Complex Dynamics of Nanoparticles in Highly Concentrated Entangled Networks Revealed by XPCS

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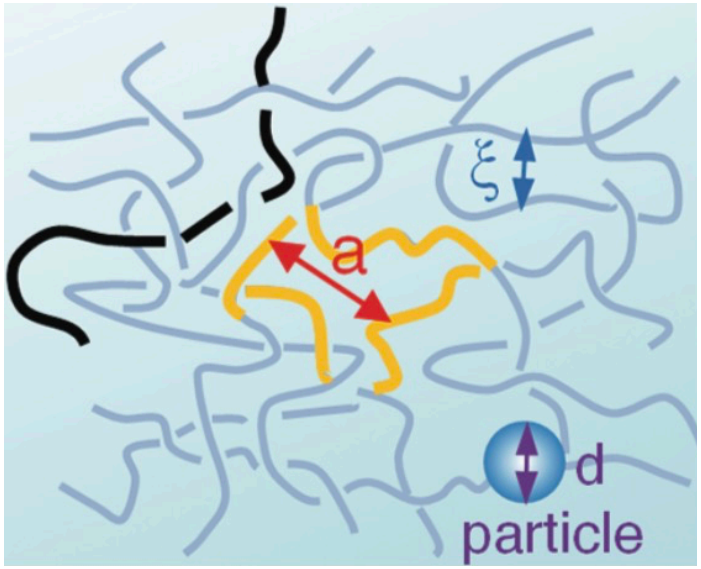
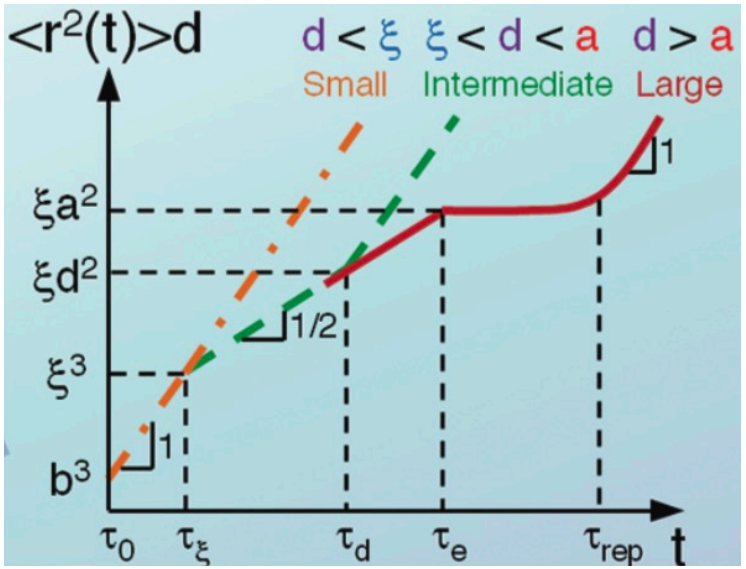
Nanorheology



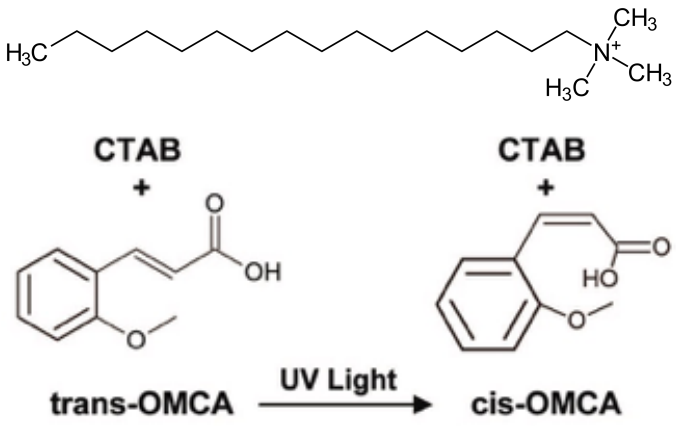


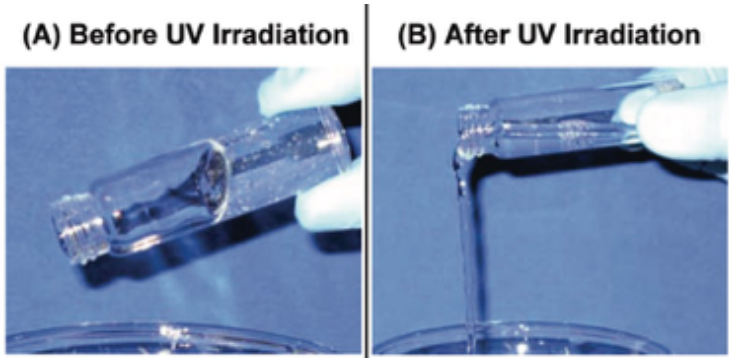
allows for studying…

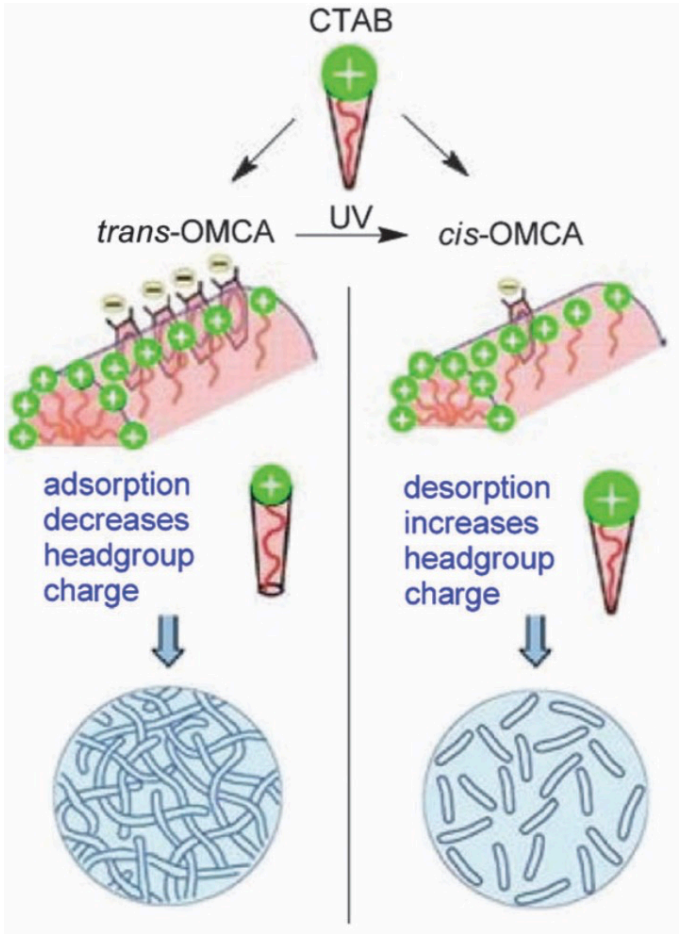
- local viscoelastic and dynamical properties of the entwined micelle network,
- interaction between network and particle dynamics.

Cai, *et al.*, *Macromolecules* **44,** 7853 (2011)

Photorheological Liquids

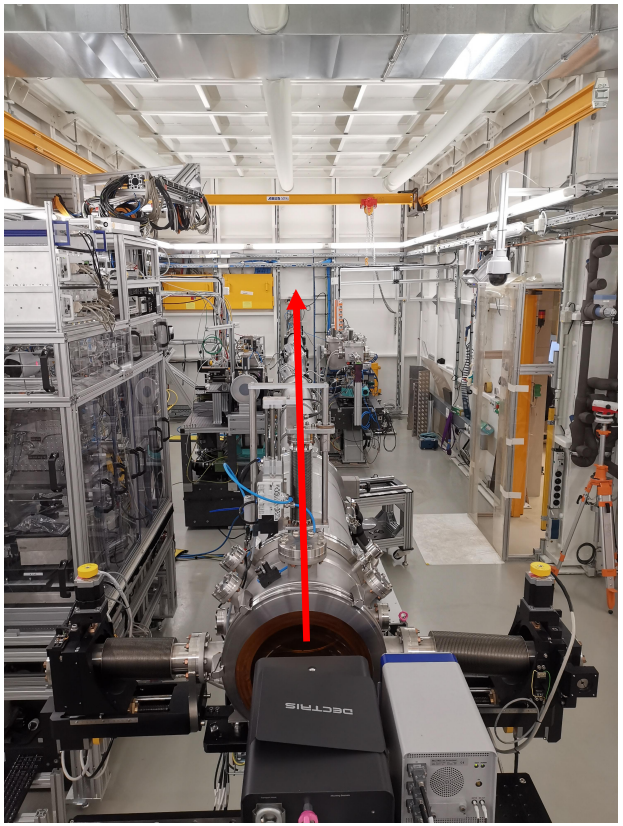






Ketner, *et al.*, *J. Am. Chem. Soc.* **129,** 1553 (2007)

Large Beam XPCS – P10 and ID02



P10 – Experimental Hutch II

	ID10	P10	ID02
photon energy in keV	8.1	8.1	12.4
Detector	Eiger 500k (PSI)	Eiger 500k (Dectris)	Eiger 500k (PSI)
maxi rep rate (Hz)	22 000	9 000	22 000
beam size A (μm^2)	10x10	75x75	30x30
detector distance R (m)	5	21	30m
pixel size (μm^2)	75x75	75x75	75x75
sample thickness (mm)	2	2	2

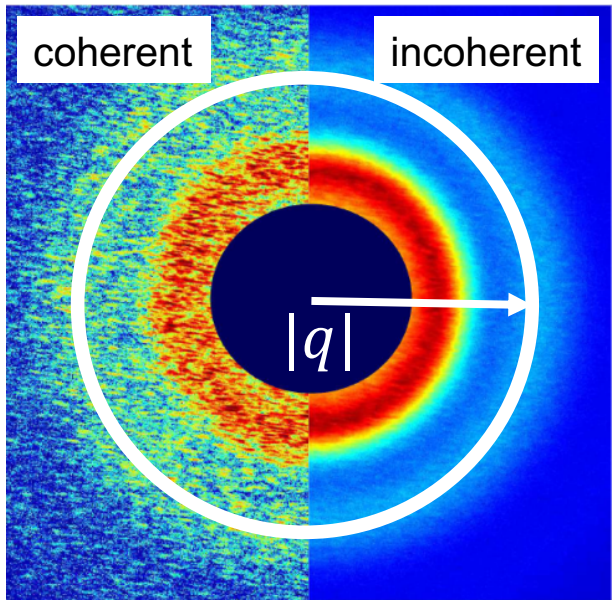
radiation sensitive samples

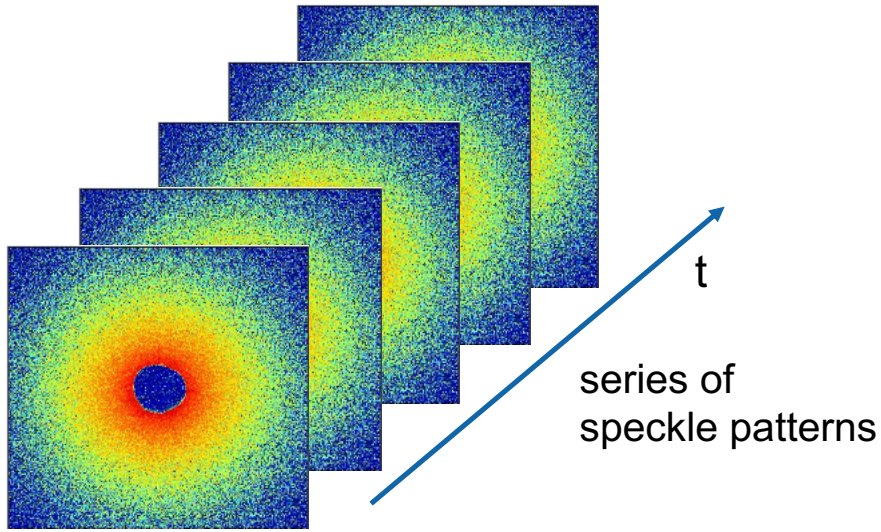
critical dose $D_c \propto \frac{F}{A}$

speckle size $s \propto \frac{R}{A}$

Meisburger *et al.*, *Biophys. J.* **104**(1), 227 (2013)

X-Ray Photon Correlation Spectroscopy (XPCS)



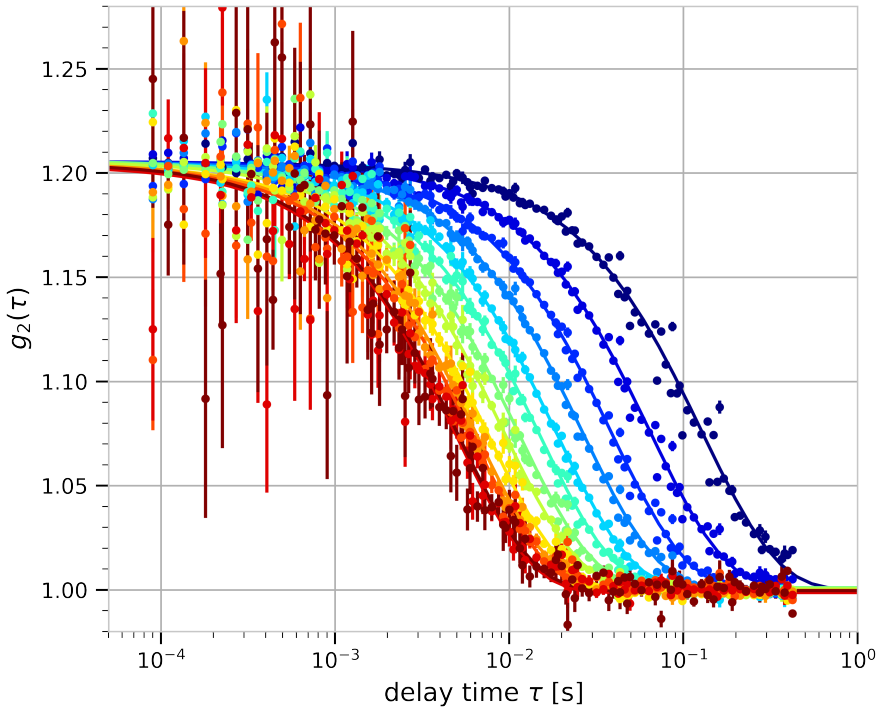


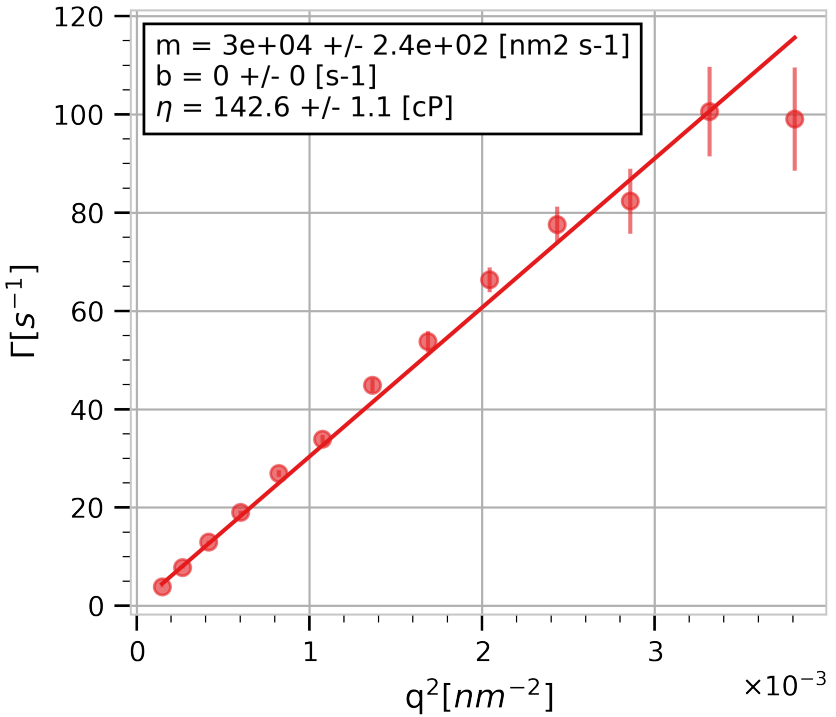
Intensity auto-correlation function

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau)\rangle_{\mathrm{pix,t}}}{\langle I(t)\rangle^2_{\mathrm{pix,t}}} = 1 + \beta_0 |g^{(1)}(\tau)|^2$$

Lee *et al.*, *Opt. Express* **21,** 24647 (2013)

Brownian Diffusion: 100nm SiO2 Spheres in Glycerol-Water Mixture





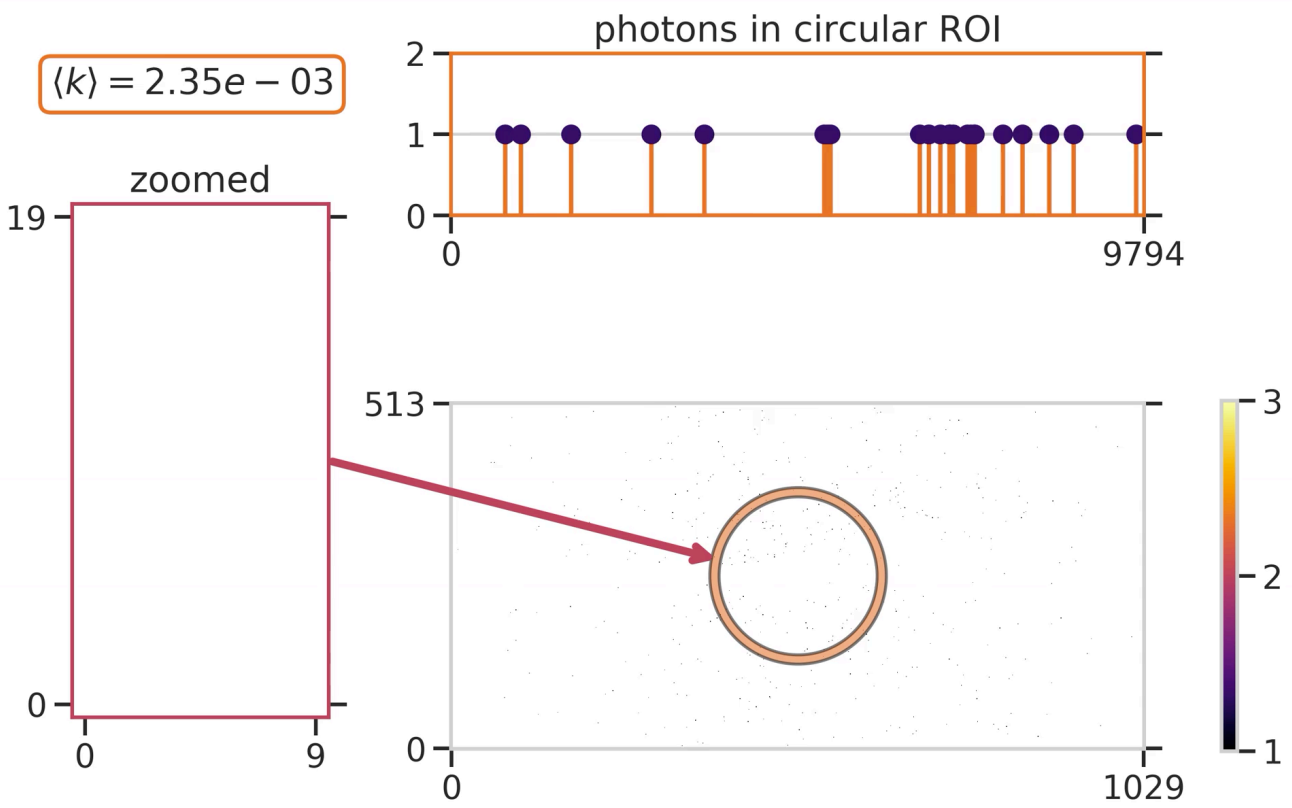
$$g^{(2)}(\tau) = 1 + \beta_0\, e^{-2(\Gamma\tau)}$$

Stokes-Einstein

$$\Gamma(q) = \tau_0^{-1} = D\, q^2\,, \quad D = \frac{k_b \mathcal{T}}{6\pi\eta_0 R_H}$$

Single Time Series for XPCS Analysis

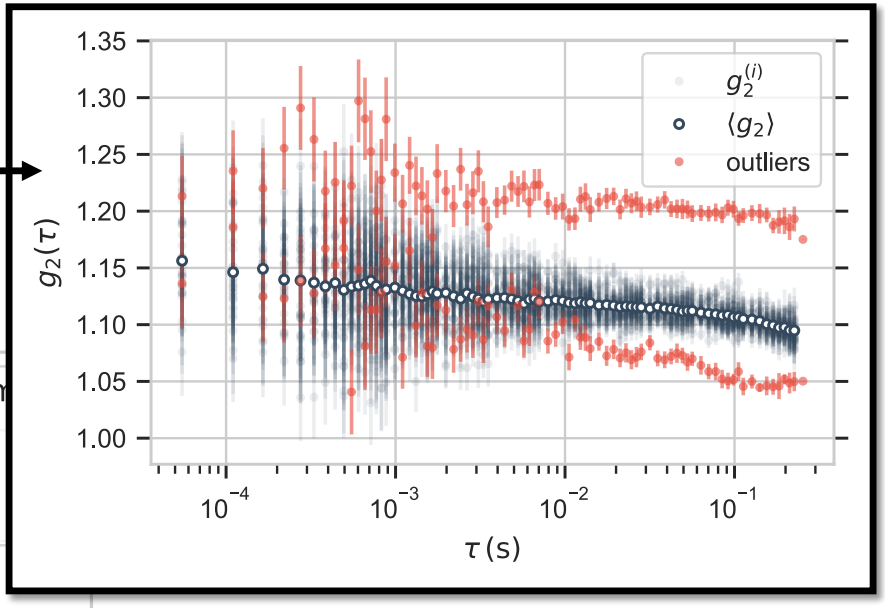
- $100nm$ (ø) SiO2 particles
  - $50mM$ OMCA:CTAB micelles
- 110µs exposure time
- $I_0 \approx 6.25 \cdot 10^{10}$ph s^{-1}

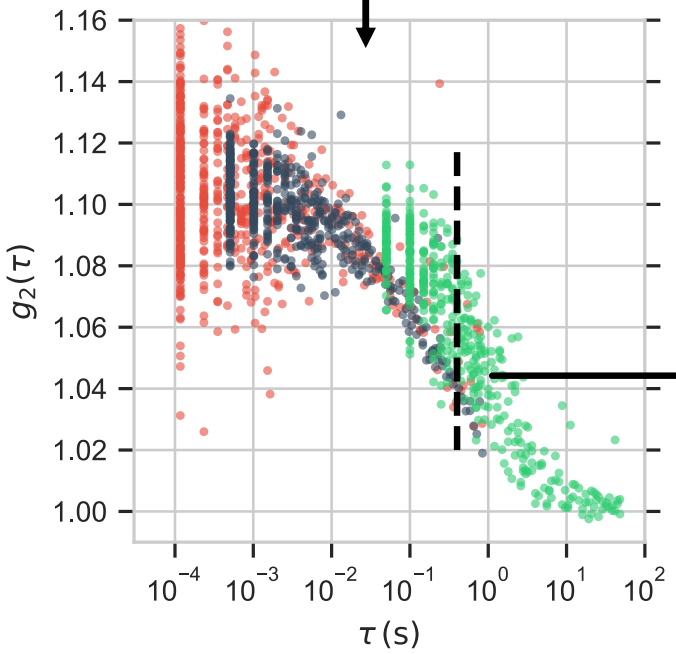


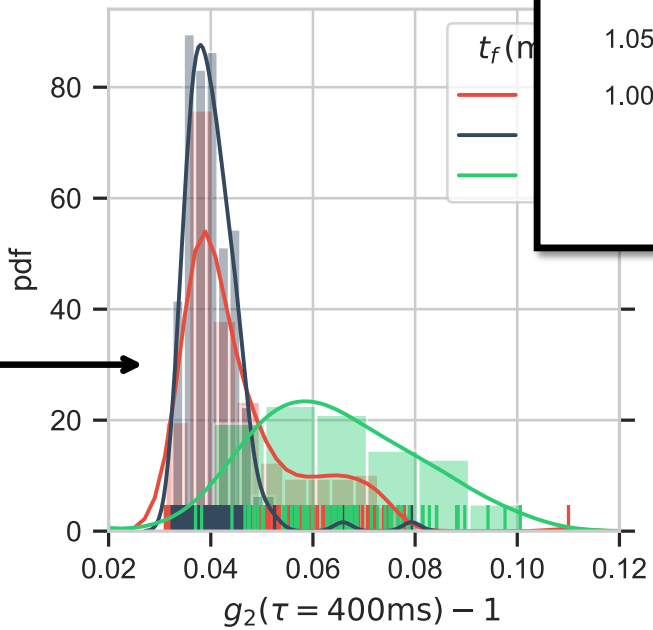
Challenge (Online) Data Analysis

identify outliers

distinguish contributions







$200 \times g_2(\tau)$ per sample

Ferroelectric materials: Gorfman *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **29,** 6680 (2018)

Building Correlation Functions

Single correlation functions measured with $40\mu s$ exposure time

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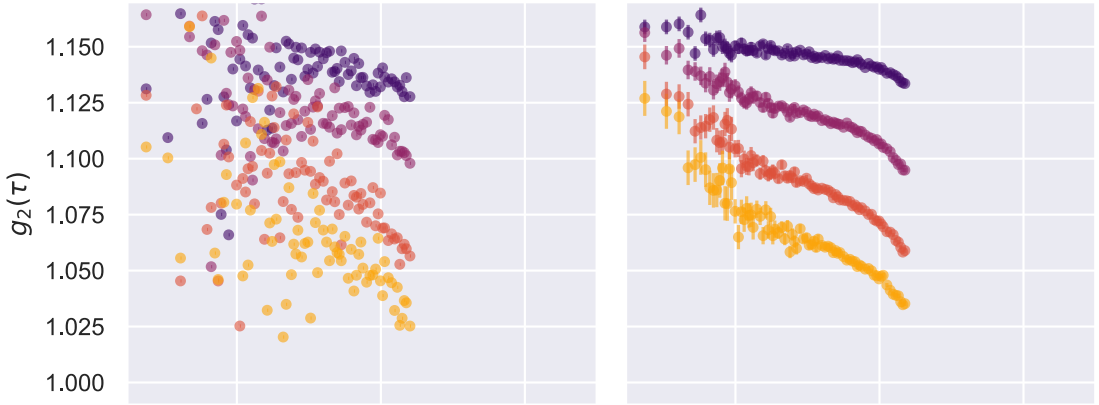
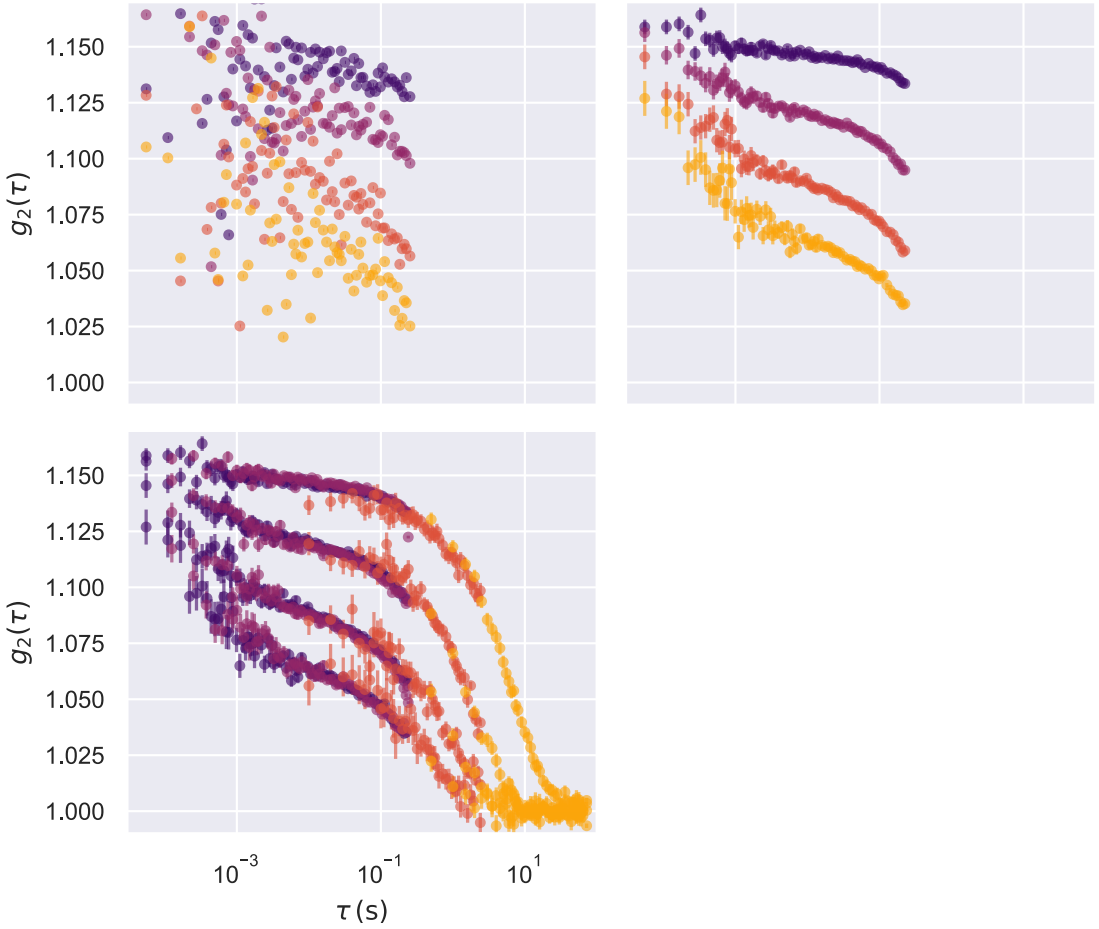


Average of 90 correlation functions measured at different positions on the sample

Building Correlation Functions

Single correlation functions measured with $40\mu s$ exposure time

Combination of measurements with $40, 110\mu s$ and $10, 500ms$



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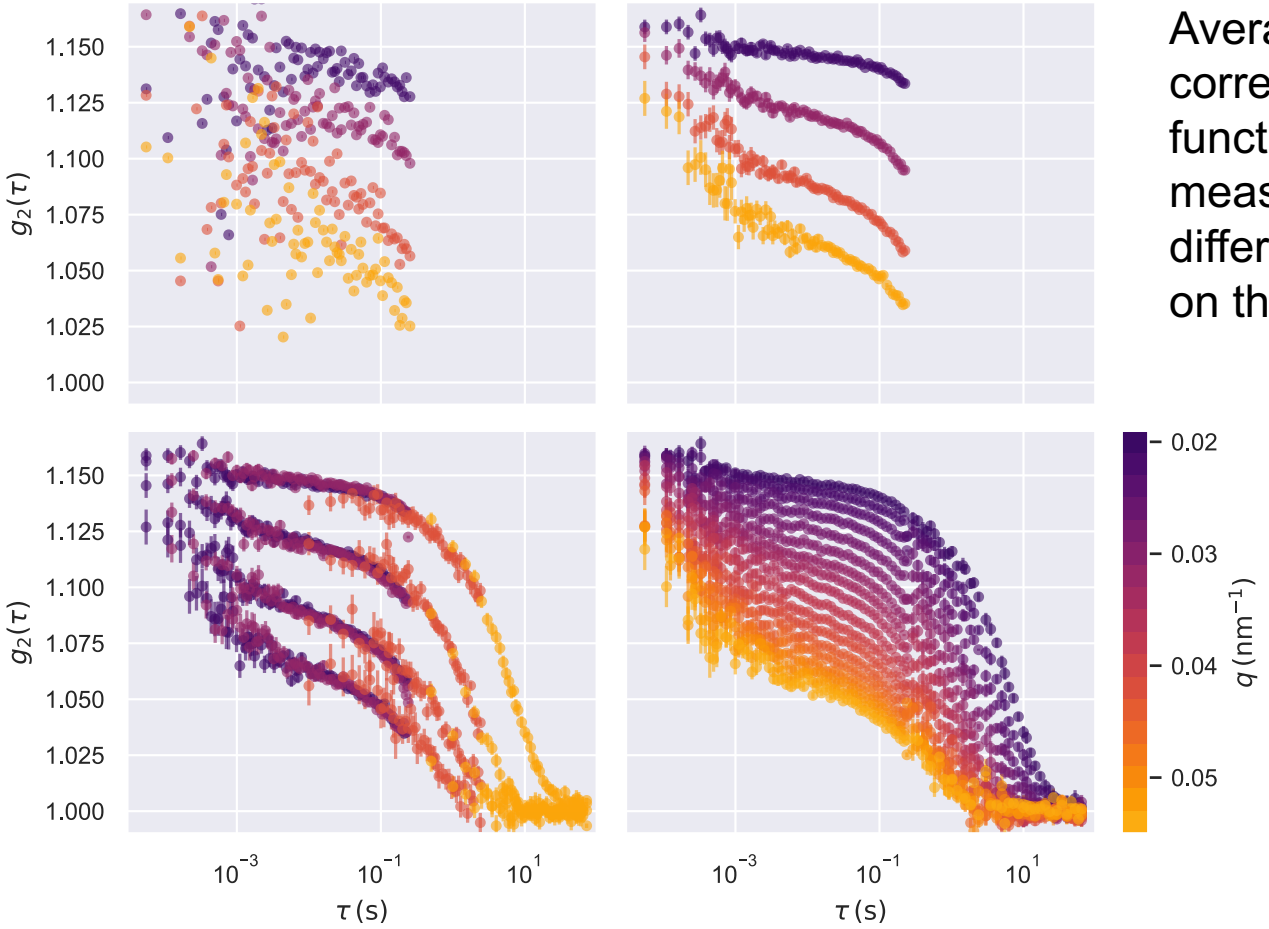
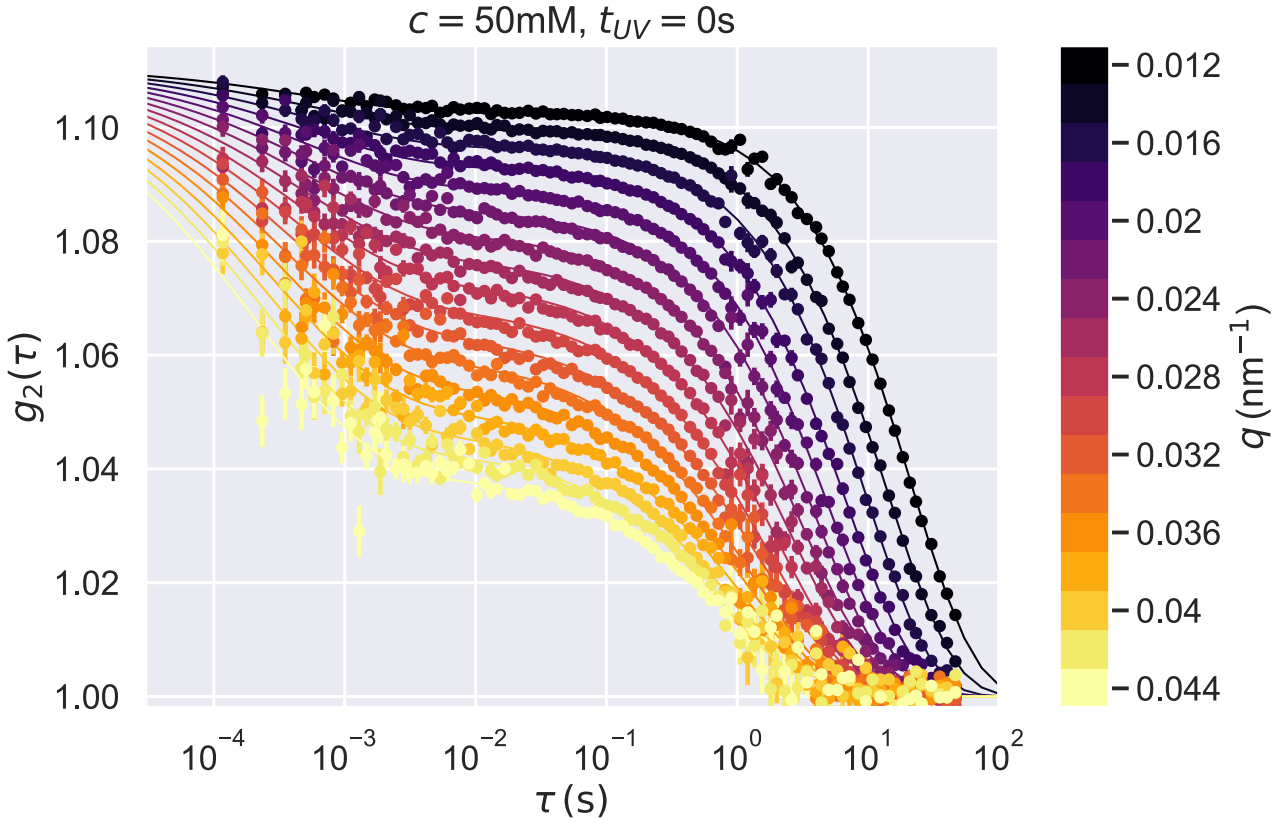


Average of 90 correlation functions measured at different positions on the sample

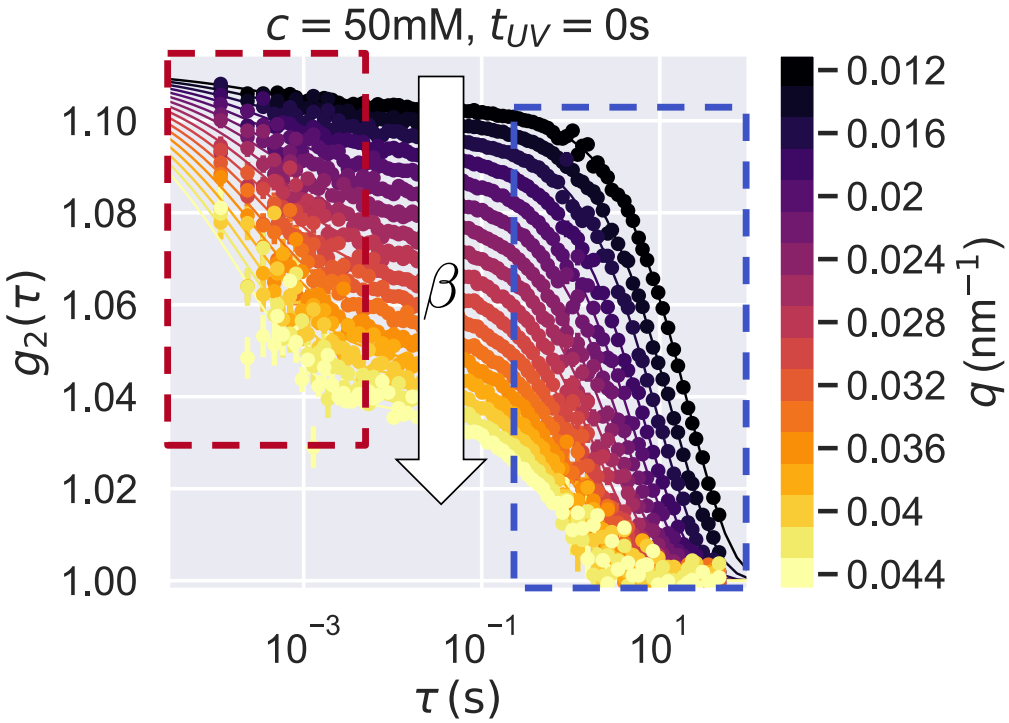
Resampling

Dynamics from microseconds to hundreds of seconds

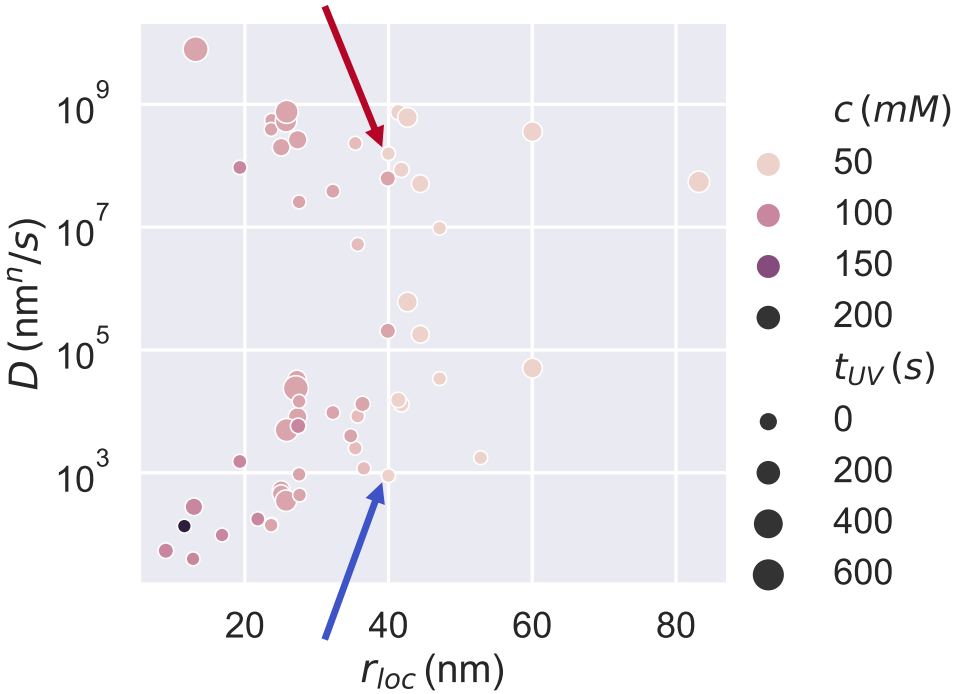


Model $$g^{(2)}(\tau) = 1 + \beta_0 \left((1-\beta)\, e^{-2(\Gamma_1 \tau)^{\gamma_1}} + \beta\, e^{-2(\Gamma_2 \tau)^{\gamma_2}} \right)$$

Model: Double Exponential Relaxation

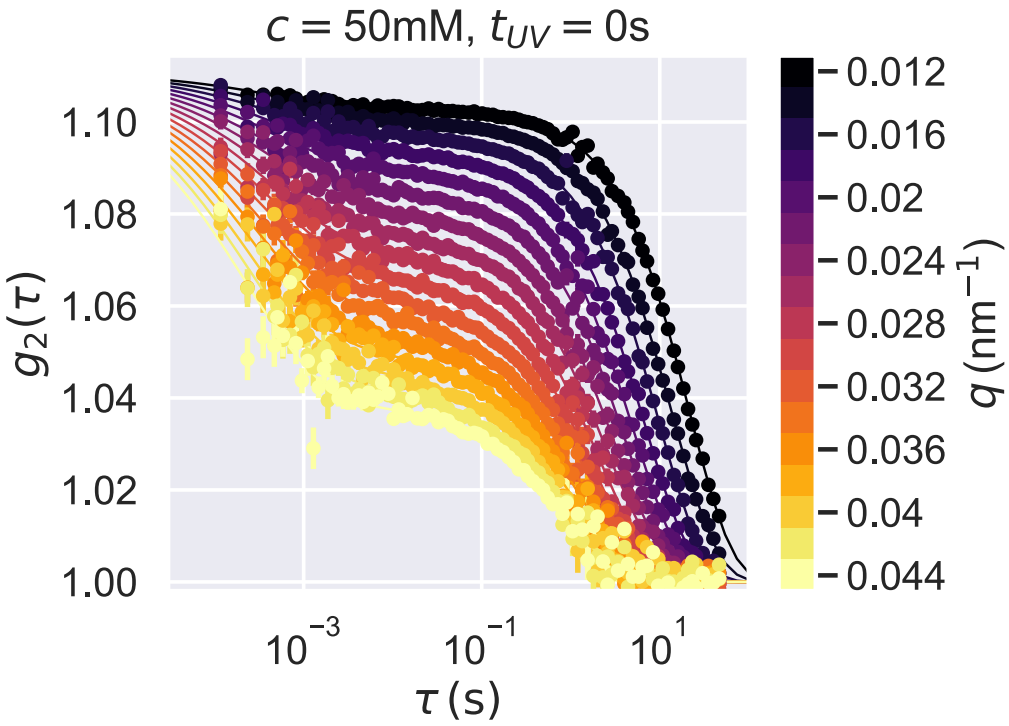


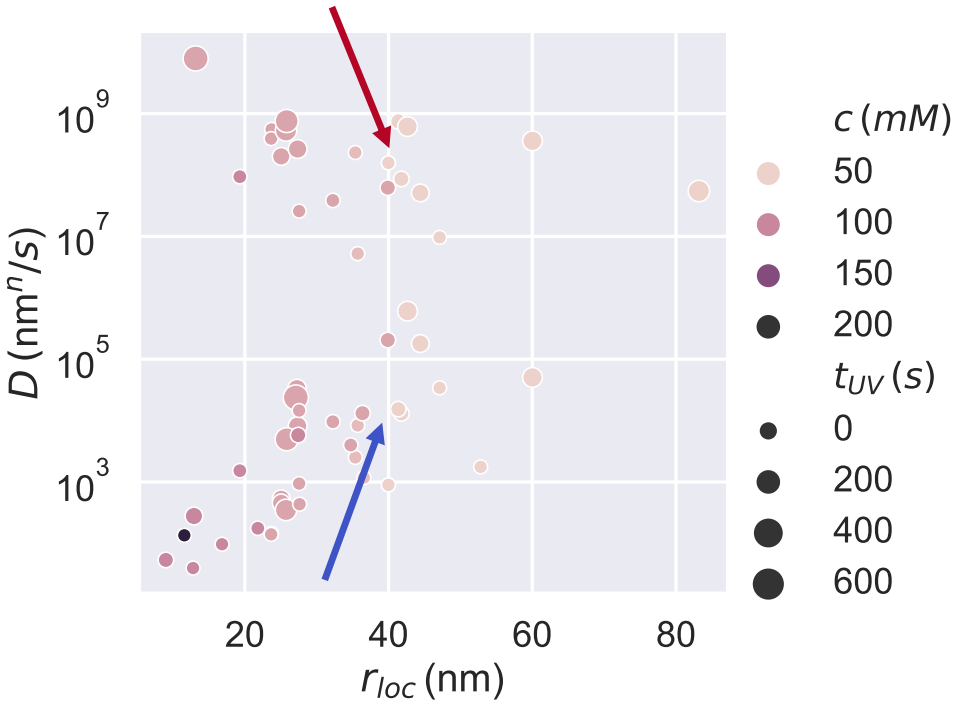
"diffusion coefficient" D: $\Gamma = Dq^n$



localization length r_{loc}: $\frac{\beta}{\beta_0} = \exp\left(-\frac{q^2 r_{loc}^2}{6}\right)$

Changing Confinement Condition





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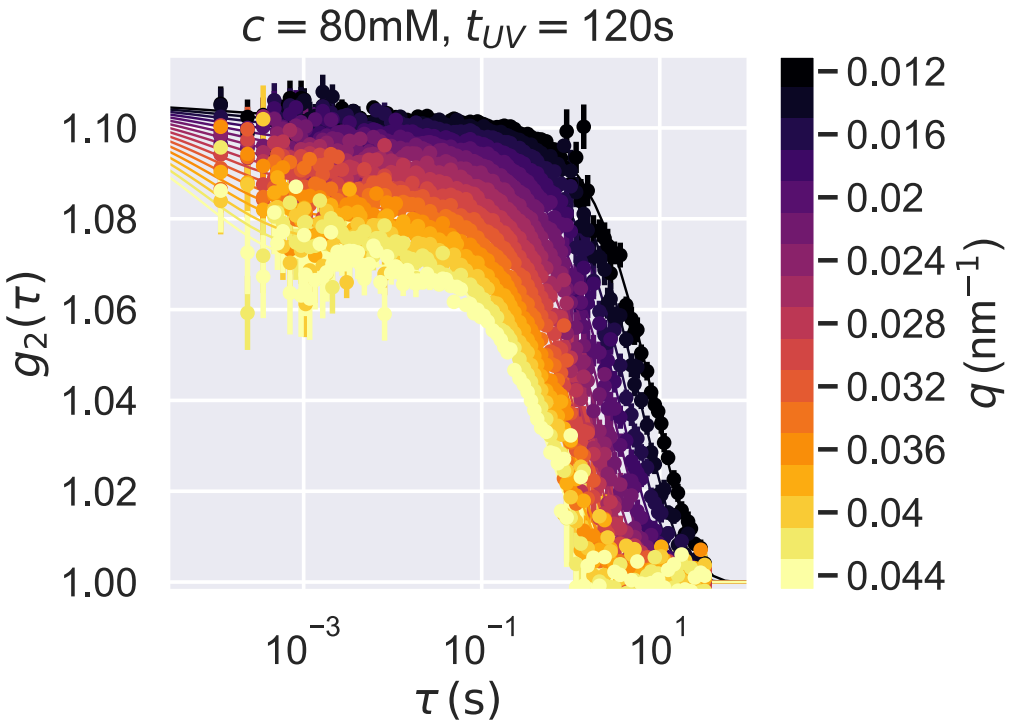

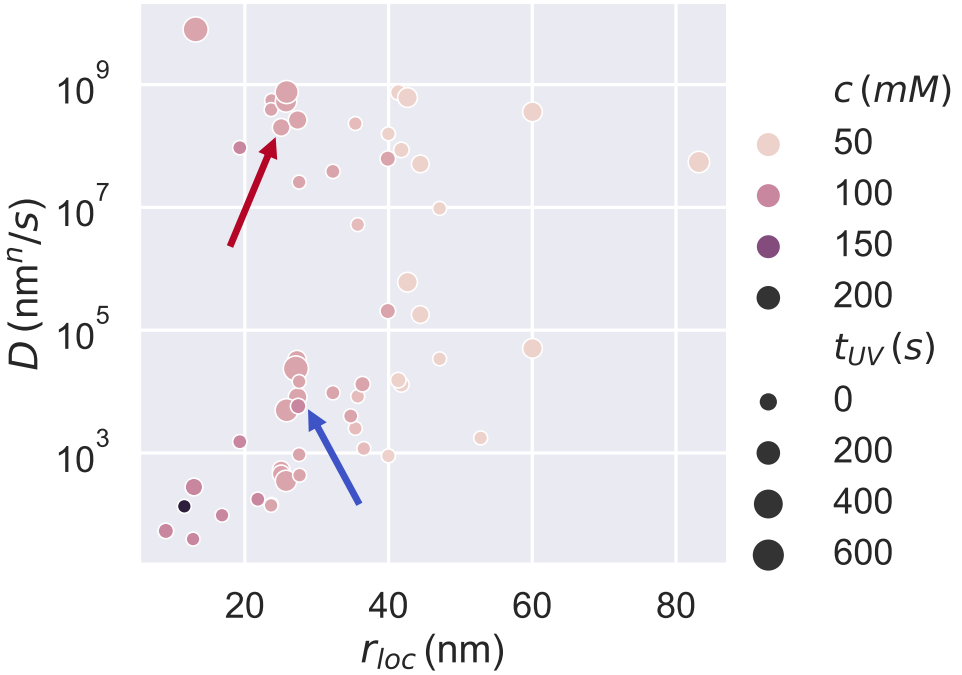

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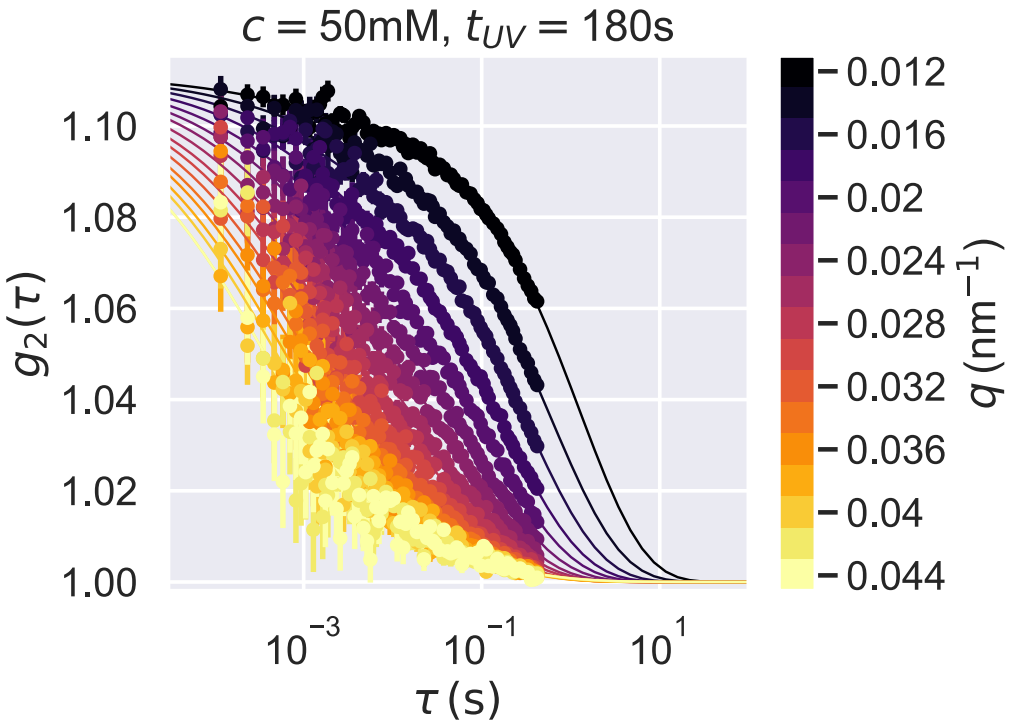

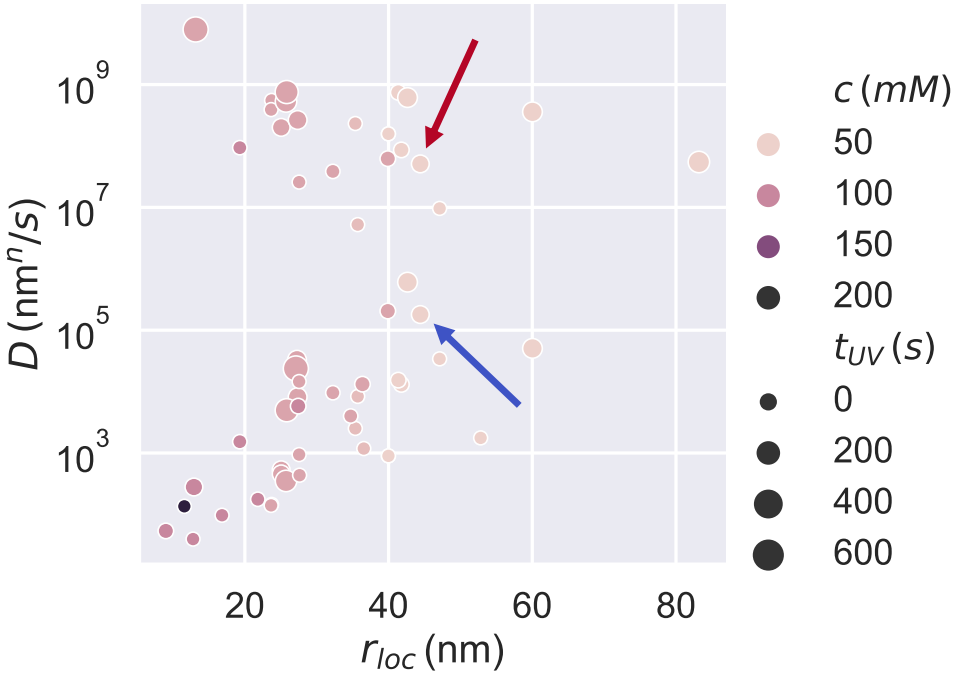

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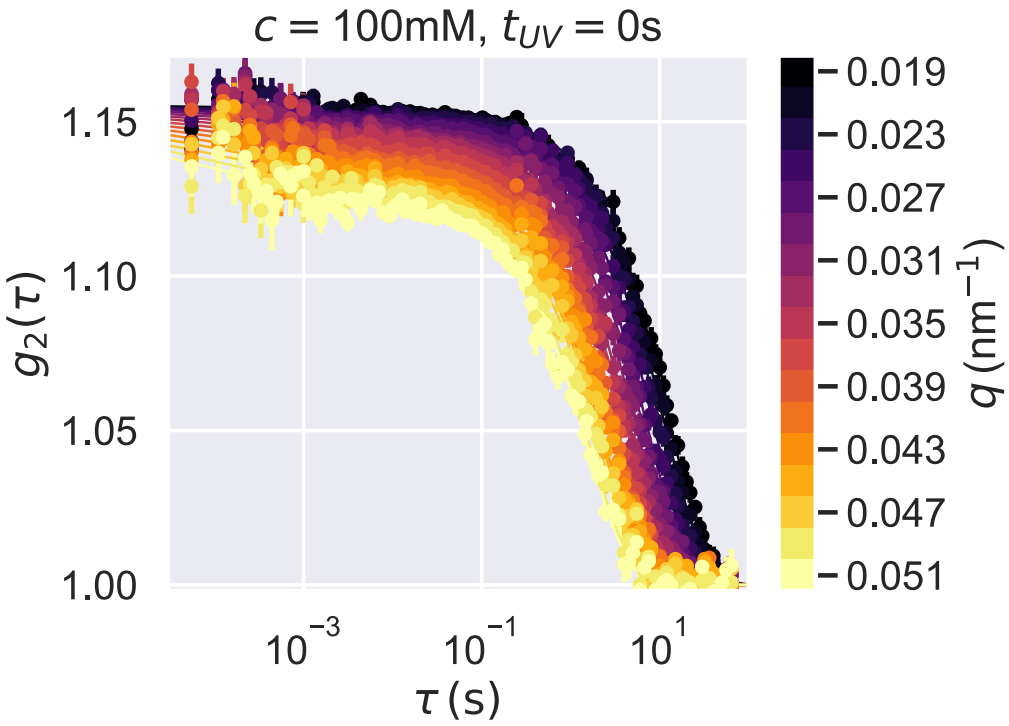
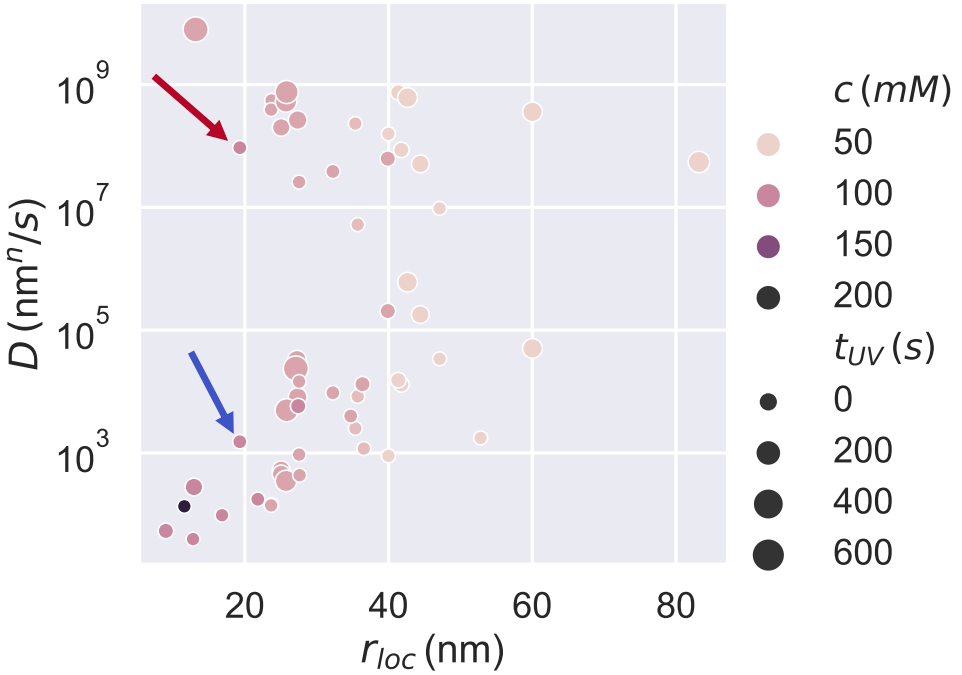
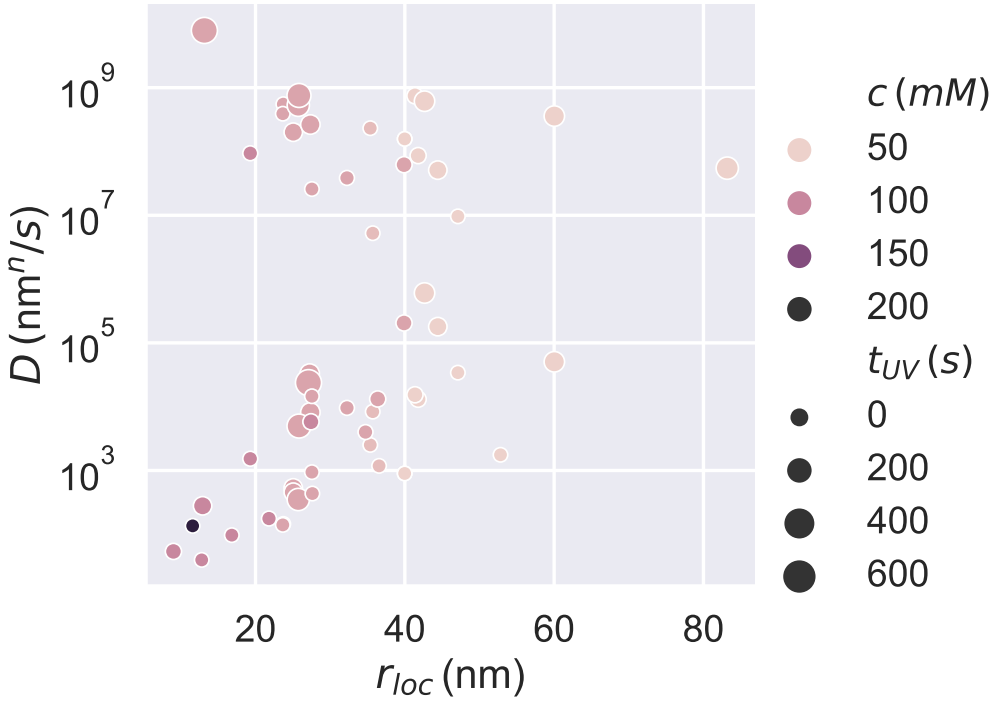
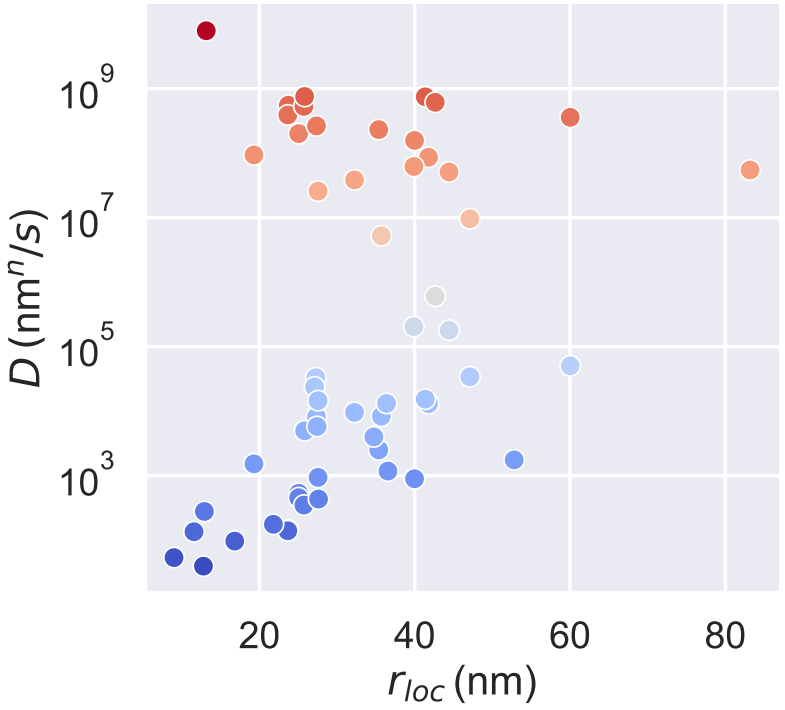




Dynamical Regimes

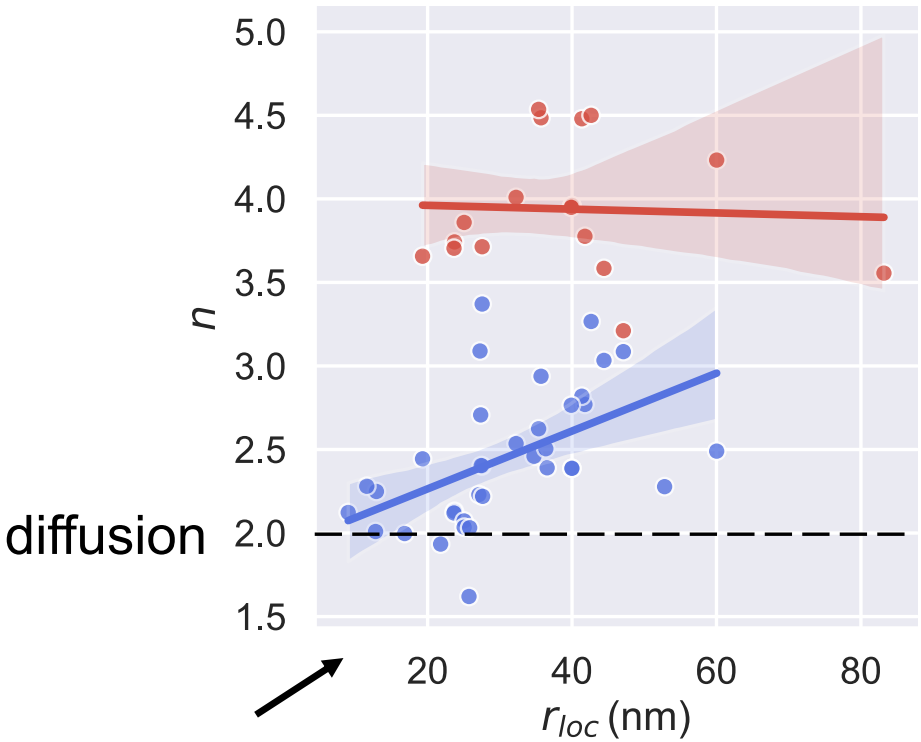


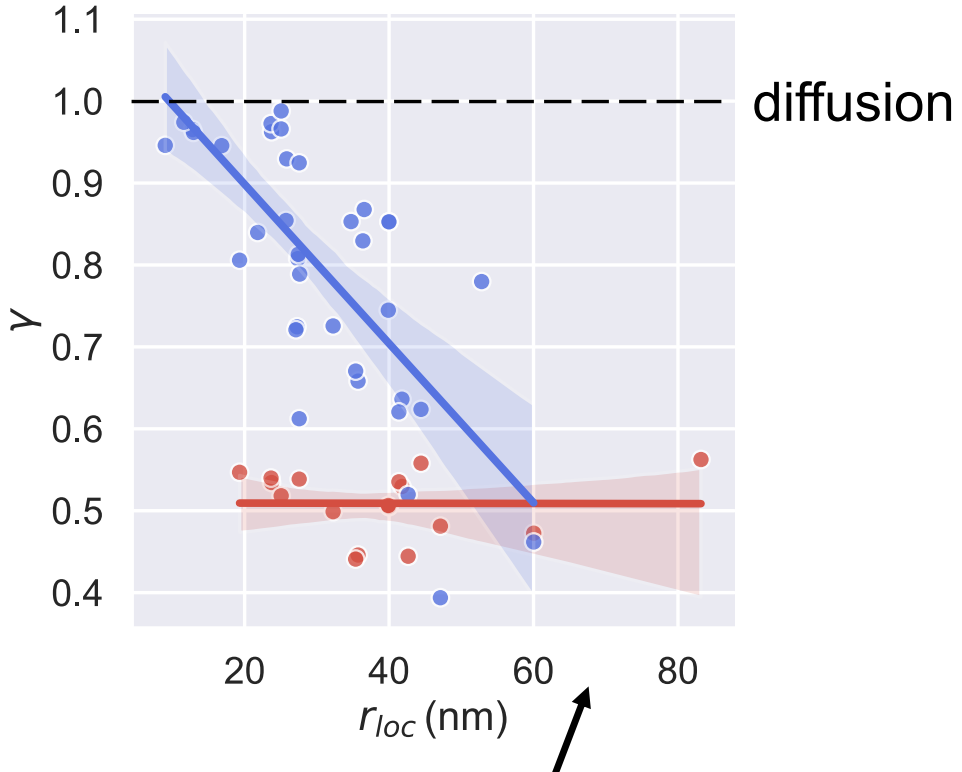
influence of microscopic entanglement strands on dynamics



macroscopic viscoelastic network properties

Transition Between Dynamical Regimes





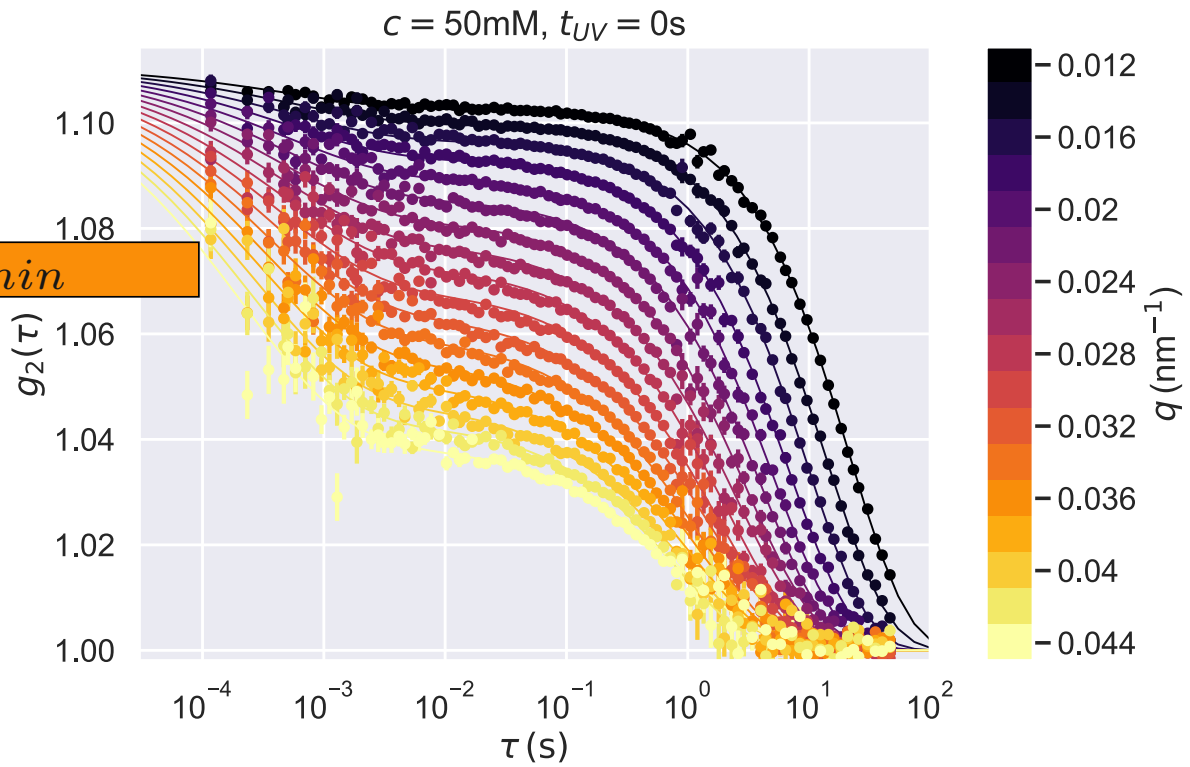
$$\Gamma = Dq^n$$

$$g^{(2)}(\tau) = 1 + \beta_0 \left((1-\beta)\, e^{-2(\Gamma_1 \tau)^{\gamma_1}} + \beta\, e^{-2(\Gamma_2 \tau)^{\gamma_2}} \right)$$

Complex Dynamics Studied with XPCS at ESRF-EBS

$\tau_{min} \propto \text{Brilliance}^{-2}$

τ_{min}



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Thank You