Polymer Dynamics: From Synthetic Polymers to Proteins

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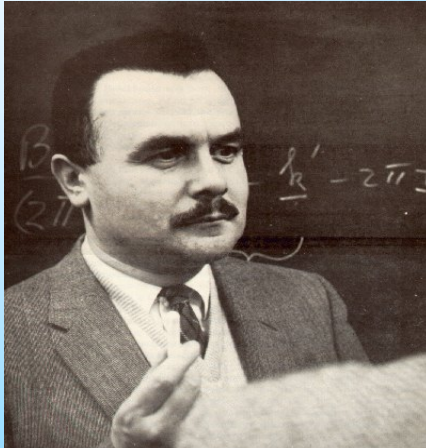
Collaborators

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M. Monkenbusch,
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A.   Wischnewski,
M. Zamponi

R. Merkel,
B. Hoffmann
Institut für Bio- und Nanosysteme

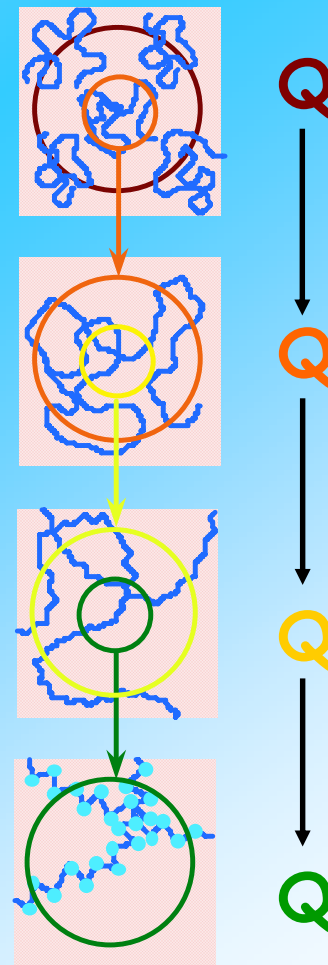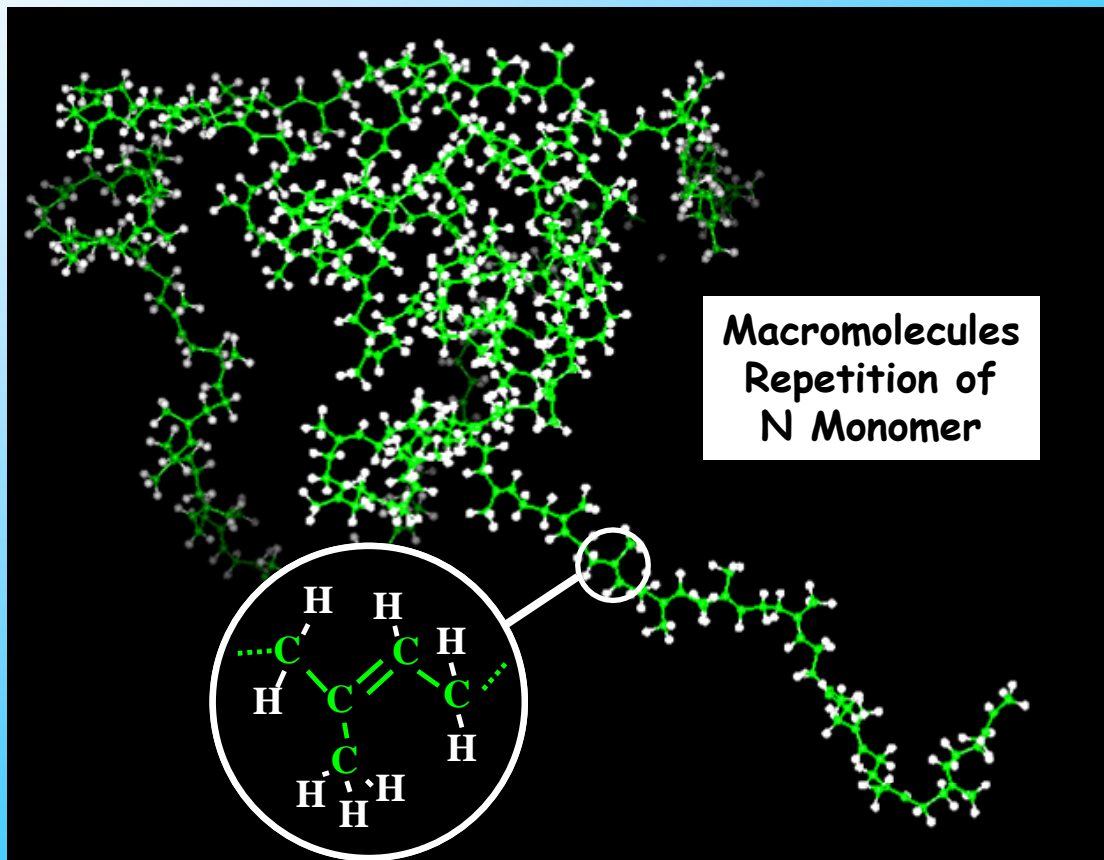B. Farago
Institute Laue Langevin Grenoble, France

B. Brockhouse
Chalk River
Canada

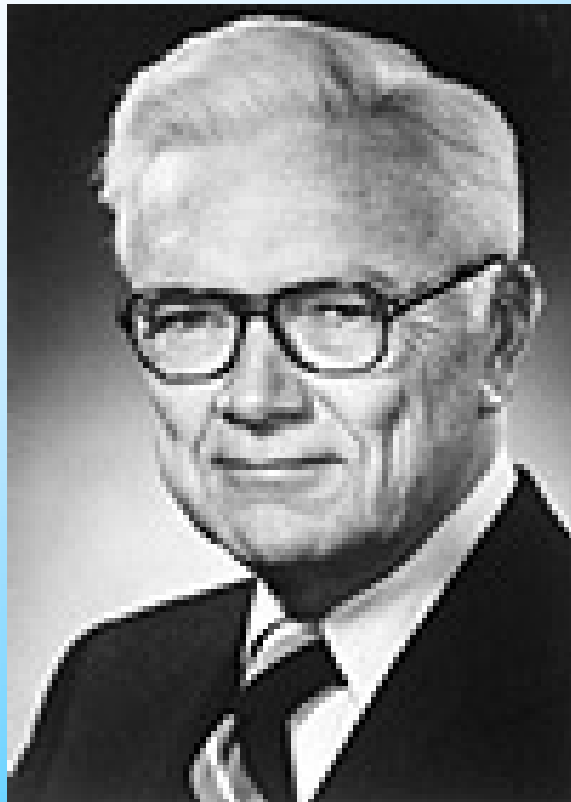Nobel prize 1994

C. Shull
Oak Ridge
USA

Neutrons tell where the atoms are and how they move

Macromolecules
Repetition of
N Monomer

Q

Q

Q

Q

Neutrons access molecular length and time scales

Only neutrons enable isotropic contrasting

Polymer Chain Conformation

Jülich 1972

P.J. Flory
Stanford
USA

Nobel prize 1974

intensity vs scattering angle
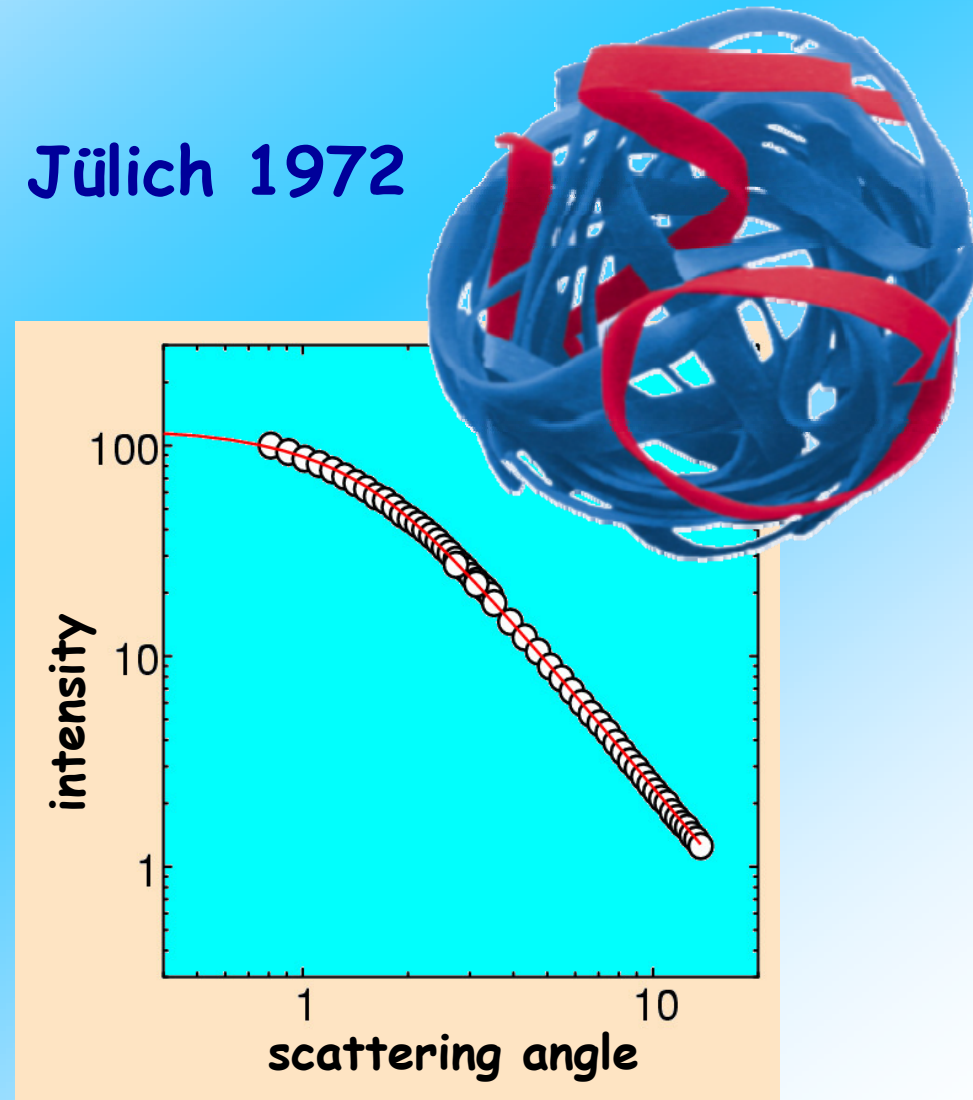
Early triumph of neutron scattering

Dynamic Structure Factor

Pair Correlations

Self Correlation

$\tau=0$ (Debye–Fktn.)

$\tau = 0.005$
$\tau = 0.010$
$\tau = 0.020$
$\tau = 0.040$
$\tau = 0.080$
$\tau = 0.160$
$\tau = 0.320$
$\tau = 0.640$
$\tau = 1.280$
$\tau = 2.560$

$\tau=\infty$ (Gauss–Fktn.)

$e^{(-D_{CM} Q^2 t)}$

$\langle r^2(t) \rangle$

$t = t'$

$t = 0$
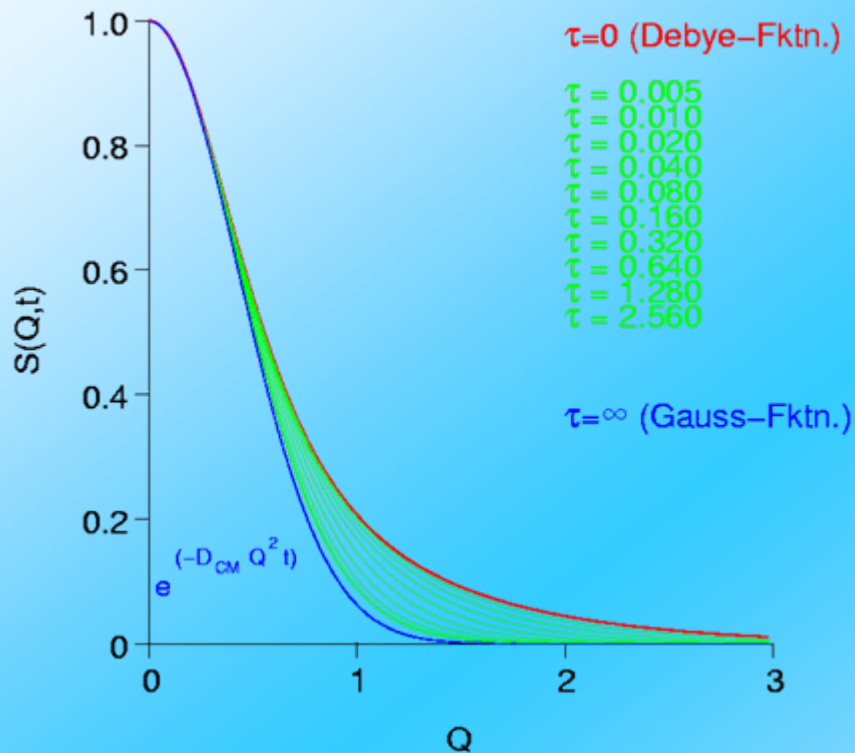
Collective Dynamics
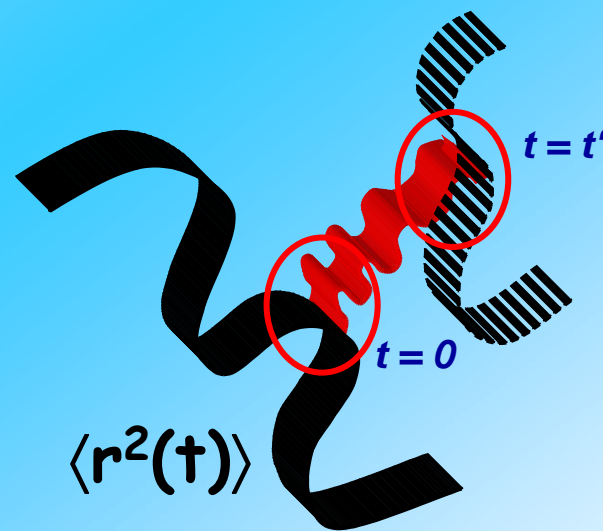
Self motion

Observation of polymer motion

Rouse Model

Gaussian chain entropic force
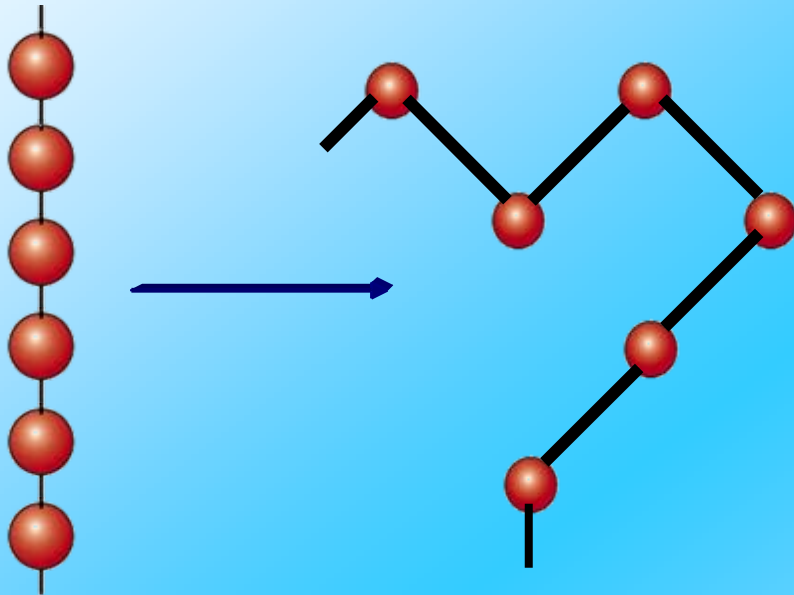
Monomeric friction entropic spring

$$\zeta v \qquad D_R \qquad \frac{3kT}{l}\Delta^2 x$$
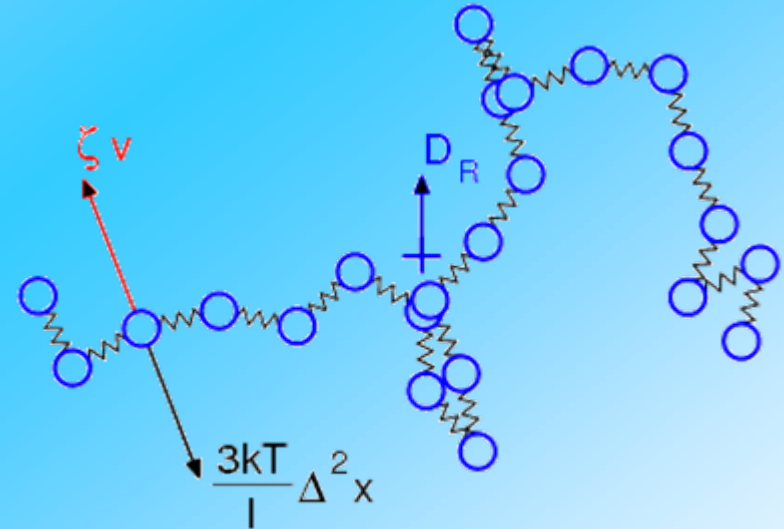
- Chain in a heat bath
- Thermally activated fluctuations
- Relaxation by viscous and entropic forces
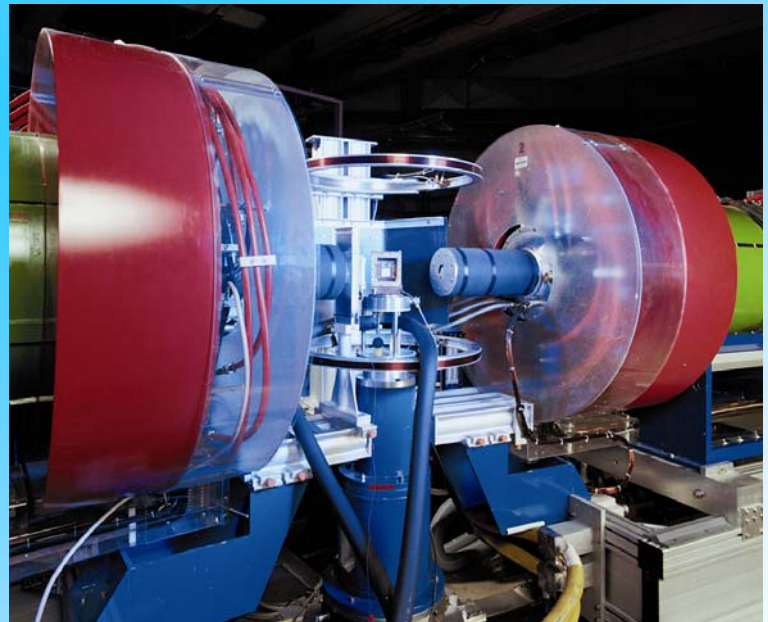- No explicit chain-chain interactions

Entropy Driven Dynamics: Rouse

Gaussian chain entropic force

Neutron Spin Echo

mean square segment displacement

$$S(Q,t) = \exp\left[-\frac{Q^2}{6}\left\langle r^2(t)\right\rangle\right]$$

$$\left\langle r^2(t)\right\rangle \approx t^{0.5}$$

Sublinear diffusion of chain segments
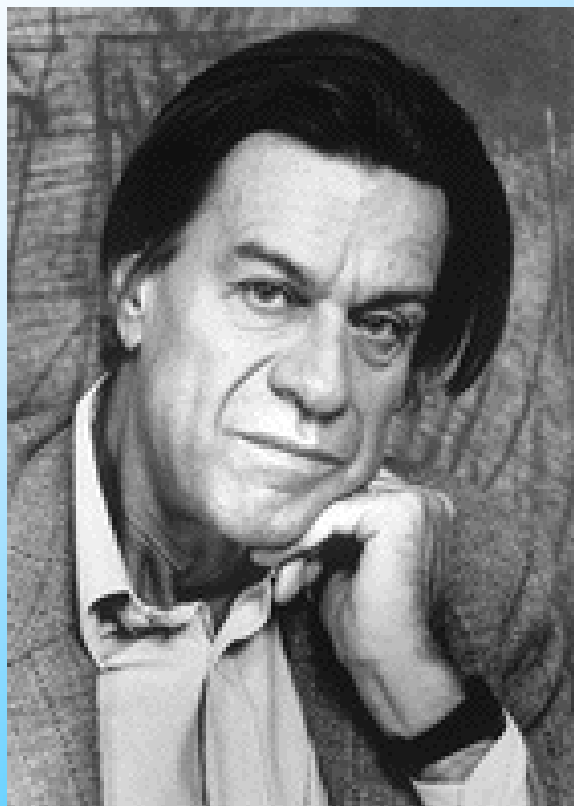
PEP $M_w = 80\ 000$ g/mol

$T = 492$ K

$t^{1/2}$

$620A^2 \rightarrow 25A$
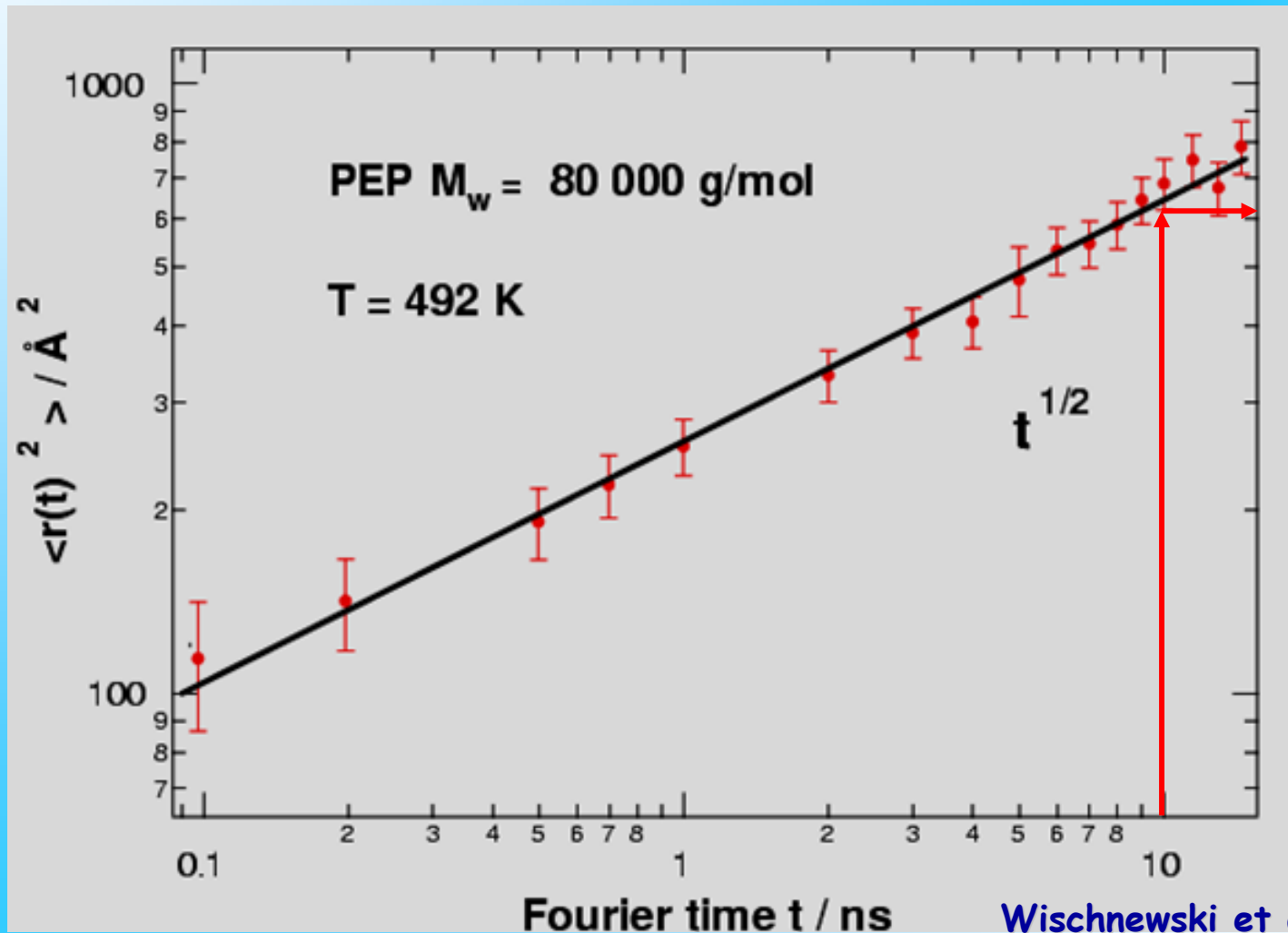
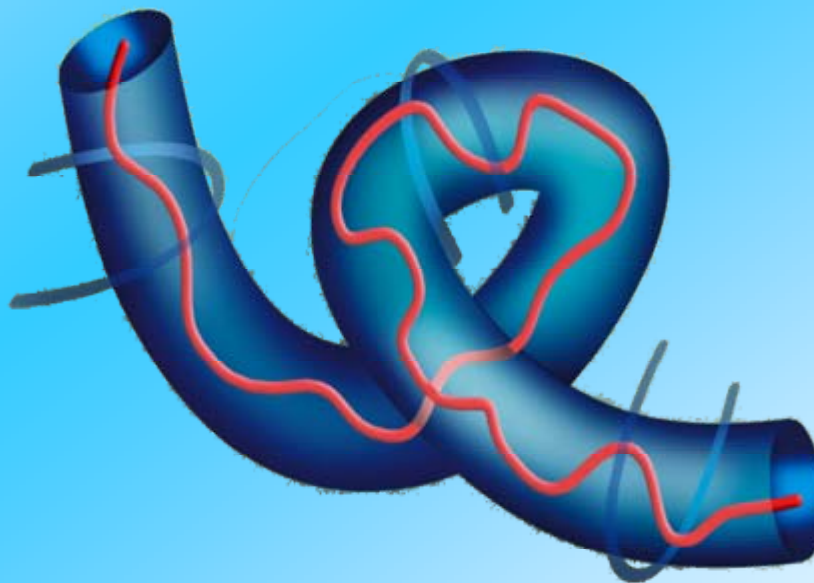Wischnewski et al., PRL 2003
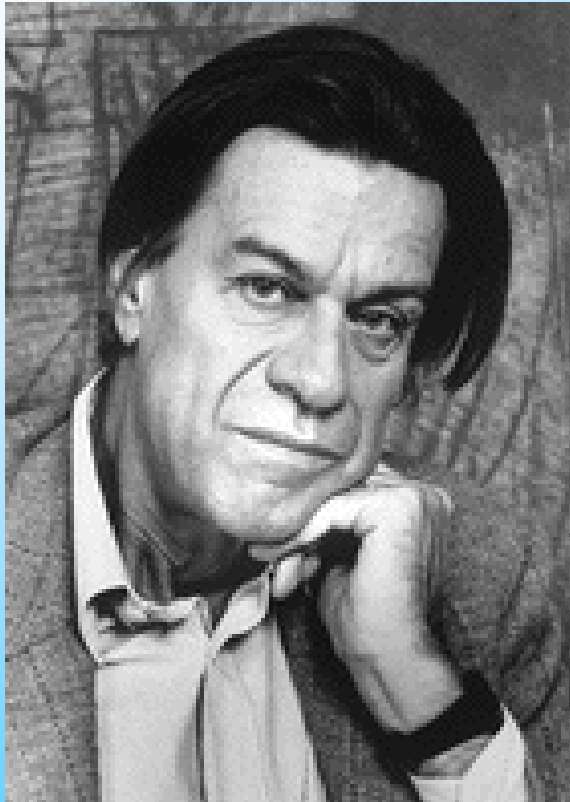
Rouse prediction verified

„entanglements"

P.G. De
Gennes
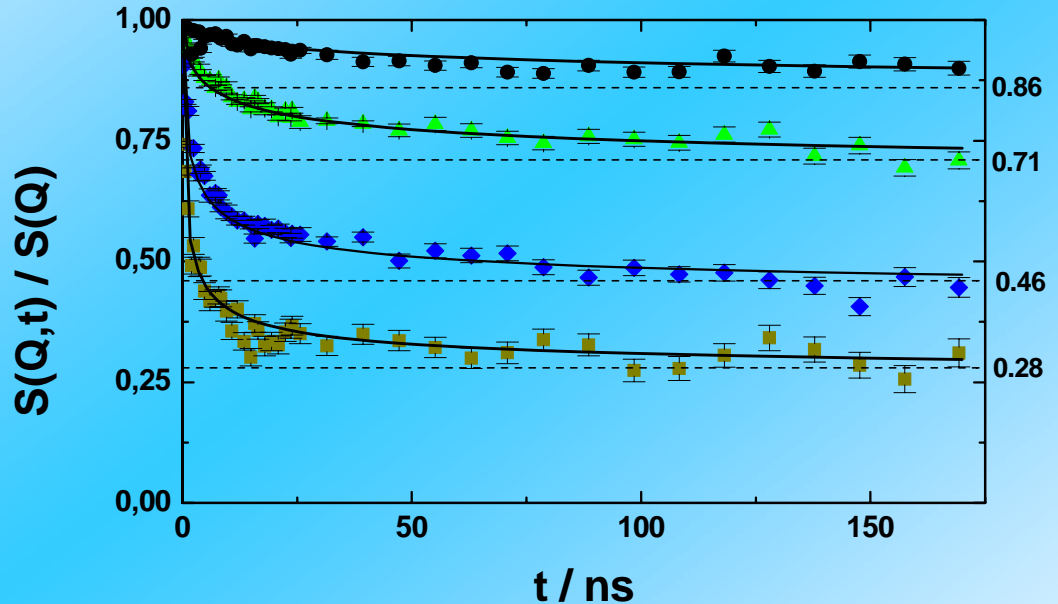ESPCI Paris
France

Nobel prize 1991

Subject of intense current research
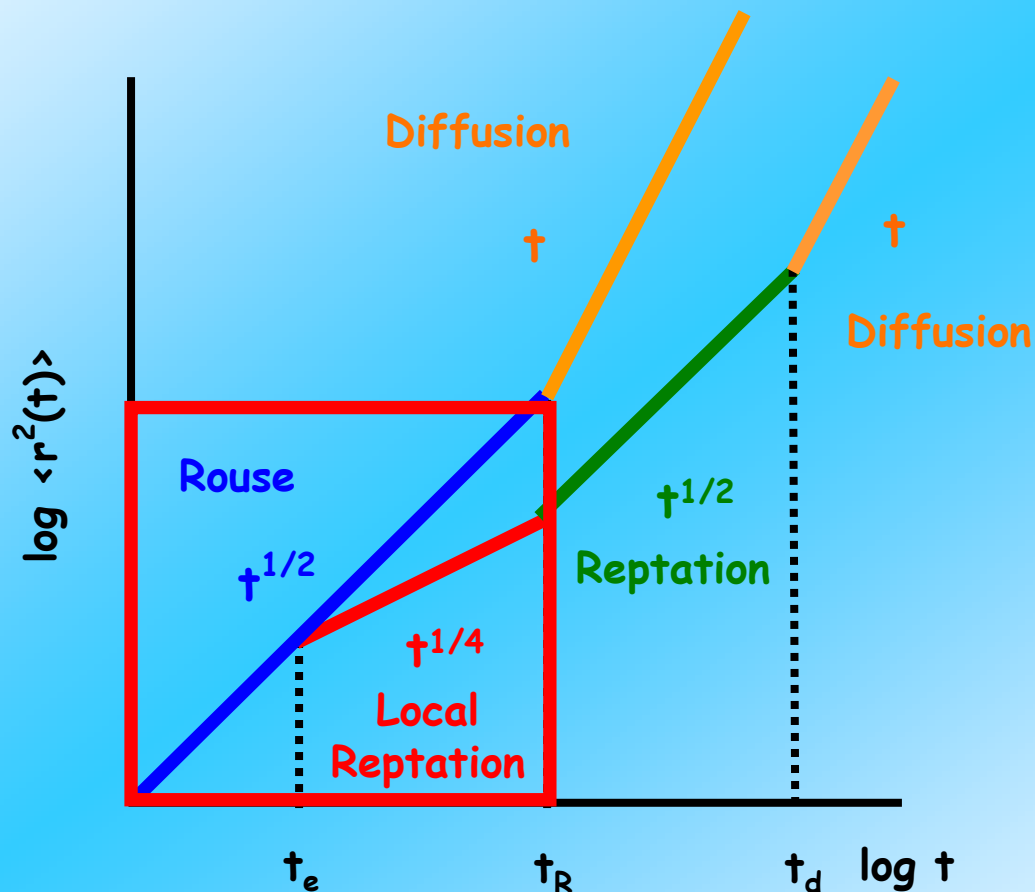
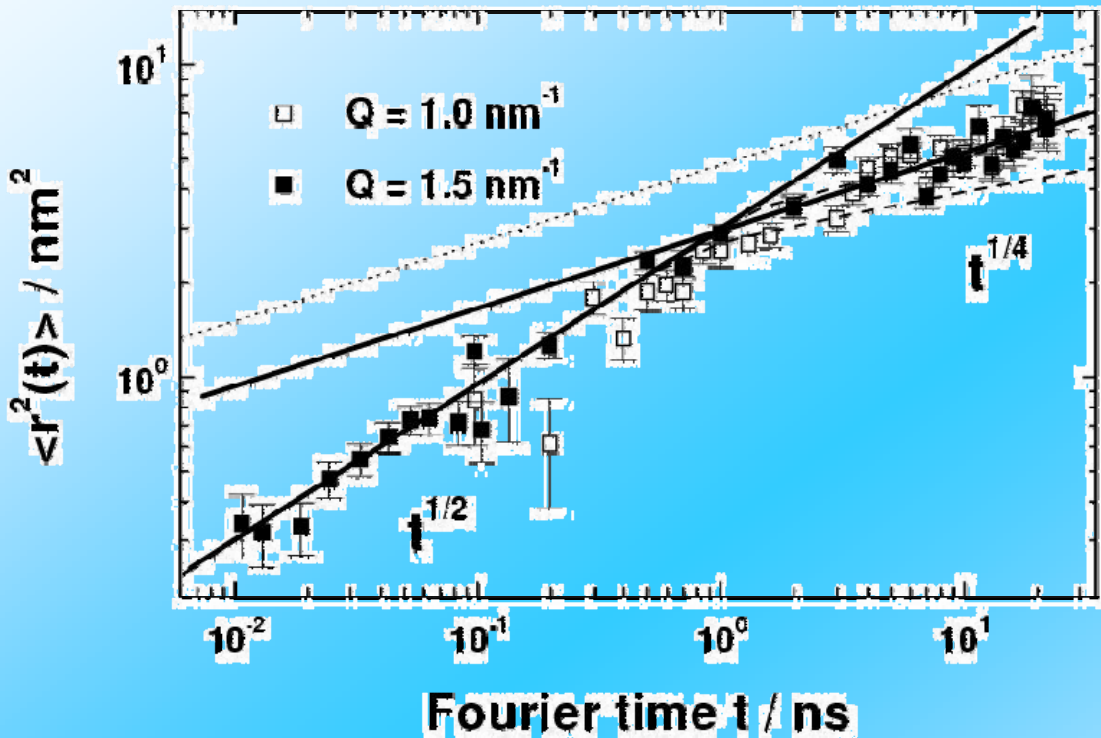**P.G. De Gennes ESPCI Paris France**

Nobel prize 1991

$$\frac{S(q,t)}{S(q)} = \left[1 - \exp\left(-\frac{q^2 d^2}{36}\right)\right] S^{\text{loc}} + \exp\left(-\frac{q^2 d^2}{36}\right) S^{\text{esc}}$$

plateau: $\exp\left(-\dfrac{d^2 Q^2}{36}\right)$

Coherent scattering: form factor of the tube

Mean squared displacement

Reptation
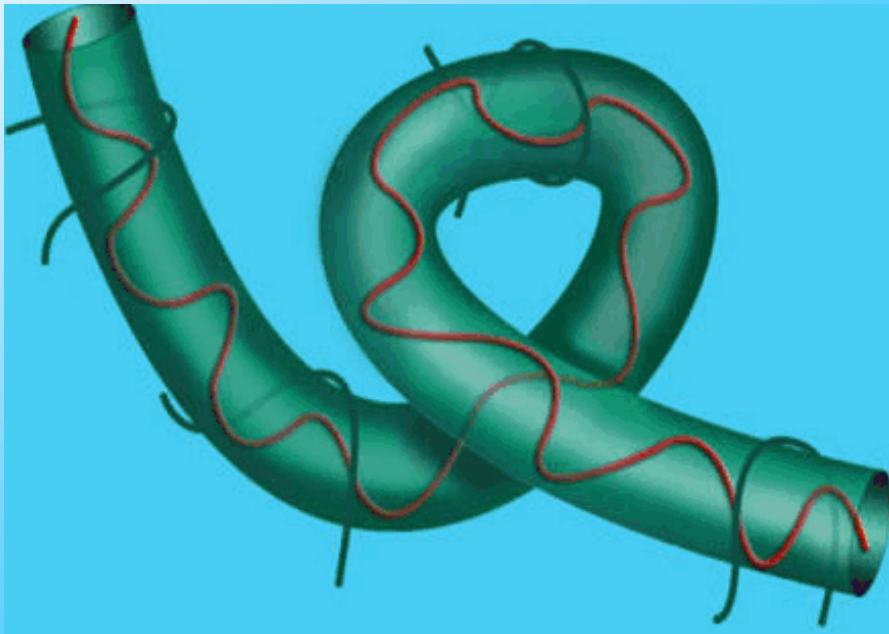## - Mean Squared Displacement

Consistent quantitative description of self and pair correlation functions in terms of reptation
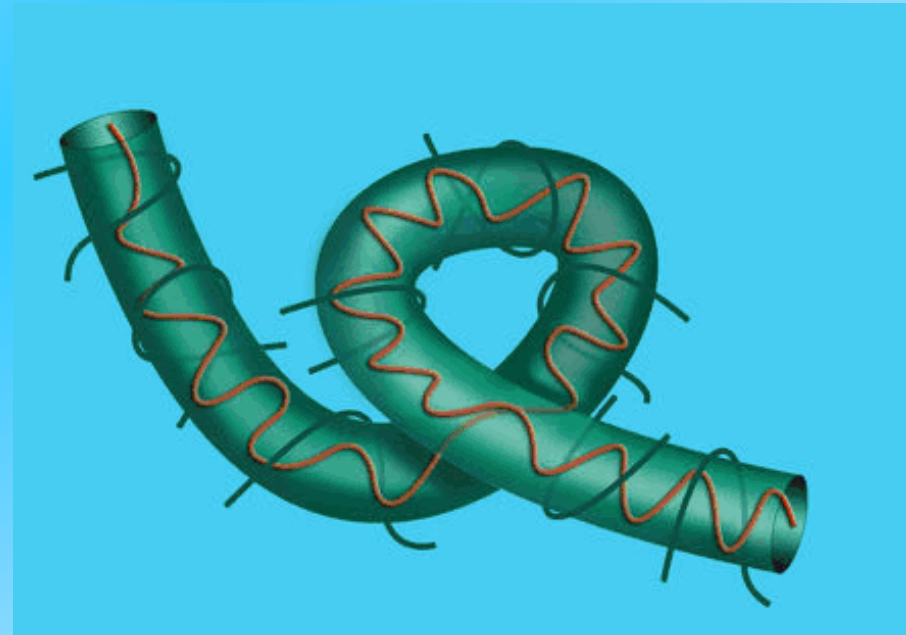
Wischnewski et al., PRL 2003

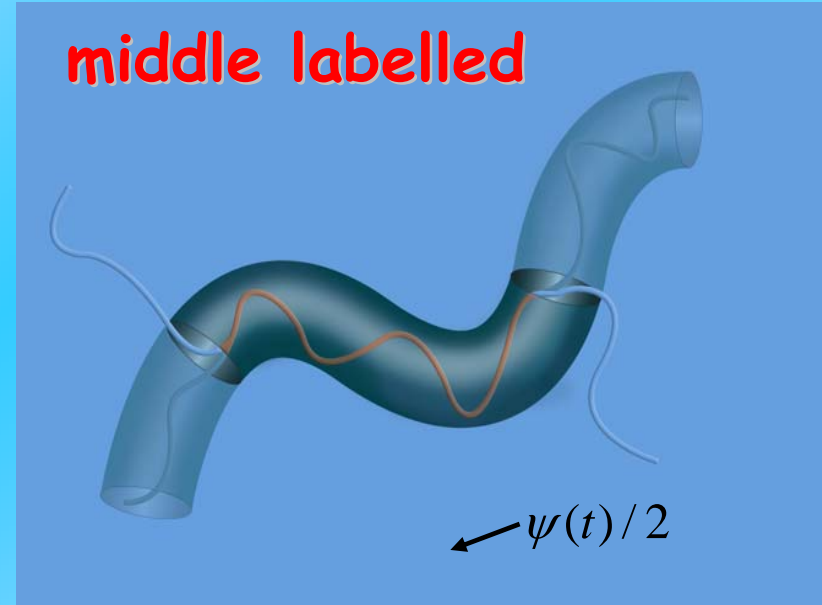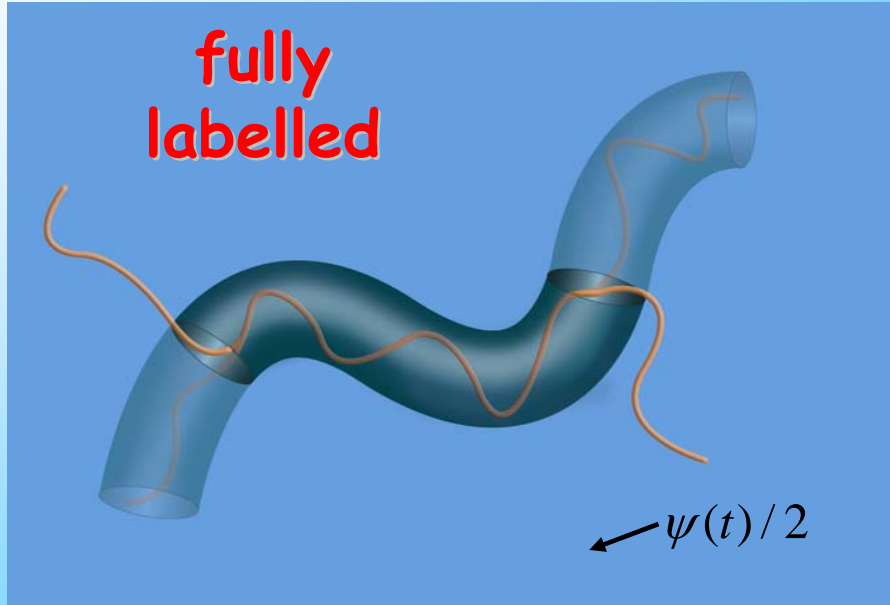**All parameters from single chain structure factor**

Limiting Processes

Contour length fluctuation

Constraint release

Reptation inherent mechanisms

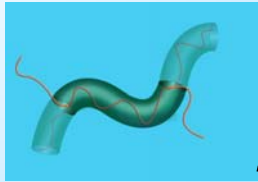# Separation of Contour Length Fluctuations (CLF)

fully labelled

$\psi(t)/2$

middle labelled

$\psi(t)/2$

$$\psi(t) = C_\mu \frac{N_e}{N} \left(\frac{t}{\tau_e} \right)^{\frac{1}{4}}$$

number of segments released from tube

A.E. Likhtman et al., Macromolecules (2002)

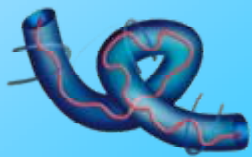# Separation of Contour Length Fluctuations (CLF)

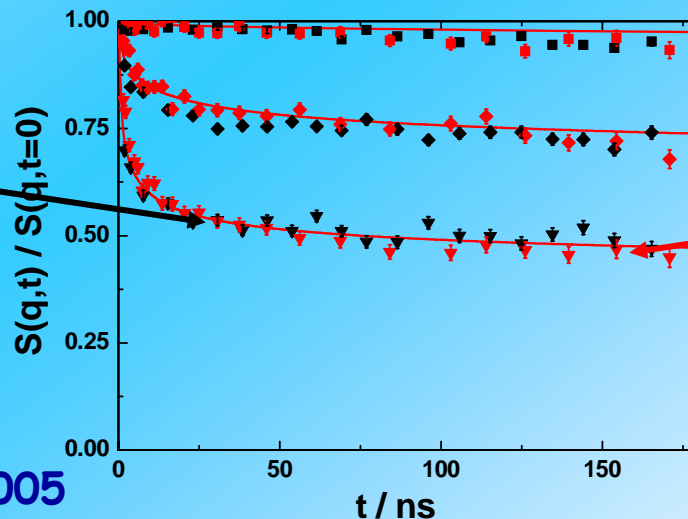

fully visible

25 kg/mol
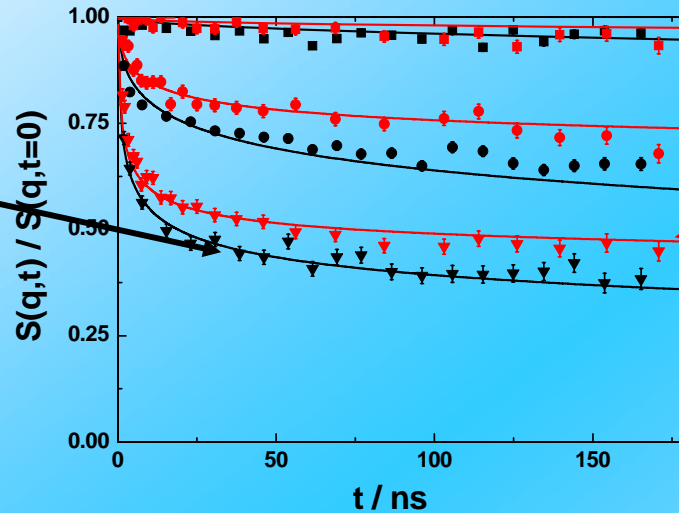
center part visible

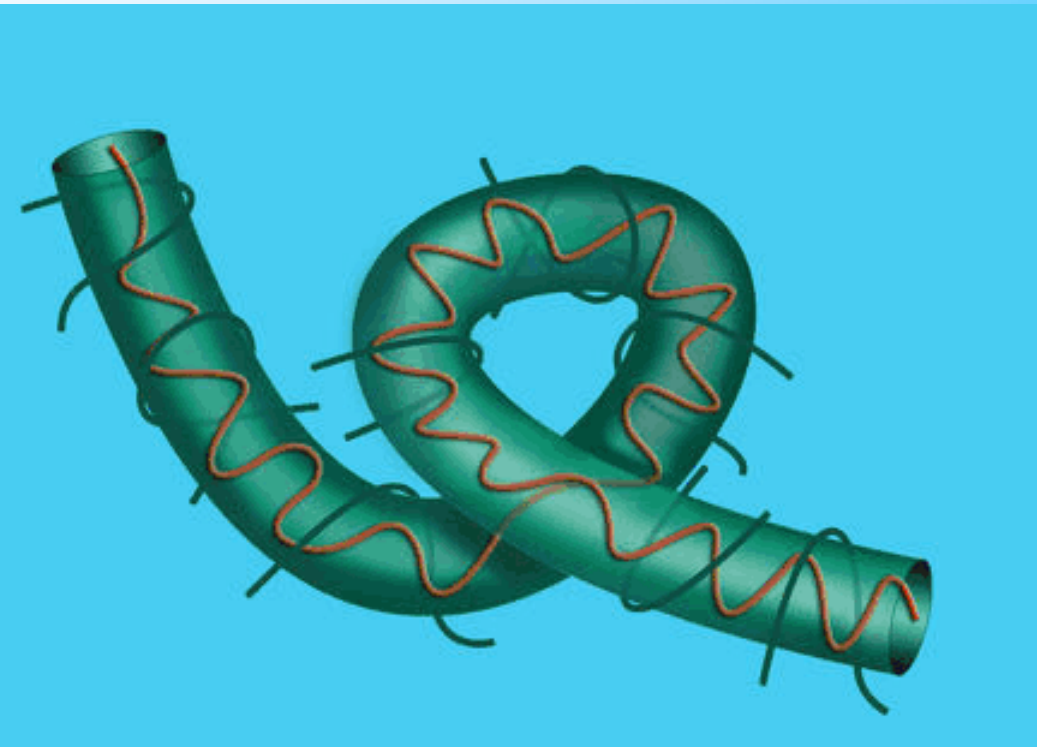4-17-4 kg/mol

very long chain

190 kg/mol

center part visible

4-17-4 kg/mol

M. Zamponi et al., EPL 2005

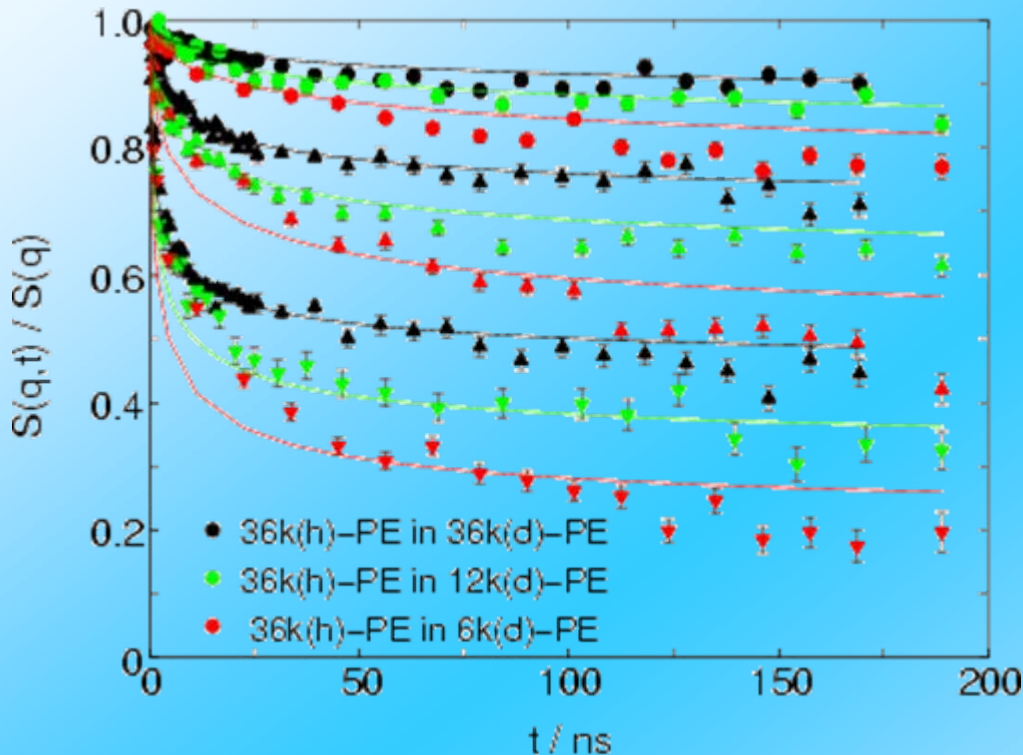**Inner part moves as infinite chain**

Common approach
➡ **CR relates to chain diffusion only**

Here:
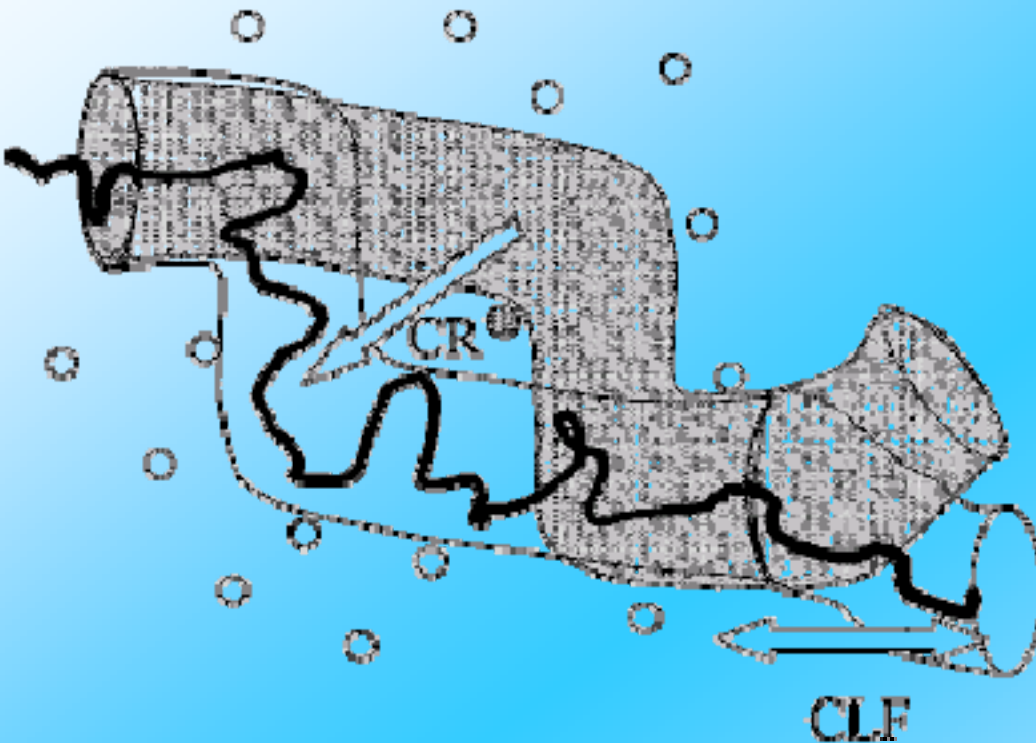➡ **CLF may play important role**

Zamponi et al. PRL 2006

Chains move away and open tube laterally

Constraint Release

fits with reptation model:
d=47Å
d=56Å
d=65Å

h-36kg/mol in
d-36kg/mol
d-12kg/mol
d-6kg/mol

Loss of confinement with decreasing matrix length

CR needs a confining chain to diffuse away; time scale:

reptation time of matrix chain

e.g.

12K τ_d = 5000 ns

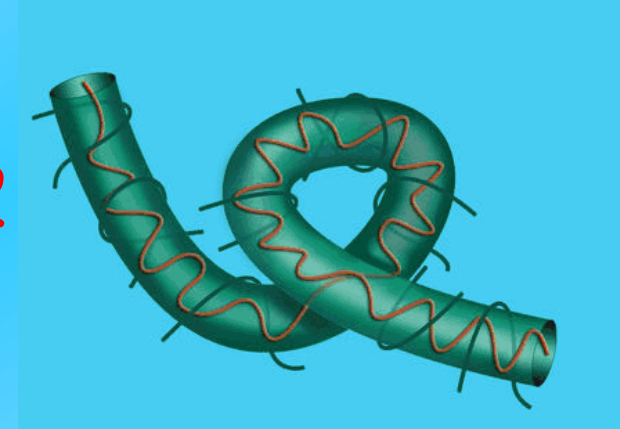**We observe strong effects on a scale of 200ns!**

a) **Long chain in short matrix no CLF of long chains**

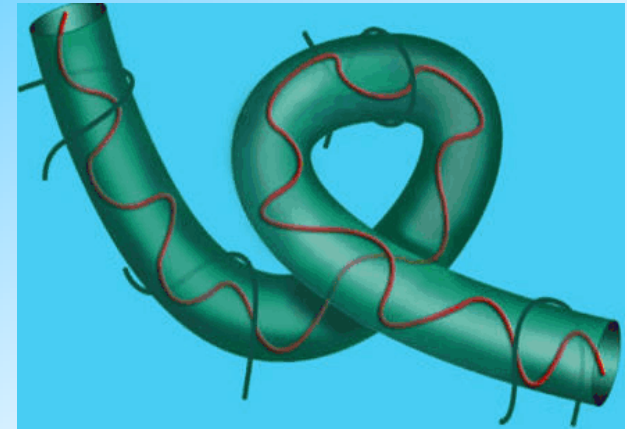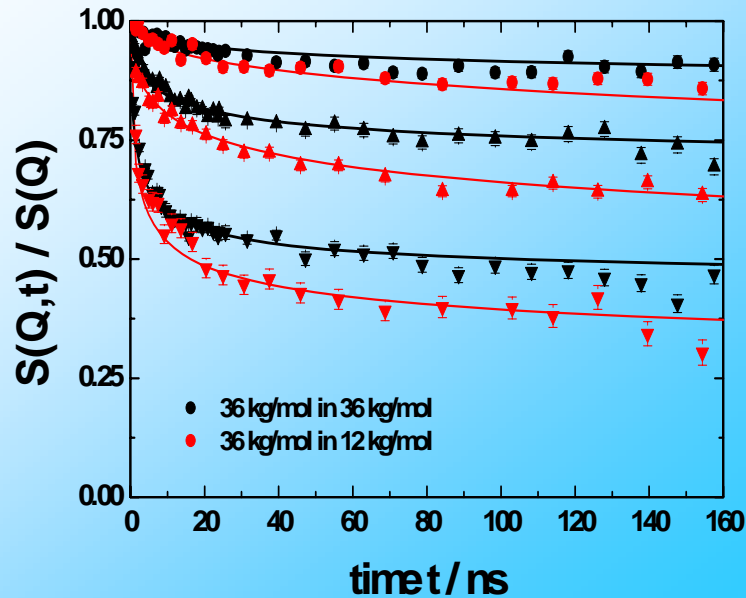36/12

Constraint release only

(end part is small)

b) **Short chain in long matrix no CR by long chains**

12/36

Contour length fluctation only

(long chains do not diffuse on our time scale)
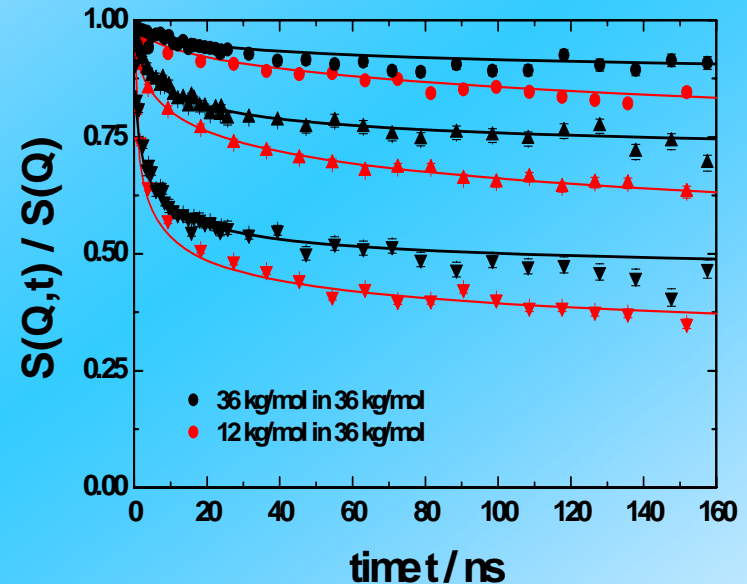
Comparison with Pure Reptation

long in short

**CR through
not by diffusion (5000ns)
but by CLF of short chains**

short in long

**CLF of short chains
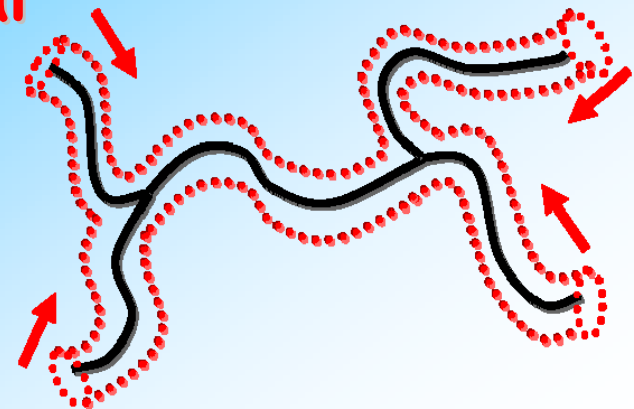no constraint release –
there are not many ends**

CR may be caused solely by CLF

Topological Constraints: Summary

NSE and synthetic chemistry

Direct visualization of
➧ **Regime of local reptation**
➧ **Limiting mechanisms**
- **contour length fluctuations**
- **constraint release**

Basic processes for the hierarchical relaxation of branched polymers

Protein motion and the coordination of biofunction

- Genome regulatory proteins

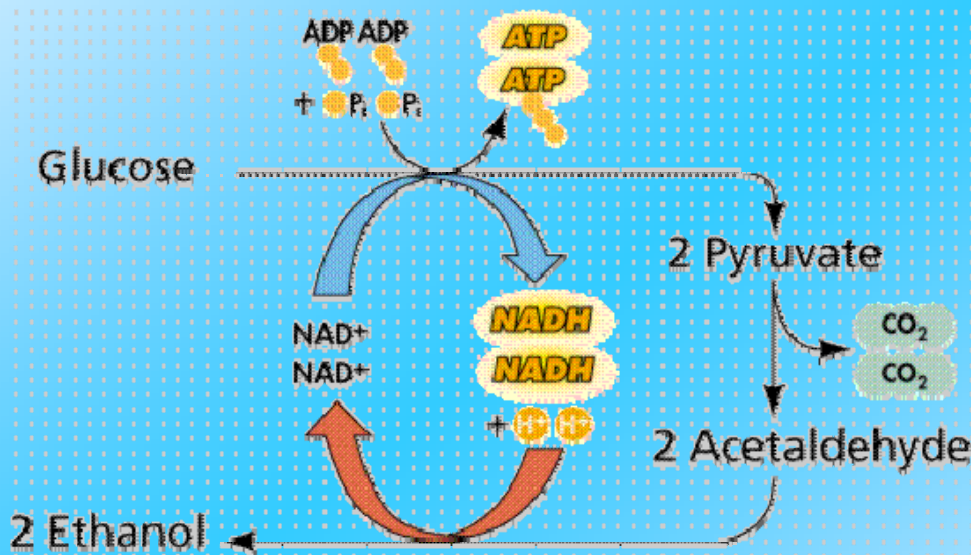- Motor proteins

- Signaling proteins

- Structural proteins

Are large scale thermal fluctuations related to functional dynamics?

Alcohol Dehydrogenase

Important enzyme e.g. prohibits poisoning by Italian red wine

In humans (Dimers)
Catalysis oxidation of ethanol

$CH_3 \, CH_2 \, OH + NAD^+ \rightarrow CH_3 \, CHO + NADH + H^+$

Alcohol Dehydrogenase
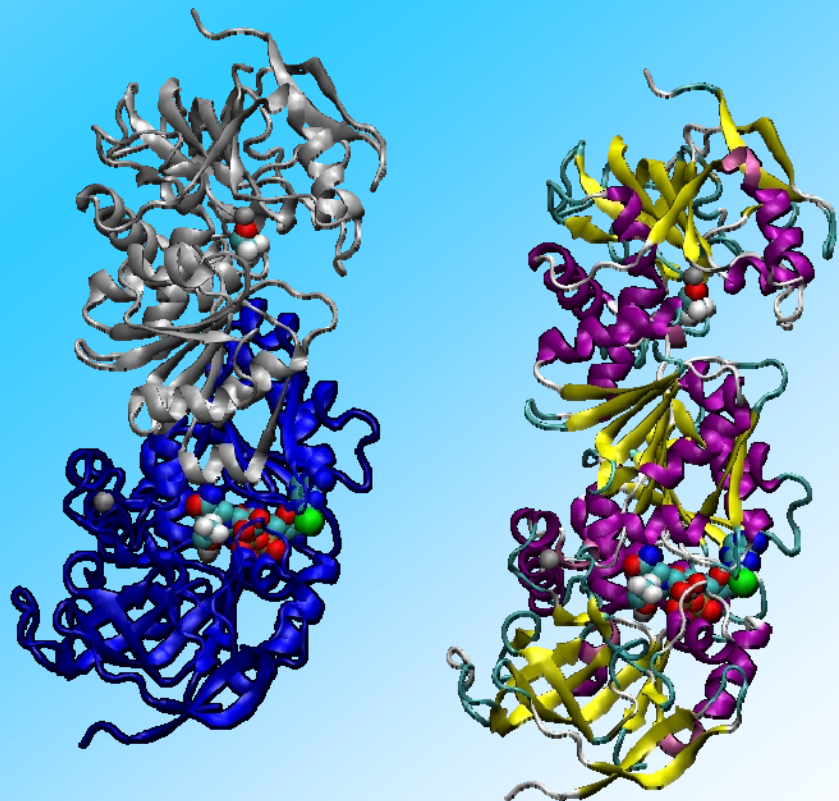
In yeast (Tetramer)

Fermentation process

$$CH_3\ CHO + NADH + H^+ \rightarrow CH_3\ CH_2\ OH + NAD^+$$
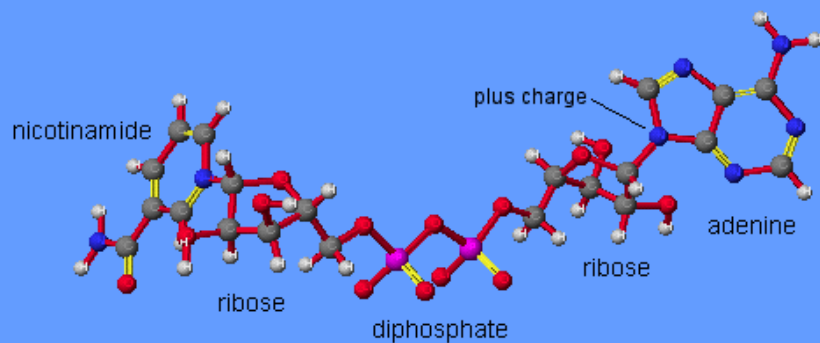

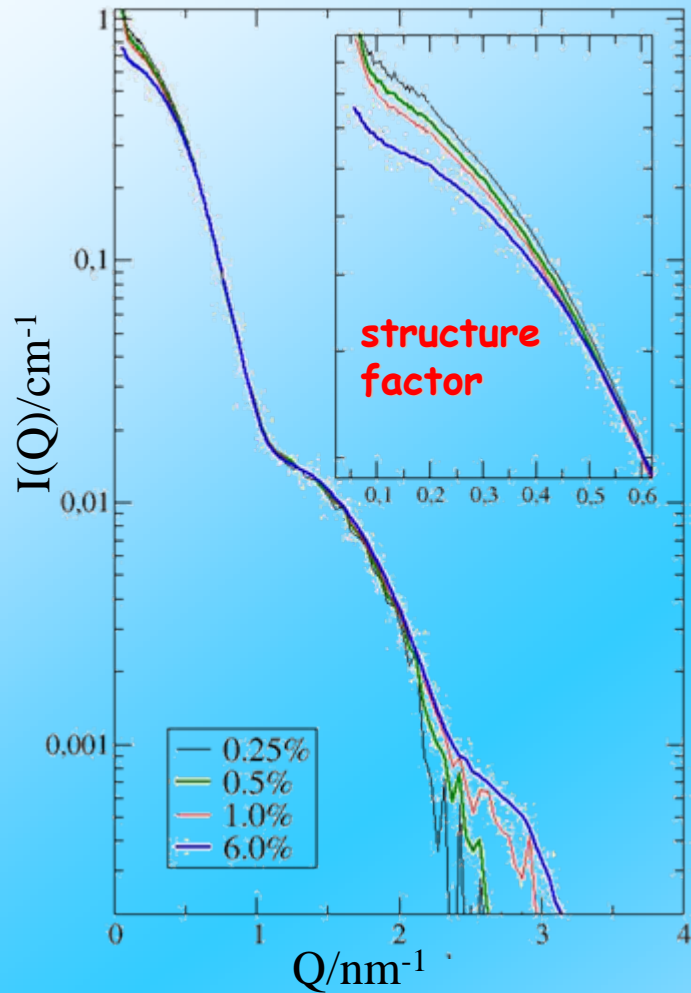**Reverse action**
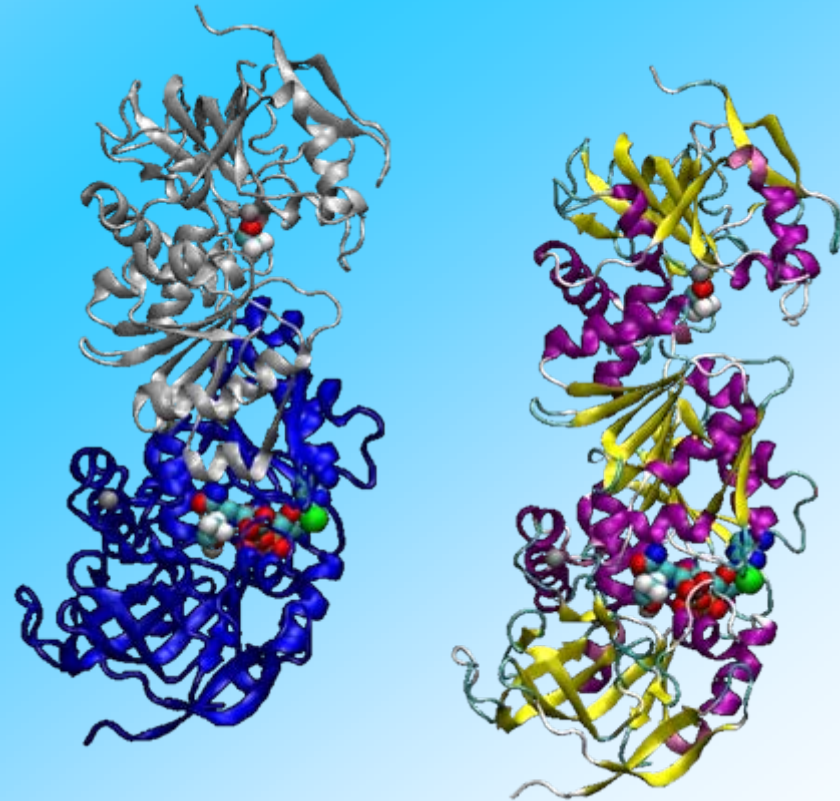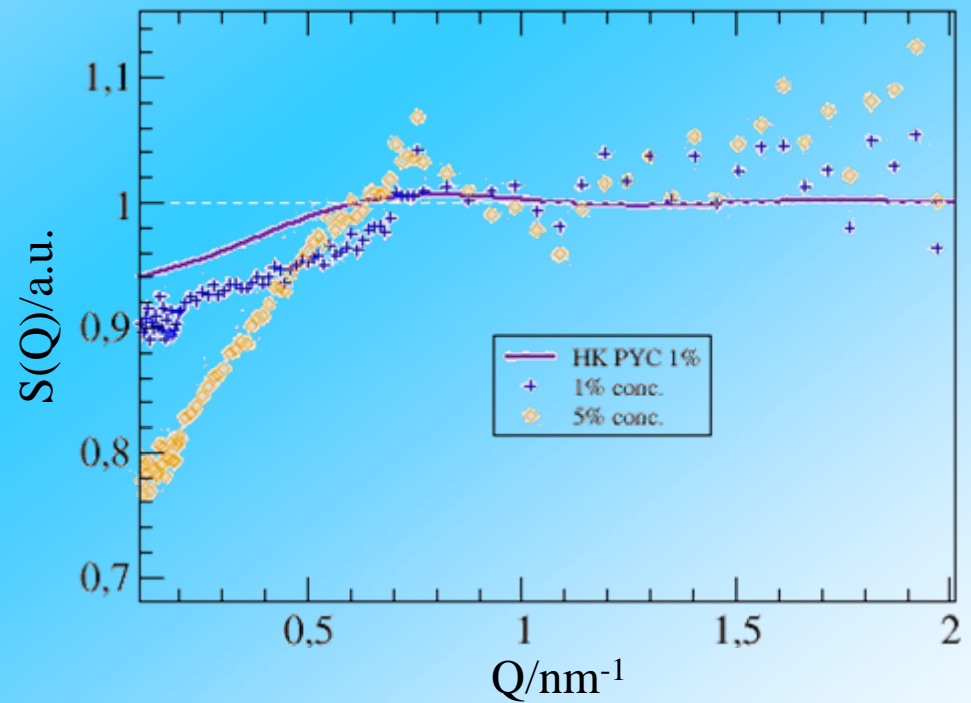
Dynamics

Internal aggregate motion

- ➡ **Rotational dynamics**
- ➡ **Influence of cofactor NADH**

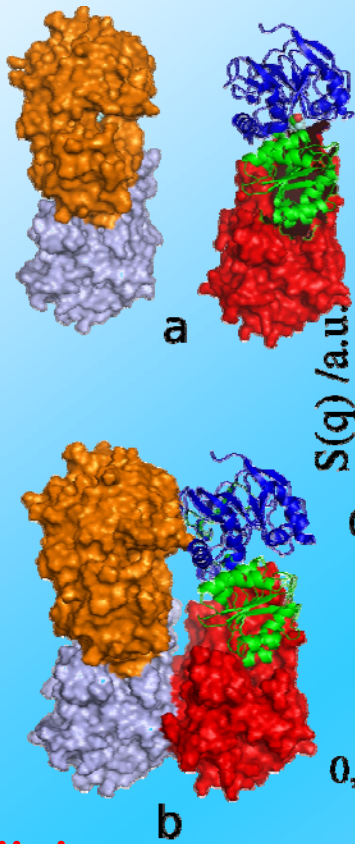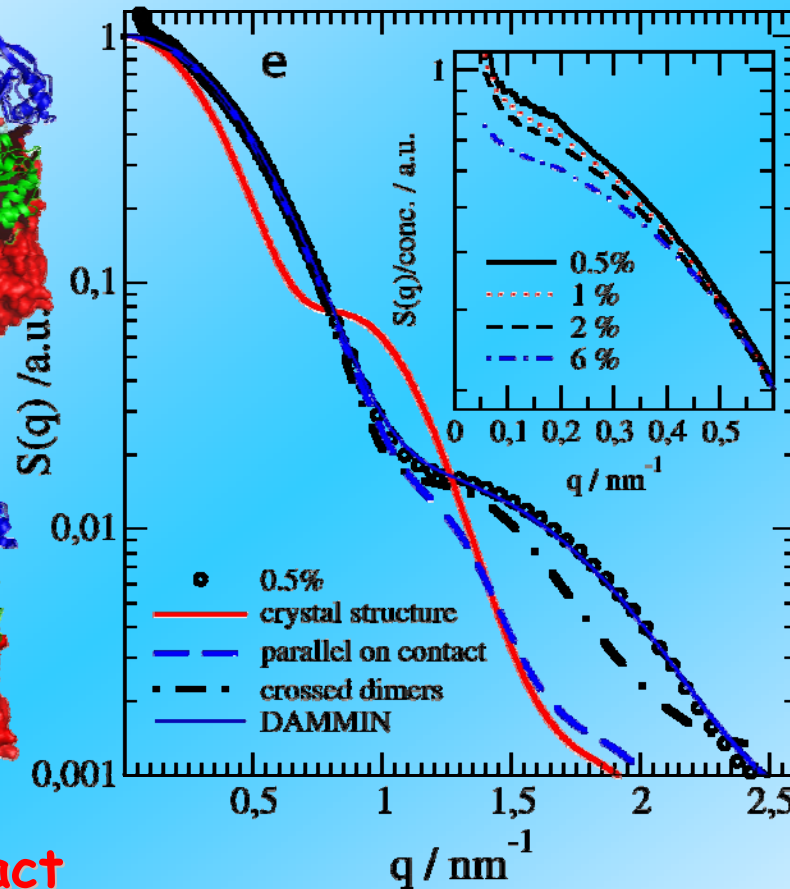Nicotinamide Adenine Dinucleotide, NAD+ Coenzyme

nicotinamide

plus charge

adenine

ribose

ribose

diphosphate

C. Ophardt, c. 2003
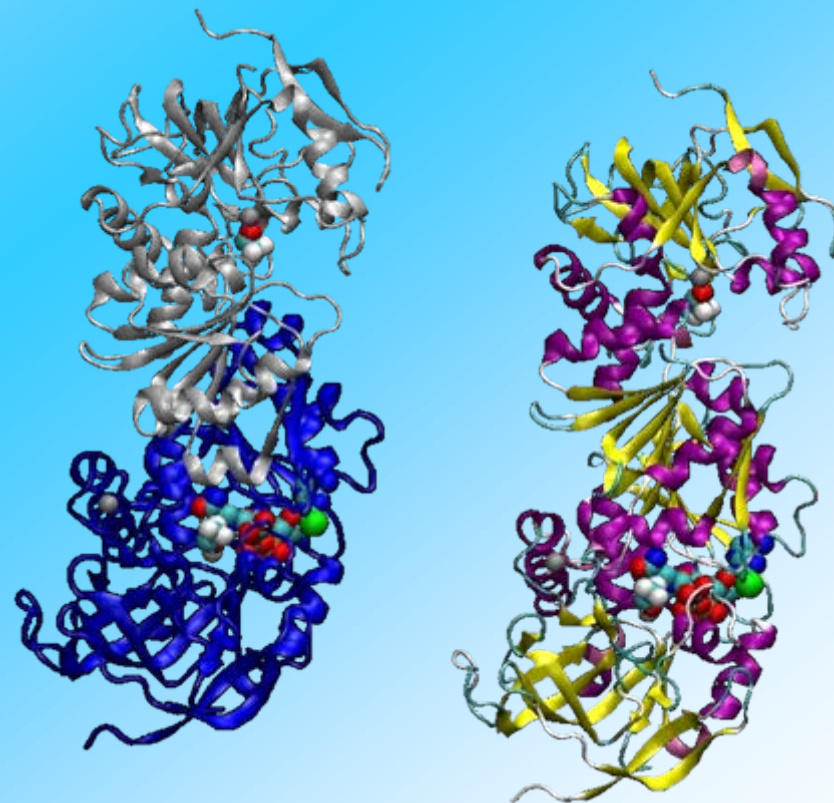
structure factor

concentration scaled

Solution Structure

crystal

DAMMIN program
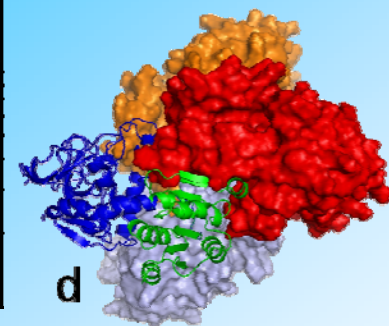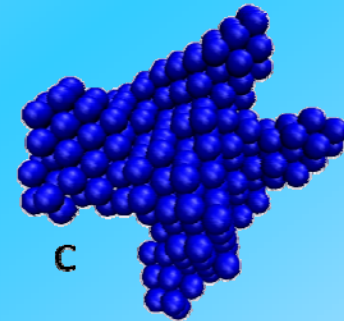

parallel on contact

Crossed dimers

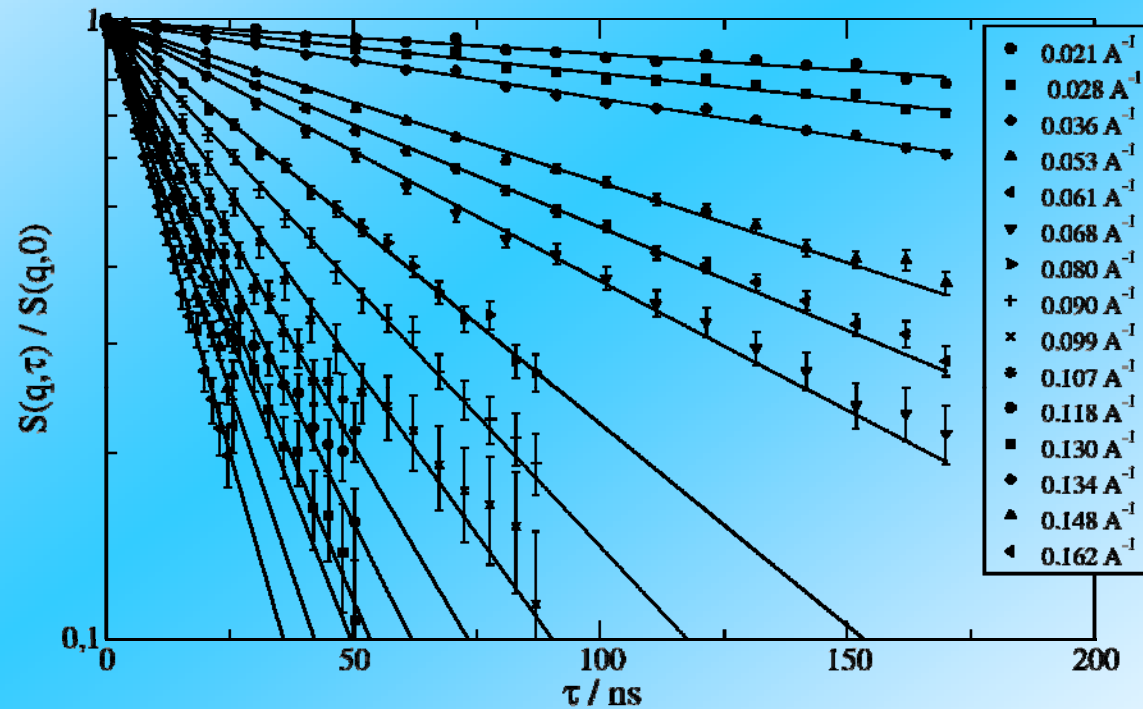**Solution structure differs from crystal: crossed dimers**

Dynamics

Translational Diffusion
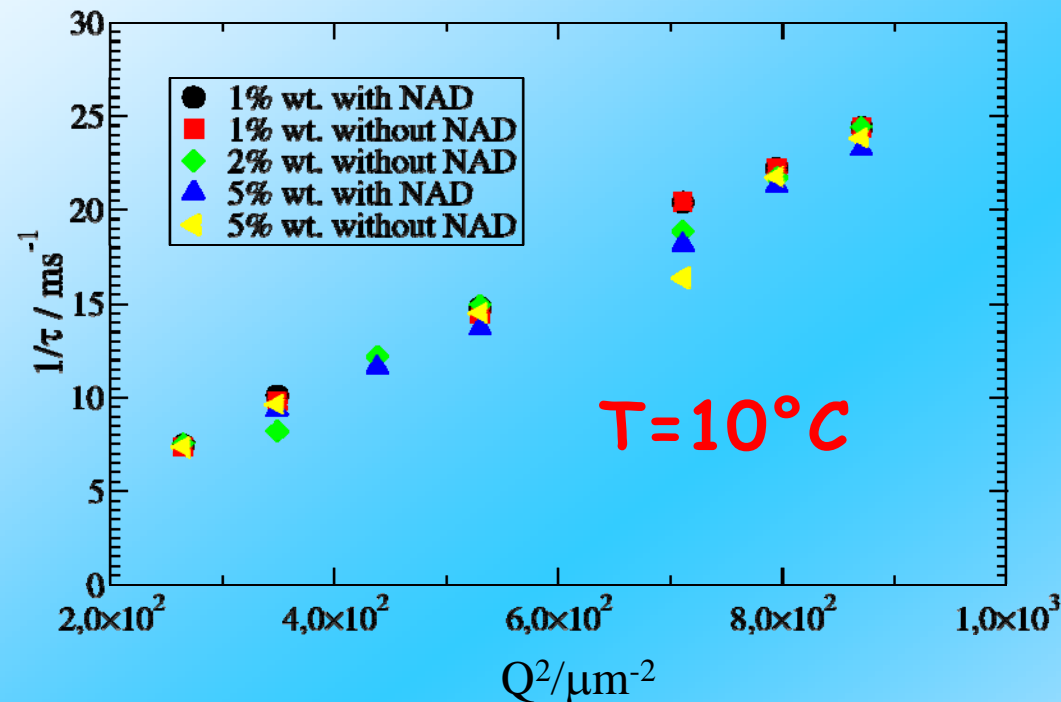
Diffusion independent of concentration

$D_{DLS} = 2.35 \pm 0.2 \text{Å}^2/\text{ns}$ at $5°C$

$R_H = 45\text{Å}$

Dynamic light scattering: photon correlation

Neutron Spin Echo Results
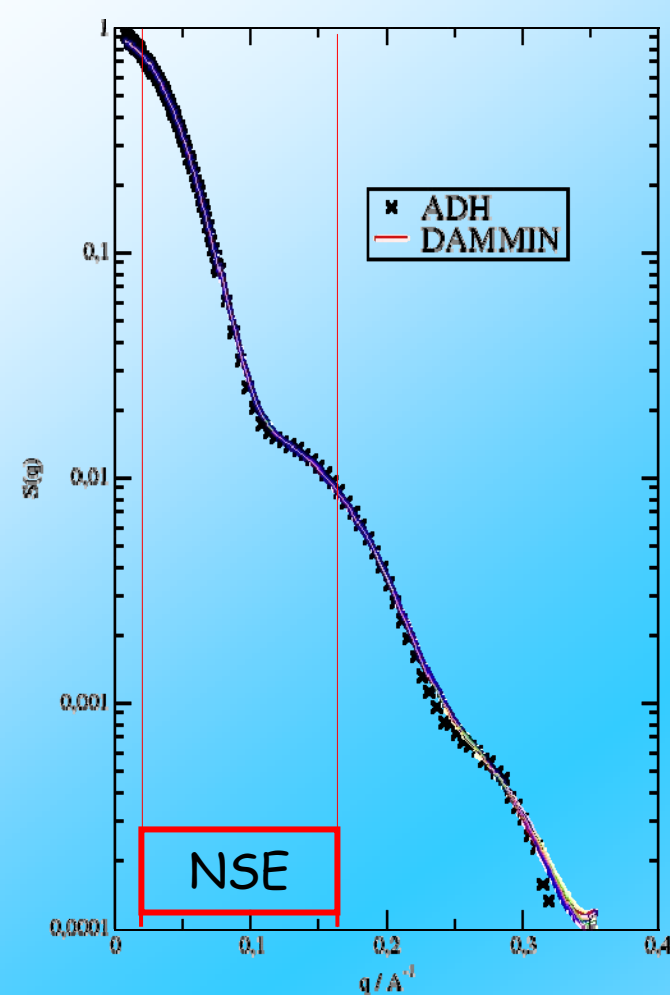
close to single exp. lineshapes
→ effective diffusion

ADH + NAD at 5% concentration

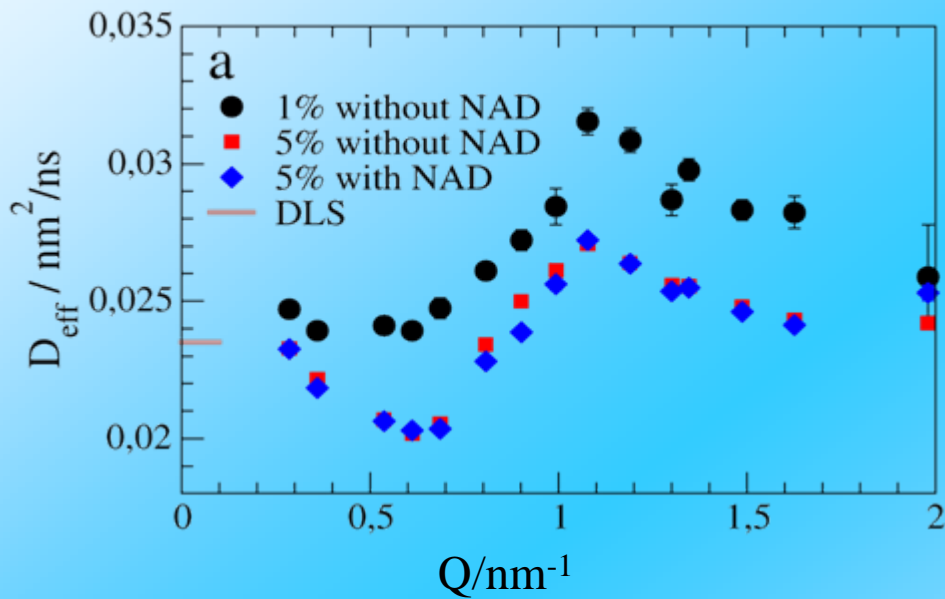# Effective Diffusion Coefficient
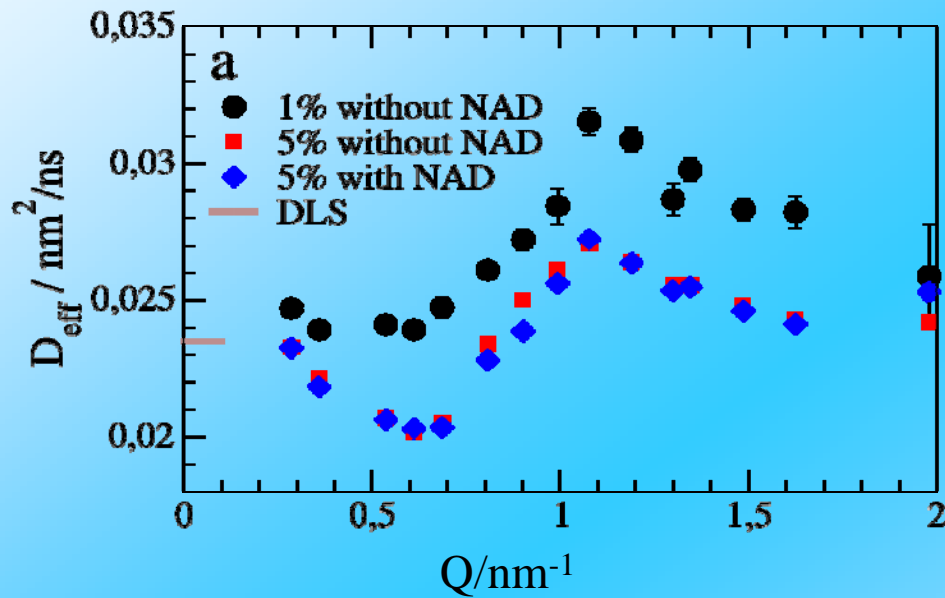
- **Strong Q modulation**
- **Significant conc. dependence**
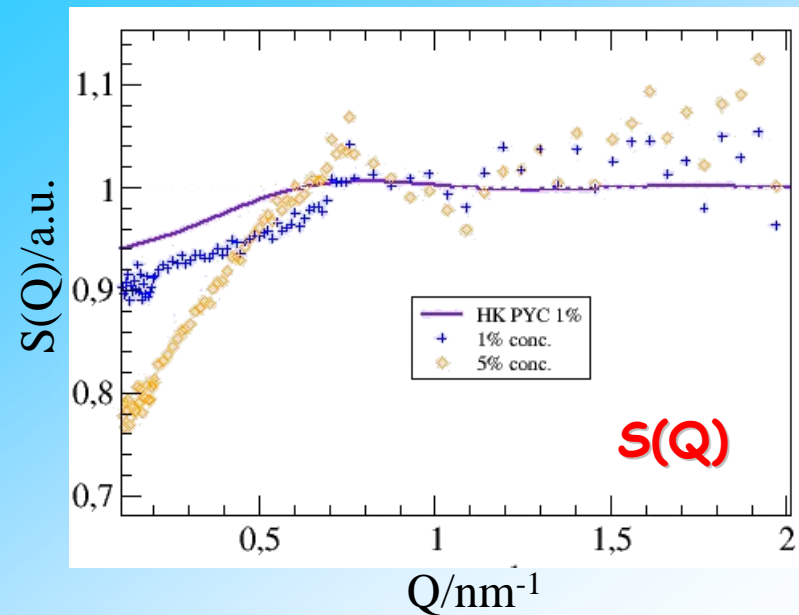- **At low Q agreement with light scattering**

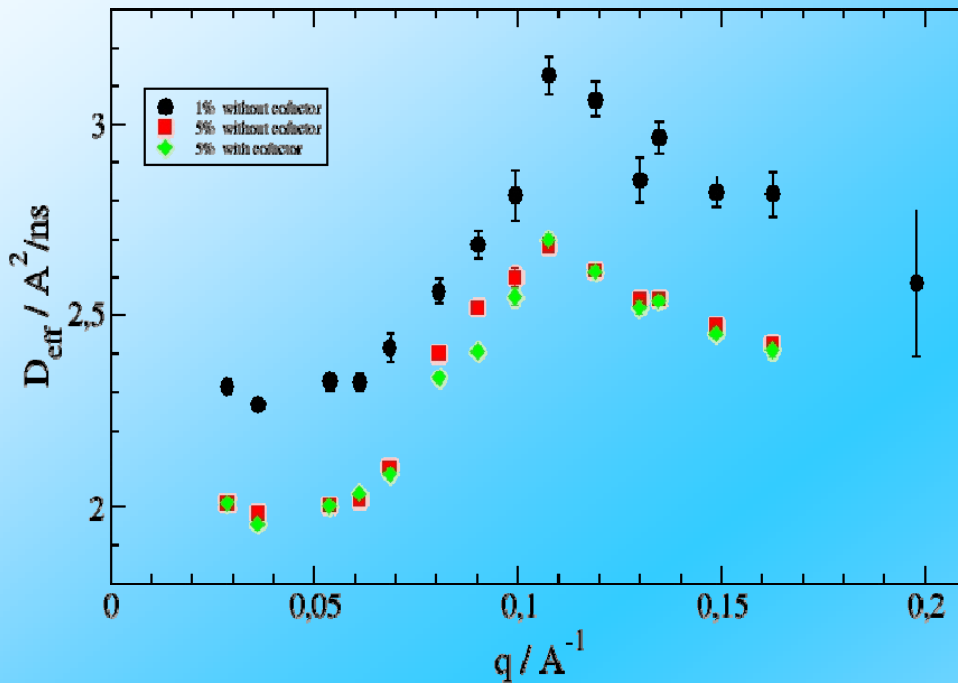**Important contributions beyond trans. diffusion**
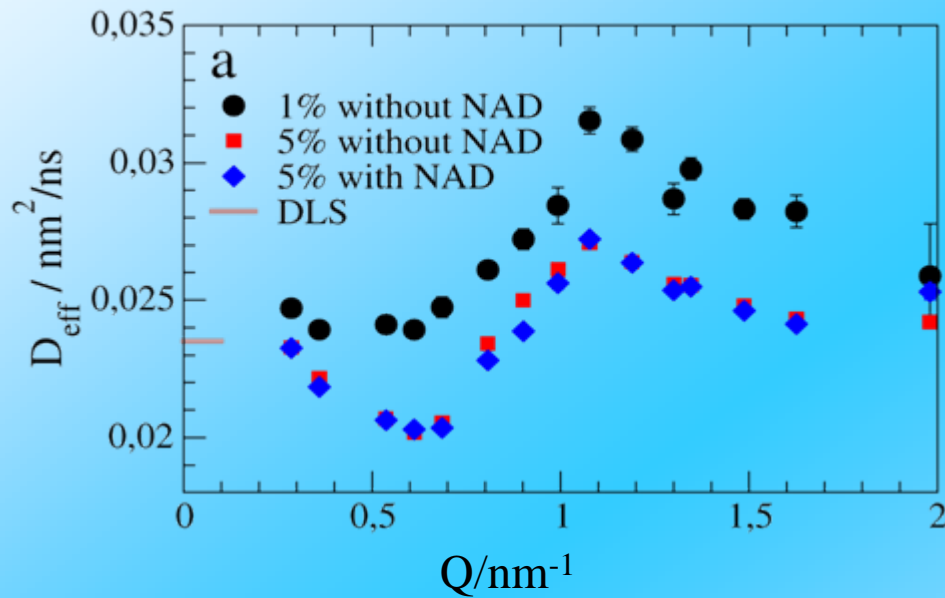
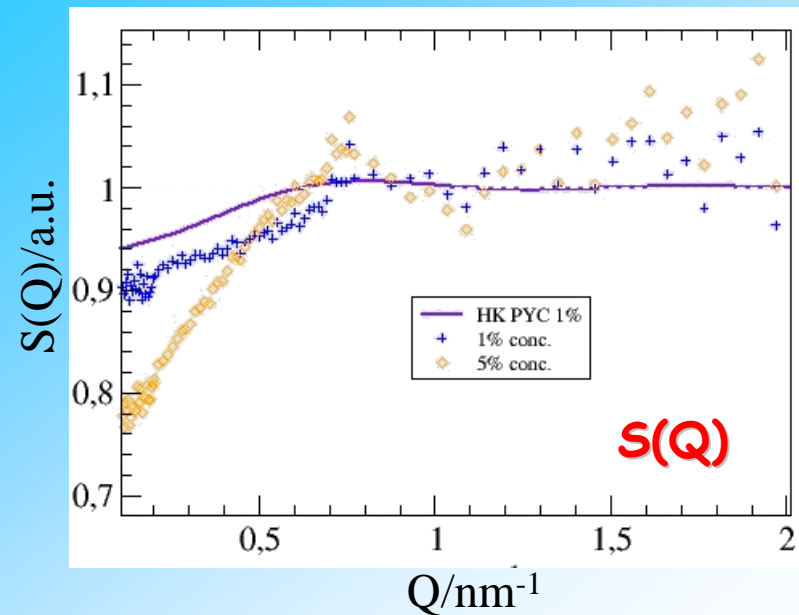$$D_{eff} = D_0 \frac{H(Q)}{S(Q)}$$

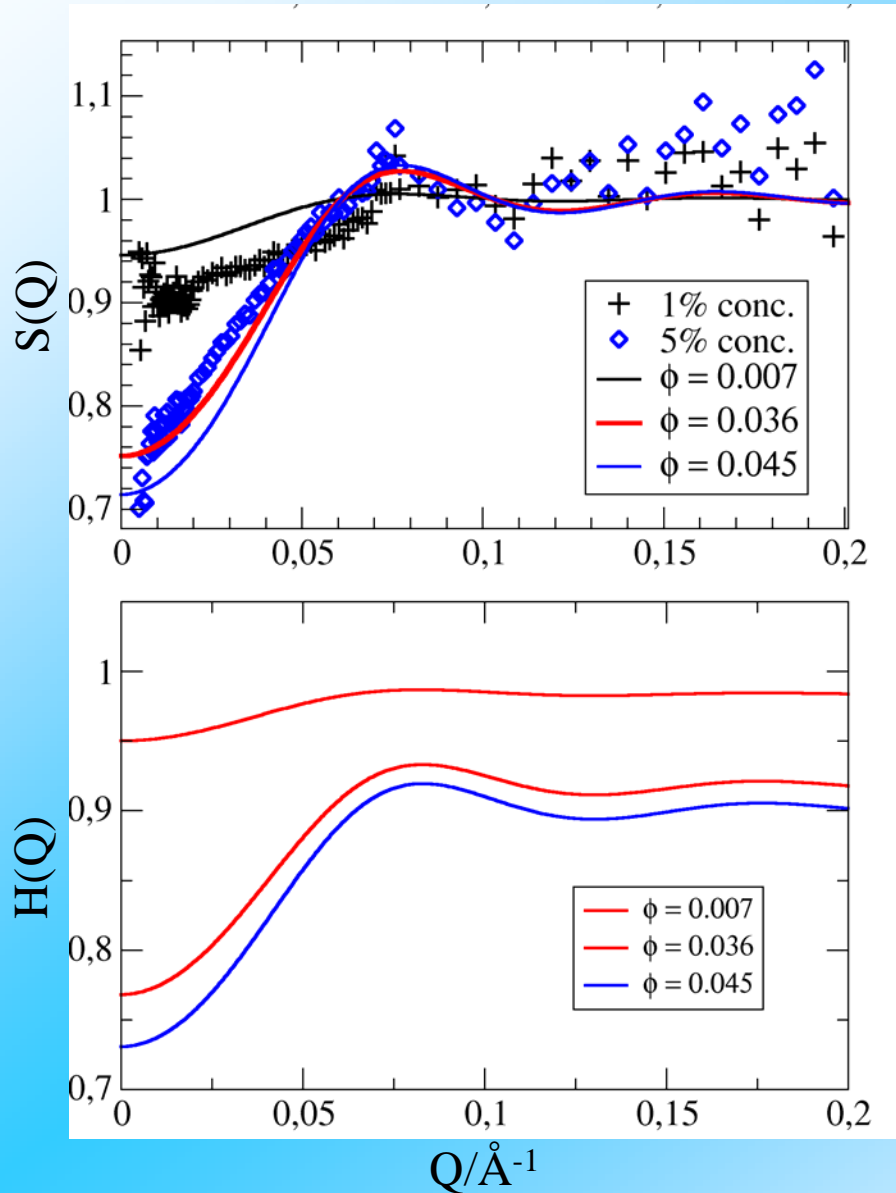$$D_{eff} = D_0 \frac{H(Q)}{S(Q)}$$

S(Q)

$$D_{eff} = D_0 \frac{H(Q)}{S(Q)}$$

S(Q)

Corrected D$_{eff}$(Q) by S(Q)
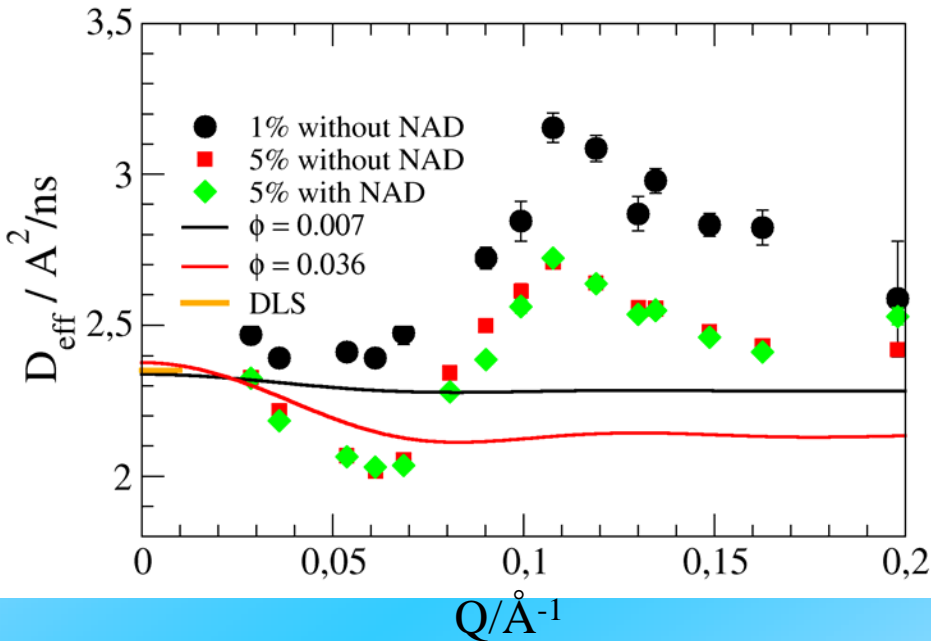
S(Q) correction removes low Q structure

$$D_{eff} = D_0 \frac{H(Q)}{S(Q)}$$

H(Q) not known

First approximation
Both H(Q) and S(Q) by Percus Yevic appr. of hard spheres

$$D_{eff} = D_0 \frac{H(Q)}{S(Q)}$$

Qualitatively correct

Low Q: very little conc. dependence

Intermediate Q: reduction slightly weaker than exp.

Higher Q: no conc. dependence

Legend:
- 1% without NAD
- 5% without NAD
- 5% with NAD
- $\phi = 0.007$
- $\phi = 0.036$
- DLS

Axes: D_{eff} / A^2/ns vs Q/Å^{-1}

Higher Q: Rotational Diffusion

First cumulant approach: $Q^2\, D_{eff} = \bar{\Gamma}(Q) = -\lim_{t \to 0} \frac{\partial}{\partial t} \frac{S(Q,t)}{S(Q,0)}$
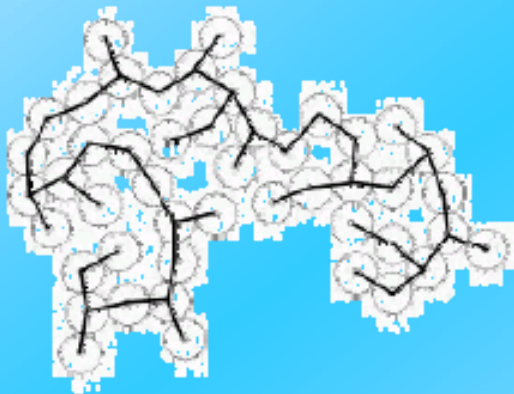
$$D_{eff}(Q) = \frac{k_B T}{Q^2} \frac{\sum_{j,k} \left\langle b_j e^{iqr_j} \begin{pmatrix} Q \\ Q \times r_j \end{pmatrix} \overleftrightarrow{H} \begin{pmatrix} Q \\ Q \times r_k \end{pmatrix} b_k e^{-iqr_k} \right\rangle}{\sum_{j,k} \left\langle b_j e^{iqr_j}\, b_k e^{-iqr_k} \right\rangle}$$

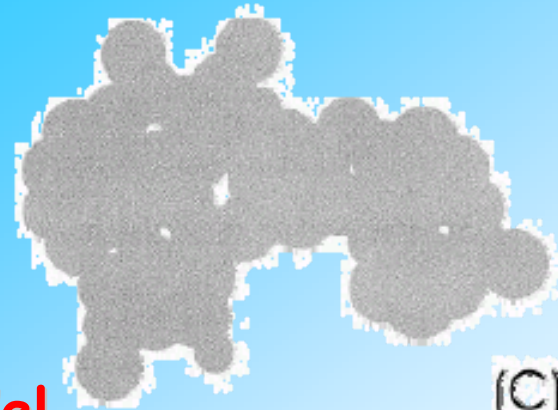$\underline{r}_j$, $\underline{r}_k$ atom positions; $b_j\, b_k$: scattering length

denominator: structure factor

First cumulant approach: $Q^2 D_{eff} = \bar{\Gamma}(Q) = -\lim_{t \to 0} \frac{\partial}{\partial t} \frac{S(Q,t)}{S(Q,0)}$

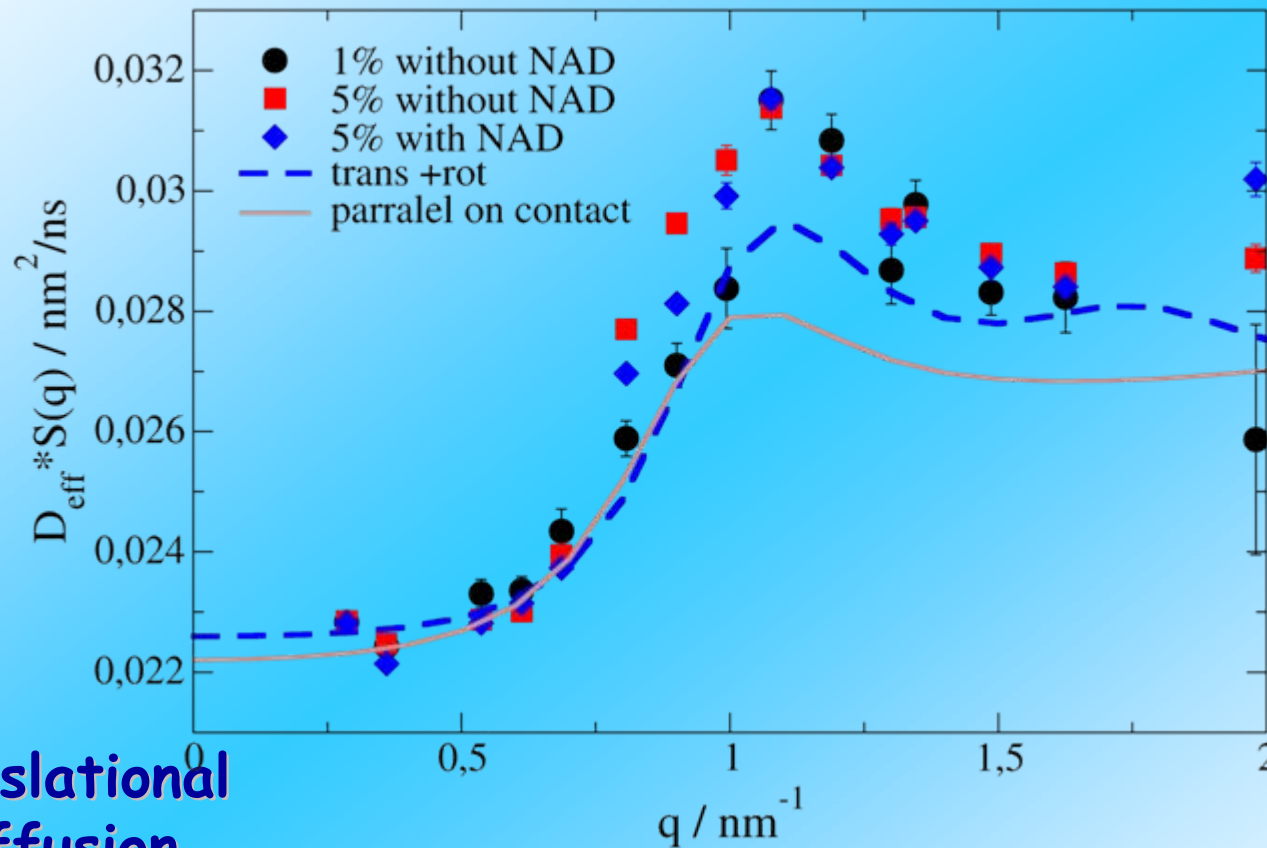**Programme HYDROPRO:**
calculates the full mobility matrix H

simplified model
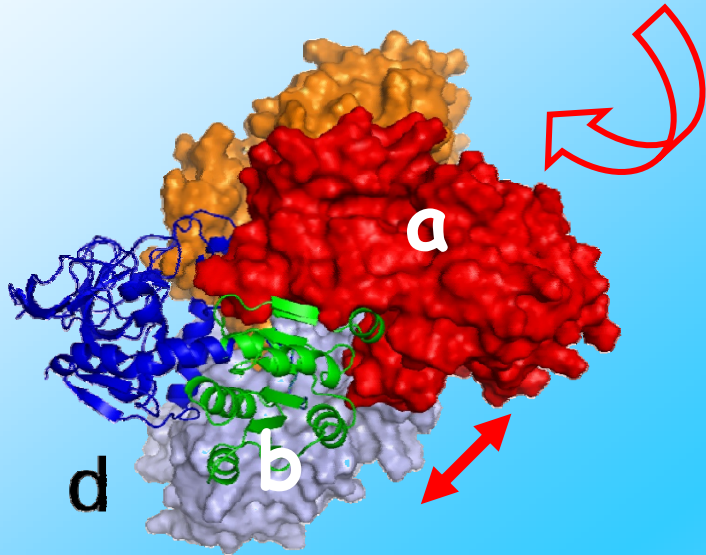of spheres

Higher Q: Rotational Diffusion

Very sensitive to correct solution structure!!

translational + rotational diffusion

translational diffusion
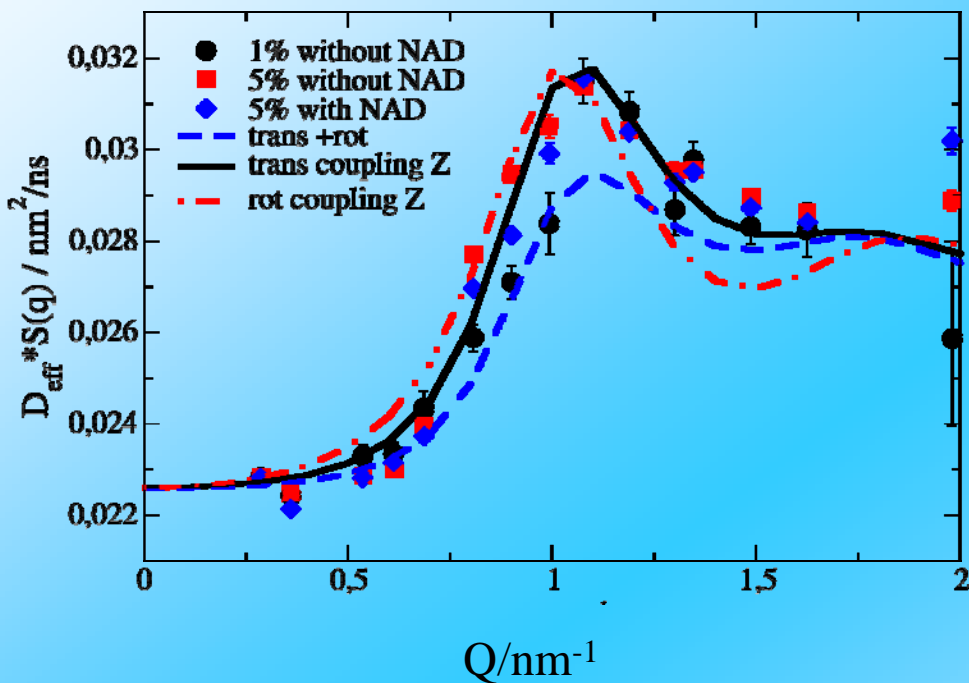
HYDROPRO result scaled to low Q trans. diffusion

Coupling term

- **elongational coupling**

- **Rotational coupling of domain motion**

$$X = T_{zz}; R_{zz}$$

$$\mathbf{T} \Rightarrow \mathbf{T} + \left\{ \begin{matrix} \mathbf{T}^{aa}_{3x3} & \mathbf{T}^{ba}_{3x3} \\ \mathbf{T}^{ab}_{3x3} & \mathbf{T}^{bb}_{3x3} \end{matrix} \right\} = \mathbf{T} + \left\{ \begin{matrix} 0 & 0 \\ 0 & 0 \\ 0 & X \\ 0 & 0 \\ 0 & 0 \\ X & 0 \end{matrix} \right\}$$

- Very consistent data sets at different concentration and cofactor

- Quantitative description by rotational diffusion of crossed dimers and rotational coupling

- NAD leads to slowing down in the low Q-flank
  - significant effect
  - points to collective origin
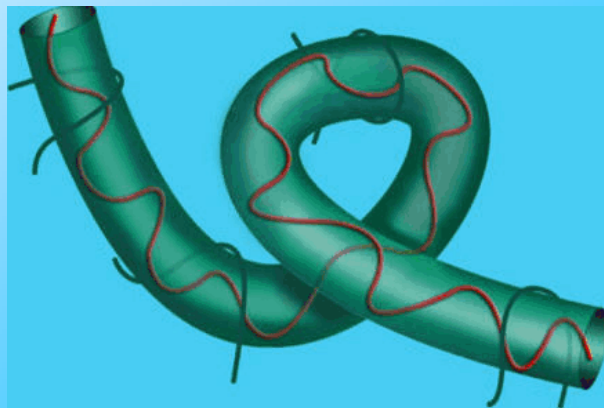
All data scaled with translational diffusion

Alcoholdehydrogenase Dynamics

➡️ **Structure in solvent different from crystal structure**

➡️ **Rigid body dynamics dominates but clear evidence for internal motion**
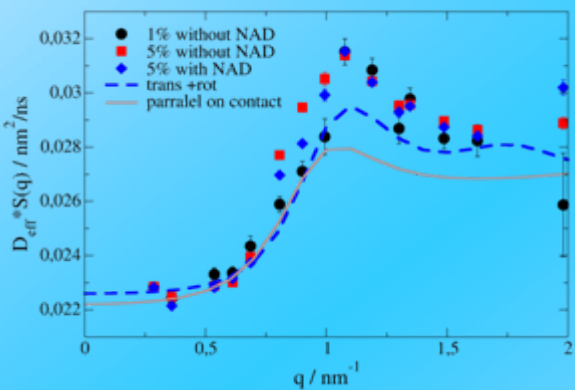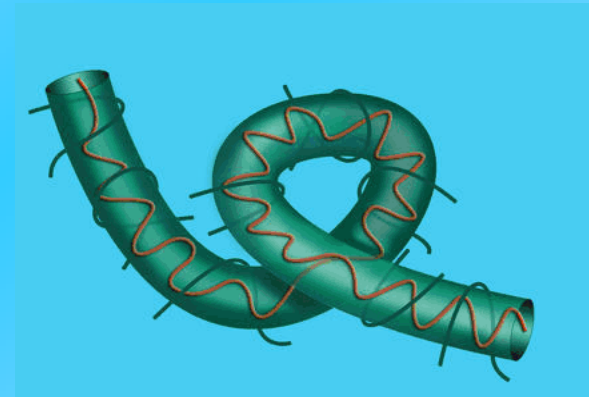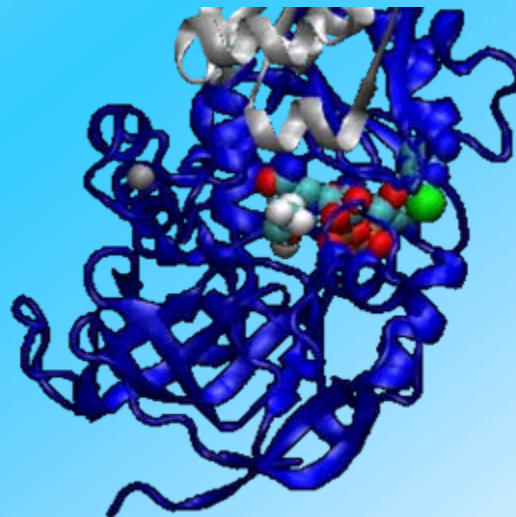
➡️ **Influence of cofactor**

Summary

Rouse
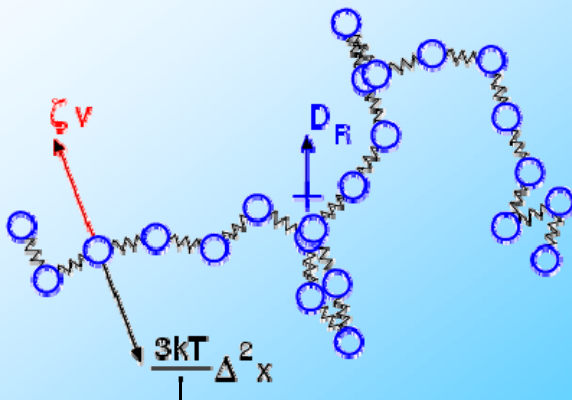
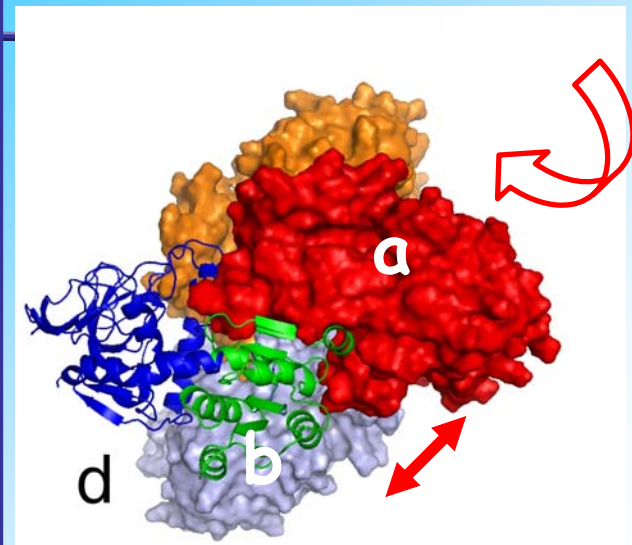## Contour Length Fluctuation

Constraint Release

Solvent Structure

Influence of Cofactor

Aggregate Motion