Extensional Flow-SANS of Wormlike Micelles

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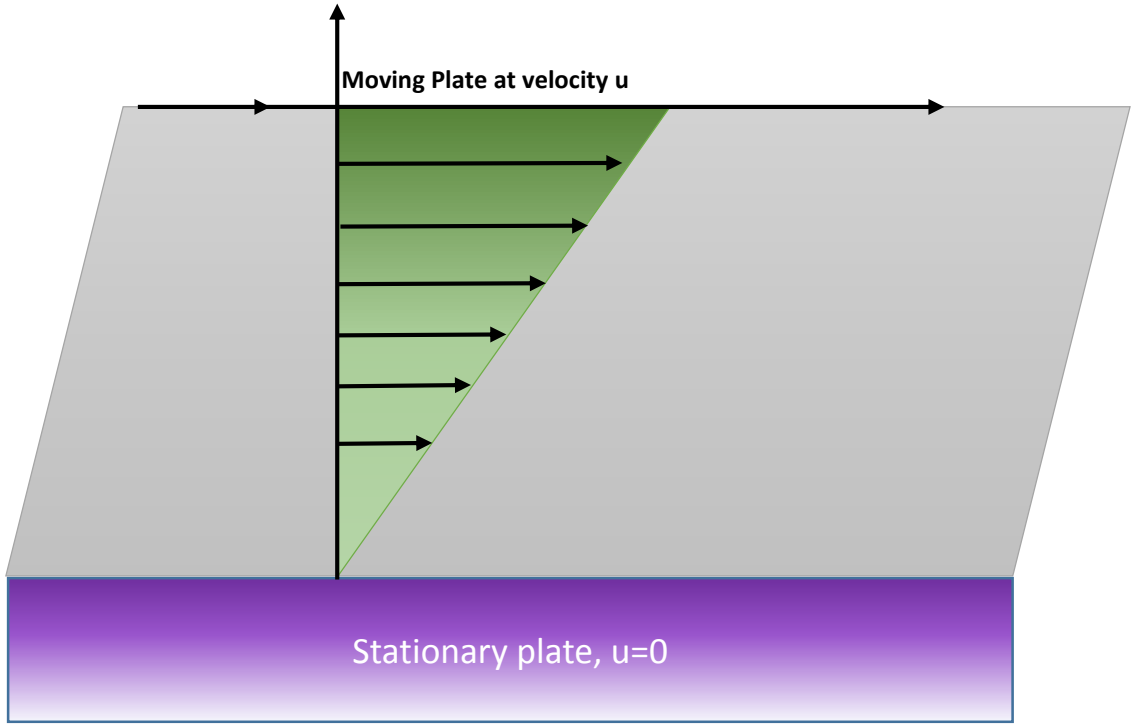
Katie Weigandt (NIST-NCNR)
NIST Symposium
August 6, 2014

NIST
National Institute of Standards and Technology
U.S. Department of Commerce

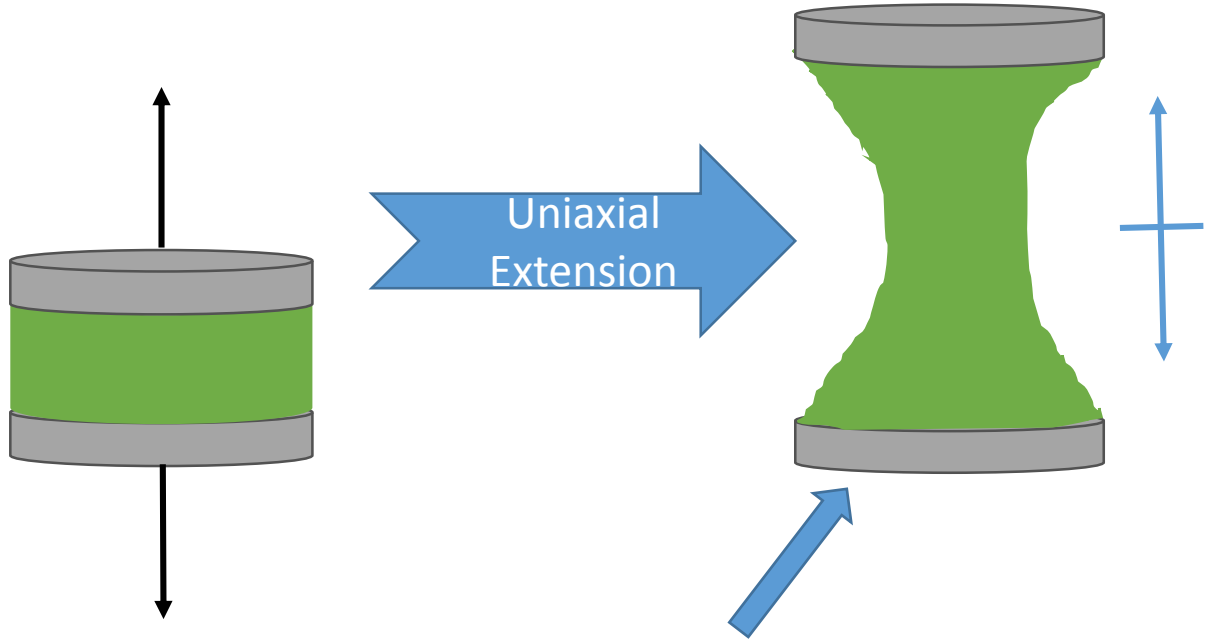
nSoft
A consortium for the advancement of neutron-based measurements for manufacturing of soft materials.

Shear vs Extensional Flow

Shear Flow



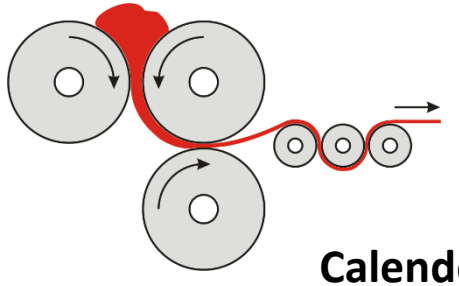
Extensional Flow



Viscoelastic Media
-Stretching Deformation

Extensional Flow Applications

Polymers, Foods, and Fabric Processing

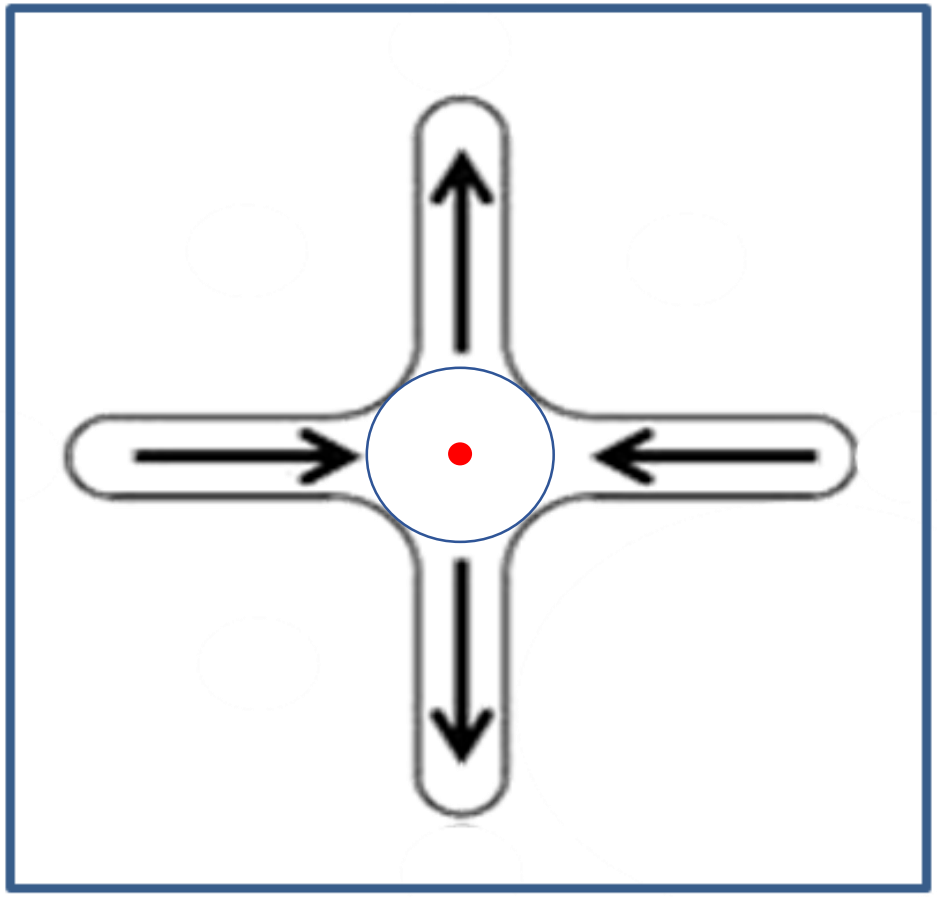


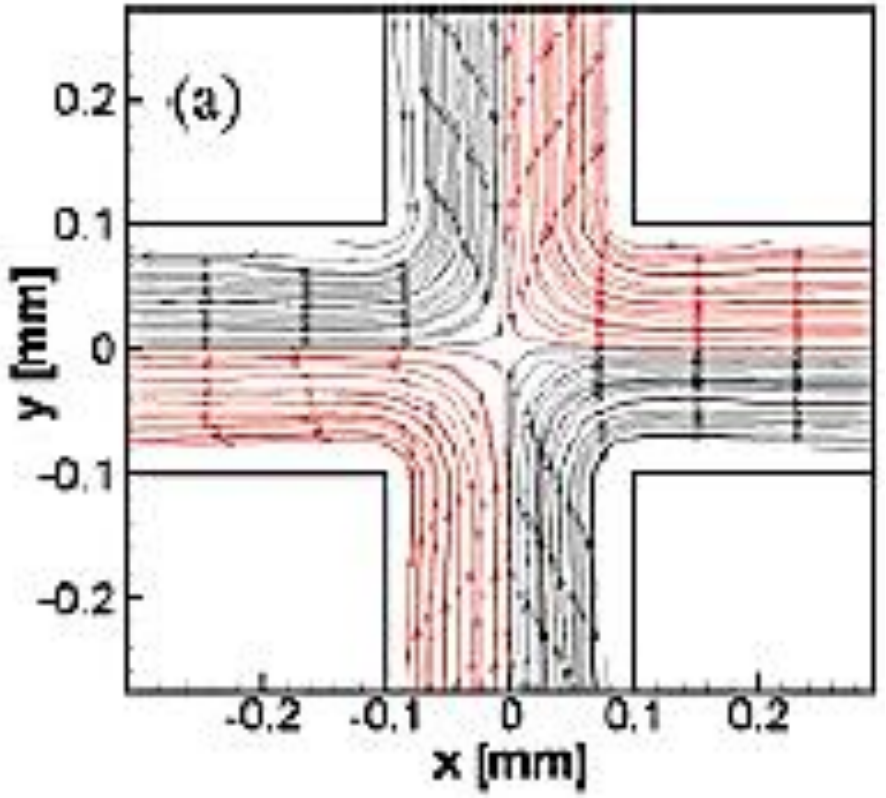
Calendering & Extrusion

Consumer Care Products & Complex Fluids

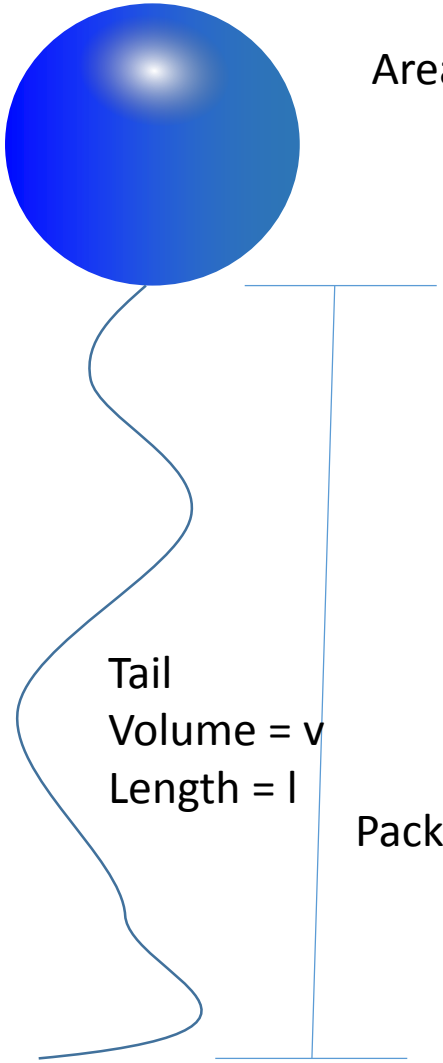
[1] http://specialtyfabricsreview.com/articles/0112_f1_engineered_fabrics.html
[2] http://www.italgi.it/e-multipla.htm
[3] http://glossary.periodni.com/glossary.php?en=calendering
[4] http://thelogisticsproject.blogspot.com/2012/05/l
[5] http://en.wikipedia.org/wiki/Soft_serve

Cross-Slot Flow Cells





Wormlike Micelles



Area of Head = a

Tail
Volume = v
Length = l

Packing Parameter

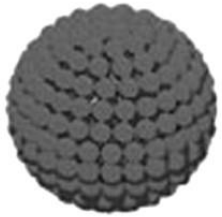
$$p = \frac{v}{al}$$

head group
(area = a)

tail
(volume = v
length = l)

packing parameter

$p = v/la$



$p<1/3$

$1/3<p<1/2$

$1/2<p<1$

$p>1$

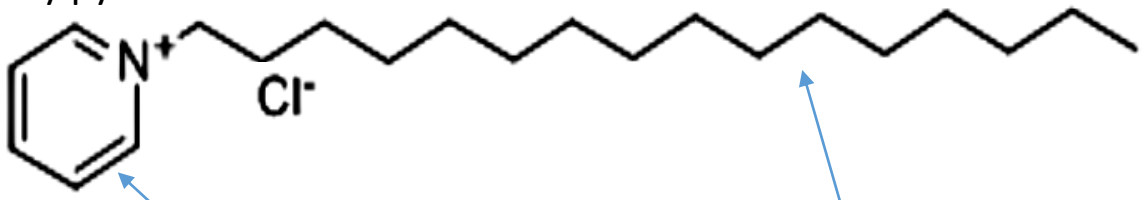
O'Reilly R Phil. Trans. R. Soc. A 2007;365:2863-2878

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

Wormlike Micelles

Surfactant *Molecule*

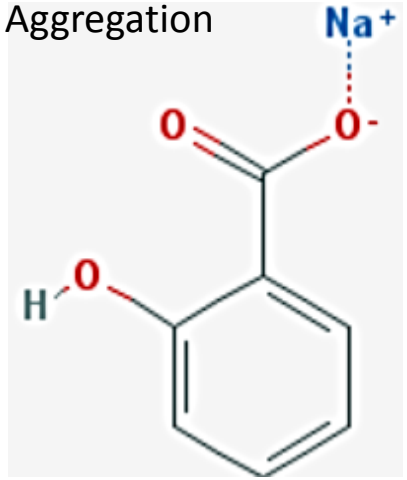
Cationic Surfactant
Cetylpyridinium Chloride



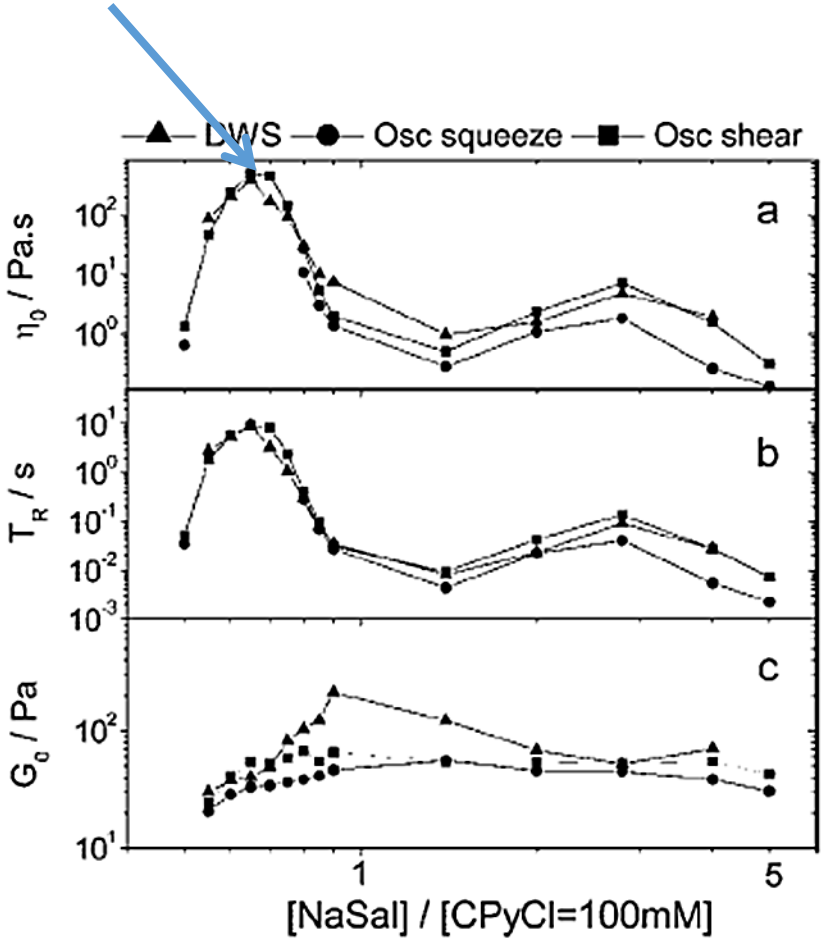
Hydrophilic Head

Hydrophobic Body

Salt Causing Aggregation



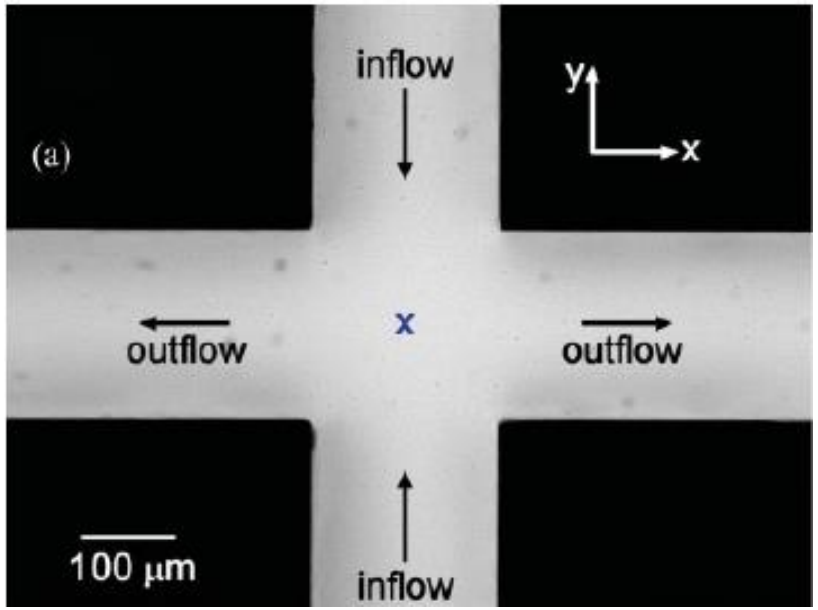
Sodium Salicylate

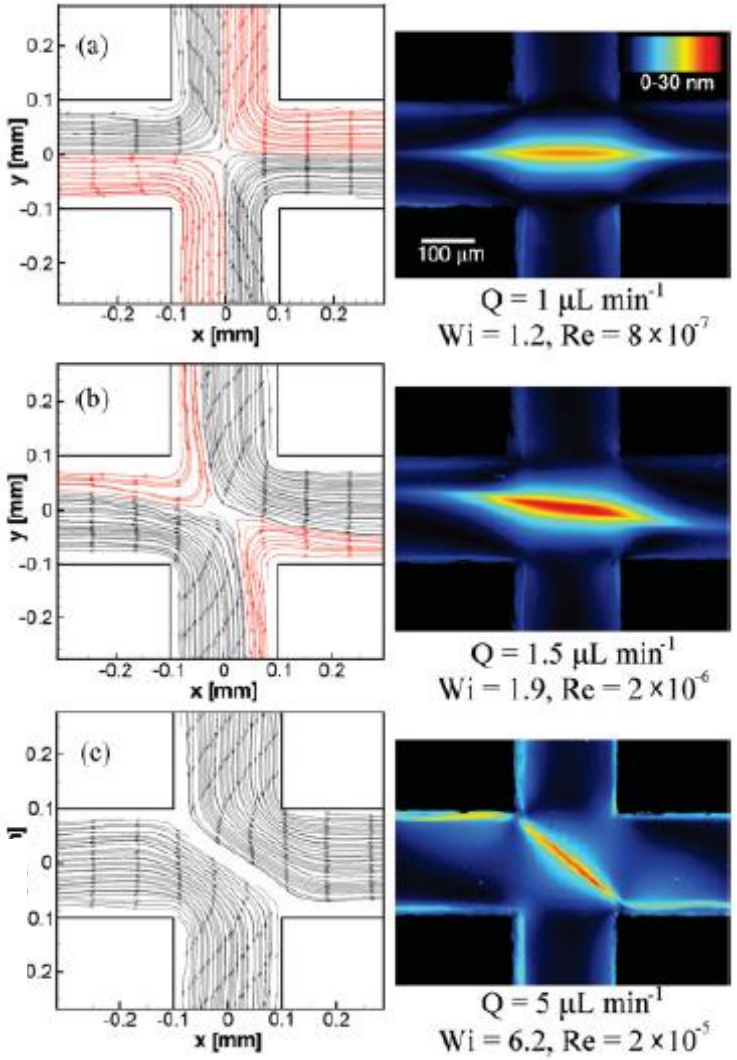


[5]Clausen, T.M. "Viscoelsatic Micellar Solutions." Journal of Physical Chemistry.

Microfluidic Flow-Cells

[4]





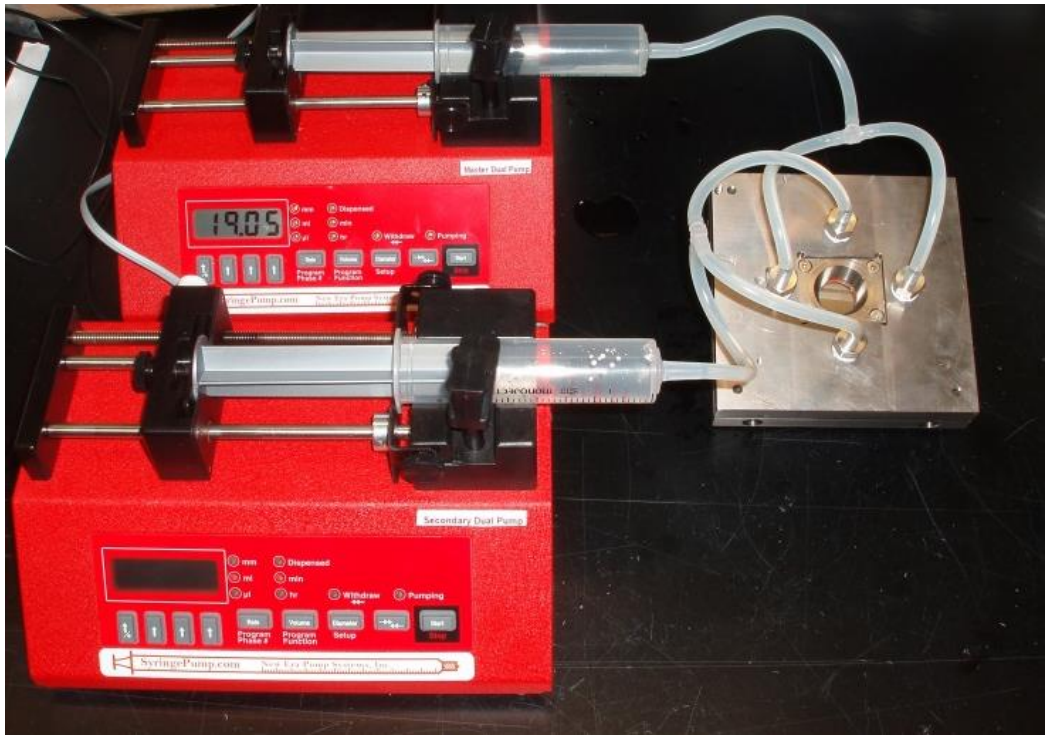
PHYSICAL REVIEW E 85, 031502 (2012)

Stagnation point flow of wormlike micellar solutions in a microfluidic cross-slot device: Effects of surfactant concentration and ionic environment

Simon J. Haward* and Gareth H. McKinley
Hatsopoulos Microfluids Laboratory, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
(Received 14 December 2011; published 14 March 2012)

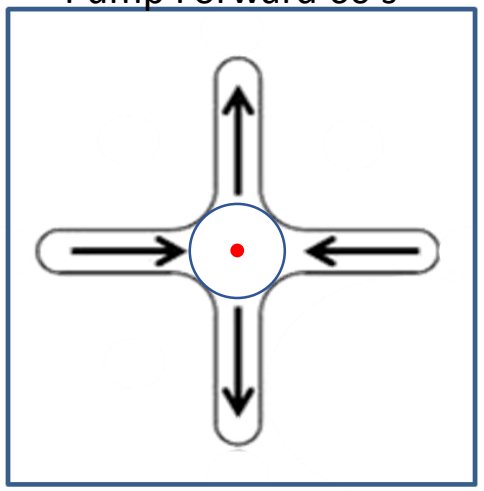
Start-Stop Extensional Flow Experiment

Syringe Pumps Manages Flow

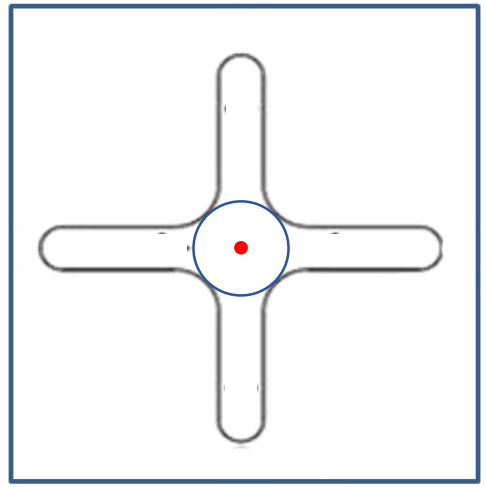


10x 1.63mm Cross-Slot

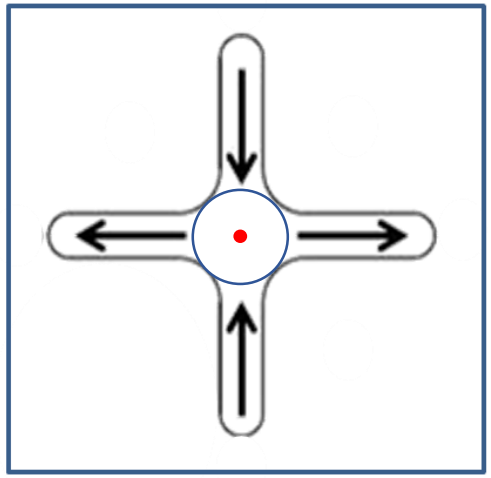
Step 1
Pump Forward 60 s



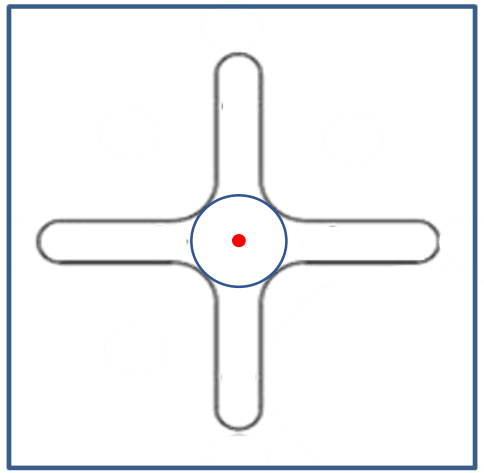
Step 2
Relax 60 s



Step 3
Reverse Pump 60 s

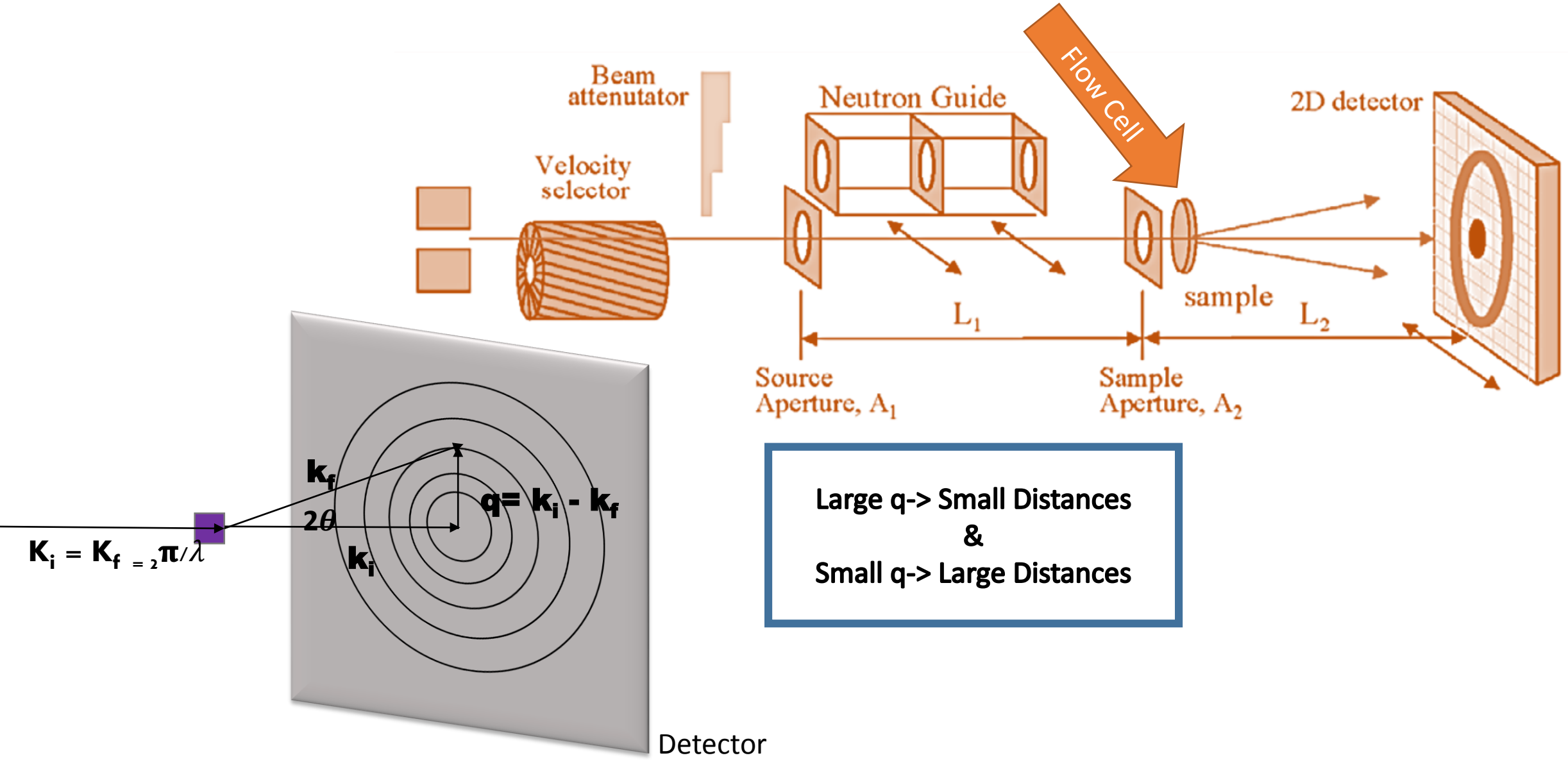


Step 4
Relax 60 s



Repeats

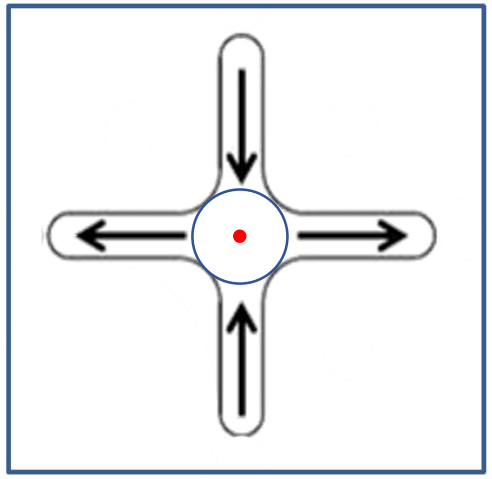
Small Angle Neutron Scattering (SANS)



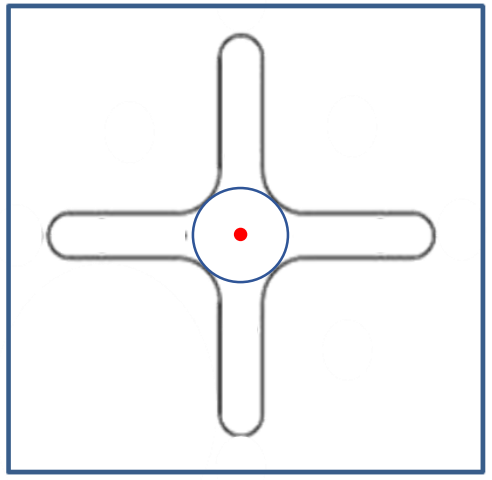
Large q-> Small Distances
&
Small q-> Large Distances

Start-Stop Extensional Flow Measurements

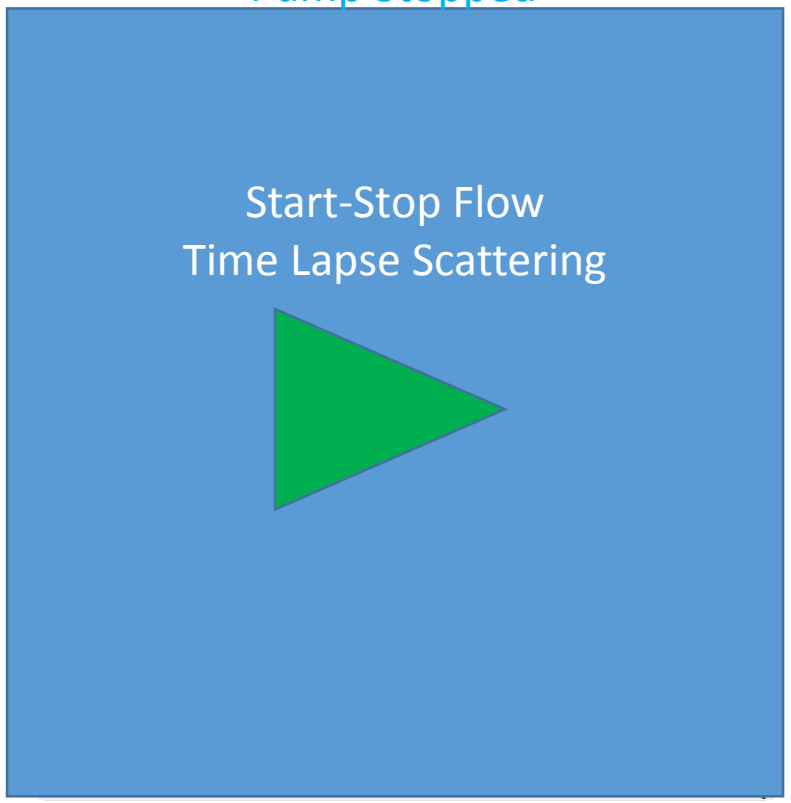
Step 3
Pump Reverse 60 s



Step 4
Relax 60 s

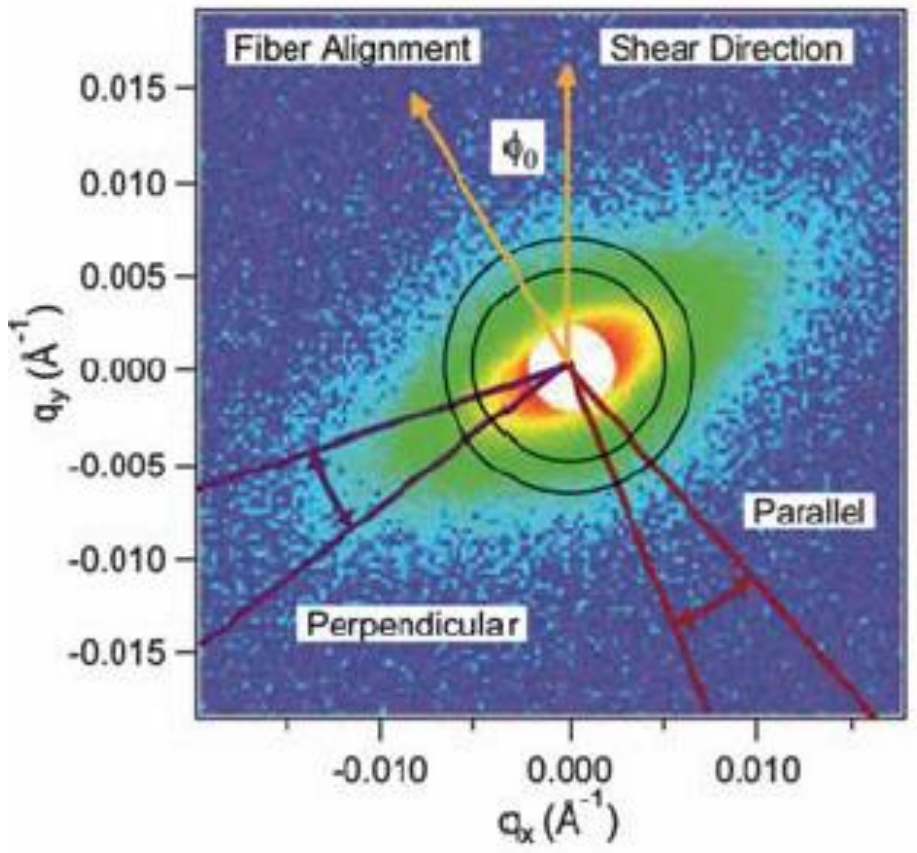


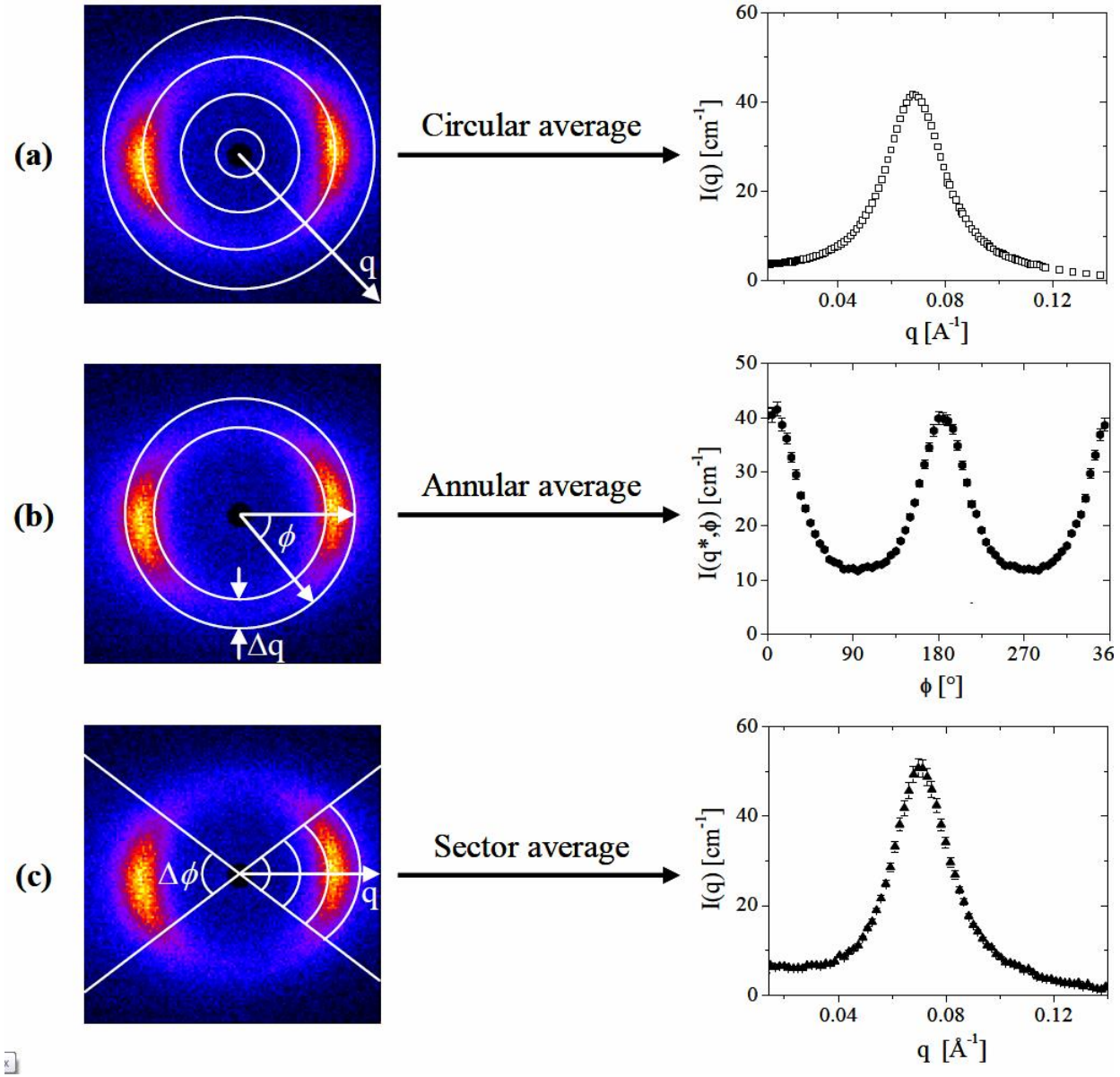
Pump Stopped



Each scattering pattern averages over 3 seconds

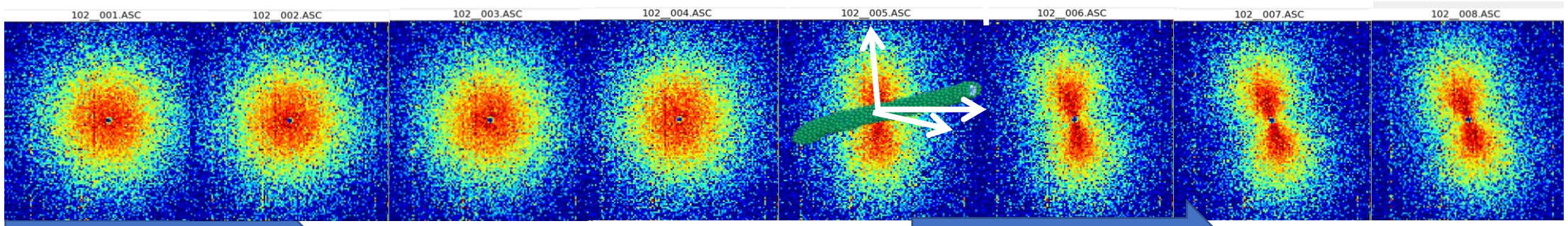
Averages for Data Analysis





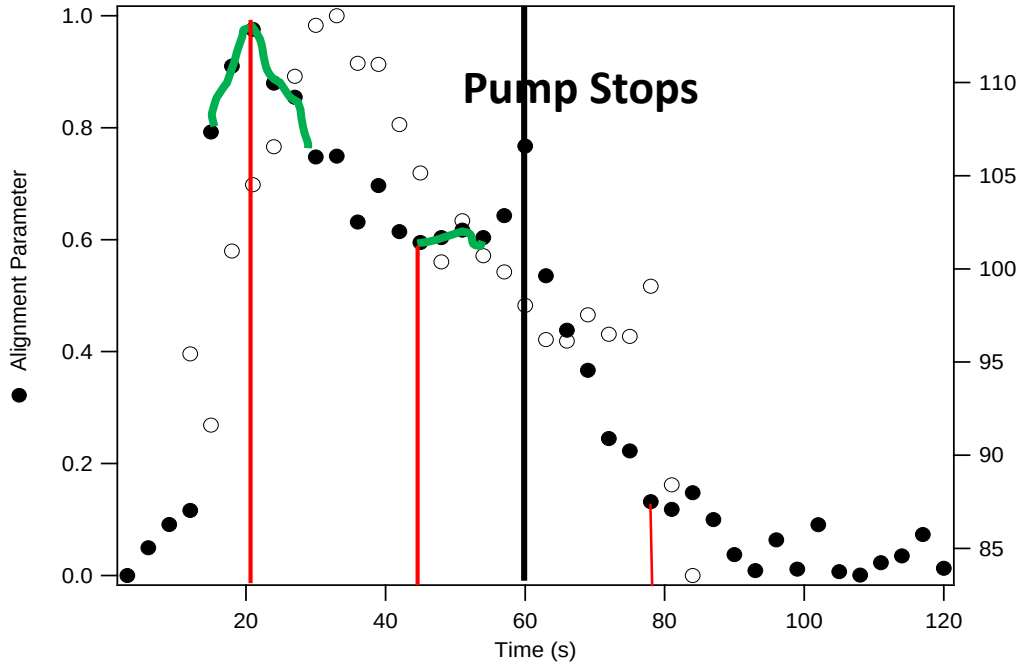
[5]SANS Team. ***In situ*** **neutron scattering study of structural transitions in fibrin networks under shear deformation. NIST NCNR, June 2012. (accessed June 6, 2014).**

Structural Transitions of Micelles



Flow Begins

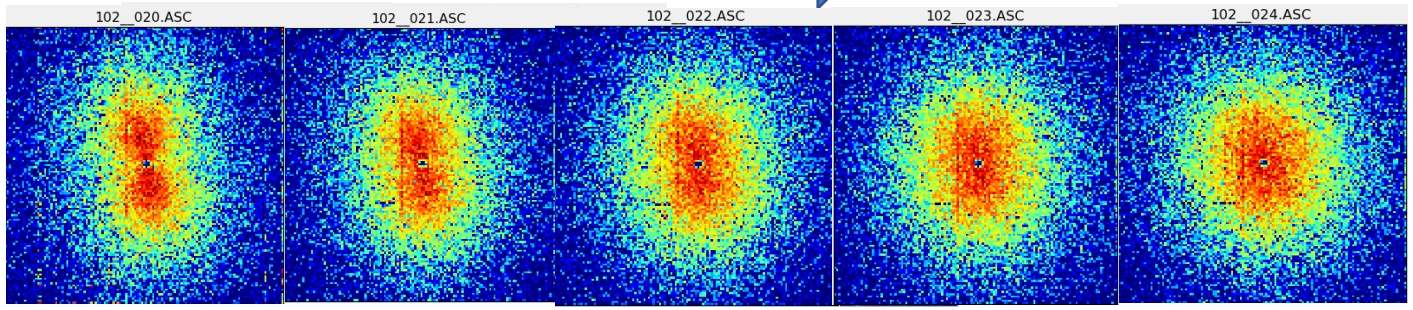
Horizontal Alignment



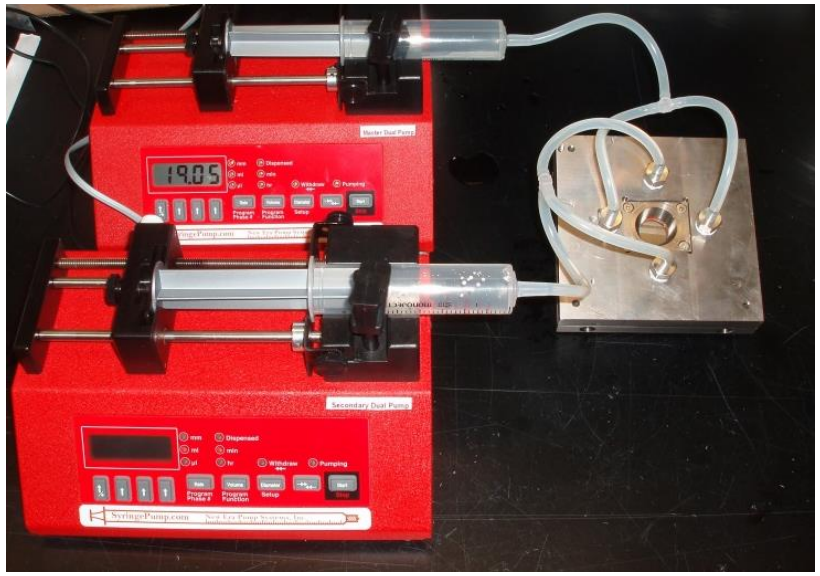
Time Dependent Alignment

Flow Stops

Relaxation



Unidirectional Flow Experiment

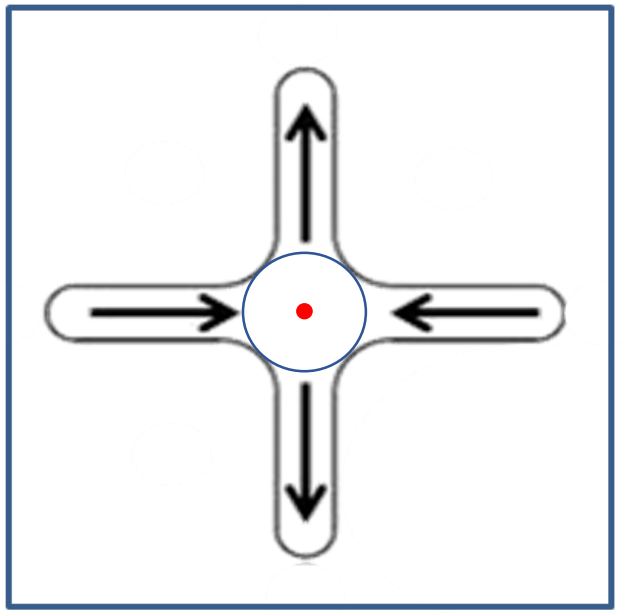


Extensional Strain Rate

$$\varepsilon = \frac{Q}{hd^2}$$

Shear Strain Rate

$$\gamma(y) = \frac{1}{2} * \frac{6Q}{w\,h^2}$$



3 Geometries:
2x 1.41 mm
2x 3.23 mm
2x 5.00 mm

1.63mm

$\dot{\varepsilon}\ (s^{-1})$	Q	$\dot{\gamma}$
ε(1/s)	Q (mL/min)	γ (1/s)
0.01	0.0978	11.04294
0.1	0.978	110.4294
0.5	4.89	552.1472
1	9.78	1104.294
5	48.9	5521.472
7.5	73.35	8282.209
10	97.8	11042.94

1.41mm

Q	$\dot{\varepsilon}\ (s^{-1})$	$\dot{\gamma}$
Q (mL/min)	ε(1/s)	γ (1/s)
0.003384	0.01	2.553191
0.03384	0.1	25.53191
0.1692	0.5	127.6596
0.3384	1	255.3191
1.692	5	1276.596
2.538	7.5	1914.894
3.384	10	2553.191

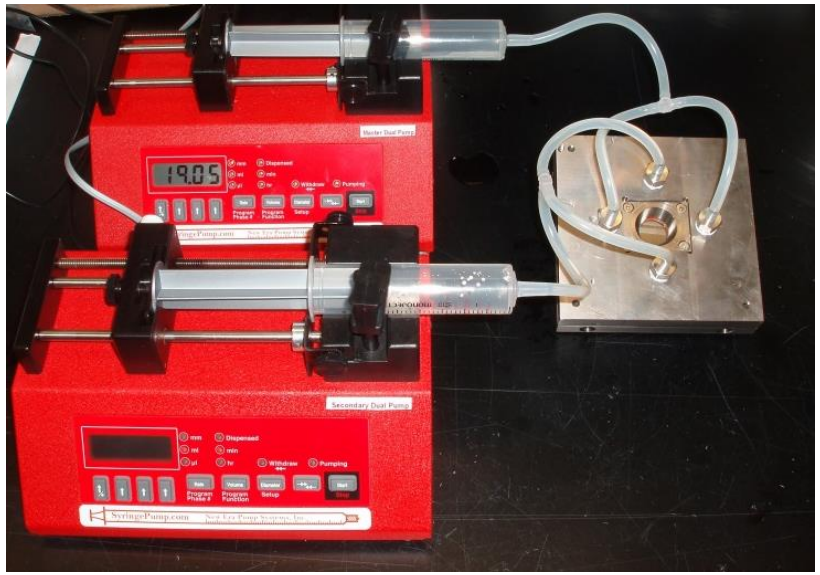
2.32mm

Q	$\dot{\varepsilon}\ (s^{-1})$	$\dot{\gamma}$
Q (mL/min)	ε (1/s)	γ (1/s)
0.007752	0.01	1.8
0.07752	0.1	18
0.3876	0.5	90
0.7752	1	180
3.876	5	900
5.814	7.5	1350
7.752	10	1800

5.00mm

Q	$\dot{\varepsilon}\ (s^{-1})$	$\dot{\gamma}$
Q (mL/min)	ε (1/s)	γ (1/s)
0.012	0.01	1.8
0.12	0.1	18
0.6	0.5	90
1.2	1	180
6	5	900
9	7.5	1350
12	10	1800

Unidirectional Flow Experiment

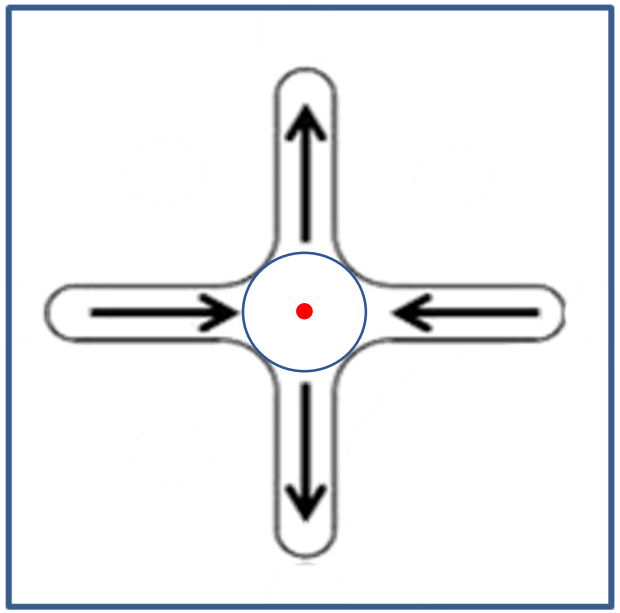


Extensional Strain Rate

$$\varepsilon = \frac{Q}{hd^2}$$

Shear Strain Rate

$$\gamma(y) = \frac{1}{2} * \frac{6Q}{w\,h^2}$$



3 Geometries:
2x 1.41 mm
2x 3.23 mm
2x 5.00 mm

0.163mm

$\dot{\varepsilon}\ (s^{-1})$ Q $\dot{\gamma}$

ε(1/s)	Q (mL/min)	γ (1/s)
0.01	0.0978	11.0
0.1	0.978	110.4
0.5	4.89	552.1
1	9.78	1104.3
5	48.9	5521.4
7.5	73.35	8282.2
10	97.8	11042.9

0.141mm

Q $\dot{\varepsilon}\ (s^{-1})$ $\dot{\gamma}$

Q (mL/min)	ε(1/s)	γ (1/s)
0.003384	0.01	2.6
0.03384	0.1	25.5
0.1692	0.5	127.7
0.3384	1	255.3
1.692	5	1276.6
2.538	7.5	1914.9
3.384	10	2553.2

0.232mm

Q $\dot{\varepsilon}\ (s^{-1})$ $\dot{\gamma}$

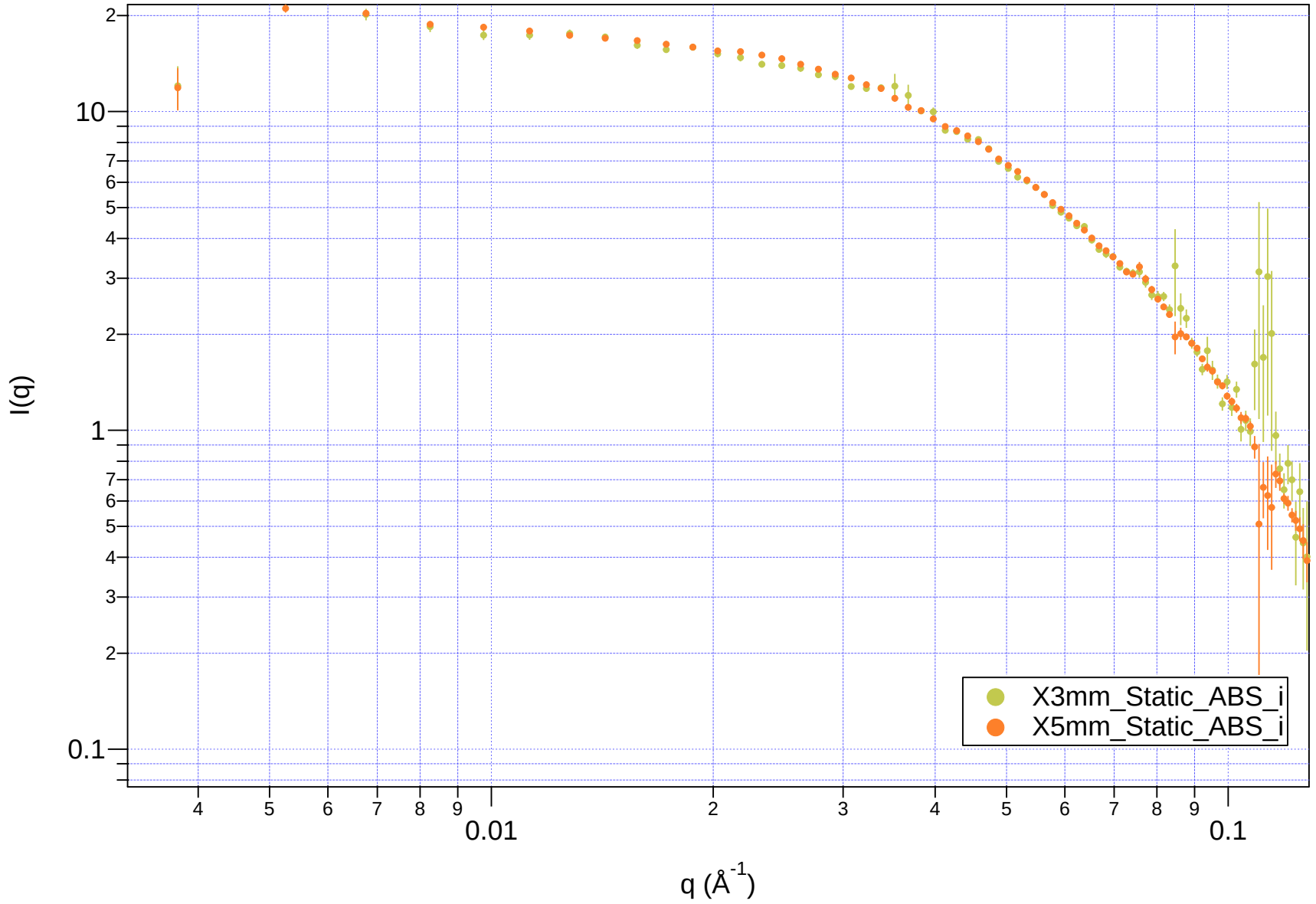
Q (mL/min)	ε (1/s)	γ (1/s)
0.007752	0.01	1.8
0.07752	0.1	18
0.3876	0.5	90
0.7752	1	180
3.876	5	900
5.814	7.5	1350
7.752	10	1800

0.500mm

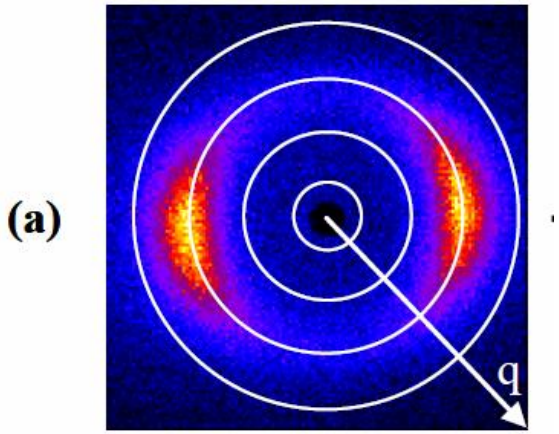
Q $\dot{\varepsilon}\ (s^{-1})$ $\dot{\gamma}$

Q (mL/min)	ε (1/s)	γ (1/s)
0.012	0.01	1.8
0.12	0.1	18
0.6	0.5	90
1.2	1	180
6	5	900
9	7.5	1350
12	10	1800

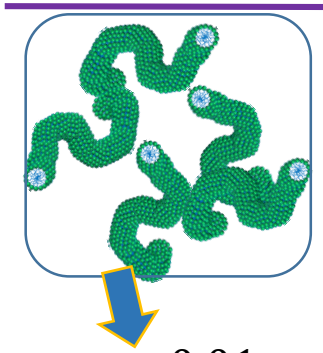
Circular Average of Static File



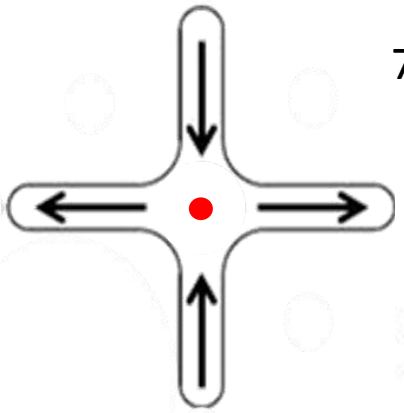
Same, so NO Multiple Scattering Effects!



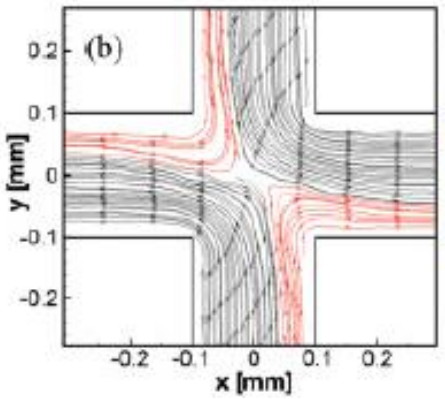
2x 1.41mm Cross-Slot

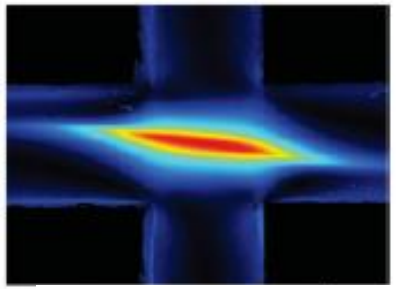


Isotropic Scattering
Indicates randomly oriented worm-like micelles



Worm-Like Micelles in D_2O
75 mM Cetylpyridinium Chloride
45 mM Sodium Salicylate

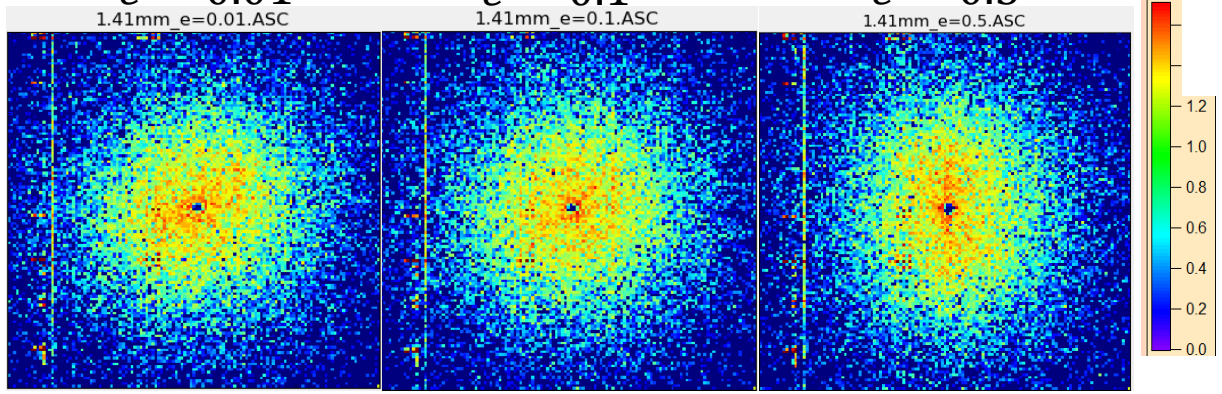




$\varepsilon = 0.01$
1.41mm_e=0.01.ASC

$\varepsilon = 0.1$
1.41mm_e=0.1.ASC

$\varepsilon = 0.5$
1.41mm_e=0.5.ASC

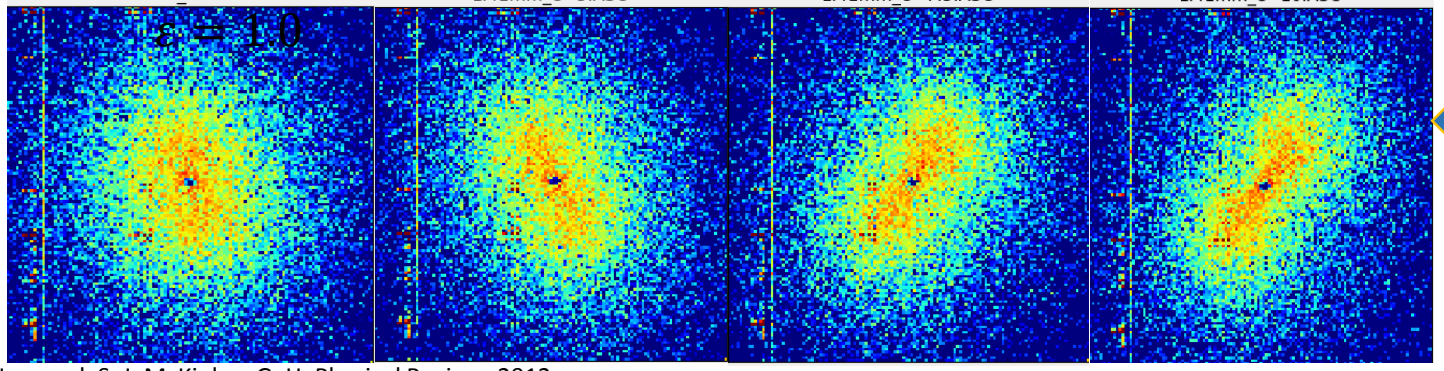


$\varepsilon = 1.0$
1.41mm_e=1.ASC

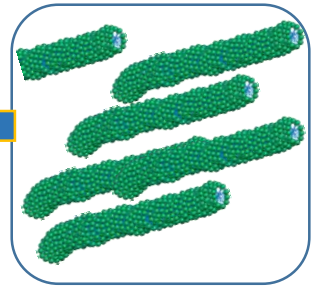
$\varepsilon = 5.0$
1.41mm_e=5.ASC

$\varepsilon = 7.5$
1.41mm_e=7.5.ASC

$\varepsilon = 10$
1.41mm_e=10.ASC

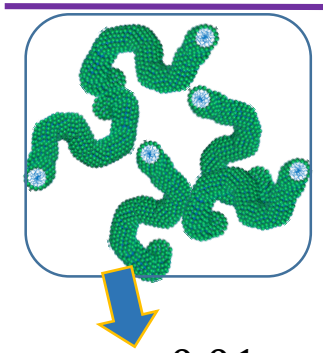


Anisotropic Scattering
Indicates oriented worm-like micelles



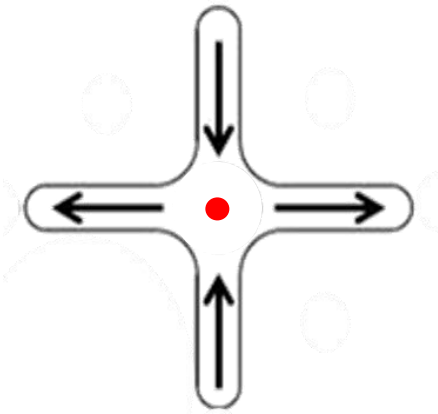
Hayward, S. J. McKinley, G. H. Physical Review. 2012.

2x 3.23mm Cross-Slot

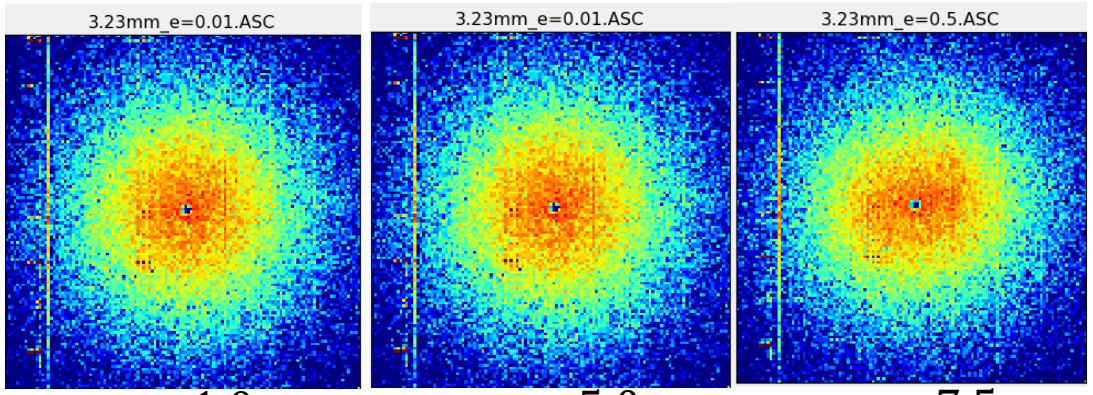


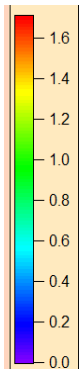
Isotropic Scattering
Indicates randomly oriented worm-like micelles

Worm-Like Micelles in D_2O
75 mM Cetylpyridinium Chloride
45 mM Sodium Salicylate

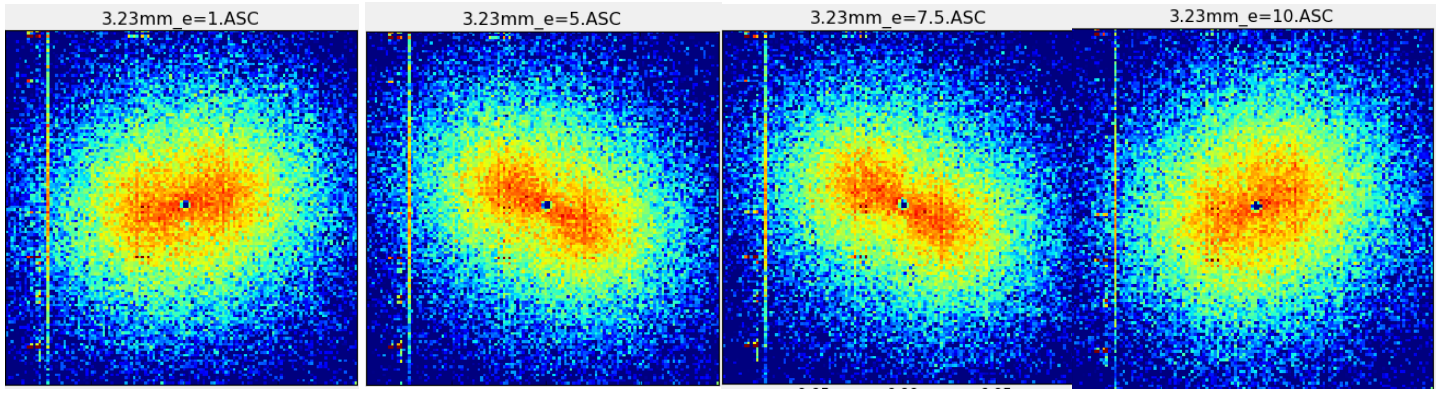


$\varepsilon = 0.01$ $\varepsilon = 0.1$ $\varepsilon = 0.5$

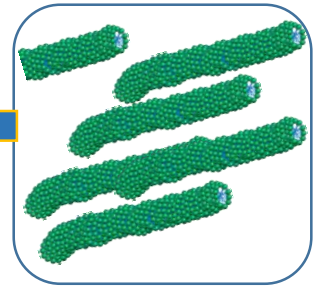




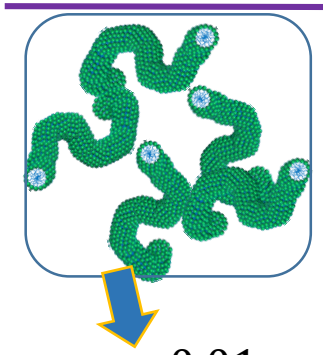
$\varepsilon = 1.0$ $\varepsilon = 5.0$ $\varepsilon = 7.5$ $\varepsilon = 10$



Anisotropic Scattering
Indicates oriented worm-like micelles

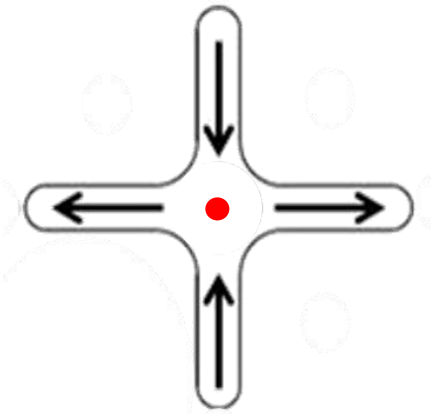


2.00x5.00mm Cross-Slot

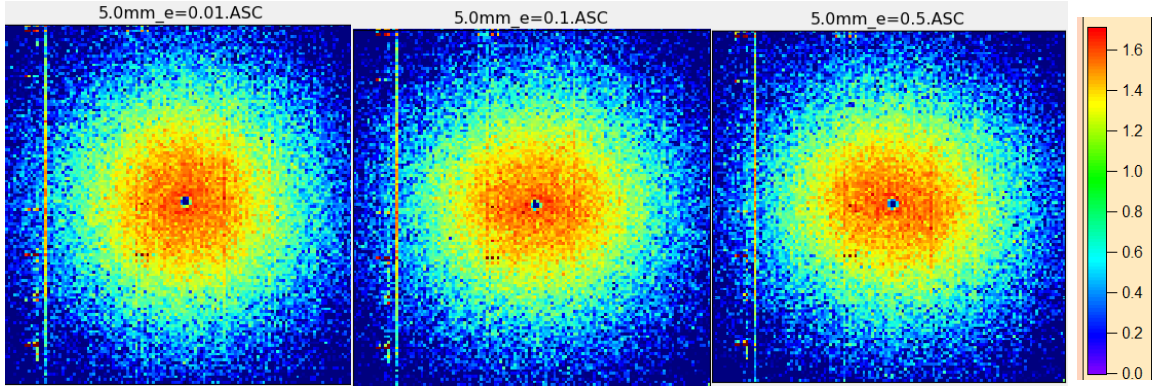


Isotropic Scattering
Indicates randomly oriented worm-like micelles

Worm-Like Micelles in D_2O
75 mM Cetylpyridinium Chloride
45 mM Sodium Salicylate

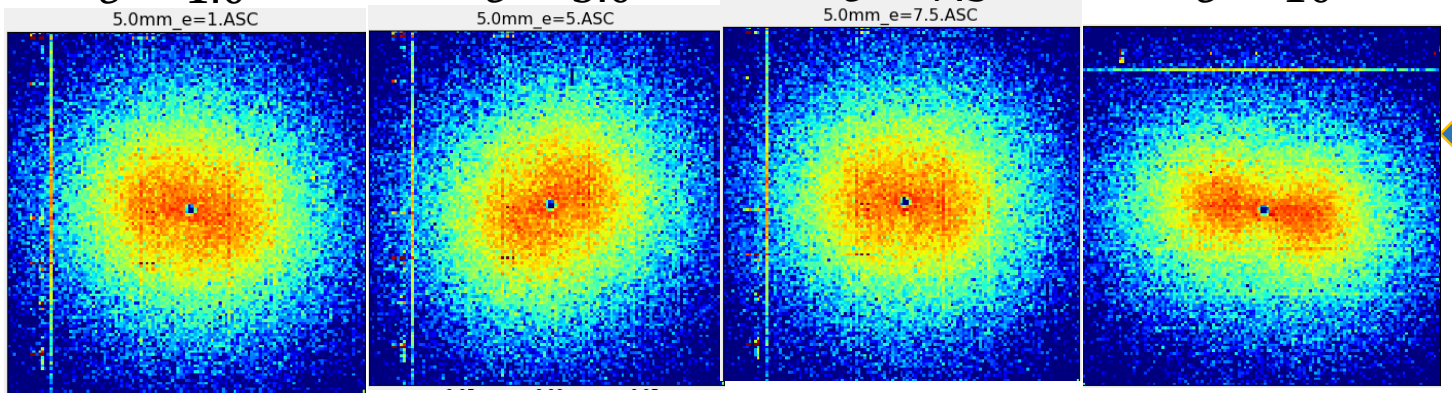


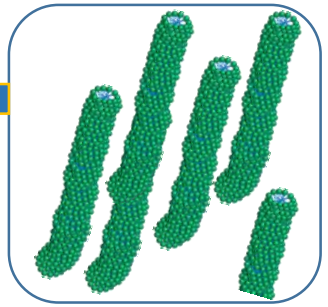
$\varepsilon = 0.01$ $\varepsilon = 0.1$ $\varepsilon = 0.5$



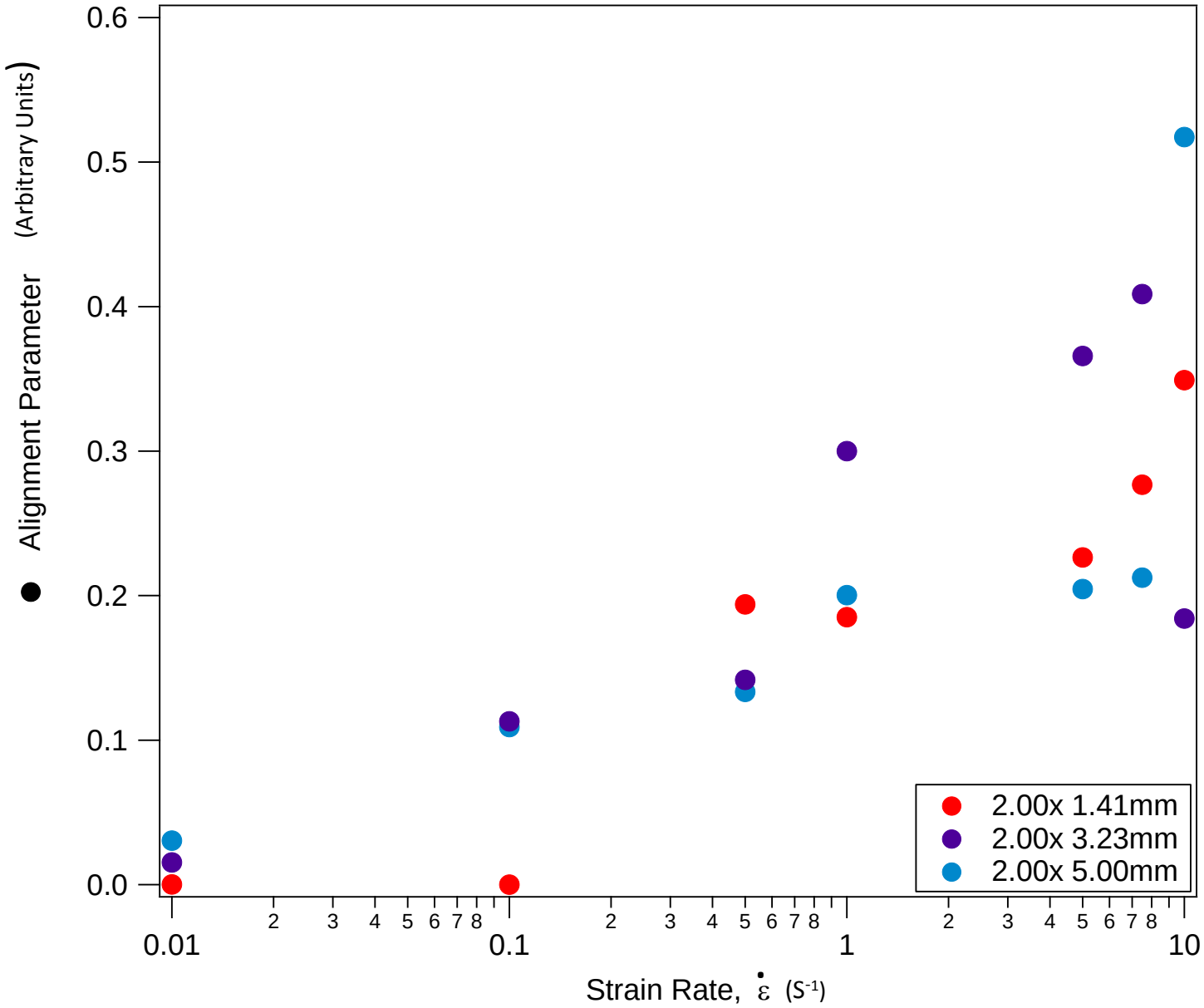
Anisotropic Scattering
Indicates oriented worm-like micelles

$\varepsilon = 1.0$ $\varepsilon = 5.0$ $\varepsilon = 7.5$ $\varepsilon = 10$





Alignment Parameters



Conclusions

- Observed a transition from a stagnation point to a flow instability
- Calculated alignment parameter and orientation of alignment
- To minimize the effect of shear strain channel height must be greater than channel width
- Future Work:
  - Analyze time-resolved data
  - Use results to optimize cross-slot geometry

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