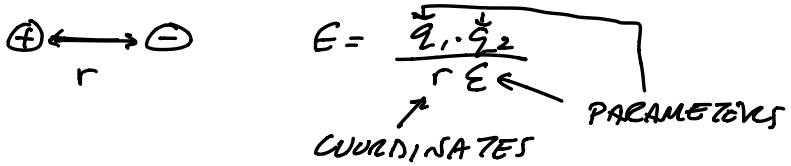
HYDROPHOBIC EFFECT AND SASA 10/22/15

TO THIS POINT WE'VE TALKED ABOUT THERMODYNAMICS (ΔS, ΔH, ΔC_p, ΔG) THAT WE CAN MEASURE. WE'VE TALKED ABOUT STRUCTURAL DETERMINATION. (X-RAY CRYSTALLOGRAPHY). HOW CAN WE LINK THEM TO UNDERSTAND FUNCTION?

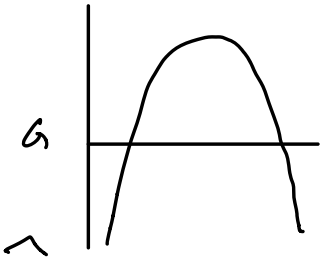
BUILD A MATHEMATICAL MODEL THAT LINKS STRUCTURE TO ENERGETICS.

G (COORDINATES, PARAMETERS)

EXAMPLE:

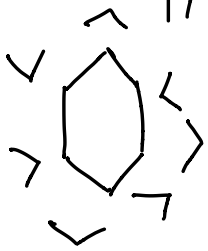


TODAY: HYDROPHOBIC EFFECT. FLESH OUT ARGUMENT THAT SHAPE OF CURVE INDICATES HYDROPHOBIC EFFECT.



SAME SHAPE OF CURVE FOR FOLDING AND SOLVENT TRANSFER

CAN WE BUILD A MODEL THAT LETS US QUANTITATIVELY RELATE TWO?



MOLECULAR NATURE HYDROPHOBIC EFFECT:

TWO VIEWS:

"CLATHRATE": MORE ORDERED (COSTS ΔS); STRONGER H-BONDS (FAVORABLE ΔH).

ΔC_p: MORE BONDS TO ABSORB ENERGY IN UNFOLDED STATE?

"DYNAMIC": RESTRICTED ROTATIONAL DEGREES OF FREEDOM

JUMP BETWEEN H-BOND STATES

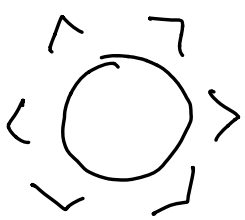
- DIRECT EVIDENCE FOR SHORTER, STRONGER H-BONDS: 10-15 / CH_4 HYDRATED

GRADDOLPHI ET AL PNAS (2006)

COMBINED SPECTROSCOPY, THERMODYNAMICS MEASUREMENTS, WITH SIMULATIONS TO GAIN MOLECULAR INSIGHT.

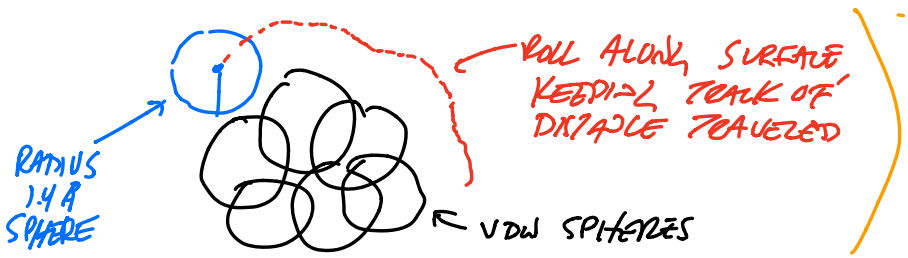
HOW WOULD YOU CALCULATE ENERGY DIFFERENCE TO TRANSFER OCTANE VS OCTANOL INTO WATER?

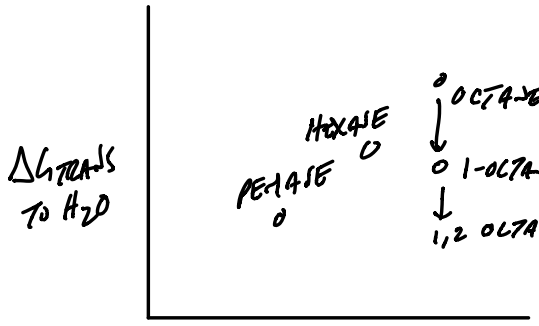
SURFACE AREA. ALL ABOUT ORDERING WATERS AT THE SOLUTE/WATER INTERFACE.



HOW MANY WATERS DO YOU ORDER?

TO CALCULATE SURFACE AREA:





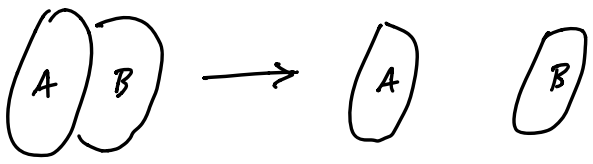
→ CAN WRITE OUT LINEAR MODEL AS FUNCTIONS OF ΔASA_{POLAR} AND $\Delta ASA_{NONPOLAR}$

$\Delta C_{p,NONPOLAR} = 0.45 \times \Delta ASA$ (IN kcal/mol)

$\Delta C_{p,POLAR} = -0.26 \times \Delta ASA$ (IN kcal/mol)

$\Delta H_{NONPOLAR}$ ...

CAN USE TO ESTIMATE ENERGY TO BURY SURFACES.



PISA SERVER WILL CALCULATE ENERGETICS OF THIS PROCESS USING SURFACE AREAS.

KEY TAKEAWAYS:

1. HYDROPHOBIC EFFECT DEPENDS ON ORDERING WATERS
2. EFFECT SIZE IS PROPORTIONAL TO SURFACE AREA
3. CAN CALCULATE SURFACE AREA CHANGE TO YIELD ESTIMATE OF $\Delta G_{HPHOBIC}$.