Polymers

(continued)

18.S995 - L14 &15

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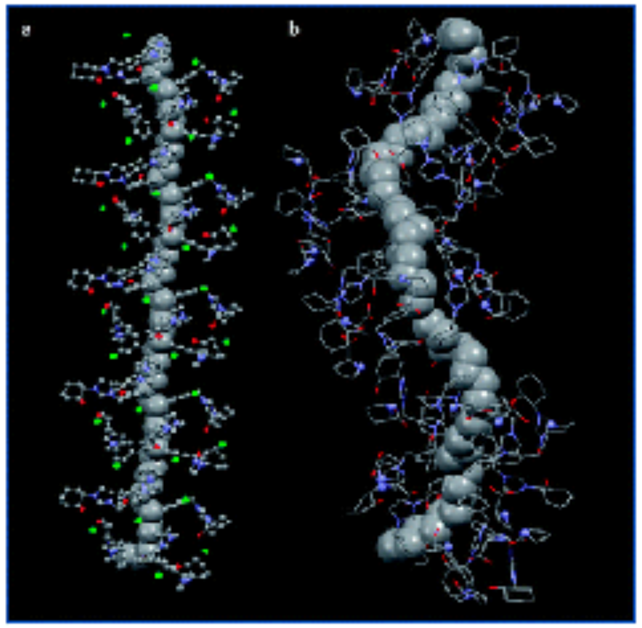
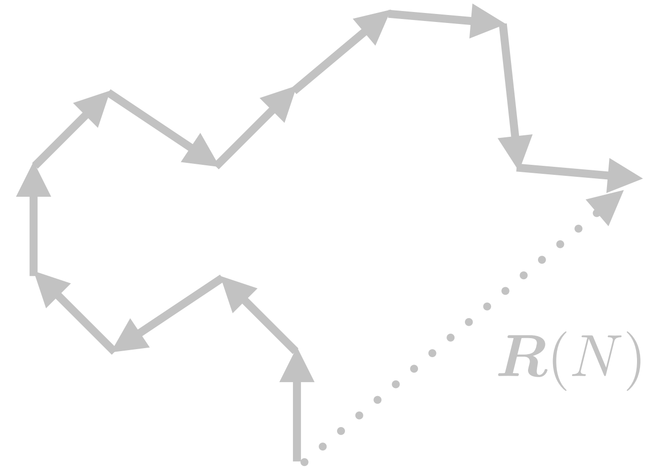
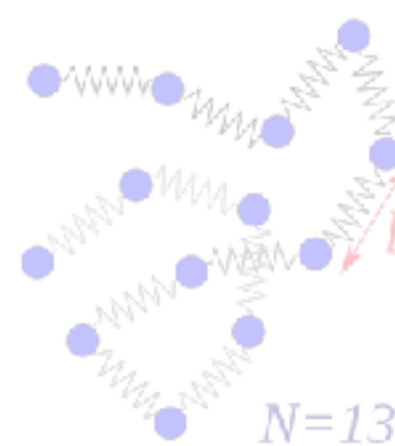
Karjalainen et al (2014) Polym Chem



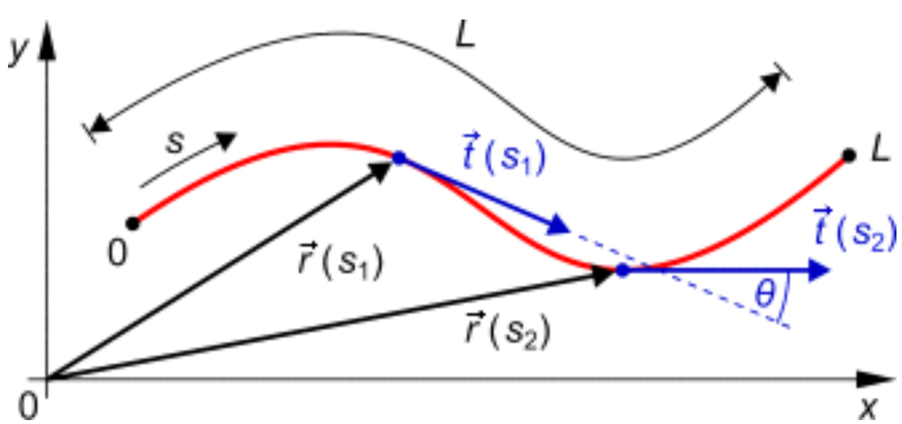
persistent RW model



mechanistic model



continuum model



http://www.uni-leipzig.de/~pwm/web/?section=introduction&page=polymers

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2.3 Continuum description

2.3.1 Differential geometry of curves

Consider a continuous curve $\boldsymbol{r}(t) \in \mathbb{R}^3$, where $t \in [0, T]$. Assume that the first three derivatives $\dot{\boldsymbol{r}}(t), \ddot{\boldsymbol{r}}(t), \dddot{\boldsymbol{r}}(t)$ are linearly independent. The length of the curve is given by

$$L = \int_0^T dt \, ||\dot{\boldsymbol{r}}(t)|| \tag{2.41}$$

where $\dot{\boldsymbol{r}}(t) = d\boldsymbol{r}/dt$ and $|| \cdot ||$ denotes the Euclidean norm. The local unit tangent vector is defined by

$$\boldsymbol{t} = \frac{\dot{\boldsymbol{r}}}{||\dot{\boldsymbol{r}}||}. \tag{2.42}$$

The unit normal vector, or unit curvature vector, is

$$\boldsymbol{n} = \frac{(\boldsymbol{I} - \boldsymbol{t}\boldsymbol{t}) \cdot \ddot{\boldsymbol{r}}}{||(\boldsymbol{I} - \boldsymbol{t}\boldsymbol{t}) \cdot \ddot{\boldsymbol{r}}||}. \tag{2.43}$$

Unit tangent vector $\hat{\boldsymbol{t}}(t)$ and unit normal vector $\hat{\boldsymbol{n}}(t)$ span the *osculating* ('kissing') plane at point t. The unit binormal vector is defined by

$$\boldsymbol{b} = \frac{(\boldsymbol{I} - \boldsymbol{t}\boldsymbol{t}) \cdot (\boldsymbol{I} - \boldsymbol{n}\boldsymbol{n}) \cdot \dddot{\boldsymbol{r}}}{||(\boldsymbol{I} - \boldsymbol{t}\boldsymbol{t}) \cdot (\boldsymbol{I} - \boldsymbol{n}\boldsymbol{n}) \cdot \dddot{\boldsymbol{r}}||}. \tag{2.44}$$

The orthonormal basis $\{\boldsymbol{t}(t), \boldsymbol{n}(t), \boldsymbol{b}(t)\}$ spans the local Frenet frame. For *plane* curves, $\dddot{\boldsymbol{r}}(t)$ is not linearly independent of $\dot{\boldsymbol{r}}$ and $\ddot{\boldsymbol{r}}$. In this case, we set $\boldsymbol{b} = \boldsymbol{t} \wedge \boldsymbol{n}$.

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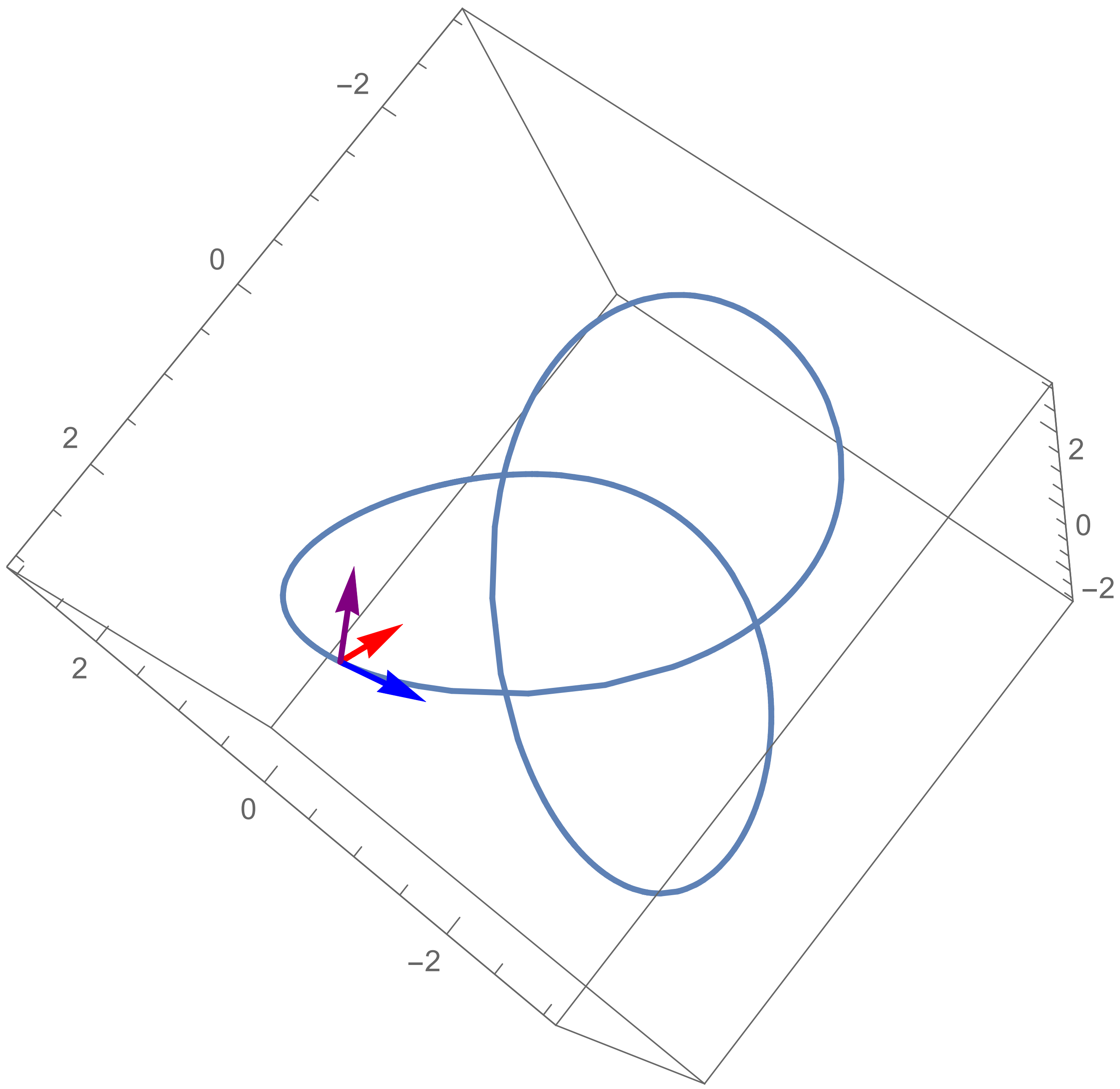
$$\boldsymbol{t} = \frac{\dot{\boldsymbol{r}}}{||\dot{\boldsymbol{r}}||}$$

$$\boldsymbol{n} = \frac{(\boldsymbol{I} - \boldsymbol{t}\boldsymbol{t}) \cdot \ddot{\boldsymbol{r}}}{||(\boldsymbol{I} - \boldsymbol{t}\boldsymbol{t}) \cdot \ddot{\boldsymbol{r}}||}$$

$$\boldsymbol{b} = \frac{(\boldsymbol{I} - \boldsymbol{t}\boldsymbol{t}) \cdot (\boldsymbol{I} - \boldsymbol{n}\boldsymbol{n}) \cdot \dddot{\boldsymbol{r}}}{||(\boldsymbol{I} - \boldsymbol{t}\boldsymbol{t}) \cdot (\boldsymbol{I} - \boldsymbol{n}\boldsymbol{n}) \cdot \dddot{\boldsymbol{r}}||}$$



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The local curvature $\kappa(t)$ and the associated radius of curvature $\rho(t) = 1/\kappa$ are defined by

$$\kappa(t) = \frac{\dot{\boldsymbol{t}} \cdot \boldsymbol{n}}{||\dot{\boldsymbol{r}}||}, \tag{2.45}$$

and the local torsion $\tau(t)$ by

$$\tau(t) = \frac{\dot{\boldsymbol{n}} \cdot \boldsymbol{b}}{||\dot{\boldsymbol{r}}||}. \tag{2.46}$$

For plane curves with constant $\boldsymbol{b}$, we have $\tau = 0$.

Given $||\dot{\boldsymbol{r}}||$, $\kappa(t)$, $\tau(t)$ and the initial values $\{\boldsymbol{t}(0), \boldsymbol{n}(0), \boldsymbol{b}(0)\}$, the Frenet frames along the curve can be obtained by solving the Frenet-Serret system

$$\frac{1}{||\dot{\boldsymbol{r}}||} \begin{pmatrix} \dot{\boldsymbol{t}} \\ \dot{\boldsymbol{n}} \\ \dot{\boldsymbol{b}} \end{pmatrix} = \begin{pmatrix} 0 & \kappa & 0 \\ -\kappa & 0 & \tau \\ 0 & -\tau & 0 \end{pmatrix} \begin{pmatrix} \boldsymbol{t} \\ \boldsymbol{n} \\ \boldsymbol{b} \end{pmatrix}. \tag{2.47a}$$

The above formulas simplify if t is the arc length, for in this case $||\dot{\boldsymbol{r}}|| = 1$.

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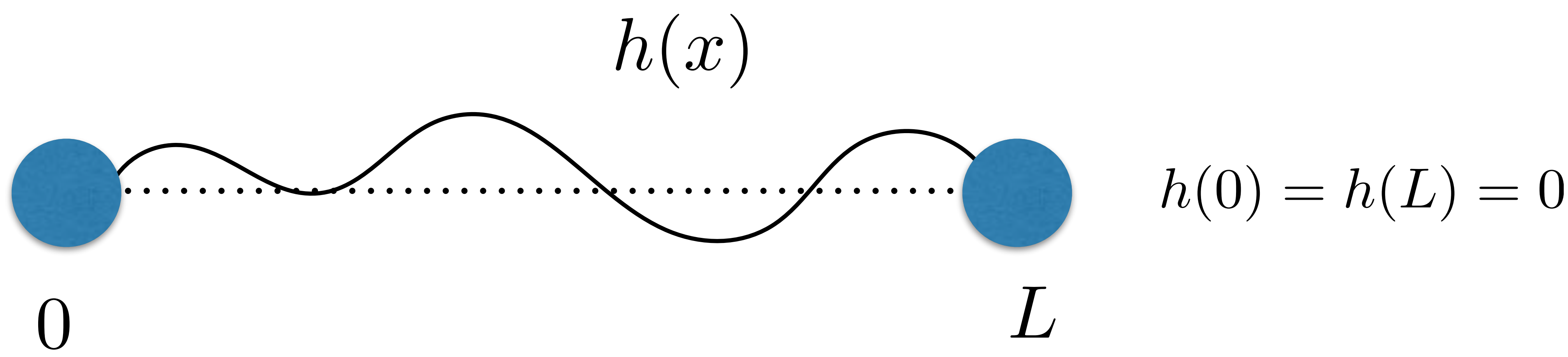
2.3.2 Stretchable polymers: Minimal model and equipartition



$$E = \gamma \left[\int_0^L dx \sqrt{1 + h_x^2} - L \right], \tag{2.48}$$

where $h_x = h'(x)$. Restricting ourselves to small deformations, $|h_x| \ll 1$, we may approximate

$$E \simeq \frac{\gamma}{2} \int_0^L dx \, h_x^2. \tag{2.49}$$

[3] γ carries units of energy/length.

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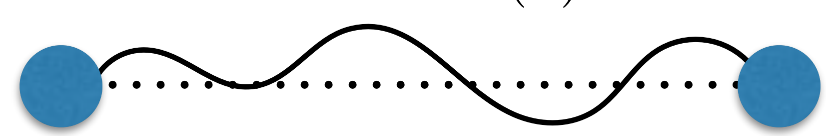

$$E \simeq \frac{\gamma}{2} \int_0^L dx\, h_x^2. \tag{2.49}$$

Taking into account that $h(0) = h(L) = 0$, we may represent $h(x)$ and its derivative through the Fourier-sine series

$$h(x) = \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi x}{L}\right) \tag{2.50a}$$

$$h_x(x) = \sum_{n=1}^{\infty} A_n \frac{n\pi}{L} \cos\left(\frac{n\pi x}{L}\right). \tag{2.50b}$$

Exploiting orthogonality

$$\int_0^L dx\ \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) = \frac{L}{2}\,\delta_{nm} \tag{2.51}$$

we may rewrite the energy (2.49) as

$$\begin{aligned} E &\simeq \frac{\gamma}{2} \sum_n \sum_m \int_0^L dx\, A_n A_m \left(\frac{n\pi}{L}\right)\left(\frac{m\pi}{L}\right) \cos\left(\frac{n\pi x}{L}\right) \cos\left(\frac{m\pi x}{L}\right) \\ &= \frac{\gamma}{2} \sum_n \sum_m A_n A_m \left(\frac{n\pi}{L}\right)\left(\frac{m\pi}{L}\right) \frac{L}{2}\,\delta_{nm} \\ &= \sum_{n=1}^{\infty} E_n, \end{aligned} \tag{2.52a}$$

where the energy E_n stored in Fourier mode n is

$$E_n = A_n^2 \left(\frac{\gamma n^2 \pi^2}{4L}\right). \tag{2.52b}$$

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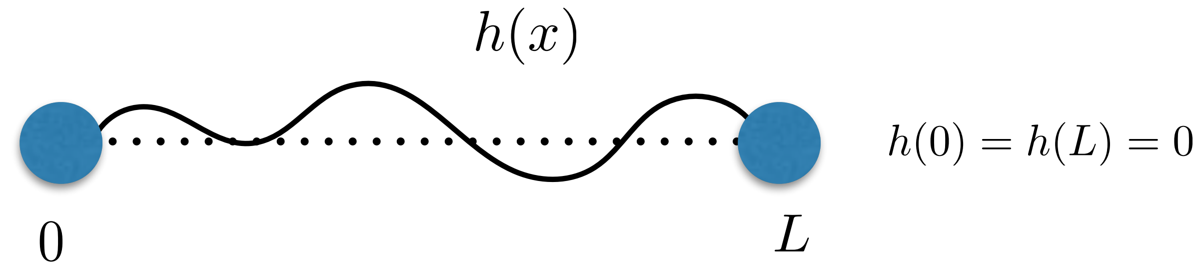


$$E \simeq \frac{\gamma}{2}\int_0^L dx\, h_x^2 \;=\; \sum_{n=1}^{\infty} E_n \qquad\qquad E_n = A_n^2\left(\frac{\gamma n^2\pi^2}{4L}\right)$$

Now assume the polymer is coupled to a bath and the stationary distribution is canonical

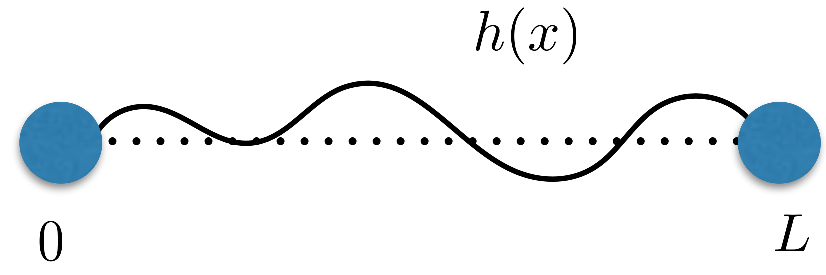
$$\begin{aligned} p(\{A_n\}) &= \frac{1}{Z}\exp(-\beta E) \\ &= \frac{1}{Z}\exp\left[-\beta\sum_{n=1}^{\infty} A_n^2\left(\frac{\gamma n^2\pi^2}{4L}\right)\right] \end{aligned} \tag{2.53}$$

with $\beta = (k_B T)^{-1}$. The PDF factorizes and, therefore, also the normalization constant

$$Z = \prod_{i=1}^{\infty} Z_n, \tag{2.54a}$$

where

$$Z_n = \int_{\infty}^{\infty} dA_n \exp\left[-\beta A_n^2\left(\frac{\gamma n^2\pi^2}{4L}\right)\right] = \left(\frac{4\pi L}{\beta\gamma n^2\pi^2}\right)^{1/2}. \tag{2.54b}$$



$h(0) = h(L) = 0$

$$E \simeq \frac{\gamma}{2}\int_0^L dx\, h_x^2 \;=\; \sum_{n=1}^{\infty} E_n \qquad\qquad E_n = A_n^2\left(\frac{\gamma n^2\pi^2}{4L}\right)$$

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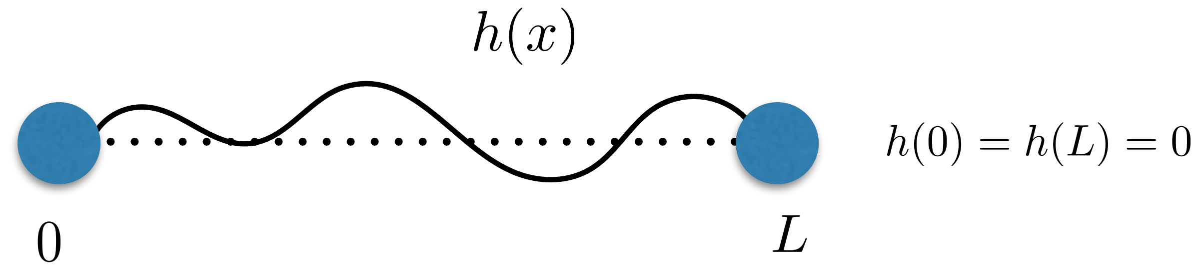
We thus find for the first to moments of A_n

$$\mathbb{E}[A_n] = 0 \tag{2.55a}$$

$$\mathbb{E}[A_n^2] = \frac{2k_BTL}{\gamma n^2\pi^2}, \tag{2.55b}$$

and from this for the mean energy per mode

$$\mathbb{E}[E_n] = \left(\frac{\gamma n^2\pi^2}{4L}\right)\mathbb{E}[A_n^2] = \frac{1}{2}k_BT. \tag{2.56}$$



We may use the equipartition result to compute the variance of the polymer at the position $x \in [0, L]$

$$
\begin{aligned}
\mathbb{E}[h(x)^2] &:= \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \mathbb{E}[A_n A_m] \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) \\
&= \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \mathbb{E}[A_n^2]\delta_{nm} \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) \\
&= \left(\frac{2k_B T L}{\gamma\pi^2}\right) \sum_{n=1}^{\infty} \frac{\sin^2(n\pi x/L)}{n^2}. \qquad (2.57)
\end{aligned}
$$

If we additionally average along x

$$
\langle \mathbb{E}[h(x)^2] \rangle = \left(\frac{k_B T L}{\gamma\pi^2}\right) \boxed{\sum_{n=1}^{\infty} \frac{1}{n^2}} = \left(\frac{k_B T L}{\gamma\pi^2}\right) \frac{\pi^2}{6} = \frac{k_B T L}{6\gamma}. \qquad (2.58)
$$

Thus, by measuring fluctuations along the polymer we may infer γ.

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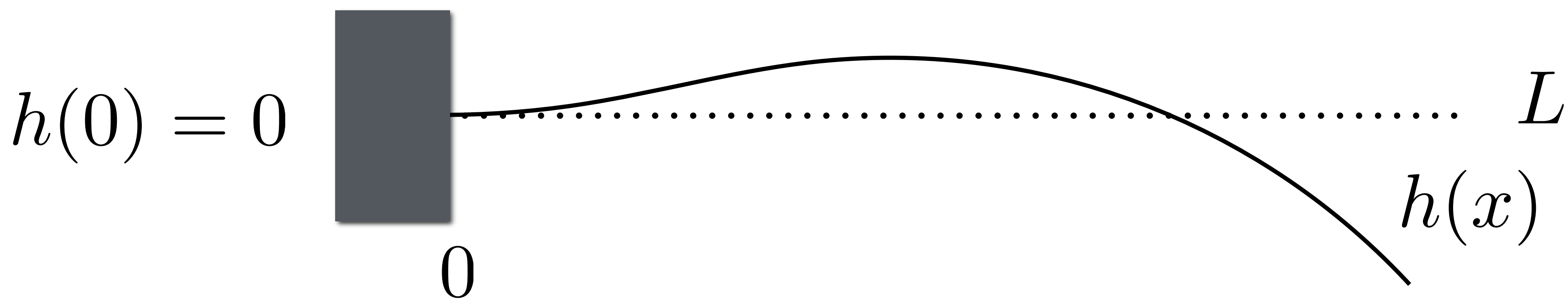
2.3.3 Rigid polymers: Euler-Bernoulli equation



$$E \simeq \frac{A}{2}\int_0^L dx\,\kappa^2, \tag{2.59}$$

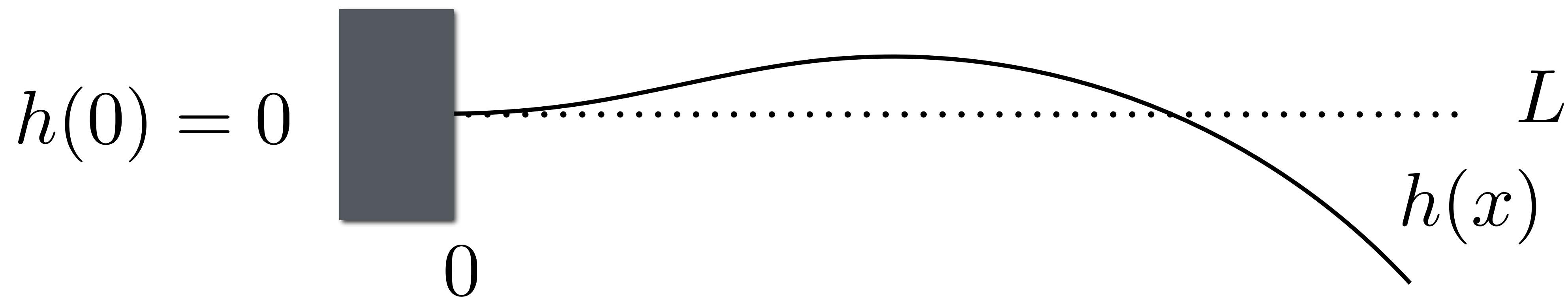
where A is the bending modulus (units energy×length). For plane curves $h(x)$, the curvature can be expressed as

$$\kappa = \frac{h_{xx}}{(1+h_x^2)^{3/2}}. \tag{2.60}$$

Focussing on the limit of weak deformations, $h_x \ll 1$, we may approximate $\kappa \simeq h_{xx}$, and the energy simplifies to

$$E \simeq \frac{A}{2}\int_0^L dx\,(h_{xx})^2. \tag{2.61}$$

Boundary conditions



$$E \simeq \frac{A}{2} \int_0^L dx \, (h_{xx})^2. \tag{2.61}$$

The exact form of the boundary conditions depend on how the polymer is attached to the plane $x = 0$. Assuming that polymer is rigidly anchored at an angle 90°, the boundary conditions at the fixed end at $x = 0$ are

$$h(0) = 0 \, , \qquad h_x(0) = 0. \tag{2.62a}$$

At the free end, we will consider flux conditions

$$h_{xx}(L) = 0 \, , \qquad h_{xxx}(L) = 0. \tag{2.62b}$$

(minimal absolute curvature at the free end)

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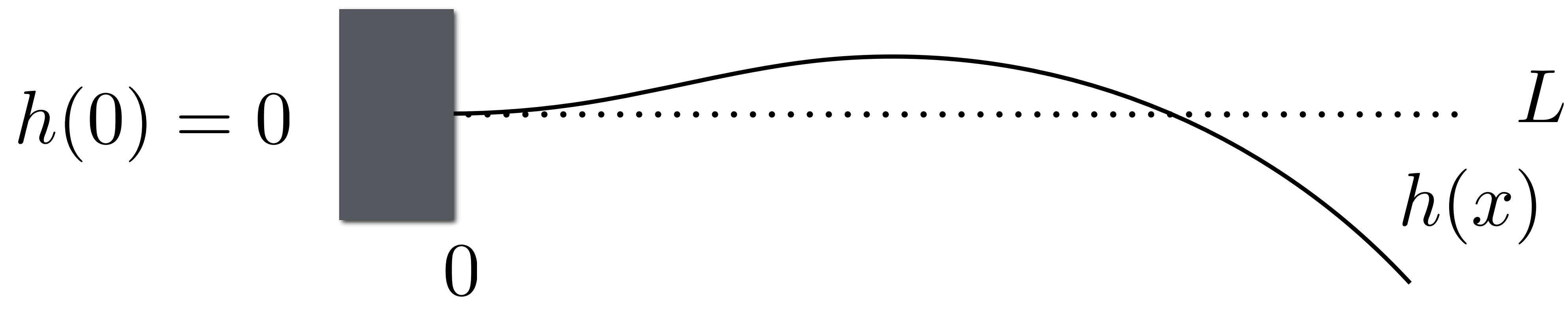
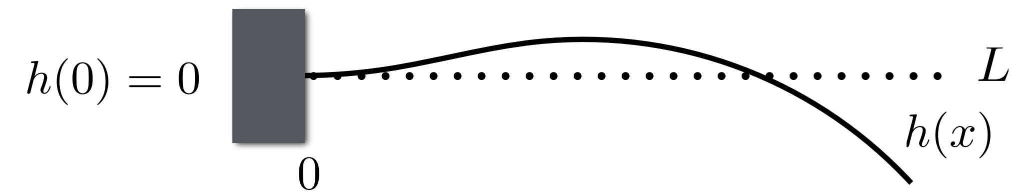
Boundary conditions



$$E \simeq \frac{A}{2} \int_0^L dx\, (h_{xx})^2. \tag{2.61}$$

By partial integrations, we may rewrite (2.61) as

$$\begin{aligned} E &\simeq \frac{A}{2} \left[h_x h_{xx} \Big|_0^L - \int_0^L dx\, h_x h_{xxx} \right] \\ &= \frac{A}{2} \left[- \int_0^L dx\, h_x h_{xxx} \right] \\ &= \frac{A}{2} \left[-h h_{xxx} \Big|_0^L + \int_0^L dx\, h h_{xxxx} \right] = \frac{A}{2} \left[\int_0^L dx\, h h_{xxxx} \right]. \end{aligned} \tag{2.63}$$



If the polymer is surrounded by a viscous solvent, an initial perturbation $h(0, x)$ will relax to the ground-state. Neglecting fluctuations due to thermal noise, the relaxation dynamics $h(t, x)$ will be of the over-damped form[4]

$$\eta h_t = -\frac{\delta E}{\delta h}, \tag{2.64}$$

where η is a damping constant, and the variational derivative is defined by

$$\frac{\delta E[h(x)]}{\delta h(y)} := \lim_{\epsilon \to 0} \frac{E[h(x) + \epsilon \delta(x - y)] - E[h(x)]}{\epsilon}. \tag{2.65}$$

Keeping terms up to order ϵ, we find for the energy functional (2.61)

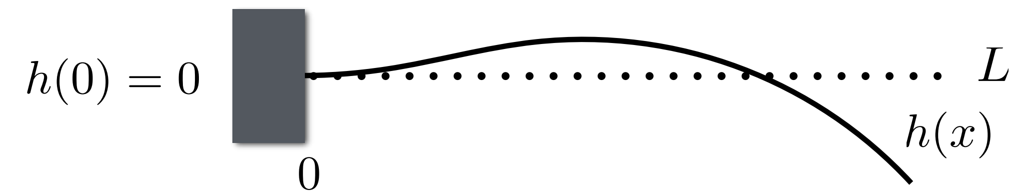
$$\begin{aligned} E[h(x) + \epsilon \delta(x - y)] - E[h(x)] &= \frac{A}{2} \int_0^L dx\, [(h + \epsilon\delta)_{xx}(h + \epsilon\delta)_{xx} - (h_{xx})^2] \\ &= \frac{A}{2} \int_0^L dx\, [2\epsilon h_{xx} \delta_{xx} + \mathcal{O}(\epsilon^2)] \end{aligned}$$

Using the integral identity

$$g(x)\ \partial_x^n \delta(x - y) = (-1)^n \delta(x - y)\ \partial_x^n g(x) \tag{2.66}$$

for any smooth function g, one obtains

$$\frac{\delta E[h(x)]}{\delta h(y)} = A \int_0^L dx\, h_{xxxx}(x)\, \delta(x - y) = A h_{xxxx}(y), \tag{2.67}$$



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so that Eq. (2.64) becomes a linear fourth-order equation

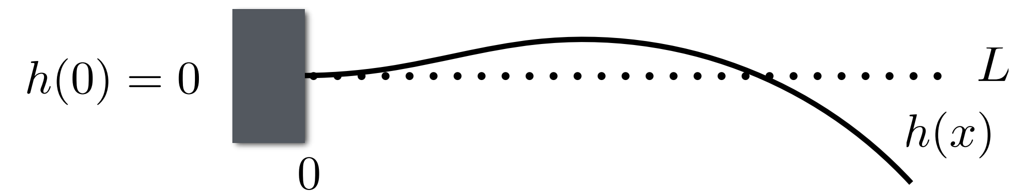
$$h_t = -\alpha h_{xxxx} \,, \qquad \alpha = \frac{A}{\eta}. \tag{2.68}$$

Inserting the ansatz

$$h = e^{-t/\tau}\phi(x) \,, \qquad h_t = -\frac{1}{\tau} e^{-t/\tau}\phi \,, \qquad h_{xxxx} = e^{-t/\tau}\phi_{xxxx}, \tag{2.69}$$

gives the eigenvalue problem

$$\frac{1}{\tau\alpha}\phi = \phi_{xxxx}. \tag{2.70}$$



Eigenvalue problem

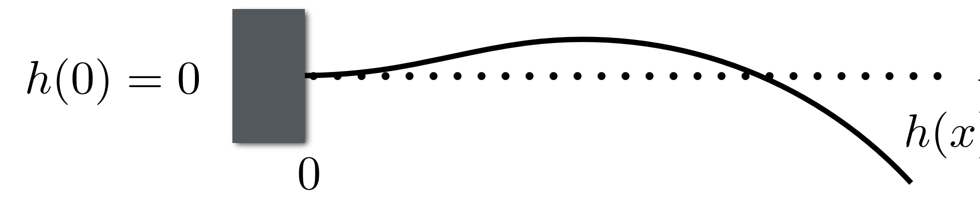
$$\frac{1}{\tau\alpha}\phi = \phi_{xxxx}. \tag{2.70}$$

for the one-dimensional biharmonic operator $(\partial_x^2)^2$, which has the general solution

$$\phi(x) = B_1 \cosh(x/\lambda) + B_2 \sinh(x/\lambda) + B_3 \cos(x/\lambda) + B_4 \sin(x/\lambda) \tag{2.71a}$$

where

$$\lambda = (\alpha\tau)^{1/4}. \tag{2.71b}$$



Inserting the first two conditions into the last two, we obtain the linear system

$$0 = B_1[\cosh(L/\lambda) + \cos(L/\lambda)] + B_2[\sinh(L/\lambda) + \sin(L/\lambda)] \tag{2.73a}$$
$$0 = B_1[\sinh(L/\lambda) - \sin(L/\lambda)] + B_2[\cosh(L/\lambda) + \cos(L/\lambda)]. \tag{2.73b}$$

For nontrivial solutions to exist, we must have

$$0 = \det \begin{pmatrix} [\cosh(L/\lambda) + \cos(L/\lambda)] & [\sinh(L/\lambda) + \sin(L/\lambda)] \\ [\sinh(L/\lambda) - \sin(L/\lambda)] & [\cosh(L/\lambda) + \cos(L/\lambda)] \end{pmatrix} \tag{2.74}$$

which gives us the eigenvalue condition

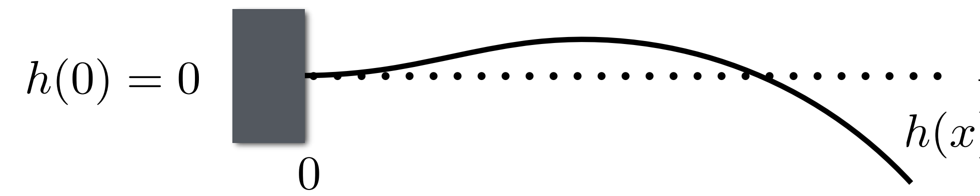
$$0 = \cosh(L/\lambda)\cos(L/\lambda) + 1. \tag{2.75}$$

This equation has solutions for discrete values $\lambda_n > 0$ that can be computed numerically, and one finds for the first few eigenvalues

$$\frac{L}{2\lambda_n} = \{0.94,\ 2.35,\ 3.93,\ 5.50,\ \ldots\}. \tag{2.76}$$

For comparison, for purely sinusoidal excitations of a harmonic string

$$L/\lambda_n \propto n.$$

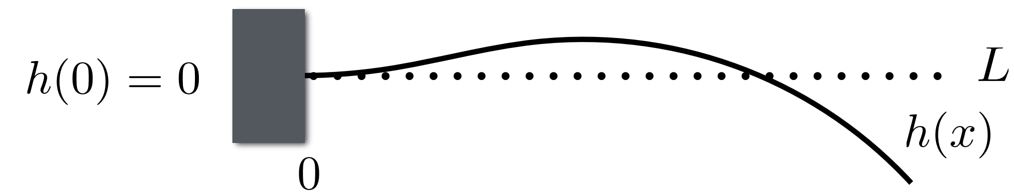


The full time-dependent solution can thus be written as

$$h(t,x) = \sum_{n=1}^{\infty} B_{1n}\, e^{-t/\tau_n} \Big\{ \cosh(x/\lambda_n) - \cos(x/\lambda_n) + \frac{\cos(L/\lambda_n) + \cosh(L/\lambda_n)}{\sin(L/\lambda_n) + \sinh(L/\lambda_n)} \left[\sin(x/\lambda_n) - \sinh(x/\lambda_n)\right] \Big\}, \quad (2.77)$$

Limit $\eta \to \infty$ or $t \to 0$

$$h(x) = \sum_{n=1}^{\infty} B_{1n} \Big\{ \cosh(x/\lambda_n) - \cos(x/\lambda_n) + \frac{\cos(L/\lambda_n) + \cosh(L/\lambda_n)}{\sin(L/\lambda_n) + \sinh(L/\lambda_n)} \left[\sin(x/\lambda_n) - \sinh(x/\lambda_n)\right] \Big\}$$



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Limit $\eta \to \infty$ or $t \to 0$

$$h(x) = \sum_{n=1}^{\infty} B_{1n} \Big\{ \cosh(x/\lambda_n) - \cos(x/\lambda_n) + \frac{\cos(L/\lambda_n) + \cosh(L/\lambda_n)}{\sin(L/\lambda_n) + \sinh(L/\lambda_n)} \left[\sin(x/\lambda_n) - \sinh(x/\lambda_n)\right] \Big\}$$

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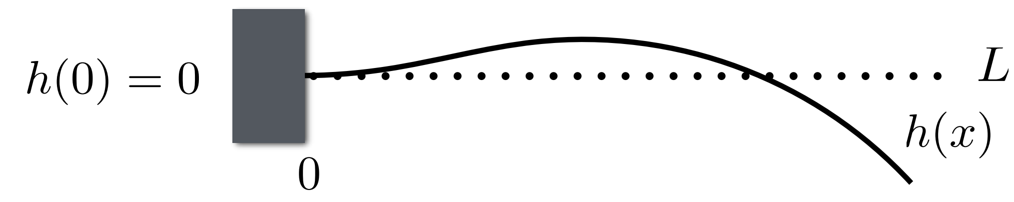

$$h(x) = \sum_{n=1}^{\infty} B_{1n} \Big\{ \cosh(x/\lambda_n) - \cos(x/\lambda_n) + \frac{\cos(L/\lambda_n) + \cosh(L/\lambda_n)}{\sin(L/\lambda_n) + \sinh(L/\lambda_n)} \left[\sin(x/\lambda_n) - \sinh(x/\lambda_n)\right] \Big\}$$

This expression can be inserted into (2.63), and after exploiting orthogonality of the biharmonic eigenfunctions

$$E \simeq \sum_{n=1} E_n \ , \qquad E_n = \frac{A}{2} \frac{L}{\lambda_n^4} B_n^2, \tag{2.79}$$

i.e., the energy per mode is proportional to the square of the amplitude, just as in the stretching case discussed in Sec. 2.3.2. It is therefore possible to compute thermal expectation values exactly from Gaussian integrals. In particular, from equipartition

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Actin in flow

PRL **108,** 038103 (2012) PHYSICAL REVIEW LETTERS week ending 20 JANUARY 2012

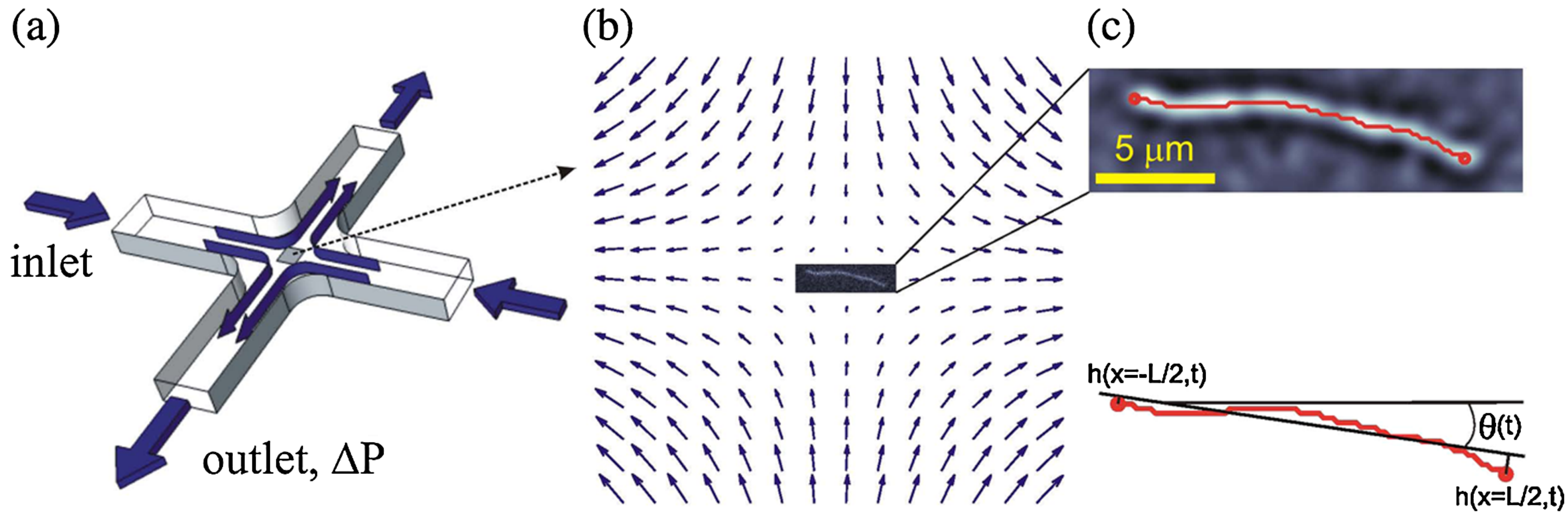

FIG. 1 (color online). Experimental setup. (a) Microfluidic cross-flow geometry controlled by a pressure difference ΔP between inlet and outlet branches. (b) Close-up of the velocity field near the stagnation point, showing a typical actin filament. (c) Raw contour (red) of an actin filament and definition of geometric quantities used in the analysis.

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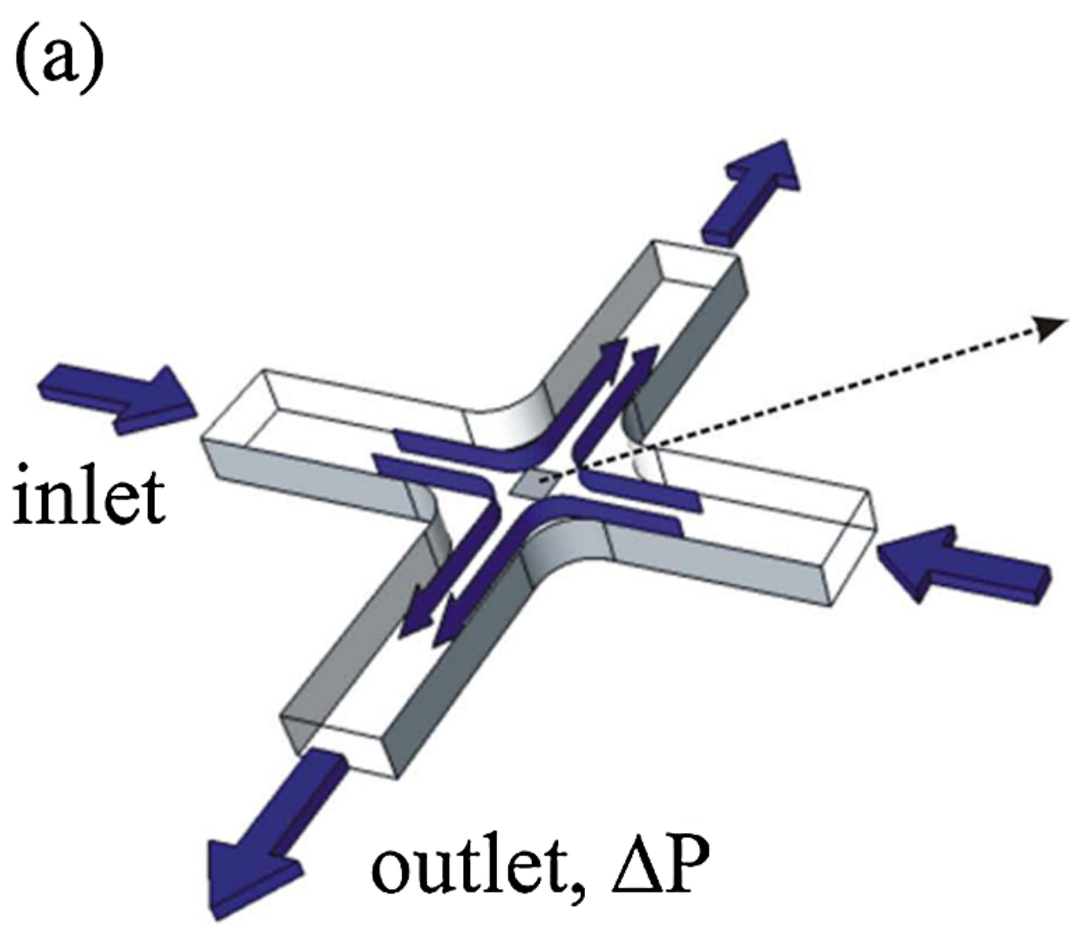
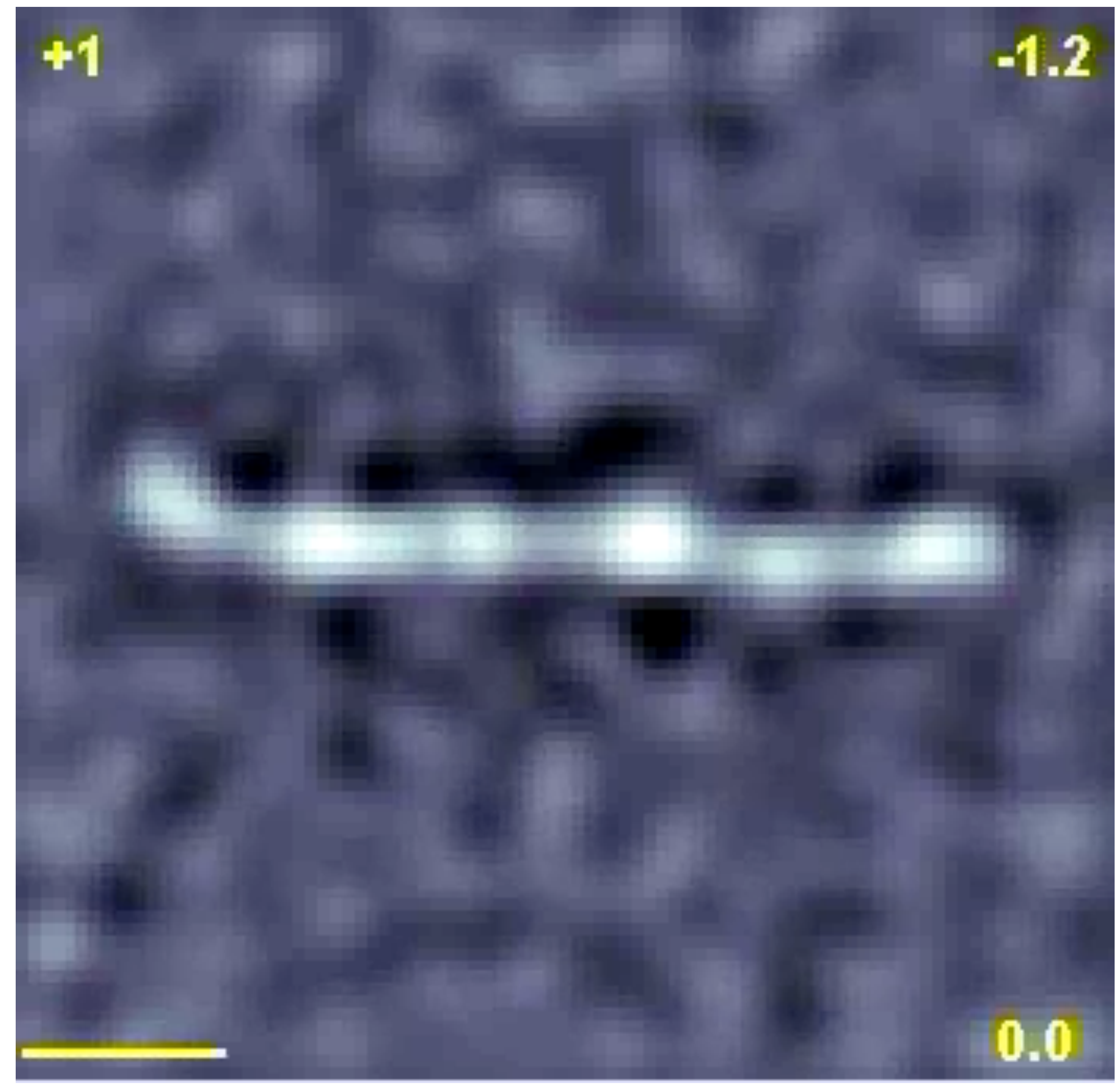
Actin in flow





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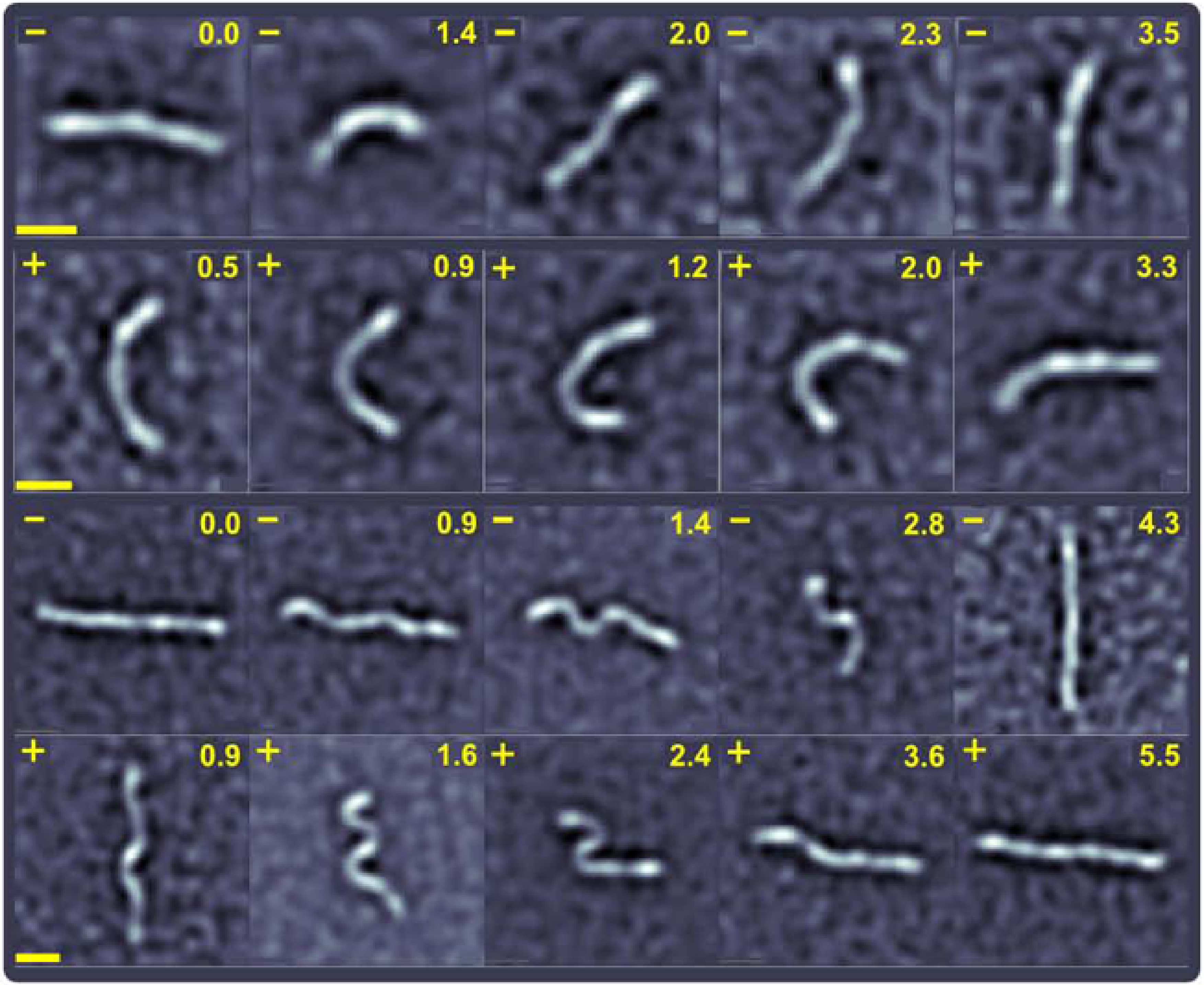
Actin in flow

(a)

(b)

(c)



Kantsler & Goldstein (2012) PRL

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Theory

$$\mathcal{E} = \frac{1}{2} \int_{-L/2}^{L/2} dx \{ A h_{xx}^2 + \sigma(x) h_x^2 \}, \tag{1}$$

where subscripts indicate differentiation. The *nonuniform* tension induced by the flow [19],

$$\sigma(x) = \frac{2\pi\mu\dot{\gamma}}{\ln(1/\epsilon^2 e)} (L^2/4 - x^2), \tag{2}$$

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Theory

of eigenfunctions $W^{(n)}$ (and eigenvalues λ_n) with boundary conditions $W_{xx}(\pm L/2) = W_{xxx}(\pm L/2) = 0$ [3,21]. Under the convenient rescaling $\xi = \pi x/L$, these obey

$$W^{(n)}_{4\xi} - \Sigma \partial_\xi[(\pi^2/4 - \xi^2) W^{(n)}_\xi] = \Lambda_n W^{(n)}. \qquad (3)$$

The eigenvalues $\Lambda_n = L^4 \lambda_n / \pi^4 A$ are functions of [22]

$$\Sigma = \frac{2\mu \dot{\gamma} L^4}{\pi^3 A \ln(1/\epsilon^2 e)}. \qquad (4)$$

When $\Sigma = 0$, the $W^{(n)}$ are eigenfunctions of the one-dimensional biharmonic equation

$$W_{\Sigma=0} = A \sin kx + B \sinh kx + D \cos kx + E \cosh kx. \quad (5)$$

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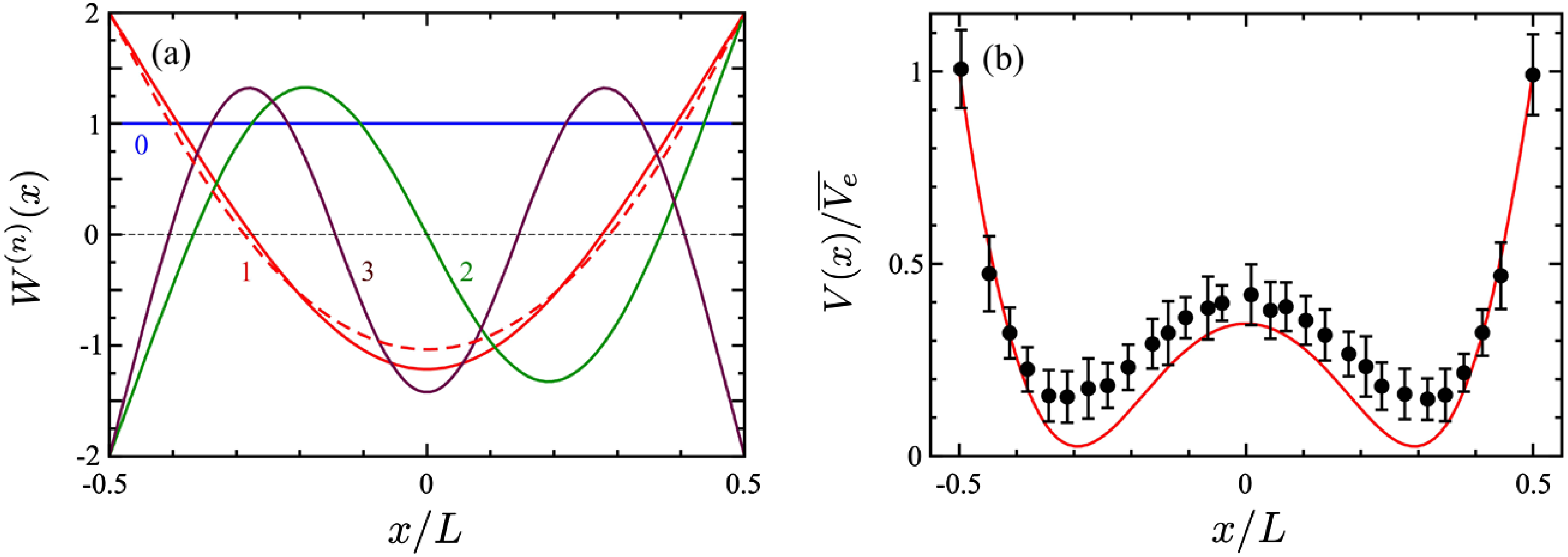
Theory vs. experiment

(and we assume they are normalized). Equipartition then yields $\langle a_m a_n \rangle = \delta_{mn} L^4/\pi^4 \ell_p \Lambda_n$, and the local variance $V(x) = \langle [h(x) - \bar{h}]^2 \rangle$ is

$$V(x;\Sigma) = \frac{L^3}{\ell_p \pi^4} \sum_{n=1}^{\infty} \frac{W^{(n)}(x)^2}{\Lambda_n(\Sigma)}.$$



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