two-Bond and One-Bond Stages

κ_v	energy difference
0.22275	0.0007881
0.44550	0.0005938
0.89100	0.0002586

We address two important inferences from Section 4.8. The first states that the decrease in the difference between the minimum surface energies for the armchair facet and zigzag one-bond stage results in longer armchair facet lengths. The disk seed simulations of Figure 4.56 support this conjecture. For $\kappa_v = 0.22275$, the armchair facet length is one unit cell. The armchair facet length for $\kappa_v = 0.44550$ is two unit cells. Finally, for $\kappa_v = 0.89100$, the armchair length is about three unit cells. Another prediction from Section 4.8 suggests that a decrease in the difference between the minimum surface energies for the zigzag two-bond and one-bond stages yields a more stable zigzag two-bond stage. At each of the intersections of the armchair and zigzag one-bond stage facets of Figure 4.56c, there is a hint of a zigzag two-bond stage. For example, moving to the right along the top of the nanocrystal, we arrive at corner where the last atom of the zigzag one-bond stage is slightly faded. Without this “semi-atom”, the neighboring atom would represent the zigzag two-bond stage. For $W_v = 0.05$ and $\kappa_v = 0.89100$, Figure 4.54c (repeated in Figure 4.58) displays clearly the zigzag two-bond stage at the corners of the nanocrystal.

4.9.4 Constant κ_v

Moving up through a given column of Tables 4.1a, 4.1b, and 4.1c results in decreasing minimum phase interface energy, increasing minimizer interface thickness, and increasing nanocrystal area. The minimum interface energy decreases by a factor of $\sqrt{2}$, while the

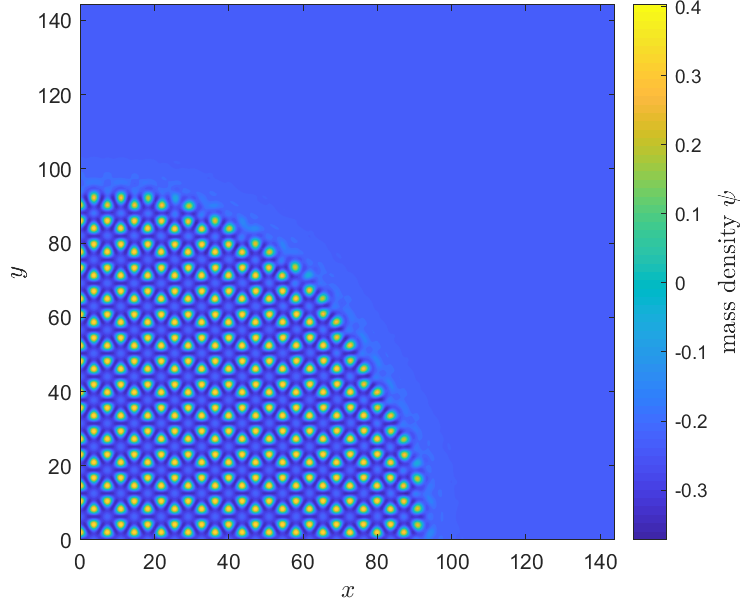


Figure 4.58: Disk Seed, Mass Density Field, $W_v = 0.05$, $\kappa_v = 0.89100$

minimizer interface thickness increases by $\sqrt{2}$. These observations concur with Subsections 4.9.1 and 4.9.2, where decreases in the minimum interface energy and increases in the minimizer interface thickness result in increased nanocrystal area. Interestingly, as we keep κ_v constant and decrease W_v , the lengths of the armchair facets in the fields of Figure 4.54 remain relatively constant. We consider the nanocrystal shapes for $\kappa_v = 0.22275$. For each of $W_v = 0.05, 0.10, 0.20$, the length of each armchair facet is one unit cell. However, since the area increases as W_v decreases, the lack of change in the length of the armchair facets actually results in a sharper nanocrystal shape and, therefore, more anisotropy. To understand this effect, we can imagine a regular dodecagon. Then, we pick six non-consecutive sides and fix their lengths. Next, we continually increase the area of the dodecagon. Concurrently, we view the dodecagon from a greater and greater distance so that the overall size looks about the same. Gradually, the sides with the fixed lengths become negligible in size. The shape appears to become a hexagon, which has greater anisotropy than a dodecagon. In conclusion, conversely, larger values of W_v result in higher isotropic energies.

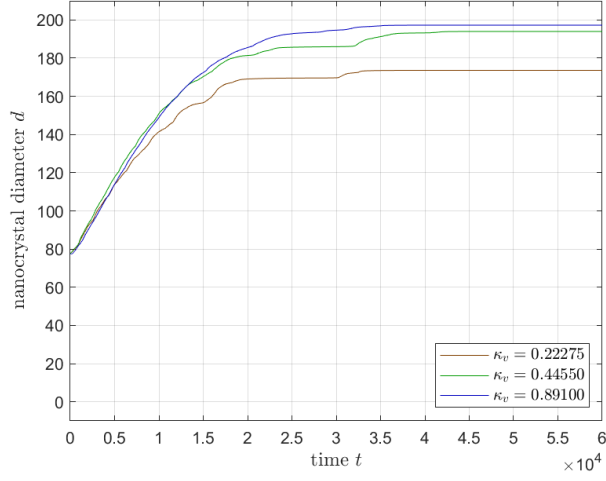
4.9.5 Nanocrystal Diameters and Free Energies

In this subsection, we investigate the changes in nanocrystal (solid region) “diameters” and total free energies over time. Although each nanocrystal begins as a disk, the shape becomes more polygonal with time. Therefore, we use the term “diameter” loosely to describe the average width of the nanocrystal.

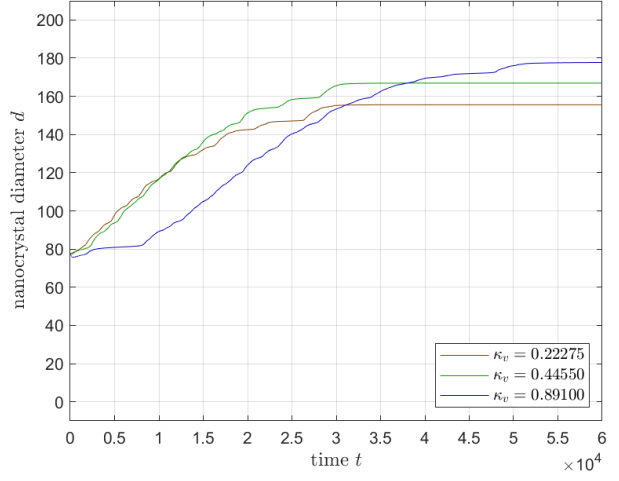
The graphs of Figure 4.59 detail the changes in nanocrystal diameters over time for the nine disk seed simulations of this section. Figures 4.59a, 4.59b, and 4.59c display the diameters for $W_v = 0.05$, $W_v = 0.10$, and $W_v = 0.20$, respectively. Note that the diameters achieved at the far right sides of each graph correspond to the equilibrium states for the simulations.

Table 4.1c indicates that, for $W_v = 0.05$ and $W_v = 0.10$, the nanocrystal areas at equilibrium are greater for larger values of κ_v . The diameters of Figures 4.59a and 4.59b reflect this trend. Furthermore, Table 4.1c indicates that, for $W_v = 0.20$, the areas decrease as κ_v increases. Figure 4.59c supports this as well. Next, Subsection 4.9.3 notes that, for $W_v = 0.20$ and $\kappa_v = 0.44550$, the nanocrystal grows very little. Figure 4.59c confirms that the corresponding nanocrystal diameter is virtually constant over time. Finally, Table 4.1c conveys that, for $W_v = 0.20$ and $\kappa_v = 0.89100$, the solid area disappears completely, while Figure 4.59c indicates that, for these same parameter values, the diameter drops to zero over time.

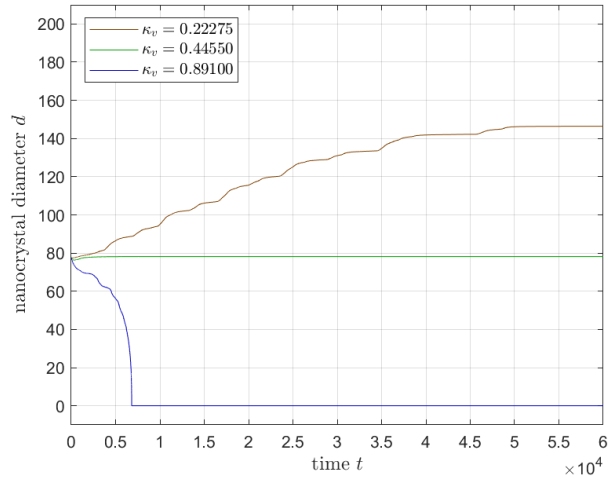
Figure 4.59 reveals that, for all pairings of W_v and κ_v , except for $W_v = 0.20$ with $\kappa_v = 0.44550$ and with $\kappa_v = 0.89100$, the diameter curves have jumps, or quick increases in value. Each jump corresponds to the attachment of new layers of atoms to particular nanocrystal facets. Due to symmetry, new atomic layers attach themselves to like facets at approximately the same time. In Table 4.1b, we see that larger values of κ_v correspond to larger minimizer interface thicknesses. For wider interfaces, more mass density configurations can occur. Therefore, as we see in Figures 4.59a and 4.59b, the diameter curves are smoother for larger value of κ_v . For $W_v = 0.20$ and $\kappa_v = 0.89100$, the nanocrystal diameter experiences drops as layers of atoms disappear (or sublime) from the nanocrystal.



(a) $W_v = 0.05$

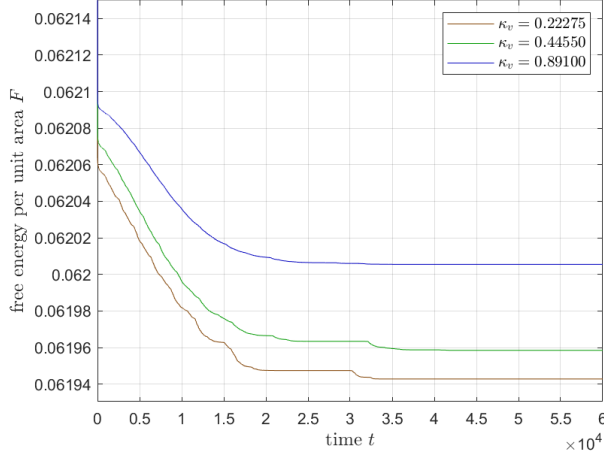


(b) $W_v = 0.10$

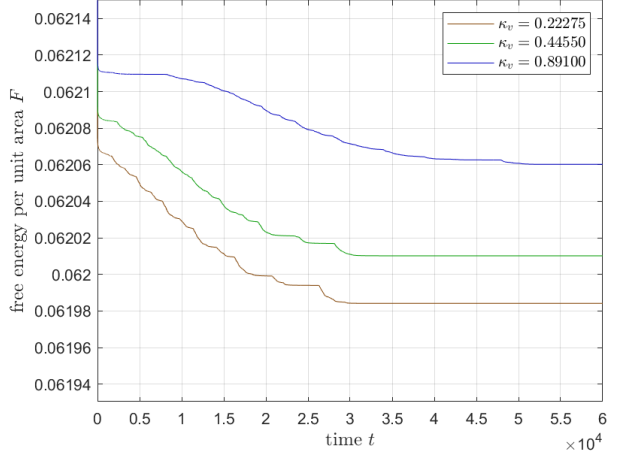


(c) $W_v = 0.20$

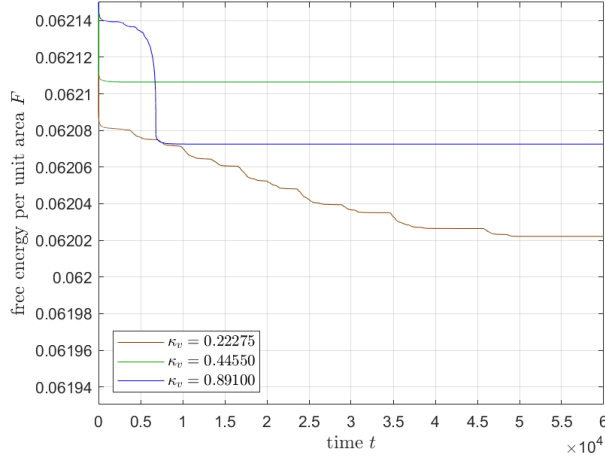
Figure 4.59: Disk Seed, Nanocrystal Diameters, Seed Multiple = 5.3441259



(a) $W_v = 0.05$



(b) $W_v = 0.10$



(c) $W_v = 0.20$

Figure 4.60: Disk Seed, Free Energies, Seed Multiple = 5.3441259

Next, Figure 4.60 graphs the free energies with respect to time for the nine simulations. These energy plots are arranged in the same fashion as the nanocrystal diameter plots of Figure 4.59. Note that these are free energies per unit area. In all cases, we see that the free energy decreases or remain relatively constant over time. This is the result of the design for the PDE's of (2.111) and (2.115) in Subsection 2.4.2.

In Figures 4.60a and 4.60b, we discover that the free energy is greater for greater values of κ_v . This may seem contradictory. For $W_v = 0.05$ and $W_v = 0.10$, Table 4.1c indicates that nanocrystal area increases as κ_v increases. As the area increases (up to a corresponding

seed multiple of 16), we expect the vapor and solid mean mass densities to converge on their equilibria. This should cause the total free energy to decrease, not increase, as κ_v increases. However, Table 4.1a tells us that the minimum phase interface energies (per unit length) increase as κ_v increases. Hence, the surface energy per unit length increases. Since the nanocrystal areas also increase, the increase in the total surface energy (per unit area) is greater still. We conjecture that this increase in total surface energy overcomes the expected decrease in free energy caused by the increasingly stable mean mass densities.

For constant values of κ_v , Table 4.1a states that the minimum phase interface energy increases as W_v increases. Examining the three graphs of Figure 4.60, we find that the free energies follow the same trend.

The free energy curves of Figure 4.60 exhibit drops at the same times where the nanocrystal diameter curves of Figure 4.59 experience bumps. In fact, except for the case where $W_v = 0.20$ and $\kappa_v = 0.89100$, if we reflect the energy graphs vertically, they form shapes very similar to those of the nanocrystal diameter curves. The free energy drops rapidly when a layer of atoms attaches to the nanocrystal. The addition of a new atomic layer establishes a more stable mass density configuration and, therefore, causes a decrease in the free energy. For $W_v = 0.20$ with $\kappa_v = 0.89100$, the free energy drops when layers of atoms disappear from the nanocrystal. Here, shrinkage results in lower free energy.

Finally, we may draw a connection between the free energy drops of Figure 4.60 and the surface energy jump discontinuities of Figures 4.21, 4.24a, 4.29, and 4.32a of Section 4.6. Both phenomena occur when a new layer of atoms form.

4.9.6 Summary

First, we recall that, for the nine cases where the initial mass densities are not at their phase equilibria, none of the nanocrystals approach a disk radius multiple of 16. Hence, for each of these cases, the simulations stall at metastable states. The battle between the different parts of the total free energy results in stagnation.

Next, increases in the *resistance to the coexistence of phases parameter* W_v and increases in the *phase interface derivative strength parameter* κ_v result in larger minimum phase

interface energies per unit length. There is strong evidence that this results in higher surface energies per unit length.

In addition, decreases in W_v and increases in κ_v result in larger minimizer phase interface thicknesses and, for lower values of W_v , larger nanocrystal areas. We surmise that larger interface thicknesses produce a larger variety of potential mass density arrangements in the phase interface regions. This usually facilitates greater nanocrystal growth. However, for $W_v = 0.20$ with $\kappa_v = 0.44550$ and $\kappa_v = 0.89100$, the surface energy per unit length is so great that the phase interface length remains constant or decreases over time. Finally, we note that wider interfaces, in particular those of $W_v = 0.05$ and $W_v = 0.10$ with $\kappa_v = 0.89100$, allow the unstable zigzag two-bond facet to occur.

Furthermore, increasing W_v or κ_v yields nanocrystals with rounder phase interfaces, and, so, the corresponding systems possess higher isotropic energies. Conversely, lower values for W_v or κ_v cause initial disk seeds to develop corners and become more polygonal in shape. This is caused by the dominance of the zigzag one-bond facet. For more rounded nanocrystals, longer armchair facets must be present to interconnect the different zigzag facets. The armchair facets are more dominant for larger W_v and κ_v values.

Finally, in nature, sharper crystals occur at lower temperatures. Therefore, decreasing parameters W_v and κ_v produces effects that are similar to those caused by decreasing the temperature.

4.10 Sinusoidal Front Seed Simulations

This section introduces simulations with initial seeds with sinusoidal fronts. Similar to the band seeds of Section 4.6, the sinusoidal seeds are oriented vertically in the computational box. The left and right sides of the seeds span one cycle of a sine wave from top to bottom. For half of these simulations, both sides are concave. We refer to these simulations as symmetric. For the asymmetric simulations, the left side of the initial seed is convex, while the right side is concave.

For both the symmetric and asymmetric cases, we present simulations where the armchair facet lies along the vertical lines, along with simulations where the zigzag facet lies along

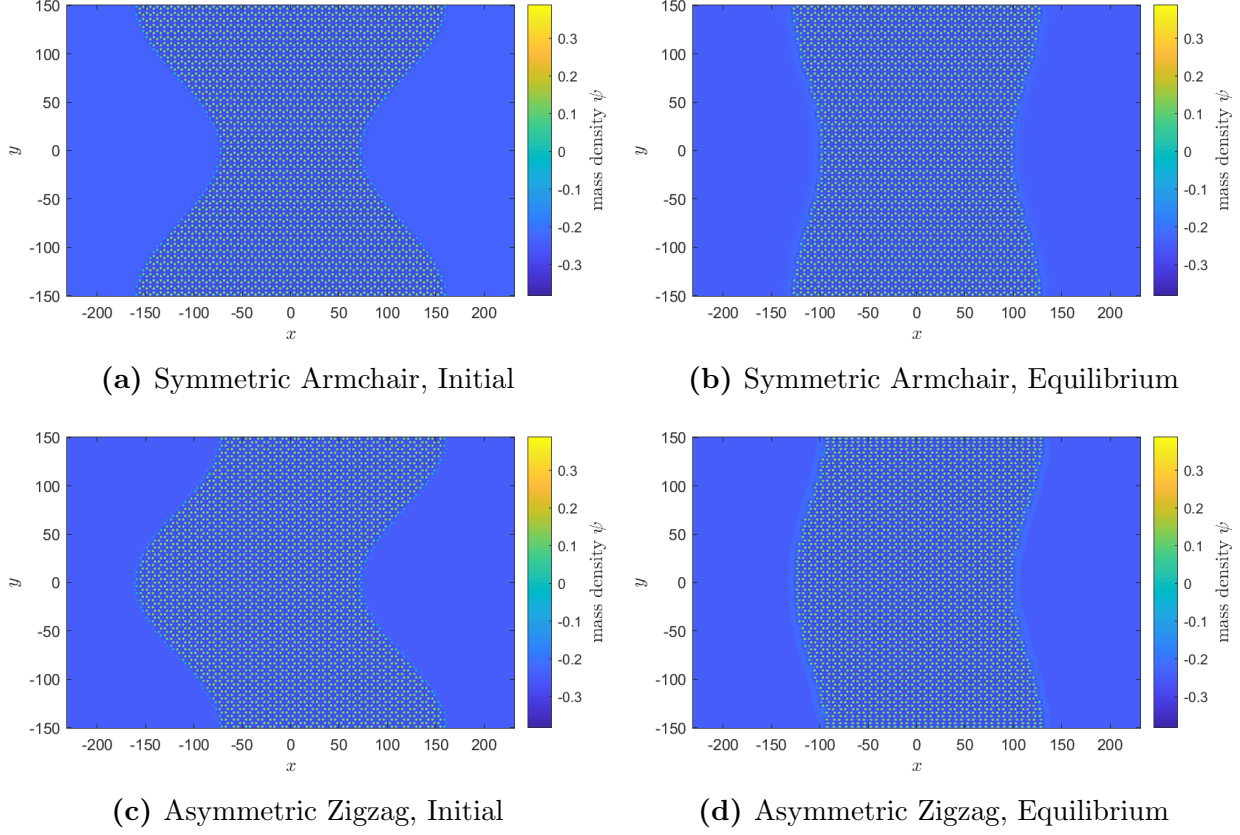


Figure 4.61: Sinusoidal Front Seeds, Mass Density Fields, Seed Multiple = 16

the vertical. We refer to the former as armchair simulations and to the latter as zigzag simulations. Figures 4.61a and 4.61b show the initial and equilibrium mass density fields, respectively, for a sinusoidal symmetric armchair simulation. Next, Figures 4.61c and 4.61d present the initial and equilibrium fields, respectively, for an asymmetric zigzag simulation. Note that, in its entirety, Figure 4.61 is a repeat of Figure 4.10 from Section 4.2.

For the armchair facet simulations, the initial seed multiple is the average number of armchair unit cell widths $\left(\frac{4\pi}{\sqrt{3}}\right)$ between the horizontal center of the computational box and the phase interface, or sinusoidal front. This average is taken over all y -values. Similarly, for the zigzag simulations, the initial seed multiple is the average number of zigzag unit cell widths (4π) between the horizontal center and the interface.

The size of the computational box is the same for every simulation. The width is given by $l_x = 64\frac{4\pi}{\sqrt{3}} \approx 464.333$ for the armchair facet simulations and by $l_x = \frac{64}{\sqrt{3}}4\pi \approx 464.333$ for the

zigzag. Note that this width is the same as the width for the disk seed simulations of Section 4.9. Similarly, the height is $l_y = 24 \cdot 4\pi \approx 301.593$ for the armchair and $l_y = 24\sqrt{3}\frac{4\pi}{\sqrt{3}} \approx 301.593$ for the zigzag. Note that, since the mass density fields are symmetric about the x -axis, we show only the top halves of the fields in the remaining simulation figures.

Now, for the initial fields of Figures 4.61a and 4.61c, the vapor and solid mean mass densities are at the phase equilibria of $\mu_{veq} = -0.22990548$ and $\mu_{seq} = -0.16894892$, respectively, from Section 2.5. Therefore, we might expect the nanocrystals to retain the same shape over time. However, the mass density fields of 4.61b and 4.61d indicate that the corresponding phase interfaces become more linear over time. The reason is surface energy. Flatter phase interfaces result in shorter phase interfaces, and shorter interfaces yield lower surface energies (per unit area). Finally, lower surface energies result in lower overall free energies. We see the flattening of the phase interface in varying degrees in all of the simulations of this section.

We now turn to analyzing sinusoidal front simulations that parallel the disk simulations of Section 4.9. We begin by choosing the same initial vapor mass density of $\mu_v = -0.219$ and the initial solid mean density of $\mu_s = -0.171$. Again, the initial vapor density is greater than the phase equilibrium $\mu_{veq} = -0.22990548$, and, so, the vapor region is supersaturated. For the symmetric and asymmetric armchair facet simulations, we use the initial seed multiples of 13.057877 and 13.052221, respectively. As with the disk simulations, we choose these multiples so that the overall mean mass density is equal to the overall density with an initial seed multiple of 16 with vapor and solid mean mass densities of $\mu_{veq} = -0.22990548$ and $\mu_{seq} = -0.16894892$, respectively. For the symmetric and asymmetric zigzag facet simulations, we use the initial seed multiples of 7.5292984 and 7.5279861, respectively. The resulting overall mean mass density corresponds to the initial seed multiple of $\frac{16}{\sqrt{3}} \approx 9.2376043$ with phase equilibrium vapor and solid mean mass densities. The selection of seed multiples for the zigzag simulations yields actual seed widths (not multiples) that are approximately the same as the widths for the armchair. The average seed width, from the horizontal center, is around 94.6 or 94.7 for all sinusoidal front simulations.

Next, the amplitudes of the sine waves are $\frac{3}{8}$ of the average seed widths. We refer to the horizontal difference between the trough and peak of the phase interface wave front as

the “nanocrystal amplitude”. Hence, for each of the sinusoidal front simulations, the initial nanocrystal amplitude is $\frac{3}{4}$ of the average seed width. Hence, these initial amplitudes are approximately 71. Note that this is similar to the initial disk seed diameter of around 77.5, which is shared by all nine of the disk seed studies of Section 4.9.

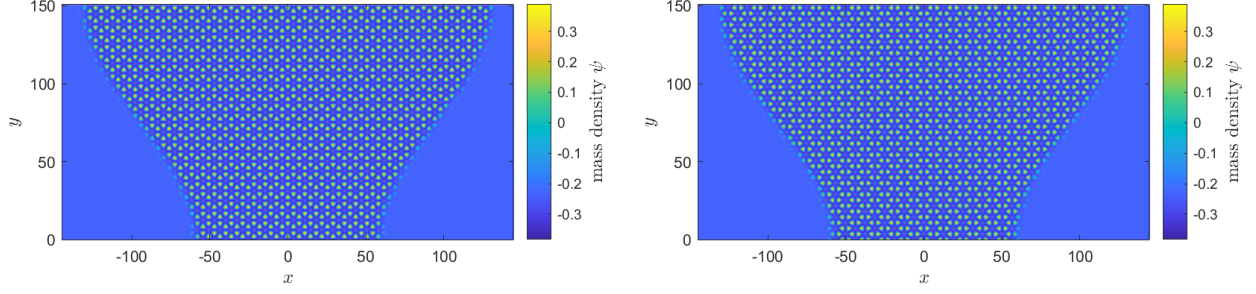
For all of the remaining simulations, the resulting initial nanocrystal areas within the computational box are approximately 57,000. In contrast, for the phase equilibrium vapor and solid mean densities of $\mu_{veq} = -0.22990548$ and $\mu_{seq} = -0.16894892$, the resulting nanocrystal area is about 70,000. We see this reflected in the areas of the four mass density fields of Figure 4.61, where the vapor and solid mean mass densities are very close to their phase equilibrium values.

For all simulations, $W_v = 0.10$. In addition, for each possible combination of the symmetric or the asymmetric front with the armchair or the zigzag facet, we consider the three values $\kappa_v = 0.22275, 0.44550, 0.89100$. The selection of initial mass densities, seed multiples, and nanocrystal amplitudes enable us to make meaningful comparisons between the sinusoidal front simulations and the three disk seed simulations with $W_v = 0.10$ in Section 4.9.

4.10.1 Symmetric Fronts

We first examine sinusoidal front simulations where the initial seeds are symmetric about the y -axis. Figure 4.62a shows the initial mass density field for the armchair simulations, while Figure 4.62b corresponds to the initial field for the zigzag. Next, Figure 4.63 displays the equilibrium mass density fields for the symmetric armchair and zigzag facet simulations for $\kappa_v = 0.22275, 0.44550, 0.89100$. The armchair simulations are on the left, while the zigzag simulations are on the right.

We first investigate the different facets that we see along the phase interfaces of the mass density fields of Figure 4.63. Due to the y -axis symmetry, we focus on the right phase interface only. We begin with the armchair simulations of Figures 4.63a, 4.63c, and 4.63e. As we might expect, since the nanocrystal is primarily vertical and the armchair facet aligns with the vertical lines, there are many armchair facets along the phase interfaces. The armchair facets become more prevalent as κ_v increases and the interface becomes more linear. If we



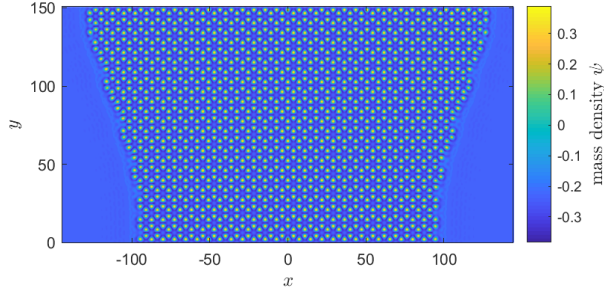
(a) Armchair Facet, Seed Multiple = 13.057877 (b) Zigzag Facet, Seed Multiple = 7.5292984

Figure 4.62: Sinusoidal Front Seed, Symmetric, Initial Mass Density Fields

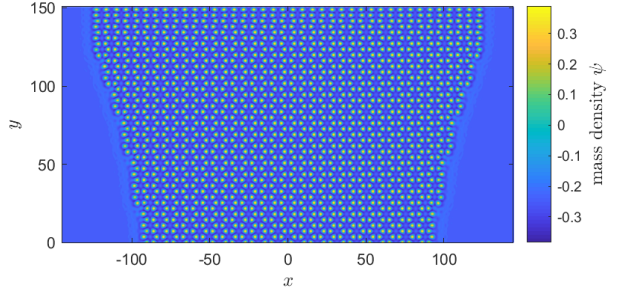
scan upward along each phase interface, we find vertical armchair facets at increasing values of x . Similar to the armchair facets of the disk seed simulations of Section 4.9, armchair facets are connected by zigzag facets and vice versa. Section 4.6 asserts that the zigzag facet two-bond stage is less prevalent than the armchair facet and the zigzag one-bond stage. We do find a zigzag two-bond stage in Figure 4.63a, but it occurs at only one atom.

More interestingly, we find top-to-top facets in the Figures 4.63a and 4.63c. For a method for identifying such a facet, we refer to the top-to-top information of Section 4.1 and Figure 4.3 therein. We see that the top-to-top facets can be found by looking for two pairs of vertically aligned atoms with two more pairs of aligned atoms directly above and offset to the right by one half of an armchair unit cell width. In Figure 4.63a, there is a top-to-top facet between $y = 25$ and $y = 60$. The length of this top-to-top facet is two top-to-top cell heights. We refer to such a facet as a “double-cell facet”. In Figure 4.63c, there are double-cell top-to-top facets between $y = 55$ and $y = 90$ and between $y = 95$ and $y = 130$. We may identify multiple instances of single-cell top-to-top facets along the phase interfaces for every armchair simulation. However, based on the armchair and zigzag unit cells sizes, we suggest that a single-cell top-to-top facet is too short to establish a meaningful trend. Again referring to Section 4.1, we note that the top-to-top facet occurs when the phase interface forms an angle of approximately 10.9° with the vertical.

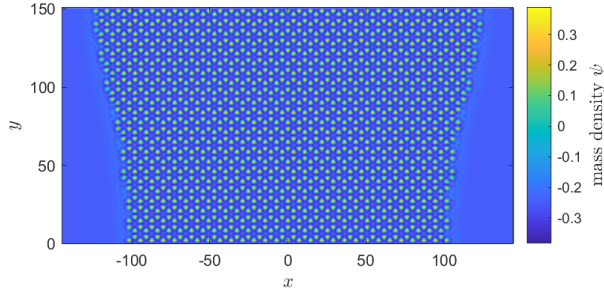
For the zigzag simulations of Figures 4.63b, 4.63d, and 4.63f, we find that the zigzag facets are dominant. Now, Section 4.6 provides evidence that the zigzag facet is more energetically stable than the armchair facet. Indeed, the zigzag facets of these zigzag simulations are more



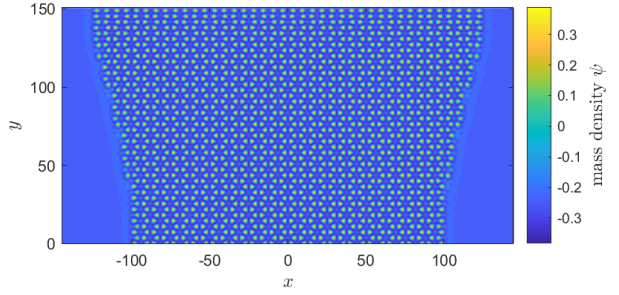
(a) Armchair Facet, $\kappa_v = 0.22275$,
Seed Multiple = 13.057877



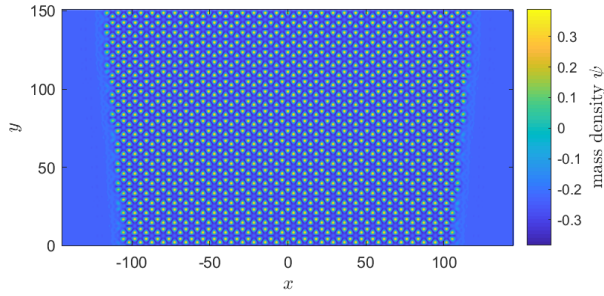
(b) Zigzag Facet, $\kappa_v = 0.22275$,
Seed Multiple = 7.5292984



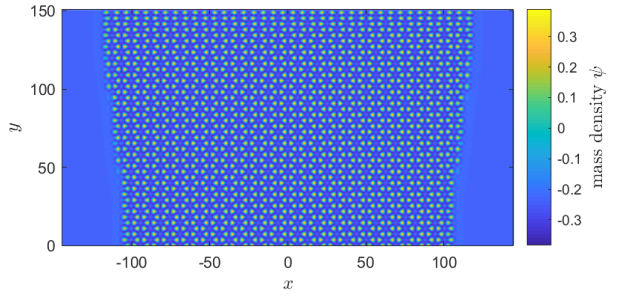
(c) Armchair Facet, $\kappa_v = 0.44550$,
Seed Multiple = 13.057877



(d) Zigzag Facet, $\kappa_v = 0.44550$,
Seed Multiple = 7.5292984



(e) Armchair Facet, $\kappa_v = 0.89100$,
Seed Multiple = 13.057877



(f) Zigzag Facet, $\kappa_v = 0.89100$,
Seed Multiple = 7.5292984

Figure 4.63: Sinusoidal Front Seed, Symmetric, Equilibrium Mass Density Fields

Table 4.3: Sinusoidal Front Seed, Symmetric, Solid Nanocrystal Areas

	Armchair Facet	Zigzag Facet
$\kappa_v = 0.22275$	68213.812	68009.936
$\kappa_v = 0.44550$	69634.009	69176.885
$\kappa_v = 0.89100$	70442.186	70063.700

prevalent than the armchair facets of the armchair simulations. In addition, we find short zigzag two-bond stages in Figures 4.63d and 4.63f. Overall, the two-bond stages are more frequent for the zigzag simulations than they are for the armchair.

Next, there is a single-cell left-to-right facet in Figure 4.63d between $y = 105$ and $y = 130$. Section 4.1 with Figure 4.4 provides a method for finding left-to-right facets. We begin by moving upward along the right interface, starting near $y = 105$. There is a zigzag one-bond stage, which is two zigzag unit cells in height. Then, directly above and $\frac{1}{3}$ of a zigzag unit cell width to the right, there is a two-bond stage. Finally, there is another one-bond stage directly above and $\frac{1}{6}$ of a zigzag unit cell width to the right. This sequence constitutes a single-cell left-to-right facet. Section 4.1 indicates that the angle between the left-to-right facet and the vertical is about 10.9° .

Table 4.3 provides the corresponding areas for the nanocrystals. Note that the layout of Table 4.3 matches that of Figure 4.63. For each simulation, the area increases significantly over time from the initial value of 57,000 to approximately 70,000. The area of 70,000 suggests that the vapor and solid mean mass densities are near the phase equilibria of $\mu_{veq} = -0.22990548$ and $\mu_{seq} = -0.16894892$, respectively. We conjecture that, unlike the disk seed simulations of Section 4.9, these sinusoidal simulations are not settling at metastable states, where the total free energy is significantly greater than the absolute minimum.

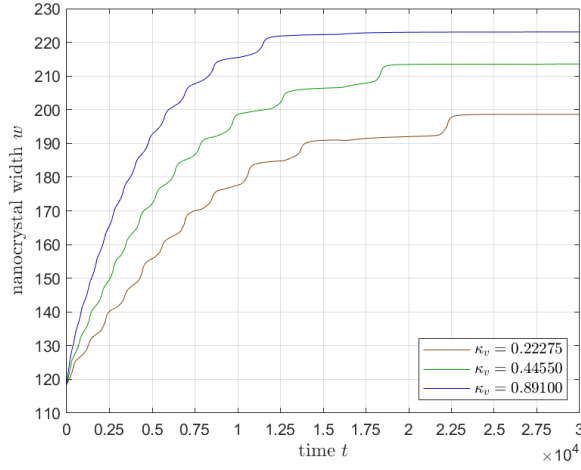
In addition, the areas in Table 4.3 indicate that the equilibrium state solid area increases as κ_v increases. This trend does echo the disk seed results of Subsection 4.9.3 for $W_v = 0.10$. However, the differences in area here are much smaller than those of the disk seed simulations for different values of κ_v . We restate our conjecture that increasing κ_v increases the phase interface width, which enables greater nanocrystal growth.

Figure 4.64 details symmetric simulation characteristics over time, including nanocrystal widths along the x -axis, nanocrystal amplitudes, and total free energies. The left column lists the characteristics for the armchair simulations and the right column itemizes the characteristics for the zigzag simulations. Figures 4.64a and 4.64b provide the nanocrystal widths along the x -axis, Figures 4.64c and 4.64d reveal the nanocrystal amplitudes, and Figures 4.64e and 4.64f display the total free energies.

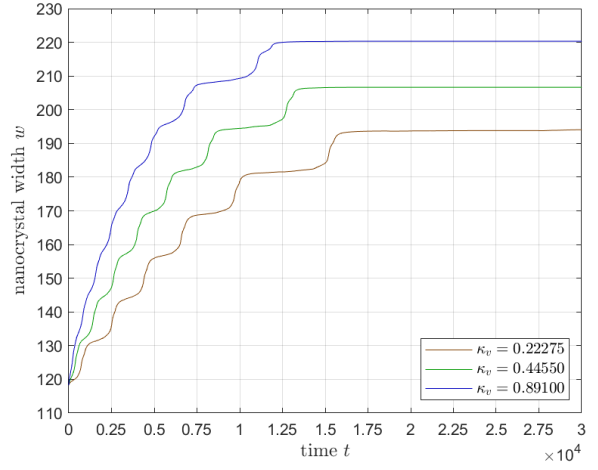
Both Figures 4.64a and 4.64b indicate multiple jumps in the nanocrystal widths over time. Each jump corresponds to the addition of new layers of atoms along the x -axis. Since the nanocrystals are symmetric about the y -axis, a layer of atoms attaches to each side of the nanocrystal at the same time and in the same way. For the armchair simulations, the thickness of one new layer of atoms corresponds to one half of an armchair unit cell width. Since each side sees an additional layer of atoms, the nanocrystal width increases by the entire armchair unit cell width, or $\frac{4\pi}{\sqrt{3}} \approx 7.255$. Indeed, the height of each jump in Figure 4.64a is about 7.255.

The addition of new atom layers along the x -axis proceeds in a similar fashion for the zigzag simulations. However, each major jump consists of two smaller “subjumps”. The earlier and larger subjump corresponds to the addition of atoms that transitions from the zigzag one-bond stage to the two-bond stage. The corresponding layer of atoms is $\frac{1}{3}$ the zigzag unit cell width. Since this occurs on both sides simultaneously, the corresponding increase in nanocrystal width is $\frac{2}{3} \cdot 4\pi \approx 8.378$. Since the two-bond stage is relatively unstable, a second layer of atoms attaches to each side of the nanocrystal soon after the first. These new layers of atoms correspond to the second, smaller subjump in nanocrystal width. Each secondary layer of atoms is $\frac{1}{6}$ the zigzag unit cell width. The simultaneous addition to both sides increases the nanocrystal width by $\frac{1}{3} \cdot 4\pi \approx 4.189$. Combining the two subjumps yields a major jump. The corresponding nanocrystal width increase equals the zigzag unit cell width $4\pi \approx 12.566$. The heights of the jumps in Figure 4.64b reflect these measurements.

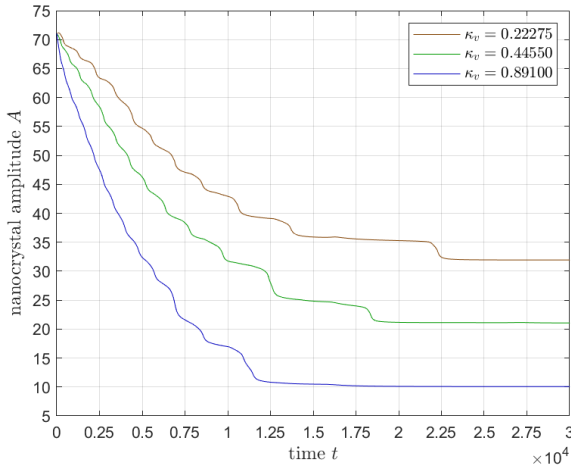
We next consider the changes in nanocrystal sinusoidal amplitudes over time. We begin with the armchair simulations. Comparing Figure 4.64c to Figure 4.64a shows that the drops in the nanocrystal amplitudes are synchronized with the jumps in nanocrystal widths



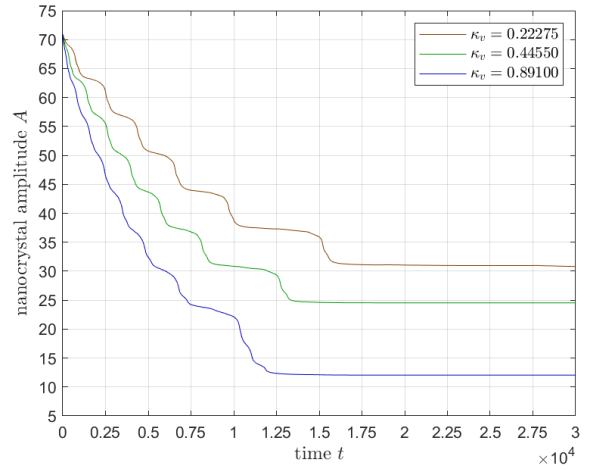
(a) Armchair Facet, Nanocrystal Widths



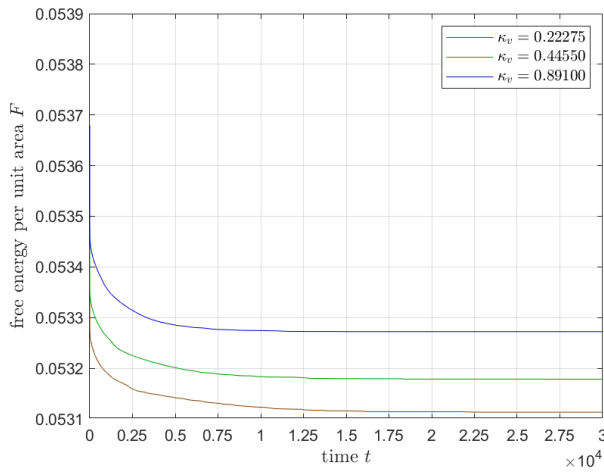
(b) Zigzag Facet, Nanocrystal Widths



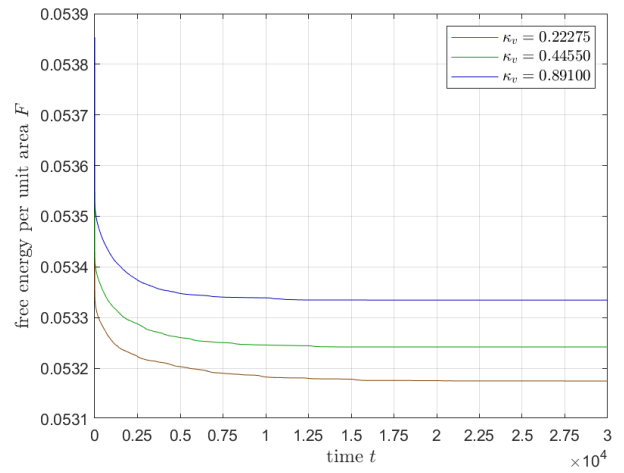
(c) Armchair Facet, Nanocrystal Amplitudes



(d) Zigzag Facet, Nanocrystal Amplitudes



(e) Armchair Facet, Free Energies



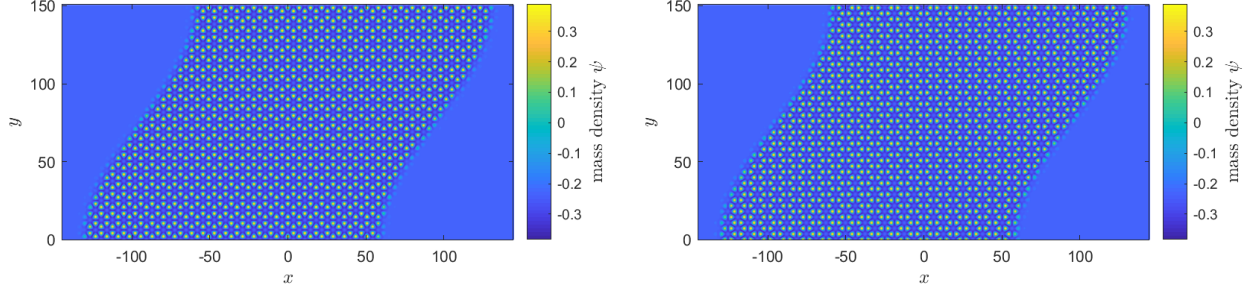
(f) Zigzag Facet, Free Energies

Figure 4.64: Sinusoidal Front Seed, Symmetric, Characteristics

along the x -axis. Note that the left and right troughs both lie along the x -axis and that atom layers attach to the left and right at the same time due to symmetry. Hence, the magnitude of a jump in nanocrystal width along the x -axis is usually twice the magnitude of the corresponding drop in amplitude. For $\kappa_v = 0.22275$, the nanocrystal widths at the top and the bottom of the computational box, at the peaks of the wave front, remain relatively constant over time. Therefore, the magnitudes of the jumps in the widths are consistently twice the magnitudes of the corresponding drops in amplitude. For $\kappa_v = 0.44550$ and $\kappa_v = 0.89100$, over time, the nanocrystal widths decrease at the top and bottom of the computational box. This causes greater decreases in the nanocrystal amplitudes. Comparing the amplitudes of Figure 4.64d to the widths of 4.64b indicates that the results are similar for the zigzag simulations.

Comparing the phase interfaces of Figure 4.63, we find that larger values of κ_v result in smaller nanocrystal amplitudes and, thus, flatter phase interfaces. First, we conjecture that larger κ_v values result in larger phase interface energies and, thus, larger surface energies per unit length. As the multimode PFC model with vapor pushes toward lower free energy, it also strives for lower surface energy per unit area. Given particular values for W_v and κ_v , the surface energy per unit length is relatively constant. Therefore, the push toward lower surface energy per unit area tends to reduce the length of the phase interfaces. For these sinusoidal simulations, shorter phase interfaces are flatter interfaces. It follows that the tendency toward flatter phase interfaces is stronger for larger values of κ_v .

Finally, Figures 4.64e and 4.64f confirm that the overall free energy per unit area is nonincreasing over time. Comparing these energies to the corresponding nanocrystal widths along the x -axis in Figures 4.64a and 4.64b reveals that very small free energy drops occur with the additions of layers of atoms. Furthermore, the free energy is greater for larger values of κ_v . Again, we assume that larger values of κ_v yield greater surface energies per unit length. Now, the phase interface lengths are lesser for flatter phase interfaces, but, as we can see in Figure 4.63, the variation in phase interface lengths is relatively small for different values of κ_v . Hence, we conjecture that, overall, the surface energy per unit area increases as κ_v increases, and, thus, larger κ_v values result in larger total free energies. Note that all of these observations concur with the disk seed free energy analyses of Subsection 4.9.5.



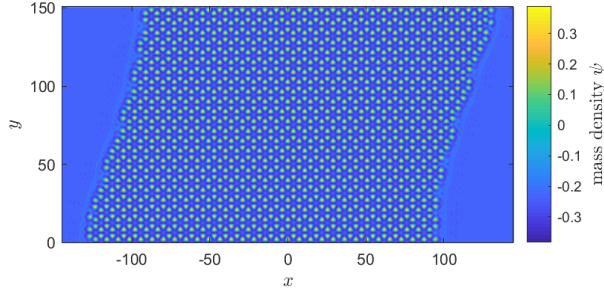
(a) Armchair Facet, Seed Multiple = 13.052221 (b) Zigzag Facet, Seed Multiple = 7.5279861

Figure 4.65: Sinusoidal Front Seed, Asymmetric, Initial Mass Density Fields

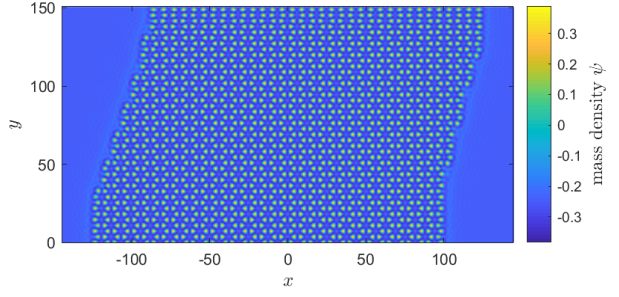
4.10.2 Asymmetric Fronts

In this subsection, we investigate sinusoidal front simulations where the initial seed is not symmetric about the y -axis. The initial seed is convex on the left and concave on the right. Figure 4.65a yields the initial mass density field for the armchair simulations, and Figure 4.65b presents the initial field for the zigzag. Then, Figure 4.66 displays the equilibrium mass density fields for the asymmetric armchair and zigzag facet simulations for $\kappa_v = 0.22275, 0.44550, 0.89100$. In Figure 4.66, the armchair simulations are on the left, while the zigzag simulations are on the right.

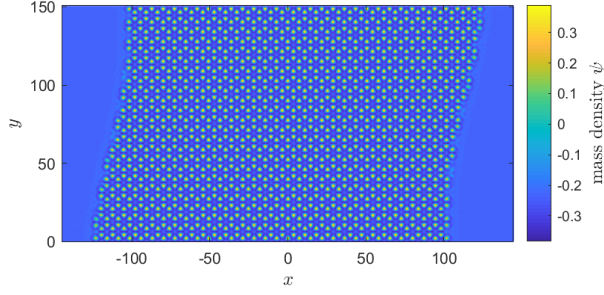
First, we compare the left and right phase interfaces of the mass density fields in Figure 4.66. We consider the midpoint between the origin and the top of the computational box at $x = 0$. We call this point P . Note that the distance between the origin and P is $\frac{1}{4}$ of the period of the phase interface sine wave. Now, roughly speaking, the asymmetric mass density fields exhibit 180° rotational symmetry about P ; that is, if we rotate a given mass density field by 180° about P , the resulting field is very similar to the original field. Investigating the mass density fields of Figure 4.66 reveals some minor discrepancies between the original mass density fields and the corresponding rotated fields. We surmise that the discrepancies originate with the design of the nanocrystal seeds of the initial mass density fields. Note that the initial seeds are convex on the left and concave on the right. This difference in concavity results in small numerical inconsistencies between the initial mass density field and the corresponding rotated form. Regardless, we often see similarities between the top



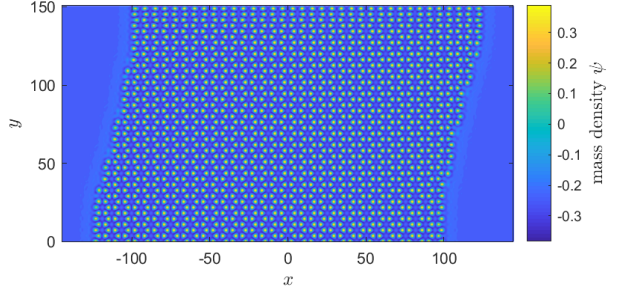
(a) Armchair Facet, $\kappa_v = 0.22275$,
Seed Multiple = 13.052221



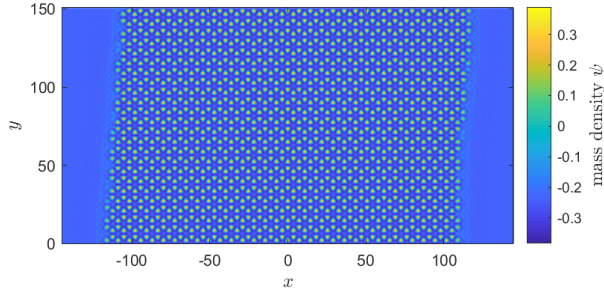
(b) Zigzag Facet, $\kappa_v = 0.22275$,
Seed Multiple = 7.5279861



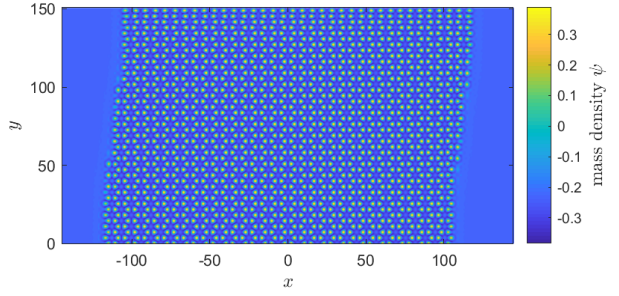
(c) Armchair Facet, $\kappa_v = 0.44550$,
Seed Multiple = 13.052221



(d) Zigzag Facet, $\kappa_v = 0.44550$,
Seed Multiple = 7.5279861



(e) Armchair Facet, $\kappa_v = 0.89100$,
Seed Multiple = 13.052221



(f) Zigzag Facet, $\kappa_v = 0.89100$,
Seed Multiple = 7.5279861

Figure 4.66: Sinusoidal Front Seed, Asymmetric, Mass Density Fields

of the left phase interface and the right interface at the x -axis and between the left interface at the x -axis and the top of the right interface.

Secondly, we analyze the similarities of the right phase interfaces of the symmetric simulations of Figure 4.63 of Subsection 4.10.1 to those of the corresponding asymmetric simulations of Figure 4.66. We first compare the right phase interfaces for the zigzag simulations with $\kappa_v = 0.44550$. The symmetric simulation appears in Figure 4.63d, and the asymmetric simulation is given by Figure 4.66d. The right interfaces are virtually identical. The same holds for the right phase interfaces of Figures 4.63f and 4.66f for $\kappa_v = 0.89100$. However, for other configurations, the right phase interfaces are slightly different. We consider the armchair simulations for $\kappa_v = 0.22275$. Figure 4.63a provides the symmetric simulation, while Figure 4.66a yields the asymmetric simulation. There is an additional layer of atoms at the top of the right interface for the asymmetric simulation in Figure 4.66a. For the zigzag $\kappa_v = 0.89100$ simulations, there is an extra layer of atoms along much of the bottom half of the right interface in the asymmetric simulation of Figure 4.66b, as compared to the corresponding symmetric simulation of Figure 4.63b. We conjecture that these discrepancies are caused primarily by the differences in the horizontal widths of the nanocrystal. For the symmetric simulations, the nanocrystals are wide at the top and bottom of the computational box, and narrow at the middle. For the asymmetric simulations, the nanocrystal widths are very similar for all values of y .

Next, we examine the facets along the phase interfaces in Figure 4.66. We rediscover many of the facet trends that we see in the symmetric simulations in Figure 4.63 of Subsection 4.10.1. While moving along each phase interface, the facets alternate between armchair and zigzag. Overall, the zigzag one-bond stage is the most prevalent. The armchair facets are more dominant in the armchair simulations of Figures 4.66a, 4.66c, and 4.66e than they are in the zigzag simulations of 4.66b, 4.66d, and 4.66f. In addition, for the armchair simulations, the armchair facets become more prevalent for greater values of κ_v , where the interface is more linear. In regard to the zigzag two-bond stage speculations of Section 4.6, we see short zigzag two-bond stages in Figures 4.66a, 4.66d, and 4.66f. Note that these three configurations correspond to the zigzag two-bond stage findings for the symmetric simulations in Subsection 4.10.1.

Table 4.4: Sinusoidal Front Seed, Asymmetric, Solid Nanocrystal Areas

	Armchair Facet	Zigzag Facet
$\kappa_v = 0.22275$	68154.485	68007.531
$\kappa_v = 0.44550$	69530.947	69263.393
$\kappa_v = 0.89100$	70456.732	70112.387

Finally, we seek top-to-top and left-to-right facets in the mass density fields in Figure 4.66. We refer to the top-to-top and left-to-right facet information of Section 4.1 and the identification methods described in Subsection 4.10.1 to identify these alternative facets. For $\kappa_v = 0.22275$, we find top-to-top facets in the armchair simulation in Figure 4.66a. There is a triple-cell top-to-top facet on the left interface between $y = 90$ and $y = 150$, and there is a double-cell top-to-top facet on the right between $y = 25$ and $y = 60$. For the $\kappa_v = 0.44550$ armchair simulation in Figure 4.66c, there is a triple-cell top-to-top facet along the left phase interface between $y = 60$ and $y = 120$. Along the right interface, there is a triple-cell top-to-top facet between $y = 30$ and $y = 90$ and a double-cell between $y = 100$ and $y = 135$. Next, we find left-to-right facets in the $\kappa_v = 0.44550$ zigzag simulation given by Figure 4.66d. There is a single-cell left-to-right facet on the left phase interface between $y = 20$ and $y = 45$ and another on the right interface between $y = 105$ and $y = 130$.

Next, Table 4.4 provides the areas for the nanocrystals at equilibrium. The layout of Table 4.4 corresponds to the layout of Figure 4.66. As with the areas in Table 4.3 for the symmetric simulations of Subsection 4.10.1, we find that the areas here are near 70,000. Again, this suggests that the vapor and solid mean mass densities are near the corresponding phase equilibria and that these asymmetric simulations arrive at a total free energy near the absolute minimum. In addition, Figure 4.66 and Table 4.4 evidence that larger values of κ_v result in larger nanocrystal areas. This also concurs with the symmetric simulation observations of Subsection 4.10.1.

We now examine asymmetric simulation trends over time. Figure 4.67 provides nanocrystal widths along the x -axis, nanocrystal amplitudes, and total free energies. The left column contains the armchair simulation data, and the right column lists the information for the zigzag simulations. Figures 4.67a and 4.67b hold the nanocrystal widths along the

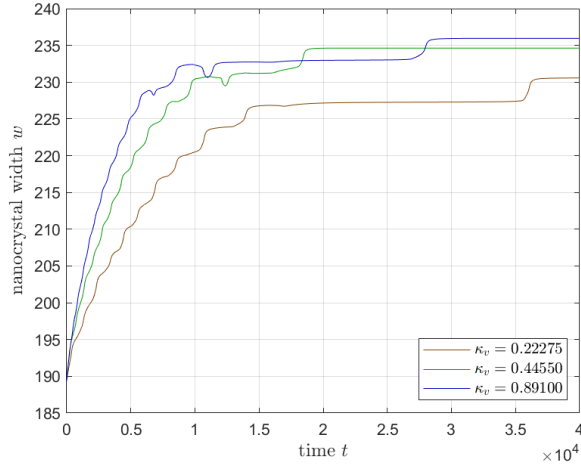
x -axis, Figures 4.67c and 4.67d display the nanocrystal amplitudes, and Figures 4.67e and 4.67f provide the free energies.

Figures 4.67a and 4.67b reveal jumps in the nanocrystal widths along the x -axis. Similar to the jumps in Figures 4.64a and 4.64b of Subsection 4.10.1, each jump here corresponds to the attachment of an additional layer of atoms along the x -axis. However, the jumps for the asymmetric simulations are smaller, and, for $\kappa_v = 0.89100$, there are also drops. Comparing the nanocrystals of the equilibrium mass density fields of Figure 4.66 to the corresponding initial fields of Figure 4.65 reveals that, along the x -axis, new layers occur primarily at the right phase interface. In fact, for larger κ_v values, atomic layers disappear from the left phase interface.

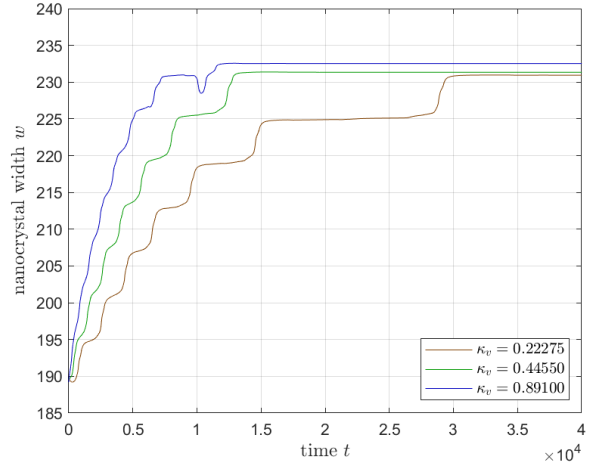
We begin with the armchair simulations. The width of one layer of atoms is one half of the armchair unit cell width. This width is given by $\frac{1}{2} \frac{4\pi}{\sqrt{3}} \approx 3.628$. Examining the nanocrystal widths along the x -axis in Figure 4.67a reveals that the jumps are approximately 3.628 in height. For $\kappa_v = 0.44550$ and $\kappa_v = 0.89100$, there are drops in the nanocrystal widths along the x -axis. However, after each drop, the thickness quickly returns to its previous level. The drop occurs when a layer of atoms detaches from the left phase interface at the x -axis. This causes an increase in the vapor phase mass density. In turn, this increase causes a new layer of atoms to form at the right phase interface along the x -axis. Hence, the nanocrystal thickness along the x -axis returns to the level achieved prior to the drop.

For the zigzag simulations, each major jump in nanocrystal width along the x -axis consists of two subjumps. The primary subjump corresponds to the atom layer that advances the facet from the zigzag one-bond stage to the two-bond stage. The width of this layer is $\frac{1}{3}$ of the zigzag unit cell width. The resulting width is $\frac{1}{3} \cdot 4\pi \approx 4.189$. The secondary subjump coincides with the transition from the two-bond to the one-bond stage. This layer of atoms is $\frac{1}{6}$ the zigzag unit cell width. The corresponding thickness is $\frac{1}{6} \cdot 4\pi \approx 2.094$. Therefore, the total jump in width along the x -axis is $\frac{1}{2} \cdot 4\pi \approx 6.283$. Reviewing Figure 4.67b, we see that the heights of the jumps match these values.

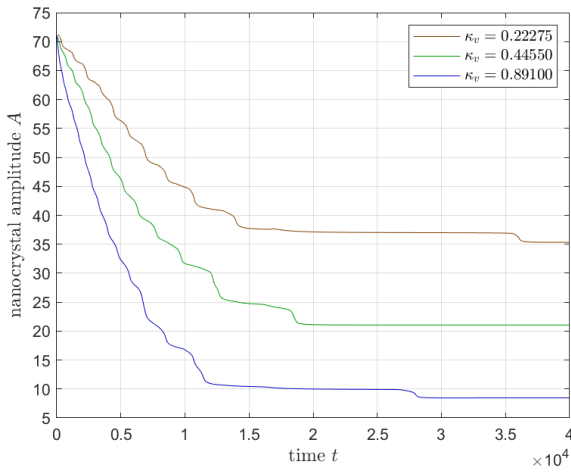
For the zigzag simulation where $\kappa_v = 0.89100$, there is an irregular sequence of changes in the phase interfaces at the x -axis between the times 6,000 and 11,600. We chronicle the events in the mass density fields of Figure 4.68, in coordination with the widths for



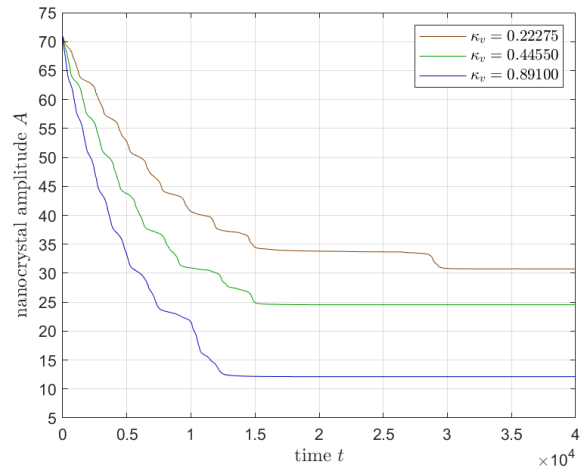
(a) Armchair Facet, Nanocrystal Widths



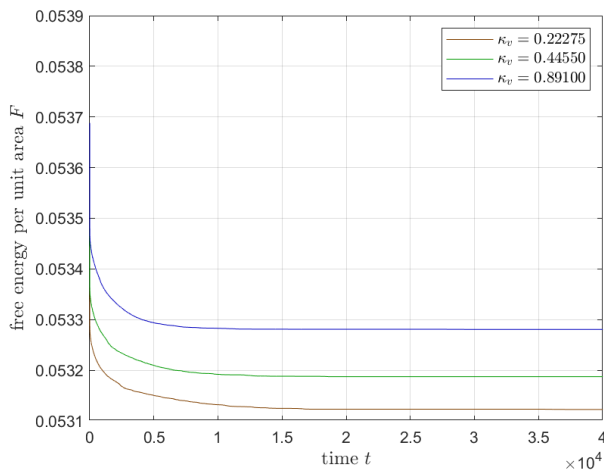
(b) Zigzag Facet, Nanocrystal Widths



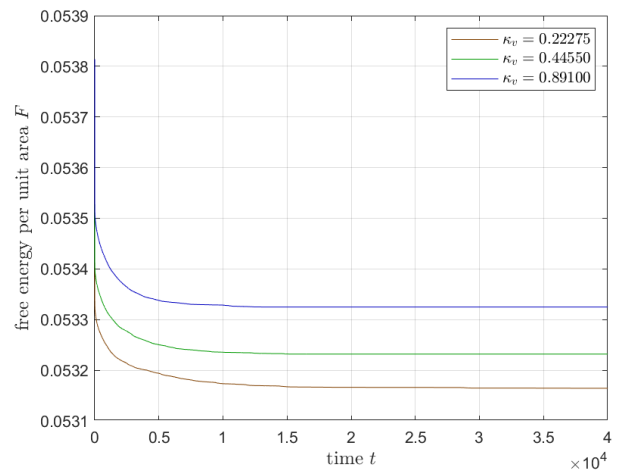
(c) Armchair Facet, Nanocrystal Amplitudes



(d) Zigzag Facet, Nanocrystal Amplitudes



(e) Armchair Facet, Free Energies



(f) Zigzag Facet, Free Energies

Figure 4.67: Sinusoidal Front Seed, Asymmetric, Characteristics

$\kappa_v = 0.89100$ in Figure 4.67b. Note that the mass density fields of Figure 4.68 are centered vertically on the x -axis. In Figure 4.68a, at time 6,000, we see that both the left and right facets are at the zigzag one-bond stage at the x -axis. After time 6,000, the left loses a layer of atoms, and the right gains a layer of atoms. Hence, both facets attain the two-bond stage, while the width along the x -axis increases by about $4.189 - 2.094 \approx 2.1$. The mass density field of Figure 4.68b shows the end result at time 6,700. Between times 6,700 and 7,300, the right interface gains another layer of atoms to achieve the one-bond stage. This results in another width increase of approximately 2.1. Figure 4.68c displays this new layer at the right. There are no significant changes along the x -axis, until time 10,000. This is unusual, because the relatively unstable zigzag two-bond stage persists at the left interface for the long interval of approximately 3,600 time units. At time 10,000, the left interface finally loses another layer of atoms to arrive at the one-bond stage. This causes the nanocrystal width along the x -axis to drop. Figure 4.68d evidences the missing layer on the left at time 10,300. The loss of this layer would result in a width decrease of approximately 4.2. However, very quickly, due to the increase in the vapor mass density, the right interface begins to gain a layer of atoms to reach the two-bond stage. The overall change in the nanocrystal width along the x -axis is negligible, as $4.189 - 4.189 = 0$. The additional atom layer is found in Figure 4.68e at time 10,700. From time 10,700 to time 11,600, the right interface gains its final layer of atoms along the x -axis, while attaining the zigzag one-bond stage. The result is a last increase of around 2.1 in nanocrystal width. Figure 4.68f shows the final, new layer on the right at time 11,600.

Next, we examine the nanocrystal sinusoidal amplitudes with respect to time. Figure 4.67c depicts the sinusoidal amplitudes for the armchair facet simulations, while Figure 4.67d shows the amplitude data for the zigzag simulations. To calculate each of these amplitudes, we take the average of the amplitudes of the left and right sinusoidal fronts. Because of the rough 180° rotational symmetry of the mass density fields, the left and right amplitudes are often similar. Next, for both symmetric and asymmetric sinusoidal simulations, we observe that new layers of atoms form at the sinusoidal troughs, while sometimes disappearing from the peaks. Hence, the sinusoidal amplitudes for the asymmetric simulations decrease over time, as do the amplitudes for the symmetric simulations of Subsection 4.10.1. In

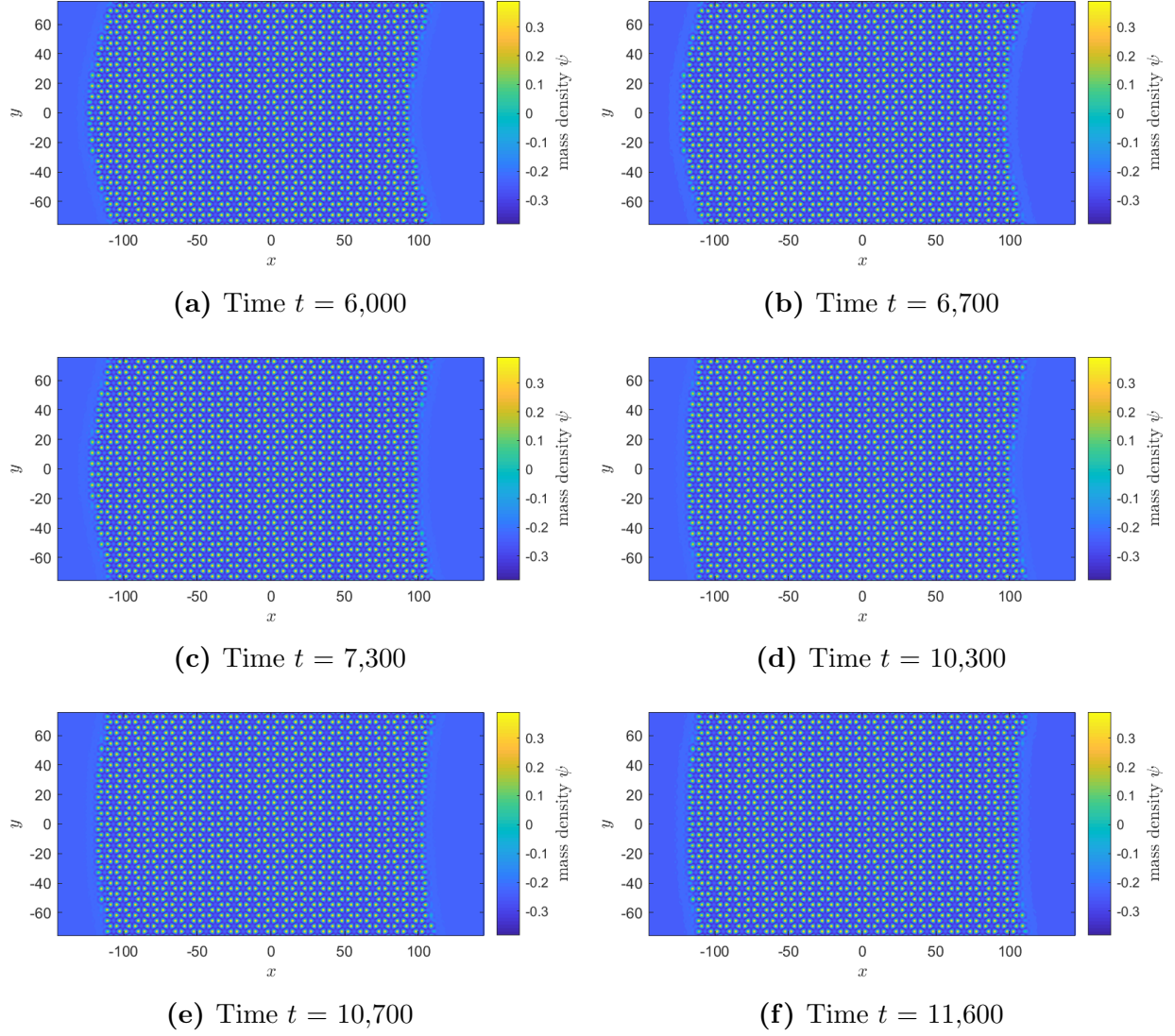


Figure 4.68: Sinusoidal Front Seed, Asymmetric, Zigzag, $\kappa_v = 0.89100$, Irregularity

addition, we note that greater values of κ_v yield lesser sinusoidal amplitudes, while lesser amplitudes correspond to phase interfaces with greater linearity. This same trend is seen in the amplitudes for the symmetric simulations of Subsection 4.10.1.

We conclude our sinusoidal amplitude analysis by comparing the nanocrystal widths at the x -axis to the amplitudes. For the armchair simulations, we compare the widths of Figure 4.67a to the corresponding sinusoidal amplitudes in Figure 4.67c. We also compare widths for the zigzag simulations in Figure 4.67b to the matching amplitudes in Figure 4.67d. Now, the additions of atom layers at the troughs coincide with both jumps in nanocrystal widths along the x -axis and drops in sinusoidal amplitudes. For the symmetric simulations, because the left and right troughs both lie along the x axis, a jump in width has twice the magnitude of the corresponding drop in amplitude. However, for these asymmetric simulations, the troughs at the left phase interface lie along the top and bottom of the computational box, while the trough on the right lies along the x -axis. Therefore, a jump in nanocrystal width along the x -axis is typically similar in magnitude to that of the corresponding amplitude drop. The first exception occurs when a layer of atoms is lost at a sinusoidal peak. The amplitude drops accordingly. However, if the loss occurs at the left peak, the nanocrystal width at the x -axis also drops. Alternatively, if the atom layer disappears only from the peaks on the right, the width remains the same. To describe the second exception, we compare the width jump along the x -axis and corresponding amplitude drop at time 36,000 for the asymmetric $\kappa_v = 0.22275$ armchair simulation. For $\kappa_v = 0.22275$, at time 36,000, the magnitude of the amplitude drop in Figure 4.67c is one half of the magnitude of the width jump in Figure 4.67a. A new layer of atoms forms at the trough at the x -axis on the right, but no new layer forms at the troughs on the left. Hence, the sinusoidal amplitude on the right decreases, while the amplitude on the left remains the same. Averaging the two amplitudes yields a drop with half the magnitude of the corresponding jump in width along the x -axis. The same sequence of events occurs for the $\kappa_v = 0.89100$ armchair simulation near time 28,000. For the $\kappa_v = 0.22275$ zigzag simulation, Figures 4.67b and 4.67d reveal that this half magnitude difference occurs at many different times.

Lastly, we consider the free energies for the asymmetric simulations. Figures 4.67e and 4.67f indicate that these energies decrease or remain constant over time. Next, we find that

the free energy is greater for larger values of κ_v . This concurs with the disk seed results in Subsection 4.9.5 and the symmetric sinusoidal data of Subsection 4.10.1. We reiterate the conjecture from these subsections stating that larger values of κ_v produce greater surface energies and, thus, greater free energies. In addition, note the similarities in the matching free energy levels for the armchair simulations in Figures 4.64e and 4.67e. The same holds for the zigzag simulation free energies of Figures 4.64f and 4.67f. Since the only difference in corresponding symmetric and asymmetric simulations is the concavity of the left phase interface, this is expected.

4.10.3 Summary

For all of the sinusoidal front simulations, the phase interfaces become flatter, or more linear, over time. Now, the multimode PFC model with vapor favors decreases in free energy, and, so, lower surface energies per unit area are usually more favorable. Lower surface energies per unit area are obtained by, among other things, shortening the phase interfaces. In these sinusoidal simulations, flatter phase interfaces correspond to shorter phase interfaces. In addition, increases in phase interface linearity are decreases in sinusoidal front amplitudes. Hence, the amplitudes also decrease over time. Finally, the phase interfaces are more linear for larger values of κ_v , because greater κ_v values result in greater phase interface energies per unit length.

In Tables 4.3 and 4.4, we find that the nanocrystal areas are approximately 70,000, which corresponds to the area for the phase equilibrium vapor and solid mean mass densities of $\mu_{veq} = -0.22990548$ and $\mu_{seq} = -0.16894892$, respectively, from Section 2.5. We surmise that, over time, each sinusoidal simulation reaches a stable state, where the total free energy is near the absolute minimum for the corresponding system. This contrasts with the disk seed simulation results of Section 4.9, where each area was significantly less than the area associated with the phase equilibrium mass densities. The disk seed simulations reach only metastable states. However, like the disk simulations, the sinusoidal nanocrystal areas increase with increases in κ_v . Larger κ_v values correspond to larger phase interfaces. This provides the opportunity for a greater variety of mass density configurations at the

interfaces. We conjecture that an increase in potential mass arrangements enables greater nanocrystal growth.

For all of the sinusoidal front simulations, new layers of atoms accumulate at the sinusoidal troughs, while, sometimes, layers disappear from the peaks. For the symmetric simulations, there are troughs at the left and right phase interfaces along the x -axis. Hence, the nanocrystal widths along the x -axis increase over time with jumps occurring at times when new atom layers form. For the asymmetric simulations, there is a peak at the left and a trough at the right on the x -axis. Since new layers of atoms form at the troughs more frequently than layers disappear from the peaks, the nanocrystal widths along the x -axis typically increase for the asymmetric simulations. However, when a layer is lost from the left peak at the x -axis, the width decreases temporarily. This loss causes the vapor mass density to increase, and, so, a new layer of atoms forms at the right interface trough. The width along the x -axis quickly returns to its previous level. Again, since new atom layers are more common than lost layers, the amplitudes of the sinusoidal fronts decrease over time. Finally, jumps in nanocrystal widths coincide with drops in amplitude.

The facets trends for the sinusoidal simulations are similar to those of the disk simulations in Section 4.9. The zigzag one-bond stage is the most common facet found in the mass density fields of Figures 4.63 and 4.66. Along the phase interfaces, the facets alternate between the armchair and zigzag facets. There are rare, short zigzag two-bond stages. The relative abundances of these different facets concur with the results of Section 4.6. We even discover top-to-top facets in some of the sinusoidal armchair simulations and left-to-right facets among the zigzag simulations.

Chapter 5

Binary Phase Field Crystal (BPFC) Model

Another method of achieving honeycomb geometry combines two mass density fields, ψ_a and ψ_b , each with triangular geometry. Field B is offset from Field A such that each triangle vertex of Field B is located at the centroid of a triangle of Field A. We refer to this as the *binary PFC model*. We derive this from the hexagonal boron nitride (*h*-BN) model designed by Taha, Mkhonta, Elder, and Huang (2017) [25] with data from [5] and [11]. In addition, we introduce a new vapor phase field configuration for the binary PFC model.

Figures 5.1a and 5.1b show examples of coupled mass density fields A and B, respectively. Figure 5.1c shows that the superposition of the two fields forms honeycomb geometry. In Figure 5.1c, the blue dots designate the peaks of ψ_a and the green represent those of ψ_b .

5.1 Binary PFC Model Parameters

Table 5.1a lists the structural parameters and values for the binary PFC model. Note that the values of ϵ , χ_3 , and χ_4 are identical to those of the multimode PFC model as listed in Table 2.3a of Subsection 2.4.1. However, $\lambda = 2.8512$ for the binary PFC model, and $\lambda = 0.02$ for the multimode model. Effectively, $c_0 = c_2 = 1$ and $c_1 = 2$ for the binary model. For the multimode PFC model, $c_0 = 142.56$. Hence, we set $\lambda = 142.56 \cdot 0.02 = 2.8512$ so that the two models are comparable in this way. Next, we add the parameters

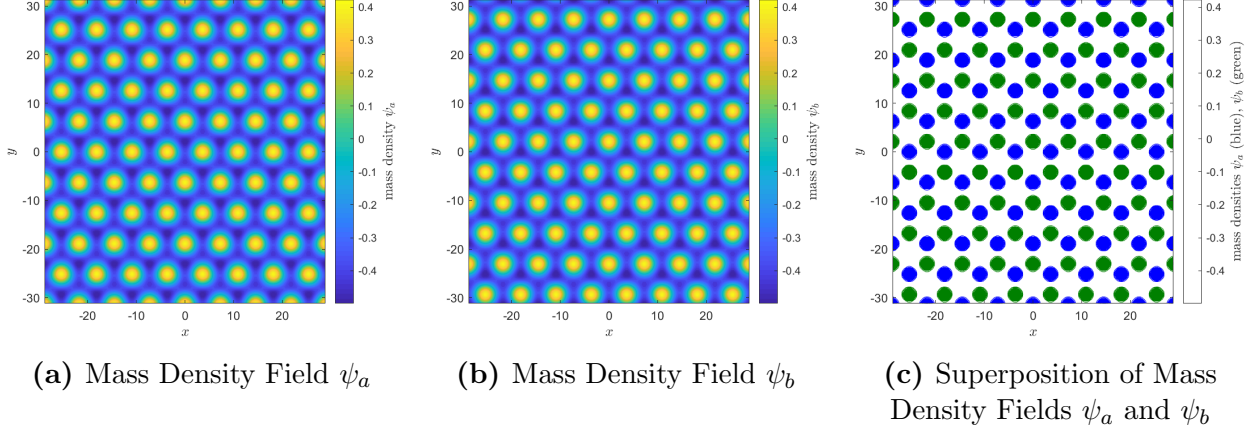


Figure 5.1: Mass Density Fields A and B

β_{11} and β_{12} of Table 5.1b for the coupling between ψ_a and ψ_b . Tables 5.1c, 5.1d, and 5.1e list the vapor phase field parameters, the mass density field initialization parameters, and the discretization parameters, respectively. Except for the initial vapor mass density $\mu_v = -0.205$, the parameters values of Tables 5.1c, 5.1d, and 5.1e match those of the multimode PFC model from Tables 2.3b, 2.3c, and 2.3d, respectively, and the values used in the simulations in Subsection 2.4.4.

5.2 Binary PFC Model Equations

We construct the binary PFC model equations by combining parts of the single-mode and multimode PFC models. Recalling (2.28) from Subsection 2.2.2, the linear differential operator for the single mode, triangular geometry is

$$C_{pfc} := (1 + \Delta)^2 = 1 + 2\Delta + \Delta^2 = \Delta^0 + 2\Delta + \Delta^2. \quad (5.1)$$

As with the other models in this study, we define a rectangular region Ω in $\mathbb{R}^2$. We require that both of our mass density fields, ψ_a and ψ_b , are Ω -periodic. We next review the multimode PFC free energy functional (2.65) from Subsection 2.3.2:

$$\mathcal{F}_{mmpfc}(t; \psi) := \int_{\Omega} \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi C \psi \right\} d\mathbf{x}, \quad (5.2)$$

Table 5.1: Binary PFC Model Parameters**(a)** Solid Phase Parameters

Parameter/Value	Description
$\epsilon = -0.15$	Temperature (scaled and shifted)
$\lambda = 2.8512$	Multimodal strength
$\chi_3 = -0.02$	Cubic term coefficient
$\chi_4 = 1.6$	Quartic term coefficient

(b) Energy Coupling Parameters

Parameter/Value	Description
$\beta_{11} = 0.05$	coupling product coefficient
$\beta_{12} = 0.06$	coupling first/second power product coefficient

(c) Vapor Phase Field Parameters

Parameter/Value	Description
$b_v = 4$	Vapor free energy scalar
$M_v = 1$	Vapor phase field mobility
$W_v = 0.1$	Resistance to coexistence of phases
$\Delta_v = 0.0387683$	Vapor free energy differential
$\kappa_v = 0.4455$	Phase interface derivative strength
$\psi_v = -0.11$	Vapor equilibrium density

(d) Mass Density Field Initialization Parameters

Parameter/Value	Description
$amp = 0.3688$	Initial solid density amplitude
$cell_x = 7.255197457$	Initial unit cell width
$cell_y = 12.5663706144685$	Initial unit cell height
$thickness = 2.756975$	Initial phase interface thickness
$\mu_s = -0.171$	Initial solid mean density
$\mu_v = -0.205$	Initial vapor density

(e) Discretization Parameters

Parameter/Value	Description
$dt = 0.1$	Time increment
$h_x \approx 0.45$	x -granularity
$h_y \approx 0.45$	y -granularity

where

$$C := \sum_{i=0}^8 c_i \Delta^i. \quad (5.3)$$

To establish the free energy functional for field ψ_a of the binary PFC model, we replace the multimode linear operator C in (5.2) with the single mode operator C_{pfc} of (5.1):

$$\mathcal{F}_{bin,a}(t; \psi_a) := \int_{\Omega} \left\{ \frac{\chi_4}{4} \psi_a^4 + \frac{\chi_3}{3} \psi_a^3 + \frac{\epsilon}{2} \psi_a^2 + \frac{\lambda}{2} \psi_a C_{pfc} \psi_a \right\} d\mathbf{x}. \quad (5.4)$$

Likewise, the free energy functional for ψ_b is:

$$\mathcal{F}_{bin,b}(t; \psi_b) := \int_{\Omega} \left\{ \frac{\chi_4}{4} \psi_b^4 + \frac{\chi_3}{3} \psi_b^3 + \frac{\epsilon}{2} \psi_b^2 + \frac{\lambda}{2} \psi_b C_{pfc} \psi_b \right\} d\mathbf{x}. \quad (5.5)$$

Next, the free energy functional for the coupling of the two fields is

$$\mathcal{F}_{bin,coup}(t; \psi_a, \psi_b) := \int_{\Omega} \left\{ \beta_{11} \psi_a \psi_b + \frac{\beta_{12}}{2} (\psi_a^2 \psi_b + \psi_a \psi_b^2) \right\} d\mathbf{x}. \quad (5.6)$$

Finally, we take the average of the free energy functionals for ψ_a and ψ_b and add the coupling free energy terms to arrive at the **binary PFC free energy functional**:

$$\begin{aligned} \mathcal{F}_{bin}(t; \psi_a, \psi_b) := & \int_{\Omega} \left[\frac{1}{2} \left\{ \frac{\chi_4}{4} \psi_a^4 + \frac{\chi_3}{3} \psi_a^3 + \frac{\epsilon}{2} \psi_a^2 + \frac{\lambda}{2} \psi_a C_{pfc} \psi_a \right\} \right. \\ & + \frac{1}{2} \left\{ \frac{\chi_4}{4} \psi_b^4 + \frac{\chi_3}{3} \psi_b^3 + \frac{\epsilon}{2} \psi_b^2 + \frac{\lambda}{2} \psi_b C_{pfc} \psi_b \right\} \\ & \left. + \beta_{11} \psi_a \psi_b + \frac{\beta_{12}}{2} (\psi_a^2 \psi_b + \psi_a \psi_b^2) \right] d\mathbf{x}. \end{aligned} \quad (5.7)$$

Hence, the free energy density is

$$\begin{aligned} f_{bin}(\psi_a, \Delta \psi_a, \Delta^2 \psi_a, \psi_b, \Delta \psi_b, \Delta^2 \psi_b) := & \frac{1}{2} \left\{ \frac{\chi_4}{4} \psi_a^4 + \frac{\chi_3}{3} \psi_a^3 + \frac{\epsilon}{2} \psi_a^2 + \frac{\lambda}{2} \psi_a C_{pfc} \psi_a \right\} \\ & + \frac{1}{2} \left\{ \frac{\chi_4}{4} \psi_b^4 + \frac{\chi_3}{3} \psi_b^3 + \frac{\epsilon}{2} \psi_b^2 + \frac{\lambda}{2} \psi_b C_{pfc} \psi_b \right\} \\ & + \beta_{11} \psi_a \psi_b + \frac{\beta_{12}}{2} (\psi_a^2 \psi_b + \psi_a \psi_b^2). \end{aligned} \quad (5.8)$$

The first two parts of the free energy density provide the standard PFC free energies for the individual mass density fields and, thus, generate triangle geometry for ψ_a and for ψ_b . These two parts are halved so that the total free energy is comparable in value to the free energy from the other PFC models in this study. The term

$$\beta_{11}\psi_a\psi_b \quad (5.9)$$

causes the two mass density fields to be offset, and the term

$$\frac{\beta_{12}}{2} (\psi_a\psi_b^2 + \psi_a^2\psi_b) \quad (5.10)$$

enforces the low density “hole” that is to form in the middle of each resulting hexagon.

We now add a vapor phase field, η , to the model, as we did for the multimode PFC model in Section 2.4. The field η outputs values in $[0, 1]$, where 0 is the solid phase, and 1 is the vapor phase. We use the vapor parameters b_v , M_v , W_v , Δ_v , κ_v , and ψ_v from the original multimode PFC model with vapor. Note that the same vapor phase field η is shared by the two mass density fields ψ_a and ψ_b . We recall the phase interpolation function

$$g(\eta) := \eta^3 (6\eta^2 - 15\eta + 10) \quad (5.11)$$

and the phase interface free energy function

$$h(\eta) := \eta^2 (\eta - 1)^2 = \eta^4 - 2\eta^3 + \eta^2 \quad (5.12)$$

from (2.93) and (2.94), respectively, of Subsection 2.4.2. From (2.96), the vapor phase field free energy density for the multimode PFC model with vapor is

$$f_{vap}(\psi) := \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v. \quad (5.13)$$

We extend (5.13) to incorporate the two mass density fields of the binary model. We take one half of the sum of the two densities to arrive at

$$f_{bin,vap}(\psi_a, \psi_b) := \frac{b_v}{4} ((\psi_a - \psi_v)^2 + (\psi_b - \psi_v)^2) + \Delta_v. \quad (5.14)$$

As with the multimode model (2.97), the phase interface free energy density is

$$f_{int}(\eta) := W_v h(\eta) + \frac{\kappa_v}{2} |\nabla \eta|^2. \quad (5.15)$$

Applying the phase interpolation function g to the solid free energy density of (5.8) and the vapor energy density of (5.14) and adding the phase interface terms of (5.15), we have the **binary PFC with vapor phase field free energy functional**

$$\begin{aligned} \mathcal{F}_{binv}(t; \psi_a, \psi_b, \eta) := & \int_{\Omega} \left[g(\eta) \left\{ \frac{b_v}{4} [(\psi_a - \psi_v)^2 + (\psi_b - \psi_v)^2] + \Delta_v \right\} \right. \\ & + (1 - g(\eta)) \left\{ \frac{1}{2} \left(\frac{\chi_4}{4} \psi_a^4 + \frac{\chi_3}{3} \psi_a^3 + \frac{\epsilon}{2} \psi_a^2 + \frac{\lambda}{2} \psi_a C_{pfc} \psi_a \right) \right. \\ & \quad + \frac{1}{2} \left(\frac{\chi_4}{4} \psi_b^4 + \frac{\chi_3}{3} \psi_b^3 + \frac{\epsilon}{2} \psi_b^2 + \frac{\lambda}{2} \psi_b C_{pfc} \psi_b \right) \\ & \quad \left. \left. + \beta_{11} \psi_a \psi_b + \frac{\beta_{12}}{2} (\psi_a^2 \psi_b + \psi_a \psi_b^2) \right\} \right. \\ & \left. + W_v h(\eta) + \frac{\kappa_v}{2} |\nabla \eta|^2 \right] d\mathbf{x}. \end{aligned} \quad (5.16)$$

By Green's first identity for periodic functions (C.4), within the integrand, the last term may be replaced with $-\frac{\kappa_v}{2}\eta(\Delta\eta)$. Then, (5.16) is equivalent to

$$\begin{aligned}
\mathcal{F}_{binv}(t; \psi_a, \psi_b, \eta) = & \int_{\Omega} \left[g(\eta) \left\{ \frac{b_v}{4} [(\psi_a - \psi_v)^2 + (\psi_b - \psi_v)^2] + \Delta_v \right\} \right. \\
& + (1 - g(\eta)) \left\{ \frac{1}{2} \left(\frac{\chi_4}{4} \psi_a^4 + \frac{\chi_3}{3} \psi_a^3 + \frac{\epsilon}{2} \psi_a^2 + \frac{\lambda}{2} \psi_a C_{pfc} \psi_a \right) \right. \\
& \quad + \frac{1}{2} \left(\frac{\chi_4}{4} \psi_b^4 + \frac{\chi_3}{3} \psi_b^3 + \frac{\epsilon}{2} \psi_b^2 + \frac{\lambda}{2} \psi_b C_{pfc} \psi_b \right) \\
& \quad \left. \left. + \beta_{11} \psi_a \psi_b + \frac{\beta_{12}}{2} (\psi_a^2 \psi_b + \psi_a \psi_b^2) \right\} \right. \\
& \left. + W_v h(\eta) - \frac{\kappa_v}{2} \eta \Delta \eta \right] d\mathbf{x}.
\end{aligned} \tag{5.17}$$

Therefore, the corresponding free energy density is

$$\begin{aligned}
f_{binv}(\psi_a, \Delta\psi_a, \Delta^2\psi_a, \psi_b, \Delta\psi_b, \Delta^2\psi_b, \eta, \Delta\eta) \\
:= & g(\eta) \left\{ \frac{b_v}{4} [(\psi_a - \psi_v)^2 + (\psi_b - \psi_v)^2] + \Delta_v \right\} \\
& + (1 - g(\eta)) \left\{ \frac{1}{2} \left(\frac{\chi_4}{4} \psi_a^4 + \frac{\chi_3}{3} \psi_a^3 + \frac{\epsilon}{2} \psi_a^2 + \frac{\lambda}{2} \psi_a C_{pfc} \psi_a \right) \right. \\
& \quad + \frac{1}{2} \left(\frac{\chi_4}{4} \psi_b^4 + \frac{\chi_3}{3} \psi_b^3 + \frac{\epsilon}{2} \psi_b^2 + \frac{\lambda}{2} \psi_b C_{pfc} \psi_b \right) \\
& \quad \left. + \beta_{11} \psi_a \psi_b + \frac{\beta_{12}}{2} (\psi_a^2 \psi_b + \psi_a \psi_b^2) \right\} \\
& + W_v h(\eta) - \frac{\kappa_v}{2} \eta \Delta \eta.
\end{aligned} \tag{5.18}$$

We now find the variational derivatives for the free energy functional $\mathcal{F}_{binv}$ with respect to ψ_a , ψ_b , and η . In Subsection 2.4.2 for the multimode PFC model with vapor, we apply Corollary E.4 to the free energy density (2.103). We perform a similar process here for the

free energy density (5.18). The resulting variational derivatives are

$$\begin{aligned}
\frac{\delta \mathcal{F}_{binv}}{\delta \psi_a} &= g(\eta) \frac{b_v}{2} (\psi_a - \psi_v) \\
&+ (1 - g(\eta)) \left\{ \frac{1}{2} (\chi_4 \psi_a^3 + \chi_3 \psi_a^2 + \epsilon \psi_a) + \beta_{11} \psi_b + \frac{\beta_{12}}{2} (2\psi_a \psi_b + \psi_b^2) \right\} \\
&+ \frac{\lambda}{2} \left\{ C_{pfc} \psi_a - \frac{1}{2} [g(\eta) C_{pfc} \psi_a + C_{pfc}(g(\eta) \psi_a)] \right\},
\end{aligned} \tag{5.19}$$

$$\begin{aligned}
\frac{\delta \mathcal{F}_{binv}}{\delta \psi_b} &= g(\eta) \frac{b_v}{2} (\psi_b - \psi_v) \\
&+ (1 - g(\eta)) \left\{ \frac{1}{2} (\chi_4 \psi_b^3 + \chi_3 \psi_b^2 + \epsilon \psi_b) + \beta_{11} \psi_a + \frac{\beta_{12}}{2} (2\psi_b \psi_a + \psi_a^2) \right\} \\
&+ \frac{\lambda}{2} \left\{ C_{pfc} \psi_b - \frac{1}{2} [g(\eta) C_{pfc} \psi_b + C_{pfc}(g(\eta) \psi_b)] \right\},
\end{aligned} \tag{5.20}$$

and

$$\begin{aligned}
\frac{\delta \mathcal{F}_{binv}}{\delta \eta} &= g'(\eta) \left\{ \frac{b_v}{4} [(\psi_a - \psi_v)^2 + (\psi_b - \psi_v)^2] + \Delta_v \right. \\
&\quad - \frac{1}{2} \left(\frac{\chi_4}{4} \psi_a^4 + \frac{\chi_3}{3} \psi_a^3 + \frac{\epsilon}{2} \psi_a^2 + \frac{\lambda}{2} \psi_a C_{pfc} \psi_a \right) \\
&\quad - \frac{1}{2} \left(\frac{\chi_4}{4} \psi_b^4 + \frac{\chi_3}{3} \psi_b^3 + \frac{\epsilon}{2} \psi_b^2 + \frac{\lambda}{2} \psi_b C_{pfc} \psi_b \right) \\
&\quad \left. - \beta_{11} \psi_a \psi_b - \frac{\beta_{12}}{2} (\psi_a^2 \psi_b + \psi_a \psi_b^2) \right\} \\
&+ W_v h'(\eta) - \kappa_v \Delta \eta.
\end{aligned} \tag{5.21}$$

Employing (5.19), (5.20), and (5.21), respectively, we define the **binary PFC model with vapor phase field PDE's** as

$$\begin{aligned}
\dot{\psi}_a &:= \Delta \frac{\delta \mathcal{F}_{binv}}{\delta \psi_a} \\
&= \Delta \left[g(\eta) \frac{b_v}{2} (\psi_a - \psi_v) \right. \\
&\quad + (1 - g(\eta)) \left\{ \frac{1}{2} (\chi_4 \psi_a^3 + \chi_3 \psi_a^2 + \epsilon \psi_a) + \beta_{11} \psi_b + \frac{\beta_{12}}{2} (2\psi_a \psi_b + \psi_b^2) \right\} \\
&\quad \left. + \frac{\lambda}{2} \left\{ C_{pfc} \psi_a - \frac{1}{2} [g(\eta) C_{pfc} \psi_a + C_{pfc}(g(\eta) \psi_a)] \right\} \right], \tag{5.22}
\end{aligned}$$

$$\begin{aligned}
\dot{\psi}_b &:= \Delta \frac{\delta \mathcal{F}_{binv}}{\delta \psi_b} \\
&= \Delta \left[g(\eta) \frac{b_v}{2} (\psi_b - \psi_v) \right. \\
&\quad + (1 - g(\eta)) \left\{ \frac{1}{2} (\chi_4 \psi_b^3 + \chi_3 \psi_b^2 + \epsilon \psi_b) + \beta_{11} \psi_a + \frac{\beta_{12}}{2} (2\psi_b \psi_a + \psi_a^2) \right\} \\
&\quad \left. + \frac{\lambda}{2} \left\{ C_{pfc} \psi_b - \frac{1}{2} [g(\eta) C_{pfc} \psi_b + C_{pfc}(g(\eta) \psi_b)] \right\} \right], \tag{5.23}
\end{aligned}$$

and

$$\begin{aligned}
\dot{\eta} &:= -\frac{\delta \mathcal{F}_{binv}}{\delta \eta} \\
&= g'(\eta) \left\{ -\frac{b_v}{4} [(\psi_a - \psi_v)^2 + (\psi_b - \psi_v)^2] - \Delta_v \right. \\
&\quad + \frac{1}{2} \left(\frac{\chi_4}{4} \psi_a^4 + \frac{\chi_3}{3} \psi_a^3 + \frac{\epsilon}{2} \psi_a^2 + \frac{\lambda}{2} \psi_a C_{pfc} \psi_a \right) \\
&\quad + \frac{1}{2} \left(\frac{\chi_4}{4} \psi_b^4 + \frac{\chi_3}{3} \psi_b^3 + \frac{\epsilon}{2} \psi_b^2 + \frac{\lambda}{2} \psi_b C_{pfc} \psi_b \right) \\
&\quad \left. + \beta_{11} \psi_a \psi_b + \frac{\beta_{12}}{2} (\psi_a^2 \psi_b + \psi_a \psi_b^2) \right\} \\
&\quad - W_v h'(\eta) + \kappa_v \Delta \eta. \tag{5.24}
\end{aligned}$$

The dot notation signifies the partial derivative with respect to time. Note that the mass density field PDE's are sixth order, while the vapor phase field PDE is fourth order. Similar to the multimode PFC model with vapor, as we prove in Subsection 2.4.3, the mass densities

ψ_a and ψ_b are each conserved, while the vapor phase field η is not conserved. Finally, the total free energy is nonincreasing over time.

5.3 Binary PFC Model Simulations

We present three simulations for the binary PFC model. In the first simulation, we begin with two different uniformly random mass density fields for ψ_a and ψ_b . The second and third simulations begin with a disk seed, or initial solid region. The remainder of the region is vapor. In the second simulation, the triangular geometries for ψ_a and ψ_b are in alignment such that the superposition of the fields yields a disk of honeycomb geometry. In the last simulation the disk seeds for each field are random. For all simulations, the initial solid mean mass density is $\mu_s = -0.171$. For the disk seed simulations, the initial vapor phase mass density is $\mu_v = -0.205$. This vapor density is higher than the vapor phase equilibrium mass density, and, so, the solid regions, or nanocrystals, grow over time. Each simulation runs until the overall free energy stabilizes at a minimum. We call this final state the “equilibrium state”.

5.3.1 Uniformly Random

For this simulation, both mass density fields, ψ_a and ψ_b , are initialized to uniformly random states. In addition, the two random fields are independent. The goal is to show that the each field forms triangular geometry and that the fields align to form honeycomb geometry. The initial fields for ψ_a and ψ_b appear in Figures 5.2a and 5.2b, respectively. Figure 5.2c provides the superposition of the two fields. Next, Figures 5.3a, 5.3c, and 5.3e display ψ_a , ψ_b , and the superposition at time 1,000. Figures 5.3a and 5.3c indicate that both mass density fields possess triangular geometry with irregularities. Figure 5.3e reveals honeycomb geometry with different orientations. Note the similarities in the grain boundaries in Figures 5.3a, 5.3c, and 5.3e. The honeycomb geometry in Figure 5.3e and the comparable grain boundaries of all three figures are the result of the coupling terms (5.6) in the free energy functional. Finally, Figures 5.3b, 5.3d, and 5.3f provide the mass density field data for time

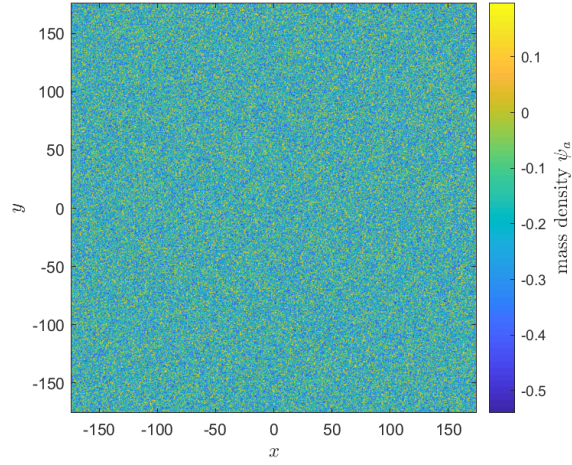
244,000, when the system is at equilibrium. We can see that there are fewer irregularities and the grain boundaries are similar in each of the mass density fields.

5.3.2 Disk Seed

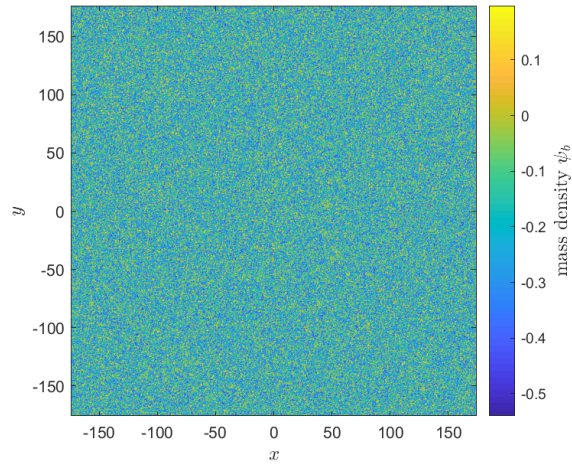
We begin with a crystal disk seed for this second simulation. Both mass density fields ψ_a and ψ_b possess triangular geometry within their respective initial solid disks. In addition, this geometry is offset so that the superposition of the two fields generates honeycomb geometry. Figures 5.4a and 5.4b yield the initial mass density fields for ψ_a and ψ_b , respectively. Figure 5.4c reveals the superposition. Figures 5.5a, 5.5c, and 5.5e display ψ_a , ψ_b , and the superposition at time 1,000. We can see that the nanocrystals, or solid regions, are larger. Finally, Figures 5.5b, 5.5d, and 5.5f reveal the field data at the equilibrium state at time 31,000. The nanocrystal is yet larger. In addition, the nanocrystal forms a dodecagon similar to the nanocrystal for the multimode PFC model with vapor simulation in Figure 2.26e of Subsection 2.4.4. However, six of the sides are very short, and, thus, the nanocrystal is almost hexagonal in shape.

5.3.3 Random Disk Seed

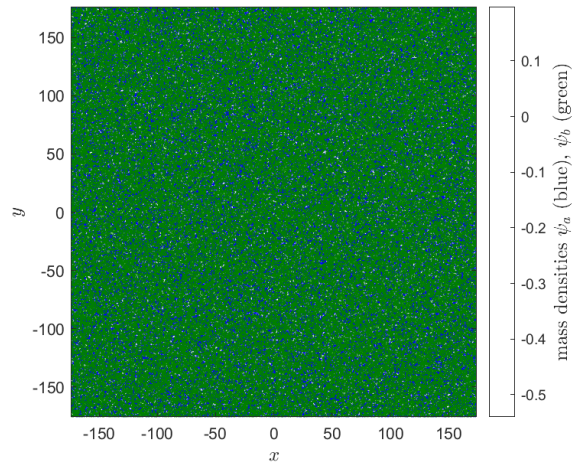
Finally, we begin with a uniformly random disk seed. Figures 5.6a and 5.6b present the initial mass density fields for ψ_a and ψ_b , respectively. These fields possess independent randomization within the disk seeds. Figure 5.6c details the superposition of ψ_a and ψ_b . Figures 5.7a and 5.7c provide the respective mass density fields at time 1,000, while Figure 5.7e shows the corresponding superposition. At this time, the triangular geometry is prevalent in both ψ_a and ψ_b . In addition, the triangular geometries are aligned so that the superposition of the two fields yields the honeycomb geometry of Figure 5.7e. As in the random simulation of Subsection 5.3.1, the grain boundaries in Figures 5.7a, 5.7c, and 5.7e are similar. We also see in these figures that the sides of the nanocrystal have become straighter. Finally, Figures 5.7b, 5.7d, and 5.7f present the field data at time 129,000, when the system is at its equilibrium. We see that no irregularities remain. In addition, the nanocrystal is larger and more polygonal.



(a) Mass Density Field A

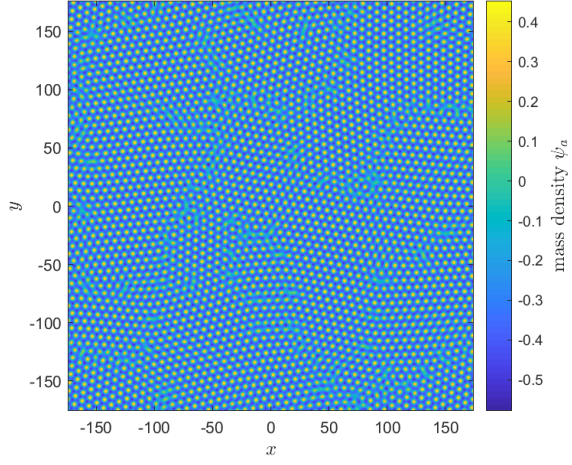


(b) Mass Density Field B

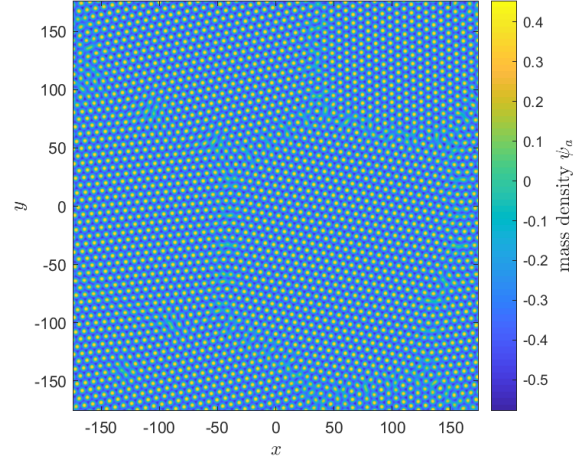


(c) Superposition of Fields

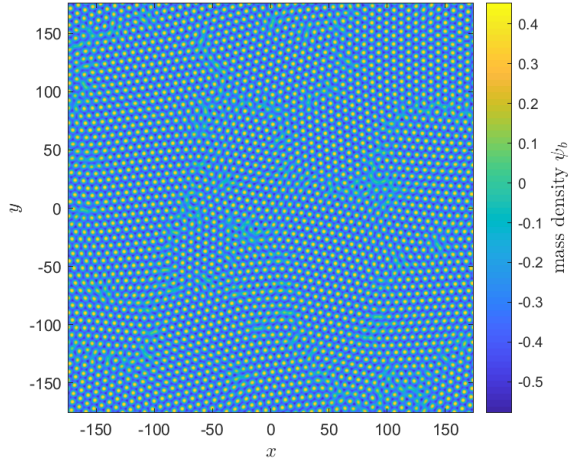
Figure 5.2: Binary PFC, Random Initial, Mass Density Fields, Time = 0



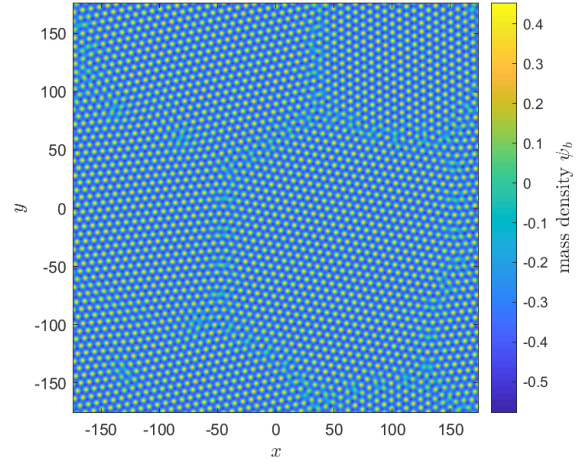
(a) Mass Density Field A, Time = 1,000



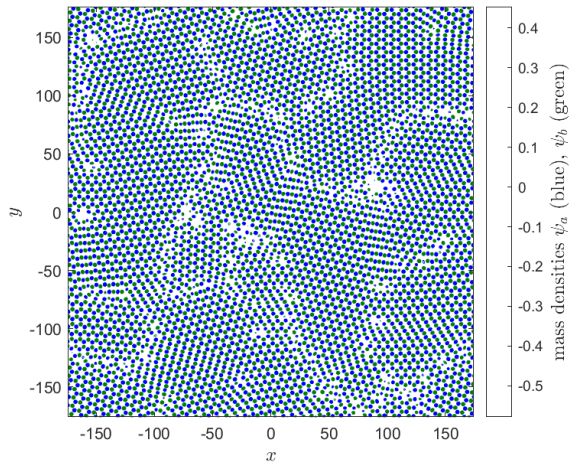
(b) Mass Density Field A, Time = 244,000



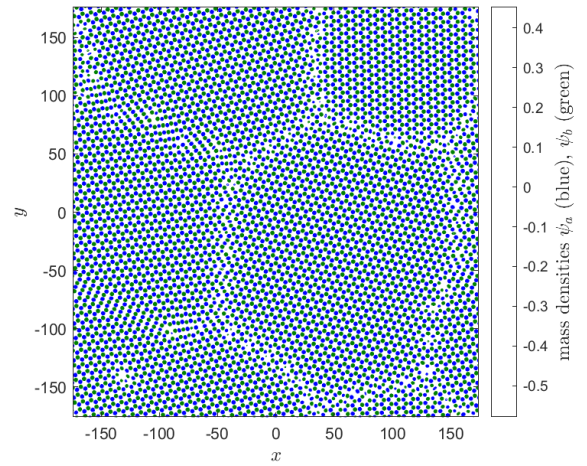
(c) Mass Density Field B, Time = 1,000



(d) Mass Density Field B, Time = 244,000

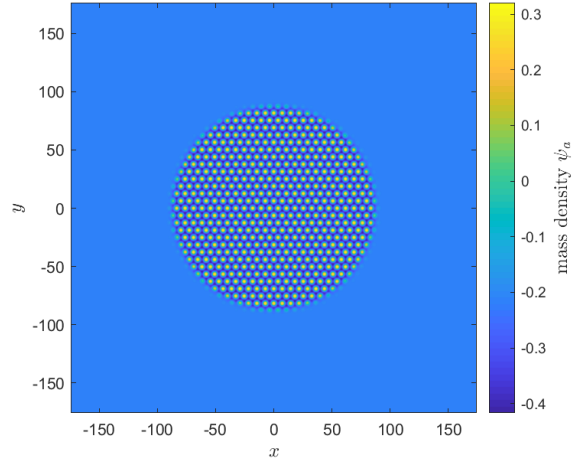


(e) Superposition of Fields, Time = 1,000

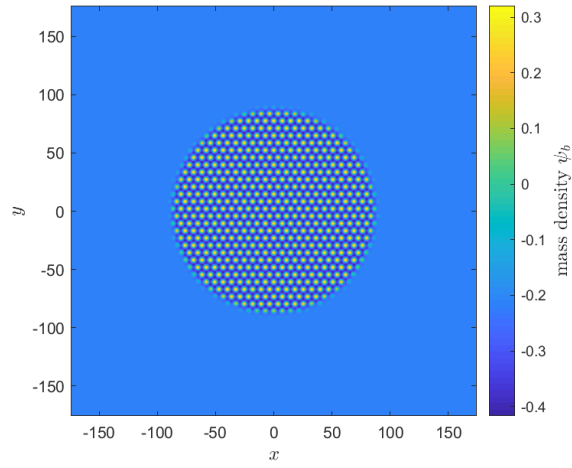


(f) Superposition of Fields, Time = 244,000

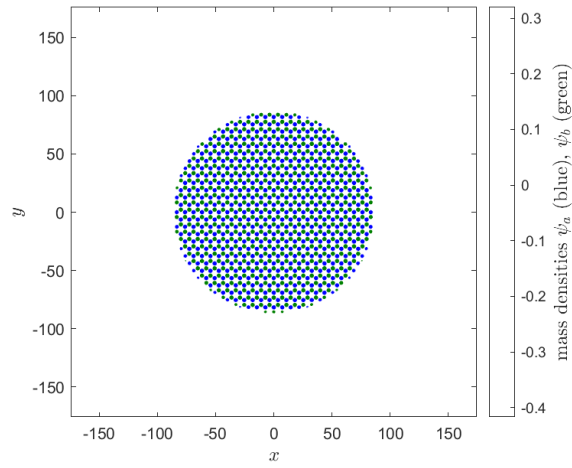
Figure 5.3: Binary PFC, Random Initial, Mass Density Fields, Time = 1,000; 244,000



(a) Mass Density Field A

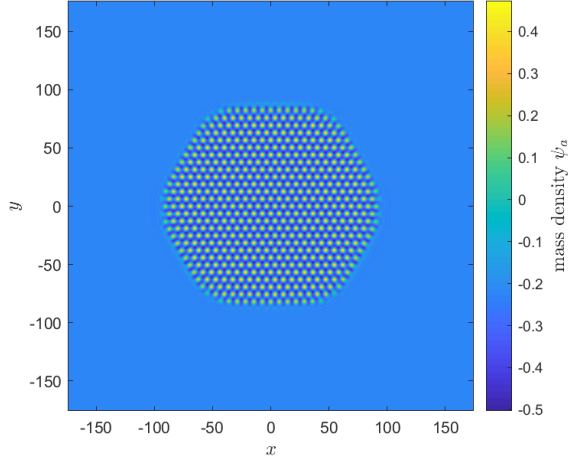


(b) Mass Density Field B

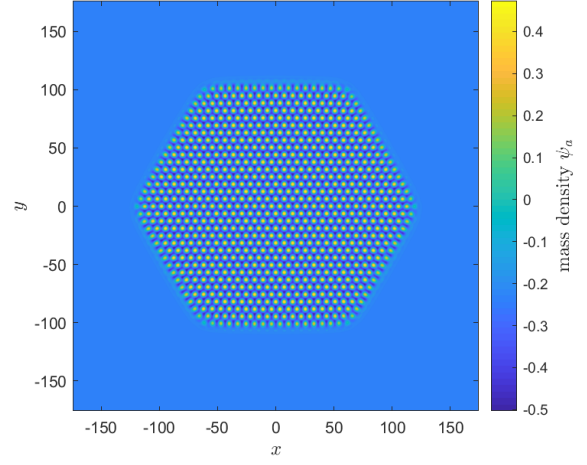


(c) Superposition of Fields

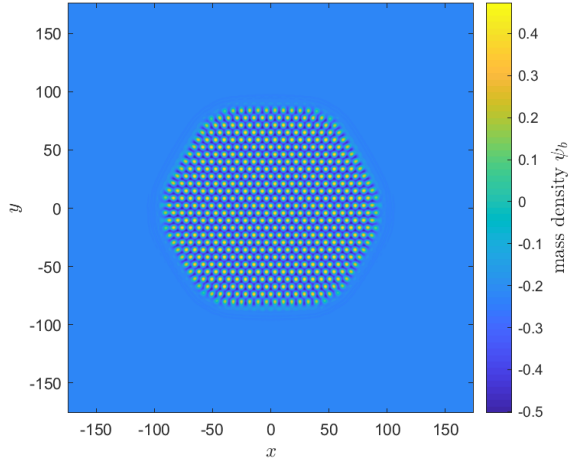
Figure 5.4: Binary PFC, Disk Seed, Mass Density Fields, Time = 0



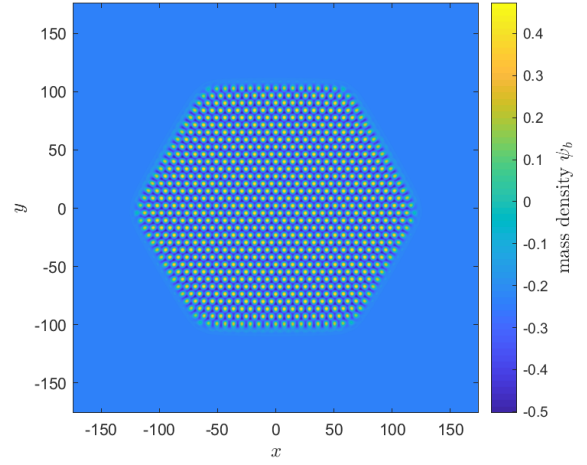
(a) Mass Density Field A, Time = 1,000



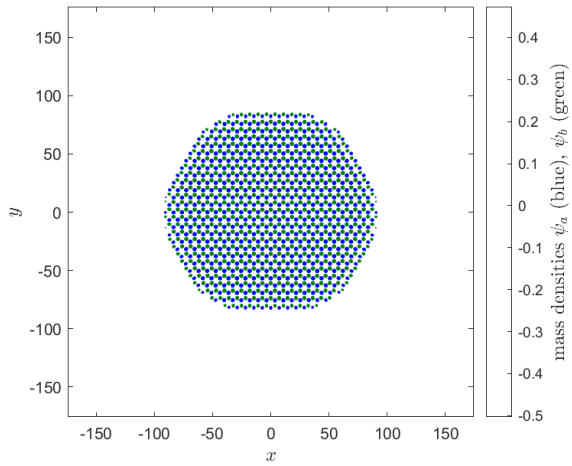
(b) Mass Density Field A, Time = 31,000



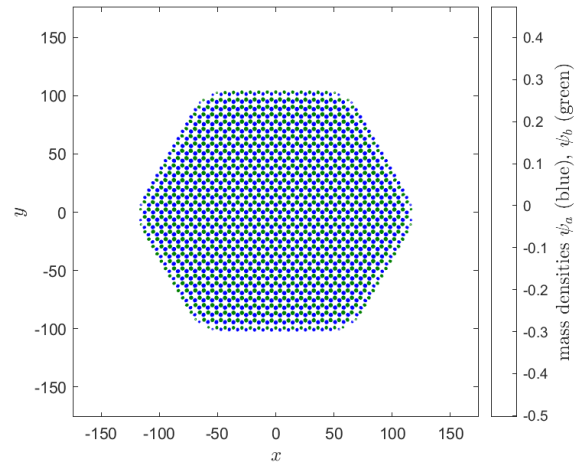
(c) Mass Density Field B, Time = 1,000



(d) Mass Density Field B, Time = 31,000

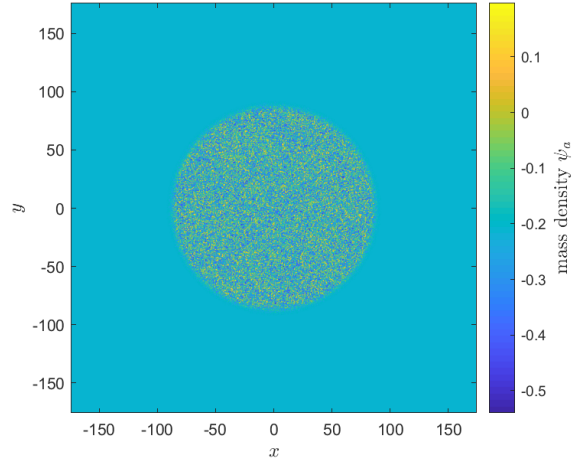


(e) Superposition of Fields, Time = 1,000

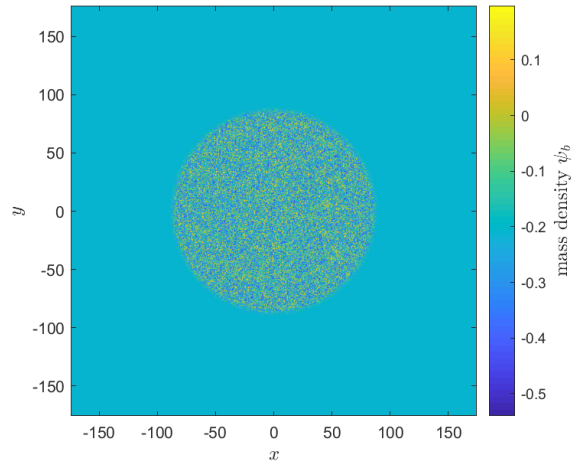


(f) Superposition of Fields, Time = 31,000

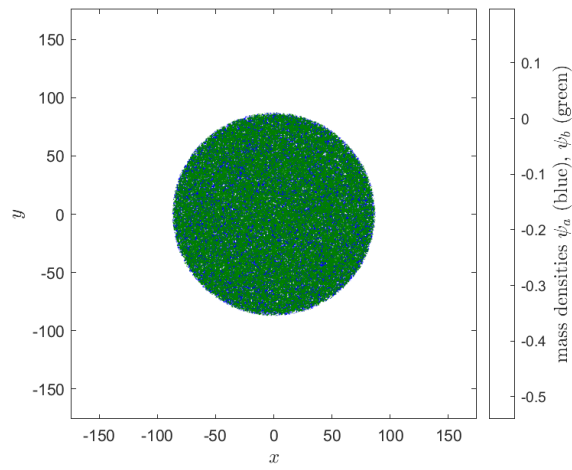
Figure 5.5: Binary PFC, Disk Seed, Mass Density Fields, Time = 1,000; 31,000



(a) Mass Density Field A

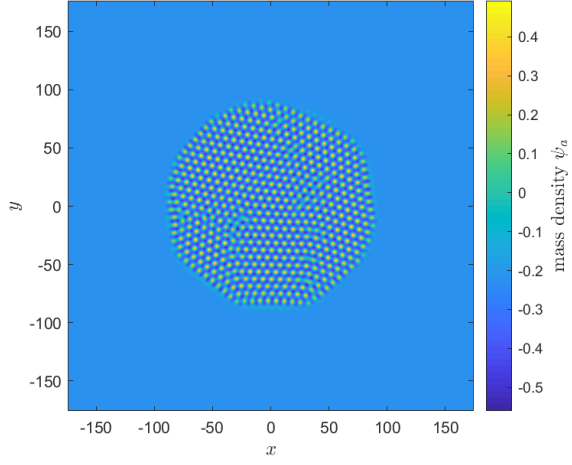


(b) Mass Density Field B

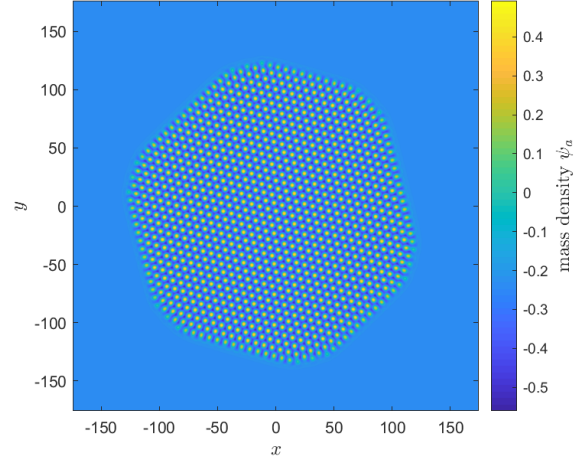


(c) Superposition of Fields

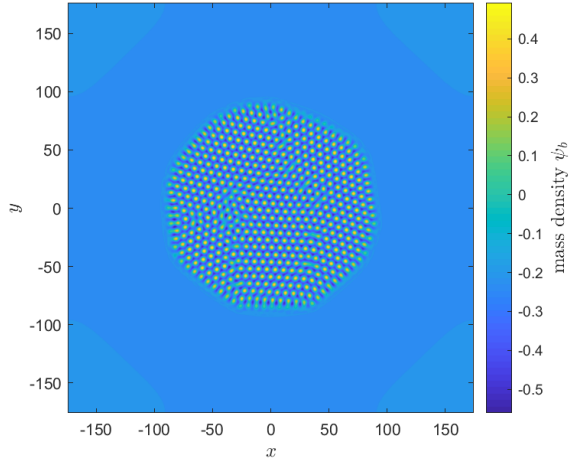
Figure 5.6: Binary PFC, Random Seed, Mass Density Fields, Time = 0



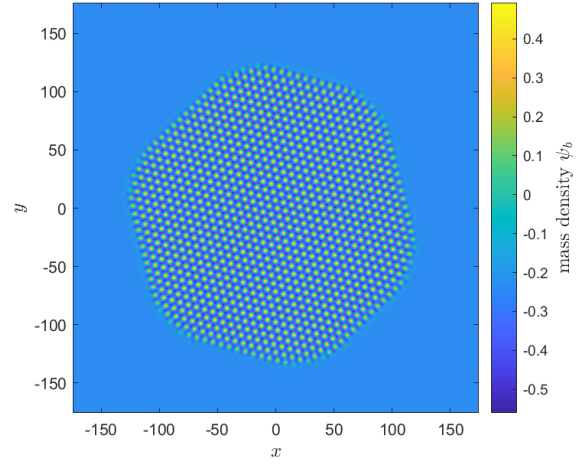
(a) Mass Density Field A, Time = 1,000



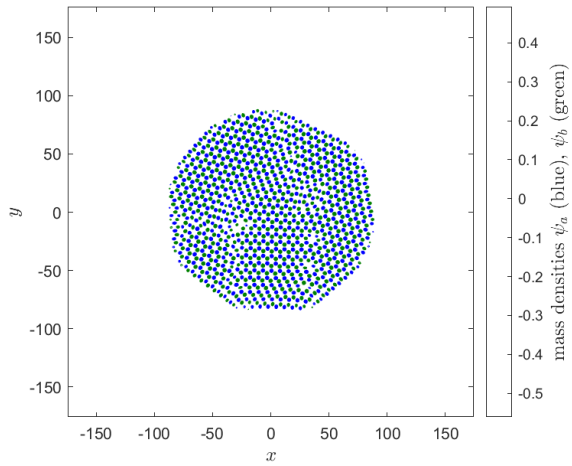
(b) Mass Density Field A, Time = 129,000



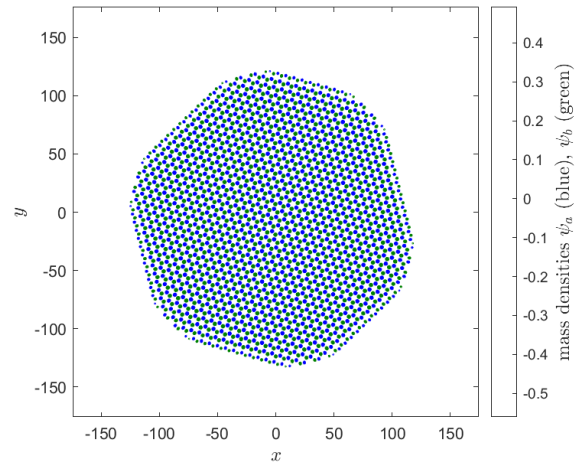
(c) Mass Density Field B, Time = 1,000



(d) Mass Density Field B, Time = 129,000



(e) Superposition of Fields, Time = 1,000



(f) Superposition of Fields, Time = 129,000

Figure 5.7: Binary PFC, Random Seed, Mass Density Fields, Time = 1,000; 129,000

5.4 Binary PFC Model Summary

The simulations indicate that the binary PFC model behaves much like the multimode PFC model. For the vapor field simulations, we find that the nanocrystal shapes are similar to those of the corresponding multimode PFC simulations. Since the individual fields have single-mode gradient free energies, we avoid the complications of designing a three-mode Fourier space multiplier. However, the binary PFC model does not provide a single mass density field to embody the honeycomb geometry.

Chapter 6

Dual-Layer Multimode PFC Model

We introduce here a *dual-layer multimode PFC model*. The purpose of this model is to simulate the formation of bilayer graphene. Each layer of graphene has honeycomb geometry. The two parallel layers of bilayer graphene are held together by van der Waals forces, which are relatively weak intermolecular attractions. The most common alignment is called Bernal, or AB, stacking [1]. For Bernal stacking, half of the carbon atoms of the upper layer align vertically with atoms of the lower layer, while the other half of the upper atoms align with the centroids of the hexagons of the lower layer. Another common type of alignment is AA stacking. In AA stacking, each of the atoms of the upper layer align with an atom in the lower layer. Figure 6.1a demonstrates Bernal stacking, while Figure 6.1b provides AA stacking. In the figures, the carbon atoms of the lower layer are blue, while the atoms of the upper layer are red. Purple represents the overlap of two atoms. The solid lines are the bonds between the carbon atoms of the lower layer, and the dashed lines designate the bonds between the upper layer atoms.

The lower and upper mass density fields are ψ_1 and ψ_2 , respectively. Since the lower and upper layers typically have different phase boundaries, we require separate vapor phase fields. We label the lower and upper vapor phase fields as η_1 and η_2 , respectively. Each layer possesses its own set of free energy density terms as defined by the multimode PFC model with vapor. In addition, we add coupling energy terms that establish the Bernal crystal alignment between the lower and upper layers. Next, we add a term to each mass density PDE that equalizes the vapor density where vapor regions overlap. Furthermore,

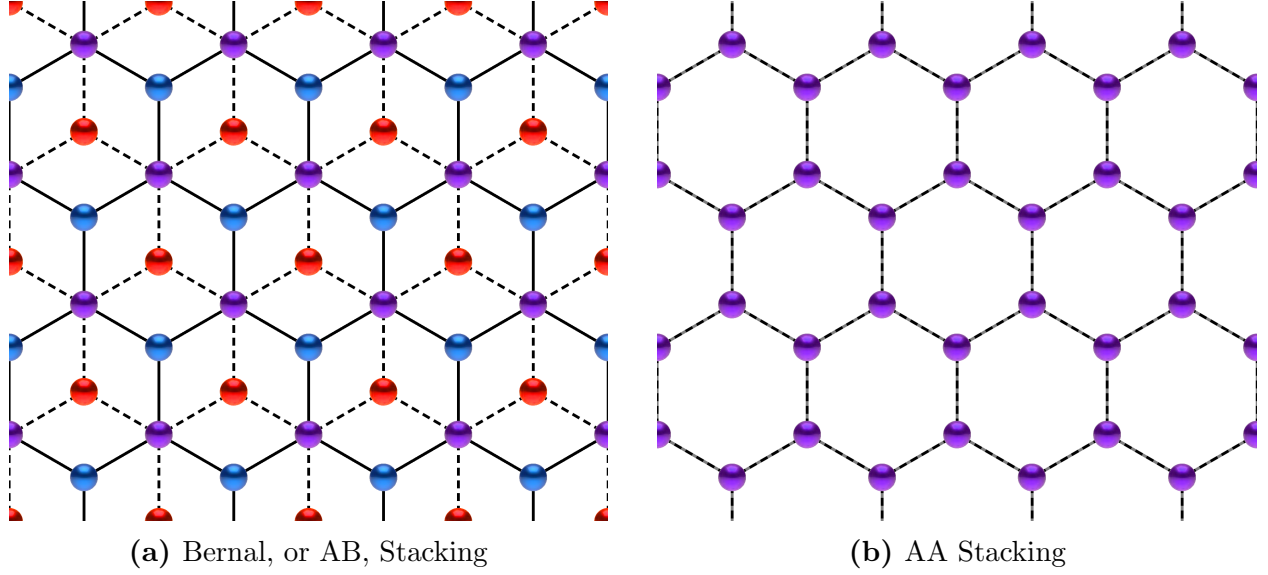


Figure 6.1: Bilayer Graphene Stacking

since bilayer graphene is typically formed on a substrate, no portion of the upper layer of graphene may overlap a region of vapor. Therefore, we design this equalizing term to effectively “sublime” any upper layer solid that resides directly above lower layer vapor.

Establishing stable Bernal stacking for this dual-layer model is challenging. We first redesign the linear differential operator from the standard multimode PFC model. The goal is to decrease the small mass density peaks at the centroids of the hexagons of the honeycomb geometry. Regardless, the Fourier multiplier for the revised linear operator still has local minima at the dominant angular frequency radii $\omega_1 = 1$, $\omega_{\sqrt{3}} = \sqrt{3}$, and $\omega_2 = 2$. Because of these modifications, we must decrease the quartic coefficient χ_4 from the homogeneous free energy to avoid triangular geometry. In turn, this decrease in χ_4 causes a change in the shape of the solid phase equilibrium free energy curve. To compensate, we decrease slightly the vapor phase free energy curve vertical offset Δ_v . Note that the standard phase equilibrium curves appear in Figures 2.30a and 2.30b in Section 2.5. Despite these modifications, we must also decrease the initial vapor and solid mean mass densities to stabilize simulations that include the vapor phase. This prevents us from generating nanocrystal growth, which is a crucial part of graphene modeling. However, further work and parameter value modifications may provide the necessary stability for nanocrystal growth.

6.1 Dual-Layer Multimode PFC Parameters

Table 6.1a catalogs the structural parameters and values for the dual-layer multimode PFC model, and Table 6.1b lists those for the vapor phase. Both the lower and upper layers of the dual-layer model share the parameter values of Tables 6.1a and 6.1b. Due to the linear differential operator revisions for stable Bernal stacking, the $c_1, c_2, \dots, c_8$ and χ_4 parameter values differ from those of the standard multimode PFC model with vapor in Table 2.3a of Subsection 2.4.1. In addition, the vapor free energy differential parameter Δ_v is smaller than the corresponding parameter in Table 2.3b. However, all of the other parameter values match. The simulations of Subsection 2.4.4 use the values $W_v = 0.1$ and $\kappa_v = 0.4455$.

Tables 6.1c and 6.1d provide the mass density field initialization parameters and the discretization parameters, respectively. Except for the initial vapor and solid mean mass densities μ_v and μ_s , the parameters values of Tables 6.1c and 6.1d match those of Tables 2.3c and 2.3d for the standard multimode PFC model with vapor.

Now, Table 6.2 holds the coupling parameters that link the lower and upper layers. The parameter α controls the rate at which the mass densities of overlapping vapor phase regions equalize. In addition, α determines how quickly a solid region sublimates when it overlaps a vapor region. The γ_{11} , γ_{12} , γ_{13} , and γ_{22} parameters are coefficients for polynomial free energy terms that establish the Bernal stacking crystal alignment. Section 6.2 describes the applications of the parameters of Table 6.2.

6.2 Dual-Layer Multimode PFC Equations

To build the dual-layer multimode PFC equations, we apply the free energy functional terms of the standard multimode PFC model with vapor. We first define a rectangular region Ω in $\mathbb{R}^2$. We stipulate that both the lower and upper layer mass density fields, ψ_1 and ψ_2 , respectively, are Ω -periodic. Each layer has a vapor phase field. The lower layer vapor phase field is η_1 , while the upper layer vapor field is η_2 . Here, η_1 and η_2 take values in $[0, 1]$, where 0 indicates the solid phase, and 1 signifies the vapor phase.

Table 6.1: Dual-Layer Multimode PFC Standard Parameters**(a)** Solid Phase Parameters

Parameter/Value	Description
$c_0 = 142.56$	Gradient coefficient 0
$c_1 = 381.898780952437$	Gradient coefficient 1
$c_2 = 329.637196825599$	Gradient coefficient 2
$c_3 = 61.6085272489722$	Gradient coefficient 3
$c_4 = -54.5946544971293$	Gradient coefficient 4
$c_5 = -32.3466037036058$	Gradient coefficient 5
$c_6 = -6.52834497352057$	Gradient coefficient 6
$c_7 = -0.466418783065528$	Gradient coefficient 7
$c_8 = 0.0000883597885397559$	Gradient coefficient 8
$\epsilon = -0.15$	Temperature (scaled and shifted)
$\lambda = 0.02$	Multimodal strength
$\chi_3 = -0.02$	Cubic term coefficient
$\chi_4 = 1.3$	Quartic term coefficient

(b) Vapor Phase Field Parameters

Parameter/Value	Description
$b_v = 4$	Vapor free energy scalar
$M_v = 1$	Vapor phase field mobility
$W_v = 0.1$	Resistance to coexistence of phases
$\Delta_v = 0.0380462643691291$	Vapor free energy differential
$\kappa_v = 0.4455$	Phase interface derivative strength
$\psi_v = -0.11$	Vapor equilibrium density

(c) Mass Density Field Initialization Parameters

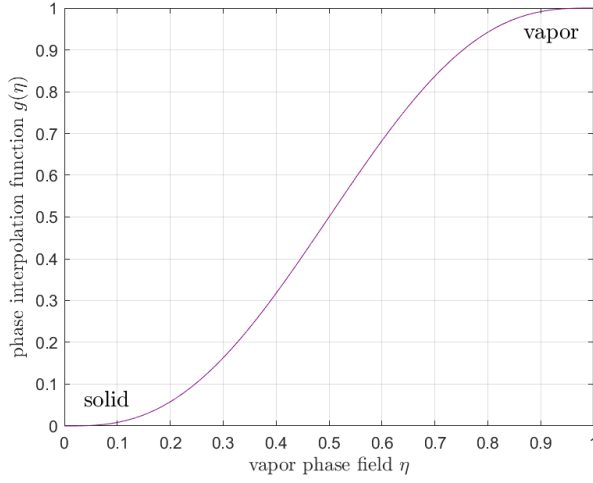
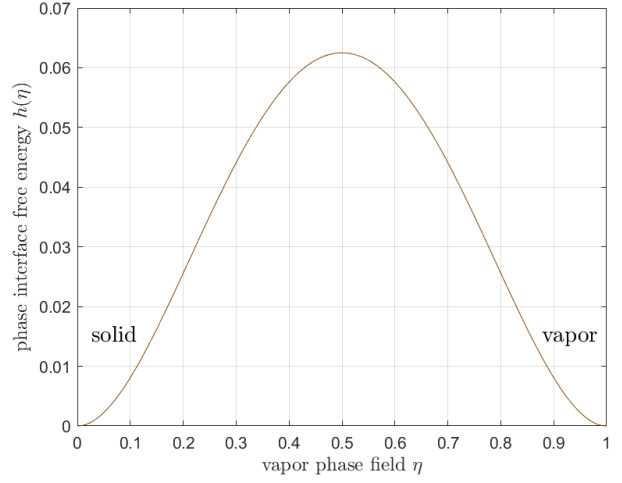
Parameter/Value	Description
$amp = 0.3688$	Initial solid density amplitude
$cell_x = 7.255197457$	Initial unit cell width
$cell_y = 12.5663706144685$	Initial unit cell height
$thickness = 2.756975$	Initial phase interface thickness
$\mu_s = -0.18$	Initial solid mean density
$\mu_v = -0.225$	Initial vapor density

(d) Discretization Parameters

Parameter/Value	Description
$dt = 0.1$	Time increment
$h_x \approx 0.45$	x -granularity
$h_y \approx 0.45$	y -granularity

Table 6.2: Dual-Layer Multimode PFC Coupling Parameters

Parameter/Value	Description
$\alpha = 0.02$	vapor density match coefficient
$\gamma_{11} = 0.015$	crystal alignment coefficient 1, 1
$\gamma_{12} = -0.03$	crystal alignment coefficient 1, 2
$\gamma_{13} = -0.15$	crystal alignment coefficient 1, 3
$\gamma_{22} = 0.01$	crystal alignment coefficient 2, 2

**(a)** Interpolation Function**(b)** Double-Well, Interface Function**Figure 6.2:** Phase Interpolation and Interface Functions

We require four vapor phase field functions for the dual-layer model. The first two are the phase interpolation and the phase interface free energy functions from (2.93) and (2.94), respectively, of Subsection 2.4.2. The corresponding definitions are

$$g(\eta) := \eta^3 (6\eta^2 - 15\eta + 10) \quad (6.1)$$

and

$$h(\eta) := \eta^2 (\eta - 1)^2 = \eta^4 - 2\eta^3 + \eta^2. \quad (6.2)$$

Figure 6.2a provides the graph for the interpolation function g , and Figure 6.2b shows the function interface energy function h .

The next two functions aid in the coupling of the lower and upper layers. The crystal alignment function,

$$p(\eta_1, \eta_2) := (1 - \eta_1)^4(1 - \eta_2)^4(5 - 4(1 - \eta_1)(1 - \eta_2)), \quad (6.3)$$

is a polynomial function on $[0, 1] \times [0, 1]$. In addition, p outputs values in $[0, 1]$. Where both layers are solid, $\eta_1 = \eta_2 = 0$, and, so, p is 1. Outside of such regions, p steeply tapers off to 0. The function p determines the regions where crystal alignment takes place. Figure 6.3a reveals the contour shape of p , while Figure 6.3b displays the curve for $\eta_1 = \eta_2$. Finally, we introduce the vapor density match function

$$r(\eta_1) := \eta_1^6(7 - 6\eta_1). \quad (6.4)$$

We see that r is a polynomial function on $[0, 1]$ that takes values in $[0, 1]$. Now, r outputs 1 within the vapor regions in the lower layer, and r diminishes quickly to 0 elsewhere. Hence, r specifies the regions of Ω where the lower and upper mass density equalization occurs. Figure 6.3c provides the curve for r .

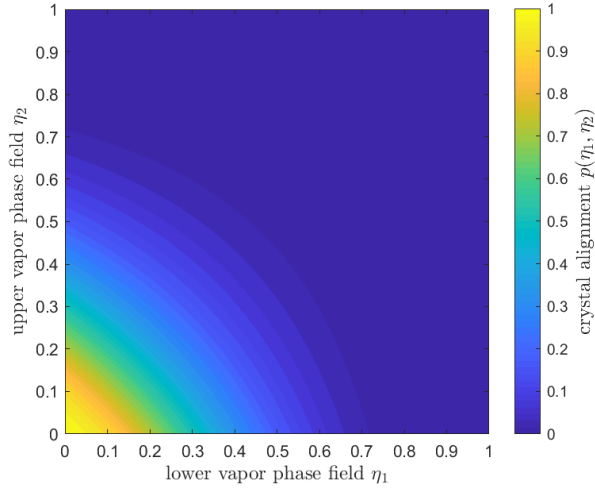
We now restate the free energy functional (2.102) from Subsection 2.4.2 for the multimode PFC model with vapor:

$$\begin{aligned} \mathcal{F}(t; \psi, \eta) := & \int_{\Omega} \left[g(\eta) \left\{ \frac{b_v}{2} (\psi - \psi_v)^2 + \Delta_v \right\} \right. \\ & + (1 - g(\eta)) \left\{ \frac{\chi_4}{4} \psi^4 + \frac{\chi_3}{3} \psi^3 + \frac{\epsilon}{2} \psi^2 + \frac{\lambda}{2} \psi C \psi \right\} \\ & \left. + W_v h(\eta) - \frac{\kappa_v}{2} \eta \Delta \eta \right] d\mathbf{x}, \quad (6.5) \end{aligned}$$

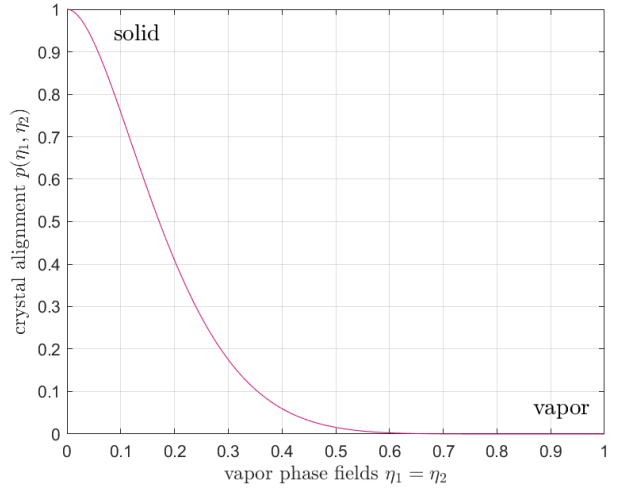
where

$$C := \sum_{i=0}^8 c_i \Delta^i. \quad (6.6)$$

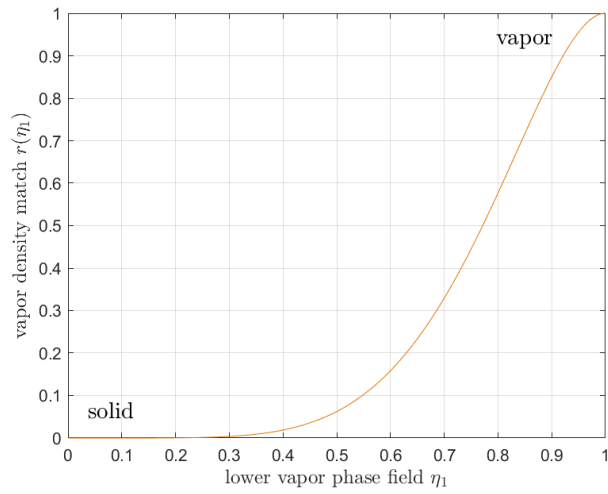
Note that the linear differential operator coefficients $c_0, c_1, \dots, c_8$ are different for this dual-layer model. However, like the standard multimode PFC model, the Fourier multiplier for the dual-layer linear operator has local minima at the dominant angular frequencies $\omega_1 = 1$,



(a) Crystal Alignment Function



(b) Crystal Alignment Function, $\eta_1 = \eta_2$



(c) Vapor Density Match Function

Figure 6.3: Lower and Upper Layer Coupling Functions

$\omega_{\sqrt{3}} = \sqrt{3}$, and $\omega_2 = 2$. By (6.5), the free energy functionals for the lower and upper mass density fields ψ_1 and ψ_2 are

$$\begin{aligned} \mathcal{F}_{d,1}(t; \psi_1, \eta_1) := & \int_{\Omega} \left[g(\eta_1) \left\{ \frac{b_v}{2} (\psi_1 - \psi_v)^2 + \Delta_v \right\} \right. \\ & + (1 - g(\eta_1)) \left\{ \frac{\chi_4}{4} \psi_1^4 + \frac{\chi_3}{3} \psi_1^3 + \frac{\epsilon}{2} \psi_1^2 + \frac{\lambda}{2} \psi_1 C \psi_1 \right\} \\ & \left. + W_v h(\eta_1) - \frac{\kappa_v}{2} \eta_1 \Delta \eta_1 \right] d\mathbf{x}, \quad (6.7) \end{aligned}$$

and

$$\begin{aligned} \mathcal{F}_{d,2}(t; \psi_2, \eta_2) := & \int_{\Omega} \left[g(\eta_2) \left\{ \frac{b_v}{2} (\psi_2 - \psi_v)^2 + \Delta_v \right\} \right. \\ & + (1 - g(\eta_2)) \left\{ \frac{\chi_4}{4} \psi_2^4 + \frac{\chi_3}{3} \psi_2^3 + \frac{\epsilon}{2} \psi_2^2 + \frac{\lambda}{2} \psi_2 C \psi_2 \right\} \\ & \left. + W_v h(\eta_2) - \frac{\kappa_v}{2} \eta_2 \Delta \eta_2 \right] d\mathbf{x}, \quad (6.8) \end{aligned}$$

respectively.

Next, the free energy functional for the Bernal stacking crystal alignment is

$$\begin{aligned} \mathcal{F}_{d,align}(t; \psi_1, \psi_2, \eta_1, \eta_2) := & \int_{\Omega} p(\eta_1, \eta_2) \left\{ \gamma_{11} \psi_1 \psi_2 \right. \\ & + \frac{\gamma_{12}}{2} (\psi_1 \psi_2^2 + \psi_1^2 \psi_2) \\ & + \frac{\gamma_{13}}{2} (\psi_1 \psi_2^3 + \psi_1^3 \psi_2) \\ & \left. + \gamma_{22} \psi_1^2 \psi_2^2 \right\} d\mathbf{x}. \quad (6.9) \end{aligned}$$

Due to the multiplier $p(\eta_1, \eta_2)$, the corresponding free energy density may be nonzero only where crystal, or solid, regions of the mass density fields overlap. In addition, the terms entail every polynomial expression, with degree less than or equal to 4, that contains both ψ_1 and ψ_2 . Through the selection of values for the alignment coefficients γ_{11} , γ_{12} , γ_{13} , and γ_{22} , we can establish a low free energy state for the Bernal stacking crystal alignment.

Finally, we combine the free energy functionals of (6.7), (6.8), and (6.9) to arrive at the **dual-layer multimode PFC free energy functional**:

$$\begin{aligned}
\mathcal{F}_d(t; \psi_1, \psi_2, \eta_1, \eta_2) := & \int_{\Omega} \left[g(\eta_1) \left\{ \frac{b_v}{2} (\psi_1 - \psi_v)^2 + \Delta_v \right\} \right. \\
& + (1 - g(\eta_1)) \left\{ \frac{\chi_4}{4} \psi_1^4 + \frac{\chi_3}{3} \psi_1^3 + \frac{\epsilon}{2} \psi_1^2 + \frac{\lambda}{2} \psi_1 C \psi_1 \right\} \\
& + W_v h(\eta_1) - \frac{\kappa_v}{2} \eta_1 \Delta \eta_1 \\
& + g(\eta_2) \left\{ \frac{b_v}{2} (\psi_2 - \psi_v)^2 + \Delta_v \right\} \\
& + (1 - g(\eta_2)) \left\{ \frac{\chi_4}{4} \psi_2^4 + \frac{\chi_3}{3} \psi_2^3 + \frac{\epsilon}{2} \psi_2^2 + \frac{\lambda}{2} \psi_2 C \psi_2 \right\} \\
& + W_v h(\eta_2) - \frac{\kappa_v}{2} \eta_2 \Delta \eta_2 \\
& + p(\eta_1, \eta_2) \left\{ \gamma_{11} \psi_1 \psi_2 \right. \\
& \quad + \frac{\gamma_{12}}{2} (\psi_1 \psi_2^2 + \psi_1^2 \psi_2) \\
& \quad + \frac{\gamma_{13}}{2} (\psi_1 \psi_2^3 + \psi_1^3 \psi_2) \\
& \quad \left. + \gamma_{22} \psi_1^2 \psi_2^2 \right\} \Big] d\mathbf{x}.
\end{aligned} \tag{6.10}$$

Therefore, the free energy density is

$$\begin{aligned}
f_d & \left(\psi_1, \Delta\psi_1, \dots, \Delta^8\psi_1, \psi_2, \Delta\psi_2, \dots, \Delta^8\psi_2, \eta_1, \Delta\eta_1, \eta_2, \Delta\eta_2 \right) \\
& := g(\eta_1) \left\{ \frac{b_v}{2} (\psi_1 - \psi_v)^2 + \Delta_v \right\} \\
& + (1 - g(\eta_1)) \left\{ \frac{\chi_4}{4} \psi_1^4 + \frac{\chi_3}{3} \psi_1^3 + \frac{\epsilon}{2} \psi_1^2 + \frac{\lambda}{2} \psi_1 C \psi_1 \right\} \\
& + W_v h(\eta_1) - \frac{\kappa_v}{2} \eta_1 \Delta\eta_1 \\
& + g(\eta_2) \left\{ \frac{b_v}{2} (\psi_2 - \psi_v)^2 + \Delta_v \right\} \\
& + (1 - g(\eta_2)) \left\{ \frac{\chi_4}{4} \psi_2^4 + \frac{\chi_3}{3} \psi_2^3 + \frac{\epsilon}{2} \psi_2^2 + \frac{\lambda}{2} \psi_2 C \psi_2 \right\} \quad (6.11) \\
& + W_v h(\eta_2) - \frac{\kappa_v}{2} \eta_2 \Delta\eta_2 \\
& + p(\eta_1, \eta_2) \left\{ \gamma_{11} \psi_1 \psi_2 \right. \\
& \quad + \frac{\gamma_{12}}{2} (\psi_1 \psi_2^2 + \psi_1^2 \psi_2) \\
& \quad + \frac{\gamma_{13}}{2} (\psi_1 \psi_2^3 + \psi_1^3 \psi_2) \\
& \quad \left. + \gamma_{22} \psi_1^2 \psi_2^2 \right\}.
\end{aligned}$$

Next, we recall the partial differential equation (PDE) (2.110) for the mass density field from Subsection 2.4.2 for the multimode PFC model with vapor:

$$\dot{\psi} := \Delta \frac{\delta \mathcal{F}}{\delta \psi}. \quad (6.12)$$

In addition, the vapor phase field PDE (2.114) for the same model is

$$\dot{\eta} := -M_v \frac{\delta \mathcal{F}}{\delta \eta}. \quad (6.13)$$

The dot notation denotes the partial derivative with respect to time. Now, for this dual-layer model, we include the vapor density equalization operations in the definitions for the lower

and upper mass density PDE's:

$$\dot{\psi}_1 := \Delta \frac{\delta \mathcal{F}_d}{\delta \psi_1} + \frac{\alpha}{2} r(\eta_1) (\psi_2 - \psi_1) \quad (6.14)$$

and

$$\dot{\psi}_2 := \Delta \frac{\delta \mathcal{F}_d}{\delta \psi_2} - \frac{\alpha}{2} r(\eta_1) (\psi_2 - \psi_1), \quad (6.15)$$

respectively. Next, the vapor phase field PDE's for the lower and upper layers are simply

$$\dot{\eta}_1 := -M_v \frac{\delta \mathcal{F}_d}{\delta \eta_1} \quad (6.16)$$

and

$$\dot{\eta}_2 := -M_v \frac{\delta \mathcal{F}_d}{\delta \eta_2}, \quad (6.17)$$

respectively. The variational derivatives can be found by expanding Corollary E.4 for four fields. Finally, the mass density field PDE's are of the 18th order, and the vapor phase field PDE's are 16th order.

Effectively, the term $\frac{\alpha}{2} r(\eta_1) (\psi_2 - \psi_1)$ is added to $\dot{\psi}_1$ and subtracted from $\dot{\psi}_2$. Necessarily, this operation transfers mass density from one layer to the other. Mass density is not conserved in the individual layer fields. Therefore, this equalization functionality cannot be included in the free energy functional $\mathcal{F}_d$. If it were included in $\mathcal{F}_d$, each mass density PDE would take the form of (6.12). Per Subsection 2.4.3, this would result in mass density conservation in each individual mass density field, and no transfer of mass would take place between layers. In Section 6.3, we prove that mass density is conserved in the sum of the mass density fields.

6.3 Dual-Layer MMPFC Mass Conservation and Non-increasing Energy

We first prove that the mass density is conserved in the sum of the lower and upper mass density fields, $\psi_1 + \psi_2$. Applying Leibniz's rule, we have

$$\frac{d}{dt} \int_{\Omega} \{\psi_1 + \psi_2\} d\mathbf{x} = \int_{\Omega} [\dot{\psi}_1 + \dot{\psi}_2] d\mathbf{x}. \quad (6.18)$$

Installing (6.14) and (6.15) yields

$$\begin{aligned} \frac{d}{dt} \int_{\Omega} \{\psi_1 + \psi_2\} d\mathbf{x} \\ = \int_{\Omega} \left[\left\{ \Delta \frac{\delta \mathcal{F}_d}{\delta \psi_1} + \frac{\alpha}{2} r(\eta_1)(\psi_2 - \psi_1) \right\} + \left\{ \Delta \frac{\delta \mathcal{F}_d}{\delta \psi_2} - \frac{\alpha}{2} r(\eta_1)(\psi_2 - \psi_1) \right\} \right] d\mathbf{x}. \end{aligned} \quad (6.19)$$

The equalization terms cancel out to give us

$$\frac{d}{dt} \int_{\Omega} \{\psi_1 + \psi_2\} d\mathbf{x} = \int_{\Omega} \left[\Delta \frac{\delta \mathcal{F}_d}{\delta \psi_1} + \Delta \frac{\delta \mathcal{F}_d}{\delta \psi_2} \right] d\mathbf{x}. \quad (6.20)$$

By the linearity of integration, we have

$$\frac{d}{dt} \int_{\Omega} \{\psi_1 + \psi_2\} d\mathbf{x} = \int_{\Omega} \Delta \frac{\delta \mathcal{F}_d}{\delta \psi_1} d\mathbf{x} + \int_{\Omega} \Delta \frac{\delta \mathcal{F}_d}{\delta \psi_2} d\mathbf{x}, \quad (6.21)$$

and, so,

$$\frac{d}{dt} \int_{\Omega} \{\psi_1 + \psi_2\} d\mathbf{x} = \int_{\Omega} 1 \cdot \Delta \frac{\delta \mathcal{F}_d}{\delta \psi_1} d\mathbf{x} + \int_{\Omega} 1 \cdot \Delta \frac{\delta \mathcal{F}_d}{\delta \psi_2} d\mathbf{x}. \quad (6.22)$$

By Green's first identity for periodic functions (C.4), we have

$$\frac{d}{dt} \int_{\Omega} \{\psi_1 + \psi_2\} d\mathbf{x} = - \int_{\Omega} \nabla 1 \cdot \nabla \frac{\delta \mathcal{F}_d}{\delta \psi_1} d\mathbf{x} - \int_{\Omega} \nabla 1 \cdot \nabla \frac{\delta \mathcal{F}_d}{\delta \psi_2} d\mathbf{x}. \quad (6.23)$$

Since $\nabla 1 = \mathbf{0}$,

$$\frac{d}{dt} \int_{\Omega} \{\psi_1 + \psi_2\} d\mathbf{x} = 0 \quad (6.24)$$

for all $t \in \mathbb{R}^+$. Therefore, mass density is always conserved in the sum of the mass density fields. For simulations with no vapor phase in the lower layer, $r(\eta_1)$ is 0 everywhere in Ω . Hence, in these cases, mass density is also conserved in each individual mass density field. However, for simulations with lower layer vapor phase regions, mass density is not conserved within the individual fields.

We now examine trends in the total free energy over time. Due to the potential transfer of mass between the two layers, it is possible for the total free energy to increase. We begin by investigating the derivative of the free energy functional $\mathcal{F}_d$ with respect to time. Expanding Corollary E.6 to four fields, we have

$$\frac{d\mathcal{F}_d}{dt} = \int_{\Omega} \left\{ \frac{\delta\mathcal{F}_d}{\delta\psi_1} \dot{\psi}_1 + \frac{\delta\mathcal{F}_d}{\delta\psi_2} \dot{\psi}_2 + \frac{\delta\mathcal{F}_d}{\delta\eta_1} \dot{\eta}_1 + \frac{\delta\mathcal{F}_d}{\delta\eta_2} \dot{\eta}_2 \right\} d\mathbf{x}. \quad (6.25)$$

The linearity of integration yields

$$\frac{d\mathcal{F}_d}{dt} = \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\psi_1} \dot{\psi}_1 d\mathbf{x} + \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\psi_2} \dot{\psi}_2 d\mathbf{x} + \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\eta_1} \dot{\eta}_1 d\mathbf{x} + \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\eta_2} \dot{\eta}_2 d\mathbf{x}. \quad (6.26)$$

Applying (6.14), (6.15), (6.16), and (6.17) gives us

$$\begin{aligned} \frac{d\mathcal{F}_d}{dt} &= \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\psi_1} \left(\Delta \frac{\delta\mathcal{F}_d}{\delta\psi_1} + \frac{\alpha}{2} r(\eta_1) (\psi_2 - \psi_1) \right) d\mathbf{x} \\ &\quad + \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\psi_2} \left(\Delta \frac{\delta\mathcal{F}_d}{\delta\psi_2} - \frac{\alpha}{2} r(\eta_1) (\psi_2 - \psi_1) \right) d\mathbf{x} \\ &\quad + \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\eta_1} \left(-M_v \frac{\delta\mathcal{F}_d}{\delta\eta_1} \right) d\mathbf{x} \\ &\quad + \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\eta_2} \left(-M_v \frac{\delta\mathcal{F}_d}{\delta\eta_2} \right) d\mathbf{x}. \end{aligned} \quad (6.27)$$

Distributing the factors in the integrands of the first two integrals, and applying the linearity of integration, we have

$$\begin{aligned}
\frac{d\mathcal{F}_d}{dt} &= \frac{\alpha}{2} \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\psi_1} r(\eta_1)(\psi_2 - \psi_1) d\mathbf{x} \\
&\quad - \frac{\alpha}{2} \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\psi_2} r(\eta_1)(\psi_2 - \psi_1) d\mathbf{x} \\
&\quad + \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\psi_1} \Delta \frac{\delta\mathcal{F}_d}{\delta\psi_1} d\mathbf{x} \\
&\quad + \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\psi_2} \Delta \frac{\delta\mathcal{F}_d}{\delta\psi_2} d\mathbf{x} \\
&\quad - M_v \int_{\Omega} \left(\frac{\delta\mathcal{F}_d}{\delta\eta_1} \right)^2 d\mathbf{x} \\
&\quad - M_v \int_{\Omega} \left(\frac{\delta\mathcal{F}_d}{\delta\eta_2} \right)^2 d\mathbf{x}.
\end{aligned} \tag{6.28}$$

Next, we apply Green's first identity for periodic functions (C.4) to the third and fourth integrals to find

$$\begin{aligned}
\frac{d\mathcal{F}_d}{dt} &= \frac{\alpha}{2} \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\psi_1} r(\eta_1)(\psi_2 - \psi_1) d\mathbf{x} \\
&\quad - \frac{\alpha}{2} \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\psi_2} r(\eta_1)(\psi_2 - \psi_1) d\mathbf{x} \\
&\quad - \int_{\Omega} \nabla \frac{\delta\mathcal{F}_d}{\delta\psi_1} \cdot \nabla \frac{\delta\mathcal{F}_d}{\delta\psi_1} d\mathbf{x} \\
&\quad - \int_{\Omega} \nabla \frac{\delta\mathcal{F}_d}{\delta\psi_2} \cdot \nabla \frac{\delta\mathcal{F}_d}{\delta\psi_2} d\mathbf{x} \\
&\quad - M_v \int_{\Omega} \left(\frac{\delta\mathcal{F}_d}{\delta\eta_1} \right)^2 d\mathbf{x} \\
&\quad - M_v \int_{\Omega} \left(\frac{\delta\mathcal{F}_d}{\delta\eta_2} \right)^2 d\mathbf{x},
\end{aligned} \tag{6.29}$$

and, so,

$$\begin{aligned}
\frac{d\mathcal{F}_d}{dt} = & \frac{\alpha}{2} \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\psi_1} r(\eta_1) (\psi_2 - \psi_1) d\mathbf{x} \\
& - \frac{\alpha}{2} \int_{\Omega} \frac{\delta\mathcal{F}_d}{\delta\psi_2} r(\eta_1) (\psi_2 - \psi_1) d\mathbf{x} \\
& - \int_{\Omega} \left| \nabla \frac{\delta\mathcal{F}_d}{\delta\psi_1} \right|^2 d\mathbf{x} \\
& - \int_{\Omega} \left| \nabla \frac{\delta\mathcal{F}_d}{\delta\psi_2} \right|^2 d\mathbf{x} \\
& - M_v \int_{\Omega} \left(\frac{\delta\mathcal{F}_d}{\delta\eta_1} \right)^2 d\mathbf{x} \\
& - M_v \int_{\Omega} \left(\frac{\delta\mathcal{F}_d}{\delta\eta_2} \right)^2 d\mathbf{x}.
\end{aligned} \tag{6.30}$$

Now, the last four integrals of (6.30) result in nonpositive values. However, for cases where the vapor phase exists in the lower layer, either of the first two integrals may result in a positive value. Hence, for such cases, the total free energy may increase. If the vapor phase is not present in the lower layer, $r(\eta_1) = 0$ everywhere in Ω , and the first two integrals are 0. In this case, the energy is nonincreasing. Due to the $\frac{\alpha}{2}r(\eta_1)(\psi_2 - \psi_1)$ terms of the PDE's (6.14) and (6.15), the vapor phase densities of the lower and upper layers approach equalization over time. Hence, $(\psi_2 - \psi_1)$ approaches 0 where there is vapor in the lower layer. Therefore, the first two integrals of (6.30) typically approach 0 as well, and the free energy trend is primarily nonincreasing.

6.4 Dual-Layer Multimode PFC Simulations

We offer three simulations for the dual-layer multimode PFC model. The first simulation starts with two independent, uniformly random mass density fields for ψ_1 and ψ_2 . The second and third simulations begin with disk seeds surrounded by vapor phase regions. For the second simulation, the initial seeds possess honeycomb geometries that are aligned according to the common Bernal stacking. However, the upper layer seed is larger than that of the lower layer. In contrast, the third simulation begins with disks containing uniformly

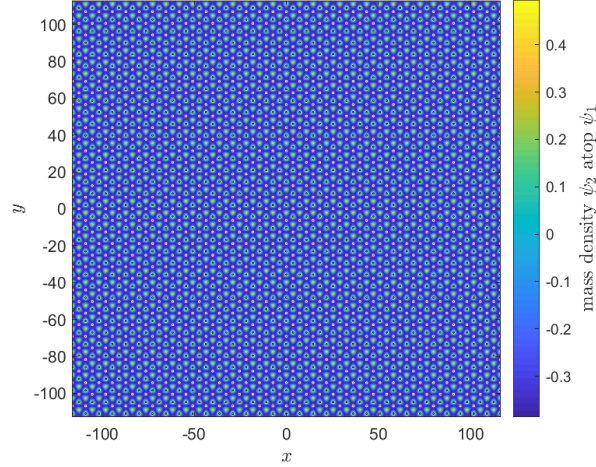


Figure 6.4: Bernal Alignment, Transparent Overlay

random mass densities, while the lower layer seed is larger than the upper layer seed. Each simulation runs to an equilibrium state where the free energy per unit area is at a numerical minimum. To see the alignment between the lower and upper layers, we provide transparent overlay figures for each time of interest. Each overlay diagram displays the lower layer mass density field in detail, while designating the peaks of the upper layer field as white circles or dots. Figure 6.4 provides an example of a transparent overlay field where the entire computational box has Bernal alignment.

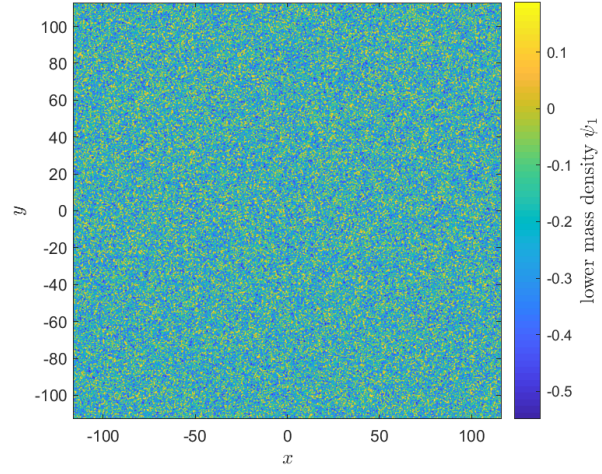
6.4.1 Uniformly Random

At the beginning of this first simulation, the mass density field of each layer holds uniformly random values. These initial layer mass densities are independent. Figures 6.5a and 6.5b provide the initial lower and upper mass density fields, respectively. Figure 6.5c shows the initial overlay diagram. Figures 6.6a, 6.6c, and 6.6e display the lower layer, upper layer, and overlay mass densities, respectively, for time 2,000. We see that the honeycomb geometry prevails in both the lower and upper layers. However, there are many irregularities in the mass densities of both layers. Figure 6.6e reveals two patches of Bernal stacking centered near $(10, -20)$ and $(70, -80)$, respectively. The system obtains its equilibrium state at time 34,000. Figures 6.6b, 6.6d, and 6.6f yield the lower layer, upper layer, and overlay

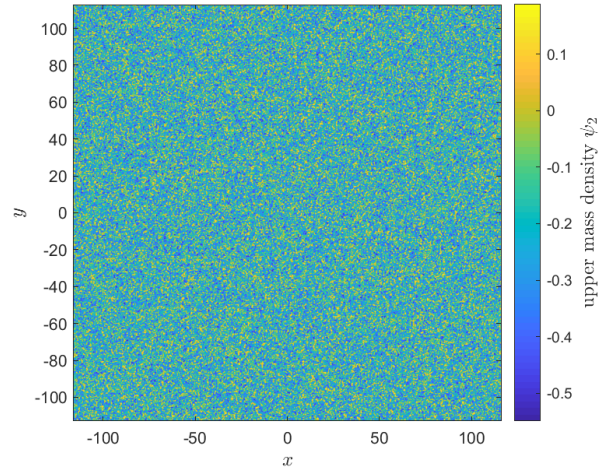
mass densities, respectively, for time 34,000. In Figures 6.6b and 6.6d, we discover that the irregularities of the honeycomb geometries of the lower and upper layer mass densities have decreased. However, a number of distinct geometrical orientations still remain. The transparent overlay for the two layers in Figure 6.6f indicates that the Bernal stacking is more prevalent. There are now three distinct regions of Bernal alignment. The region centered near $(10, -20)$ is larger and more rounded. The region containing the point $(70, -80)$ is much larger, as it extends further to the left and down. By the Ω -periodicity of the mass density fields, this same region includes the aligned area at the top right of the computational box. Finally, a new area of alignment exists around $(40, 50)$. Note that grain boundaries in the individual mass density fields result in breaks in the aligned areas.

6.4.2 Aligned Disk Seeds

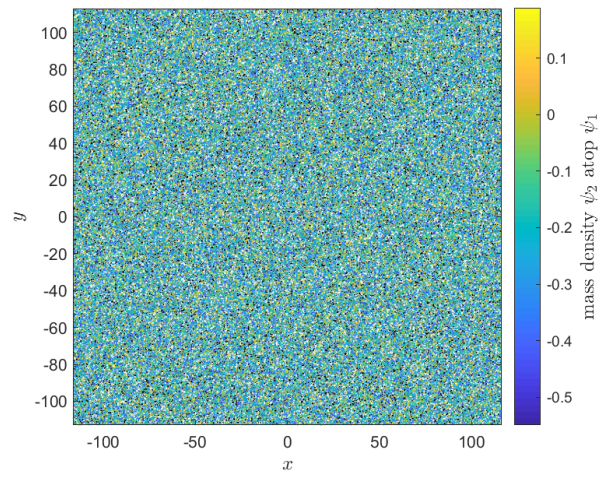
The second simulation begins with a disk seed in each of the lower and upper layers. Both seeds are centered at the origin, and the mass density forms honeycomb geometry in each seed. However, the upper layer seed is significantly larger than the lower seed. This would not occur naturally during the formation of bilayer graphene, but we include this characteristic to demonstrate the sublimation of the upper layer solid when it overlaps a vapor region. Finally, where the two seeds overlap, the geometry is aligned in the manner of Bernal stacking. Figures 6.7a and 6.7b yield the initial lower and upper mass density fields, respectively, while Figure 6.7c displays the initial transparent overlay. We can see that the upper layer disk seed is larger than that of the lower layer. In addition, where solid covers solid, Bernal stacking occurs. Next, Figures 6.8a, 6.8c, and 6.8e detail the lower layer, upper layer, and overlay mass densities, respectively, for time 500. Already, Figure 6.8c indicates that the upper layer nanocrystal is smaller than the corresponding initial seed in Figure 6.7b. However, Figure 6.8e shows that the upper solid region still overlaps vapor. At last, the system reaches an equilibrium state near time 56,000. Figures 6.8b, 6.8d, and 6.8f provide the corresponding mass density fields. Figures 6.8c and 6.8d indicate that the upper nanocrystal is even smaller than it was at time 500. Now, as the upper nanocrystal sublimates into vapor, the lower layer absorbs the extra mass density to equalize the lower and upper vapor mass densities. At the same time, the vapor becomes supersaturated. Hence, as we can see by comparing Figures



(a) Lower Layer

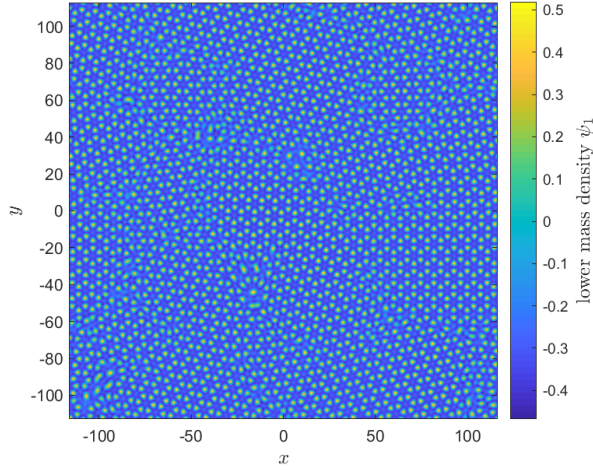


(b) Upper Layer

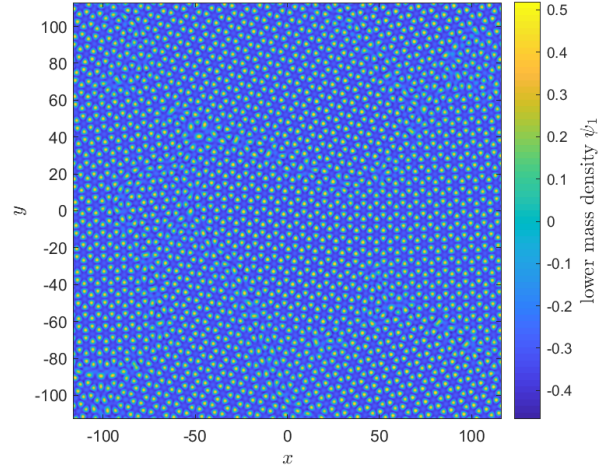


(c) Transparent Overlay

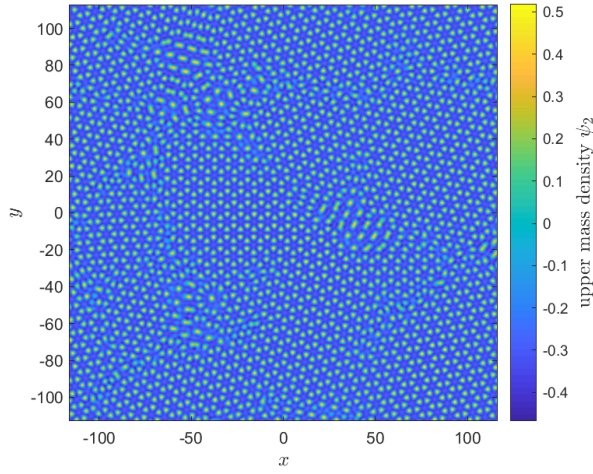
Figure 6.5: Dual MMPFC, Random Initial, Mass Density Fields, Time = 0



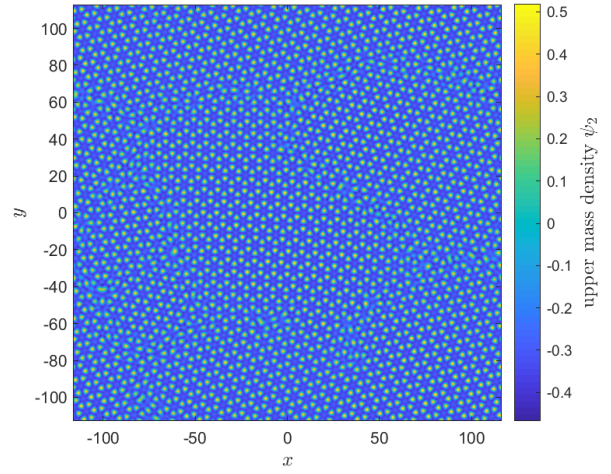
(a) Lower Layer, Time = 2,000



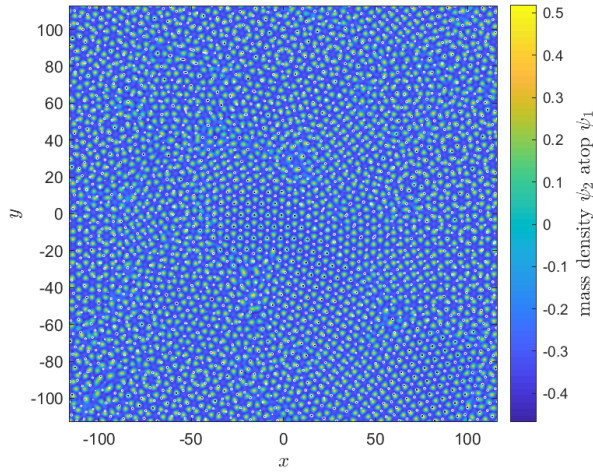
(b) Lower Layer, Time = 34,000



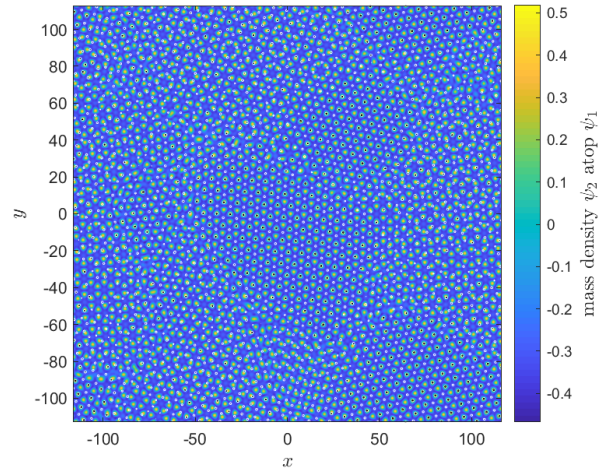
(c) Upper Layer, Time = 2,000



(d) Upper Layer, Time = 34,000



(e) Transparent Overlay, Time = 2,000



(f) Transparent Overlay, Time = 34,000

Figure 6.6: Dual MMPFC, Random Initial, Mass Density Fields, Time = 2,000; 34,000

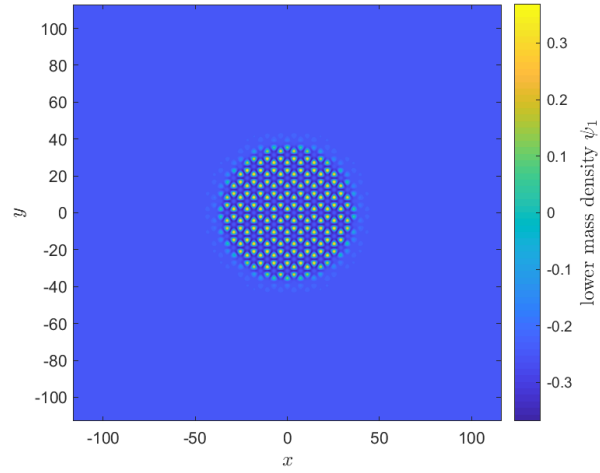
6.8a and 6.8b, the nanocrystal in the lower layer becomes larger over time. Importantly, the transparent overlay of Figure 6.8f reveals that the lower and upper nanocrystals are approximately the same size and shape. Finally, note that, in Figures 6.8e and 6.8f, the Bernal alignment prevails.

6.4.3 Random Disk Seeds

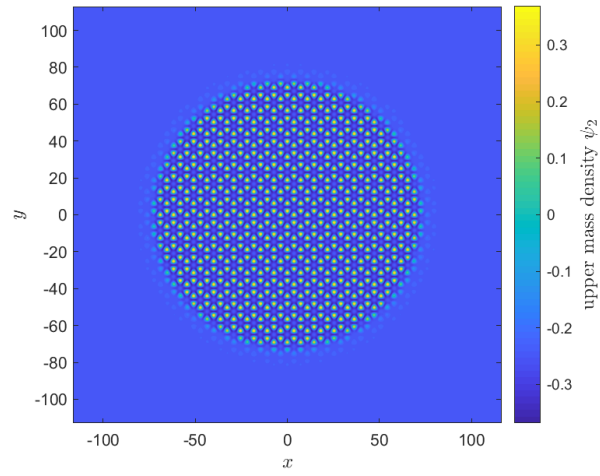
For this final simulation, as in the aligned disk seed simulation of Subsection 6.4.2, we start with a disk seed in each layer. Again, the seeds are centered at the origin. However, each initial seed possesses uniformly random mass density values, and the lower seed is larger than the upper seed. This simulation has two purposes. First, we show that solid beneath vapor is stable, and, second, we demonstrate that Bernal stacking can occur in the presence of vapor. Now, Figures 6.9a and 6.9b detail the initial lower and upper mass density fields, respectively, and Figure 6.9c provides the initial transparent overlay. Note in Figure 6.9c that the lower layer nanocrystal is larger than that of the upper layer. Figures 6.10a, 6.10c, and 6.10e display the lower layer, upper layer, and overlay mass densities, respectively, for time 1,000. Figures 6.10a and 6.10c reveal honeycomb geometry with irregularities in the solid regions of both layers. In addition, Figure 6.10e indicates a region of Bernal stacking centered near $(-20, -30)$. Figures 6.10b, 6.10d, and 6.10f provide the mass density fields and overlay for the time of 500,000. Now, Figure 6.10b reveals that the honeycomb geometry of the lower layer nanocrystal is more regular. However, Figure 6.10d shows that the honeycomb geometry of the upper solid region now has no grain boundaries. Finally, Figure 6.10f indicates that the region of Bernal stacking around $(-20, -30)$ is slightly larger than that of time 1,000 in Figure 6.10e.

6.5 Dual-Layer Multimode PFC Summary

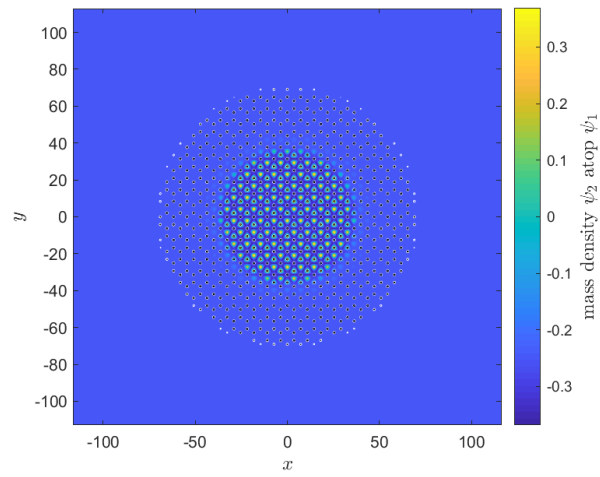
The simulations of Section 6.4 prove that the multimode PFC model can be used to produce the Bernal stacking of bilayer graphene. However, this new dual-layer multimode PFC model is complex. The multimode PFC model yields slight rises at the centroids of each of the hexagons in the solid regions. Choosing the correct γ parameter values to align mass density



(a) Lower Layer

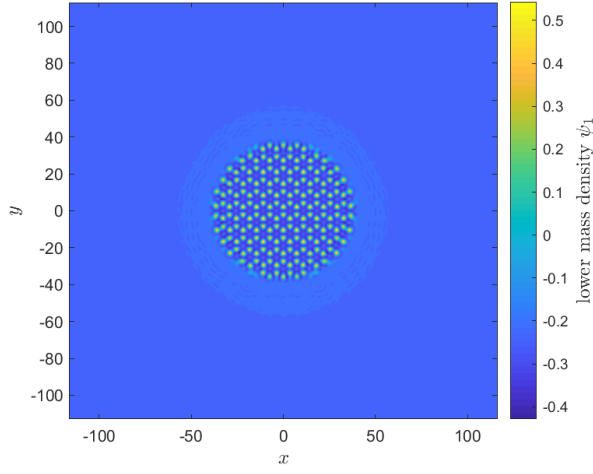


(b) Upper Layer

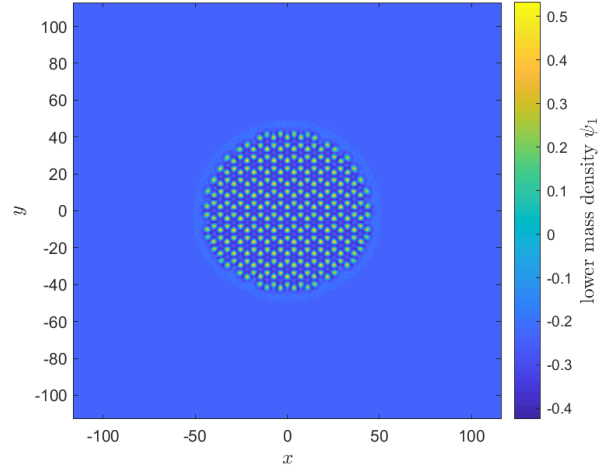


(c) Transparent Overlay

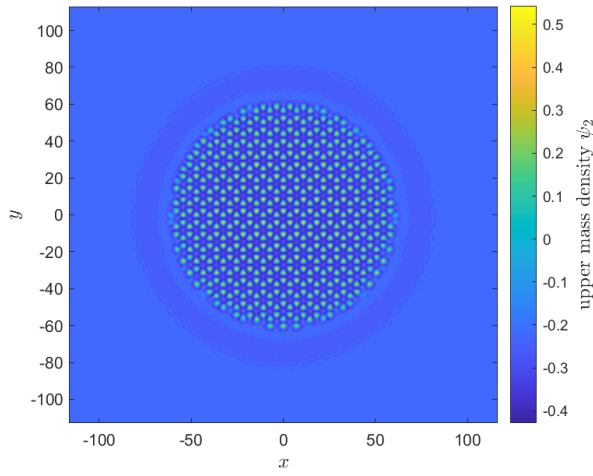
Figure 6.7: Dual MMPFC, Aligned Seeds, Mass Density Fields, Time = 0



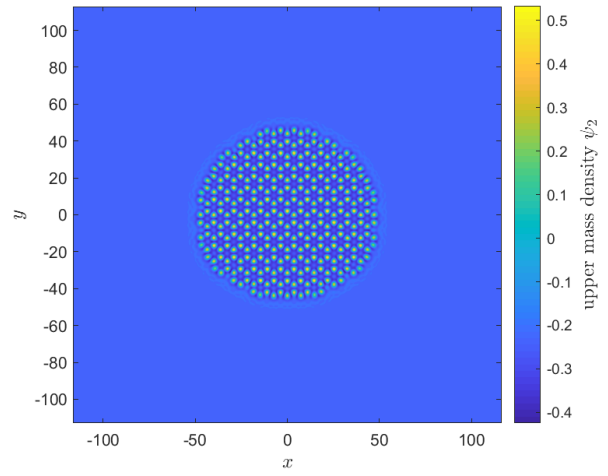
(a) Lower Layer, Time = 500



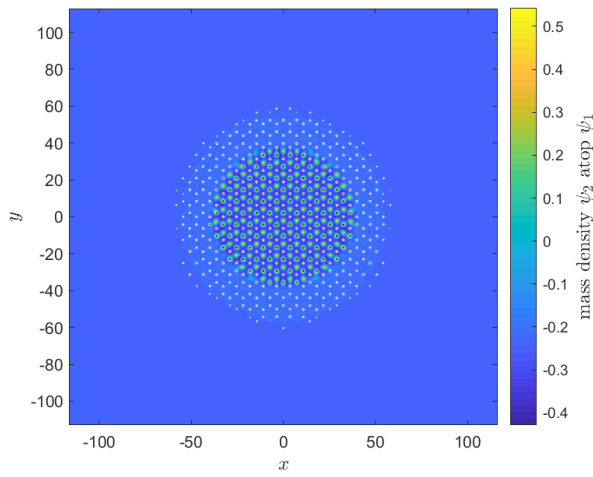
(b) Lower Layer, Time = 56,000



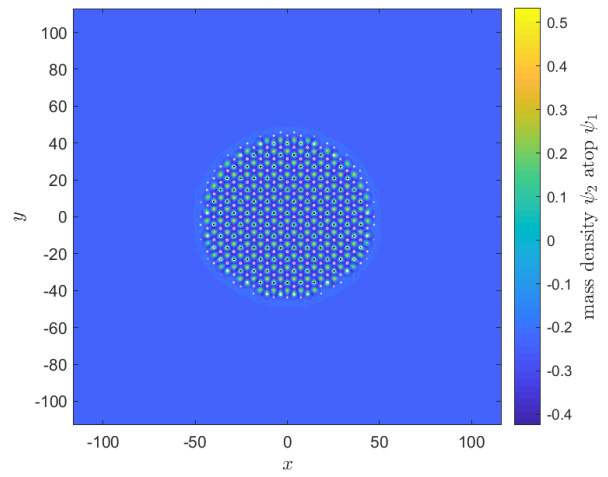
(c) Upper Layer, Time = 500



(d) Upper Layer, Time = 56,000

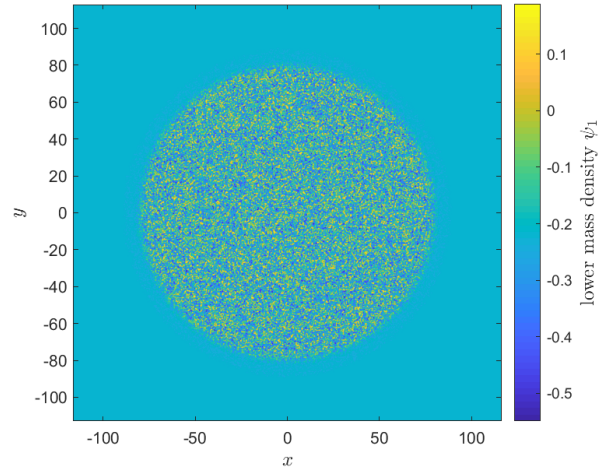


(e) Transparent Overlay, Time = 500

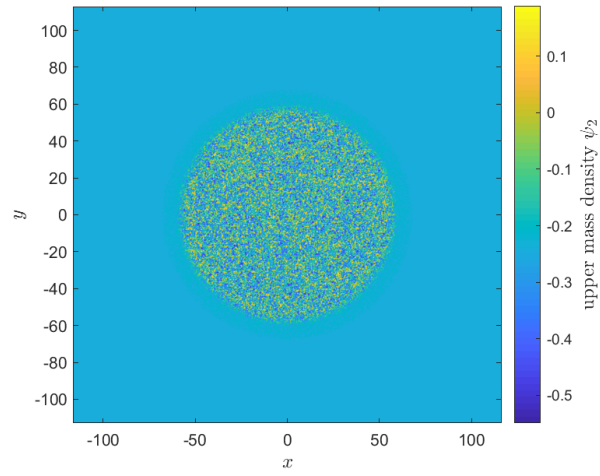


(f) Transparent Overlay, Time = 56,000

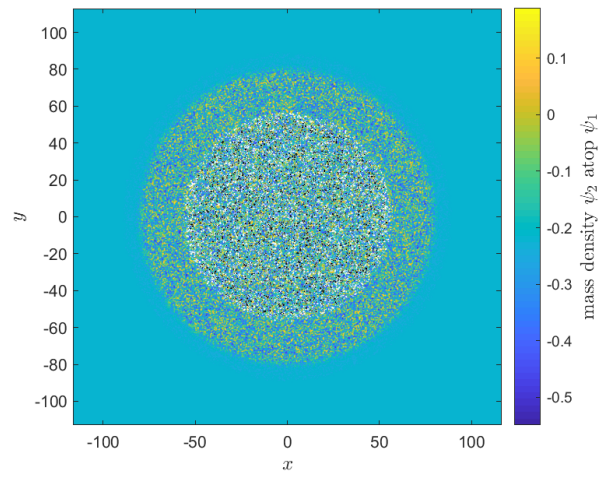
Figure 6.8: Dual MMPFC, Aligned Seeds, Mass Density Fields, Time = 500; 56,000



(a) Lower Layer

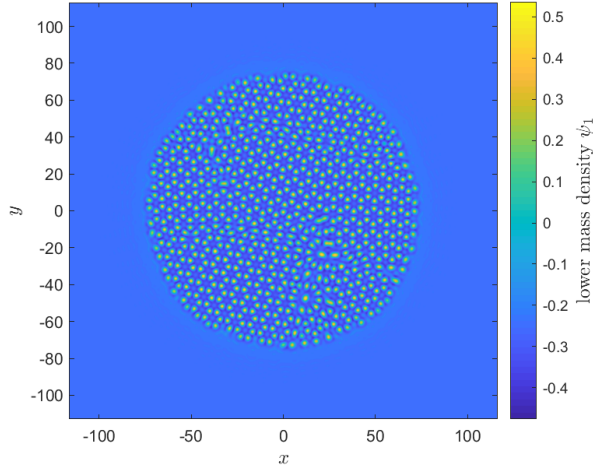


(b) Upper Layer

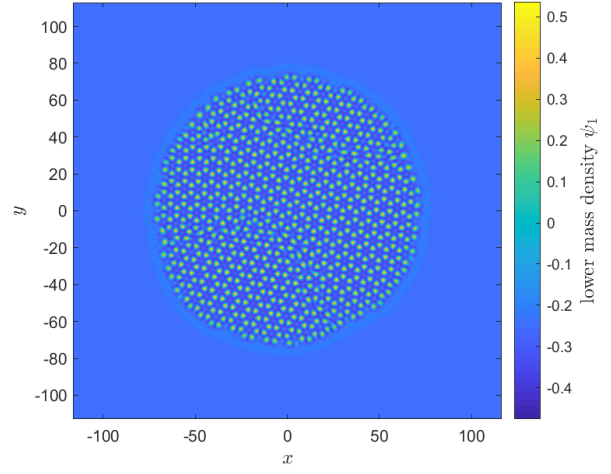


(c) Transparent Overlay

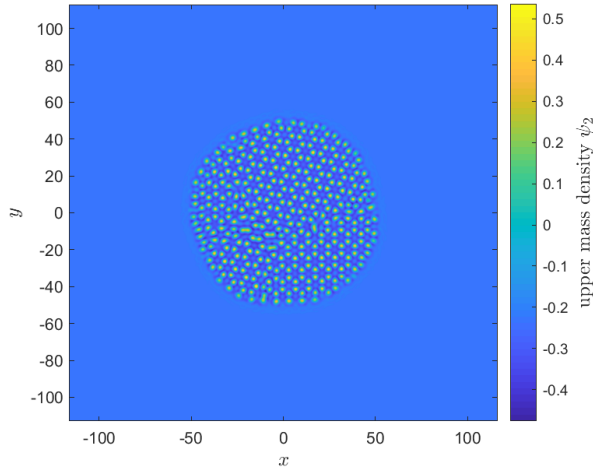
Figure 6.9: Dual MMPFC, Random Seeds, Mass Density Fields, Time = 0



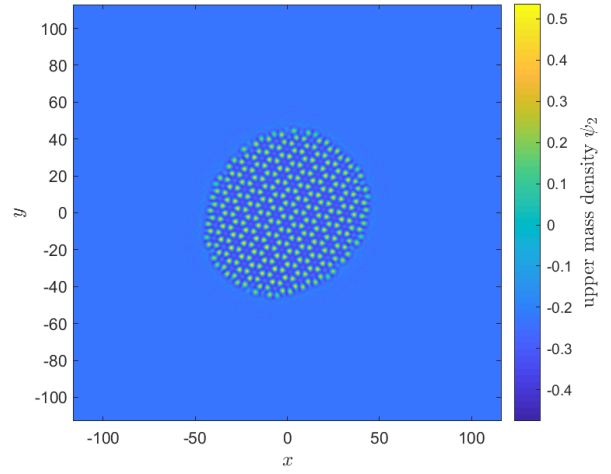
(a) Lower Layer, Time = 1,000



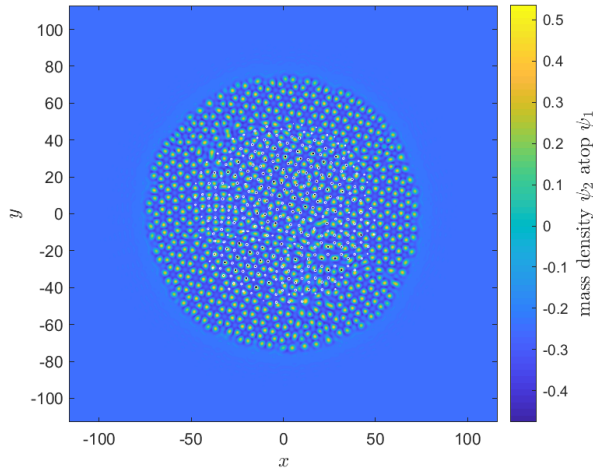
(b) Lower Layer, Time = 500,000



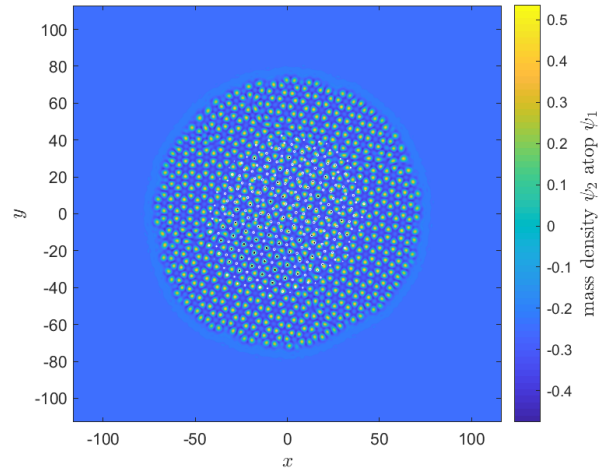
(c) Upper Layer, Time = 1,000



(d) Upper Layer, Time = 500,000



(e) Transparent Overlay, Time = 1,000



(f) Transparent Overlay, Time = 500,000

Figure 6.10: Dual MMPFC, Random Seeds, Mass Density Fields, Time = 1,000; 500,000

peaks with these centers is time-consuming. The need to decrease the initial mass densities for stability precludes simulations that yield nanocrystal growth. This growth is a major goal of graphene modeling. Regardless, this chapter provides a promising starting point for future work.

Chapter 7

Conclusions

In Chapter 2, we established the origins of the phase field crystal (PFC) model. We started with classical density functional theory (CDFT). Applying two approximations and replacing the pair correlation function and convolution with a linear differential operator, we arrived at the single-mode phase field crystal (PFC) model, which has triangular crystal geometry. To produce the multimode PFC model, which has graphene honeycomb geometry, we added two additional modes, or dominant angular frequencies, via the linear differential operator. Finally, we added a vapor phase field to complete the multimode PFC model with vapor that we used throughout this study. Additionally, we analyzed the phase field equilibrium diagram for the vapor field model and the radial distribution function for the multimode PFC model honeycomb geometry. We concluded the chapter with a simulation for the growth of graphene on a copper substrate with chemical vapor deposition (CVD). Simulations were also provided for each of the PFC, multimode PFC, and multimode PFC with vapor models. In many of our simulations, we began with uniformly random mass density fields to demonstrate the “natural” emergence of the desired crystal geometry. In summary, Chapter 2 focused primarily on the development of the multimode PFC model with vapor and the construction of crystal geometry through the manipulation of the frequency multipliers in Fourier, or k -, space.

Chapter 3 provided an alternative method for establishing the honeycomb geometry of the multimode PFC model. The linear differential operator was replaced by a pair correlation function and convolution similar to that of the CDFT. We built the Fourier transform of the

correlation function by combining Gaussian function pairs in Fourier space. In the region of the dominant angular frequencies 1, $\sqrt{3}$, and 2, the resulting Fourier transform is very similar in shape to that of the Fourier multiplier for the standard multimode PFC linear operator.

Chapter 4 examined closely the surface energy of the multimode PFC model with vapor. Through simulations, we found that the main contributor to the surface energy is the phase interface free energy:

$$\mathcal{F}_{int}(t; \eta) := \int_{\Omega} \left[W_v h(\eta) + \frac{\kappa_v}{2} |\nabla \eta|^2 \right] d\mathbf{x}. \quad (7.1)$$

In addition, the systems often reach minimum free energy equilibria where the vapor and solid regions do not attain their respective phase equilibrium mass densities. Furthermore, the phase interfaces do not always find widths that minimize the phase interface energy. The corresponding additional free energy is also part of the surface energy.

Using band seed simulations with different initial seed widths, we discovered that the surface energy is periodic with respect to the initial width. The period is related to the unit cell width for the facet. Surface energy jump discontinuities occur where new layers of atoms form. We also observed that the zigzag facet one-bond stage results in the lowest surface energy, and, thus, this one-bond stage is the most prevalent facet in disk and sinusoidal seed simulations. The armchair facet is the next most abundant. Finally, the zigzag two-bond stage occurs in relatively few simulations. Typically, the armchair and zigzag facets alternate along a given phase interface. Our disk simulations indicated that:

- larger values for W_v yield greater surface energies, narrower phase interfaces, less nanocrystal growth, and more polygonal nanocrystals (lesser isotropic energy).
- larger values of κ_v produce greater surface energies, wider phase interfaces, greater nanocrystal growth (typically), and rounder nanocrystals (greater isotropic energy).

In Chapter 5, we investigated the binary PFC model. This model incorporates two mass density fields, each with triangular geometry. Field coupling free energy terms cause the fields to align such that their superposition yields honeycomb geometry. We also added a vapor phase field to this model and noted that the nanocrystal shapes are similar to those of the multimode PFC model.

At the end of our study, Chapter 6 introduced a dual-layer multimode PFC model to simulate bilayer graphene. We implemented the common Bernal stacking via energy coupling terms, and we included vapor phase fields. We employed vapor mass density equalization. Similar to the binary PFC model, simulations demonstrated field alignment. However, this model requires additional work, as nanocrystal growth is unstable.

Through this study, we have achieved the following in the advancement of the “state-of-the-art” for the phase field crystal (PFC) model and the simulation of graphene formation:

1. We detailed a Fourier, or k -, space approach for analyzing and designing linear differential operators and pair correlation functions for PFC models. In Fourier space, the corresponding Fourier multipliers and transforms have local minima at the dominant angular frequencies, which determine the crystal geometry
2. We developed a new, higher order linear differential operator for the multimode PFC model. We also detailed a method for solving a system of linear equations to control the shape of the corresponding Fourier multiplier. Through this new operator and method, we achieved
 - (a) stable disk seed growth with a vapor phase
 - (b) graphene growth on copper substrate simulations
 - (c) a dual-layer multimode PFC model with vapor
3. We formulated a radial distribution function for the PFC model.
4. We introduced a method for building a pair correlation function for honeycomb geometry to replace the linear differential operator of the “standard” multimode PFC model. This method involves the combination of three Gaussian function pairs in Fourier space and the determination of the corresponding Gaussian parameters. One benefit of the Gaussian correlation function is the numerical stability that results from a “naturally” bounded Fourier transform (or multiplier).
5. Our surface energy study introduced new simulations and observations that may aid in future surface energy work for the PFC model:

- (a) We discovered that many systems arrive at metastable equilibrium states, which result in excess surface energy.
 - (b) We reported the effects of changes in phase interface free energy parameter values on crystal growth, isotropic energy, and facet prevalence.
6. We added a vapor phase field to the existing binary PFC model.
 7. We developed a new dual-layer multimode PFC model to simulate bilayer graphene.

Finally, future work might include:

- three-point correlation functions
- implementation of the vapor phase within the homogeneous free energy design
- dendritic growth with the added vapor phase field
- variable temperature fields
- surface energy calculations for nanocrystals with curved phase interfaces
- a height function to model graphene delamination from the copper substrate
- fine-tuning of the dual-layer multimode PFC model to establish nanocrystal growth and more prevalent Bernal stacking
- substrate coupling with the dual-layer multimode PFC model

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Appendices

A Laplacian in Two Dimensions

We define the *Laplace operator*, or *Laplacian*, in two dimensions. Let $u : \mathbb{R}^2 \rightarrow \mathbb{R}$ be differentiable as needed. Then, the Laplacian of u is defined by

$$\Delta u := \nabla^2 u = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}. \quad (\text{A.1})$$

Then, the second Laplacian of u , or biharmonic operator, is given by

$$\Delta^2 u = \Delta(\Delta u) = \frac{\partial^2}{\partial x^2} \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) + \frac{\partial^2}{\partial y^2} \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) = \frac{\partial^4 u}{\partial x^4} + 2 \frac{\partial^4 u}{\partial x^2 \partial y^2} + \frac{\partial^4 u}{\partial y^4}. \quad (\text{A.2})$$

We can continue to find additional iterations of the Laplace operator in the same way. For example, the third Laplacian is

$$\Delta^3 u = \frac{\partial^6 u}{\partial x^6} + 3 \frac{\partial^6 u}{\partial x^4 \partial y^2} + 3 \frac{\partial^6 u}{\partial x^2 \partial y^4} + \frac{\partial^6 u}{\partial y^6}. \quad (\text{A.3})$$

For the Laplacian with degree $n \geq 0$, we have

$$\Delta^n u = \sum_{i=0}^n \binom{n}{i} \frac{\partial^{2n} u}{\partial x^{2(n-i)} \partial y^{2i}}. \quad (\text{A.4})$$

Note that Δ^0 is the identity operator.

B Periodicity of Partial Derivatives

We first prove that the spatial partial derivatives of a periodic, two-dimensional function share the periodicity of the function itself.

Lemma B.1. *Spatial Derivatives of Periodic Functions Lemma*

Let $a, b > 0$. Let $u : \mathbb{R}^2 \rightarrow \mathbb{R}$ such that, for all $(x_0, y_0) \in \mathbb{R}^2$ and all $m, n \in \mathbb{Z}$,

$$u(x_0 + ma, y_0 + nb) = u(x_0, y_0). \quad (\text{B.1})$$

In addition, suppose that $\frac{\partial u}{\partial x}$ and $\frac{\partial u}{\partial y}$ exist for all $(x_0, y_0) \in \mathbb{R}^2$.

Result:

Then, for all $(x_0, y_0) \in \mathbb{R}^2$ and all $m, n \in \mathbb{Z}$,

$$\begin{aligned} \frac{\partial u}{\partial x}(x_0 + ma, y_0 + nb) &= \frac{\partial u}{\partial x}(x_0, y_0), \\ \text{and} \\ \frac{\partial u}{\partial y}(x_0 + ma, y_0 + nb) &= \frac{\partial u}{\partial y}(x_0, y_0). \end{aligned} \quad (\text{B.2})$$

Proof:

Let $(x_0, y_0) \in \mathbb{R}^2$, and let $m, n \in \mathbb{Z}$. By definition,

$$\frac{\partial u}{\partial x}(x_0 + ma, y_0 + nb) = \lim_{h \rightarrow 0} \frac{u(x_0 + ma + h, y_0 + nb) - u(x_0 + ma, y_0 + nb)}{h}. \quad (\text{B.3})$$

By the periodicity of u ,

$$\frac{\partial u}{\partial x}(x_0 + ma, y_0 + nb) = \lim_{h \rightarrow 0} \frac{u(x_0 + h, y_0) - u(x_0, y_0)}{h} = \frac{\partial u}{\partial x}(x_0, y_0). \quad (\text{B.4})$$

By the same logic,

$$\frac{\partial u}{\partial y}(x_0 + ma, y_0 + nb) = \lim_{h \rightarrow 0} \frac{u(x_0 + ma, y_0 + nb + h) - u(x_0 + ma, y_0 + nb)}{h}, \quad (\text{B.5})$$

and

$$\frac{\partial u}{\partial y}(x_0 + ma, y_0 + nb) = \lim_{h \rightarrow 0} \frac{u(x_0, y_0 + h) - u(x_0, y_0)}{h} = \frac{\partial u}{\partial y}(x_0, y_0). \quad (\text{B.6})$$

Therefore, $\frac{\partial u}{\partial x}$ and $\frac{\partial u}{\partial y}$ share the periodicity of u . Through induction, we find that multiple partial derivatives (where they exist) also share the periodicity of u . ■

Next, we consider the partial derivative with respect to time.

Lemma B.2. *Time Derivative of Periodic Functions Lemma*

Let $a, b > 0$. Let $u : \mathbb{R}^+ \times \mathbb{R}^2 \rightarrow \mathbb{R}$ such that, for all times $t_0 \in \mathbb{R}^+$, all $(x_0, y_0) \in \mathbb{R}^2$, and all $m, n \in \mathbb{Z}$,

$$u(t_0, x_0 + ma, y_0 + nb) = u(t_0, x_0, y_0). \quad (\text{B.7})$$

In addition, suppose that $\frac{\partial u}{\partial t}$ exists for all $t_0 \in \mathbb{R}^+$ and all $(x_0, y_0) \in \mathbb{R}^2$.

Result:

Then, for all $t_0 \in \mathbb{R}^+$, all $(x_0, y_0) \in \mathbb{R}^2$, and all $m, n \in \mathbb{Z}$,

$$\frac{\partial u}{\partial t}(t_0, x_0 + ma, y_0 + nb) = \frac{\partial u}{\partial t}(t_0, x_0, y_0). \quad (\text{B.8})$$

Proof:

Let $t_0 \in \mathbb{R}^+$, let $(x_0, y_0) \in \mathbb{R}^2$, and let $m, n \in \mathbb{Z}$. By definition,

$$\frac{\partial u}{\partial t}(t_0, x_0 + ma, y_0 + nb) = \lim_{h \rightarrow 0} \frac{u(t_0 + h, x_0 + ma, y_0 + nb) - u(t_0, x_0 + ma, y_0 + nb)}{h}. \quad (\text{B.9})$$

Since u possesses the same spatial periodicity at all times,

$$u(t_0, x_0 + ma, y_0 + nb) = u(t_0, x_0, y_0),$$

and, for all $h \in \mathbb{R} \setminus \{0\}$,

$$u(t_0 + h, x_0 + ma, y_0 + nb) = u(t_0 + h, x_0, y_0).$$

Therefore,

$$\frac{\partial u}{\partial t}(t_0, x_0 + ma, y_0 + nb) = \lim_{h \rightarrow 0} \frac{u(t_0 + h, x_0, y_0) - u(t_0, x_0, y_0)}{h} = \frac{\partial u}{\partial t}(t_0, x_0, y_0). \quad (\text{B.10})$$

By Lemma [B.1](#), the time derivatives of the spatial derivatives of u share the periodicity of u . ■

C Green's Identities for Periodic Functions

We derive versions of Green's first and second identities for periodic conditions. We expand Green's second identity for periodic functions to linear combinations of Laplacians of various degrees. For this investigation, let Ω be a closed, rectangular region of $\mathbb{R}^2$. We say that a scalar function u on $\mathbb{R}^2$ is “ Ω -periodic” if, when we tile $\mathbb{R}^2$ with Ω , u takes on the same values in each rectangle.

Let $u, v : \mathbb{R}^2 \rightarrow \mathbb{R}$ be Ω -periodic and sufficiently smooth. Now, let $\partial\Omega$ be the boundary of Ω , oriented in the positive sense, and let $\mathbf{n}$ be the outward pointing unit normal vector of $\partial\Omega$. We consider *Green's first identity*:

$$\int_{\Omega} (\nabla u \cdot \nabla v + u \Delta v) d\mathbf{x} = \int_{\partial\Omega} (u \nabla v) \cdot \mathbf{n} ds. \quad (\text{C.1})$$

Let $\partial\Omega_1, \partial\Omega_2, \partial\Omega_3$, and $\partial\Omega_4$ be the bottom, right, top, and left boundaries of Ω , respectively. Let $\mathbf{i}$ and $\mathbf{j}$ be the unit vectors in the positive x - and y -directions, respectively. Then, (C.1) becomes

$$\begin{aligned} \int_{\Omega} (\nabla u \cdot \nabla v + u \Delta v) d\mathbf{x} = & - \int_{\partial\Omega_1} (u \nabla v) \cdot \mathbf{j} ds + \int_{\partial\Omega_2} (u \nabla v) \cdot \mathbf{i} ds \\ & + \int_{\partial\Omega_3} (u \nabla v) \cdot \mathbf{j} ds - \int_{\partial\Omega_4} (u \nabla v) \cdot \mathbf{i} ds. \end{aligned} \quad (\text{C.2})$$

Since u and v are Ω -periodic, by Lemma B.1, all derivatives and, thus, gradients of u and of v are Ω -periodic. Since the sums, differences, and products of Ω -periodic functions are Ω -periodic, $u \nabla v$ is also Ω -periodic. Then, the values of $u \nabla v$ along the left boundary, $\partial\Omega_4$, are equal to the corresponding values of $u \nabla v$ along the right boundary, $\partial\Omega_2$. Likewise, the values of $u \nabla v$ along the bottom boundary, $\partial\Omega_1$, are equal to the corresponding values of $u \nabla v$ along the top boundary, $\partial\Omega_3$. Therefore,

$$\int_{\Omega} (\nabla u \cdot \nabla v + u \Delta v) d\mathbf{x} = 0, \quad (\text{C.3})$$

and we have *Green's first identity for periodic functions*:

$$\int_{\Omega} \nabla u \cdot \nabla v \, d\mathbf{x} = - \int_{\Omega} u \Delta v \, d\mathbf{x}. \quad (\text{C.4})$$

Applying the commutativity of the dot product for real vectors to (C.4) yields

$$\int_{\Omega} \nabla u \cdot \nabla v \, d\mathbf{x} = \int_{\Omega} \nabla v \cdot \nabla u \, d\mathbf{x} = - \int_{\Omega} v \Delta u \, d\mathbf{x}. \quad (\text{C.5})$$

Subtracting (C.4) from (C.5) yields,

$$0 = - \int_{\Omega} v \Delta u \, d\mathbf{x} + \int_{\Omega} u \Delta v \, d\mathbf{x}, \quad (\text{C.6})$$

and we have *Green's second identity for periodic functions*:

$$\int_{\Omega} u \Delta v \, d\mathbf{x} = \int_{\Omega} (\Delta u) v \, d\mathbf{x}. \quad (\text{C.7})$$

Using mathematical induction with (C.7), we prove that Green's second identity for periodic functions holds for multiple iterations of the Laplacian. Recall that Δ^0 is the identity operator.

Lemma C.1. *Green's Second Identity for Periodic Functions with Multiple Laplacians*

Result:

For all $n \geq 0$,

$$\int_{\Omega} u \Delta^n v \, d\mathbf{x} = \int_{\Omega} (\Delta^n u) v \, d\mathbf{x} \quad (\text{C.8})$$

for all smooth, Ω -periodic function $u, v : \mathbb{R}^2 \rightarrow \mathbb{R}$.

Proof by mathematical induction:

Basis Step:

For $k = 0$,

$$\int_{\Omega} u \Delta^0 v \, d\mathbf{x} = \int_{\Omega} uv \, d\mathbf{x} = \int_{\Omega} (\Delta^0 u) v \, d\mathbf{x} \quad (\text{C.9})$$

for all smooth, Ω -periodic functions $u, v : \mathbb{R}^2 \rightarrow \mathbb{R}$.

Inductive Step:

Suppose that, for some $k \geq 0$,

$$\int_{\Omega} u \Delta^k v \, d\mathbf{x} = \int_{\Omega} (\Delta^k u) v \, d\mathbf{x} \quad (\text{C.10})$$

for all smooth, Ω -periodic functions $u, v : \mathbb{R}^2 \rightarrow \mathbb{R}$. Now, let $w_1, w_2 : \mathbb{R}^2 \rightarrow \mathbb{R}$ be Ω -periodic and smooth. By Lemma B.1, $\Delta^k w_2$ is Ω -periodic and smooth. Hence, by Green's second identity for periodic functions (C.7):

$$\int_{\Omega} w_1 \Delta^{k+1} w_2 \, d\mathbf{x} = \int_{\Omega} w_1 \Delta (\Delta^k w_2) \, d\mathbf{x} = \int_{\Omega} (\Delta w_1) (\Delta^k w_2) \, d\mathbf{x}. \quad (\text{C.11})$$

By Lemma B.1, Δw_1 is a smooth, Ω -periodic function from $\mathbb{R}^2$ to $\mathbb{R}$. Then, by the inductive supposition, using Δw_1 for u and w_2 for v ,

$$\int_{\Omega} w_1 \Delta^{k+1} w_2 \, d\mathbf{x} = \int_{\Omega} (\Delta^k (\Delta w_1)) w_2 \, d\mathbf{x} = \int_{\Omega} (\Delta^{k+1} w_1) w_2 \, d\mathbf{x}. \quad (\text{C.12})$$

By the principle of mathematical induction,

$$\int_{\Omega} u \Delta^n v \, d\mathbf{x} = \int_{\Omega} (\Delta^n u) v \, d\mathbf{x} \quad (\text{C.13})$$

for all smooth, Ω -periodic function $u, v : \mathbb{R}^2 \rightarrow \mathbb{R}$ and for all $n \geq 0$. ■

We now prove that Green's second identity for periodic functions holds for all linear combinations of Laplacian operators.

Theorem C.2. *Green's Second Identity for Periodic Functions with Linear Differential Operators*

Let $u, v : \mathbb{R}^2 \rightarrow \mathbb{R}$ be Ω -periodic and sufficiently smooth. Let C be a linear combination of Laplacian operators of different, nonnegative integer degrees. Then, there exist $n \geq 0$ and $c_0, c_1, \dots, c_n \in \mathbb{R}$ such that $C = \sum_{i=0}^n c_i \Delta^i$.

Result:

Then,

$$\int_{\Omega} u(Cv) d\mathbf{x} = \int_{\Omega} (Cu)v d\mathbf{x}. \quad (\text{C.14})$$

Proof:

Now,

$$\int_{\Omega} u(Cv) d\mathbf{x} = \int_{\Omega} u \left(\sum_{i=0}^n c_i \Delta^i v \right) d\mathbf{x} = \int_{\Omega} \left(\sum_{i=0}^n c_i u \Delta^i v \right) d\mathbf{x} = \sum_{i=0}^n c_i \int_{\Omega} u \Delta^i v d\mathbf{x}. \quad (\text{C.15})$$

By Lemma C.1,

$$\int_{\Omega} u(Cv) d\mathbf{x} = \sum_{i=0}^n c_i \int_{\Omega} (\Delta^i u) v d\mathbf{x} = \int_{\Omega} \left(\sum_{i=0}^n c_i (\Delta^i u) v \right) d\mathbf{x}. \quad (\text{C.16})$$

Therefore,

$$\int_{\Omega} u(Cv) d\mathbf{x} = \int_{\Omega} \left(\sum_{i=0}^n c_i \Delta^i u \right) v d\mathbf{x} = \int_{\Omega} (Cu)v d\mathbf{x}. \quad (\text{C.17})$$

■

D Fourier Multipliers for Linear Differential Operators

We find a formula for calculating the Fourier space multipliers for linear differential operations consisting of linear combinations of Laplace operators of various degrees. Let $u : \mathbb{R}^2 \rightarrow \mathbb{R}$ be sufficiently smooth and integrable with integrable partial derivatives. Here, we use the partial derivative notation

$$u_x := \frac{\partial u}{\partial x}, u_{xx} := \frac{\partial^2 u}{\partial x^2}, u_y := \frac{\partial u}{\partial y}, \text{ and } u_{yy} := \frac{\partial^2 u}{\partial y^2}. \quad (\text{D.1})$$

First, the spatial angular frequency version of the Fourier transform in two-dimensions is given by

$$\widehat{u}(\omega_x, \omega_y) := \mathcal{F}[u](\omega_x, \omega_y) := \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_x \cdot x - i\omega_y \cdot y} u(x, y) dx dy. \quad (\text{D.2})$$

Hence, the Fourier transform of the partial derivative of u with respect to x is

$$\widehat{u}_x(\omega_x, \omega_y) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_x \cdot x - i\omega_y \cdot y} u_x(x, y) dx dy. \quad (\text{D.3})$$

We use the limit definition of the partial derivative within the integrand:

$$\widehat{u}_x(\omega_x, \omega_y) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_x \cdot x - i\omega_y \cdot y} \lim_{h \rightarrow 0} \frac{u(x+h, y) - u(x, y)}{h} dx dy. \quad (\text{D.4})$$

Pulling the limit outside the integral yields

$$\begin{aligned} & \widehat{u}_x(\omega_x, \omega_y) \\ &= \lim_{h \rightarrow 0} \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_x \cdot x - i\omega_y \cdot y} u(x+h, y) dx dy - \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_x \cdot x - i\omega_y \cdot y} u(x, y) dx dy}{h}. \end{aligned} \quad (\text{D.5})$$

For the left integral, we set $z := x + h$:

$$\begin{aligned} & \widehat{u}_x(\omega_x, \omega_y) \\ &= \lim_{h \rightarrow 0} \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_x \cdot (z-h) - i\omega_y \cdot y} u(z, y) dz dy - \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_x \cdot x - i\omega_y \cdot y} u(x, y) dx dy}{h}. \end{aligned} \quad (\text{D.6})$$

Pulling $e^{i\omega_x \cdot h}$ out of the left integral gives us

$$\begin{aligned} & \widehat{u}_x(\omega_x, \omega_y) \\ &= \lim_{h \rightarrow 0} \frac{e^{i\omega_x \cdot h} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_x \cdot z - i\omega_y \cdot y} u(z, y) dz dy - \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i\omega_x \cdot x - i\omega_y \cdot y} u(x, y) dx dy}{h}. \end{aligned} \quad (\text{D.7})$$

By the definition of the Fourier transform, we have

$$\widehat{u}_x(\omega_x, \omega_y) = \lim_{h \rightarrow 0} \frac{e^{i\omega_x \cdot h} \widehat{u}(\omega_x, \omega_y) - \widehat{u}(\omega_x, \omega_y)}{h} = \left(\lim_{h \rightarrow 0} \frac{e^{i\omega_x \cdot h} - 1}{h} \right) \widehat{u}(\omega_x, \omega_y). \quad (\text{D.8})$$

Finally, the Fourier transform for the partial derivative of u with respect to x is

$$\widehat{u}_x(\omega_x, \omega_y) = i\omega_x \widehat{u}(\omega_x, \omega_y). \quad (\text{D.9})$$

By the same logic, the Fourier transform for the partial derivative of u with respect to y is

$$\widehat{u}_y(\omega_x, \omega_y) = i\omega_y \widehat{u}(\omega_x, \omega_y). \quad (\text{D.10})$$

We now consider second partial derivatives and the Laplacian. For x , we have

$$\widehat{u_{xx}}(\omega_x, \omega_y) = \widehat{\frac{\partial}{\partial x} u_x}(\omega_x, \omega_y) = i\omega_x \widehat{u}_x(\omega_x, \omega_y) = (i\omega_x)(i\omega_x) \widehat{u}(\omega_x, \omega_y), \quad (\text{D.11})$$

and, so,

$$\widehat{u_{xx}}(\omega_x, \omega_y) = -\omega_x^2 \widehat{u}(\omega_x, \omega_y). \quad (\text{D.12})$$

Similarly,

$$\widehat{u_{yy}}(\omega_x, \omega_y) = -\omega_y^2 \widehat{u}(\omega_x, \omega_y). \quad (\text{D.13})$$

Now, by the linearity of the Fourier transform,

$$\widehat{\Delta u}(\omega_x, \omega_y) = \mathcal{F}[u_{xx} + u_{yy}](\omega_x, \omega_y) = \widehat{u_{xx}}(\omega_x, \omega_y) + \widehat{u_{yy}}(\omega_x, \omega_y). \quad (\text{D.14})$$

By (D.12) and (D.13),

$$\widehat{\Delta u}(\omega_x, \omega_y) = -\omega_x^2 \widehat{u}(\omega_x, \omega_y) - \omega_y^2 \widehat{u}(\omega_x, \omega_y) = -(\omega_x^2 + \omega_y^2) \widehat{u}(\omega_x, \omega_y). \quad (\text{D.15})$$

From now on, we treat (ω_x, ω_y) as a vector. We have

$$\boldsymbol{\omega} := (\omega_x, \omega_y), \quad (\text{D.16})$$

and

$$\omega := \sqrt{\omega_x^2 + \omega_y^2}. \quad (\text{D.17})$$

Then, the Fourier transform of the Laplacian of u is

$$\widehat{\Delta u}(\boldsymbol{\omega}) = -\omega^2 \widehat{u}(\boldsymbol{\omega}). \quad (\text{D.18})$$

Next, we use induction to prove a formula for the Fourier transform of any number of iterations of the Laplacian of u . Recall that Δ^0 is the identity operator. We use the vector form for $\boldsymbol{\omega}$.

Lemma D.1. *Fourier Transform of Multiple Laplacians Lemma*

Result:

For all $n \geq 0$,

$$\widehat{\Delta^n u}(\boldsymbol{\omega}) = (-\omega^2)^n \widehat{u}(\boldsymbol{\omega}). \quad (\text{D.19})$$

Proof by mathematical induction:

Basis Step:

For $k = 0$, we have

$$\widehat{\Delta^0 u}(\boldsymbol{\omega}) = \widehat{u}(\boldsymbol{\omega}) = (-\omega^2)^0 \widehat{u}(\boldsymbol{\omega}). \quad (\text{D.20})$$

Inductive Step:

Suppose that, for some $k \geq 0$,

$$\widehat{\Delta^k u}(\boldsymbol{\omega}) = (-\omega^2)^k \widehat{u}(\boldsymbol{\omega}). \quad (\text{D.21})$$

Replacing u with $\Delta^k u$ in (D.18) gives us

$$\widehat{\Delta^{k+1} u}(\boldsymbol{\omega}) = \widehat{\Delta(\Delta^k u)}(\boldsymbol{\omega}) = -\omega^2 \widehat{\Delta^k u}(\boldsymbol{\omega}). \quad (\text{D.22})$$

By the inductive supposition,

$$\widehat{\Delta^{k+1} u}(\boldsymbol{\omega}) = (-\omega^2) (-\omega^2)^k \widehat{u}(\boldsymbol{\omega}) = (-\omega^2)^{k+1} \widehat{u}(\boldsymbol{\omega}). \quad (\text{D.23})$$

By the principle of mathematical induction,

$$\widehat{\Delta^n u}(\boldsymbol{\omega}) = (-\omega^2)^n \widehat{u}(\boldsymbol{\omega}) \quad (\text{D.24})$$

for all $n \geq 0$. ■

Finally, we prove a formula that provides the Fourier space multiplier for any linear differential operator that is the sum of various Laplacian multiples. We define $\widetilde{C}$ to be the Fourier space multiplier. Note that the multiplier $(-\omega^2)$ in (D.19) depends only on the angular frequency radius not the vector itself. Hence, we define $\widetilde{C}$ on the real numbers instead of $\mathbb{R}^2$.

Theorem D.2. *Fourier Space Multiple for Linear Differential Operator Theorem*

Let C be a linear combination of Laplacian operators of different, nonnegative integer degrees.

Then, there exist $n \geq 0$ and $c_0, c_1, \dots, c_n \in \mathbb{R}$ such that $C = \sum_{i=0}^n c_i \Delta^i$.

Result:

Then, the Fourier space multiplier for C is

$$\tilde{C}(\omega) := \sum_{i=0}^n c_i (-\omega^2)^i. \quad (\text{D.25})$$

Proof:

By the linearity of the Fourier transform,

$$\mathcal{F}[Cu](\omega) = \mathcal{F} \left[\sum_{i=0}^n c_i \Delta^i u \right] (\omega) = \sum_{i=0}^n c_i \widehat{\Delta^i u}(\omega). \quad (\text{D.26})$$

By Lemma [D.1](#),

$$\mathcal{F}[Cu](\omega) = \sum_{i=0}^n c_i (-\omega^2)^i \widehat{u}(\omega) = \left(\sum_{i=0}^n c_i (-\omega^2)^i \right) \widehat{u}(\omega). \quad (\text{D.27})$$

Therefore, the Fourier space multiplier for C is

$$\tilde{C}(\omega) = \sum_{i=0}^n c_i (-\omega^2)^i. \quad (\text{D.28})$$

■

E Variational Derivative

We establish a method for determining the variational, or functional, derivative for functionals that have linear differential operators with Laplacians. We work in two dimensions, and we consider cases where the functional is dependent upon one or two fields. Let $u(\mathbf{x})$ and $v(\mathbf{x})$ be scalar fields on $\mathbb{R}^2$. We suppose that both u and v are sufficiently smooth and integrable. Here, $\mathbf{x} := (x, y) \in \mathbb{R}^2$. We use the following notation for partial derivatives with respect to x and y :

$$u_{x^i y^j} := \frac{\partial^k u}{\partial x^i \partial y^j} \quad (\text{E.1})$$

and

$$v_{x^i y^j} := \frac{\partial^k v}{\partial x^i \partial y^j}, \quad (\text{E.2})$$

where $i \geq 0$, $j \geq 0$, and $k = i + j$.

We begin with the single field case. We define the functional as

$$\mathcal{F}(u) := \int f(u, \Delta u, \Delta^2 u, \dots, \Delta^n u) d\mathbf{x}, \quad (\text{E.3})$$

where f is the functional density, or integrand, and n is the largest Laplacian degree. For $n = 1$, the corresponding variational derivative is given by [7]:

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial f}{\partial u} - \frac{\partial}{\partial x} \frac{\partial f}{\partial u_x} - \frac{\partial}{\partial y} \frac{\partial f}{\partial u_y} + \frac{\partial^2}{\partial x^2} \frac{\partial f}{\partial u_{x^2}} + \frac{\partial^2}{\partial x \partial y} \frac{\partial f}{\partial u_{xy}} + \frac{\partial^2}{\partial y^2} \frac{\partial f}{\partial u_{y^2}}. \quad (\text{E.4})$$

Now, Laplace operators consist purely of even partial derivatives. Since f contains only Laplacians, there are strictly even numbers of partial derivatives in f . Hence, each of the terms involving odd numbers of partial derivatives results in zero. Therefore, (E.4) simplifies to

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial f}{\partial u} + \frac{\partial^2}{\partial x^2} \frac{\partial f}{\partial u_{x^2}} + \frac{\partial^2}{\partial y^2} \frac{\partial f}{\partial u_{y^2}}. \quad (\text{E.5})$$

Extending (E.5) for all $n \geq 1$, we have

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial f}{\partial u} + \sum_{k=1}^n \sum_{j=0}^k \frac{\partial^{2k}}{\partial x^{2(k-j)} \partial y^{2j}} \frac{\partial f}{\partial u_{x^{2(k-j)} y^{2j}}}. \quad (\text{E.6})$$

Since the partial derivative is linear, it follows from (E.6) that the computation of the variational derivative is a linear operation on the functional density f . Furthermore, by the linearity of integration, the variational derivative itself is linear.

We now find the variational derivative for functionals with a density containing a single, linear Laplacian term.

Lemma E.1. *Variational Derivative for Laplacian Term Lemma*

Let $m \geq 1$, and let $g(u)$ be a sufficiently smooth and integrable scalar function on $\mathbb{R}^2$. We define the functional to be

$$\mathcal{F}(u) := \int g \Delta^m u \, d\mathbf{x}. \quad (\text{E.7})$$

Hence, the functional density is

$$f := g \Delta^m u. \quad (\text{E.8})$$

Since we wish to expand this lemma to handle functional densities with multiple Laplacian terms, we let $n \geq m$ for use in (E.6).

Result:

Then,

$$\frac{\delta \mathcal{F}}{\delta u} = (\Delta^m u) \frac{\partial g}{\partial u} + \Delta^m g. \quad (\text{E.9})$$

Proof:

Now, (E.6) gives us

$$\begin{aligned} \frac{\delta \mathcal{F}}{\delta u} &= \frac{\partial f}{\partial u} + \sum_{k=1}^n \sum_{j=0}^k \frac{\partial^{2k}}{\partial x^{2(k-j)} \partial y^{2j}} \frac{\partial f}{\partial u_{x^{2(k-j)} y^{2j}}} \\ &= \frac{\partial (g \Delta^m u)}{\partial u} + \sum_{k=1}^n \sum_{j=0}^k \frac{\partial^{2k}}{\partial x^{2(k-j)} \partial y^{2j}} \frac{\partial (g \Delta^m u)}{\partial u_{x^{2(k-j)} y^{2j}}}. \end{aligned} \quad (\text{E.10})$$

Since $\Delta^m u$ is the sum of partial derivatives with respect to x and y , $\Delta^m u$ acts as a constant in the first partial derivative. Hence,

$$\frac{\delta \mathcal{F}}{\delta u} = (\Delta^m u) \frac{\partial g}{\partial u} + \sum_{k=1}^n \sum_{j=0}^k \frac{\partial^{2k}}{\partial x^{2(k-j)} \partial y^{2j}} \frac{\partial (g \Delta^m u)}{\partial u_{x^{2(k-j)} y^{2j}}}. \quad (\text{E.11})$$

Similarly, since g contains no partial derivatives, g behaves as a constant in the summation factor

$$\frac{\partial (g \Delta^m u)}{\partial u_{x^{2(k-j)} y^{2j}}} \quad (\text{E.12})$$

for all $k = 1, 2, \dots, n$ and all $j = 0, 1, \dots, k$. Therefore,

$$\frac{\delta \mathcal{F}}{\delta u} = (\Delta^m u) \frac{\partial g}{\partial u} + \sum_{k=1}^n \sum_{j=0}^k \frac{\partial^{2k}}{\partial x^{2(k-j)} \partial y^{2j}} \left(g \frac{\partial (\Delta^m u)}{\partial u_{x^{2(k-j)} y^{2j}}} \right). \quad (\text{E.13})$$

We recall the formula for the m^{th} Laplacian of u from (A.4) of Appendix A:

$$\Delta^m u = \sum_{i=0}^m \binom{m}{i} \frac{\partial^{2m} u}{\partial x^{2(m-i)} \partial y^{2i}} = \sum_{i=0}^m \binom{m}{i} u_{x^{2(m-i)} y^{2i}}. \quad (\text{E.14})$$

Replacing $\Delta^m u$ in the sums of (E.13) yields

$$\frac{\delta \mathcal{F}}{\delta u} = (\Delta^m u) \frac{\partial g}{\partial u} + \sum_{k=1}^n \sum_{j=0}^k \frac{\partial^{2k}}{\partial x^{2(k-j)} \partial y^{2j}} \left(g \frac{\partial}{\partial u_{x^{2(k-j)} y^{2j}}} \sum_{i=0}^m \binom{m}{i} u_{x^{2(m-i)} y^{2i}} \right). \quad (\text{E.15})$$

By the linearity of the partial derivative,

$$\frac{\delta \mathcal{F}}{\delta u} = (\Delta^m u) \frac{\partial g}{\partial u} + \sum_{i=0}^m \sum_{k=1}^n \sum_{j=0}^k \binom{m}{i} \frac{\partial^{2k}}{\partial x^{2(k-j)} \partial y^{2j}} \left(g \frac{\partial u_{x^{2(m-i)} y^{2i}}}{\partial u_{x^{2(k-j)} y^{2j}}} \right). \quad (\text{E.16})$$

Now, where $k \neq m$, we have

$$\frac{\partial u_{x^{2(m-i)} y^{2i}}}{\partial u_{x^{2(k-j)} y^{2j}}} = 0 \quad (\text{E.17})$$

for all $i = 0, 1, \dots, m$ and all $j = 0, 1, \dots, k$. Then,

$$\frac{\delta \mathcal{F}}{\delta u} = (\Delta^m u) \frac{\partial g}{\partial u} + \sum_{i=0}^m \sum_{j=0}^m \binom{m}{i} \frac{\partial^{2m}}{\partial x^{2(m-j)} \partial y^{2j}} \left(g \frac{\partial u_{x^{2(m-i)} y^{2i}}}{\partial u_{x^{2(m-j)} y^{2j}}} \right). \quad (\text{E.18})$$

Furthermore, where $j \neq i$,

$$\frac{\partial u_{x^{2(m-i)}y^{2i}}}{\partial u_{x^{2(m-j)}y^{2j}}} = 0. \quad (\text{E.19})$$

Therefore,

$$\frac{\delta \mathcal{F}}{\delta u} = (\Delta^m u) \frac{\partial g}{\partial u} + \sum_{i=0}^m \binom{m}{i} \frac{\partial^{2m}}{\partial x^{2(m-i)} \partial y^{2i}} \left(g \frac{\partial u_{x^{2(m-i)}y^{2i}}}{\partial u_{x^{2(m-i)}y^{2i}}} \right). \quad (\text{E.20})$$

Next, for all $i = 0, 1, \dots, m$, we have

$$\frac{\partial u_{x^{2(m-i)}y^{2i}}}{\partial u_{x^{2(m-i)}y^{2i}}} = 1. \quad (\text{E.21})$$

Hence,

$$\frac{\delta \mathcal{F}}{\delta u} = (\Delta^m u) \frac{\partial g}{\partial u} + \sum_{i=0}^m \binom{m}{i} \frac{\partial^{2m} g}{\partial x^{2(m-i)} \partial y^{2i}}. \quad (\text{E.22})$$

Finally, by (A.4) of Appendix A,

$$\frac{\delta \mathcal{F}}{\delta u} = (\Delta^m u) \frac{\partial g}{\partial u} + \Delta^m g. \quad (\text{E.23})$$

■

We now expand Lemma E.1 to handle all functionals that have densities with linear Laplacian terms and no other derivatives of u .

Theorem E.2. *Variational Derivative for Linear Laplacian Terms Theorem*

Let $n \geq 0$. For all $i = 0, 1, \dots, n$, let $g_i(u)$ be a sufficiently smooth and integrable scalar function on $\mathbb{R}^2$. Note that g_i may be the zero function for certain values of $i = 0, 1, \dots, n$.

We define the functional to be

$$\mathcal{F}(u) := \int \left\{ g_0 + \sum_{i=1}^n g_i \Delta^i u \right\} d\mathbf{x}. \quad (\text{E.24})$$

Result:

Then,

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial g_0}{\partial u} + \sum_{i=1}^n \left\{ (\Delta^i u) \frac{\partial g_i}{\partial u} + \Delta^i g_i \right\}. \quad (\text{E.25})$$

Proof:

By the linearity of integration,

$$\mathcal{F}(u) = \int g_0 d\mathbf{x} + \sum_{i=1}^n \int g_i \Delta^i u d\mathbf{x}. \quad (\text{E.26})$$

Define $\mathcal{F}_0 := \int g_0 d\mathbf{x}$, and, for all $i = 1, 2, \dots, n$, define

$$\mathcal{F}_i(u) := \int g_i \Delta^i u d\mathbf{x}. \quad (\text{E.27})$$

Then,

$$\mathcal{F}(u) = \sum_{i=0}^n \mathcal{F}_i(u). \quad (\text{E.28})$$

By the linearity of the variational derivative,

$$\frac{\delta \mathcal{F}}{\delta u} = \sum_{i=0}^n \frac{\delta \mathcal{F}_i}{\delta u}. \quad (\text{E.29})$$

For $i = 0$, g_0 possesses no Laplacians of u , and, so, (E.6) yields

$$\frac{\delta \mathcal{F}_0}{\delta u} = \frac{\partial g_0}{\partial u} + \sum_{k=1}^n \sum_{j=0}^k \frac{\partial^{2k}}{\partial x^{2(k-j)} \partial y^{2j}} \frac{\partial g_0}{\partial u_{x^{2(k-j)} y^{2j}}} = \frac{\partial g_0}{\partial u}. \quad (\text{E.30})$$

By Lemma E.1, for all $i = 1, 2, \dots, n$,

$$\frac{\delta \mathcal{F}_i}{\delta u} = (\Delta^i u) \frac{\partial g_i}{\partial u} + \Delta^i g_i. \quad (\text{E.31})$$

Combining (E.29), (E.30), and (E.31), we have

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial g_0}{\partial u} + \sum_{i=1}^n \left\{ (\Delta^i u) \frac{\partial g_i}{\partial u} + \Delta^i g_i \right\}. \quad (\text{E.32})$$

■

We add a corollary for the common case where the functional density contains a linear operator C consisting of Laplace operators of various degrees.

Corollary E.3. *Variational Derivative for a Linear Differential Operator Corollary*

Let $n \geq 1$. Let $\lambda \in \mathbb{R}$, and, for all $i = 0, 1, \dots, n$, let $c_i \in \mathbb{R}$. We define the linear operator as

$$C := \sum_{i=0}^n c_i \Delta^i, \quad (\text{E.33})$$

where Δ^0 is the identity operator. Next, let $g(u)$ be a sufficiently smooth and integrable scalar function on $\mathbb{R}^2$. We define the functional to be

$$\mathcal{F}(u) := \int \left\{ g + \frac{\lambda}{2} u C u \right\} d\mathbf{x}. \quad (\text{E.34})$$

Result:

Then,

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial g}{\partial u} + \lambda C u. \quad (\text{E.35})$$

Proof:

Now,

$$\mathcal{F}(u) = \int \left\{ g + \frac{\lambda c_0}{2} u^2 + \sum_{i=1}^n \left(\frac{\lambda c_i}{2} u \Delta^i u \right) \right\} d\mathbf{x}. \quad (\text{E.36})$$

Define $g_0 := g + \frac{\lambda c_0}{2} u^2$, and, for all $i = 1, 2, \dots, n$, define

$$g_i := \frac{\lambda c_i}{2} u. \quad (\text{E.37})$$

Next,

$$\frac{\partial g_0}{\partial u} = \frac{\partial g}{\partial u} + \lambda c_0 u, \quad (\text{E.38})$$

and, for all $i = 1, 2, \dots, n$,

$$\frac{\partial g_i}{\partial u} = \frac{\lambda c_i}{2}. \quad (\text{E.39})$$

By Theorem E.2,

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial g}{\partial u} + \lambda c_0 u + \sum_{i=1}^n \left\{ (\Delta^i u) \frac{\lambda c_i}{2} + \Delta^i \left(\frac{\lambda c_i}{2} u \right) \right\}, \quad (\text{E.40})$$

and, so,

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial g}{\partial u} + \lambda c_0 u + \sum_{i=1}^n \left\{ \frac{\lambda c_i}{2} \Delta^i u + \frac{\lambda c_i}{2} \Delta^i u \right\} = \frac{\partial g}{\partial u} + \lambda c_0 u + \sum_{i=1}^n \lambda c_i \Delta^i u. \quad (\text{E.41})$$

Hence,

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial g}{\partial u} + \lambda c_0 \Delta^0 u + \sum_{i=1}^n \lambda c_i \Delta^i u = \frac{\partial g}{\partial u} + \sum_{i=0}^n \lambda c_i \Delta^i u. \quad (\text{E.42})$$

Finally,

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial g}{\partial u} + \lambda \left(\sum_{i=0}^n c_i \Delta^i \right) u = \frac{\partial g}{\partial u} + \lambda C u. \quad (\text{E.43})$$

■

Next, we expand the result of Theorem E.2 for two fields u and v .

Corollary E.4. *Variational Derivatives for Two Fields and Linear Laplacian Factors*
Corollary

Let $m, n \geq 0$. For all $i = 0, 1, \dots, n$, let $g_i(u, v, \Delta v, \dots, \Delta^m v)$ be a sufficiently smooth and integrable scalar function on $\mathbb{R}^2$. Note that g_i may be the zero function for certain values of $i = 0, 1, \dots, n$. We define the functional to be

$$\mathcal{F}(u, v) := \int \left\{ g_0 + \sum_{i=1}^n g_i \Delta^i u \right\} d\mathbf{x}. \quad (\text{E.44})$$

We require that, for all $j = 1, 2, \dots, m$, every occurrence of $\Delta^j v$ within a given functional density term is linear. In addition, we require that each term contains, at most, one Laplace operation on v . Hence, for each $j = 0, 1, \dots, m$, there exists a sufficiently smooth and integrable scalar function $h_j(v, u, \Delta u, \dots, \Delta^n u)$ on $\mathbb{R}^2$ such that

$$\mathcal{F}(u, v) = \int \left\{ h_0 + \sum_{j=1}^m h_j \Delta^j v \right\} d\mathbf{x}. \quad (\text{E.45})$$

Result:

Then,

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial g_0}{\partial u} + \sum_{i=1}^n \left\{ (\Delta^i u) \frac{\partial g_i}{\partial u} + \Delta^i g_i \right\}, \quad (\text{E.46})$$

and

$$\frac{\delta \mathcal{F}}{\delta v} = \frac{\partial h_0}{\partial v} + \sum_{j=1}^m \left\{ (\Delta^j v) \frac{\partial h_j}{\partial v} + \Delta^j h_j \right\}. \quad (\text{E.47})$$

Proof:

Note that all of the partial derivatives of the functional density f in (E.6) are with respect to u and to different even partial derivatives of u . It follows that, when we compute the variational derivative for $\mathcal{F}$ with respect to u , the functions $v, \Delta v, \dots, \Delta^m v$ all behave as constants. Hence, the result of Theorem E.2 holds for the variational derivative of $\mathcal{F}$ with respect to u :

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial g_0}{\partial u} + \sum_{i=1}^n \left\{ (\Delta^i u) \frac{\partial g_i}{\partial u} + \Delta^i g_i \right\}. \quad (\text{E.48})$$

Swapping u and v and swapping the g_i functions with the h_j functions yields the same outcome for the variational derivative of $\mathcal{F}$ with respect to v :

$$\frac{\delta \mathcal{F}}{\delta v} = \frac{\partial h_0}{\partial v} + \sum_{j=1}^m \left\{ (\Delta^j v) \frac{\partial h_j}{\partial v} + \Delta^j h_j \right\}. \quad (\text{E.49})$$

■

We now focus on functionals $\mathcal{F}$ and fields u and v that change over time $t \in \mathbb{R}^+$. In addition, we introduce a rectangular region Ω in $\mathbb{R}^2$. We now require that the field u is Ω -periodic; that is, if we tile $\mathbb{R}^2$ with Ω , u takes on the same values in each rectangle. We require the same spatial periodicity for v . Furthermore, we define the functional on Ω . We find that, under these circumstances, the variational derivative plays an essential role in finding the time derivative of $\mathcal{F}$. Here, we use the dot notation,

$$\dot{u} := \frac{\partial u}{\partial t} \quad (\text{E.50})$$

and

$$\dot{v} := \frac{\partial v}{\partial t}, \quad (\text{E.51})$$

for partial derivatives with respect to time.

Theorem E.5. *Variational Derivative and the Time Derivative Theorem*

Let $u(\mathbf{x})$ be an Ω -periodic scalar field on $\mathbb{R}^2$. Suppose that u is sufficiently smooth in space and time and that u is Ω -periodic throughout time. Let $n \geq 0$. For all $k = 0, 1, \dots, n$, let $g_k(u)$ be a sufficiently smooth and integrable scalar function on $\mathbb{R}^2$. Note that g_k may be the zero function for certain values of $k = 0, 1, \dots, n$. We define the functional density to be

$$f(u, \Delta u, \dots, \Delta^n u) := g_0 + \sum_{k=1}^n g_k \Delta^k u, \quad (\text{E.52})$$

and, so, the functional is

$$\mathcal{F}(t; u) := \int_{\Omega} f(u, \Delta u, \dots, \Delta^n u) d\mathbf{x}. \quad (\text{E.53})$$

Result:

Then,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \frac{\delta \mathcal{F}}{\delta u} \dot{u} d\mathbf{x}. \quad (\text{E.54})$$

Proof:

By Leibniz's rule,

$$\frac{d\mathcal{F}}{dt} = \frac{d}{dt} \int_{\Omega} f d\mathbf{x} = \int_{\Omega} \frac{\partial f}{\partial t} d\mathbf{x}. \quad (\text{E.55})$$

By the chain rule for differentiation, we have

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \frac{\partial f}{\partial u} \dot{u} + \frac{\partial f}{\partial(\Delta u)} \frac{\partial(\Delta u)}{\partial t} + \dots + \frac{\partial f}{\partial(\Delta^n u)} \frac{\partial(\Delta^n u)}{\partial t} \right\} d\mathbf{x}, \quad (\text{E.56})$$

and, so,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \frac{\partial f}{\partial u} \dot{u} + \sum_{i=1}^n \frac{\partial f}{\partial(\Delta^i u)} \frac{\partial(\Delta^i u)}{\partial t} \right\} d\mathbf{x}. \quad (\text{E.57})$$

By the definition of f (E.52), we have

$$\begin{aligned} \frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left[\frac{\partial}{\partial u} \left(g_0 + \sum_{k=1}^n g_k \Delta^k u \right) \right] \dot{u} \right. \\ \left. + \sum_{i=1}^n \left[\frac{\partial}{\partial(\Delta^i u)} \left(g_0 + \sum_{k=1}^n g_k \Delta^k u \right) \right] \frac{\partial(\Delta^i u)}{\partial t} \right\} d\mathbf{x}. \end{aligned} \quad (\text{E.58})$$

By the linearity of the partial derivative,

$$\begin{aligned} \frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n \frac{\partial (g_k \Delta^k u)}{\partial u} \right) \dot{u} \right. \\ \left. + \sum_{i=1}^n \left(\frac{\partial g_0}{\partial (\Delta^i u)} + \sum_{k=1}^n \frac{\partial (g_k \Delta^k u)}{\partial (\Delta^i u)} \right) \frac{\partial (\Delta^i u)}{\partial t} \right\} d\mathbf{x}. \end{aligned} \quad (\text{E.59})$$

Now, in the first summation, for all $k = 1, 2, \dots, n$,

$$\frac{\partial (\Delta^k u)}{\partial u} = 0, \quad (\text{E.60})$$

and, so, by the product rule for differentiation,

$$\begin{aligned} \frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n (\Delta^k u) \frac{\partial g_k}{\partial u} \right) \dot{u} \right. \\ \left. + \sum_{i=1}^n \left(\frac{\partial g_0}{\partial (\Delta^i u)} + \sum_{k=1}^n \frac{\partial (g_k \Delta^k u)}{\partial (\Delta^i u)} \right) \frac{\partial (\Delta^i u)}{\partial t} \right\} d\mathbf{x}. \end{aligned} \quad (\text{E.61})$$

Next, in the second summation, for all $i = 1, 2, \dots, n$,

$$\frac{\partial g_0}{\partial (\Delta^i u)} = 0, \quad (\text{E.62})$$

and, so,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n (\Delta^k u) \frac{\partial g_k}{\partial u} \right) \dot{u} + \sum_{i=1}^n \sum_{k=1}^n \frac{\partial (g_k \Delta^k u)}{\partial (\Delta^i u)} \frac{\partial (\Delta^i u)}{\partial t} \right\} d\mathbf{x}. \quad (\text{E.63})$$

Next, in the second and third summations, for all $i = 1, 2, \dots, n$ and all $k = 1, 2, \dots, n$,

$$\frac{\partial g_k}{\partial (\Delta^i u)} = 0, \quad (\text{E.64})$$

and, so, by the product rule,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n (\Delta^k u) \frac{\partial g_k}{\partial u} \right) \dot{u} + \sum_{i=1}^n \sum_{k=1}^n g_k \frac{\partial (\Delta^k u)}{\partial (\Delta^i u)} \frac{\partial (\Delta^i u)}{\partial t} \right\} d\mathbf{x}. \quad (\text{E.65})$$

Now, in the second and third summations, for all $i = 1, 2, \dots, n$ and all $k = 1, 2, \dots, n$, if $i \neq k$, then

$$\frac{\partial (\Delta^k u)}{\partial (\Delta^i u)} = 0. \quad (\text{E.66})$$

Hence,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n (\Delta^k u) \frac{\partial g_k}{\partial u} \right) \dot{u} + \sum_{k=1}^n g_k \frac{\partial (\Delta^k u)}{\partial (\Delta^k u)} \frac{\partial (\Delta^k u)}{\partial t} \right\} d\mathbf{x}. \quad (\text{E.67})$$

Since

$$\frac{\partial (\Delta^k u)}{\partial (\Delta^k u)} = 1 \quad (\text{E.68})$$

for all $k = 1, 2, \dots, n$,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n (\Delta^k u) \frac{\partial g_k}{\partial u} \right) \dot{u} + \sum_{k=1}^n g_k \frac{\partial (\Delta^k u)}{\partial t} \right\} d\mathbf{x}. \quad (\text{E.69})$$

Using the definition for the Laplacian (A.4) from Appendix A, we find that

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n (\Delta^k u) \frac{\partial g_k}{\partial u} \right) \dot{u} + \sum_{k=1}^n g_k \frac{\partial}{\partial t} \sum_{i=0}^k \binom{k}{i} \frac{\partial^{2k} u}{\partial x^{2(k-i)} \partial y^{2i}} \right\} d\mathbf{x}. \quad (\text{E.70})$$

By the linearity of the partial derivative,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n (\Delta^k u) \frac{\partial g_k}{\partial u} \right) \dot{u} + \sum_{k=1}^n g_k \sum_{i=0}^k \binom{k}{i} \frac{\partial}{\partial t} \frac{\partial^{2k} u}{\partial x^{2(k-i)} \partial y^{2i}} \right\} d\mathbf{x}, \quad (\text{E.71})$$

and, so,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n (\Delta^k u) \frac{\partial g_k}{\partial u} \right) \dot{u} + \sum_{k=1}^n g_k \sum_{i=0}^k \binom{k}{i} \frac{\partial^{2k} \dot{u}}{\partial x^{2(k-i)} \partial y^{2i}} \right\} d\mathbf{x}. \quad (\text{E.72})$$

Again, by (A.4),

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n (\Delta^k u) \frac{\partial g_k}{\partial u} \right) \dot{u} + \sum_{k=1}^n g_k \Delta^k \dot{u} \right\} d\mathbf{x}. \quad (\text{E.73})$$

By the linearity of integration, we have

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n (\Delta^k u) \frac{\partial g_k}{\partial u} \right) \dot{u} d\mathbf{x} + \sum_{k=1}^n \int_{\Omega} g_k \Delta^k \dot{u} d\mathbf{x}. \quad (\text{E.74})$$

Since functions dependent solely on periodic functions are themselves periodic, g_k is Ω -periodic for all $k = 1, 2, \dots, n$. In addition, since u is Ω -periodic at all times, by Lemma B.2, $\dot{u}$ is Ω -periodic. By Green's second identity for periodic functions with multiple Laplacians (Lemma C.1),

$$\int_{\Omega} g_k \Delta^k \dot{u} d\mathbf{x} = \int_{\Omega} (\Delta^k g_k) \dot{u} d\mathbf{x} \quad (\text{E.75})$$

for all $k = 1, 2, \dots, n$. Therefore,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n (\Delta^k u) \frac{\partial g_k}{\partial u} \right) \dot{u} d\mathbf{x} + \sum_{k=1}^n \int_{\Omega} (\Delta^k g_k) \dot{u} d\mathbf{x}. \quad (\text{E.76})$$

Again, the linearity of integration yields

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n (\Delta^k u) \frac{\partial g_k}{\partial u} \right) \dot{u} + \sum_{k=1}^n (\Delta^k g_k) \dot{u} \right\} d\mathbf{x}. \quad (\text{E.77})$$

Next,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left(\frac{\partial g_0}{\partial u} + \sum_{k=1}^n \left\{ (\Delta^k u) \frac{\partial g_k}{\partial u} + \Delta^k g_k \right\} \right) \dot{u} d\mathbf{x}. \quad (\text{E.78})$$

From Theorem E.2,

$$\frac{\delta \mathcal{F}}{\delta u} = \frac{\partial g_0}{\partial u} + \sum_{k=1}^n \left\{ (\Delta^k u) \frac{\partial g_k}{\partial u} + \Delta^k g_k \right\}. \quad (\text{E.79})$$

Therefore,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \frac{\delta \mathcal{F}}{\delta u} \dot{u} d\mathbf{x}. \quad (\text{E.80})$$

■

Corollary E.6. *Variational Derivative for Two Fields and the Time Derivative Corollary*

Let $u(\mathbf{x})$ and $v(\mathbf{x})$ be Ω -periodic scalar fields on $\mathbb{R}^2$. Suppose that u and v are sufficiently smooth in space and time and that u and v are Ω -periodic throughout time. Let $m, n \geq 0$. For all $k = 0, 1, \dots, n$, let $g_k(u, v, \Delta v, \dots, \Delta^m v)$ be a sufficiently smooth and integrable scalar function on $\mathbb{R}^2$. Note that g_k may be the zero function for certain values of $k = 0, 1, \dots, n$. We define the functional density to be

$$f(u, \Delta u, \dots, \Delta^n u, v, \Delta v, \dots, \Delta^m v) := g_0 + \sum_{k=1}^n g_k \Delta^k u. \quad (\text{E.81})$$

We require that, for all $j = 1, 2, \dots, m$, every occurrence of $\Delta^j v$ within a given functional density term is linear. In addition, we require that each term contains, at most, one Laplace operation on v . Hence, for each $j = 0, 1, \dots, m$, there exists a sufficiently smooth and integrable scalar function $h_j(v, u, \Delta u, \dots, \Delta^n u)$ on $\mathbb{R}^2$ such that

$$f(u, \Delta u, \dots, \Delta^n u, v, \Delta v, \dots, \Delta^m v) = h_0 + \sum_{j=1}^m h_j \Delta^j v. \quad (\text{E.82})$$

Hence, (E.81) and (E.82) are equivalent forms for f . Finally, we define the functional to be

$$\mathcal{F}(t; u, v) := \int_{\Omega} f(u, \Delta u, \dots, \Delta^n u, v, \Delta v, \dots, \Delta^m v) d\mathbf{x}. \quad (\text{E.83})$$

Result:

Then,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \frac{\delta \mathcal{F}}{\delta u} \dot{u} + \frac{\delta \mathcal{F}}{\delta v} \dot{v} \right\} d\mathbf{x}. \quad (\text{E.84})$$

Proof:

We begin in the fashion of the proof for Theorem E.5. By Leibniz's rule,

$$\frac{d\mathcal{F}}{dt} = \frac{d}{dt} \int_{\Omega} f d\mathbf{x} = \int_{\Omega} \frac{\partial f}{\partial t} d\mathbf{x}. \quad (\text{E.85})$$

By the chain rule for differentiation, we have

$$\begin{aligned} \frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \frac{\partial f}{\partial u} \dot{u} + \frac{\partial f}{\partial(\Delta u)} \frac{\partial(\Delta u)}{\partial t} + \dots + \frac{\partial f}{\partial(\Delta^n u)} \frac{\partial(\Delta^n u)}{\partial t} \right. \\ \left. + \frac{\partial f}{\partial v} \dot{v} + \frac{\partial f}{\partial(\Delta v)} \frac{\partial(\Delta v)}{\partial t} + \dots + \frac{\partial f}{\partial(\Delta^m v)} \frac{\partial(\Delta^m v)}{\partial t} \right\} d\mathbf{x}, \quad (\text{E.86}) \end{aligned}$$

and, so,

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \frac{\partial f}{\partial u} \dot{u} + \sum_{i=1}^n \frac{\partial f}{\partial(\Delta^i u)} \frac{\partial(\Delta^i u)}{\partial t} + \frac{\partial f}{\partial v} \dot{v} + \sum_{i=1}^m \frac{\partial f}{\partial(\Delta^i v)} \frac{\partial(\Delta^i v)}{\partial t} \right\} d\mathbf{x}. \quad (\text{E.87})$$

By the linearity of integration, we have

$$\begin{aligned} \frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \frac{\partial f}{\partial u} \dot{u} + \sum_{i=1}^n \frac{\partial f}{\partial(\Delta^i u)} \frac{\partial(\Delta^i u)}{\partial t} \right\} d\mathbf{x} \\ + \int_{\Omega} \left\{ \frac{\partial f}{\partial v} \dot{v} + \sum_{i=1}^m \frac{\partial f}{\partial(\Delta^i v)} \frac{\partial(\Delta^i v)}{\partial t} \right\} d\mathbf{x}. \quad (\text{E.88}) \end{aligned}$$

By the equivalent formulas for f in (E.81) and (E.82), we have

$$\begin{aligned} \frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \left[\frac{\partial}{\partial u} \left(g_0 + \sum_{k=1}^n g_k \Delta^k u \right) \right] \dot{u} \right. \\ \left. + \sum_{i=1}^n \left[\frac{\partial}{\partial(\Delta^i u)} \left(g_0 + \sum_{k=1}^n g_k \Delta^k u \right) \right] \frac{\partial(\Delta^i u)}{\partial t} \right\} d\mathbf{x} \\ + \int_{\Omega} \left\{ \left[\frac{\partial}{\partial v} \left(h_0 + \sum_{j=1}^m h_j \Delta^j v \right) \right] \dot{v} \right. \\ \left. + \sum_{i=1}^m \left[\frac{\partial}{\partial(\Delta^i v)} \left(h_0 + \sum_{j=1}^m h_j \Delta^j v \right) \right] \frac{\partial(\Delta^i v)}{\partial t} \right\} d\mathbf{x}. \quad (\text{E.89}) \end{aligned}$$

We consider the first integral of (E.89), the “ u ” integral. For all $k = 1, 2, \dots, n$, the partial derivatives of g_k are taken with respect to u and the Laplacians of u . Hence, the v factors and the Laplacian of v factors act like constants in each g_k . Similarly, in the second integral, for all $j = 1, 2, \dots, m$, the partial derivatives of h_j are taken with respect to v and the

Laplacians of v . Then, the u factors and the Laplacian of u factors behave as constants in each h_j . Therefore, each integral in (E.89) matches the form of the integral in (E.58) from the proof for Theorem E.5. For each integral in (E.89), we follow the logic of the proof for Theorem E.5, from (E.58) through to the end (E.80). The result is

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \frac{\delta\mathcal{F}}{\delta u} \dot{u} d\mathbf{x} + \int_{\Omega} \frac{\delta\mathcal{F}}{\delta v} \dot{v} d\mathbf{x}. \quad (\text{E.90})$$

Finally, by the linearity of integration, we have

$$\frac{d\mathcal{F}}{dt} = \int_{\Omega} \left\{ \frac{\delta\mathcal{F}}{\delta u} \dot{u} + \frac{\delta\mathcal{F}}{\delta v} \dot{v} \right\} d\mathbf{x}. \quad (\text{E.91})$$

■

F Periodic Convolution

In this section, we define a two-dimensional periodic convolution operation so that we may compute convolutions over rectangular regions in $\mathbb{R}^2$. We begin by defining a convolution kernel C and a scalar function u , both on $\mathbb{R}^2$. The standard convolution is defined by

$$(C * u)(\mathbf{x}) \triangleq \int_{\mathbb{R}^2} C(\mathbf{x} - \mathbf{y}) u(\mathbf{y}) d\mathbf{y} \quad (\text{F.1})$$

for all $\mathbf{x} \in \mathbb{R}^2$. We next define a rectangular region in $\mathbb{R}^2$

$$\Omega := [x_0, x_0 + a] \times [y_0, y_0 + b], \quad (\text{F.2})$$

where $(x_0, y_0) \in \mathbb{R}^2$ and $a, b \in \mathbb{R}^+$. Note that

$$\{\mathbf{x} - \mathbf{y} : \mathbf{x}, \mathbf{y} \in \Omega\} = [-a, a] \times [-b, b]. \quad (\text{F.3})$$

Additionally, we require that u is Ω -periodic; that is, if we tile $\mathbb{R}^2$ with Ω , u takes on the same values in each rectangle. Next, we define the periodic convolution kernel for Ω and C as

$$C_p(\mathbf{z}) := \sum_{m \in \mathbb{Z}} \sum_{n \in \mathbb{Z}} C(\mathbf{z} - [ma, nb]^T) \quad (\text{F.4})$$

for all $\mathbf{z} \in [-a, a] \times [-b, b]$. Finally, the periodic convolution for Ω , C , and u is defined by

$$(C_p *_\Omega u)(\mathbf{x}) \triangleq \int_{\Omega} C_p(\mathbf{x} - \mathbf{y}) u(\mathbf{y}) d\mathbf{y} = \int_{\Omega} \sum_{m \in \mathbb{Z}} \sum_{n \in \mathbb{Z}} C(\mathbf{x} - \mathbf{y} - [ma, nb]^T) u(\mathbf{y}) d\mathbf{y} \quad (\text{F.5})$$

for all $\mathbf{x} \in \Omega$. Now, we prove that, for cases where C is compactly supported in $\mathbb{R}^2$, the standard convolution and the periodic convolution are equivalent on Ω .

Theorem F.1. *Periodic Convolution Equivalency Theorem*

Let

$$\Omega := [x_0, x_0 + a] \times [y_0, y_0 + b] \quad (\text{F.6})$$

be a rectangular region in $\mathbb{R}^2$, where $(x_0, y_0) \in \mathbb{R}^2$ and $a, b \in \mathbb{R}^+$. Let C be a convolution kernel that is compactly supported in $\mathbb{R}^2$, and define the periodic convolution kernel for Ω and C as

$$C_p(\mathbf{z}) := \sum_{m \in \mathbb{Z}} \sum_{n \in \mathbb{Z}} C(\mathbf{z} - [ma, nb]^T) \quad (\text{F.7})$$

for all $\mathbf{z} \in [-a, a] \times [-b, b]$. Finally, let u be an Ω -periodic scalar function on $\mathbb{R}^2$.

Result:

Then,

$$(C * u)(\mathbf{x}) = (C_p *_{\Omega} u)(\mathbf{x}) \quad (\text{F.8})$$

for all $\mathbf{x} \in \Omega$.

Proof:

Let $\mathbf{x} \in \Omega$. By the definition of the standard convolution (F.1),

$$(C * u)(\mathbf{x}) = \int_{\mathbb{R}^2} C(\mathbf{x} - \mathbf{y}) u(\mathbf{y}) d\mathbf{y}. \quad (\text{F.9})$$

Now, we partition $\mathbb{R}^2$ into a countably infinite set of rectangles and sum the integrals over all of the rectangles. We have

$$(C * u)(\mathbf{x}) = \sum_{m \in \mathbb{Z}} \sum_{n \in \mathbb{Z}} \int_{[x_0 + ma, x_0 + (m+1)a] \times [y_0 + nb, y_0 + (n+1)b]} C(\mathbf{x} - \mathbf{y}) u(\mathbf{y}) d\mathbf{y}. \quad (\text{F.10})$$

Next, within each integral, we set $\mathbf{z} := \mathbf{y} - [ma, nb]^T$. Then, $\mathbf{y} = \mathbf{z} + [ma, nb]^T$, and $d\mathbf{y} = d\mathbf{z}$.

We now have

$$(C * u)(\mathbf{x}) = \sum_{m \in \mathbb{Z}} \sum_{n \in \mathbb{Z}} \int_{[x_0, x_0 + a] \times [y_0, y_0 + b]} C(\mathbf{x} - \mathbf{z} - [ma, nb]^T) u(\mathbf{z} + [ma, nb]^T) d\mathbf{z}, \quad (\text{F.11})$$

or, simply,

$$(C * u)(\mathbf{x}) = \sum_{m \in \mathbb{Z}} \sum_{n \in \mathbb{Z}} \int_{\Omega} C(\mathbf{x} - \mathbf{z} - [ma, nb]^T) u(\mathbf{z} + [ma, nb]^T) d\mathbf{z}. \quad (\text{F.12})$$

By the Ω -periodicity of u , $u(\mathbf{z} + [ma, nb]^T) = u(\mathbf{z})$ for all $\mathbf{z} \in \Omega$, all $m \in \mathbb{Z}$, and all $n \in \mathbb{Z}$. Therefore,

$$(C * u)(\mathbf{x}) = \sum_{m \in \mathbb{Z}} \sum_{n \in \mathbb{Z}} \int_{\Omega} C(\mathbf{x} - \mathbf{z} - [ma, nb]^T) u(\mathbf{z}) d\mathbf{z}. \quad (\text{F.13})$$

Since C is compactly supported on $\mathbb{R}^2$, $C(\mathbf{x} - \mathbf{z} - [ma, nb]^T)$ is nonzero for finitely many pairs m, n . In effect, there are only finitely many integrals in (F.13), and, so, by the linearity of integration,

$$(C * u)(\mathbf{x}) = \int_{\Omega} \sum_{m \in \mathbb{Z}} \sum_{n \in \mathbb{Z}} C(\mathbf{x} - \mathbf{z} - [ma, nb]^T) u(\mathbf{z}) d\mathbf{z}. \quad (\text{F.14})$$

Next, by (F.7), we have

$$(C * u)(\mathbf{x}) = \int_{\Omega} C_p(\mathbf{x} - \mathbf{z}) u(\mathbf{z}) d\mathbf{z}. \quad (\text{F.15})$$

Finally, by the definition of the periodic convolution (F.5),

$$(C * u)(\mathbf{x}) = (C_p *_{\Omega} u)(\mathbf{x}). \quad (\text{F.16})$$

■

Next, we consider the case where the convolution kernel C is compactly supported within $(-\frac{a}{2}, \frac{a}{2}) \times (-\frac{b}{2}, \frac{b}{2})$. This case is important for numerical work, where the grid function matrices for C and u are the same size.

Corollary F.2. *Periodic Convolution Limited Equivalency Corollary*

Let

$$\Omega := [x_0, x_0 + a] \times [y_0, y_0 + b], \quad (\text{F.17})$$

where $(x_0, y_0) \in \mathbb{R}^2$ and $a, b \in \mathbb{R}^+$. Let C be a convolution kernel that is compactly supported within $(-\frac{a}{2}, \frac{a}{2}) \times (-\frac{b}{2}, \frac{b}{2})$. Let u be an Ω -periodic scalar function on $\mathbb{R}^2$.

Result:

Then,

$$\begin{aligned}
(C * u)(\mathbf{x}) = \int_{\Omega} & \left[C(\mathbf{x} - \mathbf{y} + [-a, -b]^T) + C(\mathbf{x} - \mathbf{y} + [-a, 0]^T) + C(\mathbf{x} - \mathbf{y} + [-a, b]^T) \right. \\
& + C(\mathbf{x} - \mathbf{y} + [0, -b]^T) + C(\mathbf{x} - \mathbf{y}) + C(\mathbf{x} - \mathbf{y} + [0, b]^T) \\
& \left. + C(\mathbf{x} - \mathbf{y} + [a, -b]^T) + C(\mathbf{x} - \mathbf{y} + [a, 0]^T) + C(\mathbf{x} - \mathbf{y} + [a, b]^T) \right] u(\mathbf{y}) d\mathbf{y} \quad (\text{F.18})
\end{aligned}$$

for all $\mathbf{x} \in \Omega$.

Proof:

Let $\mathbf{x} \in \Omega$. Since C is compactly supported in $(-\frac{a}{2}, \frac{a}{2}) \times (-\frac{b}{2}, \frac{b}{2})$, C is compactly supported in $\mathbb{R}^2$. Hence, by Theorem F.1,

$$(C * u)(\mathbf{x}) = (C_p *_{\Omega} u)(\mathbf{x}) = \int_{\Omega} \sum_{m \in \mathbb{Z}} \sum_{n \in \mathbb{Z}} C(\mathbf{x} - \mathbf{y} - [ma, nb]^T) u(\mathbf{y}) d\mathbf{y}. \quad (\text{F.19})$$

Next, recall that

$$\{\mathbf{x} - \mathbf{y} : \mathbf{x}, \mathbf{y} \in \Omega\} = [-a, a] \times [-b, b]. \quad (\text{F.20})$$

Then, for all $\mathbf{y} \in \Omega$ and all $n \in \mathbb{Z}$, and for all $m \leq -2$ or $m \geq 2$,

$$\mathbf{x} - \mathbf{y} - [ma, nb]^T \notin \left(-\frac{a}{2}, \frac{a}{2}\right) \times \left(-\frac{b}{2}, \frac{b}{2}\right), \quad (\text{F.21})$$

and, so, $C(\mathbf{x} - \mathbf{y} - [ma, nb]^T) = 0$. Similarly, for all $\mathbf{y} \in \Omega$ and all $m \in \mathbb{Z}$, and for all $n \leq -2$ or $n \geq 2$,

$$\mathbf{x} - \mathbf{y} - [ma, nb]^T \notin \left(-\frac{a}{2}, \frac{a}{2}\right) \times \left(-\frac{b}{2}, \frac{b}{2}\right), \quad (\text{F.22})$$

and, thus, $C(\mathbf{x} - \mathbf{y} - [ma, nb]^T) = 0$. Now, for all $m = -1, 0, 1$ and all $n = -1, 0, 1$, there are values $\mathbf{x}, \mathbf{y} \in \Omega$ such that

$$\mathbf{x} - \mathbf{y} - [ma, nb]^T \in \left(-\frac{a}{2}, \frac{a}{2}\right) \times \left(-\frac{b}{2}, \frac{b}{2}\right), \quad (\text{F.23})$$

and, here, $C(\mathbf{x} - \mathbf{y} - [ma, nb]^T)$ may not be 0. Therefore, the shortest sum for the convolution is

$$(C * u)(\mathbf{x}) = \int_{\Omega} \sum_{m=-1}^1 \sum_{n=-1}^1 C(\mathbf{x} - \mathbf{y} - [ma, nb]^T) u(\mathbf{y}) d\mathbf{y}. \quad (\text{F.24})$$

In expanded form, we have

$$\begin{aligned} (C * u)(\mathbf{x}) = \int_{\Omega} \bigg[& C(\mathbf{x} - \mathbf{y} + [-a, -b]^T) + C(\mathbf{x} - \mathbf{y} + [-a, 0]^T) + C(\mathbf{x} - \mathbf{y} + [-a, b]^T) \\ & + C(\mathbf{x} - \mathbf{y} + [0, -b]^T) + C(\mathbf{x} - \mathbf{y}) + C(\mathbf{x} - \mathbf{y} + [0, b]^T) \\ & + C(\mathbf{x} - \mathbf{y} + [a, -b]^T) + C(\mathbf{x} - \mathbf{y} + [a, 0]^T) + C(\mathbf{x} - \mathbf{y} + [a, b]^T) \bigg] u(\mathbf{y}) d\mathbf{y}. \end{aligned} \quad (\text{F.25})$$

■

Vita

Stephen “Steve” Edward Galloway was born in Galion, OH, to parents Edward “Ed” Lee and Barbara Ann. His father was a guidance counselor and English and history teacher. His mother was a music teacher, and she has directed school and church choirs. She currently directs the choir at her church. Steve has one sister, Christy Lee Barnhart, who also taught music. Presently, she trains vocalists for high school musicals. In 2011, Steve married Lauren Mary Galloway, a medical records specialist. On May 17, 2020, Steve and Lauren welcomed into the world their first child, Graham. Steve is a Christian.

Steve grew up in East Liverpool, OH. He attended East Liverpool High School, where he desired to become a math teacher. In 1992, he graduated from Grove City College, PA, with a Bachelor of Science in Electrical Engineering. Steve was an electrical and, then, software engineer in industry for over 10 years. He was also the sole-proprietor of his own software business, and he worked as a disc jockey.

From 2010 to 2013, Steve worked as a tutor and adjunct instructor of math and computers at Butler County Community College, PA. During that time, Steve earned a Bachelor of Science in Mathematics from Slippery Rock University. During the 2013-2014 school year, Steve taught math and chemistry at Portersville Christian School. In 2014, he began his graduate work in mathematics at the University of Tennessee, Knoxville, where he has served as a graduate teaching assistant and associate. Steve earned a Master of Science in Mathematics from the university in August, 2017. Since January, 2018, under the guidance of Dr. Steven M. Wise, Steve has focused on applied mathematics and studied the phase field crystal model.