

How the H-Bond Network Leads to Anomalous Properties of Water

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In the present work the nature of anomalous properties of water is discussed. First the essential difference between the character of the dispersive interaction and H-bonding is taken into account. Isotropic dispersive interactions H-bonds have strongly anisotropic character. Due to this the chemical potential μ of water molecules can be represented as the additive combination:

$$\mu = \mu_W + \mu_H$$

where μ_W and μ_H are the contributions, caused by dispersive forces and H-bonds. From here it follows that, for example, the molecular volume ν has a similar structure:

$$\nu = \nu_W + \nu_H$$

In accordance with the principle of corresponding states, widely applicable for liquids with spherical molecules, the temperature and pressure dependencies of ν_W are expected to be argon-like:

$$\nu_W(T, P) = \nu_c f^{(Ar)}(t, p)$$

where ν_c is the critical value of ν , $f^{(Ar)}(t, p)$ is a universal function of dimensionless temperature ($t = T/T_c$) and pressure ($p = P/P_c$).

The behavior of ν_H is determined by main thermodynamic characteristics of the H-bond network, so called its structural functions: $S_1(t, p)$, $S_2(t, p)$, The first of them can be identified with the number of H-bonds per molecule ($n_H(t, p)$) and tetrahedrality parameter ($\chi_H(t, p)$). Using the Hilbert's principle, developed in the algebraic theory of invariants, one can write:

$$\nu_H(t, p) = \lambda_1 n_H(t, p) + \lambda_2 \nu_H(t, p) + \dots$$

where λ_i , $i = 1, 2, \dots$, are constants. It is shown that the approximation

$$\nu(t, p) = \nu_c f^{(Ar)}(t, p) + \lambda_1 n_H(t, p)$$

describes the non-monotonous temperature dependence of ν with very good accuracy.

Within such an approach the behavior of the molecular volume, heat of vaporization, heat capacity at constant pressure, coefficient of the surface tension and other thermodynamic variables is successfully reproduced in temperature intervals from the crystallization temperature to the critical.

Besides in the work [1], the effective cluster method for the determination of $n_H(t, p)$, $\chi_H(t, p)$ and other structural functions is developed; [1] it is shown that the properties of water near its critical point are determined by water dimers (the degree of dimerization reaches 0.9 [2]; [3] the dielectric properties of water are consistently described with its thermodynamic ones; [4] the mechanisms of the shear viscosity and self-diffusion are analyzed.

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