Colloids

- What’s a colloid?
- Colloidal Interactions and Colloidal Crystals
- Hard Spheres and thermodynamics
- Packings and the Liquid-Crystal Transition
- Hard Ellipses
- Role of Gravity
- Sedimentation Dynamics
- Sedimentation Equilibria
- Microgravity Experiments
- Crystallization Kinetics
- Phonons in hard Sphere Crystals

Colloids?

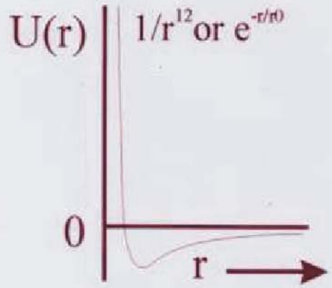
COLLOIDS. In a paper entitled "Liquid Diffusion applied to Analysis" published in 1861 in the *Philosophical Transactions,* Thomas Graham (*q.v.*) described the results of an investigation carried out with very simple means. Aqueous solutions were placed in a cylindrical vessel the bottom of which was formed by a piece of animal membrane, like pig's bladder, or by the recently invented parchment paper, and the membrane immersed in water. The amount of dissolved substance which diffused into the outer water was determined from time to time. Graham found that the numerous substances examined fell into two classes: those which diffused in appreciable amounts and those which hardly passed through the membrane in perceptible quantities. The former were without exception substances known to crystallize from their solutions, like various salts or sugar, while the latter, among which were albumin, gum arabic or gelatin, had never been known as crystals. Graham accordingly called the first class *crystalloids* and the second class *colloids* (from *colla,* glue).

Encyclopaedia Britanica 1948

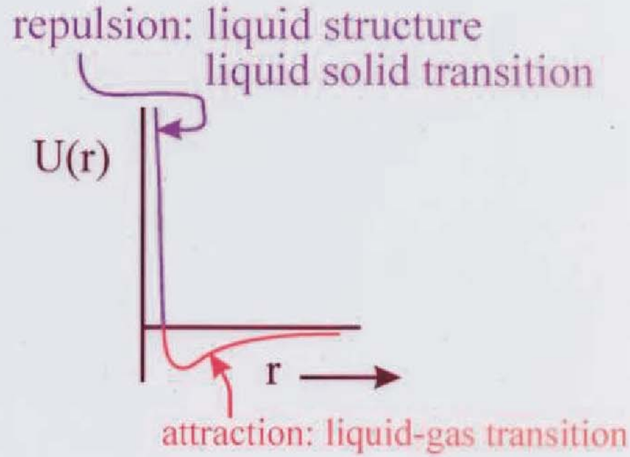
Colloidal Interactions

		Range	Strength
Van der Waals	Attractive	0.3-10nm	0-100k_BT
Electrostatic	Attractive Repulsive	0.3-1000nm	0-1000 k_BT
Depletion	Attractive	10-300nm	0-20 k_BT
Brushes	Hard repulsion Soft repulsion Soft-repulsion Reversible attraction	5-50nm	0-50 k_BT
DNA	Repulsion Specific attraction Reversible	10-5000nm	0-100 k_BT

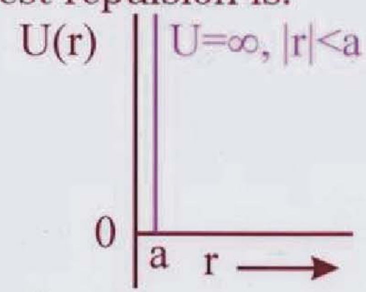
Why Hard Spheres?



typical interparticle potential



Most interesting things depend on repulsive part
simplest repulsion is:



The essence of the problem -- **Hard Spheres**

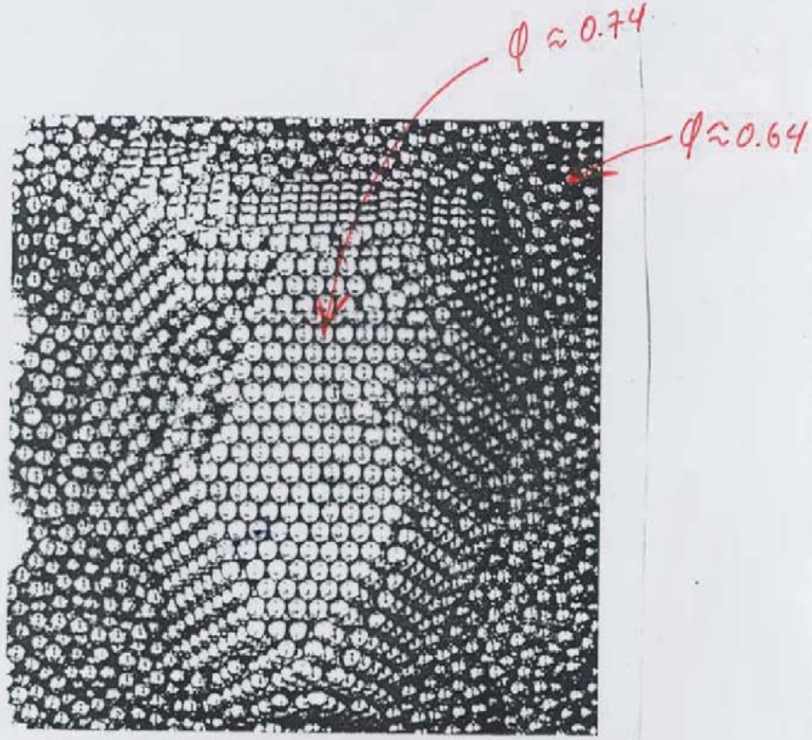


FIGURE 14. Face-centred cubic 'crystal' surrounded by 'liquid' caused by shearing ball-bearing mass. 111 face is shown at the top surface.

Gravitational Height

$$mgh = k_B T$$

Van der Waals and excluded volume

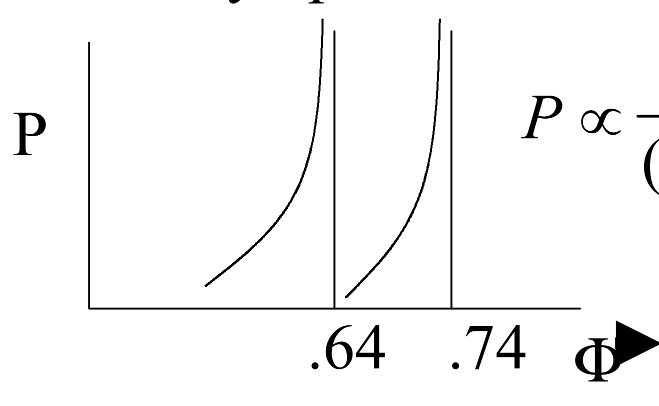
$$S = Nk_B \ln(V - Nb)$$

$$= Nk_B \ln\left(V\left(1-\phi/\phi_C\right)\right)$$

$$P = \frac{Nk_B T}{V - Nb} = \frac{Nk_B T}{V(1-\phi/\phi_C)}$$

Exact in 1D

Exact asymptotic form in any dimension

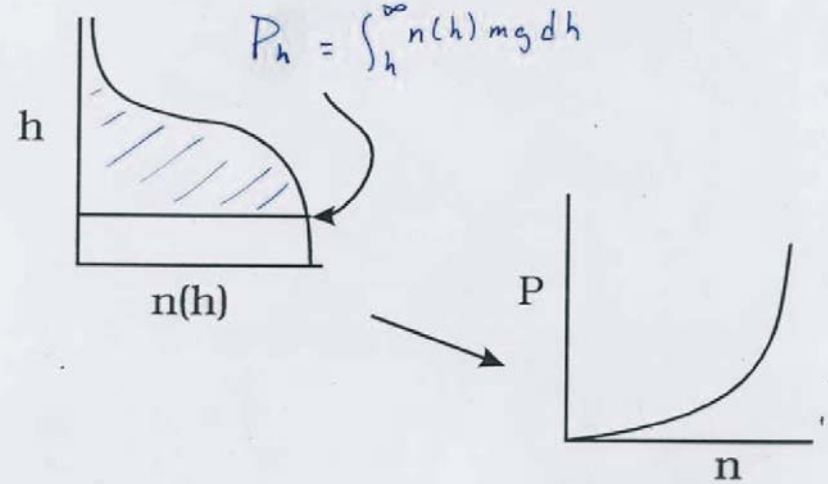


$$P \propto \frac{1}{(1-\phi/\phi_C)}$$

Sedimentation Equilibria

Profile gives Equation of State

$$P_h = \int_h^{\infty} n(h)\, mg\, dh$$

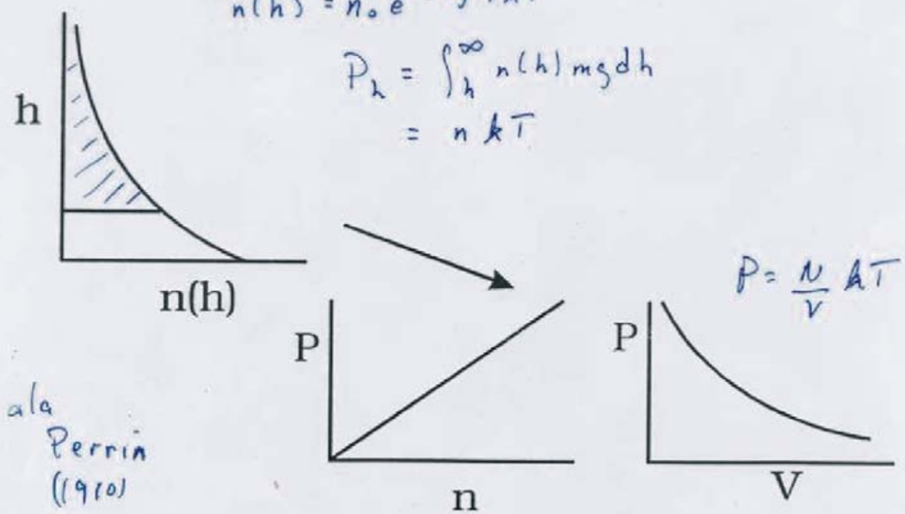


$n = \phi / v_p$

Ideal Gas

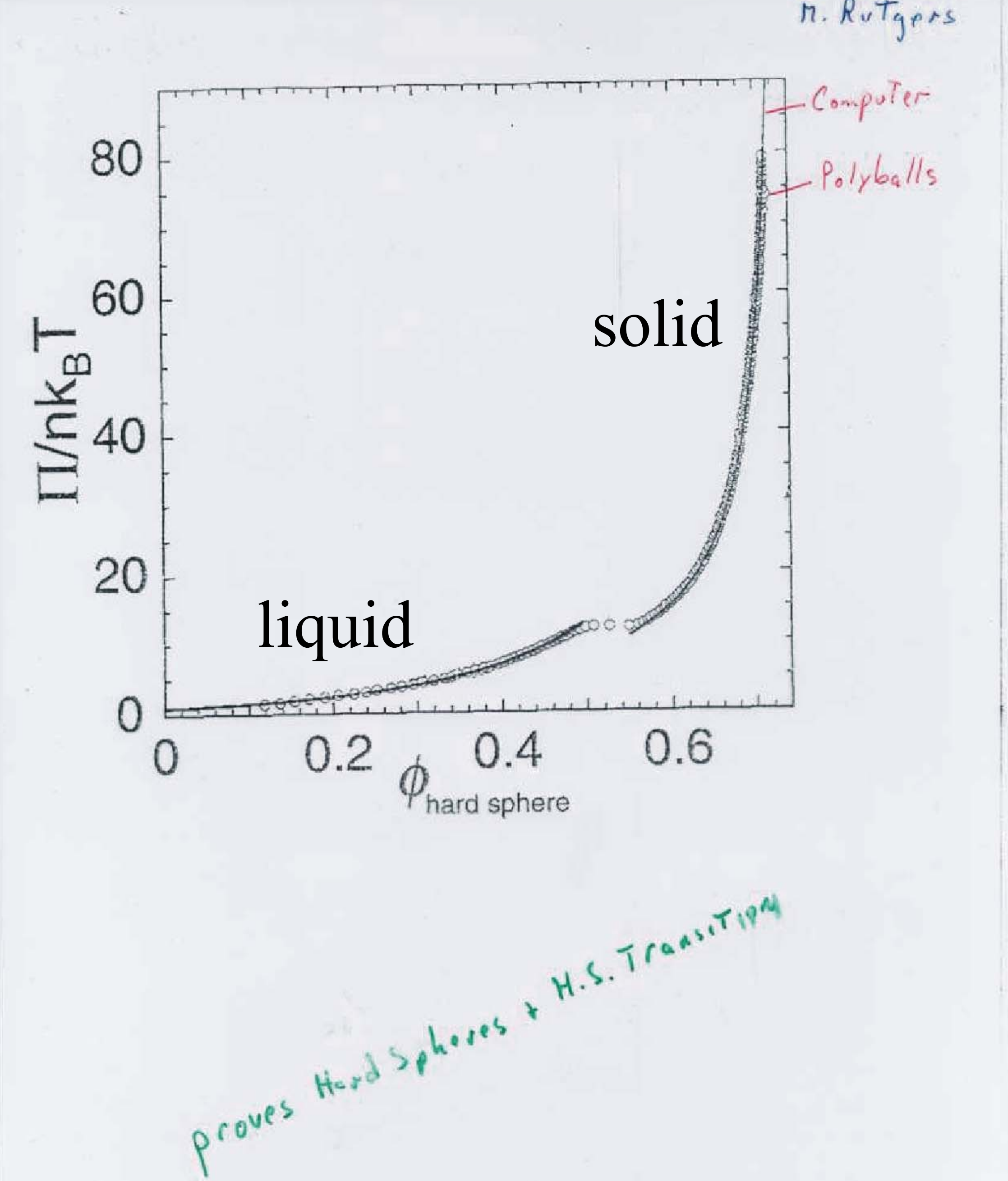
$$n(h) = n_0 e^{-mgh/kT}$$

$$P_h = \int_h^{\infty} n(h)\, mg\, dh = n\, kT$$

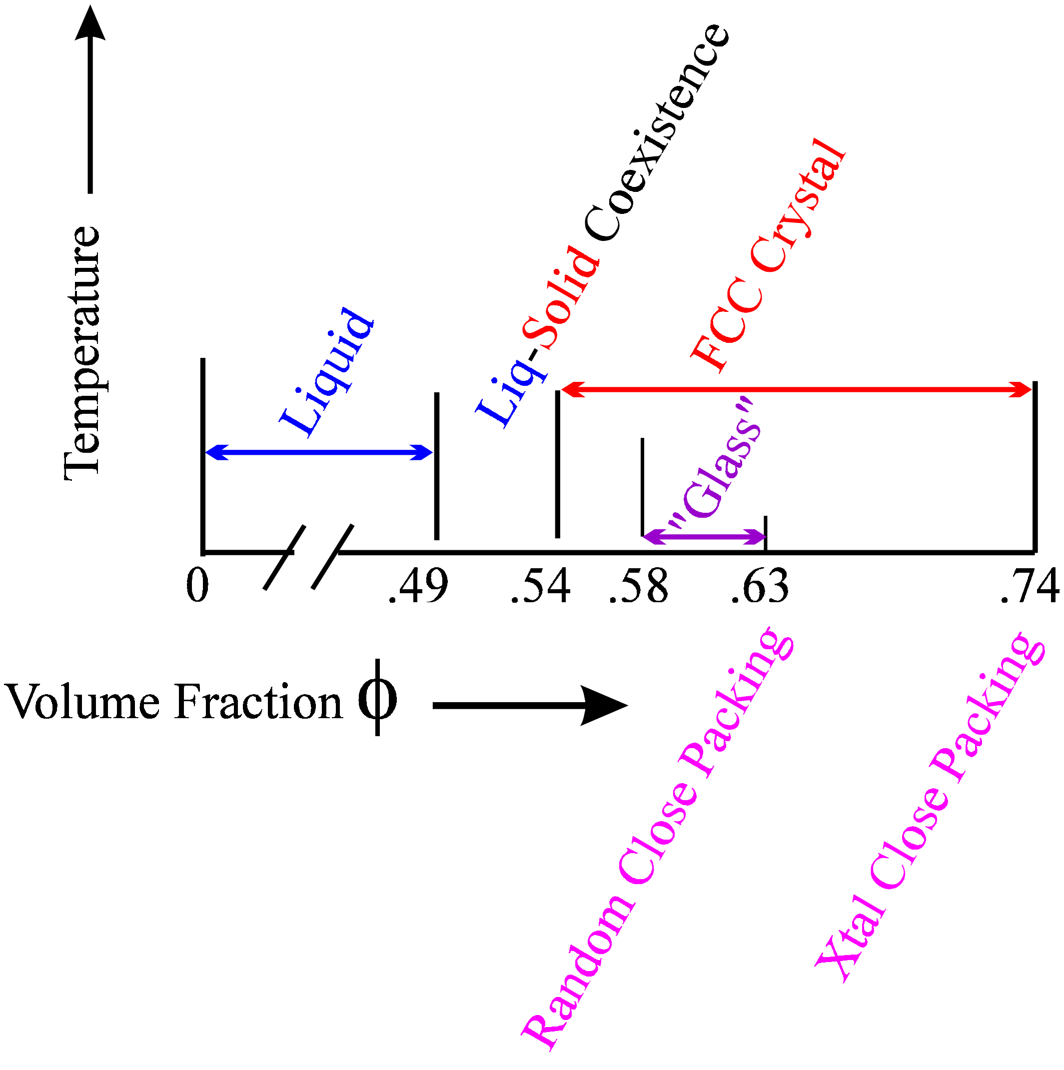


$P = \frac{N}{V} kT$

a la Perrin (1910)


M. Rutgers
Computer
Polyballs
solid
liquid
80
60
40
20
0
0
0.2
0.4
0.6
Π/nk_B T
φ_hard sphere
proves Hard Spheres + H.S. Transition

Hard Sphere Equilibrium Phase Diagram



Phase Diagram by 1g Experiment

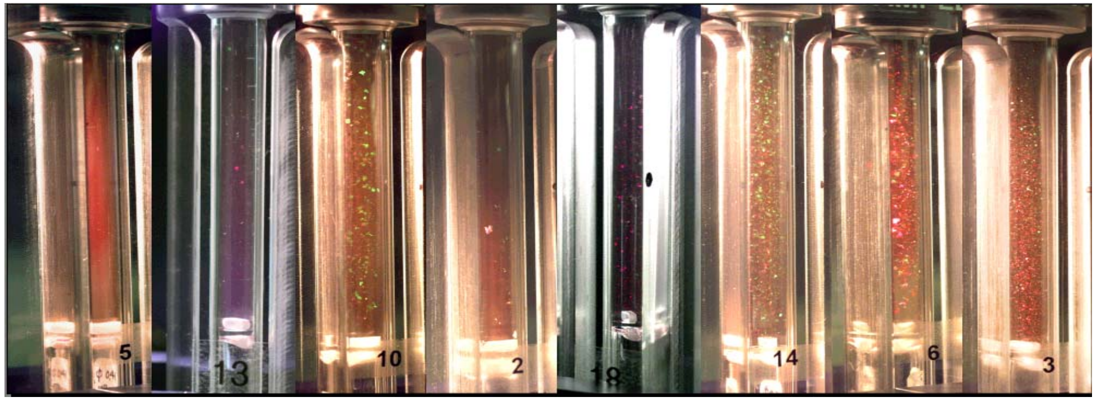
325 *nm* PMMA/decalin/CS2

0.637 0.621 | 0.595 | 0.578 0.553 | 0.528 0.512 0.502 | 0.478

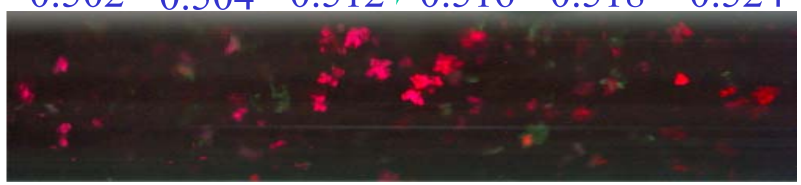
Glass Mainly | Crystal Heterogeneous | Fully crystallized | Coexistence | Liquid

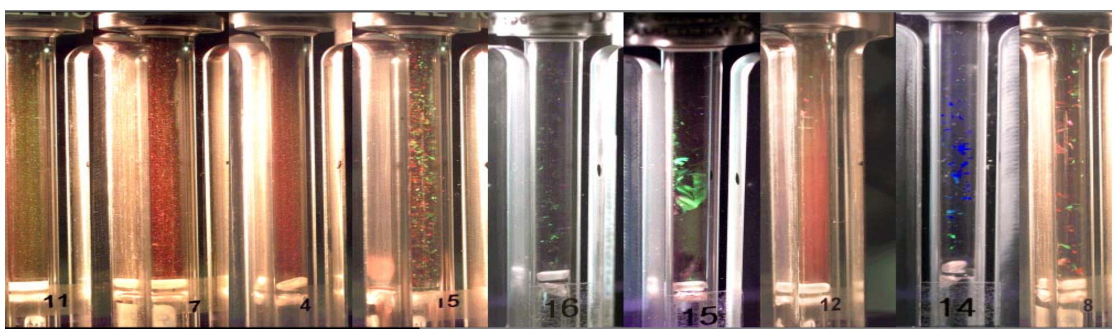
Pusey & van Megen, *Nature, 320 (1986) 340*

CDOT 1998

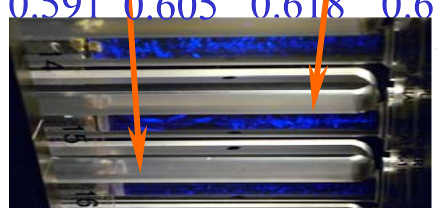


0.50 0.502 0.504 0.512 0.516 0.518 0.524 0.537

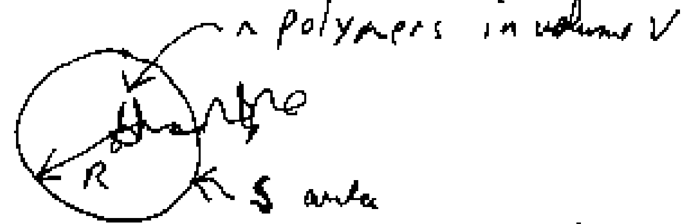




0.547 0.549 0.561 0.591 0.605 0.618 0.619 0.633 0.634



Microdomain size / Periodicity for Diblock Mesophases



$$\frac{E_{surface}}{polymer} = \frac{\gamma S}{n} = \frac{\gamma S N}{\rho V} = C\gamma N/\rho R \qquad n = \frac{\rho V}{N}$$

ρ = monomer density; N = monomers in polymer

$$\frac{E_{elastic}}{polymer} = \frac{3}{2}\left(\frac{R^2}{Na^2}\right) k_B T$$

$$C = \frac{SR}{V}$$

$= 3$ spheres
$= 2$ cylinders
$= 1$ lamellae

$$E/n = \frac{C\gamma N}{\rho R} + \frac{3}{2}\left(\frac{R^2}{Na^2}\right) k_B T$$

minimize w.r.t. R $\quad -\frac{C\gamma N}{\rho R^2} + 3\frac{R}{Na^2} k_B T = 0$

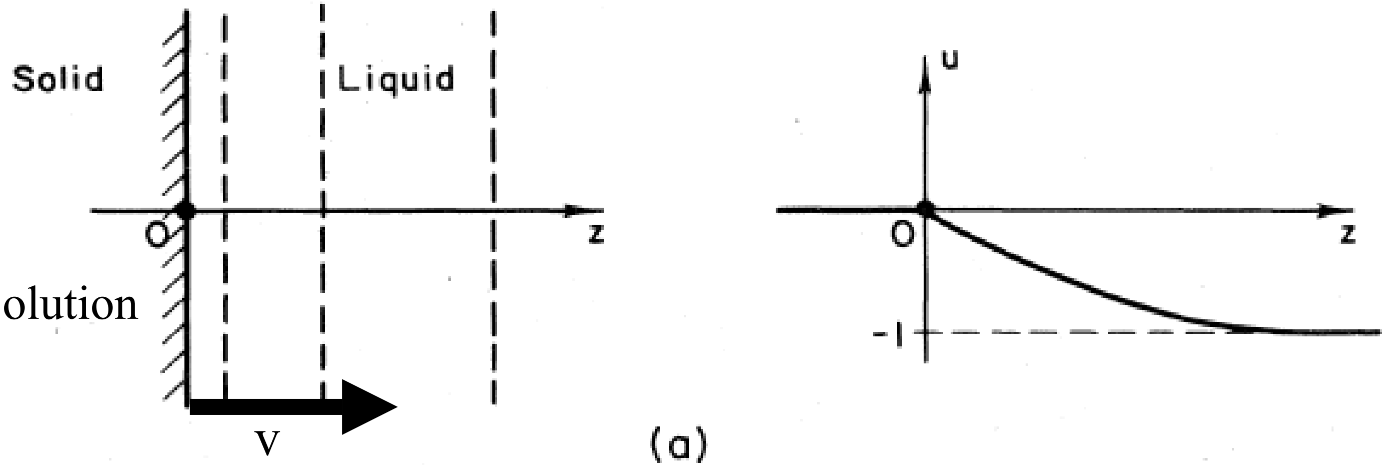
$$R^3 = N^2 \frac{C\gamma a^2}{3\rho k_B T}$$

$$\boxed{R = N^{2/3}\left(\frac{C\gamma a^2}{3\rho k_B T}\right)^{1/3}}$$

Mullins – Sekerka Instability

Planar Instability similar to dentritic instability

Quasi-steady Solution



Bulge sharpens concentration gradient, flux increases, bulge grows faster

Perturbation unstable

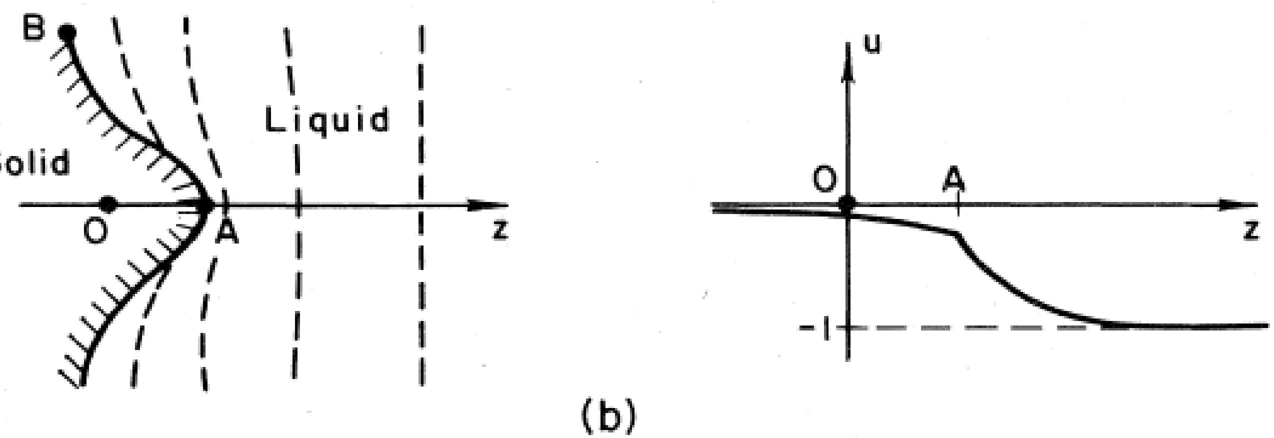
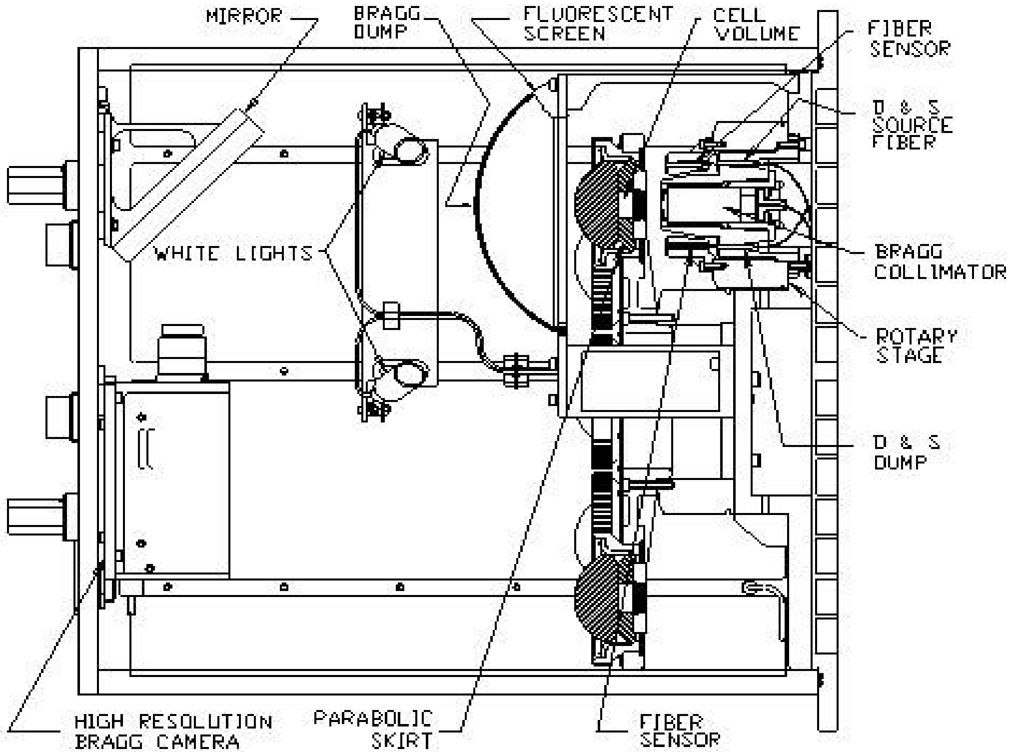
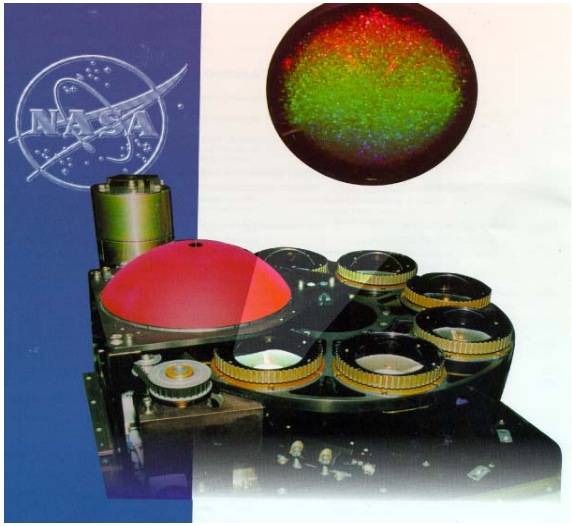


FIG. 8. Schematic illustration of the Mullins–Sekerka instability.

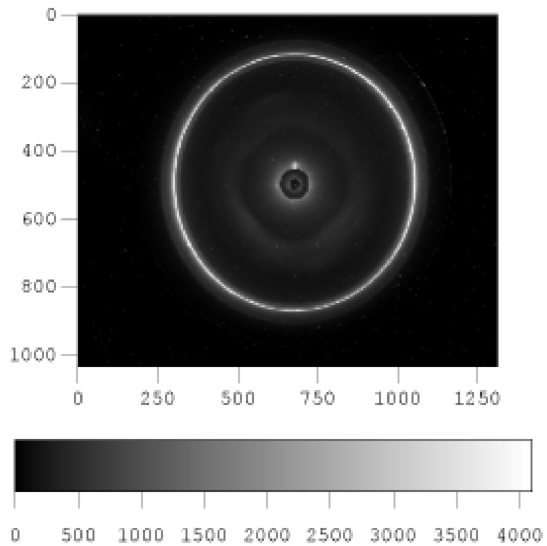
J. S. Langer

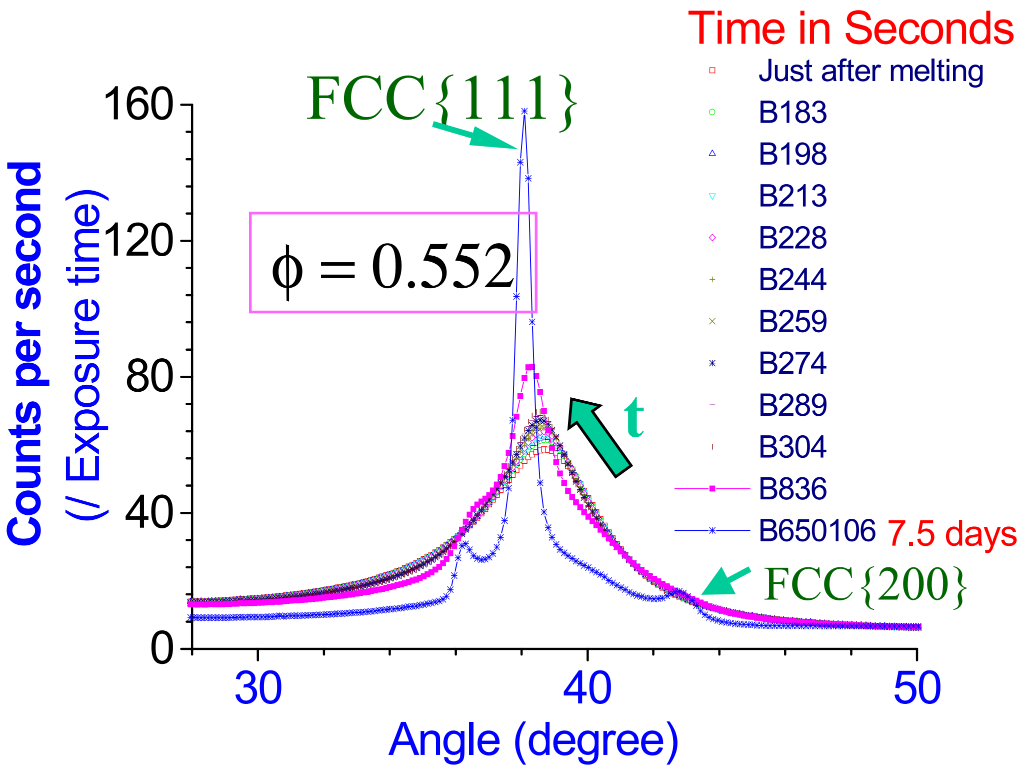
Rev. Mod. Phys., Vol. 52, No. 1, January 1980





- Bragg Scattering
- Dynamic Light Scattering
- Static Light Scattering
- Rheology

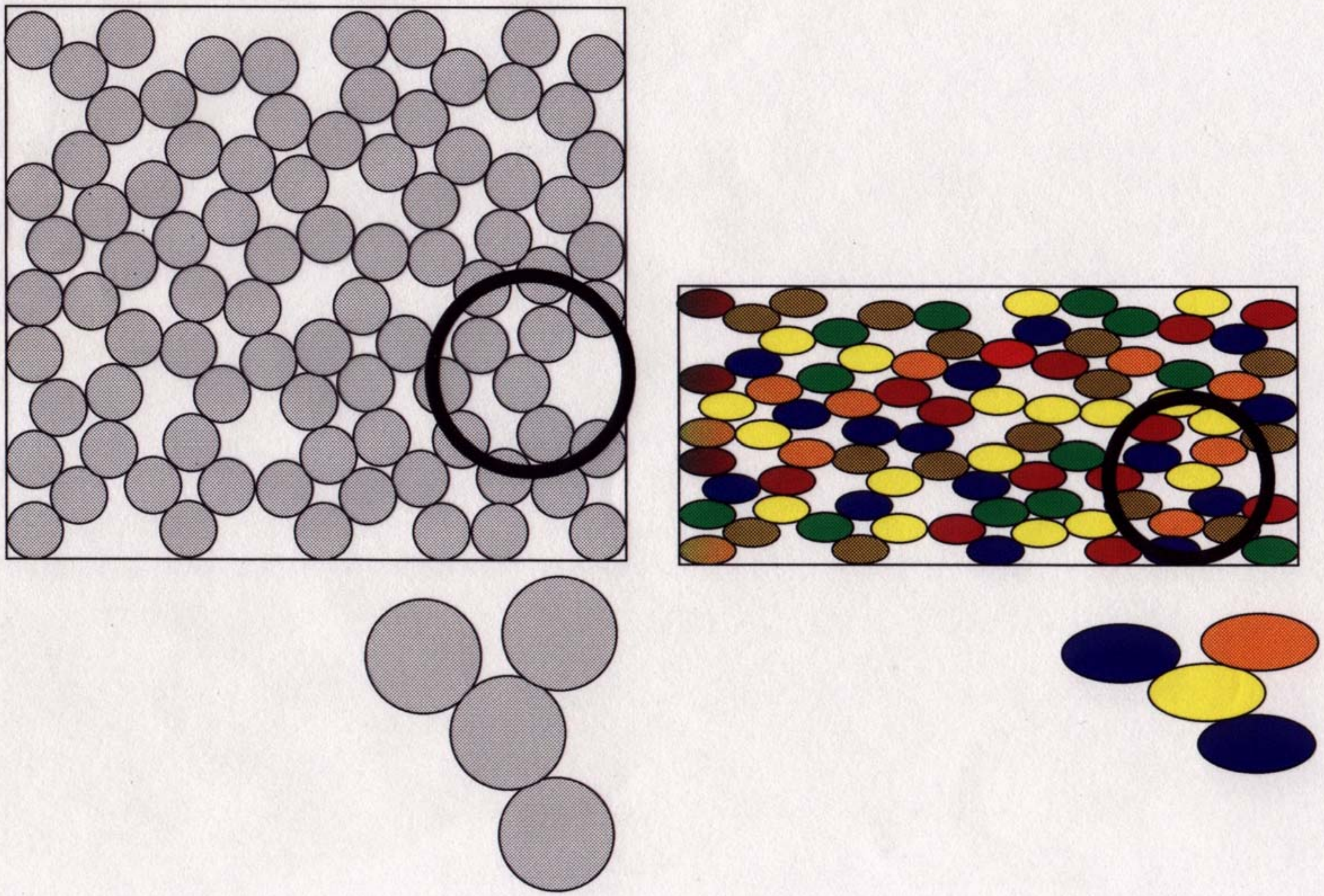

0
200
400
600
800
1000
0
250
500
750
1000
1250
0
500
1000
1500
2000
2500
3000
3500
4000


Time in Seconds
Just after melting
B183
B198
B213
B228
B244
B259
B274
B289
B304
B836
B650106 7.5 days
FCC{111}
FCC{200}
φ = 0.552
t
Counts per second
(/ Exposure time)
Angle (degree)
160
120
80
40
0
30
40
50

Do ellipsoids pack denser than spheres?

	Aspect ratio	5 litre	1 litre	0.5 litre
Regular m&m's	1.89+/- .005	.676	.671	.669
M&m minis	1.91+/- .005	.679	.672	.672
Ball bearings	1+/- .001			.636


Tubes



Jammed Configurations

Shlomo Alexander´s argument:

d degree of freedom per particle

->Nd constraint equations to define system

->Nd contacts

->2Nd neighbor-> Coordination # Z=2d

1dim

1 neighbor of 2
2 neighbor of 1

Examples: Spheres 1d Z=2
2d Z=4
3d Z=6

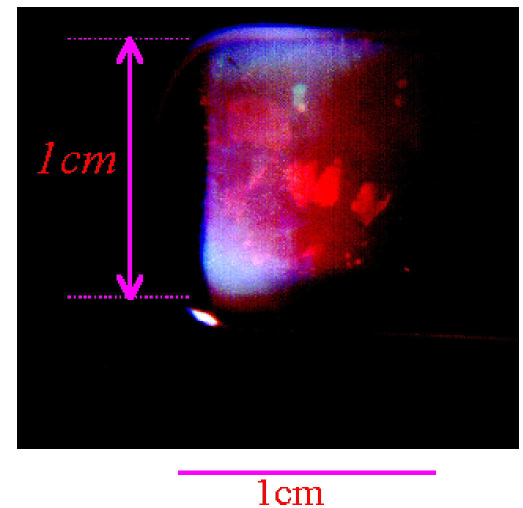
RCP has 6+ε neighbors

m&m's - 5 degrees of freedom ->10 neighbors
needs denser packing

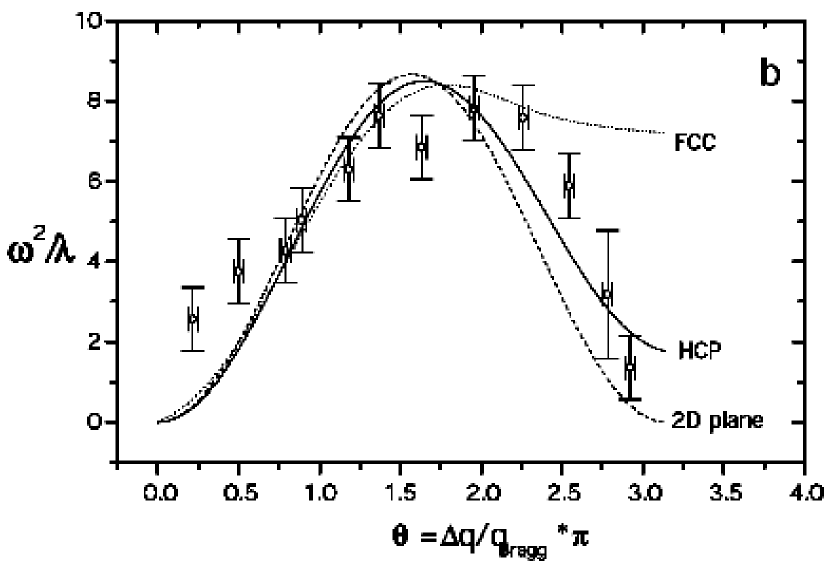
Multi-speckle Cross-correlation Spectroscopy: Phonons in an Entropic Crystal

Scattering Problems and solutions with a CCD

- Multiple scattering.. Cross-correlate in a single scattering speckle
- Non ergodicity.. ensemble average speckles with ~ same q



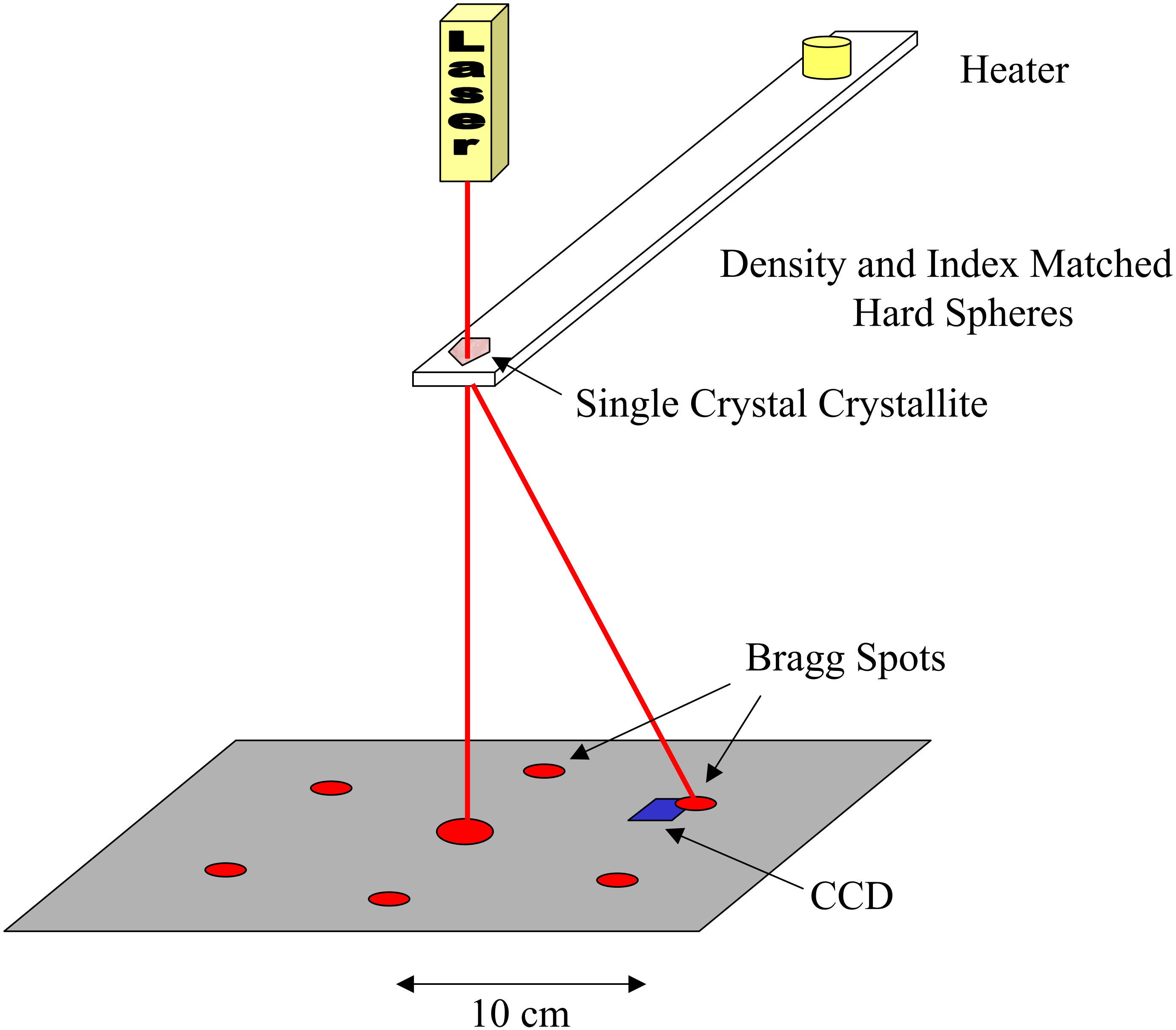
Controlled Growth of Hard Sphere Crystals in a temperature *gradient*



Phonon Spectrum for RCHP hard sphere single crystals

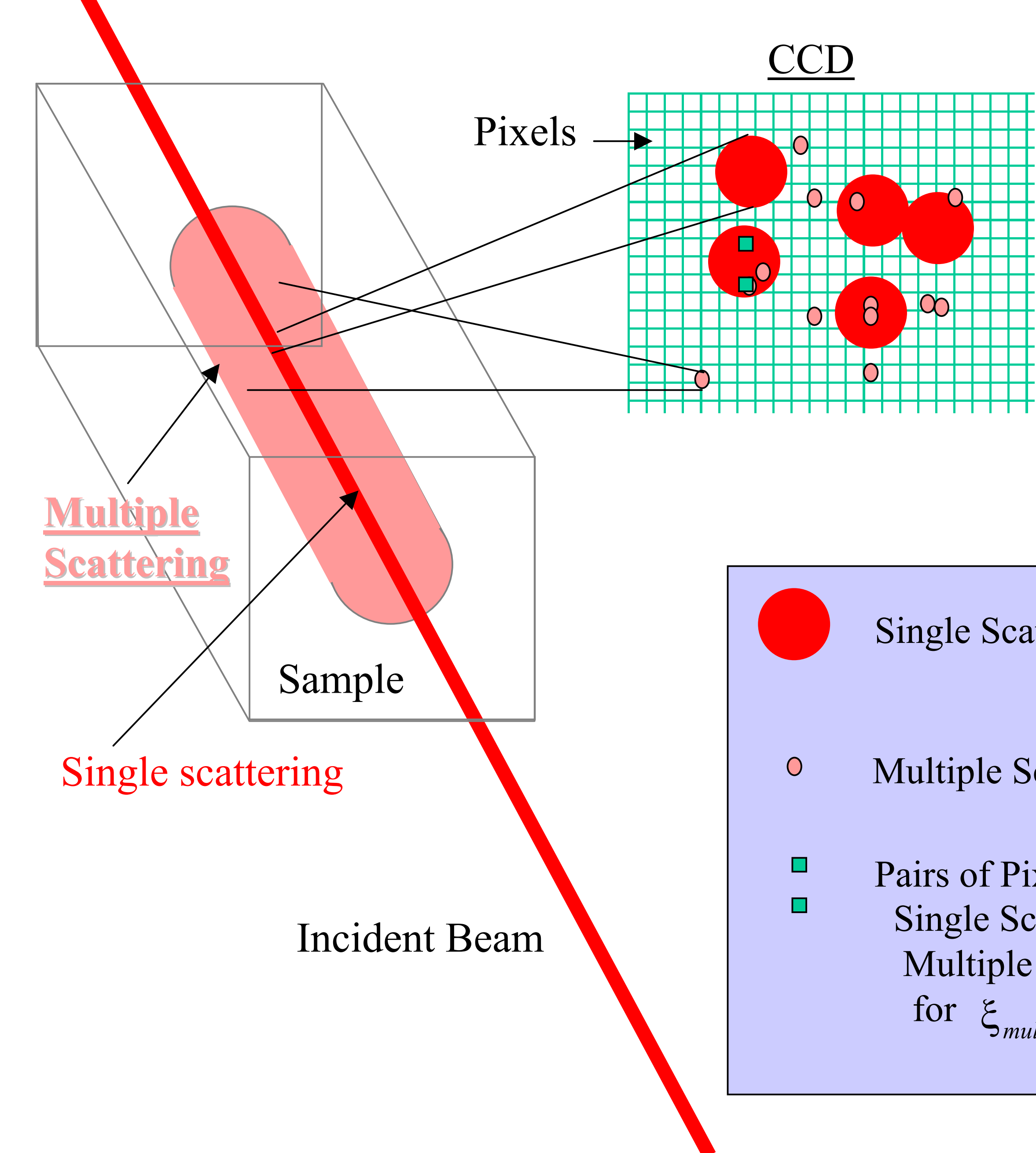
Steps:

- Grow large hard sphere single crystal
- Get rid of multiple scattering
- Ensemble average non-ergodic sample
- Separate Incoherent ($\delta r^2(t)$) from coherent phonons
- Worry about what phonons mean in a
  completely anharmonic crystal



Laser
Heater
Density and Index Matched
Hard Spheres
Single Crystal Crystallite
Bragg Spots
CCD
10 cm

Bill Meyer's Trick - Cross Correlate to eliminate Multiple Scattering

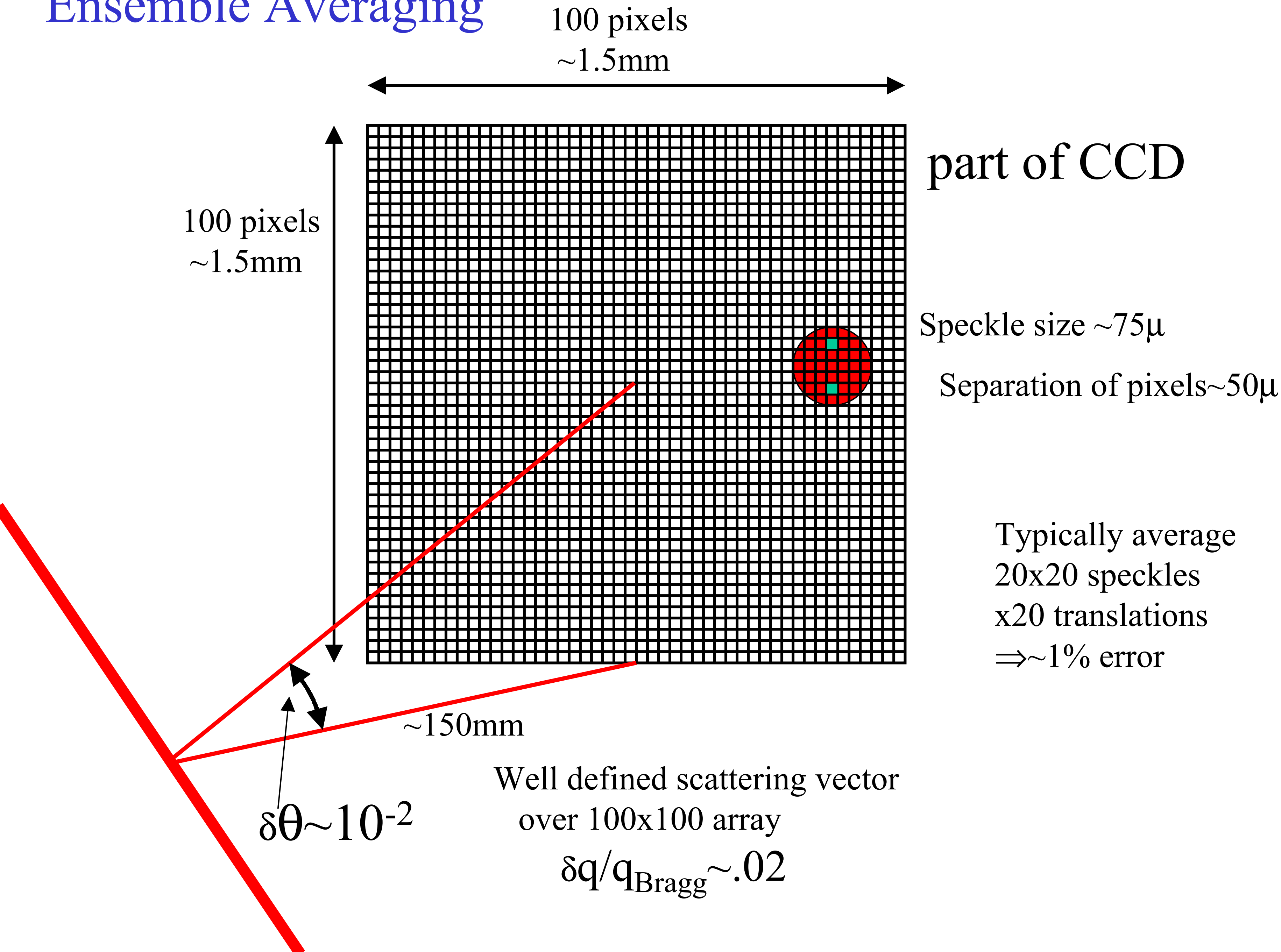


Single Scattering Speckle $\xi_{single} \sim \frac{\lambda r}{d_{beam}} \sim 120\,\mu$

Multiple Scattering Speckle $\xi_{multiple} \sim \frac{\lambda r}{l_{photon}} \sim 15\mu$

Pairs of Pixels ~ 60μ separation
Single Scattering correlated
Multiple Scattering uncorrelated
for $\xi_{multiple} < d_{pixel} < \xi_{single}$

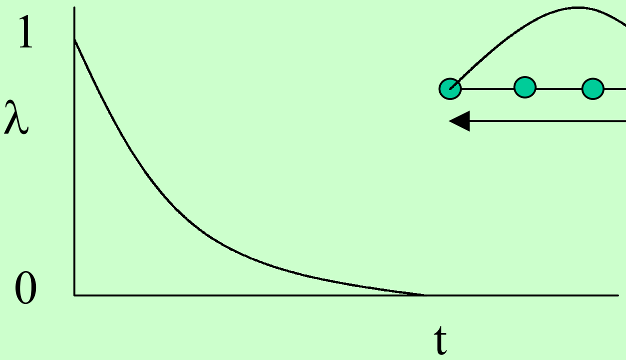
Ensemble Averaging

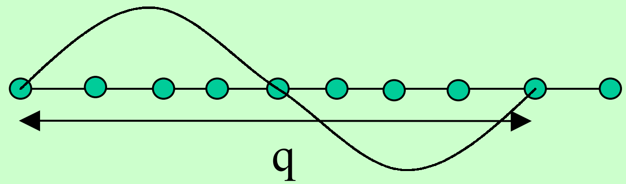


Two Contributions to Correlation Function

Coherent Scattering from Phonons

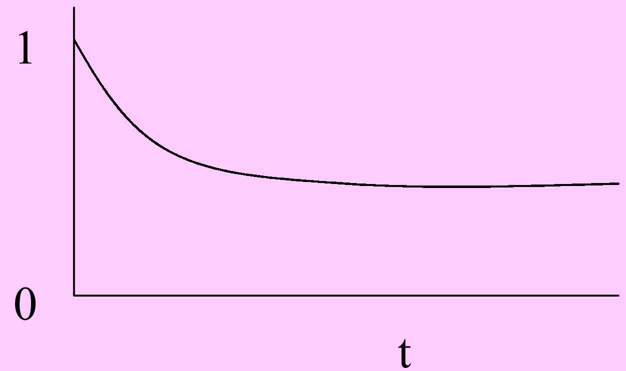
$$g_1 \sim e^{-\omega_q^2 t/\lambda}$$



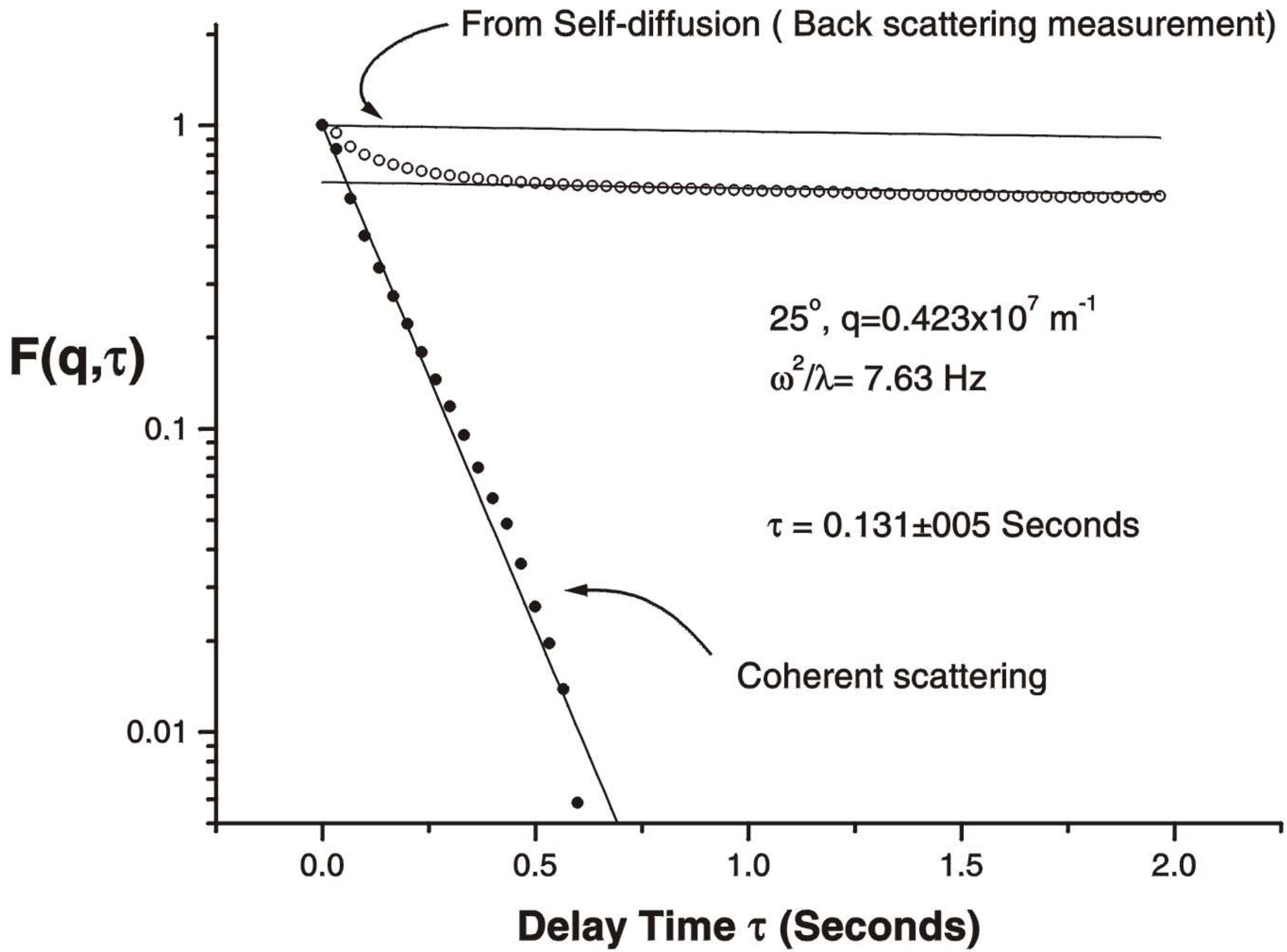


Incoherent Scattering from Polydispersity/Polyindexivity

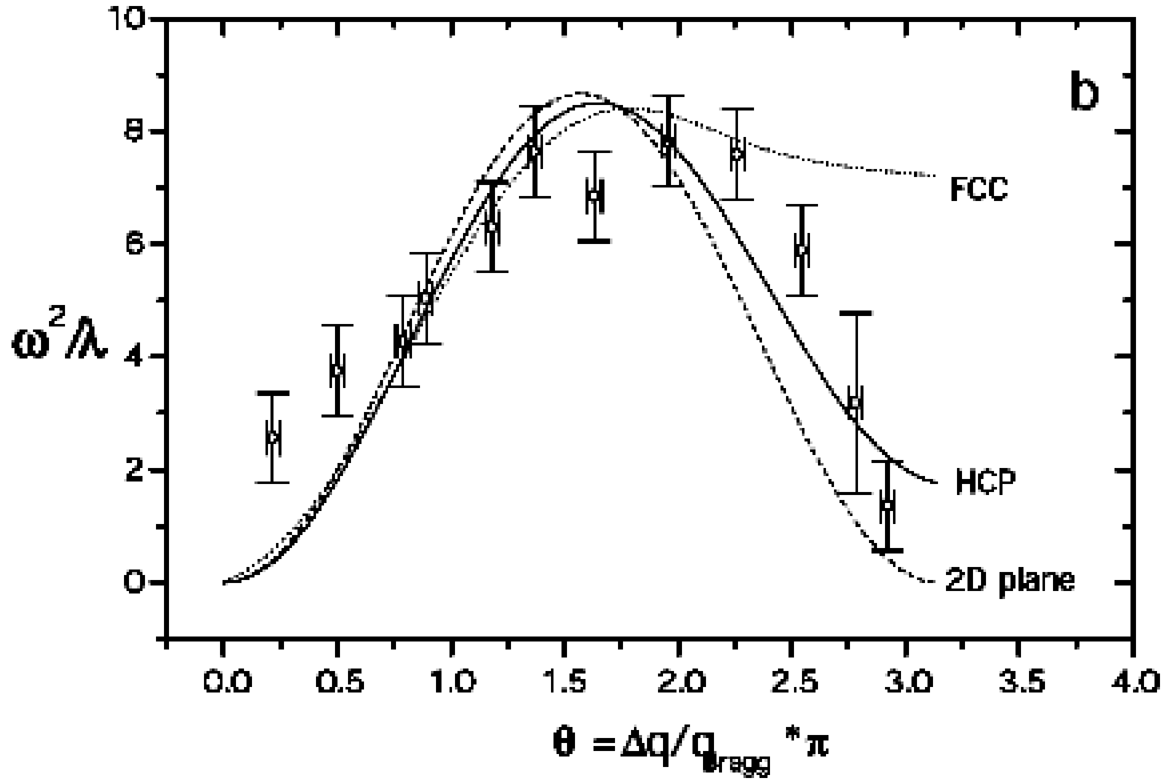
$$g_1 \sim e^{-q^2 \delta r^2 t}$$



Can get self diffusion from large angle scattering



From Self-diffusion (Back scattering measurement)
1
0.1
0.01
F(q,τ)
25°, q=0.423x10^7 m^-1
ω²/λ= 7.63 Hz
τ = 0.131±005 Seconds
Coherent scattering
0.0
0.5
1.0
1.5
2.0
Delay Time τ (Seconds)



b
FCC
HCP
2D plane
ω^2/λ
$\theta = \Delta q/q_{Bragg} * \pi$