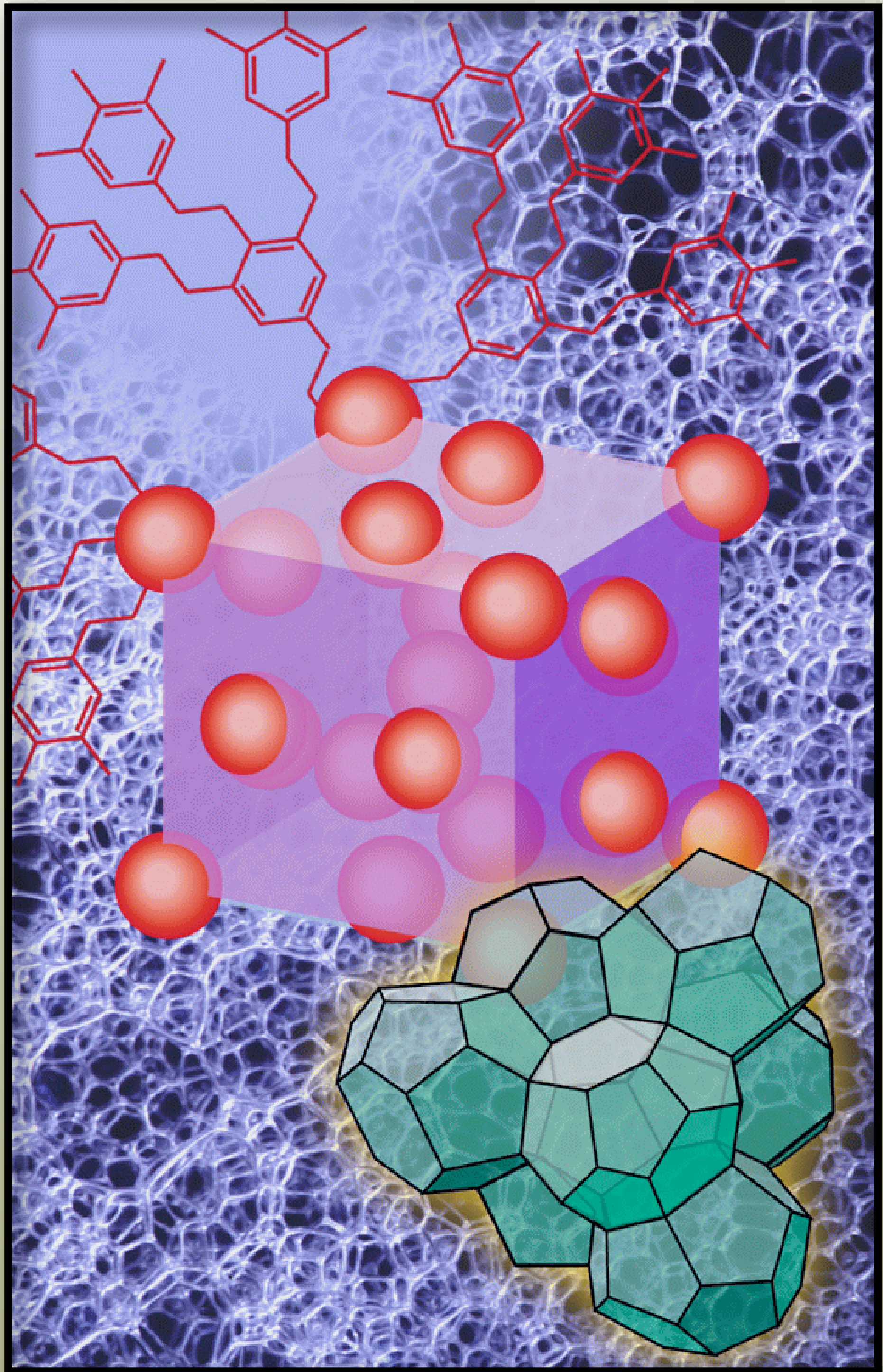
What's Kelvin's Problem?

Randall D. Kamien
Physics & Astronomy



Ziherl and RDK, *PRL* **85** (2000) 3528
Ziherl and RDK, *J. Phys. Chem.* B **105** (2001) 10147
Kung, Ziherl and RDK, *PRE* **65** (2002) 050401R
Grason, DiDonna and RDK, *PRL* **91** (2003)

www.physics.upenn.edu/~kamien/

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What's Kelvin's Problem?

Randall D. Kamien
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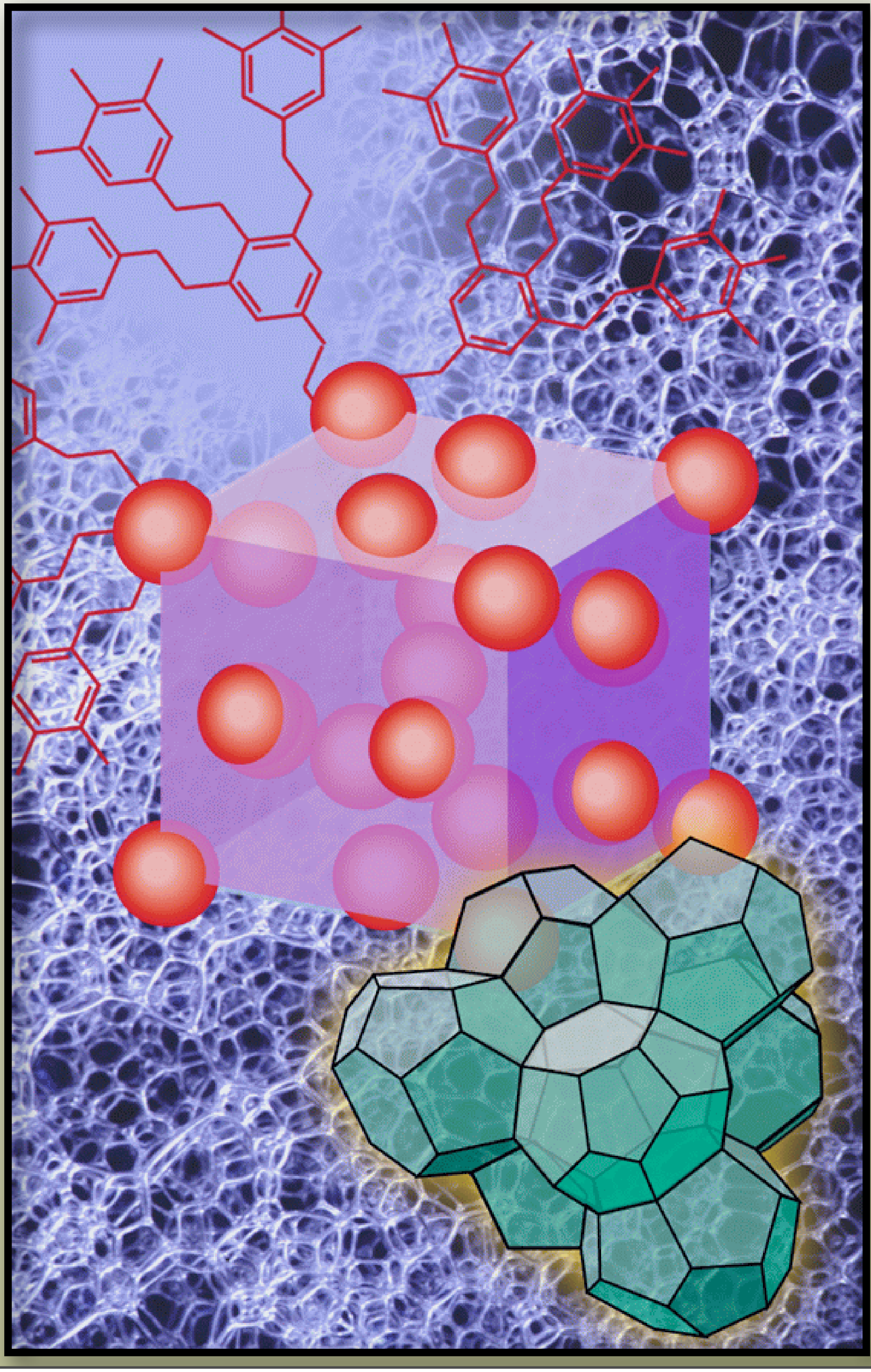
Dendrimers and Diblocks
Sphere Packings
Minimal Surfaces & Soap Froths
Diblock Copolymers
Experiment



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Grason, DiDonna and RDK, *PRL* **91** (2003)

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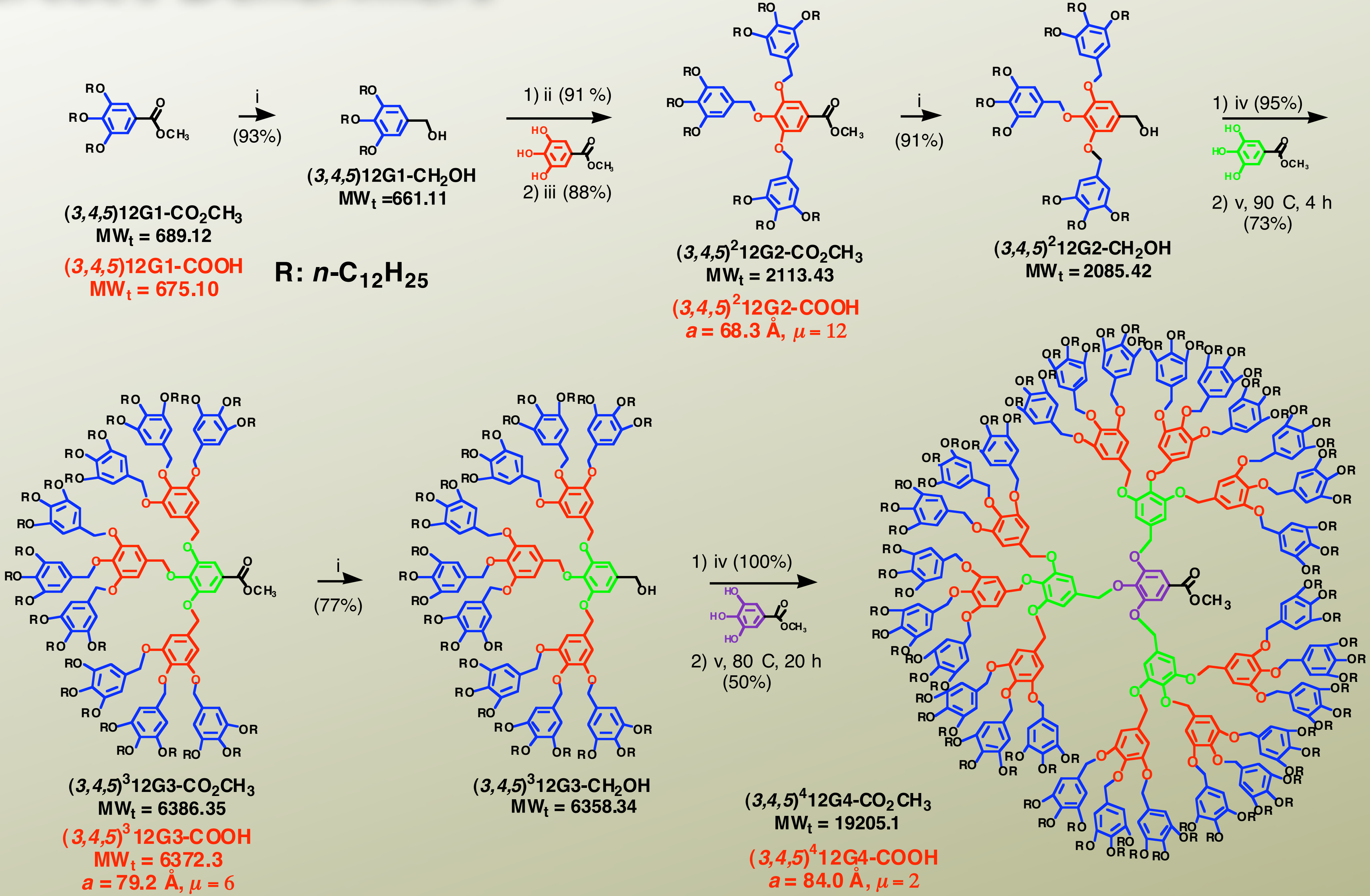
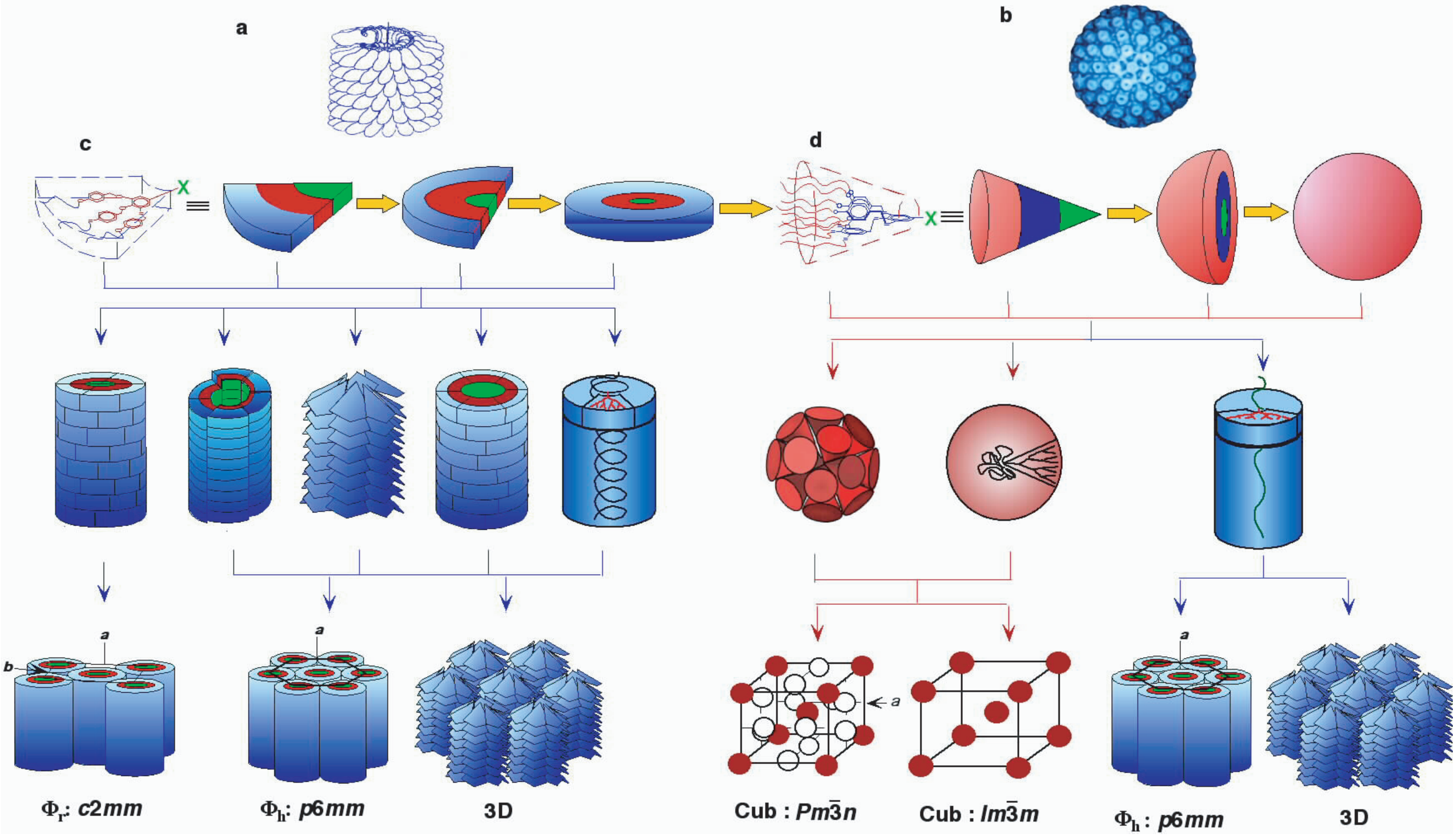
Percec's Dendrimers



Rational Design of Geometry



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New Materials

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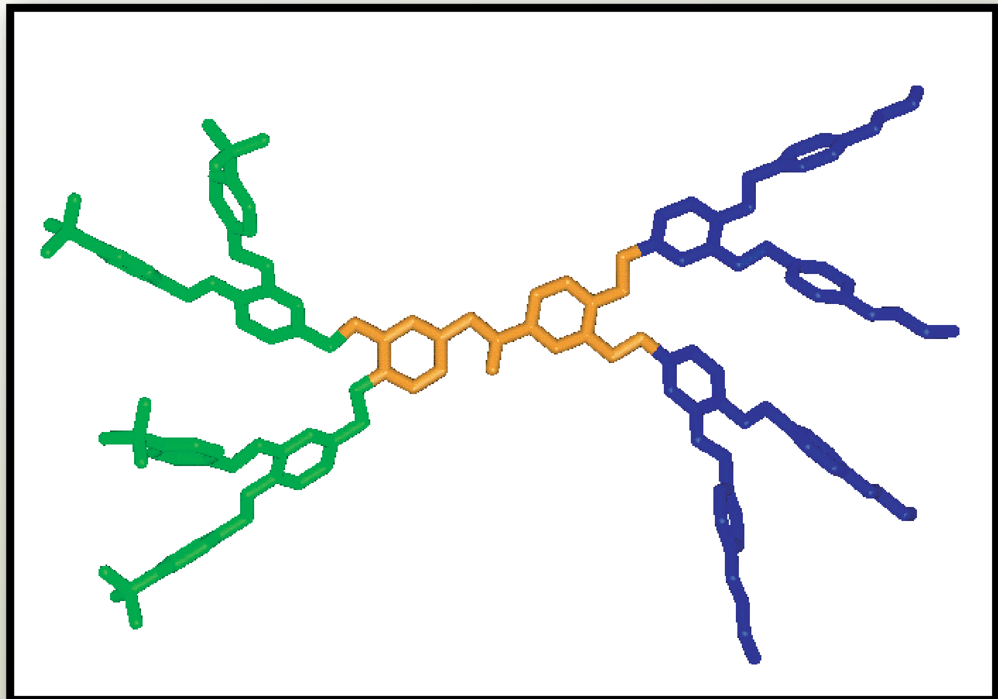
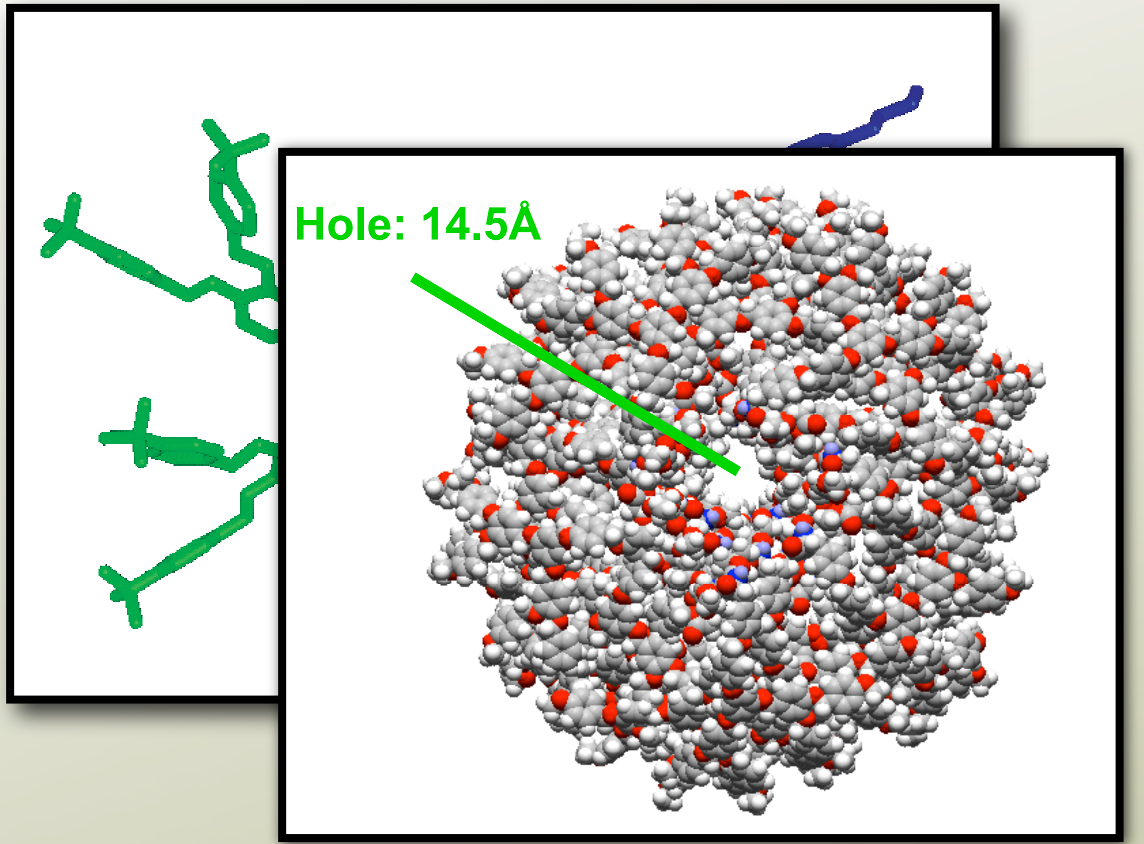
New Materials



Antimicrobials

New Materials



Nanopores and Nanoreactors

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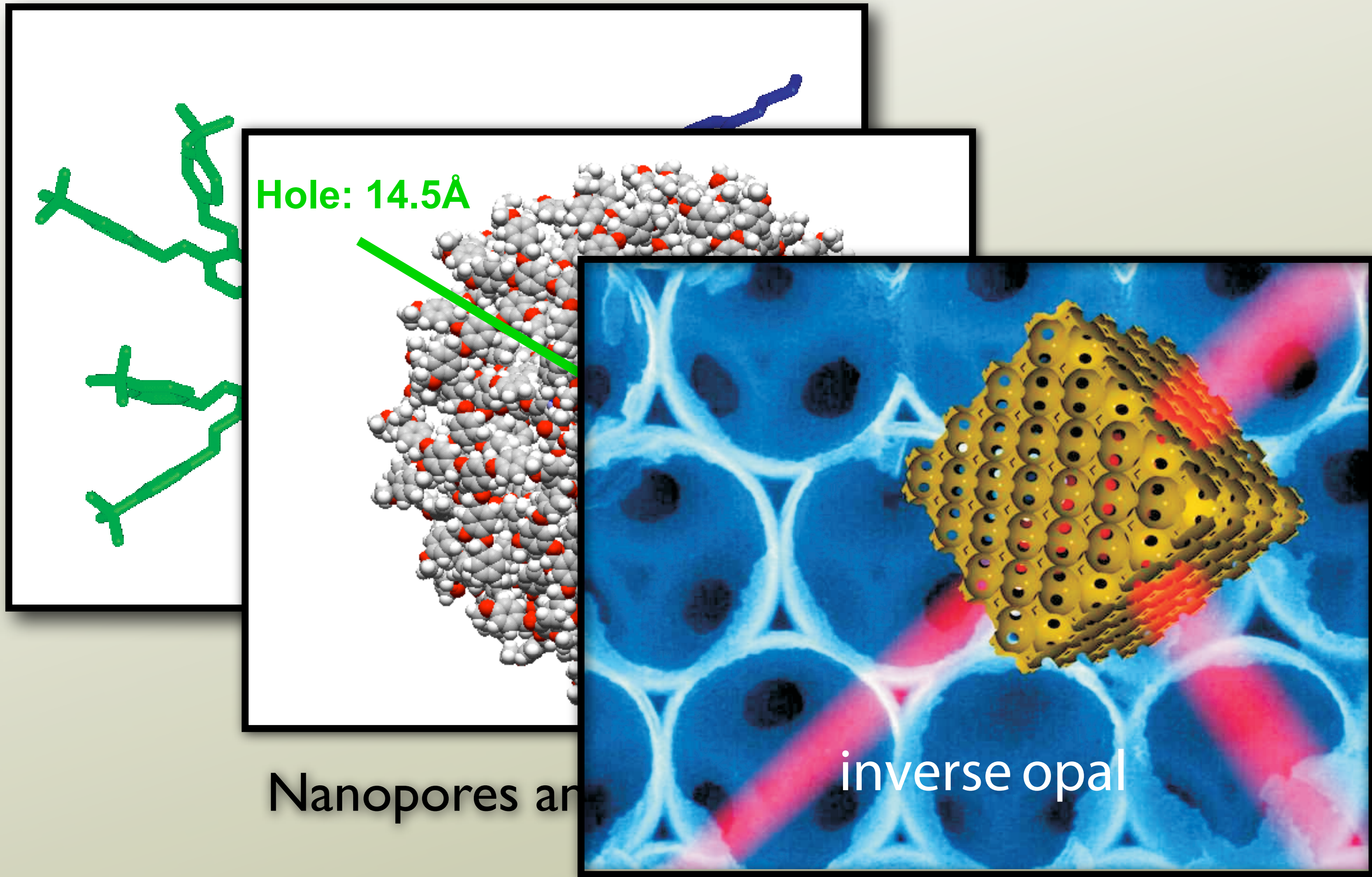
New Materials



Nanopores an

Photonic Band Gaps

Blanco, *et al.*, *Nature* 2000

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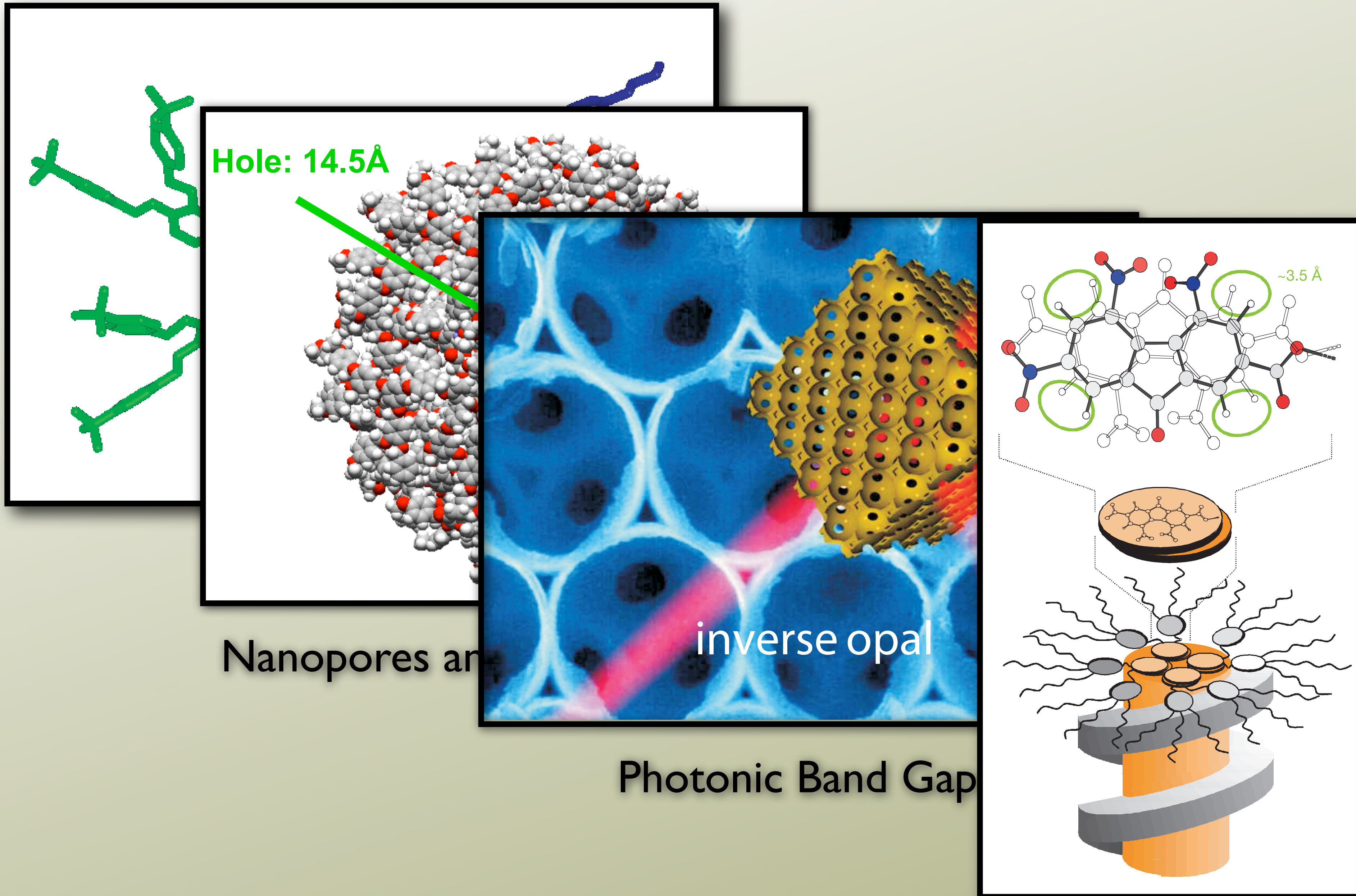
New Materials



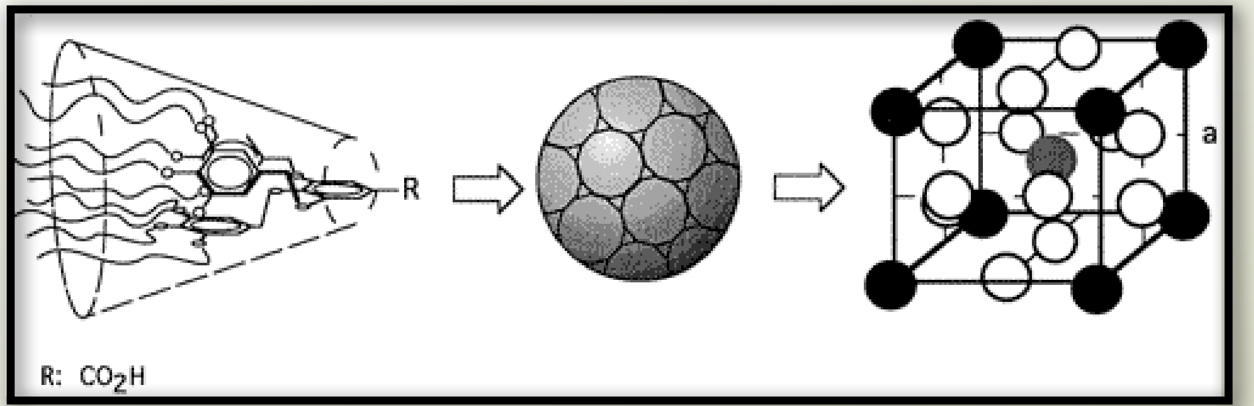
Nanopores an

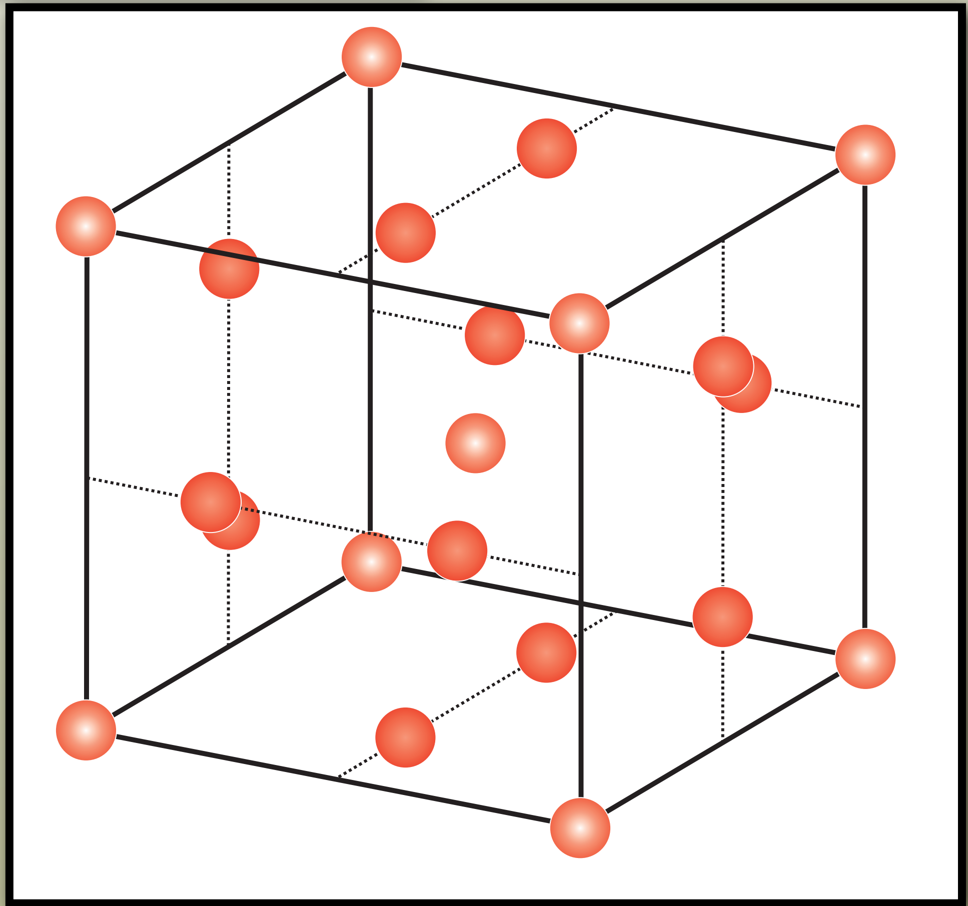
Photonic Band Gap

Percec, *et al.*, *Nature* 2002

Self-Processed Conductors

Self-Assembly of Lattices

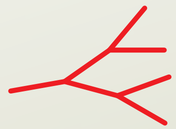




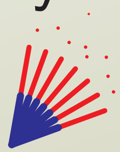
Pm$\bar{3}$n Symmetry
A15 Lattice

Self-Assembly of Macromolecular Assemblies

dendrimers

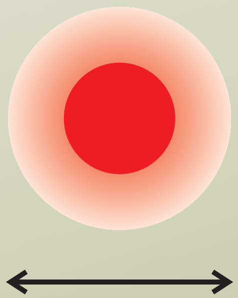


diblock
copolymers



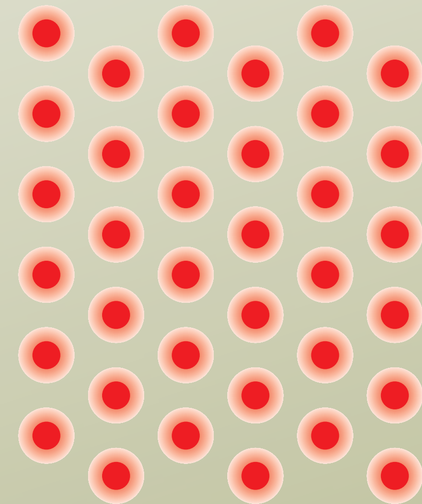
star polymers

micelles:
compact core
+ diffuse corona



a few nm

crystals



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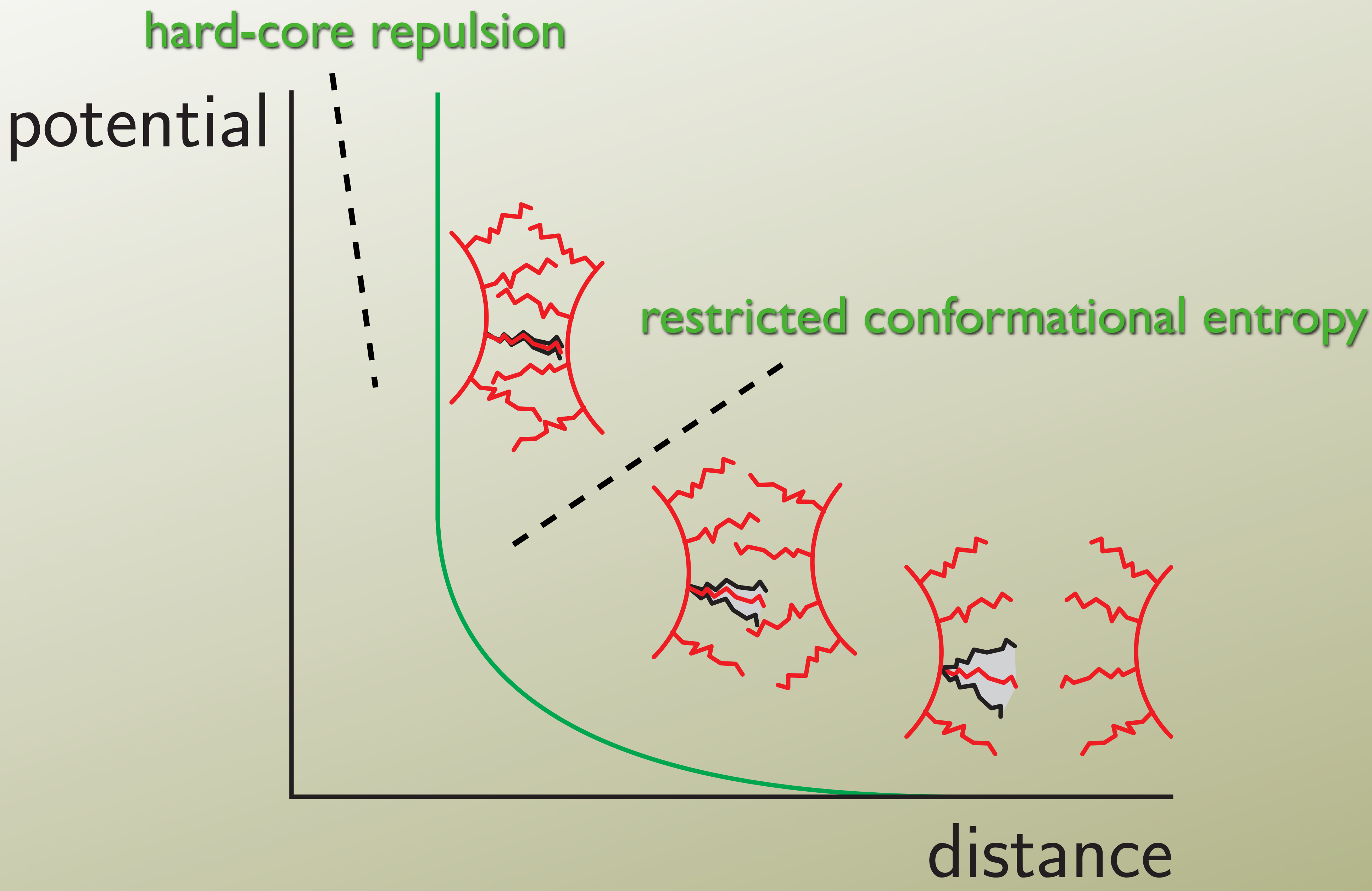
Qualitative Pair Interaction



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Phenomenological Free Energy

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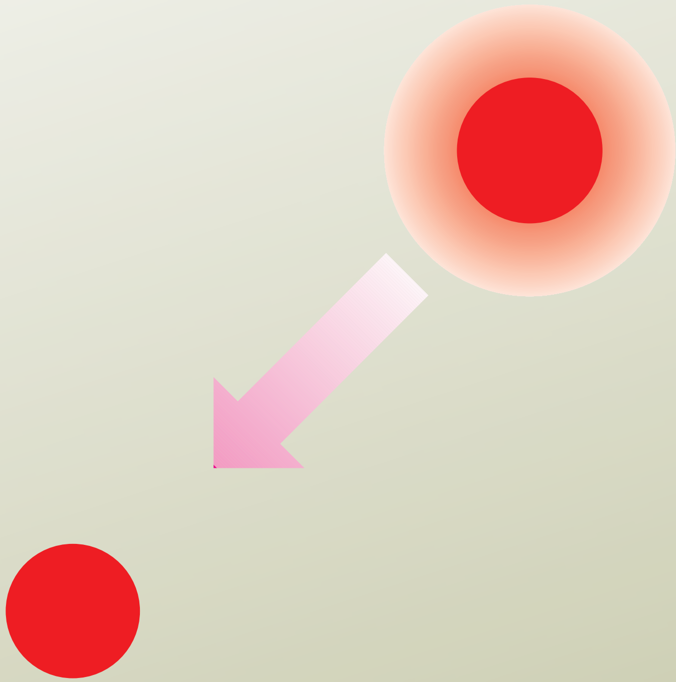
Phenomenological Free Energy



Hard Core

Bulk Free Energy

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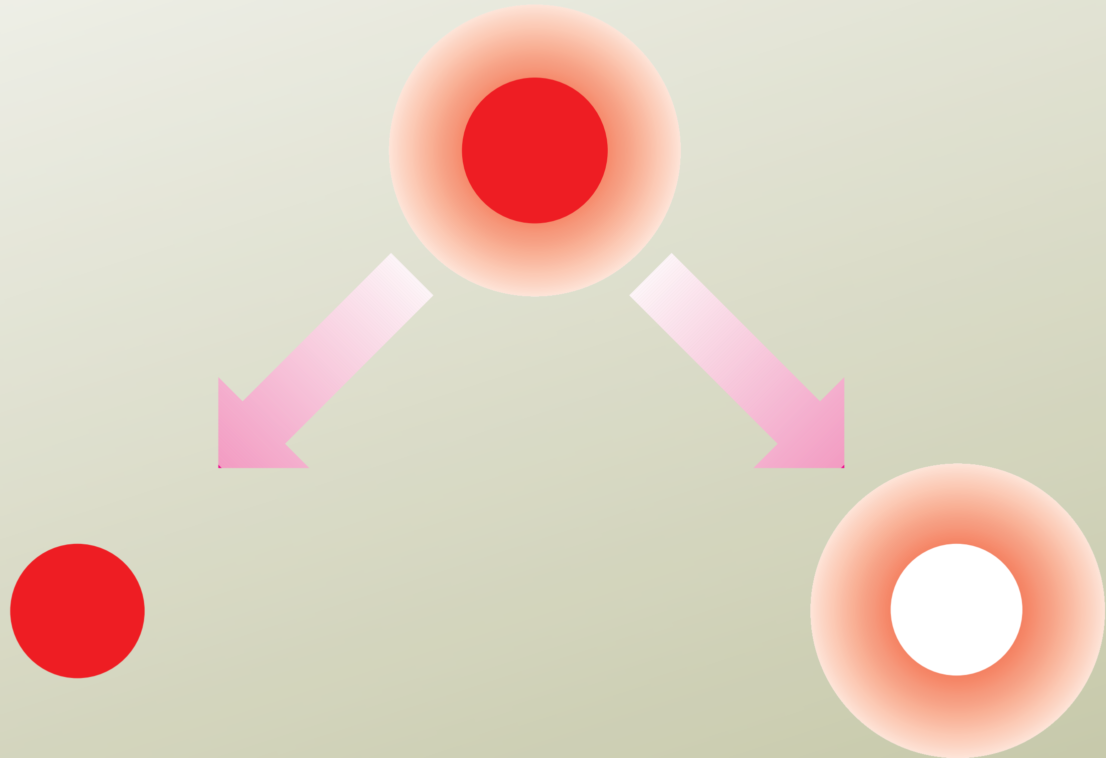
Phenomenological Free Energy

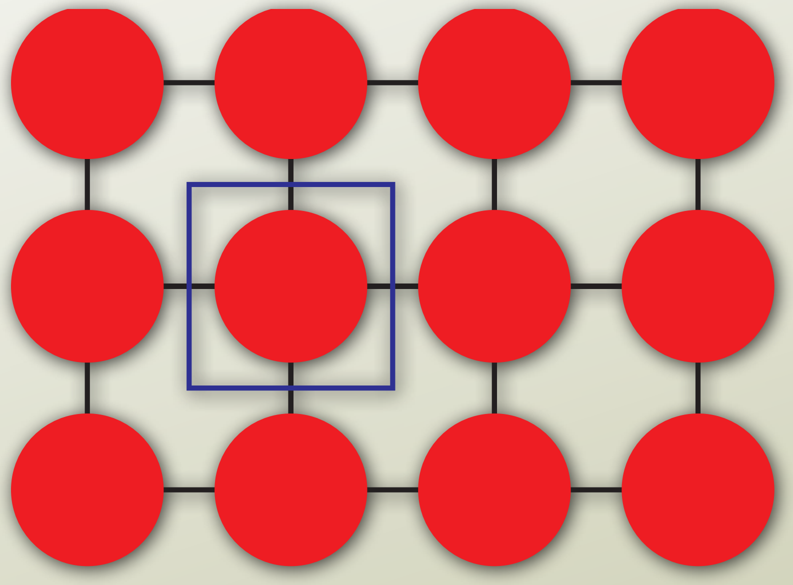


Hard Core
Bulk Free Energy

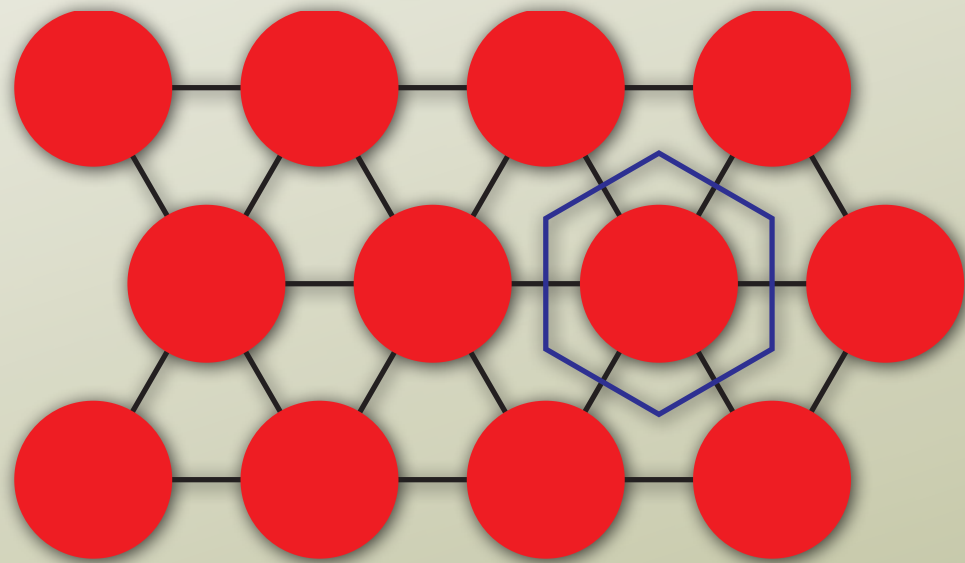
Soft Corona
Interfacial Free Energy

Positional or Bulk Entropy

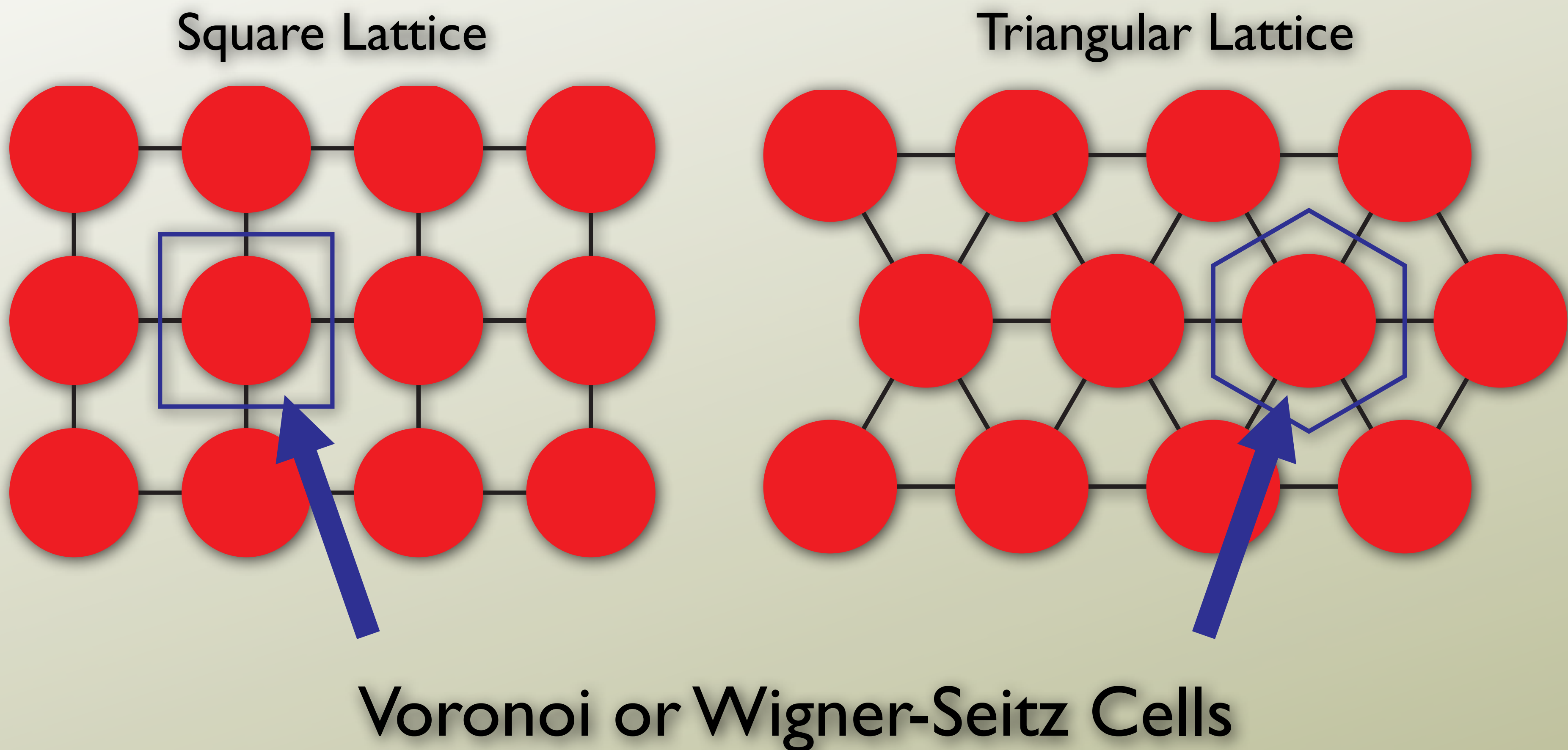
Square Lattice



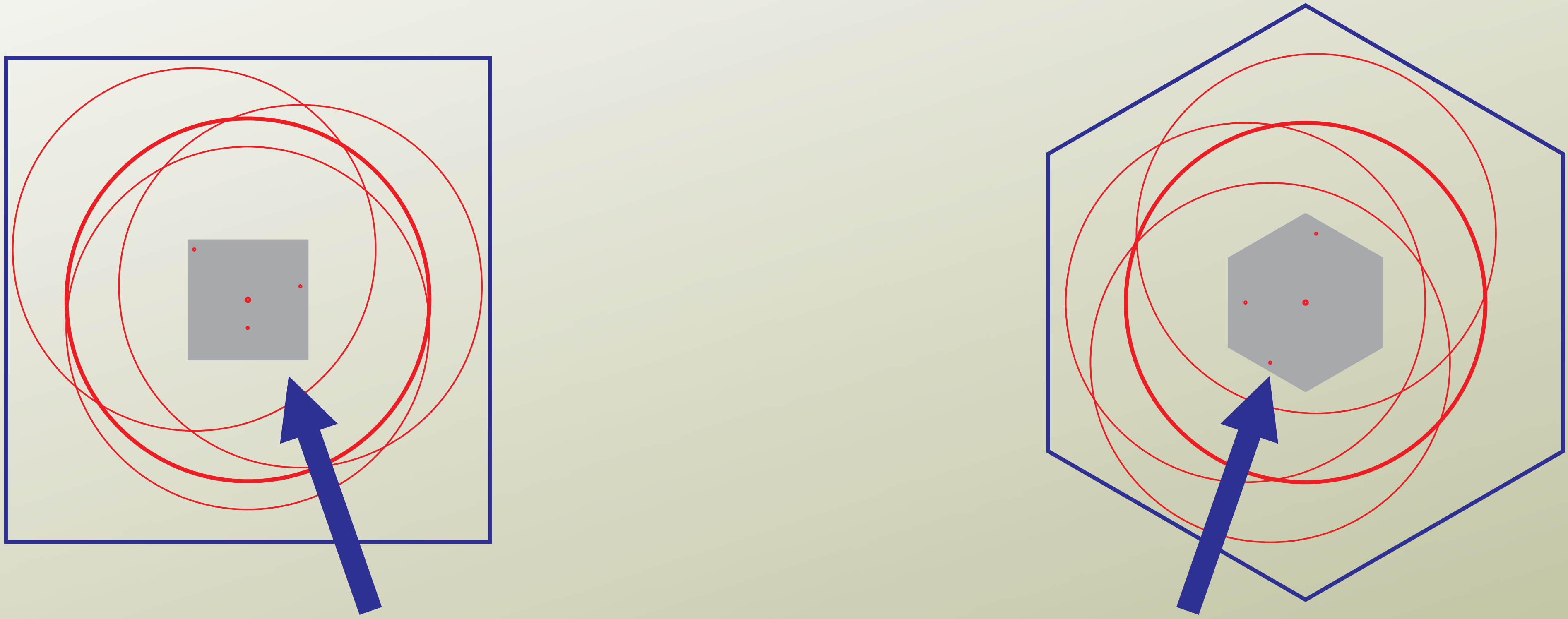
Triangular Lattice



Positional or Bulk Entropy

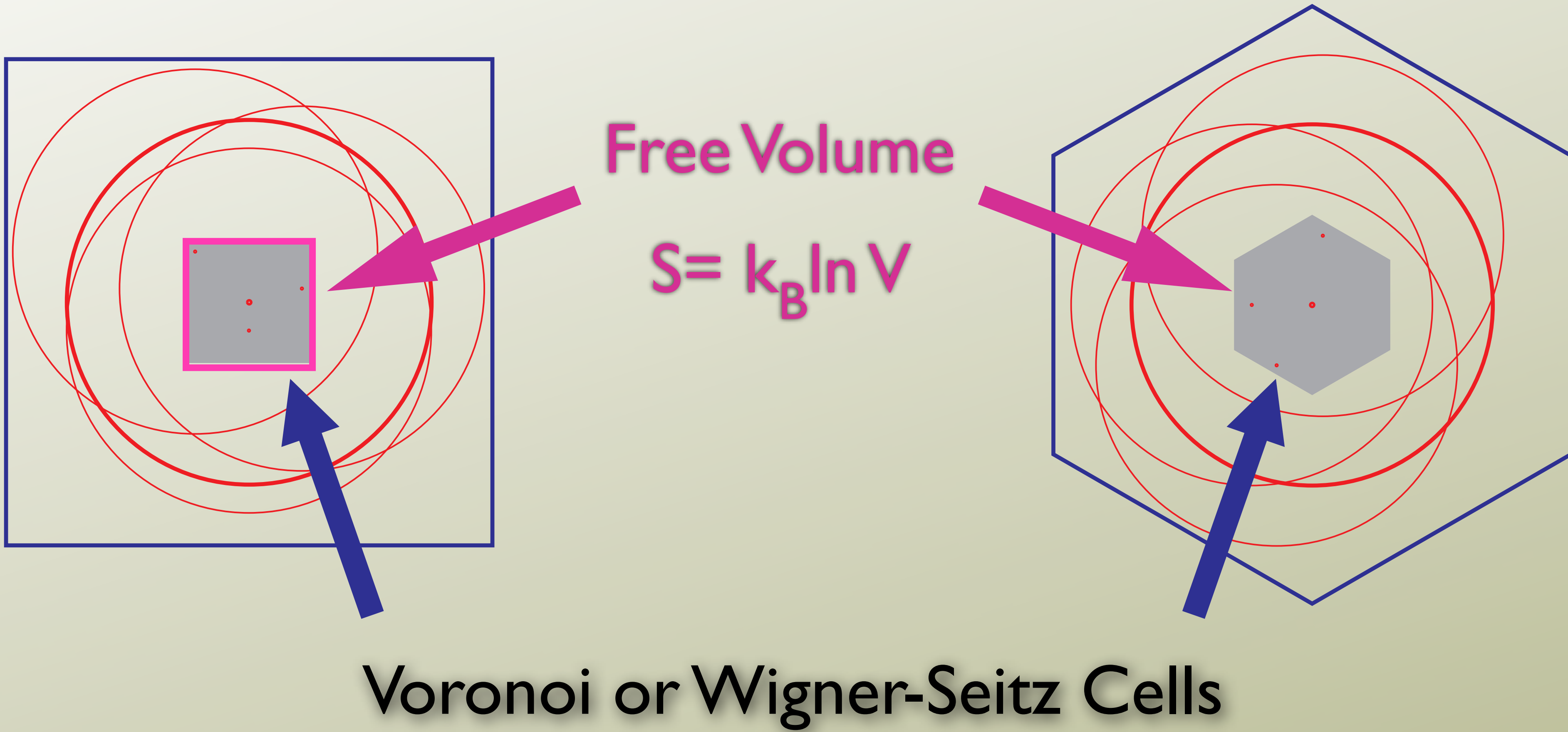


Positional or Bulk Entropy

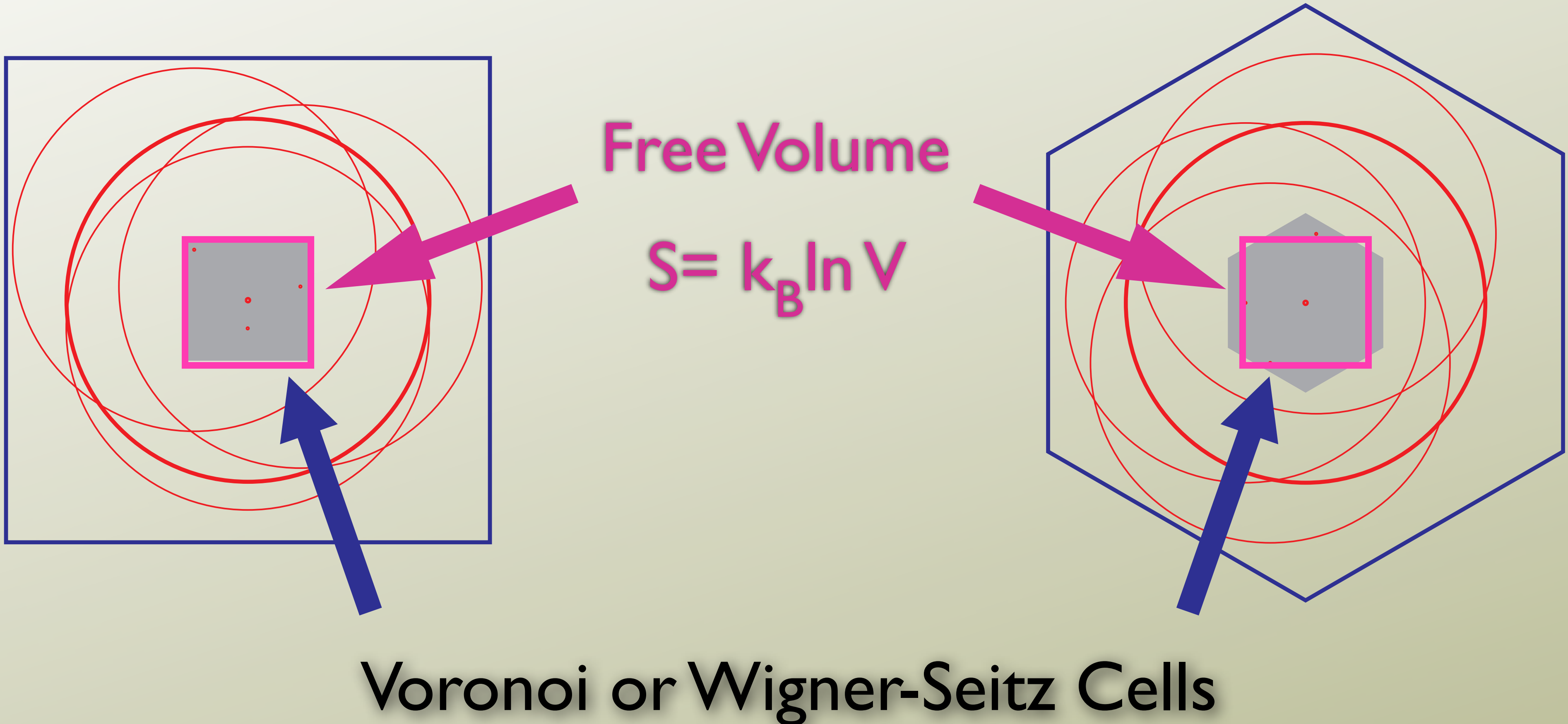


Voronoi or Wigner-Seitz Cells

Positional or Bulk Entropy



Positional or Bulk Entropy



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Johannes Kepler (1571-1630)

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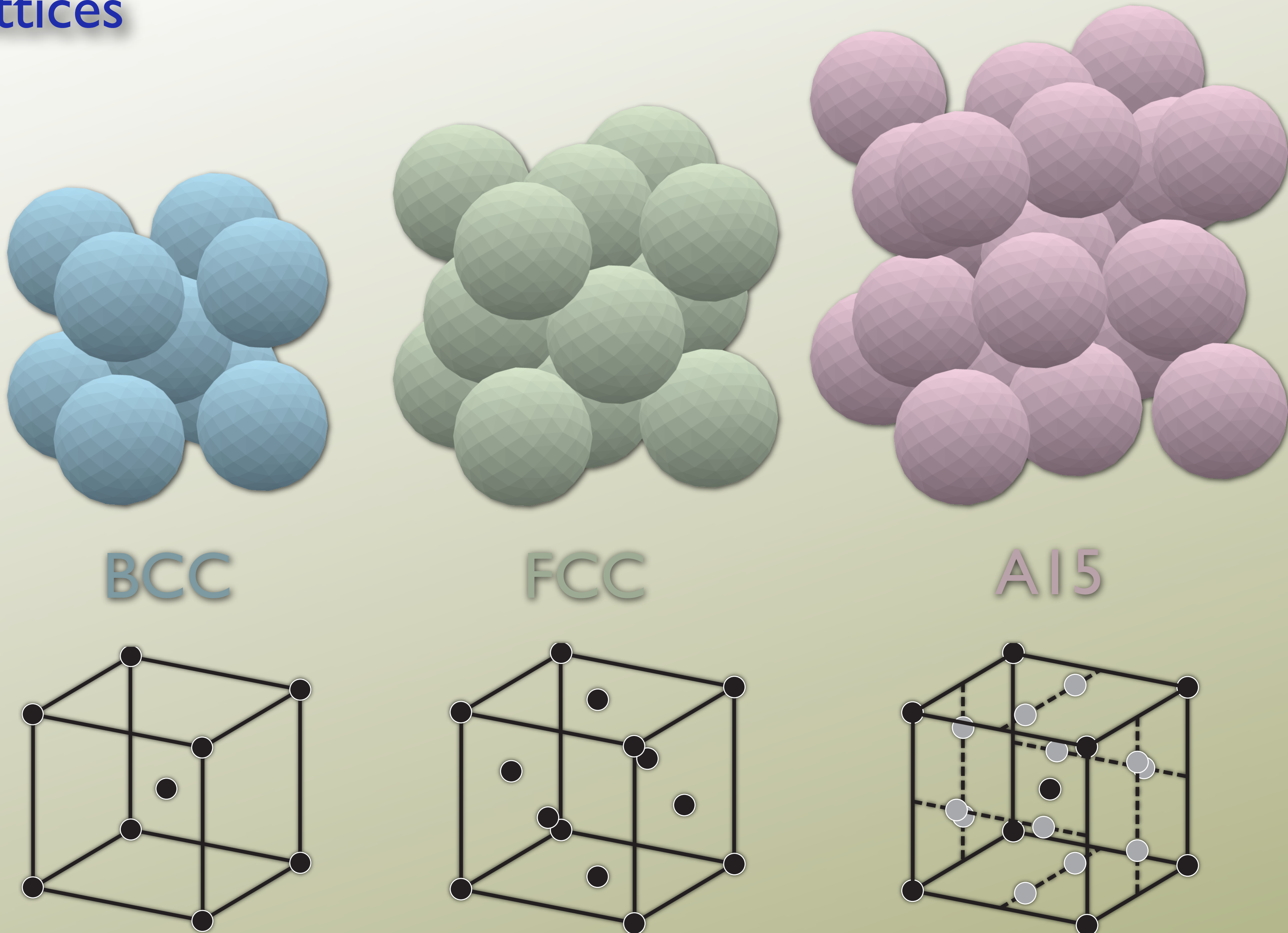
Lattices



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Cube Packing

Zentsuji, Japan

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Error Correcting Codes

Bit
Bip
Bap
Bab
Bob
Bog
Dog
Dig

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Error Correcting Codes

Bit	Bit
Bip	
Bap	Bap
Bab	
Bob	Bob
Bog	
Dog	Dog
Dig	

Detect Errors!

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Error Correcting Codes

Bit	Bit	Bit
Bip		
Bap	Bap	
Bab		Bab
Bob	Bob	
Bog		
Dog	Dog	Dog
Dig		
	Detect Errors!	Correct Errors!

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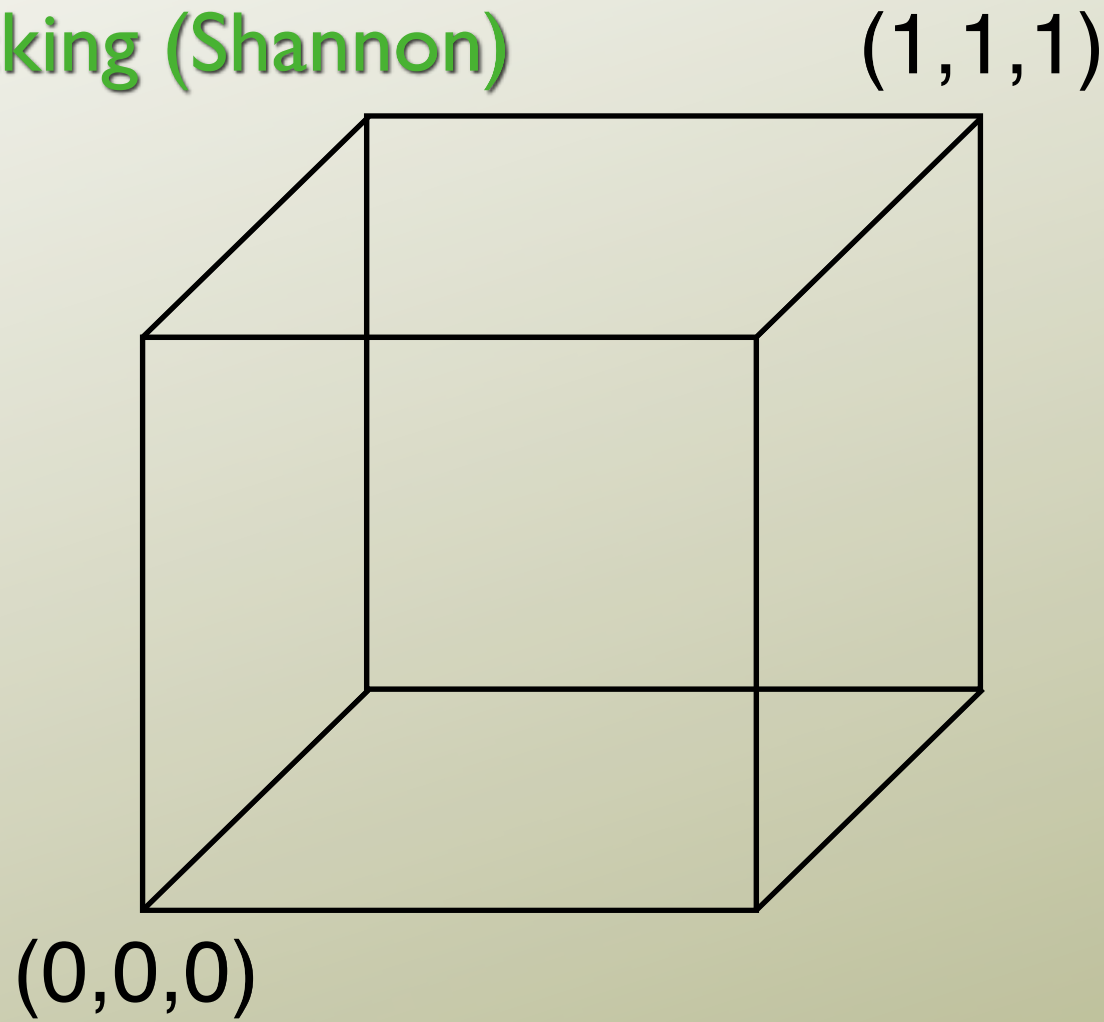
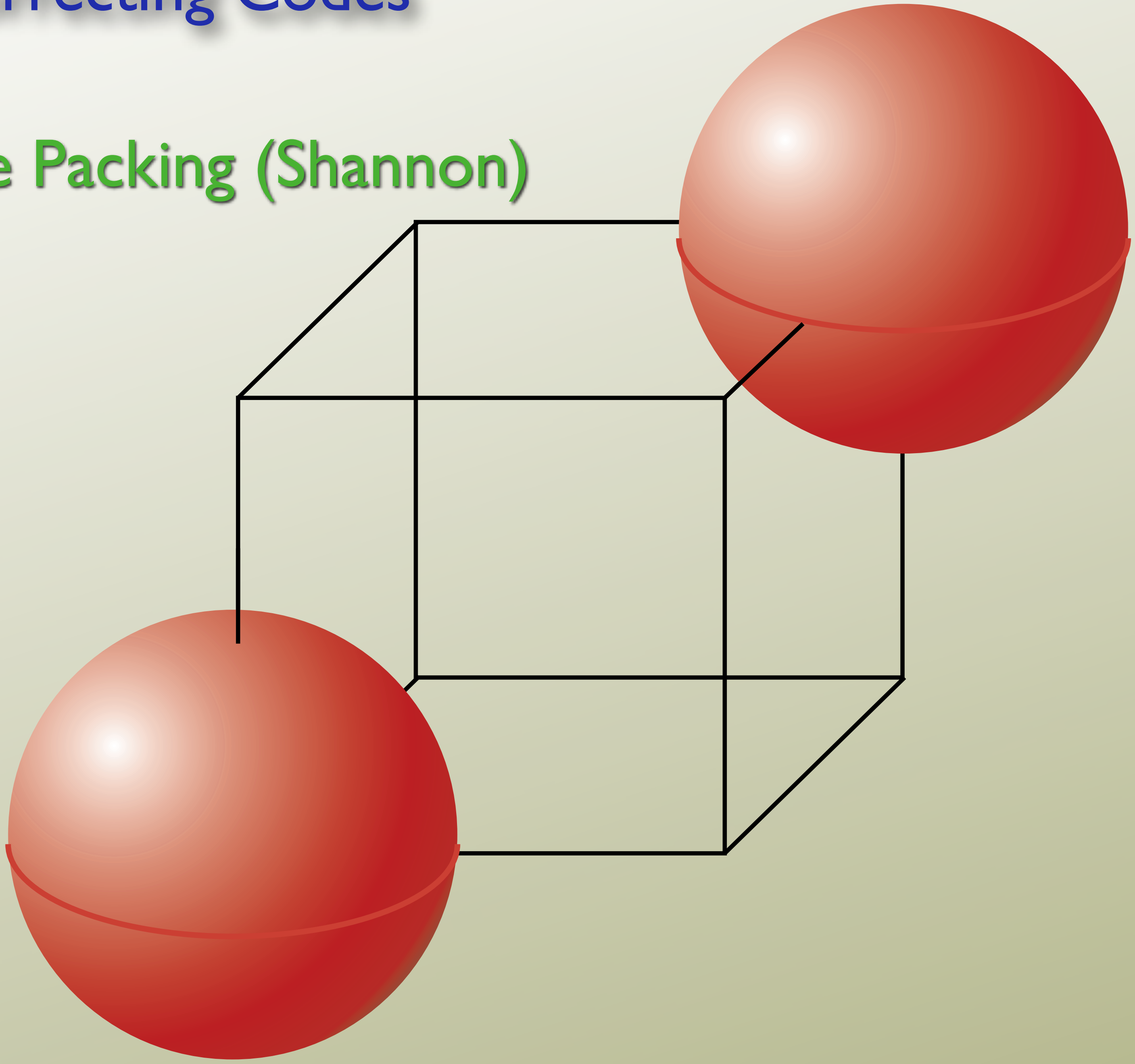
Error Correcting Codes

Sphere Packing (Shannon)



Error Correcting Codes

Sphere Packing (Shannon)



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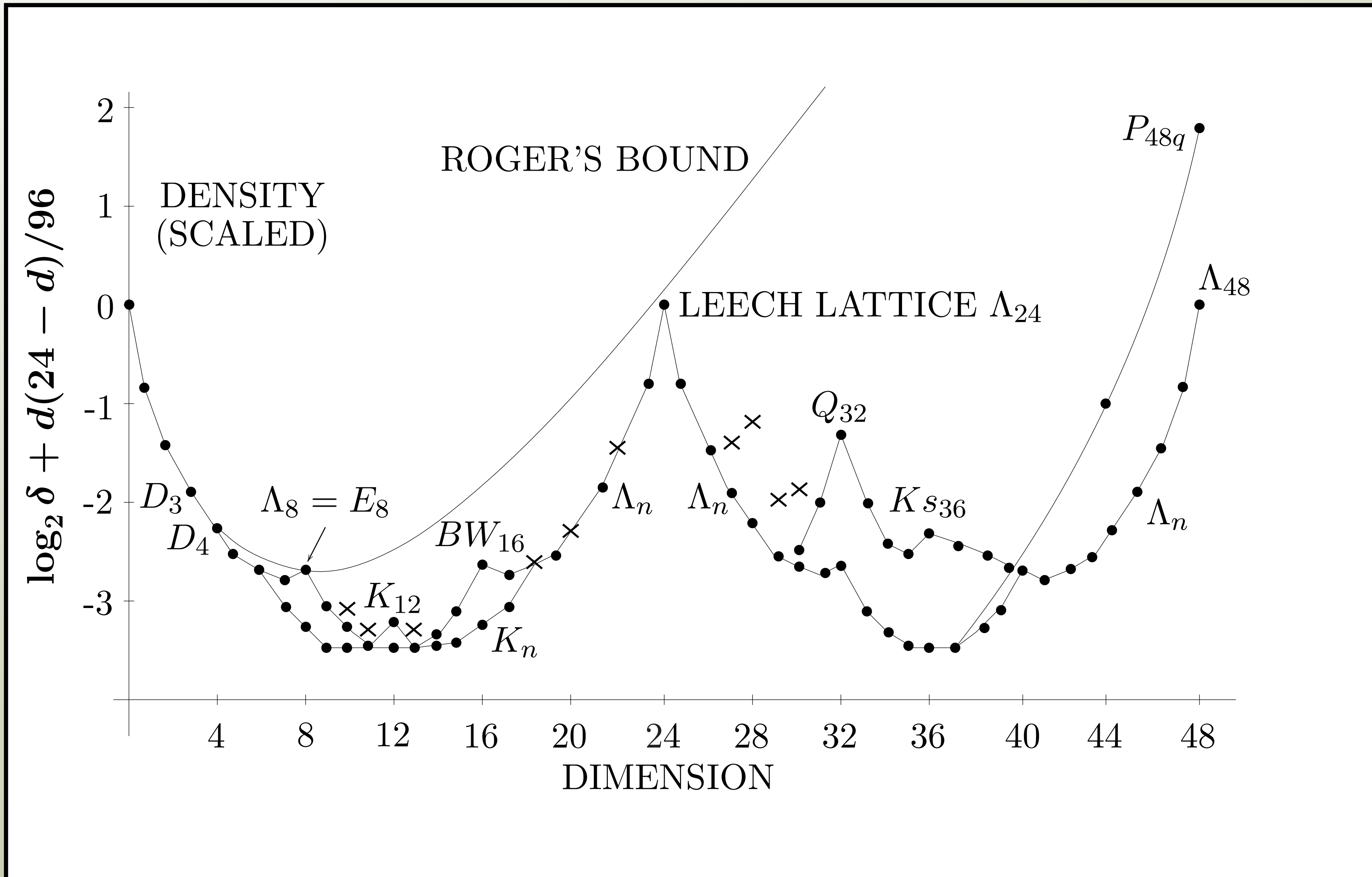
Packing Density Depends on Dimension!



Sloane, *Documenta Mathematika*, Vol. III (1998) 387

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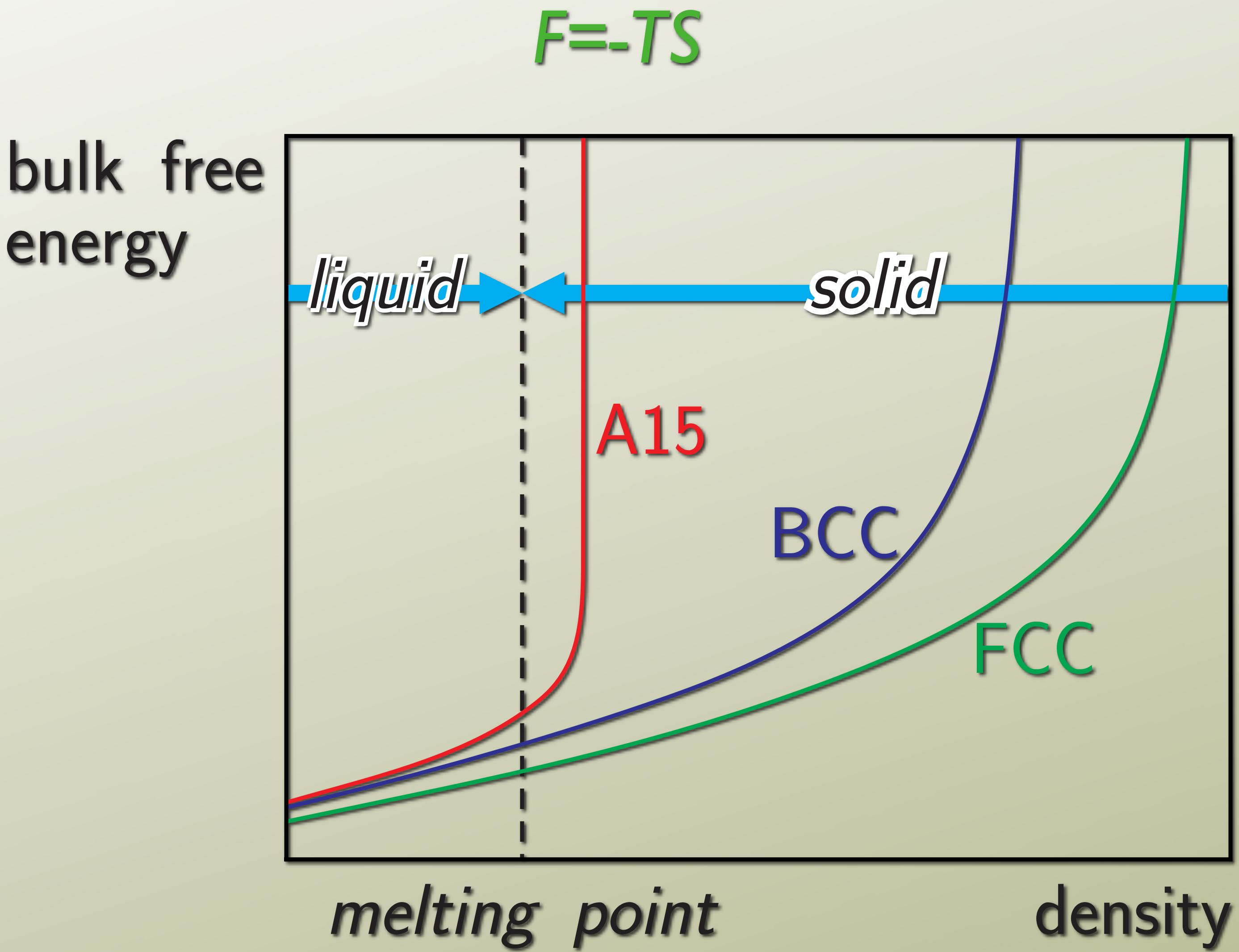
Bulk Free Energy



- *FCC has more entropy than HCP*
- *Global, not local*

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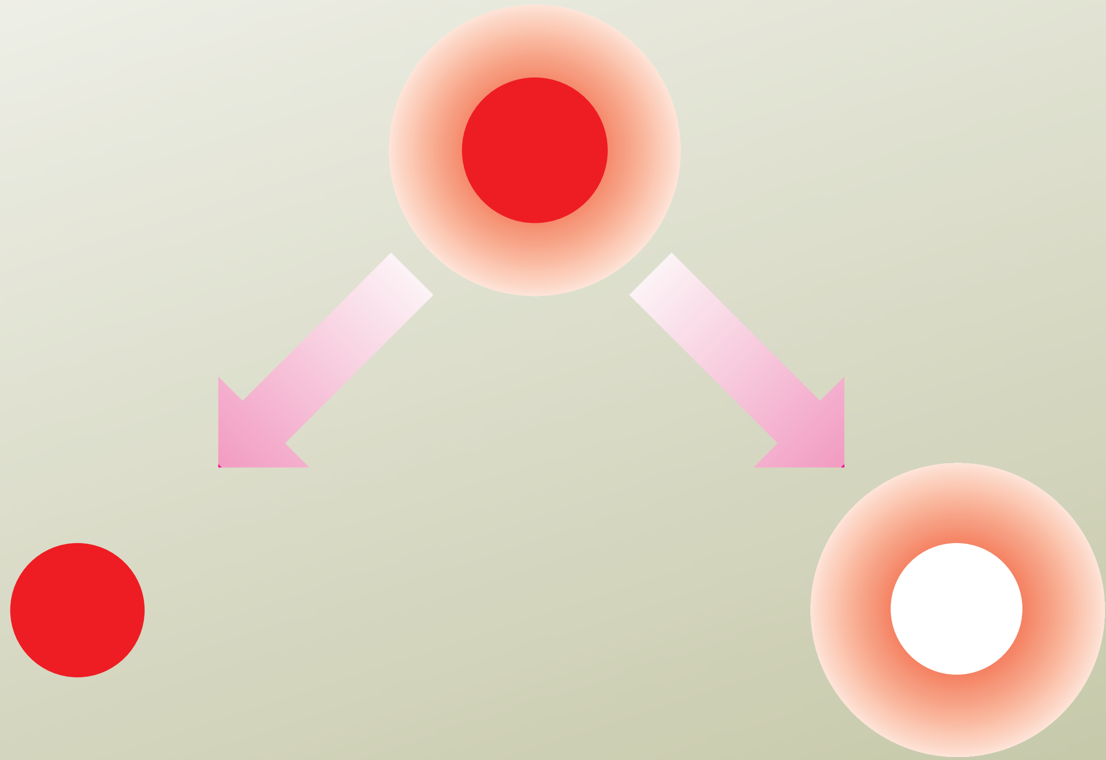
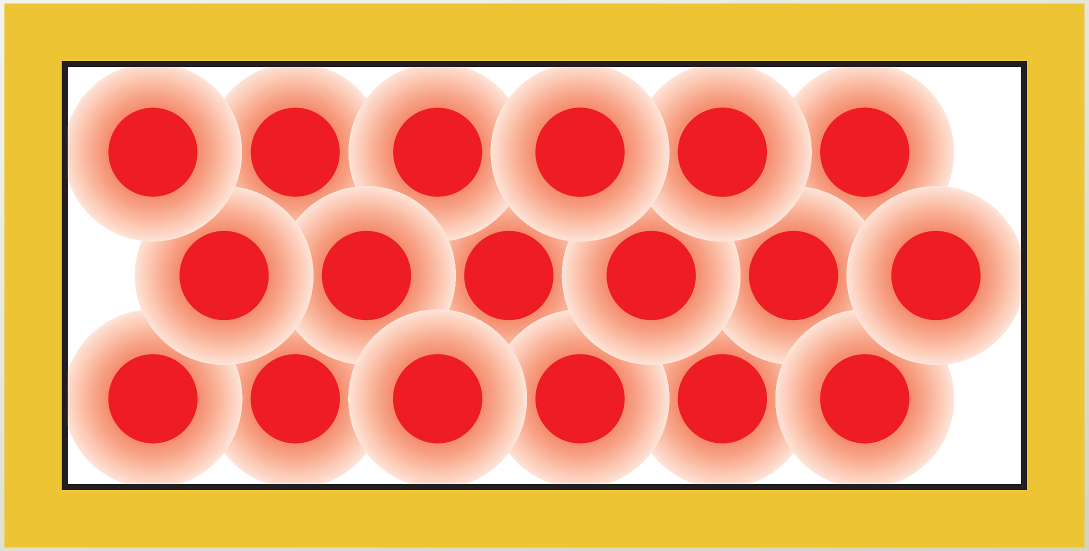
Phenomenological Free Energy



Hard Core
Bulk Free Energy

Soft Corona
Interfacial Free Energy

Minimizing the Perimeter



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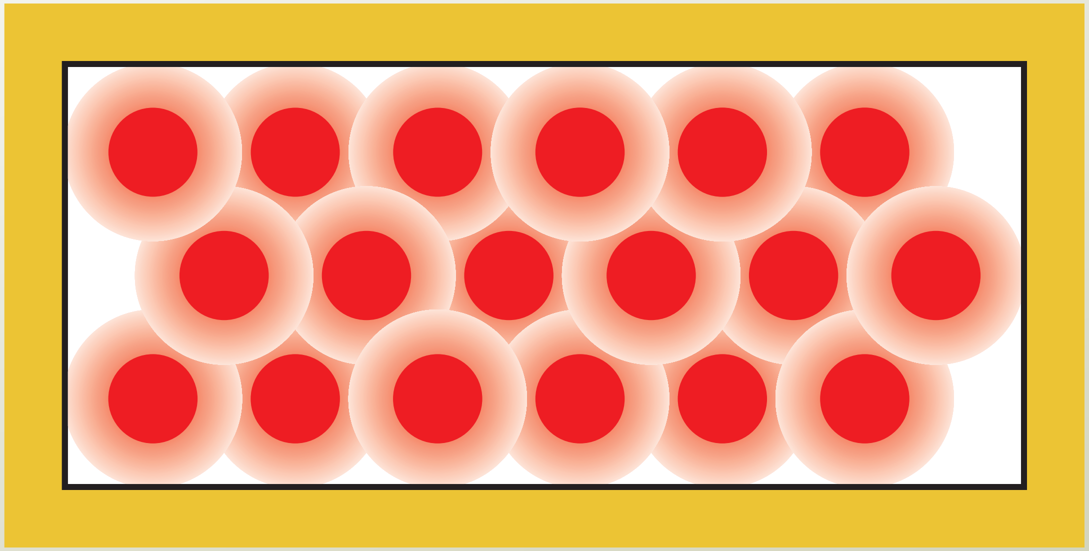
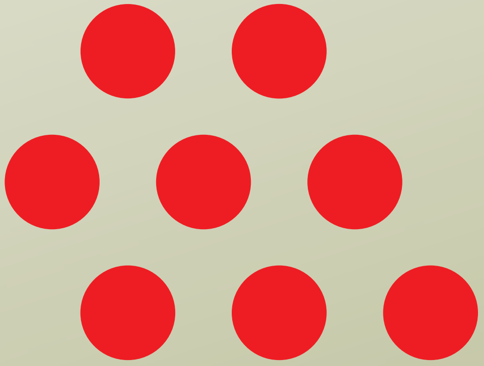
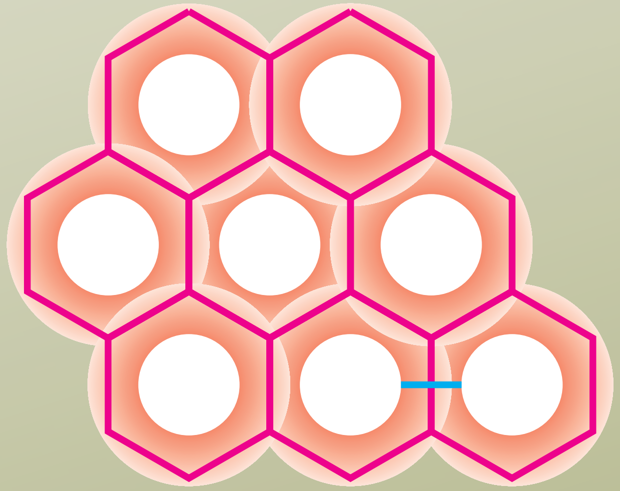
Minimizing the Perimeter

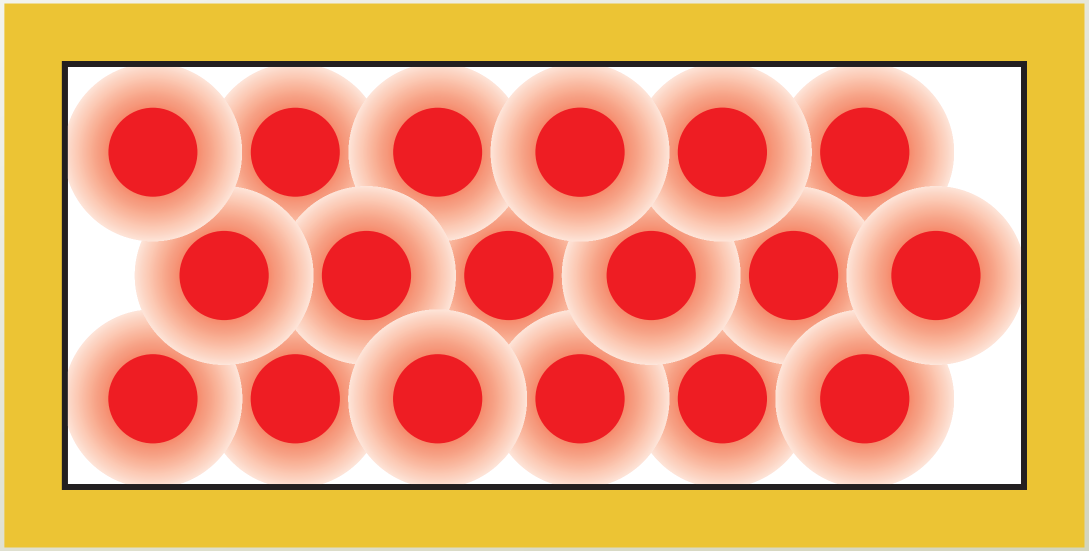


Area = hard cores + matrix of coronas

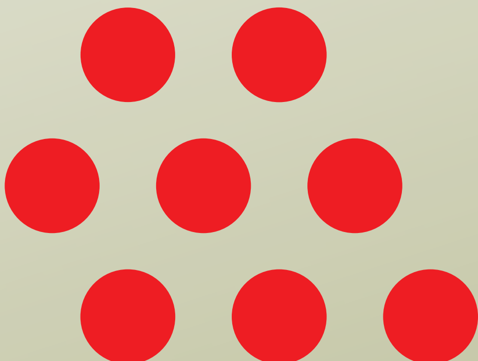


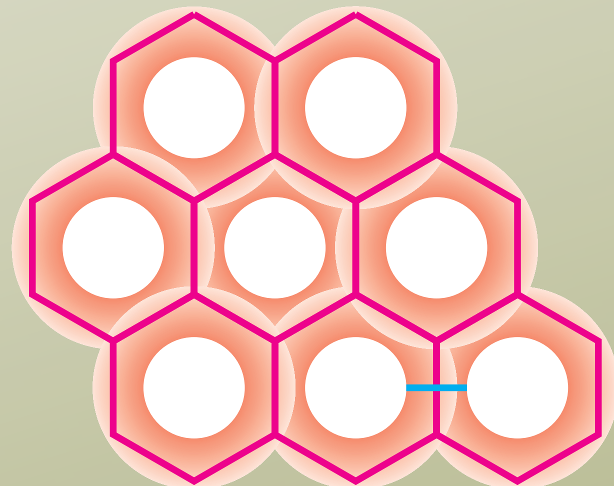


Minimizing the Perimeter



Area = hard cores + matrix of coronas





Area= perimeter x thickness

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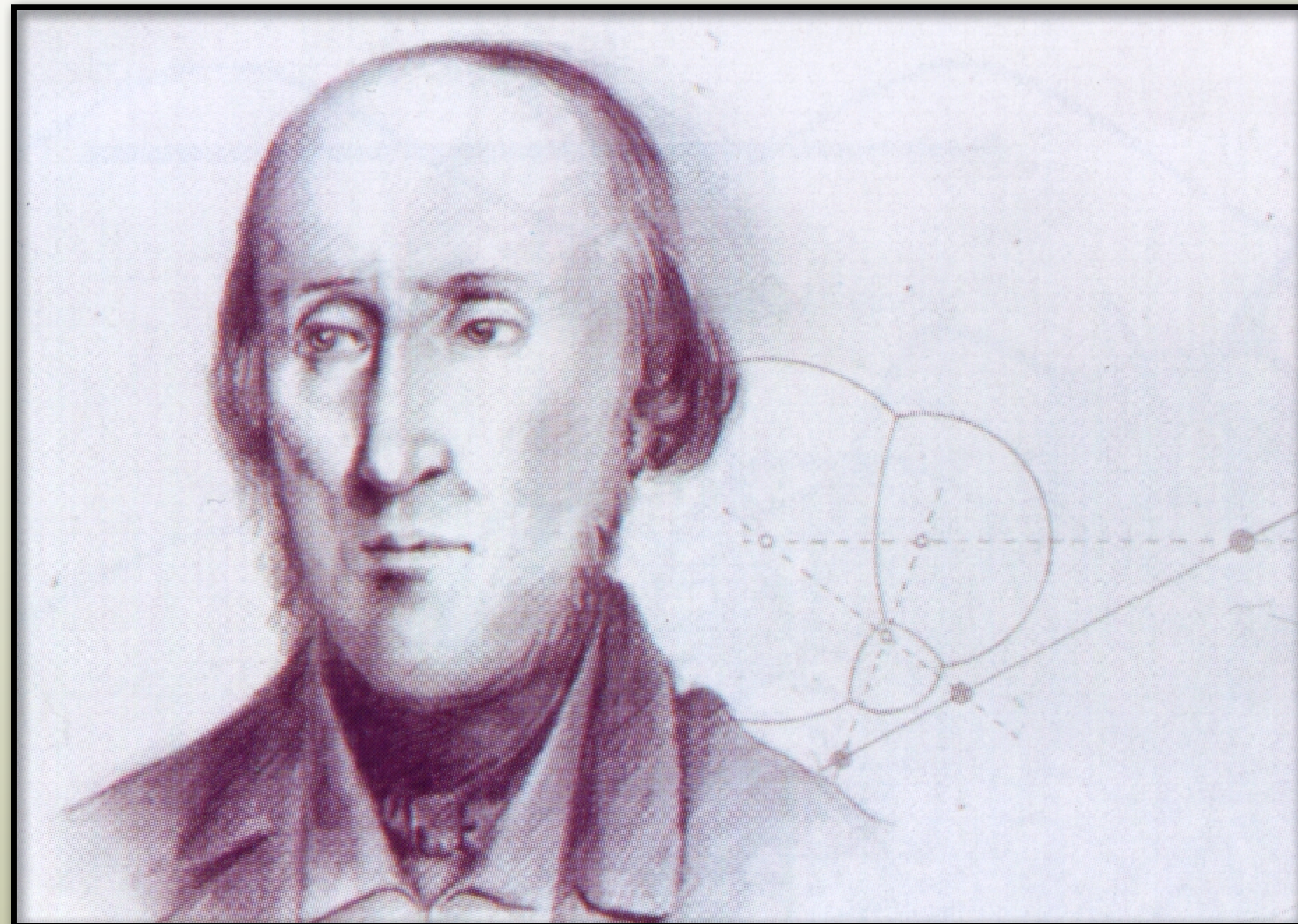

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Joseph Antoine Ferdinand Plateau (1801-1883)

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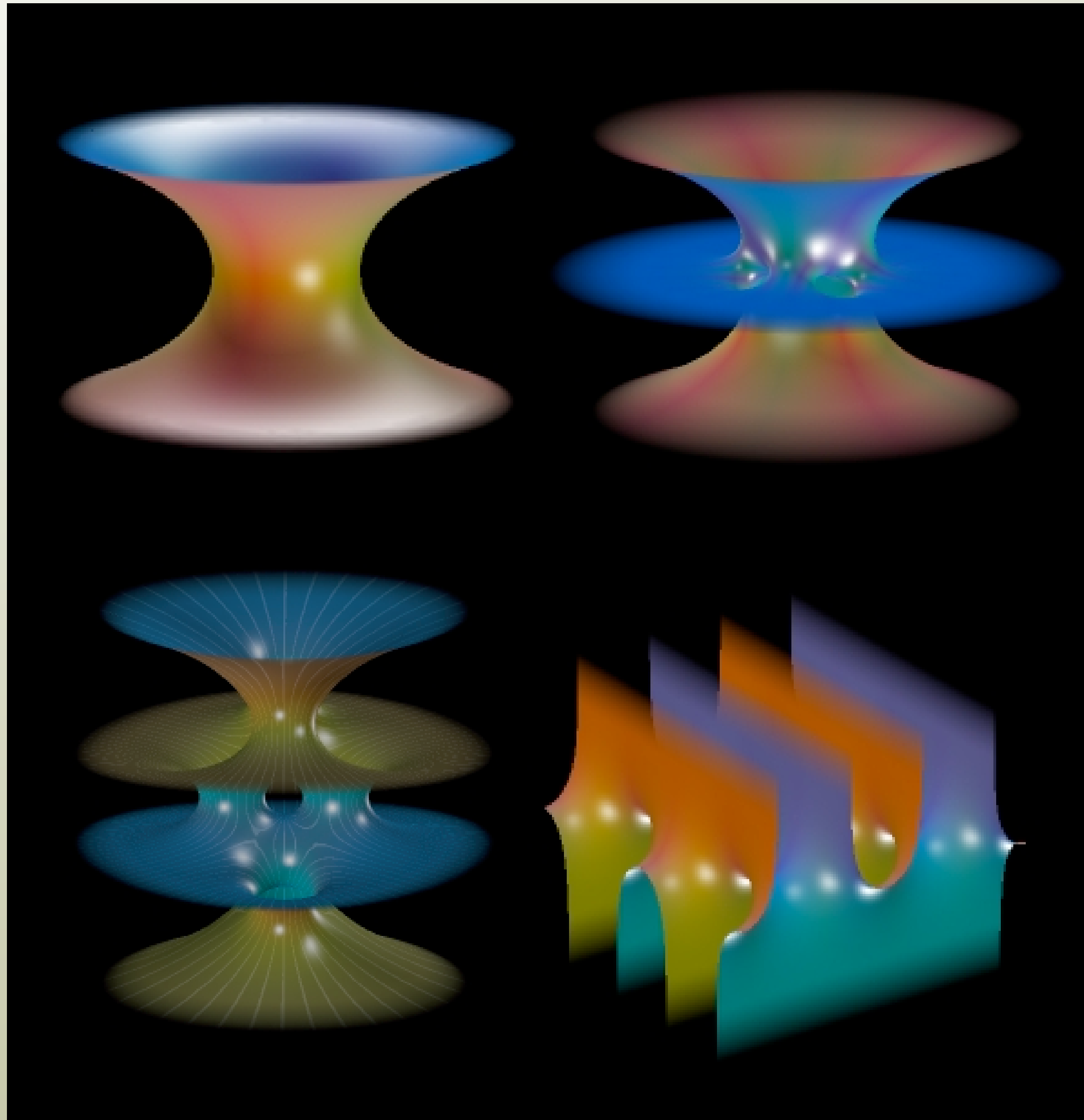
Minimal Surfaces

Catenoid



Costa-
Hoffman-
Meeks

Four-End
Handled

Scherk's
First
Surface

Graphics from MSRI - http://www.msri.org/publications/sgp/

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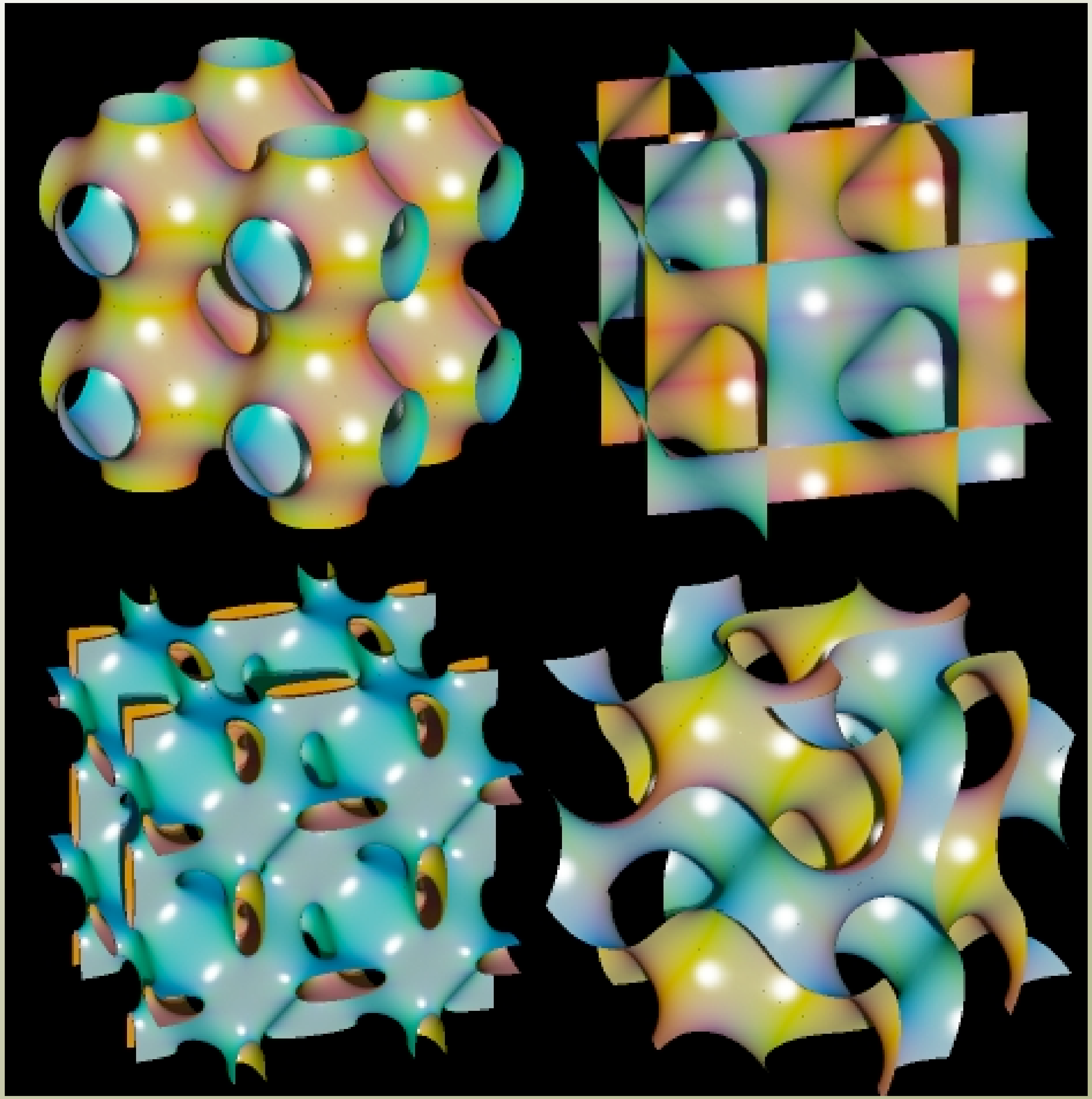
Minimal Surfaces

Schwartz P

Diamond



Neovius

Gyroid

Graphics from MSRI - http://www.msri.org/publications/sgp/

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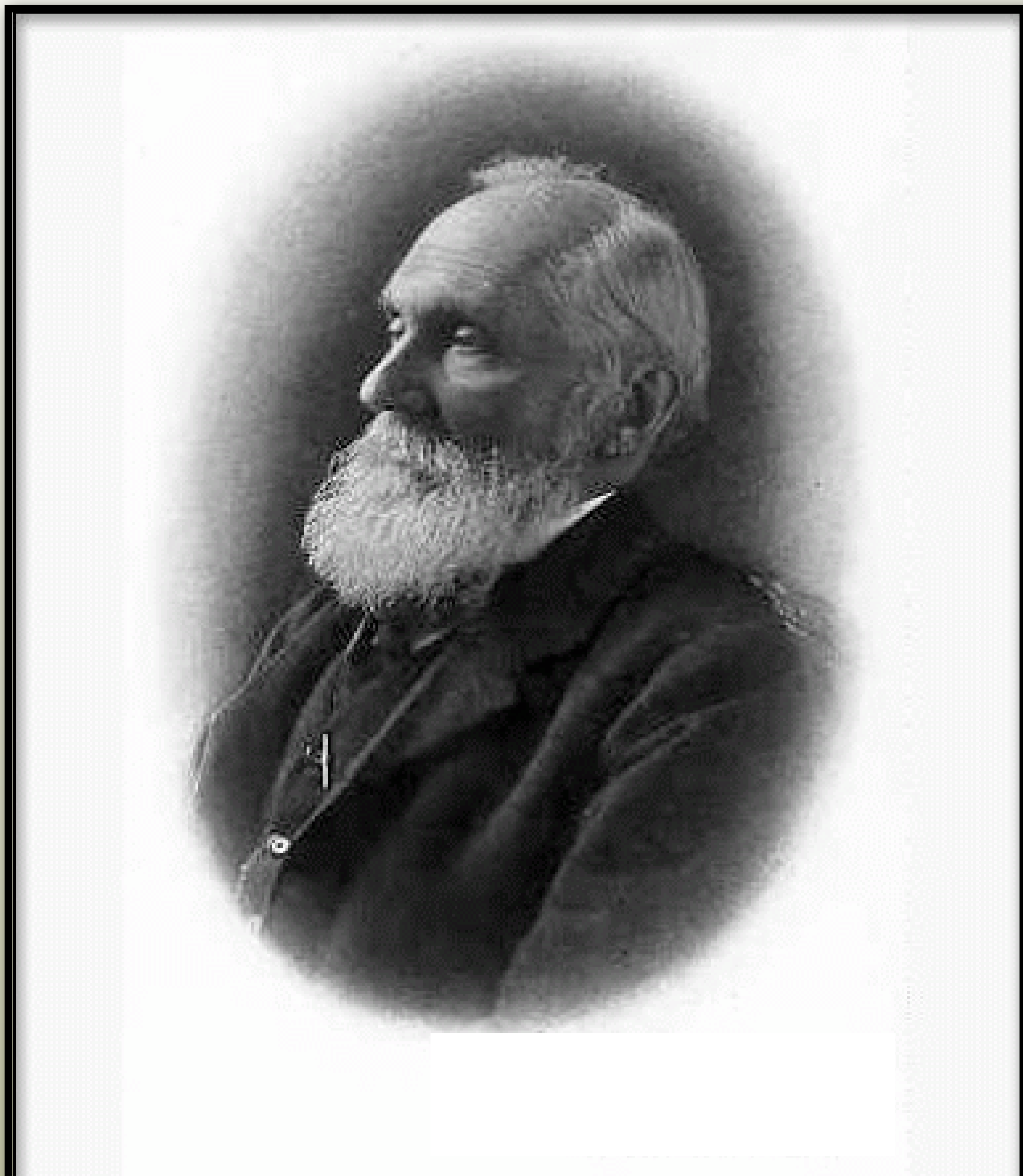
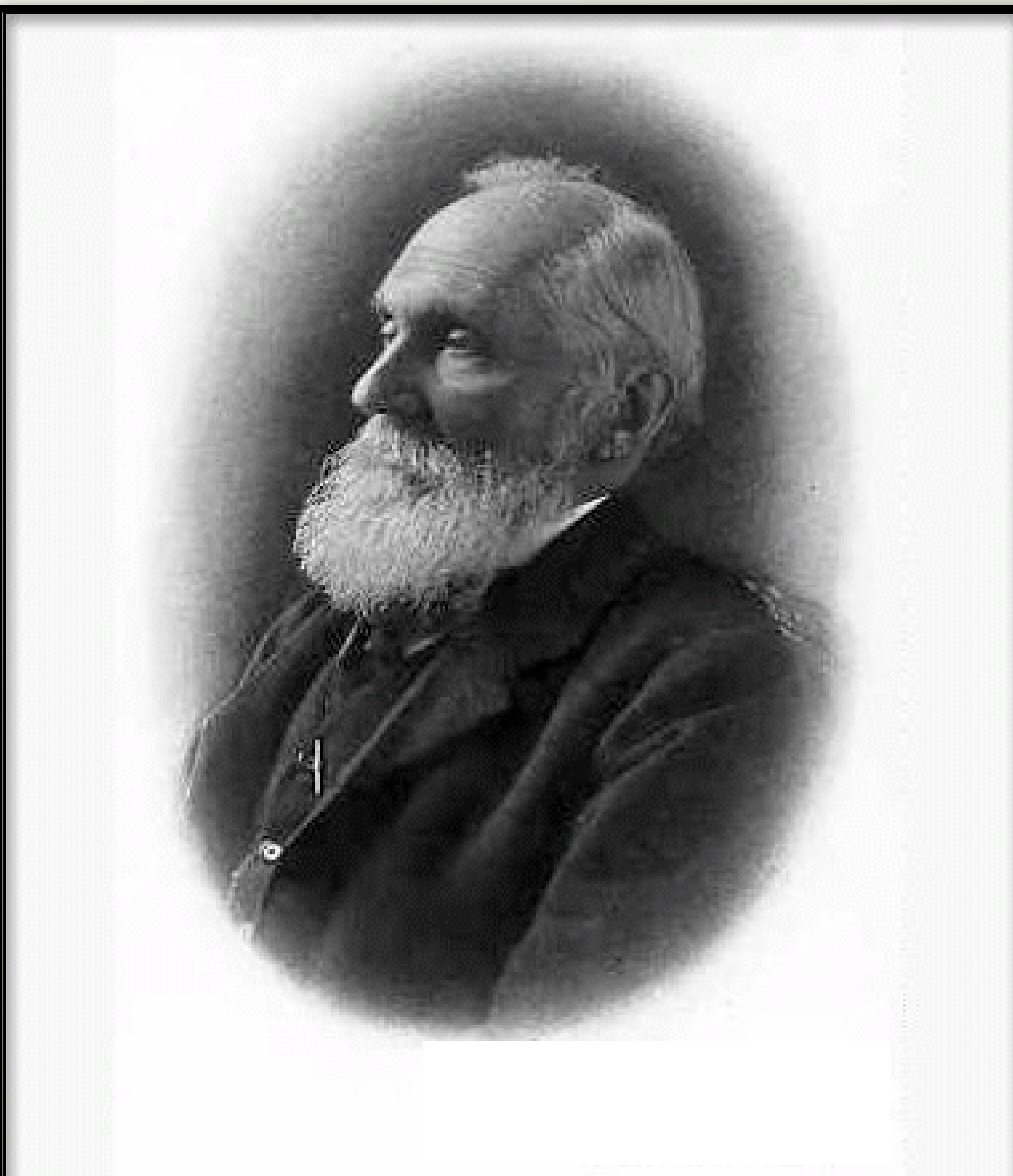


William Thomson Lord Kelvin (1824-1907)



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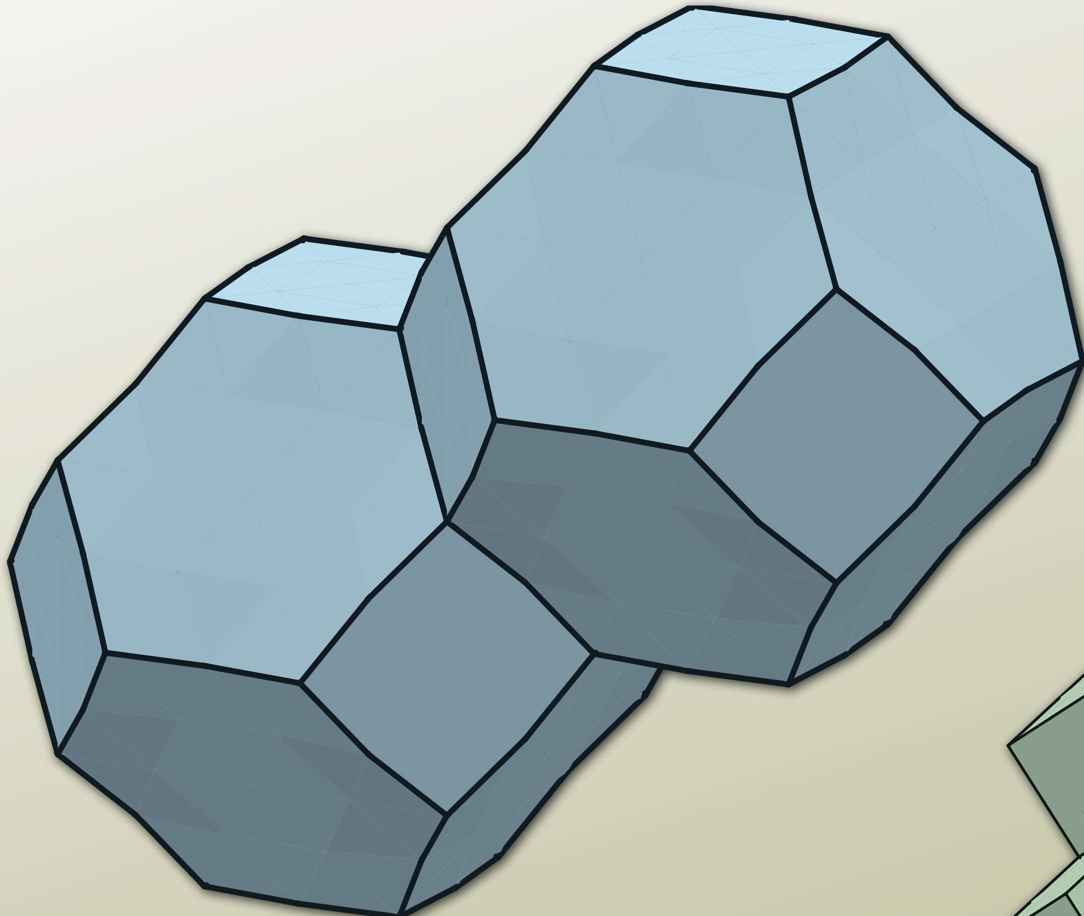
Kelvin's Problem

What regular partition of space into cells of equal volume has minimal surface area?

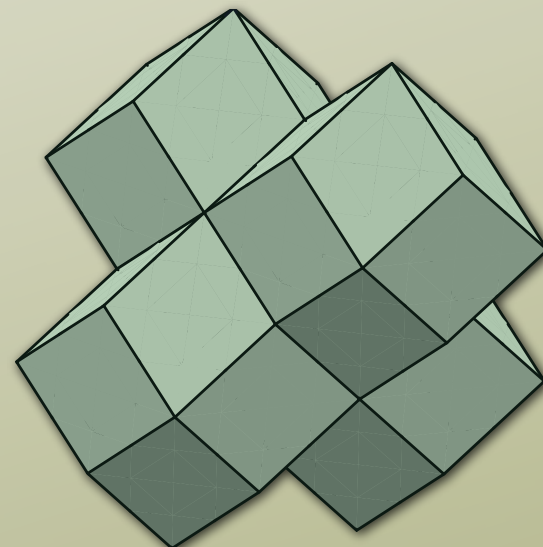
1943: Hexagon best polygon
1999: Honeycomb best (Hales)

Kelvin's Conjecture (1887)



BCC

Orthic Tetrakaidecahedra
or *decatetrahedra*



FCC

Rhombic Dodecahedra

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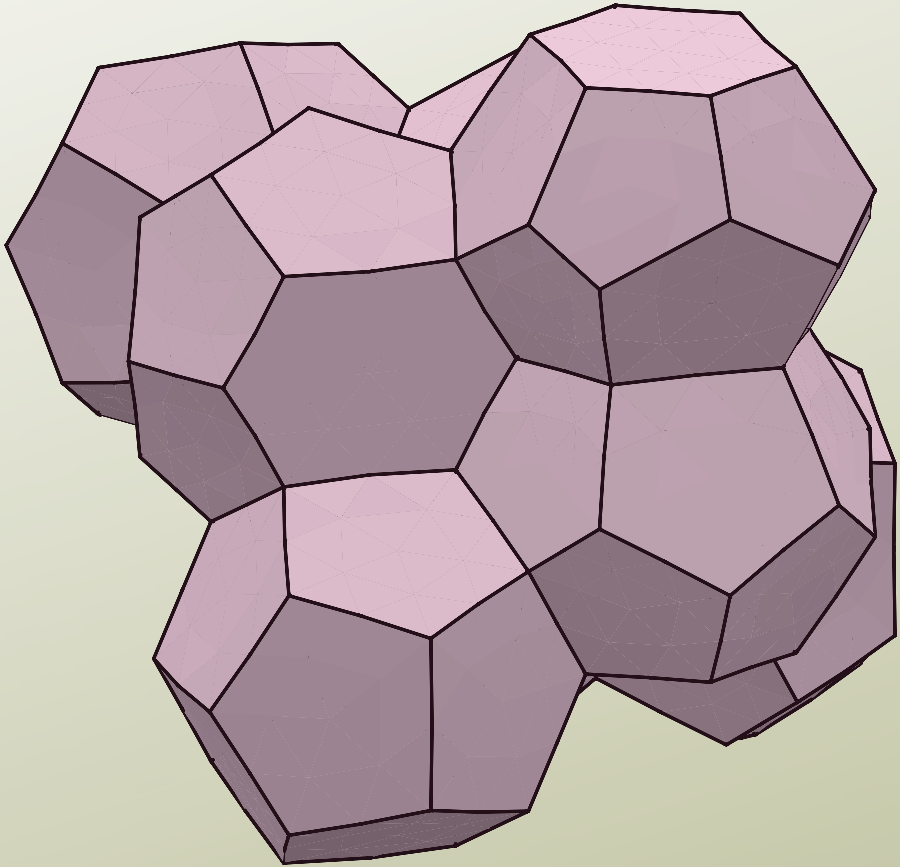
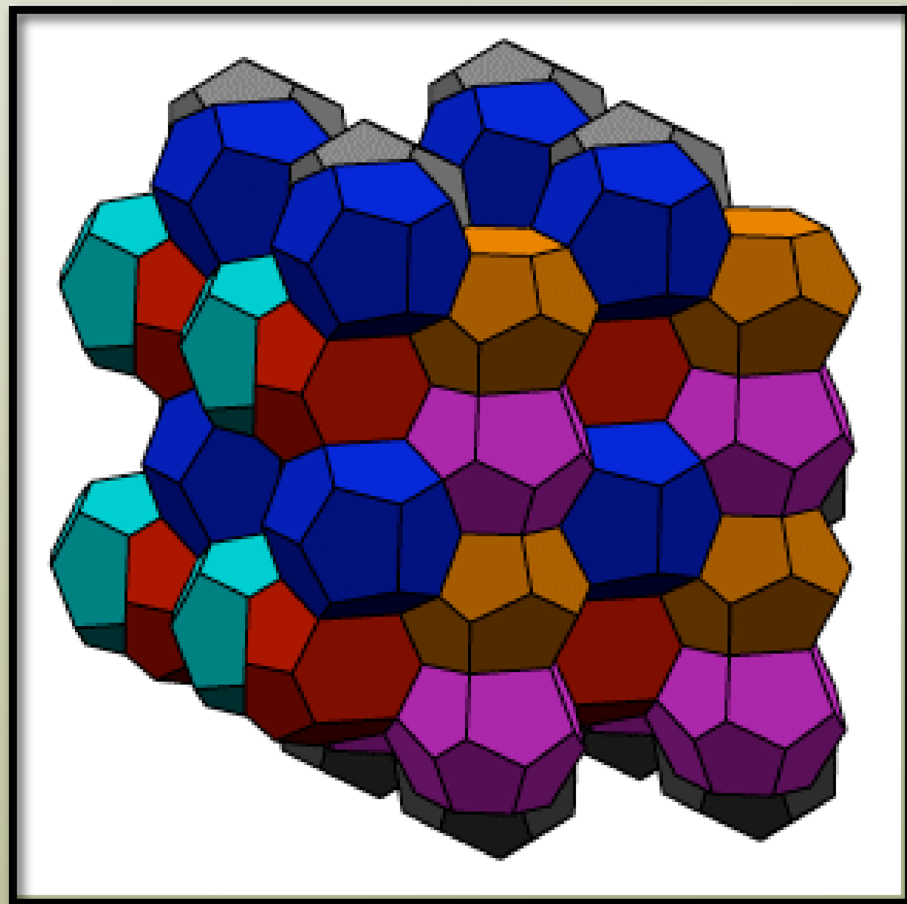
Thomson, *Phil. Mag.* **24** (1887) 503

Weaire and Phelan's Conjecture (1994)



A15

Smaller than Kelvin's!



Weaire & Phelan, *Phil. Mag. Lett.* **69** (1994) 107

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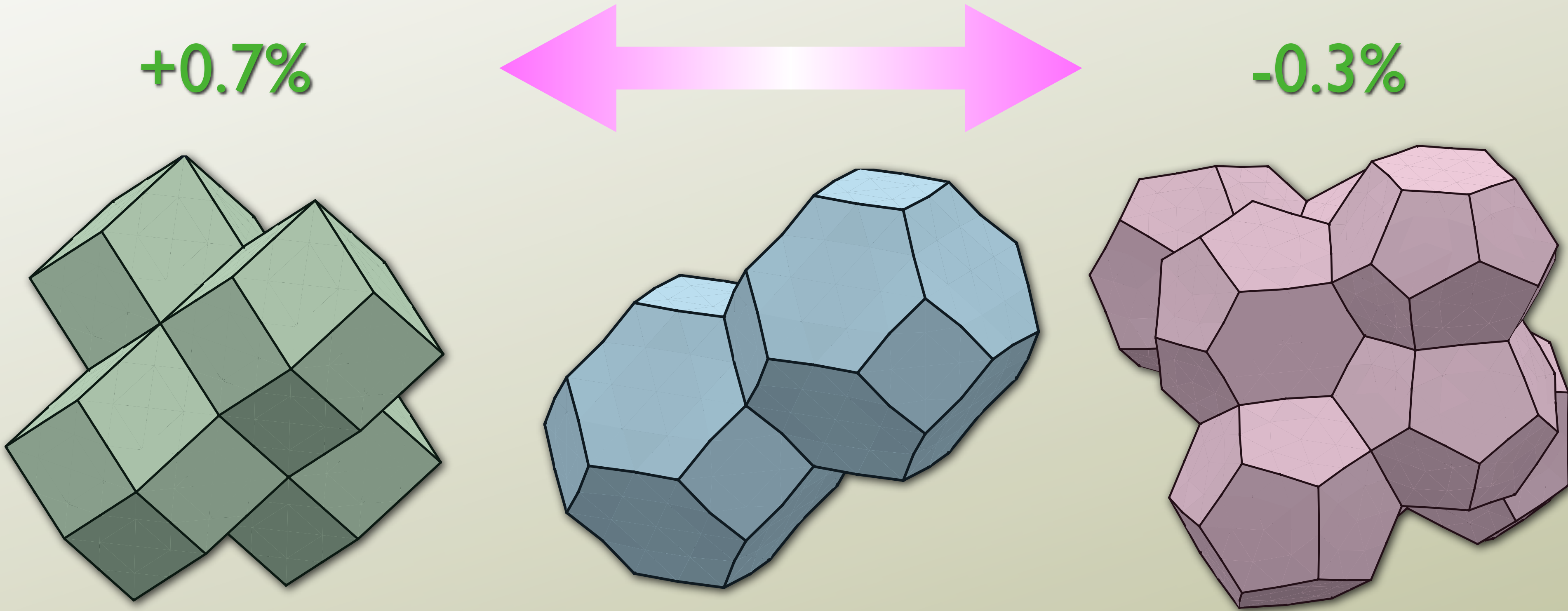
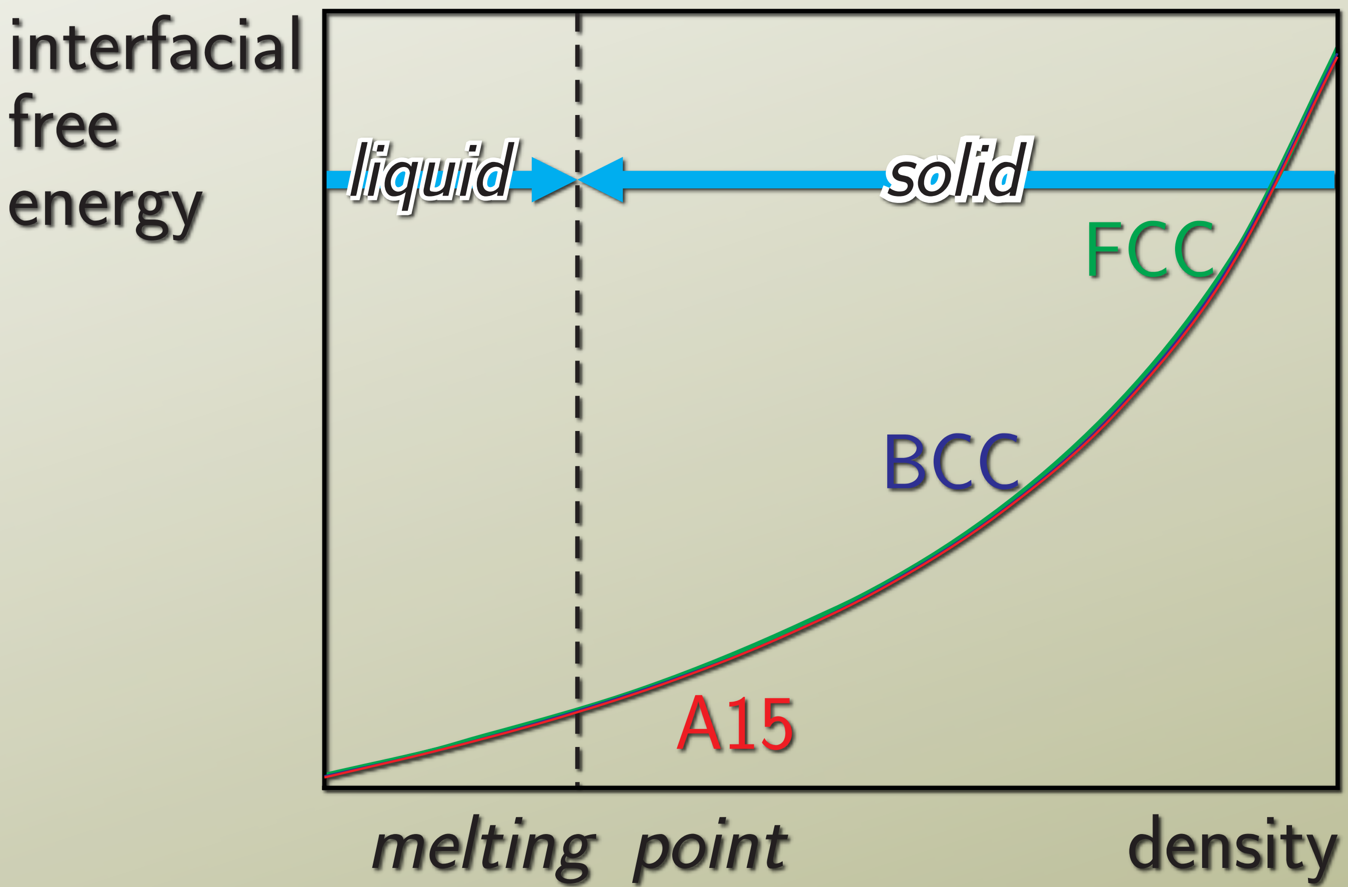
The Numbers

+0.7% -0.3%



FCC BCC A15

Interfacial Free Energy



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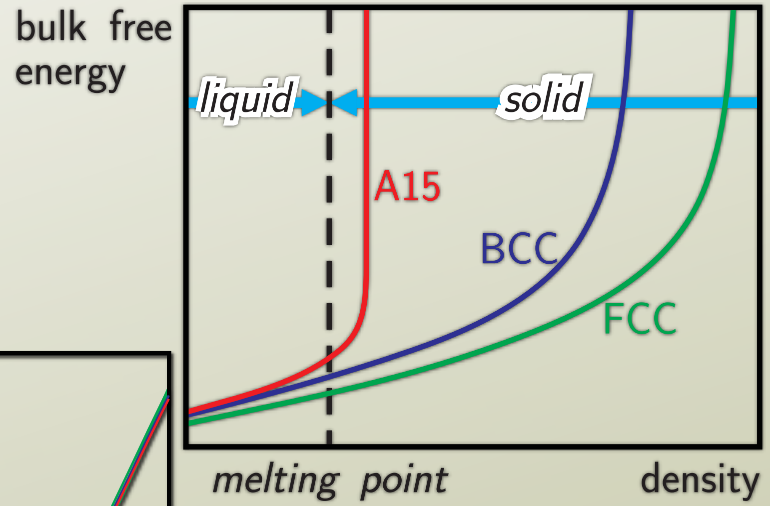
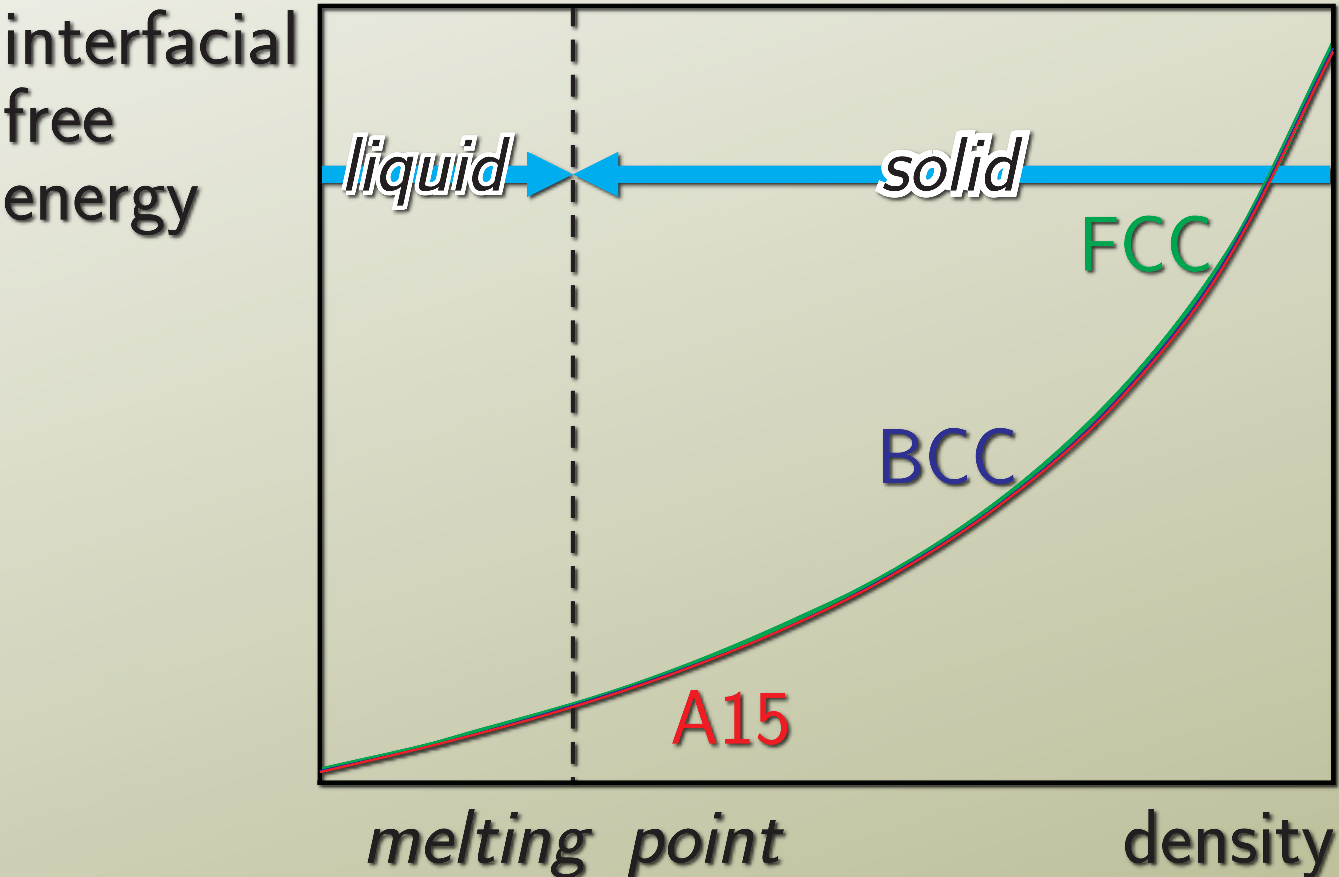
Interfacial Free Energy





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Percec's Dendrimers

Intermicellar Potential

$$U = \frac{2\ell N k_B T}{d}$$

N: chains per micelle
d: thickness of chain matrix
ℓ: Flory-like parameter

transition	ℓ	entropy per chain
FCC - BCC	$0.1R$	$0.5k_B$
BCC - A15	$0.3R$	$1.5k_B$

at melting point

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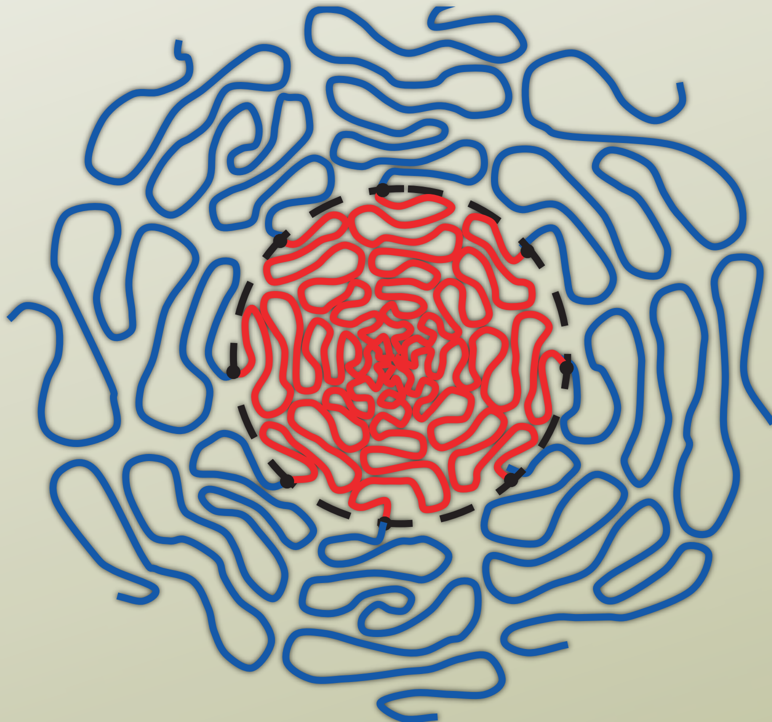
Diblock Copolymers



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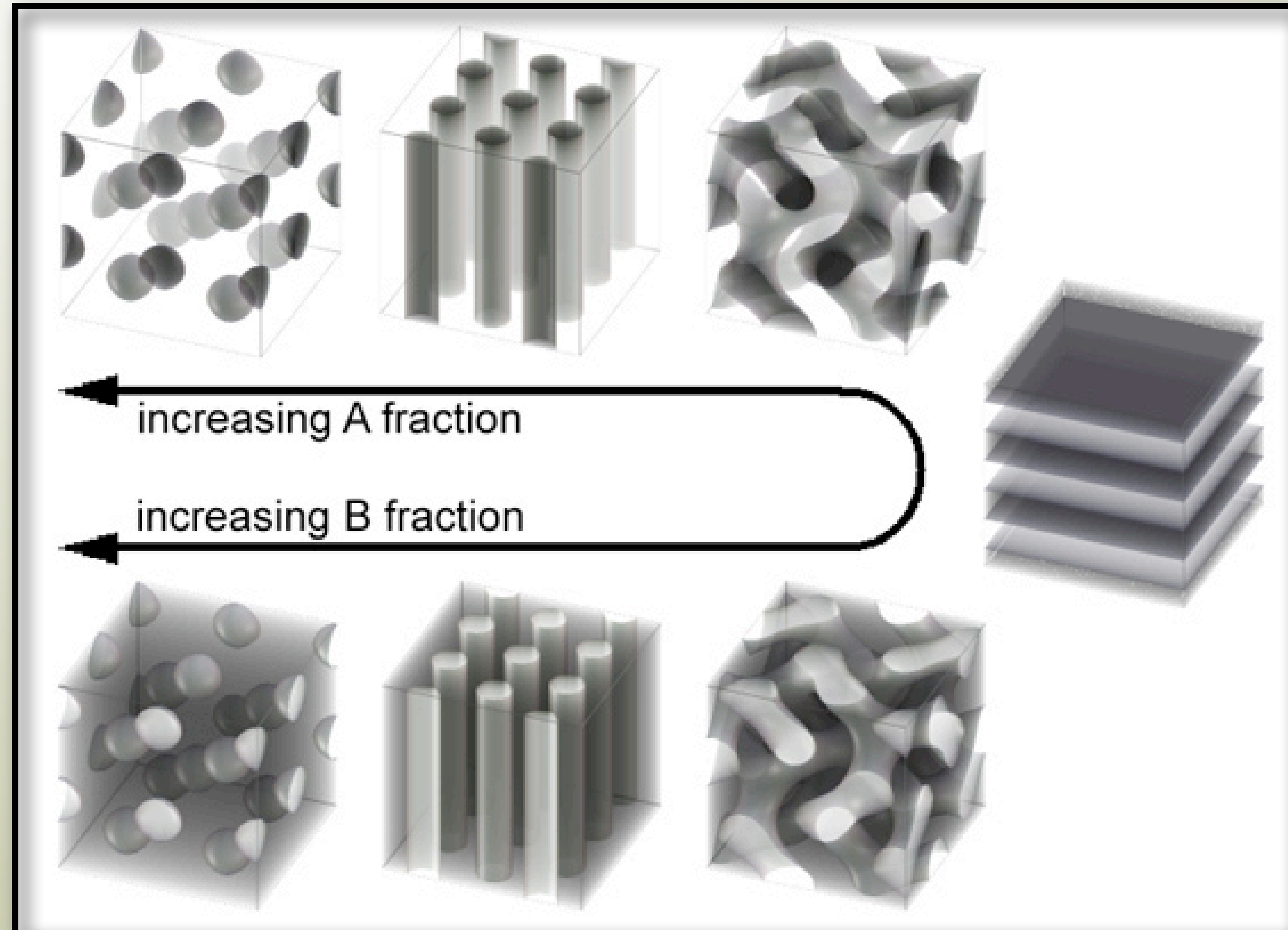
Diblock Copolymers



Graphics from MSRI - http://www.msri.org/publications/sgp/

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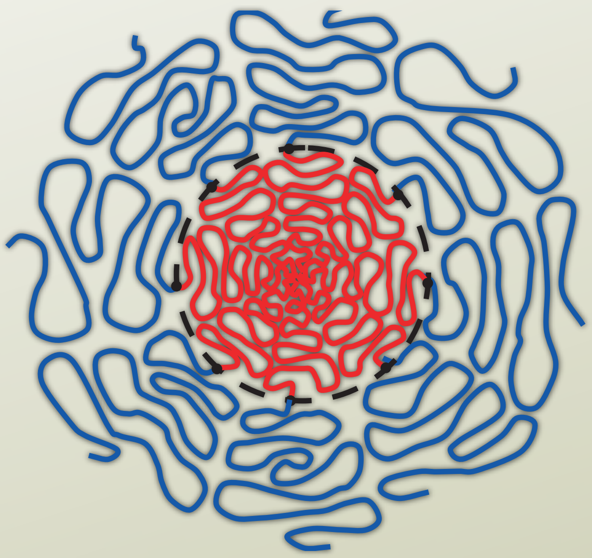
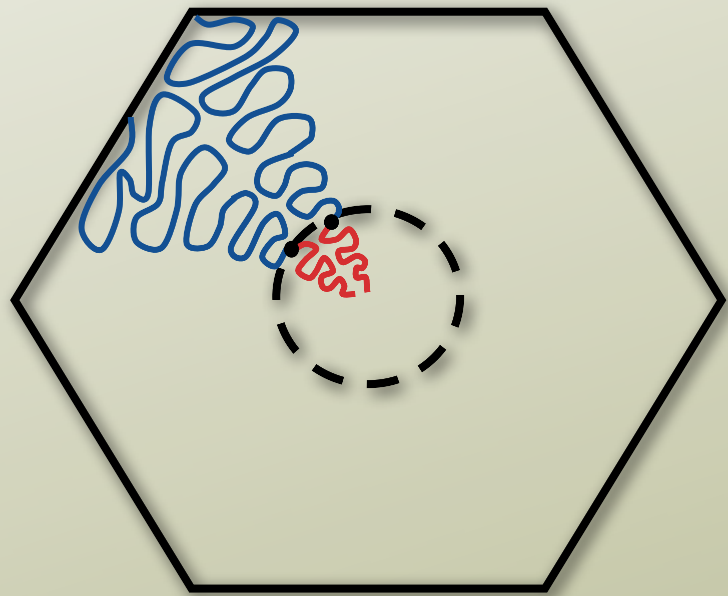
Diblock Copolymers



Spherical Micelles



Voronoi Cells

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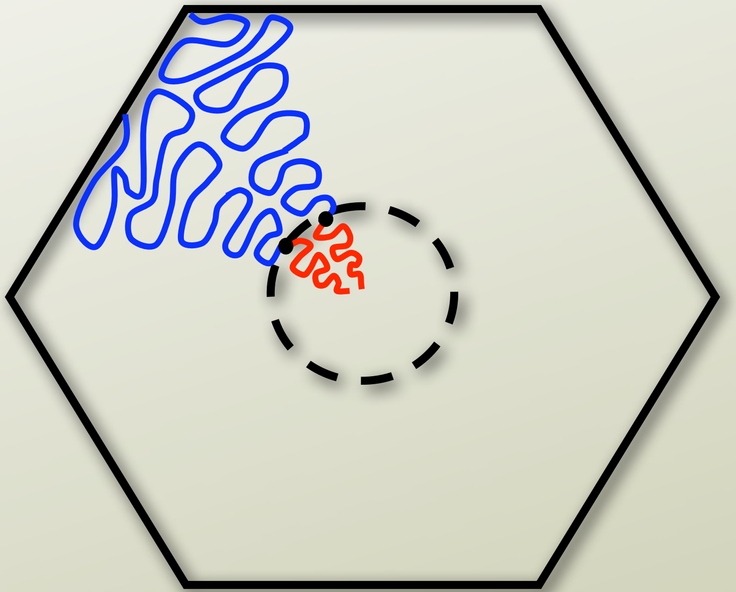
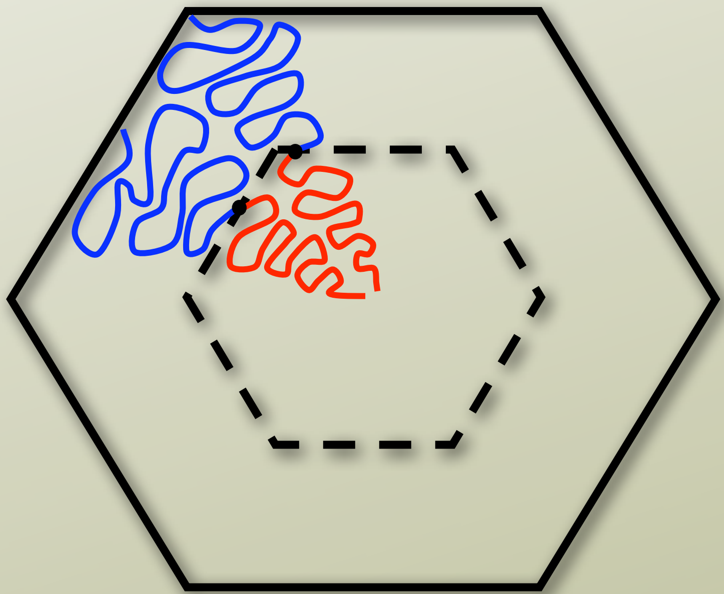
Frustration in Diblocks (Strong Segregation)

Uniform Interface Curvature vs. **Uniform Domain Thickness**





- ***As φ→0, interface ignores shape of unit cell due to high curvature***

- ***As φ→1, tension imposed by of cell wall is propagated to interface***

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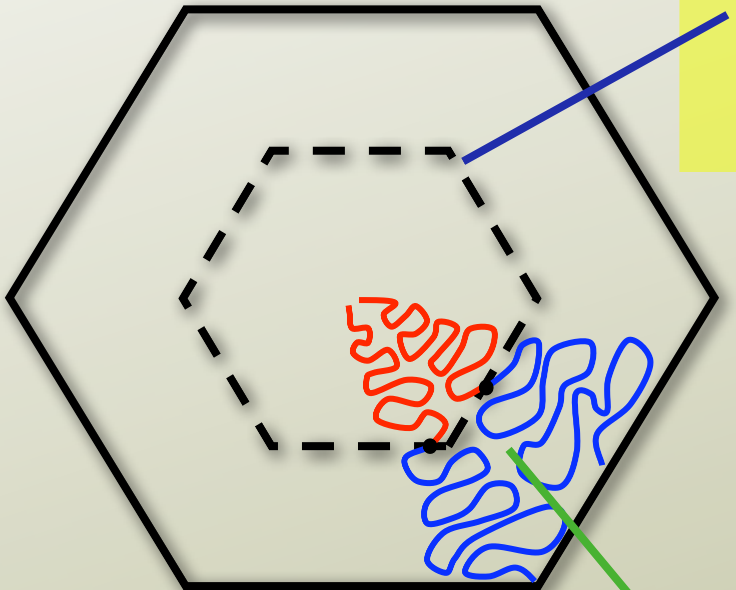
Free Energy: Tension vs. Stretching

$$f_{\text{interface}} = \frac{4\pi R^2 \widetilde{A}}{\frac{4}{3}\pi R^3} \sim \frac{\widetilde{A}}{R}$$



$$f_{\text{stretch}} = \frac{\int d\Omega\, R^5(\Omega)}{\frac{4}{3}\pi R^3} \sim \widetilde{I} R^2$$

Grason, DiDonna & RDK, *Phys. Rev. Lett.* **91** (2003)

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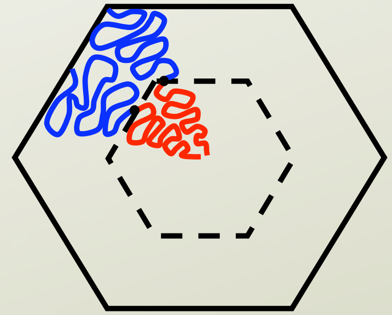
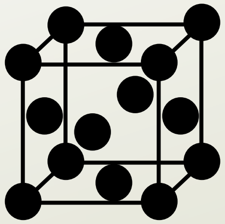
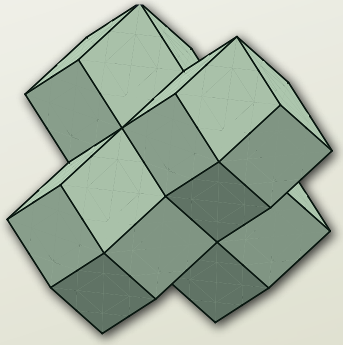
Interfacial Energy



Area: $A/V^{2/3}$

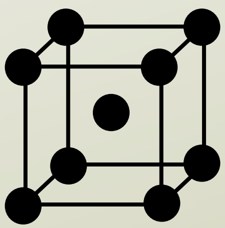
FCC

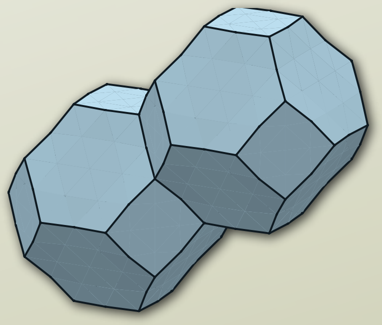




5.345 +0.91 %

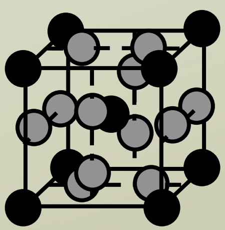
BCC

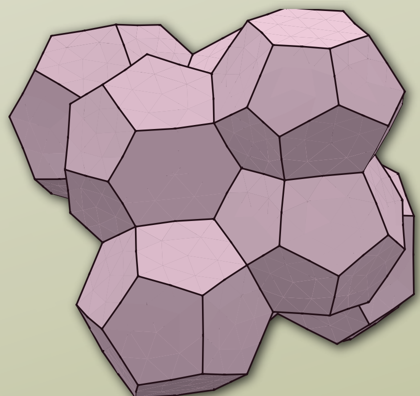




5.315 +0.34 %

A15





5.297

Weaire & Phelan, *Phil. Mag. Lett.* **69** (1994) 107

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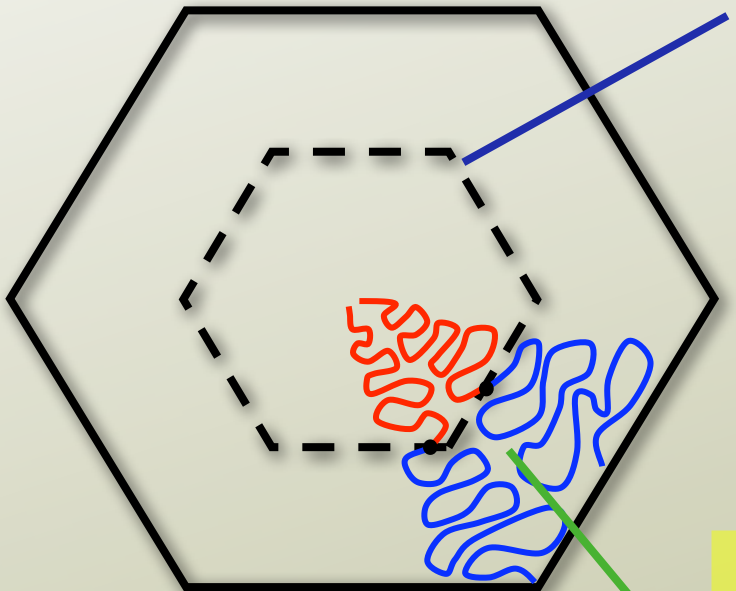
Free Energy: Tension vs. Stretching



$$f_{\text{interface}} = \frac{4\pi \boldsymbol{R}^2 \widetilde{\boldsymbol{A}}}{\frac{4}{3}\pi \boldsymbol{R}^3} \sim \frac{\widetilde{\boldsymbol{A}}}{\boldsymbol{R}}$$

$$f_{\text{stretch}} = \frac{\int d\Omega\, \boldsymbol{R}^5(\Omega)}{\frac{4}{3}\pi \boldsymbol{R}^3} \sim \widetilde{\boldsymbol{I}}\boldsymbol{R}^2$$

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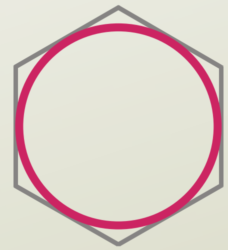
Lattice Problems

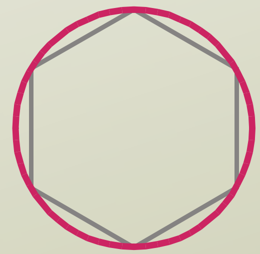
- Packing

  maximize the inradius of the Voronoi Cell



- Covering

  minimize the circumradius of the Voronoi Cell



- Quantizing

  minimize the "moment"

$$G(\Pi) = \frac{\int_{\Pi} x^2}{d\,\mathrm{Vol}(\Pi)^{(d+2)/d}}$$

- Channel Coding

  minimize the error

$$P_e = 1 - \mathcal{N}\int_{\Pi} e^{-x^2/2\sigma}$$

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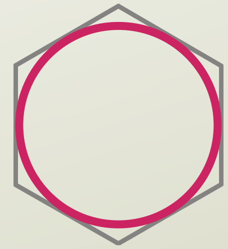
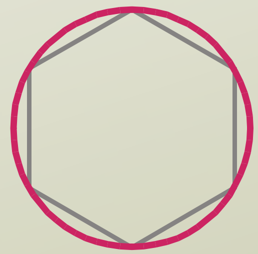
Lattice Problems

- Packing
  maximize the inradius of the Voronoi Cell



- Covering
  minimize the circumradius of the Voronoi Cell



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- Channel Coding
  minimize the error

$$P_e = 1 - \mathcal{N} \int_\Pi e^{-x^2/2\sigma}$$

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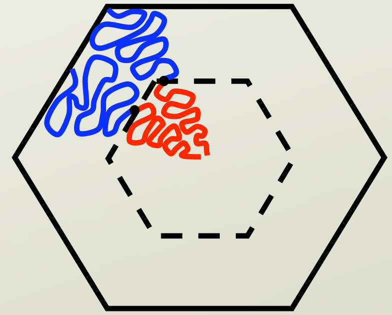
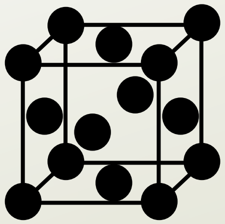
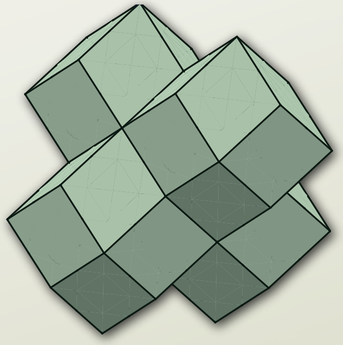
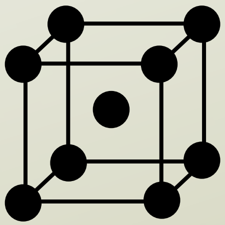
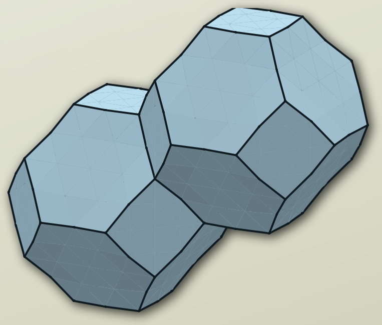
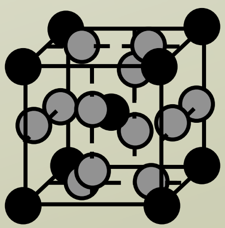
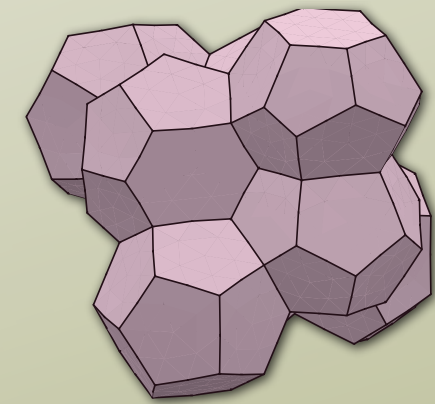
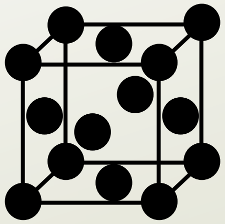
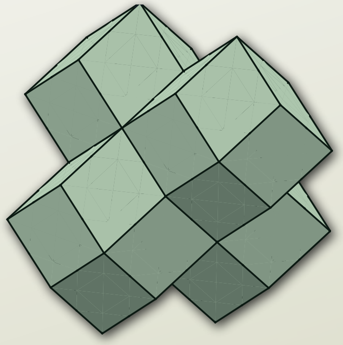
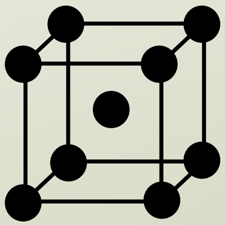
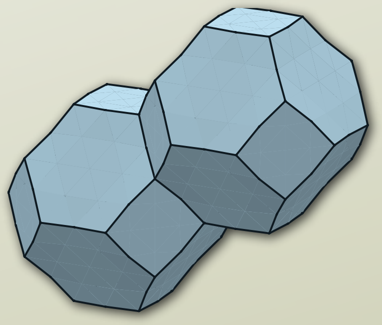
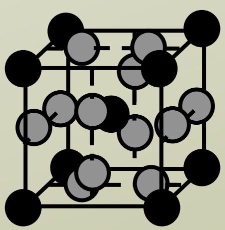
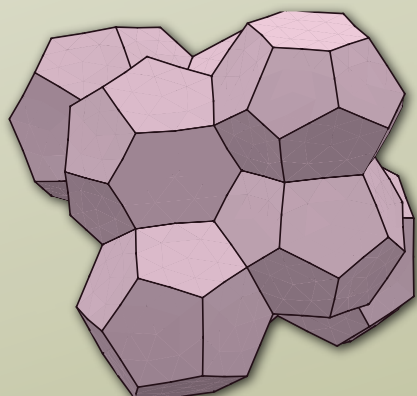
Stretching Energy



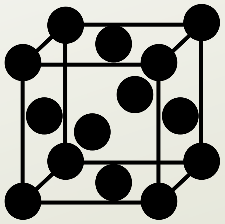
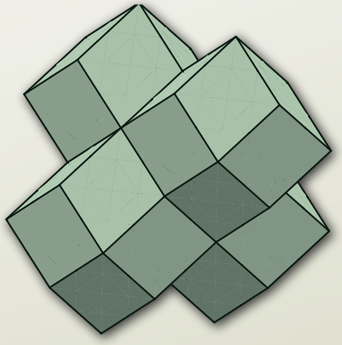
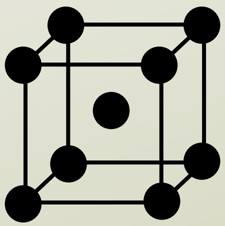
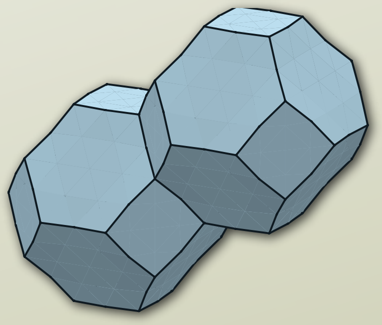
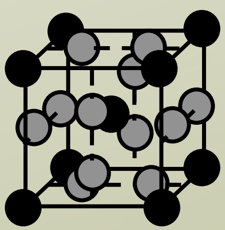
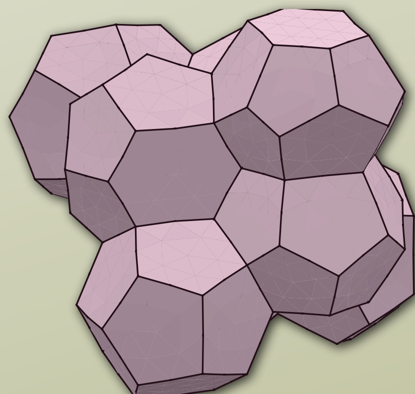
			$G(\Pi)$	
FCC			**0.0787**	+0.26 %
BCC			**0.0785**	
A15			**0.0787**	+0.26 %

Final Energy

			$G(\Pi)$	Area	Free Energy
FCC			0.0787	5.345	
BCC			0.0785	5.315	
A15			0.0787	5.297	

Grason, DiDonna & RDK, *Phys. Rev. Lett.* **91** (2003)

Final Energy

	G(Π)	Area	Free Energy
FCC  	0.0787	5.345	**1.077** *+0.61%*
BCC  	0.0785	5.315	**1.072** *+0.14%*
A15  	0.0787	5.297	**1.071**

Sphere energy: 1

Grason, DiDonna & RDK, *Phys. Rev. Lett.* **91** (2003)

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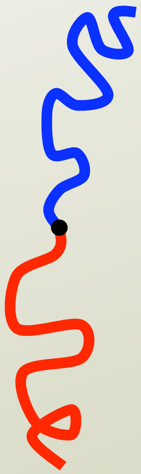
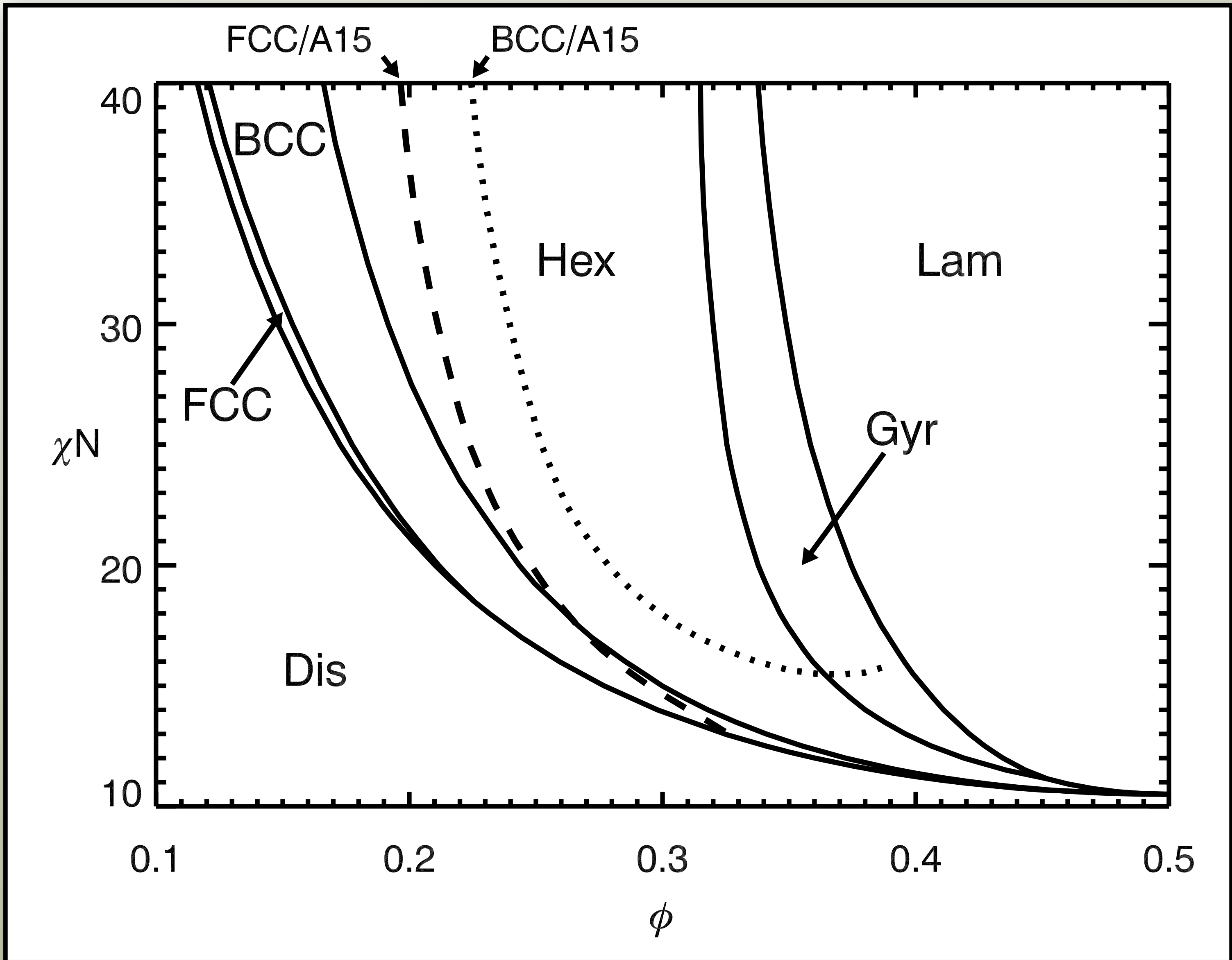
Self-Consistent Field - Linear





Matsen & Schick, *PRL* **72** (1994) 2660

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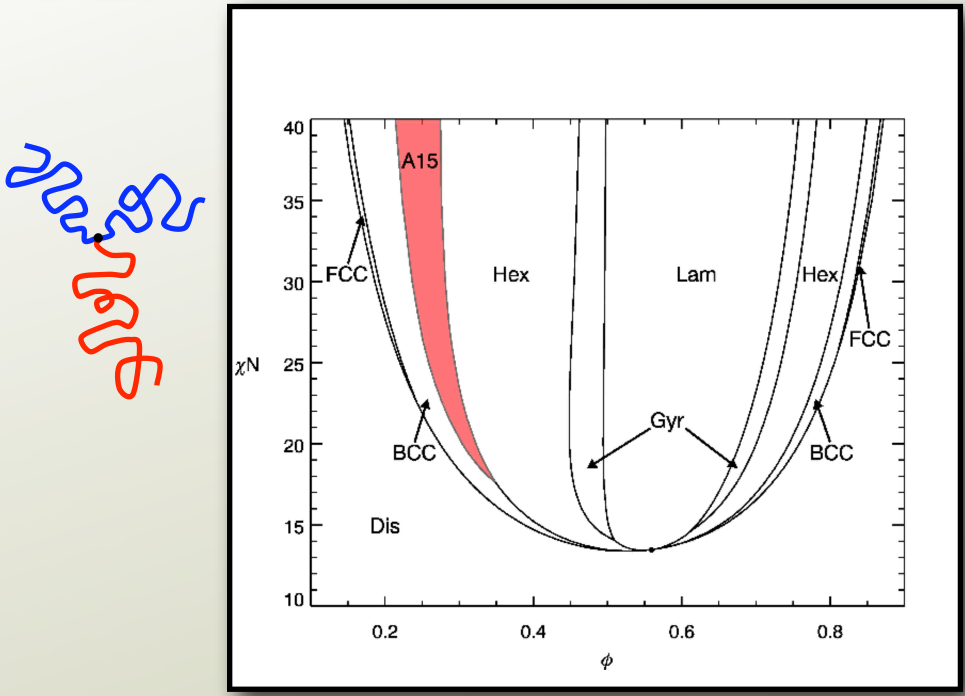
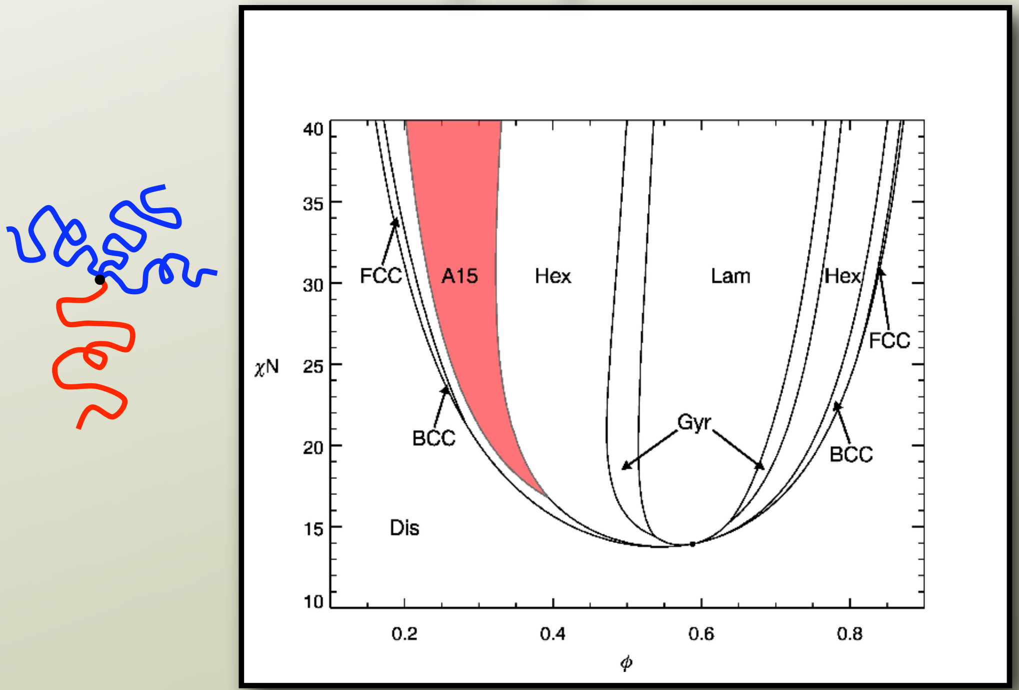
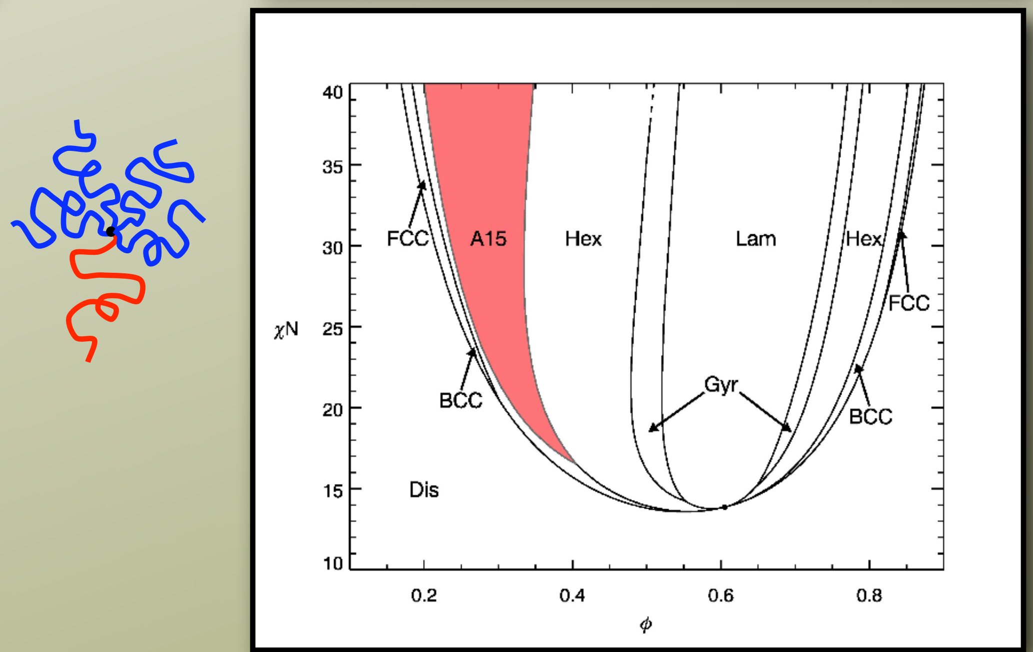
SCFT Results for Miktoarm Diblock Copolymers





As number of arms grows, region of stable A15 phase grows larger



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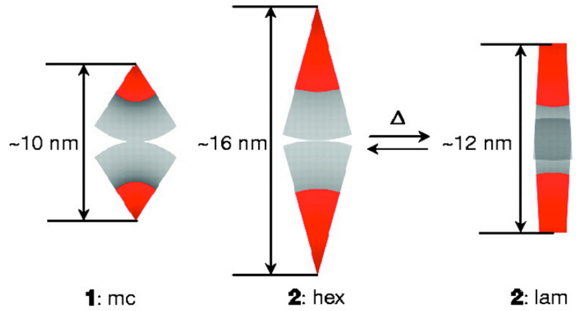
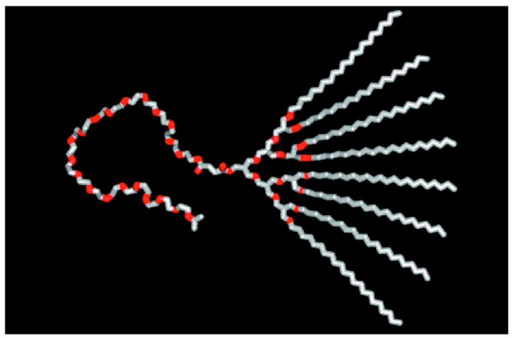
Grason & Kamien, *Macromolecules* **37** (2004) 7371.

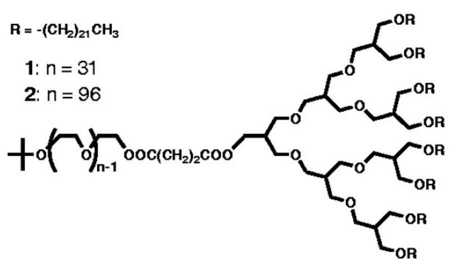
Experimental System

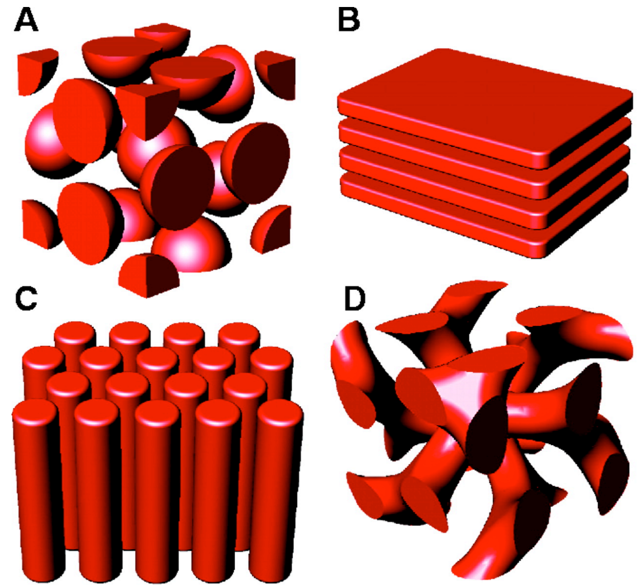
Mesophase Structure-Mechanical and Ionic Transport Correlations in Extended Amphiphilic Dendrons

B.-K. Cho,[1]* A. Jain,[1]* S. M. Gruner,[2] U. Wiesner[1]†









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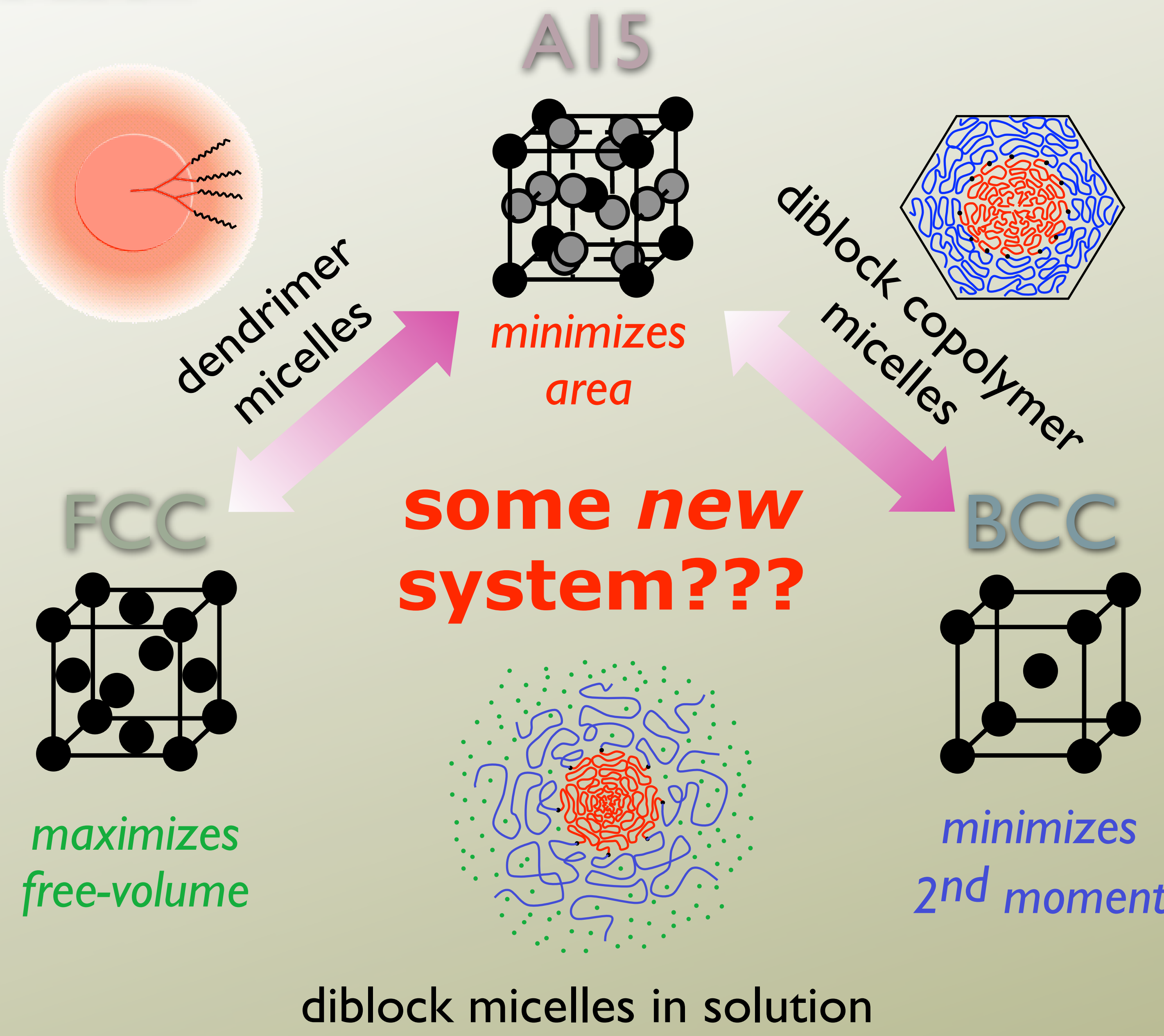
Frustration



Conclusions and Summary

mathematics
of minimal surfaces
& lattices

chemical
synthesis

thermodynamics

designer crystals

Conclusions and Summary

mathematics
of minimal surfaces
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chemical synthesis

thermodynamics

designer crystals

When you see a branch, take it

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<u>Theory</u> (www.physics.upenn.edu/~kamien/kamiengroup/)

Primoz Ziherl (University of Ljubljana)
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William Kung (Syracuse)
Brian DiDonna (Minnesota)

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Virgil Percec (PENN)

<u>Support</u>

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DMR01-29804
INT99-10017 (with Orsay)
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Petroleum Research Fund (ACS)

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