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Water: pure and as a solvent
How the microscopic structure of water is linked to its thermodynamic properties?

E. Brini,
Water is different from any other liquid

- Water has an extremely high heat capacity ($C_p$)
- Solid water (Ice I) floats on liquid water
- By mass it should not be a liquid at room temperature
- It is liquid in a wide temperature range
- It has really high surface tension

There is something weird in the energetics

Hydrogen Bond (HB):
The microscopic structure of simple (LJ) fluids
The microscopic structure of water

Hydrogen Bond (HB)

HB are about 10 times more stable than Van Der Walls interactions

Water tries to make as many HB as possible
The microscopic structure of water and its energy level

Hydrogen Bond (HB)
Water can make a lot of HB

acceptor

2 donors

acceptor

Water electron density

Tetrahedral structure

2D water

Mecedez-Benz model
The tetrahedral structure is present in ice and liquid water.

Note that there are cavities in liquid water.
Anomalous structure leads to anomalous behavior

Some examples:

- Liquid is denser than the solid
- Water is an excellent conductor of heat
- High surface tension

<table>
<thead>
<tr>
<th></th>
<th>Density / kg m(^{-3})</th>
<th>Thermal Conductivity / J (s m K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid</td>
<td>Solid</td>
</tr>
<tr>
<td>Argon</td>
<td>1407</td>
<td>1636</td>
</tr>
<tr>
<td>Water</td>
<td>997</td>
<td>920</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td></td>
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<tr>
<td>Water</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Surface tension / mJ m(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>13</td>
</tr>
<tr>
<td>Argon</td>
<td>29</td>
</tr>
<tr>
<td>Water</td>
<td>72</td>
</tr>
</tbody>
</table>
The HB network explains volume anomalies

Increasing $T$, $\rho$ increases

$T$ of max $\rho$

Normal behavior

Derivative $<0$

\[
\alpha = \frac{d h V}{d T} = \frac{d V}{d T} \frac{1}{V}
\]
Water has a weird phase diagram

Water

Exaggerated slope

(374 K; 218 atm)

(273 K; 6E-3 atm)

Normal liquid
Ice melts by compression

**Water**

Ice melts applying pressure

\[ V_{\text{liq}} < V_{\text{ice}} \]

**Normal liquid**

Other substances solidify

\[ V_{\text{liq}} > V_{\text{ice}} \]
Ice melts by compression (proof that $V_{\text{liq}} < V_{\text{ice}}$)

Clausius Clapeyron eq:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

We can measure it = -133 atm K$^{-1}$

$\Delta S = S_{\text{liq}} - S_{\text{ice}} > 0$

$\frac{dP}{dT} < 0$ (experimentally)

$\Delta V = V_{\text{liq}} - V_{\text{ice}}$ must be <0
Water has one more “energy level” than common liquid
Water as solvent: why oil and water don’t mix
Hydrophobic substances don’t like water

Hydrocarbons: small partial charges, mostly LJ interactions
\[
\Delta \mu_{S@O \to S@W}^0 = RT \ln \frac{C_{S@W}}{C_{S@O}} = + z W_{SO} - z \frac{W_{OO}}{2} + z \frac{W_{ww}}{2} - z W_{SW}
\]

\[
\Delta \mu^0 = \Delta h^0 - T \Delta s^0 \approx \Delta h^0
\]

Almost constant as function of temperature (\( \Delta h^0 = \Delta C_p(T - T_h) \)). \( \Delta C_p \gg 0 \) and \( \Delta S^0 \ll 0 \)

NOT TRUE FOR WATER:
$\Delta h^0$ and $\Delta s^0$ have a strong $T$ dependence for water

At low temperatures $S$ opposes solvation

At high temperatures $H$ opposes solvation
Water structure is different at different T, so is solvation.

Insert a hydrophobe in a “van der Waals” liquid
You brake interactions
This has an enthalpic cost

Insert a hydrophobe in the cavity
The “cage” needs to stay structured
This has an entropic cost
The $T$ dependence of $C_p$ confirms the "2 states" model

$$C_p = \left( \frac{\partial E}{\partial T} \right)_p$$ is how the system stores thermal energy

2 states model:

$$q = 1 + \gamma e^{-\varepsilon_0/kT}$$

Increase population of high energy states

Store energy in bonds that breaks (HB)
Water can’t “cage” big hydrophobic solutes

- The solute sits in DINAMIC “cages” in the solvent.
- No lost HB
- $\gamma \approx 25 \text{ cal mol}^{-1} \text{ A}^{-2}$

- Water has to sacrifice 1 HB
- HB are lost
- $\gamma \approx 75 \text{ cal mol}^{-1} \text{ A}^{-2}$
Hydrophobes attract to reduce the surface area
Water structure affects the hydrophobes conformations.

How does this affect the activity coefficient?
Ion solvation
Water has a dipole

We can see it as 2 dipoles

Equal and opposite charges are solvated differently
The balance between charge interaction and HB

Small ions = high electric field

Strongly restrict water

Big ions = small electric field

Behaves almost like a hydrophobe
Big ions sit in cages, small ions restrict water.

2 different solvation mechanisms.

Can we understand salts solubility?
Ions come in “pairs”. How does this affect their solvation?

<table>
<thead>
<tr>
<th>Solubility (M)</th>
<th>F^-</th>
<th>I^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li^+</td>
<td>0.1</td>
<td>8.8</td>
</tr>
<tr>
<td>Cs^+</td>
<td>24.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Small and Small, & Big and Big are less soluble than small and big

- Strong attraction between ions (i-i)
- Hydroph. Interaction (w-w)
- Water has to solvate them (w-i)
Balance of interactions in multi-component system

Kirkwood-Buff solution theory links structure and thermodynamics

\[ G_{ij} = \int_V \left[ g_{ij}(R) - 1 \right] dR \]

It is more or less likely to find the particle \( i \) around \( j \) compared to a random distribution?

\[ \frac{1}{kT} \frac{\partial \mu_i}{\partial \chi_i} \approx \frac{1}{\chi_i} + \frac{c_j(2G_{ij} - G_{ii} - G_{jj})}{1 + c_j \chi_i(2G_{ii} - G_{jj} - 2G_{ij})} \]

How does the chemical potential (solubility) of a substance change... \( \ldots \) depends by the balance of interactions (that determines the structure)