Density Functional Theory: Deriving Phase Field Crystals [1]

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[1]Wittkowski et al, arXiv:1207.0257, 2012

Outline

- Model
- Helmholtz Free Energy
- One Particle Density
- Introduction to DFT
- Ideal Gas
- Gradient Expansion
- PFC
- Further Work

Model

Set-up

We have a fixed number of particles N with positions $x_i \in \Lambda \subset \mathbb{R}^d$. For convenience we define

$$X_N = (x_1, \ldots, x_N) \in \Lambda^N$$

and

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

with Hamiltonian

$$H_{\Lambda^N}^{U_1}(X_N) = \underbrace{\sum_{1 \le i < j \le N} U_2(x_i - x_j)}_{\text{inter-particle interaction U}} + \underbrace{\sum_{i=1}^{N} U_1(x_i)}_{\text{external potential}}$$

$U_1 : \mathbb{R}^d \to \mathbb{R}^d$ is the external potential $U_2 : \mathbb{R}^d \times \mathbb{R}^d \to \mathbb{R}$ is the interaction potential between particles.

Canonical Gibbs Ensemble

let $\Gamma_\Lambda = \left(\Lambda \times \mathbb{R}^d\right)^N$ and equip it with the Borel σ-algebra on Γ_Λ. Then the probability measure $\gamma_{\Lambda,N}^\beta \in \mathcal{P}(\Lambda, \mathcal{B}_\Lambda)$ with density

$$\rho_{\Lambda,N}^\beta(X_N) = \frac{\exp[-\beta H_{\Lambda^N}^{U_1}(X_N)]}{N! Z_\Lambda(\beta, N)}$$

is called the canonical Gibbs ensemble.

Here $Z_\Lambda(\beta, N)$ is a normalisation factor known as the **Partition Function**.

$$Z_\Lambda(\beta, N) = \frac{1}{N!} \int_{\Lambda^N} \prod_{i=1}^{N} \exp[-\beta U_1(x_i)] \prod_{1 \leq i < j \leq N} \exp[-\beta U_2(x_i - x_j)] \mathrm{d}X_N.$$

Free Energy

Free energy is minimised at equilibrium if temperature is held constant.

We can also show [2]

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

$$= -\beta^{-1} \ln\left[\frac{1}{N!} \int_{\Lambda^N} \prod_{i=1}^{N} \exp[-\beta U_1(x_i)] \prod_{1 \le i < j \le N} \exp[-\beta U_2(x_i - x_j)] dX_N\right]$$

One-particle Density

One-particle Density

Three ways of doing this
- Integrating out $N - 1$ Variables

$$\rho_{\Lambda^N}^{(1)}(x) = N \int_\Lambda \ldots \int_\Lambda \rho_{\Lambda,N}^\beta(X_N) \mathrm{d}x_2 \ldots \mathrm{d}x_N$$

- Average over δ-functions

$$\rho_{\Lambda^N}^{(1)}(x) = \frac{1}{N! Z_\Lambda(\beta, N)} \int_{\Lambda^N} \sum_{i=0}^{N} \delta(x - x_i) \exp\left[-\beta H_{\Lambda^N}^{U_1}(X_N)\right] \mathrm{d}X_N$$

- Functional Derivative

$$\rho_{\Lambda^N}^{(1)}(x) = \frac{\delta \mathcal{F}_\beta^{\Lambda^N}[U_1]}{\delta U_1(x)}.$$

$$\int_\Lambda \rho_{\Lambda^N}^{(1)}(x) \mathrm{d}x = N$$

Introduction to Density Functional Theory

We want to express free energy as the sum of a functional of one-particle density only and another term.

$U_1(x)$ is a conjugate variable to the one-particle density $\rho^{(1)}_{\Lambda^N}(x)$. Since free energy is a functional of the external potential, we can use a Legendre transform to re-write the free energy.

$$\mathcal{F}^{\Lambda^N}_\beta[U_1] = \inf_{\tilde{\rho}(x)} \left[F_{HK}\left[\tilde{\rho}(x)\right] + \int_\Lambda U_1(x)\tilde{\rho}(x)\mathrm{d}x \right]$$

F_{HK} is known as the Hohnberg-Kohn functional and the infimum is over the space of absolutely continuous probability measure having Lebesgue density.

We can split the Hohnberg-Kohn functional into two parts an ideal gas part and an excess part

$$\mathcal{F}_\beta^{\Lambda^N}[\rho_{\Lambda^N}^{(1)}] = \mathcal{F}_{\beta,id}^{\Lambda^N}[\rho_{\Lambda^N}^{(1)}] + \mathcal{F}_{\beta,exc}^{\Lambda^N}[\rho_{\Lambda^N}^{(1)}]$$

We assume the existence of a reference density ρ_{ref} and expand the excess functional around this

$$F_{HK}[\rho_{\Lambda^N}^{(1)}] = \mathcal{F}_{\beta,exc}^{\Lambda^N}[\rho_{ref}]$$
$$+ \sum_{n=1}^{\infty} \frac{1}{n!} \int_\Lambda \cdots \int_\Lambda \frac{\delta^n \mathcal{F}_{\beta,exc}^{\Lambda^N}[\rho_{\Lambda^N}^{(1)}]}{\delta \rho_\beta^{\Lambda^N}(x_1) \ldots \delta \rho_\beta^{\Lambda^N}(x_n)}\bigg|_{\rho_{ref}} (x_1, \ldots x_n) \prod_{i=1}^{n} \Delta\rho(x_i)\mathrm{d}x_i$$

where

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

Ramakrishnan-Yussoff approximation

If the deviations from the reference density are small

$$\Delta\rho(x) \ll 1$$

we can curtail the Taylor series. We chose to ignore terms higher then $i = 2$ the $i = 1$ term vanishes as our potential is symmetric. Thus we have

$$\mathcal{F}^{\Lambda^N}_{\beta,exc}[\rho^{(1)}_{\Lambda^N}] = \mathcal{F}^{\Lambda^N}_{\beta,exc}[\rho_{ref}] - \beta^{-1} \int_\Lambda \int_\Lambda c^{(2)}(x_1, x_2)\Delta\rho(x_1)\Delta\rho(x_2)\mathrm{d}x_1\mathrm{d}x_2$$

where

$$c^{(2)}(x_1, x_2) = -\beta \frac{\delta^2 \mathcal{F}^{\Lambda^N}_{\beta,exc}[\rho^{(1)}_{\Lambda^N}]}{\delta\rho^{\Lambda^N}_\beta(x_1)\delta\rho^{\Lambda^N}_\beta(x_2)}\bigg|_{\rho_{ref}} (x_1, x_2)$$

[3]

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[3]Physics Review B, 19:5 p2775-2794,1979

Ideal Gas

In this case the internal potential, U_2, is zero

$$Z_\Lambda(\beta, N) = \frac{1}{N!} \left(\underbrace{\int_\Lambda \exp[-\beta V(x)]\mathrm{d}x}_{z(\Lambda)} \right)^N$$

Thus the free energy can be written as

$$\mathcal{F}_\beta^{\Lambda^N}[U_1] = \beta^{-1} \left(\ln[N!] - N \ln[z(\Lambda)] \right).$$

We seek to re-write the free energy in a density functional form.

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

$$\rho_{\Lambda^N}^{(1)}(x) = \frac{N \exp[-\beta U_1(x)]}{z(\Lambda)}.$$

Re-arranging we can find an expression for the external potential

$$U_1(x) = -\beta^{-1} \ln \left[\frac{\rho_{\Lambda^N}^{(1)}(x) z(\Lambda)}{N} \right].$$

We therefore find

$$\int_\Lambda \rho^{(1)}_{\Lambda^N}(x) U_1(x) \mathrm{d}x = -\beta^{-1} \int_\Lambda \rho^{(1)}_{\Lambda^N}(x) \ln\left[\rho^{(1)}_{\Lambda^N}(x)\right] \mathrm{d}x - \beta^{-1} N \ln\left[\frac{z(\Lambda)}{N}\right].$$

We recall a generalisation of Stirling's approximation [4]

$$\sqrt{2\pi N}\left(\frac{N}{e}\right)^N \exp\left[\frac{1}{12N+1}\right] \le N! \le \sqrt{2\pi N}\left(\frac{N}{e}\right)^N \exp\left[\frac{1}{12N}\right].$$

Using this and that $\int_\Lambda \rho^{(1)}_{\Lambda^N}(x)dx = N$ we can re-write the free energy as

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

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[4]Robbins, The American Mathematical Monthly 62:1, pages 26-29,1955

The Small Deviations Regime

The part of the ideal gas functional not associated with the external potential is

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

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

$$\rho_{\beta}^{\Lambda^N}(x) = \rho_{ref}(1 + \psi(x))$$

Inserting this into our ideal gas equation we have

$$\mathcal{F}_{\beta,id}^{\Lambda^N}[\rho_{\Lambda^N}^{(1)}] = \beta^{-1} \int_{\Lambda} \rho_{ref}(1 + \psi(x)) \left(\ln[\rho_{ref}(1 + \psi(x))] - 1 \right) \mathrm{d}x$$

Using the Taylor expansion of the logarithm is

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

where

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

Gradient Expansion

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

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

where we have used that

$$\Delta\rho(x_i) = \rho_{ref} \psi(x)$$

Using the definition of a convolution we have

$$\mathcal{F}_{\beta,exc}^{\Lambda^N}[\rho_{\Lambda^N}^{(1)}] = \mathcal{F}_{\beta,exc}^{\Lambda^N}[\rho_{ref}] - \rho_{ref}^2 \beta^{-1} \int_{\Lambda} \left(c^{(2)} * \psi \right)(x_1) \psi(x_1) \mathrm{d}x_1$$

Fourier Expansion

Using that the fourier transform of a convolution is the product of the fourier transforms of the functions in the convolution

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

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

$$\mathcal{F}_{\beta,exc}^{\Lambda^N}[U_1] = \mathcal{F}_{\beta,exc}^{\Lambda^N}[\rho_{ref}] - \rho_{ref}^2 \beta^{-1} \int_\Lambda \mathfrak{F}^{-1}\left[\sum_{m=0}^{\infty} c_{2m}k^{2m}\hat{\psi}(k)\right] \psi(x_1)\mathrm{d}x_1$$

Using that

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

we have

$$\mathcal{F}_{\beta,exc}^{\Lambda^N}[\rho_{\Lambda^N}^{(1)}] = \mathcal{F}_{\beta,exc}^{\Lambda^N}[\rho_{ref}] - \rho_{ref}^2 \beta^{-1} \int_\Lambda \psi(x_1) \sum_{m=0}^{\infty} c_{2m}\nabla^{2m}\psi(x_1)\mathrm{d}x_1$$

PFC

Approximate Functional

We can re-combine our ideal gas functional and our excess energy functional to give

$$F_{HK}[\rho_{\Lambda^N}^{(1)}] = F_{HK}[\rho_{ref}] - \rho_{ref}^2 \beta^{-1} \int_\Lambda \psi(x_1) \sum_{m=0}^{\infty} c_{2m} \nabla^{2m} \psi(x_1) \mathrm{d}x_1$$

$$+ \beta^{-1} \rho_{ref} \int_\Lambda a_0 \psi(x) + \frac{\psi(x)^2}{2} - \frac{\psi(x)^3}{6} + \frac{\psi(x)^4}{12}$$

$$+ O\left(\psi(x)^5\right) \mathrm{d}x$$

following [5] we curtail at fourth order in both ψ and the gradient. The functional minus the part evaluated at the reference density is

$$\Delta F_{HK}[\rho_{\Lambda^N}^{(1)}] \approx -\rho_{ref}^2 \beta^{-1} \int_\Lambda \psi(x_1) \sum_{m=0}^{2} c_{2m} \nabla^{2m} \psi(x_1) \mathrm{d}x_1$$

$$+ \beta^{-1} \rho_{ref} \int_\Lambda a_0 \psi(x) + \frac{\psi(x)^2}{2} - \frac{\psi(x)^3}{6} + \frac{\psi(x)^4}{12} \mathrm{d}x$$

[5]Stefanovic, Grant and Elder, Physics Review B, 75, 064107, 2007

discarding the linear terms we have

$$\Delta F_{HK}[\rho_{\Lambda^N}^{(1)}] \approx \beta^{-1}\rho_{ref} \int_\Lambda A\frac{\psi(x)^2}{2} + B\psi(x)\nabla^2\psi(x) + C\psi(x)\nabla^4\psi(x)$$
$$- \frac{\psi(x)^3}{6} + \frac{\psi(x)^4}{12}\mathrm{d}x$$

The classical PFC functional is given by an appropriate choice of constants and absorbing the cubic term as
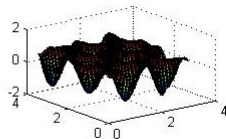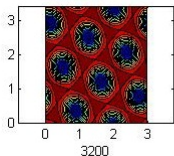
$$\mathcal{F}_{PFC}[\tilde{\psi}] = \int_\Omega \frac{\tilde{\psi}}{2}\left(\nabla^2 + 1\right)^2\tilde{\psi} - \delta\frac{\tilde{\psi}}{2} + \frac{\tilde{\psi}^4}{4}\mathrm{d}\tilde{x}$$

The PFC Equation is given [6] by H^{-1} gradient flow

$$\psi_t = \nabla^2\frac{\delta\mathcal{F}_{PFC}[\tilde{\psi}]}{\delta\tilde{\psi}(x)}$$
$$= \nabla^2\left(\left(\nabla^2 + 1\right)^2\tilde{\psi} - \delta\tilde{\psi} + \tilde{\psi}^3\right)$$

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[6]Wirth and Elsey, Pre-print, 2012

for the choice $\delta = 0.9$ and $\overline{\psi} = 0.5$ on a $6\pi \times 4\sqrt{3}\pi$ domain with periodic boundary conditions we obtain a hexagonal lattice

by altering the value of $\overline{\psi}$ we can obtain a constant density domain ($\overline{\psi} > 0.5$) or a striped pattern ($\overline{\psi} < 0.5$).

Further Work

- My Website
- Defects
- Surface Energy
- Optimisation

I would like to thank Christoph Ortner and Stefan Adams for all their help and advice.