Colloidal Fluids, Glasses, and Crystals

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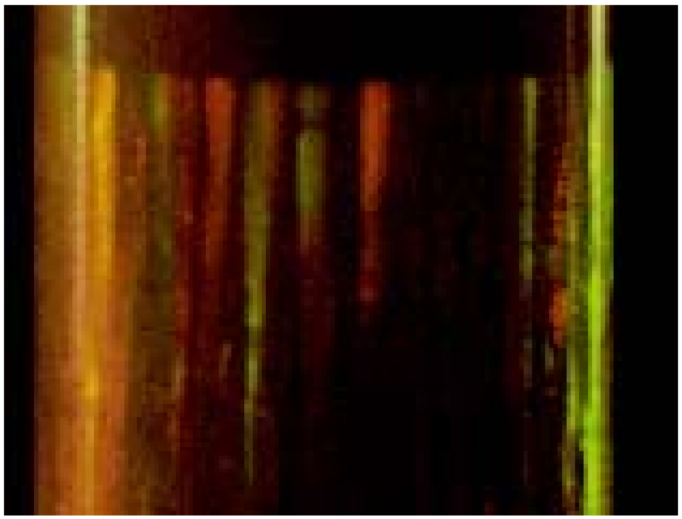
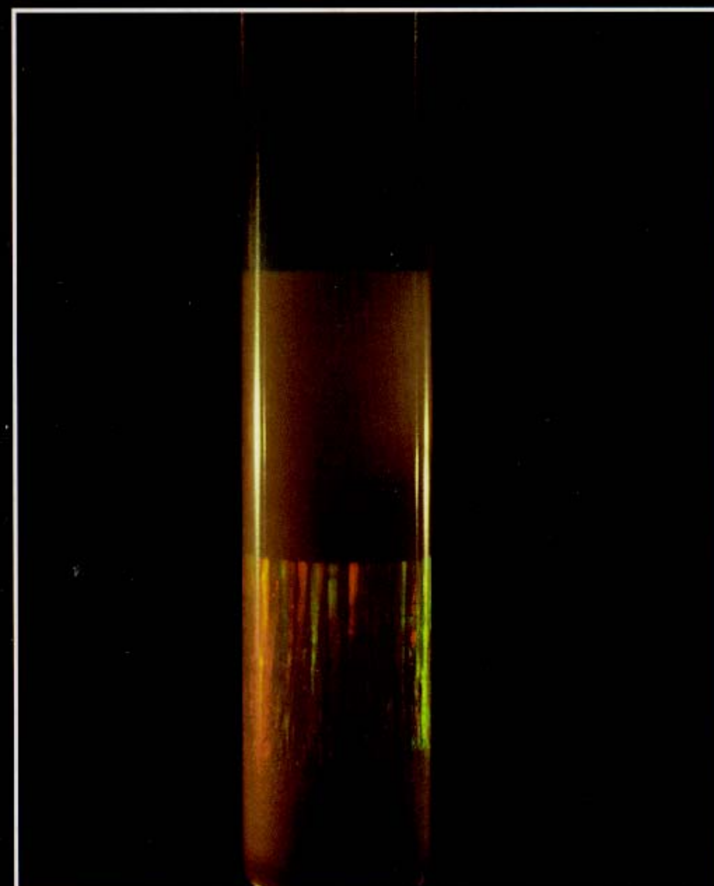


Colloidal Dispersions

W.B.RUSSEL, D.A.SAVILLE and W.R.SCHOWALTER



Thermodynamics of Hard Spheres

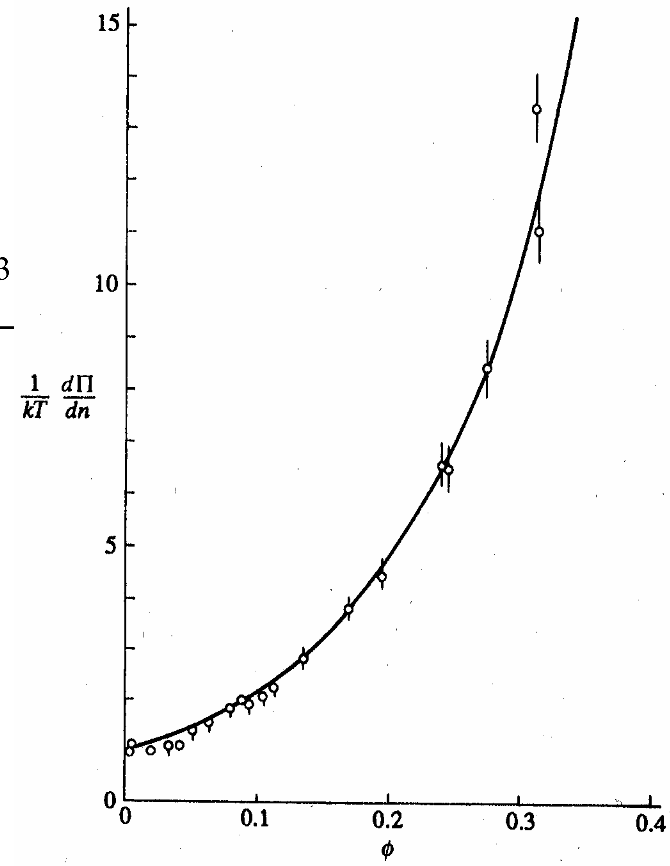
Hard-sphere interaction potential:

$$U(r) = \begin{cases} \infty & for\ r < d \\ 0 & for\ r \geq d \end{cases}$$

No exact theory available to calculate *g(r).*

Equation of state for the fluid using Percus-Yevick approximation (Carnahan &Starling, 1969):

Compressibility factor: $Z(\phi) = \dfrac{\Pi}{nkT} = \dfrac{1+\phi+\phi^2-\phi^3}{(1-\phi)^3}$

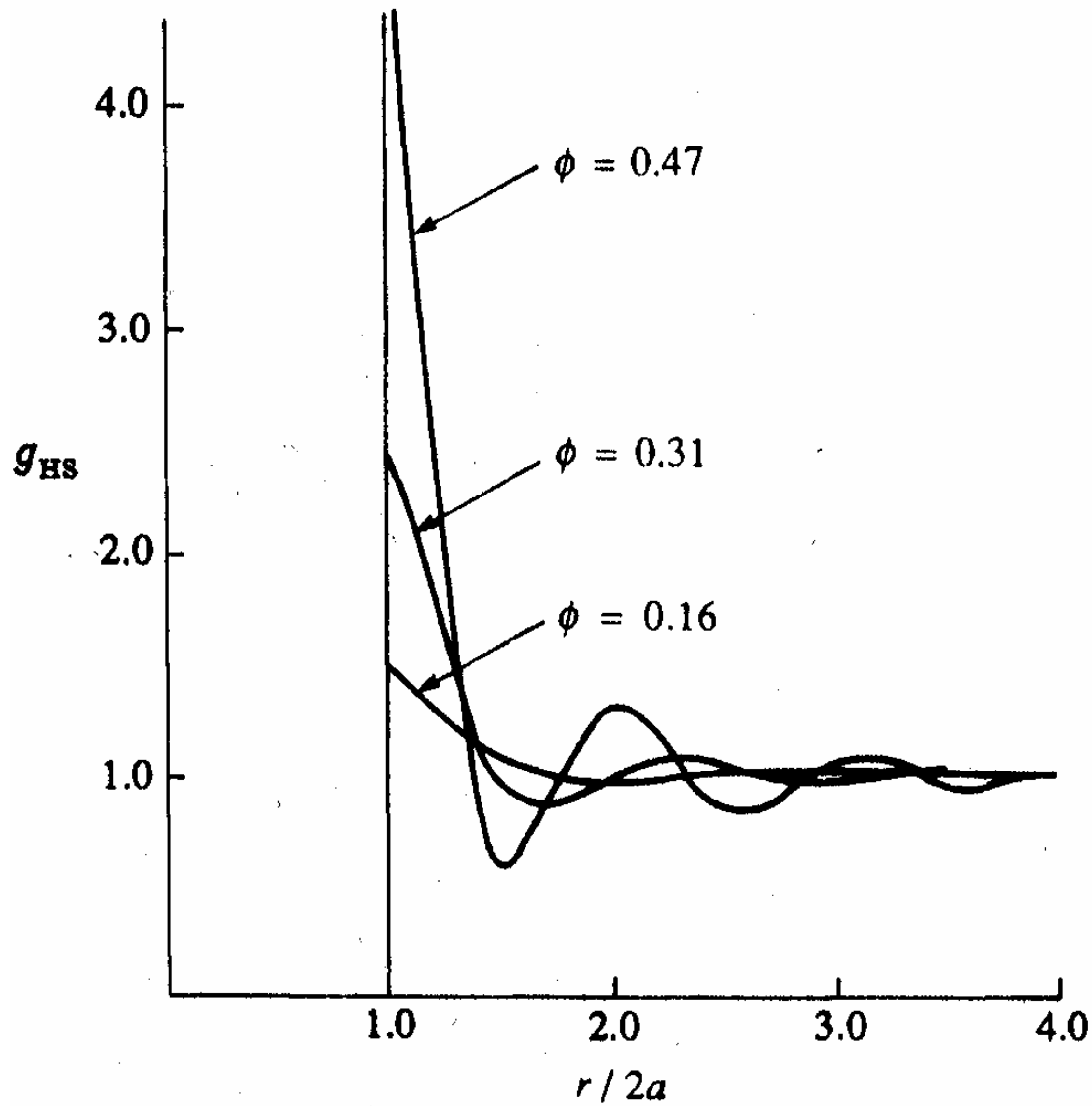


Model hard-sphere system:

Silica spheres stabilized with a thin organophilic layer and dispersed in cyclohexane (Vrij et al., 1983)

Osmotic compressibility obtained by light scattering

Radial Distribution Function of Hard Spheres
Fluid State



Smith and Henderson (1970)

Thermodynamics of Hard Spheres (cont.)

Compressibility factor for the ordered state (Hall, 1972):

$$Z(\phi) = \frac{\Pi}{nkT} = 2.558 + 0.125\beta + 0.176\beta^2 - 1.053\beta 3 + 2.819\beta^4 - 2.922\beta^5 + 1.118\beta^6 + 3(4-\beta)/\beta$$

With:

$$\beta = 4(1-\phi/0.74)$$

Coexistence of fluid and liquid for $0.5 \le \phi \le 0.55$

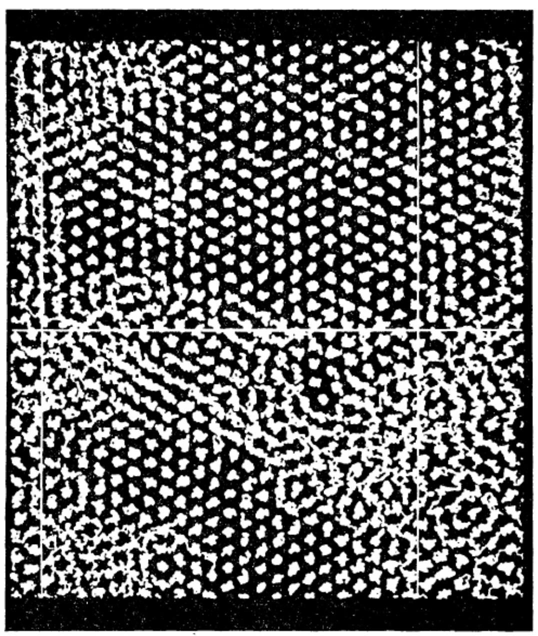
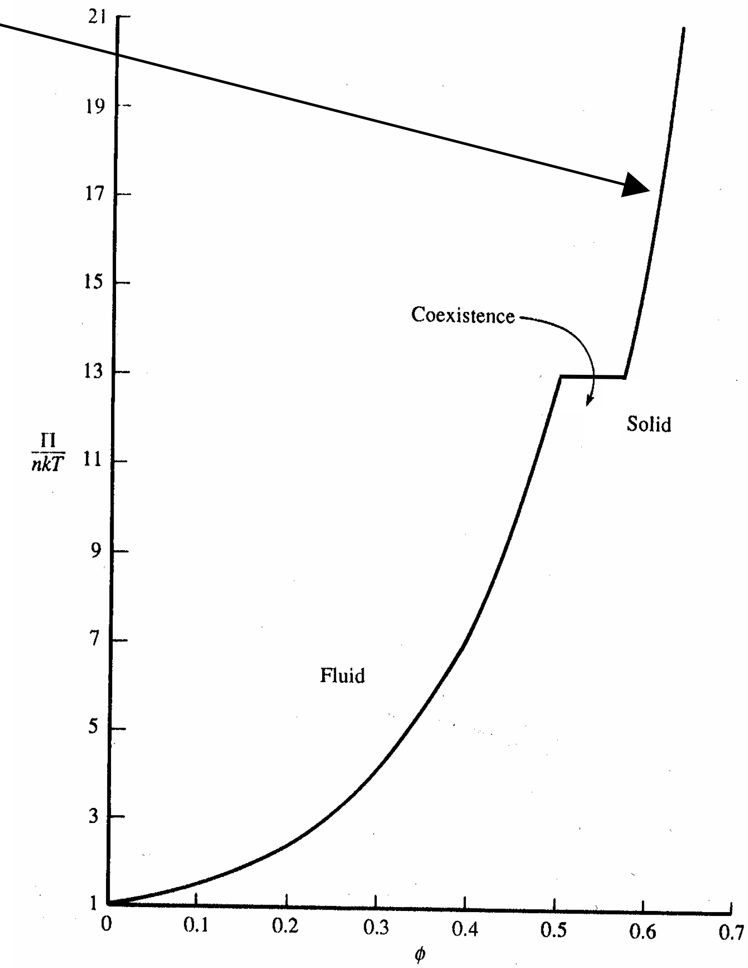
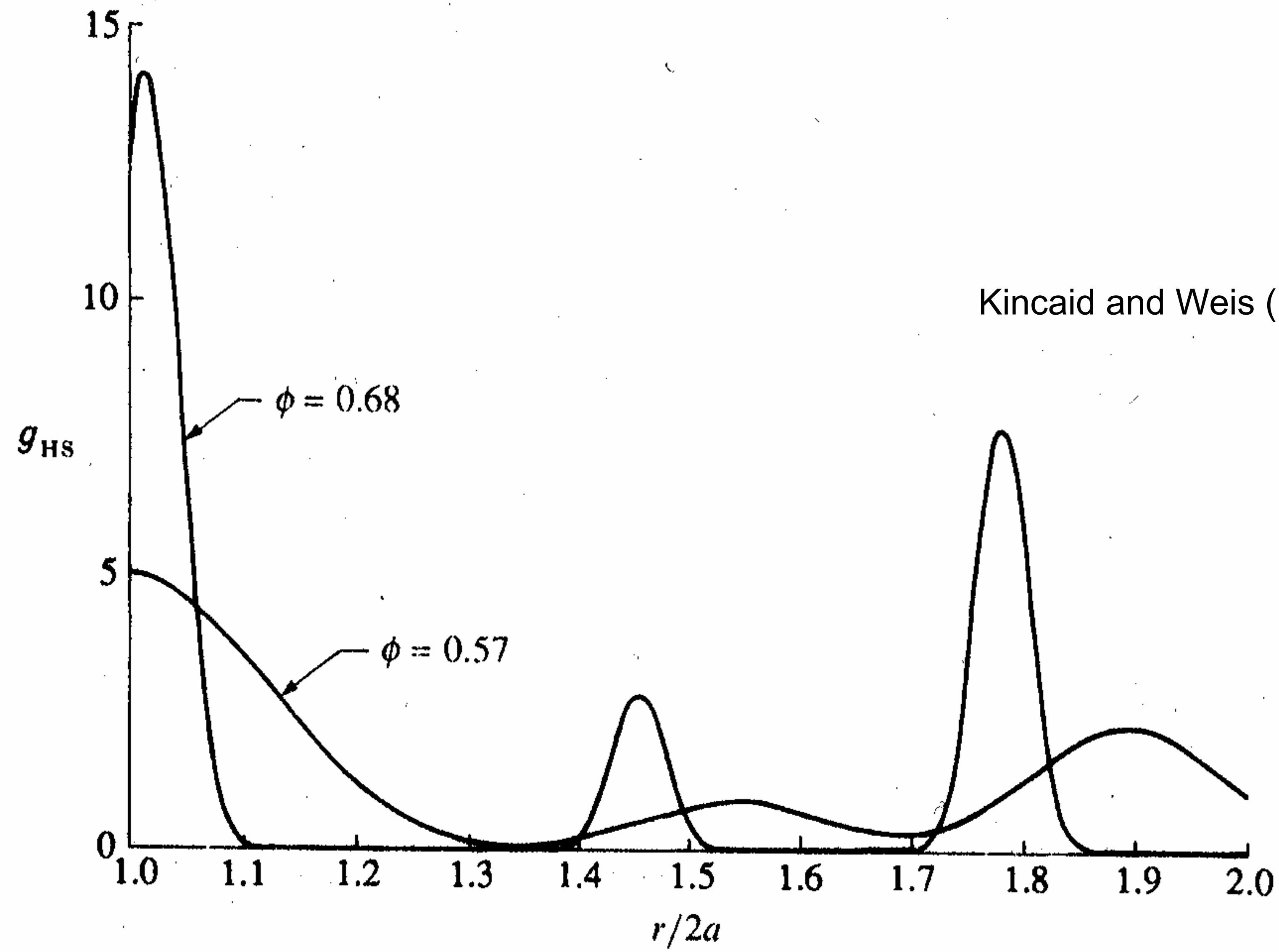


FIG. 2. The traces of the centers of particles in the phase-transition region showing fluid and crystalline regions. The horizontal and vertical lines represent an arbitrary grid.

Alder and Wainwright (1962)

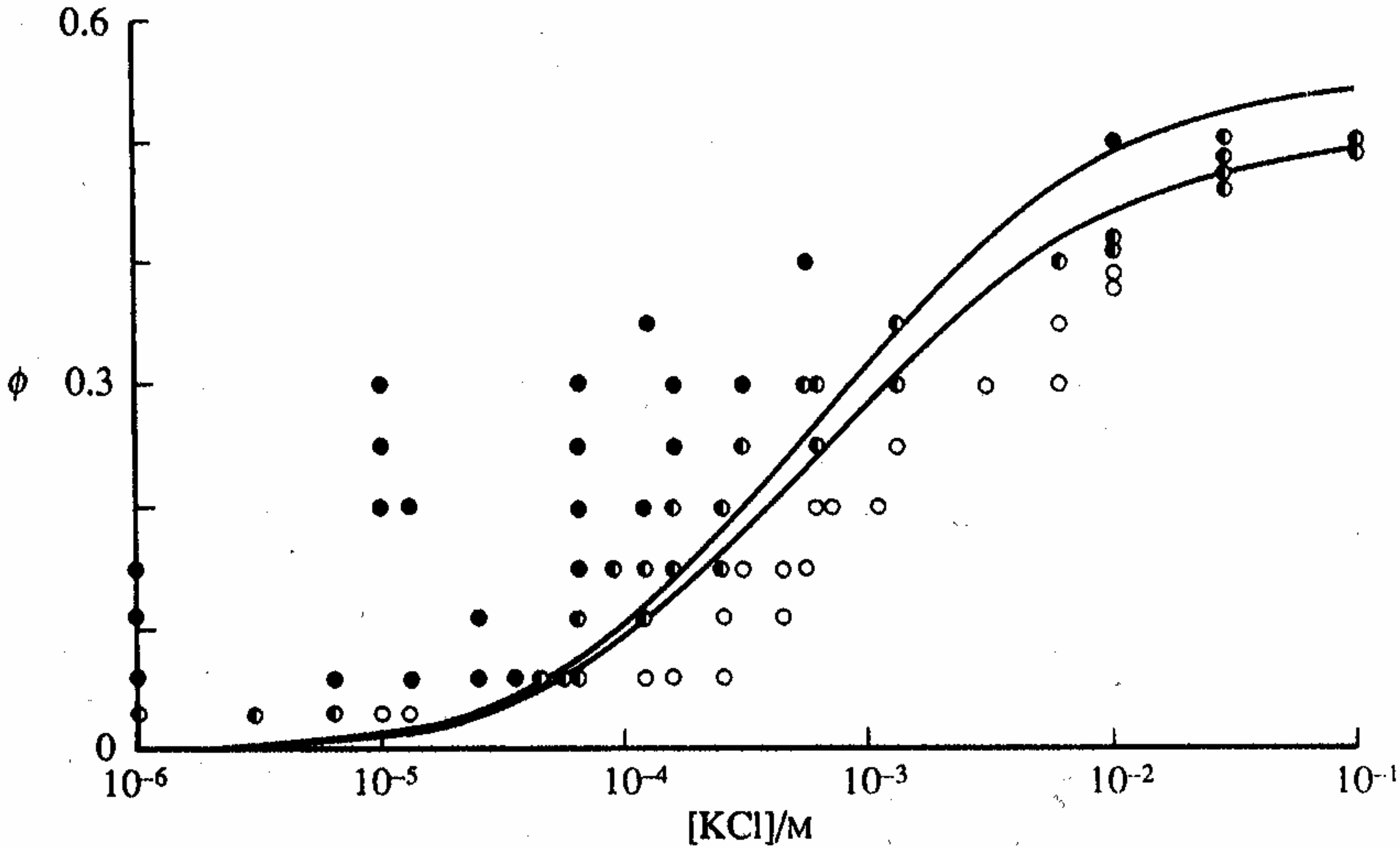


Radial Distribution Function of Hard Spheres
Solid State



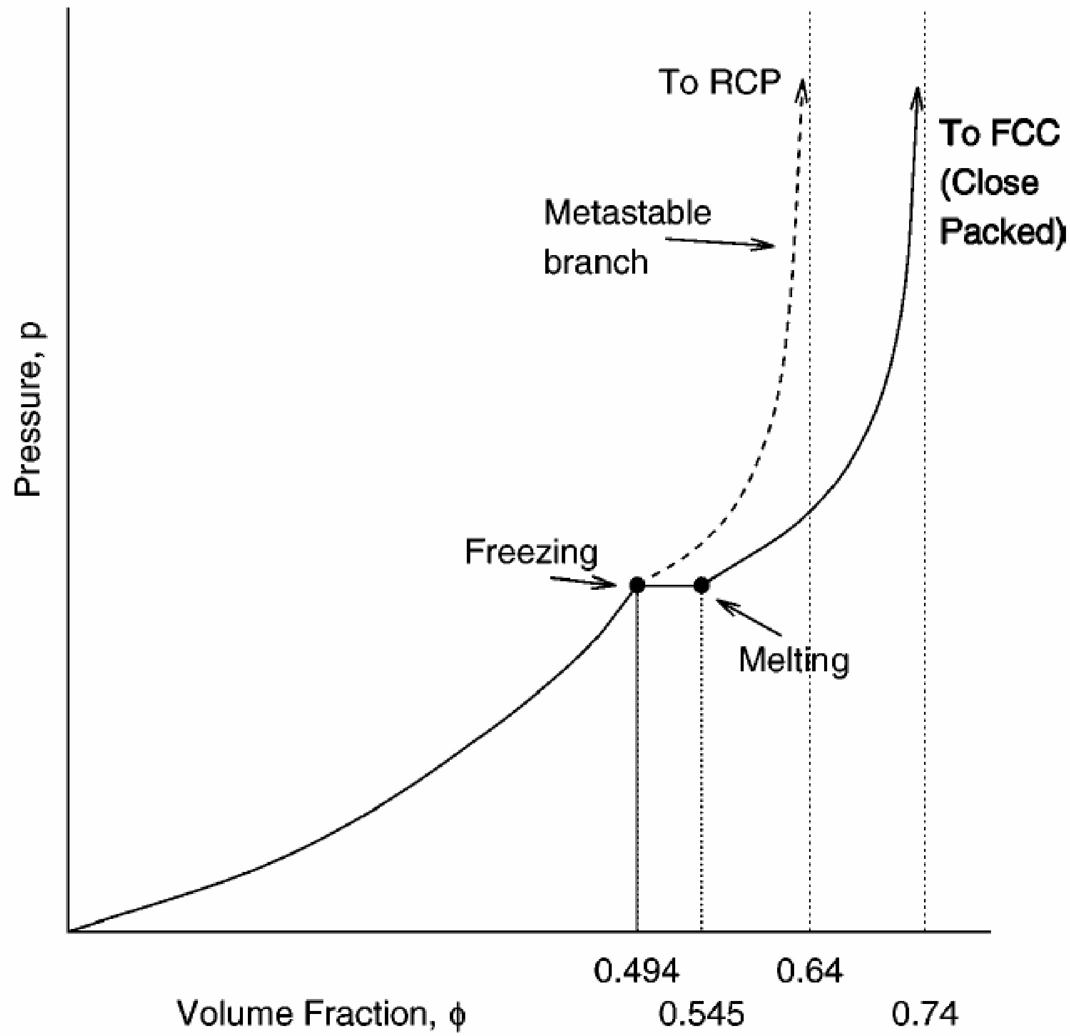
Kincaid and Weis (1977)

Phase Diagram for Charged Spheres



Order-disorder transition for charged spheres in an electrolyte solution. Data of Hachisu, Kobayashi, and Kose (1973) for polystyrene latices with a = 0.085 μm: open circles, disordered; half-filled circles, two-phase; filled circles, ordered; curves predictions of phase boundaries from perturbation theory for a =0.1 μm and $4\pi a^2 q$=5000e (Russel, 1987)

Metastability and Crystallization in Hard-Sphere Systems

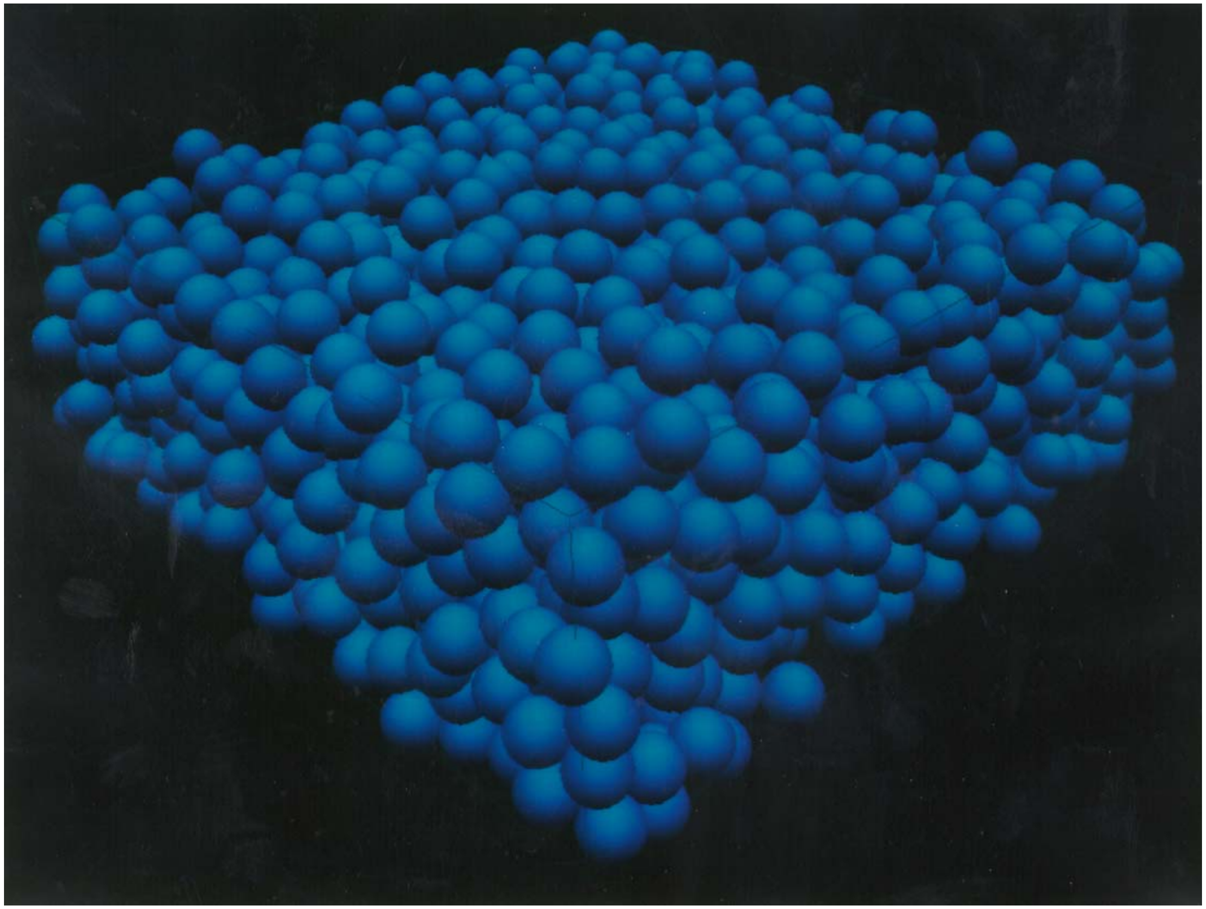


Large-scale molecular dynamics simulations. Contrary to previous studies, no evidence of a thermodynamic glass transition and after long times the system crystallizes for all ϕ above the melting point. M. D. Rintoul and S. Torquato (1996)

References

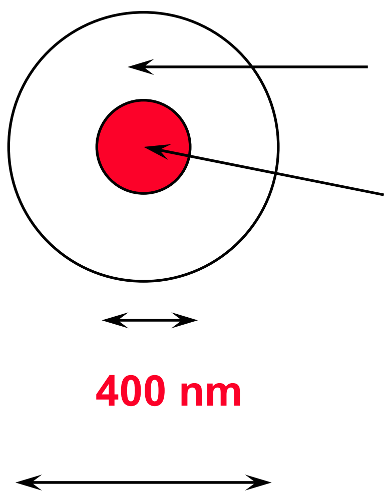
- N. F. Carnahan and K. E. Starling, *J. Chem Phys.* 51, 635 (1969)
- A. Vrij, J. W. Jansen, J. K. G. Dhont, C. Pathmamanoharan, M. M. Kops-Werkhoven, and H. M. Fijnaut, *Far. Dis.* 76, 19 (1983)
- W. R. Smith and D. Henderson, *Mol. Phys.* 19, 411 (1970)
- K. R. Hall, *J. Chem. Phys.* 57, 2252 (1972)
- J. M. Kincaid and J. J. Weis, *Mol. Phys.* 34, 931 (1977)
- W. B. Russel, *Dynamics of Colloidal Systems.* University of Wisconsin Press (1987)
- M. D. Rintoul and S. Torquato, *Phys Rev. Lett.* 77, 4201 (1996)
- B. J. Alder and T. E. Wainwright, *Phys. Rev.* 127, 359 (1962)

Colloidal glass of 1μm silica spheres



Colloidal Model System

Monodisperse Silica Spheres with a Fluorescent Core



Pure SiO_2 (n = 1.45)

SiO_2 with chemically incorporated dye (fluorescein-isothiocyanate)
Exc.: 500 nm Emm.: 520 nm

400 nm

1000 nm
Polydispersity: 2%

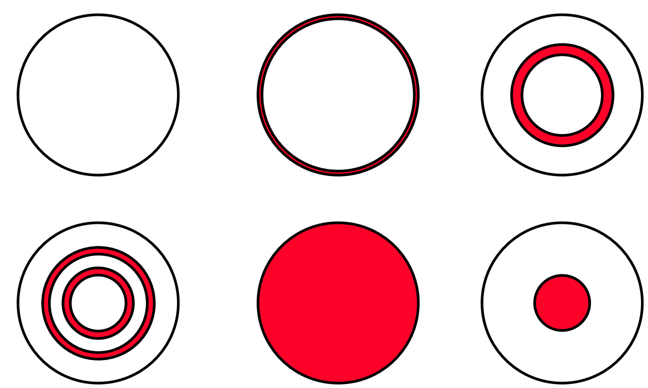
Langmuir, 8, 2921 (1992)

Interaction potential: Hard-Sphere

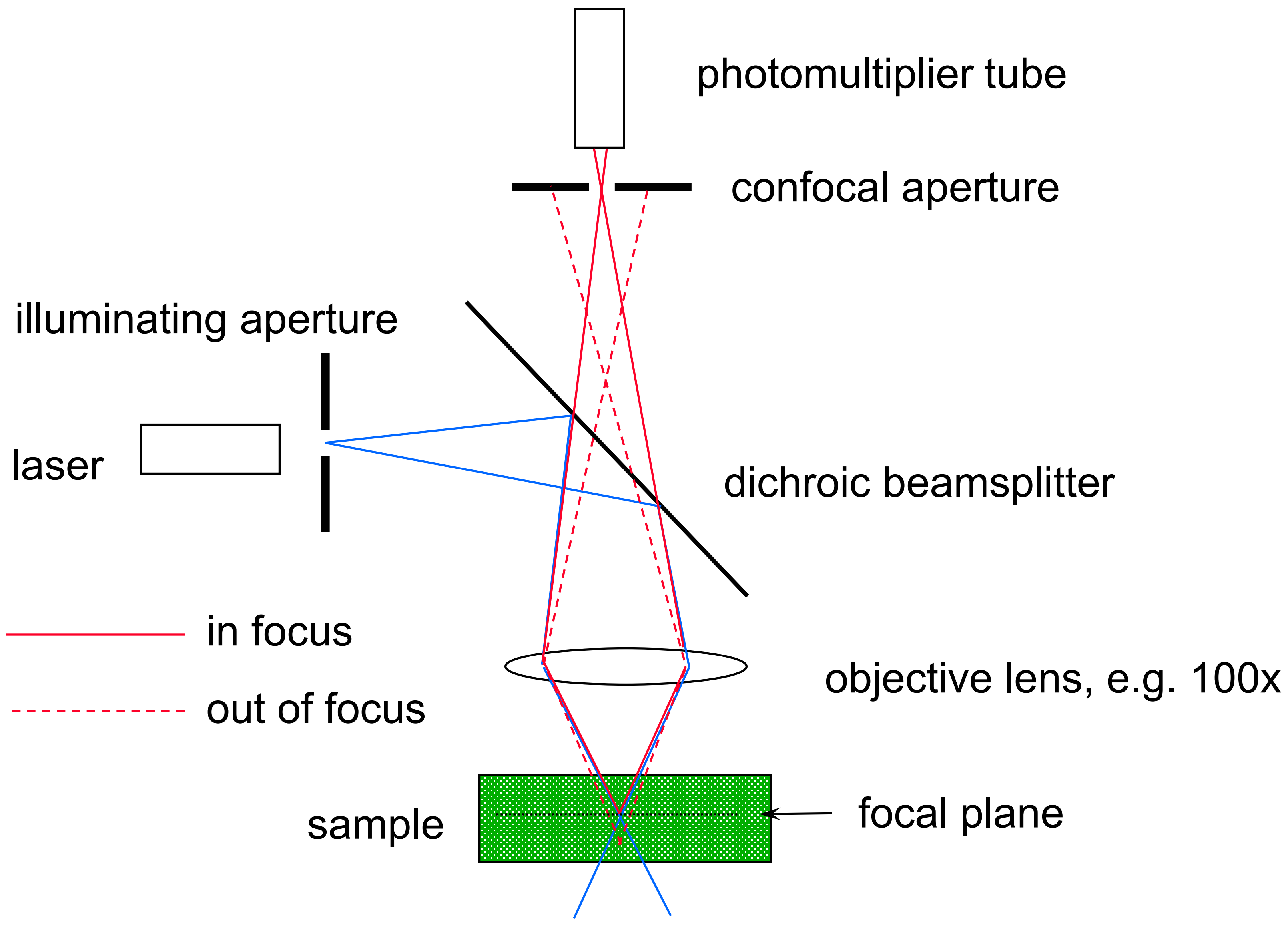
0.01M LiCl :
decreases double-layer to a few nm

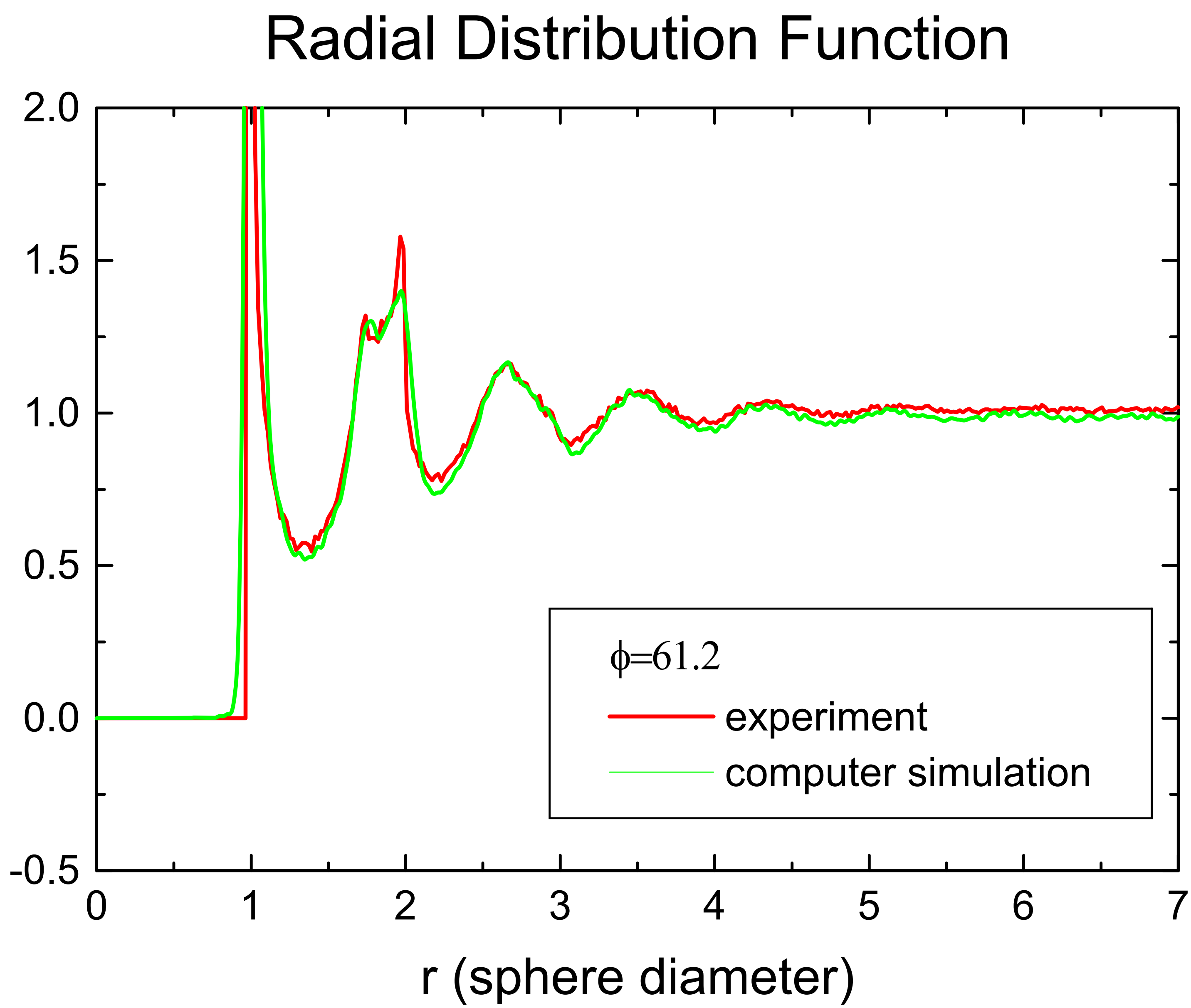
water/glycerol (16 wt% glyc.):
decreases van der Waals forces

Alfons' *SPHERES SHOP*



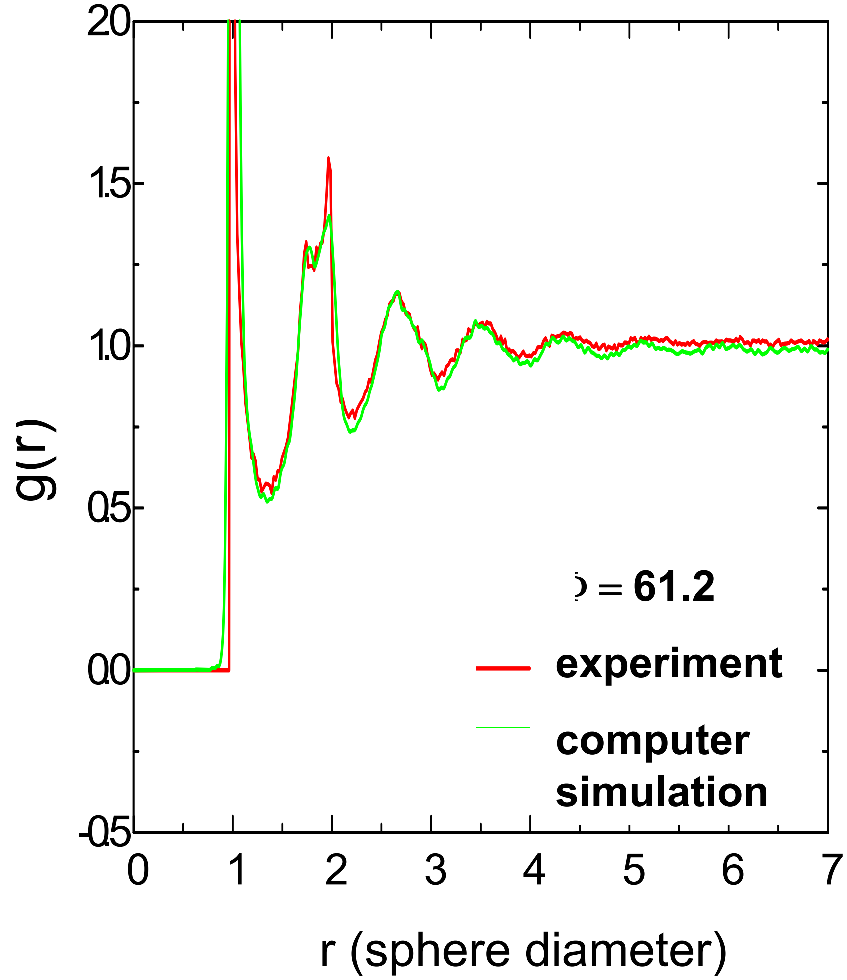
Fluorescence Confocal Scanning Light Microscope

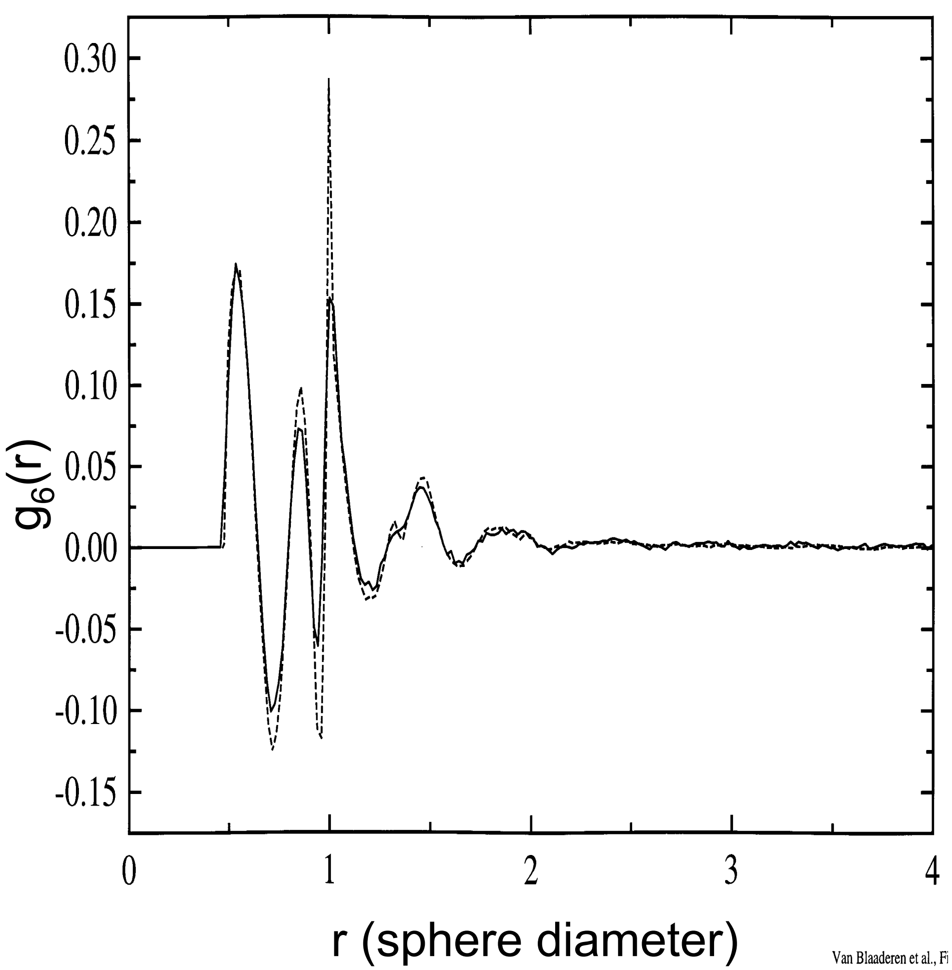




Radial Distribution Function
g(r)
r (sphere diameter)
2.0
1.5
1.0
0.5
0.0
-0.5
0
1
2
3
4
5
6
7
ϕ=61.2
experiment
computer simulation

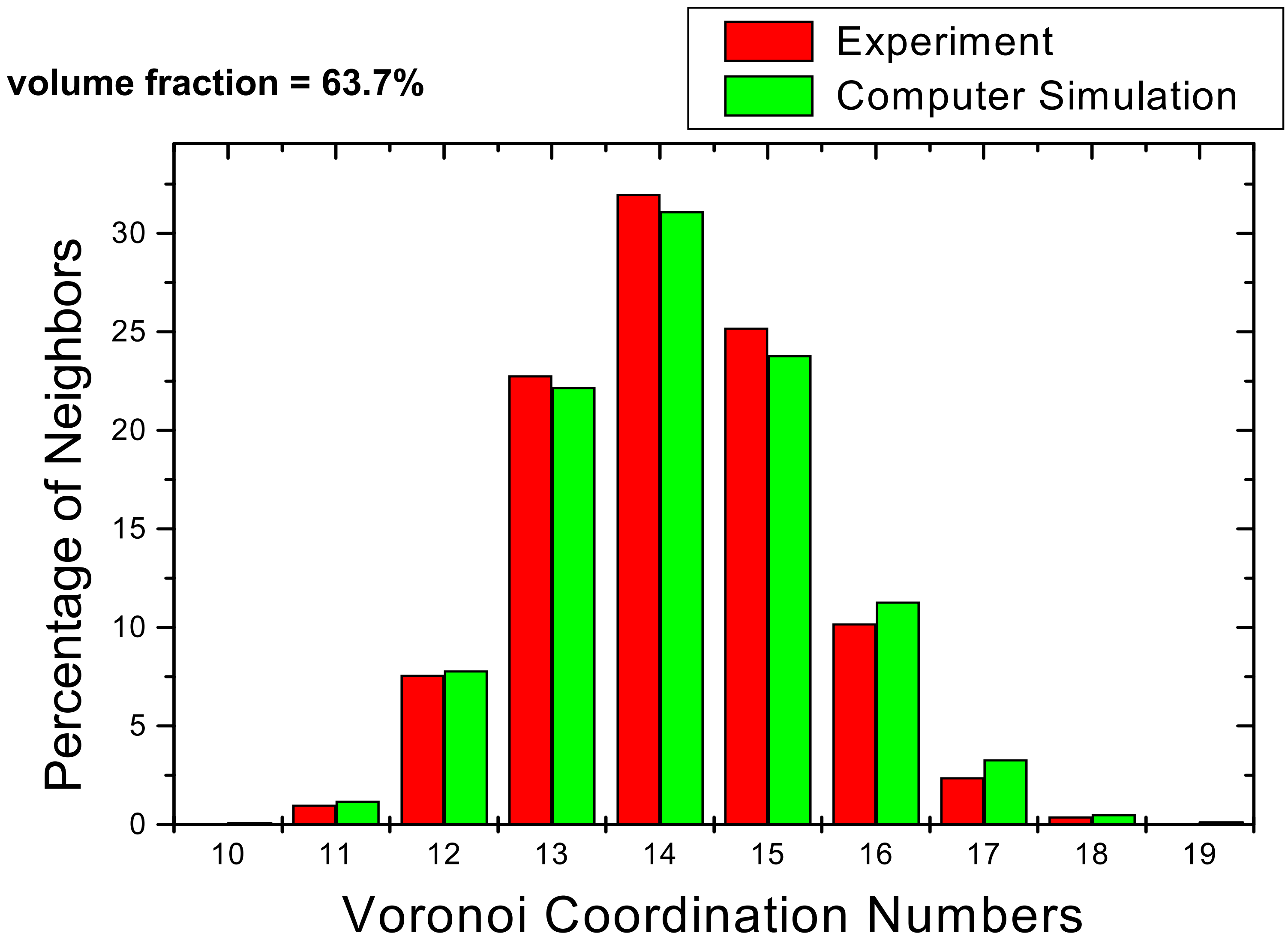
Correlation Functions



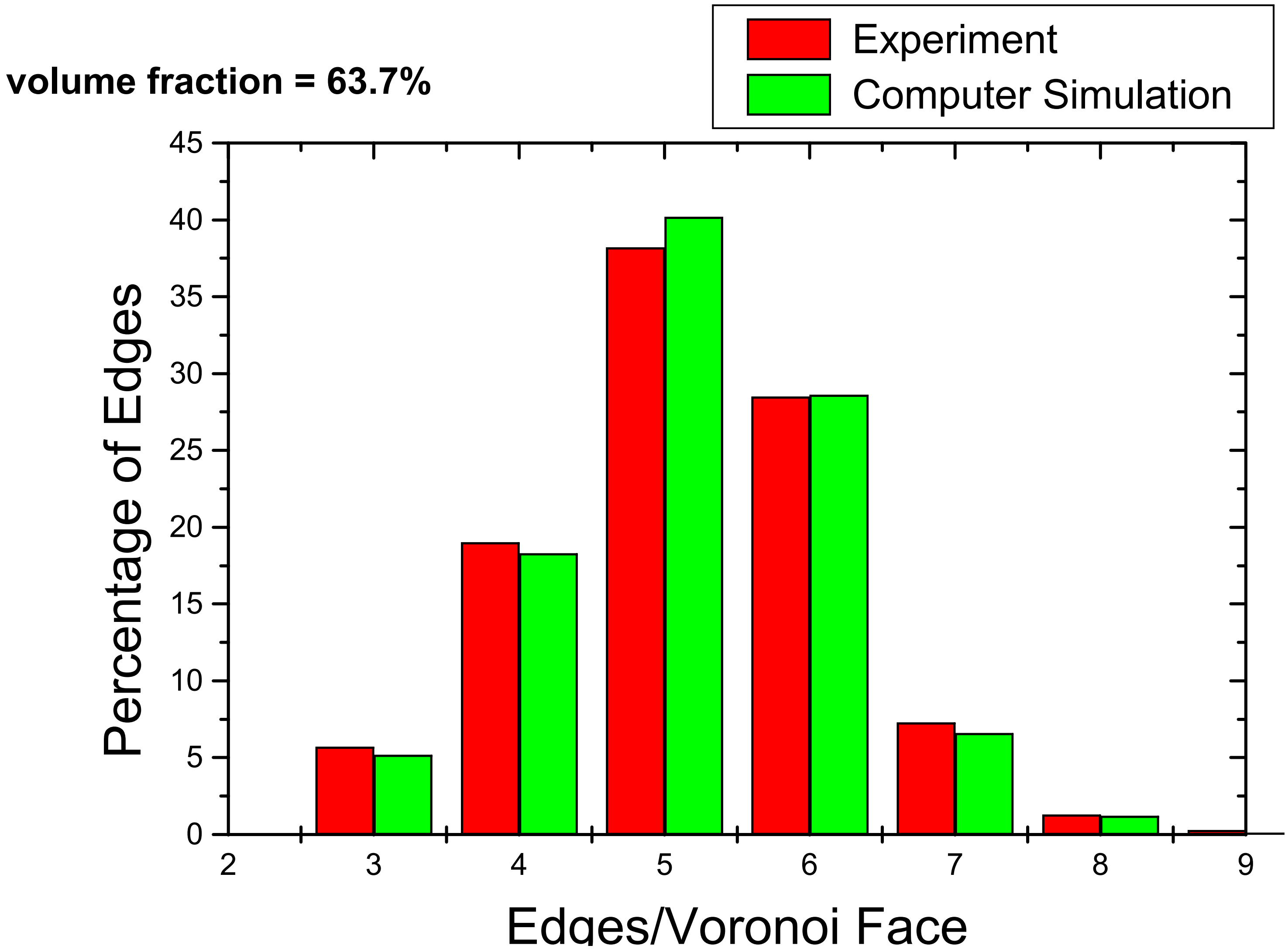


A. van Blaaderen and P. Wiltzius, Science, *270,* 1177 (1995)

Voronoi Coordination



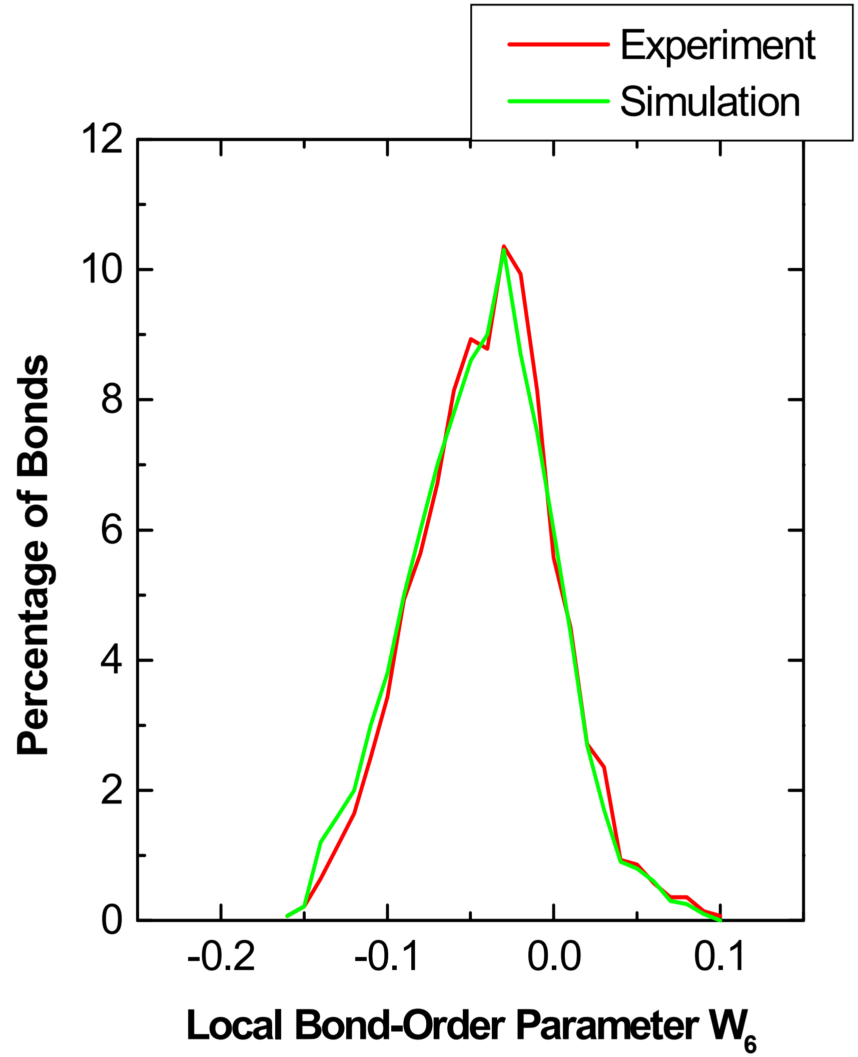
Voronoi Coordination



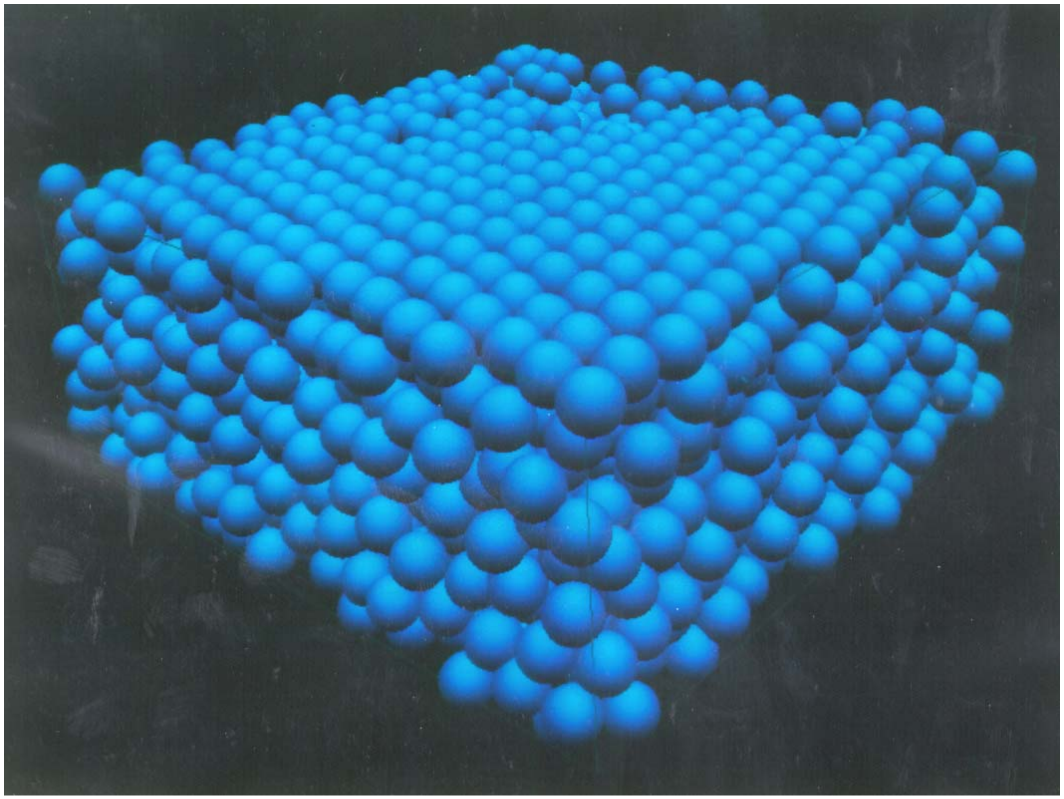
Local Bond Order Parameters

Geometry	W_6
icosahedral	-0.170
fcc	-0.013
hcp	-0.012
bcc	0.013
sc	0.013
liquid	0.000

Steinhardt, Nelson, Ronchetti (1983)



Colloidal "Crystal" of 1 μm Silica Spheres



Rendering of an experimental sediment characterized with confocal scanning optical microscopy.

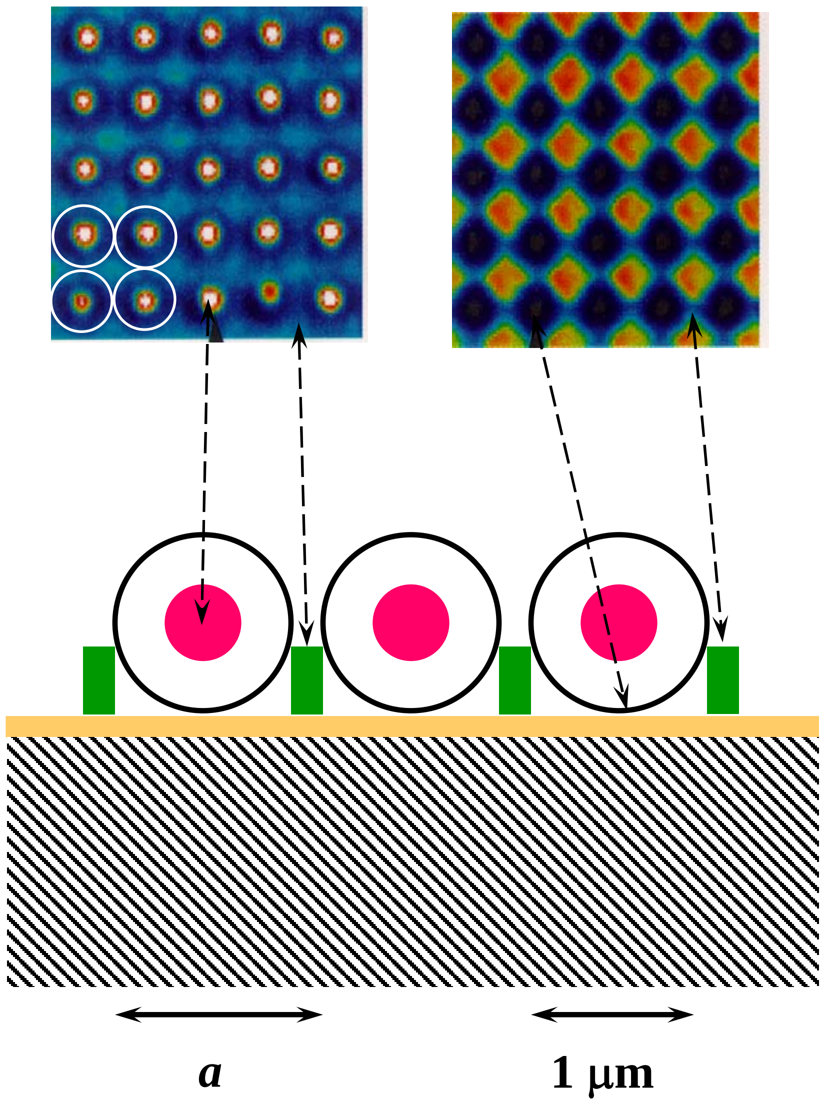
Preparation

- Sediment particles from dilute suspensions
- Form hexagonally close-packed planes

Problems

- Random stacking in gravity direction
- Polycrystalline domains

Colloidal Epitaxy



ϕ = 1%

0.01M LiCl in Glycerol/Water

Spin coated PMMA (dye doped):500 nm

Gold: ~5 nm

Cover glass: 170 μm

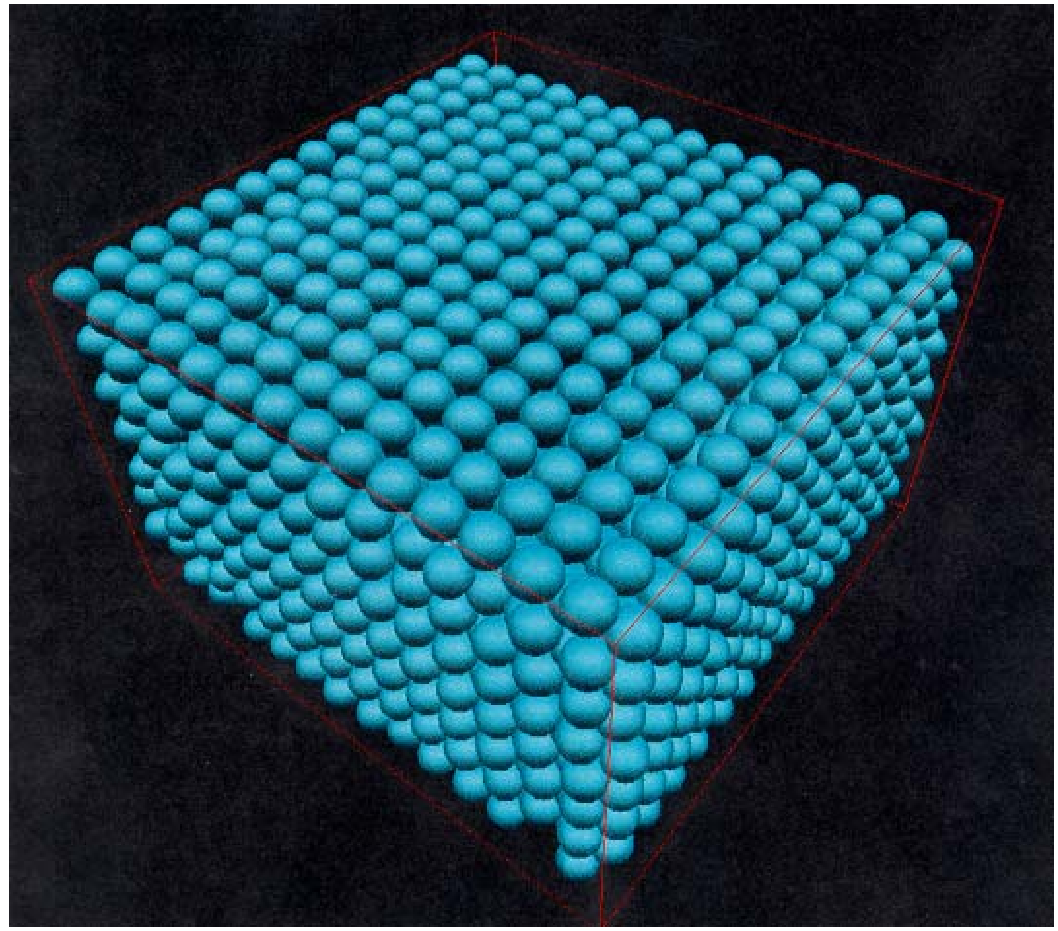
Silica sphere radii:
Fluorescent core 200 nm

Total 1050 nm

Large Single Crystal of Colloidal Silica

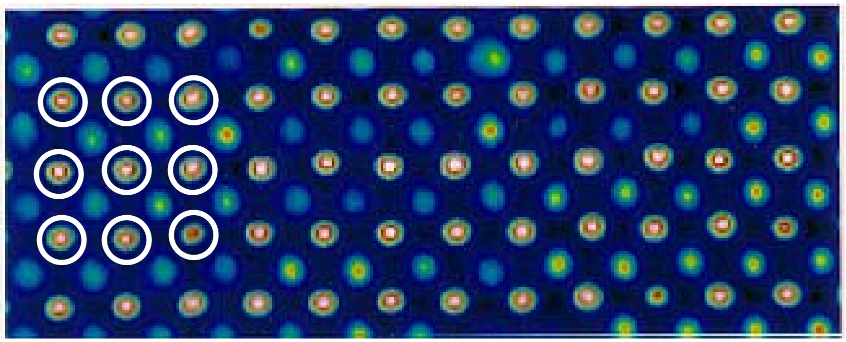
Achievement

- made 400 x 400 x 70 μm^3 single crystal of 1 μm diameter silica spheres settled onto a template with [100] pattern
- Face Centered Cubic (FCC) structure
- well oriented

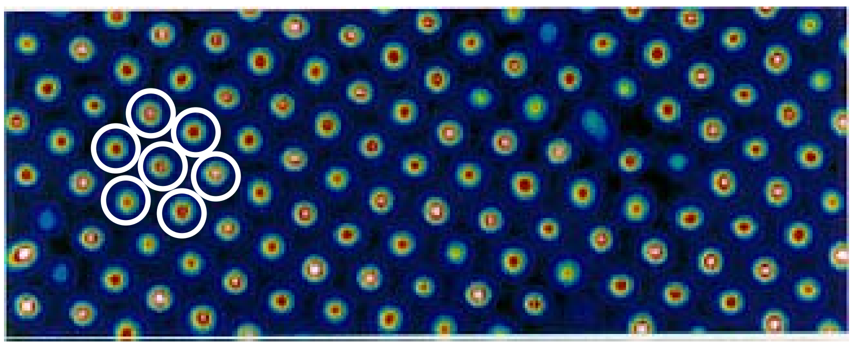


A. von Blaaderen and P. Wiltzius, Nature, 385, 321 (1997)

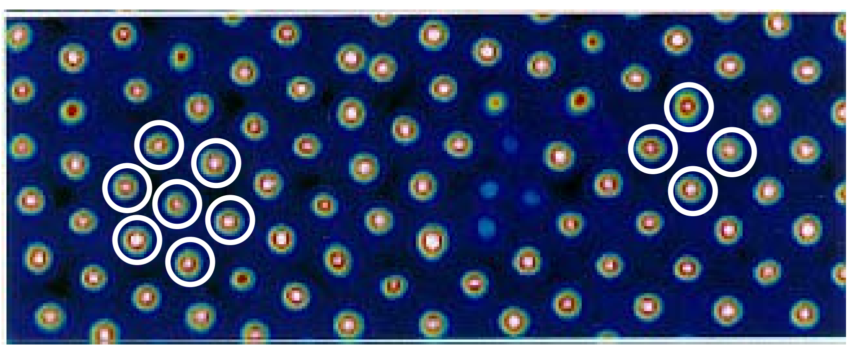
Epitaxy Issues



a = 1.35
1st layer



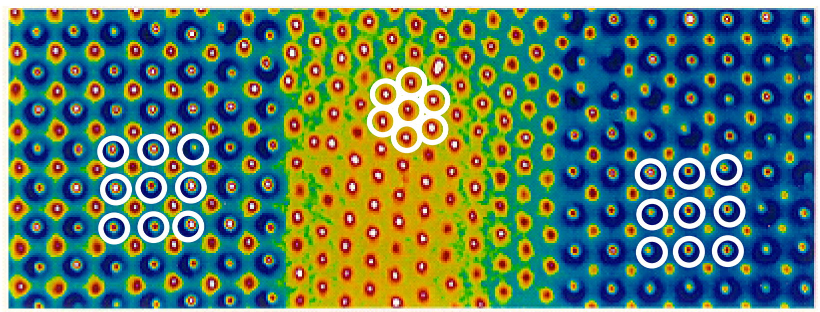
a = 1.35
10th layer



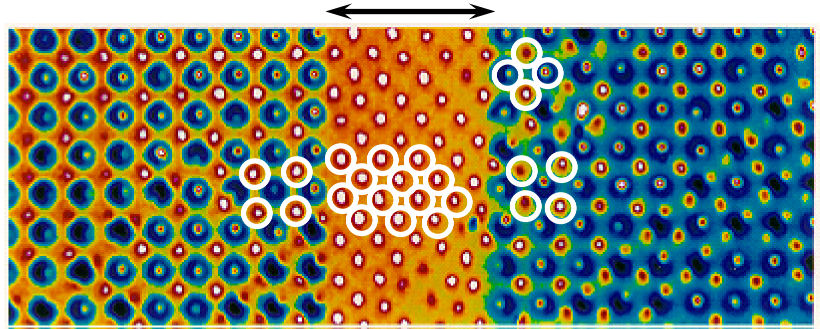
a = 1.3
1st layer

Epitaxy Issues (cont.)

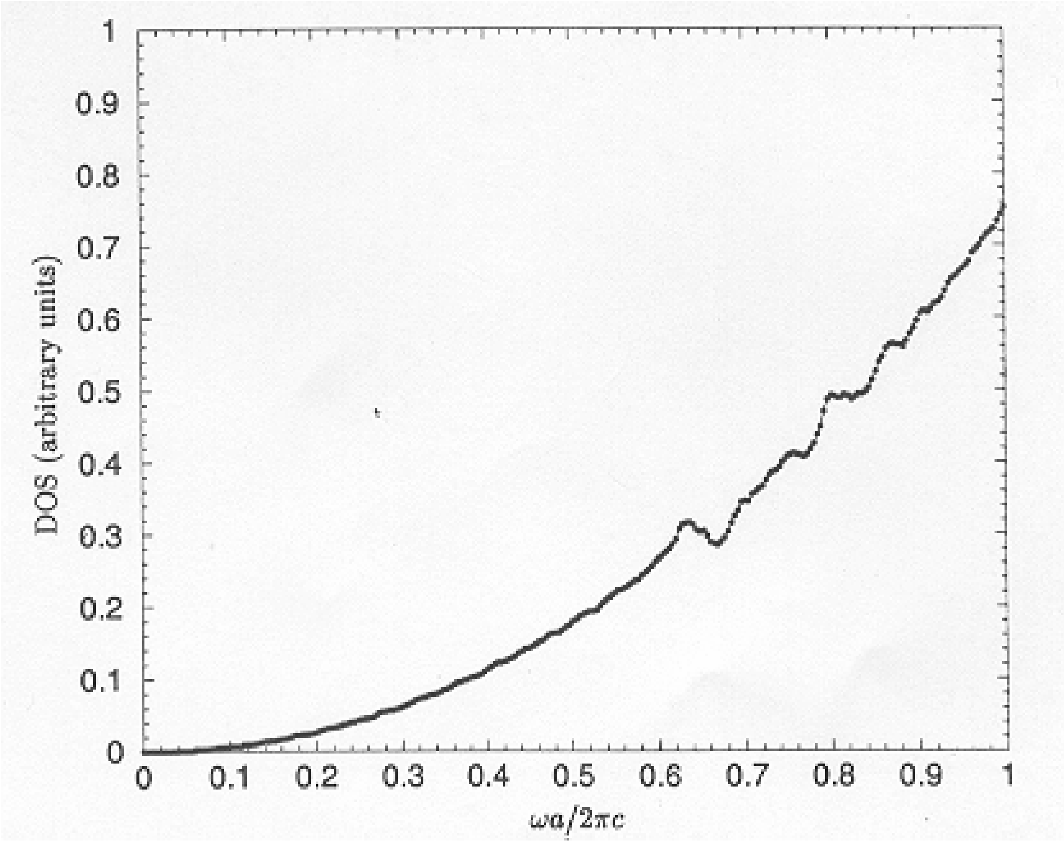
100 no template 100



100 no template 100



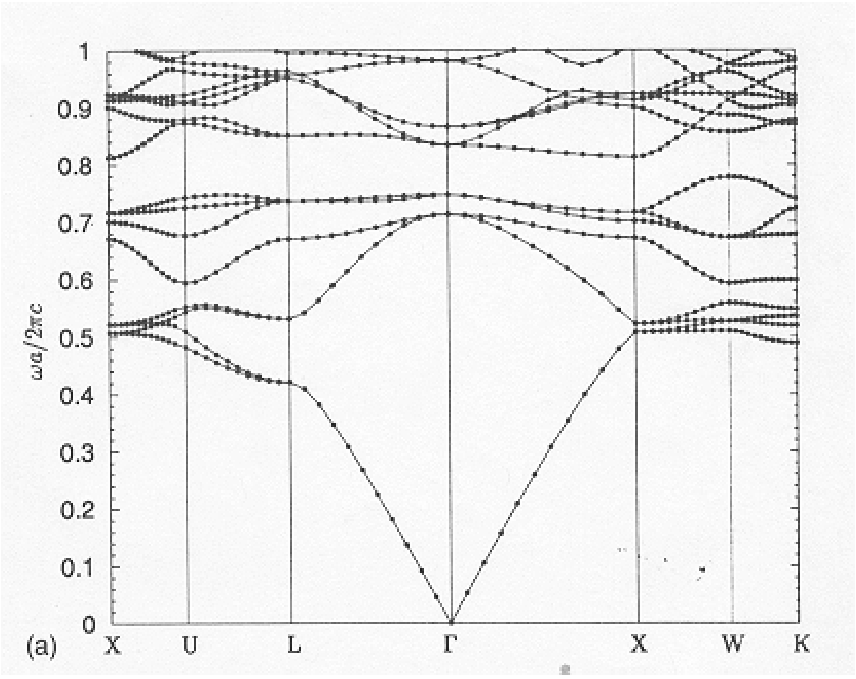
Close-packed FCC Lattice of Silica Spheres in Air

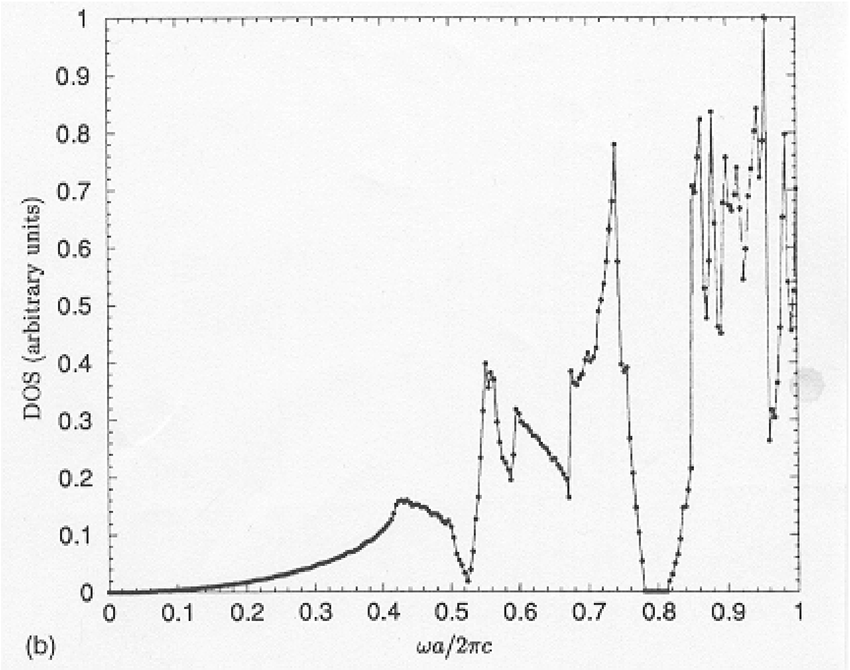


Density of Optical States

K. Busch and S. John, PRE, *58,* 3896 (1998)

Close-packed FCC Lattice of Air Spheres in Silicon





Band structure

Density of Optical States

K. Busch and S. John, PRE, *58,* 3896 (1998)

Photonic Bandgap Materials

FCC lattice of air spheres surrounded by high dielectric matrix

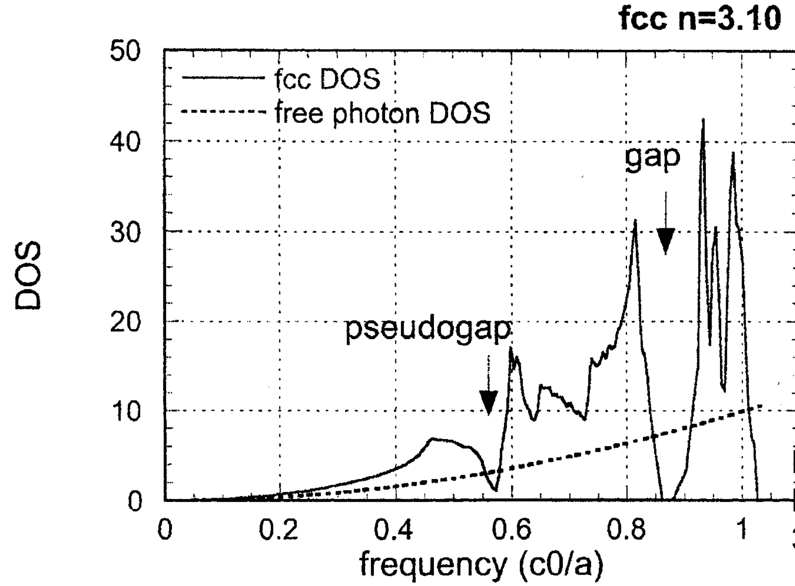
Requirements to obtain gap

$n_2/n_1>3$

FCC structure

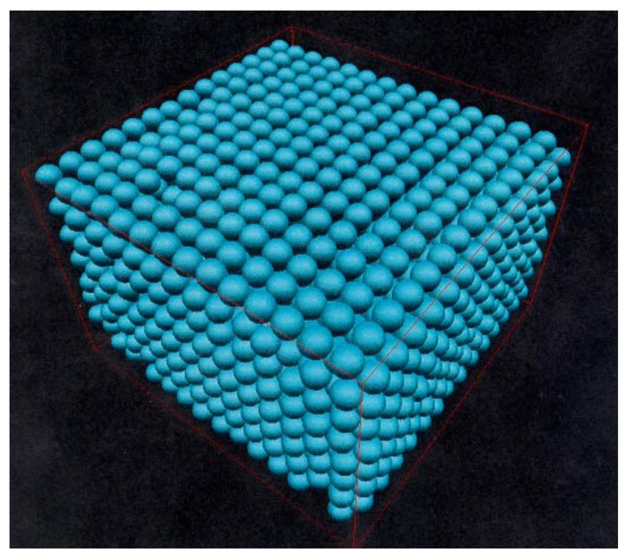
Potential Materials

TiO_2	n=2.5-2.8
CdS	n=2.5
Se	n=2.5-3.2
GaP	n=3.4
Si	n=3.5



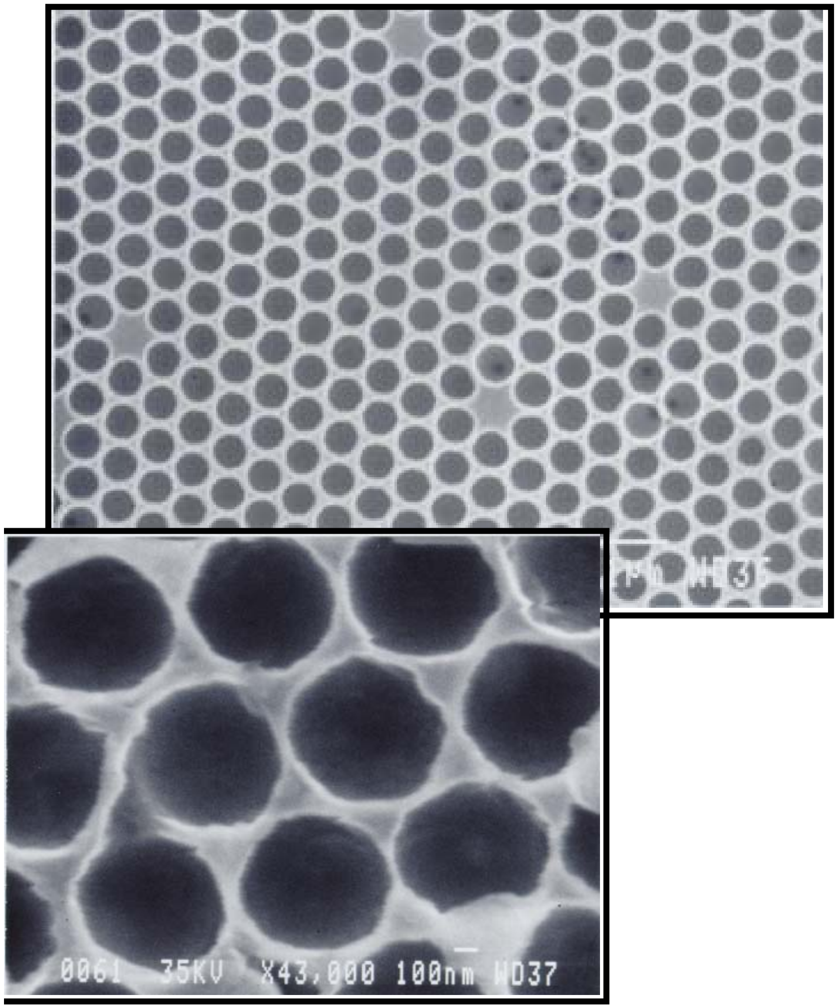
R. Biswas, et al. Phys. Rev. B **57**, 3701, (1998)

FCC crystal of 1μm silica spheres settled on template



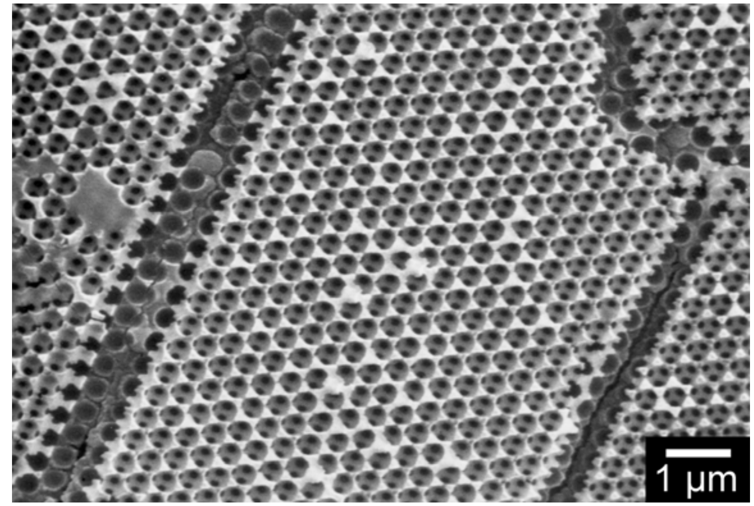
A. van Blaaderen and P. Wiltzius Nature, **385**, 321 (1997)

TiO_2 replica of colloidal assembly



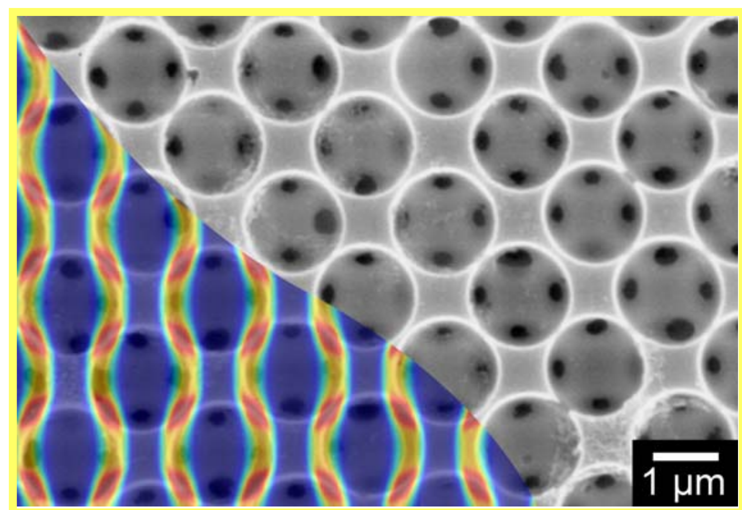
Paul Braun

Electrodeposition

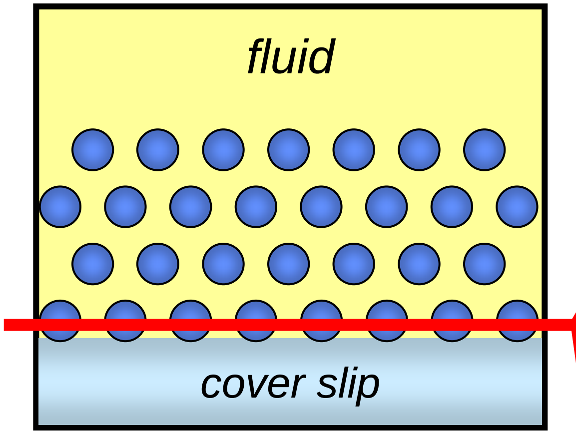


CdSe

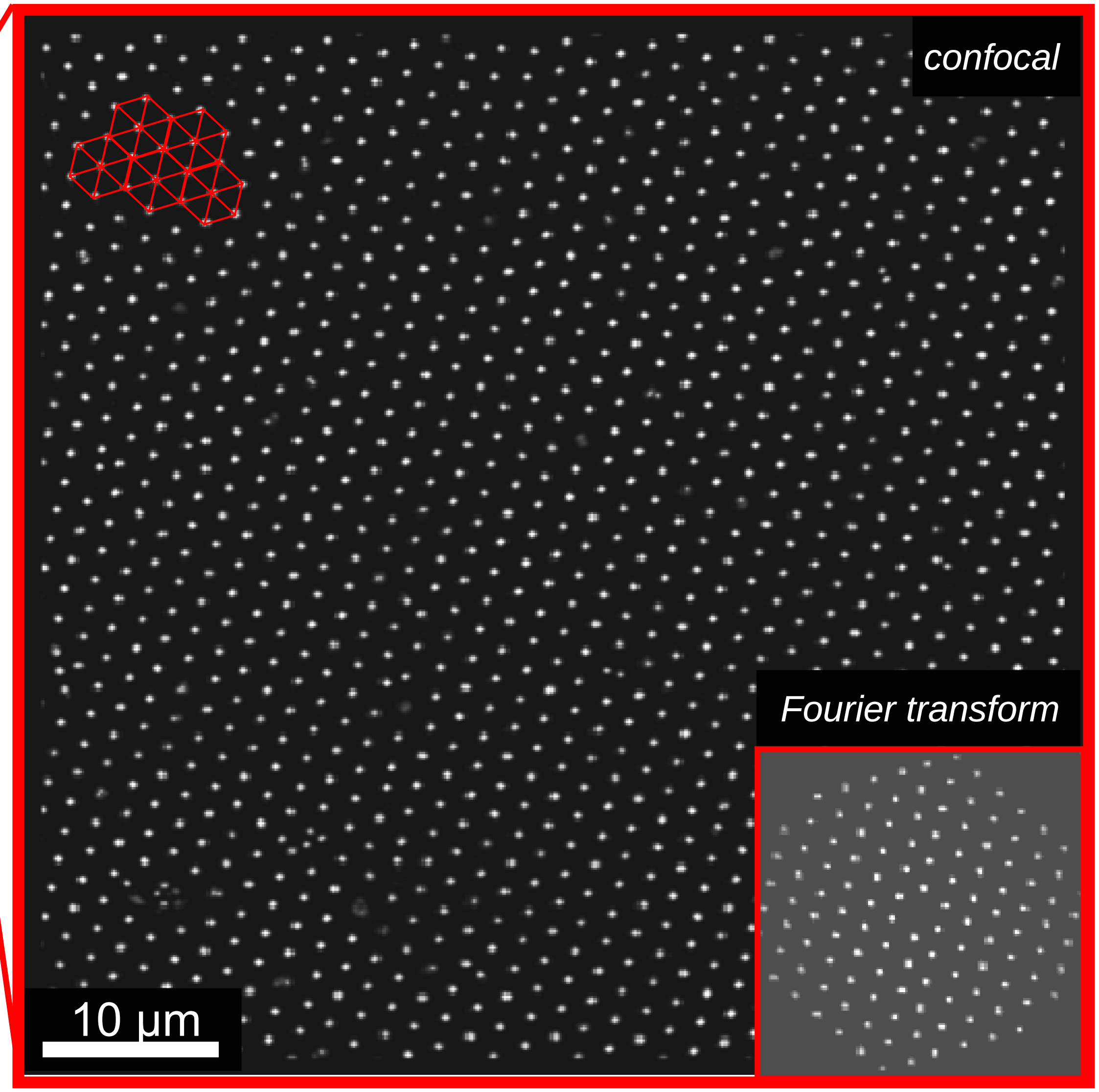
Selenium replica of silica colloid



Charge-Stabilized Colloidal Crystals

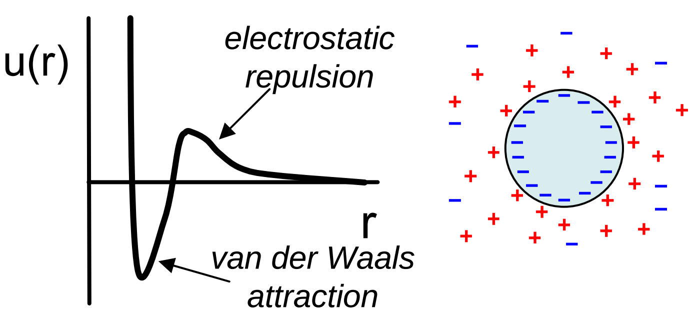


1st layer of crystal



- sediment into a crystal
- hexagonal close packing
- highly ordered in *wet* state

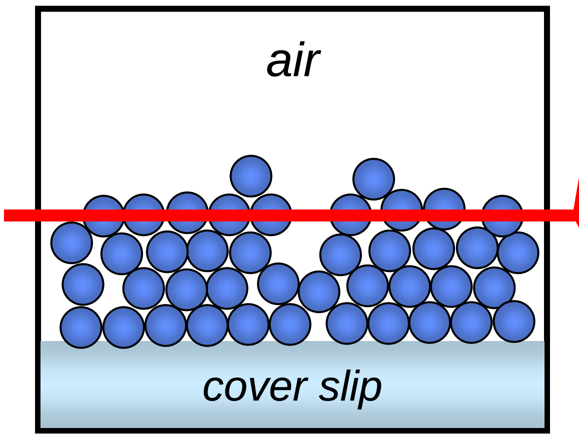
DLVO potential

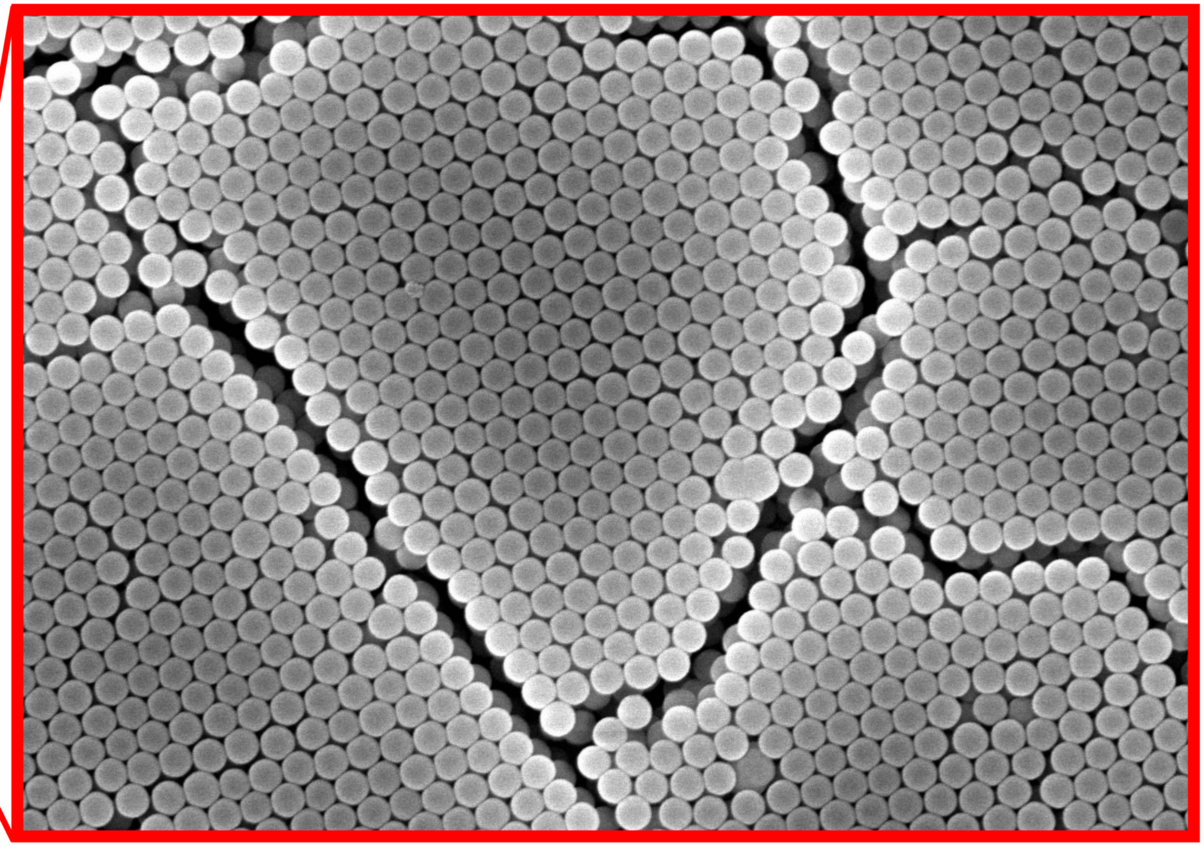


M. A. Bevan et al. To be submitted.

Wet crystal does *NOT* have…

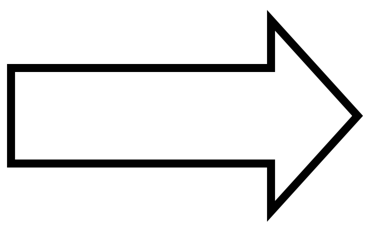
- surface-to-surface packing
- mechanical stability
- order retention when dried
- ability to be further processed





Drying Stresses:

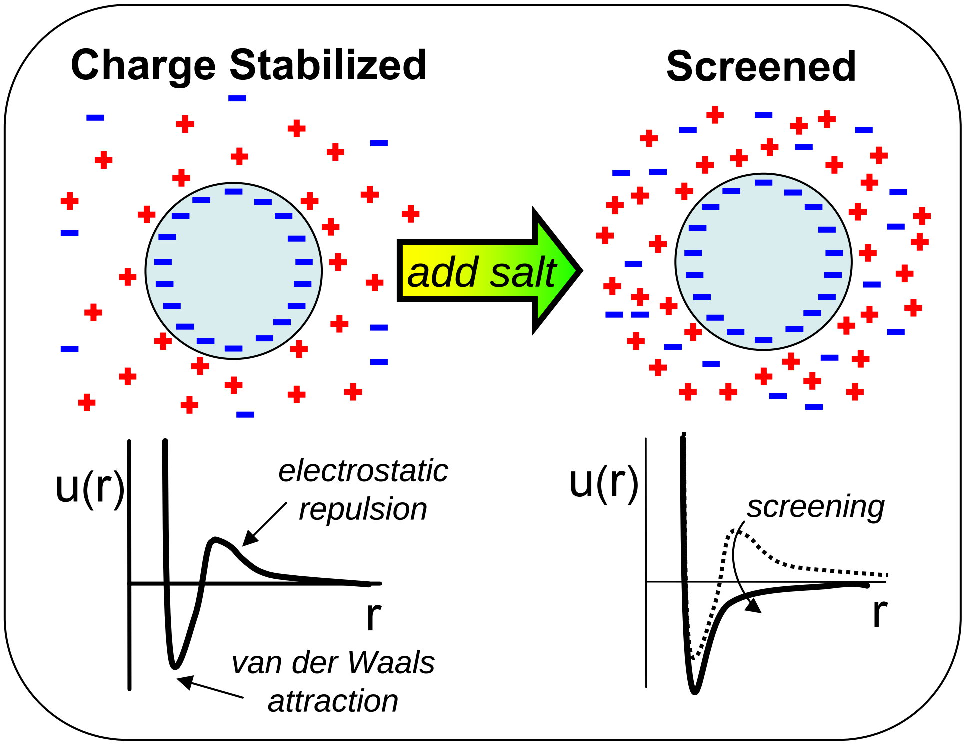
- removal of supporting fluid
- capillary forces
- convection currents

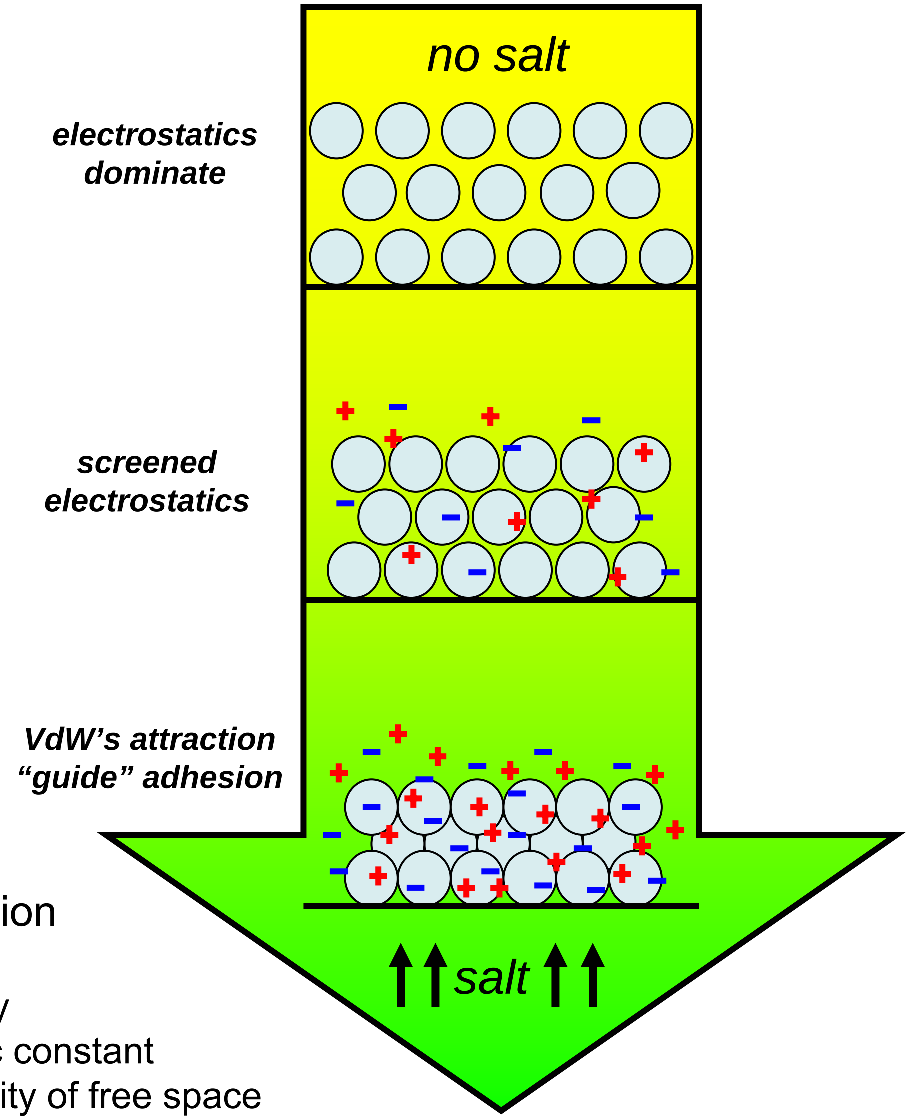


Defects and Disorder

Concept: Controlled Salt Addition

- retain order
- gain stability





<u>Debye length:</u> controls *range* of coulumbic repulsion

$$K^{-1} = \left(\frac{1}{\varepsilon \varepsilon_0 K_B T} \sum_i \rho_i z_i^2 e^2 \right)^{-1/2}$$

ρ = # density
ε = dielectric constant
ε_0 = permitivity of free space
i = index of ionic species

Measuring 2D Orientational Order

Orientation:

$$\Psi_6 = \left| \frac{1}{N} \sum_{j}^{N} \underbrace{\frac{1}{n} \sum_{k}^{n} e^{i6\theta_{jk}}}_{\psi_6} \right|$$

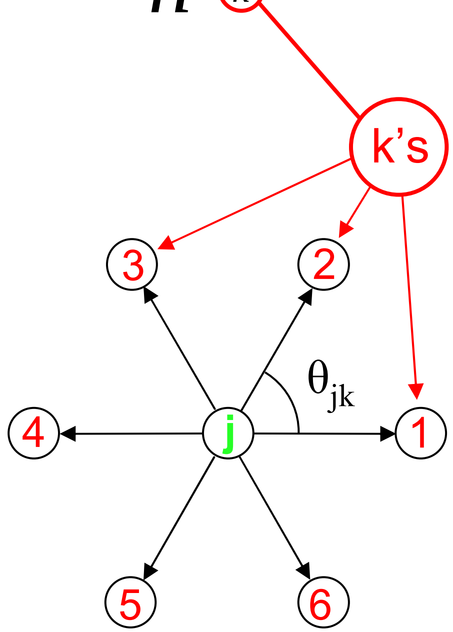
N = # particles

n = nearest neighbors

j = particle index

k = neighbor index

$$\psi_6 = \frac{1}{n} \sum_{k}^{n} \left(\cos 6\theta_{jk} + i \sin 6\theta_{jk} \right)$$



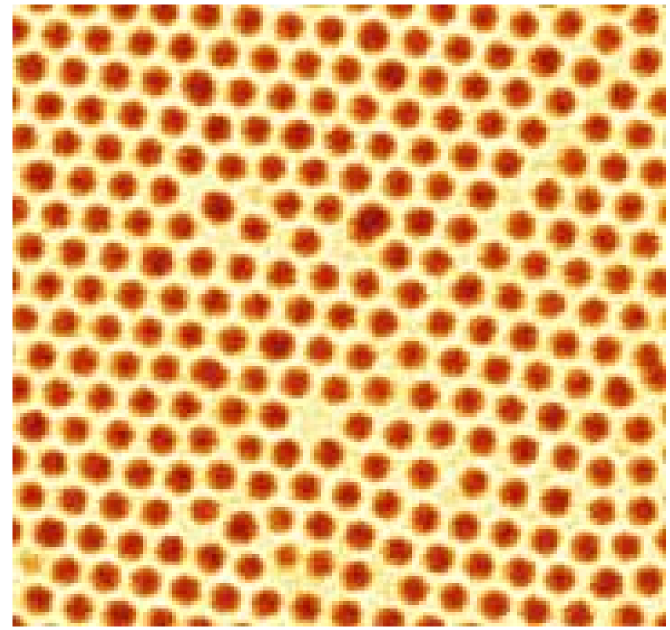
$\Psi_6 \rightarrow 1$ = perfect order

$\Psi_6 \rightarrow 0$ = non 6-fold

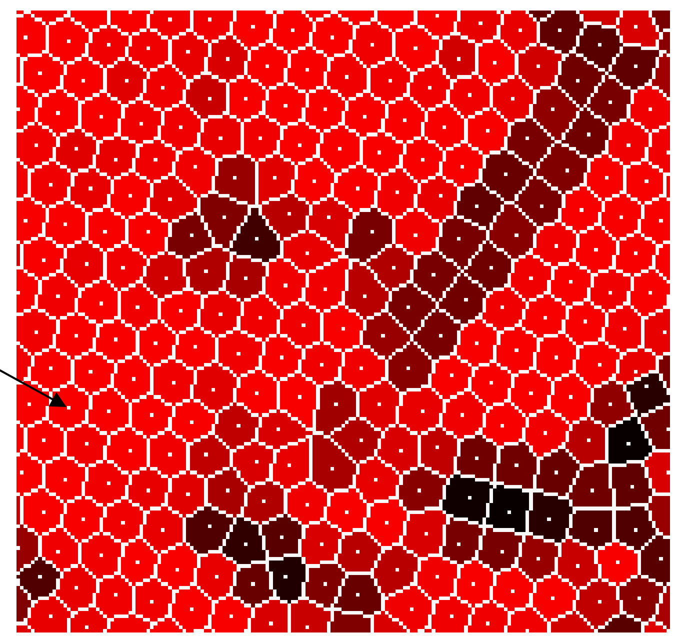
All points in the polygon are closest to this point

Nearest neighbors share sides of polygon

Confocal Image



Voronoi Plot



Measuring 2D Translational Order

Radial Distribution Function:

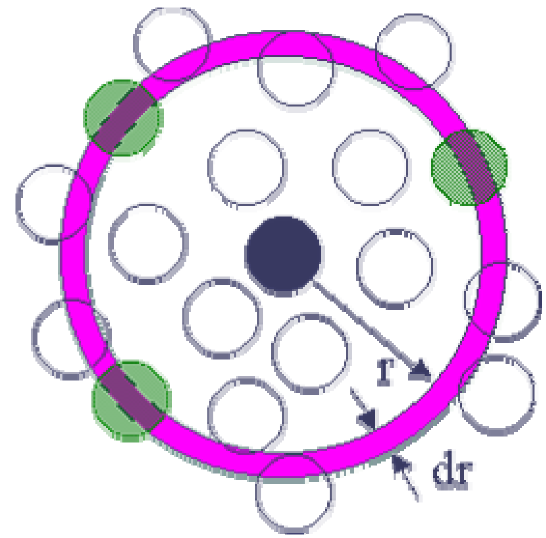
$$g(r) = \frac{\langle \rho(r) \rangle}{\rho}$$

r = radial distance from a particle

<ρ(r)> = bin averaged # density between r, r+dr

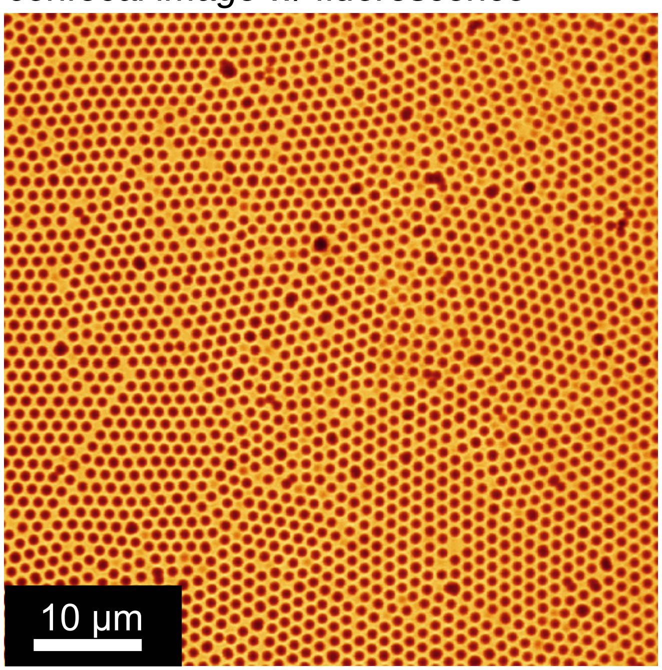
ρ = bulk # density

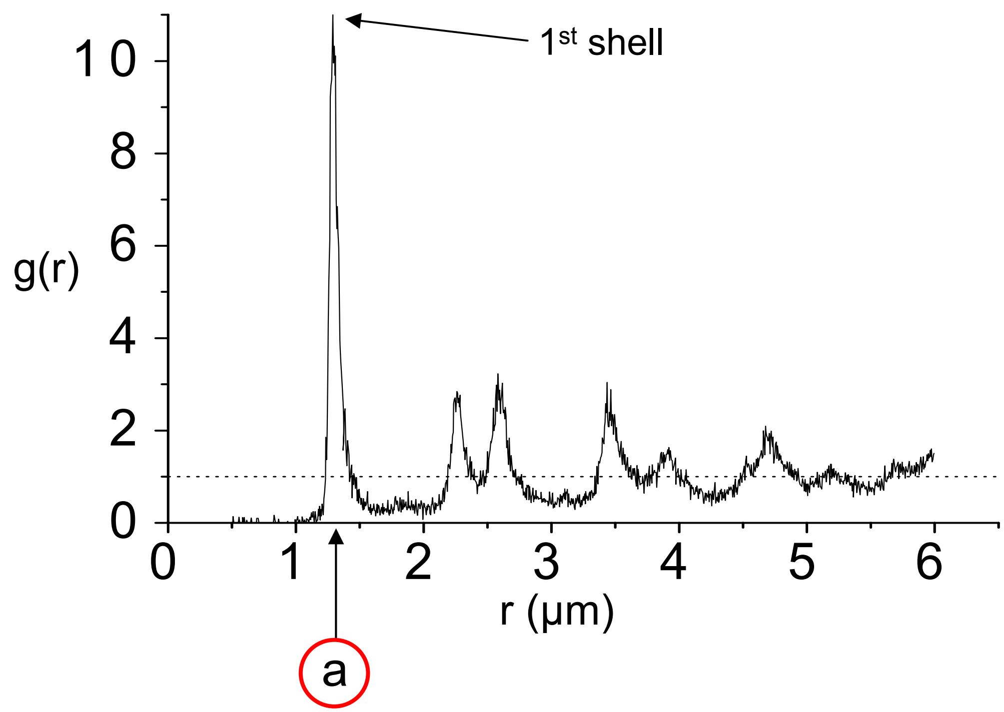
a = nearest neighbor separation



http://www.ccr.buffalo.edu/etomica/app/modules/sites/Ljmd/Background1.html

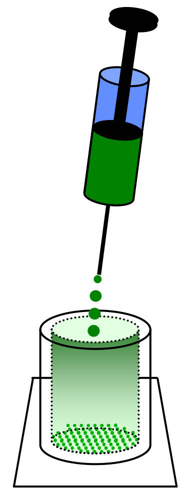
confocal image w/ fluorescence





Early Attempts: Salt Injection

[NaCl]	structure	ϕ_A	ψ_6
0 mM	crystal	0.40	0.93
0.1 mM	polycrystal	0.61	0.60
1 mM	polycrystal	0.67	0.32
10 mM	polycrystal	0.70	0.08
100 mM	gel	-	-
1000 mM	gel	0.37	0.02

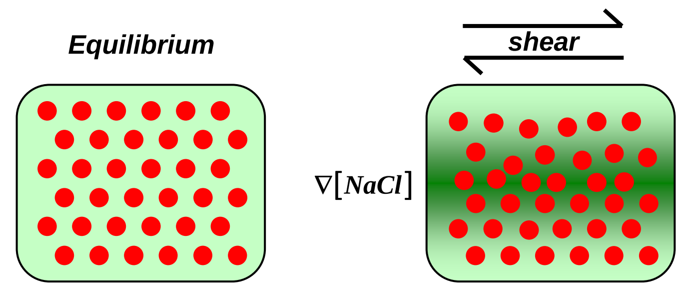


Sedimentation cell

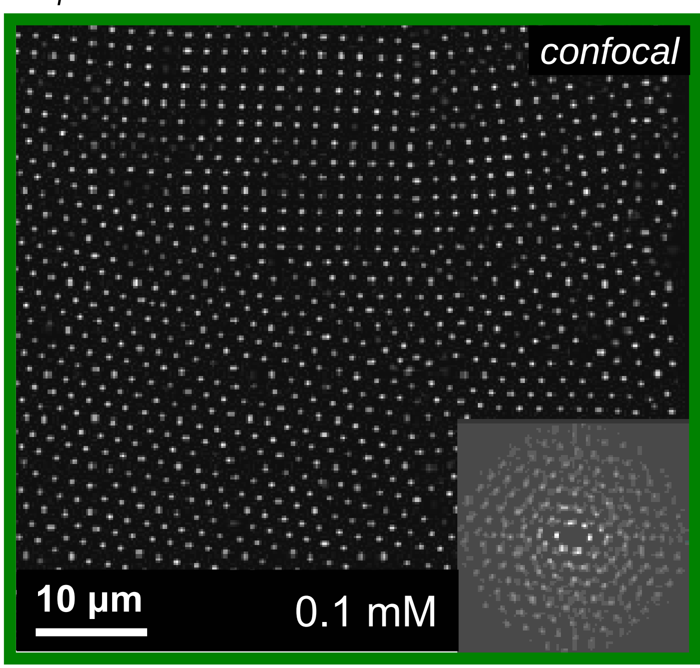
- 1.18 μm SiO_2 colloids
- H_2O with pH ~ 7
- Φ ~ 0.01

Issues:

- rate of contraction, $\left(\frac{1}{R}\frac{da}{dt}\right)$
- Brownian equilibration, $\left(\frac{D}{R^2}\right)$
- concentration gradients
- shear flow

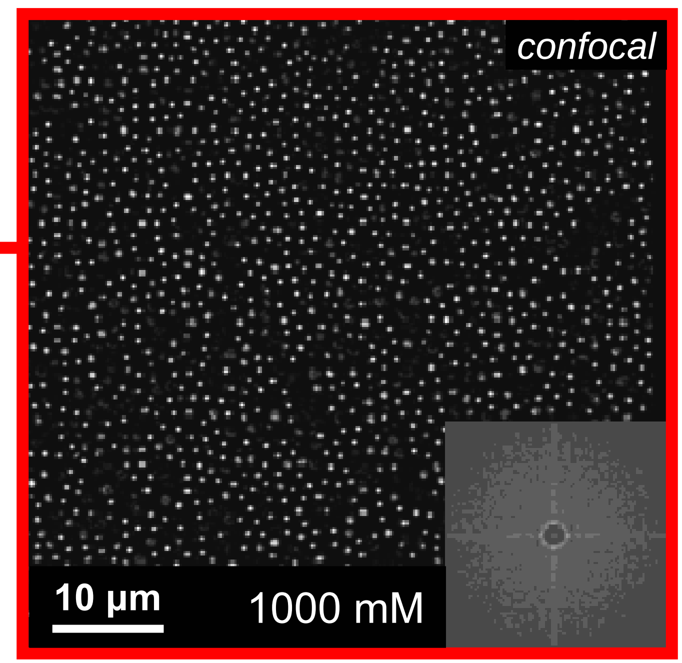


Adapted from Bevan et al.



polycrystal

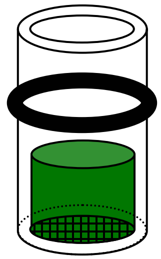
gel



Controlled Addition

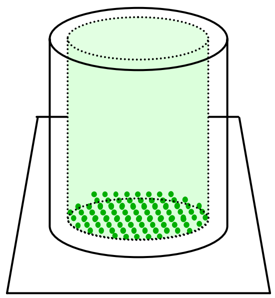
Centrifuge filter with salt solution

- 5000 NMWL cutoff
- NaCl added in steps



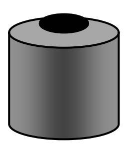
Sedimentation cell

- 1.18 μm SiO_2 colloids
- H_2O with pH ~ 7
- Φ ~ 0.01
- NO SALT

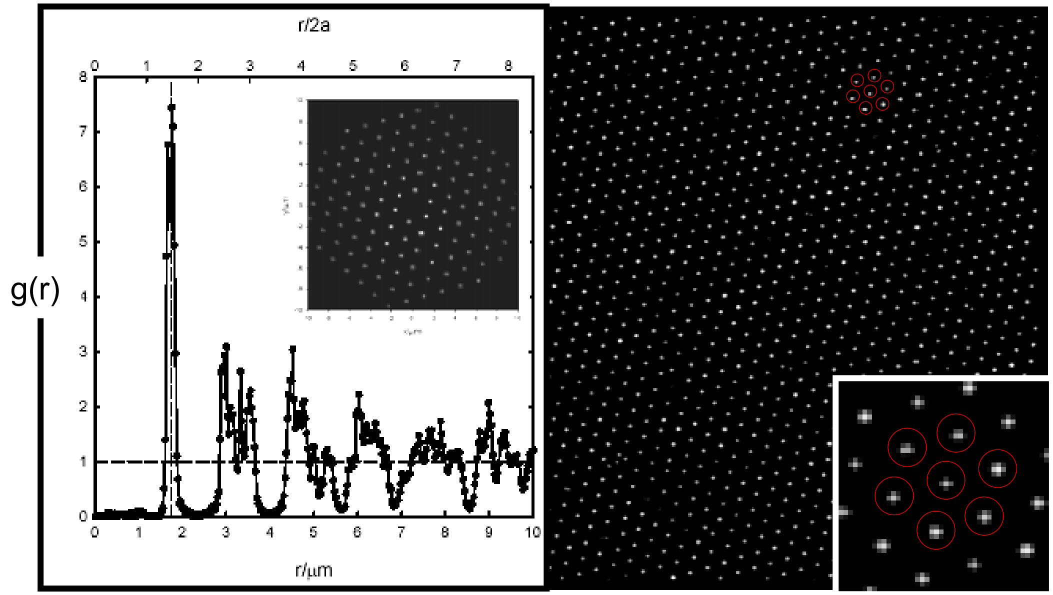


Confocal Microscope

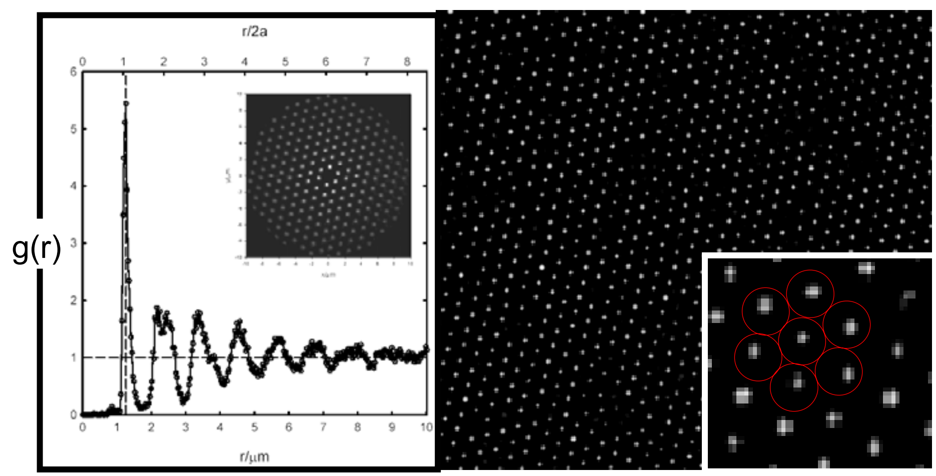
- 3D reconstructions
- fluorophore needed
- IDL; image processing



No salt

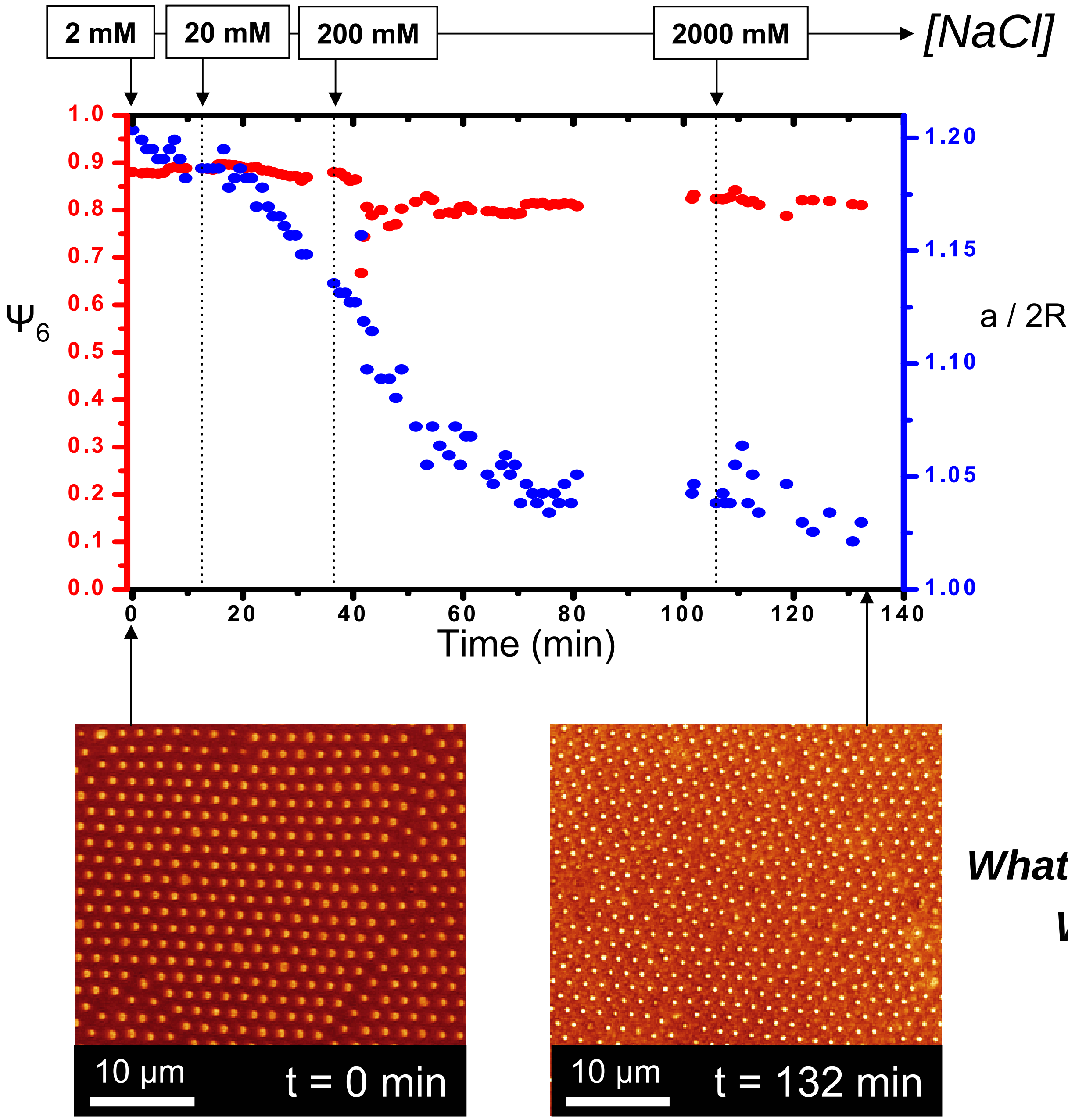


10 mM NaCl added



M. A. Bevan et al. In preparation for submission.

Tracking 2D Order



Results:

- lattice contracts
- order retained
- ∇[salt] → disorder
- shear → disorder

What about the rest of the crystal?

What's happening in 3D?

Imaging in 3D

index matching:

- decreases scattering
- increases observation range
- decreases initial order

glycerol:

n_{gly} = 1.47

η_{gly} = 934 mPas

water:

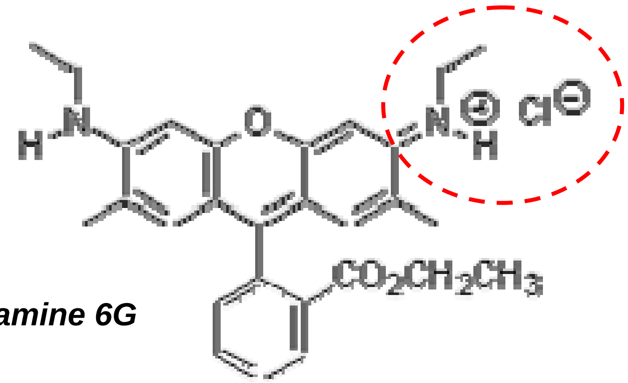
n_{wat} = 1.33

η_{wat} = 0.89 mPas

silica:

n_{silica} ~ 1.4

Rhodamine 6G



http://omlc.ogi.edu/spectra/PhotochemCAD/html/rhodamine6G.html

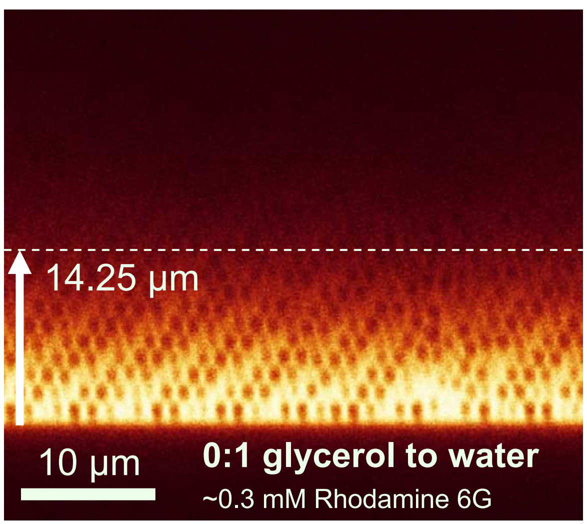
fluorescent dye:

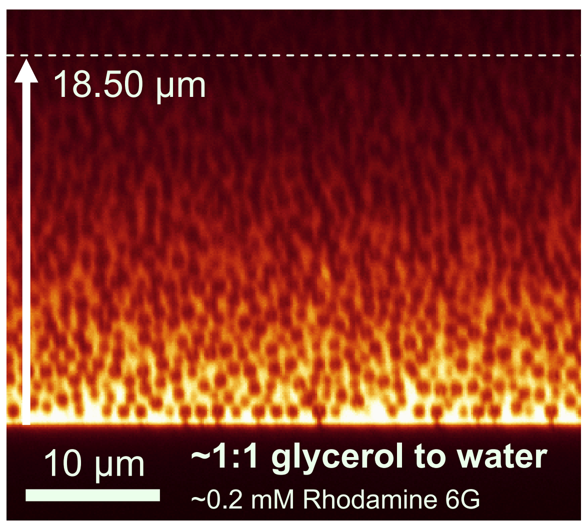
- increases contrast
- feature identification
- increases initial ionic strength
- decreases initial order

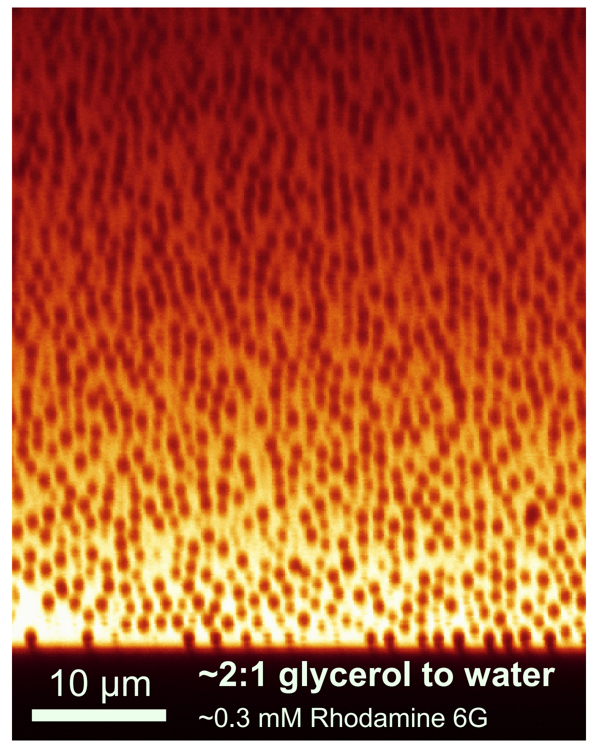
Rhodamine 6G:

disassociates in water

need ~0.1 mM for contrast

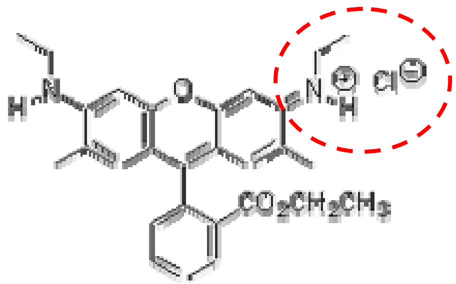






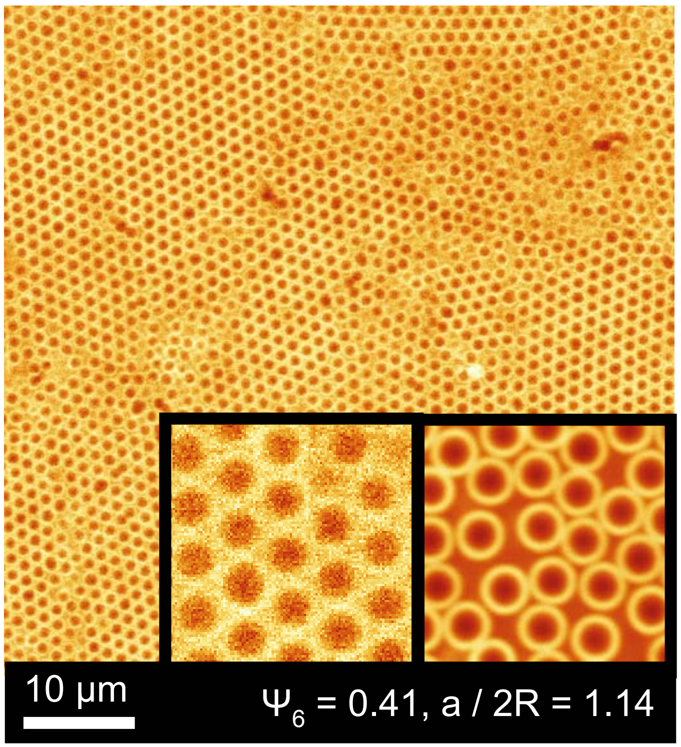
Rhodamine 6G

- water soluble
- dissociates

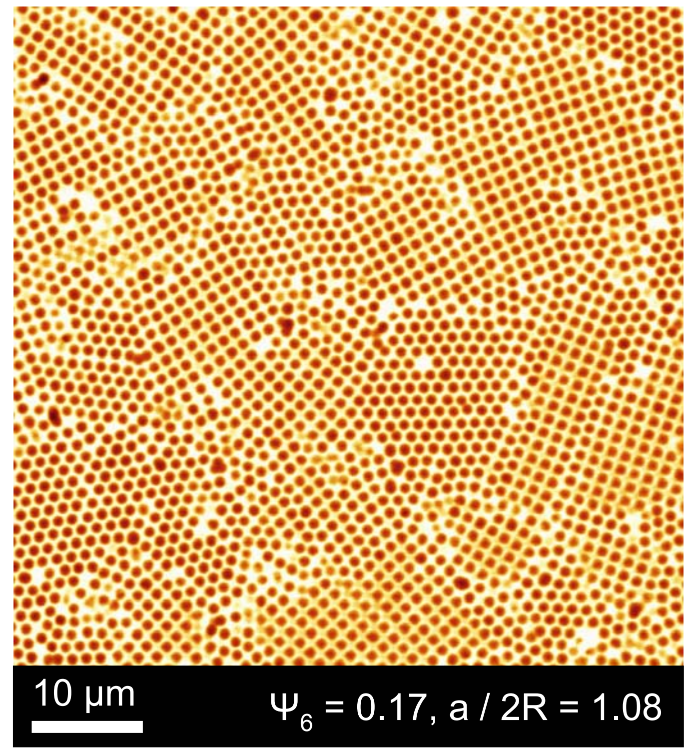


[Rhodamine]	structure	contrast
0.002 mM	crystal	NO
0.02 mM	crystal	THESHOLD
0.2 mM	crystal/gel	YES
2 mM	crystal/gel	YES

[R6G] = 0.02 mM

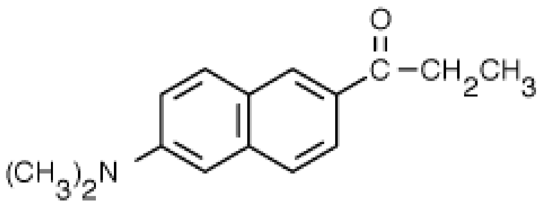


[R6G] = 0.2 mM



Prodan

- non-ionic
- water solubility?

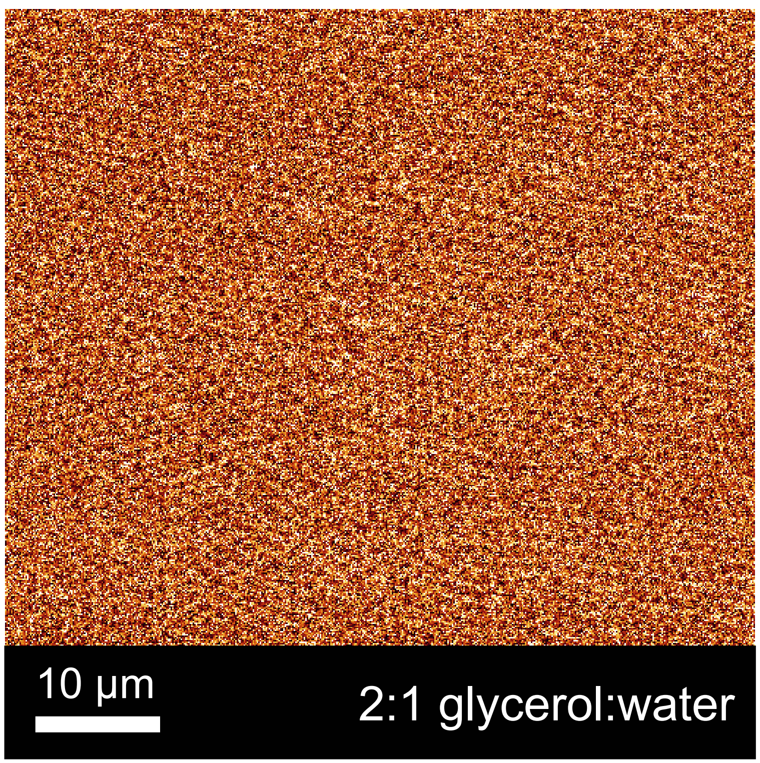


http://www.probes.com/servlets/structure?item=248

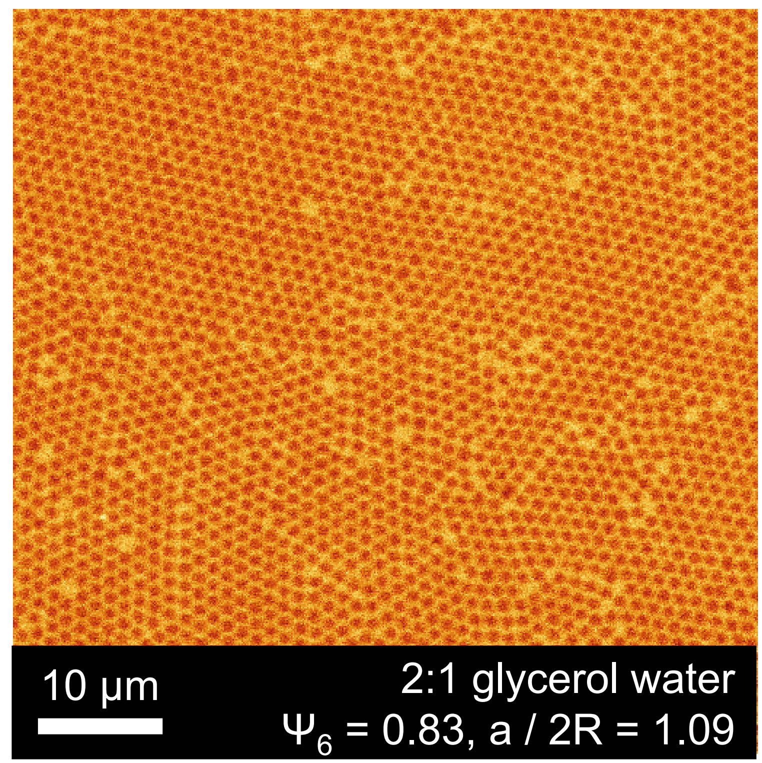
[Prodan]	glycerol:water by volume	structure	contrast
saturated*	0:1	crystal	**NO**
saturated*	2:1	crystal	**NO**

* *concentration was unable to be determined*

Single Scan: *~1 second*



25 Scan Average: *~25 seconds*



Controlled Dye Addition:

- infill 0.2 mM Rhodamine
- reduce debris
- retain order

Centrifuge filter

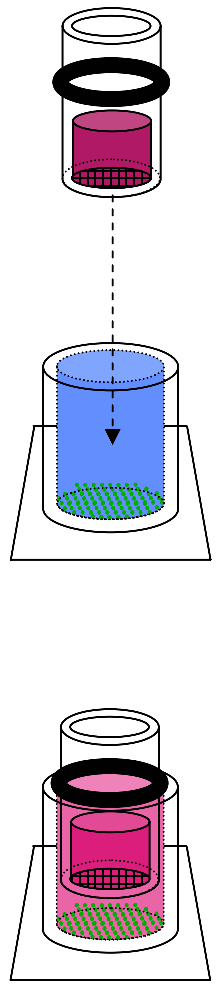
- 5000 NMWL cutoff
- 400 μL of R6G
- [R6G] = 0.45 mM

Sedimentation cell

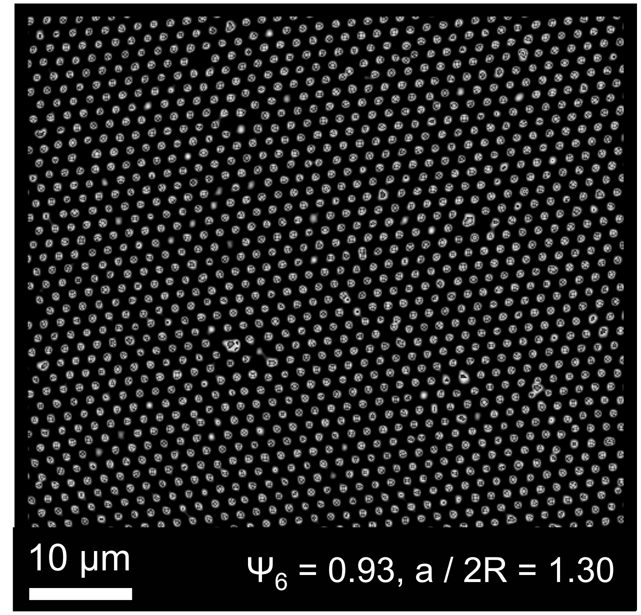
- 1.18 μm SiO_2 colloids
- H_2O with pH ~ 7
- Φ ~ 0.01

Equilibrated cell

- [R6G] ~ 0.2 mM



Initial: reflectance



Final: fluorescence