Electronic Supplementary Information for "Decoupling of viscosity and relaxation processes in supercooled water: a molecular dynamics study with the TIP4P/2005f model"

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1 Shear-viscosity determination

In this section, we describe briefly how the shear viscosity and the associated error are determined.

1.1 Green-Kubo formalism

The shear viscosity was computed using the Green-Kubo formalism:

$$\eta = \lim_{t\to\infty} \eta(t), \tag{1}$$

with

$$\eta(t) = \frac{V}{k_\mathrm{B}\cdot T}\cdot\int_0^t \left\langle p_{ij}(0)\cdot p_{ij}(u)\right\rangle\cdot \mathrm{d}u. \tag{2}$$

To get a converged value, we averaged the values obtained for 160 independent Green-Kubo integrals (see main text) for each temperature, as illustrated in Fig. 1. Then, we estimated the error associated with the average value by taking the standard deviation of this set of values, divided by the root mean square of the number of values in the set (standard error). The time interval on which the integrals are calculated were adjusted to insure a plateau is reached for each temperature.

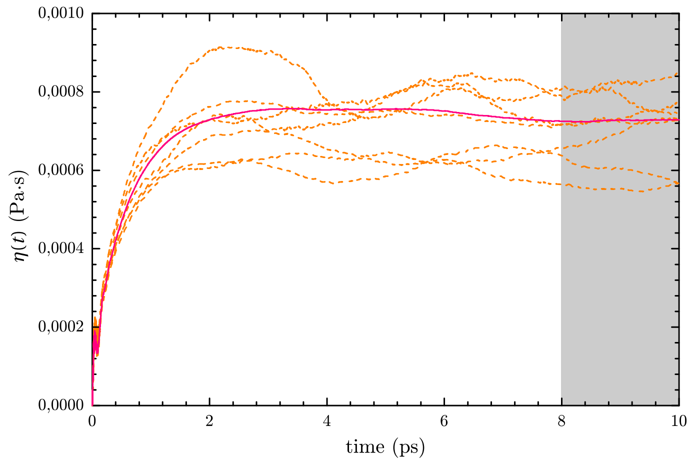

Fig. 1 Variations of the Green-Kubo integrals with time at 300 K. Dashed curves correspond to a small set of representative integrals calculated for isolated replicas, whereas the plain curve corresponds to the integral averaged over all 160 independent Green-Kubo curves. The value of viscosity is obtained by averaging the plateau value over the last 2 ps.

1.2 Steady-state shear flow

Another way to calculate the shear viscosity is to enclose the liquid between two walls and create a shear flow. The shear viscosity is then given by:

$$\eta = \frac{\sigma}{\dot{\gamma}}, \tag{3}$$

where σ and $\dot{\gamma}$ denote the shear stress applied to the walls and the shear rate of water, respectively. Both quantities were averaged over 1 ns. Three replica of the system were used at each temperature, applying shear velocities of ± 40, 70 and 100 $\mathrm{m\cdot s^{-1}}$ to the walls. As shown in Fig. 2, we checked for linearity of the shear stress with respect to the shear rate to control that the simulations remained in the linear response regime. The values of viscosities reported are averages of the values obtained for each replica. The error is then calculated as the standard error over those values.

2 Viscoelatic relaxation time

The viscoelastic relaxation time τ_M is defined as the ratio:

$$\tau_M = \frac{G_\infty}{\eta}, \tag{4}$$

where G_∞ and η denote the shear modulus of bulk water at infinite frequency and the shear viscosity. The shear modulus at infinite frequency can be computed using the stress tensor auto-correlation function, according to the relation:

$$G(t) = \frac{V}{k_B\cdot T}\cdot\left\langle p_{ij}(0)\cdot p_{ij}(t)\right\rangle, \tag{5}$$

since $G(0) = G_\infty$. However, due to zero wave vector optical phonon modes [E. Landry, M. Hussein, and A. Mc-

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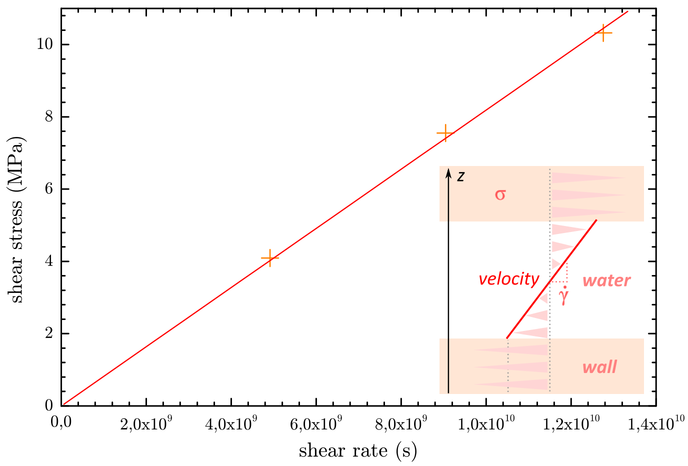

Fig. 2 Evolution of the shear stress with respect to the shear rate for different velocities applied to the walls. Points correspond to calculated values at 300 K. The line shows that all values are in the linear response regime.

Gaughey, Physical Review B **77**, 184302 (2008)], the stress tensor auto-correlation function stronlgy oscillates at short timescale, so that its initial value must be extrapolated from a model. A stretched exponential (see main text) gives good results, as shown on Fig. 3. We also tried to use a simple exponential, but the agreement with data at short timescales for low temperatures was poor. Errors were estimated using the same procedure as for the shear viscosity.

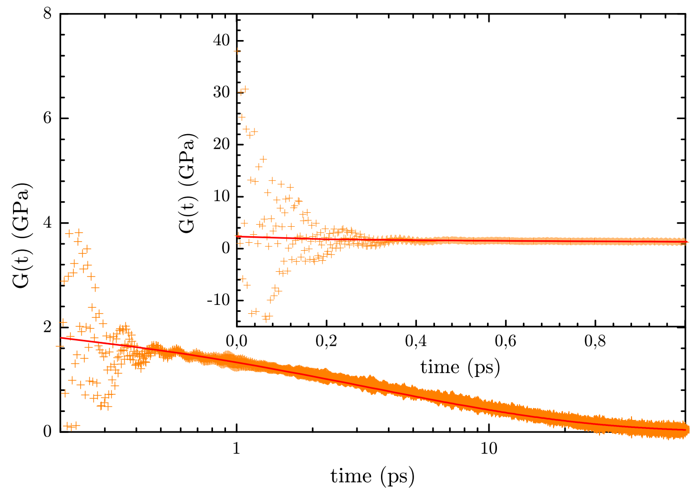

Fig. 3 Short and long-time behavior of the stress tensor auto-correlation function of bulk water at 240 K. The inset shows the short timescale behavior with the full amplitude of oscillation of the stress tensor auto-correlation function.