

Phase Field Models

Microstructures and Their Evolution

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4' 33" is a ... composition by American experimental composer **John Cage** (1912 - 92).

It was composed in 1952 for any instrument (or combination of instruments).

The score instructs the performer not to play the instrument during the entire duration of the piece.

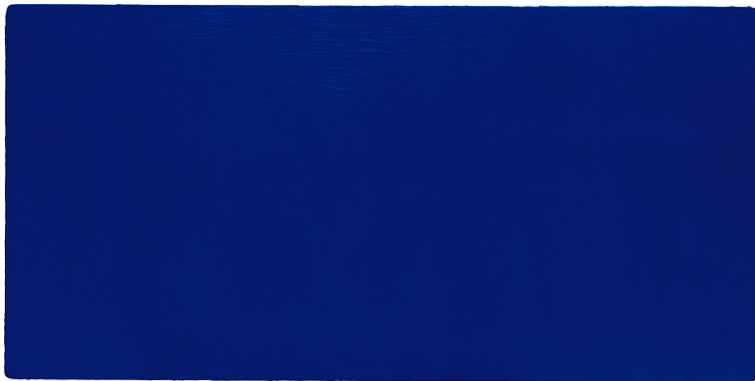
Source: Wikipedia



Yves Klein: IKB 79

Source: Tate Online

www.tate.org.uk



Yves Klein: IKB 81

Source: Yves Klein Archives

www.yveskleinarchives.org/

Art with "microstructure"

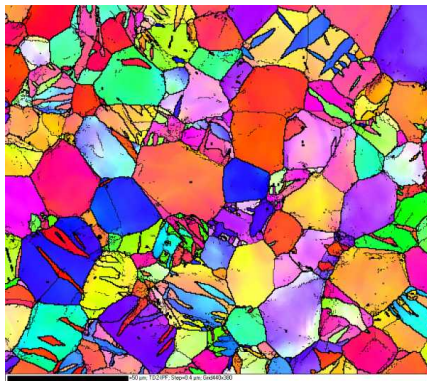


Hans Hofmann

Source: Photos of Abstract Art

www.photosofabstractart.com/

Microstructural "art"

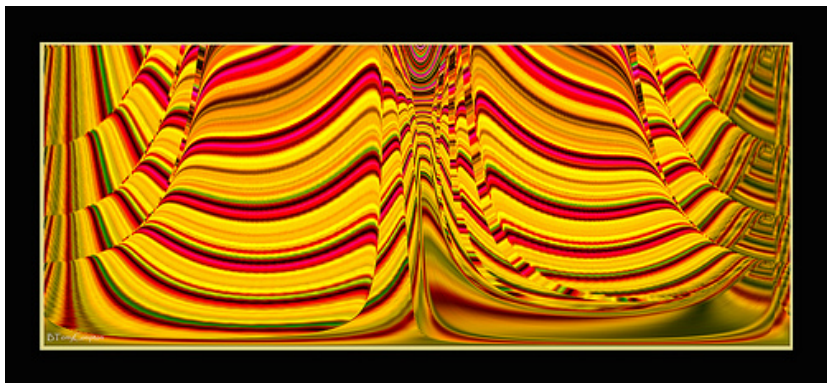


Xi-Ya Fang, Monash University

Source: Monash Universityt

mcem.monash.edu.au/assets/images/gallery/7001f3-09.jpg

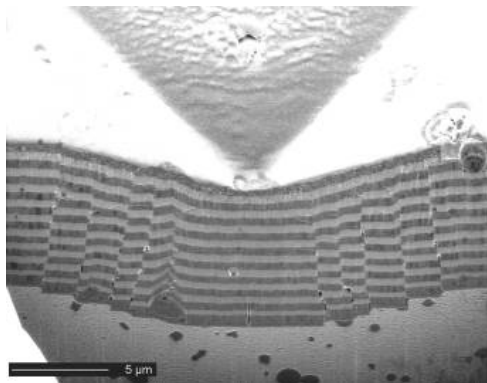
Art with "microstructure"



bterrycompton on Flickr

farm8.staticflickr.com/7023/6708508023_913b35b086.jpg

Microstructural "art"



Vikram Jayaram et al, IISc

Microstructures are everywhere

Optical microscopy: 1 - 100 μm .

Electron microscopy: Down to 10 nm.

Mesoscale: Large compared to atomic sizes and small compared to what our eyes can see.

Computational modeling has contributed much to our understanding of how they form and evolve.

- 1 **Continuum theories:** emphasis on analytical solutions
- 2 **Computational models**
 - **Atomistic models:** Molecular dynamics, Monte Carlo
 - **Continuum models:** Phase field models

Early continuum models

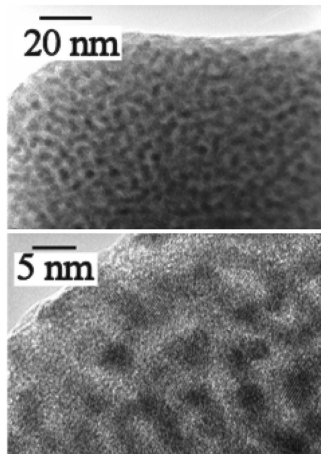
Emphasis on

- Analytical solutions.
- **Isolated features**. Specifically, their **shape**, or the dominant length scale.
 - Spherical, ellipsoidal, plate-like or rod-like particles
 - Dendrites:
 - Alternating lamellae: lamellar spacing
 - Spinodal: Maximally growing composition fluctuation.

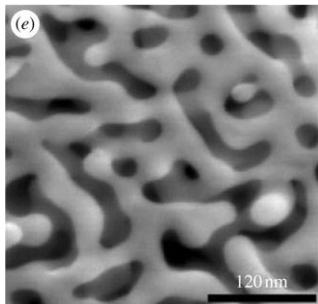
Studies of evolution of multiple features were restricted to simple shapes

e.g. Lifshitz-Slyozov-Wagner theory of coarsening of spherical particles.

Spinodal microstructures

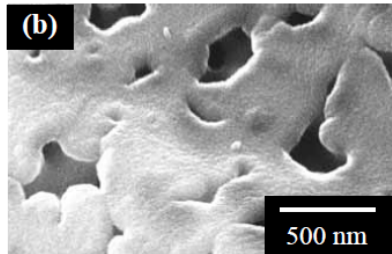
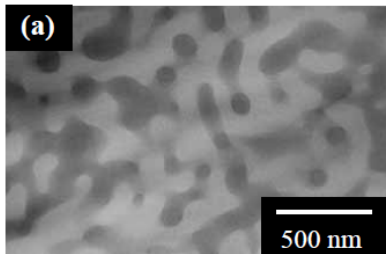


A. Chiasera et al (SPIE Newsroom, 2011)



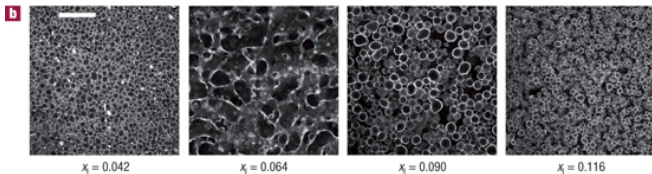
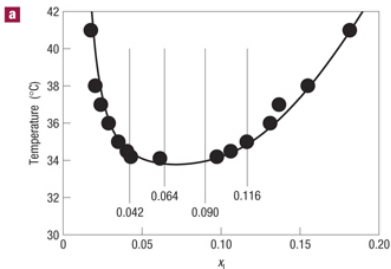
Erlebacher et al (2001)

Porous Glass



M. Suzuki et al, J. Phys. Conf. Ser. (2009)

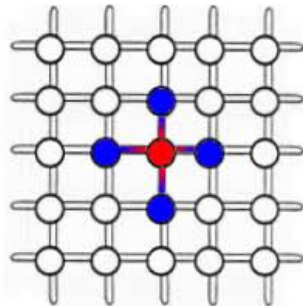
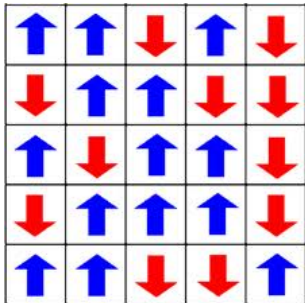
Miscibility Gap



Phase diagram of 2,6-lutidine-water system
E.Herzig, University of Edinburgh

PhD Thesis (2008), Nature Materials (2007)

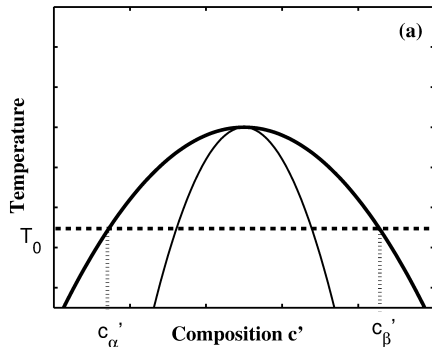
Ising model: Monte Carlo simulations



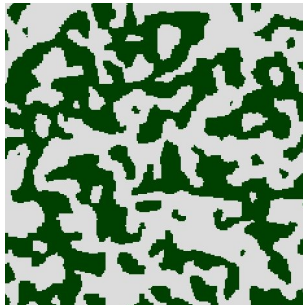
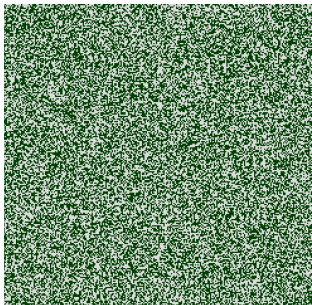
Magnet: Salvatore Torquato, Phys. Bio. (2011) - Magnet Alloy: Iyad Obeid (obeidlab.blogspot.com)

Miscibility Gap

- Nearest neighbour bonds
- e_{AA} , e_{BB} and e_{AB}
- Miscibility gap when $e_{AB} > (e_{AA} + e_{BB})/2$
- High Temperature: homogeneous alloys
- Low temperature: Co-existence of *A*-rich and *B*-rich phases



Ising model: Monte Carlo simulations



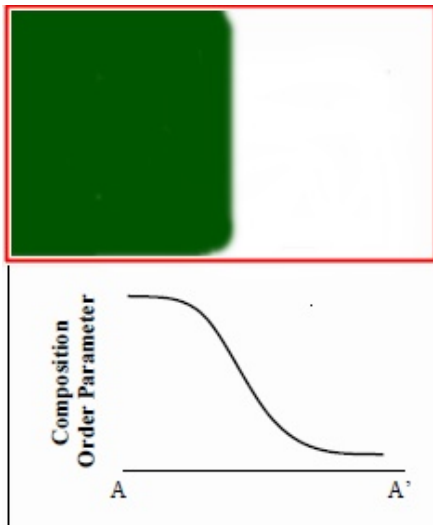
Dave Johnson

Web applet in HTML 5 (dtjohnson.net/projects/ising)

Coarse graining



Compositionally diffuse Interface



Cahn-Hilliard Model

$$F = N_v \int_V [f_o(c) + \kappa |\nabla c|^2] dV$$

F = The total free energy of the system

$f_o[c(x)]$ = Free energy density at location x
(depends on the local composition)

κ = Gradient energy coefficient

... Let's look at the details.

Free energy functional

Start with:

$$F = N_v \int_V f(\mathbf{r}) dV$$

Free energy per molecule, $f(\mathbf{r})$, must depend not only on the local composition, but also on composition derivatives.

$$f(\mathbf{r}) = f(c, p_i, q_{ij} \dots)$$

$$p_i = \partial c / \partial x_i$$

$$q_{ij} = \partial^2 c / \partial x_i \partial x_j$$

Taylor series expansion of $f(c, p_i, q_{ij})$

$$f(c, p_i, q_{ij}) = f_o(c) + L_i p_i + \kappa_{ij}^{(1)} q_{ij} + \frac{1}{2} \kappa_{ij}^{(2)} p_i p_j + \dots$$

$$f_o(c) = f(c = c, p_i = 0, q_{ij} = 0, \dots)$$

$$L_i = \left[\frac{\partial f}{\partial p_i} \right]_{(c,0,0)}$$

$$\kappa_{ij}^{(1)} = \left[\frac{\partial f}{\partial q_{ij}} \right]_{(c,0,0)}$$

$$\kappa_{ij}^{(2)} = \left[\frac{\partial^2 f}{\partial p_i \partial p_j} \right]_{(c,0,0)}$$

Symmetry arguments

Centre of symmetry: energy due to p_i and $-p_i$ must be the same.

$$L_i = 0;$$

Cubic symmetry (or, isotropy):

$$\kappa_{ij}^{(1)} = \kappa_1 \delta_{ij}$$

$$\kappa_{ij}^{(2)} = \kappa_2 \delta_{ij}$$

$$f(c, p_i, q_{ij}) = f_o(c) + \kappa_1 q_{ii} + \frac{1}{2} \kappa_2 p_i p_i$$

or,

$$f(c, p_i, q_{ij}) = f_o(c) + \kappa_1 \nabla^2 c + \frac{1}{2} \kappa_2 |\nabla c|^2$$

Divergence theorem

$$\int_V (k_1 \nabla^2 c) dV = - \int_V \left[\frac{\partial k_1}{\partial c} \right] |\nabla c|^2 + \int_S [(k_1 \nabla c) \cdot \mathbf{n}] dS$$

We now have the final form for the total free energy, F , for a system with a non-uniform composition field $c(\mathbf{r})$:

Cahn-Hilliard Model: Energy

$$F = N_V \int_V \left[f_0(c) + \kappa |\nabla c|^2 \right] dV$$

with

$$\kappa = - \frac{\partial k_1}{\partial c} + \frac{\kappa_2}{2}$$

Equilibrium interface width

Cahn-Hilliard Model: Energy

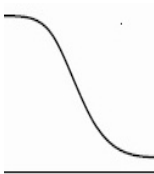
$$F = N_v \int_V [f_o(c) + \kappa |\nabla c|^2] dV$$

Too sharp



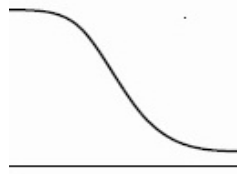
$\kappa |\nabla c|^2$ is too high

Just right



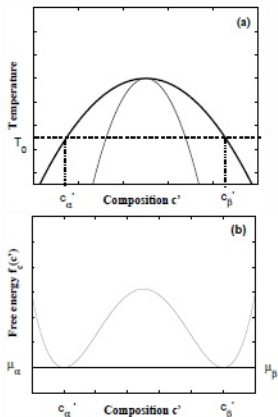
Minimizes F

Too wide



$f_o(c)$ is too high

Interfacial energy and width



$$\sigma = N_v \int_{-\infty}^{\infty} [\Delta f_0 + \kappa |\nabla c|^2] dx$$

where

$$\Delta f_0 = f_0(c) - (1 - c)\mu_A - c\mu_B$$

Cann and Hilliard show that:

$$\sigma \propto [\kappa \Delta f_0]^{1/2}$$

$$w \propto \left[\frac{\kappa}{\Delta f_0} \right]^{1/2}$$

Diffusion

Diffusive flux, \mathbf{J} :

$$\mathbf{J} = -M \nabla \mu$$

Diffusion potential, $\mu = (\mu_B - \mu_A)$:

$$\mu = \frac{\delta F}{\delta c}$$

Atomic mobility, M

Continuity equation:

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J} = \nabla \cdot [M \nabla \mu]$$

Cahn-Hilliard equation

For constant mobility, M :

Cahn-Hilliard Model: Kinetics

$$\frac{\partial c}{\partial t} = M \nabla^2 \mu$$

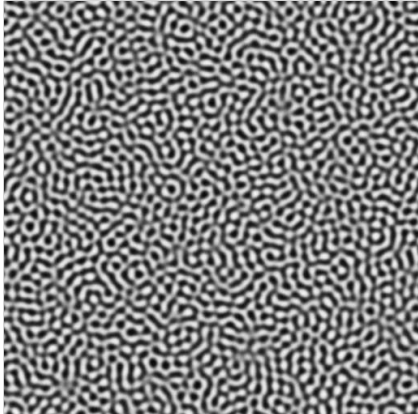
where:

$$\mu = \frac{\delta F}{\delta c} = \frac{\partial f_c}{\partial c} - 2\kappa \nabla^2 c$$

With composition, c , scaled so that $c_\alpha = 0$ and $c_\beta = 1$, the simplest approximation for $f_o(c)$ (double well potential) is:

$$f_o(c) = A c^2 (1 - c)^2$$

Spinodal decomposition: Microstructural evolution



Simulation procedure

Discretize space using a regular lattice (grid). and start with an initial composition field $c(\mathbf{r}, t = 0)$. Typically, a uniform composition (say, $c = 0.5$) with a small random fluctuation added to it.

- 1 Solve a discretized version of the Cahn-Hilliard equation numerically to go from $c(\mathbf{r}, t)$ to $c(\mathbf{r}, t + \Delta t)$.
Any suitable numerical procedure will do. We use a Fourier transform technique.
- 2 Go back to Step 1!

Store the composition field every once in a while for post-simulation data analysis and visualization.

A quick recap

- Focus on the interfaces.
Contrast with: analytical theories which focus on isolated features in simple geometries; e.g., growth of spherical particles, lamellar growth, onset of dendrite formation, etc.
- Phase field models, at their simplest, are models for the energy and dynamics of interfaces.
- Figure out what the interfaces do, where they go, without any explicit tracking of interfaces.
Contrast with: sharp interface models which tie themselves into numerical knots.
- Topological events – coalescence or splitting of microstructural features – are handled gracefully.
- Follow a transformation from the beginning to the very late stages.
Contrast with: analytical theories that examine one (small, amenable) part of a phenomenon. e.g. Nucleation, growth or coarsening.

Simulations: A framework

- 1 Define a **configuration**
- 2 Define an **energy** for the configuration
- 3 **Kinetics**: Define a rule (an elementary step) that takes the system from one configuration to the next.

Simulation framework

Classical molecular dynamics:

- 1 **Configuration:** Position and velocity of each atom
- 2 **Energy:** Sum of potential and kinetic energies of all the atoms
- 3 **Kinetics:** Solve Newton's laws of motion for each particle to go to the next step.

Monte Carlo simulation of Ising alloys:

- 1 **Configuration:** Identity of the atom at each site i
- 2 **Energy:** Ising Hamiltonian. Typically, sum of all the (nearest neighbour) bonds
- 3 **Kinetics:** a randomly chosen atoms exchanges its position with a randomly chosen neighbour (Atom exchange mechanism).

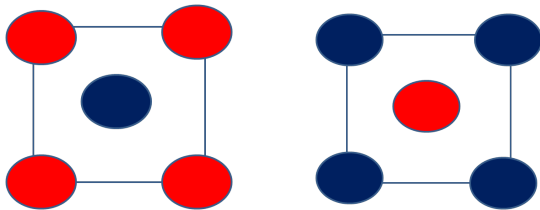
- 1 **Configuration:** Composition field, $c(\mathbf{r}, t)$, defined at every grid point
- 2 **Energy:** $F = \int [f_o(c) + \kappa |\nabla c|^2] dV$
- 3 **Kinetics:** The Cahn Hilliard equation (essentially, a modified diffusion equation)

Questions?

A second canonical model

A model for a non-conserved order parameter.

Atomic order:

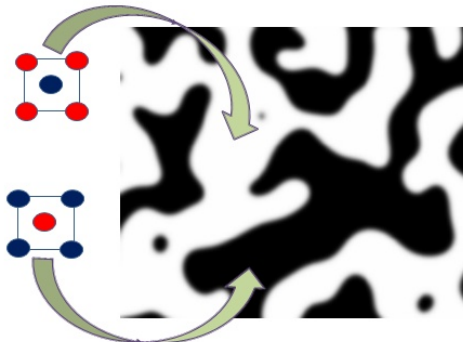


- Ferromagnetic domains in an Ising magnet
- Alloy analogue: Ordered domains

Non-conserved order parameter field $\eta(\mathbf{r}, t)$

Define a long range order parameter η that takes a value of 1 in the first variant and -1 in the second variant.

Interfaces (which, in this case, are called antiphase boundaries) are where η exhibits gradients.



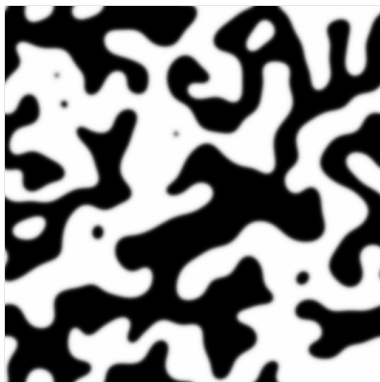
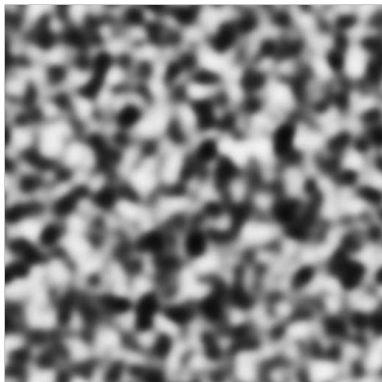
- 1 **Configuration:** $\eta(\mathbf{r}, t)$
- 2 **Energy:** Similar to the Cahn-Hilliard model, define the total free energy as a functional of $\eta(\mathbf{r}, t)$:

$$F = \int_V \left[f_\eta(\eta) + \kappa_\eta |\nabla\eta|^2 \right] dV$$

- 3 **Kinetics:** Increment the order parameter if such an increment decreases the system free energy:

$$\frac{\partial\eta}{\partial t} = -L \frac{\delta F}{\delta\eta}$$

Simulations of the Cahn-Allen model



A quick recap

- In the physics literature, the Cahn-Allen equation is also called the time-dependent Ginsburg-Landau – TDGL – equation.
- Another name: Model A, in the classification by Halperin and Hohenberg (Cahn-Hilliard model is classified as Model B).
- The two canonical models have been combined in numerous creative ways to adapt them to study of a wide variety of phenomena.
- It is easy to study effects due to elastic stresses, an electric field, etc. using these models (and others derived from them).
Typically, the additional effects are incorporated adding one or more energy terms into the equation for the free energy functional.

Where do we go from here?

- 1 Algorithm for solving Cahn-Hilliard and Cahn-Allen equations numerically.
- 2 Elastic stress effects: Precipitate shape changes, alignment, thin film instability
- 3 Grain boundary effects on spinodal decomposition
- 4 Grain boundary grooving and grain vertex pitting
- 5 With an emphasis on model development that takes into account specific details. e.g., enhanced atomic mobility at grain boundaries.

And before we end ...

Some of Yves Klein's "monochromes" have some (micro)structure.



As for John Cage, his 4' 33" still had some (micro)structure to it: it was divided into three movements, lasting 30", 2' 23" and 1' 40".