can you guess what systems that produced these patterns?
can you guess what systems that produced these patterns?

Langmuir monolayer – dipolar forces (simulation)

Turing pattern in chemical system (experiment)

Labyrinthine pattern in chemical system (experiment)

Ising model (simulation)
Self-assembled systems show similar patterns on macroscopic scales.

Langmuir monolayers

More complex three-dimensional patterns.
*time evolution of spatial patterns*

what is the main difference between the top and bottom set of pictures?
time evolution of spatial patterns

what is the main difference between the top and bottom set of pictures?

non-conserved order parameter

conserved order parameter
Dynamics of Self-Organized and Self-Assembled Structures

most material can be found in: R. C. Desai and R. Kapral, (Cambridge, 2009)

-- Introduction; binary mixtures and phase separation; order parameter; free energy and Landau expansion; free energy functional; interfacial tension

-- phase separation kinetics; Langevin Model A; Langevin Model B

-- interface dynamics at late times

-- propagating fronts; transverse front instabilities

-- competing interactions: systems with long range repulsive interactions; front repulsion

-- active materials

-- self-propelled particles
order parameter and free energy

example: binary mixture phase separation

A and B species, concentration $c = \frac{N_a}{(N_a + N_b)} = \frac{N_a}{N_0}$

off-critical quench

critical quench

Stable (single phase)

(b)

(a)

Unstable (spinodal decomposition)

Metastable (nucleation)

$l_1 + l_2$

T

c

Fe-Al alloy
mean field theory

\[ f(c, T) = k_B T \left( c \ln(c) + (1 - c) \ln(1 - c) + \chi c(1 - c) \right) \]

- coordination number
- configurational (entropic) term
- interaction term

\[ \chi = \frac{\tilde{z}}{k_B T} \left[ \epsilon_{AB} - \frac{1}{2} (\epsilon_{AA} + \epsilon_{BB}) \right] \]

thermodynamic variable conjugate to \( c \) is the chemical potential

\[ \mu = \left( \frac{\partial f}{\partial c} \right)_T \]

thermodynamic space: \( (c, \mu, T) \)

equation of state: \( \mu = \mu(c, T) \)

at the critical point

\[ \left( \frac{\partial \mu}{\partial c} \right)_{T=T_c} = 0, \quad \left( \frac{\partial^2 \mu}{\partial c^2} \right)_{T=T_c} = 0, \quad \mu_c = \mu(c_c, T_c) \]

\[ c_c = \frac{1}{2}, \quad \chi_c = 2 \]
Landau expansion

expand the free energy in a power series in $c^* = c - c_c$

$$f(c) = f(c_c) + \left( \frac{\partial f}{\partial c} \right)_{c_c}^c c^* + \frac{1}{2} \left( \frac{\partial^2 f}{\partial c^2} \right)_{c_c}^c c^{*2} + .$$

$$\left( \frac{\partial f}{\partial c} \right)_T = k_B T \left[ \ln \frac{c}{1-c} + \chi (1 - 2c) \right] \longrightarrow 0 \quad \text{at} \quad c_c = \frac{1}{2}$$

$$\left( \frac{\partial^2 f}{\partial c^2} \right)_T = k_B T \left[ \frac{1}{c} + \frac{1}{1-c} - 2 \chi \right] \longrightarrow 2k_B T (\chi_c - \chi) \quad \text{at} \quad c_c = \frac{1}{2}$$

$$\chi \sim \frac{1}{T}, \quad 2k_B T (\chi_c - \chi) \sim T \left( \frac{1}{T_c} - \frac{1}{T} \right) \sim \frac{T - T_c}{T_c} \rightarrow 0 \quad \text{as} \quad T \rightarrow T_c$$
Landau expansion of free energy

\[ f(c^*, T) = f_c + \frac{a_2}{2} c^{*2} + \frac{a_4}{4} c^{*4} + \ldots \]

\[ a_2 = a \frac{T - T_c}{T_c}, \quad a_4 > 0 \]
Landau expansion of free energy for general order parameter

general form: order parameter $\phi$

$c$ concentration

$\rho$ density

$m$ magnetization

$Q$ liquid crystal order parameter

$$f(\phi^*, T) = f_c + \frac{a_2}{2} \phi^*^2 + \frac{a_4}{4} \phi^*^4 + \ldots$$

thermodynamic space $(\phi, \left(\frac{\partial f}{\partial \phi}\right)_T, T)$

equation of state

$$\mu = \left(\frac{\partial f}{\partial \phi}\right)_T = \mu(\phi, T)$$
**Ginzburg-Landau free energy functional**

homogeneous system: free energy density

\[
f = \frac{F}{V} \quad \text{free energy}
\]

\[
\int d^d r \ f = F
\]

inhomogeneous system: \( f^* (\phi, \nabla \phi, \nabla^2 \phi, \ldots) \)

\[
\mathcal{F}[\phi(r, t)] = \int d^d r \ f^* (\phi, \nabla \phi, \nabla^2 \phi, \ldots)
\]

expand \( f \) in a power series

\[
f^* (\phi, \nabla \phi, \nabla^2 \phi, \ldots) = f(\phi) + \sum_i L_i \frac{\partial \phi}{\partial r_i}
\]

\[+ \frac{1}{2} \sum_{ij} \left[ 2 \kappa^{(1)}_{ij} \frac{\partial^2 \phi}{\partial r_i \partial r_j} + \kappa^{(2)}_{ij} \frac{\partial \phi}{\partial r_i} \frac{\partial \phi}{\partial r_j} \right] + \ldots,
\]

\[
L_i = [\partial f^*/\partial (\partial \phi/\partial r_i)]_o, \quad \kappa^{(1)}_{ij} = [\partial f^*/\partial (\partial^2 \phi/\partial r_i \partial r_j)]_o,
\]

\[
\kappa^{(2)}_{ij} = [\partial^2 f^*/\partial (\partial \phi/\partial r_i) \partial (\partial \phi/\partial r_j)]_o
\]
for an isotropic system $f$ is invariant under inversion and rotation

$L_i$ vanishes, $\kappa_{ij}^{(1)} = \kappa_1 \delta_{ij}$, and $\kappa_{ij}^{(2)} = \kappa_2 \delta_{ij}$

\[
f^*(\phi, \nabla \phi, \nabla^2 \phi, \ldots) = f(\phi) + \frac{1}{2} \kappa_2 (\nabla \phi)^2 + \kappa_1 \nabla^2 \phi + \ldots
\]

free energy functional

\[
\mathcal{F}[\phi(\mathbf{r}, t)] = \int d^d r \left[ f(\phi) + \frac{1}{2} \kappa_2 (\nabla \phi)^2 + \kappa_1 \nabla^2 \phi \right]
\]

Integrate by parts

\[
\int d^d r \kappa_1 \nabla^2 \phi = - \int d^d r \frac{\partial \kappa_1}{\partial \mathbf{r}} \cdot \nabla \phi = - \int d^d r \frac{\partial \kappa_1}{\partial \phi} (\nabla \phi)^2
\]

$\kappa \equiv \kappa_2 - 2 \frac{\partial \kappa_1}{\partial \phi}$

Ginzburg-Landau free energy functional

\[
\mathcal{F}_{GLW}[\phi(\mathbf{r}, t)] = \int d^d r \left[ f(\phi) + \frac{\kappa}{2} (\nabla \phi)^2 \right]
\]
free energy functional (continued)

expansion about the critical point \( \phi^* = (\phi - \phi_c) \)

\[
f(\phi^*) = \frac{1}{2} a_2 \phi^*^2 + \frac{1}{4} a_4 \phi^*^4
\]

free energy takes the form

\[
\mathcal{F}_{GLW}[\phi(r, t)] = \int d^d r \left[ \frac{1}{2} a_2 \phi^*^2 + \frac{1}{4} a_4 \phi^*^4 + \frac{\kappa}{2} (\nabla \phi)^2 \right]
\]

correlation length

\[
\xi = \sqrt{\kappa / |a_2|}
\]

\[
|a_2| \to 0
\]

\[
\xi \to \infty
\]
as critical point is approached
interfacial tension

where is the interface?

Gibbs equimolar dividing surface

\[
\int_{-\infty}^{z_0} dz \ (\phi(z) - \phi_+) + \int_{z_0}^{\infty} dz \ (\phi(z) - \phi_-) = 0
\]
interfacial tension (continued)

surface tension: excess surface free energy per unit area

\[ \Delta f = \begin{cases} 
(f(\phi) - f_+), & \text{for } -\infty < z < 0, \\
(f(\phi) - f_-), & \text{for } 0 < z < \infty 
\end{cases} \]

recall

\[ f(\phi) = \frac{1}{2} a_2 \phi^2 + \frac{1}{4} a_4 \phi^4 \]

\[ \frac{df}{d\phi} = 0 \rightarrow \phi_\pm = \pm \sqrt[4]{\frac{|a_2|}{a_4}} \quad \phi_- = -\phi_+ \quad f_\pm = f(\phi_\pm) \]

surface tension

\[ \tilde{\sigma} = \int_{-\infty}^{\infty} dz \left[ \Delta f + \frac{\kappa}{2} \left( \frac{d\phi(z)}{dz} \right)^2 \right] \]
Surface free energy is a minimum for the equilibrium profile

$$\frac{\delta \sigma}{\delta \phi} = 0 = \int_{-\infty}^{\infty} dz' \left[ \frac{\delta \Delta f(\phi(z'))}{\delta \phi(z)} + \frac{\kappa}{2} \frac{\delta}{\delta \phi(z)} \left( \frac{d\phi(z')}{dz'} \right)^2 \right]$$

$$0 = \int_{-\infty}^{\infty} dz' \left[ \frac{d\Delta f}{d\phi(z)} \delta(z - z') + \kappa \left( \frac{d\phi(z')}{dz'} \right) \frac{d}{dz'} \delta(z - z') \right]$$

$$0 = \frac{d\Delta f}{d\phi(z)} - \kappa \frac{d^2 \phi(z')}{dz^2}$$

or

$$\frac{d\Delta f(\phi_0)}{d\phi_0} = \kappa \frac{d^2 \phi_0}{dz^2}$$

$\phi_0$ is the equilibrium profile
multiply by \( \frac{d\phi_0}{dz} \)

\[
\frac{d\phi_0}{dz} \frac{d\Delta f(\phi_0)}{d\phi_0} = \frac{d\phi_0}{dz} \kappa \frac{d^2\phi_0}{dz^2}
\]

\[
\frac{d\Delta f(\phi_0)}{dz} = \frac{\kappa}{2} \frac{d}{dz} \left( \frac{d\phi_0}{dz} \right)^2
\]

integrate

\[
\Delta f(\phi) = \frac{\kappa}{2} \left( \frac{d\phi(z)}{dz} \right)^2
\]

substitute into surface tension equation

\[
\tilde{\sigma} = \kappa \int_{-\infty}^{\infty} dz \left( \frac{d\phi(z)}{dz} \right)^2
\]
**nonconserved and conserved order parameter dynamics**

focus on simple cases where systems can be described by a single order parameter field; accurate treatments of some real systems require several order parameters for their descriptions

*Langevin Model A – nonconserved order parameter (antiferromagnets, some chemical systems, etc.)*

equation of motion for $\phi(r, t)$

Langevin equation

$$\frac{\partial \phi}{\partial t} = -M \frac{\delta F}{\delta \phi} + \eta^*(r, t)$$

$$\langle \eta^*(r, t) \eta^*(r', t') \rangle = 2kT M \delta(r - r') \delta(t - t')$$
Model A – time-dependent Ginzburg-Landau equation

$$\frac{\delta F[\phi(r,t)]}{\delta \phi} = \frac{\delta}{\delta \phi} \int d^d r \left[ \frac{1}{2} a_2 \phi^*^2 + \frac{1}{4} a_4 \phi^*^4 + \frac{\kappa}{2} (\nabla \phi)^2 \right]$$

$$= a_2 \phi^* + a_4 \phi^*^3 - \kappa \nabla^2 \phi$$

$$\frac{\partial \phi(r,t)}{\partial t} = -M \left( a_2 \phi^* + a_4 \phi^*^3 - \kappa \nabla^2 \phi \right) + \eta^*(r,t)$$

- early times – noise important
- late times – noise can be neglected

$$\frac{\partial \phi(r,t)}{\partial t} = -M \left( a_2 \phi^* + a_4 \phi^*^3 - \kappa \nabla^2 \phi \right)$$

TDGL equation
a chemical example: bistable system: Schlögl model

\[ A \xrightleftharpoons[k_{-1}]{k_1} X, \quad 2X + B \xrightleftharpoons[k_{-2}]{k_2} 3X \]

\[ c_A = a, \quad c_B = b, \quad c_X = c \]

reaction-diffusion equation

\[ \frac{\partial c(r,t)}{\partial t} = k_1 a - k_{-1} c + k_2 b c^2 - k_{-2} c^3 + D \nabla^2 c \]

has same form as the TDGL equation

let

\[ f[c] = -k_1 a c + \frac{k_{-1}}{2} c^2 - \frac{k_2}{3} c^3 + \frac{k_{-2}}{4} c^4 \]

\[ \mathcal{F}[c(r,t)] = \int d^3r \left\{ f[c(r,t)] + \frac{1}{2} D |\nabla c|^2 \right\} \]

then RD equation can be written free energy functional form

\[ \frac{\partial c(r,t)}{\partial t} = - \frac{\delta \mathcal{F}[c(r,t)]}{\delta c(r,t)} \]
critical quench – Model A

Schlögl model

stochastic dynamics

fluctuations important at early stages if interface growth

early stage of evolution: formation of interfaces

late stage of evolution: well-defined interfaces