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energy futures lab

Oilfield Fluids: Tales of Mud and Worms

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Department of Chemical Engineering

Rideal Lecture
Wednesday 28th March 2012

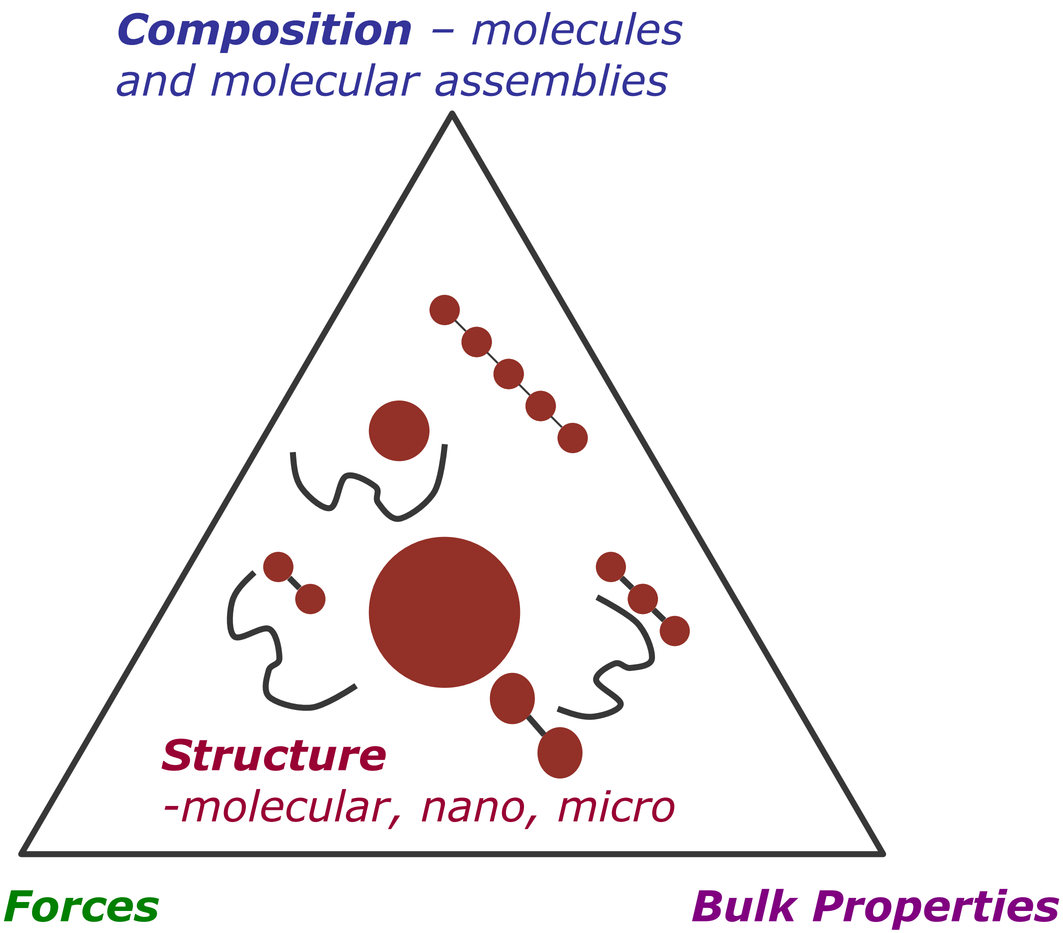
Collaborators

Schlumberger:	Louise Bailey, Isabelle Couillet, Trevor Hughes
Imperial College:	Edo Boek, John Crawshaw
Utrecht University:	Henk Lekkerkerker, Annemieke ten Brinke, Marcel Vogel, Dzina Kleshchanok
Strasbourg ICS, CNRS	Francoise Candau, Jean Candau
Twente University:	Wim Briels, Johan Padding (Eindhoven)
Bristol University:	Terence Cosgrove, Vania Croce Cecile Dreiss (KCL)

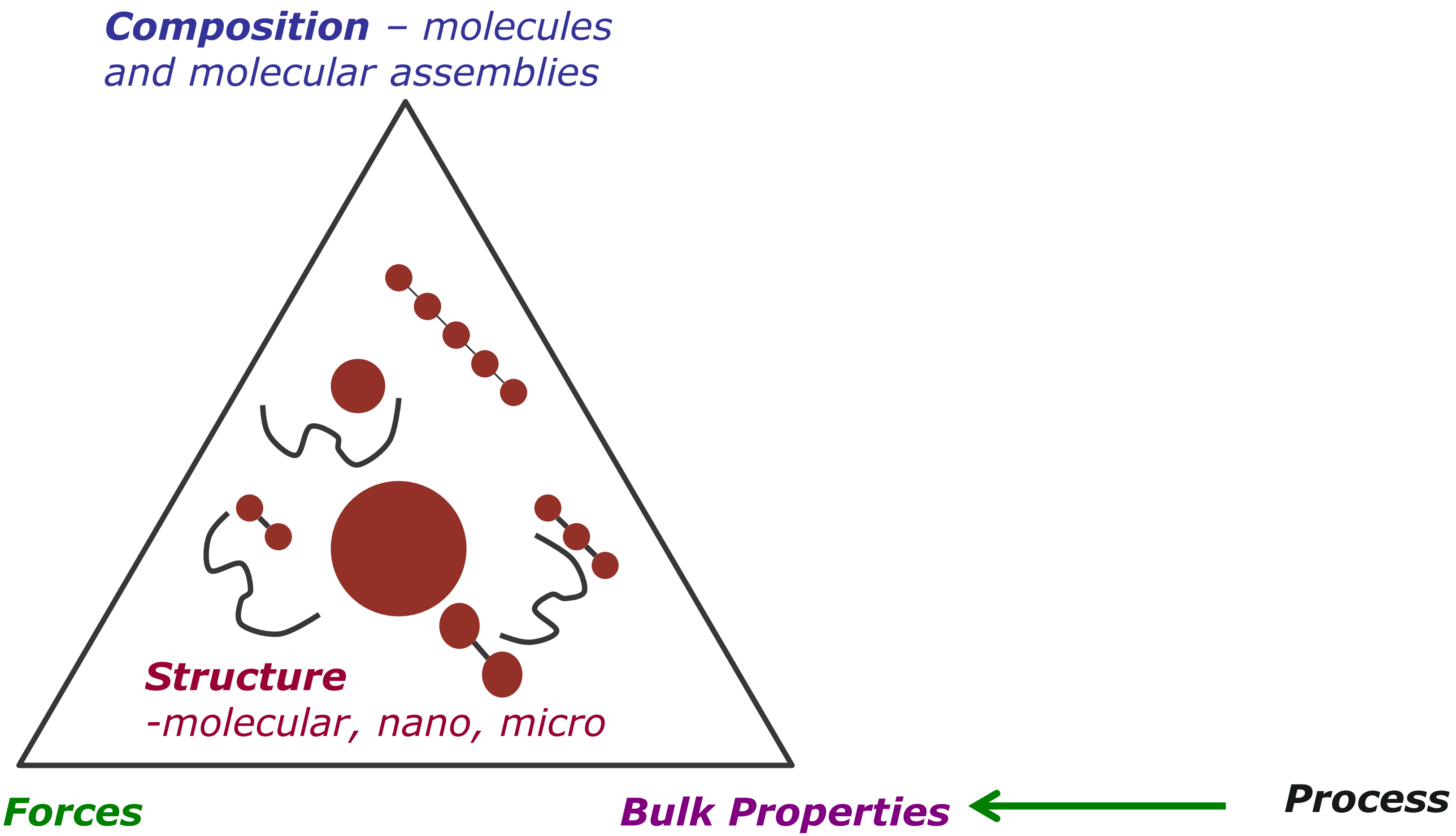
Lecture Outline

- Design of Fluids and Materials
  - Advanced Formulation and (More) Systematic Design of Fluids
- The Worm's Tale
  - Smarter Fracturing Fluids
- The Potter's Tale
  - Clays for Drilling Fluids – enhancing performance
- Some Conclusions

From Understanding to Designing Fluids



From Understanding to Designing Fluids



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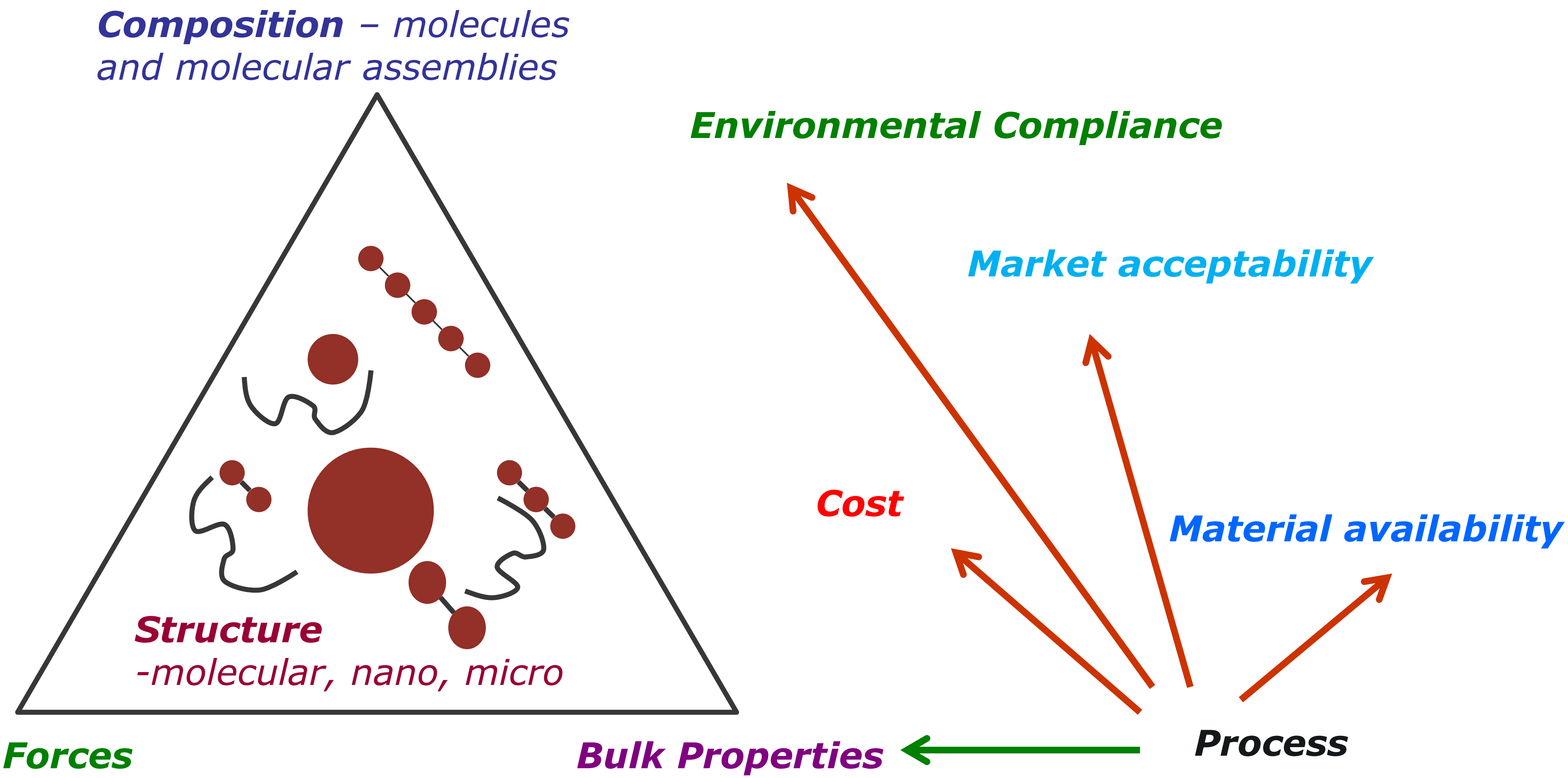
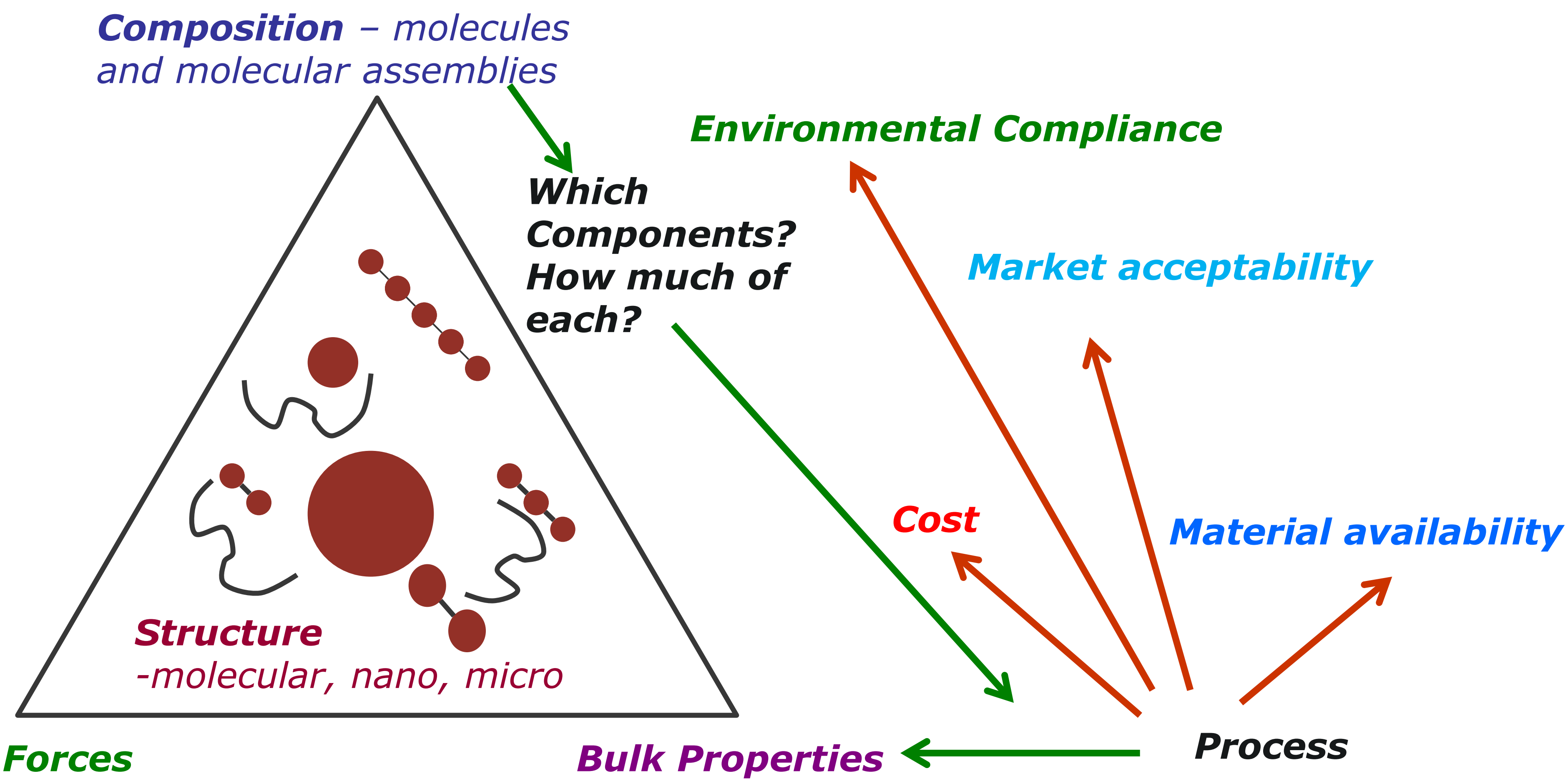
From Understanding to Designing Fluids



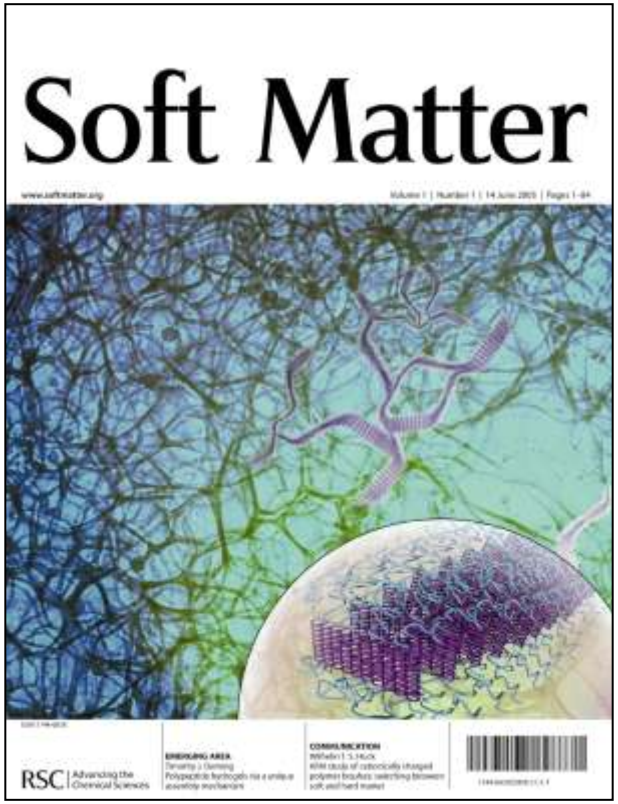
From Understanding to Designing Fluids



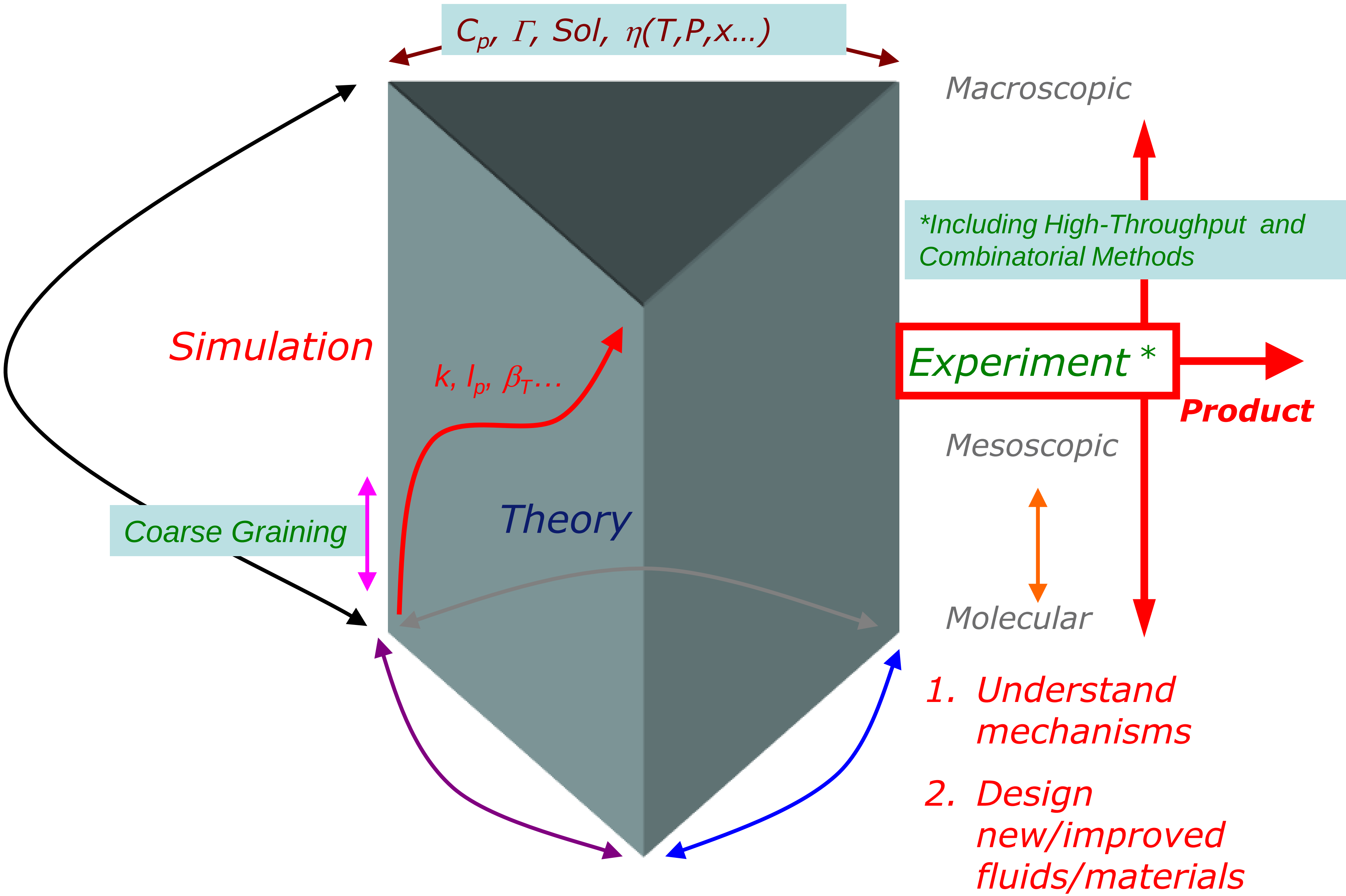
From Empirical Formulation to Systematic Fluid/Materials Design

Editorial:

G.C. Maitland
Transforming 'formulation':
systematic soft materials design
Soft Matter, 2005, **1**(2), 93 - 94



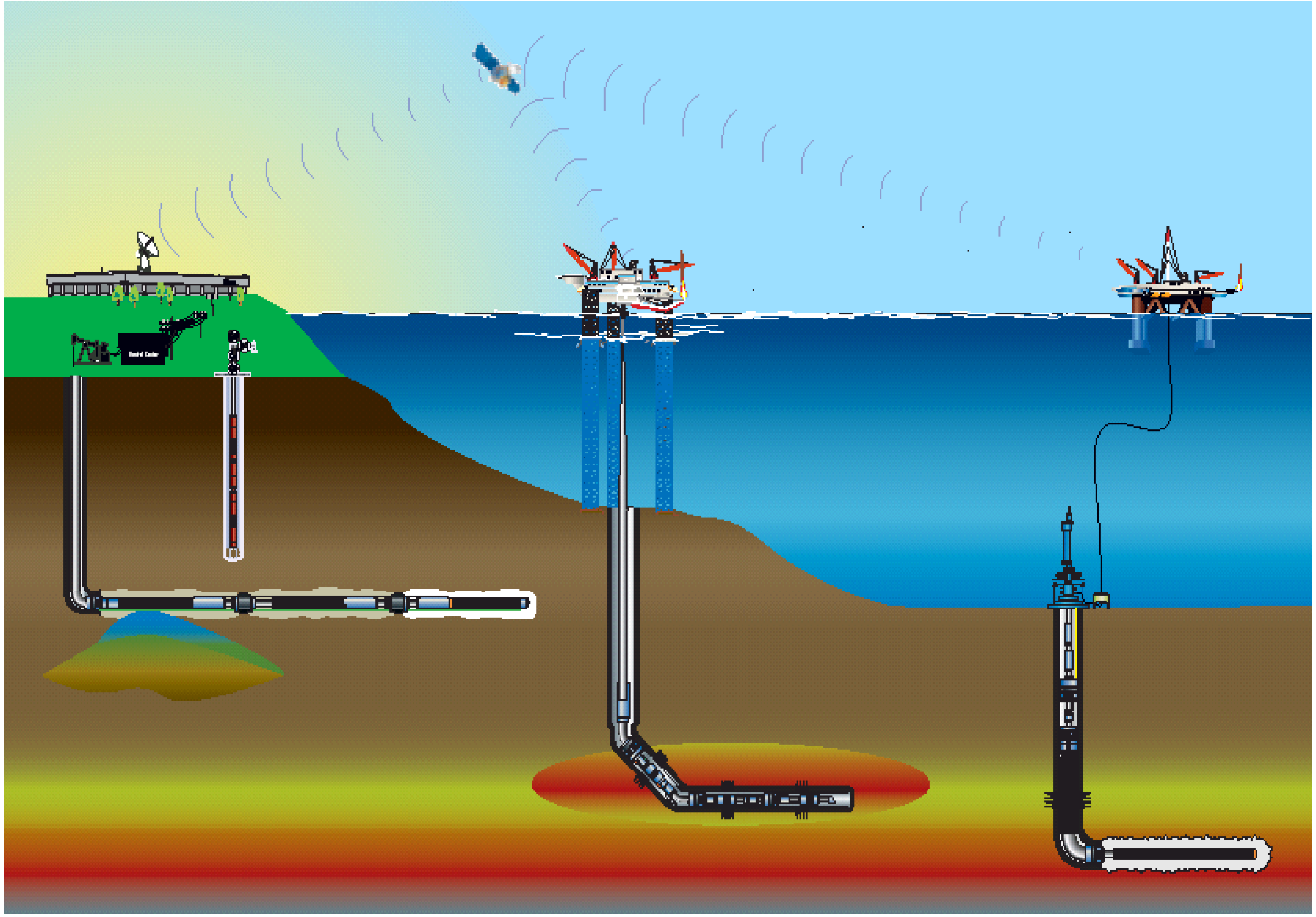
Systematic Fluid Formulation



Main building blocks for (oilfield) functional fluids

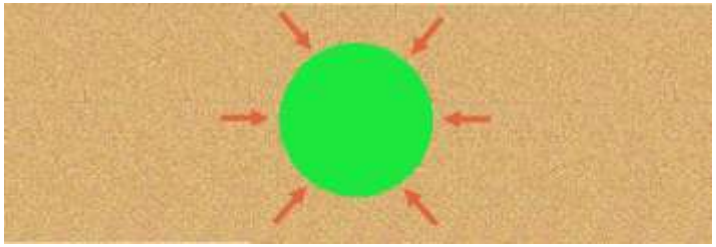
- Hydrocarbons
  - Aliphatics, aromatics, polar…
- Polymers
- Surfactants
- Colloids
  - Mineral colloids
  - Anisotropic clays…

The Worm's Tale
Stimulating an oil-gas reservoir by Hydraulic Fracturing



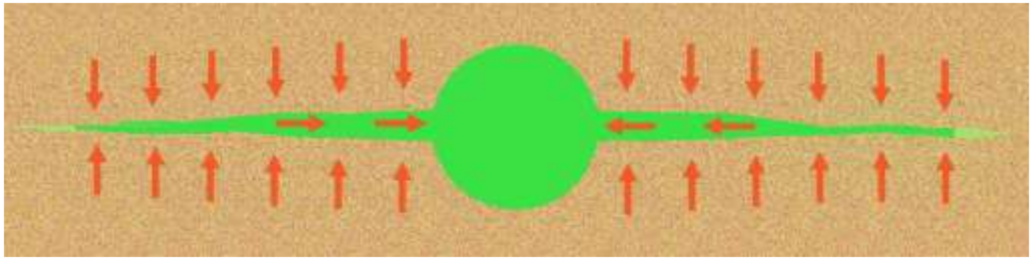
Hydraulic Fracturing

Before Treatment



Flow restricted by radial geometry

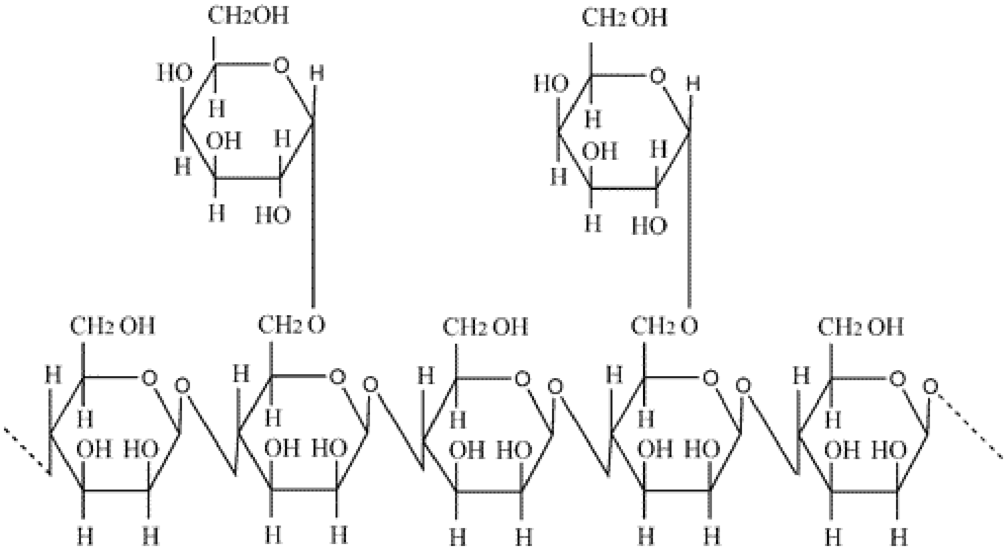
After Treatment



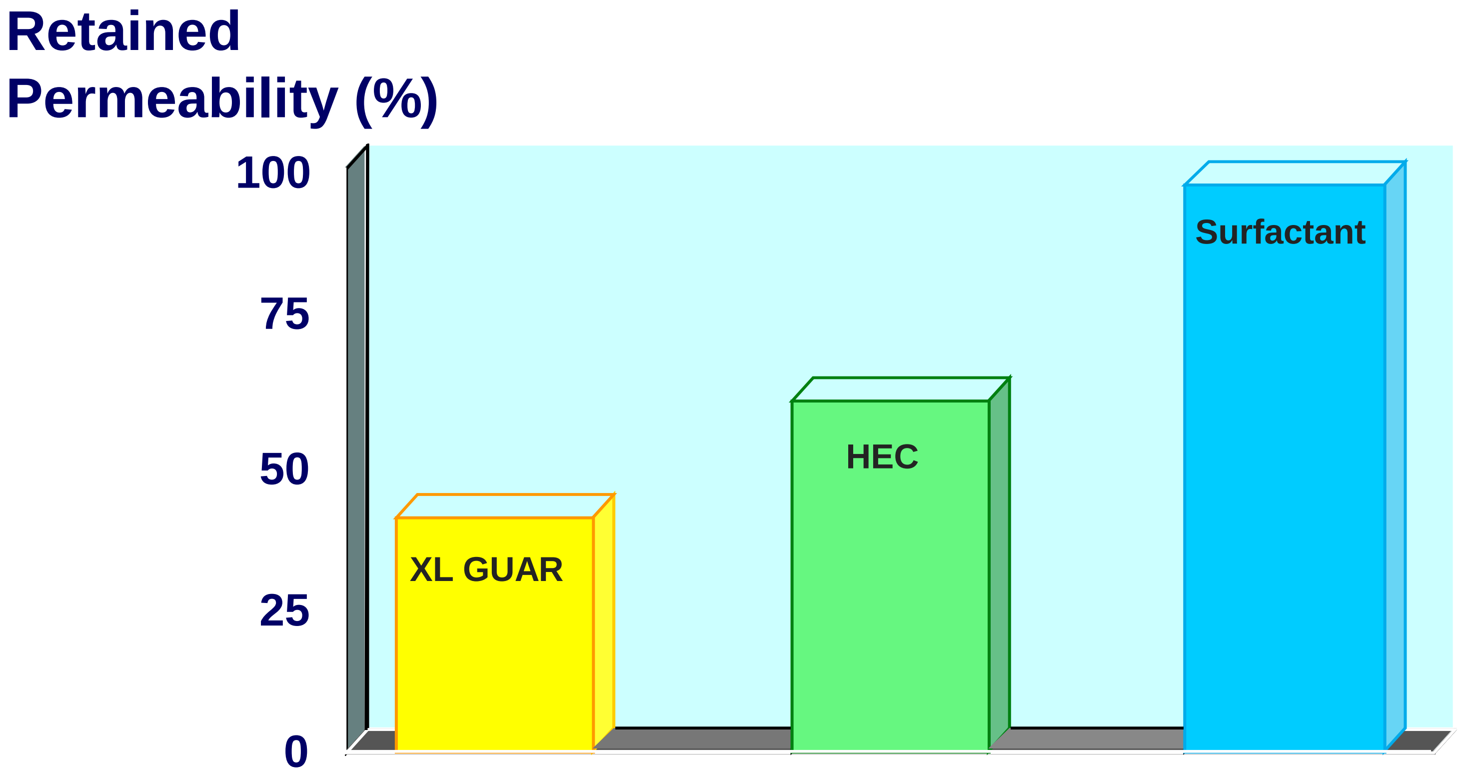
Increased productivity through fractures

Aqueous Solutions of Guar – the Standard Fracturing Fluid

Guar: Galactomannose, M ~ 10^5-10^6



The Problem -
Polymer vs Surfactant Fluids: Fracture Permeability



Low Production…Worms to the rescue!

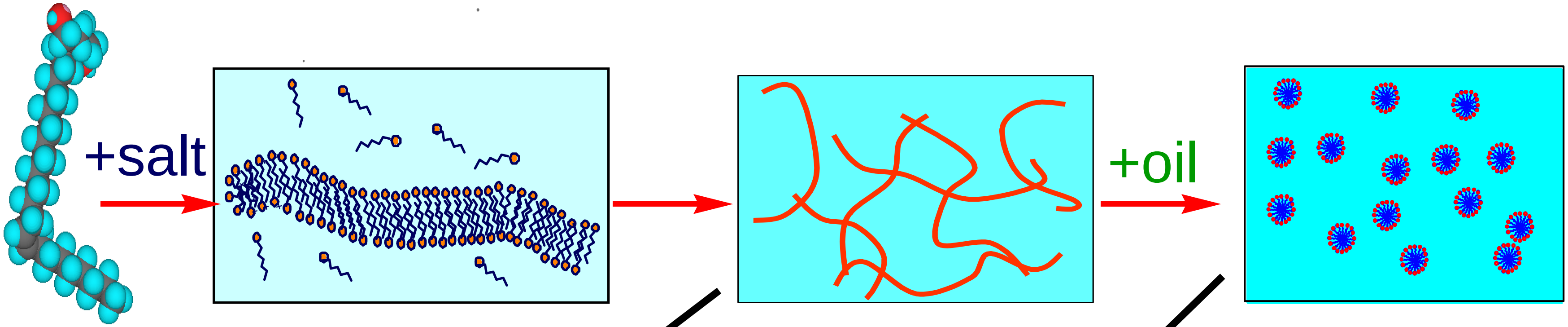
Problem:

Guar Polymer Fracturing Fluids give <50% Theoretical Production from Fractures

Solution:

Shower Gels for Deep Hot Wells - Wormlike Surfactant Micelles at $>150^{o}$C

Oil-responsive Viscoelastic Surfactants

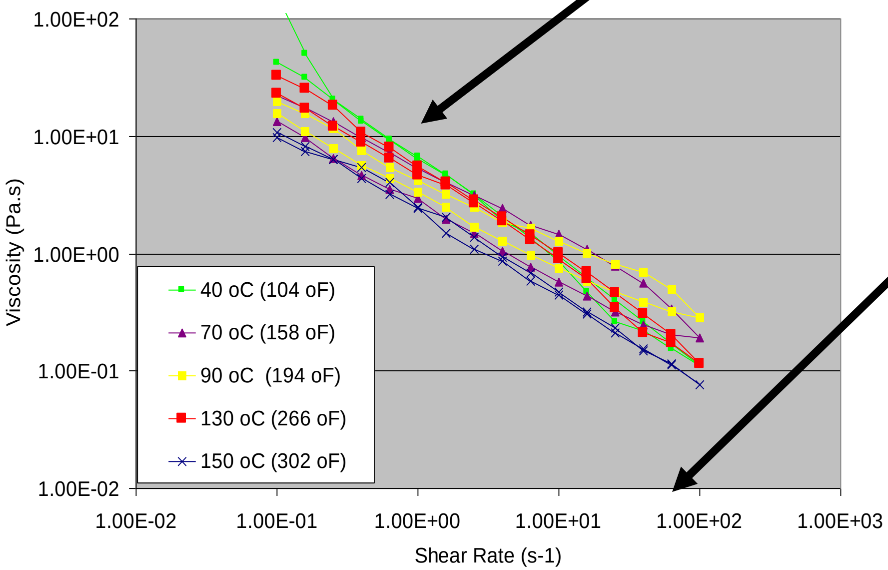


1-4wt%

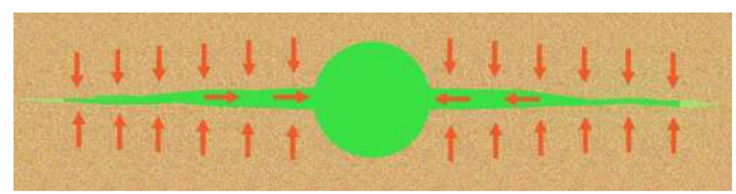
Worm-like Micelles

Network of Worm-like Micelles

Spherical Micelles

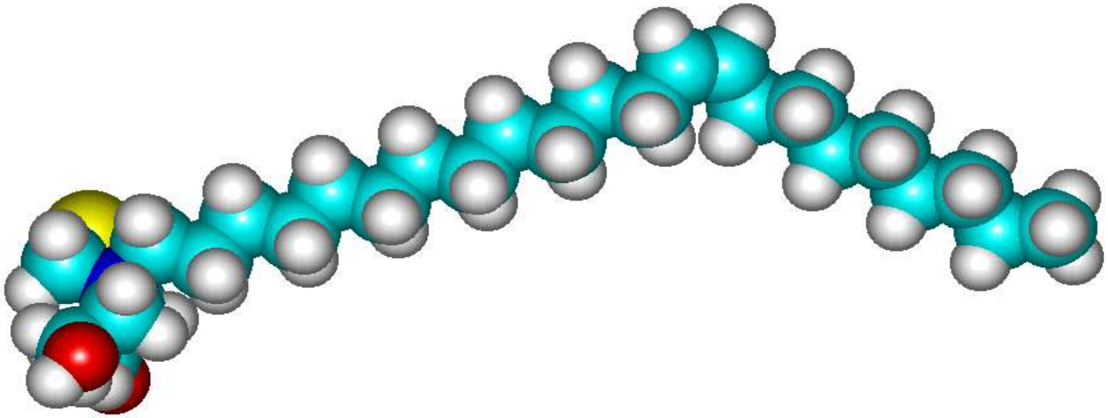


Hydraulic Fracturing



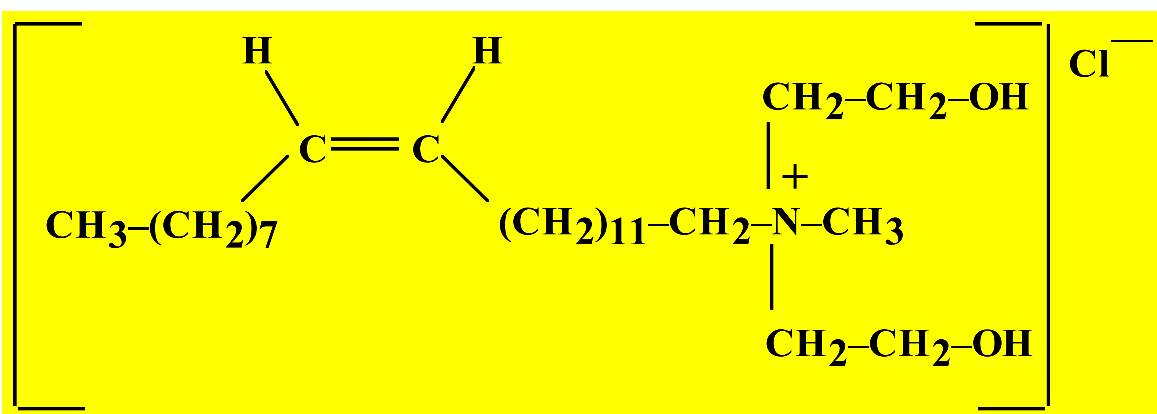
One Source of Worms...

Viscoelastic Surfactant Fracturing Fluids



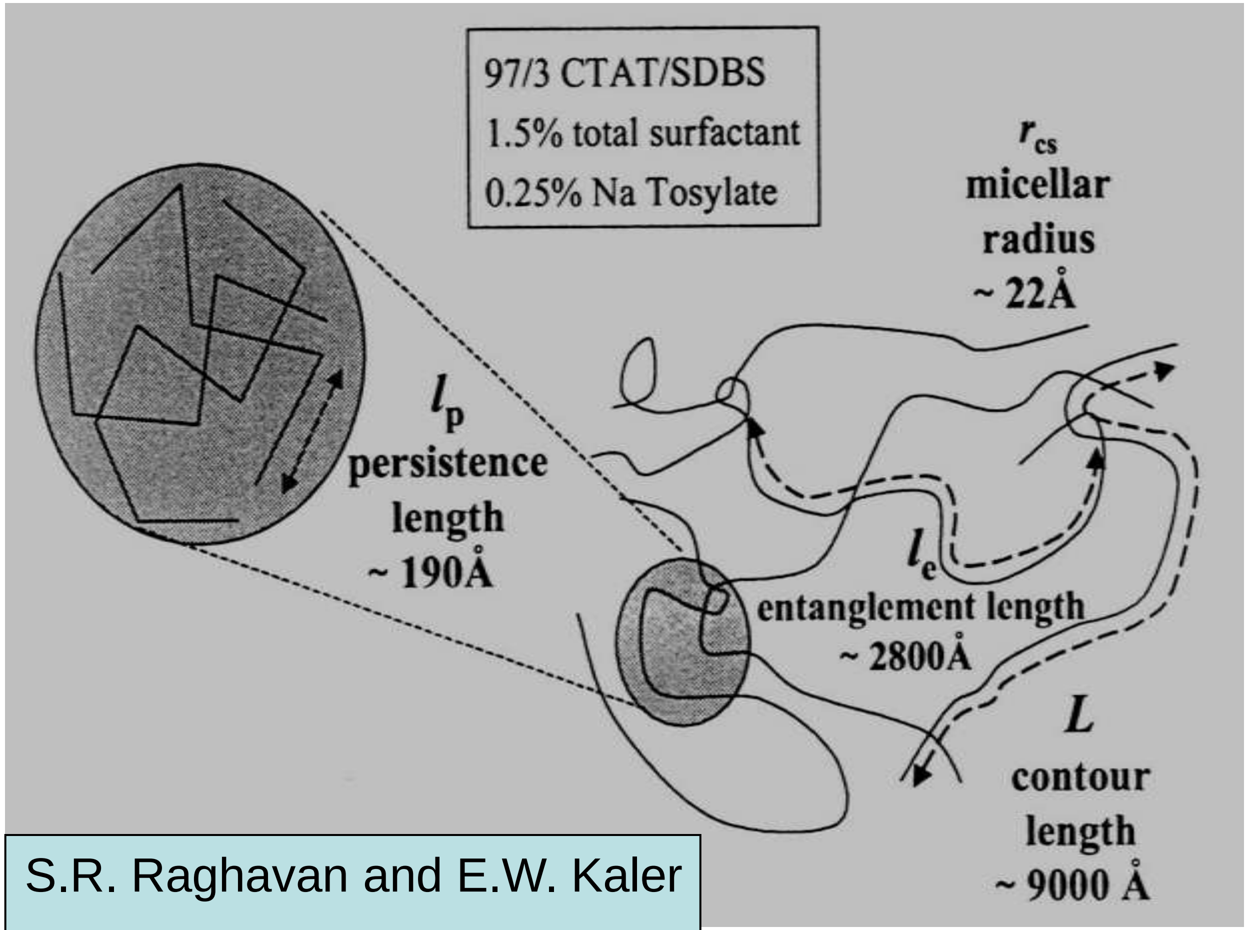
Erucyl bis (2-hydroxyethyl) methyl ammonium chloride

EHAC



- **Hydrophobic tail**
  - C_{22} chain
  - cis double bond at C_{13}
- **Hydrophilic head group**
  - quaternary ammonium with 2 hydroxyethyl groups
- **Derived from rape seed oil**
- **Blended with iso-propanol**

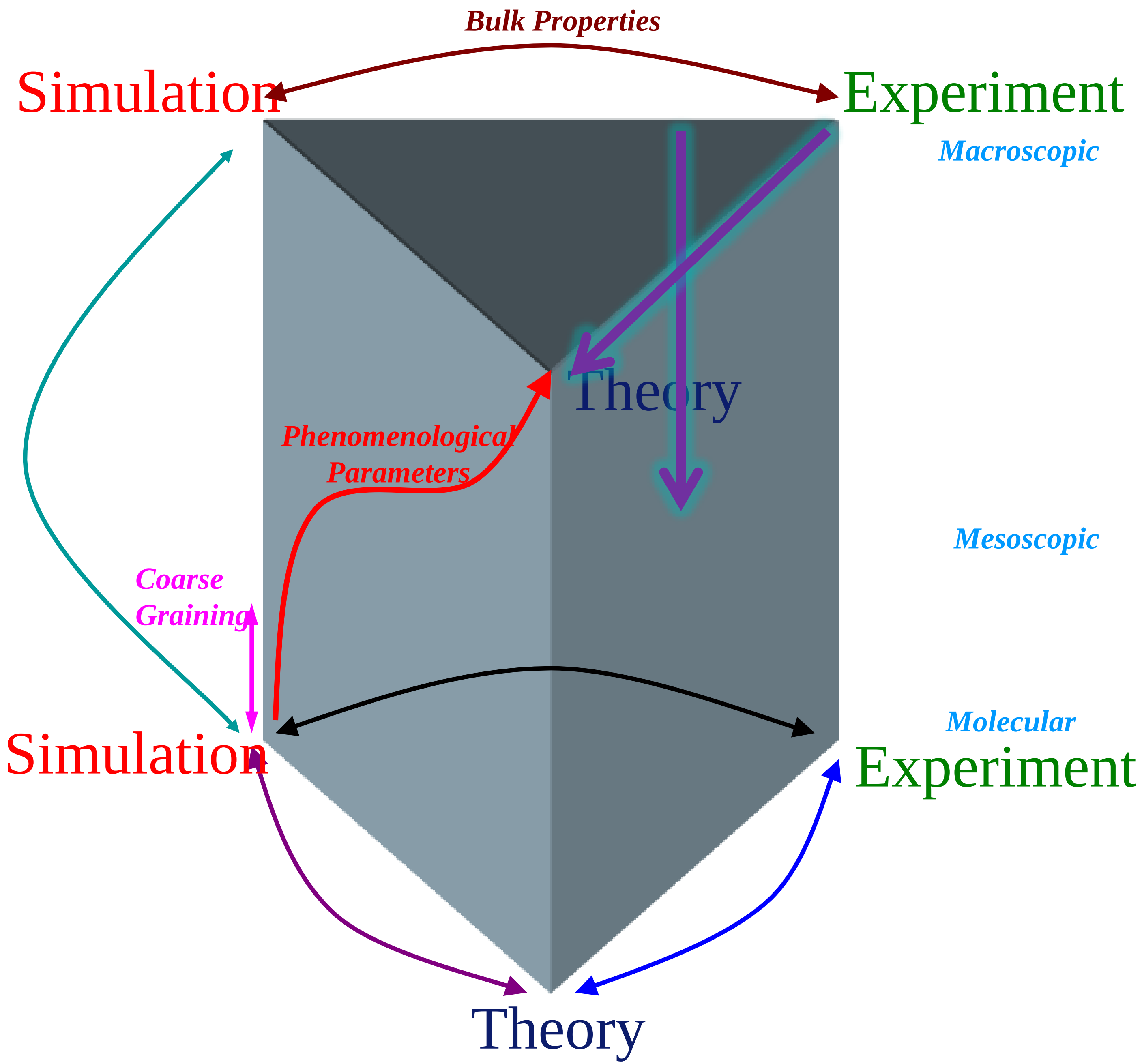
Typical Lengthscales



S.R. Raghavan and E.W. Kaler

Univ of Delaware

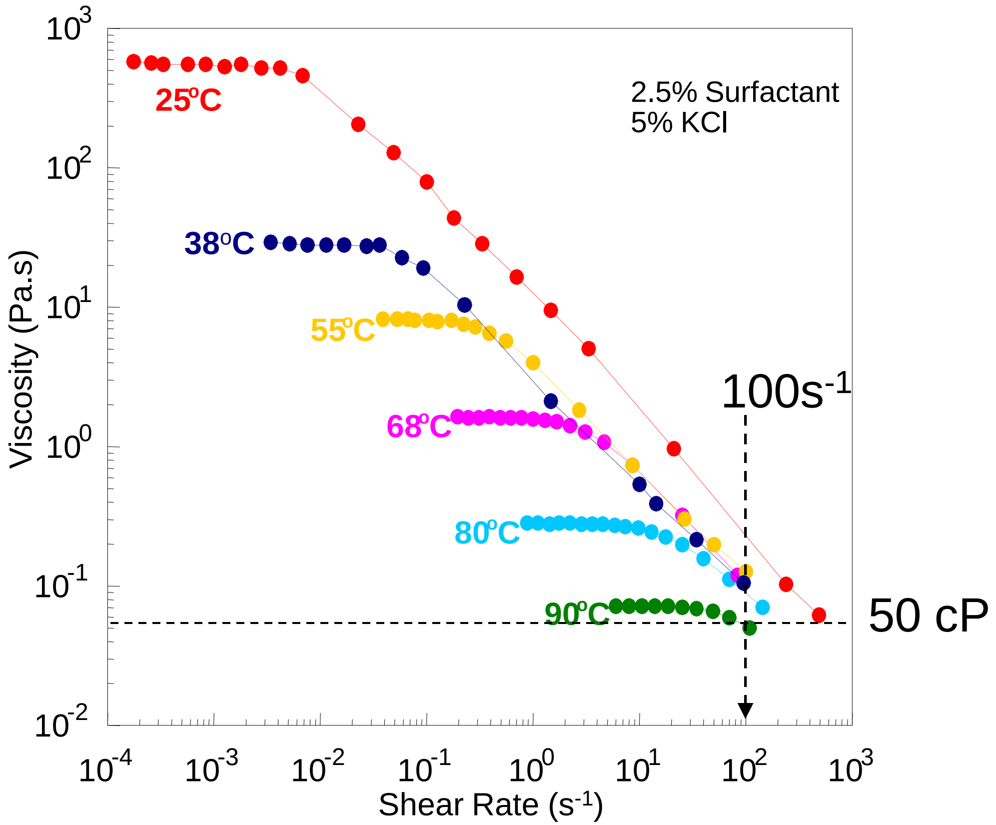
Type of Study



Bulk Rheology

Continuous Shear Flow

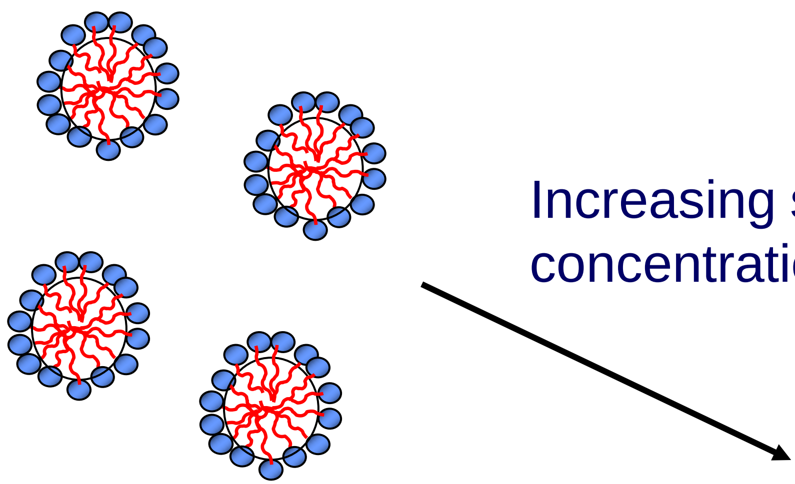
VES Shear Viscosity



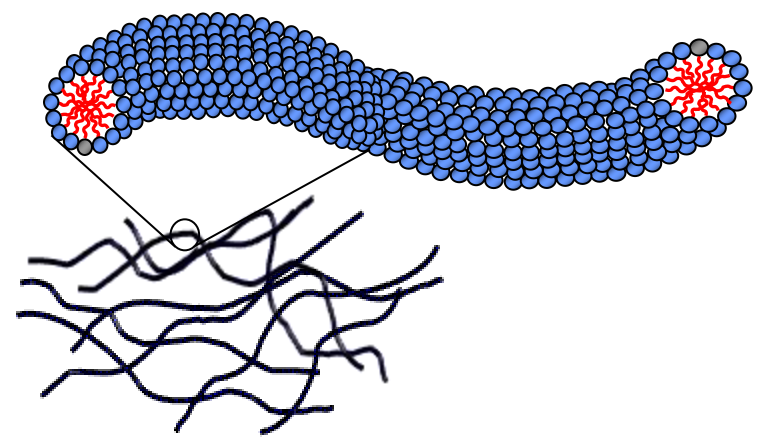
- Zero-shear viscosity, η_0 decreases as T ↑
- Relaxation time, τ_R (= $1/\gamma_c$) decreases as T ↑
- Viscosity at high shear-rates is nearly independent of T

Origin of Viscoelasticity and High Viscosity

Spherical Micelles



Increasing salt,
concentration



Transient Network
of Wormlike Micelles

Micelles are very long, 1-5 μm

Since $\tau_R \sim \eta \sim L^3$

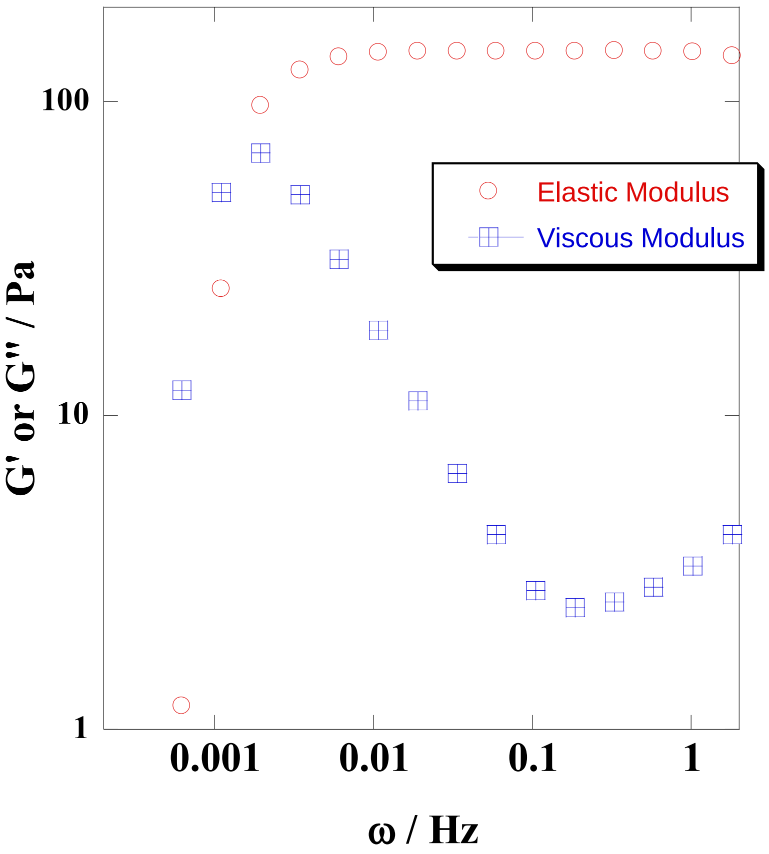
$\Rightarrow$ micelles relax slowly
$\Rightarrow$ high viscosity

After E.W. Kaler , Univ of Delaware

Bulk Rheology

Oscillatory Shear Flow

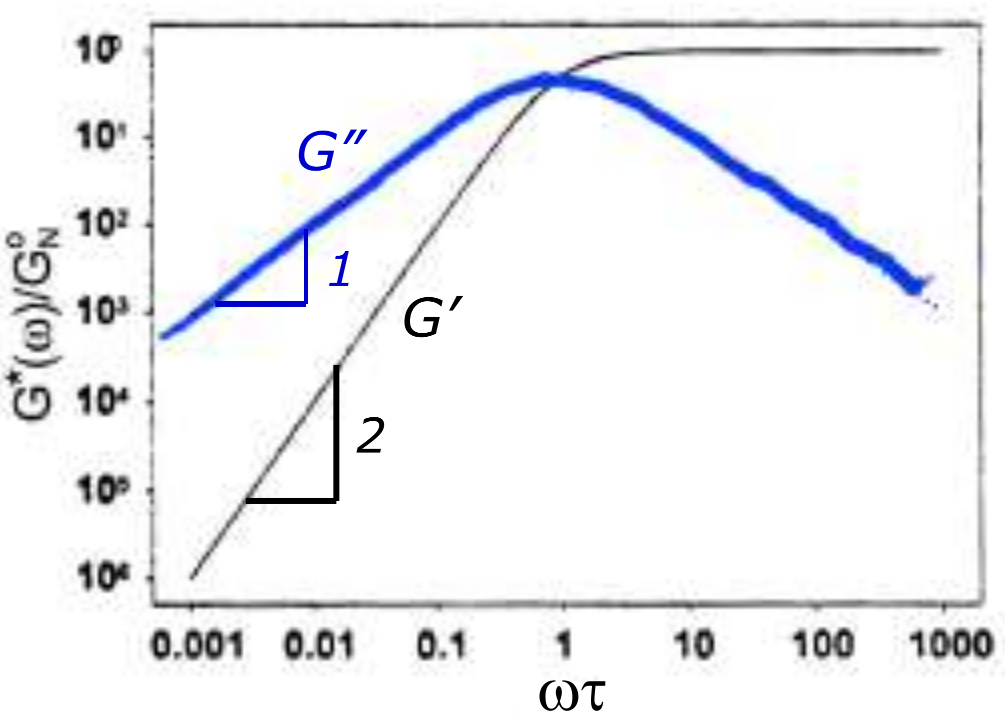
Display Simple Linear Viscoelastic Behaviour



VES Surfactant Solution

Maxwell Model for Linear Viscoelasticity

$$G' = \frac{G\ \omega^2\ \tau^2}{1 + \omega^2\tau^2} \qquad G'' = \frac{G\ \omega\ \tau}{1 + \omega^2\tau^2}$$

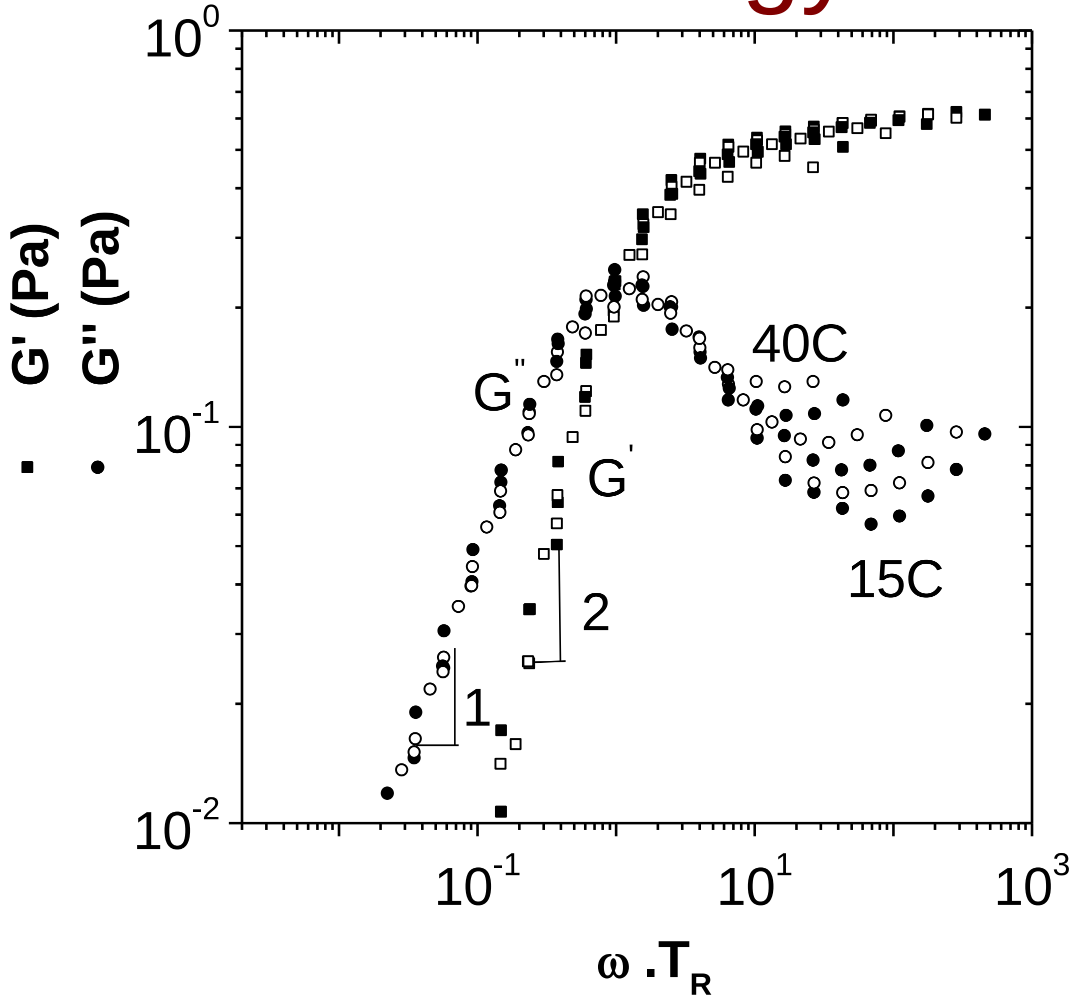


Relaxation Time

$\tau = \eta/G$

$$\tau + \frac{\eta}{G}\frac{d\tau}{dt} = \eta\frac{d\gamma}{dt}$$

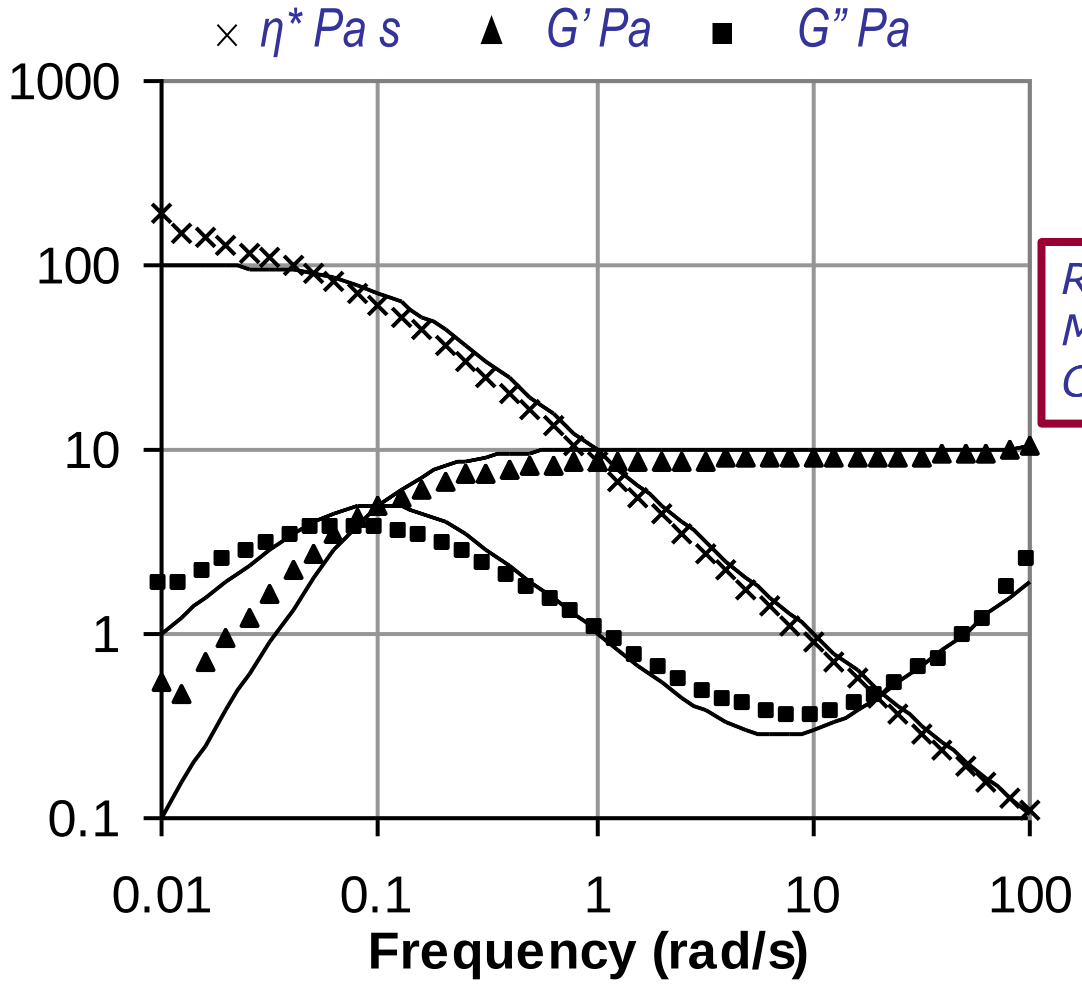
Dynamic shear rheology master curve



Rheological master curves for dynamic shear for a sample at 14.4 mM active EHAC concentration with 400mM KCl, obtained by scaling the data generated at various temperatures (15,20,25,30,35 and 40℃).

*I Couillet, T Hughes, G Maitland F Candau and S J Candau, Langmuir, **20**, 9541-9550, 2004*

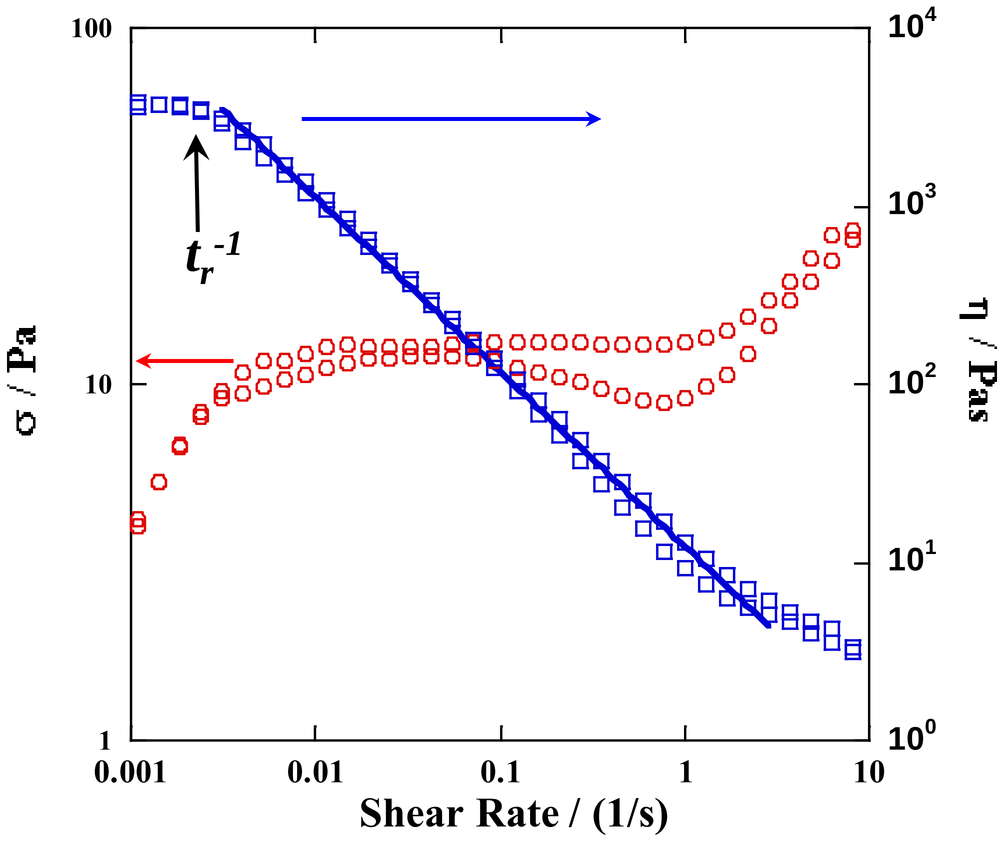
Linear Viscoelastic Regime

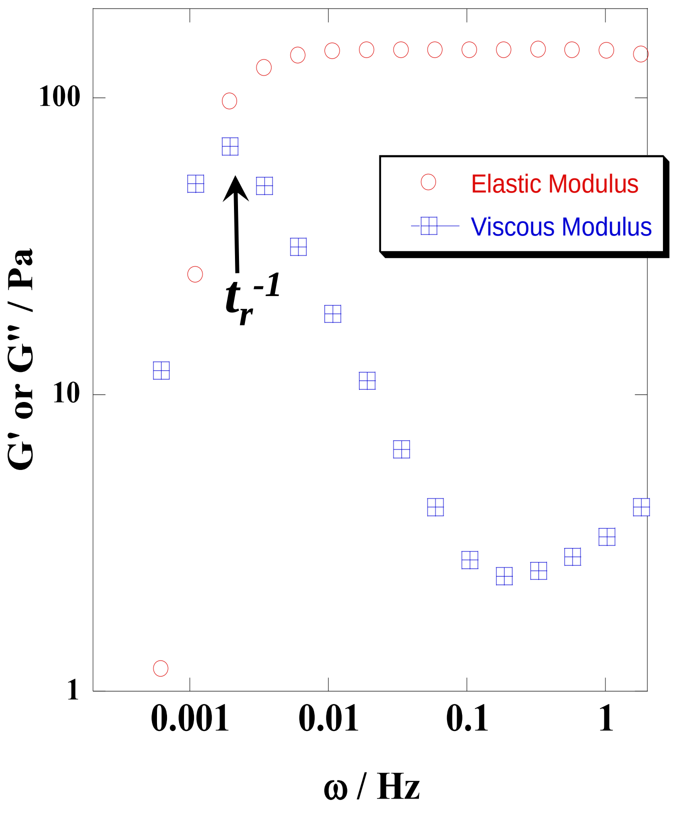


Rachel Cooke and Malcolm Mackley, Cambridge University

3 wt% EHAC surfactant, 3 wt% potassium chloride solution at 40 C.
Data fitted to a ***2 element Maxwell model*****.**

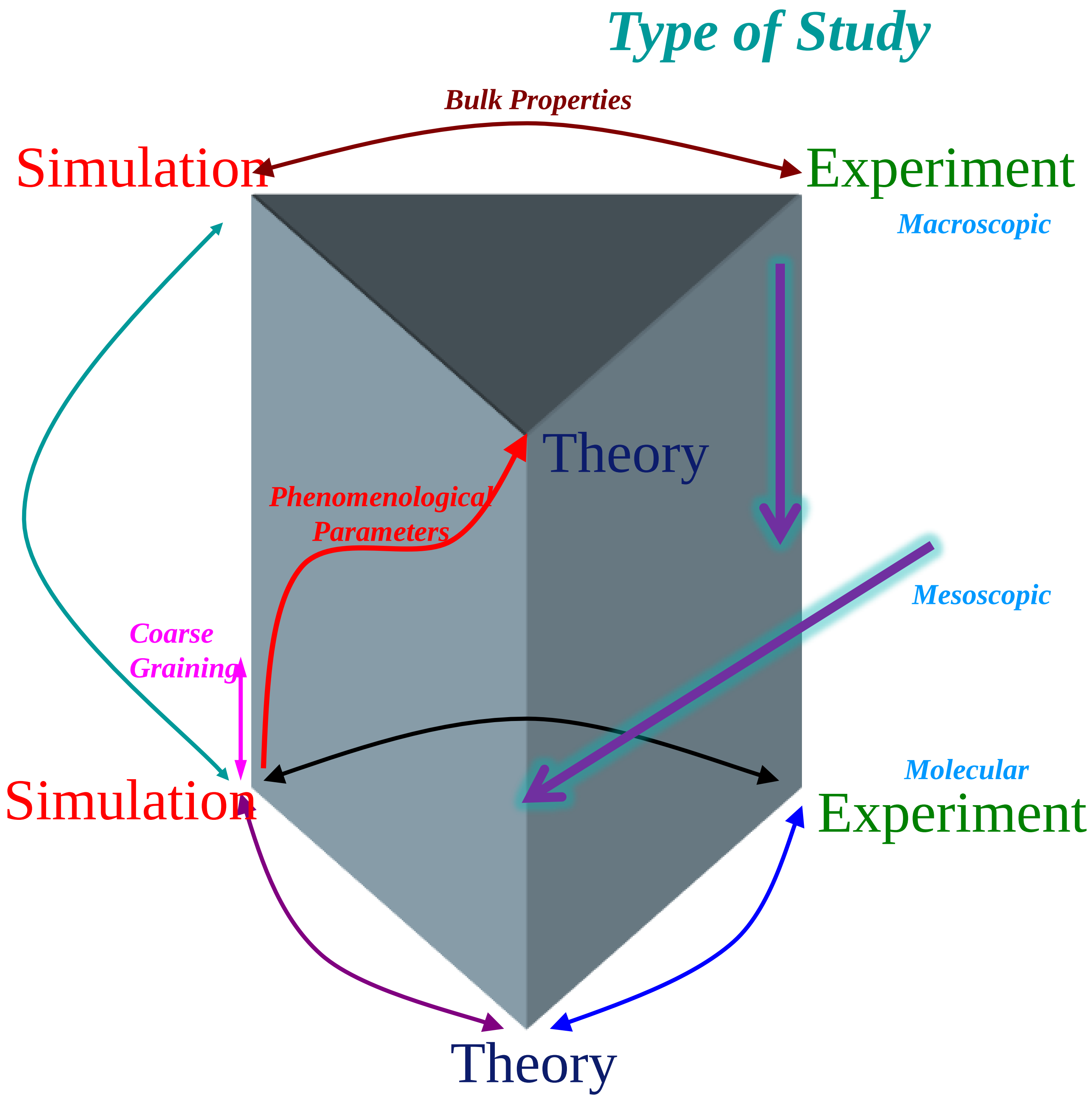
Bulk Rheology of VES Fluids





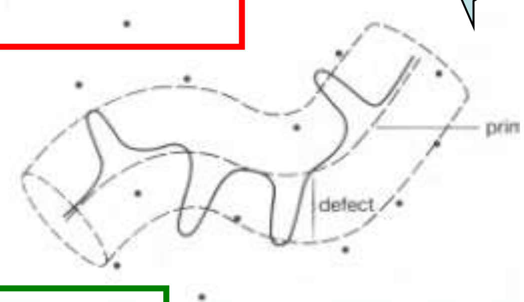
Both types of behaviour in line with the 'Reptation-Reaction' model of Cates, later adapted to η(γ) by Spenley, Cates and McLeish.

$$t_r = (\tau_R \, \tau_b)^{1/2}$$


Type of Study
Bulk Properties
Simulation
Experiment
Macroscopic
Theory
Phenomenological
Parameters
Mesoscopic
Coarse
Graining
Molecular
Simulation
Experiment
Theory

Chain Constraints – Reptation in a Tube

Repulsive interchain forces → Entanglements - moving obstacles



Obstacle course for a given chain represented by a tube

Reptation time τ_R

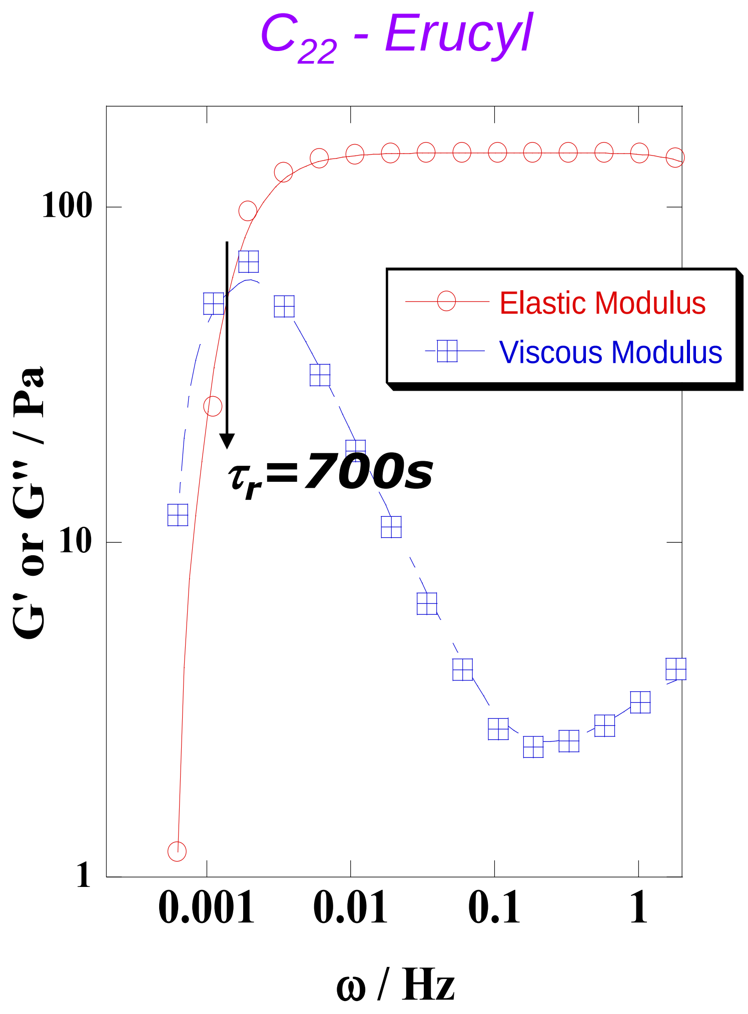
Chain reptates down the tube which is continually renewed as other chains move

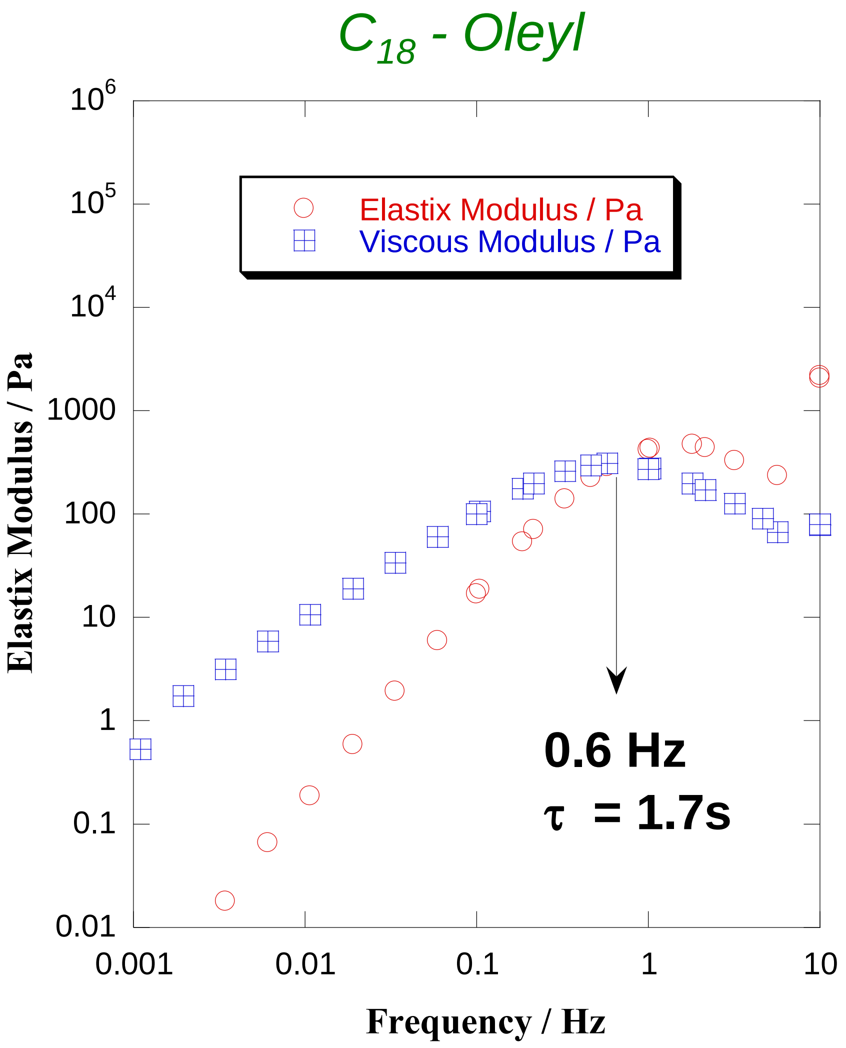
$$\eta \sim \tau_R \sim L^3$$

Cates-type models

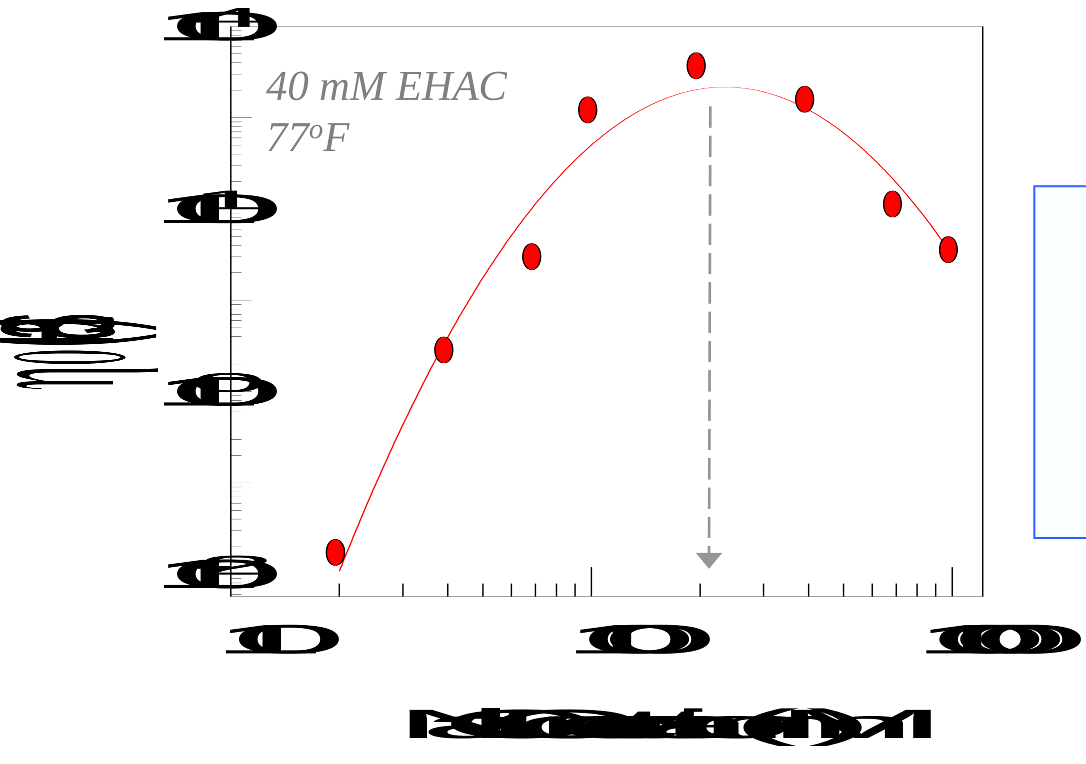
- Assume two main processes:
  - Reptation, τ_{rep}
  - Chain scission-rehealing, $\tau_{br} = (KL)^{-1}$
- Slow scission limit, $\tau_{br} >> \tau_{rep}$
  - Terminal relaxation time $\tau_R = \tau_{rep}$
  - $\eta_0 = L^3 c^{15/4}$
- Fast breaking limit, $\tau_{br} << \tau_{rep}$
  - $\tau_R = (\tau_{br}\tau_{rep})^{1/2}$
    Maxwell behaviour for G', G'' with $\tau = \tau_R$
  - $\eta_0 \sim Lc^3$
- Rouse modes at higher frequency if $\tau_{Rouse} < \tau_{br}$

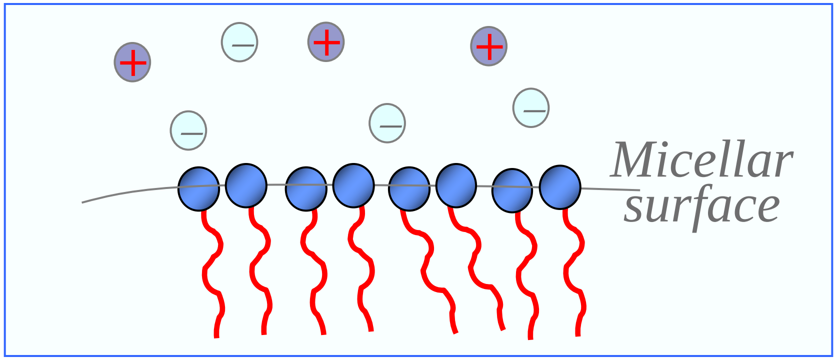
Effect of Headgroup on Relaxation Time





Screening salt: grows wormlike micelles





S.R. Raghavan and E.W. Kaler, University of Delaware

Spherical to wormlike micelles observed by SANS

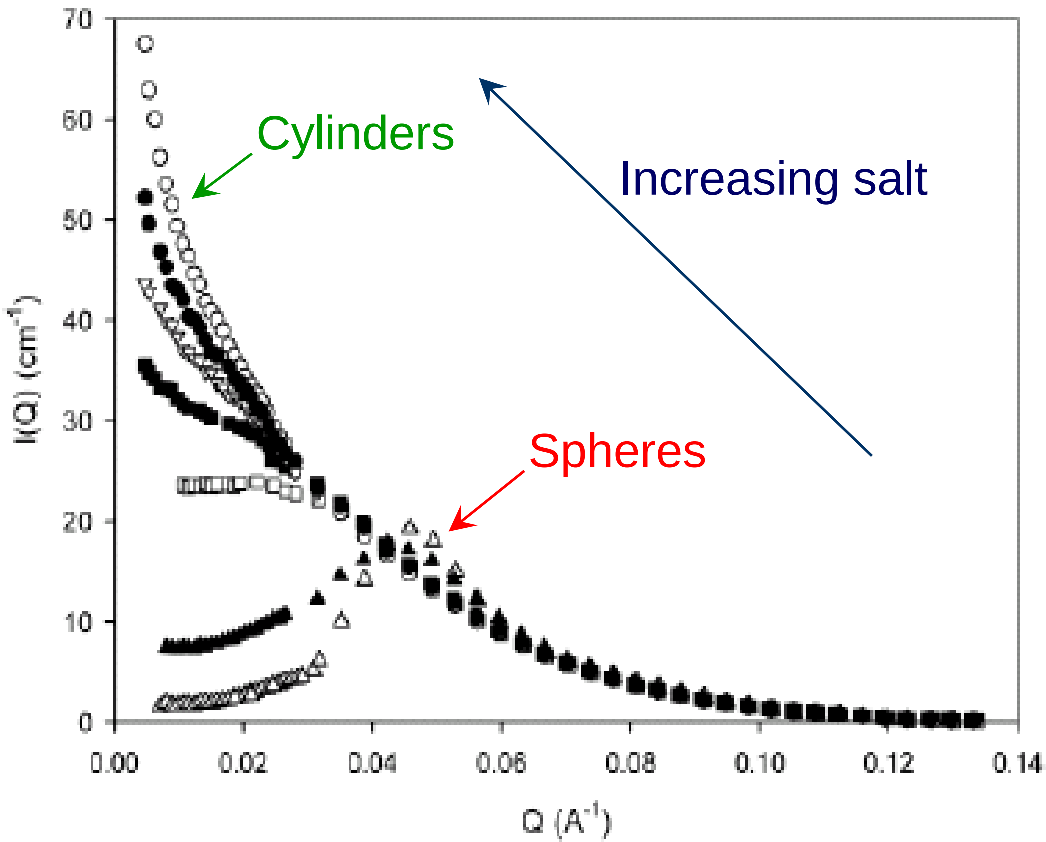


Figure 5. Scattering intensity $I(Q)$ versus scattering vector Q for polymer-like micelles formed by EHAC in D_2O as a function of KCl content at 40 °C. (△, no KCl; ▲, 0.10 wt % KCl; □, 0.25 wt % KCl; ■, 0.50 wt % KCl; ▽, 0.75 wt % KCl; ●, 1.0 wt % KCl; ○, 2 wt % KCl.)

V.Croce, T. Cosgrove, G.C. Maitland, T.L. Hughes and G. Karlsson, Langmuir **19** 8536-41 (2003)

SANS study of micelle growth – no salt

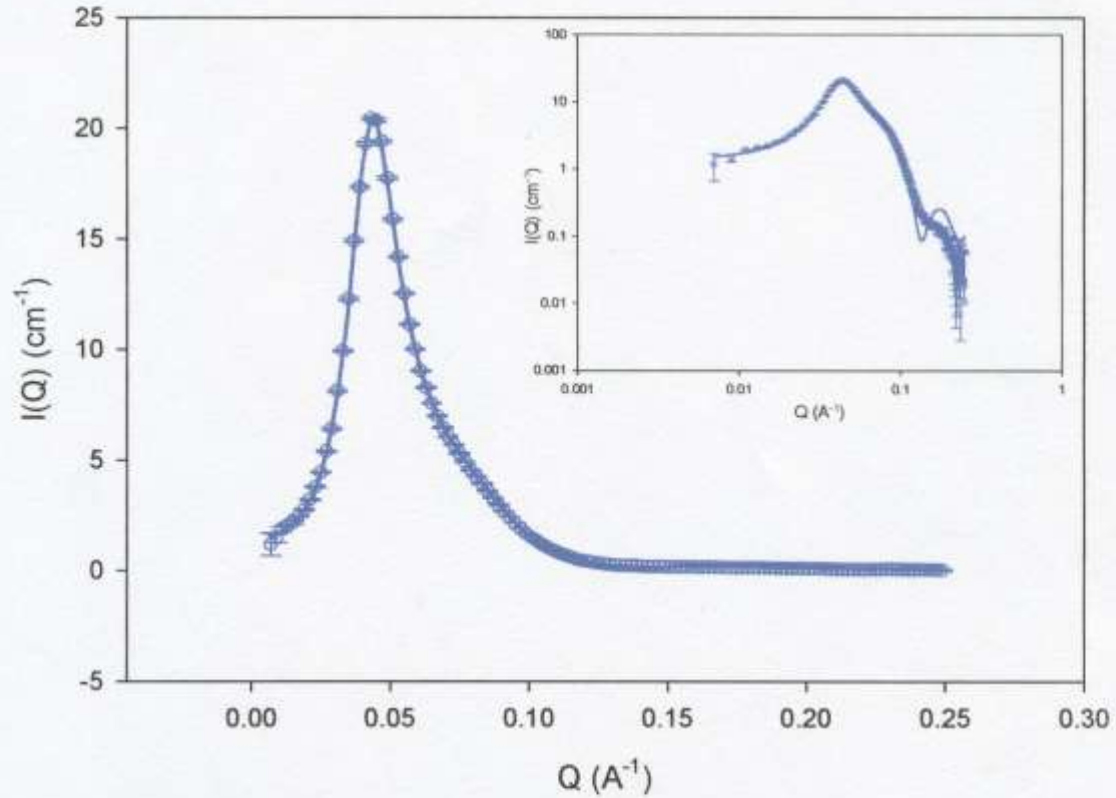


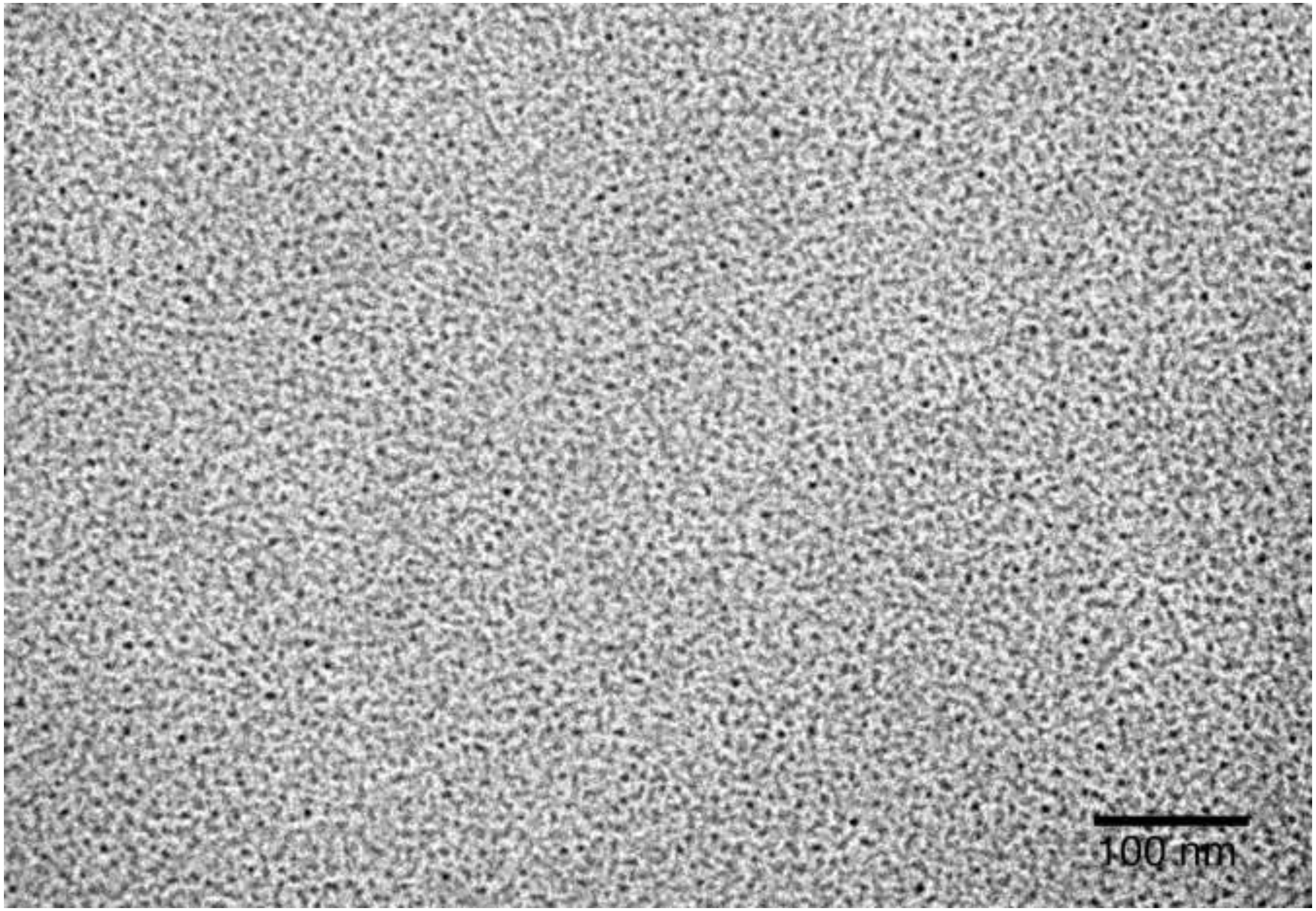
Figure 3.2.1: Scattering curve obtained for J508 micelles in D2O at a concentration of 3.96wt% without added salt.

Spherical micelles, R = 33.3 A

Data by Vania Croce, University of Bristol

V.Croce, T. Cosgrove, G.C. Maitland, T.L. Hughes and G. Karlsson, Langmuir **19** 8536-41 (2003)

4.5 wt% EHAC…no salt

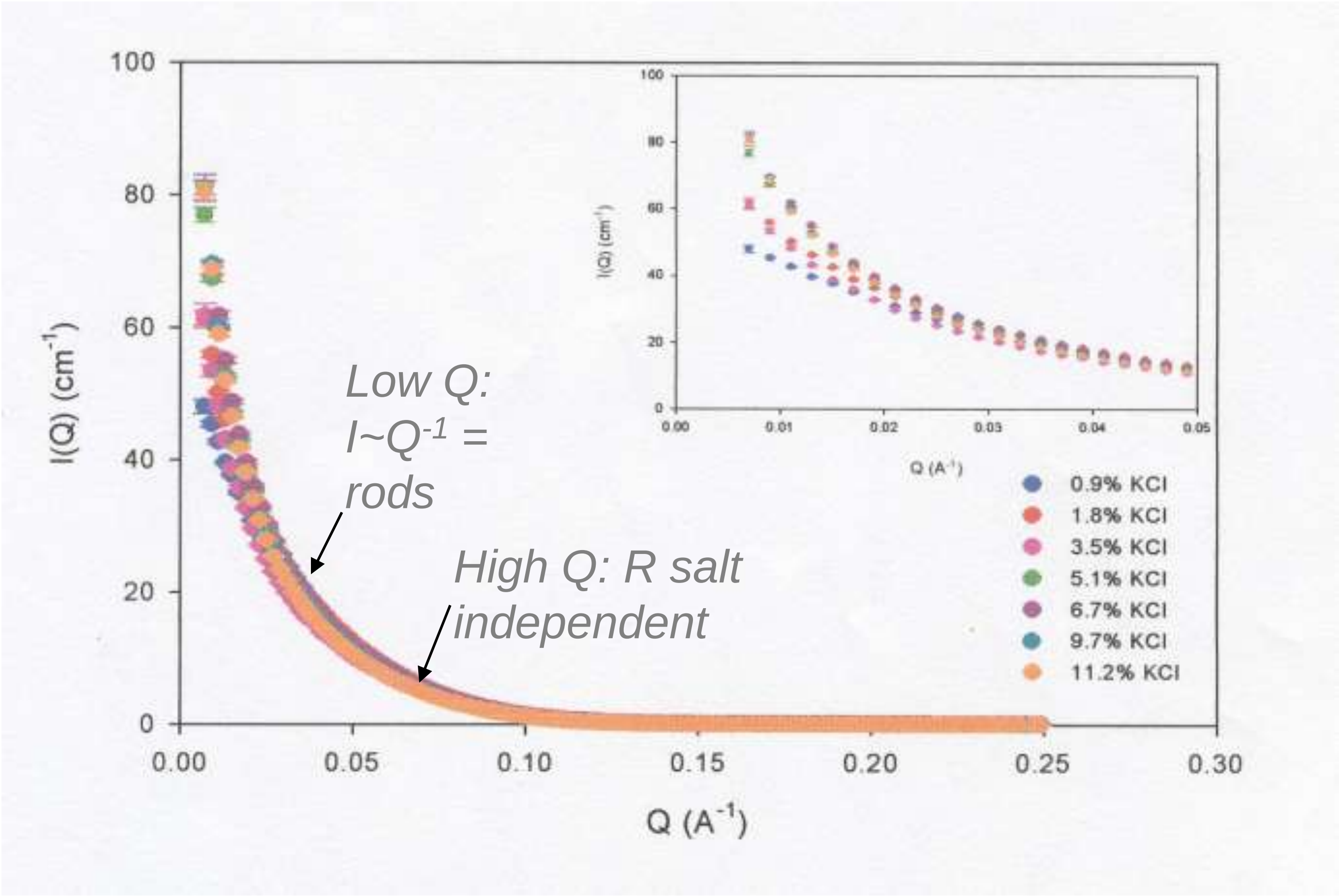


Spherical Micelles, R ~ 33A

Cryo-TEM by Goran Karlsson, Uppsala University and Vania Croce, University of Bristol

V.Croce, T. Cosgrove, G.C. Maitland, T.L. Hughes and G. Karlsson, Langmuir **19** 8536-41 (2003)

SANS study of micelle growth – added salt

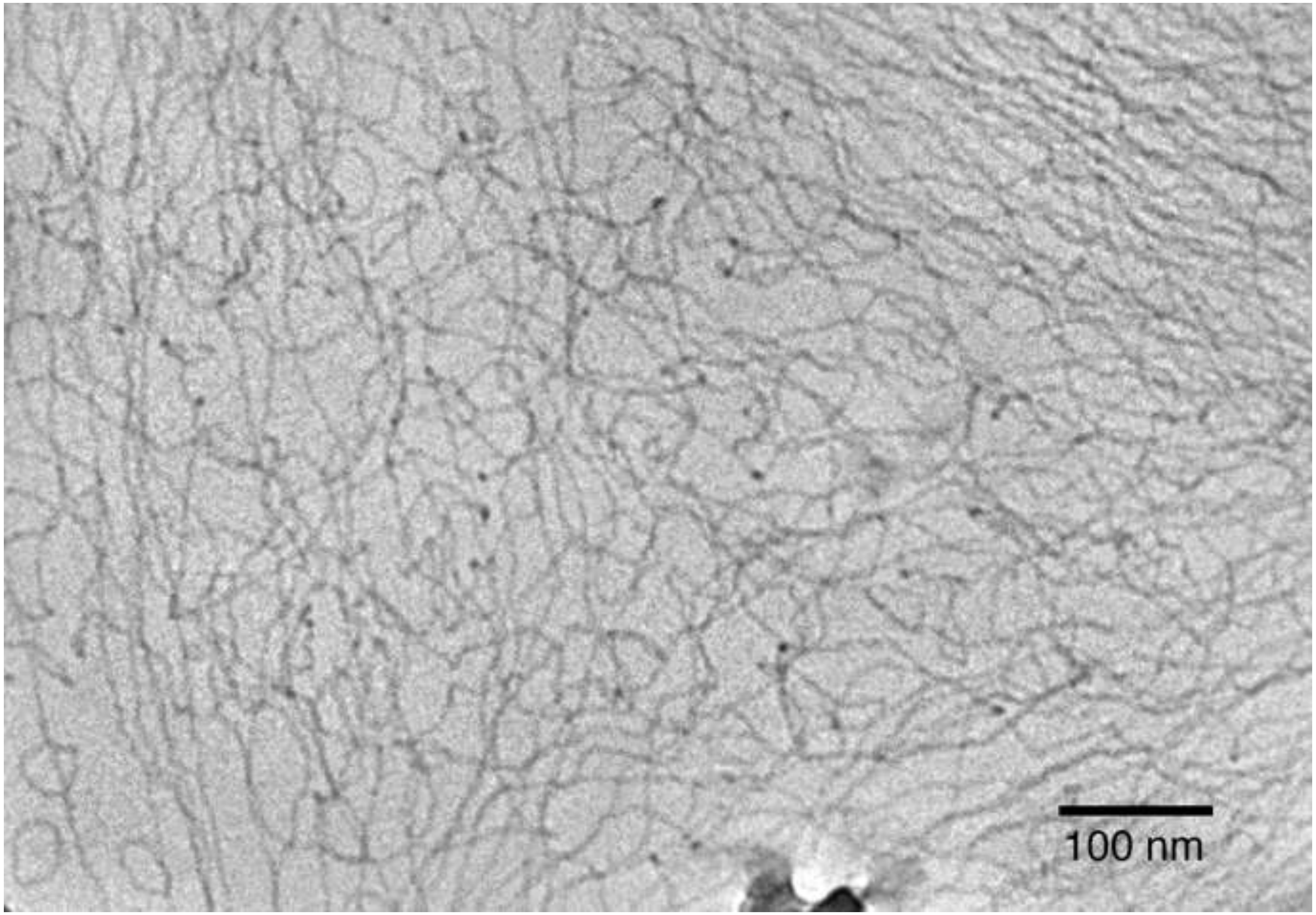


Rodlike micelles, R = 21 A

Data by Vania Croce, University of Bristol

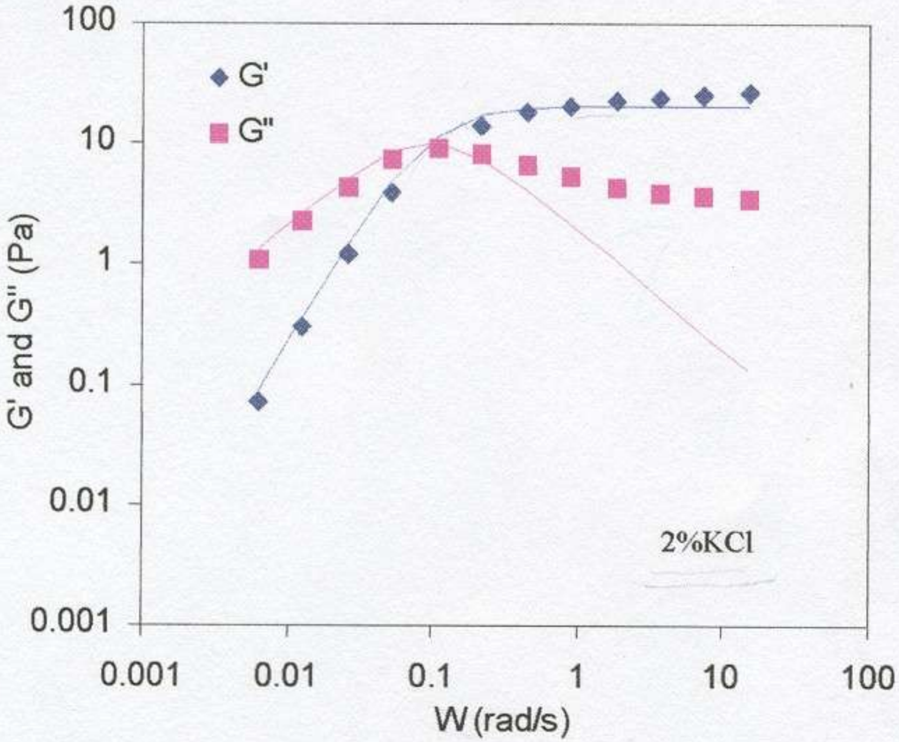
V.Croce, T. Cosgrove, G.C. Maitland, T.L. Hughes and G. Karlsson, Langmuir **19** 8536-41 (2003)

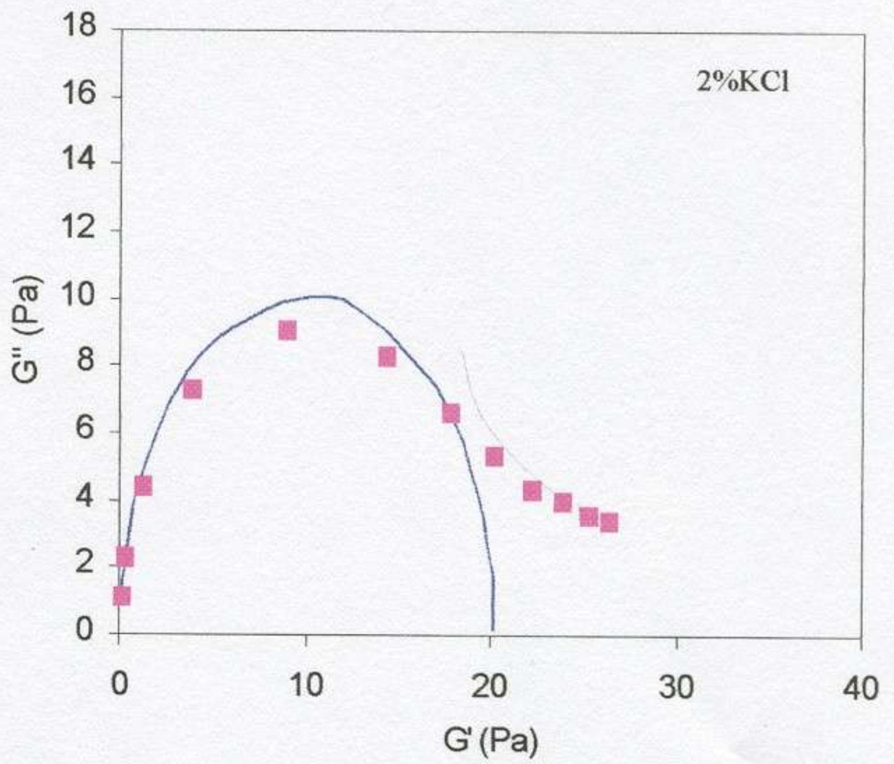
Add 2% KCl…peak viscosity



Entangled Wormlike Micelles
Cryo-TEM by Goran Karlsson, Uppsala University
and Vania Croce, University of Bristol

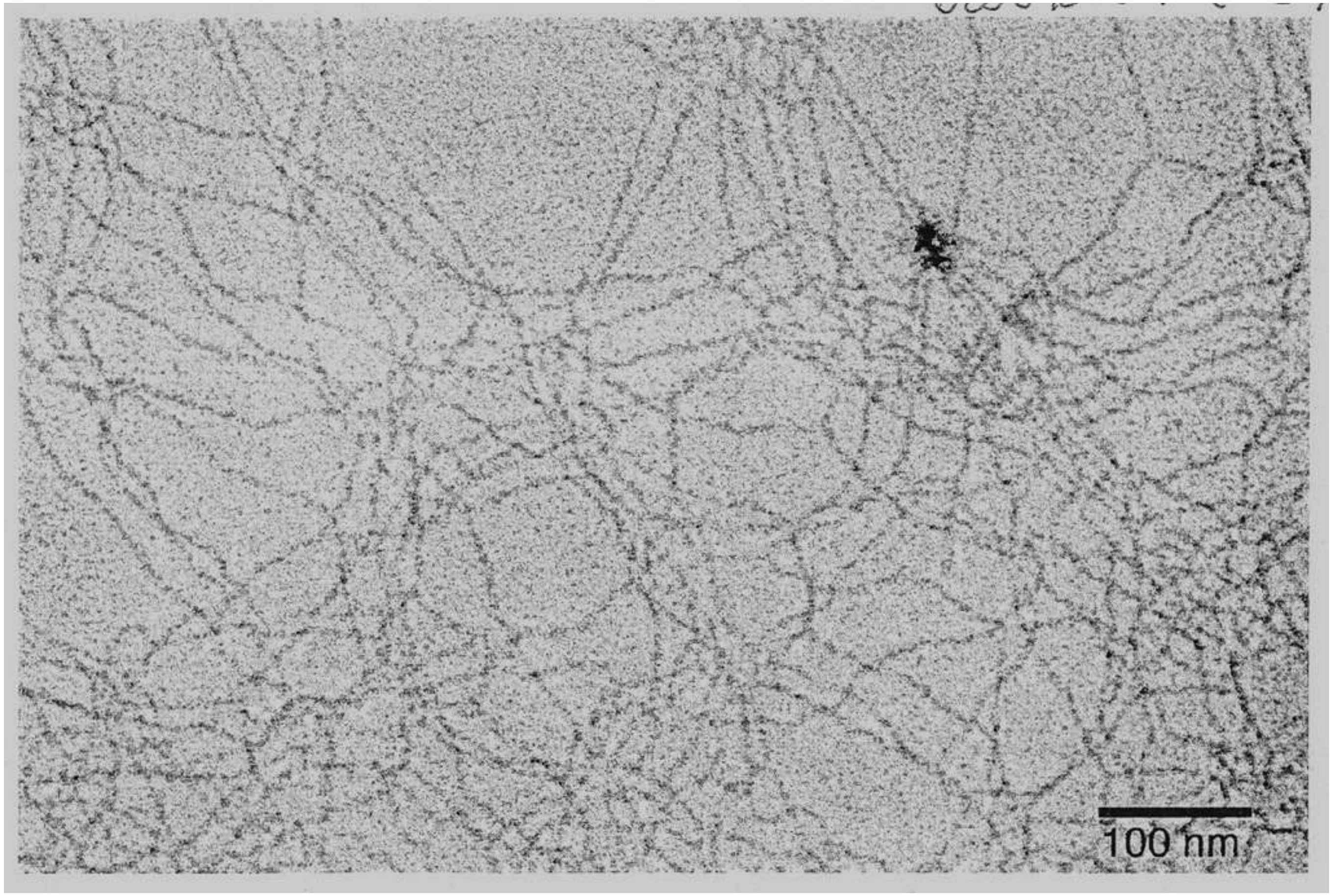
Maxwell behaviour…plus Rouse internal modes at high frequency





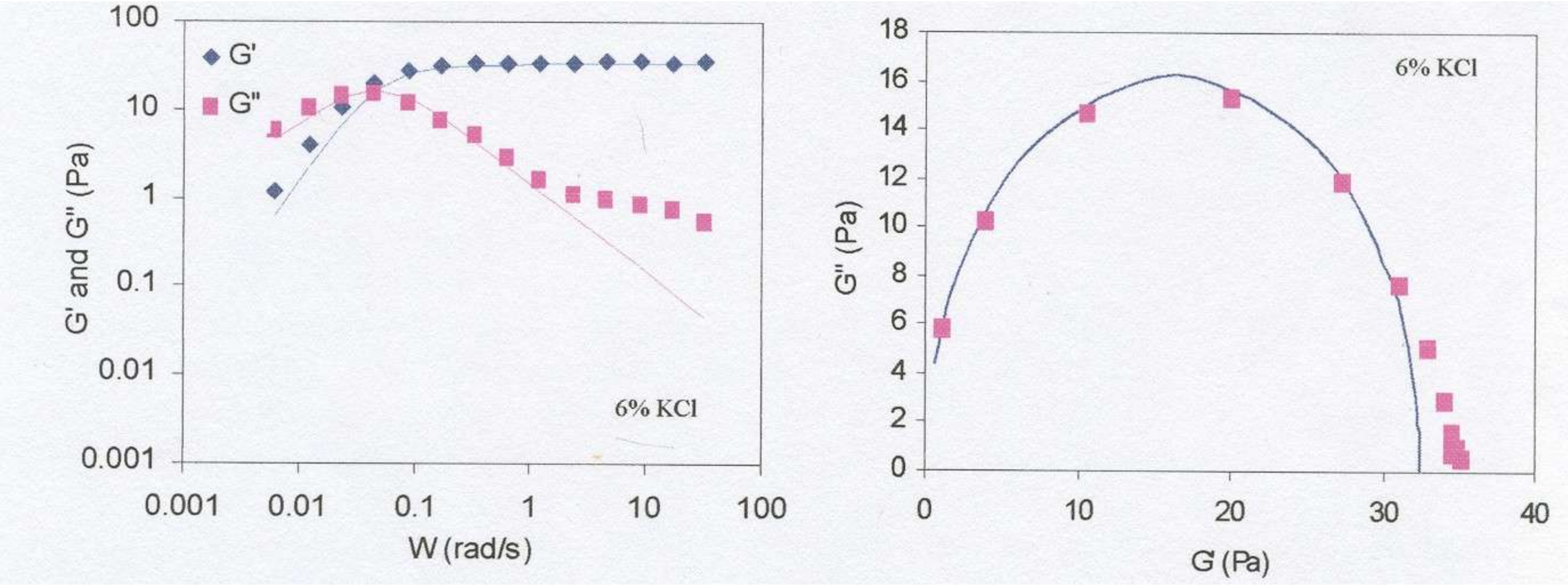
Data: Vania Croce, Univ of Bristol

6% KCl …viscosity falling... …branched micelles



Branched Wormlike Micelles
Cryo-TEM by Goran Karlsson, Uppsala University and Vania Croce, University of Bristol

6% KCl - approaching Maxwell behaviour…



Data: Vania Croce, Univ of Bristol

12% KCl – essentially Maxwell behaviour…

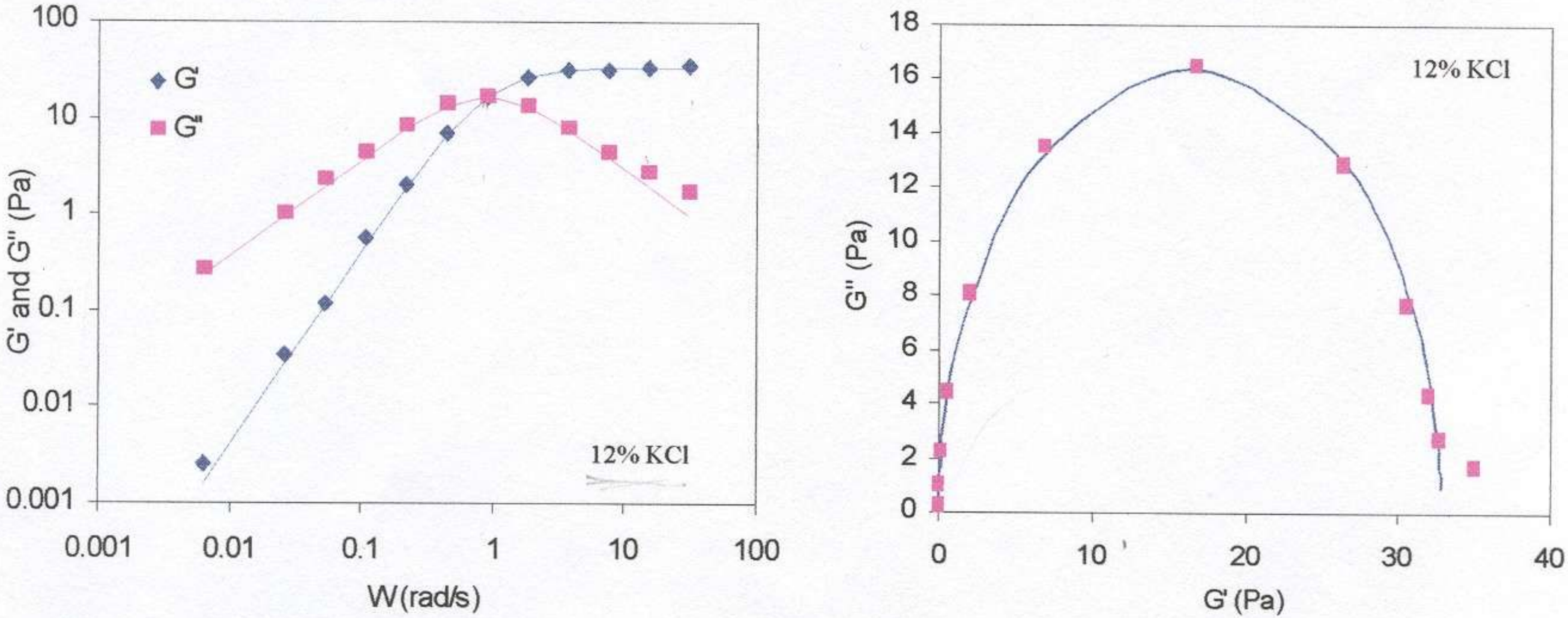
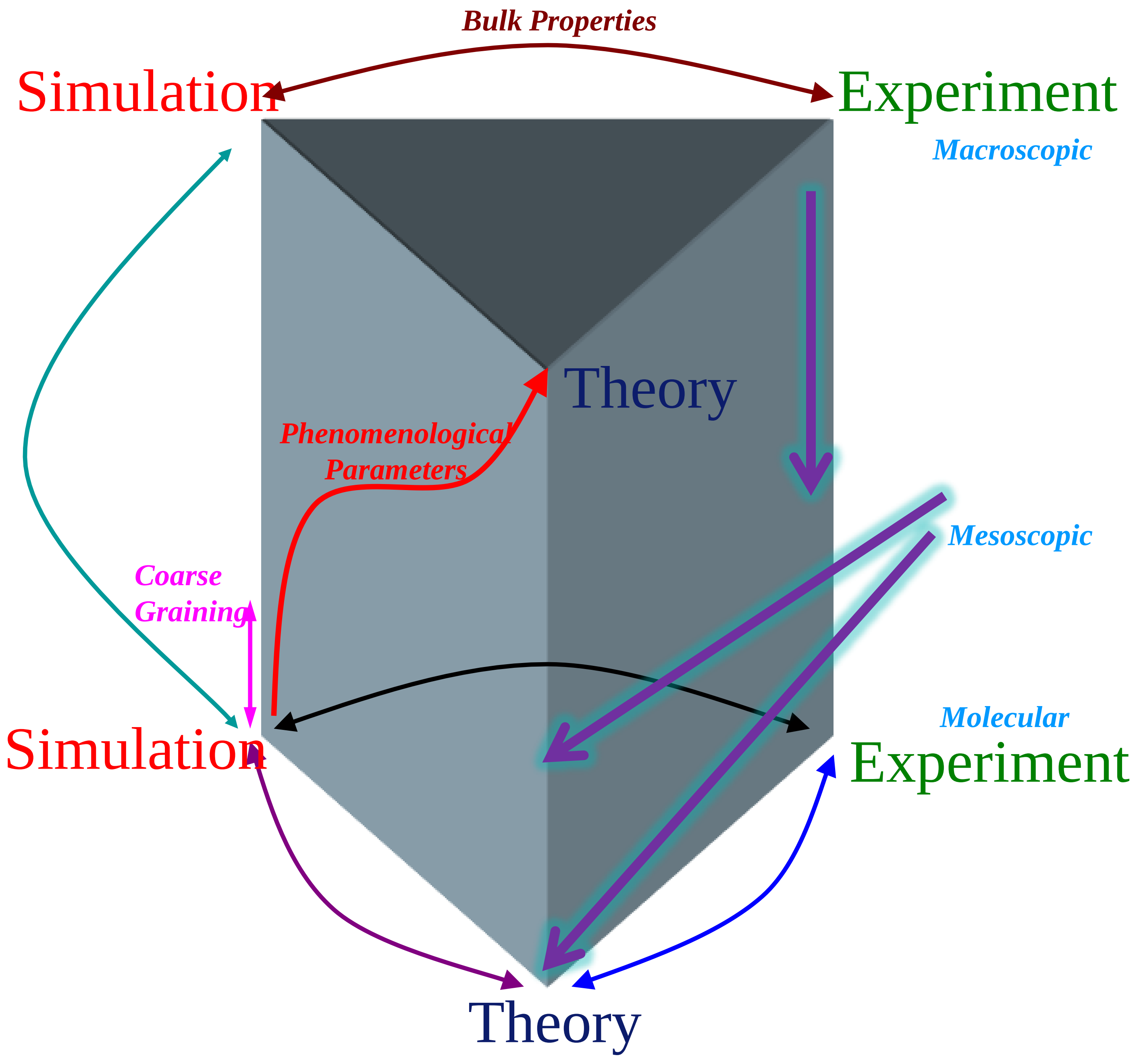


Figure 3.1.9: Evolution of G' and G'' with frequency and the Cole-Cole representation for a solution with 4.5wt % of surfactant concentration with different amounts of salt at 25 °C.

Data: Vania Croce, Univ of Bristol

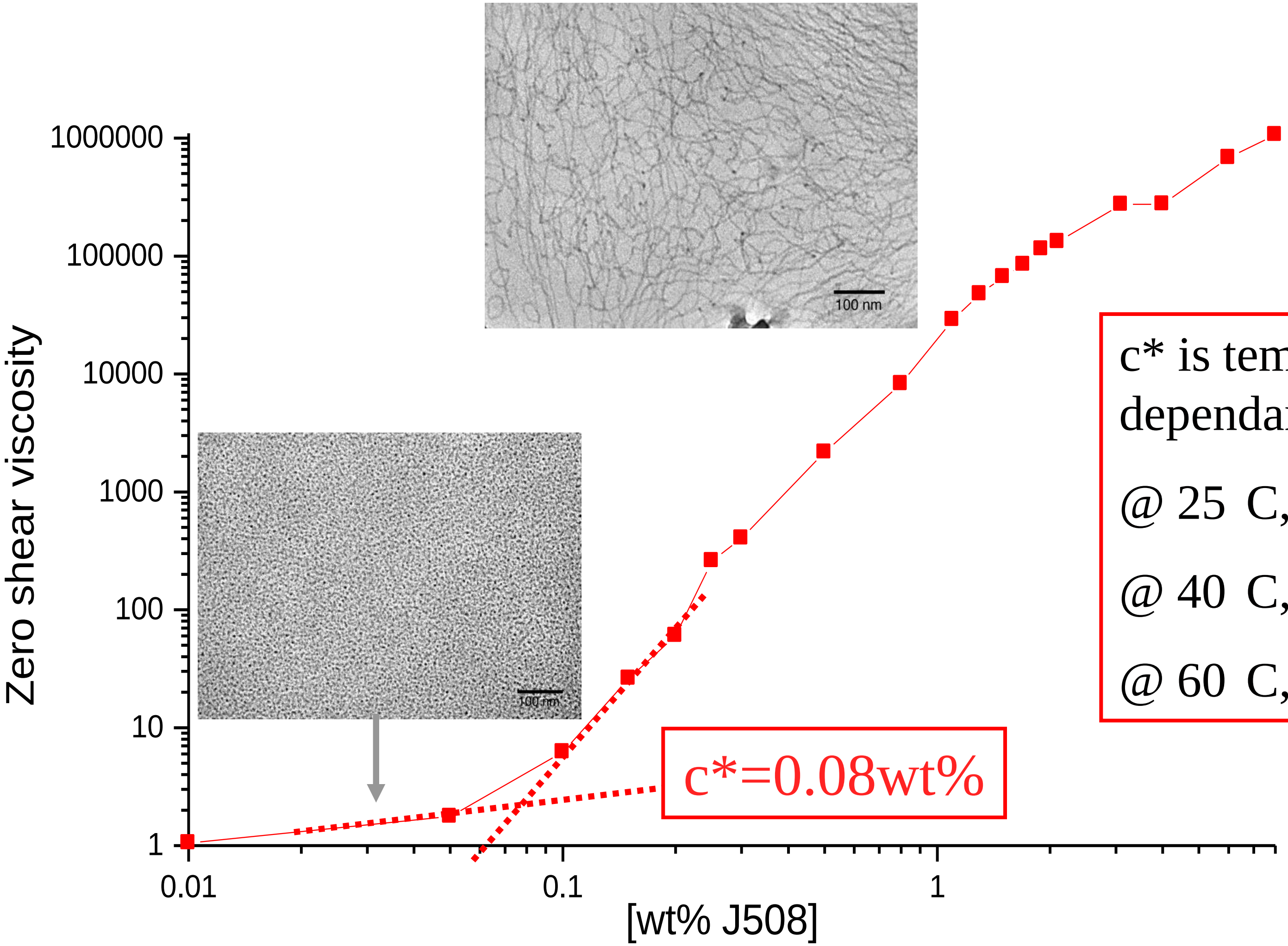
Type of Study



Probing the Microstructure

Rheology and Light Scattering

VES – onset of entanglement regime



c* is temperature dependant:

@ 25 C, c*=0.08wt%

@ 40 C, c*=0.1wt%

@ 60 C, c*=0.15wt%

CryoTEM measurements by Goran Karlsson, Uppsala University, and Vania Croce, University of Bristol

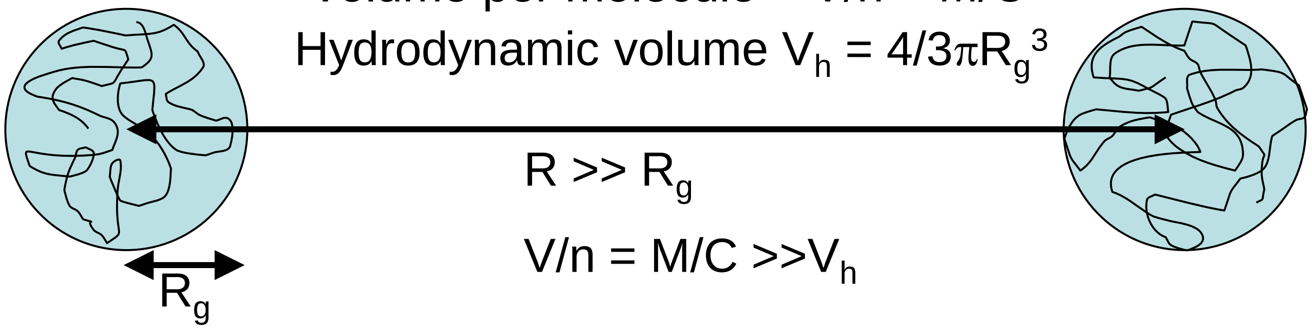
Concentration Regimes

- Dilute

Concentration $C = nM / V$

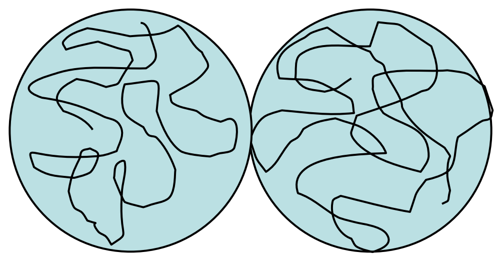
Volume per molecule = $V/n = M/C$

Hydrodynamic volume $V_h = 4/3\pi R_g^3$



- Semi-Dilute

Critical Overlap Concentration
$C^* = M / V_h$

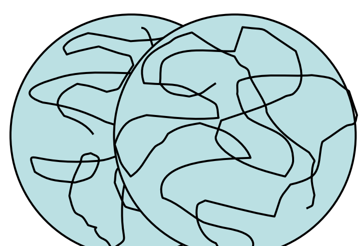


$R = R_g$

$V/n = M/C = V_h$

$C = C^*$

- Concentrated



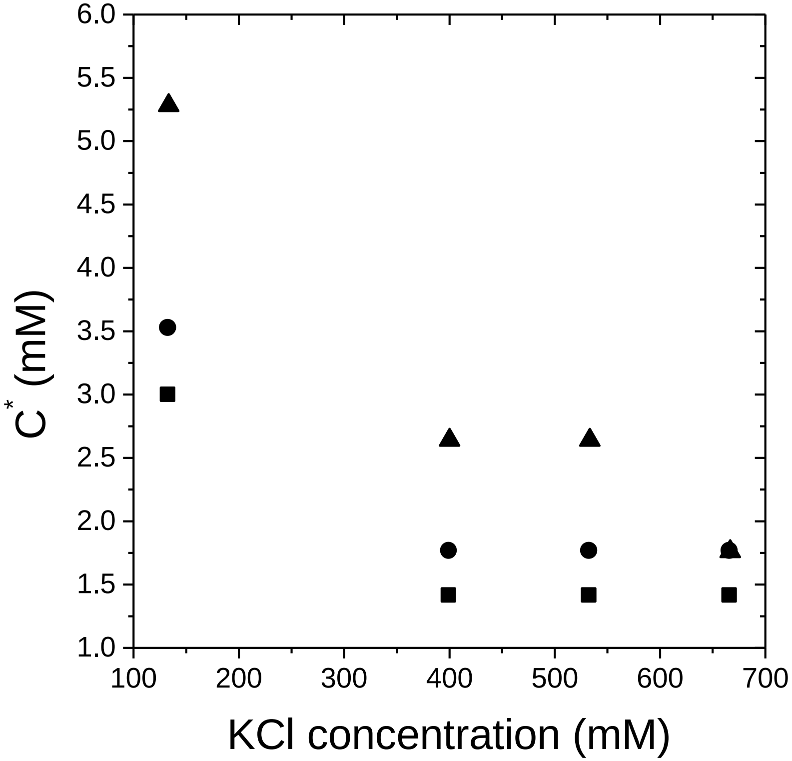
$R << R_g$

$V/n = M/C << V_h$

$C > C^*$

Critical Overlap Concentration c* versus Temperature, Salt

Note: IPA solvent reduces c by about 30%*

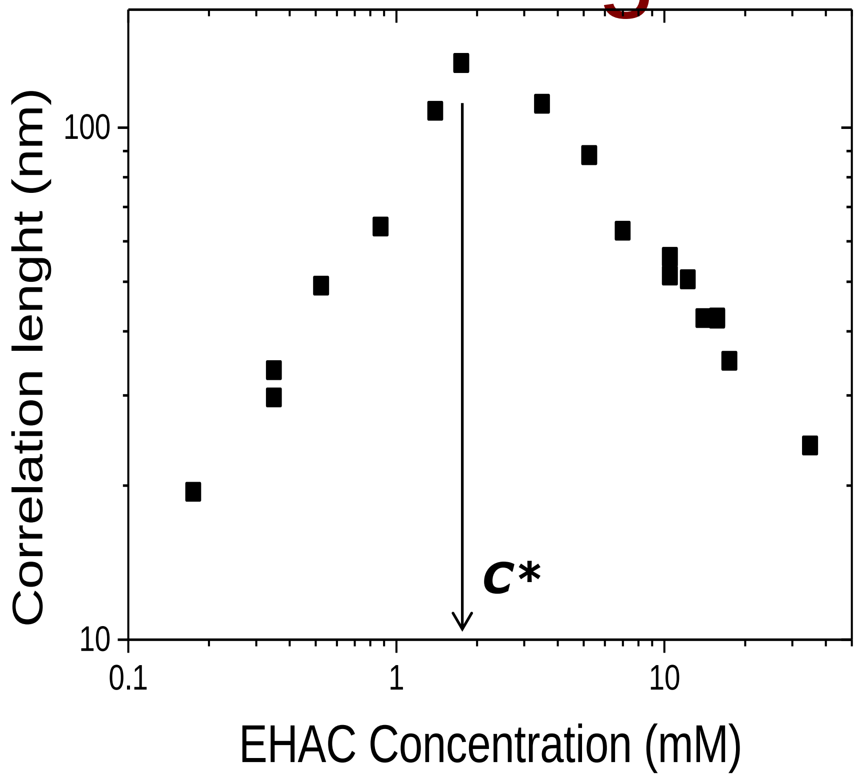


Data: Isabelle Couillet

Crossover concentration C of EHAC solutions versus KCl concentration at 25℃ ( ), 40℃ ( ) and 50℃ ( ).*

*I Couillet, T Hughes, G Maitland F Candau and S J Candau, Langmuir, **20**, 9541-9550, 2004*

Correlation length from static light scattering

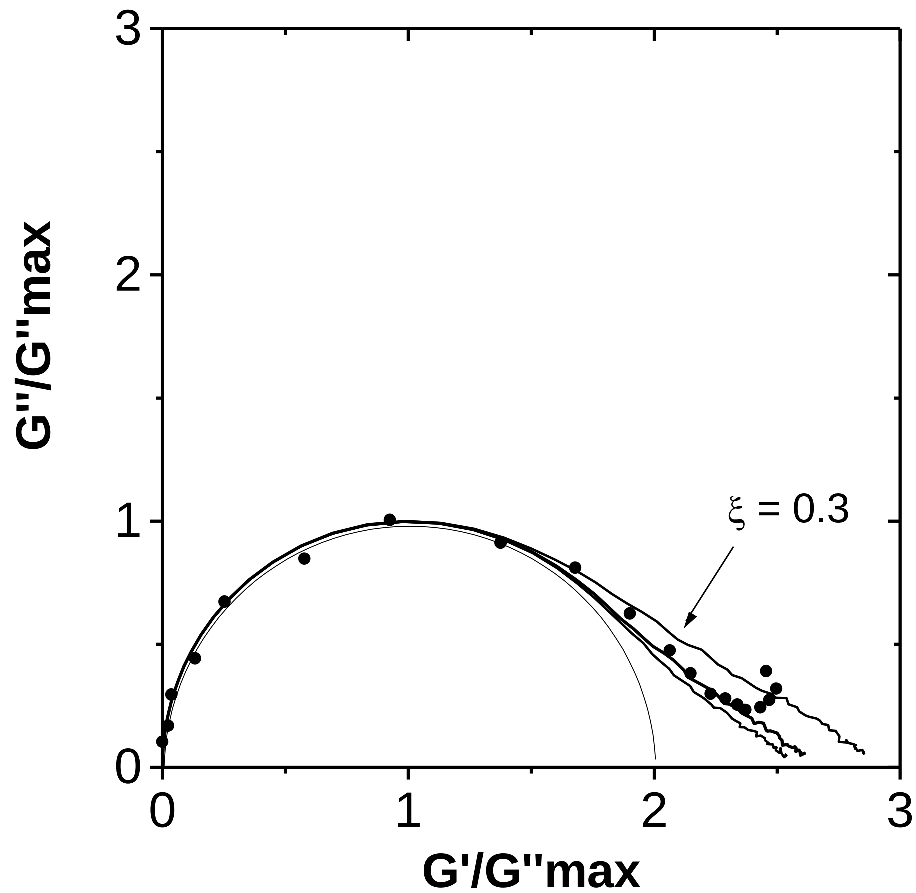


Variation of the correlation length ξ versus active EHAC concentration
With 400mM KCl at 25°C.

Correlation Length ξ from Ornstein-Zernicke Equation: $I(q)^{-1} = I(0)^{-1}[1 + q^2\xi^2]$

*I Couillet, T Hughes, G Maitland F Candau and S J Candau, Langmuir, **20**, 9541-9550, 2004*

Estimation of $\zeta = \tau_{break}/\tau_R$

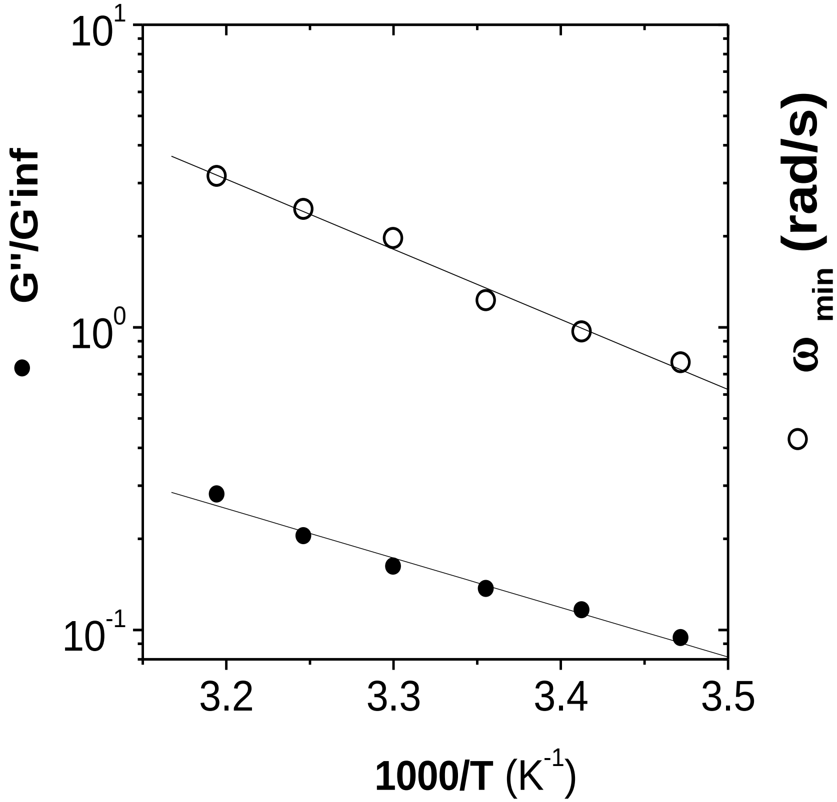


Data: Isabelle Couillet

Normalized Cole-Cole plot for a solution of EHAC at an active concentration 14.4 mM with T=15℃, [KCl]=400mM. The dotted lines are the calculated Cole-Cole plots for different values of the parameter ζ (0.1, 0.13 and 0.3).

*I Couillet, T Hughes, G Maitland F Candau and S J Candau, Langmuir, **20**, 9541-9550, 2004*

Direct Determination of E_{sciss}



$G''_{min}/G'_{inf} \sim l_e/<L>$
$\sim exp[-E_{sciss}/2kT]$

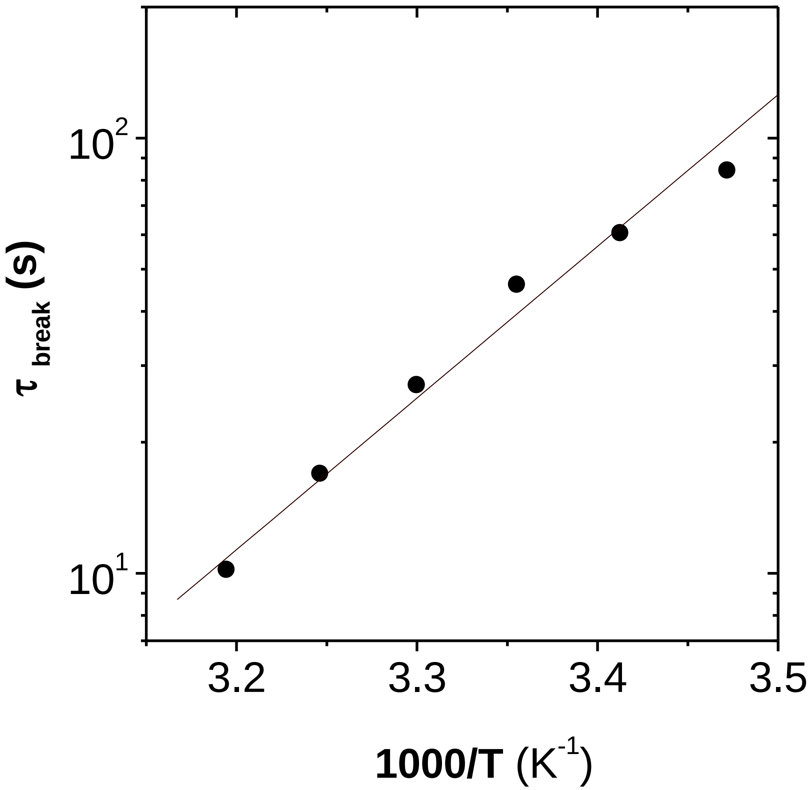
E_{sciss} = 28kT

Semi-log variation of G''_{min}/G'_{inf} ( ) and ω_m (o) as a function of $10^3/T$ for a solution with an active EHAC concentration of 14.1 mM, and 400 mM KCl

Data: Isabelle Couillet

*I Couillet, T Hughes, G Maitland F Candau and S J Candau, Langmuir, **20**, 9541-9550, 2004*

Activation Energy for Micelle Breaking



$E_{break} = 25.5kT$

$E_R = 0.5(E_{break} + E_{rep})$

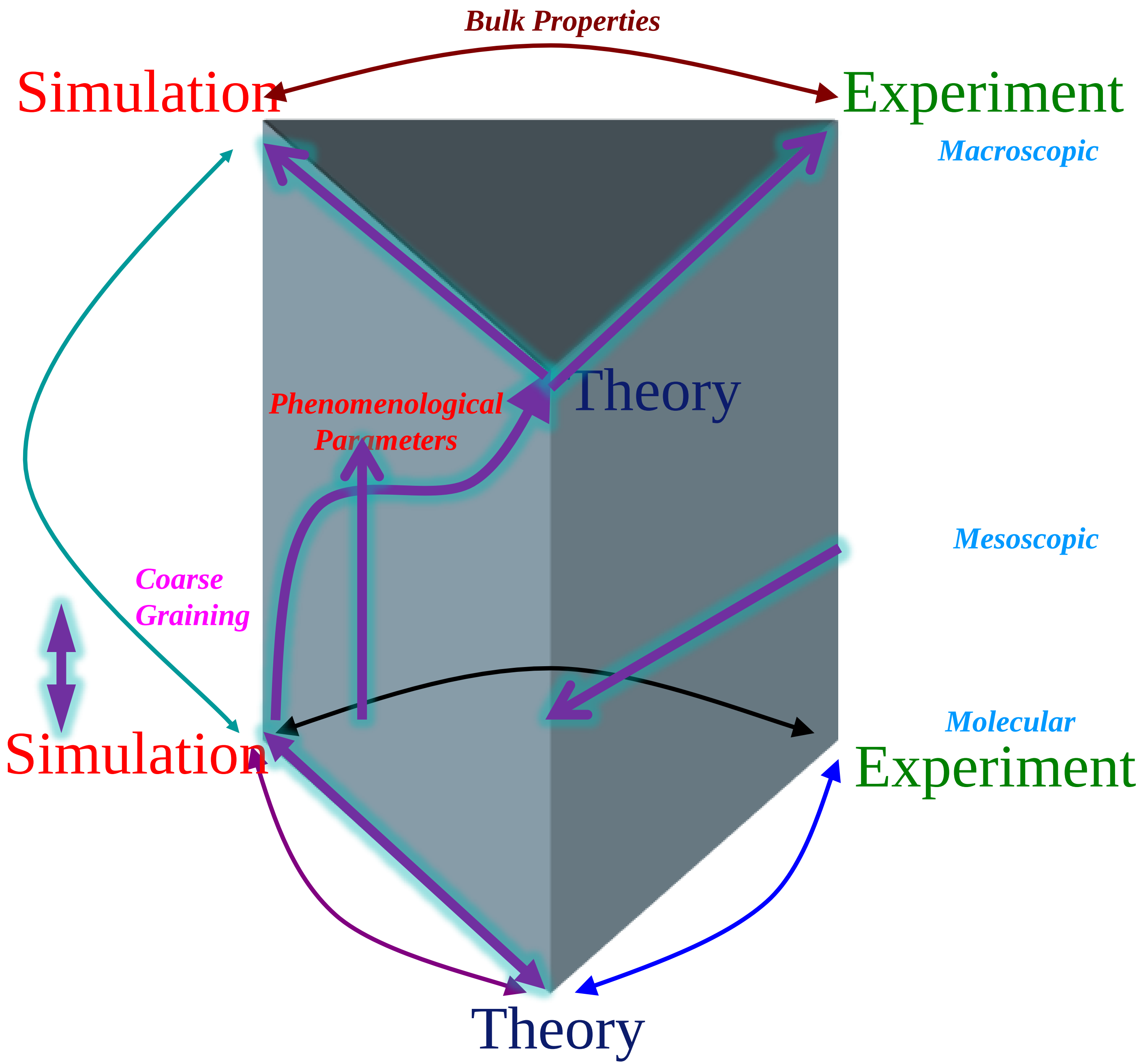
$= 0.5(E_{break} + 1.5\ E_{sciss})$

$= 34kT$

$\boldsymbol{E_{sciss} = 28kT}$

Arrhenius plot of the breaking time τ_{break} versus $10^3/T$
for active EHAC concentration of 14.1 mM and 400 mM KCl

Type of Study



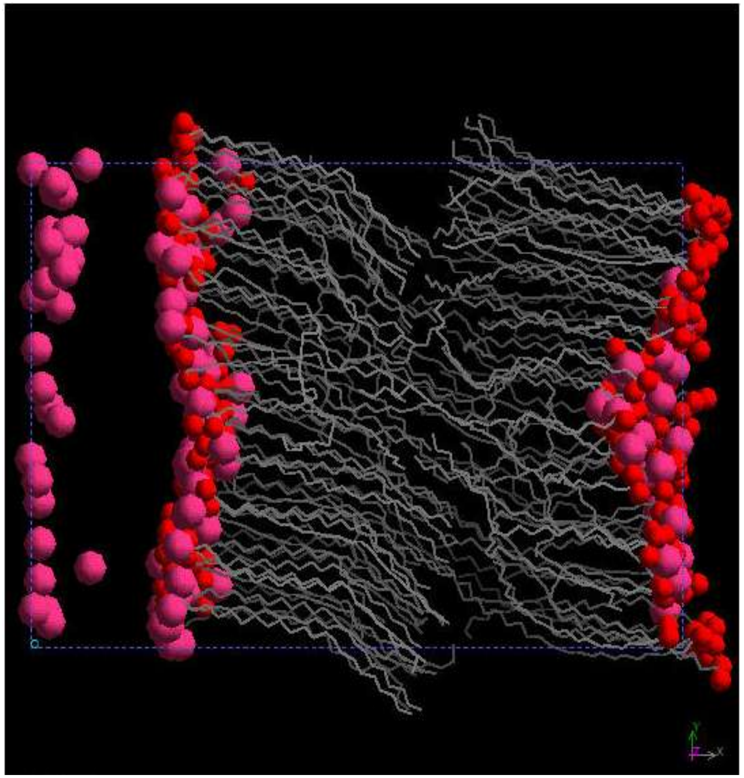
Simulation: from Micro to Meso to Macro

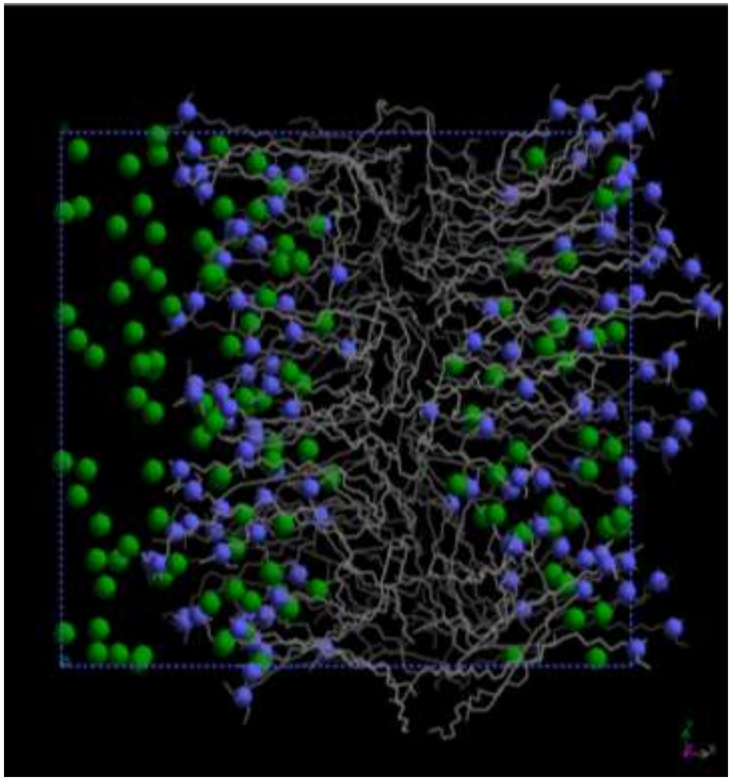
1. Micro-scale
   - Atomistic Molecular Dynamics simulation of micelles
   - Coarse-grained micelle MD
   - Output: persistence length, compressibility, scission/end cap/branching energies, …

2. Mesoscopic simulation of wormlike micellar VES fluids
   - Coarse-grained micelle MD
   - Output: rheology of bulk VES fluid

3. Macro-scale: fluid dynamics
   - flow in porous media: leak-off and clean up of frac fluid
   - particle laden flow: proppant transport, shear banding,…

MD simulation of surfactant packing





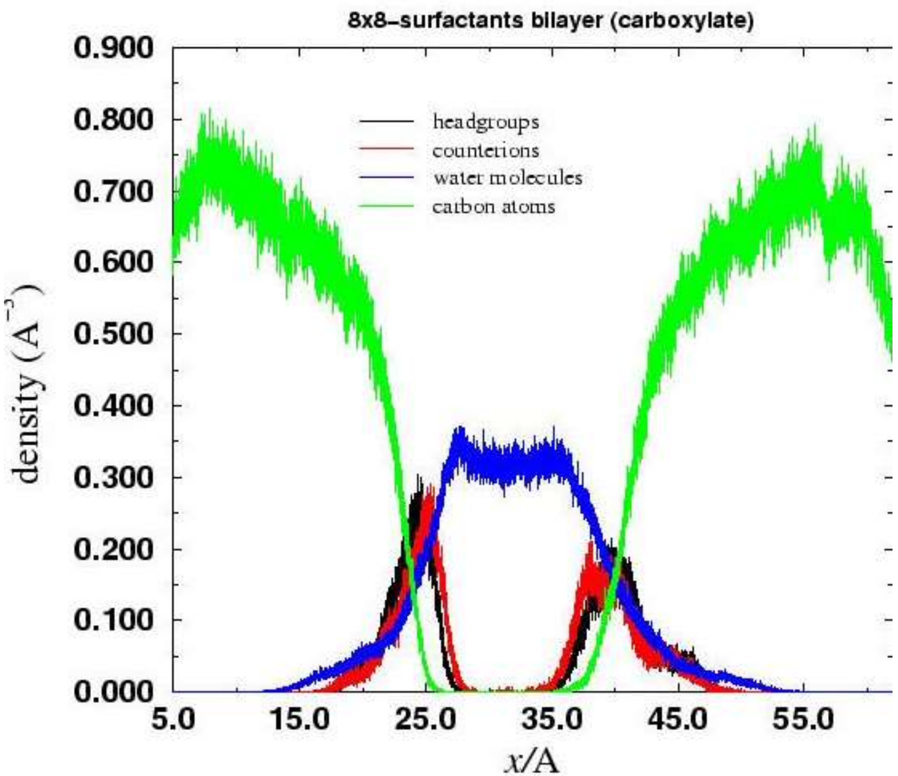
Erucate (ordered) EHAC (less ordered)

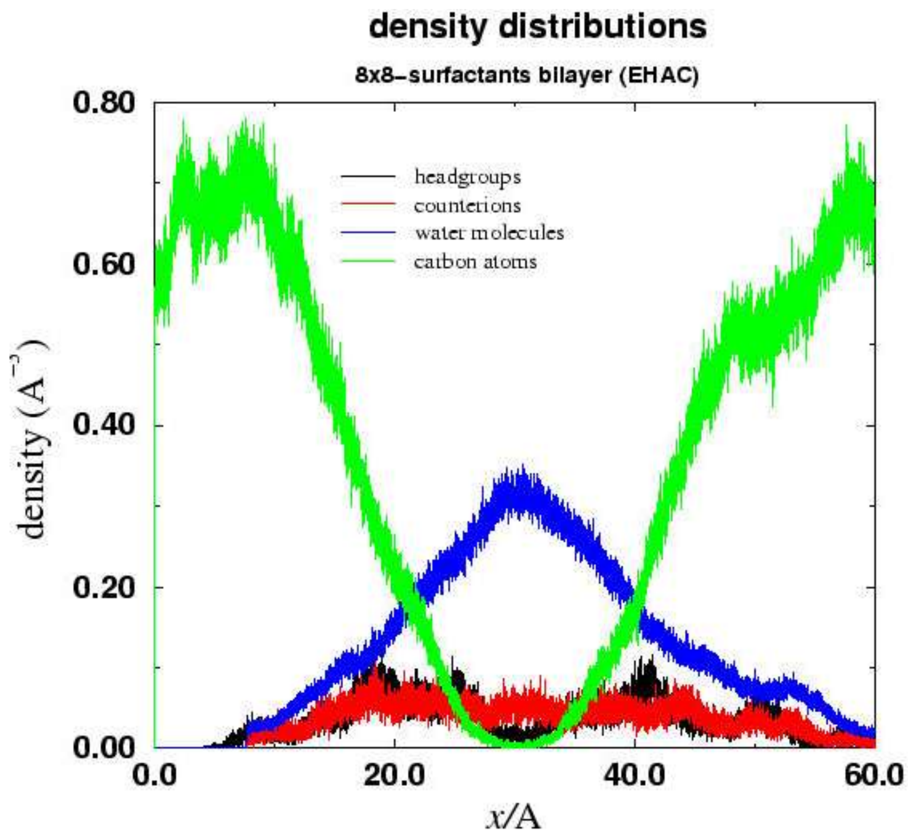
Same tail, different heads: different packing behaviour

Erucate		EHAC
0.93	$\langle \Sigma_{i,j} s_i . s_j \rangle / N^2$	0.62

ES Boek, A Jusufi, H Loewen and GC Maitland, J Phys Condens Matter, 14, 9413-9439, 2002

Density distributions

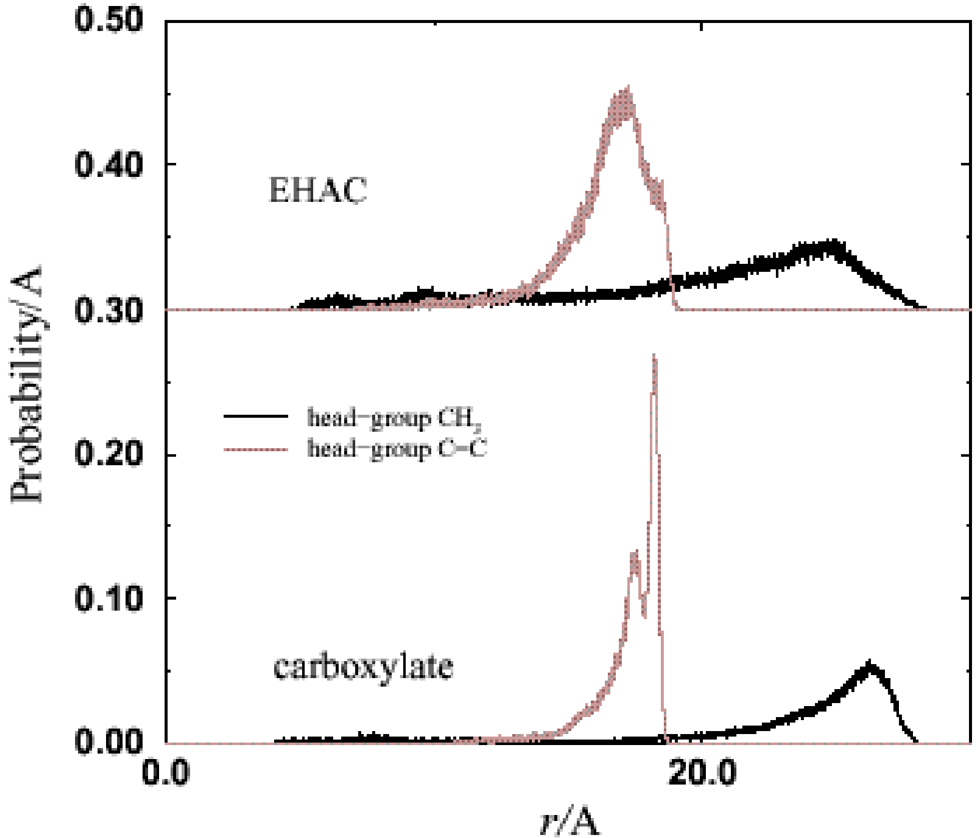




Penetration of water into membrane core
- similar to cylindrical micelles
(Watanabe & Klein, 1991)

ES Boek, A Jusufi, H Loewen and GC Maitland, J Phys Condens Matter, 14, 9413-9439, 2002

Intra-chain separations



Peaks at large r are due to fully extended chains –

at smaller distances show tendency to "fold back"

Sharper C=C peaks show that first part of chain is less flexible

ES Boek, A Jusufi, H Loewen and GC Maitland, J Phys Condens Matter, 14, 9413-9439, 2002

Control of Fluid Properties through Design of Chemical Structure

Moving from Formulation towards Molecular Engineering

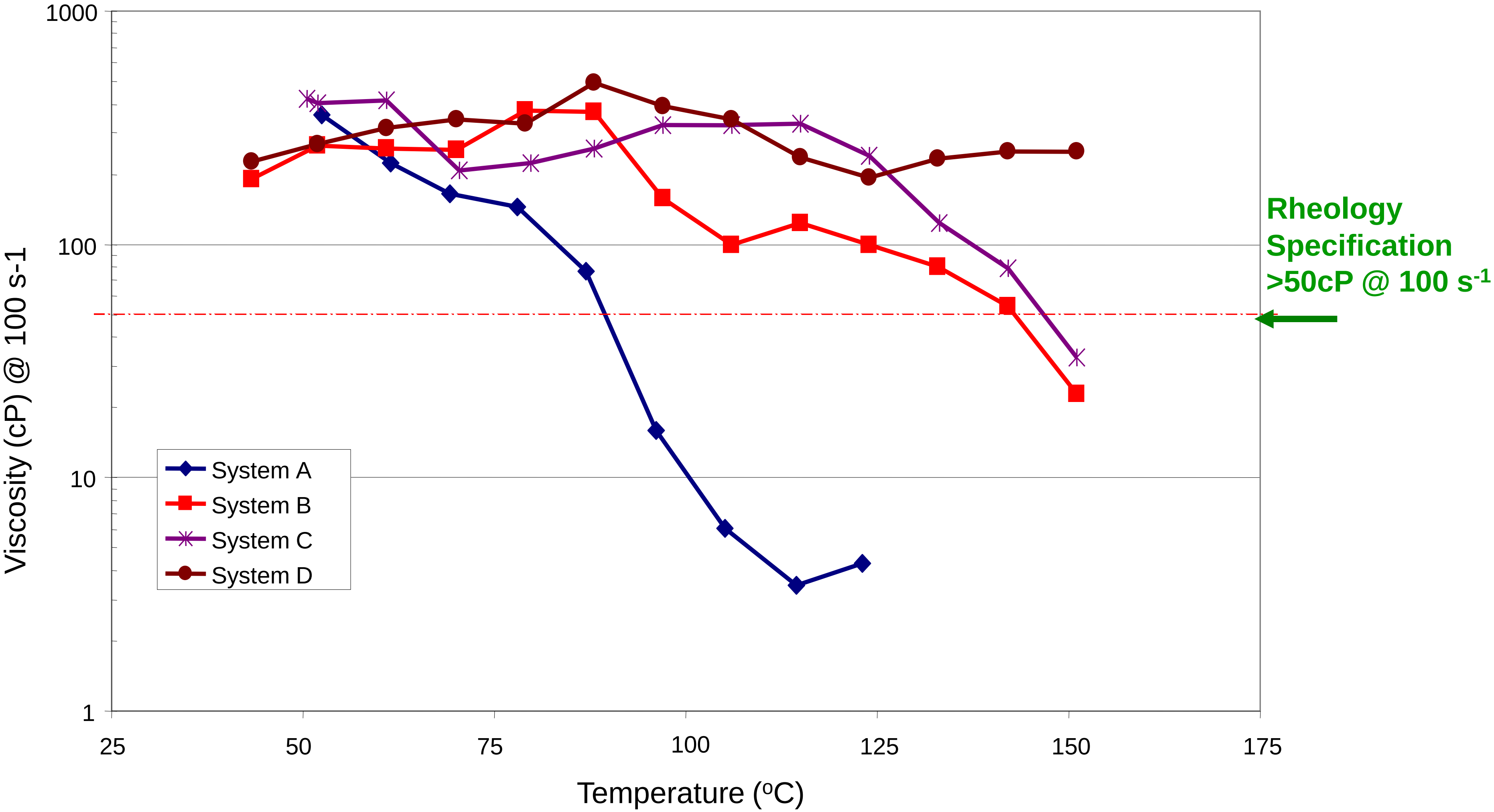
Alternative VES Structures

$R - X - Y - COO^-$

Hydrophobic Tail	*Spacer group*	*Spacer group*	*Charged group*

Tune headgroup and tail interactions to increase packing parameter, $P = V_s / la$, and so stabilise wormlike phase to higher temperatures

Improving Temperature Performance

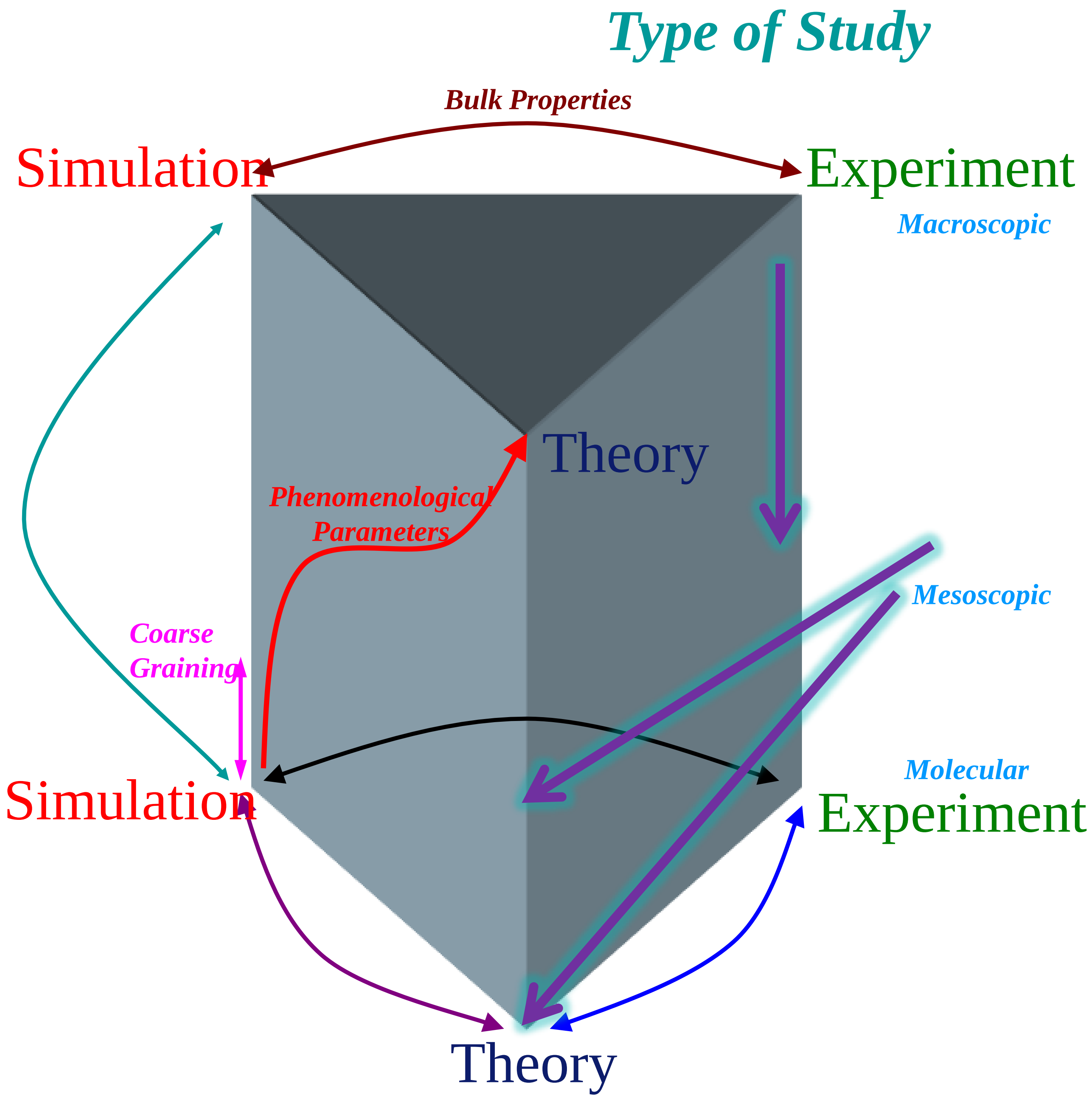


Data: T L Hughes et al, Schlumberger

The major block for using new molecules in the oilfield:

££££££££££££

Must leverage on other non-oilfield applications



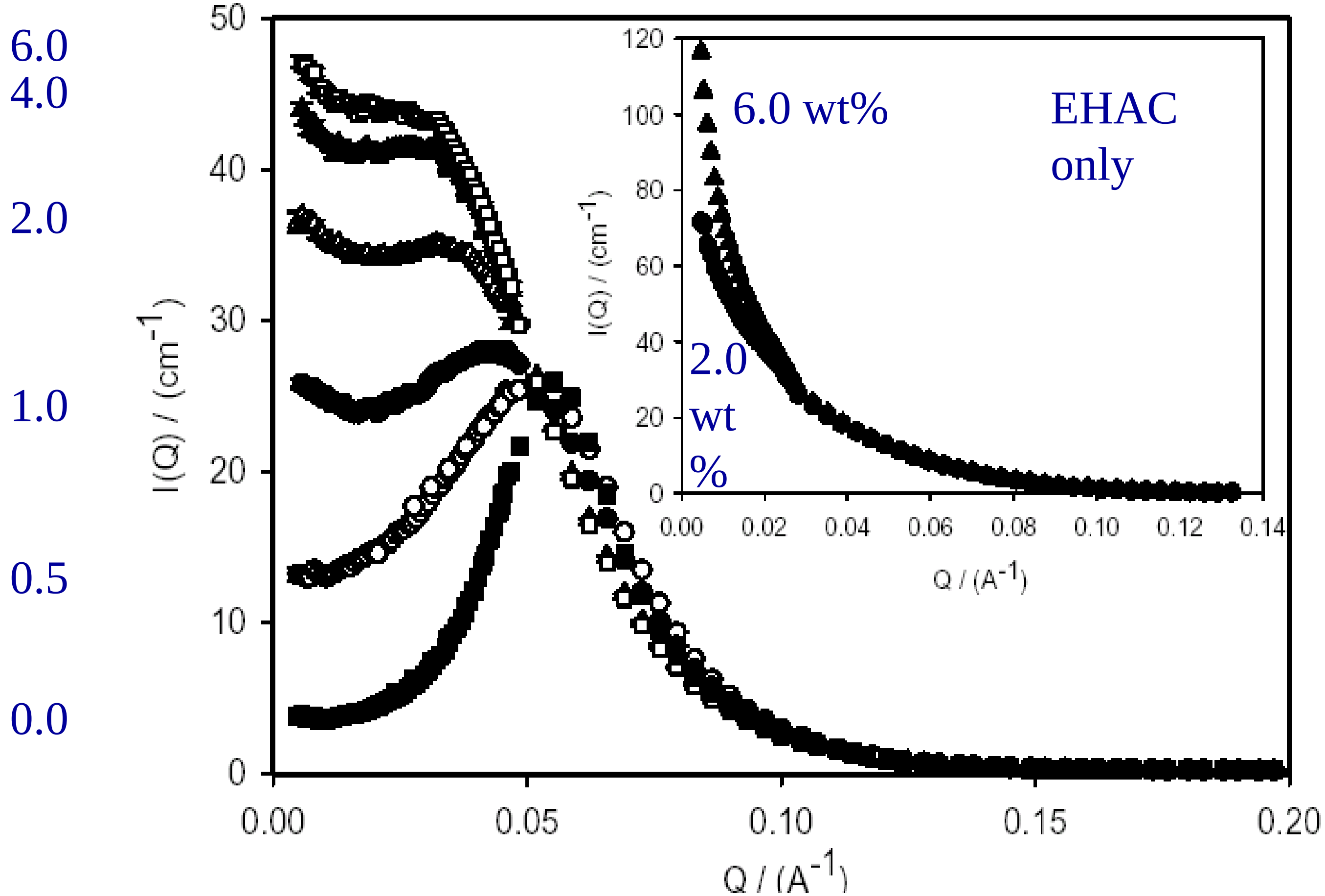
Type of Study
Bulk Properties
Simulation
Experiment
Macroscopic
Theory
Phenomenological Parameters
Mesoscopic
Coarse Graining
Molecular
Simulation
Experiment
Theory

Tuning Properties by Blends

(a) Surfactant Blends

SANS for EHAC-$C_{18}E_{18}$ mixed micelles vs [salt]

[KCl] wt%

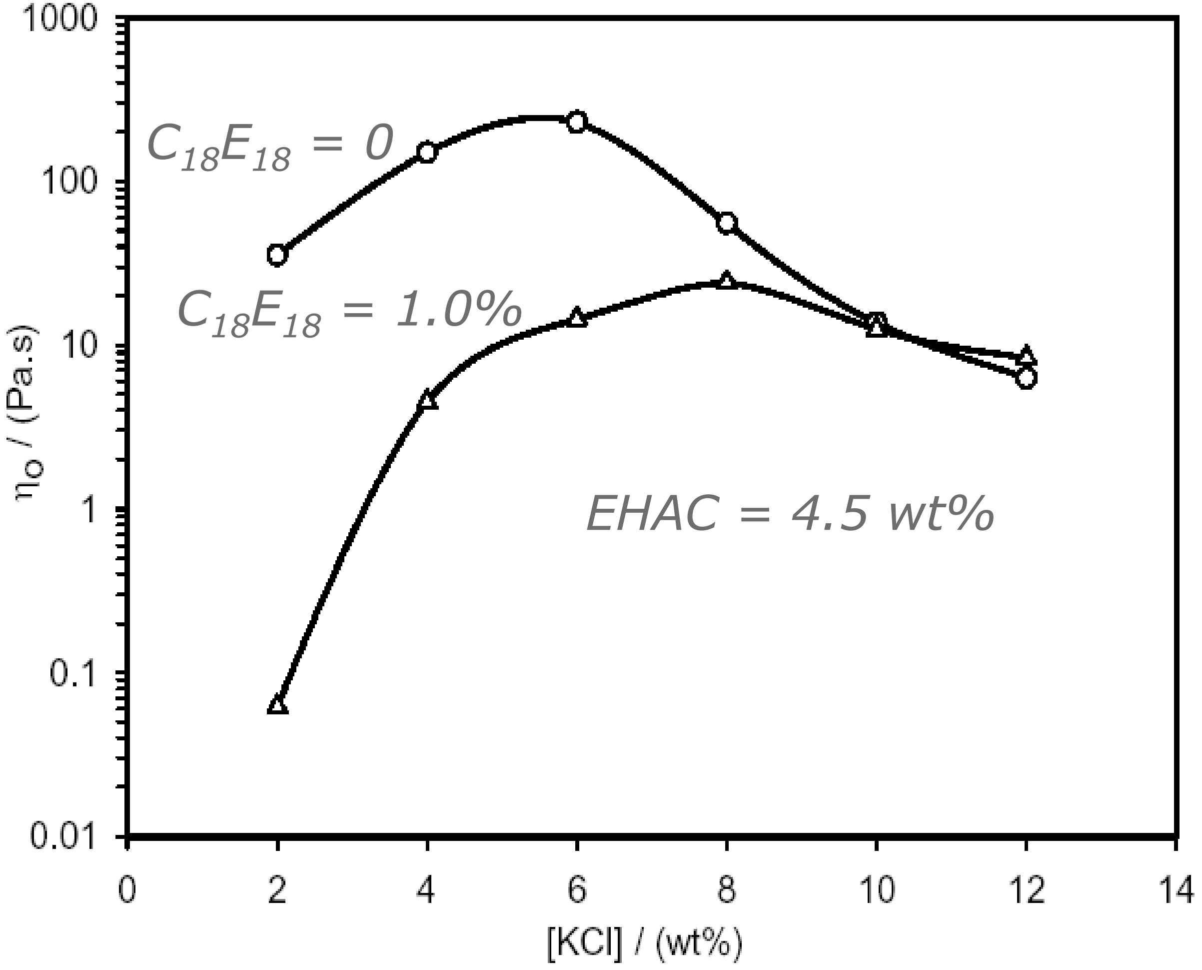


25C

4.5wt% EHAC, 4.0wt% $C_{18}E_{18}$

*V Croce, T Cosgrove, C Dreiss, G Maitland, T Hughes and G Karlsson, Langmuir, **20**, 7984-7990, 2004*

Low shear viscosity for EHAC-$C_{18}E_{18}$ mixed micelles



*V Croce, T Cosgrove, C Dreiss, G Maitland, T Hughes and G Karlsson, Langmuir, **20**, 7984-7990, 2004*

Microstructure associated with rheology changes in mixed worm-micelle fluids

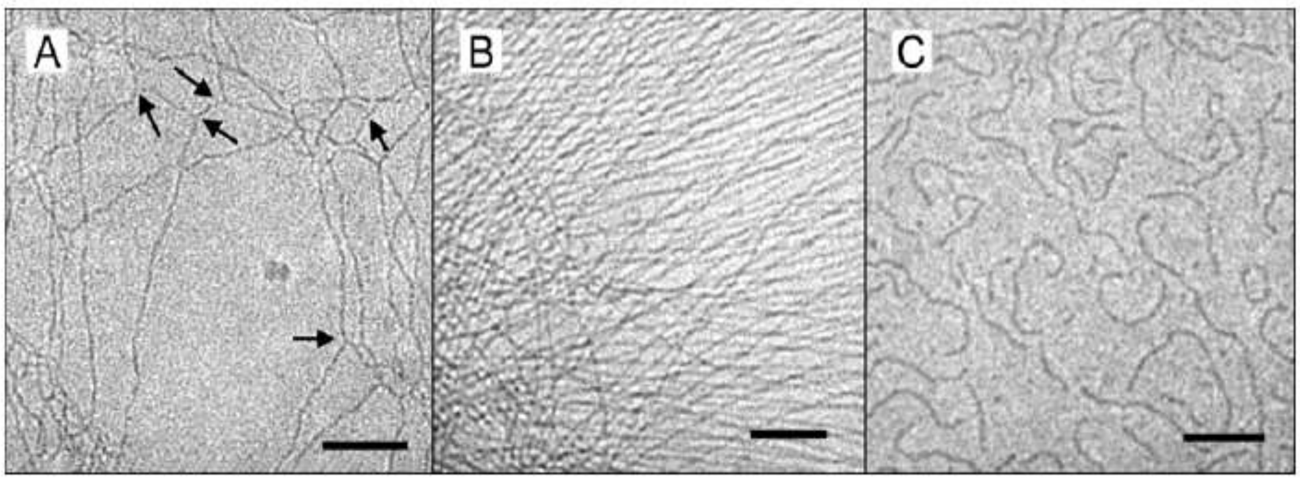


Figure 10. Cryo-TEM images with samples containing 4.5 wt% EHAC with 6.0 wt% KCl varying concentration of $C_{18}E_{18}$. (*A*: No $C_{18}E_{18}$, *B*: 1.0wt% $C_{18}E_{18}$ and *C*: 4.0 wt% $C_{18}E_{18}$). Bar = 100 nm

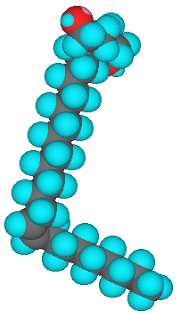
*V Croce, T Cosgrove, C Dreiss, G Maitland, T Hughes and G Karlsson, Langmuir, **20**, 7984-7990, 2004*

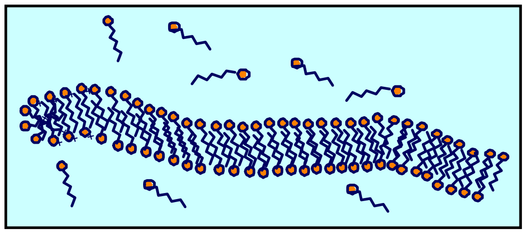
Tuning Properties by Blends

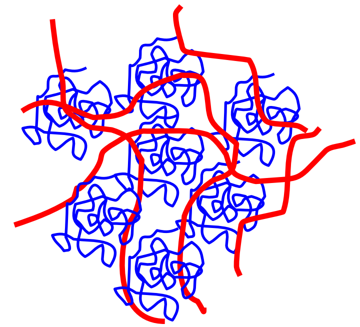
(b) Polymer-Surfactant Blends

Polymer-surfactant mixtures

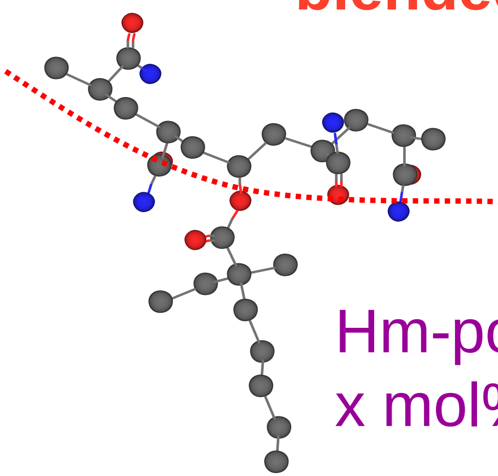
Visco-elastic surfactant (VES) - EHAC







blended with



Hm-polymer
x mol% hydrophobe

- VES/hm-polymer blend
  - visco-elastic physical gel
  - selective response to oil
  - lower concentrations of both polymer and surfactant

Hm-Polymer:Surfactant Mixtures - Enhanced linear viscoelasticity

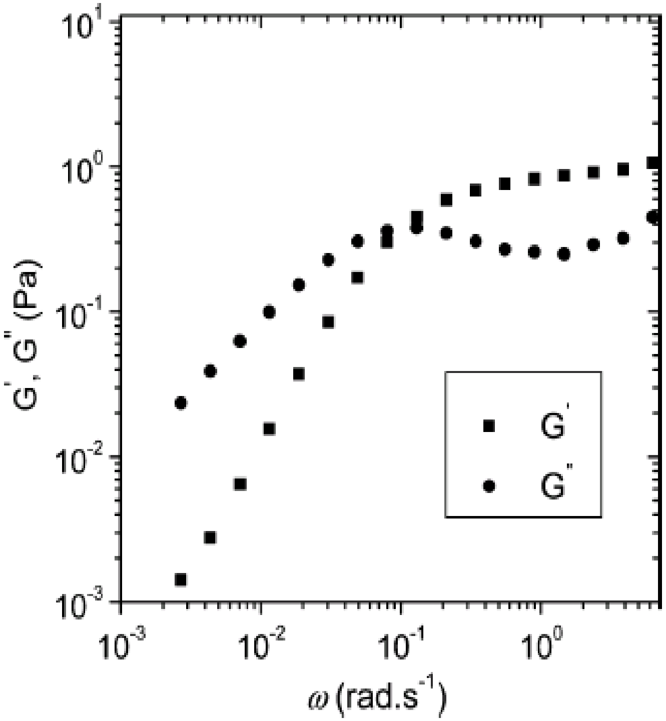
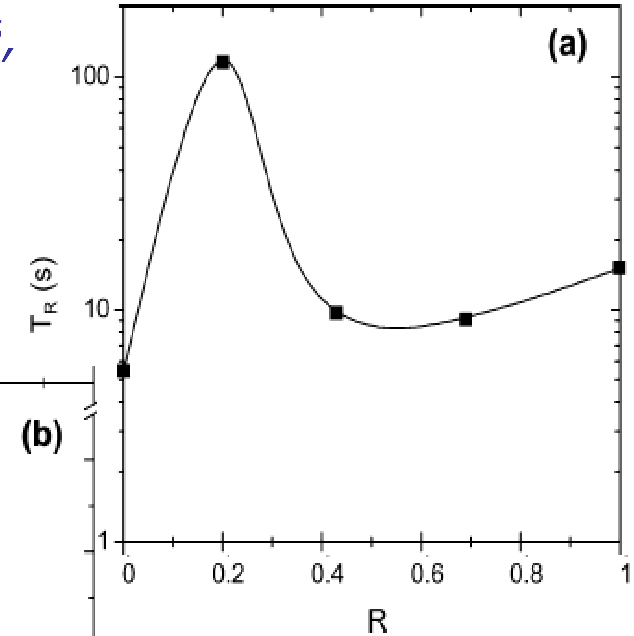


Figure 5. Storage (G') and loss (G'') moduli as a function frequency at 25 °C for a solution of 0.2 wt % hm-HPG, 0.15 % EHAC, and 3 wt % KCl ($R = 0.43$).

Hm-HPG: Mw ~ 1.8x10^6, <DP> ~ 3000, C_{22} side groups 10 per chain

R = [C_{EHAC}]/[C_{EHAC} + C_{HmHPG}]



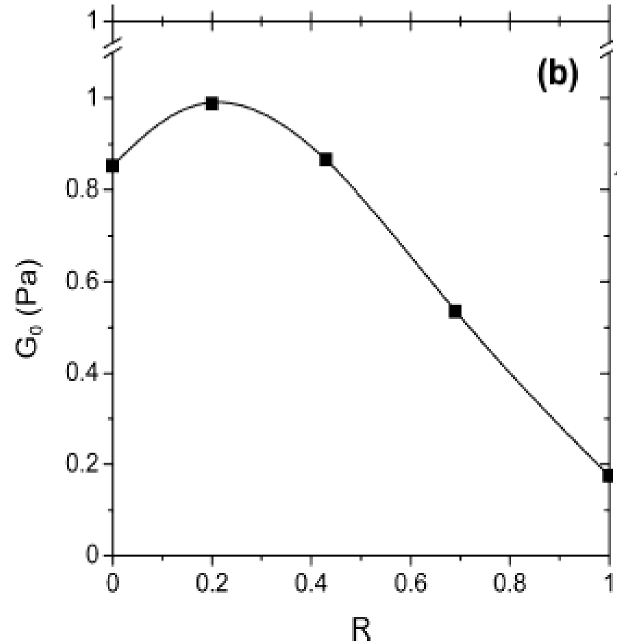


Figure 6. Terminal relaxation time (T_R, a) and pla modulus (G_0, b) vs R for systems with an overall concentr: $C_M \approx 0.35$ wt %.

*I Couillet, T Hughes, G Maitland and F Candau, Macromolecules, **38**, 5271-5282, 2005*

Hm-HPG:EHAC mixtures – shear viscosity enhancement

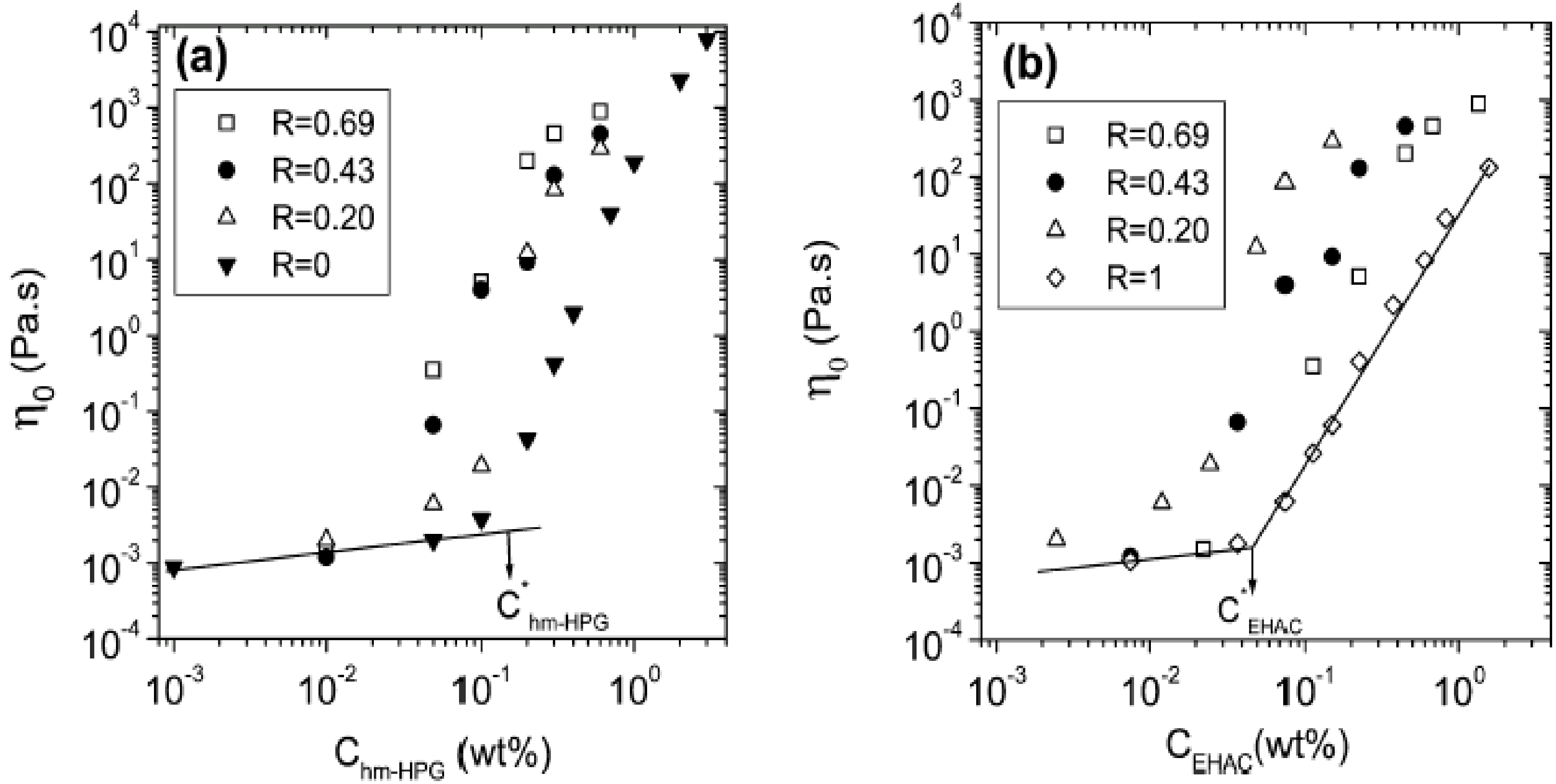


Figure 7. Zero-shear viscosity vs hm-HPG (a) and EHAC (b) concentrations for various compositions of the mixtures at 25 °C. Also are reported the variations corresponding to the single hm-HPG and EHAC components, respectively.

I. Couillet, T.L. Hughes, G.C. Maitland, F. Candau
Macromolecules, **38**, 5271-5282 (2005)

Hm-HPG:EHAC mixtures – shear viscosity

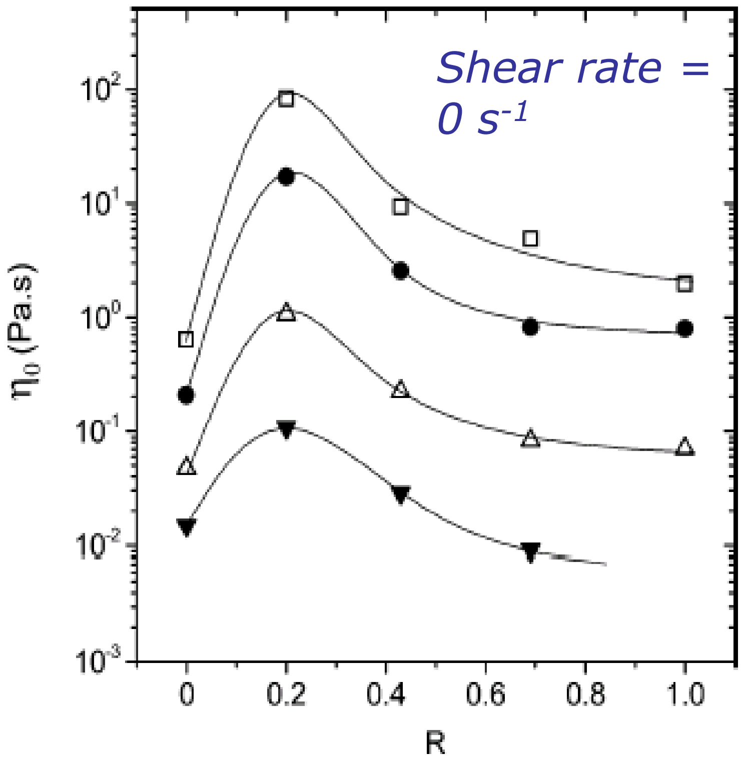


Figure 9. Zero-shear viscosity vs R at various temperatures: (□) 25 °C; (●) 40 °C; (Δ) 60 °C; (▼) 80 °C. Data are for systems with $C_M \approx 0.35$ wt %. The lines drawn through the data are guides for the eye.

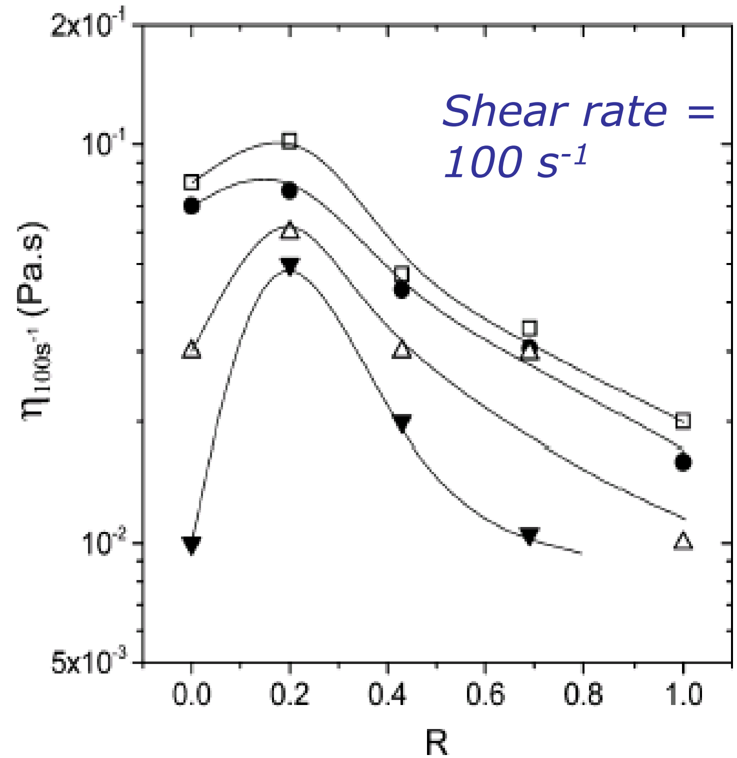
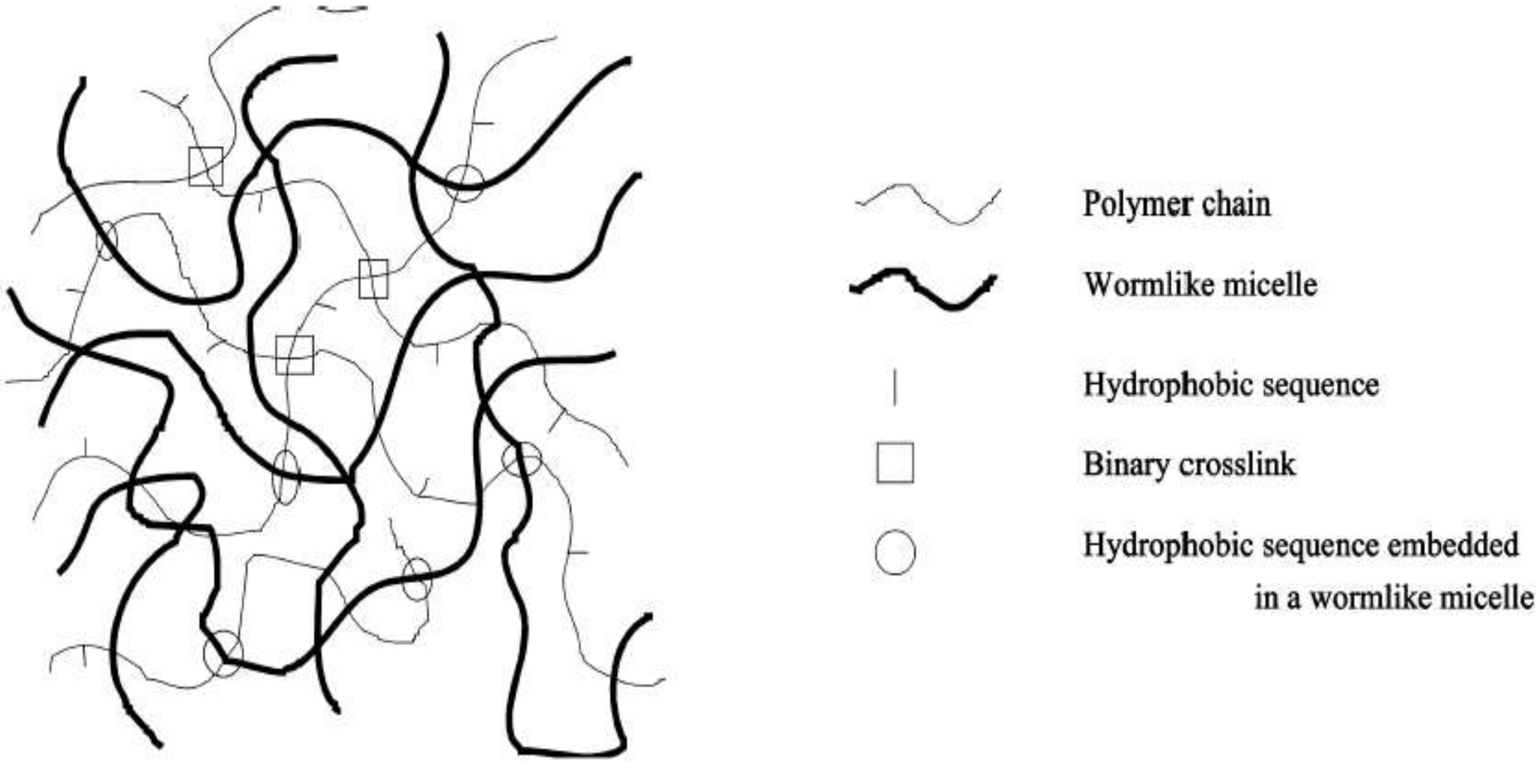


Figure 11. High shear rate viscosity vs R at various temperatures: (□) 25 °C; (●) 40 °C; (Δ) 60 °C; (▼) 80 °C. Data are for systems with $C_M \approx 0.35$ wt %. The lines drawn through the data are guides for the eye.

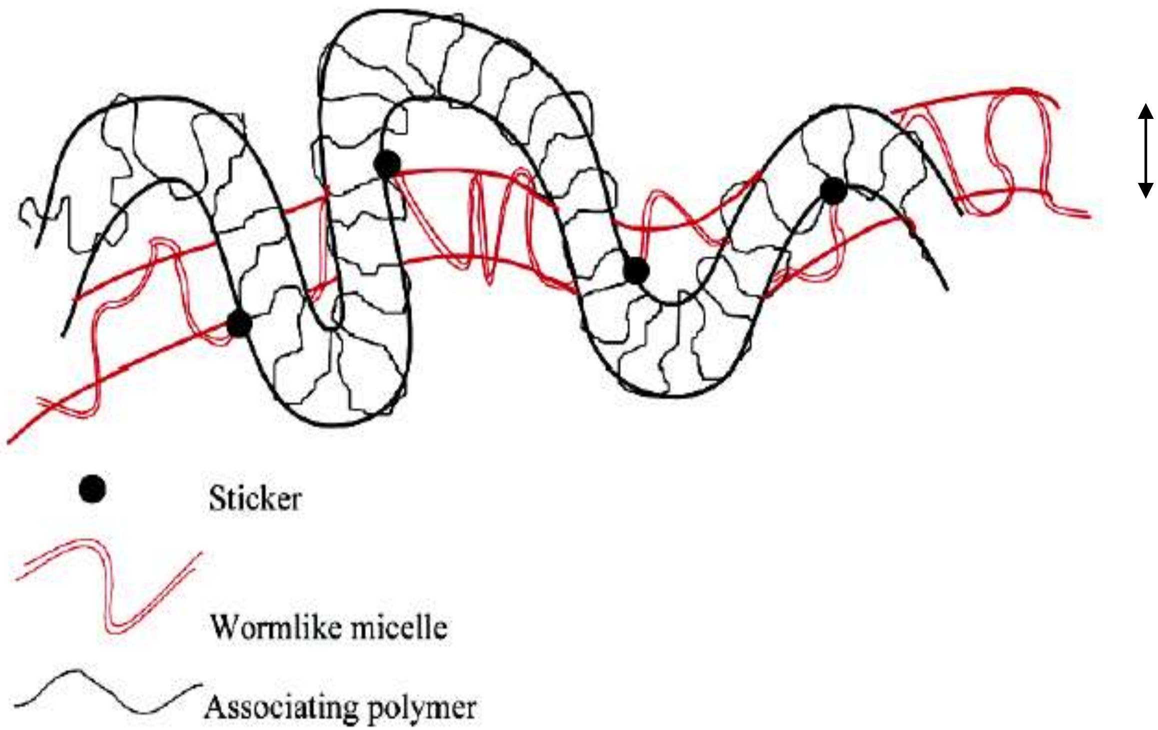
Hm-HPG: Mw ~ 1.8x10^6, <DP> ~ 3000, C_{22} side groups 10 per chain *$R = [C_{EHAC}]/[C_{EHAC} + C_{HmHPG}]$*

I. Couillet, T.L. Hughes, G.C. Maitland, F. Candau, Macromolecules, **38**, 5271-5282 (2005)

Interpenetrating network of wormlike micelles and hm chains of hm-HPG



Sticky Reptation Model for hm-polymer:wormlike micelle coupling



D ~ average mutual entanglement length

Needs quantitative model for worm-hm polymer coupled flow

The Potter’s Tale

- Or…Mud, Glorious Mud
  - – Tubular conduit for fluids…out and in
    - Macro Tubes
  - – Clay colloidal particles are everywhere
  - – Smectite montmorillonite or Bentonite
    - Clay water-based muds
    - Low permeability filtercakes
    - Soft, swellable shales

…compacted clay rocks

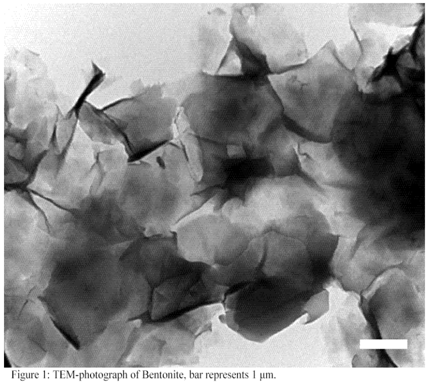
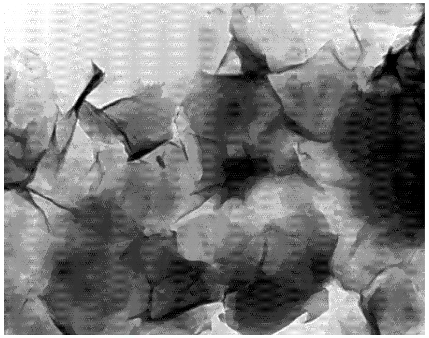
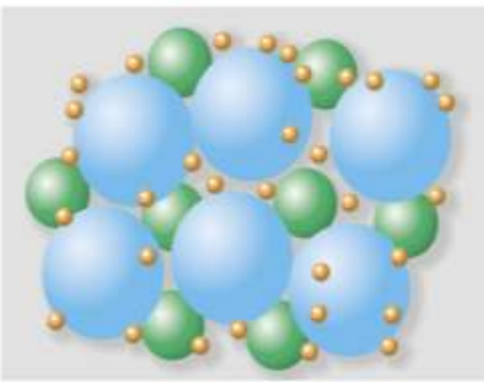
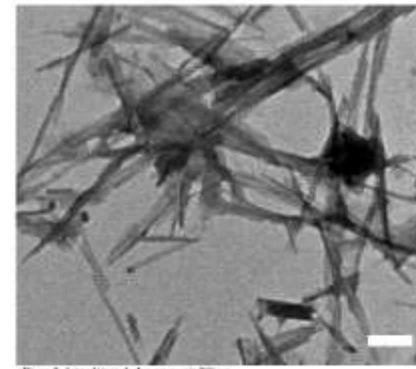


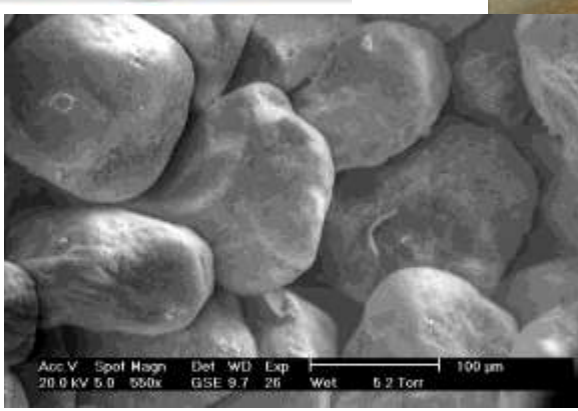
Figure 1: TEM-photograph of Bentonite, bar represents 1 μm.

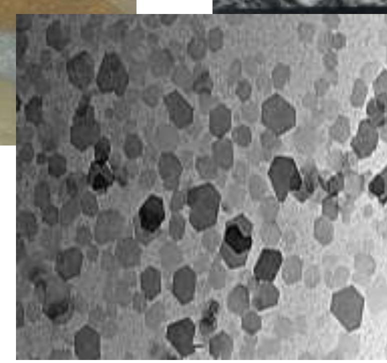
The Industrial Driver – Drilling Fluids





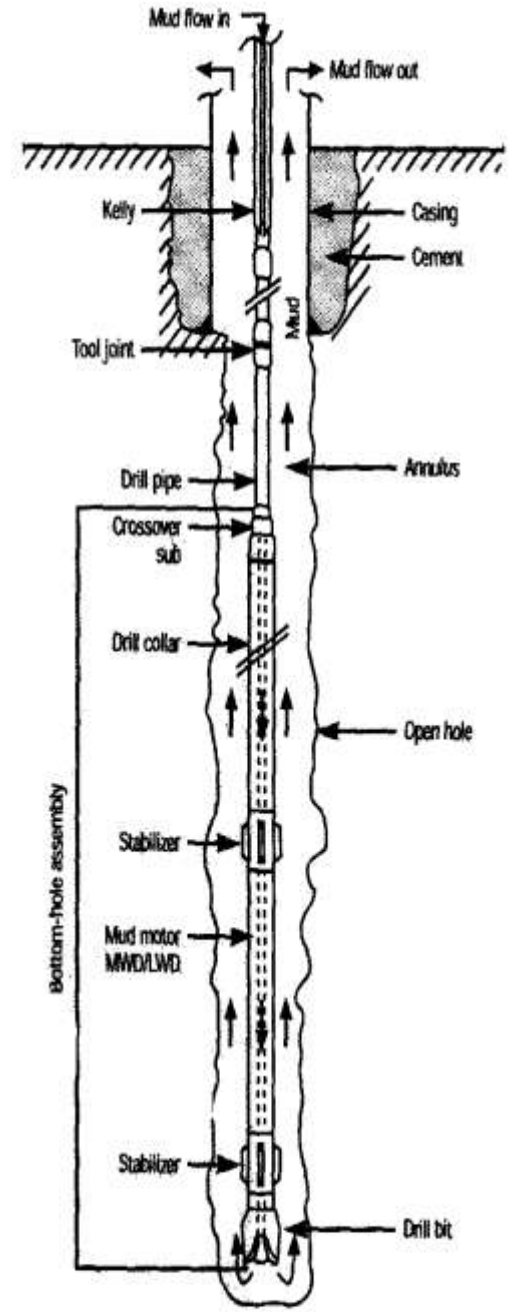






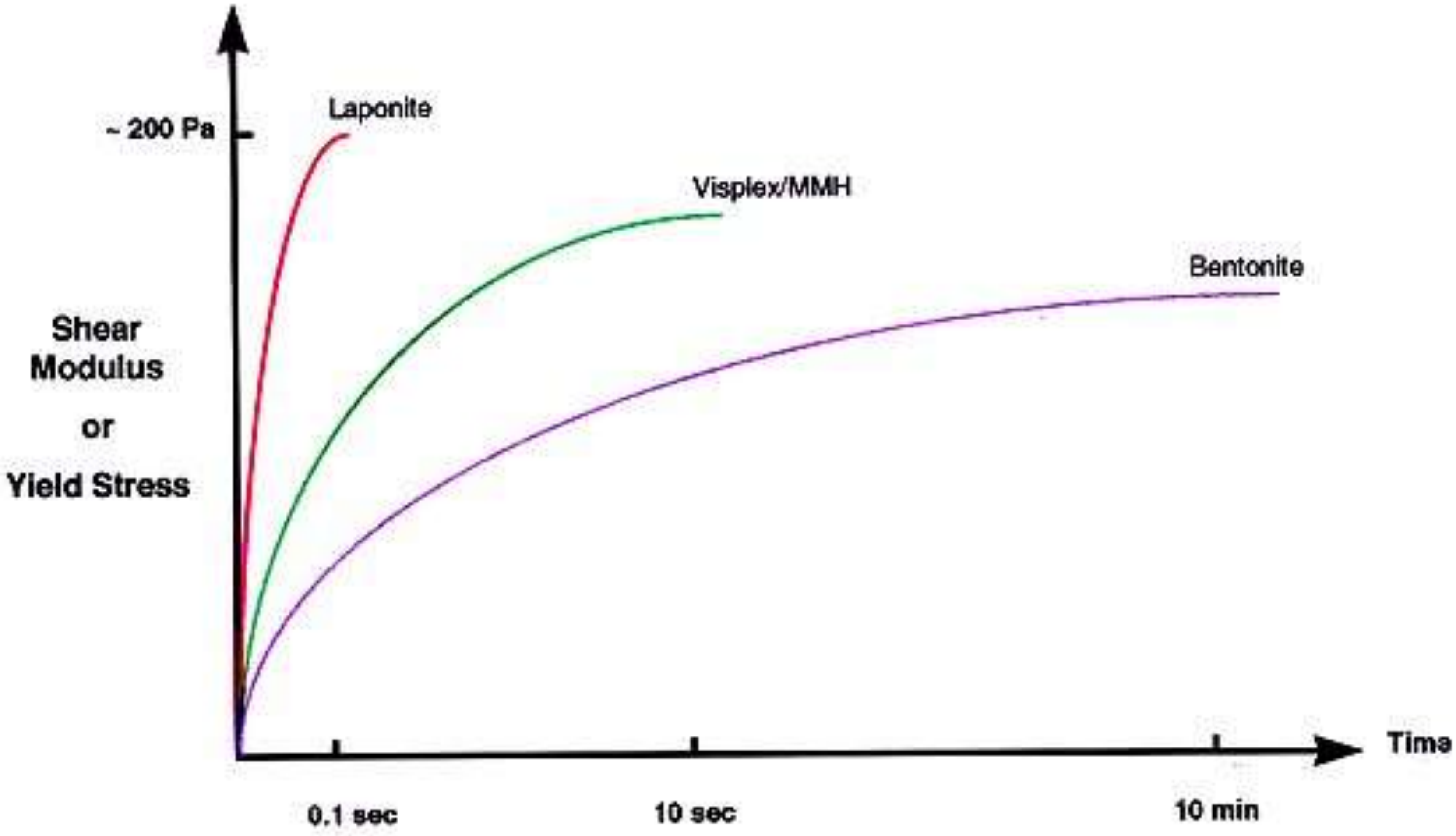
Drilling an oilwell...

- Colloidal clay oilfield drilling fluid
- Rheological behaviour critical
  - Minimize pumping energy
  - Keep cuttings suspended, even when pumps stop



Gelation of mixed colloid drilling fluids on cessation of flow

Concept: Designer Gels or Dial-a-Yield Stress



Base Clay: Montmorillonite or Bentonite

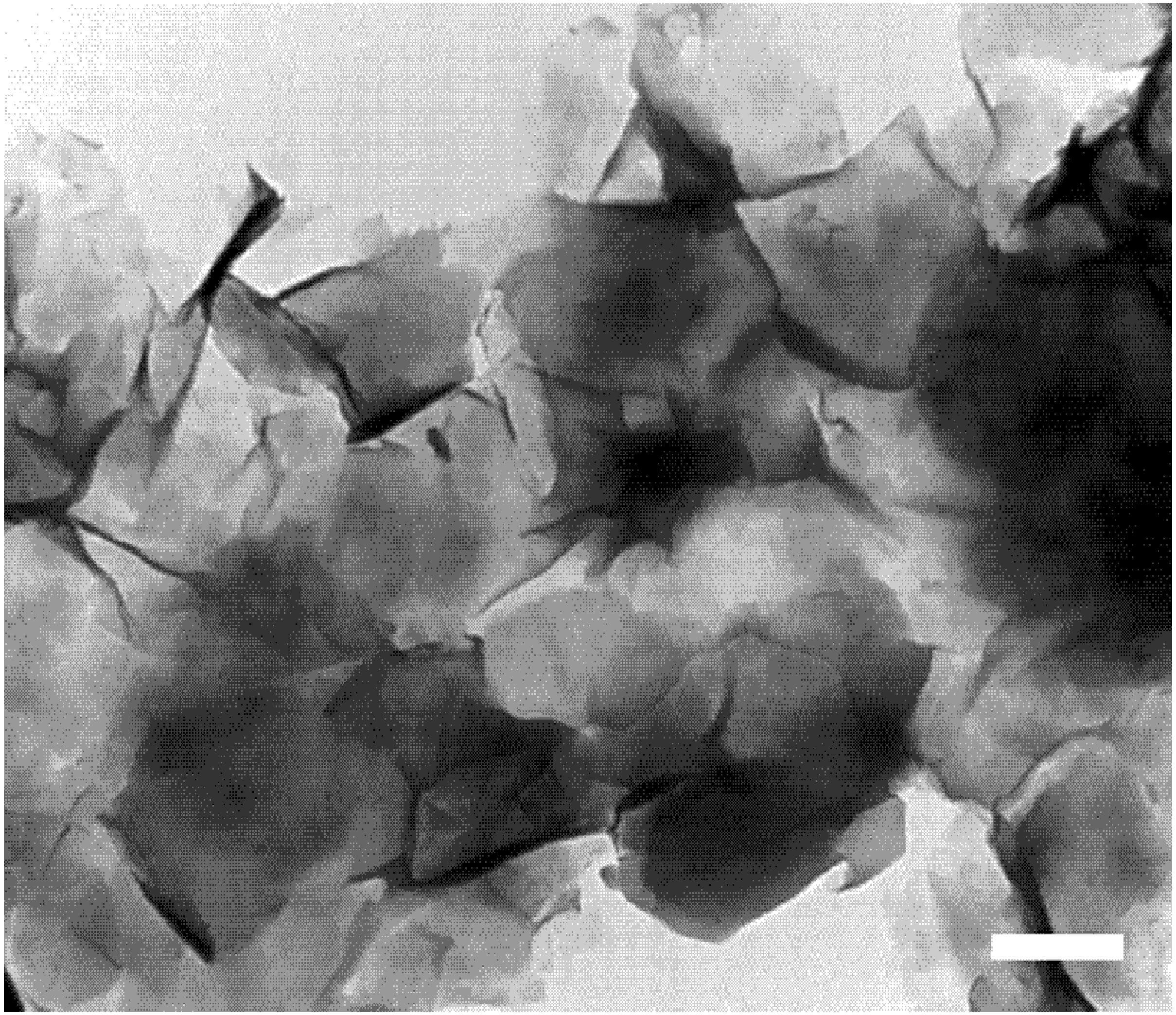
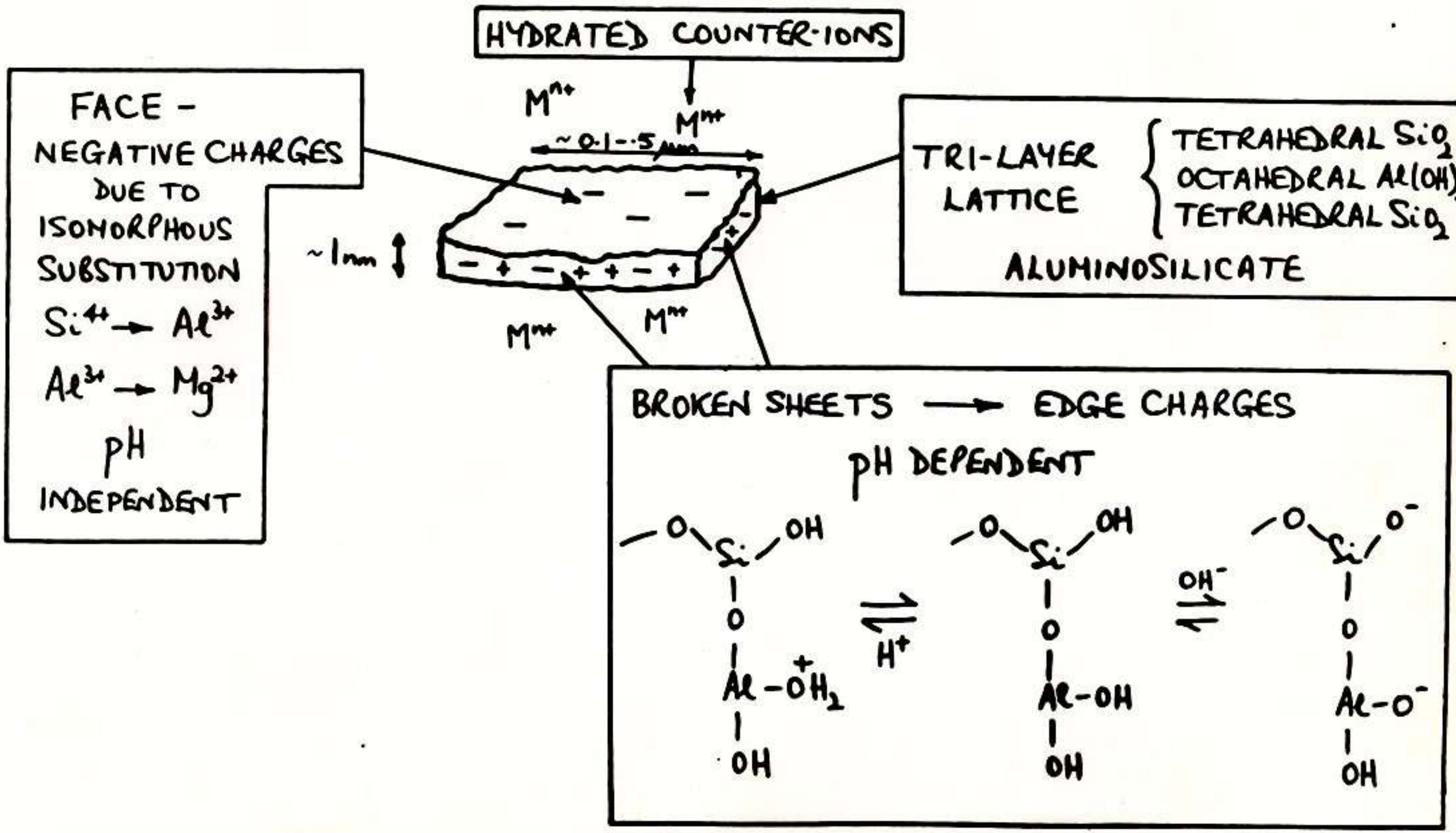


Figure 1: TEM-photograph of Bentonite, bar represents 1 µm.

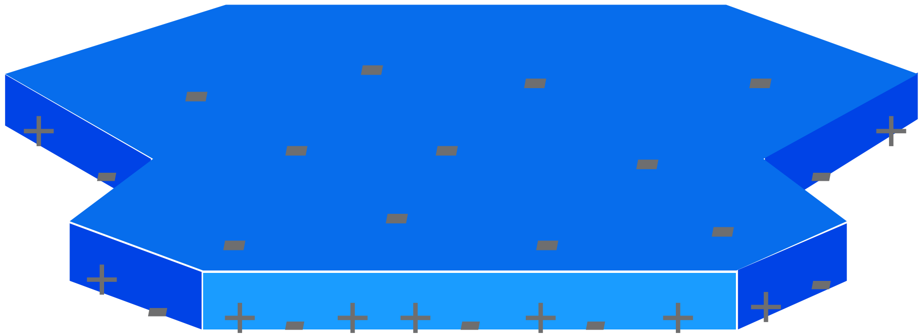
Imperial College London

100 years of living science

Montmorillonite Clay Platelets - Bentonite

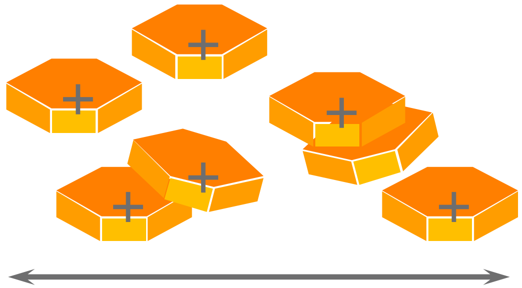


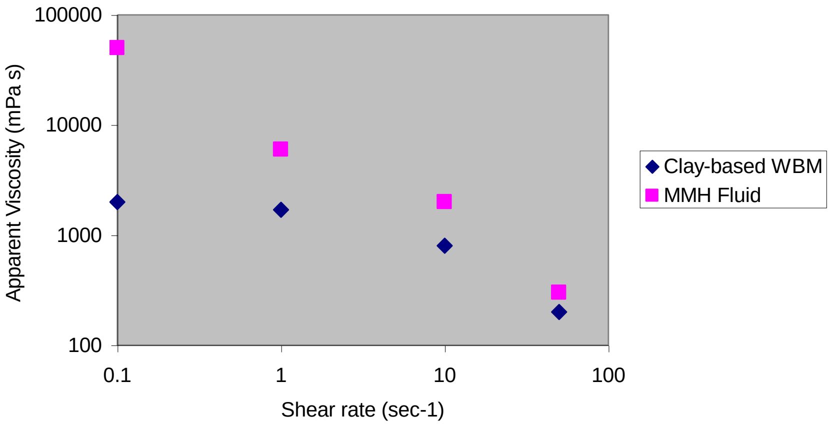
Visplex/Drillplex: Mixed Metal Hydroxide Cationic Colloid



Bentonite platelet with negative faces. Edge charges are pH-dependent.

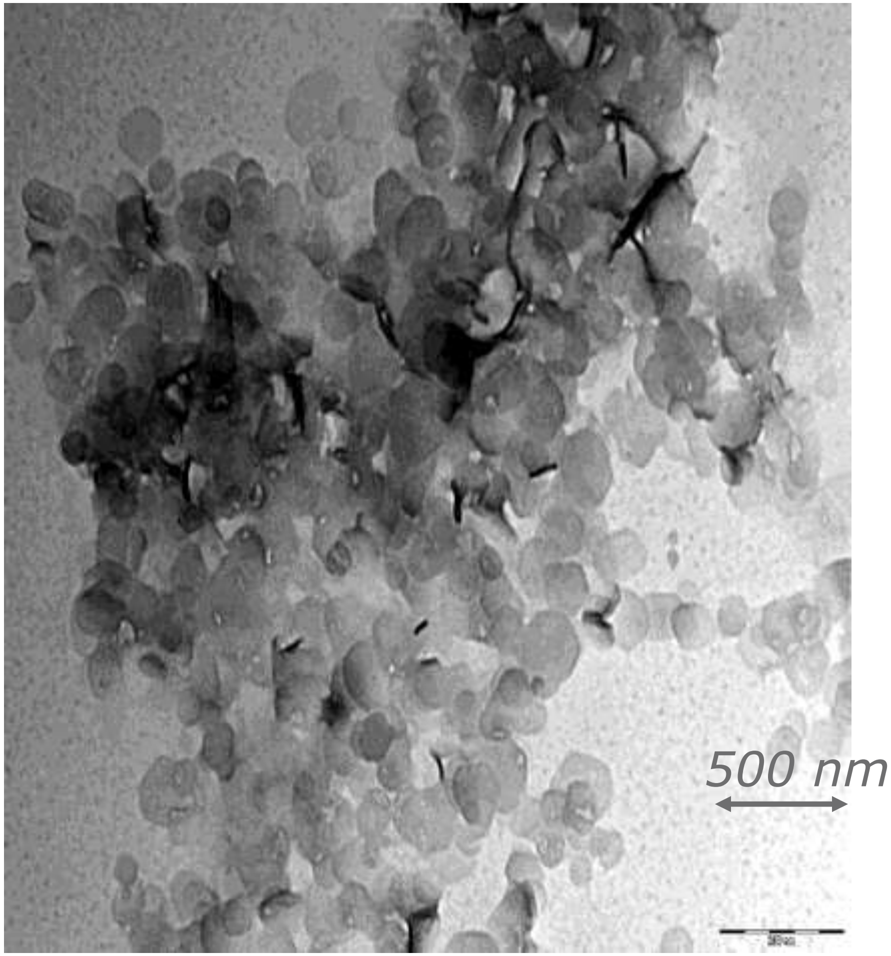
VISPLEX crystals: positive charge due to electron-deficient lattice





hexagonal plates, aspect ratio ~10
plate diameter ~100nm, Mg/Al ~ 1.0

Mixed metal oxide: TEM image



But...problems -

- *Loss of viscosity with salt, brines...seawater*
- *Gel degrades at temperatures higher than 115 ^{o}C*

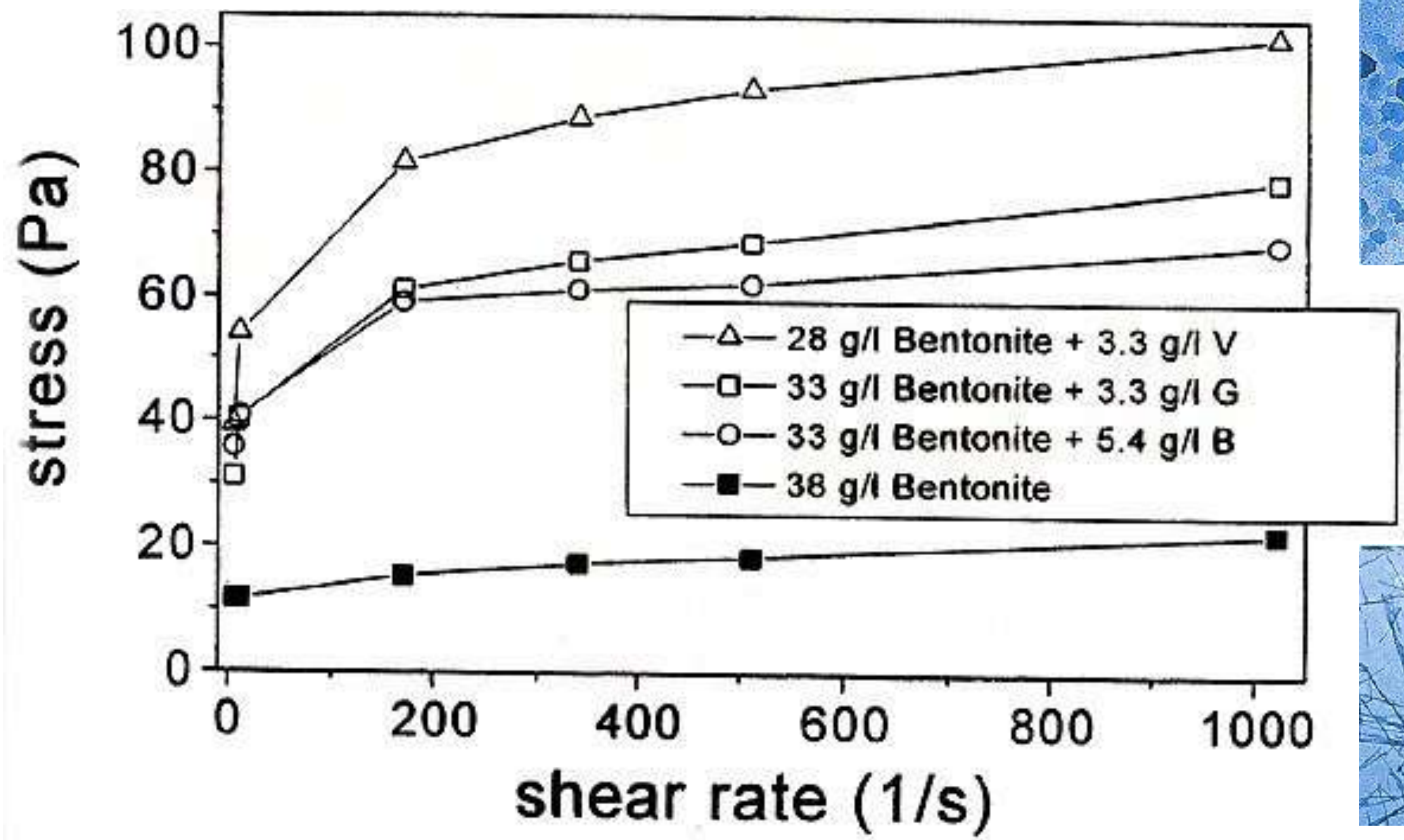
Visplex was renamed Drillplex but still these issues persisted.

Imperial College London

100 years of living science

Henk Lekkerkerker to the rescue...

Flow curves for mixtures of bentonite and various colloidal thickeners



Gibbsite

Boehmite

Felixplex Patents

(12) UK Patent (19) GB (11) 2 378 716 (13) B

(45) Date of publication: **14.01.2004**

(54) Title of the invention: Process fluid

(51) Int Cl[7]: **C09K** 7/02

(21) Application No: **0119375.4**

(22) Date of Filing: **08.08.2001**

(43) Date A Publication: **19.02.2003**

(52) UK CL (Edition W):
E1F FGP

(56) Documents Cited:

GB 2112042 A	**US 6025303 B**
US 5663122 A	**US 5532212 A**
US 4680128 A	**US 4675119 A**
US 4447341 B	**US 4230586 B**
US 4048077 B	

(58) Field of Search:
As for published application 2378716 A *viz:*
UK CL (Edition S) **E1F** FGP
INT CL[7] **C09K** 7/02
Other: **Online: WPI, EPODOC, PAJ**
updated as appropriate

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(12) **United States Patent**
Van Der Kooij et al.

(10) **Patent No.: US 7,338,922 B2**
(45) **Date of Patent: Mar. 4, 2008**

(54) **PROCESS FLUID**

(75) Inventors: **Felix Van Der Kooij**, Schiedam (NL); **Henk Lekkerkerker**, Maarn (NL); **Edo Sicco Boek**, Cambridgeshire (GB)

(73) Assignee: **M-I L.L.C.**, Houston, TX (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 410 days.

(21) Appl. No.: **10/486,043**

(22) PCT Filed: **Aug. 6, 2002**

(86) PCT No.: **PCT/GB02/03623**

§ 371 (c)(1),
(2), (4) Date: **Jul. 2, 2004**

(87) PCT Pub. No.: **WO03/014252**

PCT Pub. Date: **Feb. 20, 2003**

(65) **Prior Publication Data**

US 2004/0242431 A1 Dec. 2, 2004

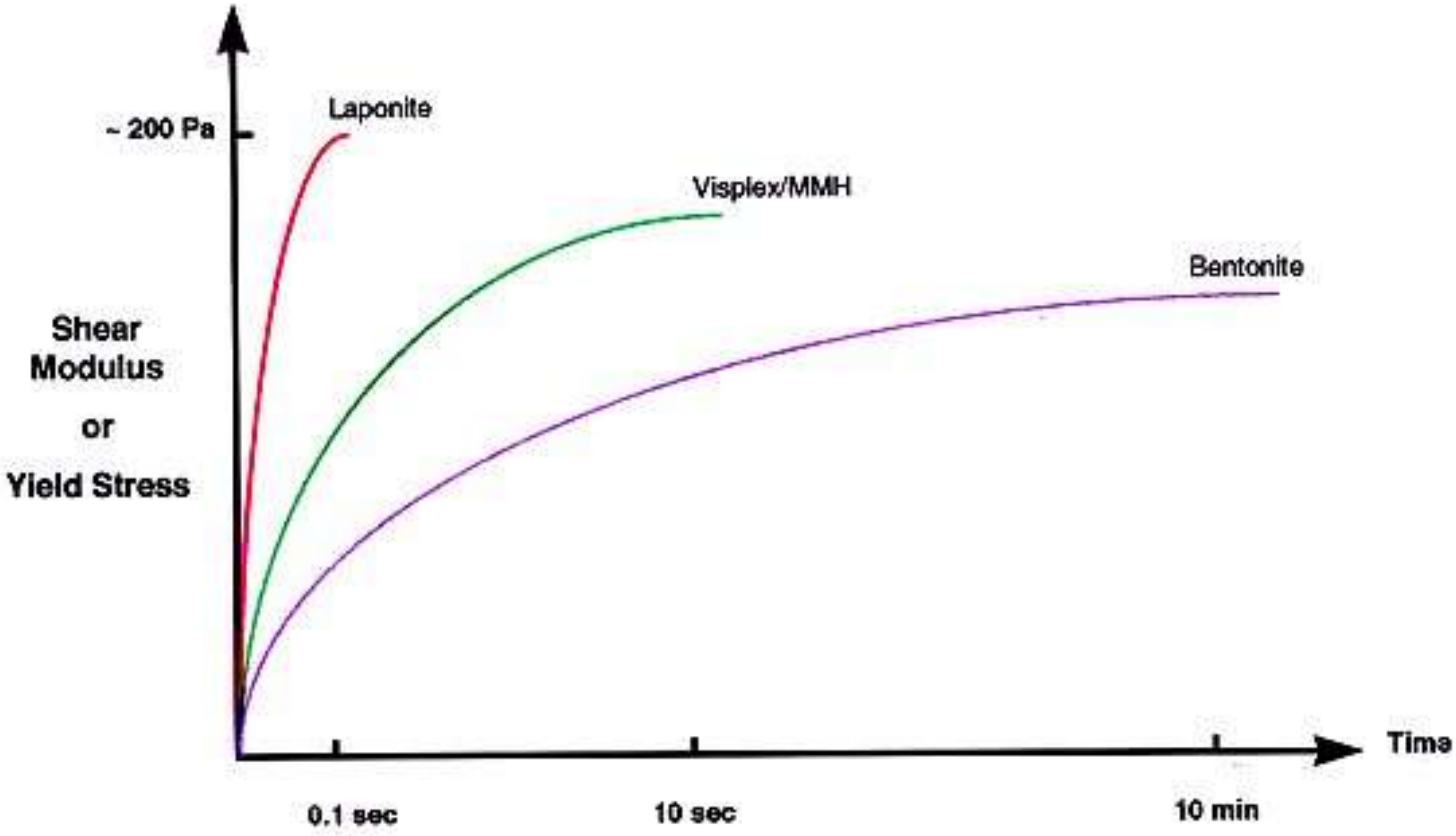
4,230,586 A		10/1980	Beetz et al.	
4,240,915 A		12/1980	Block	
4,349,443 A		9/1982	Block	
4,389,319 A		6/1983	Block et al.	
4,431,550 A		2/1984	Block	
4,447,341 A		5/1984	Block	
4,486,318 A		12/1984	Green et al.	
4,592,855 A	*	6/1986	Gioffre et al.	424/44
4,675,119 A		6/1987	Farrar et al.	
4,680,128 A		7/1987	Portnoy	
4,990,268 A		2/1991	Burba, III et al.	
5,232,627 A		8/1993	Burba, III et al.	
5,532,212 A		7/1996	Patel	
5,663,122 A		9/1997	Mueller et al.	
6,025,303 A		2/2000	Keilhofer et al.	

OTHER PUBLICATIONS

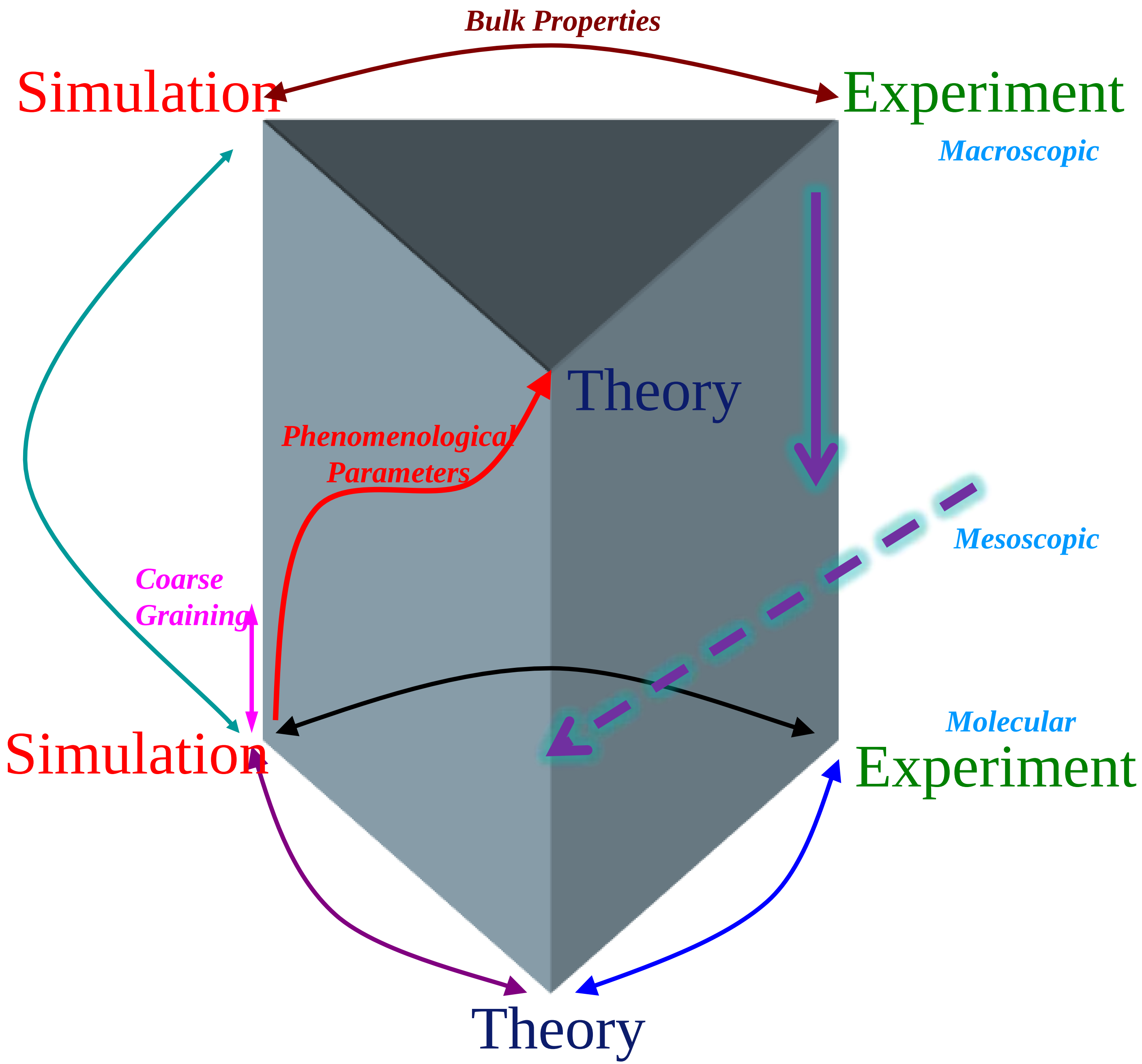
Buining et al., "Preparation of Colloidal Boehmite Needles by Hydrothermal Treatment of Aluminum Alkoxide Precursors", J. Amer. Ceram. Soc., vol. 74, No. 6, 1991, pp. 1303-1307.
Philipse et al., "Isotropic and Birefringent Dispersions of Surface Modified Silica Rods With a Boehmite-Needle Core", Langmuir, vol. 10, 1994, pp. 4451-4458.
van der Kooij et al., "Formation of Nematic Liquid Crystals in Suspensions of Hard Colloidal Platelets", J. Phys. Chem. B, vol. 102, 1998, pp. 7829-7832.
Wierenga et al., "Aqueous Dispersions of Colloidal Gibbsite Platelets: Synthesis, Characterisation and Intrinsic Viscosity Measurements", Colloids and Surfaces A, vol. 134, 1998, pp. 359-371.

Gelation of mixed colloid drilling fluids on cessation of flow

Concept: Designer Gels or Dial-a-Yield Stress



Type of Study



Shaplex: Objectives of Study

- To determine the rheology over a wide range of stress/strain-rates (using oscillatory, transient and continuous shear) of well-characterised gelling suspensions of colloids of varying shape:
  rods (boehmite), laths (hectorite), plates (gibbsite)

- To explore the rheological synergies in mixed-shape colloidal suspensions:
  2.5% w/w laths (hectorite)
  + 0.25% w/w rods (boehmite)
  or plates (gibbsite)
  or spheres (alumina-coated silica)

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Acknowledgements

Thanks to

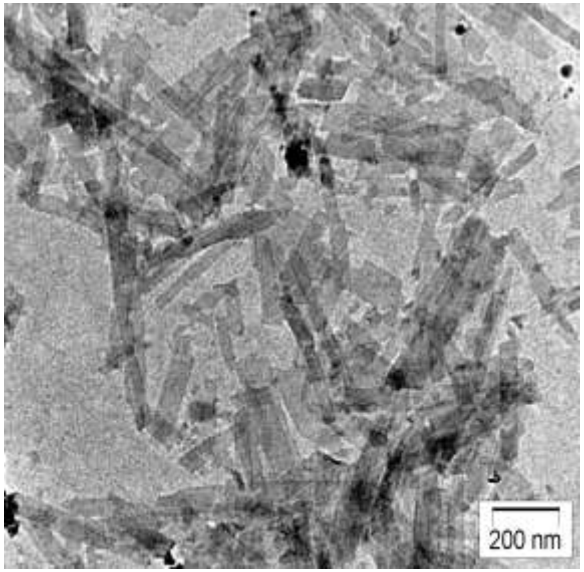
- Henk, Annemieke, Marcel and Louise for many years of fruitful collaboration
- Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and
- Schlumberger Cambridge Research,
  for financial support to Annemieke ten Brinke
- SoftComp EU 6th Framework Network of Excellence
- Edo Boek of Imperial College London (formerly Schlumberger Cambridge Research) for helpful discussions
- Dzina Kleshchanok, University of Utrecht, for producing the TEM images

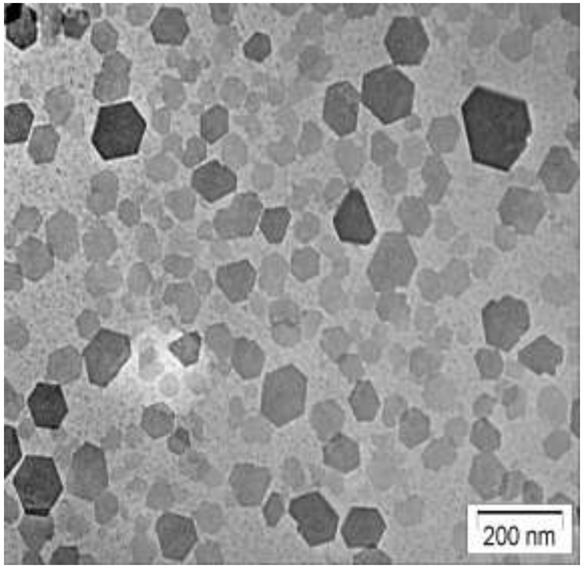
Key messages

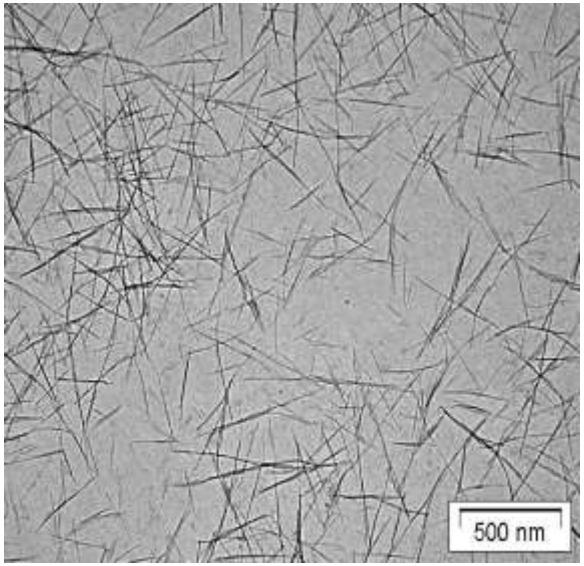
- General complex rheological behaviour of clay and clay-colloid mixtures as they transform from gels (elastoviscous solids) to weakly elastic shear-thinning liquids
- The significant enhancements to gel rheological properties caused by minor (~ 1:10 w/w) additions of a second colloidal component of varying shape
- Contrasts between hectorite and montmorillonite as the base clay
- The contrasting effect of one particular additive (silica spheres) depending on charge and clay concentration

Tuning gel behaviour by shape and charge

- Understand structure/performance relationships in mixed systems using model colloids







Hectorite *Gibbsite* *Boehmite*

Henk Lekkerkerker, Annemieke ten Brinke, Marcel Vogel (Utrecht), Louise Bailey Schlumberger

Characteristics of Particles

Property	*Particle* Hectorite	Gibbsite	Boehmite	Ludox CL
Shape	Lath	Plate	Rod	Sphere
L_1 [nm]	288	81	200	12
L_2 [nm]	43	81	10	12
d [nm]	6	6	10	12
Density [g/cm^3]	2.39	1.96	2.06	2.2
α	160	6.8	200	1.0
C* [g/100 cm^3]	1.5	28.8	1.1	220
pH	8.9	7.8	6.2	4.5
Sign of face charge	–	+	+	+
Conductivity [μS/cm]	38.1 @ 1336 ppm	80.2 @ 1154 ppm	46.0 @ 1045 ppm	
Mobility [10^{-8}m^2/Vs]	-1.2	2.8	3.9	
Zeta potential mV	-9.8	+24.0	+44.2	+42

α is the ratio of hydrodynamic volume V_h $(4\pi (L_1/2)^3/3)$ to real particle volume $(\sim L_1 L_2 d)$

C* is the 'overlap concentration' at which the hydrodynamic volumes swept out by the particle's largest dimension start to overlap = $(100\ L_1\ L_2\ 24d\ \rho)/4\pi L_1^3$

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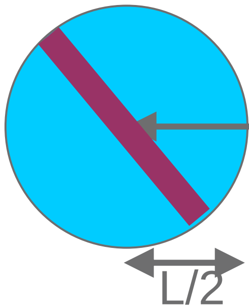
Concentration Regimes

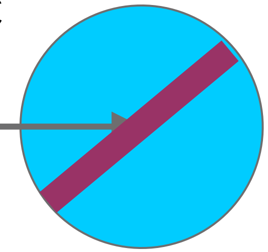
Concentration $C = nM_p / V$

Volume per molecule = $V/n = M_p/C$

Hydrodynamic volume $V_h = \pi L^3/6$

Dilute

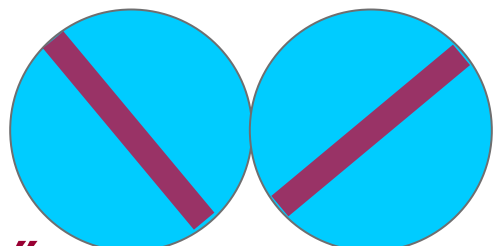




$R >> L$

$V/n = M/C >> V_h$

Semi-Dilute



Critical Overlap Concentration

$C^* = M_p / V_h$

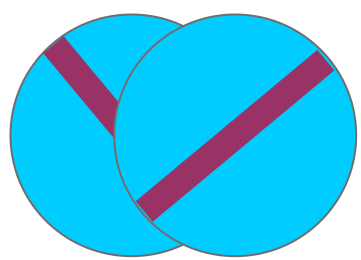
"Hydrodynamic close-packing"

$R = L$

$V/n = M/C = V_h$

$C = C^*$

Concentrated



$R << L$

$V/n = M/C << V_h$

$C >> C^*$

Multi-technique study

- *Oscillatory Shear*
- *Creep*
- *Steady Shear*
    - *Controlled Stress*
    - *Controlled Shear Rate*

- *Measurement Systems*
    - *1^o, 2^o and 4^o cone & plate*
    - *Micro-roughened and smooth*

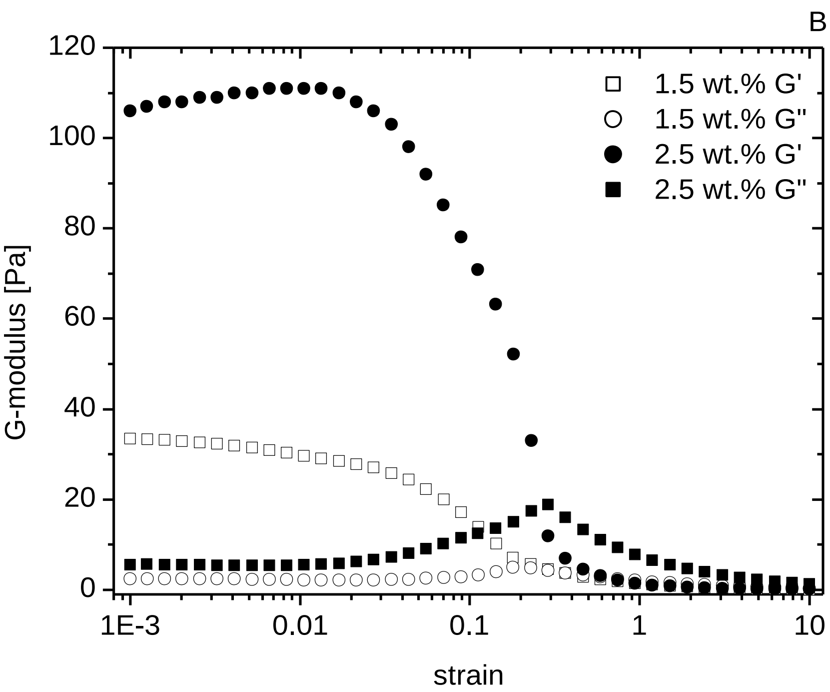
- *Controlled sample pre-shearing preparation protocols*

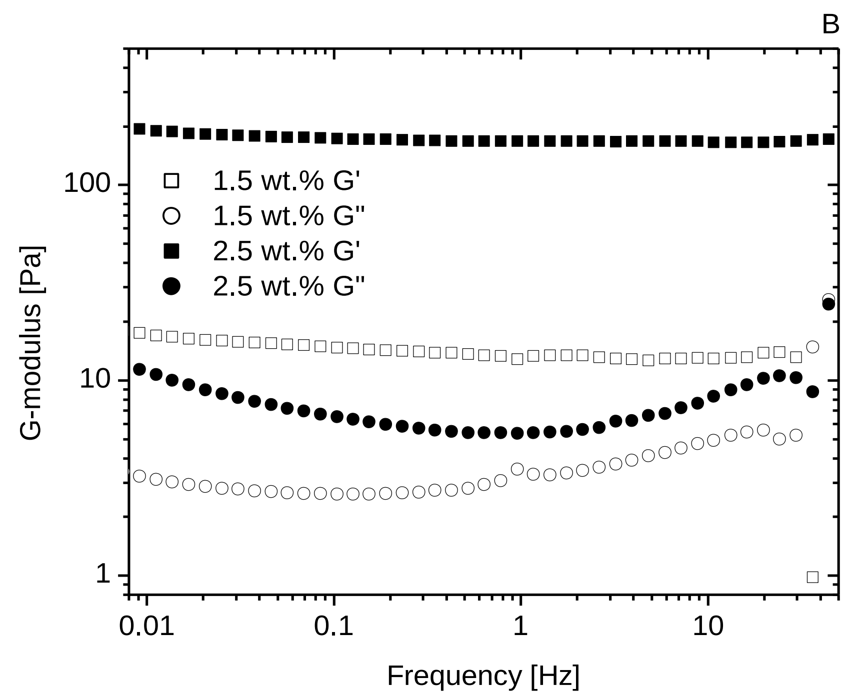
Pure Components

A few remarks...

Hectorite – Oscillatory Shear Flow

C* ~ 1.5 wt%

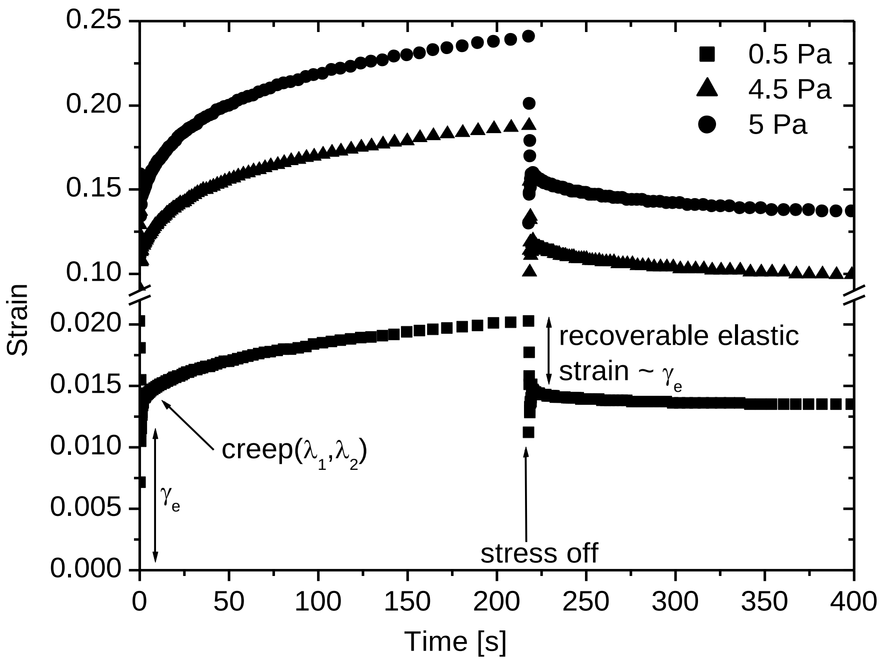


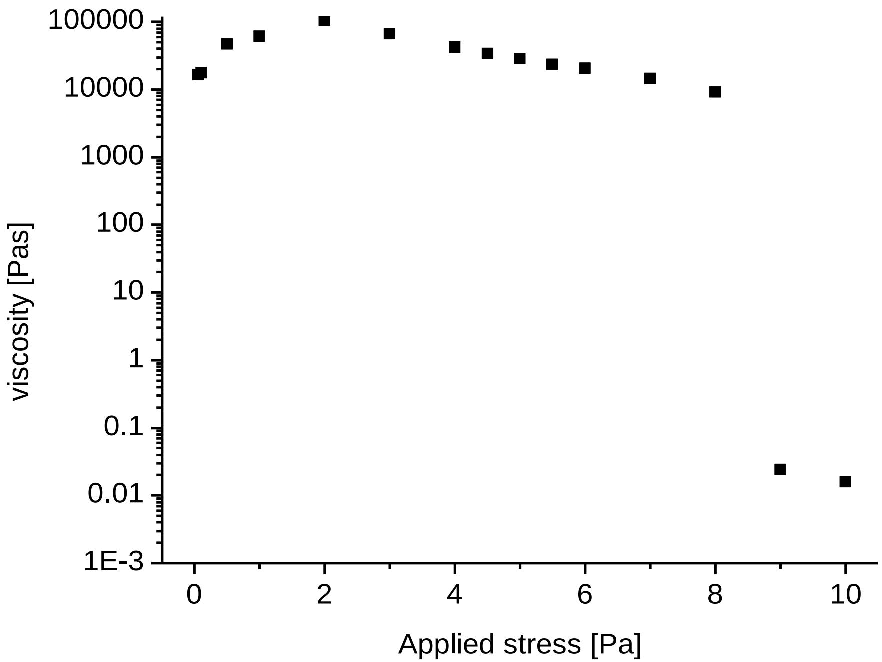


Hectorite – Gel State

Hectorite – Creep

C = 2.5 wt% = 1.7C*



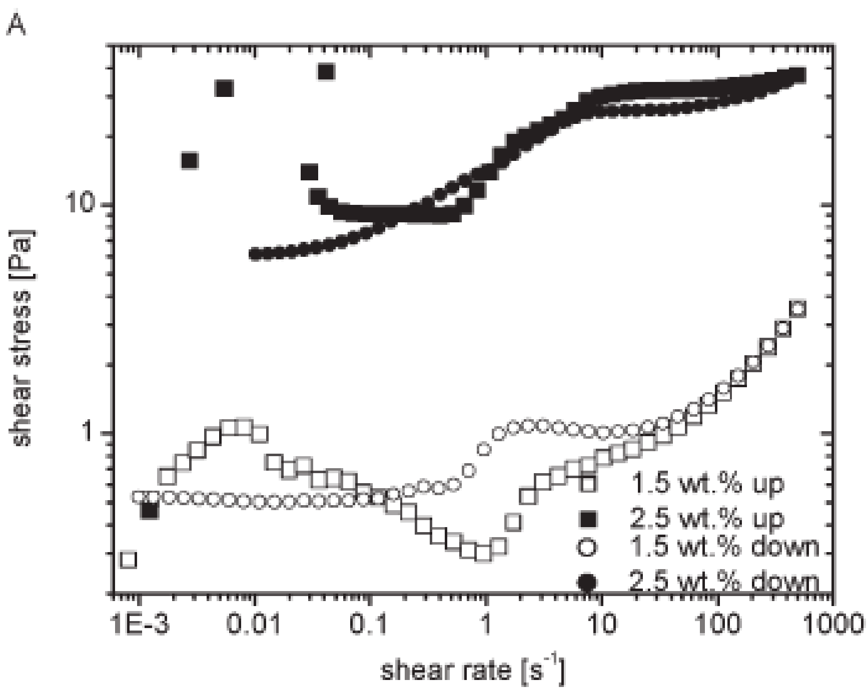


Hectorite – Transition from Gel to Sol

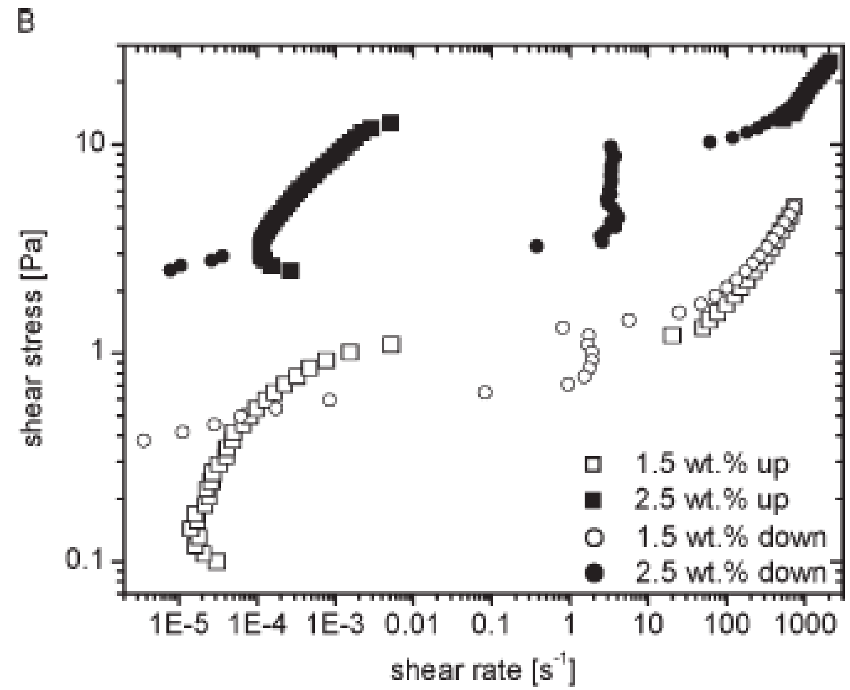
Hectorite – Continuous Shear

Recovered Gel

c* ~ 1.5 wt%



Controlled Shear Rate



Controlled Shear Stress

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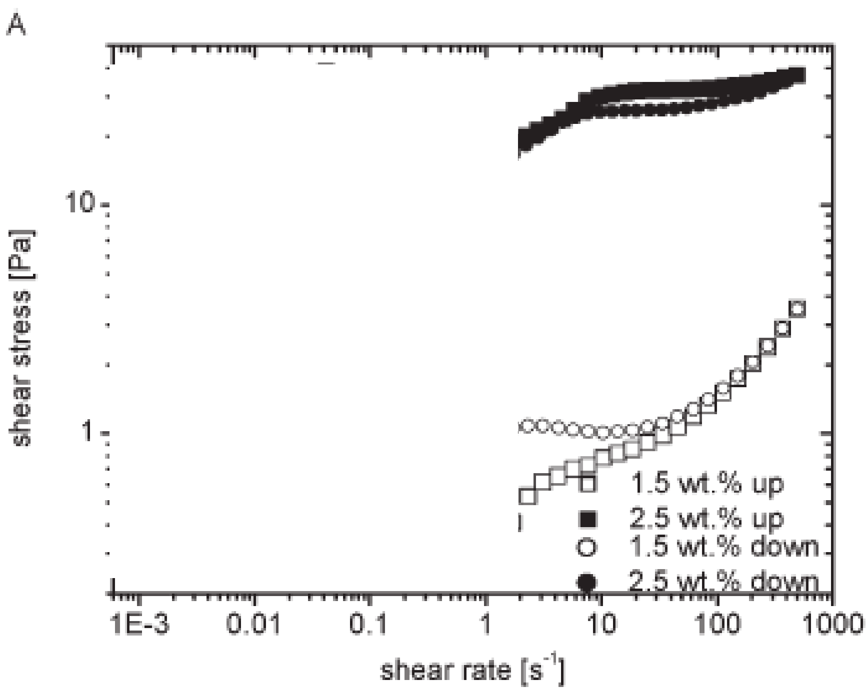
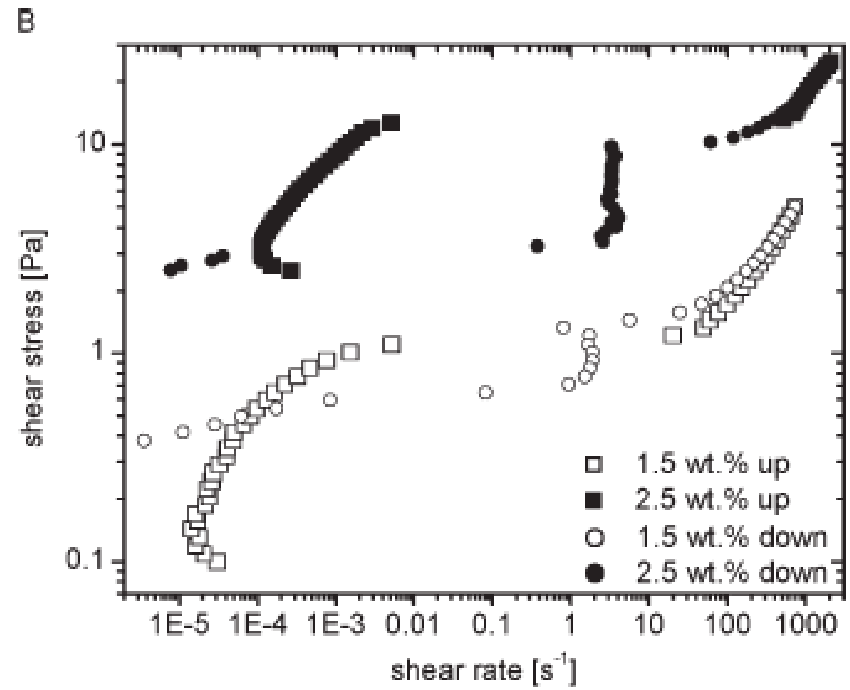
Hectorite – Continuous Shear

Recovered Gel

C* ~ 1.5 wt%

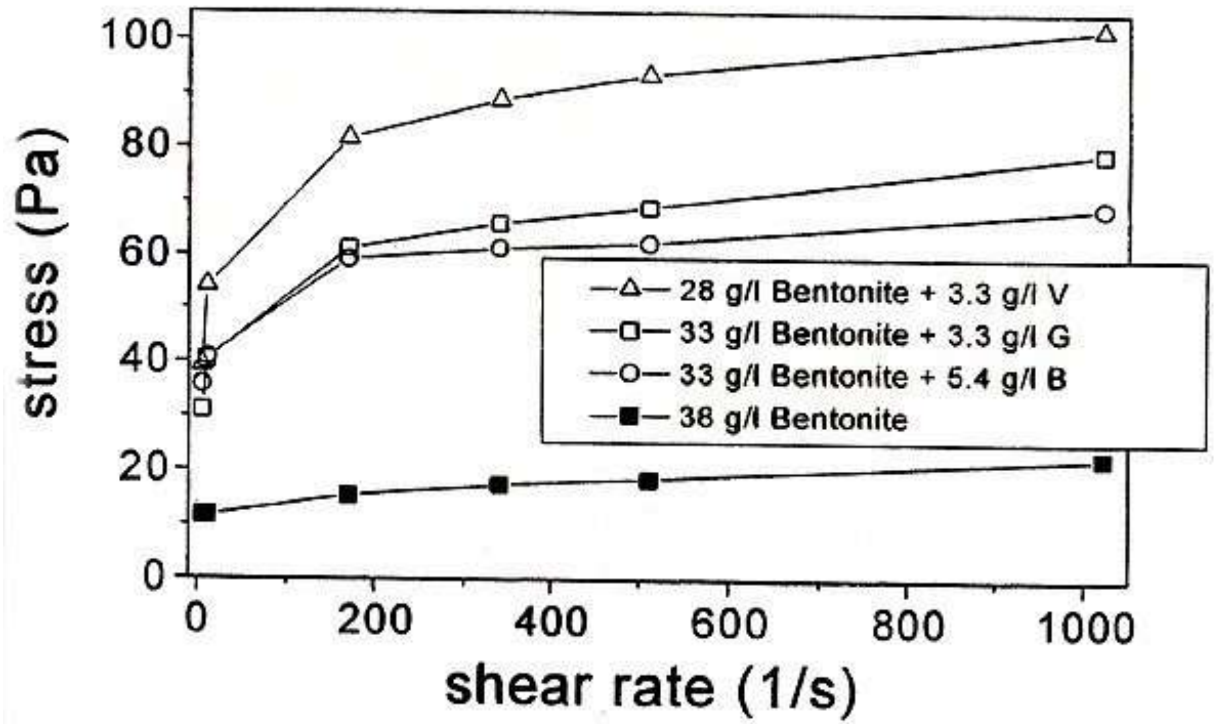


Controlled Shear Rate



Controlled Shear Stress

Fann Flow Curves Probe only the Liquid Region



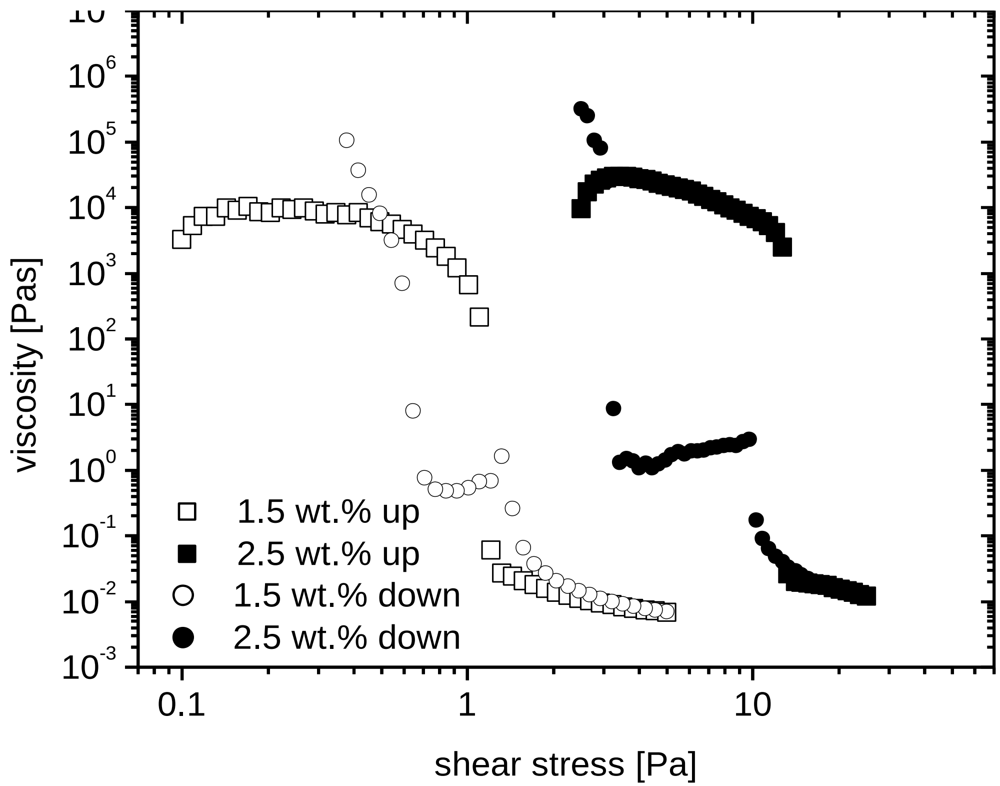
Bingham Model $\tau = \tau_y + \eta\gamma$

Herschel Bulkley Model $\tau = \tau_y + K\gamma^n$

are only the tip of the iceberg!

Hectorite – Continuous Shear

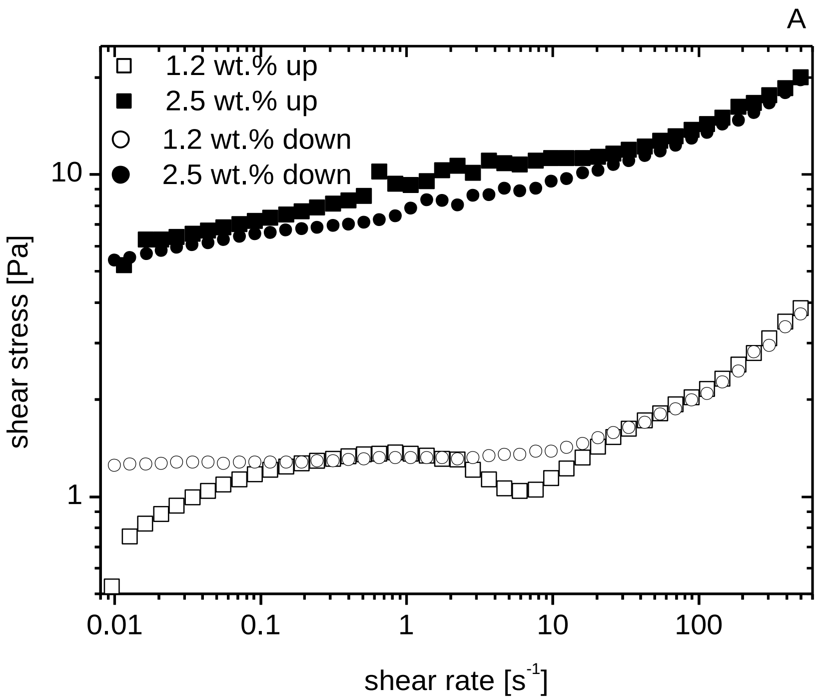
C* ~ 1.5 wt%



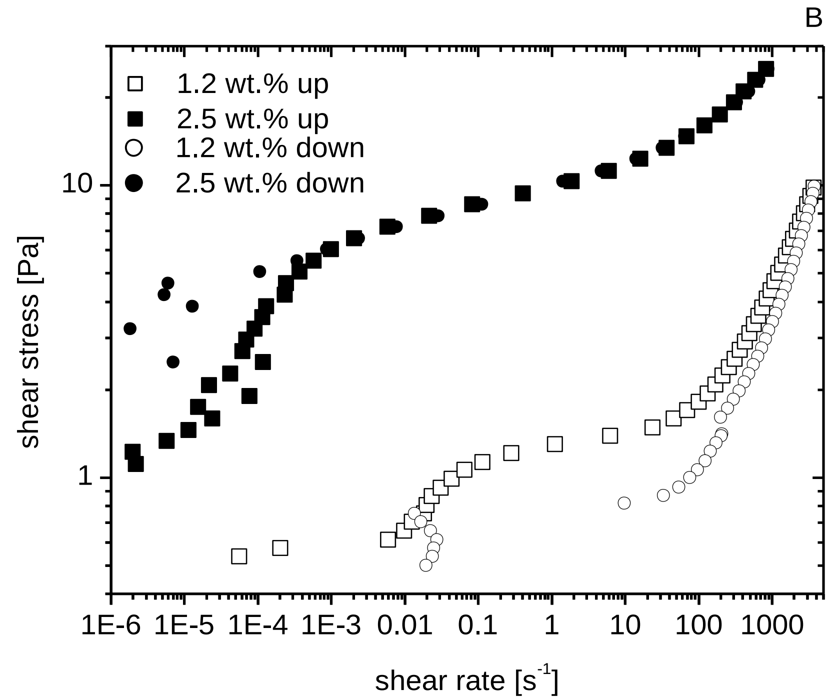
Controlled Shear Stress – Recovered Gel

Boehmite Rods – Continuous Shear

C* ~ 1.1 wt%

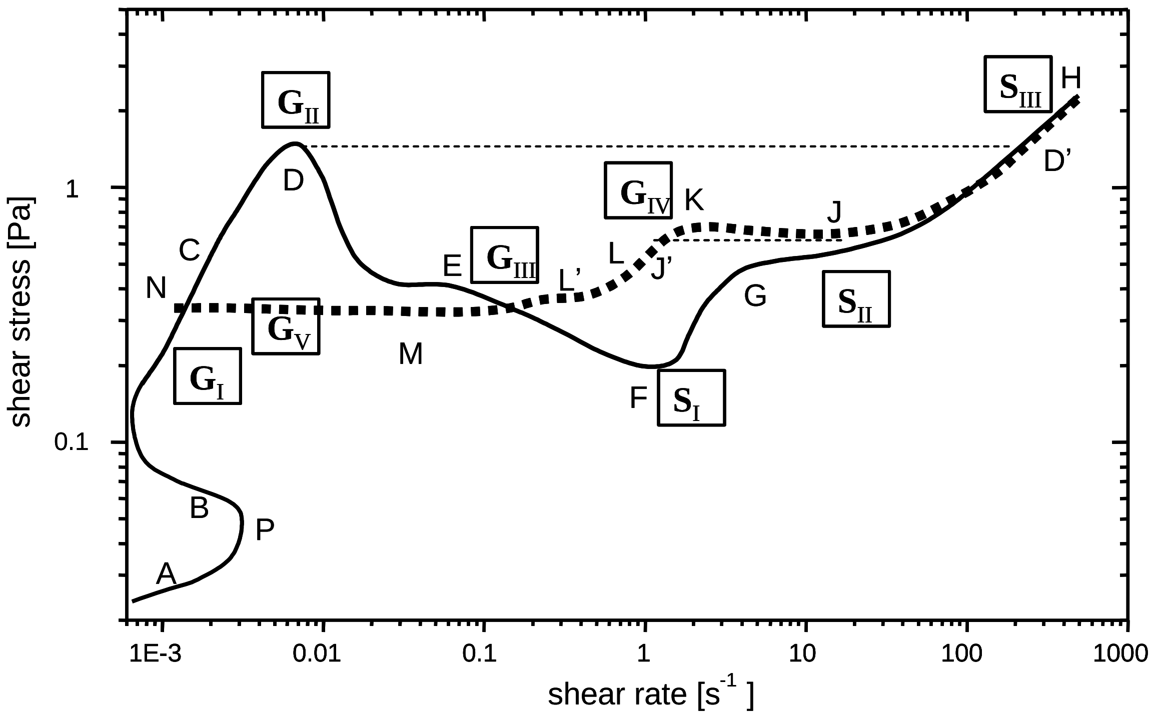


Controlled Shear Rate



Controlled Shear Stress

Continuous Shear – Generic Flow Curves



G_I = Disordered Gel G_{II} = Ordered Gel G_{III} = Breaking Gel
G_{IV} = Partially-ordered Gel G_V = Ordered Gel (not same as G_{II})

S_I = Structured Sol S_{II} = Breaking Fluid S_{III} = Dispersed, Partially-ordered Sol

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Common critical factor – yield strain

- Consistent values of G, η, 'τ_y', γ_y etc from oscillatory, transient and continuous shear experiments
- γ_y essentially independent of concentration

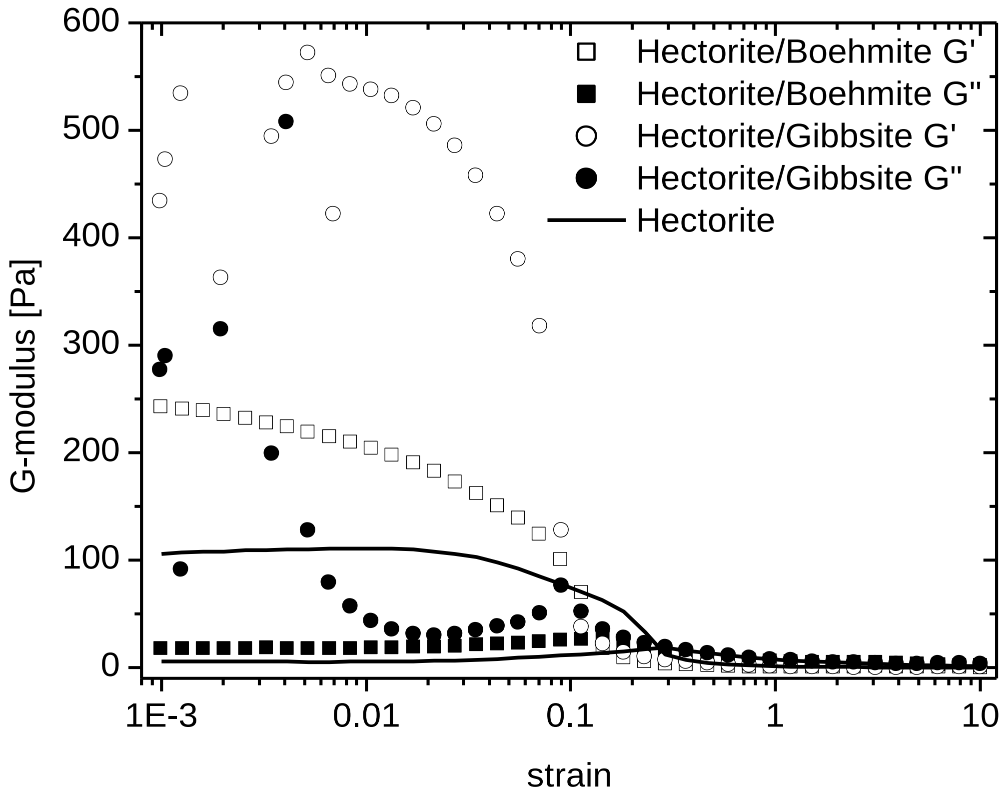
γ_y for

- Gibbsite plates 0.1 $\pm$ 0.05 (L_1 = 81nm)
- Hectorite laths 0.3 $\pm$ 0.05 (L_1 = 200 nm)
- Boehmite rods 0.45 $\pm$ 0.05 (L_1 = 288 nm)
- Same ordering as L_1 or parameter α

Mixed Shape Dispersions

Replacement of 10 wt% of the Hectorite (@ 2.5 wt%) by a second component

Mixed-shape Suspensions – Oscillatory Flow



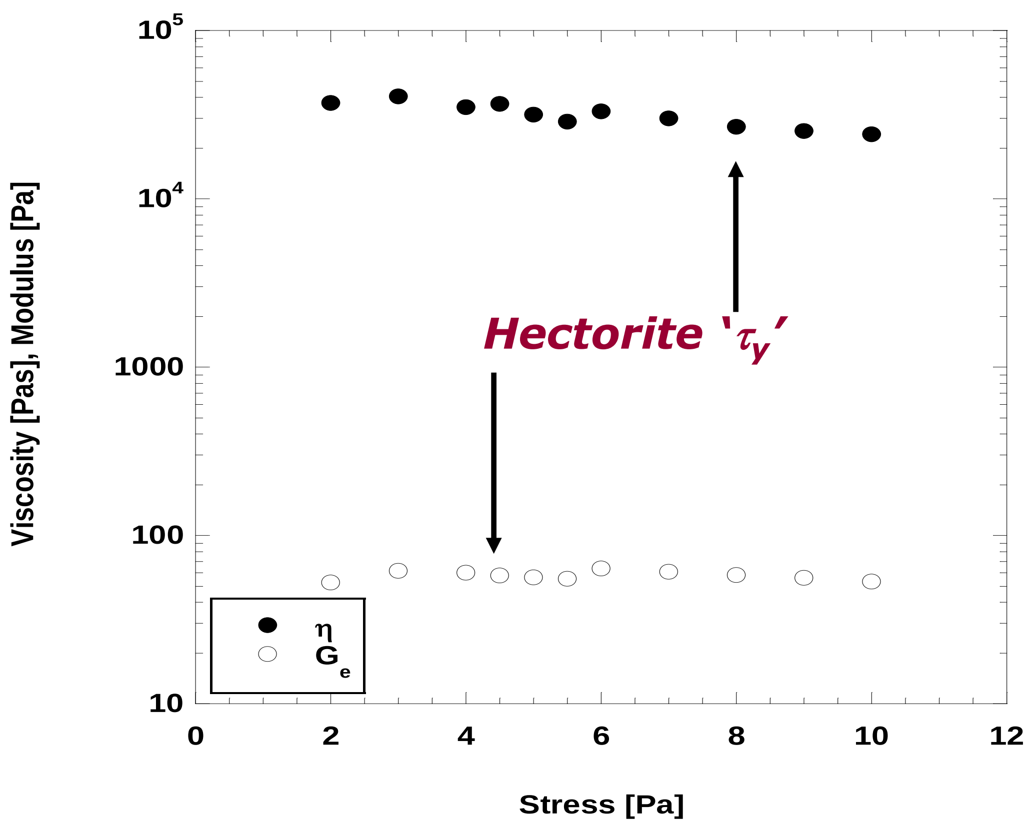
Boehmite α ***= 200***

Hectorite α ***= 160***

Gibbsite α ***= 6.8***

Hectorite 2.5 wt% (1.7c*), Minor Component 0.25 wt%

Creep viscosity η(t) and plateau modulus G_e

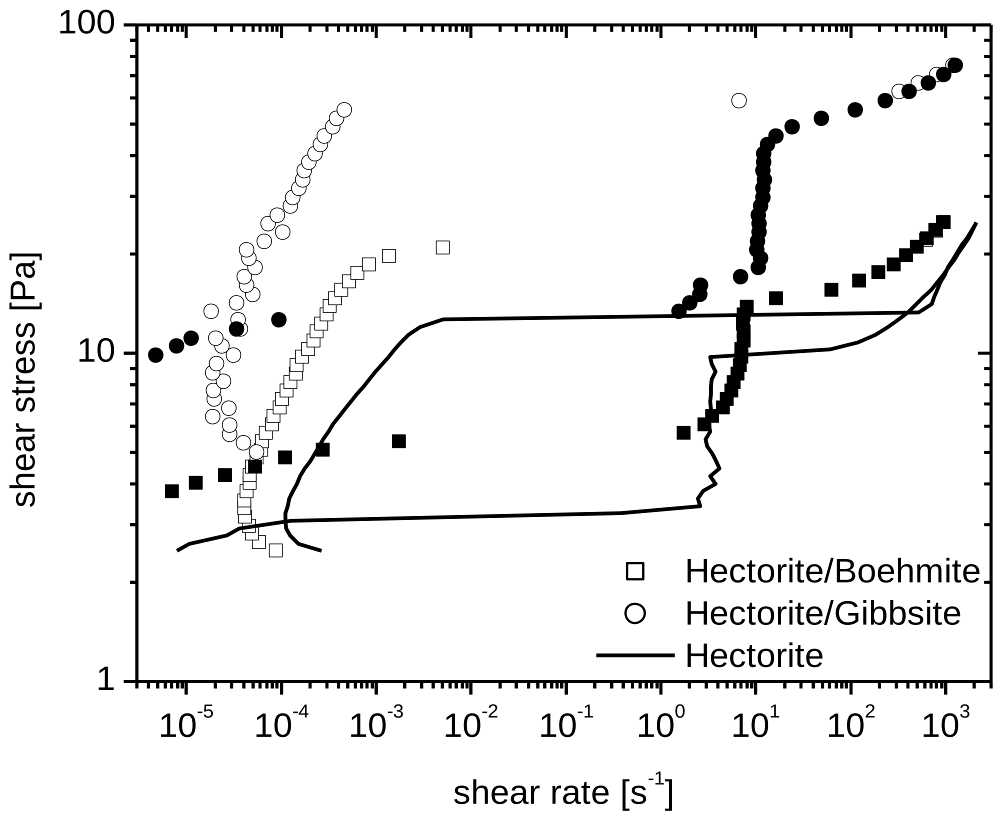


Hectorite-boehmite 10:1 mixture

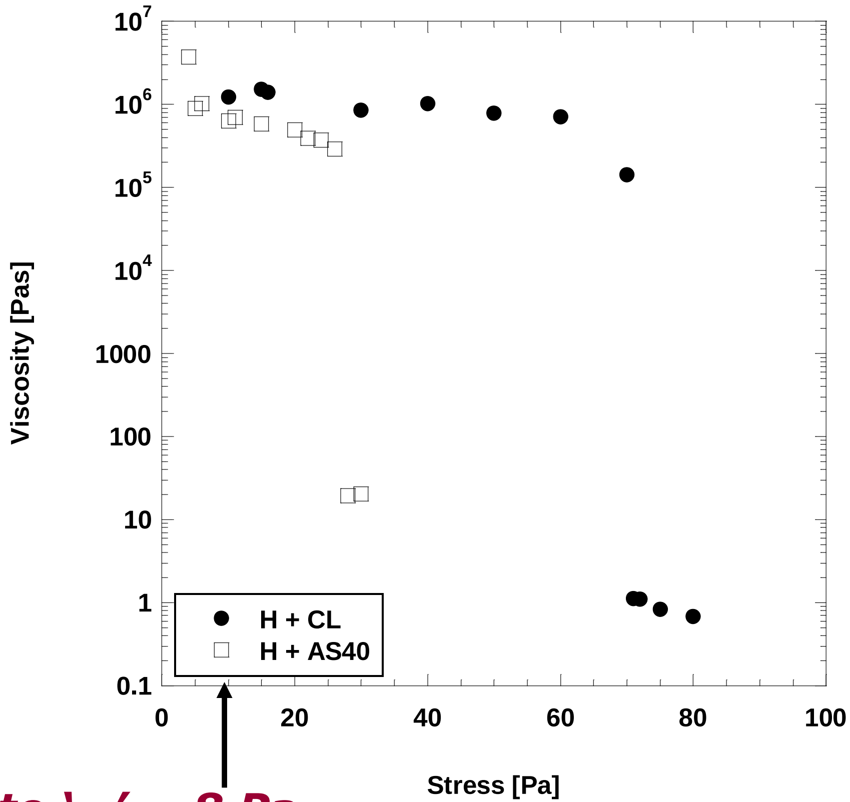
$C_{hectorite}$ = 2.5 wt% = 1.7C*

Controlled shear stress flow curves - effect of 10 wt% minor colloid

$C_{hectorite}$ = 2.5 wt% = 1.7C*



Post-creep viscosities – added silica spheres and the effect of charge



Ludox CL cationic

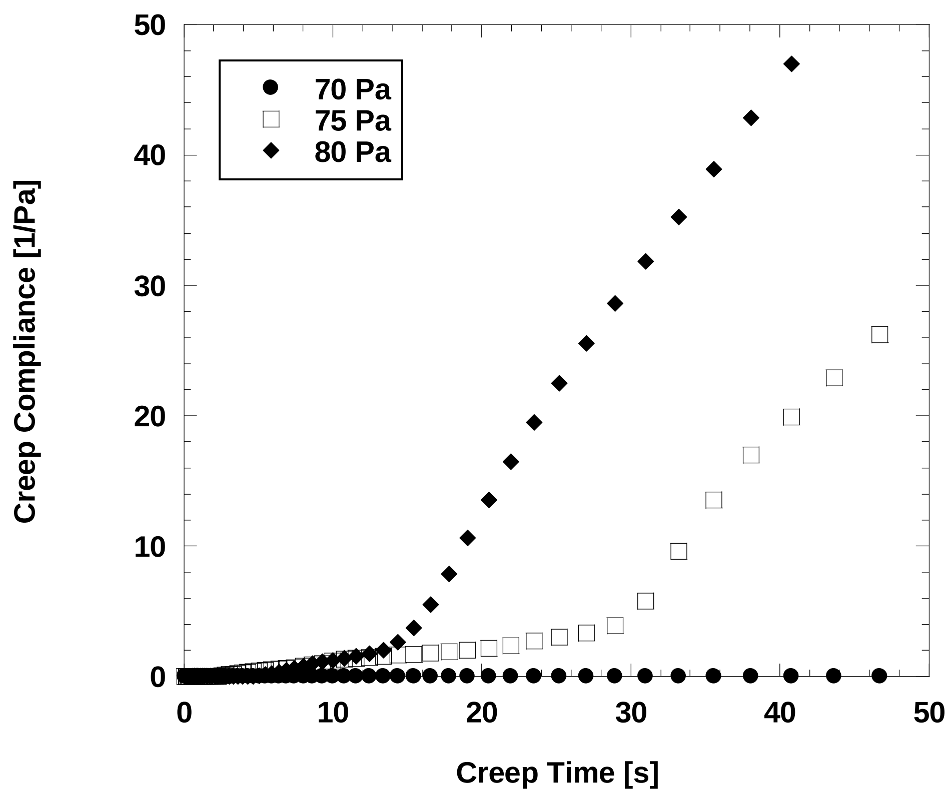
Ludox AS40 anionic

D = 12 nm for both

Pure Hectorite 'τ_y' = 8 Pa

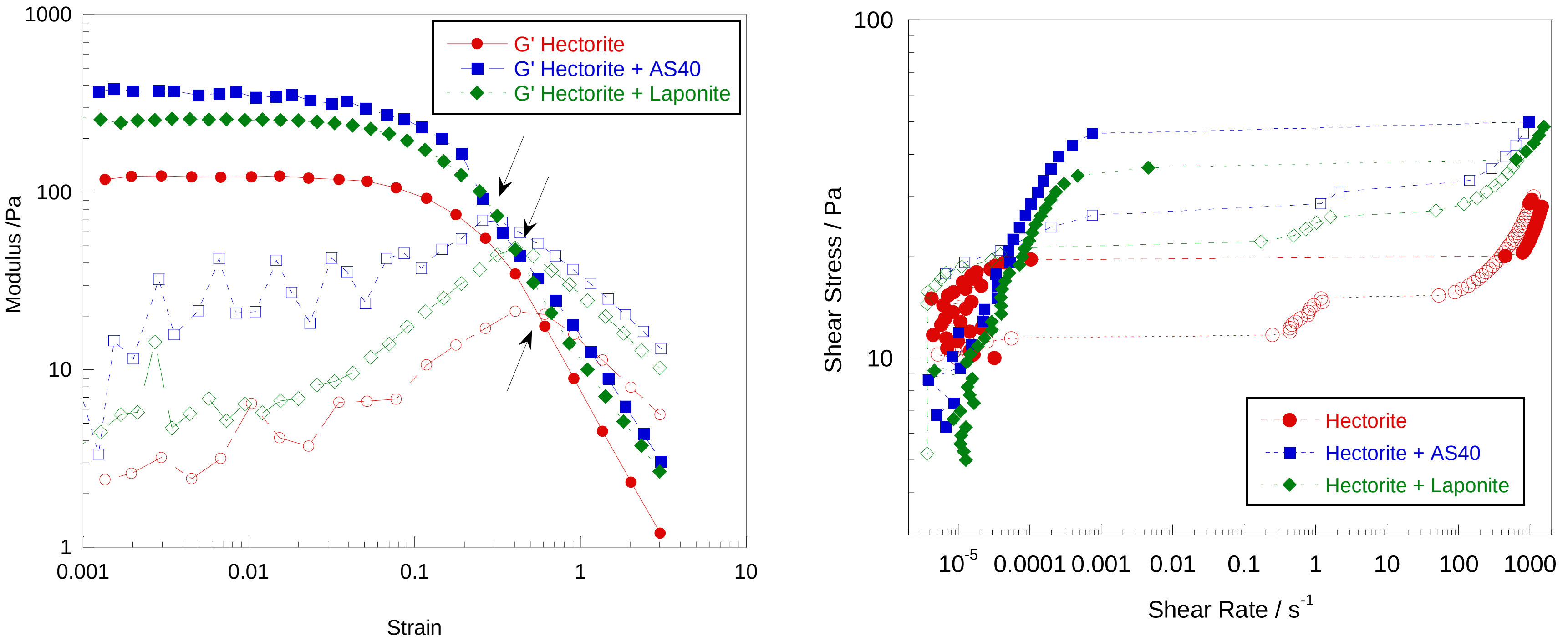
$C_{hectorite}$ = 2.8 wt% = 1.9C*

Early-time creep behaviour near ‘τ_y’



Hectorite (-ve)-Ludox CL (+ve)

Comparative anionic mixtures



Again enhancement of rheology laths + plates < spheres

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Enhancement by adding minor colloid 1:10 to 2.5 wt% Hectorite

Property / Colloids	Hectorite	Hectorite-Boehmite	Hectorite-Gibbsite	Hectorite-Ludox CL
G”	1	2	5	**30**
τ_y	1	1	2	6
G'_y	1	1	2	20
G’ (1Hz)	1	1.4	4	20
G_e (peak)	1	1	-	**1500**
$\eta(\tau \rightarrow 0)$ (Creep)	1	0.5	-	14
τ_y (Creep)	1	>1.2	-	8
$\eta(\tau \rightarrow 0)$ (Steady Shear)	1	3	10	20
τ_y (Steady Shear)	1	1.5	4.5	6
Yield Strain (Oscillatory)	1	0.6	0.3	**0.25**
Yield Strain (Cont Shear)	1	0.5	0.2	**0.06**
Relative particle concentration, n_p		2	1	**280**
Packing ratio per hectorite lath		0.8	4.5	**200**

Mixed Colloid Conclusions

- Complexity of hectorite and hectorite-aluminasol gel rheology
  - Elastoviscous solid → weakly elastic, shear-thinning liquid
  - ‘Yield Space’ rather than single Yield Stress
- Rheological behaviour and parameters by different techniques consistent if uniform sample pre-treatment used
- Major enhancements of rheology for small additions of second component (~0.1$c_{initial}$ w/w)

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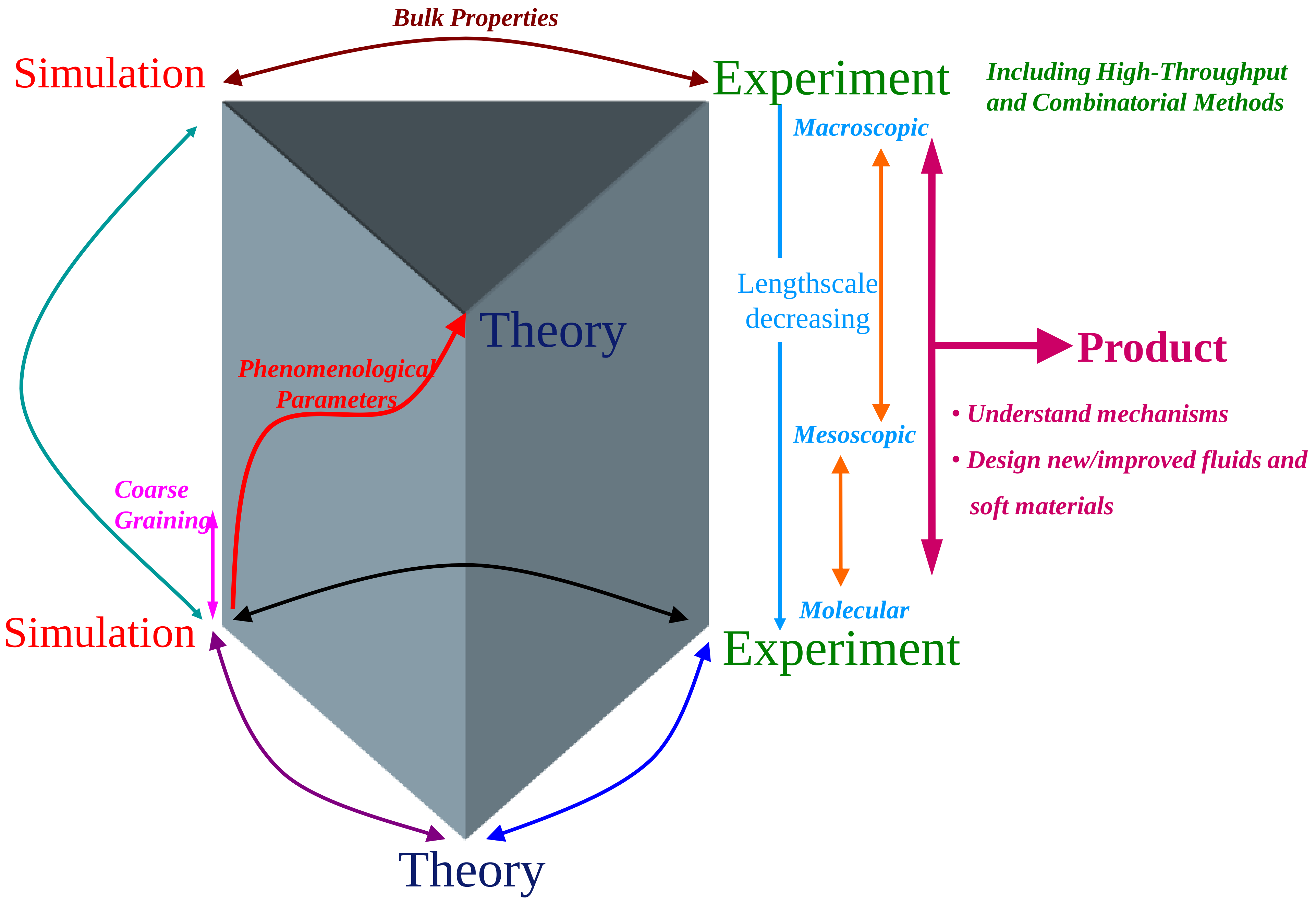
Mixed Colloid Conclusions

- Enhancements depend on second colloid shape, size, charge and number concentration
  - G', η (t→0) and 'τ_{yeff}' all increase rods < platelets < spheres,
  - Enhancements for nanospheres being typically x20 and up to x500
  - Critical parameter is γ_y, determined by size of minor component
- For a given shape, size and charge have a significant effect
- Most dramatic effects are with silica, a relativel cheap and widely available material
  - So **cost-effective** rheology enhancement and tuning of gelation characteristics looks feasible
- Qualitative physicochemical models can rationalise the observed behaviour – heteroflocculation

  – depletion or dispersion effects
  - More microstructural flow studies and quantitative models are needed

Transforming Soft Materials Formulation



Thank you all for your attention, thanks to all my collaborators, in Schlumberger, other companies, many universities...
and many thanks to the SCI and RSC Joint Colloid Groups for the 2012 Rideal Lecture Award.