

Long-range Structures in Bulk Water. A Molecular Dynamics Study

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We present recent calculations of pair correlation functions and partial structure factors derived from molecular dynamics simulations of large bulk water systems (up to 12 167 water molecules). We observe small amplitude oscillations of the pair correlation functions in the range between 10 and 20 Å.

1. Introduction

Molecular Dynamics (MD) simulations are a versatile means to investigate the structure of bulk matter by modeling small systems of its components, i.e. atoms or molecules, using periodic boundary conditions. When simulating highly polar systems like water or aqueous solutions, the size of a system which can be simulated with a reasonable effort is limited by the need to correctly evaluate the long-ranging Coulomb forces between the (partial) charges [1]. Recently there have been attempts by Trokhymchuk and coworkers to overcome this restriction by combining MD simulations with integral equation methods [2–4]. The oxygen-oxygen structure factor derived from these calculations exhibits a so called “pre-peak” at the reciprocal space vector $k \approx 0.6 \text{ Å}^{-1}$. The pre-peak corresponds to structural features with a periodicity of about 10 Å in real space, similar to those found in glasses [5].

With the advent of massively parallel computers the simulation of water systems being one or two orders of magnitude larger than the commonly used 200–500 molecules has become feasible. This allows a sufficiently accurate direct calculation of structure factors at small wave numbers ($k < 1 \text{ Å}^{-1}$). Thus the predictions by Trokhymchuk et al. [3, 4], which are based on MD simulations of a system consisting of only 200 water molecules, can be verified or falsified directly. In the following we demonstrate that long-range correlations do indeed exist, but that they are not able to produce the predicted peak in the structure factor at $k \approx 0.6 \text{ Å}^{-1}$, which is in agreement with the available experimental evidence [6, 7].

Reprint requests to Dr. E. Spohr.

2. Details of the Simulations

We have performed three simulations of large bulk water systems in cubic simulation boxes with periodic boundary conditions using either the rigid TIP4P [8] or the flexible BJH [9] water model. The two TIP4P systems consist of 12 167 water molecules in a cubic box of edge length 71.38 Å (System I) and of 2744 molecules in a cubic box with length 43.45 Å (System II). The equations of motion have been integrated for 54 and 220 ps, respectively. The *moldy* MD program [10] with a time step of 0.75 fs, employing a Beeman predictor corrector algorithm for quaternions [11, 12], has been used. The temperature has been kept at 300 K by a Nosé-Hoover thermostat [13] with an inertia parameter of $100 \text{ kJ mol}^{-1} \text{ ps}^2$. To investigate a possible model dependence of the results we have also simulated a system of 1600 BJH water molecules in a cubic box of side length 36.3 Å (System III) with our own simulation program. The Verlet algorithm [14] has been used with a time step of 0.5 fs. The temperature has been kept constant at 300 K by a Berendsen thermostat [15] with a time constant of 0.4 ps. Long-range Coulomb interactions were calculated by Ewald-summation [1, 16] in all cases.

3. Results and Discussion

The configurations from the simulations are used to calculate radial distribution functions (RDF) up to distances of $r = L/\sqrt{2}$ (with L being the box length). In the range $L/2 < r < L/\sqrt{2}$ no periodic images were included; the RDFs were normalized accordingly.

As an example, the oxygen-oxygen RDF, $g_{\text{OO}}(r)$, from simulation I (with 12 167 TIP4P water mole-

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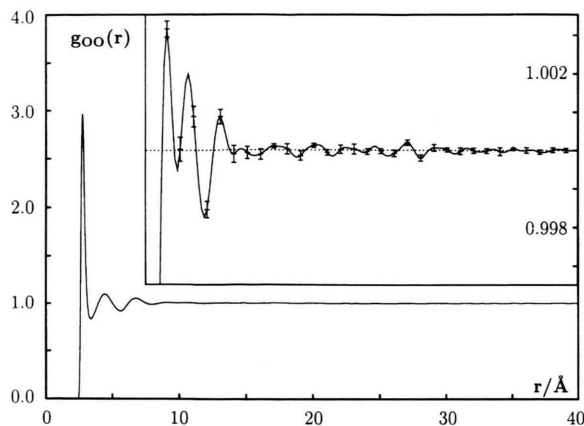


Fig. 1. Oxygen-oxygen pair correlation function g_{OO} from simulation I. The inset is a 400-fold magnification of the region between $r = 7.5$ Å and $r = 40$ Å. Errorbars represent ± 1 standard deviations of the mean value over seven 7.5-ps blocks.

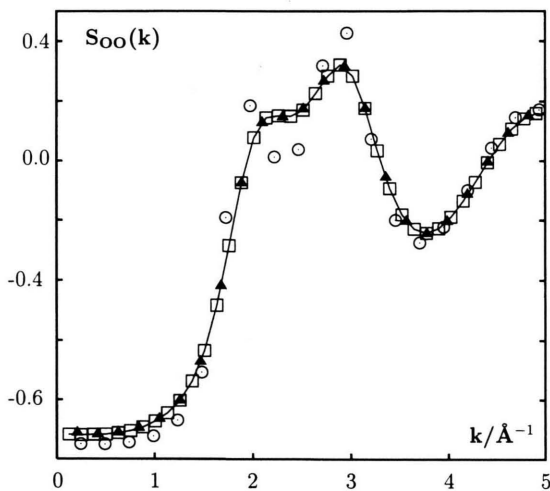


Fig. 2. Partial structure factors. Simulation I: squares and solid line, simulation II: triangles, simulation III: circles.

cules) is presented in Figure 1. The inserted plot in Fig. 1 is a 400-fold magnification of the region between 7.5 and 40 Å. Up to a distance of about 15 Å distinct oscillations are visible.

The oscillations in the region up to 30 Å are within the statistical error limits of the simulation. The inset has been filtered with a low-pass Fourier transform filter to eliminate high frequency noise.

The structure of the RDFs from simulations II and III is similar in the interesting range between 10 and 20 Å. From the (unfiltered) pair correlation functions the oxygen-oxygen partial structure factors $S_{OO}(k)$

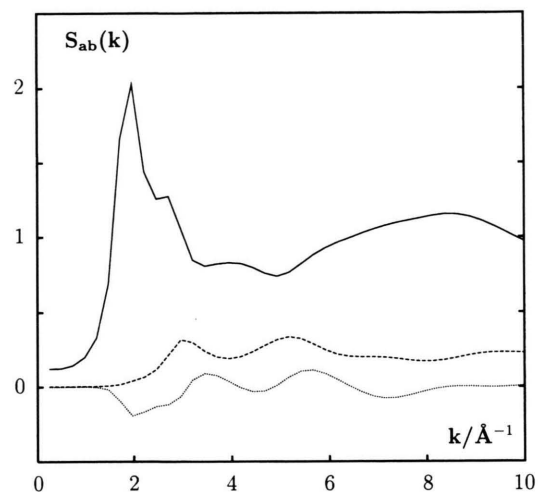


Fig. 3. Bhatia-Thornton partial structure factors. Solid line: density-density (S_{NN}); dashed line: charge-charge (S_{CC}); dotted line: density-charge (S_{NC}).

have been obtained according to

$$S_{OO}(k; L/\sqrt{2}) = \frac{4\pi\varrho_O}{k} \int_0^{L/\sqrt{2}} (g_{OO}(r) - 1) \sin(kr) r dr, \quad (1)$$

where ϱ_O is the oxygen density and $L/\sqrt{2}$ is the distance up to which the pair correlation function has been calculated. The resulting graphs are shown for all three simulations in Figure 2. The points displayed correspond to the k vectors compatible with the dimensions of the periodic boxes. The graphs of the two simulations with the TIP4P water model coincide completely, and S_{OO} from the BJH water model (simulation III) differs from the TIP4P data only in the range $1.5 \text{ Å}^{-1} < k < 3.5 \text{ Å}^{-1}$. This region represents the short to medium-ranged structural features of bulk water; it characterizes the well-known differences in the pair correlation functions between the two models in the region below 10 Å. There is definitely no indication from the direct simulations that oscillations as those proposed in [4] exist in the range $0.5 < k < 1.0 \text{ Å}^{-1}$.

From the pair correlation functions of the BJH simulation III we also calculated the Bhatia-Thornton structure factors $S_{NN}(k)$ for density-density, $S_{CC}(k)$ for charge-charge, and $S_{NC}(k)$ for density-charge correlations as described in [5]:

$$S_{NN}(k) = c_O^2 A_{OO}(k) + c_H^2 A_{HH}(k) + 2c_O c_H A_{OH}, \quad (2)$$

$$S_{CC}(k) = c_O c_H \{1 + c_O c_H [A_{OO}(k) + A_{HH}(k) - 2A_{OH}(k)]\}, \quad (3)$$

$$S_{\text{NC}}(k) = c_{\text{O}} c_{\text{H}} \{c_{\text{H}} [A_{\text{HH}}(k) - A_{\text{HO}}(k)] - c_{\text{O}} [A_{\text{OO}}(k) - A_{\text{HO}}(k)]\}. \quad (4)$$

c_{O} and c_{H} are the oxygen and hydrogen mole fractions, respectively, and $A_{\text{OO}}(k)$, $A_{\text{HH}}(k)$, $A_{\text{HO}}(k)$ the Faber-Ziman partial structure factors $A_{\alpha\beta}$ according to

$$A_{\alpha\beta}(k) = 1 + \frac{4\pi n_0}{k} \int_0^\infty [g_{\alpha\beta}(r) - 1] \sin(kr) r dr, \quad (5)$$

where n_0 is the total number density of atoms in the system. The resulting plots (Fig. 3) are similar to those presented in [4]. The density-density partial structure factor, however, does not exhibit oscillations for wave numbers below 1 \AA^{-1} and is in very good agreement with the experimental data [6, 7].

In summary, the simulations presented here show the existence of long-range correlations in bulk water. On the basis of the high statistical accuracy of the simulations it can be stated that the correlations last roughly up to 20 \AA . The amplitudes of the oscillations in this region are, however, about three orders of magnitude smaller than the amplitudes of the first and second neighbour peaks in the pair correlation functions. Detecting further oscillations would need signif-

icantly longer simulation times in order to reduce the $1/\sqrt{N}$ noise by at least one more order of magnitude. The main result of the study is that no oscillations in the low k region ($k < 1.5 \text{ \AA}^{-1}$) can be detected for at least two different commonly used water models; it thus rules out the existence of a glass-like so-called pre-peak from the simulations.

The pre-peak has been predicted by Trokhymchuk *et al.* [3] on the basis of a combination of computer simulations to obtain a short-range reference structure and an optimized cluster expansion. The same scheme was used successfully before [2] to obtain thermodynamic data. One important conclusion from the current study is thus that combinations between integral equations and computer simulations, at least with the approximations made in [2], can be useful to predict thermodynamic data but not to predict structural features.

Acknowledgements

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