MOLECULAR MECHANISMS UNDERLYING THE THERMODYNAMIC PROPERTIES OF WATER

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Background

Extensive computer simulations over the last decade have shown that the structure of pure fluids is determined primarily by short-range forces (both repulsive and attractive) [1].

The structure of an appropriately defined short-range and fluid is nearly identical to that of the considered full--range fluid [2].

The perturbation expansion about the short-range reference (SRR) rapidly converges.

For any property *X*, we may write [3] $X_{\rm full} = X_{\rm SRR} + \Delta X,$

Results

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To relate realistic water to PM's, we use reduced quantities (superscript *) referring to the critical ones (subscript c):

$$P^* = P/P_{\rm c}, \ \rho^* = \rho/\rho_{\rm c}, \ T^* = T/T_{\rm c},$$

 $\kappa^* = P_{\rm c}\kappa$

$$\alpha^* = T_{\rm c}\alpha.$$

$$c_P^r = c_P - c_V^{\text{ideal}}$$





Fig. 7: The reduced pressure of saturated vapor, P_{eq}^* , as a function of the reduced temperature, T^* . Left — the comparison of different primitive models. Right — the comparison of PM-TIP4P (PM) alone with PM-TIP4P plus dispersion (disp) and dipole-dipole (dip) terms. Inserts show the low-pressure region.

To summarize:

where ΔX includes contributions from the dispersion forces and long-range electrostatic interactions, $\Delta X =$ $X_{\rm disp} + X_{\rm el}$.

SRR is still too complex for theoretical treatment. Properties of SRR are therefore approximated by a suitable simpler model whose properties are well known.

As an example of simple model may serve hard spheres that approximate the short-range (repulsive) part of Lennard-Jones potential.

 $X_{\rm full} \approx X_{\rm simple} + X_{\rm disp} + X_{\rm el}$

Goal

To evaluate termodynamic properties of the realistic model of water by means of eqn (1) and assess the effect of individual contributions

To find a link between observed properties and individual contributions to pair interactions

We focus on the properties exhibiting anomalous behavior, namely: density, ρ , isobaric heat capacity, c_p , isothermal compressibility, κ , and isobaric thermal expansivity, α , all as functions of temperature, *T*, at constant pressure, *P*.

Fig. 2: The reduced heat capacity, c_p^r/R , as a function of the reduced temperature, T^* , at $P^* = 0$. Left — the comparison of different primitive models. Right — curves for PM-TIP4P (PM) alone or plus dispersion (disp) and dipole-dipole (dip) contributions.



Fig. 3: The reduced isothermal compressibility, κ^* , as a function of the reduced temperature, T^* . See Fig. 2 for a legend.

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The primitive model gives

• the minimum of isothermal compressibility, see Fig. 3

• density maximum at negative pressures, see Fig. 6

By adding the dispersion term we get

• the minimum of isobaric heat capacity, see Fig. 2

We fail to describe

• density maximum at positive pressures

• correct behavior of $\alpha(T)$

Conclusions

The present approach seems to be insufficient to describe the behavior of water. The following issues may play the role:

Behavior to explain:

- $\rho(T)$ has a maximum.
- $c_P(T)$ has a minimum.
- $\kappa(T)$ has a minimum.
- $\alpha(T)$ is monotonously growing and concave.

Primitive Models

We consider three realistic models of water: SPC/E, TIP4P, TIP5P [4, 5, 6]. To approximate their structure, we employ the so-called primitive models (PM's) which play here the role of the above mentioned simple models. Fig. 1 shows parent realistic and corresponding primitive models [7].



Fig. 4: The reduced isobaric thermal expansivity, α^* , as a function of the reduced temperature, T^* . See Fig. 2 for a legend.



• Primitive model itself suffers from several defects:

- The hard-sphere and square-well potentials are too crude for the correct behavior of the hydrogen bond.
- There is no force acting towards the optimum geometry. Potential well is flat.
- -Small (but important) temperature variations in the structure of fluid are not inherited from the parent model.

• Equation (1) should be questioned.

• Parent model may not fit real water – there is not enough data available for c_P and α to see the required trends.

The theoretical description (TPT2) of PM seems to be correct, an excellent agreement with Monte-Carlo data have been reported [8].

We will probably focus on the more sophisticated primitive models in our next research. Replacing the square well by the triangular one seems to be the next reasonable step. Simulations with the corresponding models have already been started. As regards the present ones, some optimizations are possible, but we



Fig. 1: Each primitive model of water consists of a hard spherical core (oxygen) and several "satellite" sites (hydrogen or auxiliary) interacting via the square-well (unlike sites) or hard-sphere (like sites) pair potential.

Fig. 5: The reduced density, ρ^* , as a function of the reduced temperature, T^* . See Fig. 2 for a legend.



Fig. 6: The isobars of the reduced density, ρ^* , of PM-TIP4P as a function of the reduced temperature, T^* . Reduced pressures, P^* , are equally spaced by 0.2.

don't expect any revolutionary improvement.

References

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