UNIVERSITY *of* CALIFORNIA · IRVINE

Phase Field Crystal (PFC) Model

and

Density Functional Theory (DFT) of Freezing

Pyrite Project Meeting October 14th 2010

Arvind Baskaran

John Lowengrub

Density functional Theory of Freezing

[Ramakrishnan and Yussouff **Phys. Rev. B 19, 2775 (1979)**]

The Free Energy of the liquid near freezing point is written as :

$$F[\rho(\mathbf{r})] = F_{id}[\rho(\mathbf{r})] + F_{ex}[\rho(\mathbf{r})] + F_{ext}[\rho(\mathbf{r})]$$

Ideal Gas

Excess /interaction

External potential

$$F_{id}[\rho(\mathbf{r})] = k_B T \int d\mathbf{r}\rho(\mathbf{r})\{\ln[\rho(\mathbf{r})\Lambda^d] - 1\}$$

Λ=thermal wavelength

$$F_{ext}[\rho(\mathbf{r})] = \int d\mathbf{r}\rho(\mathbf{r})V(\mathbf{r},t)$$

Excess Free Energy

The excess Free energy term was expanded by Ramakrishnan and Youssouf in terms of the Density difference $\Delta\rho = \rho(\mathbf{r}) - \rho$

Equilibrium density
Of liquid

$$F_{\mathrm{ex}}[\rho(\mathbf{r})] \simeq F_{\mathrm{ex}}(\rho) - \frac{k_B T}{2} \int \int d\mathbf{r} d\mathbf{r}' \Delta\rho(\mathbf{r}) \Delta\rho(\mathbf{r}') \times c_0^{(2)}(\mathbf{r} - \mathbf{r}'; \rho)$$

Direct Correlation function
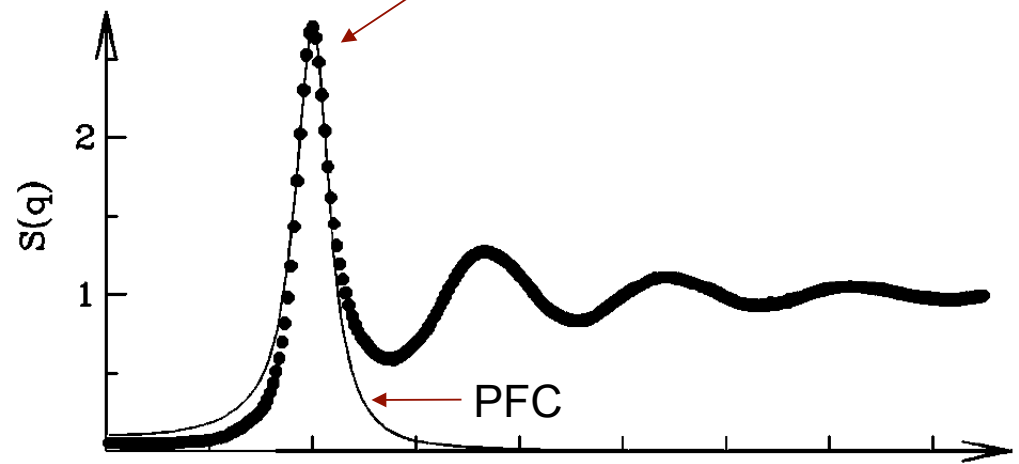
Phase Field Crystal Free Energy

The Excess Free Energy is written as :

$$\mathcal{F}_{\text{ex}}[\rho(\mathbf{r})] = F_{\text{ex}}(\rho) - \frac{k_B T}{2} \int d\mathbf{r}\, \Delta\rho(\mathbf{r})$$

$$\times(\hat{C}_0 - \hat{C}_2\nabla^2 + \hat{C}_4\nabla^4 + \cdots)\Delta\rho(\mathbf{r})$$

PFC Approximation to Direct Correlation Function :

$$\hat{c}_0^{(2)}(\mathbf{k};\rho) = \hat{C}_0 + \hat{C}_2 k^2 + \hat{C}_4 k^4$$

Captures First peak
Of Structure Factor

PFC

Phase Field Crystal Model

Choosing the scaled density difference as the filed variable : $\phi(\mathbf{r},t)=[\rho(\mathbf{r},t)-\rho]/\rho$

Mobility

$$\partial_t \phi = \nabla \cdot (M(\phi)\nabla\mu)$$

$$\mu := \delta_\phi E(\phi)$$

Temperature
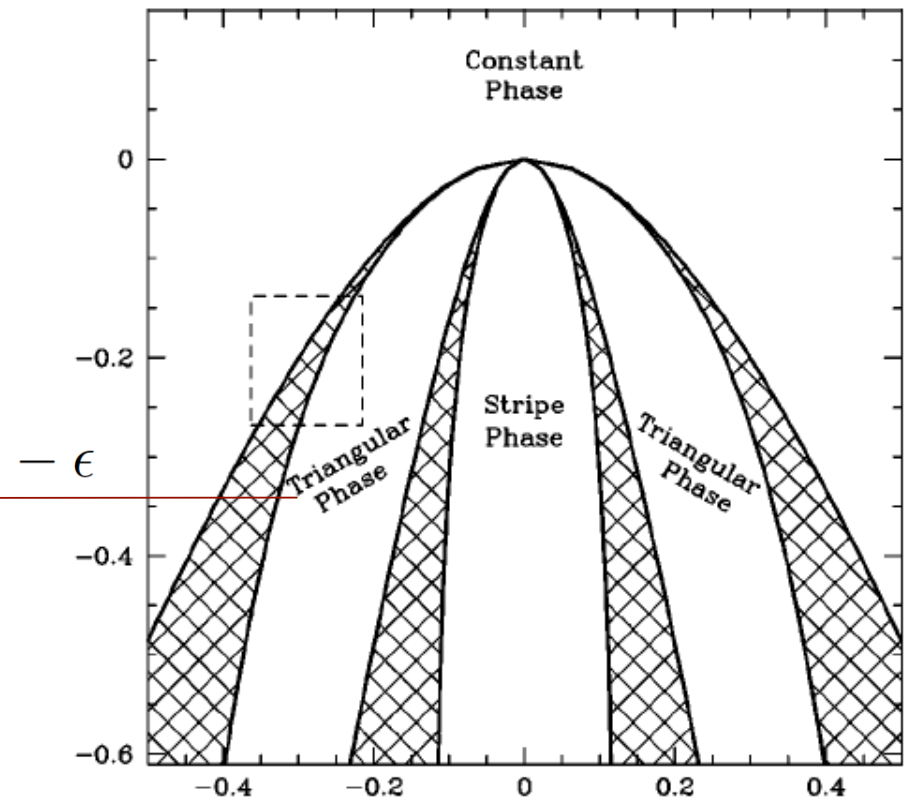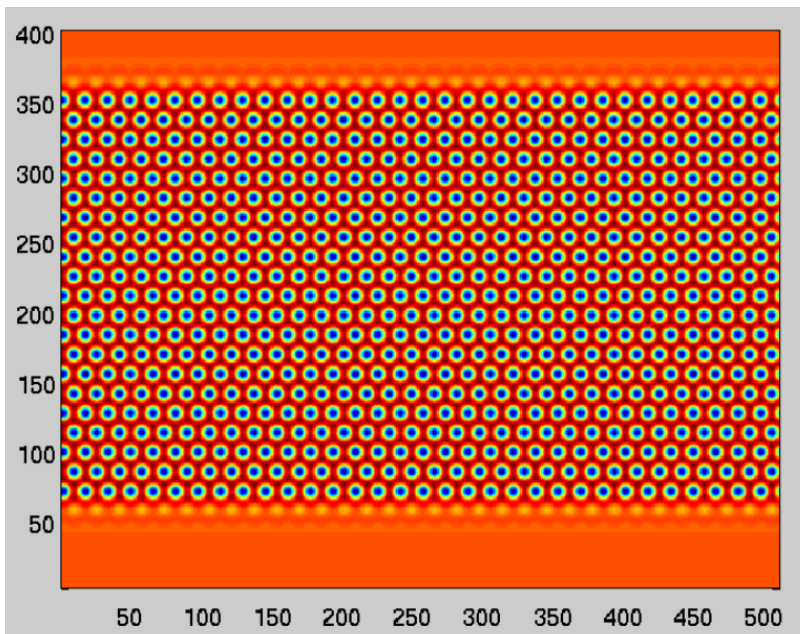
$$E(\phi) = \int_\Omega \left\{ \frac{1}{4}\phi^4 + \frac{1-\epsilon}{2}\phi^2 - |\nabla\phi|^2 + \frac{1}{2}(\Delta\phi)^2 \right\} d\mathbf{x}$$

Swift-Hohenberg

$$\epsilon \leq 1, \epsilon \in \mathbb{R}$$
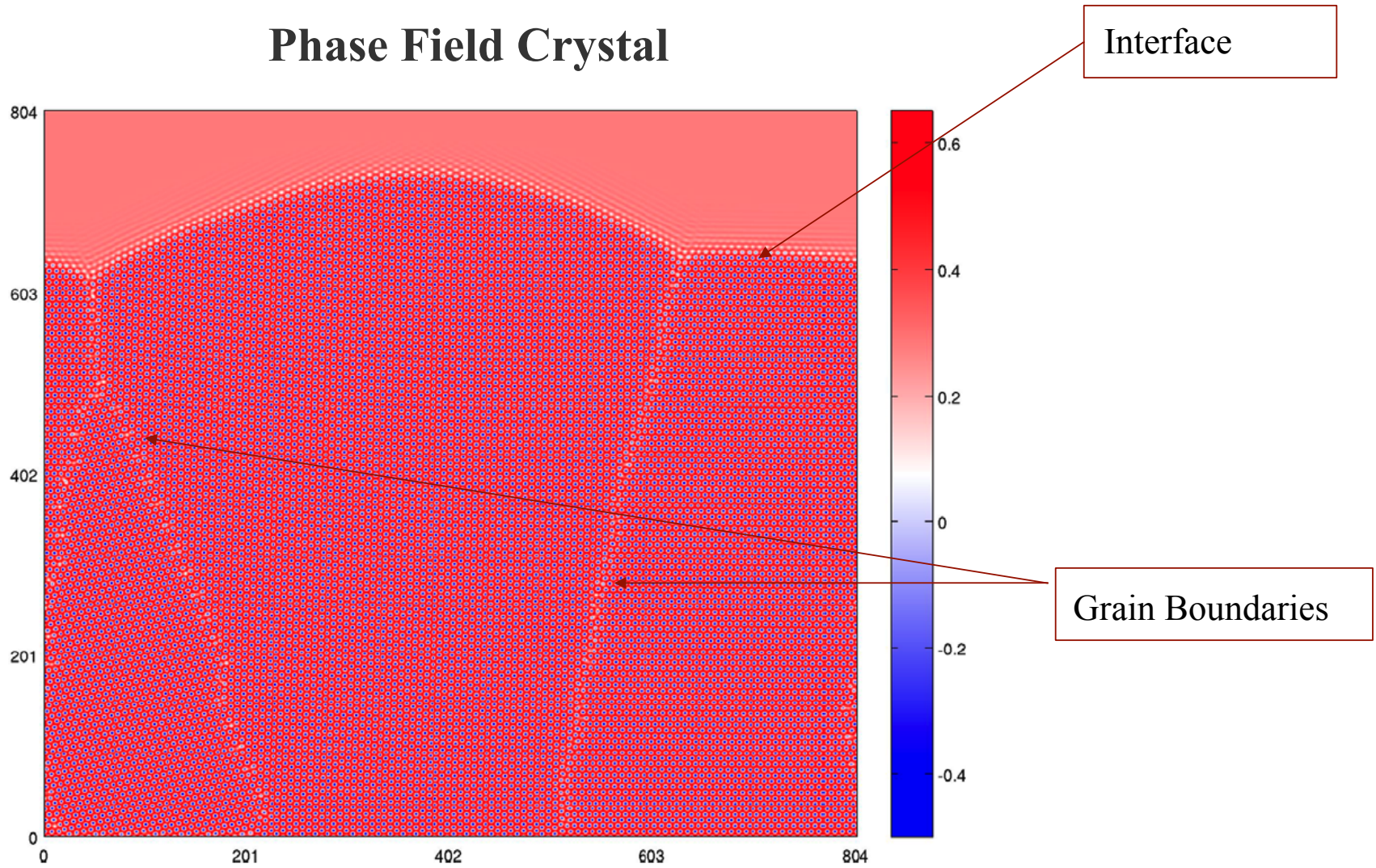
Elder et al [PRE 051606 (2004)]

Phase Diagram

$$E(\phi) = \int_{\Omega} \left\{ \frac{1}{4}\phi^4 + \frac{1-\epsilon}{2}\phi^2 - \mid \nabla\phi \mid^2 + \frac{1}{2}(\Delta\phi)^2 \right\} d\mathbf{x}$$

ϕ (average)

Phase Field Crystal

Interface

Grain Boundaries
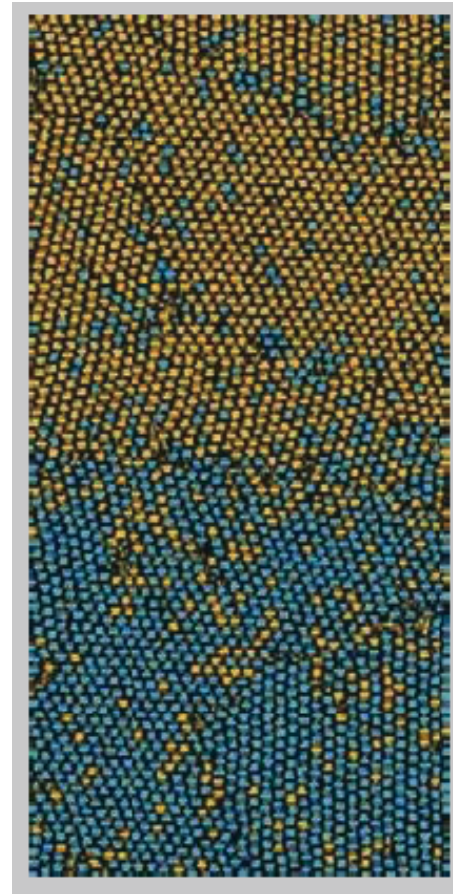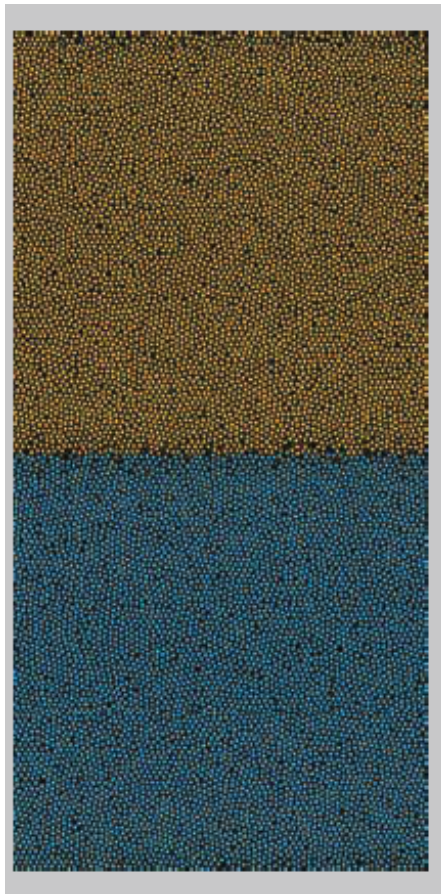
Phase Field Simulation of Binary Alloy

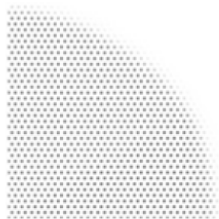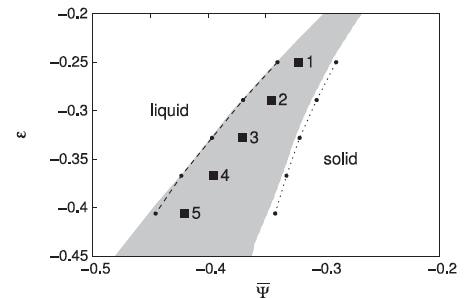[N Provatas et al JOM (2007)]

Elastic and Interfacial Energy

Elastic Interactions

$$\phi(\vec{x}) = \phi_{eq}(\vec{x} + \vec{u}) + \delta$$

$$E(\phi) = E(\phi_{eq}) + \int d\vec{x}(C_{ijkl}u_{ij}u_{kl})$$

$+ \ ...$ $\longrightarrow$ Hook's Law

Anisotropic Interfacial Energy

R. Backofan and A. Voigt J. Phys. Condens. Matter 21. (2009) 464109
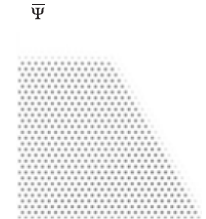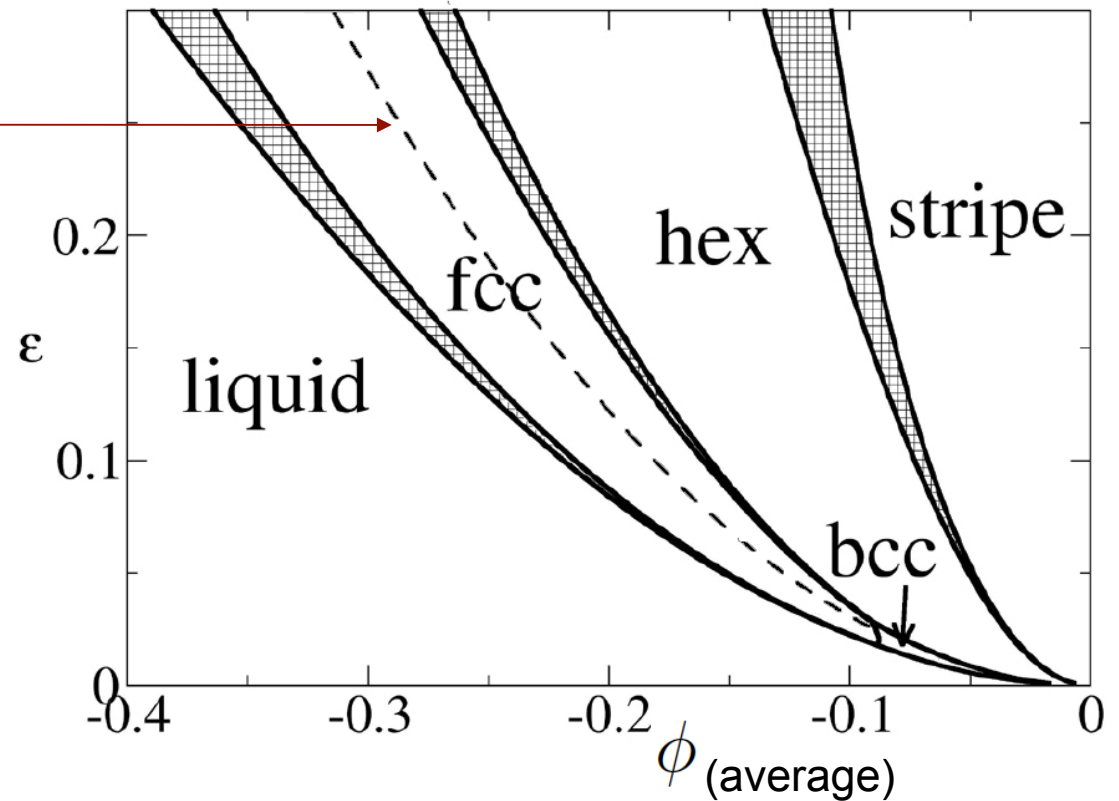
1   2   3   4   5

PFC Model in 3 – D (Phase Diagram)

The PFC Model extends directly to 3-D but generally fails to capture the FCC structure in 3-D

Unstable FCC
Region
BCC lattice is prefered

[PhD Thesis Kuo-An Wu
Northeastern University]

Phase Field Crystal Models for FCC Lattice - 1

Introduction of Two mode PFC Free energy (Kuo-An Wu et al Arxiv:1001.1349)

Standard PFC Model

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

Modified 2 Mode PFC Model with two sets of reciprocal lattice vectors for the FCC

$$F = \int d\vec{r} \frac{\psi}{2} \left[-\epsilon + (\nabla^2 + 1)^2((\nabla^2 + Q_1{}^2)^2 + R_1) \right] \psi + \frac{\psi^2}{4}$$

Equilibrium Density field of 2 Mode FCC solid :

$$\psi = \bar{\psi} + \sum_{\vec{K}=\{111\}} A\, e^{i\vec{K}\cdot\vec{r}} + \sum_{\vec{K}'=\{200\}} B\, e^{i\vec{K}'\cdot\vec{r}} + \cdots$$

Major Disadvantage is that the evolution equation is an 8th order PDE and the model does not capture structure factor of liquid

Phase Field Crystal Models for FCC Lattice - 2

Introduction of new nonlinearities into PFC Free energy (Kuo-An Wu et al

Standard PFC Model (captures only triangular lattice in 2 D)   **arXiv:1008.4019v1)**

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

Modified PFC Model that captures other symmetries (work in 2D captures square, hexagonal and triangular lattices)

$$F = \int d\vec{r} \left(\frac{\psi}{2}\left[-\epsilon + (\nabla^2 + 1)^2\right]\psi + \frac{\psi^4}{4} + \frac{g_4}{4}\psi^2\Delta^2\psi^2 + \frac{g_6}{4}\psi^2\Delta^3\psi^2 + \frac{s_4}{4}|\nabla\psi|^4 + \frac{s_6}{6}|\nabla\psi|^6 \right).$$

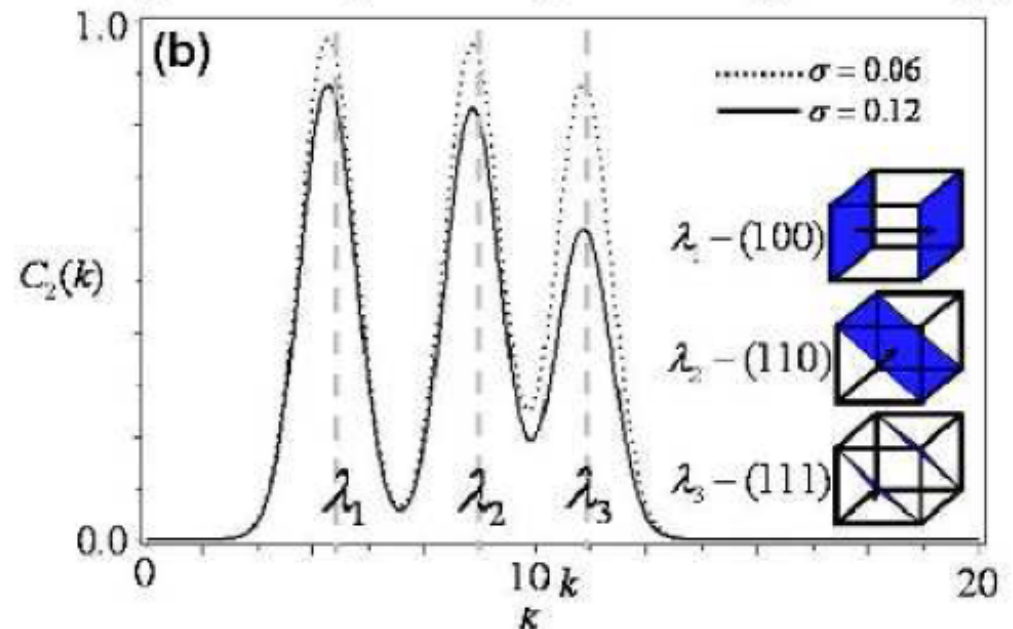This approach may be adopted to development of a future FCC model.

Phase Field Crystal Models for FCC Lattice - 3

Introduction of artificial Direct Correlation Function PFC Free energy

[arXiv:1002.3185v1]

$$\hat{c}_0^2 = \sum_i \gamma_i \exp\left(-\frac{(k-k_i)^2}{2\alpha_i^2}\right)$$

Major Disadvantage is that the model does not capture the structure factor of liquid

Phase Field Crystal Models for FCC Lattice

1)   The models concentrate of capturing the equilibrium density field correctly
     But neglect to address the physics.
     a)   The correct structure factor
     b)   The correct elastic response
     (unknown properties for all three approaches
       material properties depend on the shape of the first peak of
       structure factor)

2)   The models no longer hold the simplicity (computational) of the PFC model

Structure Factor and Direct Correlation functions for Liquids

Given a microscopic interaction potential for the liquid (say Lennard Jones) the
Direct correlation function can be computed using the Ornstein Zernike relation
Using an approximate closure relation.
[See " Introduction to Liquid state physics " by Norman H. March]

$$h(r) = c(r) + \rho \int c(r - r')h(r')dr' \qquad \hat{h}(k) = S(k) - 1$$

direct correlation function   Structure factor

Percus-Yevick (PY) approximation

$$c(r) = \left(1 - e^{\beta\phi(r)}\right)(h(r) + 1)$$

analytically solvable for hard sphere interactions

Several such methods have been used to study the freezing of Lennard Jones
Liquids using Density Functional Theory.
[See Phys Rev E 50 4801 (1994)]

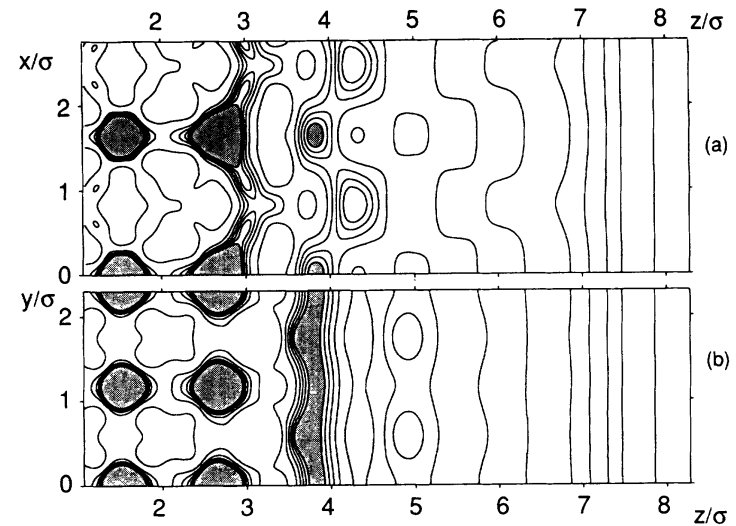The Lennard Jones Liquid
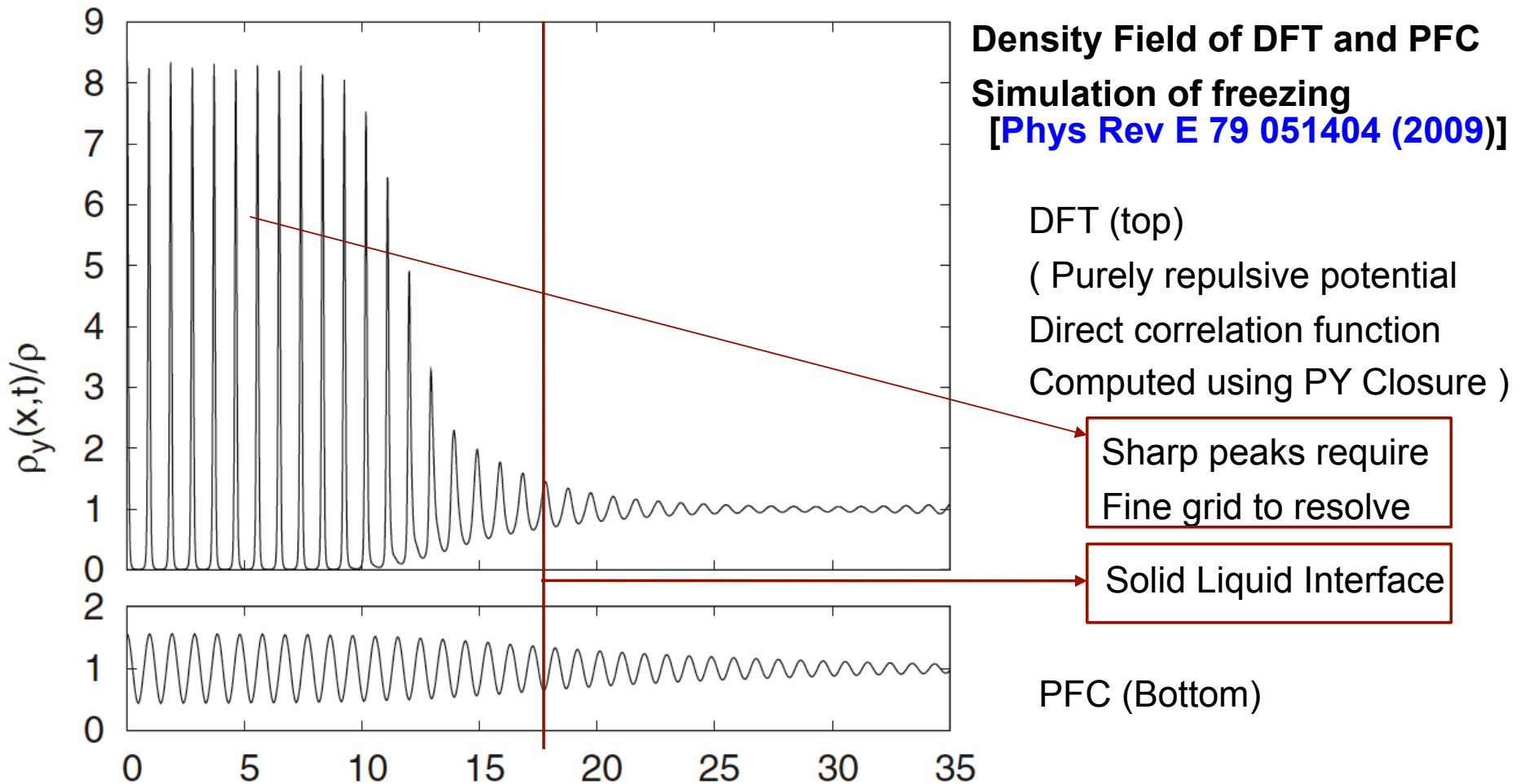naturally freezes into an FCC solid.

FIG. 6. (110) surface of a LJ crystal at $\tau = 10^{-4}$: Contour
plots of the density in a $(1\bar{1}0)$ plane (a) and a (001) plane (b).
Both planes are normal to the surface and hit the lattice sites.
Lines correspond to densities $\rho\sigma^3 = 0.05 + n0.25$, $n = 0, \ldots, 6$.
The shaded areas correspond to $\rho\sigma^3 > 1.55$.

Phys Rev E 50 4801 (1994)

Numerical Difficulty in DFT approach

Density Field of DFT and PFC

Simulation of freezing
 [Phys Rev E 79 051404 (2009)]

DFT (top)

(Purely repulsive potential

Direct correlation function

Computed using PY Closure)

Sharp peaks require
Fine grid to resolve

Solid Liquid Interface

PFC (Bottom)

Proposed DFT Approach

1) Use DFT for Freezing to construct Free energy (same as PFC)

2) Approximate the Excess Energy term truncated at two particle direct correlation (same as PFC)

3) Approximate the Direct correlation function numerically using Lennard Jones or Modified Lennard Jones (Yukawa Potential) for two body interaction.

4) Evolve the density field using a gradient model or a more sophisticated Dynamic Density Functional Theory (DDFT) Model for the density field.

$$\frac{\partial \rho}{\partial t} = \nabla \cdot \left(M \nabla \frac{\delta E}{\delta \rho} \right)$$

Gradient descent (M constant)

$$\frac{\partial \rho}{\partial t} = \nabla \cdot \left(\rho \nabla \frac{\delta E}{\delta \rho} \right)$$

DDFT

Advantages of DFT approach

1)   It captures the relevant physics naturally due to design based on microscopic interactions

2)   Extension to Multiple species is straight forward based on the
DFT for freezing of Binary alloys and Binary LJ interactions
[J. Chem. Phys. 90, 1188 (1989)]

$$F_{ex} = \int dr dr' \ (\delta\rho_A(r)C_{AA}(r-r')\delta\rho_A(r') + \delta\rho_B(r)C_{BB}(r-r')\delta\rho_B(r') + 2\delta\rho_A(r)C_{AB}(r-r')\delta\rho_B(r'))$$

3)   Potential models for Iron Pyrite based on Modified Buckingham Potentials
have shown promising results in ab initio MD simulations

Philpott et al.   J. Chem. Phys. 120, 1943 (2004) ,

Zhang et al   J. Electrochemical Society, 152 10 A1955-A1962 2005

de Leeuw et al.   J. Phys Chem, 104 7969-7976 2000

$$\Phi_{ij}(r_{ij}) = A_{ij}e^{-r_{ij}/\rho_{ij}} - \frac{C_{ij}}{r_{ij}^6}$$