

SUPPLEMENTARY INFORMATION

Exploring the validity of the Stokes-Einstein relation in
supercooled water using nanomolecular probes

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S1 Langevin dynamics

In order to analytically model the observed probe dynamics we used the Langevin equation

$$m\ddot{\mathbf{r}}(t) = -\zeta\dot{\mathbf{r}}(t) + \mathbf{R}(t), \quad (\text{S1.1})$$

where $\mathbf{r} = (x, y, z)$ is the position, ζ is the friction coefficient and $\mathbf{R}(t)$ is a randomly non-correlated fluctuating force that fulfills $\langle \mathbf{R}(t) \rangle = 0$ and $\langle R_i(t)R_j(s) \rangle = 2\zeta k_B T \delta_{ij} \delta(t-s)$, the latter criteria being a result of the fluctuation-dissipation theorem¹. Adopting the formalism in Ref. 2, we have in the diffusive limit (also known as the overdamped or zero-mass limit):

$$\dot{\mathbf{r}}(t) = \frac{1}{\zeta} \mathbf{R}(t) = \quad (\text{S1.2a})$$

$$= \sqrt{\frac{2k_B T}{\zeta}} \mathbf{W}(t) = \sqrt{2D} \mathbf{W}(t), \quad (\text{S1.2b})$$

$$\Rightarrow \Delta x(t) = \sqrt{2D\Delta t} W(t), \quad (\text{S1.2c})$$

where $\mathbf{W}(t)$ is white noise with $\langle \mathbf{W}(t) \rangle = 0$ and $\langle W_i(t)W_j(s) \rangle = \delta_{ij} \delta(t-s)$. In the second step of eq. (S1.2b) viscous flow is assumed with the friction coefficient given by Stokes law, $\zeta = 6\pi\eta R_h$, followed by substitution with the Stokes-Einstein relation, eq. (4).

Furthermore, the last equation (eq. (S1.2c)) is the displacement along one dimension, assuming small time steps Δt . The total mean-square displacement (MSD) for small Δt in three dimensions is thus given by

$$\langle \Delta r(t)^2 \rangle = \langle (\Delta x(t)^2 + \Delta y(t)^2 + \Delta z(t)^2) \rangle. \quad (\text{S1.3a})$$

For the numerical calculation of the above MSD we utilized the Matlab code given in Ref. 2.

Lastly, at large t the analytical form of the MSD, that can be derived from eq. (S1.1), reduces to

$$\lim_{t \rightarrow \infty} \langle \Delta r(t)^2 \rangle = 6Dt, \quad (\text{S1.4a})$$

hence reflecting the linear time dependence that is characteristic of diffusive motion.

S2 The mean-squared displacement

While dynamics captured by DLS is readily analyzed in terms of the intensity autocorrelation function g_2 , it may also be converted into the mean-squared displacement (MSD), i.e. by substitution of eq. (S1.4a) and eq. (3) into the exponential decays of eq. (2) and solving for the MSD^{3,4}. The resulting MSD as a function of time for the three probe sizes at different temperatures are given in Fig. S1. For PHF (Fig. S1c) we show here only the MSD for the fast g_2 component at short times, for which the amplitude of the slow component is nearly constant and equals its contrast (i.e. β_2 in eq. (2b)). The MSD provides additional information from the g_2 functions since it is averaged over all momentum transfers Q . Within the experimental window, all probes display MSD with linear time dependence, indicating diffusive motion. The diffusive character of the MSD is further emphasized and consistent with the numerically calculated MSD based on Langevin dynamics (see section S1), as shown by the black solid lines at the highest and lowest temperature (299 K and 260 K). In accordance with the $1/Q^2$ -dependence of the relaxation time constant, the above observations further confirm the translational motion of all studied probes as overall diffusive in nature, which in the view of the Langevin

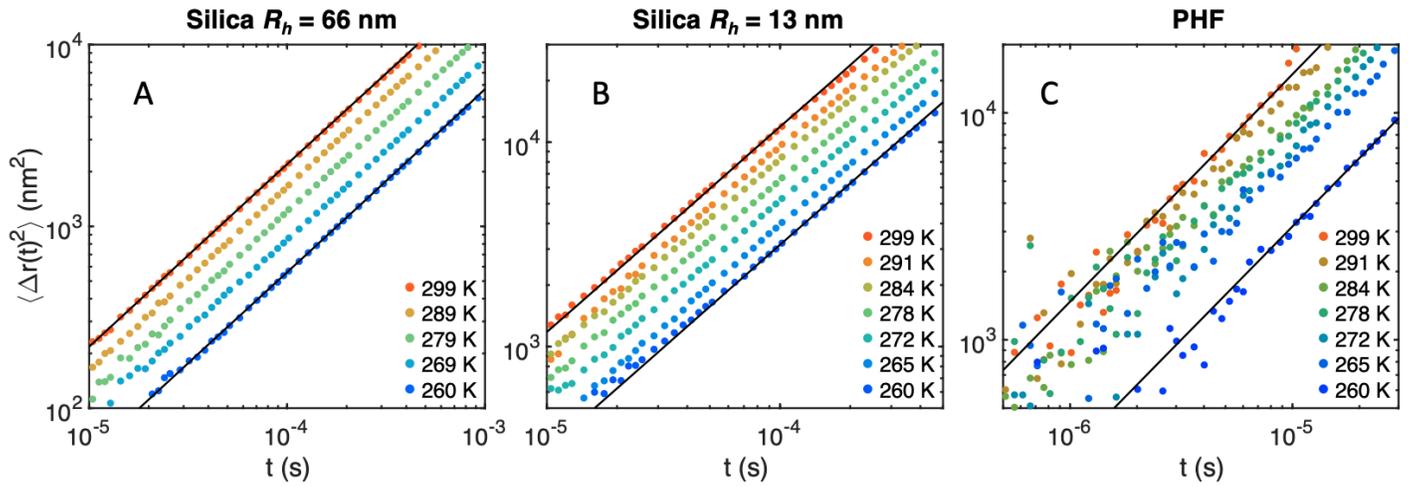


Fig. S1 The DLS data of the probe dynamics presented in the form of the mean-squared displacement (MSD), $\langle \Delta r(t)^2 \rangle$, at different temperatures. Unlike the g_2 functions in Fig. 1, the MSD is averaged over all scattering angles and thus represents the dynamic information independent of the momentum transfer Q . Experimental data is indicated by solid dots while the solid black lines refer to fitted numerical results based on Langevin dynamics (see section S1)². Panel (a) shows the MSD of silica spheres with $R_h = 66$ nm, (b) silica spheres with $R_h = 13$ nm and (c) the fast component of PHF.

dynamics framework suggests that the probe motion is predominantly driven by random fluctuations of the surrounding water molecules and governed by viscous flow.

References

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