Week 1-3

Calculating Equilibrium Crystal Structure

Epitaxy

Self-assembly

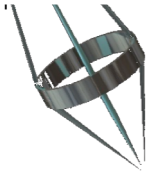
Chapter 2.5-2.8

Summary: Comparison of Bond Strengths

Bond strength determines the physical properties of materials

Bond type	Material	Melting point (°C)	Boiling point (°C)	Sublimation point* (°C)	Density+ (g/cm^3) STP	Bond energy* (kJ/mol)
Covalent	Si	1414	3265		2.33	222
	Ge	938	2833		5.35	188
	GaAs	1238			5.32	210
Ionic	NaCl	801	1413		2.17	787
	LiF	845	1676		2.64	1046
van der Waals	Anthracene	216	340		1.28	129
	Alq_3			350		162
	PTCDA			550	1.70	240
	Pentacene	>300		372	1.3	166
Hydrogen	Water	0	100		1	21
	Ammonia	−77	−33		0.82 (*s*)	46
	Ethanol	−114	78		0.79 (*l*)	38

*Approximate values are given for sublimation points and several bond energies.
+STP = standard temperature and pressure, *s* = solid, *l* = liquid.



Calculating Equilibrium Crystal Structure

- Why do we need to do this?
  - Morphology determines optical and electrical properties of thin films
  - To understand anisotropies in dielectric constants, optical properties and transport, we must understand their relationships to structure
  - Can use structure as a predictive tool for behavior of organics
  - Can use energetic calculations to find routes to improved structure via annealing, self-assembly, etc.
- But the problem requires large computational resources
  - Each molecule has shape
  - Molecules have 6 degrees of freedom to seek equilibrium (3 rotational, 3 translational)

Practical Solutions Require Significant Simplifications

Atom-Atom Potentials For Calculating Equilibrium vdW Crystal Structure

- Definition of a molecular solid: Atoms within a molecule are closer than nearest atoms on different molecules
- The atom-atom potential method is used to calculate equilibrium structures of molecular solids
  - Assumes that the total binding energy between molecules is equal to the sum of the vdW atom potentials of each molecular pair between these molecules.

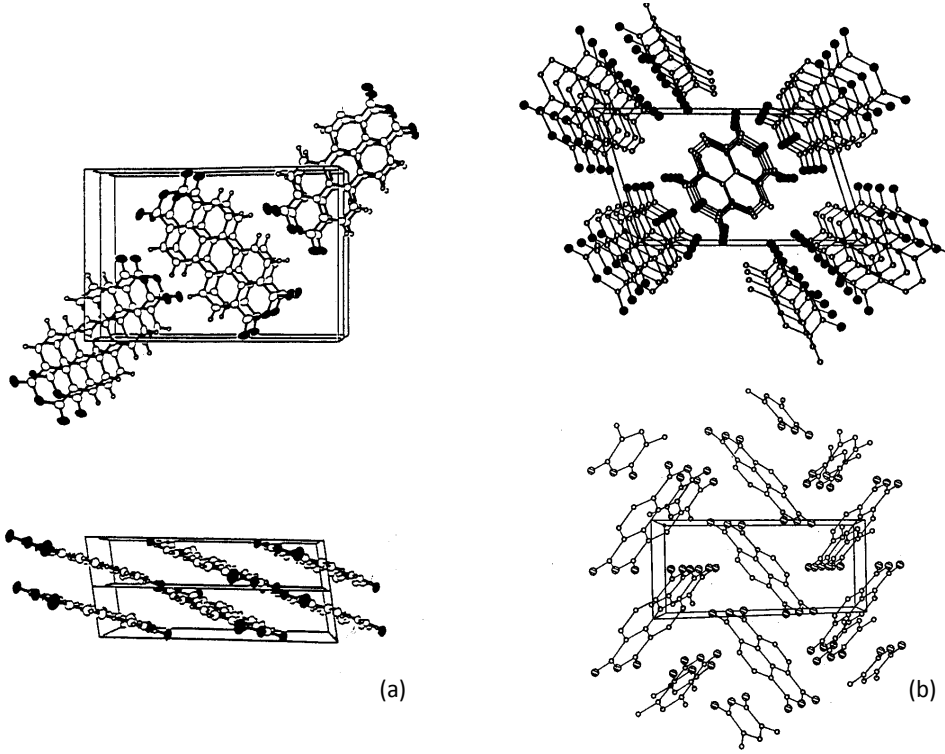
$$U(R_{ij}) = \frac{1}{2}\sum_{m,n} U(r_{mn})$$: Total binding energy of two molecules separated by $R_{ij}=R_i - R_j$ with atom m on molecule i, n on molecule j with vdW attraction $U(r_{mn})$

$$U_{crystal} = \frac{1}{2}\sum_{i \neq j} U(R_{ij})$$: Total crystal energy

$$\frac{\partial U_{crystal}}{\partial R_{ij}} = 0$$: Equilibrium crystal configuration

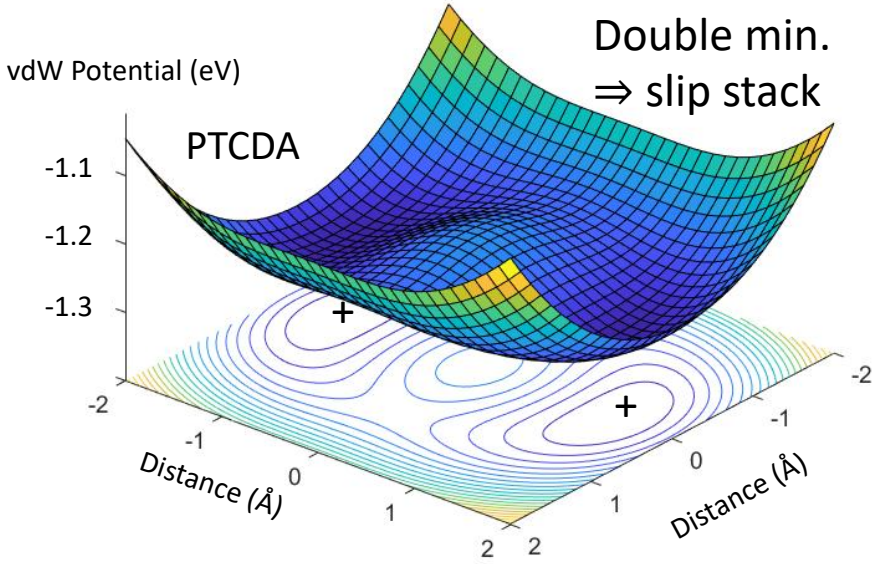
- Atom-atom potential method too cumbersome for practical structures (6 dof/molecule!)
- Results in closest possible packing arrangements like ideal gas; maximizes coordination no.
- Assumes T=0 (model is static, no vibrational modes)
- Ignores U_{coul}, $U_{fixed\ dip}$, U_{hydro}
- Gives no clue as to how to achieve the structure
- ε,σ isotropic but potentials are not
- $1/r^6 \Rightarrow$ nearest neighbors only
- No charge transfer between molecules

Examples: PTCDA and NTCDA

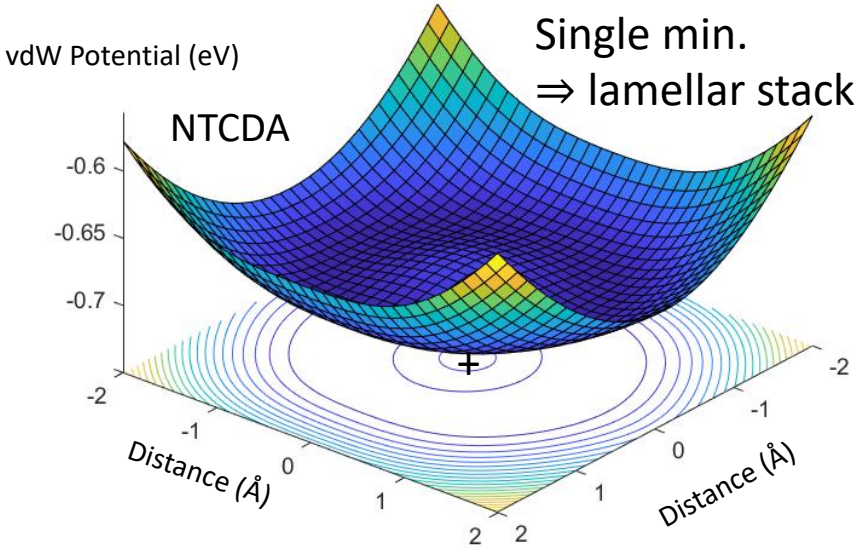


PTCDA NTCDA

Equilibrium crystal structures



Double min.
⇒ slip stack

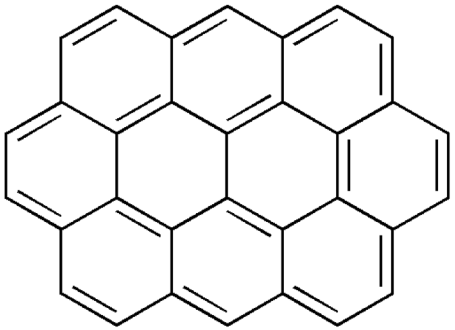


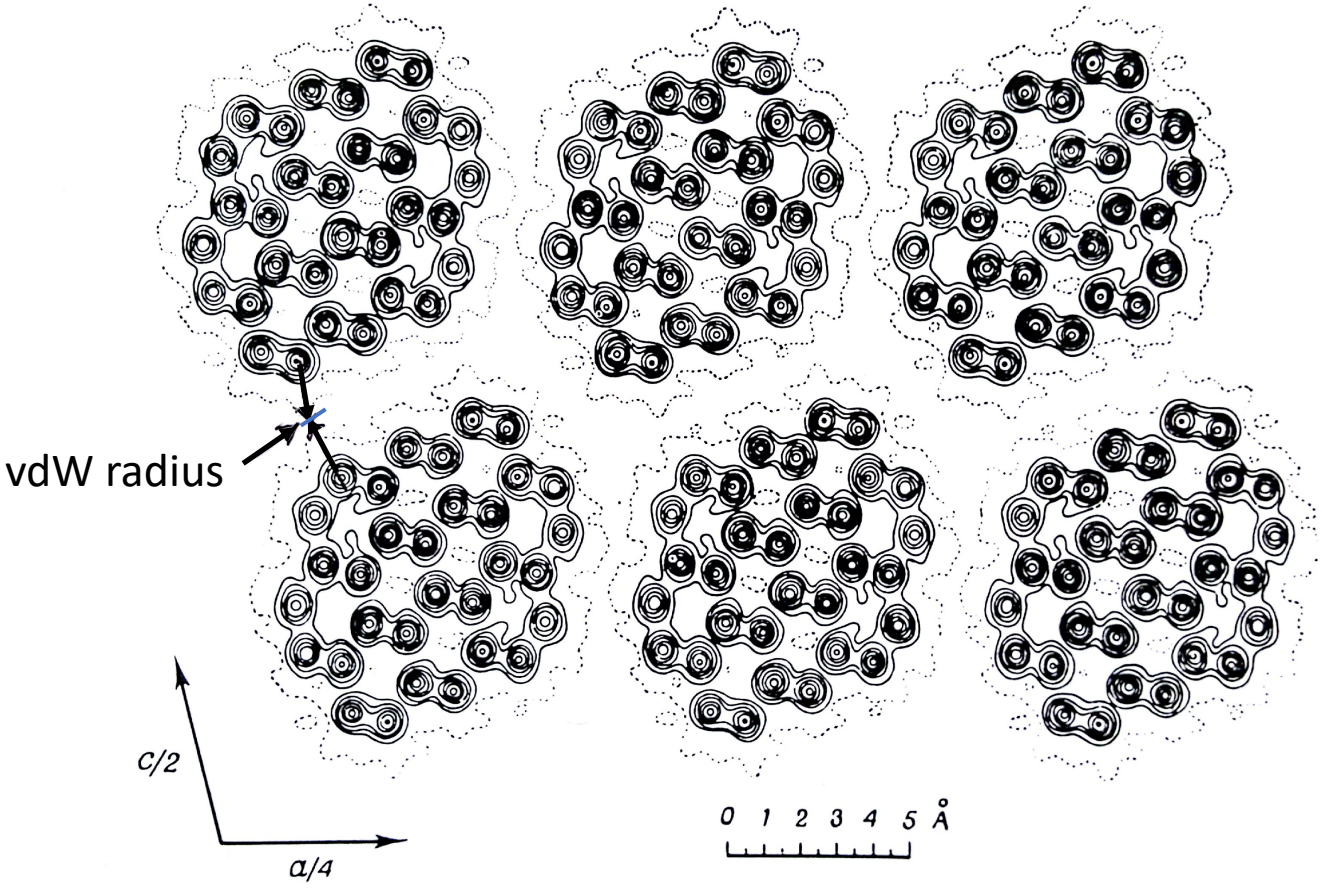
Single min.
⇒ lamellar stack

Molecule-molecule (dimer) potential surfaces

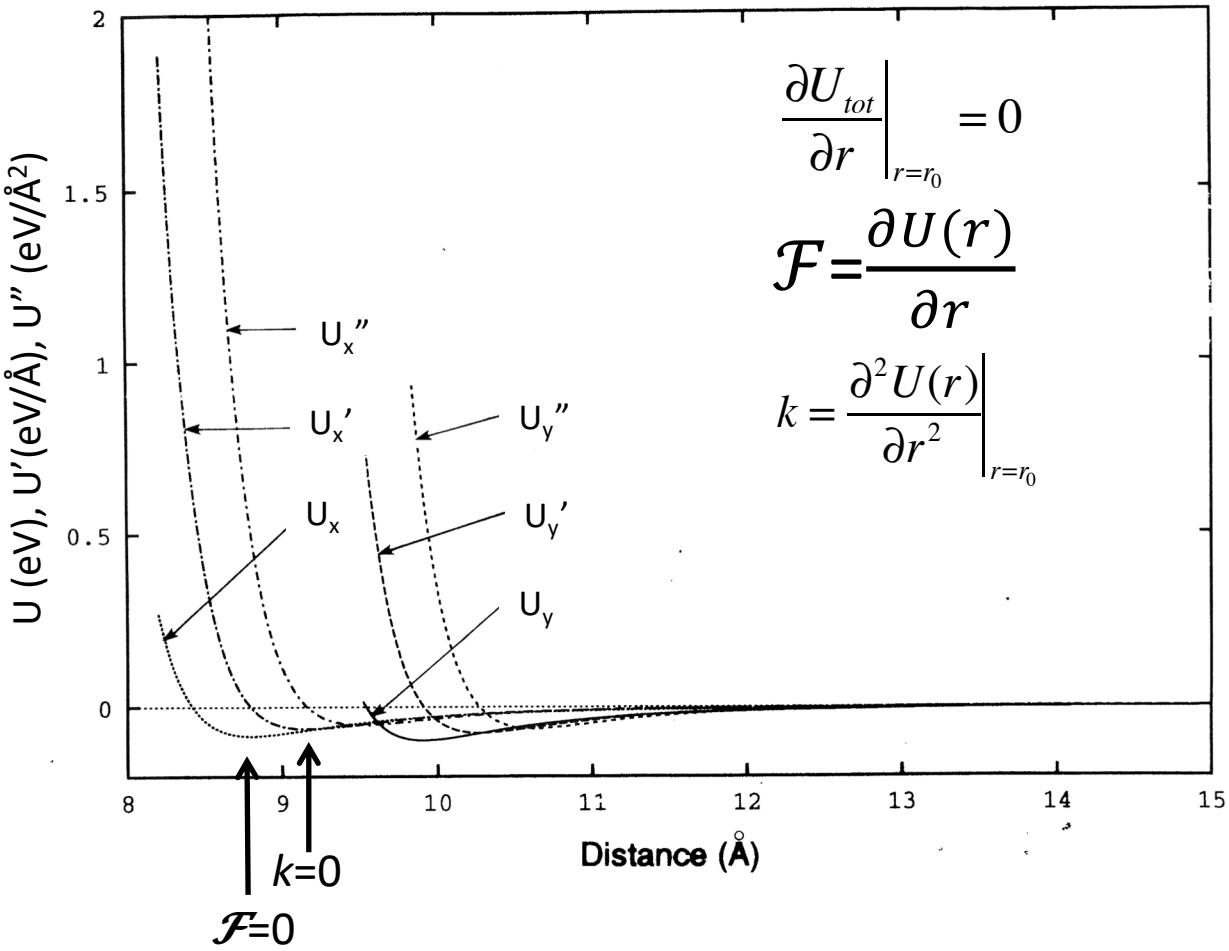
An example of close packing

Ovalene





Energy, Force, Elastic Constants of PTCDA



$$\left.\frac{\partial U_{tot}}{\partial r}\right|_{r=r_0} = 0$$

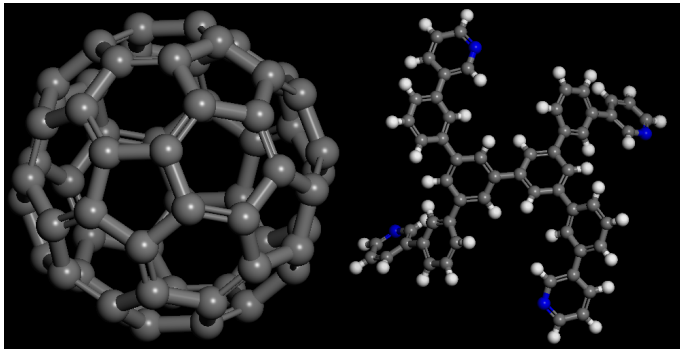
$$\mathcal{F} = \frac{\partial U(r)}{\partial r}$$

$$k = \left.\frac{\partial^2 U(r)}{\partial r^2}\right|_{r=r_0}$$

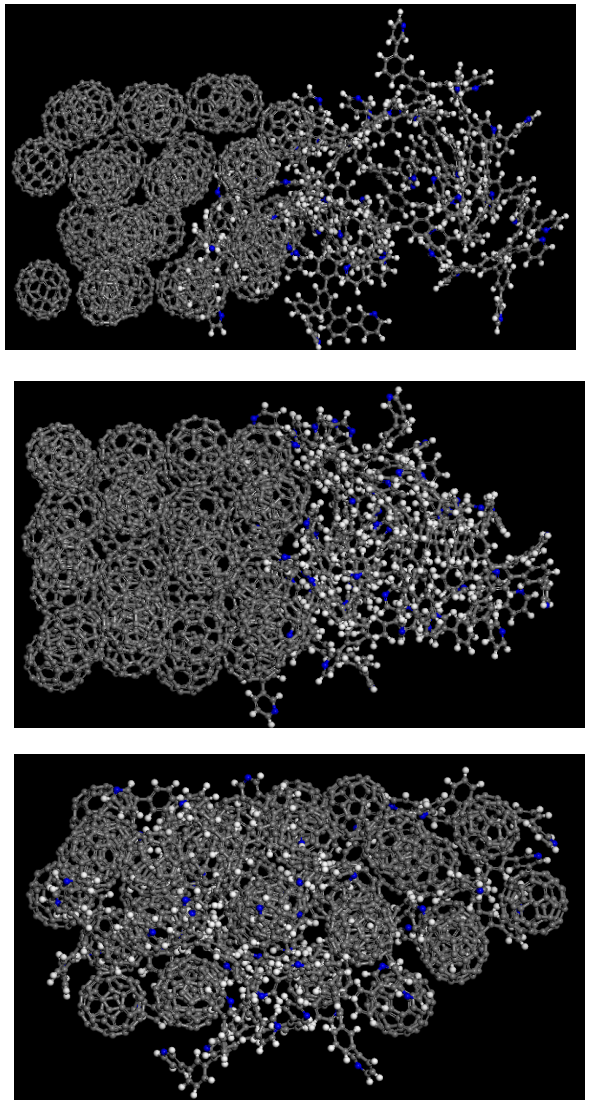
Molecular Dynamics Simulations

- Includes thermodynamics (i.e. temperature) in the atom-atom potential calculations to determine the likely lowest energy structures
- Calculationally intense

Example: Blending at a bilayer interface C_{60} + BP4mPy with increasing annealing temperature.



Simulated annealing at an interface

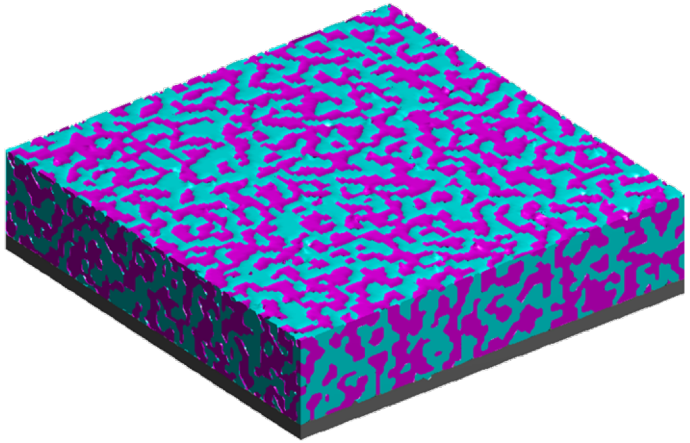


Song & Forrest, Nano Lett. 16, 3905 (2016)

3D complexity Using MD Calculations

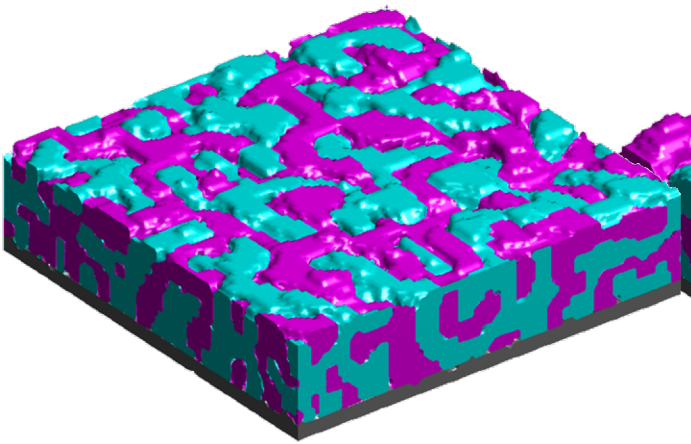
Phase Separation → Surface Morphology

Initial configuration: mixed layer

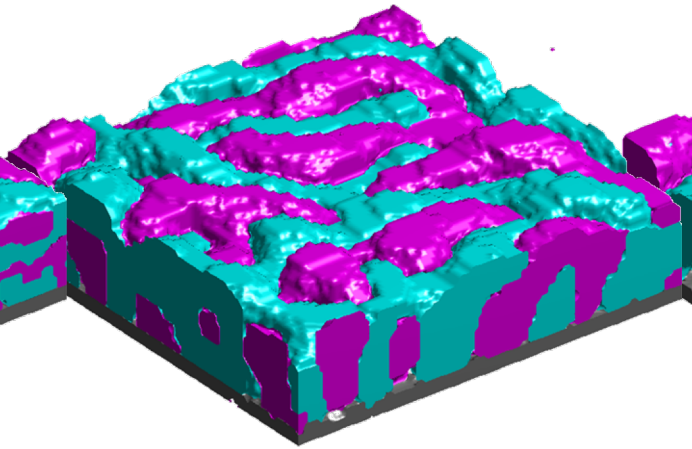


Annealed configuration

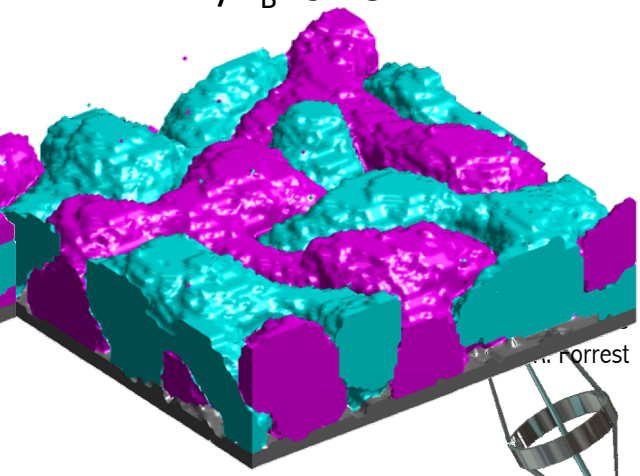
kT/E_B=0.067



kT/E_B=0.10



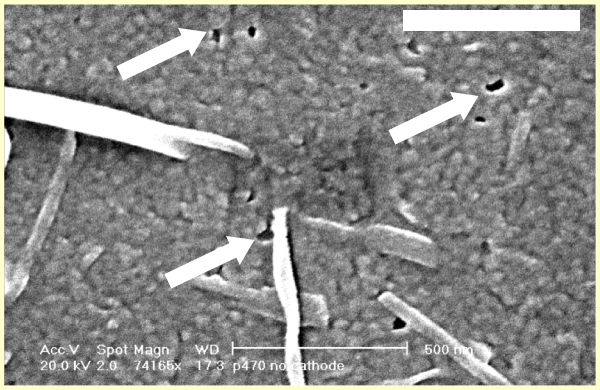
kT/E_B=0.13

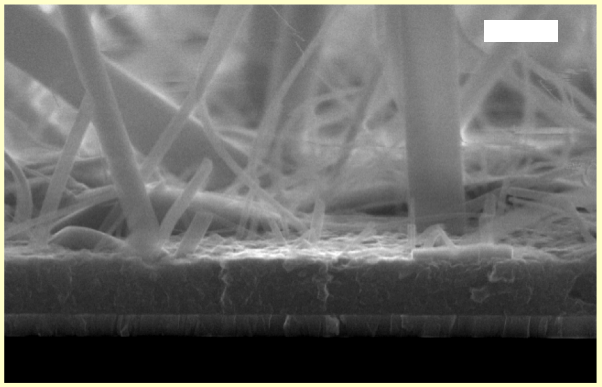


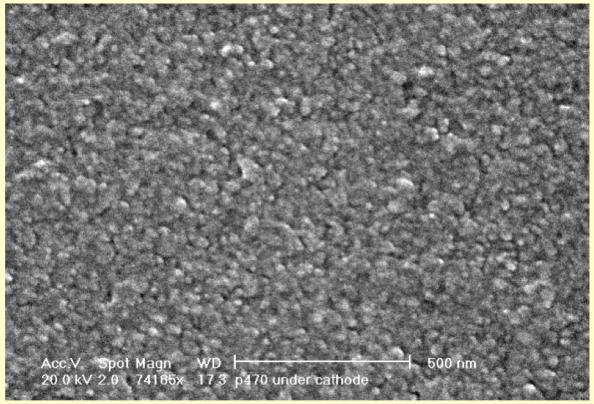
Yang & Forrest, ACS Nano, 2, 1022 (2008)

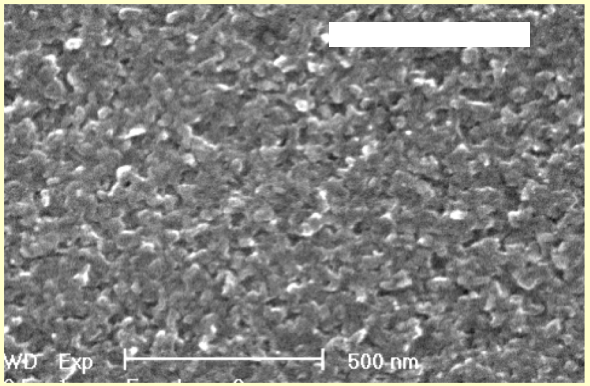
Bulk Heterojunction Formation:
Annealing with Metal Stressor Cap

Annealed-no metal cap



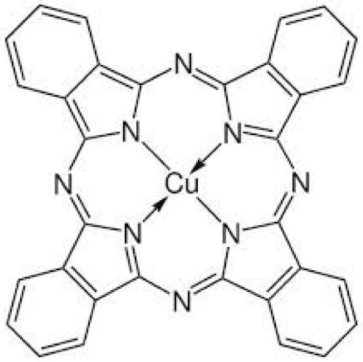






Annealed-metal cap

Not annealed



Cu phthalocyanine (CuPc)

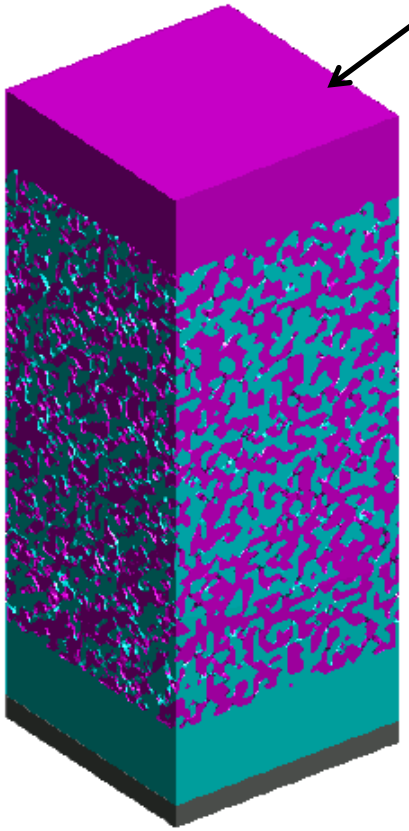
Stephen R. Forrest

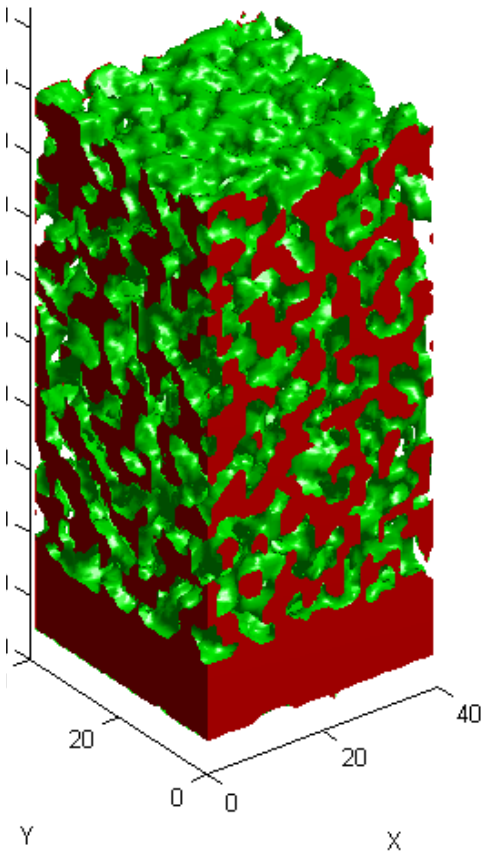
Peumans, et al. 2003. *Nature,* 425**,** 158.

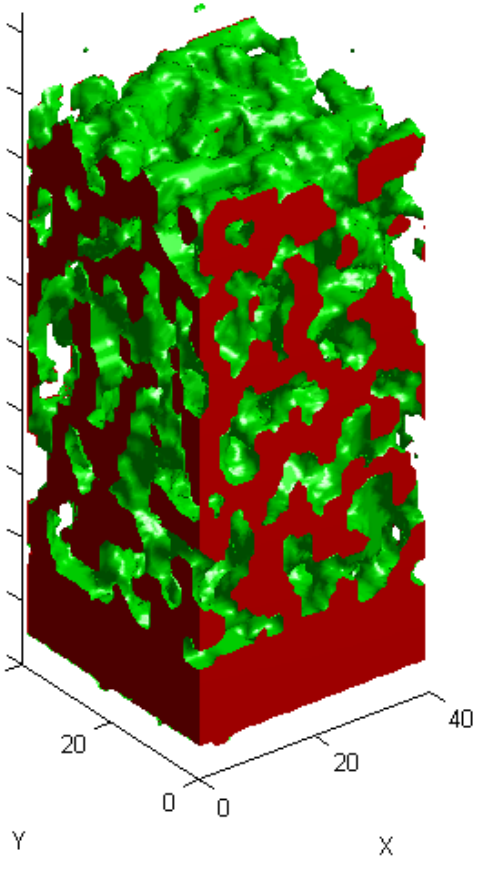
Calculating annealing of a binary blend

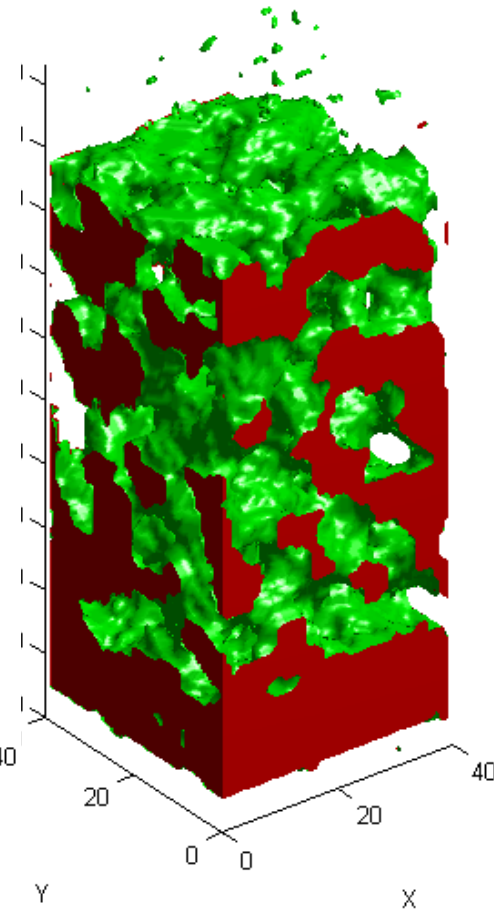
Qualitatively accurate representation by MD

Ag cap holds surface flat









1000Å Ag

CuPc:PTCBI

ITO

kT/E_B=0.067

η_{ED}=77%

kT/E_B=0.10

η_{ED}=55%

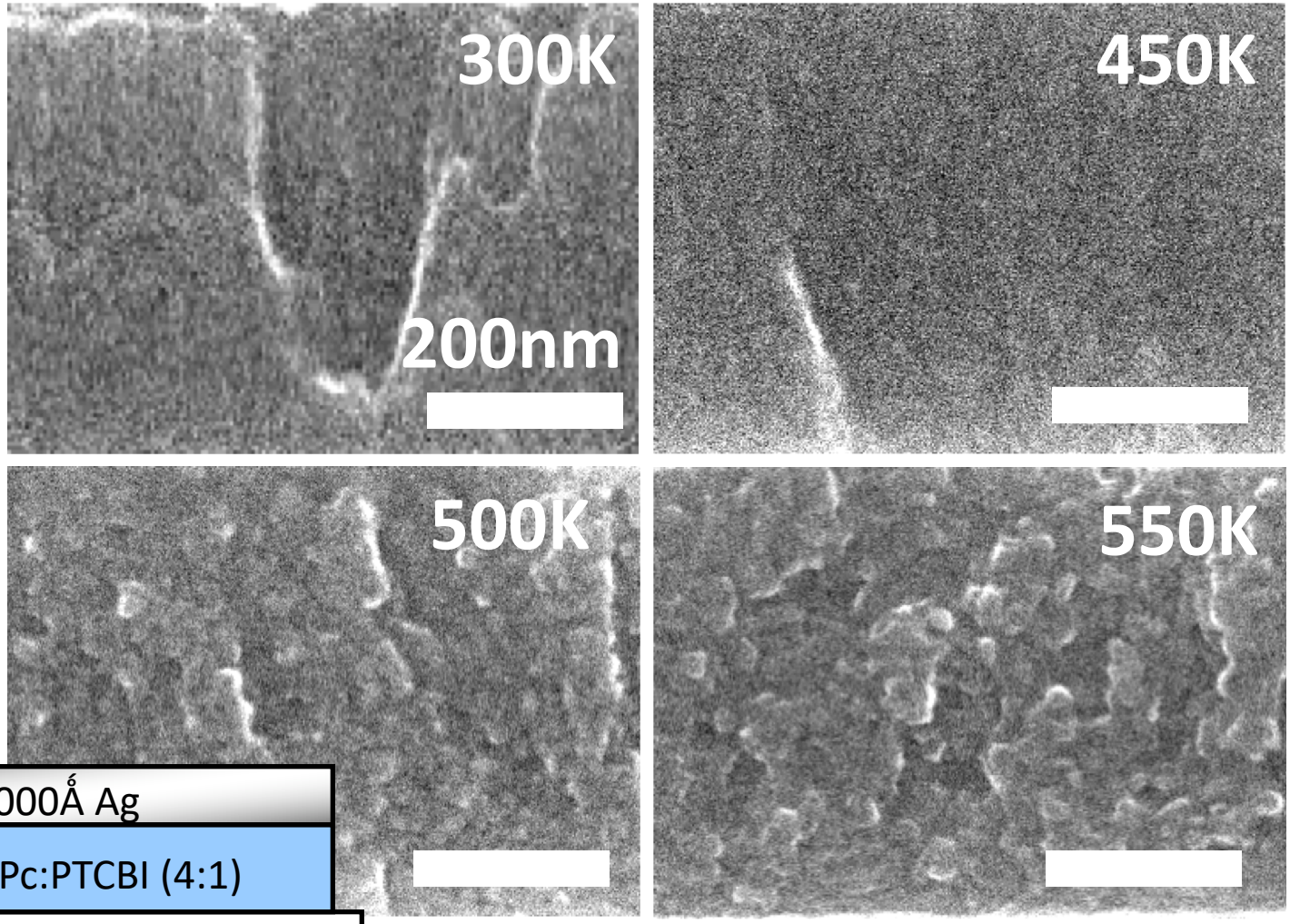
kT/E_B=0.13

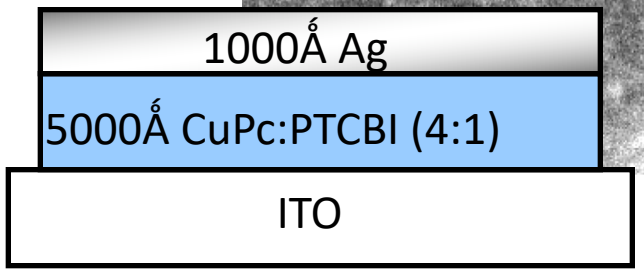
η_{ED}=43%

Peumans, et al. 2003. *Nature,* 425**,** 158.

Phase Segregation in Confined Films

SEM of cross-section shows increasing grain size

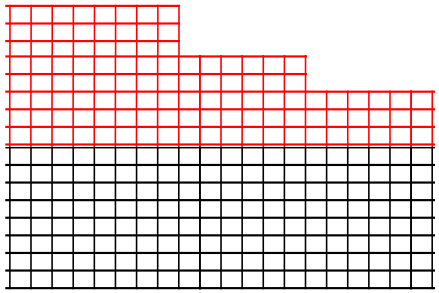




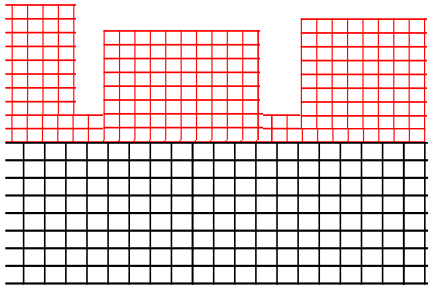
Peumans, P. et al. 2003. *Nature,* 425**,** 158.

Growth Modes of Materials: Epitaxy

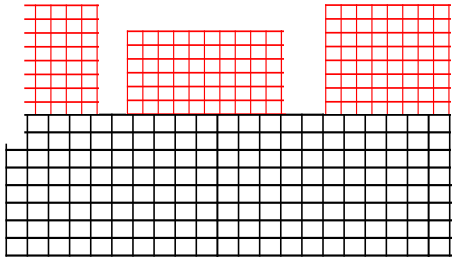
- **Epitaxy**: the growth of a layer whose structure mimics that of the underlying lattice



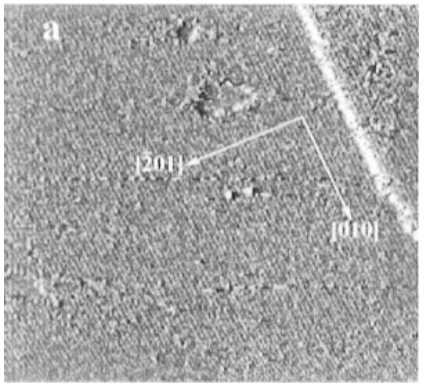
Layer-by-layer
(Franck-van der Merwe)



Wetting layer+islands
(Stranski-Krastonow)

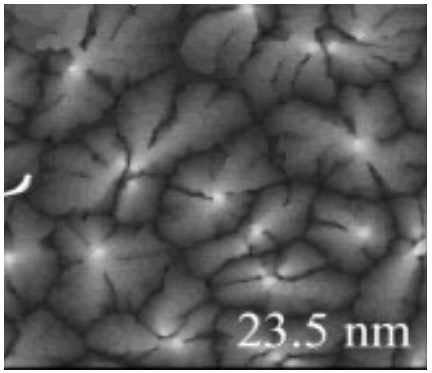


Island
(Volmer-Weber)



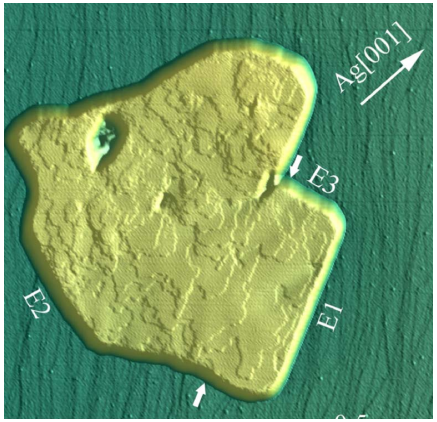
PTCDA on Graphite

Kendrick, et al. Appl. Surf. Sci., 104/105 586 (1996)



Pentacene on polyimide

Yang, et al. Adv. Func. Mater., 15, 1806 (2005)



Oligoethylene on Ag

Zhong, et al. Phys. Rev. B, 77 113404 (2008)

Matthews-Blakeslee Strain Limit

At a critical degree of strain, the lattice relaxes via dislocations

$$Strain = f = \frac{a_E - a_S}{a_S} = \frac{\Delta a}{a_S}$$

Δa = lattice mismatch

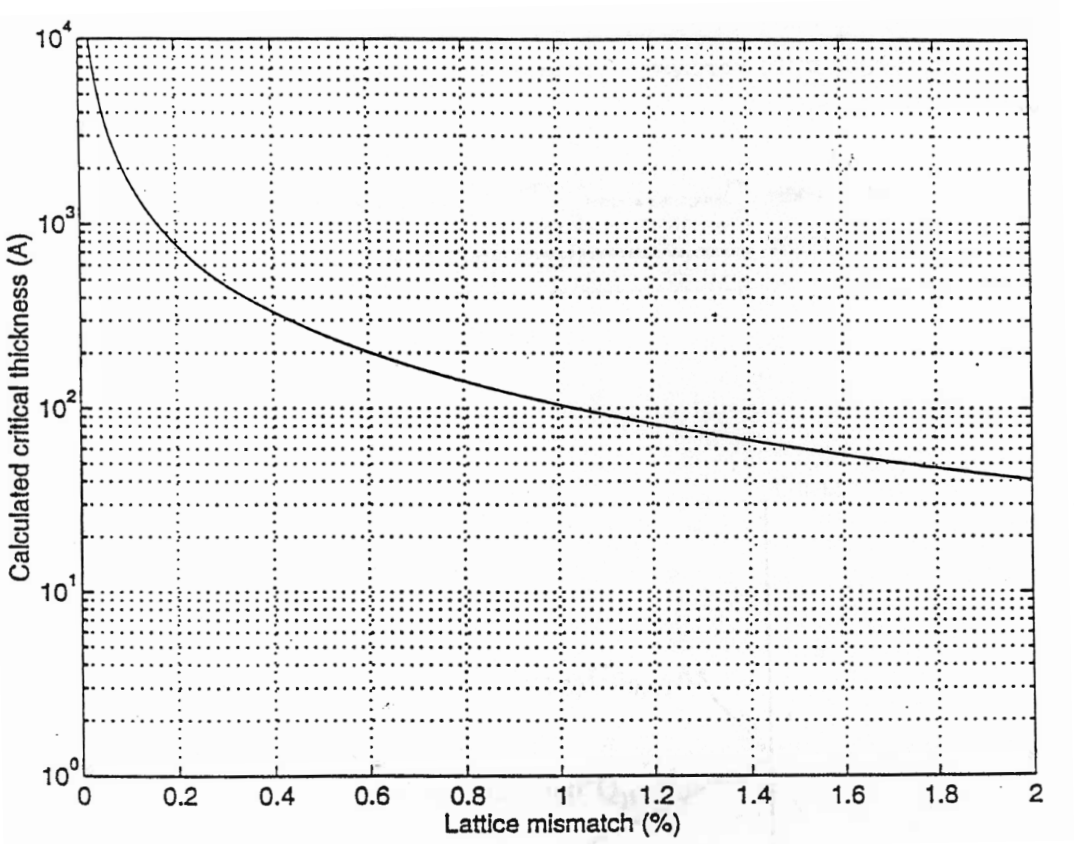
Critical thickness leading to lattice dislocations

When force due to strain = tension in dislocation

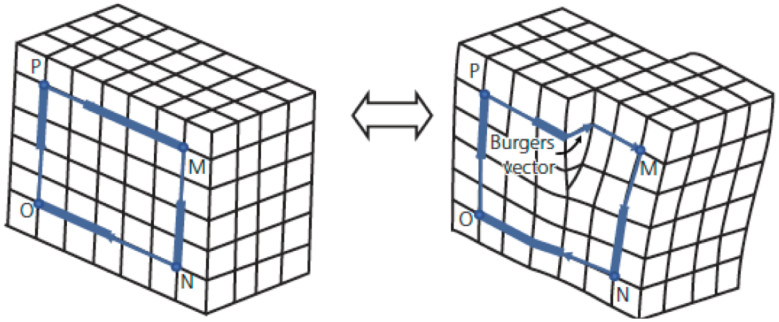
$$t_c = \frac{a_e(1-\nu/4)}{4\sqrt{2}\pi f(1+\nu)}\left(\ln\frac{\sqrt{2}t_c}{a_e}+1\right)$$

ν=Poisson's ratio

a_e=magnitude of the **Burger's vector** of the dislocation



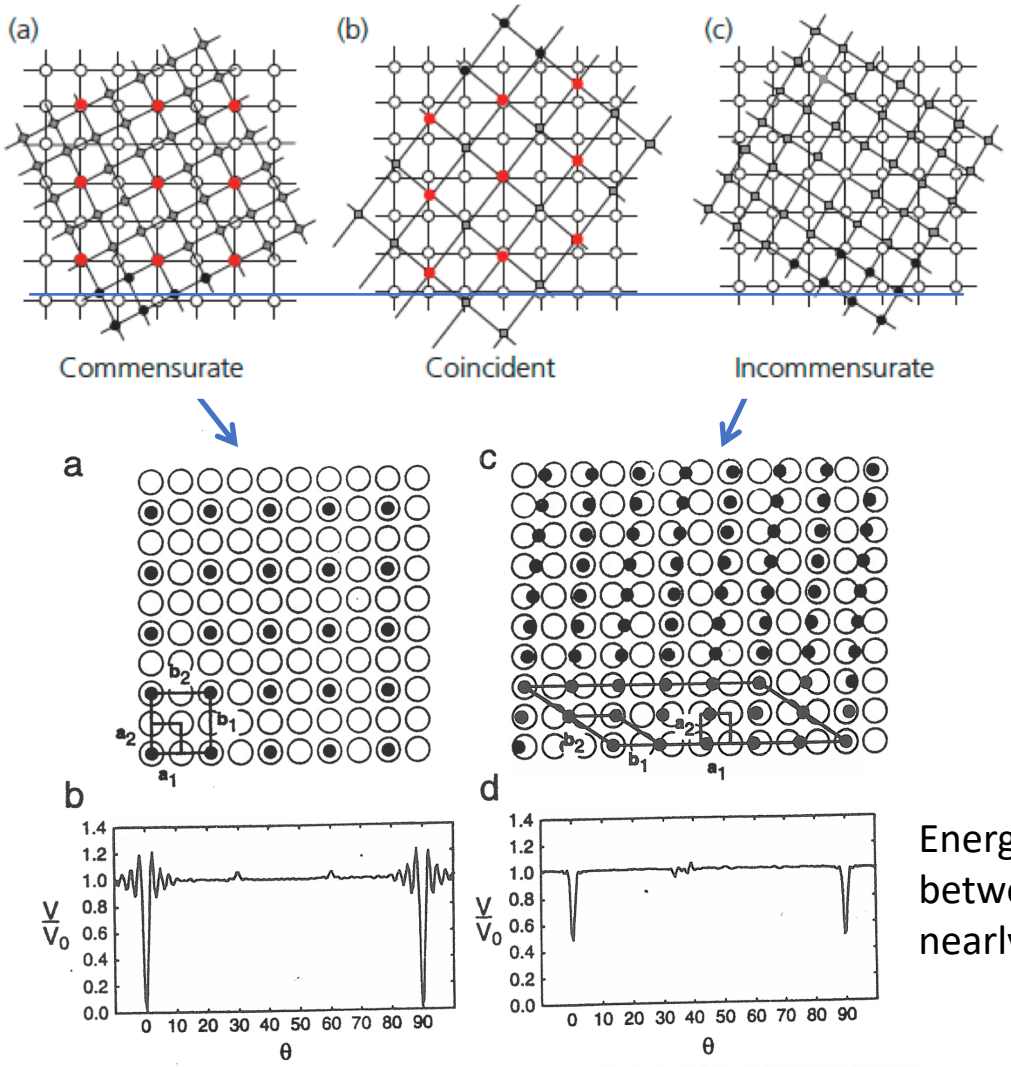
Matthews & Blakeslee, J. Cryst. Growth, 27, 118 (1974)



Burger's vector definition

Defect formation depends on bond strength, energy of defect formation, *size of lattice*

Commensurality Looking From the Top

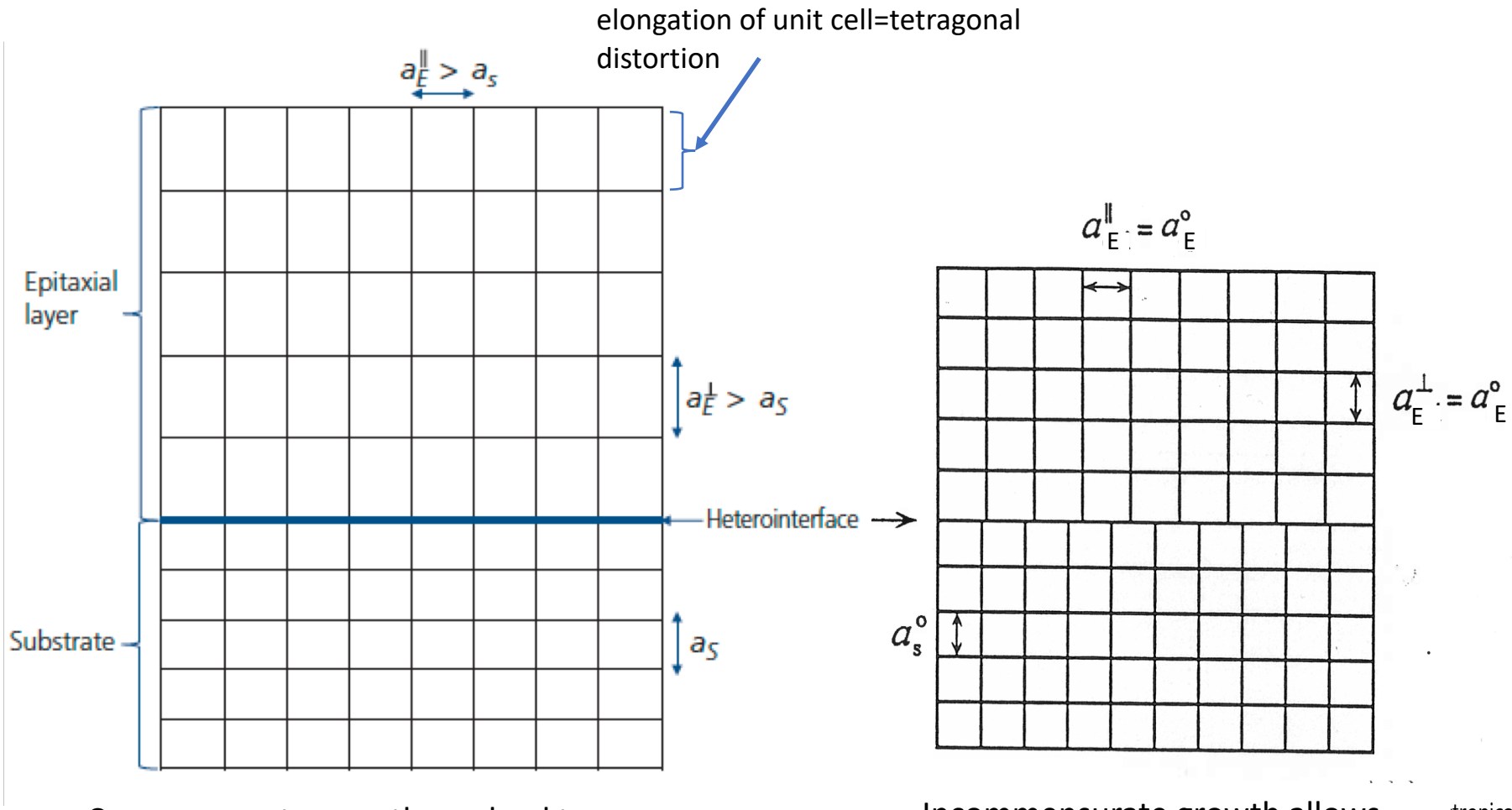


Energy vs. rotational angle between commensurate & nearly commensurate lattices

Energy minima deeper for commensurate (equilibrium) structures

Hiller, A. C. & Ward, M. D. 1996. *Phys. Rev. B,* 54**,** 14037.

Commensurality in X-section View



Commensurate growth can lead to lattice distortion to accommodate strain

Incommensurate growth allows epitaxial lattice to relax to its equilibrium dimensions

tronics
Forrest

Organic systems often incommensurate but align to substrate in order to minimize energy: Quasi-epitaxial growth

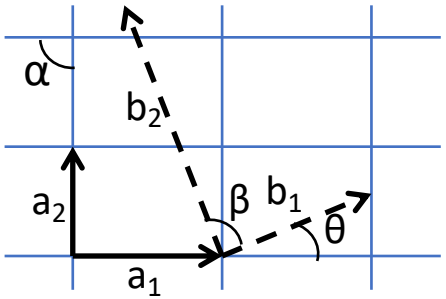
- Rarely is there an appropriate substrate to initiate epitaxy
- Growth can occur relatively free of defects (very large Matthews-Blakeslee critical thickness) when the force constant within a layer is greater than between the layer and substrate

$$\Rightarrow U''_{\text{int}\,ra} >> U''_{\text{int}\,er}$$: Condition for **quasi-epitaxy**

- That is, lattice stiffness exceeds interaction between layers, allowing for slippage between epitaxy and substrate
- Fundamentally a "guided self-assembly" process
- Large molecules more readily form ordered layers on substrates due to overlap with multiple lattice constants

Lattices related by transformation matrix, **T**

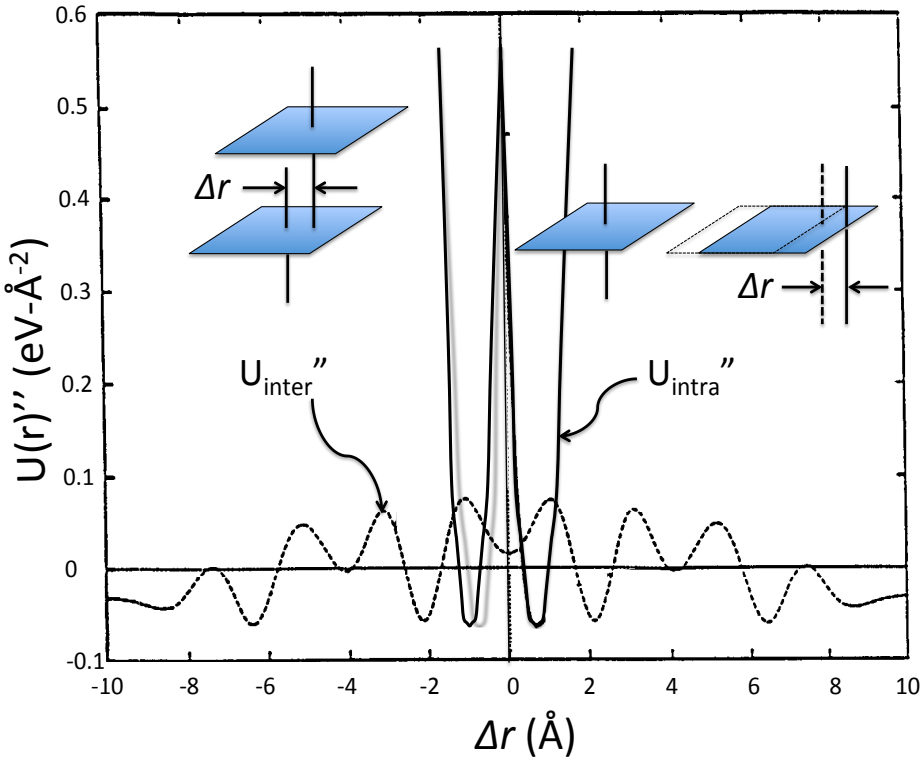
$$\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \mathbf{T} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \qquad \mathbf{T} = \begin{pmatrix} t_{11} & t_{12} \\ t_{21} & t_{22} \end{pmatrix}$$



-**Commensurate**: all t's are integers (i.e. det(**T**)= integer)
-**Coincident**: one direction of overlayer lies along a substrate direction (i.e. det(**T**)= simple fraction)
-**Incommensurate**: no t's are integers (i.e. det(**T**)= irrational no.)

Quasi-epitaxial growth condition

PTCDA



$$\Rightarrow U''_{intra} >> U''_{inter}$$

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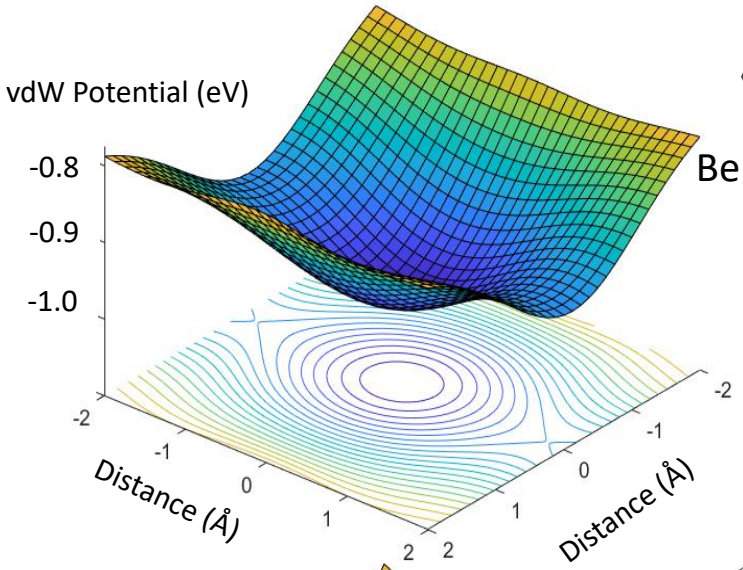
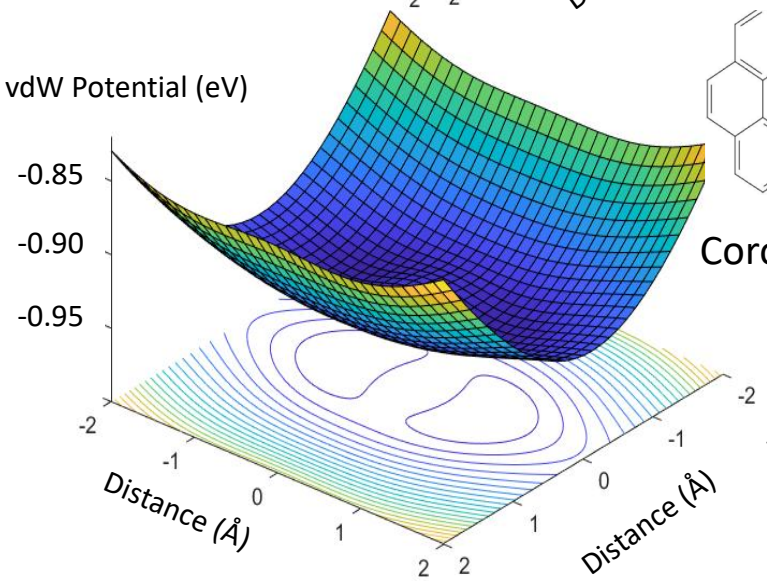
Intralayer elastic constant (i.e. stiffness) greater than interlayer (with substrate) elastic constant

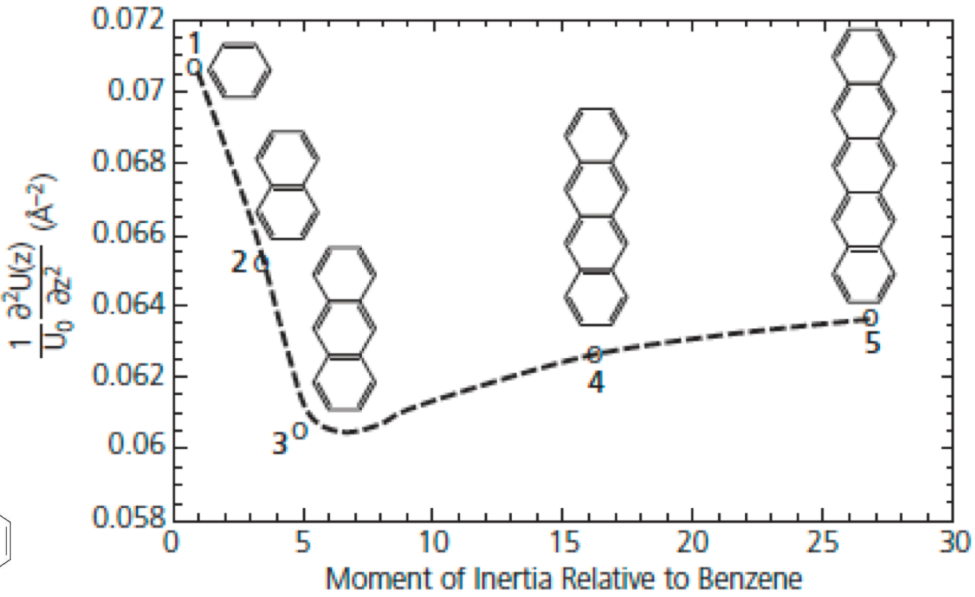
Larger molecules have lower intermolecular strain



Benzene



Coronene

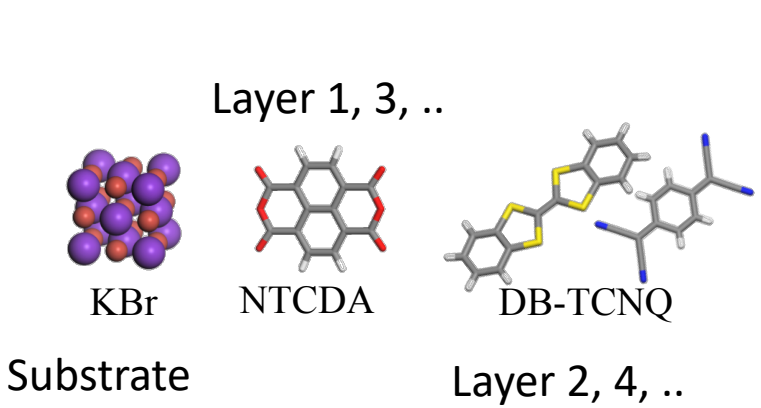


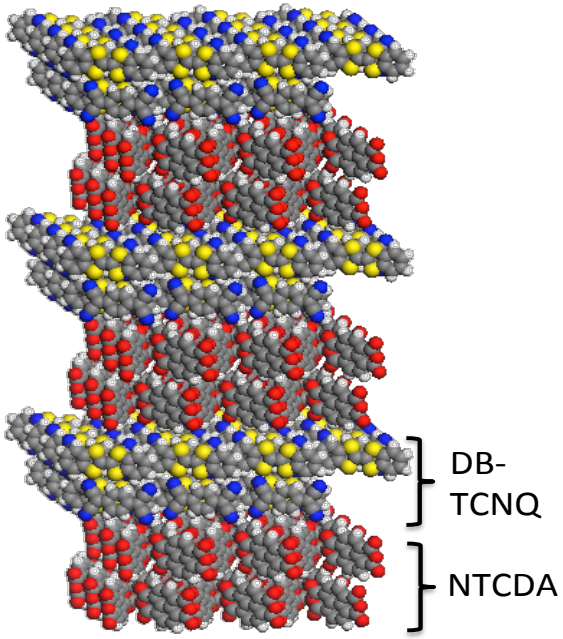
"Longer" molecules can accommodate more strain with substrate

"Rounder" molecules have broader and more uniform energy surfaces
⇒ easier to slide on substrate

Example of ordered q-e growth

- OVPD growth of DB-TCNQ on NTCDA on KBr
- Deep alternating layer stacks grown
- Congruent growth of the two component salt, DB-TCNQ observed
  (**Congruent growth** = ordered growth of 1 DB per 1 TCNQ molecule in each monolayer)
- 5 nm/layer
- Order maintained throughout stacks, orientation of one layer on another also maintained even when incommensurate
- Layer ordering measured using in-situ reflection high energy elctron diffraction (RHEED)



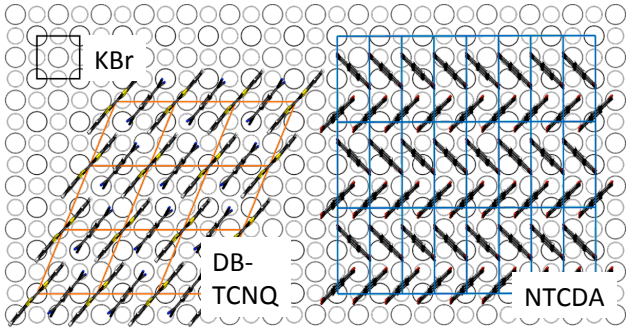


Organic Electronics
Stephen R. Forrest

Lunt, et al, 2011. *Rev. B,* 83**,** 064114.

Measurement and atom-atom calculations predict similar lattice angle alignments

Measured lattice alignments



Coincident

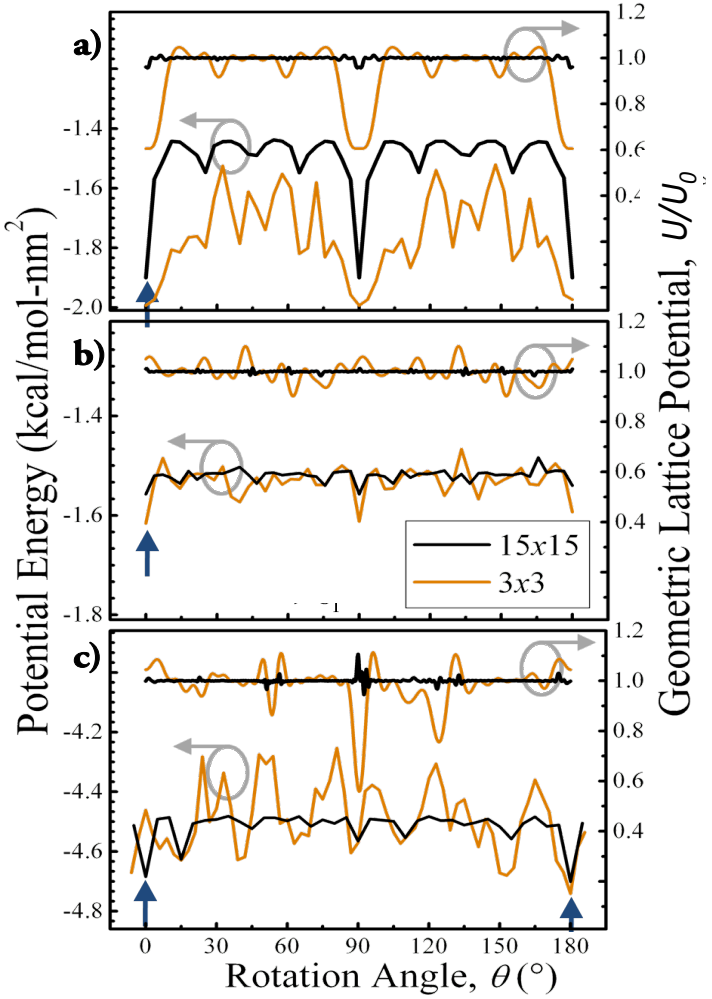
$$\mathbf{T}_{\text{KBr-NTCDA}} = \begin{pmatrix} 1.99\pm0.01 & 0\pm0.009 \\ 0\pm0.01 & 0.753\pm0.008 \end{pmatrix}.$$

Incommensurate

$$\mathbf{T}_{\text{KBr-TCNQ}} = \begin{pmatrix} 1.38\pm0.02 & 0\pm0.02 \\ 0.63\pm0.03 & 1.47\pm0.02 \end{pmatrix}.$$

Quasi-epitaxial

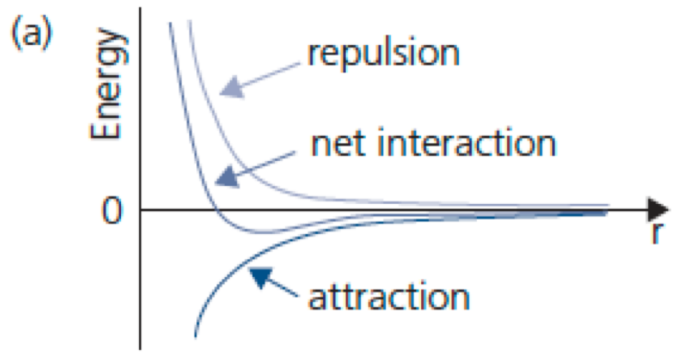
$$\mathbf{T}_{\text{NTCDA-TCNQ}} = \begin{pmatrix} 0.70\pm0.01 & 0\pm0.02 \\ 0.32\pm0.02 & 1.96\pm0.04 \end{pmatrix}.$$



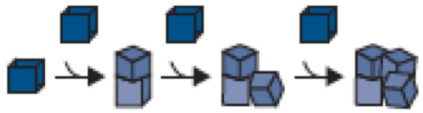
Atom-atom energy calculations show preferred interlayer orientations to minimize energy

Lunt, et al, 2011. *Rev. B,* 83**,** 064114.

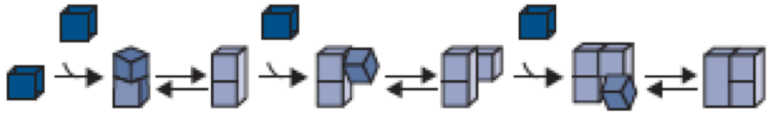
Self-Assembly



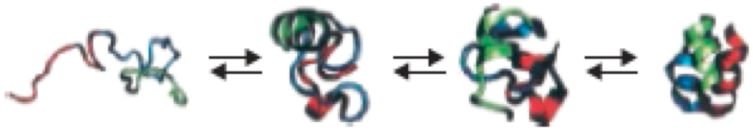
(b) Irreversibility gives glasses.



(c) Reversibility gives crystals ...



(d) ... and ordered macromolecules.



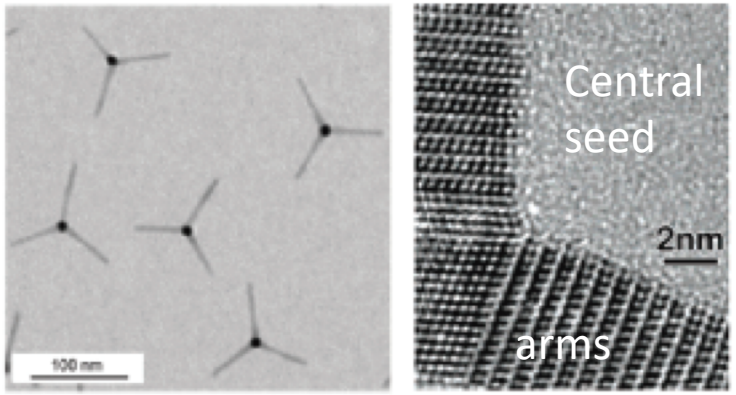
Balance of attractive and repulsive forces drives SA

Whitesides & Boncheva, PNAS, 99 4769 (2002)

Self-assembly

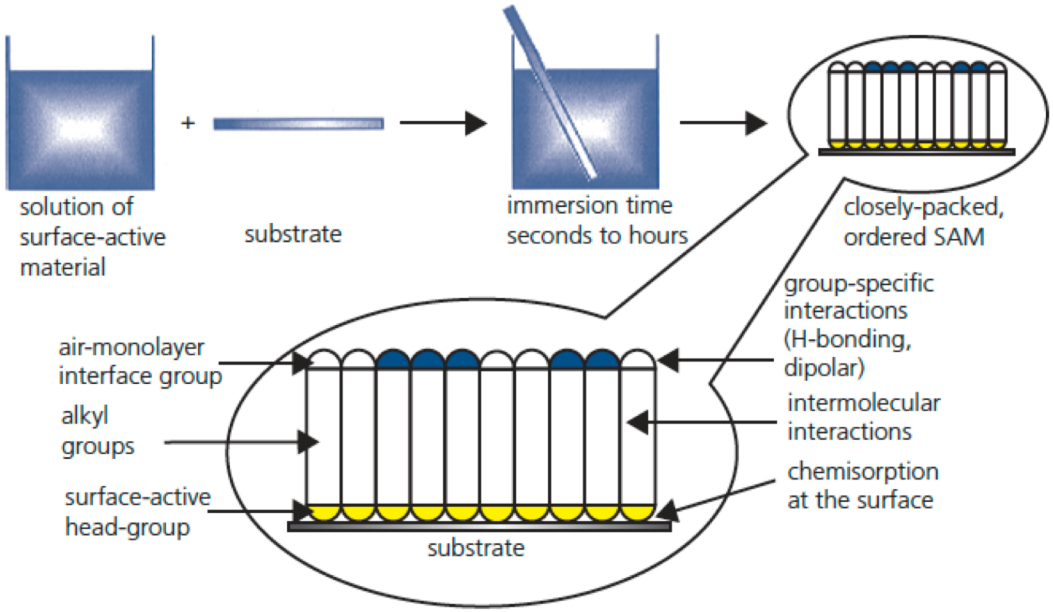
- The process where structure is guided by cohesion and symmetry of components
- It can be spontaneous
- It can occur over multiple length scales, from nano to cm.

SA of CdSe tetrapods



Nelson, et al. Nano Lett., 7, 2951 (2007)

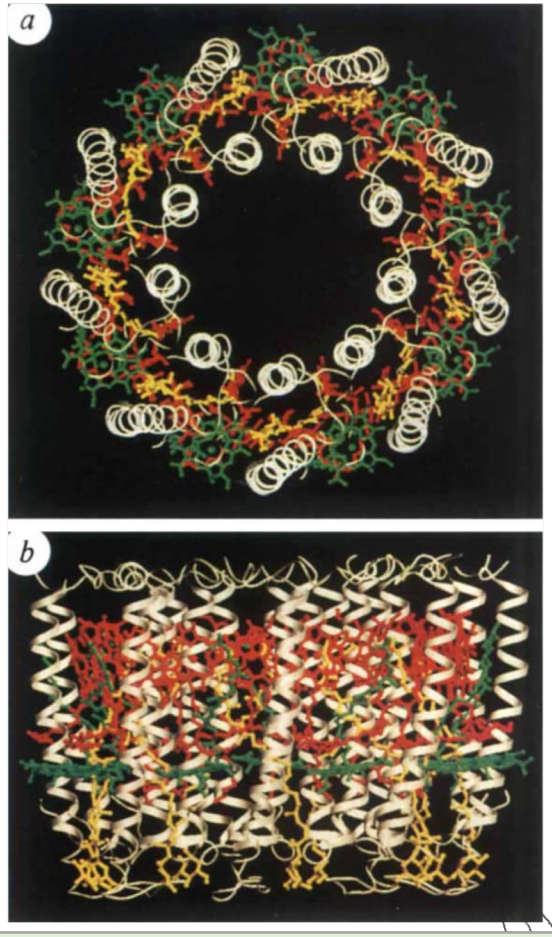
Self-Assembly: Two Examples



Guided SA

- Functionalized molecules assemble side-by-side due to vdW attraction
- Directionality provided by end group functionalization

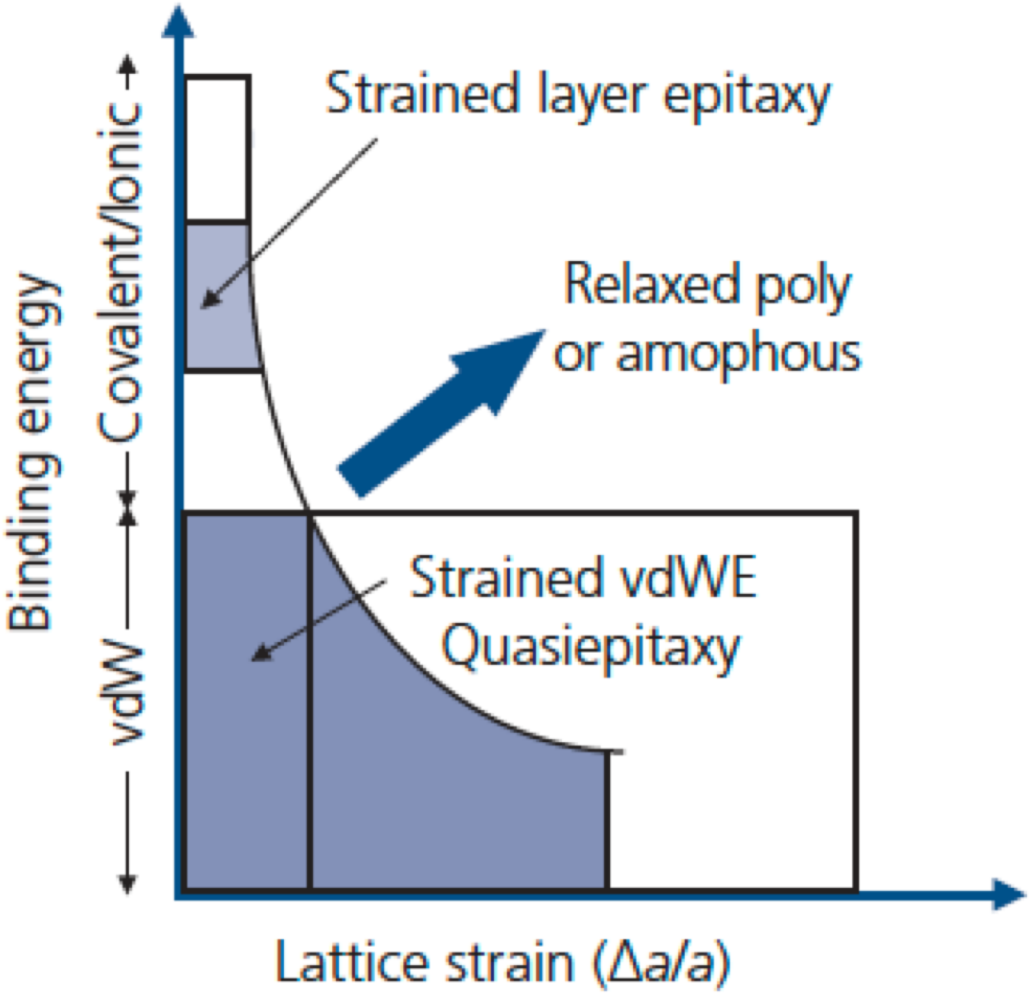
Ullman, Chem. Rev. 96, 1533 (1996).



- Photosynthetic complexes are assembled over multiple scales:
- Single porphyrin molecules at pico/nano scale
- Protein scaffolds (the spirals and colored strands) at 10 micron scale

McDermott et al., Nature 374, 517 (1995).

The Universe of Structure



What we learned

- We introduced several classes of organic compounds useful in OE, and established a common language
- We quantified important binding properties of crystals (covalent, ionic, van der Waals, H-bonds) and the crystal structures they produce
- We showed how layers grown onto surfaces can replicate, or are guided by the underlying substrate structure (epitaxy, vdW epitaxy, quasi-epitaxy)
- We described the process of self-assembly resulting from a balance between cohesive and repulsive forces that can produce ordered structures over multiple length scales.