What can NMR tell us about shear banding and ordering?

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1. Introduction to nuclear spin interactions
   spectroscopic tools

2. Rheo-NMR: microscopy and velocimetry
   velocity probability distributions
   timescale of NMR velocimetry

3. Ordering in entangled polymer melts
   complete rank-2 alignment tensor

4. CTAB/D_2O shear banding and ordering
   complexity of shear banding
   near an I-N transition

5. CPyCl-NaSal in 0.5M NaCl/D_2O
   complexity of shear banding
   far from an I-N transition

Acknowledgements

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Maria Kilfoil

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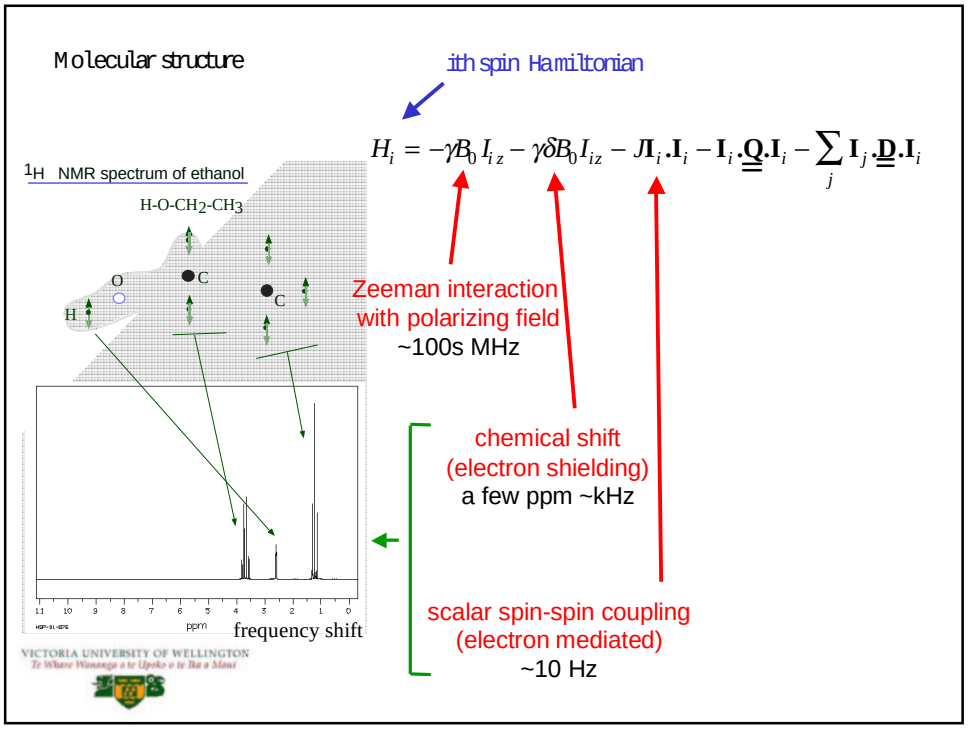
Molecular structure
ith spin Hamiltonian
$H_i = -\gamma B_0 I_{iz} - \gamma\delta B_0 I_{iz} - J\mathbf{I}_i.\mathbf{I}_i - \mathbf{I}_i.\underline{\underline{\mathbf{Q}}}.\mathbf{I}_i - \sum_j \mathbf{I}_j.\underline{\underline{\mathbf{D}}}.\mathbf{I}_i$
^{1}H NMR spectrum of ethanol
H-O-CH$_2$-CH$_3$
O
C
C
H
ppm
frequency shift
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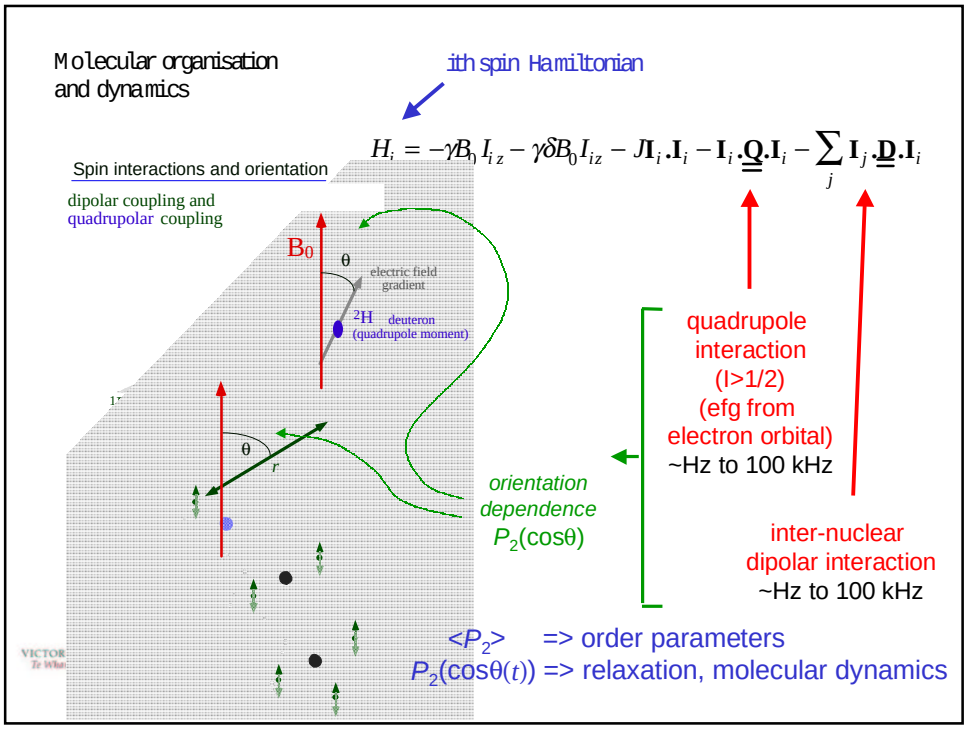
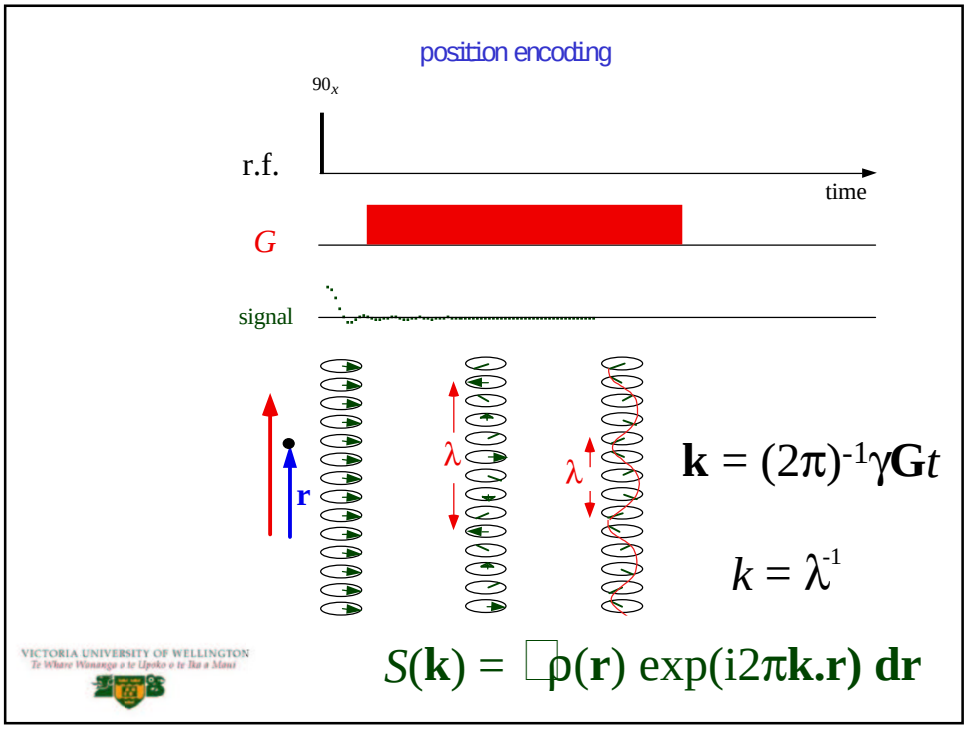
Zeeman interaction
with polarizing field
~100s MHz
chemical shift
(electron shielding)
a few ppm ~kHz
scalar spin-spin coupling
(electron mediated)
~10 Hz


Molecular organisation
and dynamics
ith spin Hamiltonian
$H_i = -\gamma B_0 I_{iz} - \gamma\delta B_0 I_{iz} - J\mathbf{I}_i.\mathbf{I}_i - \mathbf{I}_i.\underline{\underline{\mathbf{Q}}}.\mathbf{I}_i - \sum_j \mathbf{I}_j.\underline{\underline{\mathbf{D}}}.\mathbf{I}_i$
Spin interactions and orientation
dipolar coupling and
quadrupolar coupling
B$_0$
θ
electric field
gradient
^{2}H deuteron
(quadrupole moment)
θ
r
orientation
dependence
$P_2(\cos\theta)$
quadrupole
interaction
(I>1/2)
(efg from
electron orbital)
~Hz to 100 kHz
inter-nuclear
dipolar interaction
~Hz to 100 kHz
<P_2> => order parameters
$P_2(\cos\theta(t))$ => relaxation, molecular dynamics


position encoding
90_x
r.f.
time
G
signal
r
λ
λ
$\mathbf{k} = (2\pi)^{-1}\gamma\mathbf{G}t$
$k = \lambda^{-1}$
$S(\mathbf{k}) = \int \rho(\mathbf{r}) \exp(i2\pi\mathbf{k}.\mathbf{r})\, d\mathbf{r}$
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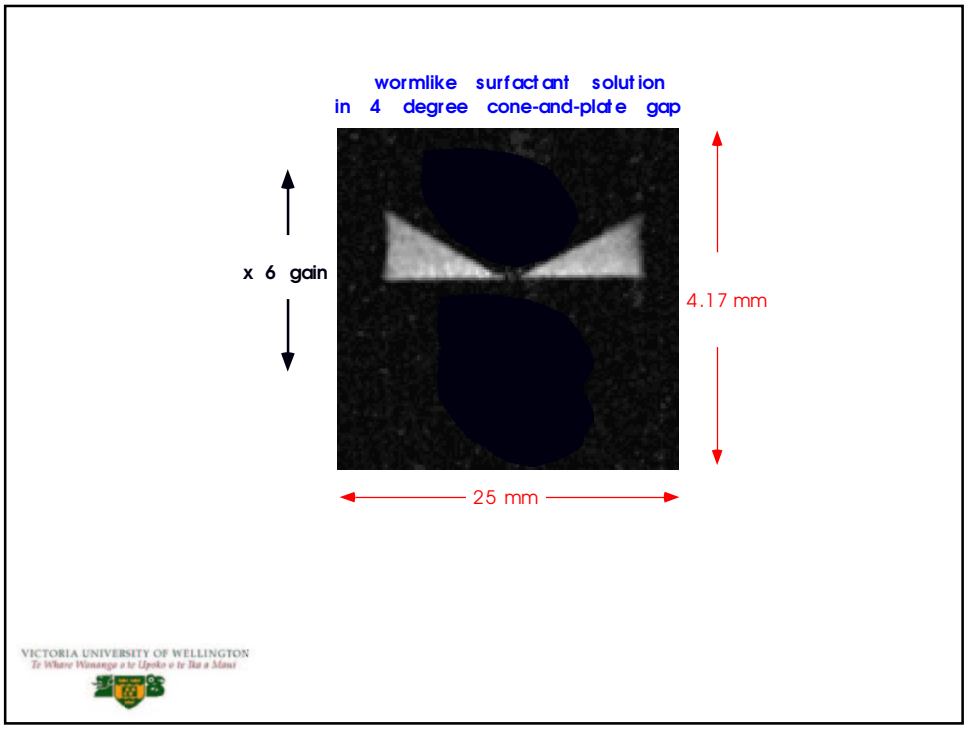
wormlike surfactant solution
in 4 degree cone-and-plate gap
x 6 gain
4.17 mm
25 mm
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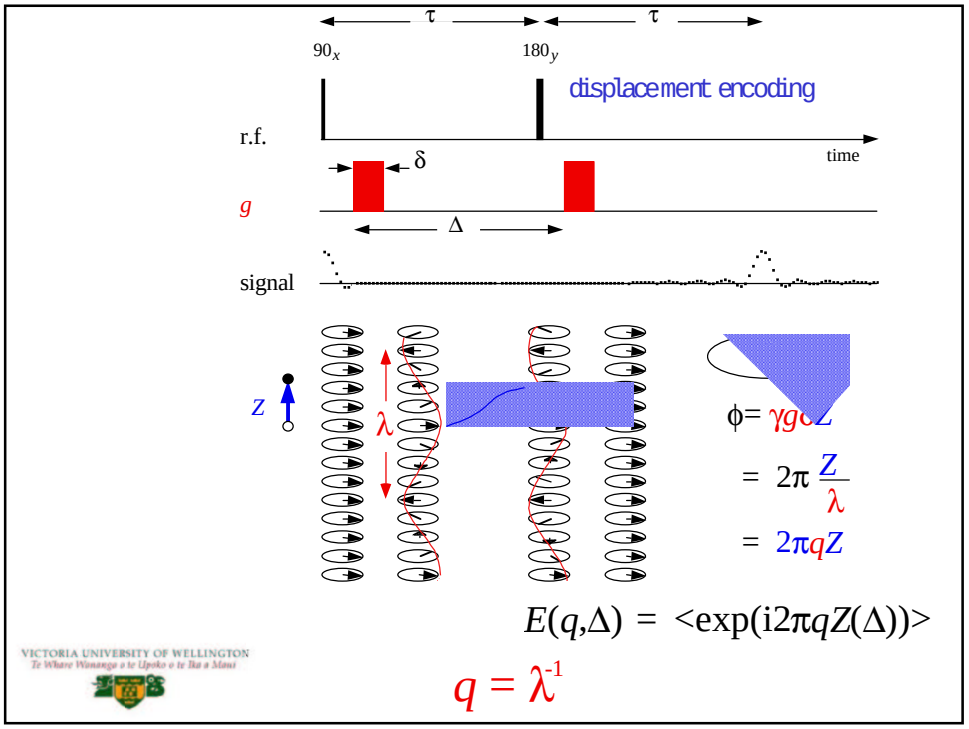
τ
τ
90x
180y
displacement encoding
r.f.
time
δ
g
Δ
signal
Z
λ
ϕ= γgδZ
= 2π Z/λ
= 2πqZ
E(q,Δ) = <exp(i2πqZ(Δ))>
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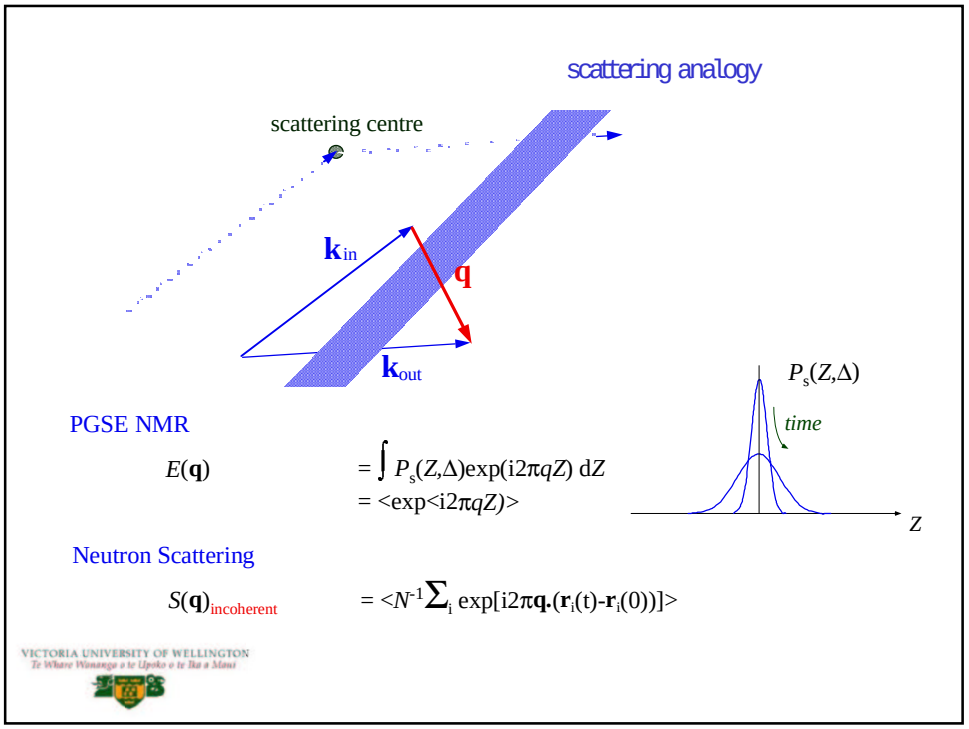
q = λ-1


scattering analogy
scattering centre
kin
q
kout
Ps(Z,Δ)
time
Z
PGSE NMR
E(q)
= ∫ Ps(Z,Δ)exp(i2πqZ) dZ
= <exp<i2πqZ)>
Neutron Scattering
S(q)incoherent
= <N-1Σi exp[i2πq.(ri(t)-ri(0))]>
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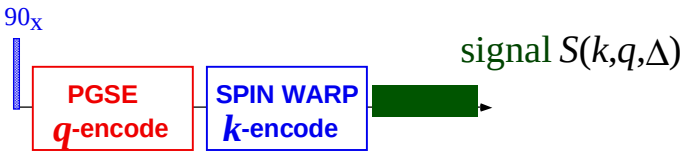
The spatial domain -
-localised velocimetry



$$F_k\{S(k,q,\Delta)\} = E(q,\Delta)$$ for each pixel

$$F_q\{E(q,\Delta)\} = \overline{P}_s(Z,\Delta)$$ for each pixel

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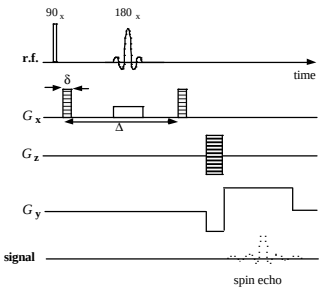
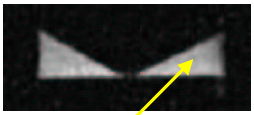
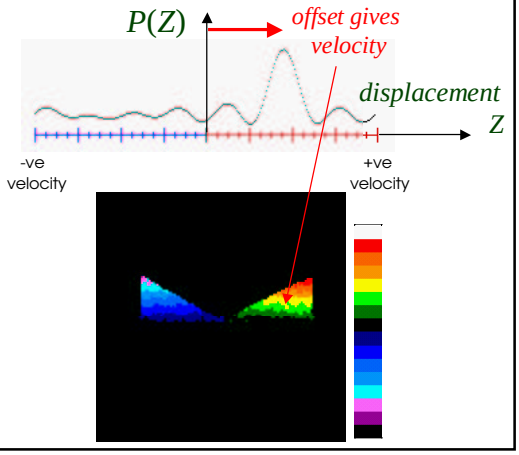




probability distribution from a single pixel



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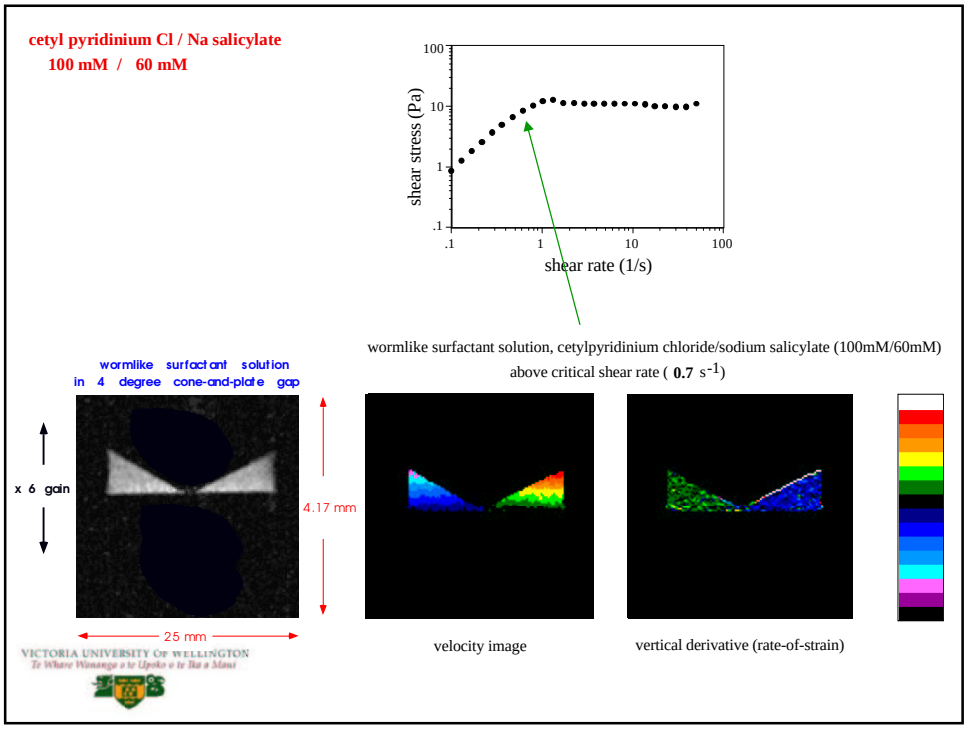
cetyl pyridinium Cl / Na salicylate
100 mM / 60 mM
shear stress (Pa)
shear rate (1/s)
wormlike surfactant solution, cetylpyridinium chloride/sodium salicylate (100mM/60mM)
above critical shear rate (0.7 s-1)
wormlike surfactant solution
in 4 degree cone-and-plate gap
x 6 gain
4.17 mm
25 mm
velocity image
vertical derivative (rate-of-strain)
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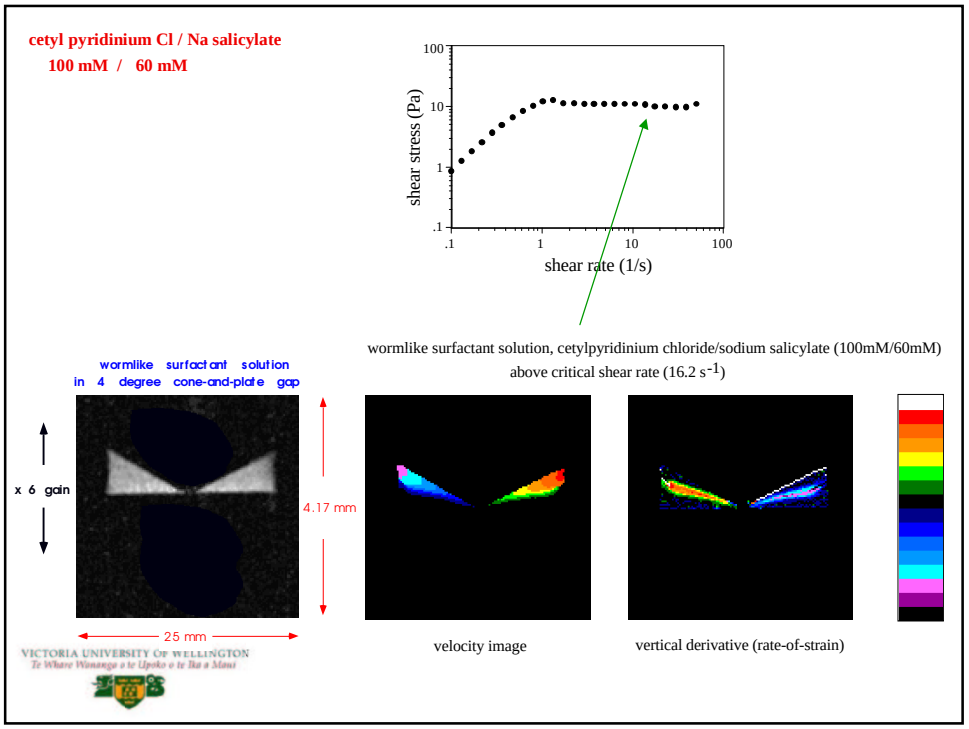
cetyl pyridinium Cl / Na salicylate
100 mM / 60 mM
shear stress (Pa)
shear rate (1/s)
wormlike surfactant solution, cetylpyridinium chloride/sodium salicylate (100mM/60mM)
above critical shear rate (16.2 s-1)
wormlike surfactant solution
in 4 degree cone-and-plate gap
x 6 gain
4.17 mm
25 mm
velocity image
vertical derivative (rate-of-strain)
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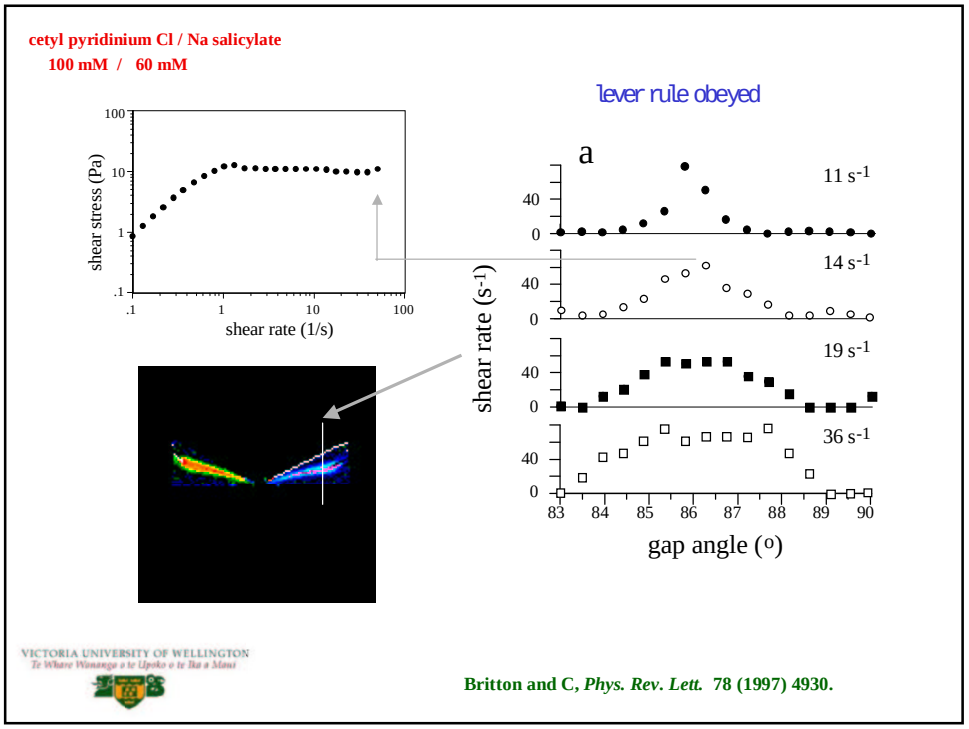
cetyl pyridinium Cl / Na salicylate
100 mM / 60 mM
lever rule obeyed
shear stress (Pa)
shear rate (1/s)
a
11 s-1
14 s-1
19 s-1
36 s-1
shear rate (s-1)
gap angle (o)
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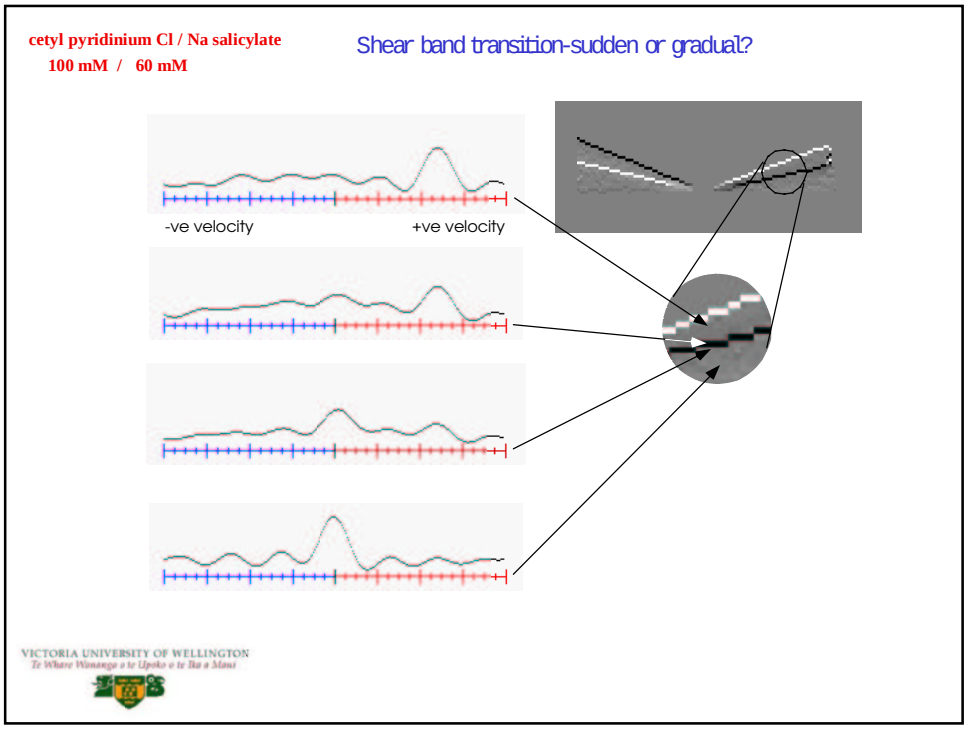
Britton and C, Phys. Rev. Lett. 78 (1997) 4930.


cetyl pyridinium Cl / Na salicylate
100 mM / 60 mM
Shear band transition-sudden or gradual?
-ve velocity
+ve velocity
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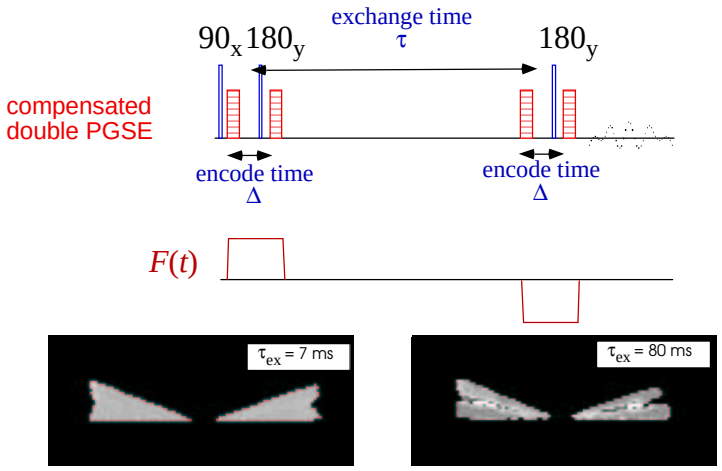
The temporal domain -
-fluctuations in translational motion



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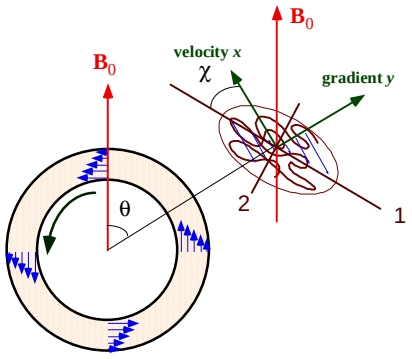
Britton and C, *Eur. Phys. Journal* B7, 237-249 (1999)

accessing the full deformation tensor



alignment tensor

$S_{\alpha\beta}=\langle u_\alpha u_\beta-\delta_{\alpha\beta}/3\rangle$

$S_{xx}=\langle u_x^2-1/3\rangle$

$S_{xy}=\langle u_x u_y\rangle$

linear entangled polymer melts
deformation under shear

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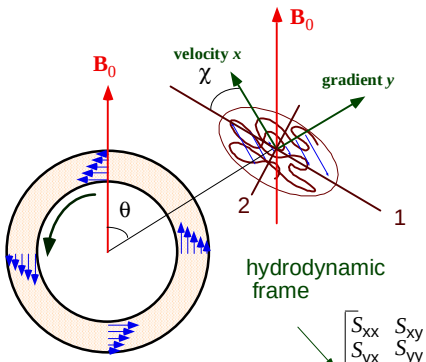
accessing the full deformation tensor



alignment tensor

$S_{\alpha\beta}=\langle u_\alpha u_\beta-\delta_{\alpha\beta}/3\rangle$

$S_{xx}=\langle u_x^2-1/3\rangle$

$S_{xy}=\langle u_x u_y\rangle$

molecular frame

hydrodynamic frame

$$\begin{bmatrix} S_{xx} & S_{xy} & 0 \\ S_{yx} & S_{yy} & 0 \\ 0 & 0 & S_{zz} \end{bmatrix} = R_3(\chi)\begin{bmatrix} S_{11} & 0 & 0 \\ 0 & S_{22} & 0 \\ 0 & 0 & S_{33} \end{bmatrix} R_3^{-1}(\chi)$$

$$\begin{bmatrix} H_{Zeeman} & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{bmatrix} = R_z(\theta)\begin{bmatrix} S_{xx} & S_{xy} & 0 \\ S_{yx} & S_{yy} & 0 \\ 0 & 0 & S_{zz} \end{bmatrix} R_z^{-1}(\theta)$$

measurement frame

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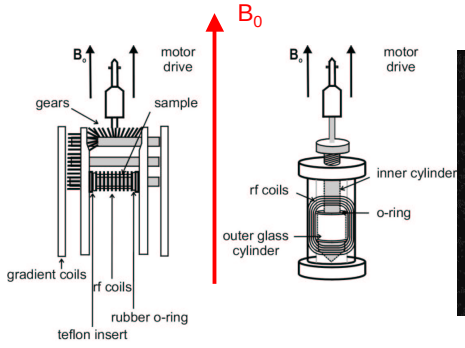
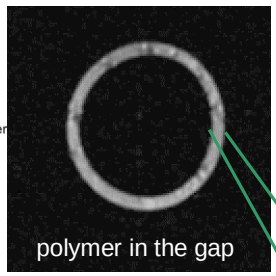
selecting the required alignment:

vorticity, or gradient/velocity along B_0

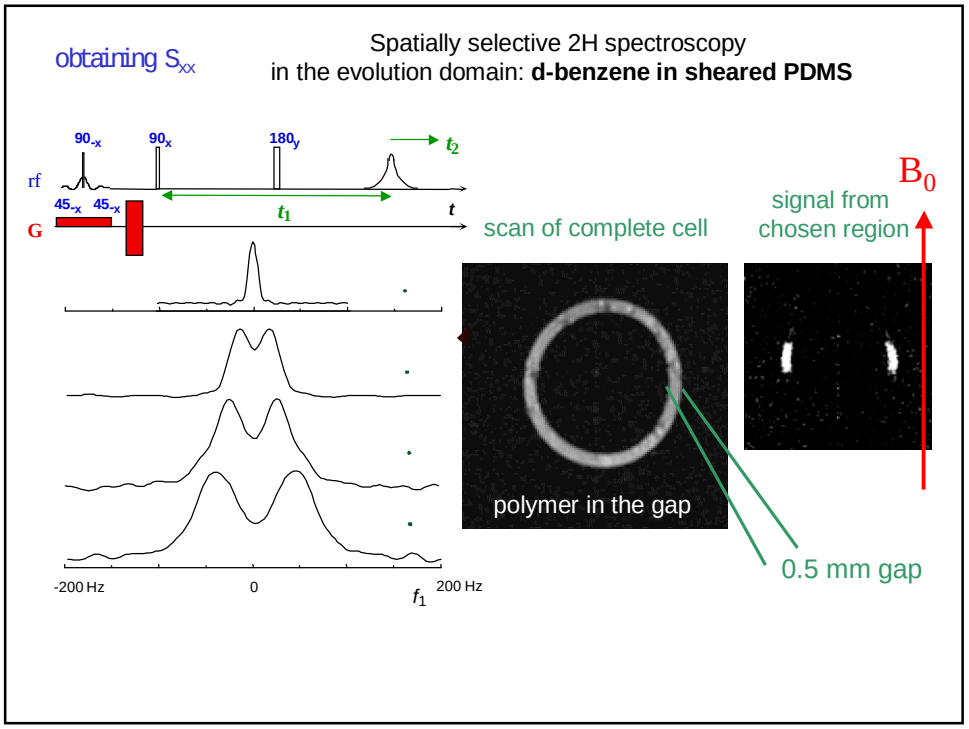


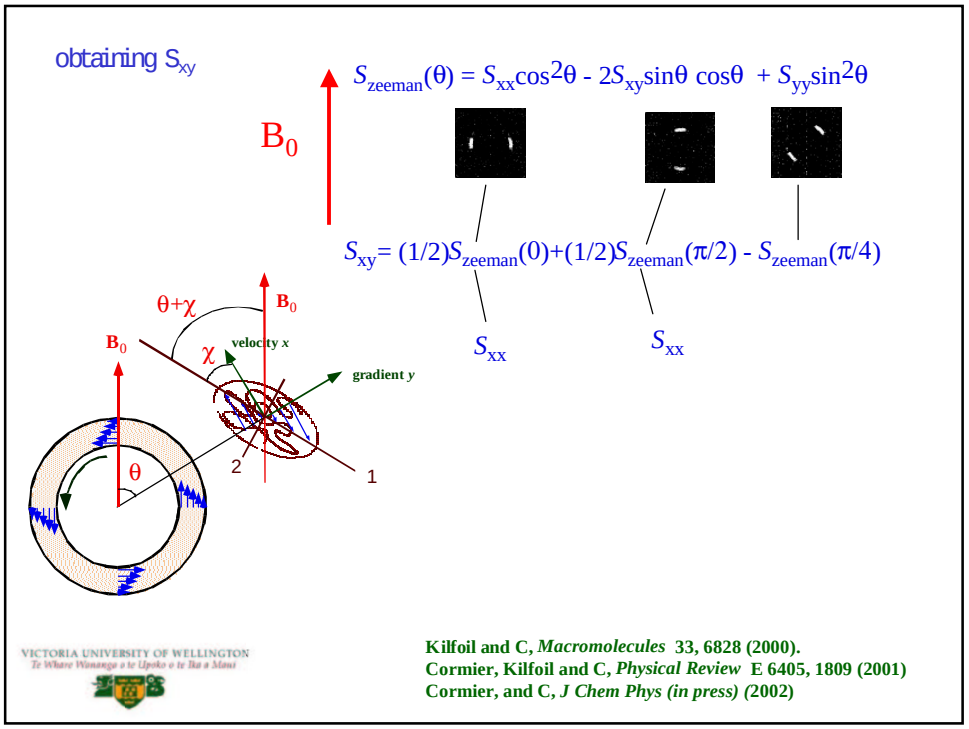
horizontal and vertical couette cells

polydimethylsiloxane-650 kD
(~65 entanglements)



0.5 mm gap


obtaining S_{xx}
Spatially selective 2H spectroscopy
in the evolution domain: **d-benzene in sheared PDMS**
90_{-x}
90_x
180_y
t_2
rf
45_{-x} 45_{-x}
t_1
t
G
-200 Hz
0
f_1
200 Hz
scan of complete cell
signal from
chosen region
B_0
polymer in the gap
0.5 mm gap


obtaining S_{xy}
$S_{zeeman}(\theta) = S_{xx}\cos^2\theta - 2S_{xy}\sin\theta\cos\theta + S_{yy}\sin^2\theta$
B_0
$S_{xy} = (1/2)S_{zeeman}(0) + (1/2)S_{zeeman}(\pi/2) - S_{zeeman}(\pi/4)$
S_{xx}
S_{xx}
$\theta+\chi$
B_0
B_0
χ
velocity x
gradient y
θ
2
1
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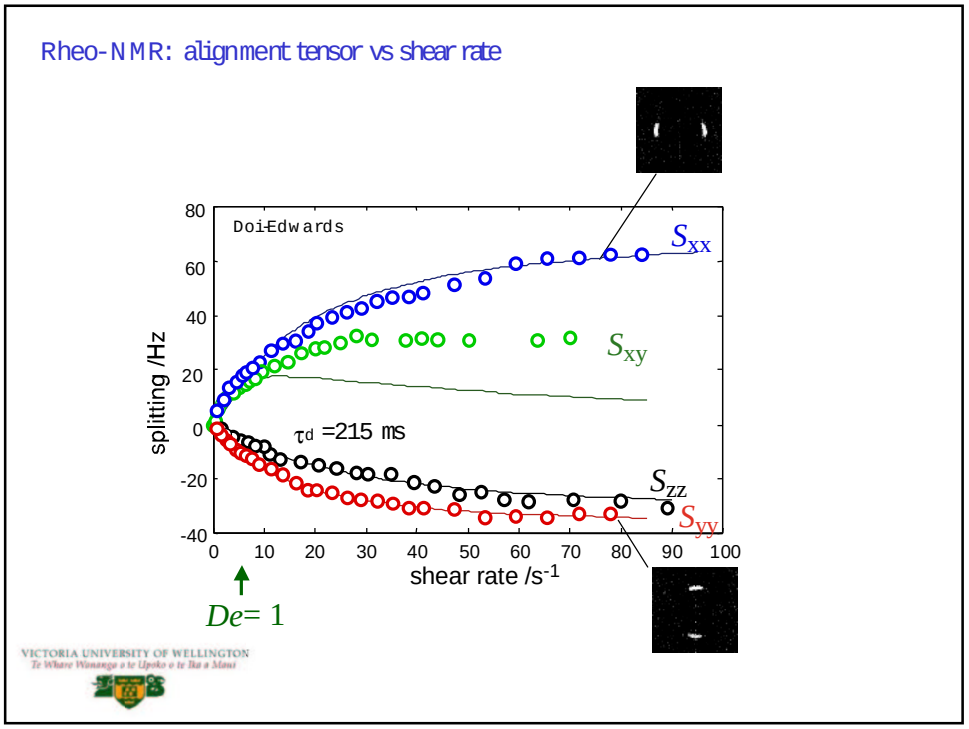
Kilfoil and C, *Macromolecules* 33, 6828 (2000).
Cormier, Kilfoil and C, *Physical Review* E 6405, 1809 (2001)
Cormier, and C, *J Chem Phys (in press)* (2002)


Rheo-NMR: alignment tensor vs shear rate
Doi-Edwards
S_{xx}
S_{xy}
S_{zz}
S_{yy}
τ_d =215 ms
splitting /Hz
shear rate /s^{-1}
80
60
40
20
0
-20
-40
0 10 20 30 40 50 60 70 80 90 100
De= 1
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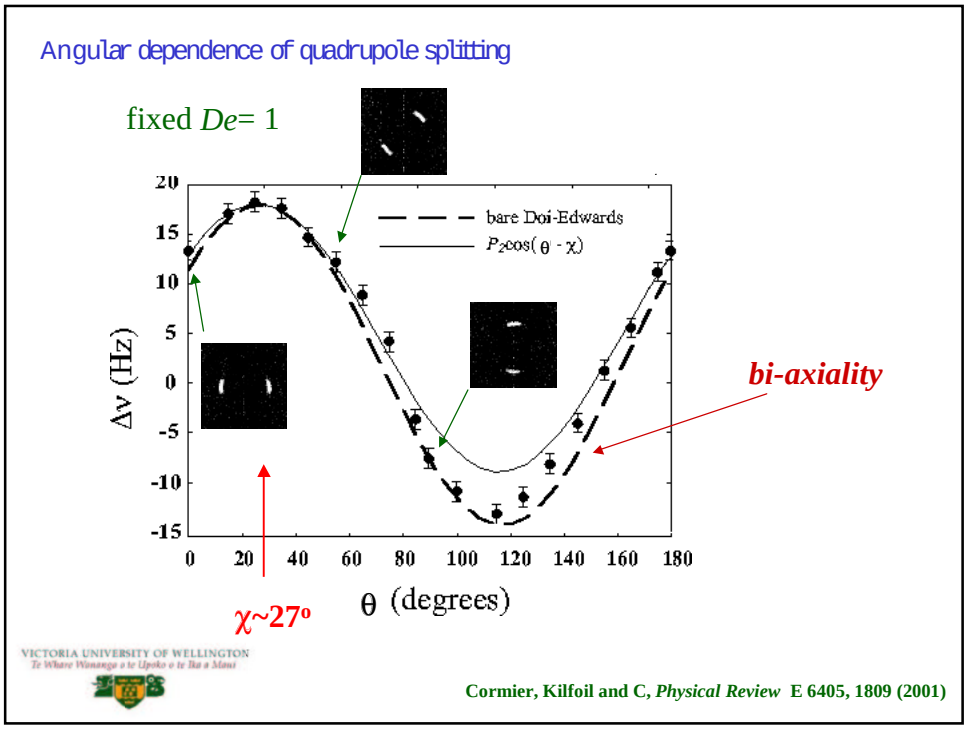
Angular dependence of quadrupole splitting
fixed De= 1
bare Doi-Edwards
$P_2\cos(\theta - \chi)$
$\Delta\nu$ (Hz)
20
15
10
5
0
-5
-10
-15
0 20 40 60 80 100 120 140 160 180
θ (degrees)
χ~27°
bi-axiality
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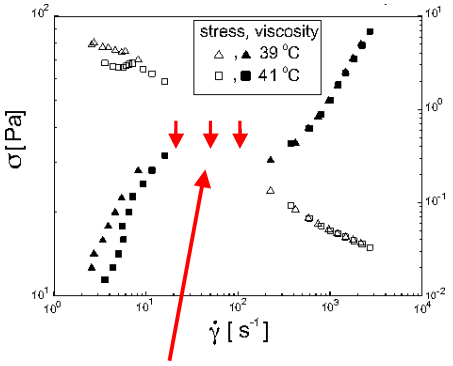
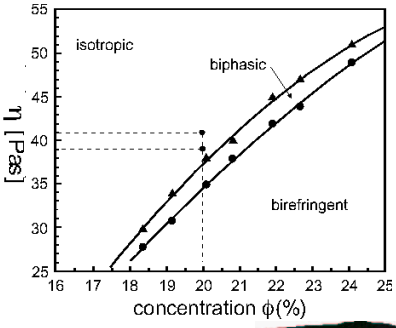
Cormier, Kilfoil and C, *Physical Review* E 6405, 1809 (2001)

Shear banding close to an I-N transition

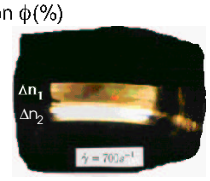
CTAB/D_2O across a Couette cell gap

Cappelaere, Berret, Decruppe, Cressely. and Lindner, *Phys. Rev. E*, 56 (1997) 1869.





use deuteron NMR to investigate orientational order



"classic flow-induced birefringence"

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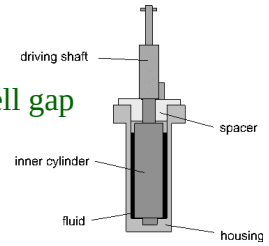
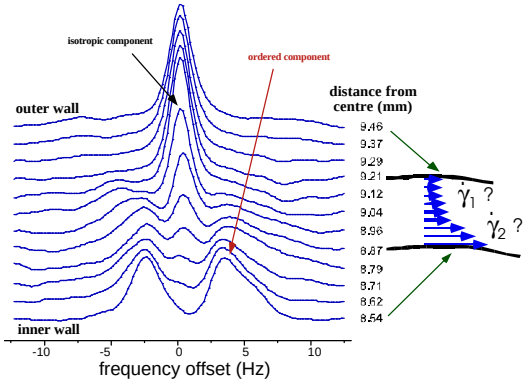
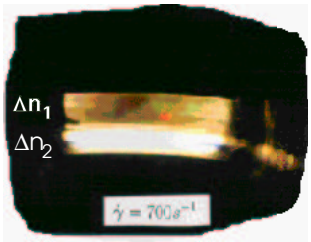
Shear banding close to an I-N transition

CTAB/D_2O: ^2H spectroscopy across a Couette cell gap







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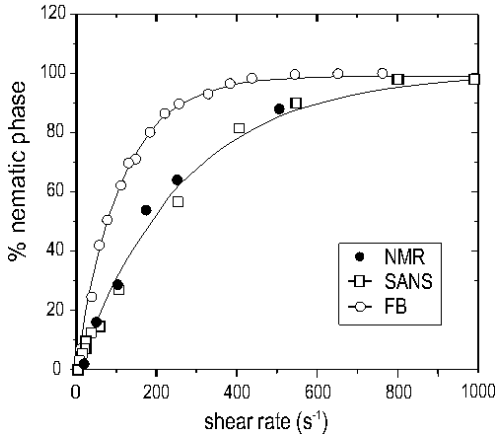
Fischer and C, *Europhysics Letters*, 50, 803 (2000)
Physical Review E, 6401, 1501 (2001)

Shear banding close to an I-N transition

CTAB/D_2O: ^2H spectroscopy
quantitation of nematic phase



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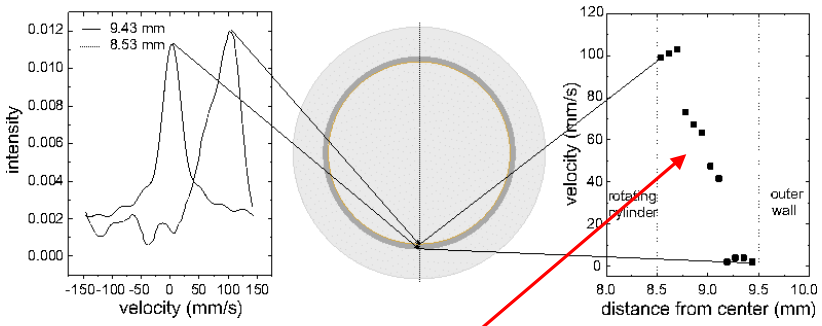
Shear banding close to an I-N transition

CTAB/D_2O: ^2H velocimetry across a Couette cell gap



Velocity distribution is "messy" near shear band

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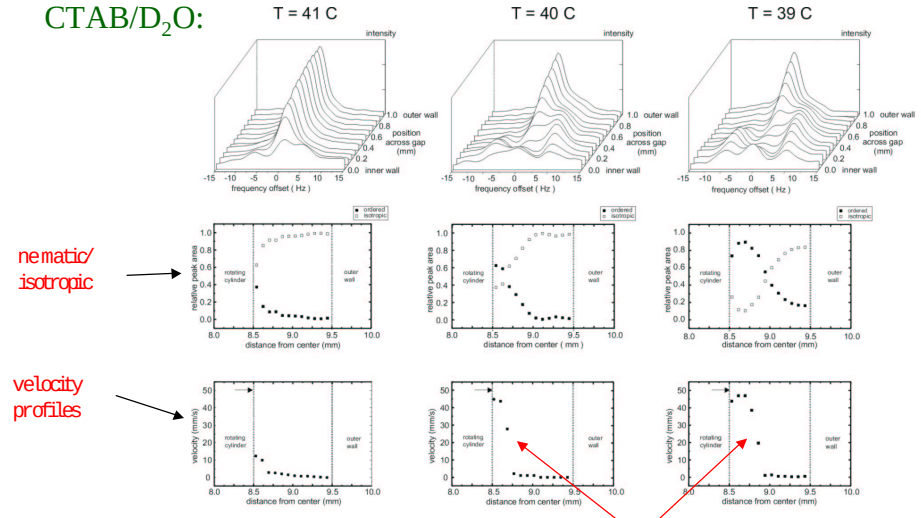
Shear banding close to an I-N transition -fixed strain rate 51 s^{-1}

$CTAB/D_2O$:



~ 200 s^{-1}

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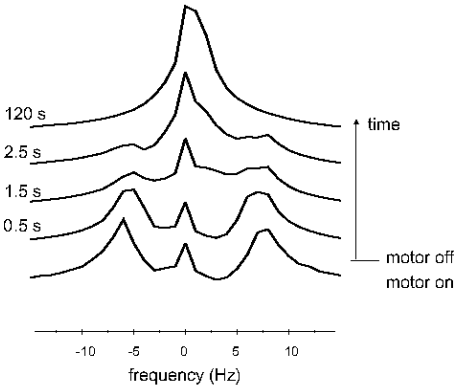
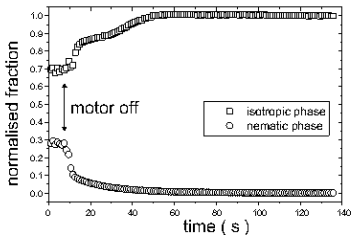
relaxation of the nematic state on shear cessation



non-equilibrium nematic state relaxes to isotropic state



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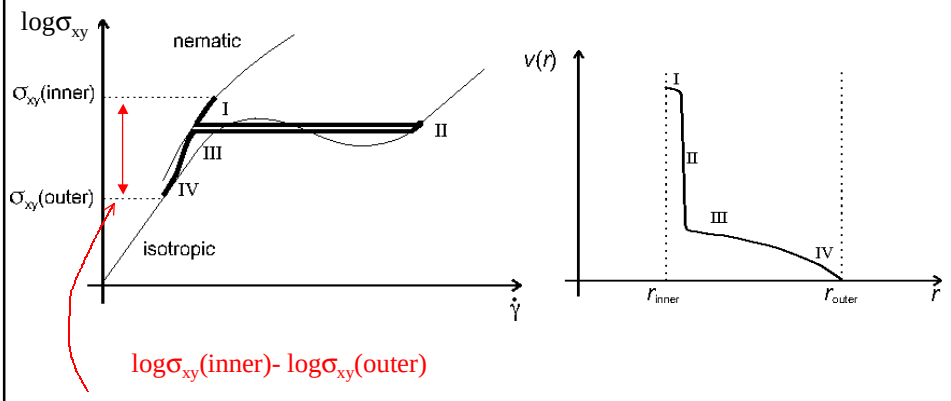
simple phenomenological model

CTAB/D_2O-strain rate controlled



logσ_{xy}(inner)- logσ_{xy}(outer)

is fixed at 2log(r_{outer}/r_{inner})

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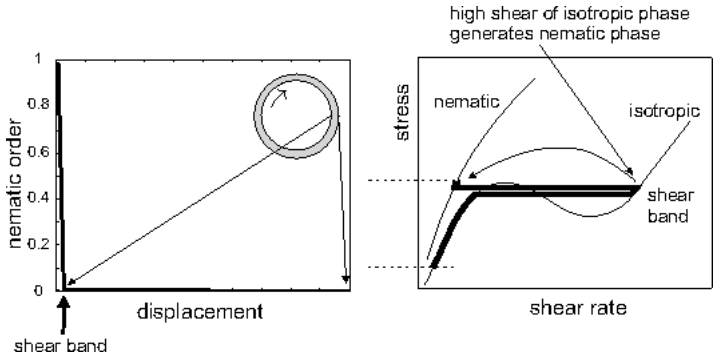
simple phenomenological model

CTAB/D_2O

CTAB/D_2O-strain rate controlled



generation
and stress migration

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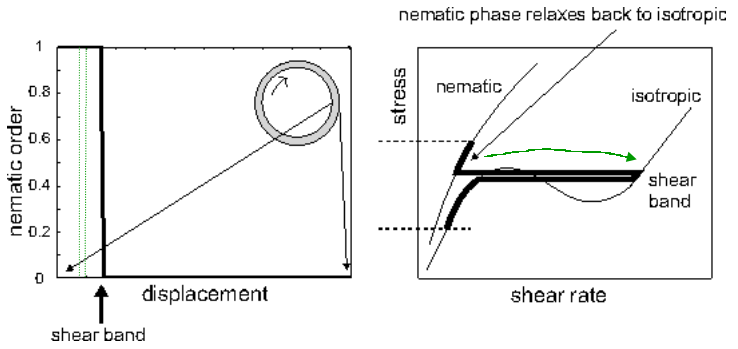
simple phenomenological model

CTAB/D_2O

CTAB/D_2O-strain rate controlled



relaxation
and stress jump

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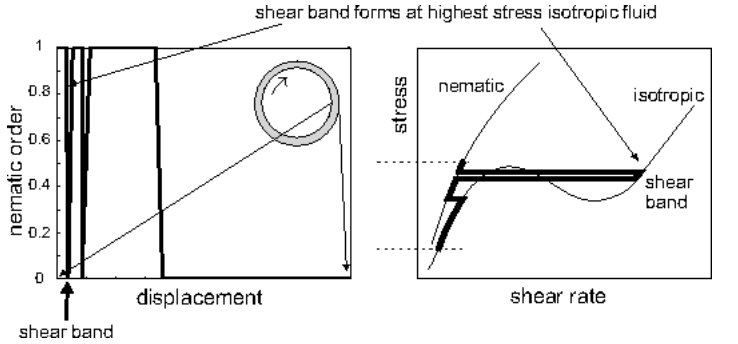
simple phenomenological model

CTAB/D_2O



steady state
competition

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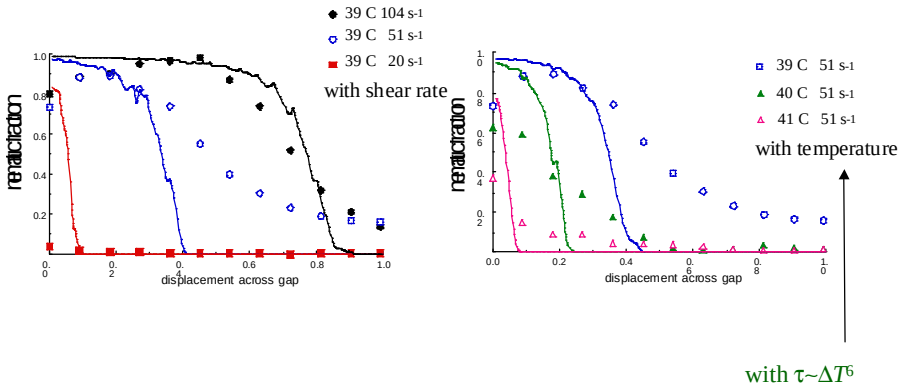
Shear banding close to an I-N transition

CTAB/D_2O: model predictions and comparison with experiment
nematic fraction across gap



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Shear banding far from an I-N transition

CPyCl/NaSal in 0.5M NaCl/D_2O
across a Couette cell (17mm/19 mm) gap
10% concentration (I-N at around 30%)

classical Maxwell-Cates system extensively studied by Berret and co-workers
-stress plateau
-shear bands observed by NMR velocimetry
-birefringence not conclusive

NMR strategy
-use deuteron NMR to investigate ordering
-NMR velocimetry by ^2H NMR
-careful analyis of pixel velocity distributions
-^1H NMR spectroscopy of micelles

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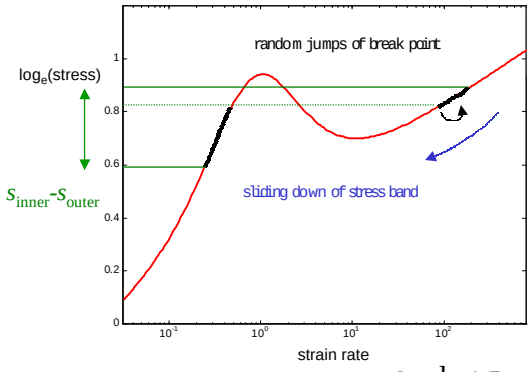
Shear banding model

10% CPyCl/NaSal in 0.5M NaCl/D_2O



$$\sigma = \frac{\dot{\gamma}}{1+(1-b)\dot{\gamma}^2} + \varepsilon\dot{\gamma}^{\alpha}$$

"Johnson-Segelman"

ε=1.7
α =0.1
b=0.89

$$s = \log\sigma, \qquad s_{inner} - s_{outer} = 2\log\left(\frac{R_{outer}}{R_{inner}}\right)$$

fixed by geometry

$$\omega_{inner} = \int_{s_{outer}}^{s_{inner}} \dot{\gamma}(s)\,ds$$

fixed for strain rate controlled

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