The RENS method of Magazu et al.

Instead of aiming at the complete intermediate scattering function $I(Q, t, \tau_c)$, Magazu et al. determine only the average system relaxation time $\tau_{RENS}(T_{on})$ at a single temperature point T_{on} from a particular instrumental resolution τ_{res}. From the instrumental width of the energy resolution function ΔE (FWHM), and the observed onset temperature T_{on} a correlation time $\tau_{RENS}(T_{on})$ is estimated. Their basic assumption is: $\tau_c(T_{on}) \approx \tau_{RENS}$. The 'elastic' onset temperatures of various hydrated lysozyme samples obtained at different 'resolution times' using several instruments are then compared with the average correlation times derived by Chen et al. based on a full dynamic analysis [PNAS 2006]. Four data points of $\tau_{RENS}(T_{on})$ are presented as the figure below shows, which tend to agree with Chen's results. In particular the fourth data point reproduces the kink in the temperature dependence, suggesting a change in the slope of the Arrhenius plot.

We first consider the formal analysis of the data in comparison with ERS: The equivalent instrumental resolution time t_Δ is called τ_{RES} in their notation. It is instructive to cite the statement, which is central to their analysis, revealing how the instrumental resolution time is calculated: "The characteristic resolution time τ_{RES} was evaluated considering a normalized Gaussian behavior for the resolution function in ω-space in which the line-width of the function is $\Delta\omega$. More specifically it results, that HWHM = 1,17 $\Delta\omega$ and τ_{RES} = 1,66 / HWHM, in which the half weight at half maximum is the elastic energy resolution (!) of the spectrometer. Finally, to transform the micro-electronvolts into picoseconds, we adopt the common relationship $E = \hbar\omega$".

This rather floppy statement neither explains the factors 1,17 and 1,66 properly, nor does it reveal the formula with correct units, from which τ_{RES} and $\tau_{RENS}(T_{on})$ are finally calculated. In our view there is a numerical error by a factor of two in their calculation, the factor 1,66

should be replaced by 0,83: The half width (HWHM) was confused with full width (FWHM). The first factor 1,17 = $\sqrt{}$(2 ln2) transforms the Gaussian σ_ω value (= $\Delta\omega$) to a HWHM. The factor of 0,83 obtains, if the time scale is set by $\tau_{res} = 1/(\sqrt{2}\ \Delta\omega)$, which is identical with the definition given in Doster et al 2003. There we have shown (equ. 10 and fig. 2), that to determine $\tau_c(T_{on})$ requires a proper definition of T_{on}. Magazu et al. simply equate τ_{RES} with the relaxation time $\tau_{RENS}(T_{on})$ at the elastic onset temperature. This is the second error. The total error in determining the 'exponential' relaxation time at T_{on} then amounts to a factor of 2,5 since $\tau_c\ (T_{on}) = 5/2\ \tau_{RENS}(T \approx T_{on})$. The agreement with Chen's data is thus artificial.

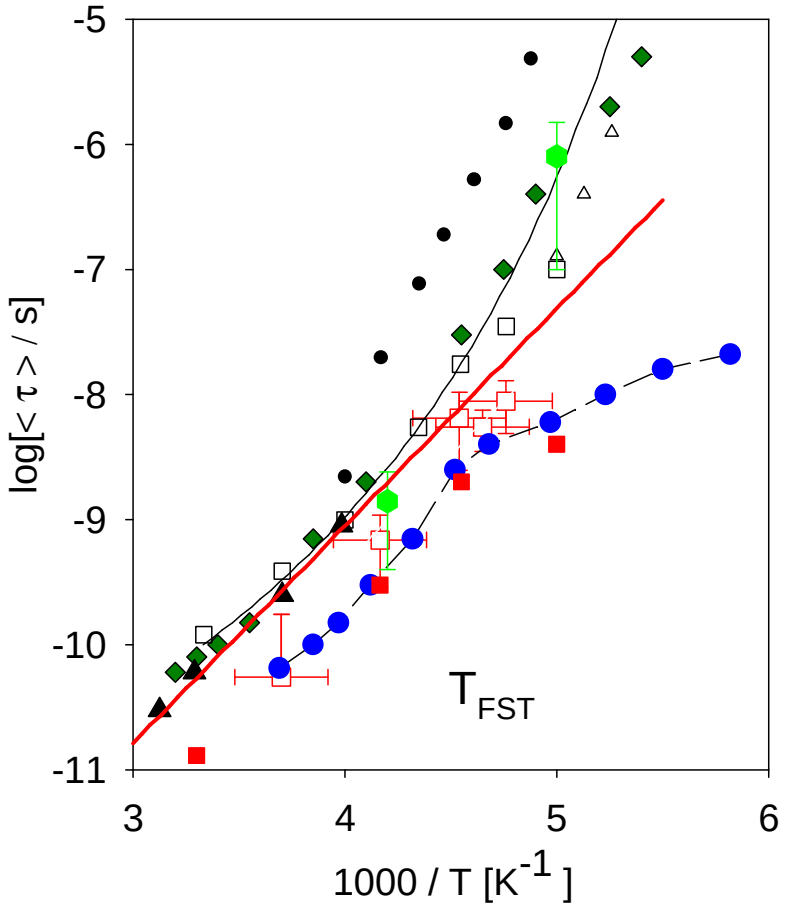
Moreover, an essential result of Chen's dynamic analysis is the stretched exponential shape of the relaxation function. As shown in the figure, the stretching of the relaxation time spectrum tends to lower the apparent T_{on}. This suggests that the apparent onset temperatures of Magazu et al. are too low. Chen et al. present a sophisticated analysis of the spectrum, where the correlation time of hydration water varies with Q due to translational diffusion: The correlation time decreases with increasing Q. These important aspects cannot be addressed with RENS, which is Q-independent. The most important deficiency of RENS is the somewhat arbitrary definition of the onset temperature. Their most important data point, suggesting a dynamic cross-over, results from a HFBS study performed by Chen et al. and by Sokolov et al.. In both studies the onset temperature for lysozyme hydration water and lysozyme is given by $T_{on} \approx$ 220 K. Magazu by contrast chooses T_{on} = 200 K without explaining the discrepancy.

Moreover, the data by Chen represent the hydration water spectrum, while Magazu cites experiments with hydrated lysozyme, where the protein contribution was not subtracted.

The figure compares the average water relaxation times of Chen et al to RENS results by Magazu et al. and to our corrected RENS, assuming exponential relaxation. Error bars were estimated by accounting for uncertainties in determining T_{on} and the resolution of the

spectrometers. The ERS data agree with the RENS results and those of Chen et al. at high temperatures.

The corrected RENS data however show no sign of a dynamic cross-over at 220 K. The same conclusion was obtained in our previous dynamic analysis of D-PC hydration water, which is also shown. Our average correlation times of protein hydration water agree with D-NMR results of Vogel et al. and with dielectric relaxation . The corrected RENS correlation times however are by a factor of two lower than those of the full dynamic analysis of D-PC hydration water. The difference can be removed by taking into account the stretched-exponential relaxation with a stretching exponent of $\beta = 0{,}5$. The average relaxation time, is related to τ_c by $\langle\tau_c\rangle = \tau_c / \beta$.



from Doster et al. JCP (2013) 139, 145105: Arrhenius plot of the average relaxation time of protein hydration water: red squares: RENS (Magazu), open red squares: RENS (Doster) , blue circles: FST, Chen et al. PNAS 2006, black open squares: CPC hydration water, Doster et al. PRL 2010, 104 198101