Molecular Dynamics and Self-Diffusion in Supercritical Water

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The dynamics of the hindered molecular translations and librations and their dependence on temperature and density has been investigated for supercritical water in the range $630 < T < 780 \, \text{K}$ and $0.166 < \rho < 1.284 \, \text{g/cm}^3$ in terms of velocity autocorrelation functions obtained from molecular dynamics simulations. Calculated self-diffusion coefficients of supercritical water agree well with available experimental data and results of other simulations. The validity of the Stokes-Einstein relation has been tested using the experimental data on viscosity of supercritical water.

I. Introduction

The knowledge of physico-chemical properties of aqueous systems at high temperatures and pressures has long been considered of great importance for geochemistry, chemical and power engineering, and environmental chemistry [1–3]. In recent years supercritical water has become a subject of ever growing scientific interest as a medium for chemical reactions [4]. Flameless oxidation in supercritical water already emerges as a promising advanced technology for the effective destruction of a wide variety of hazardous wastes [5]. Spontaneous ignition of diffusion flames in supercritical aqueous media has also been observed [6].

Due to the large compressibility of water under supercritical conditions, small changes in pressure can produce substantial changes in density which, in turn, affect diffusivity, viscosity, dielectric and solvation properties, thus dramatically influence the kinetics of chemical reactions in supercritical water. Although, kinetics of such reactions is now extensively studied (e.g., [7, 8]), many important questions still remain unanswered. For instance, it is not well understood to what extent diffusion controls the reaction rate [4], and in most cases there is no data on diffusion of aqueous species under supercritical conditions.

On the other hand, Molecular Dynamics (MD) computer simulation technique is now routinely applied to various complex aqueous systems under normal conditions (e.g., [9, 10]), providing many fundamental correlations between molecular-scale microscopic properties of the systems, (e.g., positions, velocities, and orientations of individual particles) and their macroscopic, experimentally measurable properties. The same approach can contribute significantly to a better understanding of the dynamic behavior of supercritical aqueous fluids on a molecular level. However,
extensive simulations of water covering wide ranges of thermodynamic conditions were started only recently [11 - 14].

This paper presents the results of MD simulations of pure supercritical water in a range of densities varying about an order of magnitude form a relatively dilute vapor to a highly compressed liquid. Dynamics of translational and librational movements of individual molecules is discussed in terms of velocity autocorrelation functions. Self-diffusion coefficients obtained from the simulations are compared with experimental data from NMR spin-echo measurements in compressed supercritical water [15].

II. Molecular Dynamics Simulations

Five simulation runs were performed using a standard NVE-ensemble MD algorithm (e.g., [16]). The systems studied in the simulations consisted of 200 water molecules in a cubic box with the side length adjusted to give the required density. The densities of every run are given in Table I and correspond to a pressure range 0.25 ≤ P ≤ 25 kbar. The flexible BJH water model [19] was employed to calculate the intermolecular interaction energy. This model has already been successfully used in numerous MD simulations of aqueous systems at normal temperatures [9, 10].

Due to the stability requirements of the integration procedure at high temperatures, the molecular equations of motion were integrated with the time-step of 1.5 × 10^-16 s, which is somewhat smaller than normally used in room-temperature simulations with the BJH potential (2.5 × 10^-16 s, [9]). The simulations extended to about 15000 time-steps after a pre-equilibration of approximately the same length. Ewald summation in tabulated form was used for the coulombic part of the interactions, and the "shifted-force" method (see e.g. [16]) was used for the other parts of the BJH potential. With this procedure, the total energy change ΔE/E during the simulation was smaller than 5 × 10^-5 in all cases and the average temperature remained constant without rescaling, which is very important for the reliability of the dynamical properties reported here calculated from velocity autocorrelation functions.

Thermodynamic and structural results of the present simulations are discussed in detail elsewhere [14] together with the results of our previous Monte Carlo simulations of water under similar thermodynamic conditions [20]. Our aim here is to discuss the dynamics of molecules in supercritical water.

The dynamical behavior of a fluid can be monitored in terms of molecular center of mass velocity autocorrelation functions (VACF), which are calculated according to:

\[ \langle v(0) \cdot v(t) \rangle = \frac{1}{N N_T \sum_{i=1}^{N_T} \sum_{j=1}^{N} v_i(t) \cdot v_j(t + t) } \]

where \( N \) denotes the number of particles, \( N_T \) the number of time average and \( v_j(t) \) the velocity of particle \( j \) at time \( t \).

The velocity autocorrelation functions for water molecules at different temperatures and densities calculated from MD simulations are shown in Fig. 1. Obviously, the VACFs decay faster at the higher density. The density dependence of these functions is very similar to that for water at normal temperatures [21], in agreement with the similarity in the pressure induced changes of the structural properties [14]. At the liquid-like density of 0.9718 g/cm³ (run D), where a comparison with previous normal-temperature simulations of Jancsó et al. [21] can be made, the effect of temperature on the VACFs is also in close agreement with the results of Stillinger and Rahman [17] who simulated water at temperatures up to 600 K and a density of 1 g/cm³ using a BNS water model.

The pronounced effects of temperature and density are also reflected in the spectral densities of the hindered translational motions for the water molecules which have been calculated by Fourier transformation:

![Normalized center of mass velocity autocorrelation functions for the water molecules under supercritical conditions](image)
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Fig. 2
Fourier transform of the VACFs, in arbitrary units, for supercritical water at liquid-like densities. A similar spectrum for normal liquid water obtained by Jancsó et al. [21], is given for comparison

\[
f(v) = \sqrt{\frac{2\pi c}{\langle v(0) \cdot v(t) \rangle}} \int_0^\infty \cos(2\pi c v t) dt
\]

from the normalized velocity autocorrelation functions. The spectra for the two high-density simulations (runs D and E) are shown in Fig. 2 as dotted and dash-dotted lines, respectively. A similar spectrum obtained by Jancsó et al. [21] from MD simulations of normal liquid water are given for comparison in Fig. 2 as a solid line. In normal liquid water, the peaks at \( \approx 60 \text{ cm}^{-1} \) and around \( \approx 200 \text{ cm}^{-1} \) are usually assigned to the intermolecular hydrogen bond oxygen hydrogens bending motions and hydrogen bond oxygen stretching motions, respectively (see, e.g., [22]).

As can be seen in Fig. 2, both peaks have completely disappeared at supercritical temperatures, indicating a significant break down of the hydrogen bond structure of water even at liquid-like densities. The lower-density spectra for the MD runs A –C (out of scale in Fig. 2) follow the same trend. On the other hand, a detailed analysis of atom-atom radial distribution functions and intermolecular energy distribution functions [14, 20] clearly indicates, that hydrogen bonding persists at these supercritical temperatures in the whole density range presently studied.

The same temperature dependence of the power spectra of velocity autocorrelation functions has been observed earlier by Stillinger and Rahman [17] in MD simulations of water at elevated temperatures using BNS and ST2 potentials.

It is important to note that the decrease (with increasing density and temperature) of the spectral densities in the frequency range corresponding to the hydrogen bond bending and stretching motions is quite similar to the effect of dissolved Li\(^+\) ions as obtained by Szász and Heinzier [23] from a MD simulation of a 2.2 molal LiI solution with the ST2 water model. At normal temperature this similarity has already been noted by Jancsó et al. [21].

Rotational relaxation of water molecules is often discussed in terms of angular momentum autocorrelation func-

tions (e.g., [17]). As the BJH water model used in the present simulations allows distortions of the individual water molecules, a slightly different approach has been used. In order to separate the various modes of molecular librations (hindered rotations) and intramolecular vibrations the scheme proposed by Bopp et al. [24, 25] has been employed. The instantaneous velocities of the two hydrogen atoms of a water molecule in the center-of-mass system are projected onto the instantaneous unit vectors: i) perpendicular to the O – H bonds in the plane of the molecule \( (\mathbf{p}_1 \text{ and } \mathbf{v}_1) \), and ii) perpendicular to the plane of the molecule \( (\mathbf{p}_2 \text{, and } \mathbf{v}_2) \).

Using capital letters to denote the projections of the hydrogen velocities onto the corresponding unit vectors, the following quantities are defined:

\[
R_x = V_1 - V_2, \quad R_y = P_1 + P_2, \quad R_z = P_1 - P_2.
\]

where \( R_x, R_y, \text{and } R_z \) approximate the instantaneous rotations around the three principal axes of the water molecule, as defined in the insertion of Fig. 3. The normalized velocity autocorrelation functions calculated in this way for water molecules under the supercritical thermodynamic conditions presently studied are shown in Fig. 3. The differences between \( x, y, \text{and } z \) reflect the different moments of inertia around the three axes.

Fig. 3
Velocity autocorrelation functions for the three libration modes of water molecules at supercritical temperatures and different densities. The librations are calculated separately for the three components in a molecule fixed coordinate system as defined in the insertion.
The Fourier transformations of these velocity autocorrelation functions result in the spectral densities of the corresponding motions. They are shown in Fig. 4 for the librational modes around the three principal molecular axes. At high temperatures a density decrease causes a significant red shift of the librational frequencies around the \( x \) - and \( y \)-axes, and the maxima completely disappear at the lowest density studied (not shown in Fig. 4). The same trend is seen for the librations around the dipole moment axis \( (z) \), where the maximum disappears already at much higher densities. This means that the water molecule is able to rotate freely around this axis, even when its rotation around the other two axes is still hindered by the neighboring molecules.

The effects of temperature and density on the geometry and the intramolecular vibrations of individual water molecules, obtained from the present MD simulations, are analyzed elsewhere [14, 20].

Self-diffusion coefficients can be determined from MD simulations through the velocity autocorrelation functions, Eq. (1), with the help of the Green-Kubo relation (e.g., [16]):

\[
D = \lim_{t \to \infty} \frac{1}{3} \langle \mathbf{v}(0) \cdot \mathbf{v}(t') \rangle dt'.
\] (4)

The self-diffusion coefficients \( D_{\text{MD}} \), calculated from the present simulations, are compared with the available measurements for supercritical water [15] in Table 1. We estimate the statistical uncertainty of calculated values to be about 10%, i.e., comparable with the accuracy of experimental data. Thus, the simulated values of \( D \) agree very well with experiments. The density studied experimentally is \( \leq 0.7 \, \text{g/cm}^3 \), and for the two points of higher density (runs D and E) an extrapolation has been made using the semiempirical fit equation given by Lamb et al. [15]. The discrepancies for these two points can be ascribed to the significant density extrapolation, although it has been noted earlier that the BJH water potential somewhat underestimates self-diffusion coefficients at liquid-like densities and normal temperatures [21].

On the other hand, it is quite surprising that three other high-temperature MD simulations [11, 13, 17] at a normal liquid density, \( \rho = 1 \, \text{g/cm}^3 \), with three different intermolecular potentials, resulted in self-diffusion coefficients virtually identical to that of run D. This seems to indicate that all the intermolecular potentials are able to reproduce correctly the temperature dependence of the self-diffusion coefficients up to supercritical temperatures at least at liquid-like densities. It may be also an indication of the fact that calculations of self-diffusion coefficients from MD simulations are not very sensitive to the details of the particular intermolecular potential used.

The self-diffusion coefficient is often related to the shear viscosity \( \eta \) through the hydrodynamic Stokes-Einstein equation:

\[
D = k_B T/(C_{\text{SE}} \pi \eta a),
\] (5)

where \( a \) is the hydrodynamic radius, \( C_{\text{SE}} = 6 \) for stick boundary conditions, \( C_{\text{SE}} = 4 \) for slip boundary conditions, and other symbols have their usual meaning.

From the structural results of the simulations [14, 20] a value of \( a = 1.4 \, \text{Å} \) can be estimated. Available subcritical measurements of self-diffusion [27, 28] and viscosity [18] can be adequately fitted with a single value of \( C_{\text{SE}} = 4.8 \). Using these data and supercritical viscosity measurements of Dudzik and Frank [18] the values indicated in Table 1 as \( D_{\text{SE}} \) have been obtained. It can be seen that this procedure gives reasonable results at all but the highest and the lowest densities studied. At the lowest density (run A) direct experimental measurements [15] are available, which indicate that \( D_{\text{SE}} \) underestimates the real value of \( D \) by about 40%. At the highest density (run E) both \( D_{\text{SE}} \) and \( D_{\text{exp}} \) are close to each other and significantly differ from the simulated \( D_{\text{MD}} \) value. However, at this point both \( D_{\text{SE}} \) and \( D_{\text{exp}} \) are the results of long-range density extrapolations, so no final conclusion on the validity of the Stokes-Einstein relation can be drawn.

It is instructive to calculate the values of \( C_{\text{SE}} \) using the simulated self-diffusion coefficients and experimental data.
on viscosity [18]. The results are given in the last line of Table 1. The density dependence of \(C_{SE}\) obtained in this way is in good qualitative agreement with calculations of Lamb et al. [15], who used a temperature-dependent hydrodynamic radius \(\alpha\). However, the extremely high value of \(C_{SE}\) for run E may indicate that the self-diffusion coefficient of water at this thermodynamic point lies in reality somewhere between \(D_{MP}\) and \(D_{SE}\).

IV. Conclusions

In this paper the results of molecular dynamics computer simulations of pure supercritical water in a wide range of temperatures and densities have been presented, with particular emphasis on the dynamics of single molecular movements. The hindered molecular translations and librations and their dependence on temperature and density for supercritical water have been analyzed in terms of velocity autocorrelation functions and the corresponding power spectra. Calculated self-diffusion coefficients of supercritical water are in a good agreement with available experimental data and results of other simulations. A strong density dependence of the Stokes-Einstein coefficient seems to indicate that the hydrodynamic Stokes-Einstein equation cannot be directly applied under supercritical conditions over a wide range of temperatures and, especially, densities.

It is obvious that computer simulations of supercritical water and aqueous solutions are just at the beginning as far as their practical relevance is concerned. However, the results presented here seem to demonstrate that simulation methods can contribute significantly to a better understanding of the properties of these complex chemical systems. Being a source of information intermediate between theory and experiment, computer simulations can greatly stimulate the development of both theoretical and experimental studies of the supercritical aqueous fluids in the near future.

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References


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