Phase Field Crystal (PFC) model.

The Application of Lagrange Multipliers in PFC

物理數學報告 111022138李偉誠

Outline

- Free Energy
- Lagrange Multiplier
- Density Functional Theory
- Phase Field Crystal

Free Energy

- $F = U - TS$, Helmholtz Free Energy
- $G = H - TS$, Gibbs Free Energy

U： Internal Energy

T： Absolute Temperature

S： Entropy

H：Enthalpy

- The meaning of minimized free energy is thermal equilibrium

(Different free energy with different constraints)

Helmholtz’s： Constant T & Constant V

Gibbs’： Constant T & Constant P

Lagrange Multiplier

- Lagrange Multiplier is a way to find an extreme value

$f(x_1, x_2 \dots x_i \dots)$ is a Multivariable function.

$g(x_1, x_2 \dots x_i \dots) = 0$ is the constraint of the problem we deal with.

Define $f^*(x_1, x_2 \dots \dots x_i \dots \dots, \lambda) = f(x_1, x_2 \dots \dots x_i \dots \dots) + \lambda g(x_1, x_2 \dots \dots x_i \dots \dots)$

And we'll get $\frac{\partial f^*(x_1, x_2 \dots\dots x_i \dots\dots, \lambda)}{\partial x_i} = 0$ & $\frac{\partial f^*(x_1, x_2 \dots\dots x_i \dots\dots, \lambda)}{\partial \lambda} = 0$

Using blackboard to show example & explanation of why Lagrange Multiplier works.

Classical Density Functional Theory

$$F[\rho] = F_{\text{ideal}}[\rho] + F_{\text{int}}[\rho]$$

$$F_{\text{ideal}}[\rho] = k_B T \int d\vec{r}\, \rho(\vec{r}) \ln \rho(\vec{r}) \Lambda^3 - \rho(\vec{r})$$

Functional Taylor expansion around ρ_0

$\delta\rho(\vec{r}_i)$

$$F_{\text{int}}[\rho] = F_{\text{int}}(\rho_0) + \sum_{n=1}^{\infty} \frac{1}{n!} \prod_{i=1}^{n} \int d\vec{r}_i \boxed{(\rho(\vec{r}_i) - \rho_0)} \left. \frac{\delta^n F_{\text{int}}[\rho]}{\delta\rho(\vec{r}_1) \cdots \delta\rho(\vec{r}_n)} \right|_{\rho_0}$$

$$= F_{\text{int}}(\rho_0) - k_B T \sum_{n=1}^{\infty} \frac{1}{n!} \prod_{i=1}^{n} \int d\vec{r}_i\, \delta\rho(\vec{r}_i)\, c^{(n)}(\vec{r}_1, \cdots, \vec{r}_n)$$

$$\frac{\Delta F[\rho]}{k_B T} = \int d\vec{r}\, \rho(\vec{r}) \ln \frac{\rho(\vec{r})}{\rho_0} - \delta\rho(\vec{r}) - \frac{1}{2} \iint d\vec{r}_1\, d\vec{r}_2 \delta\rho(\vec{r}_1)\, \delta\rho(\vec{r}_2) c^{(2)}(|\vec{r}_1 - \vec{r}_2|)$$

Classical Density Functional Theory

- Constraint：

$$\int dr\rho(r) = N$$

- Define a new functional：

$$\Omega[\rho] = F[\rho] - \mu\left(\int dr\rho(r) - N\right)$$

- Variational method

Phase Field Crystal Model

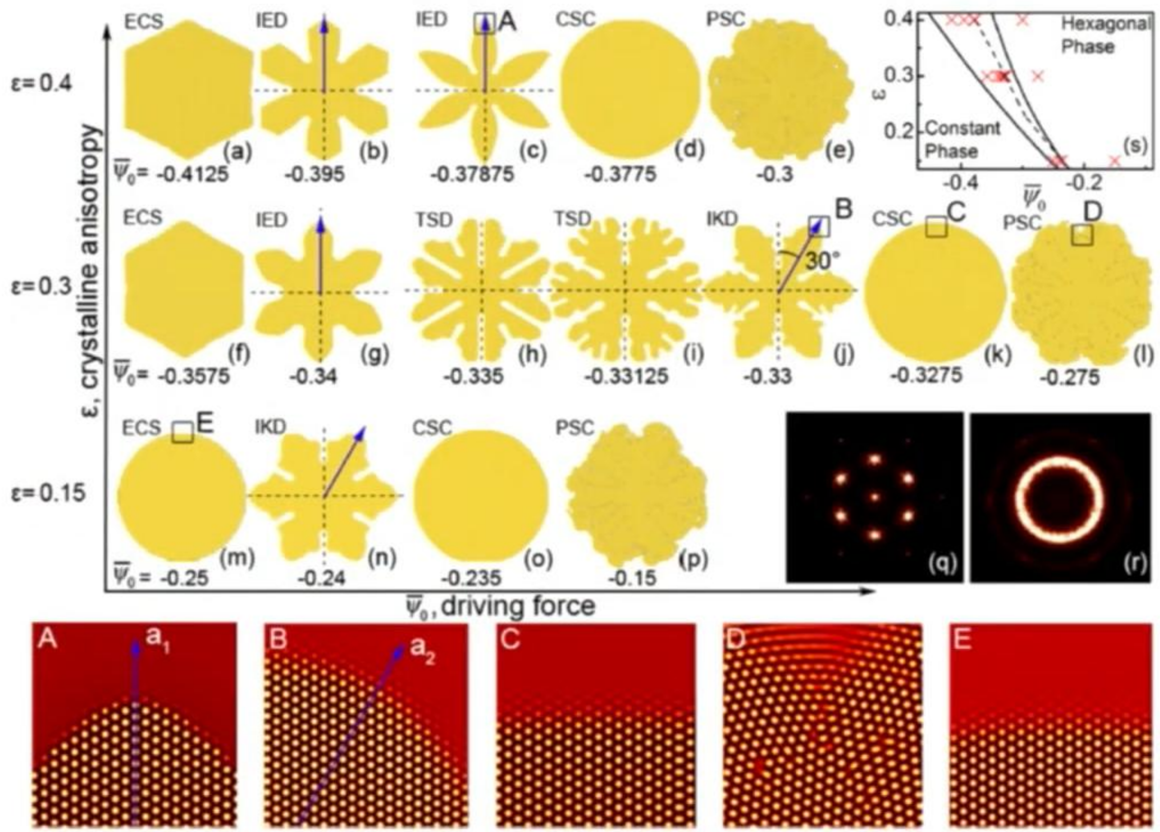
- Based on cDFT
- Lower power terms of cDFT
- Density waves

$$\delta\rho(\vec{r}) = \rho_o \sum_{\vec{K}_i} A_i(z) \cdot e^{i\vec{K}_i \cdot \vec{r}}$$

Phase Field Crystal Model

$$F = \int d\vec{r} \left\{ \frac{\psi}{2} \left[-\epsilon + (\nabla^2 + 1)^2 \right] \psi + \frac{\psi^4}{4} \right\}$$

$$\frac{\partial \psi}{\partial t} = \nabla \cdot \nabla \frac{\delta F}{\delta \psi}$$



Tang *et al.*
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Solidification of 2D hexagonal lattices in a liquid near equilibrium and far-from equilibrium.

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