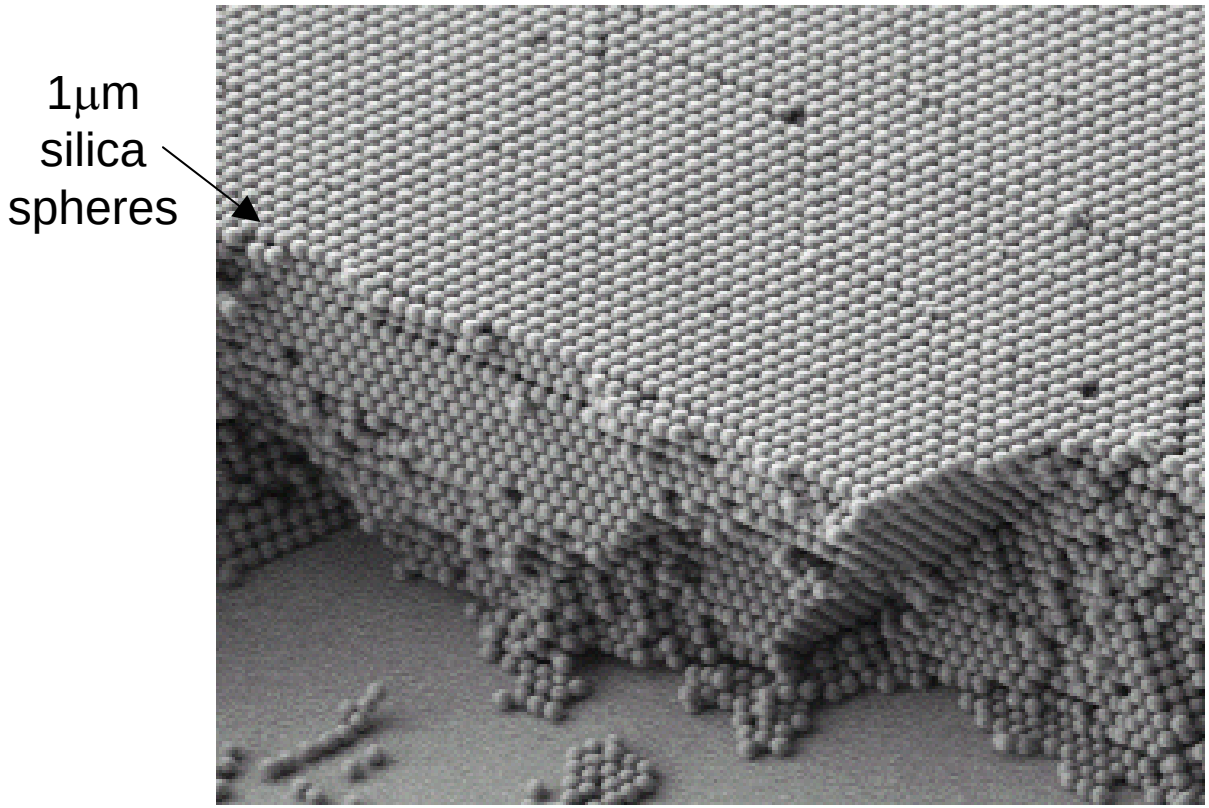
Opaline Photonic Crystals: How Does Self-Assembly Work?

David J. Norris

Chemical Engineering & Materials Science, University of Minnesota



See: D. J. Norris, E. G. Arlinghaus, L. Meng, R. Heiny, L. E. Scriven, *Adv. Mater.* (in press).

What is Self-Assembly?

VIEWPOINT

Self-Assembly at All Scales

George M. Whitesides* and Bartosz Grzybowski

Science ***295****, 2418 (2002).*

Definition: "Self-assembly is the autonomous organization of components into patterns or structures without human intervention."

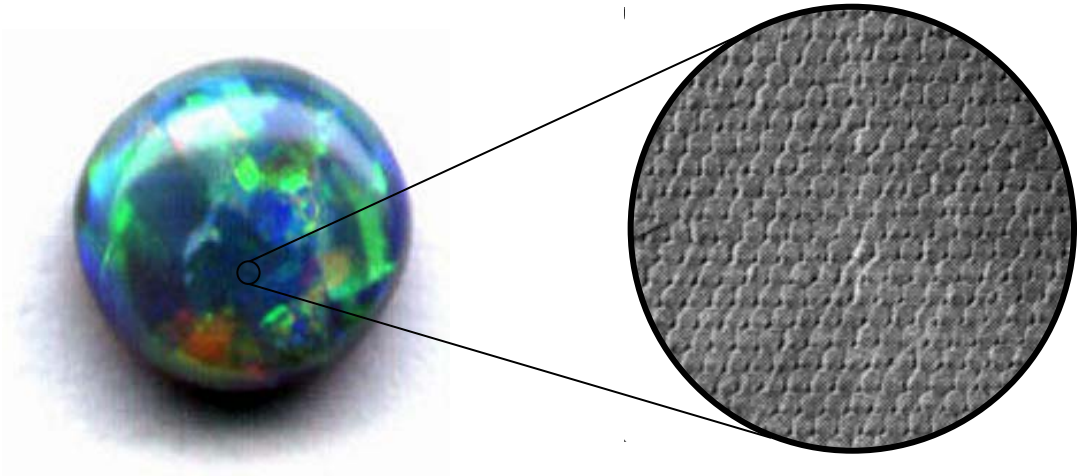
Further: Includes "processes that involve pre-existing components (separate or distinct parts of a disordered structure), are reversible, and can be controlled by proper design of the components."

→ spontaneous ordering of "building blocks"

Examples: Formation of molecular crystals
Folding of globular proteins

Background:

Use self-assembly to obtain photonic crystals?



natural gemstone opal

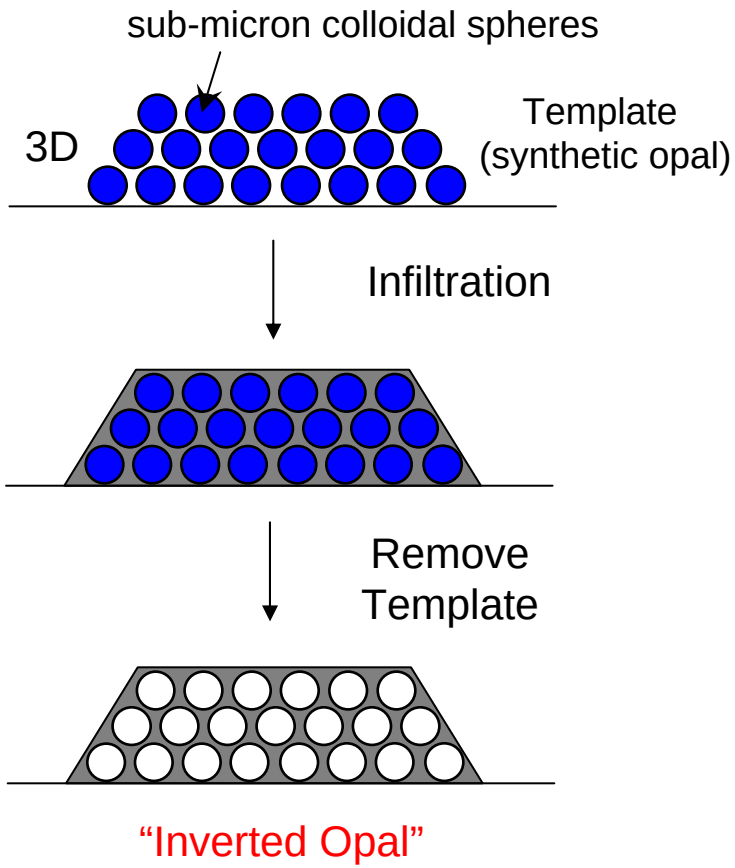
0.2μm silica (glass) spheres

*Sanders; Nature **204**, 1151 (1964)*

Motivation: Ideal material for controlling light

- Light now used in telephone & internet traffic
- Need small circuits to control these optical signals
- Photonic crystals in future optical technologies?

Our Approach to Photonic Crystals: Colloidal Self-Assembly



Literature Results:

O. D. Velev *et al.*, *Nature* **1997**, *389*, 447.
D. Pine *et al.*, *Nature* **1997**, *389*, 948.
G. Stucky *et al.*, *Science* **1998**, *279*, 548.
A. Stein *et al.*, *Science* **1998**, *281*, 538.
W. Vos *et al.*, *Science* **1998**, *281*, 802.
A. A. Zakhidov *et al.*, *Science* **1998**, *282*, 897.
T. E. Mallouk *et al.*, *Science* **1999**, *283*, 963.
V. L. Colvin *et al.*, *PRL* **1999**, *83*, 300.
A. Blanco *et al.*, *Nature* **2000**, *405*, 437.

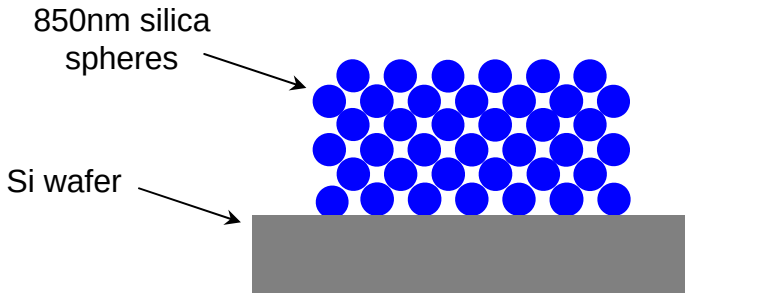
Theory: inverted opals have a PBG

Haus *et al.*, PRB, **45**, 13962 (1992).
Busch and John, PRE, **58**, 3896 (1998).

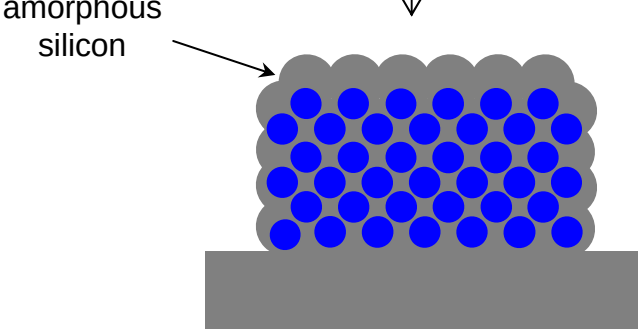
Requires refractive index > 2.85

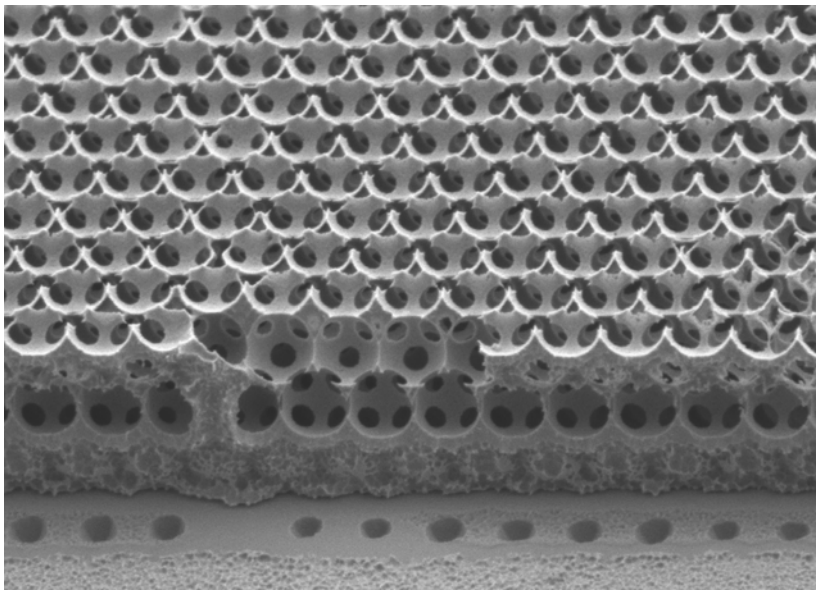
Silicon Inverted Opal

in collaboration with X. –Z. Bo and J. Sturm (Princeton)

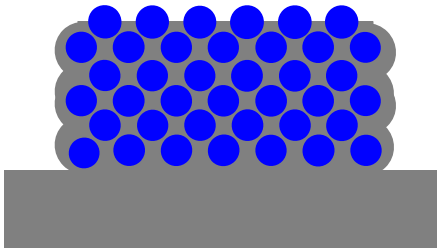


Si deposition

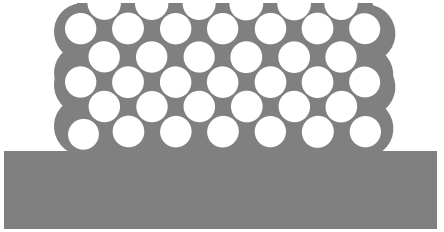




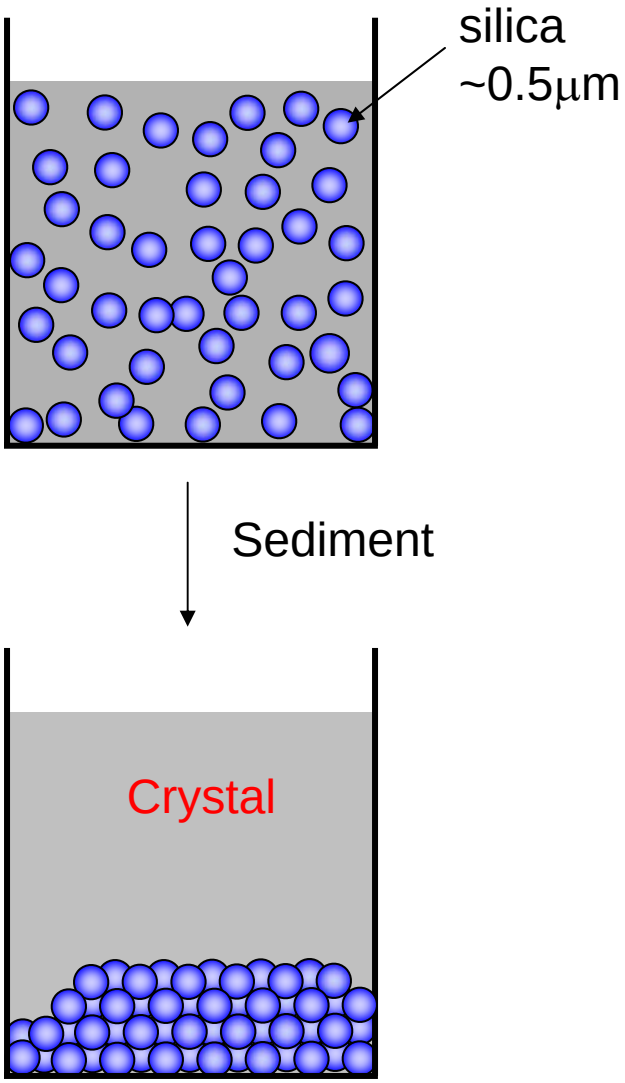
reactive ion etch

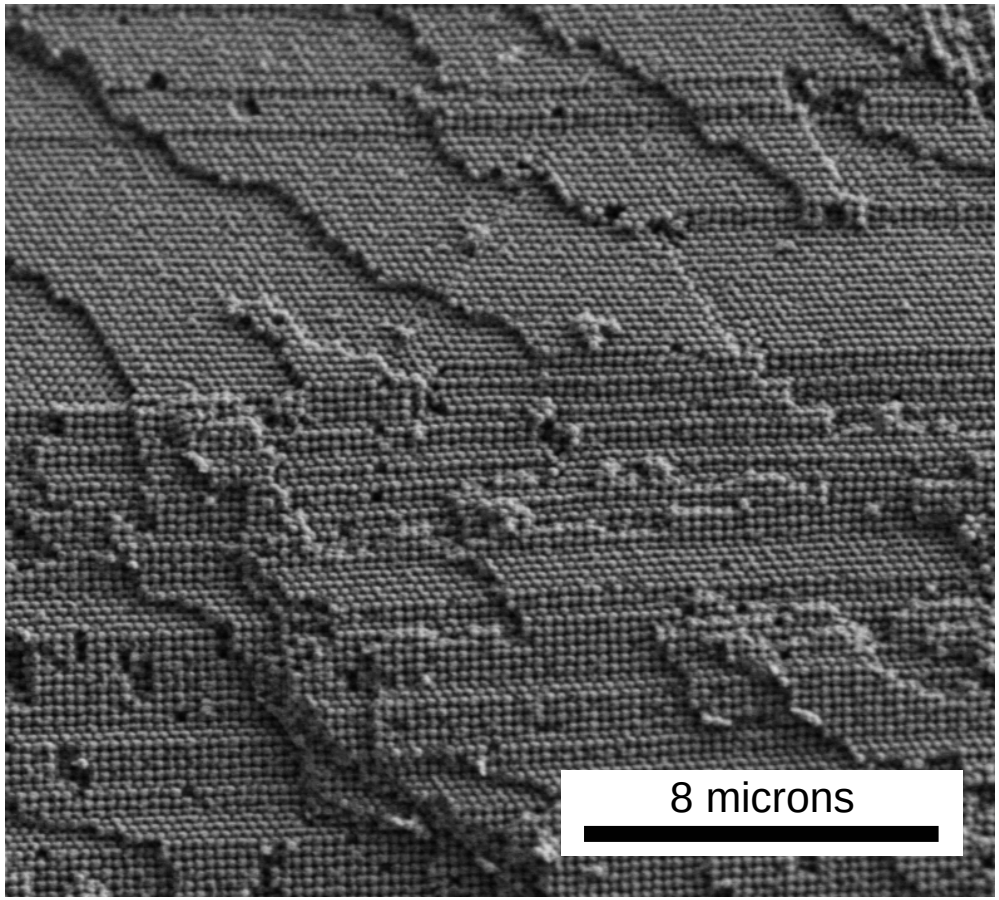


acid etch



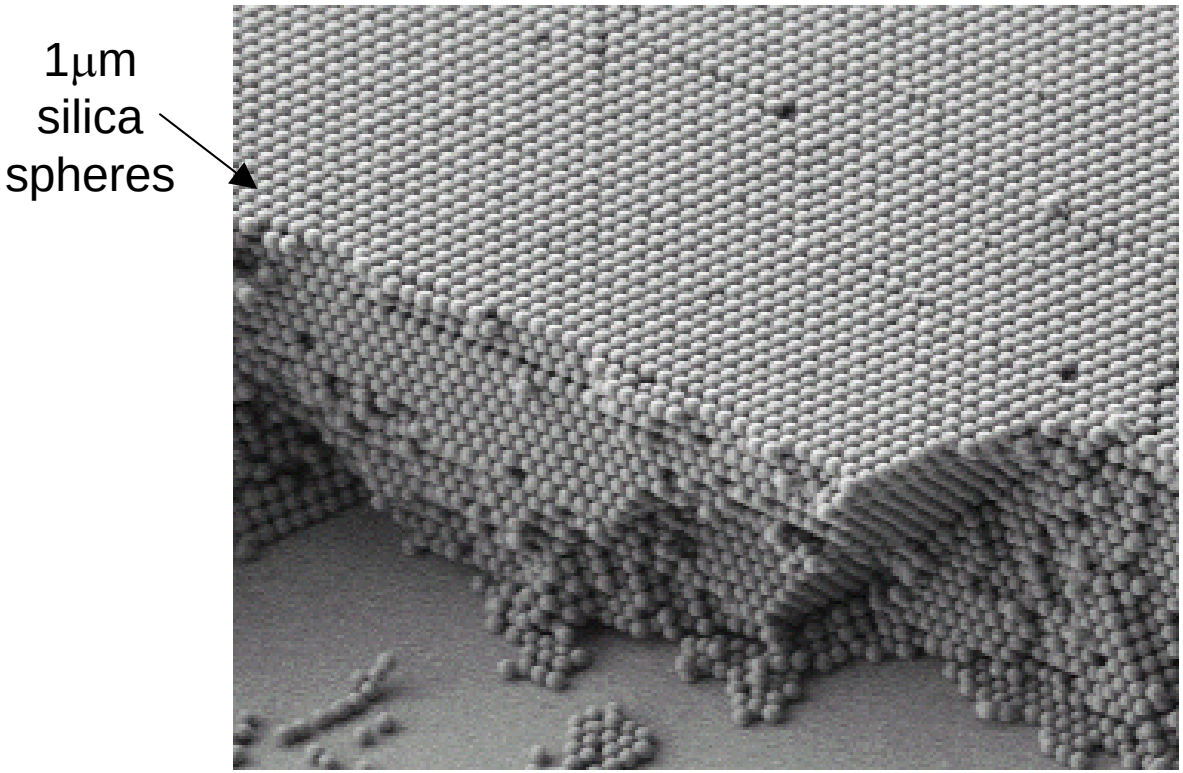
Sedimentation: Synthetic Opals





dry and collect sediment → synthetic opal

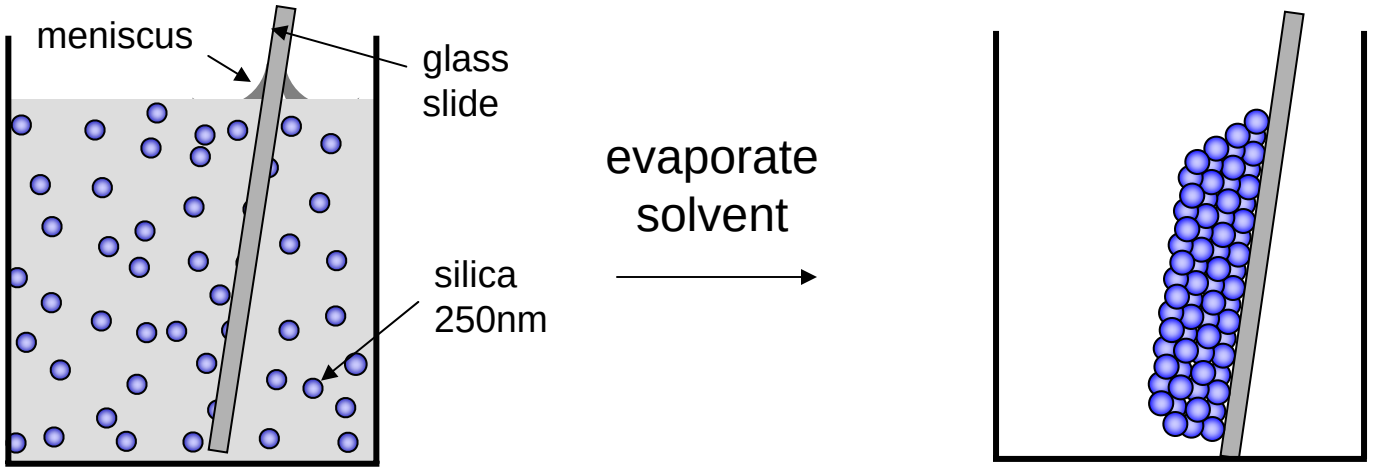
Even Better: Thin Opaline Films



Opaline films

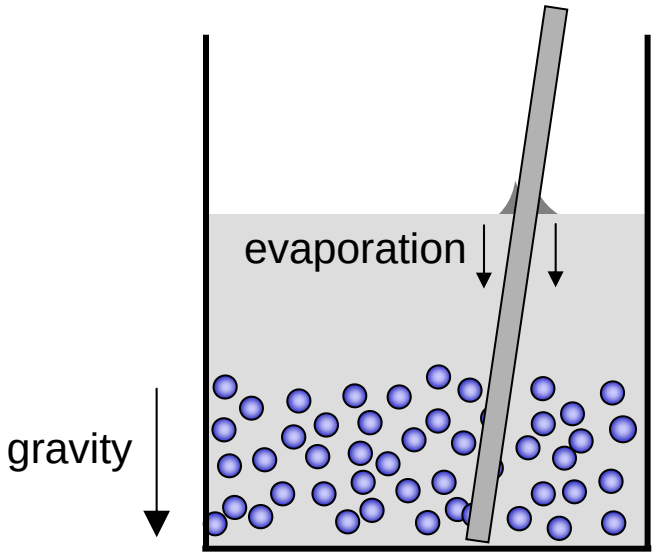
Convective Self-Assembly

Colvin *et al.*, *Chem. Mater.* (1999)



- Capillary forces during drying cause assembly in the meniscus
- Extremely flat, large-area opals of controllable thickness
- Limited by gravity to spheres <400nm?

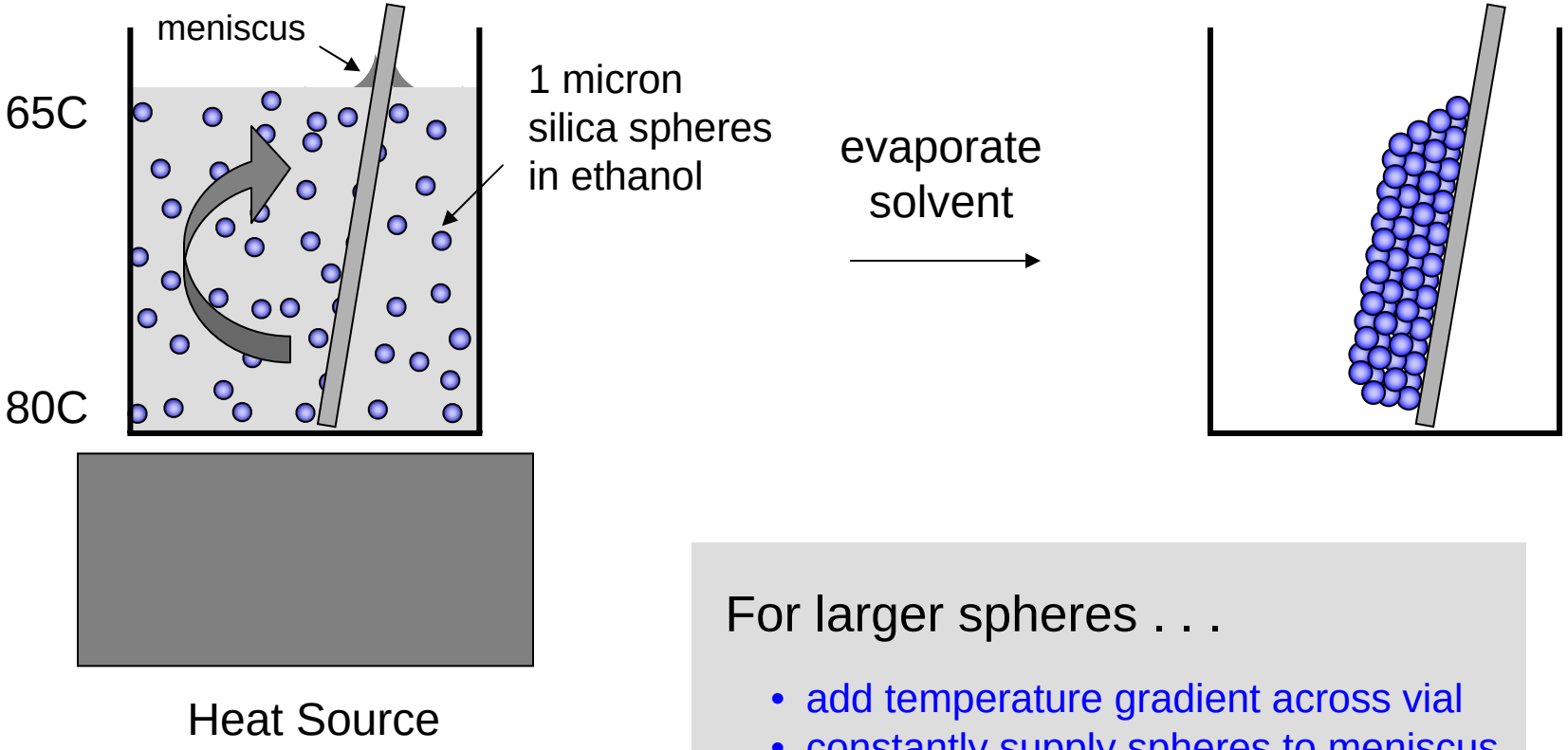
Problem with larger spheres: sedimentation



For larger spheres . . .

- spheres sediment away from the meniscus region
- deposition cannot take place

Add Temperature Gradient

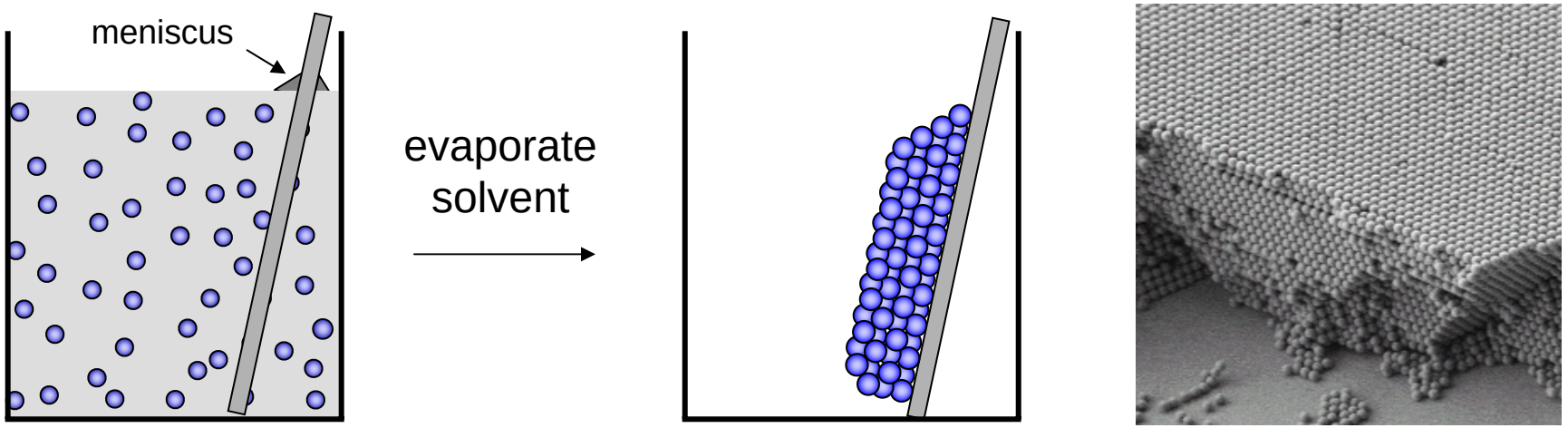


For larger spheres . . .

- add temperature gradient across vial
- constantly supply spheres to meniscus
- make large sphere planar opals

Large sphere opals are necessary to have photonic band gap at $\lambda = 1.5\mu m$.

But how does the assembly process work?

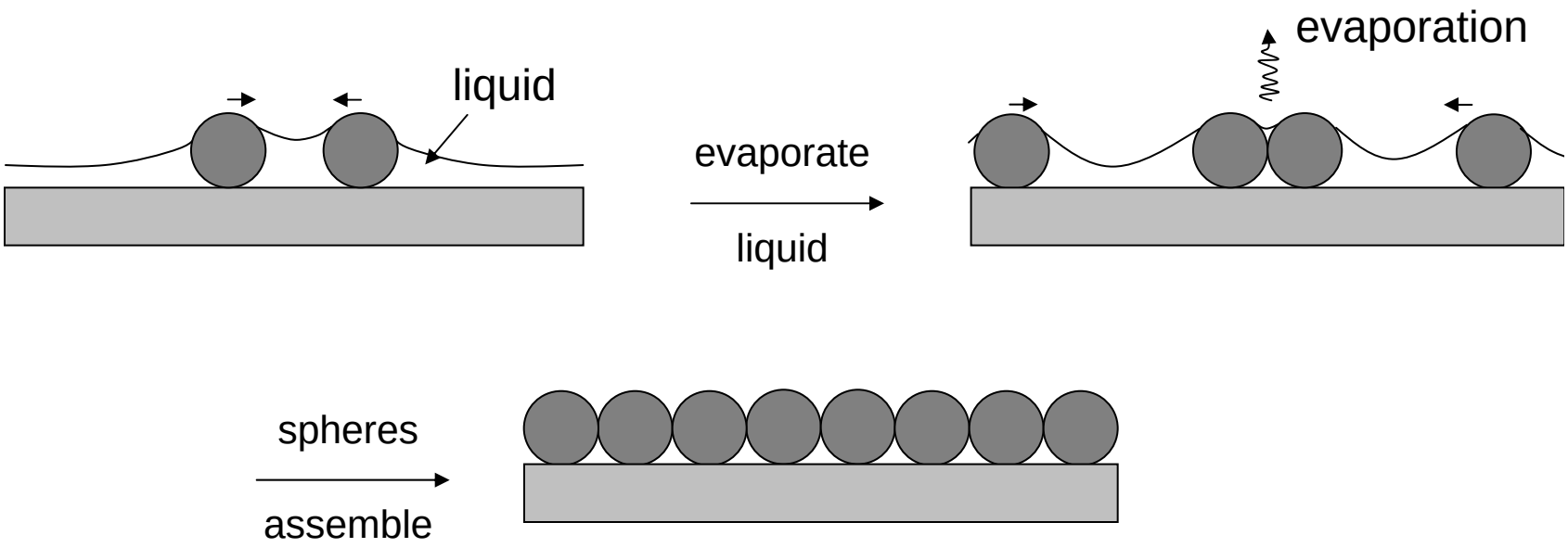


Questions:

- Mechanism that controls the formation of multilayers?
- With understanding, can we reduce disorder?
- Assemble other structures?

Consider connections to three related areas:

1. Monolayer formation *(Denkov, Kralchevsky, Nagayama, Velev, and coworkers)*



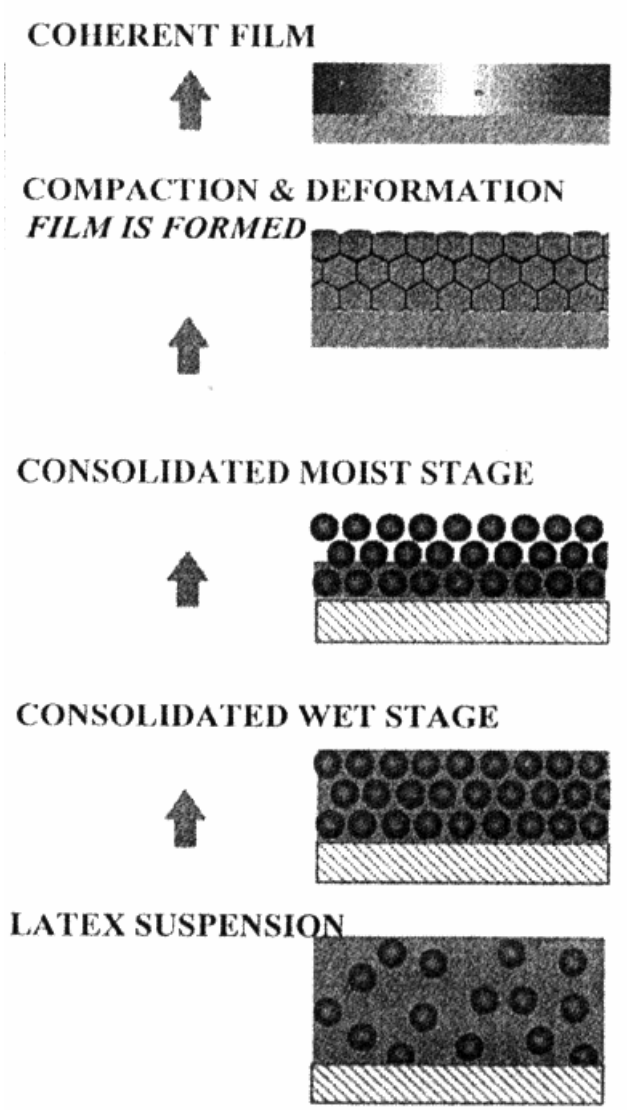
- Liquid interface induces partially immersed spheres to close-pack
- Liquid evaporating from the spheres brings in more liquid
- Liquid flow brings in more spheres
- Ordered monolayer develops

But what about multilayers?

Consider connections to three related areas:

2. “Latex” Coatings

- Heavily studied
- Industrially important
- 3 stages: consolidation
  compaction
  coalescence
- Ordering has been observed
- Solvent evaporation causes viscous drag that forms “pack”
- If evaporation is halted, spheres redisperse
- Solvent flow is important!

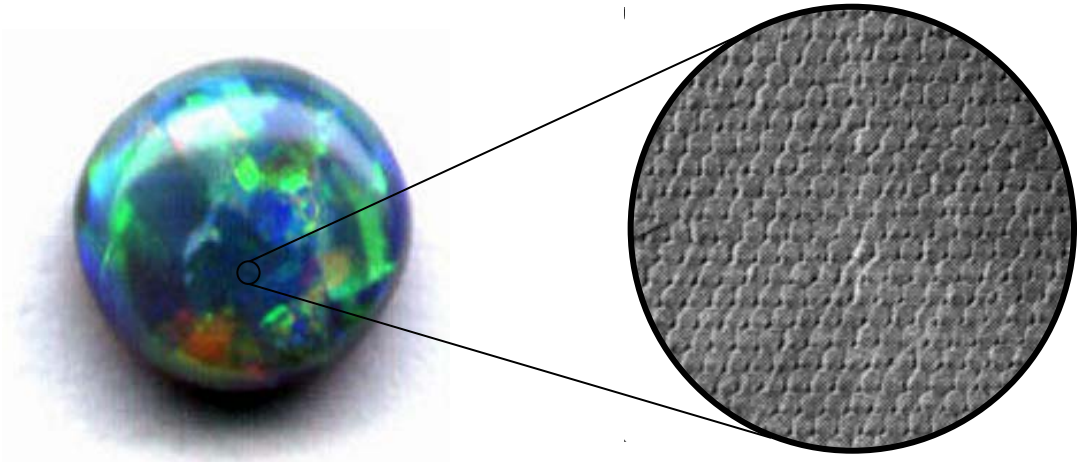


from Z. Huang, Ph.D. Thesis, Univ. of Minnesota, 2001.

see J. L. Freddie, Mater. Sci. Eng. R ***1997****, 21,* 10.

Consider connections to three related areas:

3. Opals & Colloidal Crystals



natural gemstone opal

0.2μm silica (glass) spheres

*Sanders; Nature **204**, 1151 (1964)*

Unlike deformable latex spheres, here we have non-deformable “hard spheres”

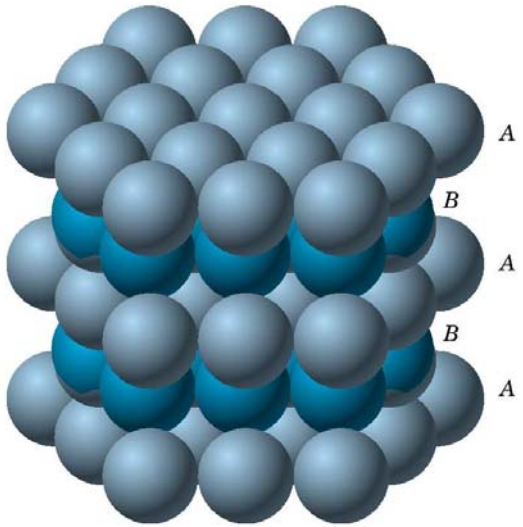
How do “hard-spheres” pack?

hexagonal
sheets of spheres

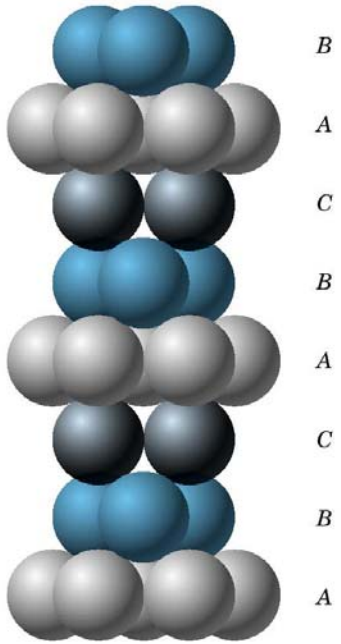
↓

stack

2 possibilities



HCP



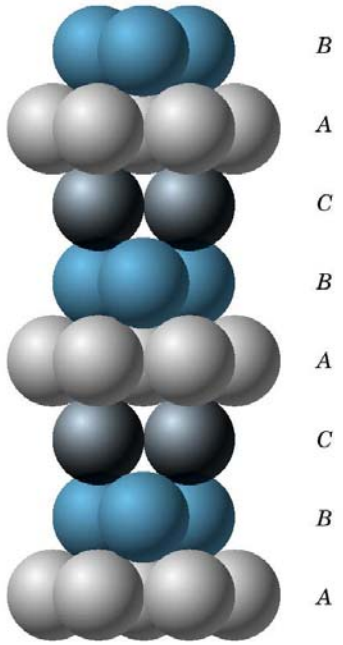
FCC

- Two possible crystal structures: HCP and FCC
- Both have the same packing volume (74%) at zero temperature.
- Also can have randomly stacked (i.e. *ABACBCAC* . . .) or random hexagonal close-packed (RHCP).

Theory

Thermodynamics: FCC slightly lower in free energy

- See: Woodcock, *Nature*, **385**, 141 (1997).
  Bolhuis *et al.*, *Nature*, **388**, 235 (1997).
  Mau and Huse, *Phys. Rev. E*, **59**, 4396 (1999).
- Subtle effect: differences in 3rd nearest neighbors
- Energy difference small: ~10^{-3} $k_b T$

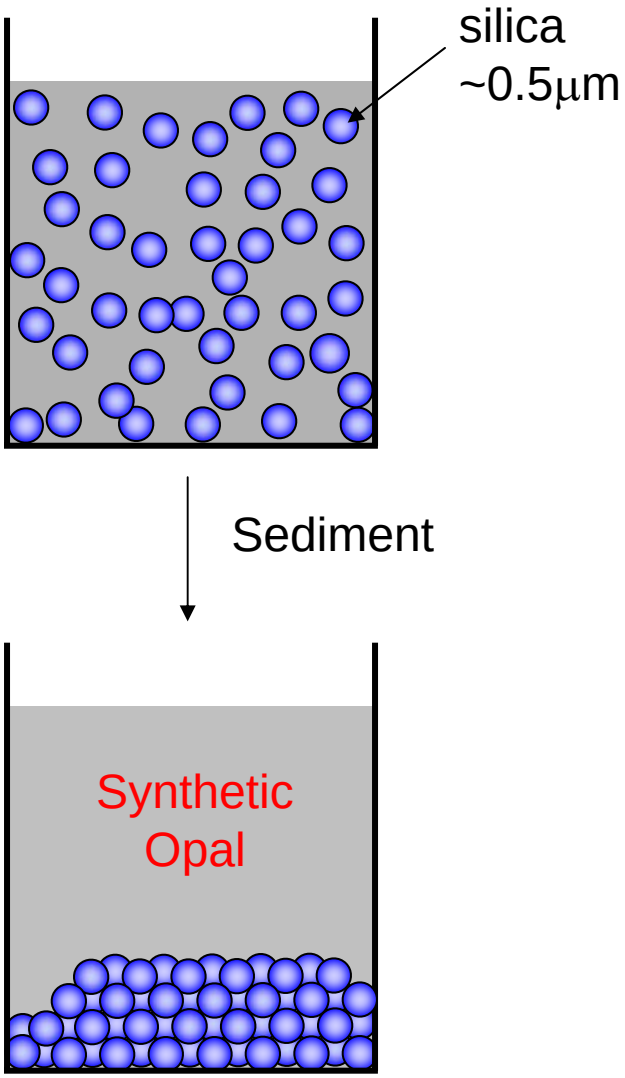


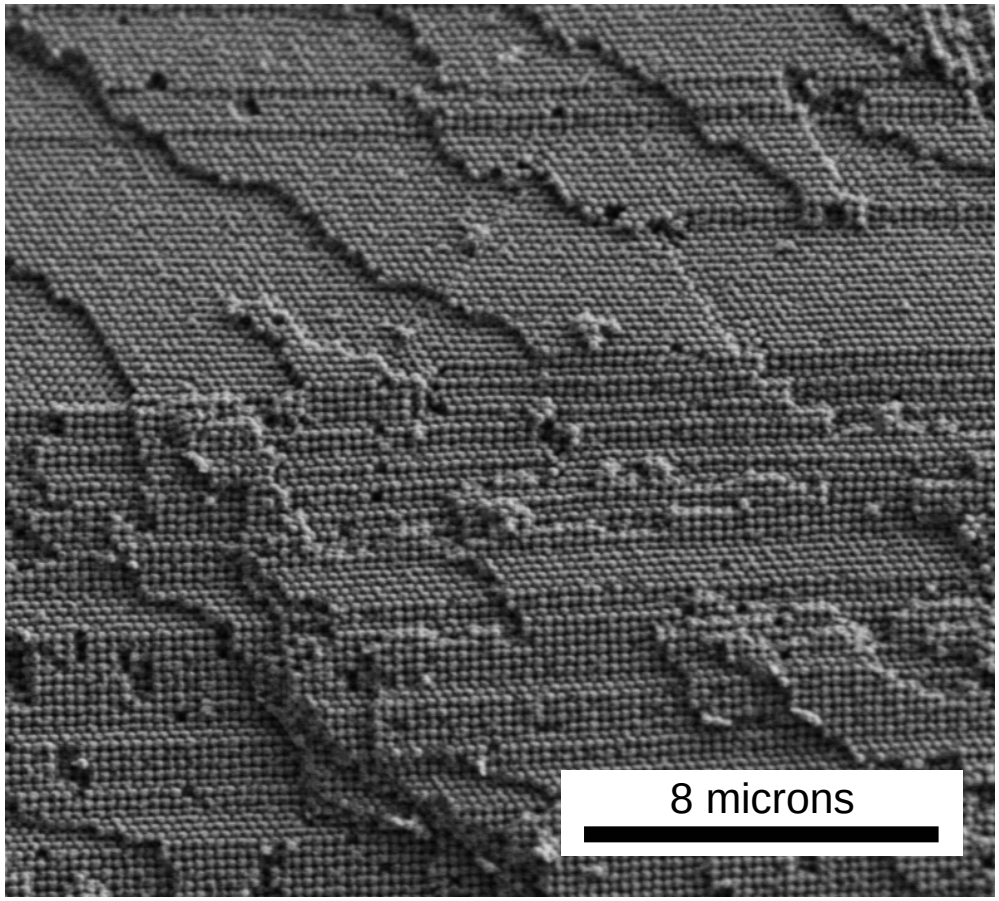
FCC

Natural Opals

- Most natural opals are RHCP
- Although in rare cases, FCC is observed
- See: Sanders, *Nature*, **204**, 1151 (1964).
  Sanders, *Acta Cryst. A*, **24**, 427 (1968).

Sedimented synthetic opals





structure depends on sedimentation time

Sedimented synthetic opals

VOLUME 63, NUMBER 25 PHYSICAL REVIEW LETTERS 18 DECEMBER 1989

Structure of Crystals of Hard Colloidal Spheres

P. N. Pusey,[1] W. van Megen,[1,2] P. Bartlett,[3] B. J. Ackerson,[1,4]
J. G. Rarity,[1] and S. M. Underwood[2]

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[2]*Department of Applied Physics, Royal Melbourne Institute of Technology, Melbourne, Victoria, Australia*
[3]*School of Chemistry, Bristol University, Bristol, BS8 1TS, United Kingdom*
[4]*Department of Physics, Oklahoma State University, Stillwater, Oklahoma 74078*

(Received 23 June 1989)

We report light-scattering measurements of powder diffraction patterns of crystals of essentially hard colloidal spheres. These are consistent with structures formed by stacking close-packed planes of particles in a sequence of permitted lateral positions, A,B,C, which shows a high degree of randomness. Crystals grown slowly, while still containing many stacking faults, show a tendency towards face-centered-cubic packing; possible explanations for this observation are discussed.

- Opals sedimented over months: preference for FCC
- Thermodynamics controlling crystal structure?

But important side comment . . .

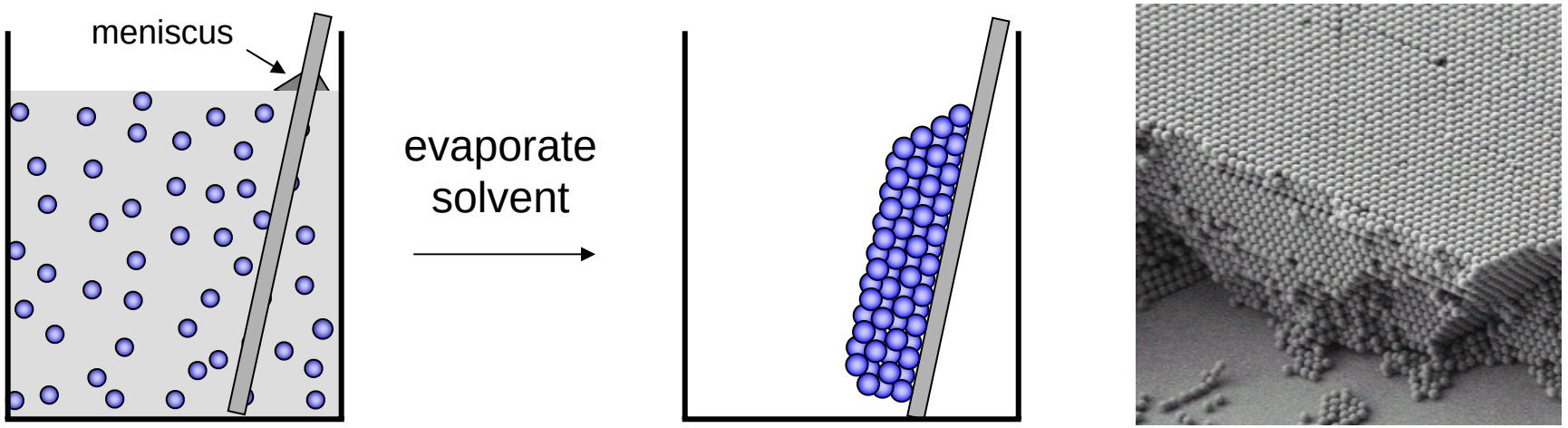
Structure of Crystals of Hard Colloidal Spheres

P. N. Pusey,[1] W. van Megen,[1,2] P. Bartlett,[3] B. J. Ackerson,[1,4] J. G. Rarity,[1] and S. M. Underwood[2]

Thus there appears to be a correlation between structure and the rate at which the crystals have grown. For crystals which grow at the maximum rate the stacking is essentially completely random, $\alpha = 0.5$. We expect this finding to be generic for hard spheres: It is difficult to imagine a mechanism by which such a completely random stacking would be influenced by minor departures of the interparticle potential from the hard-sphere form, for example, slight softness or attraction,[5,6] or by a small polydispersity. However, such factors could be responsible for the tendency towards the fcc structure, $\alpha > 0.5$, observed in crystals grown at lower concentrations where, under the influence of a smaller "supersaturation," the particles presumably have more time to explore possible lattice sites. On the other hand, it may be that the true equilibrium structure of hard-sphere crystals is fcc, but that the difference in free energies between this and other structures is very small. In fact, several calculations[19] have indicated that the free energies (per particle) of fcc and hcp hard-sphere crystals are the same within an uncertainty of no more than $\sim 2 \times 10^{-3} k_B T$. Thus long-lived nonequilibrium states are easily achieved. Nonequilibrium hydrodynamic interactions (on settling) or macroscopic shear deformations[20] may favor the formation of certain structures which will persist and be hard to distinguish from true equilibrium states. Clearly to test these conjectures will require a very detailed study of the interparticle interaction and a more quantitative analysis of the nucleation and growth processes.

Solvent flow may be important! →

Back to convective assembly:

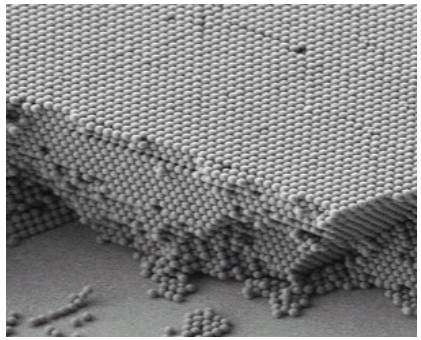


Questions:

- Mechanism that controls the formation of multilayers?
- With understanding, can we reduce disorder?
- Assemble other structures?

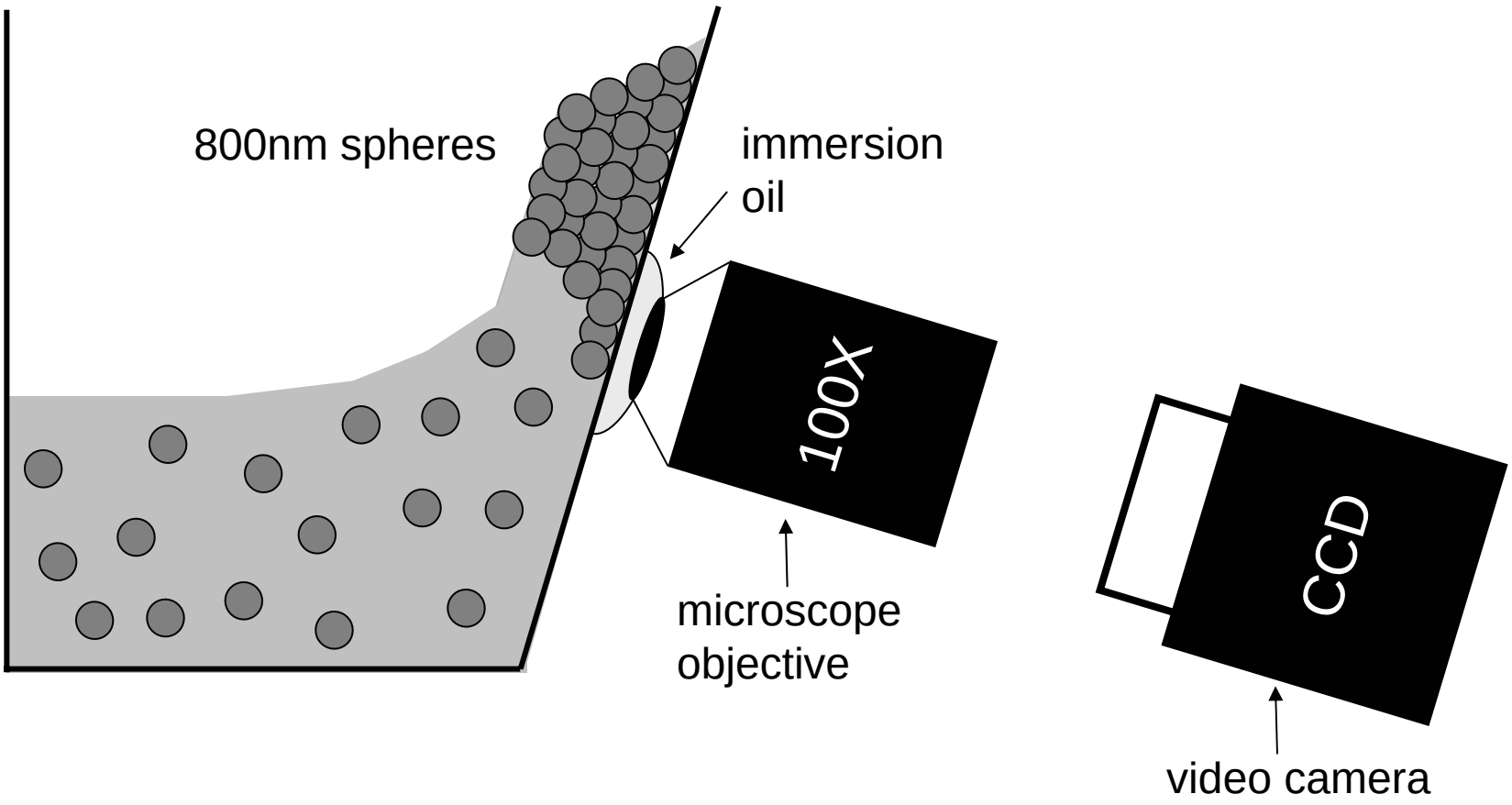
Summary of observations:

thermodynamics	→	favors FCC slightly
natural opals	→	typically random (RHCP)
synthetic opals (quick sedimentation)	→	random (RHCP)
synthetic opals (slow sedimentation)	→	FCC
opaline coatings (made in hours)	→	FCC??

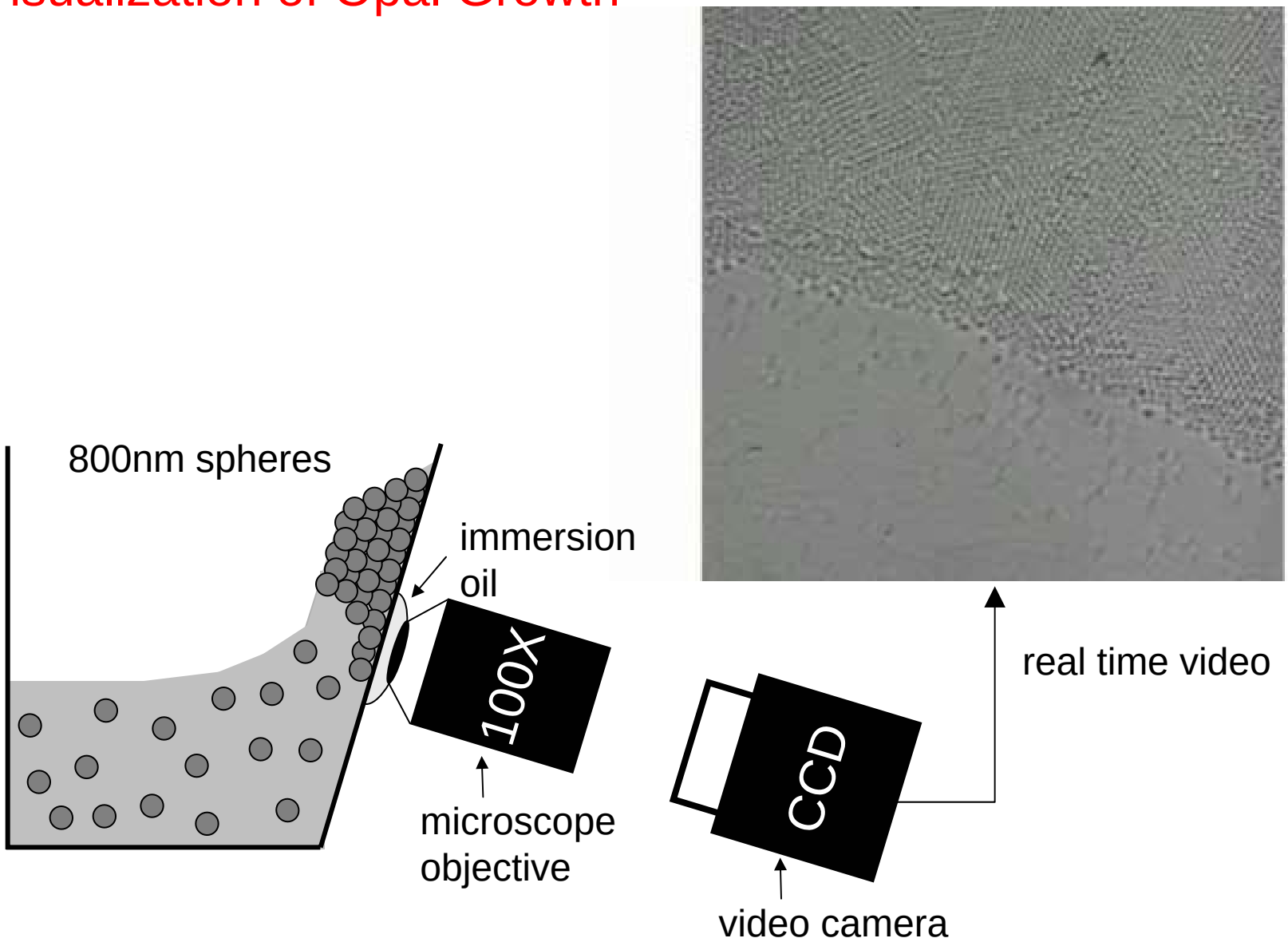


What is controlling crystal structure in convective assembly?

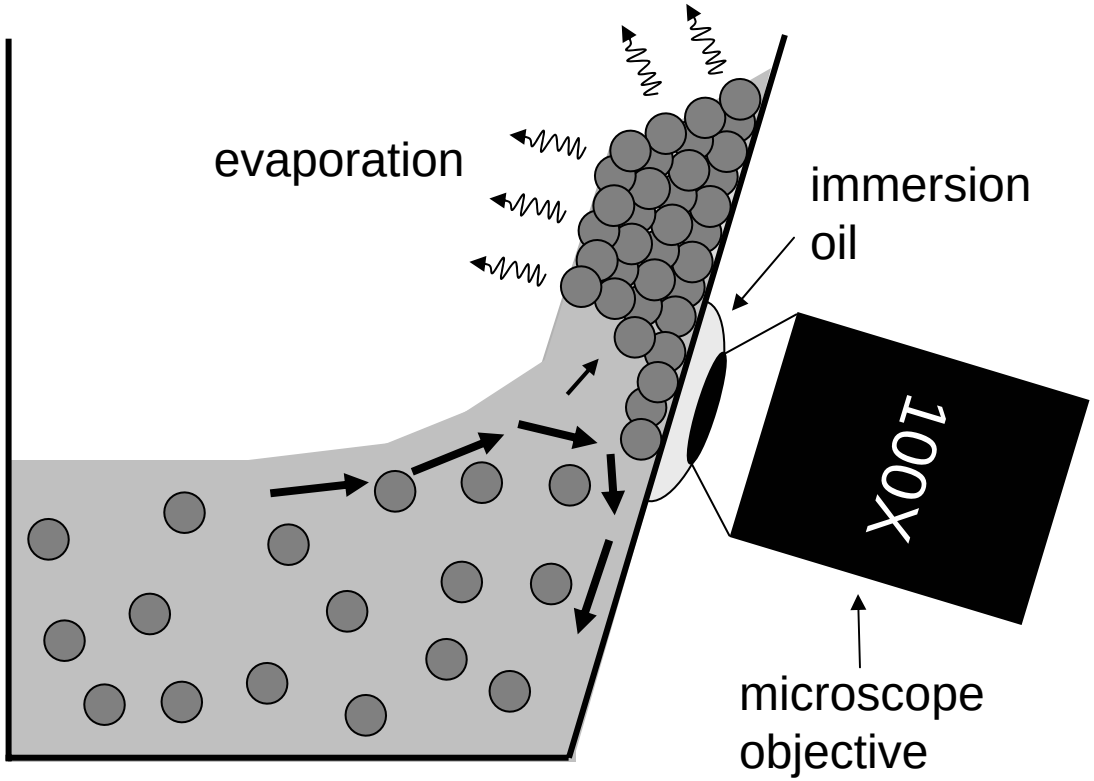
To study: visualize opal growth



Visualization of Opal Growth



Analysis

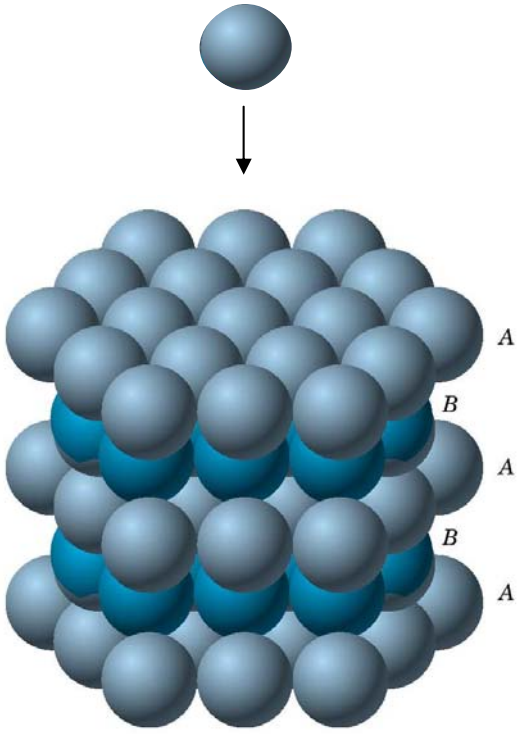


- Evaporation causes dramatic flows of fluid and spheres
- Spheres get sucked into place by the flow
- Unlikely that structure forms in thermodynamic equilibrium
- But, we obtain the lowest energy form - FCC

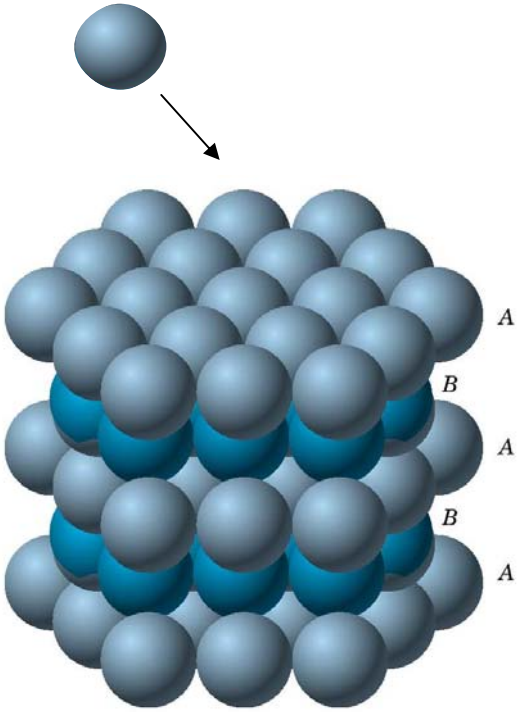
WHY??

Fluid-Driven Assembly

- Solvent flow drives the assembly
- Solvent flow controls the crystal structure?
- Consider two cases . . .

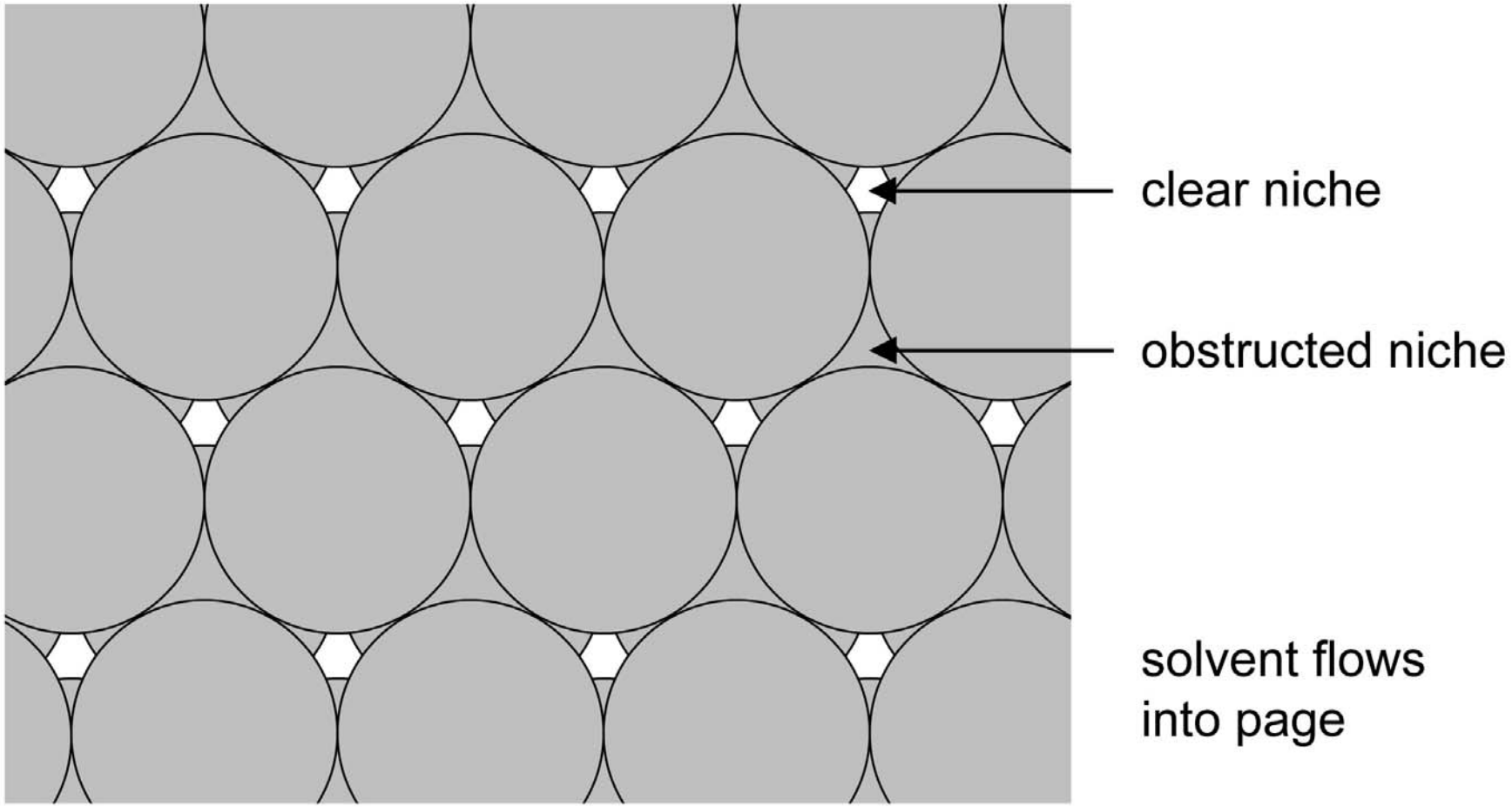


flow into crystal face

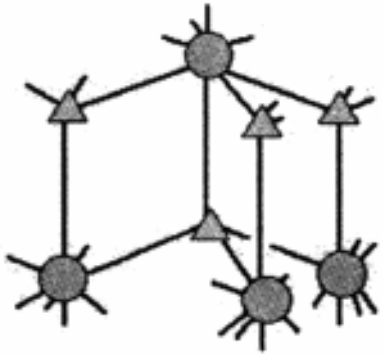


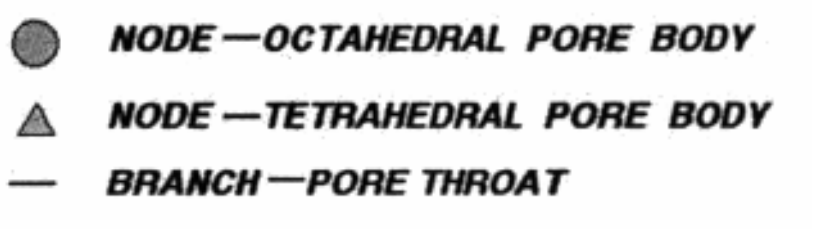
flow with component
along the crystal face

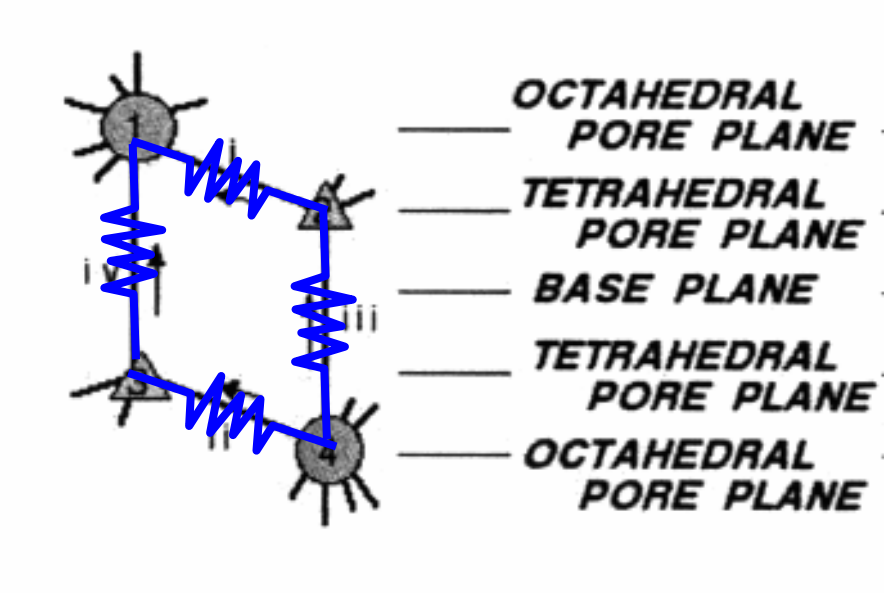
Solvent Flow Into Crystal Face

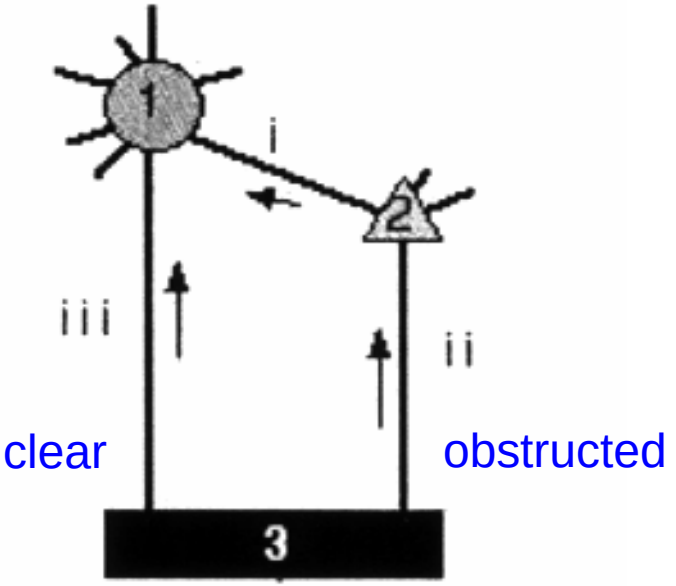


Model Flow Though Interstitials ("Resistors in Parallel")



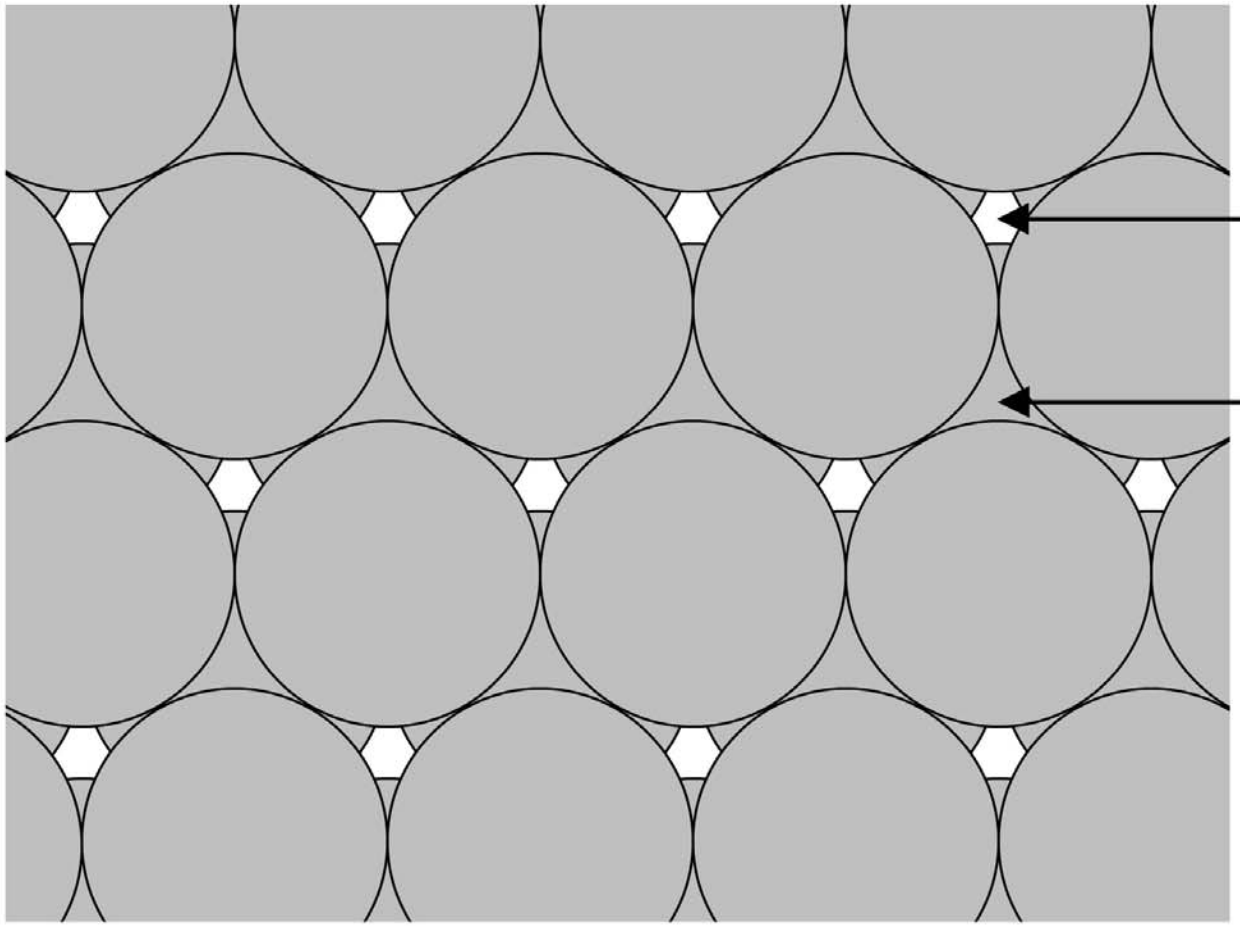






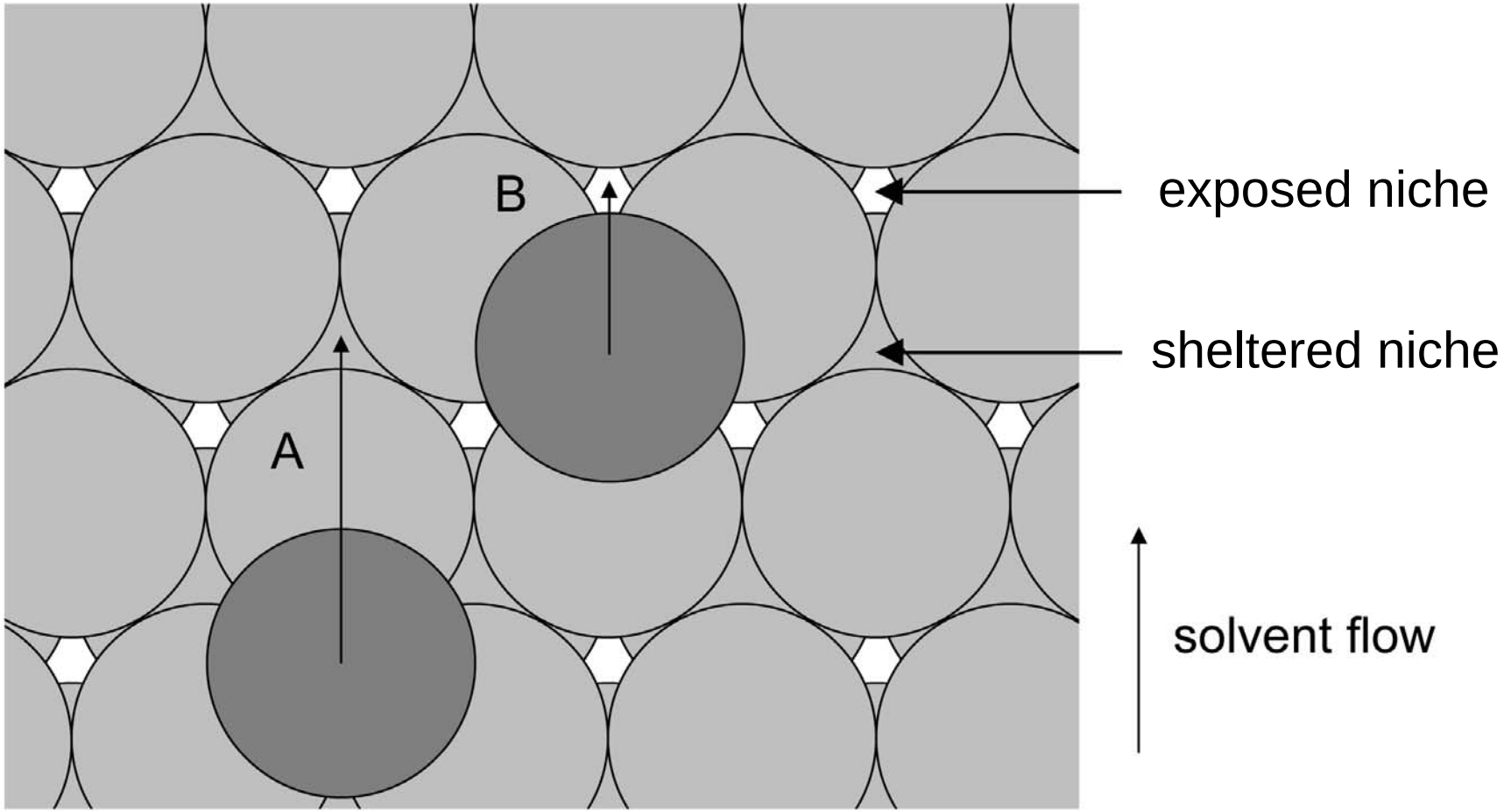
from E. G. Arlinghaus, Ph.D. Thesis, University of Minnesota, 2004.

Solvent Flow Into Crystal Face

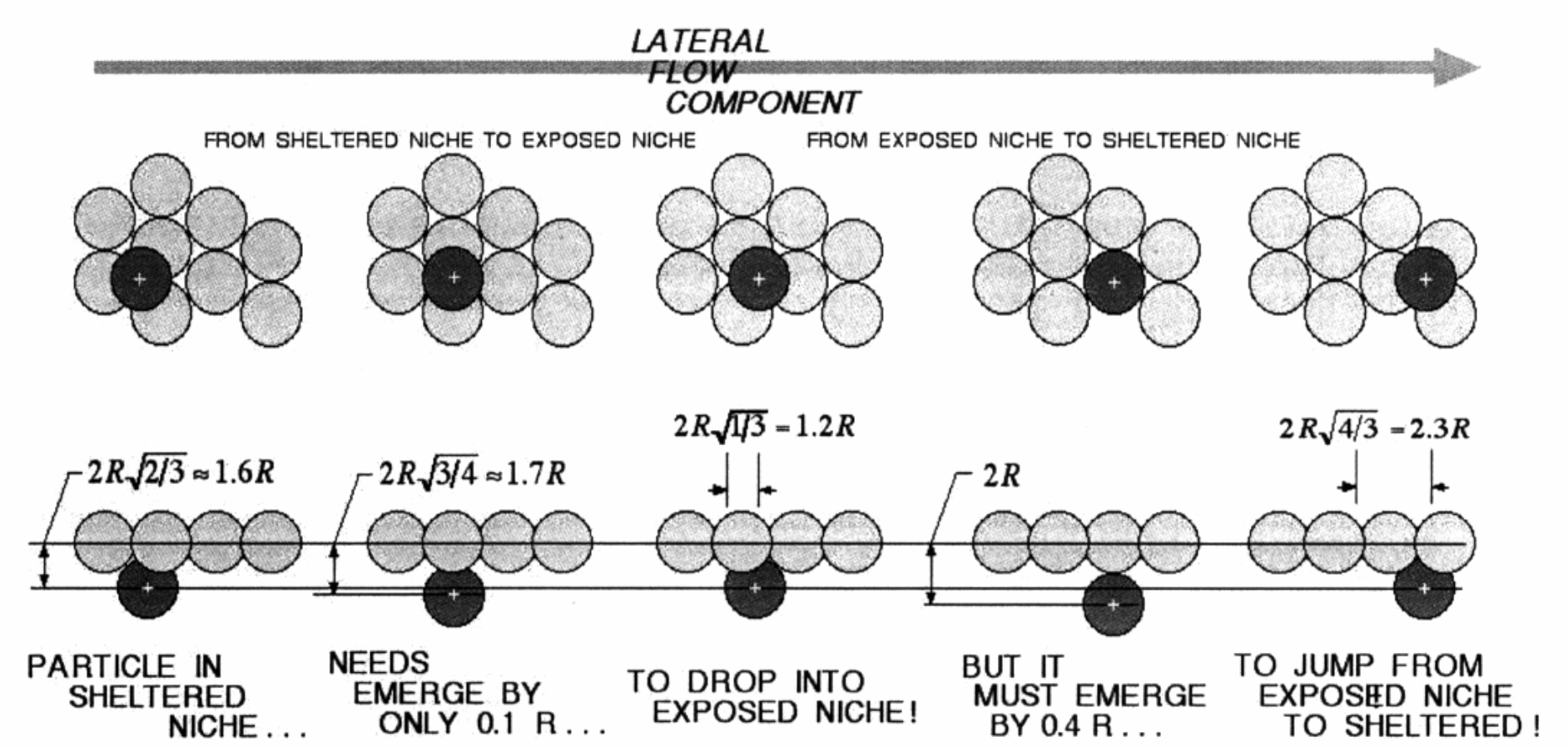


Could explain FCC structure!

Lateral Solvent Flow



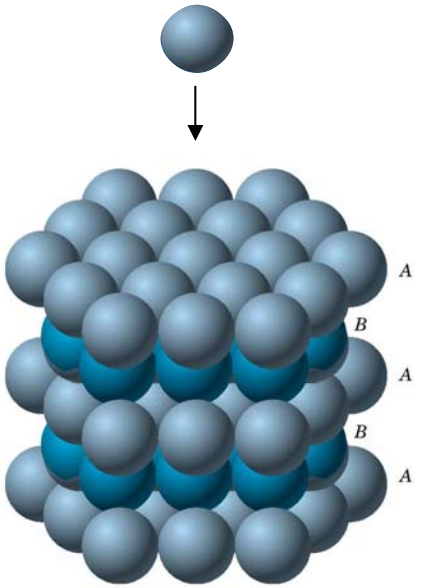
Lateral Solvent Flow



Could explain FCC structure!

from E. G. Arlinghaus, Ph.D. Thesis, University of Minnesota, 2004.

Concluding Thoughts:



- Both possibilities lead to FCC structure!
- Are these flow mechanisms playing a role?
- If so, it is non-traditional self-assembly
- Further work necessary to understand
- Utilize to further eliminate defects in our opals?
- Use fluid flow to create other structures?
- Use different shape building blocks?
- What new materials will this allow us to create?

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Y. Jun
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Prof. L. E. Scriven

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