PATTERN FORMATION IN MESOPHASES

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KINETIC EQUATION

\[ \tau_0 \frac{\partial \psi(r, t)}{\partial t} = \epsilon \psi - \frac{\xi_0^2}{4k_0^2} \left( q_0^2 + \nabla^2 \right)^2 \psi + g_2 \psi^2 - \psi^3 \]

Stationary solution \( g_2 = 0 \)

- \( \epsilon < 0 \): \( \psi = 0 \)
- \( \epsilon > 0 \): \( \psi(\vec{r}, t) = \epsilon^{1/2} A_0 \sin(\vec{q}_0 \cdot \vec{r}) + O(\epsilon^{3/2}) \).

Stripe pattern oriented along an arbitrary \( \vec{q}_0 \).

Smectic or lamellar phase (1D crystal).

Stationary solution \( g_2 \neq 0 \)

- \( -|\epsilon_m(g_2)| < \epsilon < \epsilon_M(g_2) \): \( \psi(\vec{r}, t) = \sum_{n=1}^{6} A_n e^{i\vec{q}_n \cdot \vec{x}} + \text{c.c.} \)

Hexagonal pattern. Columnar phase (2D crystal).
ORDER AT FINITE WAVEVECTOR

Block Copolymers

[Kim, ..., de Pablo, Nealy, 2003]

Amphiphilic systems

Liquid crystalline elastomers

[Gido and Thomas, 1994]

[Forster et al. 2001]

[Dalhaimer, Discher, Lubensky, 2007]
APPLICATIONS IN NANOTECHNOLOGY

[T. Thurn-Albrecht et al., Science 290, 2126 (2000); B. Stipe et al., Nature Photonics 4, 484 (2010), exceeding 1TB/in²]

[C.T. Black, APL 2005: PS-PMMA]

[Park, Yoon, and Thomas, Polymer 2003]
DIFFERENCES WITH $q=0$ SYSTEMS

Domain coarsening

Topological defects

Pinning and structural glass

Anisotropic rheology
ENERGETICS

Order parameter

\[ \psi \propto \rho_a - \rho_b \]

Free energy

- Ohta-Kawasaki

\[
F[\psi] = \int dr \left( \frac{-\tau}{2} \psi^2 + \frac{u}{4} \psi^4 + \frac{K}{2} (\nabla \psi)^2 \right) + \frac{B}{2} \int drdr' \psi(r) G(r-r') \psi(r')
\]

with \( \nabla^2 G(r - r') = -\delta(r - r') \).

- Leibler/Swift-Hohenberg (weak segregation limit)

\[
F[\psi] = \int dr \left( \frac{-\tau}{2} \psi^2 + \frac{u}{4} \psi^4 + \frac{K}{2} \left[ (\nabla^2 + q_0^2) \psi \right]^2 \right)
\]

\( \tau \) is temperature difference with microphase separation temperature, \( q_0 \) is the characteristic wavenumber.
PHASE DIAGRAM

Study the evolution of a perturbation of $\psi_0$:

$$
\delta \psi_q(x, t) = \psi_q e^{i q \cdot x} e^{\sigma_t}
$$

Re $\sigma_q$ gives exponential growth or decay. Im $\sigma_q = -\omega_q$ gives oscillations, waves $e^{i (q \cdot x - \omega_q t)}$

Im $\sigma_q = 0 \rightarrow$ Stationary Instability
Im $\sigma_q \neq 0 \rightarrow$ Oscillatory Instability
Parabolic approximation:

For $R$ near $R_c$ and $q$ near $q_c$,

\[ \text{Re } \sigma_q = \frac{1}{\tau_0} \left[ \epsilon - \xi_0^2 (q - q_c)^2 \right] \]

\[ \epsilon = \frac{R - R_c}{R_c} \]
NONLINEARITY

Parabolic approximation:

For $R$ near $R_c$ and $q$ near $q_c$,

$$\text{Re } \sigma_q = \frac{1}{\tau_0} \left[ \epsilon - \xi_0^2 (q - q_c)^2 \right]$$

$$\epsilon = \frac{R - R_c}{R_c}$$

Near threshold separation of scales:

1. $|q_{N-} - q_{N+}| \sim \sqrt{\epsilon}$. Slow modulations around periodic solutions with $q_c$.
2. Modulations are slow: grow in a time scale $\epsilon$.
Slightly above threshold ($\varepsilon \ll 1$):

- Continuum of modes around $k_0$.
- Other symmetries: rotational invariance ...

\[
\frac{\partial \hat{\psi}(k)}{\partial t} = \left[ \varepsilon - \xi_0^2 (k - k_0)^2 \right] \hat{\psi}(k) + \ldots
\]

\[
\xi_0^2 = \frac{1}{2} \left( \frac{\partial^2 \varepsilon_c(k)}{\partial k^2} \right) \bigg|_{k_0}.
\]

$\xi_0$ is the coherence length that determines the “rigidity” of the pattern (mean field correlation length).
Assume weak distortion,

\[ \psi = A(X, Y, T)e^{ik_0x} + \text{c.c.} \]

with

\[ A(X, Y, T) = A(\epsilon^{1/2}x, \epsilon^{1/4}y, \epsilon t). \]

Ginzburg-Landau equation (in original variables),

\[ \frac{\partial A}{\partial t} = \epsilon A + \xi_0^2 \left( \partial_x - \frac{i}{2k_0} \partial_y^2 \right)^2 A - 3|A|^2 A \]
SECONDARY INSTABILITIES

Zig-zag (transverse) instability

“Wavelength selection” problem

Eckhaus (longitudinal) instability
Boundary conditions. At small $\epsilon$, they reduce the band of allowable solutions. No sharp selection.

Dynamical: front propagation. Studied in one dimension.

Set by defects (targets, grain boundaries select wavelength).

Statistical: initial conditions and domain coarsening.
DOMAIN COARSENING

- A single time dependent length $l(t)$ emerges, the linear scale of the structure.
- In the self-similar range, $t \to \infty$, $l(t) \to \infty$, and all other scales of microscopic origin become irrelevant (cf. correlation length divergence near a critical point).
- Scaling functions are introduced. For example for the domain size distribution ($R$ the linear size of a domain),

$$p(R, t) = G \left( \frac{R}{t^x} \right) \quad l(t) \sim t^x.$$

- Universality classes have been introduced according to the value of $x$
  - Purely relaxational dynamics, $x = 1/2$.
  - Relaxational dynamics with global conservation law, $x = 1/3$.
  - Binary fluids (non-variational modes), $x = 1$. 

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CURVATURE SCALING FUNCTION

Curvature distribution function

Scaled curvature distribution function
Moments of the distribution of domain curvatures,

\[ m_n(t) = \int_0^{\kappa_c(t)} d\kappa \kappa^n P(\kappa, t) \]

\[ P(\kappa, t) = t^x f(\kappa t^x) \]

**Coarsening mechanism**

- Experiments in thin films (hexagonal) \( x = 1/4 \)
- Domain wall relaxation, \( x = 1/2 \) or \( x = 1/4 \).
- Numerically: no fluctuations \( x = 1/5 \), fluctuations \( x = 1/4 \).
- Dislocation or disclination motion \( x = 1/2 \).
THE ROLE OF DEFECTS

- Large gradients (locally) - not close to equilibrium, but very slow on a microscopic scale.
- Large numbers of interacting defects: microstructure.
- Defects control slow relaxation.
ENVELOPE DESCRIPTION OF DEFECT MOTION

[Siggia and Zippelius, 1981]

Point defect in the envelope field,

$$\psi = Ae^{i\vec{k} \cdot \vec{x}} = \rho(\vec{x})e^{i\theta(\vec{x})}e^{i\vec{k} \cdot \vec{x}}.$$  

$$\oint \nabla \theta \cdot d\vec{l} = \pm 2\pi.$$  

Climb velocity is found,

$$v \propto (k - k_0)^{3/2}.$$  

Phase $\theta$ plays the role of the displacement field $u$. 
Order parameter expanded in slowly varying amplitudes:

\[ \psi = A e^{ik_0 x} + B e^{ik_0 z} + \text{c.c.} \]

where

\[ A = A(\epsilon^{1/2} x, \epsilon^{1/4} y, \epsilon^{1/4} z, \epsilon t) \]

\[ B = B(\epsilon^{1/4} x, \epsilon^{1/4} y, \epsilon^{1/2} z, \epsilon t) \]
\[ \frac{\partial A}{\partial t} = \epsilon A + \xi_0^2 \left( \partial_x - \frac{i}{2k_0} \partial_y^2 \right)^2 A - 3 |A|^2 A - 6 |B|^2 A, \]
\[ \frac{\partial B}{\partial t} = \epsilon B + \xi_0^2 \left( \partial_y - \frac{i}{2k_0} \partial_x^2 \right)^2 B - 3 |B|^2 B - 6 |A|^2 B. \]
WHY DOES A BOUNDARY MOVE?
Linear relaxation rate \( \sigma \propto q^4 \).

Nonlinear uniform translation mode,

\[
v_{gb}(t) = \left( \frac{\xi_0^2}{4k_0^2} q^4 \right) \frac{(\epsilon/4)[k_0\delta x(t)]^2}{\int_{-\infty}^{\infty} dx \left[ (\partial_x A_0)^2 + (\partial_x B_0)^2 \right]} \sim \frac{\delta x(t)^2 q^4}{\sqrt{\epsilon}} \propto \frac{\kappa^2}{\sqrt{\epsilon}}
\]

\[
v_{gb}(t) = \text{Mobility} \times \text{Time dependent driving force}
\]

If this motion dominates asymptotically, \( x = 1/3 \).
For small $\epsilon \sim 0.1$, the decoupling between slowly varying amplitudes and the phase of the lamellae already breaks down.
NON ADIABATIC EFFECTS

- Seek dominant, non-perturbative corrections to

\[
\frac{\partial A}{\partial t} = \epsilon A + \xi_0^2 \left( \partial_x - \frac{i}{2k_0} \partial_y^2 \right)^2 A - 3|A|^2 A - 6|B|^2 A
\]
\[
- \int_{x}^{x+\lambda_0} \frac{dx'}{\lambda_0} \left( A^3 e^{i2k_0 x'} + A^* e^{-4ik_0 x'} \right),
\]

\[
\frac{\partial B}{\partial t} = \epsilon B + \xi_0^2 \left( \partial_y - \frac{i}{2k_0} \partial_x^2 \right)^2 B - 3|B|^2 B - 6|A|^2 B
\]
\[
- 3 \int_{x}^{x+\lambda_0} \frac{dx'}{\lambda_0} \left( A^2 Be^{2ik_0 x'} + A^* e^{-2ik_0 x'} \right).
\]

- Assume that \( A \) and \( B \) may change over a wavelength,

\[
\int_{x}^{x+\lambda_0} dx' A^3 e^{i2k_0 x'} \approx -i e^{2iX/\sqrt{\epsilon}} A^2 \frac{\partial A}{\partial X}
\]
As $\epsilon \rightarrow 0$, interface width $\xi_0/\epsilon^{1/2} \gg \lambda_0$.

Grain boundary velocity contains a dependence on both $x$ and $X$:

$$v_{gb} \int dX \left( A_0' + B_0' \right) = T_1 + T_2 + \ldots + e^{-1/\sqrt{\epsilon}} \sin(2k_0x) \left( N_1 + N_2 + \ldots \right).$$

$$v_{gb} = \frac{\epsilon}{3k_0^2} \kappa^2 - \frac{p(\epsilon)}{D(\epsilon)} \cos(2k_0x_{gb} + \phi) \quad p(\epsilon) \sim \epsilon^2 e^{-\alpha/\sqrt{\epsilon}}$$
CONSEQUENCES OF NON ADIABATICITY

- Grain boundary located at potential minima - decoupling between grain boundary location and lamellar phase lost.
- Continuous motion in $X$, $T$ only in the limit $\epsilon \to 0$.
- Pinning forces with periodicity $1/k_0$, even in the absence of any external fields or impurities.
- Glassy states as $\epsilon$ is increased.
- Domain coarsening affected: effective exponents may depend on $\epsilon$ and on the existence of random forces.
EFFECTIVE COARSENING EXPONENTS

\[ \rho_d(t) \]

- \( \varepsilon = 0.4, F = 0.01 \) \( \varepsilon^{5/4} \)
- \( \varepsilon = 0.4, F = 0.03 \) \( \varepsilon^{5/4} \)
- \( \varepsilon = 0.15, F = 0.04 \) \( \varepsilon^{5/4} \)
- \( \varepsilon = 0.04, F = 0.05 \) \( \varepsilon^{5/4} \)
- \( \varepsilon = 0.4, F = 0 \) \(-1/5\)
- \(-1/4\)
- \(-1/3\)
- \(-1/3\)
PINNING AND BIFURCATION CHARACTER

\[ D v_{gb} = -p_{hex} \sin [2k_0 x_{gb} \sin(\theta/2)] , \]

with (Peierls force),

\[ p_{hex} \sim A_0^4 e^{-2ak_0 \sin(\theta/2)\xi} \]

Supercritical bifurcation (e.g., lamellar phase)

\[ \xi \sim 1/\sqrt{\epsilon} \quad p_{lam} \sim e^{-1/\sqrt{\epsilon}} \rightarrow 0. \]

Subcritical bifurcation (e.g., hexagonal phase)

\[ \xi \rightarrow \xi_0 = \frac{15\lambda_0}{8\sqrt{6\pi}g_2} , \quad p_{hex} \text{ finite.} \]
REVERSIBLE/HAMILTONIAN MODES

Block Copolymers

Amphiphilic systems

Liquid crystalline elastomers

[Kim, ..., de Pablo, Nealy, 2003]

[Gido and Thomas, 1994]

[Forster et al. 2001]

[Dalhaimer, Discher, Lubensky, 2007]
MESOSCOPIC REVERSIBLE STRESSES

NORMAL FLUID

- Local equilibrium in the rest frame, 
  \[ s = s(u, \rho) \quad T \frac{ds}{dt} = \frac{du}{dt} + p \frac{d1/\rho}{dt} \]
- Conservation laws (e.g., momentum density \( g = \rho v \))
  \[ \partial_t g_i = -\partial_j \sigma_{ij} \]
- Reversible stress: \( \sigma_{ij}^R = \rho v_i v_j + p \delta_{ij} \)
MESOSCOPIC REVERSIBLE STRESSES

NORMAL FLUID

- Local equilibrium in the rest frame,
  \[ s = s(u, \rho) \quad T\frac{ds}{dt} = \frac{du}{dt} + p\frac{\partial u}{\partial \rho} \]
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CAHN-HILLIARD FLUID


\[ s = s(u, \rho, \psi, \partial_i \psi) \]

\[ \sigma_{ij}^R = \rho v_i v_j + p\delta_{ij} - \frac{\partial s}{\partial (\partial_i \psi)} \partial_j \psi \]

needed so that advection of \( \psi \) does not cause entropy production.

GENERAL CASE

Reversible motion requires (Maxwell type relation)

\[ \frac{\partial \dot{\psi}}{\partial v_i} = \frac{\partial \dot{g}_i}{\partial (\partial_j \xi_j)} \quad \xi_j = \frac{\partial s}{\partial (\partial_j \psi)} \]

If \( \psi \) has a reversible current
\[ \partial_t \psi + v \cdot \nabla \psi = \ldots \frac{\partial \psi}{\partial v_i} = -\partial_i \psi \]
and non classical stresses result.

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MESOSCOPIC DISSIPATIVE STRESSES

\[ T \dot{S}_{\text{prod}} = \int d\vec{r} \left\{ - \left( J_i^\psi - v_i \psi \right) \partial_i \mu + \left( \sigma_{ij} - \sigma_R^{ij} \right) \partial_i v_j \right\} \]

Broken Symmetry incorporated in dissipative fluxes.

MESOSCOPIC DISSIPATIVE STRESSES

\[ T \dot{S}_{\text{prod}} = \int d\vec{r} \left\{ - \left( J_i^\psi - \nu_i \psi \right) \partial_i \mu + \left( \sigma_{ij} - \sigma_{ij}^R \right) \partial_i \nu_j \right\} \]

Broken Symmetry incorporated in dissipative fluxes.


Lamellar phase: uniaxial fluid

\[
J_i^{\psi D} = - [\Lambda_L q_i q_j + \Lambda_T (\delta_{ij} - q_i q_j)] \partial_j \mu \\
\sigma_{ij}^{D} = \alpha_1 q_i q_j q_k q_l D_{kl} + \alpha_4 D_{ij} \\
+ \alpha_{56} (q_i D_{kj} + q_j D_{ki}) q_k \\
D_{ij} = \partial_i \nu_j + \partial_j \nu_i
\]

Cahn-Hilliard (isotropic) fluid

\[
J_i^{\psi D} = - \Lambda q^2 \partial_i \mu \\
\sigma_{ij}^{D} = \alpha_4 D_{ij}
\]
Characteristic decay times determined by decay of transverse perturbations.

Transverse scattering intensity,

\[ S(Q) = \frac{k_B T}{\xi} \frac{Q^4 + 2(Q/\lambda)^2}{Q^4 + 2(Q/\lambda)^2} \]

For a block copolymer in weak segregation,

\[ \lambda \sim \frac{R_g N^{1/4}}{\sqrt{\epsilon}} \gg k_0^{-1} \]

ORIENTATION SELECTION UNDER SHEAR

In this low frequency formulation, both orientations are degenerate.

Uniaxial form of dissipative stress leads to viscosity contrast. Hydrodynamic instability under shear.

Extended to uniaxial viscoelasticity. Hydrodynamic instability under shear when viscoelastic contrast is appreciable.
SUMMARY

Modulated phases (mesophases) share some of the phenomenology of pattern formation and phase transition kinetics, but:

- Continuum of degenerate phases (wavelength and orientation) - wavelength and orientation selection.

- Specific classes of topological defects and motion - beyond phase boundary motion.

- Pinning, structural glasses, and non universal growth.

- New hydrodynamic models, and rich rheology (complex fluids and biological materials).