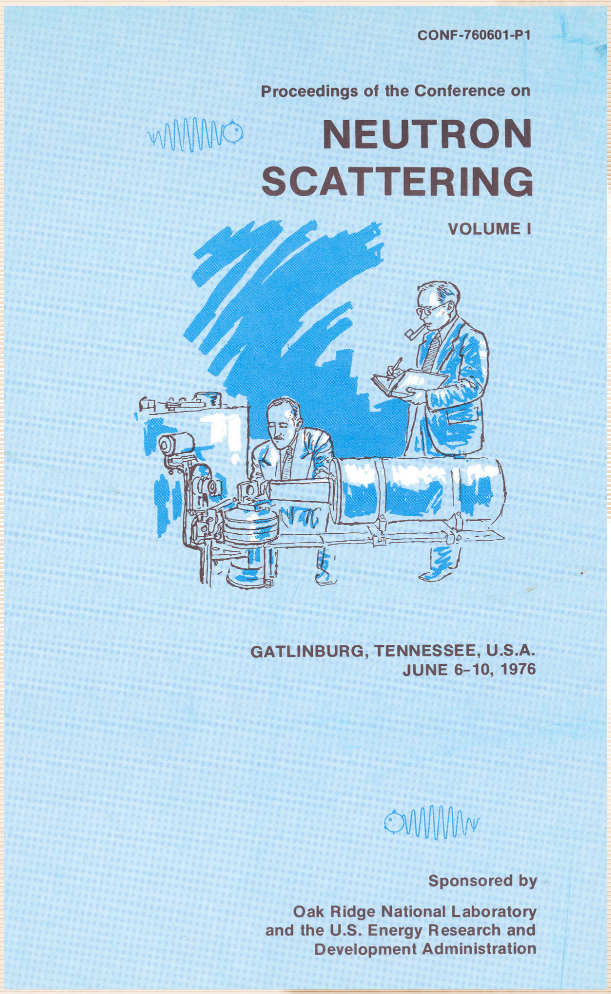
NIST Neutron Research at NIST NCMR

A Symposium honouring Mike Rowe & Jack Rush

Neutron Scattering in Soft Matter Science

D. Richter

Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany



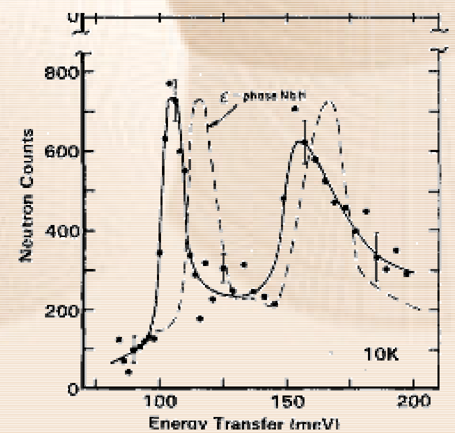
- H in metals
- OECD Megascience Forum
- NSE instrument
- Promoting neutrons

H in Metals

BT4 at NIST

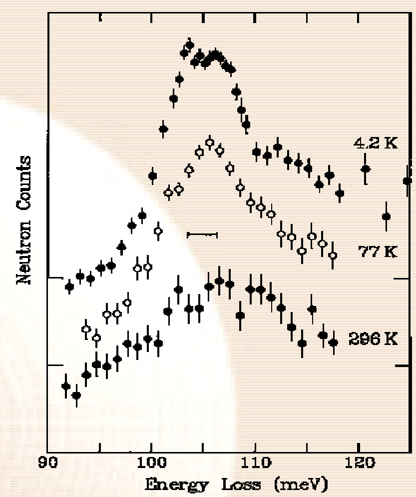
Numerous joint publications

Example:



Physical Review B **27**, 927 (1983)

H trapped at O-impurity in Nb



Europhysics Letters **48**, 187 (1999)

Exited state tunneling of trapped H

Three-tier global strategy

3 next generation sources in Asia, USA and Europe

Maximum utilization of current front rank facilities

Maintain local neutron infrastructure as far as possible

Neutron Instrumentation

NSE with worldwide highest
Field integral (Resolution)

IN 11 => 0.2 Tm

IN15 => 0.27 Tm

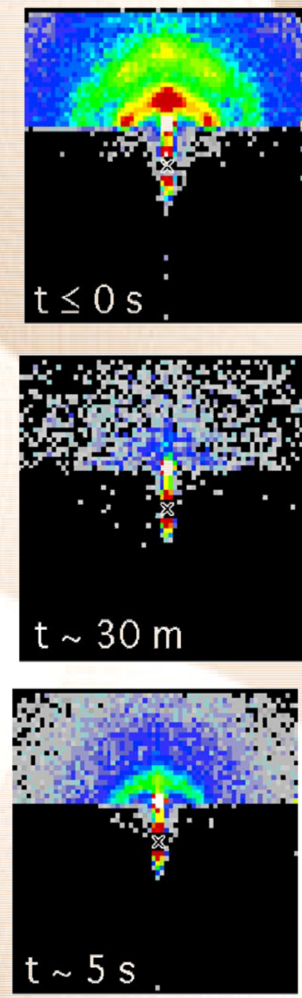
JNSE/NIST => 0.5 Tm

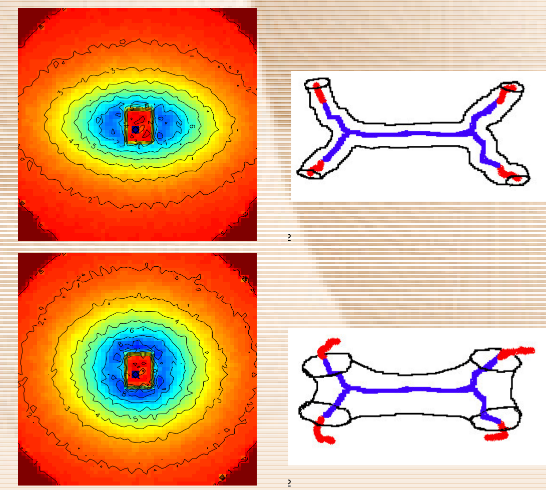
Multidetektor ($32x32cm^2$)

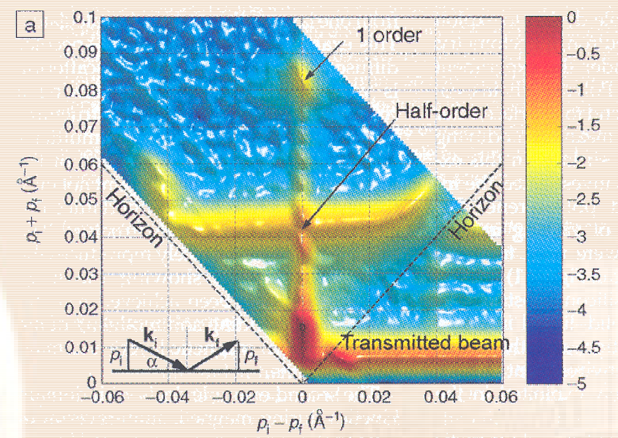
Most modern compensated
Field design

State of the art NSE

Promoting Neutrons



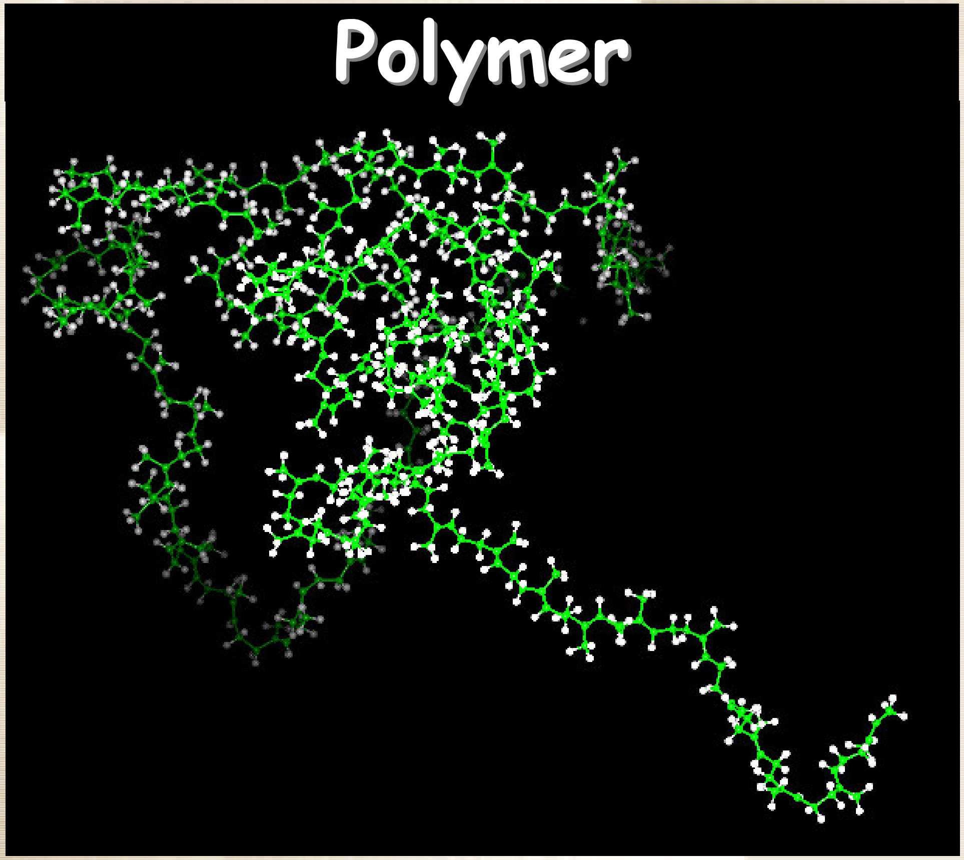




MRS Special: Neutrons in Materials Science

Neutron Scattering in Soft Matter Science

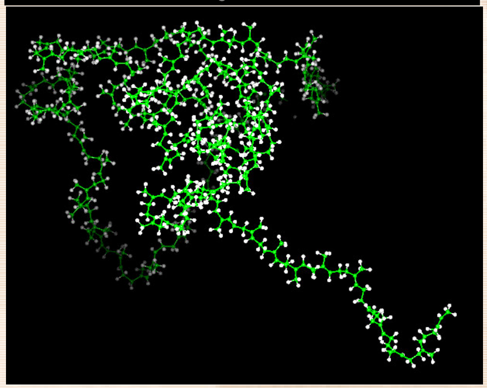
What is Soft Condensed Matter?



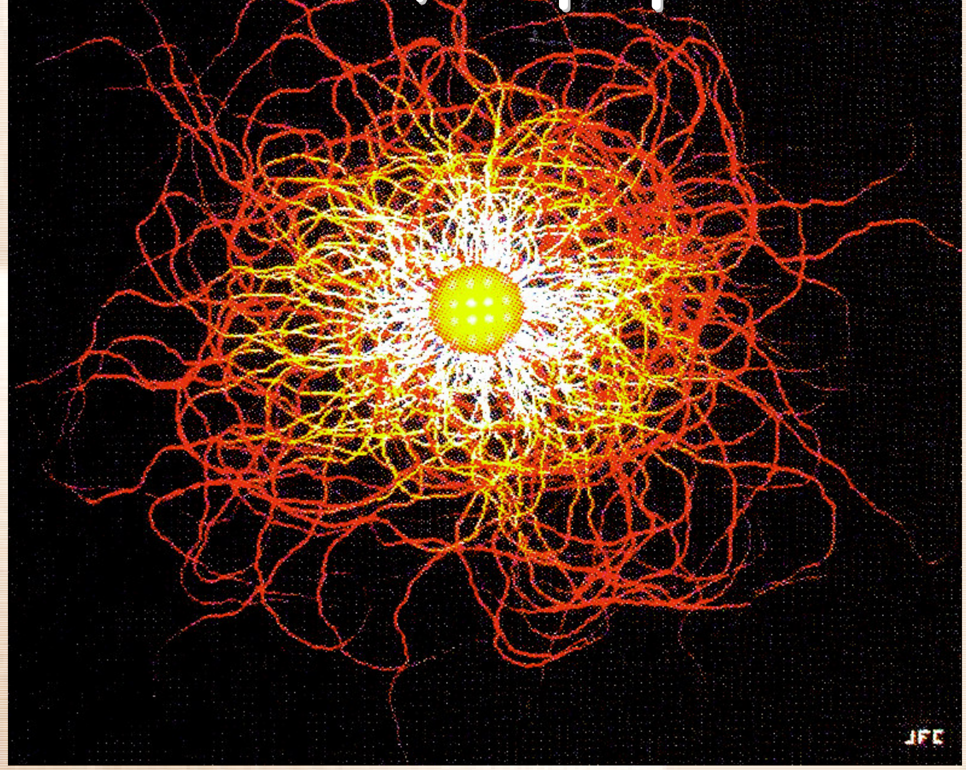
Structural units: large molecules or aggregates molecules

What is Soft Condensed Matter?

Polymer



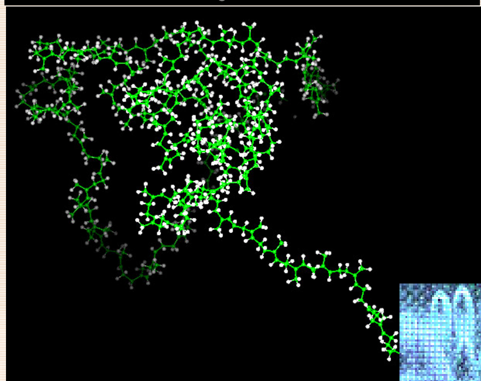
Surfactants. Micellar solutions, amphiphilics



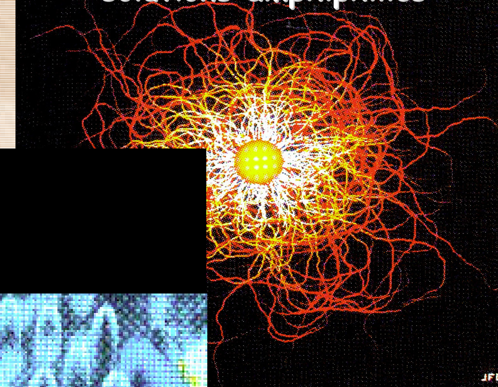
Structural units: large molecules or aggregates molecules

What is Soft Condensed Matter?

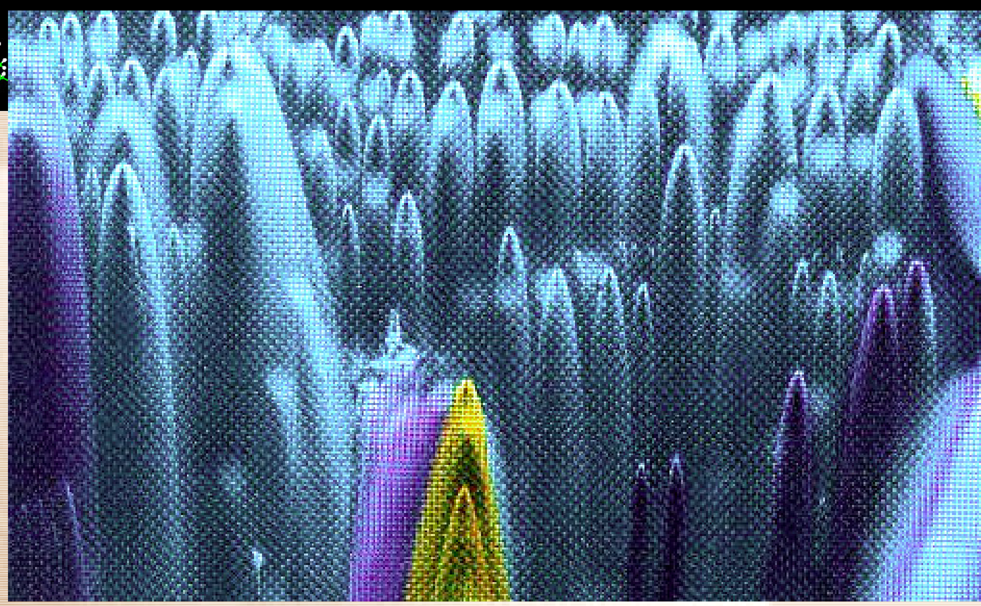
Polymer



Surfactants micellar solutions amphiphilics

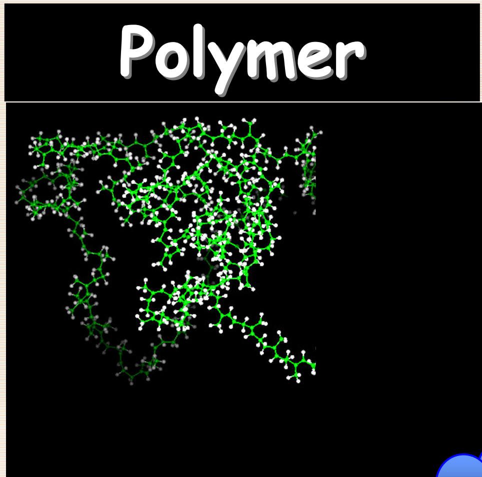


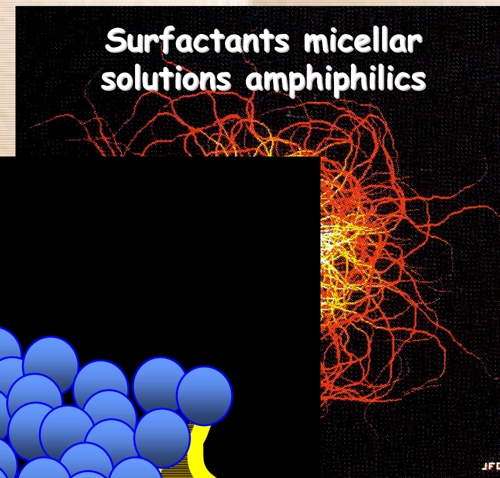
Liquid crystals

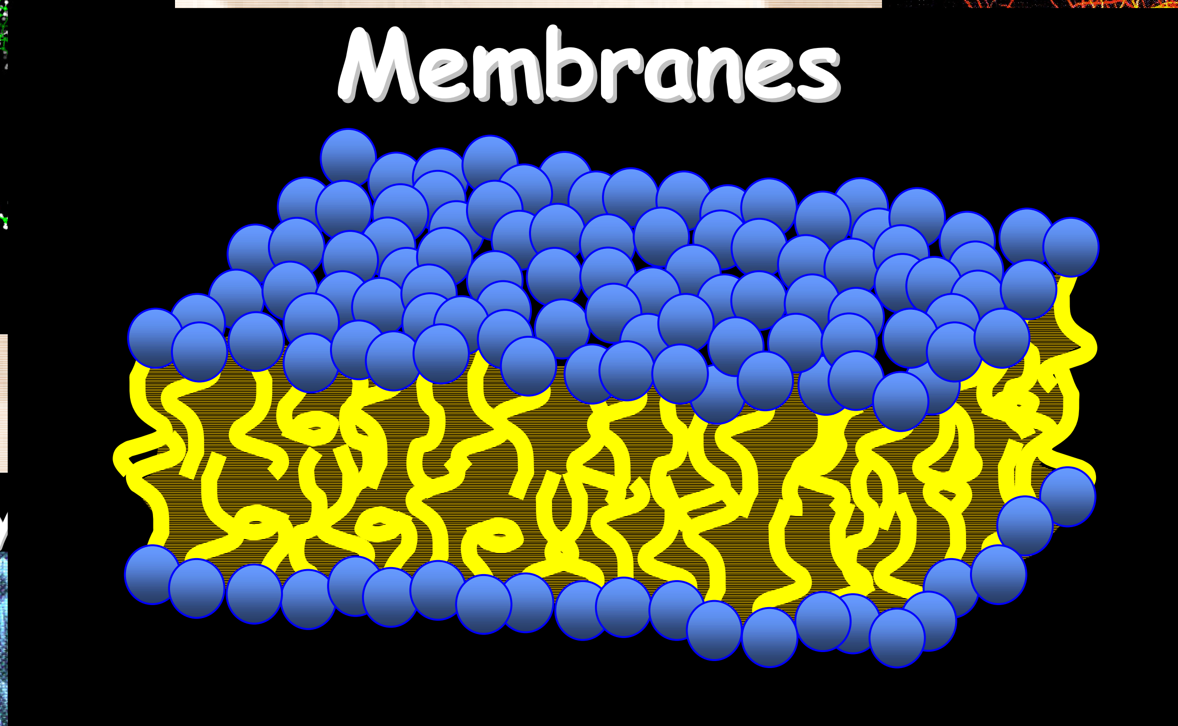


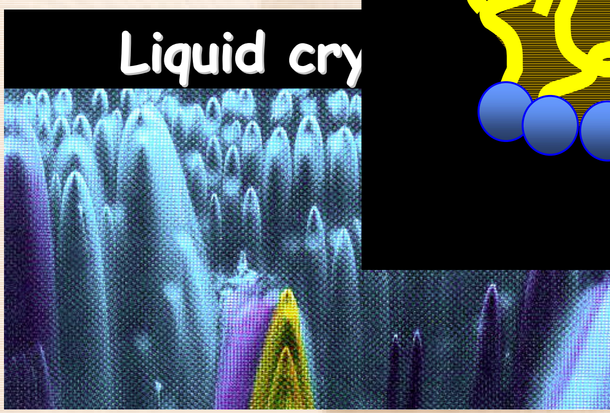
Structural units: large molecules or aggregates molecules

What is Soft Condensed Matter?





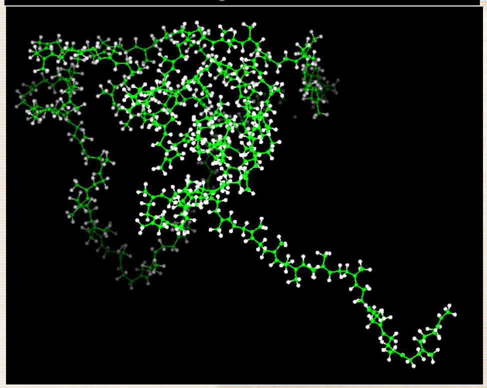




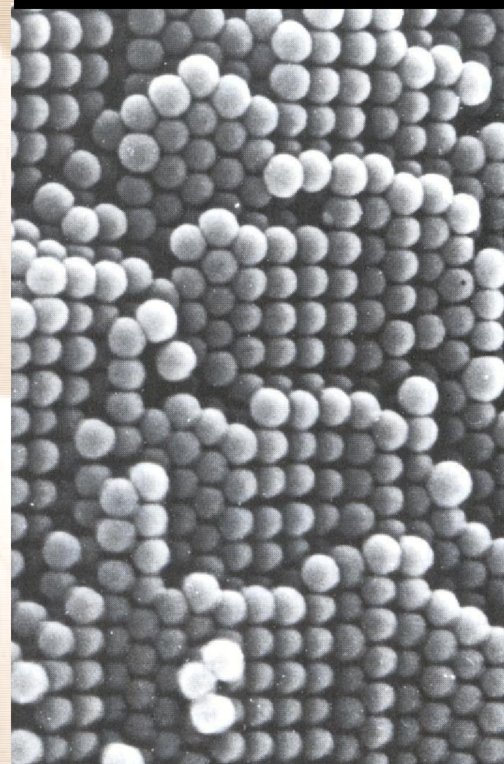
Structural units: large molecules or aggregates molecules

What is Soft Condensed Matter?

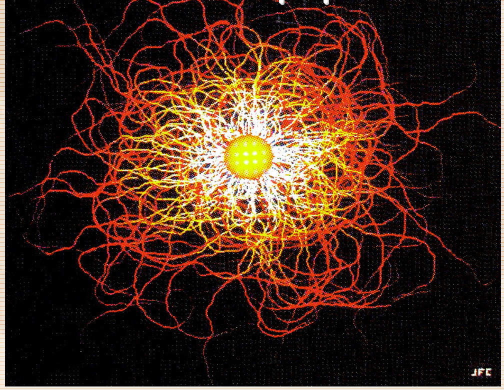
Polymer



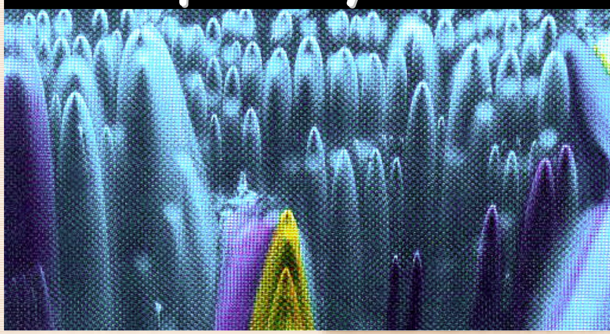
Colloids



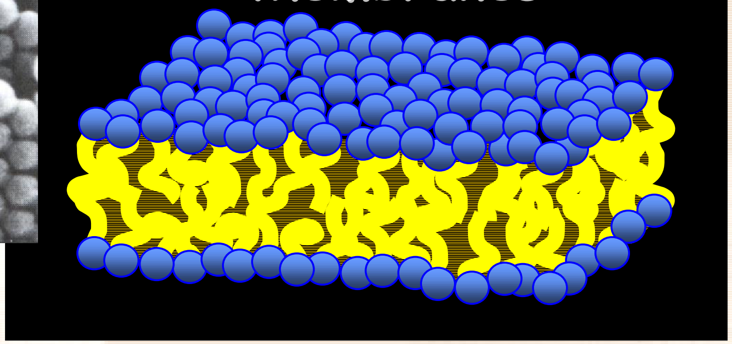
Surfactants micellar solutions amphiphilics



Liquid crystals



Membranes



Structural units: large molecules or aggregates molecules

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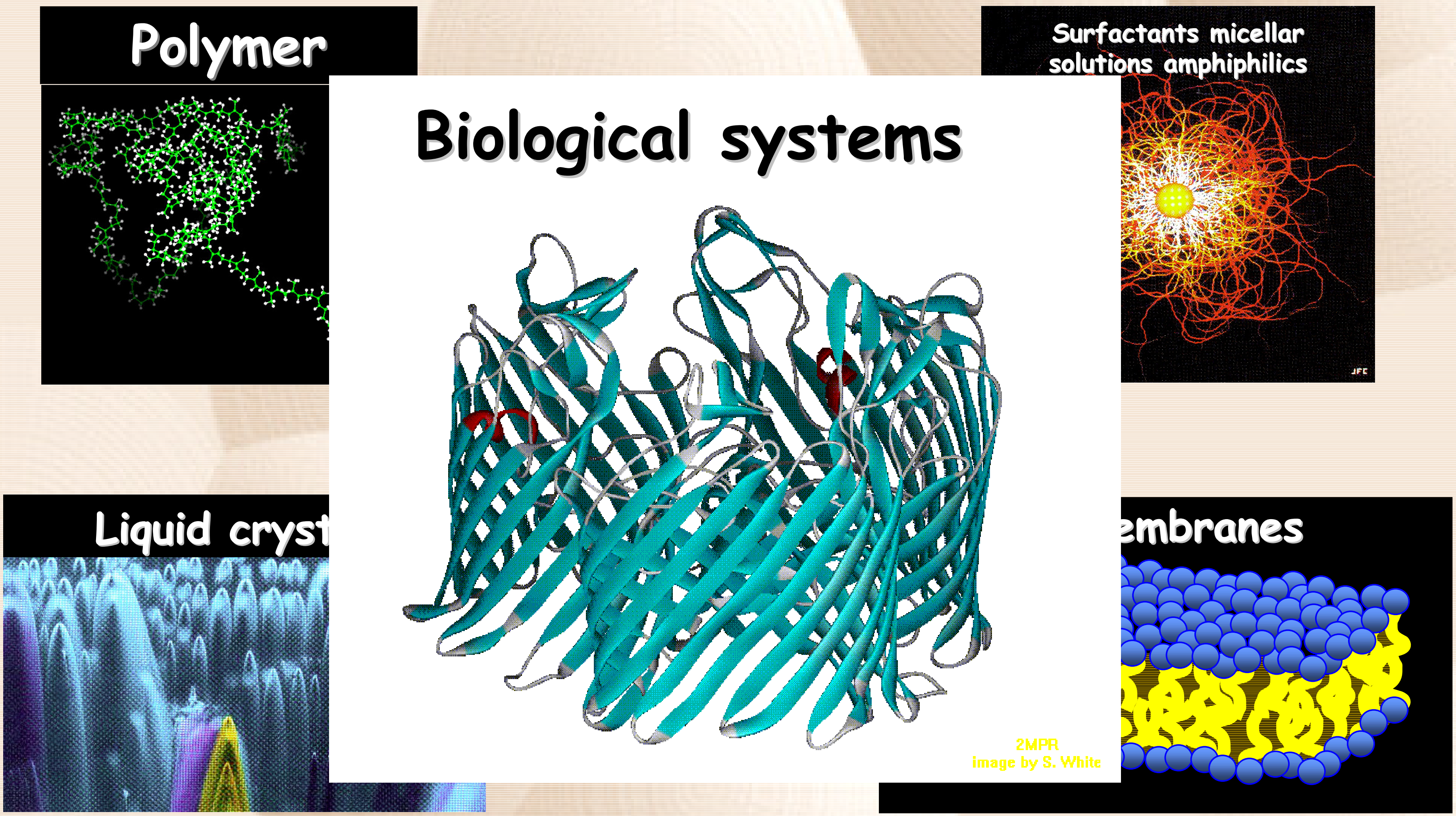


Structural units: large molecules or aggregates molecules

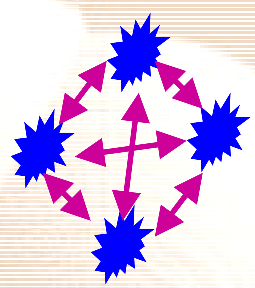
What is Soft Condensed Matter?

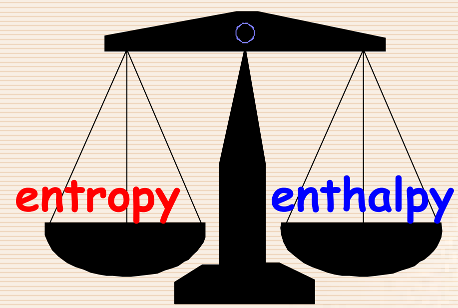
unifying principles

large number of internal degrees of freedom

weak interaction between the structural units

delicate balance entropic ⟷ enthalpic contrib. to free energy



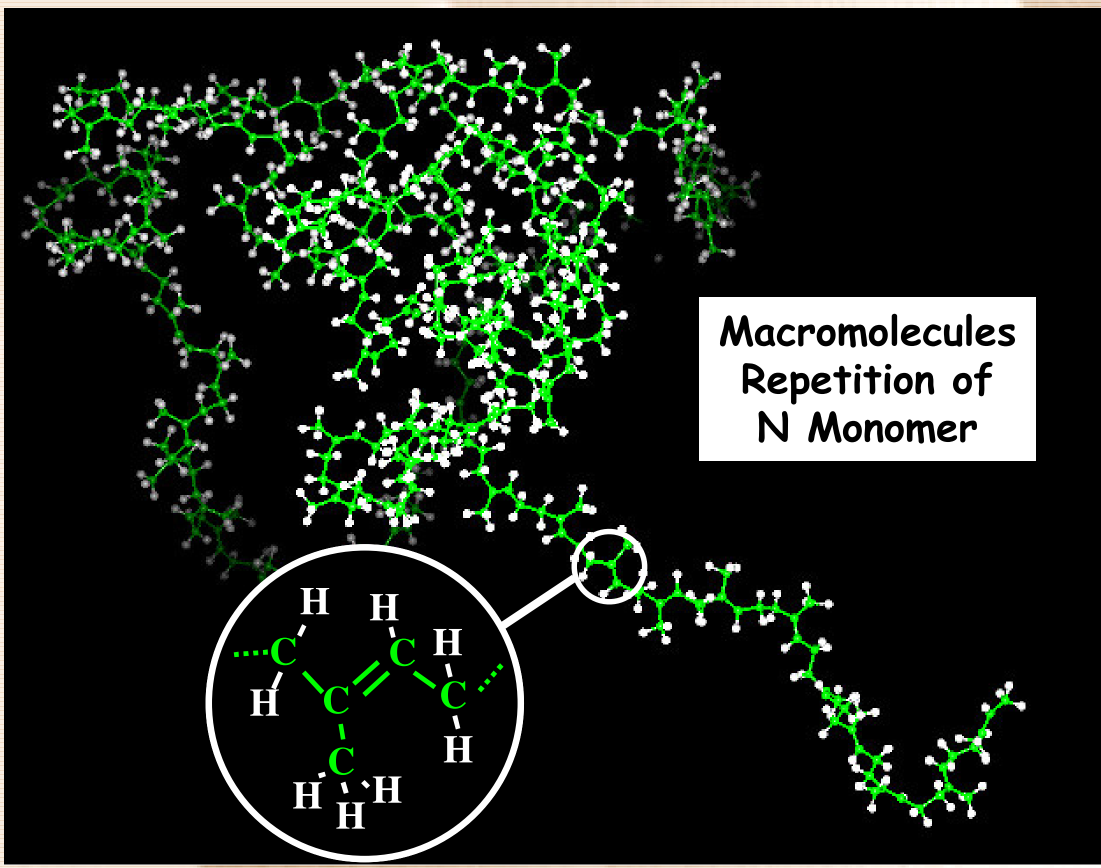


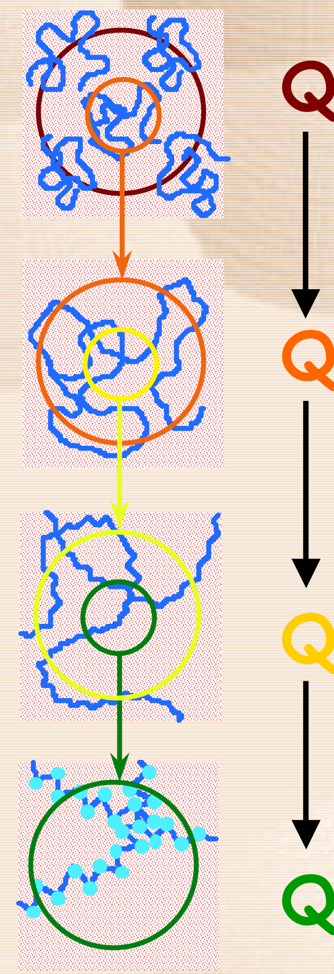
Statistical physics: universal properties

Soft Condensed Matter: Challenges

- Interplay : specific and universal
- Bridge the huge gap in the length and time scale: individual molecular units to the mesoscopic structures
- Fundamental understanding of interplay between enthalpy and entropy
- Out of equilibrium systems
- Concepts of SM for biological systems

Neutrons and Soft Matter

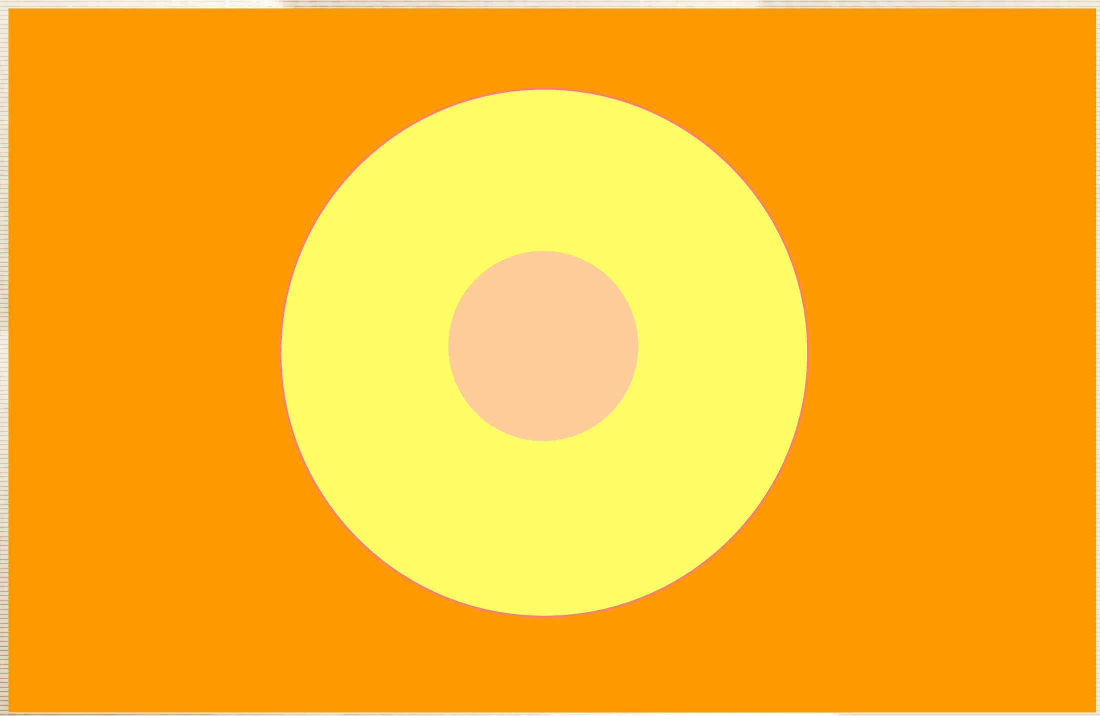




Neutrons access molecular length and time scales

Neutrons and Soft Matter

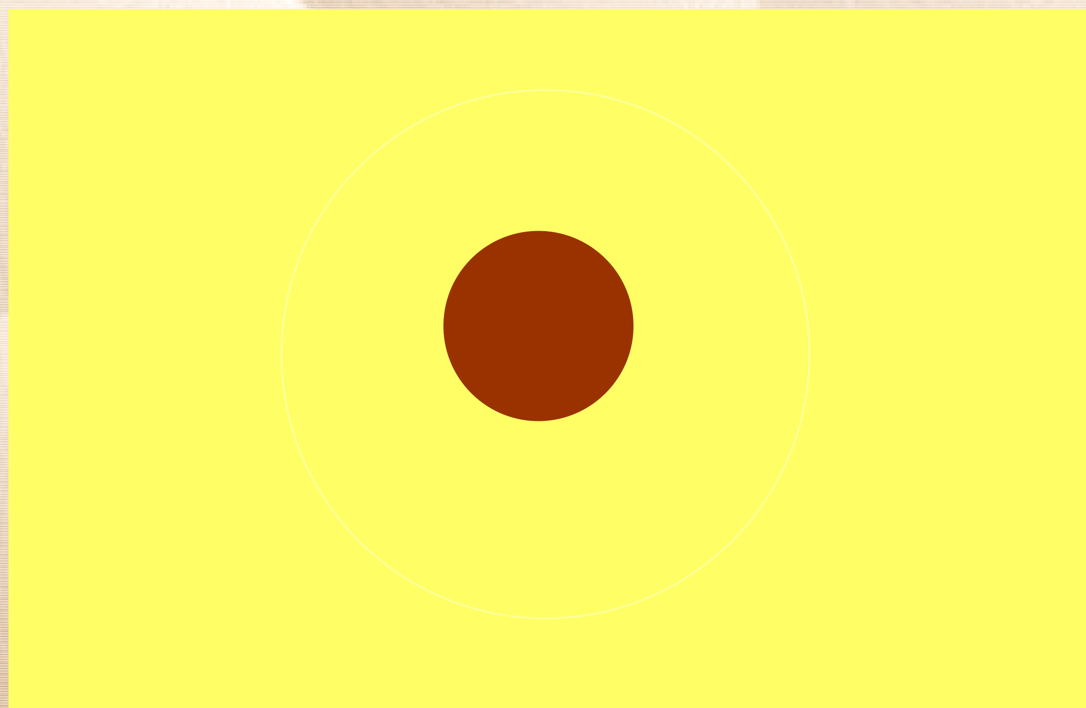
Hydrogen deuterium contrast



Neutrons enable contrasting on molecular scale

Neutrons and Soft Matter

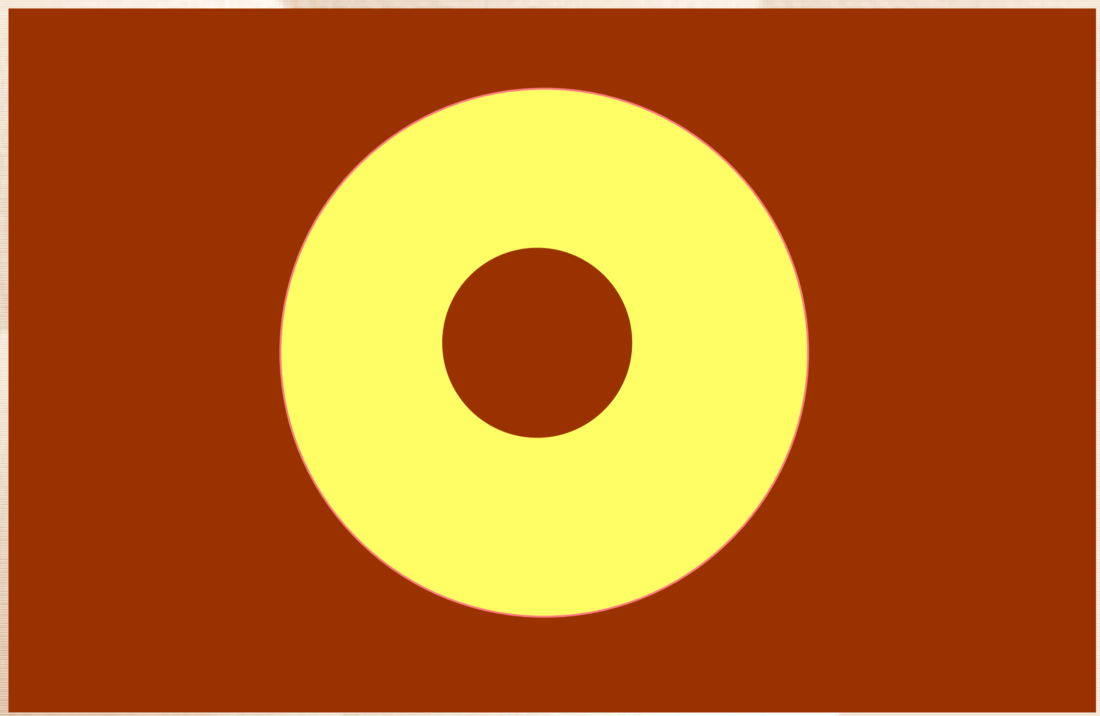
Contrast variation



Neutrons enable contrasting on molecular scale

Neutrons and Soft Matter

Contrast variation



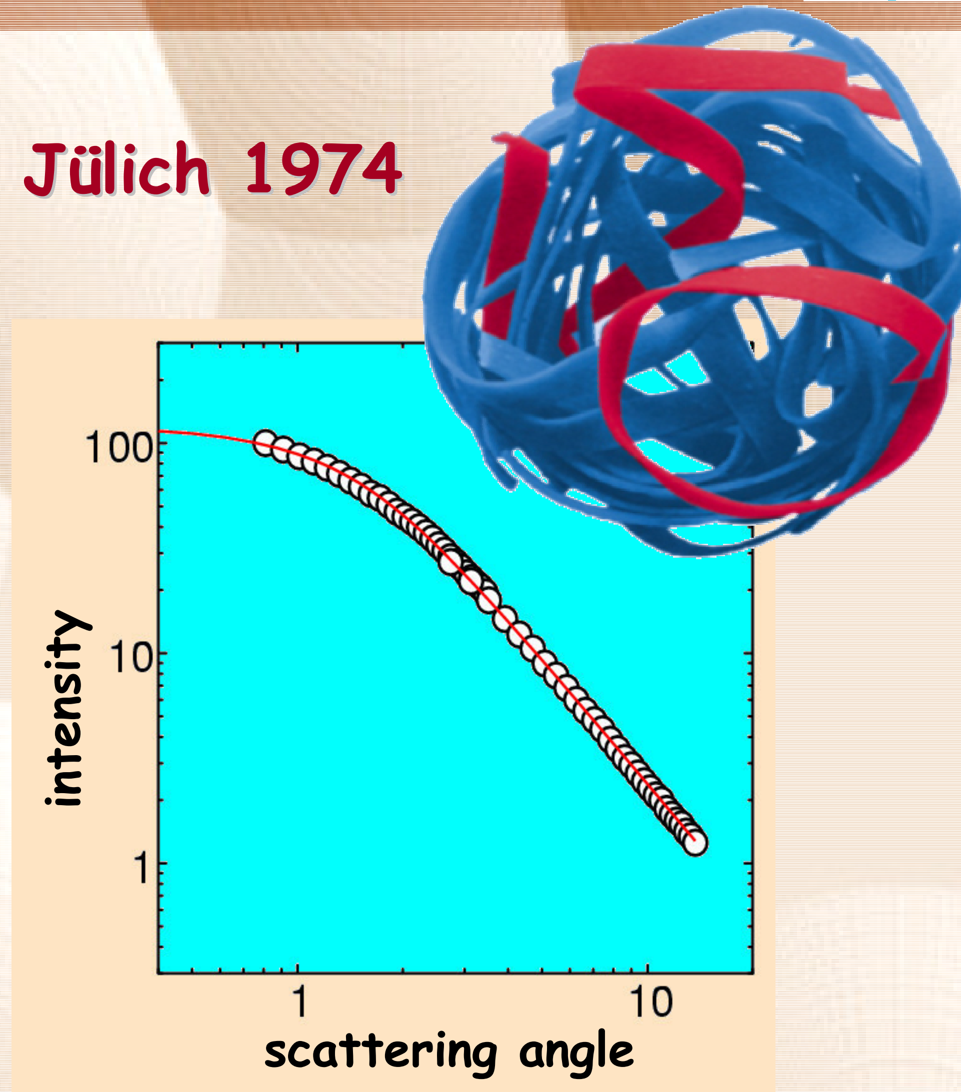
Neutrons enable contrasting on molecular scale

Polymer Chain Conformation

P.J. Flory
Stanford
USA

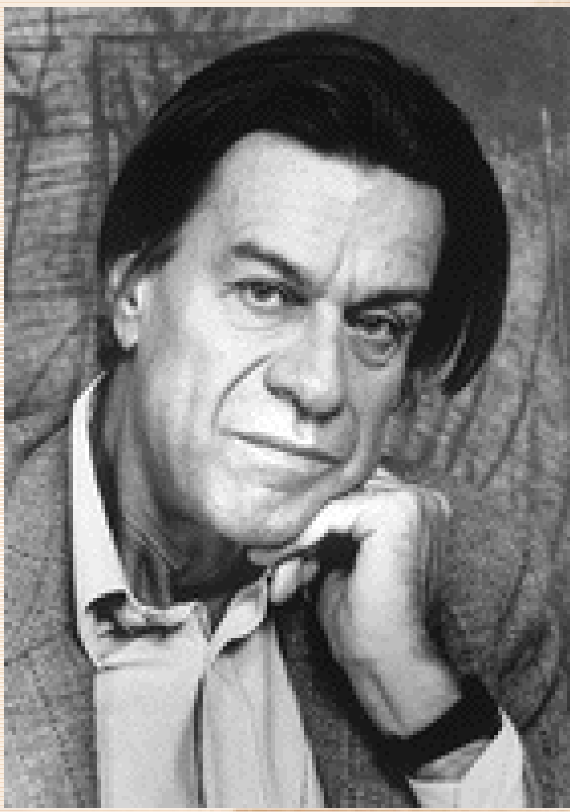
Nobel prize 1974

Jülich 1974



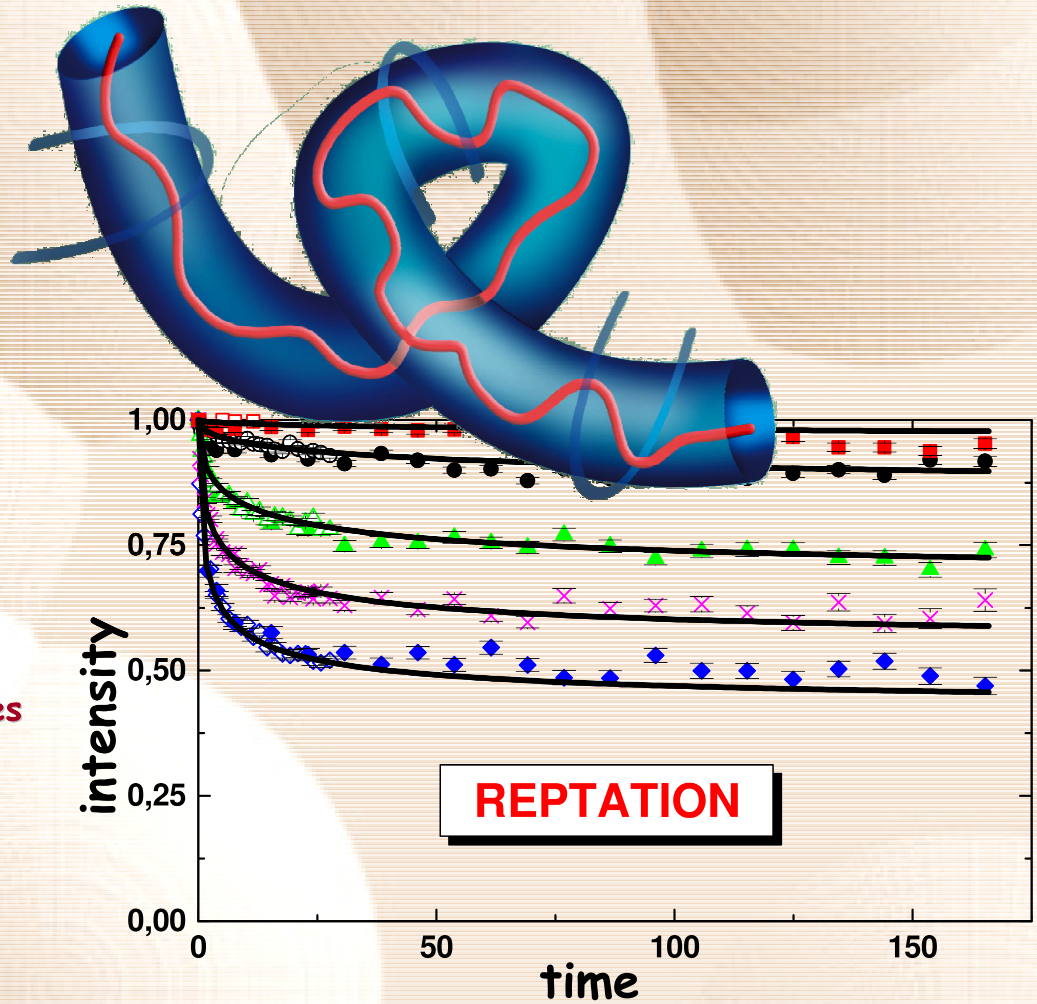
Early triumph of neutron scattering

Polymer Chain Dynamics



P.G. De Gennes
ESPCI Paris
France

Nobel prize 1991



Subject of intense current research

Neutrons in Soft Matter Science

Multiscale dynamics

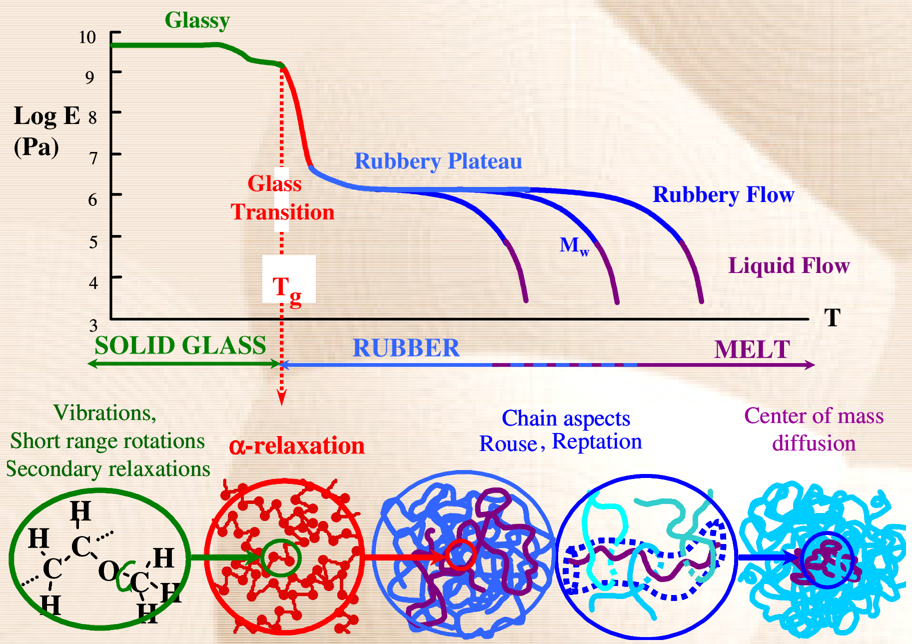
Real time kinetic &
non equilibrium processes

Soft Matter Challenges

Key components

Self-assembly

Polymer Dynamics



Example:
viscoelastic and mechanical properties of polymers

Molecular Origin?

with

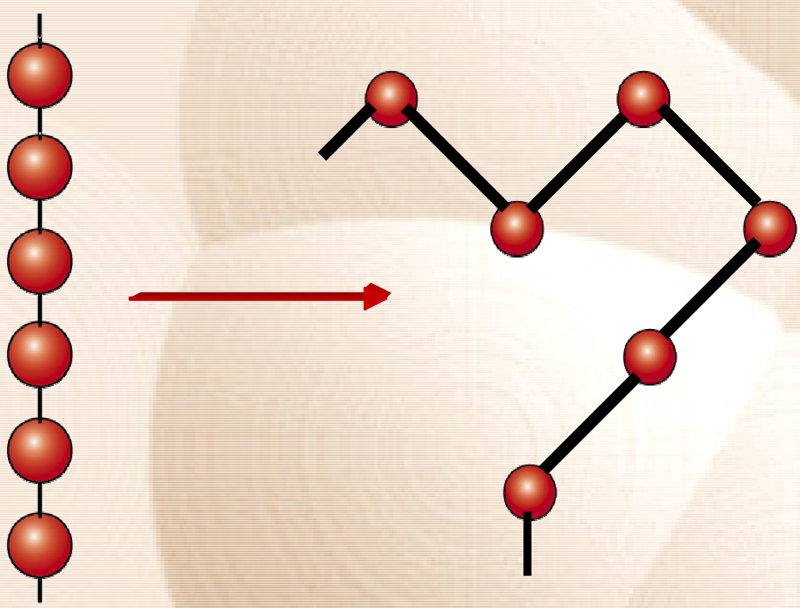
A. Wischnewski	*FZ Jülich*
M. Monkenbusch	*FZ Jülich*
L. Willner	*FZ Jülich*
M. Zamponi	*FZ Jülich*

Space time resolution on a molecular scale

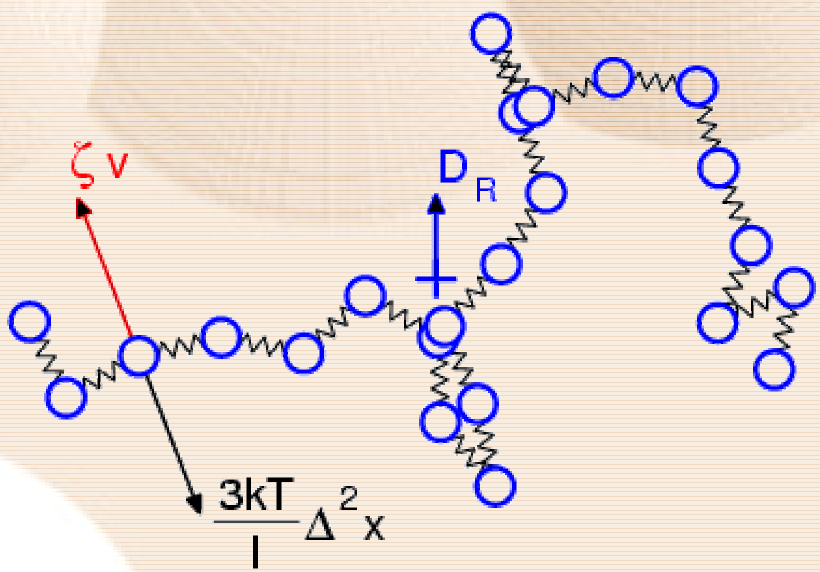
Entropy Driven Dynamics: Rouse

Gaussian chain

entropic Force



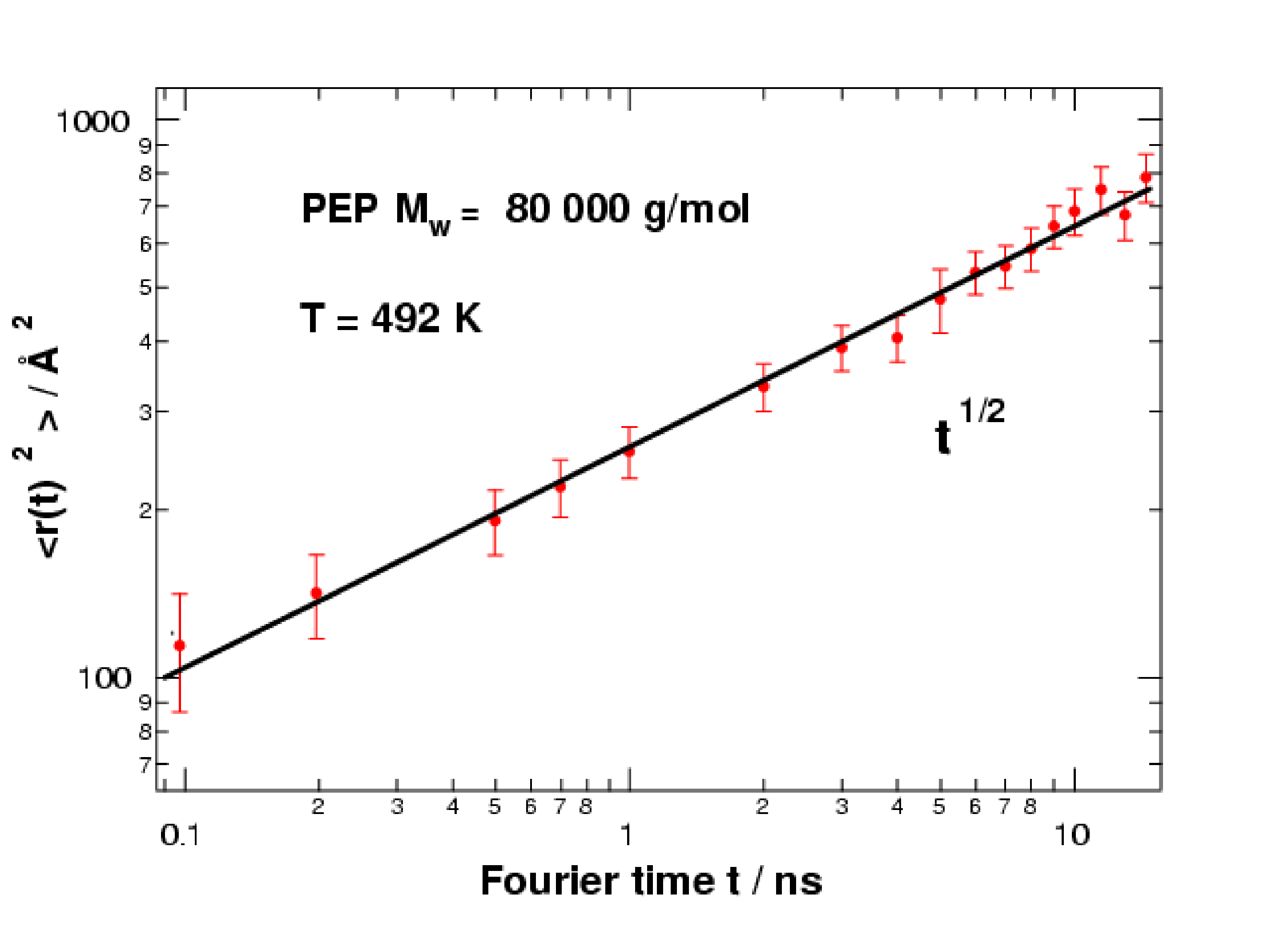
friction



entropic spring

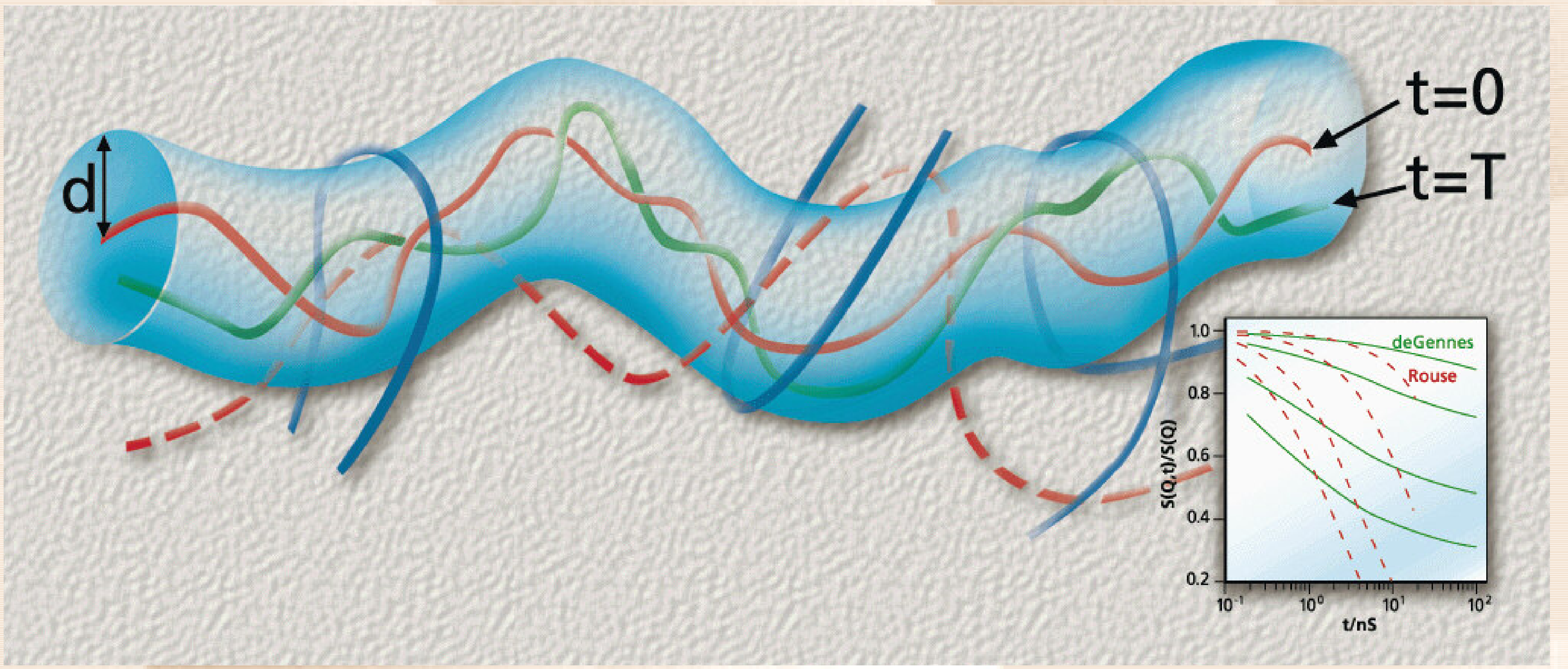
Entropic and frictional forces

Linear Chain Dynamics in the Melt



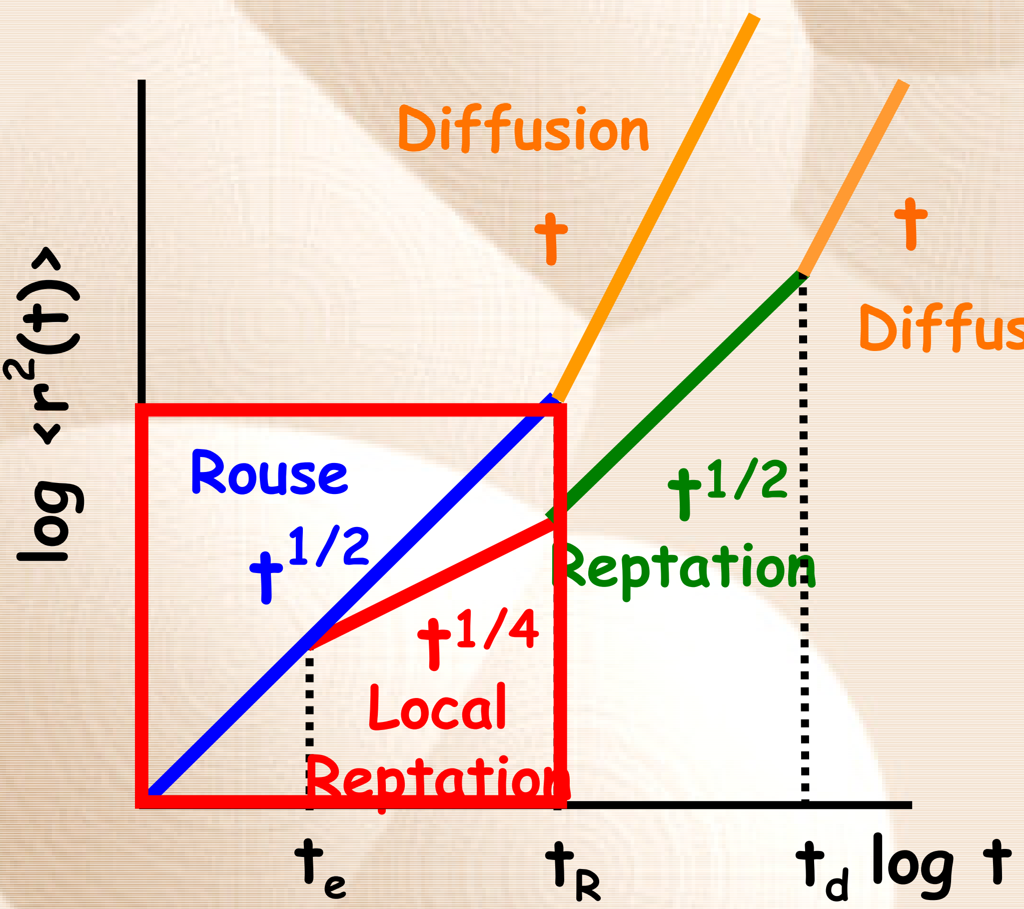
Rouse model

Topologically constraint Motion
- The Effect of Chain Length



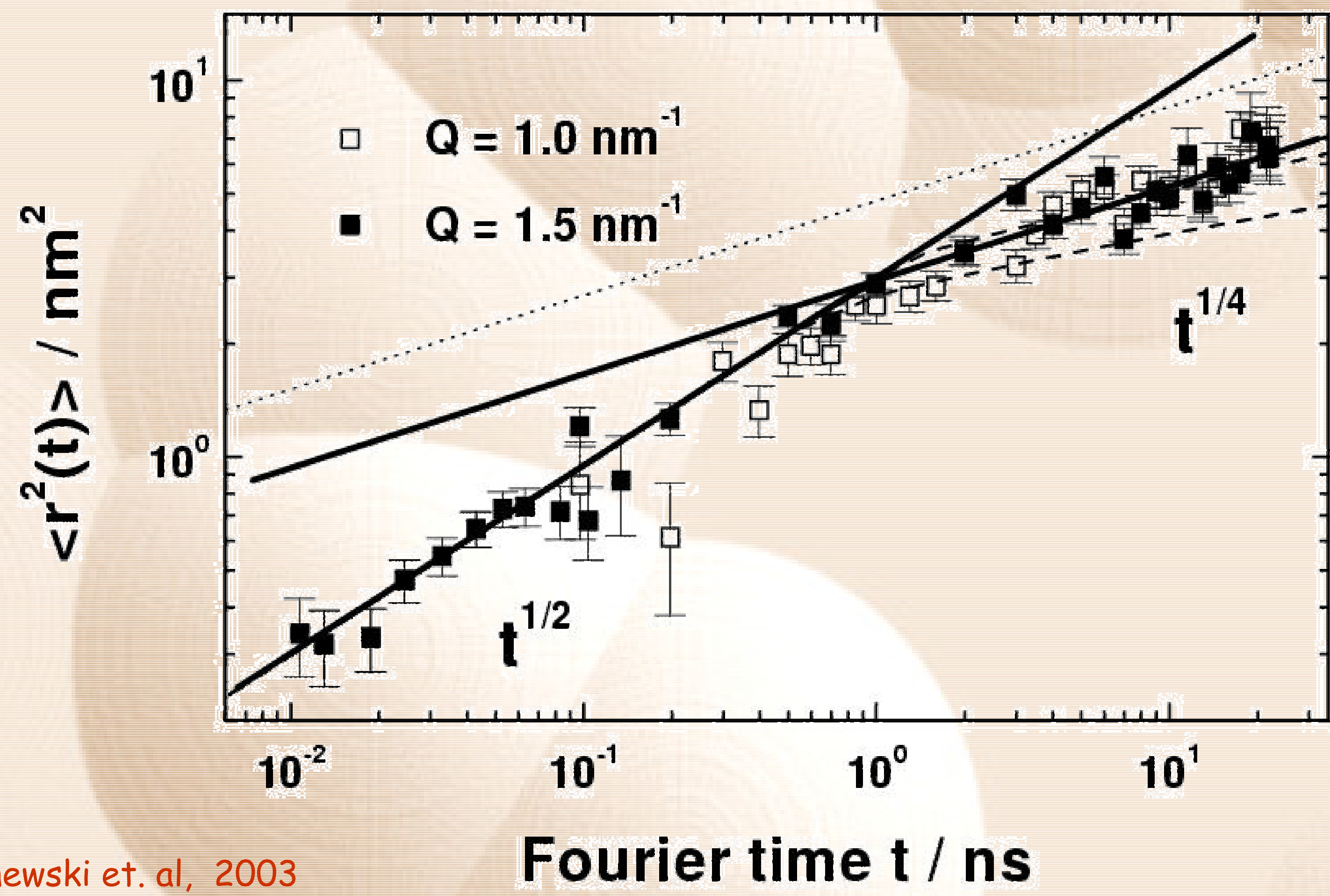
Reptation: relaxation in tube - creep out of tube

Topologically constraint Motion
- Self-Motion



Mean squared displacement

Topologically constraint Motion
- Reptation



Wischnewski et. al, 2003

Mean squared displacement

Neutrons in Soft Matter Science

Multiscale dynamics

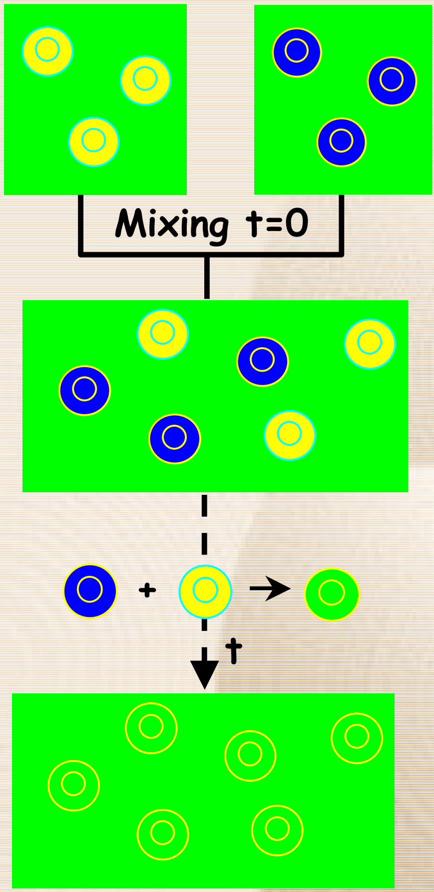
Real time kinetic & non equilibrium processes

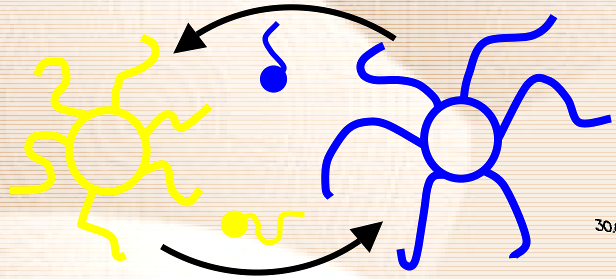
Soft Matter Challenges

Key components

Selfassembly

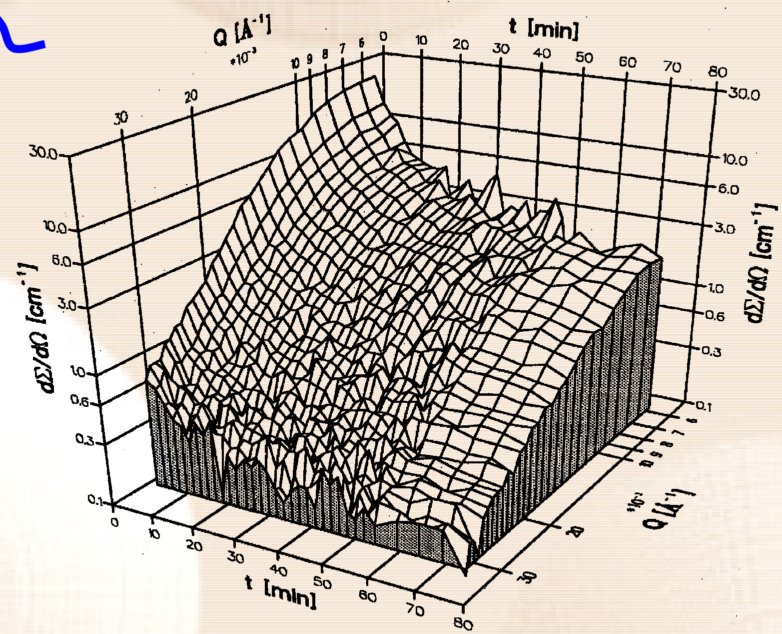
Kinetic Studies
- Recent Example: Micellar exchange kinetics





Recent example:
Micellar exchange kinetics

SANS



Contrast and real time capabilities

What to Expect from Theory?

Halperin and Alexander 1989:

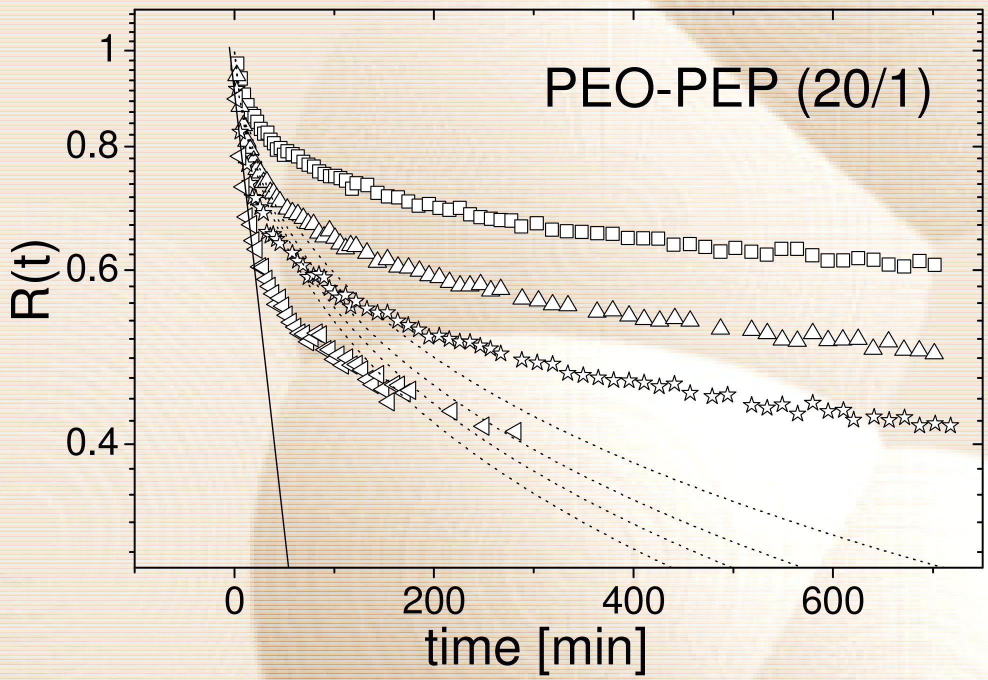
Only unimer exchange relevant for polymeric micelles

(Aniansson-Wall mechanism):

$$E_A \sim N_B^{2/3}\gamma$$

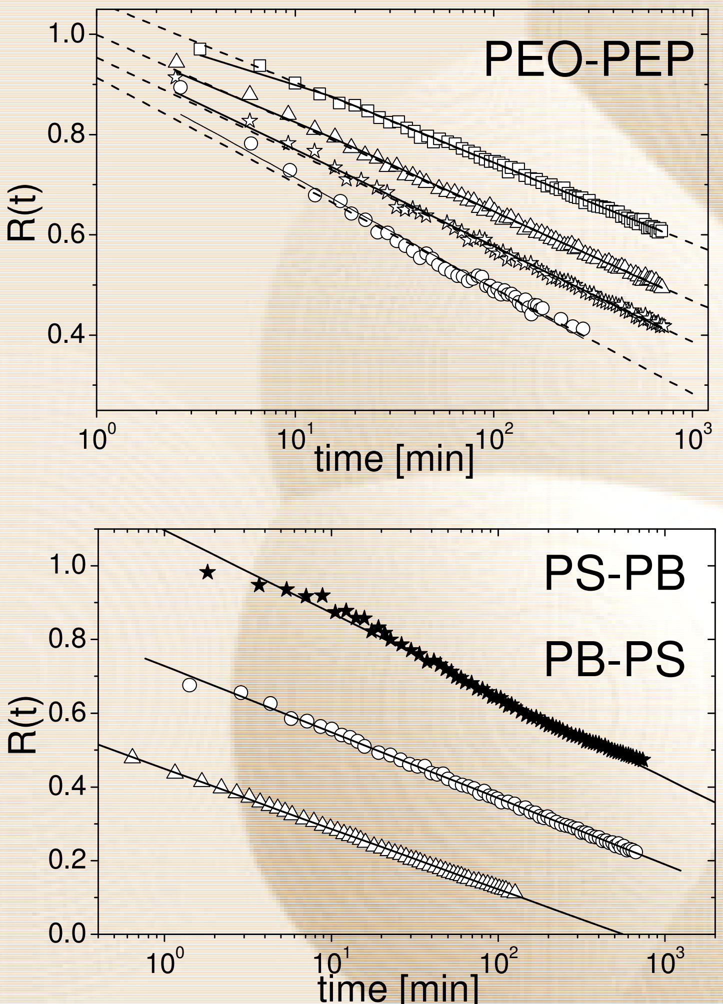
- Single exponential relaxation for unimer exhange

Kinetic Studies
- Micellar exchange kinetics



- Cannot be described with a single exponential!
- Polydispersity provides no explanation
- Extremely broad distribution of rates

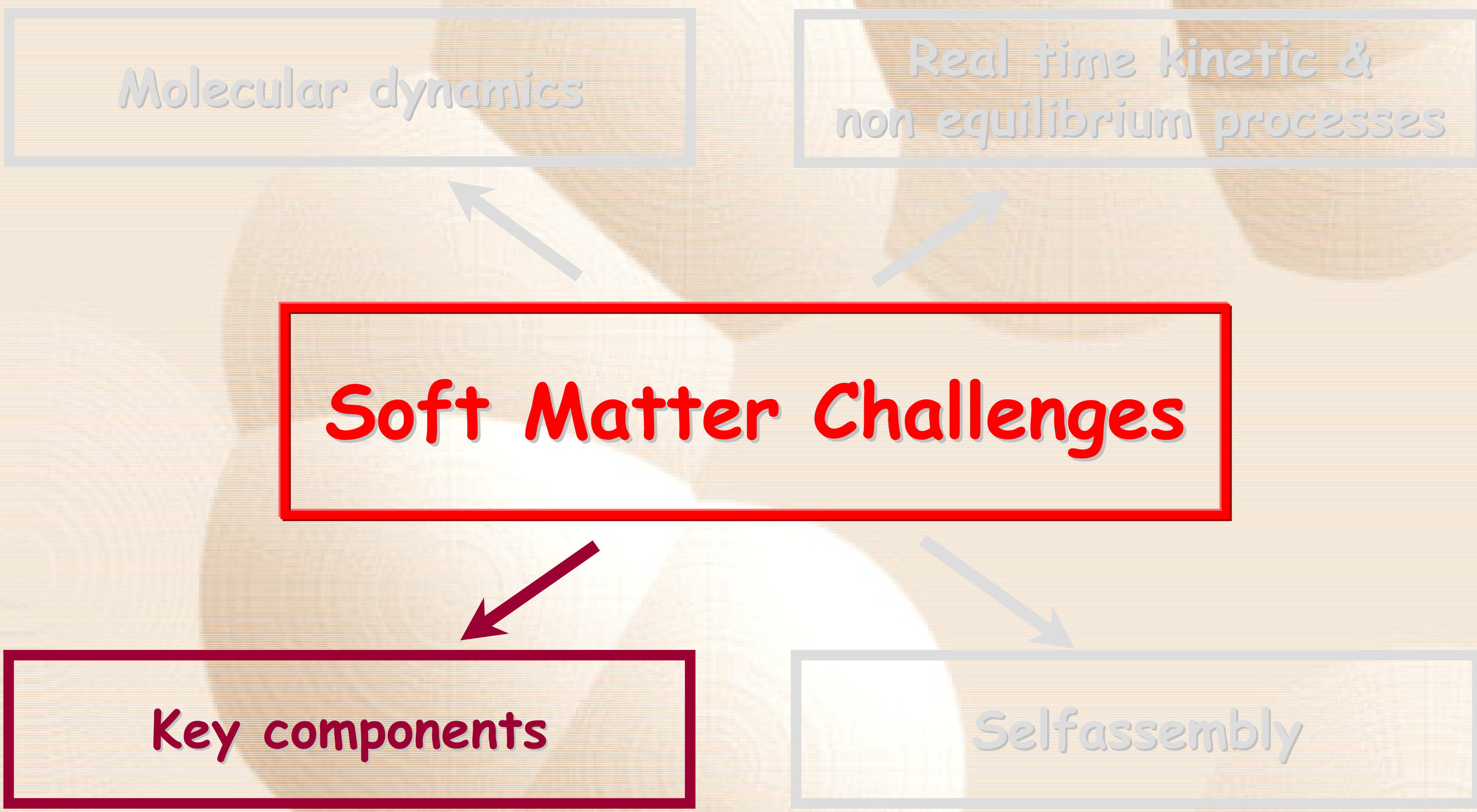
Kinetic Studies
- Micellar exchange kinetics



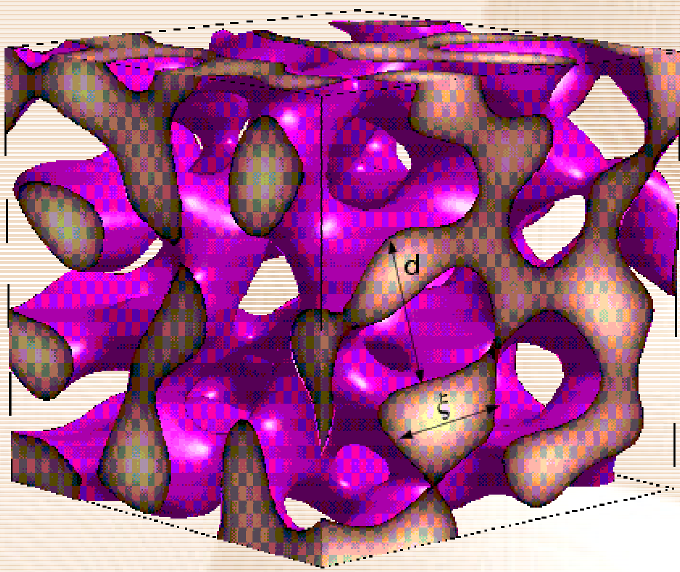
Logarithmic time dependence

- independent of system
- escape time Halperin: minutes
- confinement in micellar core ?
- hierachical processes ?

Neutrons in Soft Matter Science

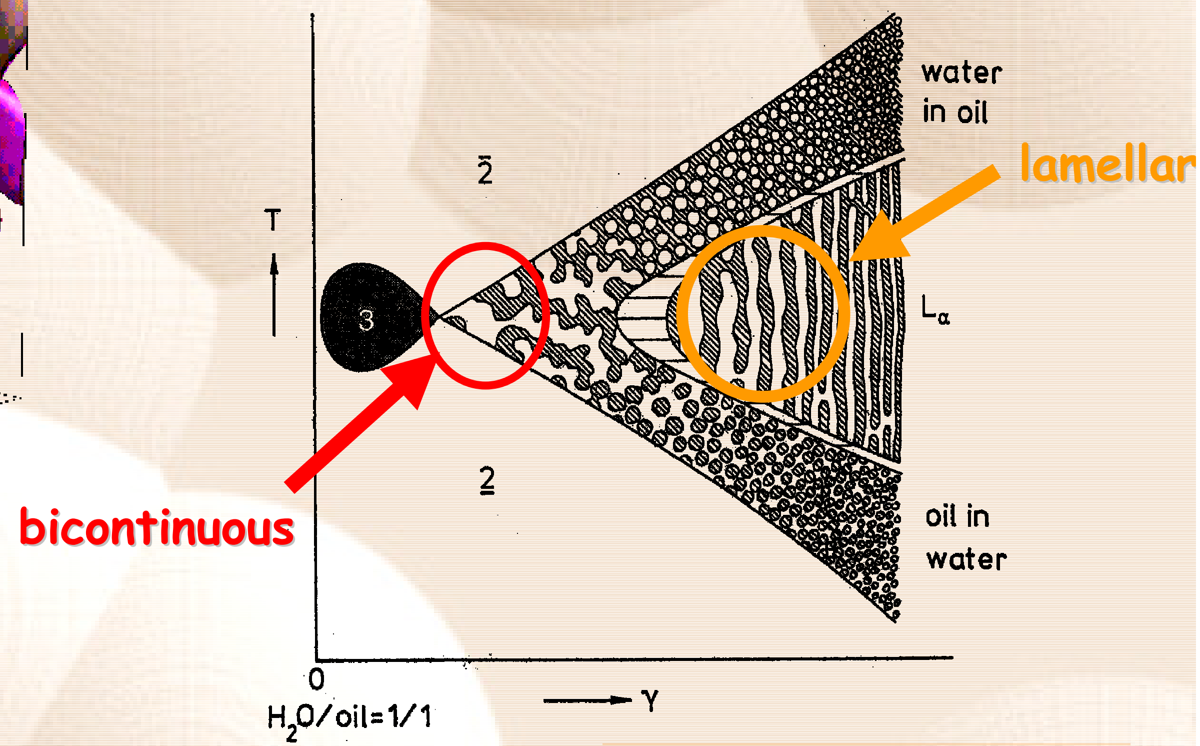


Microemulsions



with

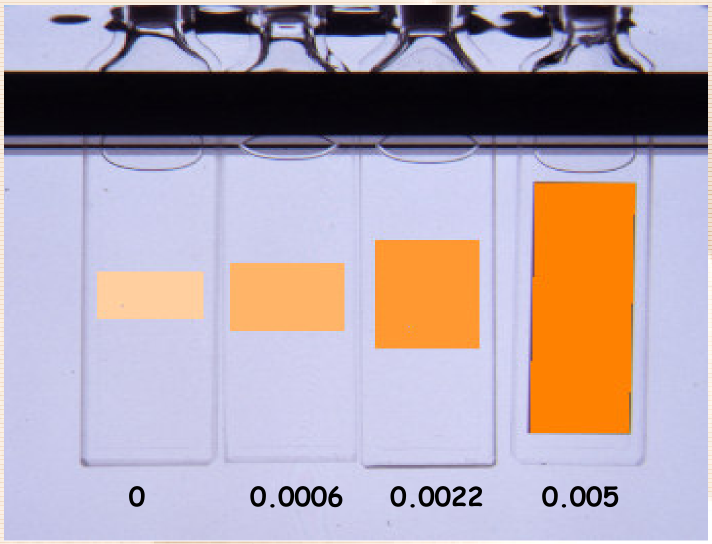
H. Endo	(Jülich)
M. Monkenbusch	(Jülich)
G. Gompper	(Jülich)
J. Allgaier	(Jülich)
R. Strey	(Köln)
T. Sottmann	(Köln)



← Structure length, d   Surfactant concentration →

Phase diagram: $\phi_{H20} = \phi_{oil}$

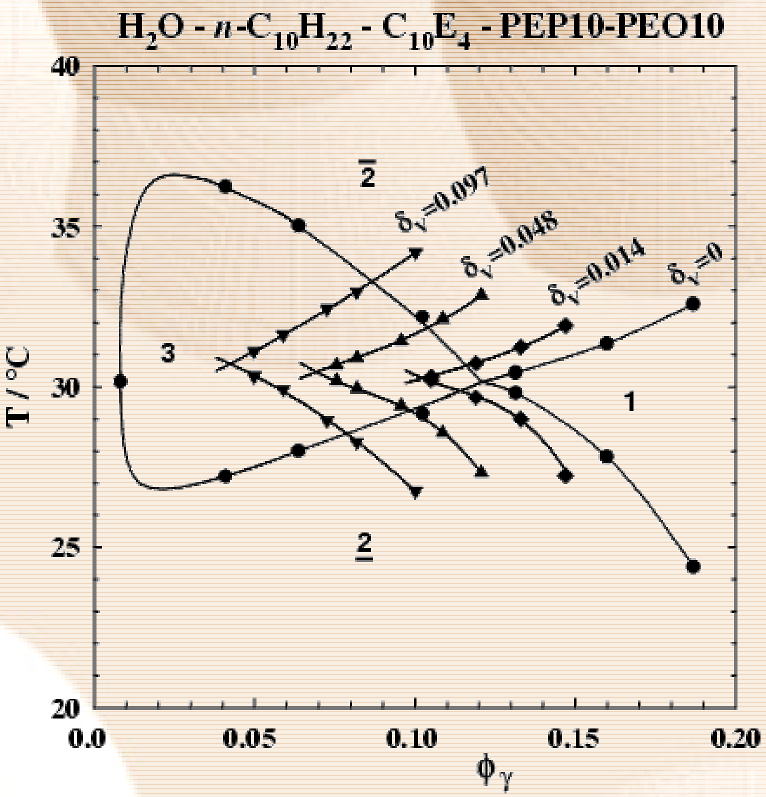
Observing Key Components



→ Polymer Fraction →

New Macromolecular Surfactant PEO-PEP

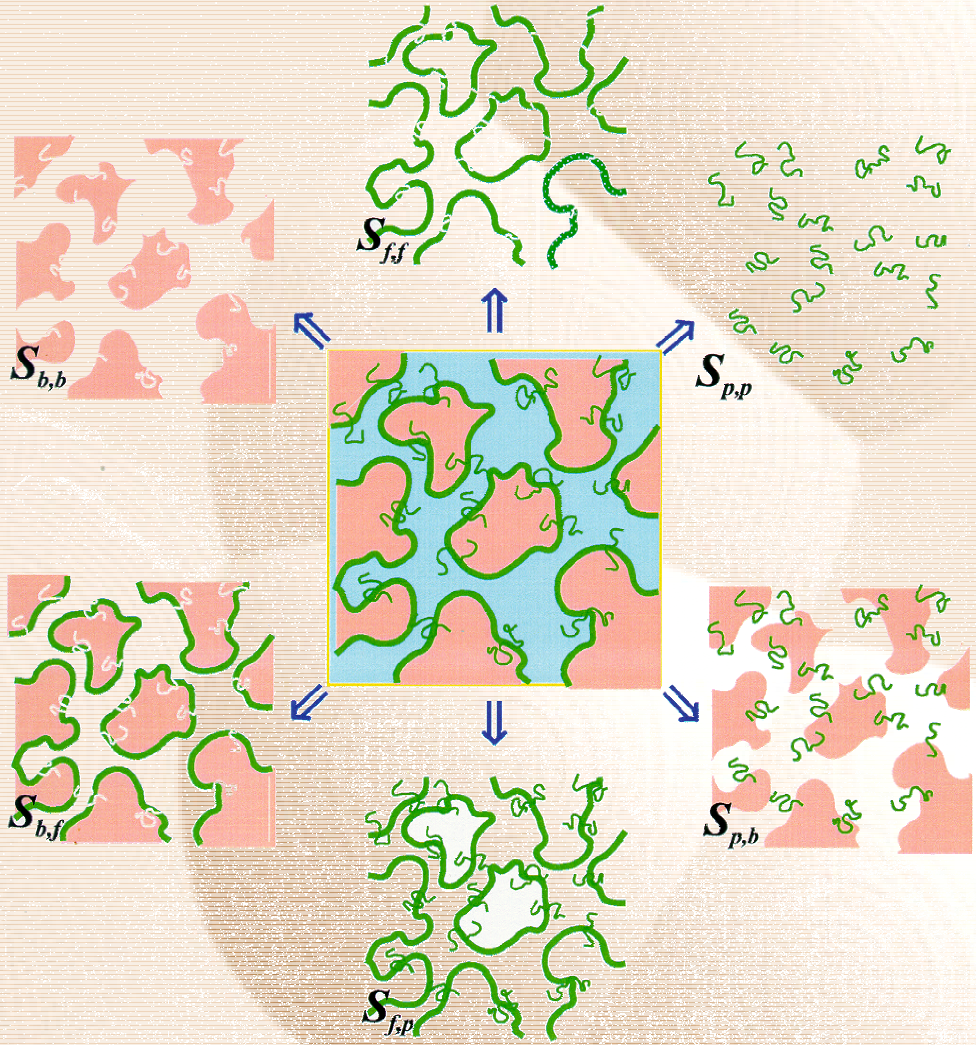
$(-CH_2-CH(CH_3)-CH_2-CH_2-)_n-O-(-CH_2-CH_2-O-)_m H$



Jakobs et al. Langmuir 15, 6707 (1999)

Emulsification boosting

Inherently Small Cross Sections



Vastly different

Cross sections

2-d contrast variation

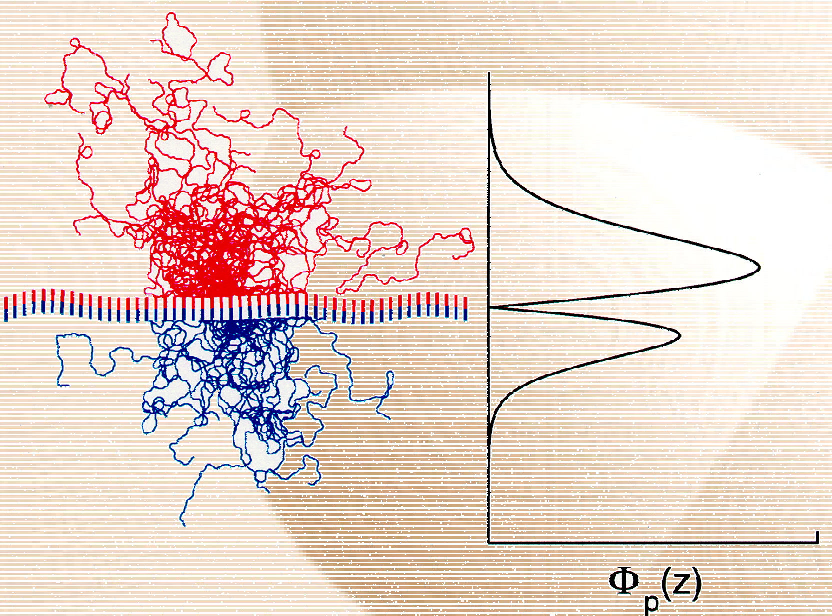
Observation of key components in multicomponent systems

Observing Key Components

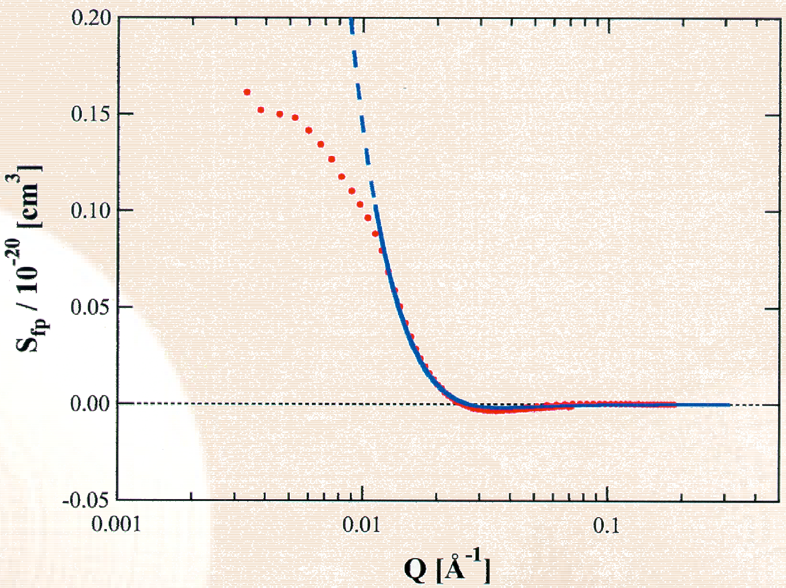
S_{pf}: polymer- film interference

- Polymer scattering amplitude

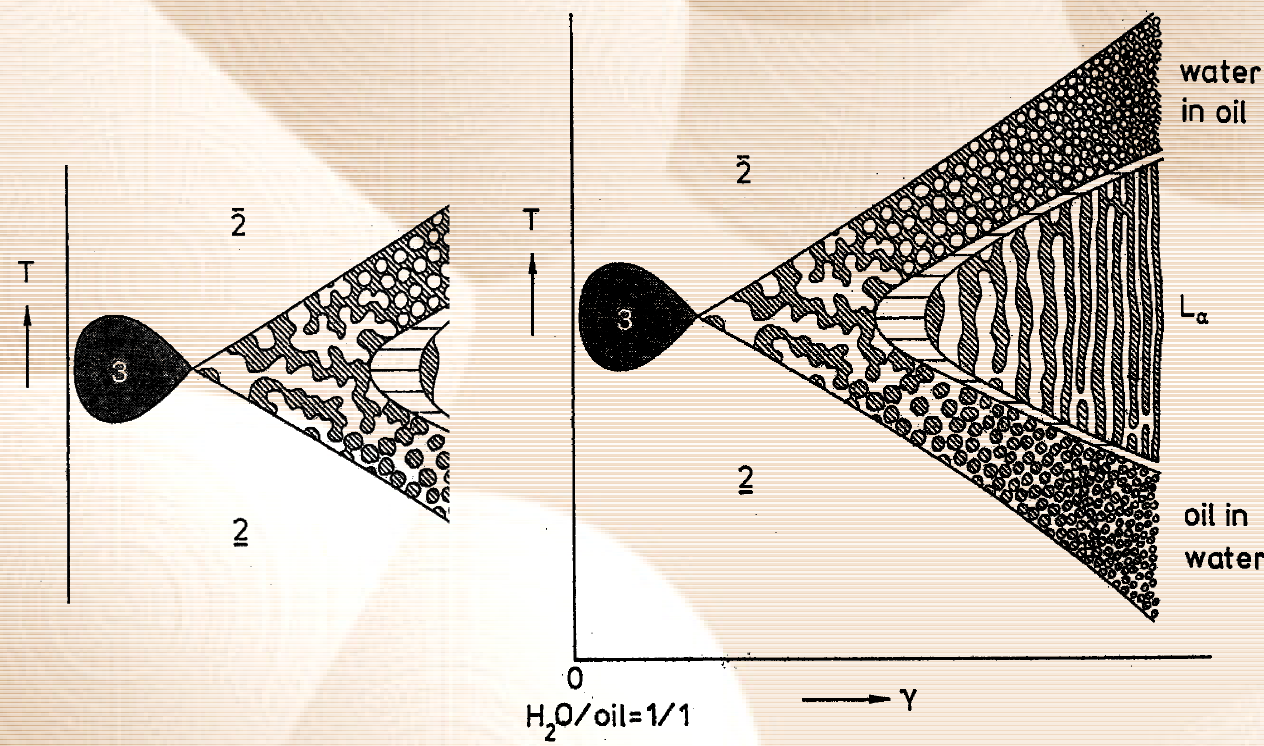
polymer mushroom



polymer film scattering

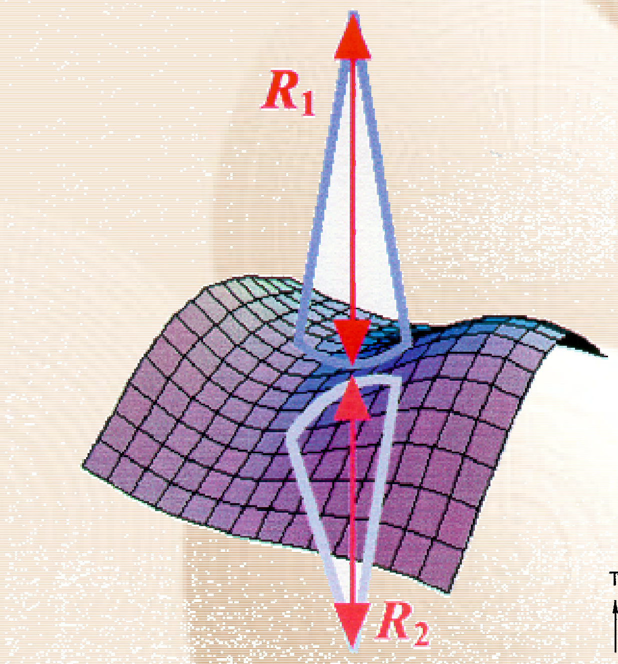


Polymer density distribution at interface


T
3
2̄
2
water
in oil
L_α
oil in
water
0
H_2O/oil=1/1
Y

Theoretical Implications

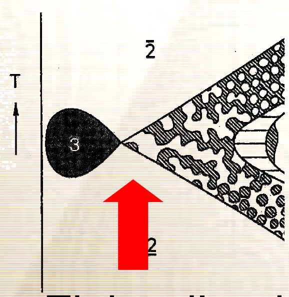
$c_i = 1/R_i$



curvature energy (Helfrich)

$$H = \int ds \left[\frac{\kappa}{2} \left(C_1 + C_2 - 2C_0 \right)^2 + \bar{\kappa}\, C_1\, C_2 \right]$$

$\bar{\kappa}$ **:determines phase boundary**

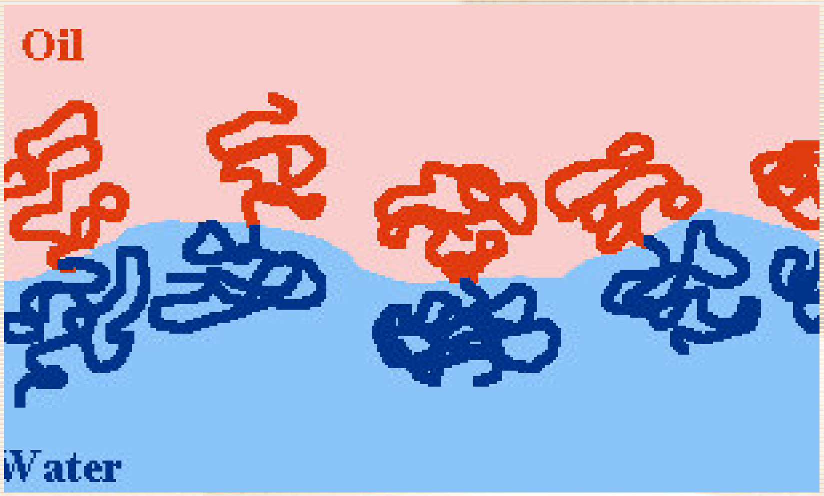


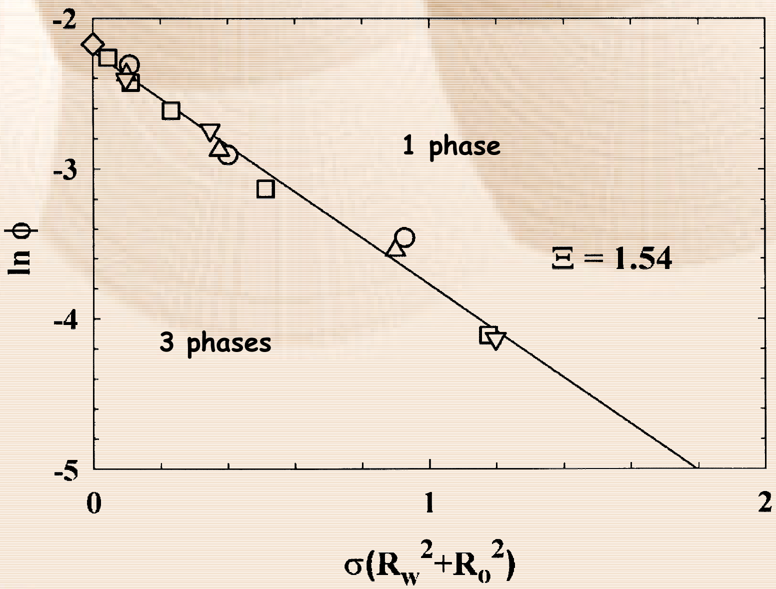
Fish tail point

$$\ln \phi_{fish-tail} = \frac{4\pi\, \bar{\kappa}}{\bar{\alpha}\, k_B T} \qquad \bar{\alpha} = \frac{10}{3}$$

Microemulsions: governed by surface elasticity

Explanation: Polymer Changes Membrane Elasticity





$$\kappa_{eff} = \kappa + \frac{k_B T}{12}\left(1 + \frac{\pi}{2}\right) \sigma \left(R_\omega^2 + R_o^2\right)$$

$$\bar{\kappa}_{eff} = \bar{\kappa} - \frac{k_B T}{6} \sigma \left(R_\omega^2 + R_o^2\right)$$

$$\ell n\, \phi_{fish-tail} = \ell n\, \phi_0 - \Xi\, \sigma \left(R_w^2 + R_0^2\right)$$

Influence on emulsification boundary is universal effect

Neutrons in Soft Matter Science

Molecular dynamics

Real time kinetic &
non equilibrium processes

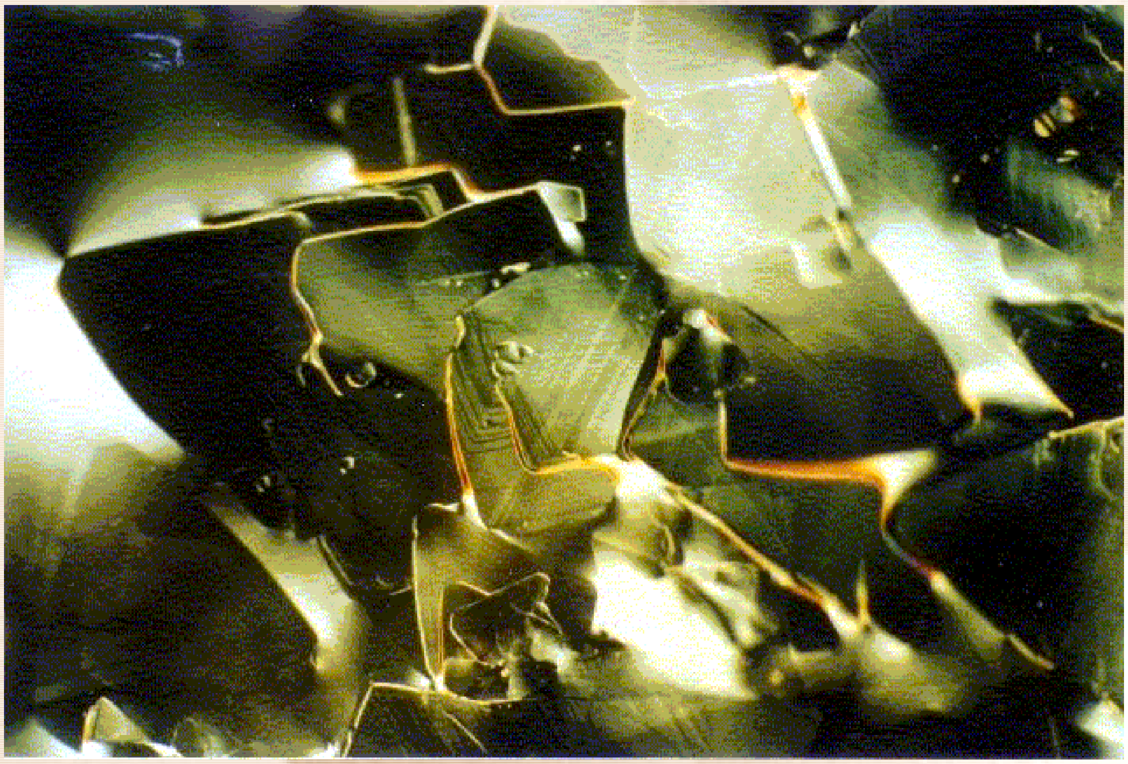
Soft Matter Challenges

Key components

Self-assembly

Wax Control by Self-Assembling Polymers - A Scientific Approach

Wax crystal in Diesel oil plug filters



with

L.J. Fetters	(Exxon)
J. Huang	(Exxon)
M. Monkenbusch	(Jülich)
L. Willner	(Jülich)

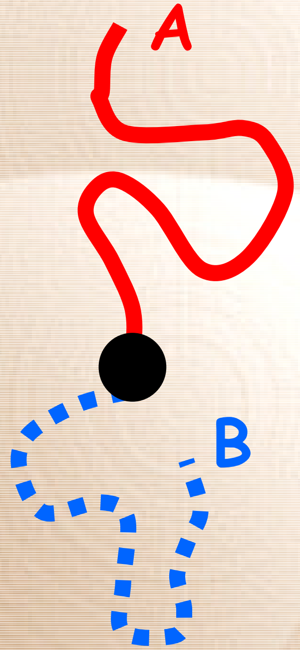
Neutron discover and tailor antifreeze for Diesel

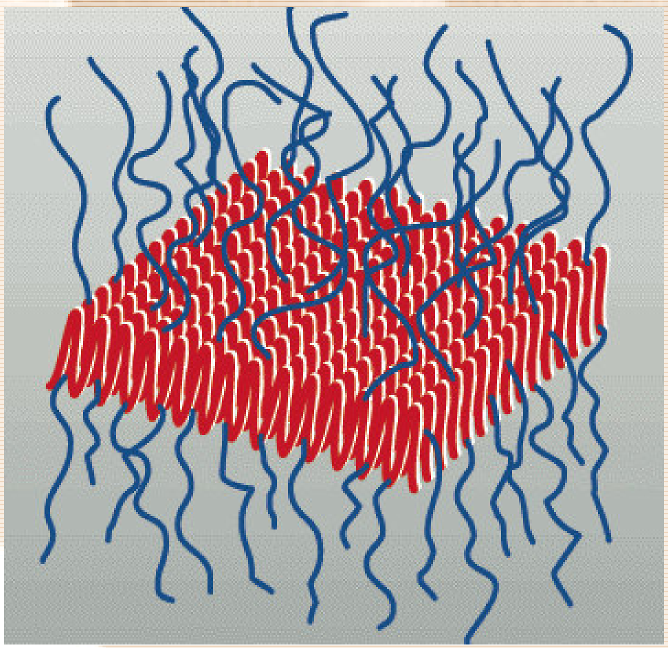
Wax Crystal Modification:
- A Scientific Approach

PE - PEP

PE - PEB

diblocks





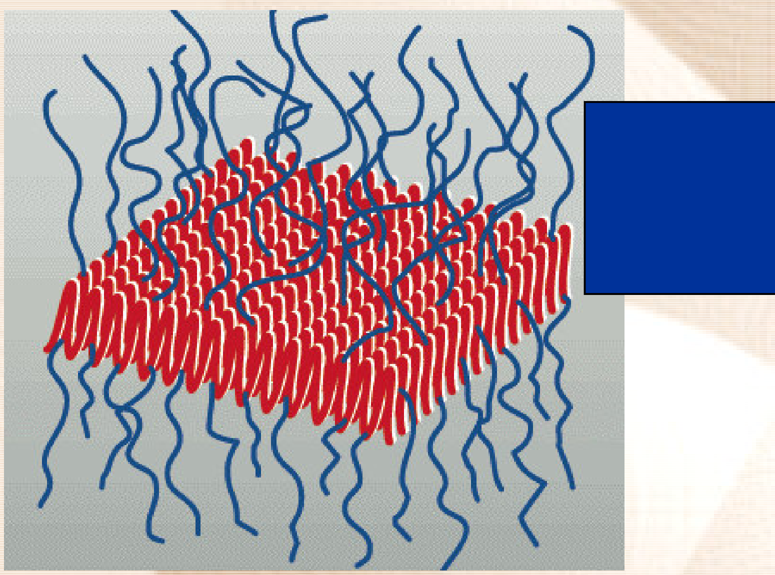
Richter et al., Macromolecules 30 (1997) 1053

Leube et al., Engergy&Fuel 14 (2000) 419

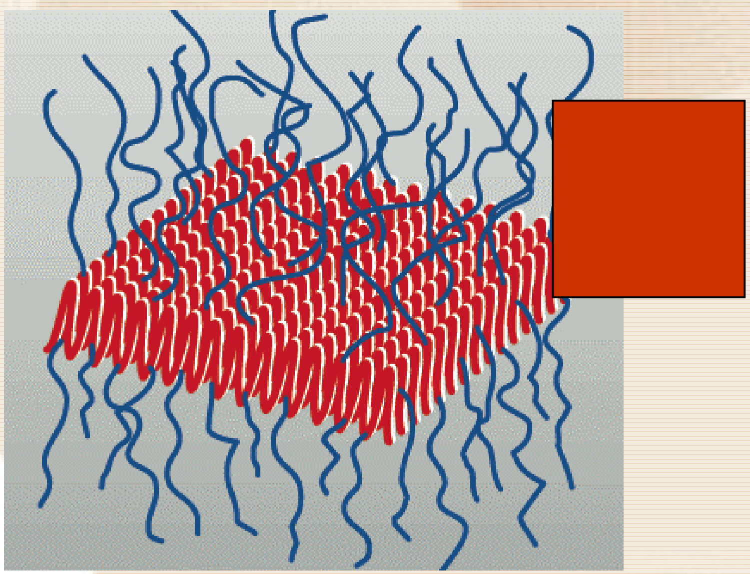
SANS deciphers structures with contrast variation

PE-PEP Diblocks as Wax Crystal Modifiers

Core Contrast

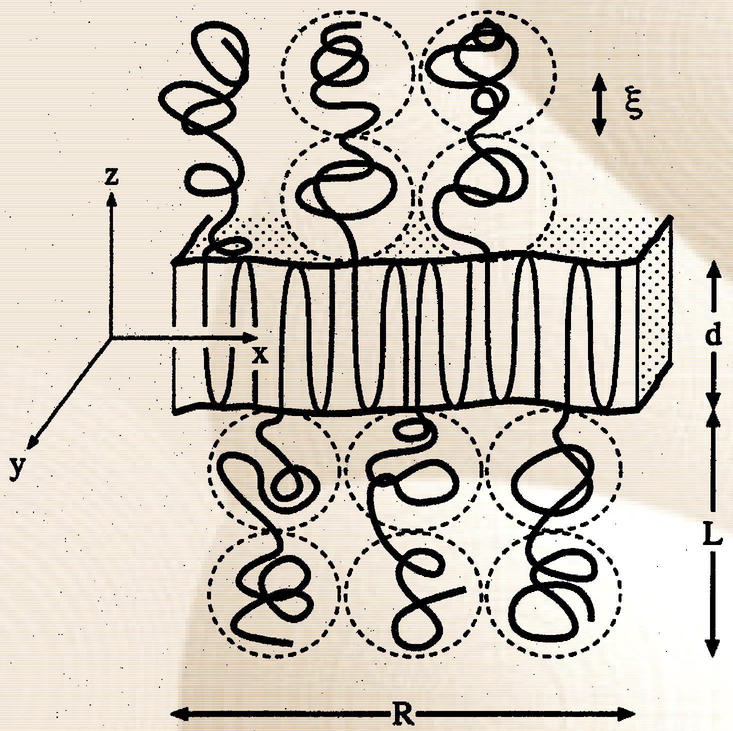


Brush Contrast



SANS deciphers structures with contrast variation

Thermodynamics of Platelet Formation



structural data for different compositions identify the contributions

Brush: loss of entropy due to chain stretching

Core: crystallisation enthalpy

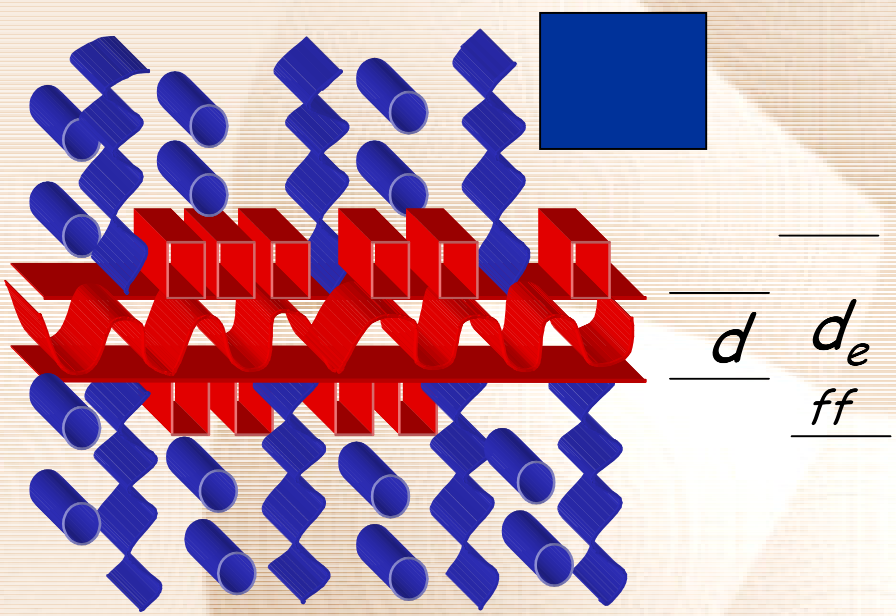
chain folding

ethylene side chains (defects)

Basis for predictions on size and surface

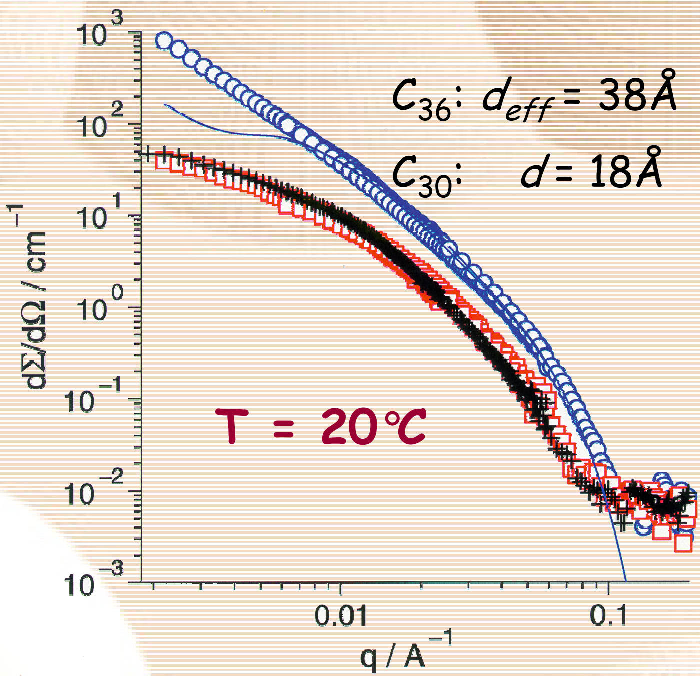
Interaction with Wax

contrast effective thickness change



acts as wax nucleator

results on $PE_{1.5}$ PEP_5 with C_{30}, C_{36}



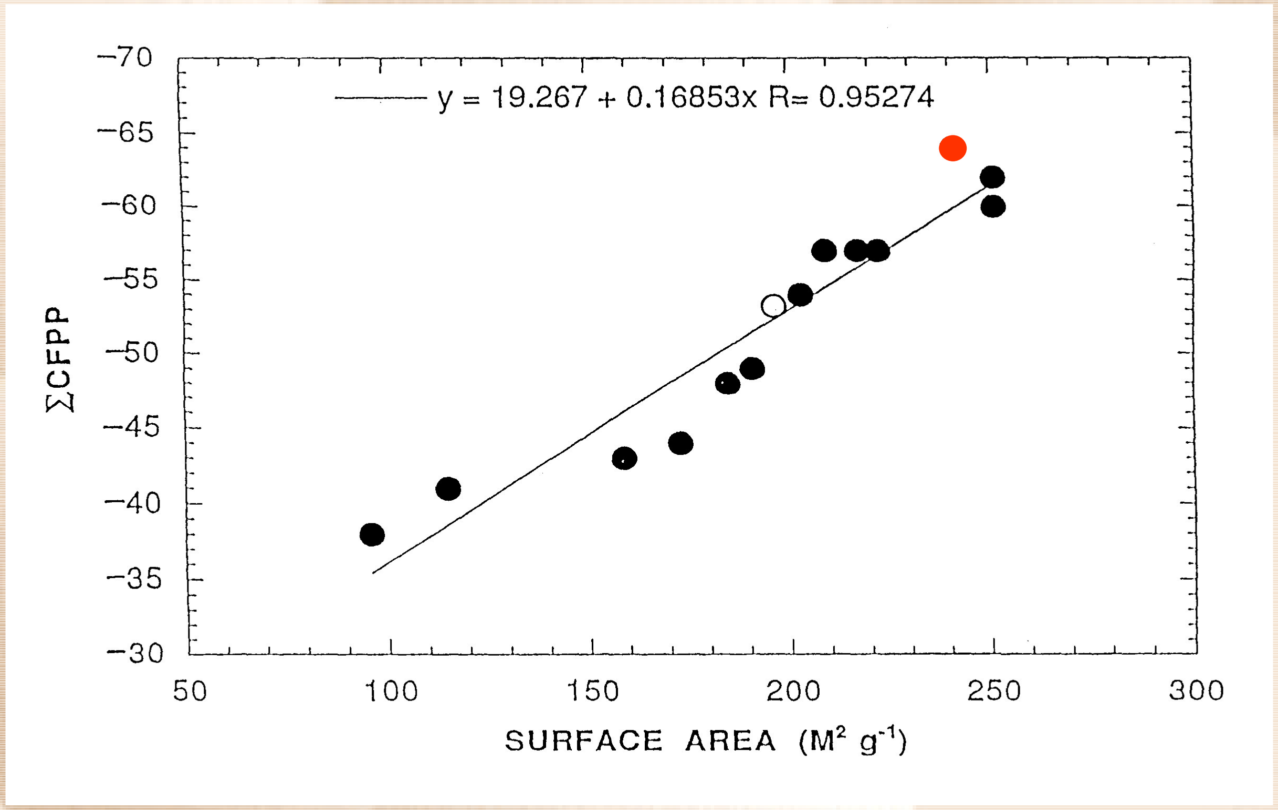
C_{36}: 83% aggregation

C_{30}: no aggregation

Wax and core visible – thickening of core

Correlations with ΣCFPP

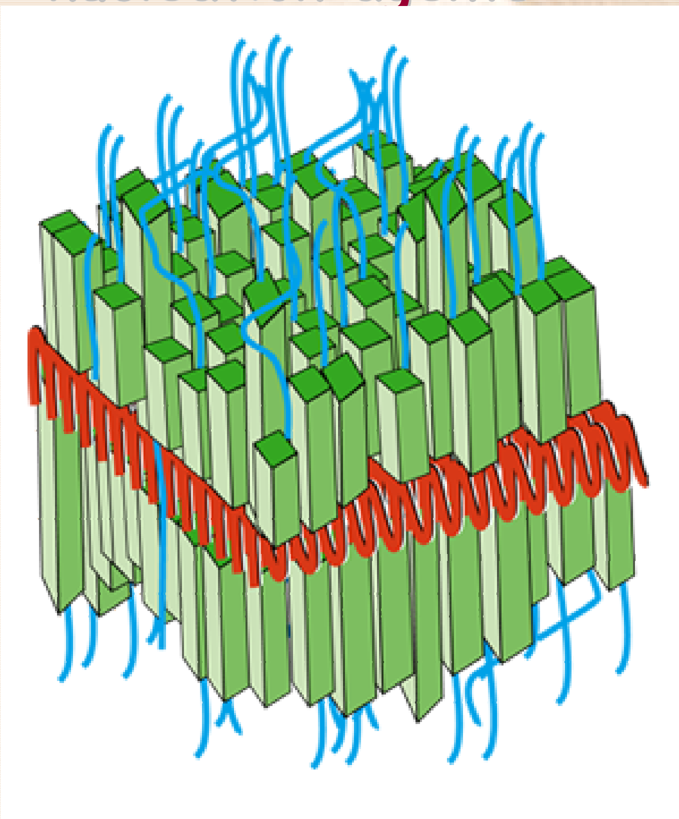
predictive power of SANS based free energy



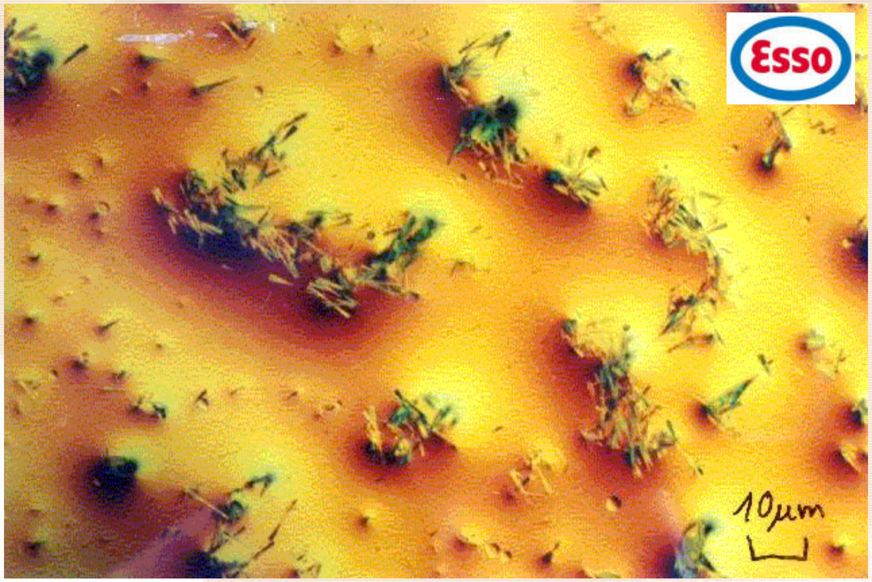
wax crystal supression by nucleation at PE surface

Antifreeze for Diesel

polymer aggregates
nucleation agents

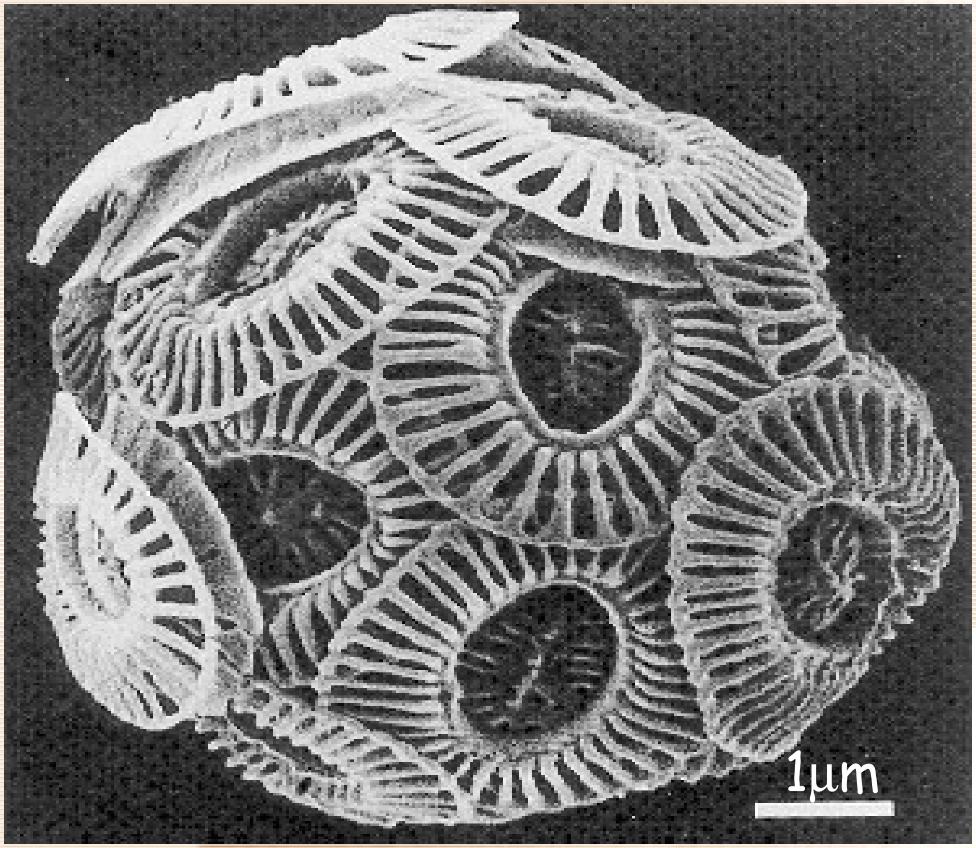


supression of
large crystals



4 years from discovery to commercialization

Selfassembly: Biomineralisation

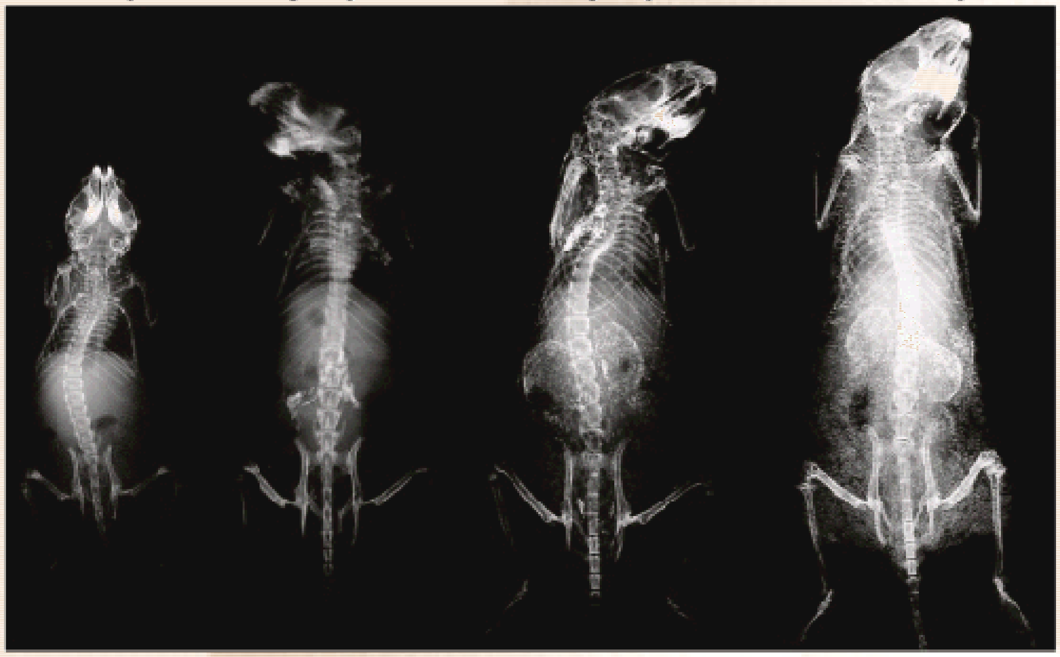


SEM of *Emiliana* Cocosphere

Biomineralisation

Nature tailors crystal growth (e.g. in bones and teeth) using associating polymers

Selfassembly: Biomineralisation



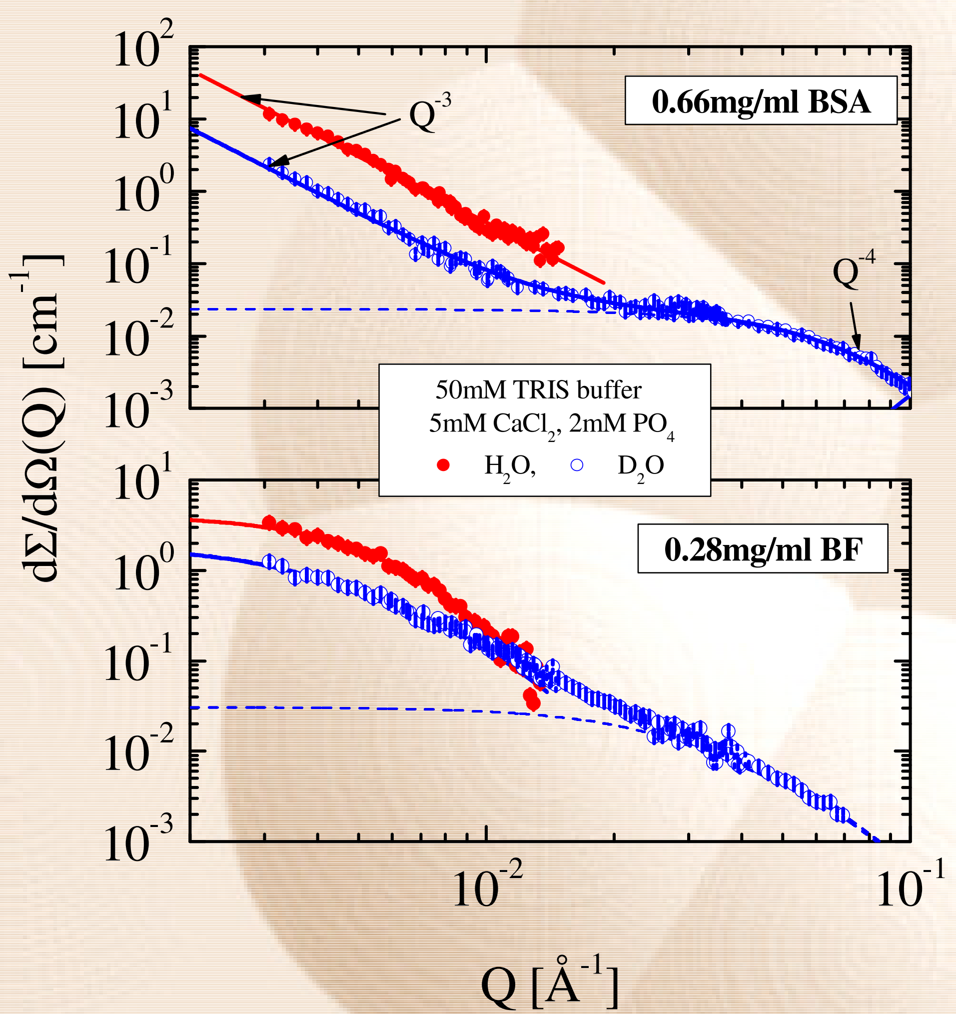
Problem

Patients with long term dialysis display down regulated fetuin expression leading to calcification of soft tissue

D. Schwahn, H. Endo (FZ Jülich) and
H. Heiß, Jahnen-Dechant (RWTH Aachen)

Calcification of fetuin deficient mouse

Precipitation Mechanism



Albumin

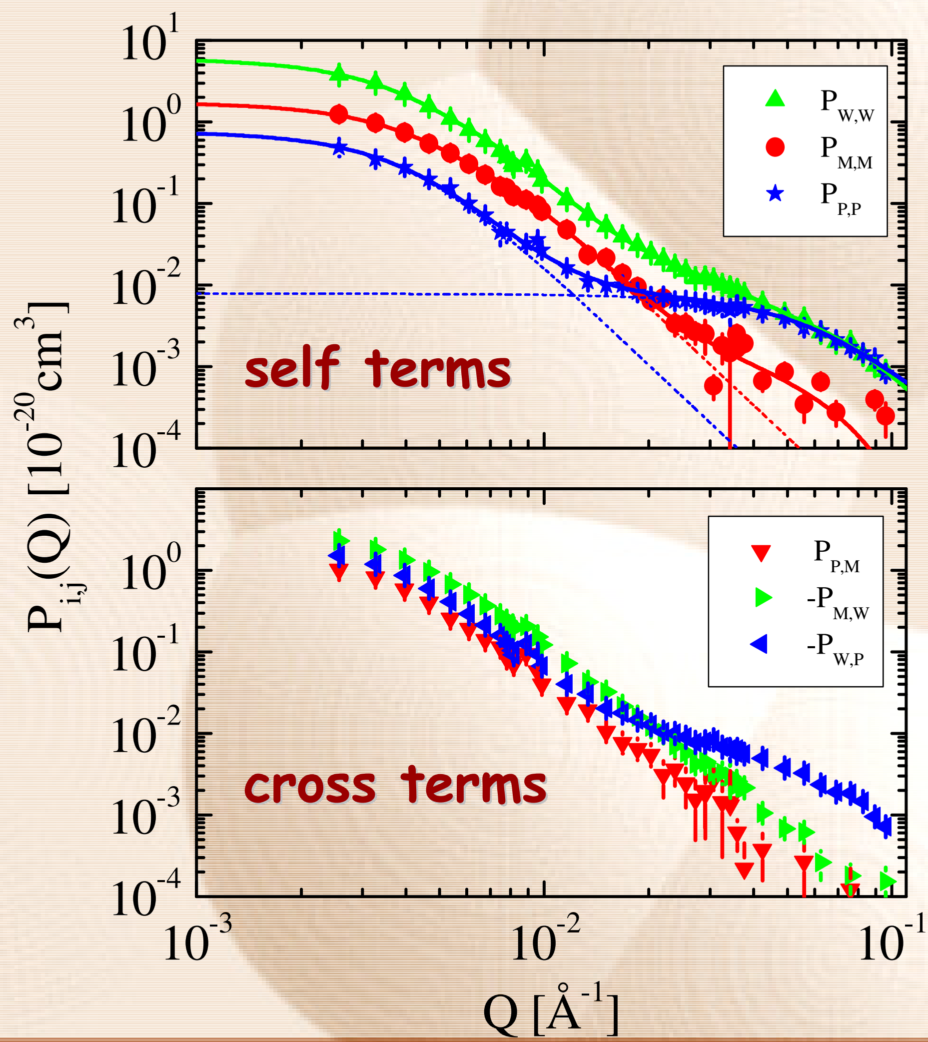
- Large μm sized minerals
- Q^{-3} → porous structure

Fetuin

- Stable 100nm particles

SANS experiments

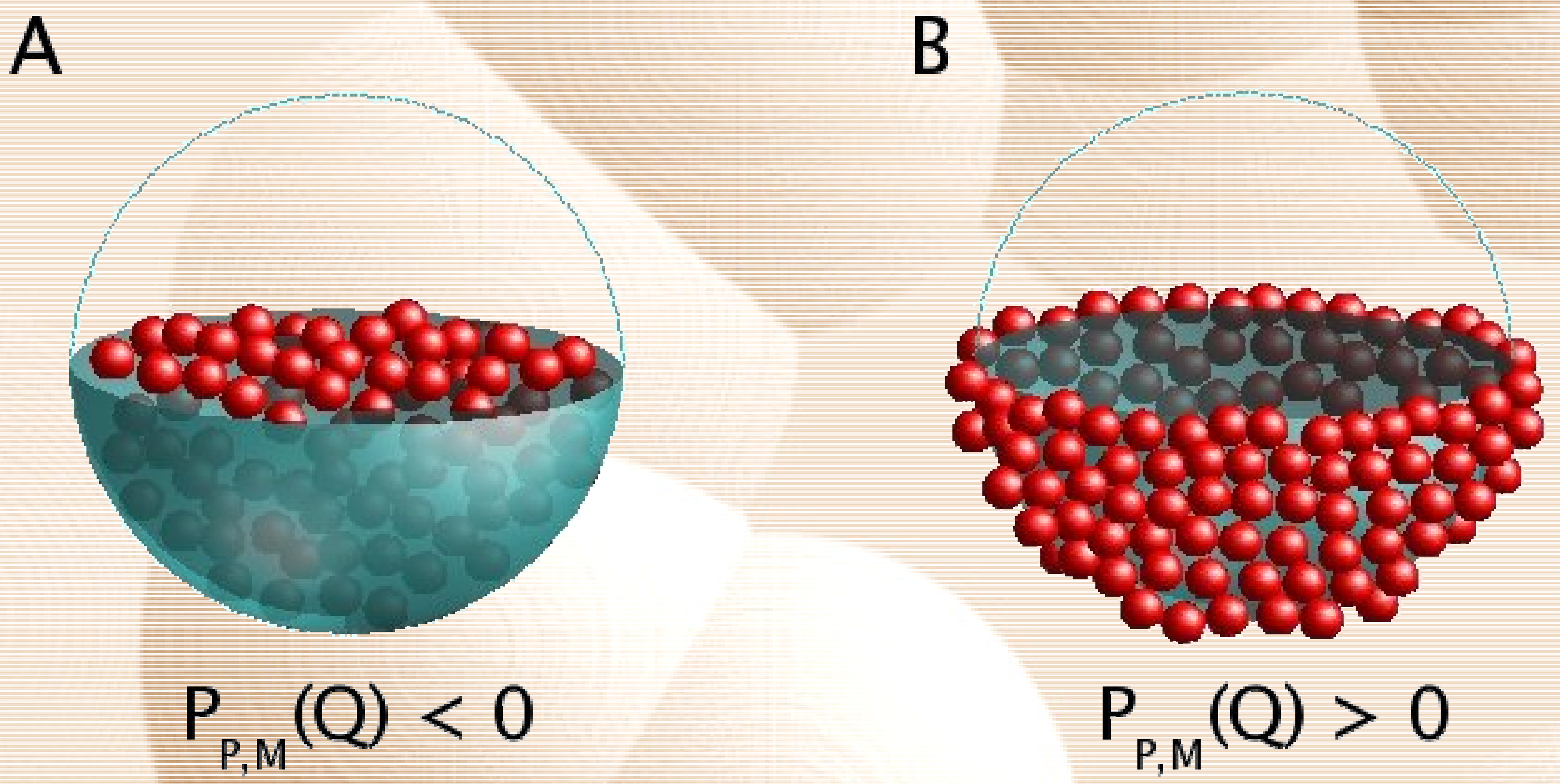
Partial Structure Factors from Contrast Variation



- Bimodal protein distribution in solution
  - free proteins
  - proteins associated with mineral

positive P_{PM} at higher Q
→ protein outside mineral

Association Mechanism



in the Porod regime

Dense layer of proteins at the surface

Soft Condensed Matter

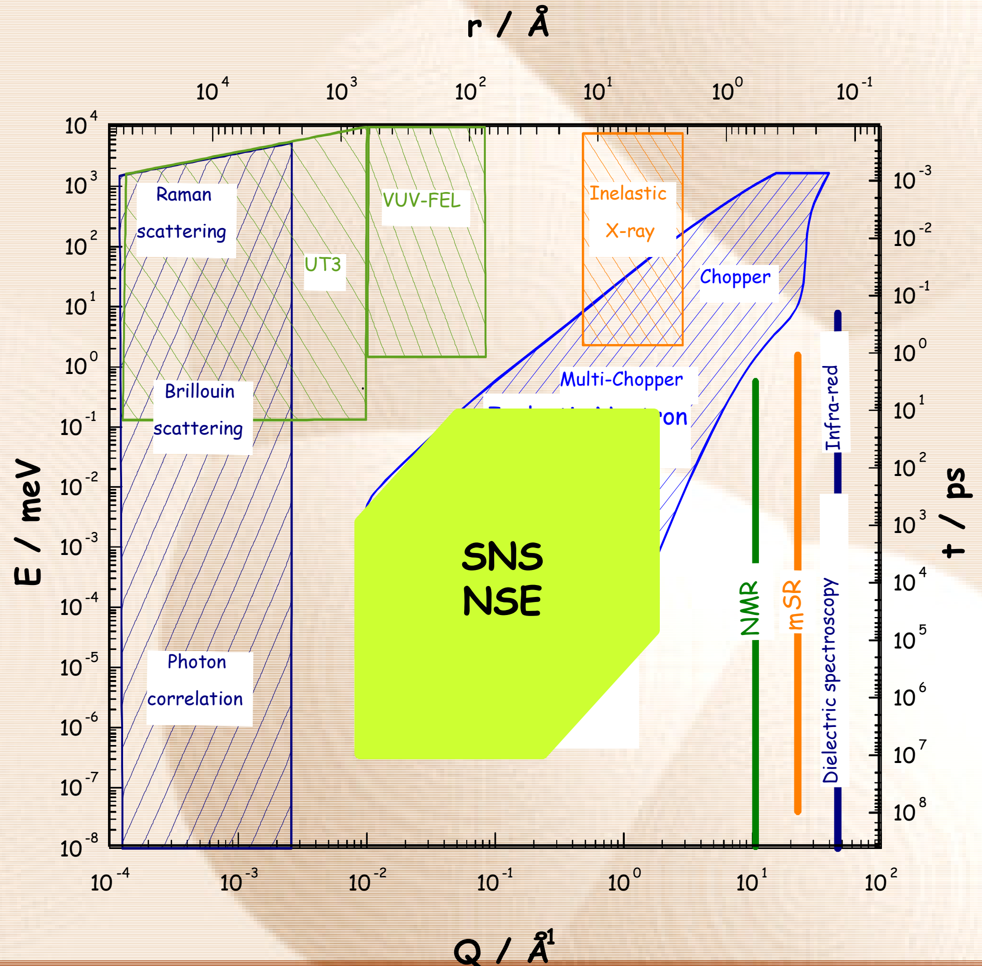
broad + rich field with close links to application and likely biology

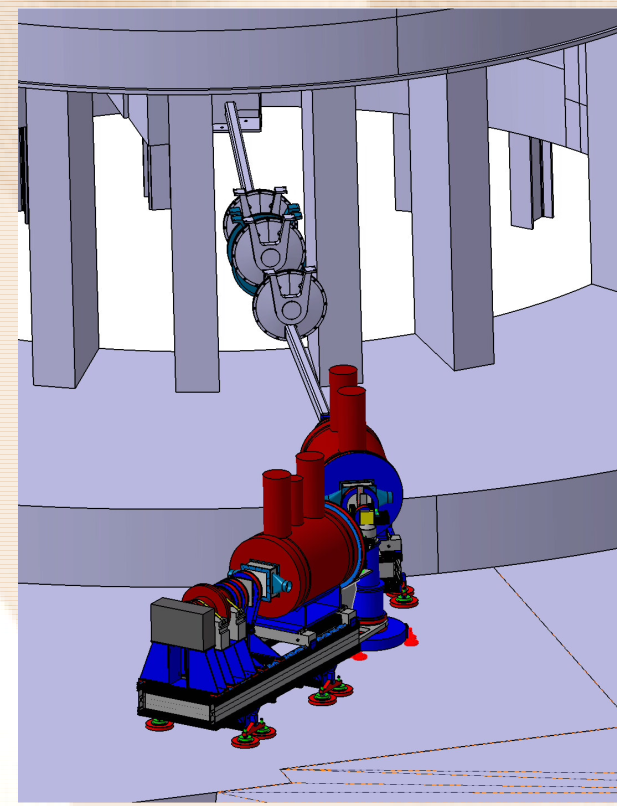
Neutrons:
- proper length + time scales
- H/D contrast

Decisive role in combination with
- advanced chemistry
- computer simulations and modellisation

Soft Matter Dynamics: The Future

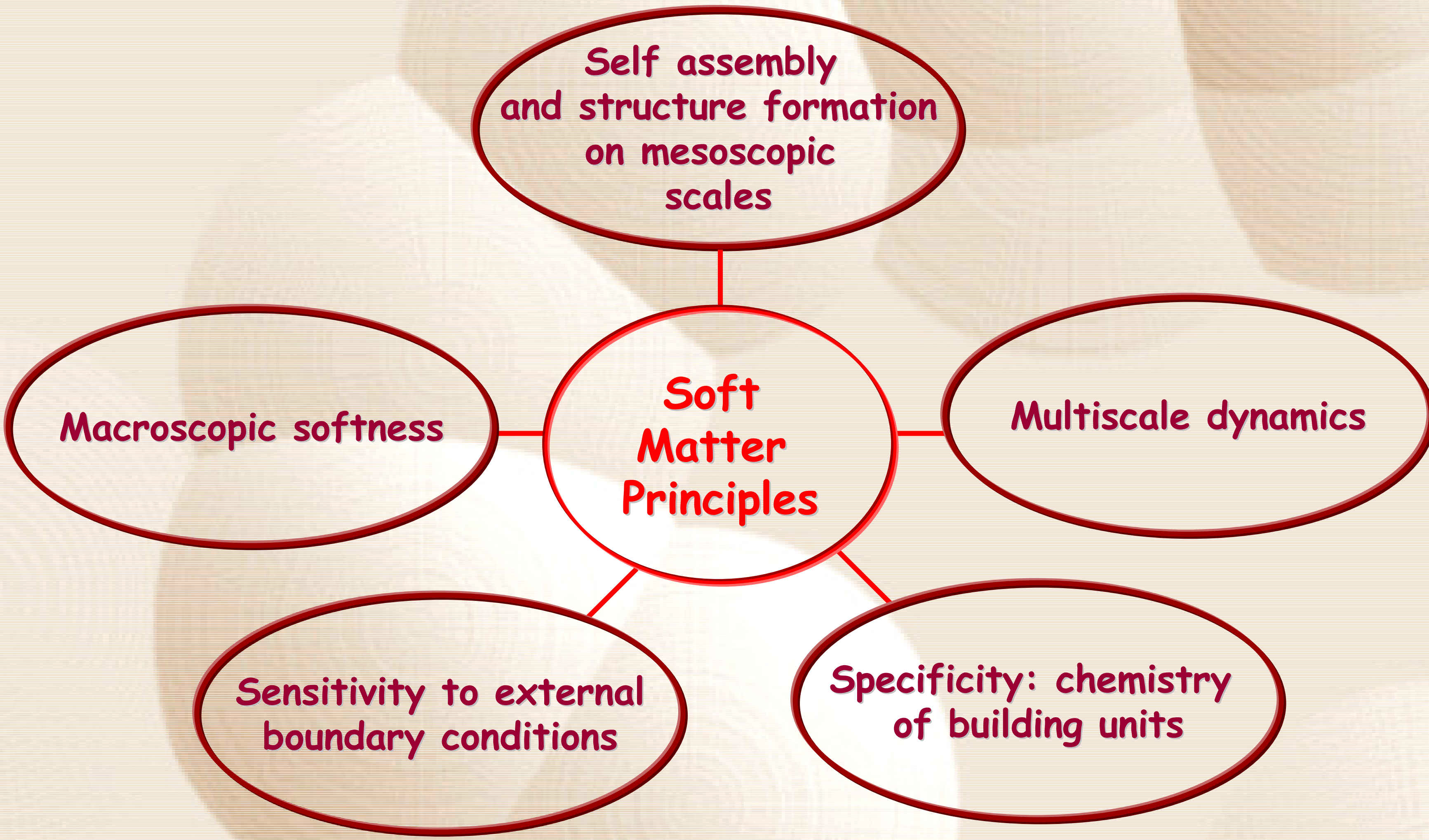
NSE at SNS: From ps to µs





Best in resolution and dynamic range

What is Soft Condensed Matter?



Interplay between specific and universal