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System size and trajectory length dependence of the static structure factor and the diffusion coefficient as calculated from molecular dynamics simulations: The case of SPC/E water

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ABSTRACT

The effect of the applied trajectory length on the convergence of the self-diffusion coefficient was examined for the SPC/E water model in the NVT ensemble with different system sizes at 293 K. Temperature dependence and isotope effects, via using D_2O instead of H_2O, were also investigated. A simulation for the polarizable SWM4-DP model was also carried out to compare the effect of different potential models. Radial distribution functions and the neutron weighted structure factor were also calculated; they were found to be insensitive to changing the system size in the range of 216 to 16,000 molecules. On the other hand, the diffusion coefficient is rather sensitive to the applied trajectory length, system size and the method of calculation. The diffusion coefficient is therefore not appropriate for assessing, and distinguishing between, potential models of water, whereas the structure factor could serve as a more stable measure.

1. Introduction

Molecular dynamics (MD) computer simulation of aqueous systems, including protein solutions, has been (and will increasingly be) an indispensable technique for the investigation of these materials. A key element of such computations is the water interaction potential model applied. Therefore, precise knowledge concerning the behavior of the potentials, with respect to changing system size and simulation length, is of utmost importance.

Properties of the SPC/E [1–5] and SWM4-DP [6] water potential models have already been investigated thoroughly. The SPC/E model was chosen here, too, for its simplicity and popularity when studying aqueous systems, while the polarizable SWM4-DP model was selected as this model performed very well in our previous investigations regarding the structure of salt solutions [7,8]. As we could not find systematic data for the system size and trajectory length dependence of the static structure factor and the diffusion coefficient, we decided to perform a new investigation, first on pure water. Our aim was not so much to give any further information on these specific models, but rather, to exploit them as examples for studying the effects of different simulation parameters.

The system-size dependence of the self-diffusion coefficient was studied earlier by Dünweg [9] for polymers, by Yeh [10] for TIP3P water and Lennard–Jones fluids under periodic boundary conditions and by Spångberg [11] for dilute (single ion) aqueous Li^+ and Mg^{2+} solutions. An analytic correction based on hydrodynamic arguments, proportional to $1/L$ (where L is the simulation box size), was found. However, unfortunately, it is quite common in water simulation literature that the finite-size effect is neglected when the self-diffusion coefficient is calculated. One of our aims therefore is to draw attention to the importance of this, apparently not unknown, finite-size effect.

We found that apart from the applied system size, the simulation trajectory length influences strongly the actual value of the self-diffusion constant. Another aim of ours was then to study the dependence of the self-diffusion coefficient on the calculation method applied (mean square displacement vs. velocity auto correlation function) and the convergence of its value depending on the applied trajectory length and sampling interval.

The effects of temperature and isotopic substitution were also touched upon for one system size. Concerning the latter, it is known that classical molecular dynamics simulations can distinguish only between time-dependent properties of the isotopic compounds as the auto-correlation function, self-diffusion coefficient etc., but no difference is expected between equilibrium static properties such as the radial distribution function [12] (assuming identical interaction parameters and only the mass being different).

For studying the system-size effect also of static structural properties, the radial distribution function and the neutron weighted static structure factor were calculated and compared.

2. Simulation details

The primary water potential in our investigations was the SPC/E model [1], at a temperature of 293 K. All simulations were carried out in

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Table 1
Basic parameters of the simulation models: name, chemical composition, number of molecules (*N*), temperature, potential model, time step (*dt*), data collection length for the coordinates and velocities.

Name	System	*N*	*T* (K)	Potential	*dt* (fs)	Length for coord. (ns)	Length for vel. (ps)
H1	H_2O	216	293	SPC/E	2	8.2	1000
H2	H_2O	518	293	SPC/E	2	8	400
H3	H_2O	2000	293	SPC/E	2	8	200
H4	H_2O	16,000	293	SPC/E	2	8	100
H1-O	H_2O	216	298	SPC/E	1.25	6	625
D1	D_2O	216	293	SPC/E	2	8	1000
H3-T	H_2O	2000	298	SPC/E	2	8	200
SWM4-DP	H_2O	2000	293	SWM4-DP	2	8	200

the NVT ensemble under periodic boundary conditions with an atomic number density of $\rho = 0.099$ Å^{-3}. Four different system sizes, over a rather wide range, were used, containing 216, 518, 2000 and 16,000 water molecules; these systems are denoted by H1, H2, H3 and H4, respectively, corresponding to the increasing number of molecules. To investigate the temperature dependence, the H3-T model at 298 K was created; otherwise, the calculation was identical to that on the H3 model. The isotope effect was examined by substituting hydrogen atoms by deuterium. Model D1 is identical to H1, except that the mass of H atoms (1.00800 amu) changes to the mass of D atoms (2.014102 amu). Lennard–Jones (LJ) parameters for D_2O were the same as for H_2O and the same molecular geometry was assumed. Simulation H1-O was performed with 216 water molecules at 298 K, using slightly different run parameters by applying long-range dispersion correction for the energy (as implemented in the molecular dynamics simulation package 'GROMACS') and shorter (1.25 fs) time step, as in this calculation we tried to reproduce the simulations performed by Svishchev and Kusalik [13] to make the comparison with the results of these authors more accurate. For a comparison with a different potential model, the GROMACS-adapted [14] version of the SWM4-DP potential was chosen (calculation name: 'SWM4-DP'); this simulation, in terms of system size and temperature, was identical to H3. In our version of the SWM4-DP model the Drude particle was massless, no second thermostat for the oxygen-Drude pair was introduced and a time step of $dt = 2$ fs was applied (see Table 1 for the summary of systems used).

All the molecular dynamics simulations were carried out by the GROMACS simulation package [15], using the leap-frog algorithm for integrating Newton's equations of motion, with a time step $dt = 2$ fs, if not stated otherwise. Essential simulation parameters of the models are listed in Table 1. All simulations used the 6–12 LJ potential with a cutoff of 0.9 nm. The rigid molecular geometry was enforced by the SETTLE [16] algorithm. Calculations H1, H2, H3, H4, D1, H3-T and SWM4-DP were carried out with the same parameters (except for the differences explicitly given in Table 1), using particle-mesh Ewald [17] summation for the long range Coulomb-forces with interpolation order 4 and a grid size of 0.12 nm. The relative strength of the electrostatic interaction at the cutoff is ~10^{-5}, providing an accuracy of $5 \cdot 10^{-3}$ which is still better than the accuracy of the Lennard–Jones calculations. LJ parameters for the SPC/E oxygen were $\sigma = 0.316557$ nm and $\varepsilon = 0.650194$ kJ/mol, whereas they were set to be $\sigma = 0.31803$ nm and $\varepsilon = 0.861141024$ kJ/mol for the SWM4-DP water model. Temperature was held constant with the help of a Berendsen thermostat [18] using a temperature coupling time constant of $\tau_T = 0.1$ ps.

The equilibration stage, i.e., the first 400 ps of the simulation, was discarded; data collection was carried out for the following 6–8.2 ns, as it is given in Table 1. Coordinates were collected at each time step for each system, apart from the largest H4 model, where only every 10th configuration was kept. (The size of the configuration files for the already mid-size 2000 molecule systems was around 300 GB, which made the storage and handling of the file difficult.) Velocities for the calculation of the diffusion coefficient were collected for much shorter time periods (see Table 1), via restarting the simulation from the beginning of the data collection period.

3. Radial distribution functions and static structure factors

The average partial radial distribution functions, $g_{ij}(r)$, were calculated for 4000 configurations (spanning 8000 ps in time) of the model systems, consecutive sample configurations being $\Delta t = 2$ ps (or in case of H1-O, 1.25 ps) apart. As it can be seen in Fig. 1a, there is virtually no difference regarding the partial $g(r)$'s. In Fig. 1b the effect of slightly different parameters and temperature (H1 and H1-O), and isotope substitution (D1) can be seen. There is no difference between H1, H1-O and D1 models, indicating that such small differences in terms of the parameters and the 5 K temperature difference did not have a visible effect on the $g(r)$. (Note that isotopic substitution using classical MD stimulation was not expected to result in any structural change.) There is no visible difference between the corresponding partial $g(r)$-s of the H3 and H3-T model, so the 5 K temperature increase for H3-T does not have any effect (not shown).

On the other hand, there is a large difference between the size-wise and temperature-wise equal H3 and SWM4-DP models in terms of the radial distribution functions (Fig. 2a), especially in the O-H and H-H partials. The neutron weighted total structure factor is very different, too (Fig. 2b). This can be attributed partially to the fact that even the equilibrium geometry of the two models is different: in the SPC/E model, $d_{OH} = 0.1$ nm and $\beta_{HOH} = 109.47°$ whereas in the SWM4-DP model $d_{OH} = 0.09572$ nm and $\beta_{HOH} = 104.52°$.

The effect of the trajectory length was also investigated for the small H1 model. The average $g(r)$ and $S(Q)$ were calculated for 10, 20, 50, 100

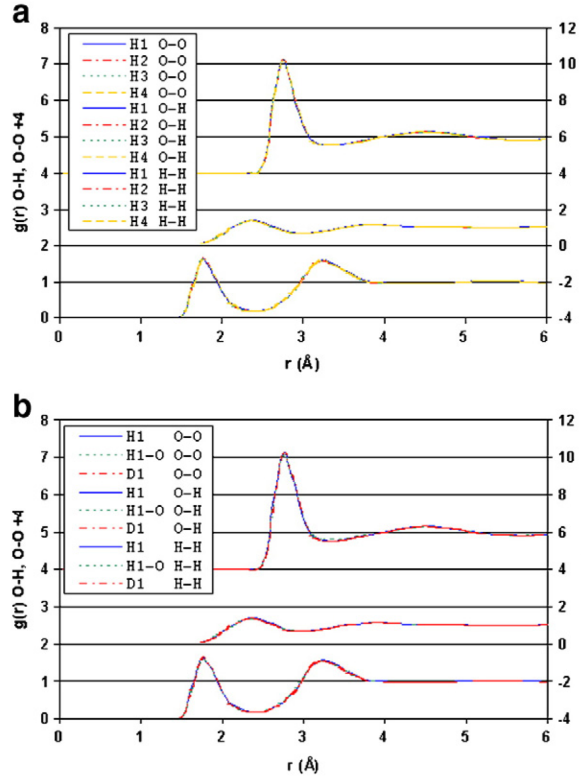

Fig. 1. Partial radial distribution functions for the various models. (a) The effect of system size for the 293 K H1, H2, H3 and H4 models. (b) The effect of temperature and slightly different run parameters (H1 and H1-O) and the isotope effect (D1) for the 216 molecules models. The O-H (O-D) partials are plotted against the left axis with no shift and the O-O partials shifted by 4 on the same axis, the H-H (D-D) partials are plotted against the right axis for the sake of clarity.