

Confined Water

Marie Claire Bellissent-Funel, J. Teixeira and S. Chen, the famous neutron scattering water experts, picked up the sample and the scientific approach of H. Middendorf about ten years later. H₂O is studied absorbed by perdeuterated C-phycocynin. The old paper of Middendorf was not cited however. The authors perform a decent dynamic analysis of the neutron scattering spectra at different temperatures again with a striking result concerning the Q-dependent line-width: The width of the hydration water spectrum, in contrast to bulk water, levels off below $Q = 1 \text{ \AA}^{-1}$. (black dots). There is even a well-defined cross-over at $Q = 1 \text{ \AA}^{-1}$. The conclusion is: The protein hydration water is “confined” by the protein. This seems a great application of the Dianoux-Volino model: The water performs a free diffusion inside a solid sphere of a given size (cross-over). A Gaussian confinement in a harmonic potential does not have an upper limit and does not lead to a low Q plateau. What is wrong?

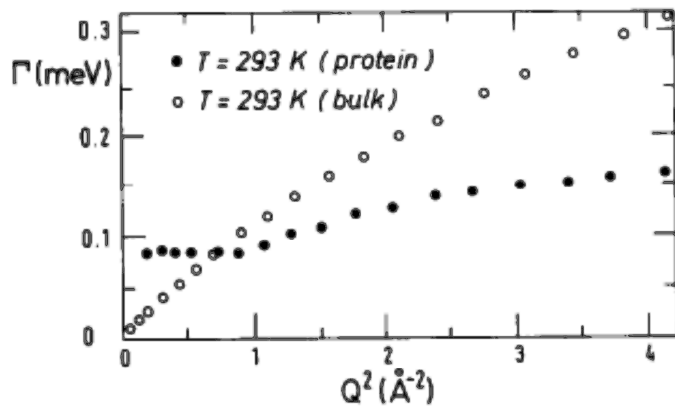
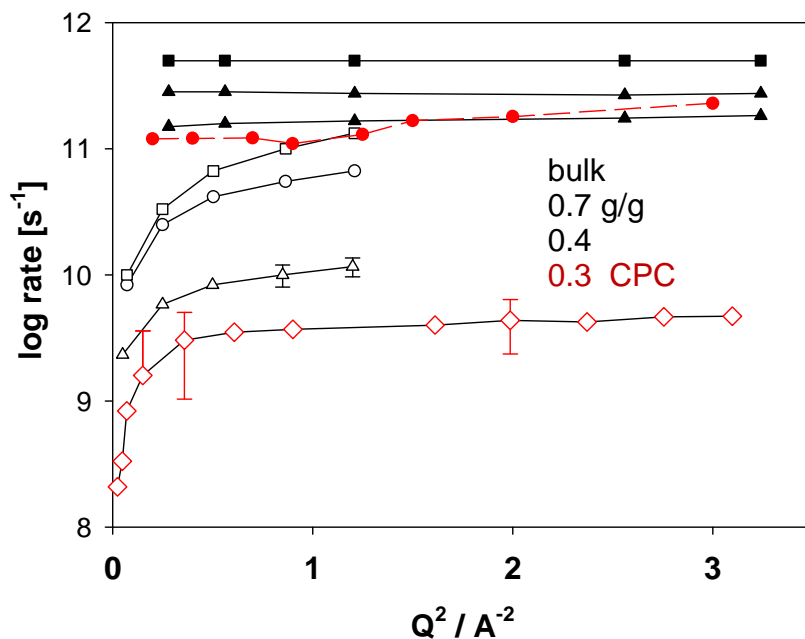


Fig. 4. HWHM of the Lorentzian quasi-elastic line Γ versus Q^2 , for $T = 293 \text{ K}$.

The full red points in the figure below were taken from the above study (Doster, BBA 2005)



and Doster et al (Phys.Rev. Lett 2010). The black points (open and full) were derived from our spectral analysis of H₂O hydrated myoglobin at various degrees of hydration (Doster, BBA 2005). The spectrum can be fitted by two Lorentzian components as bulk water (Deriu), a broadline due to rotation and a narrow line from translation. The rotational width is independent of Q. The translational width goes with Q² at low Q (diffusion) and saturates at high Q due to the cage effect (Settles /Doster, Faraday Discussion 103, 1996).

Bellissent-Funel et al. thus seem to confuse the fast Q-independent process of water reorientation with the slower translational diffusion, which they could not resolve in their experiment. The slightly Q-dependent linewidth is most likely resulting from a well-known artefact of a standard unconstrained fitting procedure, which tends to assign part of the amplitude increase with Q² to the linewidth.

This work thus shows that hydration water performs reorientational motions, which has nothing to do with confinement. I have not seen a single valid application of the DV model in neutron scattering data. As already mentioned in my comment on Middendorfs work (see 1980), low Q spectra are generally prone to artefacts such as multiple scattering or a vanishing incoherent cross section of the sample .

I am discussing this old paper because Jose Teixeira insisted on its validity at a Les Houches seminar (2013) as a proof of confined hydration water. The neutron scattering spectra of protein hydration water were first properly discussed by Settles et al in (1996) Faraday Discussion 103 and by Doster/Settles in BBA (2005).

These problems were corrected by a very nice paper in 2000 by Dellerue and Bellissent in Chemical Physics 218, 315 (2000) Relaxation Dynamics of Water at a Protein Surface.

Relaxational dynamics of water molecules at the surface of a C-phycocyanin protein is studied by high resolution quasi-elastic neutron scattering. The neutron quasi-elastic spectra are well described by the α -relaxation process of mode coupling theory of supercooled liquids. The relaxation times of interfacial water exhibit a power law dependence on the wave vector Q. The average diffusion coefficient is 10 times lower than that of bulk water. This confirms that there is a retardation of water molecules at the protein surface which is in good agreement with the results of water at the surface of hydrophilic model systems.