Microrheology: Basic Principles

Translational and Rotational Motion of Probe Particles in Soft Materials

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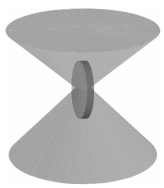
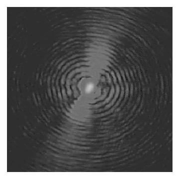
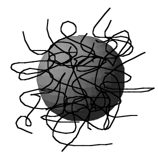





Thermal Diffusion Microrheology: Idea and Inspiration

While examining dynamics of soft materials in 1993…

Rheology of Glassy Colloidal Dispersions of Hard Spheres
Mechanical Rheometer

Measure Moduli: $G'(\omega)$, $G''(\omega)$

Diffusing Wave Spectroscopy
Dynamic Light Scattering

Measure Diffusion: Brownian Motion of Uniform Spheres

→ **Get *G'*, *G''* of glasses from light scattering!?!**

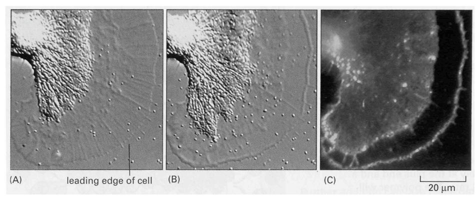
Microrheology

Study of mechanical shear response of materials at the micro-scale

How can you build a rheometer to probe rheological properties of soft materials in very small volumes?

For example, what are viscoelastic properties inside cells?
Rheology of scarce and valuable biomolecules?
Screening of material properties using small volumes?

Growth Cone of a Nerve Cell



Alberts, et al *Molecular Biology of the Cell*

Traditional mechanical rheometers are not suited for this!
Exploit sensitivity and wide dynamic range of optical methods!

Experimental Methods of Microrheology

Microscale probe particle approach:
- Put microscale tracer particles into material to be studied
- Measure motion of particle (strain) in response to driving stress

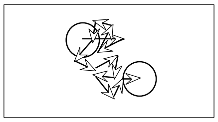
Thermal: let $k_B T$ excite probe particles
("passive") watch motion (light scattering, optical microscopy)
Advantages: no external driving is required
$k_B T$ excitations are always linear
$k_B T$ excitations cover very broad freq. range

Forced: apply optical/magnetic forces to probe particles
("active") watch motion (usually optical microscopy)
Advantages: particles can be held/moved where desired
make particle motion easier to detect

Many exciting new uses are being found!

Simple Translational Diffusion of Microparticles

Thermal fluctuations cause microspheres to move in a random walk



Entropic excitation of liquid molecules cause net force fluctuations on microspheres

microsphere radius: $a \sim 1\ \mu$m
liquid viscosity: η

Mean square displacement describes ensemble-averaged motion

3D $\quad <\Delta \boldsymbol{r}^2(t)> = 6Dt \quad$ square of displacement grows linearly with time

Stokes-Einstein Relation connects diffusion coefficient D with thermal energy, viscosity, and particle size

$$D = k_B T/(6\pi\eta a) \qquad \text{(sphere)}$$

Typical value at room temperature $T = 298$ K for $a = 1\ \mu$m, $\eta = 1$ cP (water):

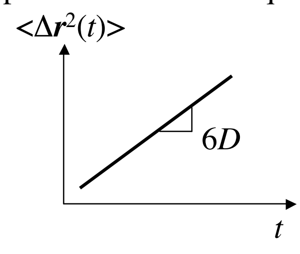
$$D = 0.2\ \mu\text{m}^2/\text{s}$$

Principle of Thermal Microrheology

T.G. Mason and D.A. Weitz, PRL **74** 1250 (1995).

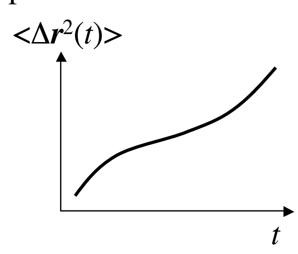
Brownian Motion in a Viscoelastic Complex Fluid
Measure mean square displacement (msd): $<\Delta \boldsymbol{r}^2(t)>$

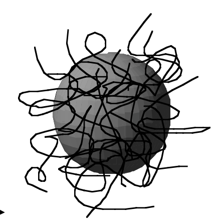
Sphere in a viscous liquid



Stokes-Einstein Relation
$\Rightarrow \eta$

Sphere in a viscoelastic material





Generalized Stokes-Einstein Relation
$\Rightarrow G^*(\omega), J(t), \ldots$

Add probe microspheres, measure translational $<\Delta \boldsymbol{r}^2(t)>$, and apply **Generalized Stokes-Einstein Relation (GSER)**

Assumptions of Thermal Microrheology

Validity of Generalized Stokes-Einstein Relation

At Equilibrium: No External Driving Forces/Torques
No flow or convection-- diffusive transport

Continuum Approximation
Treat the complex fluid as a continuum around the probe
Good approximation: probe particle size >> elastic structure size
Example: 1 μm sphere in a polymer sol’n with mesh size = 20 nm

Stick Boundary Conditions
Assume both viscous and elastic coupling by stick
Generally OK, but sphere coating can matter

Flow Field Pattern in Complex Fluid outside Probe
Don’t know the flow field outside a sphere for arbitrary material
Assume flow field resembles that of viscous liquid
Generally OK for liquid-based materials

Generalized Stokes Einstein Relation (GSER)

Langevin force equation: thermal driving with memory damping

velocity of spherical particle

$$m\dot{v}(t) = F_{\mathrm{R}}(t) - \int_0^t \zeta(t - t')v(t')dt'$$

inertia

random thermal driving force

memory function

geometry

frequency-dependent shear viscosity η

coupling

Used for describing long time tails in particle diffusion

(e.g. R. Klein)

Generalized Stokes Einstein Relation (GSER)

Unilateral Laplace transform into *s*-frequency domain:

$$\tilde{v}(s) = \frac{\tilde{F}_{\mathrm{R}}(s) + mv(0)}{\tilde{\xi}(s) + ms}$$

retain initial conditions

Find LT of the velocity autocorrelation function:

$$\langle v(0)\tilde{v}(s)\rangle = \frac{m\langle v(0)v(0)\rangle}{\tilde{\xi}(s) + ms} = \frac{k_{\mathrm{B}}T}{\tilde{\xi}(s) + ms}$$

causality: $\langle v(0)\tilde{F}_{\mathrm{R}}(s)\rangle = 0$

energy equipartition: $m\langle v(0)v(0)\rangle = k_{\mathrm{B}}T$

Microrheology: Basic Principles

Generalized Stokes Einstein Relation (GSER)

T.G. Mason and D.A. Weitz, PRL **74** 1250 (1995).

Stokes drag for a sphere in a viscous liquid (stick boundary cond.):

$$\tilde{\xi}(s) = 6\pi a\tilde{\eta}(s)$$

Assume that the simple drag equation can be generalized to all frequencies

Express modulus using mean square displacement:

$$\langle v(0)\tilde{v}(s)\rangle = s^2\langle\Delta\tilde{\boldsymbol{r}}^2(s)\rangle/6 \qquad \text{(3D)}$$

(GSER)

$$\tilde{G}(s) = s\tilde{\eta}(s) = \frac{k_{\mathrm{B}}T}{\pi as\langle\Delta\tilde{\boldsymbol{r}}^2(s)\rangle}$$

Neglecting inertia (OK for $s < 10^7$ Hz)

Estimate $G^*(\omega)$ using log slope of $\langle\Delta \boldsymbol{r}^2(t)\rangle$

Analytical continuation: $s = i\omega$

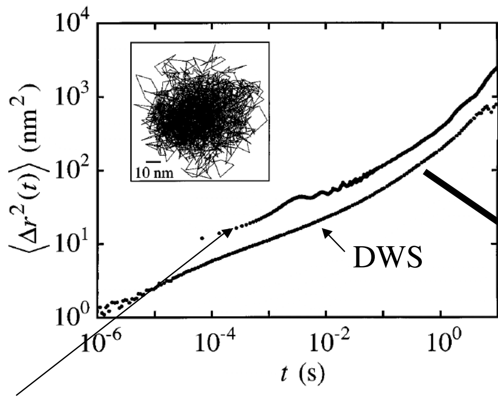
Reverse transform to time-domain to get creep compliance:

$$J(t) = \frac{\pi a}{k_{\mathrm{B}}T}\langle\Delta\boldsymbol{r}^2(t)\rangle$$

Microrheology: Basic Principles

Particle Tracking Thermal Microrheology

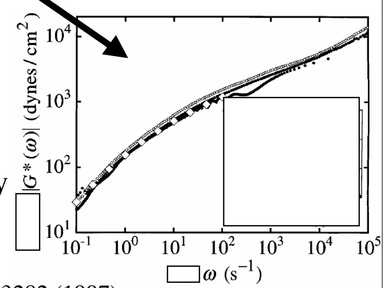
Dilute Polystyrene Beads in Aqueous Polyethylene Oxide Solution



MW = 500,000 PEO
3% by mass

$a = 0.46\ \mu$m (upper curve)
$a = 0.26\ \mu$m (lower curve)

GSER

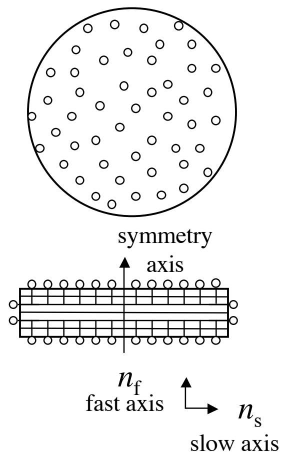


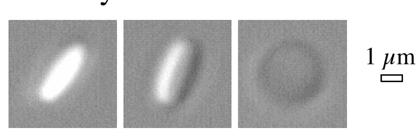
Laser Deflection Particle Tracking (LDPT)
Quad. photodiode detection of 2d trajectory
Scattered laser beam deflected by sphere

T.G. Mason, et al., *PRL* **79** 3282 (1997).

Anatomy of a Wax Microdisk

Short right circular cylinders with flat faces





Smectic layering of wax into planes
Molecular and disk axes are parallel

Molecular alignment creates an anisotropic surface tension

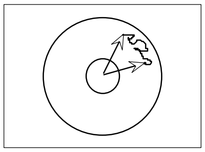
Surface tension overcomes in plane bulk yield stress to create a circular perimeter

Surface tension does not overcome interplanar bulk yield stress: disks stay flat

Birefringent:
$\Delta n = n_s - n_f \approx 0.1$

Simple Rotational Diffusion of Microparticles

Thermal fluctuations cause re-orientation of microparticles



Reorienting collisions of liquid molecules cause net torque fluctuations on microparticles

Unit vector rigidly attached to the sphere diffuses over surface of unit sphere ↗

microsphere radius: $a \sim 1\ \mu$m
liquid viscosity: η

Mean square angular displacement describes ensemble-averaged rotation

1D $\quad \langle \Delta\theta^2(t) \rangle = 2\Theta t \quad$ square of anglular displacement grows linearly with time

Rotational Stokes-Einstein Relation connects the rotational diffusion coefficient Θ with thermal energy, viscosity, and particle size

$$\Theta = k_B T/(8\pi\eta a^3)$$

sphere: $\Theta_{xx} = \Theta_{yy} = \Theta_{zz}$

Typical value at room temperature $T = 298$ K for $a = 1\ \mu$m, $\eta = 1$ cP (water):

$$\Theta = 0.2\ \mathrm{rad}^2/\mathrm{s}$$

Rotational Diffusion Microrheology

Can we measure the linear viscoelasticity of complex fluids by examining the rotational diffusion of tracer microparticles?

Example:
microdisk in a polymer entanglement solution

Procedure

- Tracer particle is embedded in a viscoelastic complex fluid
- Thermal torque kicks → broadband rotational fluctuations
- Measure time-dependent orientation (real-space/scattering)
- Compute mean square angular displacement: $\langle \Delta\theta^2(t) \rangle$
- Use Rotational Generalized Stokes-Einstein Relation (R-GSER) (Treat complex fluid as a homogeneous continuum material)
- Obtain viscoelastic shear modulus as a function of frequency

Rotational Generalized Stokes Einstein Relation (R-GSER)

Langevin torque equation: thermal driving with memory damping

angular velocity
$v = \mathrm{d}\theta/\mathrm{d}t$

$$I\dot{v}(t) = \tau_{\mathrm{R}}(t) - \int_0^t \mathrm{d}t' \zeta_{\mathrm{R}}(t - t') v(t')$$

rotational inertia

random thermal driving torque

rotational memory function

geometry

frequency-dependent shear viscosity η

coupling

Rotational Generalized Stokes Einstein Relation (R-GSER)

Unilateral Laplace transform into s-frequency domain:

$$\tilde{v}(s) = \frac{\tilde{\tau}_{\mathrm{R}}(s) + I v(0)}{\tilde{\zeta}_{\mathrm{R}}(s) + Is}$$

Find LT angular velocity autocorrelation function:

$$\langle v(0)\tilde{v}(s)\rangle = \frac{I\langle v(0)\tilde{v}(0)\rangle}{\tilde{\zeta}_{\mathrm{R}}(s) + Is} = \frac{k_{\mathrm{B}}T}{\tilde{\zeta}_{\mathrm{R}}(s) + Is}$$

causality: $<v(0)\tau_{\mathrm{R}}(s)> = 0$

rotational energy equipartition: $I\langle v(0)\tilde{v}(0)\rangle = k_{\mathrm{B}}T$

Rotational Generalized Stokes Einstein Relation (R-GSER)

Rotational Stokes drag for a sphere in a viscous liquid (stick):

$$\tilde{\xi}_{\mathrm{R}}(s) = 8\pi a^3 \tilde{\eta}(s)$$

Assume that this rotational drag equation can be generalized to all frequencies

Express modulus using mean square rotational displacement:

$$\langle v(0)\tilde{v}(s)\rangle = s^2\left\langle \Delta\tilde{\theta}^2(s)\right\rangle \Big/ 2$$

Rotation of the major symmetry axis (1D)

$$\boxed{\tilde{G}(s) = s\tilde{\eta}(s) \cong \frac{k_{\mathrm{B}}T}{4\pi a^3 s\left\langle \Delta\tilde{\theta}^2(s)\right\rangle}}$$

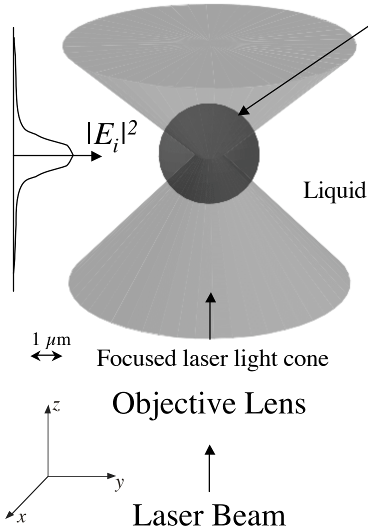
Neglect inertia (OK for $s < 10^7$ Hz)

Reverse transform to time-domain to get creep compliance:

$$J(t) = \frac{4\pi a^3}{k_{\mathrm{B}}T}\left\langle \Delta\theta^2(t)\right\rangle$$

Basic Principles of Laser Tweezers

Focus laser beam using microscope's objective lens

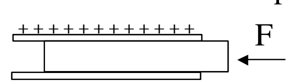


Dielectric microsphere is trapped in the region of highest electric field by strong gradient forces in *x*, *y*, & *z* when $\varepsilon_{\mathrm{sphere}} > \varepsilon_{\mathrm{liquid}}$

Energy ~ $-\varepsilon E^2 \cdot$ Volume

Focusing must be strong so *z*-gradient forces overcome radiation pressure: Use high mag. and high N.A. lens

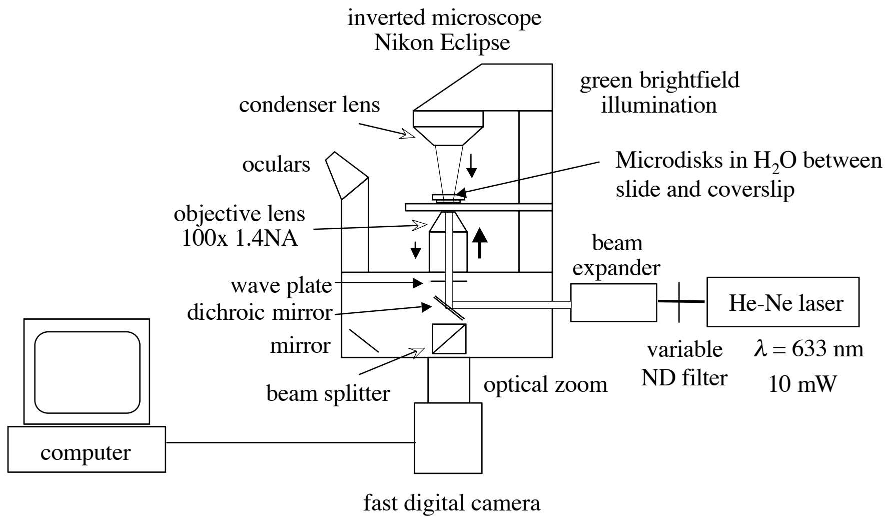
Analogy: dielectric slab in a capacitor



Store more energy when slab is pulled into region of high *E*-field

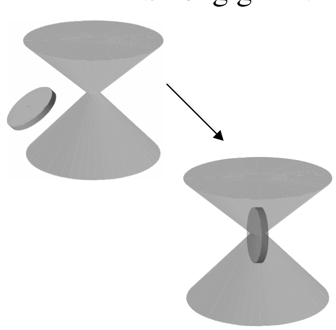
Laser Tweezers and Fast Digital Microscopy Apparatus

Expanded laser beam is focused by a microscope's objective lens
to create high electric field gradients in *x*, *y*, & *z*



Applying Laser Tweezers to Dielectric Microdisks

Move a diffusing microdisk near the focal spot of the laser
Strong gradients in the electric field trap the disk



Disk aligns "on edge" in the trap

Maximizes the volume of highest dielectric constant in the brightest part of the focused beam

- Gradient forces in xy-plane center disk
- Symmetry axis is ⊥ to beam direction
- Gradient forces in *z* balance radiation pressure

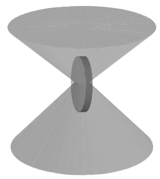
First observation of 3D trapping of a microdisk!

Disk thickness is comparable to wavelength of light

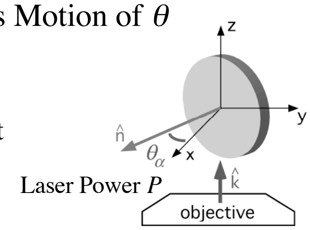
Microdisk's alignment facilitates the study of 1D rotational dynamics:
3 Euler angles for arbitrarily shaped particle –> 1 angle θ

Angular Equation of Motion of a Tweezed Microdisk

Langevin Torque Equation Describes Motion of θ



$$I\ddot{\theta} = \tau_R - \zeta\dot{\theta} + \tau_{light}$$



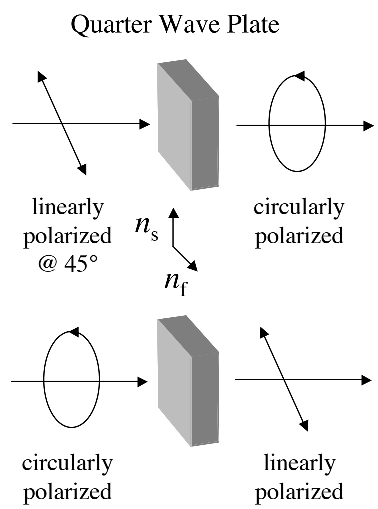
$I\ddot{\theta}$	Rotational Inertia	$\sim \rho a^5 \ddot{\theta}$	10^{-20} erg for 1 rad/s^2
τ_R	Random Thermal Torque	$\sim k_B T$ (white noise)	4×10^{-14} erg
$\zeta\dot{\theta}$	Viscous Drag Torque	$\sim \eta a^3 \dot{\theta}$ (Stokes law)	10^{-14} erg for 1 rad/s
τ_{light}	Optical Torque	$\sim \left(P/\hbar\omega_o\right) \; \hbar \; f\left(\Delta n, \theta\right)$	$<10^{-13}$ erg for 1 mW

photons / s — ang mom per photon — birefringence, orientation, polarization

Changing Light Polarization with Birefringent Wave Plates

Birefringence: anisotropy in a material's dielectric constant

Light waves travel at different speeds along different molecular axes



Sinusoidal oscillation of *E*-field in a plane is converted into circular oscillation

Optical angular momentum is transferred to the wave plate as CP light leaves plate

∴ Light exerts a small torque on plate

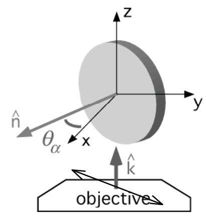
R.A. Beth, Phys. Rev. **50**, 115 (1936).

Circular oscillation of *E*-field is converted into sinusoidal oscillation in a plane

Optical angular momentum is transferred to the wave plate independent of its orientation

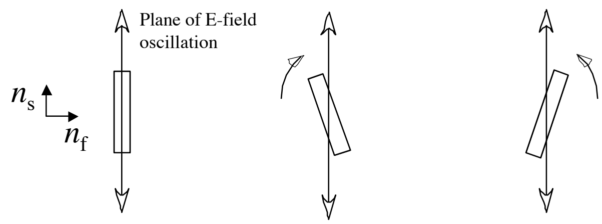
Tweezing Birefringent Wax Microdisks

Linearly Polarized (LP) Laser Light



Optical angular momentum transfer:
Harmonic angular restoring force for θ

top view:

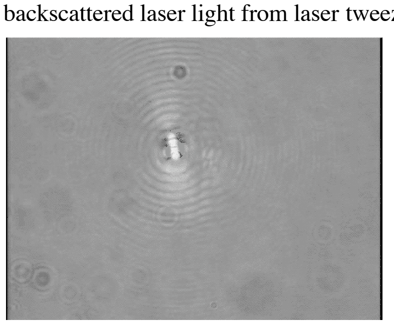


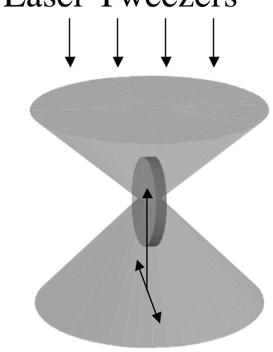
polarization out:	linear	r.h. elliptical	l.h. elliptical
torque:	0	CW restoring	CCW restoring

Constrained Rotational Diffusion of a Wax Microdisk Trapped Using Linearly Polarized Laser Tweezers

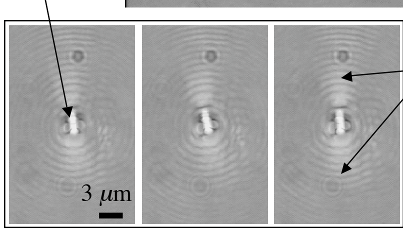
Green brightfield illumination
Red backscattered laser light from laser tweezer

disk (on edge)
in tweezer





Z. Cheng, P.M. Chaikin, and T.G. Mason, PRL **89** 108303 (2002).



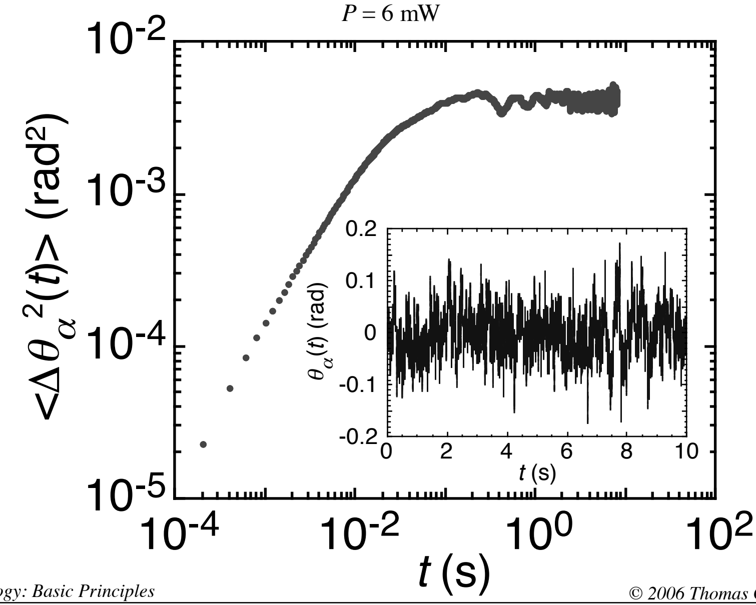
Light Streak !

Refracted light from the disk forms a natural optical lever for measuring its orientation: θ

Microdisk Dynamics in an Orientational Trap

Linearly polarized tweezer

$P = 6$ mW



Rotational - Harmonically Bound Brownian Particle

Torque equation for a rotationally trapped microdisk:

rot. inertia — rot. visc. friction factor — laser power — retardation

$$I\ddot{\theta}_\alpha = \tau_R - \varsigma\dot{\theta}_\alpha - \frac{2P_{\text{eff}}}{\omega_o}\sin(R)\sin(2\theta_\alpha)$$

white noise thermal driving torque — optical frequency

Linearize, neglect inertia, apply equipartition, & solve for the mean square angular displacement (MSAD):

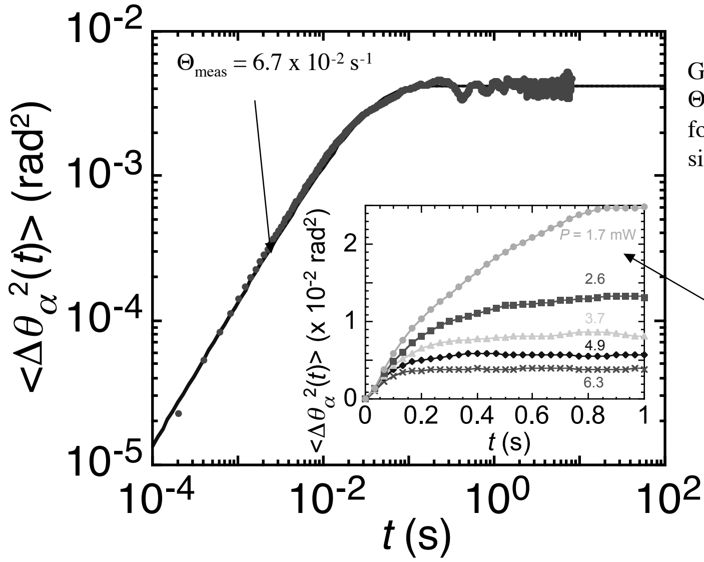
$$\left\langle \Delta\theta_\alpha{}^2(t)\right\rangle = \frac{2k_B T}{\kappa}\left[1 - \exp(-\kappa t / \varsigma)\right]$$

where $\kappa \equiv 4P_{\text{eff}}\sin(R)/\omega_o$ optical rotational spring constant

$\varsigma = 8\pi\eta a^3 H(\rho)$ rotational friction factor (Perrin)

geometrical function of aspect ratio ρ

R-HBBP: Comparison of Experiment with Theory

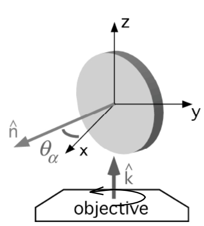


Good agreement:
Θ_{pred} = 4.3 x 10^{-2} s^{-1}
for an ellipsoid of
similar aspect ratio

Inset: Disk is more strongly aligned at higher laser power

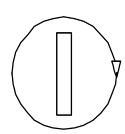
Tweezing Birefringent Wax Microdisks

Circularly Polarized (CP) Laser Light



Disk's symmetry axis rotates
in the xy-plane

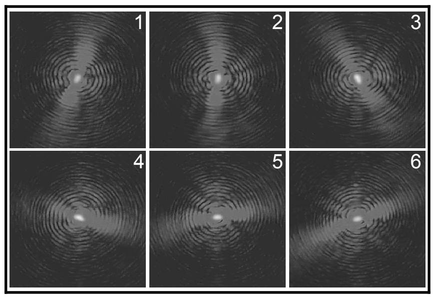
Some CP light gets converted to elliptical or linear polarization:
Torque on disk is due to change in photon angular momentum

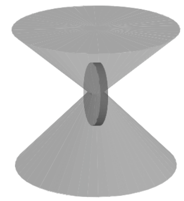


Symmetry: torque is independent of disk's orientation θ
Direction of rotation controlled by handedness of CP light

Microdisk in a Circularly Polarized Tweezer

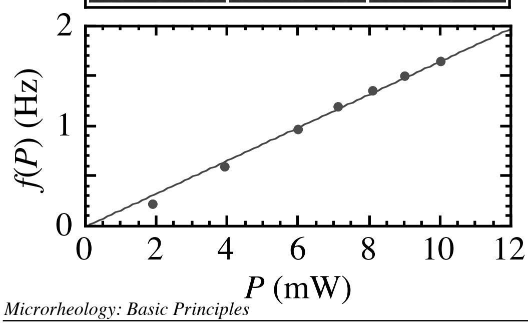
Light torques drive continuous rotation





"Colloidal Lighthouse"

Light Flashes From the Microscope Slide

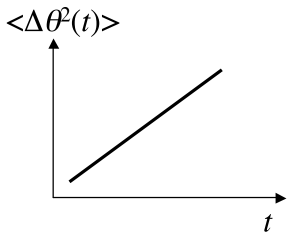


rotation frequency is proportional to laser power

Rotational Diffusion Microrheology

Z. Cheng and T.G. Mason, Phys. Rev. Lett. **90**, 018304 (2003).

We can measure a simple liquid's shear viscosity η by examining the rotational diffusion of a tracer microparticle



Measure $<\Delta\theta^2(t)>$ using Light Streak Tracking

Slope gives Θ

Stokes-Einstein Relation tells us η

Can we measure a complex fluid's frequency-dependent viscoelasticity by examining the rotational diffusion of a nonspherical microparticle?

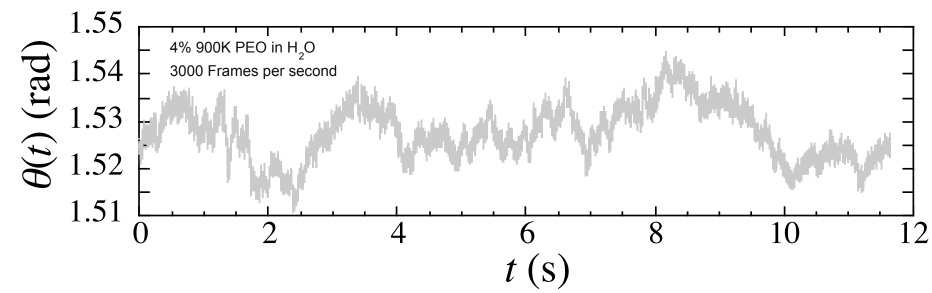
Example:
Microdisk in a polymer solution

Polymer entanglements ⇒ high freq. elasticity
$<\Delta\theta^2(t)>$ will not be a simple straight line

Rotational Diffusion Microrheology Experiment

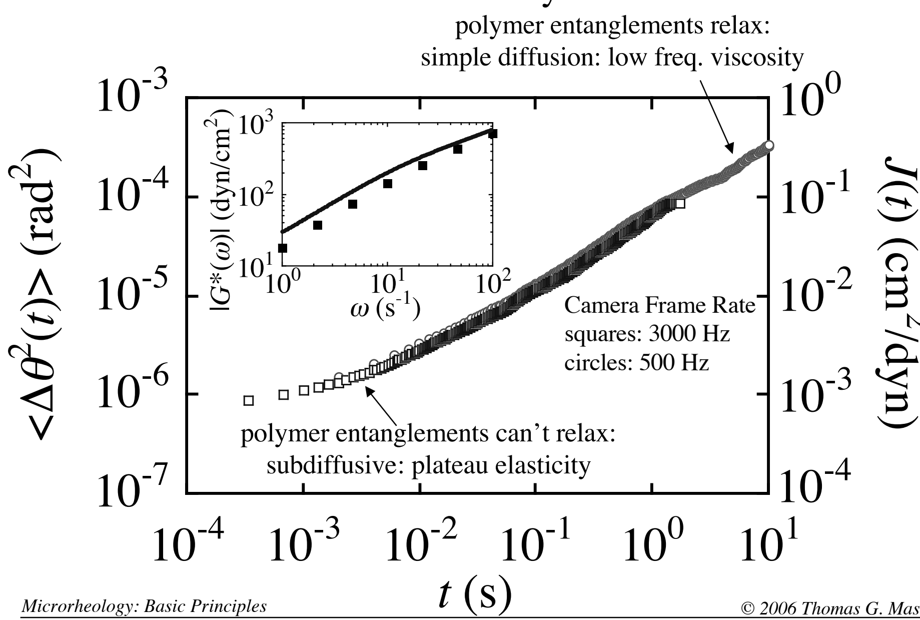
Perform Light Streak Tracking on a 1-eicosene microdisk
in a viscoelastic aqueous polyethylene oxide (PEO) solution

Viscoelastic drag torque dominates optical torque
(lower laser power after aligning disk on edge)



Fluctuations are small and bounded at shorter times
Fluctuations wander more like a random walk at longer times (1 s)

Mean Square Angular Displacement and Creep Compliance of a Microdisk in a Polymer Solution



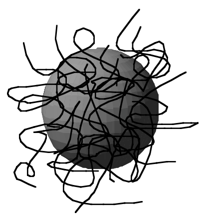
Conclusions

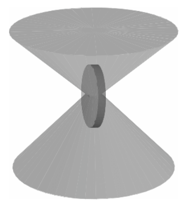
Translation and Rotational Motion of Probe Particles
Yields Quantitative Rheology of Microscale Rheological Properties

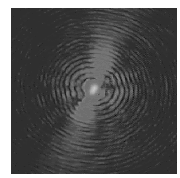
Microrheology is Expanding our Understanding of New Complex Fluids

-Biopolymer Solutions
-Novel Synthetic Materials
-Product Formulations

Many Opportunities Remain: Science and Applications







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