Rods, Rotations, Gels

Soft-Matter Experiment and Theory from Penn.

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The Penn Team

- Theory
  - TCL
  - Randy Kamien
  - Andy Lau
  - Fangfu Ye
  - Ranjan Mukhopadhyay
  - David Lacoste
  - Leo Radzihovsky
  - X.J. Xing
- Experiment
  - Arjun Yodh
  - Dennis Discher
  - Jerry Gollub
  - Mohammad Islam
  - Ahmed Alsayed
  - Zvonimir Dogic
  - Jian Zhang
  - Mauricio Nobili
  - Yilong Han
  - Paul Dalhaimer
  - Paul Janmey

Outline

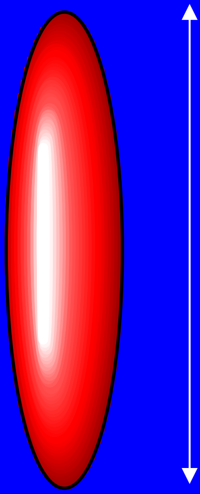
- Some rods
- Rotational and Translational Diffusion of a rod - 100th Anniversary of Einstein's 1906 paper
- Chiral granular gas
- Semi-flexible Polymers in a nematic solvent
- Nematic Phase
- Carbon Nanotube Nematic Gels

Comments

- Experimental advances in microsocpy and imaging: real space visualization of fluctuating phenomena in colloidal systems
- Wonderful “playground” to for interaction between theory and experiment to test what we know and to discover new effects
- Simple theories - great experiments

Rods

PMMA Ellipsoid

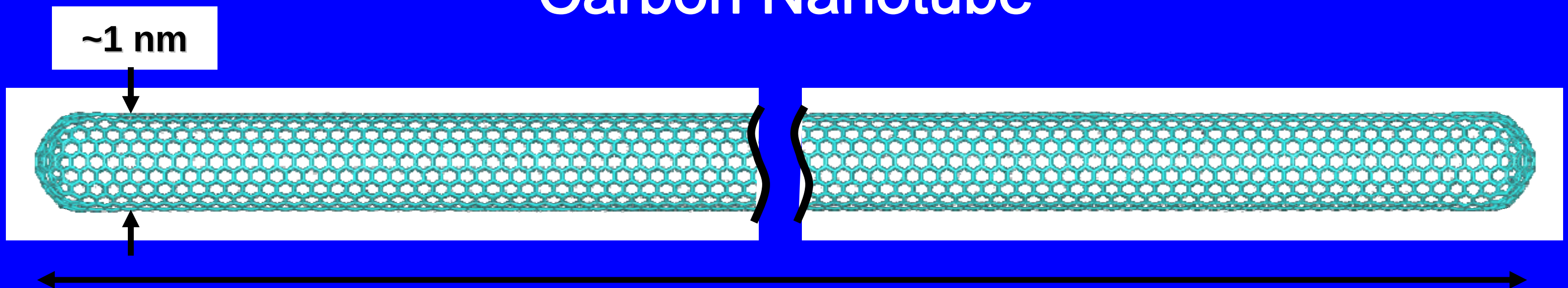


1 μm

fd Virus

900 nm

Carbon Nanotube



100 nm – 10,000 nm

Einstein – Brownian Motion

1. "On the Movement of Small Particles Suspended in Stationary Liquid Required by the Molecular Kinetic Theory of Heat", Annalen der Physik 17, 549 (1905);

$$\dot{x} = \Gamma f; \quad \Gamma = (6\pi\eta a)^{-1}$$

$$\left\langle (\Delta x)^2 \right\rangle = 2Dt; \;\; D = k_B T \Gamma$$

a = particle radius; η = viscosity; f = force

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Langevin Oscillator Dynamics

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2$$
$$p = mv = m\dot{x}$$

$$\dot{p} = -kx - \gamma v + \varsigma$$
$$\langle \varsigma(t)\varsigma(t')\rangle = 2\gamma T\delta(t-t')$$
$$\gamma = 6\pi\eta a$$

Ignore inertial terms:

$$\dot{x} = -\Gamma kx + \xi; \quad \Gamma = \gamma^{-1}$$
$$\langle \xi(t)\xi(t')\rangle = 2T\Gamma\delta(t-t')$$
$$\langle |x(\omega)|^2\rangle = \frac{2T}{k}\frac{\Gamma k}{\omega^2 + \Gamma^2 k^2}$$

$$\langle x^2\rangle = \int \frac{d\omega}{2\pi}\langle |x(\omega)|^2\rangle = \frac{k_B T}{k}$$

Dynamics must retrieve equilibrium static fluctuations: sets scale of noise fluctuations to be $2T\Gamma$

P. Langevin, Comptes Rendues 146, 530 (1908)
Uhlenbeck and Ornstein, Phys. Rev. 36, 823 (1930)

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Diffusion with no potential

$$k \to 0: \quad \dot{x} = \xi$$

$$\left\langle [x(t) - x(0)]^2 \right\rangle$$

$$= \int \frac{d\omega}{\pi} \frac{2k_B T\Gamma}{\omega^2}\left(1 - e^{-i\omega t}\right)$$

$$= 2k_B T\Gamma t = 2Dt$$

Gaussian probability distribution

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

$$D = \frac{k_B T}{6\pi\eta a} = \frac{1}{N_{\text{AVG}}} \frac{RT}{6\pi\eta a}$$

Measurement of D gives Avogrado's number

R = Gas constant

Density Diffusion

$$n(x,t) = \left\langle \sum_\alpha \delta\left(x - x_\alpha(t)\right) \right\rangle$$

$$\dot{x}_\alpha = \xi_\alpha; \quad x_\alpha(t+\Delta t) = x_\alpha(t) + \int_t^{t+\Delta t} \xi_\alpha(t')dt'$$

$$n(x,t+\Delta t) = \left\langle \sum_\alpha \delta\left(x - x_\alpha(t+\Delta t)\right) \right\rangle$$

$$= \left\langle \sum_\alpha \delta\left(x - x_\alpha(t)\right) \right\rangle - \partial_x \left\langle \sum_\alpha \dot{x}_\alpha \delta\left(x - x_\alpha(t)\right) \right\rangle$$

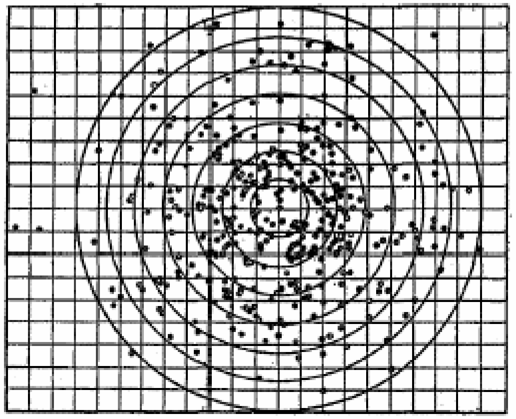
$$+ \frac{1}{2}\partial_x^2 \left\langle \sum_\alpha \delta\left(x - x_\alpha(t)\right) \int_t^{t+\Delta t}\int_t^{t+\Delta t} \xi_\alpha(t_1)\xi_\alpha(t_2)\, dt_1 dt_2 \right\rangle$$

$$\partial_t n(x,t) = -\partial_x nv + D\partial_x^2 n(x,t)$$

$$\partial_t n(\mathbf{r},t) = -\nabla \cdot n\mathbf{v} + D\nabla^2 n(\mathbf{r},t)$$

J. Perrin Expts. (1908)

$$n(r,t) = \frac{N_0}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$



Déplacements (en μ) compris entre :	n observé.	n calculé.
0 et 2	24	27
2 et 4	76	71
4 et 6	90	84
6 et 8	67	76
8 et 10	45	54
10 et 12	34	30
12 et 14	20	14
14 et 16	4	5
16 et ∞	5	4

$N_{AVG} = 7.05 \times 10^{23}$

Rotational Diffusion

"On the Theory of Brownian Motion," ibid. **19**, 371 (1906):
Idea of Brownian motion of arbitrary variable,
application torotational diffusion of a spherical particle.

$$\dot{\theta} = \Gamma_\theta \tau; \quad \Gamma_\theta = \left(8\pi\eta a^3\right)^{-1}$$

$$\left\langle (\Delta\theta)^2 \right\rangle = 2D_\theta t; \quad D_\theta = k_B T \Gamma_\theta$$

τ = torque

P. Zeeman and Houdyk, Proc. Acad. Amsterdam, **28**, 52 (1925)
W. Gerlach, Naturwiss **15**,15 (1927)
G.E. Uhlenbeck and S. Goudsmit, Phys. Rev. **34**,145 (1929)
F. Perrin, Ann. de Physique 12, 169 (1929)
W.A. Furry, "Isotropic Brownian Motion", Phys. Rev. **107**, 7 (1957)

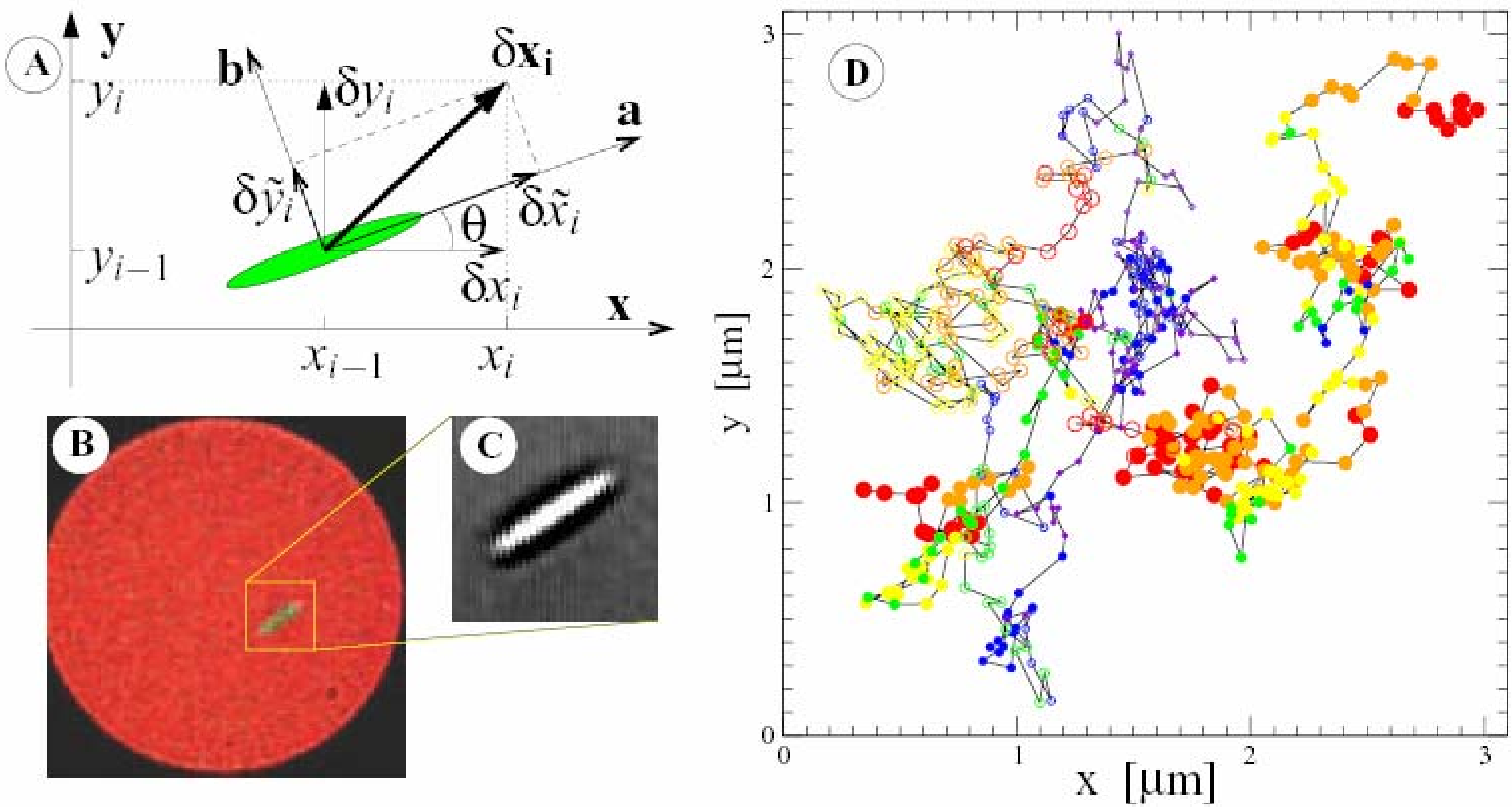
Diffusion of Anisotropic Particles

1. Brownian motion of an anisotropic particle: F. Perrin, J. de Phys. et Rad. V, 497 (1934); VII, 1 (1936).

Interaction of Rotational and Translational Diffusion: Stephen Prager, J. of Chem. Physics 23, 12 (1955)

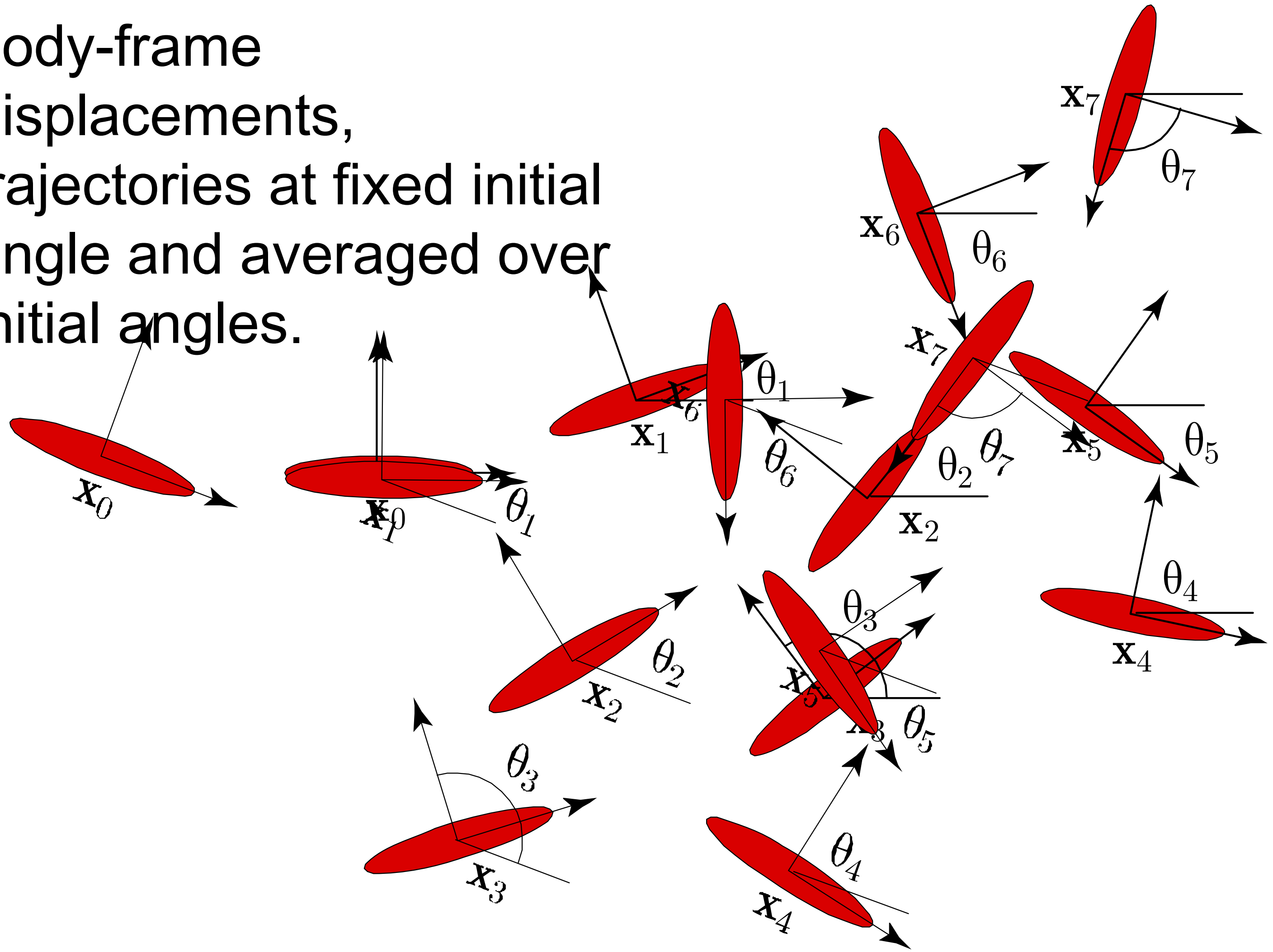
Diffusion of a rod

Han, Alsayed,Nobili,Zhang,TCL,Yodh



Defining trajectories

Can extract lab- and body-frame displacements, trajectories at fixed initial angle and averaged over initial angles.



Rotational Langevin (2d)

$$I\ddot{\theta} = -\frac{\partial H}{\partial \theta} - \Gamma_\theta \dot{\theta} + \Gamma_\theta \xi_\theta = \dot{p}_\theta$$

$$\dot{\theta} = -\Gamma_\theta \frac{\partial H}{\partial \theta} + \xi_\theta \rightarrow \boxed{\dot{\theta} = \xi_\theta}$$

$$\left\langle \xi_\theta(t) \xi_\theta(t') \right\rangle = 2 k_B T \Gamma_\theta \delta(t - t')$$

$$\left\langle [\theta(t) - \theta(0)]^2 \right\rangle \equiv \left\langle [\Delta\theta]^2 \right\rangle = 2 D_\theta t$$

$$D_\theta = \frac{\left\langle [\Delta\theta]^2 \right\rangle}{2t}$$

$$\left\langle \cos[n\Delta\theta] \right\rangle = \exp[-n^2 D_\theta t]$$

Translation and Rotation

Anisotropic friction coefficients $\dot{x}_{\parallel} = -\Gamma_a f_{\parallel}; \quad \dot{x}_{\perp} = -\Gamma_b f_{\perp}$

Lab-frame equations

$$\dot{x}_i = -\Gamma_{ij}(\theta)\frac{\partial H}{\partial x_j} + \xi_i$$

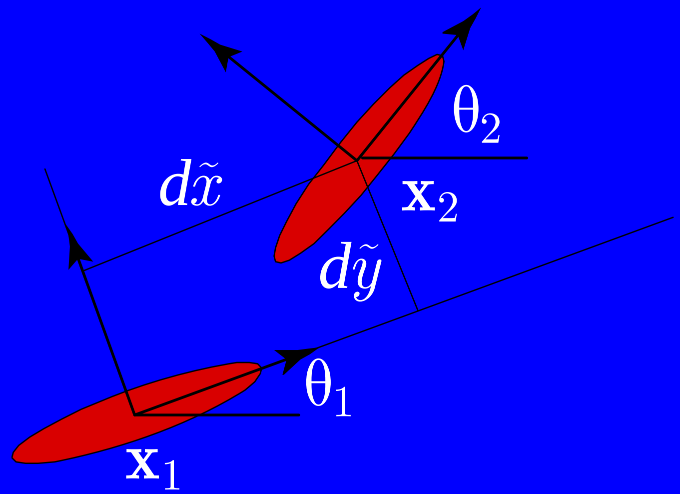
$$\Gamma_{ij}(\theta) = \Gamma_a n_i(\theta) n_j(\theta) + \Gamma_b [\delta_{ij} - n_i(\theta) n_j(\theta)]$$

$$\left\langle \xi_i(t)\xi_j(t')\right\rangle_{\theta_0} = 2k_B T \Gamma_{ij}(\theta(t))\delta(t-t')$$

In lab-frame, noise depends on angle: expect anisotropic crossover

F. Perrin, J. de Phys. et Rad. **V**, 497 (1934); **VII**, 1 (1936).

Body-frame equations



Body frame : $\tilde{x}$ and $\tilde{y}$ are are independent; simple Langevin equations with constant diffusion.

$$\begin{pmatrix} \delta\tilde{x} \\ \delta\tilde{y} \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \delta x \\ \delta y \end{pmatrix}$$

$$\tilde{x}_i(t) = \sum_n \delta\tilde{x}_{ni}$$

$$\partial_t \tilde{x}_i = \tilde{\xi}_i; \quad \left\langle \tilde{\xi}_i(t)\tilde{\xi}_i(t') \right\rangle = 2k_B T \tilde{\Gamma}_{ij}$$

$$\tilde{\Gamma}_{ij} = \begin{pmatrix} \Gamma_a & 0 \\ 0 & \Gamma_b \end{pmatrix}$$

$$\left\langle [\Delta\tilde{x}]^2 \right\rangle = 2D_a t; \quad \left\langle [\Delta\tilde{y}]^2 \right\rangle = 2D_b t$$

Anisotropic Crossover

$$D_{ij}(t,\theta_0) = \frac{1}{2t}\left\langle [\Delta x_i(t)][\Delta x_j(t)] \right\rangle_{\theta_0}$$
$$= \bar{D}\delta_{ij} + \frac{\Delta D}{2t}\tau_4(t)\begin{pmatrix} \cos 2\theta_0 & \sin 2\theta_0 \\ \sin 2\theta_0 & -\cos 2\theta_0 \end{pmatrix}$$

$$\bar{D} = (D_a + D_b)/2$$
$$\Delta D = D_a - D_b$$
$$\tau_n(t) = \frac{(1 - e^{-nD_\theta t})}{nD_\theta}$$

1. Diffusion tensor averaged over angles is isotropic.
2. Lab-frame diffusion is anisotropic at short times and isotropic at long times
3. Body-frame diffusion tensor is constant and anistropic at all times

$$\bar{D}_{ij} = \frac{1}{2\pi}\int d\theta_0 D_{ij}(t,\theta_0) = \bar{D}\delta_{ij}$$
$$\left\langle [\Delta \tilde{x}]^2 \right\rangle = 2D_a t; \quad \left\langle [\Delta \tilde{y}]^2 \right\rangle = 2D_b t$$

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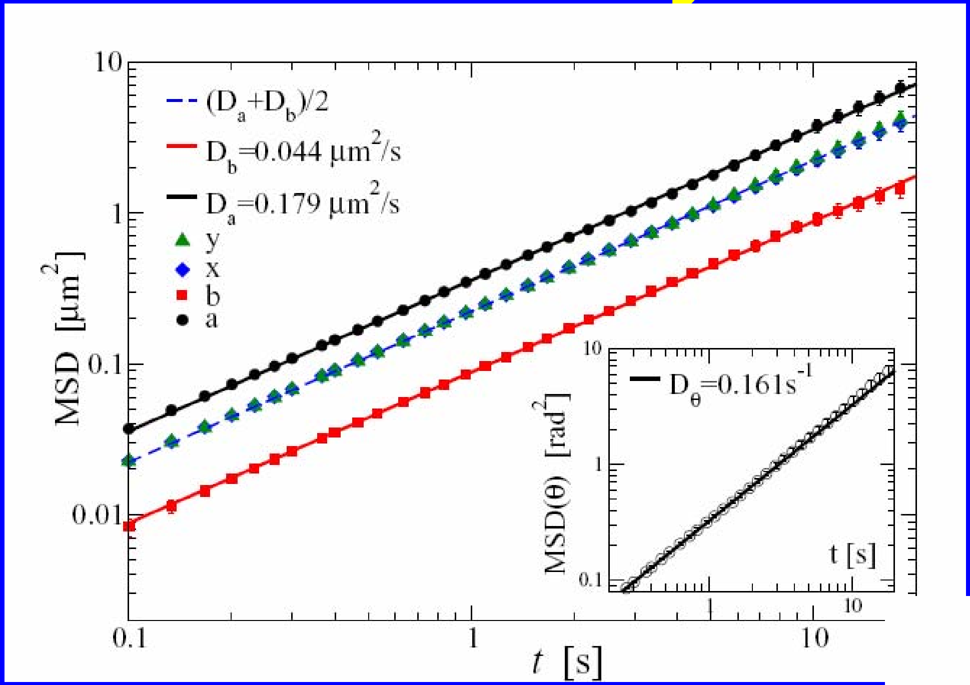
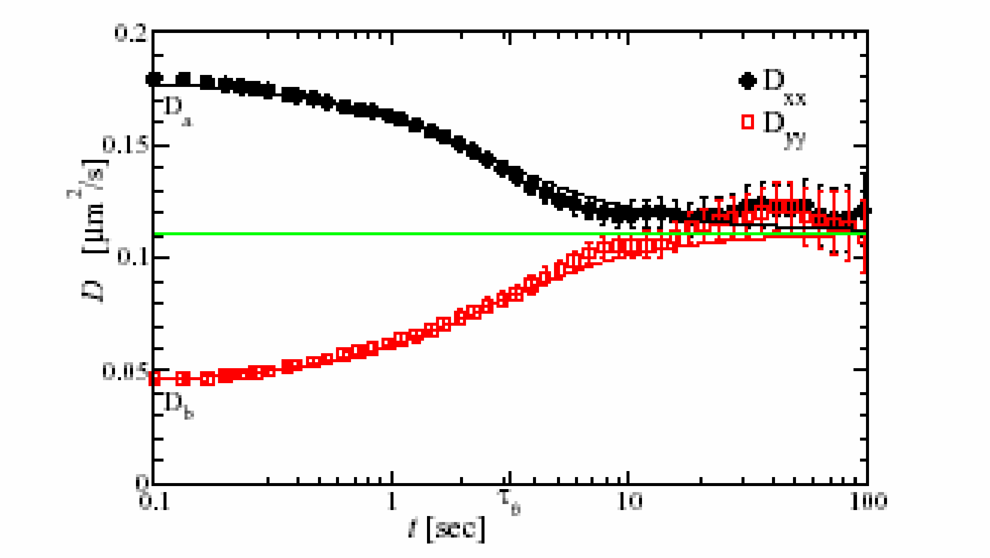
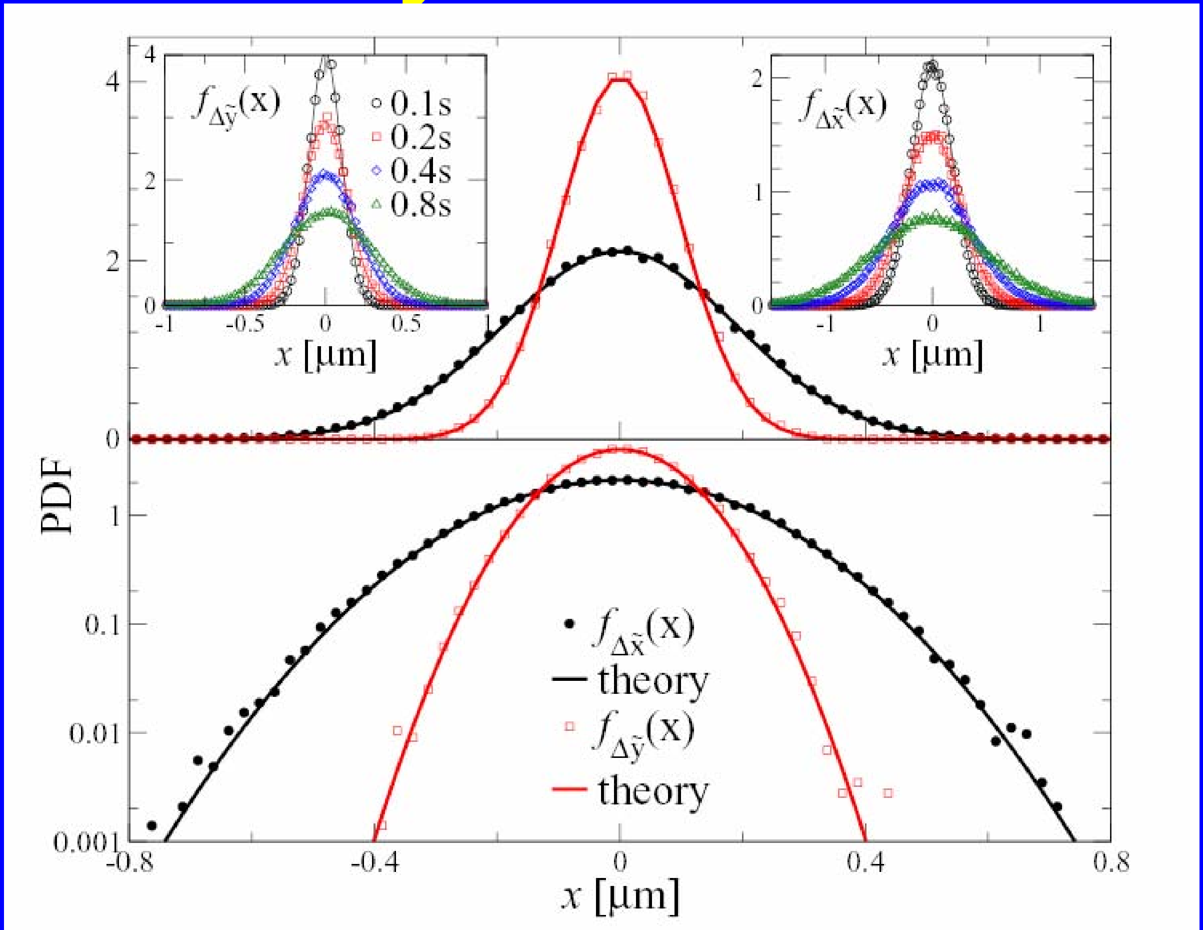
Lab- and body-frame diffusion





Gaussian Body Frame Statistics



$$\partial_t \tilde{x}_i = \tilde{\xi}_i;$$

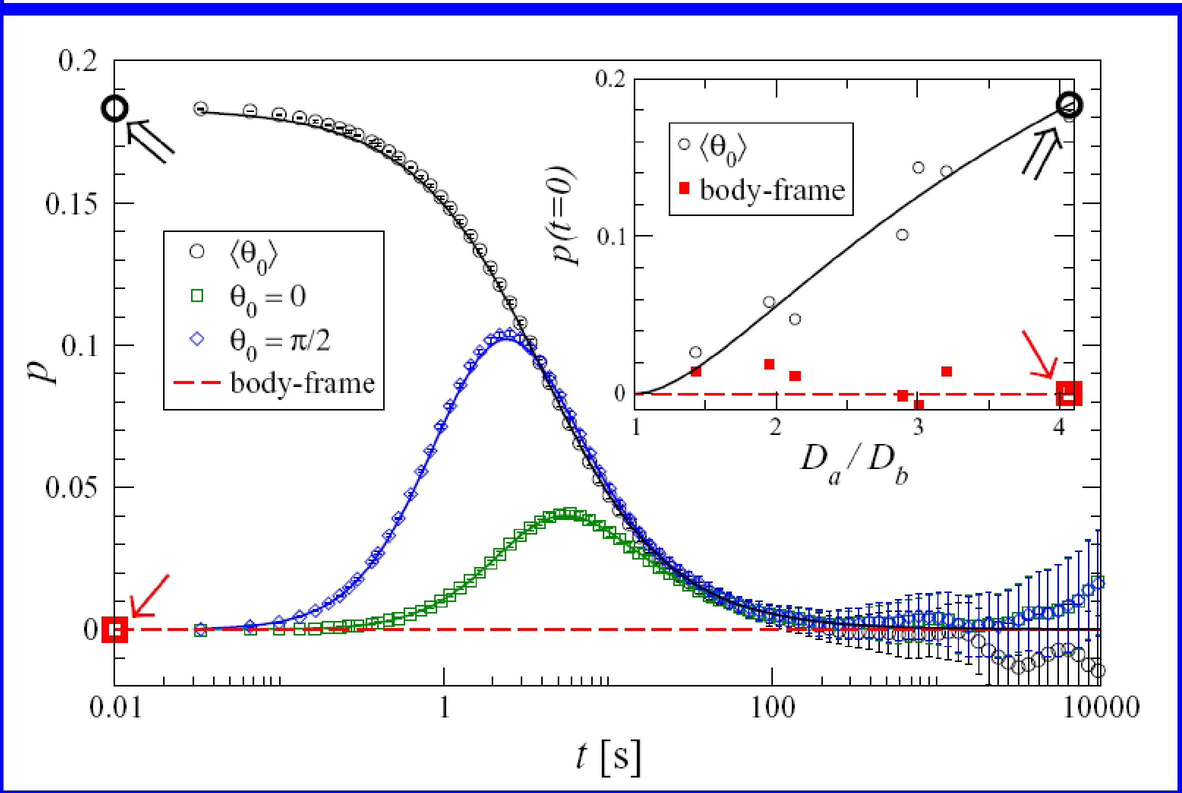
$$\left\langle \tilde{\xi}_i(t)\tilde{\xi}_i(t')\right\rangle = 2k_B T\tilde{\Gamma}_{ij}$$

$$P(\tilde{x}_i) = \frac{1}{\sqrt{4\pi D_i t}}\exp\left(-\frac{\tilde{x}_i^2}{4D_i t}\right)$$

Non-Gaussian lab-frame statistics

$$C^{(4)}_{\theta_0} = \left\langle [\Delta x(t)]^4 \right\rangle - 3\left\langle [\Delta x(t)]^2 \right\rangle^2$$
$$= \tfrac{1}{2}(\Delta D)^2\,[3(\tau_\theta t - \tau_\theta \tau_4(t) - \tau_4^2(t))$$
$$+ (\tau_\theta \tau_4(t) - \tau_\theta \tau_{16}(t) - 3\tau_4^2(t))\cos 4\theta_0]$$

$$p(t) = \frac{C^{(4)}_{\theta_0}(t)}{3\left\langle [\Delta x(t)]^2 \right\rangle^2} \to \frac{(D_a - D_b)^2}{2(D_a + D_b)^2}$$



Fixed q0: Gaussian at short times – same as body frame; Gaussian at long times – central limit theorem.
Average q0: nonGaussian at short times, Gaussian at long times

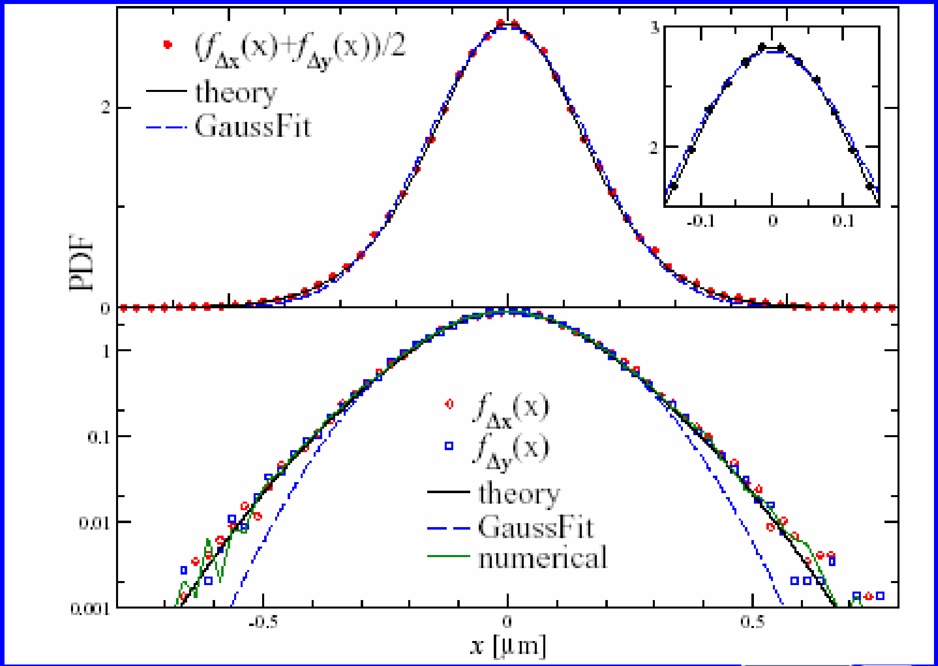
Non-Gaussian Distribution.

$$f_{\Delta x}(x) = \langle \delta(x - \Delta x(t)) \rangle = \int \frac{dk}{2\pi} e^{ikx} \left\langle e^{-ik\Delta x(t)} \right\rangle$$

$$= \left\langle \int \frac{dk}{2\pi} e^{\frac{(ik)^2}{2!} C^{(2)}_{\theta_0}(t) + \frac{(ik)^4}{4!} C^{(4)}_{\theta_0}(t) + \cdots} \right\rangle_{\theta_0}$$

$$\xrightarrow{t \to 0} \int_0^{2\pi} \frac{d\theta}{2\pi} \frac{e^{-\frac{x^2}{2\sigma^2(\theta)}}}{\sqrt{2\pi}\sigma(\theta)},$$

Probability distribution at fixed angle and small t is Gaussian. The average over initial angles is not



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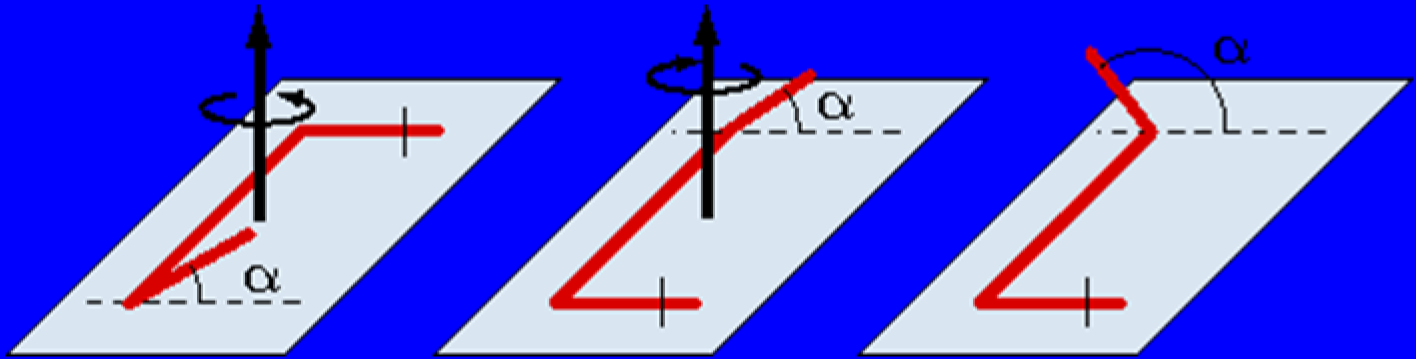
Rattleback gas

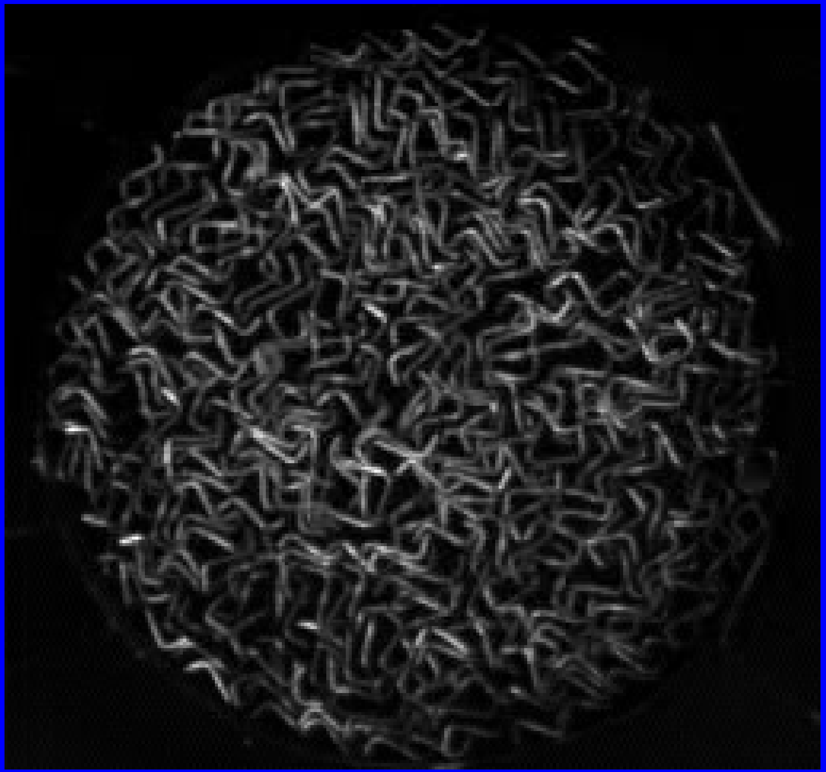
Tsai, J.-C., Ye, Fangfu , Rodriguez, Juan , Gollub, J.P., and Lubensky, T.C., A Chiral Granular Gas, *Phys. Rev. Lett.* **94**, 214301 (2005).

Chiral Rattlebacks spin in a preferred direction; Achiral ones do not.

Chiral wires spin in a preferred direction on a vibrating substrate



Rattleback gas II



Spin angular momentum dynamics

$l = nI\Omega =$ Spin angular momentum

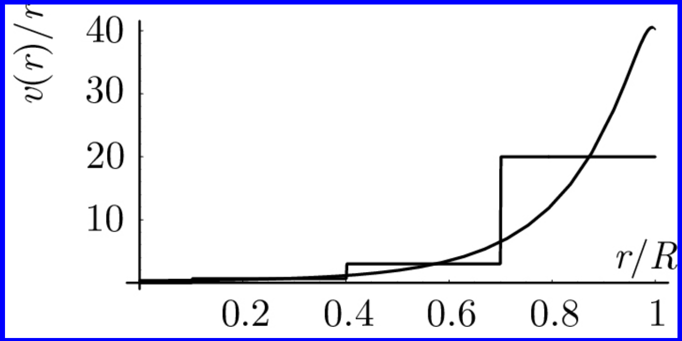
$\Omega =$ Spin angular frequency

$$l(\mathbf{x},t) = \left\langle \sum_\alpha p_{\theta\alpha} \delta\left(\mathbf{x} - \mathbf{x}_\alpha(t)\right) \right\rangle$$

$$I\ddot{\theta} = -\frac{\partial H}{\partial \theta} - \Gamma_\theta \dot{\theta} + \Gamma_\theta \xi_\theta = \dot{p}_\theta$$

$$\begin{aligned} \partial_t l &= -n\Gamma_\theta \Omega + \partial_i \partial_j \left\langle \sum_\alpha D_{ij}(\theta_\alpha) p_{\theta\alpha} \delta(\mathbf{x} - \mathbf{x}_\alpha(t)) \right\rangle \\ &= -n\Gamma_\theta \Omega + \bar{D} \nabla^2 l \\ &= -\partial_j (l v_j) - \Gamma \Omega + D_\Omega \nabla^2 \Omega \end{aligned}$$

Rattleback gas III



$l = I\Omega =$ Spin angular momentum

$g_i = \rho v_i =$ Center-of-mass mometum

$\Omega =$ Spin angular frequency

$\omega = (\nabla \times \mathbf{v})_z / 2 =$ CM angular frequency

$$\partial_t l = -\partial_j (l v_j) - \Gamma^\Omega \Omega - \Gamma(\Omega - \omega) + D_\Omega \nabla^2 \Omega + \tau$$

Substrate friction

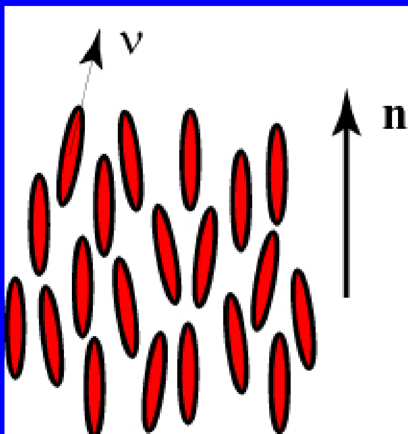
Spin-vorticity coupling

Vibrational torque

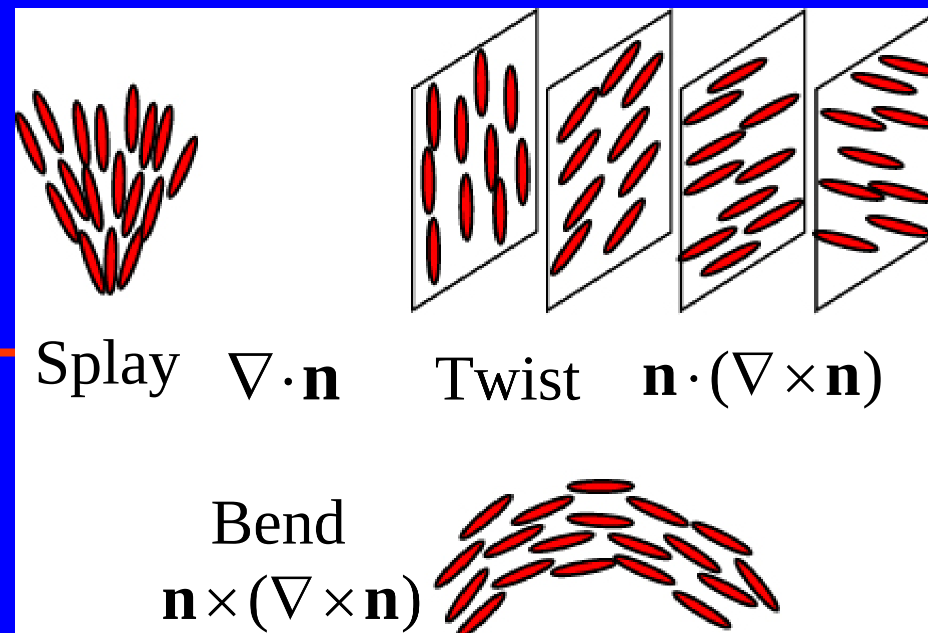
$$\partial_t g_i = -\partial_j (g_i v_j) - \partial_i p + \eta \nabla^2 v_i - \Gamma^v v_i + \tfrac{1}{2} \varepsilon_{ij} \partial_j \Gamma(\Omega - \omega)$$

B.C.: $\Omega(R) = \omega(R) = v(R) / R; \quad \partial_r v = -\ell^{-1} v$

Nematic phase



Order Parameter $Q_{ij} = S(n_i n_j - \frac{1}{3}\delta_{ij}) = \langle \nu_i \nu_j - \frac{1}{3}\delta_{ij} \rangle$

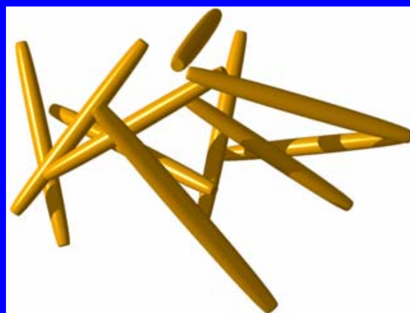


$$F = \frac{1}{2} \int d^3x \left\{ K_1 (\nabla \cdot \mathbf{n})^2 + K_2 [\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 + K_3 [\mathbf{n} \times (\nabla \times \mathbf{n})]^2 \right\}$$

Frank free energy

$\mathbf{n}$ =Frank director

Isotropic-to-Nematic Transition



increasing concentration →

D - rod diameter
L – rod length

$\phi(\theta)$–orientational distribution functions

ϕ_{I-N} - rod concentration at I - N phase transition

$$\phi_{I-N} = 4\frac{D}{L} \text{ when } \frac{L}{D} \gg 1$$

order parameter S :

$$S = \frac{1}{2}\int d\theta \sin\theta\, \phi(\theta)(3\cos^2\theta - 1)$$

Onsager *Ann. N. Y. Acad. Sci.* 51, 627 (1949)

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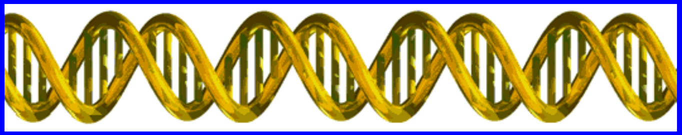
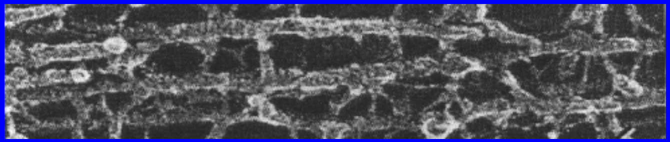
Semi-flexible biopolymers

DNA



16 micron length
2 nm in diameter
40 nm persistence length

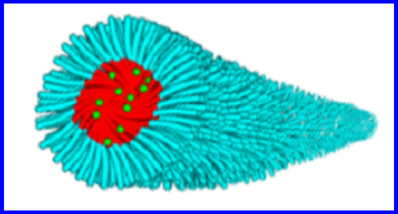
Neurofilament



5 - 20 micron length
12 nm in diameter
~ 220 nm persistence length

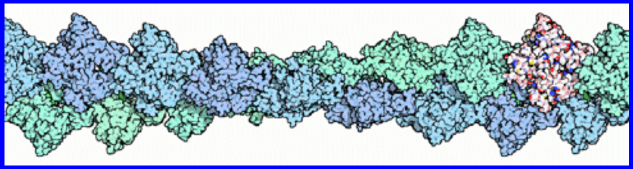
Wormlike Micelle

(polybutadiene-polyethyleneoxide)



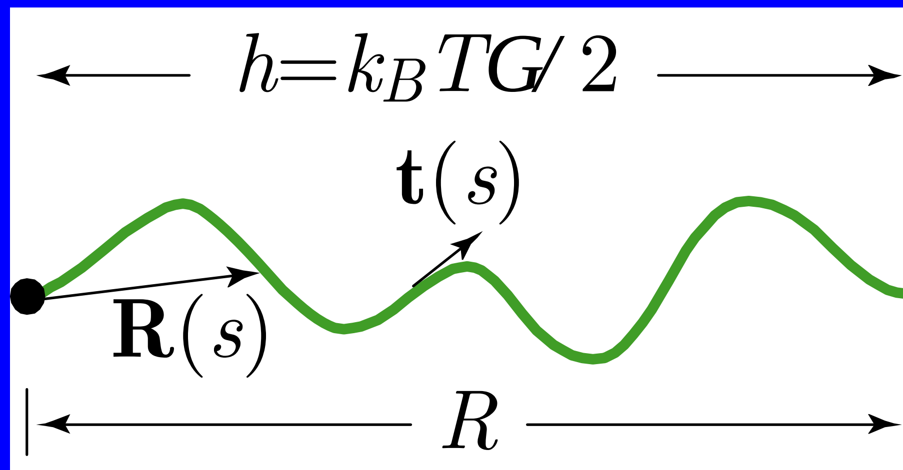
10 – 50 micron length
~ 15 nm in diameter
~ 500 nm persistence length

Actin



2 – 30 micron length
7-8 nm in diameter
~ 16 micron persistence length

Semi-flexible Polymer in Aligning Field



$$\frac{d\mathbf{R}}{ds} = \mathbf{t}(s)$$

$$|\ \mathbf{t}(s)\ | = 1;$$

$$\mathbf{t}(s) = (\mathbf{t}_{\perp}(s), \sqrt{1 - |\ \mathbf{t}_{\perp}(s)\ |^2})$$

Fluctuations

$$H = \frac{k_B T}{2}\int ds\left[l_P\left(\frac{d\mathbf{t}}{ds}\right)^2 - \Gamma\,|\,\mathbf{t}_z\,|^2\right]$$

$$\approx \frac{k_B T}{2}\int ds\left[l_P\left(\frac{d\mathbf{t}_\perp}{ds}\right)^2 + \Gamma\,|\,\mathbf{t}_\perp\,|^2\right]$$

$l_p = \kappa / k_B T =$ Persistence length

$\Gamma = h / k_B T =$ Alignment parameter

$\lambda = \sqrt{\frac{l_p}{\Gamma}} =$ Odijk deflection length

$\Gamma > 0$

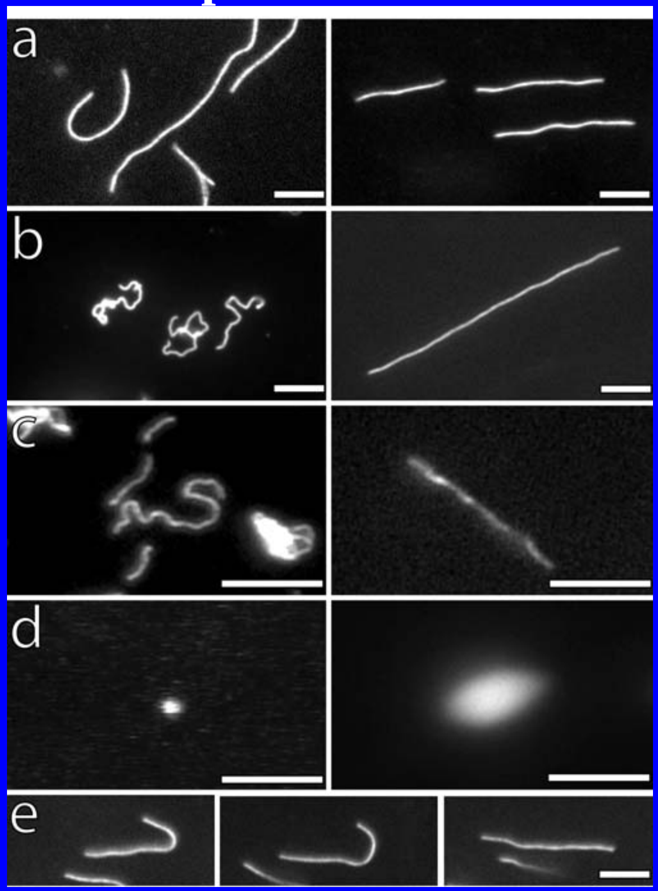
$\Gamma = 0$

$$\langle \mathbf{t}(s)\cdot\mathbf{t}(0)\rangle = e^{-s/2l_p}$$

$$\langle t_x(z)t_x(0)\rangle = \frac{\lambda}{2l_p}e^{-|z|/\lambda}$$

Polymers in fd-virus suspensions

Isotropic Nematic



Actin
16 μm

Wormlike
Micelle
500 nm

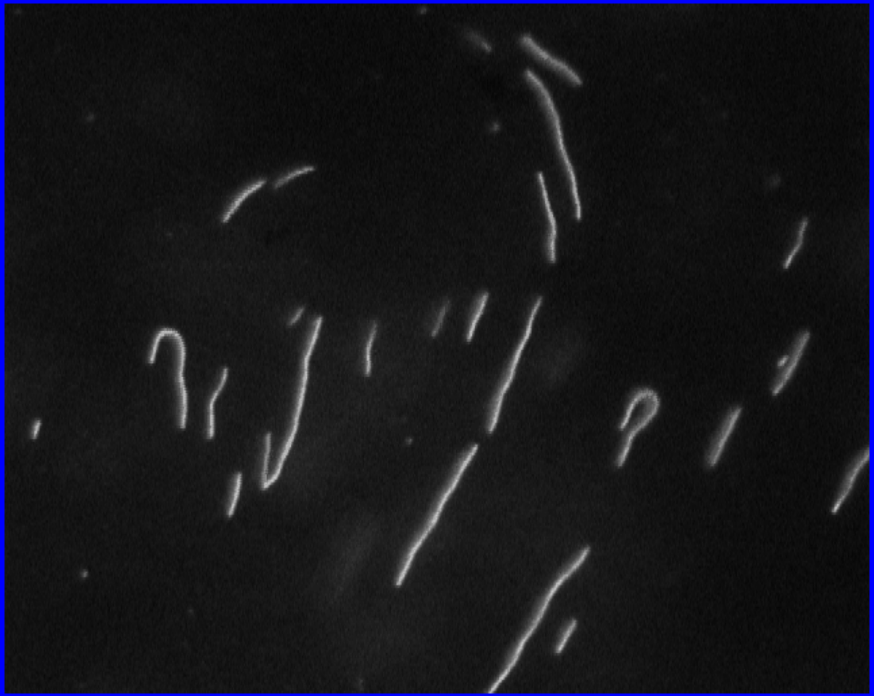
Neurofilament
200 nm

DNA
50 nm

Hairpin
defects

10 μm 10 μm

Actin in Nematic Fd



Dogic Z, Zhang J, Lau AWC, Aranda-Espinoza H, Dalhaimer P, Discher DE, Janmey PA, Kamien RD, Lubensky TC, Yodh AG, Phys. Rev. Lett. 92 (12): 2004

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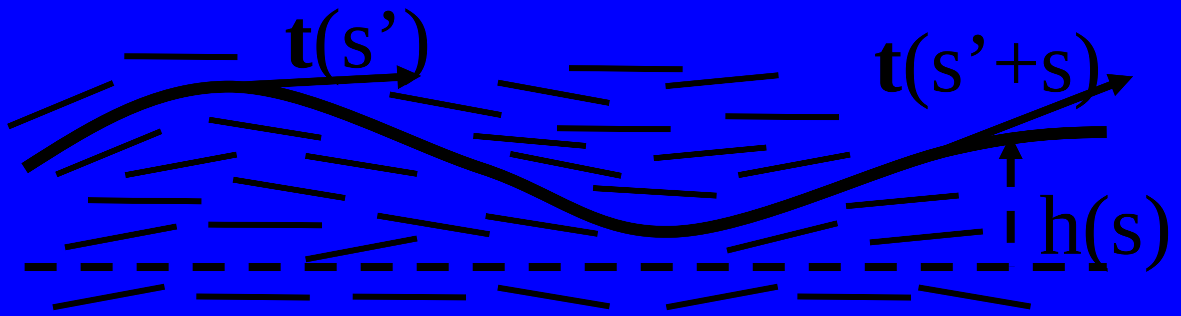
Tangent-tangent correlations

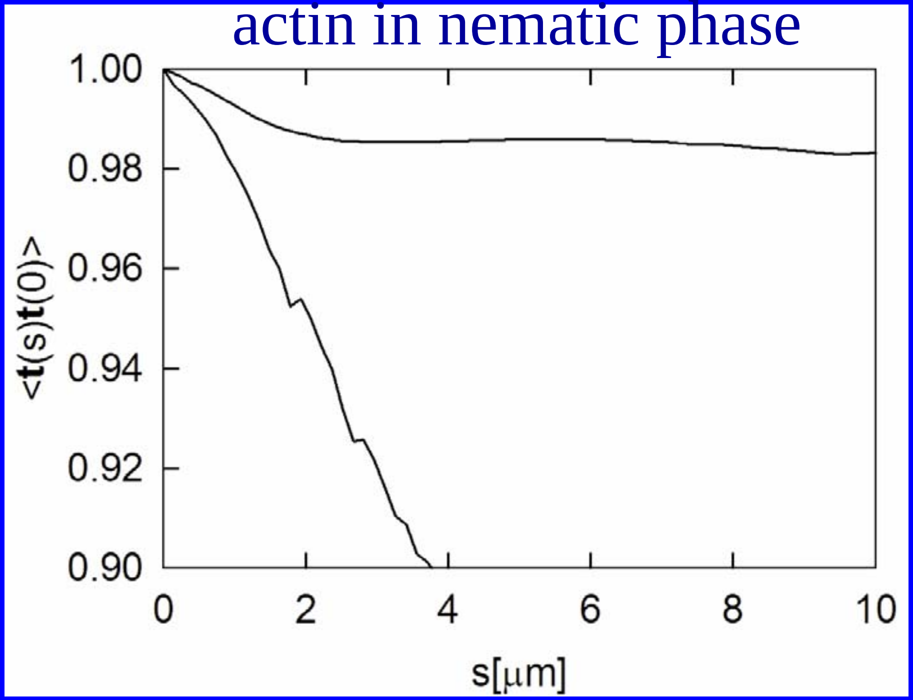


Isotropic phase – quasi 2D

$$\langle \mathbf{t}(s) \cdot \mathbf{t}(0) \rangle = e^{-s/2l_p}$$

Orientational correlations decay exponentially

l_p – persistence length of actin in isotropic phase



Polymer in nematic solvent

Bending energy　Coupling energy　Elastic energy

$$F/T = \frac{l_p}{2}\int_0^L dz\left(\frac{d\mathbf{t}_\perp}{dz}\right)^2 + \frac{\Gamma}{2}\int_0^L dz\left[\mathbf{t}_\perp(z) - \delta\mathbf{n}(0,z)\right]^2 + \frac{1}{2}K\int d^3x\,(\nabla\mathbf{n})^2$$

$l_p =$ Persistence length

$\Gamma =$ Coupling constant

$K =$ Elastic constant

$$\lambda = \sqrt{\frac{l_P}{\Gamma}} = \text{ Odijk length}$$

$$\left\langle t_x(z)t_x(z+z')\right\rangle = \frac{\lambda}{2\ell_p}e^{-z/\lambda} + \frac{1}{4\pi^2 K\lambda}\int_0^\infty dx\,\frac{\cos(xz/\lambda)\log(1+D^2/x^2)}{(1+x^2)[1+x^2+\alpha x^2\log(1+D^2/x^2)]}$$

Penn
University of Pennsylvania