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Crystal Model Based on Dynamic Density Functional Theory (DDFT)

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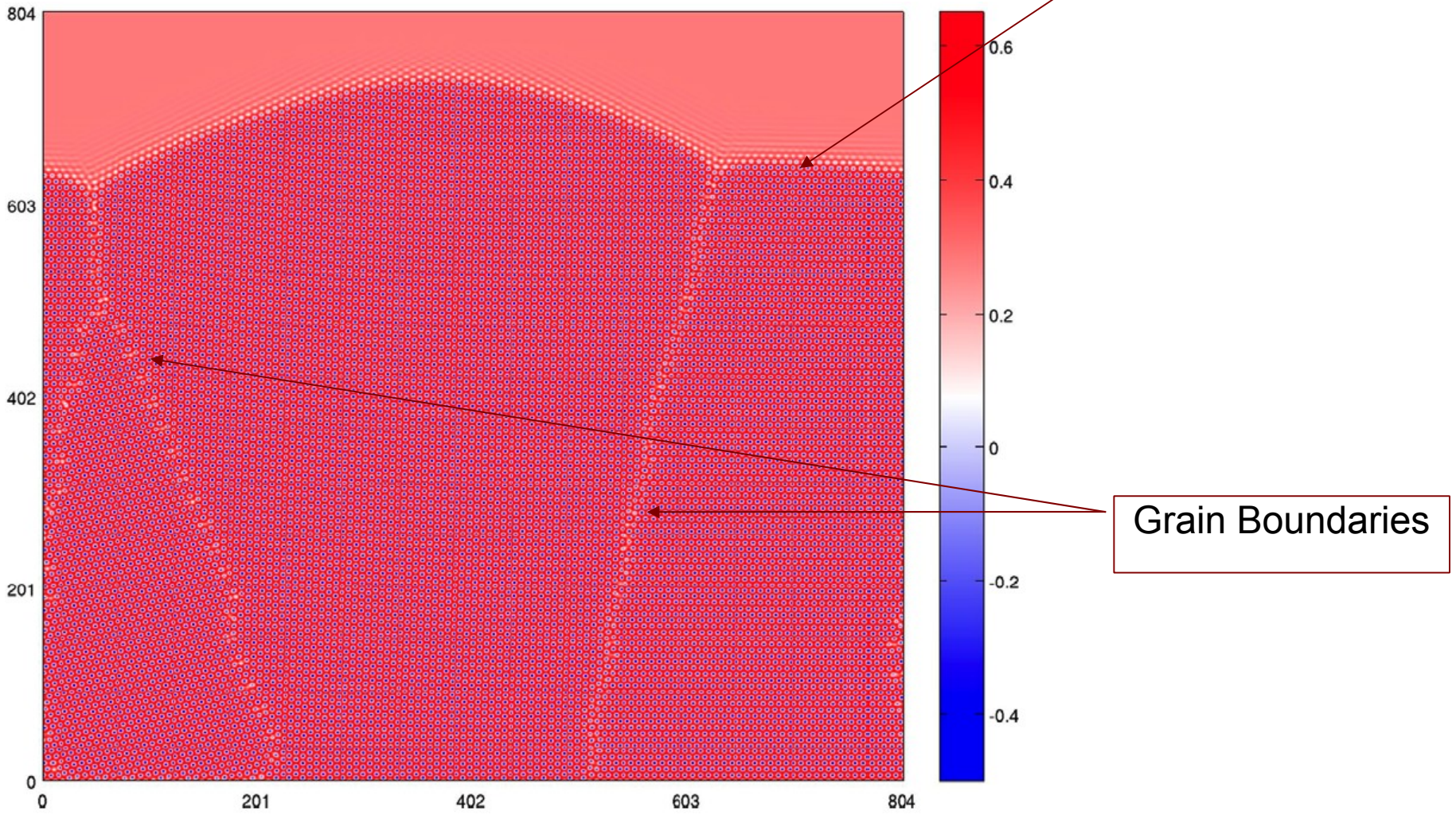
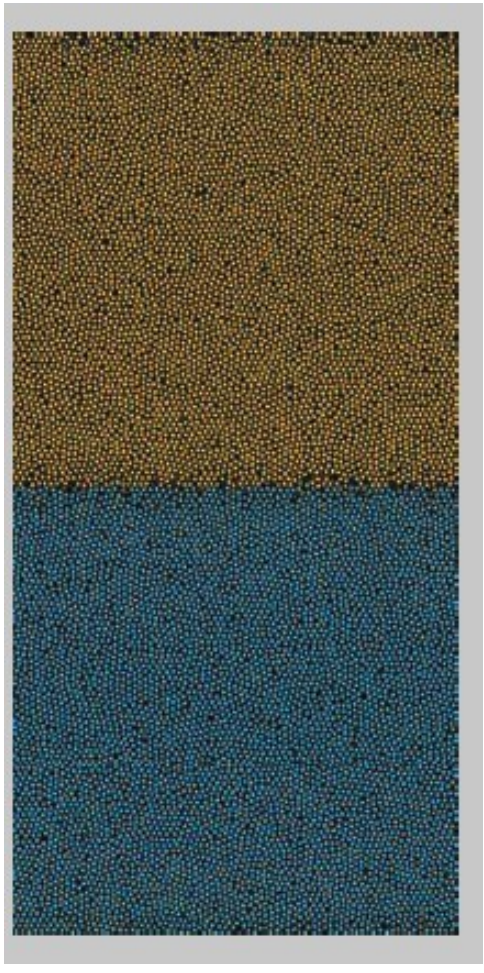
Pyrite Project Meeting December 7th 2010

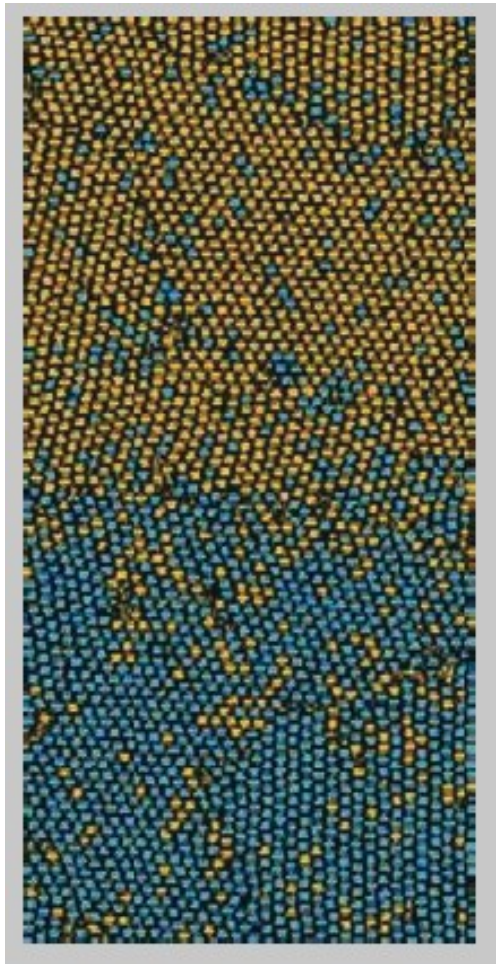
Phase Field Crystal



Phase Field Simulation of Binary Alloy

[N Provatas et al JOM (2007)]





Density functional Theory of Freezing

[Ramakrishanan and Youssouf **Phys. Rev. B 19, 2775 (1979)**]

The Free Energy of the liquid near freezing point is written as a functional of The scaled atomic density :

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

Density | Ideal Gas | Excess | External potential

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

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

0

Excess Free Energy Approximation

(truncated Taylor Expansion)

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

Equilibrium density
Of liquid

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

Direct Correlation function

Rescaled DDFT Model

$$\partial_t \rho = D\nabla^2 \frac{\delta \mathcal{F}[\rho]}{\delta \rho}$$

Restated With new variable

$$\phi(\mathbf{r},t) = \frac{(\rho(\mathbf{r},t) - \rho_{eq})}{\rho}$$

Ideal gas term

Excess Energy Term

$$\partial_t \phi = D\nabla^2 \left[\phi - \frac{1}{2}\phi^2 + \frac{1}{3}\phi^3 - \rho_{eq}\left(c_o^{(2)} \star \phi\right) \right]$$

Direct Correlation Function

Ornstein Zernike Relation :

$$h(\mathbf{r}) - c_o^{(2)}(\mathbf{r}) = \rho_{eq} \int h(\mathbf{r}')c_o^{(2)}(\mathbf{r}-\mathbf{r}')d\mathbf{r}'$$

Total correlation function

Percus Yevick (PY) Closure Relation :

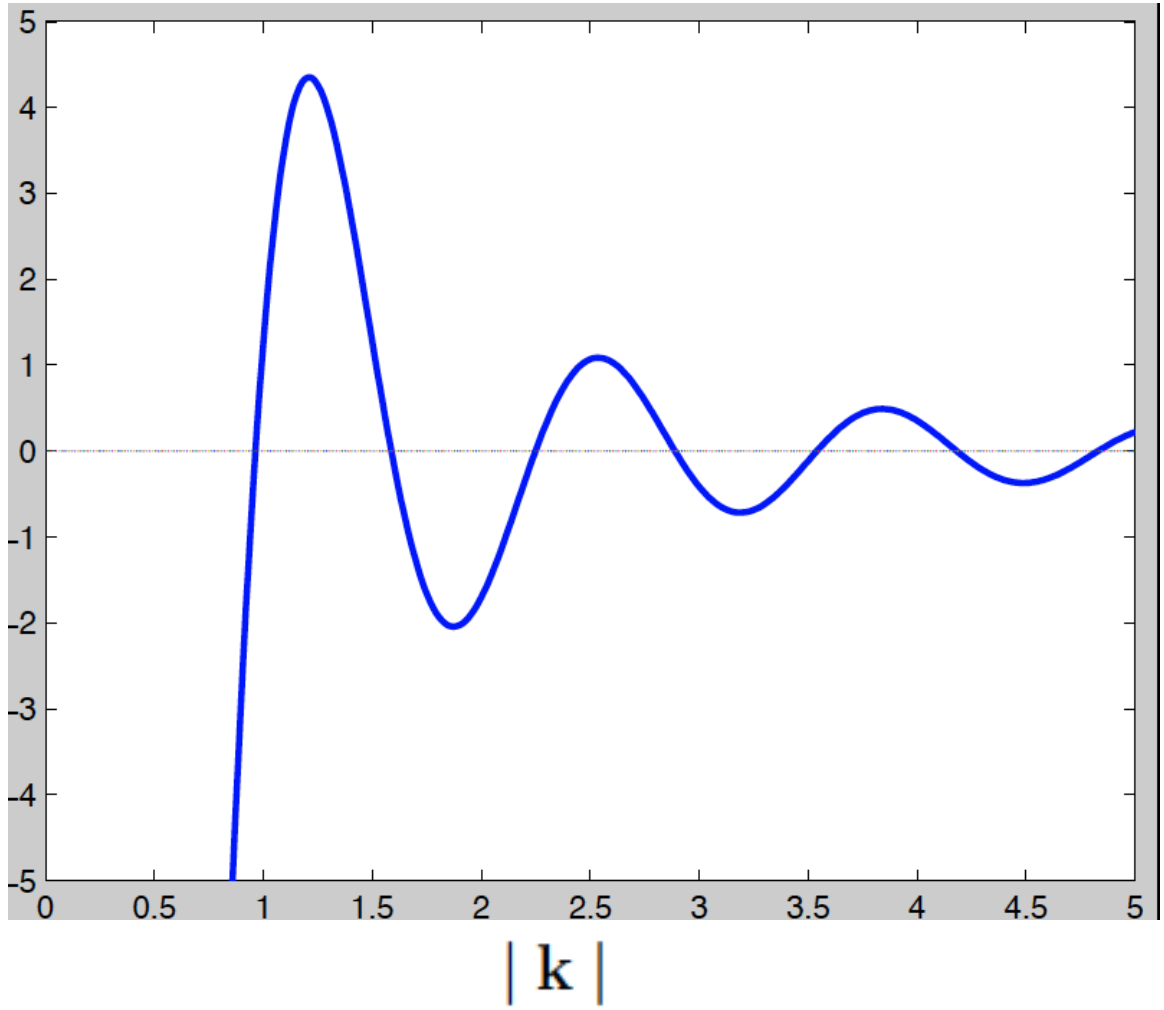
$$c_o^{(2)} = \left[\exp\left(-\frac{u(\mathbf{r})}{kT}\right) - 1\right]\left[h(\mathbf{r}) - c_o^{(2)}(\mathbf{r}) + 1\right]$$

Pair Potential

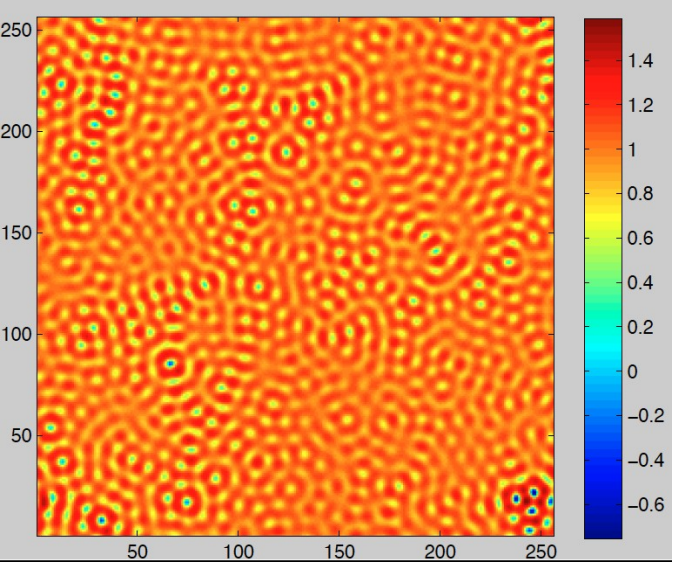
Direct Correlation Function for Hard Sphere with PY Closure

$$u(\mathbf{r}) = \begin{cases} \infty & |\,\mathbf{r}\,| < \sigma \\ 0 & |\,\mathbf{r}\,| \geq \sigma \end{cases}$$

$\hat{c}_o^{(2)}(\mathbf{k})$

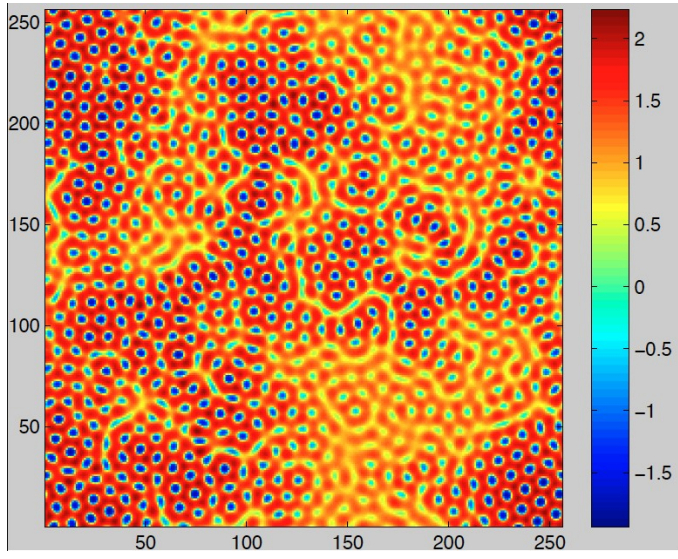


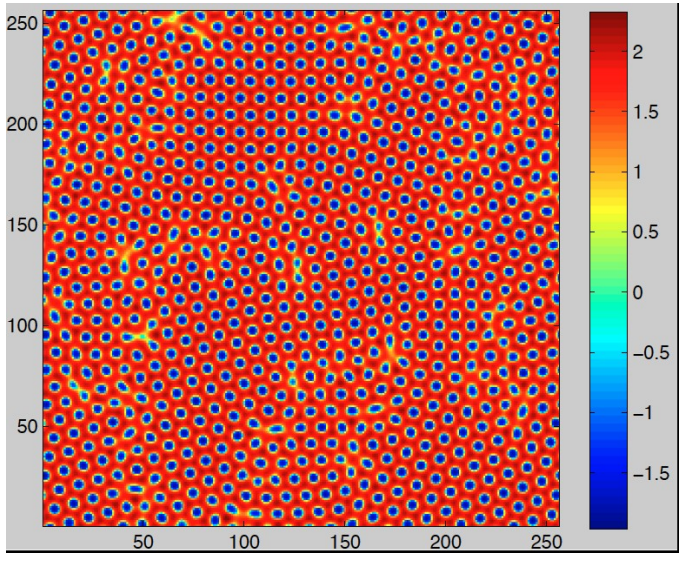
DDFT Simulation of Freezing of a Supercooled Hard Sphere Fluid



5000
Time steps

10000
Time steps





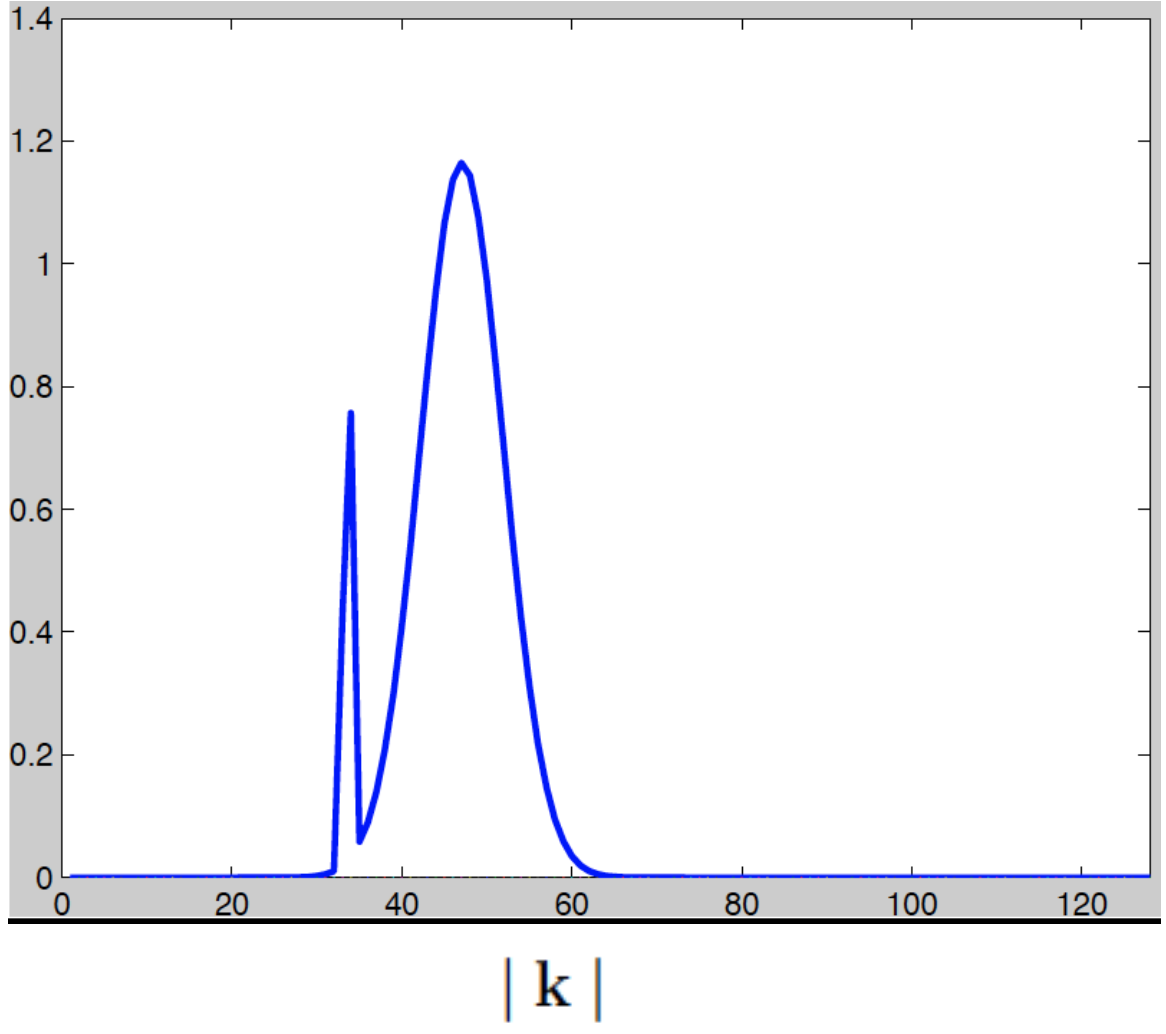
50000
Time steps

Direct Correlation function for Square Lattice (constructed)

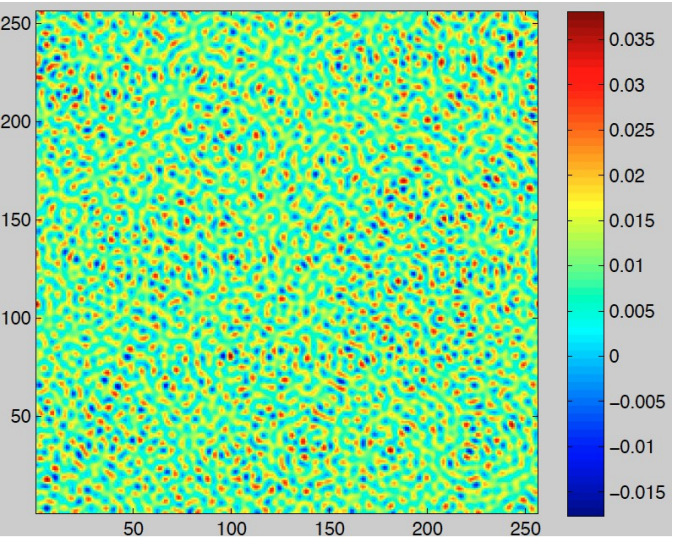
$$\hat{c}_0^2 = \sum_i \gamma_i \exp\left(-\frac{(k-k_i)^2}{2\alpha_i^2}\right)$$

[Following Greenwood et al arXiv:1002.3185v1]

$\hat{c}_o^{(2)}(\mathbf{k})$

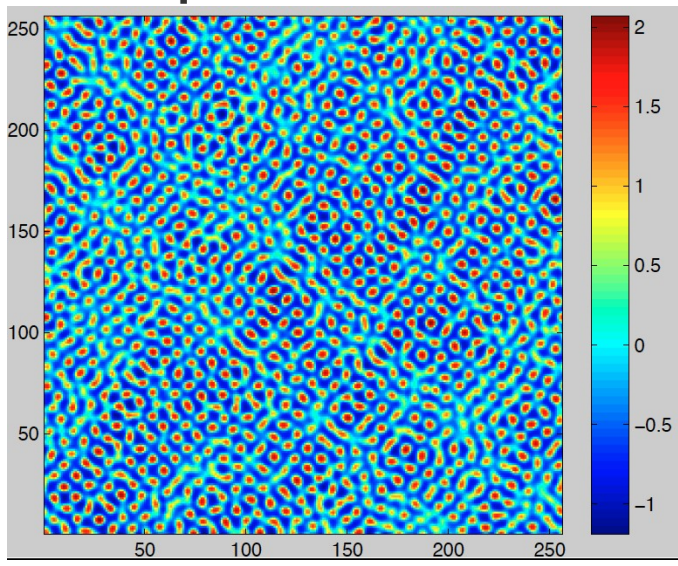


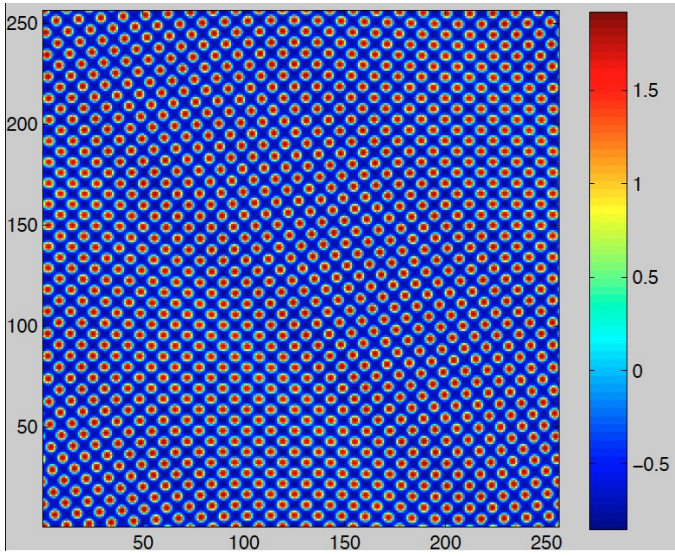
Simulation of Freezing of a Supercooled Fluid into a Square Lattice



5000
Time steps

10000
Time steps





50000
Time steps

Phase Field Crystal Free Energy

The Excess Free Energy is written as :

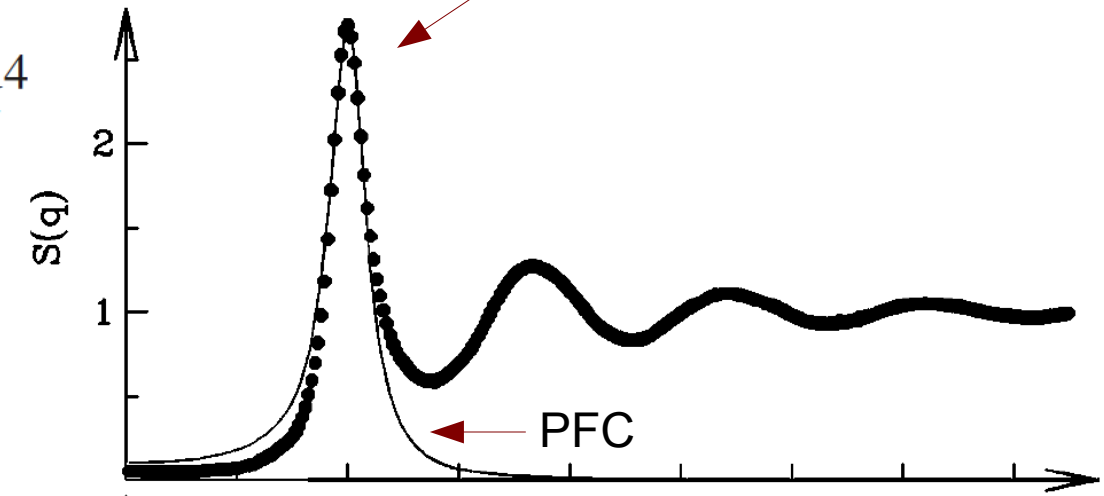
$$\mathcal{F}_{\text{ex}}[\rho(\mathbf{r})] = F_{\text{ex}}(\rho) - \frac{k_B T}{2}\int d\mathbf{r}\Delta\rho(\mathbf{r})$$

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

PFC Approximation to Direct Correlation Function :

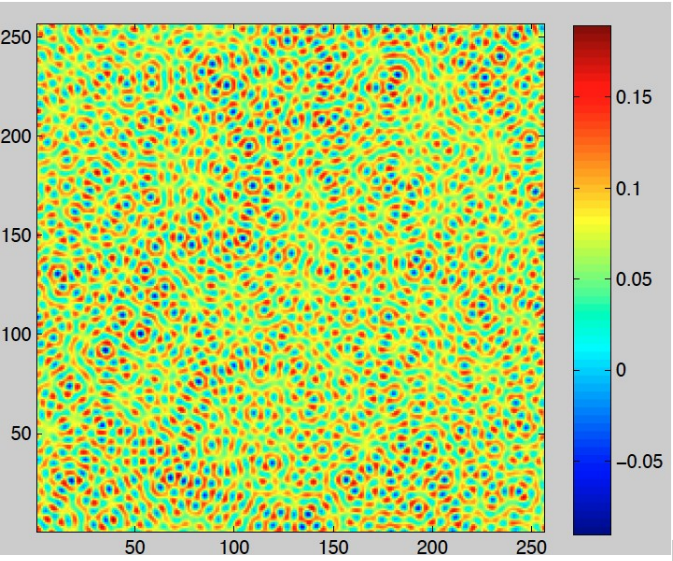
$$\hat{c}_0^{(2)}(\mathbf{k};\rho) = \hat{C}_0 + \hat{C}_2 k^2 + \hat{C}_4 k^4$$

Captures First peak
Of Structure Factor



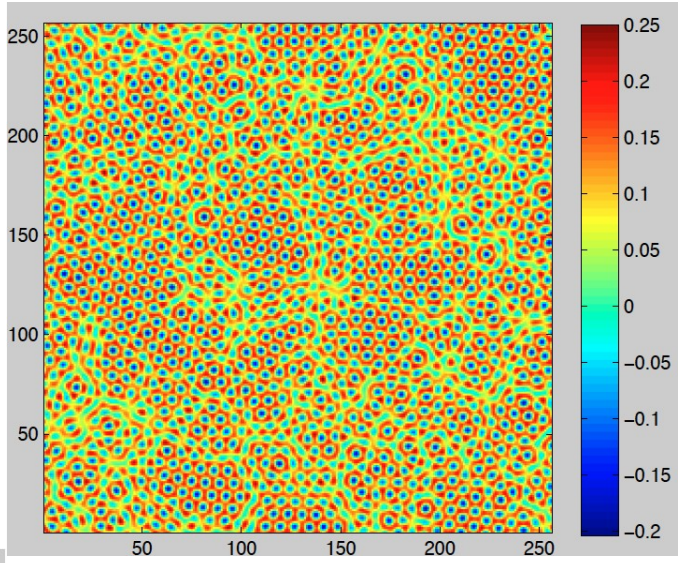
Elder et al [PRE 051606 (2004)]

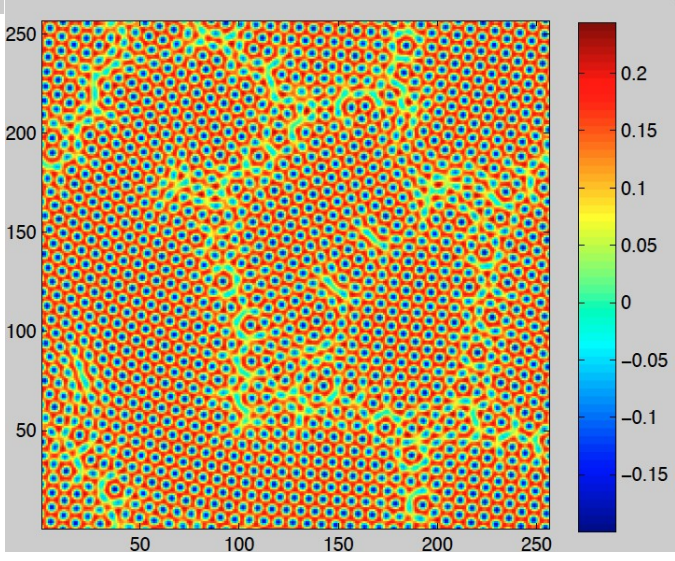
PFC Simulation of Freezing of a Supercooled Fluid



10000
Time steps

20000
Time steps





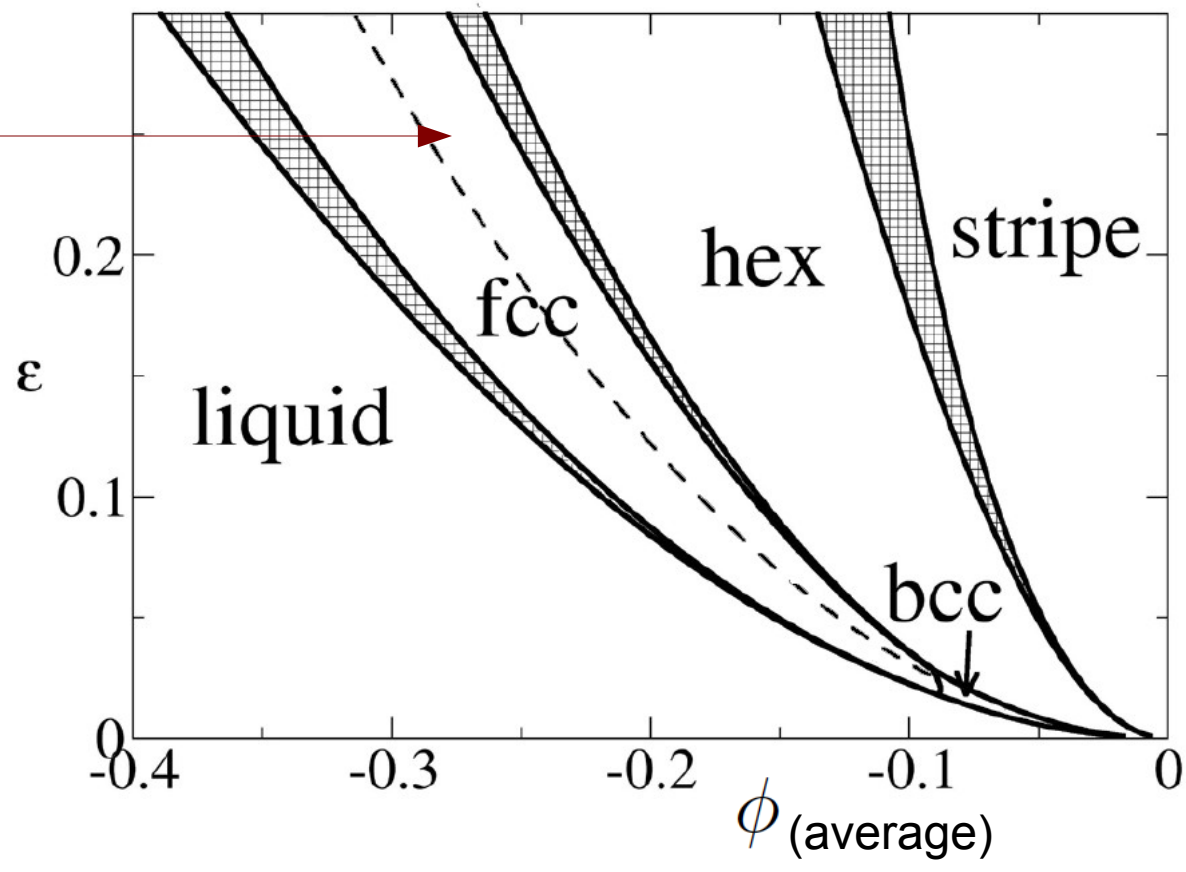
50000
Time steps

PFC Model in 3 – D (Phase Diagram)

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

Unstable FCC
Region
BCC lattice is prefered

[PhD Thesis Kuo-An Wu
Northeastern University]



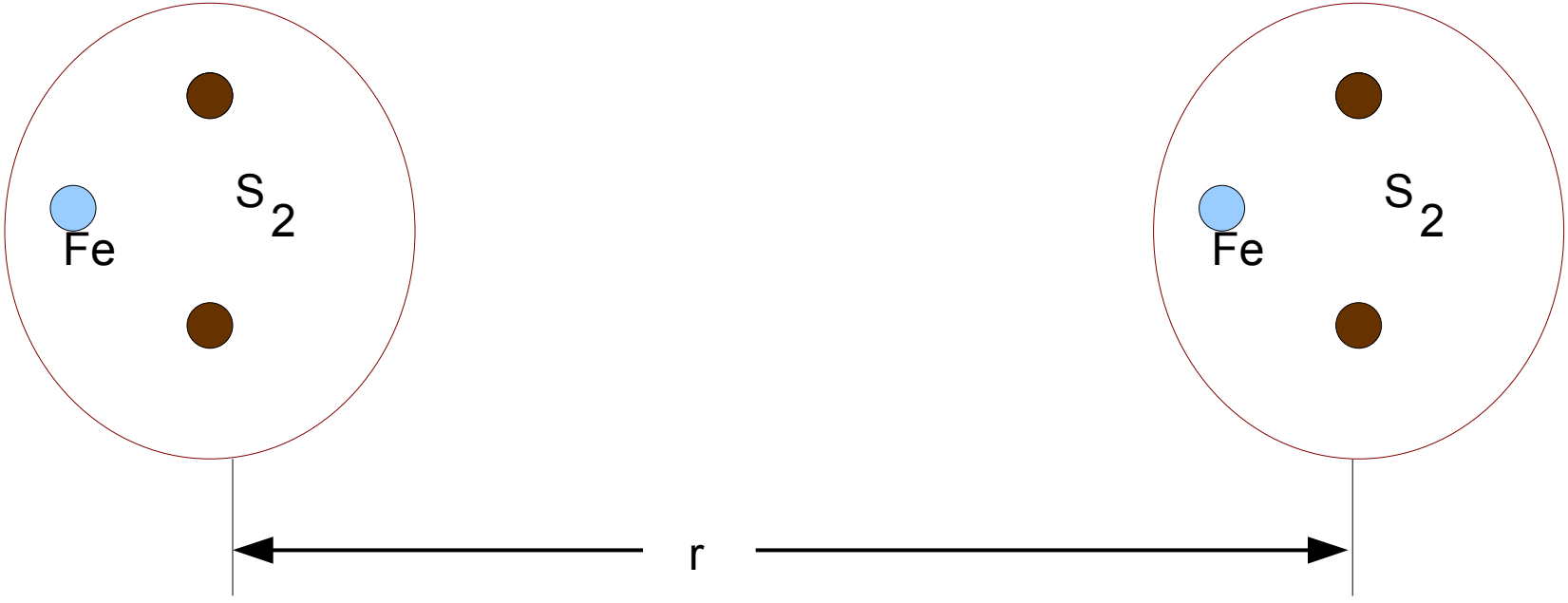
Main Accomplishments Since Last Meeting

1) Development of a Algorithm that simulates solidification of a fluid given the Direct correlation function of the fluid phase in 2-D.
(a spectral method with Crank Nicholson like time integration)

2) Development of a Numerical Ornstein Zernike Solver based on the algorithm Proposed by Labik et al in **[Molecular Physics 1985 (56) 701 -715]**

3) Development of a 3-D Code for simulation of solidification.

Plan for Developing a Pyrite Model



In Collaboration with Ruqian Wu 's Group :

Step 1 : Treat Ferrite as a molecule and determine Pair potential using DFT

Step 2 : Develop a model for surface re-arrangements of Sulphur

Step 3 : Add internal degrees of freedom for the Fe S2 molecule (relative orientation etc)

Alternative Approach for Developing a Pyrite Model

1) Use Existing Molecular Dynamics Models to obtain pair potentials
For pairwise interaction of Fe-Fe, S-S and Fe – S to model crystallization.

2) For simulation of solidification from an ink the treatment of the Solvent Solute interaction is the key ingredient which needs careful modeling.

Relative Comparison of Approaches

DFT Approach:

1) The pair potentials are calculated from DFT rather than modeled
2) Simpler implementation as the Molecule is assumed to be rigid. But certain defects are hard to capture
3) Solute/Solvent interaction (growth from an ink) is not straight forward.

Alternative Approach:

1) The pair potentials are modeled
2) Molecules not rigid and hence order In the crystal must follow from the Pair interactions. Thus defects are naturally captured.
3) Solute/Solvent interaction can be modeled.