Pre-MidSem Revision

21.09.24

LS2103

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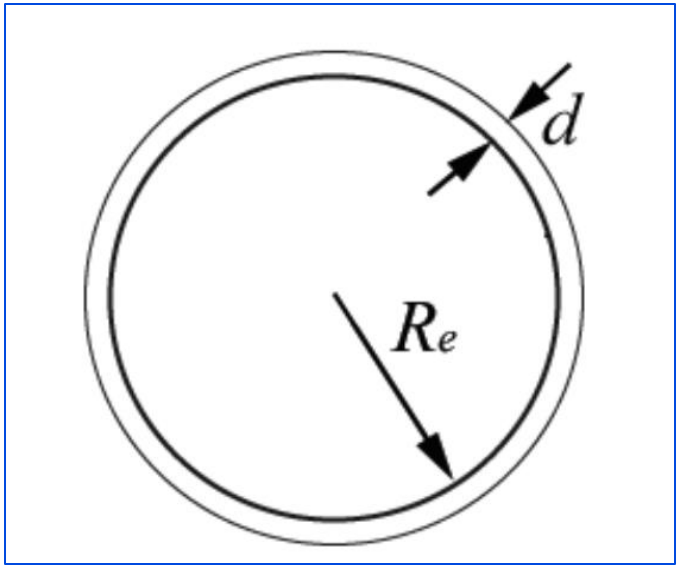
Scales and Approximations

The mass of water within the hydration layer of thickness *d* surrounding a near-spherical cell of radius R_e = 50 nm is estimated to be 1.76 x 10^{-17} grams.

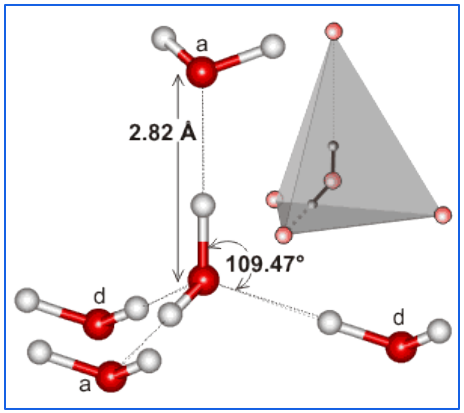
The hydration layer is 2 water molecules thick, and the density of water is 1.0 g cm^{-3}.

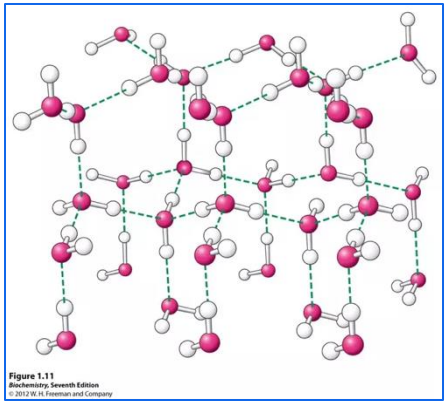
Since *d* is much smaller than R_e,
the volume of the layer may be approximated as ($4\pi R_e^2.d$).

Estimate the diameter of a water molecule, in Angstroms, from this information.



Hydrophobicity: **entropic cost** of solvation

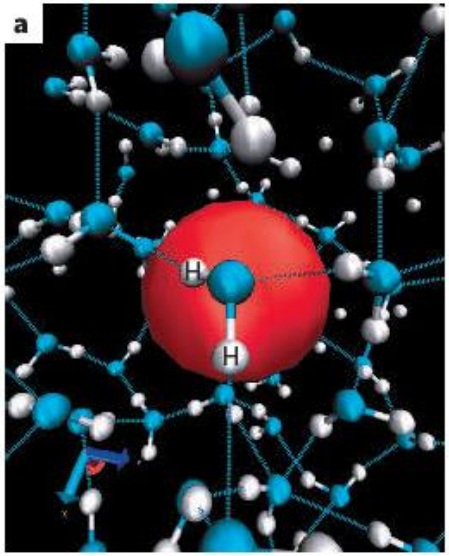




H_2O form tetrahedral structure

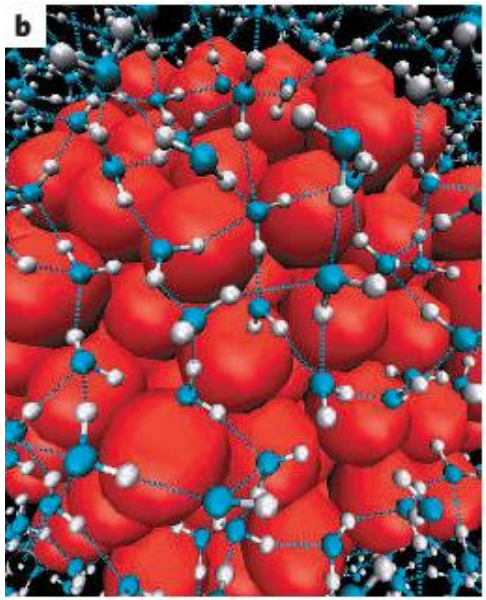
Network of hydrogen bonded molecules

Small (water unfriendly) solute



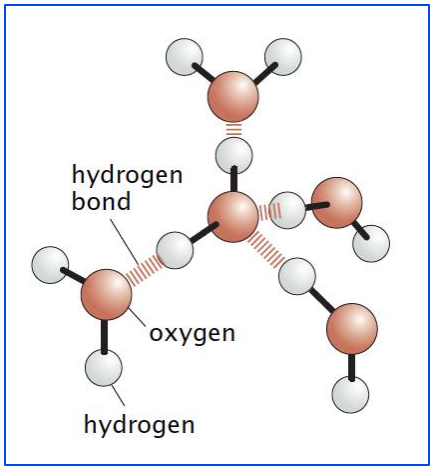
VS.

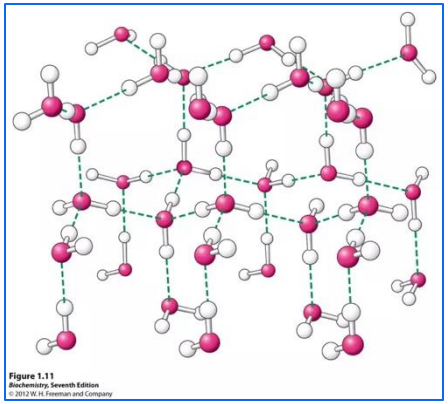
Large solute



Hydrophobicity: **entropic cost** of solvation

radius
~ 1 Å





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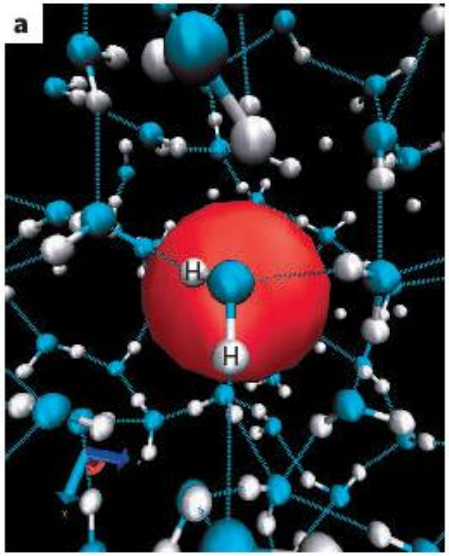
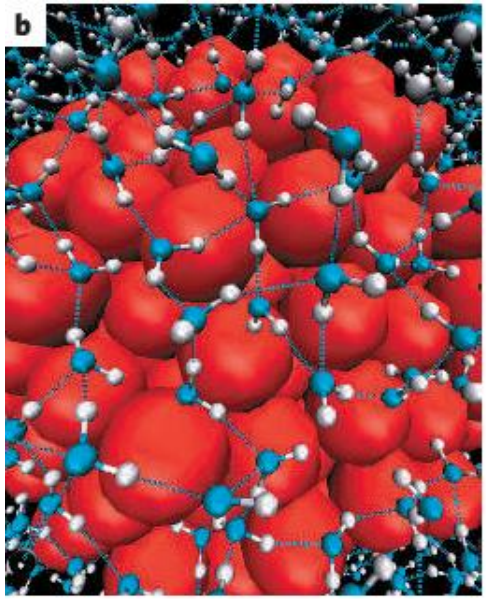


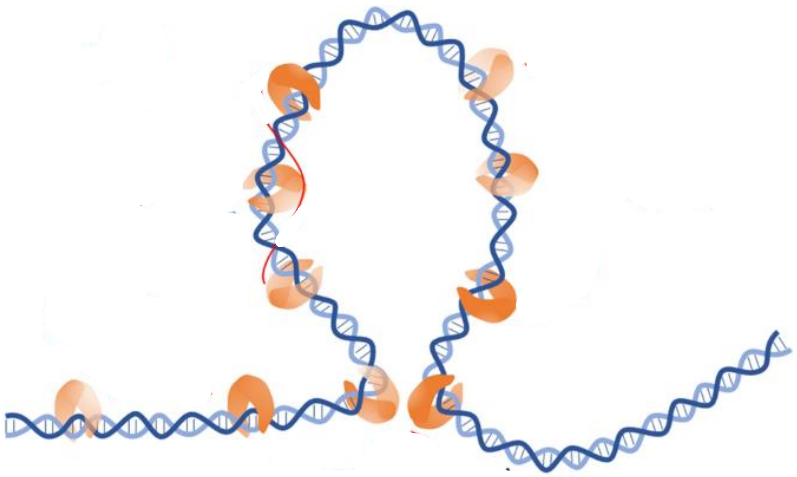
VS.



Entropy estimates

$$S = k_B \ln(\Omega)$$

Protein binding sites on DNA:



Representative image from:
Park et al., J. Korean. Phys. Soc., **78**, 408–426 (2021): review

Entropy of composite systems:

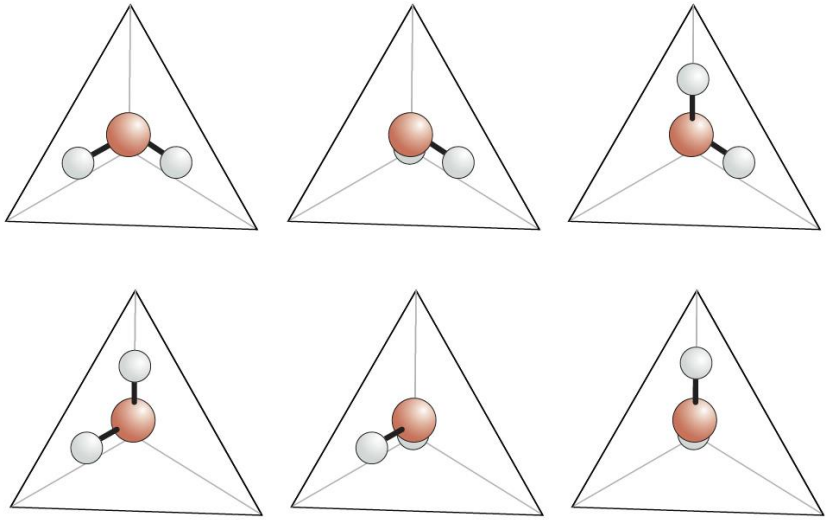
For the composite system,

$$\Omega_{(total)} = \Omega_1 \times \Omega_2$$

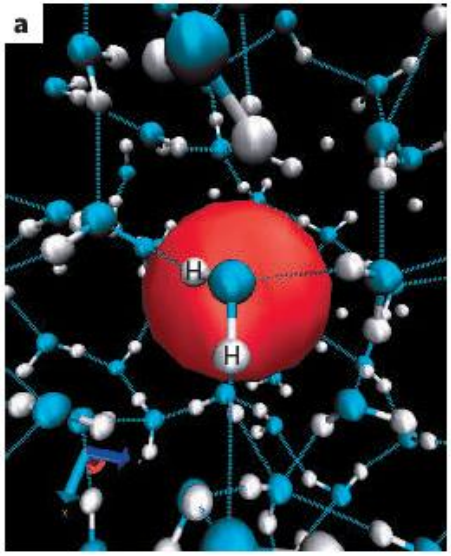
$$S_{tot} = k_B \ln \Omega = S_1 + S_2$$

Entropy is additive

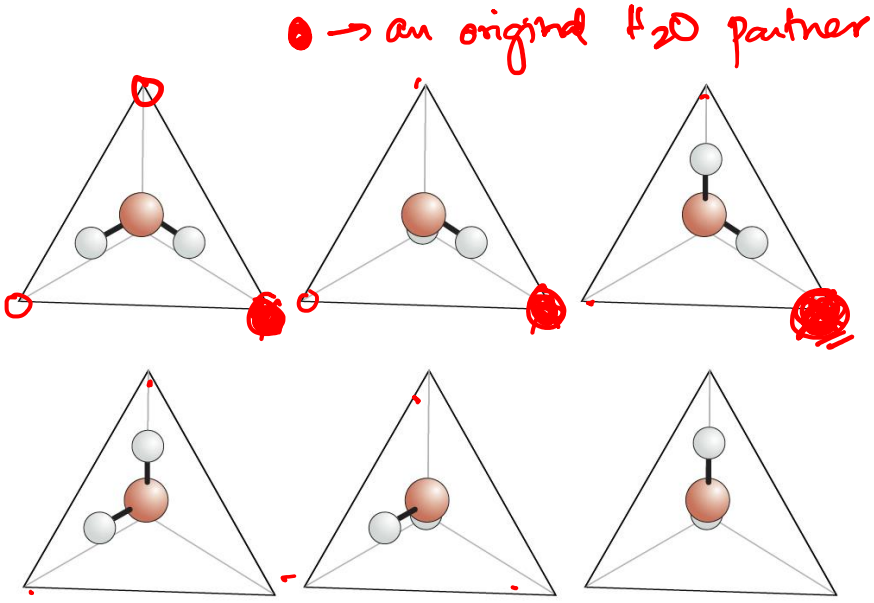
Approximating the entropic cost



6 possible molecular orientations

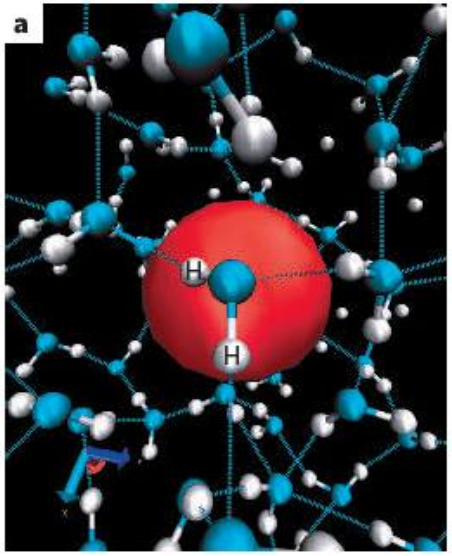


Approximating the entropic cost of hydrophobic solvation



$\Omega_{original} = 6$

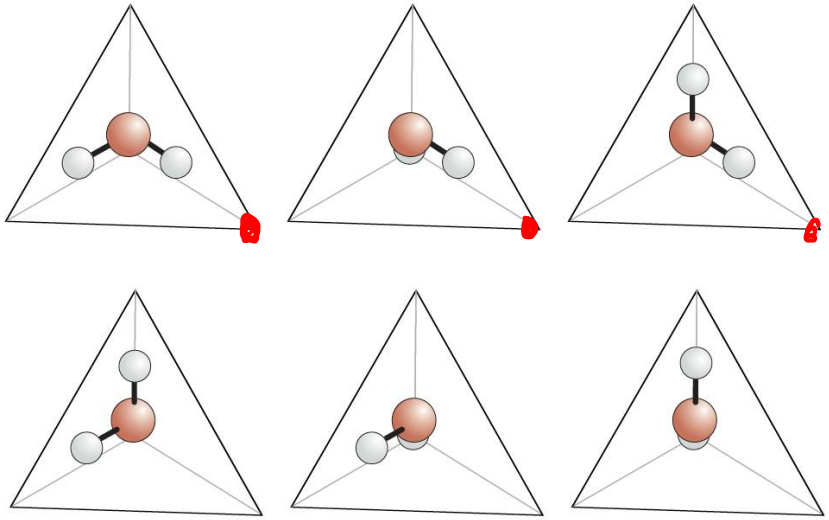
$\Omega_{reduced} = 3$



6 possible molecular orientations

When one site is replaced,
3 orientations are lost.

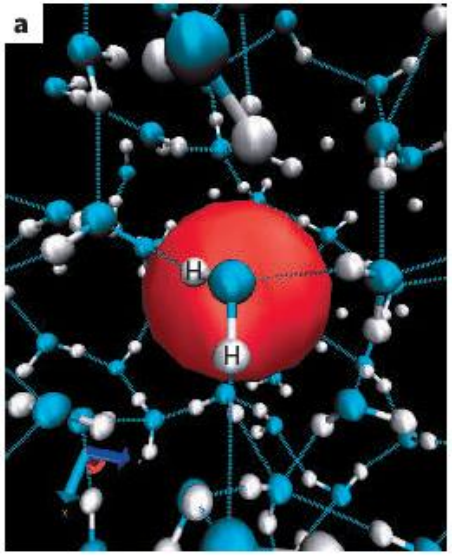
Approximating the entropic cost of hydrophobic solvation



Water molecule orientations

$$\Delta S_{hydrophobic} = S_{reduced} - S_{original}$$

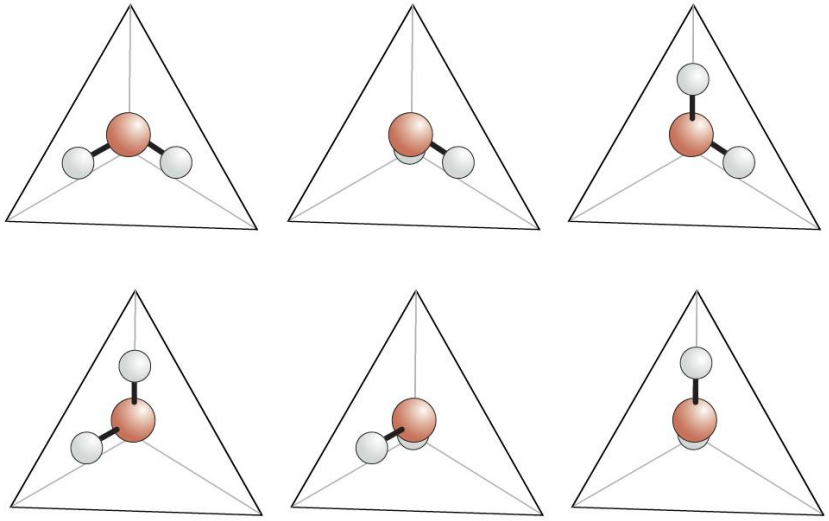
$$= -R_B \ln 2$$



When ‘n’ molecules lose one H-bonding partner,

$$\Delta S_{hydrophobic(n)} = -n R_B \ln 2$$

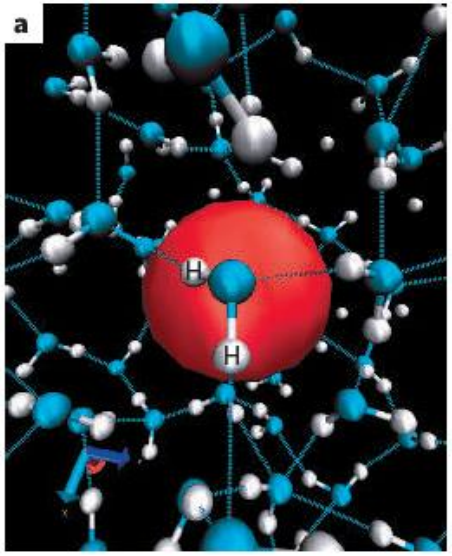
Approximating the entropic cost of hydrophobic solvation



If enthalpic (energetic) cost is insignificant,

$$\Delta G_{hydrophobic} = -T\Delta S_{hydrophobic}$$

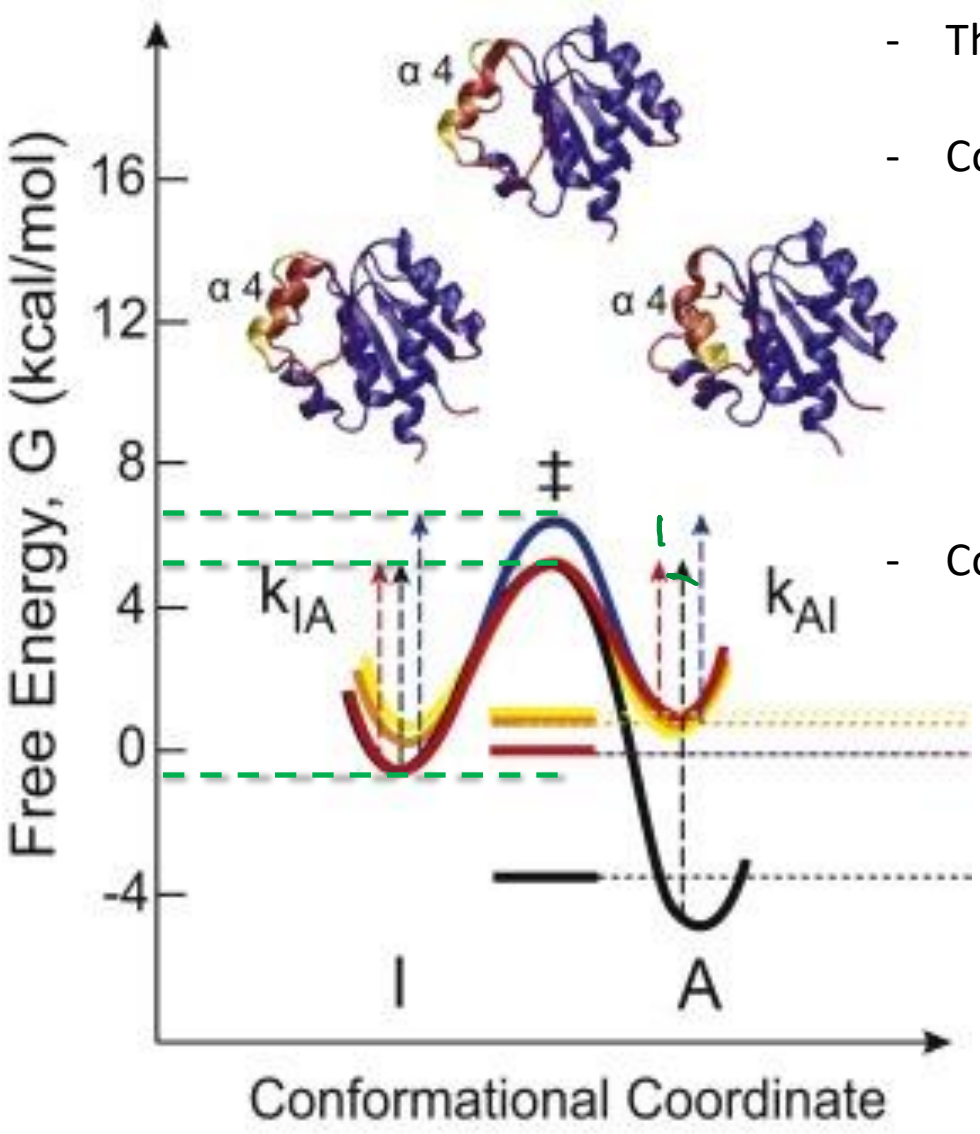
$$= n k_B T \ln(2)$$



Now 'n' is proportional to the area (A) of hydrophobic solute, ie. the hydrophobic entropy penalty is,

$$\Delta G_{hydrophobic} = (\text{cost per unit area}) \times A$$

(RT) is the energy scale in *molecular* biology



- This diagram shows *four* energy landscapes
- Compare the population ratio of states 'I' to 'A' in the three systems
- Compare the rates of transitions from I → A