

Water Dipole Rotations modeled as auto regressive Processes

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1 Abstract

Continuum models of electrolyte/surface interactions are required for understanding water at surfaces, but can be notoriously complicated. In this study, we examine the limits of applicability and origin of information loss when using the equations of Brownian motion to predict water orientation dynamics in MD simulations of bulk liquid TIP4P water. The Brownian motion model is equivalent to assuming that the orientation of each water follows via a Gaussian autoregressive(AR) process in the presence of a time-dependent external field. We applied a standard Gaussian process regression to determine the temperature and time-scale dependence of the thermal noise. Temperature-dependent trends show a fairly constant friction coefficient. Residual plots show that adding memory to the fit (e.g.AR1, AR2, etc.) does little to improve the predictability of the model. This result is explained in the context of the dipole-dipole and dipole-field correlation functions, which are dominated by short-time, collisional relaxation on the femto-second scale.

2 Introduction

The prevalence of water in a variety of chemical and biological processes has provided inspiration for the experimental and theoretical effort aimed at understanding its behavior. Water often plays a key role in hydrophobic and hydrophilic surface interactions during protein folding, separation and catalysis.[1]. A very relevant problem is addressing the difference in the dynamic and static behavior of bulk and interfacial water located near surfaces. There is a general consensus that the dynamics of interfacial water are slower[2] than bulk's, but the associated length and time scales are still a topic of debate[3]. Experiments have also shown that waters response to a perturbation caused by a change in a nearby solutes charge is bimodal; There is a short lived inertial component on the femtosecond scale followed by a slower response due to collective rotational relaxation.[4, 5, 6]

Water gets its unique properties from its ability to dynamically form hydrogen bond networks[7]. Water molecules are also involved in long range electrostatic and multipolar interactions[8]. This makes modeling the collective dipole orientation dynamics of water

near charged surfaces quite a challenge[3, 1, 9]. Continuum models can accurately model long range effects but have difficulty with describing short range effects caused by individual water molecules.[10]. Explicit models usually provide more realistic results but carry a significant computational expense[11] that scales with the size of the system.

Modeling the collective dipole orientation dynamics of water molecules may provide valuable insight about intermolecular interactions occurring near charged surfaces. The most prominent theoretical model for water reorientation is Debye’s small step diffusion model[12]. Debye’s model describes a probability function that strictly depends on the angular orientation of dipole moments in the presence of an external perturbation [12]. Debye’s model offers an intuitive approach to understanding water reorientations but cannot account for large-amplitude angular jumps that involve hydrogen bond partner exchanges[7]. The short scale solvation dynamics of water have also been studied via simple Brownian oscillator models that decouple the short term librational motion from the larger timescale diffusive motion.[4] Results from these studies show that the high degree of networking present in water makes it difficult to describe solvation dynamics via single molecule reorientations.

This study aims to gain some insight on the strengths and weaknesses of the Brownian motion assumption. This is done by first assuming that the orientation of each water follows via a Gaussian autoregressive process in the presence of a time-dependent external field(figure 1a). The study then attempts to compare the effect of the short range, long range and total electric field on individual water dipole reorientations; This will provide an opportunity to determine if there is a quantifiable difference between the local and long range behavior for the Brownian model. Temperature and timescale dependent trends are also analyzed to provide further context.

Correlation functions and residual plots were used to understand the limits of applicability and origin of information loss in the brownian assumption. Residual plots for all three electric field variants show that changing the order parameter (e.g. AR1, AR2, etc.) causes a minimal improvement in the predictability of the model. The total electric field provided the smallest residuals for all considered time steps and generated the most accurate prediction for the friction coefficient $\frac{\beta\sigma^2\Delta t}{2}$. Results also show that increasing memory of fit(e.g. AR1, AR2, etc.) causes a significant increase in the accuracy of the friction coefficient when the short range electric field is used to do the fitting. This suggest that the Short range and total electric field can provide unique information that can be beneficial for analyzing collective dipole relaxation.

3 Methods

3.1 Bulk Water Molecular Dynamics(MD) Simulations

The gromacs simulation suite and the OPLS-AA all atom force field were used to generate constant volume and temperature trajectories of TIP4P water at 1 bar and temperatures ranging from 300K to 450K. The trajectories were then used to compute the the dipole moments on individual water molecules using the formula below.

$$\mu_a = \sum_{i:a} q_i \cdot r_i \quad (1)$$

μ_a represents the dipole on a single water molecule and q_i and r_i represent the charges and positions of its atoms(respectively).

The total electric field on individual water molecules was computed from the charges (q) and forces (F) generated from gromacs using,

$$E_a = \sum_{i:a} \frac{F_i}{q_i} \quad (2)$$

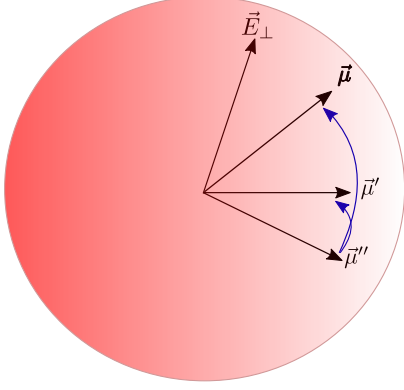
E_a represents the electric field on a single water molecule and F_i and q_i represent the electrostatic forces and charges respectively. The short range electric field was computed using the short term contribution to the Ewald summation.[13] The long range component of the electric field is generated by subtracting the short range term from the total electric field value generated from gromacs.

3.2 Brownian Model

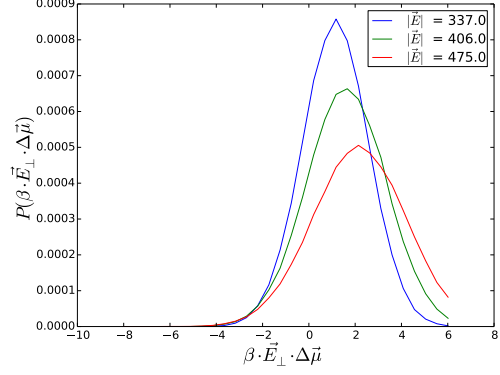
The implemented model treats the reorientation of bulk water dipoles (μ) as an isotropic auto-regressive process. There is also a mean field term (\vec{E}_\perp) that is varied to include the short range, long range and total contributions from the electric field

$$\Delta\mu_t = \alpha_0 \vec{E}_\perp + \alpha_1 \Delta\mu_{t-1} + \alpha_2 \Delta\mu_{t-2} + \dots + Z_t \quad (3)$$

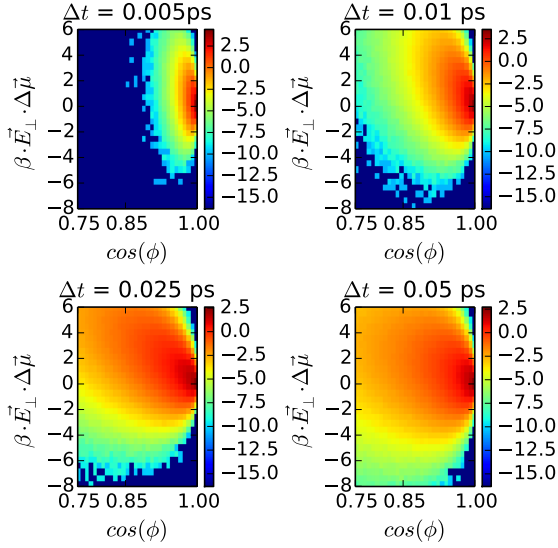
$\Delta\mu_t$ is the change in the dipole orientation in one dimension(x, y, z), α_i 's are a fitting parameters, Z_t is a random number with zero mean. For pure Brownian motion $\alpha_0 = \frac{\beta\sigma^2 \cdot \Delta t}{2}$ is the friction coefficient and $\langle Z_t^2 \rangle = \sigma^2 \Delta t$; $\beta = \frac{1}{k_b T}$ where k_b is Boltzmann's constant. This fit is implemented for \vec{E}_\perp of the short range, long range and total electric field values at time steps ranging from 0.01 - 10 ps and temperatures ranging from 275 - 450 k.



(a) Gaussian autoregressive (AR) process for dipole moment μ in the presence of perpendicular electric field (\vec{E}_\perp). μ' and μ'' represent values from the previous two time steps (AR2 process).



(b) Probability of the change in energy ($\beta \cdot \vec{E} \cdot \Delta \vec{\mu}$) associated with a constant electric field (\vec{E}) and dipole reorientation ($\Delta \vec{\mu}$); $\beta = \frac{1}{k_b T}$ where k_b is Boltzmann's constant; Figure is plotted at different magnitudes of the total electric field ($|\vec{E}|$) in units of $\frac{k_j}{\text{mol} \cdot \text{nm} \cdot e}$.



(c) Two dimensional histogram showing the probability (log-scale) of the cosine of the angle (ϕ) between μ and μ' at different values of $\beta \cdot \vec{E} \cdot \Delta \vec{\mu}$ and timesteps ranging from 0.005 - 0.05 picoseconds

4 Results

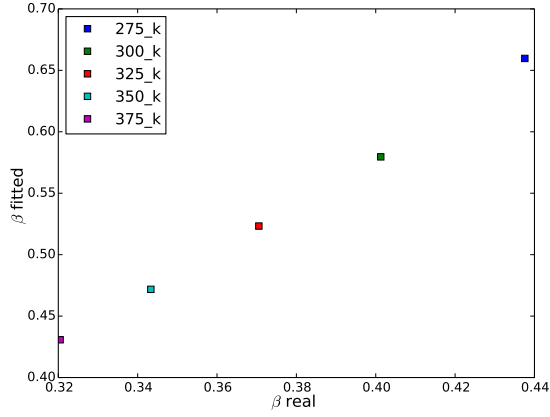
Reproducibility of the friction coefficient $\frac{\beta\sigma^2}{2}$ was used as a benchmark for the accuracy of the model. Temperature dependent fits for an AR1 model yielded fairly accurate friction coefficients as can be seen in figure 1b which plots the fitted β values determined from $\frac{\alpha_0}{\langle Z_t^2 \rangle / 2}$ vs the expected result. The fit was also performed for an AR0 model ($\Delta\mu_t = \alpha_0 \vec{E}_\perp + Z_t$) in order to determine the role of adding memory to the fit. The AR0 model shown in figure 1a seems to be less accurate than the AR1 model which suggests that adding memory can improve predictability. The results of an AR10 model are also plotted in 1c; results show a significantly higher fitted β values which can be attributed to a proportional decrease in the computed residuals(σ^2).

Results from timescale dependent fits were not as straightforward; The accuracy of the fit seems to be heavily dependent on the time scale of the orientations. Shorter time steps ranging from 0.01 - 0.05 picoseconds provide accurate values for the friction coefficient while longer time-steps ranging from 1.0 to 10.0 picoseconds provide inaccurate results. These results suggest the Brownian assumption holds true in the femtosecond scale that is characterized molecular friction and ultrafast solvent dynamics[5]; This might be promising for gaining some insight on short lived processes such as aqueous charge transfer[14] and rotational dynamics of small particles[6].

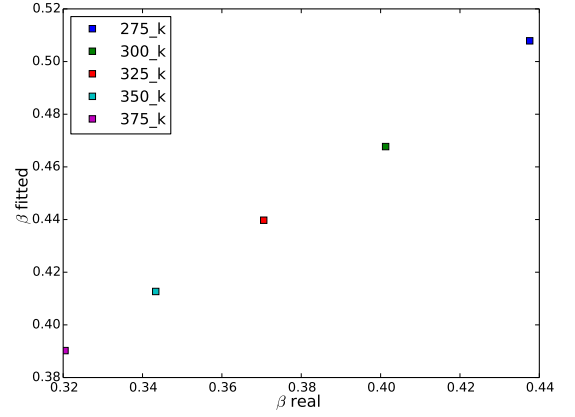
The lack of accuracy at larger timescales(1.0–10ps) is discouraging but can be explained in the context of the dipole-dipole and dipole-field correlation functions. The correlation time between the change in dipole moment $\Delta\mu$ and normal component of all electric field variants used (\vec{E}_\perp) are short lived and reside on the femtosecond scale as seen in figure 2; The same is true for autocorrelation of $\Delta\mu$. These short lived correlations limit the predictability of the model at larger time scales.

The shorter time steps were further analyzed to provide some insight on the role of the mean field variants. The total electric field provided the smallest residual values for all time steps (figure 4). Comparing the accuracy of the autoregressive fit for all the electric field variants also revealed some interesting trends. The total electric field provides the most accurate results at time steps between 0.025 and 0.05 picoseconds. The short range electric field provides the most accurate results at 0.01 picoseconds. The long range part of the electric field did not provide accurate values for any of the time steps.

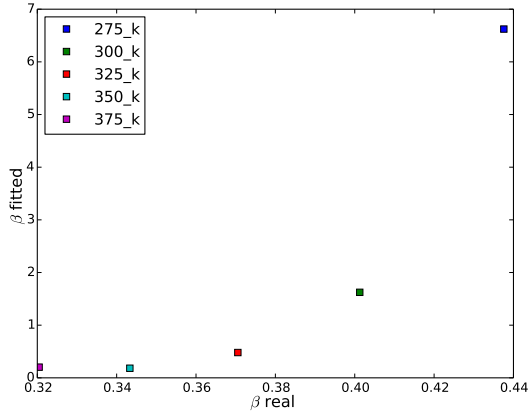
In order to probe the limits of applicability and origin of information loss, residual values of an order one(AR1) and order 10(AR10) fit were computed for all the electric field variants. Residual plots in figure 5 show that changing the order of the fit does not cause a significant improvement in the residual for any of the field variants. Changing the order parameter did cause a significant increase in the accuracy of the friction coefficient for the short range electric field. This result was not reproducible for the total and long range electric values which suggests that the short range electric field can provide unique information about the water reorientations. This result is promising because experiments



(a) AR0 Model

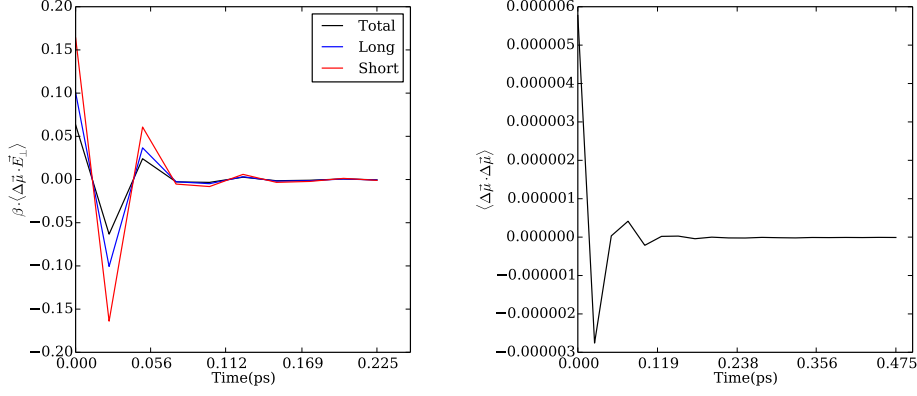


(b) AR1 Model



(c) AR10 Model

Figure 1: Temperature dependent values of β fitted determined from $\frac{\alpha_0}{\langle Z_t^2 \rangle / 2}$ Vs. β expected; Subplots show the effect of adding memory ($AR10 > AR1 > AR0$) to the autoregressive(AR) model



(a) Cross correlations between the change in dipole moment $\Delta \mu$ and normal electric field \vec{E}_{\perp} for the total, long and short range electric fields; $\beta = \frac{1}{k_b T}$ where k_b is Boltzmann's constant

(b) Auto correlation function for the change in dipole moment $\Delta \vec{\mu}$ in units of $nm^2 e^2$ where e is electron charge.

Figure 2: cross correlation and auto correlation functions at a time step of 0.025 picoseconds

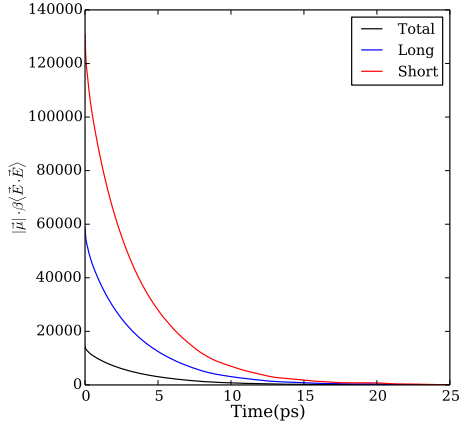


Figure 3: Auto correlation of the total (black), long range (blue) and short range (red) electric fields (\vec{E}) in units of $\frac{kJ}{mol \cdot nm \cdot e_0}$

have shown that almost half of waters solvation response to atomic solutes lies in the femtosecond timescale[5] which is dominated by local electrostatics.

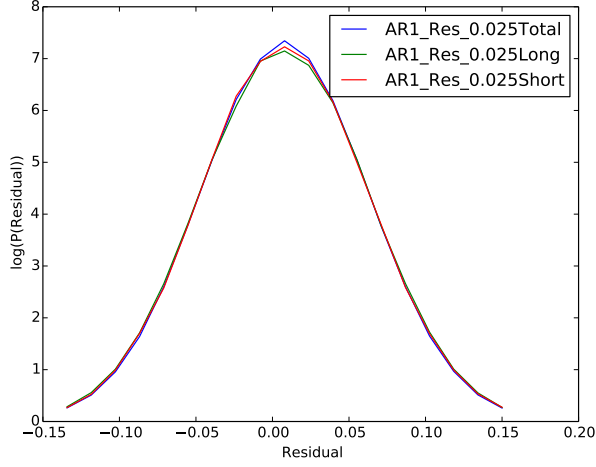
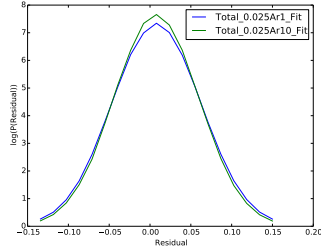
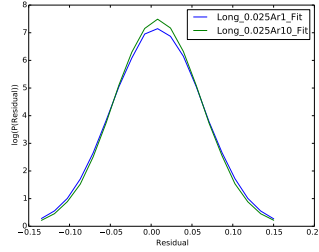


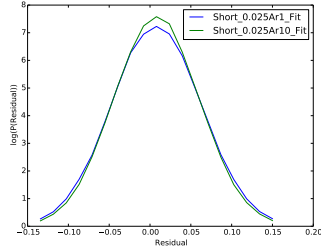
Figure 4: Comparison of residuals in units of (nm^2e^2) for all electric field variants(long range, short range and total) at a 0.025 picoseconds time step



(a) Total electric field



(b) Long range Electric Field



(c) Short range Electric Field

Figure 5: Effect of adding memory(AR1 vs AR10) on the computed residuals with units of (nm^2e^2) and a timestep of 0.025 picoseconds

5 Conclusion

Results show that simulate bulk TIP4P water reorientations are undergoing Brownian motion in the presence of a mean field; This is only true for a narrow range of time steps(0.01 - 0.05 picoseconds). Dipole-field correlation functions show that the correlations between water reorientations and electric field variants are extremely short; The same is true for the water-water autocorrelations. Residual plots for all three electric field variants(long range, short range, total) did not increase the predictability of the fit for small(AR1) or large order fits(AR10). The study did show that changing the order of the fit causes a significant increase in the accuracy of the friction coefficient for the short range electric field. These results suggest that the Short range and total electric field will be beneficial for analyzing collective dipole relaxation.

References

- [1] Bertil Halle. Protein hydration dynamics in solution: a critical survey. *Philosophical Transactions of the Royal Society of London B: Biological Sciences*, 359(1448):1207–1224, 2004.
- [2] Priyanka Dutta, Mohsen Botlani, and Sameer Varma. Water dynamics at protein–protein interfaces: Molecular dynamics study of virus–host receptor complexes. *The Journal of Physical Chemistry B*, 118(51):14795–14807, 2014.
- [3] Matthias Heyden, Douglas J Tobias, and Dmitry V Matyushov. Terahertz absorption of dilute aqueous solutions. *The Journal of chemical physics*, 137(23):235103, 2012.
- [4] Minhaeng Cho, Sandra J Rosenthal, Norbert F Scherer, Lawrence D Ziegler, and Graham R Fleming. Ultrafast solvent dynamics: Connection between time resolved fluorescence and optical kerr measurements. *The Journal of chemical physics*, 96(7):5033–5038, 1992.
- [5] Ralph Jimenez, Graham R Fleming, PV Kumar, and M Maroncelli. Femtosecond solvation dynamics of water. *Nature*, 369(6480):471, 1994.
- [6] JS Baskin, M Chachisvilis, M Gupta, and AH Zewail. Femtosecond dynamics of solvation: microscopic friction and coherent motion in dense fluids. *The Journal of Physical Chemistry A*, 102(23):4158–4171, 1998.
- [7] Damien Laage and James T Hynes. On the molecular mechanism of water reorientation. *The Journal of Physical Chemistry B*, 112(45):14230–14242, 2008.
- [8] CJF Böttcher, OC Van Belle, P Bordewijk, A Rip, and David D Yue. Theory of electric polarization. *Journal of The Electrochemical Society*, 121(6):211C–211C, 1974.
- [9] Stefania Perticaroli, Lucia Comez, Marco Paolantoni, Paola Sassi, Laura Lupi, Daniele Fioretto, Alessandro Paciaroni, and Assunta Morresi. Broadband depolarized light scattering study of diluted protein aqueous solutions. *The Journal of Physical Chemistry B*, 114(24):8262–8269, 2010.
- [10] Thomas Simonson. Macromolecular electrostatics: continuum models and their growing pains. *Current opinion in structural biology*, 11(2):243–252, 2001.
- [11] Linda Yu Zhang, Emilio Gallicchio, Richard A Friesner, and Ronald M Levy. Solvent models for protein–ligand binding: Comparison of implicit solvent poisson and surface generalized born models with explicit solvent simulations. *Journal of Computational Chemistry*, 22(6):591–607, 2001.

- [12] Peter Josef William Debye. *Polar molecules*. Chemical Catalog Company, Incorporated, 1929.
- [13] Ulrich Essmann, Lalith Perera, Max L Berkowitz, Tom Darden, Hsing Lee, and Lee G Pedersen. A smooth particle mesh ewald method. *The Journal of chemical physics*, 103(19):8577–8593, 1995.
- [14] Michael J Weaver. Dynamical solvent effects on activated electron-transfer reactions: principles, pitfalls, and progress. *Chemical reviews*, 92(3):463–480, 1992.