# Dynamical Arrest of Electron Transfer in Super-cooled Water: Supplement

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The dielectric properties of SPC/E water have been obtained from MD simulations based on the formalism described previously in refs 1–7 for polar molecular fluids. In particular, static dielectric properties and dielectric dispersion of water from simulations have been previously reported in refs 2,5–8. In this communication, the static dielectric constant of water is calculated from rms fluctuations of the overall dipole moment $M(t)$ of water in the simulation box with the corrections for the cut-off of electrostatic interactions according to Neumann.[9] Figure 1 shows the average $\langle M(0)^2 \rangle$, reduced by the number of particles in the box $N$ and the dipole moment $\mu$ of the water molecule, vs the length of MD simulation. A good convergence of the static dielectric constant has been achieved at all temperatures studied.
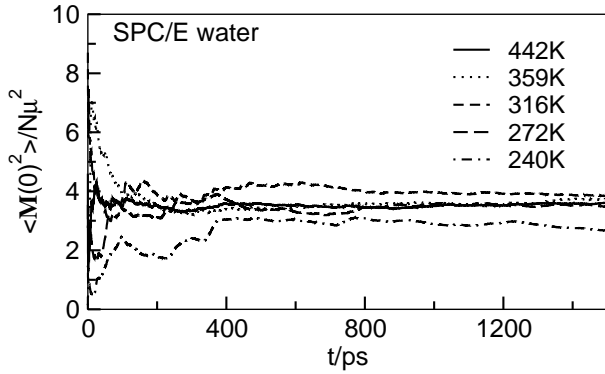


FIG. 1: Convergence of the mean-squared fluctuation of the total dipole moment of SPC/E water in NVE MD simulations.

The dielectric spectrum is obtained from the autocorrelation function

$$C_M(t) = (N\mu^2)^{-1}\langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle \qquad (1)$$

calculated on MD trajectories (Figure 2). The correlation function $C_M(t)$ was fitted to a multiexponential decay function

$$C_M(t) = \sum_{j=1}^{P} a_j e^{-t/\tau_j} \qquad (2)$$

used to generate the Laplace-Fourier transform

$$\tilde{C}_M(z) = \int_0^\infty C_M(t) e^{-izt} dt. \qquad (3)$$

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This function is then used to calculate the dielectric spectrum according to the equation given by Neumann and Omelyan:[2,9]

$$\frac{\epsilon(z) - 1}{\epsilon(z)} = \frac{9y\chi(z)}{1 + 9y\chi(z)} \qquad (4)$$

where

$$\chi(z) = C_M(0) - iz\tilde{C}_M(z) \qquad (5)$$

and

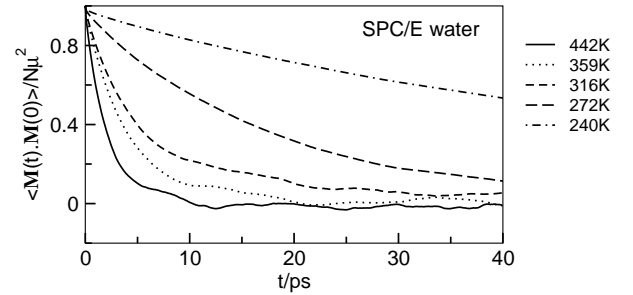$$y = (4\pi/9)\rho\mu^2/k_B T. \qquad (6)$$



FIG. 2: Autocorrelation function of the total dipole moment of SPC/E water at temperatures indicated on the plot.

The dielectric loss function turns out to be well reproduced by a single-exponential Debye form for all temperatures studied. The peak of the dielectric loss function is used to obtained the Debye relaxation time $\tau_D$ which is approximated by the Vogel-Fulcher (VF) fit: $\ln(\tau_D(T)/\text{ps}) = -0.51 + 961/(T - 88)$ (Figure 3). Also shown is the Debye relaxation time of super-cooled water as reported by Bertolini *et al.*[10] The discrepancies between MD simulations and experiment can be traced back to the approximate nature of the SPC/E force field (e.g., SPC/E water in non-polarizable) and to the fact that our simulations refer to constant-volume conditions whereas the experiment was done at constant pressure. Note that constant-volume MD simulations by Neumann[6] using the TIP4P force field of water give results (half-filled circles in Figure 3) in better agreement with those reported in the laboratory experiment.[10]

We have also calculated the one-particle rotational correlation function

$$C_1(t) = \langle \mathbf{m}(t)\mathbf{m}(0) \rangle / \langle \mathbf{m}(0)^2 \rangle. \qquad (7)$$
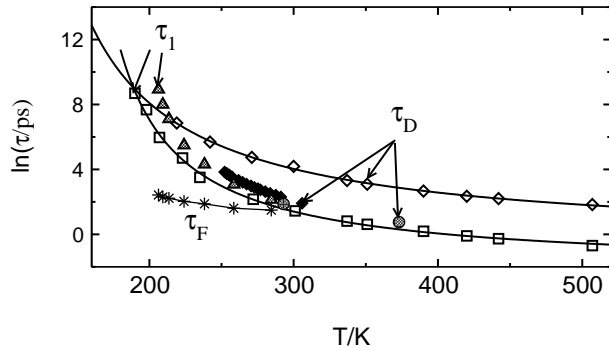
FIG. 3: Relaxation times $\tau_1$ (one-particle orientational relaxation, eq 7), and $\tau_D$ (Debye dielectric relaxation) vs $T$. The solid lines indicate the VF fits. The solid points refer to (constant pressure) experimental dielectric relaxation of supercooled water[10] and half-filled circles are results of MD simulations of TIP4P water by Neumann.[6] Half-filled triangles refer to one-particle rotational relaxation times $\tau_1$ reported by Sciortino *et al.*[11] Starts indicate the stretched exponential relaxation time $\tau_F$ of the intermediate scattering function of SPC/E water reported by Sciortino *et al.*[11]

$C_1(t)$ was fitted by a combination of the Gaussian and stretched exponential decay functions[11]

$$C_1(t) = [1 - A]\, e^{-(t/\tau_G)^2} + A e^{-(t/\tau_1)^\beta}. \qquad (8)$$

The relaxation time $\tau_1(T)$ shows a super-Arrhenius temperature dependence which can be approximated by the VF law: $\ln(\tau_1(T)/\text{ps}) = -2.15 + 578/(T - 137)$ (Figure 3). Our rsults for $\tau_1(T)$ (squares in Figure 3) agree resonably well with similar data previously reported by Sciortino *et al* (half-filled trianges in Figure 3).[11]

Figure 3 also shows the stretched exponential relaxation time $\tau_F(T)$ extracted from the time evolution of the incoherent intermediate scattering function $F_s(Q_{\max}, t)$ obtained from MD simulations of supercooled SPC/E water ($Q_{\max}$ is the position of the maximum of $F_s(Q_{\max}, t)$).[11] Among the relaxation times obtained from simulations, $\tau_F(T)$ and $\tau_D(T)$ change in the most similar fashion. However, they cannot be superimposed on one master curve as is often the case with other glass-formers.[12]

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