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Early Stages of the Shear Banding Instability in a Shear-thinning Surfactant Solution

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Outline

I. Introduction. Shear banding. Wormlike micelles.

II. Experiments: shear band formation kinetics in worms.
metastability / instability.

III Theory: Initial stage of unstable banding kinetics.

[preamble: analogy with Cahn-Hilliard fluid-fluid demixing instability]

our work: non-local Johnson-Segalman model,
with 2-fluid coupling to concentration.

IV Conclusions. Outlook.

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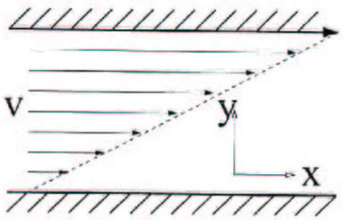
Shear banding instability

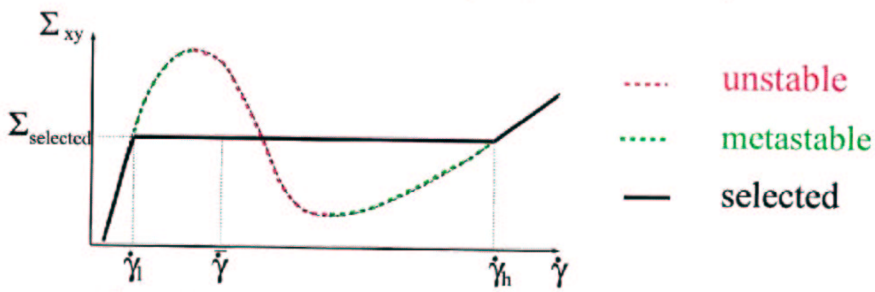
- "Usual" steady shear: *homogeneous*



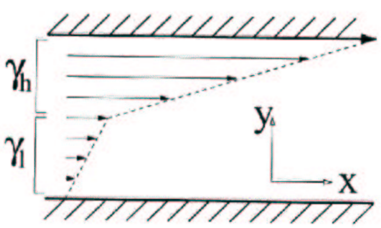
strain rate $\dot\gamma = \partial_y v$

stress $\Sigma = \Sigma(\dot\gamma)$

- But if underlying flow curve $\Sigma_{xy}(\dot\gamma)$ has −ve slope...



- ...see shear-induced "phase separation"...



...steady state is *banded*

[Spenley, Cates, McLeish. '93]

[Olmsted, Goldbart. '90, '92]

- Here study initial instability...

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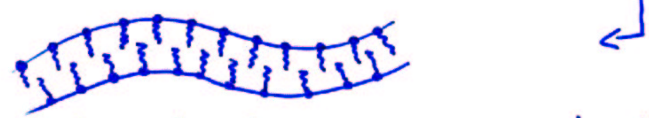
Wormlike micelles : surfactant in H_2O (+salt..)

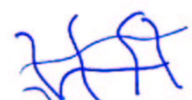
- low surfactant concentration $\phi \to 0$

  individual surfactant molecules

- $\phi > \phi_{cmc}$: reversible assembly → spheres, worms, sheets..



- Semidilute $\phi > \phi^* > \phi_{cmc}$: worms entangle



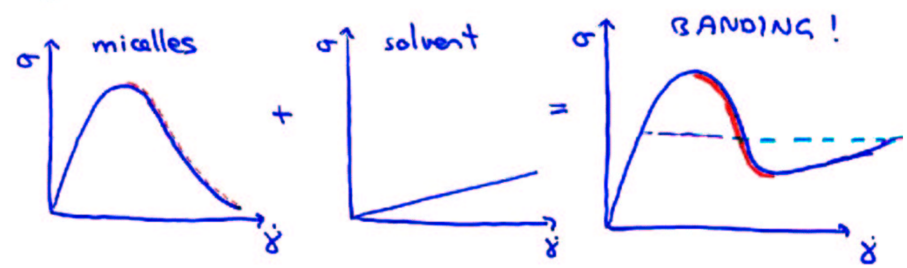
Dynamics: reptate τ_d

break / recombine τ_b

Rheology (Cates 87, 90)

Linear: maxwell $G(t) = G_0 \exp\left(\frac{-t}{\sqrt{\tau_d \tau_b}}\right)$ if $\tau_b \ll \tau_d$

Non-Linear:



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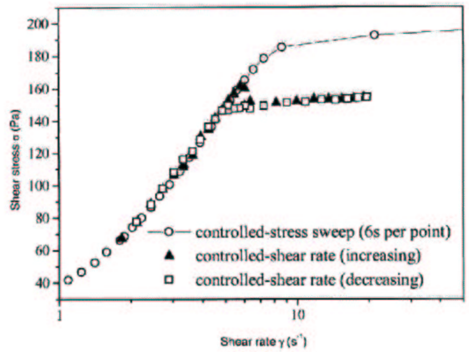
Experiments: wormlike micelles

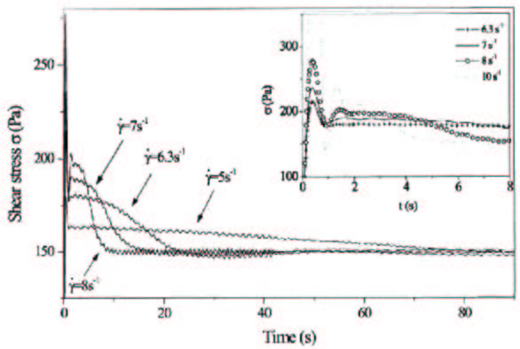
[Lerouge, Decruppe. '01] [Lerouge *et al.* '00] [Berret. '97] [Grand *et al.* '97] [Berret, Porte. '00] Below data: [Lerouge. PhD thesis, Univ. of Metz '00]

- $\Sigma_{xy}, \dot{\gamma}$ sweeps ("flow-curves")



CTAB(0.3M) $+NaNO_3$(1.79M) $+H_2O$. 30°C

- $\dot{\gamma}$-jumps ("start-up") Metastable



CTAB(0.3M) $+NaNO_3$(1.79M) $+H_2O$. 30°C

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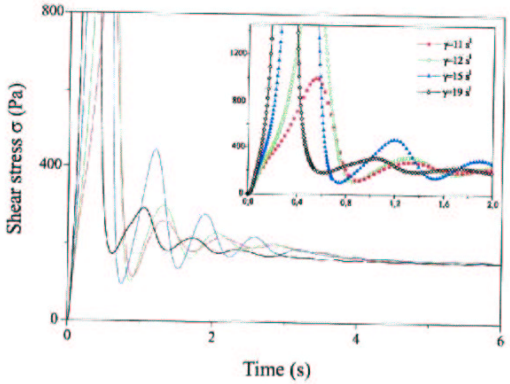
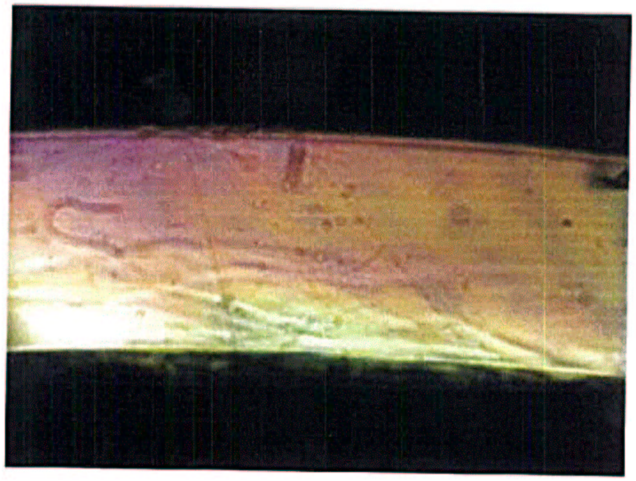
Experiments (cont.)

- $\dot{\gamma}$-jumps ("start-up") Unstable



CTAB(0.3M) $+NaNO_3$(1.79M) $+H_2O$. 30°C



CTAB(0.1M) +NaSal(0.08M) $+H_2O$. 30°C

15. COMPORTEMENT RHÉO-OPTIQUE TRANSITOIRE S.A.L.S. Lerouge

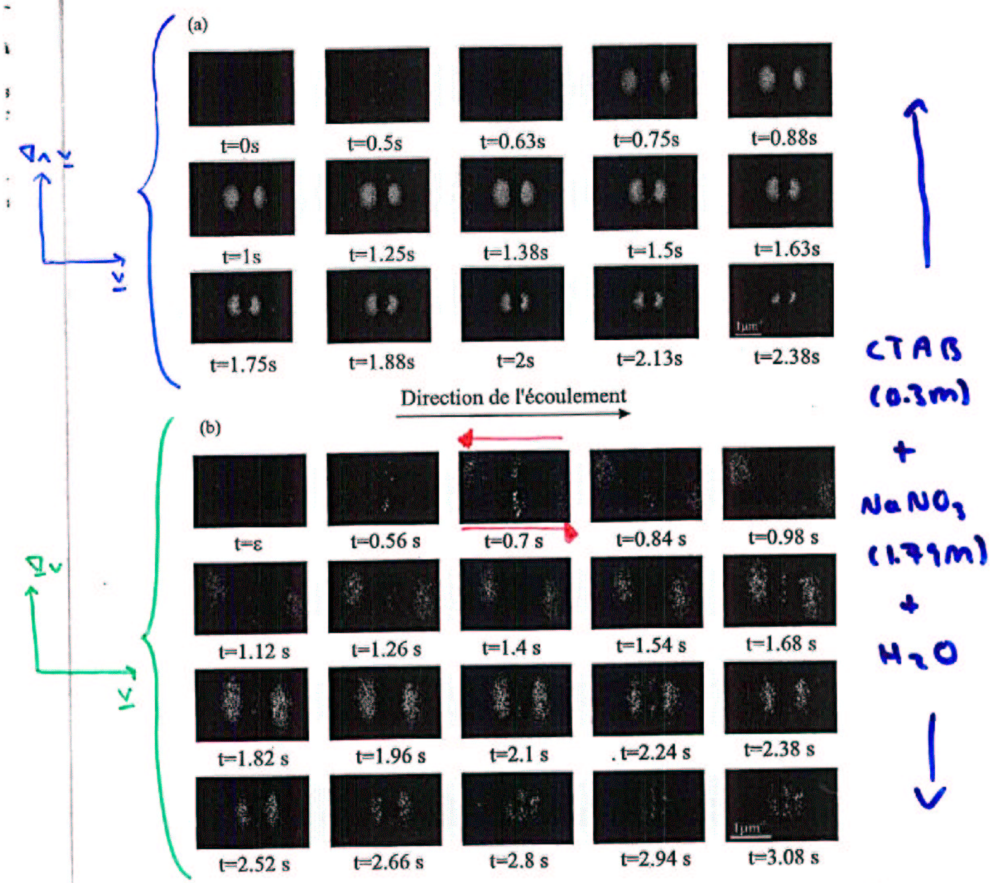
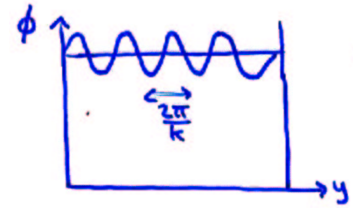


Figure 15.15: *Diffusion de la lumière aux petits angles sous écoulement. Le taux de cisaillement imposé est 10 s^{-1}. Les graphes (a) et (b) correspondent respectivement aux plans d'observation $(\vec{v}, \vec{\omega})$ et $(\vec{v}, \vec{\nabla} v)$.*

Analogy? Cahn-Hilliard demixing instability [$\dot{\gamma} = 0$]

2-fluid mixture of micelles (volume fraction ϕ) and solvent



Initial state = homogeneous + noise

$$\phi(y,t) = \bar{\phi} + \mathrm{Re}\sum_k \delta\phi_k e^{\omega_k t} e^{iky}$$

growth rate.

Stable ?

Dynamics: Cahn-Hilliard equation:

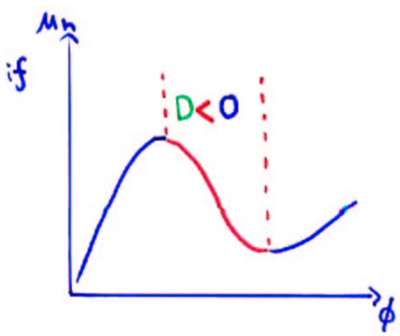
$$\partial_t \phi = m\, \partial_y^2 \frac{\delta F}{\delta \phi}, \quad \text{free energy } F = \int dr \left[f_h(\phi) + \frac{\kappa}{2} |\partial_y \phi|^2 \right]$$

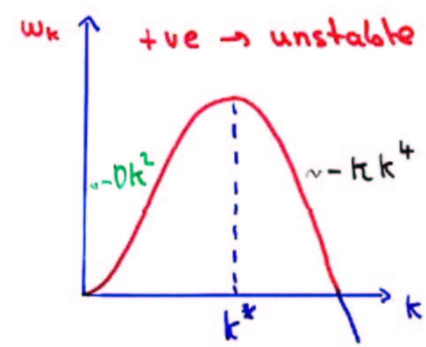
Gives growth rate $\omega_k = -Dk^2 - \kappa k^4$

sign? negative

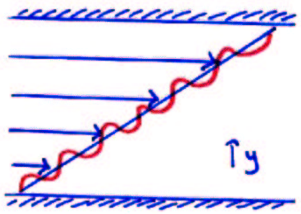
with diffusion coefficient $D = \frac{d^2 f_h}{d\phi^2} = \frac{d\mu_h}{d\phi}$

if





Simplest transcription of CH theory → shear banding



homogeneous + noise

$$\begin{pmatrix}\dot\gamma\\ \Sigma_{xy}\end{pmatrix} + \sum_k \begin{pmatrix}\delta\dot\gamma\\ \delta\Sigma_{xy}\end{pmatrix}_k e^{\omega_k t} e^{iky}$$

stable ?

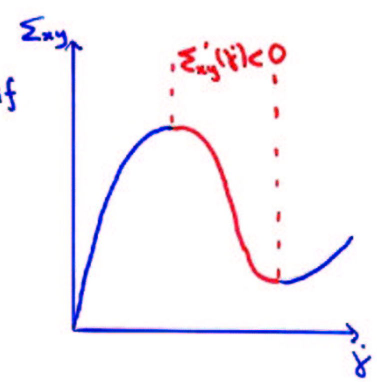
Force balance $\rho\,\partial_t\dot\gamma = \partial_y^2\,\Sigma_{xy}$

Constitutive $\Sigma_{xy} = \Sigma_{xy}(\dot\gamma)$

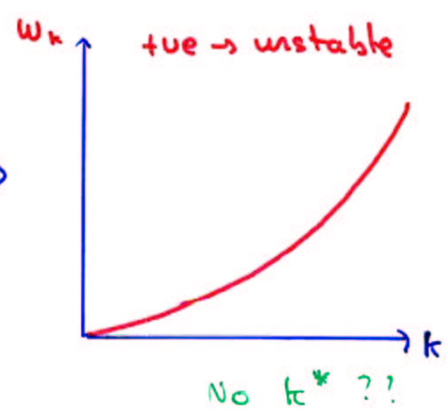
$$\left.\begin{matrix}\rho\,\partial_t\dot\gamma = \partial_y^2\,\Sigma_{xy}\\ \Sigma_{xy} = \Sigma_{xy}(\dot\gamma)\end{matrix}\right\}\ \rho\,\partial_t\dot\gamma = \Sigma'_{xy}(\dot\gamma)\,\partial_y^2\,\dot\gamma + O((\partial_y\dot\gamma)^2)$$

$\Rightarrow$ growth rate $\omega_k = -\dfrac{\Sigma'_{xy}(\dot\gamma)}{\rho}\,k^2$

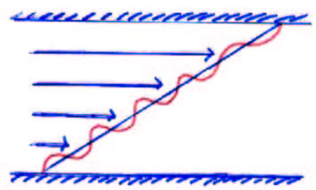
if



$\Rightarrow$



diffusive Johnson-Segalman model.



homogeneous + noise

$$\begin{pmatrix}\dot\gamma\\ \underline{\underline{W}}\end{pmatrix} + \sum_k \begin{pmatrix}\delta\dot\gamma\\ \delta\underline{\underline{W}}\end{pmatrix}_k e^{\omega_k t} e^{iky}$$

Dynamical equations:

1) Fluid velocity $\rho\, D_t \underline{v} = \nabla\cdot\underline{\underline{\Sigma}} - \nabla p$ Force balance

2) Viscoelastic stress $\underline{\underline{\Sigma}} = G(\phi)\,\underline{\underline{W}} + \eta(\phi)\,\dot\gamma\,\hat{\underline{x}}\,\hat{\underline{y}}$

micellar Newtonian

↙

d-JS: $\overset{\nabla}{\partial_t}\underline{\underline{W}} = a\,(\underline{\underline{D}}\cdot\underline{\underline{W}} + \underline{\underline{W}}\cdot\underline{\underline{D}}) + 2\underline{\underline{D}} - \dfrac{\underline{\underline{W}}}{\tau(\phi)} + \dfrac{l^2}{\tau(\phi)}\,\partial_y^2\,\underline{\underline{W}}$

translation, rotation

SLIP

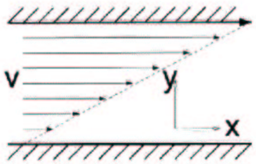
stretch

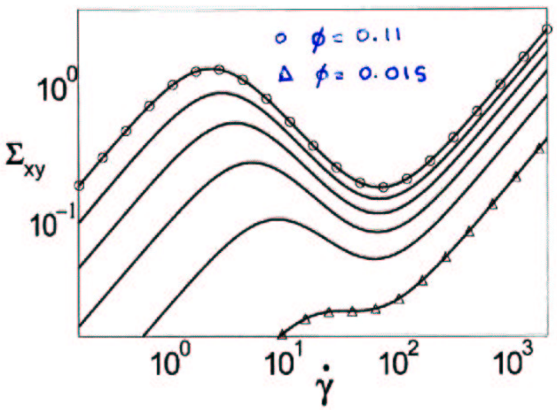
$2\underline{\underline{D}} = \nabla\underline{v} + (\nabla\underline{v})^T$

maxwell time, relaxation

mesh size l: interfaces

Solve for time-independent...



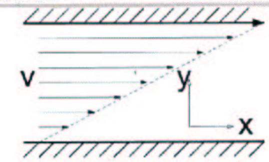


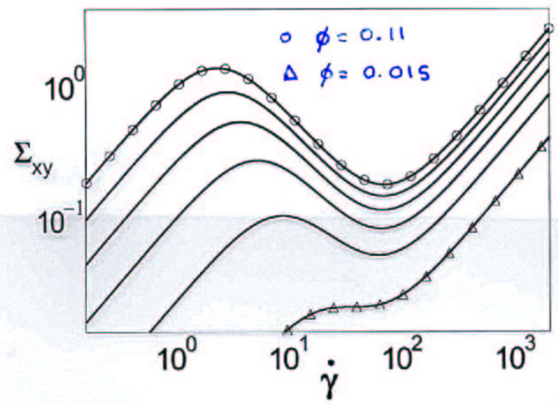
Units:

$G(\phi = 0.11) = 1$

$\tau(\phi = 0.11) = 1$

Solve for time-independent...

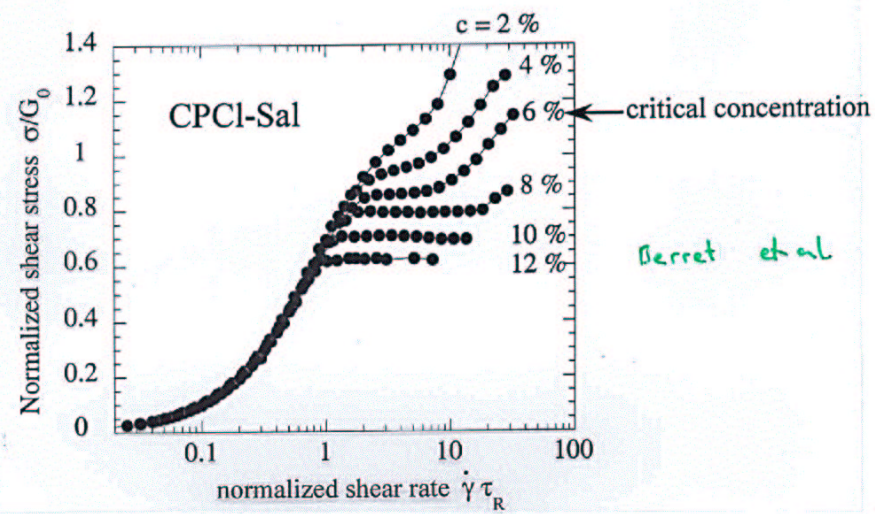




Units:

$G(\phi = 0.11) = 1$

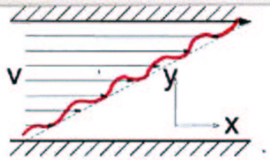
$\tau(\phi = 0.11) = 1$



Berret et al

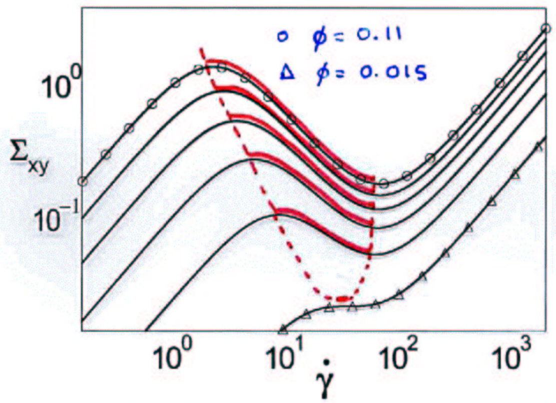
Solve for time-independent...

Linear stability analysis:



$$\omega_k \begin{pmatrix} \delta\dot\gamma \\ \delta\underline{\underline{W}} \end{pmatrix} = \underline{\underline{M}}_k \begin{pmatrix} \delta\dot\gamma \\ \delta\underline{\underline{W}} \end{pmatrix} + O\left(\begin{pmatrix} \delta\dot\gamma \\ \delta\underline{\underline{\Sigma}} \end{pmatrix}\right)^2$$

growth rate; stability matrix



— unstable

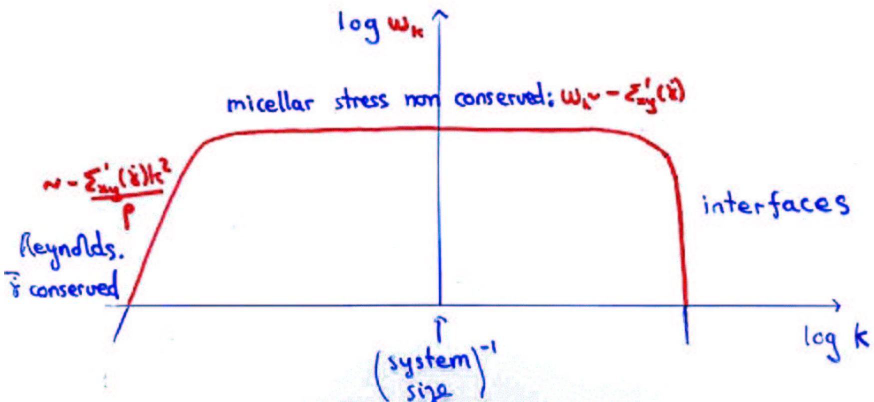
Units:

$G(\phi = 0.11) = 1$

$\tau(\phi = 0.11) = 1$

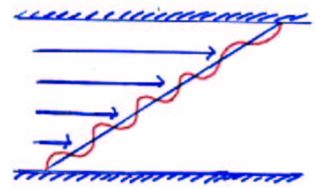
---- spinodal

→ unstable, $\omega_k > 0$ if $\Sigma'_{xy}(\dot\gamma) < 0$



No selected k^* ....

diffusive Johnson-Segalman model. + concentration (ϕ) coupling.



homogeneous + noise

$$\begin{pmatrix} \bar{\dot\gamma}_{cm} \\ \bar{\underline{\underline{W}}} \\ \bar\phi \end{pmatrix} + \sum_k \begin{pmatrix} \delta\dot\gamma_{cm} \\ \delta\underline{\underline{W}} \\ \delta\phi \end{pmatrix}_k e^{\omega_k t} e^{iky}$$

$\underline{v}_{rel} = 0$; from $\underline{v}_{rel}$

Dynamical equations:

1) Fluid velocity $\rho D_t \underline{v}_{cm} = \nabla \cdot \underline{\underline{\Sigma}} - \nabla p$ Force balance

$+ \phi$ coupling

2) Viscoelastic stress $\underline{\underline{\Sigma}} = G(\phi)\underline{\underline{W}} + \eta(\phi)\dot\gamma \hat{x}\hat{y}$

micellar; Newtonian

d-JS: $\overset{\circ}{\delta_t}\underline{\underline{W}} = a(\underline{\underline{D}}\cdot\underline{\underline{W}} + \underline{\underline{W}}\cdot\underline{\underline{D}}) + 2\underline{\underline{D}}_m - \dfrac{\underline{\underline{W}}}{\tau(\phi)} + \dfrac{l^2}{\tau(\phi)}\partial_y^2 \underline{\underline{W}}$

translation, rotation; SLIP; stretch; maxwell time, relaxation; mesh size l: interfaces

$2\underline{\underline{D}} = \nabla\underline{v} + (\nabla\underline{v})^T$

3) micellar volume fraction $D_t\phi = -\nabla\cdot\phi(1-\phi)\underline{v}_{rel}$

Dynamics of $\underline{v}_{cm}$ & $\underline{v}_{rel}$: 2-fluid model.

[de Gennes '76, Milner '93]

• Force balance for micelles

$$\phi\rho D_t \underline{v}_m = \underbrace{-\zeta \underline{v}_{rel}}_{\text{Drag}} + \underbrace{\nabla\cdot G(\phi)\underline{\underline{W}}}_{\text{visco-elastic}} + \underbrace{2\nabla\cdot\eta_m(\phi)\underline{\underline{D}}_m}_{\text{Newtonian (Rouse...)}} - \phi\nabla\frac{\delta F}{\delta\phi} - \underbrace{\phi\nabla p}_{\text{pressure}}$$

$$F = \begin{cases} \int d\underline{r}\left[f_n(\phi) + \frac{\kappa}{2}|\nabla\phi|^2\right] & \text{osmotic} \\ \quad + & \\ \frac{1}{2}\int d\underline{r}\; G(\phi)\,\mathrm{Tr}\left[\underline{\underline{W}} - \log\underline{\underline{W}}\right] & \text{elastic}\end{cases}$$

• Force balance for solvent

$$(1-\phi)\rho D_t\underline{v}_s = \underbrace{\zeta\underline{v}_{rel}}_{\text{Drag}} + \underbrace{2\nabla\cdot\eta_s(\phi)\underline{\underline{D}}_s}_{\text{Newtonian}} - \underbrace{(1-\phi)\nabla p}_{\text{pressure}}$$

+ Add $\rightarrow$ $D_t\underline{v}_{cm}$ force balance

−: Subtract $\rightarrow$ $\underline{v}_{rel}$ $\Rightarrow$ $D_t\phi = -\nabla\phi(1-\phi)\underline{v}_{rel}$ continuity

→ Final dynamical equations

• Viscoelastic constitutive equation

$D_t\underline{\underline{W}} = d - JS$ as before (but $\underline{v}_{cm} \to \underline{v}_m$)

• Force balance

$$\rho D_t\underline{v} = \nabla\cdot G(\phi)\underline{\underline{W}} + \text{Newtonian} \boxed{-\phi\nabla\frac{\delta F}{\delta\phi}} - \nabla p$$

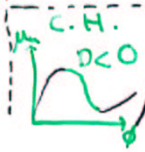
• Continuity

$$D_t\phi = -\nabla\frac{\phi(1-\phi)}{\zeta}\left\{-\nabla\frac{\delta F}{\delta\phi}\boxed{+\frac{1}{\phi}\nabla\cdot G(\phi)\underline{\underline{W}} + \text{Newtonian}}\right\}$$

Homogeneous constitutive curves as before

But now: fluctuations coupled (except for $\zeta\to\infty$, D fixed)

$$\underline{\underline{M}}_k = \begin{array}{c|c|c} & \delta\dot\gamma \quad \delta\underline{\underline{W}} & \delta\phi \\ \hline \delta\dot\gamma,\ \delta\underline{\underline{W}} & \text{"mechanical"} & \text{coupling of flow} + \phi \\ \hline \delta\phi & \text{coupling of flow} + \phi & \text{C.H.} \end{array}$$



Normal stress$_{yy}$ ↑

ϕ ↑

[Schmitt, Marques, Lequeux ; Helfand-Fredrickson]

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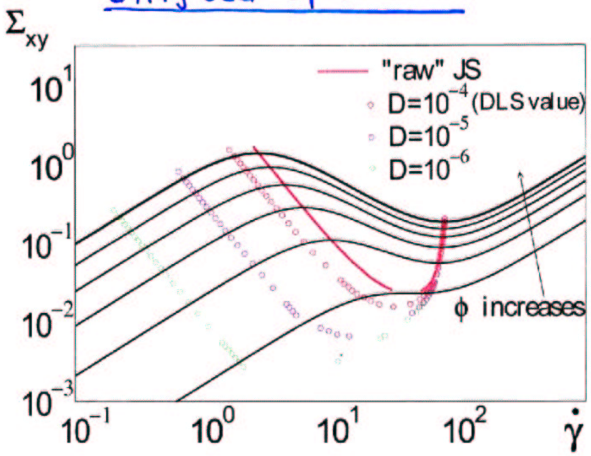
Shifted Spinodals:



lower spinodal: $\bar{D}\,\Sigma'_{xy}(\dot\gamma) + \frac{G'(\phi)}{\tau} N'_{yy}(\dot\gamma) = 0$

C.H. mechanical coupling

$\Rightarrow$ at $\Sigma'_{xy}(\dot\gamma)=0$ in uncoupled limit $\tau \to \infty$

Coupling shifts it by $O\left(\frac{G'(\phi)}{\tau D}\right) = O\left(\frac{G'(\phi)}{f''(\phi)}\right)$

Qualitatively 2 different types of system: expected eigenvector

o far from C.H. → mechanical, perturbed by $\phi \to \left(d\dot\gamma, d\underline{\underline{\Sigma}}, d\phi\right)$

o close to C.H. → (for low $\dot\gamma$): C.H. perturbed by flow → $\left(d\dot\gamma, d\underline{\underline{\Sigma}}, d\phi\right)$

[Clarke+McLeish, Milner, Onuki]

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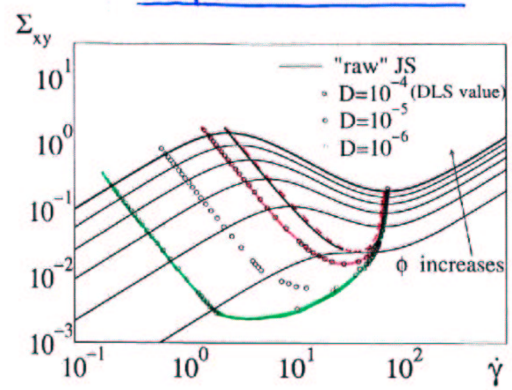
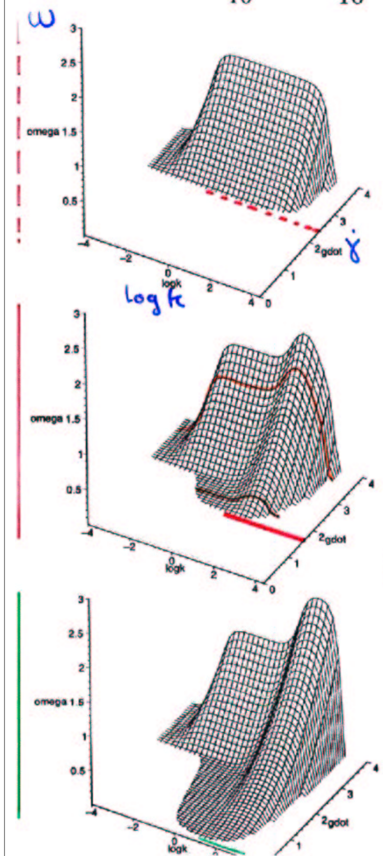
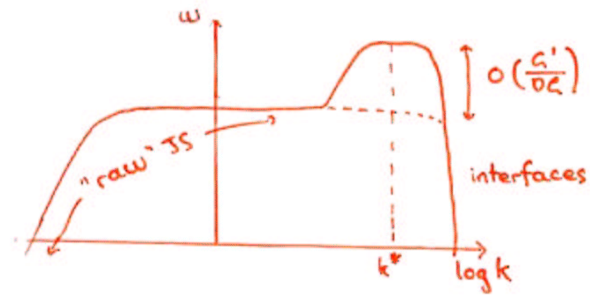
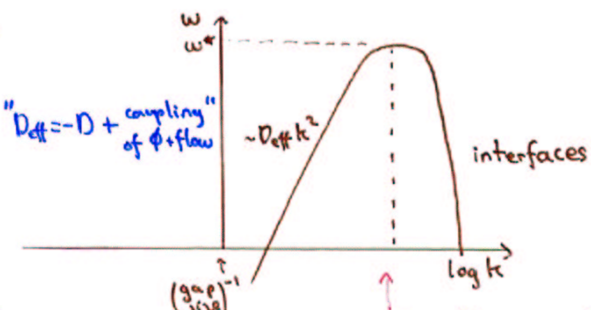
Dispersion Relations









"$D_{eff} = -D +$ coupling of ϕ+flow"

Selected $k^* \sim \left(\frac{\omega^*}{D_{eff} \times \text{interface width}}\right)^{\frac{1}{4}}$

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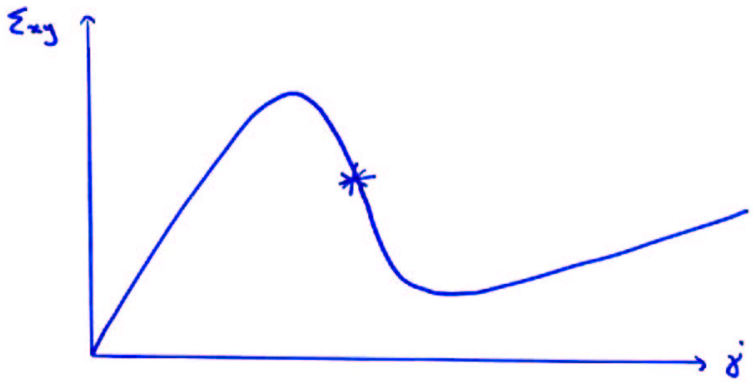
So far we've considered ...



... fluctuations about intrinsic constitutive curve.

Can use these to define spinodal,

for slow $\dot\gamma$ sweeps towards unstable region.

But : inside unstable region:

must consider $\dot\gamma$ startup quenches . . .

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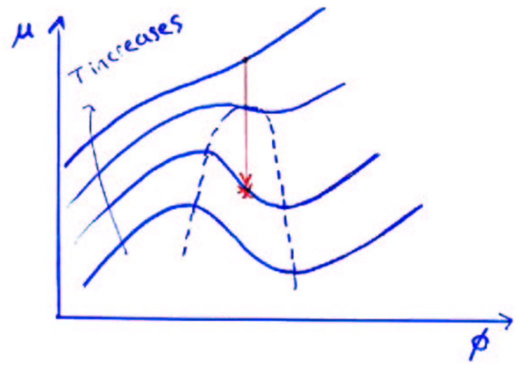
$\dot\gamma$ startup - Quench into unstable region

- Cahn-Hilliard analogy (?) - again !



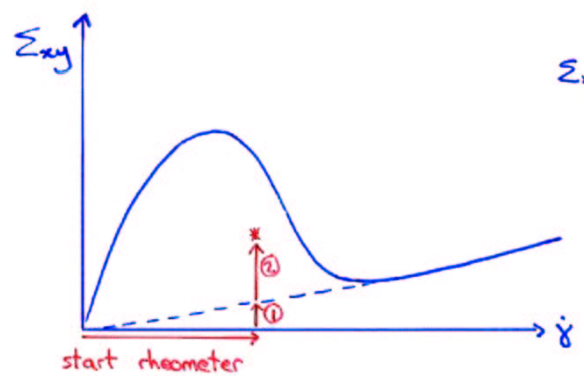
T quench :

Usually assume heat out quickly

$T_{conduction} \ll \frac{1}{\omega^*} = \tau_{instability}$

time-scales separate

- Our case - more complicated !



$$\Sigma_{xy} = \underbrace{\eta\dot\gamma}_{\text{"instant"}} + \underbrace{G(\phi)\,W_{xy}}_{\text{Maxwell time},\ \tau}$$

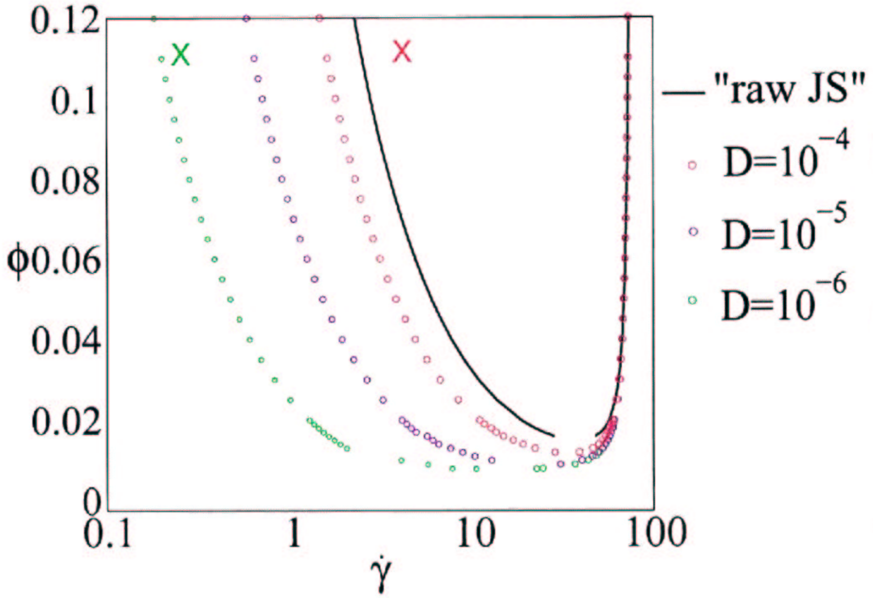
①, ②

But $\omega^* = O\left(\frac{1}{\tau}\right)$

time-scales comparable.

$\longrightarrow$ explicitly consider time dependent background $\begin{pmatrix} \bar{\dot\gamma} \\ \bar{\underline{\underline{W}}}(t) \\ \bar\phi \end{pmatrix}$

Spinodals in $\phi - \dot\gamma$ space



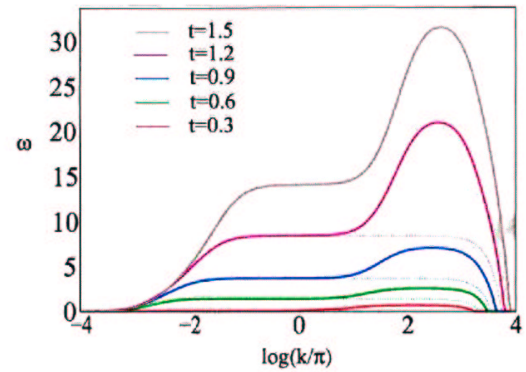
Now consider shear start-up for

X a type A system [expect eigenvector $(\delta\dot\gamma, \delta\sigma, {\scriptstyle \delta\phi})$]

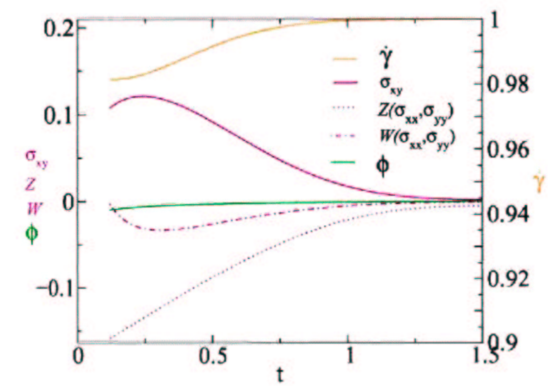
X a type B system [expect eigenvector $({\scriptstyle \delta\dot\gamma}, {\scriptstyle \delta\sigma}, \delta\phi)$]

Shear start-up type A; expect $(\delta\dot\gamma, \delta\sigma, {\scriptstyle \delta\phi})$

- Dispersion relation



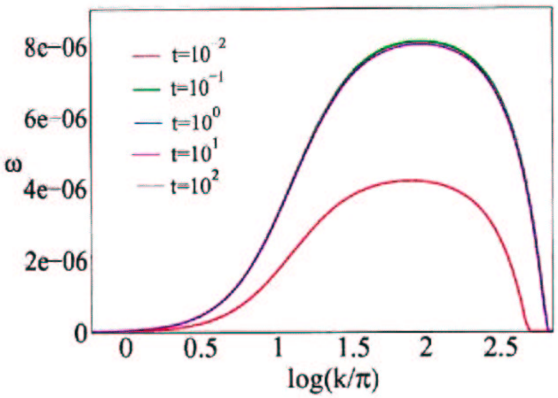
- Eigenvector at peak of dispersion relation



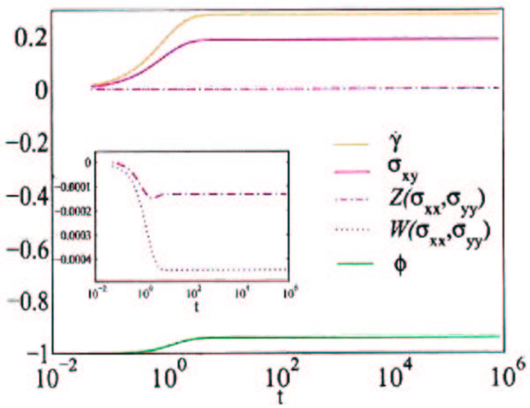
Find $(\delta\dot\gamma, \delta\sigma, {\scriptstyle \delta\phi})$ as expected

Shear start-up type B; expect $(\delta\dot{\gamma}, \delta\sigma, \delta\phi)$

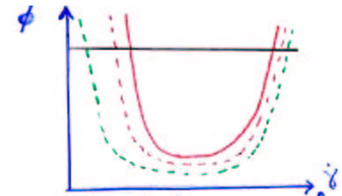
- Dispersion relation



- Eigenvector at peak of dispersion relation

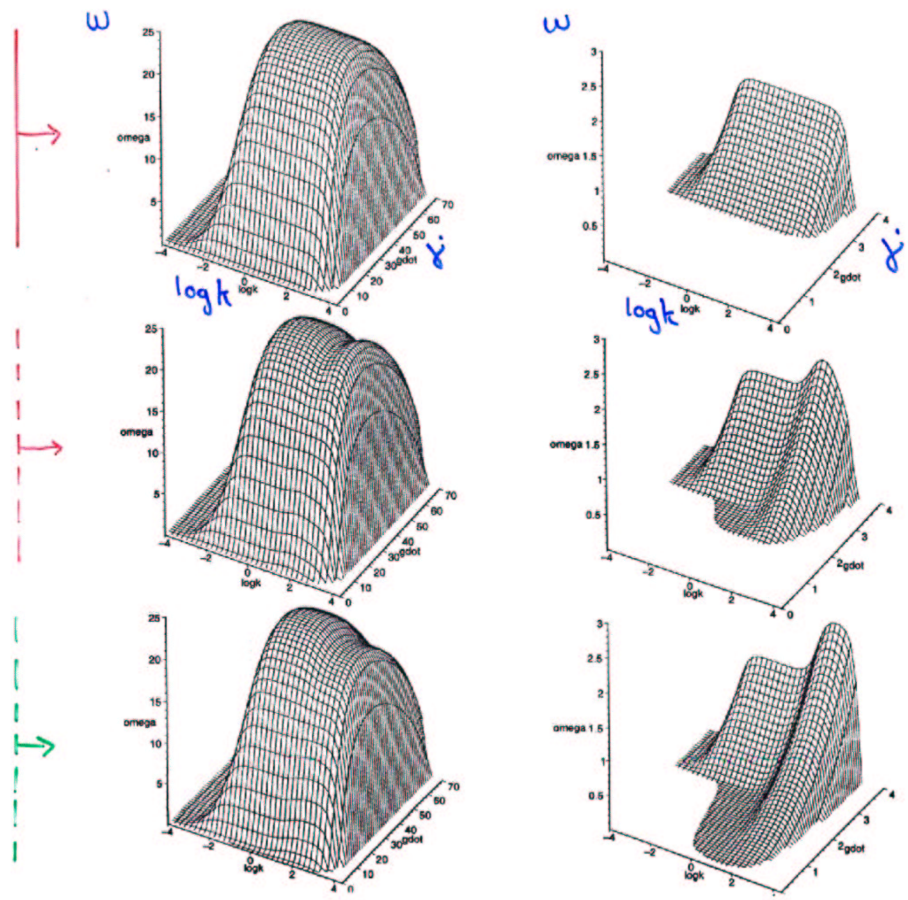


Find $(\delta\dot{\gamma}, \delta\sigma, \delta\phi)$ as expected

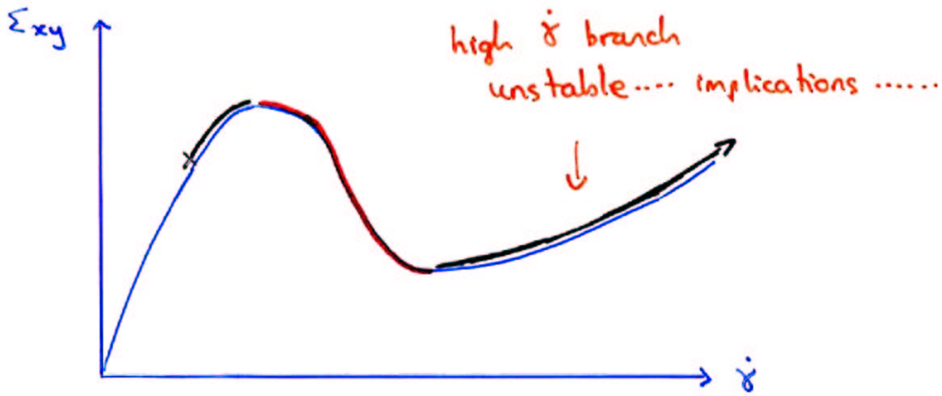


... more complicated −ve feedback at large $\dot{\gamma}$

(effect of ϕ fluct. on velocity field seen by micelles ...)



And sometimes even:



— "raw JS instability"

— Extra instability via coupling to ϕ

Conclusions

- Purely mechanical instability is enhanced by coupling to concentration
  & then has a selected wavevector k^*
- Two extreme types of instability...
  mechanical, slightly perturbed by ϕ coupling
  Cahn-Hilliard, slightly perturbed by flow
  Smooth cross-over between these two types.

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Extensions, outlook

- whole $\underline{v}, \nabla \underline{v}$ plane
- $\int dt$ to find "static" $S(\underline{q}, t)$
- later stages of unstable kinetics
- metastable kinetics.
- steady state phase diagram.
- other models, ideally microscopic..
- Implications of unstable high $\dot{\gamma}$ branch.