PATTERN FORMATION IN MESOPHASES

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KINETIC EQUATION

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

Stationary solution $g_2 = 0$

- $\epsilon < 0$: $\psi = 0$
- $\epsilon > 0$: $\psi(\vec{r}, t) = \epsilon^{1/2} A_0 \sin(\vec{q_0} \cdot \vec{r}) + \mathcal{O}(\epsilon^{3/2})$.

  Stripe pattern oriented along an arbitrary $\vec{q_0}$.
  Smectic or lamellar phase (1D crystal).

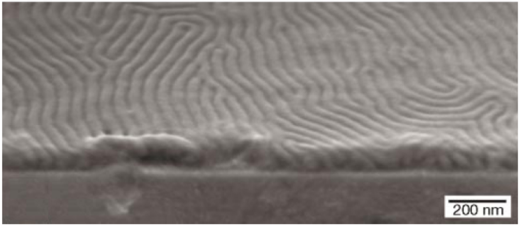
Stationary solution $g_2 \neq 0$

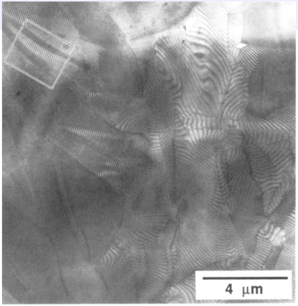
- $-|\epsilon_m(g_2)| < \epsilon < \epsilon_M(g_2)$: $\psi(\vec{r}, t) = \sum_{n=1}^{6} A_n e^{i\vec{q}_n \cdot \vec{x}} + \mathrm{c.c.}$.

  Hexagonal pattern. *Columnar phase (2D crystal)*.

ORDER AT FINITE WAVEVECTOR

Block Copolymers

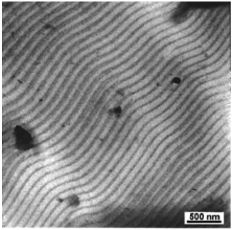




[Kim, ..., de Pablo, Nealy, 2003]

[Gido and Thomas, 1994]

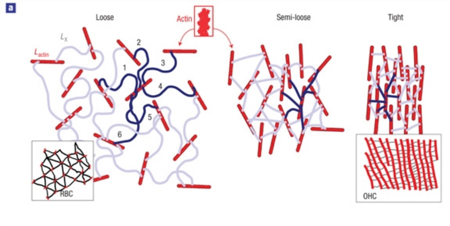
[Forster et al. 2001]



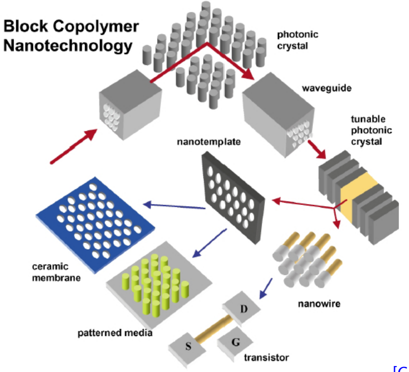
Amphiphilic systems

Liquid crystalline elastomers

[Dalhaimer, Discher, Lubensky, 2007]

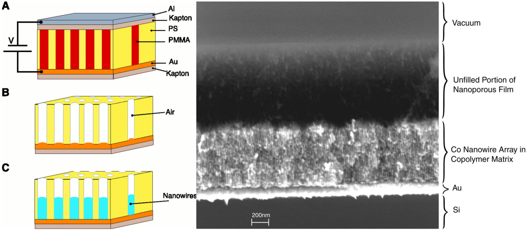


APPLICATIONS IN NANOTECHNOLOGY

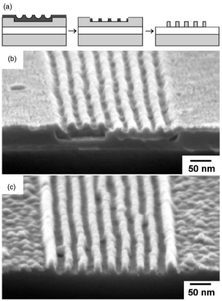


[Park, Yoon, and Thomas, Polymer 2003)]

[T. Thurn-Albrecht *et al.*, Science **290**, 2126 (2000); B. Stipe *et al.* Nature Photonics **4**, 484 (2010), exceeding 1TB/in^2]

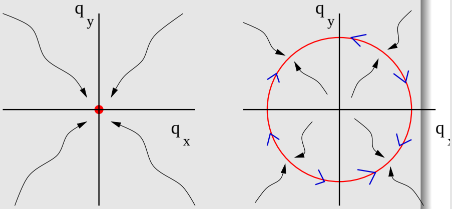


[C.T. Black, APL 2005: PS-PMMA]

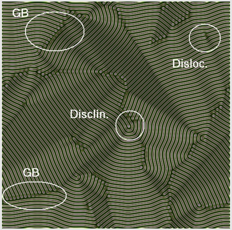


DIFFERENCES WITH q=0 SYSTEMS

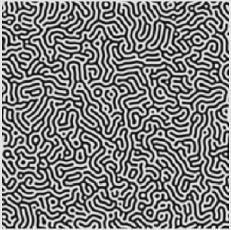
Domain coarsening



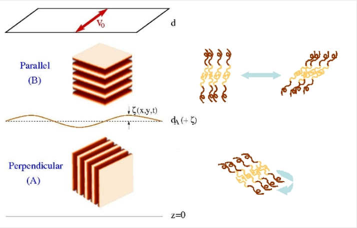
Topological defects



Pinning and structural glass



Anisotropic rheology



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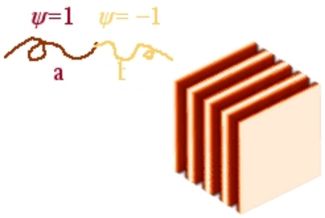
ENERGETICS



Order parameter

$$\psi \propto \rho_a - \rho_b$$

Free energy

- Ohta-Kawasaki

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

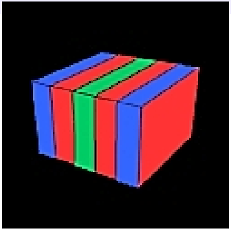
with $\nabla^2 G(r-r') = -\delta(r-r')$.

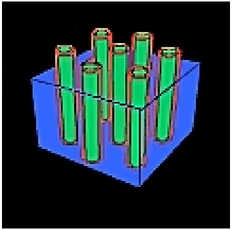
- Leibler/Swift-Hohenberg (weak segregation limit)

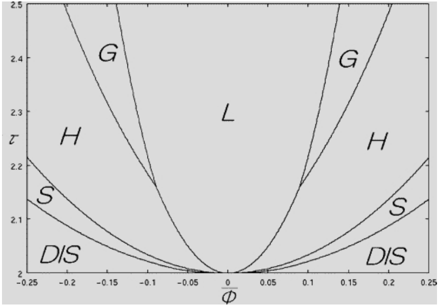
$$F[\psi] = \int dr \left(\frac{-\tau}{2}\psi^2 + \frac{u}{4}\psi^4 + \frac{K}{2}\left[\left(\nabla^2 + q_0^2\right)\psi\right]^2 \right)$$

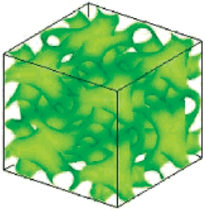
τ is temperature difference with microphase separation temperature, q_0 is the characteristic wavenumber.

PHASE DIAGRAM





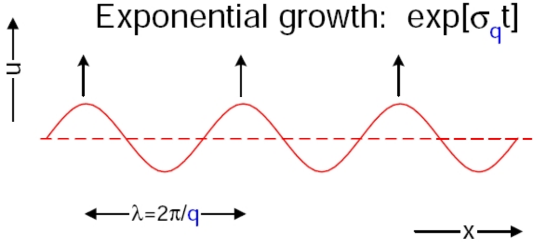




[K. Yamada, M. Nonomura, and T. Ohta, Macromolecules **37**, 5762 (2004)].

LINEAR STABILITY ANALYSIS

Study the evolution of a perturbation of ψ_0:



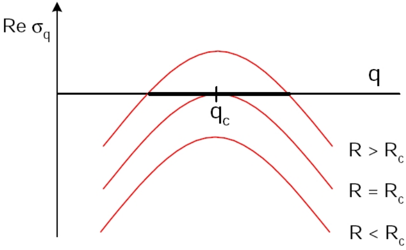
$$\delta\psi_{\mathbf{q}}(\mathbf{x}, t) = \psi_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{x}} e^{\sigma}$$

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

$$\begin{array}{lcl} \text{Im } \sigma_{\mathbf{q}} = 0 & \rightarrow & \text{Stationary Instability} \\ \text{Im } \sigma_{\mathbf{q}} \neq 0 & \rightarrow & \text{Oscillatory Instability} \end{array}$$

NONLINEARITY

Parabolic approximation:



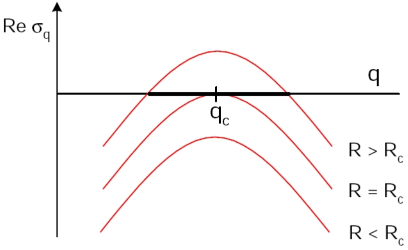
For R near R_c and q near q_c,

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

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

NONLINEARITY

Parabolic approximation:



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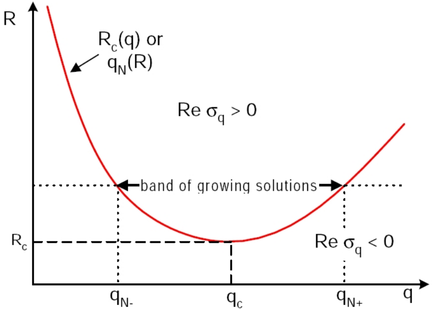

Near threshold separation of scales:

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 ϵ

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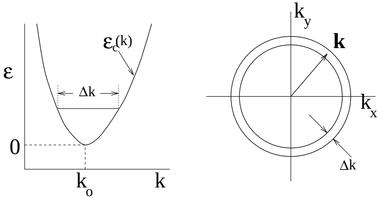
NONLINEARITY

Slightly above threshold ($\varepsilon \ll 1$):

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



(a) (b)

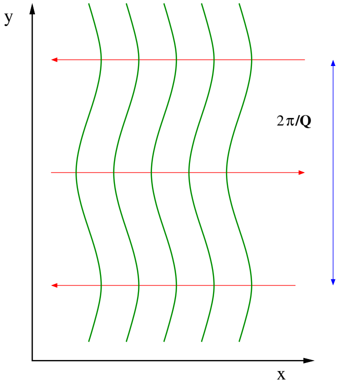
- Linear evolution.

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

$$\xi_0^2 = \frac{1}{2} \left(\frac{\partial^2 \varepsilon_c(k)}{\partial k^2} \right)_{k_0}.$$

ξ_0 is the coherence length that determines the "rigidity" of the pattern (mean field correlation length).

AMPLITUDE EQUATIONS



- Assume weak distortion,

$$\psi = A(X,Y,T)e^{ik_0x} + \mathrm{c.c.}$$

with

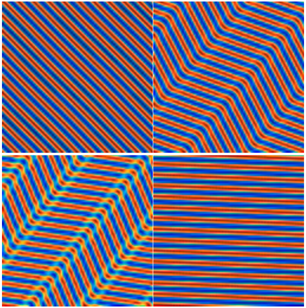
$$A(X,Y,T) = A(\epsilon^{1/2}x, \epsilon^{1/4}y, \epsilon t).$$

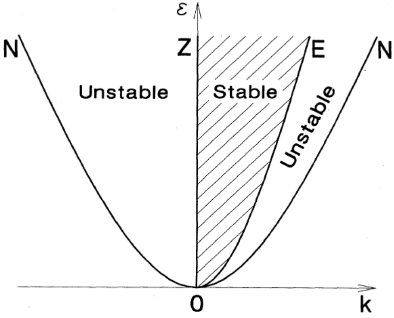
- Ginzburg-Landau equation (in original variables),

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

SECONDARY INSTABILITIES

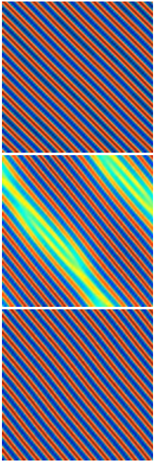
Zig-zag (transverse) instability





"Wavelength selection" problem

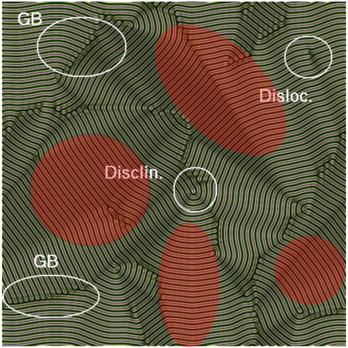
Eckhaus (longitudinal) instability



PATTERN SELECTION - LARGE DOMAIN

- Boundary conditions. At small ϵ, 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).

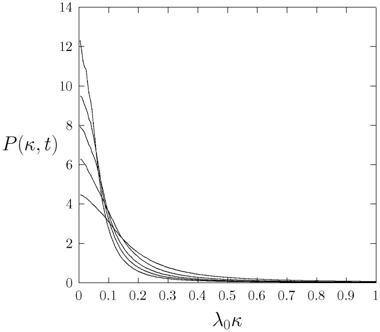
- Scaling functions are introduced. For example for the domain size distribution (R the linear size of a domain),

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

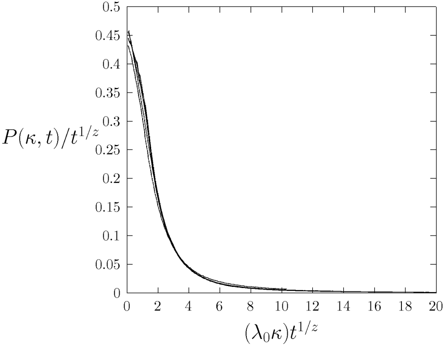
- Universality classes have been introduced according to the value of x
  - Purely relaxational dynamics, $x = 1/2$.
  - Relaxational dynamics with global conservation law, $x = 1/3$.
  - Binary fluids (non-variational modes), $x = 1$.

CURVATURE SCALING FUNCTION

Curvature distribution function



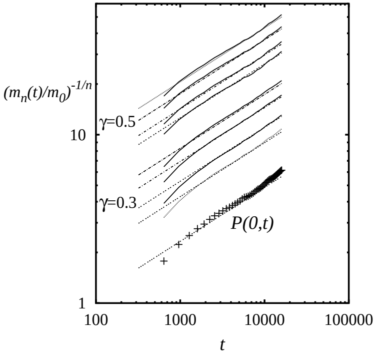
Scaled curvature distribution function



MOMENTS OF CURVATURE DISTRIBUTION

Moments of the distribution of domain curvatures,

$$m_n(t) = \int_0^{\kappa_c(t)} d\kappa \ \kappa^n P(\kappa, t) \quad P(\kappa, t) = t^x f(\kappa t^x)$$



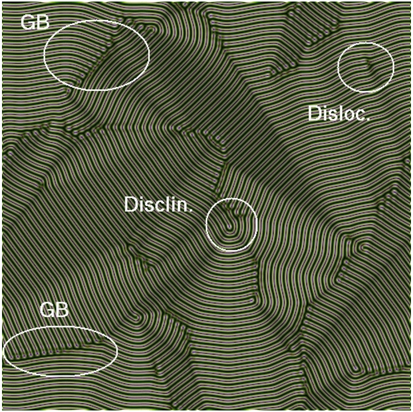
Coarsening mechanism

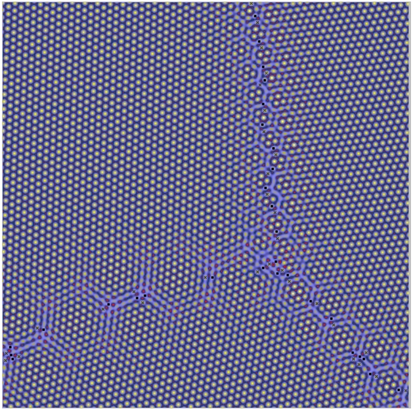
- Experiments in thin films (hexagonal) $x = 1/4$
- Domain wall relaxation, $x = 1/2$ or $x = 1/4$.
- Numerically: no fluctuations $x = 1/5$, fluctuations $x = 1/4$.
- Dislocation or disclination motion $x = 1/2$.

What is the mechanism ?

$x \simeq 1/3$

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]

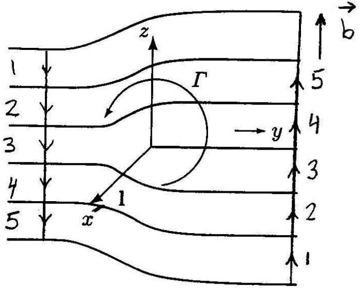
Point defect in the envelope field,

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

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

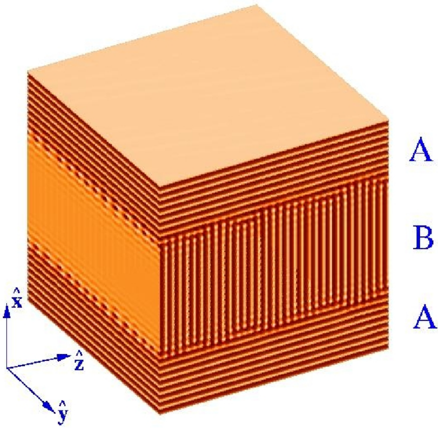
Climb velocity is found,

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



Phase θ plays the role of the displacement field u.

ENVELOPE DESCRIPTION OF GRAIN BOUNDARY



Order parameter expanded in slowly varying amplitudes:

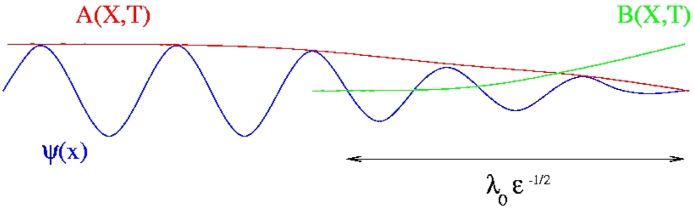
$$\psi = A e^{ik_0 x} + B e^{ik_0 z} + \mathrm{c.c.}$$

where

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

$$B = B(\epsilon^{1/4} x, \epsilon^{1/4} y, \epsilon^{1/2} z, \epsilon t)$$

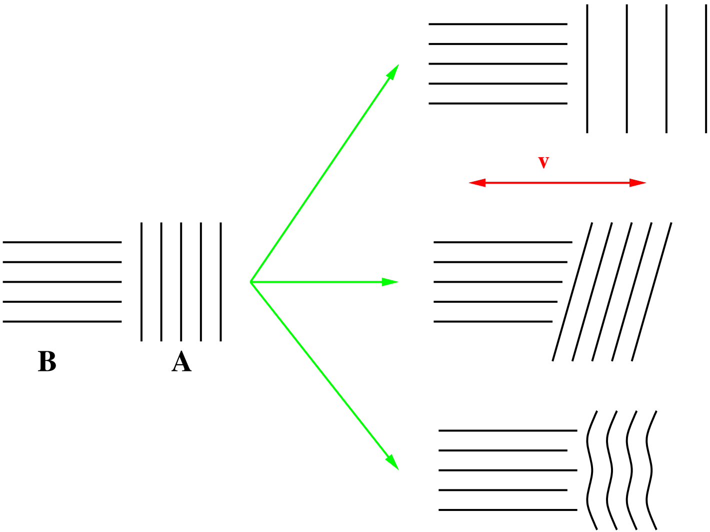
ENVELOPE DESCRIPTION OF GRAIN BOUNDARY



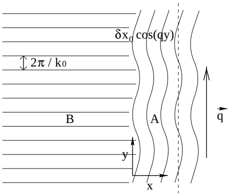
$$\frac{\partial A}{\partial t} = \epsilon A + \xi_0^2 \left(\partial_x - \frac{i}{2k_0} \partial_y^2 \right)^2 A - 3|A|^2 A - 6|B|^2 A,$$

$$\frac{\partial B}{\partial t} = \epsilon B + \xi_0^2 \left(\partial_y - \frac{i}{2k_0} \partial_x^2 \right)^2 B - 3|B|^2 B - 6|A|^2 B.$$

WHY DOES A BOUNDARY MOVE?



GRAIN BOUNDARY MOTION



- Linear relaxation rate $\sigma \propto q^4$.
- Nonlinear uniform translation mode,

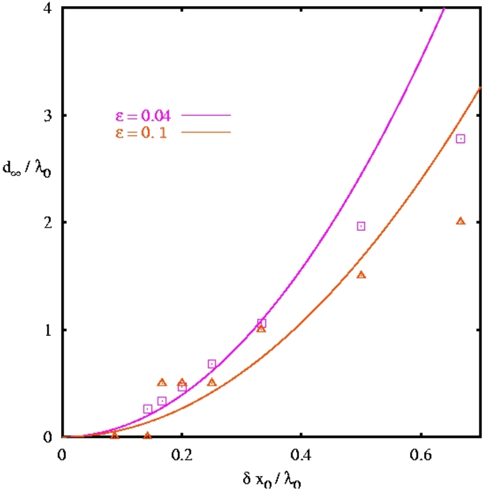
$$v_{gb}(t) = \left(\frac{\xi_0^2}{4k_0^2} q^4\right) \frac{(\epsilon/4)[k_0 \delta x(t)]^2}{\int_{-\infty}^{\infty} dx \left[(\partial_x A_0)^2 + (\partial_x B_0)^2\right]} \sim \frac{\delta x(t)^2 q^4}{\sqrt{\epsilon}} \propto \frac{\kappa^2}{\sqrt{\epsilon}}$$

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

If this motion dominates aymptotically, $x = 1/3$.

NON ADIABATIC COUPLING

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

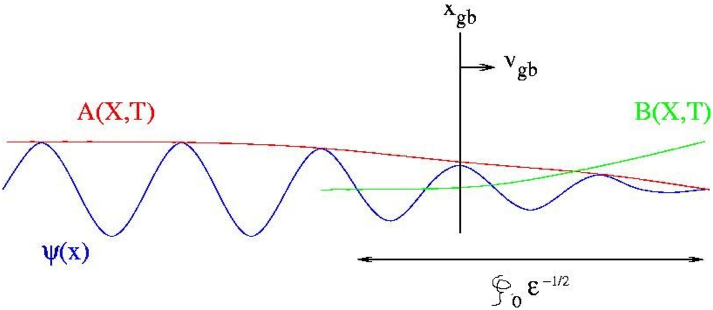
$$\begin{aligned}\frac{\partial A}{\partial t} &= \epsilon A + \xi_0^2 \left(\partial_x - \frac{i}{2k_0}\partial_y^2\right)^2 A - 3|A|^2 A - 6|B|^2 A \\ &- \int_x^{x+\lambda_0} \frac{dx'}{\lambda_0} \left(A^3 e^{2ik_0 x'} + A^{*\,3} e^{-4ik_0 x'}\right),\end{aligned}$$

$$\begin{aligned}\frac{\partial B}{\partial t} &= \epsilon B + \xi_0^2 \left(\partial_y - \frac{i}{2k_0}\partial_x^2\right)^2 B - 3|B|^2 B - 6|A|^2 B \\ &- 3\int_x^{x+\lambda_0} \frac{dx'}{\lambda_0} \left(A^2 B e^{2ik_0 x'} + A^{*\,2} B e^{-2ik_0 x'}\right).\end{aligned}$$

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

$$\int_x^{x+\lambda_0} dx' A^3 e^{i2k_0 x'} \approx -i e^{2iX/\sqrt{\epsilon}} A^2 \frac{\partial A}{\partial X}$$

NON ADIABATIC EFFECTS



- As $\epsilon \to 0$, interface width $\xi_0/\epsilon^{1/2} \gg \lambda_0$.
- Grain boundary velocity contains a dependence on both x and X:

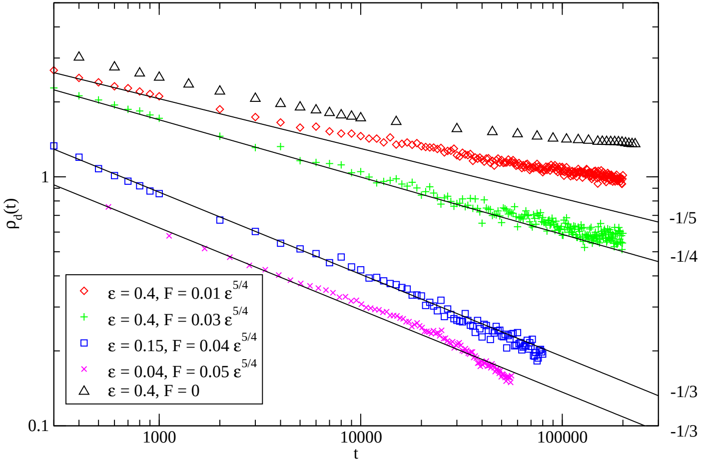
$$v_{gb} \int dX \left({A'_0}^2 + {B'_0}^2\right) = T_1 + T_2 + \ldots + e^{-1/\sqrt{\epsilon}} \sin(2k_0 x) \left(N_1 + N_2 + \ldots\right).$$

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

CONSEQUENCES OF NON ADIABATICITY

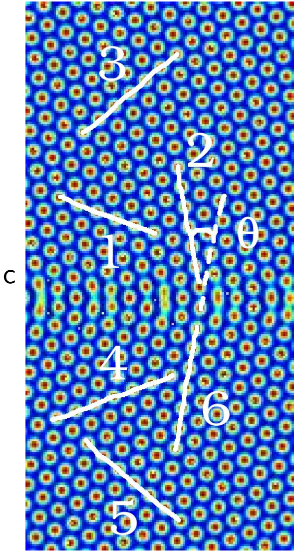
- Grain boundary located at potential minima - decoupling between grain boundary location and lamellar phase lost.
- Continuous motion in X, T only in the limit $\epsilon \to 0$.
- Pinning forces with periodicity $1/k_0$, even in the absence of any external fields or impurities.
- Glassy states as ϵ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

EFFECTIVE COARSENING EXPONENTS



MINNESOTA

PINNING AND BIFURCATION CHARACTER



$$Dv_{gb} = -p_{hex} \sin\left[2k_0 x_{gb} \sin(\theta/2)\right],$$

with (Peierls force),

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

Supercritical bifurcation (e.g., lamellar phase)

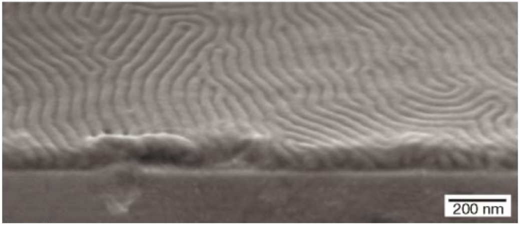
$$\xi \sim 1/\sqrt{\epsilon} \quad p_{lam} \sim e^{-1/\sqrt{\epsilon}} \to 0.$$

Subcritical bifurcation (e.g., hexagonal phase)

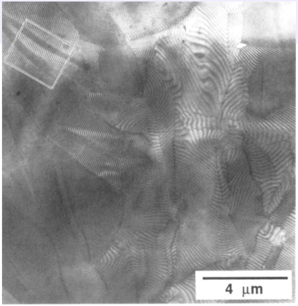
$$\xi \to \xi_0 = \frac{15\lambda_0}{8\sqrt{6}\pi g_2}, \quad p_{hex} \text{ finite.}$$

REVERSIBLE/HAMILTONIAN MODES

Block Copolymers

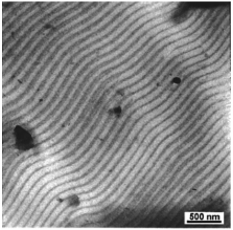


[Kim, ..., de Pablo, Nealy, 2003]



[Gido and Thomas, 1994]

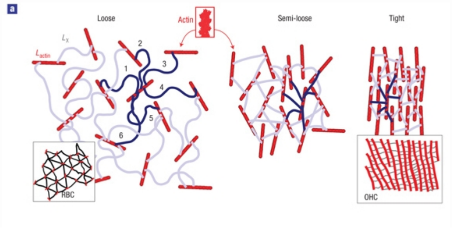
[Forster et al. 2001]



Amphiphilic systems

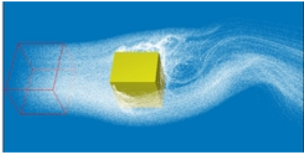
Liquid crystalline elastomers

[Dalhaimer, Discher, Lubensky, 2007]



MESOSCOPIC REVERSIBLE STRESSES

NORMAL FLUID



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

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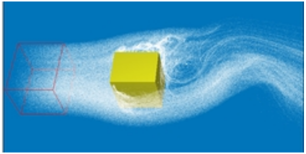

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CAHN-HILLIARD FLUID

[M. Gurtin, D. Polignone, JV, Math. Models and Meth. Appl. Sci. 6, 816 (1996)]

$$s = s(u, \rho, \psi, \partial_i\psi)$$

$$\sigma^R_{ij} = \rho v_i v_j + p\delta_{ij} - \frac{\partial s}{\partial(\partial_i\psi)}\partial_j\psi$$

needed so that advection of ψ does not cause entropy production.

GENERAL CASE

Reversible motion requires (Maxwell type relation)

$$\frac{\partial\dot{\psi}}{\partial v_i} = \frac{\partial\dot{g}_i}{\partial\left(\partial_j\xi_j\right)} \qquad \xi_j = \frac{\partial s}{\partial(\partial_j\psi)}$$

If ψ has a reversible current $\partial_t\psi + \mathbf{v}\cdot\nabla\psi = \ldots \; \frac{\partial\dot{\psi}}{\partial v_i} = -\partial_i\psi$ and non classical stresses result.

MESOSCOPIC DISSIPATIVE STRESSES

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

Broken Symmetry incorporated in dissipative fluxes.

cf. [P. Martin, O. Parodi, P. Pershan, Phys. Rev. A 6, 2401 (1972)]

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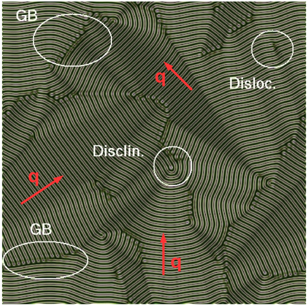


Lamellar phase: uniaxial fluid

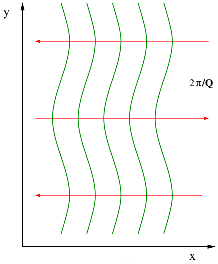
$$\begin{aligned} J_i^{\psi\ D} &= -\left[\Lambda_L q_i q_j + \Lambda_T(\delta_{ij} - q_i q_j)\right]\partial_j\mu \\ \sigma_{ij}^D &= \alpha_1 q_i q_j q_k q_l D_{kl} + \alpha_4 D_{ij} \\ &\quad + \alpha_{56}\left(q_i D_{kj} + q_j D_{ki}\right) q_k \end{aligned}$$

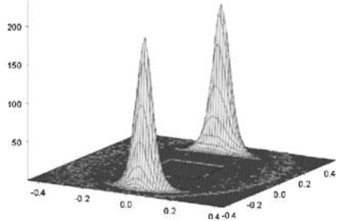
$$D_{ij} = \partial_i v_j + \partial_j v_i$$

Cahn-Hilliard (isotropic) fluid

$$\begin{aligned} J_i^{\psi\ D} &= -\Lambda q^2 \partial_i\mu \\ \sigma_{ij}^D &= \alpha_4 D_{ij} \end{aligned}$$

REVERSIBLE MODES AND LINEAR RESPONSE





[L. Wu, T. Lodge, F. Bates, J. Rheol. 49, 1231 (2005)]

Characteristic decay times determined by decay of transverse perturbations.

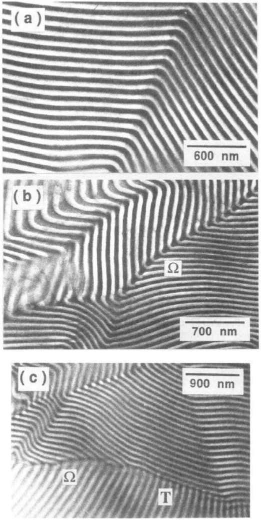
Transverse scattering intensity,

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

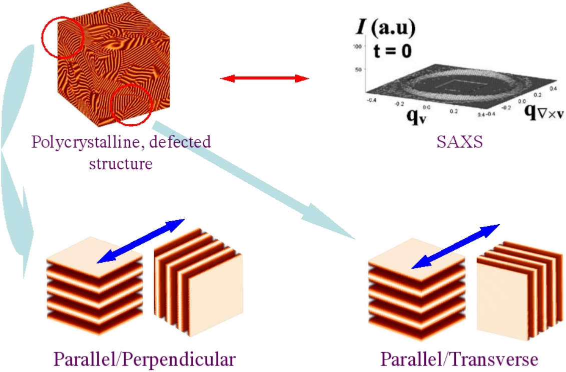
For a block copolymer in weak segregation,

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

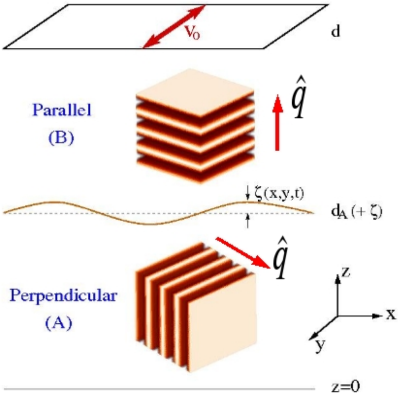
ORIENTATION SELECTION UNDER SHEAR



[S. Gido, E.L. Thomas, Macromolecules 27, 6137 (1994).]



RHEOLOGY AND ORIENTATION SELECTION



- 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).