XPCS and Shear Flow

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Outline

- Background: XPCS & rheology
- XPCS during shear
  - Unidirectional shear flow
  - Oscillatory shear flow
- XPCS following shear
  - Slow materials
  - Fast materials
- Generic needs
- Conclusions

XPCS & rheology

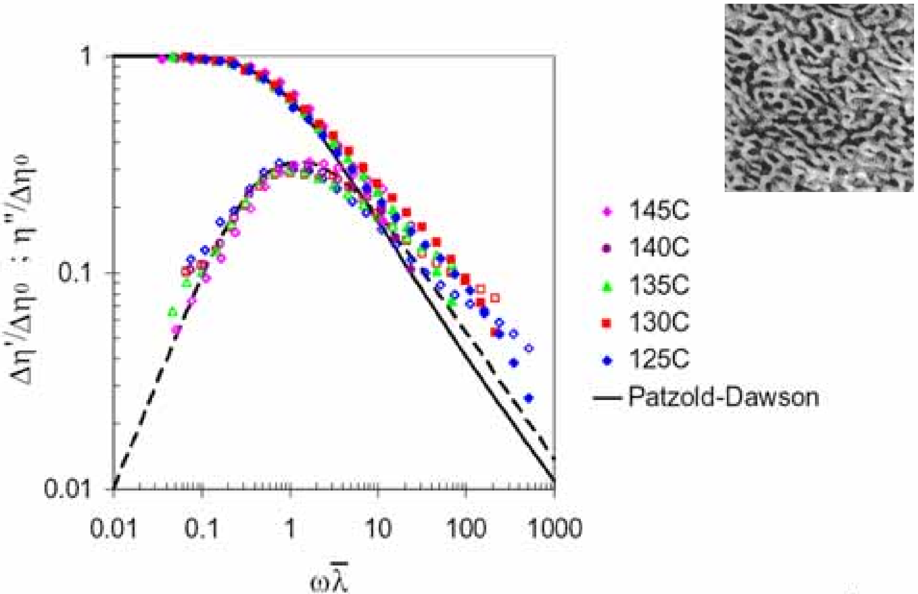
- Complementary methods for probing structural dynamics of soft materials/complex fluids
  - Polymers, colloids, emulsions, gels, self-assembled fluids, etc.
- ‘Sweet spot’ of XPCS:
  - 10s to 100s of nanometers
  - ~ 0.01 to 100 seconds
  - *Similarity to scales that govern rheology*

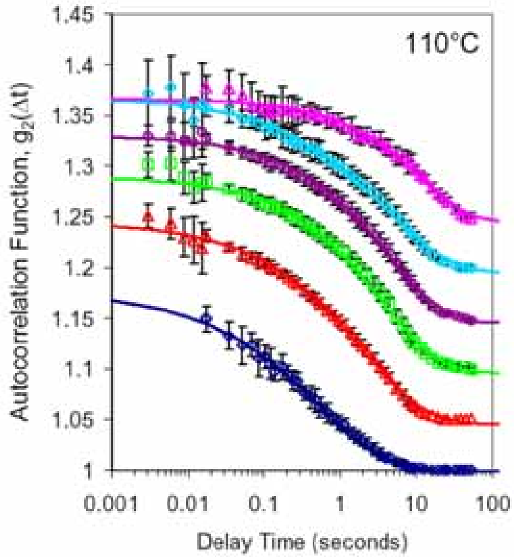
Linear & nonlinear rheology

- Linear viscoelasticity
  - Small deformations or deformation rates
  - Stress linear in applied deformation
  - Probes structural dynamics at equilibrium
  - *Conceptual alignment with XPCS*
- Nonlinear viscoelasticity
  - Large deformations or deformation rates
  - Nonlinear mechanical response
  - *Fluid structure strongly perturbed away from equilibrium*

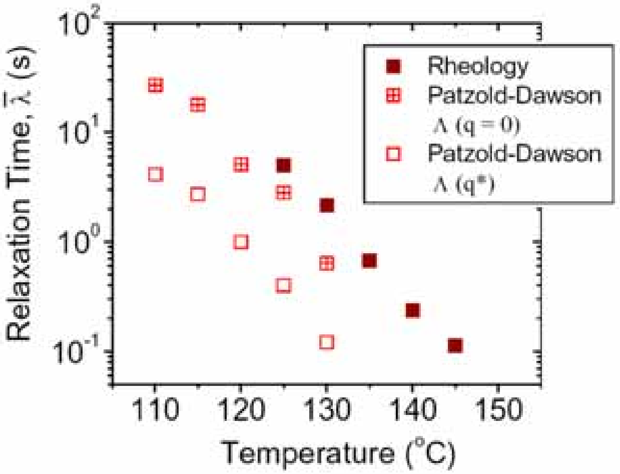
Linear viscoelasticity & XPCS

Polystyrene-polyisoprene bicontinuous microemulsion:





Landau-Ginzberg theory for microemulsion predicts inter-relationship between dynamic structure factor and linear viscoelastity.



Brinker, Mochrie & Burghardt, *Macromolecules*, **40**, 5150 (2007).

Nonlinear viscoelasticity

- Superposition rheology:
  - Apply steady shear at high rates to perturb fluid structure, access nonlinear regime
  - Superimpose *small-amplitude* oscillation; analyze using linear viscoelastic concepts
  - *What is the nature of microscopic relaxation processes in a sample pushed far from equilibrium?*

- XPCS during shear… another route to approach this idea?

XPCS during shear flow

Fluerasu and coworkers:

$$|g_1(\mathbf{q},t)|^2 = \underset{\substack{\nearrow \\ \text{‘Diffusion’}}}{|g_{1,D}(\mathbf{q},t)|^2} \cdot \underset{\substack{\uparrow \\ \text{‘Transit’}}}{|g_{1,T}(\mathbf{q},t)|^2} \cdot \underset{\substack{\nwarrow \\ \text{‘Shear’}}}{|g_{1,S}(\mathbf{q},t)|^2}$$

For simple Brownian diffusion (e.g. dilute colloids):

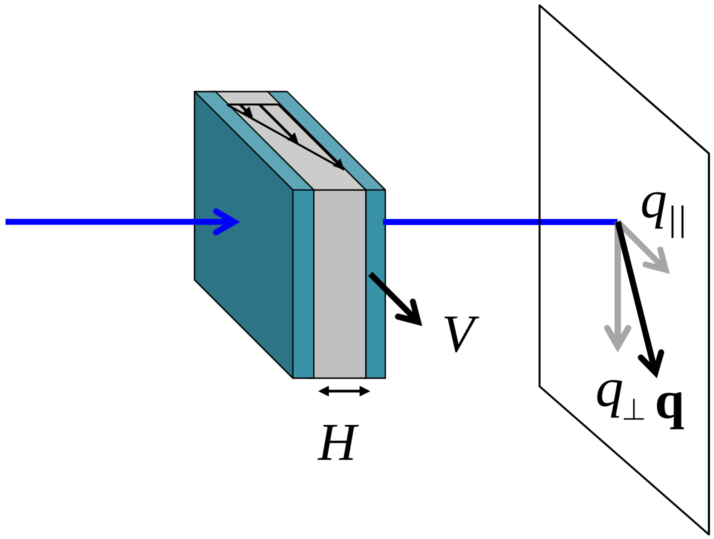
$$|g_{1,D}(\mathbf{q},t)|^2 = \exp\left[-2Dq^2t\right]$$

‘Transit’ term reflects de-correlation as particles enter/leave volume; characteristic time scale ~ w/V (w = beam width; V = char. velocity)

‘Shear’ term may be calculated given variation of velocity over scattering volume. Fluerasu and coworkers: pressure-driven (Poiseuille) flow.

Busch et al. Eur Phys J E, 26, 55 (2008); Fluerasu et al. J Synch Rad, 15, 378 (2008); Fluerasu et al. New J Phys, 12, 035023 (2010)

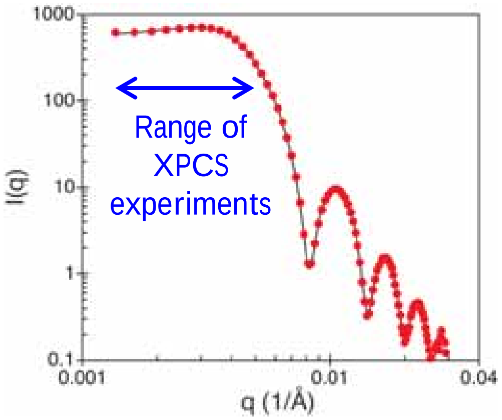
XPCS during homogenous shear



$$\left|g_{1,S}(\mathbf{q},t)\right|^2 = \frac{\sin^2\left(q_{||}\dot{\gamma}Ht/2\right)}{\left(q_{||}\dot{\gamma}Ht/2\right)^2}$$

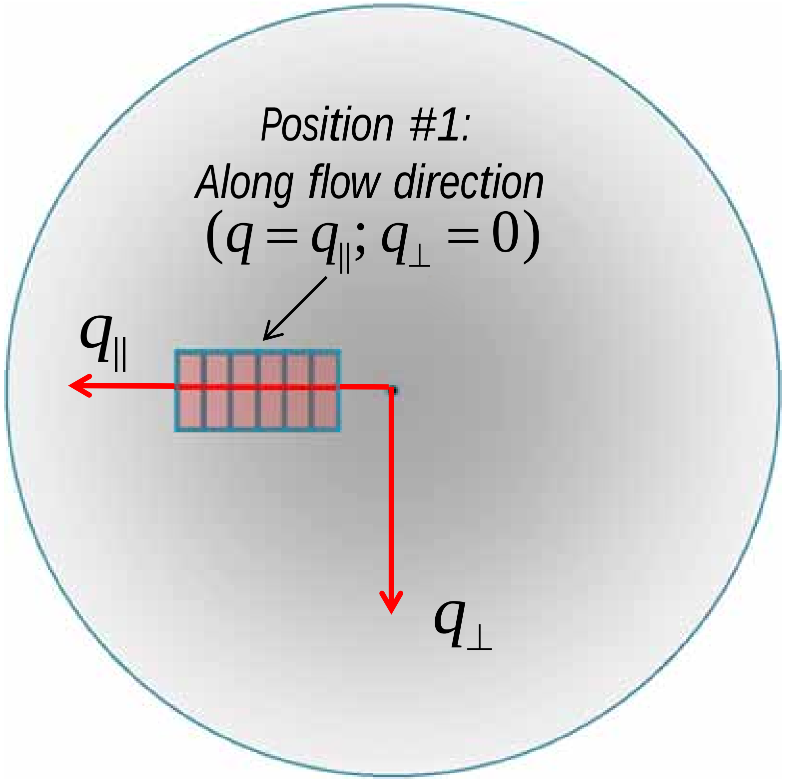
Homogeneous shear flow experiments:

- Rotating disk shear cell
- PS/glycerol latex dispersion (ϕ = 0.13; a = 55 nm)
- APS 8ID-I; SMD CCD, 128 x 1024 pixel ROI; 330 Hz
- M. Sikorski, A. Sandy, S. Narayanan
- Transit time effects should be negligible

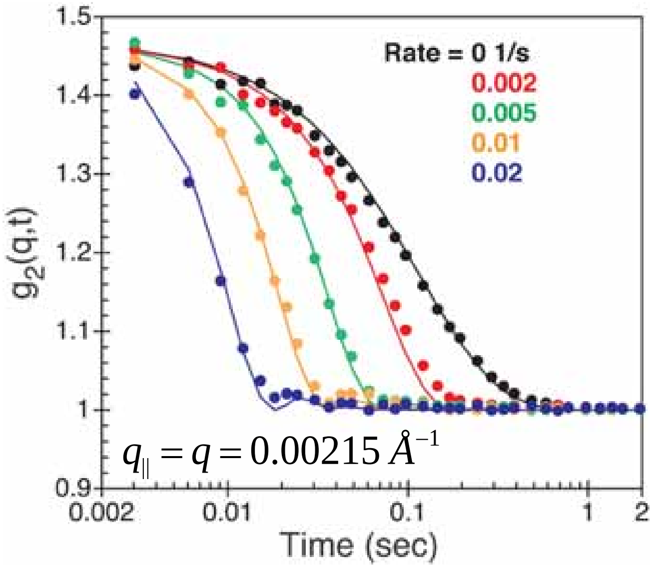


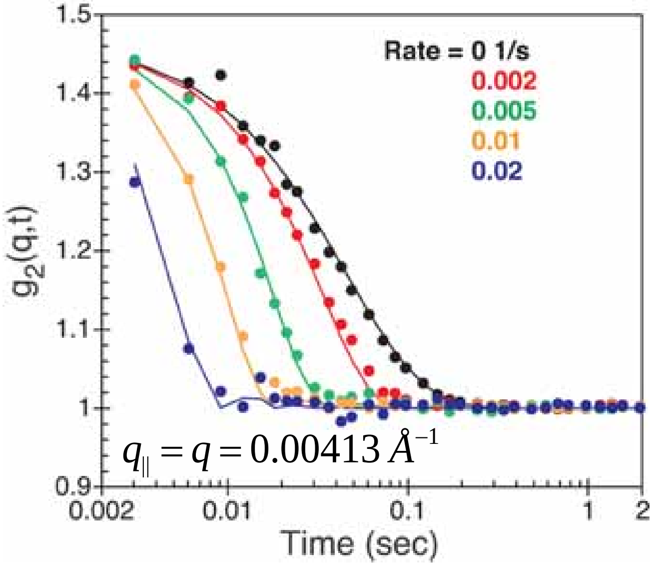
XPCS during homogenous shear

$$g_2(\mathbf{q},t) = 1 + \beta \exp\left[-2Dq^2 t\right] \frac{\sin^2\left(q_{\parallel}\dot{\gamma}Ht/2\right)}{\left(q_{\parallel}\dot{\gamma}Ht/2\right)^2}$$



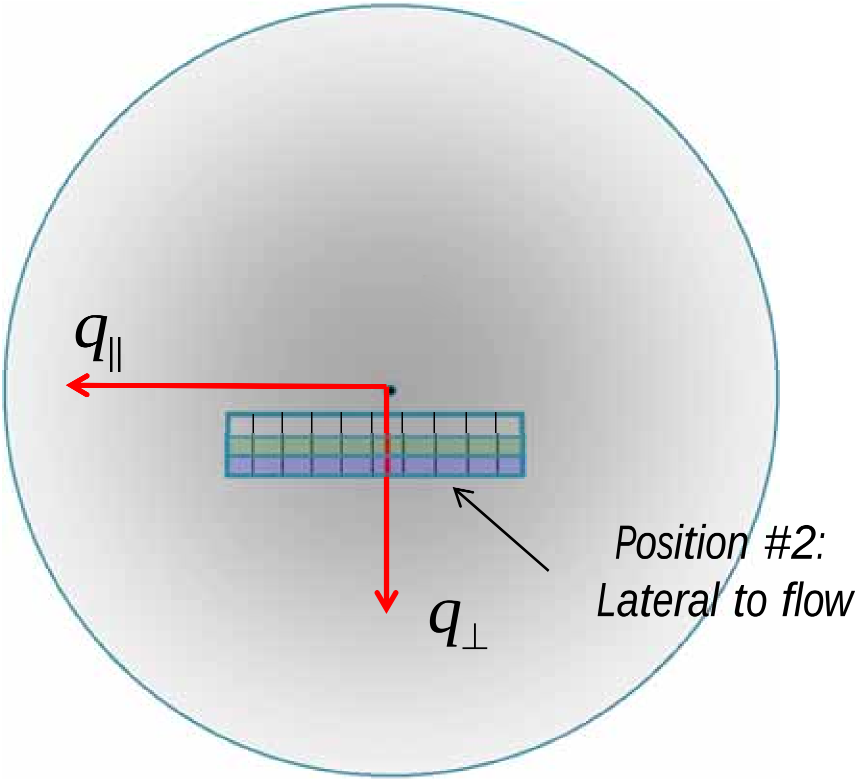
Position #1:
Along flow direction
$(q = q_{\parallel};\ q_{\perp} = 0)$



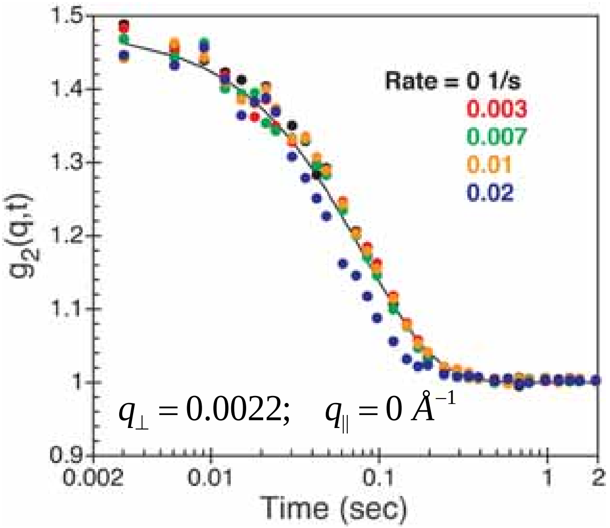


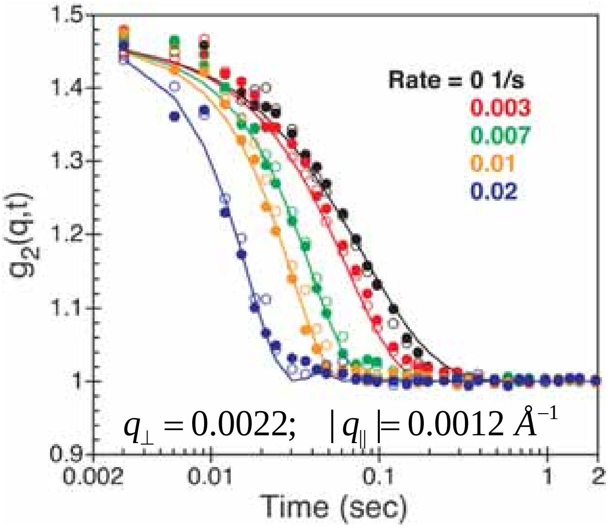
XPCS during homogenous shear

$$g_2(\mathbf{q},t)=1+\beta\exp\left[-2Dq^2t\right]\frac{\sin^2\left(q_\parallel\dot{\gamma}Ht/2\right)}{\left(q_\parallel\dot{\gamma}Ht/2\right)^2}$$



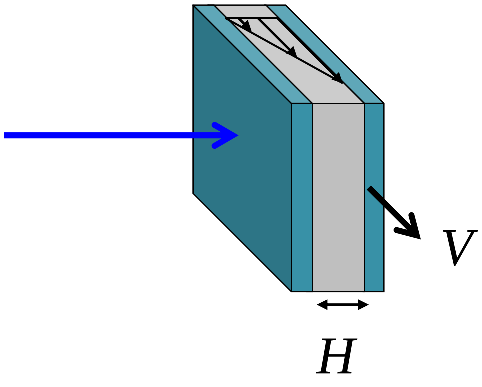
Position #2: Lateral to flow



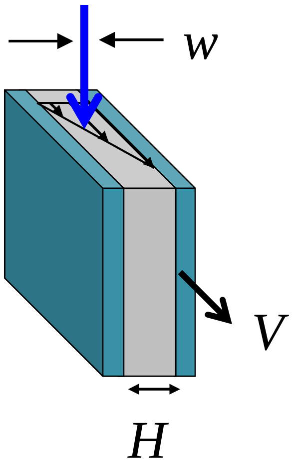


Homogenous shear observations

- Shear dominates decay of autocorrelation function, even at low rates
- Even at low rates, shear effects leak into data in ‘magic direction’
- Alternate configuration of shear flow XPCS?



$$\tau_S \sim \frac{1}{q_{\|}\dot{\gamma}H}$$

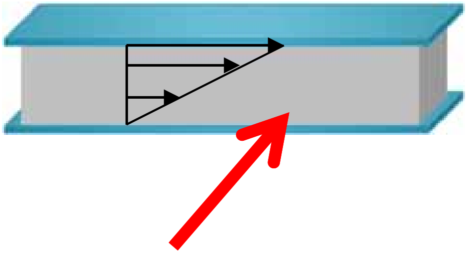


$$\tau_S \sim \frac{1}{q_{\|}\dot{\gamma}w}$$

Shear XPCS 'from the side'

- Advantages
  - Wider shear rate range accessible (wide enough?)
  - *If* interested in velocity gradient measurement, better view to resolve shear-banding
- Issues
  - Harder to produce; require free surfaces at sides to avoid parasitic velocity gradients along beam direction
  - Sample thickness/x-ray absorption?
  - May help mitigate shear effects in magic direction, but still have transit term to consider

Best case scenario for 'superposition experiment'?



Beam width = w

Positioned near bottom (fixed) plate

Shear: $\tau_S = \dfrac{1}{q_{\|}\dot{\gamma} w}$

Transit: $\tau_T = \dfrac{w}{V} = \dfrac{w}{\dot{\gamma} w} = \dfrac{1}{\dot{\gamma}}$

Diffusion: τ_D

For shear not to be 'limiting', require:

$$\tau_T < \tau_S \Rightarrow q_{\|} < \frac{1}{w}$$

(~ 1 pixel width on SMD CCD detector)

To 'cleanly' resolve diffusive dynamics without impact of transit time, require:

$$\tau_D < \tau_T \Rightarrow \boxed{\tau_D \dot{\gamma} < 1}$$

XPCS during oscillatory shear

- Autocorrelation function under shear:

$$\left|g_{1,S}(\mathbf{q},t)\right|^2 = \frac{\sin^2\left(q_{\parallel}\dot{\gamma}Ht/2\right)}{\left(q_{\parallel}\dot{\gamma}Ht/2\right)^2}$$

Note: loss of correlation really driven by applied *strain*:

$$\gamma(t) = \dot{\gamma}t$$

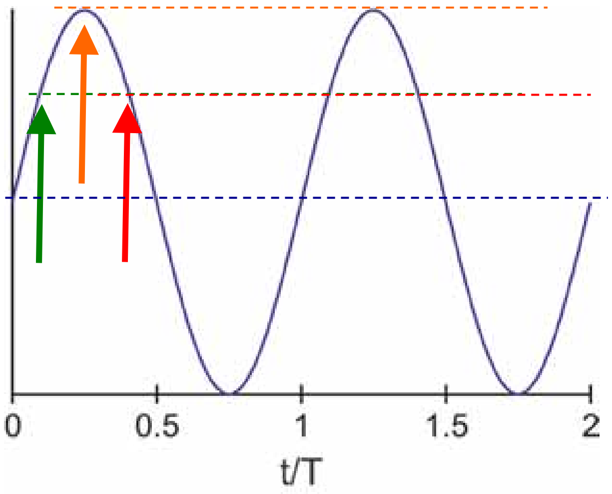
$$\left|g_{1,S}(\mathbf{q},t)\right|^2 = \frac{\sin^2\left(q_{\parallel}H\gamma(t)/2\right)}{\left(q_{\parallel}H\gamma(t)/2\right)^2}$$

- Oscillatory shear flow: $\gamma(t) = \gamma_0 \sin\omega t$

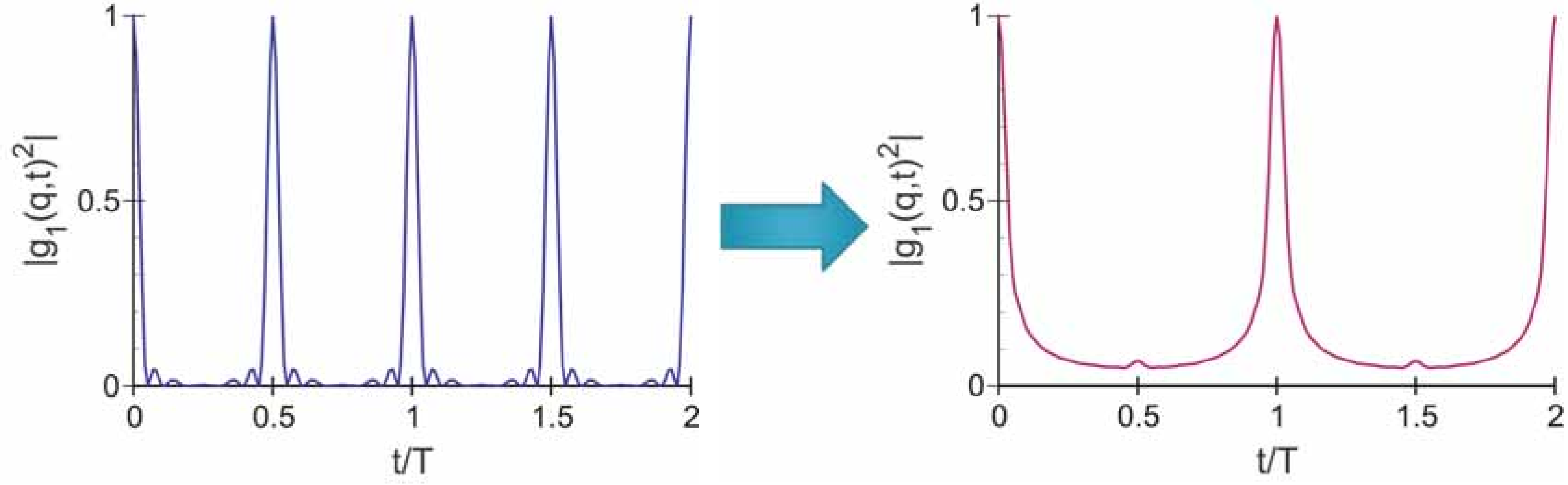
$$\left|g_{1,S}(\mathbf{q},t)\right|^2 = \frac{\sin^2\left(q_{\parallel}H\gamma_0\sin\omega t/2\right)}{\left(q_{\parallel}H\gamma_0\sin\omega t/2\right)^2}$$

If there's no diffusive motion, autocorrelation function will be *periodic*.

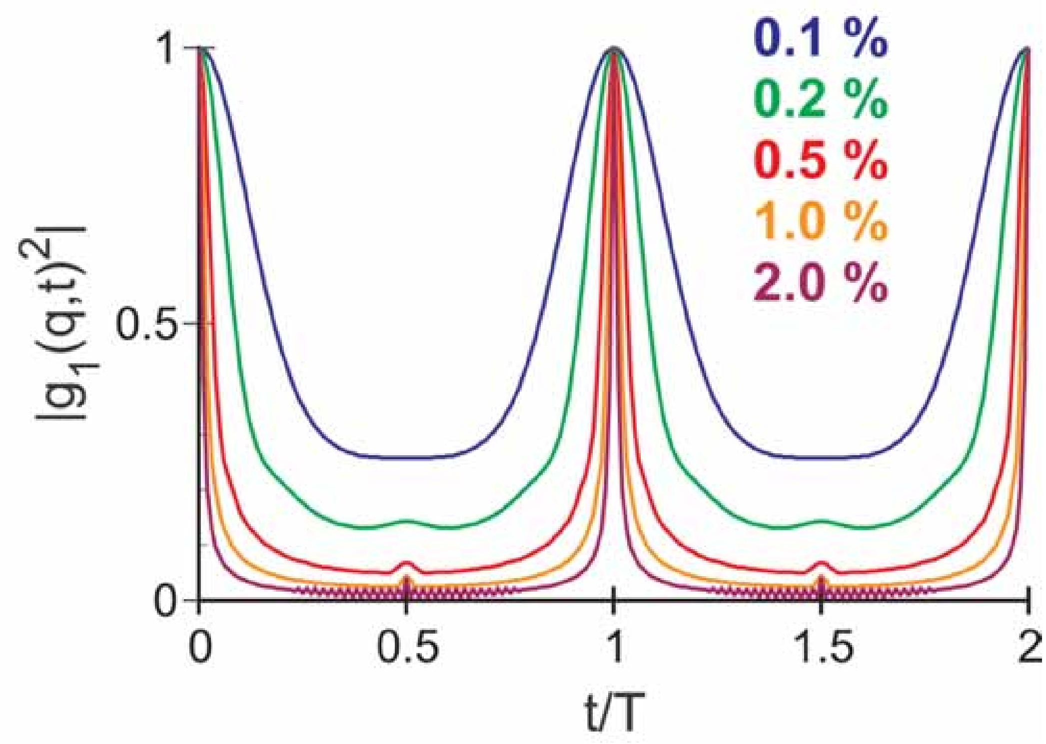
Oscillatory shear correlation



Computed using representative parameters:
H = 0.4 mm
$q_{||}$ = 0.01 nm^{-1}
γ_0 = 0.5 %



Oscillatory shear: impact of strain

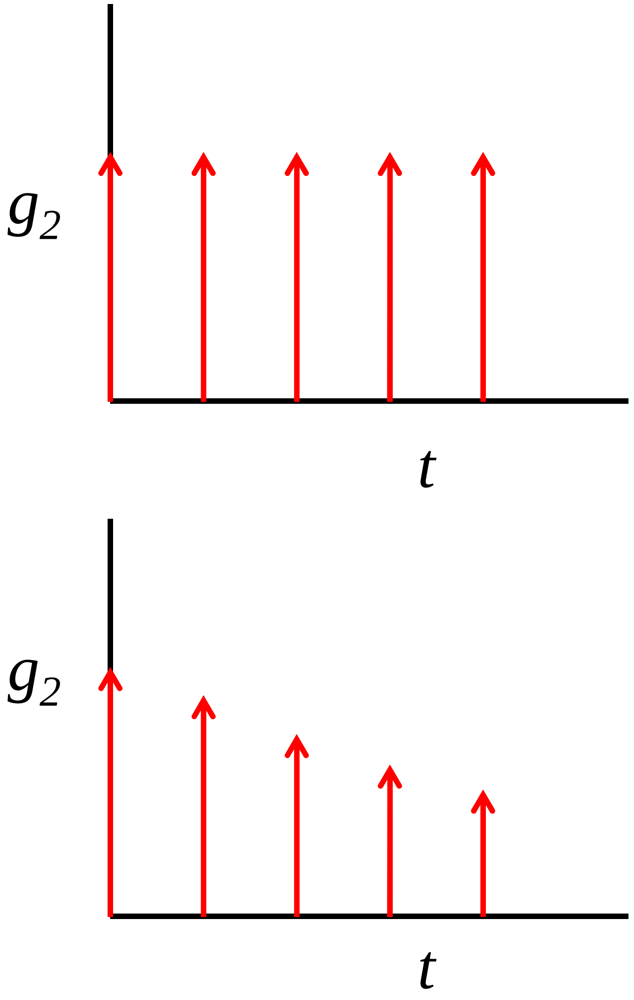


<u>Comments</u>:

- It doesn’t take much shear strain to de-correlate speckle pattern
- *In absence of internal structural dynamics*, autocorrelation function will oscillate indefinitely, returning to its initial value once every strain period.

Possible application of XPCS in oscillation

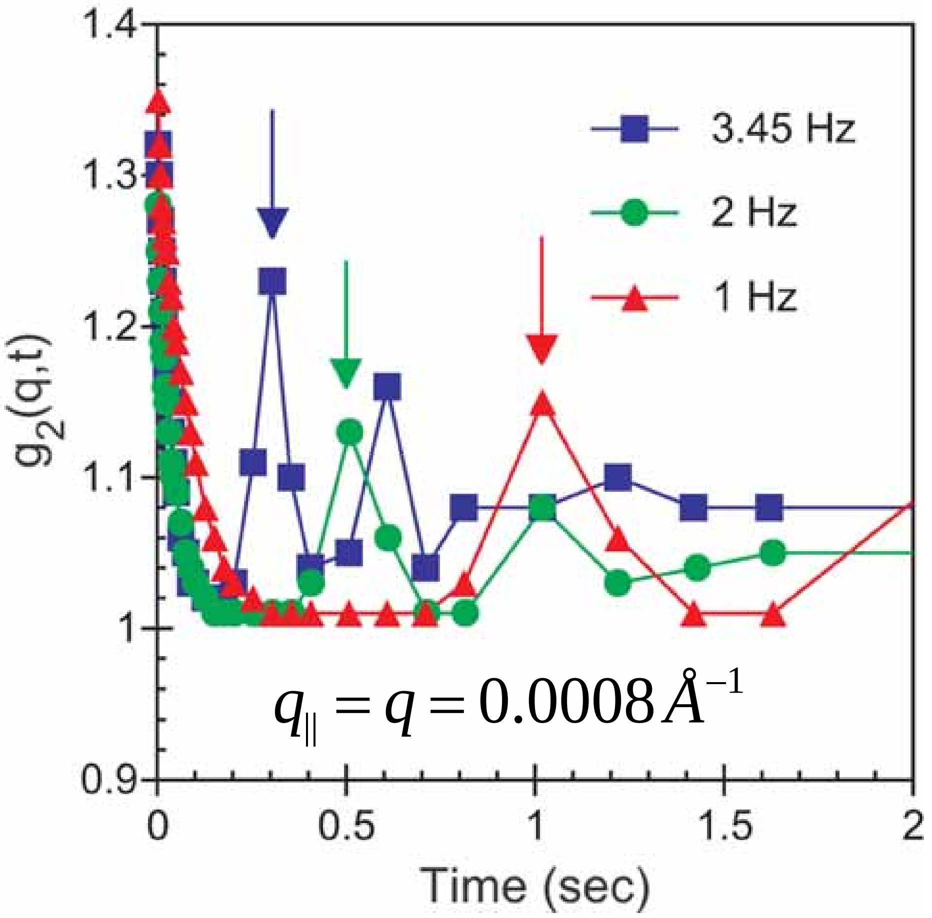
- Consider soft solids (e.g. weak particulate gels)
  - At low strains, no diffusive dynamics; deformation perfectly reversible at all structural scales
  - At larger strains, applied shear disrupts structure, leads to irreversibility in structural dynamics
  - Potentially sensitive way to study onset of microscopic yielding processes in detail.



Trial experiments

- R. Leheny, J. Harden & S. Ramakrishnan
- Gels of silica nanoparticles in decalin induced by polymer depletion forces
- In 'aged' state, negligible relaxation of intensity autocorrelation function over time scales of tens of seconds
- XPCS performed using fast CCD, similar experimental setup as in earlier homogeneous shear studies (input oscillatory waveforms imperfect due to mechanical backlash)

Oscillatory data

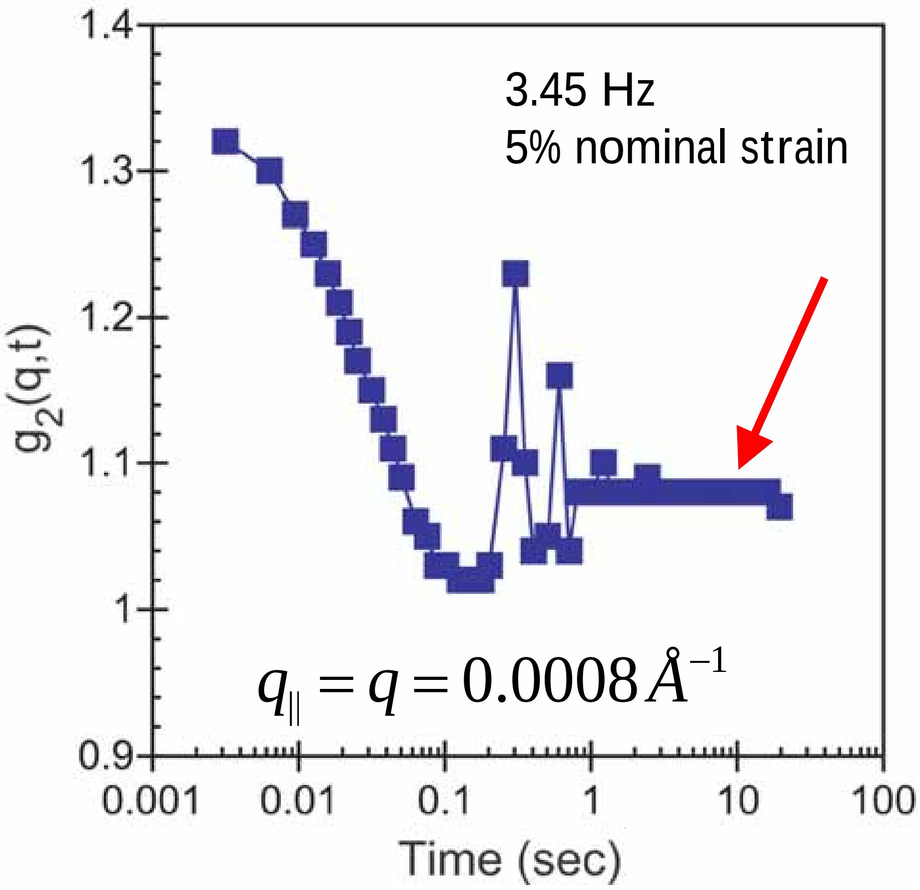


$$q_{\|} = q = 0.0008\,\AA^{-1}$$

Nominal strain = 5%
Estimated actual strain ~ 2%

- Oscillation in g_2 is clear, time scales correct
- Details obscured by smoothing from multi-tau correlator algorithm

Oscillatory data… long time



$$q_{\parallel} = q = 0.0008\,\mathring{A}^{-1}$$

- At long times, observe time-average of oscillatory response due to poor time resolution

- Constant value suggests that oscillatory shear at this strain level is not introducing irreversible changes to fluid structure

XPCS following shear

- Accessing nonlinear phenomena during shear looks to be difficult due to dominant direct effect of shear on autocorrelation function
- Alternative: induce structural changes through vigorous *pre*-shearing; use XPCS following shear to interrogate dynamic consequences
- When sample dynamics are slow, this is straightforward

XPCS following flow

- Chung et al, *PRL* **96**, 228301 (2006)
- Silica/polystyrene depletion gel in decalin

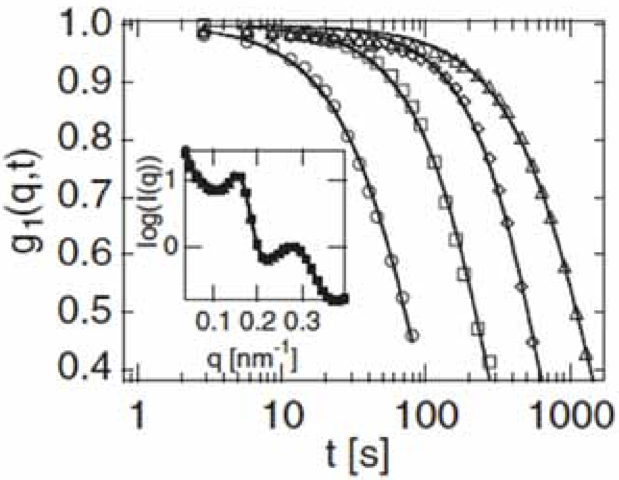


FIG. 1. XPCS intermediate scattering functions at $q = 0.09\ \mathrm{nm}^{-1}$ for gel A following the application of strong shear for recovery times $t_d = 800$ (circles), 2500 (boxes), 6100 (diamonds), and 13 000 s (triangles). The solid lines are the results of fits to a compressed exponential form. The inset shows the x-ray scattering intensity for these different times.

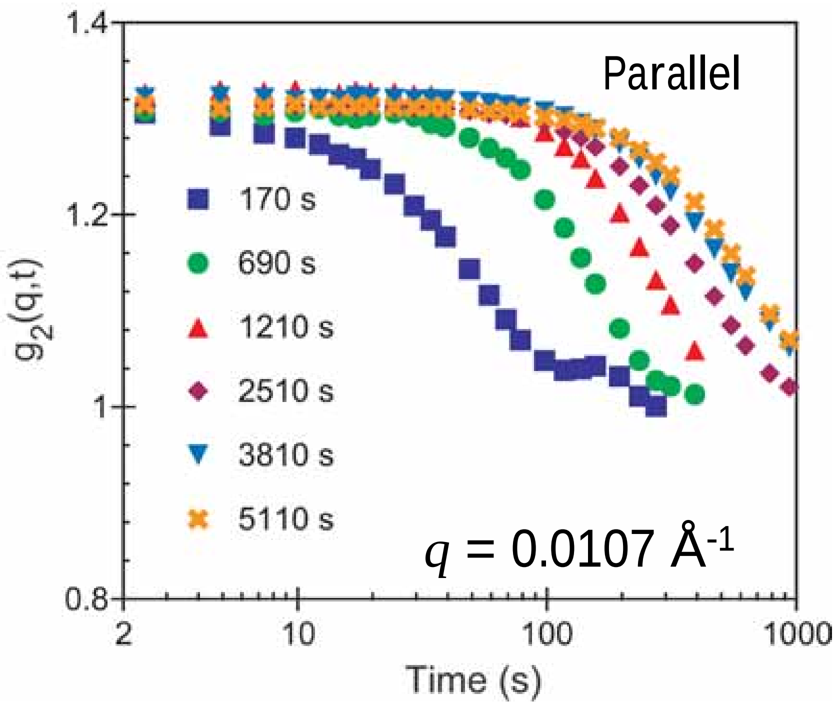
- Severe, but poorly defined flow history as sample was mixed and extruded into sample cell from syringe

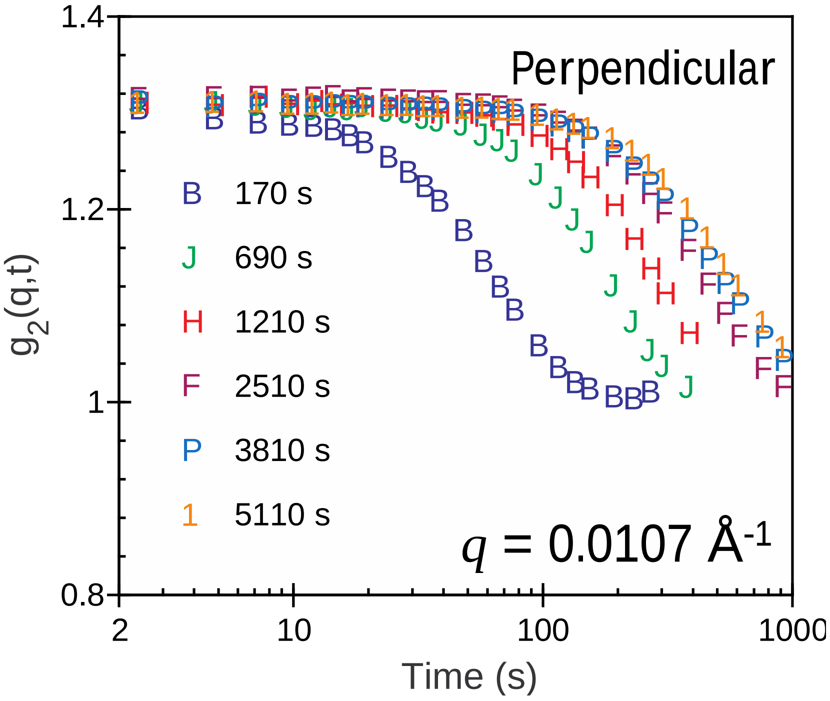
- XPCS used to monitor evolution of sample's dynamics over extended period following flow cessation

- Soft-glassy concepts

Similar experiment, controlled flow history

- Approx. 100 seconds of shear at 2 s^{-1}
- 6 sequential series of XPCS data acquisition
- Detector sectioned into regions parallel & perpendicular to flow direction





What about faster samples?

- This approach already works well for ‘sluggish’ samples using existing XPCS capabilities
  - Slow evolution of slow dynamics
- Many samples will have faster relaxation times, and will relax back to equilibrium structure and dynamics on such faster time scales
  - Substantially greater experimental challenge
  - Alternate experimental/analysis strategies
    - Two-time correlation function?
  - *Demanding & potentially productive application for enhanced XPCS capabilities?*

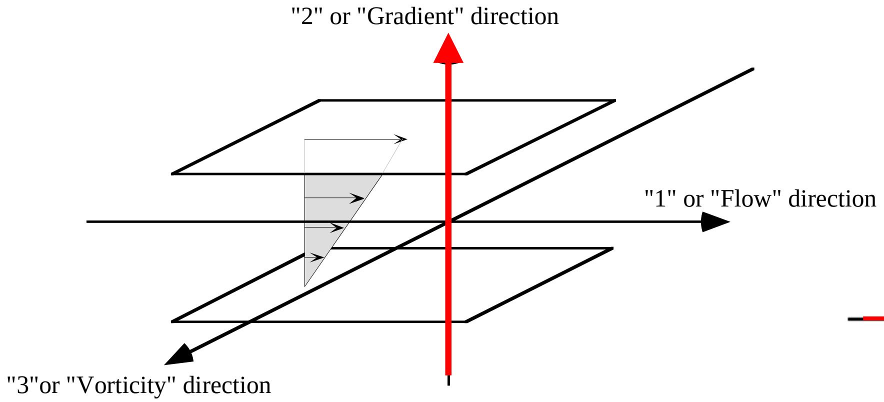
General issues/needs from shear flow perspective

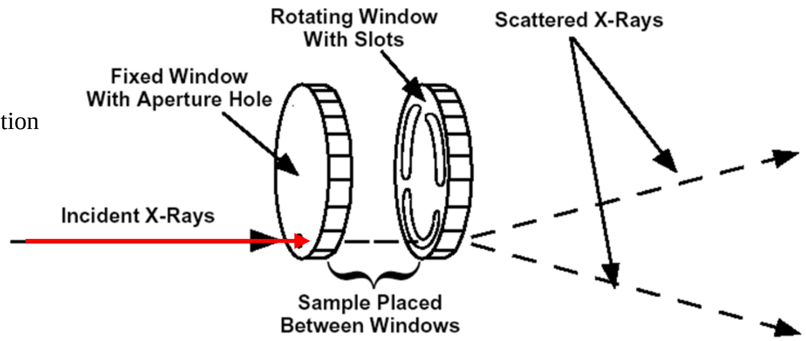
- Higher energy (than APS 8ID-I)
  - Reduced x-ray absorption facilitates shear flow devices
- Faster detectors
  - Autocorrelation functions measured during shear naturally involve fast time scales
- Higher flux of coherent photons will enable more demanding applications
- Ever present beam damage concerns… shear flow helps here

Acknowledgments

- APS Sector 8
  - Marcin Sikorski, Alec Sandy, Suresh Narayanan & Ray Ziegler
- APS XSD Visitor Program
- S. Ramakrishnan, J. Harden & R. Leheny

Sealed rotating disk shear cell for solutions





Shear banding in complex fluids

Uniform shear:

- Localized band of high velocity gradient
- Constitutive instability and/or phase separation