Water Dynamics in Confinement: Insights from NMR experiments

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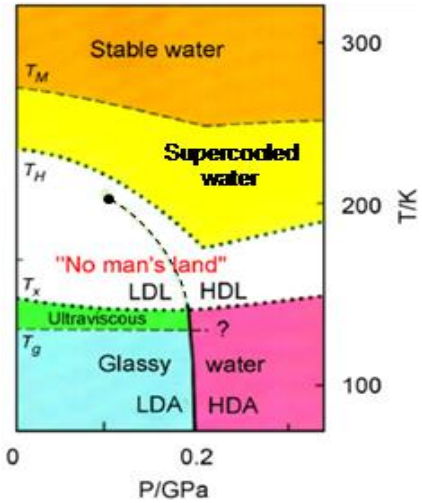
Outline

TECHNISCHE UNIVERSITÄT DARMSTADT

- Introduction
- Basics of ^{2}H NMR Experiments
- Water dynamics in protein matrices
- Water dynamics in silica matrices
- Summary

Bulk Water



Water anomalies:

Controversial discussion about the origin

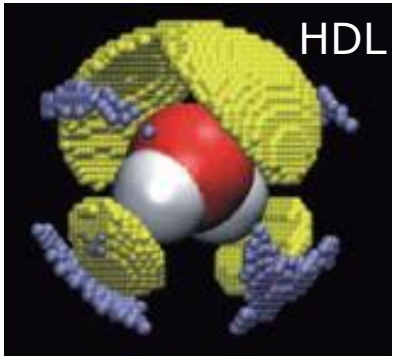
Stanley et al.:

- Liquid-liquid phase transition (HDL-LDL)
- Existence of a second critical point

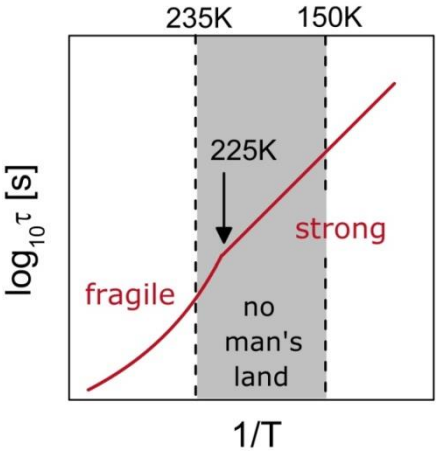
Nature (98), PNAS (05)

Structure

Changes in the order of the HB network



Paschek et al., CPC 08



Dynamics

Fragile-strong transition

Angell Science (08)

Confined Water

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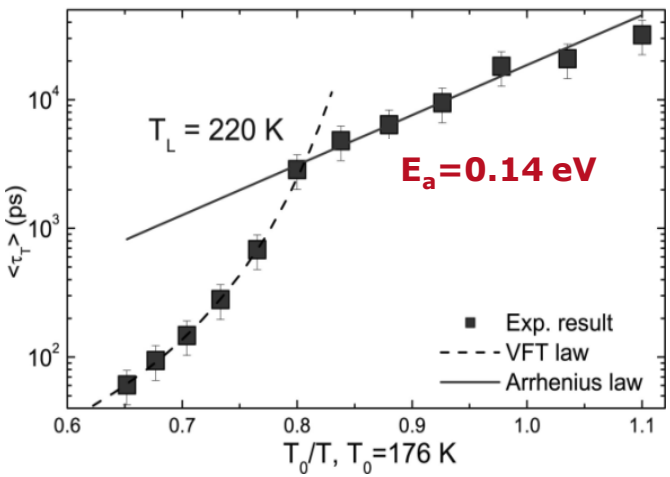
QENS

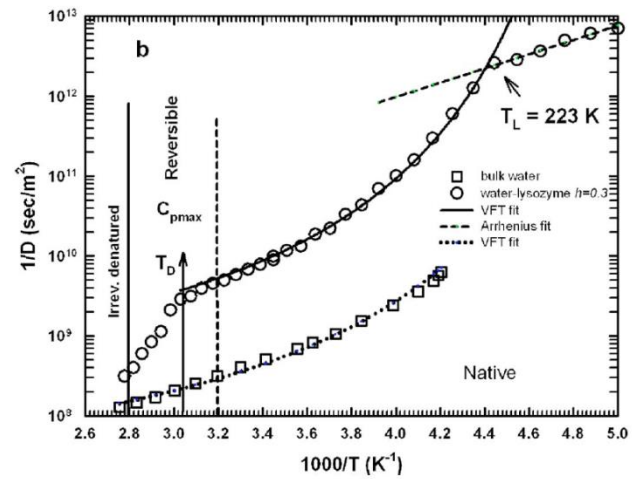
Hydrated lysozyme (h=0.3 g/g)



Chen et al., PNAS (06)

NMR diffusometry

Hydrated lysozyme (h=0.3 g/g)



Mallamace et al., JCP (07)

Evidence for a fragile-strong transition

Confined Water

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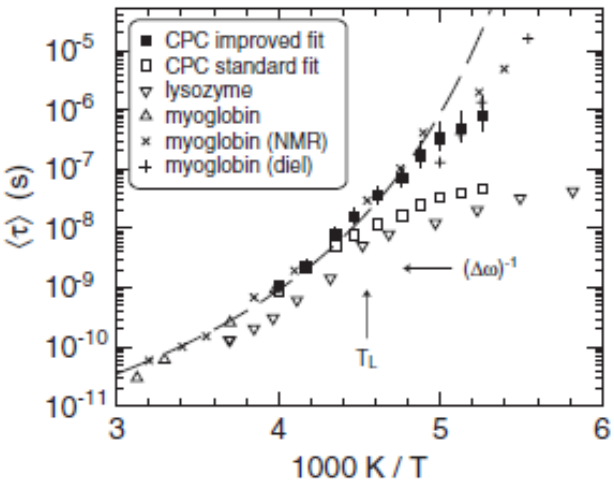
QENS

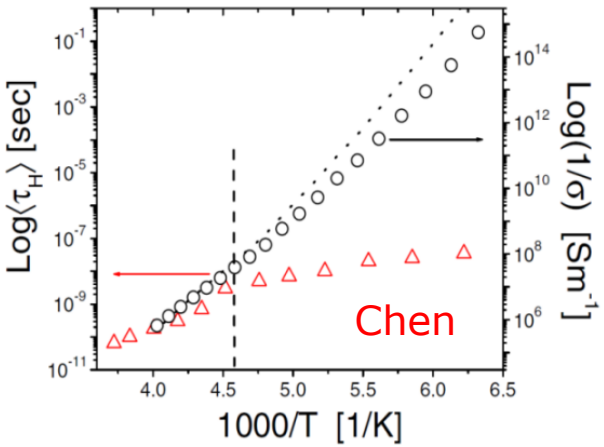
Hydrated C-phycocyanin (h=0.3)
Hydrated myoglobin (h=0.35)



Doster et al., PRL 10

Conductivity

Hydrated lysozyme (h=0.4)



Pawlus et al., PRL (08)

No evidence for a fragile-strong transition

Confined Water

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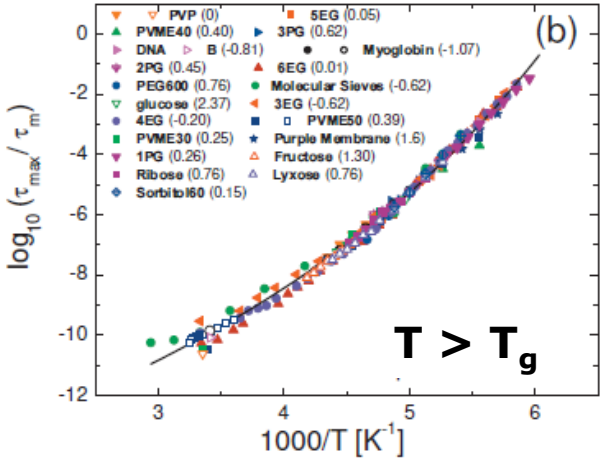
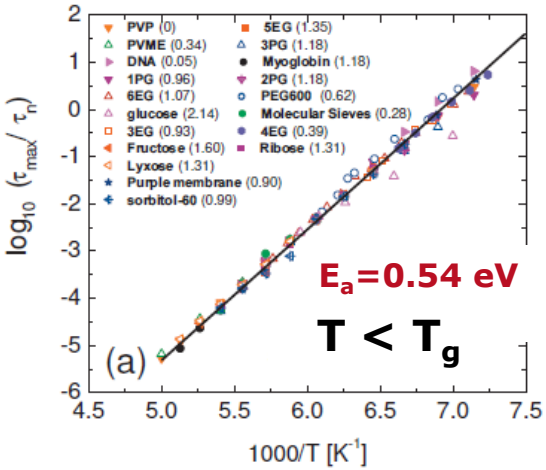
Dielectric spectroscopy



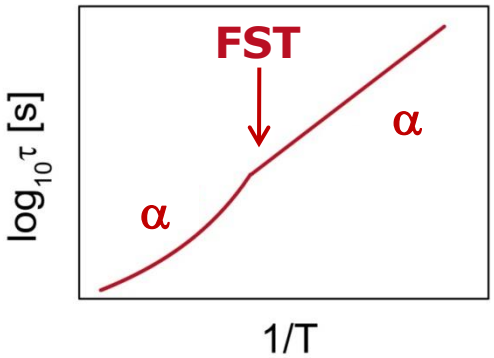


Cerveny et al., PRE (08)

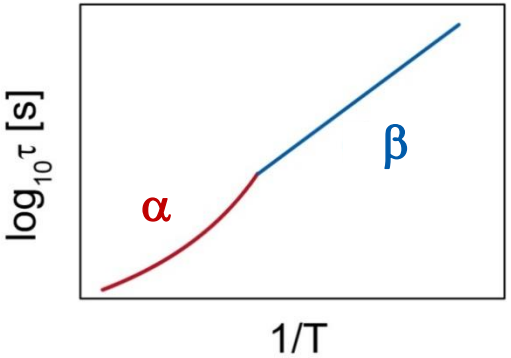
Crossover in the temperature dependence at $T \approx T_g$

Universal hydration water dynamics at $T > T_g$ and at $T < T_g$

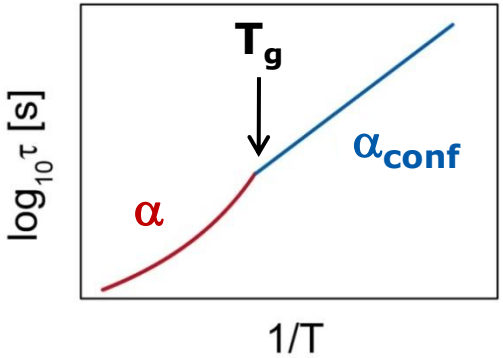
Confined Water



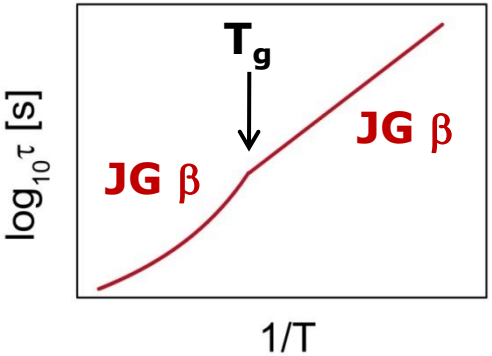
Chen et al., PNAS (05)
Liu et al., PRL (05)
Kumar et al., PRL (06)
Mallamace et al., JCP (07)



Cerveny et al., PRL (04)
Swenson et al., PRL (06)
Pawlus et al., PRL (08)



Cerveny et al., PRB (08)



Capaccioli et al., JPC B (07)
Ngai et al, JPC B (08)

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Basics of ^{2}H NMR Experiments

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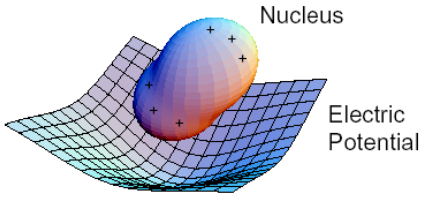
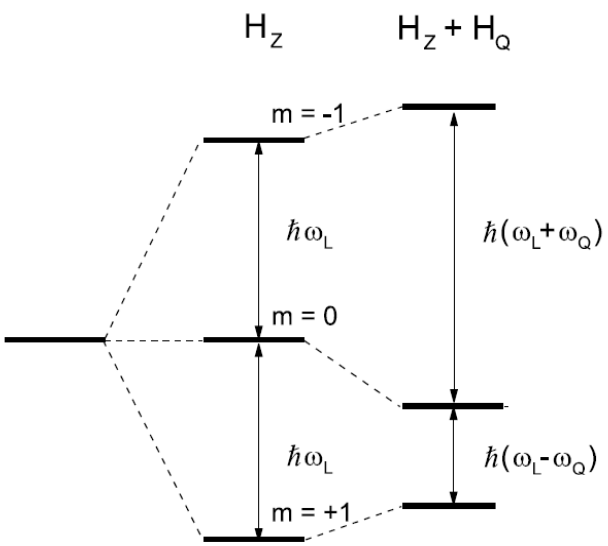
Quadrupolar Interaction

^{2}H: nuclear spin I=1

quadrupole moment Q





$$H_Q = \frac{eQ}{2I(2I-1)\hbar}\mathbf{IVI} \qquad V_{\alpha\beta} = \frac{\partial^2\Phi}{\partial r_\alpha \partial r_\beta}$$

Φ: electric potential

$$\omega(\theta,\phi) = \pm\, \delta/2\, [3\cos^2\theta - 1 - \eta \sin^2\theta \cos(2\phi)]$$

(θ,ϕ): polar coordinates of $\mathbf{B}_0$ in PAS of EFG tensors

δ: anisotropy parameter, η: asymmetry parameter

Basics of ^{2}H NMR Experiments

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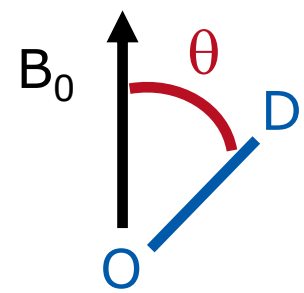
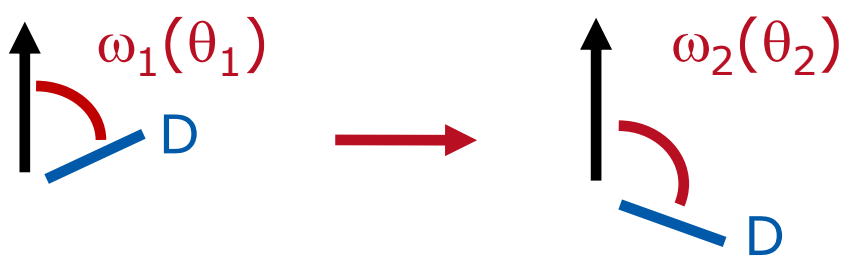
Quadrupolar Interaction for D_2O ($\eta \approx 0$)

The resonance frequency ω depends on the orientation of the O-D bond:

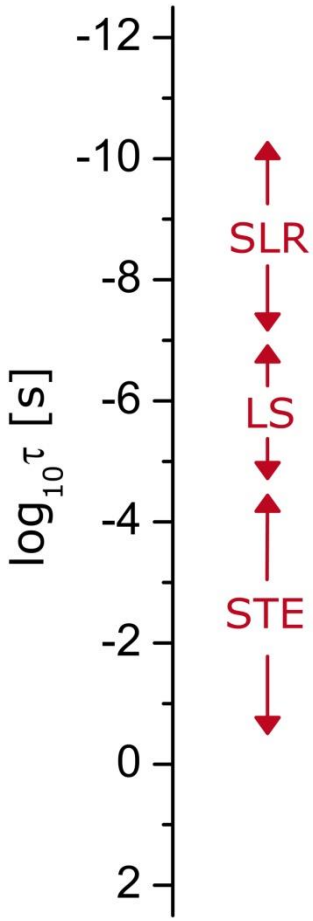
$$\omega(\theta) = \pm \delta/2\,(3\cos^2\theta - 1)$$



Molecular reorientation renders ω time dependent



Basics of ^{2}H NMR Experiments



Spin-lattice relaxation

$$1/T_1 = C \cdot [J(\omega_L) + 4J(2\omega_L)] \qquad J(\omega) = \int_0^\infty F_2(t)\cos(\omega t)dt$$

T_1 minimum at $\omega_L\tau = 0.6 \rightarrow \tau \approx 10^{-9}$ s

Line-shape analysis

$$\omega(\theta) = \pm \delta/2 \,(3\cos^2\theta - 1)$$

Motional narrowing at $\delta\tau = 0.6 \rightarrow \tau \approx 10^{-6}$ s

Stimulated-echo experiments

$$F_2(t_m) = \langle \omega(0) \cdot \omega(t_m) \rangle$$

$1/\delta \leq \tau \leq T_1 \rightarrow \tau \approx 10^{-3}$ s

^{2}H NMR Spin-Lattice Relaxation

$$\frac{1}{T_1} = \frac{2}{15}\delta^2\left[J_2(\omega_0) + 4J_2(2\omega_0)\right] \qquad J_2(\omega) = \int_0^\infty F_2(t)\cos(\omega t)dt \qquad F_2(t) = \frac{\langle P_2[\cos(\theta(0)]P_2[\cos(\theta(t)]\rangle}{\langle P_2[\cos(\theta(0)]P_2[\cos(\theta(0)]\rangle}$$

Exponential correlation function (BPP)

$$F_2(t) = e^{-t/\tau} \qquad J_{BPP}(\omega) = \frac{\tau}{1+\omega^2\tau^2}$$

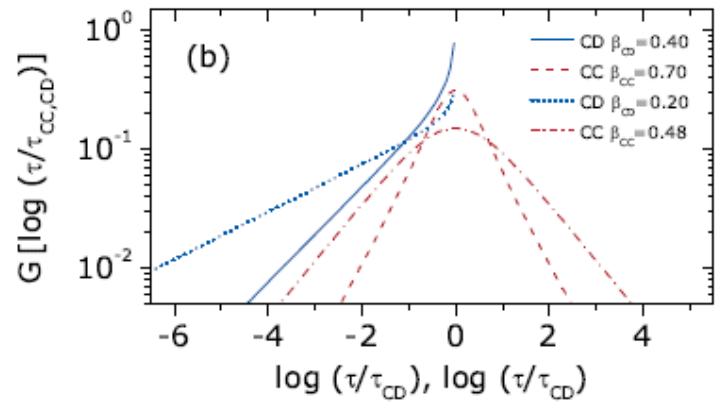
Distribution of correlation times G(log τ)

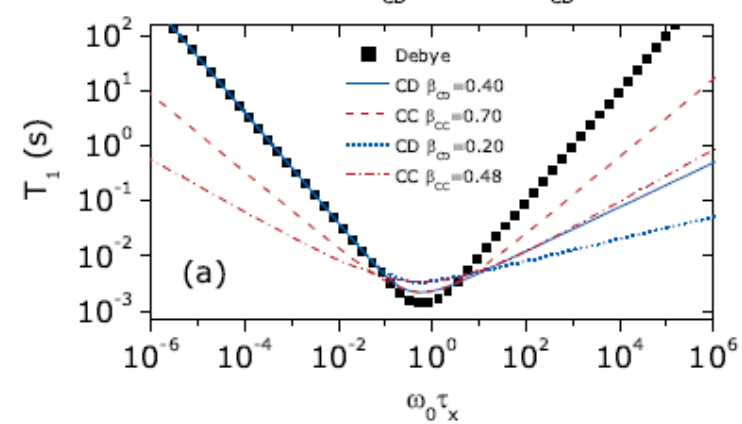
Cole-Davidson spectral density

$$J_{CD}(\omega) = \omega^{-1}\sin[\beta_{CD}\arctan(\omega\tau_{CD})]/(1+\omega^2\tau_{CD}^2)^{(\beta_{CD}/2)}$$

Cole-Cole spectral density

$$J_{CC}(\omega) = \frac{\omega^{-1}\sin(\frac{\beta_{CC}\pi}{2})(\omega\tau_{CC})^{\beta_{CC}}}{1+(\omega\tau_{CC})^{2\beta_{CC}} + 2\cos(\frac{\beta_{CC}\pi}{2})(\omega\tau_{CC})^{\beta_{CC}}}.$$





^{2}H NMR Line-Shape Analysis

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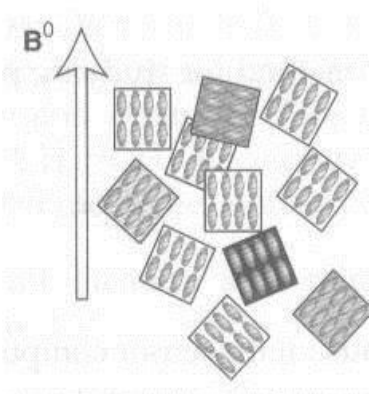
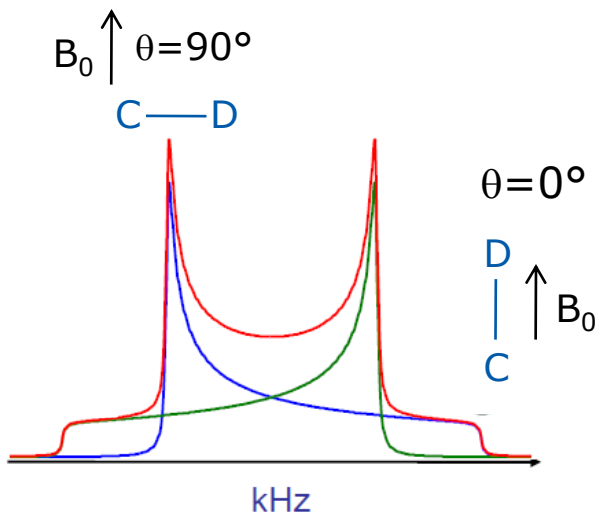
Limit of slow motion: $\tau >> 1/\delta \approx 1\mu s$ (η=0)

In crystalline powders and amorphous materials, a distribution of molecular orientations exists (powder average)

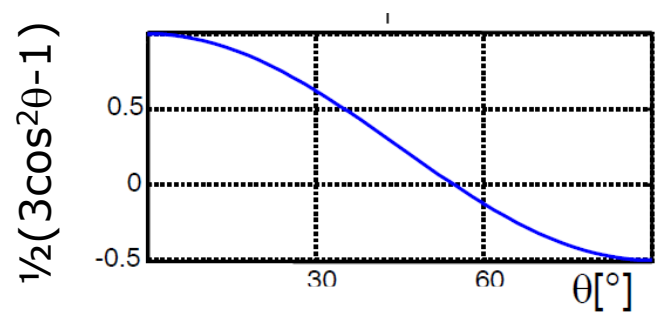
Due to the dependence of the frequency on the orientation, broad powder spectra are observed



M.H. Levitt
Spin Dynamics



$$\omega(\theta) = \pm \delta/2\ (3\cos^2\theta - 1)$$



^{2}H NMR Line-Shape Analysis

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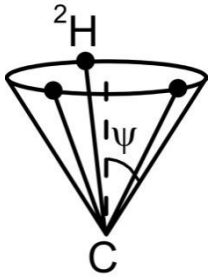
Limit of fast motion: $\tau << 1/\delta \approx 1\mu s$ ($\eta=0$)

Isotropic Reorientation: $\bar{\delta} = 0,\ \bar{\eta} = 0$

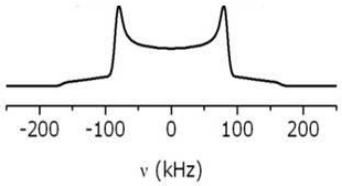
Uniaxial Reorientation: $\bar{\delta} = \delta/2\,(3\cos^2\Psi - 1)$ $\quad \bar{\eta} = 0$

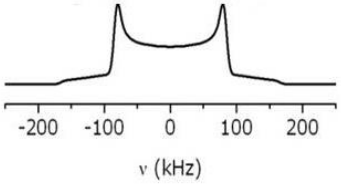


Isotropic | **Uniaxial**

$\tau << 1/\delta$ — high temperature

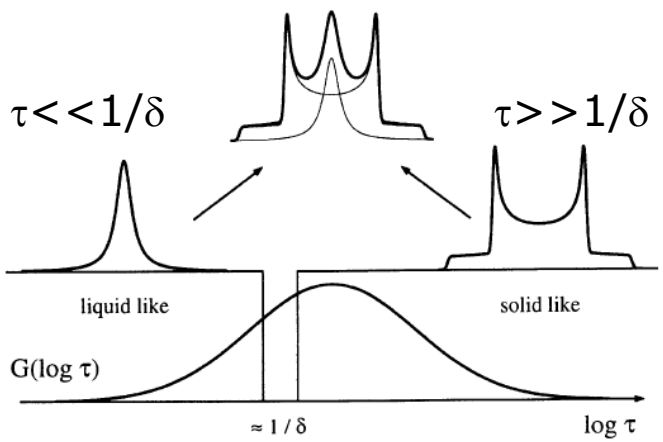
$\tau >> 1/\delta$ — low temperature

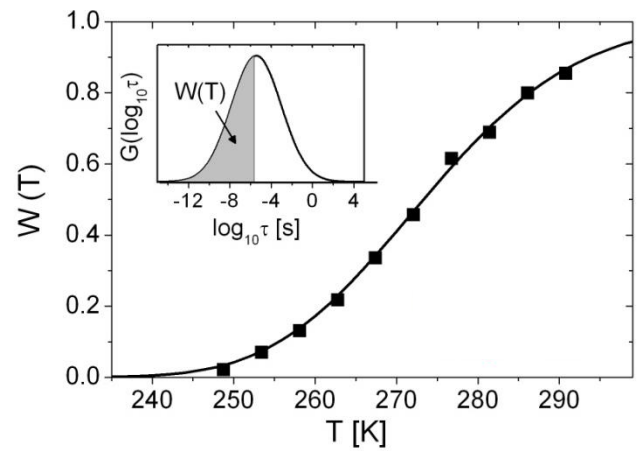




^{2}H NMR Line-Shape Analysis

If a broad distribution of correlation times G(log τ) exists,
e.g., because of a broad distribution of activation energies $g(E_a)$





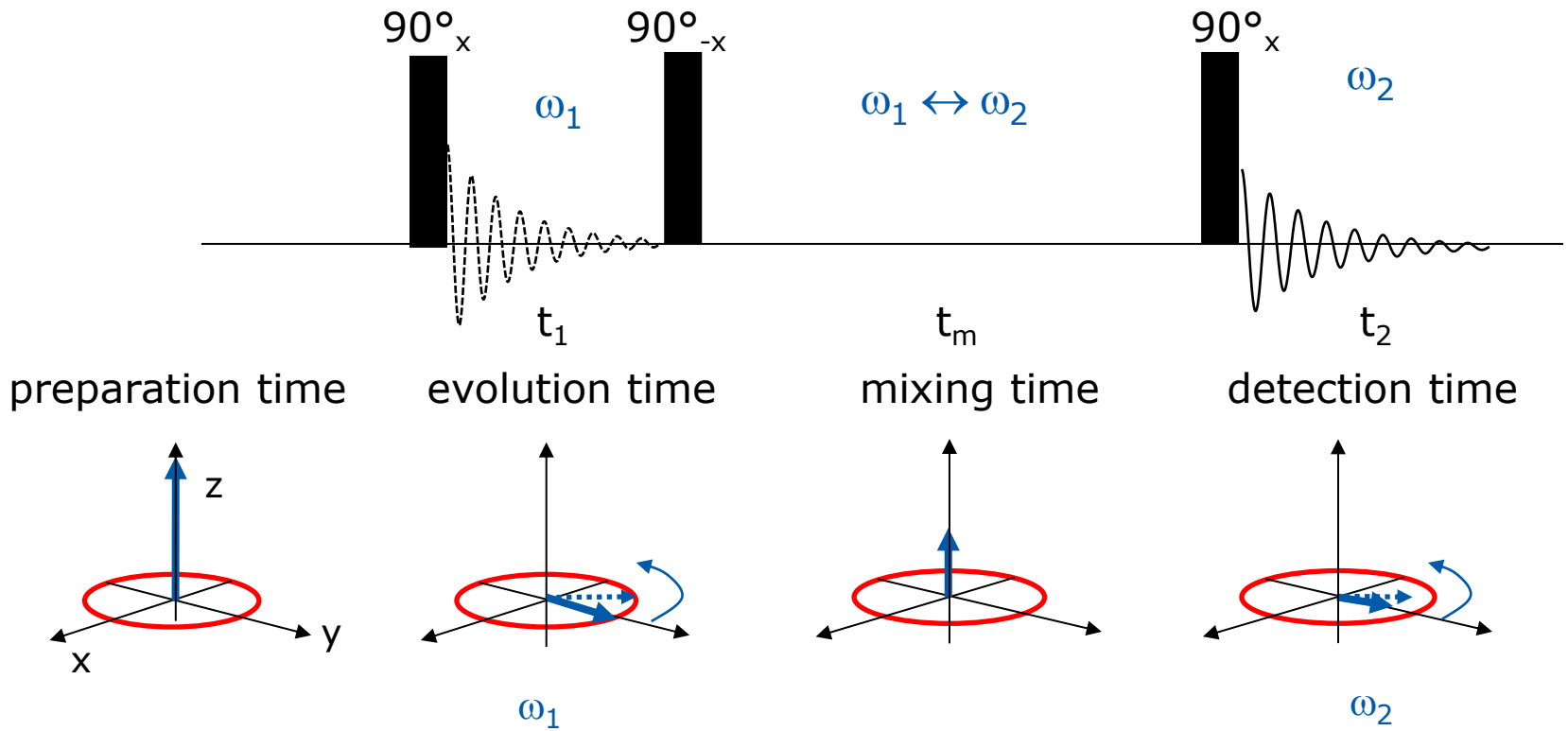
Weighted superposition of a broad line and a narrow line

(two-phase spectra)

$g(E_a)$ can be determined from the weight of the narrow line:

$$g(E_a) = \frac{dW(T)}{dT}$$

2D ^{2}H NMR Experiments



Evolution (t_1) and detection (t_2) times are limited by T_2

Mixing time t_m is limited by $T_1 >> T_2$

2D ^{2}H NMR Experiments

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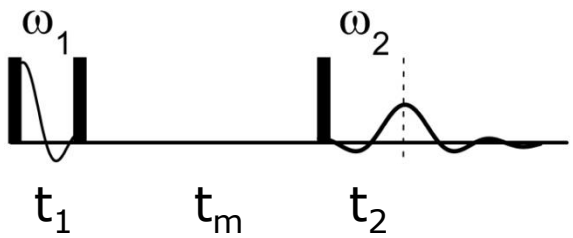
Stimulated-echo sequence:
t_m: mixing time



$t_1, t_2 < t_m \approx \tau < T_1$

$t_m \approx 10^{-5}\text{-}10^{0}$ s

Measure and correlate the frequencies at two times:

$$F_2^{SS}(t_m;t_p) = \langle \sin(\omega_1 t_1)\cdot\sin(\omega_2 t_2)\rangle$$

$$F_2^{CC}(t_m;t_p) = \langle \cos(\omega_1 t_1)\cdot\cos(\omega_2 t_2)\rangle$$

Analysis in frequency domain:

Vary t_1 and t_2 for constant t_m

2D NMR spectrum $S(\omega_1,\omega_2)$ results from 2D Fourier transformation

Analysis in time domain:

Vary t_m for constant $t_1 = t_2 \equiv t_p$

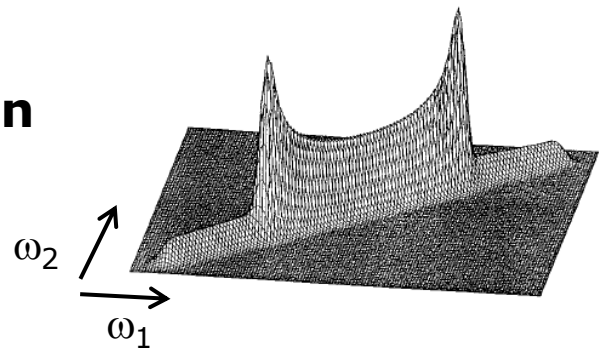
Rotational correlation function is obtained from analysis of echo height

$$F_2(t_m;t_p) = \langle \cos[(\omega_2-\omega_1)t_p]\rangle$$

2D ^{2}H NMR Spectra

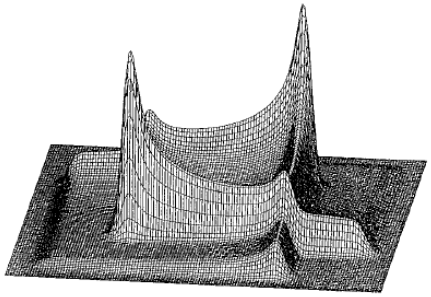
No reorientation

$(\omega_1 = \omega_2)$

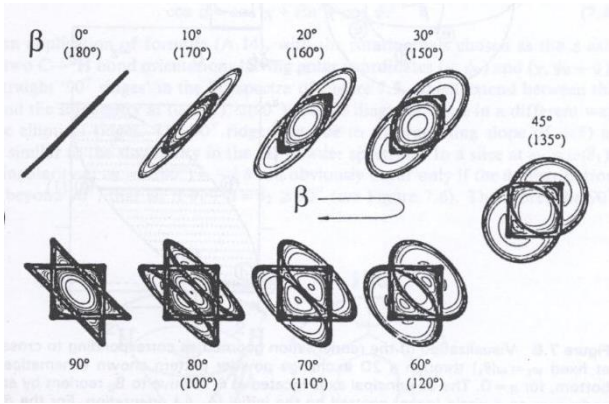


Isotropic reorientation

$(\omega_1 \neq \omega_2)$



Defined jump-angle β



Schmidt-Rohr and Spiess
Multidimensonal NMR and Polymers

$S(\omega_1,\omega_2)$ measures the joint probability of finding a frequency ω_1 before the mixing time t_m *and* frequency ω_2 after this period

^{2}H NMR Stimulated-Echo Experiments

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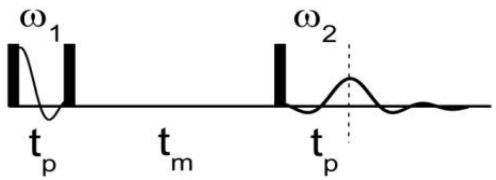
Meaning of the evolution time

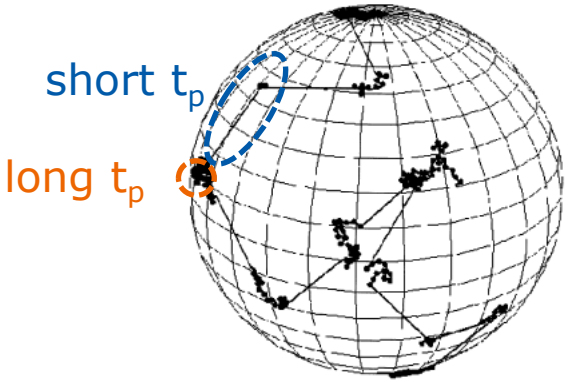


$$F_2(t_m; t_p) = \langle \cos[(\omega_2 - \omega_1)t_p] \rangle$$

Variation of the evolution time enables adjustment of angular resolution of stimulated-echo experiments

short t_p : poor resolution (large angles)

long t_p: high resolution (small angles)



^{2}H NMR Stimulated-Echo Experiments

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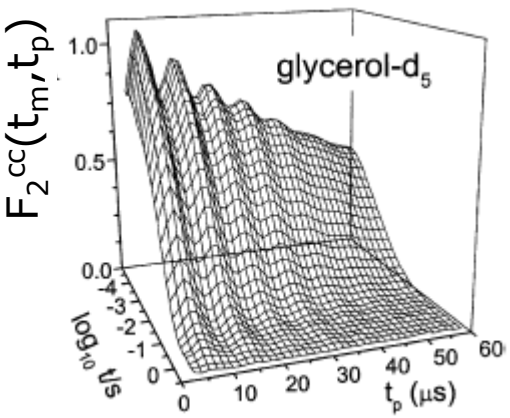
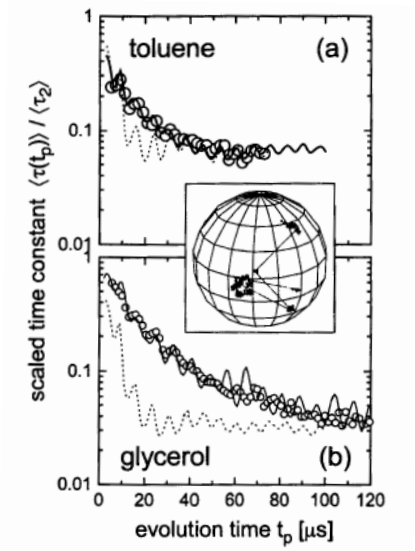
Meaning of the evolution time

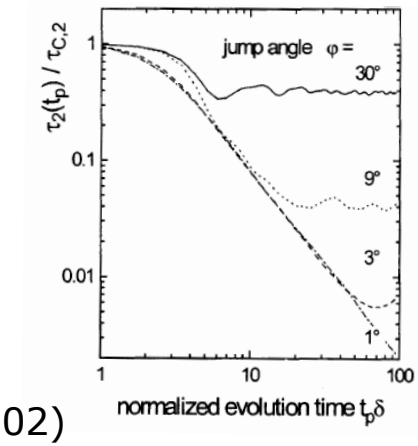
Structural relaxation of supercooled liquids





Determination of jump angle φ:

$$\frac{\tau(t_p \to \infty)}{\tau(t_p \to 0)} = \frac{3}{2}\sin^2\varphi$$



Böhmer, Springer (2002)

Evolution-time dependence $\tau(t_p)$ provides access to jump angles

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Biological Background

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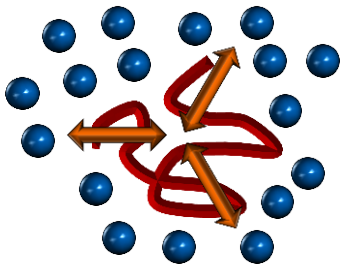
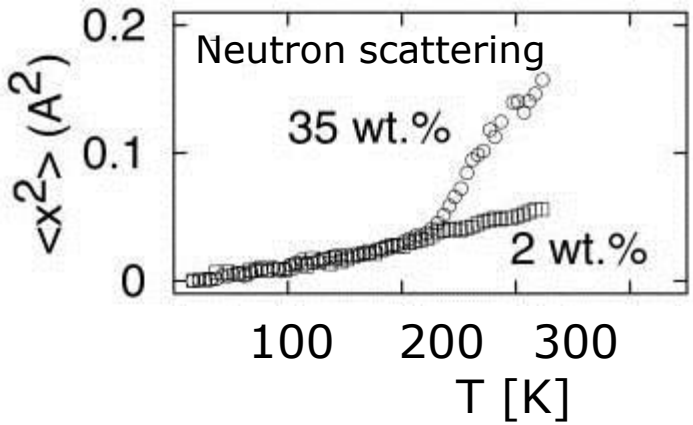
Interactions between protein and water are essential for biological functions



Slaving

Frauenfelder



Bacteriorhodopsin

Temperature-dependent experiments yield valuable insights

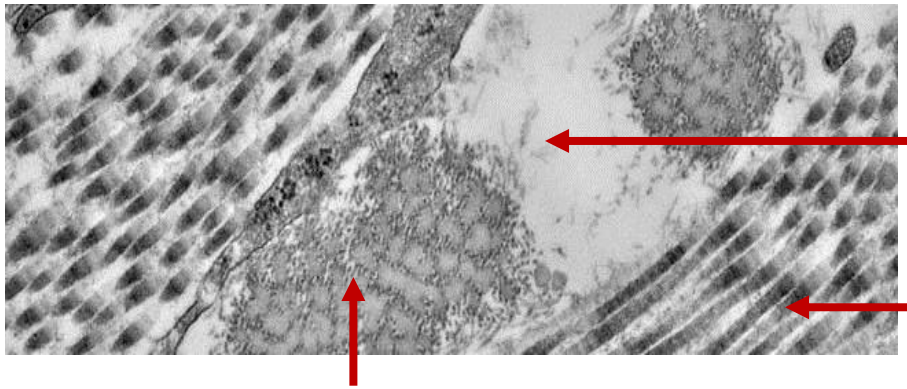
Fenimore et al., PNAS (2002)

Hydrated proteins:

Dynamical transition at 200-220 K

is often accompanied by an onset of the biological function

Biological Background



Connective Tissue

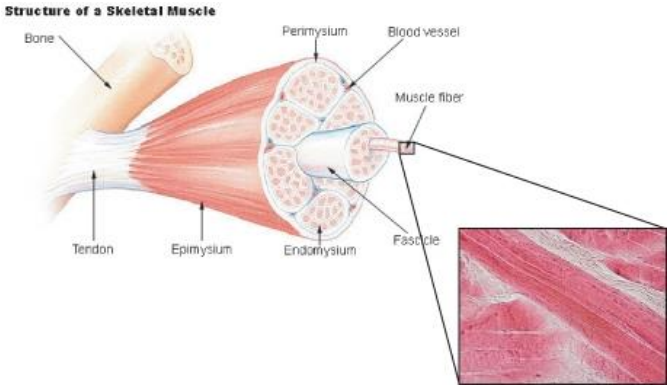
amorphous
ground substance

collagen fibers
(tensile strength)

elastin fibers (elasticity)

Skeletal Muscle

myoglobin
warrants oxgen
transport



Samples

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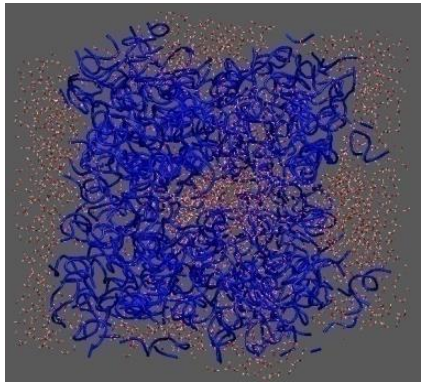
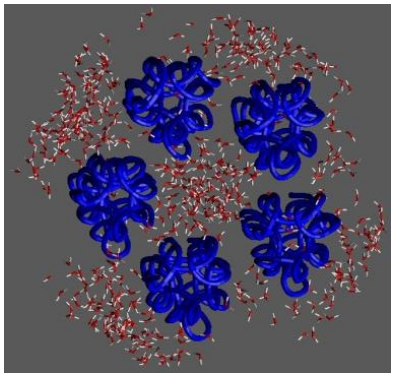
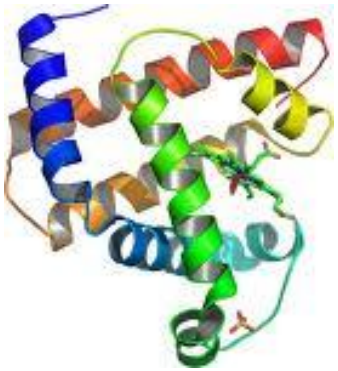
Elastin + D_2O



Collagen + D_2O



Myoglobin + D_2O



^{2}H NMR studies on the dynamical behaviors of protein-water mixtures

Low hydration levels h= 0.2-1.0 (g water/ g protein)

^{2}H NMR Spin-Lattice Relaxation

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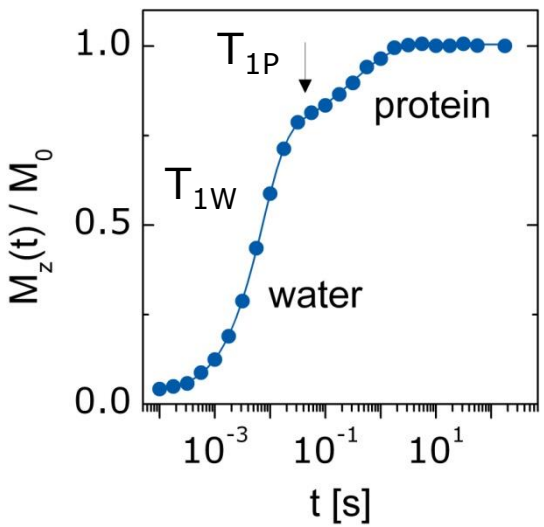
Due to proton exchange, a fraction of deuterons arrives at proteins



Collagen + D_2O

M. V.,
PRL 101, 225701 (08)

Magnetization builds up in two steps:

1. step (T_{1W}): supercooled water
2. step (T_{1P}): protein

Signal from protein hydration waters can be singled out in partially relaxed experiments

^{2}H NMR Spin-Lattice Relaxation

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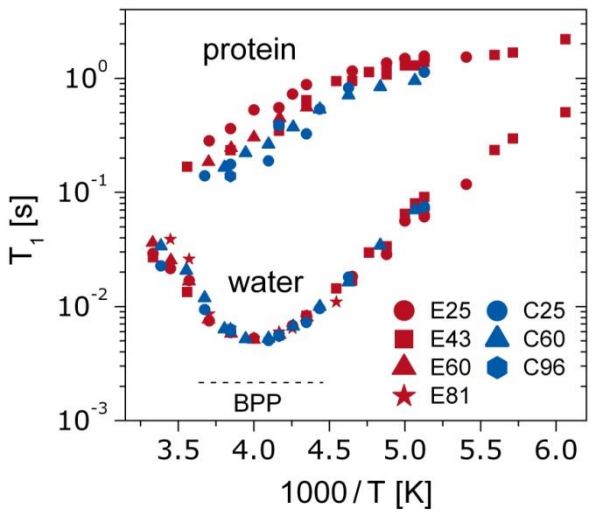
Elastin/Collagen + D_2O



$\omega_L = 2\pi \cdot 76.8$ MHz

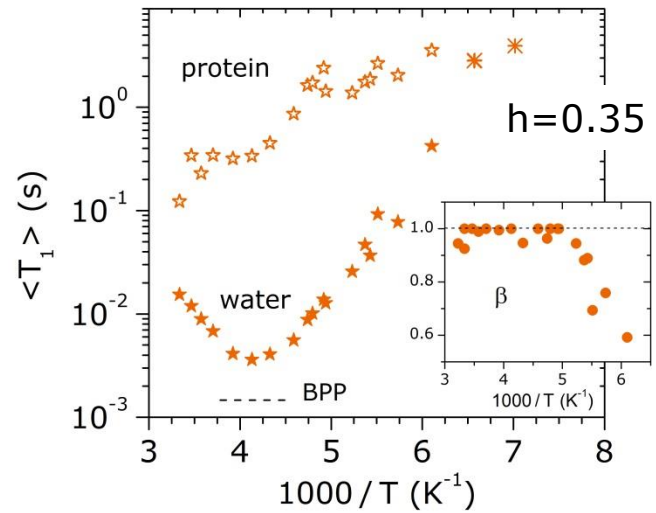
$$1/T_1 = C \cdot [J(\omega_L) + 4J(2\omega_L)]$$

$$J(\omega) = \int_0^\infty F_2(t)\cos(\omega t)dt$$

BPP: $\mathbf{F_2(t) = e^{-t/\tau}}$

$$J_{BPP}(\omega) = \frac{\tau}{1+\omega^2\tau^2}$$

Myoglobin + D_2O



$\omega_L = 2\pi \cdot 46.1$ MHz

Highly comparable water dynamics

Very broad distribution G(log τ)

^{2}H NMR Spin-Lattice Relaxation

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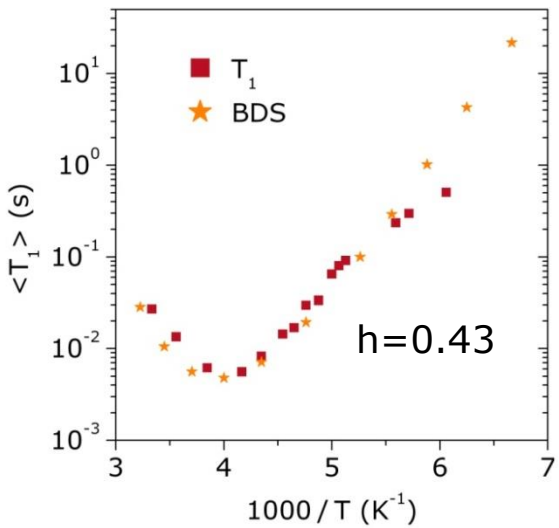
Elastin + D_2O

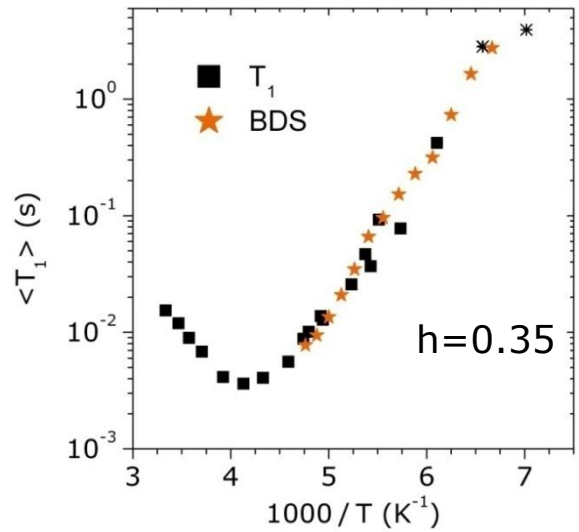


DS: Gainaru et al.

$$g(E) \propto \exp\left(\frac{E-E_a}{2\sigma^2}\right)$$

E_a=6330K
σ=580K

Myoglobin+ D_2O



DS: Jansson & Swenson

$$\varepsilon_{CC} = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+(i\omega\tau_{CC})^{\alpha_{CC}}}$$

Cole-Cole
$\alpha_{CC} = 0.48$

NMR and DS yield nicely consistent results

^{2}H NMR Spin-Lattice Relaxation

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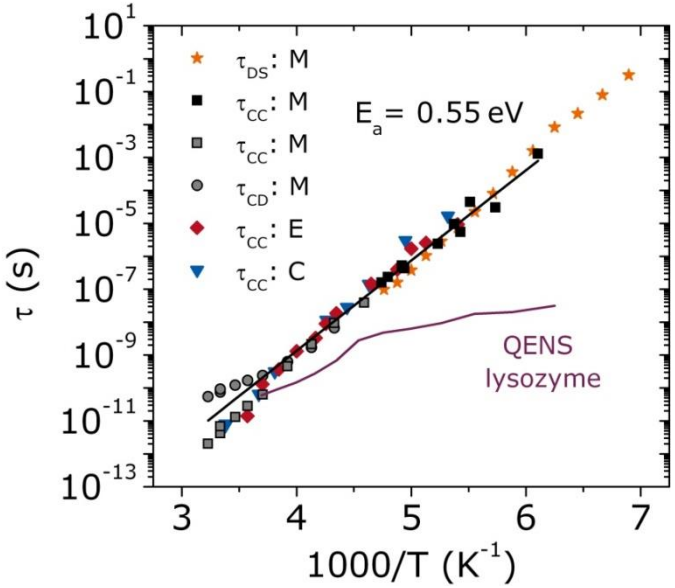
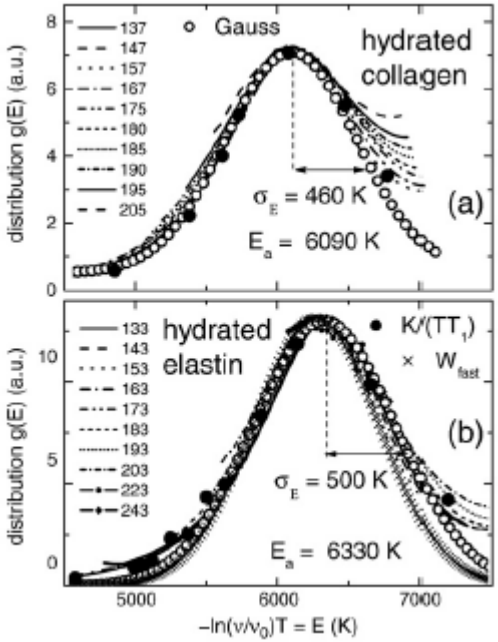
Collagen/Elastin/Myoglobin + D_2O



Lusceac et al. (BBA 10)

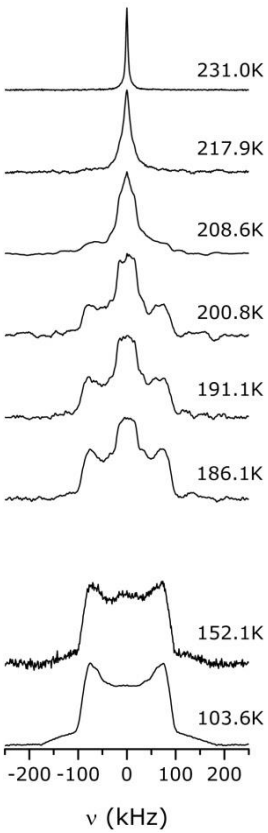


Lusceac et al. (JNCS 11)

No indication of a fragile-strong transition at ca. 225 K

Gaussian distribution of activation energies $g(E_a)$

^{2}H NMR Line-Shape Analysis



Myoglobin + D_2O

T ≥ 210K:

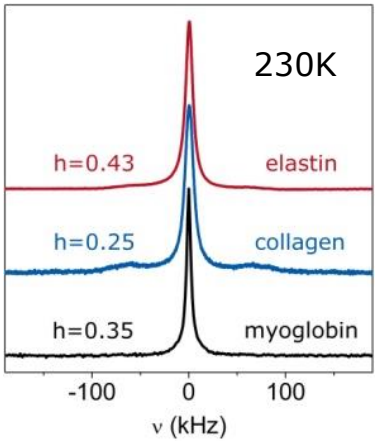
Fast isotropic reorientation
($\tau < 1/\delta \approx 1\mu s$)

210K ≥ T ≥ 140K:

Fast anisotropic reorientation
($\tau < 1/\delta \approx 1\mu s$)

140K > T:

Absence of reorientation on a time scale of $1/\delta \approx 1\mu s$

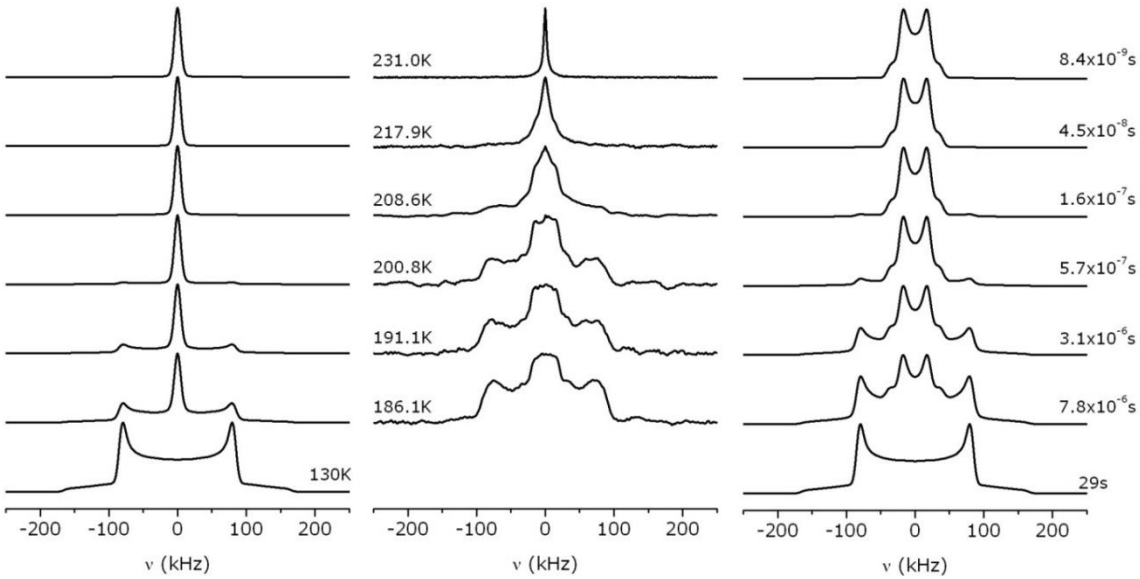


Lusceac et al.
(BBA 10)

Mechanism for water dynamics changes at ~ 210-220 K

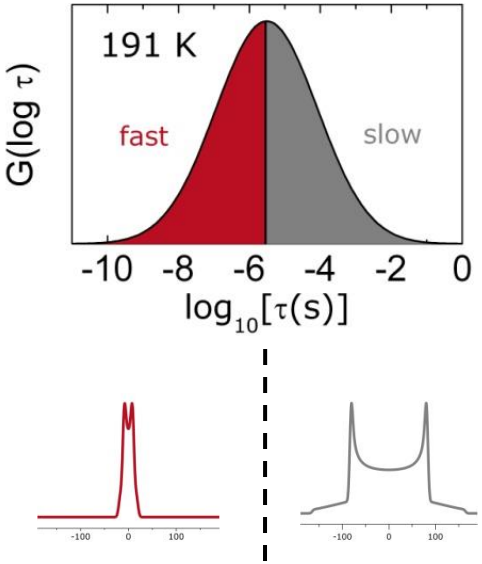
^{2}H NMR Line-Shape Analysis

isotropic **Myoglobin+D_2O** anisotropic



Lusceac et al. (JPC B 10)

Coexistence of $\tau<1/\delta$ and $\tau>1/\delta$



$\tau\approx1/\delta$

Crossover from isotropic to anisotropic rotational motion on the microseconds time scale upon cooling through T≈210-220 K

Mechanisms for Low-Temperature Motion

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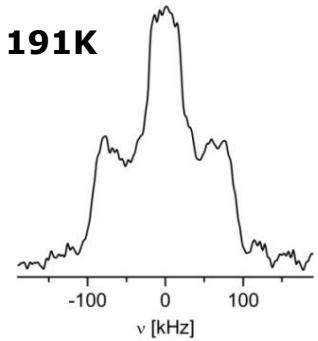
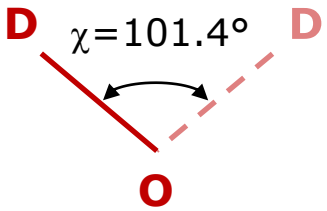
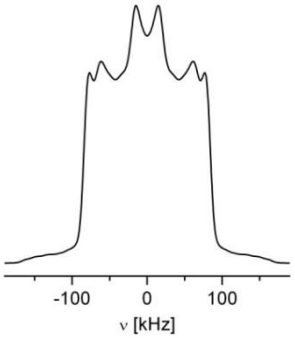
Myoglobin + D_2O (h=0.35)

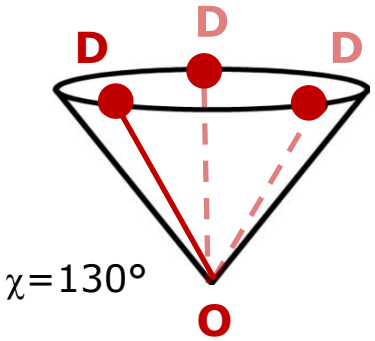


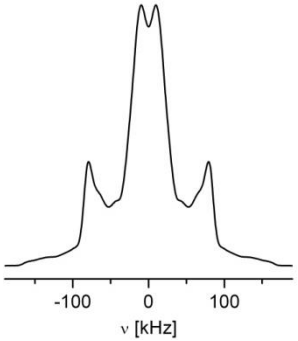
π flip



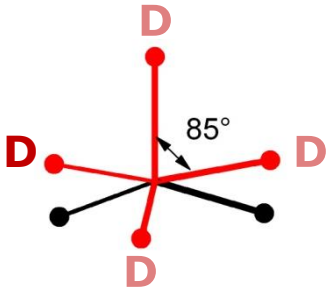


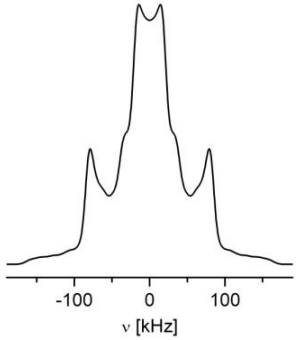
3-site jump





distorted tetrahedral jump





Anisotropic large-angle (90-130°) jumps with a distribution of geometries ?

2D ^{2}H NMR Spectra

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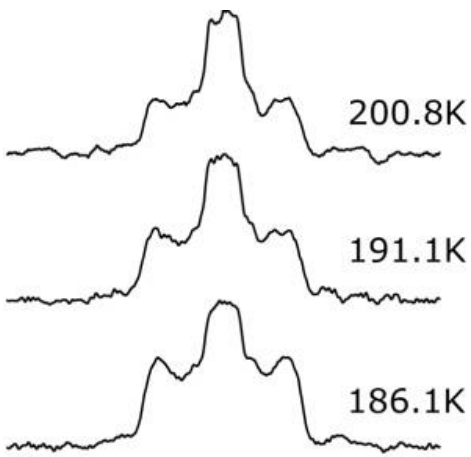
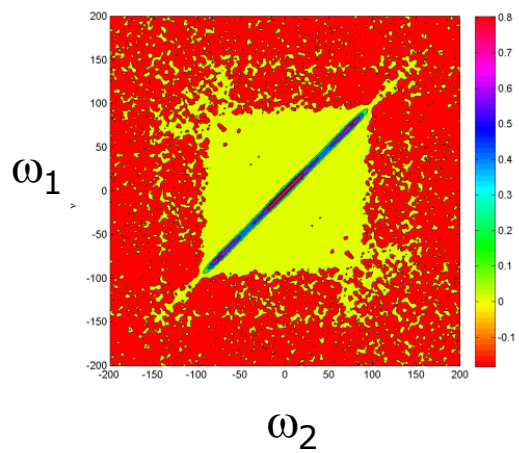
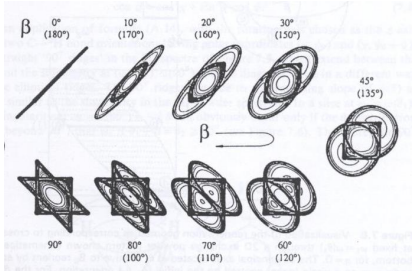
Myoglobin + D_2O

1D Spectrum



2D Spectrum





T=176 K
t_m=10 ms

Lusceac et al., JPC B (2010)

Below 200 K, water shows anisotropic reorientation, which has a large amplitude, but no well-defined geometry

^{2}H NMR Stimulated-Echo Decays

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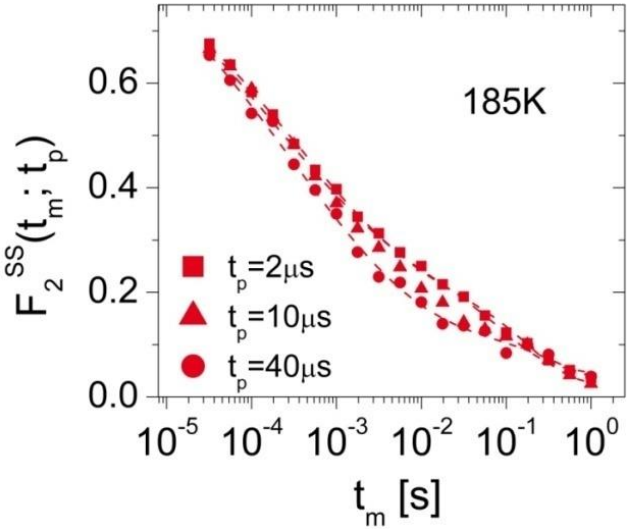
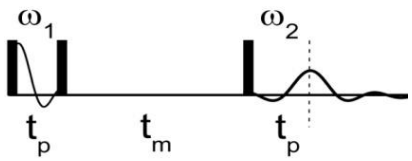
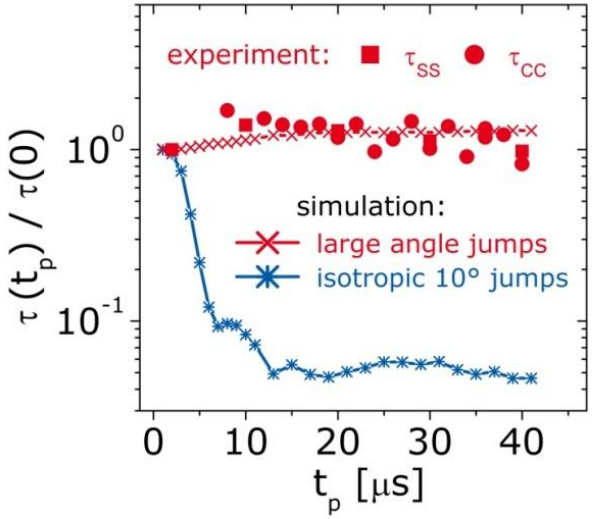
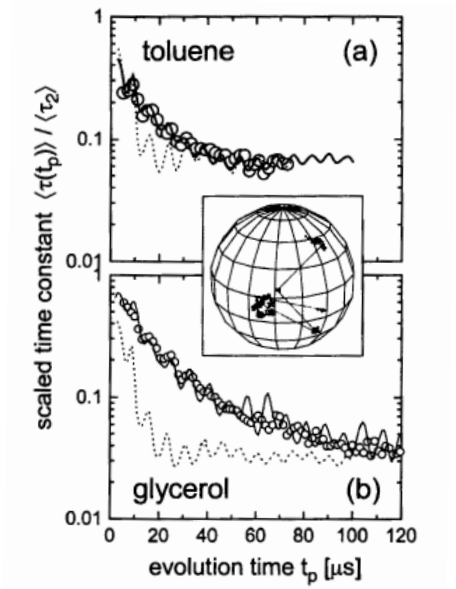
Elastin + D_2O







Böhmer, Springer (2002)



Low-temperature water reorientation is characterized by:

Non-exponentiality

Large-angle jumps

M.V. PRL (2008)

^{1}H NMR Diffusometry

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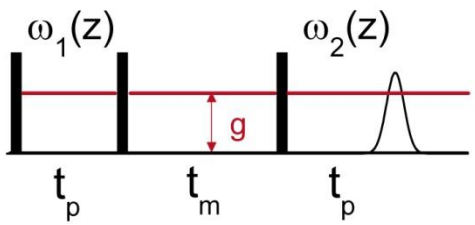
Application of a magnetic field with a field gradient **g**=(0,0,g):

$$\omega(z) = -\gamma(B_0 + gz)$$

Investigation of translational diffusion

Static field gradients (SFG)

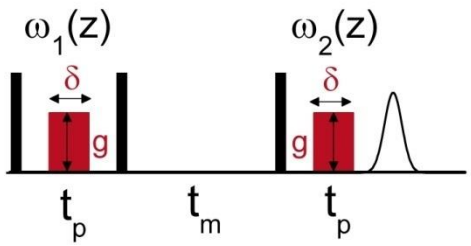


higher gradients, more stable

$t_p \leq T_2$

$t_m \leq T_1$

Pulsed field gradients (PFG)



higher SNR, spectral resolution

For normal diffusion: ($t_m >> t_p$)

$$S = S_0 \exp\left(-q^2 D t_m\right)$$

$q = g\gamma t_p$ bzw. $q = g\gamma\delta$

$D = 10^{-15} - 10^{-9}$ m²/s

$1/q \approx 100$ nm

^{1}H SFG NMR Diffusometry

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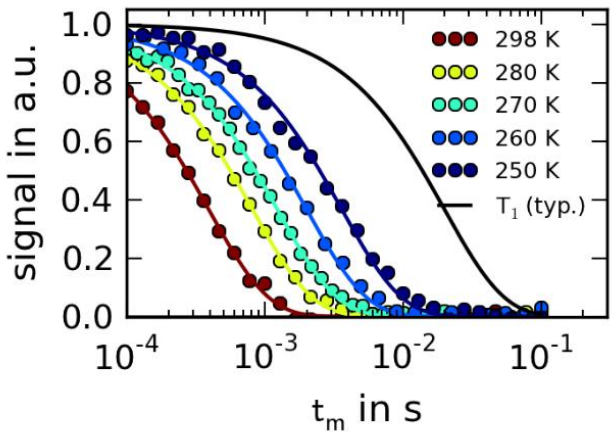
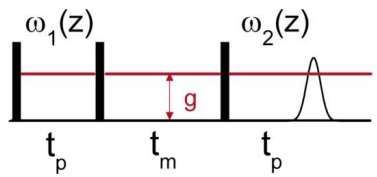
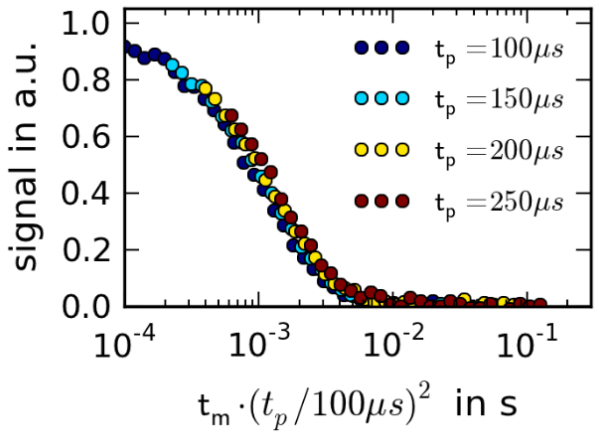
Myoglobin + H_2O: high temperatures





$$S = S_0 \exp\left(-q^2 D t_m\right)$$

$$q = g\gamma t_p$$



Rosenstihl et al. (JCP 11)

Hydration water shows long-range translational diffusion

^{1}H SFG NMR Diffusometry

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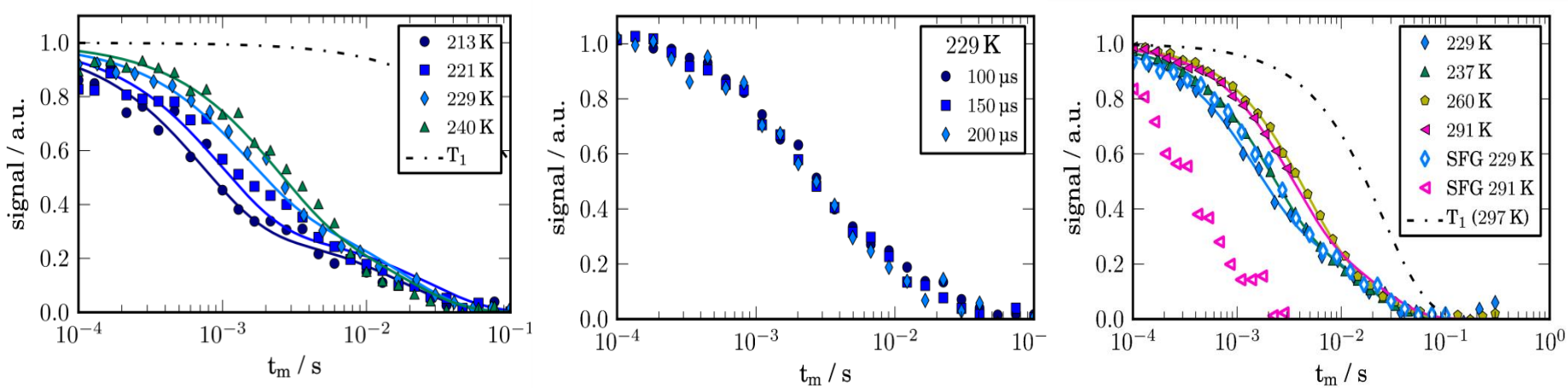
Myoglobin + H_2O: low temperatures

gradient field | **gradient field** | **homogeneous field**



Rosenstihl et al. (JCP 11)

At low temperatures, stimulated-echo amplitude does not decay due to water diffusion, but rather due to cross relaxation

^{1}H SFG NMR Diffusometry

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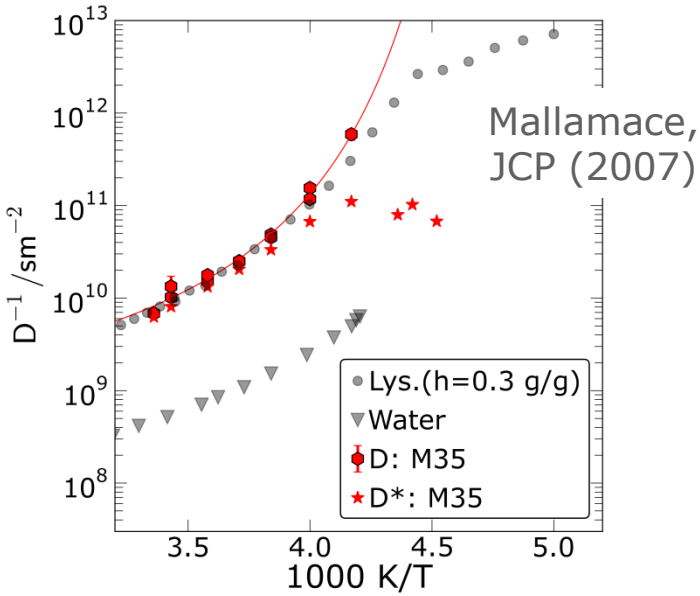
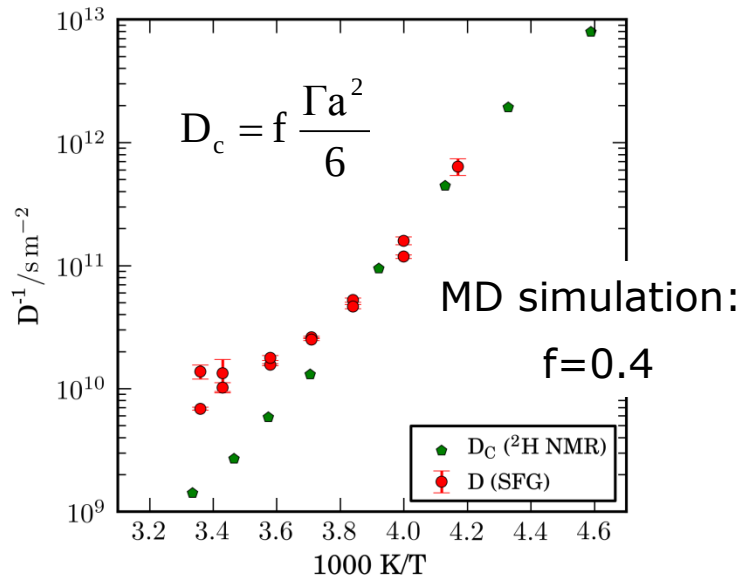
Temperature-dependent diffusion coefficients



Kink in temperature dependence due to onset of cross relaxation

Translational motion vs. rotational motion



Different temperature dependence of rotational and translational motion

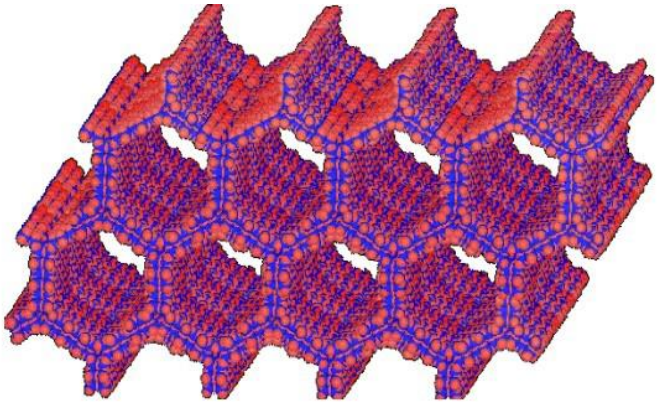
Outline

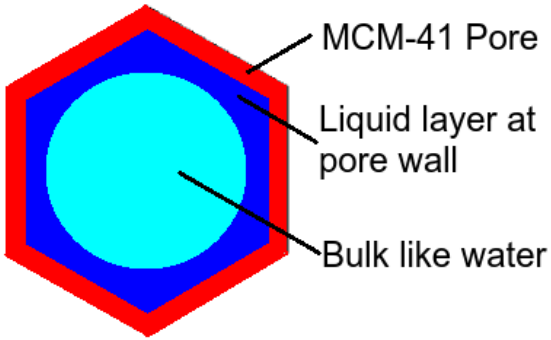
TECHNISCHE UNIVERSITÄT DARMSTADT

- Introduction
- Basics of ^{2}H NMR Experiments
- Water dynamics in protein matrices
- Water dynamics in silica matrices
- Summary

Samples

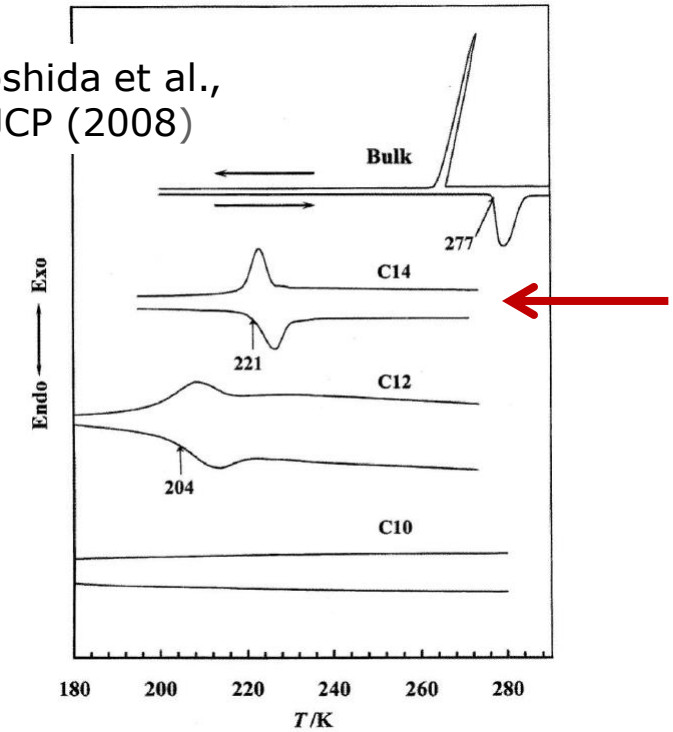
D_2O (80% & 90%) in MCM-41 (C14)



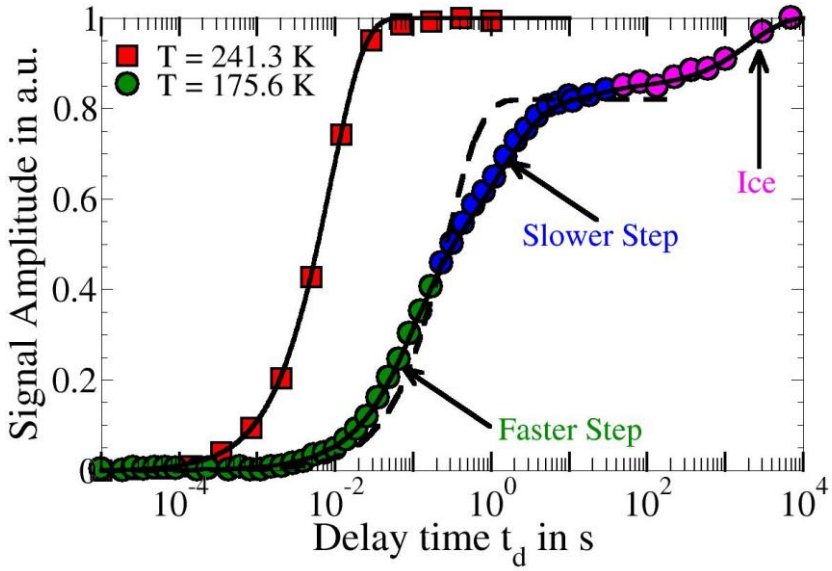


Pore diameter: 2.9 nm

Yoshida et al., JCP (2008)



^{2}H NMR Spin-Lattice Relaxation



Buildup of magnetization occurs in

- 1 step at high temperatures
- 3 steps at low temperatures

In the following: suppression of ice signal

^{2}H NMR Spin-Lattice Relaxation

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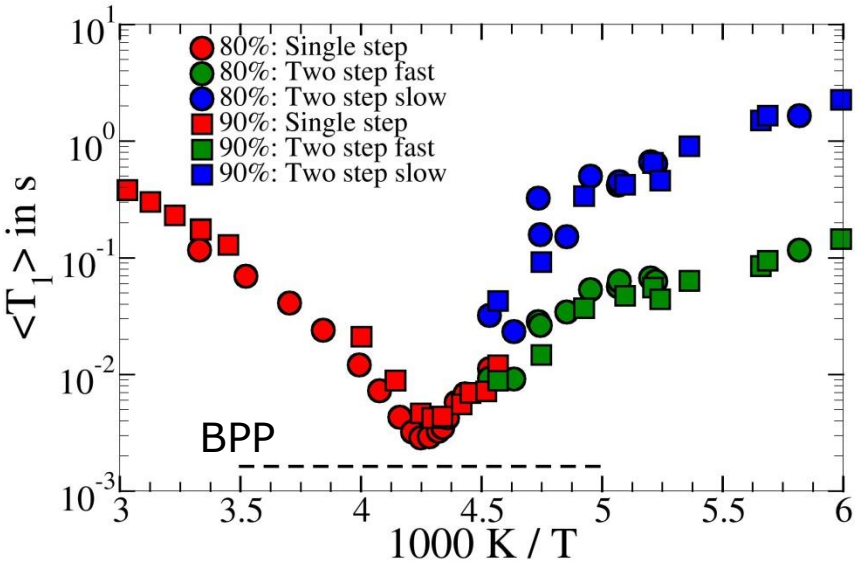
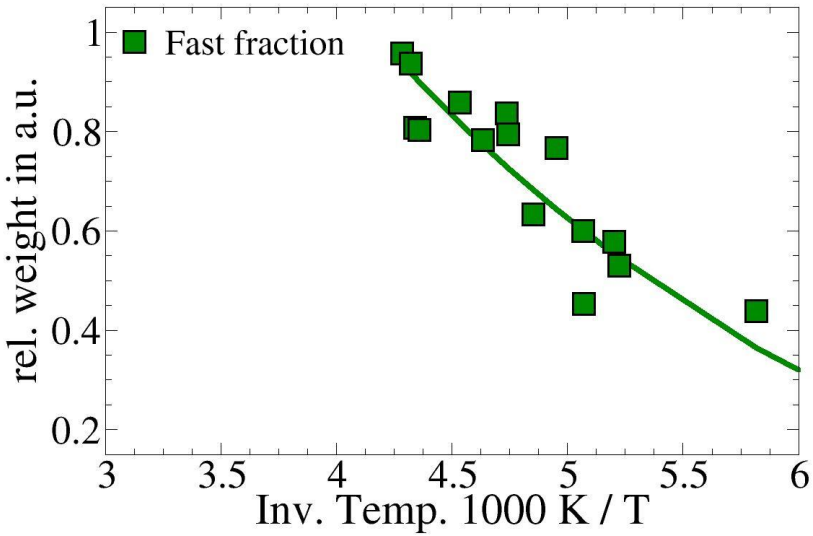
Relaxation times



Height of first relaxation step



Dynamically distinguishable water species

Kink in the temperature dependence at T~210 K

Fast relaxation step vanishes upon cooling

^{2}H NMR Spin-Lattice Relaxation

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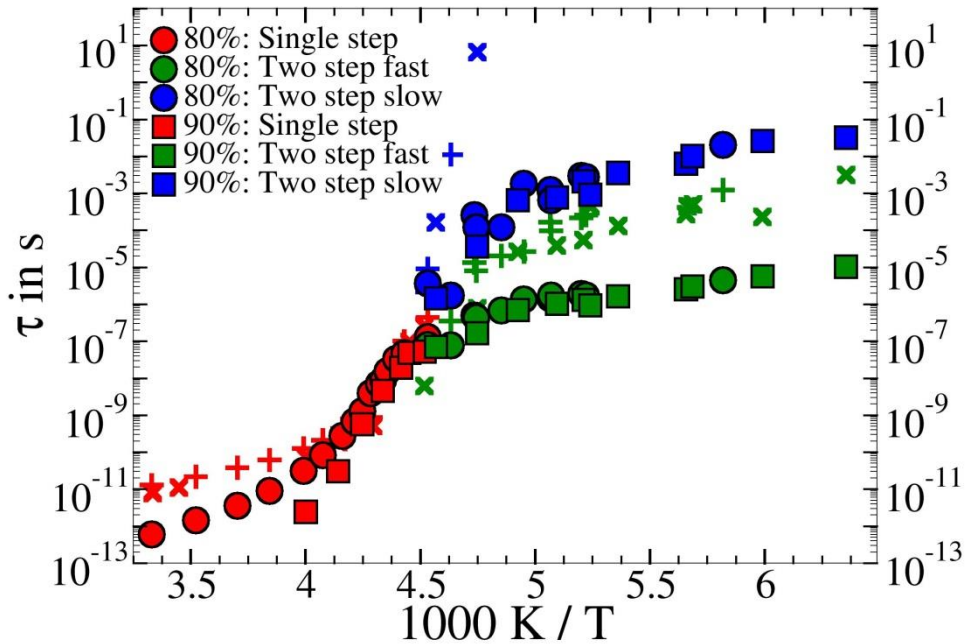
Correlation times

Cole-Cole spectral density

(symbols)

β_{CC}=0.59 (80%)

β_{CC}=0.40 (90%)



Cole-Davidson spectral density

(crosses)

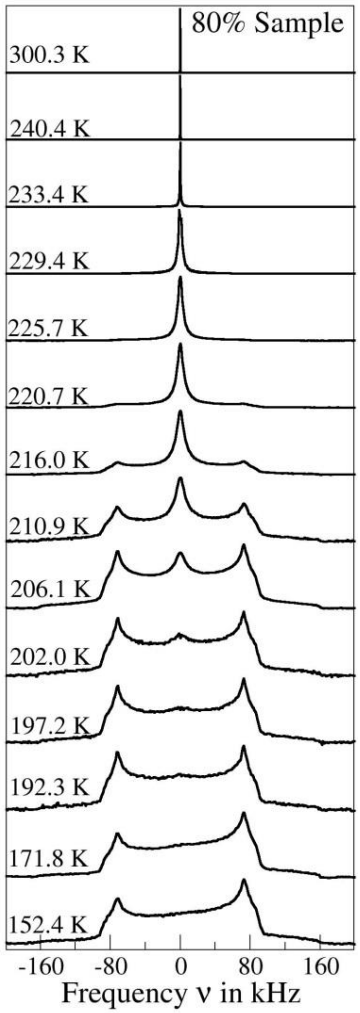
β_{CD}=0.30 (80%)

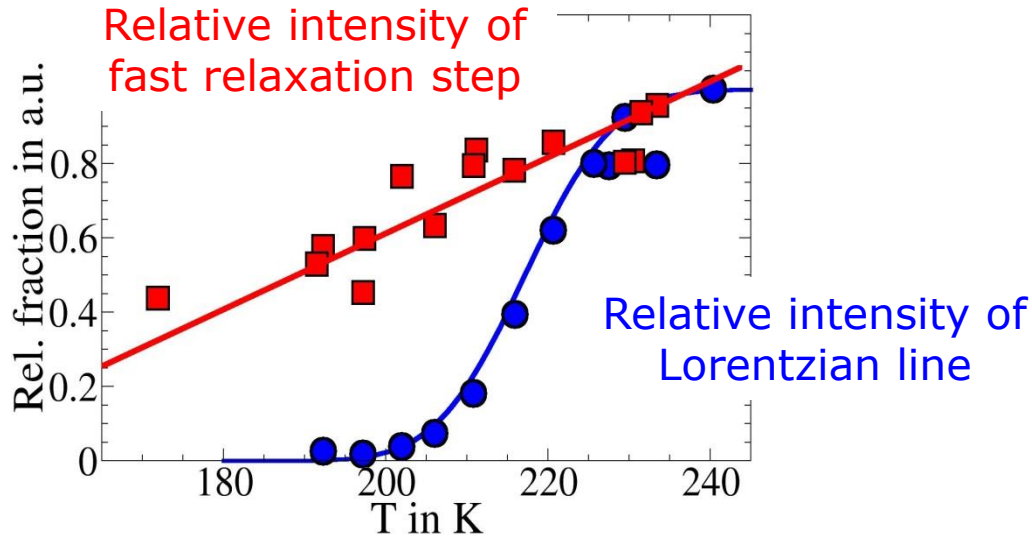
β_{CD}=0.18 (90%)

Kink in temperature dependence at 210 K ???

Distribution of correlation times G(log τ)

^{2}H NMR Line-Shape Analysis





A fraction of water molecules shows liquid-like dynamics down to T~200 K

Dynamically distinguishable water molecules: continuous and/or bimodal distribution G(log τ) ?

^{2}H NMR Stimulated-Echo Decays

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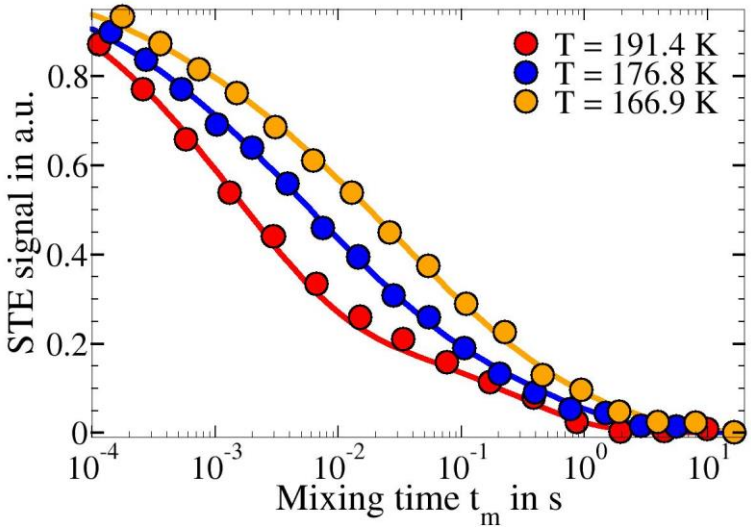
Correlation functions

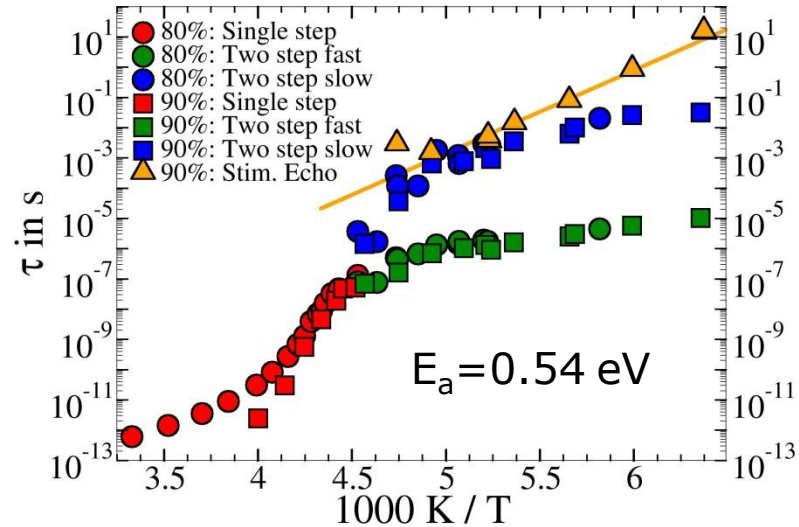


$$F_2^{CC}(t_m;t_p) = \langle \cos(\omega_1 t_p)\cdot\cos(\omega_2 t_p)\rangle$$

Non-exponential correlation function

Finite plateau at intermediate times

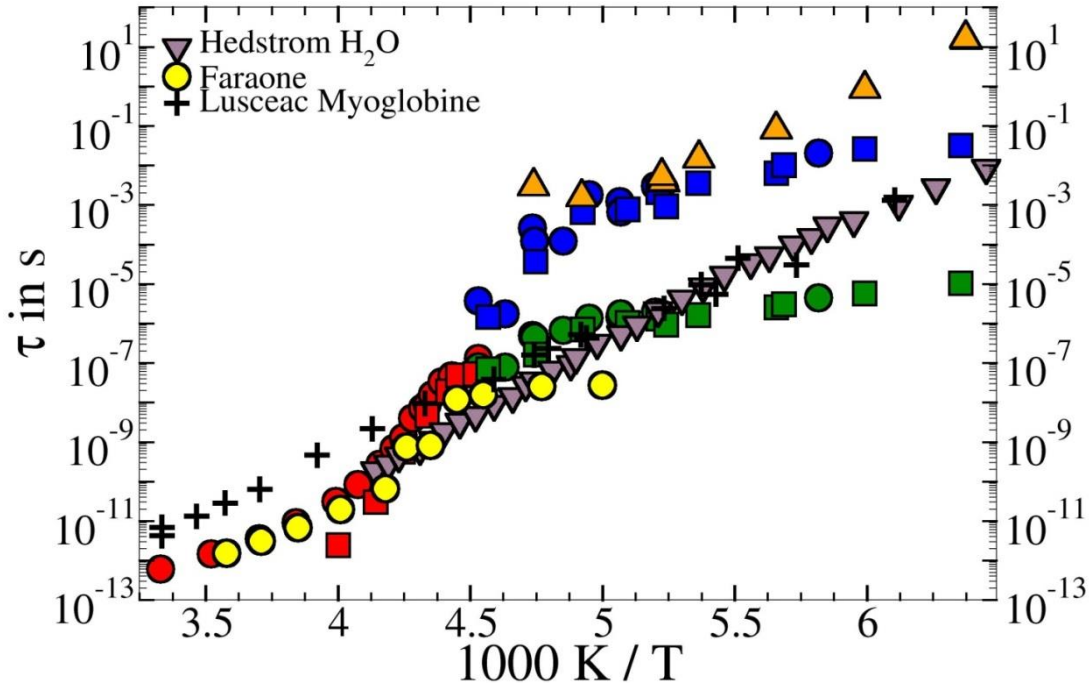
Temperature dependence



$$F_2^{CC}(t_m) = (1-F_\infty)\cdot\exp\left[-\left(\frac{t_m}{\tau_K}\right)^\beta\right] + F_\infty$$

Diverse temperature dependence from spin-lattice relaxation and stimulated-echo experiments

Comparison of Correlation Times



Temperature dependence:

Consistent with neutron scattering data at high temperatures

Consistent with dielectric spectroscopy data at low temperatures

^{2}H NMR Stimulated-Echo Decays

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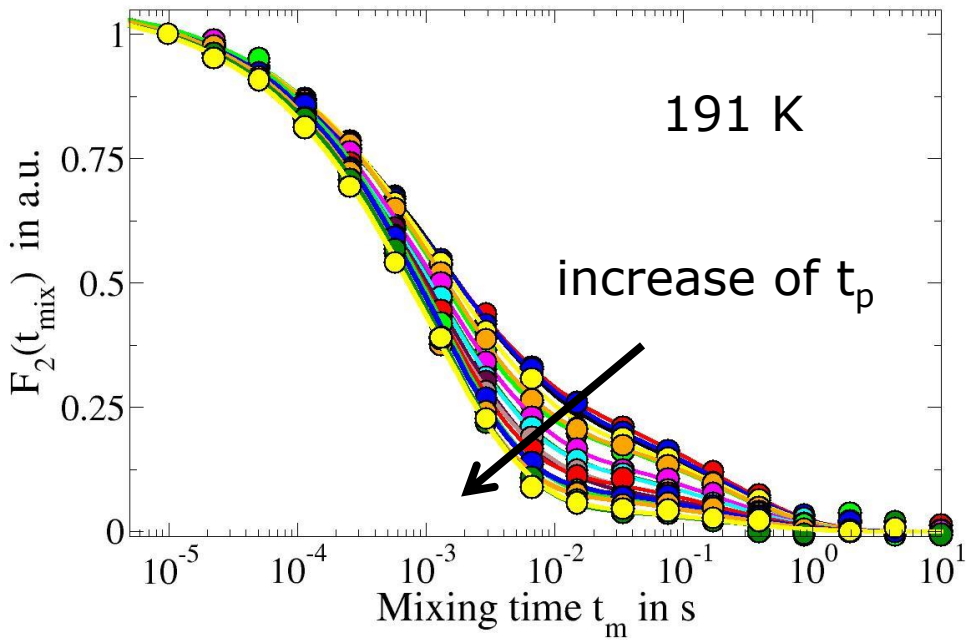
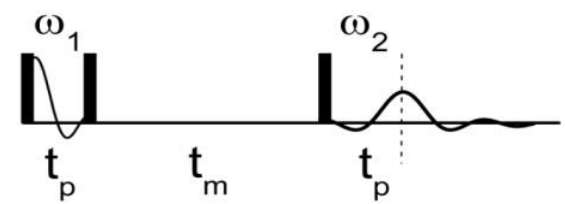
Evolution-time dependence





$$F_2^{CC}(t_m;t_p) = \langle \cos(\omega_1 t_p) \cdot \cos(\omega_2 t_p) \rangle$$

$$F_2^{CC}(t_m) = (1 - F_\infty) \cdot \exp\left[-\left(\frac{t_m}{\tau_K} \right)^\beta \right] + F_\infty$$

Plateau height decreases with increasing angular resolution

^{2}H NMR Stimulated-Echo Decays

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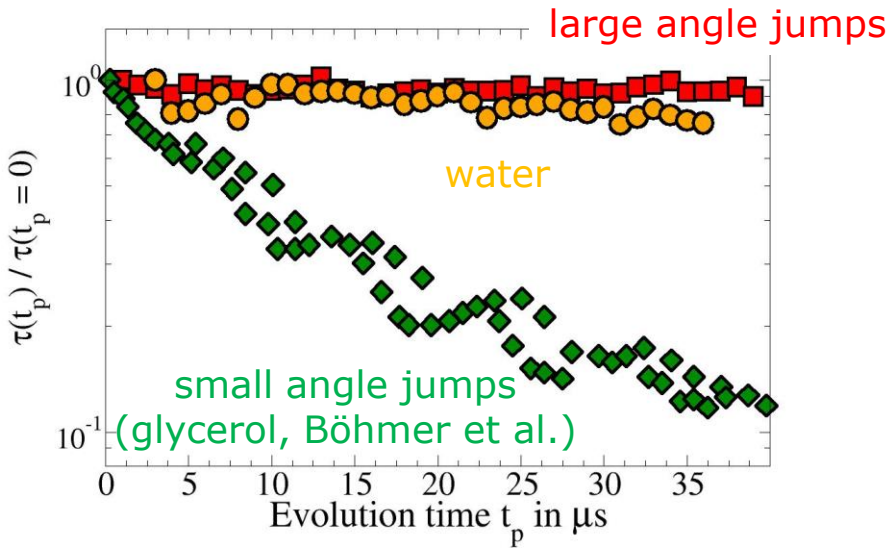
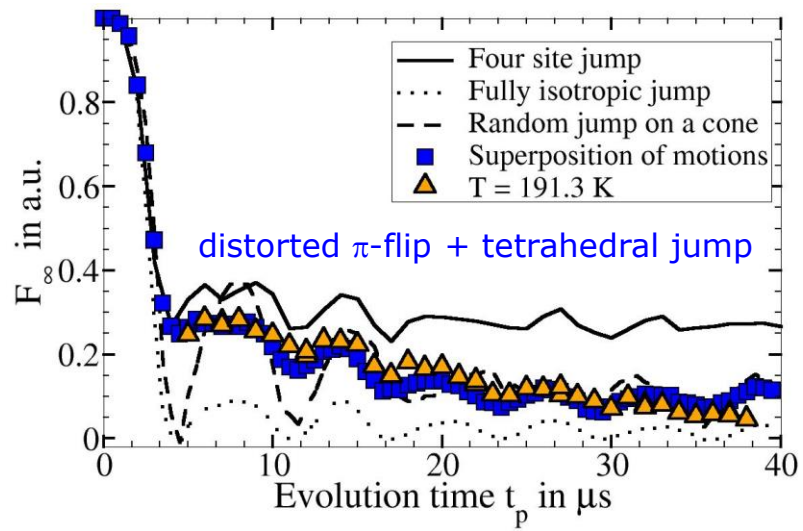
Evolution-time dependence

Correlation times



Plateau height



Large-angle jumps

Distorted anisotropic motion

Summary

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Water in protein matrices

shows no fragile-strong transition but a crossover from isotropic to anisotropic reorientation

The change of mechanism for rotational motion may be related to a crossover from diffusive motion to localized motion

Water in silica matrices

exhibits distinguishable dynamical processes

The processes dominating above and below ~210K, respectively, have different temperature dependence

All surface waters

show universal low-temperature dynamics which involves large-angle jumps with distributions of motional geometries and correlation times

Thank You

TECHNISCHE UNIVERSITÄT DARMSTADT

Prof. R. Böhmer (Dortmund)
Prof. J. Swenson (Gotheborg)
Prof. G. Buntkowsky (Darmstadt)

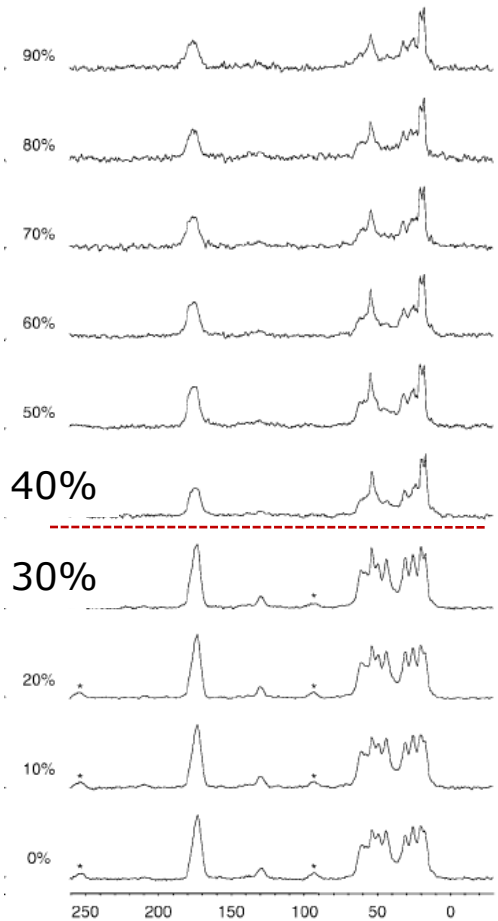
CONFINE DYNAMICS

Research unit 1583

DFG Deutsche Forschungsgemeinschaft

Dr. Sorin Lusceac
Dr. Markus Rosenstihl
Kerstin Kämpf
Matthias Sattig

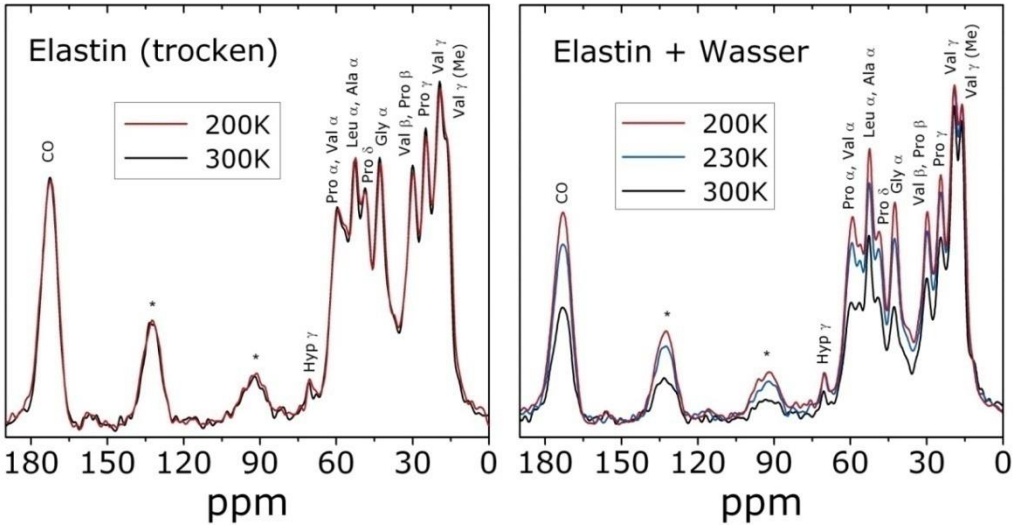
^{13}C CPMAS NMR Spectra



Perry et al., BJ (2002)

Hydrated Elastin (h=0.6 g/g)

^{13}C MAS NMR



Lusceac et al., BBA (2010)

Elastin dynamics:

- requires an existence of a hydration shell
- freezes in upon cooling through 200-230 K