Coherent Soft X-ray Scattering for Studying Nanoscale Materials

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Introduction and motivations

Reminders about x-ray coherence

X-ray resonant (magnetic) scattering

Speckle phenomena

Nanoscale complexity: examples and applications

Collaborators

University of Washington
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- Karine Chesnel

IBM/Hitachi
- Eric Fullerton
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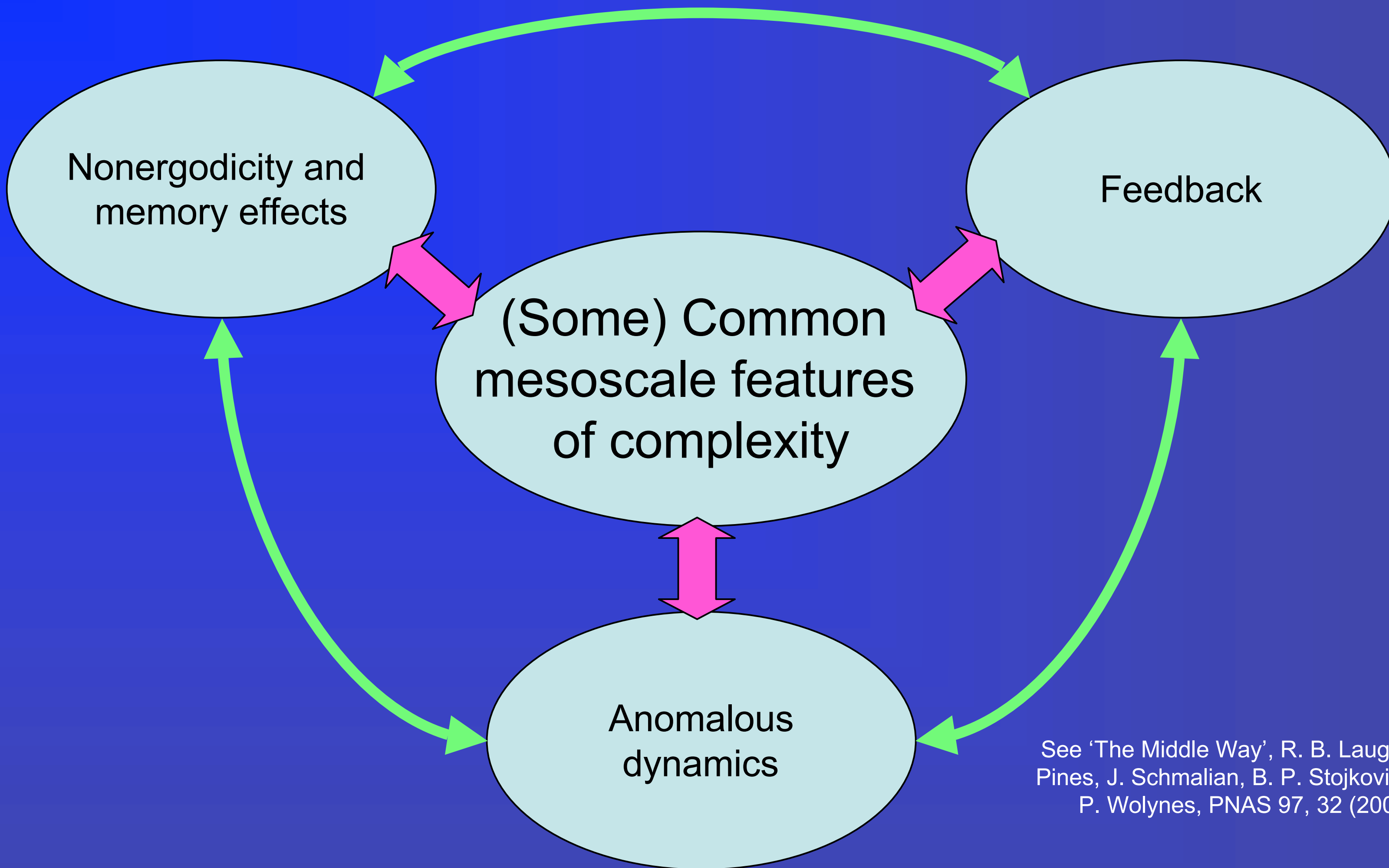
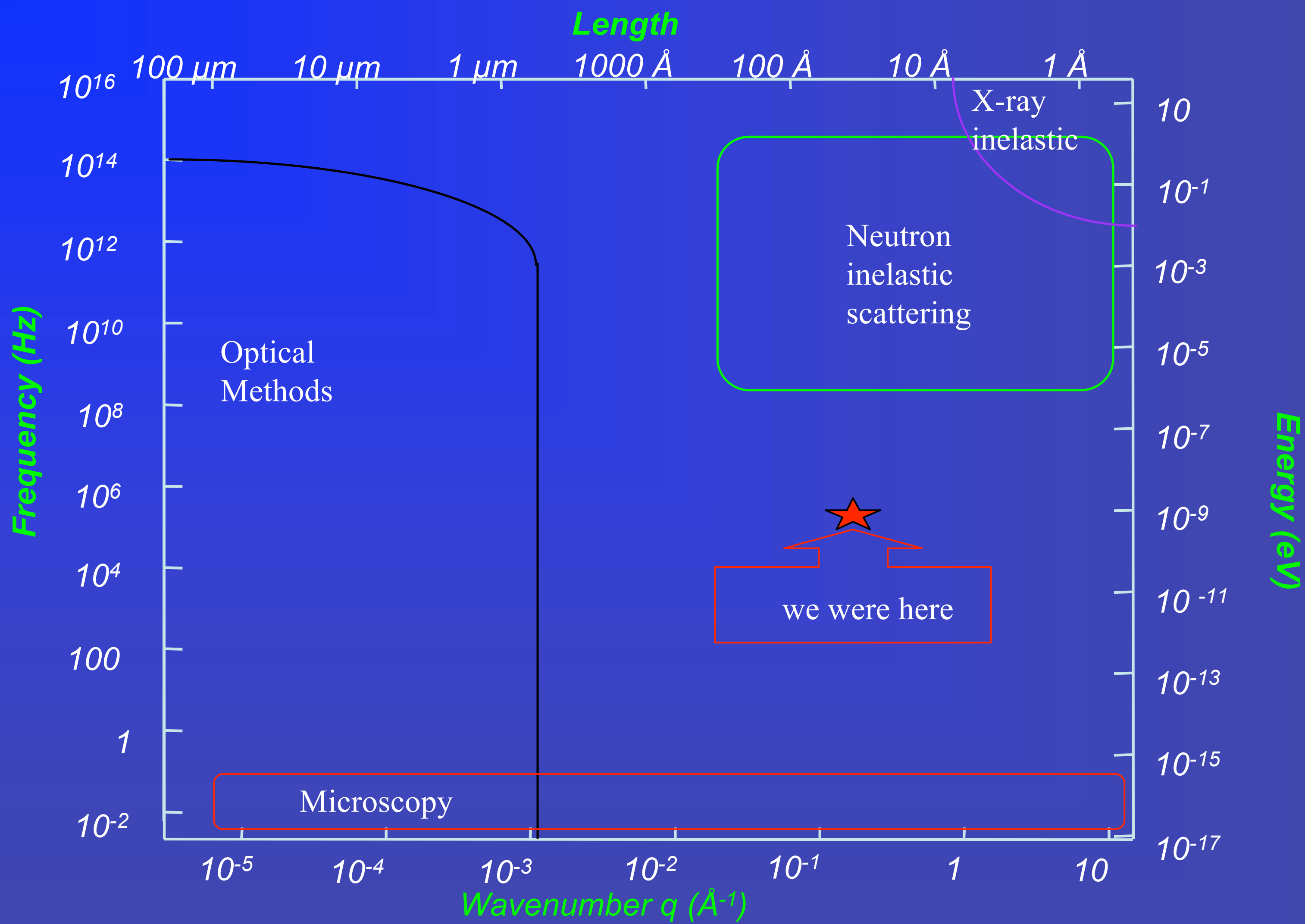
What Drives Material Complexity?



See ‘The Middle Way’, R. B. Laughlin, D. Pines, J. Schmalian, B. P. Stojkovic´i, and P. Wolynes, PNAS 97, 32 (2000).

These issues are often statistical in nature and can be usefully probed in terms of statistical averages, such as space-time correlation functions: $S(q, t, T, H, E, j, \ldots)$

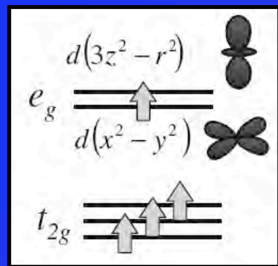
Probing Hierarchies in Space and Time

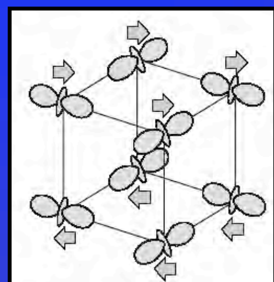


★ "Soft X-ray Dynamic Light Scattering from Smectic A Films", A.C. Price, L.B. Sorensen, S.D. Kevan, J.J. Toner, A. Poniewrski, and R. Holyst, Phys. Rev. Lett., **82**, 755 (1999).

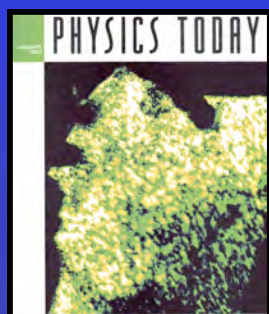
Probing Hierarchies in Space and Time

example: CMR manganites

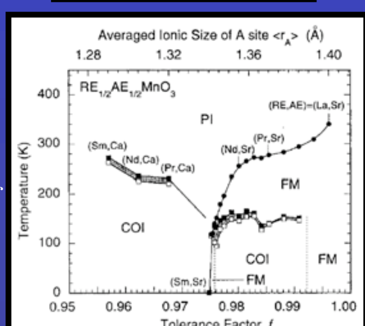




Ishihara and Maekawa, Rep. Prog. Phys. **65** (2002) 561–598



Mathur and Littlewood, Physics Today, Jan. 2003, p. 25.



Kuwahara and Tokura, in *CNR, Charge Ordering and Related Properties of Manganites*, p. 217.

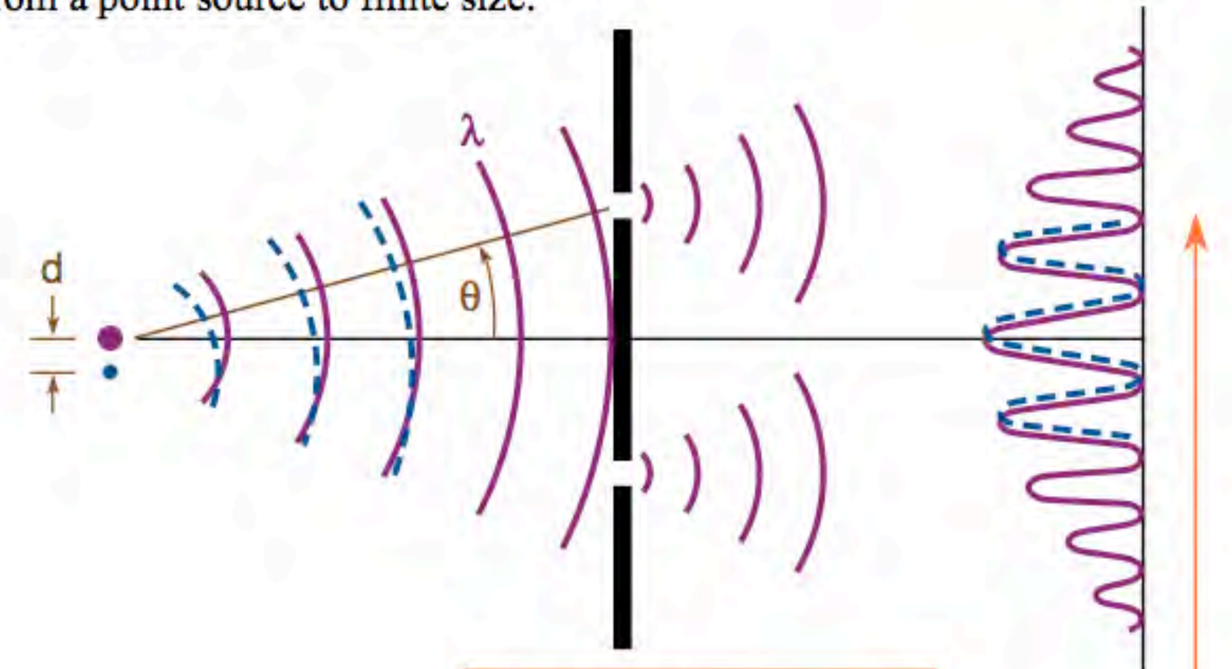
Spatial scale	Energy/time scale	Phenomenology
0.1 nm	~1 eV, 1 fsec ~1 fsec	crystal field, intra-atomic exchange and multiplets
1-2 nm	1-100 meV 100 fs – 1 ps	t-J-ology; charge, spin, orbital order; polarons, magnons, orbitons, ….
10-1000nm	< 1 neV? >1 μs?	Mesophase separation; Percolation; domain switching
Macroscopic	static/low frequency driven	CMR, etc.

Surprise! Soft x-rays provide the tools to probe this entire hierarchy!

Some Reminders About Coherence: lecture 2, slide 3

Young's Double Slit Experiment: Spatial Coherence and the Persistence of Fringes

Persistence of fringes as the source grows from a point source to finite size.



$$\boxed{d \cdot 2\theta|_{FWHM} \simeq \lambda/2}$$

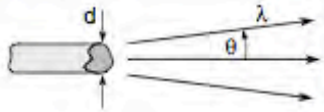
$$\boxed{\lambda_{coh} = \lambda^2/2\Delta\lambda = \frac{1}{2} N_{coh}\lambda}$$

Professor David Attwood
Univ. California, Berkeley

Some Reminders About Coherence: lecture 2, slide 2

Chapter 8

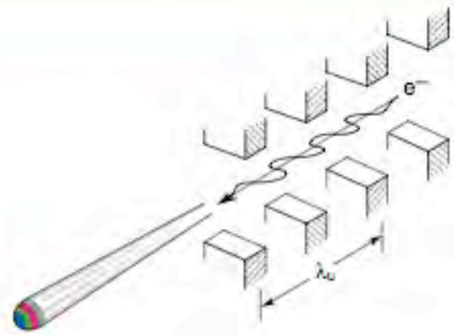
COHERENCE AT SHORT WAVELENGTHS

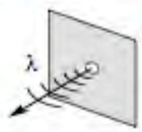


$$l_{coh} = \lambda^2/2\Delta\lambda \ \{\text{temporal (longitudinal) coherence}\} \qquad (8.3)$$

$$d \cdot \theta = \lambda/2\pi \ \{\text{spatial (transverse) coherence}\} \qquad (8.5)$$

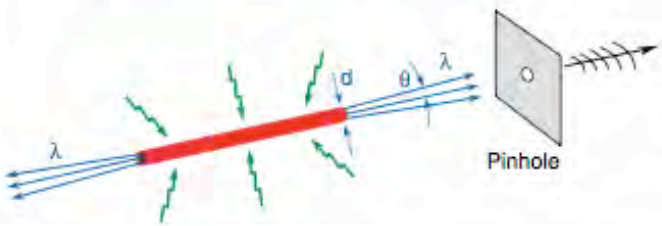
$$\text{or } d \cdot 2\theta\big|_{FWHM} = 0.44\,\lambda \qquad (8.5^*)$$





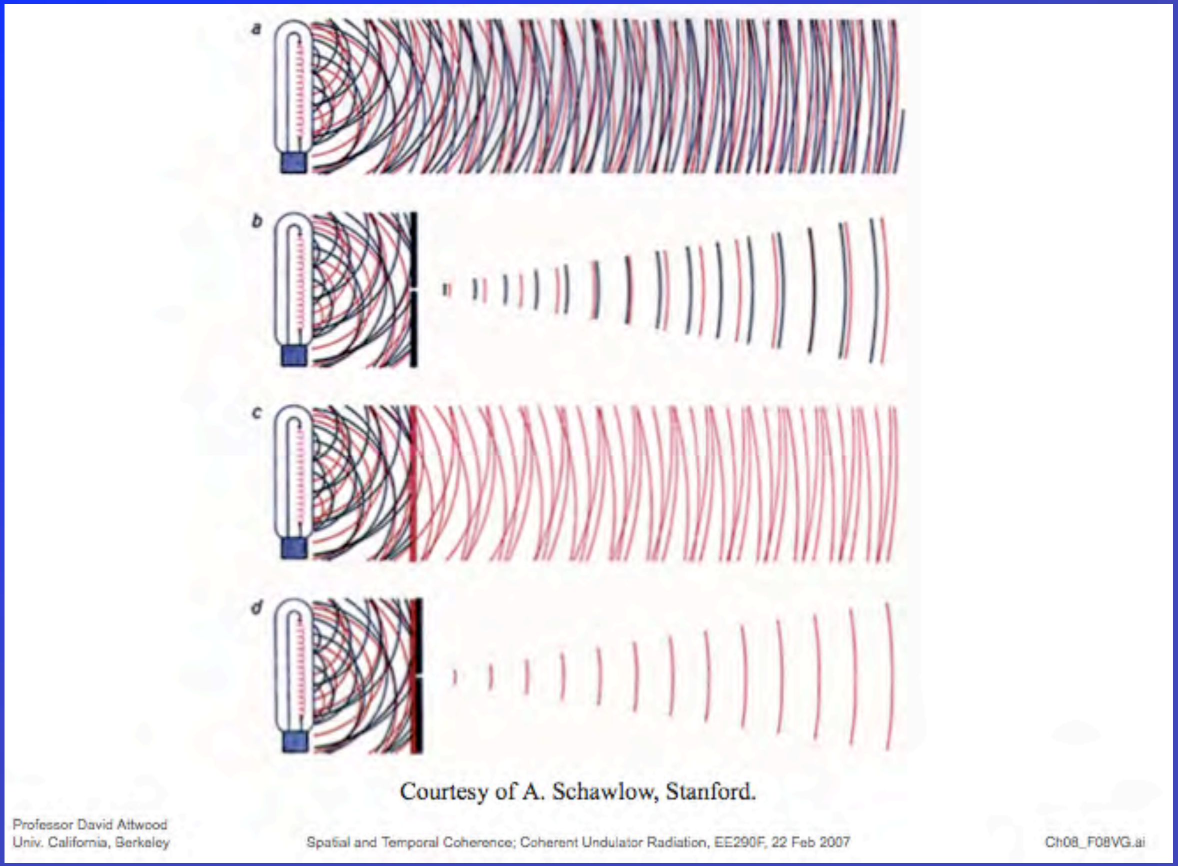
$$\bar{P}_{coh,N} = \frac{(\lambda/2\pi)^2}{(d_x\theta_x)(d_y\theta_y)}\,\bar{P}_{cen} \qquad (8.6)$$

$$\bar{P}_{coh,\lambda/\Delta\lambda} = \frac{e\lambda_u I\eta(\Delta\lambda/\lambda)N^2}{8\pi\epsilon_0 d_x d_y}\cdot\left[1-\frac{\hbar\omega}{\hbar\omega_0}\right]f(K) \qquad (8.9)$$



$$P_{coh} = \frac{(\lambda/2\pi)^2}{(d_x\theta_x)(d_y\theta_y)}\,P_{laser} \qquad (8.11)$$

Some Reminders About Coherence: lecture 2, slide 4



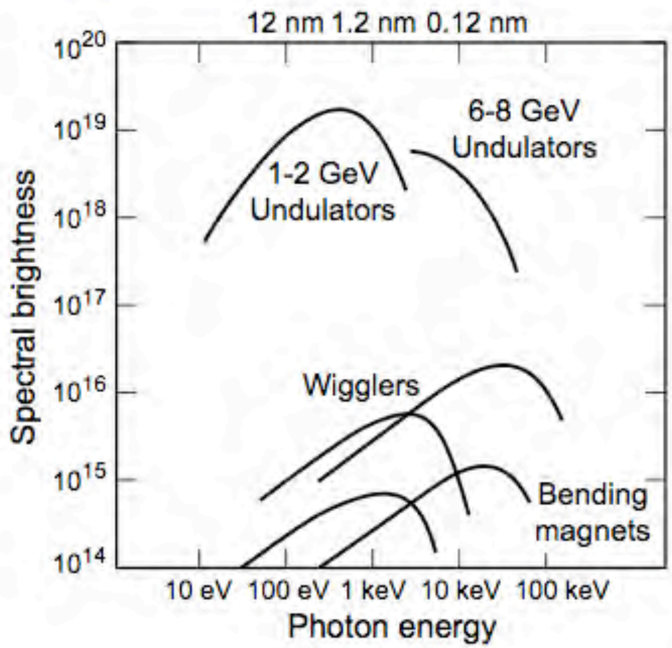
Extracting the coherent fraction from a partially coherent source:

$$F_{coh} = B \times (\lambda/2)^2 \times (\delta E/E) \times \text{beamline efficiency}$$

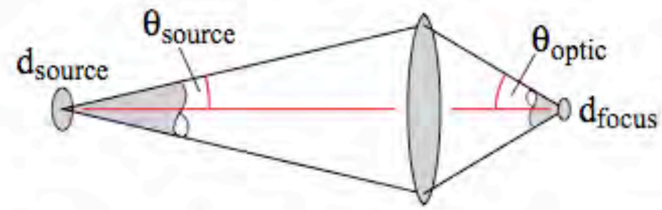
spectral brightness   transverse acceptance   longitudinal acceptance

Coherent Scattering is a 'Brightness Experiment'

Spectral Brightness is Useful for Experiments that Involve Spatially Resolved Studies



- Brightness is conserved (in lossless optical systems)



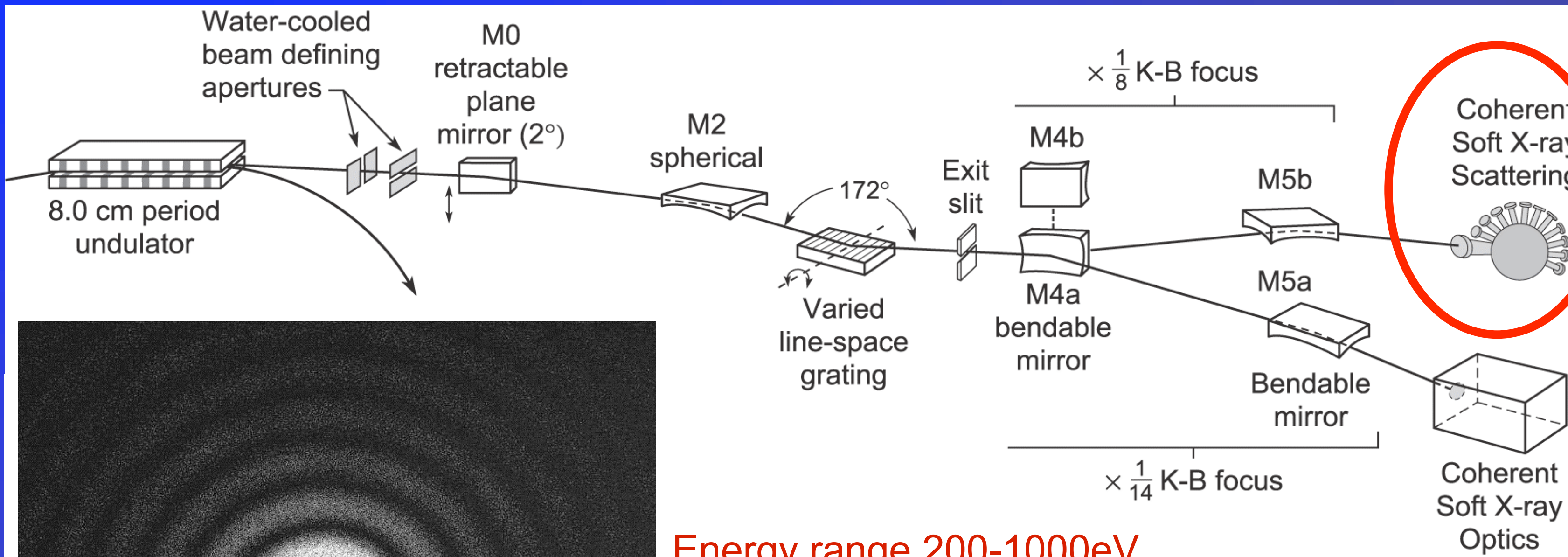
$$d_{source} \cdot \theta_{source} = d_{focus} \cdot \theta_{optic}$$

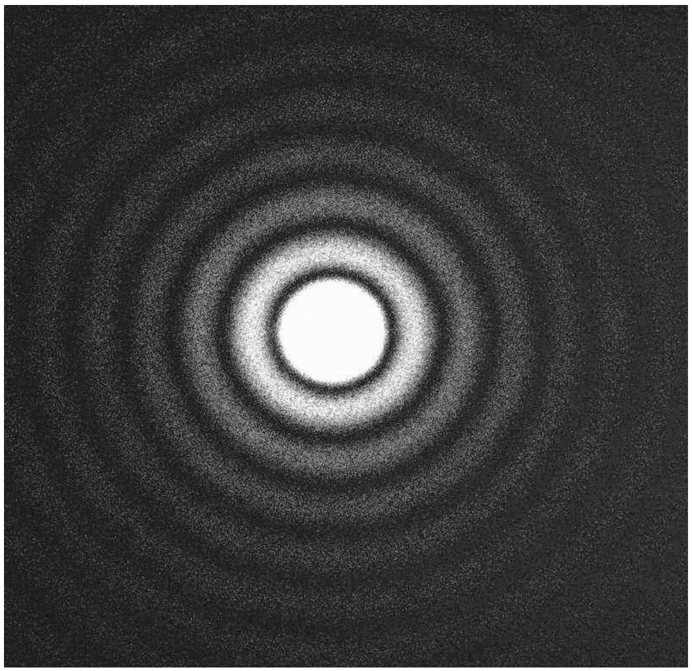
Smaller after focus

Large in a focusing optic

- Starting with many photons in a small source area and solid angle, permits high photon flux in an even smaller area

ALS Coherent Soft X-ray Beamline (the current generation)





Energy range 200-1000eV

Moderate dispersion

8x demagnification of the source

Quality optics to preserve coherence

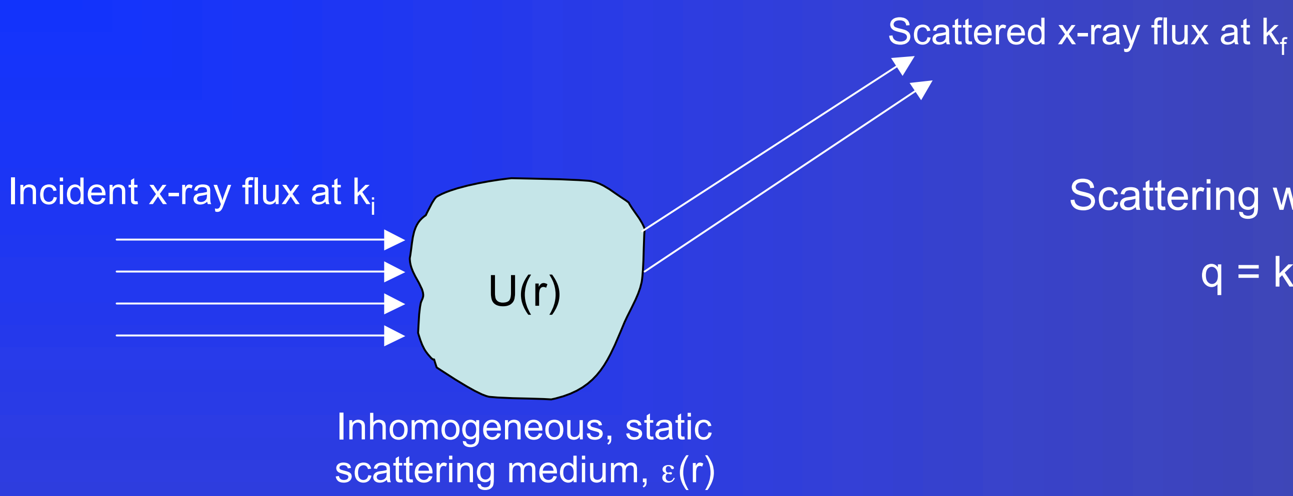
Coherent flux at 500eV: ~ 5×10^{10} ph/sec/0.1%BW

λ = 2.48 nm (500 eV)
d = 2.5 μm

Rosfjord et al. (2004)

Coh_Optics_BLwGraf.4.03.ai

X-ray Scattering in One Slide



Scattering wave vector

$q = k_f - k_i$

In the Born approximation, the scattering rate is determined by Fermi's Golden Rule

$$W_{if} = \frac{2\pi}{\hbar} \left| \left\langle k_i \middle| U(r) \middle| k_f \right\rangle \right|^2 \rho\left(E_f\right) \propto \frac{d\sigma}{d\Omega dE}$$

The measured scattering rate is related to a correlation function of the dielectric density

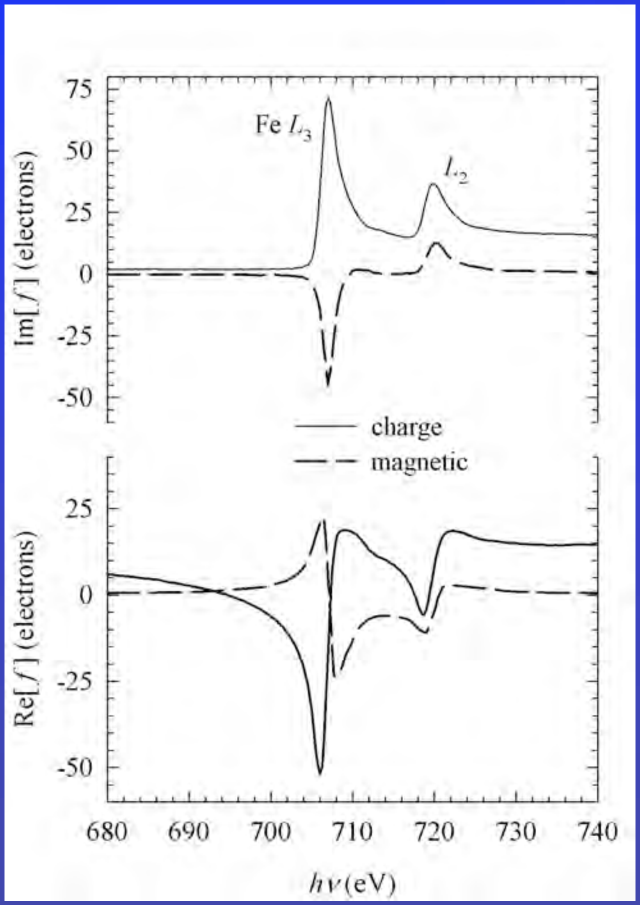
$$S(q) \propto \int_V d\vec{r} e^{i\vec{q}\cdot\vec{r}} \left\langle \varepsilon(\vec{0}) \varepsilon(\vec{r}) \right\rangle$$

Fourier decompose the medium into microscopic gratings of wave vector q. According to the Laue condition, these gratings Bragg scatter at a scattering wave vector q. The scattering rate at q depends on the density and amplitude of these microscopic gratings. An incoherent scattering experiment, therefore, provides a statistical average of the microscopic structure as a function of q through the structure factor S(q).

Resonant X-ray Scattering in One Slide

$$S(q) \propto \int_V d\vec{r} e^{i\vec{q}\cdot\vec{r}} \left\langle \varepsilon(\vec{0}) \varepsilon(\vec{r}) \right\rangle$$

X-rays scatter off inhomogeneities in the dielectric function of a material.



Iron L-edge ($2p \rightarrow 3d$) Magneto-optical Constants
Kortright and Kim, PRB 62 12216 (2000).

Materials are very polarizable near x-ray absorption edges:

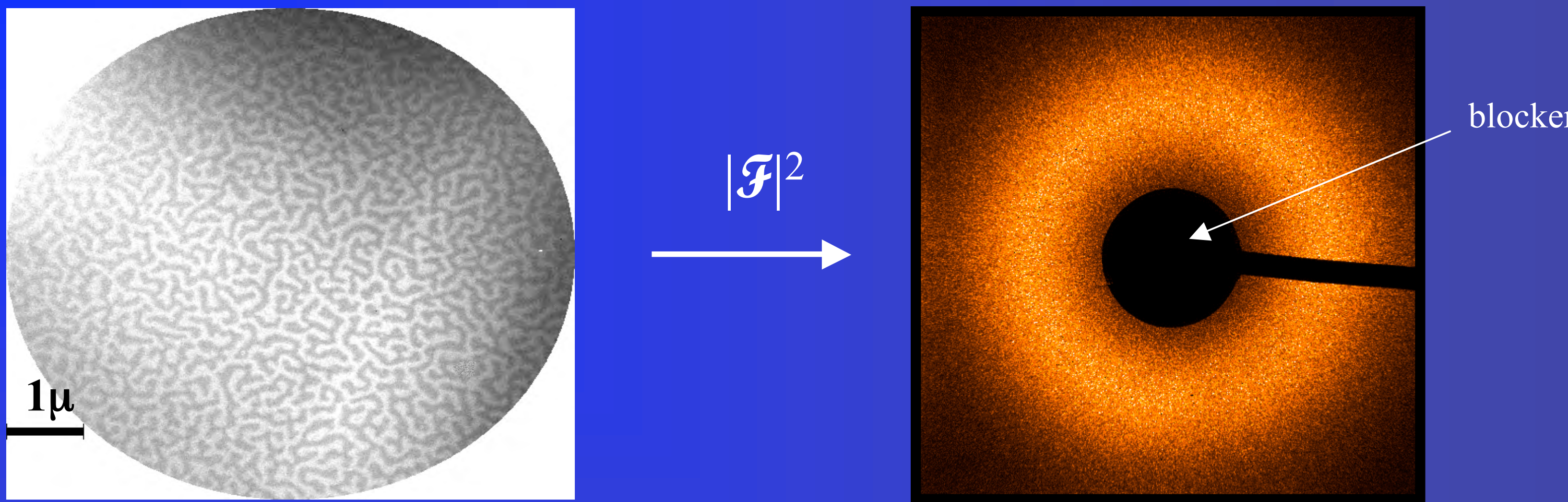
$$\frac{d\sigma}{d\Omega} \sim \left| f_o + f' + if'' \right|^2$$

This enhanced polarizability can be used to

- increase the scattering rate
- achieve elemental and structural sensitivity
- achieve magnetic scattering contrast

in precisely the same was as in many other techniques discussed in this class.

Diffuse Soft X-ray Scattering from a Pt:Co Multilayer

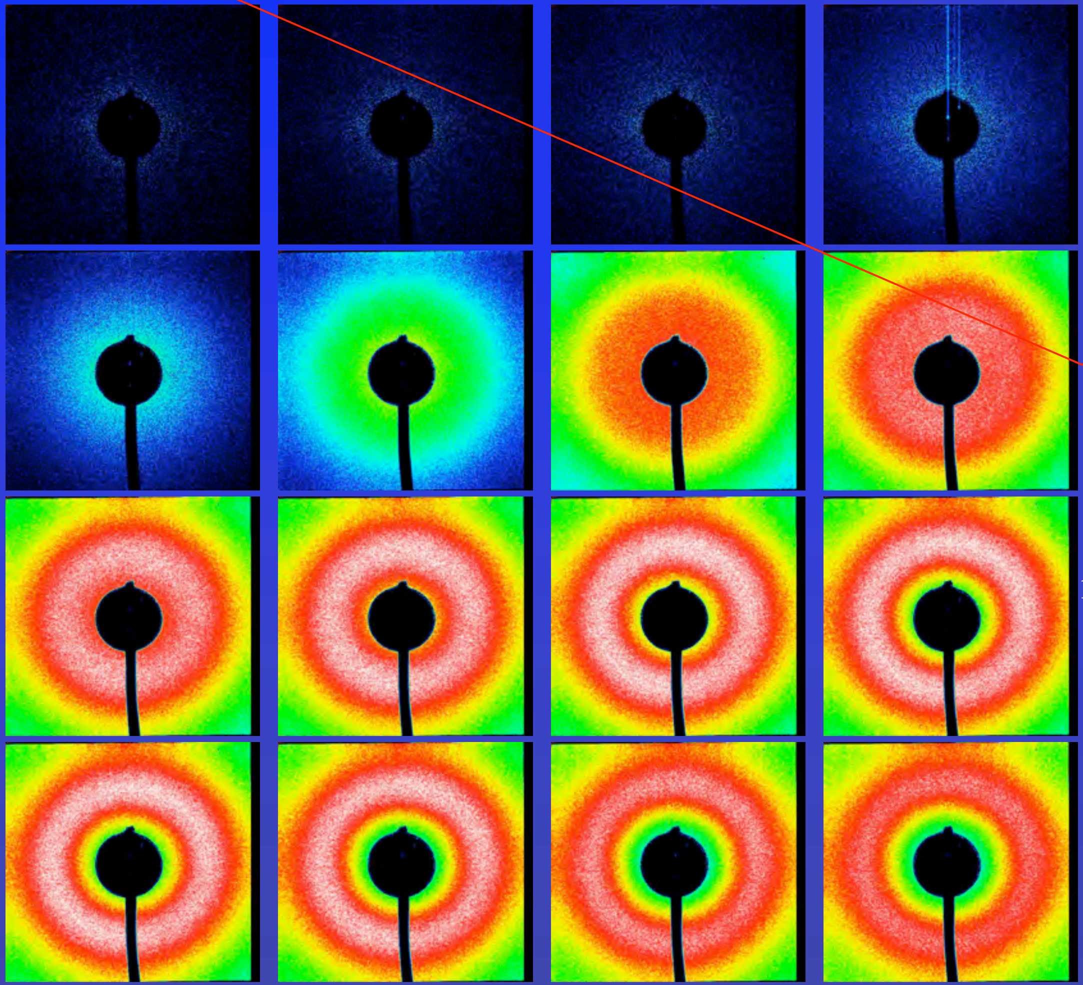


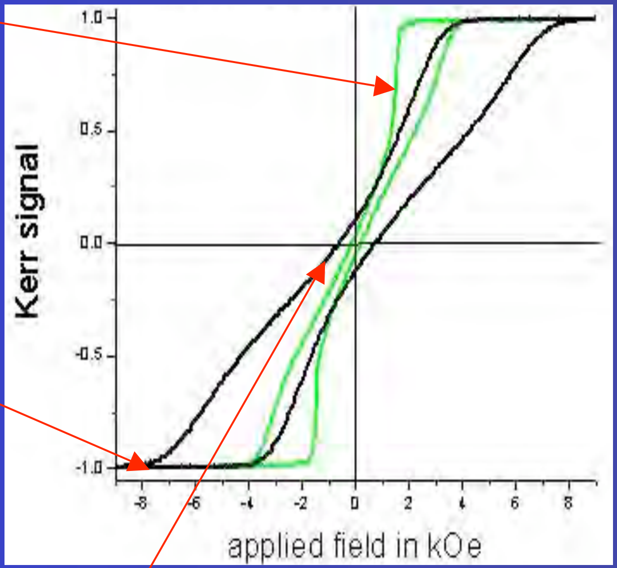
- Scattering pattern = diffraction pattern of the average magnetic domain structure;
- Collected in transmission through the film and its supporting silicon nitride membrane;
- Domain size inversely related to angular width of the ‘doughnut’;
- Contrast provided by huge x-ray magneto-optic effects near the cobalt L-edge.

All Around the Magnetization Loop

saturation

nucleation

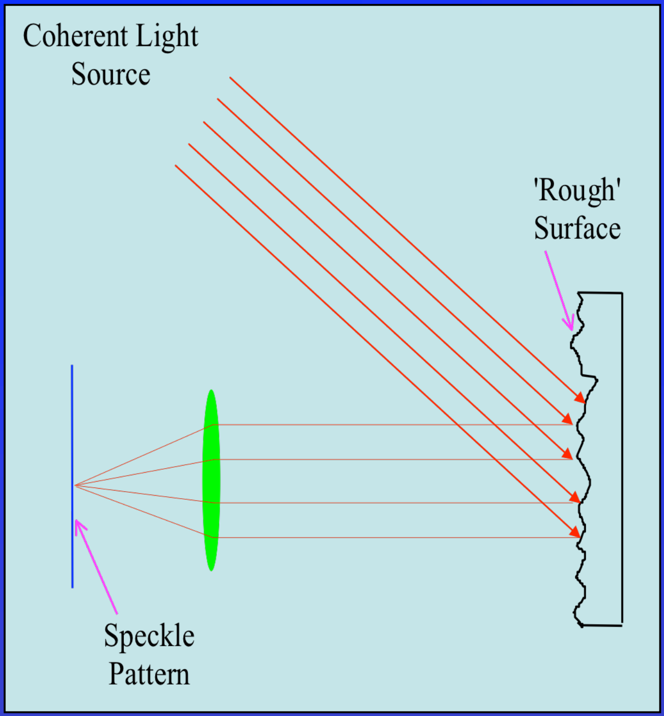




remanence

. . . . and on and on (Gb after Gb).

Speckle-Diffraction Patterns

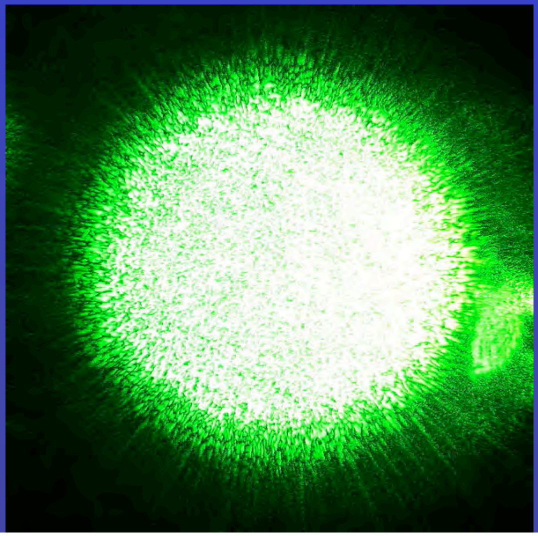


- Since laser light is coherent, amplitudes from different points on the surface add to form a diffraction pattern of the entire illuminated area.

- Since the surface is rough on the sale of λ, the phases of the reflected amplitudes fill the interval $[0,2\pi]$ completely and randomly.

- This is not quite holography - there is no reference beam and we do not encode the phase of the scattered beam.

- Note the increasing size of a speckle with distance and the weird parallax effect.



Speckle pattern of a ground glass screen illuminated with a green laser pointer (from Wikipedia, of course).

Single-Point Speckle Statistics

A speckle pattern arises when a large number of wavelets with random phase is added together. Assuming a scalar electric field

$$E(\vec{r}) = \sum_{k=1}^{N} \left|E_k(\vec{r})\right| e^{i\varphi_k(\vec{r})} \qquad I(\vec{r}) \propto \left|E(\vec{r})\right|^2$$

In phasor language, this corresponds to the summation of random phasors in 2D, which is the same as the 2D random walk. The statistics of the resulting patterns are well-known - and actually do not offer much direct information about the scattering object. For example, for single-point statistics:

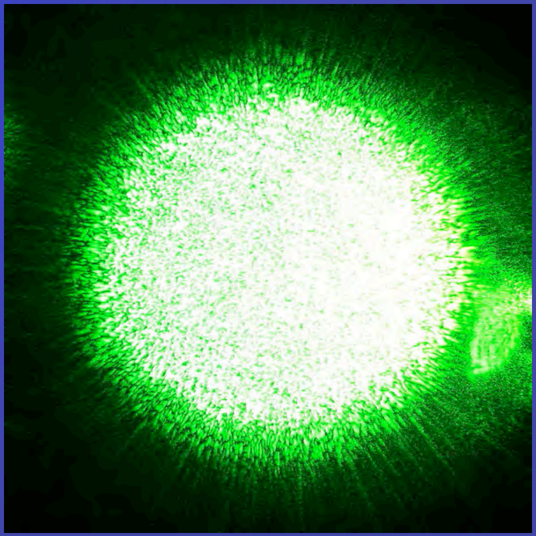
Intensity histogram:

$$P(I) = \frac{1}{\sigma_I} e^{-\frac{I}{\sigma_I}} \qquad I > 0$$

Intensity standard deviation:

$$\sigma_I \equiv \sqrt{\left\langle \left(I - \langle I \rangle\right)^2 \right\rangle} = \langle I \rangle$$

. . . In the ideal case, the fringes have unit visibility.



Two-Point Speckle Statistics

The graininess in a speckle pattern is not random noise - it is correlated. What is the 'size' of a speckle? This is defined by a correlation function, which compares a function to a shifted version of itself:

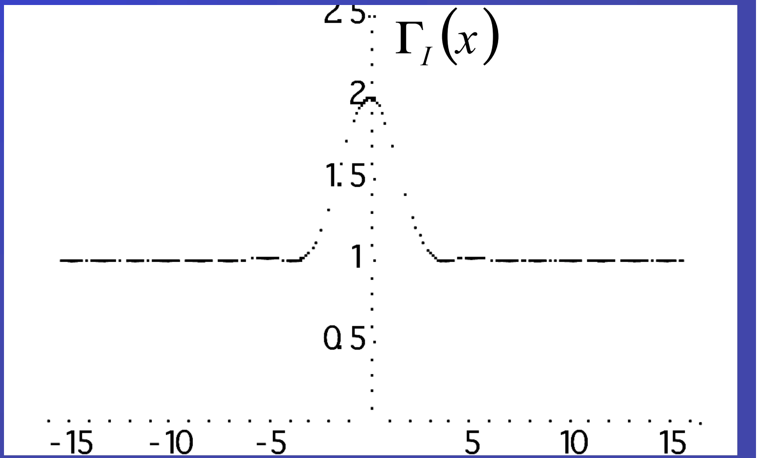
$$\Gamma_I(\vec{r}) = \frac{\int I(\vec{\rho})I(\vec{\rho}+\vec{r})d\vec{\rho}}{\int I(\vec{\rho})^2 d\vec{\rho}}$$

For well-behaved light (Gaussian circular statistics), this can be written as something that looks a lot like a far-field diffraction integral:

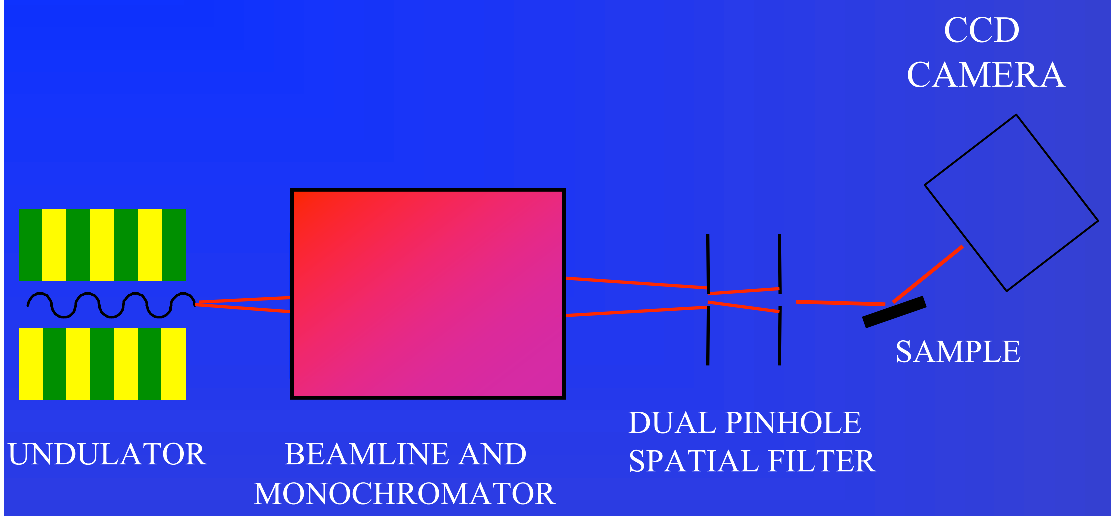
$$\Gamma_I(\vec{r}) = 1 + \left| \frac{\int I(\vec{\rho})\exp\left[i\frac{2\pi}{\lambda z}\vec{\rho}\cdot\vec{r}\right]d\vec{\rho}}{\langle I \rangle} \right|^2$$

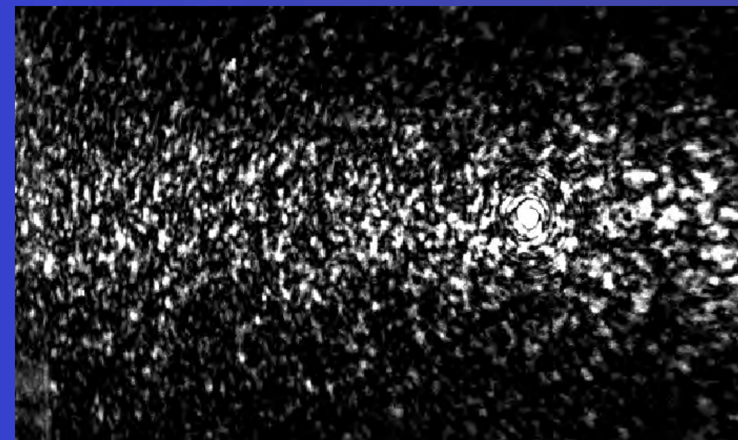
For a circular illumination pattern, this correlation function looks like an Airy-function diffraction patterns, with a constant background = 1. This peak provides an operational definition of a 'speckle'. It's width is nominally λ/d, where d is the diameter of the circular illumination - just like in diffraction.

This is an illustration of the Zernike-van Cittert theorem. There is still no information here about the sample. Another theorem indicates that higher correlation functions also do not contain specific information about the sample.

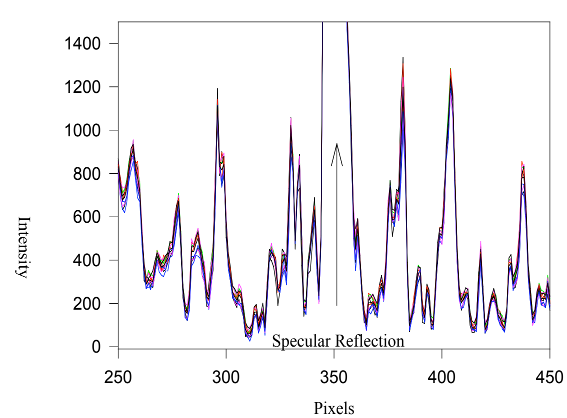


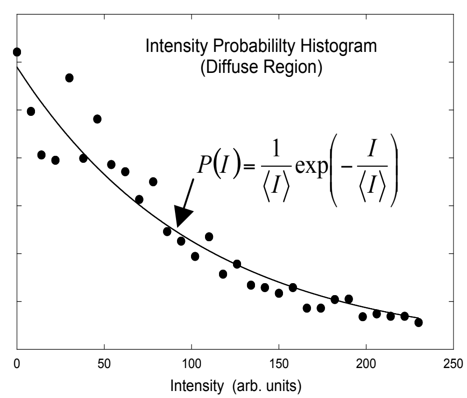
Static Soft X-ray Speckle from Roughened Silicon

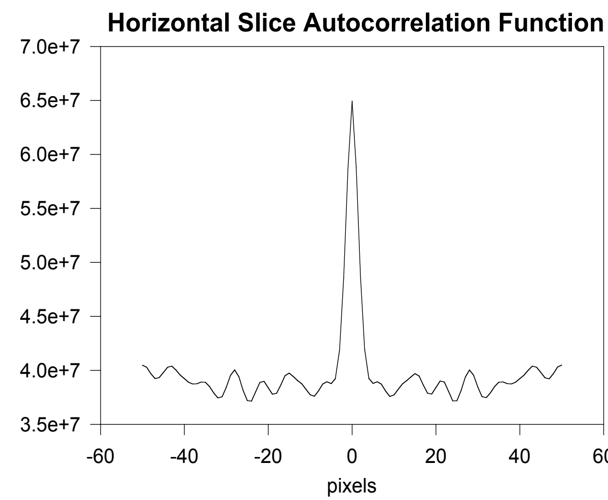




$\lambda = 80$ Å $P = 20\mu m$ $\sigma \sim 30$ Å



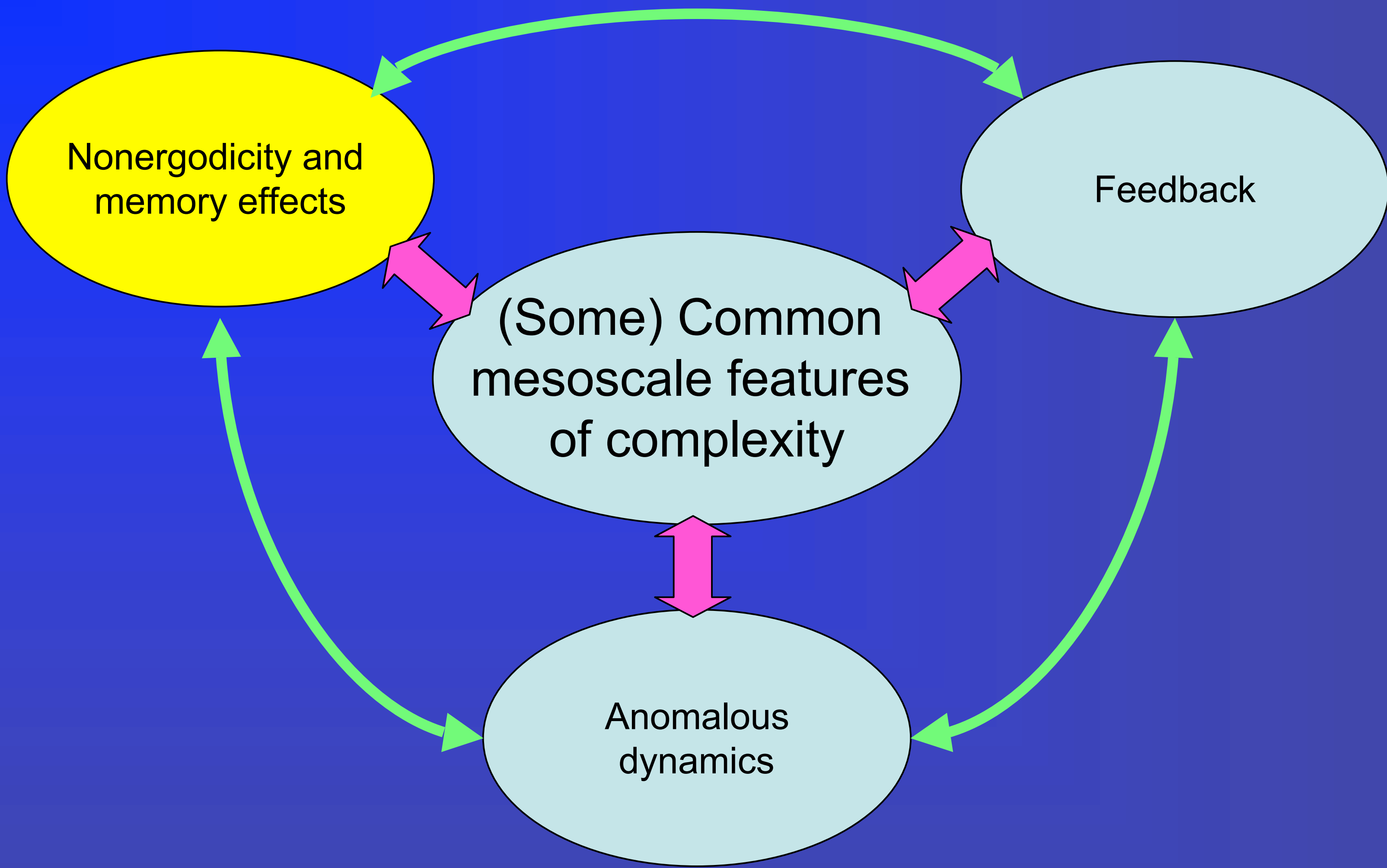




Speckle is repeatable . . . has the right histogram . . . **and** is correctly correlated

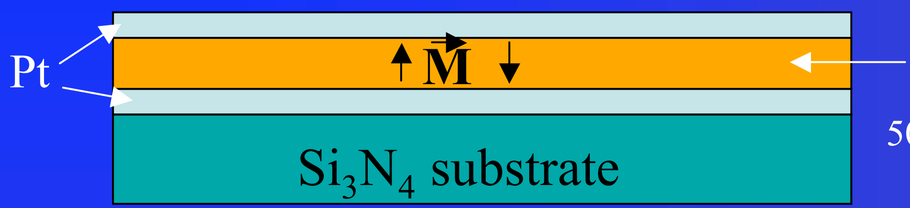
So, how do we extract useful material information from speckle patterns, or more generally, from coherent scattering data?

What Drives Material Complexity?



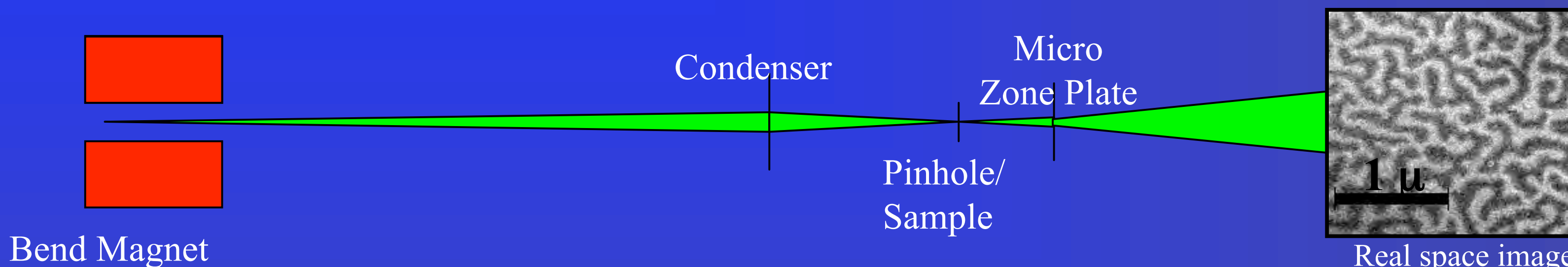
These issues are often statistical in nature and can be usefully probed in terms of statistical averages, such as space-time correlation functions: S(q, t, T, H, E, j, . . .)

Magnetic Domains in Real and k-Space

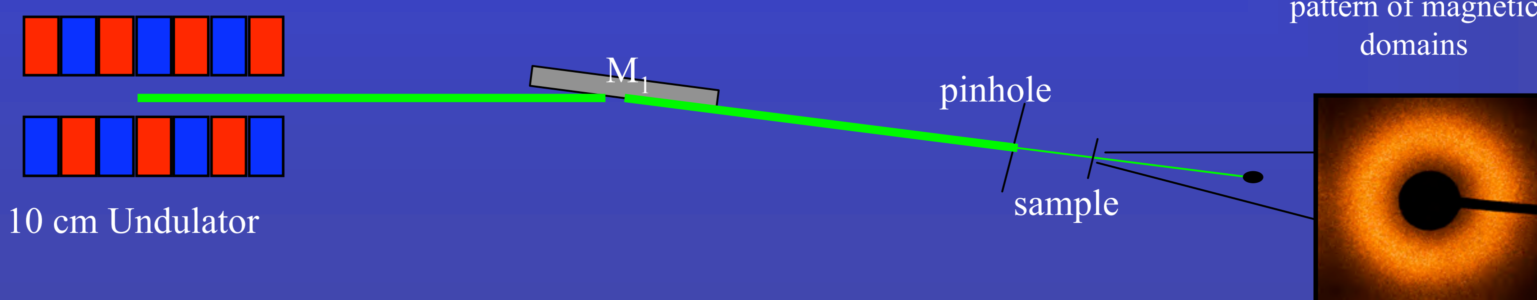


Co:Pt multilayer
50 repeats (7Å Pt + 4Å Co)

Magnetic contrast attained by operating near the Co L-edge



ALS XM-1 X-ray Microscope



ALS BL7.0.1 (past) – BL9.0.1 ‘Blowtorch’ (recent) – BL12.0.2 CSX Beamline (current)

Static Soft X-ray 'Speckle Metrology' of Thin Film Ferromagnets

- While the statistics of a fully-developed speckle pattern provide no information about the scattering medium, the pattern itself is the diffraction pattern of the illuminated volume and can in principle be inverted using phase retrieval methods.

- Speckle patterns have been extensively used to deduce how a system changes under external stresses. There are several such application in optical metrology.

- We can combine the submicron magnetic sensitivity of soft x-rays to measure how a magnetic system changes under the influence of an applied magnetic field. In providing ensemble-averaged information, this coherent scattering approach has advantages in speed and precision over real-space probes.

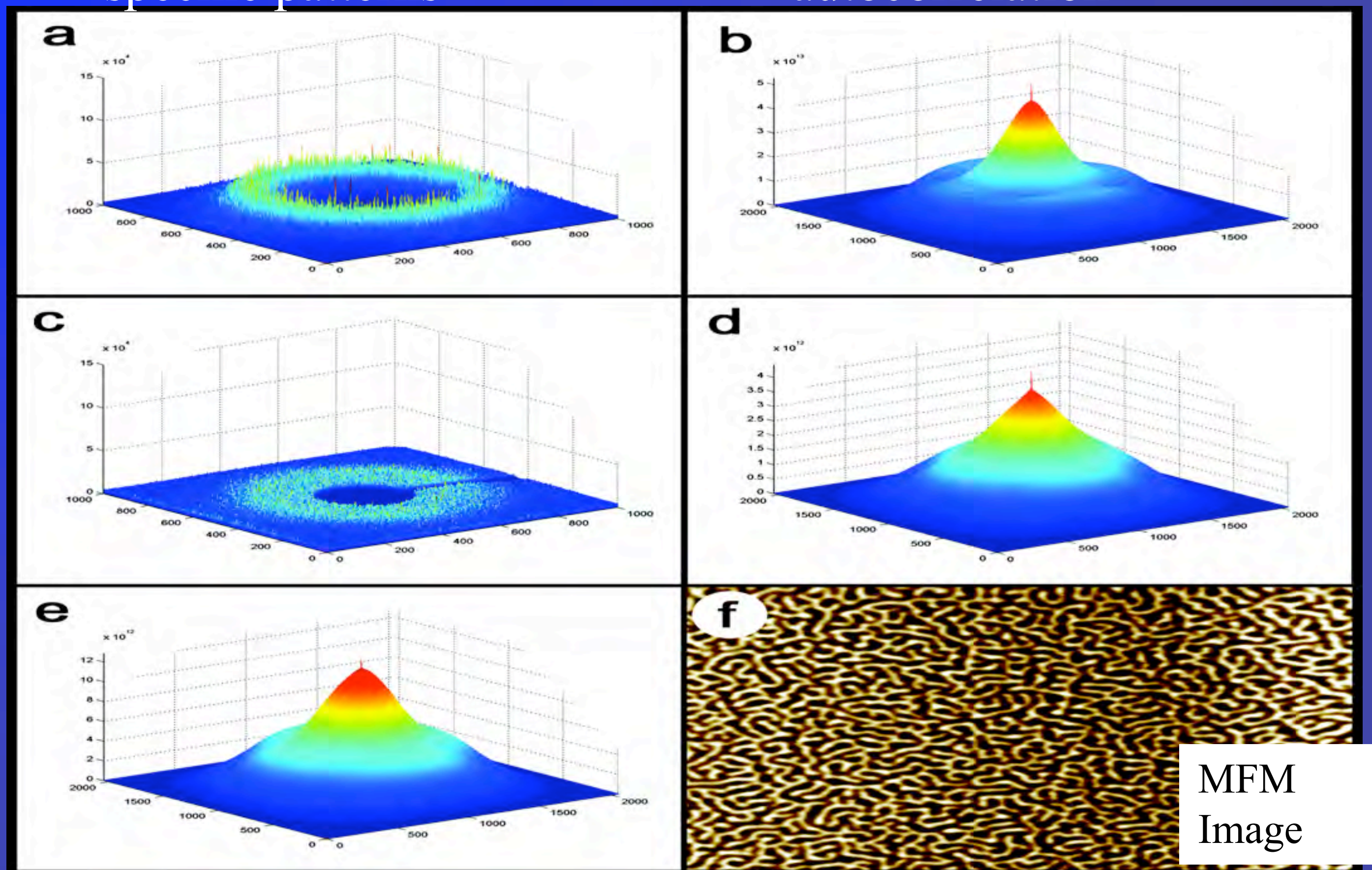
‘Speckle Metrology’ of Thin Film Ferromagnets

speckle patterns | autocorrelation

H=0 kG

H=2 kG

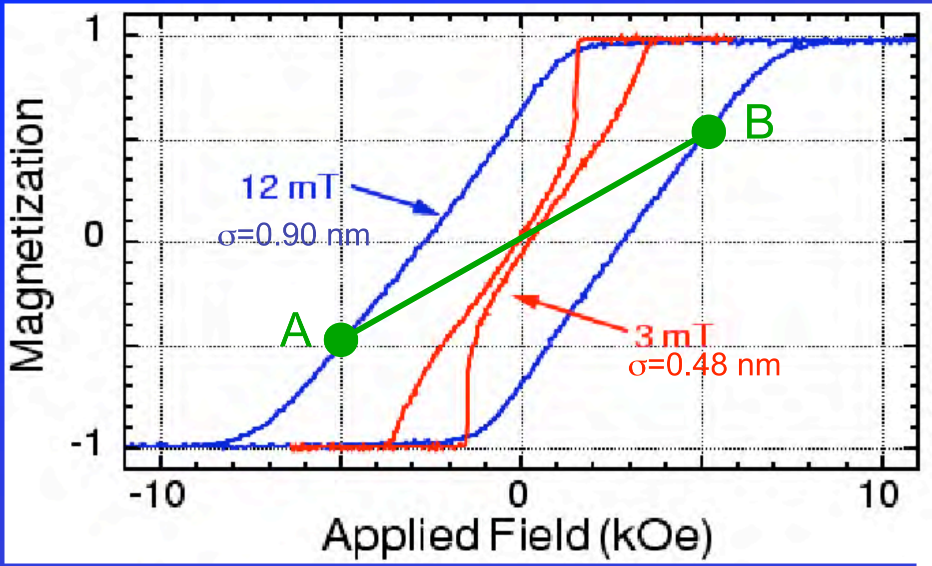
cross-cor



Generalized correlation coefficient integrates the speckle peaks:

$$< \rho(A,B) >= \frac{\sum\left[A\otimes B-(A\otimes B)_{bkg}\right]}{\sqrt{\sum\left[A\otimes A-(A\otimes A)_{bkg}\right]\sum\left[B\otimes B-(B\otimes B)_{bkg}\right]}}$$

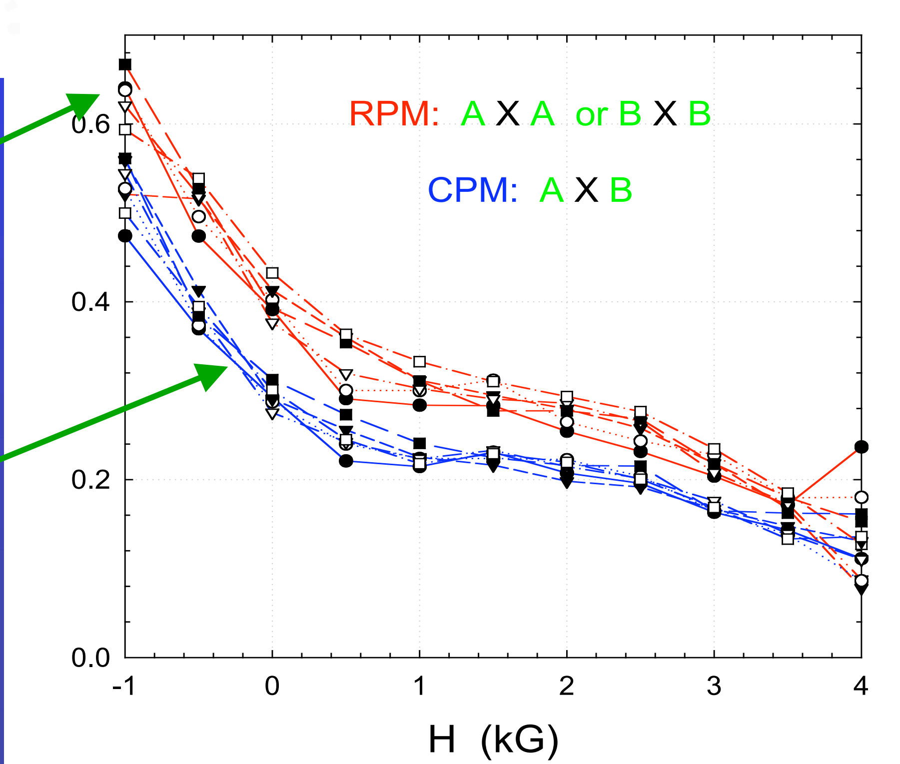
Microscopic Return and 'Conjugate' Point Memory



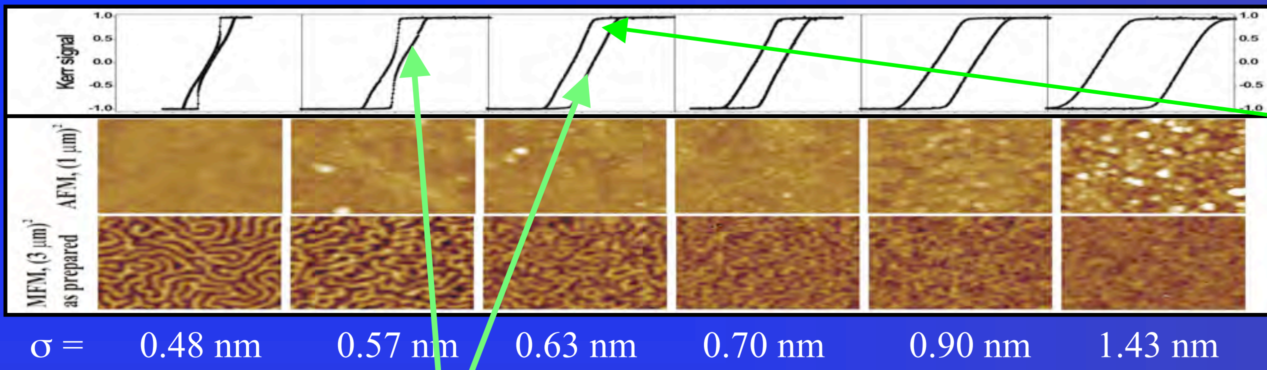
σ = 0.63 nm ('8.5 mT'):
Rougher films exhibit significant microscopic RPM and CPM, while smooth films do not.

Best memory near onset of reversal: first domains to nucleate have better memory.

Conjugate point memory is systematically ~20% lower than return point memory.



How (Dirty) Magnets Forget

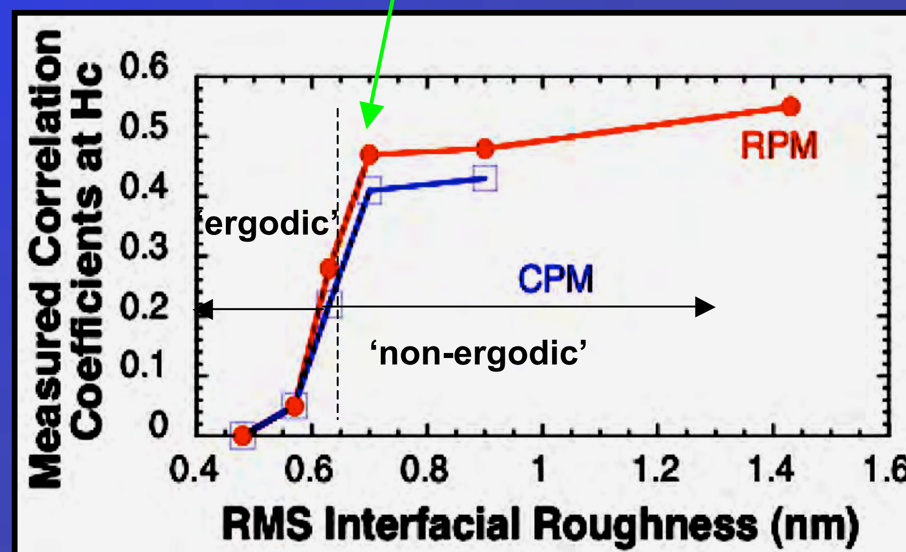


Roughness where a nucleation event disappears from the magnetization loop corresponds to an abrupt onset of RPM.

Theory of ‘crackling noise’ by Sethna* predicts an abrupt transition as a function of structural heterogeneity between a smooth magnetization loop and one with a distinct nucleation event, where a single Barkhausen cascade becomes macroscopic.

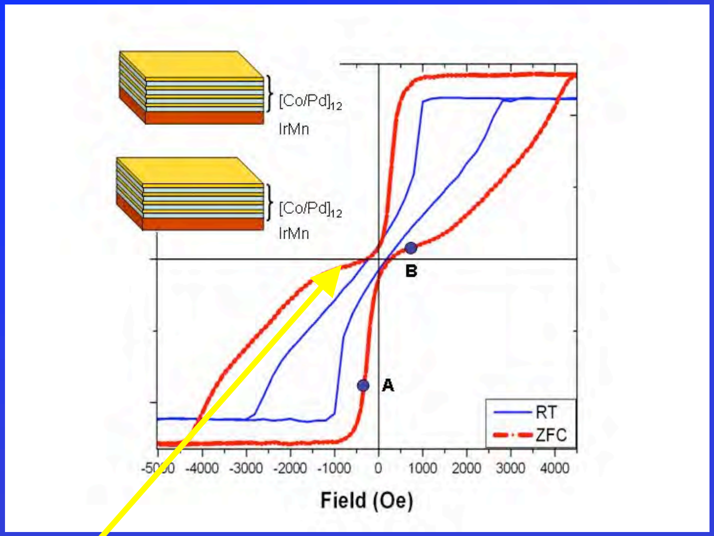
Multilayer perfection plays the role of a non-thermal parameter that allows us to control ergodic or nonergodic behavior.

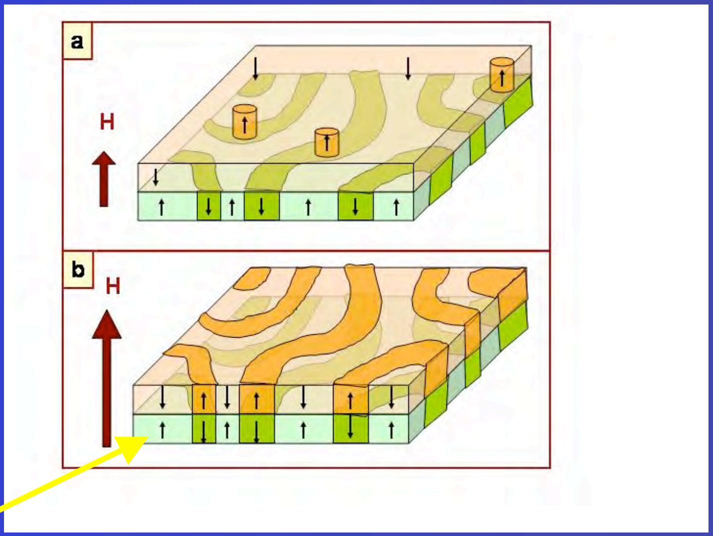
This T=0, random field Ising theory i) does not include dipolar interactions and thus does not predict measured loops very well, ii) predicts perfect return point memory, and iii) predicts zero complementary point memory.



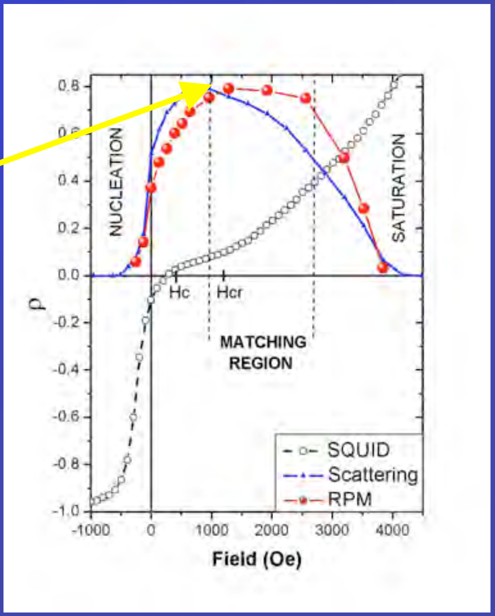
* see, for example, Sethna, Dahmen, and Myers, Nature **410**, 252 (2001).

Controlling Mesoscopic Memory with Exchange Bias Structures



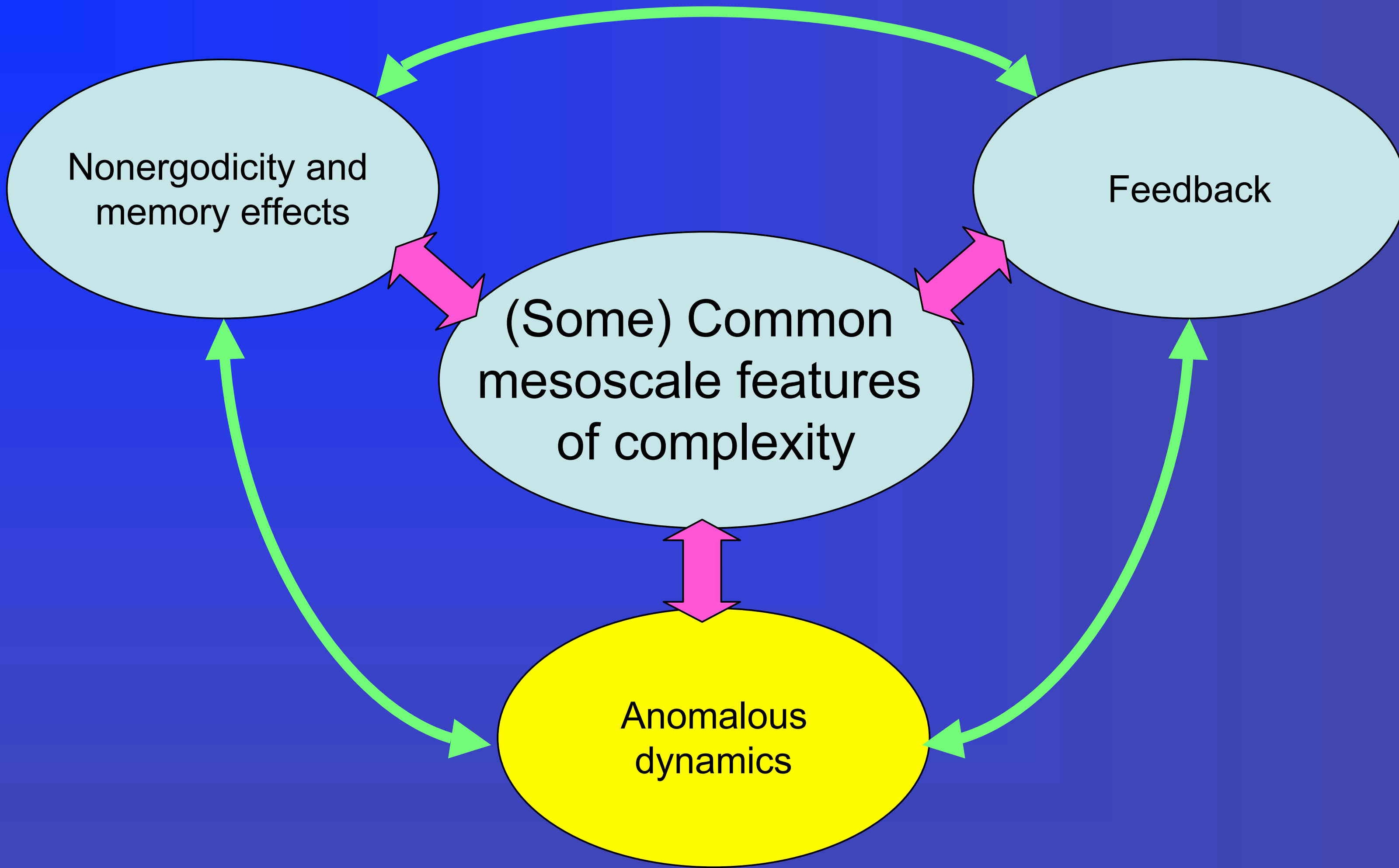


‘Plateau’ in the magnetization loop after zero-field cooling caused by a ‘template’ of uncompensated spins in the AF layer which ensures good mesoscopic memory.



K. Chesnel, submitted.

What Drives Material Complexity?



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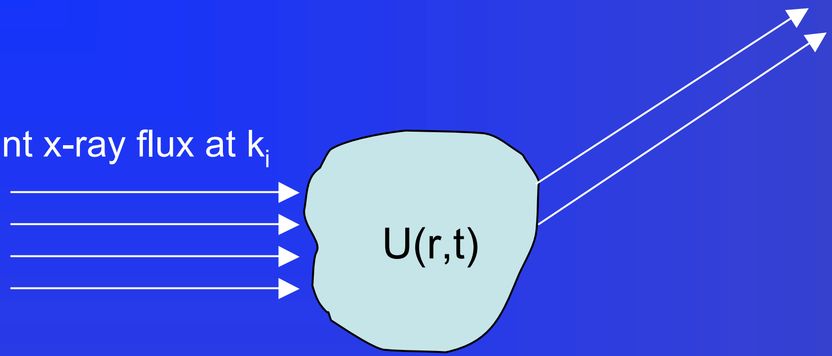
Dynamic X-ray Scattering in One Slide

Scattered x-ray flux at k_f

Incident x-ray flux at k_i



Inhomogeneous, fluctuating scattering medium, $\varepsilon(r)$

Scattering wave vector

$q = k_f - k_i$

In the Born approximation, the scattering rate is determined by Fermi's Golden Rule

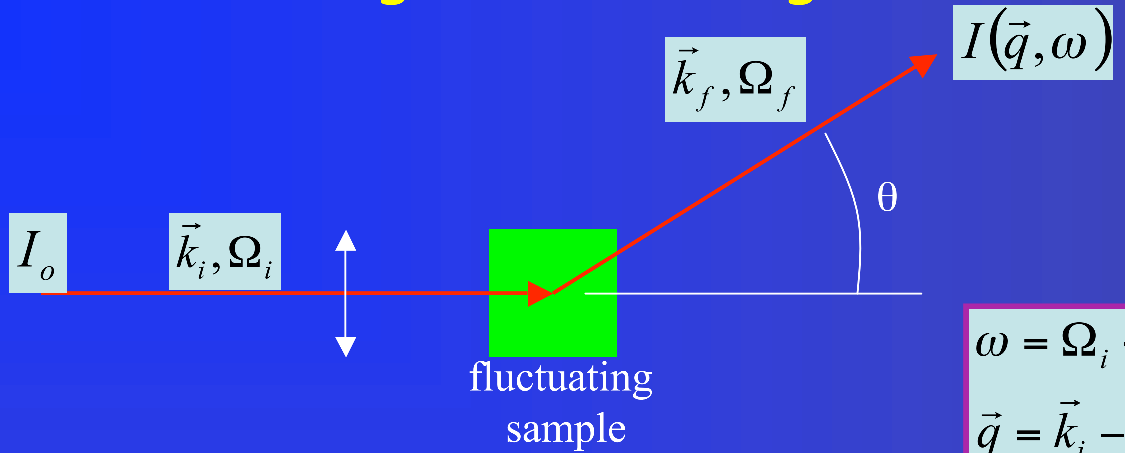
$$W_{if} = \frac{2\pi}{\hbar} \left| \left\langle k_i \middle| U(r,t) \middle| k_f \right\rangle \right|^2 \rho\left(E_f\right) \propto \frac{d\sigma}{d\Omega dE}$$

The measured scattering rate is related to a correlation function of the dielectric density

$$S(q,t) \propto \int_V d\vec{r} e^{i\vec{q}\cdot\vec{r}} \left\langle \varepsilon(\vec{0},0)\varepsilon(\vec{r},t) \right\rangle$$

Now the microscopic gratings are fluctuating in both space and time. With coherent illumination, the scattering rate at q depends on the instantaneous density and amplitude of the gratings providing a statistical average of the microscopic spatiotemporal structure through the intermediate scattering function S(q,t).

Light Scattering Demo



$$\omega = \Omega_i - \Omega_f$$

$$\vec{q} = \vec{k}_i - \vec{k}_f$$

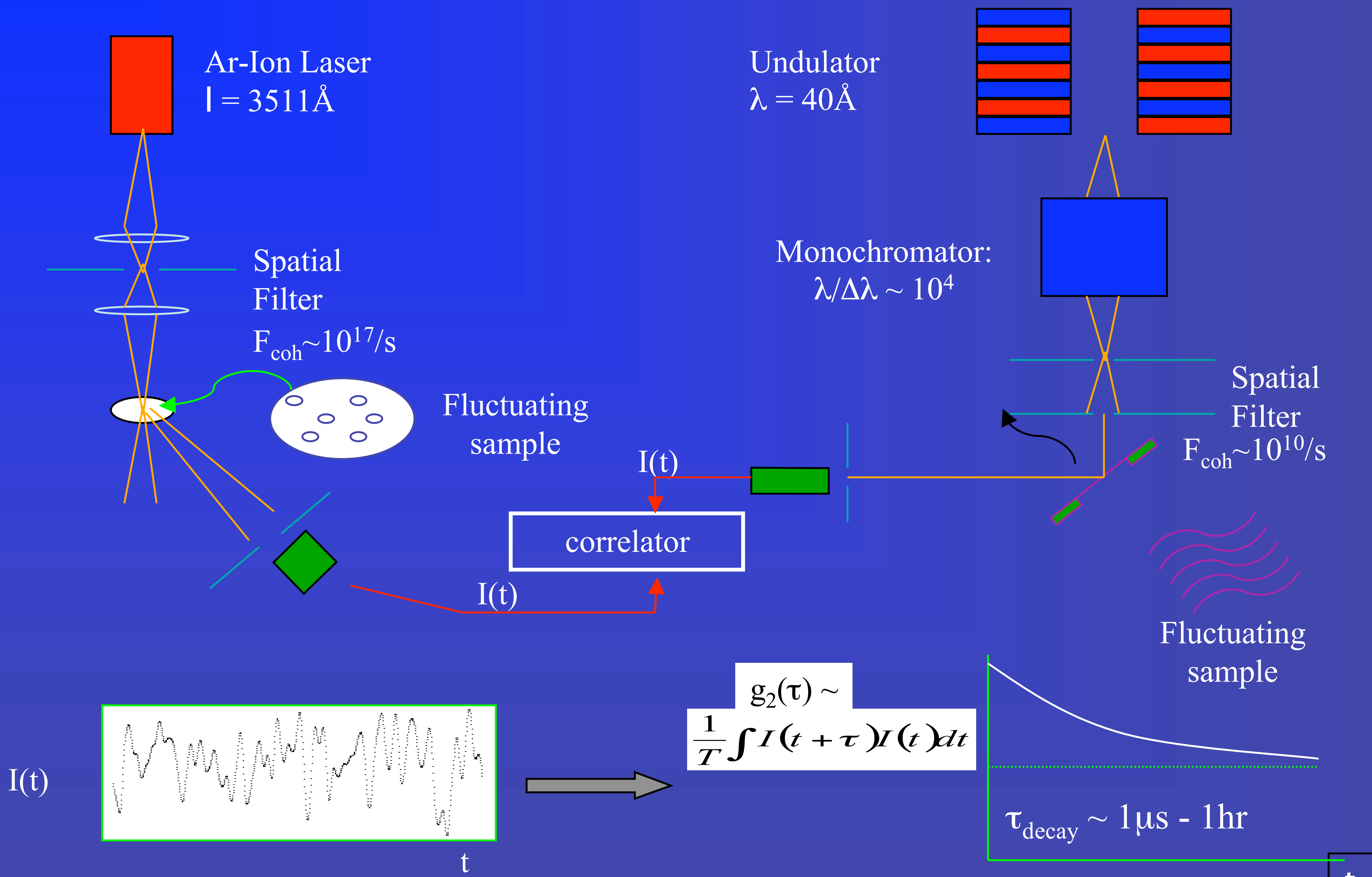
- The fact that the incident beam has a high degree of transverse and longitudinal coherence means that waves scattered from the entire illuminated volume interfere;

- Thermal fluctuations drive the normal modes of the sample, and photons are scattered quasi-elastically, essentially through a Doppler shift;

- As the scattering from a particular normal mode selected by the scattering geometry gets stronger and weaker, the number of singly scattered photons follows the driven modulation;

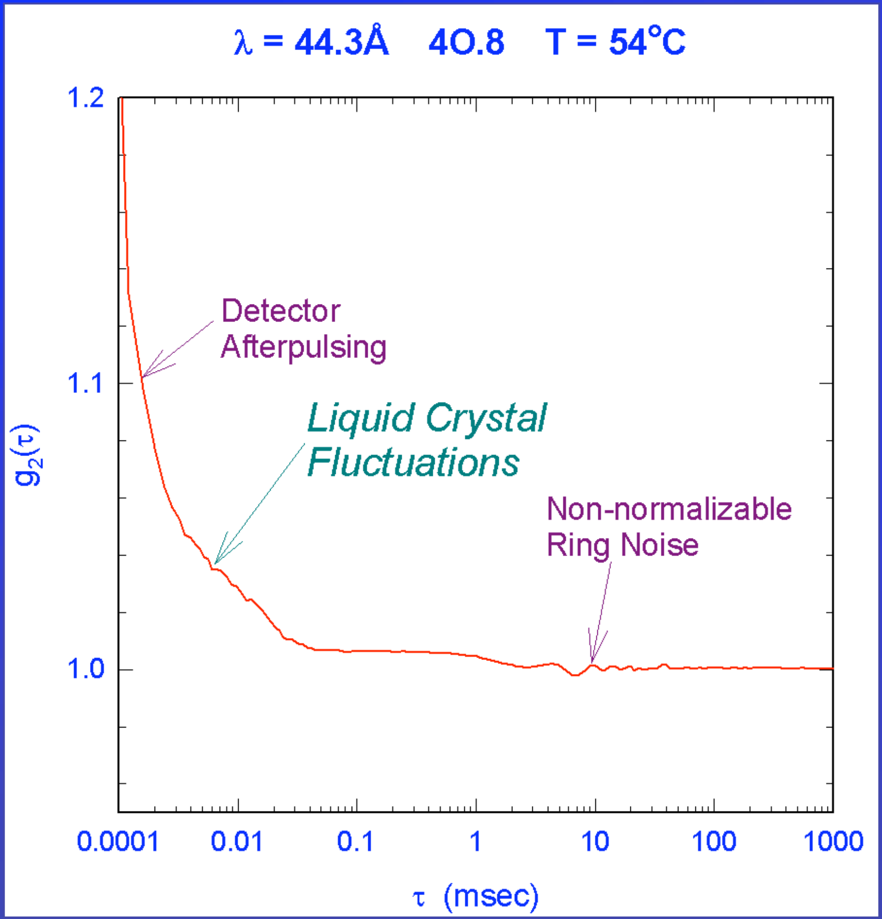
- By measuring the fluctuations in the scattered light in terms of an intensity autocorrelation function, we can determine the fluctuations in the sample.

Dynamic Light Scattering



$g_2(t)$ is the time Fourier transform of the dynamical structure factor, $S(q,\omega)$.

Fast Times at the ALS
Drumhead Modes of a Tethered Membrane



"Soft X-ray Dynamic Light Scattering from Smectic A Films", A.C. Price, L.B. Sorensen, S.D. Kevan, J.J. Toner, A Poniewrski, and R. Holyst, Phys. Rev. Lett., **82**, 755 (1999).

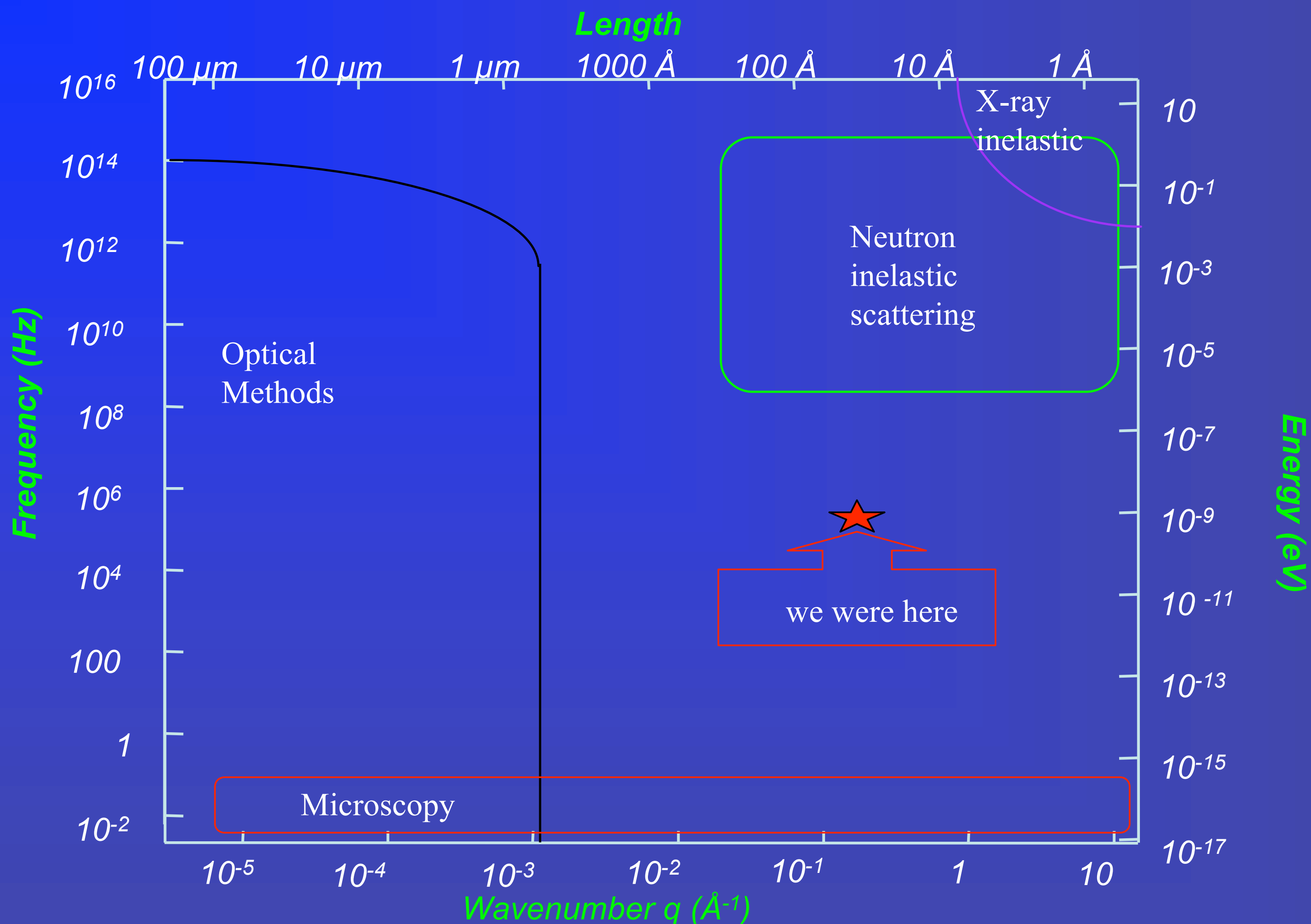
- The slow mode corresponds to the over-damped, uniform drumhead motion of a tethered membrane. The measured decay time is in excellent accord with theory;

- In the quasi-Bragg geometry, we have no sensitivity to the bulk moduli B and K since the surface tension dominates the restoring force.

- The fastest commercial digital correlator operates with 5 ns time resolution.

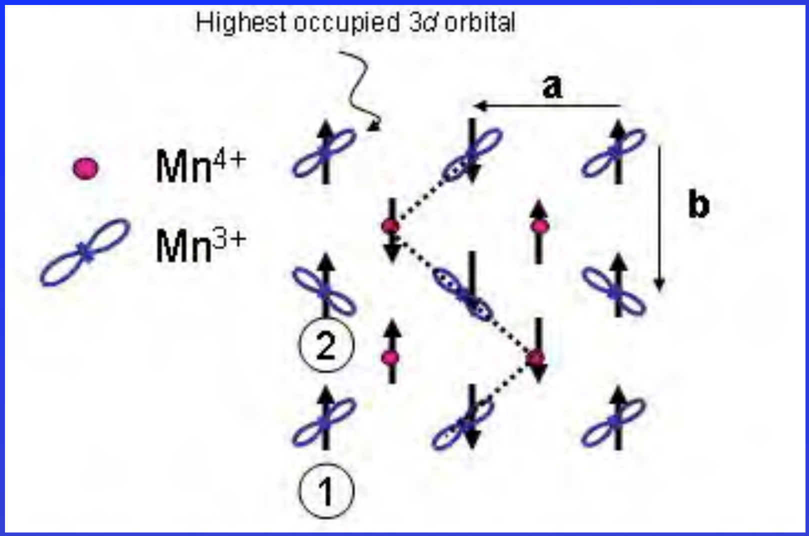
- Non-CW-nature of the source causes some difficulty

Probing Hierarchies in Space and Time



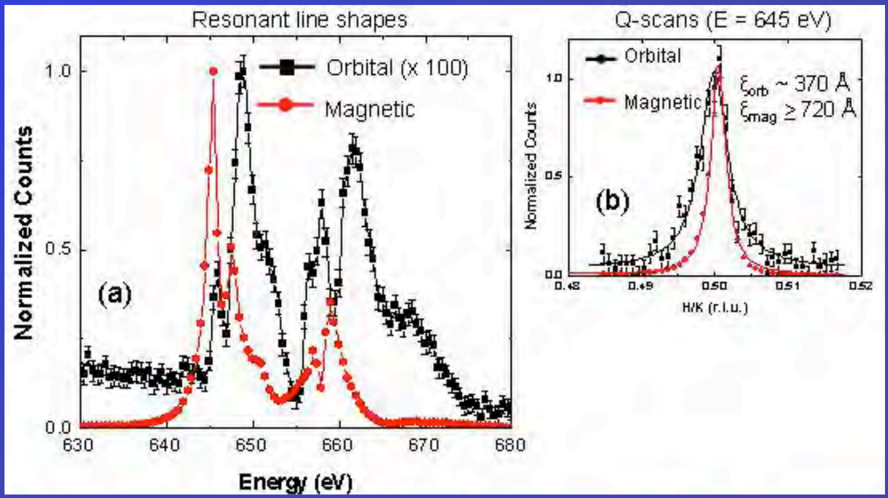
★ "Soft X-ray Dynamic Light Scattering from Smectic A Films", A.C. Price, L.B. Sorensen, S.D. Kevan, J.J. Toner, A. Poniewrski, and R. Holyst, Phys. Rev. Lett., **82**, 755 (1999).

L-edge Structure in Orbital Ordered Manganites



'Conventional' picture of spin and charge ordering in $Pr_{0.5}Ca_{0.5}MnO_3$

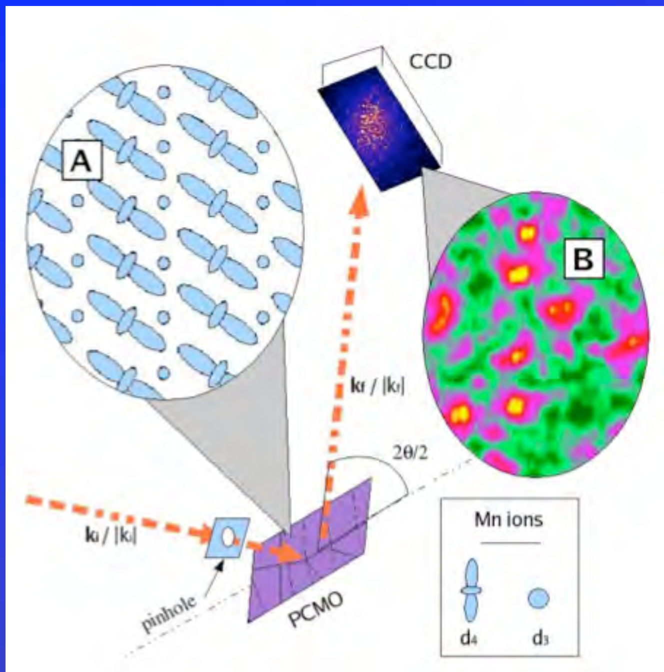
- Mn 3d orbital physics helps determine the overall ground state;
- L-edge anomalous diffraction offers a direct probe of how the atomic interactions couple to nanoscale spin and charge structures.



Resonant diffraction from magnetic- and charge-ordered superstructures (from X1B at the NSLS)

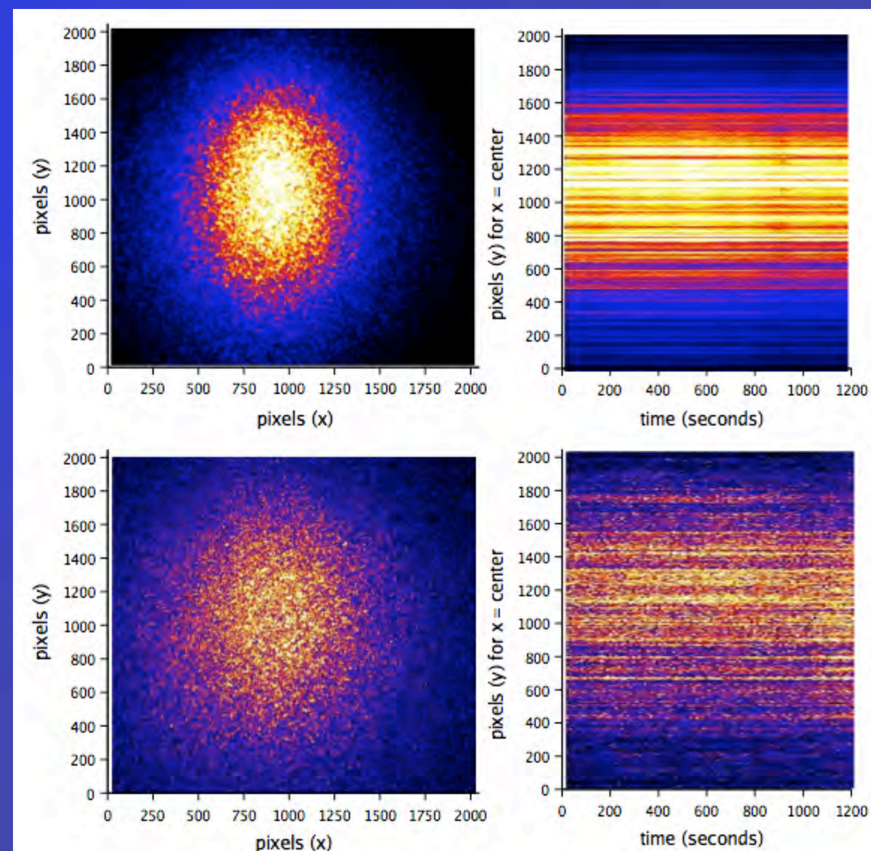
K.J. Thomas, J.P. Hill, S.Grenier, Y.-J. Kim, P. Abbamonte, L. Venema, A. Rusydi, Y. Tomioka, Y. Tokura, D.F. McMarrow, G. Sawatzky, and M. van Veenendaal, PRL 92, 237204 (2004).

How Does an Orbital Lattice Melt?



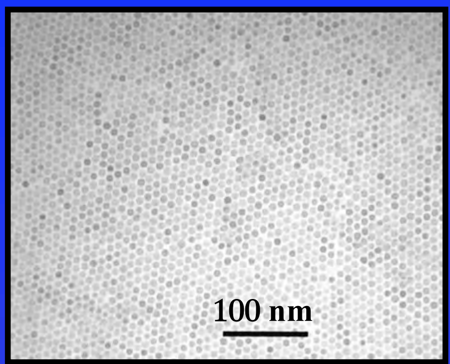
Schematic of scattering geometry sampling the (0,1/2,0) orbital-order Bragg peak that is broadened by finite-sized orbital domains.

Left: Images of the OO Bragg peak well below (top) and near the ordering transition. Right: Intensity vs time for a line of pixels through the middle of the Bragg peak indicating that the system remains mostly static even though the orbital peak broadens due to reduced OO correlation length.

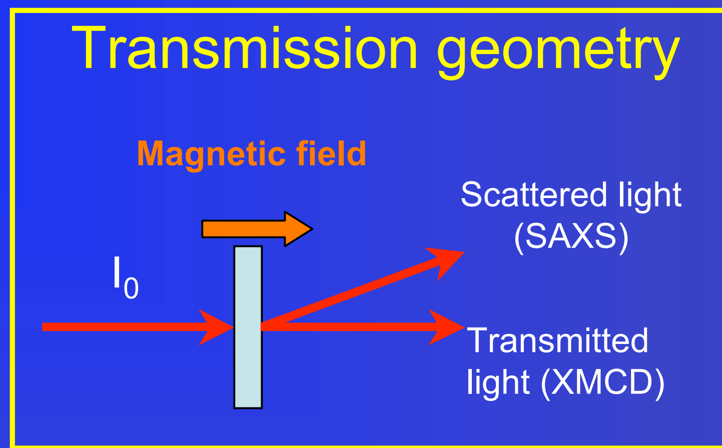


Fluctuations in Cobalt and Fe_3O_4 Nanocrystal Lattices

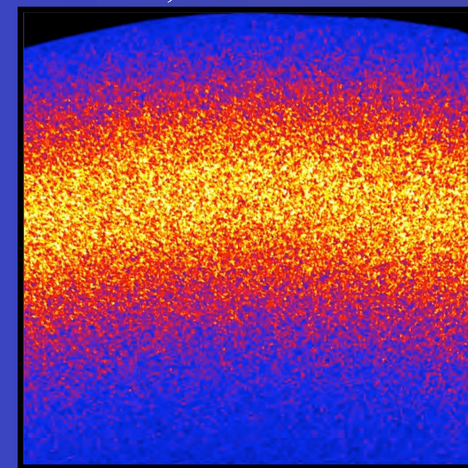
'representative' TEM



Puntes, Krishnan, and Alivisatos, Science 291, 2115 (2001).



Speckle pattern at the Co L_3 resonance, from K. Chesnel



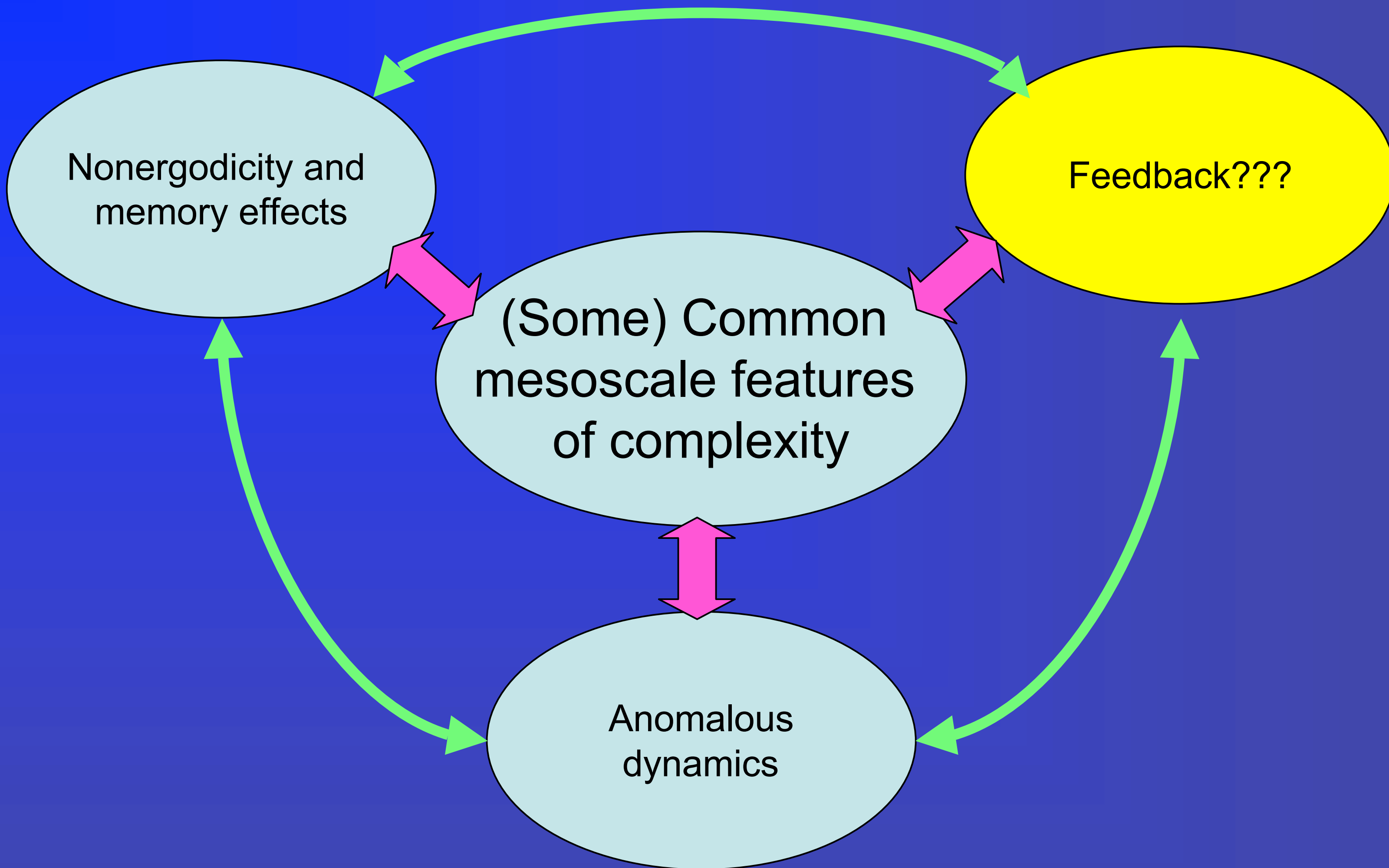
~10^3 photons/sec/speckle

14 nm diameter Co nanocrystals have a blocking temperature of ~200K, above which the particles are superparamagnetic:

- At low T, does the nanoparticle lattice exhibit significant microscopic return point memory?
- Can we detect superparamagnetic fluctuations?
- Can we measure the full intermediate scattering function, S(q,t), to probe the microscopic switching dynamics?

We want an EPU for Christmas (but we knew that a long time ago and it's not going to happen that soon).

What Drives Material Complexity?



I believe that feedback, as very generally defined, plays a key role in both nonergodicity and anomalous dynamics. . . but I have not been able to think of a direct probe of microscopic feedback mechanisms.

Conclusions: Coherence ➠ Correlations ➠ Complexity

Scattering coherent soft x-rays off complex materials maps their complexity into an easily-measured far-field speckle diffraction pattern with atomic, structural, and magnetic contrast.

These speckle patterns can be analyzed using various correlation function techniques to probe the microscopic memory and slow dynamics that are hallmarks of complexity.

Other lectures in this course have introduced the notion of phase retrieval and holographic imaging, in which such speckle patterns are inverted into real-space images. In that way, coherent x-rays provide a unification between real- and momentum-space material probes.