# Nonequilibrium soft matter: self-propelled, drifting, and stuck


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IITK-ICTS Nonequilibrium Statistical Physics 2 Feb 2010


Support: DST, CEFIPRA, JCBose

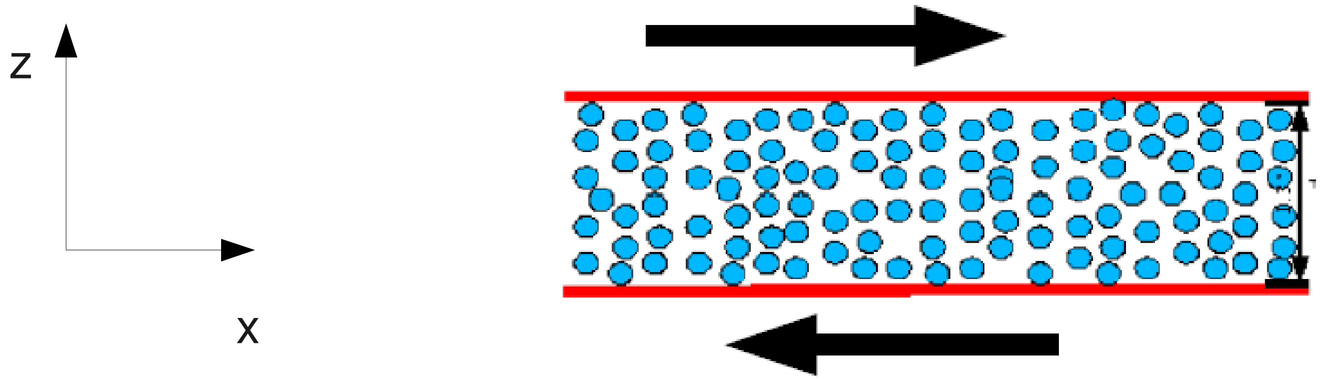
# Outline: in three parts

- Active matter
  - swimmers, motors, cytoskeleton — self-propelled
- Driven particulate flows
  - sedimentation, electrophoresis — drifting
- Confined liquids
  - friction, the glass transition — stuck

# Stuck: viscosity of confined fluids

Saroj Nandi, Sarika Bhattacharyya, SR 2010

# Confined fluids and glassiness




Granick et al. 1990s:
surface force apparatus
shear measurements
simple organic liquids

Confine to 3 – 10 molecular layers

- huge viscosity enhancement
- shear thinning at modest flow rates
- not crystallization
- confinement promotes the glass transtion

# Stuck: confined liquids and the glass transition

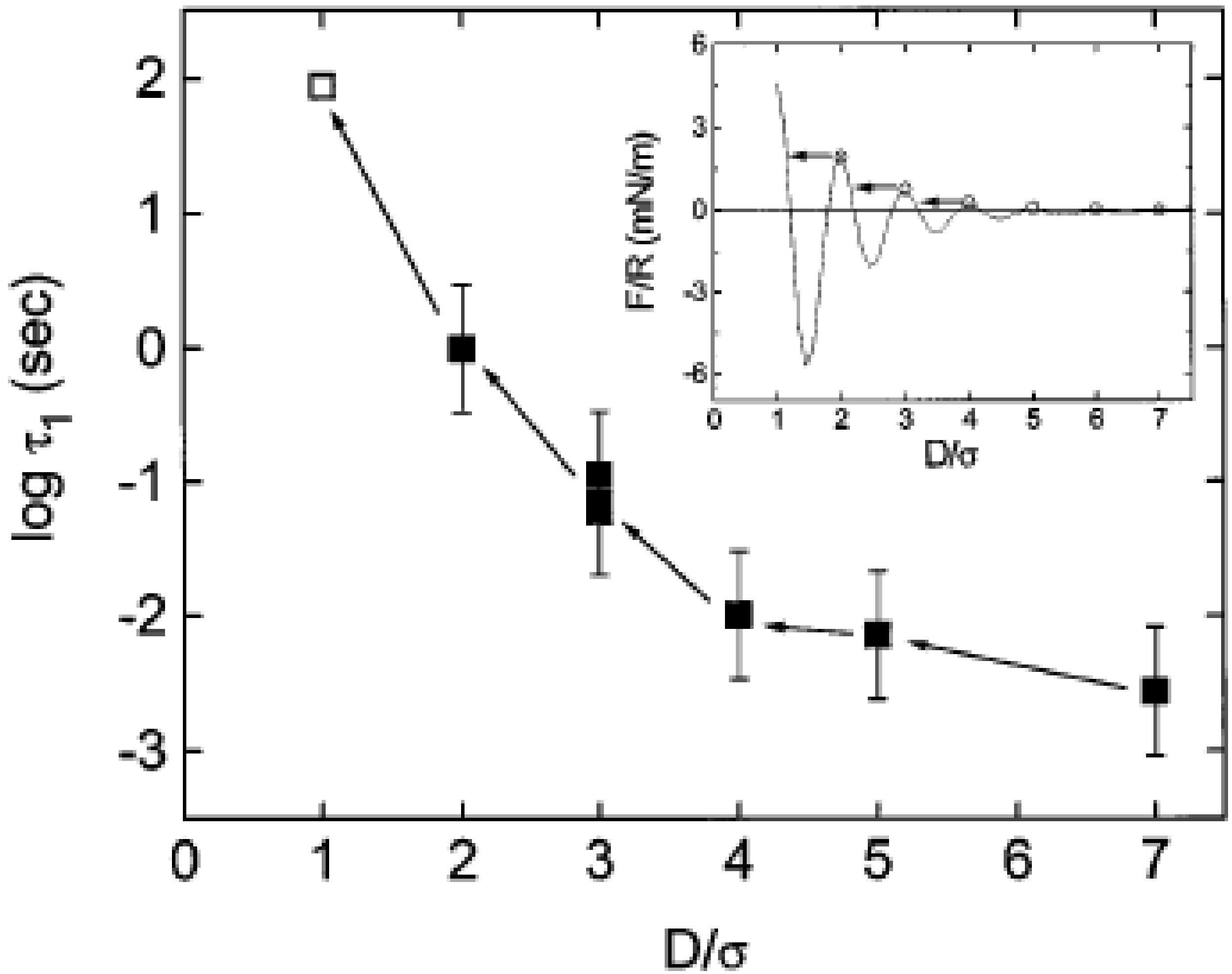



FIG. 2. Longest relaxation time $\tau_1$ plotted logarithmically against film thickness expressed in multiples of the molecular dimension of OMCTS. Data at different thickness were ac-

Macroscopic relaxation time
Demirel, Granick
PRL **77** (1996) 2261

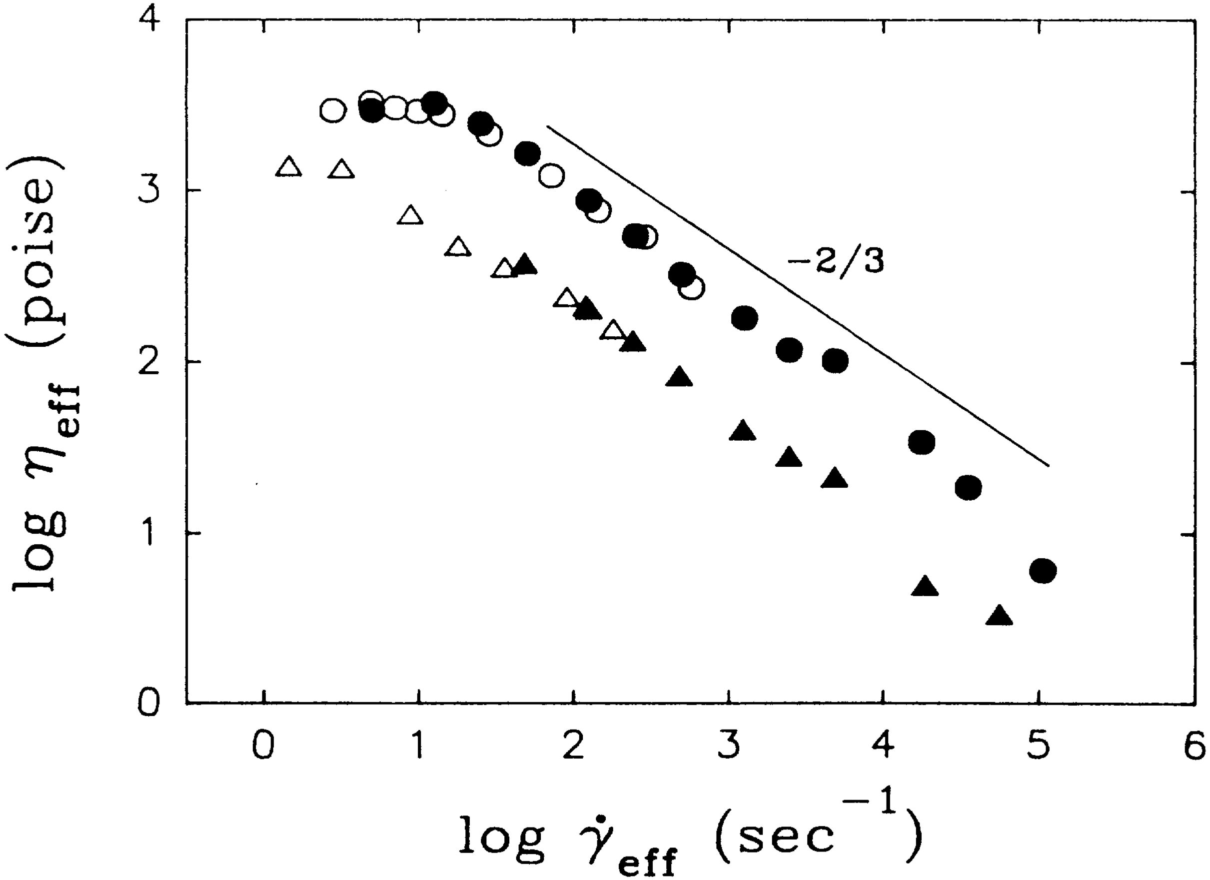



FIG. 2. Log-log representation of changes in the effective viscosity as a function of strain rate. Circles: dodecane film specified in Fig. 1. Triangles: OMCTS film of thickness 2.7 nm and net normal pressure 0.14 MPa. Open symbols: amplitude varied at constant frequency. Solid symbols: frequency varied at constant amplitude.

Strong shear-thinning
Hu *et al.* PRL **66** (1991) 2758

# Prelude to theory

- Velocity along x, gradient along z
  - modes with wavevector along x involved
  - layering not central issue
- Confinement: momentum sink, density diffuses
  - emergence of zero-wavenumber friction?
  - slowing down: feedback of density diffusivity

# Related work

- Krakoviack 2007
  - Microscopic approach to mode-coupling theory
  - Disordered confining medium: random potential
- Biroli-Reichman
  - Inhomogeneous mode-coupling theory
- Karmakar *et al.* 2009
  - System smaller than critical droplet can't relax
  - Indrani *et al.* 1991: first sign that small is slow

# Possible mechanisms

- Suppressed modes NO
  - Confinement cuts off long-wavelength modes
  - Naively, this should speed up dynamics
- No-slip boundary conditions NO
  - Should yield diffusivity ~ $\text{gap}^2$
  - Trivial, kinematic effect, scales out, can't feed back
- Periodic potential of walls YES
  - Slows down some density modes
  - Should enhance MCT feedback

S Nandi, S Bhattacharyya, SR 2010

# Mode-coupling theory for beginners

- Maxwell: step shear-strain $\varepsilon$ on a fluid
  - $G_{inf}$ = infinite-freq shear modulus
  - Instantaneous response $\sigma = G_{inf}\,\varepsilon$
  - Wait a time $\tau$, strain unrecoverable
  - Therefore strain rate = $\varepsilon/\tau$, viscosity $\eta = G_{inf}\,\tau + \eta_0$ (bare)
- Plausibly: $\tau = A\,\eta$
  - $\eta = G_{inf}\,\tau + \eta_{0/}/(1 - A\,G_{inf})$ diverges at large A

Geszti 1983

# Mode-coupling for beginners contd.

The stress tensor $\sigma$, strain tensor $\epsilon$ and infinite frequency shear modulus is $G_\infty$, then $\dot{\epsilon} = \epsilon/\tau$ and $\frac{\sigma}{G_\infty} = \epsilon$

$$\frac{\sigma}{G_\infty \tau} = \frac{\epsilon}{\tau} = \dot{\epsilon} \Rightarrow \delta\eta = G_\infty \tau$$

$$\eta = \eta_0 + \delta\eta \quad (1)$$

$$\Rightarrow \eta = \frac{\eta_0}{1 - AG_\infty} \quad (2)$$

$T \downarrow$ or density $\uparrow \Rightarrow G_\infty \uparrow \rightarrow \eta$ diverges.

(T. Geszti, J. Phys. C: Solid State Phys. 16, 5805 (1983))

# How does confinement affect this?

- Walls impose periodic potential $u^{ext}(r)$
  - Some density modes frozen
  - density $\rho(r,t) = m(r) + \delta\rho(r,t)$
  - m(r) stands in for $u^{ext}(r)$
- Redo mode-coupling theory in terms of m(r)
  - increase amplitude of m(r) --> MCT glass transition
  - enough to do one-dimensional theory

S Nandi, S Bhattacharyya, SR 2010

# Technical details

Density field ρ, velocity field v

free energy functional $F^u[\rho]$ includes wall potential $u^{ext}(r)$

bare viscosities η, ζ, combination = $D_L$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$

$$\frac{\partial \rho \mathbf{v}}{\partial t} = \eta \bigtriangledown^2 \mathbf{v} + (\zeta + \eta/3)\nabla(\nabla \cdot \mathbf{v}) - \rho \nabla \frac{\delta F^u}{\delta \rho}$$

$$\beta F^u = \int_{\mathbf{r}} \left[ \rho(\mathbf{r},t) \ln \left( \frac{\rho(\mathbf{r},t)}{\rho_0} \right) - \delta\rho(\mathbf{r},t) \right] - \frac{1}{2} \int_{\mathbf{r},\mathbf{r}'} c(r-r')\delta\rho(\mathbf{r},t)\delta\rho(\mathbf{r}',t) + \beta \int_{\mathbf{r}} u^{\mathrm{ext}}(\mathbf{r})\delta\rho(\mathbf{r},t)$$

# Mode-coupling equations as in Krakoviack 2007

- Stresses ~ m $\delta\rho$ and $\delta\rho$ $\delta\rho$
- Autocorrelate m $\delta\rho$
  - damps momentum at zero wavenumber
  - thus density diffuses
- Autocorrelate $\delta\rho$ $\delta\rho$
  - enhance viscosity and hence friction
  - Effect enhanced as m increases

S Nandi, S Bhattacharyya, SR 2010

# Results of mode-coupling with walls

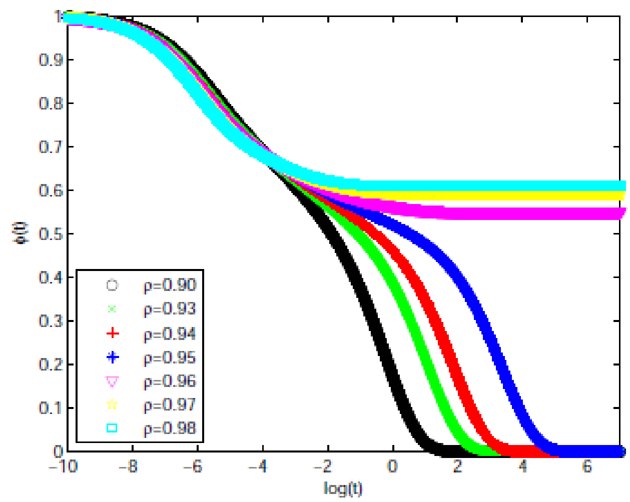



FIG. 4: The correlation function as a function of the logarithm of time for various density

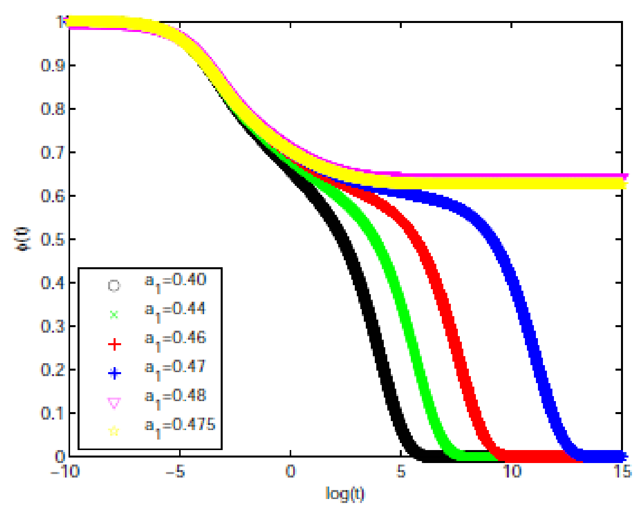



FIG. 5: Change of potential strength at a particular density when the fluid is in liquid state.

Extension to shear, higher dimension:
straightforward but complicated
will see shear-thinning at low flow-rates etc

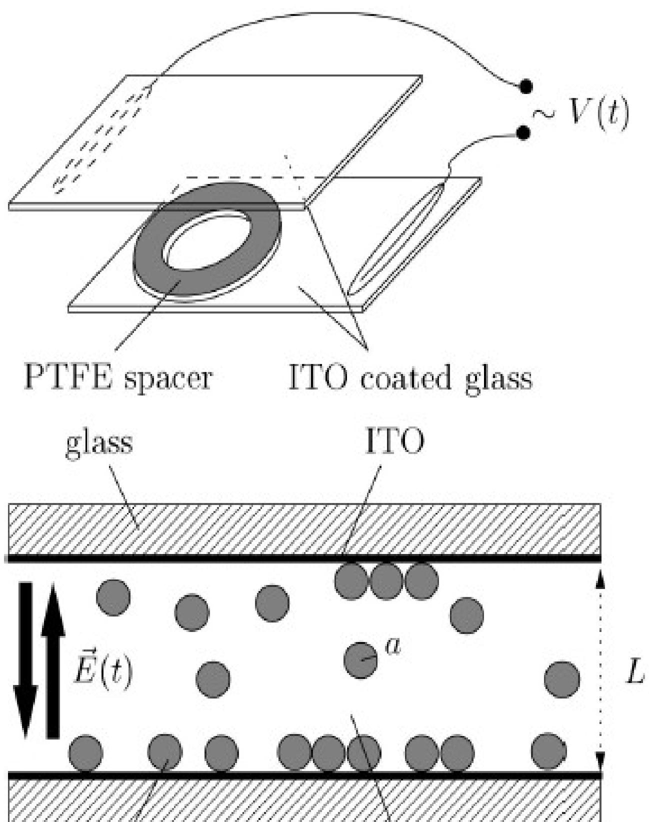
# Drifting: noise in electrophoresis

Suropriya Saha and SR `arxiv:0907.0469`

# Background: colloids in electric fields

## Aggregation in AC field

NADAL, ARGOUL, HANUSSE, POULIGNY, AND AJDARI PHYSICAL REVIEW E **65** 061409



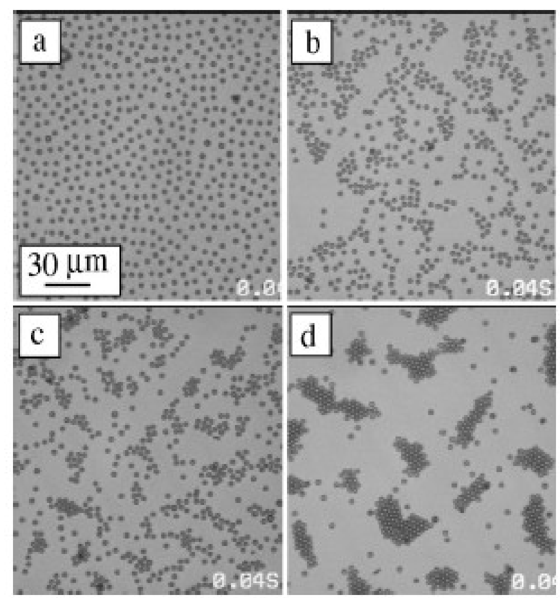




FIG. 2. Stationary patterns on the bottom plate obtained with a dispersion of latex particles, $a=1.5\ \mu$m in diameter, for different frequencies. (a) $\nu=2$ kHz, (b) $\nu=1.5$ kHz, (c) $\nu=1.3$ kHz, (d) $\nu=1$ kHz. $E_o=V_o/L=185$ V cm$^{-1}$.

# Background: colloids in electric fields

Aggregation morphology changes with frequency

11624 *Langmuir, Vol. 21, No. 25, 2005* *Negi et al.*

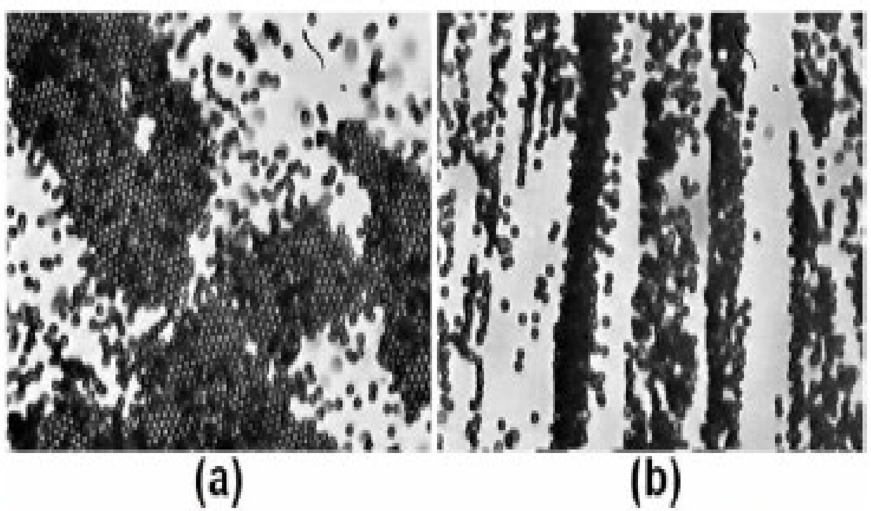



**Figure 1.** Morphology of the clusters depends on the frequency of the applied electric field. (a) Randomly shaped isotropic cluster. Frequency = 1 kHz, applied voltage = 3 V. (b) Elongated cluster. Frequency = 100 kHz, applied voltage = 6 V. The particles shown here have diameter 2.1 $\mu$m.

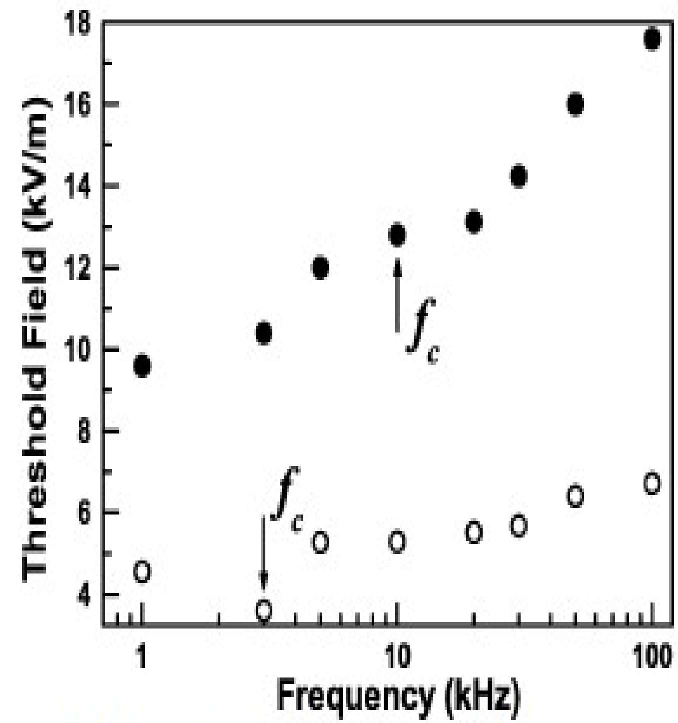
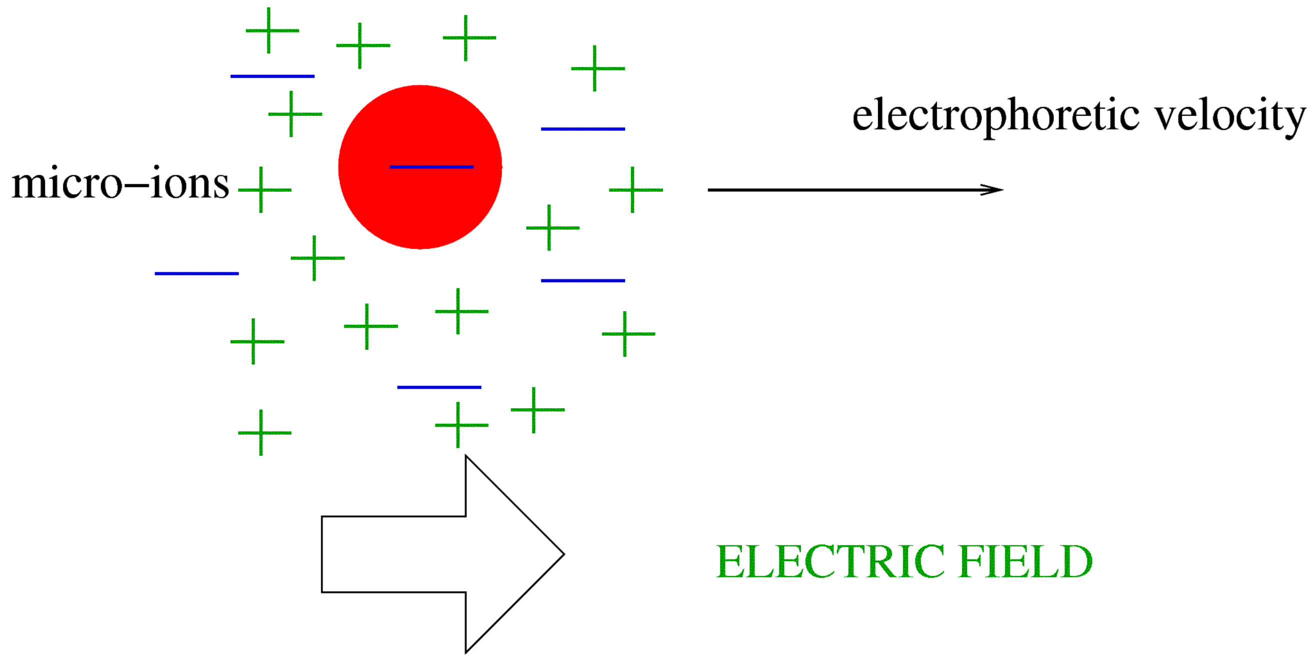



**Figure 2.** Threshold field increases with frequency for both 2.1 $\mu$m (open circles) and 0.98 $\mu$m (filled circles) particles.

# Background: colloids in electric fields

electrophoresis




- Controlled colloidal assembly
- Separation technologies
- Low-Re number mixing, pumping

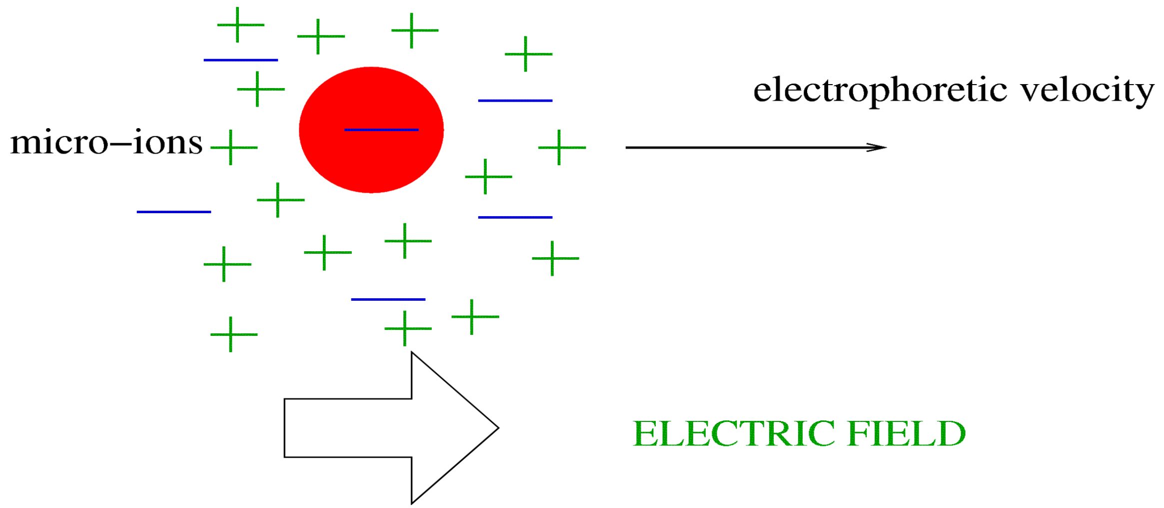
# Background: colloids in electric fields

A hard problem

- Colloids, counterions, impurity ions
- Interactions: Coulomb + hydrodynamic
- Electrostatic stresses
- Noise

# This work

Simple model problems: focus on noise

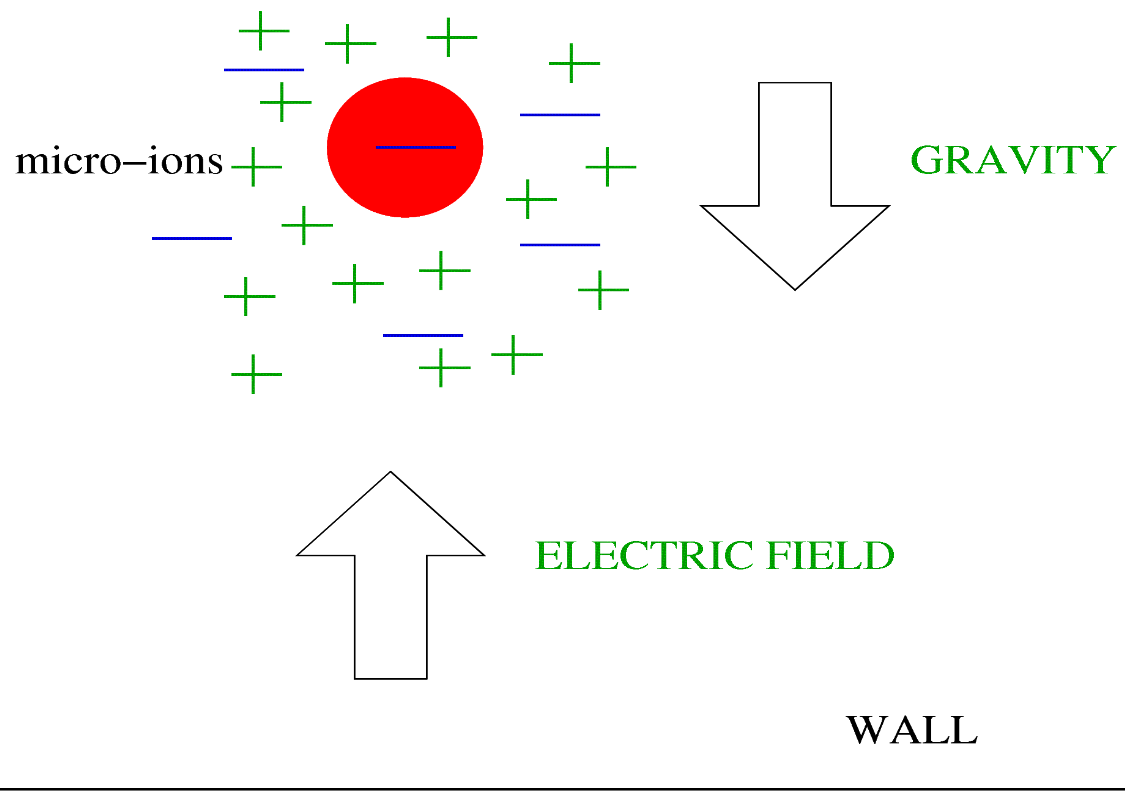



One colloid + micro-ions + electric field + Stokes flow

Suropriya Saha and SR `arxiv:0907.0469`

# This work

Simple model problems: focus on noise




One colloid + micro-ions + electric field + gravity + wall + Stokes flow

Suropriya Saha and SR `arxiv:0907.0469`

# This work: result summary

S Saha and SR
arxiv:0907.0469

- Large excess noise in effective colloid dynamics
  - variance ~ (electric field)$^2$
  - 1 to 1000 times thermal noise strength
  - strongly anisotropic
- "Temperature" from correlation/response ratio
  - Strongly frequency dependent
  - anisotropic
- Superdiffusion for times upto ~ $1/(D\,\kappa^2)$; $\kappa$ = 1/Debye length
- $V_{eff}$ from colloid position pdf: shallower than in Squires 2001

Nonequilibrium signatures from measurements on colloid position alone

# This work: result summary

S Saha and SR
arxiv:0907.0469

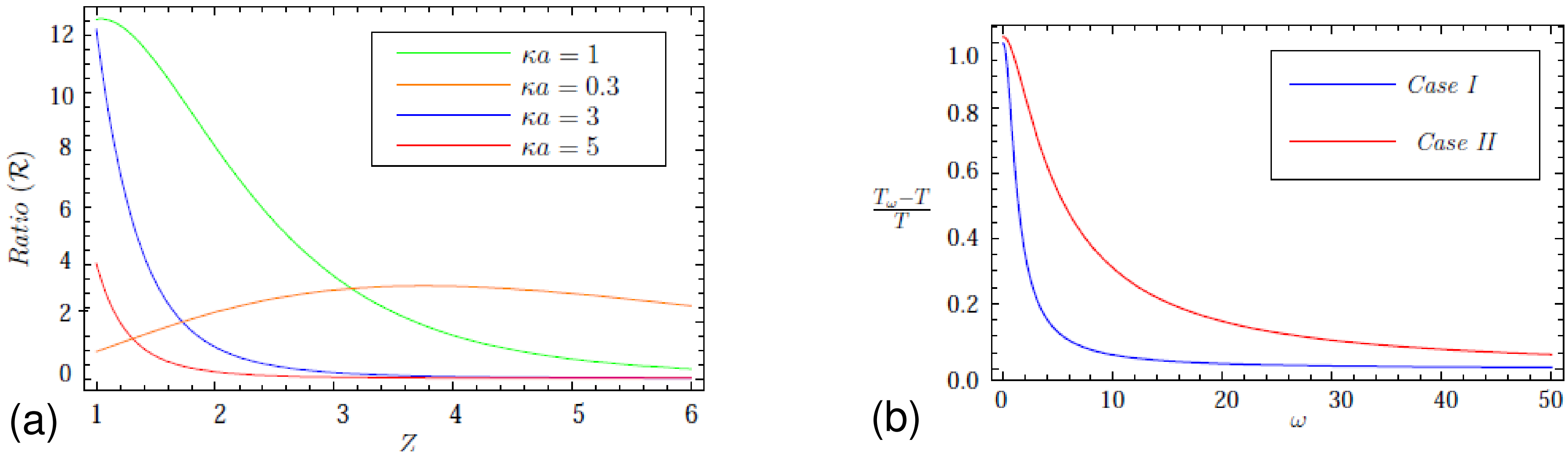



FIG. 1: (a) Ratio $\mathcal{R}$ of excess to thermal noise strength versus particle position $Z$ for various values of $\kappa a$; (b) Fractional excess "temperature" $(T_\omega - T)/T$ versus frequency $\omega$

# This work: result summary

S Saha and SR
arxiv:0907.0469

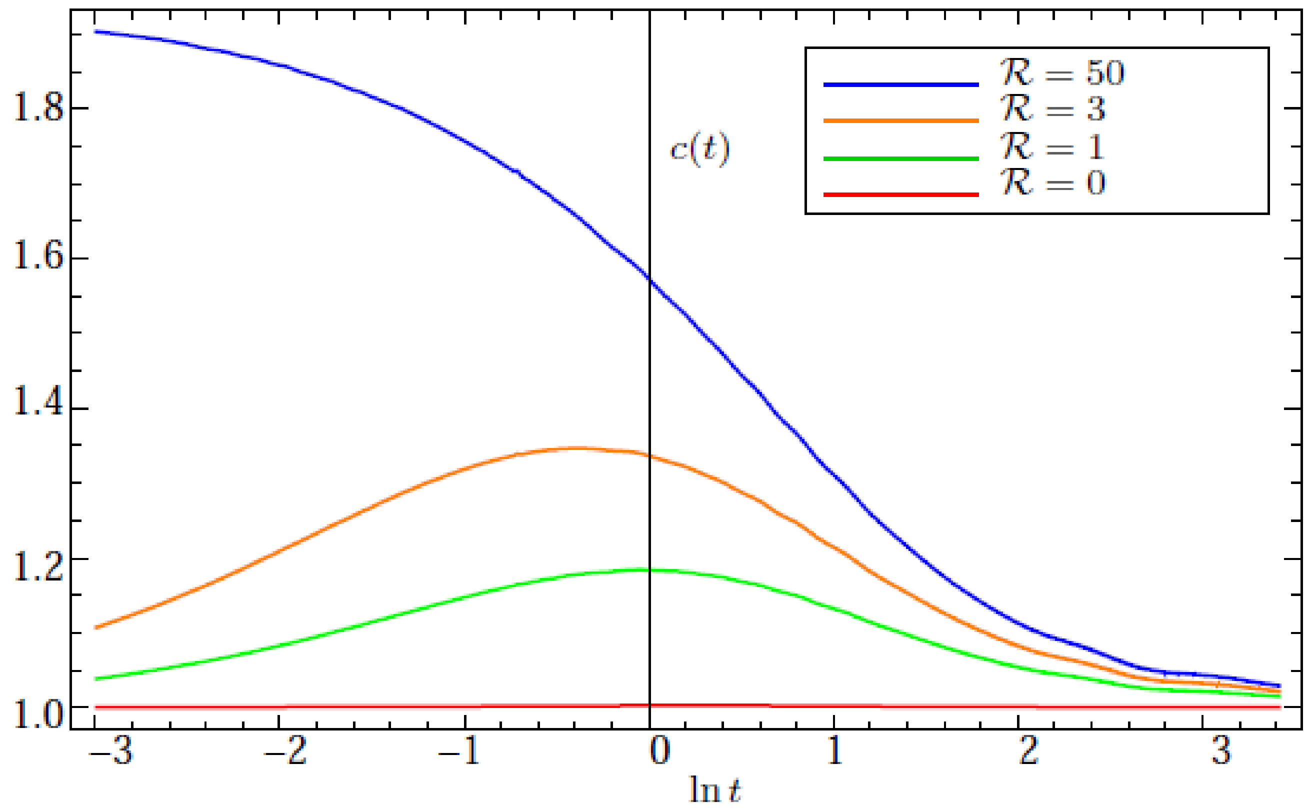



FIG. 2: The regimes of the effective exponent $c(t) \equiv d \ln \Delta R^2 / d \ln t$ for the mean square displacement $\Delta R^2$ for various values of $\mathcal{R}_{zz}$.

# Detailed theory

Want effective Langevin equation for colloid

$$\frac{d\boldsymbol{R}}{dt} = \boldsymbol{v}_0 + \boldsymbol{f} + \zeta$$

$\boldsymbol{R}$ = colloid position, $\boldsymbol{v}_0(\boldsymbol{R})$ = drift velocity

$\boldsymbol{f}$ = thermal noise, $\zeta$ = noise due to electric field

Where does this come from?

Why a noise due to E field?

# Detailed theory

Assume colloid carried by fluid

$$\frac{d\boldsymbol{R}}{dt} = \boldsymbol{v}(\boldsymbol{R}(t))$$ = fluid velocity at colloid location

Stokes equation + electrostatic force density + thermal noise

$$\eta\nabla^2\boldsymbol{v} - \boldsymbol{\nabla}p + \rho\boldsymbol{E} + \sqrt{2k_BT\eta}\boldsymbol{\xi} = 0; \boldsymbol{\nabla}\cdot\boldsymbol{v} = 0$$

Leads to extra noise

ρ = total charge density: colloid + all micro-ions

ξ = thermal noise, Gaussian, spacetime white, solenoidal

# Detailed theory: charge conservation, Gauss, Ohm

$$\frac{\partial n^+}{\partial t} = D\nabla^2 n^+ - \mu\nabla\cdot(n^+\boldsymbol{E}) + \boldsymbol{\nabla}\cdot(\sqrt{2n^+D}\boldsymbol{f}^+)$$

$$\frac{\partial n^-}{\partial t} = D\nabla^2 n^- + \mu\nabla\cdot(n^-\boldsymbol{E}) + \boldsymbol{\nabla}\cdot(\sqrt{2n^-D}\boldsymbol{f}^-)$$

$$\boldsymbol{\nabla}\cdot\boldsymbol{E} = \frac{\rho}{\epsilon_0}$$

$n^+$, $n^-$ ionic number densities     $\boldsymbol{E}$ = total electric field

$\boldsymbol{f}^+$ and $\boldsymbol{f}^-$ are independent Gaussian noise

$\mu = D/ek_BT$

# Detailed theory: solution method

- Linearize everywhere
- Continuity equations: charge densities in terms of noise sources
- Insert into electrostatic force density in Stokes equation

•Fluctuating charge density δρ leads to fluctuating force density

δρ E in Stokes equation

•Solve Stokes to get velocity field; evaluate at colloid position

Thermal noise

$$\frac{d\boldsymbol{R}}{dt} = \boldsymbol{v}_0 + \boldsymbol{f} + \zeta$$

From δρ E in Stokes

# Detailed theory: what Squires did

Squires 2001

$$\frac{d\boldsymbol{R}}{dt} = \boldsymbol{v}_0(\boldsymbol{R})$$

Let vertical coordinate = h

$$v = -b_\perp(h)F_\mathrm{g} + M_\perp(h)E_\infty$$

b, M are ordinary and electrophoretic mobilities

$$\frac{\partial P}{\partial t} = 0 = -\frac{\partial}{\partial h}\left[v(h)P - D_\perp(h)\frac{\partial P}{\partial h}\right]$$

$$D_\perp = k_\mathrm{B} T b_\perp(h)$$

Squires retains only equilibrium thermal noise

# Detailed theory: what Squires did

Squires 2001

$$v = -b_\perp(h)F_g + M_\perp(h)E_\infty \qquad D_\perp = k_B T b_\perp(h)$$

$$\frac{\partial P}{\partial t} = 0 = -\frac{\partial}{\partial h}\left[v(h)P - D_\perp(h)\frac{\partial P}{\partial h}\right]$$

$$\Phi_{ps}(h) = F_g h - \int^h \frac{M_\perp(h')E_\infty}{b_\perp(h')}\mathrm{d}h'$$

This effective potential misses the nonequilibrium noise

# Detailed theory: effect of nonequilibrium noise

$$\mathcal{R}_{ij} \equiv \frac{\int_0^\infty \mathrm{d}t \langle \zeta_i(0)\zeta_j(t)\rangle}{\frac{1}{3}\int_0^\infty \mathrm{d}t \langle f_k(0) f_k(t)\rangle}$$

Relative strength of driven and equilibrium noises

$$\mathcal{R}_{zz}/\mathcal{R}_{xx} \simeq 8$$

$$\mathcal{R}_{zz} \propto \frac{\epsilon E_0^2 \kappa^{-1} a a_{mic}}{k_B T}$$

$a$ = colloid radius, $a_{mic}$ = microion radius

Excess noise is *not* a temperature: anisotropic, frequency dependent

See this by fluctuation-dissipation ratio

# Detailed theory: not an effective temperature

$S_\omega$, $\chi_\omega$: correlation and response functions of colloid position at frequency $\omega$

Define "effective temperature" $\omega S_\omega / 2\mathrm{Im}\chi_\omega \equiv T_\omega$

Find
$$\frac{T_\omega - T}{T} = \frac{\sqrt{2}\mathcal{R}_{zz}(\kappa a)^3}{\Omega\sqrt{\Omega + (\kappa a)^2}}$$

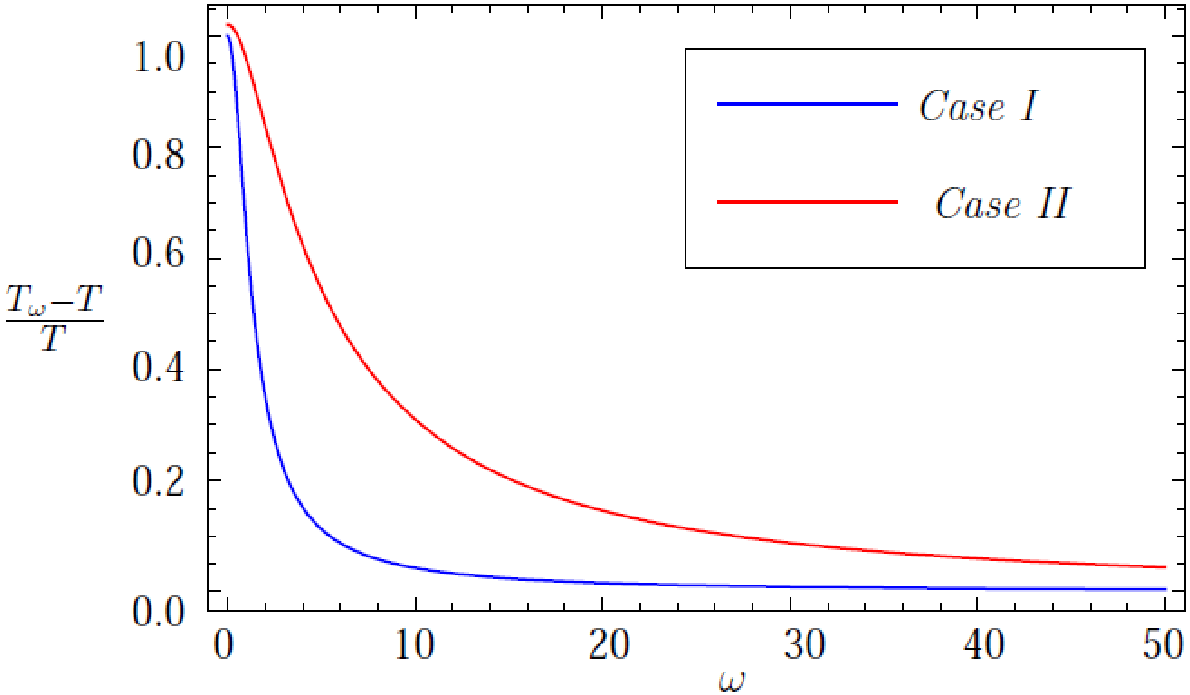
$$\Omega \equiv \sqrt{(\kappa a)^4 + \omega^2/(D\kappa^2)^2}$$

For freely electrophoretically moving colloid, must introduce trap to calculate response

Also calculate mean-square displacement vs time, get results shown earlier

# Recall results

S Saha and SR
arxiv:0907.0469




FD ratio far from constant: not to be interpreted as temperature
Fast degrees of freedom at equilibrium

# Recall results

S Saha and SR
arxiv:0907.0469

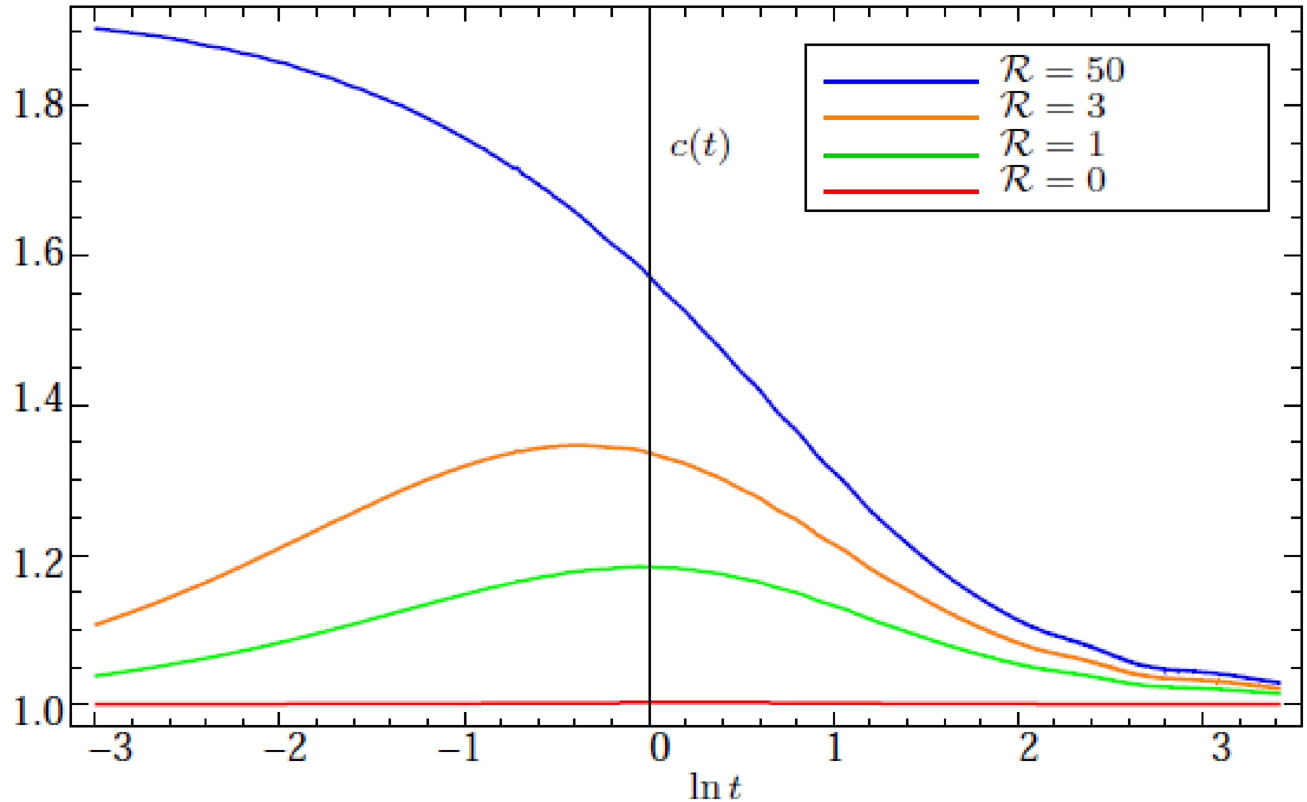
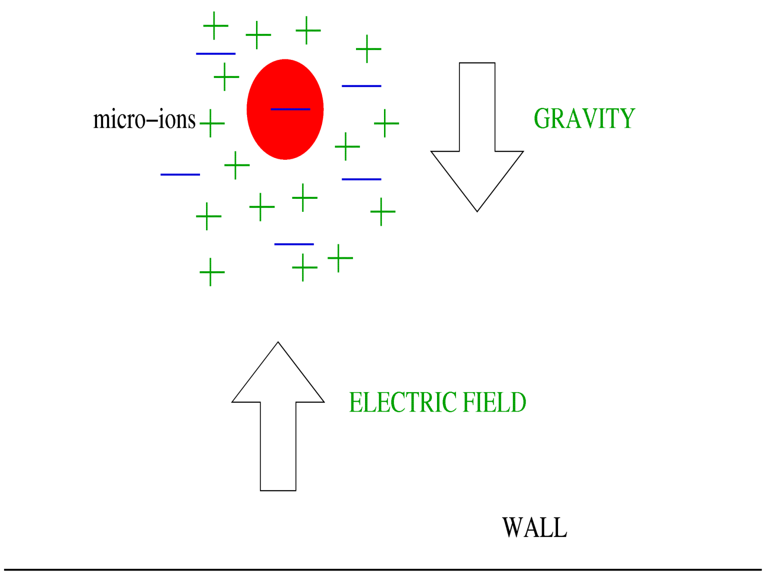
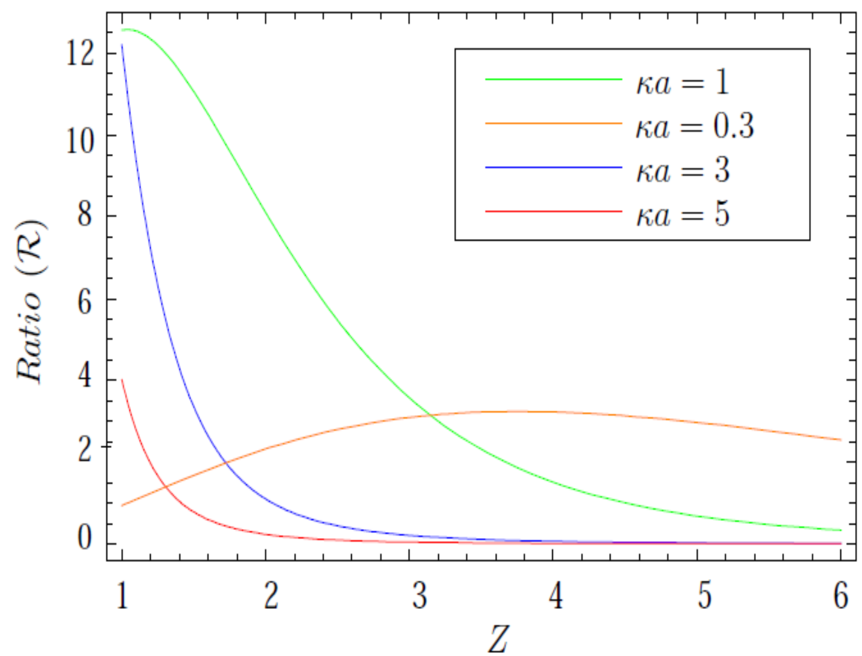



FIG. 2: The regimes of the effective exponent $c(t) \equiv d \ln \Delta R^2 / d \ln t$ for the mean square displacement $\Delta R^2$ for various values of $\mathcal{R}_{zz}$.

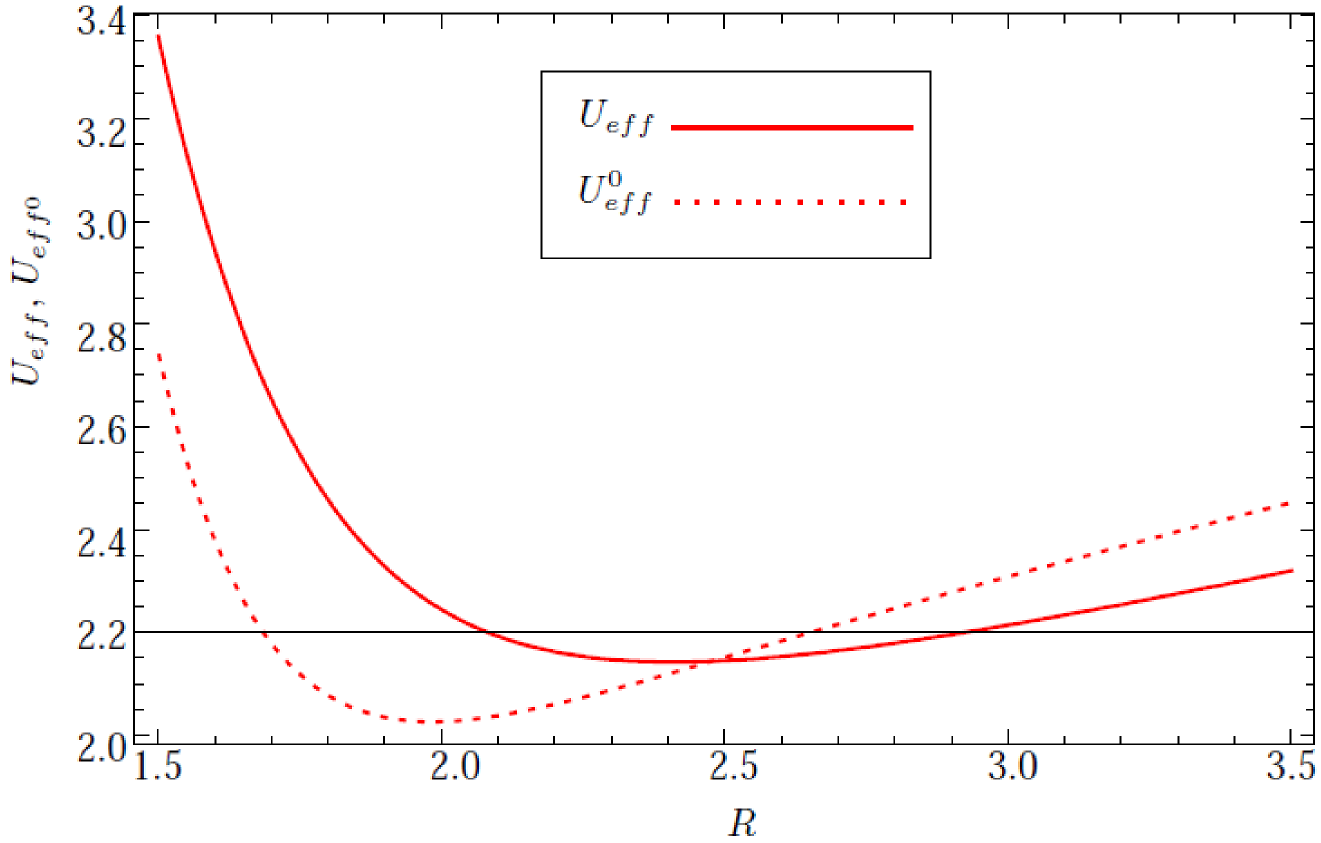
# Detailed theory: electrostatically levitated particle




Impose no slip, no penetration at wall by method of images
electric field normal to wall: for details see `arxiv:0907.0469`

# Detailed theory: effective potential




Fokker-Planck equation from effective Langevin equation: get effective potential from log of stationary solution: significantly shallower than Squires's $\Phi_{ps}$ because of excess noise. For details see arxiv:0907.0469

# Drifting: outlook

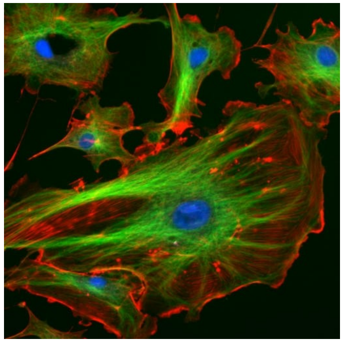
- Built statistical dynamics of single colloid in static electric field.
- Not an effective Gibbsian equilibrium problem
- Effective Langevin equation for colloid gets nonequilibrium noise from Brownian motion of micro-ions in field
- Strong departures from FD theorem; testable in experiments
- Role of this noise in field-induced colloidal ordering?
- Many colloids? Particle shape? AC fields?

# Self-propelled: actively moving particles

Toner, Tu, SR Ann Phys NY 2005

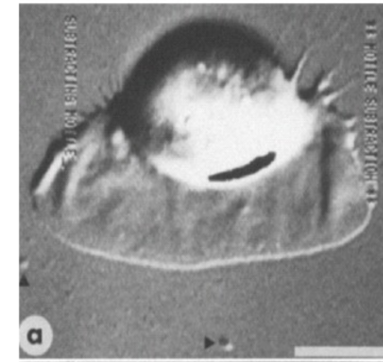
Juelicher et al Phys Rep 2007; Joanny & Prost HFSP Jour 2009

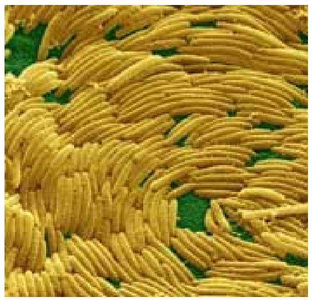
SR: Annual Review of Condensed Matter Physics 2010



active cytoskeleton
http://commons.wikimedia.org/wiki/Image:FluorescentCells.jpg

lamellipodium
Small *et al.* J Cell Biol **129** (1995) 1275

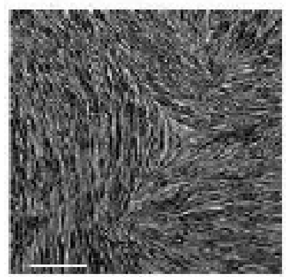




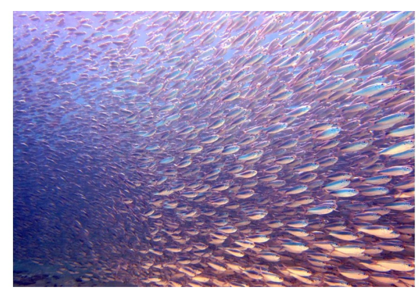
myxococcus
www.bio.indiana.edu/facultyresearch/faculty/Velicer.html

# ORDERED ACTIVE MATTER ON MANY SCALES

Melanocytes
Kemkemer *et al.* EPJE 1999



Fish shoals
www.flickr.com/photos/pmforster/496918483



Vibrated rods
Narayan *et al.* 2007

Starling flock over Rome
http://angel.elte.hu/starling/

The Mechanics and Statistics of Active Matter
SR: *Annual Review of Condensed Matter Physics* 2010

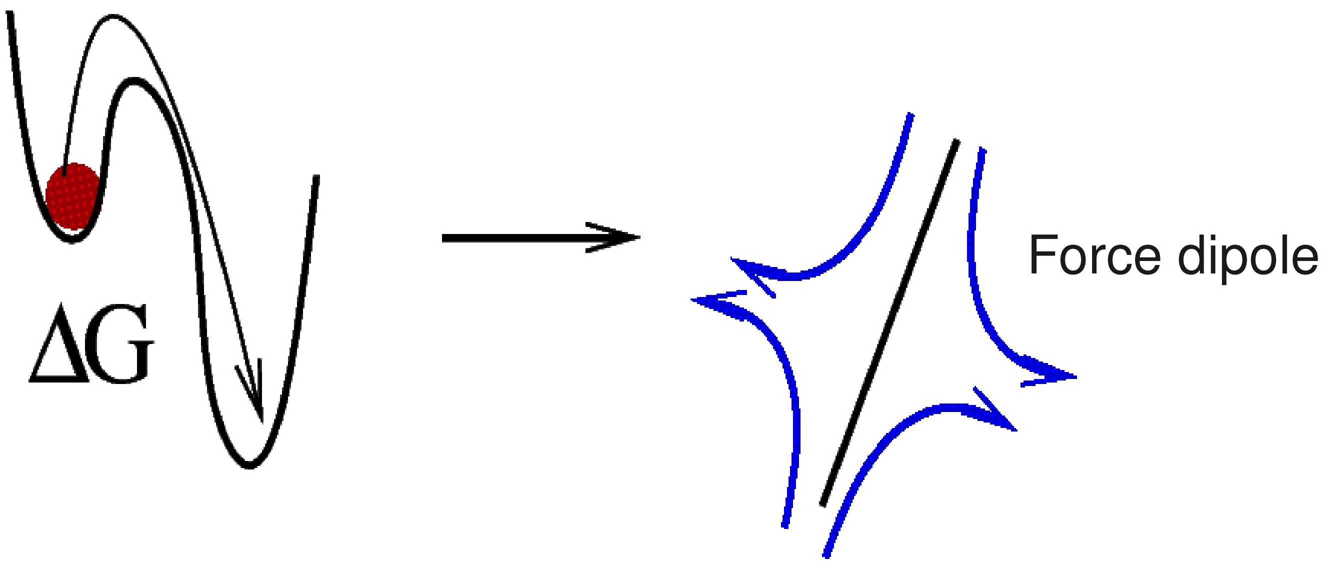
# Who should care and why

- Physicists, engineers, materials scientists
  - new kind of matter, new laws
  - order, fluctuations and response?
  - phases and phase transitions
  - uses: stirring, pumping, swarming
  - inanimate mimics of active matter?

# Who should care and why

- Cell biologists, biochemists, ethologists
  - collective dynamics of motors
  - single and collective cell mechanics
  - mechanism for strong inhomogeneity
  - biofilms, quorum sensing
  - tissue mechanics and growth
  - animal flocks, swarms, migration

# A minimal active particle

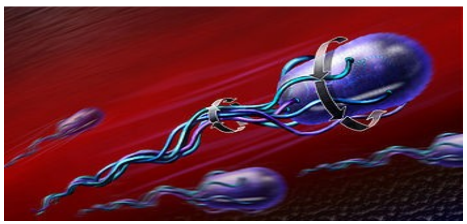


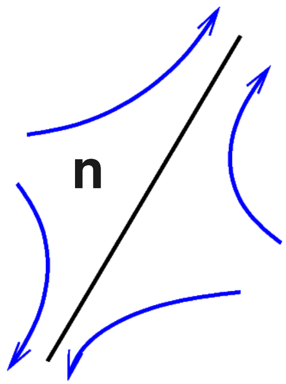

Active particles consume free-energy
Move and stir surrounding medium
Require no *external* force:
Lighthill; Brennen & Winet 1977; Pedley and Kessler 1992

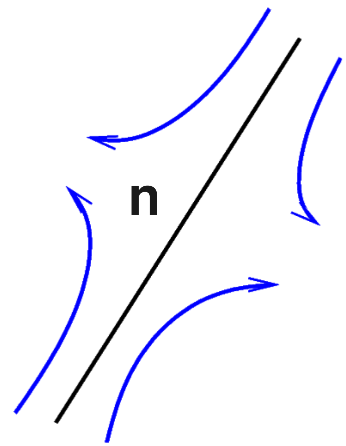
# Elementary active objects

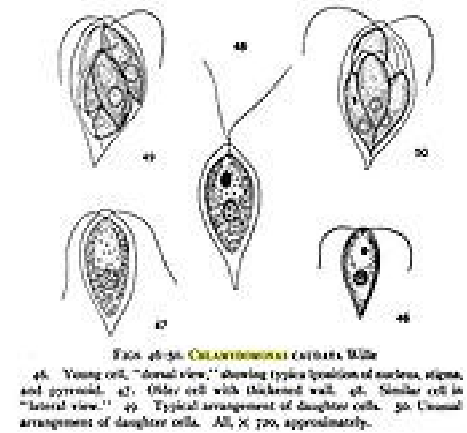
http://en.wikipedia.org/wiki/Escherichia_coli

http://en.wikipedia.org/wiki/Chlamydomonas

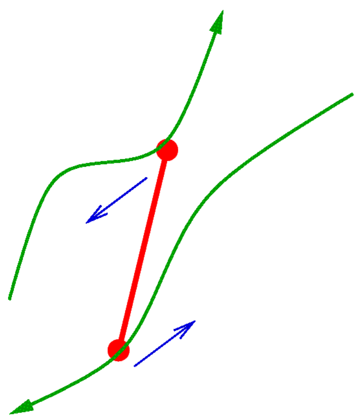




T E Hazen, Bull. Torrey Botan Club. April, 1922, pp. 87-92



Bipolar motor cluster
tugging on cytoskeleton

Flock: spontaneously ordered collection of active particles

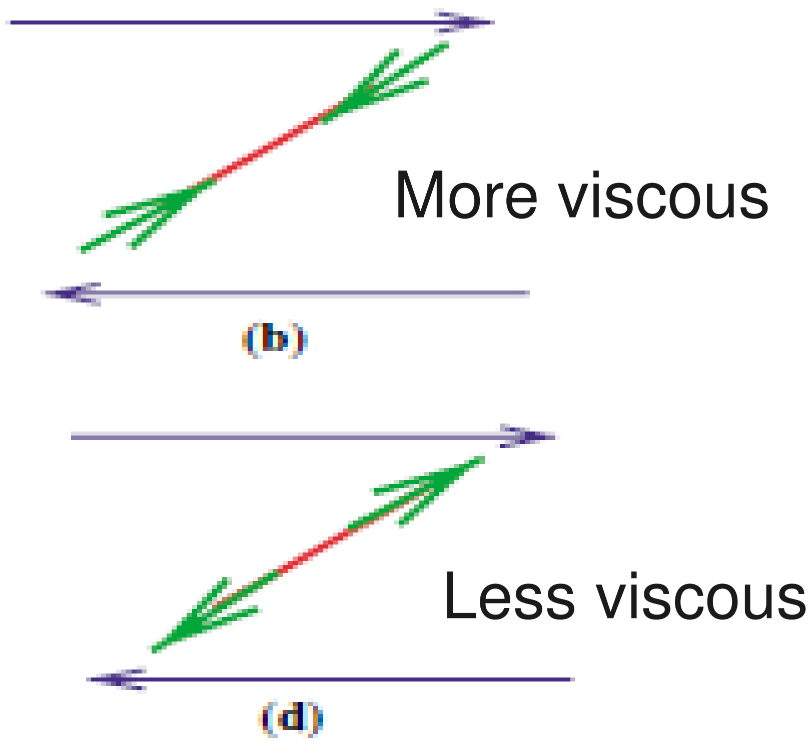
Self-driven particles: permanent force dipoles
bacteria: tensile; algae, motors + filaments: contractile

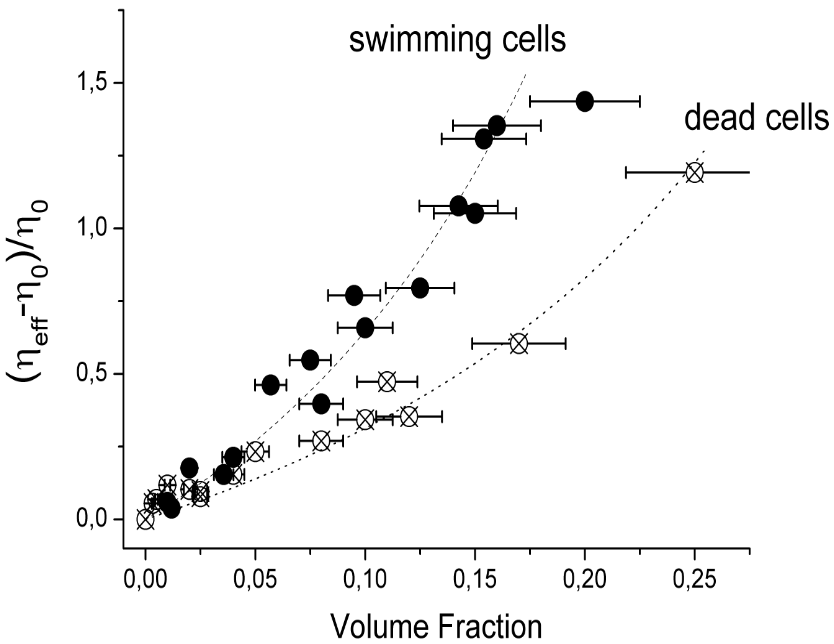
Active stresses,
active currents

# Many predictions

- Bacteria can't swim straight in bulk viscous fluid
- Experiments: low-Re turbulence in microorganisms
- Confinement stabilizes
- Flocks have giant density fluctuations
- Granular experiments confirm
- Oscillations, contractile ring (Curie/Dresden/ESPCI)

# Swimming alters viscosity: experiments!



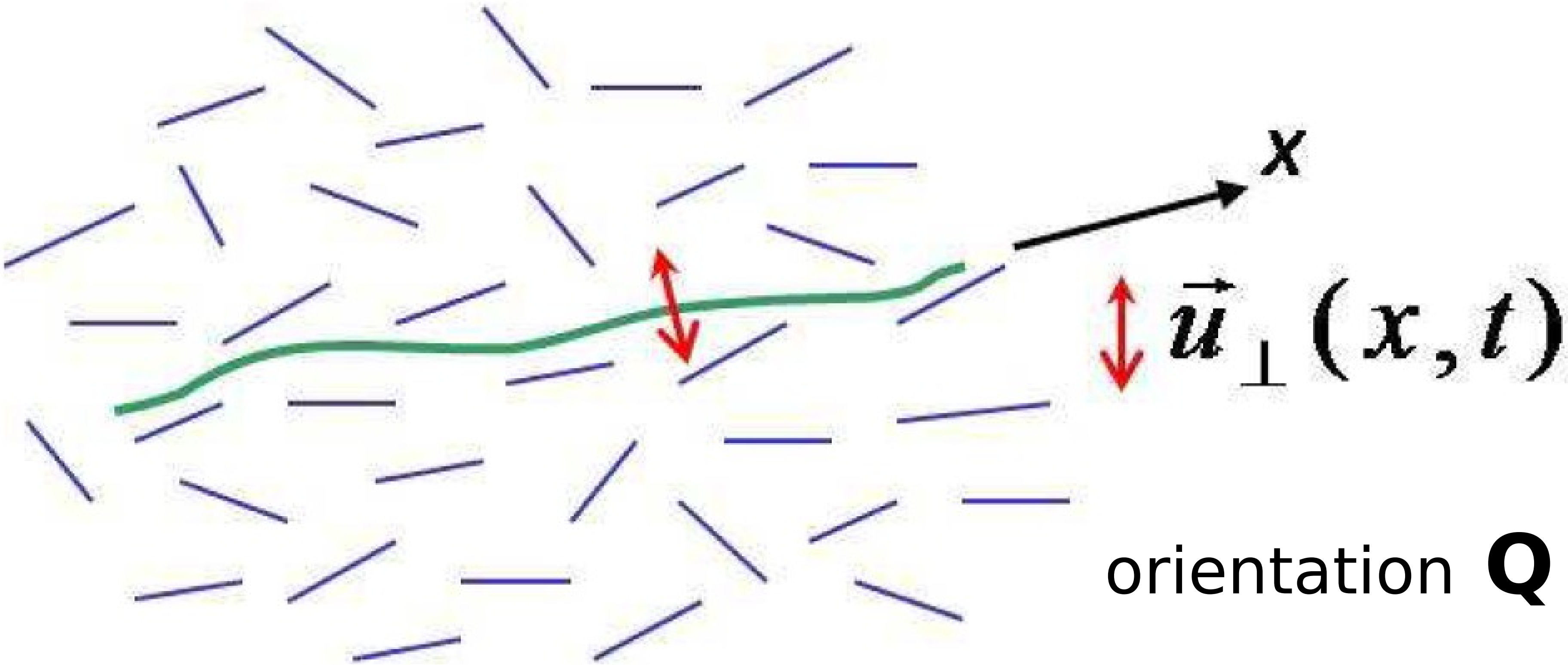

Prediction: Hatwalne, SR, Rao, Simha PRL 2004

Expts: Rafai *et al.* `arxiv 0909.4193v1;` Sokolov & Aranson PRL 2009

Commentary by SR -- `www.condmatjournalclub.org/?p=760`

Microrheology: Wu-Libchaber PRL 2000; U Penn PRE 2009

# A filament in an active medium




What happens to a stiff filament surrounded by activity?
How does actin-myosin activity affect microtubules?

Kikuchi, Ehrlicher, Koch, SR, Rao, Kaes PNAS **106** (2009) 19776-19779

# A simple model

$$\partial_t \mathbf{u}_\perp - \mathbf{v}_\perp(x, \mathbf{r}_\perp = \mathbf{0}, t) = -\frac{1}{\gamma}\delta F/\delta \mathbf{u}_\perp + \mathbf{f}_\perp$$

$$\partial_t \mathbf{Q} = -\frac{1}{\zeta}\delta F/\delta \mathbf{Q} + \boldsymbol{\eta},$$

$\mathbf{u}_\perp(x, t)$ transverse fluctuations

$\mathbf{v}$ hydrodynamic velocity field

$\mathbf{Q}$ nematic order parameter

$F[\mathbf{u}_\perp, \mathbf{Q}]$ free-energy functional

Free-energy: ordering, elasticity, anchoring

$$F[\mathbf{u}_\perp, \mathbf{Q}] = F_f[\mathbf{u}_\perp] + F_{LD}[\mathbf{Q}] + F_{anc}[\mathbf{u}_\perp, \mathbf{Q}]$$

$$F_f[\mathbf{u}_\perp] = \int_0^L dx[(\sigma/2)\,(\partial_x \mathbf{u}_\perp)^2 + (\kappa/2)(\partial_x^2 \mathbf{u}_\perp)^2]$$

$$F_{LD}[\mathbf{Q}] = \int dx \int d^2 r_\perp [(a/2)\mathbf{Q}^2 + (K/2)(\nabla \mathbf{Q})^2]$$

$F_{anc}[\mathbf{u}_\perp, \mathbf{Q}]$ Favours normal or parallel alignment of medium and filament

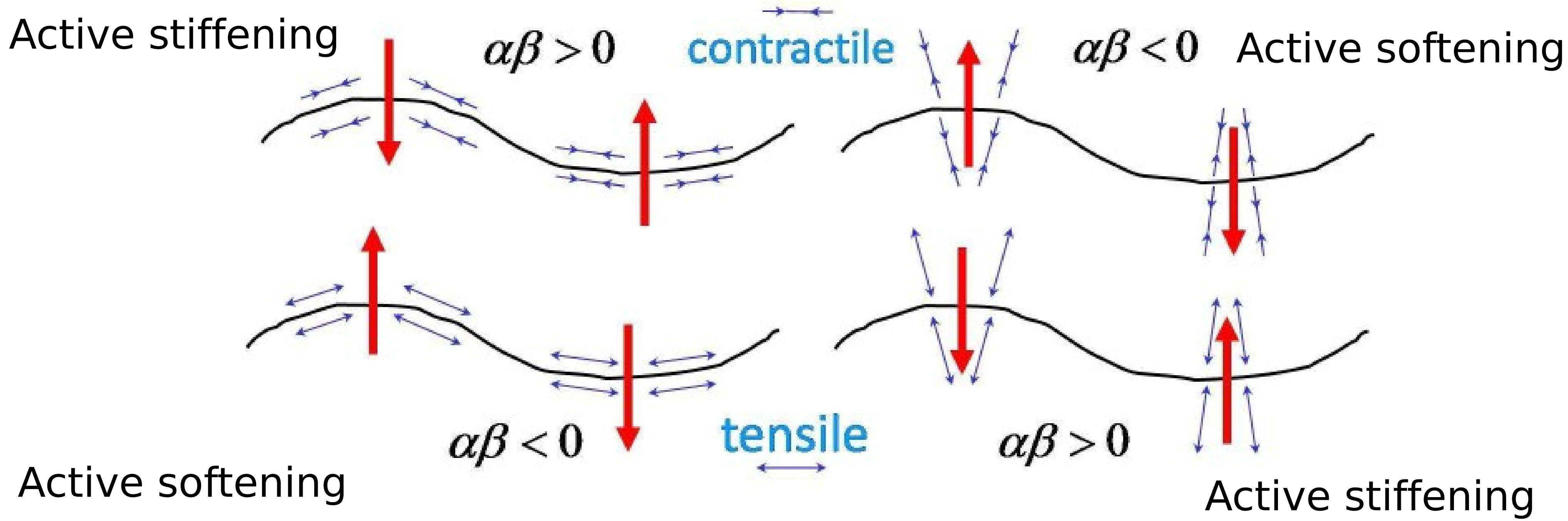
# Where's activity?

$$\mathbf{v}_\perp(x, \mathbf{r}_\perp, t) = -(W c_0/\Gamma)\partial_x \mathbf{Q}_{x\perp}(x, \mathbf{r}_\perp, t)$$

Force balance: friction against active stresses
"Rouse" approximation: local damping

Combine these elements

# Interplay: anchoring and activity




- Stiffening: strictly nonequilibrium effect
- At equilibrium, coupling to additional degree of freedom always reduces elastic constant
- Buckling: provides basis for Brangwynne *et al*. 2008

# Fluctuation-dissipation ratio

$$R_{q_x\omega} = \frac{N_1\gamma}{k_BT}\left[1 + \frac{\alpha\left(\alpha N_2/N_1 + \beta\right)(\zeta/K)^2 q_x^2 \Sigma(q_\omega)}{1 - \alpha\beta(\zeta/K)^2 q_x^2 \Sigma(q_\omega)}\right]$$

- A mess: should be unity if effective temperature
- Depends on activity through Σ
- Can turn negative at finite frequency
- Close analogy: Martin *et al* PNAS '01 auditory hair cells

Kikuchi, Ehrlicher, Koch, SR, Rao, Kaes PNAS **106** (2009) 19776-19779

# Conclusion to part 3

- Theory of mechanics and statistics of living matter
- Relevance: flocks, cytoskeleton, analogues
- Predictive: now some confirmation in experiments
- Many obvious extensions
- Need: clean experiments on model systems