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Water dynamics in a concentrated aqueous solution of perdeuterated poly(N-isopropylacrylamide) across the cloud point

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In aqueous solutions of the thermoresponsive polymer poly(N-isopropylacrylamide) (PNIPAM), the interaction between water and the polymer changes strongly at the demixing transition. Cooperative dehydration causes the polymer chains to collapse and aggregate. Recent quasi-elastic neutron scattering experiments have shown that the susceptibility spectra of hydration water occur at lower frequencies than those of bulk water and that their relative population decreases abruptly at the cloud point [1,2].

In the present study, we investigate the low frequency water dynamics on a perdeuterated PNIPAM sample in H₂O using the backscattering spectrometer SPHERES at FRM II with an increased energy resolution near the elastic line of $\sim 0.65 \mu\text{eV}$ (FWHM). Deuteration suppresses incoherent scattering from the polymer. We find that, below the cloud point, the previously observed frequency dependence of the relaxation of the hydration water extends to lower frequencies. Below, but even more strongly above the cloud point, an additional slow process is detected and is tentatively attributed to strongly bound water.

1. M. Philipp, C. M. Papadakis et al., J. Phys. Chem. B 2014, 118, 4253
2. B.-J. Niebuur, C. M. Papadakis et al., Macromolecules 2019, 52, 1942

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