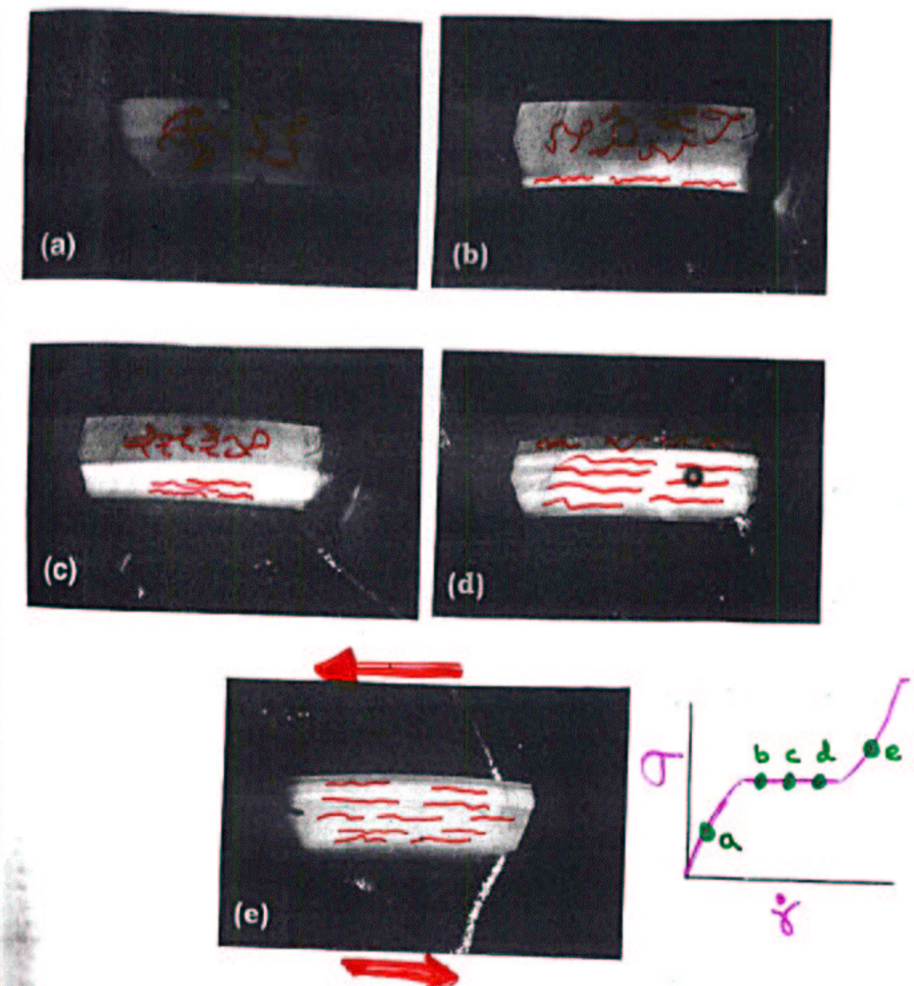
PHENOMENOLOGY OF (Simple!) Shear-Banding

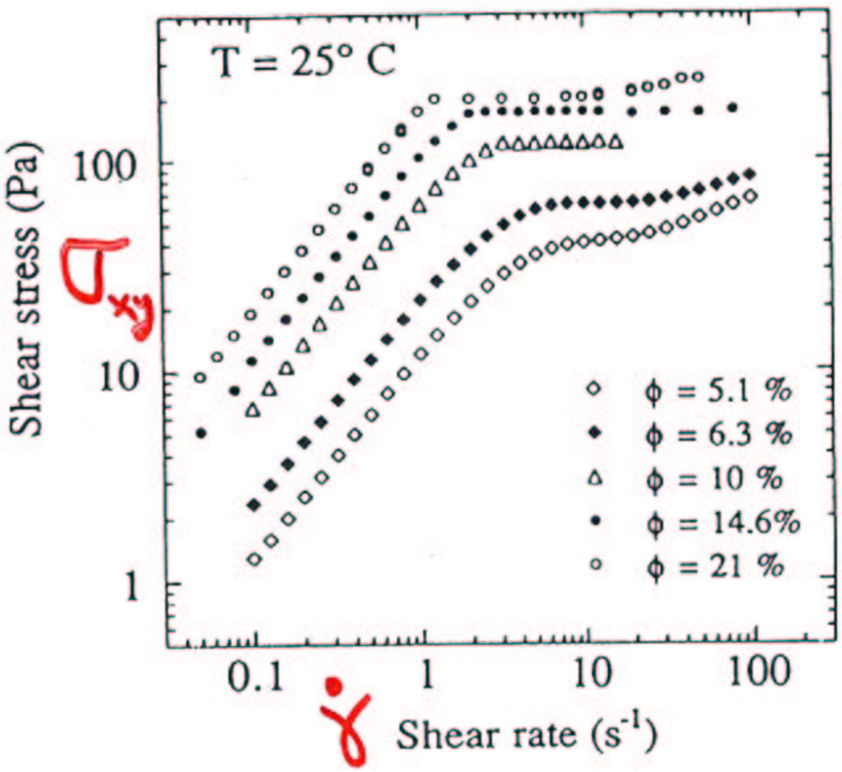
- coexistence conditions & geometries
- 'phase diagram' $\rightleftharpoons$ flow curve
  "tutorial" – Are flow curves useful?
- examples – calculation / exp'ts / vorticity banding
- complications
- kinetics ?
- Summary … where next ?



Cappelaere et al, PhysRev E56 (1997) 1869
Worms: CTAB-D_2O, 18%

FIG. 5. Photographs of the 1.5-mm gap of a Couette shearing cell containing a CTAB-D_2O solution at $\phi = 18\%$. The five photographs correspond to the different domains (I–III) of the curves flow (see Fig. 4): (a) domain I, (b)–(d) domain II, and (e) domain III.

Berret, Porte, Roux
J. de Physique 4 (1994) 1261

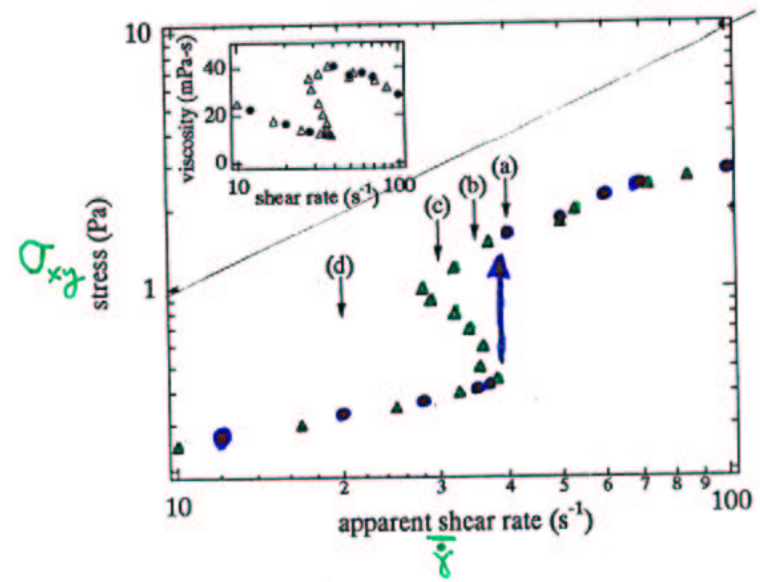


CpCl/NaSal

Worms:

$$\sigma = \eta \dot{\gamma}$$

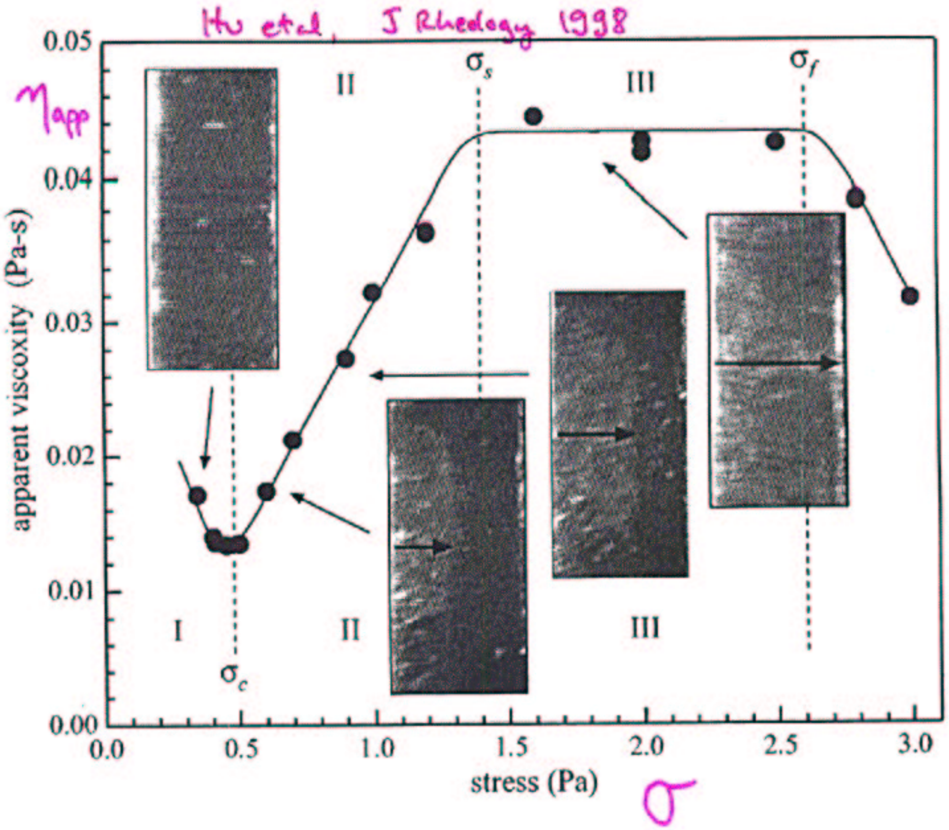
(Boltenhagen, Hu, Matthys & Pine)



▲ controlled stress

● controlled strain rate

TTAA / NaSal + H_2O
worm-like micelles



VOLUME 80, NUMBER 12 PHYSICAL REVIEW LETTERS 23 MARCH 1998

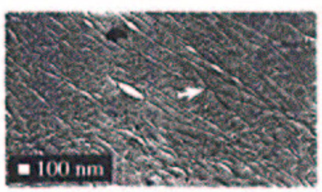
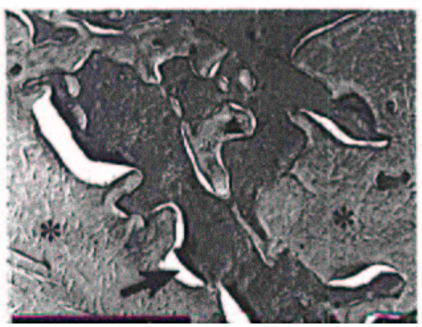


FIG. 2. Sheared 10 mM TTAA/NaSal wormlike micelles (arrow) aligned from the top left to the bottom right.

Keller, etal.



Spherical micelle solutions

PHYSICAL REVIEW E VOLUME 61, NUMBER 6 JUNE 2000

Nonhomogeneous textures and banded flow in a soft cubic phase under shear

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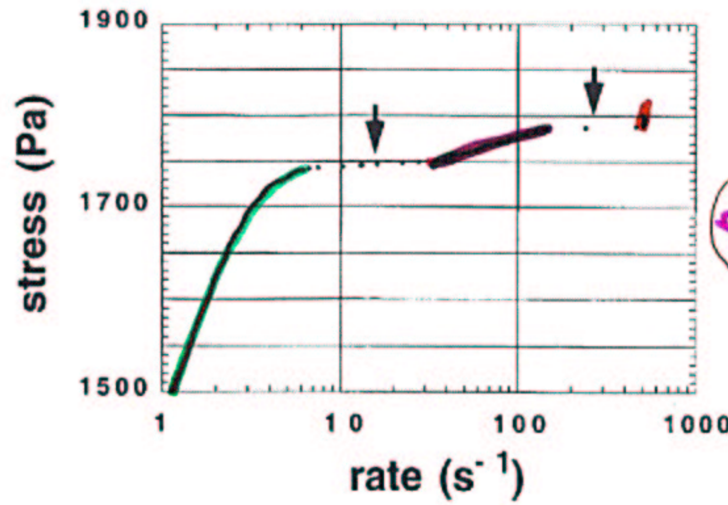
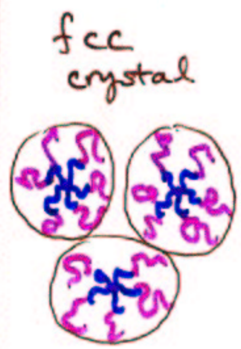
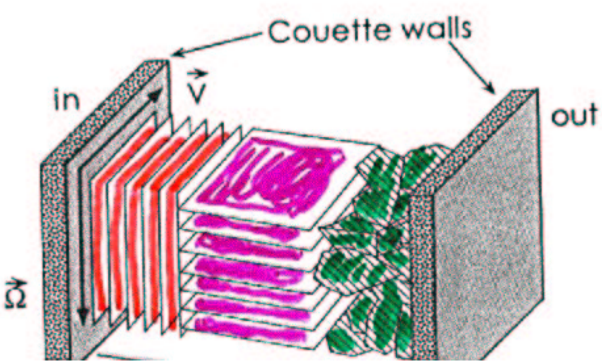
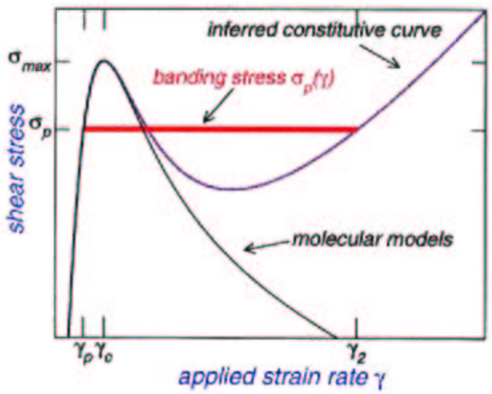
(Received 30 August 1999)



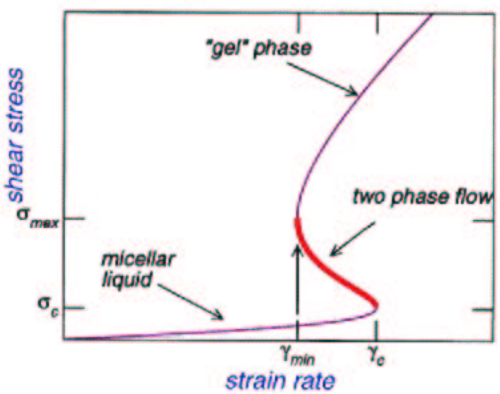




"Typical" Flow Curves

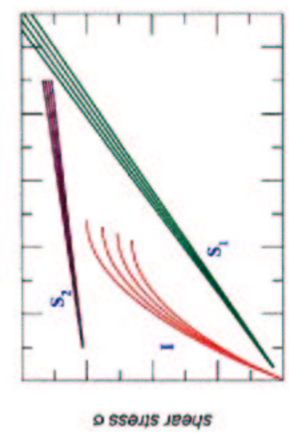


Shear thinning systems (wormlike micelles, [Spenley, *et al.* 1993]).



Shear-thickening systems (wormlike micelles [Boltenhagen *et al.* 1997; Goveas and Pine 1999)].

Phenomenology



- I Newtonian:
- S_1 flow-induced phase:
- S_2 flow-induced "gel":

A hypothetical fluid:

- Identify dynamical variables (flow, composition, and structural information).
- "Phases" =steady state solutions to equations of motion:

$$\partial_t \phi = \nabla \cdot M \nabla \frac{\delta F}{\delta \phi} = 0 \quad \text{(composition)}$$

$$\rho \partial_t \mathbf{v} = \nabla \cdot \boldsymbol{\sigma} = 0 \quad \text{(flow)}$$

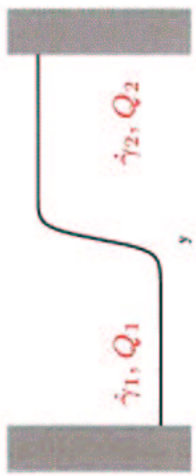
$$\partial_t \mathbf{Q} = \ldots = 0 \quad \text{(microstructure)}$$

- Calculate steady state flow curves as a function of concentration.

Coexistence Conditions

1. Stationary states $\partial_t \mathbf{Q} = 0.$
2. Stress Balance $\nabla\cdot\boldsymbol{\sigma} = 0 \Rightarrow \sigma_{xy} = constant$
3. No concentration flux: $\nabla\cdot\mathbf{J} = 0 \Rightarrow \mu = \dfrac{\delta F}{\delta\phi} = constant$ ("chemical potential")

Phase coexistence implies a stationary interface:



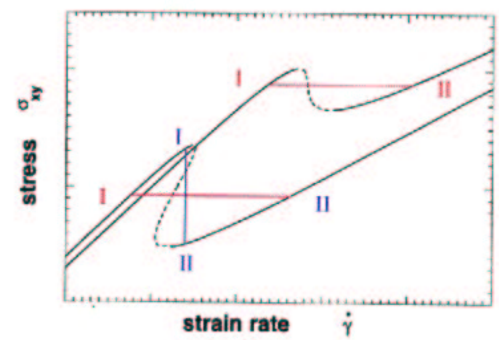
Analog of minimizing free energy, or common tangent construction.

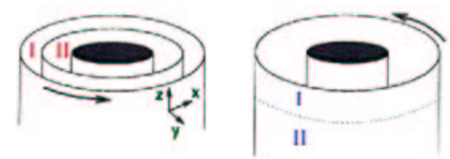
[Kramer 1981; Pomeau 1986, PDO and PMG 1992; Spenley *et al.* 1996; PDO & CYDL 1997; CYDL, PDO, and RCB 2000].

Shear Banding in Complex Fluids 1

Coexistence Geometries

Unlike equilibrium, the definition of field and density variables depends on the geometry of phase coexistence.



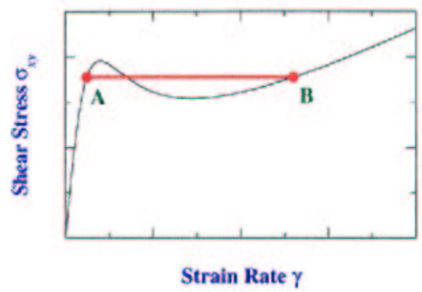


Phase separate according to $\bar\phi = \alpha\,\phi_I + (1-\alpha)\,\phi_S$.

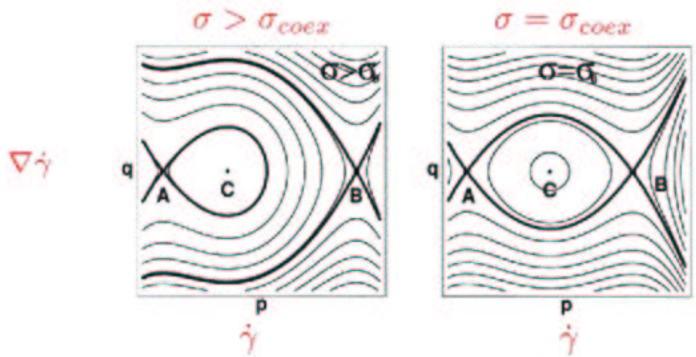
Common Stress	Common Strain Rate
Annular layering	Vorticity Layering
$\bar{\dot\gamma} = \alpha\,\dot\gamma_I + (1-\alpha)\,\dot\gamma_{II}$	$\bar\sigma = \alpha\,\sigma_I + (1-\alpha)\,\sigma_{II}$
σ is a "field variable"	$\dot\gamma$ is a "field variable"
$\dot\gamma$ is a "density variable"	σ is a "density variable"
Seen in wormlike micelles and lamellar systems	Seen in surfactant onion systems

Shear Banding in Complex Fluids 8

Stress Selection

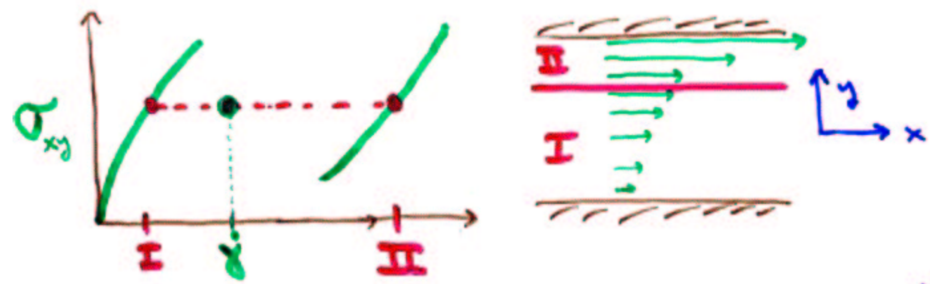


$$\sigma = \sigma_{hom}(\dot\gamma) - D\nabla^2\dot\gamma$$



- Selection condition is heteroclinic orbit condition.
- Not equal areas construction.
- Generally non-integrable dynamics.
- Unique (isolated) σ_{coex} for all differential models [CYDL/PDO/RCB *PRL* 84 (2000) 642.].
- Analog of Gibbs Phase Rule.
- Gradient terms $\nabla^2\dot\gamma$ can change selected stress σ_{coex}.

Coexistence Conditions?



$\nabla \cdot \sigma = 0$

Need another condition!!

$$\sigma_{xy}(\dot\gamma_I) = \sigma_{xy}(\dot\gamma_{II}) = \sigma^*$$

$$[\sigma_{zy}]_I^{II} = 0 \checkmark$$

$$[\sigma_{yy}]_I^{II} = 0 \checkmark \quad \text{(pressure)}$$

a) Gradient terms $\sigma^* = \sigma_h(\dot\gamma) - \nabla^2\dot\gamma$

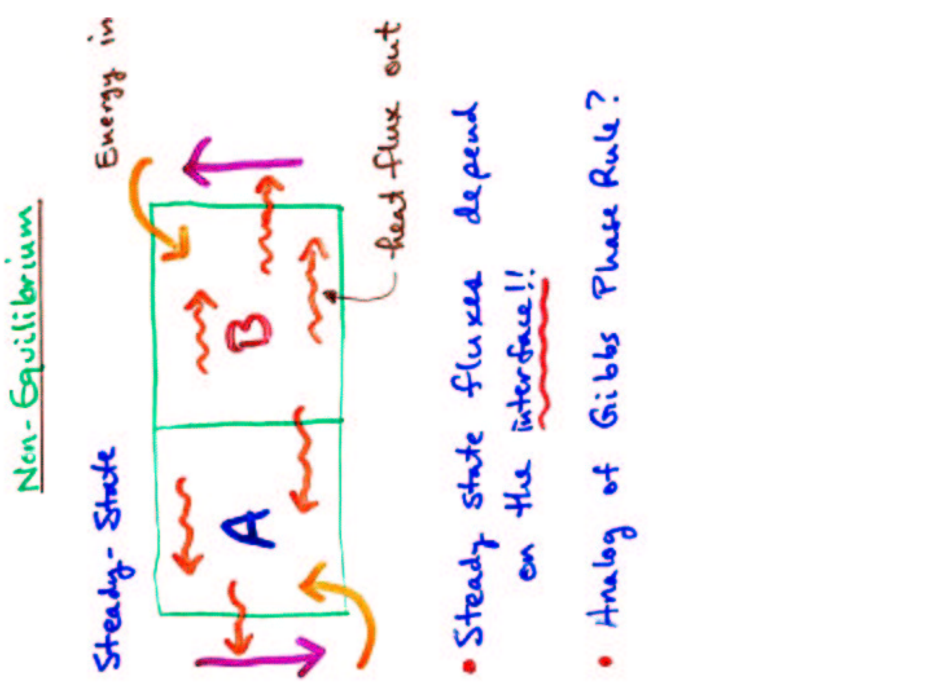
b) Interface Equation of motion

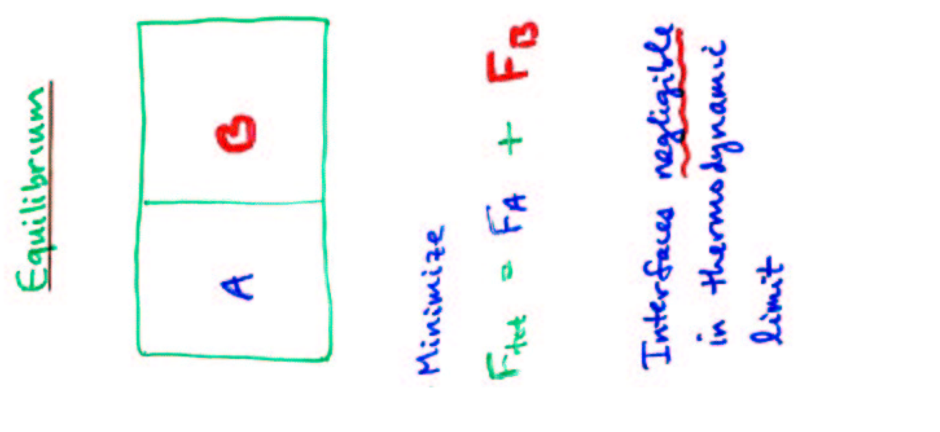
$$\partial_t h = f(h, \dot\gamma, \sigma^*) = 0$$

[A Ajdari, Goveas / Pine]

c) Interfacial Stress

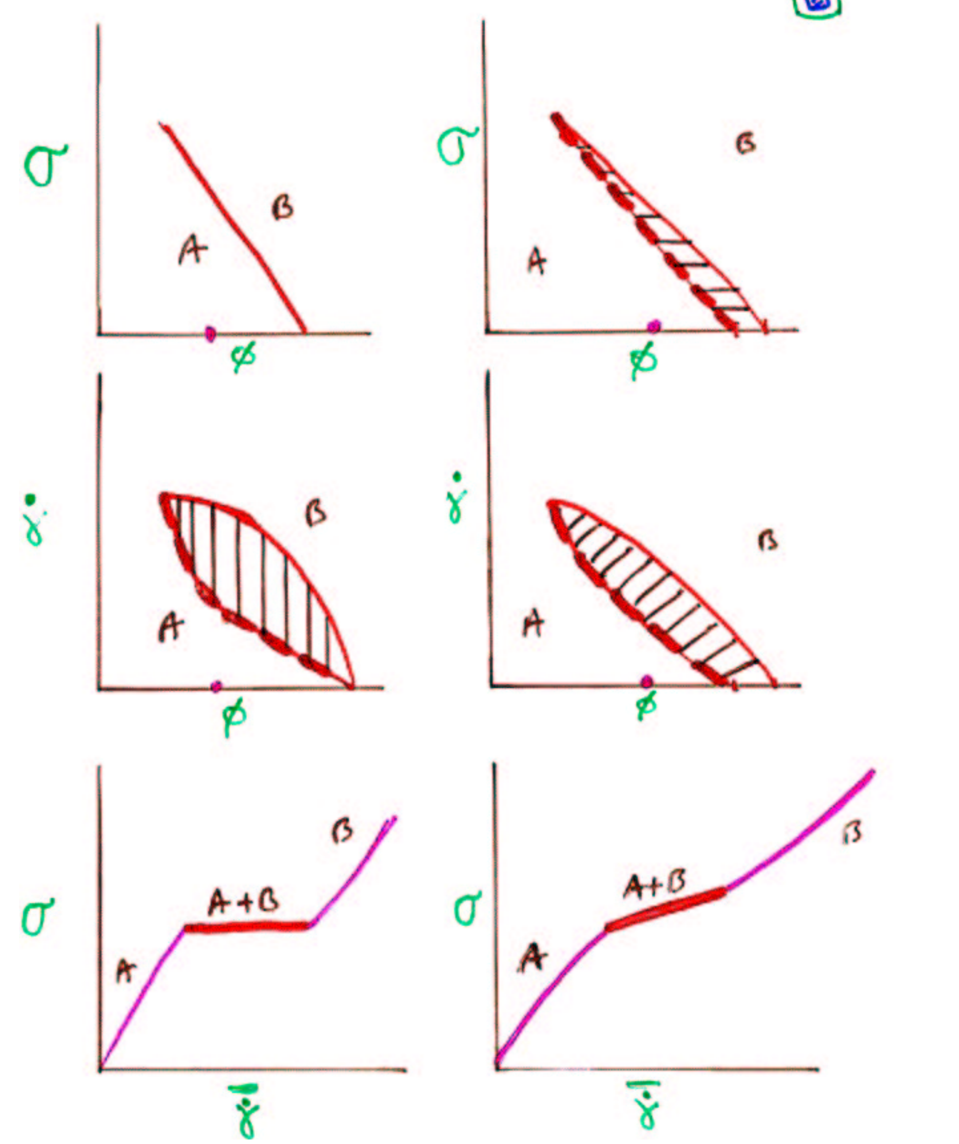
$$\sigma^* = \sigma_h(\dot\gamma) + \delta(y - y_{int})\,\sigma_{int}(\dot\gamma)$$

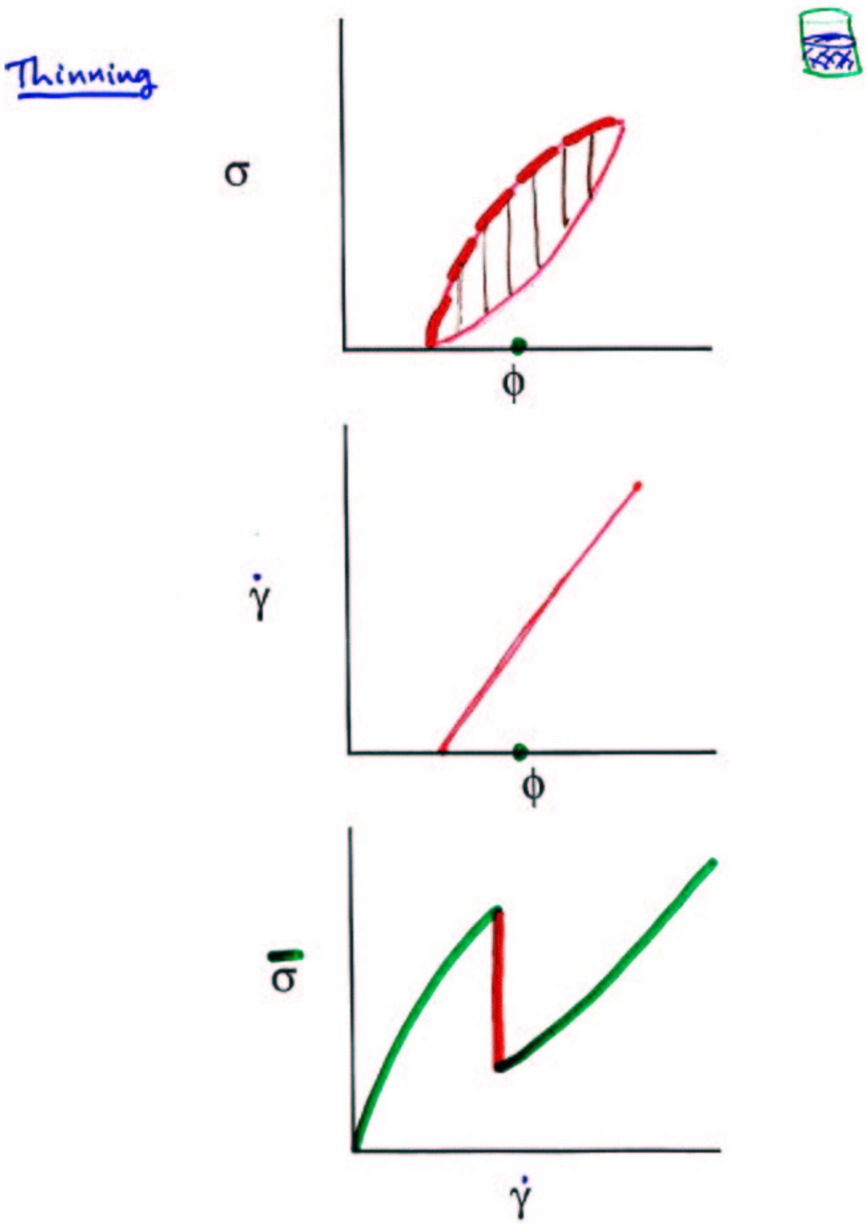


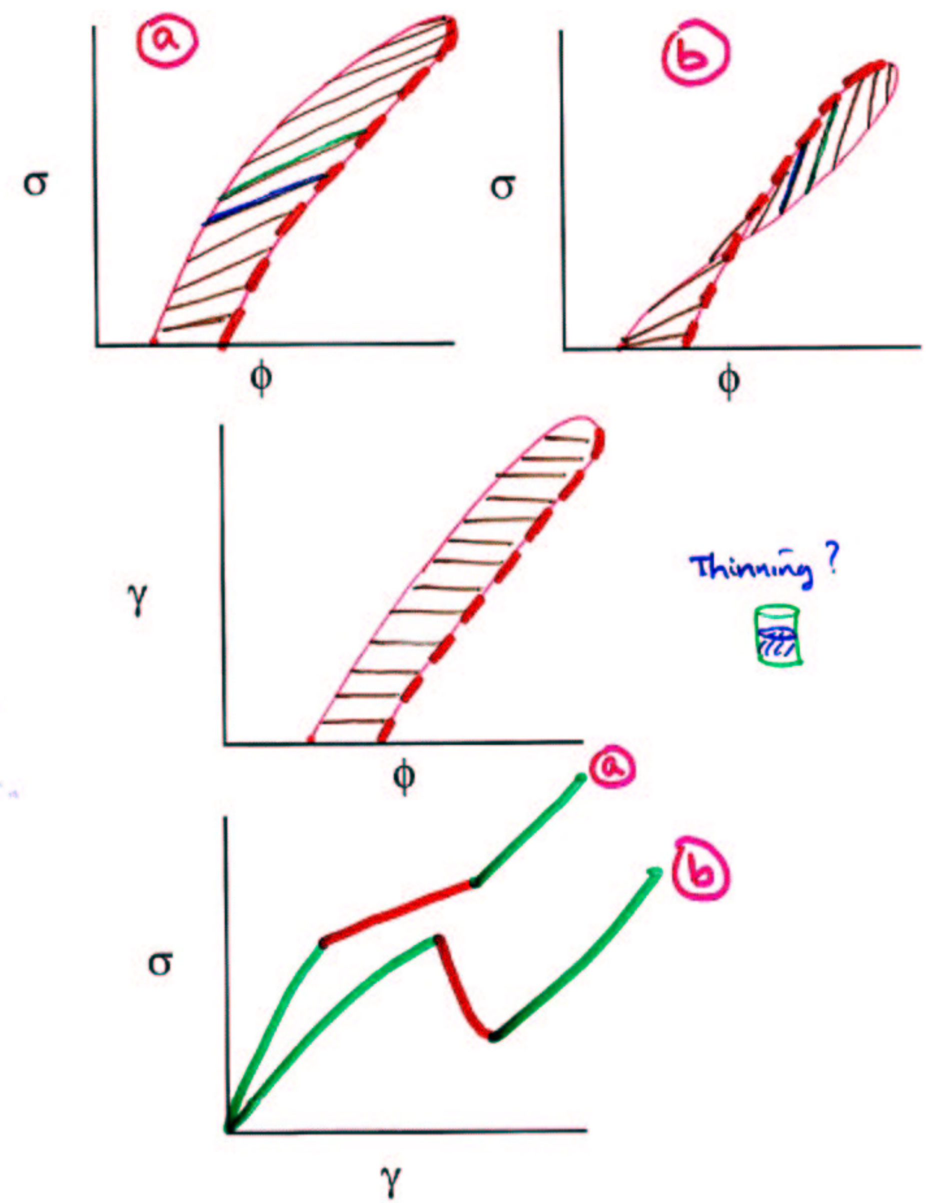


Concentration - Dependence

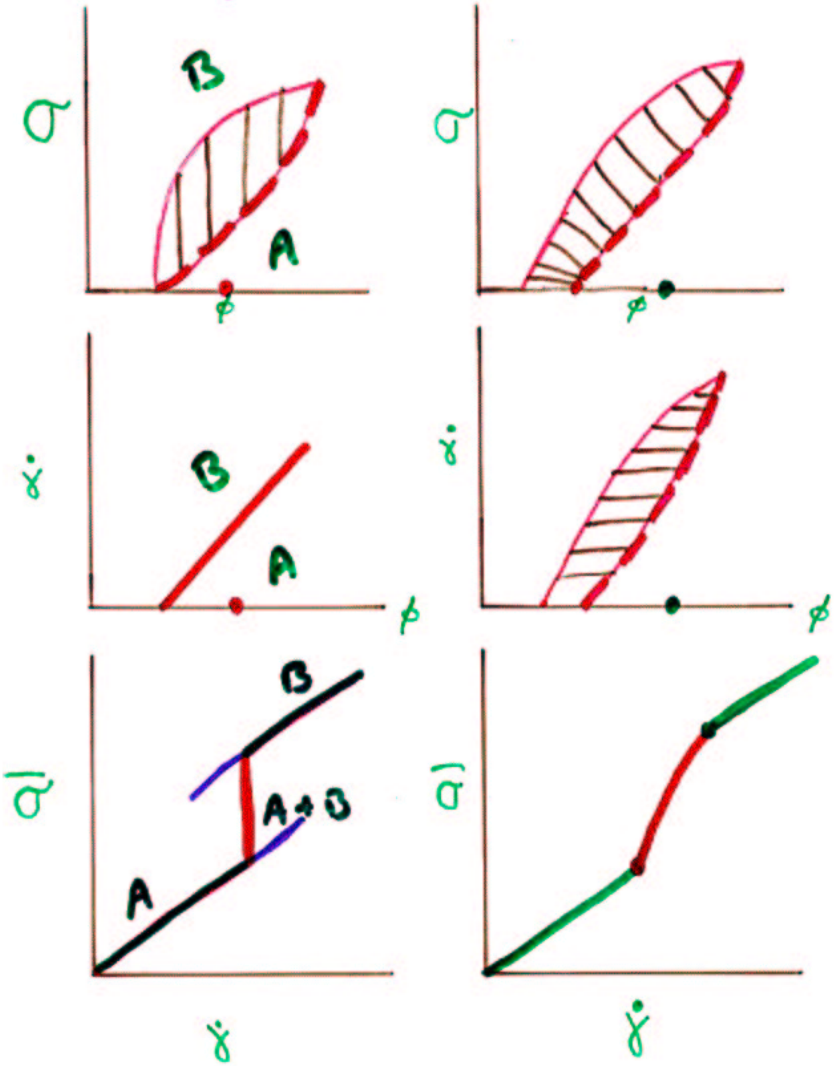
[Schmitt et al 1994; PDol(CYDL]



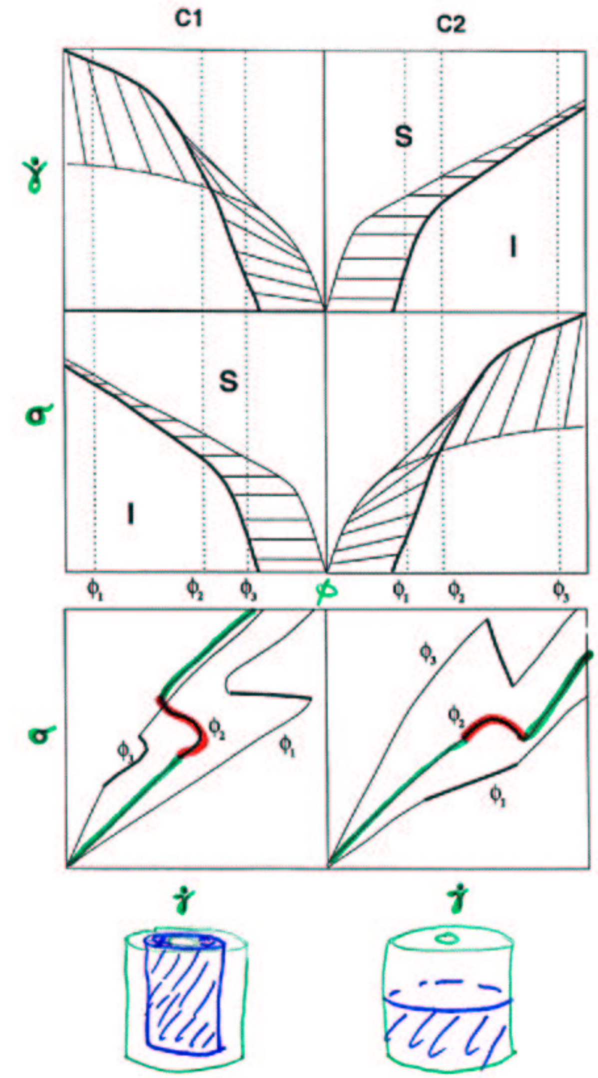

Thinning
σ
φ
γ̇
φ
σ̄
γ̇

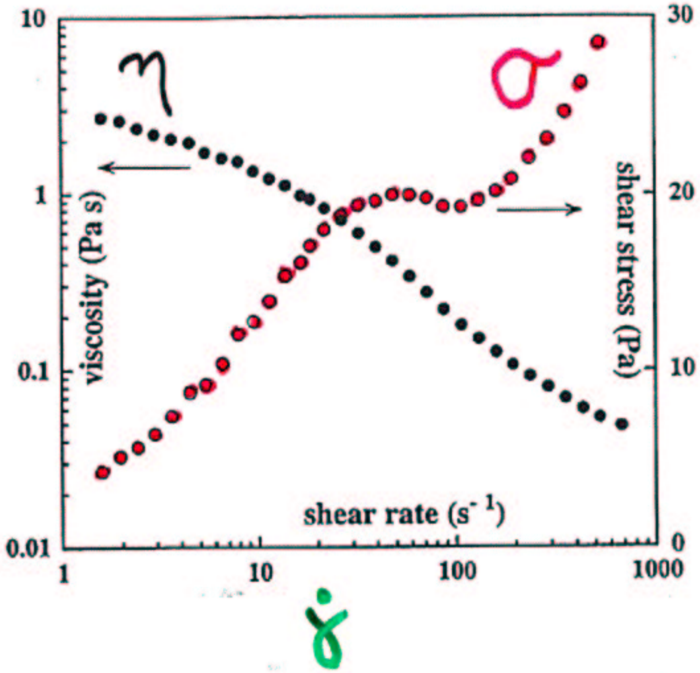

a
b
σ
φ
σ
φ
γ
φ
Thinning ?
a
b
σ
γ

Thickening: common $\dot{\gamma}$



Mix & Match!!

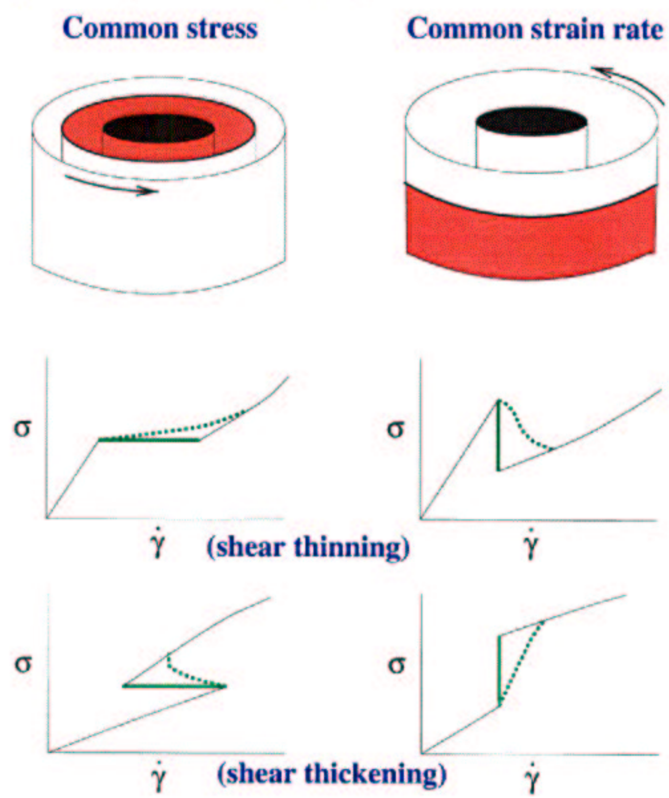




Please plot $\sigma(\dot\gamma)$!!

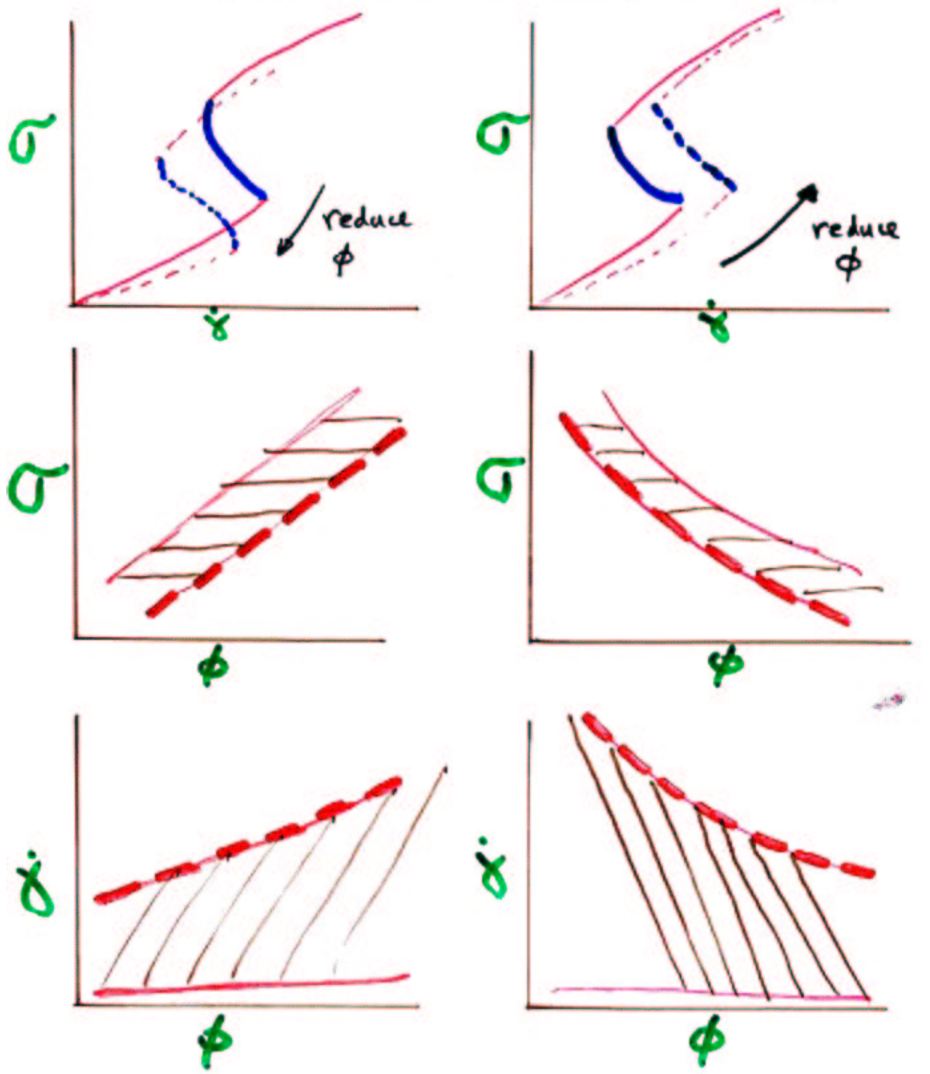
Typical Rheological Signatures

[PDO, *Europhysics Letters* **48** (1999) 339]



worms, liquid crystals	colloids, onions, hexagonal micelles
worms	onions

Pine et al: Thickening Micelles?



VORTICITY BANDING?

I

II

$\dot\gamma_I = \dot\gamma_{II}$

$\nabla \cdot \sigma = 0 \qquad \nabla \parallel \hat{z}$

$[\sigma_{xz}]_I^{II} = 0$ ✓

$[\sigma_{yz}]_I^{II} = 0$ ✓

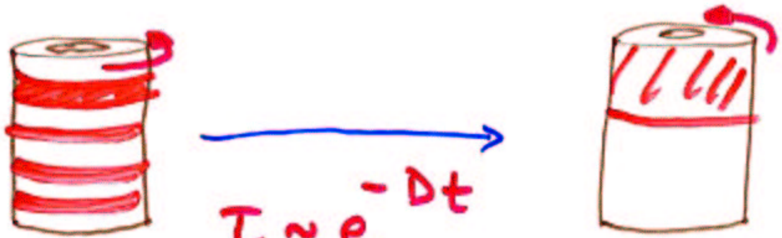
$[\sigma_{zz}]_I^{II} = 0$ pressure

- Need an auxiliary equation / degree of freedom for interface construction
  - concentration ϕ
  - L.C. order Q
  - polymer stress Σ_p
  - ⋮
- Inferred if

- Observed:
  - Lamellar Systems [Roux, Panizza, Bonn...]
  - Colloids [Chen / Zukowski]
  - Hex. Micelles (?) [Ramos et al.]

VORTICITY BANDS

- Expect slow kinetics (in Couette)



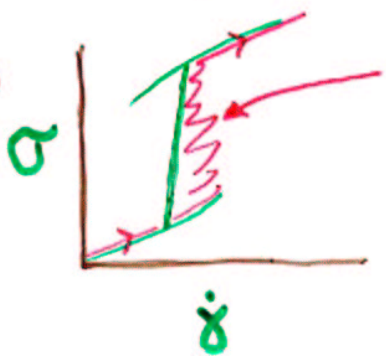
$\tau \sim e^{-Dt}$

D: $\partial_t Q = \ldots\ldots + D\nabla^2 Q$

1D coarsening

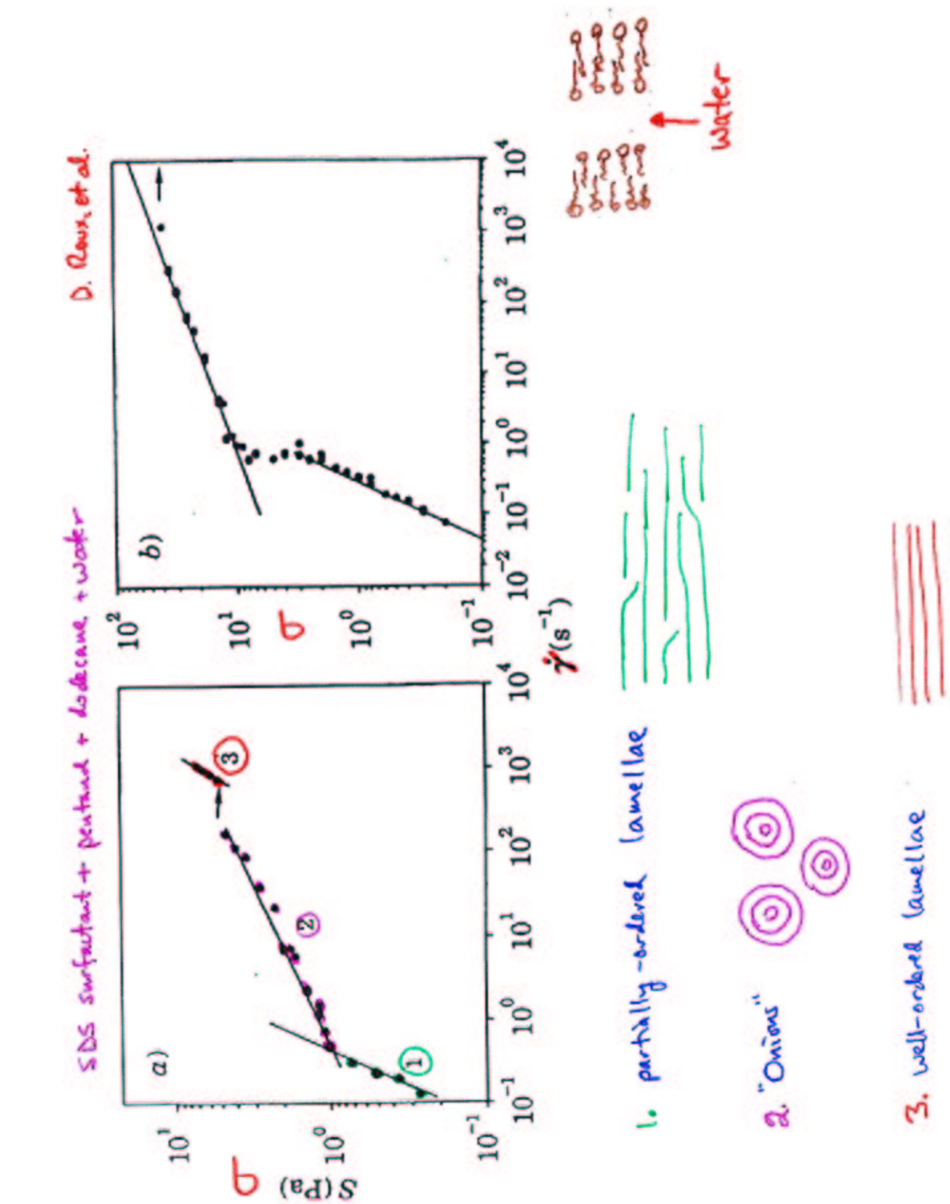
- Curvature of Couette Flow accelerates coarsening of gradient banding

[Radulescu (PDO, JNNFM '00)]

- 

steady states

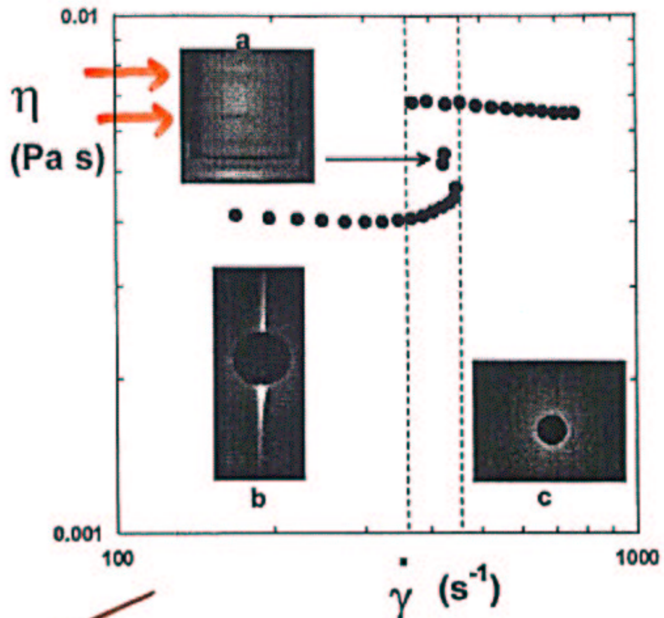
controlled stress sweeps?

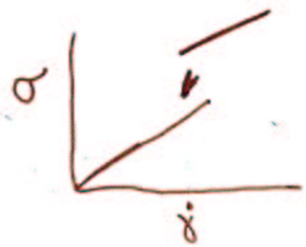


PRE 2001

G. CRISTOBAL, J. ROUCH, P. PANIZZA, AND T. NARAYANAN

SDS/octane/brine

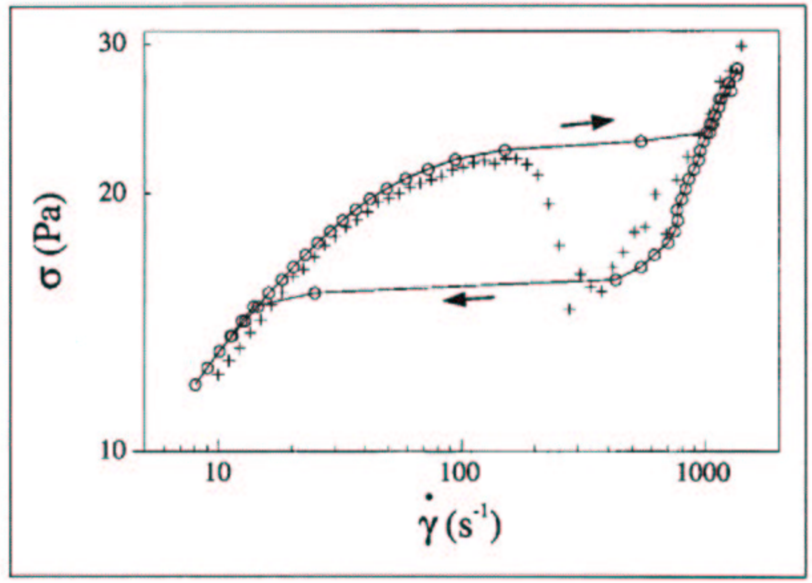




- Steady state not achieved?
- Observe bands under controlled σ or $\dot{\gamma}$.

"true" steady-state flow curve?

Hexagonal Micellar Phases

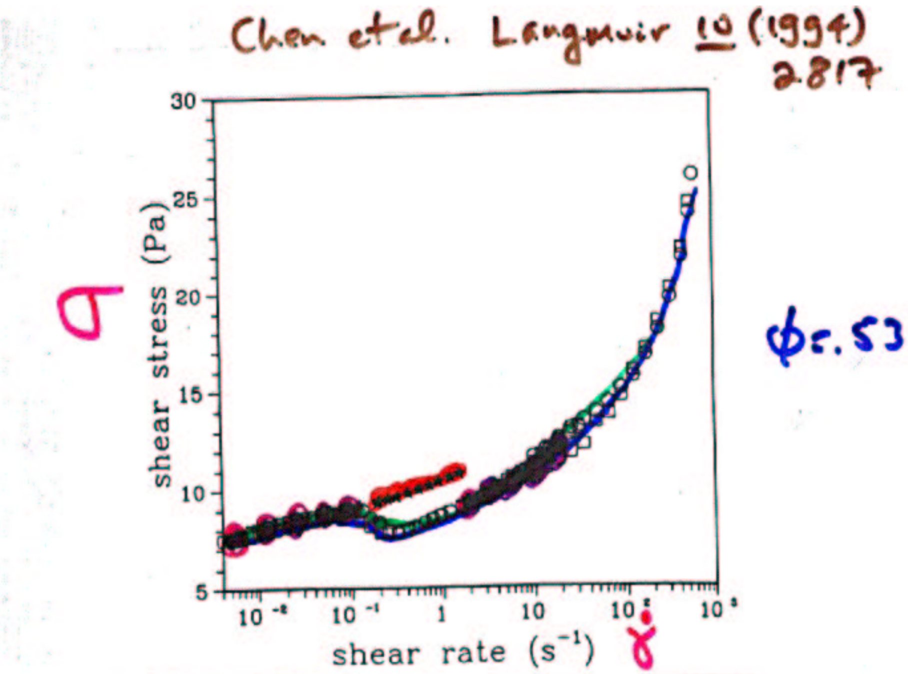


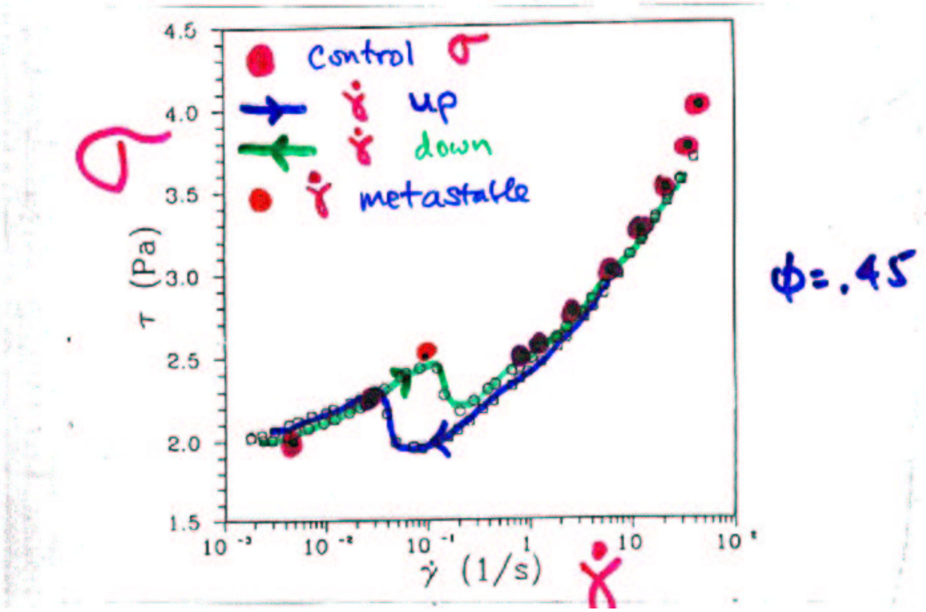
Ramos/Molino/Porte, *Langmuir* **16** (2000) 5846, SDS/pentanol/cyclohexane/brine.

Controlled stress (solid lines) and controlled strain rate experiments.

Shear-melting of hexagonal phase.

Band orientation not determined [flow curves suggest common strain rate, or vorticity banding].





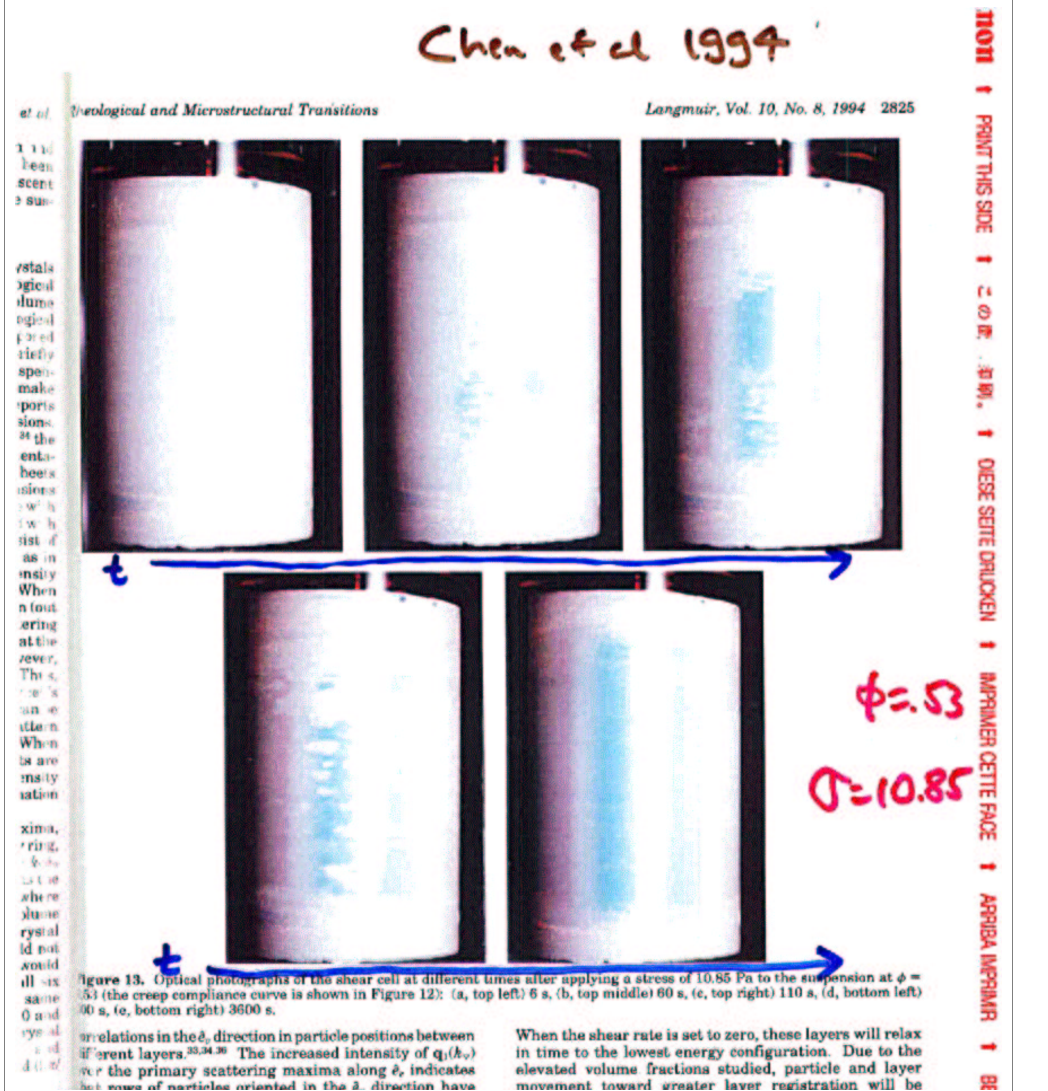
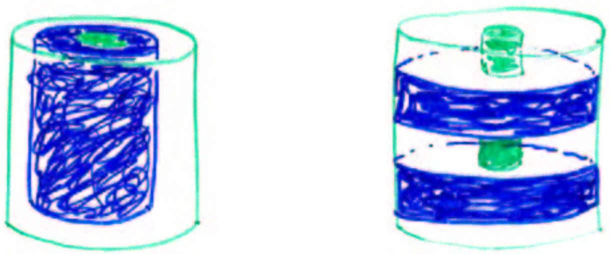


Figure 13. Optical photographs of the shear cell at different times after applying a stress of 10.85 Pa to the suspension at ϕ = .53 (the creep compliance curve is shown in Figure 12): (a, top left) 6 s, (b, top middle) 60 s, (c, top right) 110 s, (d, bottom left) 300 s, (e, bottom right) 3600 s.

Which coexistence is "preferred"?

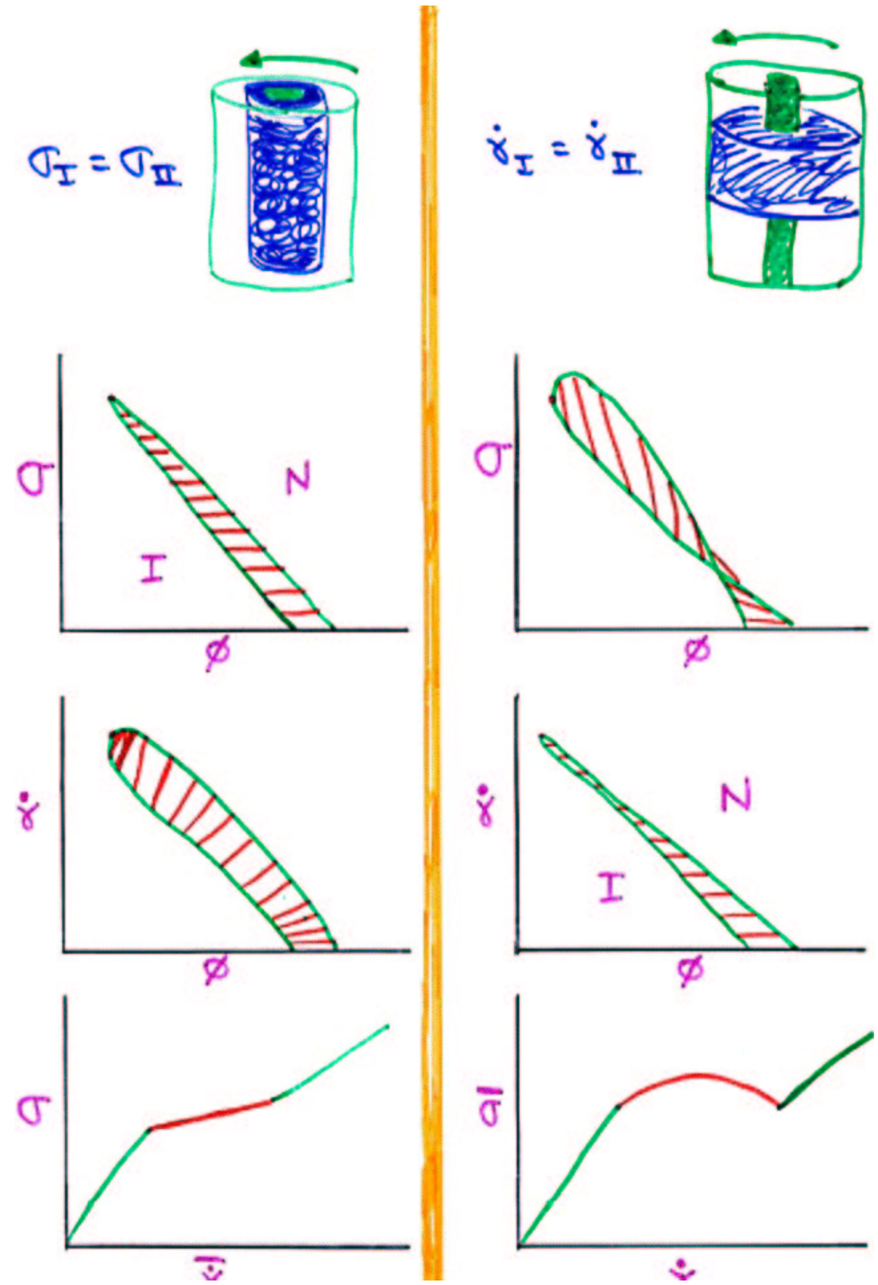


common σ common $\dot{\gamma}$

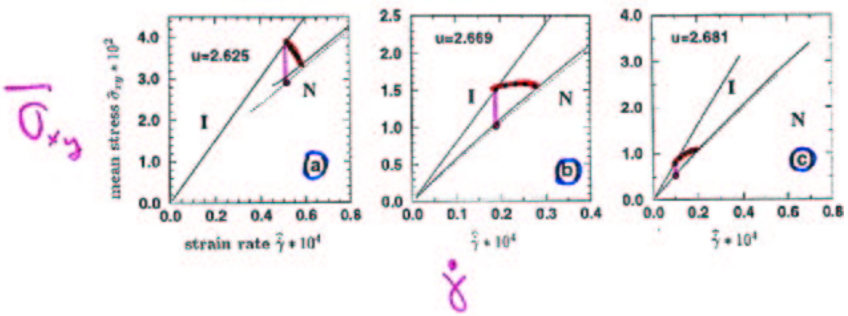
- Boundary conditions?

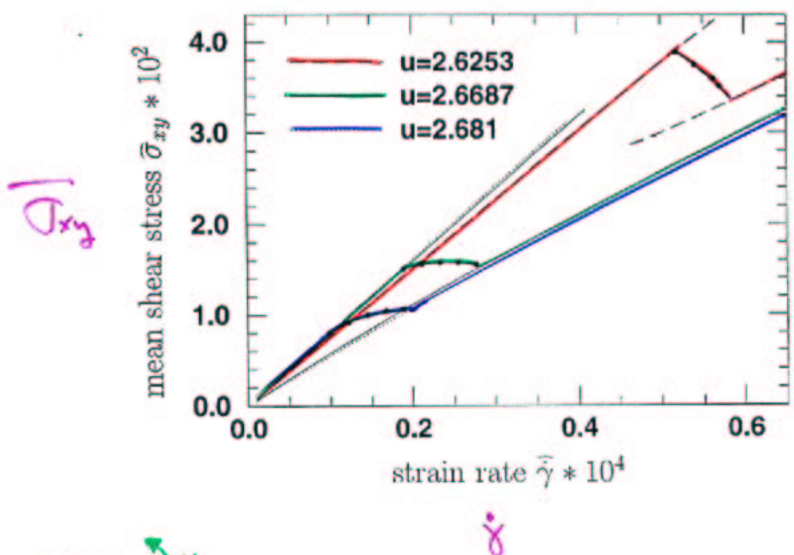
Couette, Cone & plate } "natural" asymmetry for common stress.

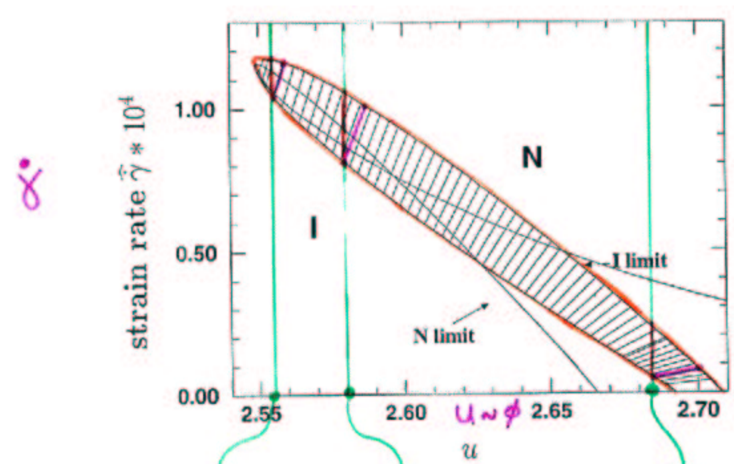
- Compare chemical potentials?

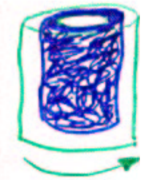


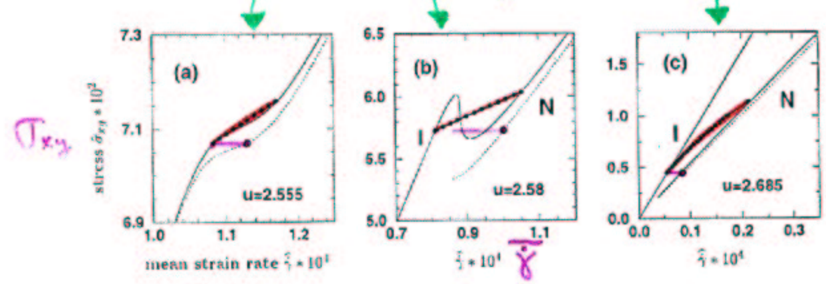
Fixed Strain-Rate Coexistence

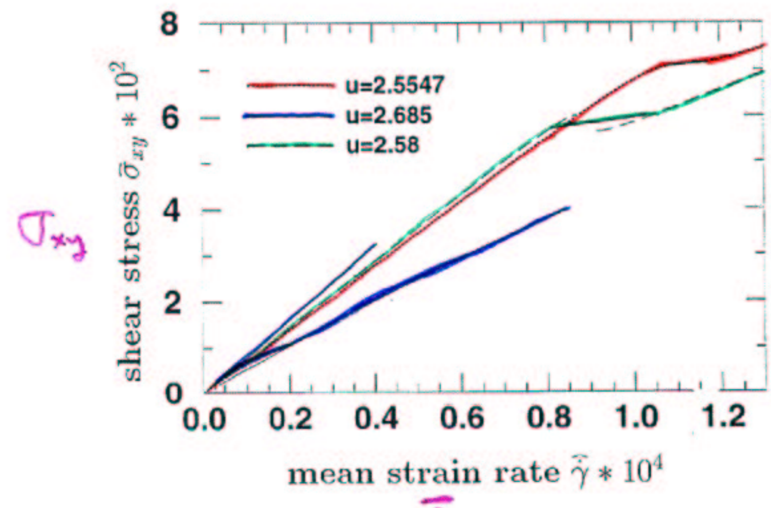








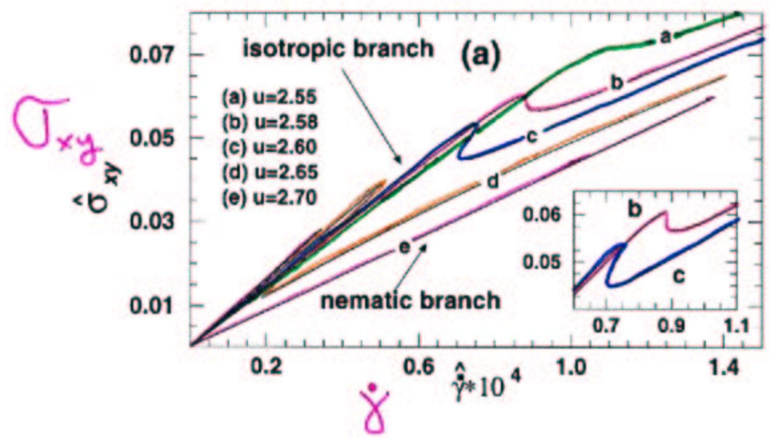


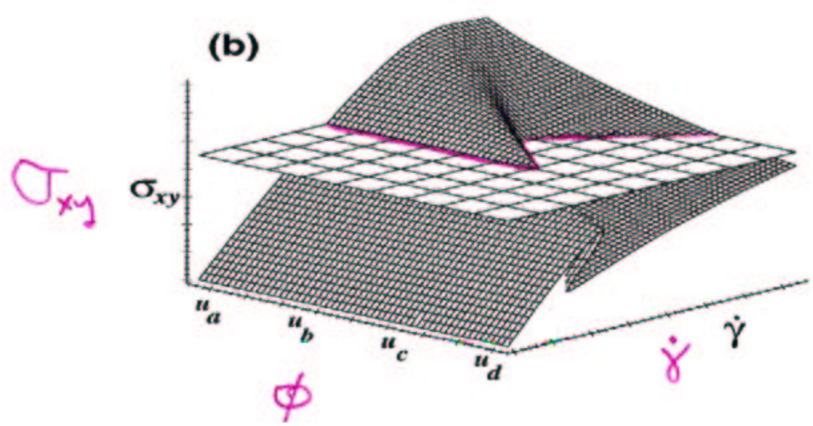


Doi Model in Shear $\mathbf{v} = \dot{\gamma} y \hat{\mathbf{x}}$

Homogeneous steady states for a given ϕ:

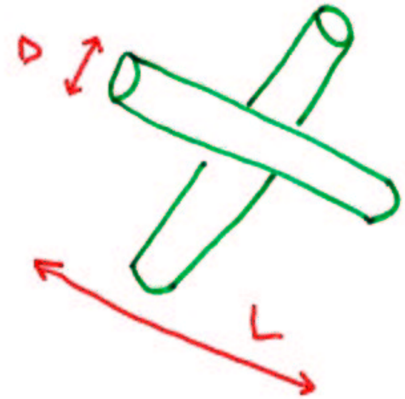
$$\sigma(\phi, \dot{\gamma}, \mathbf{Q}) = \sigma_{xy} \quad \text{(applied stress)}$$
$$\partial_t Q_{\alpha\beta} = 0$$

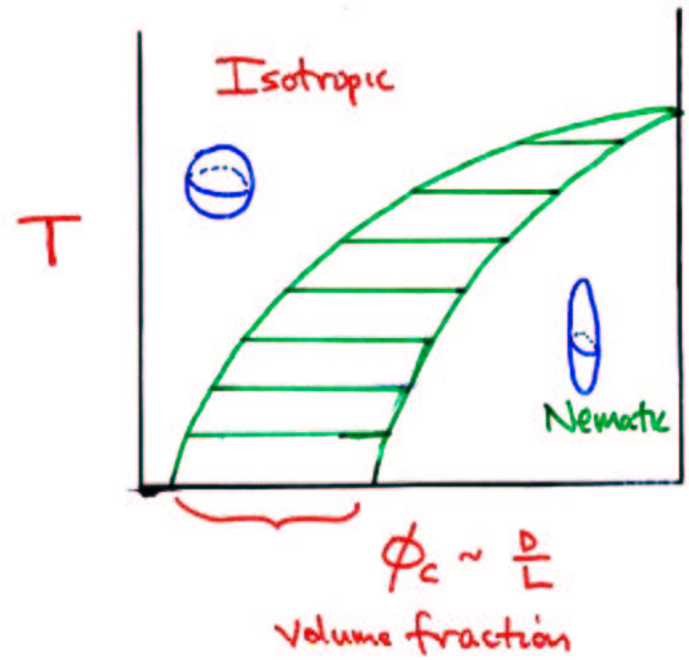




I-N Transition in Solutions

(L. Onsager 1949)
(Doi, 1981)





Complications: many ☹

- Callaghan / Fischer CTAB / D_2O

  nematic gel ?!

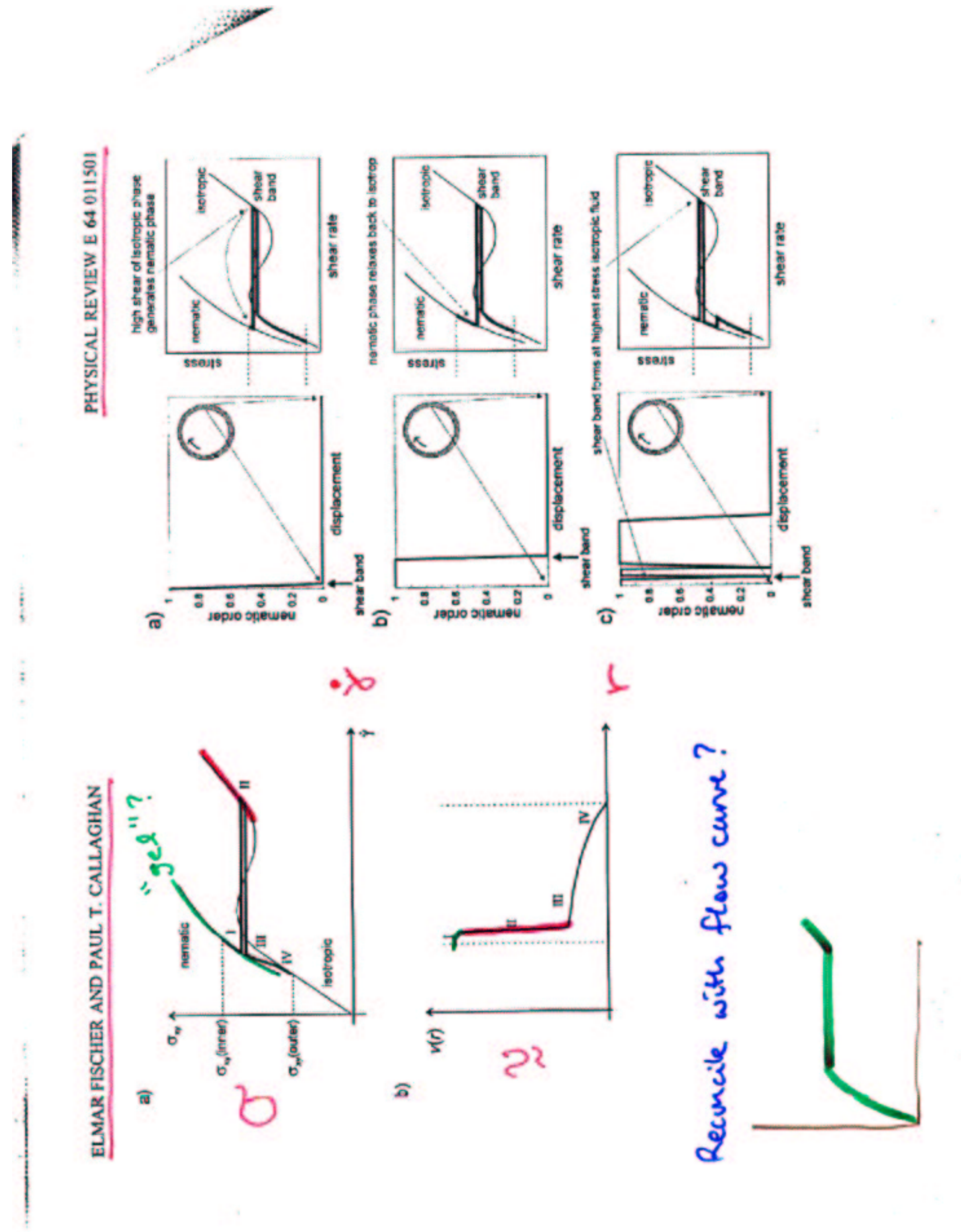
- Lerouge, Decruppe, Berret

  CTAB / $NaNO_3$ "exploding bands"

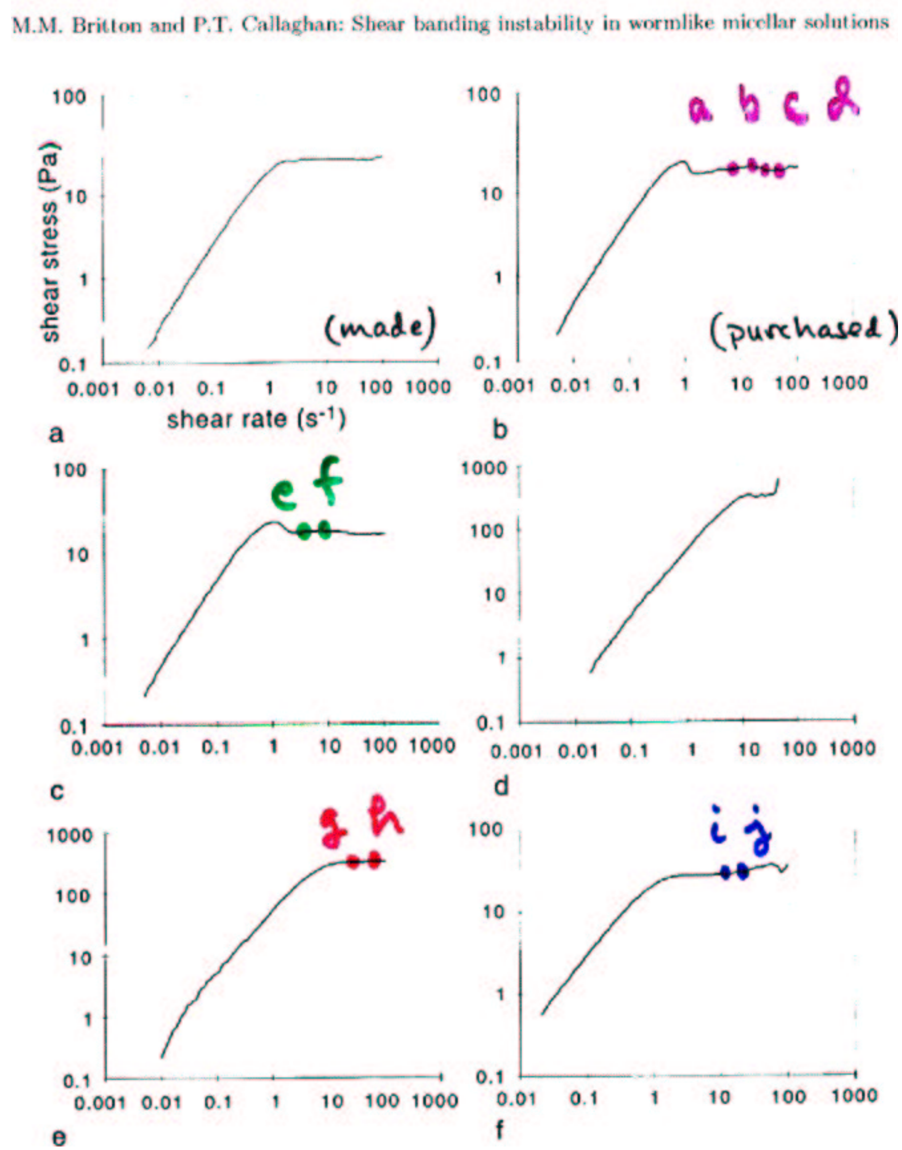
  CTAB / KBr { 3 bands ? Unstable interface ?

- Britton / Callaghan CPCl / NaSal

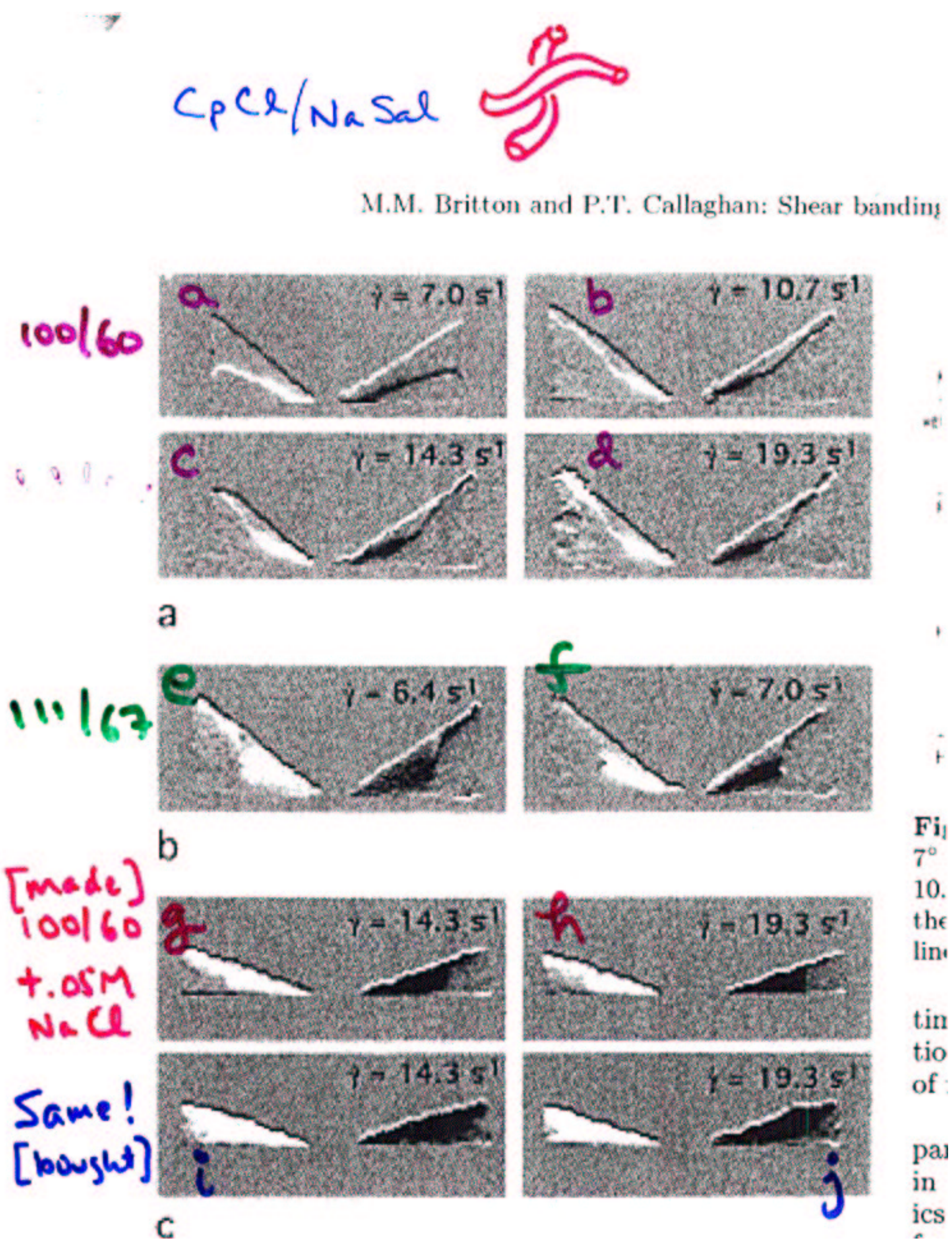
  vorticity + gradient banding together ?!



OMPORTEMENT RHÉO-OPTIQUE TRANSITOIRE
S Lerouge (Metz) Thesis, 2000
CTAB (.3M) / NaNO3 (1.79M)
B
A
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
t=ε
t=1s
t=2s
t=3s
t=4s
t=5s
t=6s
t=7s
t=8s
t=15s
t=35s
t=40s
t=55s
t=70s
t=80s
t=95s
t=120s
t=150s
t=170s
t=180s
"Exploding Bands"
[Concentration ?]
[unstable branch?]
σ
γ̇
[PRE 2001, Decruppe, Lerouge, Berret]

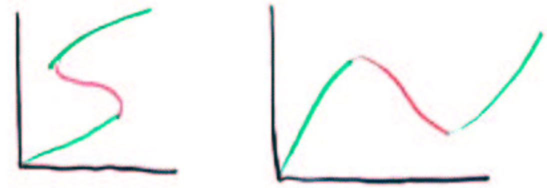


M.M. Britton and P.T. Callaghan: Shear banding instability in wormlike micellar solutions
shear stress (Pa)
shear rate (s⁻¹)
(made)
(purchased)
a b c d
e f
g h
i j
a
b
c
d
e
f



Instabilities?

"constitutive"

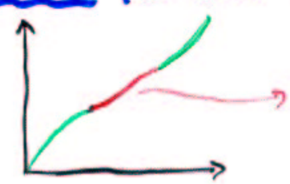


Need $\dot\gamma$ + additional quantity:

$$\sigma = \begin{cases} \eta\dot\gamma + \sigma_p, & \partial_t \sigma_p = \dots \\ \eta\dot\gamma + \sigma(Q), & \partial_t Q = \dots \\ \int K(\ell)\, P(\ell)\, d\ell + \eta\dot\gamma, & \partial_t P(\ell) = \dots \end{cases}$$

[Note: All (most) phase transitions have "mechanical" instabilities !!]

concentration (or other non-mechanical ...)



$$\partial_t \phi = \begin{cases} D\nabla^2\phi \dots \\ D\phi \dots \end{cases}$$

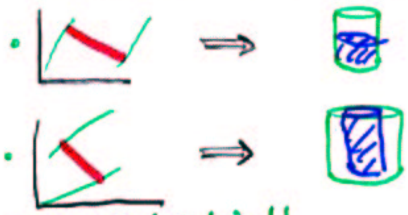
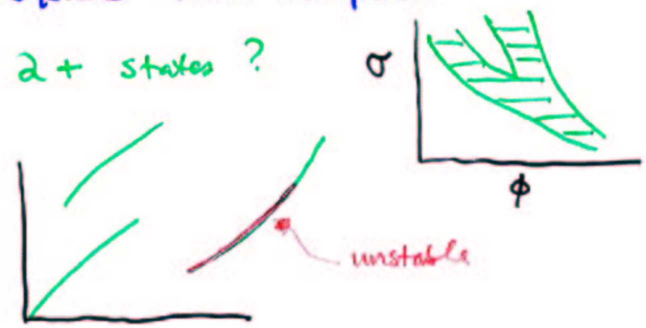
$D < 0$

Schmitt/Marques/Lequeux - Relate instability to unstable wavevector ...

Kinetics?

- "spinodal" vs "nucleated"?
  [Grand, et al. Berret, Porte]
- initial length scale?
  [S Fielding]
- band motion ⟹ Determine gradient terms $D\nabla^2 \underline{\underline{\Sigma}}$?
  [O Radulescu, S Lerouge ...]
- coarsening: gradient vs. vorticity?
- slow!

Summary

- "simple" banding
  - flow curves ⇌ phase diagram
  - Selection criteria (interfaces)
  - 
  - concentration!!
- most systems more complex?
  2+ states ?
  

- need more experiments on vorticity banding
- kinetics - slow
  many hysteresis effects
  interplay with oscillatory states?