Supplementary Information for:
Water diffusion in single suspended phase-separated aerosols

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S1 Aerosol trapping chamber

Figure S1 Aerosol trapping chamber - (a) Overview, 1-Top cover with coverslip, 2-Chamber exterior, 3-Exhaust port, 4-Bottom baffle, 5&6-Fixing bolts and nuts, 7-Inlets for aerosols, nitrogen, and other possible substances; (b) Profile, 8-Bottom coverslip, 9-Top coverslip, 10-Inner cylinder baffle, 11-Rubber O-rings, 12&13-Fixing bolts and nuts. The path of incoming aerosol droplets and mixture of dry and wet nitrogen is expressed with red arrowed lines. The aerosols were generated from desired mother solutions by a medical ultrasonic nebulizer (Mint PN100). The radii of the generated droplets are 4~10 μm with a median of 5 μm.
S2 Raman spectra of phase-separated aerosols

Figure S2 Raman spectra of aerosols with various morphologies - (a) Spectrum of homogenous aerosol. The high-quality WGMs indicates a spheric shape and the internal isotropy. (b) Spectrum of core-shell aerosol. The weak but noticeable WGMs indicates the symmetry of the particle remains, albeit the destruction of internal isotropy. (c) Spectrum of partly engulfed aerosol. No WGMs indicates the destruction of both isotropy and symmetry in the particle.
S3 Raman spectra of bulk mother solutions

Figure S3 Raman spectra of bulk solutions containing H₂O or D₂O - As O-D and O-H have different energy levels, the H₂O and D₂O solutions have strikingly different Raman peaks which respectively locates at 640∼660 nm and 605∼625 nm. Thus, the rise and fall of O-D/O-H peaks in Raman spectra can be used to trace water diffusion within aerosols.
S4 Influence of WGMs on peak area

Figure S4 Influence of WGMs of the calculated $\phi_{OD}$ - (a) The temporal variations of fractional concentration of water molecules within the droplet. The peak areas of O-D band and O-H band are calculated with excluding the WGMs in the Raman spectra. The results have no appreciable discrepancy with that in Fig. 6B in the main text. (b) The deviations of $\phi_{OD}$ when considering or ignoring the contribution of WGMs. It shows that the deviations are incredibly trivial of which the maximum is merely $7 \times 10^{-3}$. 

![Graphical representation of the data](image-url)
S5 Fickian fitting

Figure S5 Fitting the observed $\phi_{OD}$ with the modified Fickian diffusion model
- An example of fitting the observed $\phi_{OD}$ data with the modified Fickian diffusion model. The data points are from H$_2$O+AS+DLT (Stage I). It shows the model works well with the data. The fitted parameter $\chi$ indicates the diffusion extent and $a^2/(\pi^2 D_w)$ means the time of diffusing to an isotropically stable state.

\[ \chi = 0.73 \pm 0.016 \]
\[ \pi D_w / a^2 = (9.19 \pm 0.56) \times 10^{-5} \]
\[ R^2 = 0.94 \]
S6 Comparison of the water diffusion coefficients

Table S1 Water diffusion coefficients of aerosols measured with various methods

<table>
<thead>
<tr>
<th>Aerosol</th>
<th>RH (%)</th>
<th>$D_w$ (m$^2$s$^{-1}$)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O+CA</td>
<td>60</td>
<td>2.51 × 10$^{-11}$</td>
<td>isotope exchange</td>
<td>Davies et al.$^1$</td>
</tr>
<tr>
<td>H$_2$O+Sucrose</td>
<td>50</td>
<td>1.01 × 10$^{-13}$</td>
<td>RH oscillation</td>
<td>Preston et al.$^2$</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3.98 × 10$^{-12}$</td>
<td>isotope exchange</td>
<td>Davies et al.$^1$</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.17 × 10$^{-13}$</td>
<td>diffusion model</td>
<td>Zobrist et al.$^3$</td>
</tr>
<tr>
<td>H$_2$O+Sucrose+CA</td>
<td>40</td>
<td>1.01 × 10$^{-13}$</td>
<td>isotope exchange</td>
<td>Davies et al.$^1$</td>
</tr>
<tr>
<td>H$_2$O+AS+OA</td>
<td>60</td>
<td>1.32 × 10$^{-15}$</td>
<td></td>
<td></td>
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<tr>
<td>H$_2$O+AS+DLT</td>
<td>60</td>
<td>5.36 × 10$^{-16}$</td>
<td>isotope exchange</td>
<td>This work</td>
</tr>
<tr>
<td>H$_2$O+AS+HEX</td>
<td>60</td>
<td>2.25 × 10$^{-16}$</td>
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<td></td>
</tr>
<tr>
<td>H$_2$O+AS+DLT+H$^+$</td>
<td>60</td>
<td>3.99 × 10$^{-15}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For H$_2$O+CA droplet, according to the results of Davies et al.$^1$, the calculated $\tau_{\text{mixing}}$ is $\sim$20 s which is in the same order magnitude as the observed $\tau_{\text{OD}}$ ($\sim$80 s) in this work. For the phase-separated droplets, the measured $D_w$ is considerably lower than the values of homogenous droplets studied in literature works, which indicates the occurrence of the water diffusion limitations.
S7 RH correction

The equilibrium vapor pressures of D\textsubscript{2}O and H\textsubscript{2}O are slightly different at the same temperature conditions. Thus, after switching from H\textsubscript{2}O to D\textsubscript{2}O, the RH probe measurement needs to be corrected. The relationship of the two equilibrium vapor pressures can be specified as

\[
\ln \frac{p^0_{\text{H}_2\text{O}}}{p^0_{\text{D}_2\text{O}}} = A + \frac{B}{C + T} = \Lambda,
\]

where \(A = -0.30661\), \(B = 9.14056\), \(C = 75.753\), \(T\) is in Celsius, \(p^0_{\text{H}_2\text{O}}\) is the equilibrium vapor pressure of H\textsubscript{2}O, and \(p^0_{\text{D}_2\text{O}}\) is the equilibrium vapor pressure of D\textsubscript{2}O.

If not correcting the RH (i.e. not changing the setting value of RH after switching the moisture), the actual RH value will be \(e^\Lambda\) times the readout of the RH probe. Therefore, to keep a constant RH condition, the RH setting value should be corrected as \(RH_{\text{post}} = RH_{\text{pre}} \cdot e^\Lambda\), where \(RH_{\text{post}}\) is the setting value after moisture switching and \(RH_{\text{pre}}\) is the setting value before switching.
S8 Reagents and sample preparation

The mother solutions used to generate the aerosol droplets were prepared by double-distilled water (18.2 MΩ cm; Milli-Q; MilliporeSigma, Burlington, MA, United States). Solute citric acid was purchased from Beijing Modern Oriental Fine Chemical Co., Ltd. (Beijing, China); Oleic acid was purchased from Xilong Scientific Co., Ltd. (Guangdong, China); Diethyl-L-tartrate was purchased from Shanghai D&B Biotechnology Co., Ltd. (Shanghai, China); 1,2,6-hexanetriol was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China); Ammonium sulfate was purchased from Tong Guang Fine Chemical Co. (Beijing, China). The D$_2$O was purchased from Cambridge Isotope Laboratories, Inc. (Andover, USA).

References

