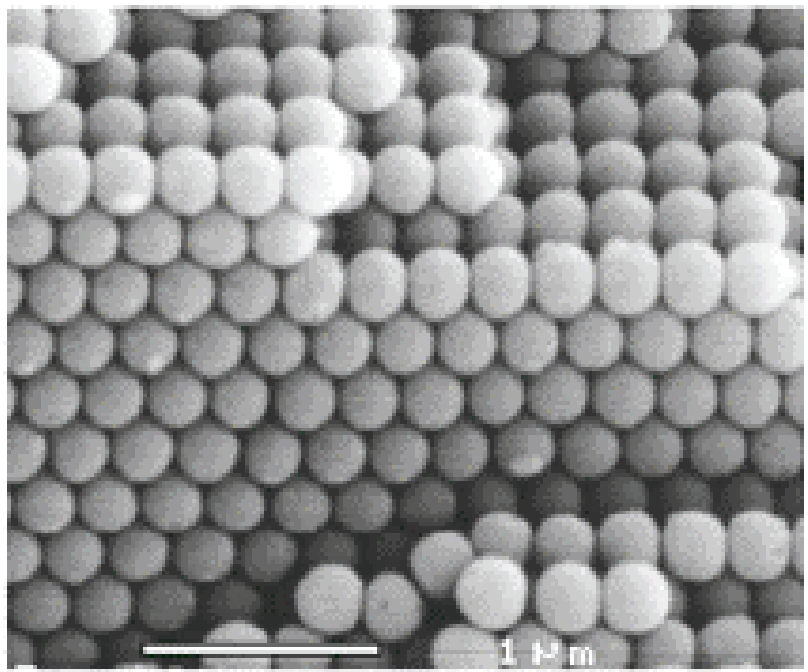
Colloidal crystals



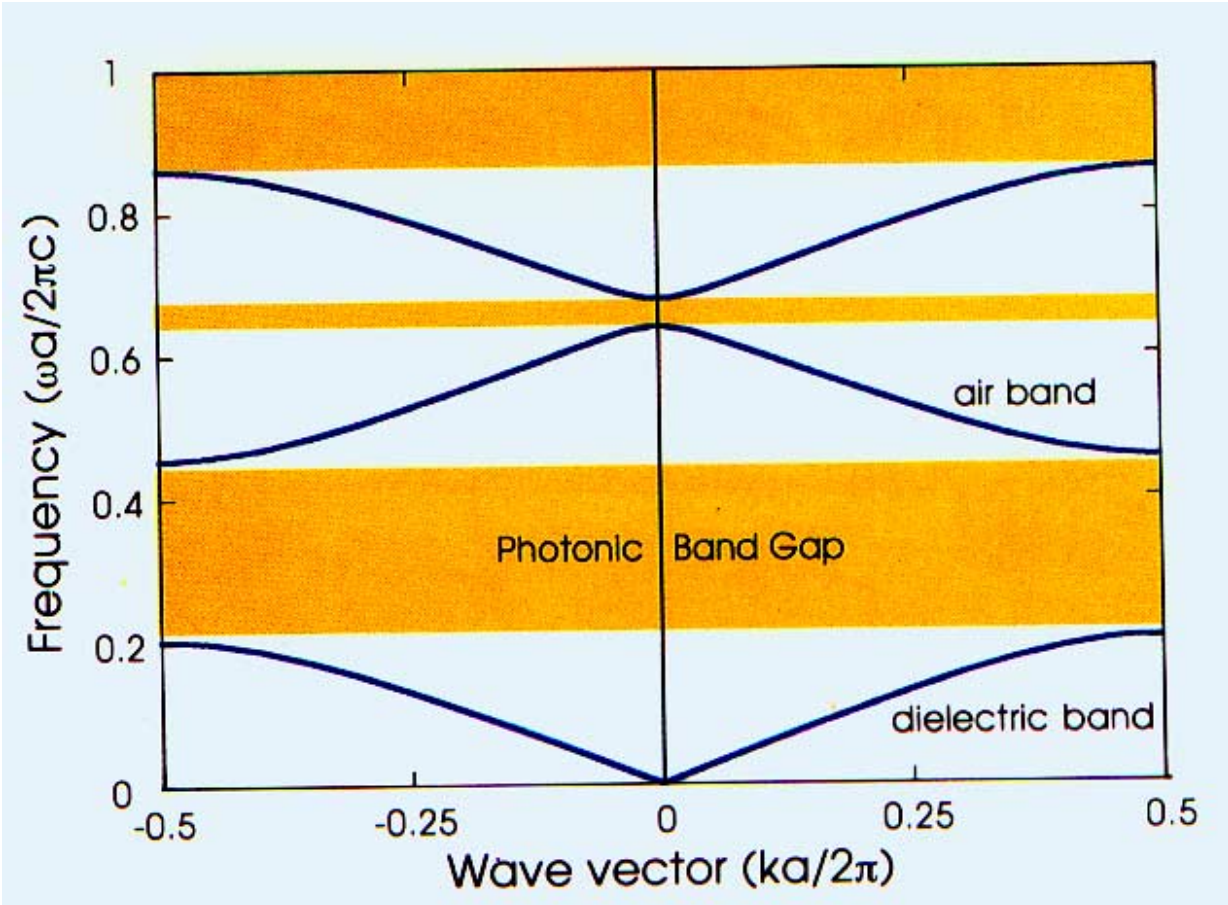
Reasons to make arrays of spheres

Photonic band gap

Normally

$$\nu = \frac{cn}{\lambda}$$

If a material has a periodic variation in the refractive index, there can be a photonic band gap.

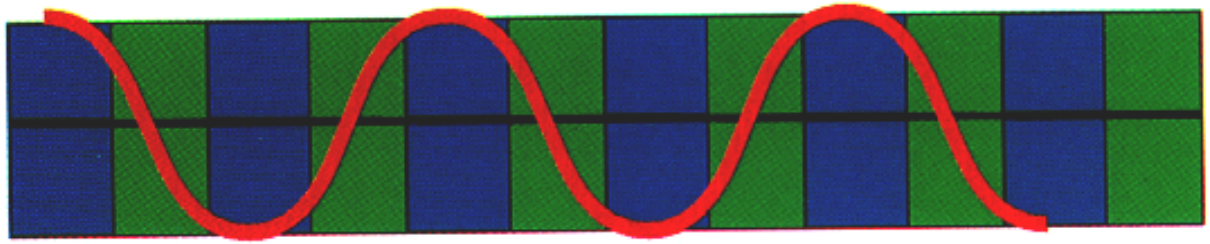


lattice constant = a

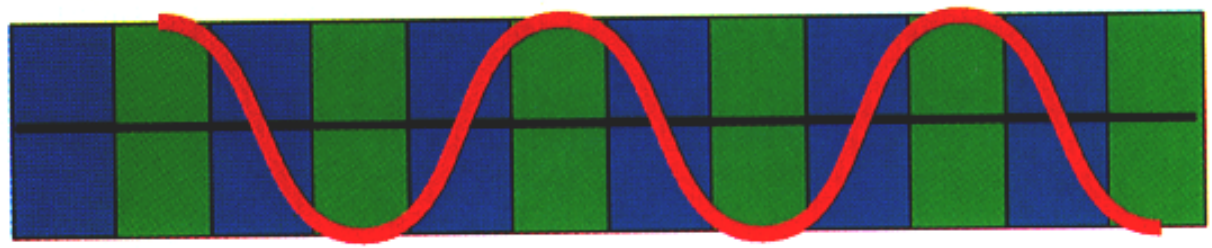
John Joannopoulos, Robert Meade, Joshua Winn, *Photonic Crystals* (1995), p. 42

Origin of the band gap

(a) E-field for mode at top of band 1



(b) E-field for mode at bottom of band 2



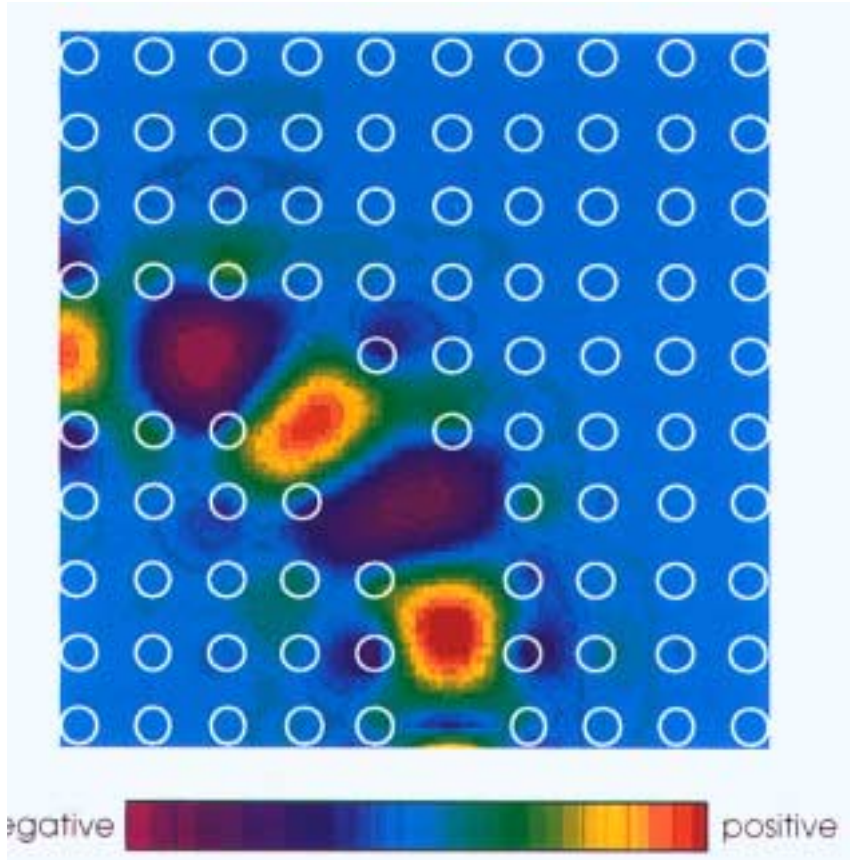
At $ka/2\pi = 0.5$, $\lambda = 2a$. There are two modes with this λ. The top one (a) resides mostly in the high-index material, while the bottom one (b) resides mostly in the low-index material. Consequently, the two modes have a different refractive index, which causes them to have a different frequency and energy.

John Joannopoulos, Robert Meade, Joshua Winn, *Photonic Crystals* (1995), p. 42

Making waveguides with photonic crystals

If a line of lattice sites are removed, light can be confined to the line “defect.”

Light can be steered through very sharp corners with almost no loss.



To learn all about photonic crystals take EE 316/MSE 346 “Nanophotonics”

John Joannopoulos, Robert Meade, Joshua Winn, *Photonic Crystals* (1995), p. 42

Arrays of nanocrystals could be artificial crystals

Three things determine the electronic structure of a crystal

1. The energy levels of the atoms or lattice sites

2. The coupling between adjacent sites

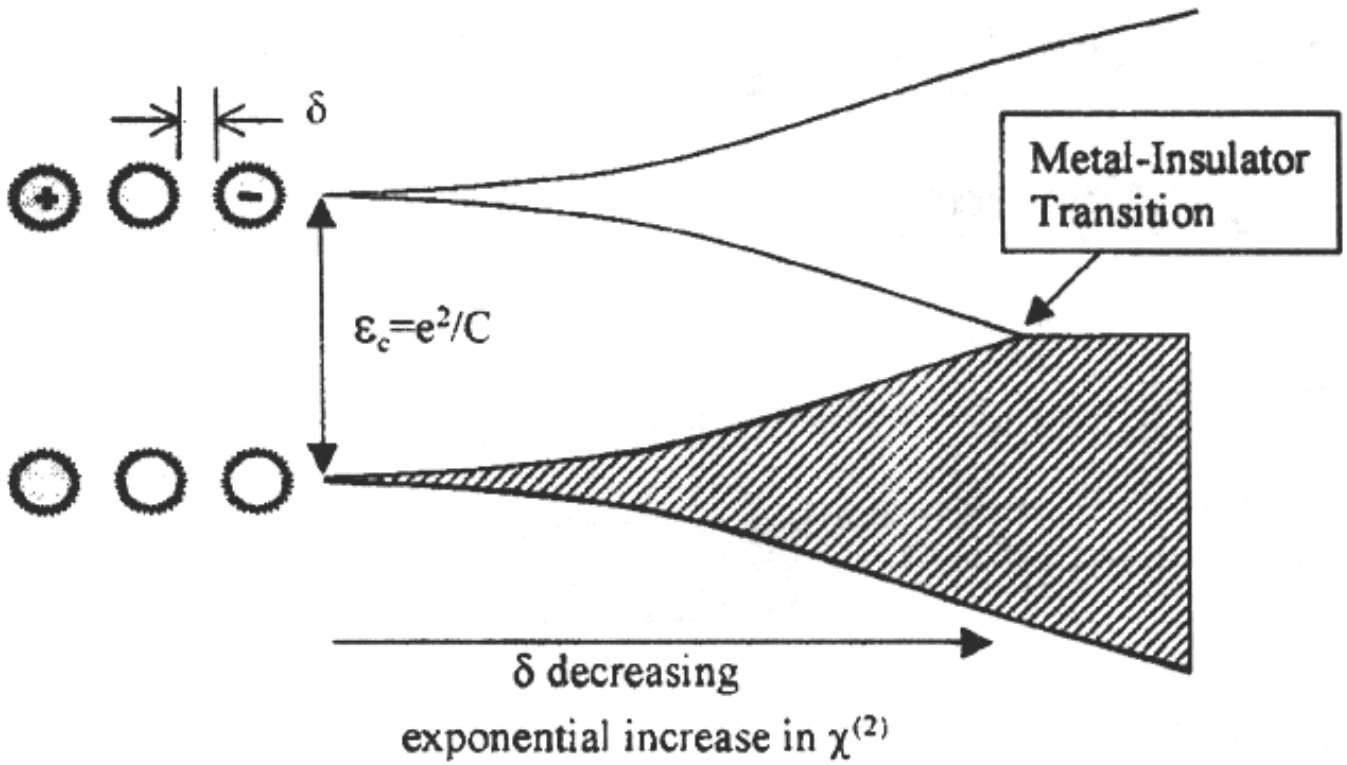
3. The symmetry of the solid.

A remarkably large number of materials with a wide range of properties can be made with the atoms in the periodic table.

New materials could be made if we could independently adjust each of the three parameters. One way to do this is to make arrays of nanocrystals, which can be thought of as artificial atoms.

James Heath et al., “Architectonic Quantum Dot Solids”, *Acc. Chem. Res.* **32** (1999) p. 415.

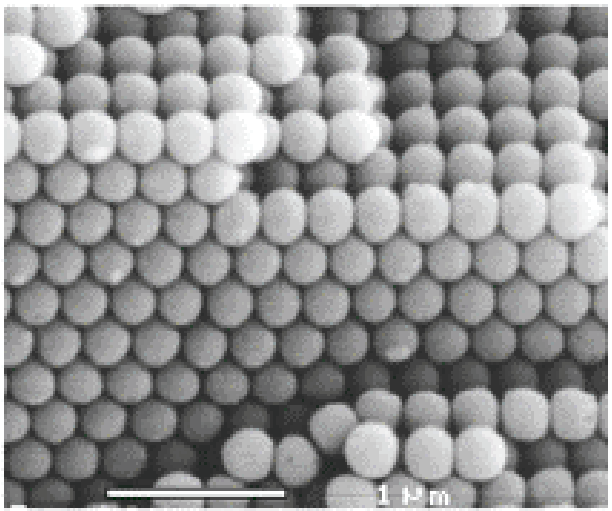
Tuning a crystal through a metal-insulator transition



James Heath et al., *Acc. Chem. Res.* **32** (1999) p. 415.

Making colloidal crystals (synthetic opals)

SiO_2 Opal

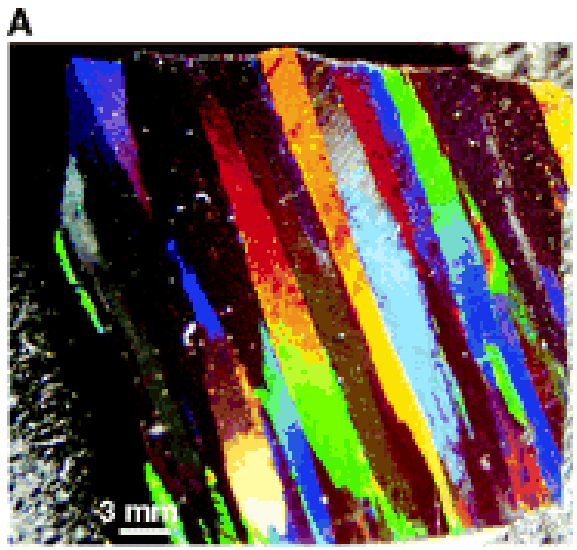


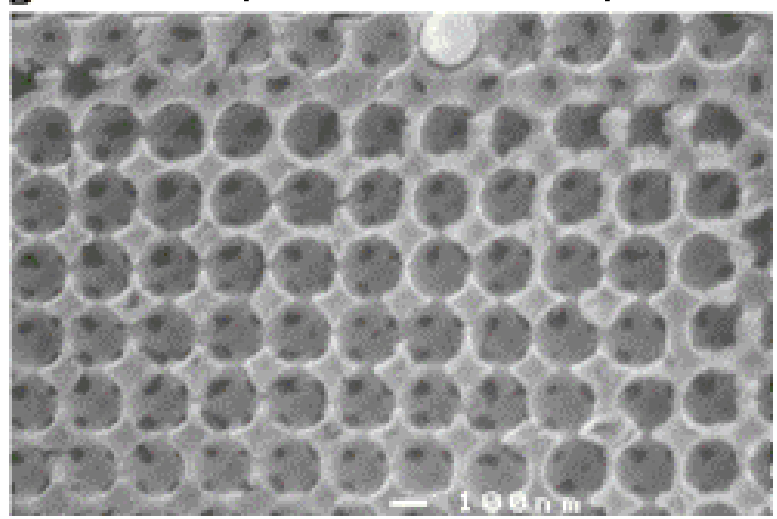
This opal was grown by slow crystallization of a monodispersed SiO_2 colloid over a period of 10 months in a 1-m-long glass cylinder.

The inverse opal or graphite shown below was made by chemical vapor deposition into an SiO_2 opal. After the graphite was formed, the SiO_2 was etched out with HF.

Graphite Inverse Opal

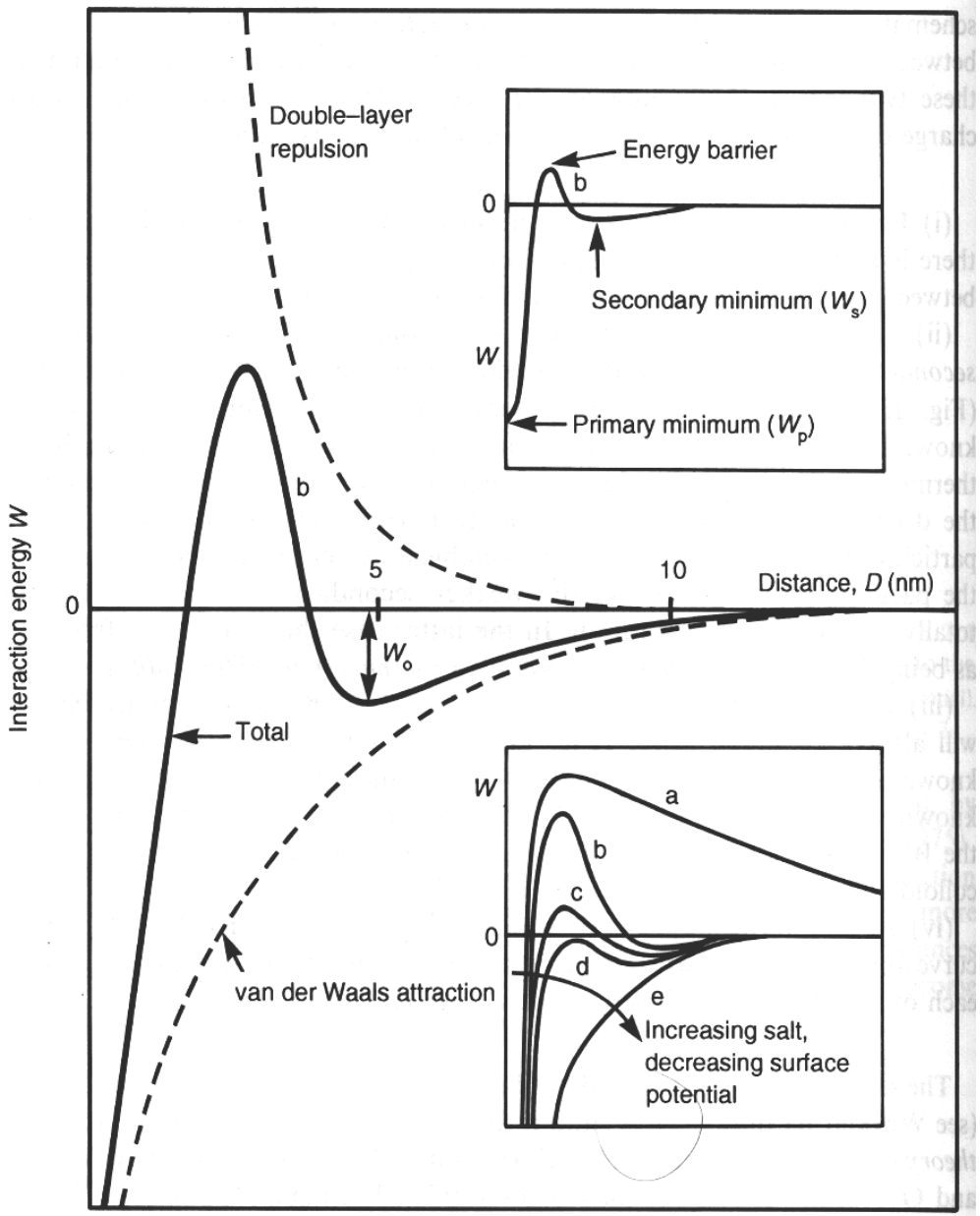
The photograph shows that the lattice reflects light and that the grains have mm dimensions.





Anvar Zakhidov et al., *Science* **282** (1998) p. 897.

Interactions between colloidal particles



VDW interactions pull particles together.

If the particles are charged,
coulomb repulsion can keep them apart.

In most cases, pH determines the charge on the surface.

Salt can be used to screen Coulomb repulsion.

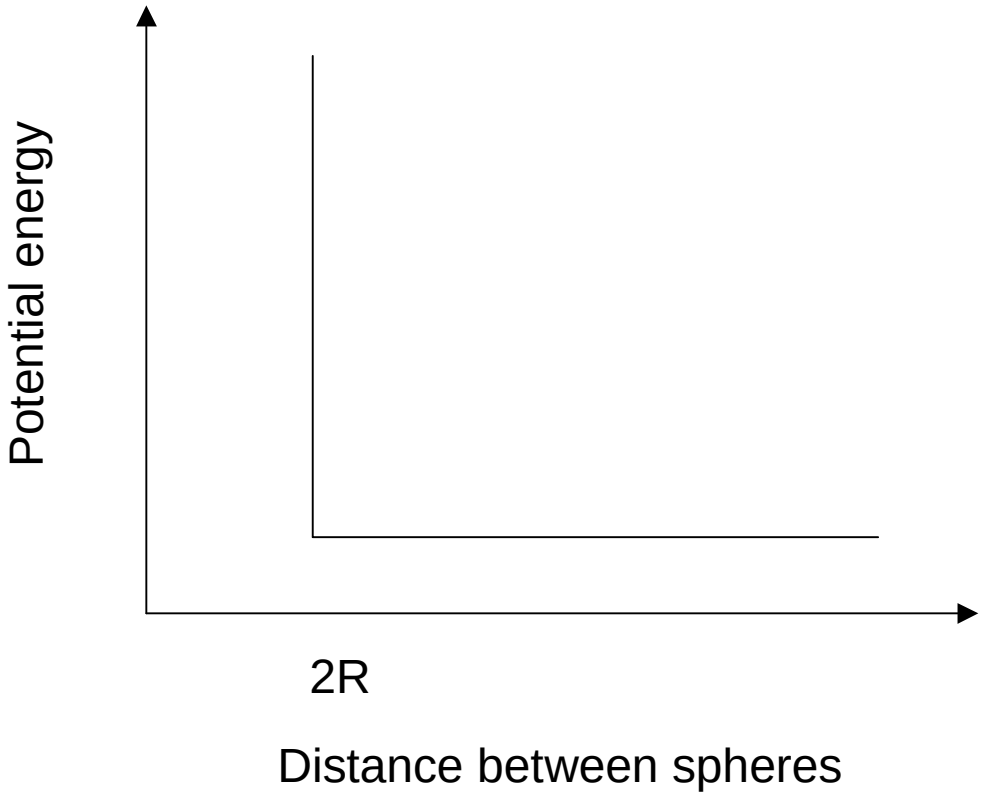
Jacob Israelachvili
Intermolecular and Surface Forces
p. 248.

Strong repulsion limit

If the spheres are charged, then they repel each other. An ordered structure will form rapidly so that the distance between sphere can be maximized. The crystal fills the container it is in.

Unfortunately, in this case the spheres do not touch. If the liquid is removed, the structure is destroyed.

Hard sphere limit



The spheres don’t attract each other at all. If they touch, they strongly repel because they cannot interpenetrate each other.

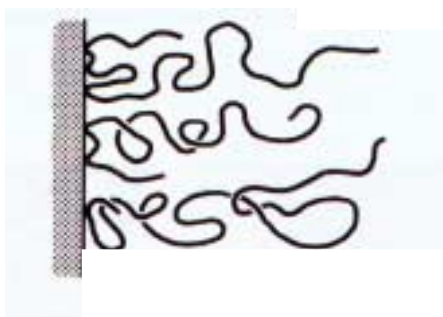
Achieving the hard sphere limit

Most people achieve the hard sphere limit by:

1. Using spheres made of materials that are not easy to polarize (e.g. SiO_2)

2. Matching the refractive indices of the sphere and the solvent (This results in the VDW interactions between the spheres being almost exactly the same as those between a sphere and the solvent.)

3. Grafting polymer chains to the surface. (If the spheres get too close the side chains are compressed and their entropy is reduced.)



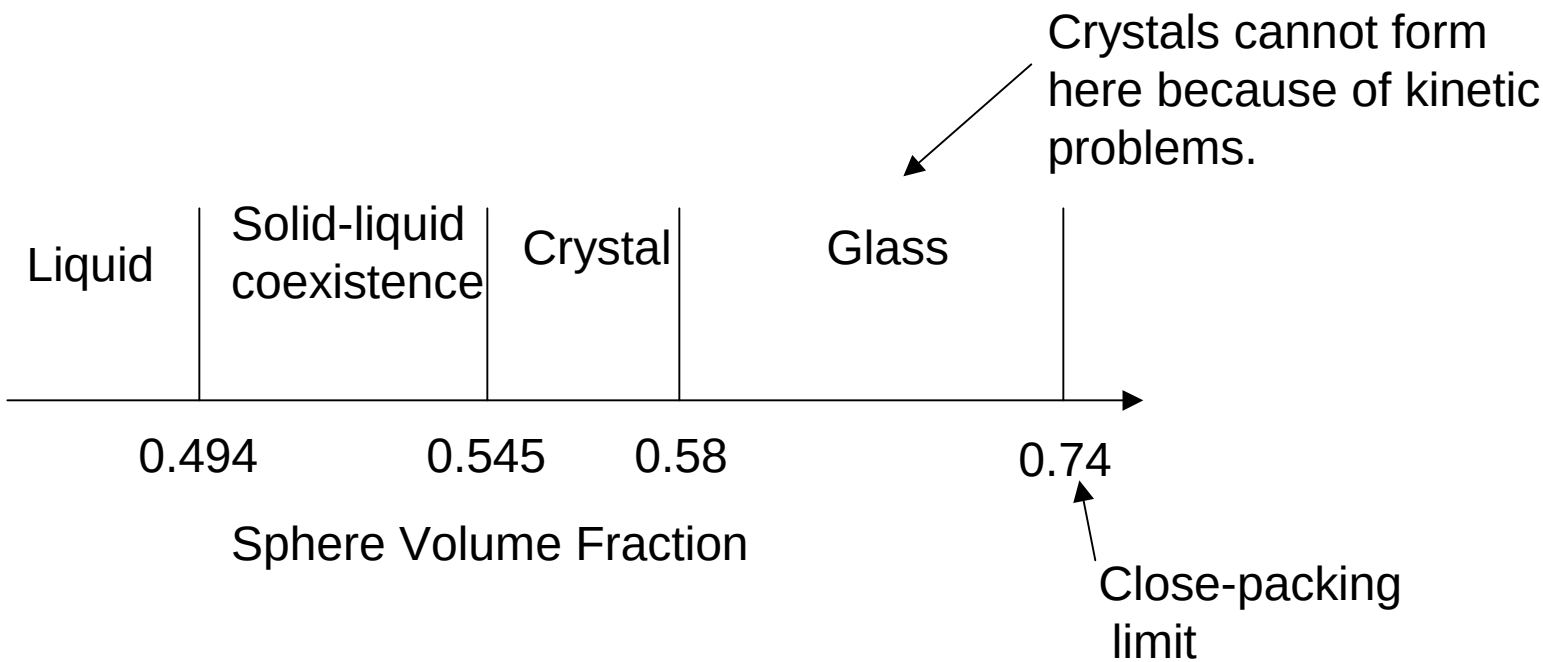
Why do hard-sphere colloidal crystals form?

Since the interactions between spheres are negligible, enthalpy does not play a role in determining whether or not a crystal will form.

Surprisingly, crystals form because they have more entropy.

In a disordered structure, some spheres are pinned at a certain site.
In an ordered structure, there is more room for each sphere to rattle around, so there is more conformational entropy.

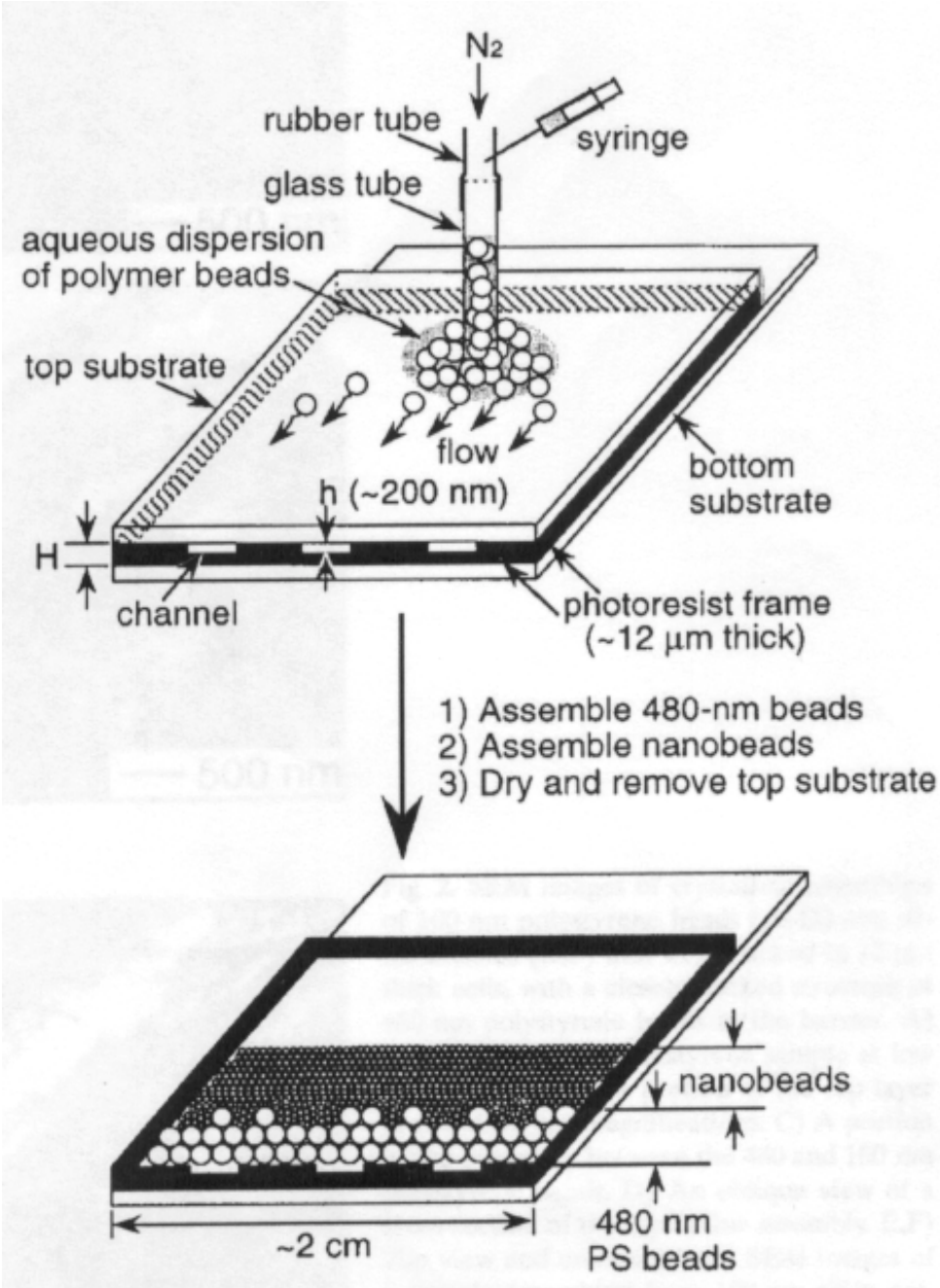
Phase diagram of hard spheres in a solvent



The phase does not depend on temperature because there is no ethalpy term in the free energy. (G = -TS)

P.N. Pusey, *Nature* **320** (1986) p. 340.

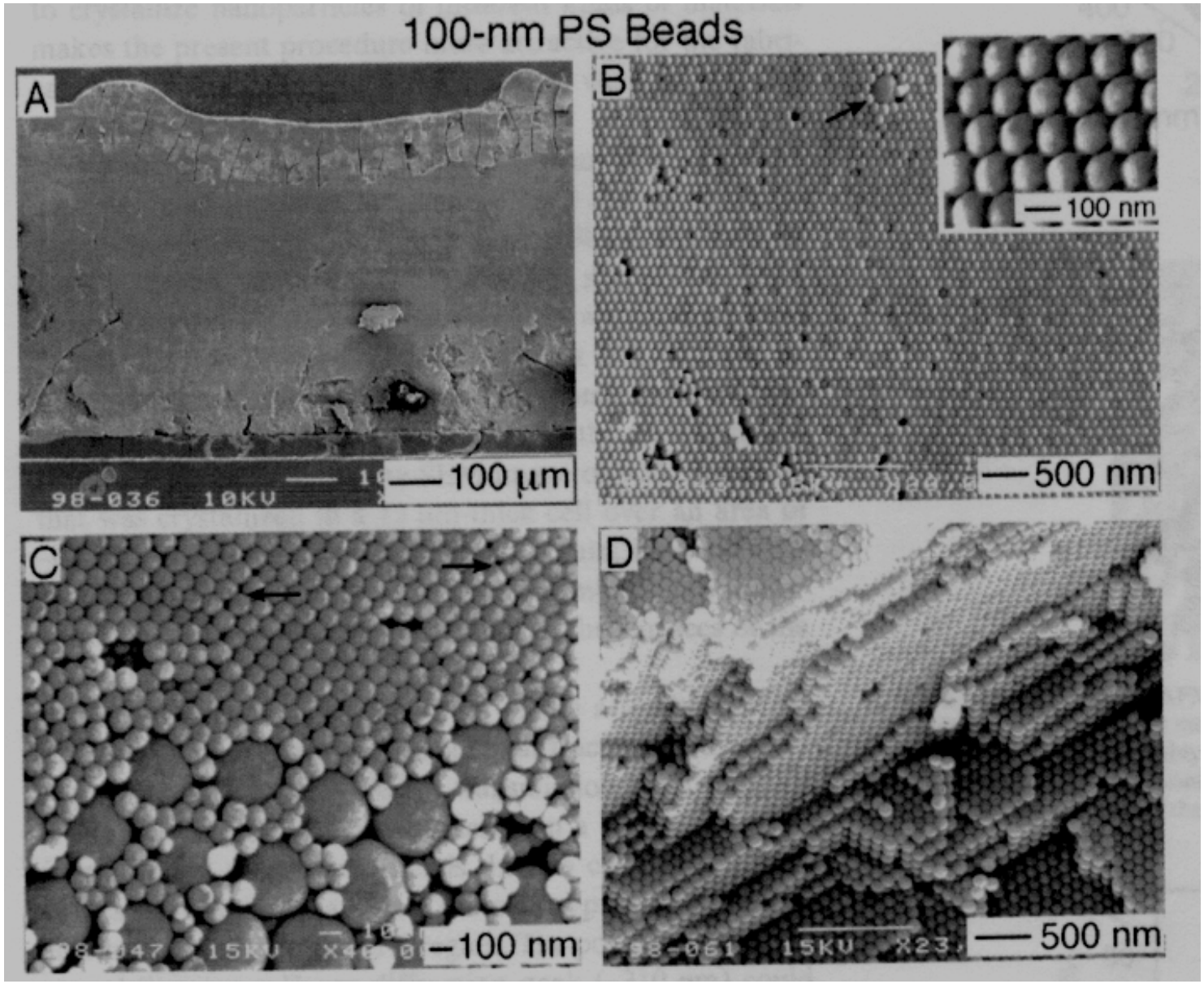
Colloidal-crystal thin films



The large beads at the bottom stop the smaller beads from passing through, but allow the watert to pass.

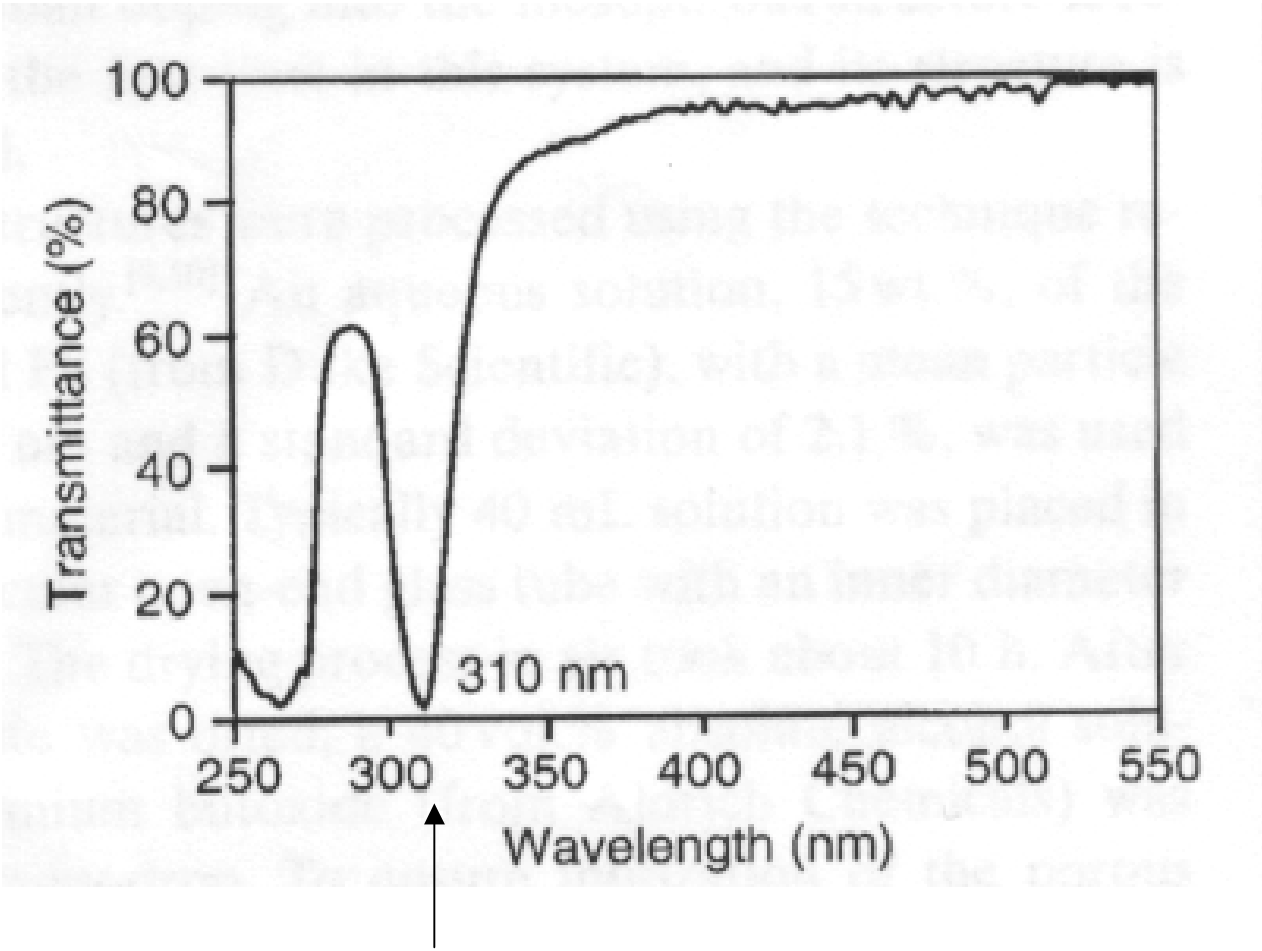
Byron Gates, Younan Xia
Advanced Materials **11** (1999) p. 466.

Colloidal crystal thin films



Byron Gates, Younan Xia
Advanced Materials **11** (1999) p. 466.

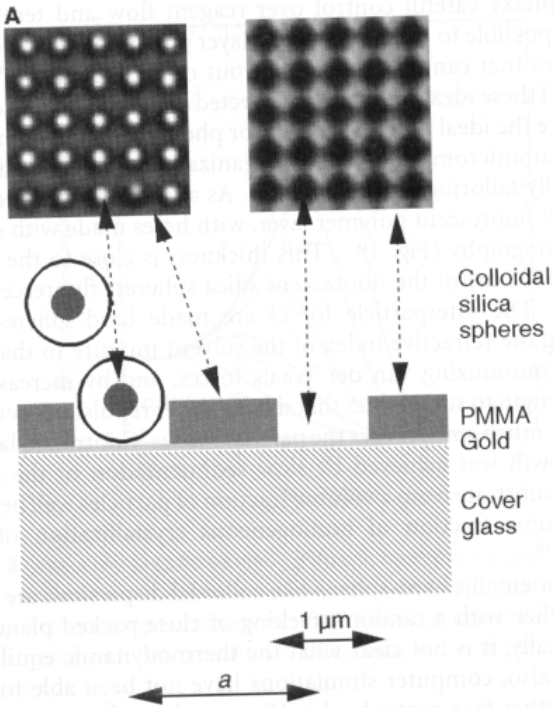
Diffraction off of the thin film



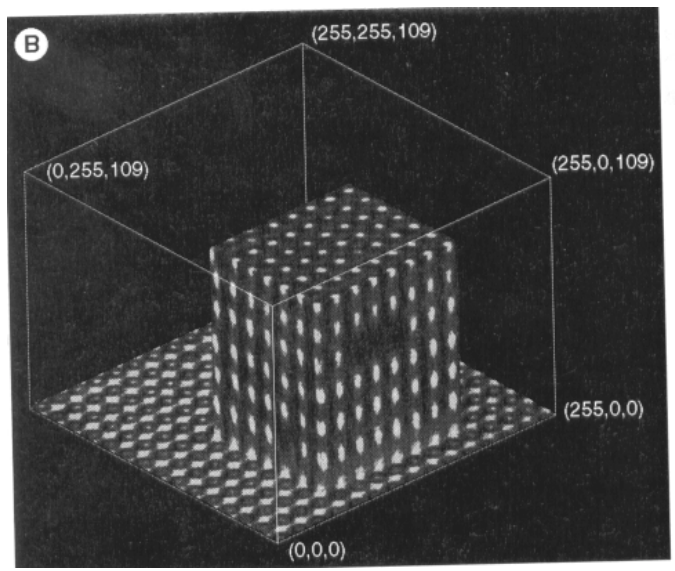
Light is Bragg reflected.

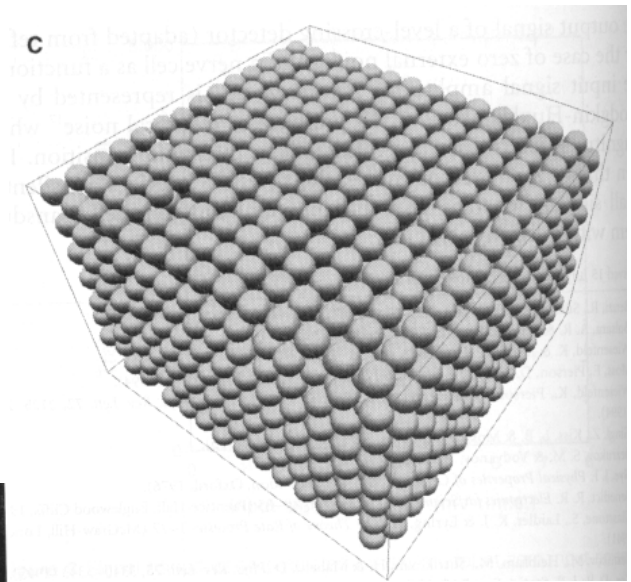
Byron Gates, Younan Xia
Advanced Materials **11** (1999) p. 466.

Epitaxial growth of colloidal crystals



Confocal micrograph of a crystal

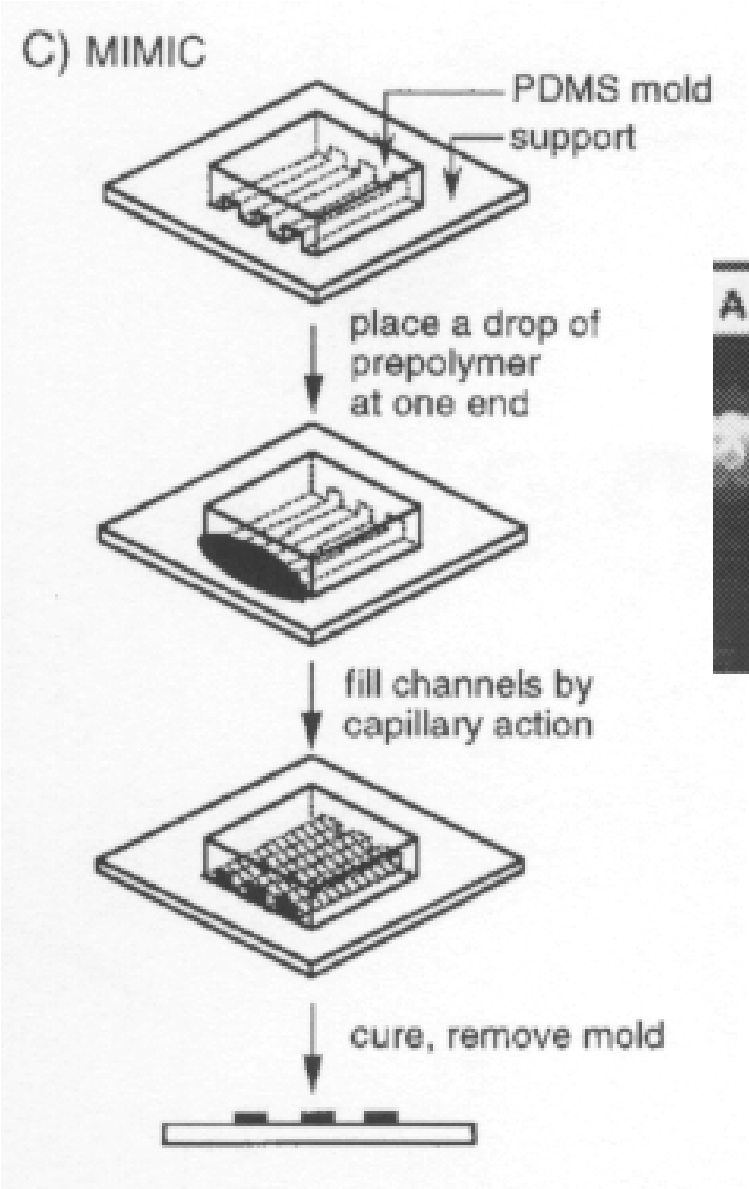


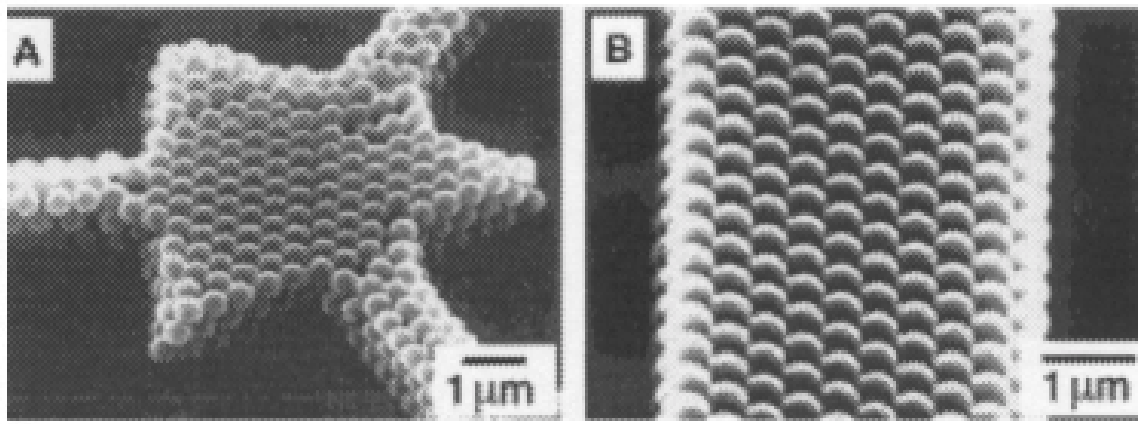


Computer generated picture of experimental data

Van Blaaderen et al., *Nature* 385 (1997) p. 321.

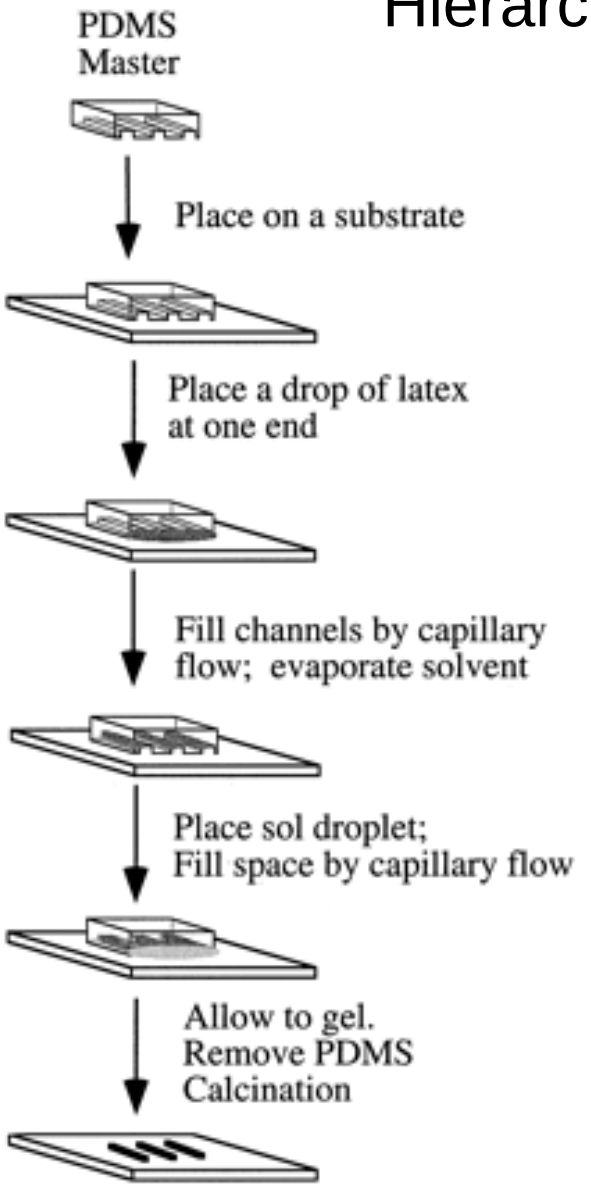
Controlling the shape of colloidal crystals with micromolding



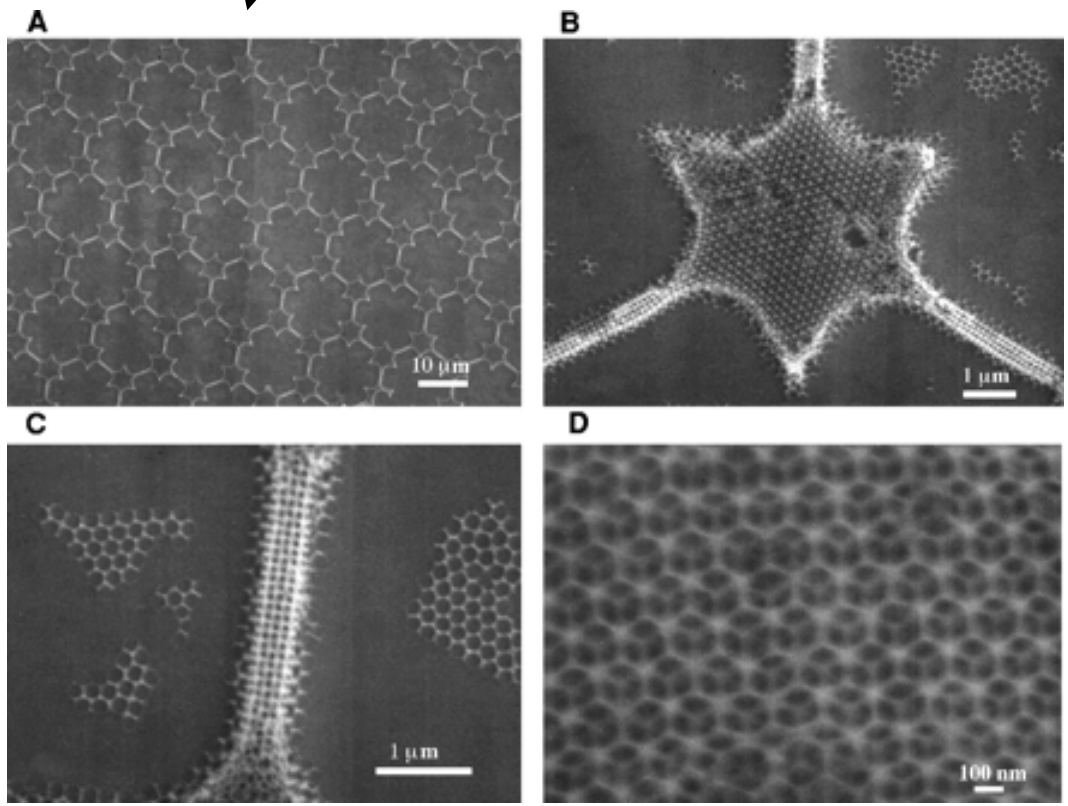


Whitesides, *Angew. Chem. Int. Ed*. **37** (1998) p. 550.

Hierarchically ordered materials



The stamp controls mm-size features

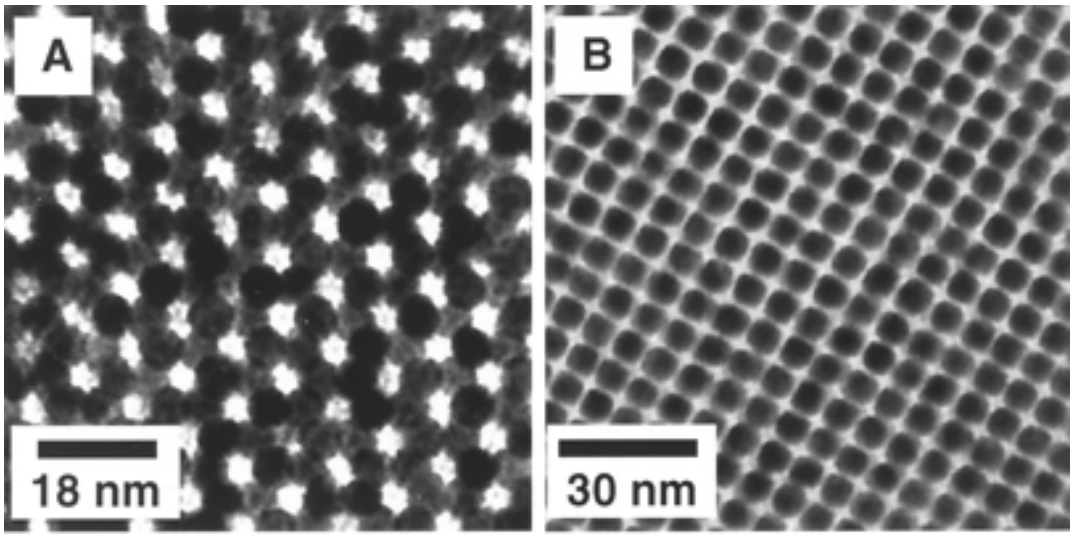


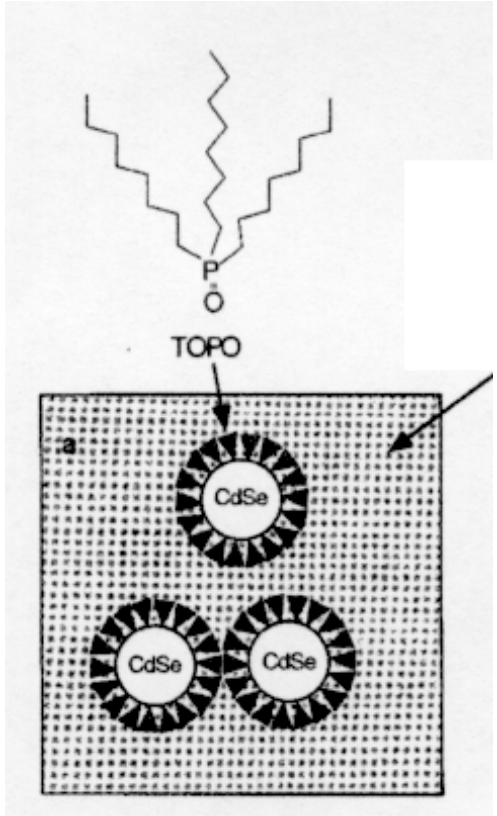
Polystyrene sphere determine the structure on the 100-nm length scale.

The block copolymer-silica solution self-assembles on the 10-nm length scale.

Peidong Yang et al.
Science **282** (1998) p. 2244.

Periodic arrays of nanocrystals





Self-assembly of superlattices readily occurs when a dispersion of monodisperse nanocrystals is spread on a substrate and the carrier solvent is allowed to slowly evaporate. The spheres don't touch each other because they are surrounded by organic surfactants like the ones shown to the right.

The nanocrystals shown above are magnetic $Fe_{50}Pt_{50}$ particles. IBM is exploring the use of these materials for magnetic recording.

Chris Murray et al. *Science* **287** (2000) p. 1989.
Science **270** (1995) p. 1335.

Conclusions

• Periodic crystals with periodicities from ~ 5 to 1000 nm can be made with spheres.

• The degree of order is usually far from perfect, but can be enhanced with patterned substrates.

• My opinion is that lithography techniques will probably be necessary to build the photonic crystals that most people want. I don't yet see how the defects that are needed to make waveguides, cavities, etc. can be self-assembled.

• Self-assembly faces stiff competition in the > 100 nm regime because optical lithography works well there.