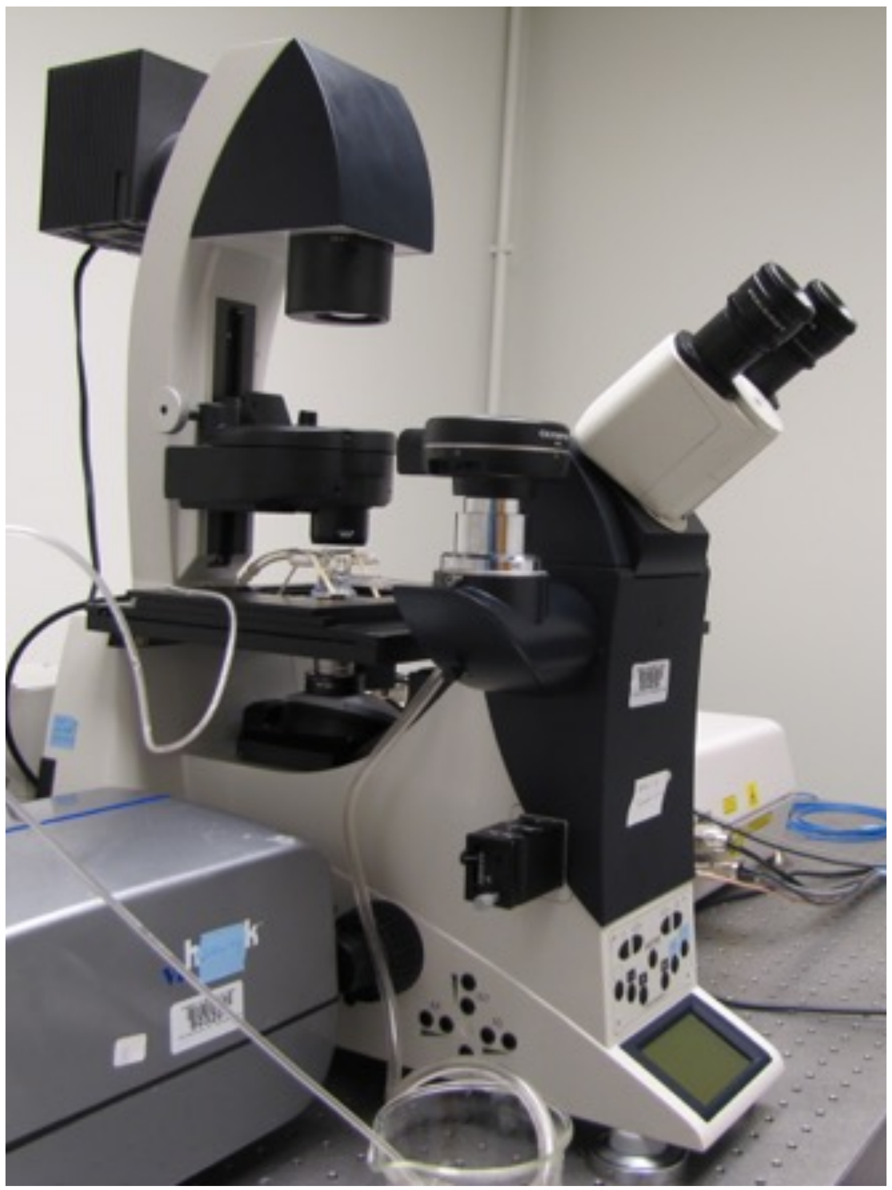
Differential dynamic microscopy: scattering in an optical microscope



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Structure and Dynamics of Soft Matter
CNMS User Meeting 2015

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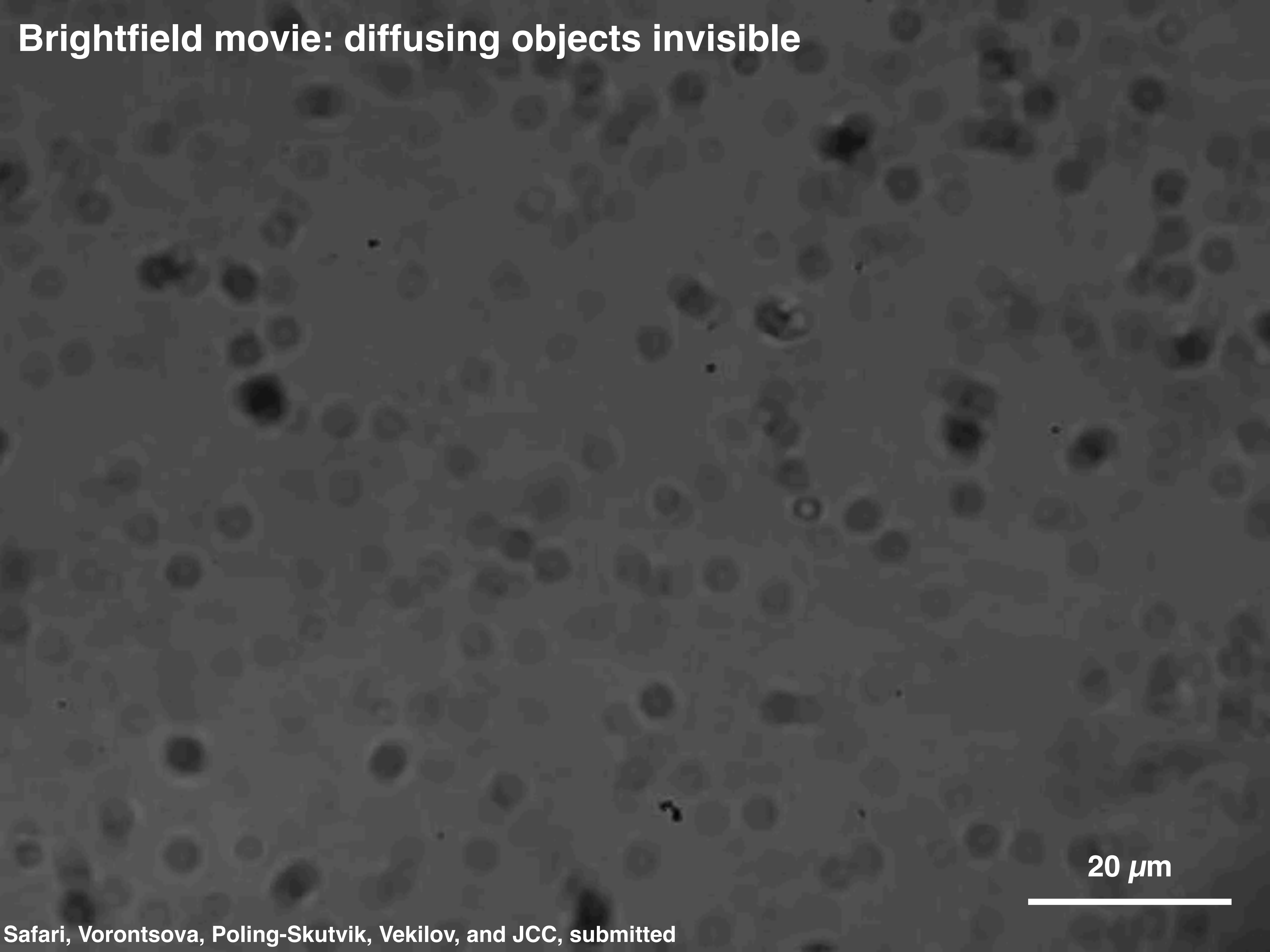
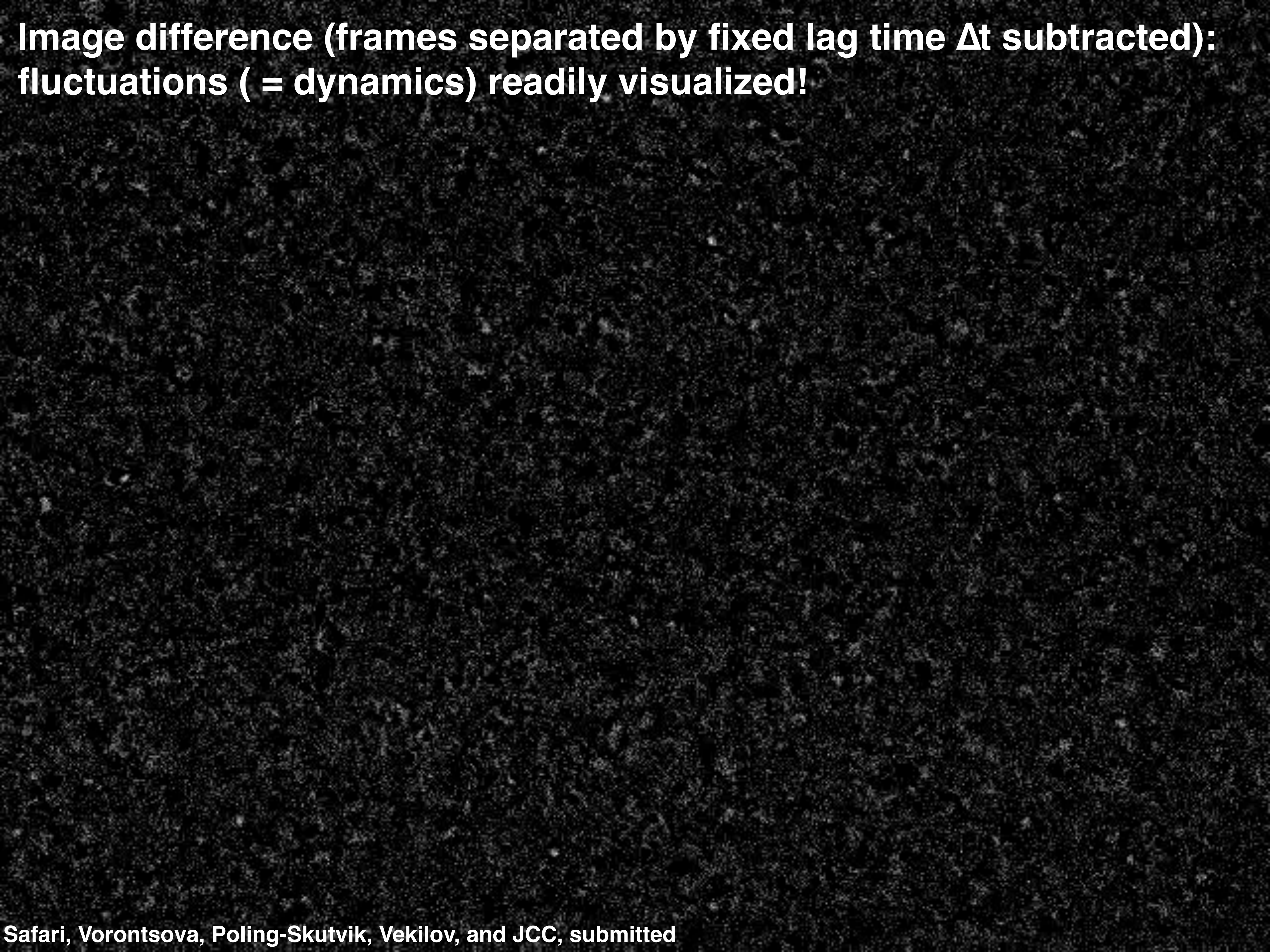
Brightfield movie: diffusing objects invisible



Safari, Vorontsova, Poling-Skutvik, Vekilov, and JCC, submitted

Image difference (frames separated by fixed lag time Δt subtracted): fluctuations (= dynamics) readily visualized!



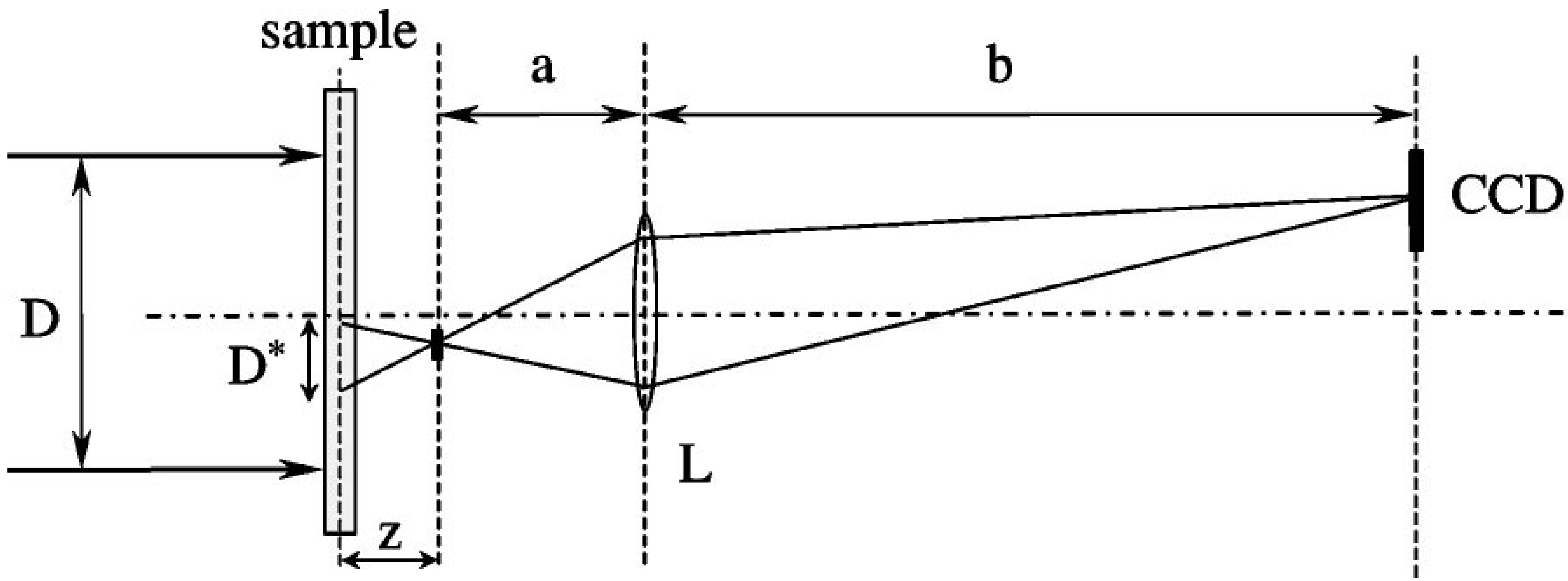
Safari, Vorontsova, Poling-Skutvik, Vekilov, and JCC, submitted

Outline of the tutorial

1. Theory
    i. Heterodyne near-field scattering
    ii. Differential dynamic microscopy
2. Techniques and methods
    i. Brightfield DDM
    ii. Variants: fluorescence, confocal DDM, polarized DDM, ghost-particle velocimetry
3. Applications
    i. Complex fluids: nanoparticles, colloids, liquid crystals
    ii. Biological systems: bacteria and proteins
    iii. Complex geometries

Heterodyne near-field scattering (HFNS) 1

Near-field scattering (NFS): light scattered from a large collimated beam collected by a close-placed CCD, in which each pixel can be reached by light scattered over all angles



Heterodyne detection: weak fluctuating scattered beam interferes with strong transmitted beam:

intensity $f(\mathbf{r},t) = i_0(\mathbf{r}) + e_0(\mathbf{r})e_S^*(\mathbf{r},t) + e_0^*(\mathbf{r})e_S(\mathbf{r},t) + |e_S(\mathbf{r},t)|^2$

$e_0(\mathbf{r})$: static electric field associated with transmitted beam
$e_S(\mathbf{r},t)$: time-dependent forward-scattered field

Brogioli, Vailati, and Giglio, *Appl. Phys. Lett.* **81**, 4109-4111 (2002)
Ferri, Giglio, *et al.*, Phys. Rev. E **70**, 041405 (2004)

HFNS 2

Subtract the average static contribution: $i_0(\mathbf{r}) = |e_0(\mathbf{r})|^2 = \langle f(\mathbf{r},t)\rangle_t$

$$\delta f(\mathbf{r},t) = f(\mathbf{r},t) - \langle f(\mathbf{r},t)\rangle_t = e_0(\mathbf{r})e_S^*(\mathbf{r},t) + e_0^*(\mathbf{r})e_S(\mathbf{r},t)$$

Fourier transform the image difference:

$$\delta F(\mathbf{q},t) = E_0(\mathbf{q}) * E_S^*(-\mathbf{q},t) + E_0^*(-\mathbf{q}) * E_S(\mathbf{q},t)$$

$$\sim E_S^*(-\mathbf{q},t) + E_S(\mathbf{q},t)$$ (NF: narrow E_0 spectrum)

necessary condition: $z < D/2\theta_{\max}$

Power spectrum of the heterodyne signal:

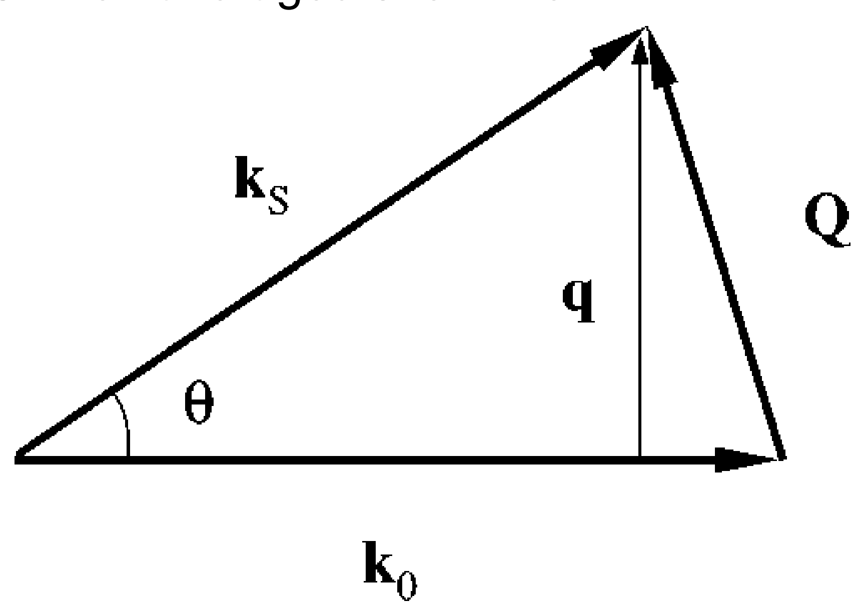
$$|\delta F(\mathbf{q},t)|^2 \sim |E_S(\mathbf{q},t)|^2 + |E_S(-\mathbf{q},t)|^2 + E_S(-\mathbf{q},t)E_S(\mathbf{q},t) + E_S^*(-\mathbf{q},t)E_S^*(\mathbf{q},t)$$

vanishes when averaged over time

Mean spectrum:

$$S(q) = \left\langle |\delta F(\mathbf{q},t)|^2 \right\rangle_{t,q}$$ with $I_s(Q) \sim S[q(Q)]$

$$q = Q\sqrt{1-(Q/2k)^2}$$



HNFS 3

Apply a differential double-frame analysis (frames separated by time Δt):

intensity in frame 1:

$$f_1(\mathbf{r}, t) = i_0(\mathbf{r}) + e_0(\mathbf{r})e_1^*(\mathbf{r}, t) + e_0^*(\mathbf{r})e_1(\mathbf{r}, t)$$

intensity in frame 2:

$$f_2(\mathbf{r}, t + \Delta t) = i_0(\mathbf{r}) + e_0(\mathbf{r})e_2^*(\mathbf{r}, t + \Delta t) + e_0^*(\mathbf{r})e_2(\mathbf{r}, t + \Delta t)$$

Calculate the intensity difference:

$$\delta f(\mathbf{r}, t, \Delta t) = e_0(\mathbf{r})e_2^*(\mathbf{r}, t+\Delta t) + e_0^*(\mathbf{r})e_2(\mathbf{r}, t+\Delta t) - e_0(\mathbf{r})e_1^*(\mathbf{r}, t) - e_0^*(\mathbf{r})e_1(\mathbf{r}, t)$$

Following the same analytical method:

$$|\delta F(\mathbf{q}, t, \Delta t)|^2 = |\alpha_1|^2 + |\alpha_2|^2 + \underline{\alpha_1\alpha_2^* + \alpha_1^*\alpha_2}$$

$$\alpha_1 = E_1^*(-\mathbf{q}, t) + E_1(\mathbf{q}, t)$$

$$\alpha_2 = E_2^*(-\mathbf{q}, t + \Delta t) + E_1(\mathbf{q}, t + \Delta t)$$

Double frame analysis removes some of the limitations associated with fluctuations in the intensity signal, but Δt must be carefully chosen

Differential dynamic microscopy (DDM)

Differential dynamic microscopy: dynamic heterodyne near-field scattering: fluctuations in the Fourier intensity difference spectrum signal are analyzed as a function of Δt

$$|\delta F(\mathbf{q}, t, \Delta t)|^2 = |\alpha_1|^2 + |\alpha_2|^2 + \underline{\alpha_1 \alpha_2^* + \alpha_1^* \alpha_2}$$

"vanishing" terms (in temporally-averaged HFNS) describe decorrelation of intensity fluctuations

Cerbino and Trappe showed, for a collection of scattering particles, a single Fourier decay mode satisfied:

$$|\delta F(q; \Delta t)|^2 = A(q)\left[1 - \underline{\exp\left(-\Delta t / \tau(q)\right)}\right] + B(q)$$

More generally, this is the intermediate scattering function measured in dynamic light scattering

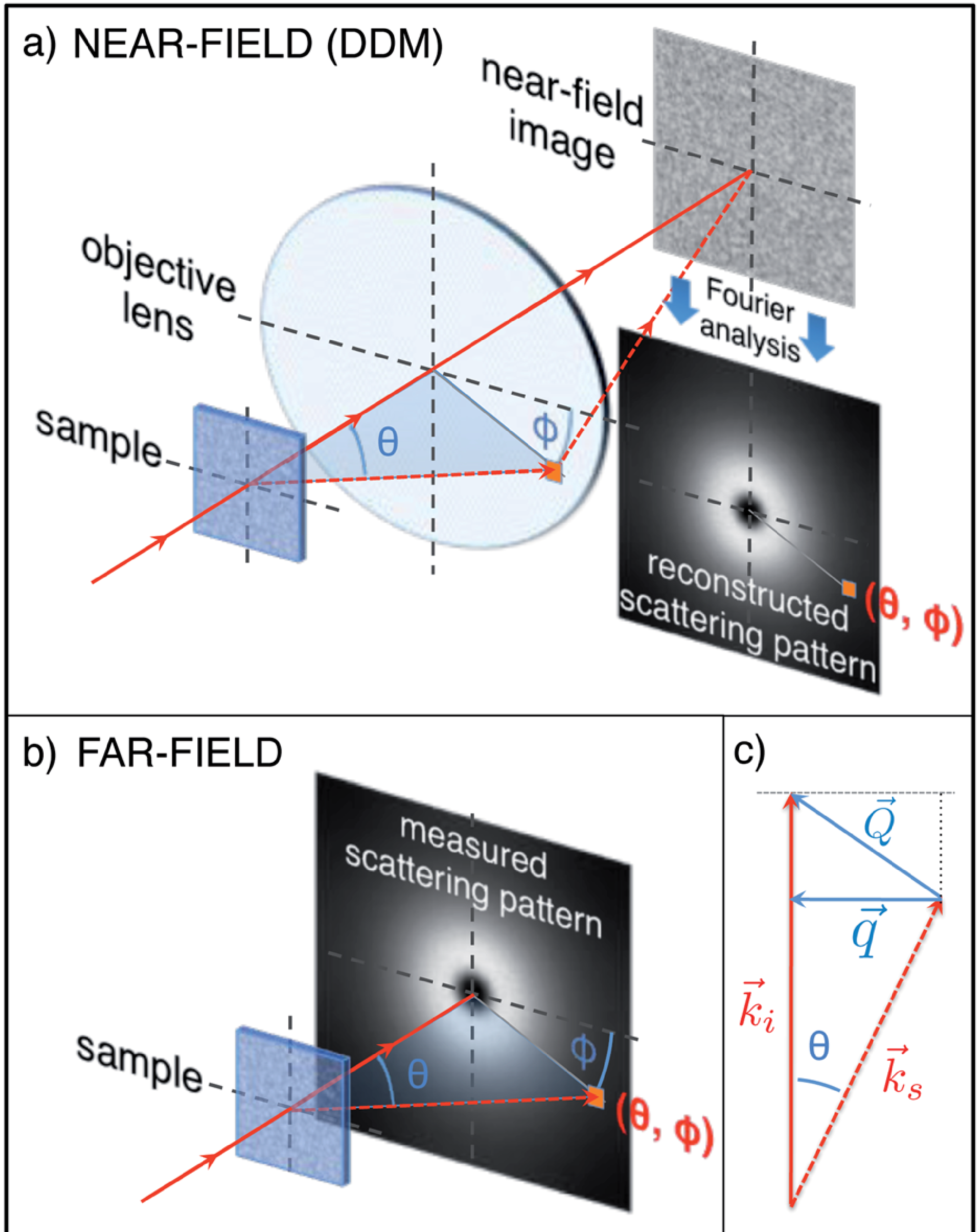
$$|\delta F(q; \Delta t)|^2 = A(q)\left[1 - f(q; \Delta t)\right] + B(q)$$

intermediate scattering function ISF

References:
Cerbino and Trappe, *Phys. Rev. Lett.* **100**, 188102 (2008)
Giavazzi, Cerbino, *et al.*, *Phys. Rev. E* **80**, 031403 (2009)

Methods and variations

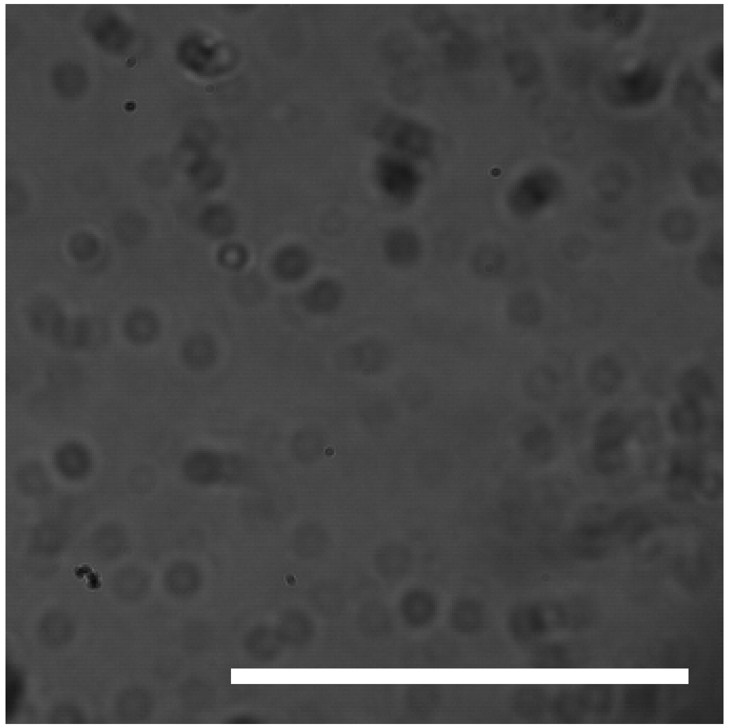
white light illumination

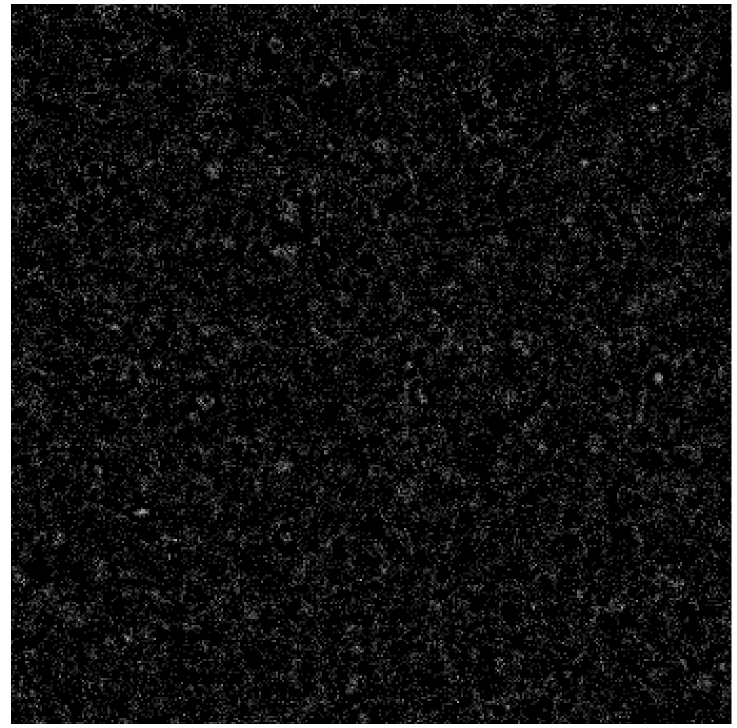


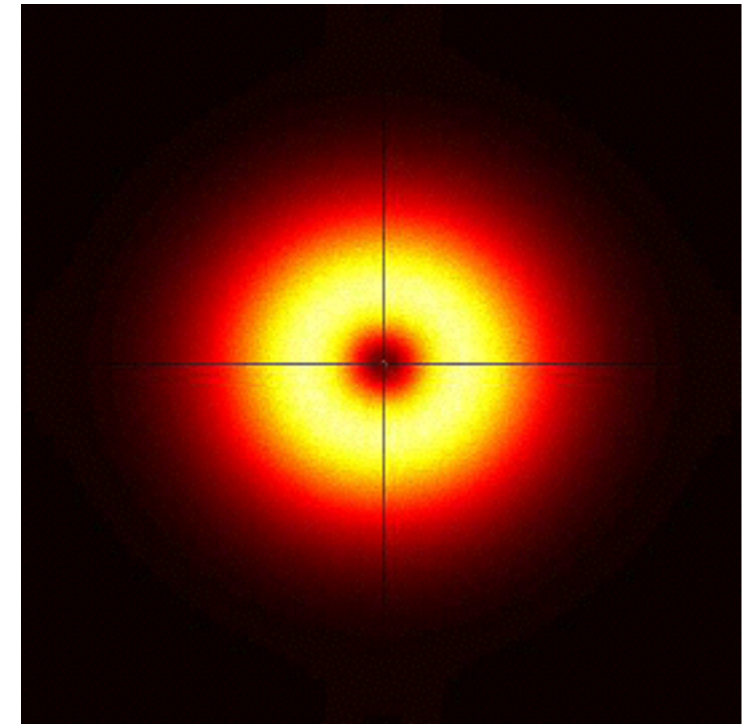
inelastic scattering

Giavazzi, Cerbino, *et al.*, *Soft Matter* **10**, 3938-3949 (2014)

Brightfield DDM: processing







1. Subtract images separated by fixed lag time:

$$\delta f(x, y; \Delta t) = f(x, y; t + \Delta t) - f(x, y; t)$$

2. Fourier transform image differences:

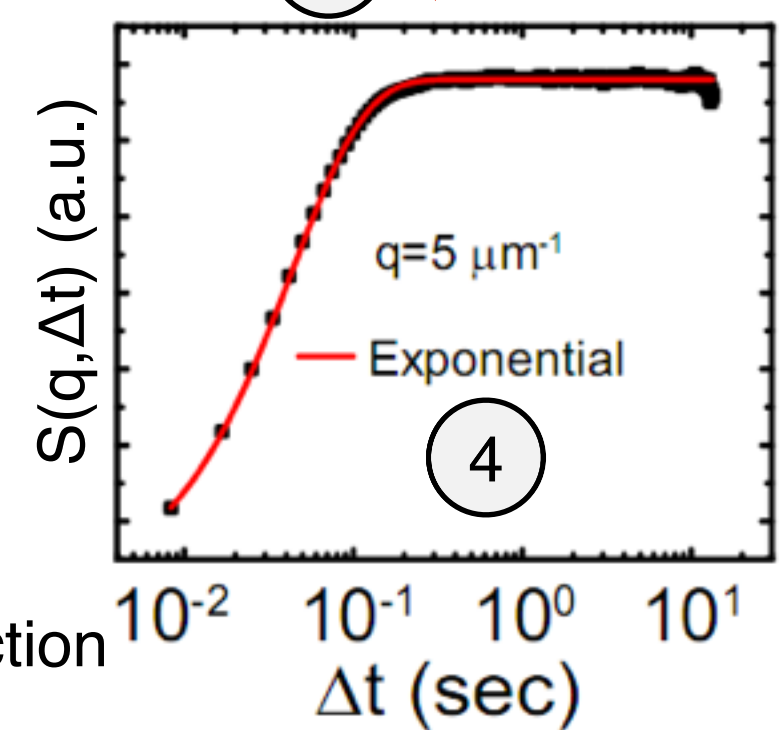
$$S(u_x, u_y; \Delta t) = \left\langle \left| \delta I(u_x, u_y; \Delta t) \right|^2 \right\rangle$$

3. Azimuthally average to obtain image structure function:

$$S(u_x, u_y; \Delta t) \rightarrow S(q, \Delta t)$$

4. Fit structure function to obtain intermediate scattering function

$$S(q, \Delta t) = A(q) \left[1 - f(q, \Delta t)\right] + B(q)$$



Framework also works for other linear space-invariant imaging methods (fluorescence DDM)

Example: particle dynamics

System: polystyrene nanoparticles (73 nm and 420 nm)

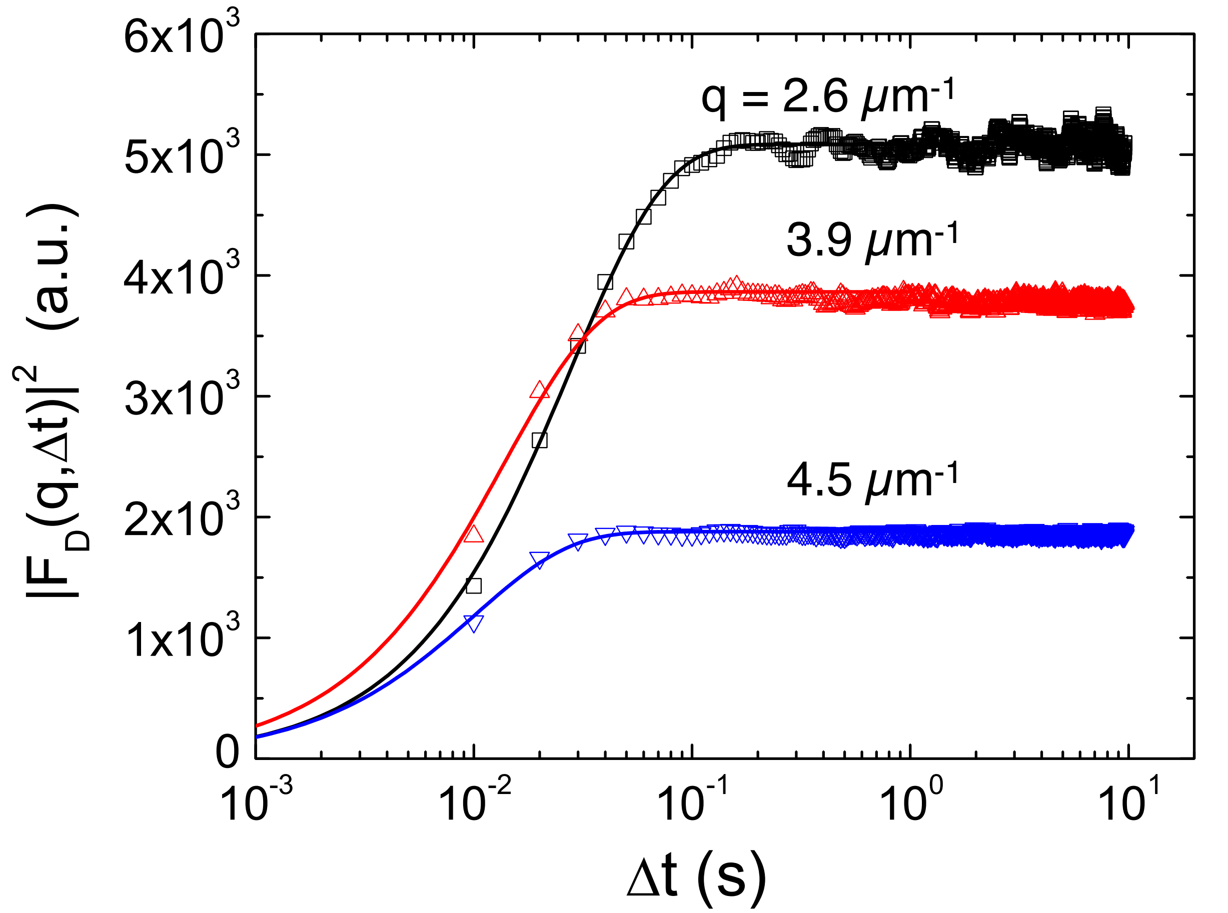
Fitting model:

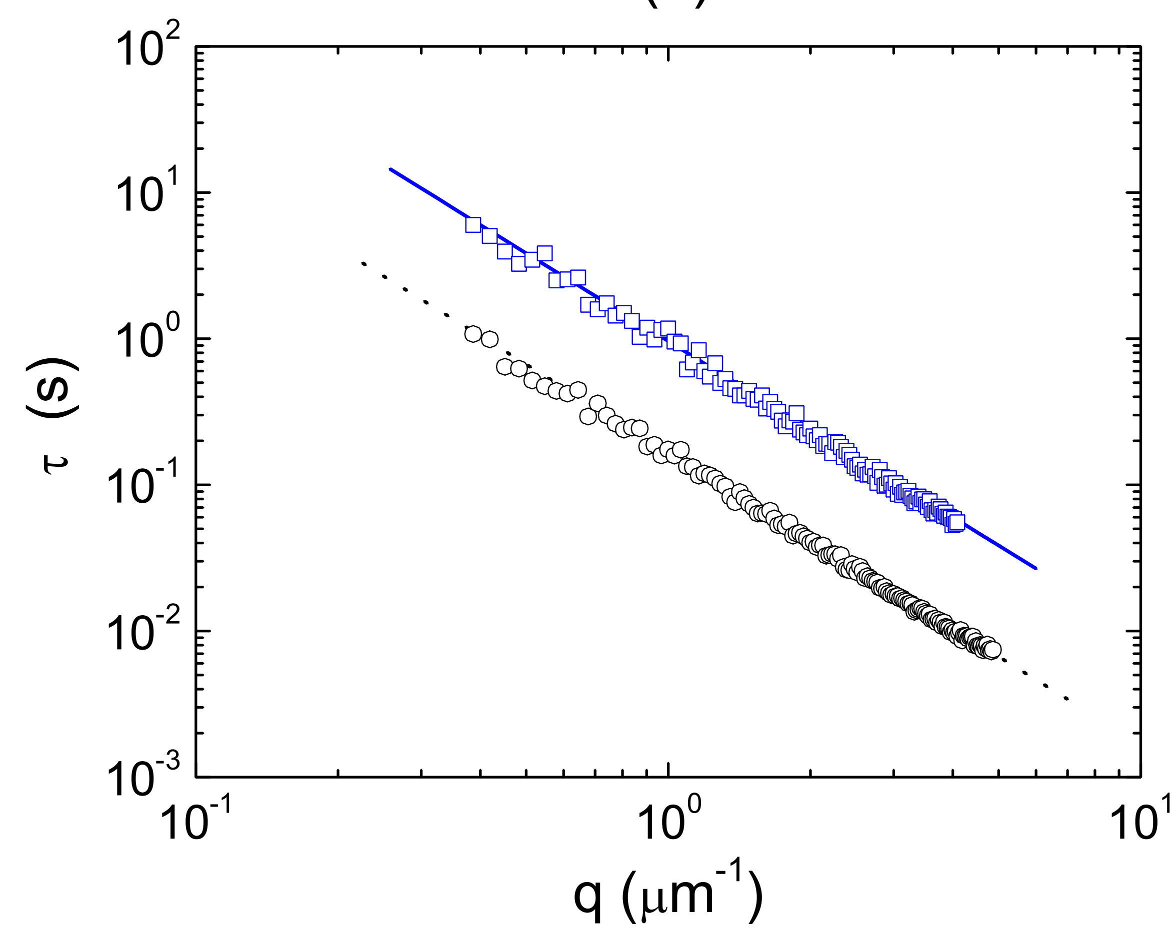
signal

$$S(q, \Delta t) = A(q)\left[1 - \exp\left\{-\frac{\Delta t}{\tau(q)}\right\}\right] + B(q)$$

camera noise

Key result: Diffusivity of submicron particles can be measured using DDM





Cerbino and Trappe, *Phys. Rev. Lett.* **100**, 188102 (2008)

Considerations for running experiments

1. Range of accessible wave vectors

Acquisition frame rates: 63, 120 fps

$$q_{\min} = \frac{2\pi}{\max(l_x, l_y)}$$

$q_{min} \approx 0.1\ \mu m^{-1}$

$$q_{\max} = \min\left(\sqrt{\text{frame rate}/D}, 2\pi n \sin(\theta_{\max})/\lambda\right)$$

$q_{max} \approx 4—12\ \mu m^{-1}$

2. Signal-to-noise ratio

$$\frac{A(q)}{B(q)} \geq$$

0.07 (f-DDM)

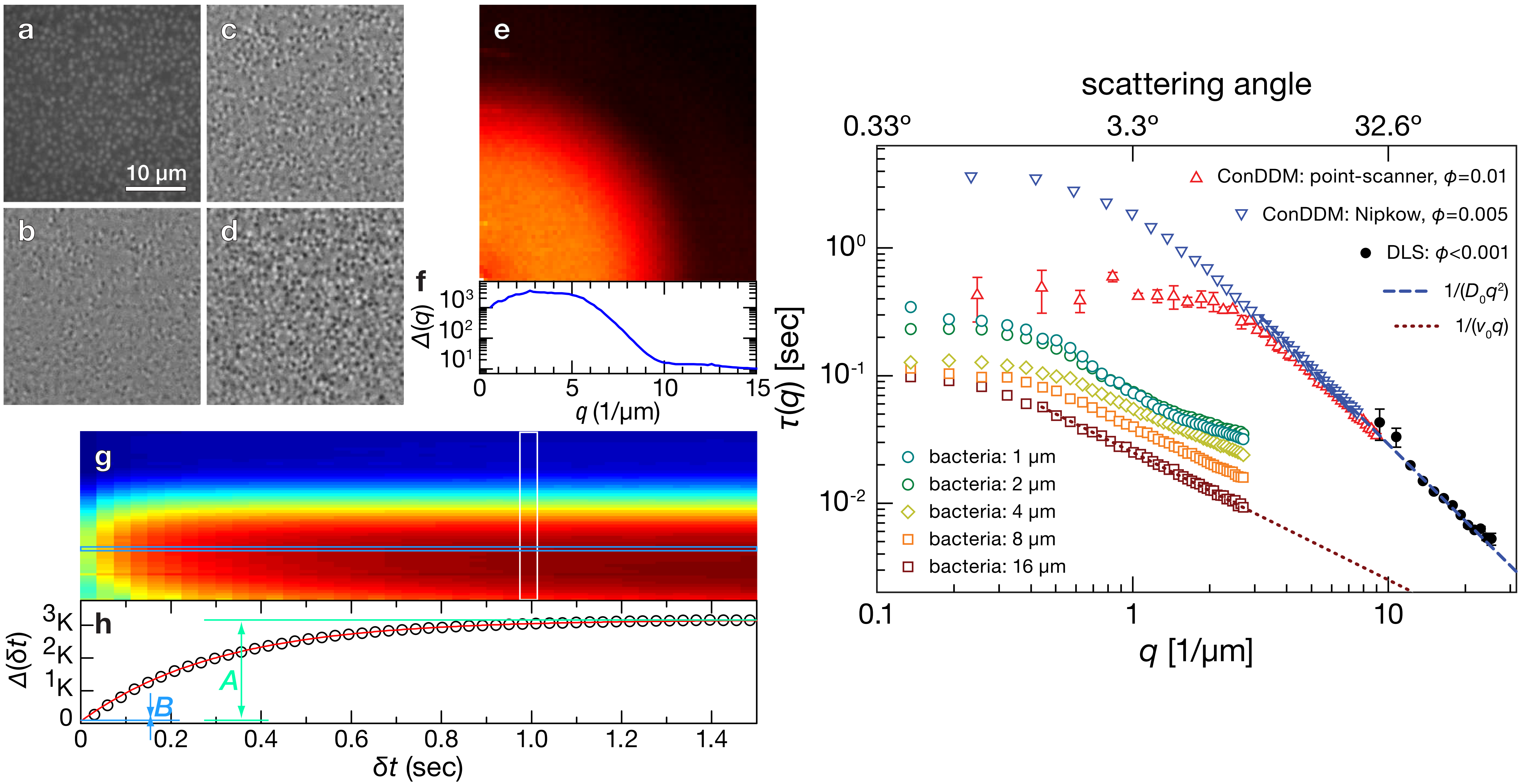
0.2 (b-DDM)

NP diameter	Volume fraction, φ	Diffusion coefficient ($\mu m^2\ s^{-1}$)		
		b-DDM	f-DDM	DLS
400 nm	1×10^{-3}	0.96 ± 0.06	0.95 ± 0.04	—
	1×10^{-4}	0.94 ± 0.05	0.95 ± 0.06	—
	1×10^{-5}	0.95 ± 0.03	0.94 ± 0.05	0.92 ± 0.06
	1×10^{-6}	0.93 ± 0.02	0.96 ± 0.06	0.97 ± 0.05
200 nm	1×10^{-3}	1.88 ± 0.10	1.89 ± 0.10	—
	1×10^{-4}	1.89 ± 0.12	1.92 ± 0.10	—
	1×10^{-5}	1.92 ± 0.06	1.92 ± 0.11	2.01 ± 0.06
	1×10^{-6}	1.93 ± 0.07	1.89 ± 0.27	2.01 ± 0.05
100 nm	1×10^{-3}	3.83 ± 0.11	3.91 ± 0.14	—
	1×10^{-4}	3.79 ± 0.09	3.71 ± 0.20	—
	1×10^{-5}	3.60 ± 0.14	Immeasurable	3.83 ± 0.06
	1×10^{-6}	3.60 ± 0.34	Immeasurable	3.87 ± 0.09

He, Spannuth, JCC, and Krishnamoorti, *Soft Matter* **8**, 11933-11938 (2012)

Variants: confocal DDM

Modification: analyze time series of confocal micrographs

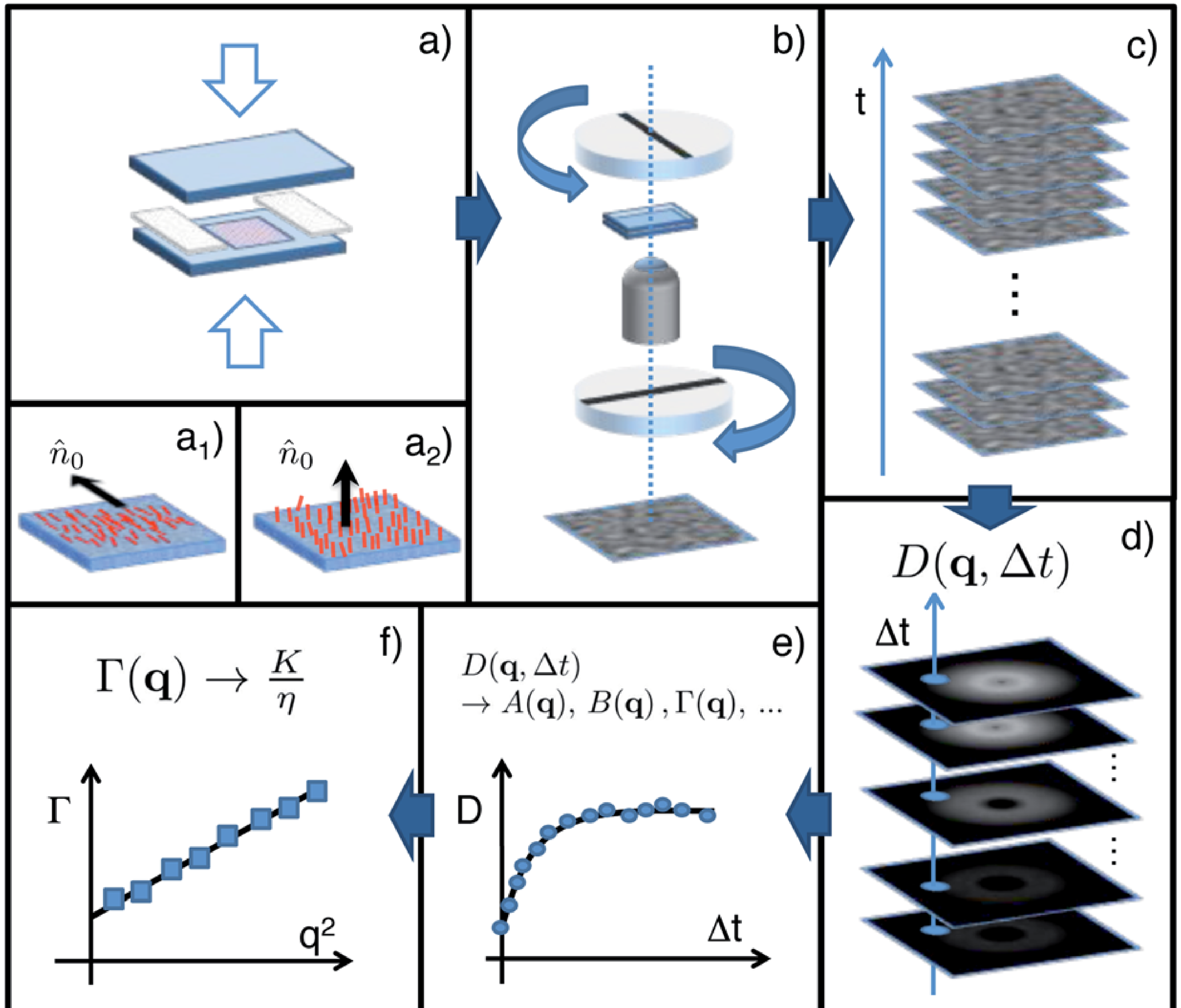


Useful for: obtaining structure factors and dynamics in dense and/or opaque samples that are multiply-scattering

Lu, Cerbino, *et al.*, *Phys. Rev. Lett.* **108**, 218103 (2012)

Variant: polarized DDM

Modification: insert polarizer and analyzer into the beam path



Useful for: optically-anisotropic systems (liquid crystals)

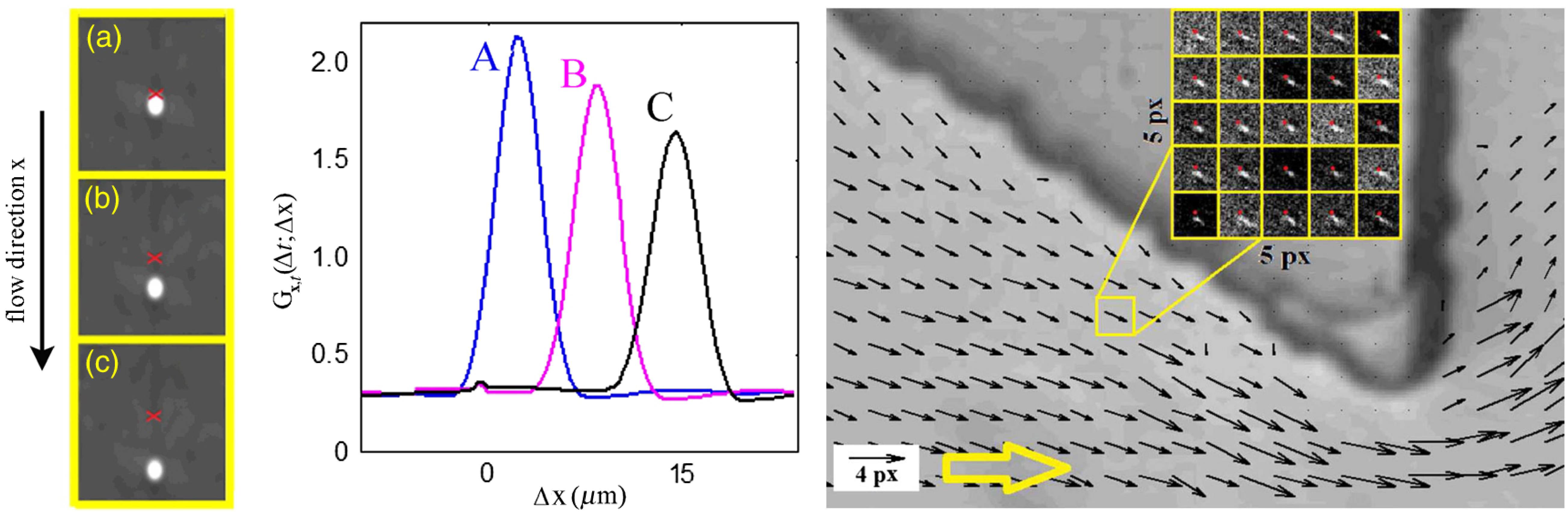
Giavazzi, Cerbino, *et al.*, *Soft Matter* **10**, 3938-3949 (2014)

Variant: ghost-particle velocimetry

Modification: use cross-correlation to analyze the NF speckle pattern

$$G_{\mathbf{x},t}\left(\Delta t;\Delta\mathbf{x}\right) = i(t,\mathbf{x}+\mathbf{\Delta x})i(t+\Delta t,\mathbf{x}+\mathbf{\Delta x})$$

Velocity: obtained from well-defined peak at $\mathbf{\Delta x} = \mathbf{V}\Delta t$

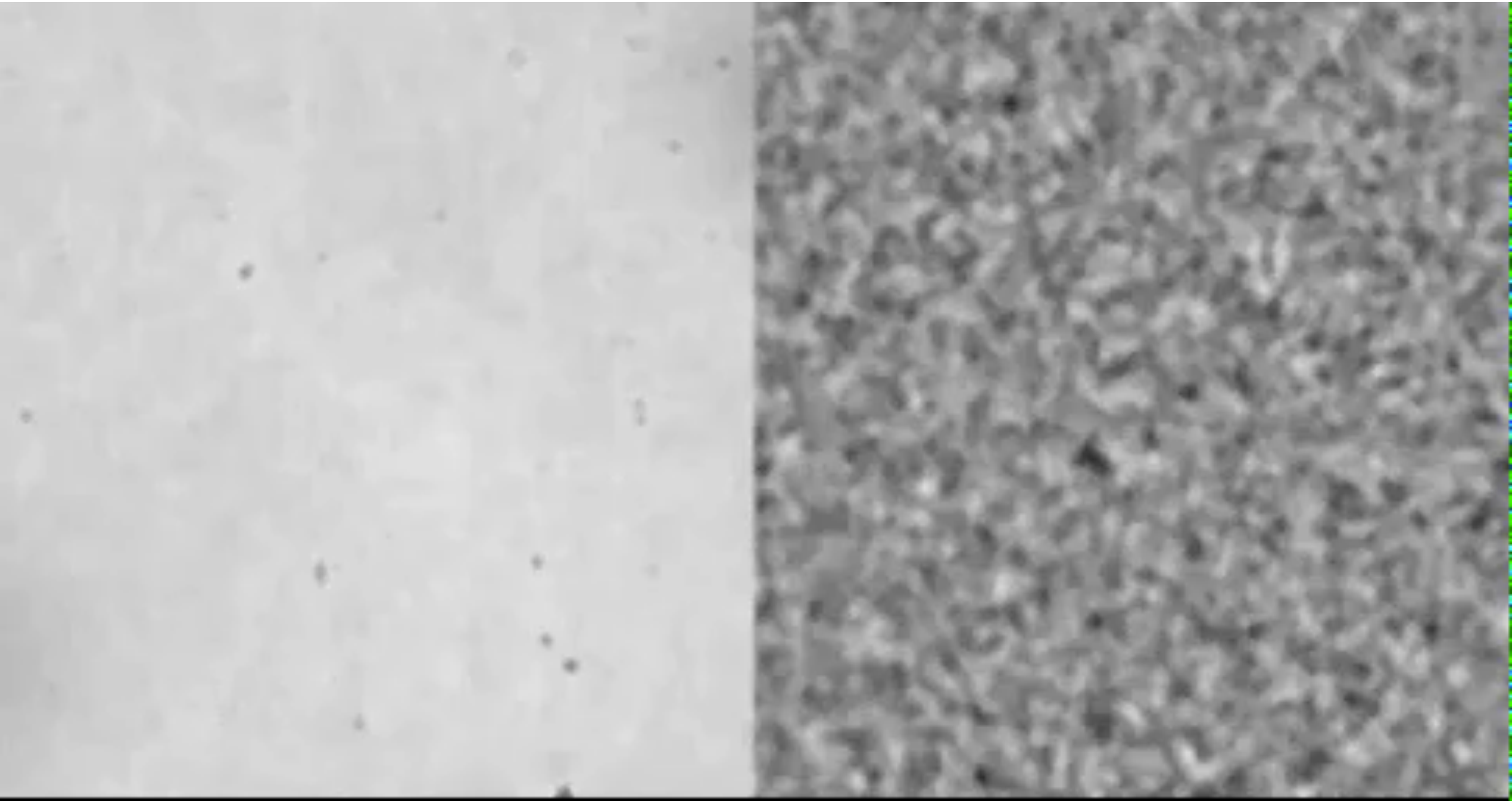


Useful for: obtaining flow profiles in turbid flowing systems

Buzzacaro, Secchi, and Piazza, *Phys. Rev. Lett.* **111**, 048101 (2013)

Application area 1: complex fluids

73 nm polystyrene nanoparticles in water



Cerbino and Trappe, *Phys. Rev. Lett.* **100**, 188102 (2008)

I: static structure factor

System: index-matched PMMA particles in a ternary solvent mixture

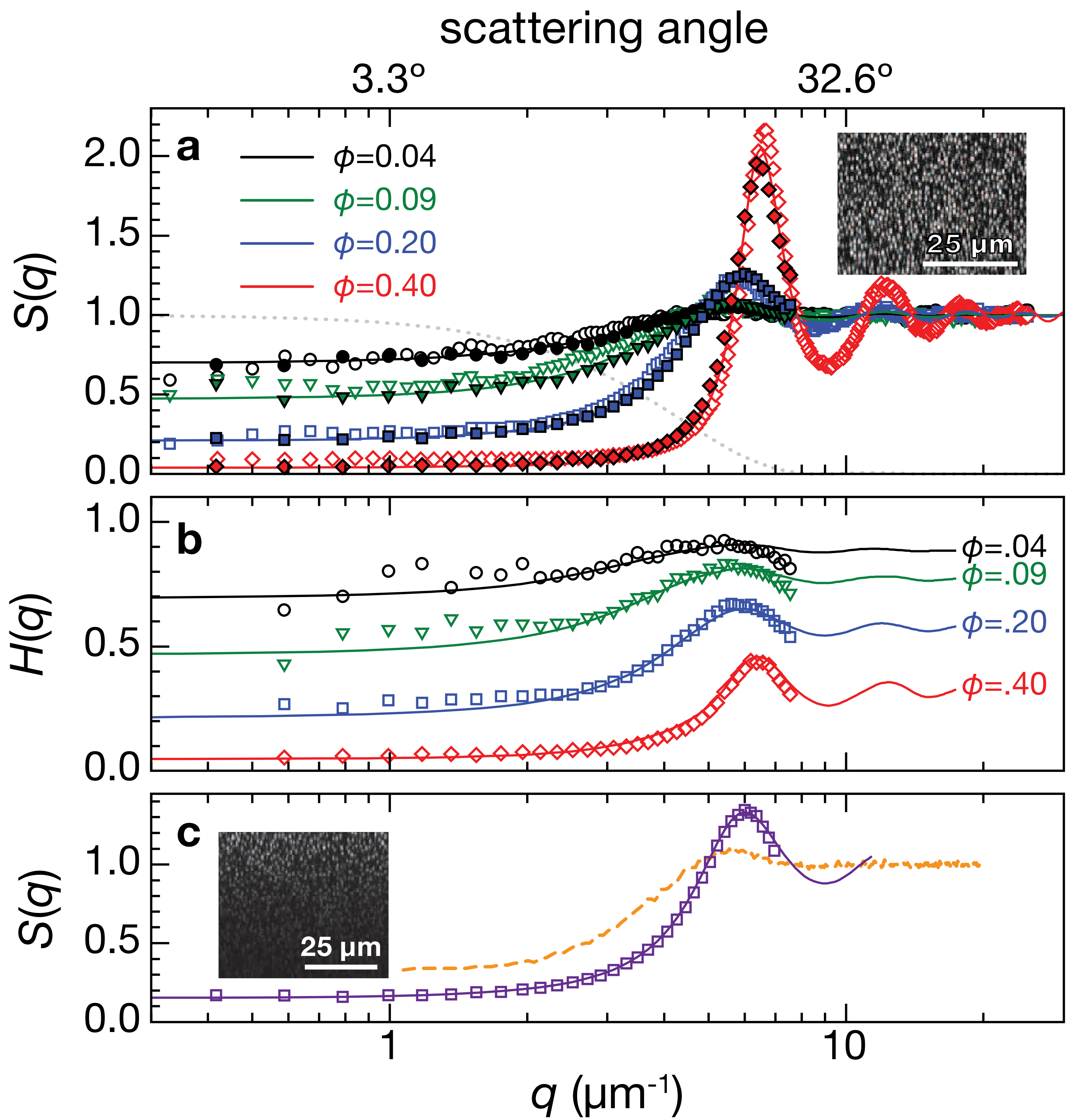
Method: confocal DDM

Representative data: measurements of the (static) structure function S(q)

$$S(q) = \phi_{\rm dil} A(q) / \phi A_{\rm dil}(q)$$

Key result: simultaneous measurements of S(q) and τ(q) allow direct measurements of hydrodynamics

$$\tau_S(q) = (D_0 q^2)^{-1} S(q) / H(q)$$



Lu, Weitz, Cerbino, *et al.*, *Phys. Rev. Lett.* **108**, 218103 (2012)

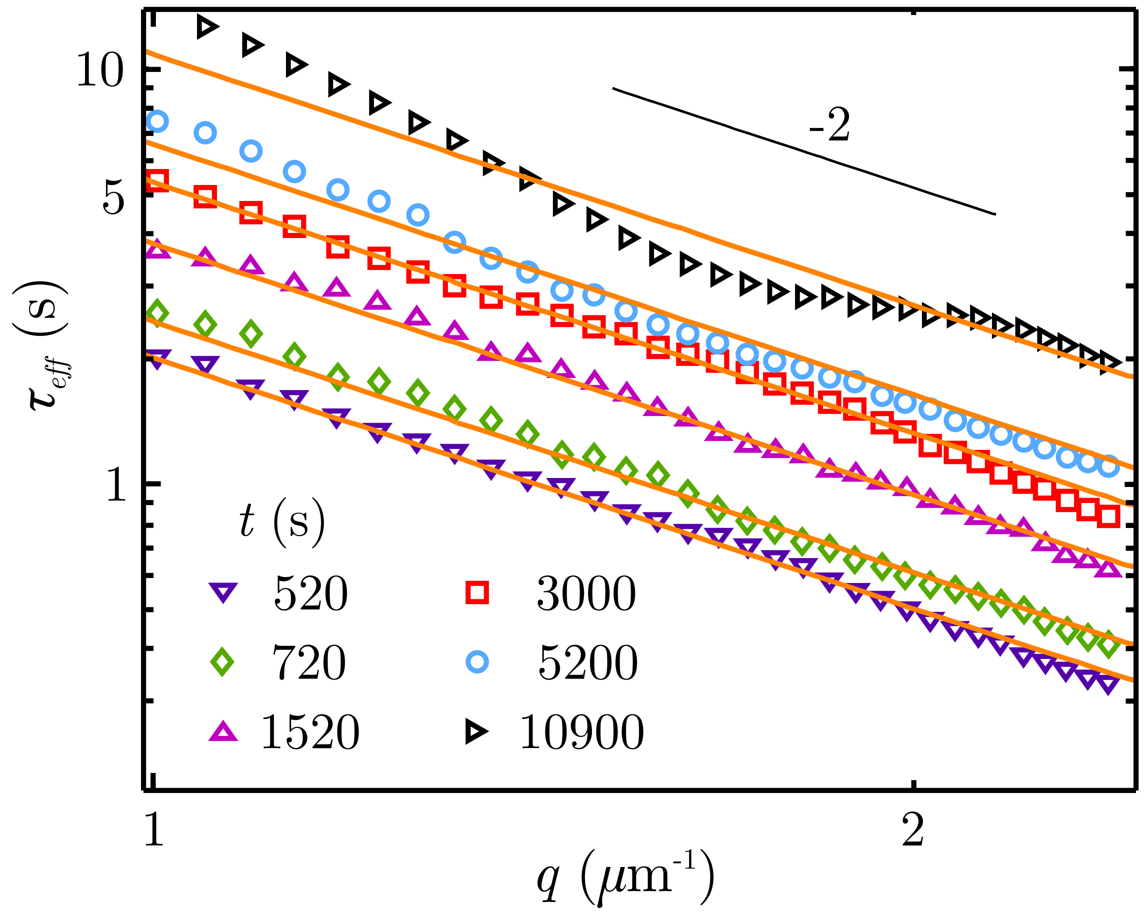
I: fractal aggregation

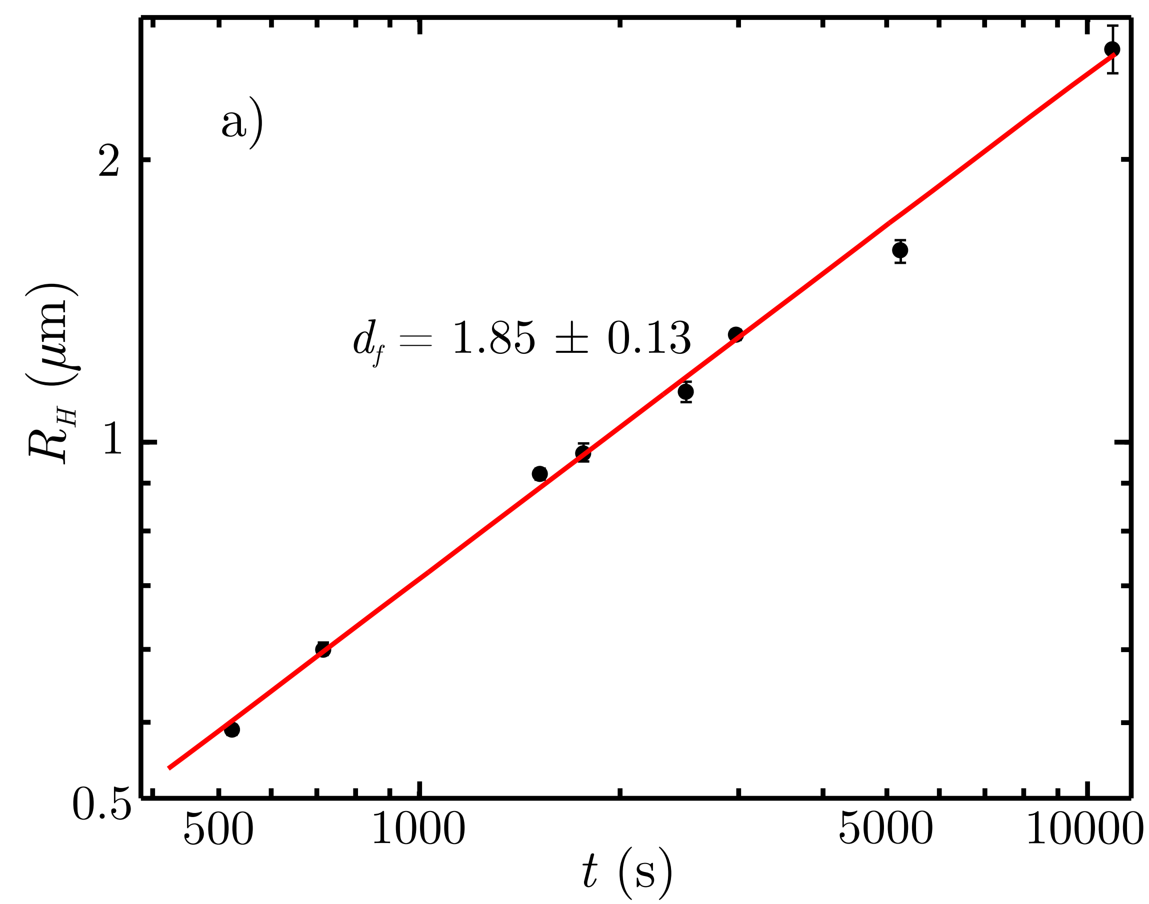
System: polystyrene nanoparticles aggregated with $MgCl_2$

Method: brightfield DDM

Representative data: measurements of τ_{eff} versus q

Key result: Clusters grow with a fractal dimension consistent with diffusion-limited cluster aggregation





Ferri, Cerbino, *et al.*, *Eur. Phys. J. Special Topics* ***199***, 139-148 (2011)

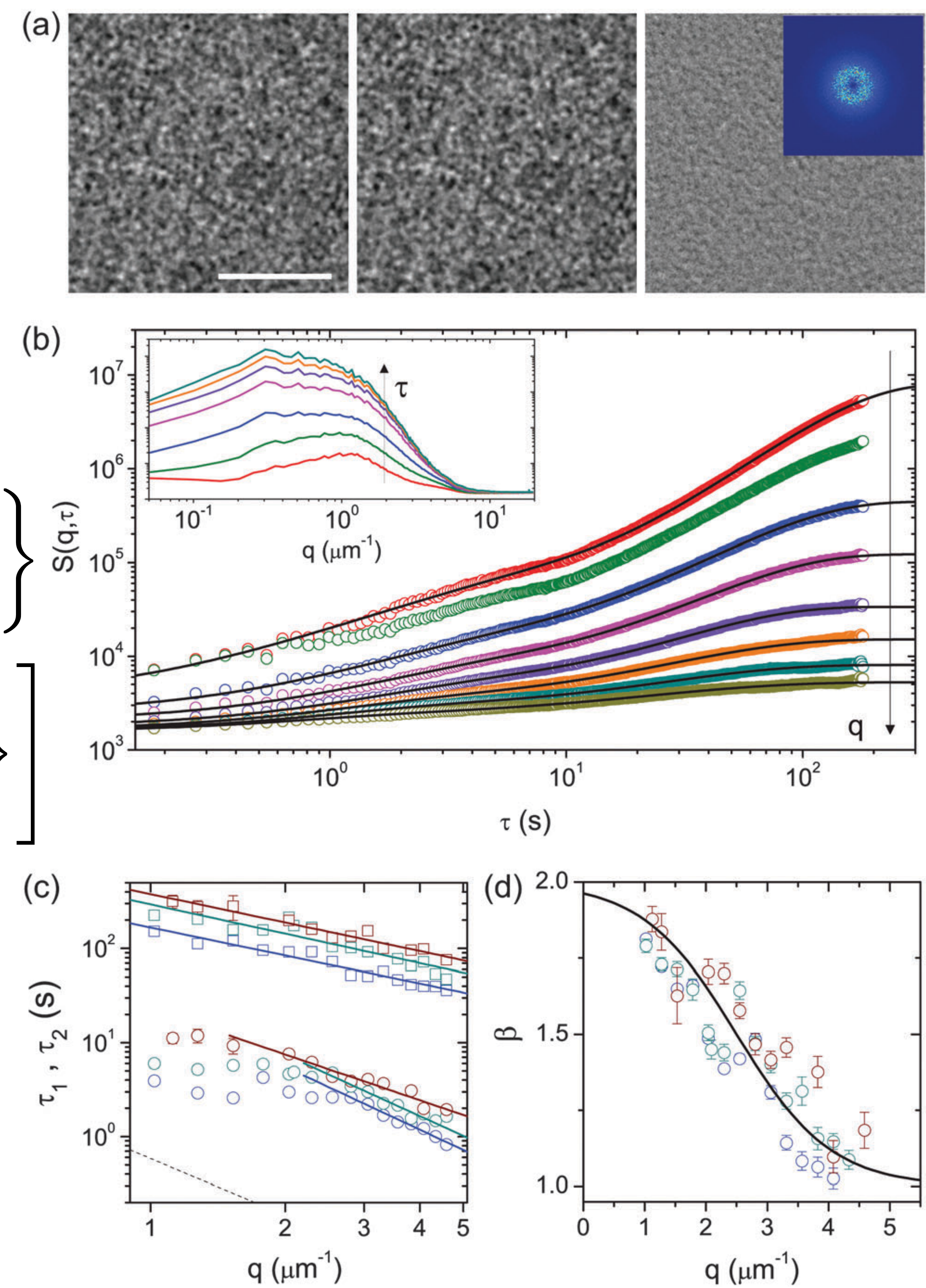
I: arrested dynamics

System: thermoreversible colloidal gel (nanoemulsion o/w droplets with thermoresponsive end-functionalized polymers)

Method: brightfield DDM

Fitting model:

$$S(q,\Delta t) = A(q)\left[1 - a(q)\exp\left\{-\left(\frac{\Delta t}{\tau_1(q)}\right)\right\} -(1-a(q)\exp\left\{-\left(\frac{\Delta t}{\tau_2(q)}\right)^{\beta}\right\}\right]$$



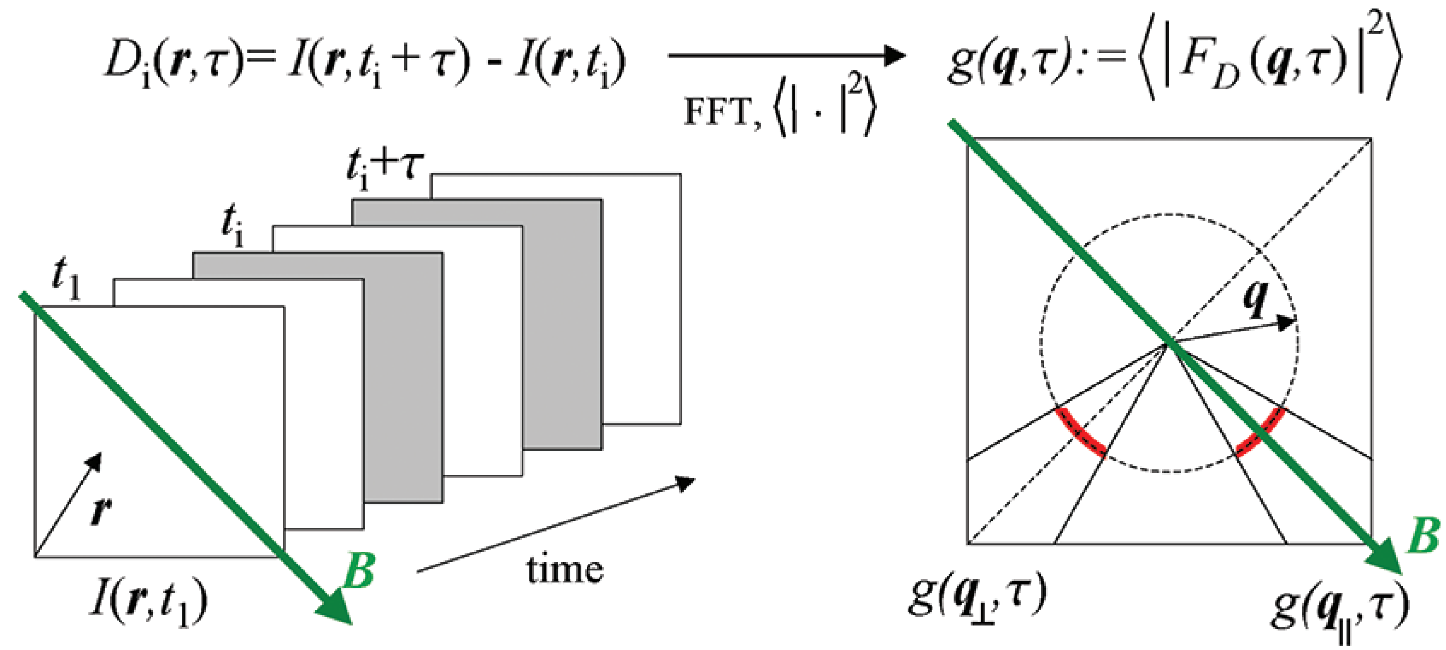
Key result:
Coarsening dynamics exhibit two distinct time scales, slow and fast

Gao, Kim, and Helgeson, *Soft Matter* **11**, 6360-6370 (2015)

I: anisotropic colloids

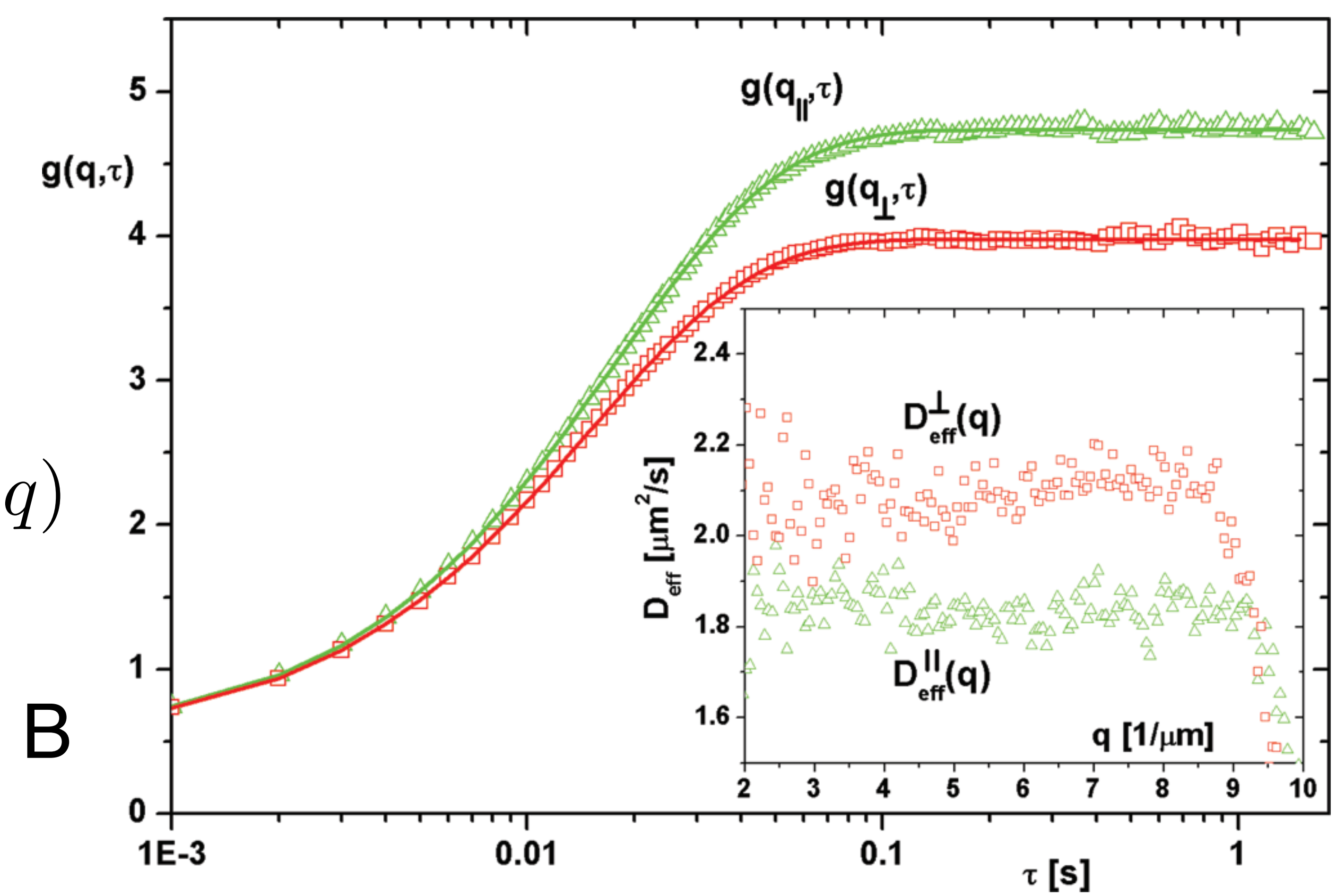
System:
Silica-coated hematite nanoparticles
(a = 175 nm, b = 52 nm)

Method: brightfield DDM



Representative data:
q = 5.56 μm^{-1}
magnetic field B = 430 mT

$$S(\mathbf{q},\Delta t) = 2N|A(\mathbf{q}|^2 S(\mathbf{q})\left[1 - \mathrm{Re}(f(\mathbf{q},\Delta t))\right] + \tilde{\mathbf{B}}(q)$$



Key result:
$D_\parallel$, $D_\perp$ as a function of field strength B

Reufer, Poon, *et al.*, *Langmuir* **28**, 4618-4624 (2012)

I: liquid crystals

System: liquid crystals (6CB)

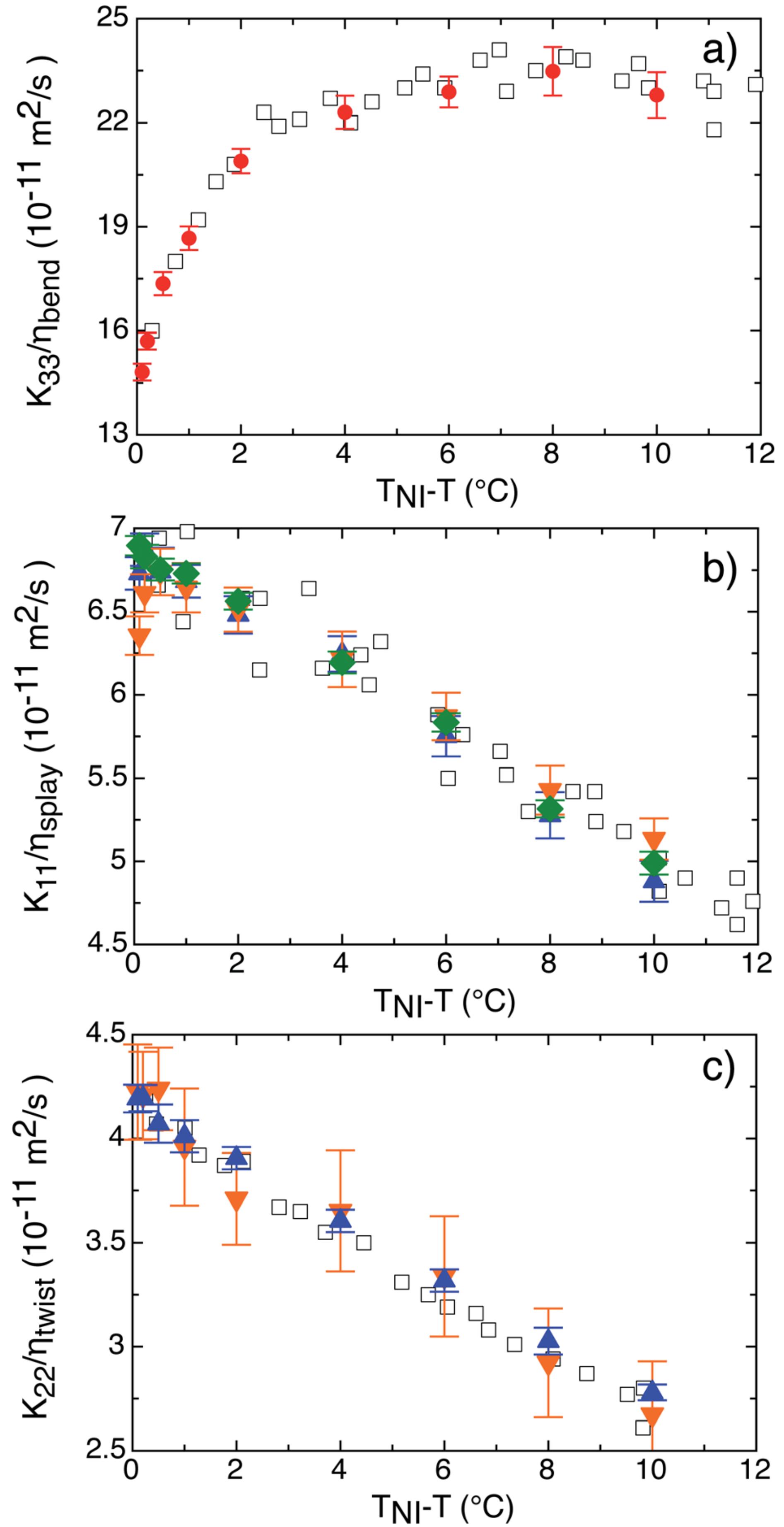
Method: polarized DDM

Fitting model for the ISF:

$$g(\mathbf{q}, \Delta t) = g_1(\mathbf{q}) \exp\{-\Gamma_1(\mathbf{q})\Delta t\} + g_2(\mathbf{q}) \exp\{-\Gamma_2(\mathbf{q})\Delta t\}$$

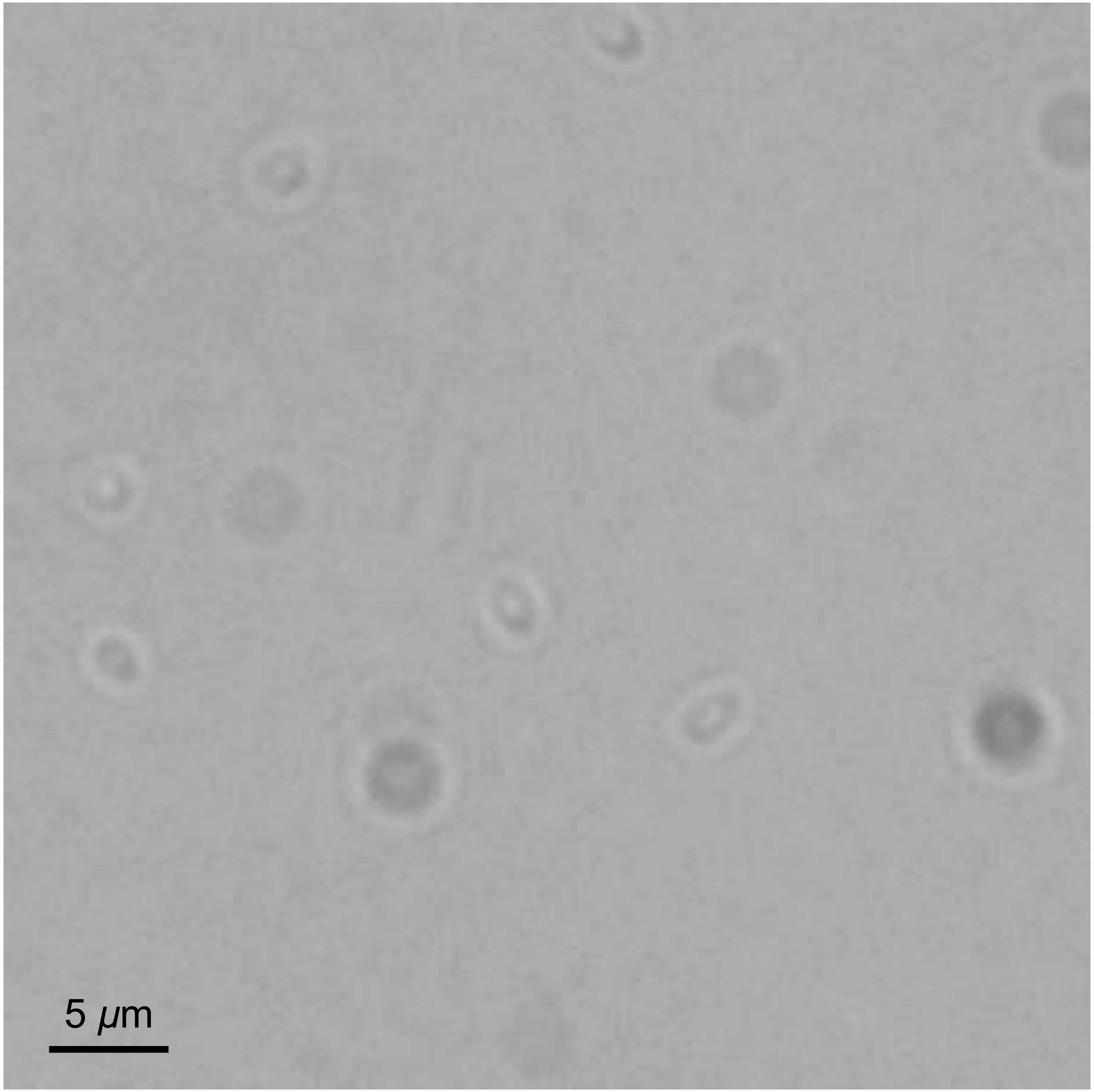
Relationship between Γ_1, Γ_2 and elastic constants depends on polarizer configuration

Key result: elastic constants K_{11}, K_{22}, K_{33} as a function of temperature



Giavazzi, Cerbino, *et al.*, *Soft Matter* **10**, 3938-3949 (2014)

Application area 2: biofluids



Movie: M. Gibiansky, JCC, and F. Jin (old, not DDM, but shows my point)

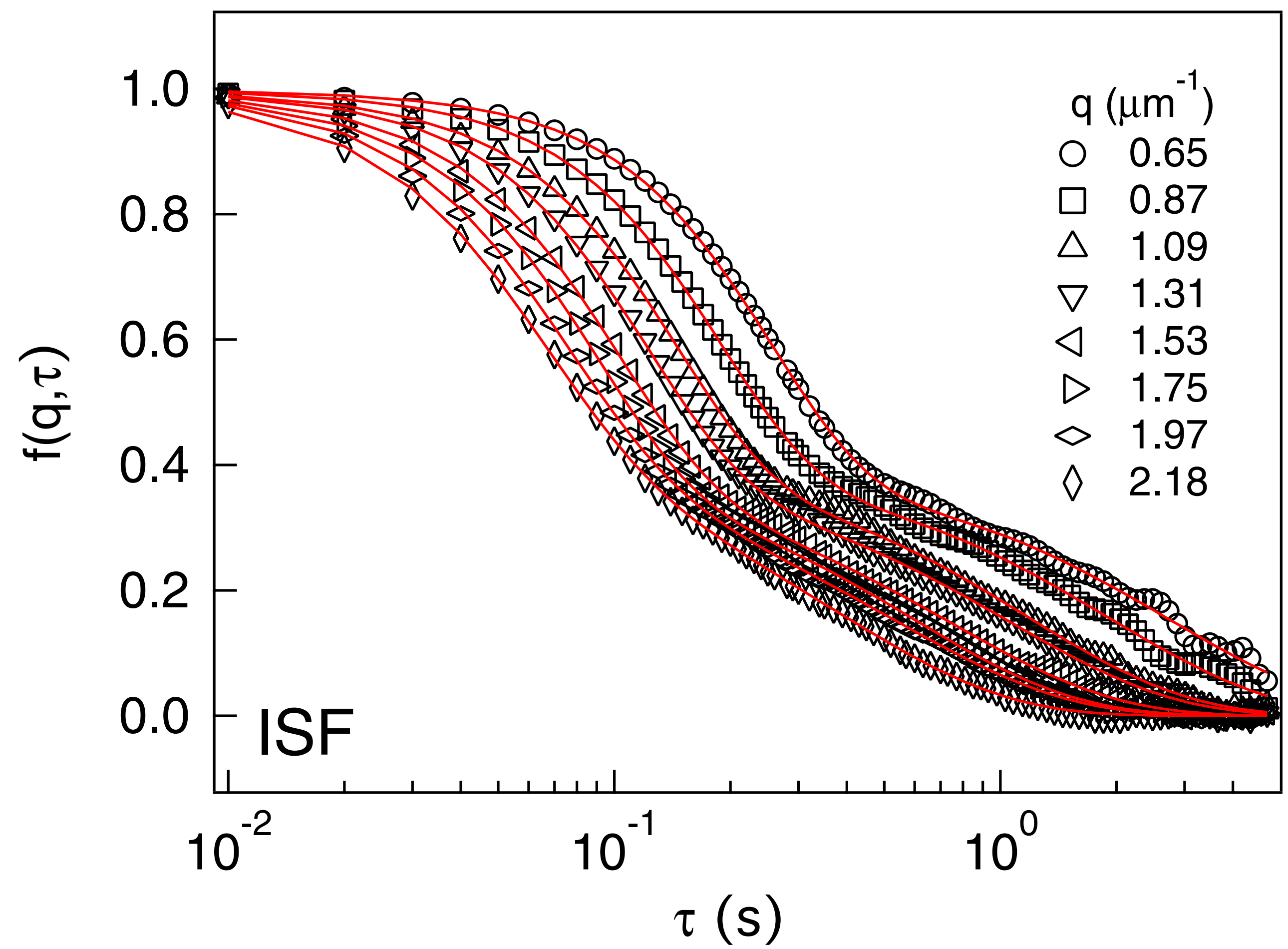
II: bacterial dynamics (i)

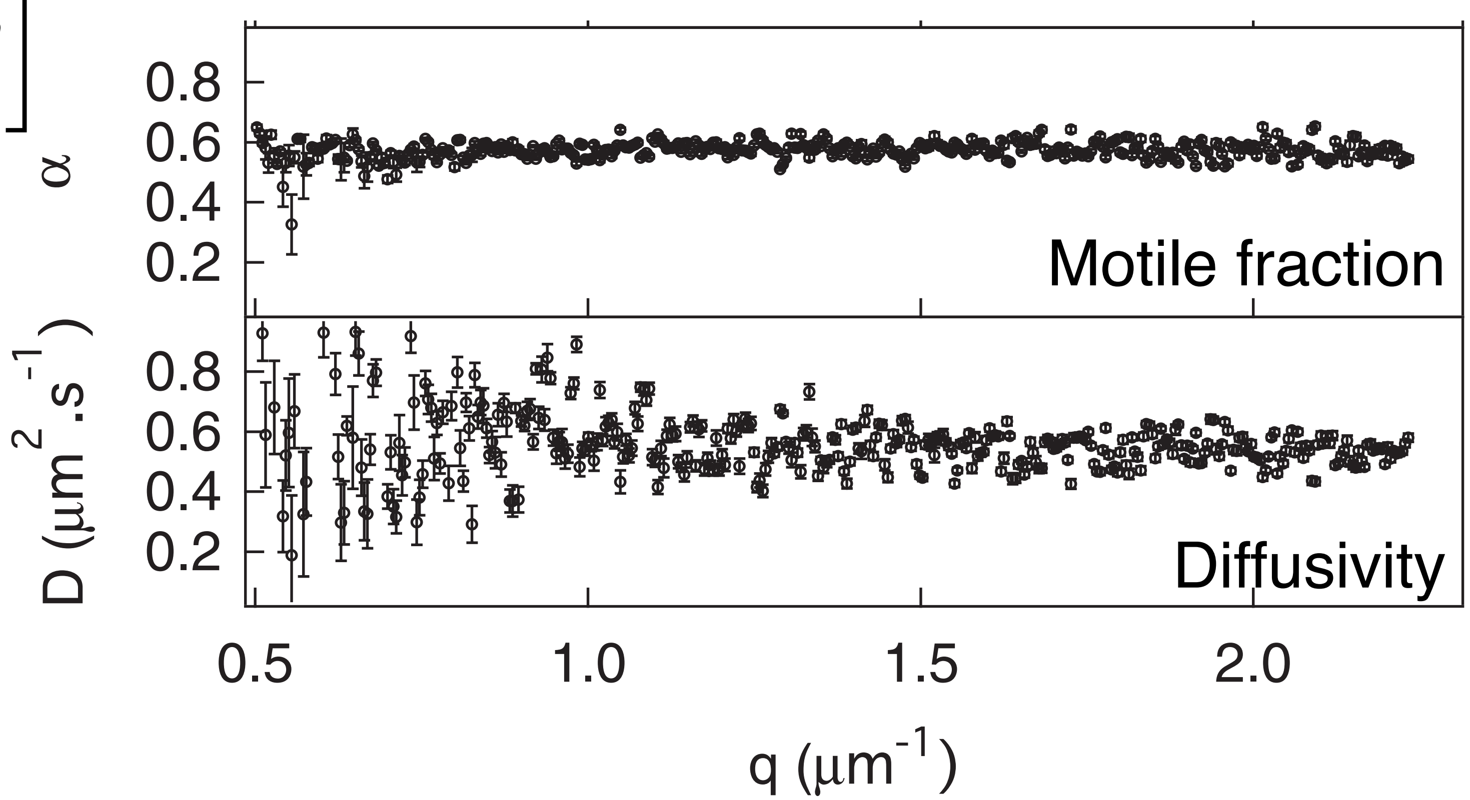
System: swimming *Escherichia coli* bacteria

Method: brightfield DDM

Fitting model for the ISF:

$$f(q,\Delta t) = e^{-Dq^2\Delta t}\left[(1-\alpha) + \alpha\int_0^\infty P(v)\frac{\sin(qv\Delta t)}{qv\Delta t}\,dv\right]$$



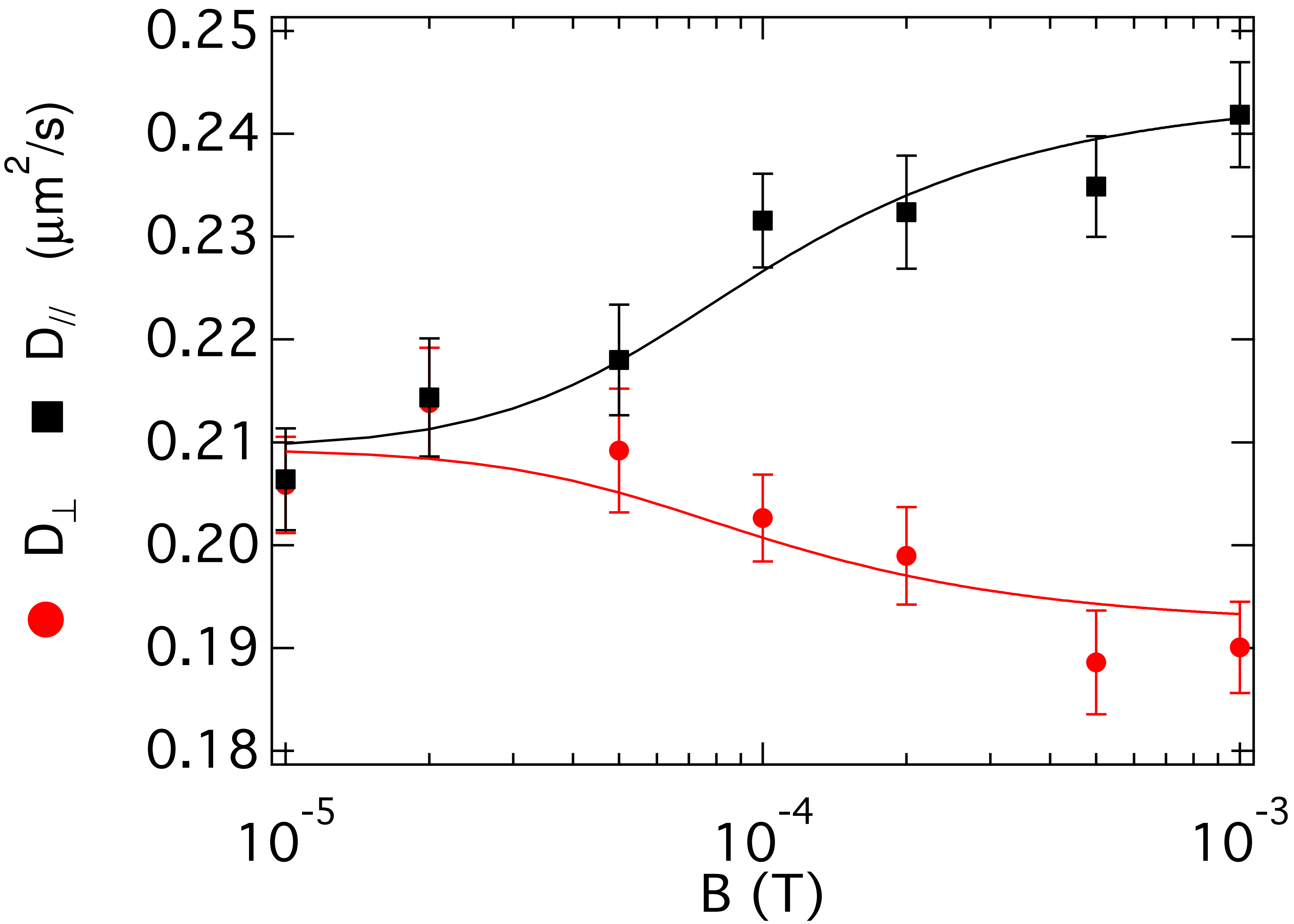


Key result:
Diffusivity and motile fraction of swimming cells as a function of swimmer volume fraction

Wilson, Poon, *et al.*, *Phys. Rev. Lett.* **106**, 018101 (2011)

II: bacterial dynamics (ii)

System: magnetotatic *Magnetospirillum gryphiswaldense* bacteria



Key result: Diffusion coefficients of nonmotile cells

$$D_{\parallel} = D_{\text{iso}} + \frac{2}{3}\left(D_a - D_b\right) S_2(h)$$

$$D_{\perp} = D_{\text{iso}} - \frac{1}{3}\left(D_a - D_b\right) S_2(h)$$

Reufer, Poon, *et al.*, *Biophys. J.* **106**, 37-46 (2014)

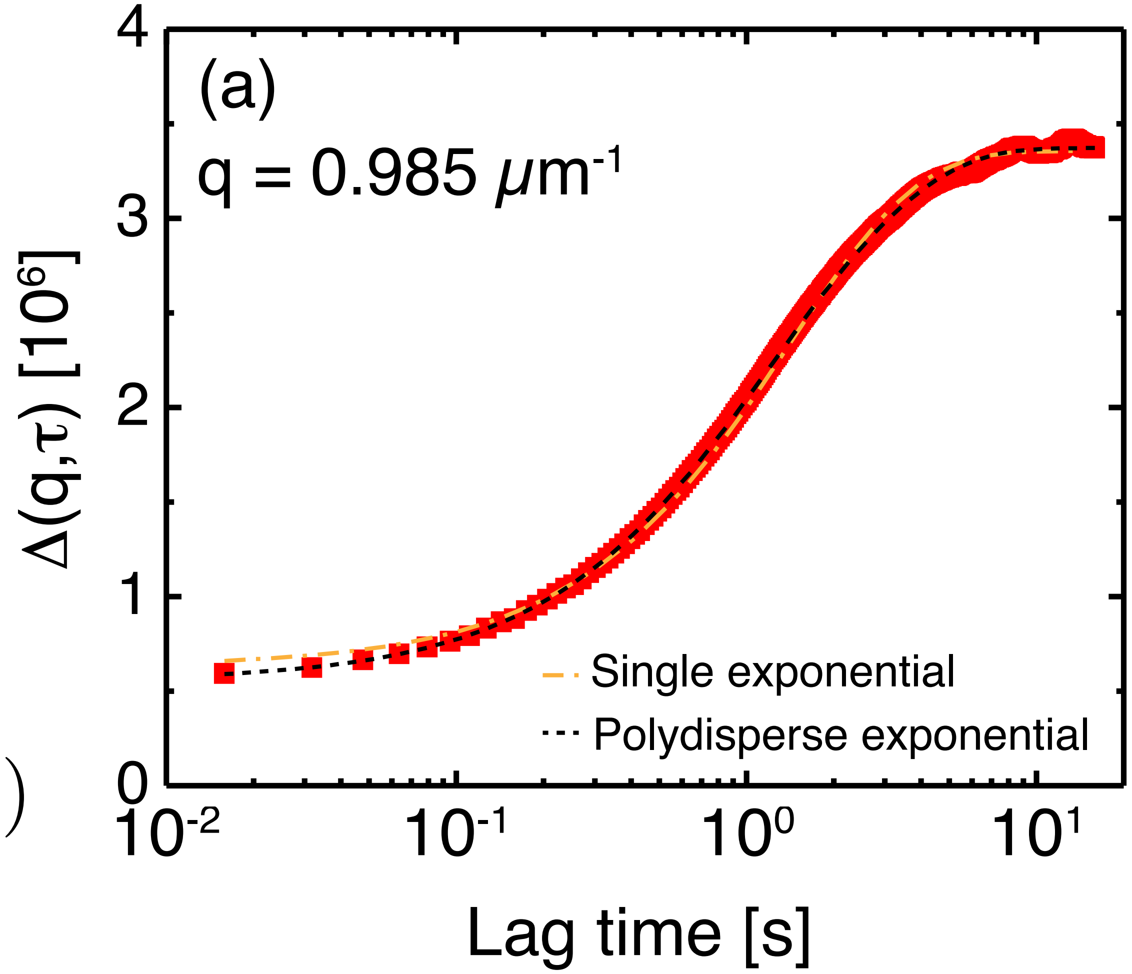
II: protein cluster diffusivity

System: protein-rich polydisperse liquid clusters in hemoglobin solutions

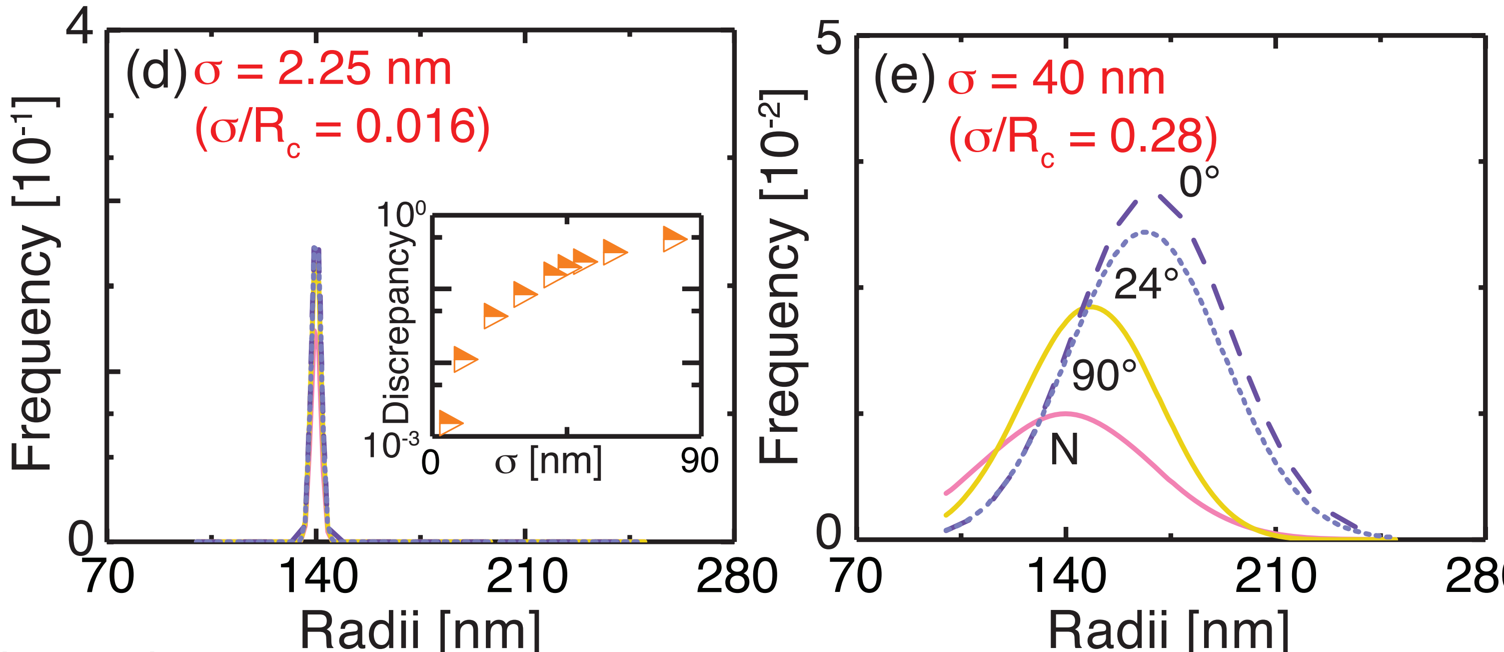
Method: brightfield DDM

Fitting function: polydisperse cumulant-fitting model (from Frisken, *J. Appl. Opt.* (2006))

$$S(q,\Delta t) = A(q)\left[1-\exp\left\{-\frac{\Delta t}{\tau_c(q)}\right\}\times\left(1+\frac{\mu(\Delta t)^2}{2}\right)\right]+B(q)$$

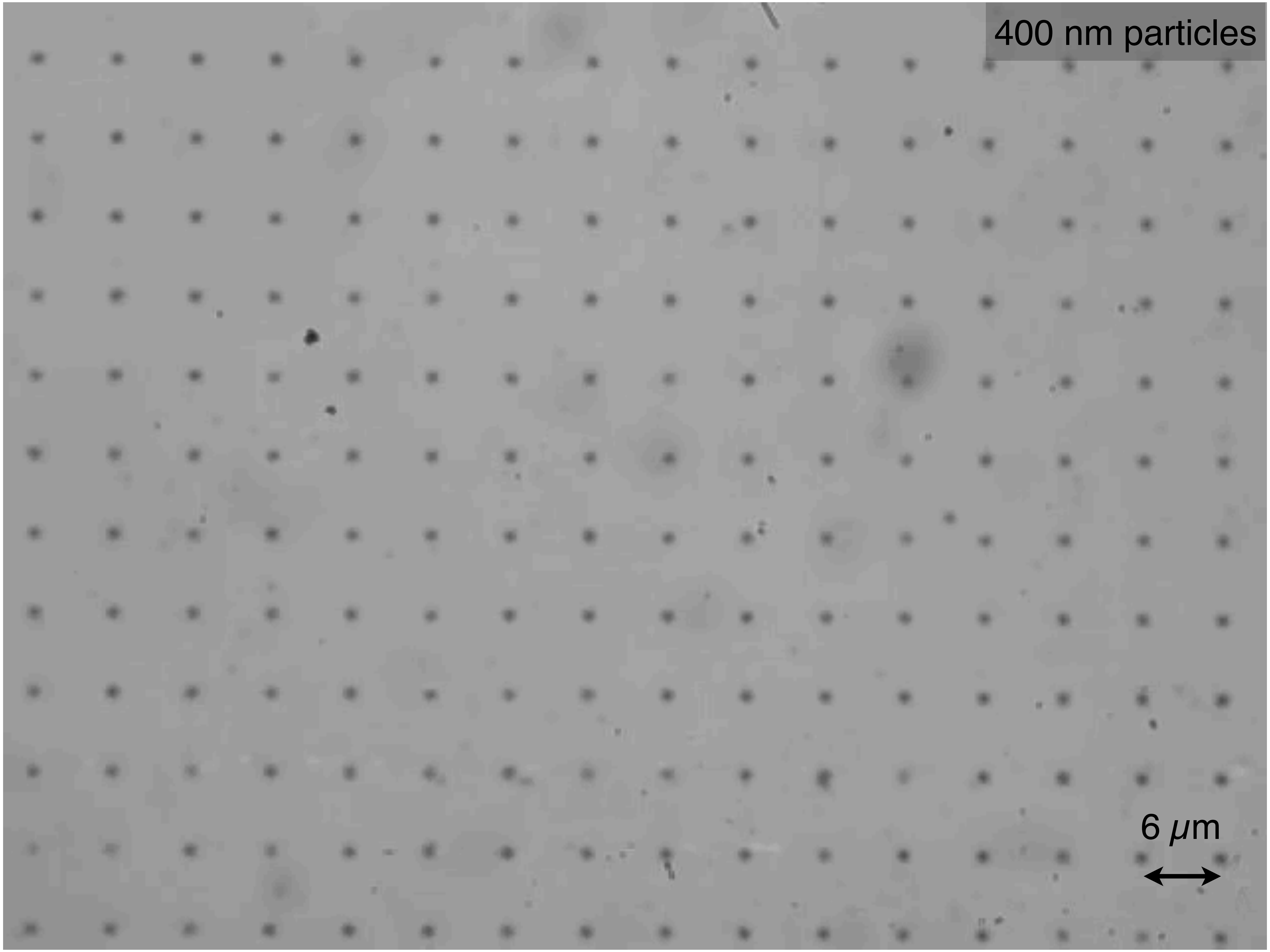


Key result: effects of cluster polydispersity more pronounced in DDM than in DLS (lower scattering angles)



Safari, Vorontsova, Poling-Skutvik, Vekilov, and JCC, submitted

Application area 3: complex geometries



Movie credit: K. He; fabrication credit: K. He and S. T. Retterer

He, Babaye Khorasani, Retterer, Thomas, JCC, and Krishnamoorti, *ACS Nano* **7**, 5122-5130 (2013)

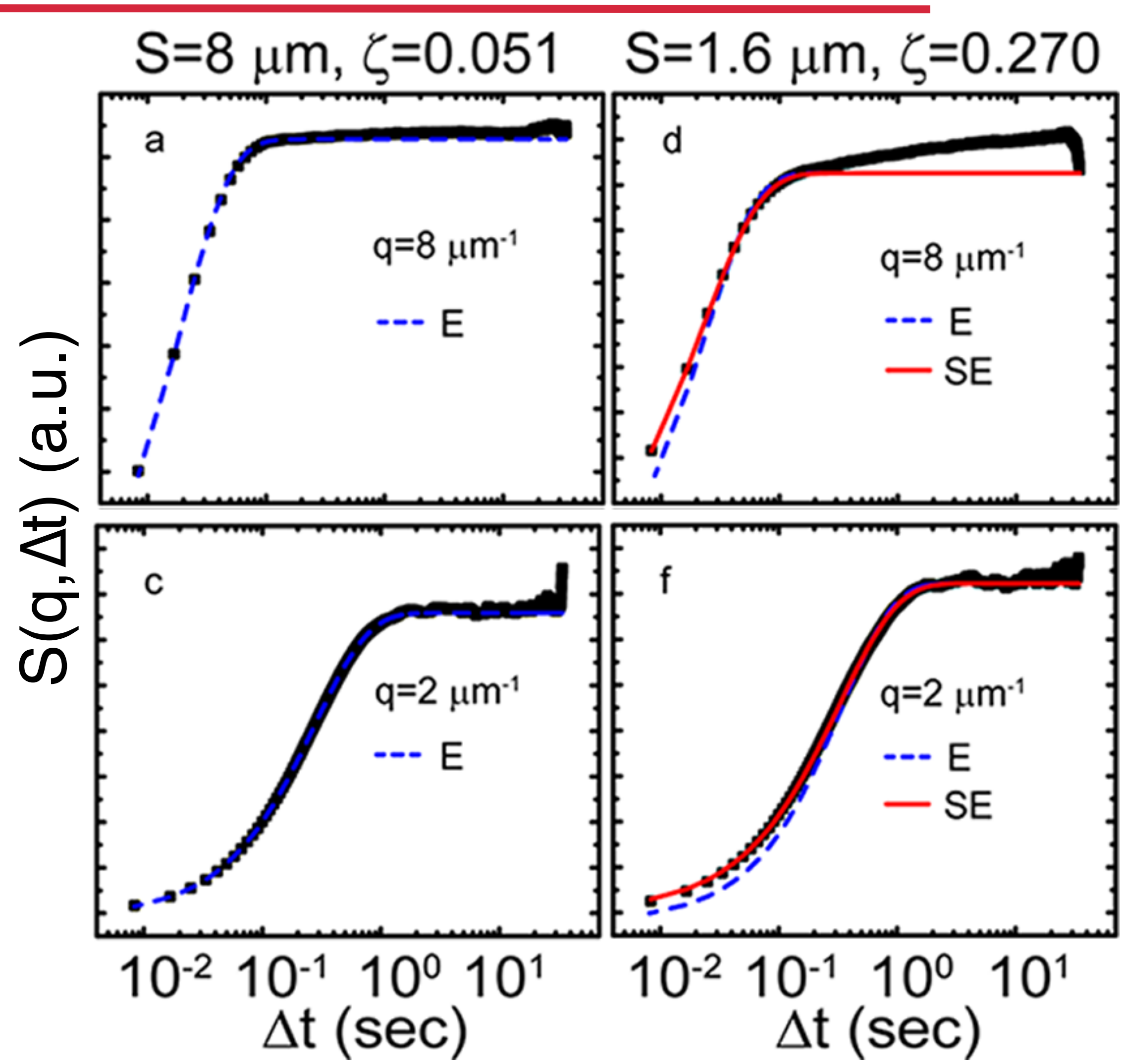
III: complex geometries (i)

System: Polystyrene nanoparticles diffusing in an array of nanoposts (edge-to-edge spacing: > 1 μm)

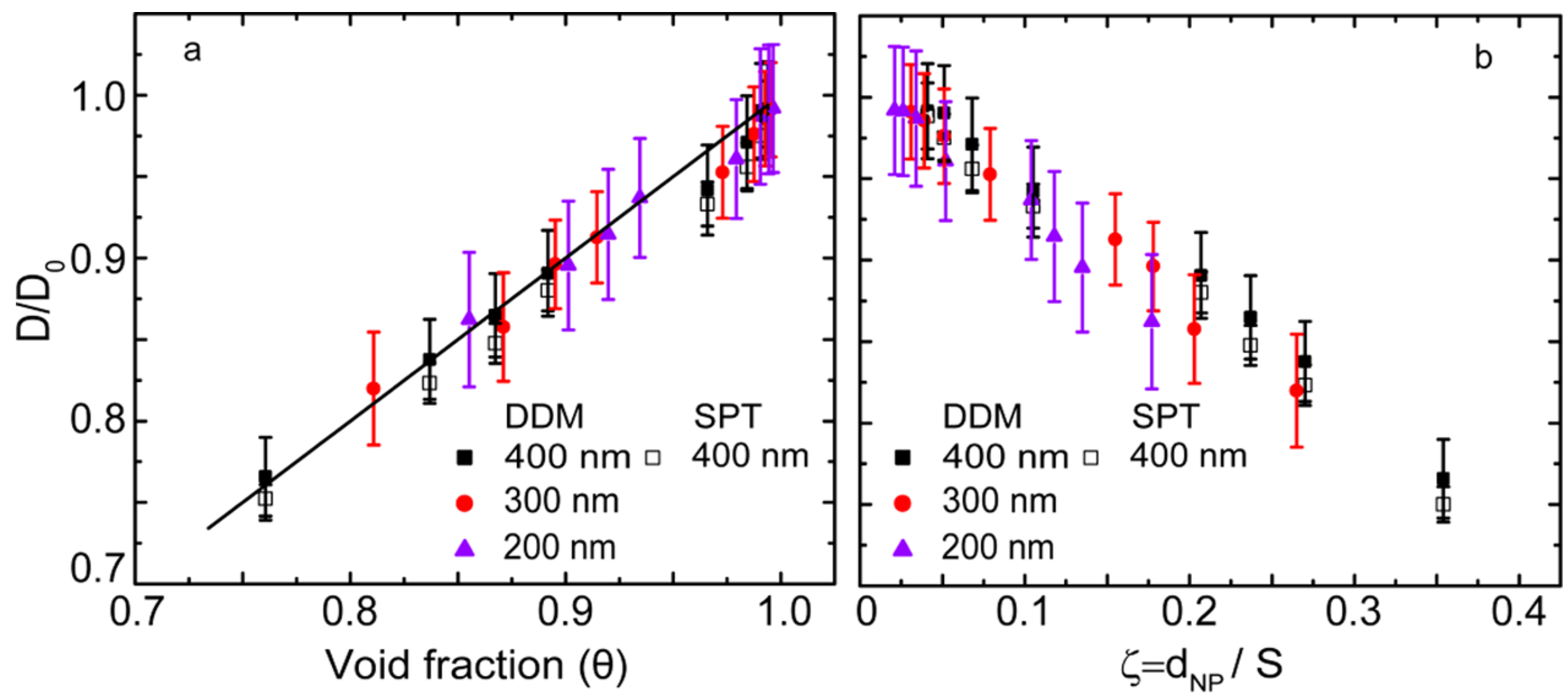
Method: Fluorescence DDM

Fitting model:

$$S(q,\Delta t) = A(q)\left[1 - \exp\left\{-\left(\frac{\Delta t}{\tau(q)}\right)^{r(q)}\right\}\right] + B(q)$$



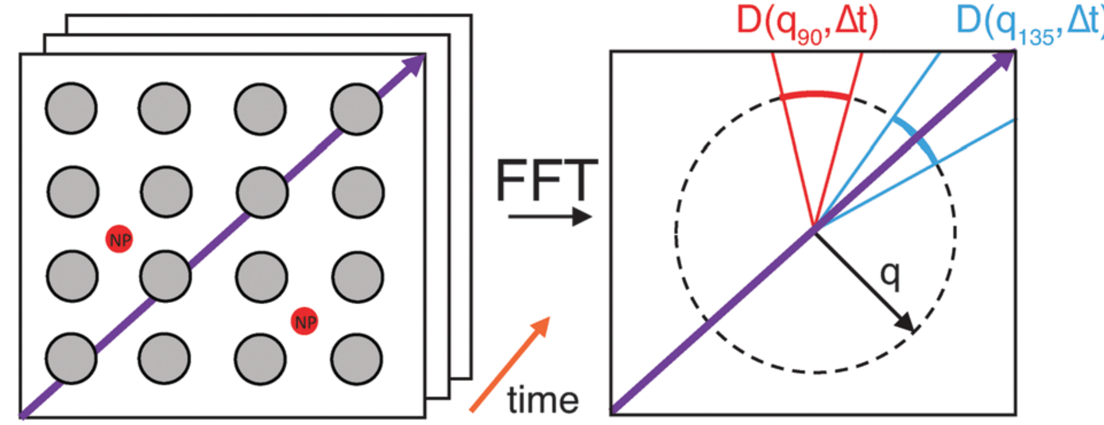
Key result: Particle diffusion slows and stretches in confinement



He, Babaye Khorasani, Retterer, Thomas, JCC, and Krishnamoorti, *ACS Nano* **7**, 5122-5130 (2013)

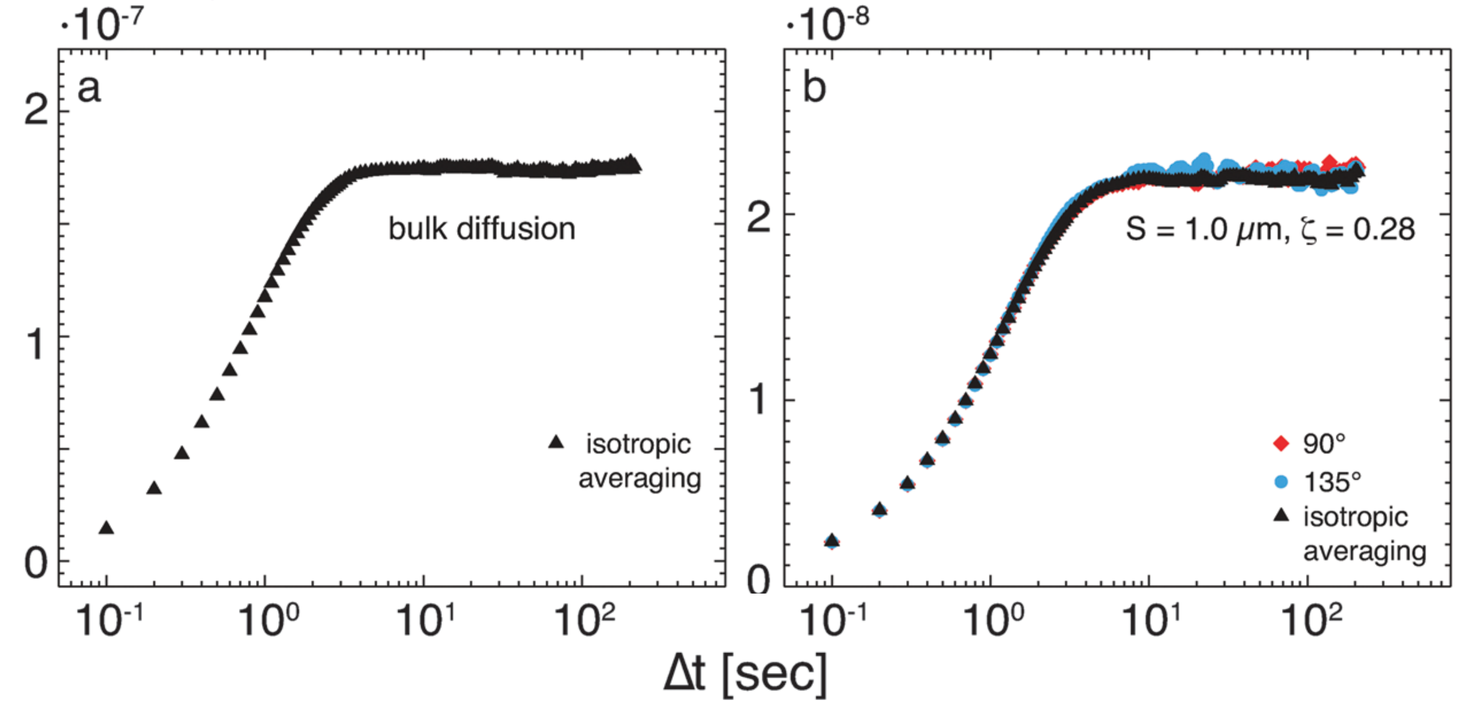
Applications: complex geometries (ii)

System: Polystyrene nanoparticles diffusing in an array of nanoposts (edge-to-edge spacing: < 1 μm)

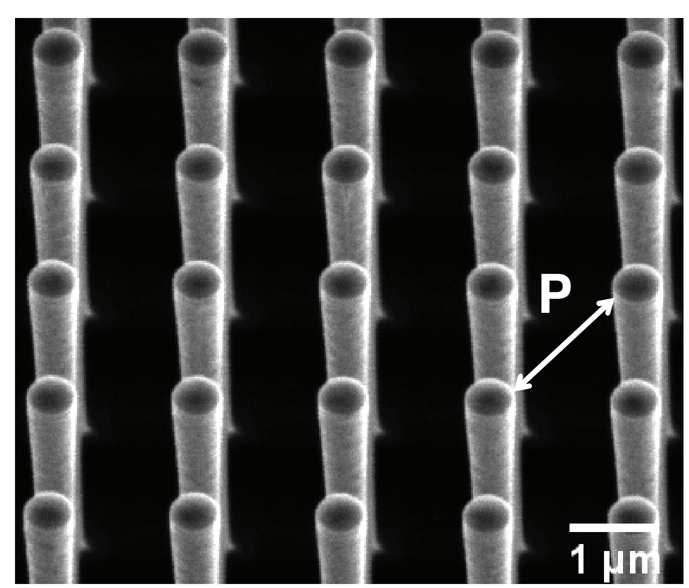


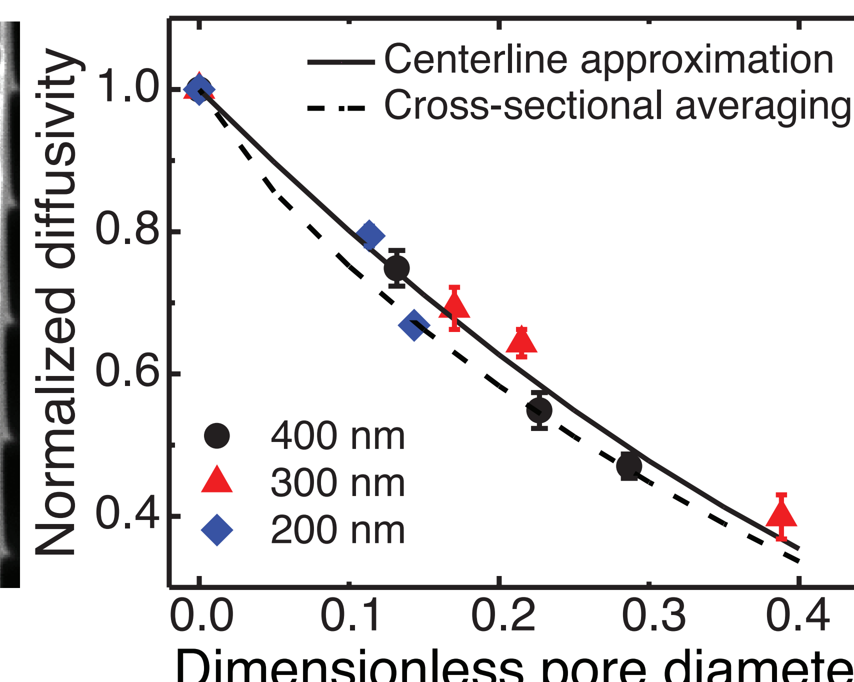
Method: Fluorescence DDM

Representative DDM data: isotropic dynamics in nanopost arrays



Key result: Hydrodynamic models for slit diffusion describe slowing of diffusion in nanopost arrays





Jacob, He, Retterer, Krishnamoorti, and JCC, *Soft Matter* Advance Article (2015)

Conclusions, thoughts, and opportunities

- Differential dynamic microscopy (DDM) yields measurements of dynamics of nanoscale ($\gtrsim$50 nm) objects over a wave vector range of (approximate) $0.1 \leq q \leq 10\ \mu m^{-1}$
- **Advantages of DDM**
  - Submicron (sub-optical-resolution) dynamics
  - Simple equipment (white light source, microscope, camera)
  - Challenging samples: dense, opaque, multiply-scattering
- **Disadvantages of DDM**
  - Inversion problem (but builds on years of DLS analysis)
- **Opportunities and challenges**
  - Other soft materials (polymers? emulsions? cells?)
  - Further adaptions of existing light-scattering methods

Backup DDM slides

Practical considerations for DDM expts

1. Finite thickness of sample chamber:

$$L_{\min} > \frac{1}{\Delta q}$$ (Δq: wavevector uncertainty)

2. Temporal incoherence: minimize source numerical aperture

$$N_A \ll 1$$

3. Spatial incoherence: examine wave vectors satisfying

$$q \ll \frac{1}{\Delta\lambda}$$ (microscope lamp: Δλ ≈ 0.1 μm)

4. Sufficient heterodyne signal: ratio of signal-to-noise terms

$$\frac{A(q)}{B(q)} > 0.05$$

5. Minimum and maximum wave vectors

$$q_{\min} = \frac{2\pi}{\max\left(l_x, l_y\right)} \qquad q_{\max} = \min\left(\sqrt{\text{frame rate}/D}, 2\pi n \sin\left(\theta_{\max}\right)/\lambda\right)$$

1—3: Giavazzi, Cerbino, *et al.*, *Phys. Rev. E* **80**, 031403 (2009)
4, 5: JCC and collaborators