17TH ADVANCED BEAM DYNAMICS WORKSHOP ON
FUTURE LIGHT SOURCES

Frequencies and Wavevectors for Scattering Probes of Condensed Matter

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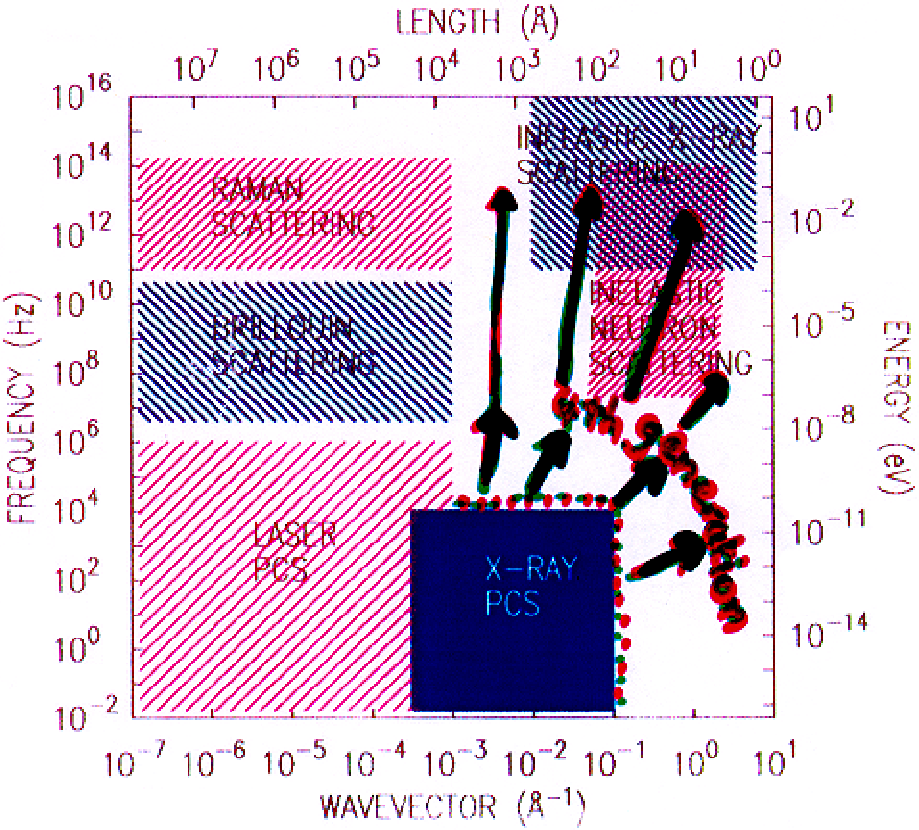
APRIL 6-9, 1999
ARGONNE NATIONAL LABORATORY, ARGONNE, IL U.S.A.

FREQUENCIES AND WAVEVECTORS FOR SCATTERING PROBES OF CONDENSED MATTER



XPCS require both spatial & temporal partial cohe

At LCLS/G4

X-RAY PHOTON CORRELATION SPECTROSCOPY WOULD ENABLE STUDIES OF ~~SLOW~~ DYNAMICS AT LARGE Q'S AND IN OPAQUE MATERIALS

- CRITICAL DYNAMICS OF POLYMER BLENDS
- BLOCK COPOLYMER DYNAMICS
- DYNAMICS NEAR THE GLASS TRANSITION OF COLLOIDAL SUSPENSIONS
- DNA MOTION INSIDE A HYDROGEL
- DYNAMICS OF "FROZEN" PHASE HETEROPOLYMER GELS

⋮

REQUIREMEN SAMPLES SURVIVE BEYOND 1 PULSE* i.e. 2 pulses @ least

* pulse if defined below.

Lateral Extent of a Coherent Wave-Packet

$$l_T \simeq \frac{\lambda R}{2\sqrt{\pi}\sigma}$$

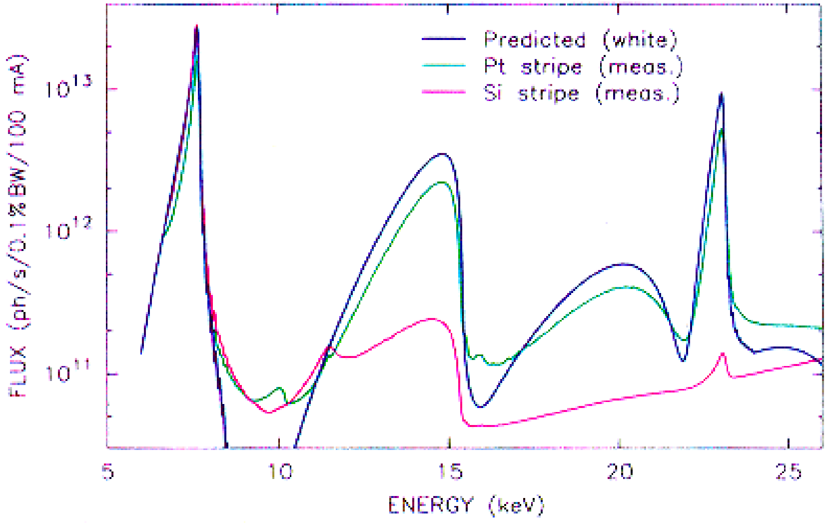
$R \approx 55\,\mathrm{m}$ Distance Source-Observer
$\lambda \approx 1.6\,\text{Å}$ Wavelength
$\sigma_h \approx 350\,\mu\mathrm{m}, \sigma_v \approx 50\,\mu\mathrm{m}$ Vertical and Horizontal 1-σ Source Sizes
$l_{Th} \approx 7\,\mu\mathrm{m}, l_{Tv} \approx 50\,\mu\mathrm{m}$

$$\Downarrow$$

Transversely Coherent Flux $\propto$ Source Brilliance B

$$\frac{l_{Th}\, l_{Tv}}{d_h\, d_v}\Phi_{tot} \propto \frac{\lambda^2\,\Phi_{tot}}{\sigma_h\,\sigma_v}\,\frac{R}{d_h}\,\frac{R}{d_v} \propto \lambda^2\,\frac{\Phi_{tot}}{\sigma_h\,\sigma_v\,\theta_h\,\theta_v} \propto \lambda^2\,B$$

d_h, d_v Slit Sizes
Φ_{tot} Total Photon Rate
θ_h, θ_v Opening Angles



$$\theta_h = \theta_v = \frac{270\,\mu m}{27.5\,m}$$

$$B_{peak} = 1.19 \cdot 10^{19}\,\frac{photons/s}{mm^2\,mrad^2\,100\,mA\,0.1\%bw}$$

Length of a Coherent Wave-Packet

$$l_L \simeq \left(\frac{\lambda}{2\pi}\right) \Big/ \left(\frac{\Delta E}{E}\right)$$

$\Delta E/E \approx$ [redacted] 1.5×10^{-4} Relative Energy Bandwidth (HWHM)

$l_L \approx$ [redacted] 1620 Å using a monochromator

$\Delta E/E \simeq 1.3\times10^{-2}$ $\ell_L \simeq 20$Å using a mirror/entire first harmonic

Constraint on Q

To see coherence effects, require optical path differences of scattered X-rays to be not too many times larger than l_L.

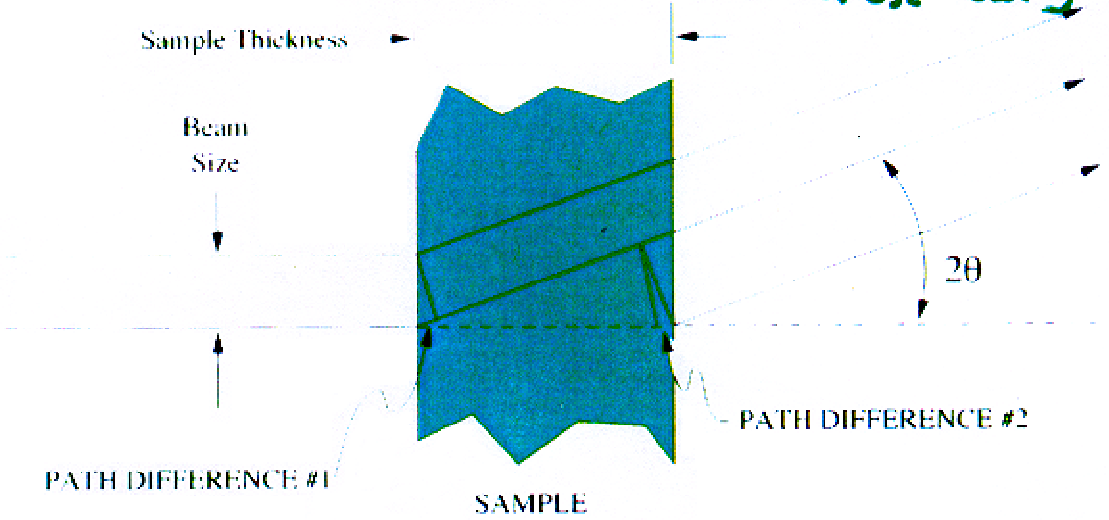
$$\Downarrow$$

$$2W\sin^2(\theta) \lesssim \frac{\lambda^2}{\Delta\lambda} \quad \text{and} \quad d_{h,v}\sin(2\theta) \lesssim \frac{\lambda^2}{\Delta\lambda}.$$

$W \approx 1.5$ mm Sample Width

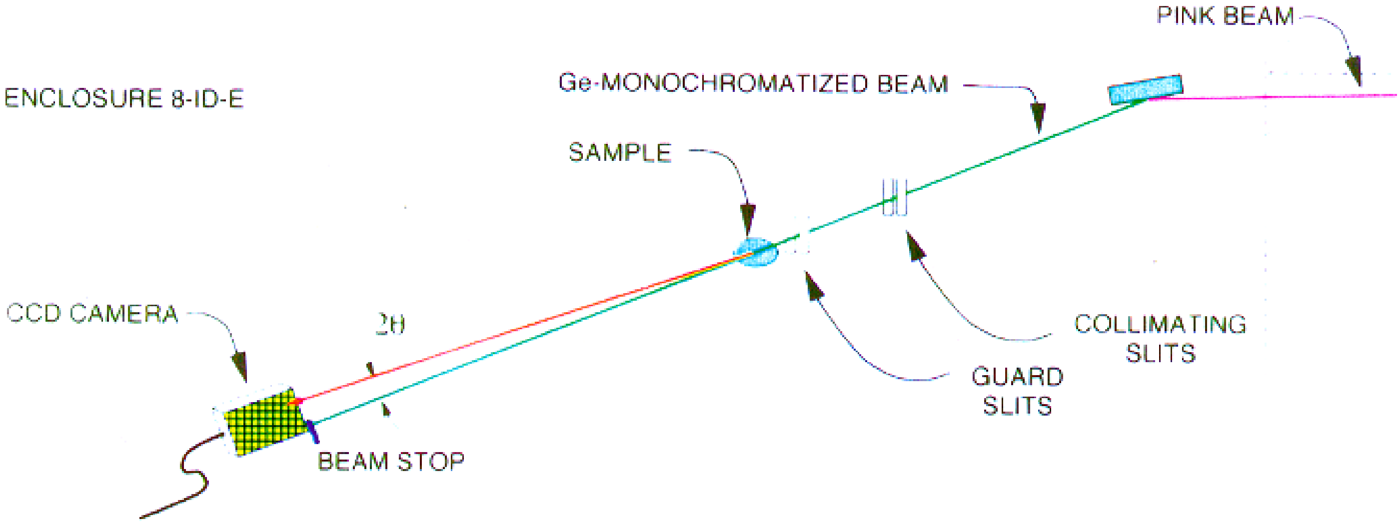
$d_{h,v}$ Vertical and Horizontal Slit Sizes

easily satisfied at Q's of interest using mono

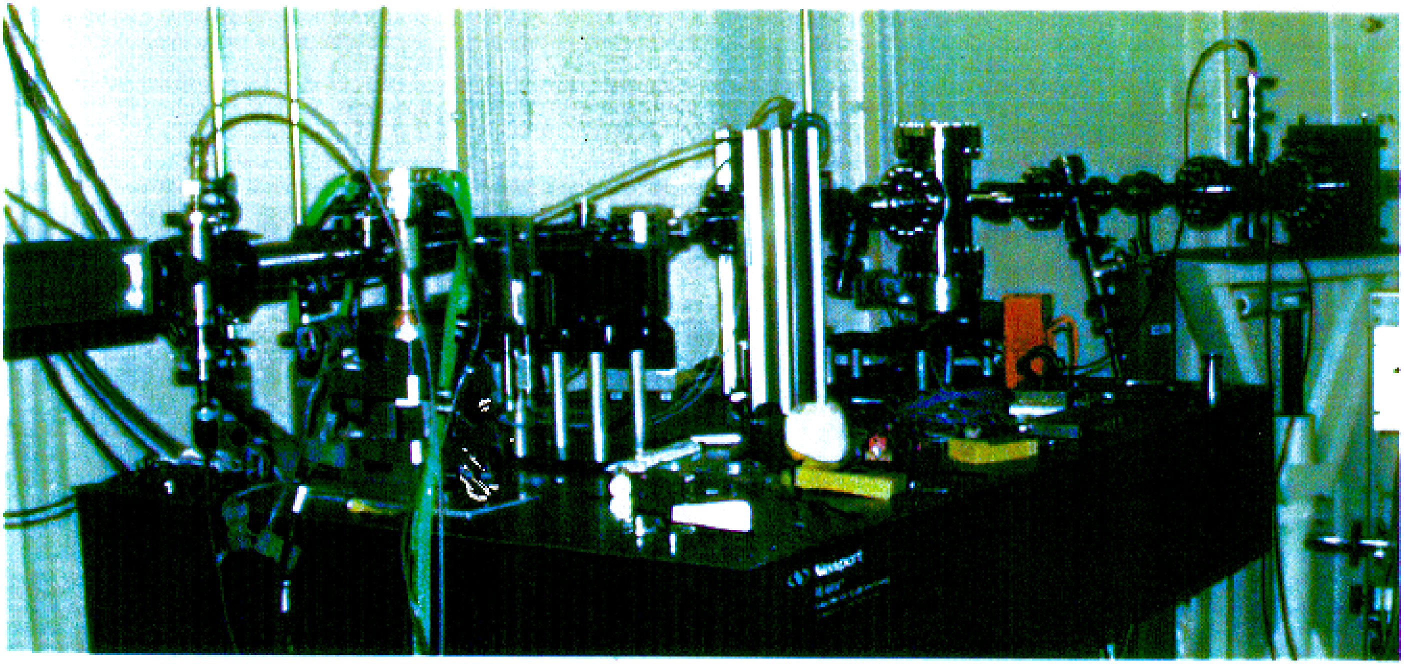


marginal at Q's of interest using entire first harmonic

BEAMLINE SCHEMATIC



The Experiment

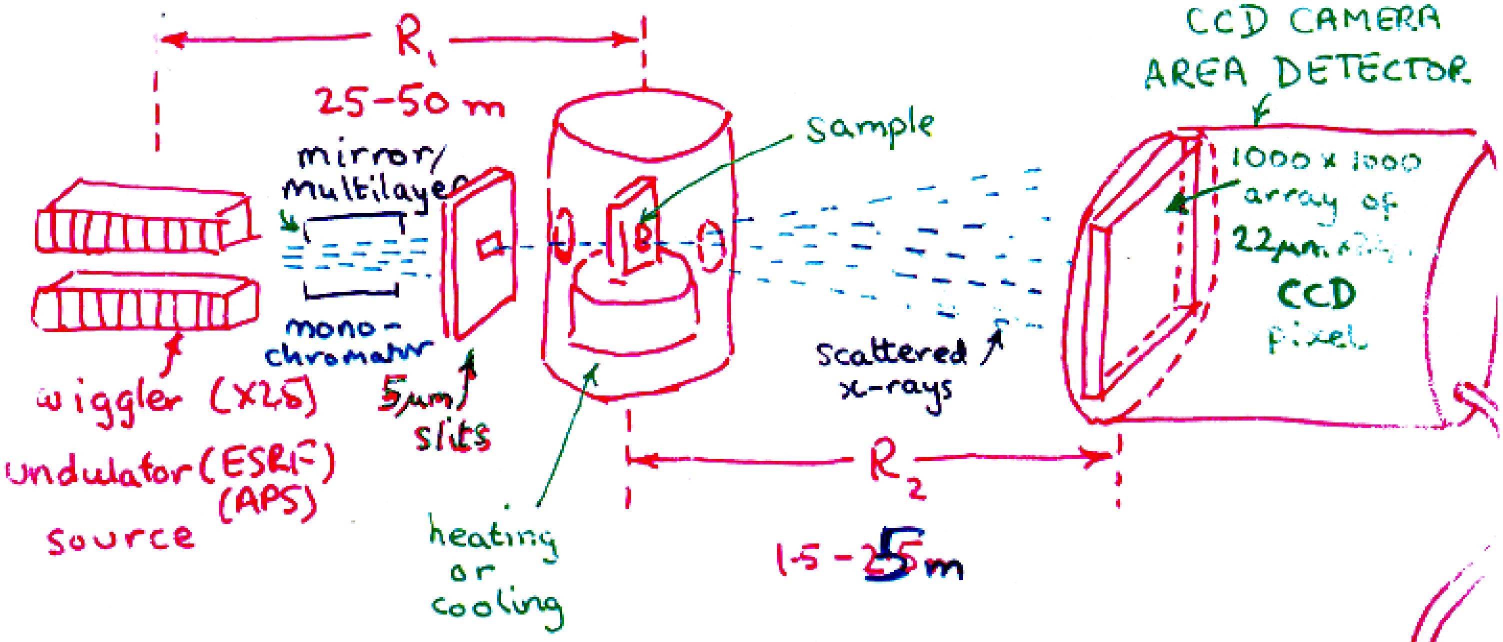


THIRD GENERATION SYNCHROTRON PRODUCE COHERENT X-R

- HIGH-COUNT RATES.... ($\sim 10^{11}$ PER SECOND AT APS)
  BUT FAR LESS THAN FOR A LASER

- EMPLOYING AN AREA DETECTOR IS
  VERY HELPFUL ... BY A FACTOR OF 10^5

- EXPERIMENTAL SETUP...



- BEAMLINE 8-ID HAS RECENTLY COME "ON-LINE" AT APS

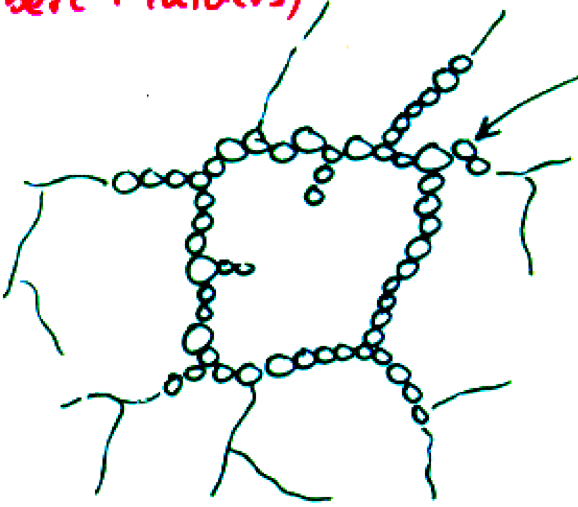
- SAMPLES
  - aerogel (8-ID, APS)
  - colloidal suspensions (8-ID, APS)
  - polymer micelles (ID-10, ESRF)
  - polymer blends (8-ID, APS)

MIT - McGill - IBM Beamline

* FUNDED BY NSF INSTRUMENTATION PROGRAM AND DOE FACILITIES INITIATIVE

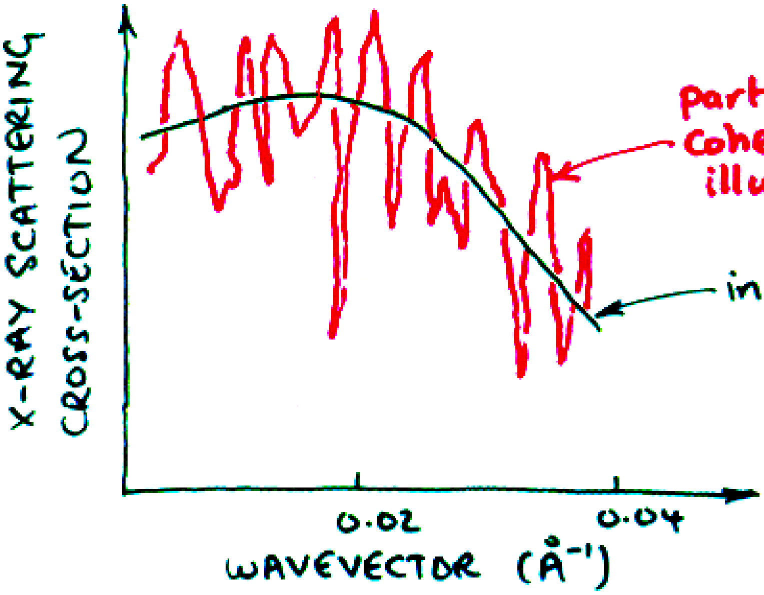
- AEROGEL

(Norbert Mulders)



20Å SiO_2 spheres in a static, random network of strands

- here : a strong diffuse scatterer of x-rays
- fine way to characterize beam coherence



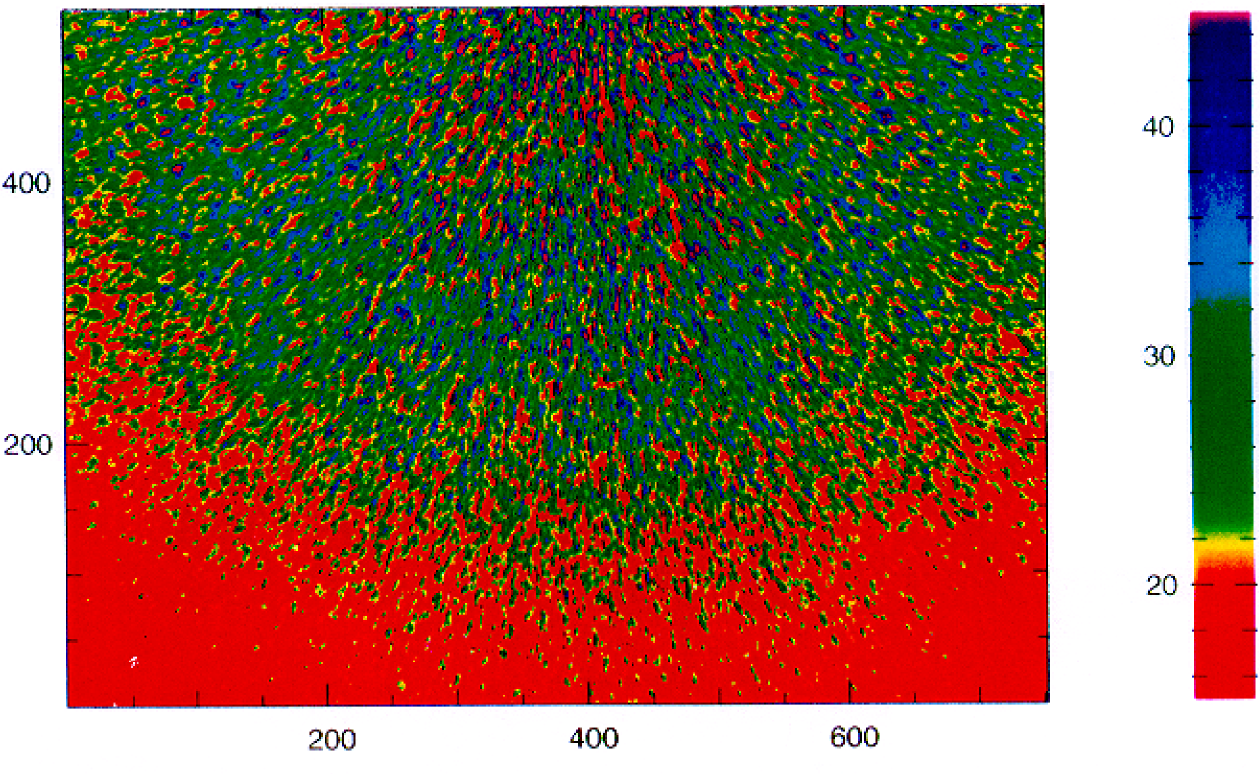
- UNDER COHERENT ILLUMINATION A RANDOM SAMPLE PRODUCES A RANDOM DIFFRACTION PATTERN THAT DEPENDS ON THE SPECIFIC ARRANGEMENT OF MATERIAL IN THE SAMPLE

i.e. SPECKLE

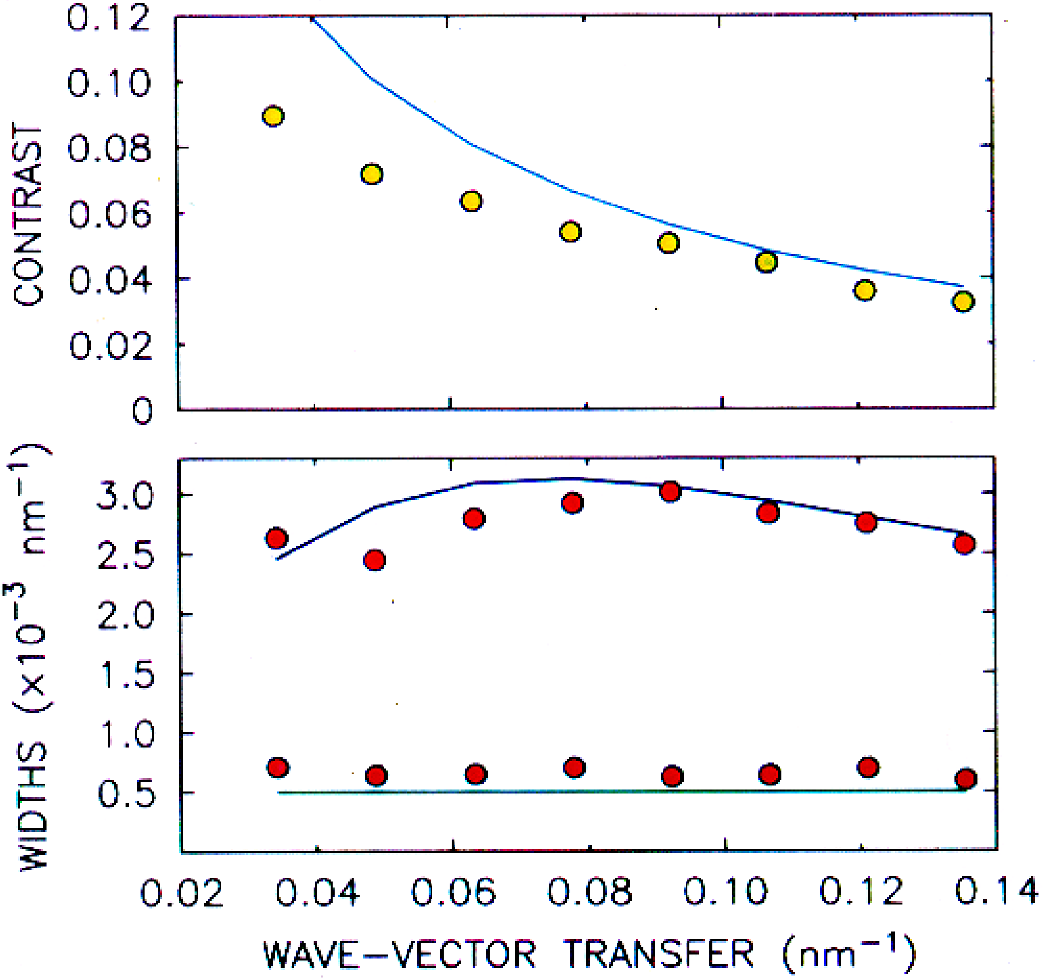
Pink beam data

Speckle

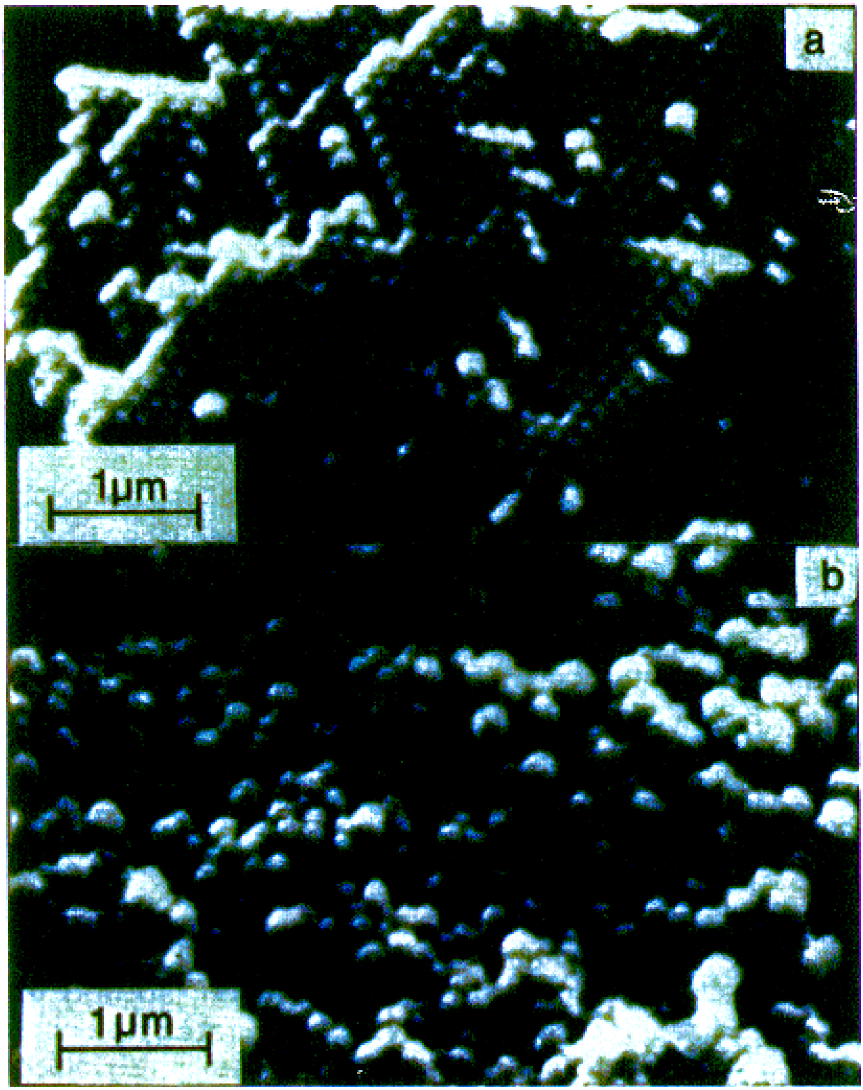
Objects viewed in highly coherent light acquire a peculiar granular appearance.



Pink beam data & predictions



Colloidal Suspension

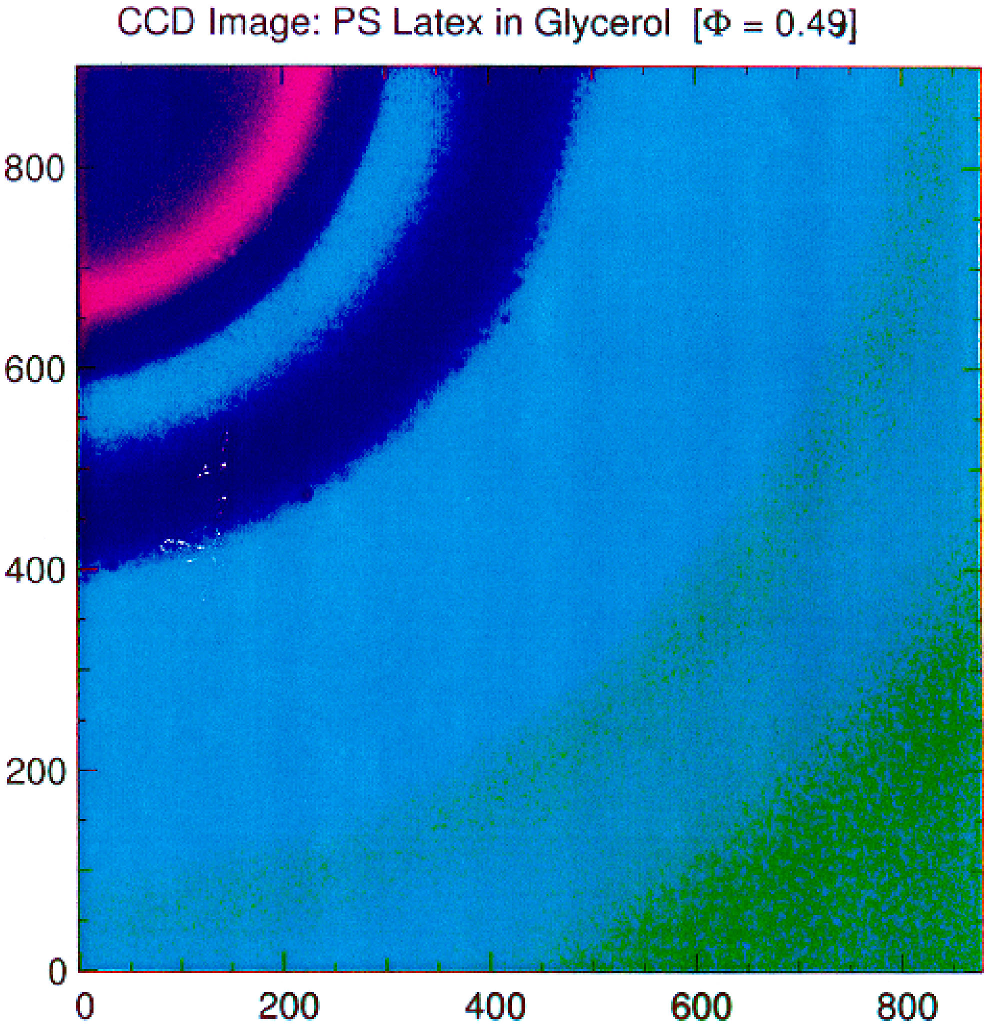


Our System

Polystyrene Latex Spheres ['particles']

of Radius 67 nm

Suspended in Glycerol



The Scattering Cross Section

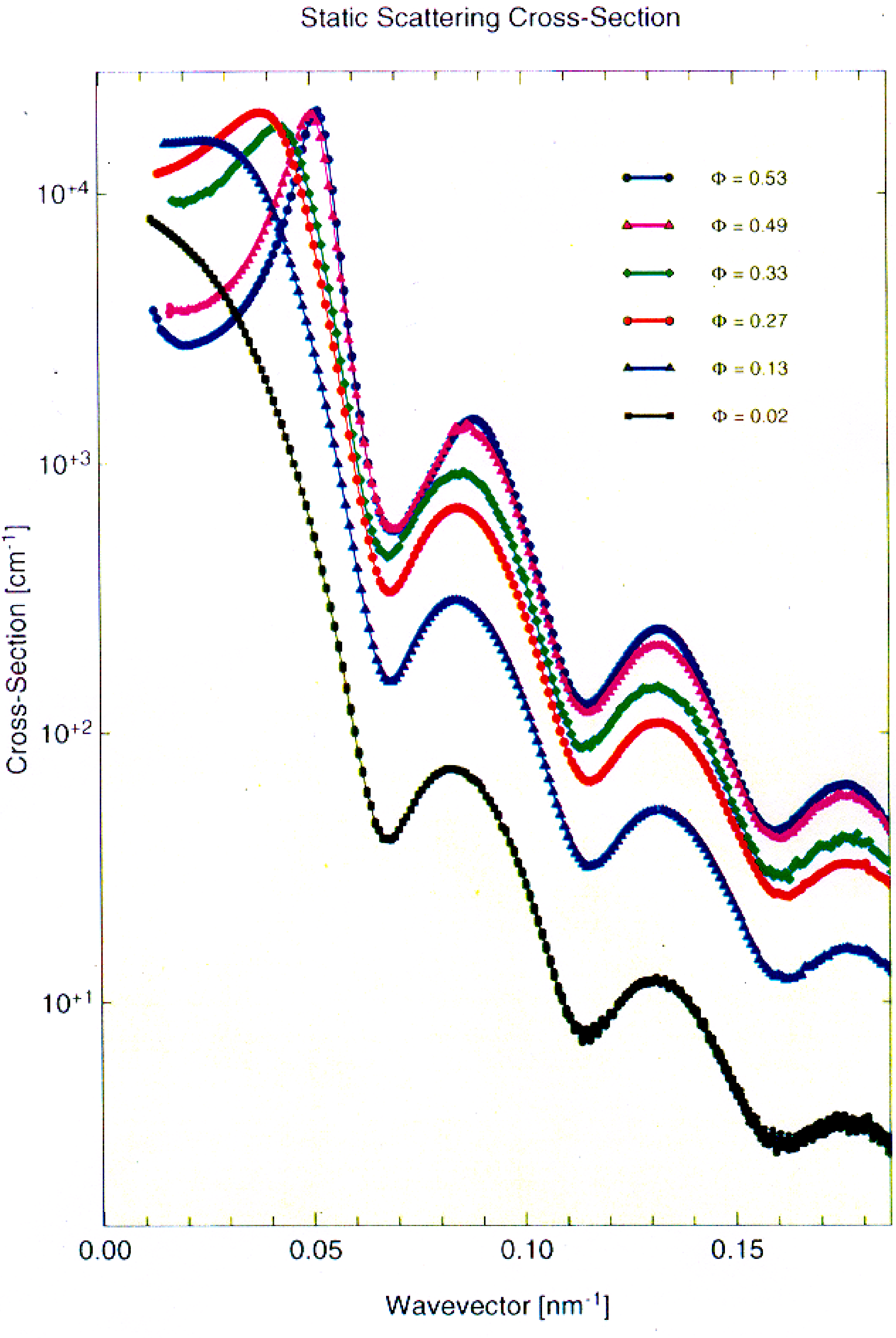
$$\frac{1}{V}\frac{d\sigma}{d\Omega} = {r_0}^2\,\phi\,(\rho_{PS} - \rho_{Gl})^2\,\nu\,|F(Q)|^2\,S(Q)$$

V Scattering Volume
ν Volume of Polystyrene Sphere
ϕ Volume Fraction of Polystyrene
ρ_{PS}, ρ_{Gl} Material Densities
r_0 Thomson Radius

Form Factor $|F(Q)|^2$

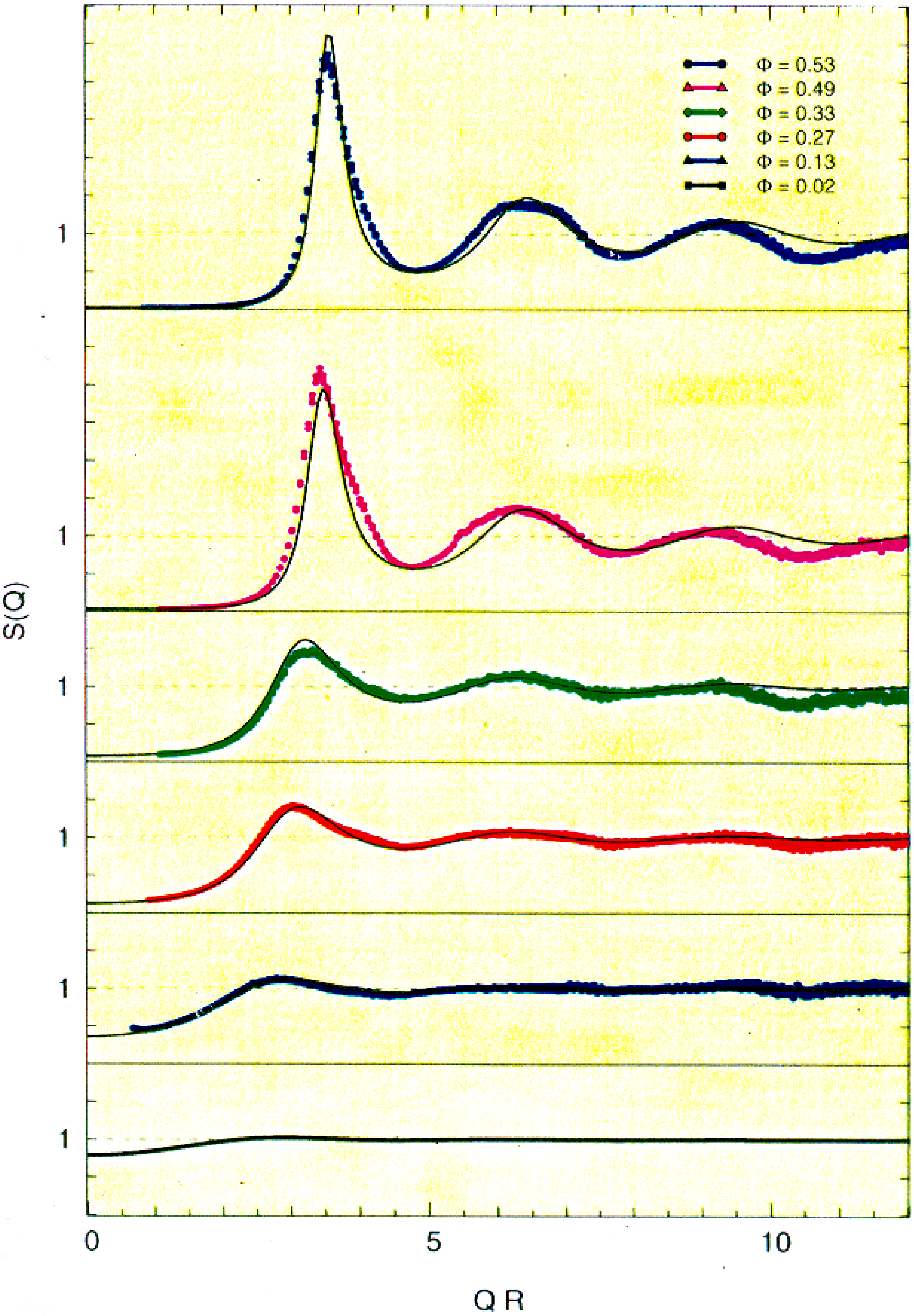
Determined from the Scattering Function
in the Dilute Limit

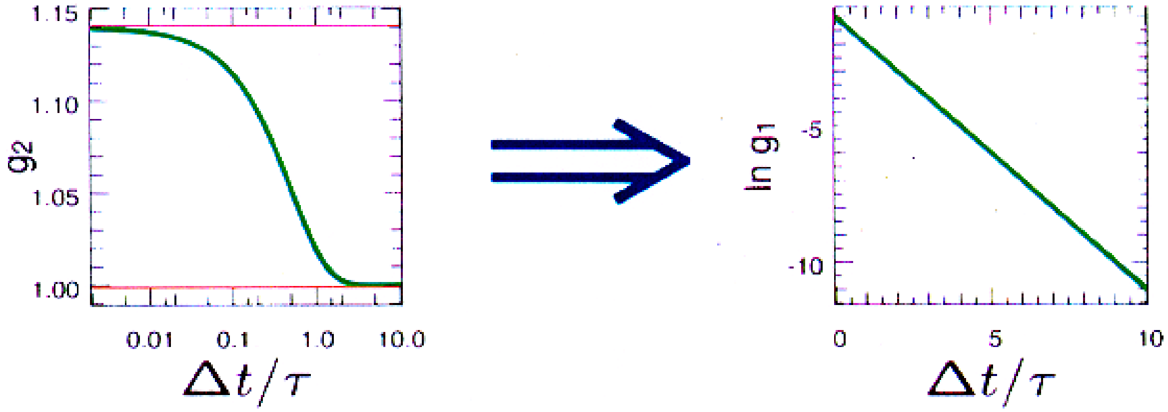
Structure Factor $S(Q)$


Static Scattering Cross-Section
Cross-Section [cm^{-1}]
10^{+4}
10^{+3}
10^{+2}
10^{+1}
$\Phi = 0.53$
$\Phi = 0.49$
$\Phi = 0.33$
$\Phi = 0.27$
$\Phi = 0.13$
$\Phi = 0.02$
0.00
0.05
0.10
0.15
Wavevector [nm^{-1}]

Peak in S(Q) develops as the fluid of colloidal particles approaches a crystal phase (nascent Bragg peak

Suspension of PS Latex in Glycerol: Structure Factor





The Measured Quantity

Normalized Intensity Time-Autocorrelation Function

$$g_2(\Delta t) = \frac{\langle I(t+\Delta t)\ I(t)\rangle_t}{\langle I(t)\rangle_t^2}$$

Field Time-Correlation Function g_1

Derived from Siegert Relation

$$g_2(\Delta t) = 1 + |g_1(\Delta t)|^2$$

Relation to the Dynamic Structure Factor

$$S(Q, \Delta t) = S(Q, 0)\, g_1(Q, \Delta t)$$

Simplest Functional Form

$$g_2(\Delta t) = a + \left|\sqrt{\beta}\ \mathrm{exp}(-\Delta t/\tau)\right|^2$$

β Contrast

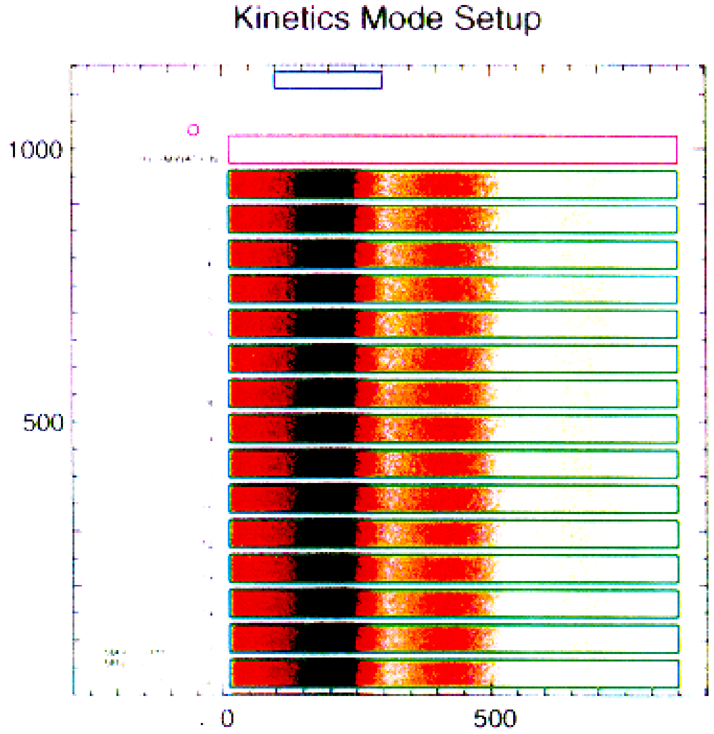
τ Decay Time

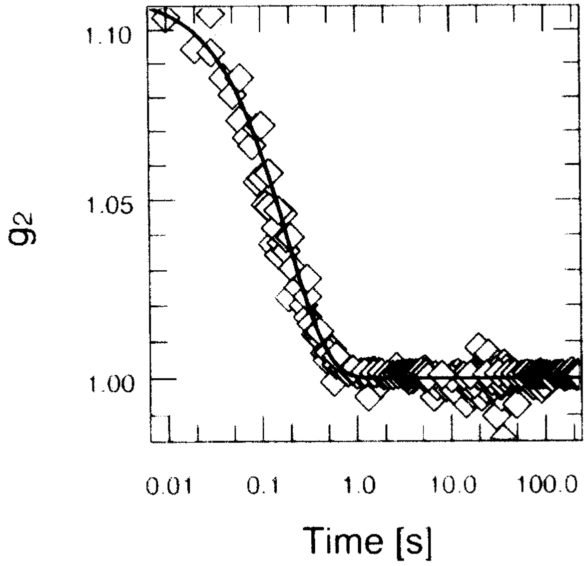
$a \approx 1$ Baseline

CCD Detector Kinetics Mode

Illuminating a stripe of the CCD detector and using the remainder of the CCD as memory, it is possible to acquire CCD images in rapid succession:
10 ms, 30 ms, 100 ms, ... exposure times with 60 μs shifting times.

Shown here are 15 time slices separated from one another by 500 ms.





Calculating g_2

(1)
Calculation of the Intensity Time Correlation Function Pixel-by-Pixel

(2)
Averaging over Pairs of Equal Delay Time

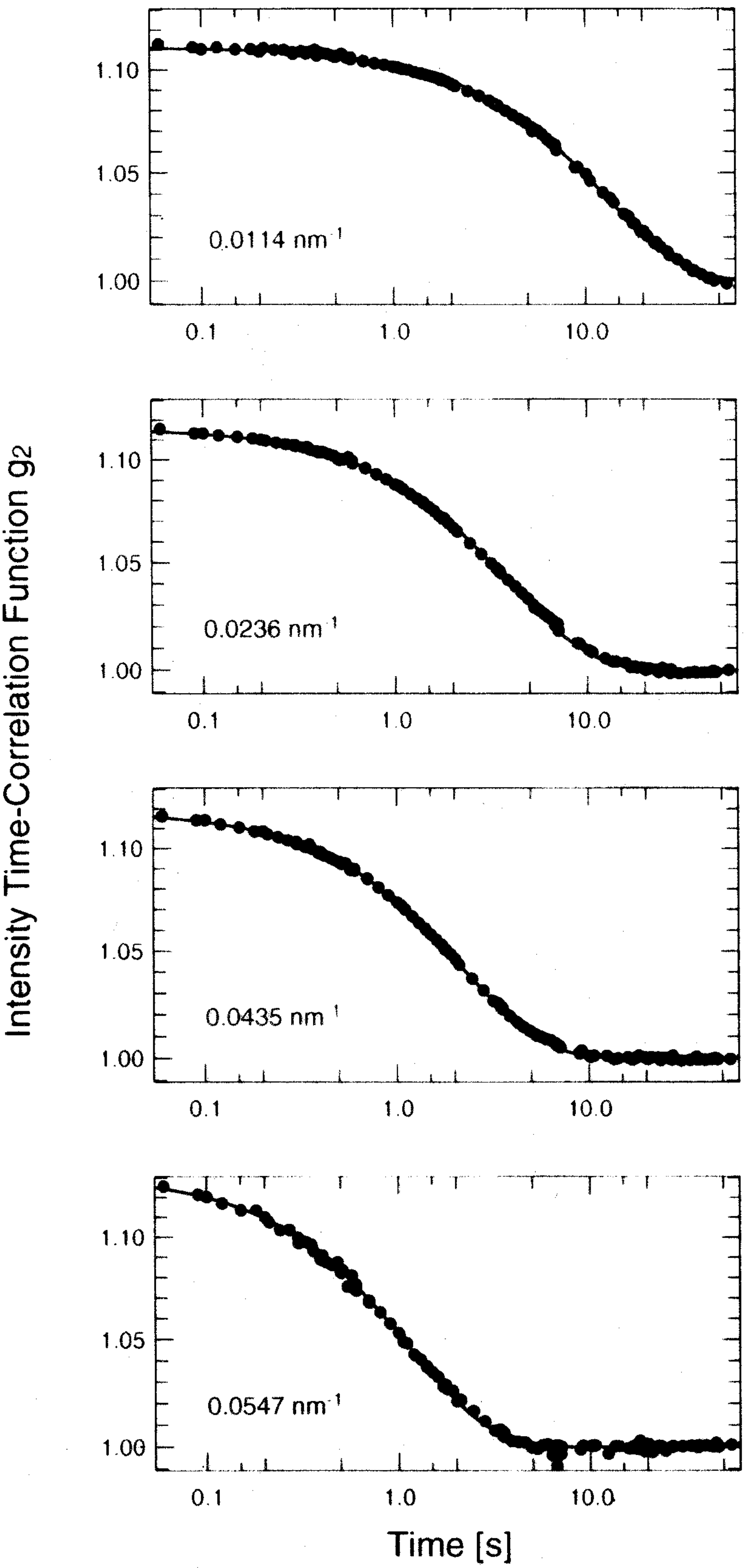
(3)
Averaging over Small Ranges of Wavevectors

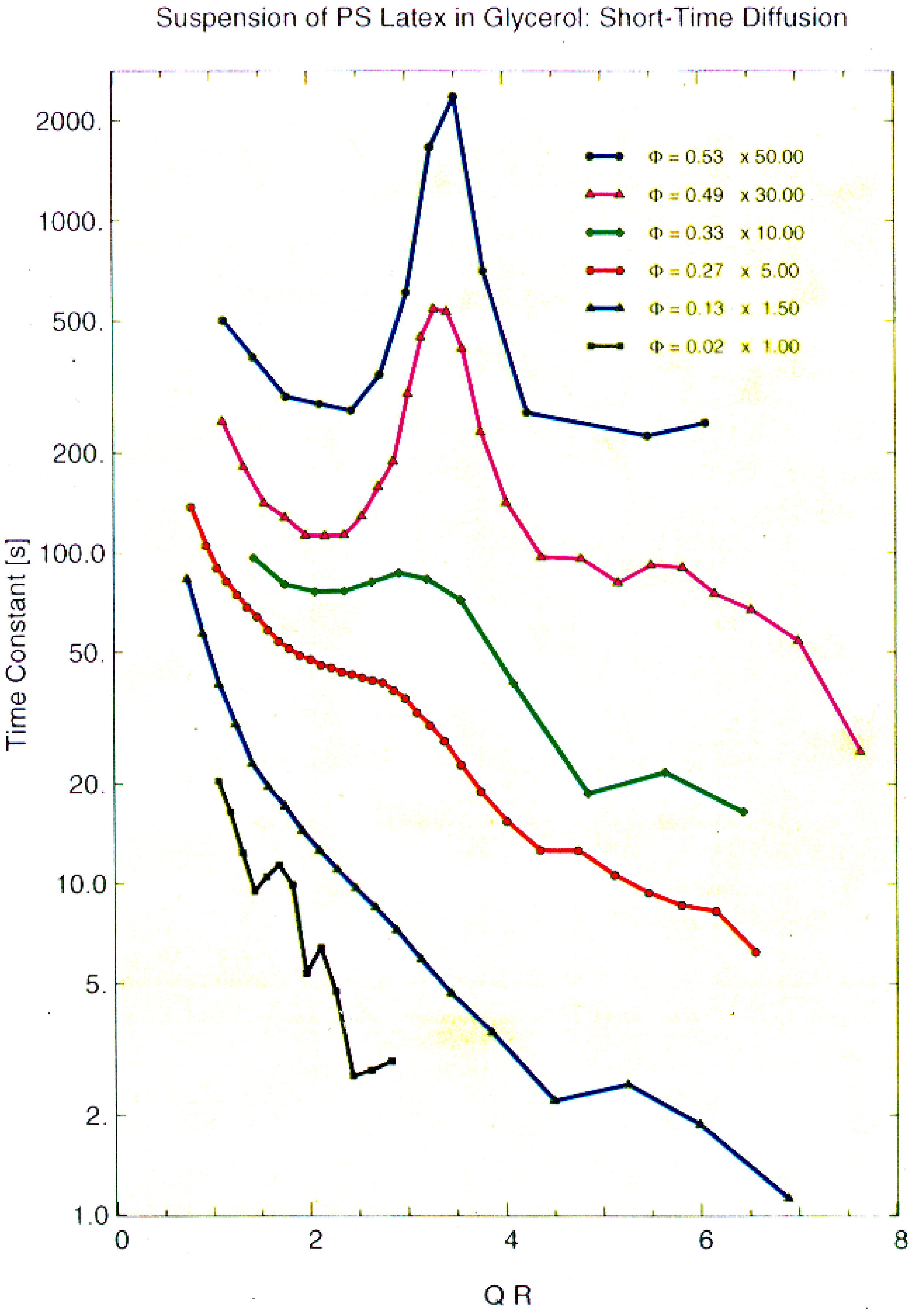
(4)
Matching Slice-Slice Correlation with Frame-Frame Correlations

(5)
Averaging of Sets of Data Acquisition Sequences

(6)
Matching Set-Averages of Different Exposure Times

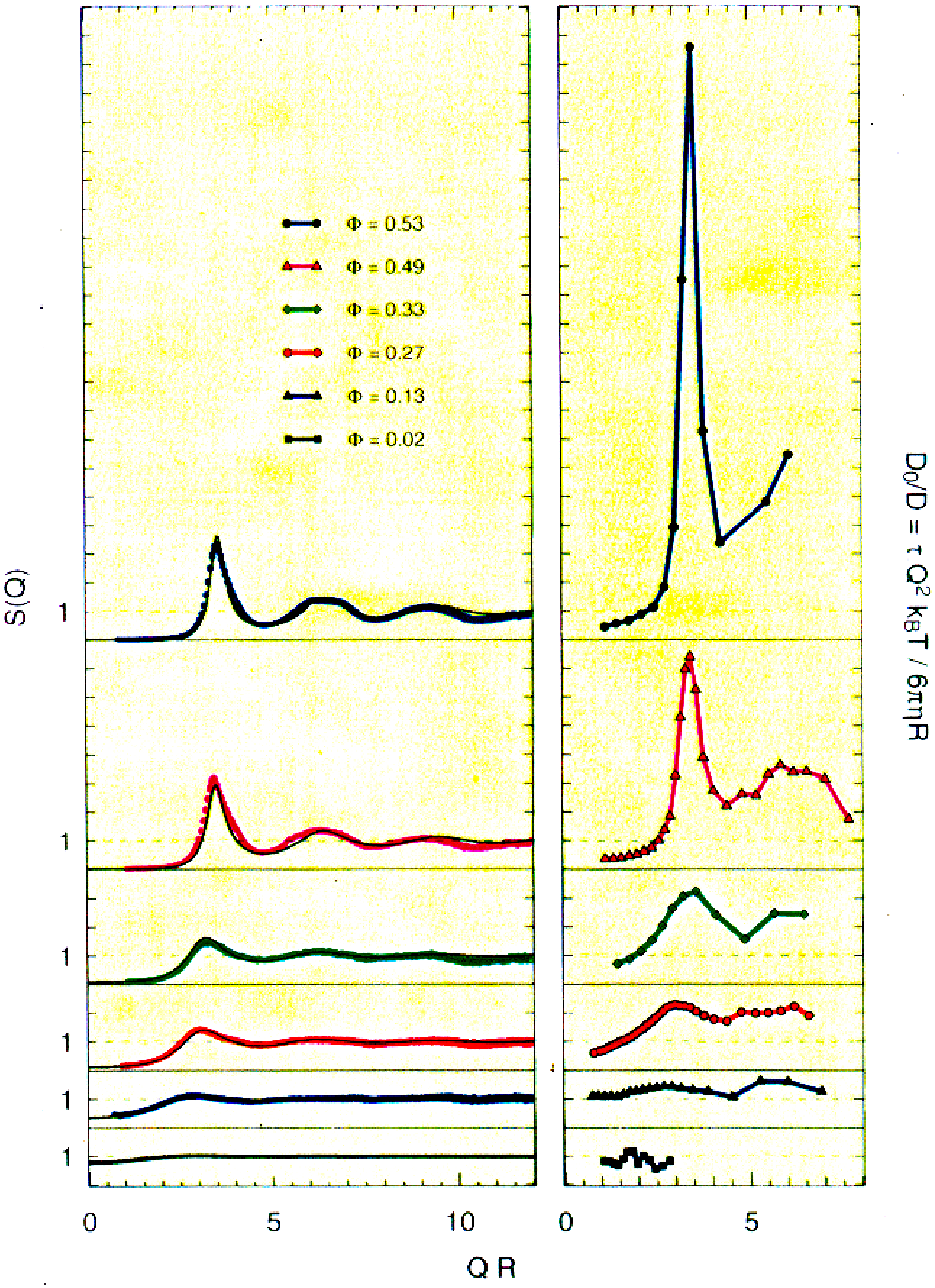
Polystyrene Latex in Glycerol [$\Phi = 0.27$] at -5°C




Suspension of PS Latex in Glycerol: Short-Time Diffusion
Φ = 0.53 x 50.00
Φ = 0.49 x 30.00
Φ = 0.33 x 10.00
Φ = 0.27 x 5.00
Φ = 0.13 x 1.50
Φ = 0.02 x 1.00
Time Constant [s]
2000.
1000.
500.
200.
100.0
50.
20.
10.0
5.
2.
1.0
0
2
4
6
8
Q R

Locally solid-like configurations – corresponding to the peak in $S(Q)$ – persist for a long time – corresponding to the peak in $D_0/D(Q)$

Static Structure Factor and Short-Time Diffusion



Dynamic Structure Factor $S(Q,\omega)$

$$S(Q) = \int_{-\infty}^{+\infty} \mathrm{d}\omega\, S(Q,\omega)$$

Sum Rule

$$\frac{Q^2\, k_B\, T}{M} = \int_{-\infty}^{+\infty} \mathrm{d}\omega\, \omega^2 S(Q,\omega)$$

Small Frequencies ω

$$S(Q,\omega) \simeq \frac{S(Q)}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2}$$

$\longrightarrow$ Does NOT obey the sum rule.

Simple Remedy: $S(Q,\omega) \approx 0$ for $\omega > \omega_c$

$$\Downarrow$$

$$\frac{k_B\, T}{D} \simeq \frac{2M\, \omega_c\, S(Q)}{\pi}$$

Diffusion Coefficient acquires Wavevector Dependence

$1/D \propto S(Q)$

- More elaborate theories indicate

$$\frac{D_0}{D} = \frac{S(Q)}{H(Q)}$$

result of hydrodynamic interactions

- Physically... density fluctuations corresponding to wavevectors which are close to wavevectors of incipient crystal are favorable free-energetically –

So there's a peak in S(Q) –

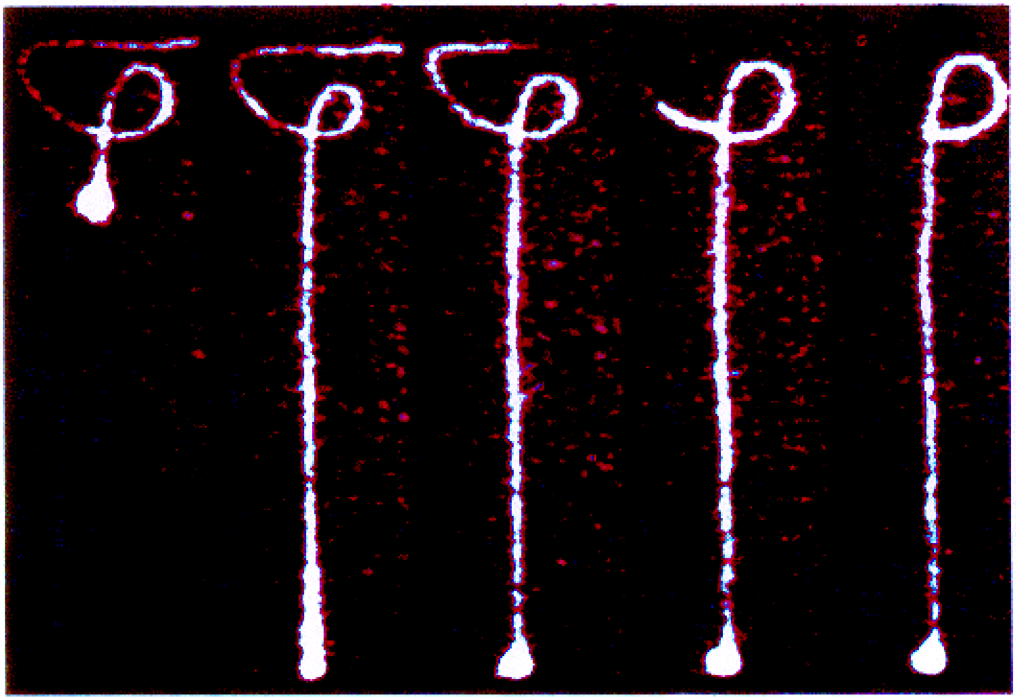
not surprisingly, these modes are also long-lived –

So there's a peak in $D_0/D(Q)$

Reptation model of polymer dynamics

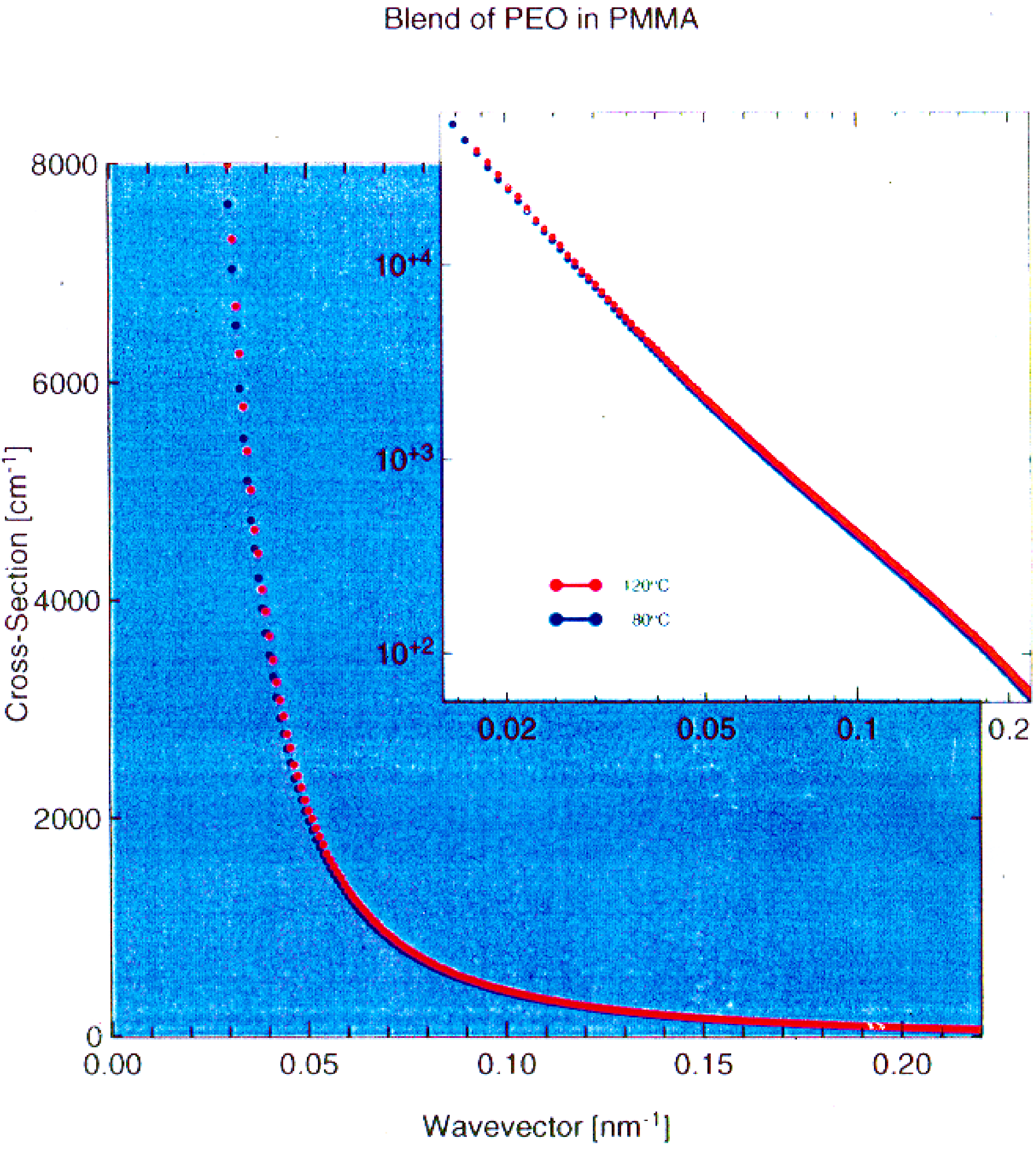
- snake-like motion (reptation) within the tube defined by entanglements with neighboring polymers

- evidence for the "tube" comes from neutron spin-echo measurements and microscopy of fluorescence-labelled DNA in a solution of unlabelled DNA

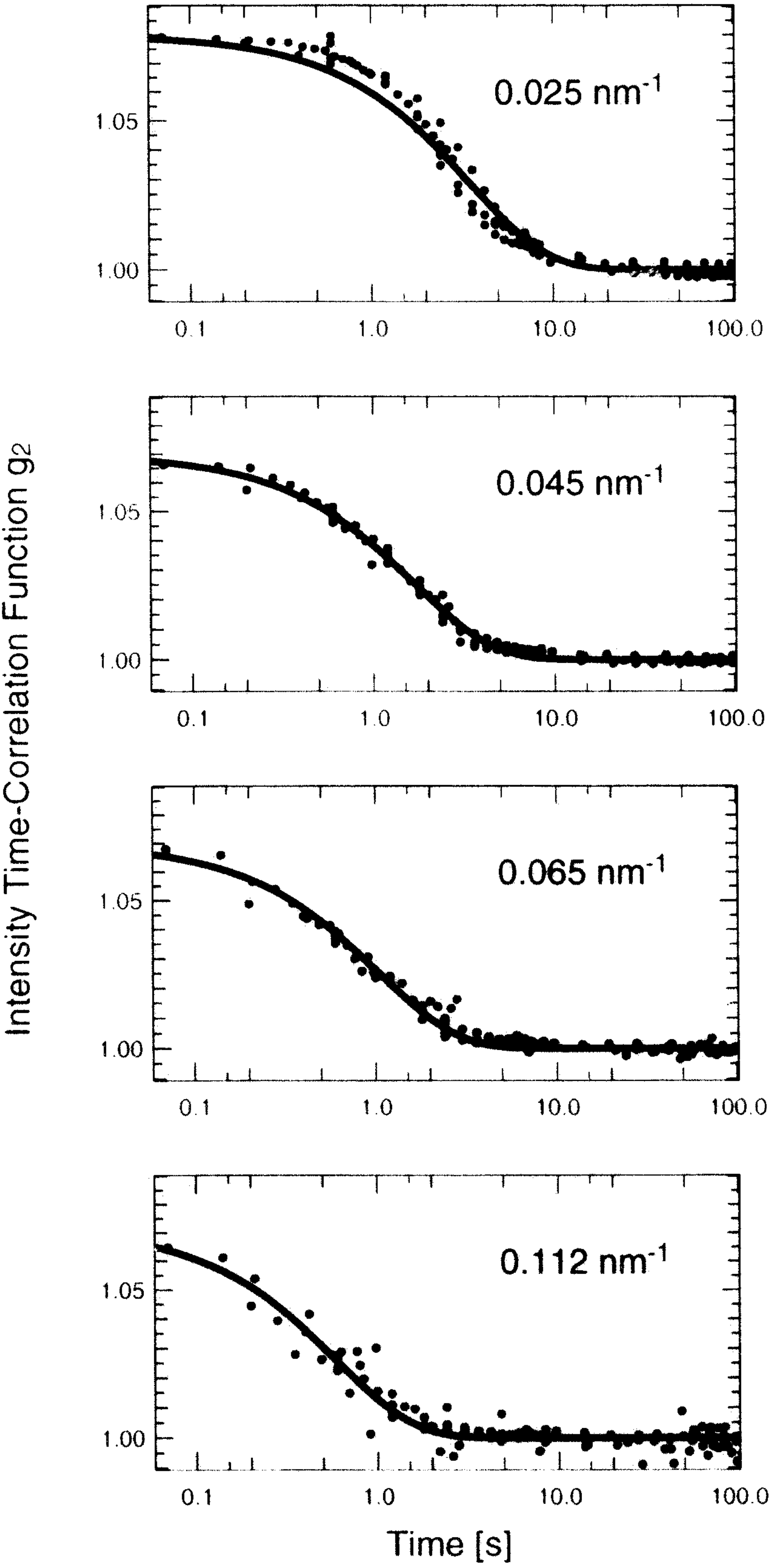


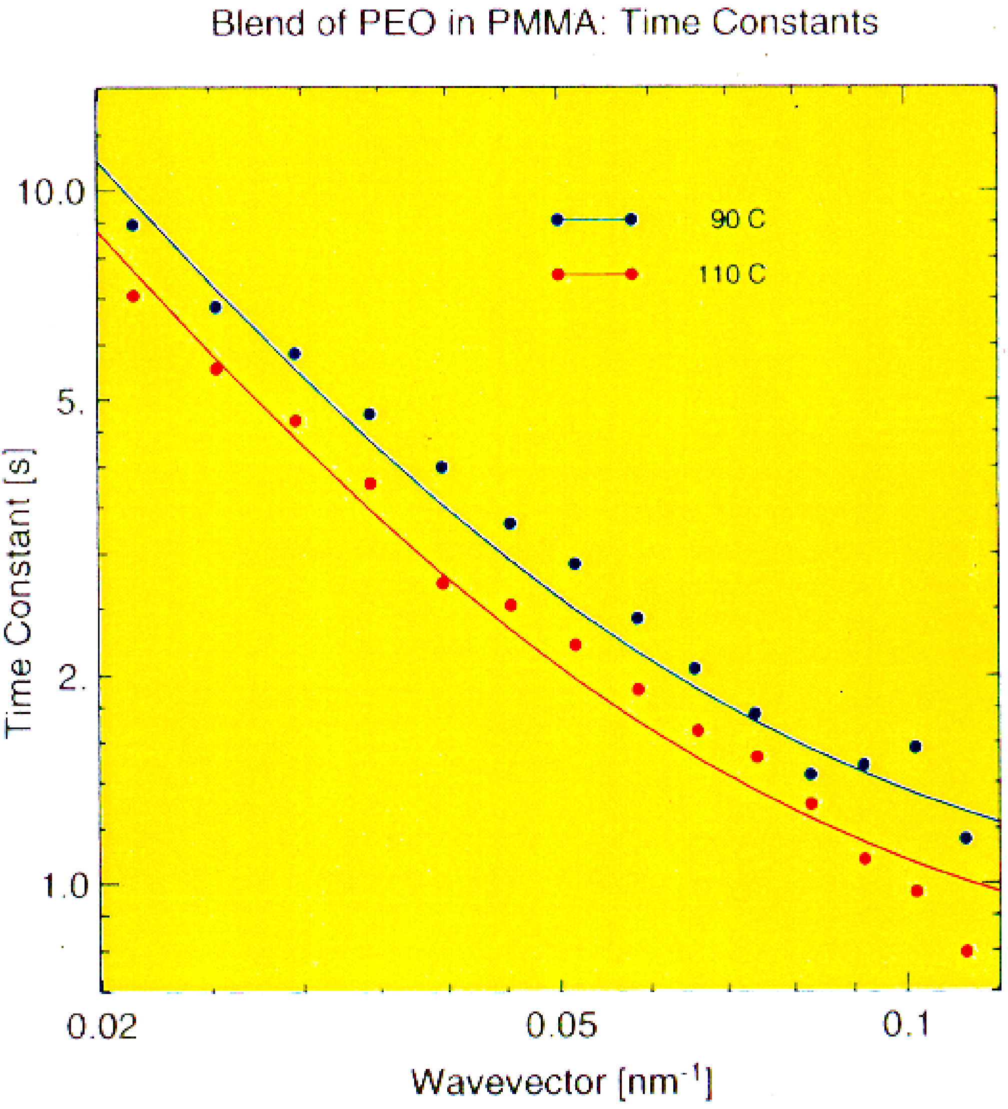
T. Perkins, D. E. Smith and S. Chu, Science **264**, 819 (1994)

- **diffusive motion away from the original tube has not been characterized**


Blend of PEO in PMMA
8000
6000
4000
2000
0
Cross-Section [cm-1]
0.00
0.05
0.10
0.15
0.20
Wavevector [nm-1]
10+4
10+3
10+2
0.02
0.05
0.1
0.2
120°C
80°C

Blend of PEO in PMMA: Equilibrium Fluctuations at 90°C




Blend of PEO in PMMA: Time Constants
90 C
110 C
Time Constant [s]
10.0
5.
2.
1.0
0.02
0.05
0.1
Wavevector [nm^{-1}]

Single Chain in a Melt

Dynamic Structure Factor

Doi and Edwards
The Theory of Polymer Dynamics

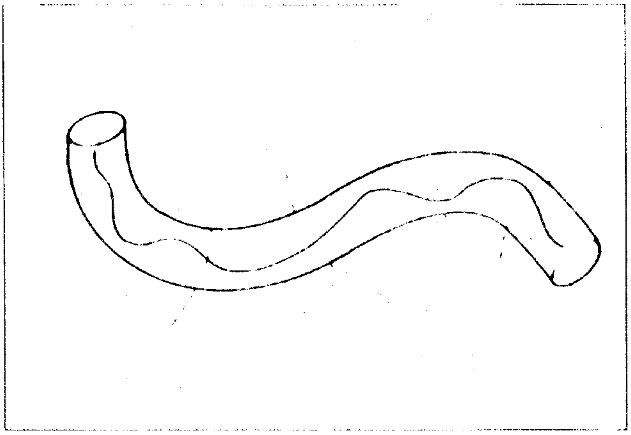
$$\boldsymbol{\mathcal{S}}(q,t) = \sum_{p=1}^{\infty} \frac{2\mu N}{\alpha_p^2(\mu^2+\alpha_p^2+\mu)} \, \sin^2\alpha_p \, \exp\left(-\frac{4\alpha_p^2}{\pi^2}\frac{t}{\tau_d}\right)$$

$$\alpha_p \tan\alpha_p = \mu \qquad \mu = \frac{1}{2}(qR_g)^2$$

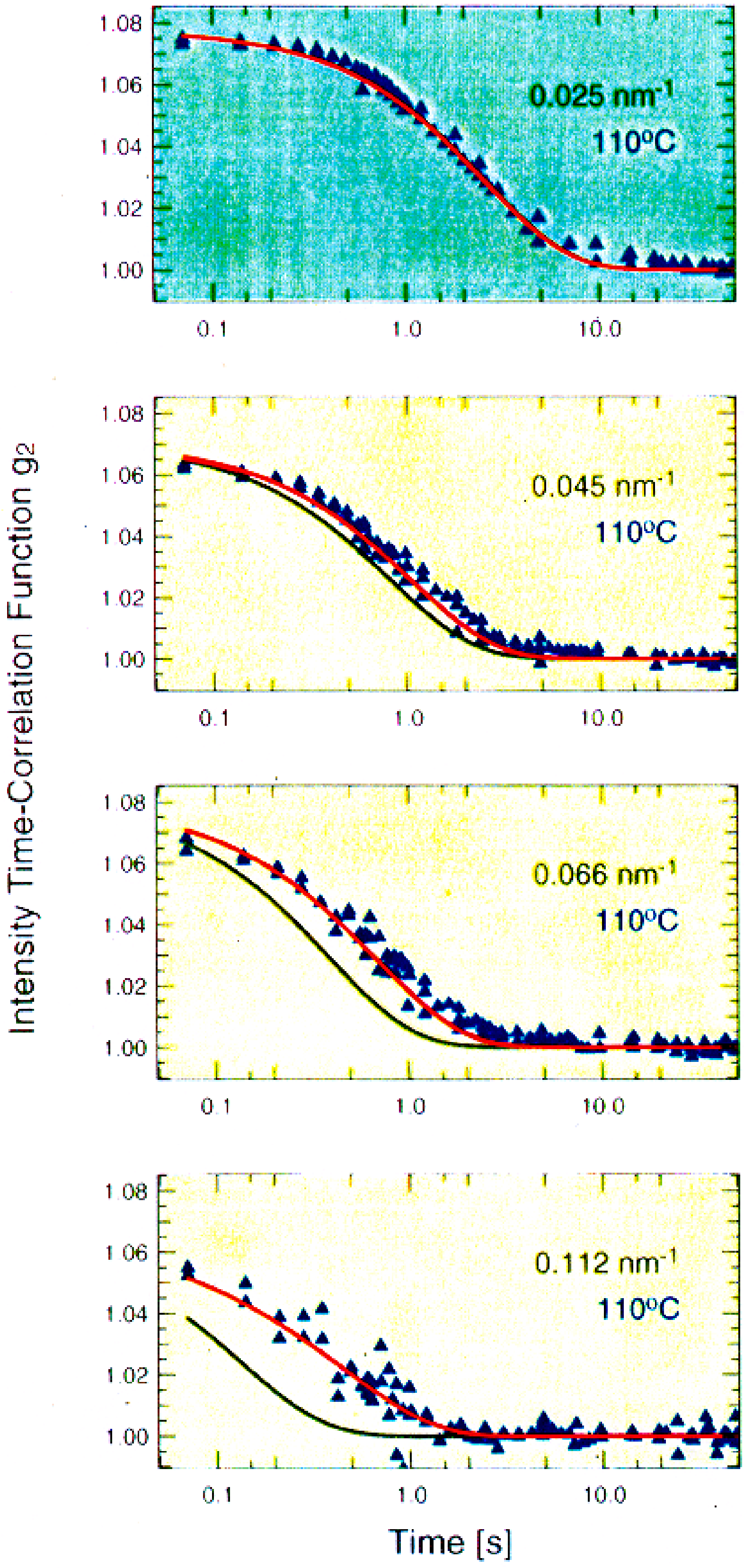
Simplest among the Available Models – Neglecting
Polydispersity
Interaction between Chains
Asymmetry of Mixture

$$\Downarrow$$

Quantitative Description of Wavevector Dependence



Single-Chain Reptational Diffusion in Melt Versus Brownian Motion



Future Work on Entangled Polymeric Systems

Slow Dynamics (0.07 – 100s) on
Small Length Scales (100 – 1000 Å)

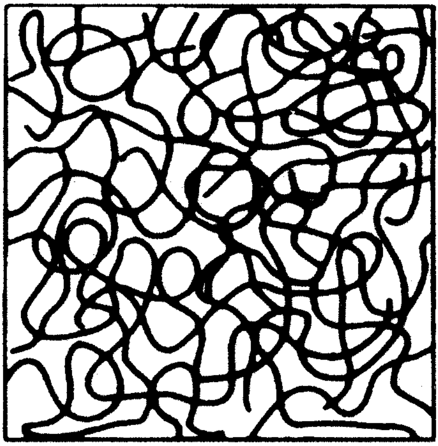
Temperature Dependence

More Temperature Points

Comparison with Rheology

Monodisperse PEO-PMMA Blend

More Detailed Comparability with Theory



So... How well are we doing really?

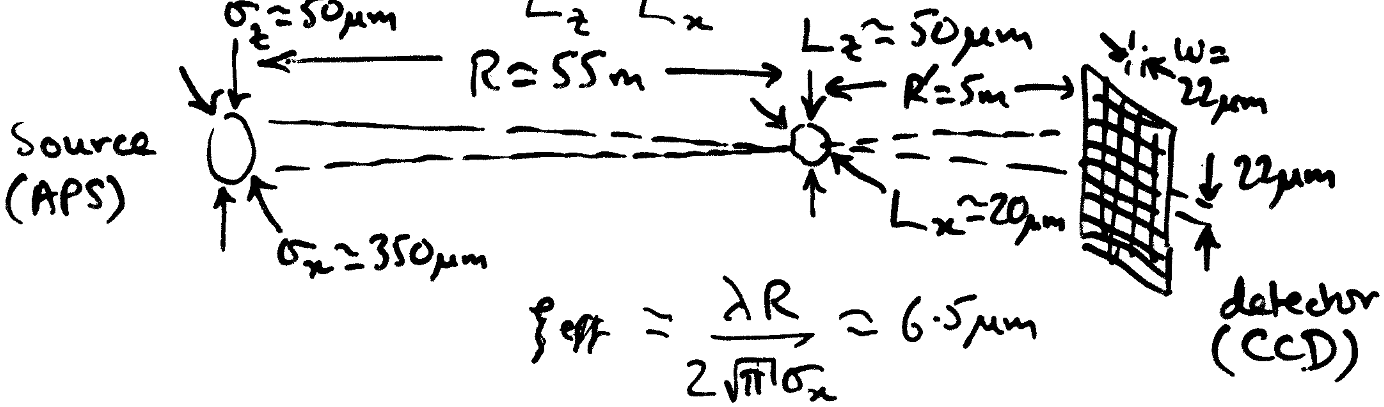
i.e. How well do we understand XPCS and can we extrapolate to LCLS/G4?

1. Expected flux thru 20μm x 50μm slits in BW of 2.5×10^{-4} is $\sim 2\times10^{10}$ x-rays per sec

(not worrying about less that perfect reflectivity of mirror & mono & attenuation of Be windows)

we typically get $0.7 \rightarrow 1.0\times10^{10}$ x-rays per sec

2. Expected contrast with 20μm x 50μm slits is $\beta \simeq \frac{\zeta_{eff}}{L_z}\frac{\xi_{eff}}{L_x}$



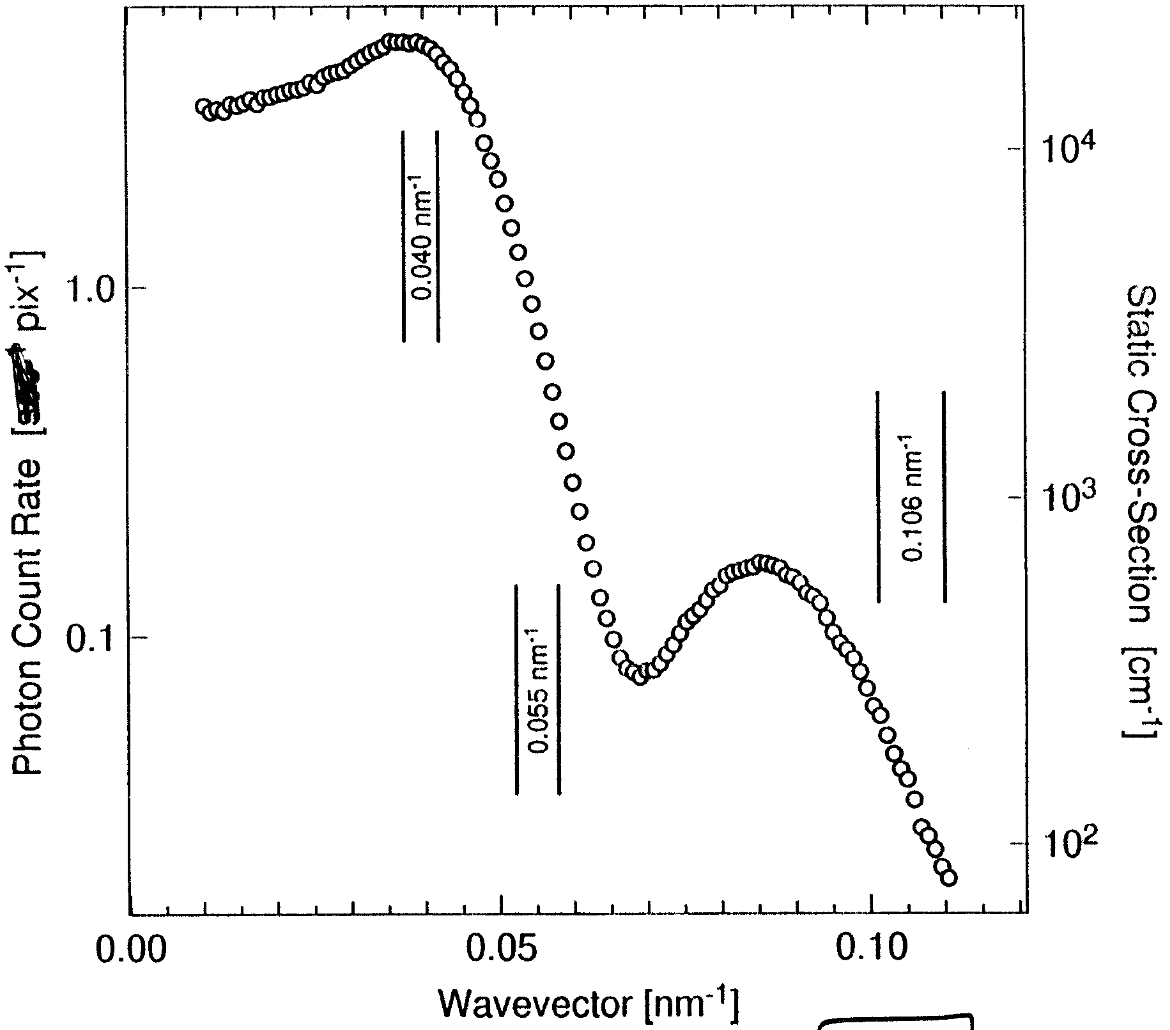
$$\xi_{eff} \simeq \frac{\lambda R}{2\sqrt{\pi}\,\sigma_x} \simeq 6.5\mu m$$

$$\zeta_{eff} \simeq \frac{\lambda R}{2\sqrt{\pi}\sqrt{\sigma_z^2+\left(\frac{Rw}{R'}\right)^2/6}} \simeq 20\mu m$$

so $\beta \simeq 0.13$ expected

$\beta \simeq 0.11$ observed

3. Signal-to-Noise in XPCS
Is it what we expect?



Jakeman has shown that $\sqrt{\mathrm{var}\, g_2} \simeq \frac{1}{\bar{n}\sqrt{M}}$

$\bar{n}$ = counts per pixel per accumulation time

M = # of measurements of g_2 = $N_p N_t$

with N_p = # of pixels, N_t = # of time pairs

$\simeq$ 1000 typical

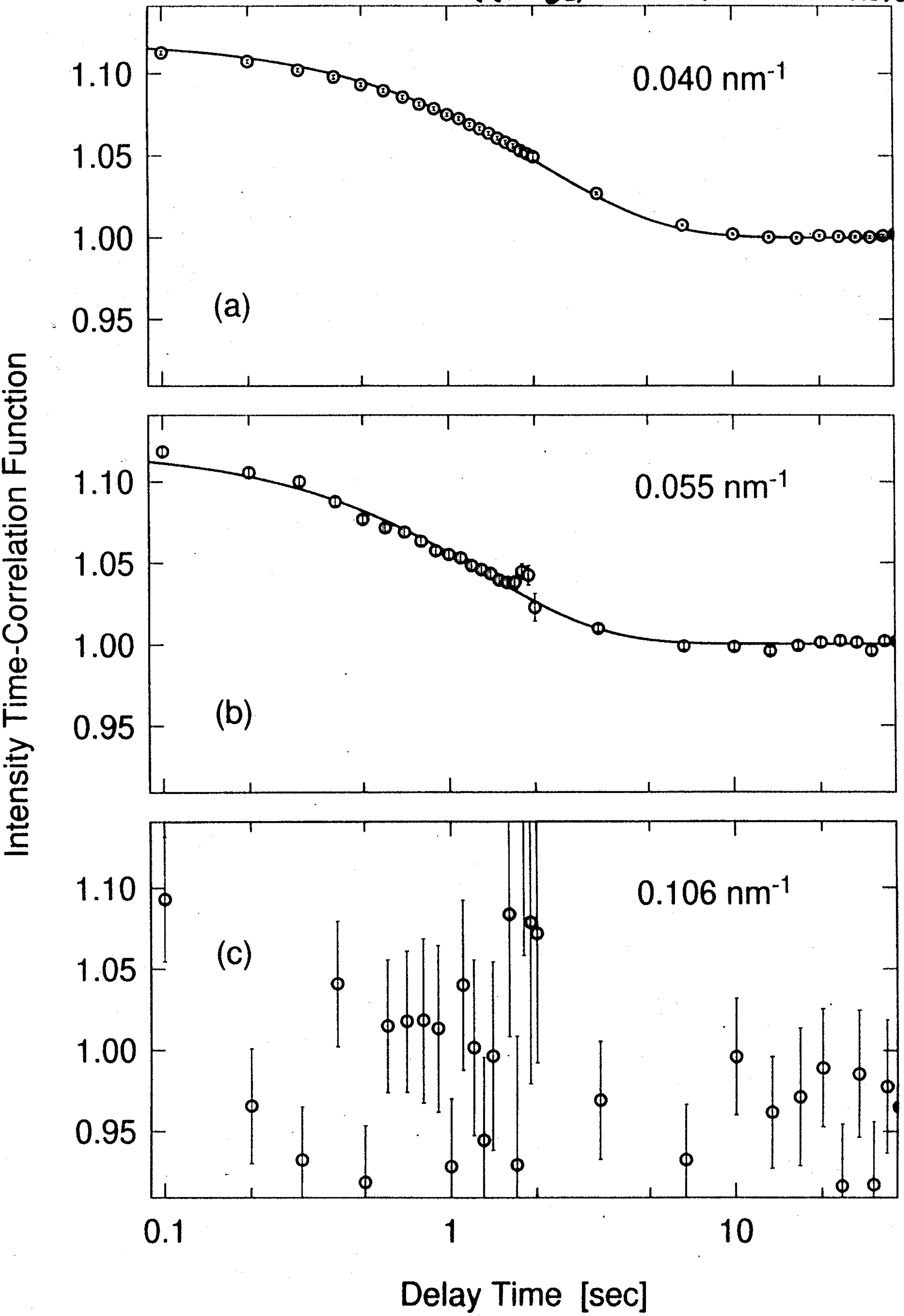
$\simeq$ 6000 is 10 minutes of data acquisition ×2 in real time

then $\sqrt{\mathrm{var}\, g_2} \simeq 0.001$

note $\frac{S}{N} \simeq \frac{\beta}{\sqrt{\mathrm{var}\, g_2}}$

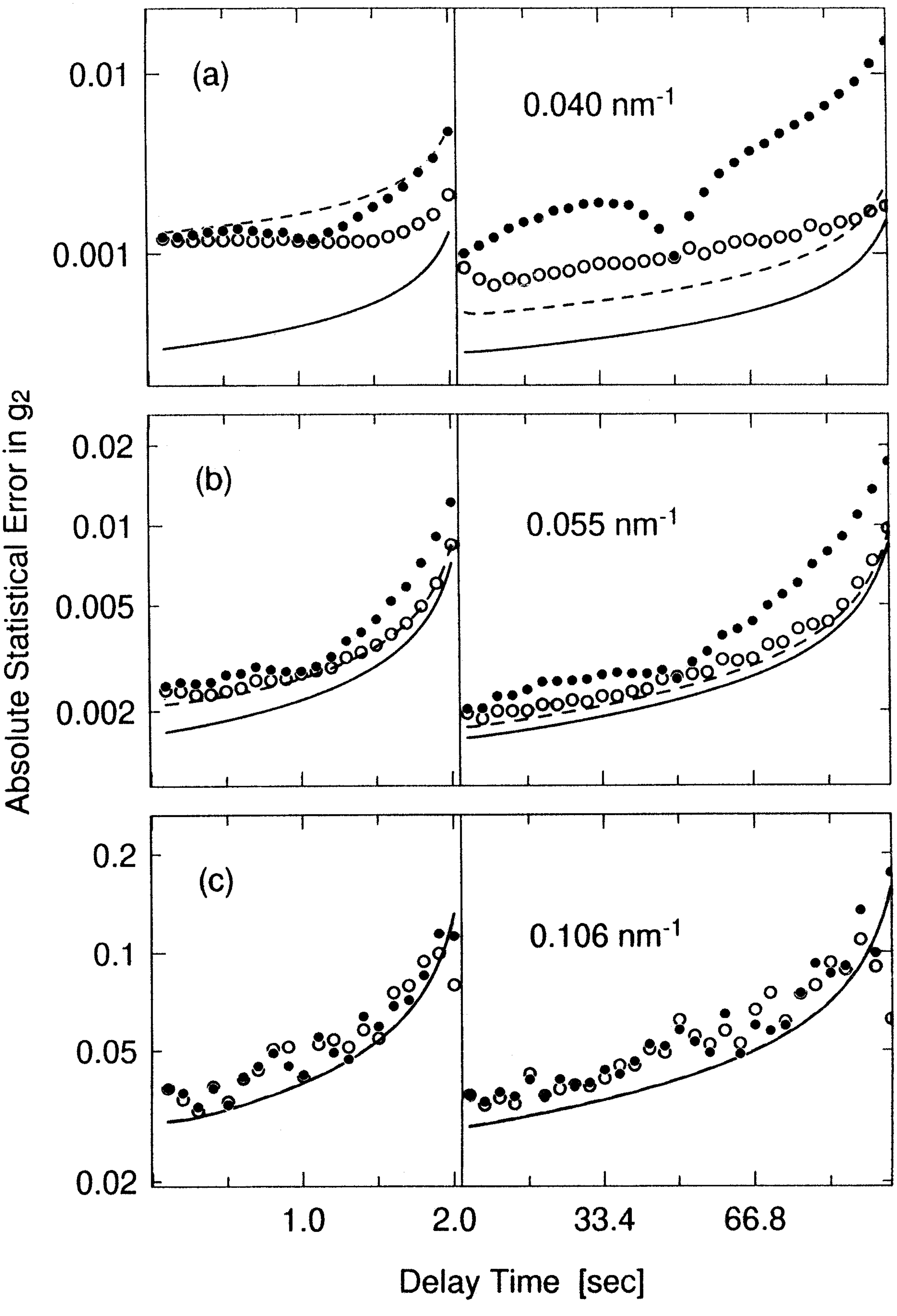
Here are the g_2's at the 3 Q's… from 100ms data + experimental error estimators

Note that $\frac{\text{signal}}{\text{noise}} \simeq \frac{g_2 - 1}{\sqrt{(\mathrm{Var}\, g_2)}}$



and here are the expected (theoretical)
errors and the experimental error estimators
(dashed lines) (open circles)

..... comparison reveals good agreement



Conclusion: we understand errors

4. Note ~~that~~ the detector overall efficiency @ 100ms exposures in kinetics mode

is

$$\eta \simeq \frac{1}{5} \times \left(\frac{1600\,\text{ms}}{1.6+1.6\,\text{s}}\right) \times \frac{1}{16} = \frac{1}{160}$$

↗ x-ray detection efficiency

↑ fraction of experiment data is being acquired

↑ area of detector used

Note for (esp.) Mike Hart $\frac{S}{N} \propto \sqrt{N_p}$ pixels × CCD

So the more, the better.

@ 10 ms $\eta \simeq \frac{1}{1600}$

Conclusion

More suitable detectors are needed $\boxed{\text{now}}$

<u>and</u> for LCLS/94

ALSO

nota bene

Coherent beams with larger sizes means less flux (damage) of samples

BUT then need finer detector resolution

5. Now we are in a good position to address XPCS @ LCLS/94

(a) What is S/N for a speckle pattern obtained in 1 pulse – containing (say) 10^{12} photons?

$\frac{\Delta E}{E}$ should be $10^{-5}_{-13?}$

⋮

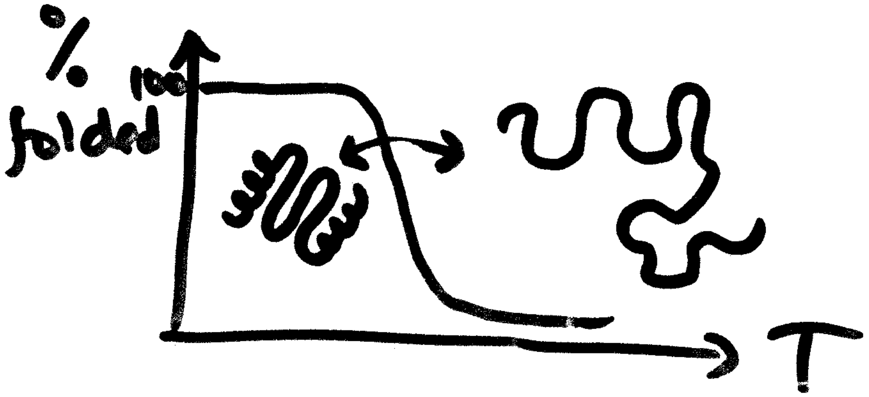
Suppose that $\Sigma_1 = 2 \times 10^{-2}$ cm^{-1}

≏ typical cross-section for conc. protein solution

at $Q = 0.5 \rightarrow 1.0$ Å^{-1}

$L \simeq 6 \rightarrow 12$ Å^{-1}

e.g. to look ~~to~~ at protein folding/unfolding dynamics



So $\bar{n} = n_i \, \Sigma_1 \, \Lambda_{eff} \, \Delta\Omega$

$\uparrow$ 10^{12} coherent photons i.e. $\beta = 1$

$\uparrow$ $2 \times 10^{-2}\,\mathrm{cm}^{-1}$

$\uparrow$ effective sample thickness $\simeq 0.03\,\mathrm{cm}$

$\uparrow$ pixel solid angle $\simeq 2 \times 10^{-11}$ sterads (say)

then $\bar{n} \cong 1.2 \times 10^{-2}$

$$\sqrt{\operatorname{var} g_2} = \frac{1}{\bar{n}\sqrt{N_p}}$$

$$= \frac{1}{12}$$

Here we are interested in spatial g_2 and N_p = # of n.n. pairs on CCD $\simeq 10^6$ – using entire area

$$S/N = \frac{\beta}{\sqrt{\operatorname{var} g_2}} = 12$$

in ONE shot

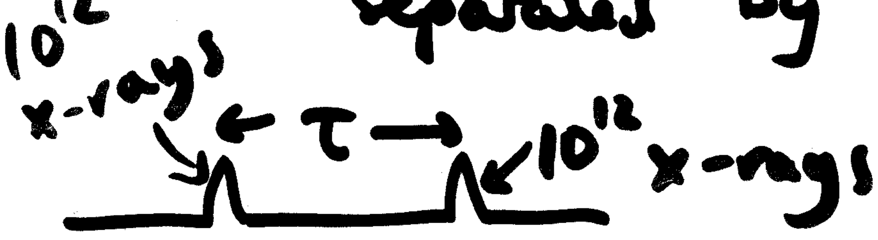
- averaging over many shots – studying a sample under flow for example will allow S/N to be improved greatly

(b) How can we do time correlations?

A PULSE TRAIN IS REQUIRED

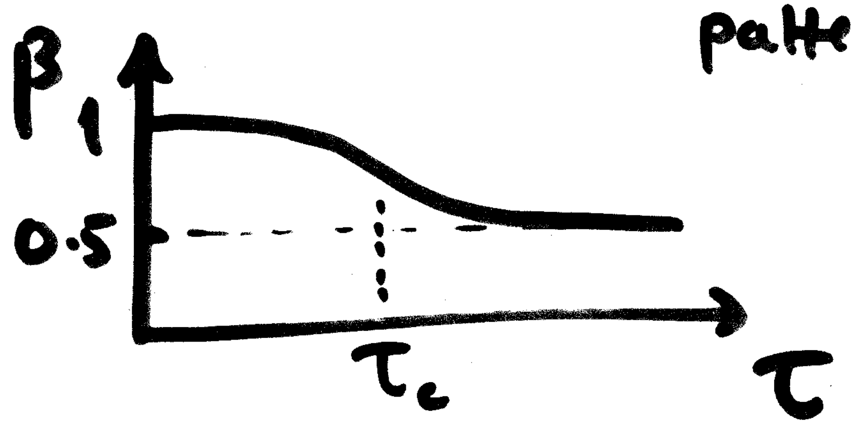
Suppose 2 x-ray pulses separated by time τ

both scatter into CCD



(i) $\tau \to 0$ Same speckle pattern ($\beta = 1$)

(ii) $\tau \to \infty$ Sum of 2 speckle patterns ($\beta = 0.5$)



- This method will allow τ_c to be determined within range that τ can be varied over.
  (I suppose the 2 pulses are within the pattern that repeats at 120Hz so $\tau \simeq 10^{-9}$s say)
- Ideally $\tau = 10^{-12} \to 10^{-6}$s or longer
  maybe a challenge... ?

- The CCD does NOT need to be exceptionally fast – it's read out @ 120 Hz
- Sample needs to survive τ, then can be changed e.g. flow

Conclusions

XPCS @ LCLS/G4 appears straightforward

- if pulse structure can be easily changed to vary τ
- if samples can survive 1 pulse for $\tau \sim 10^{-6}$ secs after that pulse and first pulse does not change the physics or chemistry or biology...

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