# Condensed Matter Physics

## Superalloy and Phase field theories

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# Diffusion

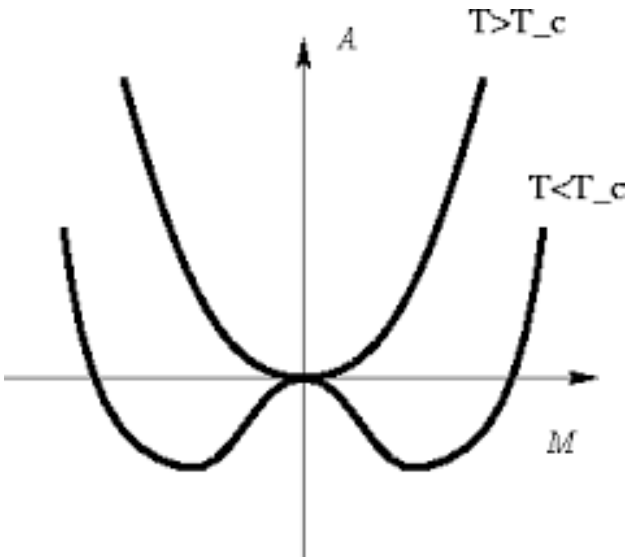
$$\frac{\partial c(r,t)}{\partial t} = \nabla \left\{ M \nabla \frac{\delta G}{\delta c(r,t)} \right\}$$

$$G = \iiint \left[ g_0(c) + \frac{\beta}{2} (\nabla c)^2 \right] \mathrm{d}^3 r$$

# Magnetism Landau theory

Phenomenological $F(M)$ relation that is invariant for $M \longleftrightarrow -M$

$$\frac{F}{V} = f_0 + A(T)M^2 + \frac{B(T)}{2}M^4$$




$$A(T) = a(T - T_c), \qquad B = const > 0$$

# Ginzburg-Landau theory

Energy of the domain wall

$$F = F_0 + \int \left[ A(T)M^2 + \frac{B(T)}{2} M^4 + l^2 a(\bigtriangledown M)^2 \right] dV$$

In equilibrium

$$\frac{\delta F}{\delta M} = 0$$

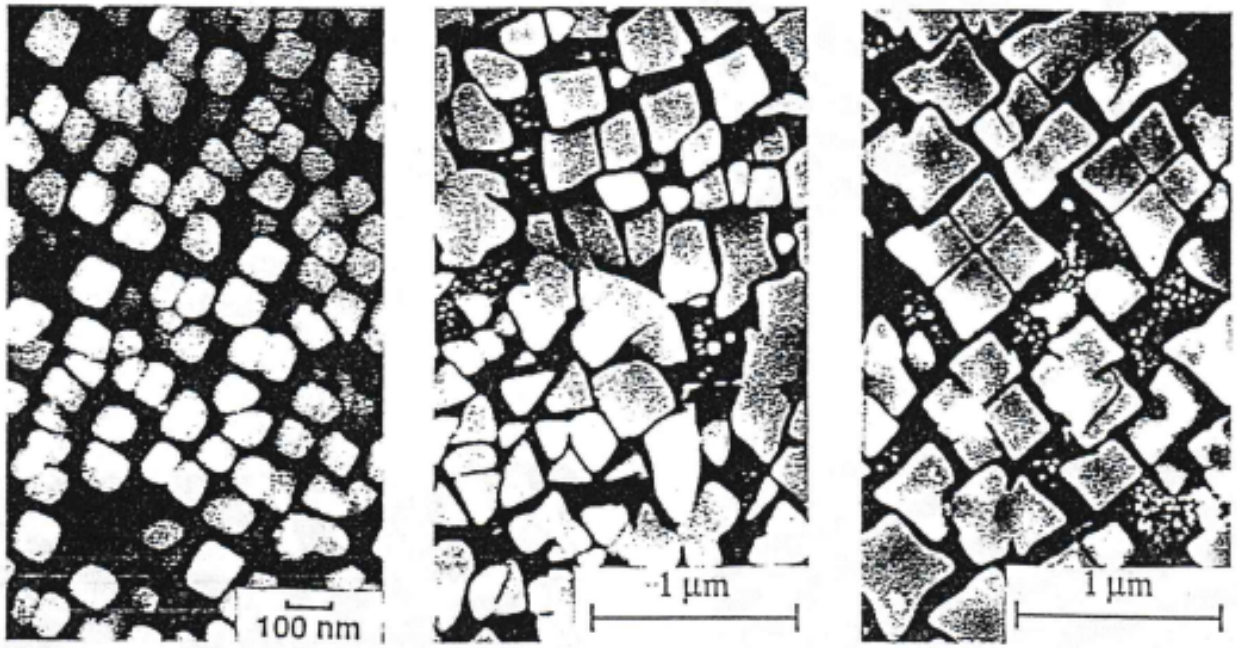
Close to equilibrium

$$\frac{\partial M}{\partial t} = -D \frac{\delta F}{\delta M}$$

Allen-Chan equation, order parameters $\psi_p$

$$\frac{\partial \psi_p}{\partial t} = -\hat{M}_{pq} \frac{\delta F}{\delta \psi_q}$$

# $Ni_3Al$ superalloy



# $Ni_3Al$ superalloy

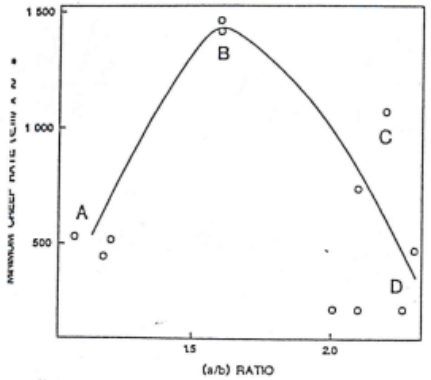



Figure 1 - The correlation between the minimum creep rate $\dot{\varepsilon}_m$ and the aspect ratio a/b of the rafted $\gamma'$ particles.


b) Region B;

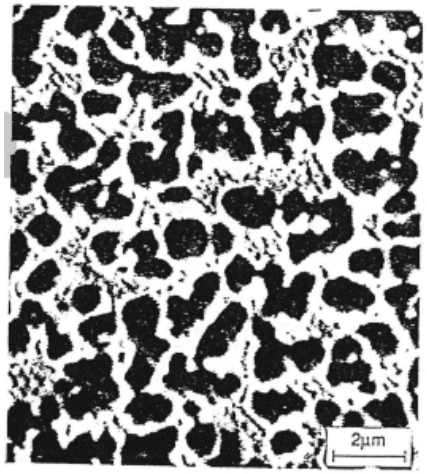



Figure 2 - Different morphological


c) Region C;

# $Ni_3Al$ superalloy

Structural parameter

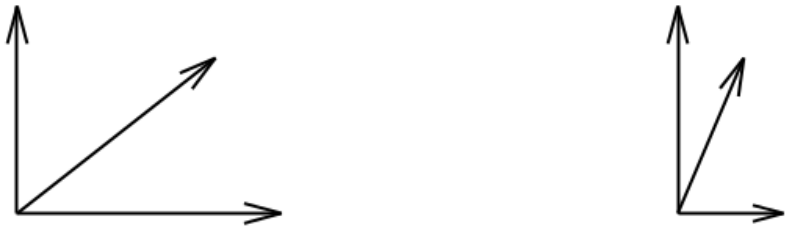


*Figure:* cubic phase — $\eta'$ tetragona phase

$\eta_i = \frac{a}{a_0} - 1$: structural parameter ($i = 1, 2, 3$)

$$\frac{\partial c(r,t)}{\partial t} = M\nabla^2 \frac{\delta F}{\delta c(r,t)}$$

$$\frac{\partial \eta_p(r,t)}{\partial t} = -\hat{L}_{pq} \frac{\delta F}{\delta \eta_q(r,t)} \qquad (p, q = 1, \ldots)$$

At local equilibrium

$$\frac{\delta F}{\delta \eta} = 0 \tag{1}$$

# $Ni_3Al$ superalloy

The equations are deterministic
We add noise

$$\frac{\partial c(r,t)}{\partial t} = M\nabla^2 \frac{\delta F}{\partial c(r,t)} + \xi(r,t)$$

$$\frac{\partial \eta_p(r,t)}{\partial t} = \hat{L}_{pq} \frac{\delta F}{\partial \eta_q} + \xi_p(r,t)$$

with (fluctuation dissipation theorem)

$$\langle \xi(r,t), \xi(r',t') \rangle = -2k_B T M \nabla^2 \delta(r-r')\delta(t-t')$$

$$\langle \xi_p(r,t), \xi(r',t) \rangle = 2k_B T \hat{L}_{pq} \delta_{pq} \delta(r-r')\delta(t-t')$$

Form of free energy

$$F = \iiint \left[ \frac{1}{2}\alpha_{ij}\nabla_i c \nabla_j c + \frac{1}{2}\sum_{p=1}^{N} \beta_{ij}\nabla_i \eta_p \nabla_j \eta_p + f(c, \eta_1, \ldots \eta_N) \right] \mathrm{d}^3 r$$

# $Ni_3Al$ superalloy

$$
\begin{aligned}
f(c,\eta_1,\eta_2,\eta_3) \quad = \quad & A_1(c) + \frac{A_2(c)}{2}(\eta_1^2+\eta_e^2+\eta_3^2) + \\
& \frac{A_3(c)}{4}(\eta_1^4+\eta_2^4+\eta_3^4) + \frac{A_4(c)}{4}(\eta_1^2+\eta_e^2+\eta_3^2)^2 + \\
& \frac{A_5(c)}{6}\eta_1^2\eta_2^2\eta_3^2 + \frac{A_6(c)}{6}(\eta_1^6+\eta_2^6+\eta_3^6) + \\
& \frac{A_7(c)}{6}(\eta_1^2+\eta_e^2+\eta_3^2)^3 + \dots
\end{aligned}
$$

Simplest possible case
Minima

$$\eta_1 = \eta_2 = \eta_3 = 0$$

$$\eta_1 = \pm\eta_0, \qquad \eta_2 = 0, \qquad \eta_3 = 0$$

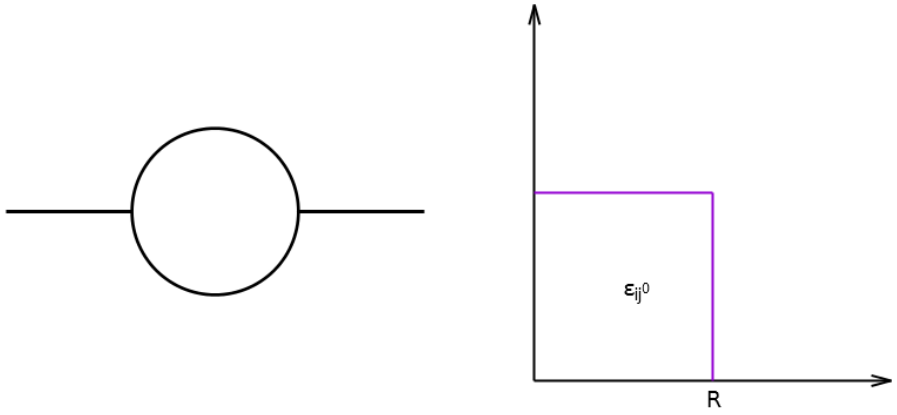
$$\eta_2 = \pm\eta_0, \qquad \eta_1 = 0, \qquad \eta_3 = 0$$

$$\eta_3 = \pm\eta_0, \qquad \eta_2 = 0, \qquad \eta_1 = 0$$

# $Ni_3Al$ superalloy

$$f(c,\eta_1,\eta_2,\eta_3) = \frac{1}{2}A_1(c-c_1)^2 + \frac{1}{2}A_2(c-c_2)(\eta_1^2+\eta_2^2+\eta_3^2) - \frac{1}{4}A_3(\eta_1^4+\eta_2^4+\eta_3^4) + \frac{1}{6}A_4(\eta_1^2+\eta_2^2+\eta_3^2)^2$$

Adding elastic energy




$$\varepsilon_{ij}^0 = \varepsilon_{ij}^{00}\Theta(\vec{r})$$

# $Ni_3Al$ superalloy

We can introduce

$$\varepsilon^0_{ij} = (c(\vec{r}) - c_2)\varepsilon^{00}_{ij}$$

$$\varepsilon^1_{ij} = \sum \eta^2_p(r)\varepsilon^{00}_{ij}(p)$$

with this the elastic energy density

$$\frac{1}{2}\varepsilon_{ij}L_{ijkl}\varepsilon_{kl}$$

with

$$\varepsilon_{ij} = \varepsilon^0_{ij} + \varepsilon^1_{ij}$$

Numerical method

$$\frac{\partial \tilde{c}(\vec{k},t)}{\partial t} = -Mk^2\left\{\frac{\delta F}{\delta c}\right\}_k + \tilde{\xi}(\vec{k},t)$$

$$\frac{\partial \tilde{\eta}_p(\vec{k},t)}{\partial t} = -L_{pq}\left\{\frac{\delta F}{\delta \eta_q}\right\}_k + \tilde{\xi}(\vec{k},t)$$

# $Ni_3Al$ superalloy

$$\langle \xi(\vec{k},t), \xi(\vec{k}',t') \rangle = 2k_B TMk^2 N \delta_{k,k'} \delta(t-t')$$

$$\langle \xi(\vec{k},t), \xi(\vec{k}',t') \rangle = 2k_B TL_{pq} \delta_{pq} N \delta_{k,k'} \delta(t-t')$$

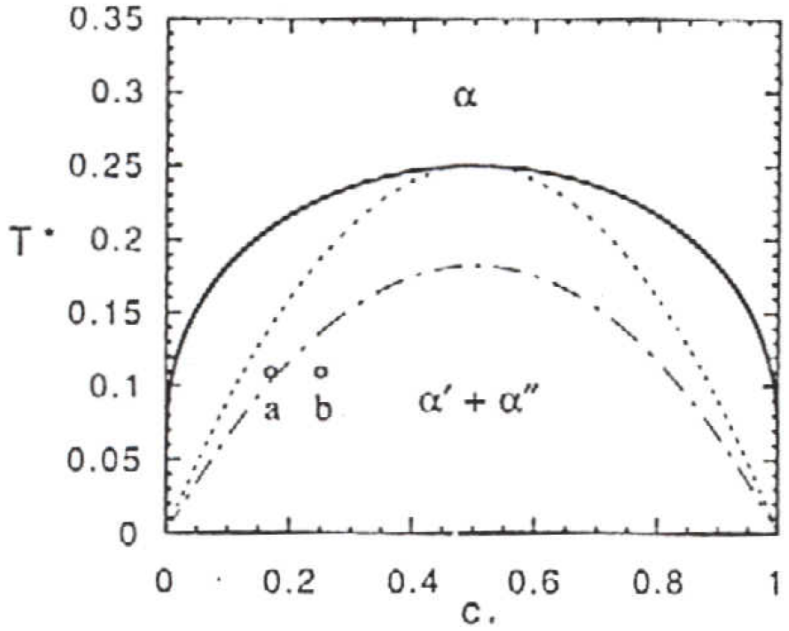



*Figure:* Phase diagram of the model system. The thick line, dotted line, and dot-dashed line represent the miscibility gap, spinodal congruent order $\leftrightarrow$ disorder transition lines, respectively. $T^*$ is the reduced temperature and $c$ is the composition.

# $Ni_3Al$ superalloy

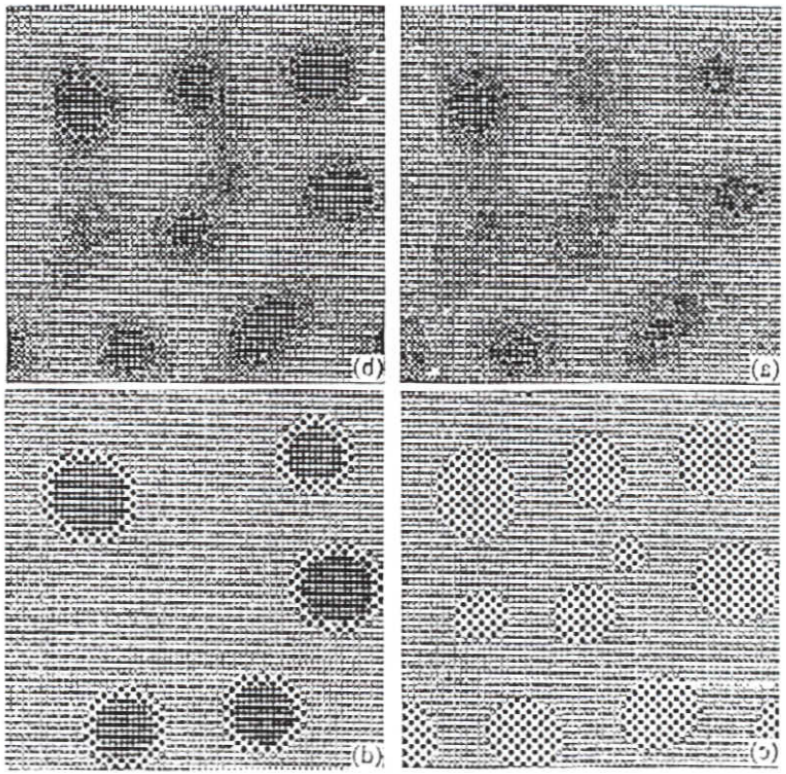



*Figure:* Temporal evolution of occupation probabilities for an alloy with a composition $c = 0.175$. (a) $\tau = 370$; (b) $\tau = 460$; (c) $\tau = 470$; (d) $\tau = 800$. Different values of occupation probabilities are represented by shades of gray. The completely dark shade represents $n(r) = 1.0$ and the completely white shade represents $n(r) = 0.0$.

# $Ni_3Al$ superalloy

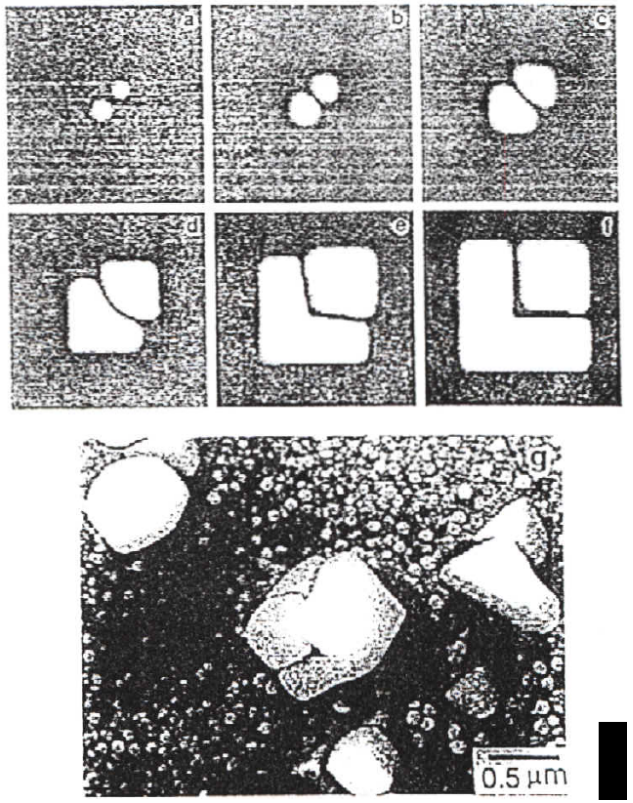



*Figure:* (a)-(f) Formation of a typical ”split” pattern through shape transition and spatial rearrangement of two growing coherent ordered particles which are ”out-of-phase” with respect to each other, (a)-(f) correspond to $\tau = 0,\ 5,\ 20,\ 100,\ 500$. (g) SEM image of a similar particle configuration in Ni-Co-Al-Ti (Courtesy of Y. S. Yoo and D. Y. Yoon [1]).

# $Ni_3Al$ superalloy

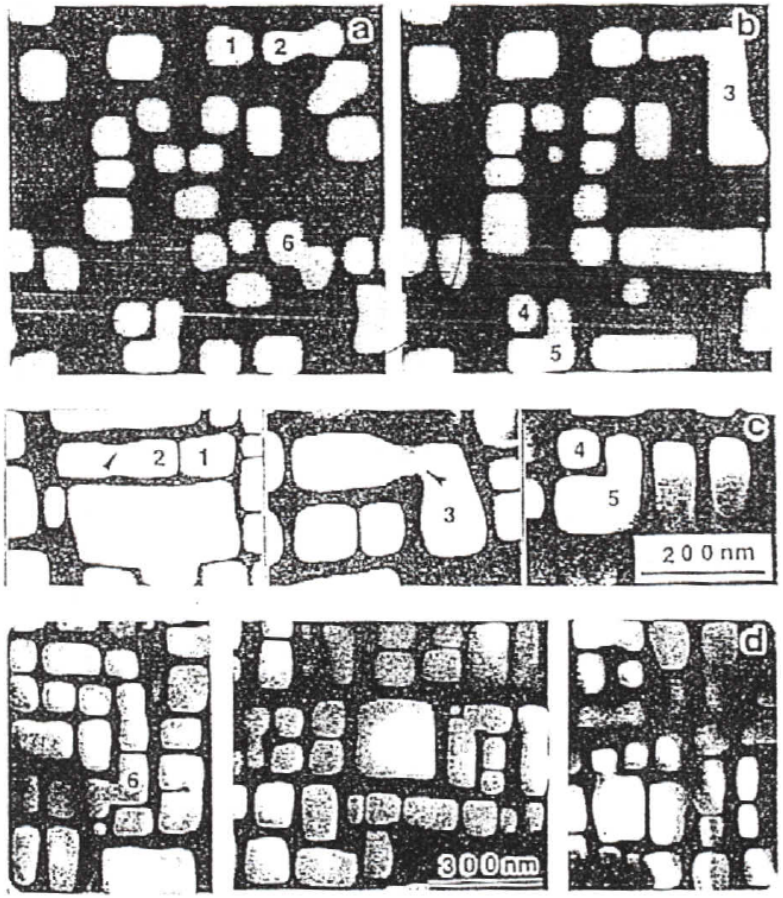



*Figure:* Comparison between the simulation predictions and experimental observations. (a)-(b) Repeats of Fig. 6 (c) and (d). (c)-(d) Dark field TEM images showing the aligned precipitates witl ”odd” shapes in Ni9.5Al-5.4Mo (Courtesy of G. Kostorz [8]).

# Solidification

Early models:

Two fields, concentration $c$, solid liquid phase order parameter $\phi$

$$\frac{\partial \phi}{\partial t} = -M_\phi \frac{\delta F}{\delta \phi} + \xi$$

$$\frac{\partial c}{\partial t} = \bigtriangledown \left[ M_c \bigtriangledown \frac{\delta F}{\delta c} \right] + \xi_c$$

The free energy has the form

$$F = \int \left[ \frac{\alpha}{2} (\bigtriangledown \phi)^2 + \frac{\beta}{2} (\bigtriangledown c)^2 + g(\phi, c, T ...) \right] dV$$

The function $f$ has one or 2 minima depending on the temperature
Generalization for multi components and phases is straightforward.

# Solidification

Recent approach: adding an orientation field $\Theta$
The model of Warren et. al (2003)

$$F = \int \left[ \frac{\epsilon}{2}(\vartheta - \Theta)|\bigtriangledown \phi|^2 + \eta(\phi)|\bigtriangledown \Theta|^2 + H(\phi)|\bigtriangledown \Theta| + \frac{\beta}{2}(\bigtriangledown c)^2 + g(\phi, c, T...) \right] dV$$

Evolution equations:

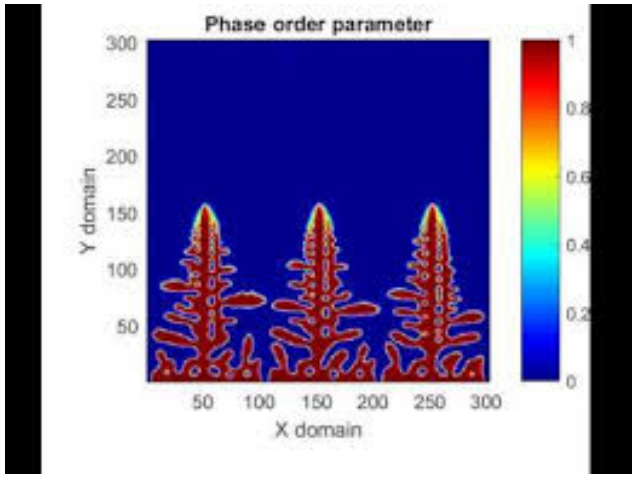
$$\frac{\partial \phi}{\partial t} = -M_\phi \frac{\delta F}{\delta \phi} + \xi_\phi = M_\phi \left[ \bigtriangledown \left( \frac{\partial f}{\partial \bigtriangledown \phi} \right) - \frac{\partial f}{\partial \phi} \right] + \xi_\phi$$

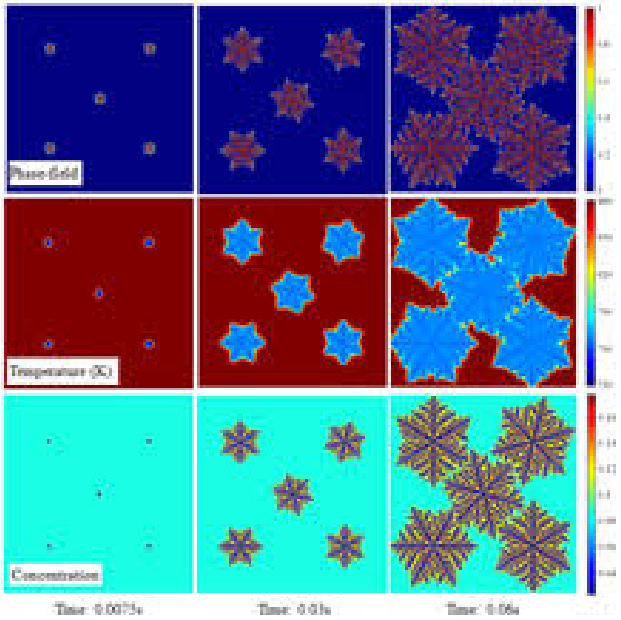
$$\frac{\partial c}{\partial t} = \bigtriangledown \left[ M_c \bigtriangledown \frac{\delta F}{\delta c} \right] + \xi_c = \bigtriangledown \left\{ Dc(c-1) \bigtriangledown \left[ \left( \frac{\partial f}{\partial c} \right) - \left( \frac{\partial f}{\partial \bigtriangledown c} \right) \right] \right\} + \xi_c$$

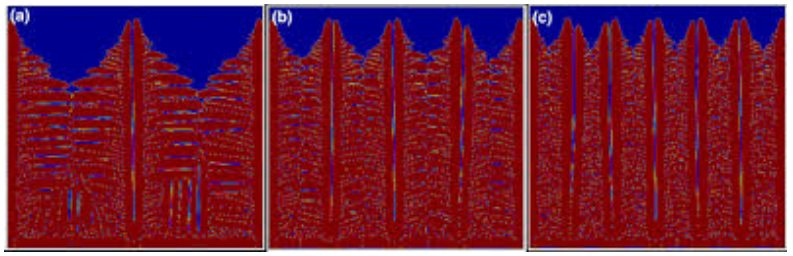
$$\frac{\partial \Theta}{\partial t} = -M_\Theta \frac{\delta F}{\delta \Theta} + \xi_\Theta = M_\Theta \left[ \bigtriangledown \left( \frac{\partial f}{\partial \bigtriangledown \Theta} \right) - \frac{\partial f}{\partial \Theta} \right] + \xi_\Theta$$

# Solidification

Results:



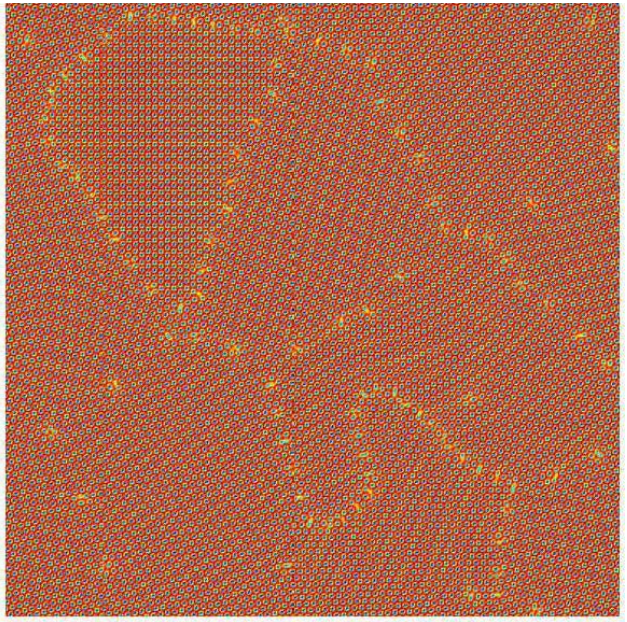
# Phase field crystal

Free energy:

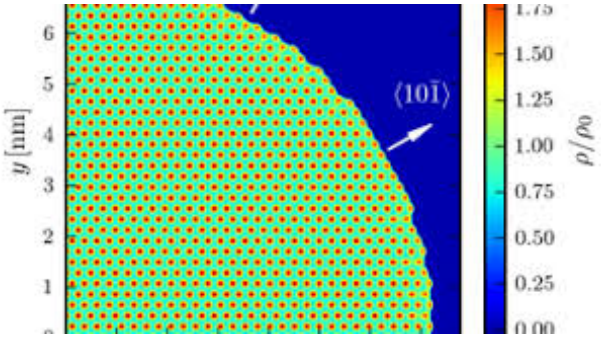
$$F = \int \left[ \frac{1}{2} n(-\beta + (k_0^2 + \nabla^2)^2) n + \frac{a}{4} n^4 \right] dV$$

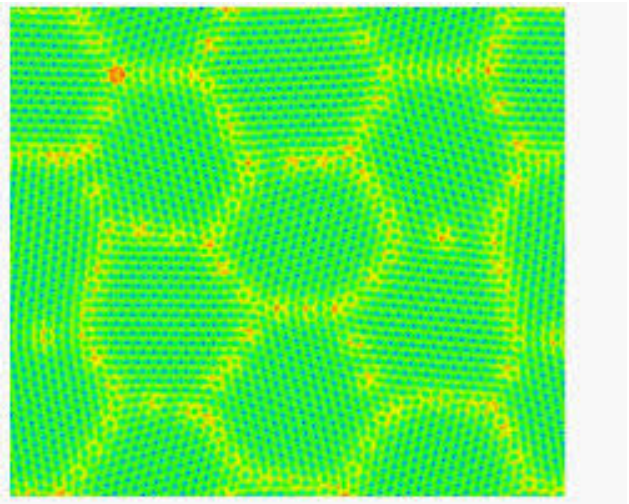
Conserved quantity

$$\frac{\partial n}{\partial t} = M \triangle \frac{\delta F}{\delta n}$$



# Phase field crystal



# Superconductivity, Ginzburg Landau theory

$$F = F_0 + \int \left[ a(T)|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m}|(-i\hbar \bigtriangledown -2e\underline{A})\psi|^2 + \frac{B^2}{2\mu} \right] dV$$

where $a(T) = a_0(T - T_c)$
Equilibrium

$$\frac{\delta F}{\delta \psi} = 0 \quad \frac{\delta F}{\delta \underline{B}} = 0$$

$$a(T)\psi + \beta|\psi|^2\psi + \frac{1}{2m}(-i\hbar \bigtriangledown -2e\underline{A})^2\psi = 0$$

$$\bigtriangledown \times \underline{B} = \mu_0 \underline{j}; \quad \underline{j} = \frac{2e}{m} Re\{\psi^*(-i\hbar \bigtriangledown -2e\underline{A})\psi\}$$