Scientific Opportunities with the ERL--Soft Materials and Nanoscience

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UCSD

This dynamic shampoo's **cleansing power comes from deep within the earth. Magnetite, a polarizing mineral that infuses positive energy while repelling negative charges, combines with special cleansing and conditioning forces. Proteins fill in ravaged hair to smooth and soothe. With each shampoo, hair feels stronger, looks better. Micro-magnets expel oils and residues. Damage is repaired. Shine is an absolute blast. This is the positron effect of Energizing Shampoo.**

DIRECTIONS: Lather into wet hair for 30 seconds. Feel the power? Rinse compietely. Follow with Restructuring Conditioner.

INGREDIENTS: Aqueous (Water) Extracts of *Rosemary (Rosmannus Officinalis) Oil, *Coltsfoot Leaf (Tussilago Farfara), *Sage Leaf (Salvia Officinalis), *Clary (Salvia Sclarea), *Thyme (Thymus Vulgaris) Oil, *Soybean Protein (Glycine Soja), C12-14 Olefin Sulfonate (coconut derived), Cocamidopropyl Betaine, **__**Magnetite (Fe_3O_4)**__, Citric Acid (corn), Lactoferrin (Metalloprotein), Carbomer, Mica, Sodium Hydroxymethylglycinate, Sodium Chloride (sea salt), Grapefruit Seed.

* Certified Organic

** Nature's Remedy for Beautiful Hair

7 19237 18048 3

PLEASE RECYCLE · PLEASE RECYCLE

GIOVANNI HAIR CARE
P.O. Box 6990
Beverly Hills, CA 90212
MADE IN U.S.A.

giovannicosmetics.com

Motivation

- Near atomic-scale imaging with hard x-rays - a grand challenge.
- Enables breakthrough science - ability to penetrate, high accuracy elemental, chemical and structural characterization.
- Critical development for DOE User Facilities - APS, CNM, LCLS, and NSLS-II

Need to identify Problems which are….

- Of great scientific/technological importance
- Cannot be done easily in other ways
- Has a potentially large interested scientific community
- Overcomes the natural resistance to scattering and other complicated techniques

Coherence

(Beware of what you wish for, you might actually get it!!)

- Provides great new capabilities--->Imaging, Dynamics
- Can make life difficult!!
- Conventional SAXS, reflectivity and GISAXS give GLOBAL statistical information

SAXS

$$S(\mathbf{Q}) = |f(\mathbf{Q})|^2 \Sigma \Sigma \exp(i\mathbf{Q}.\mathbf{l})\exp(-i\mathbf{Q}.\mathbf{l}')$$

Scattering from a surface:

$$S(\mathbf{Q}) = |\langle A_{substrate}(\mathbf{Q}) \rangle|^2$$

$$A_{substrate}(\mathbf{Q}) = i\rho_0/Q_z \int\int dX\, dY \exp(-iQ_z h(\mathbf{R})) \exp(-i\mathbf{Q}.\mathbf{R})$$

For Gaussian Roughness

$$S(\mathbf{Q}) = A_0\rho_0^2/Q_z^2 \int\int dX\, dY \exp[-{}^1/_2 Q_z^2 G(\mathbf{R})] \exp(-i\mathbf{Q}.\mathbf{R})$$

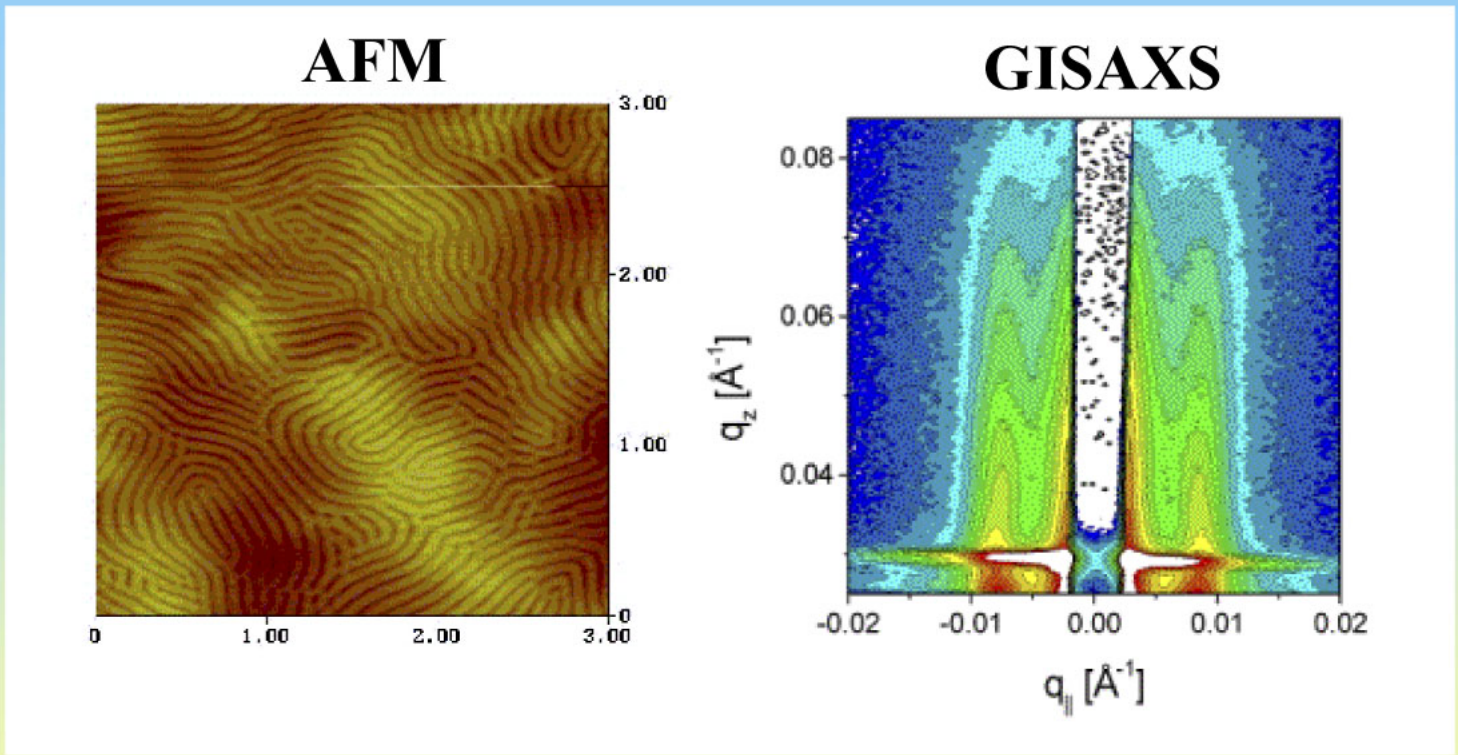
Bimodal Roughness (Islands)

$$S(\mathbf{Q}) = A_0\rho_0^2/Q_z^2 \exp[(-iQ_z\Delta] \int\int dX\, dY\, \gamma\,(\mathbf{R}) \exp(-i\mathbf{Q}.\mathbf{R}) + c.c.$$

GISAXS

$$S(\mathbf{Q}) = |\langle f(\mathbf{Q})\Sigma \exp(i\mathbf{Q}.\mathbf{l}) + A_{substrate}(\mathbf{Q}) \rangle|^2 |T(\alpha)|^2 |T(\beta)|^2$$

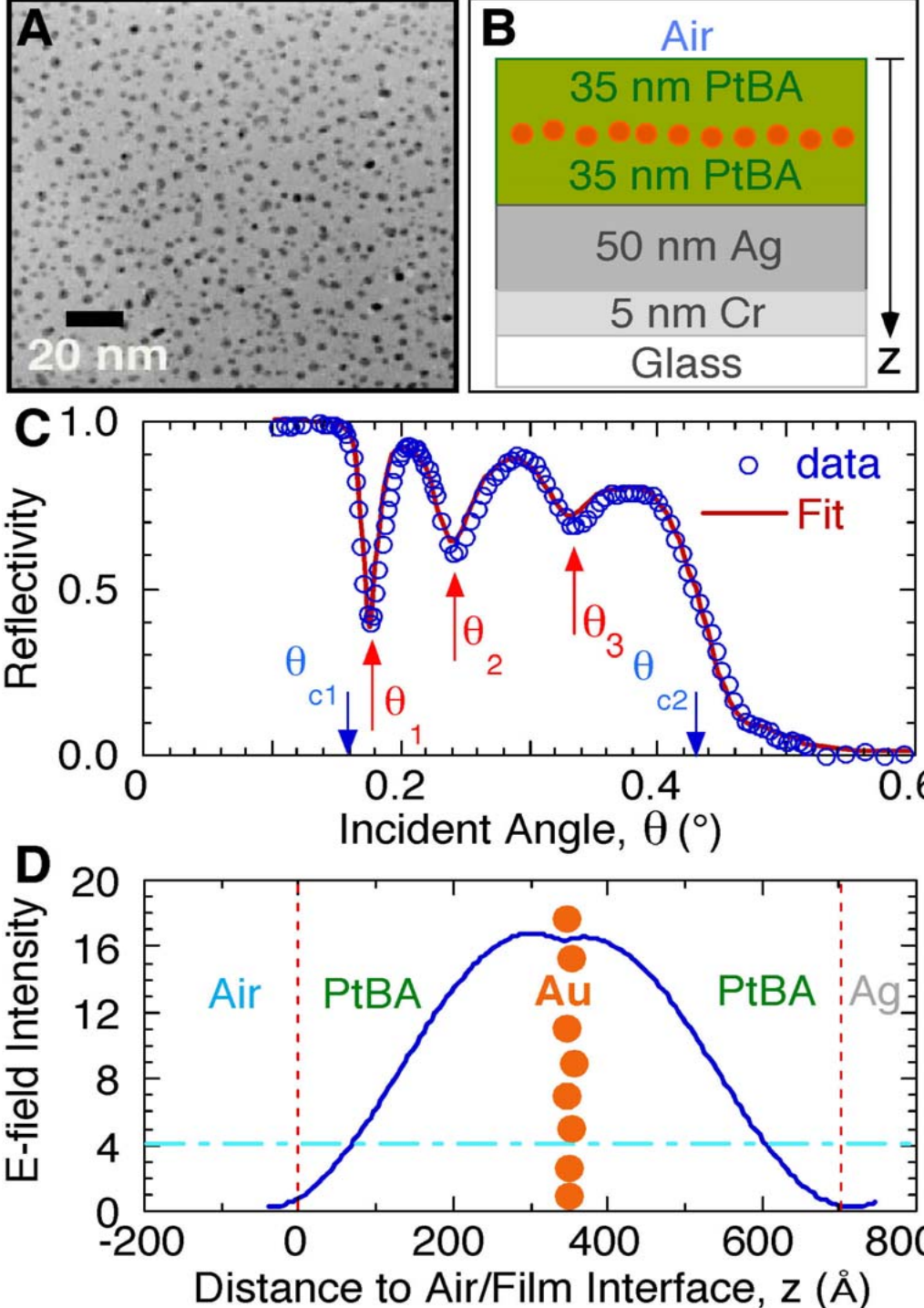
Block copolymer thin films: PS-PB



Smilgies, Busch, Posselt, Papadakis, SRN 15(5), p. 35-41 (2002).

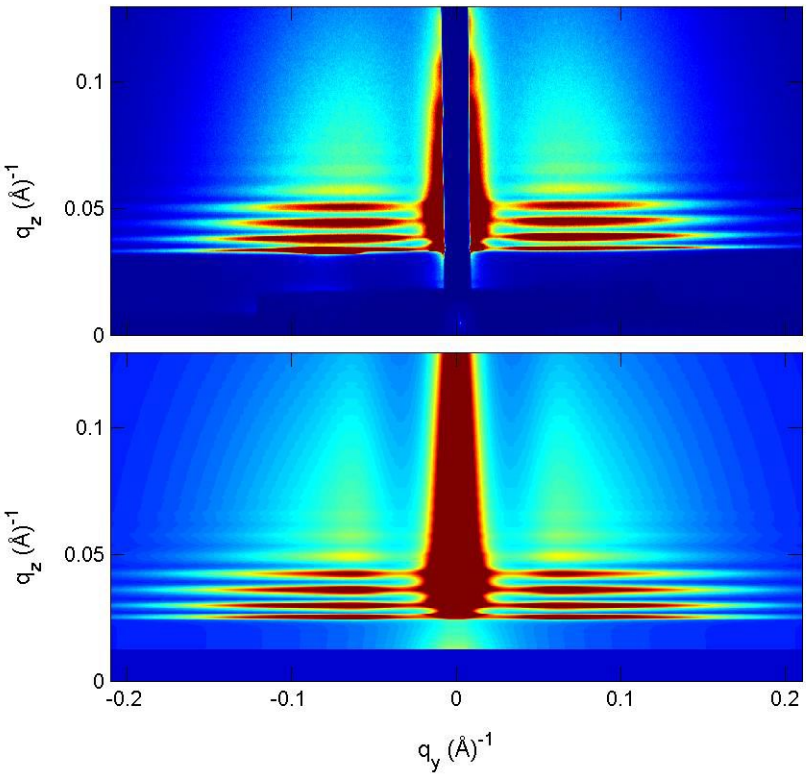
Lamellar spacing: 850 Å

CHESS D-line: ML optics + CCD



Gold colloids in Polymer films
Jin Wang, S.Narayanan, D.R.Lee, R.S.Guico and S.K.S. (2003)

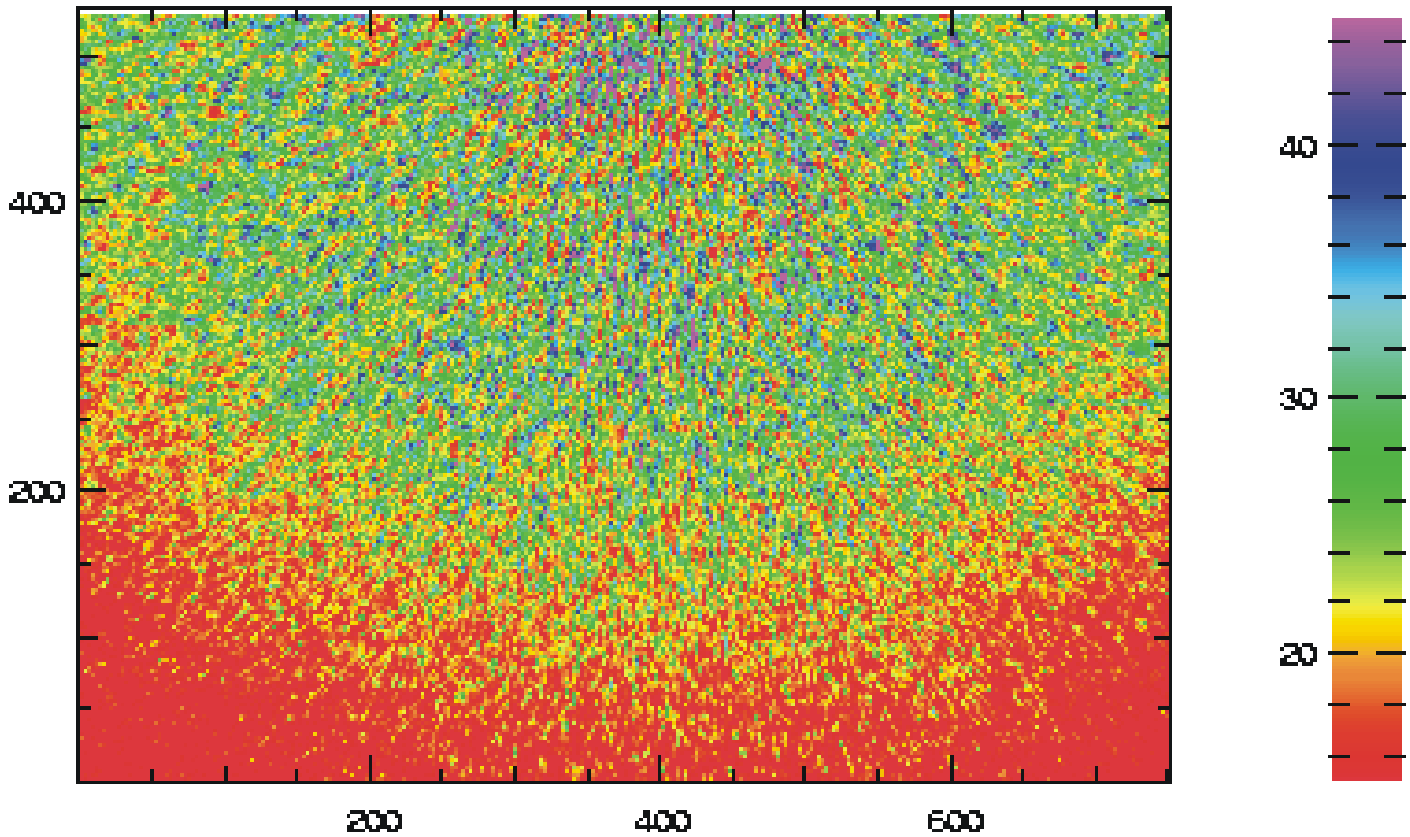
GISAXS measurement (top) and calculation (bottom)



For a completely coherent beam everything interferes with everything else (maybe even what you're NOT interested in) giving SPECKLE!

May want *tunable* coherence!

X-ray speckle pattern from a static silica aerogel



We may write: (Sinha,Tolan,Gibaud Phys. Rev. 1998)

$$I(\mathbf{q}) = \text{Constant} \times \iint d\mathbf{r}\, d\mathbf{r}' \exp[i\,\mathbf{q}.(\mathbf{r}'-\mathbf{r})]\, \rho(\mathbf{r})\rho(\mathbf{r}')\, \Gamma_s(\mathbf{r}, \mathbf{r}', 0)\, W_1(\mathbf{r}'-\mathbf{r}) W_2(\mathbf{r}'-\mathbf{r}) W_3(\mathbf{r}, \mathbf{r}')$$

Where

$$\Gamma_s(\mathbf{r}, \mathbf{r}', 0) = \Psi_s(\mathbf{r}_{\perp 1})\, \Psi_s^*(\mathbf{r}'_{\perp 1}) g(\mathbf{r}'_{\perp 1} - \mathbf{r}_{\perp 1}) \exp[i\beta(r_{\perp 1}^2 - r'^2_{\perp 1})]$$

$$W_1(\mathbf{r}'-\mathbf{r}) = \int d(\Delta\omega)\, F(\Delta\omega) \exp[-i\,\Delta\omega/\varpi\, \mathbf{q}.(\mathbf{r}'-\mathbf{r})]$$

$$W_2(\mathbf{r}'-\mathbf{r}) = \iint d\mathbf{u} \exp\{ ik_2^2/2[\mathbf{u}.(\mathbf{r}'-\mathbf{r})]\} \qquad k_2 = (2\pi/\lambda L_2)^{1/2}$$

$$W_3(\mathbf{r}, \mathbf{r}') = \exp[ik_2^2/2(r_{\perp 2}^2 - r'^2_{\perp 2})]$$

If translational invariance is satisfied for statistical average:

$\langle \rho(\mathbf{r})\rho(\mathbf{r}') \rangle = C(\mathbf{r}'-\mathbf{r})$ (**NOT true for imaging specific systems)

Define $\mathbf{R} = \mathbf{r}'-\mathbf{r}$

Then we have

$I(\mathbf{q}) = A \int d\mathbf{R} \exp[i\,\mathbf{q}.\mathbf{R}]\, C(\mathbf{R})\, \Phi(\mathbf{R})$

$\Phi(\mathbf{R})$ defines the *Coherence Volume*

$$\Phi(\mathbf{R}) = \int d\mathbf{r}\, \Psi_s(\mathbf{r}_{\perp 1})\, \Psi_s^*([\mathbf{r}+\mathbf{R}]_{\perp 1}) g(\mathbf{R}_{\perp 1}) \exp[i\beta(r_{\perp 1}^2 - [r+R]_{\perp 1}^2)]\, W_1(\mathbf{R})\, W_2(\mathbf{R}) \exp[ik_2^2/2(r_{\perp 2}^2 - [r+R]_{\perp 2}^2)]$$

$$W_1(\mathbf{R}) = \int d(\Delta\omega)\, F(\Delta\omega) \exp[-i\, \Delta\omega/\varpi\, \mathbf{q}.\mathbf{R}]$$

$$W_2(\mathbf{R}) = \iint d\mathbf{u} \exp\{ ik_2^2/2[\mathbf{u}.\mathbf{R}]\} \qquad k_2 = (2\pi/\lambda L_2)^{1/2}$$

So we can write:

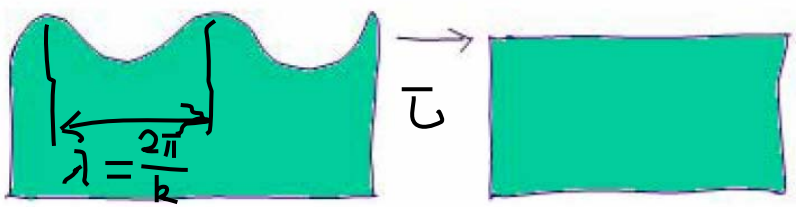
$$I(\mathbf{q}) = A \int d\mathbf{K}\, S(\mathbf{K})\, \Phi(\mathbf{K}-\mathbf{q})$$

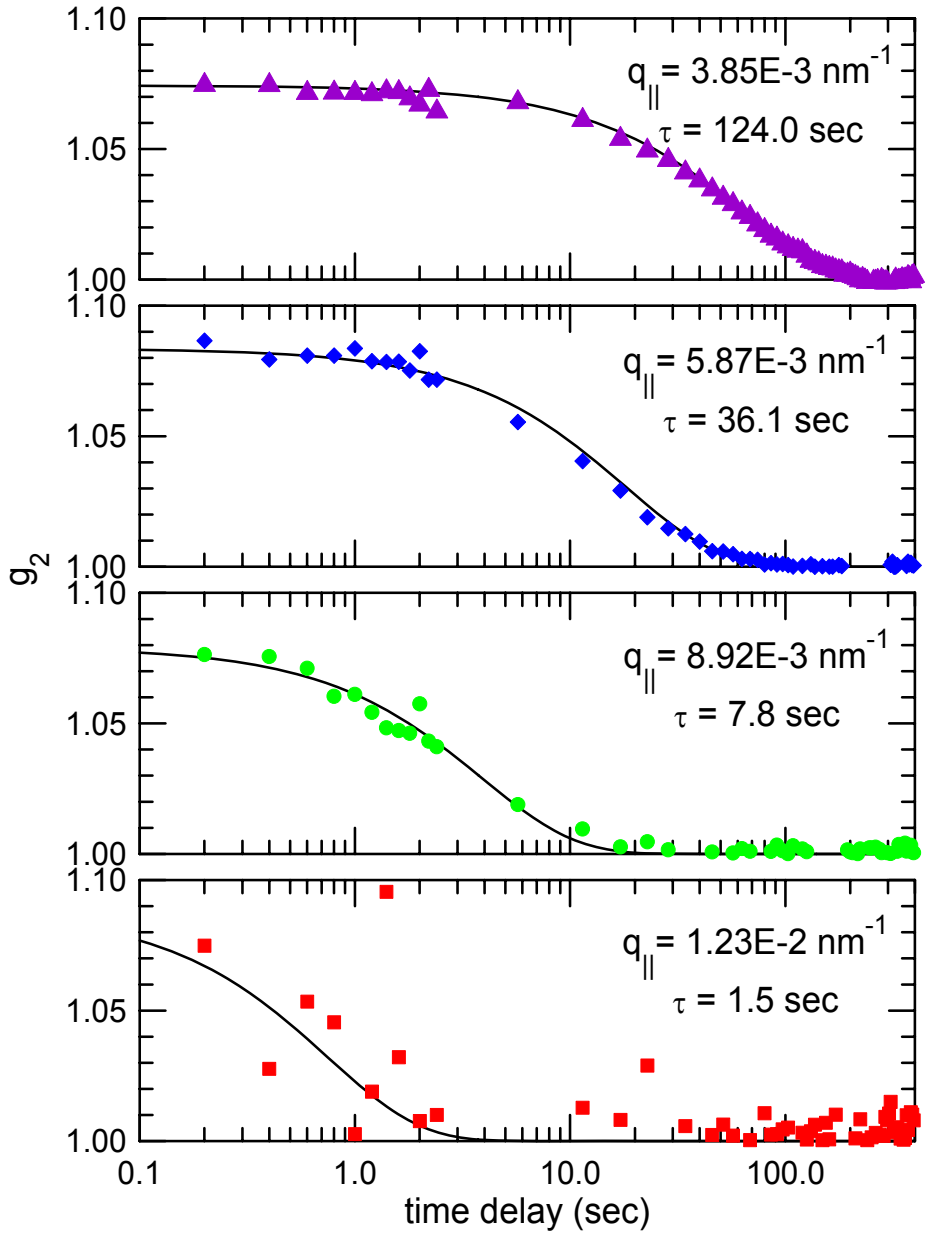
as in conventional “Resolution Function” calculations!

Intensity Autocorrelation

$$g_2(q,\tau) = \frac{\langle I(q,t)I(q,t+\tau)\rangle}{\langle I(q,t)\rangle^2}$$

$$g_2(q,\tau) = 1 + \beta e^{-2t/\tau}$$

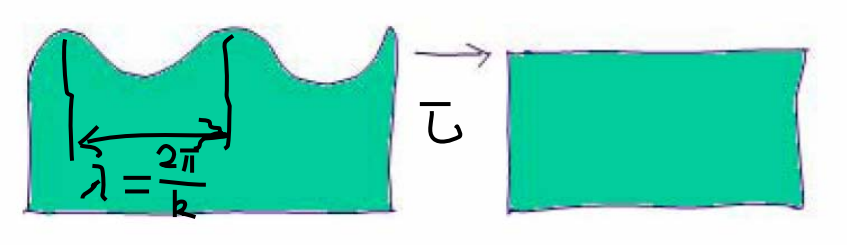


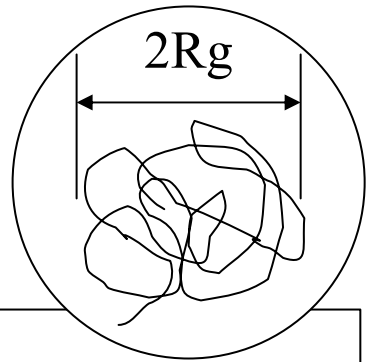


Hyunjung Kim, et.al., PRL 90, 68302 (2003)

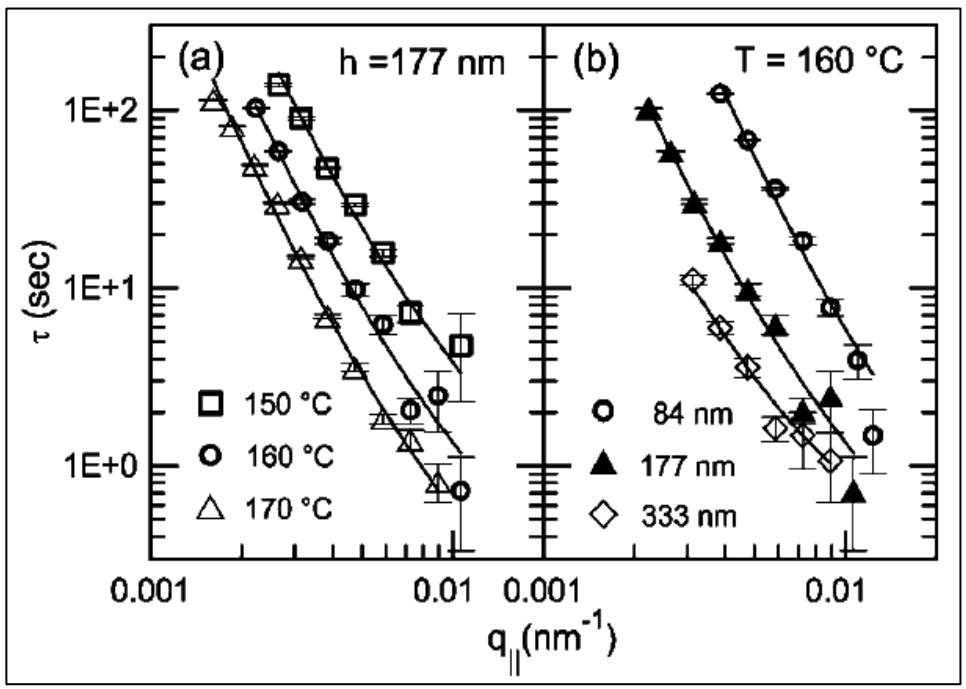
Over Damped Surface Capillary Waves

- Time required for a surface mode of wave length $\lambda=2\pi/k$ to relax.





- Supported polystyrene (PS) films (thickness >> Rg)



$$\tau(q_{||}) \cong \frac{2\eta H}{\gamma q_{||} F}$$

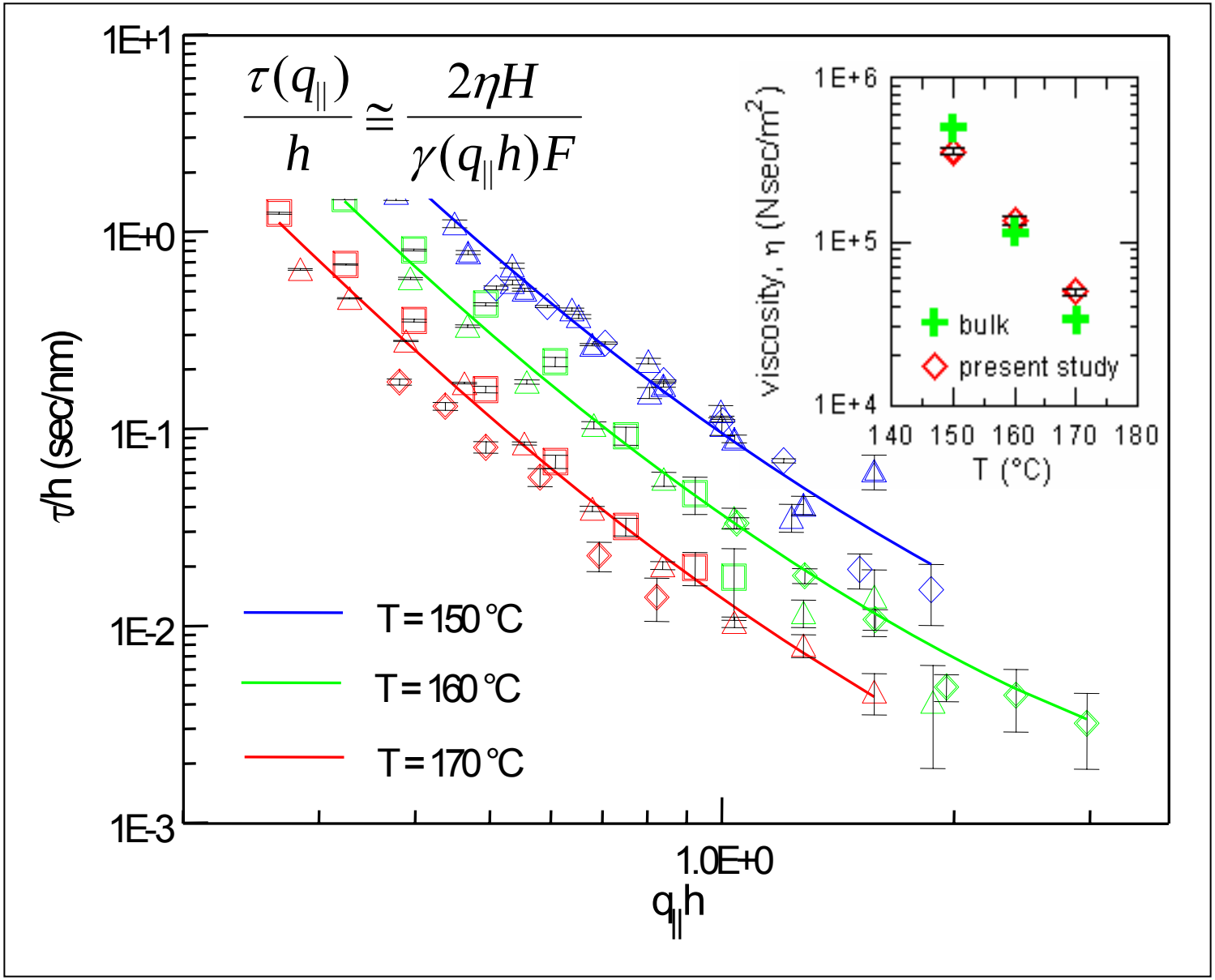
$$F = \sinh(q_{||}h)\cosh(q_{||}h) - (q_{||}h)$$

$$H = \cosh^2(q_{||}h) + (q_{||}h)^2$$

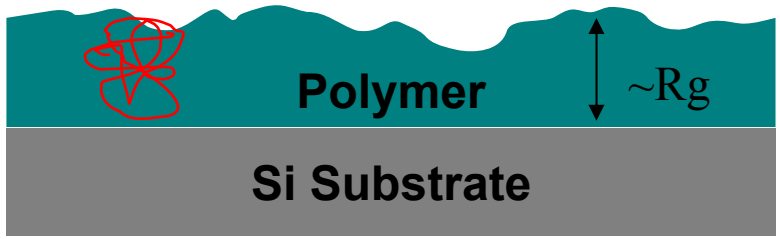
η : viscosity

γ : surface tension

h : film thickness


$\frac{\tau(q_{||})}{h} \cong \frac{2\eta H}{\gamma(q_{||}h)F}$
1E+1
1E+0
1E-1
1E-2
1E-3
τ/h (sec/nm)
1.0E+0
$q_{||}h$
T = 150 °C
T = 160 °C
T = 170 °C
1E+6
1E+5
1E+4
viscosity, η (Nsec/m²)
bulk
present study
140 150 160 170 180
T (°C)

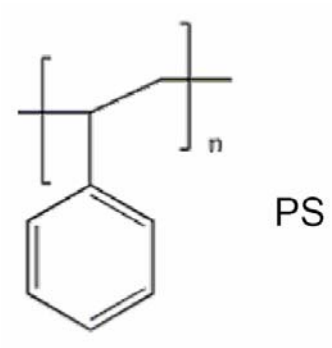
What might happen to ultra-thin films ?



? Interaction with substrate (Van de Waals force)

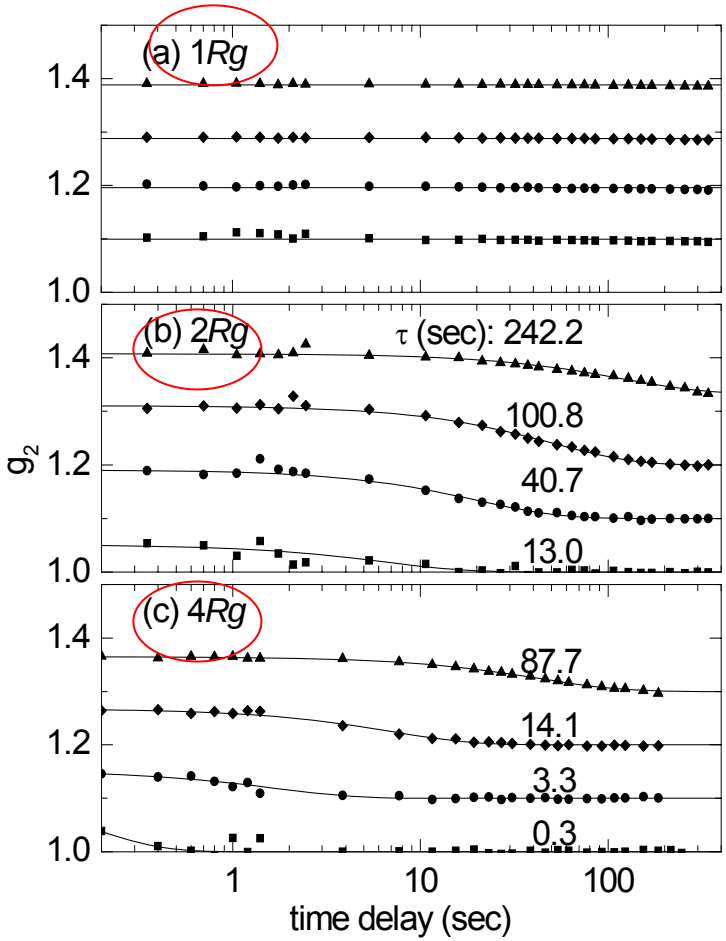
? Absorption of segments onto substrate

? Viscoelasticity



$$Rg = 6.7\left(\frac{N}{6}\right)^{\frac{1}{2}}$$

Mw	Rg (A)	Thickness
65K	68	Rg, 2Rg,4Rg
123K	94	Rg,2Rg,4Rg
400K	170	Rg,2Rg,4Rg
650K	217	2Rg,4Rg
900K	255	Rg,2Rg,4Rg



PS123K @ 195C : wave vector 3.3 (▲), 5.4 (↗), 7.7 (↘) and 10 (→) x 10^{-4} A^{-1}

$$g_2(q,\tau) = \frac{\langle I(q,t)I(q,t+\tau)\rangle}{\langle I(q,t)\rangle^2}$$

$$g_2(q,\tau) = 1 + \beta e^{-2t/\tau}$$

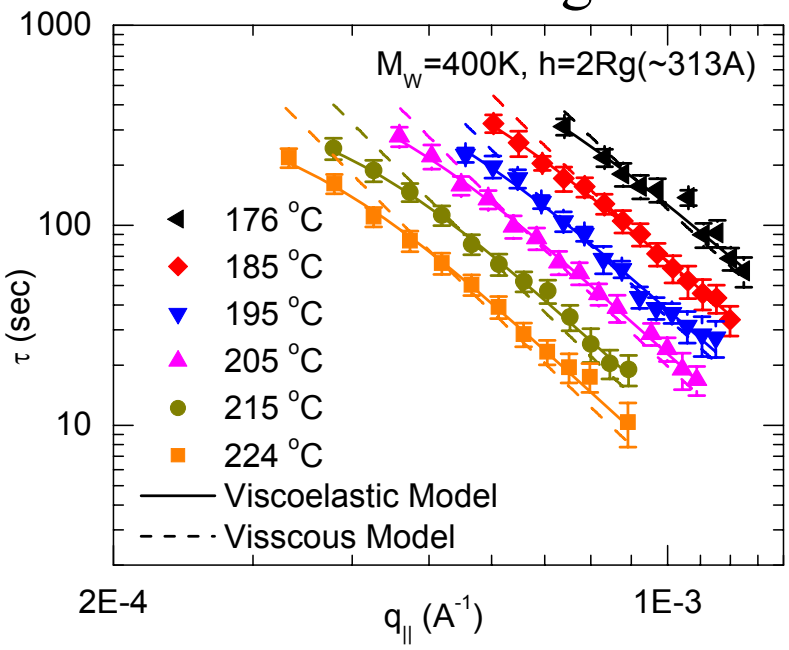
- 1Rg film: static. Polymer chains are stuck on substrate. Viscosity is very tremendously large
- 2Rg and 4Rg films : dynamic
- 2Rg film is slower than 4Rg; chains have less mobility than those in 4Rg films.

Thermal Driven Capillary Wave Relaxation Time

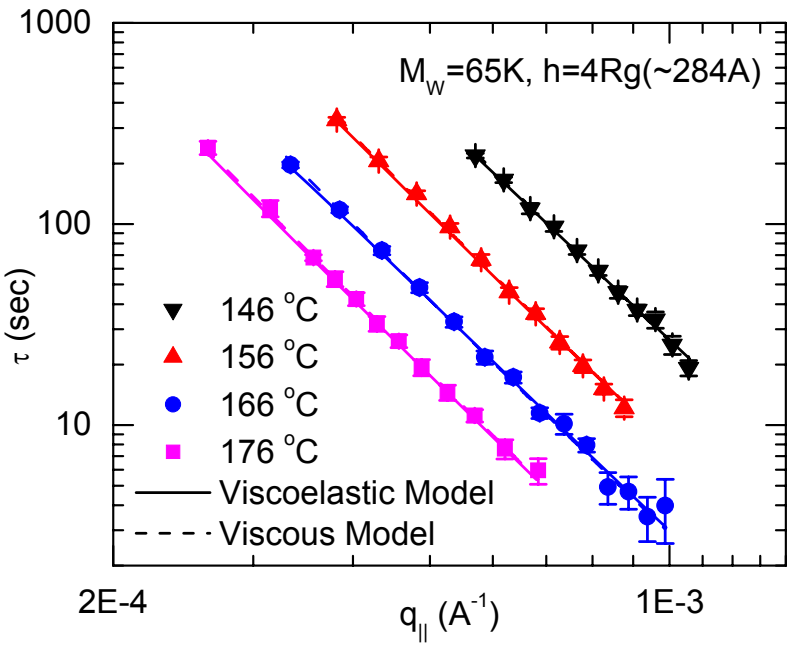
400K Rg= 170 A

65K Rg=68 A

Thickness = 2Rg



Thickness = 4Rg

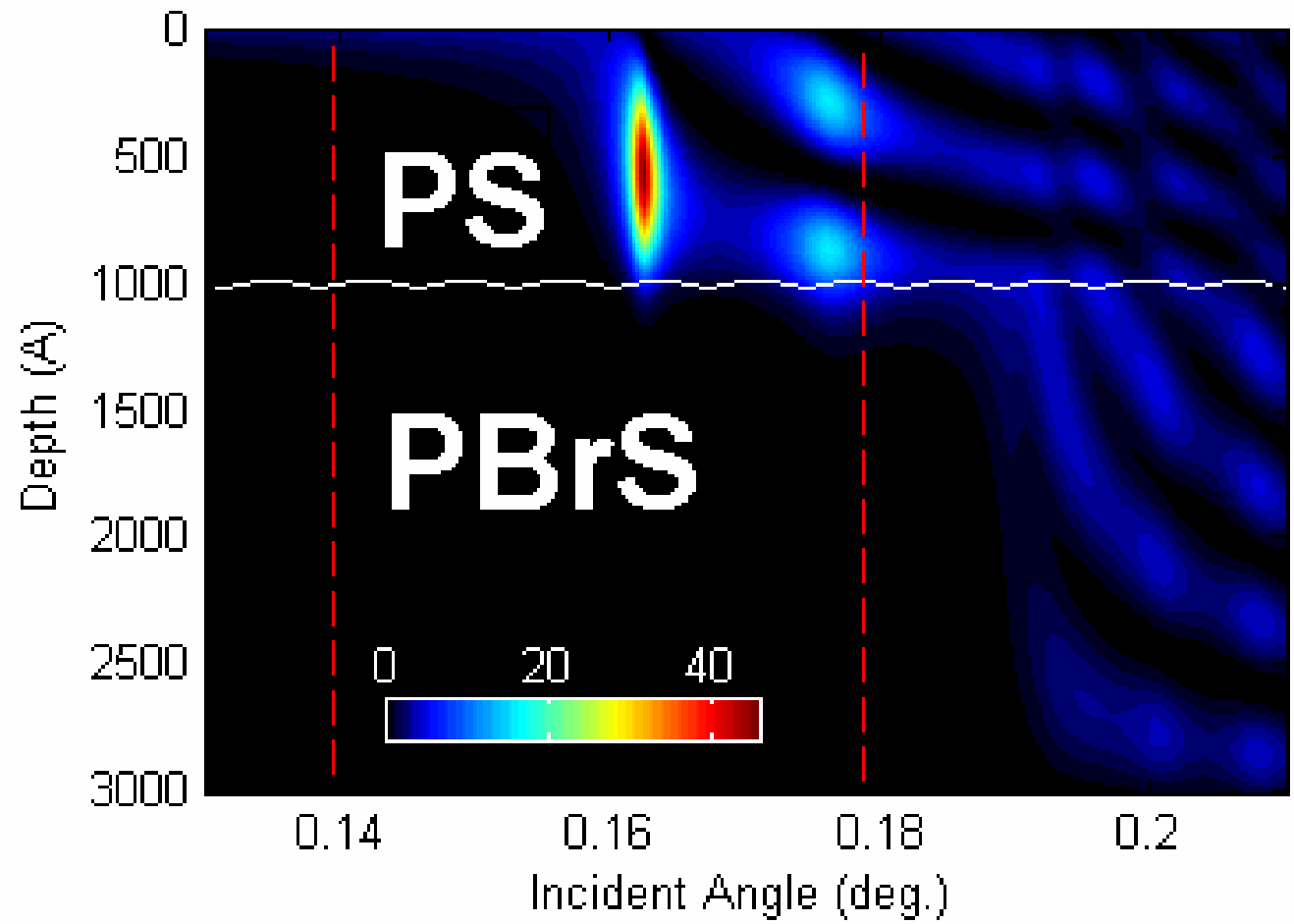


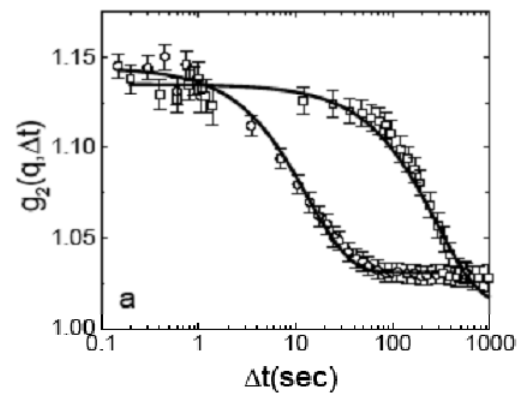
Viscoelastic model:

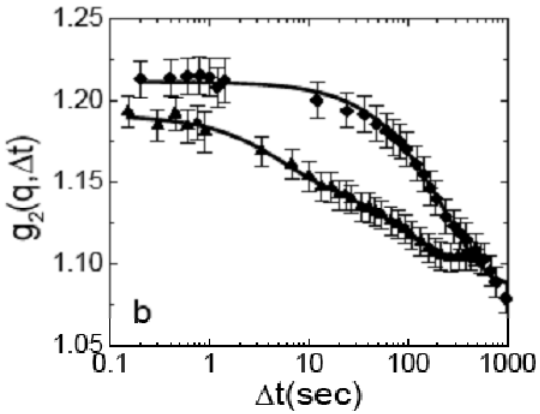
$$\tau(q_{\|}) \cong \frac{2\eta H}{\gamma q_{\|} F} \Big/ \left(1 + \frac{2\mu H}{\gamma q_{\|} F}\right)$$

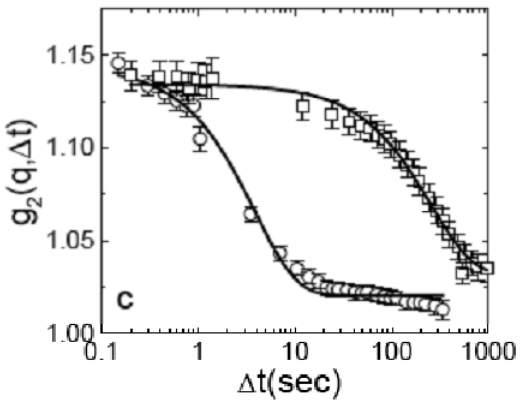
Viscous model:

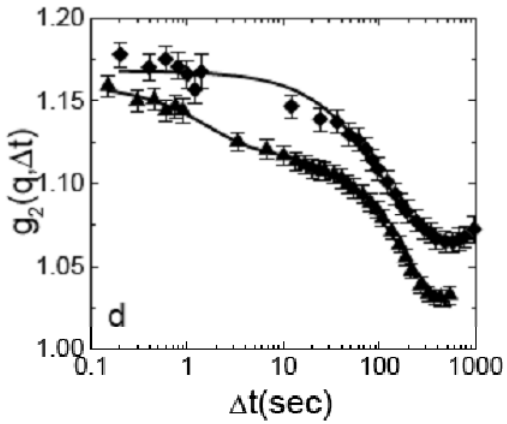
$$\tau(q_{\|}) \cong \frac{2\eta H}{\gamma q_{\|} F}$$

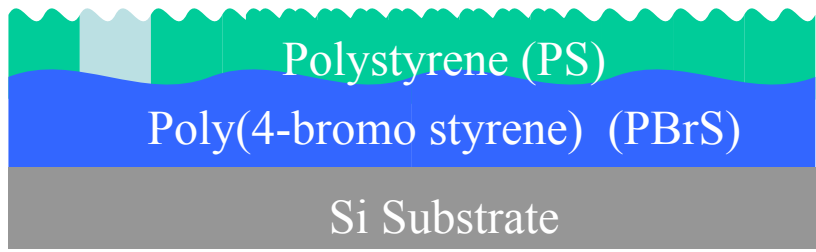

0
500
1000
1500
2000
2500
3000
Depth (A)
PS
PBrS
0
20
40
0.14
0.16
0.18
0.2
Incident Angle (deg.)

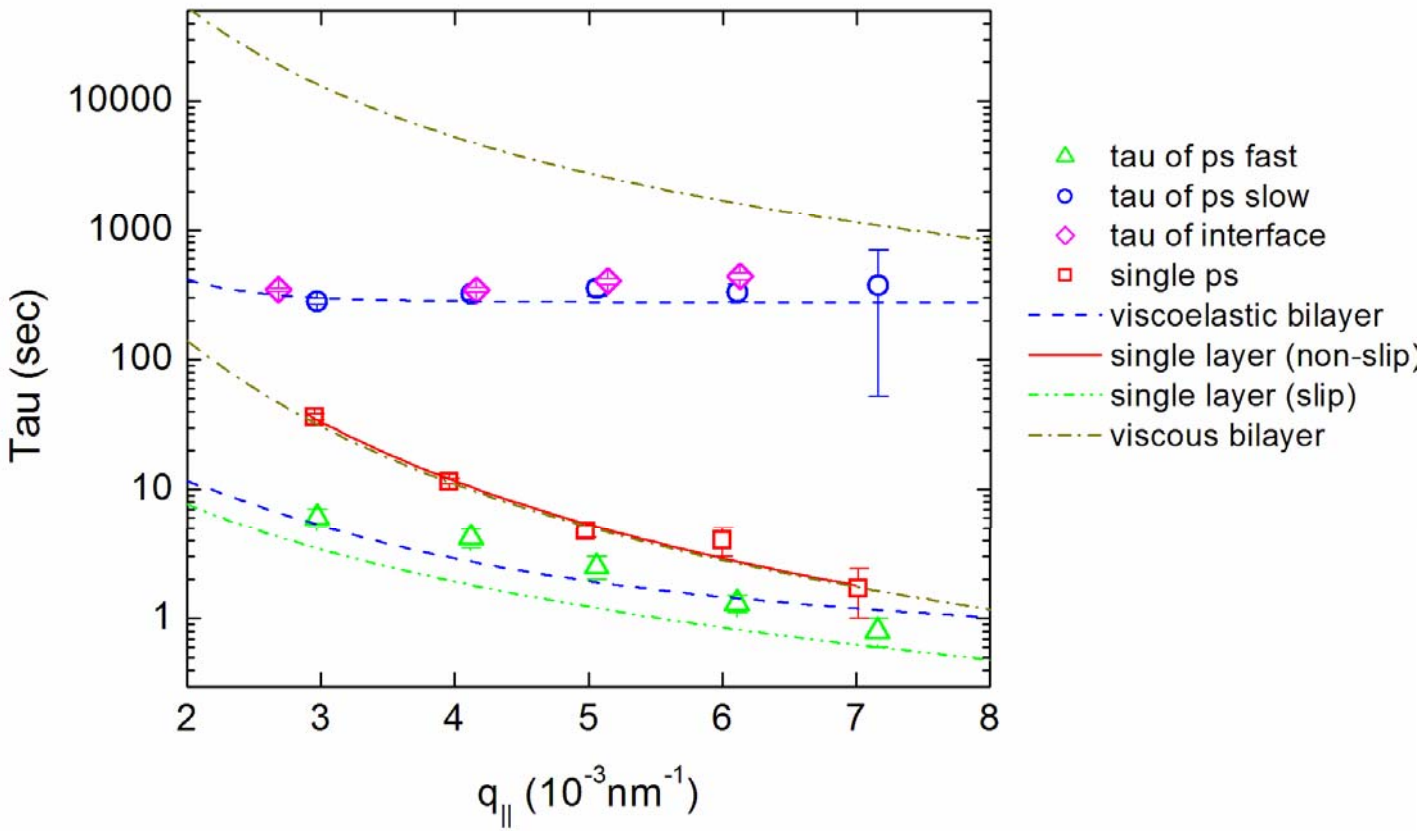

a
$g_2(q,\Delta t)$
Δt(sec)

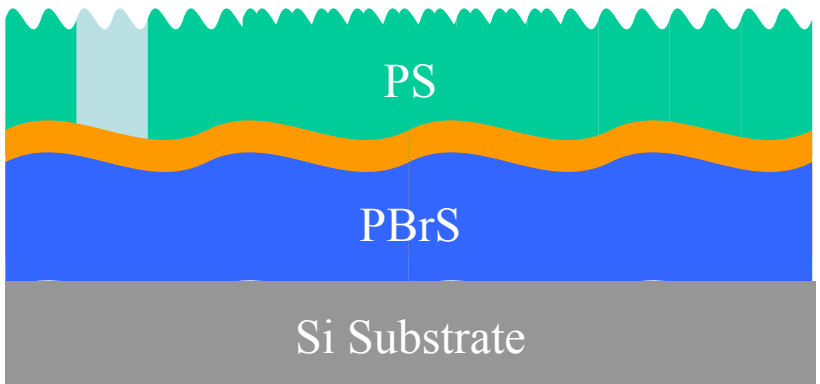

b
$g_2(q,\Delta t)$
Δt(sec)

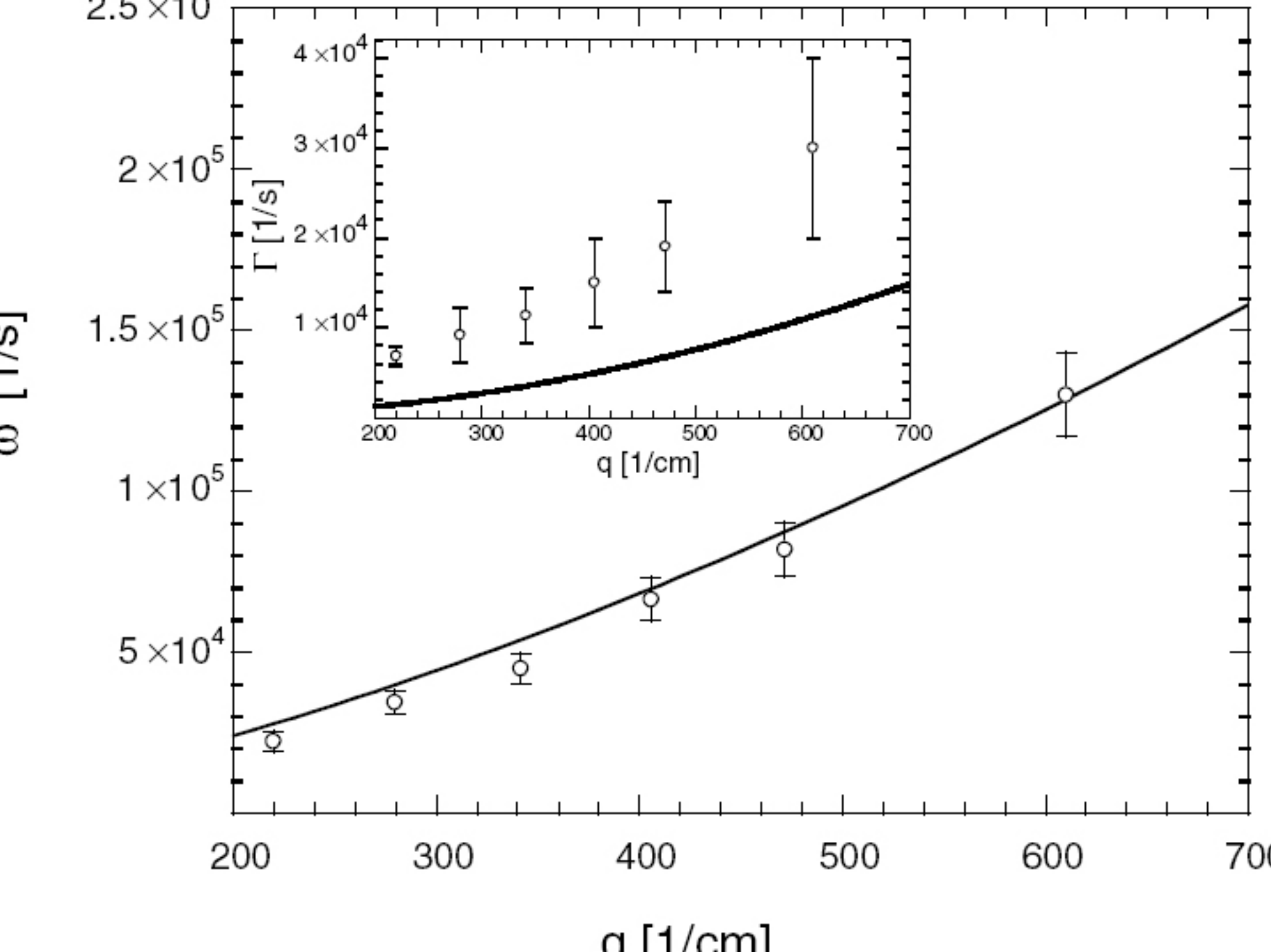

c
$g_2(q,\Delta t)$
Δt(sec)


d
$g_2(q,\Delta t)$
Δt(sec)


Polystyrene (PS)
Poly(4-bromo styrene) (PBrS)
Si Substrate


Tau (sec)
10000
1000
100
10
1
2
3
4
5
6
7
8
$q_{||}$ (10^{-3}nm^{-1})
tau of ps fast
tau of ps slow
tau of interface
single ps
viscoelastic bilayer
single layer (non-slip)
single layer (slip)
viscous bilayer


PS
PBrS
Si Substrate


2.5×10
2×10^5
1.5×10^5
1×10^5
5×10^4
ω [1/s]
200
300
400
500
600
700
q [1/cm]
4×10^4
3×10^4
2×10^4
1×10^4
Γ [1/s]
200
300
400
500
600
700
q [1/cm]

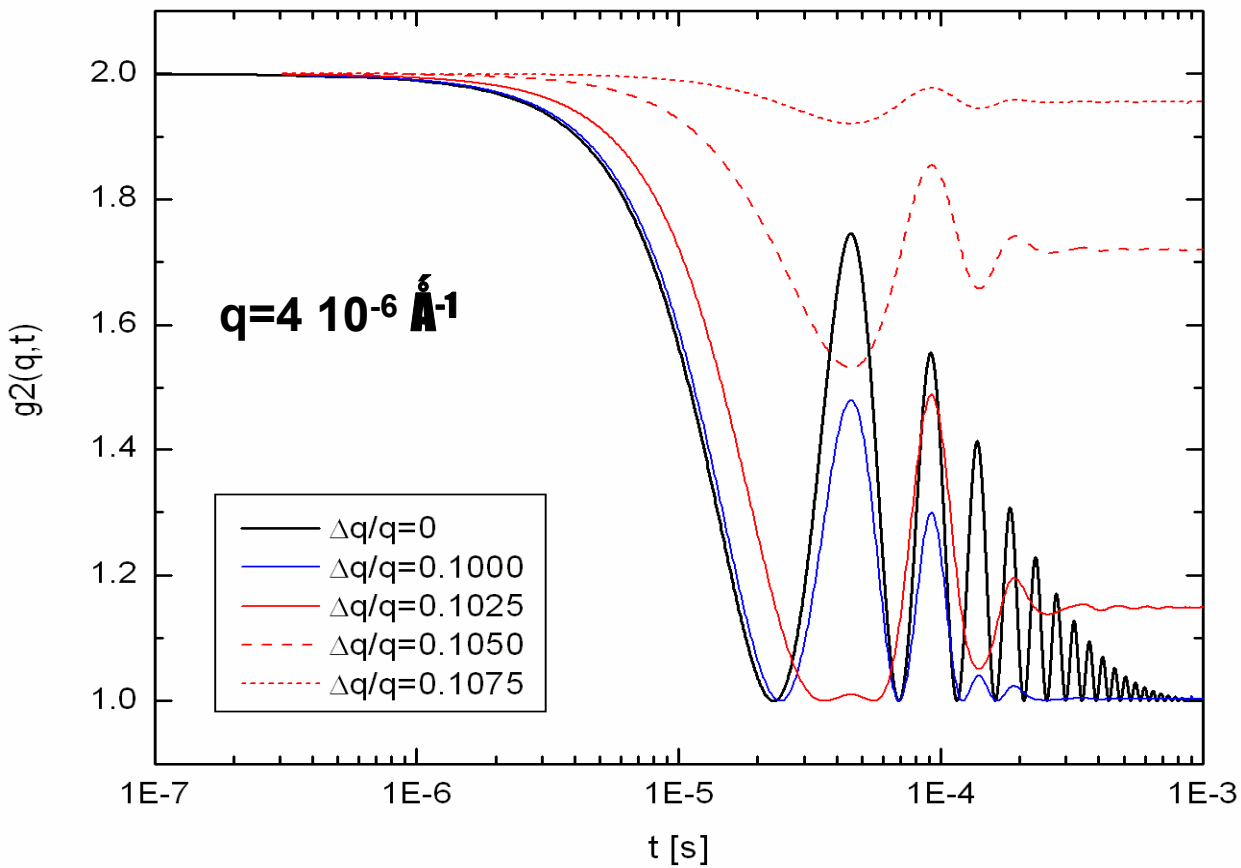
XPCS is currently a very intensity limited technique at 3rd generation sources

- So with ERL we could go to much larger q values (current limit~ 7*10-3 nm-1)

…needs better longitudinal resolution

- And shorter time scales (10-9 secs or smaller).

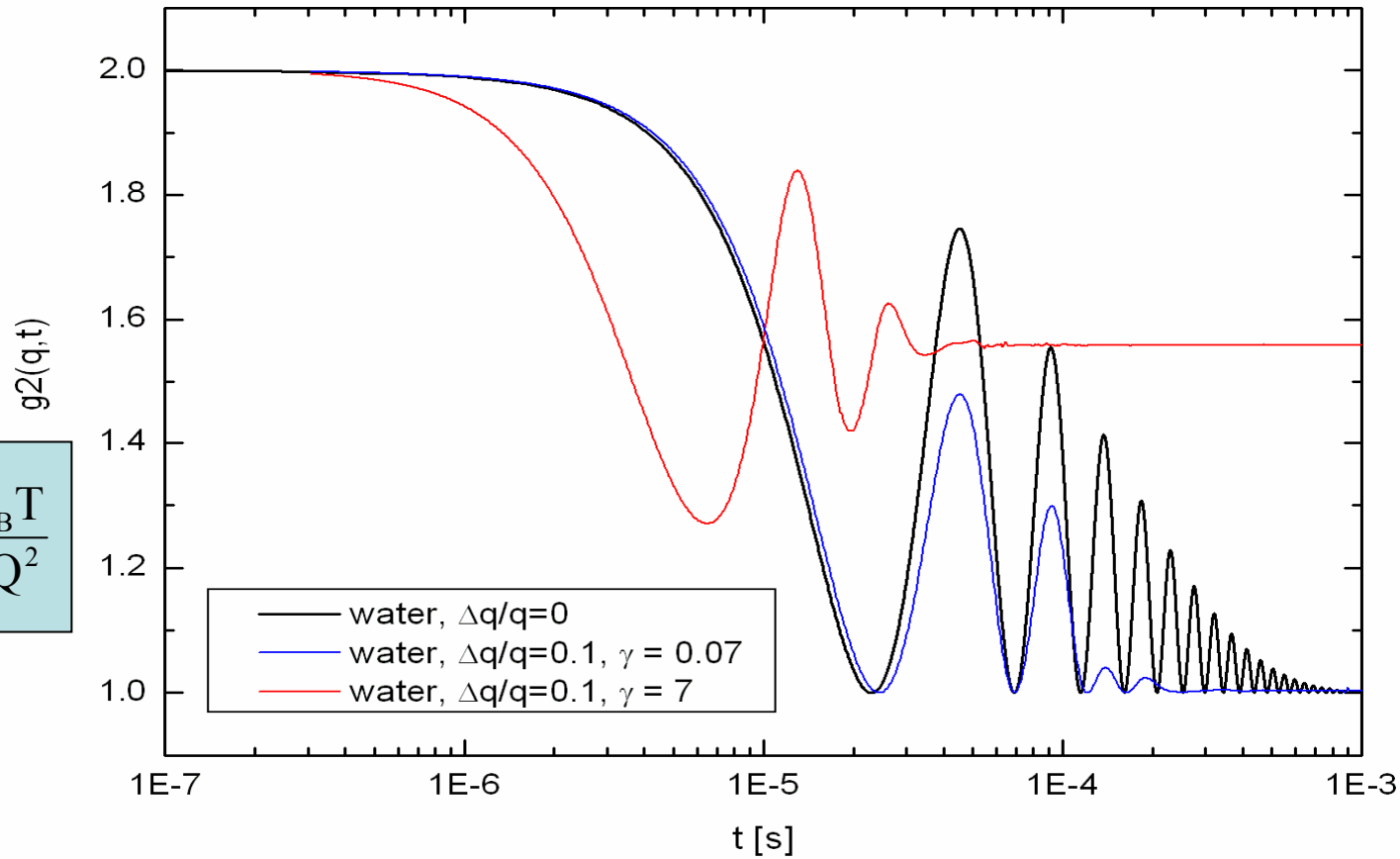
Transition Homodyne-Heterodyne (i)



$$G_1(r,\tau) = \left(\frac{k_0 r_l \rho}{2\pi L_1 L_2 q_z}\right) e^{-q_z^2\sigma^2}\left[F(Q_x,Q_y) + q_z^2 \iint d\tilde{Q}_x d\tilde{Q}_y C_{zz}(\tilde{Q}_x,\tilde{Q}_y) F(\tilde{Q}_x - Q_x, \tilde{Q}_y - Q_y)\right]$$

Transition Homodyne-Heterodyne (ii)

$$C_{zz}(Q,0) = \frac{k_B T}{\gamma Q^2}$$



$$G_1(r,\tau) = \left(\frac{k_0 r_l \rho}{2\pi L_1 L_2 q_z}\right) e^{-q_z^2\sigma^2}\left[F(Q_x,Q_y) + q_z^2 \iint d\tilde{Q}_x d\tilde{Q}_y C_{zz}(\tilde{Q}_x,\tilde{Q}_y,\tau) F(\tilde{Q}_x - Q_x, \tilde{Q}_y - Q_y)\right]$$

Other uses of Homodyne

- Dynamically: measuring velocity gradients
- Static systems or dynamic systems (if can get information quickly enough): holography

What about Nanobeams?

- Studying inhomogeneous systems
- Layering and Dynamics of liquids in confinement
- Reflectivity/Diffraction Studies of FET's
- X-ray Fluorescence Correlation Spectroscopy XFCS

(Wang, Sood et al., PRL 80, 1110 (1997))

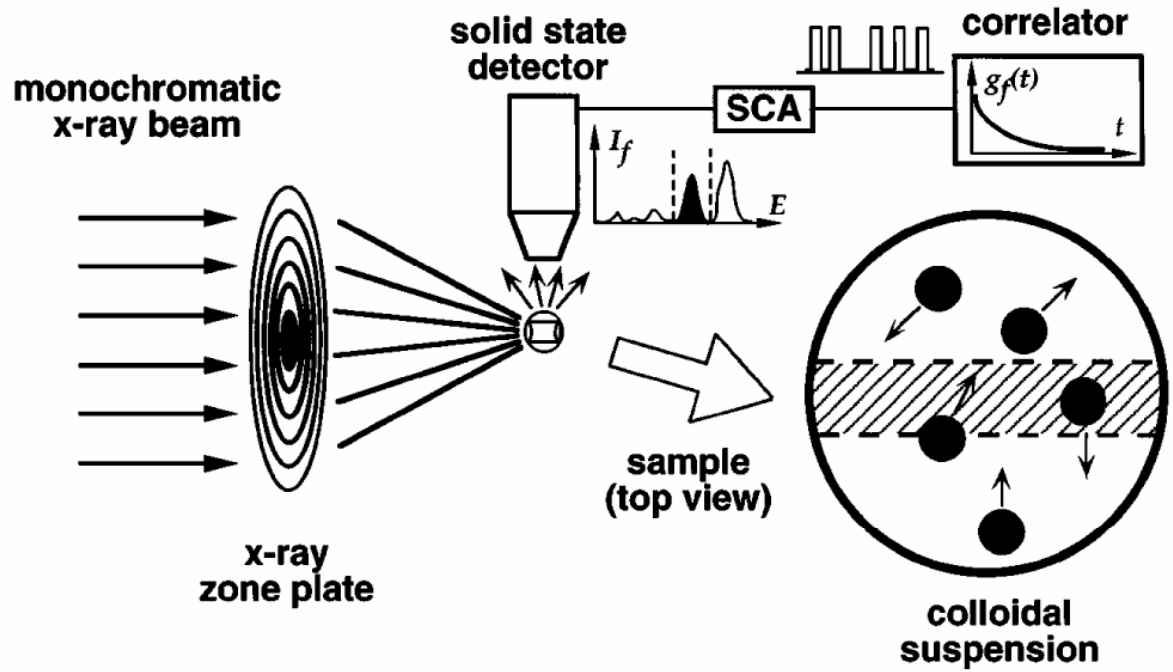


FIG. 1. Schematic of the experimental setup. The microfocused beam was obtained by first monochromating the beam from the undulator using a Si(111) double-crystal monochromator and then transmitting through a transmission Fresnel zone plate. A magnified view of sample is also sketched in the figure, where the shaded region outlines the x-ray illuminated area in the sample.

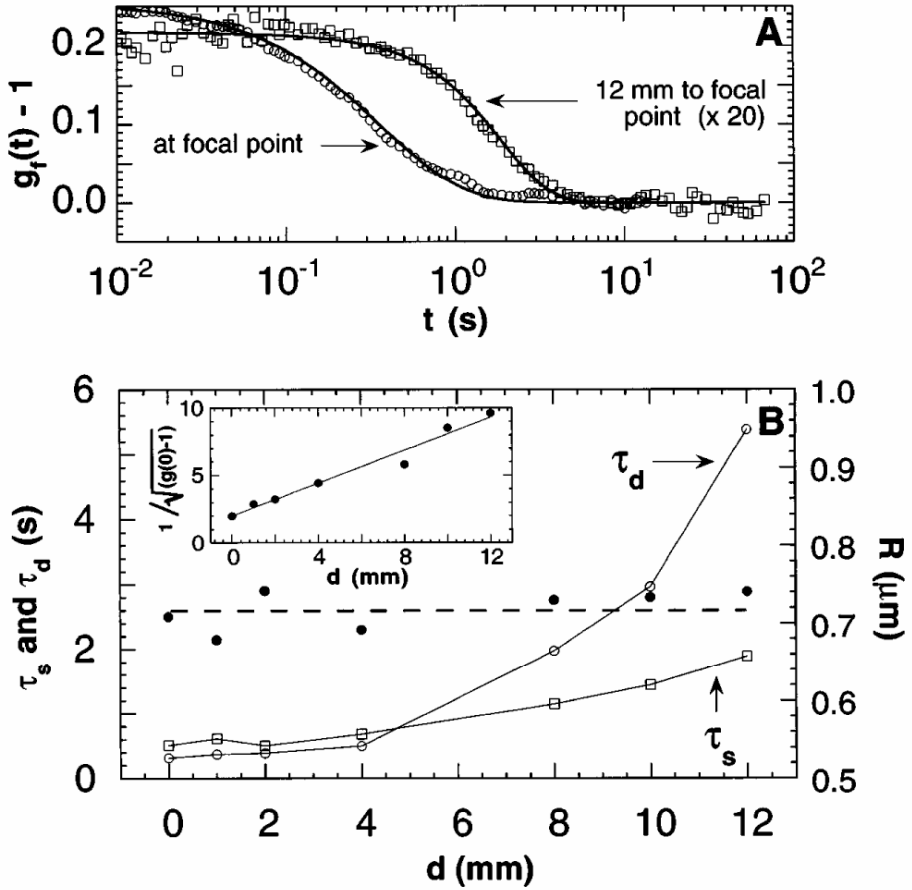
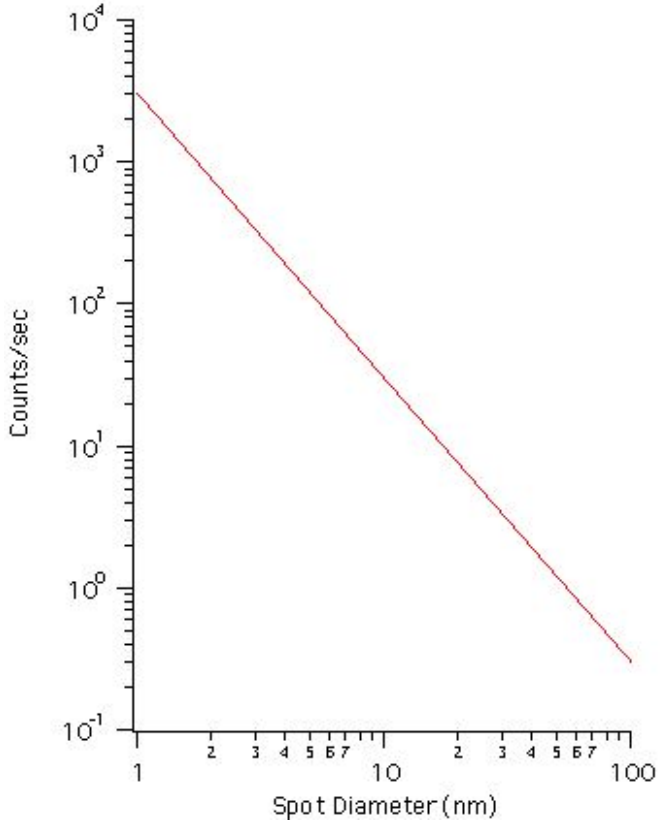


FIG. 3. Experimental results for sample 4 measured at different positions, on the zone plate axis, at a distance d to the focal point. (A) The experimental (circles and rectangles) and theoretical (line) fluorescence autocorrelation functions at and 12 mm away from the focal point. (B) The fitting parameters τ_d (circles), τ_s (rectangles), and derived values of R (dots) at each position are shown. The solid lines connecting data points are for guiding the eye. The dashed line represents the mean value of R. The inset for (B) shows the relationship between $[g_f(0) - 1]^{-1/2}$ and d (dots) and the linear function fit (solid line).

Detectability Limits for a Nanoprobe at the APS

Courtesy **Gene Ice**.



Fluorescent signal from a single atom.

$$Signal = \frac{K_\alpha I E \Omega}{4\pi A}$$

~ 3000 cps for a single atom, λ = 1 Å

- K_α = fluorescence cross-section
- I = 2×10^6 ν/s/nm^2/mrad^2/0.1%bw
- E = emittance product
- A = probe cross section (nm^2)
- Ω = detector solid angle ~ $4\pi/6$

Can we do anything more with Speckle?

$$I(\mathbf{q},\mathbf{t}) = \text{Constant} \times \iint d\mathbf{R} \exp[i\,\mathbf{q}.R)] \langle \rho(\mathbf{r},\mathbf{t})\rho(\mathbf{r}+\mathbf{R},\mathbf{t}) \rangle$$

$$\iint I(\mathbf{q},0)I(\mathbf{q}+\mathbf{Q},t)\, d\mathbf{q} \exp[-i\mathbf{Q}.\mathbf{R}]\, d\mathbf{R} = \langle \rho(\mathbf{r},\mathbf{0})\rho(\mathbf{r}+\mathbf{R},\mathbf{0}) \rangle \langle \rho(\mathbf{r},\mathbf{t})\rho(\mathbf{r}+\mathbf{R},\mathbf{t}) \rangle$$

Variance of speckle intensity fluctuations as fn. of q:

$V = \langle I^2(\mathbf{q}) \rangle / \langle I(\mathbf{q}) \rangle^2 - \mathbf{1}$

----> medium range order in amorphous materials
M.Treacy and J.M. Gibson, Acta Cryst. A52, 212 (1996)

Speckle from Quantum Coherent Systems

Could we observe quantum zero point motion using XPCS?

He atom motions in the Bose-Einstein
Condensed State?

Could we observe electron motion in metals and superconductors with attosecond XPCS?

Answer: NO!!

Hard x-ray phase contrast image: 2005

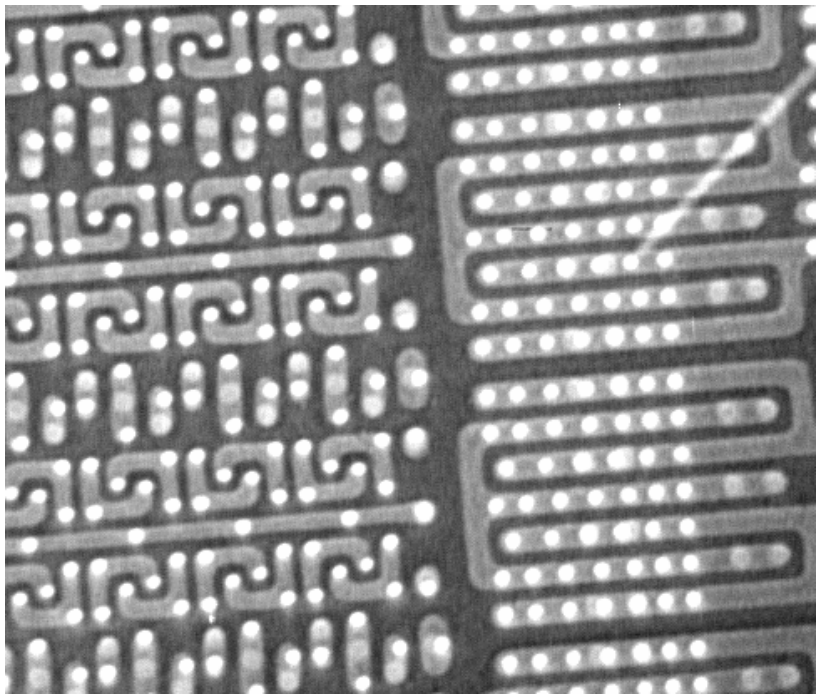
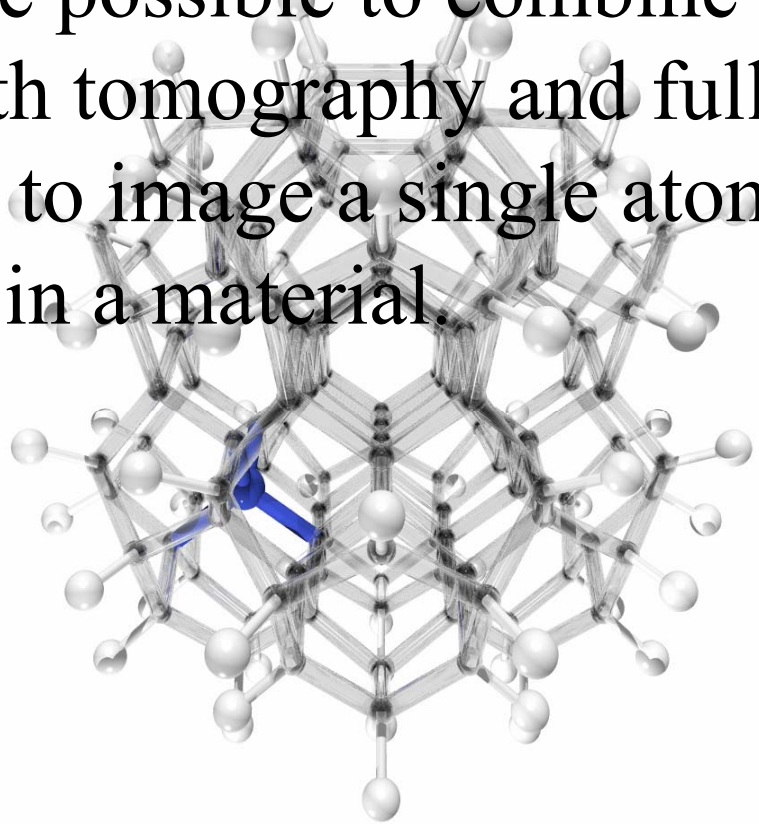


Image of buried wire & vias in circuits
with 60 nm resolution.
Courtesy W. Yun, Xradia, Inc.

Imaging a Single Embedded Atom

- It should be possible to combine high flux density with tomography and full-field techniques to image a single atom or defect embedded in a material.

- structure (strain)
- valence states
- spin ?



Diamond nanocrystal doped with a single atom.
Courtesy Amanda Barnard

Nanopatterning of Nanowires

- X-ray induced persistent photocurrent in AlGaAs:Si - DX centers are efficiently excited by hard x-rays.
- Possibility for direct write of nanowires with lateral

Current persists >17 hrs after x-rays are turned off at 185 K.

Soh, et al, JAP, 90, 6172 (2001).

QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.

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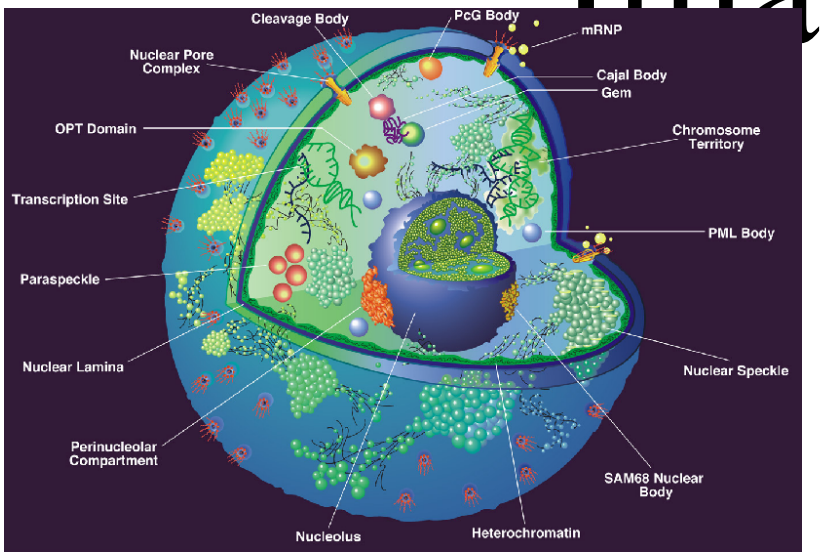
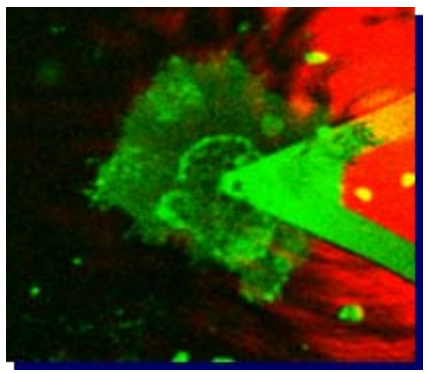
Nano-Bio-Medical Imaging



Some important length scales:

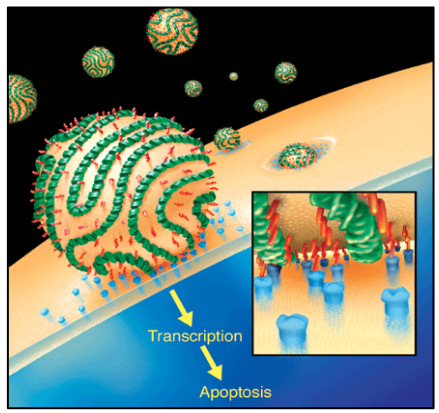
- Mitochondria - sub-micron
- Membrane thickness - sub-10 nm

Targeted drug delivery

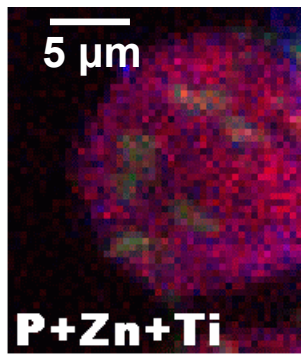


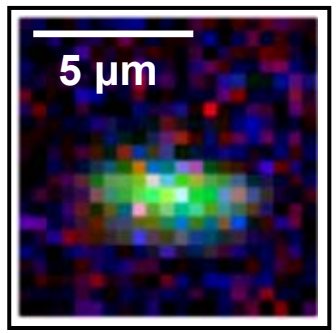
AFM guided drug delivery in osteoblast

In-vivo cell biology



TiO_2-DNA nanoparticles localized at mitochondria. Woloschak, et al





T. Paunesku et al, *Nature Materials 2, 343-346*