April 12: Phase Field, Fluid Flow, Electrochemistry

- How the (Cahn Hilliard) Phase Field method works
- Phase Field - Fluid Flow coupling
- Electromigration and charge transfer
- Low resolution transport-limited electrochem results
- Phase Field and Fluid-Structure Interactions

Phase Field

A diffuse interface method
Free energy:

$$\mathcal{F} = \int \left[\frac{\alpha}{2} |\nabla \phi|^2 + \beta \Psi(\phi) \right] dV$$

- First term is gradient penalty
- Second term is homogeneous free energy: $\Psi(\phi) = \phi^2 (1-\phi)^2$

Interface thickness:

$$\epsilon \sim \sqrt{\frac{\alpha}{\beta}}$$

Interfacial energy:

$$\gamma \sim \sqrt{\alpha \beta}$$

Phase Field

"Chemical" potential

$$\mu = \frac{\delta \mathcal{F}}{\delta \phi} = \beta \Psi'(\phi) - \alpha \nabla^2 \phi$$

Conservation equation

$$\frac{\partial \phi}{\partial t} = \nabla \cdot (\kappa \nabla \mu)$$

expands to

$$\frac{\partial \phi}{\partial t} = \nabla \kappa \cdot \nabla \left(\beta \Psi'(\phi) + \alpha \nabla^2 \phi \right) + \kappa \left(\beta \nabla^2 \Psi(\phi) + \alpha \nabla^2 \nabla^2 \phi \right)$$

Simulation:

- Increase interface thickness
- Preserve interfacial energy
- Keep thickness smaller than the smallest feature (diffusion)

Phase Field and Fluid Flow

Add convection to conservation equation

$$\frac{\partial \phi}{\partial t} + \vec{u} \cdot \nabla \phi = \nabla \kappa \cdot \nabla \left(\beta \Psi'(\phi) + \alpha \nabla^2 \phi \right) + \kappa \left(\beta \nabla^2 \Psi(\phi) + \alpha \nabla^2 \nabla^2 \phi \right)$$

Navier-Stokes

$$\frac{D\vec{u}}{Dt} = -\nabla p + \nu \nabla^2 \vec{u} + \rho \vec{g} + F_{int}$$

Coupling between phase, velocity

$$F_{int} = -\phi \nabla \mu$$

Velocity-Phase Coupling

2-D Oscillating Droplet

- Benchmark liquid-liquid code
- Square initial condition
- Analytical solution: Rayleigh and Lamb
- Numerical solution: Jacqmin

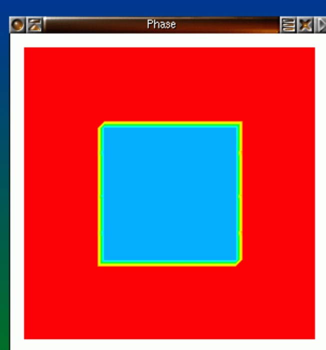
Our results:

- Close to analytical
- Diffusion causes early rounding

Velocity-Phase Coupling

Oscillating liquid drop benchmark

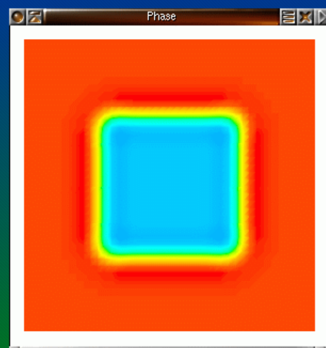
Results: 40x40, t=0



Velocity-Phase Coupling

Oscillating liquid drop benchmark

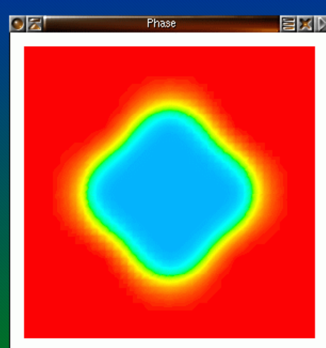
Results: 40x40, t=0.0005



Velocity-Phase Coupling

Oscillating liquid drop benchmark

Results: 40x40, t=0.0127



Electrochemistry: Fe-FeO

Extra term in the conservation equation:

$$\frac{\partial C_i}{\partial t} = \nabla \cdot (\kappa(\nabla \mu_i + z_i F \nabla V))$$

Conservation of charge

$$\frac{D\rho_f}{Dt} = -\vec{\nabla} \bullet \left(\sum \vec{J}_i z_i F\right)$$

Assuming rapid charge redistribution

$$0 = \vec{\nabla} \bullet \left(\sigma_{eff}(C)\, \vec{\nabla} \phi\right)$$

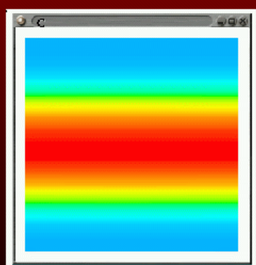
where

$$\sigma_{eff}(C) \equiv \frac{\tilde{z}(C)}{z_{Fe}(C)} \sigma_{Fe}(C) + \sigma_e(C)$$

$$\tilde{z}(C) \equiv z_{Fe}(C) - \frac{M_{Fe}}{M_O} z_O$$

Simulation Results

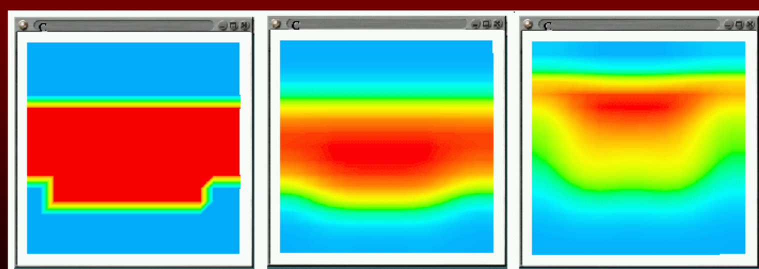
- Perturbed cathodic and anodic interfaces
- 16x16 nodes, Lx=Ly=1cm
- Symmetry boundary conditions used for C
- Steady-state shown below for no voltage



Simulation Results

Perturbed Cathodic Interface

- Shown below:
  - C at t=0
  - C at t=1660s, no voltage
  - C at t=1660s, 1 volt



Simulation Results

Perturbed Anodic Interface

- Shown below:
  - C at t=0
  - C at t=1660s, no voltage
  - C at t=1660s, 1 volt