STRUCTURE & RHEOLOGY OF LAMELLAR MESOPHASES

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Acknowledgements:

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F. Thakkar, A. Debnath, (MD) M. Hulgi (Experiments)

B. Murch, P. Verstrete (Discussions)

V. M. Naik (Discussions)

भारत सरकार
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GOVERNMENT OF INDIA
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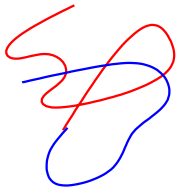
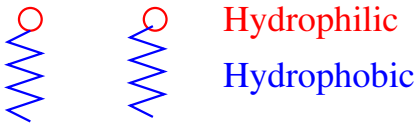
Department of Science and Technology
Technology Bhavan, New Mehrauli Road
New Delhi - 110016

Surfactant solutions:

A−A−A−A−B−B−B−B−B



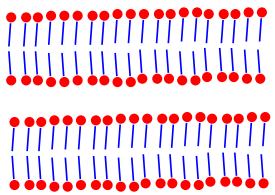
Block Copolymers



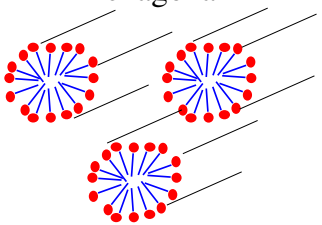
Surfactants

Surfactant mesophases

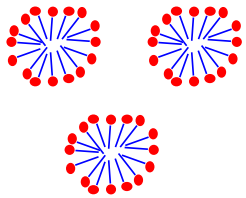
Lamellar



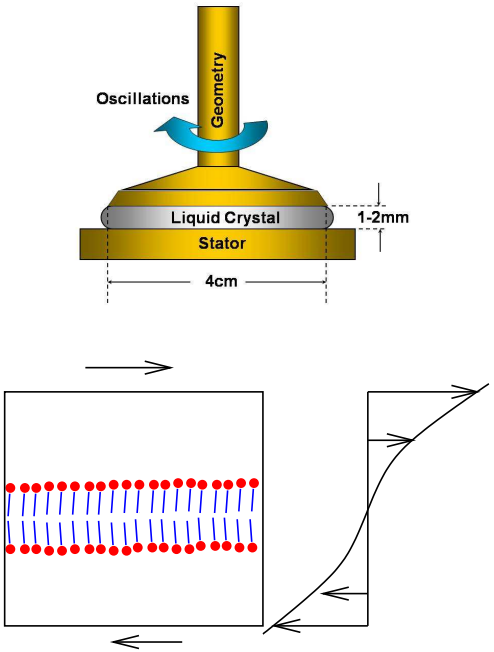
Hexagonal

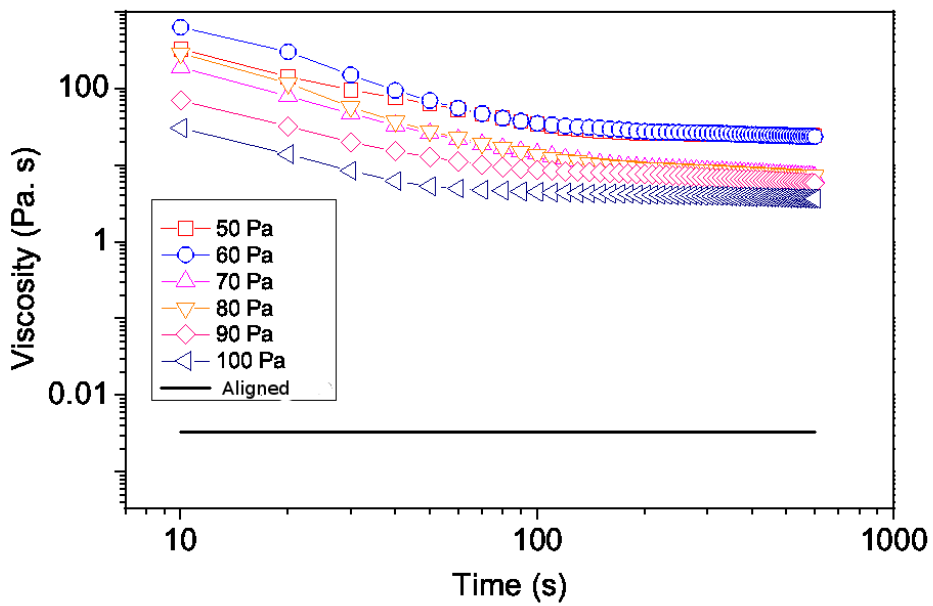


Micellar



Complex rheology: Triton-X-100/Oleic Acid/Water



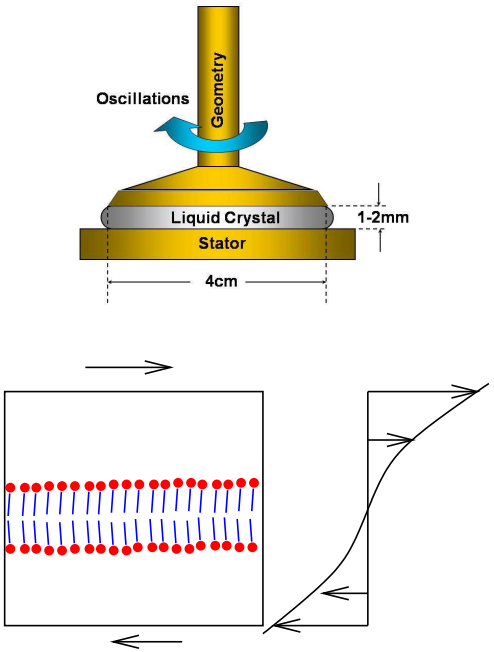


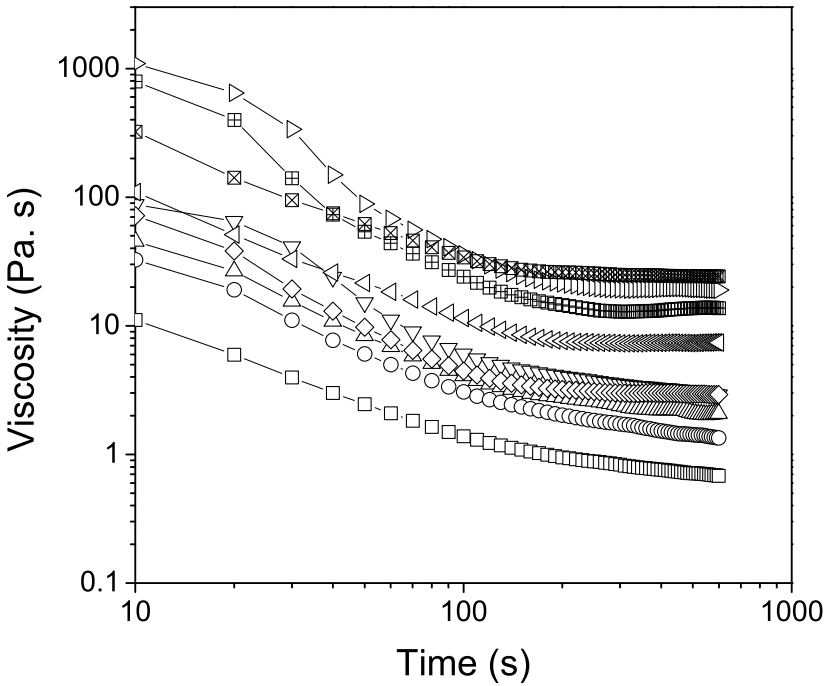
$$\frac{1}{\mu} = \frac{f_w}{\mu_w} + \frac{f_o}{\mu_o}$$

$(\square 50Pa)$; $(\circ 60Pa)$; $(\triangle\ 70Pa)$; $(\triangledown 80Pa)$; $(\diamond 90Pa)$; $(\triangleleft 100Pa)$.

M. Hulgi, ME Thesis, Indian Institute of Science, 2010.

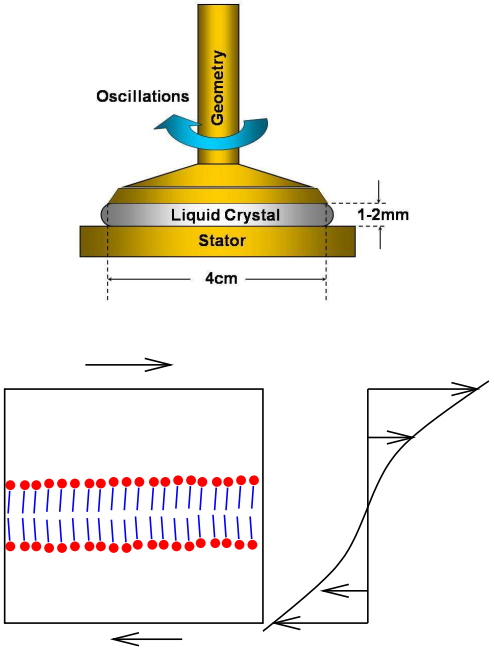
Evolution of viscosity under shear: Shear stress 50 Pa.

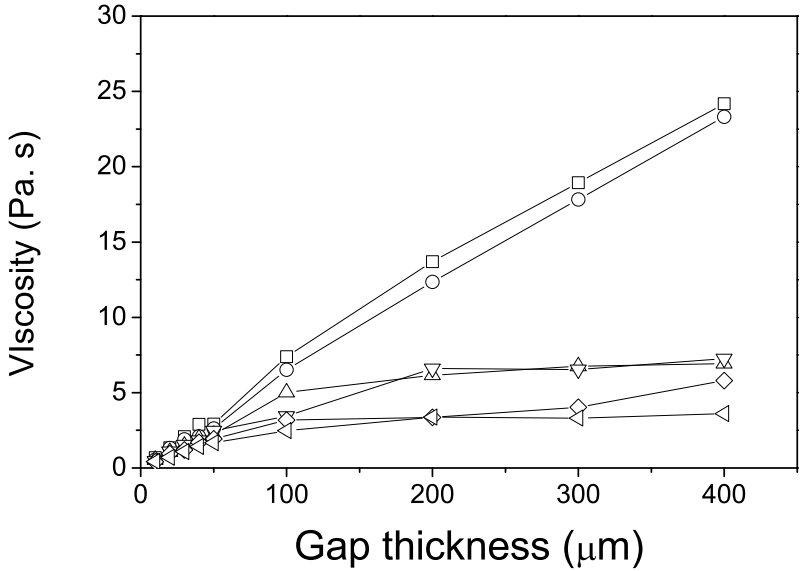




($\square$ – – – 10μ), ($\circ$ – – – 20μ), ($\triangle$ – – –30μ), ($\triangledown$ – – – 40μ), ($\diamond$ – – – 50μ), ($\triangleleft$ – – – 100μ), ($\triangleright$ – – – 200μ), ($\boxplus$ – – – 300μ) and ($\boxtimes$ – – – 400μ)

Complex rheology: Triton-X-100/Oleic Acid/Water 60:30:10



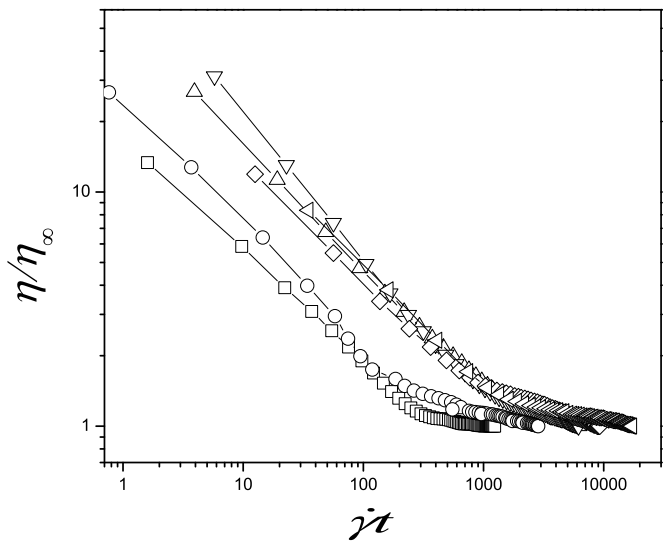


$$\frac{1}{\mu} = \frac{f_w}{\mu_w} + \frac{f_o}{\mu_o}$$

($\square 50Pa$); ($\circ 60Pa$); ($\triangle$ $70Pa$); ($\triangledown 80Pa$); ($\diamond 90Pa$); ($\triangleleft 100Pa$).

M. Hulgi, ME Thesis, Indian Institute of Science, 2010.

Evolution of steady viscosity under shear:



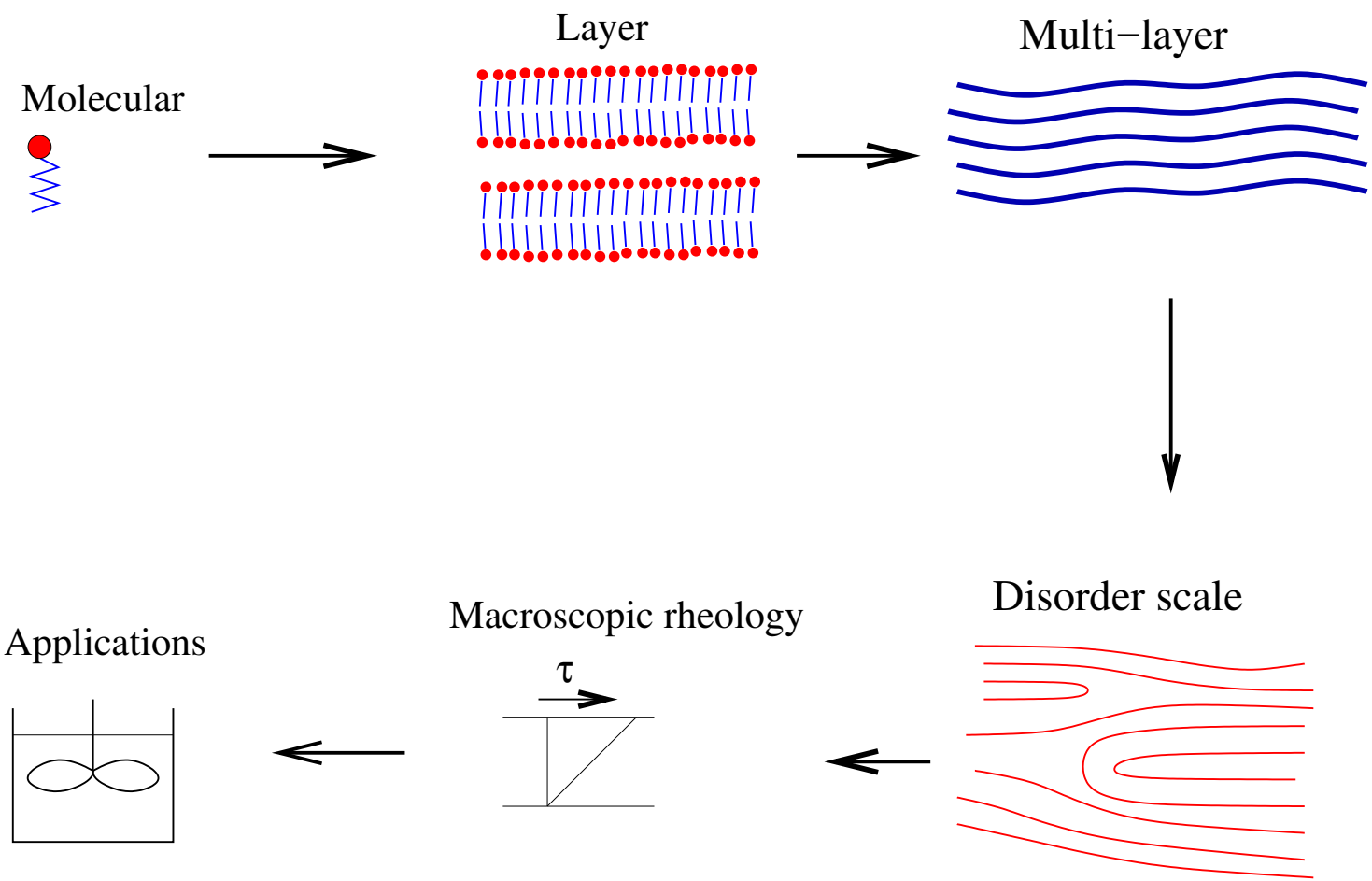
Initial slopes:

Shear stress (Pa)	**Slopes**
50	-1.19 ± 0.22
60	-1.13 ± 0.23
70	-1.03 ± 0.19
80	-1.08 ± 0.22
90	-0.98 ± 0.33
100	$-0.903 \pm 0.20.$

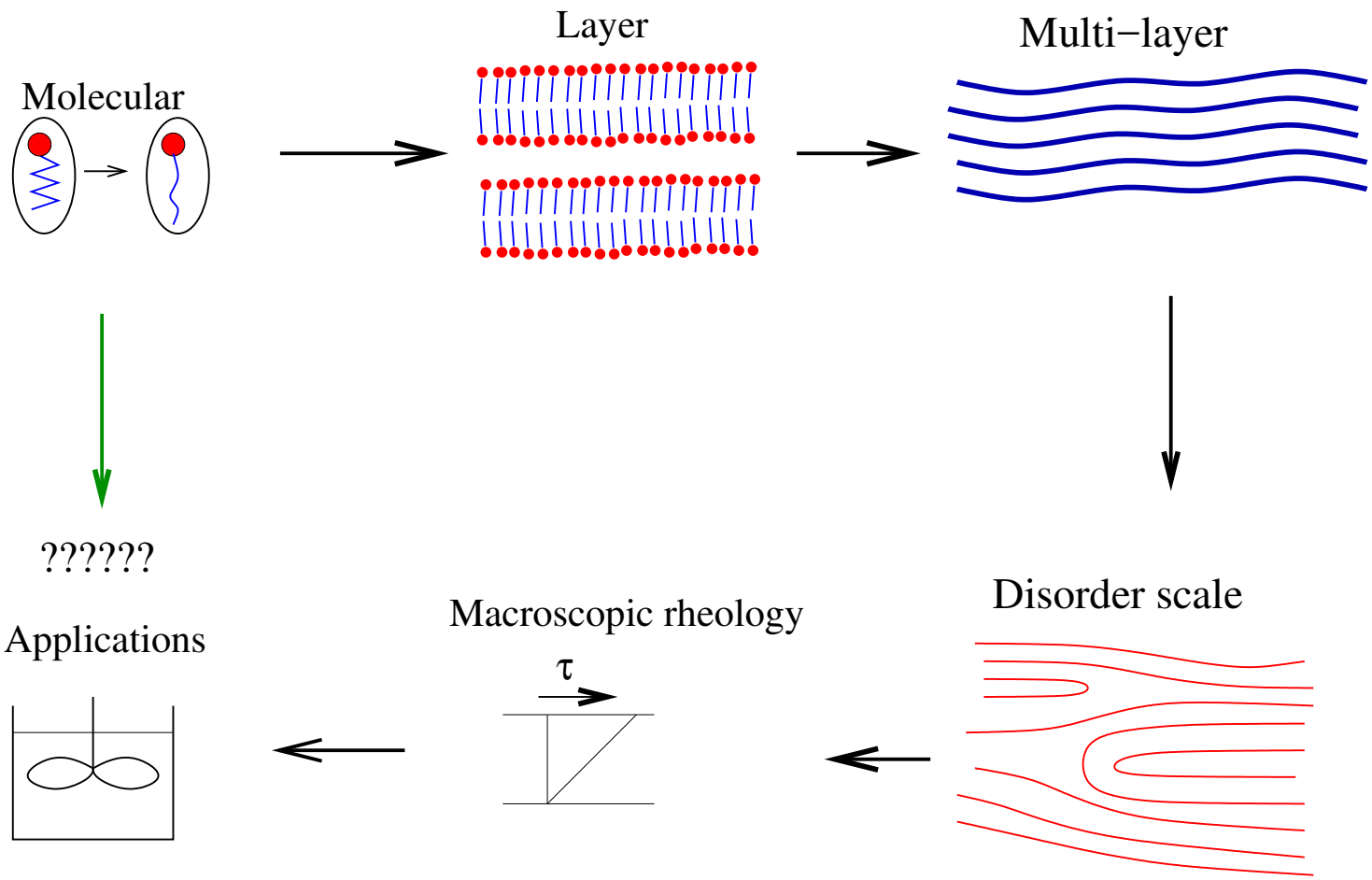
Gap thickness 400 microns.

$(\square - - - 50Pa)$, $(\circ - - - 60Pa)$, $(\triangle - - -70Pa)$, $(\triangledown - - - 80Pa)$, $(\diamond - - - 90Pa)$, $(\triangleleft - - - 100Pa)$.

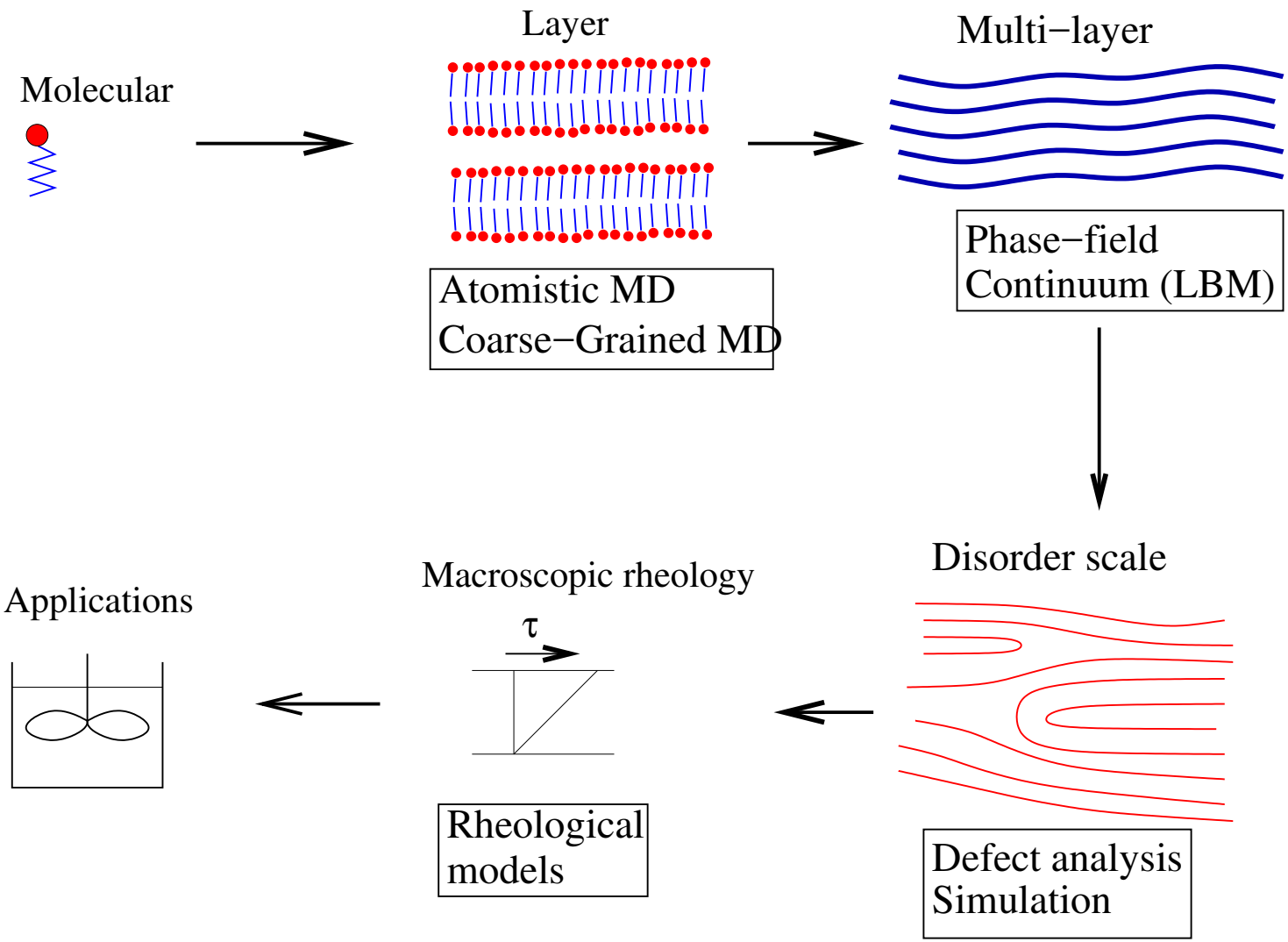
Multi-scale structures



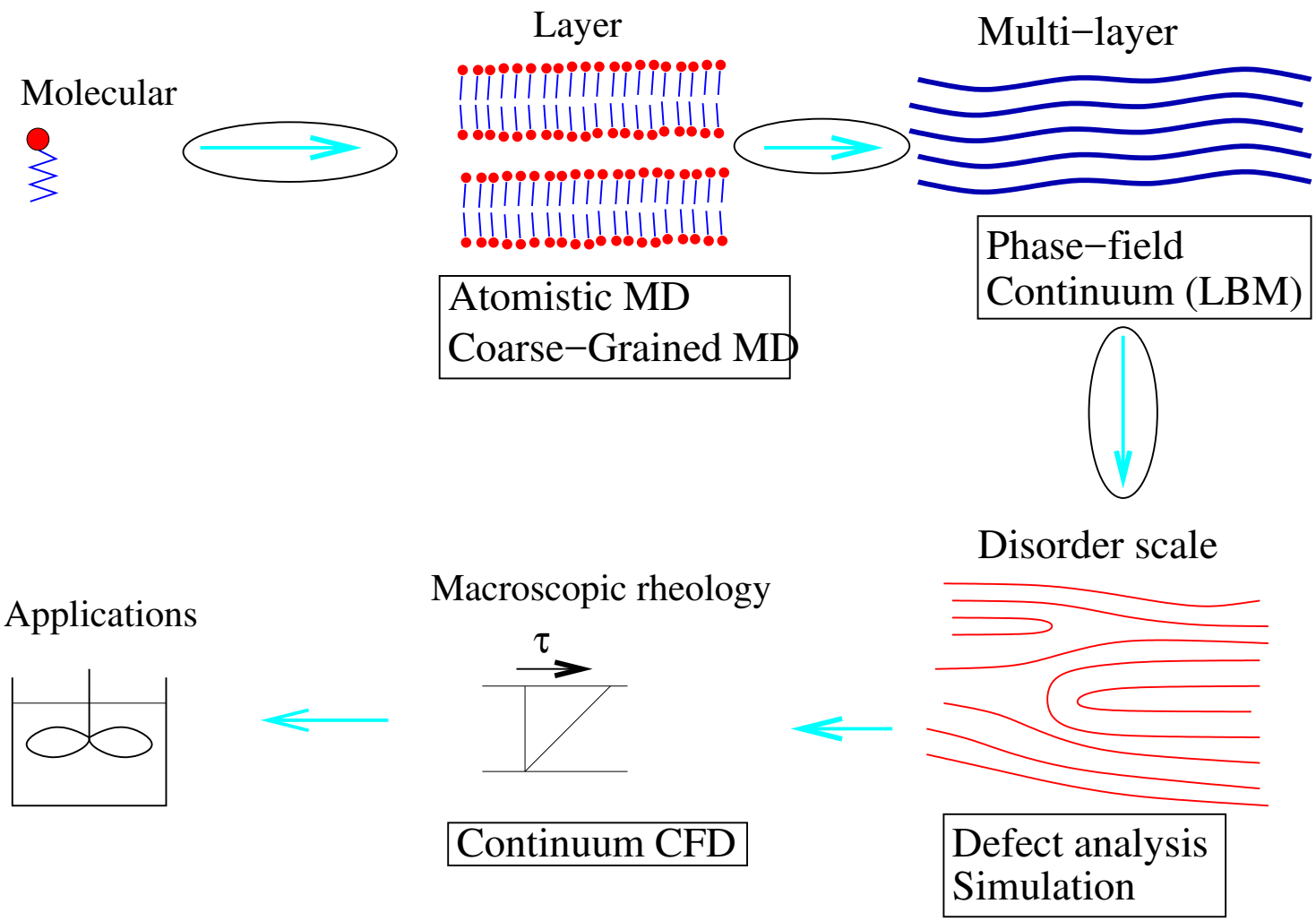
Structure-function relationships



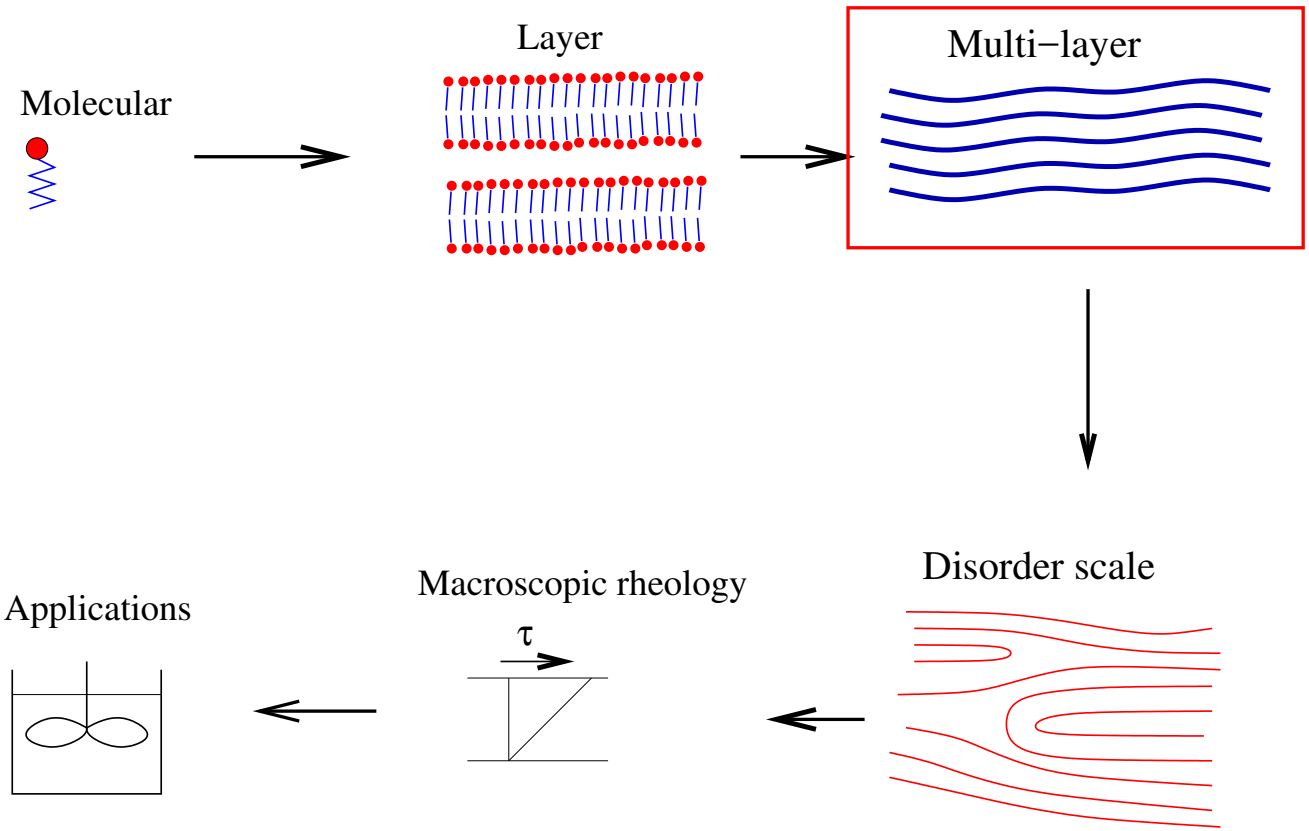
Structure-function relationships



Structure-function relationships



Mesoscale description:

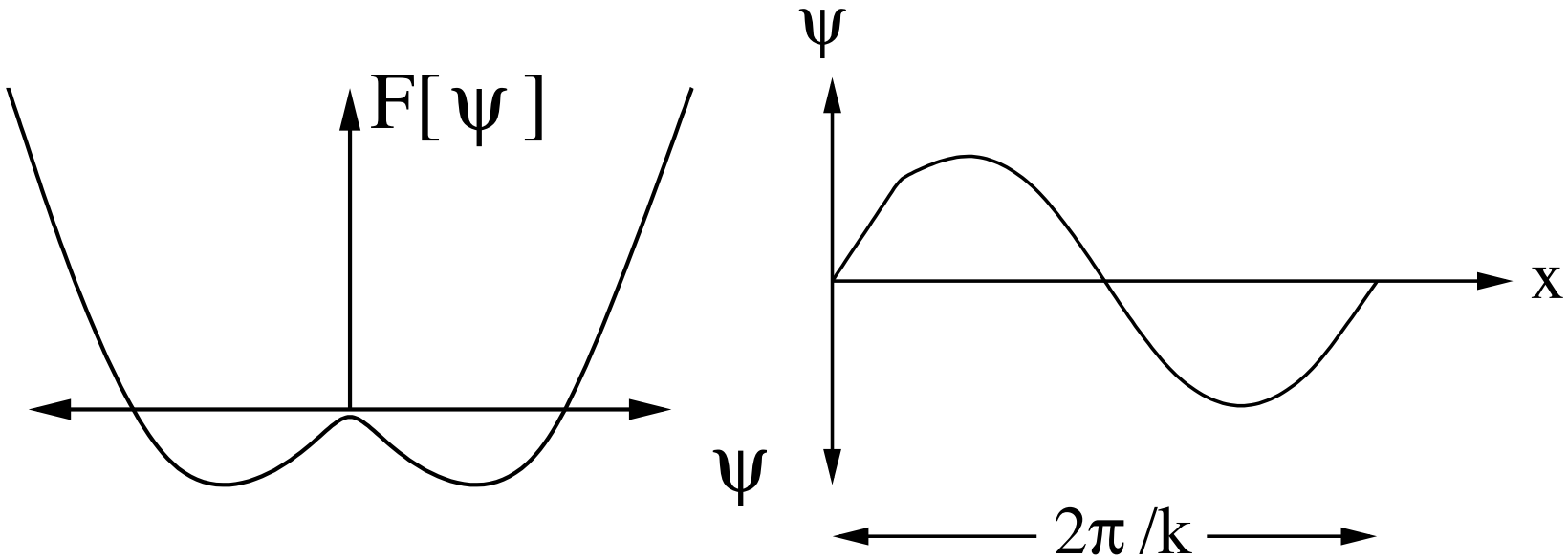


V. Kumaran , Y. K. V. V. N. Krishna Babu and J. Sivaramakrishna, J. Chem. Phys., **130**, *114907, (2009);*

V. Kumaran , J. Chem. Phys., **130**, *224905, (2009).*

Mesoscale description:

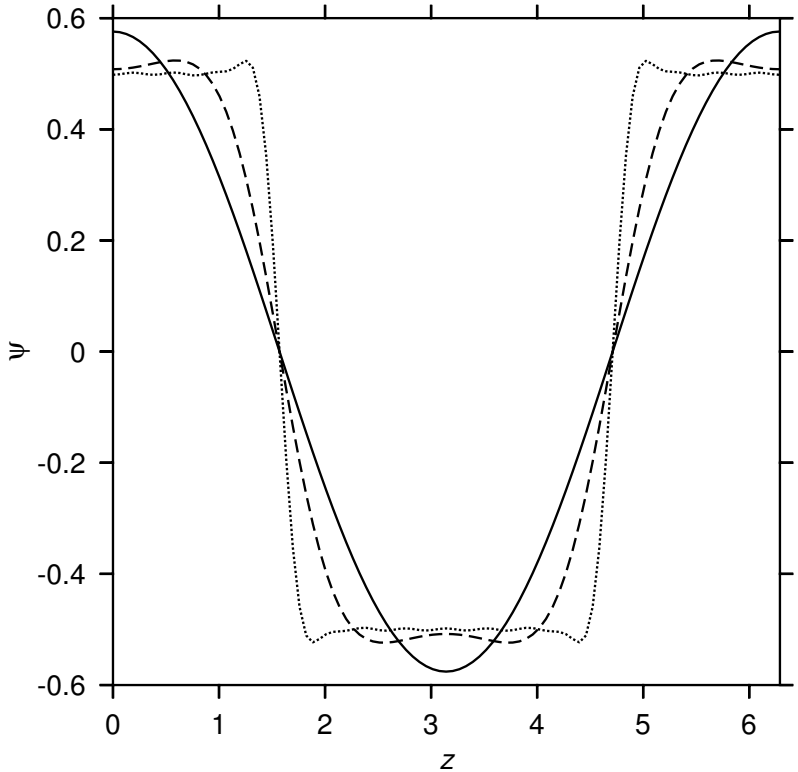
- Assume total density $c_w + c_o$ is a constant.
- Define a concentration field $\psi = (c_w - c_o)/(c_w + c_o)$.
- Free energy functional
  $F[\psi] = A \int dV \left[-\frac{1}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{g}{2}(\nabla\psi)^2 + \frac{r}{2}[(\nabla^2 + k^2)\psi]^2 \right]$



Mesoscale simulations:

Free energy functional

$$F[\psi] = A \int dV \left[-\frac{1}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{g}{2}(\nabla\psi)^2 + \frac{r}{2}[(\nabla^2 + k^2)\psi]^2 \right]$$



Free energy functional

$F[\psi] = A \int dV \left[-\frac{1}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{g}{2}(\nabla\psi)^2 + +\frac{r}{2}[(\nabla^2 + k^2)\psi]^2 \right]$

Minimisation of free energy functional:

$$-\psi + \psi^3 - g\nabla^2\psi + r(\nabla^4 + 2k^2\nabla^2 + k^4)\psi = 0$$

Free energy functional

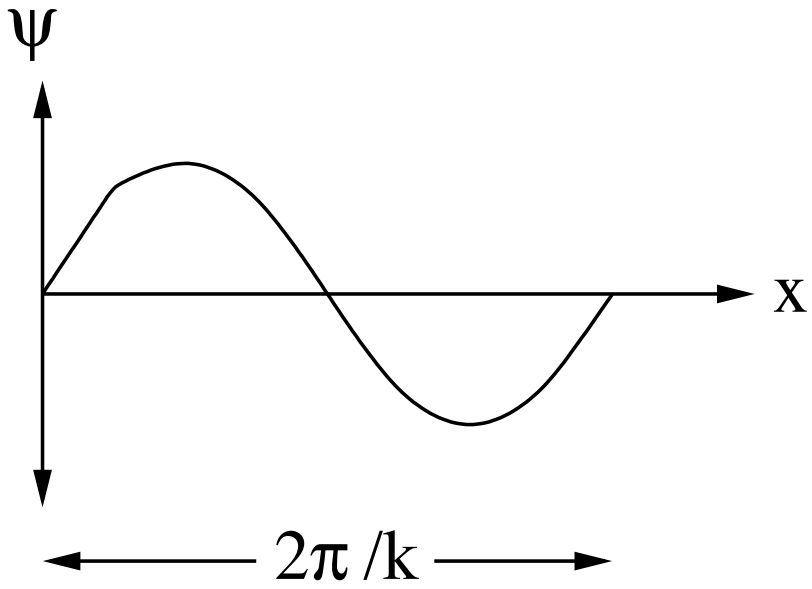
$$F[\psi] = A \int dV \left[-\tfrac{1}{2}\psi^2 + \tfrac{1}{4}\psi^4 + \tfrac{g}{2}(\nabla\psi)^2 + \tfrac{r}{2}[(\nabla^2 + k^2)\psi]^2 \right]$$

Minimisation of free energy functional:

$$-\psi + \psi^3 - g\nabla^2\psi + r(\nabla^4 + 2k^2\nabla^2 + k^4)\psi = 0$$

Limit $r \gg 1$:

$$\psi = \psi_1 \exp(\imath k x)$$



Free energy functional

$$F[\psi] = A \int dV \left[-\tfrac{1}{2}\psi^2 + \tfrac{g}{2}(\nabla\psi)^2 + \tfrac{1}{4}\psi^4 + \tfrac{r}{2}[(\nabla^2 + k^2)\psi]^2 \right]$$

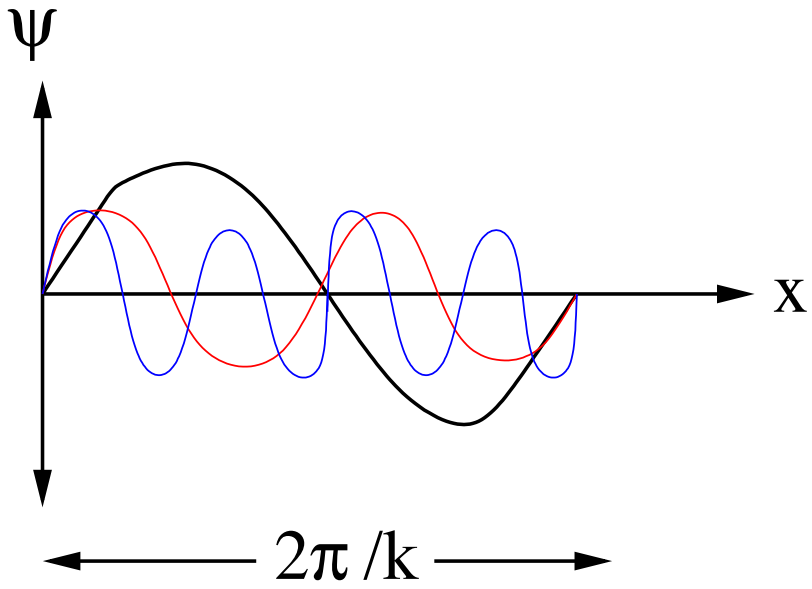
Minimisation of free energy functional:

$$-\psi + \psi^3 - g\nabla^2\psi + r(\nabla^4 + 2k^2\nabla^2 + k^4)\psi = 0$$

Limit $r \gg 1$:

$$\psi = \psi_1 \exp(\imath k x)$$

Non-linear interactions



Concentration field:

$$\psi = \sum_{n=0}^{\infty} \psi_n \exp(\imath nkz)$$

Insert into equation:

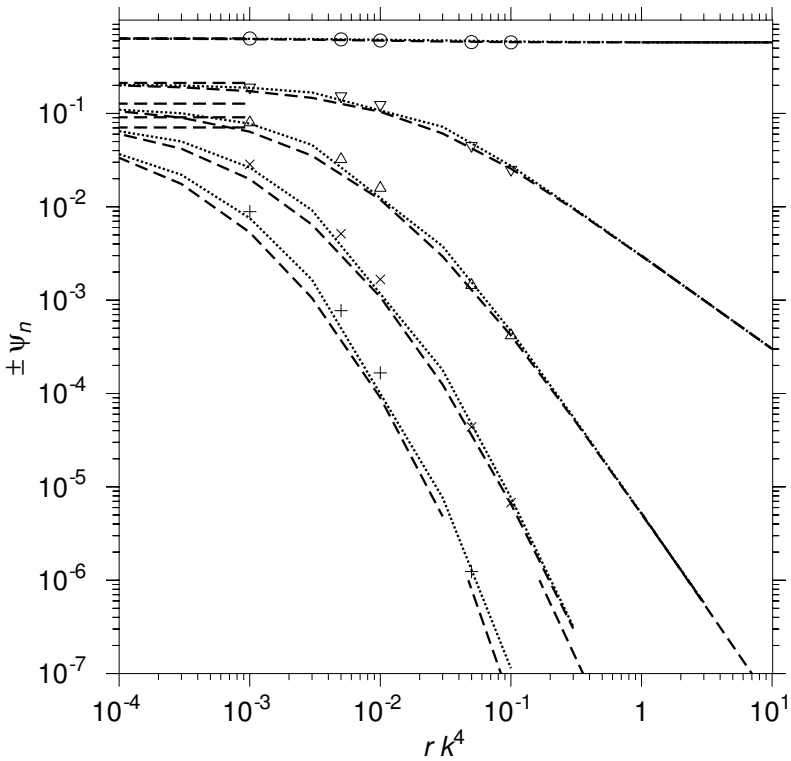
$-\psi + \psi^3 - g\nabla^2\psi$

$r(\nabla^4 + 2k^2\nabla^2 + k^4)\psi = 0$

Solve non-linear simultaneous eqns for ψ_n.

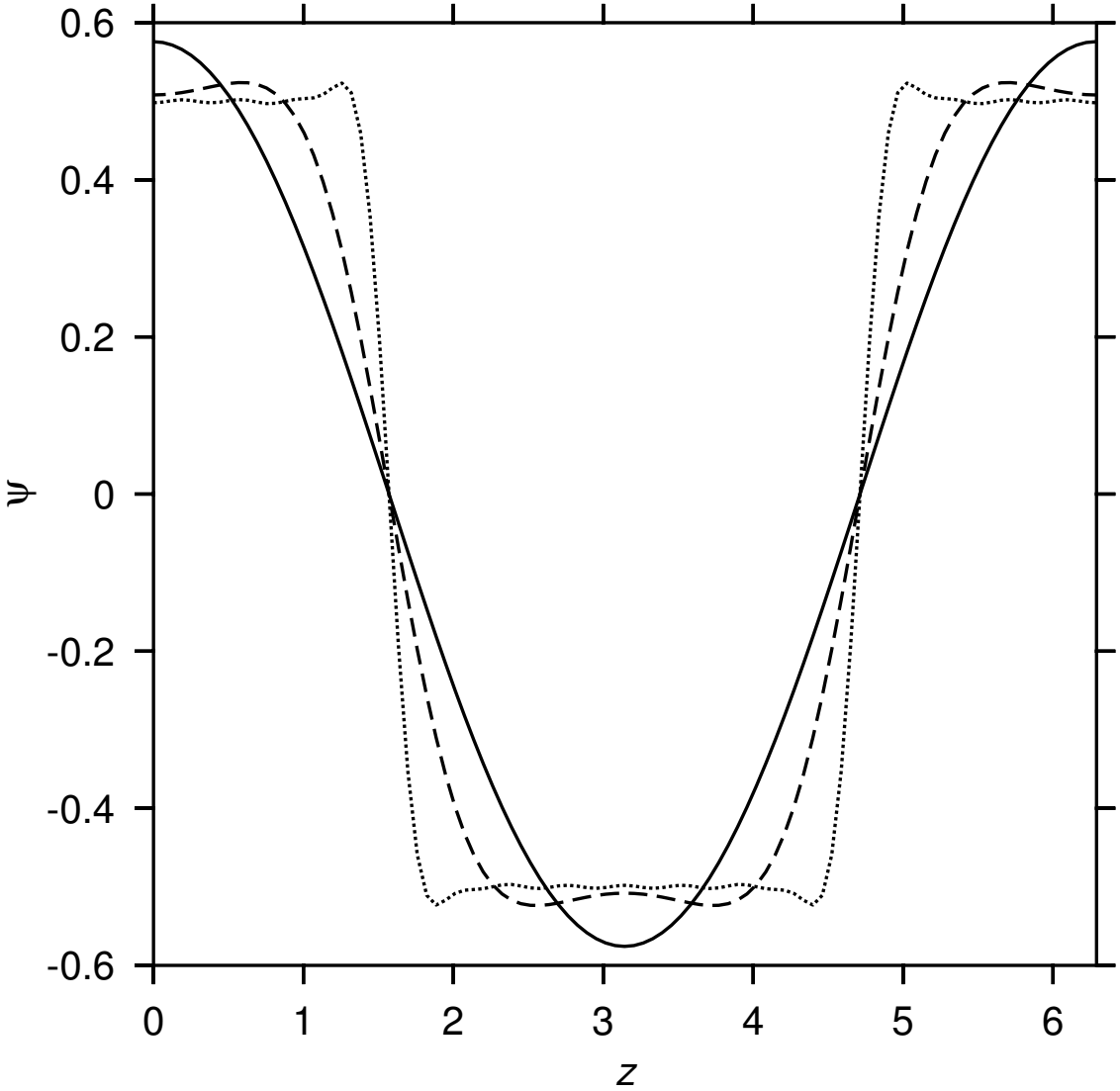
$r \ll 1$ step profile $\psi_n = (2/n\pi)$.

$r \gg 1$ sine profile $\psi_n \propto r^{-(n-1)/2}$.



Symbols simulations; $\cdots$ solution of non-linear equations, $- - -$ Asymptotic results for $r \ll 1$.

Concentration profiles:



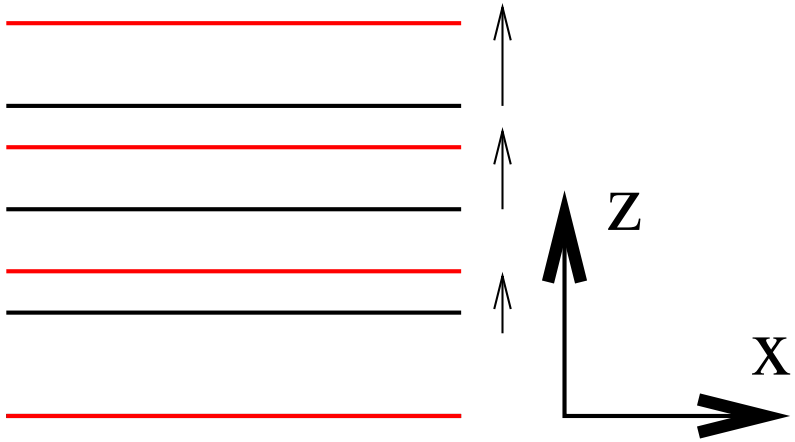
Solid line — $(rk^4) = 1$;
Broken line — $(rk^4) = 10^{-2}$;
Dotted line — $(rk^4) = 10^{-4}$.

Energy scale A: Response to collective excitations

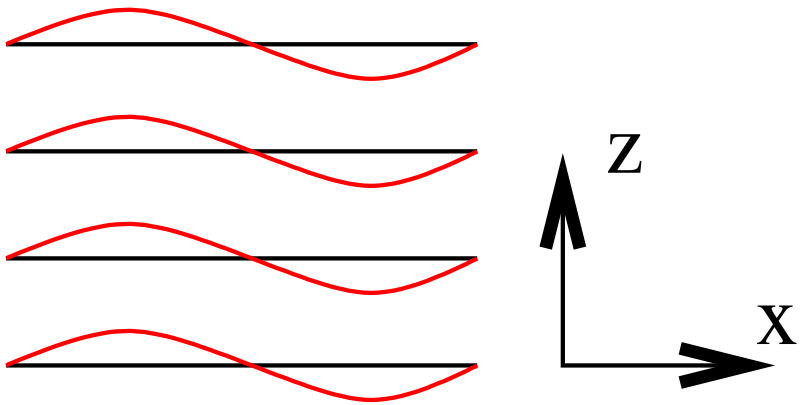
Free energy functional

$$F[\psi] = A \int dV \left[-\frac{1}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{g}{2}(\nabla\psi)^2 + \frac{r}{2}[(\nabla^2 + k^2)\psi]^2 \right]$$

Normal:

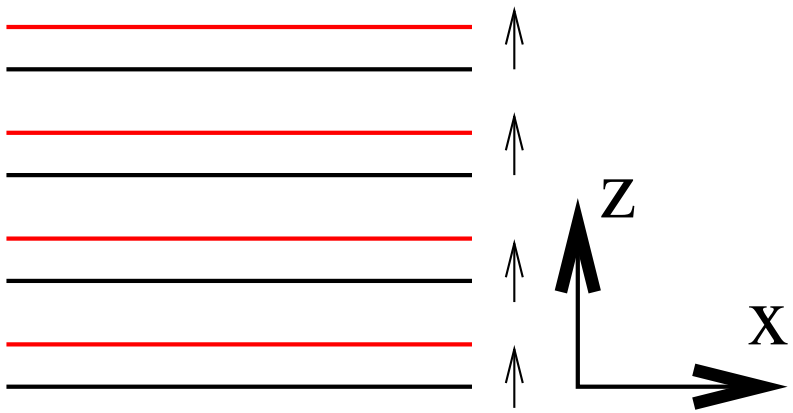


In-plane:



Collective excitations:

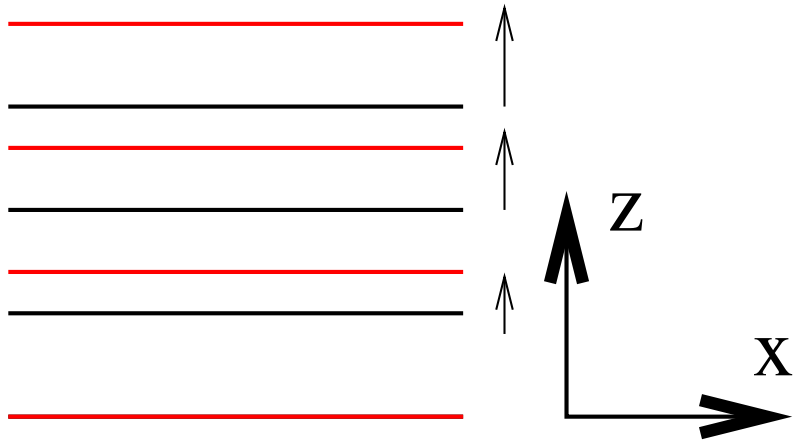
Normal displacement field



Constant u — no energy penalty

Collective excitations:

Normal displacement field

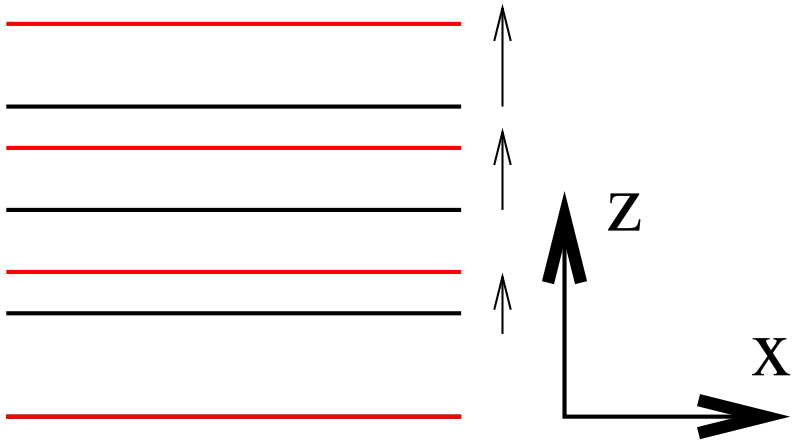


$u \propto z$

$$f \propto \left(\frac{\partial u}{\partial z}\right)^2$$

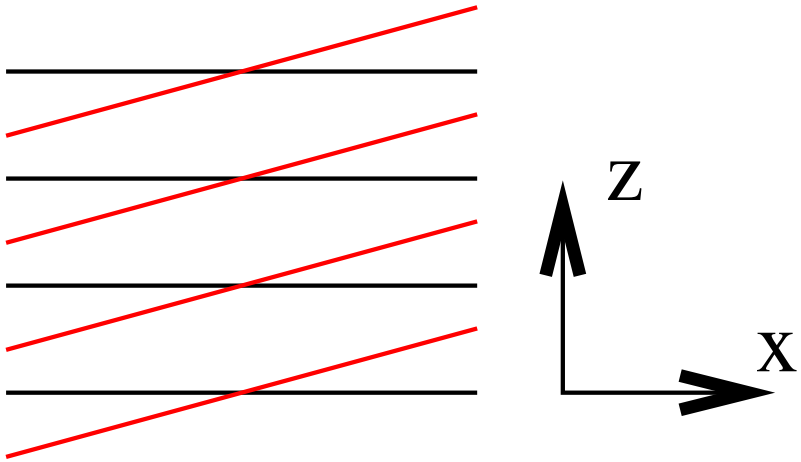
Collective excitations:

Normal displacement field



$$f \propto \left(\frac{\partial u}{\partial z}\right)^2$$

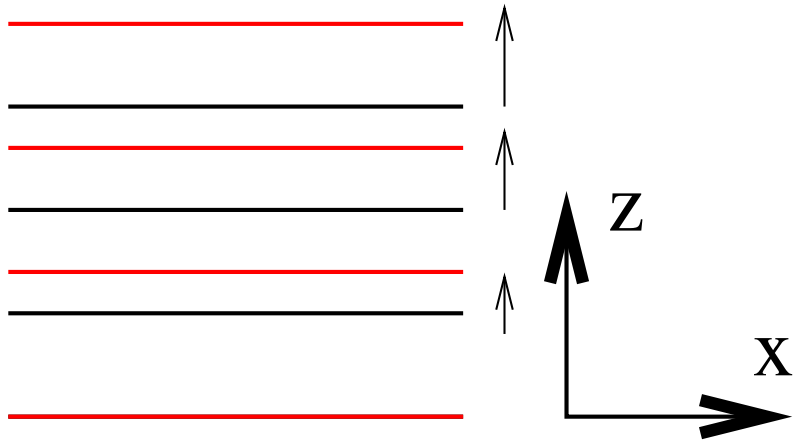
In-plane displacement



$u \propto x$ no energy penalty

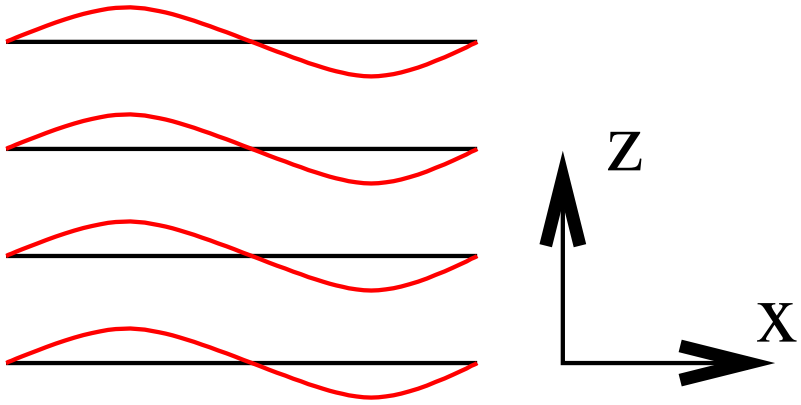
Collective excitations:

Normal displacement field



$$f \propto \left(\frac{\partial u}{\partial z}\right)^2$$

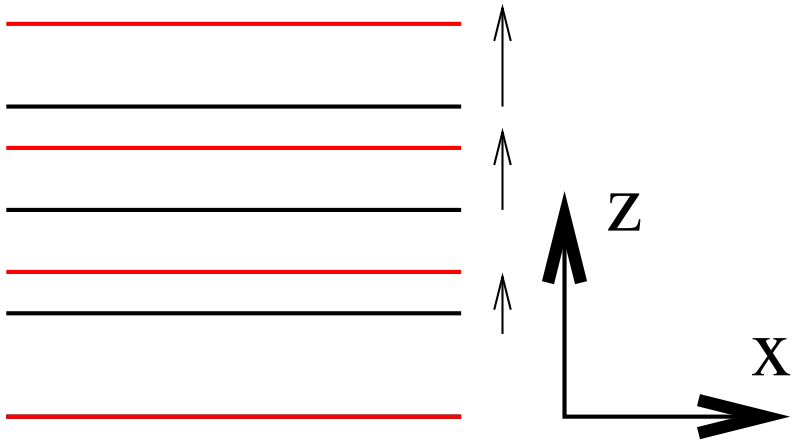
In-plane displacement



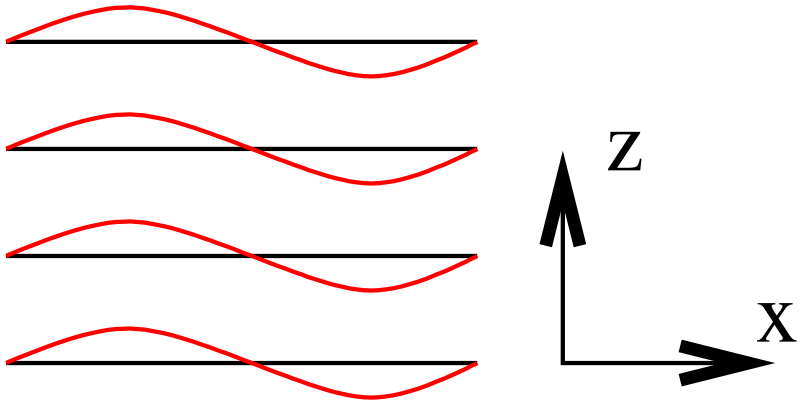
$$f \propto \left(\frac{\partial^2 u}{\partial x^2}\right)^2$$

Collective excitations:

Normal displacement field



In-plane displacement



$$f \propto \left(\frac{\partial u}{\partial z}\right)^2$$

$$f \propto \left(\frac{\partial^2 u}{\partial x^2}\right)^2$$

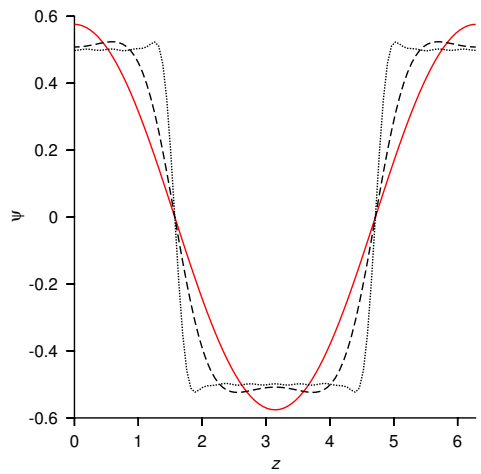
Free energy functional

$$F = \int dV \left(\frac{B}{2}\left(\frac{\partial u}{\partial z}\right)^2 + \frac{K}{2}\left(\nabla_\perp^2 u\right)^2\right)$$

Collective excitations ($r \gg 1$):

Assume displacement field $u(\mathbf{x}, t)$:

$$\psi = \psi_1 \exp\left(-\imath k(z - u(x, y, z, t))\right)$$



Free energy functional

$$F[\psi] = A \int dV \left[-\tfrac{1}{2}\psi^2 + \tfrac{1}{4}\psi^4 + \tfrac{g}{2}(\nabla\psi)^2 + \tfrac{r}{2}[(\nabla^2 + k^2)\psi]^2\right]$$

Square gradient term:

$$(\nabla^2 + k^2)\psi = \psi_1 \left(2k^2 \partial_z u - k^2 (\nabla u)^2 + \imath k \nabla^2 u\right)$$

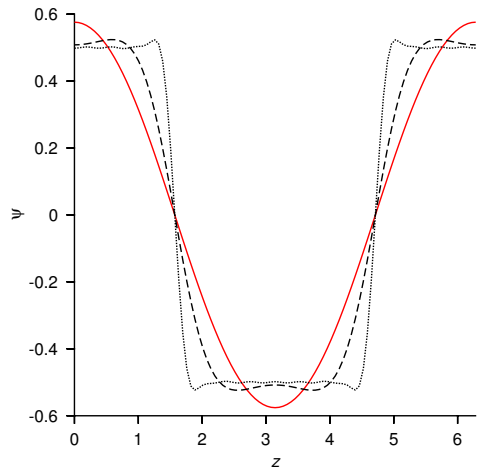
$$= \psi_1 (2k^2 E_{zz}(u) + \imath k \nabla^2 u)$$

where $E_{zz}(u) = (\partial_z u - (1/2)(\nabla u)^2)$ is frame-invariant strain.

Collective excitations ($r \gg 1$):

Assume displacement field $u(\mathbf{x}, t)$:

$$\psi = \psi_1 \exp\left(-\imath k(z - u(x, y, z, t))\right)$$



Free energy functional:

$$\langle F \rangle_{cg} = A \int dV \left(-\frac{\psi_1^2}{2} + \frac{\psi_1^4}{4} + (r/2)\psi_1^2 (4k^4 E_{zz}(u)^2 + k^2 (\nabla^2 u)^2) \right)$$

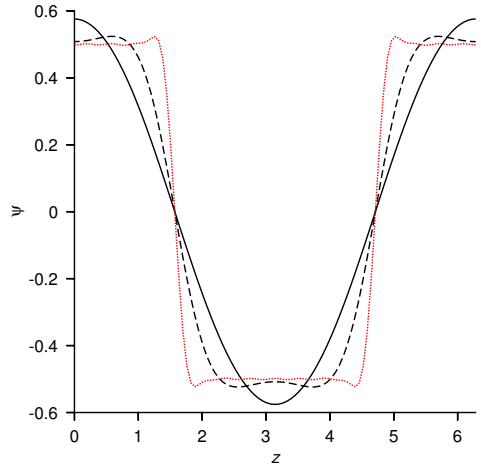
Bending and layer compression moduli:

$$\begin{aligned} B &= 4rAk^4\psi_1^2 \\ K &= rAk^2\psi_1^2 \end{aligned}$$

Collective excitations ($r \sim 1$):

Assume displacement field $u(\mathbf{x}, t)$:

$$\psi = \sum_n \psi_n \exp\left(-\imath n k (z - u(x, y, z, t))\right)$$



$$F[\psi] = A \int dV \left[-\tfrac{1}{2}\psi^2 + \tfrac{1}{4}\psi^4 + \tfrac{g}{2}(\nabla\psi)^2 + \tfrac{r}{2}[(\nabla^2 + k^2)\psi]^2\right]$$

$$\begin{aligned}\langle F\rangle_{cg} = \quad & A \int dV \textstyle\sum_n \psi_n^2 \left[2rn^4(\frac{\partial u}{\partial z} - (1/2)(\nabla u)^2)^2 + (r/2k^2)n^2(\nabla^2 u)^2\right. \\ & \left. +2rn^2(1-n^2)(\tfrac{\partial u}{\partial z} - (1/2)(\nabla u)^2) - gn^2(\tfrac{\partial u}{\partial z} - (1/2)(\nabla u)^2)\right]\end{aligned}$$

$$\begin{aligned} B &= rA\textstyle\sum_n 4n^4k^4\psi_n^2 \qquad K = rA\textstyle\sum_n n^2k^2\psi_n^2 \\ g &= \frac{2r\sum_n n^2(1-n^2)\psi_n^2}{\sum_n n^2\psi_n^2} = -g_0 \end{aligned}$$

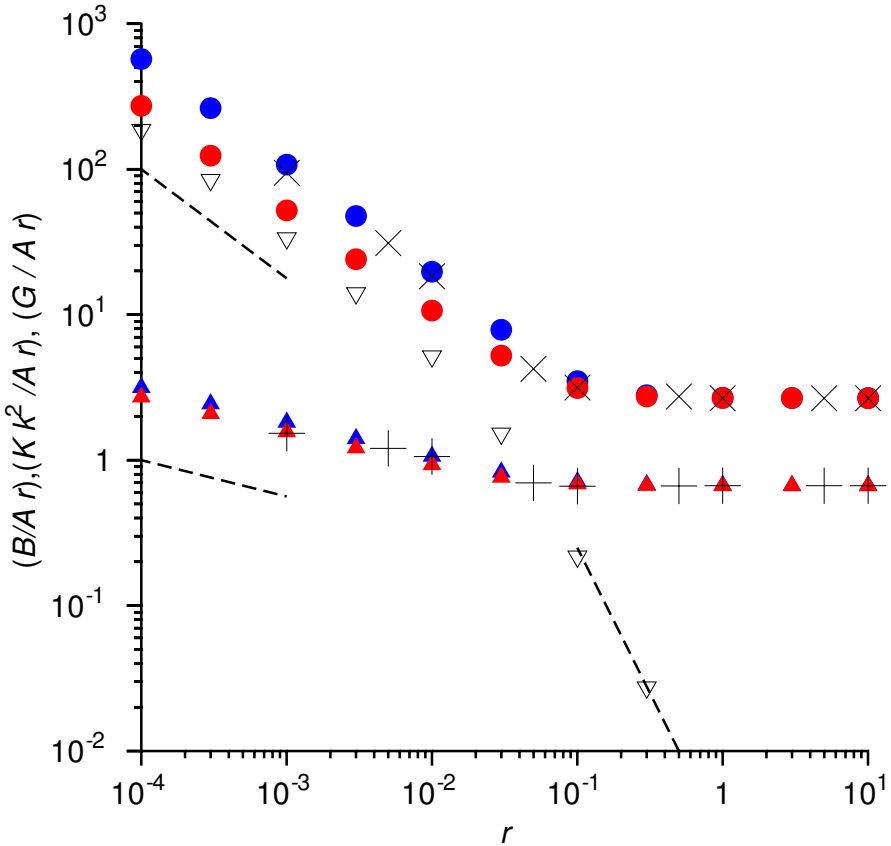
Collective excitations:

Compression & Bending moduli:

Scaling:

$(r \gg 1) \rightarrow \psi_1 = (1/\sqrt{3})$
$B = (4rk^4 A/3)$
$K = (rk^2 A/3)$

$r \ll 1 \rightarrow \psi_n = (2/\pi n)$
$B \propto r^{-1/4}$
$K \propto r^{-3/4}$



$\circ$ — (B/Ar) $\triangle$ — (Kk^2/Ar); $g = -g_0$, $g = 0$. ∇ — Spurious linear coefficient.

Simulations: $\times$ (B/Ar), $+$ (Kk^2/Ar).

Dynamical response:

Concentration equation:

$$\frac{\partial \psi}{\partial t} + \mathbf{v}.\nabla\psi = \nabla.\left(\Gamma\nabla\left(\frac{\delta F}{\delta\psi}\right)\right)$$

Fluid mass equation:

$$\nabla\cdot\mathbf{v} = 0$$

Fluid momentum equation:

$$\rho(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v}) = -\nabla p + \mu\nabla^2\mathbf{v} + (\nabla\psi)\frac{\delta F}{\delta\psi}$$

Dynamical response:

Concentration equation:

$$\frac{\partial \psi}{\partial t} + \mathbf{v}.\nabla\psi = \nabla.\left(\Gamma\nabla\left(\frac{\delta F}{\delta\psi}\right)\right)$$

$\psi = \sum \psi_n \exp\left(\imath nk(z-u)\right)$, linearise.

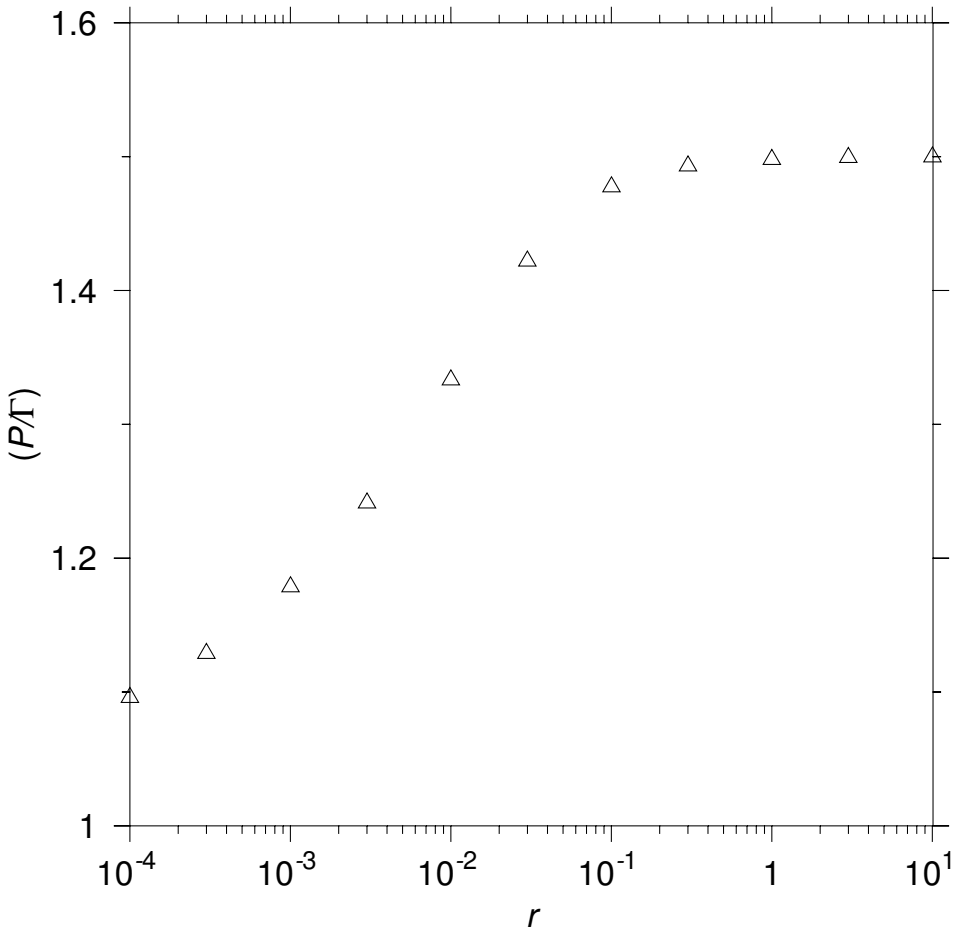
Displacement equation:

$$P(\frac{\partial u}{\partial t} - v_z) = -f_z$$

Force density:

$f_z = (B\partial_z^2 u - K\nabla^4 u) = -(\delta\langle F\rangle_{cg}/\delta u)$

$$P = \frac{\Gamma}{\left(\sum_n \psi_n^2\right)}$$



Dynamical response:

Fluid momentum equation:

$$\frac{\partial \mathbf{v}}{\partial t} = -\nabla p + \eta \nabla^2 \mathbf{v} + (\nabla \psi) \frac{\delta F}{\delta \psi}$$

Substitute $\psi = \sum \psi_n \exp\left(\imath n k (z - u)\right)$ and expand to linear order in u, and take long wavelength limit.

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\nabla p + \eta \nabla^2 \mathbf{v} + \mathbf{e}_z f_z$$

where

$$\begin{aligned} B &= rA \textstyle\sum_n 4 n^4 k^4 \psi_n^2 \\ K &= rA \textstyle\sum_n n^2 k^2 \psi_n^2 \end{aligned}$$

Force density $f_z = (B \partial_z^2 u - K \nabla^4 u)$

Linear response:

$u = \tilde{u} \exp(st) \exp(\imath(q_x x + q_z z))$; $\mathbf{v} = \tilde{\mathbf{v}} \exp(st) \exp(\imath(q_x x + q_z z))$

Layer displacement equation:

$$\frac{\partial u}{\partial t} - v_z = P^{-1} f_z \qquad \Bigg| \qquad s\tilde{u} - \tilde{v}_z = -(Bq_z^2 + Kq^4)\tilde{u}$$

Momentum equations:

$$\rho \frac{\partial v_z}{\partial t} = \mu \nabla^2 v_z - \frac{\partial p}{\partial z} + f_z \qquad \Bigg| \qquad \rho s \tilde{v}_z = -\imath q_z \tilde{p} + \mu q^2 \tilde{v}_z - P^{-1}(Bq_z^2 + Kq^4)\tilde{u}$$

$$\rho \frac{\partial v_x}{\partial t} = \mu \nabla^2 v_x - \frac{\partial p}{\partial x} \qquad \Bigg| \qquad s\tilde{v}_x = -\imath q_x \tilde{p} + \mu q^2 \tilde{v}_x$$

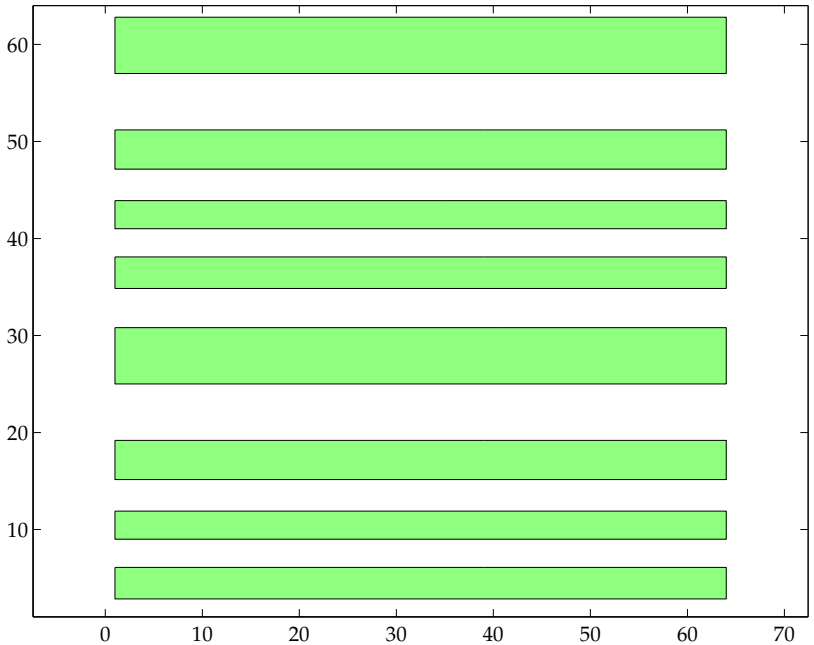
Dispersion relation:

$$(s + \nu q^2)(s + P^{-1}(Bq_z^2 + Kq^4)) + q_x^2(Bq_z^2 + Kq^4) = 0$$

Linear response:

Compression

$u = \tilde{u} \exp(st) \exp(\imath q z)$

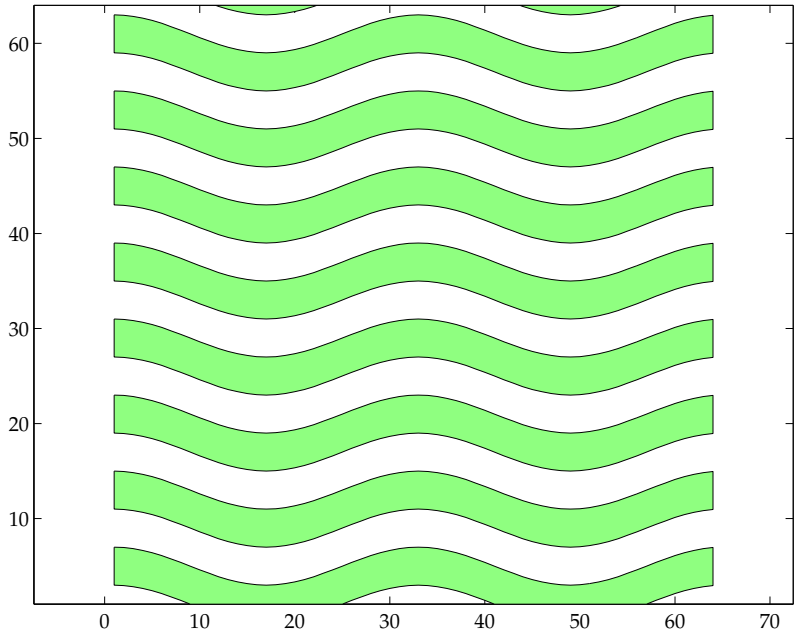


Growth rate:

$s = -\nu q_z^2, s = -P^{-1} B q_z^2.$

Bending

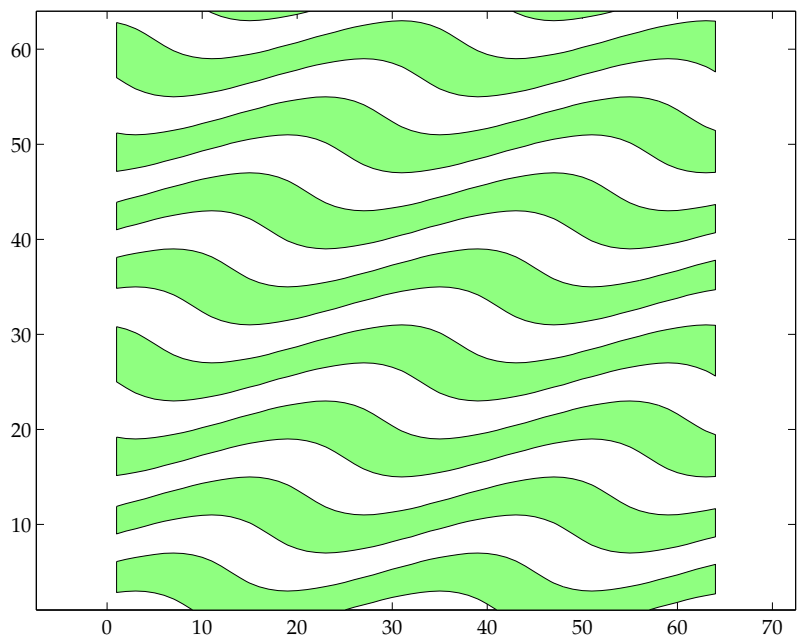
$u = \tilde{u} \exp(st) \exp(\imath q x)$

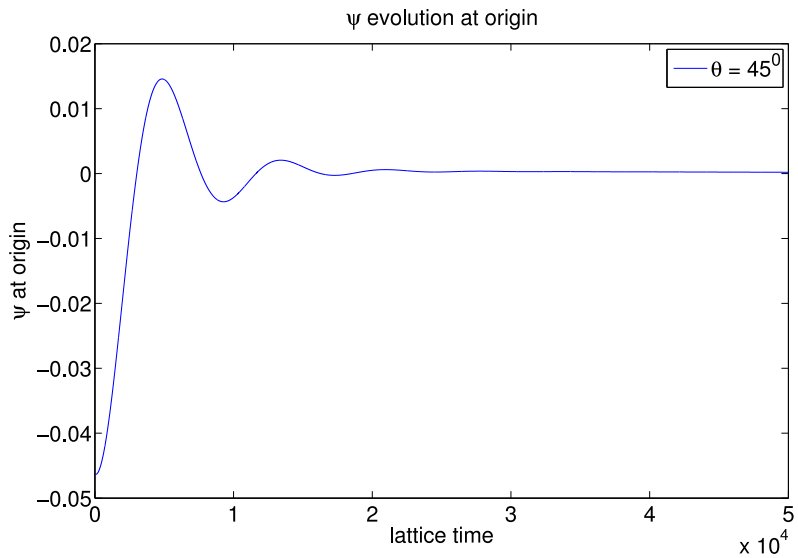


Growth rate

$s = (q^2/2)(-\nu \pm \sqrt{\nu^2 - 4K}).$

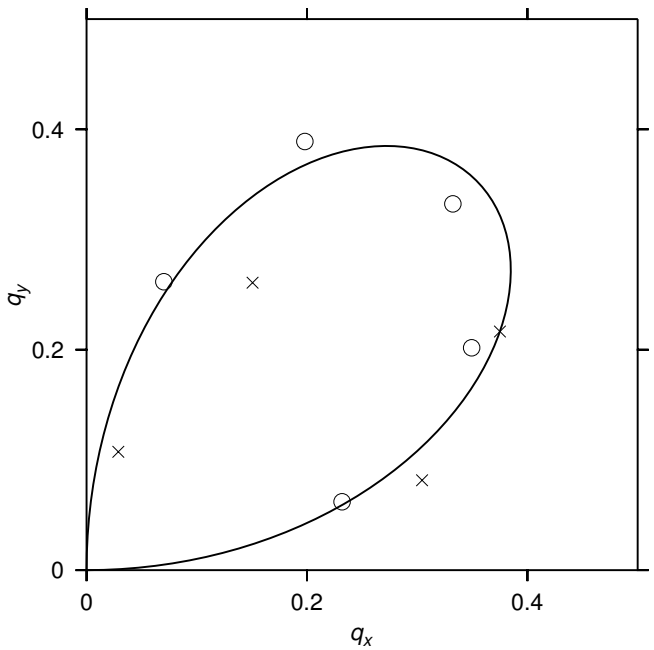
Linear response:





$$s = \pm \imath c_2 - (\nu q^2/2) - (BP^{-1}q_z^2/2)$$

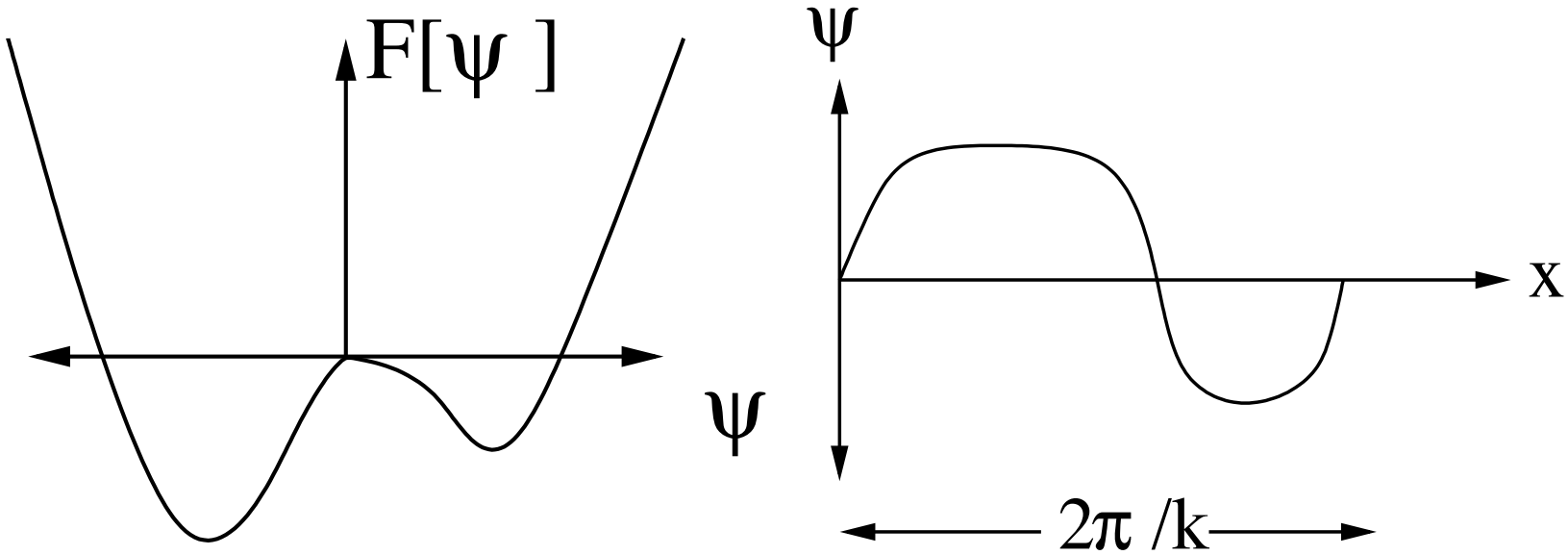
$$c_2 = \sqrt{Bq_x q_z}$$



Asymmetric bilayer:

Modified free energy functional:

$$F[\psi] = A \int dV \left(-\frac{\psi^2}{2} + \frac{c\psi^3}{3} + \frac{\psi^4}{4} + \frac{g}{2k^2}(\nabla\psi)^2 + \frac{r}{2k^4}((\nabla^2 + k^2)\psi)^2 \right)$$



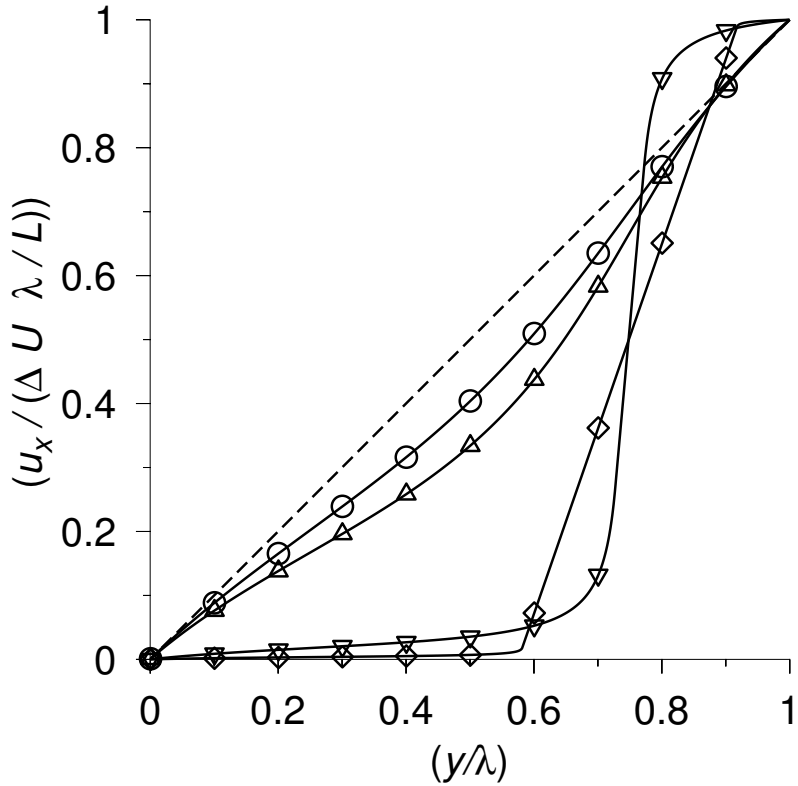
Viscosity constrast:

Dependence on concentration:

$$\mu = \mathrm{Max}[\mu_0(1+\mu_1\psi(\mathbf{x},t)), 0.01\mu_0]$$

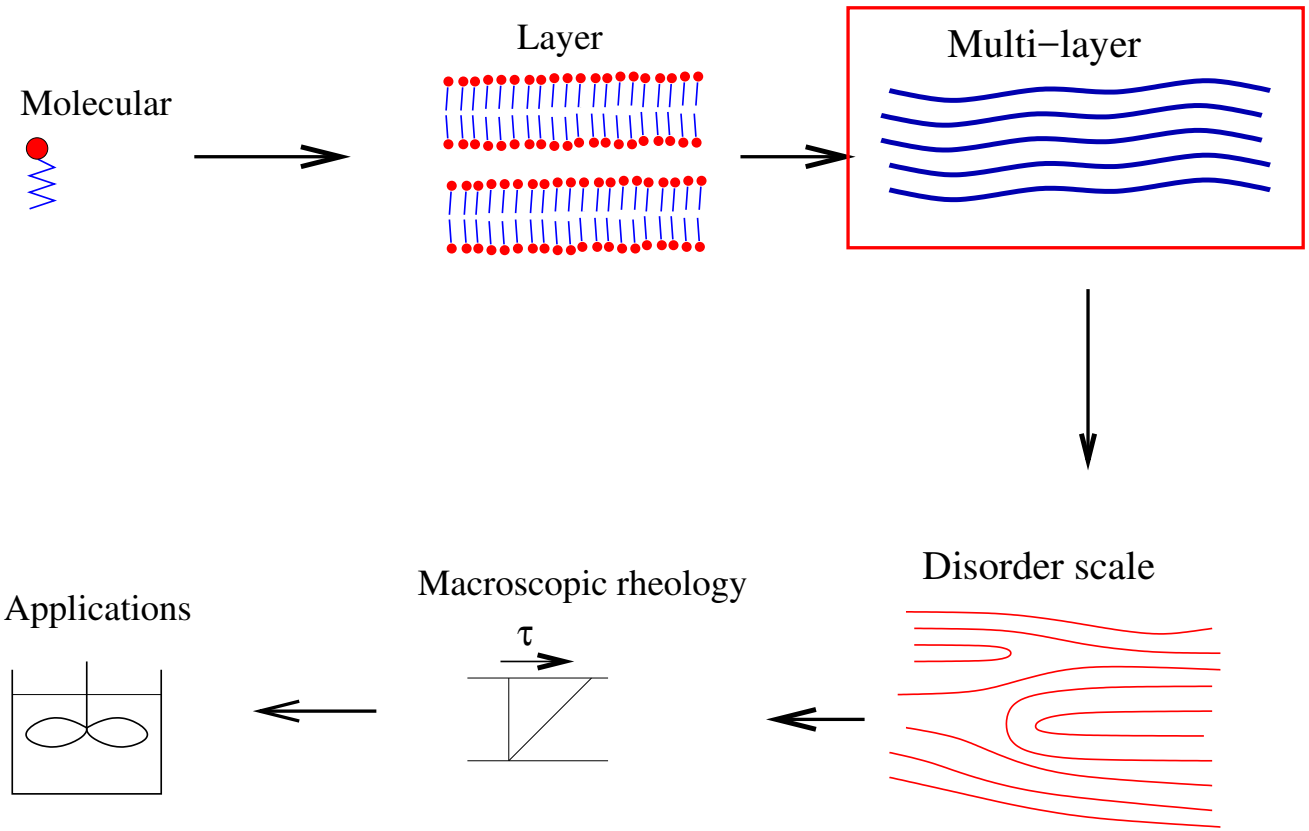
Average viscosity:

$$\bar{\mu} = \left(\frac{1}{\lambda}\int_0^\lambda dy \frac{1}{\mu(y)}\right)^{-1}$$



$$\mu_1 = 0.32(\circ), 0.53(\triangle), 1.07(\nabla), 2.13(\diamond)$$

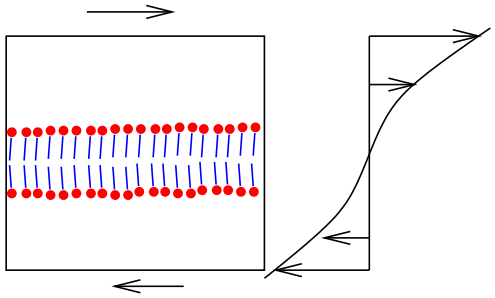
Rheology at mesoscale:



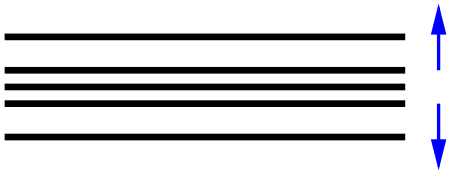
V. Kumaran , S. K. Jariwala & S. Hussain, Chem. Eng. Sci., **56**, *5663, (2001);*

V. Kumaran & D. S. S. Raman, Phys. Rev. E, **83**, *031501, (2011).*

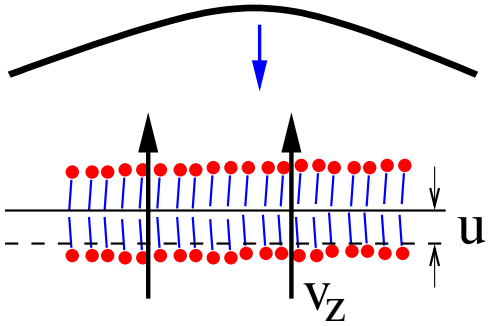
Dimensional parameters:



- Fluid: Viscosity μ, density ρ.
- Viscosity contrast: $\Delta\mu$.



- Bilayers: Layer spacing λ.
- Bilayers:
  Compression mod B,
  Bending mod $K \sim (B/\lambda^2)$.



- Coupling: Permeation constant P.

Mesoscale simulations: Dimensional analysis:

Dimensional parameters:

Wavelength $\lambda = (2\pi/k)$

System size L

Free energy density $A \leftrightarrow B$ Bending modulus

Interface sharpness r

Onsagar coeff $\Gamma \leftrightarrow D$ Diffusion coeff

Viscosity μ

Viscosity constrast $\mu_r = (\Delta\mu/\mu)$

Dimensionless groups:

Size $(L/\lambda) = 16, 32, 64, 128.$

$Re = (\rho L^2 \dot{\gamma}/\mu) = 1$

$\Sigma = (\rho A \lambda^2/\mu^2) = 10^{-2} - 10^{-6}$

$\mathrm{Er} = (\bar{\mu}\dot{\gamma}/B)$

$\mathrm{Sc}\Sigma = (A\lambda^2/\mu D) = 1 - 100$

Viscosity contrast $\mu_r = 0 - 2.$

Conservation equations:

$\frac{\partial \psi}{\partial t} + \mathbf{v}.\nabla\psi = \nabla.\left(\Gamma\nabla\left(\frac{\delta F}{\delta\psi}\right)\right)$

$\rho(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v}) = -\nabla p + \mu\nabla^2\mathbf{v} + (\nabla\psi)\frac{\delta F}{\delta\psi}$

$\nabla^* = \lambda\nabla$, $k^* = (k\lambda)$, $t^*_\psi = (t\Gamma A/\lambda^2) = (tD/\lambda^2)$.

$\mathbf{v}^* = (\mathbf{v}/V_\psi)$ where $V_\psi = (A\lambda/\mu)$

Scaled equations:

$$\Sigma\left(\frac{\partial \mathbf{u}^*}{\partial t^*} + \mathbf{v}^*\cdot\nabla\mathbf{v}^*\right) = -\nabla^* p^* + \nabla^{*2}\mathbf{v}^* + \nabla^*\psi\left(-\psi + \psi^2 + \frac{r}{k^{*4}}(\nabla^{*2} + k^{*2})^2\psi\right)$$

$$\mathrm{Sc}\Sigma\left(\frac{\partial \psi}{\partial t^*} + \mathbf{v}^*\nabla^*\psi\right) = \nabla^{*2}\left(-\psi + \psi^3 + \frac{r}{k^{*4}}(\nabla^{*2} + k^{*2})\psi\right)$$

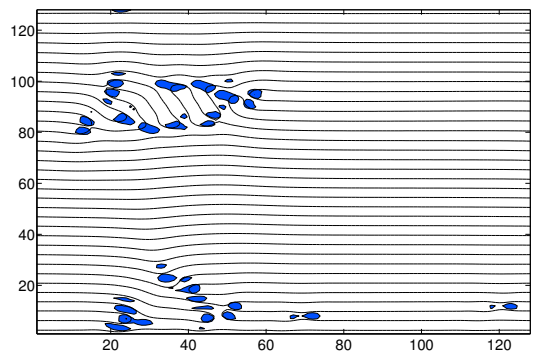
Σ Reynolds number based on layer spacing & V_ψ.

$\mathrm{Sc}\Sigma$ Peclet number based on layer spacing & V_ψ.

Macroscopic measure of dis-ordering & Rheology:

Ordered lamellar phase, free energy

$$F[\psi] = \int dV(-\frac{\psi^2}{2}+\frac{\psi^4}{4}+\frac{r}{2}((\nabla^2+k^2)\psi)^2)$$

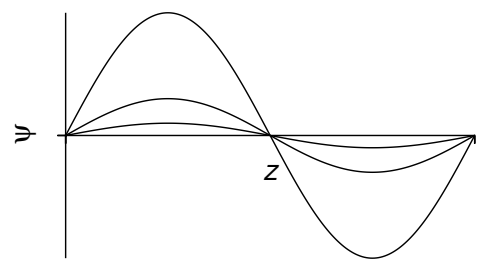


Define local defect density field

$$f = -\frac{\psi^2}{2} + \frac{\psi^4}{4} + \frac{r}{2}((\nabla^2 + k^2)\psi)^2$$

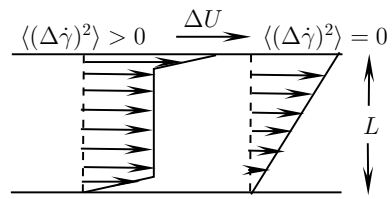
Extent of coarsening

$\langle\psi^2\rangle = \frac{1}{V}\int dV\psi^2$



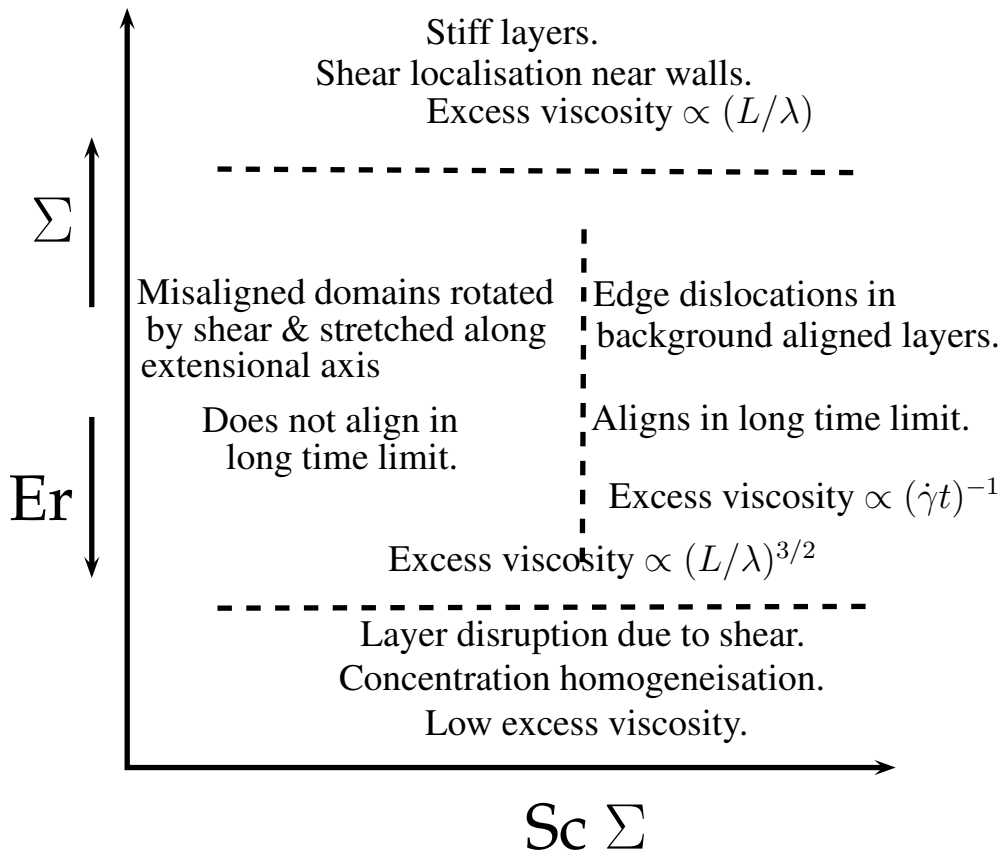
Departure from linear shear:

$\langle(\Delta\dot{\gamma})^2\rangle = \frac{1}{V\bar{\dot{\gamma}}^2}\int dV(v_x - \dot{\gamma}y)^2$



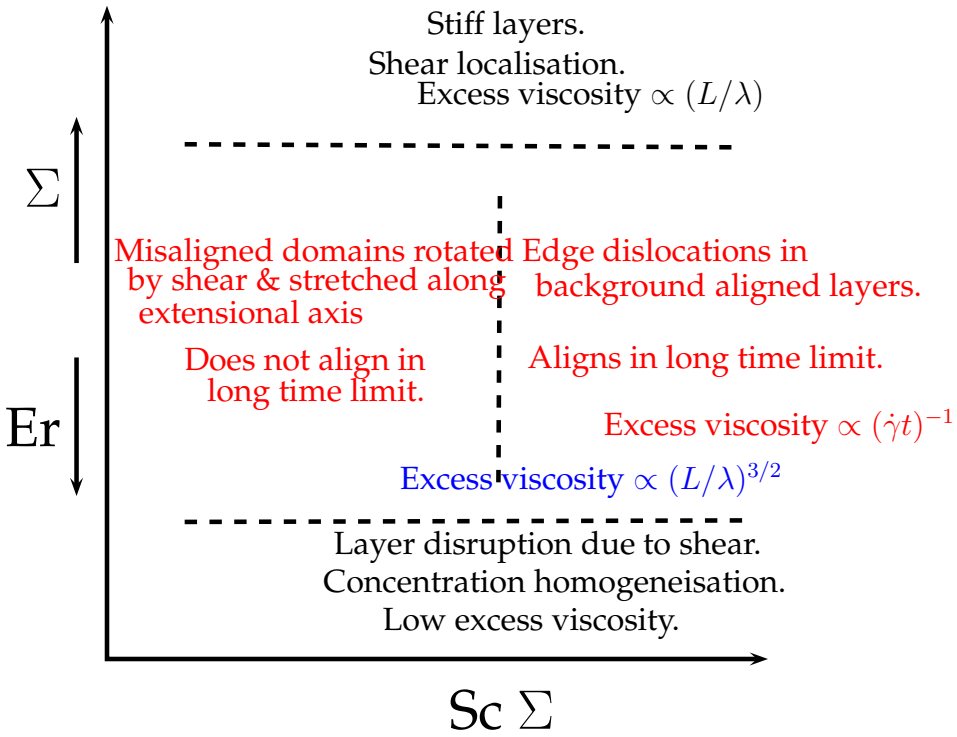
$\mu = (\tau/(\Delta V_x/L)); \mu^* = (\mu/\mu_{al})$

Structure-rheology relationship:



$Re = (\rho L^2 \dot{\gamma}/\mu) = 1$, $\Sigma = (\rho A \lambda^2/\mu^2)$ $\mathrm{Sc}\Sigma = (A\lambda^2/\mu D)$,
$\mathrm{Er} = (\bar{\mu}\dot{\gamma}/B)$

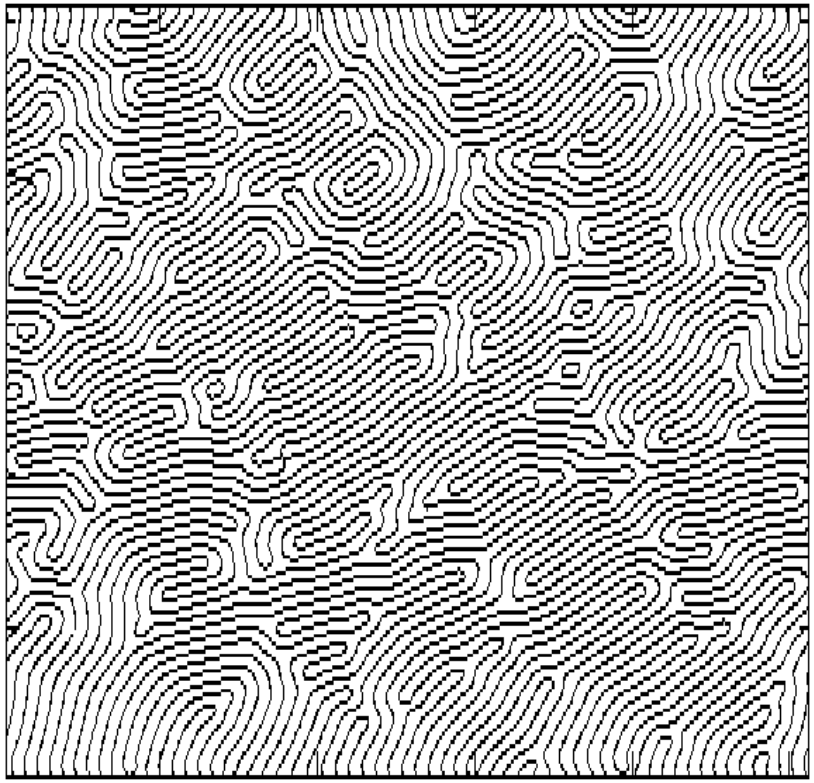
Structure-rheology relationship:



$r = 1$, $\Sigma = 4 \times 10^{-3}$, $3.41 \leq \mathrm{Sc}\Sigma \leq 51.2$.

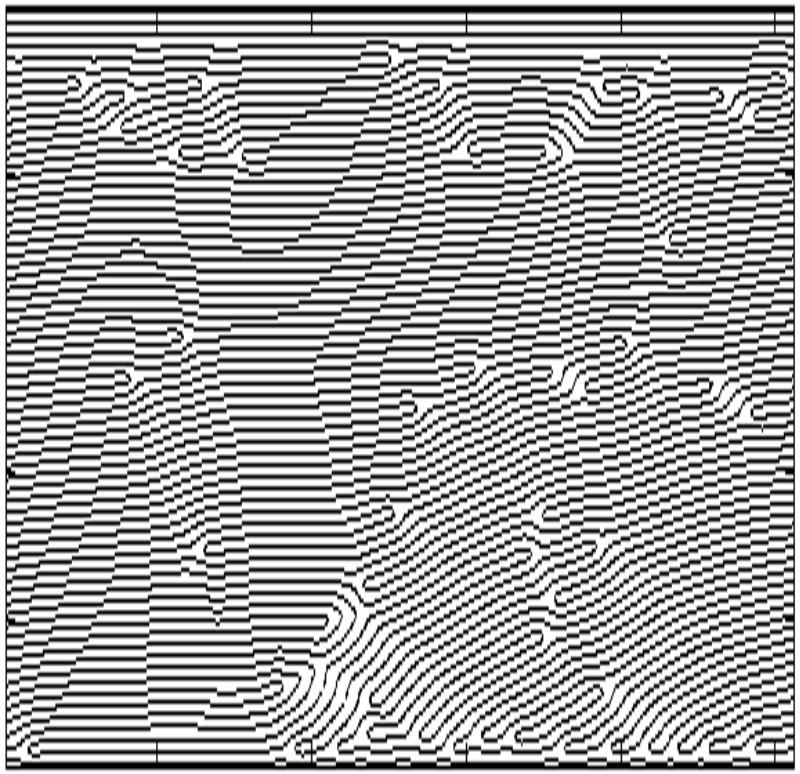
Different types of ordering:

$Sc\Sigma = 3.41$, t=7.8125:



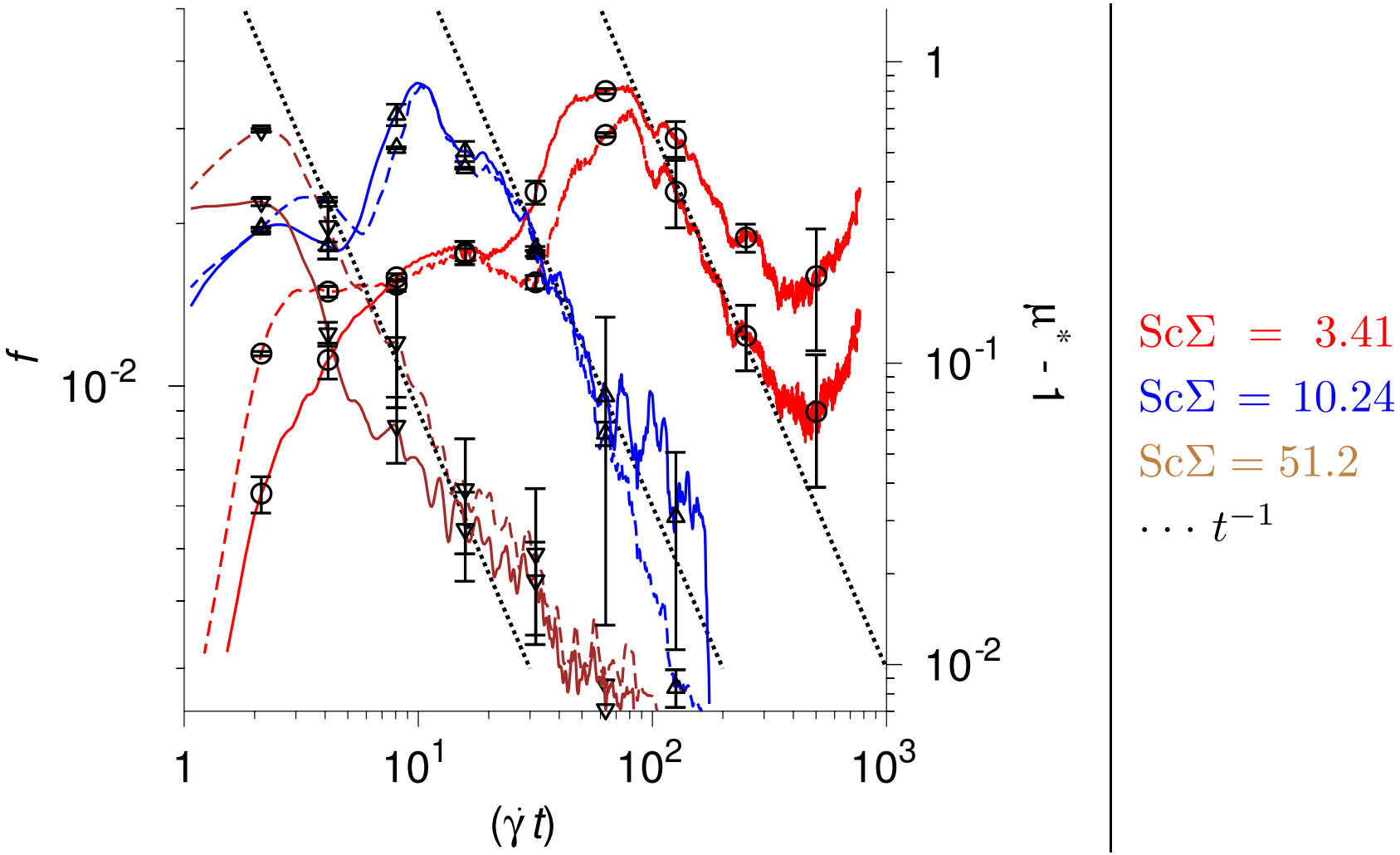
Grain-boundary coarsening.

$Sc\Sigma = 5.0$, t=7.8125:



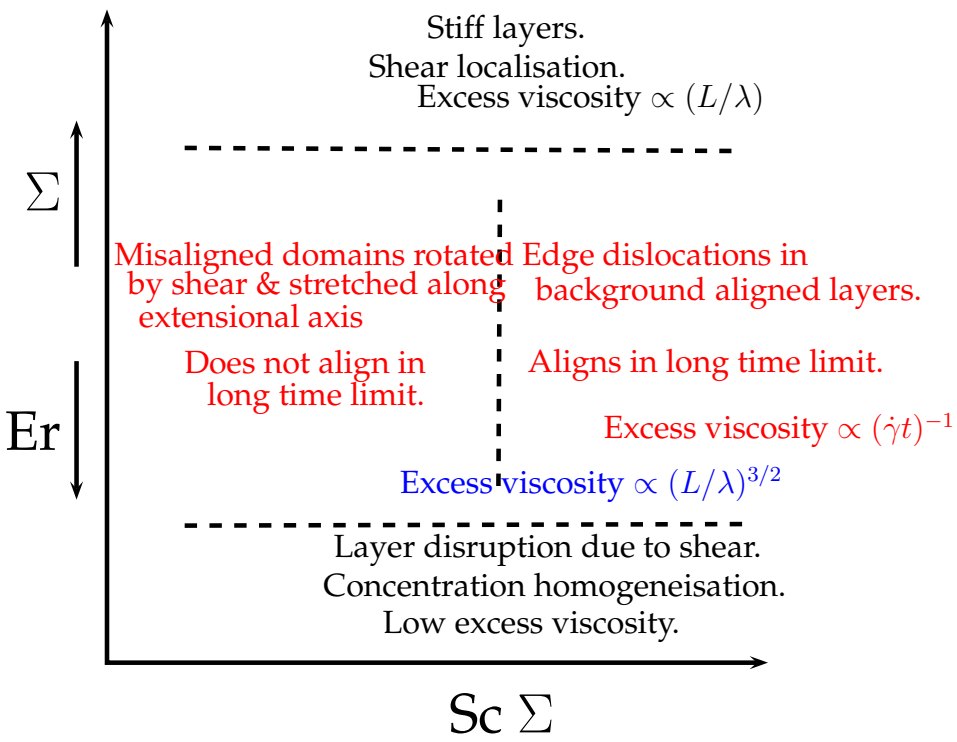
Isolated edge dislocation.

Time evolution of structure and rheology:



- - - $f = -\frac{\psi^2}{2} + \frac{\psi^4}{4} + \frac{r((\nabla^2+k^2)\psi)^2}{2}$; — $\mu^* - 1 = (\mu/\mu_{al}) - 1$.

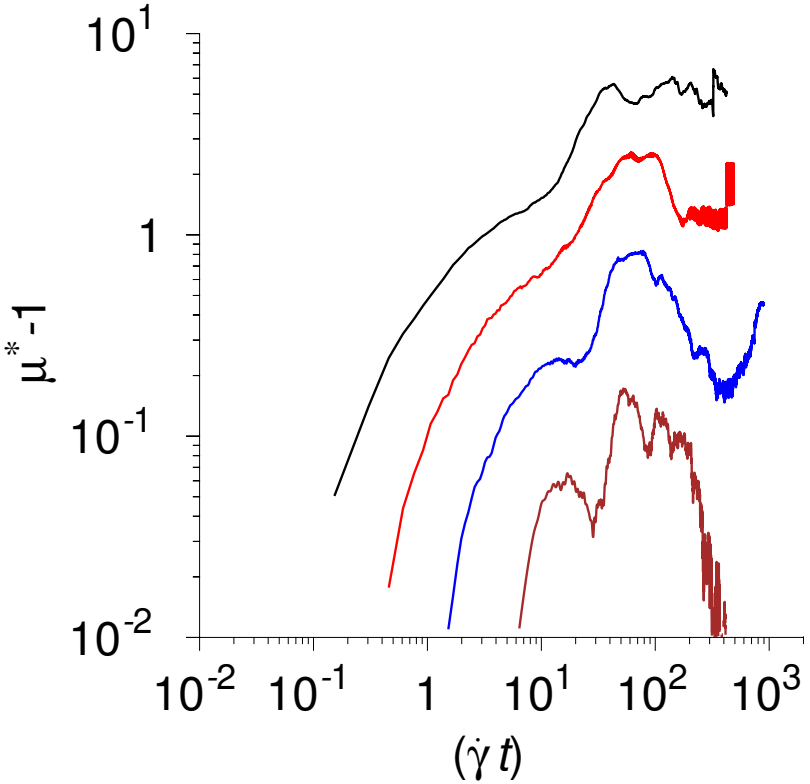
Structure-rheology relationship:



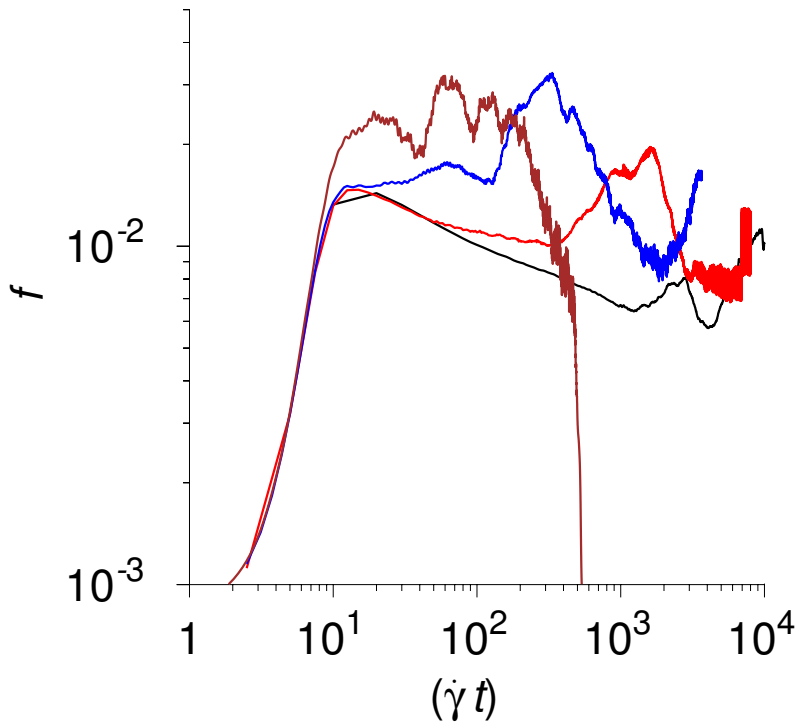
$r = 1$, $\Sigma = 4 \times 10^{-3}$, $3.41 \leq \mathrm{Sc}\Sigma \leq 50.2$, $16 \leq (L/\lambda) \leq 128$.

Structure-rheology relationship: $\mathrm{Sc}\Sigma = 3.41$

$(L/\lambda) = 128, 64, 32, 16.$



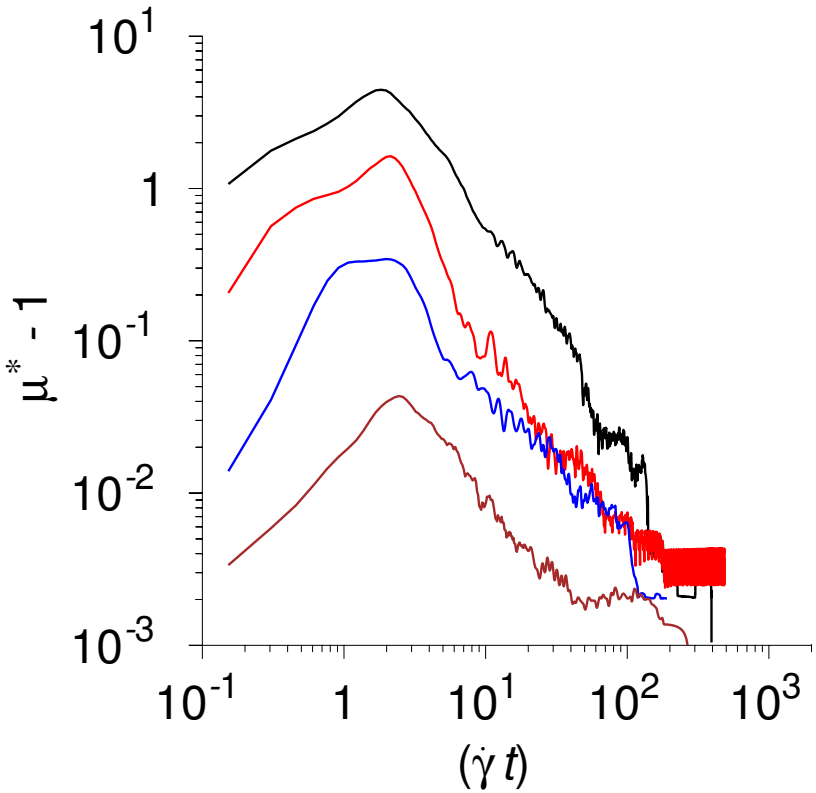
— $\mu^* - 1 = (\mu/\mu_{al}) - 1,$



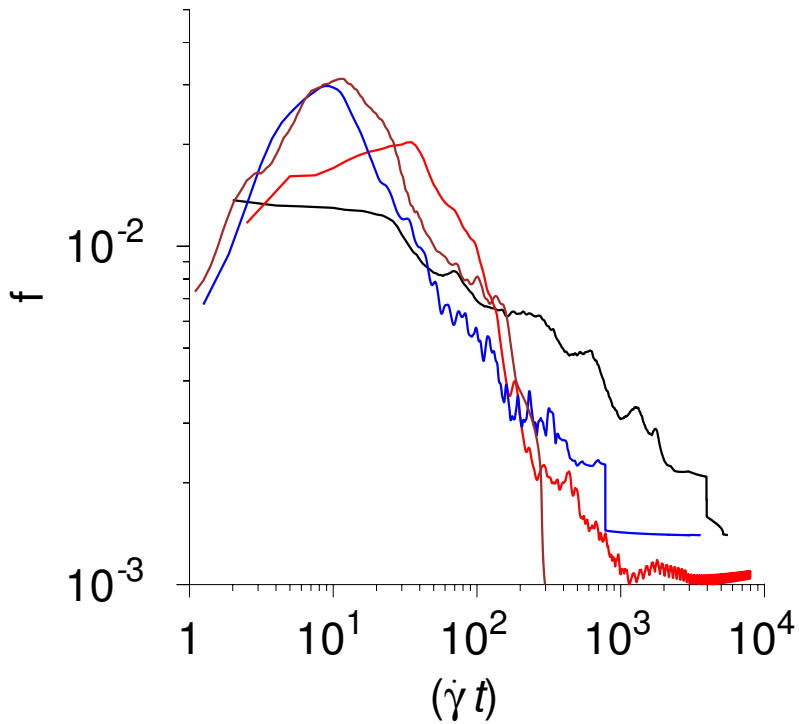
$$f = -\frac{\psi^2}{2} + \frac{\psi^4}{4} + \frac{r((\nabla^2 + k^2)\psi)^2}{2}.$$

Structure-rheology relationship: $\mathrm{Sc}\Sigma = 51.24$

$(L/\lambda) = 128, 64, 32, 16.$



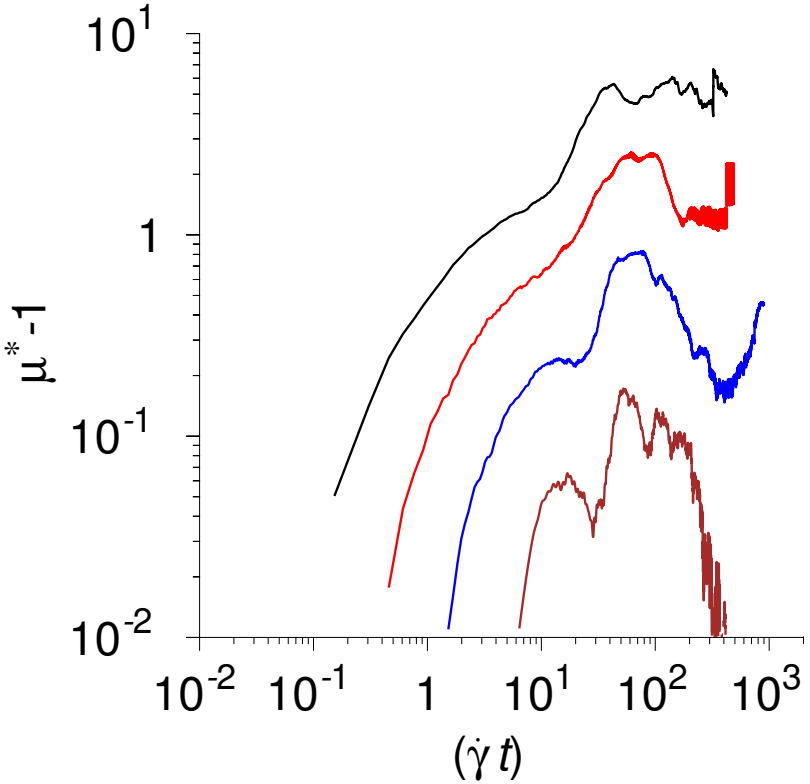
— $\mu^* - 1 = (\mu/\mu_{al}) - 1,$



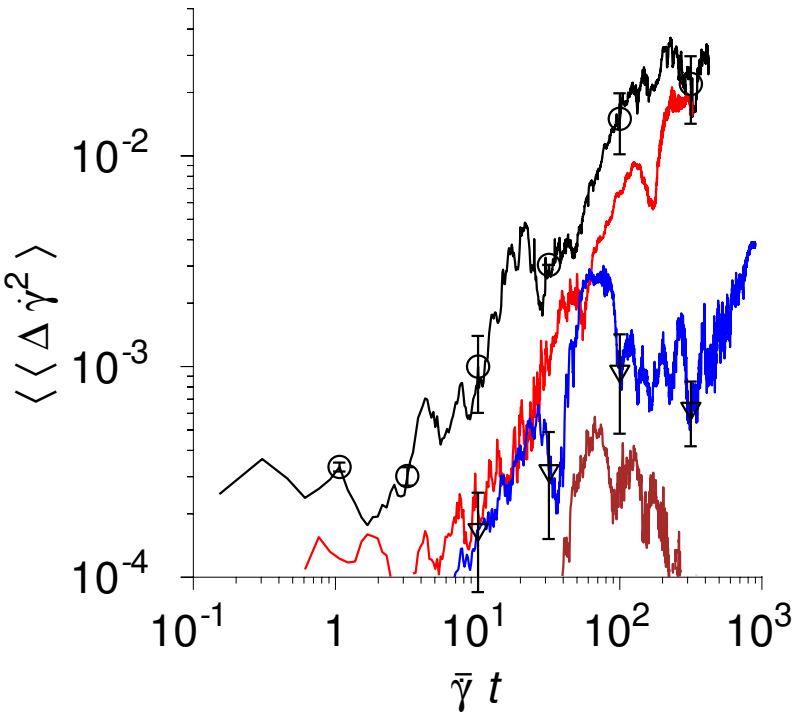
$$f = -\frac{\psi^2}{2} + \frac{\psi^4}{4} + \frac{r((\nabla^2 + k^2)\psi)^2}{2}.$$

Structure-rheology relationship: $\mathrm{Sc}\Sigma = 3.41$

$(L/\lambda) = 128, 64, 32, 16.$



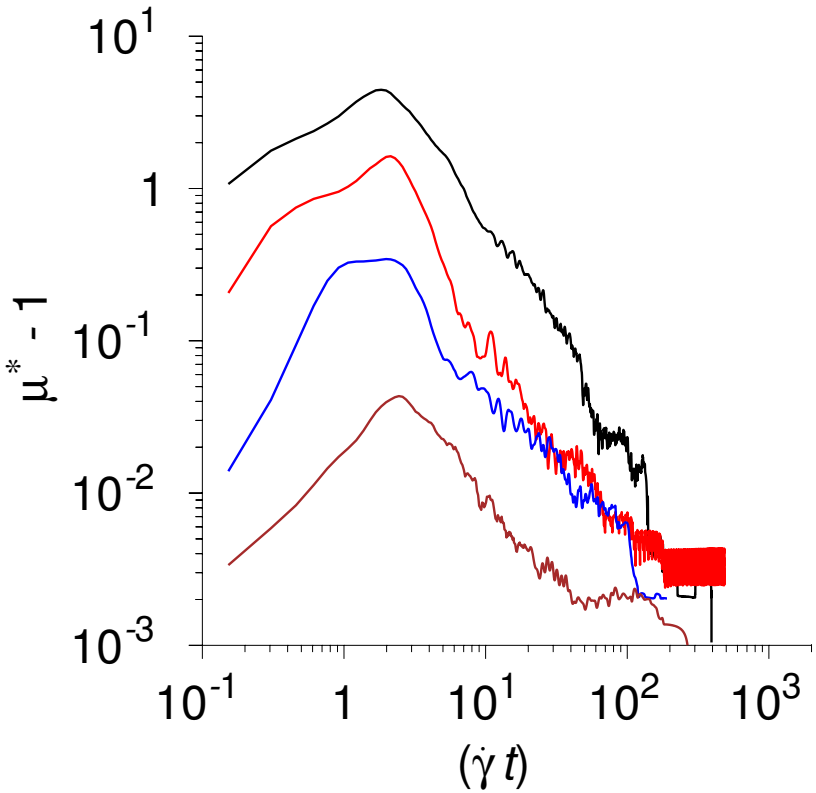
— $\mu^* - 1 = (\mu/\mu_{al}) - 1,$



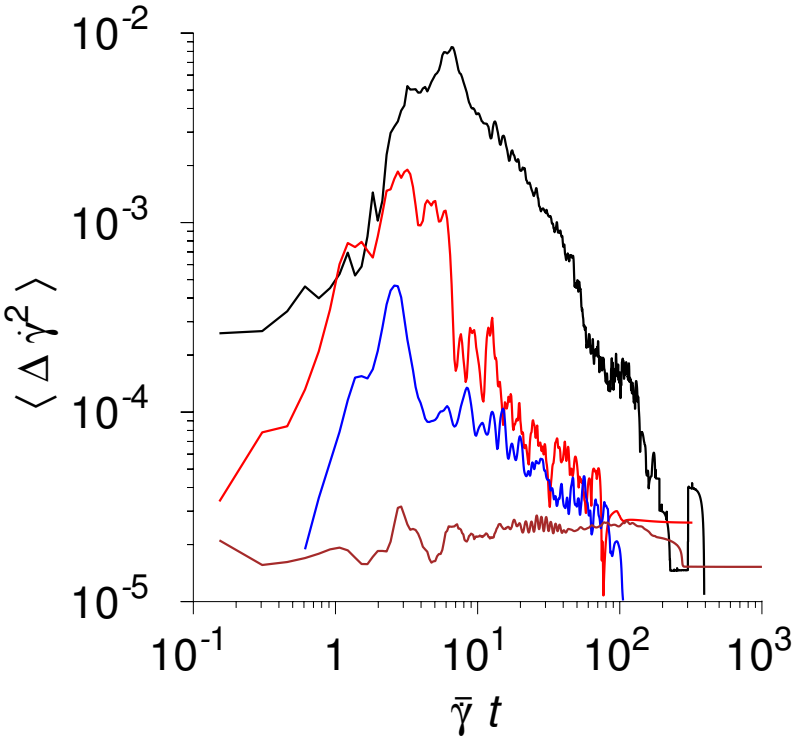
$\langle(\Delta\dot\gamma)^2\rangle = \frac{1}{V(L\dot\gamma)^2}\int dV(v_x - \dot\gamma y)^2$

Structure-rheology relationship: $\mathrm{Sc}\Sigma = 51.24$

$(L/\lambda) = 128, 64, 32, 16.$

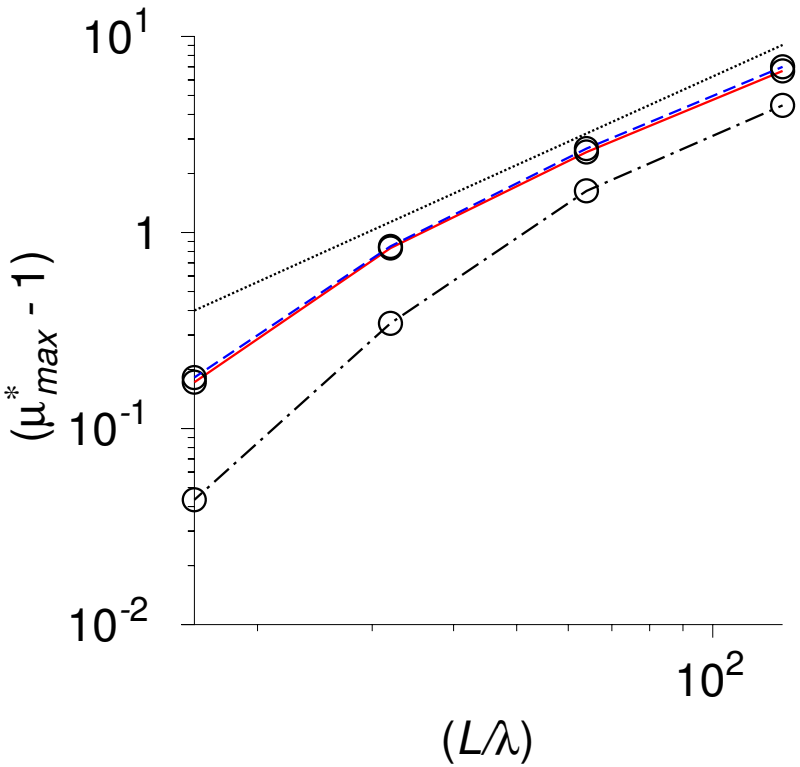


$\mu^* - 1 = (\mu/\mu_{al}) - 1,$



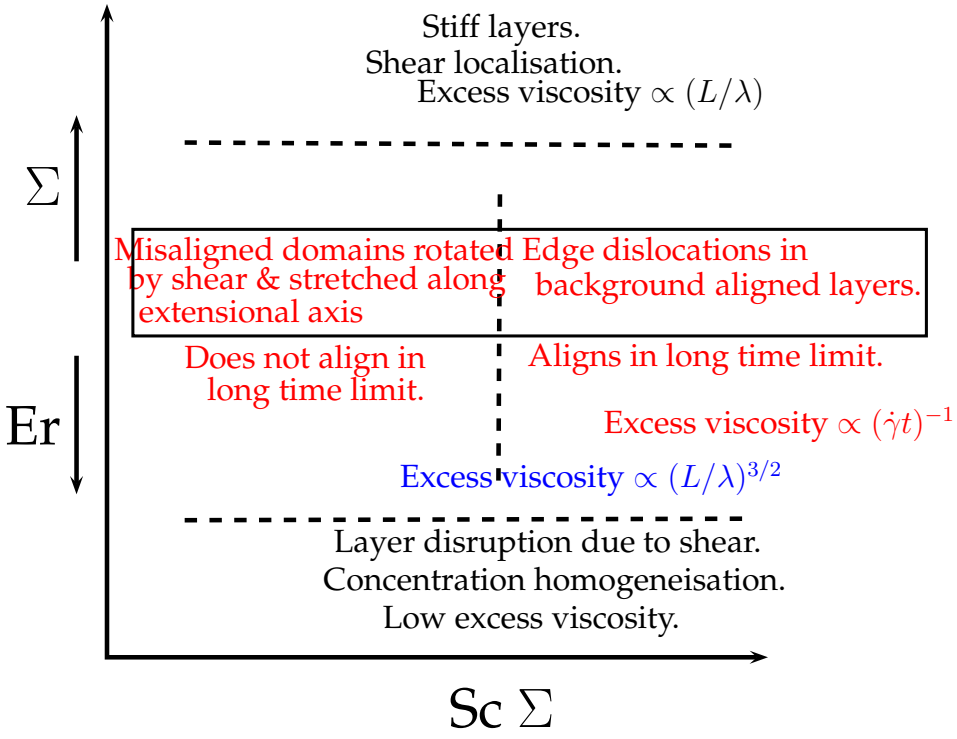
$\langle (\Delta\dot{\gamma})^2 \rangle = \frac{1}{V(L\dot{\gamma})^2} \int dV (v_x - \dot{\gamma} y)^2$

Maximum viscosity: System size dependence $(L/\lambda)^{3/2}$



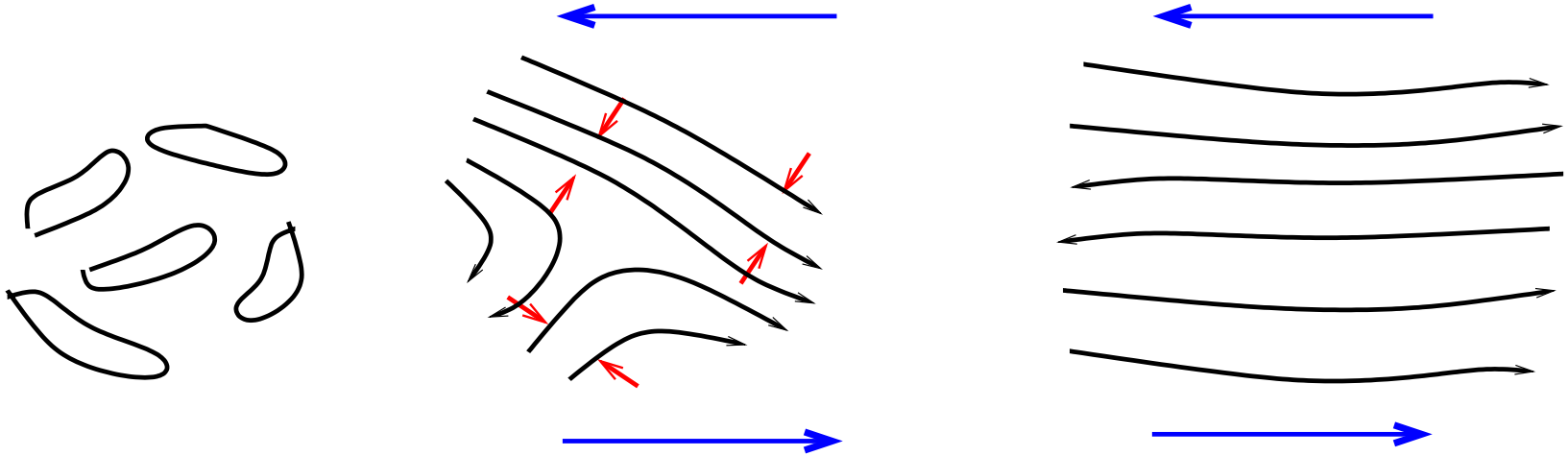
$\Sigma = 4 \times 10^{-3}$, $\mathrm{Sc}\Sigma = 3.41$, $\mathrm{Sc}\Sigma = 10.24$, $\mathrm{Sc}\Sigma = 51.2$.

Correlation between structure and rheology:

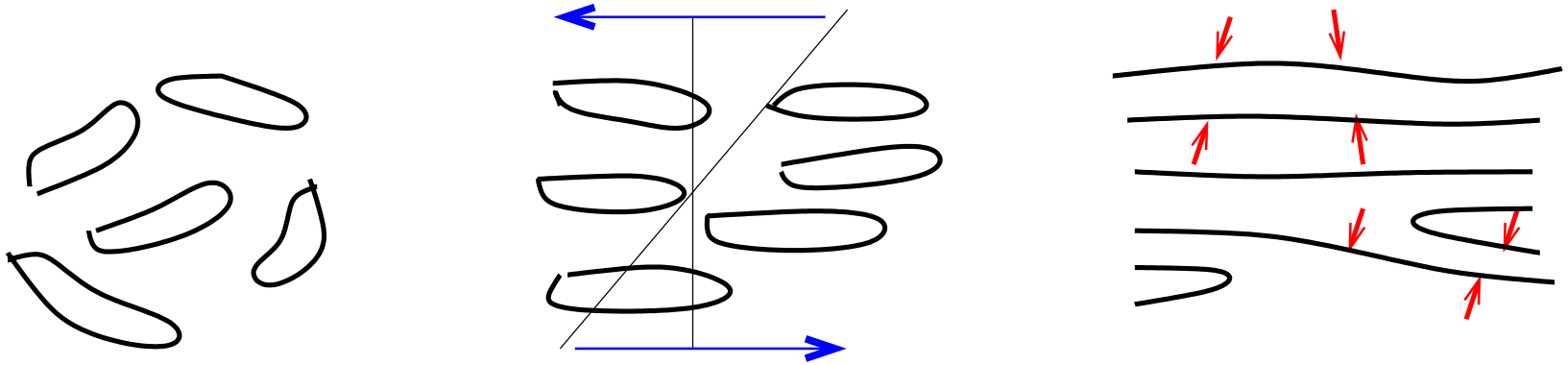


Different types of ordering:

Low Schmidt (ν/D) number: Grain boundary coarsening.

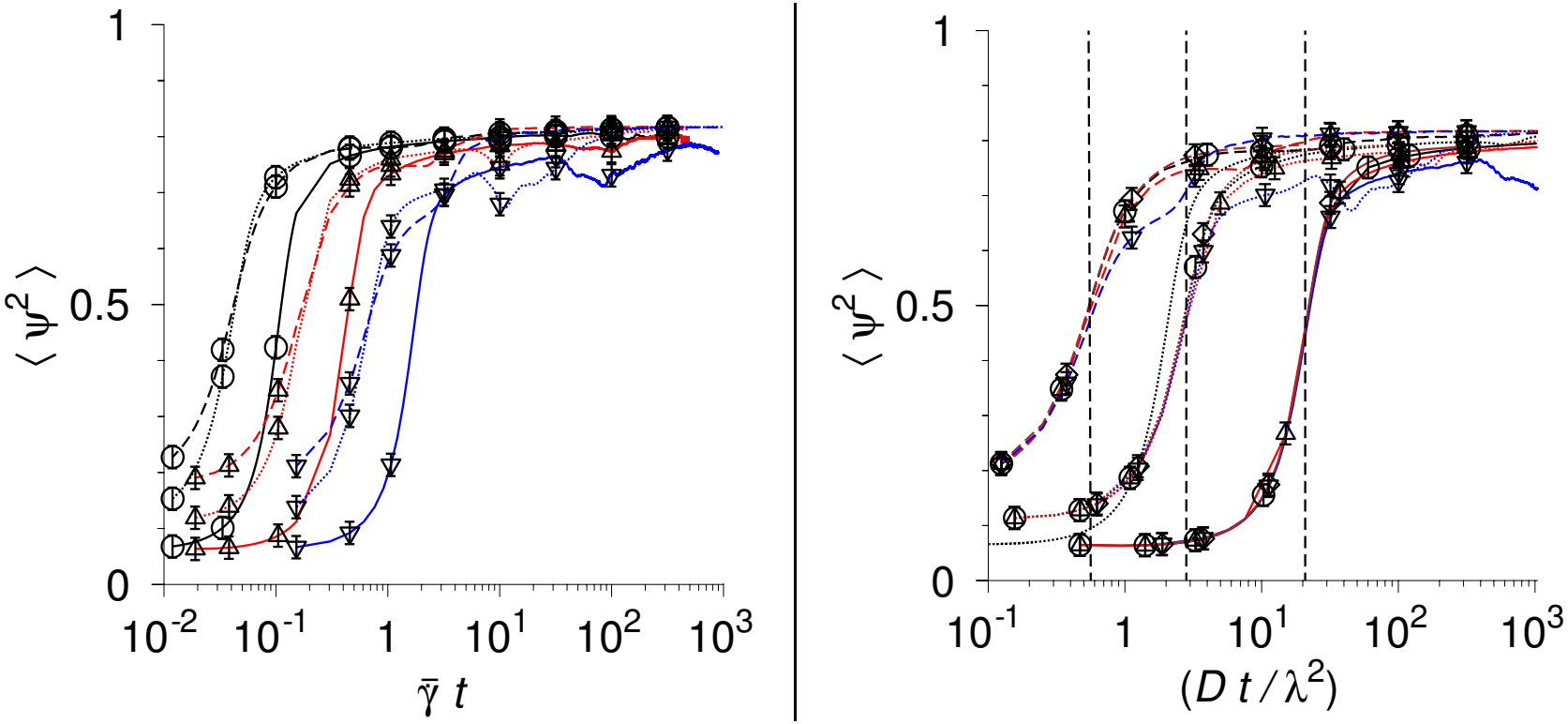


High Schmidt (ν/D) number: Edge dislocation.



Structure-rheology relationship: Early stage coarsening.

$\langle \psi^2 \rangle = \frac{1}{V} \int dV \psi^2$



— $\mathrm{Sc}\Sigma = 3.41$, $\cdots$ $\mathrm{Sc}\Sigma = 10.24$, - - - $\mathrm{Sc}\Sigma = 51.2$.

$(L/\lambda) = 128, 64, 32, 16.$

Structure-rheology relationship: Crossover between two regimes:

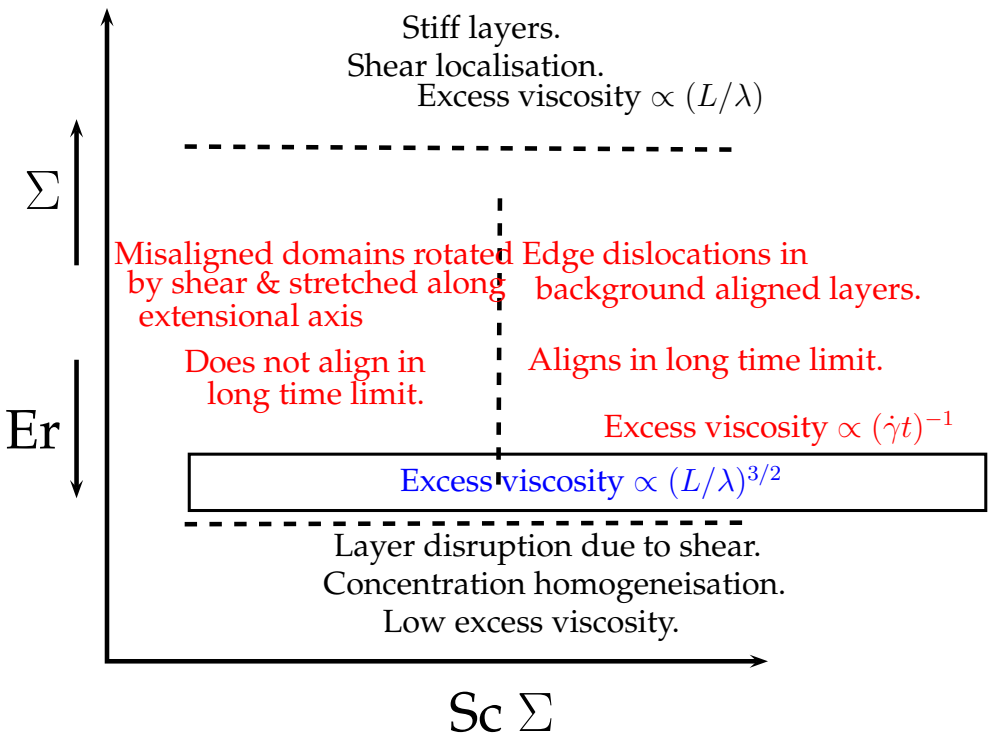
$$\mathrm{Sc}\Sigma = \frac{A\lambda^2}{\mu D} = \frac{(A/\mu)}{D/\lambda^2}$$

Constant Reynolds number $\mathrm{Re} = (\rho L^2 \dot{\gamma}/\mu) = 1$.

$$\Rightarrow \mathrm{Sc}\Sigma = \frac{(A/\rho L^2 \dot{\gamma})}{(D/\lambda^2)} = \frac{\tau_D}{\tau_{\dot{\gamma}}}$$

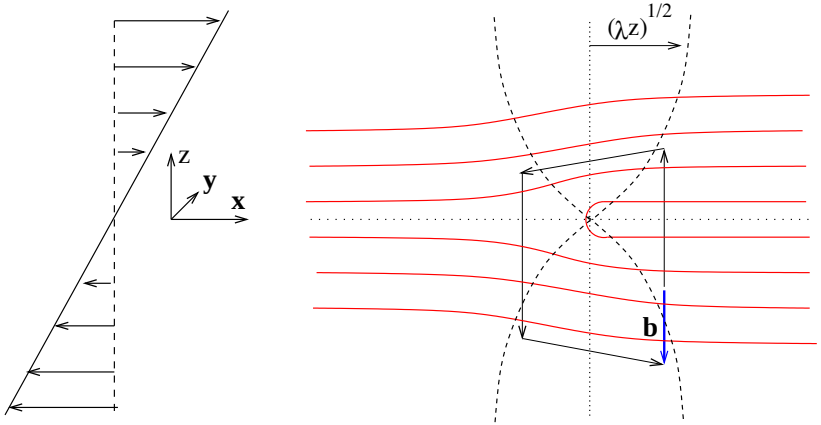
Cross-over when diffusion time over one layer comparable to time for shear propagation over system height.

Correlation between structure and rheology:



Defects in lamellar phases:

Edge dislocation:



Multiscale modeling: Defect dynamics.

Concentration field:

$$F[\psi] = A \int dV \left(-\frac{\psi^2}{2} + \frac{\psi^4}{4} + \frac{g(\nabla\psi)^2}{2k^2} + \frac{r}{2k^4} \left((\nabla^2 + k^2)\psi \right)^2 - \mathbf{f}\cdot\nabla\psi \right),$$

$$\frac{\partial\psi}{\partial t} + \mathbf{v}\cdot\nabla\psi = \Gamma\nabla^2 \frac{\delta F}{\delta\psi},$$

$$\rho \left(\frac{\partial\mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v} \right) = -\nabla p + \mu\nabla^2\mathbf{v} + \nabla\psi\frac{\delta F}{\delta\psi},$$

Fourier expansion:

$$\psi_= \sum_n \psi_n \exp\left(\imath nkz\right); \mathbf{f} = \sum_n \mathbf{f}_n \exp\left(\imath nkz\right).$$

Multiscale modeling: Defect dynamics.

Layer displacement field & momentum equations:

$$P\left(\frac{\partial u}{\partial t} - v_z\right) = B\frac{\partial^2 u}{\partial z^2} - K\frac{\partial^4 u}{\partial x^4} + f_u,$$

$$\rho\left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v}\right) = -\nabla p + \mu\nabla^2\mathbf{v} - \left(B\frac{\partial^2 u}{\partial z^2} - K\frac{\partial^4 u}{\partial x^4} + f_u,\right)$$

Force density f^u:

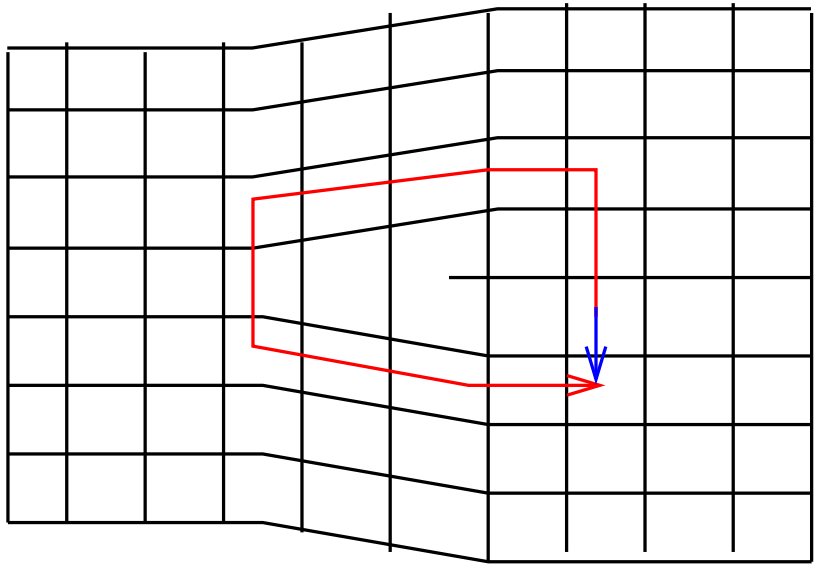
$$f_u = \sum n^2 k^2 \psi_{-n}(\mathbf{f}_n\cdot\mathbf{e}_z),$$

Point defect:

$$f_u = Bb\delta(x)\delta(z)$$

Defects in isotropic solids:

Edge dislocation:



Stress equation:

$$\nabla \cdot \sigma + \mathbf{f}_u = 0$$

Isotropic material:

$$\sigma = G\nabla \mathbf{u} + K\mathbf{I}\nabla \cdot \mathbf{u}$$

$$G'\nabla^2 \mathbf{u} + \mathbf{f}_u = 0$$

Point force:

$$\mathbf{f}_u = G'\mathbf{b}\delta(x)\delta(z)$$

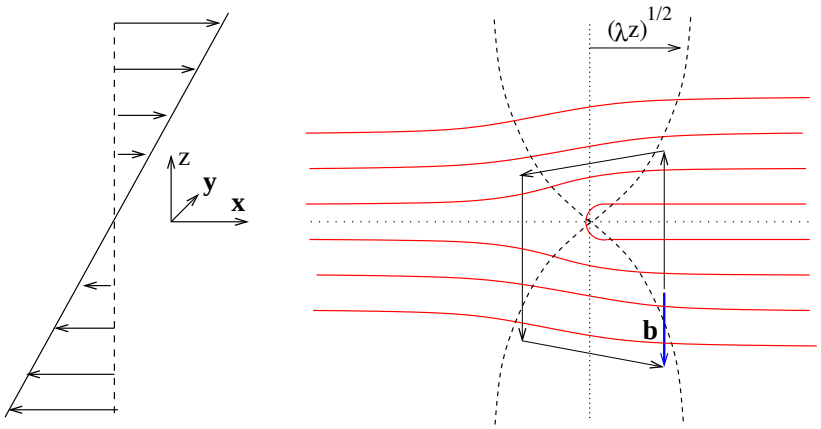
Solution: $\mathbf{u} = G'\mathbf{b}\log(\mathbf{x})$

Defects in lamellar phases:

Stress equation: $\nabla \cdot \sigma + \mathbf{f}_u = 0$

Lamellar mesophase:

Edge dislocation:



$$B\left(\frac{\partial^2 u}{\partial z^2} - \lambda^2 \frac{\partial^4 u}{\partial x^4}\right) + f_u = 0$$

Point force: $f_u = Bb\delta(\mathbf{x})$

$$B\left(\frac{\partial}{\partial z} + \lambda^2 \frac{\partial^2}{\partial x^2}\right)\left(\frac{\partial}{\partial z} - \lambda^2 \frac{\partial^2}{\partial x^2}\right) u + f_u = 0$$

$u = \pm(b/4)\mathrm{erf}(x/2\sqrt{\lambda|z|})$

$u \sim z^{-1/2}$ for $|z| \to \infty$

Theory of Elasticity, Landau and Lifshitz, Oxford, 1989.

Defects in lamellar phases: Effect of flow.

Leading solution:

$$u^{(0)} = \pm\frac{b\,\mathrm{erf}(x/2\sqrt{\lambda|z|})}{4} = \pm\frac{b\mathrm{erf}(\eta)}{4}$$

First correction:

$$P(\dot{\gamma}z\frac{\partial u^{(0)}}{\partial x} - v_z^{(1)}) = B\left(\frac{\partial^2 u^{(1)}}{\partial z^2} - \lambda^2\nabla^4 u^{(1)} \underline{-3\frac{\partial u^{(0)}}{\partial x}\frac{\partial^2 u^{(0)}}{\partial x \partial z}}\right)$$

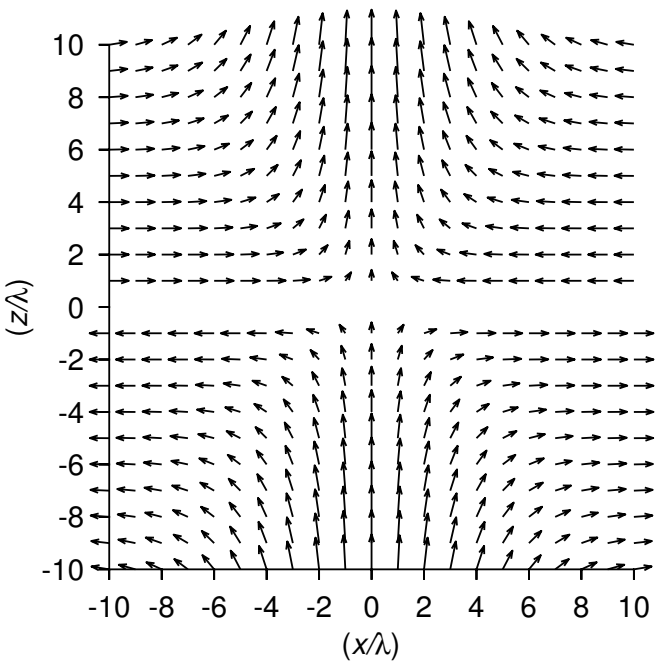
$$-\nabla p + \mu\nabla^2\mathbf{v}^{(1)} + P\left(\dot{\gamma}z\frac{\partial u^{(0)}}{\partial x} - v_z^{(1)}\right)\mathbf{e}_z = 0.$$

Solution for velocity field:

$$v_z^{(1)} = \frac{b\dot{\gamma}\exp(-\eta^2)}{4\sqrt{\pi}}\left(\frac{\sqrt{|z|}}{\sqrt{\lambda}} + \frac{\mu}{P}\left(\frac{(2\eta^2-1)}{2\lambda^{3/2}|z|^{1/2}}\right)\cdots\right)$$

$$v_x^{(1)} = \mp\frac{b\dot{\gamma}\,\mathrm{erf}(\eta)}{4} \pm \frac{b\eta\dot{\gamma}}{4\exp(\eta^2)\sqrt{\pi}} + \frac{\mu}{P}\left(\frac{b\eta\dot{\gamma}(2\eta^2-1)}{8\exp(\eta^2)\lambda\sqrt{\pi}z}\right).$$

Defects in lamellar phases: Effect of flow.



Velocity:

$$v_z^{(1)} = (b\dot{\gamma}\exp(-\eta^2)/4\sqrt{\pi})(\sqrt{|z|}/\sqrt{\lambda})$$

$$v_x^{(1)} = \mp(b\dot{\gamma}\mathrm{erf}(\eta)/4) \pm \frac{b\eta\dot{\gamma}}{4\exp(\eta^2)\sqrt{\pi}}$$

Shear stress:

$$\sigma_{xz}^{v} = -(b\mu\eta\dot{\gamma}/4\sqrt{\pi}\lambda\exp(\eta^2))$$

Dissipation rate:

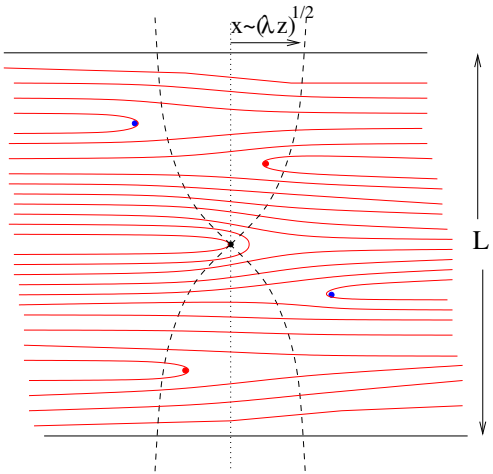
$$D = \int dV \sigma_{xz}(\partial v_z^{(1)}/\partial x)$$

Effective viscosity:

$$\mu_{eff} = \mu\left(1 + \frac{Cnb_{av}^2 L^{3/2}}{\lambda^{3/2}}\right)$$

Defects in lamellar phases: Effect of flow.

Divergence cut-off due to defect interactions:



Interaction region $x \sim (\lambda|z|)^{1/2}$.

Defect density n.

Non-interacting: $nL^{3/2}\lambda^{1/2} \ll 1$.

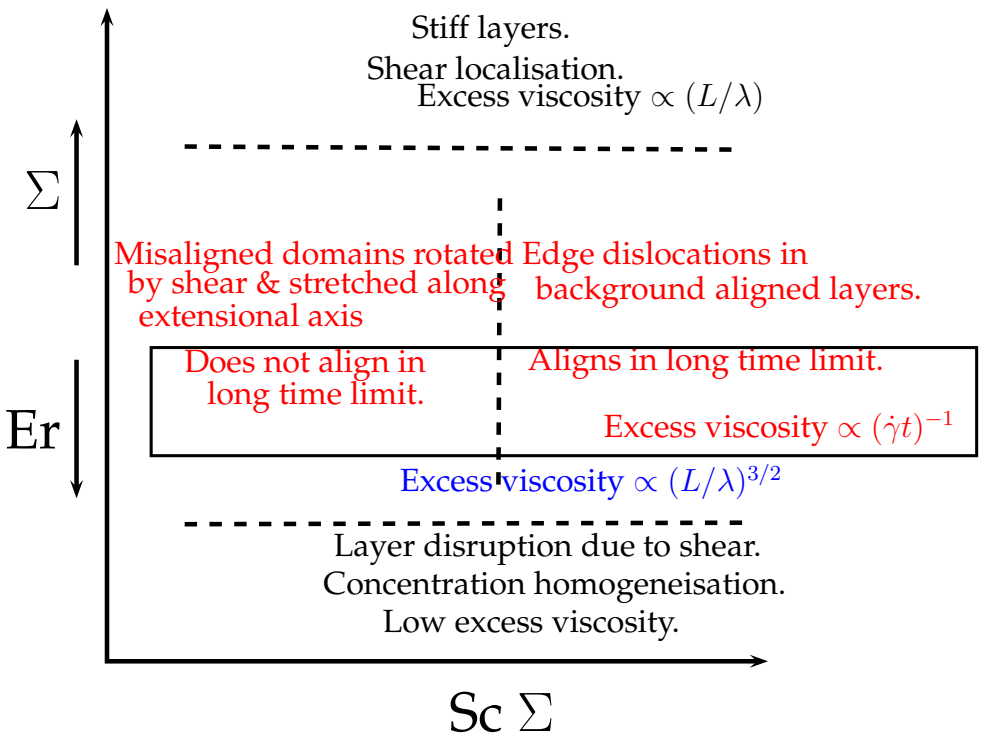
Interacting: $nL^{3/2}\lambda^{1/2} \gg 1$.

Weak flow approximation — layer configuration not significantly affected by flow.

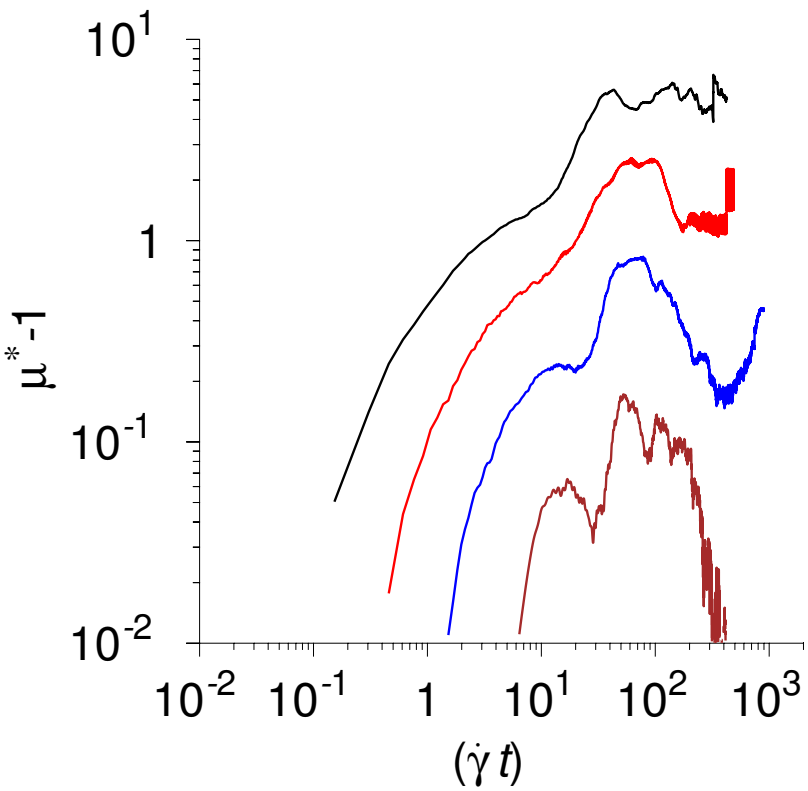
$$\frac{\sigma_{xy}^{(v)}}{\sigma_{xy}^{(e)}} \sim \frac{\mu\dot{\gamma}}{B}\left(\frac{z}{\lambda}\right)^{3/2} = \mathrm{Er}(z/\lambda)^{3/2}$$

Weak flow approximation fails for $(z/\lambda) \sim \mathrm{Er}^{-2/3}$.

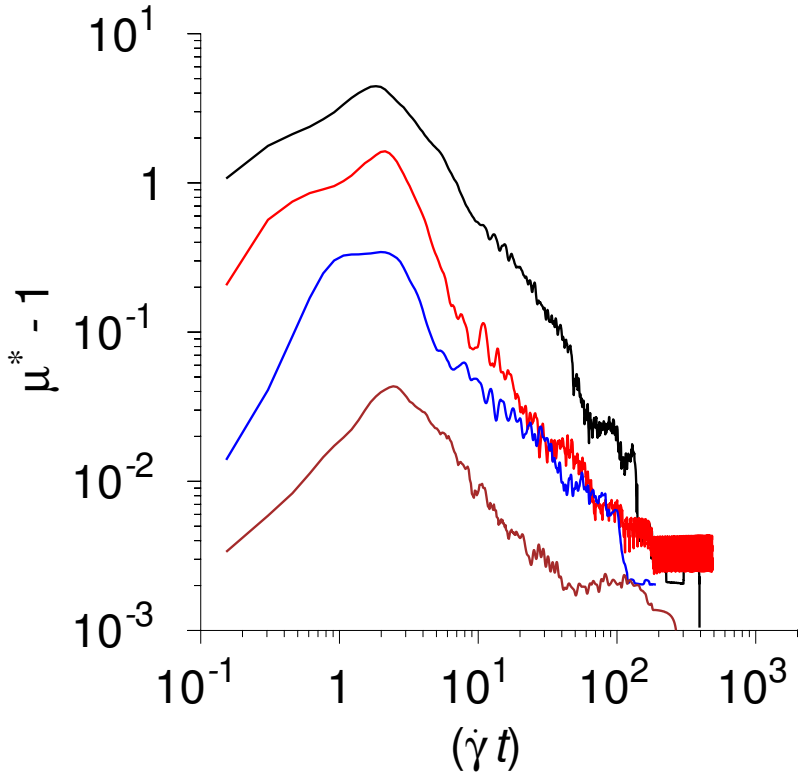
Correlation between structure and rheology:



Structure-rheology relationship: $(L/\lambda) = 128, 64, 32, 16$.



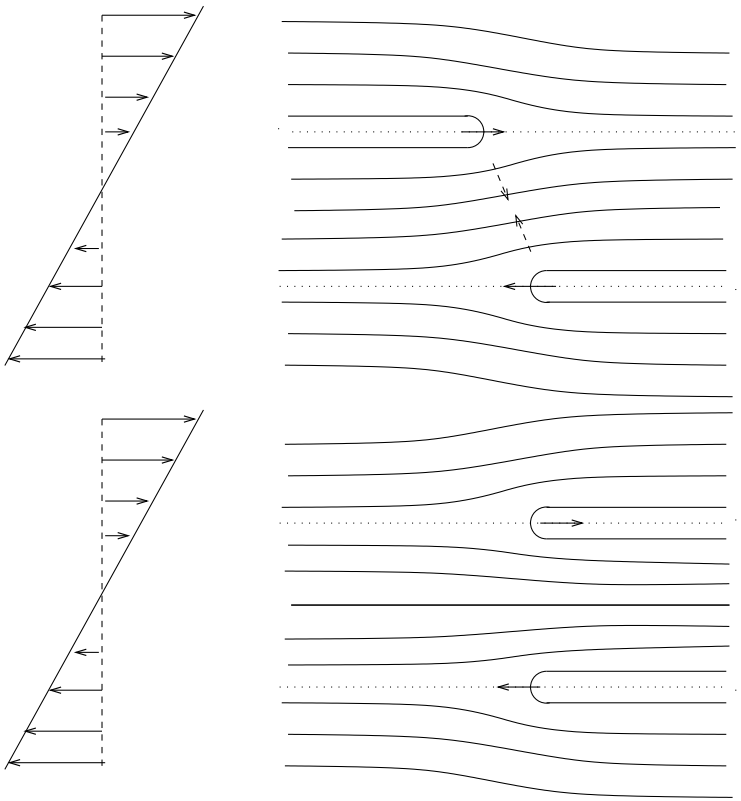
$\mathrm{Sc}\Sigma = 3.41$



$\mathrm{Sc}\Sigma = 51.2$

— $\mu^* - 1 = (\mu/\mu_{al}) - 1$,

Defect interactions:



Peach-Koehler force:

$$f_z = -\sigma_{xz} b = \frac{b_1 b_2 \mu \eta \dot{\gamma}}{4\sqrt{\pi}\lambda \exp\left(\eta^2\right)}$$

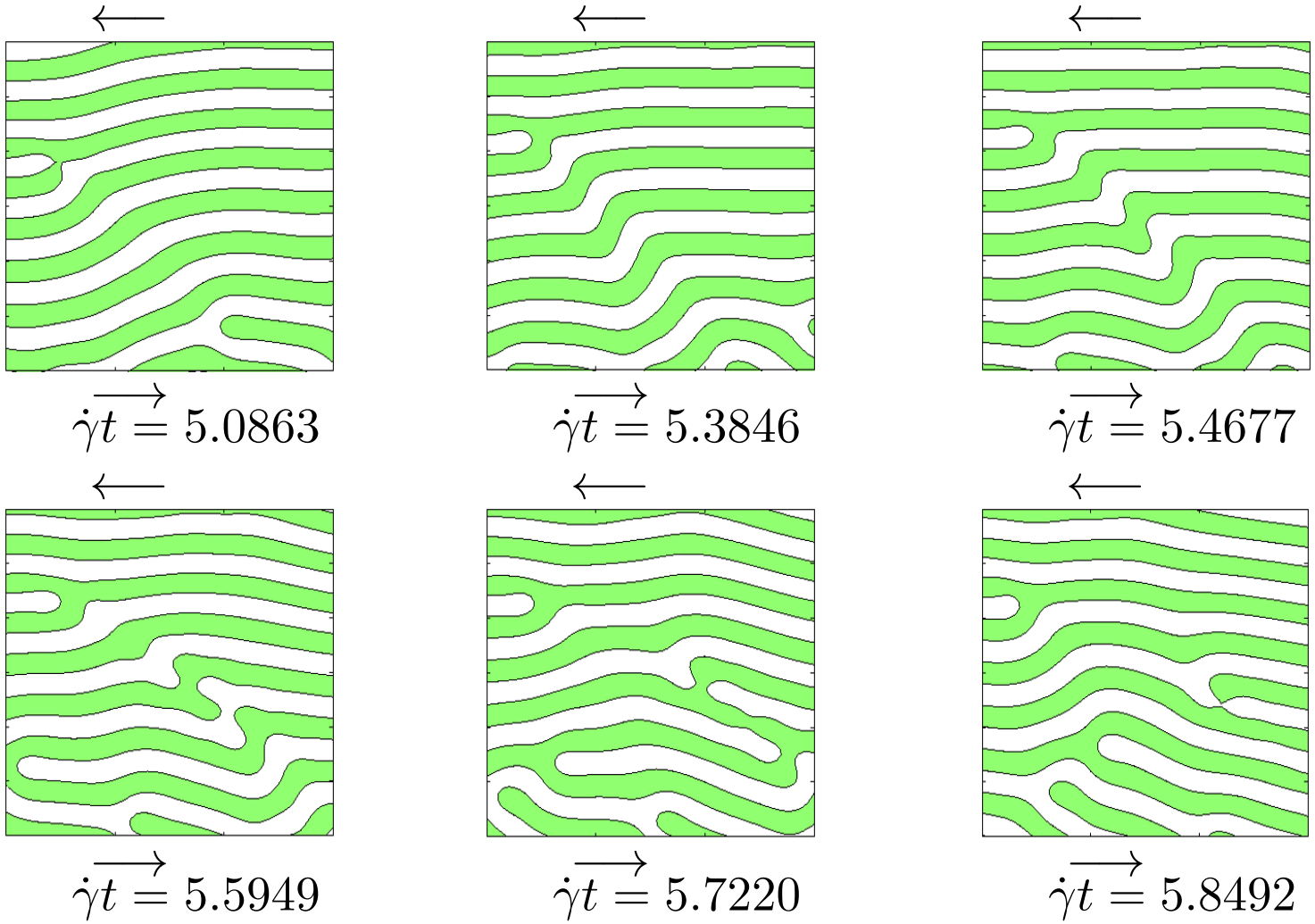
Defect mobility:

$$v_z = \frac{2 f_z}{P_d}$$

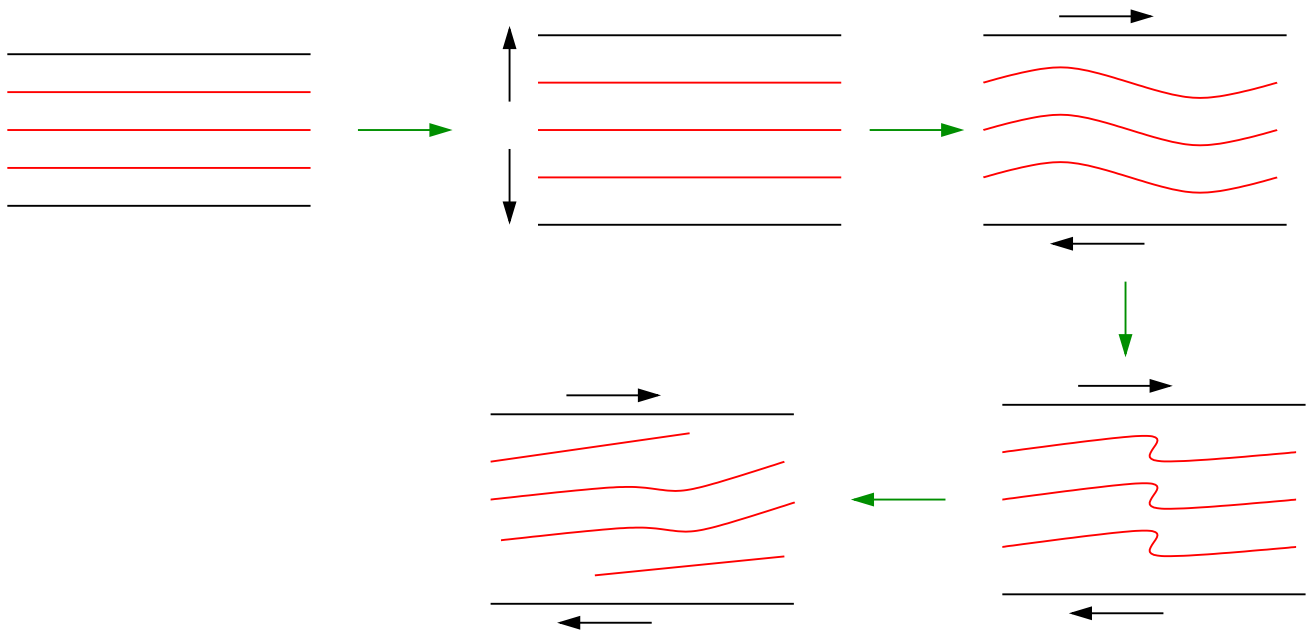
Defect separation:

$$\frac{2}{3}\left(|\Delta z|^{3/2} \Big|_{\Delta x = -\infty}^{\Delta x = 0} \right) = \frac{b_1 b_2 \mu}{2 P_d \sqrt{\pi \lambda}}.$$

Defect creation due to shear: Buckling instability:



Undulation instability in lamellar liquid crystals



$$F = \int dV B \left[\left(\frac{\partial u}{\partial z} - \frac{1}{2} \left(\frac{\partial u}{\partial x} \right)^2 \right)^2 + \frac{K}{2} (\frac{\partial^2 u}{\partial x^2})^2 \right]$$

Instability of layered fluids:

Imposed dilation $u = \mathcal{D}z + u'$ linear approximation:

$$-\frac{\delta F}{\delta u'} = B\frac{\partial^2 u'}{\partial z^2} - \frac{B}{2}\frac{\partial}{\partial z}\left(\frac{\partial^2 u'}{\partial x^2}\right) - B\mathcal{D}\left(\frac{\partial^2 u'}{\partial x^2}\right) - K\frac{\partial^4 u'}{\partial x^4}$$

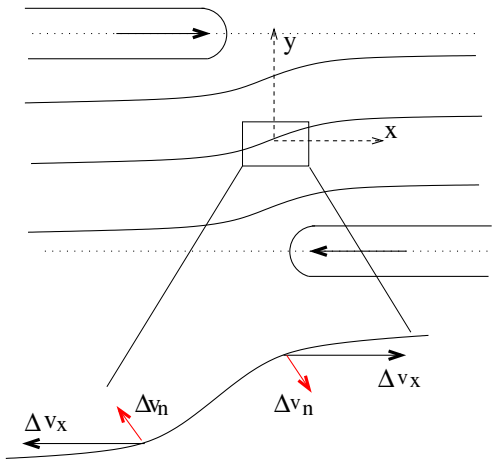
Normal mode analysis $u' = \tilde{u}(t)\exp\left(\imath(k_x x + k_z z)\right)$:

Dispersion relation:

$$\frac{D\tilde{u}}{Dt} = (-Bk_z^2 + (B/2)\imath k_z k_x^2 + B\mathcal{D}k_x^2 - Kk_x^4)\tilde{u}$$

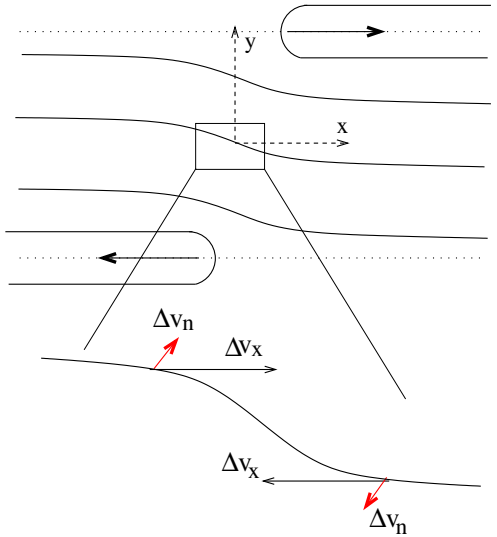
- $\mathcal{D} > (Kk_x^2/B)$ Unstable
- $k_x \sim (1/L)$; $(K/B) \sim \lambda^2 \Rightarrow \mathcal{D} > (\lambda^2/L^2)$ Unstable.

Defect creation:



Compression between defects:

Stabilising



Extension between defects:

Destabilising

$$T_{\text{flow}} \sim \int_C dz(P\Delta v_x)u \sim \int_C dz(P\dot{\gamma}u^2) \sim \frac{P\dot{\gamma}b^3}{96}$$

$$T_{\text{restoring}} \sim \int_{\text{C}} xdxK\partial_x^4 u \sim \frac{Kb^3}{96\sqrt{3}\lambda^2\pi z^2}$$

Defect dynamics:

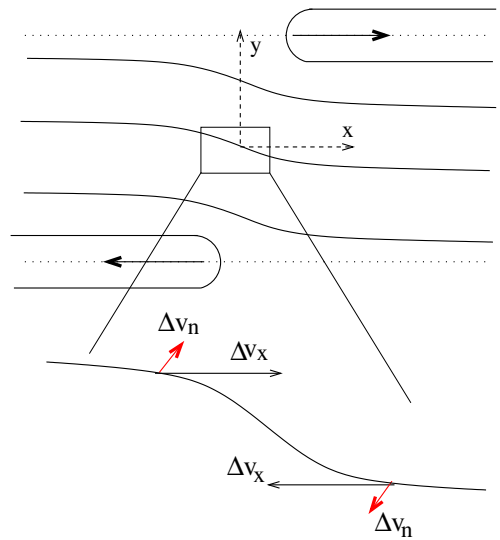
Instability $T_{\text{flow}} \gtrsim T_{\text{restoring}} \Rightarrow$

Fixed separation:

$$\dot{\gamma} \gtrsim (K/\sqrt{3}\pi\lambda^2 z^2 P) \gtrsim (B/\sqrt{3}\pi z^2 P)$$

Fixed strain rte

$$(z^2/\lambda^2) \gtrsim C(A\lambda^2/\mu D)(\mu/\rho\dot{\gamma}L^2)(L^2/\lambda^2)$$
$$\gtrsim C(\text{Sc}\Sigma/\text{Re})(L^2/\lambda^2)$$



Defect creation:

$$(L^2/\lambda^2) \gtrsim C(\text{Sc}\Sigma/\text{Re})(L^2/\lambda^2)$$
$$\text{Sc}\Sigma \lesssim (1/C)$$

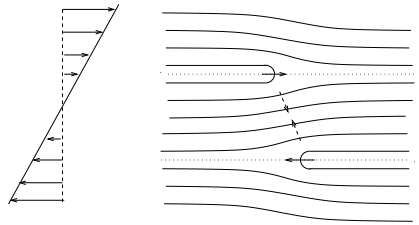
No defect creation:

$$(L^2/\lambda^2) \lesssim C(\text{Sc}\Sigma/\text{Re})(L^2/\lambda^2)$$
$$(\text{Sc}\Sigma/\text{Re}) \gtrsim (1/C)$$

Defect dynamics:

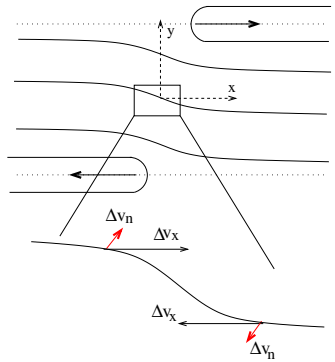
Rate of cancellation:

$$\mathcal{D} = 2\int_0^{c_{\mathcal{D}}\lambda} dz\dot{\gamma}zn^2 = n^2\dot{\gamma}c_{\mathcal{D}}^2\lambda^2$$



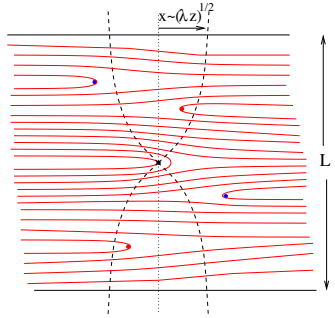
Defect creation: Cut-off by system size

$$\mathcal{C} = 2\int_{CL(\mathrm{Sc}\Sigma/\mathrm{Re})}^{L} n^2\dot{\gamma}zdz \sim n^2\dot{\gamma}L^2(1-(C\mathrm{Sc}\Sigma/\mathrm{Re}))$$



Defect creation: Cut-off by defect interactions

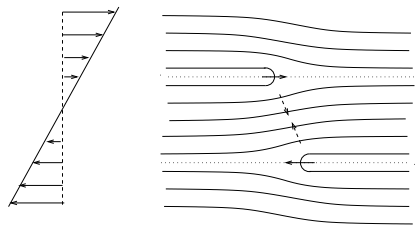
$$\mathcal{C} = 2\int_{CL(\mathrm{Sc}\Sigma/\mathrm{Re})}^{c_{\mathcal{C}}n^{-1/2}} n^2\dot{\gamma}zdz \sim n\dot{\gamma}(c_{\mathcal{C}}^2 - \frac{CnL^2\mathrm{Sc}\Sigma}{\mathrm{Re}})$$



Defect dynamics:

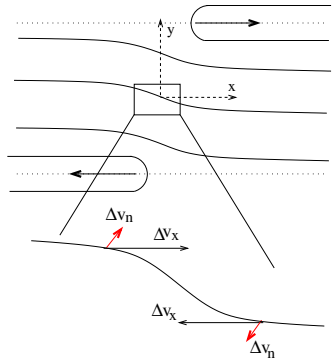
Rate of cancellation:

$$\mathcal{D} = 2\int_0^{c_{\mathcal{D}}\lambda} dz\dot{\gamma}zn^2 = n^2\dot{\gamma}c_{\mathcal{D}}^2\lambda^2$$



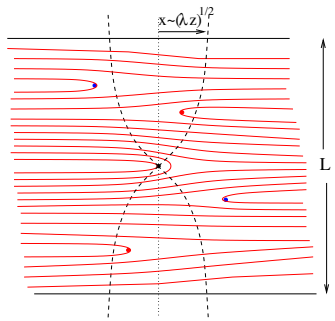
Defect creation: Cut-off by system size

$$\mathcal{C} = 2\int_{CL(\mathrm{Sc}\Sigma/\mathrm{Re})}^{L} n^2\dot{\gamma}zdz \sim n^2\dot{\gamma}L^2(1-(C\mathrm{Sc}\Sigma/\mathrm{Re}))$$



Defect creation: Cut-off by defect interactions

$$\mathcal{C} = 2\int_{CL(\mathrm{Sc}\Sigma/\mathrm{Re})}^{c_{\mathcal{C}}n^{-1/2}} n^2\dot{\gamma}zdz \sim n\dot{\gamma}(c_{\mathcal{C}}^2 - \frac{CnL^2\mathrm{Sc}\Sigma}{\mathrm{Re}})$$

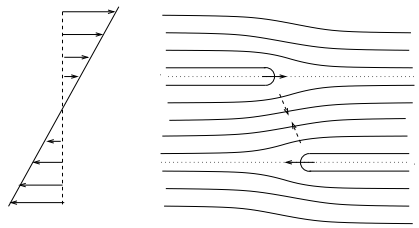


Defect number decreases/increases exponentially.

Defect dynamics:

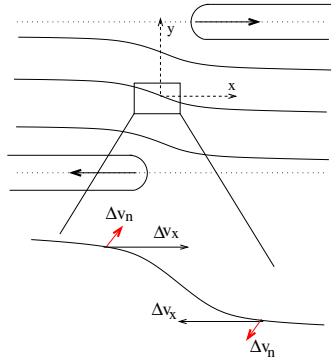
Rate of cancellation:

$$\mathcal{D} = 2\int_0^{c_{\mathcal{D}}\lambda} dz\dot{\gamma}zn^2 = n^2\dot{\gamma}c_{\mathcal{D}}^2\lambda^2$$



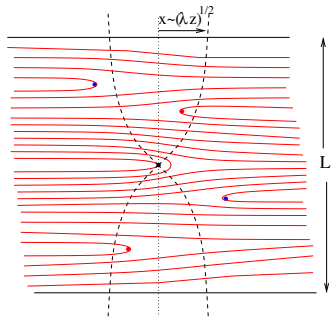
Defect creation: Cut-off by system size

$$\mathcal{C} = 2\int_{CL(\mathrm{Sc}\Sigma/\mathrm{Re})}^{L} n^2\dot{\gamma}zdz \sim n^2\dot{\gamma}L^2(1-(C\mathrm{Sc}\Sigma/\mathrm{Re}))$$



Defect creation: Cut-off by defect interactions

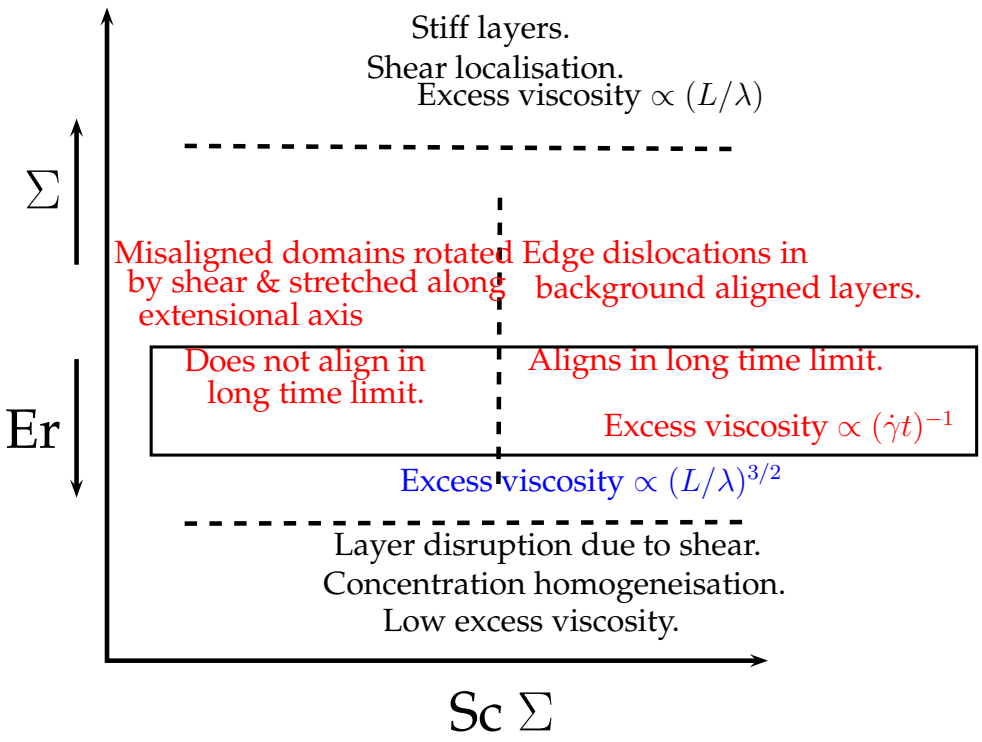
$$\mathcal{C} = 2\int_{CL(\mathrm{Sc}\Sigma/\mathrm{Re})}^{c_{\mathcal{C}}n^{-1/2}} n^2\dot{\gamma}zdz \sim n\dot{\gamma}(c_{\mathcal{C}}^2 - \frac{CnL^2\mathrm{Sc}\Sigma}{\mathrm{Re}})$$

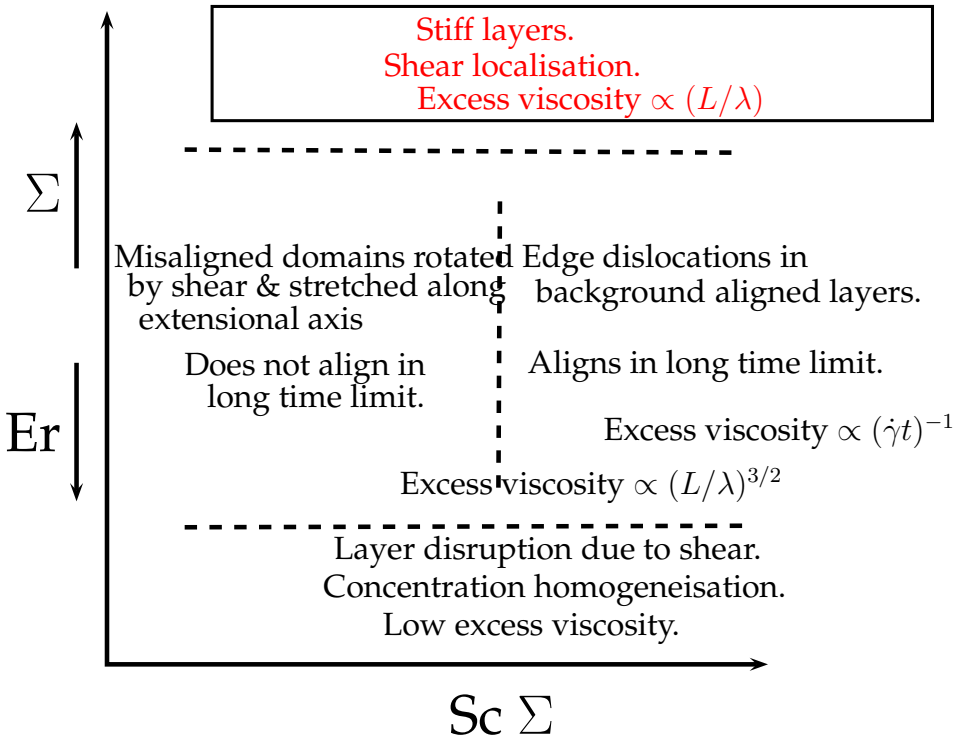


Steady state: $n_s = \frac{c_{\mathcal{C}}^2}{c_{\mathcal{D}}^2\lambda^2 + CL^2(\mathrm{Sc}\Sigma/\mathrm{Re})}$

Rheological model:

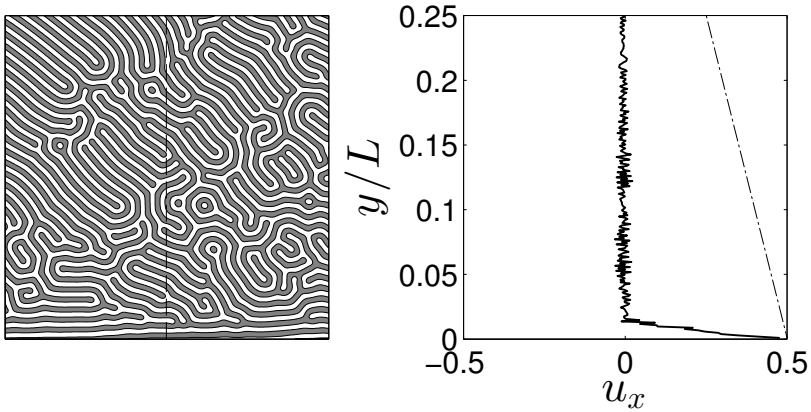
1. For $(C\mathrm{Sc}\Sigma/\mathrm{Re}) \lesssim 1$, no defect creation.
   - Viscosity $\propto nL^{3/2}\lambda^{1/2}$.
   - Defect density $n \to 0$ in long time limit.
   - $(dn/dt) \propto -n^2$
   - Defect density $n(t) \propto (1/t)$.
2. For $(C\mathrm{Sc}\Sigma/\mathrm{Re}) \lesssim 1$,
   - $n_s = \frac{c_{\mathcal{C}}^2}{c_{\mathcal{D}}^2\lambda^2 + CL^2(\mathrm{Sc}\Sigma/\mathrm{Re})}$
   - $\frac{dn}{dt} = \frac{n(n_s - n)}{n_s\tau}$
   - $n = \frac{n_s \exp(-t/\tau)}{1+\exp(-t/\tau)}$
   - $\tau = (\dot{\gamma}c_{\mathcal{C}}^2)^{-1}$


Stiff layers.
Shear localisation.
Excess viscosity $\propto (L/\lambda)$
Σ
Misaligned domains rotated by shear & stretched along extensional axis
Edge dislocations in background aligned layers.
Does not align in long time limit.
Aligns in long time limit.
Excess viscosity $\propto (\dot{\gamma}t)^{-1}$
Er
Excess viscosity $\propto (L/\lambda)^{3/2}$
Layer disruption due to shear.
Concentration homogeneisation.
Low excess viscosity.
Sc Σ

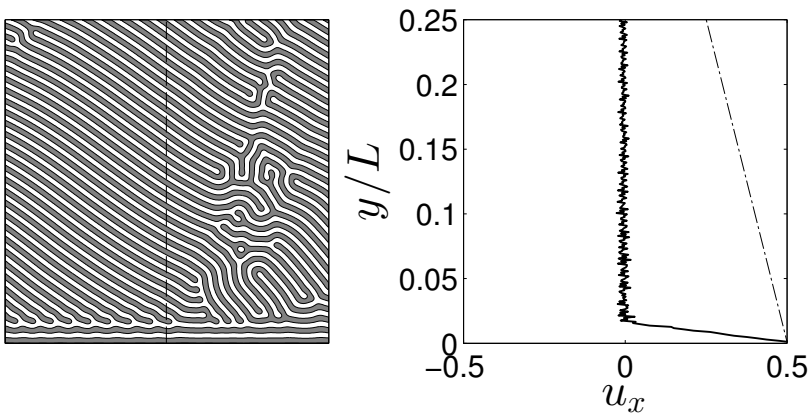


Ordering at large Σ.

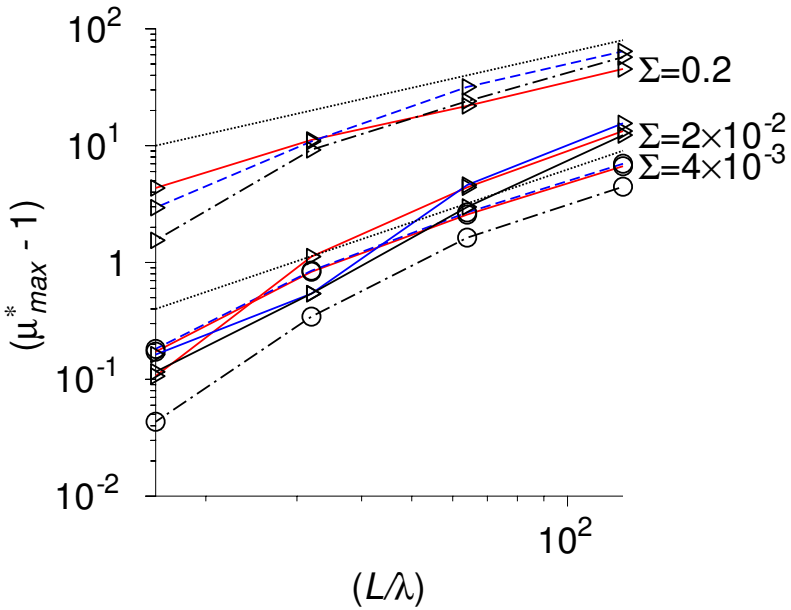
Structure & Rheology: High Σ.



$\Sigma = 0.2; \mathrm{Sc}\Sigma = 0.33$

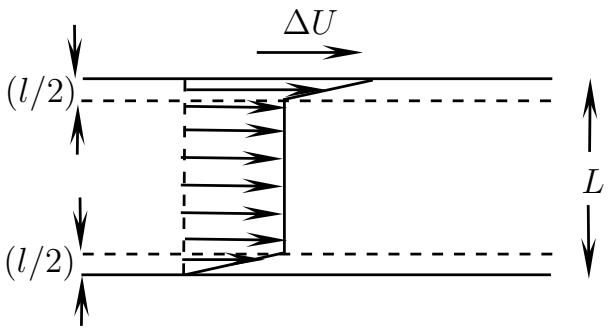


$\Sigma = 0.2; \mathrm{Sc}\Sigma = 5$



$\mathrm{Sc}\Sigma = 3.41$, 10.24, 51.2.

Structure & Rheology: High Σ.

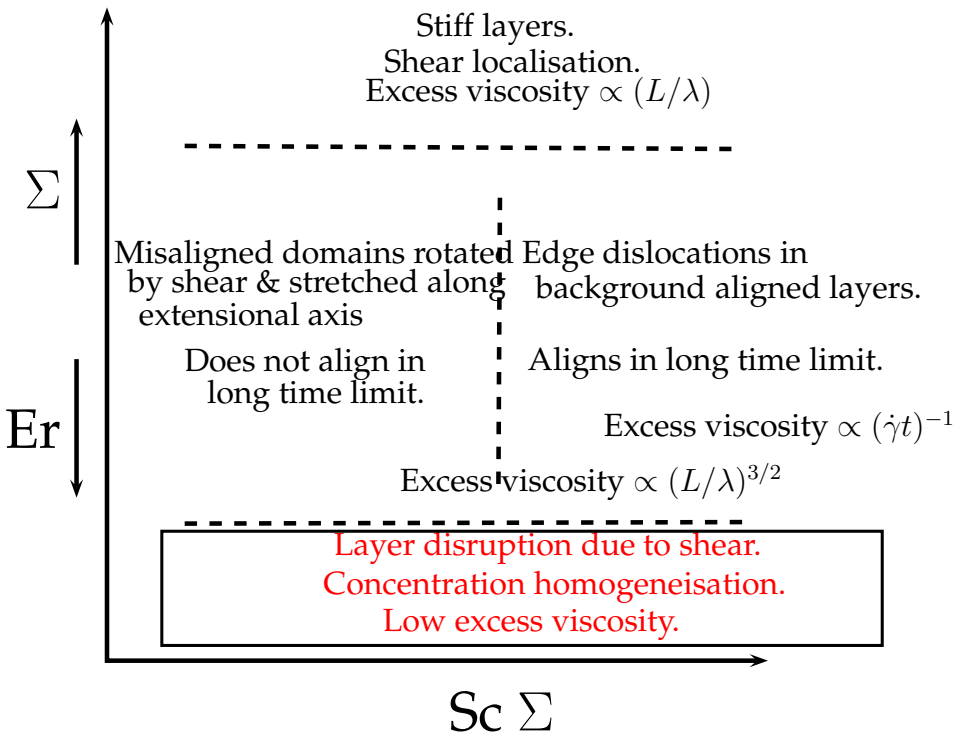


Stress balance condition:

$\tau = (\mu_{al}\Delta U/l) \sim B \Rightarrow l = (\mu_{al}\Delta U/B)$

Apparent viscosity

$\mu^* = \frac{\tau}{\mu_{al}\Delta U/L} \sim \frac{\mu_{al}L}{l} \sim \frac{BL}{\mu_{al}\Delta U}$


Stiff layers.
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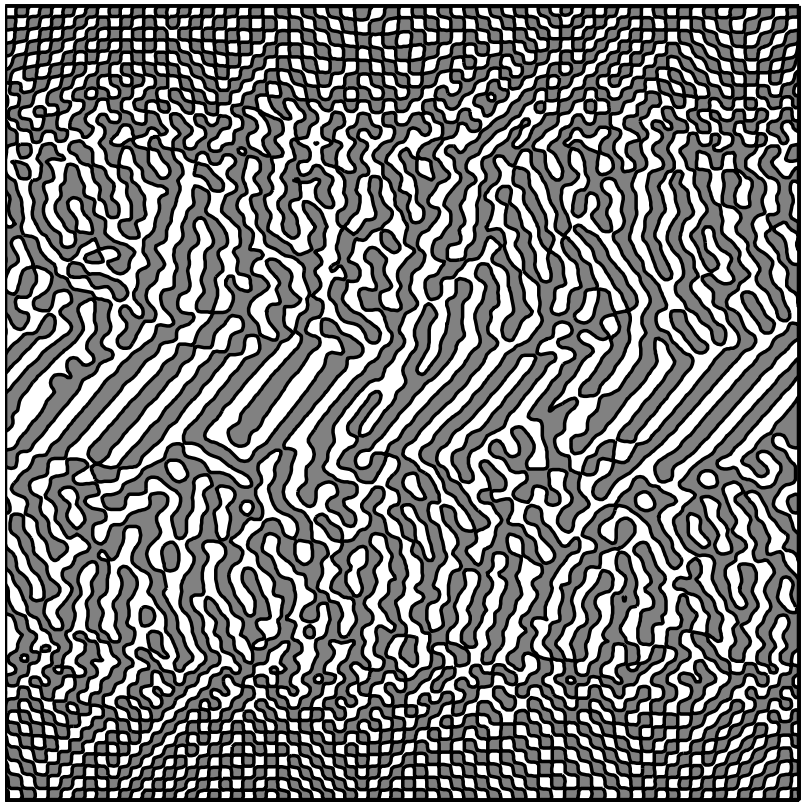
Excess viscosity $\propto (\dot{\gamma}t)^{-1}$
Er
Excess viscosity $\propto (L/\lambda)^{3/2}$
Layer disruption due to shear.
Concentration homogeneisation.
Low excess viscosity.
Sc Σ

$\Sigma = (\rho A \lambda^2/\mu^2) \ll 1$:

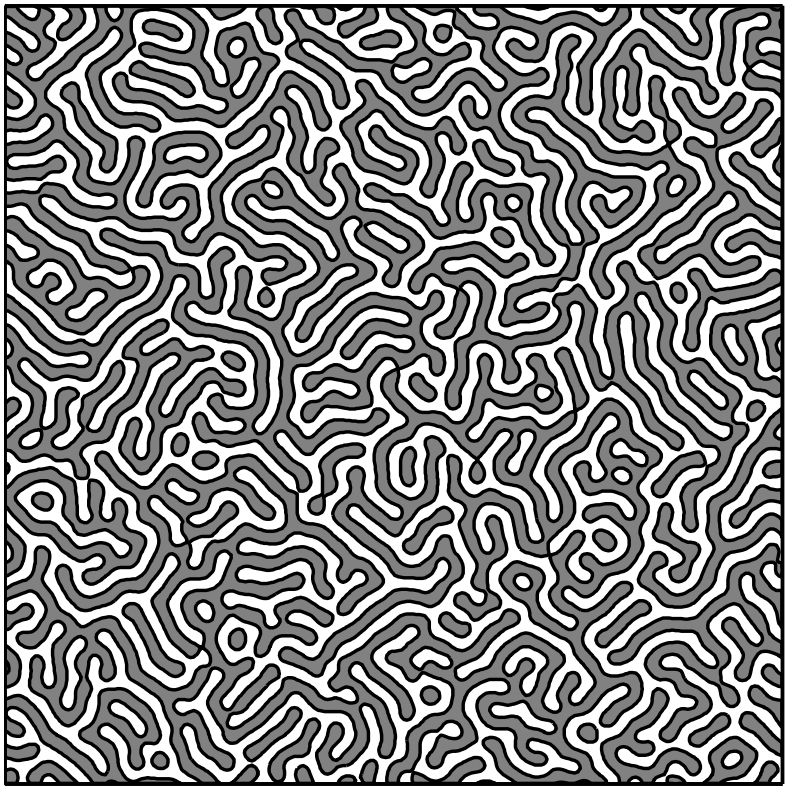
Coarsening with shear:



$\Sigma = 2 \times 10^{-6}$, $\mathrm{Sc}\Sigma = 3.81$

Shear melting of layers.

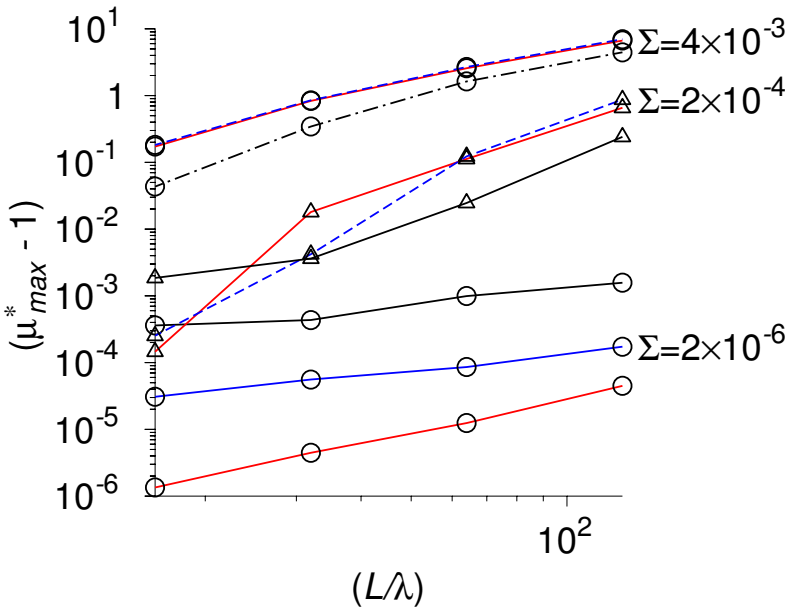
Coarsening without shear:



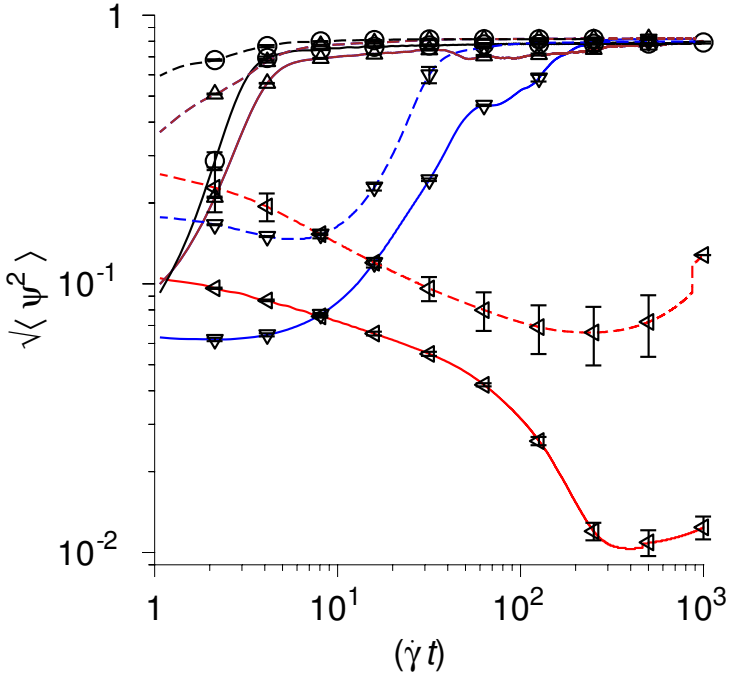
$\Sigma = 2 \times 10^{-6}$, $\mathrm{Sc}\Sigma = 3.81$

No layer melting.

Concentration homogenisation due to shear:



$\mathrm{Sc}\Sigma = 3.41, 10.24, 50.2$

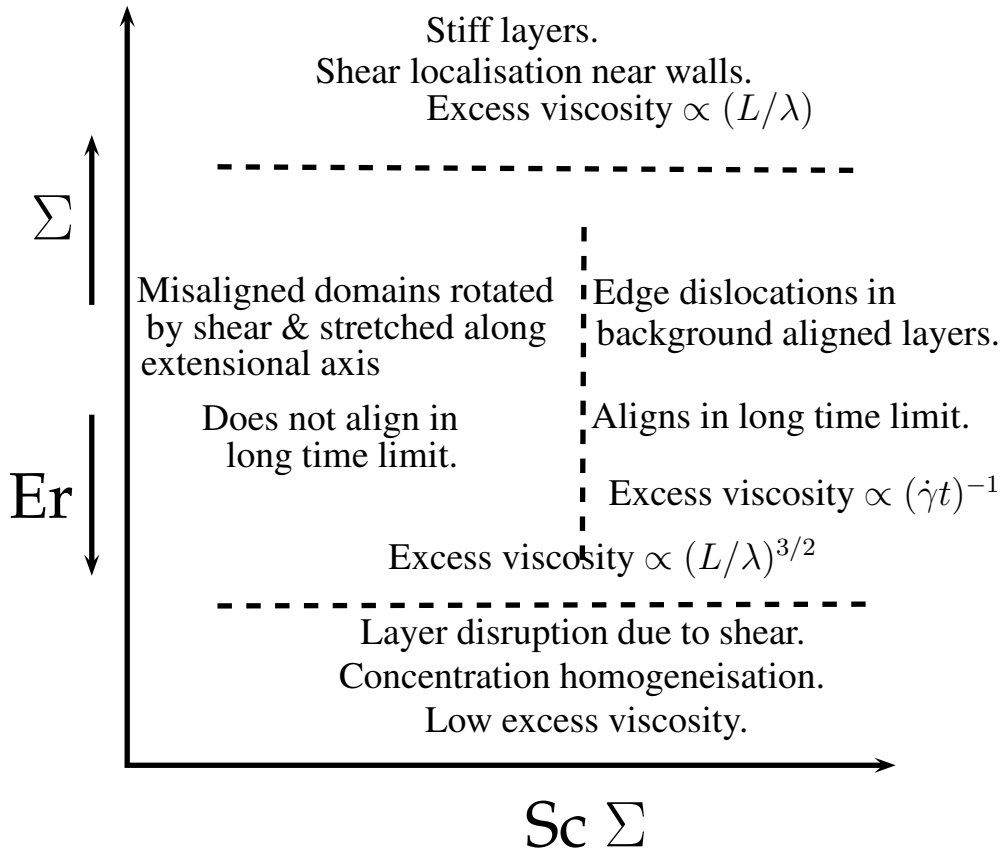


— $\mathrm{Sc}\Sigma = 3.41$; - - - $\mathrm{Sc}\Sigma = 51.2$

$\Sigma = 4 \times 10^{-3}, 2 \times 10^{-3},$

$2 \times 10^{-4}, 2 \times 10^{-6}.$

Summary:



Thank you.