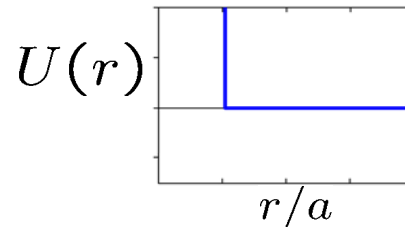
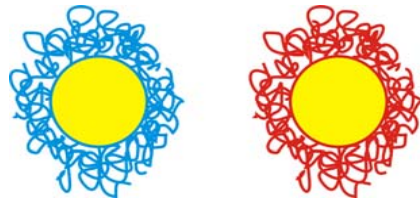
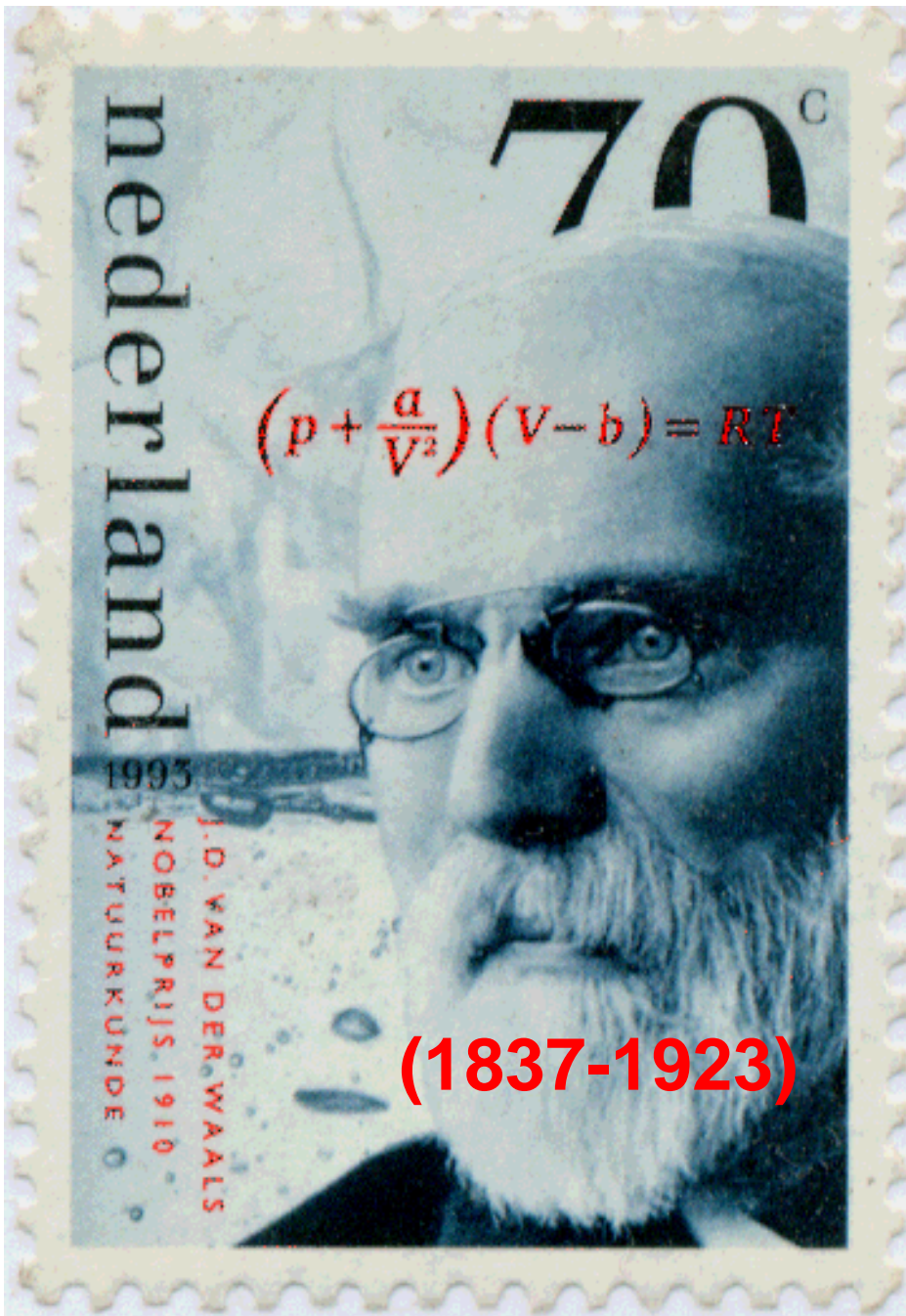


# The Program

- Lecture 1: Phase transitions in atomic and molecular systems
- Lecture 2: Colloids as atoms
- **Lecture 3: Hard spheres**



- Lecture 4: Hard spheres + attraction
- Lecture 5: Rods
- Lecture 6: Platelets



Over  
De continuïteit van den gas –  
en vloeistofoestand.

Proefschrift Leiden, 1873.

Condensatie vereist  
attractie en repulsie

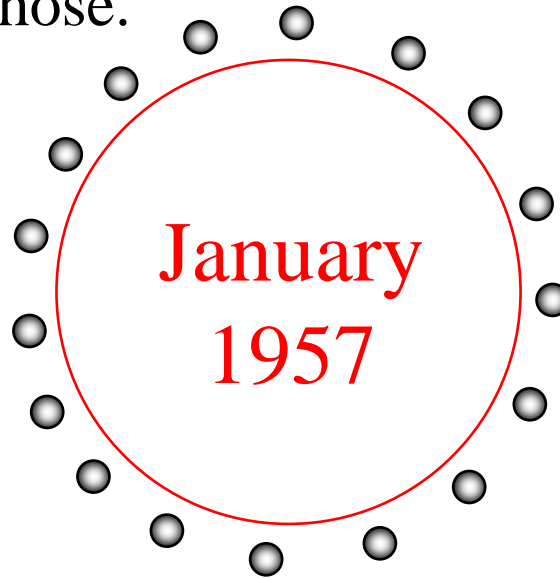
maar kristallisatie...

# Geen attractie, toch faseovergang!?



George E. Uhlenbeck  
(1900-1988)

“...the transition goes a little bit **against intuition**; that is why so many people have difficulty with it, and surely, I am one of those.”



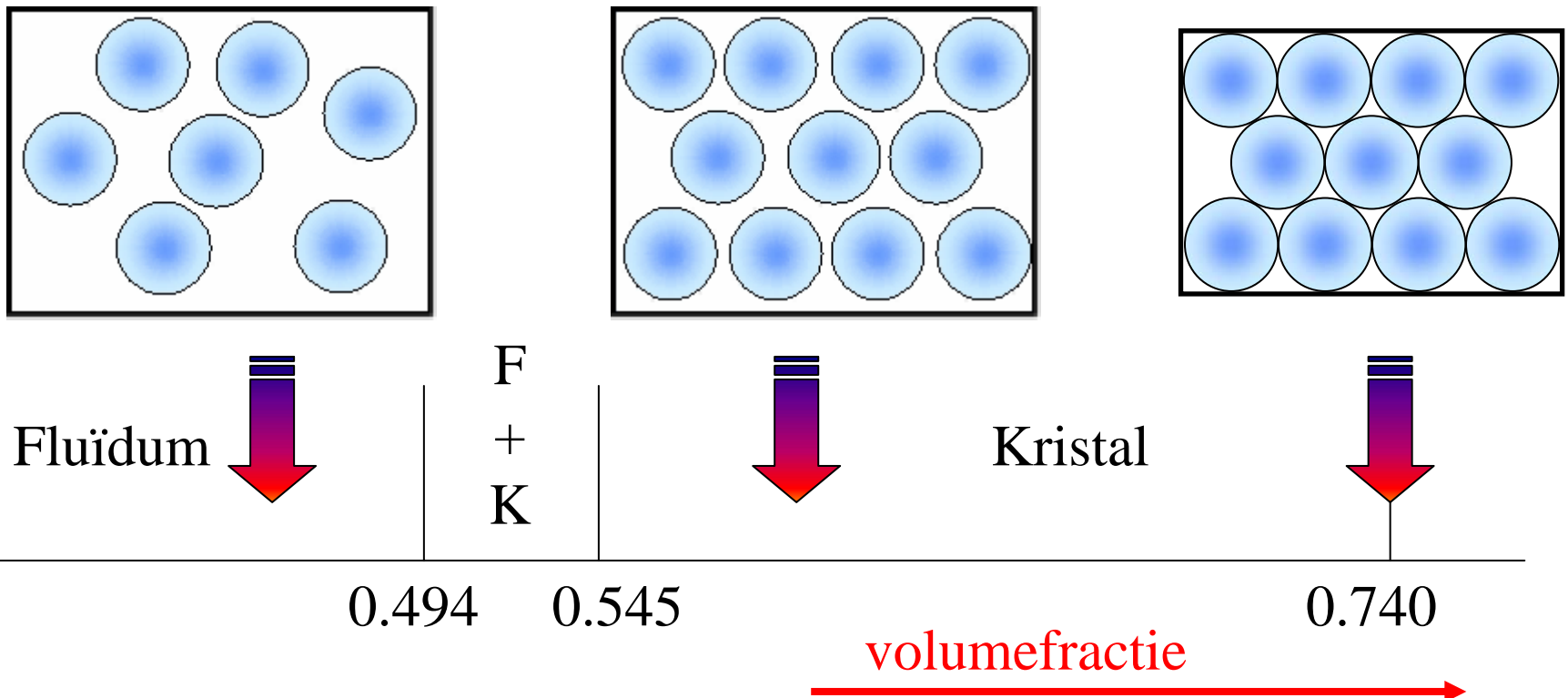
“I think it is quite **unnecessary** to have an **attractive force** to achieve a crystalline phase and one can produce simple intuitive arguments for that.”



*John G. Kirkwood*  
(1907-1959)

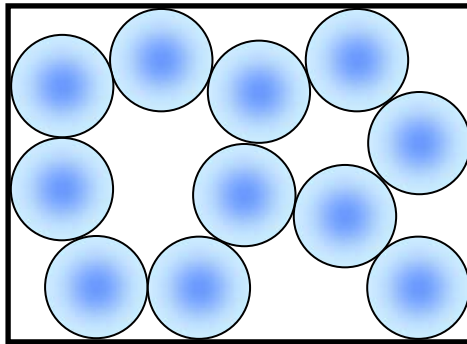
# Harde bollen met thermische beweging

Computersimulaties: Alder & Wainwright (1957)  
Wood & Jacobson (1957)

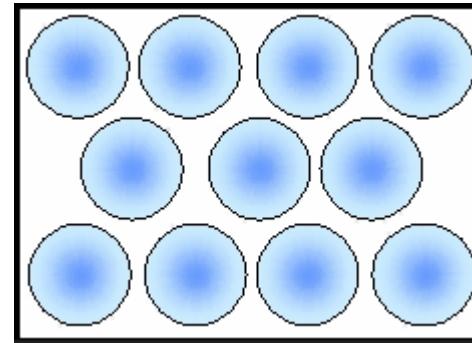


# Ordering door entropie

**Fluidum:**  
**wanordelijke stapeling**

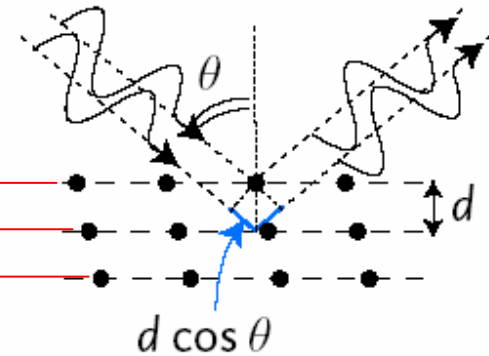
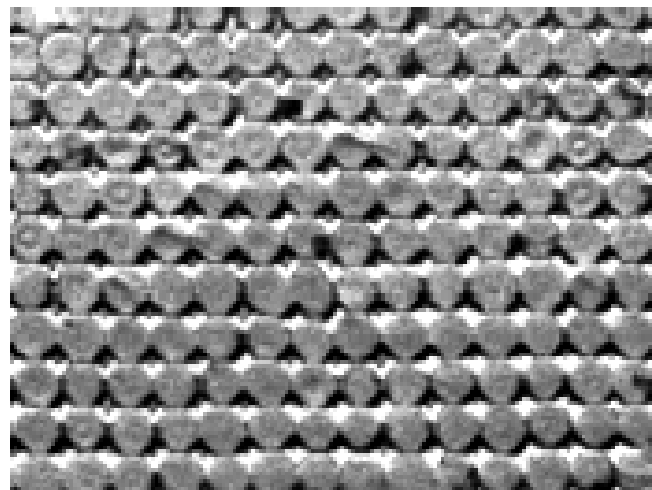
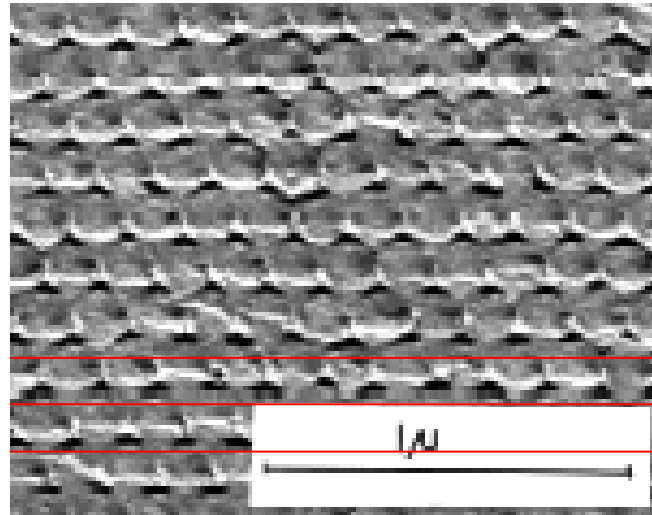
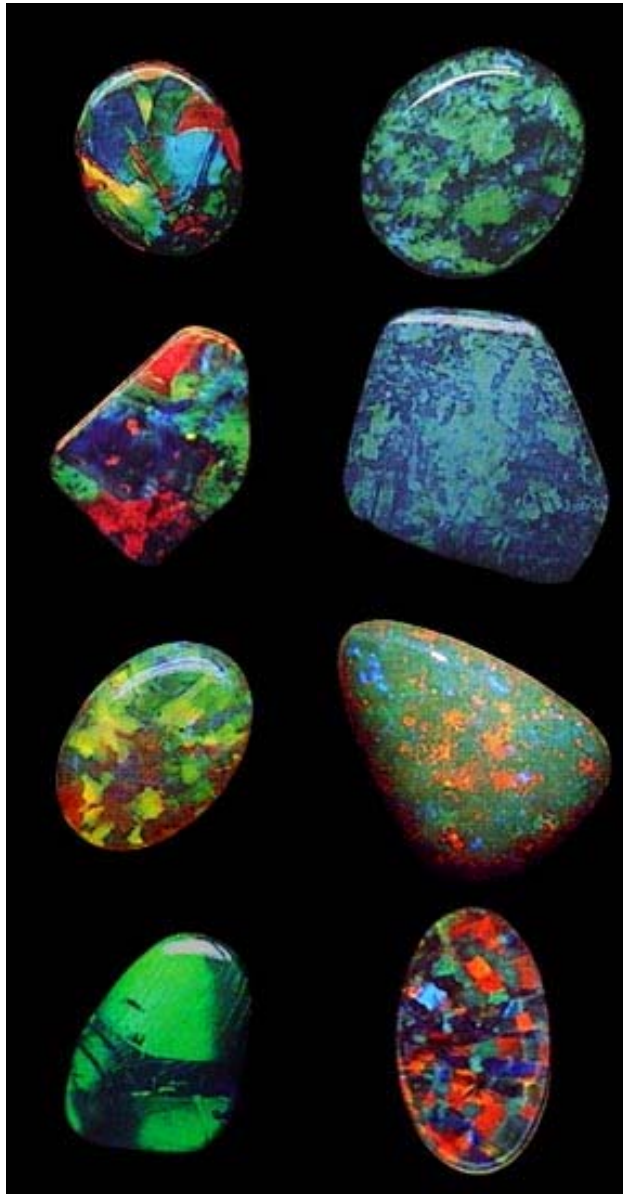


**Kristal:**  
**geordende stapeling**



	<b>Fluidum</b>	<b>Kristal</b>
$S_{\text{stapeling}}$	hoog	laag
$S_{\text{vrij volume}}$	laag	hoog

# Opaal: geordende silicabollen

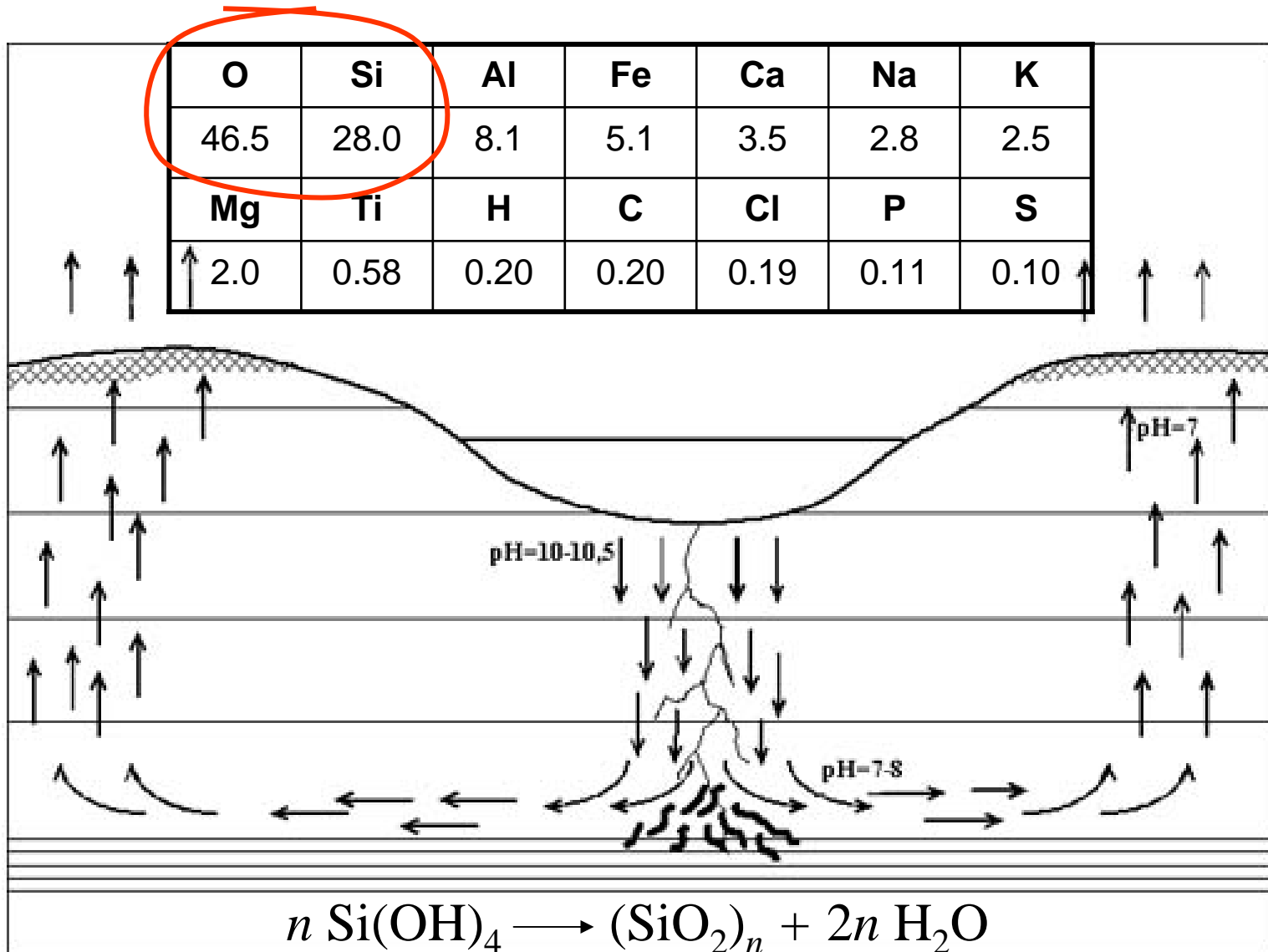


wet van Bragg  
(1912):

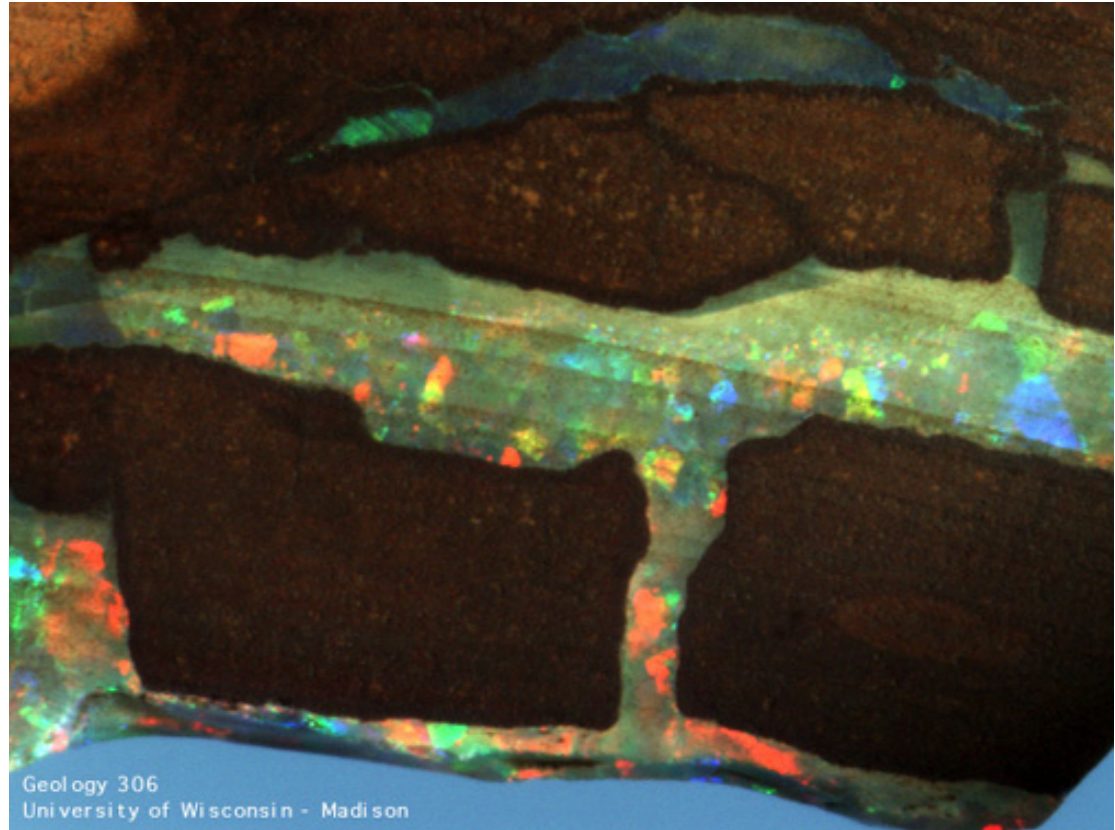
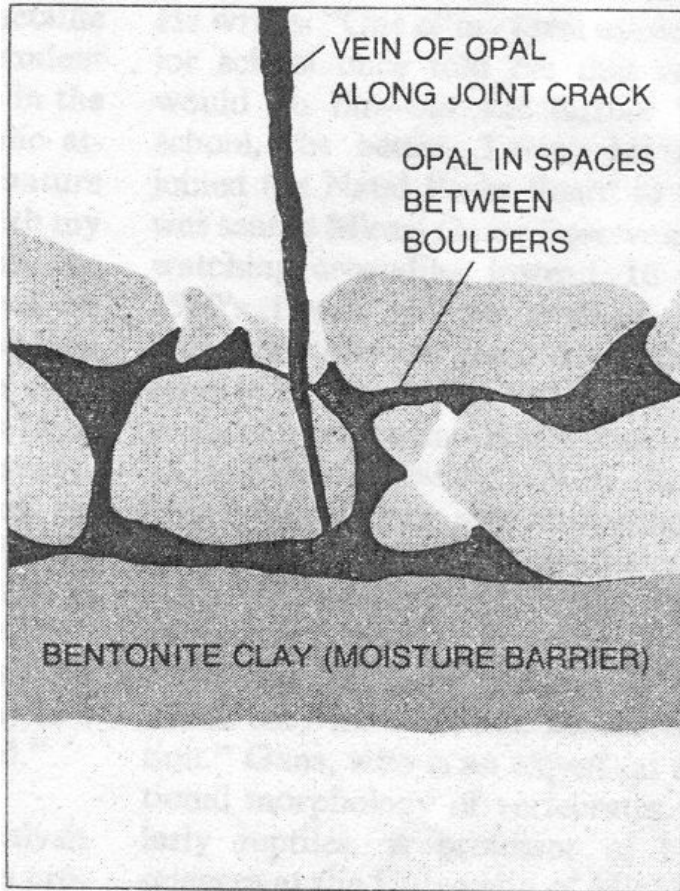
$$2d \cos \theta = \lambda$$

Sanders (1968)

# Geochemical formation of opal

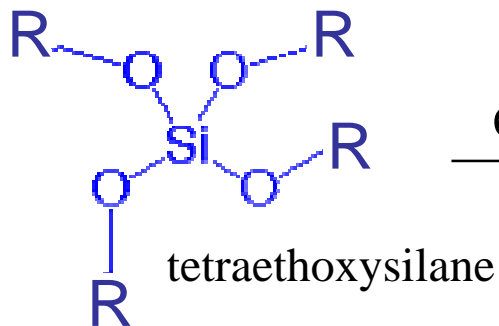


# Geochemie

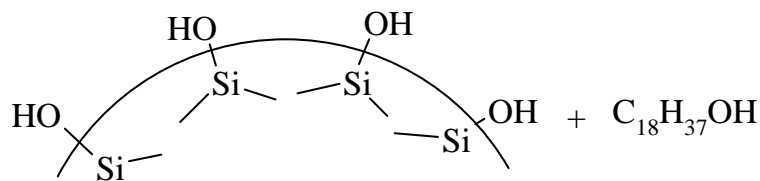
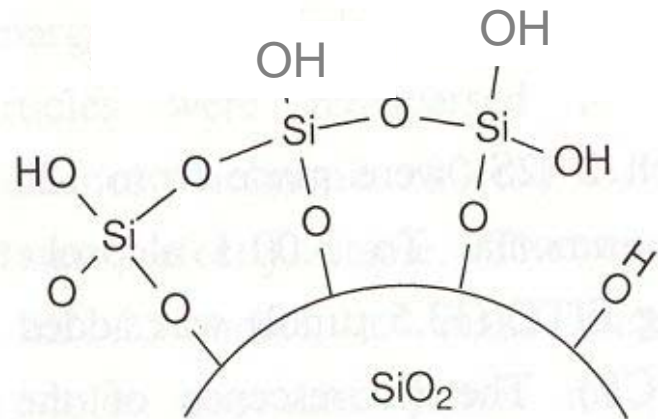




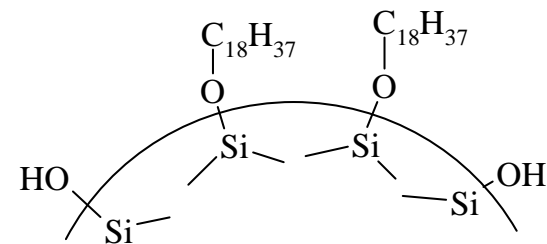
# Silica particles in the laboratory: Stöber-synthesis



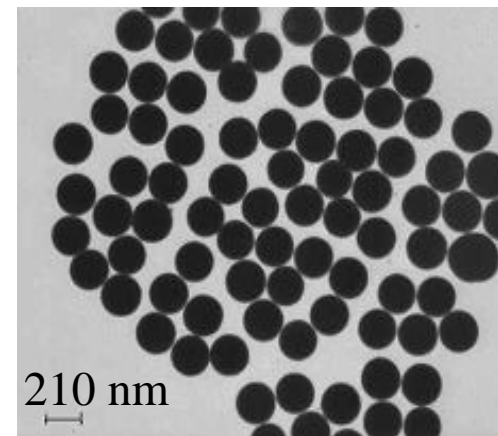
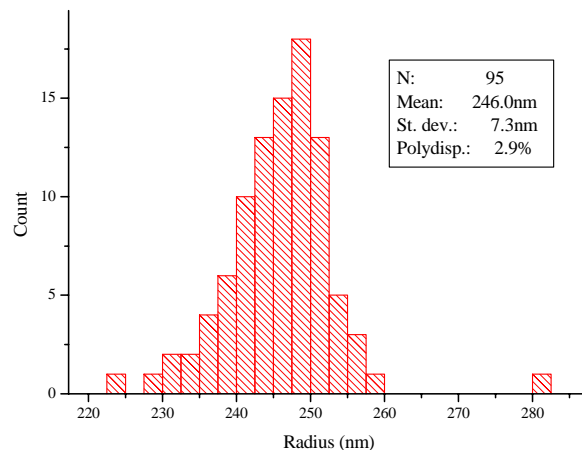
ethanol + ammonia



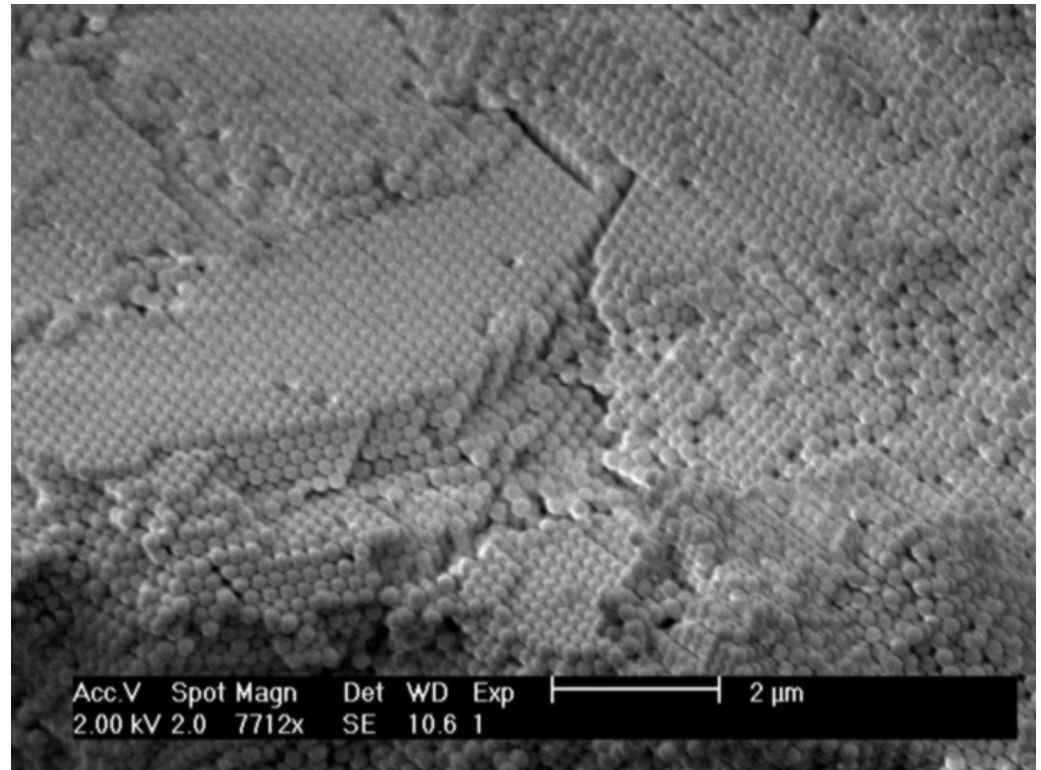
$\Delta T$   
(frituur)



zeer monodispers!



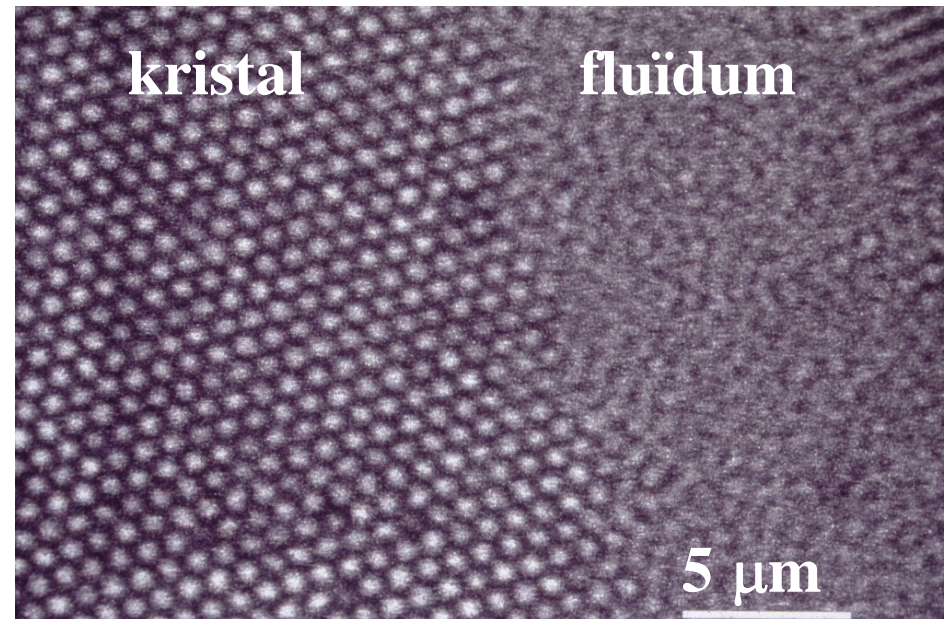
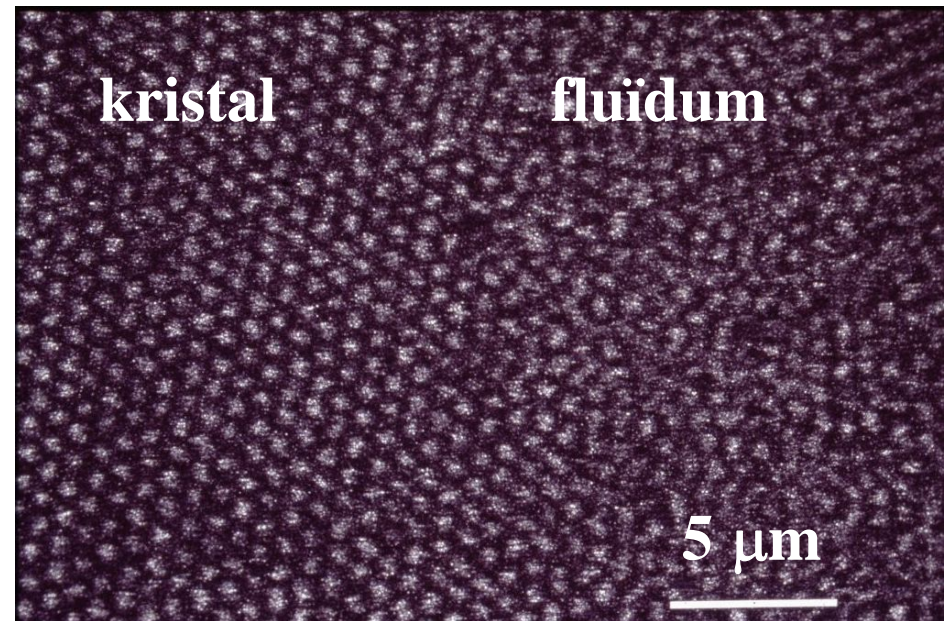
# Kristallen van colloïdale bollen

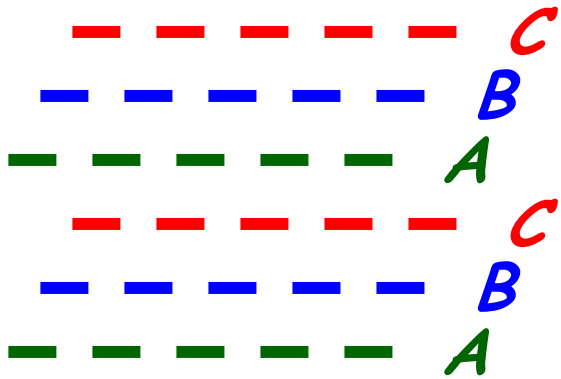
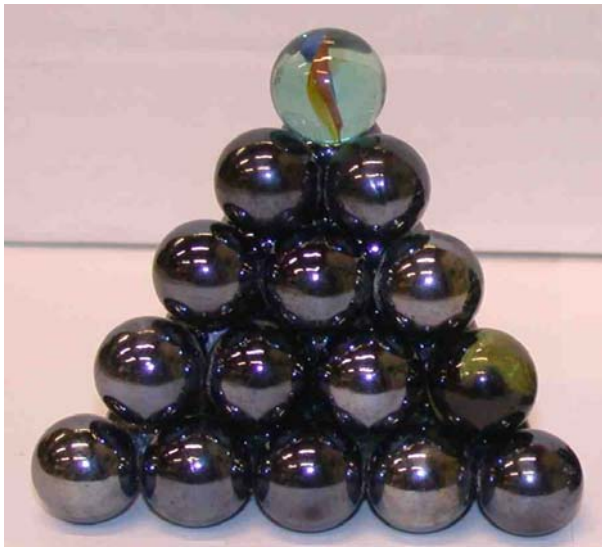


# Confocale Fluorescentie -microscopie

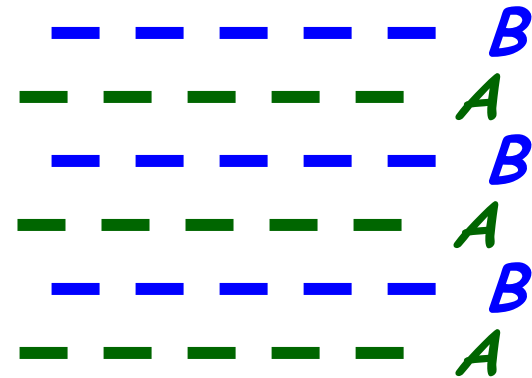


Verhaegh en Van Blaaderen (1994).





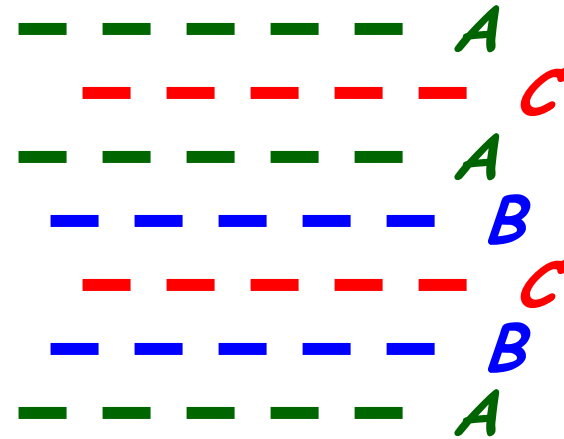
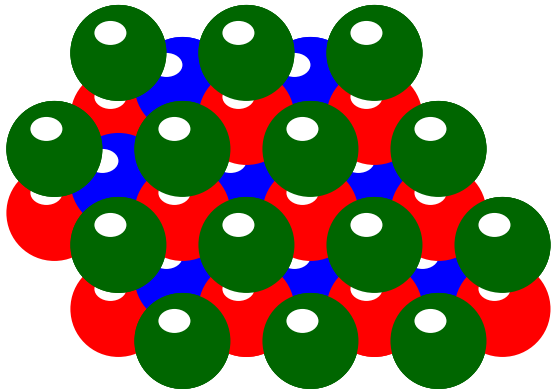
**Face-centred  
cubic (fcc)**



**Hexagonal close  
packed (hcp)**



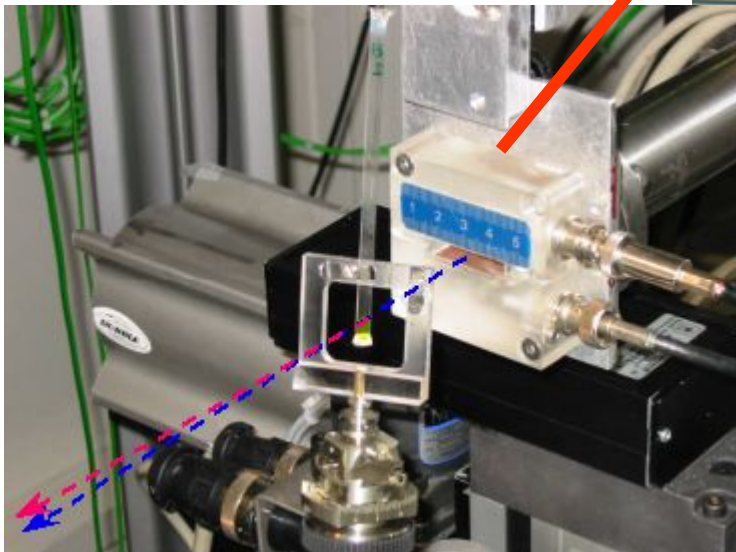
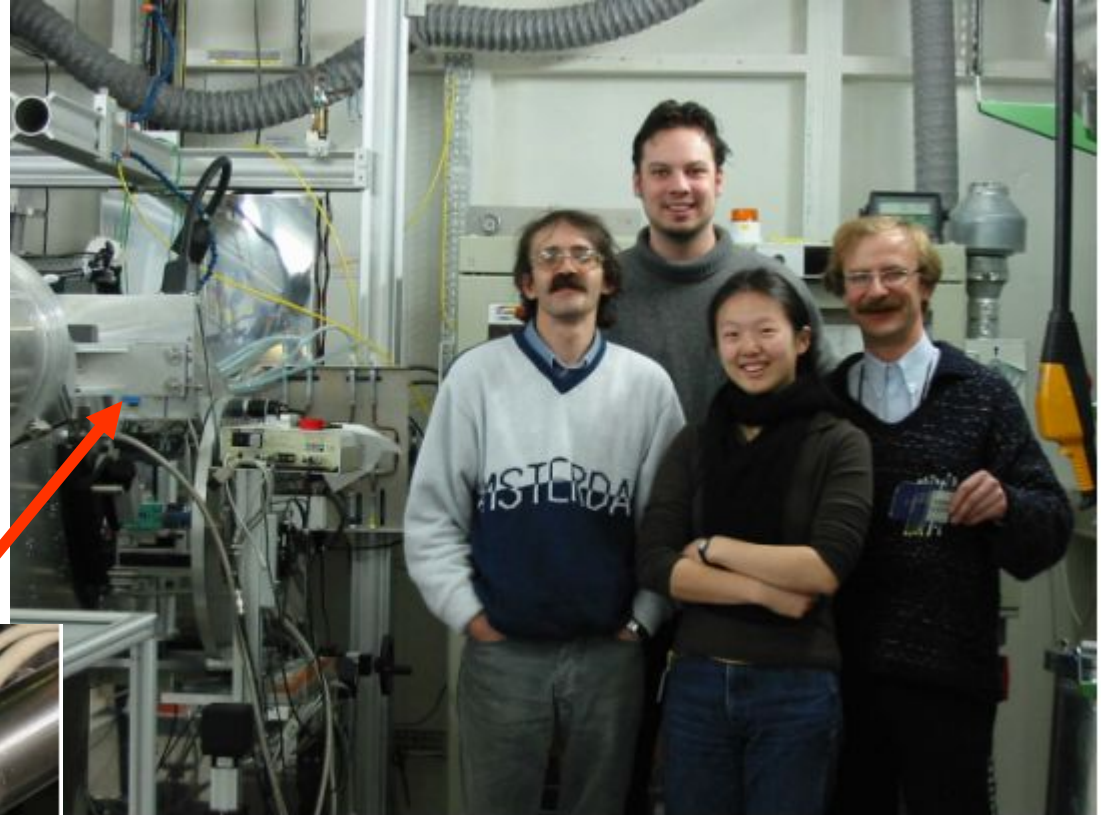
FCC or HCP ?



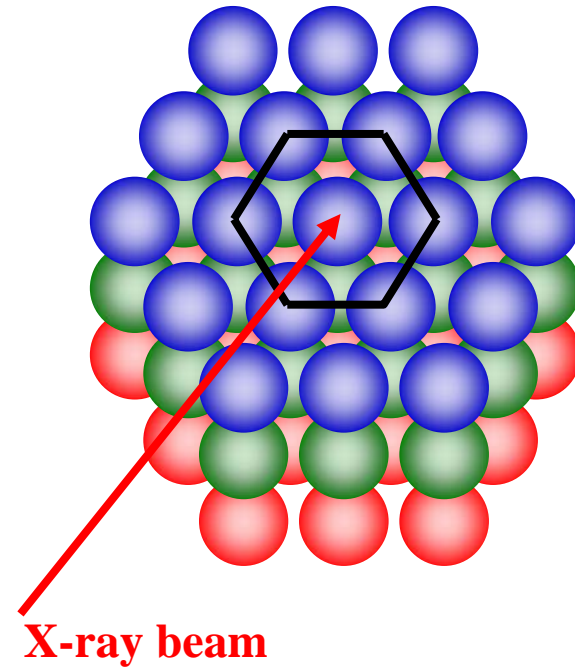
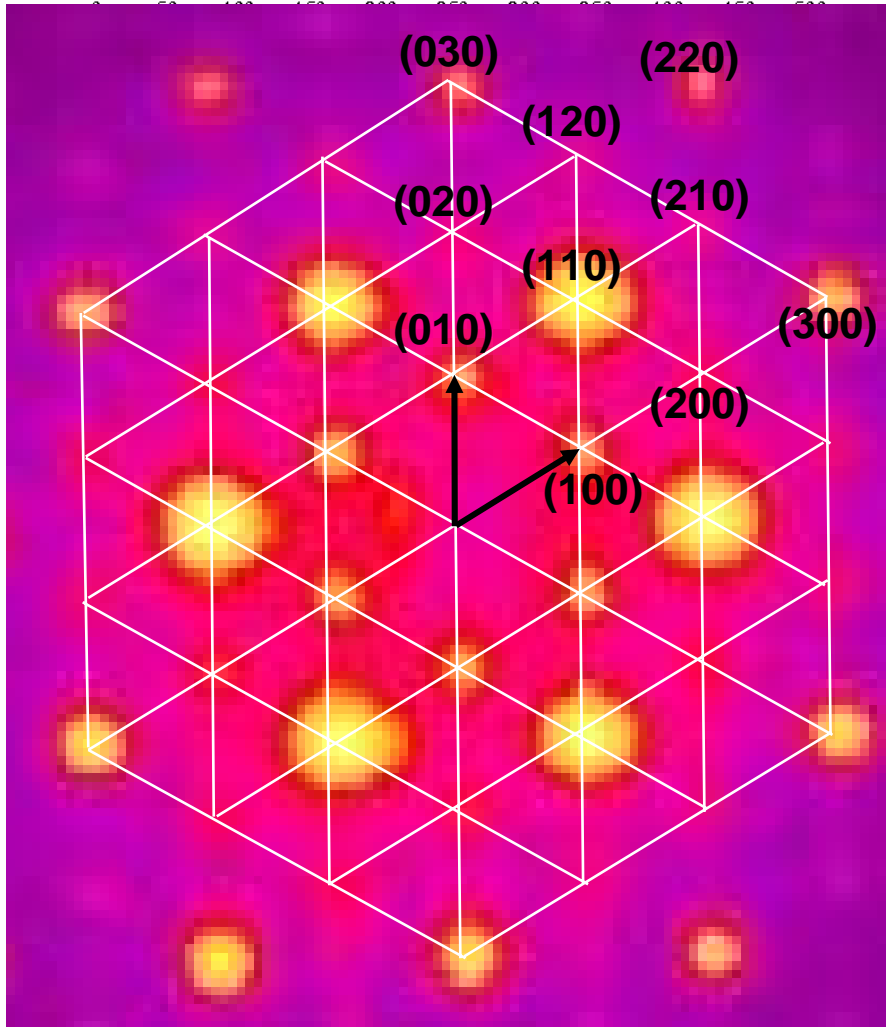
**Random hexagonal  
close packed (rhcp)**

**All three (fcc, hcp & rhcp)  
have the same packing ratio...**

# Synchrotron Röntgenverstrooiing



European Synchrotron  
Radiation Facility, Grenoble



Close-packed crystals:  $h - k = 3n$      $h - k \neq 3n$

FCC:	...ABCABC...	1	0
HCP:	...ABABAB...	1	0.25
RHCP:	...ABACBC...	1	0...0.25

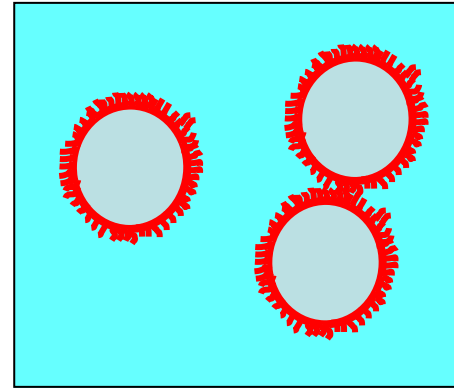
- *Petukhov, Aarts, Dolbnya, de Hoog, Kasapidou, Vroege, Bras, HNWL, Phys.Rev.Let., 88, 208301 (2002);*
- *Petukhov, Dolbnya, Aarts, Vroege, HNWL, Phys.Rev.Let., 90, 028304 (2003).*



# Samples

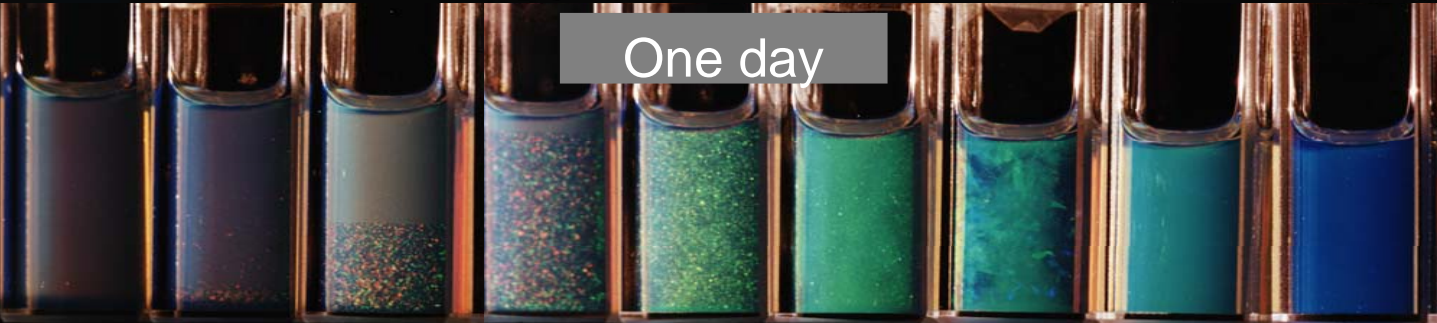
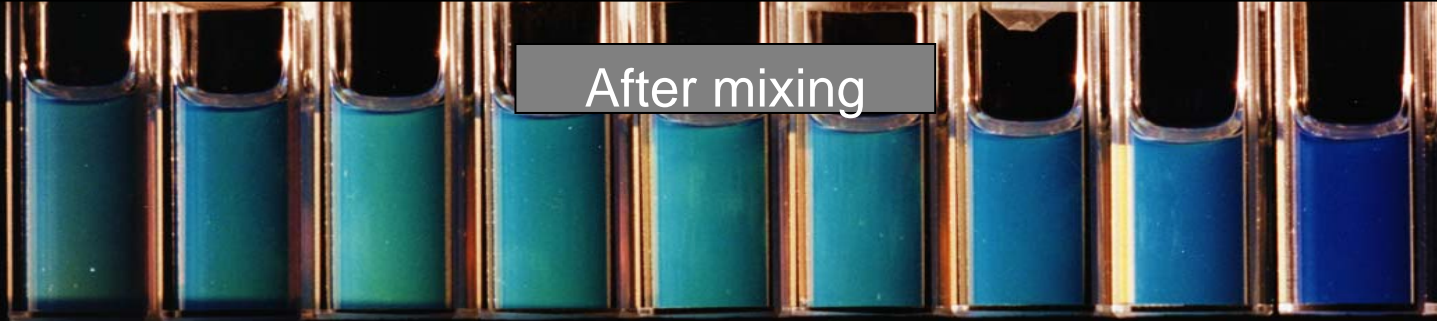
## Hard-sphere colloids:

Sterically-stabilised poly-methylmethacrylate (PMMA) colloidal “hard spheres”



- Suspend in mixtures of organic liquids –  
match refractive index and/or density
- No attraction, nearly hard-sphere repulsion ( but ? charge ? )
- Radius  $R \approx 0.2 \text{ to } 1 \mu\text{m}$
- Polydispersity  $\sim 0.05$

# Hard-sphere colloidal crystals and glasses



Fluid  
 $\phi < 0.494$

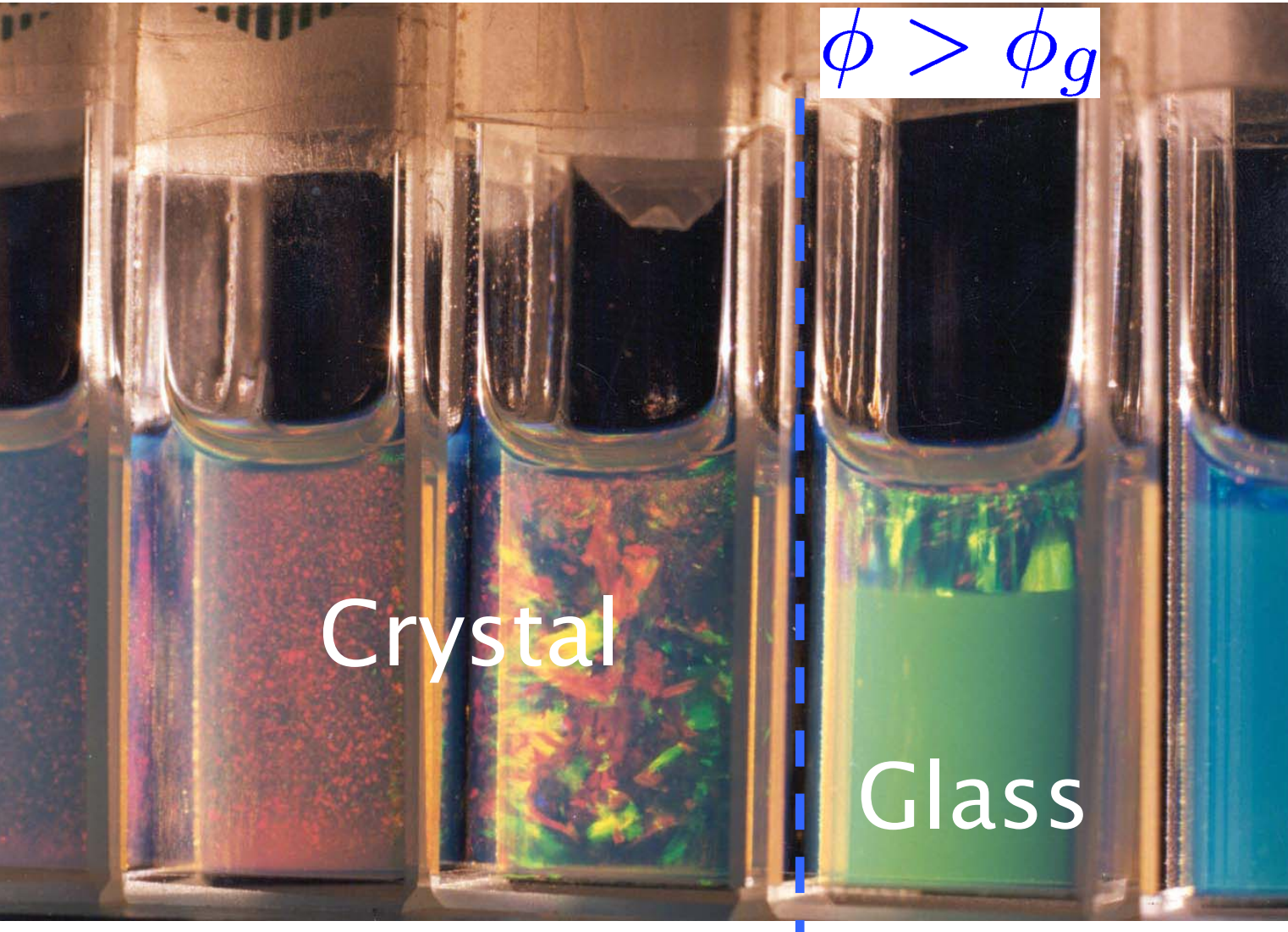
Fluid +  
Crystal

Crystal  
 $\phi > 0.545$

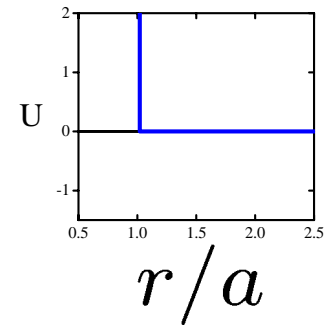
Glass  
 $\phi > 0.58$

# Repulsive glass

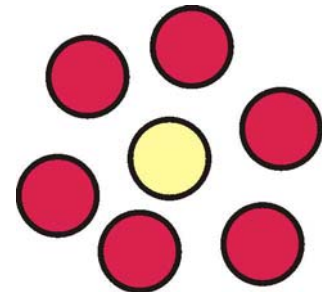
High-density kinetically-arrested disordered solid

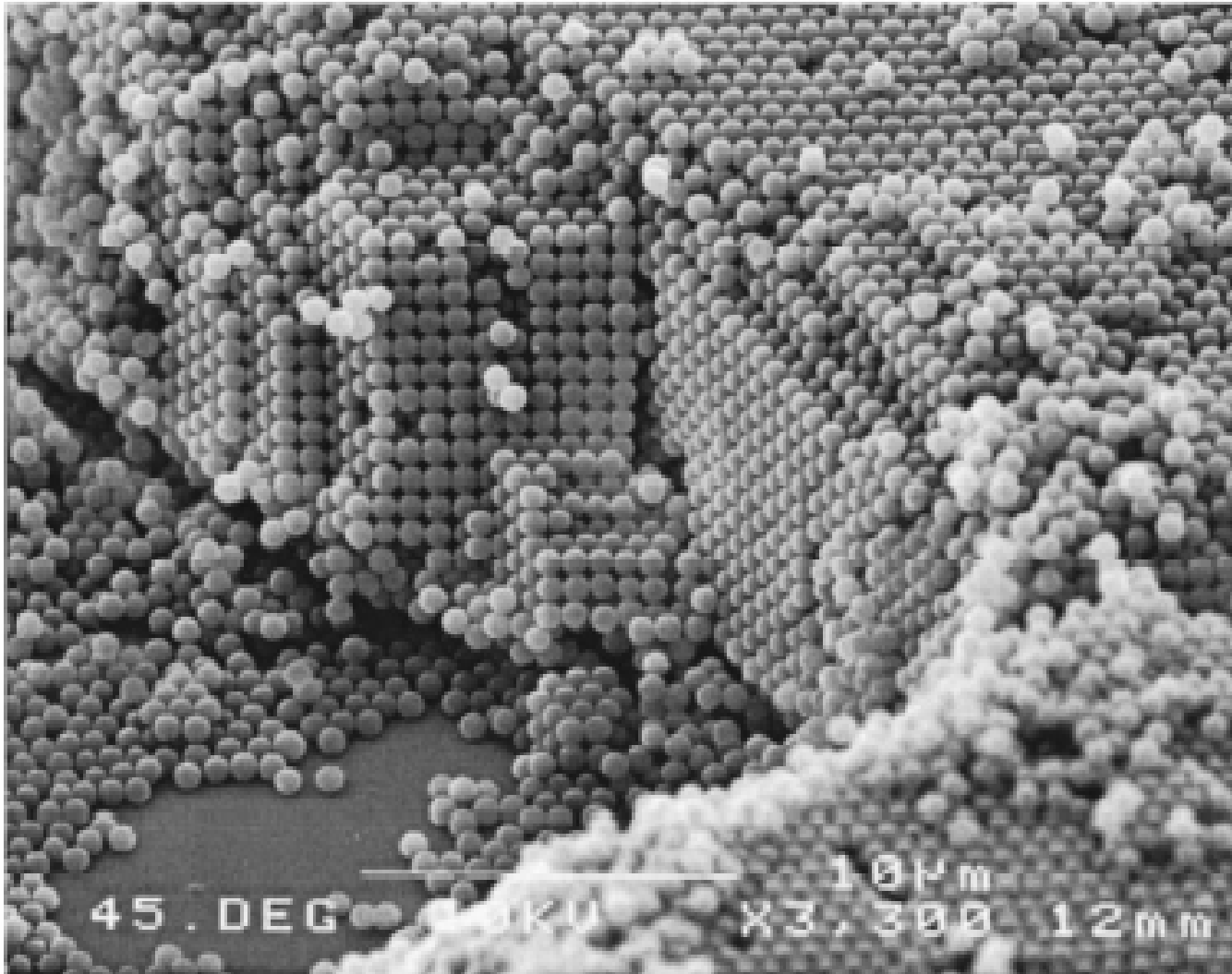


Hard sphere

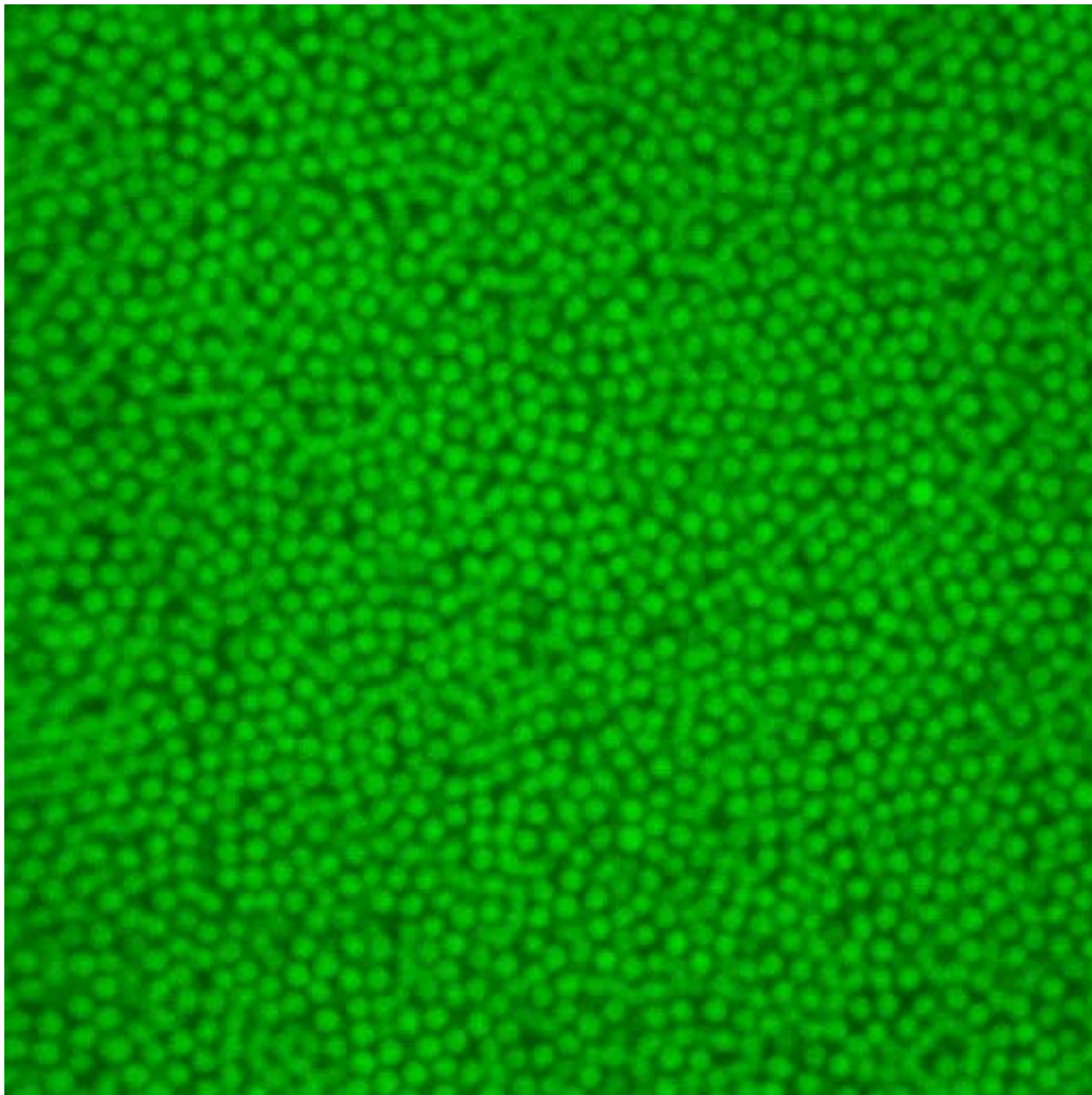


Repulsions  
dominant



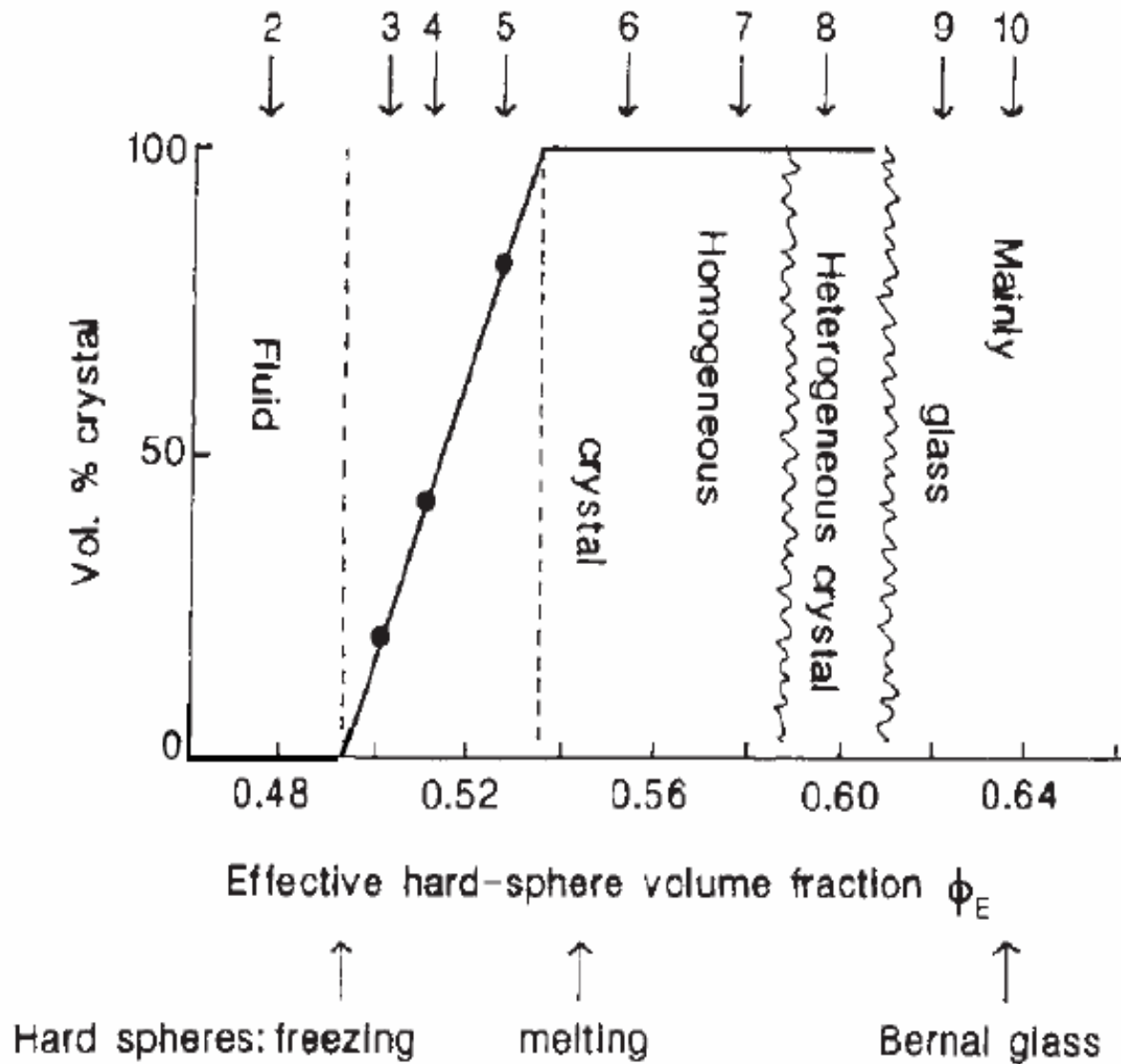


(b) R.M. Amos et al., PRE **61**, 2929 (2000)



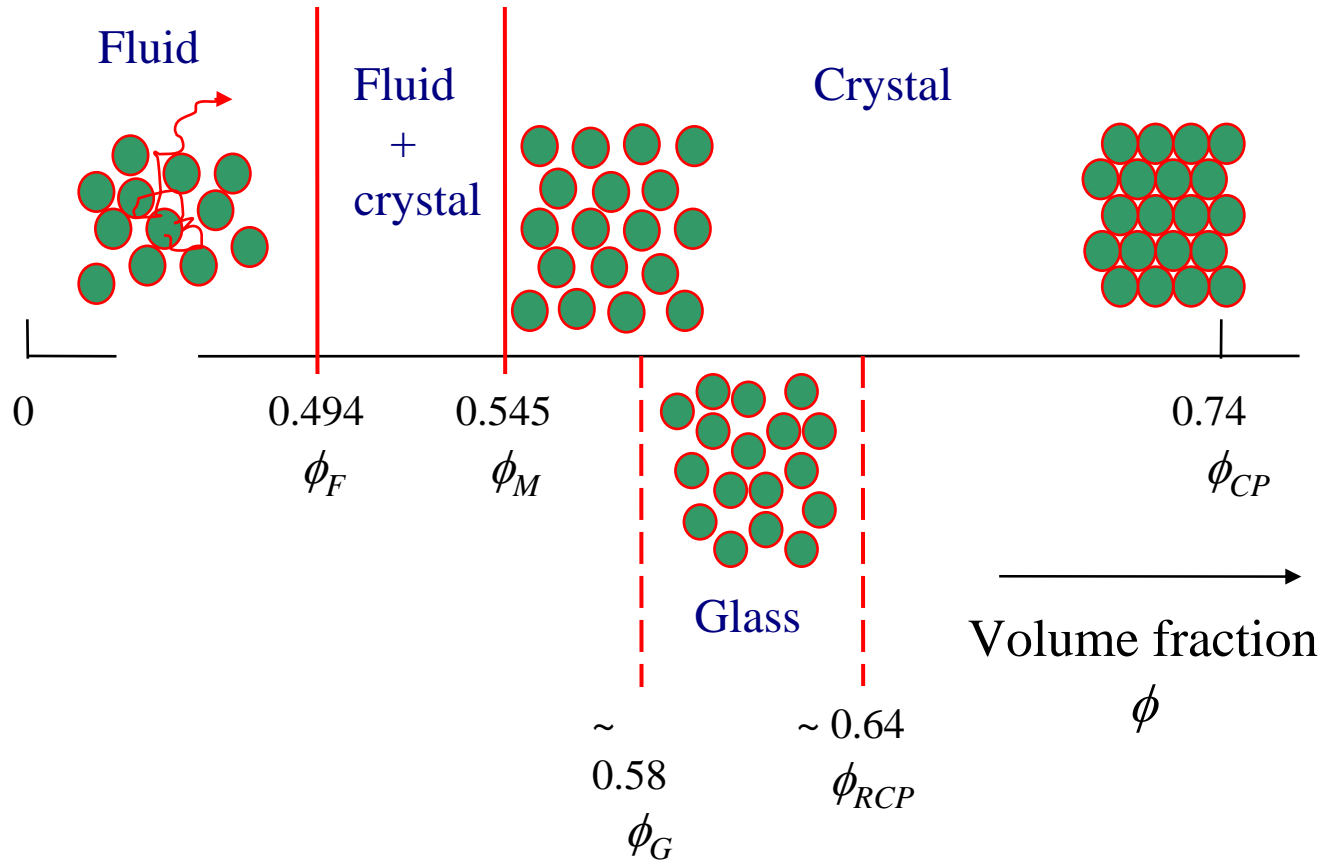
Fluorescent PMMA, Volkert de Villeneuve

# Observed phase behaviour



# Phase behaviour of hard spheres

Only one variable: volume fraction  $\phi = \frac{N}{V} \frac{4}{3} \pi R^3$



The end of lecture 3