

Q1. In line 57, what does “these two experimental systems” refer to? Similarly, which method does “measurements” refer to in line 59?

We thank the reviewer for pointing out these ambiguities. In the original manuscript, “these two experimental systems” referred to the solution-disk and electrodynamic balance (EDB) systems mentioned in the preceding sentence, whereas “measurements” referred to measurements based on H₂O/D₂O isotope exchange. We agree that the original wording did not clearly distinguish the experimental systems and the measurement method. We have therefore revised the relevant descriptions in the Introduction to make these terms explicit at first mention.

First, when the isotope-exchange method is introduced in Lines 46–48, we now specify that the method developed by Price et al. (2014) was applied to solution disks. The sentence has been revised to:

10 “Price et al. subsequently developed a Raman isotope-tracer method that monitors H₂O/D₂O exchange in a solution disk, which enabled direct retrieval of water diffusion behaviour in highly viscous solutions and quantitative characterisation of the dependence of the water diffusion coefficient on RH (Price et al., 2014).”

Second, in Line 55, we have replaced “the method” with “the isotope-exchange method”.

Third, the original expression “The relatively large sample or droplet size in these two experimental systems substantially
15 prolongs the time required for complete H₂O/D₂O exchange” has been revised to identify the two systems explicitly:

“The relatively large sample size in solution-disk experiments or droplet size in EDB experiments substantially prolongs the time required for complete H₂O/D₂O exchange.”

Finally, the sentence describing the measurement time for solution disks has been revised to clarify that the reported duration refers specifically to the isotope-exchange measurement:

20 “For solution disks, when the water diffusion coefficient is on the order of $10^{-16} \text{ m}^2 \text{ s}^{-1}$, the H₂O/D₂O isotope-exchange measurement takes approximately 8 days (Price et al., 2014).”

These revisions clarify the distinction between the isotope-exchange measurement method and the experimental systems in which it has been implemented.

25 **Q2. Why does the combination of optical tweezers and Raman isotope tracing show a relatively short equilibration time? What process does “equilibration” describe here?**

We thank the reviewer for pointing this out. The term “equilibration time” in the original manuscript was insufficiently defined and could therefore be ambiguous. In Davies and Wilson (2016), the authors noted that, compared with the isotope-exchange measurements performed on solution disks by Price et al. (2014), “the time scales for equilibration are much
30 shorter”, allowing water diffusion coefficients down to approximately $\sim 10^{-17} \text{ m}^2 \text{ s}^{-1}$ to be measured within a single day rather than over periods of weeks (Davies and Wilson, 2016). Here, this equilibration refers to the $\text{H}_2\text{O}/\text{D}_2\text{O}$ isotope-exchange process used to determine the water diffusion coefficient. The shorter timescale is associated with micrometre-sized droplets in optical-tweezer measurements, where the time required for $\text{H}_2\text{O}/\text{D}_2\text{O}$ exchange is substantially reduced compared with isotope-exchange measurements using the larger solution disks in Price et al. (2014).

35 To make this point clear when these experimental approaches are first introduced in Lines 46-50, we have added the following sentence to the Introduction: “In optical tweezer experiments, the use of micrometre-sized droplets substantially shortens the time required for $\text{H}_2\text{O}/\text{D}_2\text{O}$ exchange compared with isotope-exchange measurements using the solution disks (Davies and Wilson, 2016).”, after “This isotope tracer method was later applied to both optical tweezer systems and EDB (Davies and Wilson, 2016; Nadler et al., 2019), extending direct measurements of water diffusion coefficients to suspended
40 single droplets.”

We have also revised the ambiguous term “equilibration time” in Line 65. The revised sentence now reads:

“The combination of optical tweezers and Raman isotope tracing offers several advantages for measuring the water diffusion coefficient, including relatively simple modelling, shorter isotope-exchange times in micrometre-sized droplets, and the ability to probe supersaturated states (Davies and Wilson, 2016).”

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Q3. Is the diffusion process temperature-dependent?

We thank the reviewer for pointing this out. Yes, water diffusion is temperature-dependent, as previous studies of highly viscous aqueous and sucrose-containing systems have reported (Zobrist et al., 2011; Price et al., 2014). We also recognise that the literature datasets compared in our manuscript were obtained at different temperatures, whereas this information was not clearly indicated in the original figure. We have therefore added the corresponding experimental temperatures to the revised figure and its caption.

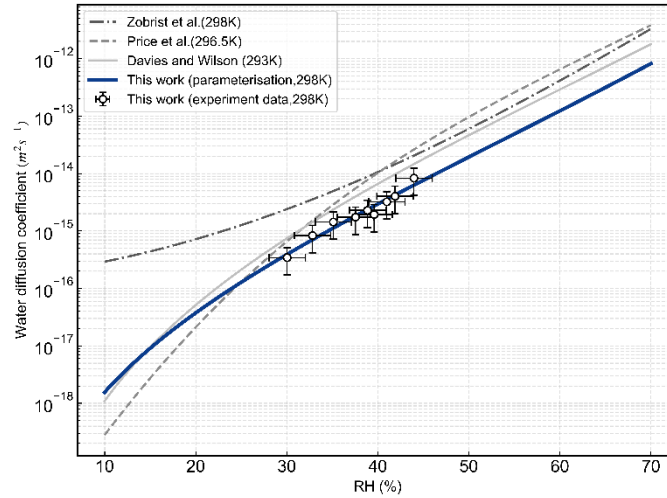


Figure 3.1: Measured water diffusion coefficients in sucrose droplets at different RH in this study and comparison with parameterisations reported by Zobrist et al., Price et al., and Davies and Wilson (Zobrist et al., 2011; Price et al., 2014; Davies and Wilson, 2016).

Q4. At $RH < 30\%$, the results obtained using the characteristic-time-based method differ considerably from those of Zobrist et al. Which results are more reliable?

We thank the reviewer for raising this important question. We consider that the experimental evidence currently available, together with the results reported in previous studies, is insufficient to determine which set of water diffusion coefficients obtained by different methods more accurately represents the true D_w at $RH < 30\%$. In fact, the differences in D_w obtained using different experimental methods at low RH have already been reported in previous studies of sucrose systems (Price et al., 2014; Nadler et al., 2019). Previous studies have compared the results of Zobrist et al. (2011) with water diffusion coefficients derived from H_2O/D_2O isotope-exchange measurements and reported differences of several orders of magnitude at low water activity (Nadler et al., 2019). We therefore do not consider the currently available evidence sufficient to conclude that one method is more reliable than the other.

These differences may arise from how the two experimental methods constrain water diffusion. Zobrist et al. (2011) induced water uptake or loss in individual sucrose droplets by changing ambient RH and retrieved the water diffusion coefficient from the time-dependent evolution of droplet size using a mass transport model. During this process, both the droplet's total water content and sucrose concentration change continuously, creating a time-dependent radial composition gradient. Consequently, the retrieval of D_w involves both the thermodynamic relationship between water activity and solution composition and the dependence of the diffusion coefficient on composition. In contrast, Price et al. (2014) and subsequent studies employed H_2O/D_2O isotope exchange and characterised water diffusion within the droplet by monitoring the temporal evolution of its isotopic composition (Davies and Wilson, 2016; Nadler et al., 2019). At a given RH, this method changes the isotopic composition of the water molecules, rather than relying on bulk water uptake or loss driven by a substantial change in RH. Nadler et al. attributed the large difference between the two methods to the different assumptions employed in the corresponding models. In the mass transport model involving changes in ambient RH, the droplet radius varies as RH changes, and the model involves moving and nonlinear boundary conditions. By contrast, the isotope-exchange model assumes a constant droplet radius at fixed RH and therefore involves a fixed, linear boundary condition.

The experimental method used in the present study is likewise based on H_2O/D_2O isotope exchange, and the CT method provides a new approach to retrieving D_w from the temporal evolution of the isotope exchange process within this experimental framework. Therefore, the present study is more directly comparable methodologically with previous isotope exchange measurements. In the revised Discussion, we therefore restrict our interpretation to an objective description of the differences reported between the experimental methods at low RH and the possible reasons for these differences. We do not use the present measurements to determine which method is more accurate. We also clarify the RH range directly investigated in this study and the corresponding scope of applicability of our conclusions.

Reference

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