MESOSCALE TRANSPORT AND RHEOLOGY

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MESOSCALE THEMES

1 Nonequilibrium evolution

- Slow ("hydrodynamic") but unstable motion of collective variables: interfaces, topological defects, structural variables.
- Classical macroscopic transport models need to incorporate discontinuities (interfaces), singularities (defects), and generally solve moving boundary problems.
- Various mesoscale regularization schemes.

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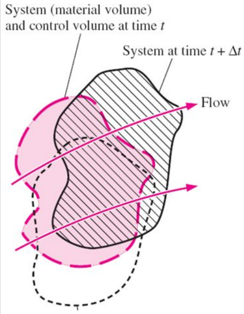
- Various mesoscale regularization schemes.

2 Multiple scales and their decoupling

Microscopic Laws	Mesoscopic Lawlessness (cf. R. Laughlin)
Macroscopic Laws	

Often it is not clear how to decouple time and length scales.

LOCAL EQUILIBRIUM



Local center of mass frame

$$Tds = du + p\, d(1/\rho)$$

Laboratory frame - conservation laws

$$Td(\rho s) = d(\rho e) - v_i dg_i - \mu d\rho$$

$$e = u + \frac{1}{2}v^2 \quad g_i = \rho v_i$$

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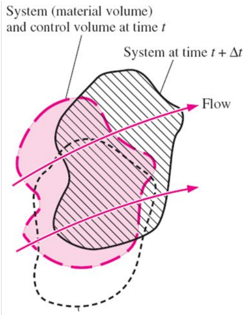


Local center of mass frame

$$T\frac{ds}{dt} = \frac{du}{dt} + p\frac{d1/\rho}{dt}$$

Laboratory frame - conservation laws

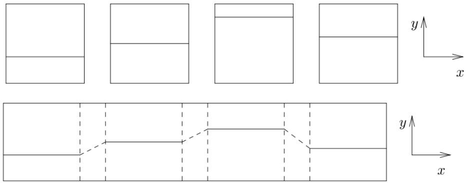
$$Td(\rho s) = d(\rho e) - v_i dg_i - \mu d\rho$$

$$e = u + \frac{1}{2}v^2 \quad g_i = \rho v_i$$

STRUCTURAL VARIABLES
BROKEN SYMMETRIES

$$Td(\rho s) = d(\rho e) - v_i dg_i - \mu d\rho - \xi_i d\left(\partial_i \varphi\right)$$

Translational symmetry



$$E\{h(x)\} = \frac{\sigma}{2} \int dx |\nabla h(x)|^2$$

$$\xi_i = \sigma \partial_i h(x)$$

$$\varphi = h(x)$$

STRUCTURAL VARIABLES
BROKEN SYMMETRIES

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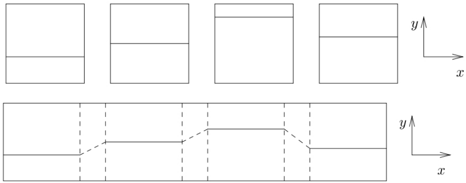


$$E = \frac{1}{2}\int dx \left[B(\partial_y u)^2 + K(\partial_x^2 u)^2\right]$$

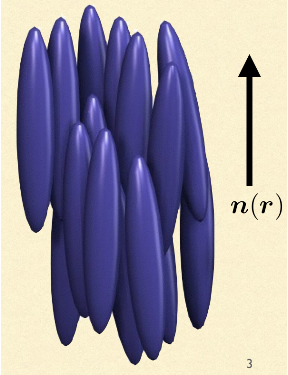
$$\xi_i = B\delta_{iy}\partial_y u - K\delta_{ix}\partial_x^3 u$$

$$\varphi = u(x, y)$$

STRUCTURAL VARIABLES
BROKEN SYMMETRIES

$$Td(\rho s) = d(\rho e) - v_i dg_i - \mu d\rho - \xi_i d\left(\partial_i \varphi\right)$$

Rotational symmetry



$$E\left[\hat{\boldsymbol{n}}(\mathbf{x})\right] = \frac{1}{2}\int d\mathbf{x} K_{ijkl}(\partial_i n_j)(\partial_k n_l)$$

$$Td(\rho s) = \ldots - h_{ij} d(\partial_j n_i)$$

$$h_{ij} = \left(\frac{\partial E}{\partial(\partial_j n_i)}\right)_{\rho,s,g_i} = K_{jikl}\partial_k n_l$$

$$\varphi = \hat{\boldsymbol{n}}(\mathbf{x})$$

NONEQUILIBRIUM

Thermodynamic driving forces are gradients of intensive parameters, including $\partial_i \xi_i$, $\partial_j h_{ij}$, etc.

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Structural stresses - Legendre transform

$$df = \ldots + g_i dv_i + \varphi d(\partial_i \xi_i)$$

Reversible stresses (low frequency/quasistatic) follow from Maxwell relation

$$\frac{\partial^2 f}{\partial(\partial_j \xi_j)\partial v_i} = \frac{\partial g_i}{\partial(\partial_j \xi_j)} \qquad \frac{\partial^2 f}{\partial v_i \partial(\partial_i \xi_i)} = \frac{\partial \varphi}{\partial v_i}.$$

$$\underbrace{\frac{\partial \dot{g}_i}{\partial(\partial_j \xi_j)}}_{\text{Reversible force}} = \underbrace{\frac{\partial \dot{\varphi}}{\partial v_i}}_{\text{Advection} \quad \partial_t \varphi + \mathbf{v}\cdot\nabla\varphi = \ldots}$$

Ginzburg Landau type

$$\mathcal{F} = \frac{1}{2}\int dx \left[K|\nabla\psi|^2 + g(\psi)\right] \qquad \partial_t\psi + v_i\partial_i\psi = L\nabla^2\frac{\delta F}{\delta\psi}$$

$$\xi_j = \frac{\partial f}{\partial(\partial_j\psi)} = K\partial_j\psi \qquad \frac{\partial\dot{\psi}}{\partial v_i} = -\partial_i\psi$$

Maxwell relation:

$$\partial_t g_i = \ldots - K(\nabla^2\psi)\partial_i\psi \quad \text{or} \quad \sigma_{ij}^R = K(\partial_i\psi)(\partial_j\psi)$$

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Orientational order

$$\frac{\partial\dot{g}_i}{\partial(\partial_j h_{kj})} = \frac{\partial\dot{n}_k}{\partial v_i}$$

$$\partial_t n_k - \lambda_{kij}\partial_i v_j + X^D_k = 0, \qquad \frac{\partial\dot{n}_k}{\partial v_i} = \lambda_{kmi}\partial_m\delta(\mathbf{x}-\mathbf{x}')$$

$$\partial_t g_i + \partial_i p - \partial_l\lambda_{mli}\partial_n h_{mn} = \partial_j\sigma^D_{ij}$$

CONTINUUM MECHANICS

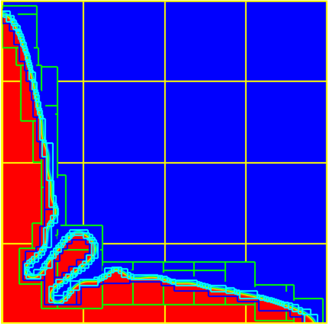
$$s = s(e, \rho, \varphi, \partial_i \varphi) \quad \dot{s} = \ldots - \frac{\sigma_{ij} - p\delta_{ij}}{T} \partial_i v_j - \frac{\xi_i}{T} \dot{(\partial_i \varphi)} - \frac{\mu_\varphi}{T} \dot{\varphi}$$

$$\dot{(\partial_i \varphi)} = \partial_i \dot{\varphi} - (\partial_i v_j)(\partial_j \varphi)$$

$$\dot{s} = \ldots - \frac{\sigma_{ij} - p\delta_{ij} - \xi_i \partial_j \varphi}{T} \partial_i v_j + \partial_i (J_i^\varphi - \varphi v_i) \left(\frac{\mu_\varphi}{T} - \partial_i \frac{\xi_i}{T} \right)$$

Reversible stress when entropy/free energy depends on gradients of order parameter

CAHN-HILLIARD FLUID



Non classical stress:

$$(\sigma_{ij})^R = p\delta_{ij} + \xi_i \partial_j \varphi$$

so that (Ginzburg-Landau)

$$\partial_j (\sigma_{ij})^R = \partial_i p + K(\nabla^2 \psi)\, \partial_i \psi$$

- High order in gradients - negligible except at interfaces.
- In the limit of a sharp interface

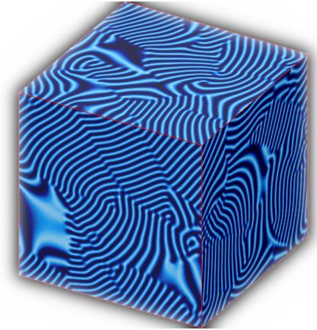
$$K(\nabla^2 \psi)\, \partial_i \psi \simeq K |\nabla \psi|^2 \kappa \hat{\mathbf{n}} \simeq \sigma \kappa \delta(\zeta) \hat{\mathbf{n}}$$

$$\sigma = K \int_{-\infty}^{\infty} dz \left(\frac{d\psi_0}{dz} \right)^2$$

Normal stress discontinuity at the interface.

RHEOLOGY - UNIAXIAL FLUID

$$\mathcal{F} = \int d\mathbf{x} \left\{ \frac{1}{2} \left[(q_0^2 + \nabla^2)\psi \right]^2 - \frac{\epsilon}{2}\psi^2 + \frac{g}{4}\psi^4 \right\} \qquad \partial_t \psi + v_i \partial_i \psi = -L \frac{\delta \mathcal{F}}{\delta \psi}$$



$$\psi_0(\mathbf{x}) = \epsilon^{1/2} A_0 \cos(\mathbf{q}_0 \cdot \mathbf{x}) + \dots$$

Reversible stress

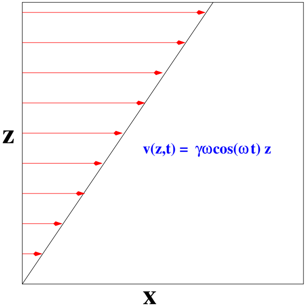
$$\psi(\mathbf{x} + \mathbf{u}(\mathbf{x})) = \psi(\mathbf{x}), \qquad \sigma_{ij} = \frac{\delta \mathcal{F}}{\delta(\partial_i u_j)}$$

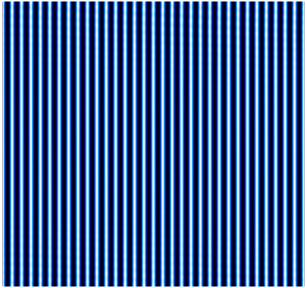
$$\sigma_{ij} = \left[\partial_i (q_0^2 + \nabla^2)\psi \right] \partial_j \psi - \left[(q_0^2 + \nabla^2)\psi \right] \partial_i \partial_j \psi$$

Complex modulus

$$\sigma_{ij}(\mathbf{k}, \omega) = G_{ijkl}(\mathbf{k}, \omega) \gamma_{kl}(\mathbf{k}, \omega) \qquad G_{ijkl}(\mathbf{k}, \omega) = G'_{ijkl}(\mathbf{k}, \omega) + i G''_{ijkl}(\mathbf{k}, \omega)$$

Order parameter relaxation causes viscoelastic response

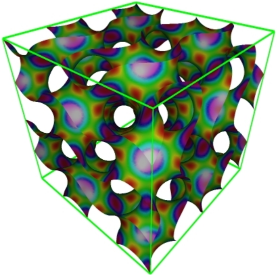




$$G' = \frac{4\epsilon}{3}\left(2q_x^2 q_z^2 + \mathcal{O}(\gamma^2)\right)$$

$$G'' = \frac{32\epsilon\gamma^2}{3} q_x^4 q_z^4 \frac{\omega}{\epsilon^2 + \omega^2}$$

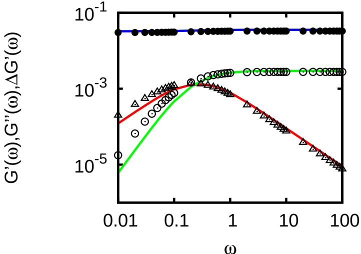
GYROID - PERIODIC MINIMAL SURFACE ($Ia\bar{3}d$)

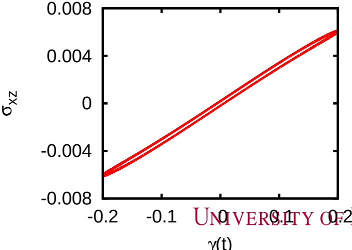


$$\psi(\mathbf{r}) = \overline{\psi} + \left[\sum_{j=1}^{12} A_j e^{i\mathbf{q}_j\cdot\mathbf{r}} + \sum_{k=1}^{6} B_k e^{i\mathbf{p}_k\cdot\mathbf{r}} + \mathrm{c.c.}\right]$$

with 18 reciprocal lattice vectors with $q^2 = 3p^2/4 \neq 1$.

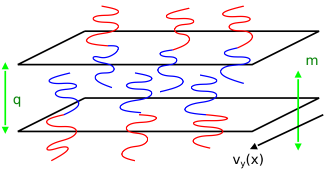
$$G' = \sum_{j=1}^{8} \Gamma_j \left[\frac{(\omega/\lambda_j)^2}{1+(\omega/\lambda_j)^2} - 1\right] + 8q_0^2\left(\phi_a^2 + \frac{2}{3}\phi_b^2\right), \qquad G'' = \sum_{j=1}^{8} \Gamma_j \left[\frac{\omega/\lambda_j}{1+(\omega/\lambda_j)^2}\right]$$



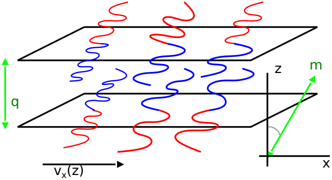


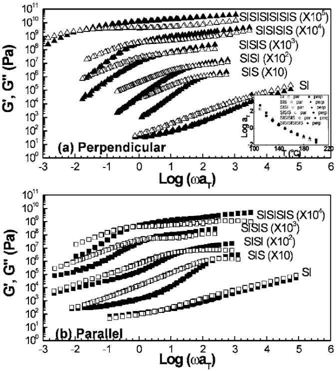
BLOCK COPOLYMER RHEOLOGY

Perpendicular Orientation



Parallel Orientation



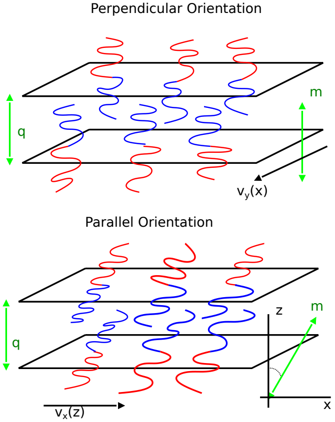


[L. Wu, T.P. Lodge, and F. Bates, J. Rheol. **49**, 1231 (2005)]

$$G_{ijkl}(t) = G_{11}(t)q_iq_jq_kq_l + G_4(t)(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}) + G_{56}(t)\left[q_i(q_k\delta_{jl}+q_l\delta_{kj})+q_j(q_k\delta_{il}+q_l\delta_{ki})\right]$$

Perpendicular G_4. Parallel $G_4 + G_{56}$.

BLOCK COPOLYMER RHEOLOGY



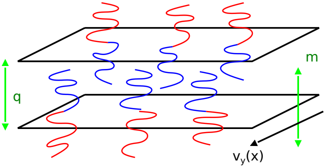
Two order parameters:

- Lamellar planes $\psi(\mathbf{x}, t)$
- End-to-end polymer chain orientation

$$Q_{ij}(\mathbf{x}, t) = \langle m_i m_j - \frac{1}{3}\delta_{ij} \rangle$$

BLOCK COPOLYMER RHEOLOGY

Perpendicular Orientation



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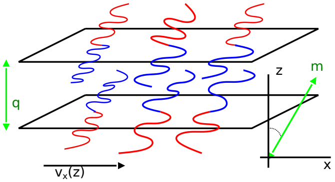


Two order parameters:

- Lamellar planes $\psi(\mathbf{x}, t)$
- End-to-end polymer chain orientation

$$Q_{ij}(\mathbf{x}, t) = \langle m_i m_j - \frac{1}{3}\delta_{ij} \rangle$$

Free energy:

- Uniaxial state

$$\mathcal{F}_S = \int d\mathbf{x} \left\{ \frac{1}{2} \left[(q_0^2 + \nabla^2)\psi \right]^2 - \frac{\epsilon}{2}\psi^2 + \frac{g}{4}\psi^4 \right\}$$

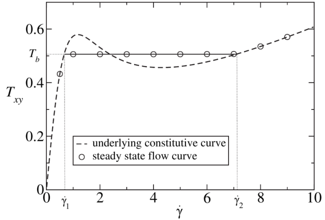
- Some model for polymer chains $\mathcal{F}_Q(Q_{ij}, \partial_k Q_{ij})$
- Minimal coupling $-\partial_i \psi Q_{ij} \partial_j \psi$

Only simple chain diffusive relaxation studied so far (Maxwell viscoelasticity)

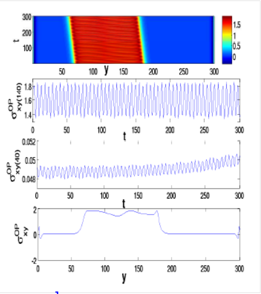
[C. Yoo, and J. Viñals, Macromolecules **45**, 4848 (2012), S. Yabunaka and T. Ohta, Soft Matter **9**, 7479 (2013)].

RHEOCHAOS AND SHEAR BANDING

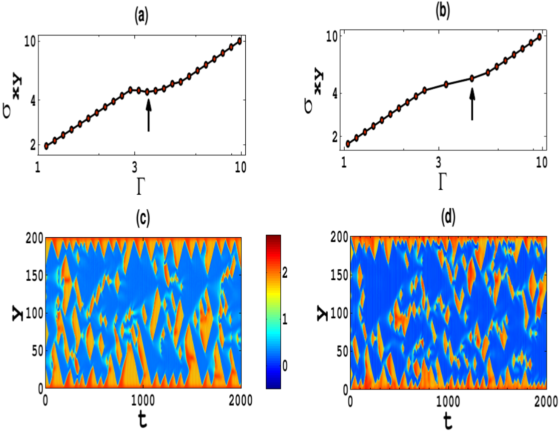
- Shear instability to bands of different shear rates. Non monotonic shear stress/shear rate curve due to the microstructural response of the fluid.
- Observed in many complex fluids: wormlike micelles, liquid crystalline polymers, colloidal suspensions, soft glasses.
- Elastic bursts, and rheochaos.
- Introduce a structure order parameter Q_{ij} *instead of* phenomenological constitutive laws for the flow curve.



[S. Fielding, Phys. Rev. Lett. **95**, 134501 (2005)]



[C. Dasgupta]

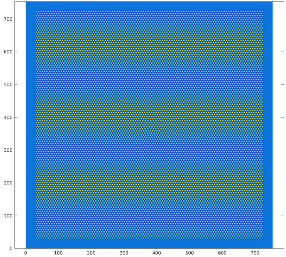


$$\sigma_{ij}^{R} = \alpha_0 \frac{\delta F}{\delta Q_{ij}} + \alpha_1 \left[Q_{ik} \frac{\delta F}{\delta Q_{kj}} \right]$$

TOPOLOGICAL DEFECT MOTION AT THE MESOSCALE

Hexagonal phase

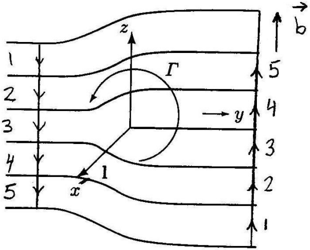
$$\mathcal{F}_S = \int d\mathbf{x} \left\{ \frac{1}{2} \left[(q_0^2 + \nabla^2)\psi \right]^2 + g(\psi) \right\}$$



ψ around "defects" is regular.
Envelope equations on the other hand

$$\psi(\mathbf{x}, t) = A(\mathbf{X}, T) e^{i\mathbf{q}\cdot\mathbf{x}} = \rho(\mathbf{X}, T) e^{i\theta(\mathbf{X}, T)} e^{i\mathbf{q}\cdot\mathbf{x}}$$

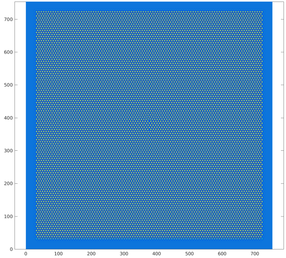
$$\oint \nabla\theta \cdot d\mathbf{l} = \pm 2\pi.$$

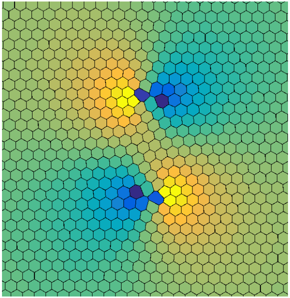


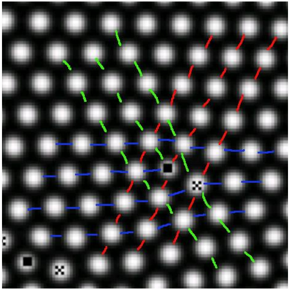
Hexagonal phase

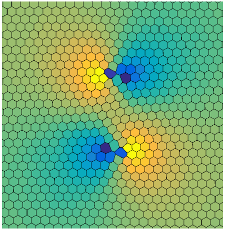
$$\mathcal{F}_S = \int d\mathbf{x} \left\{ \frac{1}{2} \left[(q_0^2 + \nabla^2)\psi \right]^2 + g(\psi) \right\}$$

$$\sigma_{ij} = \left[\partial_i (q_0^2 + \nabla^2)\psi \right] \partial_j \psi - \left[(q_0^2 + \nabla^2)\psi \right] \partial_i \partial_j \psi$$

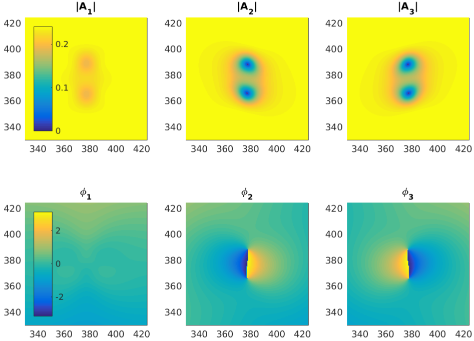


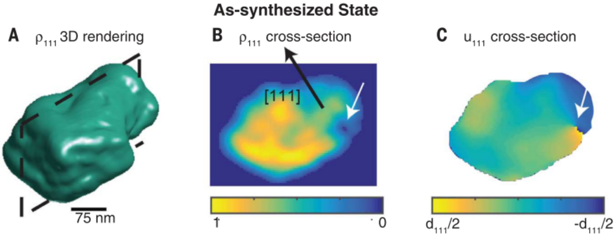






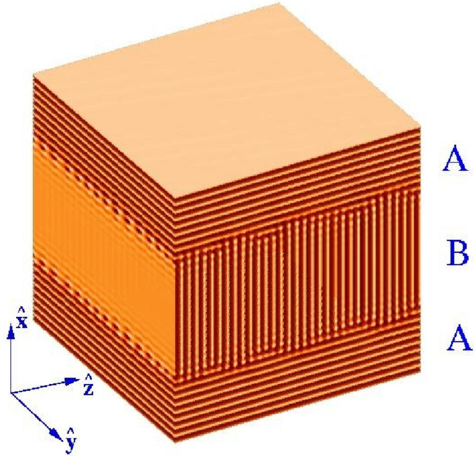
[A. Skaugen and L. Angheluta]





[A. Yau, W. Chak, M. Kanan, G.B. Stephenson, Science **356**, 739 (2017)]

REDUCTION FROM MESOSCALE TO MACROSCALE



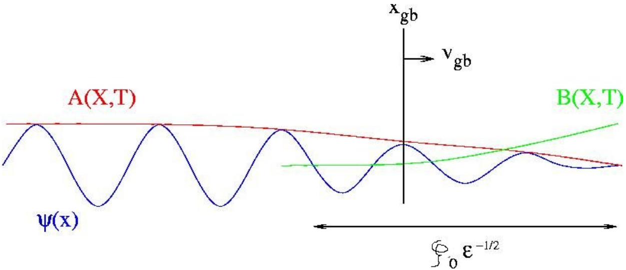
Order parameter expanded in slowly varying amplitudes:

$$\psi = Ae^{ik_0x} + Be^{ik_0z} + \mathrm{c.c.}$$

where

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

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

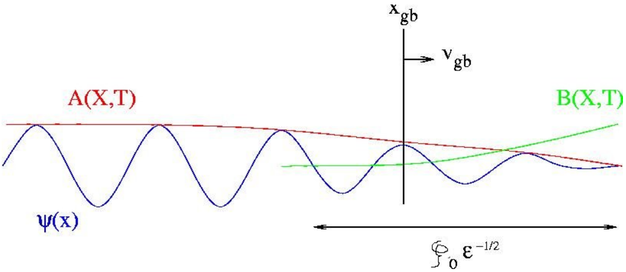


$$\frac{\partial A}{\partial t} = \epsilon A + \xi_0^2 \left(\partial_x - \frac{i}{2q_0} \partial_y^2 \right)^2 A - 3|A|^2 A - 6|B|^2 A,$$

$$\frac{\partial B}{\partial t} = \epsilon B + \xi_0^2 \left(\partial_y - \frac{i}{2q_0} \partial_x^2 \right)^2 B - 3|B|^2 B - 6|A|^2 B.$$

Two, coupled, Ginzburg-Landau equations!

CAREFUL ...



- As $\epsilon \to 0$, interface width $\xi = \xi_0/\epsilon^{1/2} \gg \lambda_0$.
- Null terms in the solvability condition to derive GL look like (e.g.,)

$$\int_{x}^{x+\lambda_0} dx' A^3 e^{2iq_0x'} = 0.$$

- What if $A(X,x)$ is allowed to have some residual dependence on x (the $\mathcal{O}(1)$ scale) ?

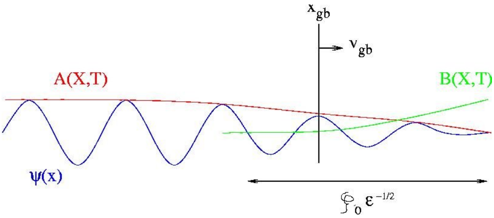
NONPERTURBATIVE CORRECTIONS

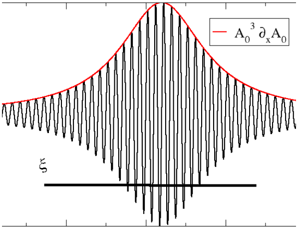
Allowing this possibility, the lowest order envelope equations are

$$
\begin{aligned}
\frac{\partial A}{\partial t} &= \epsilon A + \xi_0^2 \left(\partial_x - \frac{i}{2q_0} \partial_y^2 \right)^2 A - 3|A|^2 A - 6|B|^2 A \\
&- \int_x^{x+\lambda_0} \frac{dx'}{\lambda_0} \left(A^3 e^{2iq_0 x'} + A^{*\,3} e^{-4iq_0 x'} \right),
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial B}{\partial t} &= \epsilon B + \xi_0^2 \left(\partial_y - \frac{i}{2q_0} \partial_x^2 \right)^2 B - 3|B|^2 B - 6|A|^2 B \\
&- 3 \int_x^{x+\lambda_0} \frac{dx'}{\lambda_0} \left(A^2 B e^{2iq_0 x'} + A^{*\,2} B e^{-2iq_0 x'} \right).
\end{aligned}
$$

Assume an interface, and project amplitude equations onto $\partial_x A_0$ and $\partial_x B_0$





Estimate terms of the type

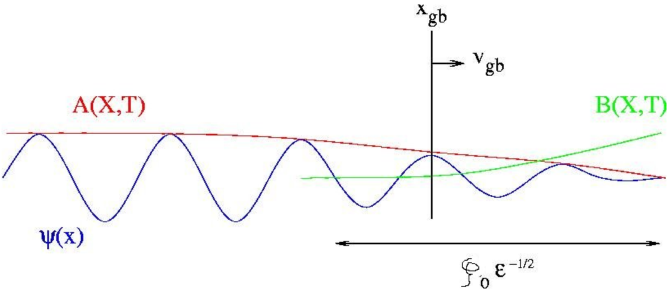
$$\int_{\infty}^{\infty} dx A_0^3 \left(\partial_x A_0\right) e^{2iq_0 x} \quad \text{when} \quad \xi q_0 \gg 1$$

Continue x into complex plane, and assume that envelope on real axis results from a singularity at $z = x_{gb} + i\alpha\xi$. Then

$$\int_{\infty}^{\infty} dx A_0^3 \left(\partial_x A_0\right) e^{2iq_0 x} \approx i(\sqrt{\epsilon})^4 e^{-2q_0 \alpha \xi} e^{2iq_0 x_{gb}}$$

Depends explicitly on x_{gb} and is of the order of $e^{-\xi} = e^{-\xi_0/\sqrt{\epsilon}}$.

LAW OF BOUNDARY MOTION



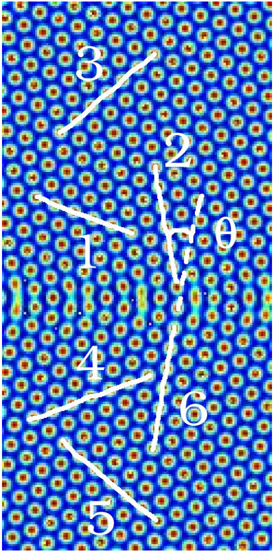
For a grain boundary, we find,

$$v_{gb} = \frac{\epsilon}{3k_0^2 D(\epsilon)} \kappa^2 - \frac{p(\epsilon)}{D(\epsilon)} \cos(2k_0 x_{gb} + \phi)$$

The function $D(\epsilon)$ is a friction coefficient, and $p(\epsilon)$ is a pinning force

$$p(\epsilon) \sim \epsilon^2 e^{-\alpha/\sqrt{\epsilon}}.$$

$p(\epsilon) \to 0$ exponentially as $\epsilon \to 0$ (essential singularity). Grows quickly with ϵ.



$$v_{gb}(t) = \frac{\Delta f}{D(\epsilon)} - \frac{p(\epsilon)}{D(\epsilon)} \sin\left[2q_0 x_{gb}(t)\sin(\theta/2)\right],$$

with (Peierls stress)

$$p \sim A_0^4 e^{-2aq_0 \sin(\theta/2)\xi}.$$

Supercritical (second order)

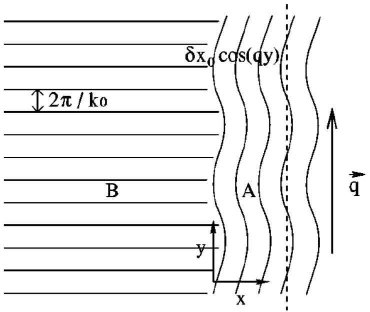
$$\xi \sim 1/\sqrt{\epsilon} \quad p \sim e^{-1/\sqrt{\epsilon}} \to 0.$$

Subcritical (first order)

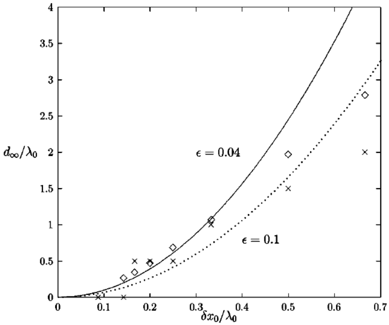
$$\xi \to \xi_0 = \frac{15\lambda_0}{8\sqrt{6}\pi g_2} \quad \text{finite}.$$

BOUNDARY PINNING

Relaxation of a weakly distorted boundary,



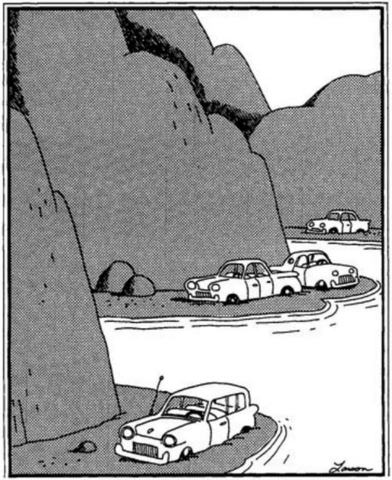
Boundary relaxes **and** moves to the right.



$\epsilon = 0.04$ - smooth curve. Agrees with analytic calculation.
$\epsilon = 0.1$, steps.

SUMMARY

1. Linear response/irreversible thermodynamics are widely used frameworks for the construction of nonequilibrium theories at the mesoscale.
2. Nontrivial response/rheology can be described from the existence of structural fields and the resulting micro stresses.
3. The mesoscale provides useful regularization schemes for the study of the dynamical evolution of moving boundaries and topological defects.
4. No general theoretical framework exists at the mesoscale. Not generally possible to decouple it from micro and macro scales. A large amount of phenomenology is required.



The fords of Norway