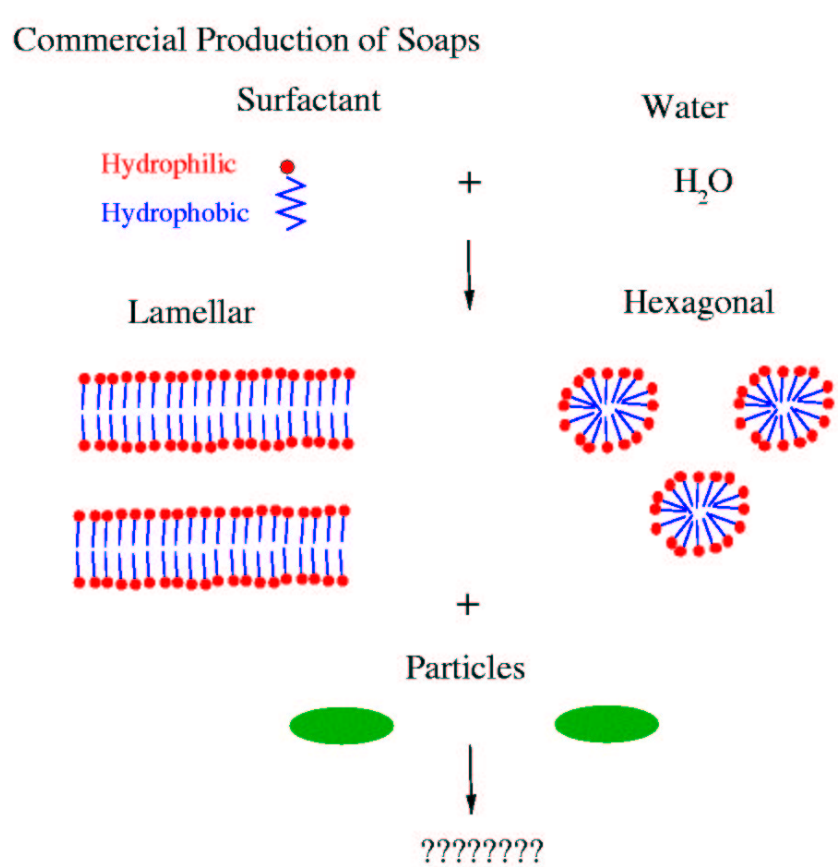
STRESS TRANSMISSION BY A DEFECT NETWORK IN A LIQUID CRYSTALLINE PHASE

V. Kumaran[2], Prabhu R. Nott[2], Sriram Ramaswamy[2], Geetha Basappa[1], Suneel[2]

[1] Department of Physics
[2] Department of Chemical Engineering
Indian Institute of Science
Bangalore 560 012
India

Collaborative Project with Unilever Research India



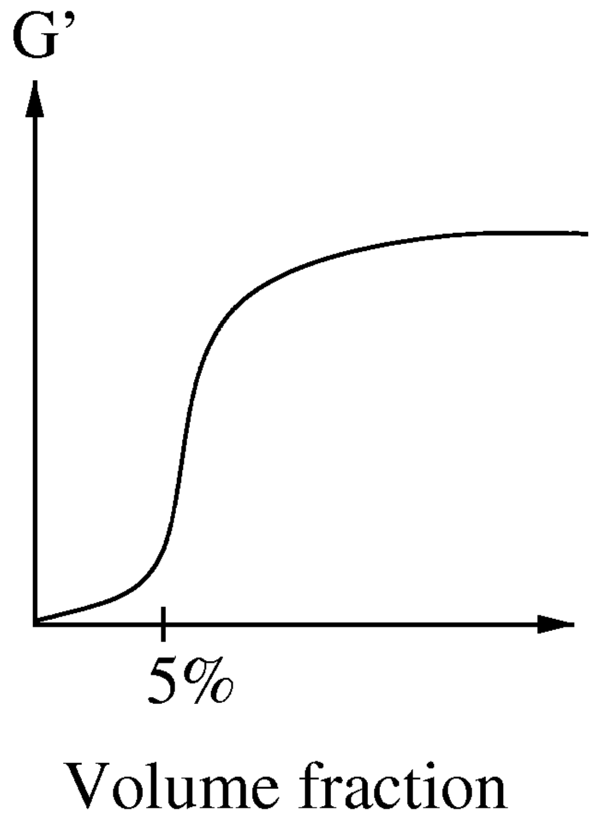
Manufacture of Personal Wash Bars

- Raise yield stress and shear modulus (to provide rigidity to the bar) with as little solids content as possible.
- Develop constitutive models for the rheology of particle laden liquid crystalline phases for use in the process design.
- Presently used rheological models for soft solids extremely inadequate for reliable, predictive equipment design.

Objectives

1. Develop a microscopic understanding of the relation between the structure and rheology of particle laden liquid crystalline phases.
2. Develop the links between microscopic structure and macroscopic rheology which can be used for design of materials with appropriate phase composition and particle concentration to provide required macroscopic properties.
3. Incorporate this understanding into macroscopic rheological models for liquid crystalline phases with suspended particles which can be used for flow computations.

Motivation Experiments by Shouche et al and Khakhar

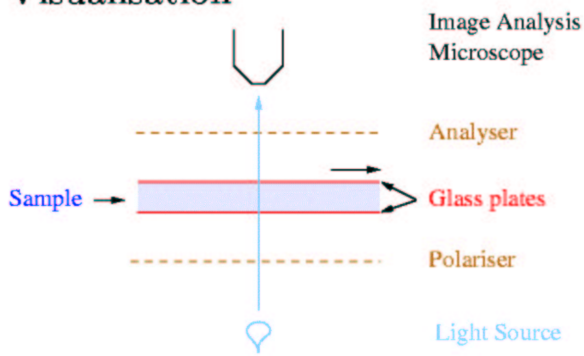


Outline of presentation

1. Rheological measurements of lamellar phases with and without particles.
2. Visualisation of the structures formed during shear of the lamellar phase.
3. Effect of added particles.
4. Estimation of the elasticity from the structures formed.
5. Dynamical evolution of structures under shear.
6. Conclusions.

Experimental studies

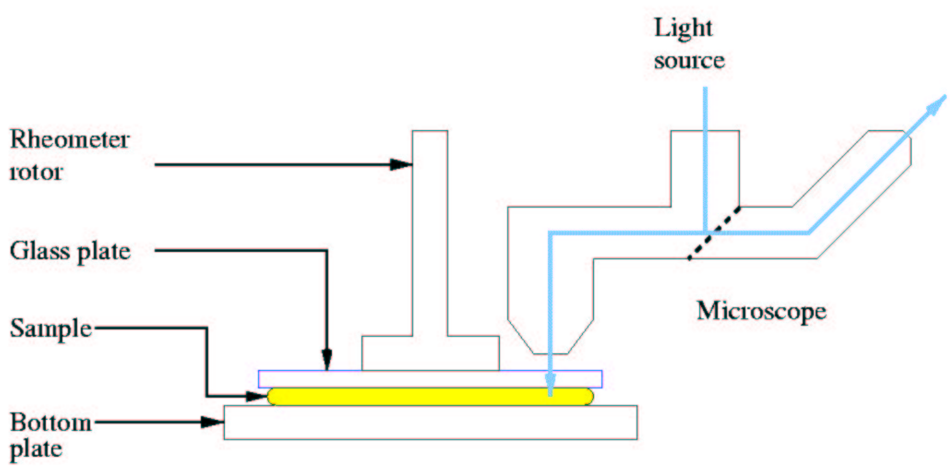
Visualisation



Rheology — Rheolyst AR1000 Rheometer

- Geometries — parallel plate, cone & plate, Couette.
- Steady shear, oscillatory $10^{-4} - 100Hz$.
- Storage G' and loss G'' moduli, viscosity, frequency dependences.

Simultaneous visualisation and rheology



- Rheolyst AR1000 Rheometer.
- Top plate modified by sticking a glass plate on the metal disk.
- Bottom reflecting plate.
- Custom built microscope.

Rheological Measurements

System

- Sodium dodecyl ether sulphate (SLES) + Water

$$CH_3 - (CH_2)_{10} - [OC_2H_4] - SO_4^- Na^+$$

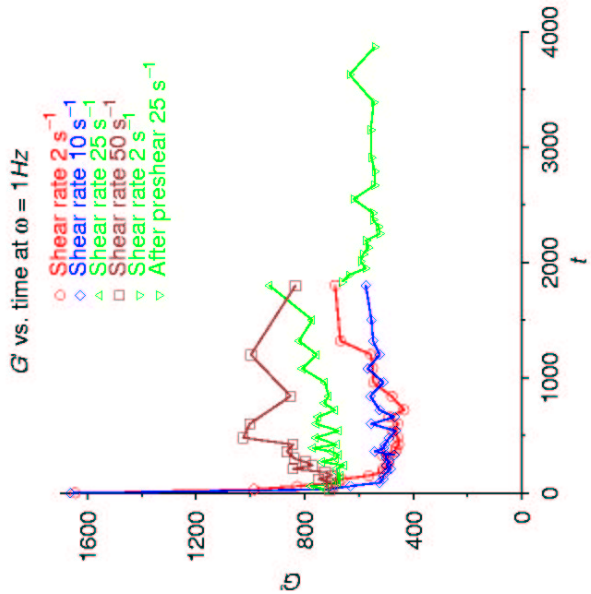
- Phases (% of SLES)

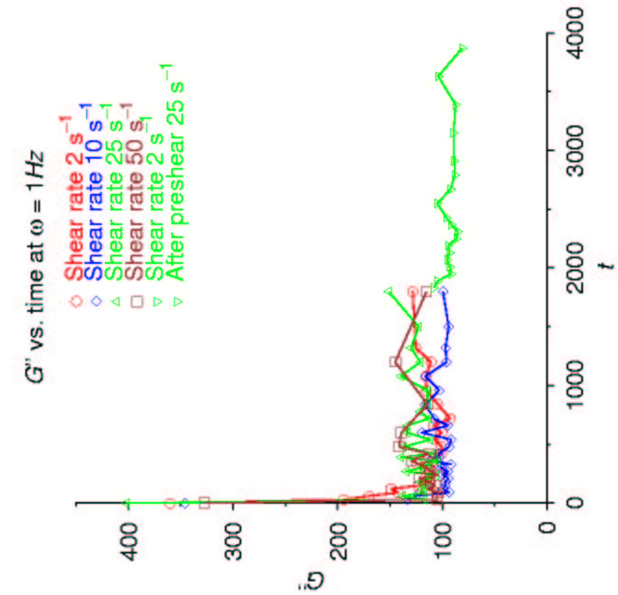
$$I \sim 37 \rightarrow H \sim 58 \rightarrow H + L \sim 63 \rightarrow L \sim 81 \rightarrow L + K$$

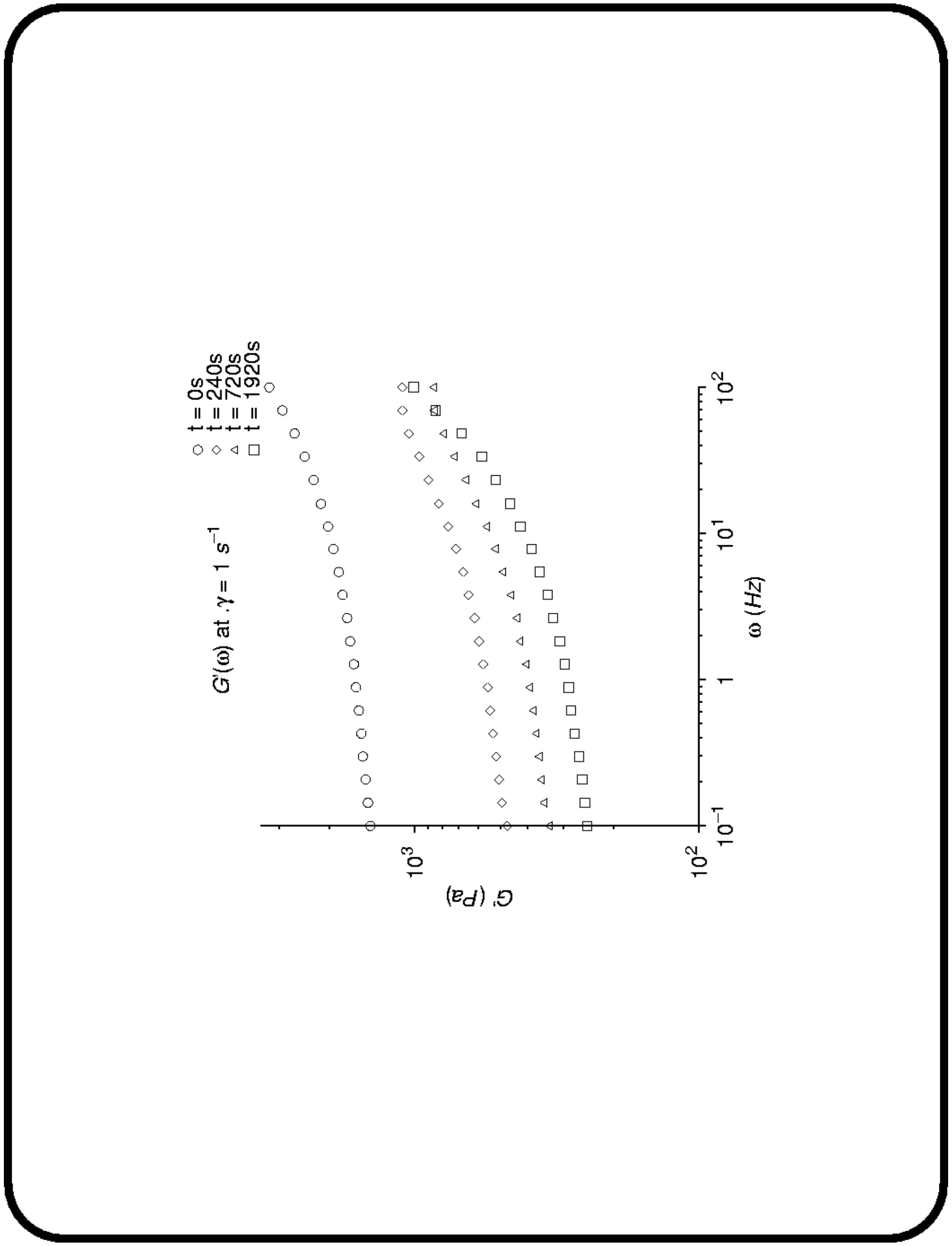
- Operating concentration SLES : $\mathrm{H_2O}$ = 72.3:26.8
- Dispersed particles: 19 μ silica particles, 9.5 μ polystyrene particles.

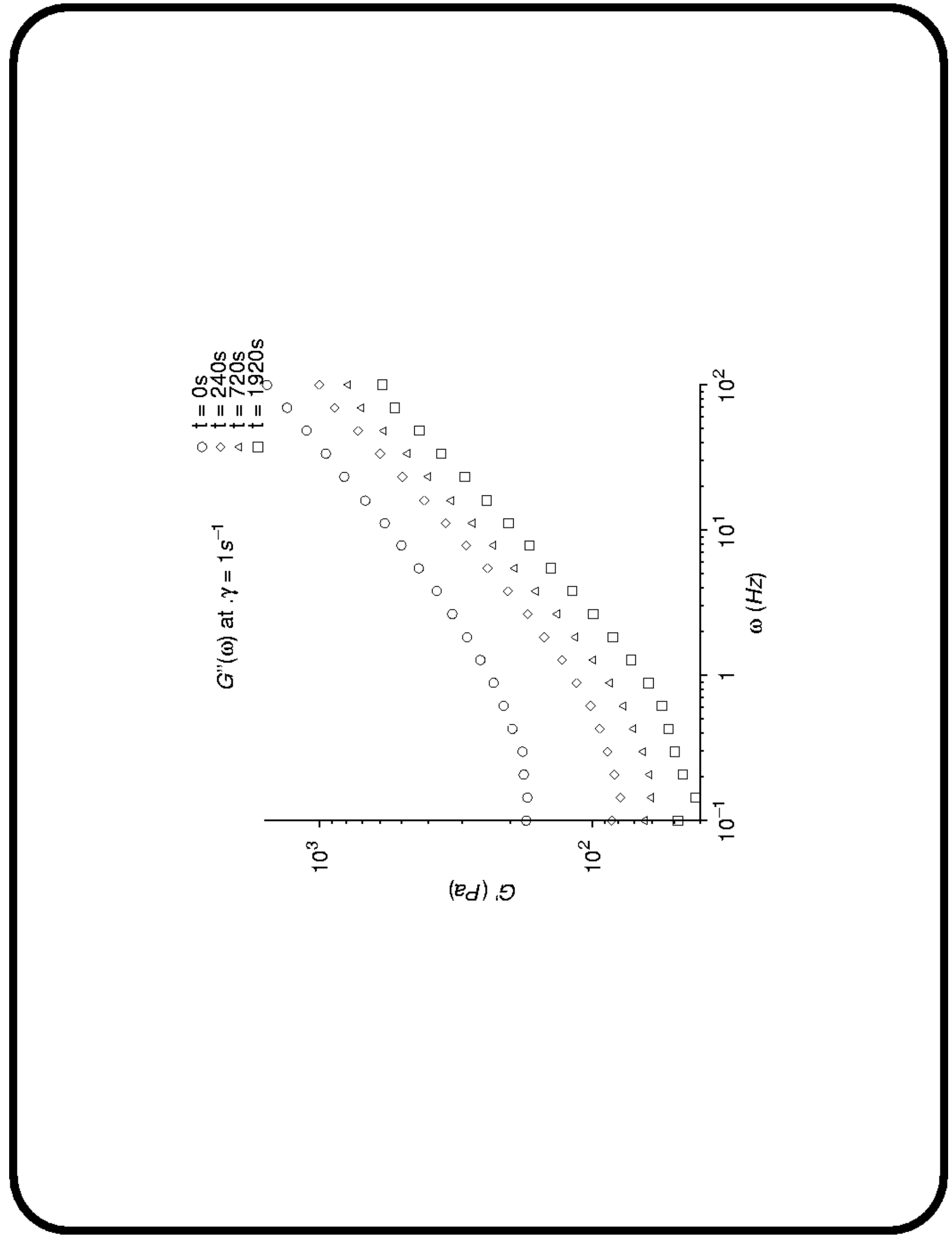
Protocol for rheology experiments

- Place sample in the parallel plate geometry of the rheometer (in disordered state.
- Steady shear for time interval Δt.
- Stop steady shear and determine storage and loss modulus using oscillatory measurements in the rheometer.
- Steady shear for next interval Δt followed by oscillatory measurements.
- Plot storage and loss moduli versus total time of shear.


G' vs. time at ω = 1 Hz
Shear rate 2 s⁻¹
Shear rate 10 s⁻¹
Shear rate 25 s⁻¹
Shear rate 50 s⁻¹
Shear rate 2 s⁻¹
After preshear 25 s⁻¹
G'
t
0
400
800
1200
1600
1000
2000
3000
4000


G'' vs. time at ω = 1 Hz
Shear rate 2 s⁻¹
Shear rate 10 s⁻¹
Shear rate 25 s⁻¹
Shear rate 50 s⁻¹
Shear rate 2 s⁻¹
After preshear 25 s⁻¹
G''
t
0
100
200
300
400
1000
2000
3000
4000


G'(ω) at ·γ = 1 s⁻¹
t = 0s
t = 240s
t = 720s
t = 1920s
G' (Pa)
ω (Hz)


G''(ω) at ·γ = 1s⁻¹
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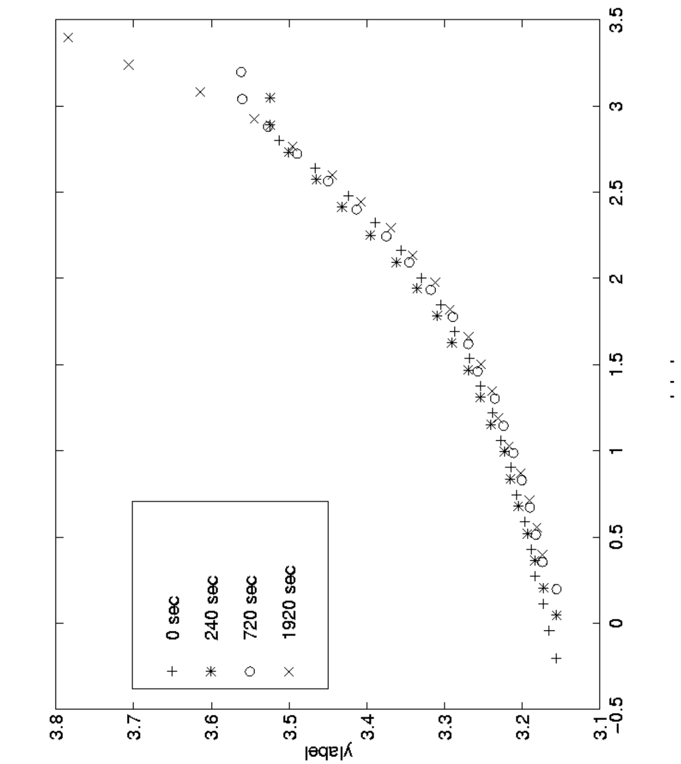
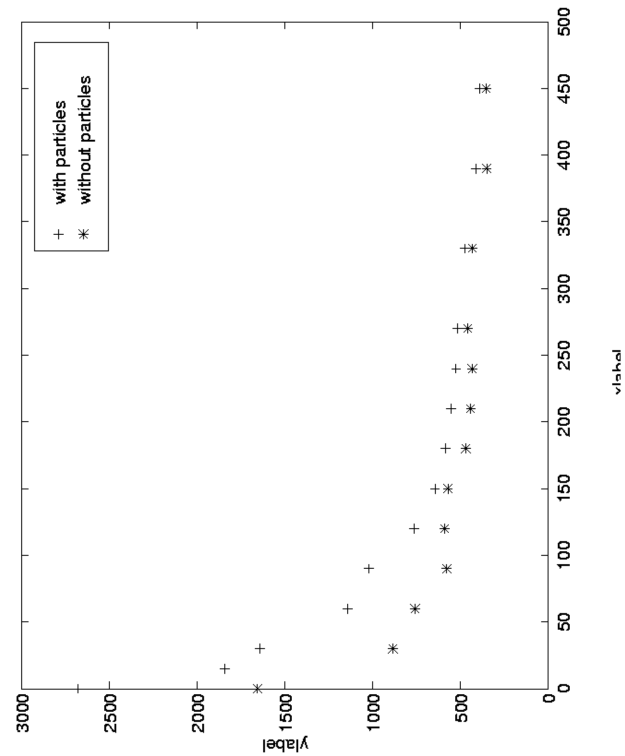
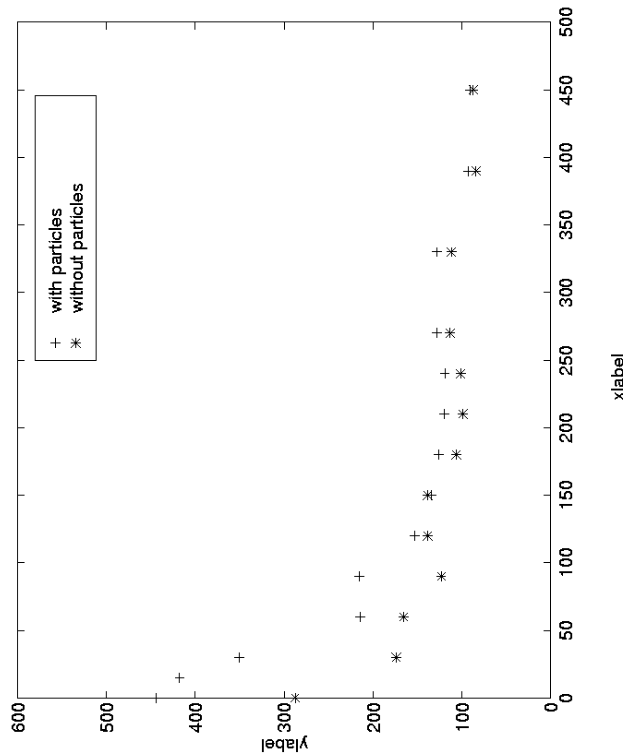
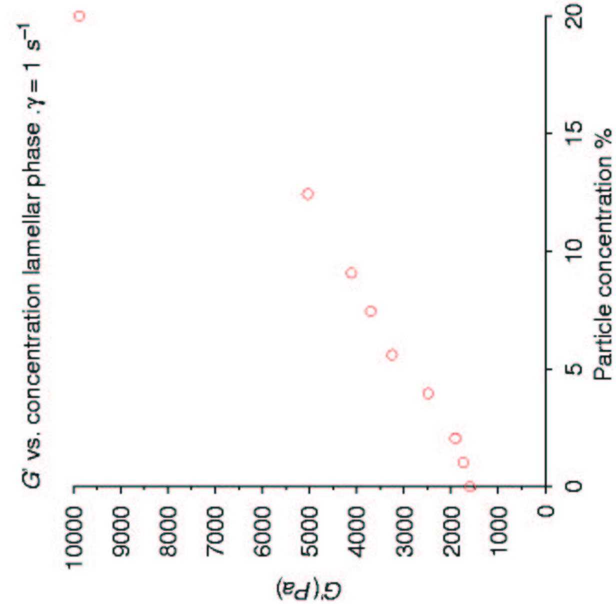
G' (Pa)
ω (Hz)


0 sec
240 sec
720 sec
1920 sec
ylabel


with particles
without particles
ylabel

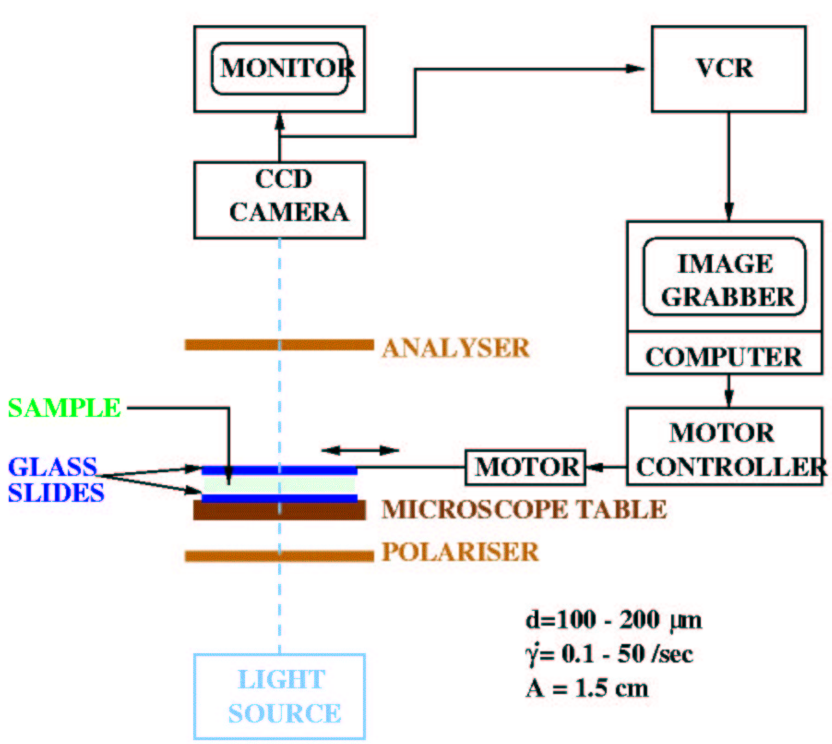

with particles
without particles
xlabel
ylabel

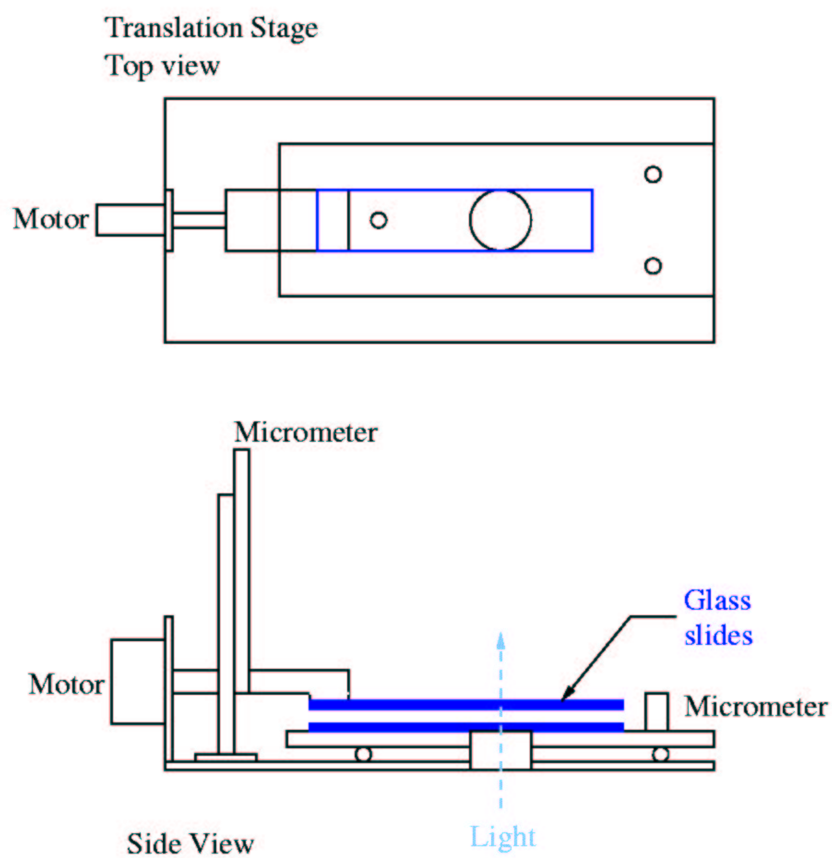

G' vs. concentration lamellar phase :γ = 1 s^-1
Particle concentration %
G'(Pa)

Conclusions (Rheological Measurements)

1. Storage and loss moduli decrease as system is sheared, reach what appears to be a steady state value, and then appear to increase on further shearing.
2. At any point in time, frequency dependence of moduli are similar to those seen in typical soft solids.
3. Transient dynamical properties depend on history of shear.
4. Shear treatment affects microstructure, which in turn affects properties. Working in of defects at late times?
5. Presence of particles increases storage and loss moduli at early and intermediate times, but qualitative decrease of moduli with shear treatment maintained.

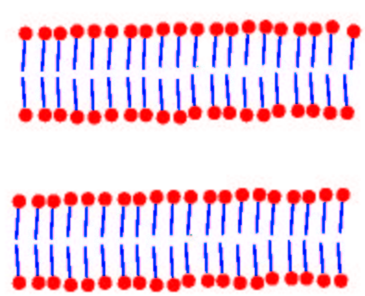
RHEO - OPTICS EXPERIMENTAL SETUP



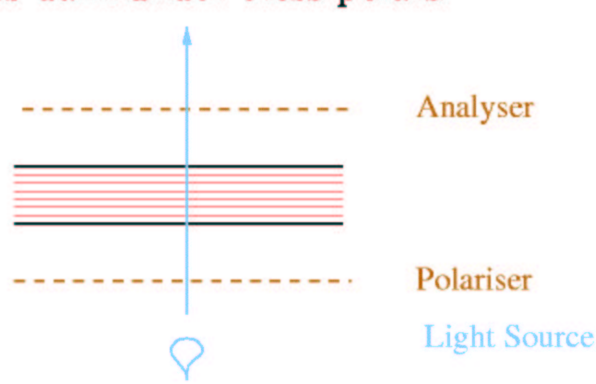


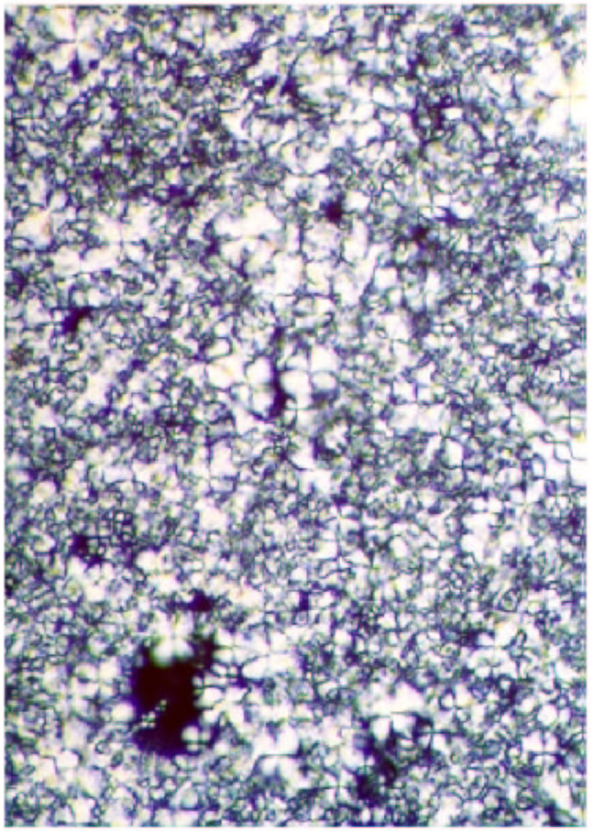
Lamellar liquid crystals

- Anisotropic liquids with surfactants stacked in form of lamellae.

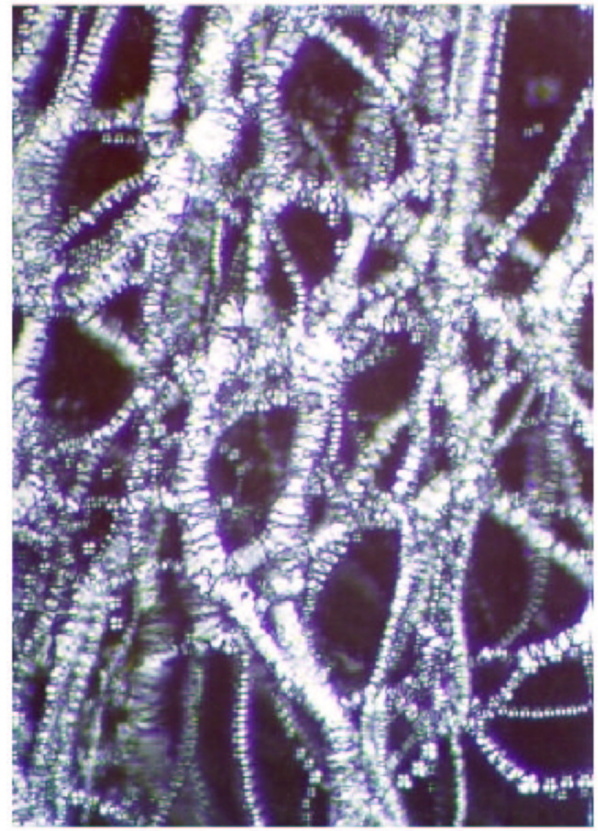


- Ordered phases dark under cross polars.

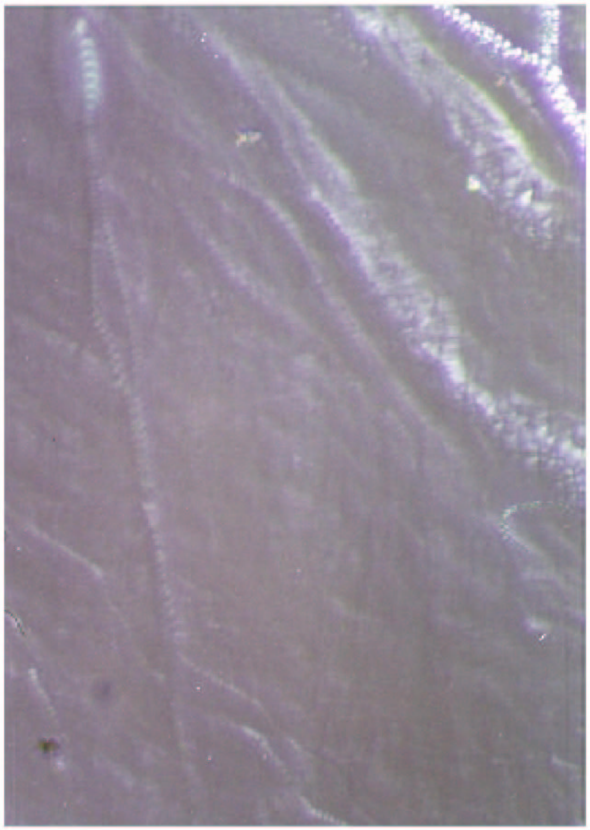




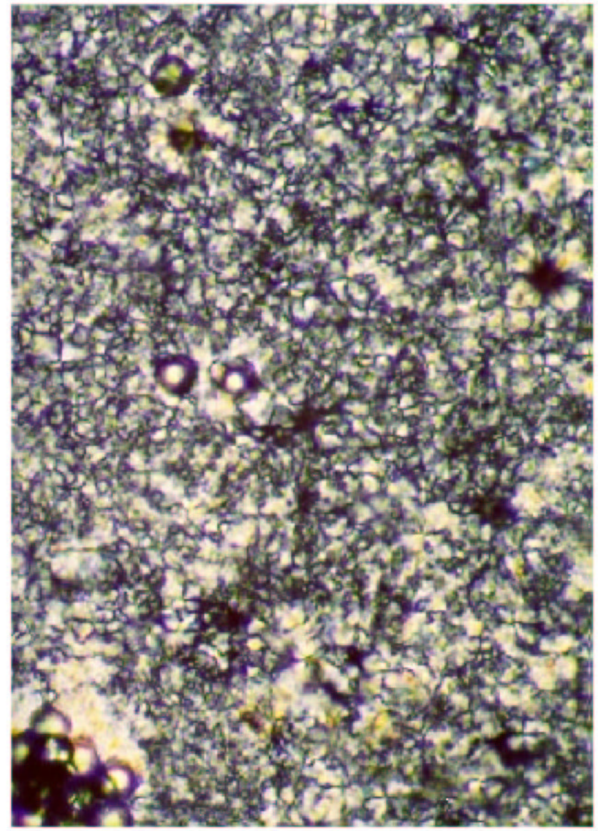
Pure SLES before shearing



Pure SLES after shearing 58 s^{-1} for 1 minute

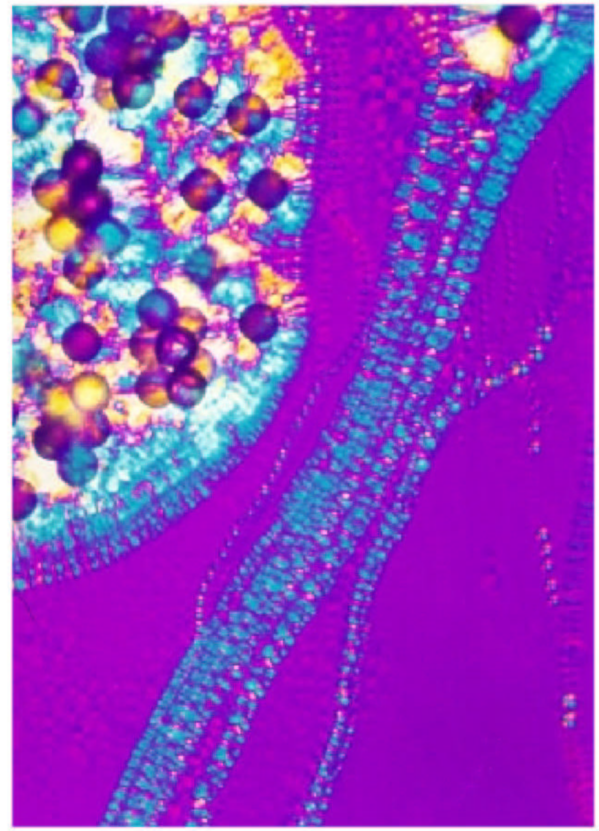


Pure SLES after shearing 58 s^{-1} for 13 minute

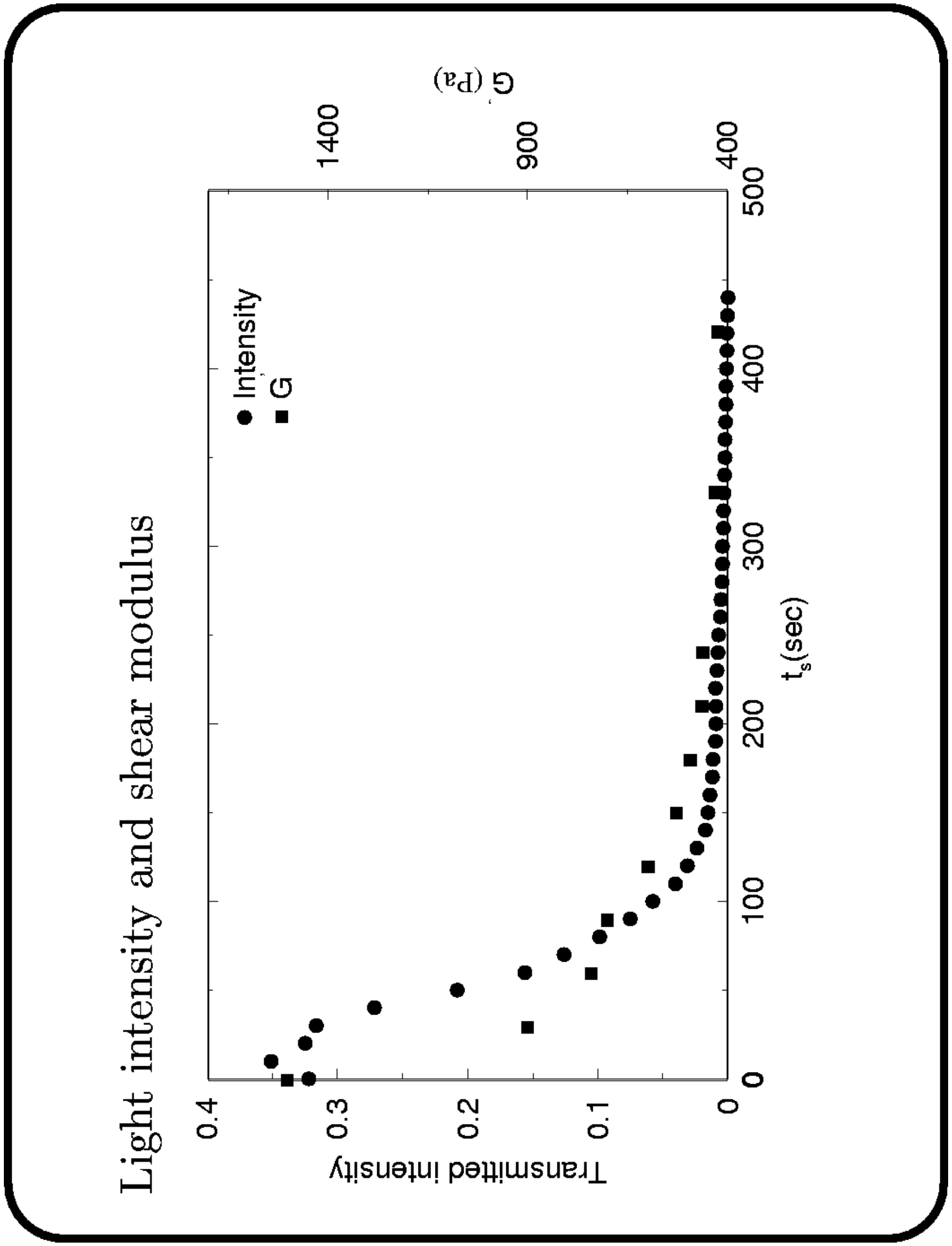


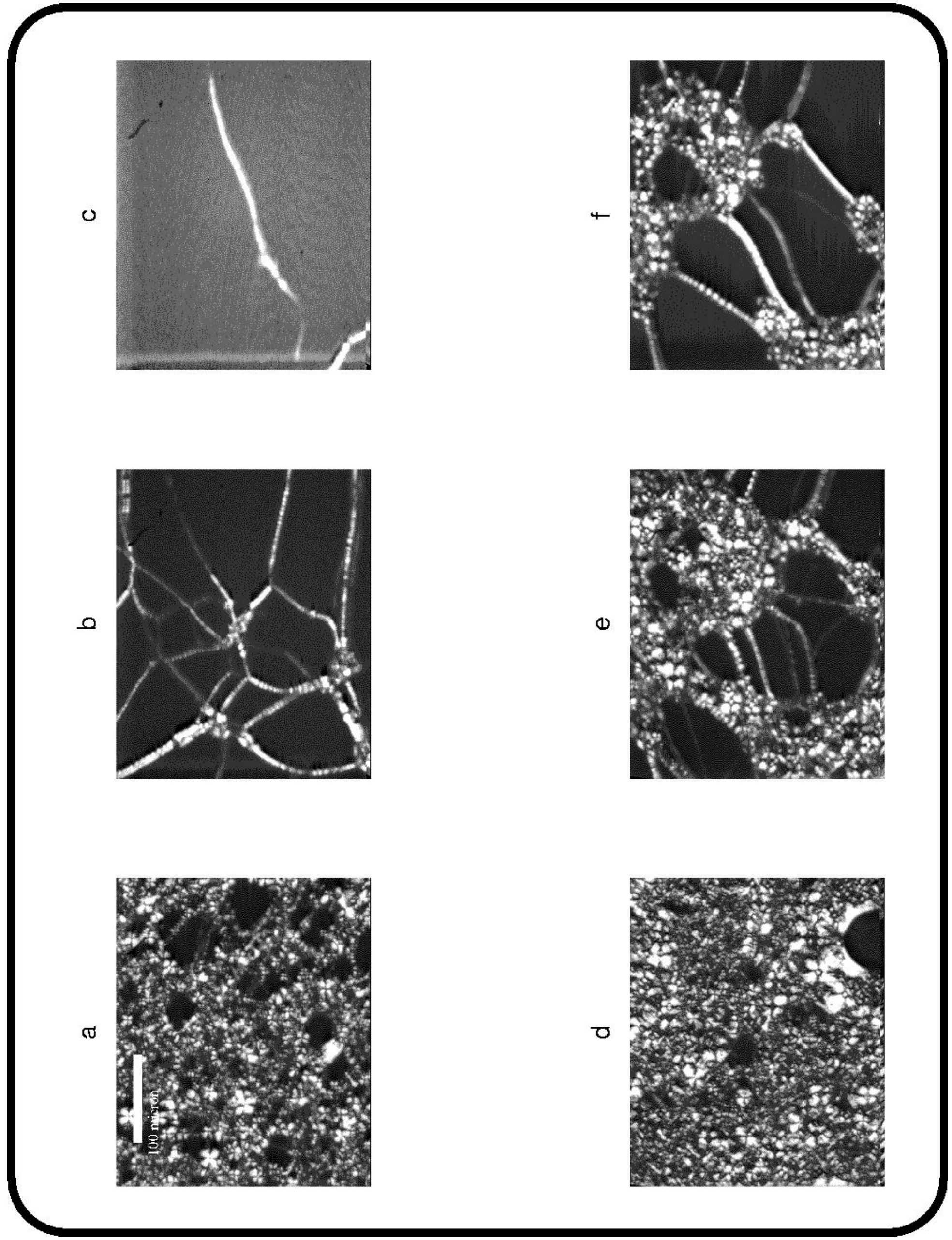
SLES + 0.5 % silica particles before shearing

SLES + 0.5 % silica particles after shearing 8 minutes



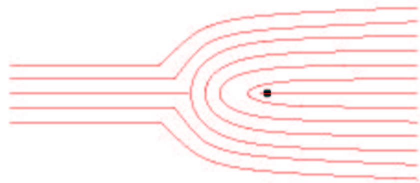
SLES + 0.5 % silica particles after shearing 11 minutes


Light intensity and shear modulus
Transmitted intensity
0.4
0.3
0.2
0.1
0
0
100
200
300
400
500
t_s(sec)
G' (Pa)
1400
900
400
Intensity
G'

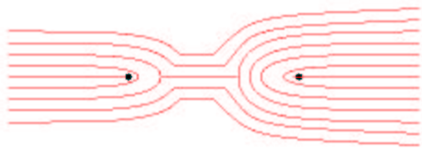

a
b
c
d
e
f
100 micron

Oily streak defects

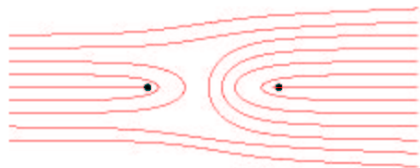
- Edge dislocation



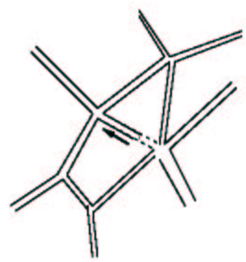
- Pairs of edge dislocations — energetically favourable



- Oily streaks



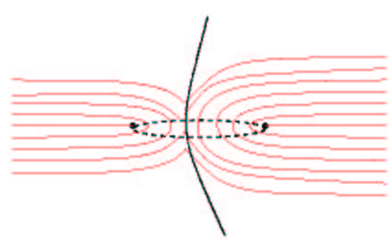
- Streaks under cross polars.



Focal Conic defects

- Pairs of edge dislocations

- Disclination lines break up into ellipse and hyperbola



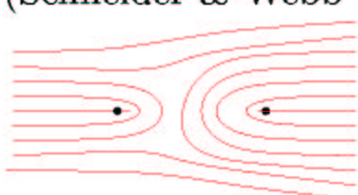
- Appears as a four brush structure under cross polars.

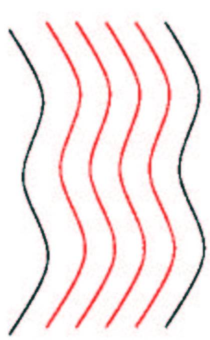
- Onion structures in sheared liquid crystals

Striated oily streaks

Undulating pair of disclinations

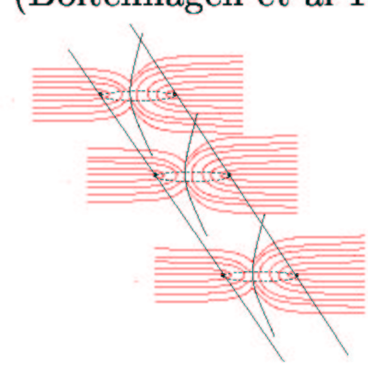
(Schneider & Webb 1984)



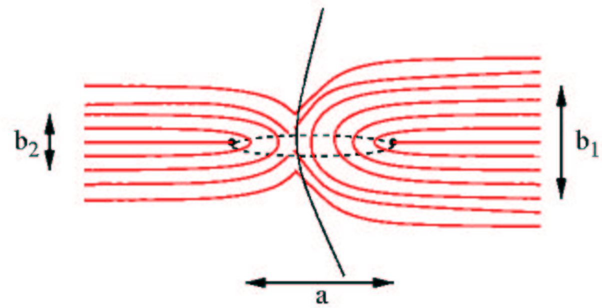


Arrays of focal conics

(Boltenhagen et al 1991)



Energetics of defects (Boltenhagen et al 1991)



- Ellipse with major and minor axes $a = (b_1 + b_2)/2$ and $b = \sqrt{b_1 b_2}$.
- Eccentricity $e = (b_1 - b_2)/(b_1 + b_2)$.

Energetics of defects (Boltenhagen et al 1991)

- Bending energy

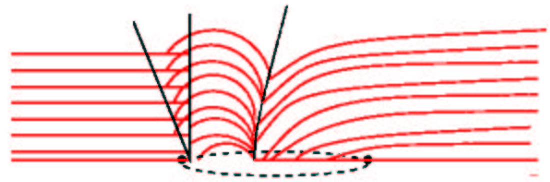
$$f_B = \frac{1}{2}K\left(\frac{1}{R_1} + \frac{1}{R_2}\right)^2 + \frac{\bar{K}}{R_1 R_2}$$

- Bending energy of edge dislocations (per length) of major axis a, eccentricity e

$$F_B = 4\pi K(1 - e^2)a\left[\log(a/r_c) + 1 - 2\frac{\bar{K}}{K}\right]$$

- Bending energy of edge dislocations of length l is $\sqrt{KB}bl$, where b is the Burgers vector.

Energetics of defects



- Compression energy of focal conics

$$E_c = Bh^2 \left[\frac{e}{\sqrt{1-e^2}} - \frac{a}{h} \right]^5$$

- Network, compression screened at length l.
- Combining the two, we get a compression energy increase proportional to e^5 as eccentricity $e = b/(b_1 + b_2)$ increases.
- Stabilises oily streaks at higher values of Burgers vector b.
- For $B \sim 10^5 Pa$, $l \sim 50\mu m$, the minimum b for stable oily streaks is $O(10\mu m)$.

Stress transmission by oily streak network

- Network of oily streaks with mesh size l and tension Γ has shear modulus $G' = (\Gamma/l^2)$.
- Estimation of line tension Γ.
  - Compression energy in an oily streak in a sample of width h

$$E = Bh^2 \left[\frac{e}{\sqrt{1-e^2}} - \frac{a}{h} \right]^5$$

  - Network, compression screened at length l.
  - For $B \sim 10^5 Pa$, $l \sim 50\mu m$ and $a \sim 5 - 10\mu m$, $G' \sim 10^2 - 10^3 Pa$.
  - Correct order of magnitude.

Rheological measurements

- Shear modulus curve suggests that the rheological state is a function of the applied strain rate, and not just of the material properties.
- If stress is transmitted by defects, defect density depends on strain rate.
- It is known that shear anneals defects, but shear should also work in defects.
- Defect density higher at higher strain rates.
- Mechanism?

Undulation instability in lamellar liquid crystals

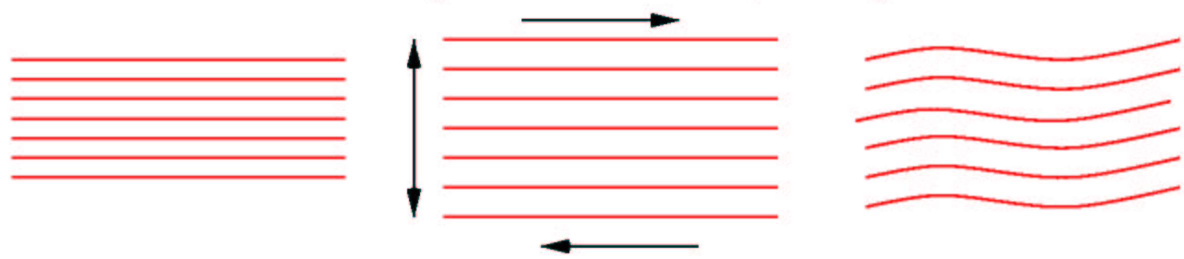
- Scalar field u describes displacement of layers from their equilibrium position.
- Expansion or contraction perpendicular to the layers

$$S = \left(\partial_z u - \frac{1}{2}(\nabla_\perp u)^2\right)$$

- Bending of layers, the curvature is given by

$$\kappa = \nabla_\perp^2 u$$

Undulation instability in lamellar liquid crystals



$$\text{Free energy} F = \int dV B \left[\left(\partial_z u - \frac{1}{2} (\nabla_\perp u)^2 \right)^2 + \frac{K}{2} (\nabla_\perp^2 u)^2 \right]$$

Dilation $\partial_z u = D$

$$F = \int dV \left[-\frac{B}{2} D (\nabla_\perp u)^2 + \frac{K}{2} (\nabla_\perp^2 u)^2 \right]$$

Unstable if

$$k_\perp = \sqrt{\frac{BD}{K}}$$

Undulation instability in lamellar liquid crystals

Upper cut off of instability based on system size:

- A perturbation of length $L_\perp$ along the layers propagates a distance $(L_\perp^2/\lambda)$ perpendicular to the layers.
- For a thickness h perpendicular to the layers, the cut off for waves along the layers is $L_\perp = \sqrt{h\lambda}$.
- Cut off for wave vector $k_\perp = \sqrt{BD/K} > 1/\sqrt{h\lambda}$.
- Minimum dilation $D > (K/B\lambda h)$.

Undulation instability in lamellar liquid crystals

- Undulation caused by a normal stress due non - uniformity in the boundaries as the system is sheared.
- Normal stress $\propto \eta\dot{\gamma}$ (viscosity $\times$ strain rate).

$$D = \frac{a\eta\dot{\gamma}}{B}$$

- Unstable if $\dot{\gamma} > \dot{\gamma}_c$, where

$$\dot{\gamma}_c \sim \frac{K}{\eta\lambda h}$$

- Using numerical values used earlier, we find $\dot{\gamma}_c$ is in the range of $1 - 10s^{-1}$.

Conclusions

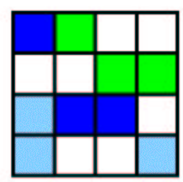
1. Evolution and annealing of defect structure — network of oily streaks under shear.
2. Two different types of defects — striated oily streaks and lines of focal conic defects.
3. Rheology and visualisation → stress transmitted due to defect lines, not background lamellar phase.
4. Further shearing works in defects, possibly due to working in of defects by the undulation instability.
5. Particles move to nodes of defect structure, decrease rate of coarsening of defects.

Requirement of simulations

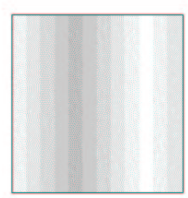
- Should predict anisotropic properties.
- Alignment under shear.
- Variation of storatge and loss moduli under shear.
- Annealing and introduction of defects under shear.
- Flow around particles.
- Flow through complex geometries.

Simulation and Analysis

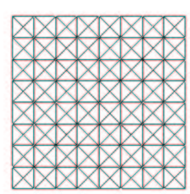
1. Microscopic Lattice Monte Carlo simulations



2. Continuum Monte Carlo simulations



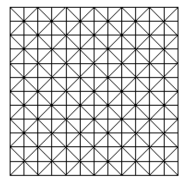
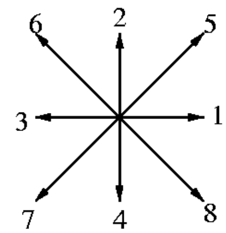
3. Lattice Boltzmann simulations



4. Macroscopic continuum model — Conservation equations for layer normal $\mathbf{n}$, spacing w and velocities $\mathbf{u}$ and $\mathbf{v}$ of surfactants.

Lattice Boltzmann simulations

- Define 'distribution function' $f_i(\mathbf{x}, t)$ for discrete velocity directions on a lattice.

- Relation to macroscopic properties

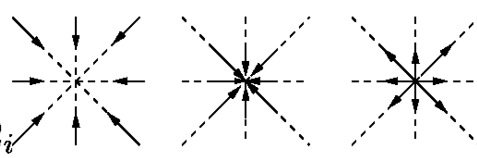
$$\rho = \sum_i f_i$$

$$\rho u_\alpha = \sum_i f_i e_{i\alpha}$$

$$\rho u_\alpha u_\beta - T_{\alpha\beta} = \sum_i f_i e_{i\alpha} e_{i\beta}$$

- Streaming, collision and re-distribution steps.

  $f_i(\mathbf{x} + \mathbf{e}_i, t{+}1) = f(\mathbf{x}, t) + \Omega_i$



- BGK approximation $\Omega_i = -\frac{(f_i - f_i^{eq})}{\tau}$
- f_i^{eq} sum of velocity moments chosen to satisfy

$$\sum_i f_i^{eq} = \rho$$

$$\sum_i f_i^{eq} e_{i\alpha} = \rho u_\alpha$$

$$\sum_i f_i^{eq} e_{i\alpha} e_{i\beta} = \rho u_\alpha u_\beta + \rho C_s^2 \delta_{\alpha\beta}$$

- Can show above scheme correctly reproduces macroscopic Navier - Stokes equations with kinematic viscosity $\nu = (\tau - 0.5) C_s^2$.

Lattice Boltzmann for lamellar phase

- Free energy functional
  $F[\psi] = \int dV \left[\frac{r}{2}\psi^2 + \frac{u}{4}\psi^4 + c[(\nabla^2 + q_0^2)\psi]^2\right]$
- Two distributions $f(\mathbf{x}, t)$ for total density and $g(\mathbf{x}, t)$ for order parameter.
-

$$\sum_i g_i^{eq} = \psi$$

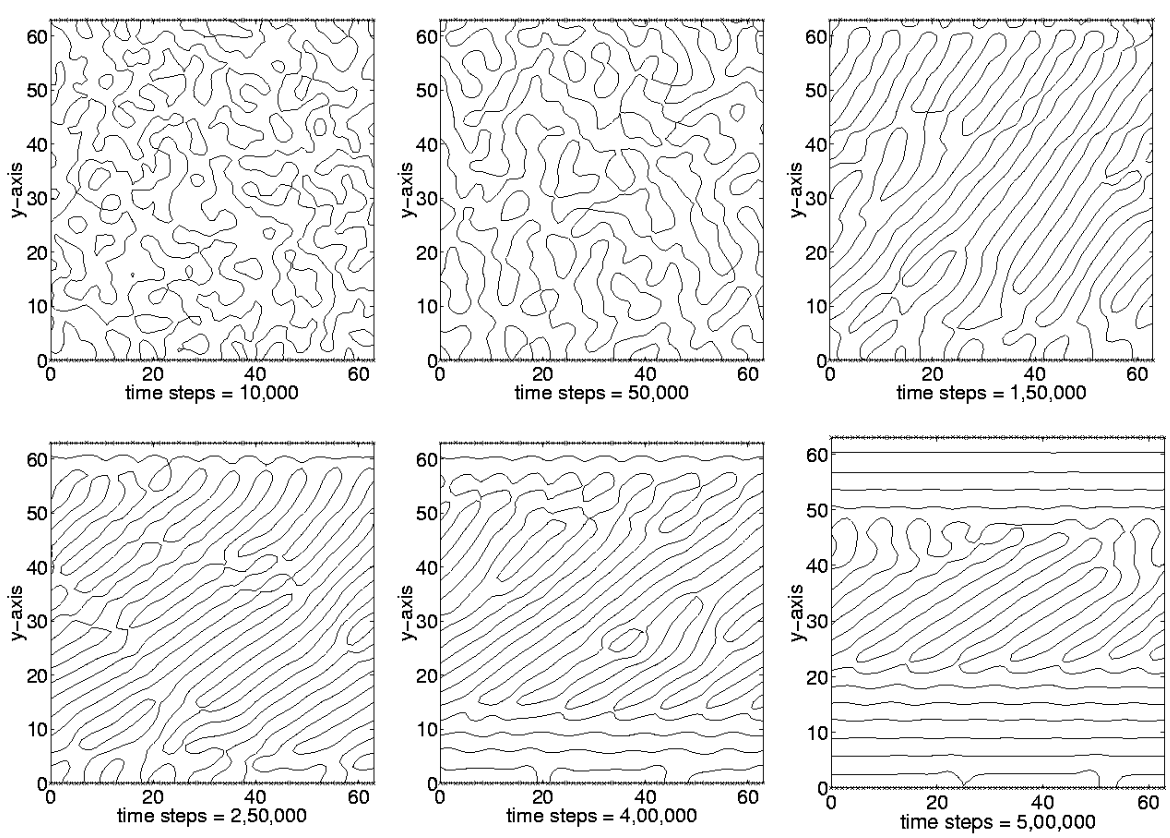
$$\sum_i g_i^{eq} e_{i\alpha} = \psi u_\alpha$$

- Second moment relations

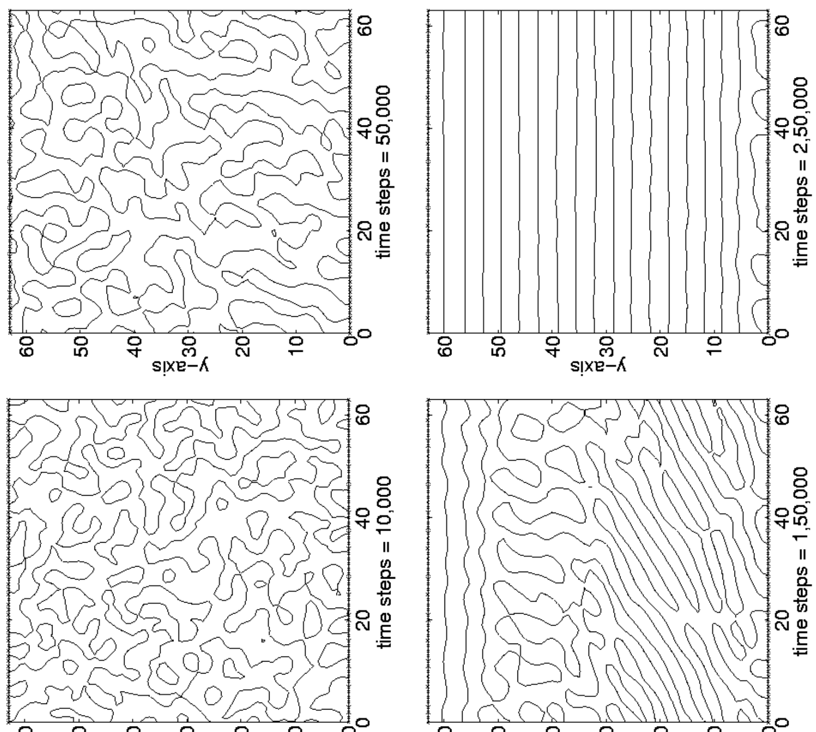
$$\sum_i f_i^{eq} e_{i\alpha} e_{i\beta} = \rho u_\alpha u_\beta + \mathcal{F}[f(\psi)]$$

$$\sum_i g_i^{eq} e_{i\alpha} e_{i\beta} = \psi u_\alpha u_\beta + \mathcal{G}[f(\psi)]$$

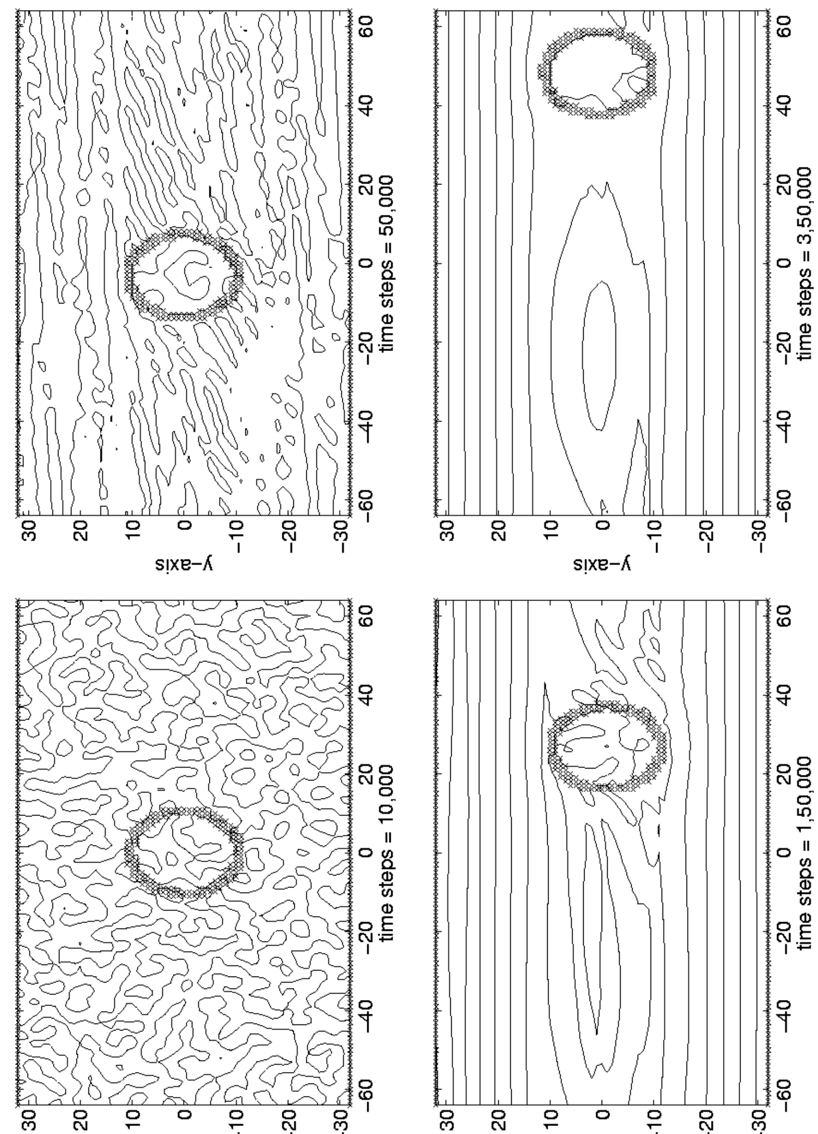
Shear alignment of the lamellar phase (Re = 1.0)

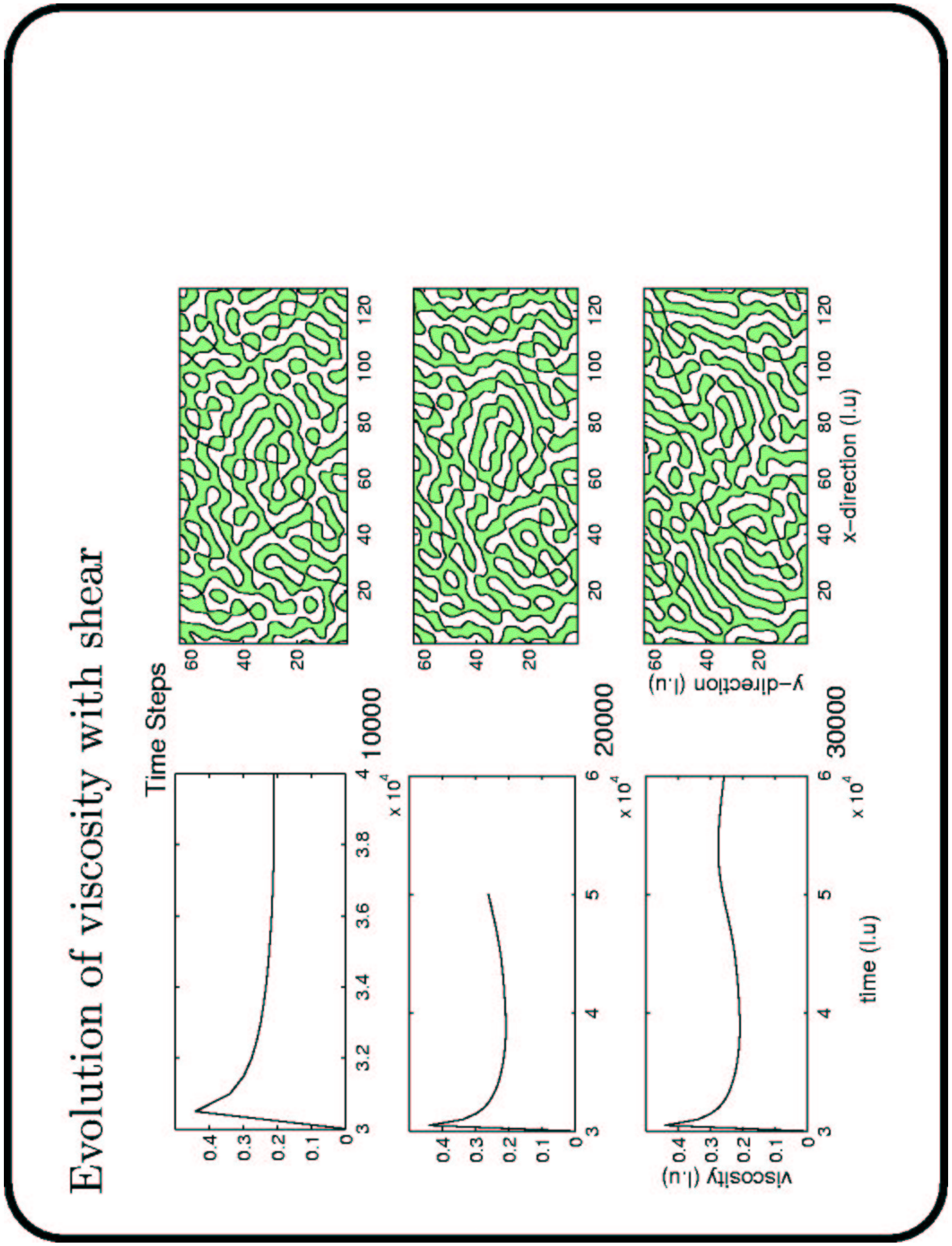


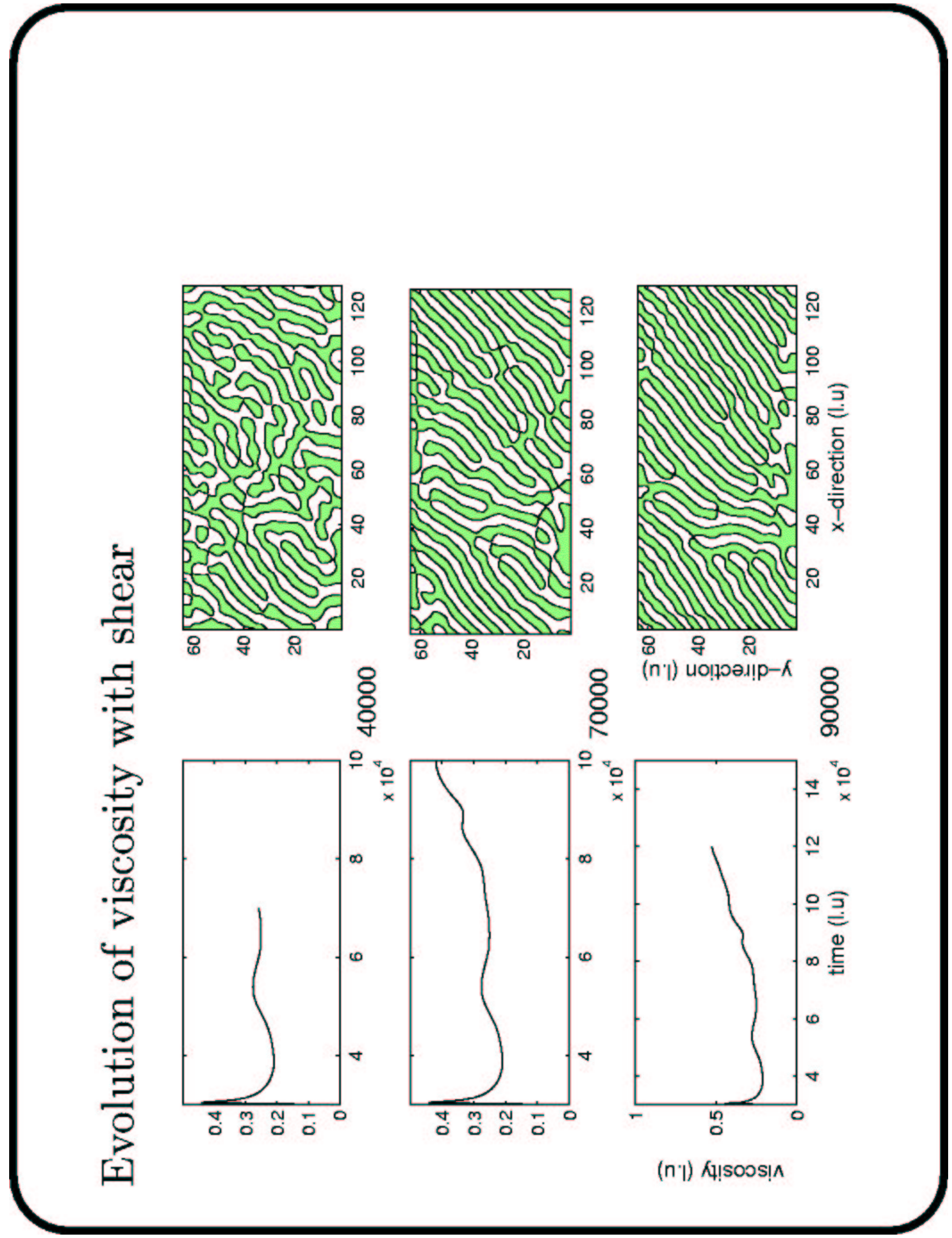
Shear alignment of the lamellar phase (Re = 2.0)



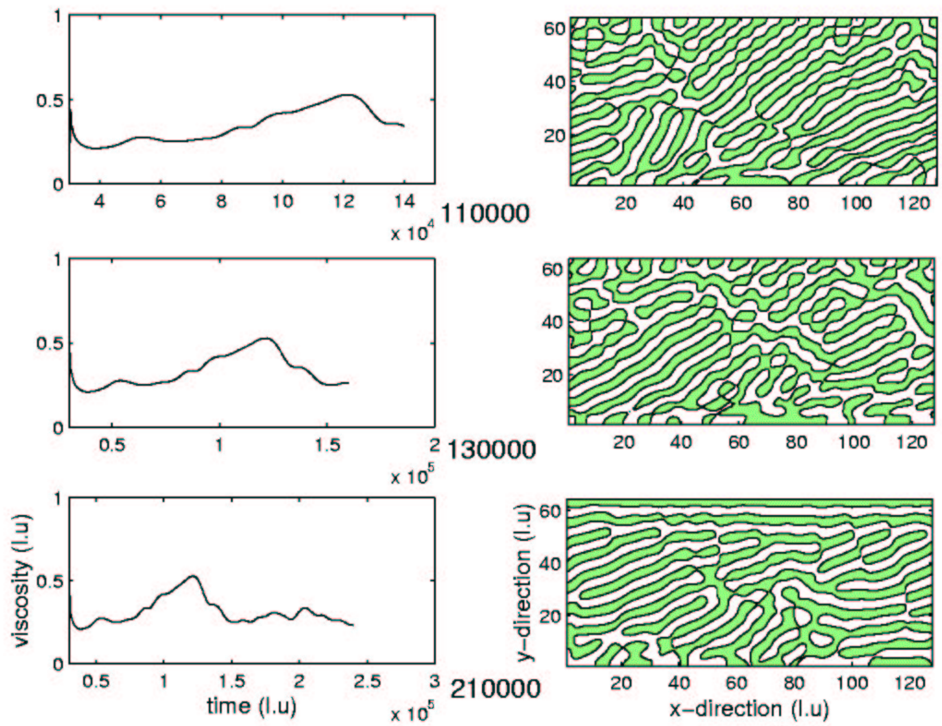
Flow around a particle



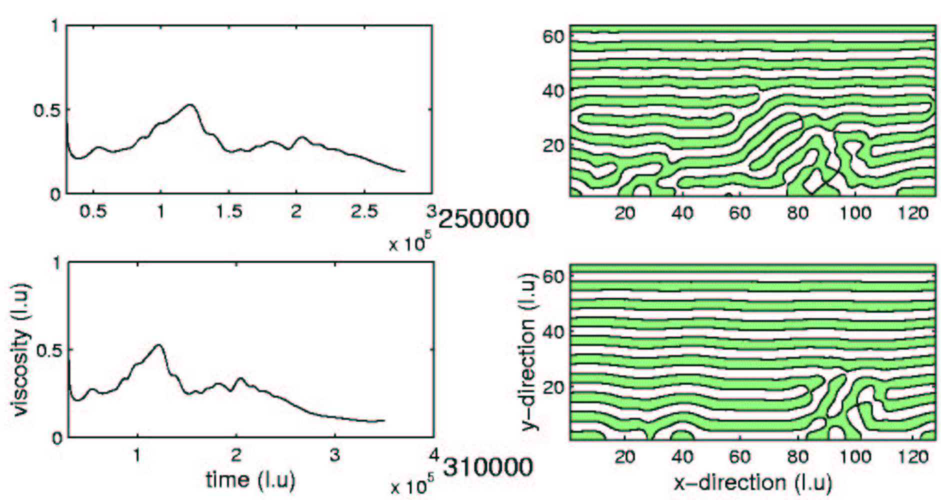

Evolution of viscosity with shear
Time Steps
10000
20000
30000
viscosity (l.u)
time (l.u)
y−direction (l.u)
x−direction (l.u)


Evolution of viscosity with shear
40000
70000
90000
viscosity (l.u)
time (l.u)
y−direction (l.u)
x−direction (l.u)

Evolution of viscosity with shear

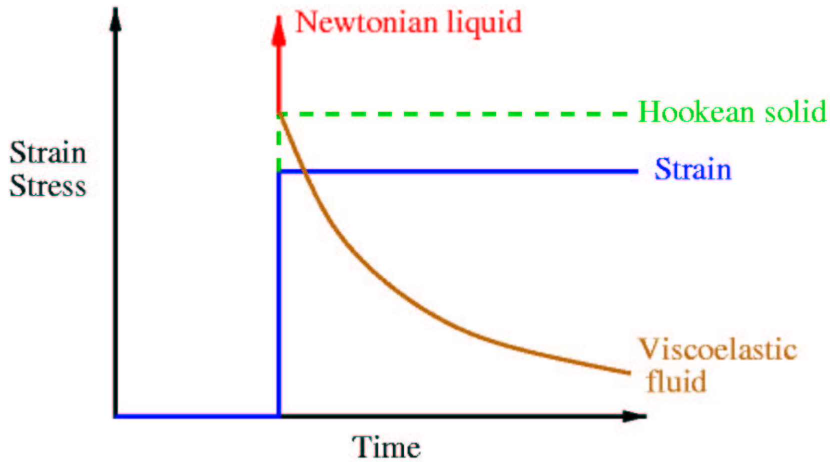


Evolution of viscosity with shear



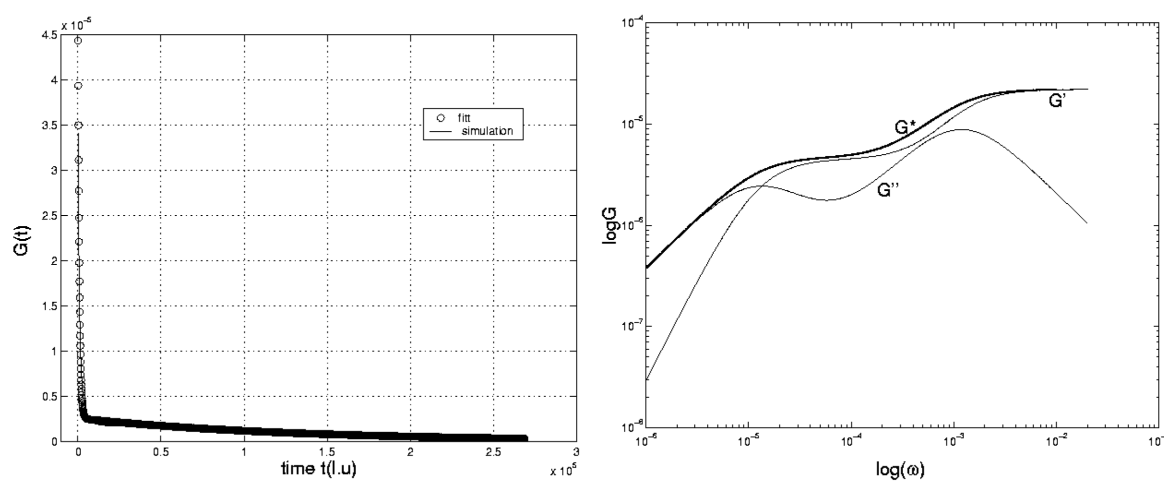
Storage and loss moduli

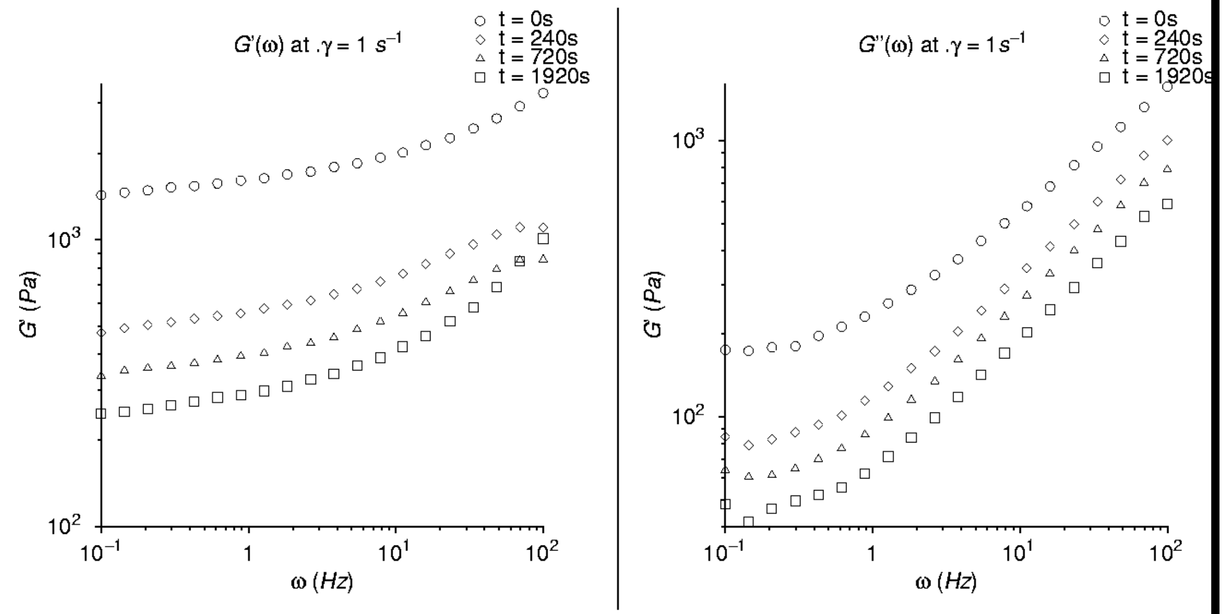
Apply a step strain on the sample, and determine evolution of stress.



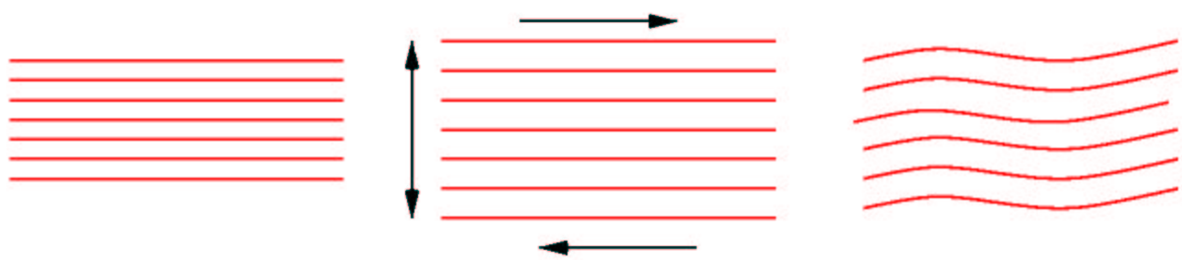
Determine storage and loss moduli from inverse Fourier transform of step strain date.

Storage and loss moduli

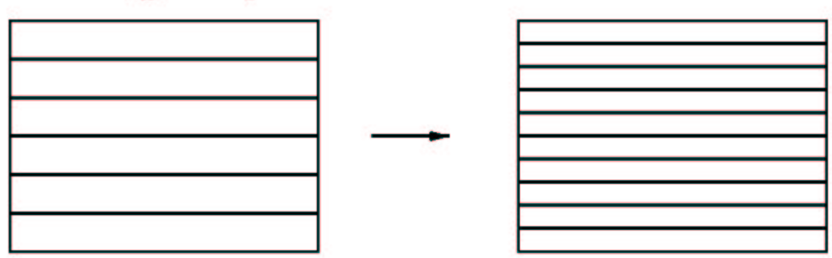




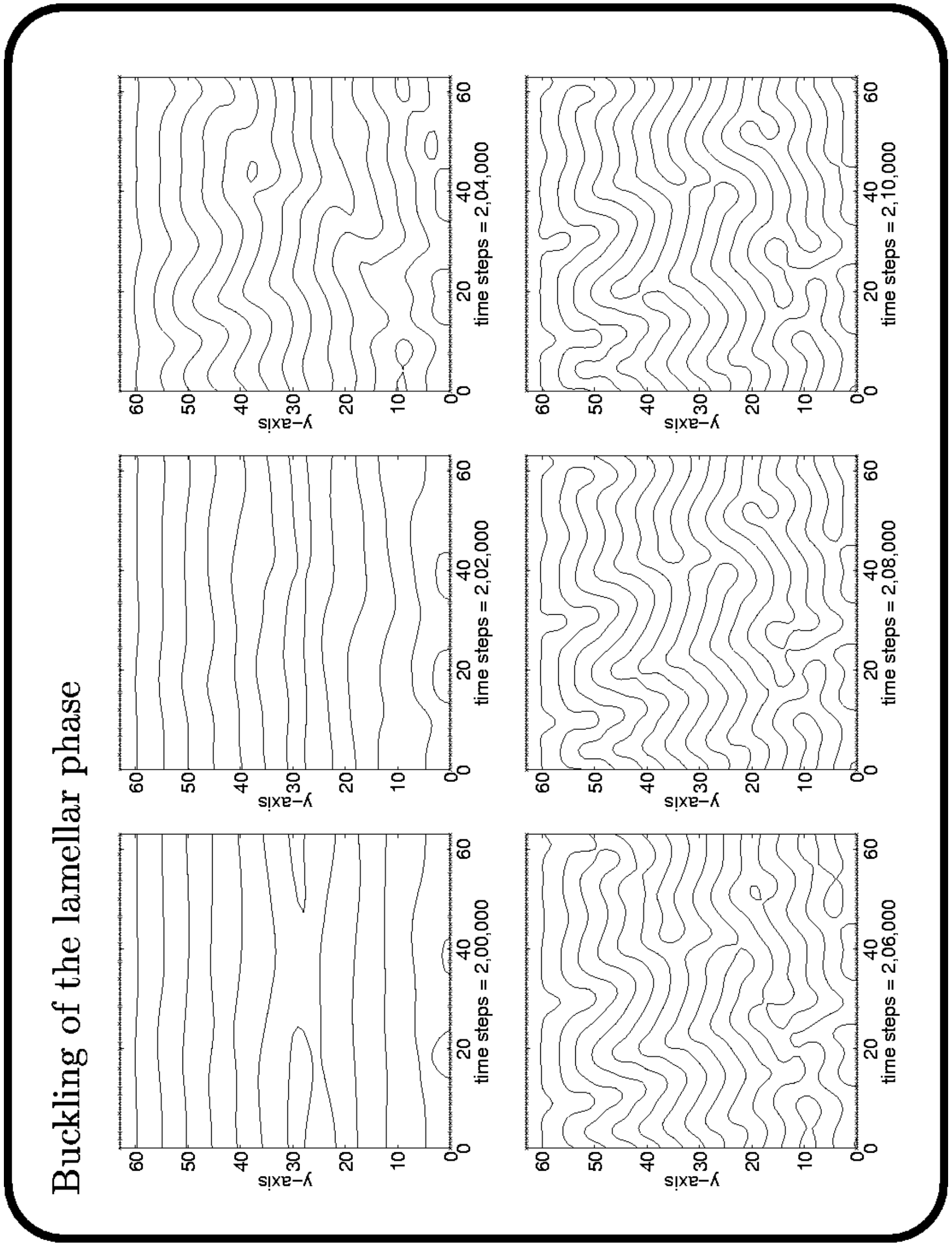
Introduction of defects — Undulation instability of layers



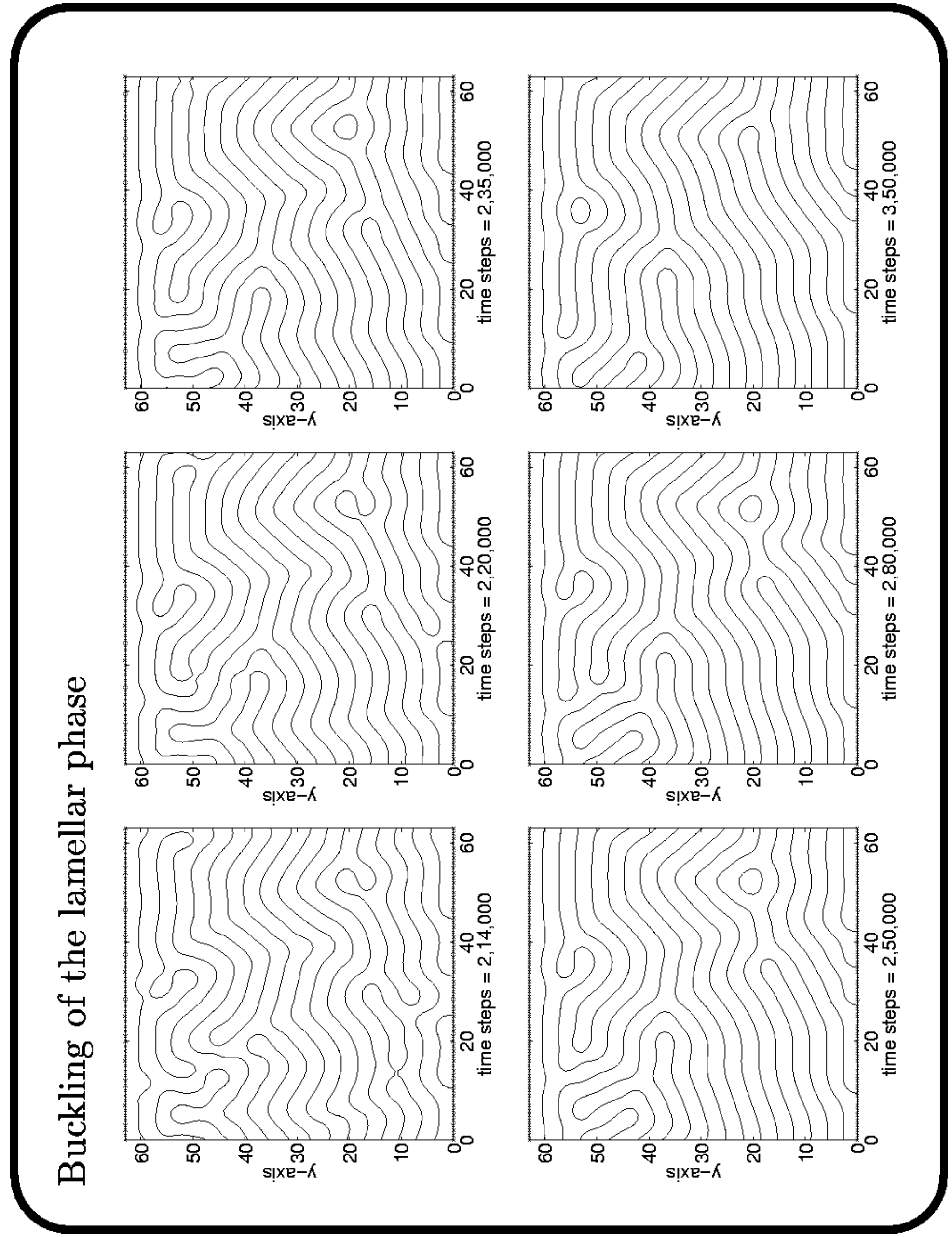
Buckling of layers



- Start with an initial equilibrium configuration with five layers in a box.
- Instanteneously change the free energy functional so that the equilibrium state corresponds to nine layers in the box.



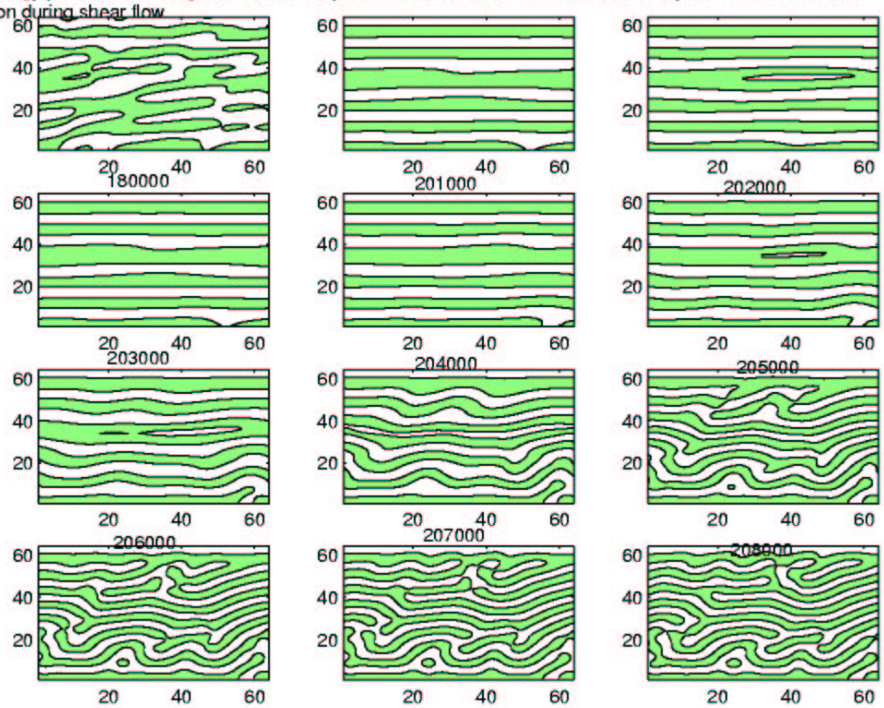
Buckling of the lamellar phase
time steps = 2,00,000
time steps = 2,02,000
time steps = 2,04,000
time steps = 2,06,000
time steps = 2,08,000
time steps = 2,10,000
y−axis



Buckling of the lamellar phase
time steps = 2,14,000
time steps = 2,20,000
time steps = 2,35,000
time steps = 2,50,000
time steps = 2,80,000
time steps = 3,50,000
y−axis

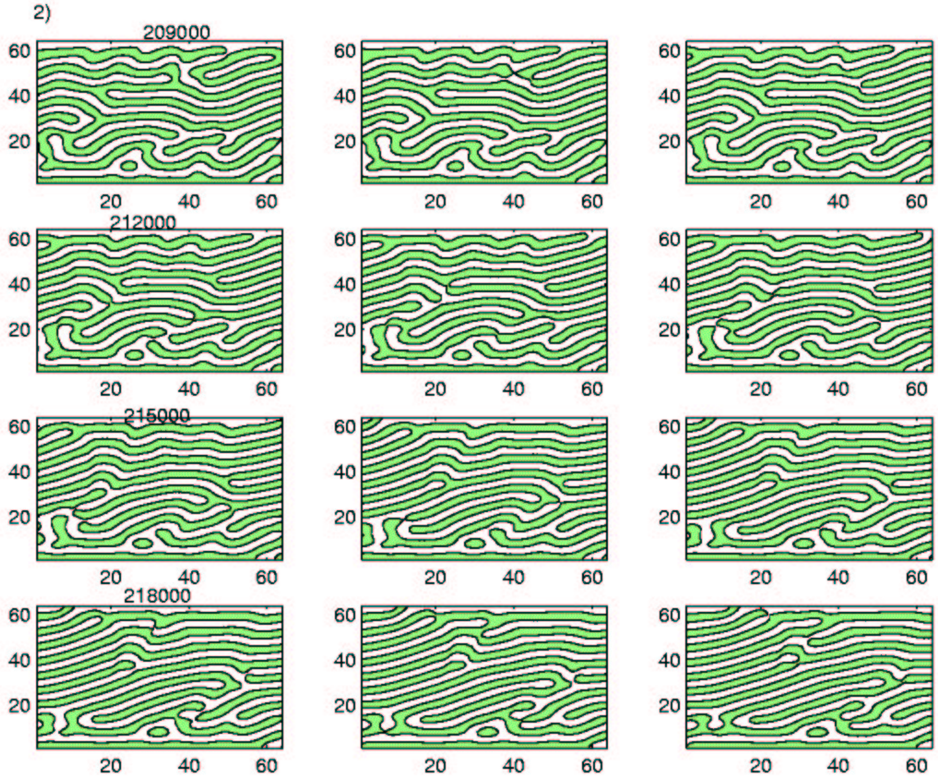
Buckling in presence of shear

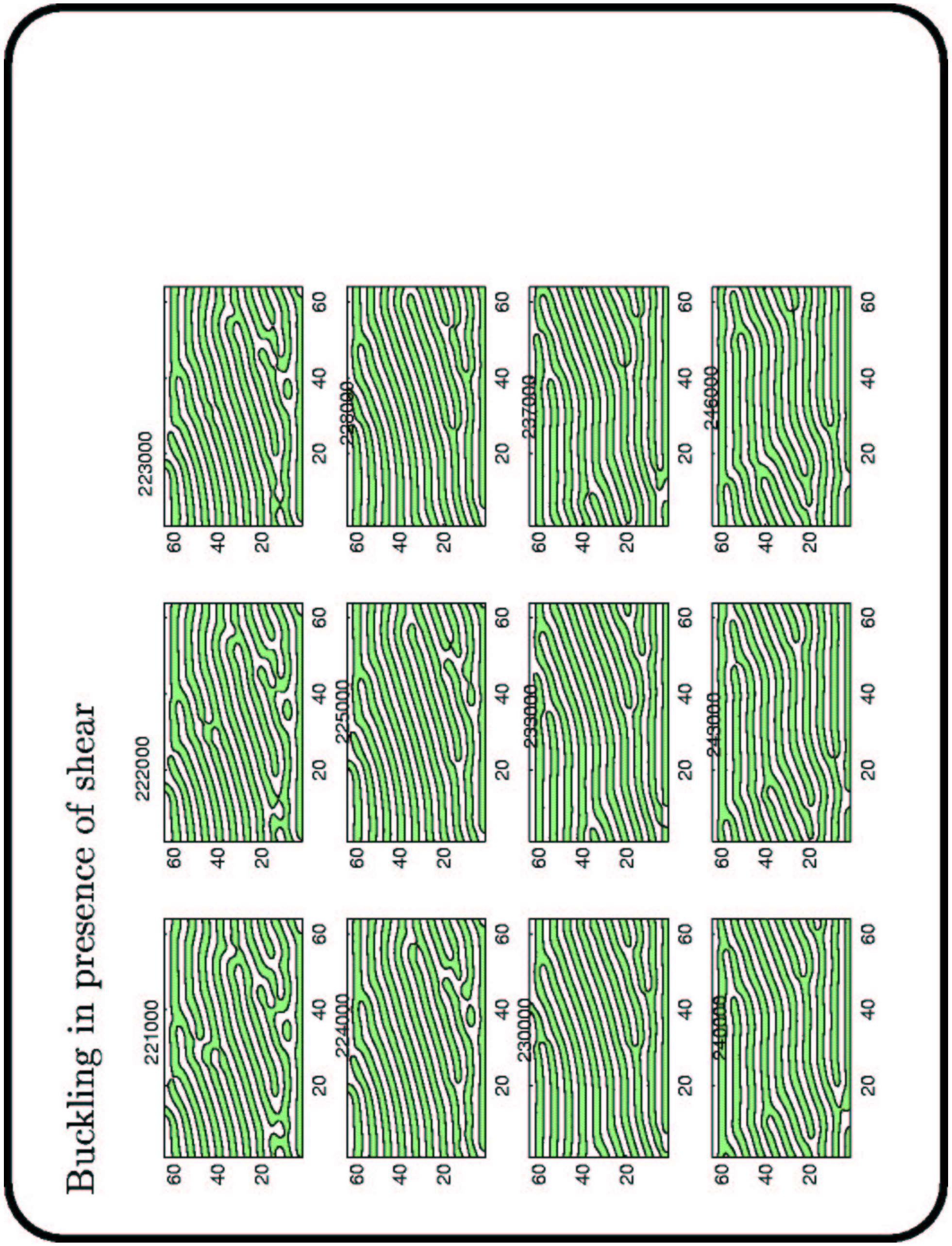
The shearstress is pallied upto two lakh iter for a free energy parameter corresponding to 5 lamallae then free energy paramter is changed to that correspond to nine lamallae and the shear is kept on so as to simulate dialation during shear flow

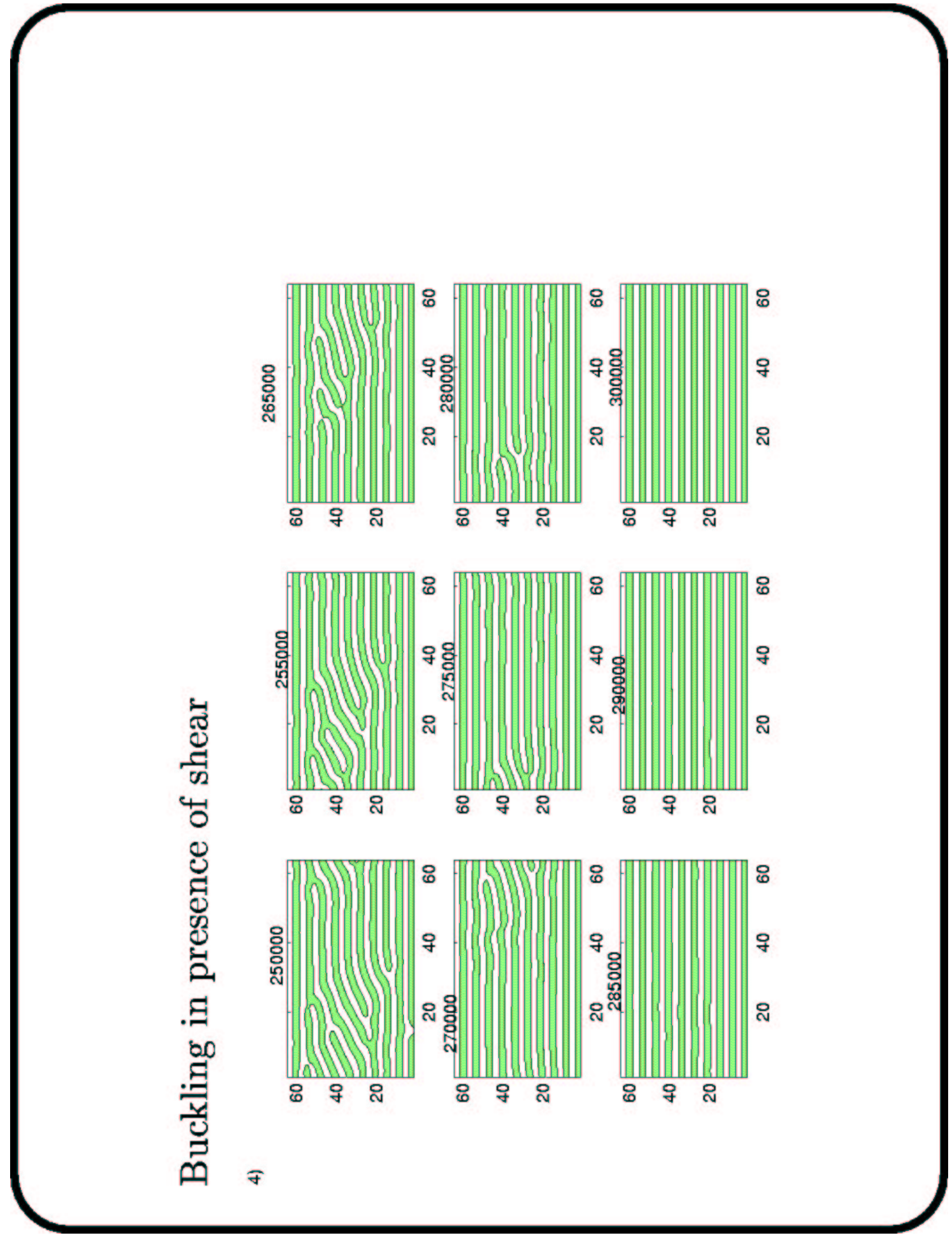


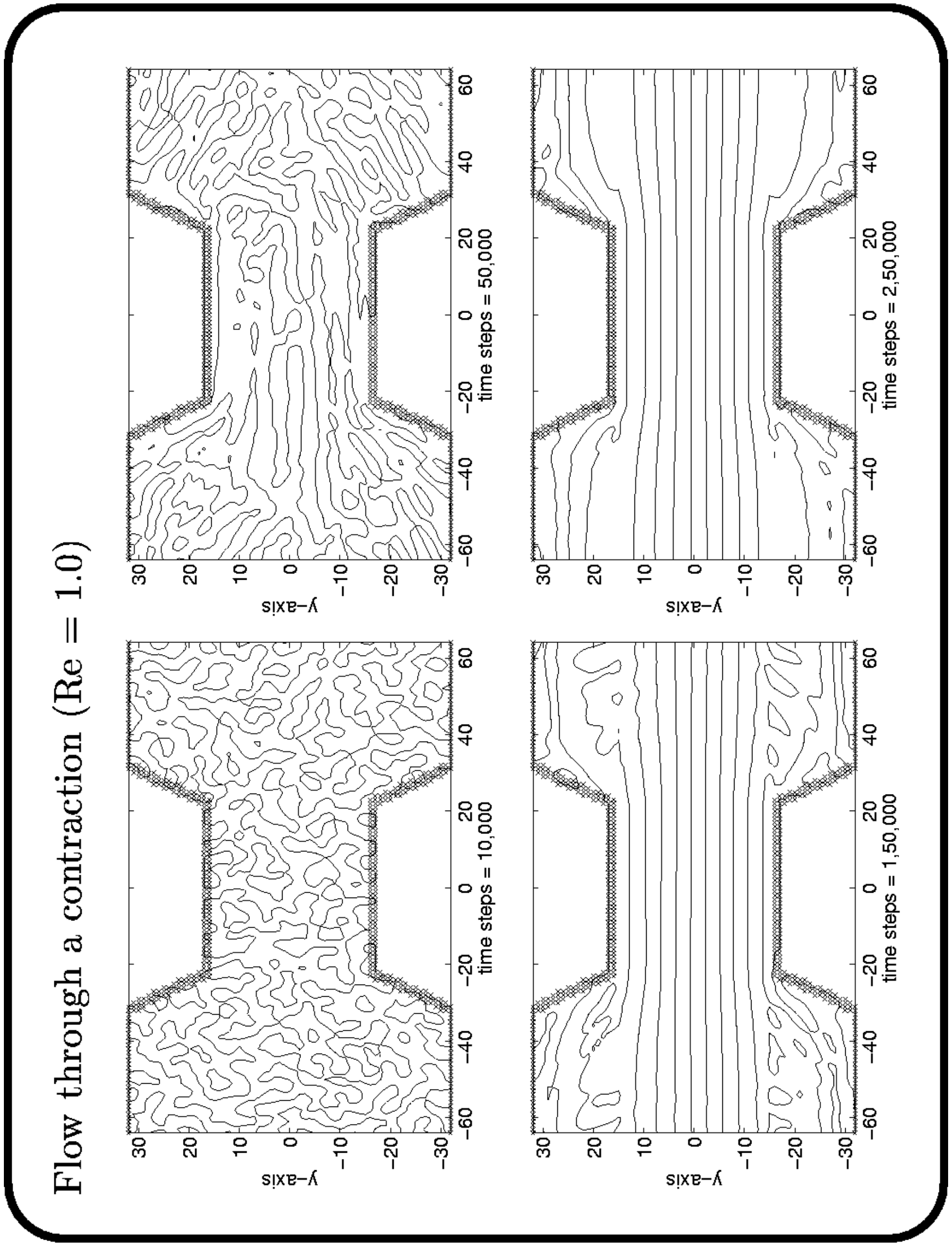
Buckling in presence of shear

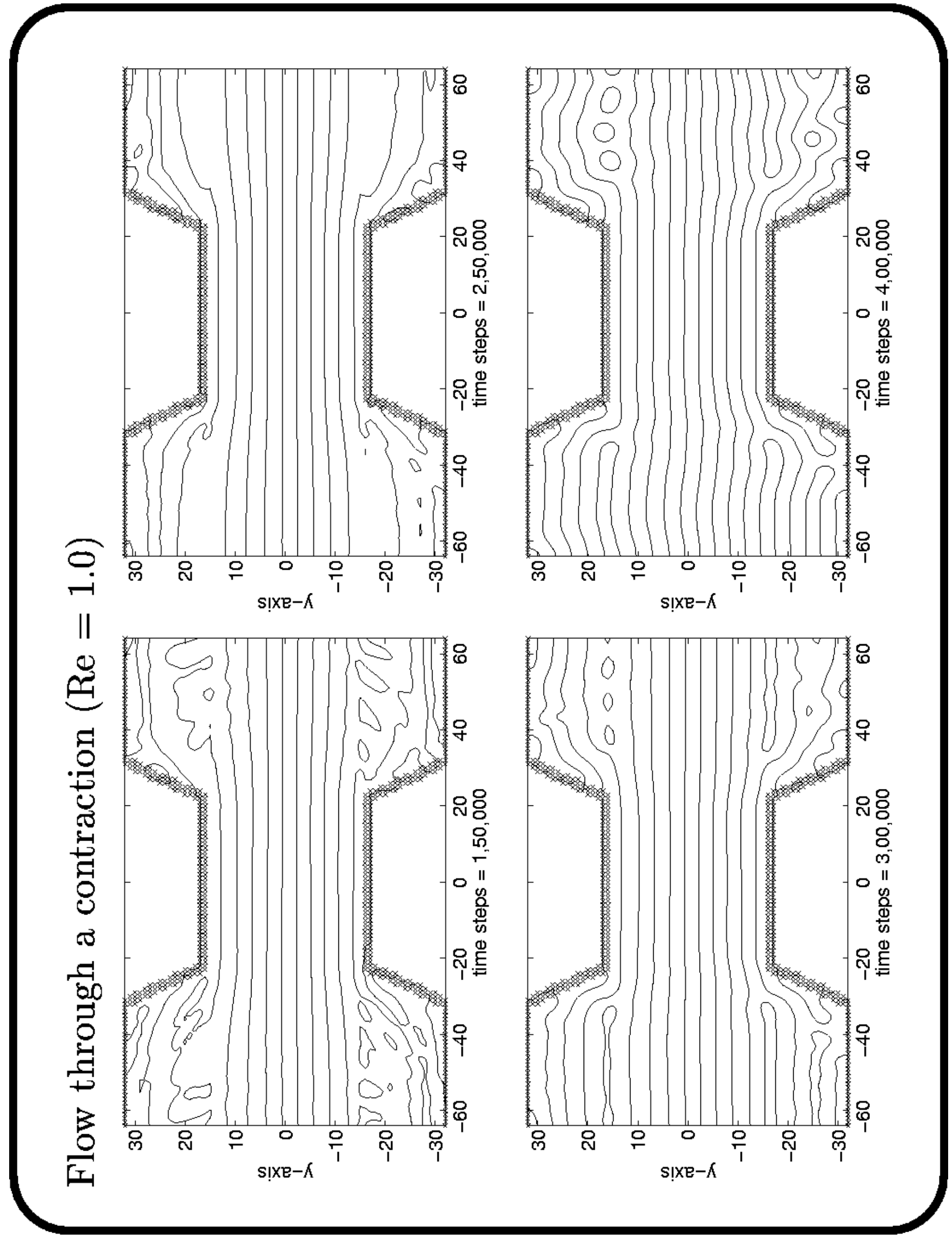
2)




Buckling in presence of shear
221000
222000
223000
224000
225000
230000
237000
243000

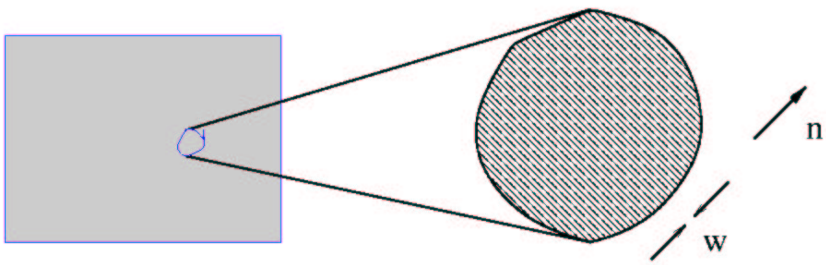

Buckling in presence of shear
4)
250000
255000
265000
270000
275000
280000
285000
290000
300000


Flow through a contraction (Re = 1.0)
time steps = 10,000
time steps = 50,000
time steps = 1,50,000
time steps = 2,50,000
y−axis


Flow through a contraction (Re = 1.0)
time steps = 1,50,000
time steps = 2,50,000
time steps = 3,00,000
time steps = 4,00,000
y−axis

Continuum macroscopic model

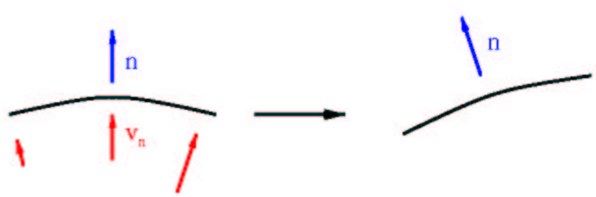
Variables



- Fluid velocity $\mathbf{u}(\mathbf{x})$
- Local unit normal direction $\mathbf{n}(\mathbf{x})$
- Local layer spacing $w(\mathbf{x})$
- Surfactant concentration along layers c
- Velocity of surfactants $\mathbf{v}(\mathbf{x})$ with components v_n and $\mathbf{v}_t$ along normal and tangential directions.

Evolution equation for $\mathbf{n}$, $\mathbf{w}$ and c

$$\frac{D\mathbf{n}}{Dt} = \nabla_s v_n$$

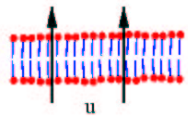


$$\frac{Dw}{Dt} = \mathbf{n}.\nabla v_n$$

$$\frac{Dc}{Dt} + \nabla_s(.\mathbf{v}_t c) = 0$$

Stress balance for fluid phase (normal direction)

$$-\mathbf{n}.\nabla p + \chi(u_n - v_n) = 0$$

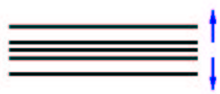


Stress balance for fluid phase (tangential direction)

$$(\mathbf{I} - \mathbf{nn}).(-\nabla p + \eta \nabla^2 \mathbf{u} + \chi_t(\mathbf{u} - \mathbf{v})) = 0$$

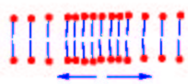
Stress balance for surfactant (normal direction)

$$B\nabla_s.\mathbf{n} + K\kappa - \chi(u_n - v_n) = 0$$



Stress balance for surfactant (tangential direction)

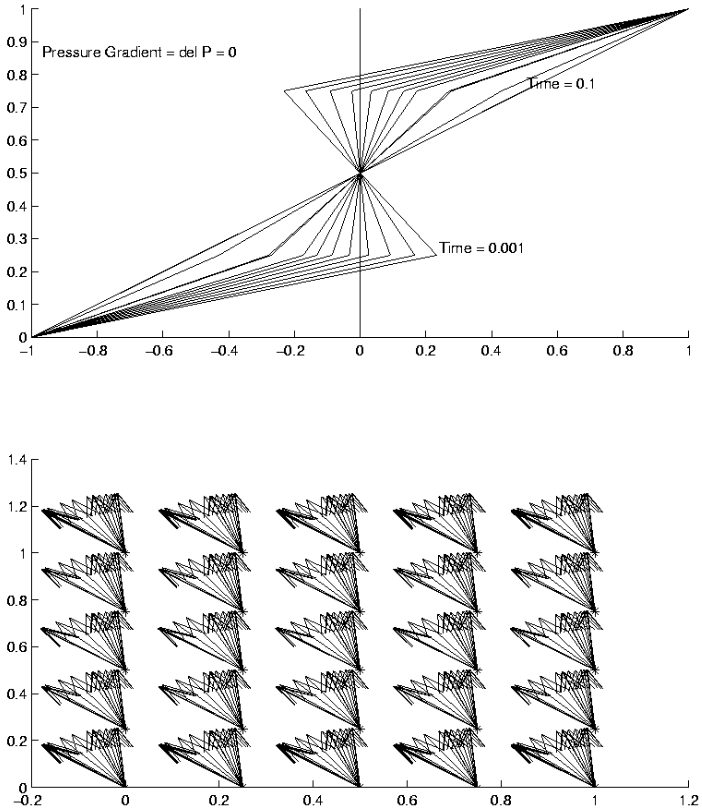
$$-\nabla_s \Pi + \chi_t(\mathbf{u}_t - \mathbf{v}_t) = 0$$



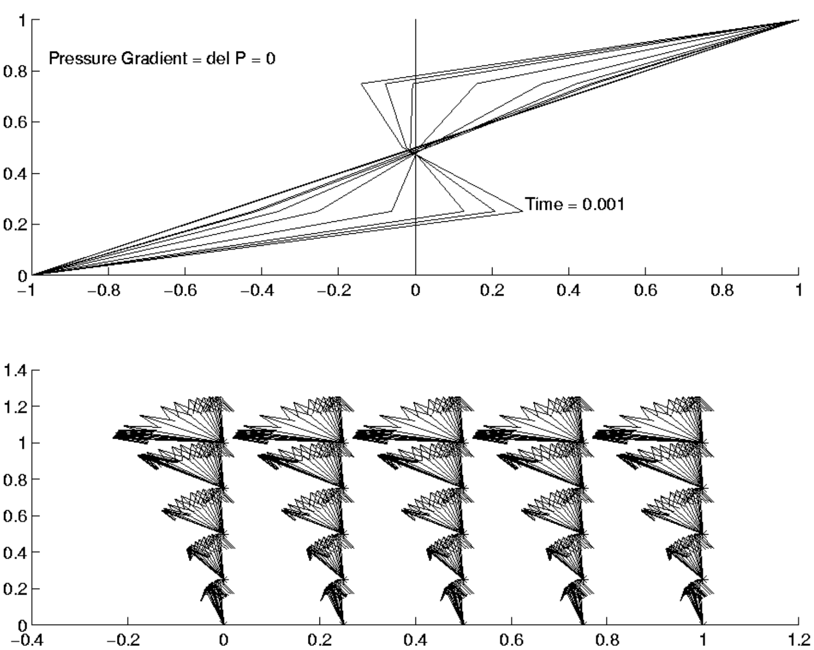
Continuum Macroscopic model

- Given initial configurations for w, $\mathbf{n}$ and c, $\mathbf{v}$ and $\mathbf{u}$, equations can be solved for time evolution of these parameters.
- Equations simplify in the case c is a constant, and $\mathbf{v}_t = \mathbf{u}_t$.
- Predicts simple effects observed, such as alignment of layers under shear.
- Particles can be incorporated using boundary conditions at the surface for unit normal and concentration fields.
- Necessary to incorporate defects within this description!

Shear alignment of lamellar phase



Shear alignment of lamellar phase



Conclusions

- Formulation of Lattice Boltzmann simulations for determining dynamical properties.
- Predicts all qualitative effects observed in lamellar phase rheology in two dimensions.
- Larger 3D computation carried out using parallel computer.
- Coarse grained macroscopic model for the lamellar phase. Microscopic parameters such as local unit normal and layer spacing incorporated in the model.
- Macroscopic model correctly predicts effects such as shear alignment. Work in progress to incorporate defects in this model.