Glass transition and functionality of hydrated proteins

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Functionality related to dynamics

Simplest characterization of dynamics:

Debye-Waller or Lamb-Mössbauer factor

$\exp(-Q^2 \langle u^2 \rangle/3)$

mean square displacement (MSD)

Definition of MSD ambiguous: mean over what?

- Average over sample atoms: **how weighted? Homogeneity?**
- Average over **what time?**
- Is Q^2u^2 **really << 1? Heterogeneity?**

Averaging time: defined by the experiment

Mössbauer spectr.: $t \sim 1\ \mu s$

Bragg diffraction: $t \sim \infty$

amorphous matter: energy/time analysis

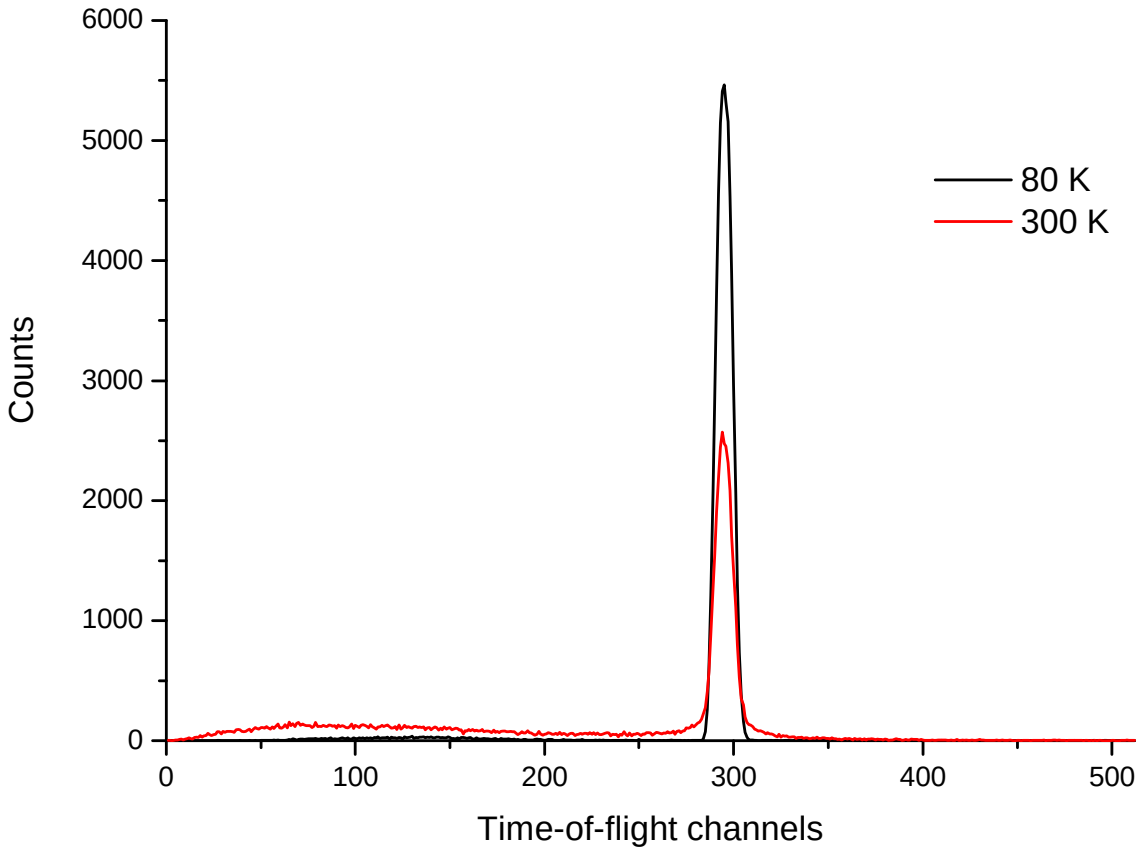
"Dynamic transition"

observed in the temperature dependence of MSD or DW

Goal: some additional experimental look

Time-of-flight inelastic neutron spectroscopy:

variable averaging time domain ~ 1 – 100 ps

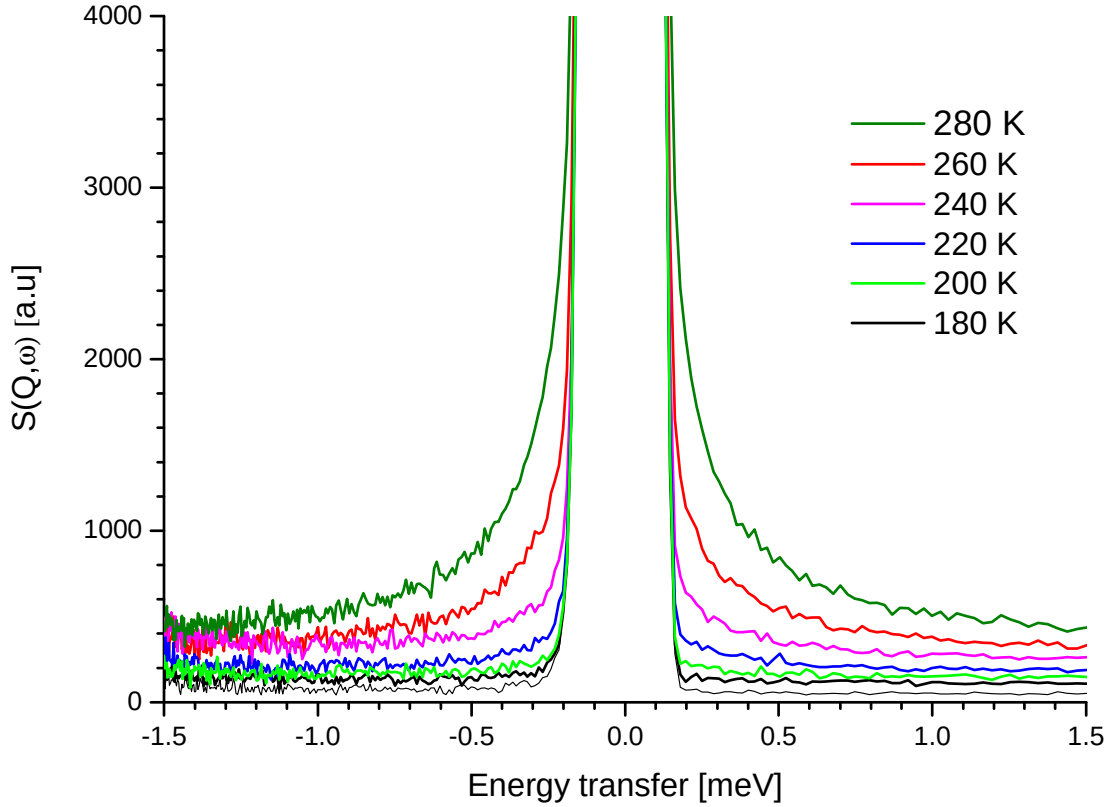


Additional dynamic process: “β relaxation”

time domain: t > 5 ps

approx. power law shape, “relaxation time” poorly defined

$< >_t$ for times up to ~t obtained by $\int Sd(\hbar\omega)$ for $|\omega| < 1/t$



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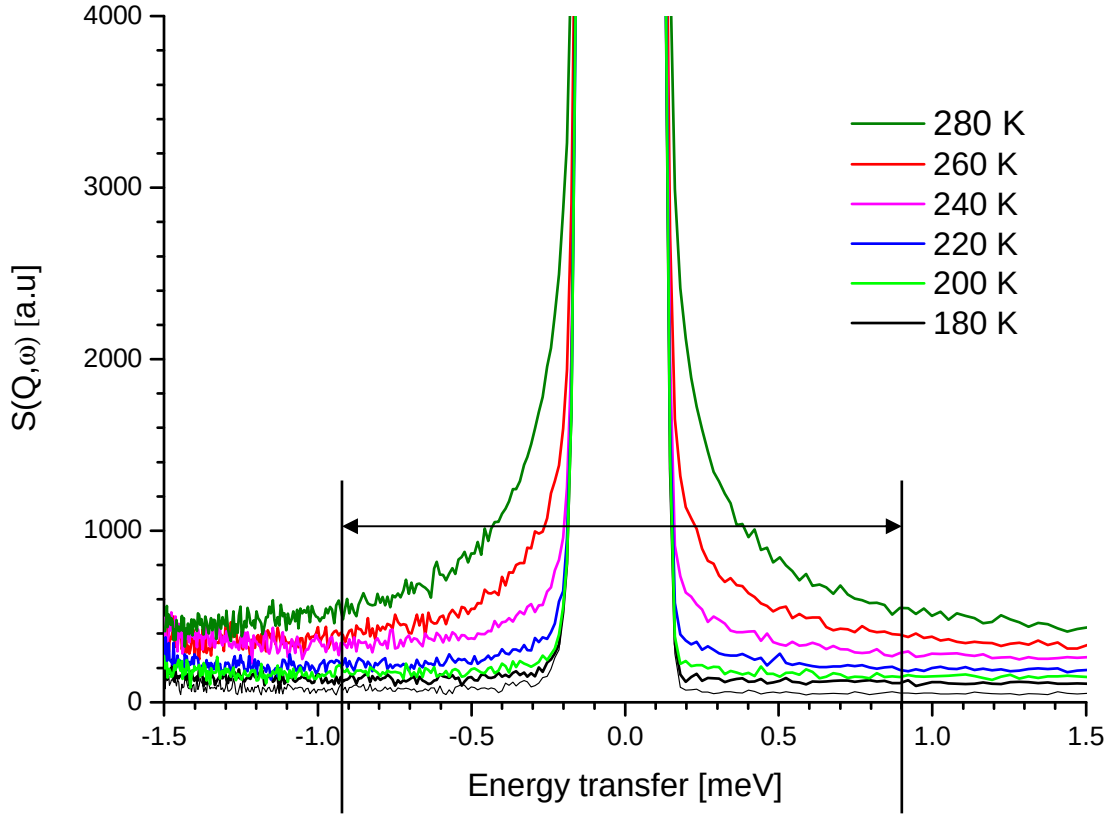
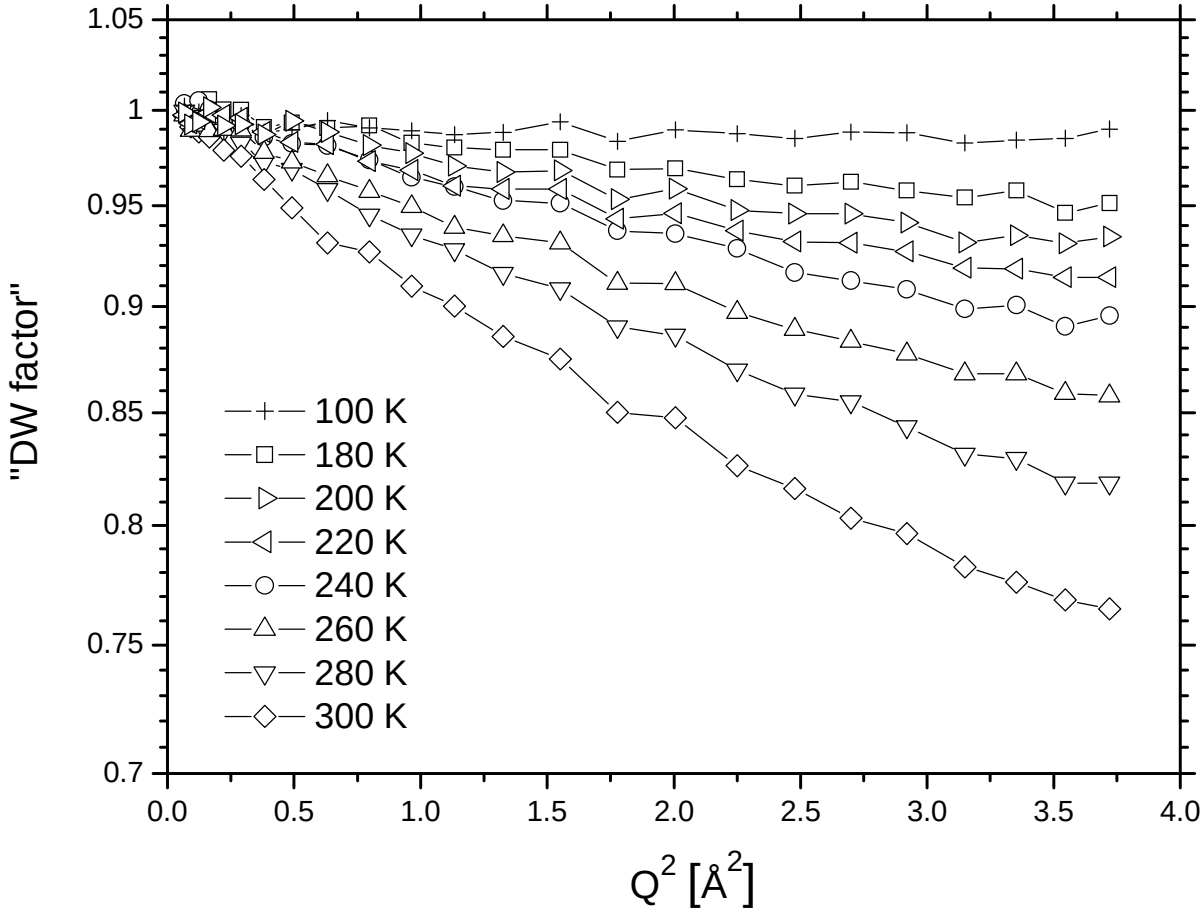


“Debye-Waller factor”

evaluated for two definitions of “elasticity”: 5 ps and 100 ps

$< u^2 >$: initial slope of reasonably straight lines

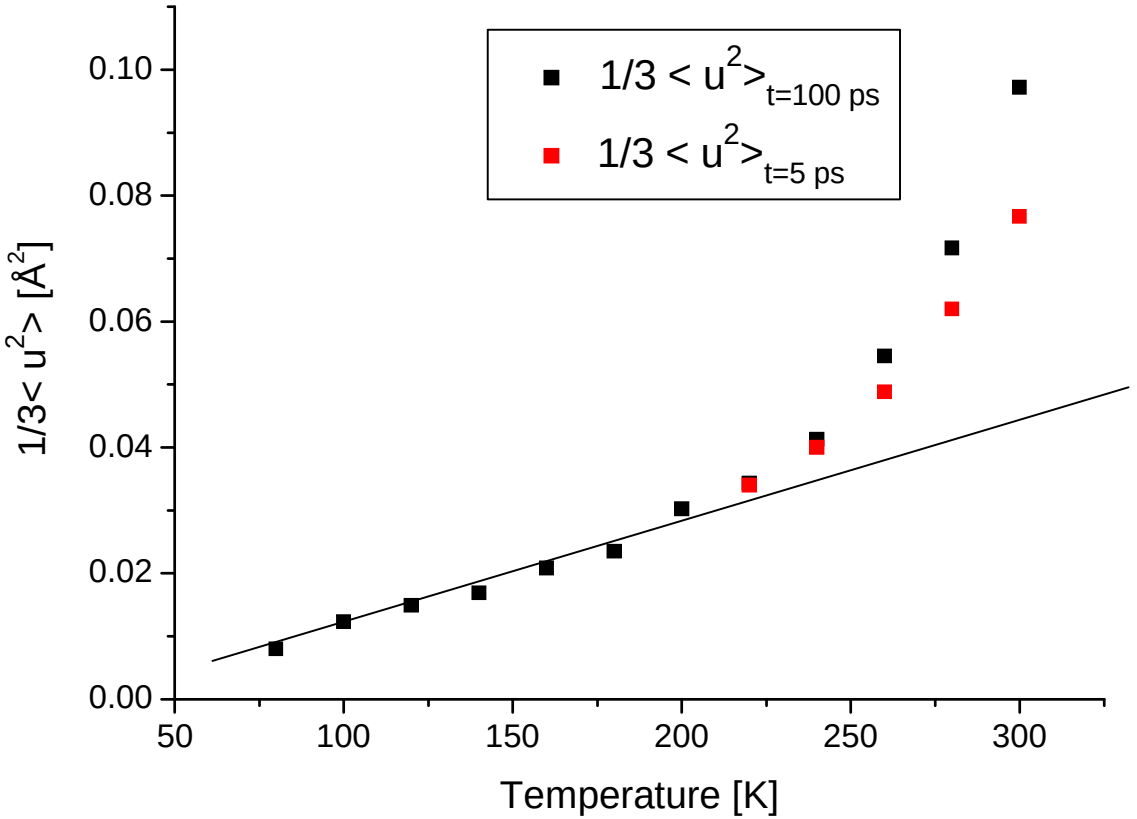


t ~ 100 ps

MSD shows:

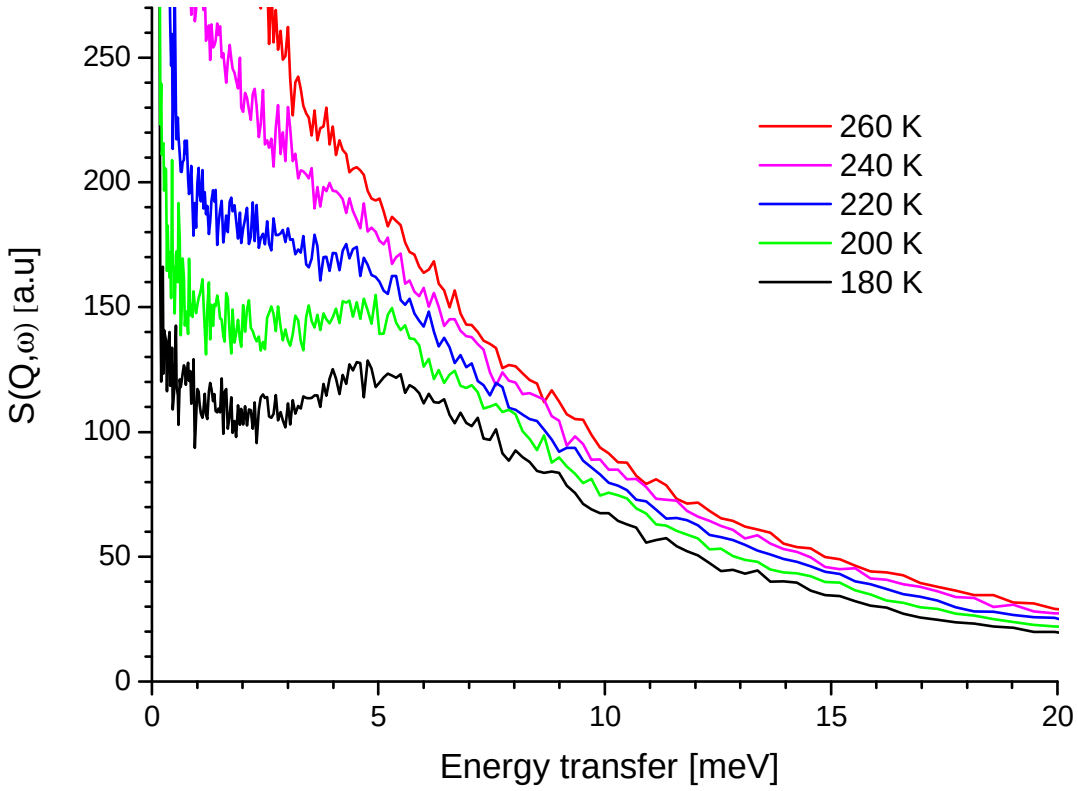
same “transition temperature” T* for both times

i.e. change in purely vibrational behavior at T*



Energy spectrum shows apparent Boson peak below T*

not checked if it is in excess of Debye sp.



Habitual data analysis leads to common signatures of the “dynamic transition” in hydrated proteins:

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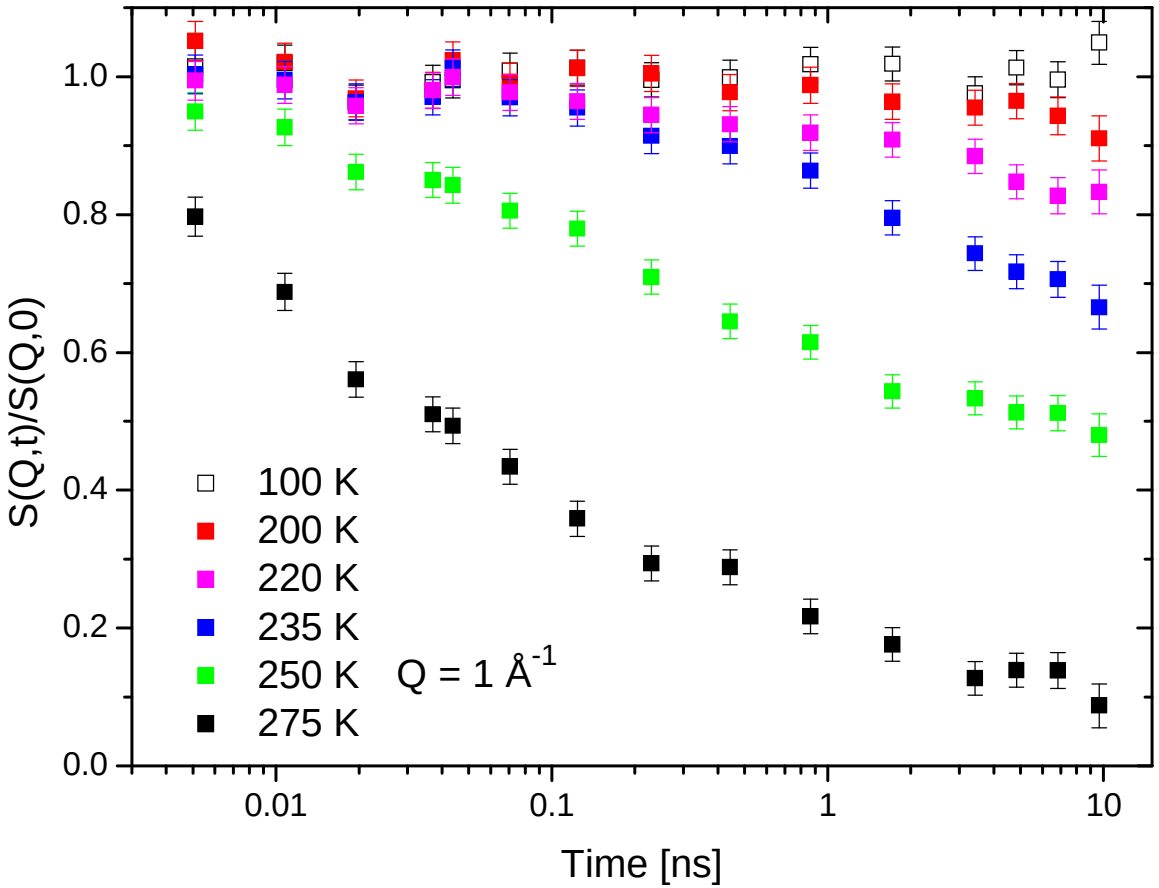
… but the sample was just an archetypical glass: glycerol

… the apparent $T^* \sim T_g$

Neutron Spin Echo study of a real hydrated protein

NSE: direct measurement of DW factor vs. time in a broad range

but: Q range limited to < ~ 1 $Å^{-1}$



Myoglobin + H_2O

Time dependence spans a large time domain

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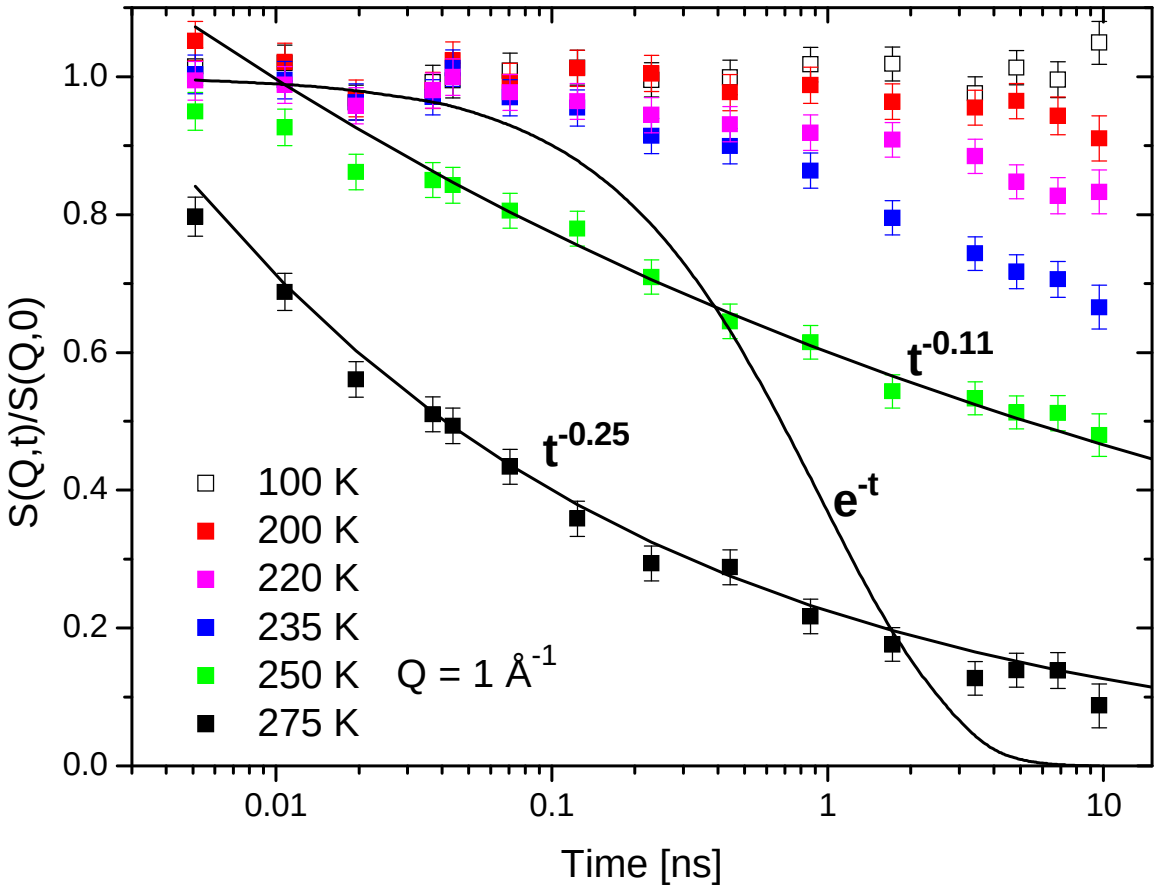

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Complex relaxation line shapes

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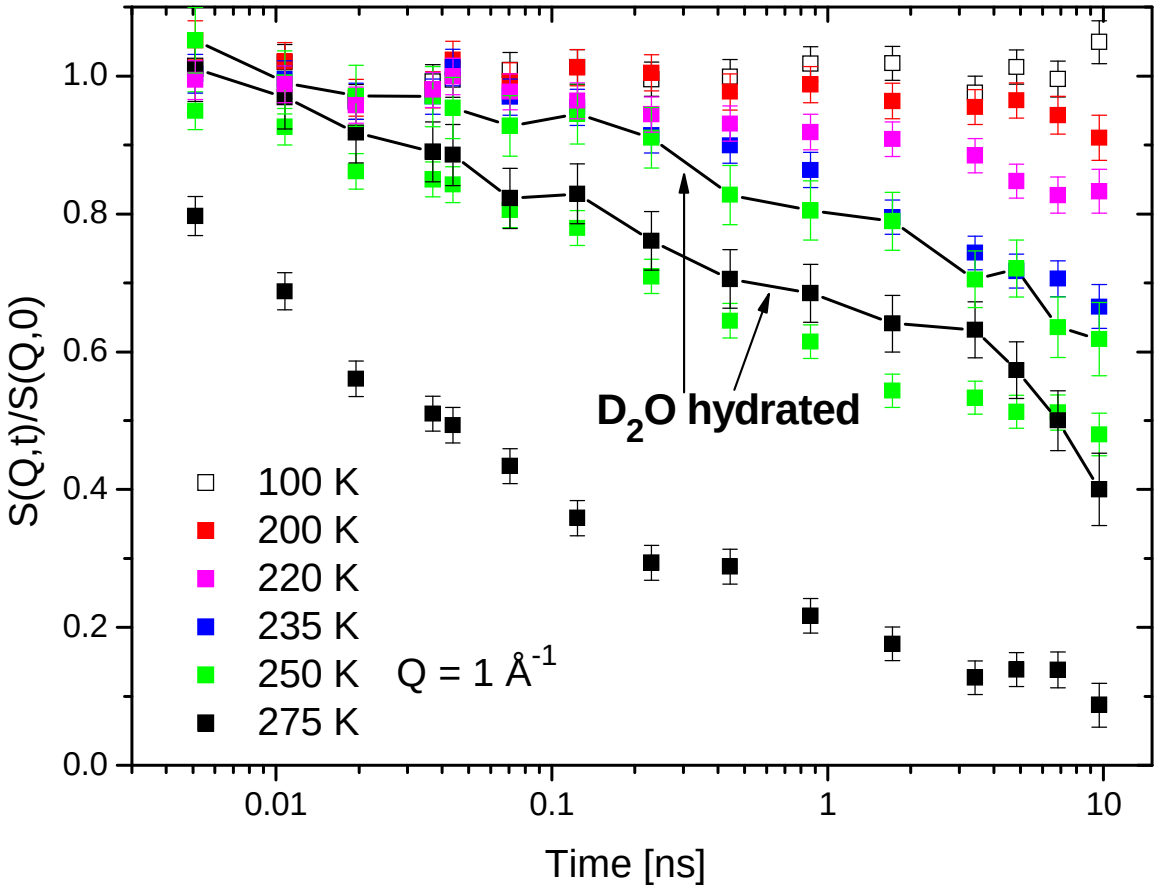

D_2O hydration: signal from protein dominates

Dynamics of protein and hydration water are different

Indirect evidence from Q dependence: **more dynamic heterogeneity**

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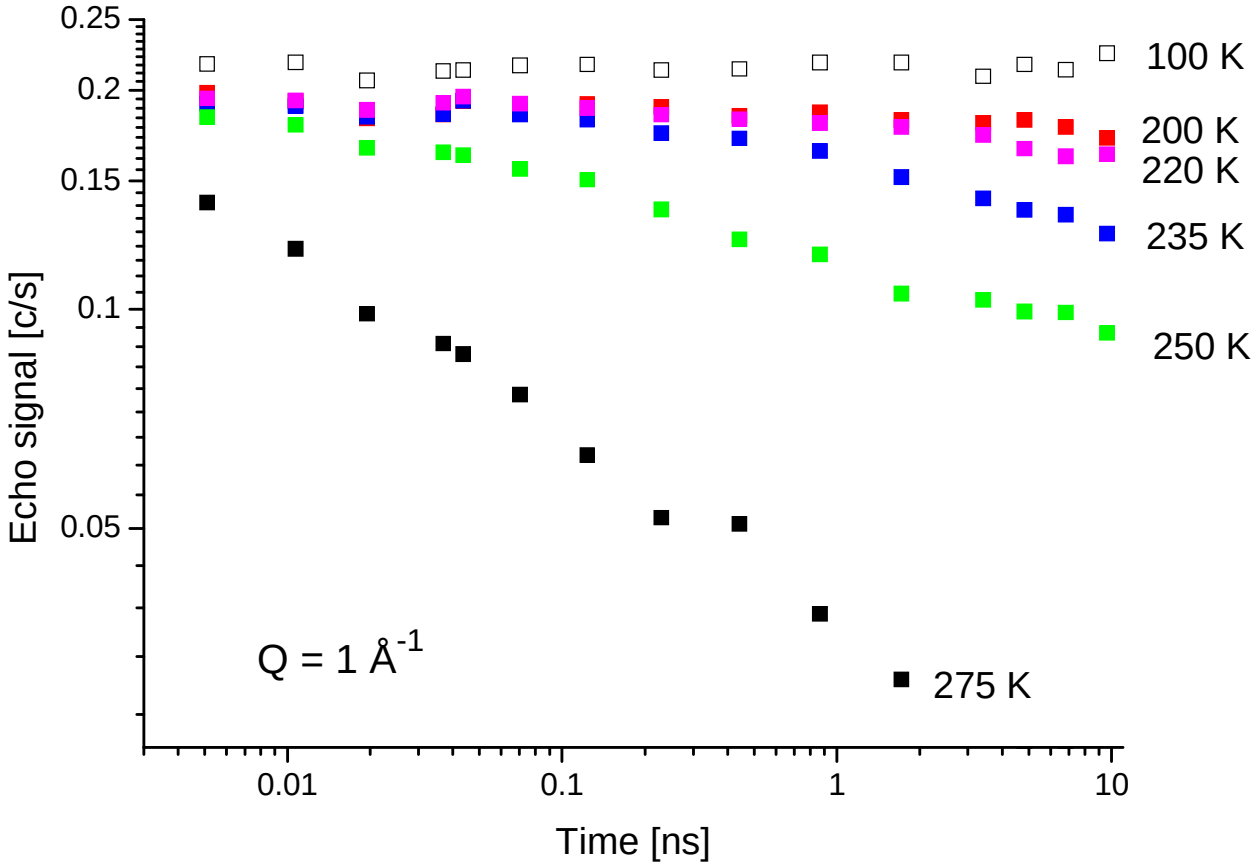

DW factor: S(Q,t)

Q range below that of of previous studies

Complex Q dependence due to dynamic hetero-geneity

Apparent transition temperature slightly time dependent

Conclusions:

The canonical “glass transition” shows key signatures of the “dynamic transition” in hydrated proteins

….and vice versa

Dynamic heterogeneity (at least at small Q’s i.e. r > ~ 3 Å) makes the data incompatible with the assumption of a single $< u^2 >$: complexity

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The canonical “glass transition” shows key signatures of the “dynamic transition” in hydrated proteins

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Dynamic heterogeneity (at least at small Q’s i.e. r > ~ 3 Å) makes the data incompatible with the assumption of a single $< u^2 >$: complexity

“The truth is rarely pure and never simple”

Oscar Wilde