Excluded-Volume Interactions

We saw previously that the probability distribution of the end-to-end vector $\mathbf{R}$ has the Gaussian form

$$P(R) \sim \mathrm{e}^{-3R^2/2N\ell^2} \ .$$

We are free to interpret the argument of the exponential as the Boltzmann factor of an effective free energy $F(R)$,

$$F(R) = -k_B T \ln P(R) = k_B T \frac{3R^2}{2N\ell^2}$$

which has the form of a (Hookean) entropic spring, with a minimum at $R = 0$. It costs entropy to extend the chain.

Let us now consider how excluded-volume interactions change this free energy. We imagine that there is a pairwise interaction of the form

$$\frac{1}{2} v k_B T \int_0^N dn \int_0^N dm \ \delta(\mathbf{R}_n - \mathbf{R}_m)$$

where we have called the amplitude of the interaction vk_BT for convenience, and abstracted it into a delta function potential.

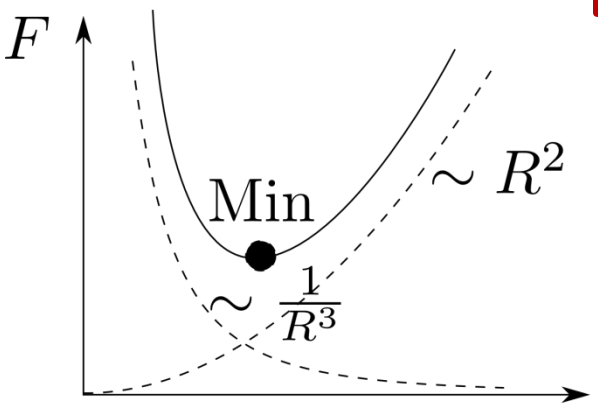
Excluded-Volume Interactions - continued

Using the mean-field arguments of van der Waals, we estimate the contribution of these interactions to the free energy as

$$vk_BT \cdot N \cdot \frac{N}{R^3} \sim k_BT \frac{vN^2}{R^3}$$

where the local segment concentration is N/R^3 (in three dimensions). The total free energy in this *Flory theory* is thus

$$F_{\text{tot}} = k_BT \left[\frac{3R^2}{2N\ell^2} + \frac{vN^2}{R^3} \right]$$



We see a competition between entropy, which favours the smallest R, and excluded-volume effects that tend to swell the chain. Differentiating to find the optimum, R^*, we obtain

$$R^* \sim N^{3/5}$$

Note: $3/5 > 1/2$, so excluded-volume interactions have swollen the chain from its ideal random-walk size.

Excluded-Volume Interactions - continued

Generalizing this to d-dimensions, the only change is that the local concentration is N/R^d, so the balance of terms is

$$\frac{R^2}{N} \sim \frac{N^2}{R^d} \Rightarrow R^{d+2} \sim N^3 \Rightarrow R \sim N^{3/(d+2)}$$

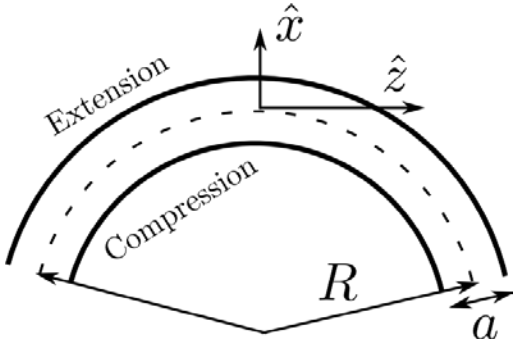
Thus, Flory theory predicts the exponent values

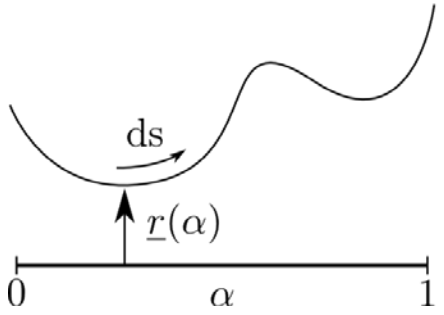
$$R \sim N^{\nu} \qquad \nu = \frac{3}{d+2}$$

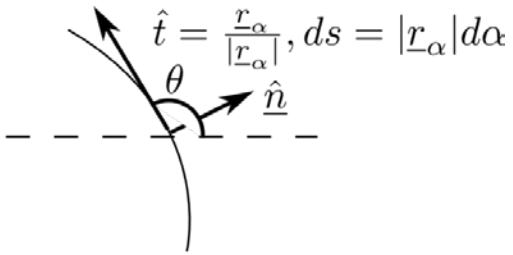
This relation is remarkably accurate:

$d = 1$	$R \sim N$	correct
$d = 2$	$R \sim N^{3/4}$	exact (solved)
$d = 3$	$R \sim N^{3/5}$	numerical solution (0.589)
$d = 4$	$R \sim N^{1/2}$	correct
$d > 4$	$R \sim N^{3/(d+2)}$	wrong (should be $N^{1/2}$)

Geometry and Elasticity







First, some differential geometry. Consider a curve $\mathbf{r}(\alpha)$ in a plane that is parameterized by $\alpha \in (0, 1)$. The differential of arclength is

$$ds = |d\mathbf{r}| = \sqrt{g} d\alpha \qquad g = \mathbf{r}_\alpha \cdot \mathbf{r}_\alpha$$

with $\mathbf{r}_\alpha \equiv \partial \mathbf{r} / \partial \alpha$ and g is the metric. The unit tangent to the curve is

$$\hat{\mathbf{t}} = \frac{\mathbf{r}_\alpha}{\sqrt{g}}$$

The tangent and normal vectors rotate as we move along the curve according to the *Frenet-Serret* equations

$$\frac{\partial}{\partial s} \begin{pmatrix} \hat{\mathbf{t}} \\ \hat{\mathbf{n}} \end{pmatrix} = \begin{pmatrix} 0 & -\kappa \\ \kappa & 0 \end{pmatrix} \begin{pmatrix} \hat{\mathbf{t}} \\ \hat{\mathbf{n}} \end{pmatrix}$$

where κ is the curvature.

More on Differential Geometry of Curves

If the tangent vector makes an angle θ with respect to a fixed axis (e.g., the x-axis), then it is easy to show that

$$\kappa = \frac{\partial \theta}{\partial s} \quad \text{where in general} \quad \frac{\partial}{\partial s} = \frac{1}{\sqrt{g}} \frac{\partial}{\partial \alpha}$$

In the "Monge representation", where we have a function $h(x)$ with no overhangs as a function of an external parameter x,

$$\mathbf{r}(x) = x\hat{\mathbf{e}}_\mathbf{x} + h(x)\hat{\mathbf{e}}_\mathbf{y}$$

$$\mathbf{r}_x = \hat{\mathbf{e}}_\mathbf{x} + h_x\hat{\mathbf{e}}_\mathbf{y}$$

$$\hat{\mathbf{t}} = \left[\hat{\mathbf{e}}_\mathbf{x} + h_x\hat{\mathbf{e}}_\mathbf{y}\right] / \sqrt{1 + h_x^2}$$

$$\text{so} \qquad \theta = \tan^{-1} h_x$$

and the curvature is

$$\kappa = \frac{h_{xx}}{(1 + h_x^2)^{3/2}} \simeq h_{xx}$$

The Persistence Length

Let us look at the example of an elastic filament, weakly deformed, to understand a bit more about curvature and variational principles. The simplest elastic energy is (Landau & Lifshitz, etc.)

$$E = \frac{A}{2}\int_0^L ds\kappa^2$$

where A is an elastic modulus and s is arclength. Note that the units of A are energy·length, so we can always express A as k_BTL_p, where L_p is the *persistence length*. This has physical meaning in that if the curvature $\kappa \sim 1/R \sim 1/L$ then $E \sim A \cdot L \cdot 1/L^2 \sim A/L$, and if we ask that such bending cost k_BT, then the length scale is on which this occurs is $L \sim A/k_BT$. Thus the persistence length is the length over which thermal energy can induce a filament-length bend.

DNA	$L_p \sim 50$ nm (~ 150 base pairs)
actin	$L_p \sim 10 - 15$ μm
microtubules	$L_p \sim 5$ mm

Note the definition of the Young's modulus:

$$\frac{\text{Force}}{\text{area}} = E\frac{\Delta L}{L}$$

and a force/area is an energy/volume. Since $[A]$ = energy · length, we conclude

$$A \sim E \cdot \text{radius}^4$$

A Simple Application to the Elastic Filament

Returning to the elastic energy if the slope is small everywhere, we can approximate this as

$$E \simeq \frac{A}{2}\int_0^L dx h_{xx}^2$$

To find equilibria of this energy functional we need to look at the variation δE when h is changed by δh. Repeatedly integrating by parts, we find

$$\delta E = A\int dx h_{xx}\delta h_{xx} = A\left\{h_{xx}\delta h_x\Big|_0^L - \int dx h_{3x}\delta h_x\right\}$$

$$= A\left\{h_{xx}\delta h_x\Big|_0^L - h_{xxx}\delta h\Big|_0^L + \int dx h_{4x}\delta h\right\}$$

Functional Differentiation- continued

$$\delta E = A\left\{ h_{xx}\delta h_x\Big|_0^L - h_{xxx}\delta h\Big|_0^L + \int dx h_{4x}\delta h \right\}$$

This implies that the functional derivative of E is

$$\frac{\delta E}{\delta h} = A h_{4x}$$

If the "surface" terms vanish for arbitrary δh and δh_x then we require

$$h_{xx}(0) = h_{xx}(L) = 0 \qquad [Ah_{xx}] = \text{energy} = \text{torque}$$
$$h_{3x}(0) = h_{3x}(L) = 0 \qquad [Ah_{3x}] = \text{energy/length} = \text{force}$$

These are the *natural boundary conditions* of no torque and no force at the (free) ends. If this is the case, the ∂_{4x} is a self-adjoint operator and its eigenfunctions are real. These are eigenfunctions satisfying

$$AW_{4x} = k^4 W$$

just as $\sin qx$ and $\cos qx$ are eigenfunctions satisfying $f_{xx} = -q^2 f$.

The Biharmonic Eigenfunctions

A simple superposition of $\sin kx$ and $\cos kx$ will not work, as this can not allow successive derivatives to vanish. Instead,

$$W(x) = A \sin kx + B \cos kx + D \sinh kx + E \cosh kx$$

An exercise for the student is to show that the boundary conditions imply

$$\cos kL \cosh kL = 1$$

This yields an infinite discrete set of wavenumbers k analogous to the trigonometric numbers $n\pi/L$.
If we express $h(x)$ as a sum of biharmonic eigenfunctions

$$h(x) = \sum_n a_n W^{(n)}(x) \qquad \text{then} \qquad h_{4x} = \sum_n a_n \lambda_n W^{(n)}(x)$$

where λ_n is the nth eigenvalue.

The Biharmonic Eigenfunctions

This impliest that the bending energy can be separated into modes:

$$\frac{A}{2}\int dx h_{xx}^2 = \frac{A}{2}\int dx h h_{4x} = \frac{A}{2}\int dx \sum_m \sum_n a_m a_n \lambda_n W^{(m)} W^{(n)}$$

$$= \frac{A}{2}\sum_n \lambda_n a_n^2$$

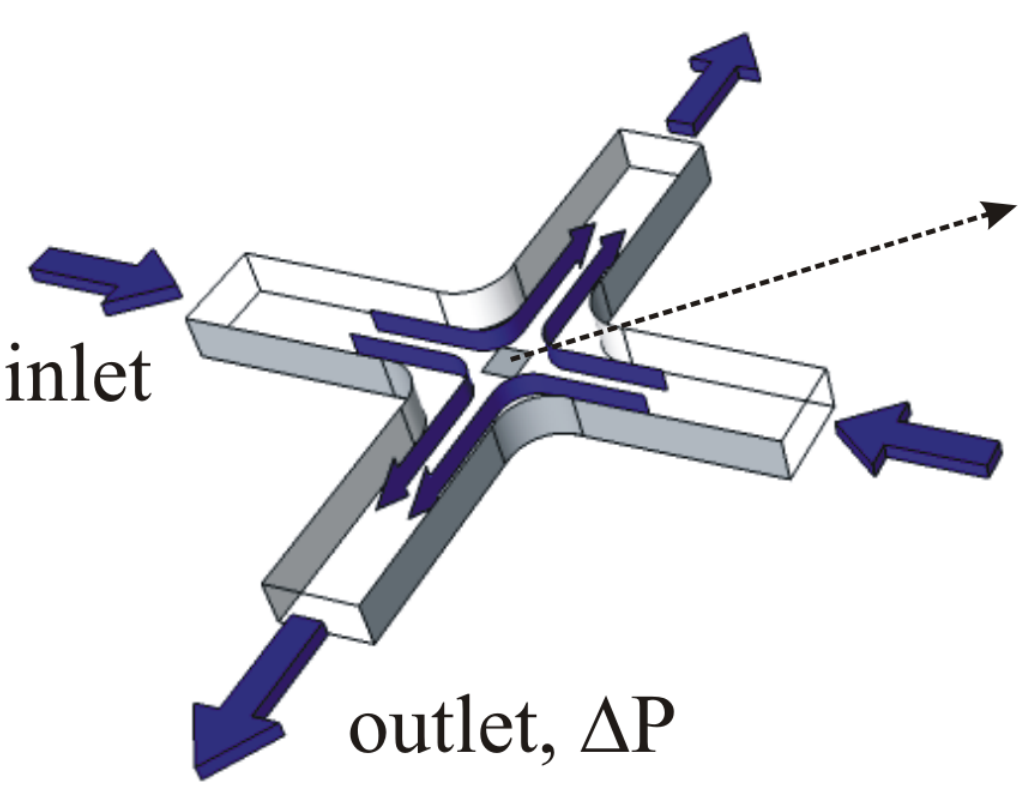
by the orthogonality of the Ws (and their assumed normalization). And we can compute the variance:

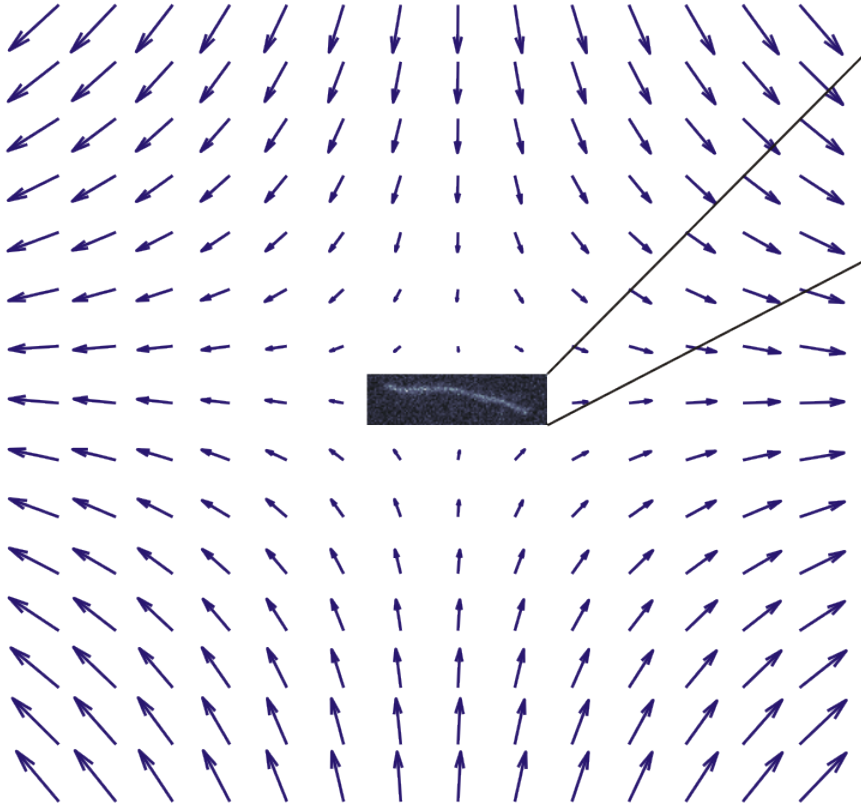
$$h^2(x) = \sum_m \sum_n a_m a_n W^{(m)}(x) W^{(n)}(x)$$

and, since the a_m are independent, Gaussianly distributed variables,

$$\langle h^2(x) \rangle = \frac{k_B T}{A} \sum_n \frac{W^{(n)}(x)^2}{\lambda_n}$$

Fluctuations, Dynamics, and the Stretch-Coil Transition of Actin Filaments in Extensional Flows





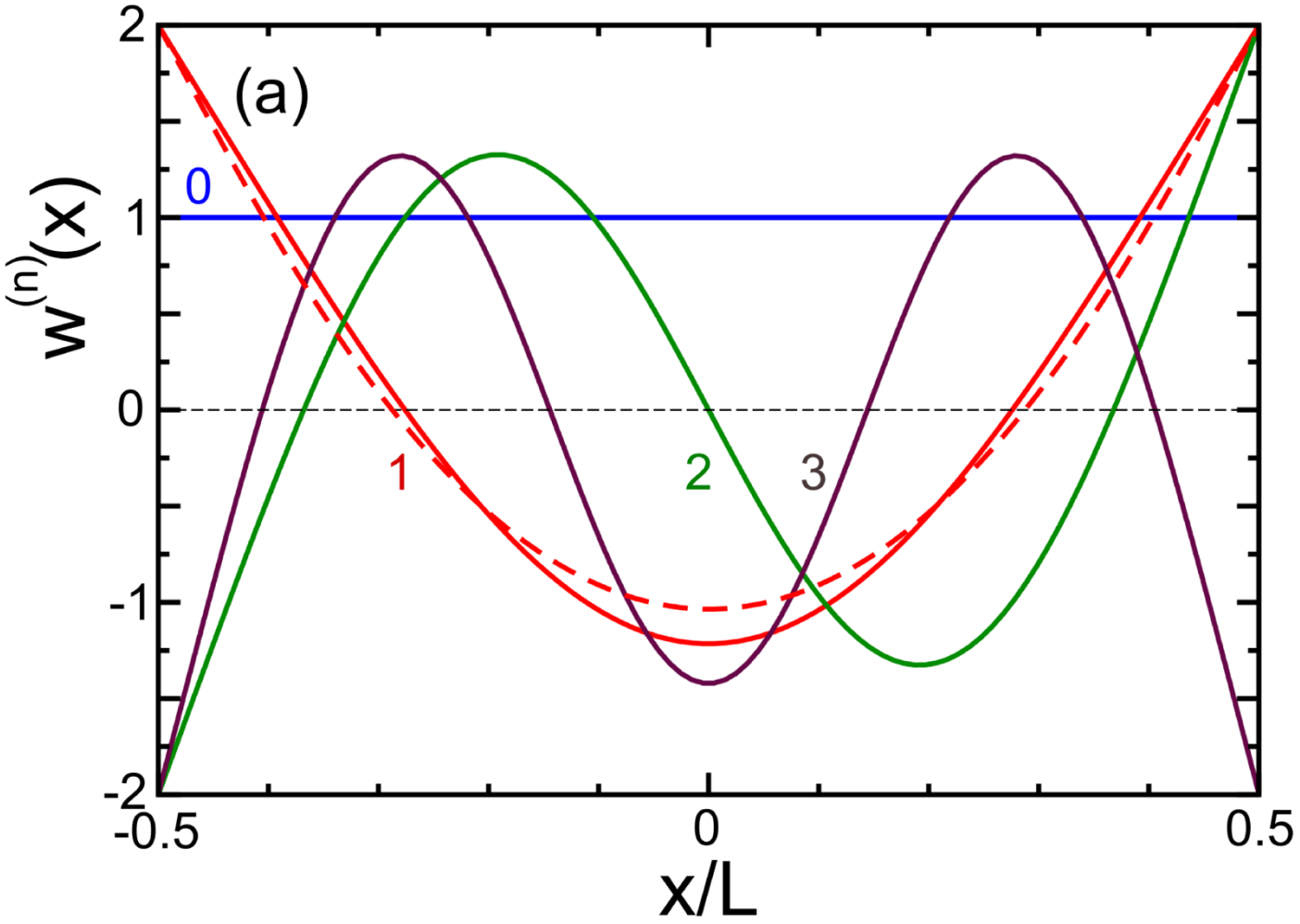
Kantsler and Goldstein, *PRL* **108**, 038103 (2012)

Fluctuations and Dynamics Under Extension

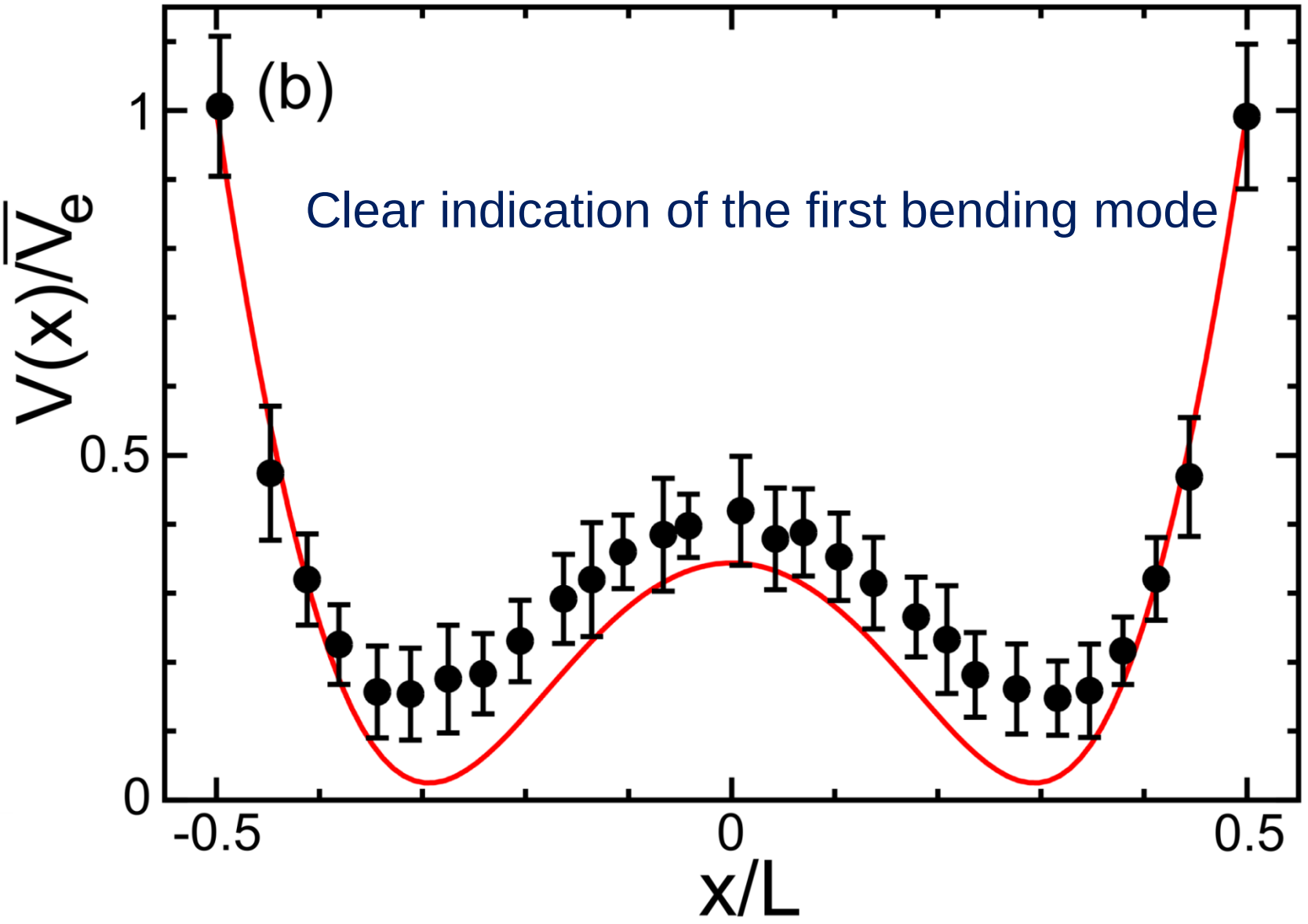
When Σ=0, these are the biharmonic eigenfunctions:

$$W(x) = A\cos kx + B\sin kx + D\cosh kx + E\sinh kx$$

$$\cos kL \cosh kL = 1$$

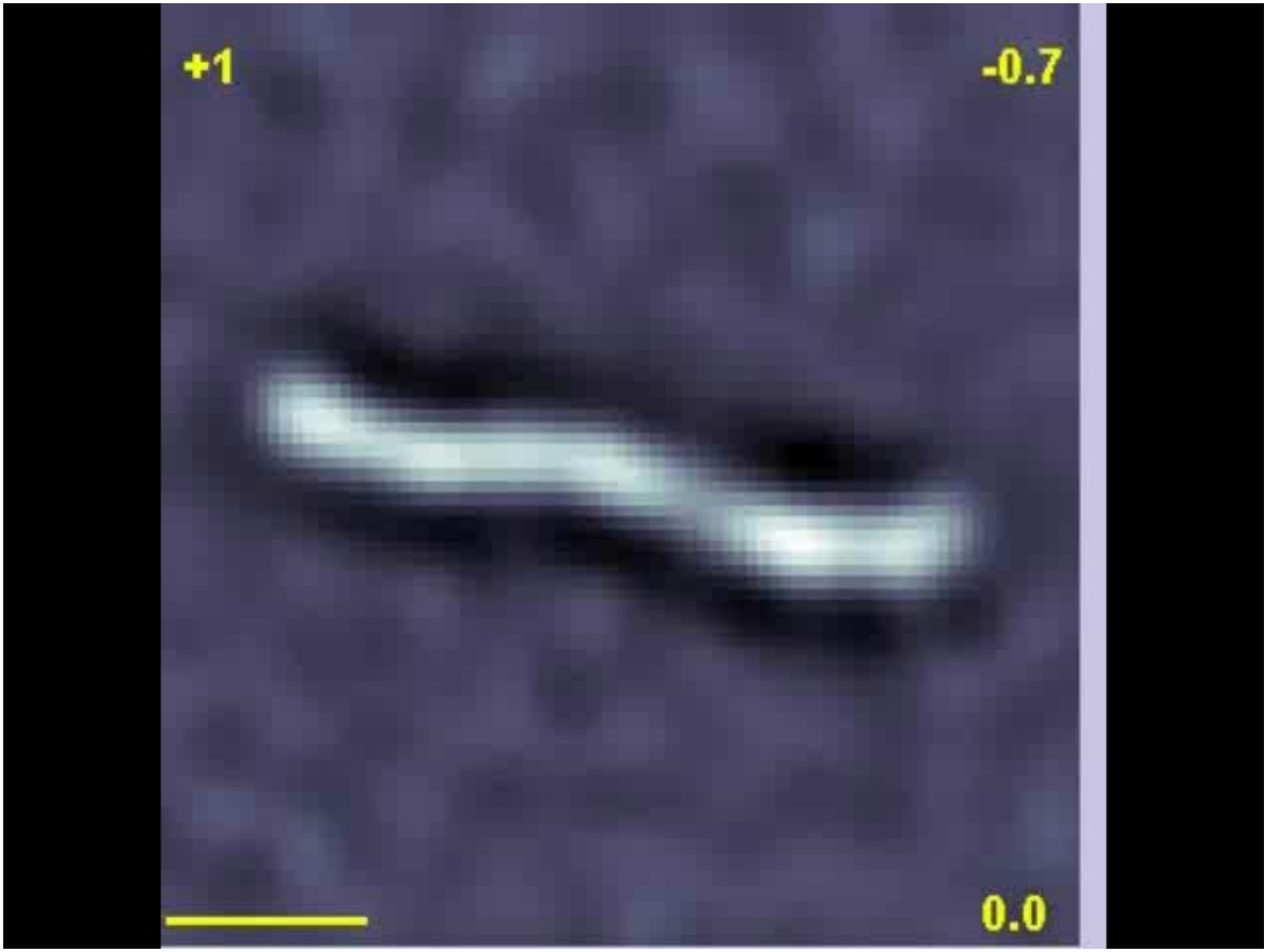


Arclength-Resolved Fluctuations

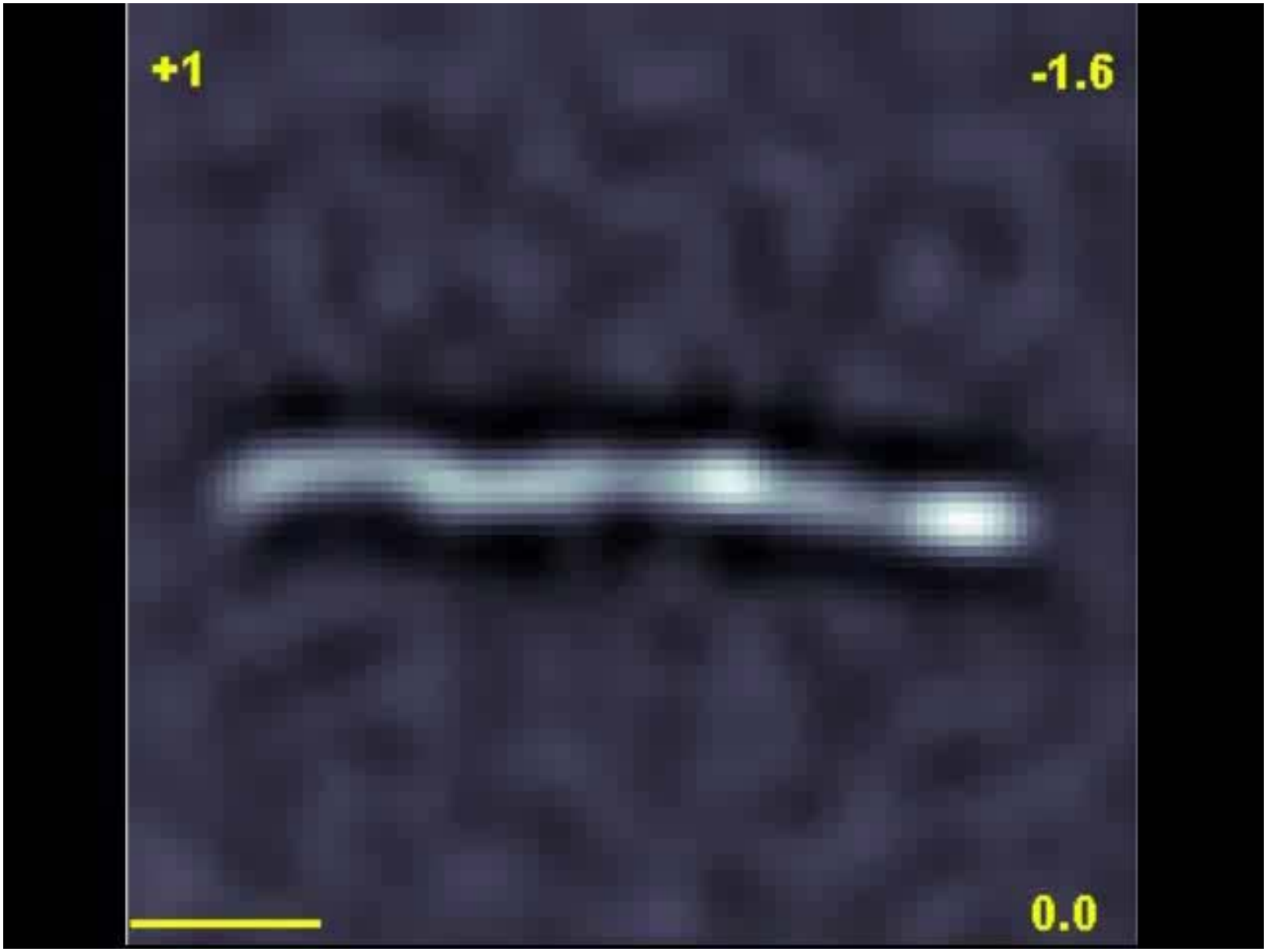


Kantsler and Goldstein, *PRL* (2012)

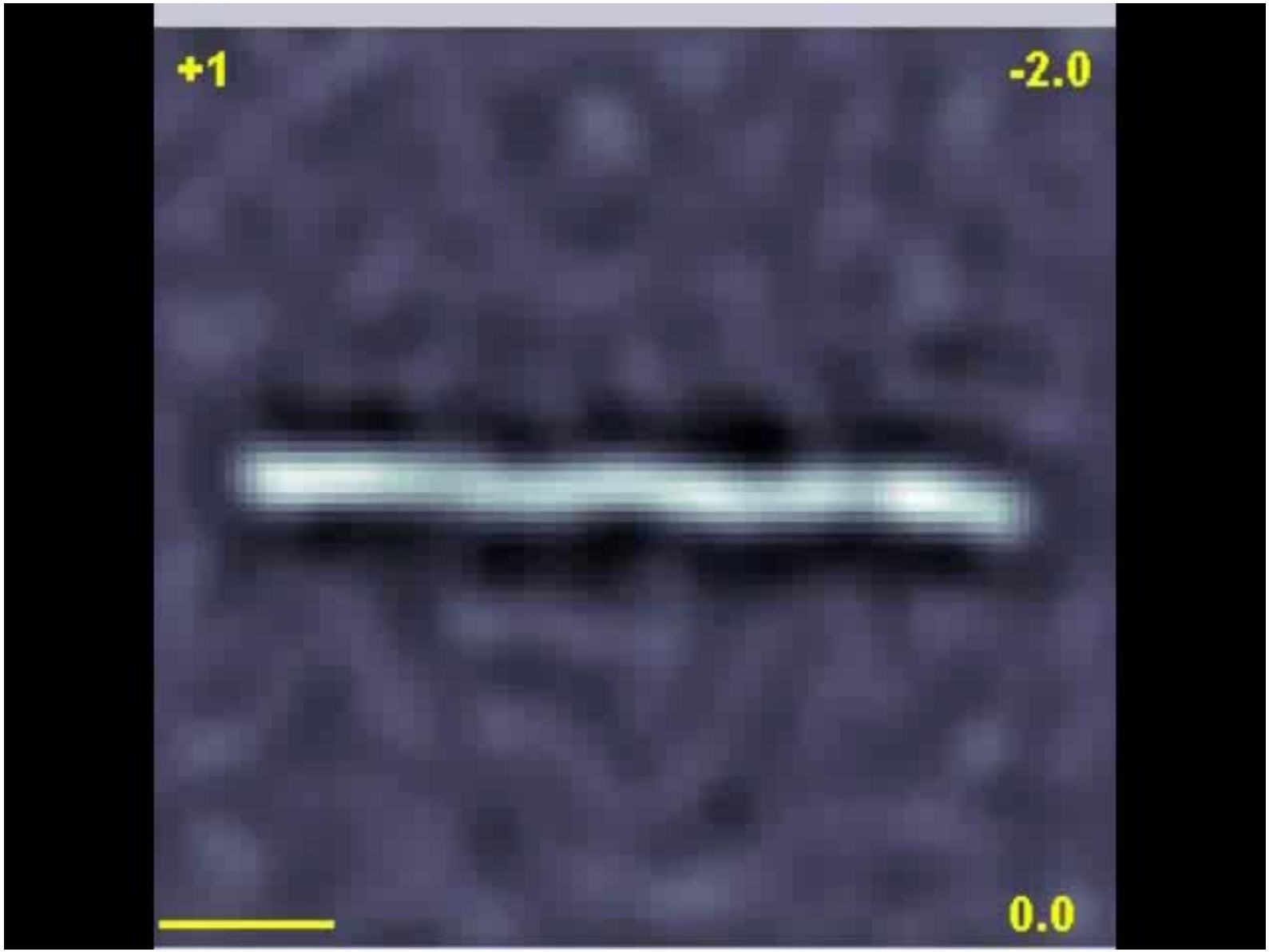
The Stretch-Coil Transition of Actin (Σ=2.2)



Σ=15



Σ=50



The Stretch-Coil Transition of Actin