Post-Graduate Seminar: Deriving Phase Field Crystals

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Outline

- Derivation of PFC from DFT
- Numerical Approach
- Results
- Preliminary Results
- Another Method
- Further Work

Derivation of PFC from DFT: Statistical Mechanics

Start from statistical mechanics following [1]. $N \in \mathbb{N}$ particles with positions x_i in a d-dimensional box $\Lambda \subset \mathbb{R}^d$.

$$H_{\Lambda^N}^{U_1}(X_N) = \sum_{i=1}^{N} U_1(x_i) + \sum_{1 \leq i < j \leq N} U_2(|x_i - x_j|)$$

where $X_N = (x_1, .., x_N) \in \Lambda^N$ and $U_1 : \mathbb{R}^d \to \mathbb{R}$, $U_2 : \mathbb{R}^d \to \mathbb{R}$.

Let $\Gamma_\Lambda = \Lambda^N$ and equip it with the Borel σ-algebra $\mathcal{B}_\Lambda$ on Γ_Λ. Then the probability measure $\gamma_\Lambda^{\beta,\mu} \in \mathcal{P}(\Gamma_\Lambda, \mathcal{B}_\Lambda)$ with density

$$\hat{\rho}_\beta^{\Lambda^N}(X_N) = \exp\left[-\beta H_{\Lambda^N}^{U_1}(X_N)\right] (N! Z_\Lambda(N, \beta))^{-1}$$

is called the canonical ensemble.

[1] A. González, J.A. White. The extended variable space approach to density functional theory in the canonical ensemble, Journal of Physics: Condensed Matter 14, pages 11907-11919, (2002).

Derivation of PFC from DFT:Free Energy

The normalisation constant $Z_\Lambda(N,\beta)$ is called the partition function.

$$Z_\Lambda(N,\beta) = \frac{1}{N!}\int_{\Lambda^N} \exp\left[-\beta H_{\Lambda^N}^{U_1}(X_N)\right] \mathrm{d}X_N \tag{1}$$

and

$$\beta = \frac{1}{k_B T}.$$

Following page 23 of [2] the (Helmholtz) free energy can be written as

$$\mathcal{F}_\beta^{\Lambda^N}[U_1] = -\beta^{-1}\ln[Z_\Lambda(\beta,N)]. \tag{2}$$

[2] S. Adams. Lectures on Mathematical Statistical Mechanics, Communications of the Dublin Institute for Advanced Studies, Series **A**, No. 30, (2006).

Derivation of PFC from DFT: Density

$$\begin{aligned}\rho^{\Lambda}_{\beta,N}(x) &= \int_{\Lambda^N} \sum_{i=1}^{N} \delta(x - x_i)\hat{\rho}^{\Lambda^N}_{\beta}(X_N)\mathrm{d}X_N \\ &= N \int_{\Lambda} \dots \int_{\Lambda} \hat{\rho}^{\Lambda^N}_{\beta}(X_N)\mathrm{d}x_2 \dots \mathrm{d}x_N \\ &= \frac{\delta \mathcal{F}^{\Lambda^N}_{\beta}[U_1]}{\delta U_1(x)}\end{aligned}$$

where importantly

$$N = \int_{\Lambda} \rho^{\Lambda}_{\beta,N}(x)\mathrm{d}x.$$

Derivation of PFC from DFT: The Kohn-Hohenberg Functional

Theorem

There exists a functional $\mathcal{F}_{HK}$ purely a functional of density, minimised at the equilibrium density (see Section 4 of [a]).

[a] W.S.B. Dwandaru, M. Schmidt. Variational Principle of Classical Density Functional Theory via Levy's Constrained Search Method, Physical Review E, 83, 061133, (2011).

Free energy is minimised at equilibrium at constant temperature (see Section 1.3 of [3]), so at equilibrium

$$\mathcal{F}_{\beta}^{\Lambda^N}[U_1] = \mathcal{F}_{HK}[\rho^{\Lambda}_{\beta,eq,N}] + \int_{\Lambda} U_1(x)\rho^{\Lambda}_{\beta,eq,N}(x)\mathrm{d}x.$$

We can split this functional into two

$$\mathcal{F}_{HK}[\rho^{\Lambda}_{\beta,N}] = \mathcal{F}_{\beta,id}[\rho^{\Lambda}_{\beta,N}] + \mathcal{F}_{\beta,exc}[\rho^{\Lambda}_{\beta,N}].$$

[3] M. Plischke, B. Bergerson. Equilibrium Statistical Physics, 3rd Edition, World Scientific, (2006).

Derivation of PFC from DFT: The Excess Functional

Following Section 2 of [4] assume a constant reference density and perform a formal expansion of the excess free energy around it and curtail at 2nd order

$$\mathcal{F}_{\beta,exc}[\rho_{\beta,\mu}] \approx \mathcal{F}^{(0)}_{\beta,exc}(\rho_{ref}) - \frac{1}{2}\beta^{-1}\int\int c^{(2)}(x_1 - x_2)\Delta\rho_{\beta,\mu}(x_1)\Delta\rho_{\beta,\mu}(x_2)\mathrm{d}x_1\mathrm{d}x_2.$$

$$\Delta\rho_\beta(x) = \rho^{\Lambda}_{\beta,N}(x) - \rho_{ref}.$$

Consideration of translational and rotational symmetry gives $c^{(1)} = 0$

[4] H. Emmerich, H. Löwen, R. Wittkowski, T. Gruhn, G.I. Tóth, G. Tegze, L. Gránásy. Phase-field-crystal models for condensed matter dynamics on atomic length and diffusive time scales; an overview, arXiv:1207.0257,(2012)

Derivation of PFC from DFT: The Ideal Gas

We now consider the ideal gas contribution, i.e. $U_2(x_1, x_2) = 0$. Using the formula (2) for free energy and the partition function (1) we have

$$\mathcal{F}_\beta^{\Lambda^N}[U_1] = \beta^{-1}\left(\ln[N!] - N \ln\left[\underbrace{\int_\Lambda \exp\left[-\beta U_1(x)\right] \mathrm{d}x}_{z(\Lambda)}\right]\right). \quad (3)$$

Using the definition of the one-particle density as the functional derivative of the free energy we can find the density

$$\rho_{\beta,N}^{\Lambda}(x) = \frac{N \exp[-\beta U_1(x)]}{z(\Lambda)}$$

Derivation of PFC from DFT: Density Functional

Using that the integral of $\rho^{\Lambda}_{\beta,N}(x)$ is N we can re-write (3)

$$\mathcal{F}^{\Lambda^N}_{\beta}[U_1] = \beta^{-1}\left(\ln[N!] - N\ln N\right) + \beta^{-1}\int_{\Lambda}\rho^{\Lambda}_{\beta,N}(x)\ln\left[\rho^{(1)}(x)\right]\mathrm{d}x$$
$$+\int_{\Lambda}\rho^{\Lambda}_{\beta,N}(x)U_1(x)\mathrm{d}x.$$

Derivation of PFC from DFT: Stirling's Approximation

We have Stirling's approximation (see [5])

$$\ln[N!] = N \ln N - N + O(\ln N).$$

using this in our functional and discarding the external energy term the ideal gas part of our Hohenberg-Kohn functional is

$$\mathcal{F}_{\beta,id}[\rho_{N_1}] = \beta^{-1} \int_\Lambda \rho_{N_1}(x) \left(\ln\left(\rho_{N_1}(x)\right) - 1\right) \mathrm{d}x. \tag{4}$$

[5] H. Robbins. A remark on stirling's formula, The American Mathematical Monthly, 62:1, pages 26-29, (1955).

Derivation of PFC from DFT: Density Approximation

If we know the reference density is constant and the deviation from the density is small we can re-write the density as

$$\rho_{N_1} = \rho_{ref}(1 + \psi(x)).$$

Inserting this into our ideal gas equation functional and Taylor expanding the logarithm we have

$$\mathcal{F}_{\beta,id}[\rho_{N_1}] = \mathcal{F}_{\beta,id}[\rho_{ref}] + \beta^{-1}\rho_{ref}\int_{\Omega} a_0\psi(x) + \frac{\psi(x)^2}{2} - \frac{\psi(x)^3}{6} + \frac{\psi(x)^4}{12} + O\left(\psi(x)^5\right) \mathrm{d}x$$

where

$$a_0 = \ln\left[\rho_{ref}\right].$$

Derivation of PFC from DFT: Excess Functional Approximation

If we use the same approximation for the density in our expression for the excess energy

$$\mathcal{F}_{\beta,exc}[\rho_{N_1}] = \mathcal{F}_{\beta,exc}[\rho_{ref}] - \frac{\rho_{ref}^2 \beta^{-1}}{2} \int_\Omega \int_\Omega c^{(2)}(x_1, x_2)\psi(x_1)\psi(x_2)\mathrm{d}x_1\mathrm{d}x_2.$$

Using the definition of a convolution and that the Fourier transform of a convolution is the product of the Fourier transforms of the functions in the convolution we have

$$\mathcal{F}_{\beta,exc}[\rho_{N_1}] = \mathcal{F}_{\beta,exc}[\rho_{ref}] - \frac{\rho_{ref}^2 \beta^{-1}}{2} \int_\Omega \mathfrak{F}^{-1}\left[\hat{c}^{(2)}(k)\hat{\psi}(k)\right]\psi(x_1)\mathrm{d}x_1.$$

Derivation of PFC from DFT: Gradient Expansion

Then expand $\hat{c}^{(2)}$ as a Taylor series around $k = 0$ and use that odd terms vanish by symmetry of $\hat{c}^{(2)}$

$$\mathcal{F}_{\beta,exc}[\rho_{N_1}] = \mathcal{F}_{\beta,exc}[\rho_{ref}] - \frac{\rho_{ref}^2 \beta^{-1}}{2} \int_\Omega \mathfrak{F}^{-1} \left[\sum_{m=0}^{\infty} c_{2m} k^{2m} \hat{\psi}(k) \right] \psi(x_1) \mathrm{d}x_1.$$

Using that

$$\mathfrak{F}^{-1} \left[k^{2m} \hat{\psi}(k) \right] = (-1)^m \nabla^{2m} \psi(x)$$

we have

$$\begin{aligned} \mathcal{F}_{\beta,exc}[\rho_{N_1}] = \mathcal{F}_{\beta,exc}[\rho_{ref}] \\ - \frac{\rho_{ref}^2 \beta^{-1}}{2} \int_\Omega \psi(x_1) \sum_{m=0}^{\infty} c_{2m} (-1)^m \nabla^{2m} \psi(x_1) \mathrm{d}x_1. \end{aligned}$$

Derivation of PFC from DFT: Combining the Functionals

We can re-combine our ideal gas functional and our excess energy functional and following [6] we curtail at fourth order in both ψ and the gradient. We know the terms c_i alternate in sign and we discard the linear terms. The functional minus the part evaluated at the reference density is

$$\Delta\mathcal{F}_{HK}[\rho_{N_1}] \approx \beta^{-1}\rho_{ref}\int_{\Omega} A\psi(x)^2 + B\psi(x)\nabla^2\psi(x) + C\psi(x)\nabla^4\psi(x) - \frac{\psi(x)^3}{6} + \frac{\psi(x)^4}{12}\mathrm{d}x. \tag{5}$$

We would like to reformulate our functional difference to be of the form

$$\tilde{\mathcal{F}} = \int \left(\frac{\tilde{\psi}}{2}\left(-\ell + \left(k_0^2 + \nabla^2\right)^2\right)\tilde{\psi} + \frac{\tilde{\psi}^4}{4} \right) \mathrm{d}\tilde{x}. \tag{6}$$

[6] K.R. Elder, N. Provatas, J. Berry, P. Stefanovic, M. Grant. Phase Field Crystal and Classical Density Functional Theory, Physical Review B 75, 064107, (2007)

Derivation of PFC from DFT: Reformulating the Functional

Substitution of $\tilde{\psi} = \alpha(1 - 2\psi(x))$ in (6), neglecting constant contributions and terms linear in ψ and terms that vanish on the boundary shows this is equivalent to (5) divided by $12\rho_{ref}\beta^{-1}C^2$.

Using the transforms ${k_0}^2 x_i = \tilde{x}_i$, and $\tilde{\psi} = {k_0}^2 u$ (6) can be re-written as

$$\tilde{\mathcal{F}}[u] = {k_0}^{8-2d} \int_\Omega \frac{u}{2}\left(\Delta + 1\right)^2 u - \frac{\ell}{2{k_0}^4}u^2 + \frac{1}{4}u^4 \mathrm{d}\tilde{x}.$$

Derivation of PFC from DFT: The PFC functional

The PFC functional

$$\mathcal{F}[u] = \int_\Omega \frac{u}{2}\left(\Delta + 1\right)^2 u - \frac{\delta}{2}u^2 + \frac{1}{4}u^4 \mathrm{d}x \tag{7}$$

where $u : \mathbb{R}^d \to \mathbb{R}$ is a density perturbation.

We minimise the functional whilst conserving the integral of u

$$\bar{u} = \frac{1}{|\Omega|}\int_\Omega u \mathrm{d}x.$$

This functional is minimised by 3 different phases:

- a striped phase,
- a hexagonal phase
- a constant phase

see [7].

[7] Modelling elastic and plastic deformations in non-equilibrium processing using phase field crystals, K.R. Elder, Martin Grant. Physical Review E, 70, 051605, (2004).

Numerical Approaches: Idea

We seek to minimise the PFC functional whilst conserving the integral of u.

Classical gradient flow

$$u^{n+1} = u^n - \nabla \mathcal{F}(u^n)$$

We wish to choose a different metric i.e.

$$u^{n+1} = u^n - M^{-1} \nabla \mathcal{F}(u^n)$$

which is equivalent to

$$\langle M(u^{n+1} - u^n), u^{n+1} - u^n \rangle = -\langle \delta \mathcal{F}(u^n), u^{n+1} - u^n \rangle$$

Numerical Approaches: Definitions

First we define a quadratic functional

$$\Phi(v,u) = \frac{1}{2}\|\Delta v + v\|_{L^2}^2 + \langle \delta\mathcal{F}(u), v\rangle + \frac{\gamma}{2}\|v\|_{L^2}^2.$$

c.f.

$$\mathcal{F}[u] = \int_\Omega \frac{u}{2}\left(\Delta + 1\right)^2 u - \frac{\delta}{2}u^2 + \frac{1}{4}u^4 \mathrm{d}x$$

We also define the inner product

$$\langle M_\gamma v, v\rangle = \|\Delta v + v\|_{L^2}^2 + \gamma\|v\|_{L^2}^2$$

where we have a norm

$$|||v|||^2 = \langle M_1 v, v\rangle.$$

and the dual norm

$$|||\delta\mathcal{F}(u)|||_* = \sup_{|||\varphi|||=1} -\langle \delta\mathcal{F}(u), \varphi\rangle.$$

Numerical Approaches: Lemma 1

We know

$$\exists! v = \operatorname{argmin} \Phi(v, u).$$

Lemma 1

In 2 (or 3) dimensions, for sufficiently large $\gamma(\|u\|_{L^\infty}, |||\delta\mathcal{F}(u)|||_*)$.
If $\|u\|_{L^\infty}, |||\delta F(u)|||_* < \infty$, $\beta > 0$

$$\mathcal{F}(u+v) \leq \mathcal{F}(u) - \beta\langle M_\gamma v, v\rangle$$

.

Numerical Approaches: Numerical Schemes

We now know we can find the minimum of $\mathcal{F}$ by minimising Φ .

$$\Phi(u, v) = \frac{1}{2}\langle M_\gamma v, v\rangle + \langle \delta\mathcal{F}(u), v\rangle.$$

We can show that minimising this functional is equivalent to solving the problem

$$\langle M_\gamma v, v\rangle = -\langle \delta\mathcal{F}(u), v\rangle.$$

This is equivalent to

$$\left(\Delta^2 + 2\Delta + (1+\gamma)\right) v = -(\Delta+1)^2 u + \delta u - u^3. \qquad (8)$$

We now discretise in space to introduce the discrete Laplacian, for which we use the central difference method. Since we are using a domain which is a periodic box we transform into Fourier space and use the Fast Fourier Transform.

Numerical Approach: Fourier transform of the Laplacian

To solve our equation in Fourier space, we need the Fourier transform of the discrete Laplacian.

Using the linearity of the Fourier transform, after some changes of variable we can show

$$\widehat{\Delta_h U_j^n} = F[k]\widehat{U^n}[k]$$

where

$$F[k] = \sum_{i=1}^{d} \frac{2}{h_i^2}\left(\cos\left[\frac{2\pi k_i}{m_i}\right] - 1\right).$$

and we see that in k-space the action of the operator Δ_h becomes multiplication by $F[k]$.

Numerical Methods: Equation in Fourier Space

The Fourier transform of equation (8) after re-arrangement and discretising in space is

$$\hat{V}_j = -\frac{(F+1)^2\hat{U}_j - \delta\hat{U}_j + \widehat{U_j^3}}{(F^2+2F+(1+\gamma))}.$$

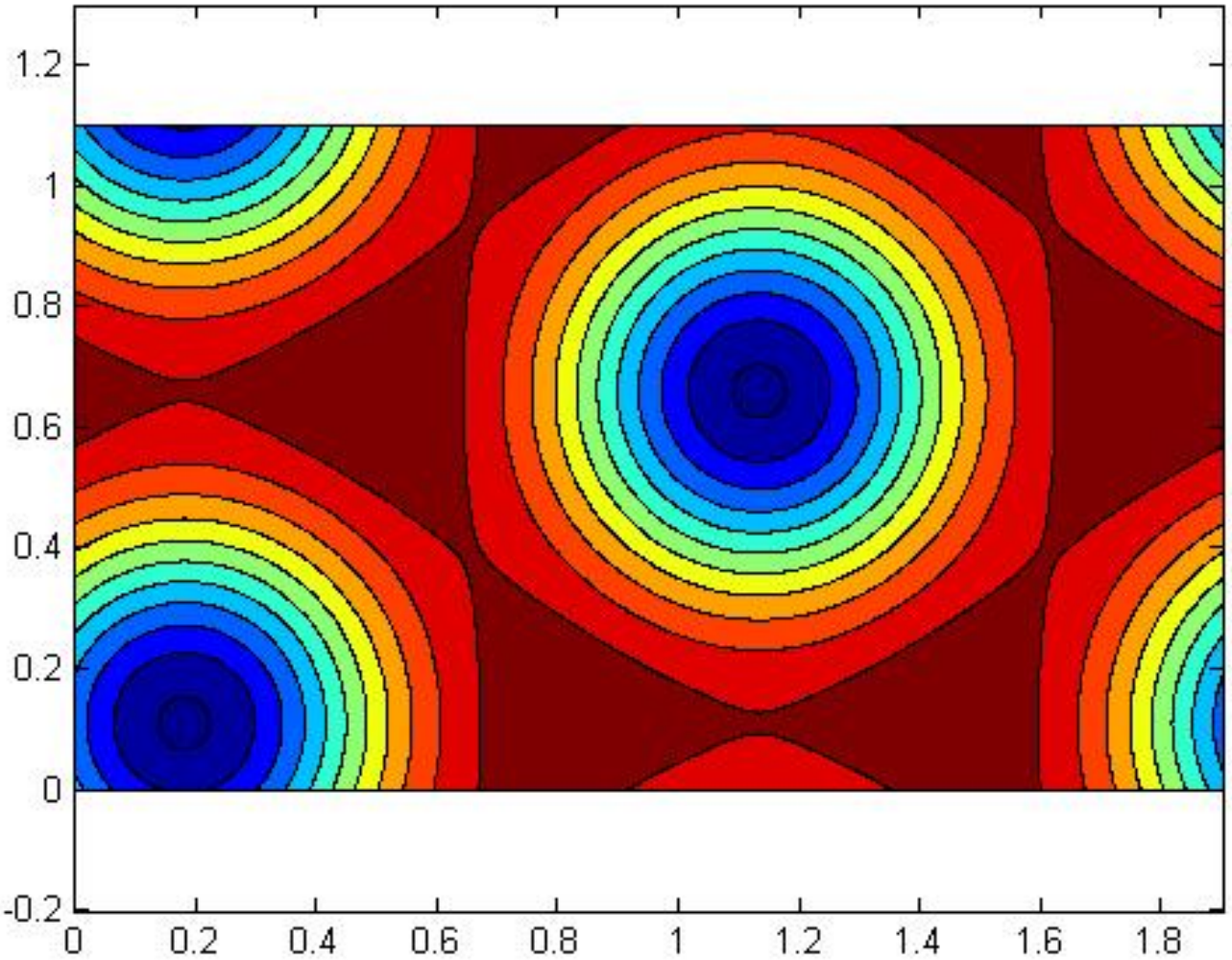
We know $u^{n+1} = u^n + v$. Thus

$$\hat{U}_j^{n+1} = \hat{U}_j^n - \frac{(F+1)^2\hat{U}_j^n - \delta\hat{U}_j^n + \widehat{U_j^n{}^3}}{(F^2+2F+(1+\gamma))}.$$

We enforce conservation of u using

$$\hat{U}_j^{n+1}[0] = \hat{U}_j^n[0]$$

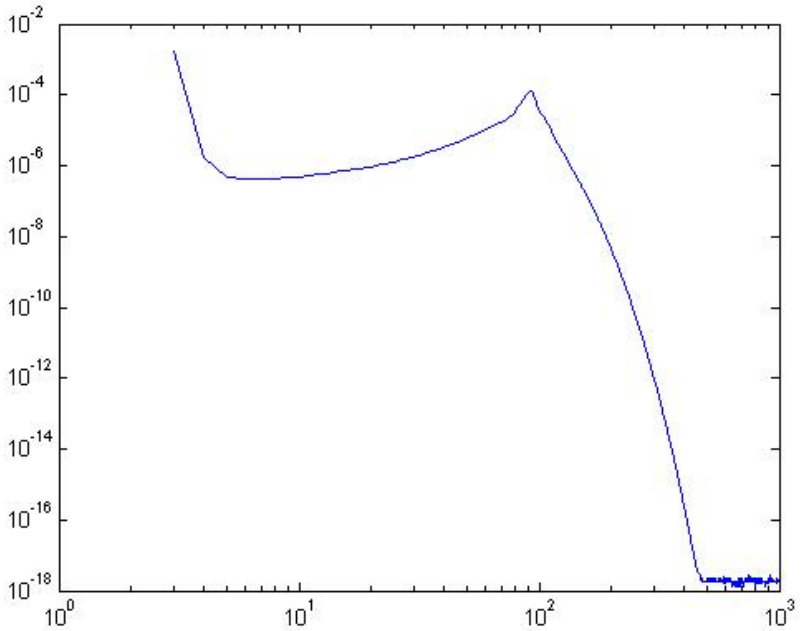
Results: Unit Cell



Results: Errors

We show below the graph of the error against the time step on a log-log scale, where the error is given as

$$e^{n+1} = \frac{\left\| u^{n+1} - u^n \right\|_{L^\infty}}{\left\| u^{n+1} \right\|_{L^\infty}}$$

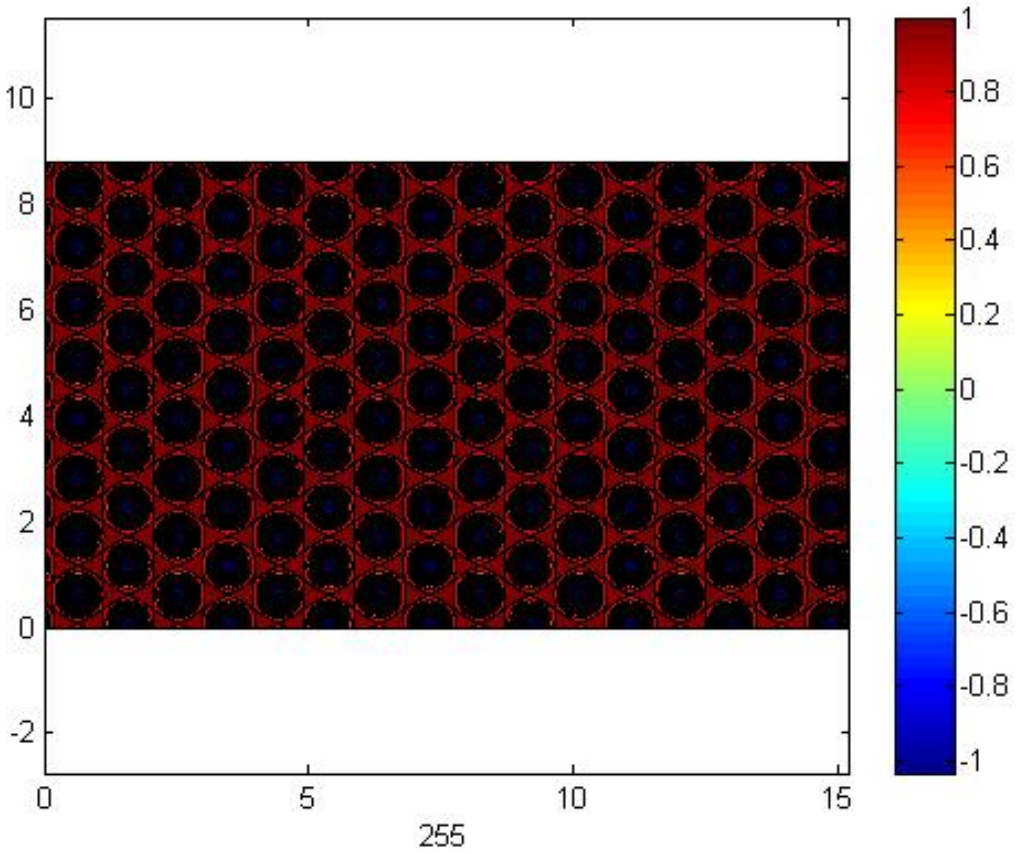


Results: Video

movie

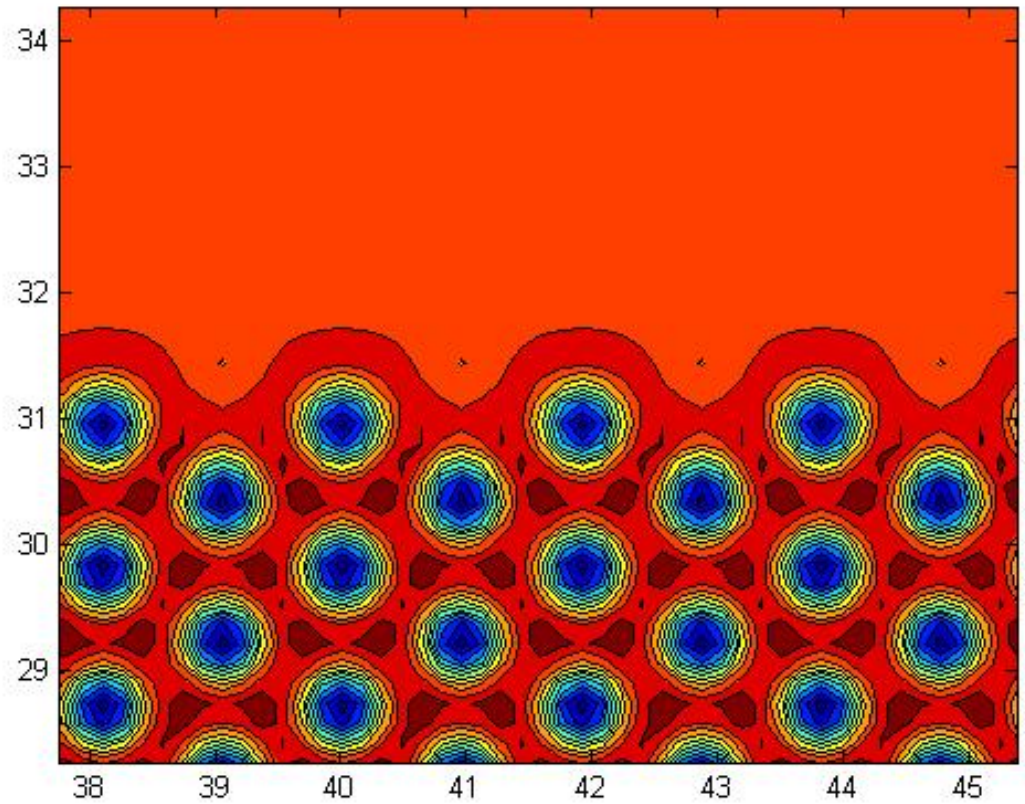
Results: Lattice

We have created a unit cell, now we can create a lattice of arbitrary size by placing unit cells side by side.



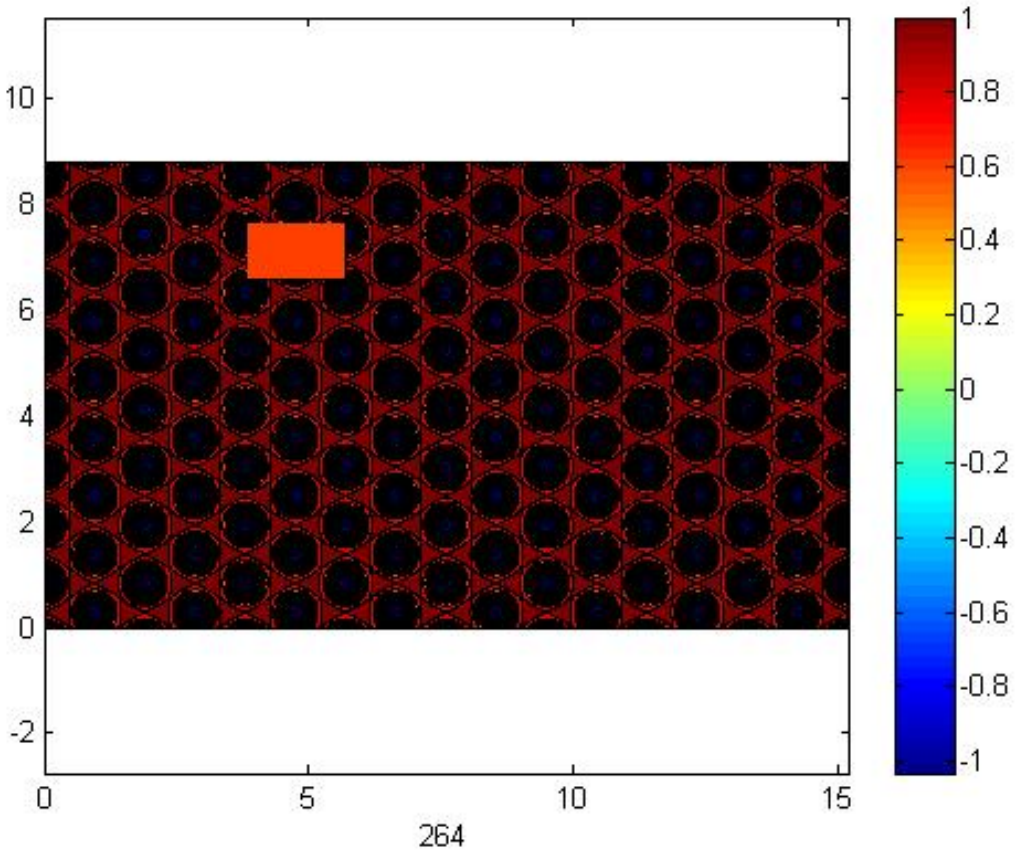
Results: Surfaces

We have a minimising constant phase, this is typically taken to be the liquid phase. We wish to embed the lattice in a liquid. The value to create an interface is $\bar{u} = 0.7$



Preliminary Results: Site Vacancy

We can simulate a site vacancy by creating a lattice and then removing half a unit cell and setting $\bar{u} = 0.7$ in the gap.



Another Method: The PFC Equation

The classical way of minimising our functional (7) whilst enforcing conservation of $\bar{u}$ is to take the H^{-1} gradient flow, i.e.

$$u_t = \Delta \frac{\delta \mathcal{F}}{\delta u}[u].$$

This leads to the equation

$$u_t = \Delta \left((\Delta + 1)^2 u - \delta u + u^3 \right)$$

known as the PFC equation.

Another Method: The Method of Elsey and Wirth

In [8] they add and subtract a stabilising constant to the PFC equation. They then discretise in time and use a convex-concave splitting to give

$$\frac{u^{n+1}-u^n}{\tau} = \Delta\left((\Delta+1)^2 u^{n+1} - \delta u^{n+1} + Cu^{n+1} - Cu^n + (u^n)^3\right).$$

Re-arranging, discretising in space and evaluating in Fourier space gives

$$\widehat{U^{n+1}}[k] = \frac{\hat{U}^n[k] + \tau F\left(\widehat{(U^n)^3}[k] - C\hat{U}^n[k]\right)}{1 - \tau F\left((F+1)^2 - \delta + C\right)}.$$

[8] M. Elsey, B. Wirth. A simple and efficient scheme for phase field crystal simulation, pre-print, (2012).

Further Work

- Coarse Graining PFC
- Grain Boundaries
- Elastic Deformations
- Finding Faster Minimisation Technique

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