

# MO Theory of $\pi$ -electrons in conjugated and aromatic molecule : Hückel model.

Hückel model : uses hybridization and the localized VB model to describe the  $\sigma$ -bonded skeleton and MO theory to describe the delocalized  $\pi$ -electrons.

For the  $\pi$ -electrons, Hückel makes the following simplifying assumptions : <sup>rigid framework which determines shape of molecule</sup>

- all C atoms are identical  $\rightarrow \alpha$  is same for each A.O.
- all overlap integrals are zero,  $S=0$
- all resonance integrals between neighboring carbons are equal, call this  $\beta$ .
- all other resonance integrals are zero.

This gives a simple structure to the determinant :

- 1) all diagonal elements are  $\alpha - E$
- 2) all off-diagonal elements between neighboring atoms are  $\beta$
- 3) all other elements are 0.

example: butadiene  
 We have 4  $\pi$ -electrons:  
 Hückel energies are



$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

Solution is  $E = \alpha \pm 1.62\beta$  and  $E = \alpha \pm 0.62\beta$   
 Since  $\beta < 0$  the  $\pi$ -electrons in butadiene have  
 total energy  $E_{\pi} = 2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta)$   
 $= 4\alpha + 4.48\beta$

What should we compare this to?  
 In ethene we have  $E_{\pi} = 2(\alpha + \beta)$  (pg. 91)  
 so that two individual  $\pi$ -bonds has energy  $4\alpha + 4\beta$ .

thus we can say the delocalization energy in  
 butadiene is  $0.48\beta$ , which is approximately 110 kJ/mol  
 this is the extra stabilization energy due to conjugation.

example: cyclobutadiene

Hückel  $\pi$ -electron energies are

$$\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

$E = \alpha \pm 2\beta$  and  $E = \alpha$   
 doubly degenerate

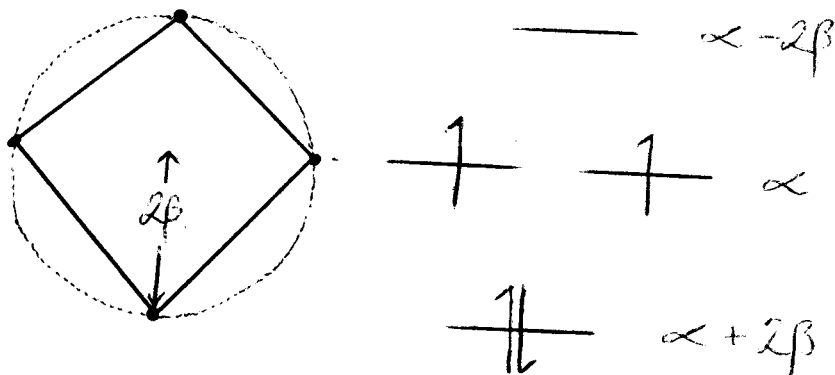
Hence  $E_{\pi} = 2(\alpha + 2\beta) + 2\alpha = 4\alpha + 4\beta$   
no extra stabilizing energy!

## Hückel model for monocyclic polyenes :

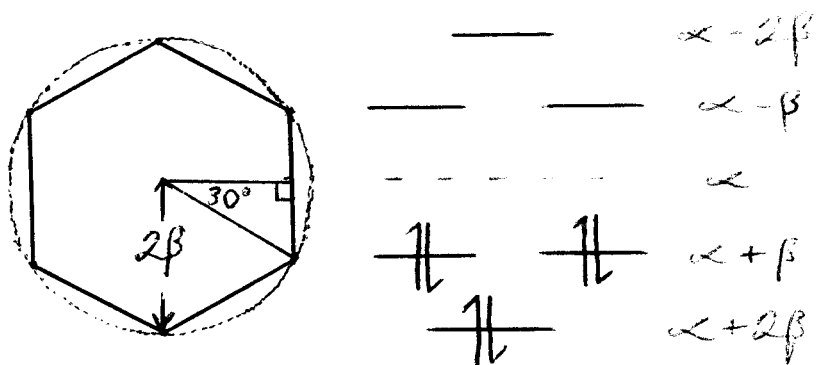
The matrix method works but the  $\pi$ -electron MO energies can also be obtained using a graphical method.

Inscribe a regular polygon with the shape of the polyene in a circle of radius  $2\beta$  with one vertex pointing downwards. Draw a horizontal line at each point for which the polygon touches the circle. The lines give the energy levels with the center of the circle corresponding to energy  $\alpha$ .

Example: cyclobutadiene

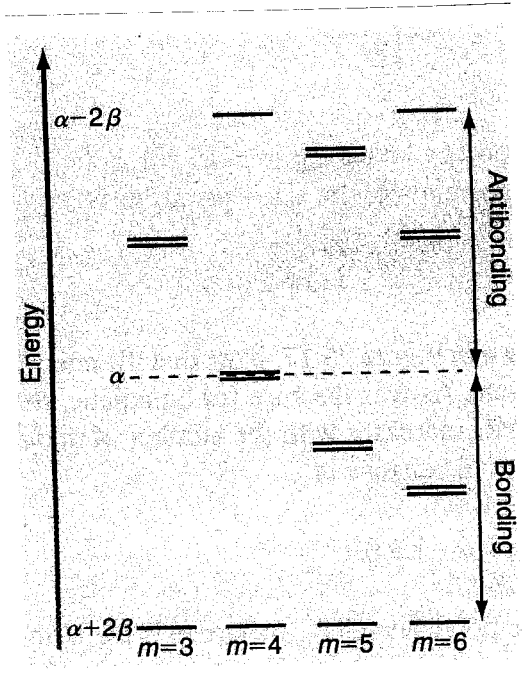


Example: benzene



The  $\pi$ -electron energy levels are summarized in the following plot: which leads to the Hückel rules for a monocyclic conjugated system with  $N$   $\pi$ -electrons

- if  $N = 4n + 2$  the molecule is stabilized through  $\pi$ -delocalization
- if  $N = 4n + 1$  the molecule is a free radical
- if  $N = 4n$  the molecule has two unpaired electrons and is very reactive.



**FIGURE 25.18**  
The energy of the  $\pi$  MOs is shown for cyclic polyenes described by the formula  $(CH)_m$  with  $m = 3$  to  $6$   $\pi$  bonded carbons. The doubly degenerate pairs are shown slightly separated in energy for clarity.

ex  $C_3H_3^+$  is more stable than  $C_3H_3$  or  $C_3H_3^-$ .

ex cyclobutadiene is a diradical and is very reactive.

ex  $(CH)_5^-$  is more stable than  $(CH)_5$  or  $(CH_5)^+$ .

These predictions have been verified by experiment and demonstrate that the Hückel model has predictive power.


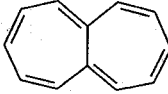
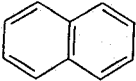
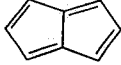
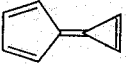
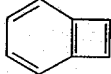

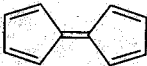


Resonance stabilization energy in aromatic compounds due to the presence of closed circuits of delocalized electrons.

Compare the  $\pi$  network energy to the same molecule in a linear form using Hückel

This measure is in good agreement with experimental data from thermochemistry, reactivity, and NMR.

Molecules with negative resonance stabilization energies are called antiaromatic.

One weakness of the Hückel model is that it only treats the  $\pi$ -electrons. The  $\sigma$ -framework strain energy of cyclobutadiene (arising from  $90^\circ$  instead of  $120^\circ$  bond angles) is not taken into account. This is fixed in the modified extended Hückel method developed by Rald Hoffmann (Nobel Prize 1981)

	Benzene 0.065		Heptalene -0.004
	Naphthalene 0.055		Pantelene -0.018
	Calicene 0.043		Benzocyclobutadiene 0.065
	Azulene 0.023		Fulvalene -0.033
	Fulvene -0.002		Cyclobutadiene -0.268

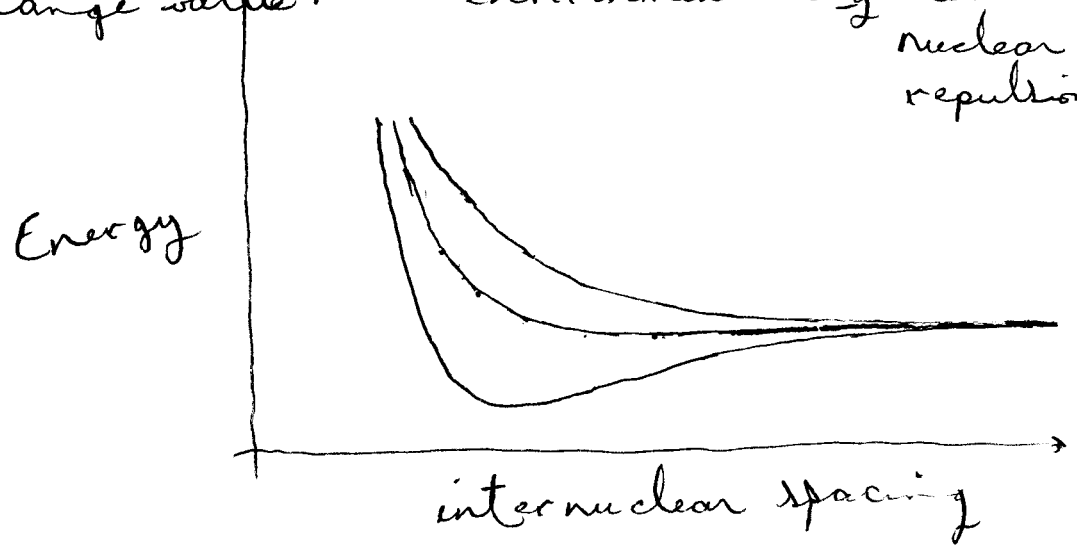
units of  $\beta$  per  $e^-$

# Bonding in Solids - Metals, Conductors, Semiconductors, Insulators

We can explain the difference between conductors, semiconductors, and insulators from simple LCAO-MO considerations.

Up until now, we have been building the MO's assuming a particular internuclear separation. The  $S \approx 0$  approx gave us bonding and antibonding energies of  $E = \alpha \pm \beta$  where  $\alpha$  is the energy of an electron in an atomic orbital in the molecular environment.

Since  $\alpha = \frac{1}{2}(E_{\text{bonding}} + E_{\text{antibonding}})$ , this is, for different internuclear separation, the average of the bonding and antibonding energies. Why does it change value? : environment (eg nuclear-nuclear repulsion)



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We consider a specific example that demonstrates the contrasts among a conductor, a semiconductor, and an insulator. In solids, separate bands are generated from different AOs, such as the  $3s$  and  $3p$  AOs on Mg. Magnesium, with the  $[\text{Ne}]3s^2$  atomic configuration, has two  $3s$  valence electrons that go into a band generated from the overlap of the  $3s$  electrons on neighboring Mg atoms. Because  $N$  Mg atoms generate  $N$  MOs, each of which can be doubly occupied, the  $2N$  Mg valence electrons completely fill the  $3s$ -generated band (lower band in Figure 14.21). If there were a gap between this and the next highest band (upper band in Figure 14.21), which is generated from the  $3p$  elec-

FIGURE 14.20

MOs generated in an atom chain using the Hückel model. As  $N$  becomes very large, the energy spectrum becomes continuous. The energy range of the MOs is shown in units of  $\beta$ .

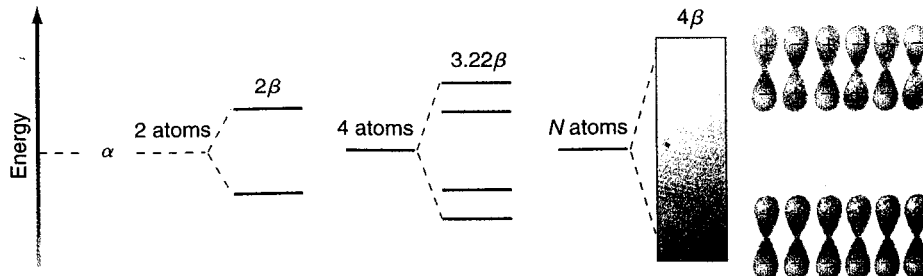
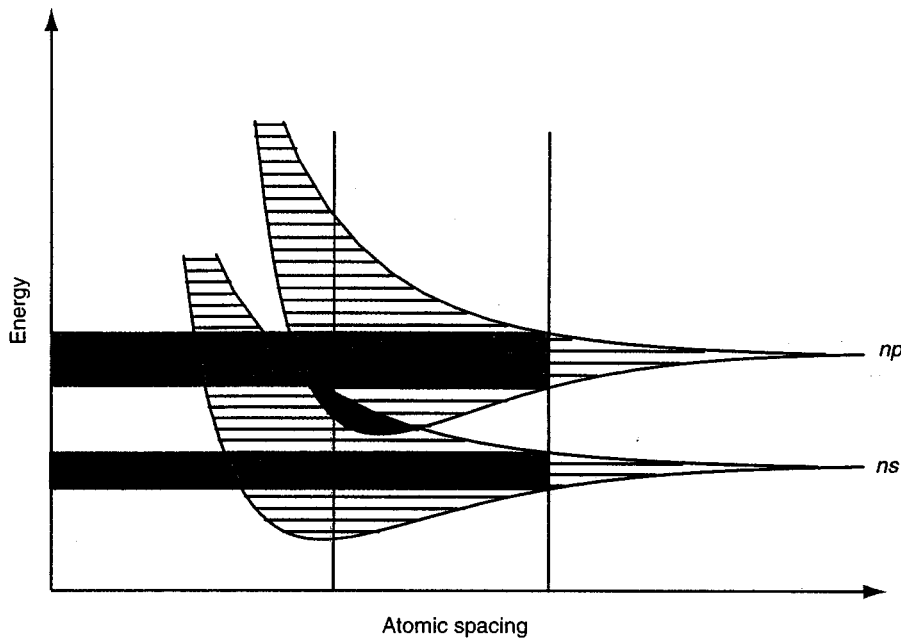


FIGURE 14.21

Bands generated from two different AOs are shown. The width in energy of the band depends on the atomic spacing. For the equilibrium spacing indicated by the red bar, the two bands overlap and all energy values between the top and bottom of the yellow shaded area are allowed because the two bands overlap. This is not true for significantly larger or shorter atomic spacings, and the solid would exhibit a band gap at the spacing indicated by the blue bar. In this case the two narrow bands indicated by the green areas do not overlap.



trons, Mg would be an insulator. However, in this case, the  $3s$  and  $3p$  bands overlap, and the result is that the unoccupied states in the overlapping bands are only infinitesimally higher in energy than the highest filled state. For this reason, Mg is a conductor.

If there is a gap between a completely filled band and the empty band of next higher energy, the solid is either an insulator or a semiconductor. The distinction between a semiconductor and an insulator is the width of the energy gap. If  $E_{gap} \gg kT$  at temperatures below the melting point of the solid, the material is an insulator. Diamond is an insulator at 300 K because it has a large band gap. However, if at elevated temperatures  $E_{gap} \sim kT$ , the Boltzmann distribution [Equation (2.2)] predicts that it will be easy to promote an electron from the filled valence band to the empty conduction band. In this case, the highest filled state is infinitesimally lower in energy than the lowest unfilled state, and the solid is a conductor. Silicon and germanium are called semiconductors because they behave like an insulator at low temperatures and like a conductor at higher temperatures.

Now for solids:  $n$  AOs combine to give  $n$  MOs. Think about sodium with a single valence electron  $3s^1$ . As we bring more and more atoms together with a fixed lattice spacing, the MO energies only spread out a finite amount, hence we get a band.

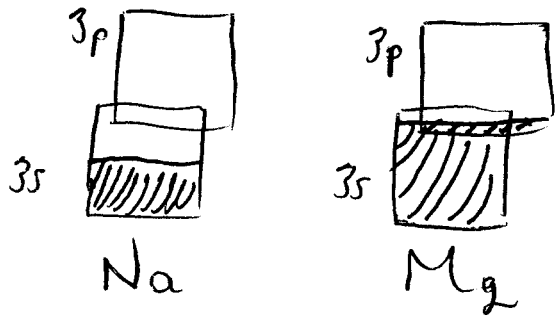
To think about this, consider the lattice spacing to be very large. Then the width is essentially zero even though there are many, many MOs.

To a first approx. we can just "fill in" the region between the diatomic MO energies with a continuum of bands.

Na: band is only  $1/2$  filled  $\rightarrow$  the empty orbitals permit the movement of electrons by promoting electrons to the open levels at almost no energy cost. Conducting.

Mg:  $3s^2 \rightarrow$  filled band  $\rightarrow$  no conduction?   
 $3p$  band overlaps (see handout)

But if the gap is big (see handout) get insulator.





# Intermolecular Forces

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there are 4 forces in nature:

1. Strong Force: binds protons and neutrons together in the nucleus.
2. Weak Force:  $\beta$ -decay
3. Electromagnetic: electricity, magnetism, light
4. Gravity: mass

1, 2 are very short ranged ( $< 10^{-5}$  nm), while 3, 4 are very long ranged (infinitely long).

## History of Intermolecular Forces

18<sup>th</sup>/19<sup>th</sup> century: researchers studied the capillary rise of liquids in glass tubes.

In 1808 Clairaut suggested that capillarity could be explained if the attraction between the liquid and glass molecules was different from the attraction of the liquid molecules for themselves.

It was also noticed that the height of rise of a liquid column does not depend on the capillary wall thickness, which led to the conclusion that these forces must be of very short range.

During the 19<sup>th</sup> century it was believed that one simple 12  
universal force law would eventually be found to account  
for all intermolecular attractions.

It was proposed that the interaction potential  
between two molecules was of the form

$$U(r) = - \frac{C m_1 m_2}{r^n} \quad \text{with } n=4 \text{ or } 5.$$

This contrasts with gravity,  $U(r) = - \frac{G m_1 m_2}{r}$   
or electrostatics,  $U(r) = - \frac{C q_1 q_2}{r}$ , both of which have  $n=1$ .

Why was  $n=4$  or  $5$  suggested? The reason is because  
if the intermolecular forces are to be short ranged,  $n > 3$ .

Suppose the potential between two molecules is  $U(r) = - \frac{C}{r^n}$ .  
and consider a region of space where the number  
density of these molecules is  $\rho$ . This region could be  
a solid, liquid, or gas, or even a large region in  
outer space.

Let us add up all the interaction energies of one  
particular molecule with all the other molecules in  
the system.

The number of molecules in a region of space between  $r$  and  $r+dr$  away is  $\rho 4\pi r^2 dr$ . The total interaction energy is thus

$$-\int_{\sigma}^L U(r) \rho 4\pi r^2 dr = -4\pi C \rho \int_{\sigma}^L \frac{dr}{r^{n-2}}$$

$$= \frac{-4\pi C \rho}{(n-3) \sigma^{n-3}} \left[ 1 - \left(\frac{\sigma}{L}\right)^{n-3} \right] \text{ where } \sigma \text{ is the diameter of the molecules and } L \text{ is the size of the system.}$$

Since  $\sigma < L$ , large distance contributions disappear only for  $n > 3$ . In this case we get  $\frac{-4\pi C \rho}{(n-3) \sigma^{n-3}}$ .

But for  $n < 3$ , the  $(\sigma/L)^{n-3}$  term dominates, meaning the contribution from more distant molecules dominates over that of nearby molecules. Then the size of the system must be taken into account, for example for gravitational forces ( $n=1$ ) where distant planets, stars, and even galaxies are interacting with each other.

Modern theories ~~are~~ of intermolecular forces predict that  $n > 3$ . Therefore the molecular properties of solids, ~~solids~~ liquids, and gases do not depend on the volume of material or on the size of the container (unless there are extremely small), but only on the forces between molecules in close proximity to one another.

Only with the development of quantum theory was it possible to understand the origin of intermolecular forces and derive expressions for their interaction potentials.

• All intermolecular forces are essentially electrostatic in origin. They are sub-divided into different categories even though they all have the same origin.

- covalent
- ionic
- van der Waals
- hydrophobic
- hydrogen bonding
- solvation

### Look at van der Waals forces

Like gravity, the van der Waals, a dispersion, force acts between all atoms and molecules.

It plays ~~a~~ <sup>a</sup> role in adhesion, surface tension, physical adsorption, ...

Their origin can be understood at a conceptual level as follows: for a non-polar atom such as helium, the time average of its dipole moment is zero, but at any instant there exists a finite dipole moment given by the instantaneous positions of the electrons about the nuclear protons.

This instantaneous dipole generates an electric field that polarizes any nearby neutral atom, inducing a dipole moment in it. The resulting interaction between the two dipoles gives rise to an instantaneous attractive force between the two atoms, and the time-average of this force is finite.

The distance dependence is  $r^{-6}$ .

At very small interatomic distances the electron clouds of atoms overlap, and a strong repulsive force results.

There is no general equation to describe this repulsion,

$r^{-12}$  is most commonly used only for computational efficiency (just  $r^{-6}$  squared).

# Hydrophobic Effect

I6

Due to van der Waals interactions, water and oil molecules attract one another, but water has a stronger attraction for itself because of H-bonding.

Each water molecule can participate in 4 H-bonds; sharing its two H atoms with two neighboring water molecules, and sharing two additional H-atoms associated with two other neighbors.

When water molecules encounter a non-polar molecule, it would appear that one or more H-bonds are lost. However, if the non-polar solute molecule is not too large, it is possible for water molecules to pack around it without giving up any of their H-bonding sites. This structure is called a clathrate cage.

This restructuring of water around non-polar solutes is entropically unfavorable because it imposes a new, more ordered, structure of the surrounding water molecules.

For example, the transfer free energy of n-butane from bulk liquid into water at 298 K is

$$\Delta G = \Delta H - T\Delta S = -4.2 + 28.7 = +24.5 \text{ kJ/mol}$$

The decrease in entropy contributes 85% of this interaction. For many other hydrocarbons (eg. benzene) it is closer to 100%.

The low solubility of non-polar molecules in water and the largely entropic nature of the solubilization free energy is known as the hydrophobic effect (Walter Kauzmann, 1959).

However, this picture breaks down for an extended oily region, because not all H-bonds can persist near its surface. This loss of H-bonds is an enthalpic effect, and drives the segregation of oil from water.

At ~~what~~ what size does this cross-over from entropy dominated to enthalpy-dominated solvation energy occur?

For the entropy-dominated region, the number of water molecules affected by the solute is proportional to the volume of the solute. (why?)

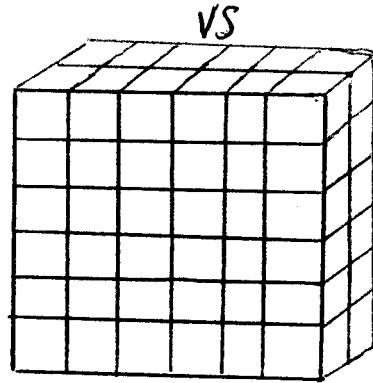
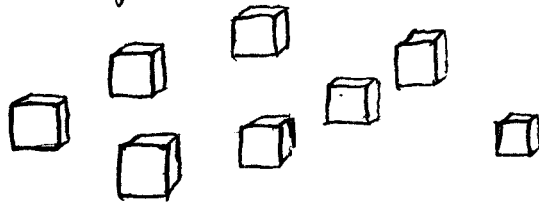
The proportionality constant can be estimated from the solvation free energies of small alkanes as  $C_v \approx 1 \times 10^8 \text{ J m}^{-3}$ .

For the enthalpy-dominated region, the number of water molecules affected is proportional to the surface area of the solute/water interface. (why?)

This proportionality constant can be estimated from the surface tension of oil/water interfaces as  $C_A \approx 6 \times 10^{-2} \text{ J m}^{-2}$ .

Work out the crossover length scale :

Consider cubic solutes of size  $L$ . If  $n$  of them are ~~the~~ separately solubilized in water, the energy cost is  $C_v \cdot n \cdot L^3$



If, instead, they pack together to avoid contact with water, the solvation energy is what?

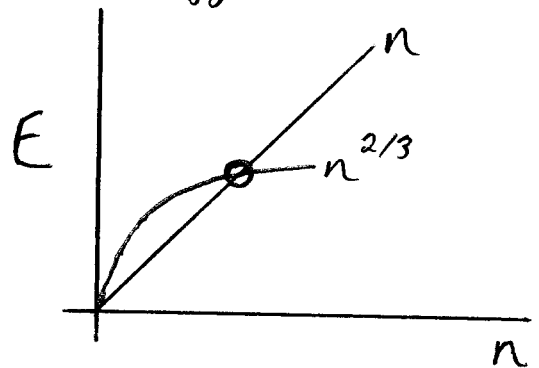
Volume of big cube is  $nL^3$ . Side length is thus  $n^{1/3}L$  and the surface area is  $6n^{2/3}L^2$ . Energy is  $C_A 6n^{2/3}L^2$ .

Equate to find crossover.

$$\text{Get } n = \left( \frac{6C_A}{C_v L} \right)^3$$

Thus crossover size is  $n^{1/3}L$

$$\text{which is } \frac{6C_A}{C_v} = 3.6 \times 10^{-9} \text{ m} = 3.6 \text{ nm.}$$



At this crossover length scale, solvation free energy of a hydrophobic object changes from being proportional to the solute volume, to being proportional to the solute surface area.