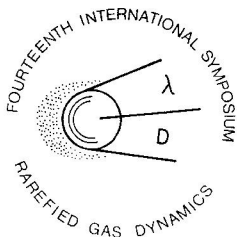


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MOLECULAR DYNAMICS SIMULATION STUDY OF AGGREGATION PHENOMENA IN SUPERCOOLED WATER

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SUMMARY The temperature dependence of several structural and dynamical correlation functions of supercooled water has been studied by molecular dynamics (MD) simulations. Particularly, the aggregation of water molecules with four hydrogen bonds and some percolation theory aspects are discussed.

INTRODUCTION

The investigation of water on a molecular level is of great biological, chemical as well as technical importance, since water is a major constituent of our planet. Moreover water shows a fascinating anomalous behaviour in its normal liquid range, which becomes even more pronounced in the supercooled liquid region. Such anomalies are (a) density maximum at about 4 °C, (b) negative volume of melting, (c) isothermal compressibility minimum at about 46 °C, (d) a possible thermodynamic singularity at - 45 °C. Also, studying supercooled water is essential to understand the nucleation behaviour of ice crystals and cloud formation in high atmosphere [1], [2]. Homogeneous nucleation of ice crystals can occur by an intermediate formation of supercooled water during the phase change from water vapour to ice - the so-called condensation freezing. Supercooled water is found in the atmosphere down to - 40 °C. It is widely agreed that the anomalous behaviour of water is connected with the presence of the spacefilling random network of hydrogen bonds [3]. This network shows a preference for local tetrahedral (icelike) geometry. It has been shown, that there are regions of water molecules with four hydrogen bonds, which show decreased local density and increased local order [4]. The clustering behaviour of such fourbonded water molecules is strongly cooperative (i.e. nonlinear) and is of main interest in this study. Therefore, intensive molecular dyna-

mics simulations for different temperatures were made, using an ST2-interaction potential [5]. Here we concentrate on the temperature dependence of several correlation functions. To test the percolation model of Stanley and Teixeira [6], [7] intensive percolation theory analyses were done.

DESCRIPTION OF THE MD-SIMULATION METHOD

To study the temperature behaviour in the supercooled region, we performed eight simulation runs ranging from 287 K to 235 K. The density has been kept constant at $\rho = 1.0 \text{ g/cm}^3$. The Newton equations of motion were solved for a system of 216 water molecules in a cubic box, using Verlet form of the constraint dynamics algorithm. Moreover, the calculations were based on periodic boundary conditions and the use of neighbour lists. Penetrating into the temperature region of supercooled water, we are faced with strongly increasing relaxation times. Therefore, the lengths of the simulation runs cover time intervals which increased from about 20 ps to 150 ps. The cut-off radius for direct interactions was reduced to oxygen separations of $R_c = 7.8 \text{ \AA}$. To include long range interactions, a reaction field method was implemented. This method had been examined carefully by Steinhäuser [8]; including the use of a tapering function to smooth the cutoff. The timestep size for the integration of the equations of motion was $\Delta t = 1.22 \cdot 10^{-15} \text{ sec}$. The simulation runs were performed on a VAX 780 with attached array processor FPS 164.

PAIR DISTRIBUTION FUNCTIONS AND TIME-DEPENDENT CORRELATION FUNCTIONS

The microscopic structure of fluids is usually characterized by pair distribution functions $g_{\alpha\beta}(R)$, which describe deviations from the uniform local distribution of the constituents: $4\pi R^2 \rho g_{\alpha\beta}(R) dR$ gives the number of particles β one finds on average within a distance R and $R+dR$ from a reference particle α (ρ is the average number density of particles β).

Fig. 1 shows oxygen-oxygen distribution functions $g_{oo}(R)$, which become more pronounced, when decreasing the temperature. Experimentally accessible is the Fourier transformed of $g(R)$, the so-called structure factor $S(Q)$, which can be written as

$$S(Q) = \frac{1}{N} \left\langle \sum_{k,l} \exp(i \underline{Q} \cdot \underline{R}_{kl}) \right\rangle, \quad (1)$$

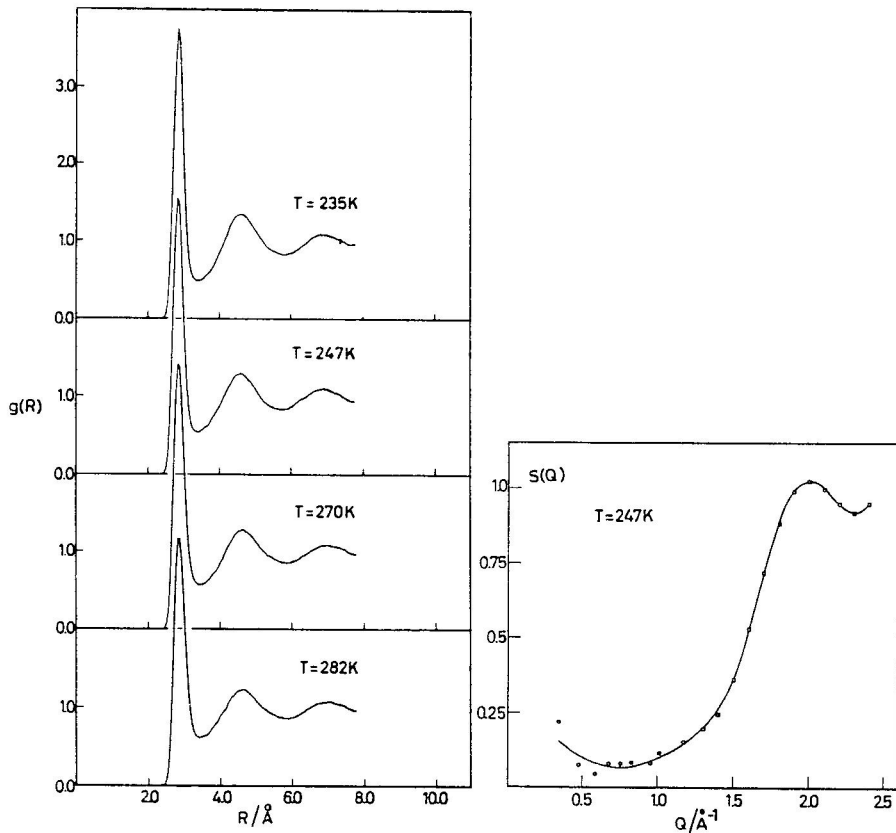


Fig. 1: Oxygen pair correlation function and structure factor from oxygen positions

where the sum includes all pairs of molecules k and l and R_{kl} is the corresponding oxygen distance vector; N is the particle number. As mentioned before, the existence of a thermodynamic singularity at -45°C has been postulated, which manifests itself by a rapidly increasing isothermal compressibility κ_T . This quantity is a measure for the occurring long range density fluctuations and is related to $S(Q)$ by

$$S(Q=0) = \rho k_B T \kappa_T \quad (2)$$

(k_B is the Boltzmann constant). In accordance with these considerations small angle x-ray scattering experiments on supercooled water by Bosio et al. [9] revealed an increase of $S(Q)$ for $Q \rightarrow 0$, which becomes stronger with decreasing temperatures.

From these measurements a typical correlation length of about 8 Å is extracted for the density fluctuations.

Fig. 1 also shows $S(Q)$ for our simulation run at $T = 247$ K. For small Q formula (1) is used, whereas for $Q > 1.2$ Å⁻¹ a direct Fourier transformation of $g_{oo}(R)$ from Fig. 1 can be utilized. The qualitative behaviour of $S(Q)$ is in accordance with the scattering experiments, indicating the presence of long range fluctuations in our model liquid.

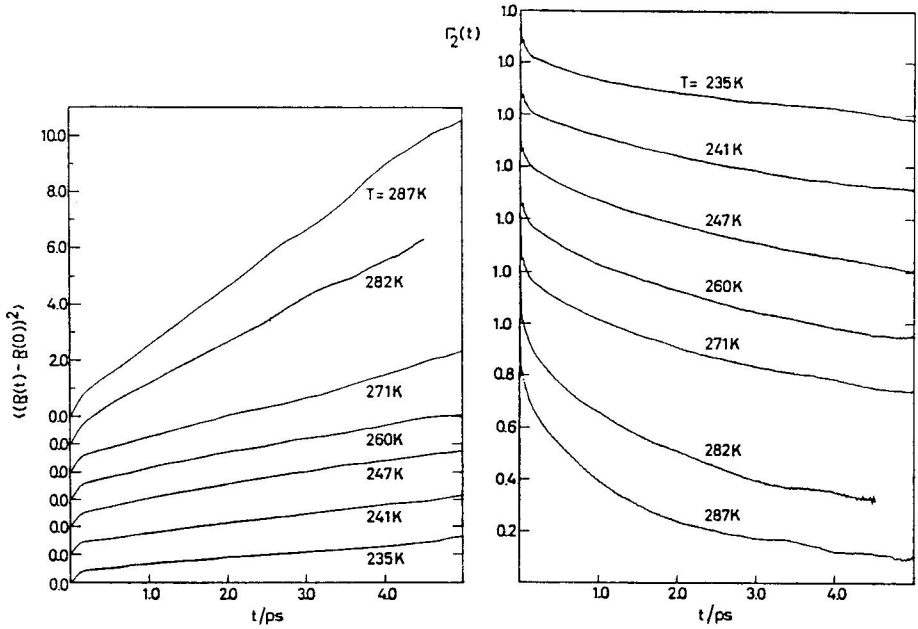


Fig. 2: Mean squared displacement of the oxygens and dipole direction correlation function $\Gamma_2(t)$

The mean squared displacements $\langle \Delta R^2 \rangle$ of the oxygens at various temperatures are shown in Fig.2. As one can see, the mobility of the water molecules is reduced drastically, when decreasing the temperature, leading to a nearly vanishing long time slope (self diffusion coefficient) at $T = 235$ K. The initial parabolic course of $\langle \Delta R^2 \rangle$ is explained by a nearly free flight motion for very short times within the cage of nearest neighbors. The reorientational motion has been studied by calculating time autocorrelation functions $\Gamma_1(t)$ for Legendre polynomials $P_1(\cos\theta)$ of order 1 of different molecule fixed unit vectors $\underline{\mu}_i$

$$\Gamma_1(t) = \langle P_1(\underline{\mu}_i(t_0) \underline{\mu}_i(t_0 + t)) \rangle . \quad (3)$$

At very short times, the functions $\Gamma_2(t)$ in Fig. 2 show a fast librational decay, which is followed by a nearly exponential decline at longer times. When decreasing the temperature, the libration amplitude decreases and the long time decay slows down. Both observations indicate the transition to a more solid like orientational motion.

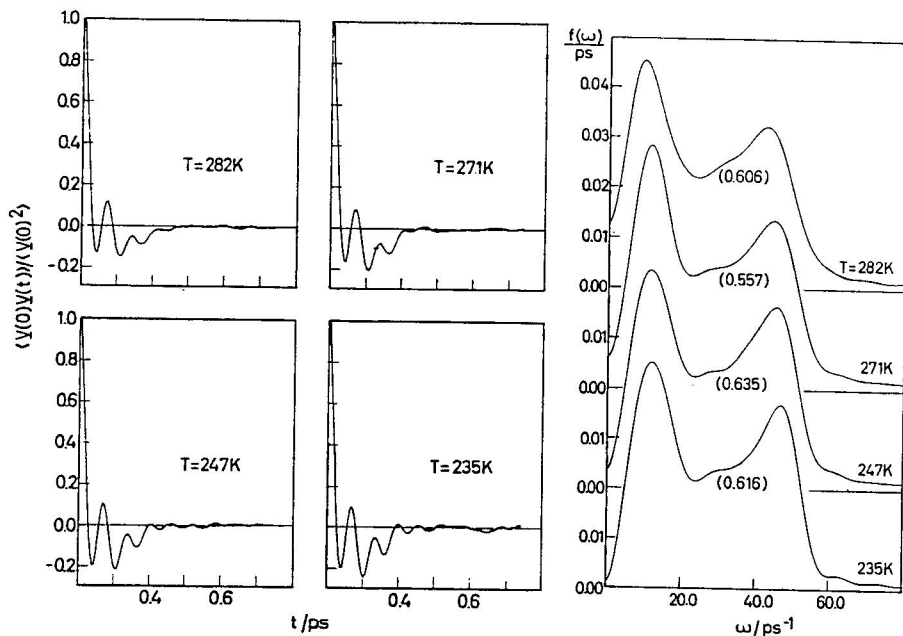


Fig. 3: Velocity autocorrelation function of the oxygen motion and power spectrum $f(\omega)$

In Fig. 3 the velocity autocorrelation functions (vacf) of the oxygen motion at four different temperatures are given. These functions characterize the short time behaviour of the translational motion of the water molecules. The general form of the vacf's can be described as a strongly damped low frequency oscillation with one negative period, superimposed by more persistent high frequency oscillations. The low frequency contribution equals the vacf's observed in simple dense liquid noble gas. The negative region can therefore be explained by the 'back-scattering' of the reference particle in the cage of its neighbors. The additional high frequency motion may be

assigned to the intermolecular vibrations of hydrogen bonded water molecules. At first glance, the temperature dependence is very weak, but one can see, that oscillations become more persistent and their number increases from about three at $T = 282$ K to about five at $T = 235$ K. Obviously, the motion becomes more solid like.

The temperature influence shows up more clearly, when calculating the power spectrum $f(\omega)$, which is obtained as the Fourier transformed of the vacf's:

$$f(\omega) = \int \cos(\omega t) \langle \underline{V}(0) \underline{V}(t) \rangle \langle \underline{V}(0)^2 \rangle^{-1} dt. \quad (4)$$

Fig. 3 shows the two maxima, which are typical for cold water [5]. The high frequency peak - assigned to the intermolecular vibration of hydrogen bonded molecules - becomes more pronounced and is shifted to higher frequencies, when the temperature is lowered. This indicates a less damped, more solid like vibrational motion. Of course, it is possible to extract macroscopic observable quantities from the shown functions. These quantities are discussed in detail and compared with experimental values in ref. [10].

SOME PERCOLATION THEORY ASPECTS

The percolation model of Stanley and Teixeira [6], [7] associates the possible thermodynamic singularity with a percolation threshold for clusters of four-bonded water molecules at -45 °C. In this model the fraction f_j of molecules with j intact bonds is given by the binomial distribution law

$$f_j(p) = \binom{z}{j} p^j (1-p)^{z-j} \quad (5)$$

with $p = \langle n_{HB} \rangle / z$, $z = 4$. $\langle n_{HB} \rangle$ is the average number of hydrogen bonds. For a quantitative description of the hydrogen bond network the distribution functions W_M^N and W_S^C are introduced. W_M^N gives the weight fraction of water molecules belonging to 'nets' of M molecules and W_S^C the weight fraction of four-bonded molecules which belong to 'clusters' of S molecules. Explicit formulas for an ice I_h lattice are given in [11]. Using this weight fractions one is able to define average network and cluster sizes.

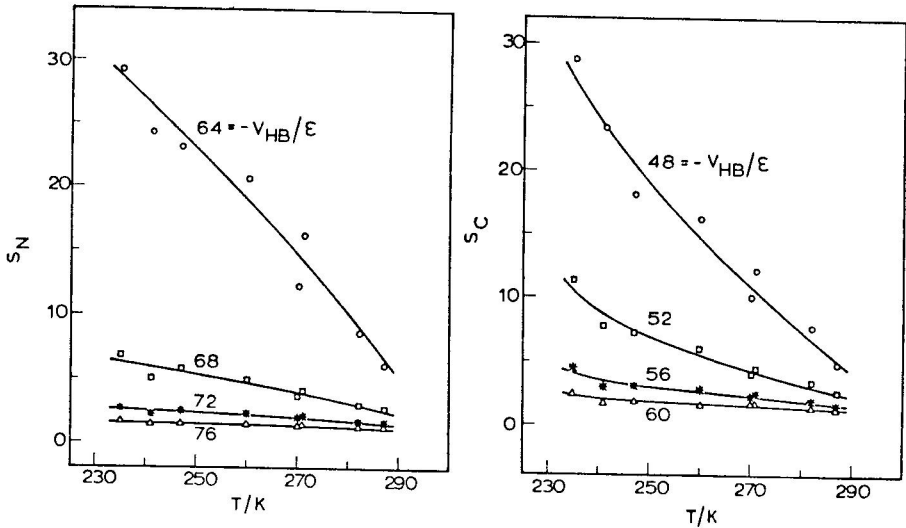


Fig. 4: Temperature dependence of S_N and S_C for different V_{HB} -definitions ($\epsilon = 0.07575^N \text{ kcal/mol}$)

$$S_N = \frac{\sum' M W_M^N}{\sum' W_M^N}, \quad (6)$$

$$S_C = \frac{\sum' S W_S^C}{\sum' W_S^C}. \quad (7)$$

The primes indicate that the spanning networks are omitted from the sums. In a number of papers it could be shown that many of the assumptions and predictions such as the percolation threshold and even the critical exponents characterizing the singular behaviour at the percolation threshold [12] could be reproduced, when analyzing the molecular dynamic data. In this study we were mainly interested in the strongly cooperative clustering behaviour of four-bonded water molecules [13]. The average hydrogen bond numbers $\langle n_{HB} \rangle$ are calculated for various V_{HB} -values and show only a weak temperature dependence. In contrast to this behaviour, the temperature dependence of the average network and cluster size as shown in Fig. 4 is strong, especially when V_{HB} approaches the percolation threshold. Fig. 4 presents the S_N -values below the bond percolation threshold at $\langle n_{HB} \rangle = 1.53$ and the S_C -values below the size percolation point for the four-bonded molecules at $\langle n_{HB} \rangle = 3.18$. A more detailed description, especially for the percolation theory aspect may be found in [10].

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