Sintering Process of Pyrite Nano Particles: A Phase Field Model

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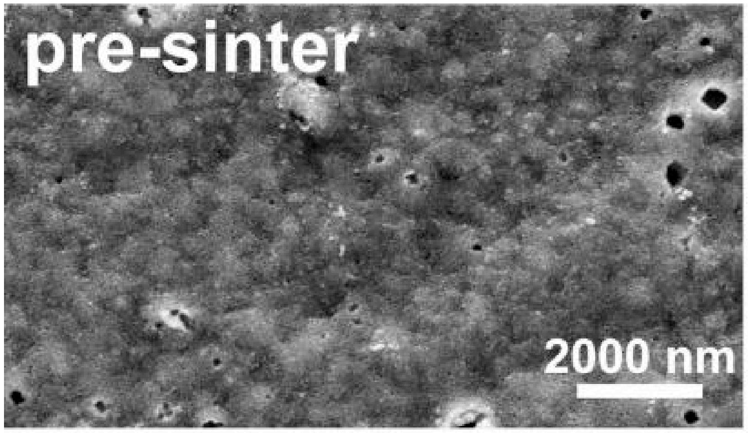
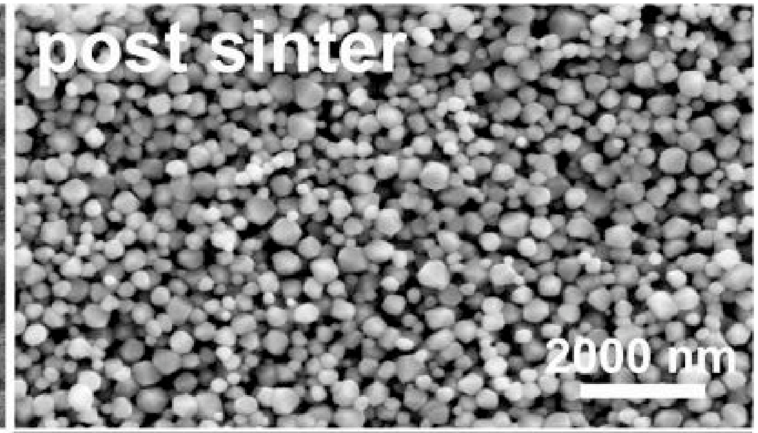
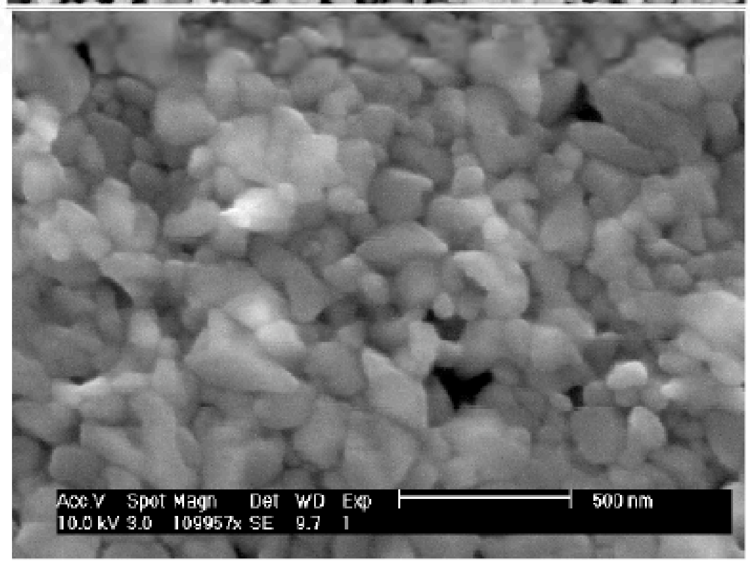
Motivation

S_2





H_2S

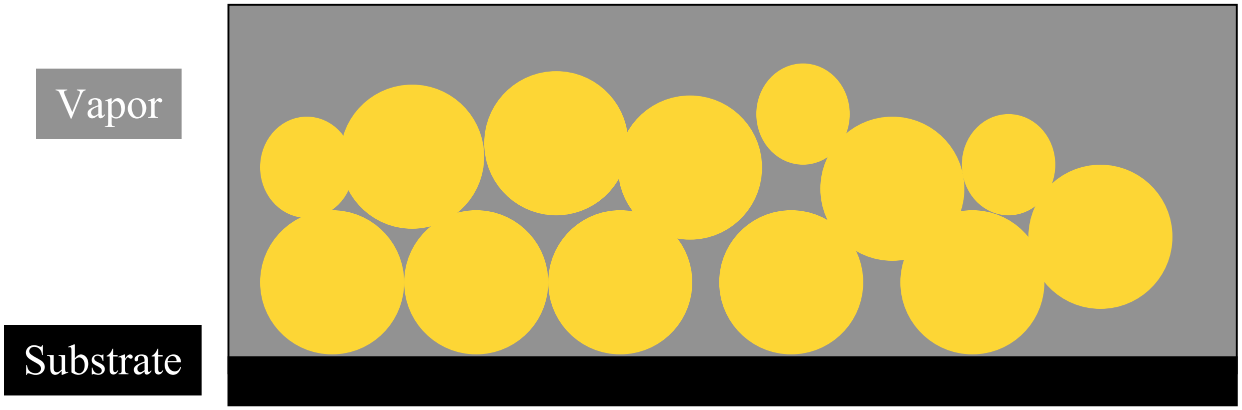


Motivation

We want to model the sintering process and study the effect of different vapors on the surface energy anisotropy, mobility? and how these anisotropies effect the densification during the annealing?

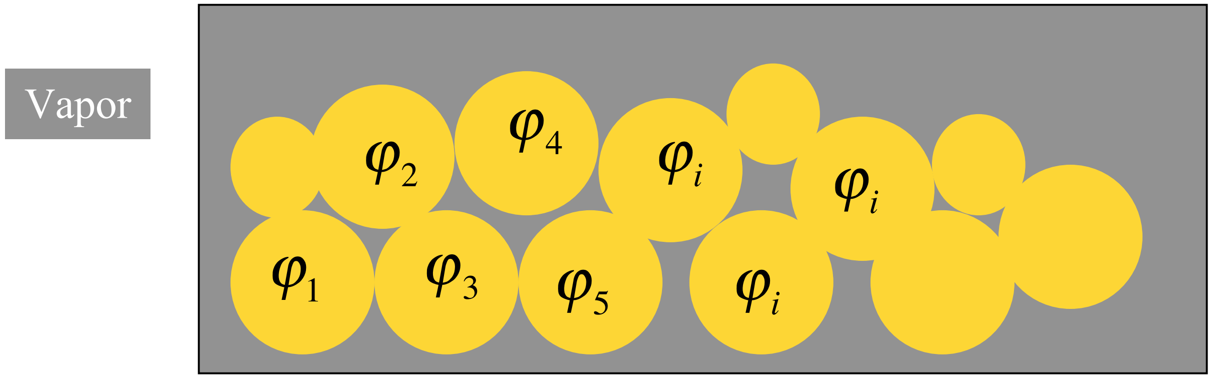
We study the effect of anisotropic surface energy and kinetics on the sintering evolution by diffusive interface phase field models

Sintering



Mass is conserved

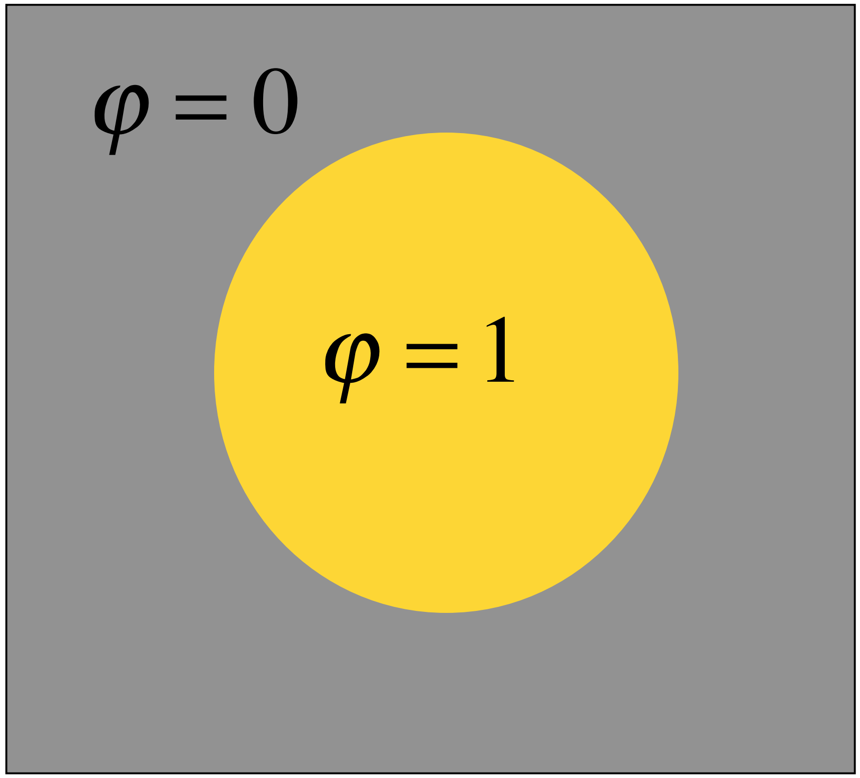
Sintering



$$\sum \varphi_i = cte$$

Phase Field Model

Vapor



Classical Diffuse Interface Model

Cahn-Hilliard system

$$f(\varphi,\nabla\varphi,\nabla^2\varphi) = f_0 + \sum_i L_i \frac{\partial\varphi}{\partial x_i} + \sum_{ij} \kappa_{ij}^{(1)} \frac{\partial^2\varphi}{\partial x_i \partial x_j} + \frac{1}{2}\sum_{ij} \kappa_{ij}^{(2)} \frac{\partial\varphi}{\partial x_i}\frac{\partial\varphi}{\partial x_j}$$

$$E(\varphi) = \int_\Omega \left(f_0(\varphi) + \kappa\,|\nabla\varphi|^2 \right) d\Omega$$

$$f_0 = \varphi^2 (1-\varphi)^2 / 4 \qquad \epsilon^2 = 2\kappa$$

$$\frac{\partial\varphi}{\partial t} = \frac{1}{\epsilon^2}\nabla\cdot(M(\varphi)\nabla\mu)$$

Cahn, 1958

$$\mu = \frac{\partial E}{\partial\varphi} = f_0{}'(\varphi) - \epsilon^2\Delta\varphi \qquad M(\varphi) = 4\varphi(1-\varphi)$$

Anisotropic Surface Energy

$$E[\varphi] = \int_\Omega \left(f_0 + \frac{\epsilon^2}{2} |\Gamma(\mathbf{n}) \nabla \varphi|^2 \right) d\Omega$$

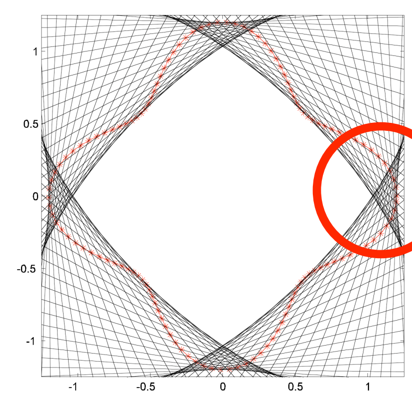
Kobayashi, 1993

$$E[\varphi] = \int_\Omega \Gamma(\mathbf{n}) (f_0 + \frac{\epsilon^2}{2} |\nabla \varphi|^2) d\Omega$$

Torabi et al., 2009.

$$\Gamma(n) = 1 + \epsilon_4 (4 \sum_{i=1}^{d} n_i^4 - 3)$$

$$\Gamma(\theta) = 1 + \epsilon_4 cos 4\theta$$



ill-posed $\Gamma + \Gamma'' < 0$

Anisotropic Surface Energy

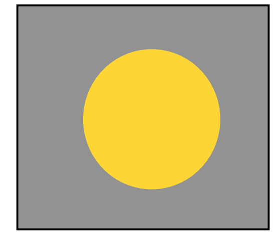
Add high order **regularization** term to the **strongly anisotropic energy**

$$\frac{\delta^2}{2}\int_\Omega \left(\frac{f_{0'}(\varphi)}{\epsilon^2} - \Delta\varphi\right)^2 \, d\Omega$$

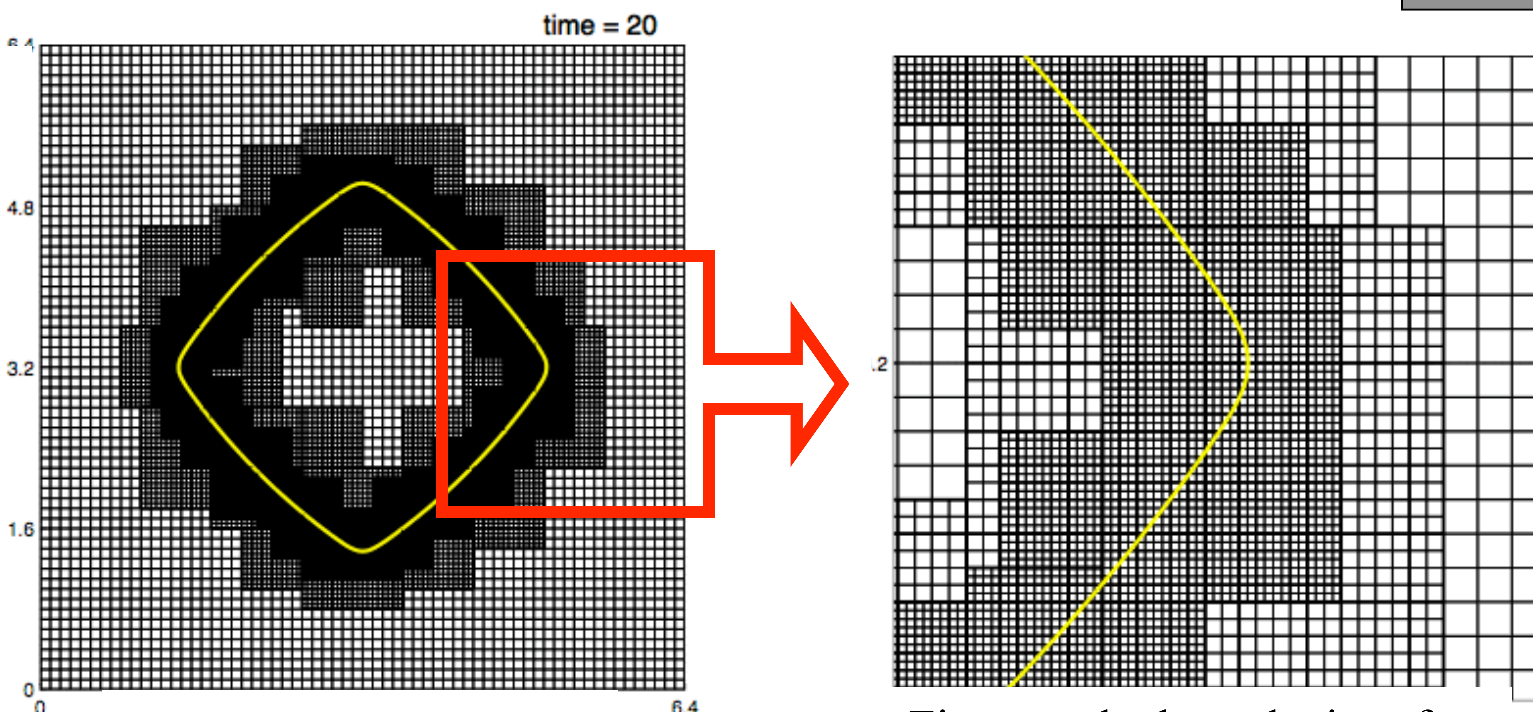
DeGiorgi, 1991;
Du, Liu, Wang, 2004

$$\frac{\partial \varphi}{\partial t} = \frac{1}{\epsilon^2}\nabla\cdot(M(\varphi)\nabla\mu)$$

Numerical Analysis



Adaptive, Nonlinear Multigrid, Finite Difference Method



Two level of refinement. Finer mesh along the interface

2^{nd} order accurate in time and space

Wise, et al, 2007

Is there any **Natural** way to address the anisotropy?

Extended Cahn-Hilliard Model

Cubic Symmetry

$$f(\varphi,\nabla\varphi,\nabla^2\varphi) = f_0 + \frac{1}{2}\sum_{ij}\kappa_{ij}\frac{\partial\varphi}{\partial x_i}\frac{\partial\varphi}{\partial x_j}$$

$$+\sum_{ijkl}\bar{\gamma}_{ijkl}\frac{\partial^2\varphi}{\partial x_i\partial x_j}\frac{\partial^2\varphi}{\partial x_k\partial x_l}$$

Abinandanan et al., 2001

$$+\sum_{ijkl}\bar{\lambda}_{ijkl}\frac{\partial^2\varphi}{\partial x_i\partial x_j}\frac{\partial\varphi}{\partial x_k}\frac{\partial\varphi}{\partial x_l}+\sum_{ijkl}\bar{\alpha}_{ijkl}\frac{\partial\varphi}{\partial x_i}\frac{\partial\varphi}{\partial x_j}\frac{\partial\varphi}{\partial x_k}\frac{\partial\varphi}{\partial x_l}$$

$$E(\varphi) = \int_\Omega\Big(f_0(\varphi)+\kappa\,|\nabla\varphi|^2+\bar{\gamma}_{ijkl}\varphi_{ij}\varphi_{kl}+\bar{\lambda}_{ijkl}\varphi_{ij}\varphi_k\varphi_l+\bar{\alpha}_{ijkl}\varphi_i\varphi_j\varphi_k\varphi_l\Big)d\Omega$$

$$\varphi_i = \partial\varphi/\partial x_i \qquad \varphi_{ij} = \partial^2\varphi/\partial x_i\partial x_j$$

ECH for Cubic Crystals

$$(\bar{\gamma},\bar{\lambda},\bar{\alpha}) \sim \delta^2(\gamma,\lambda,\alpha)$$

$$E(\varphi) = \int_\Omega \Big(f_0(\varphi) + \frac{\epsilon^2}{2} |\nabla\varphi|^2$$

$$+\frac{\delta^2}{2}\Big(\gamma_{11}(\Delta\varphi)^2 + 2(\gamma_{12}-\gamma_{11})\varphi_{11}\varphi_{22} + 4\gamma_{44}\varphi_{12}^2$$

$$+\lambda_{11}|\nabla\varphi|^2\,\Delta\varphi + (\lambda_{12}-\lambda_{11})(\varphi_{11}\varphi_2^2 + \varphi_{22}\varphi_1^2) + 4\lambda_{44}\varphi_{12}\varphi_1\varphi_2$$

$$+\alpha_{11}|\nabla\varphi|^4 + 2(\alpha_{12}+2\alpha_{44}-\alpha_{11})\varphi_1^2\varphi_2^2\Big)\Big)d\Omega$$

$$\mu = f_{0'}(\varphi) - \epsilon^2 \nu + \delta^2\Big(\gamma_{11}\Delta\nu + 2(\gamma_{12}+2\gamma_{44}-\gamma_{11})\omega_{12}$$

$$+2(\lambda_{44}-\lambda_{12})(\varphi_{11}\varphi_{22}-\omega^2)$$

$$-6\alpha_{11}(\varphi_1^2\varphi_{11}+\varphi_2^2\varphi_2) - 2(\alpha_{12}+2\alpha_{44})(\varphi_1^2\varphi_{22}+\varphi_2^2\varphi_{11}+4\varphi_1\varphi_2\varphi_{12})\Big)$$

$$\nu = \Delta\varphi,\ \ \omega_{12} = \partial^2\omega/\partial x_1\partial x_2,\ \ \omega = \varphi_{12} = \partial^2\varphi/\partial x_1\partial x_2$$

ECH Model

- The biggest advantage is having **well posed** model and **no need to regularize the energy**.
- The model can be used in **energy stable schemes: Energy splits** into purely convex and concave pieces.
- The energy is always **non-increasing in time**, **regardless of the time step size**

$$E(\varphi^{n+1}) \leq E(\varphi^{n})$$

Energy Stable Scheme

$$E_c = \int_\Omega \Big(\frac{1}{4}\varphi^2(1-\varphi)^2 + \frac{\varphi^2}{8} + \frac{\epsilon^2}{2} |\nabla\varphi|^2$$

$$+\frac{\delta^2}{2}\Big(\gamma_{11}(\varphi_{11}^2+\varphi_{22}^2) + 4\gamma_{44}\varphi_{12}^2 + \gamma_{12}(\varphi_{11}+\varphi_{22})^2\Big) d\Omega$$

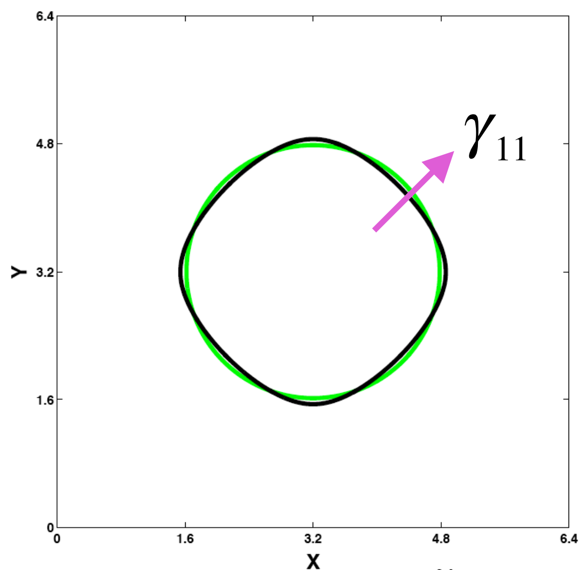
$$E_e = \int_\Omega \Big(\frac{\varphi^2}{8} + \frac{\delta^2}{2}\gamma_{12}(\varphi_{11}^2+\varphi_{22}^2)\Big) d\Omega$$

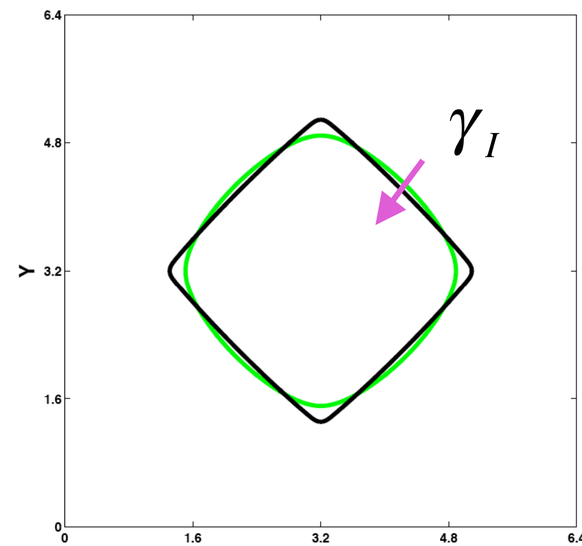
$$\boxed{\gamma_{11}, \gamma_{44}, \gamma_{12} > 0}$$

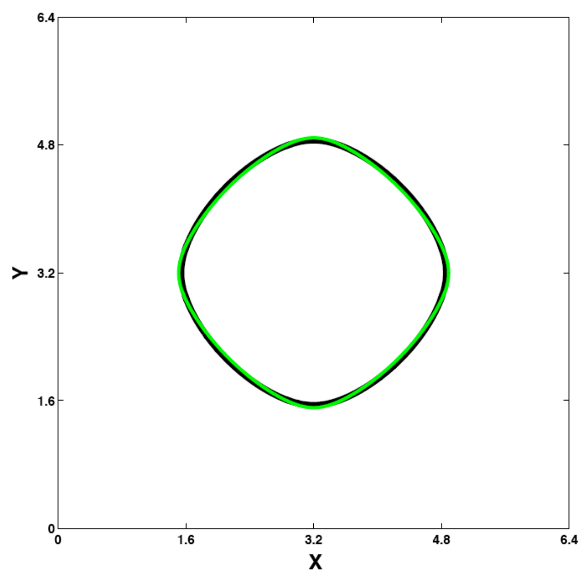
Numerical Results

Are the so many Coefficients?

Effect of Coefficients







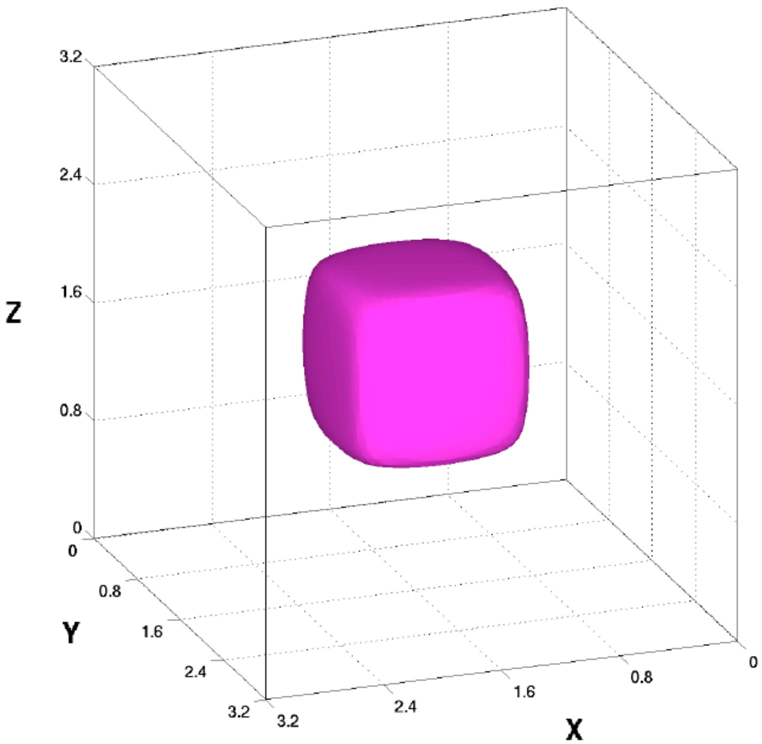
$$R_\gamma = \gamma_I / \gamma_{11}$$

$$\gamma_I = 2(\gamma_{12} + 2\gamma_{44} - \gamma_{11})$$

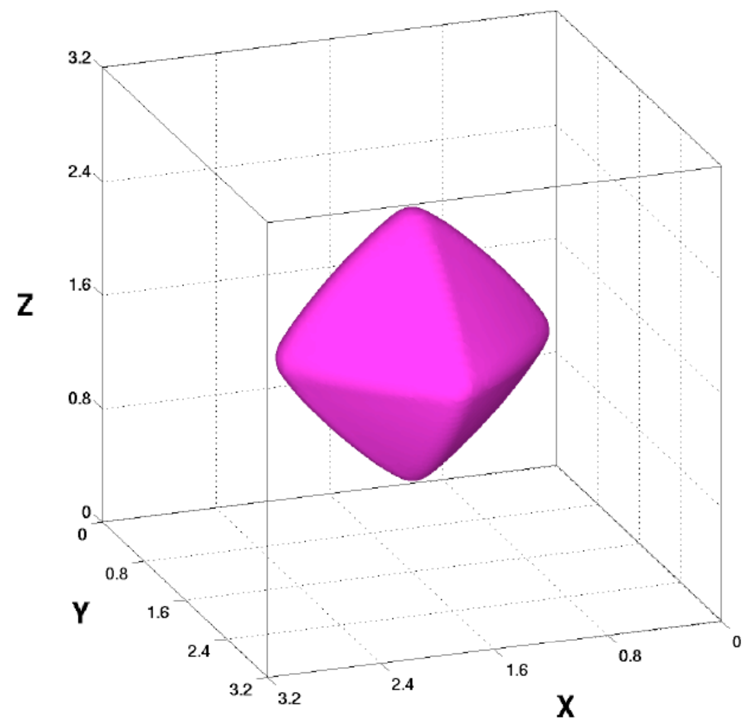
$$\delta = 0.1$$
$$\epsilon = 0.001$$
$$h = 0.1$$
$$s = 0.001$$

γ

Numerical Results in 3D



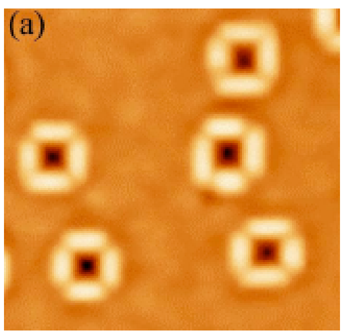
(a) $\gamma_m = -1.4$

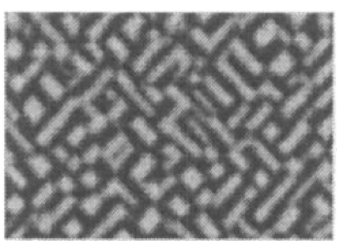


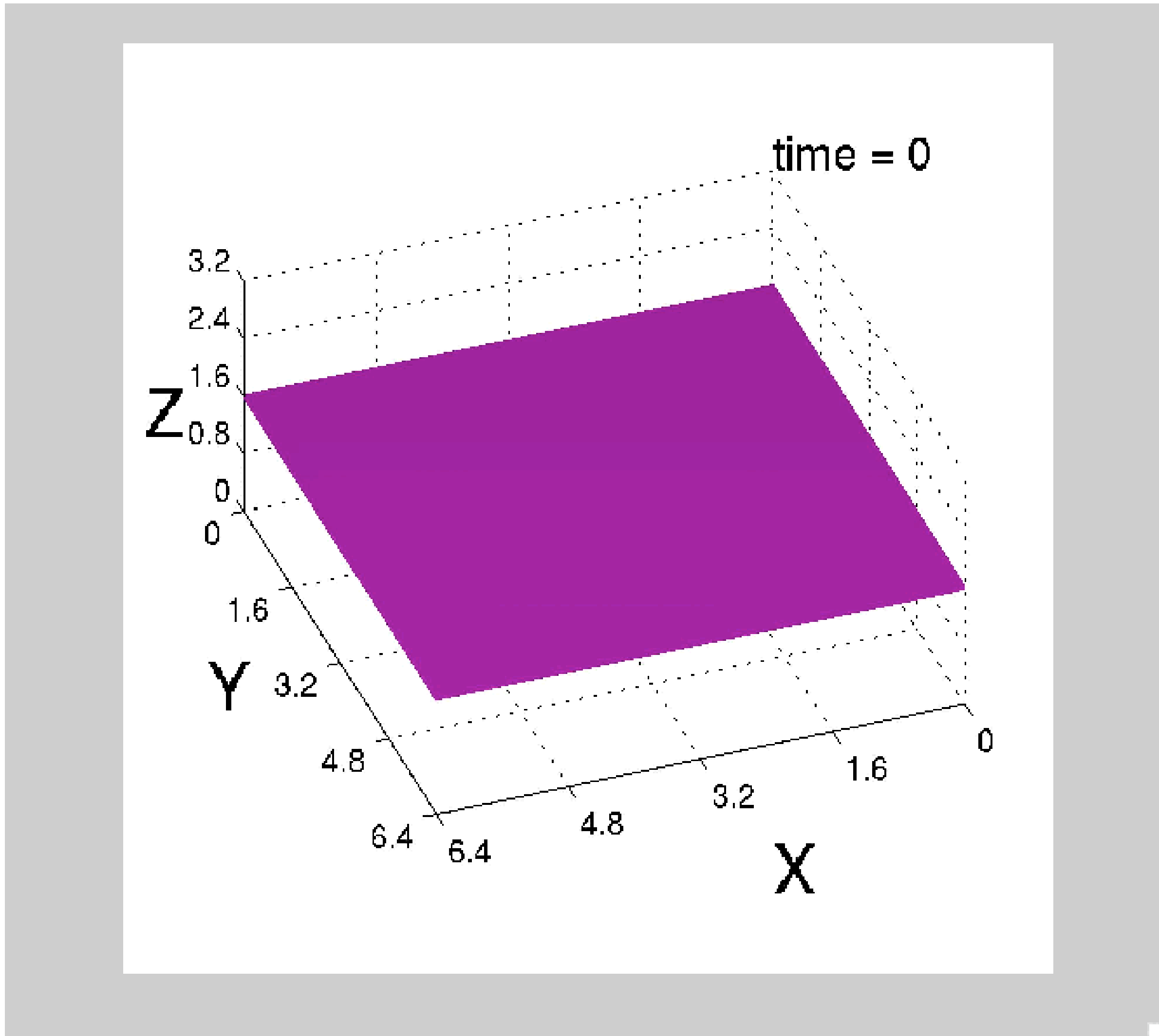
(b) $\gamma_m = 1.4$

3D Evolution for flat Interface

$\{105\} < 100 >$







$M = 1$

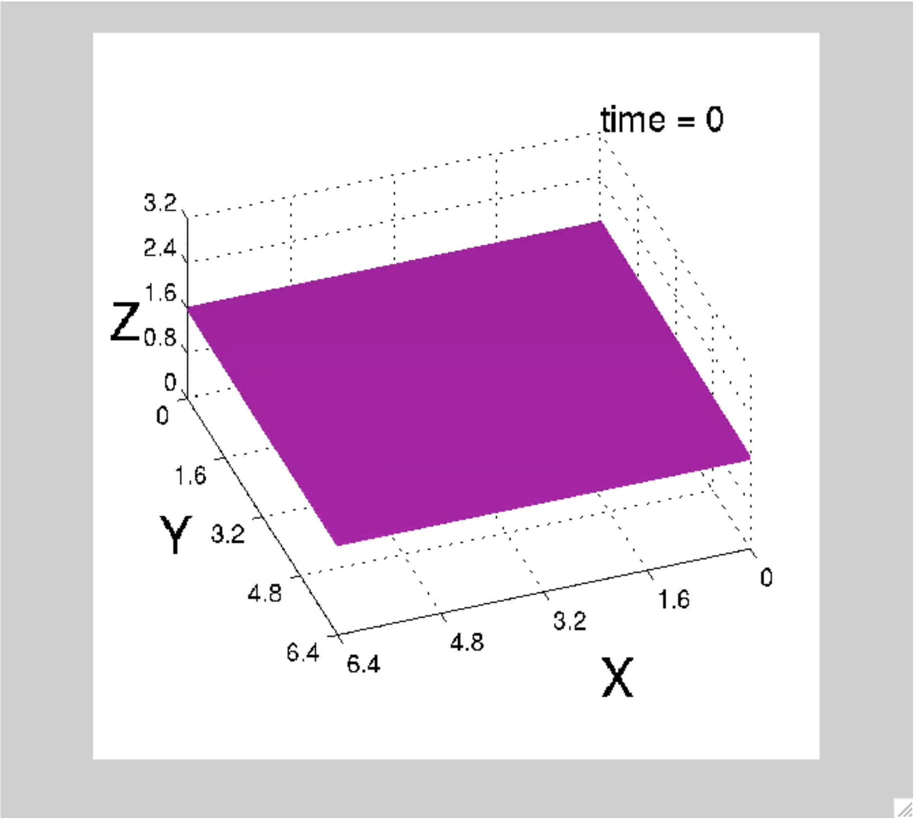
$\gamma_{11} = 1$

$\gamma_m = 1.4$

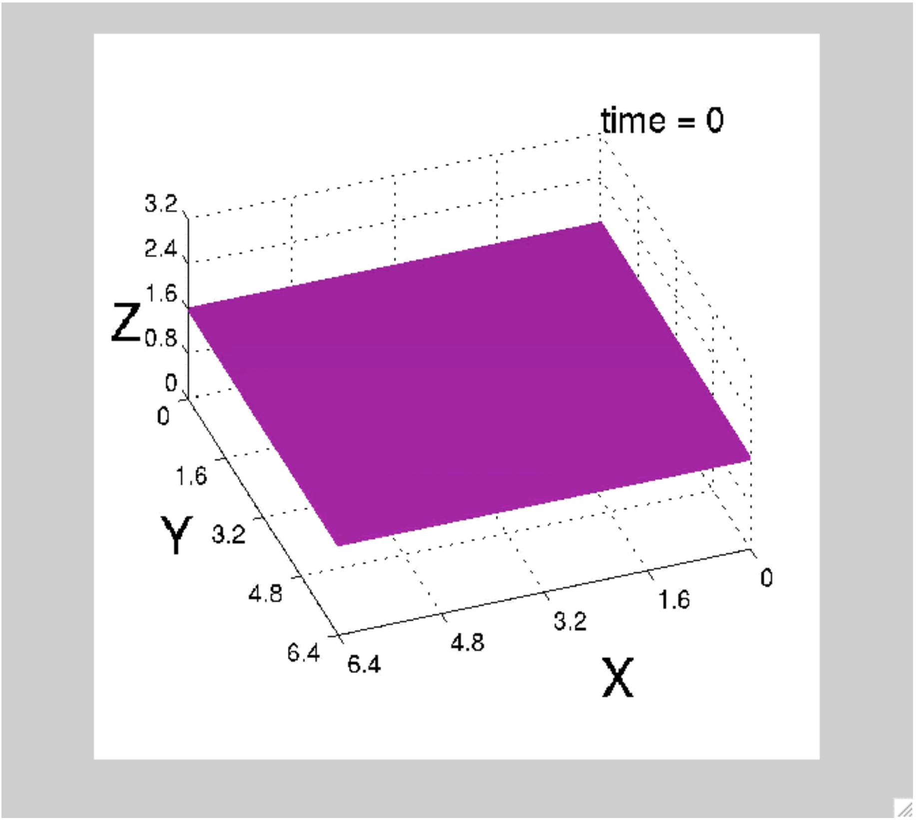
$\{111\}$

$< 110 >$

Effect of Mobility

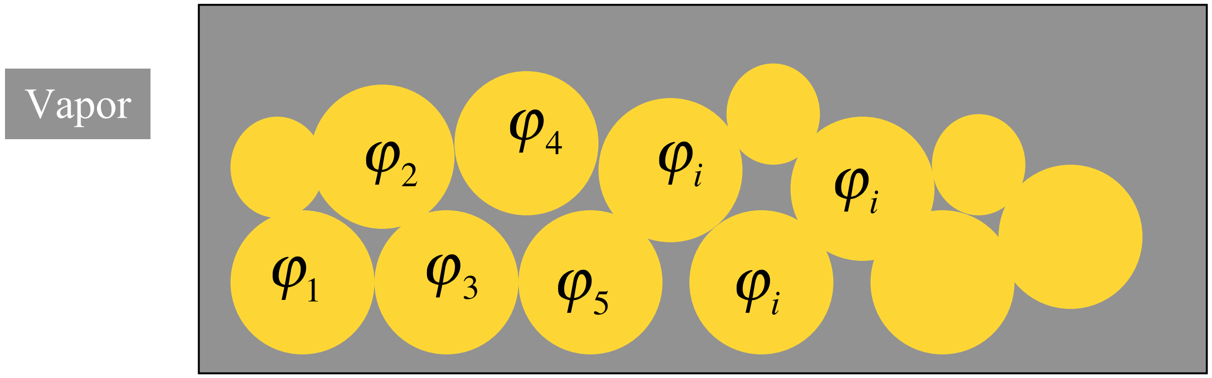


$M = 50$



$M = 1$

Sintering



$$\sum \varphi_i = cte$$

Thank You