Equation of state and the topology of hydrogen bonding networks in water at high temperatures and pressures

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Atomistic computer simulations of water using two different intermolecular potentials for H_2O were carried out for over 50 thermodynamic states covering a very wide range of conditions: $573 \leqslant T \leqslant 1273$ K; $0.02 \leqslant \rho \leqslant 1.67$ g/cm^3; $0.01 \leqslant P \leqslant 10$ GPa. Good agreement of the simulated thermodynamic and structural properties of water with available experimental data assures a reliable quantitative statistical analysis of intermolecular hydrogen bonding between H_2O molecules and the topology of the H-bonding networks formed under these conditions [1]. The effect of temperature on the energetic, geometric, and angular characteristics of H-bonding in water is much more profound than the effect of density along any supercritical isotherm over the entire density range from dilute gas-like (≈ 0.03 g/cm^3) to highly compressed liquid-like (≈ 1.5 g/cm^3) thermodynamic states. Both above and below the H-bonding network percolation threshold, the fractions of water molecules engaged in a certain specific number of H-bonds closely follow the universal binomial distributions as functions of the average number of H-bonds per one H_2O molecule in that state, $\langle n_{\mathrm{HB}} \rangle$, as predicted by a simple independent bond theory [2]. The universality of these distributions is preserved even when dynamic criteria of H-bonding lifetimes are additionally applied.

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[1] Kalinichev A G 2001 *Rev. Mineral. Geochem.* **42** 83–129
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