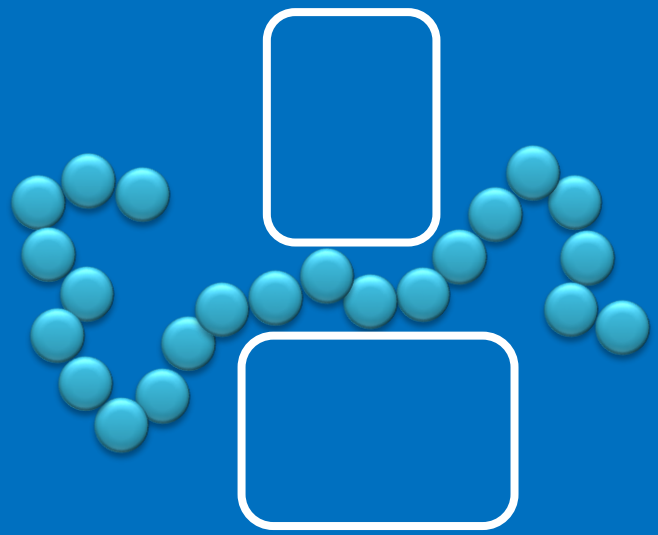
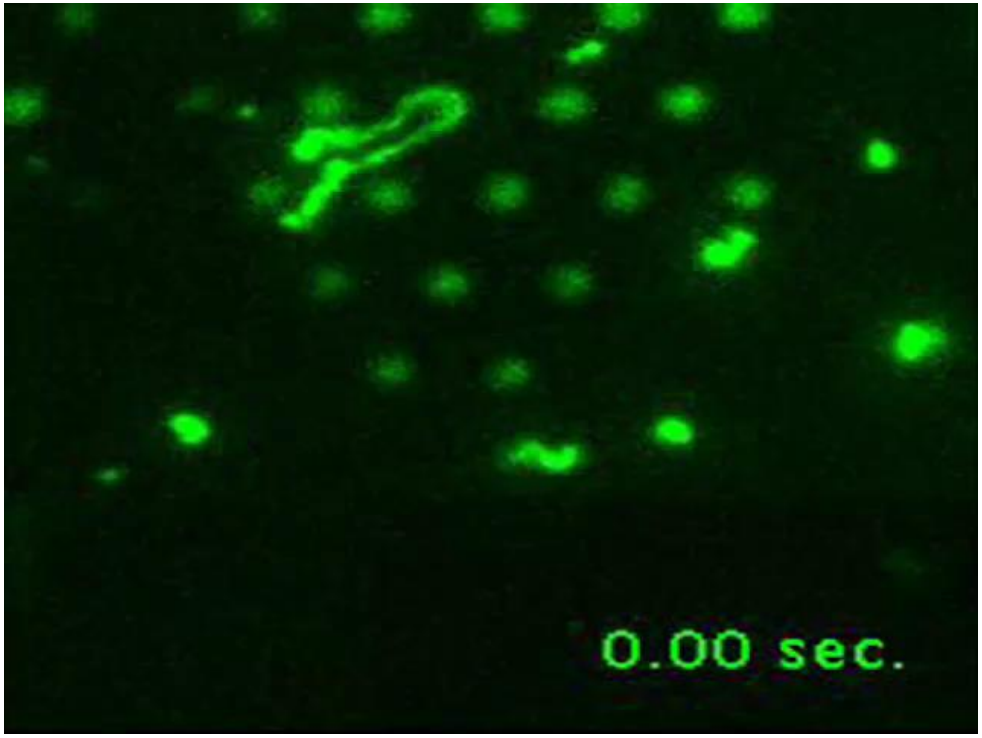
Chemical Potential Formalism for Entropic Effects in Confined Polymers

Cheng-Hung Chang 張正宏

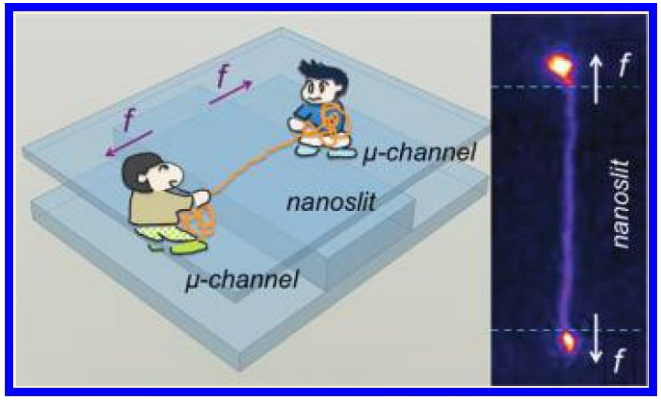
Institute of Physics,
National Chaio Tung university
Taiwan



Experimental motivations

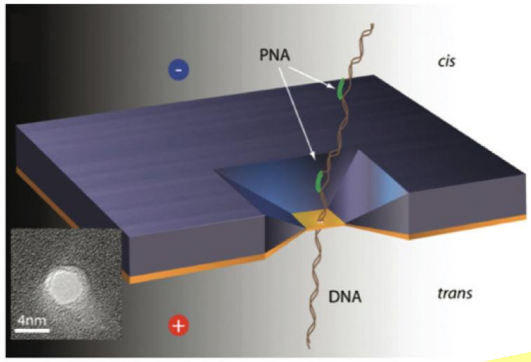


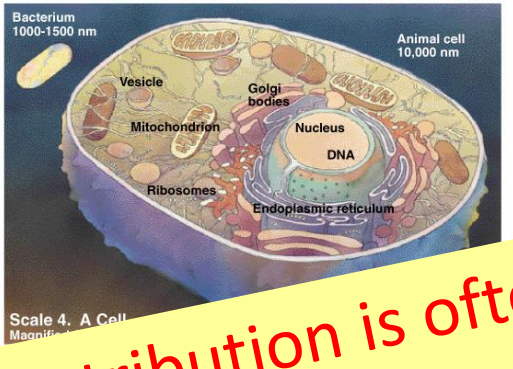
A DNA is pulled into and escapes from a nanoslit. Chia-Fu Chou's lab (Academia Sinica, Taiwan)

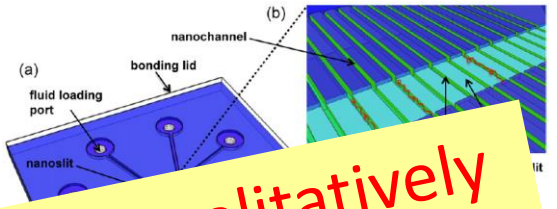


Both tug-of-war and recoiling processes are caused by entropic forces.

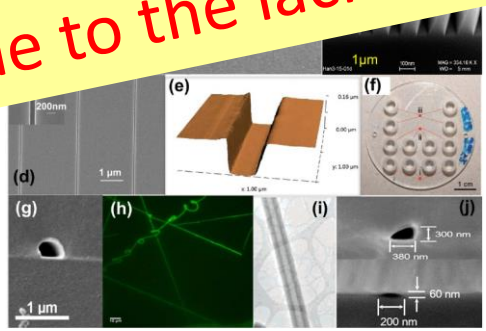
The entropic effect for confined polymers

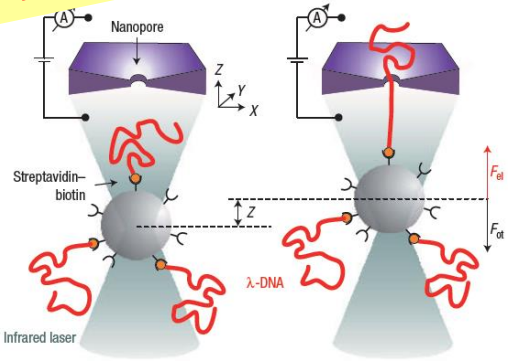


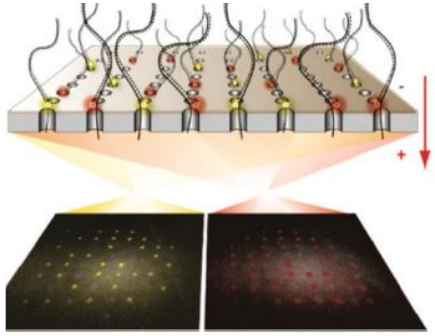


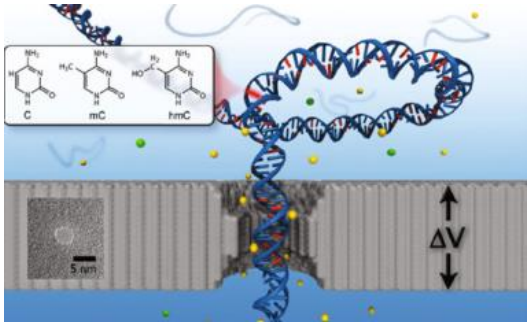


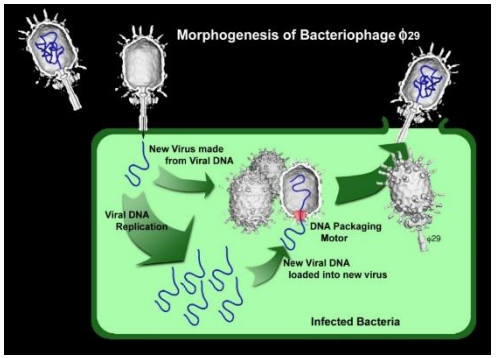
RNA











How much is its contribution is often only qualitatively reported, due to the lack of a simple method.

Experiments for entropic forces

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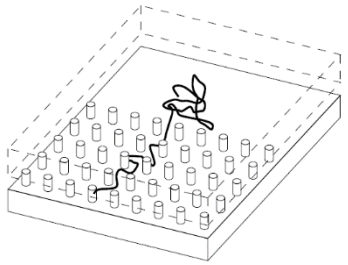

≈ 0.04 pN

Confinement-Induced Entropic Recoil of Single DNA M… …tructure

S. W. P. Tu…

School of A…

Inferred from empirical friction forces or polymer extension

No theoretical justifications yet.

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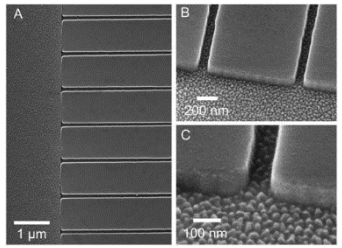
Conformation… …DNA Molecules U… …ng Entropically I… …ion in Nanocha…

J. T. Mannion, C. H. R…

School of Applied an…

Goal:

- propose a simple approach
- justify experimental values



≈ 0.22 pN

NANO LETT… Letter

pubs.acs.org/NanoLett

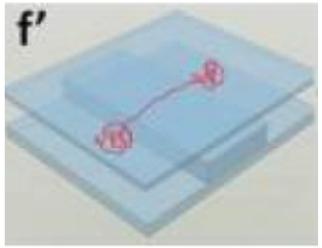
Entropy-Driven Single Molecule Tug-of-War of DNA at Micro–Nanofluidic Interfaces

Jia-Wei Yeh,[†,‡,¶] Alessandro Taloni,[‡,#,¶] Yeng-Long Chen,[†,‡,⊥] and Chia-Fu Chou*[,‡,§,∥]

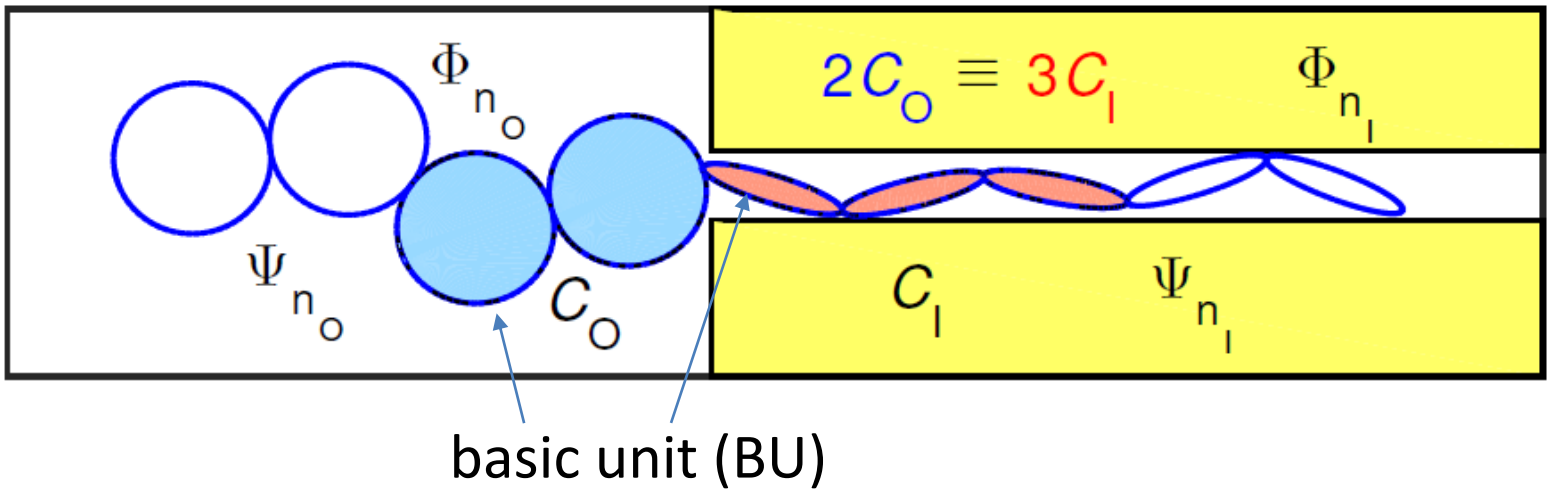
[†]Department of Physics, National Taiwan University, Taipei, Taiwan

[‡]Institute of Physics, [§]Research Center for Applied Sciences, and [∥]Genomics Research Center, Academia Sinica, Taipei, Taiwan

[⊥]Department of Chemical Engineering, National Tsing-Hua University, Hsinchu, Taiwan

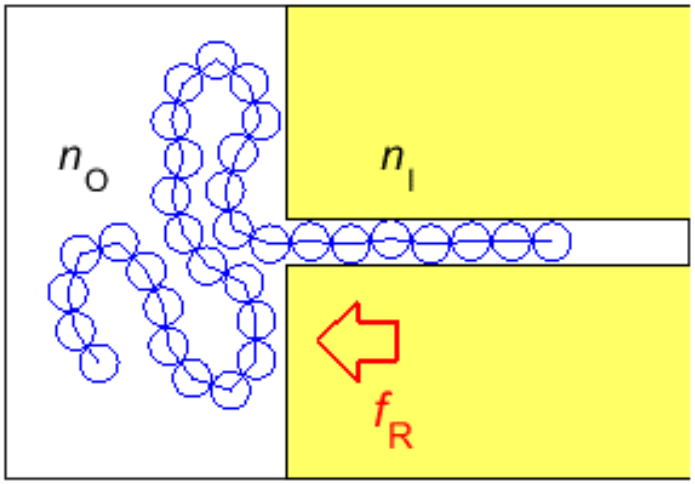


≈ 0.17 ~ 0.51 pN



	Outside the channel	Inside the channel
coarse-grained BU	C_O	C_I
number of BU	n_O	n_I
configuration number of BU	Ω_{n_O}	Ω_{n_I}
excess configuration number caused by adding an extra BU outside/inside the channel	$\Phi_{n_O} = \frac{\Omega_{n_O+1}}{\Omega_{n_O}}$	$\Phi_{n_I} = \frac{\Omega_{n_I+1}}{\Omega_{n_I}}$

Entropic recoiling force



If $C_{\mathrm{I}} = C_{\mathrm{O}}$

Entropic free energy

$$-\tilde{T}\mathrm{S} = -k_B\tilde{T}\ln\left(\Omega_{n_{\mathrm{I}}}\Omega_{n_{\mathrm{O}}}\right)$$

k_{B} = Boltzmann's constant

$\tilde{T}$ = Kelvin temperature

The entropic recoiling force describes the tendency of a chain to escape from a channel,

$$\tilde{f}_R = \frac{-\tilde{T}\Delta S}{l} = \left(\frac{k_{\mathrm{B}}\tilde{T}}{l}\right)\ln\left(\frac{\Omega_{n_{\mathrm{I}}-1}\Omega_{n_{\mathrm{O}}+1}}{\Omega_{n_I}\Omega_{n_O}}\right), \qquad (1)$$

when the chain is shifted a distance *l* (BU size) out of the channel.

A dimensionless version of force

$$f_R = \frac{\tilde{f}_R l}{\varepsilon} = T\ln\left(\frac{\Omega_{n_I-1}\Omega_{n_O+1}}{\Omega_{n_I}\Omega_{n_O}}\right) = T\ln\left(\frac{\Phi_{n_o}}{\Phi_{n_I-1}}\right) \qquad (2)$$

with $T = \tilde{T}/\tilde{T}_{\mathrm{room}}$ and $\varepsilon \equiv k_B\tilde{T}_{\mathrm{room}}$.

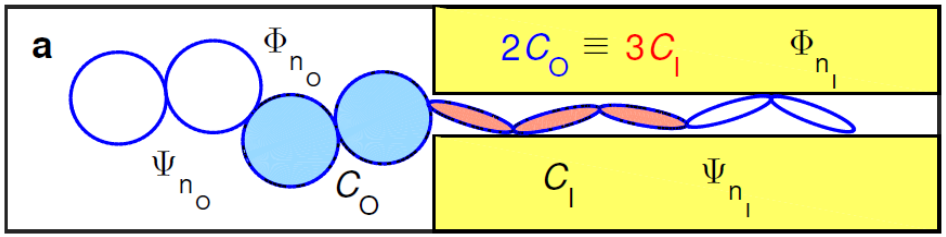
If f_R' is the force of a second chain of the same form as (2), then

$$f_R = f_R' + T\ln(\alpha_R) \qquad (3)$$

with $\alpha_R \equiv \dfrac{\Phi'_{n_I-1}\Phi_{n_O}}{\Phi_{n_I-1}\Phi'_{n_O}}$.

If $C_{\mathrm{I}} \neq C_{\mathrm{O}}$

$$f_R = T\ln\left(\frac{\left(\tilde{\Phi}_{n_O}\right)^{n_o}}{\left(\tilde{\Phi}_{n_I-1}\right)^{n_i}}\right) \quad (4)$$



$(n_o, n_i) = (2,3)$

$$\begin{cases} \tilde{\Phi}_{n_I} \equiv \dfrac{g_{n_I+1}\Omega_{n_I+1}}{g_{n_I}\Omega_{n_I}} = \Psi_{n_I}\Phi_{n_I} \\ \tilde{\Phi}_{n_O} \equiv \dfrac{g_{n_O+1}\Omega_{n_O+1}}{g_{n_O}\Omega_{n_O}} = \Psi_{n_O}\Phi_{n_O} \end{cases} \qquad \begin{cases} \Psi_{n_O} \equiv \dfrac{g_{n_O+1}}{g_{n_O}} \\ \Psi_{n_I} \equiv \dfrac{g_{n_I+1}}{g_{n_I}} \end{cases}$$

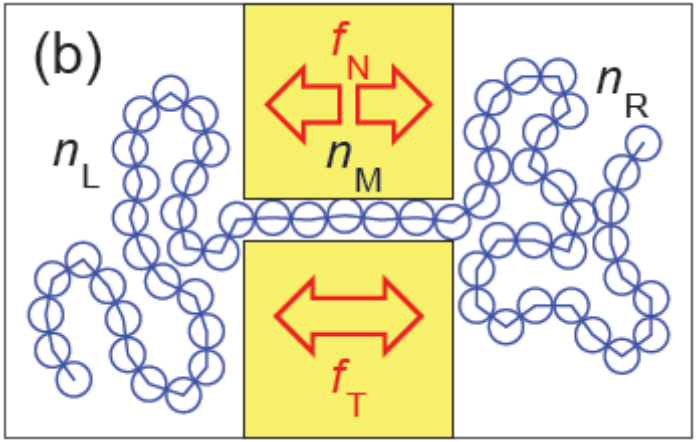
Two forces of this form are related by

difference btw C_{I} and C_{O}

$$f_R = f_R' + T\ln(\tilde{\alpha}_R) \qquad \tilde{\alpha}_R = G\bar{\alpha}_R = \gamma\alpha_R \qquad (5)$$

$$G \equiv \frac{g'_{n_I-1}{}^{n_i} g_{n_O}{}^{n_o}}{g_{n_I-1}{}^{n_i} g'_{n_O}{}^{n_o}} \qquad \bar{\alpha}_R \equiv \frac{\Phi'_{n_I-1}{}^{n_i}\Phi_{n_O}{}^{n_o}}{\Phi_{n_I-1}{}^{n_i}\Phi'_{n_O}{}^{n_o}} \qquad \gamma \equiv G\frac{\bar{\alpha}_R}{\alpha_R}.$$

Entropic drift & tension forces



The entropic drift force describes the tendency of the drift of the whole chain from the right to the left space,

$$f_D = T\ln\left(\frac{\Omega_{n_R-1}\Omega_{n_L+1}}{\Omega_{n_R}\Omega_{n_L}}\right) = T\ln\left(\frac{\Phi_{n_L}}{\Phi_{n_R-1}}\right). \qquad (6)$$

The entropic tension force is the tendency of polymer stretching inside the channel,

$$f_T = T\ln\left(\frac{\Omega_{n_L+1}\Omega_{n_I-1}\Omega_{n_R} + \Omega_{n_L}\Omega_{n_I-1}\Omega_{n_R+1}}{\Omega_{n_L}\Omega_{n_I}\Omega_{n_R}}\right)$$
$$= T\ln\left(\frac{\Phi_{n_L} + \Phi_{n_R}}{\Phi_{n_I-1}}\right). \qquad (7)$$

All these forces are related to a second force of the same type by

$$f_{\mathrm{X}} = f_{\mathrm{X}}^{\ominus} + T\ln(\alpha) \qquad \text{with } \alpha = \gamma\beta, \quad \mathrm{X} \in \{\mathrm{R}, \mathrm{D}, \mathrm{T}\}. \tag{8}$$

desired force

reference force

Upper & bottom bounds of forces (candidates for reference forces)

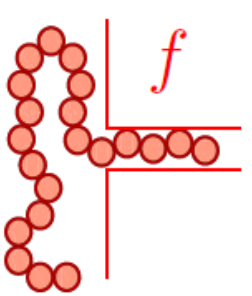
Force range	Strip (2D)	Tube (3D)	Slit (3D)
$\begin{bmatrix} \bar{f}_{\mathrm{R}}^{(\mathrm{NSC})} \\ \underline{f}_{\mathrm{R}}^{(\mathrm{NSC})} \end{bmatrix}$	$\begin{bmatrix} T\ln\left(\frac{2\pi l}{d}\right) \\ T\ln\left(\frac{\pi l}{d}\right) \end{bmatrix}$	$\begin{bmatrix} T\ln\left(\frac{16l^2}{d^2}\right) \\ T\ln\left(\frac{8l^2}{d^2}\right) \end{bmatrix}$	$\begin{bmatrix} T\ln\left(\frac{2l_q}{d}\right) \\ T\ln\left(\frac{l_q}{d}\right) \end{bmatrix}$
$\begin{bmatrix} \bar{f}_{\mathrm{D}}^{(\mathrm{NSC})} \\ \underline{f}_{\mathrm{D}}^{(\mathrm{NSC})} \end{bmatrix}$	$\begin{bmatrix} T\ln 2 \\ -T\ln 2 \end{bmatrix}$	$\begin{bmatrix} T\ln 2 \\ -T\ln 2 \end{bmatrix}$	$\begin{bmatrix} T\ln 2 \\ -T\ln 2 \end{bmatrix}$
$\begin{bmatrix} \bar{f}_{\mathrm{T}}^{(\mathrm{NSC})} \\ \underline{f}_{\mathrm{T}}^{(\mathrm{NSC})} \end{bmatrix}$	$\begin{bmatrix} T\ln\left(\frac{4\pi l}{d}\right) \\ T\ln\left(\frac{2\pi l}{d}\right) \end{bmatrix}$	$\begin{bmatrix} T\ln\left(\frac{32l^2}{d^2}\right) \\ T\ln\left(\frac{16l^2}{d^2}\right) \end{bmatrix}$	$\begin{bmatrix} T\ln\left(\frac{4l_q}{d}\right) \\ T\ln\left(\frac{2l_q}{d}\right) \end{bmatrix}$

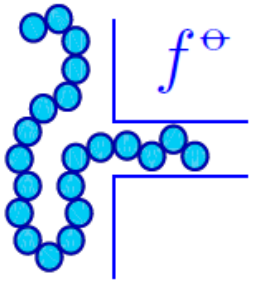
A correspondence between the entropic force for confined polymers & the chemical potential for solutions.

$$f = f^{\ominus} + T\ln(\alpha), \quad \alpha = \gamma\beta$$

$\gamma = 1$

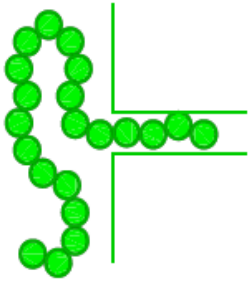
granular chain





inter-unit factor β

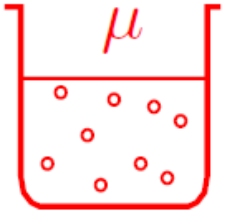
intra-unit factor γ

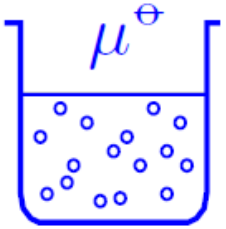


$$\mu = \mu^{\ominus} + R\tilde{T}\ln(a), \quad a = rc$$

$r = 1$

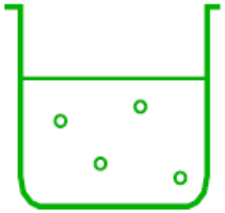
dilute solution



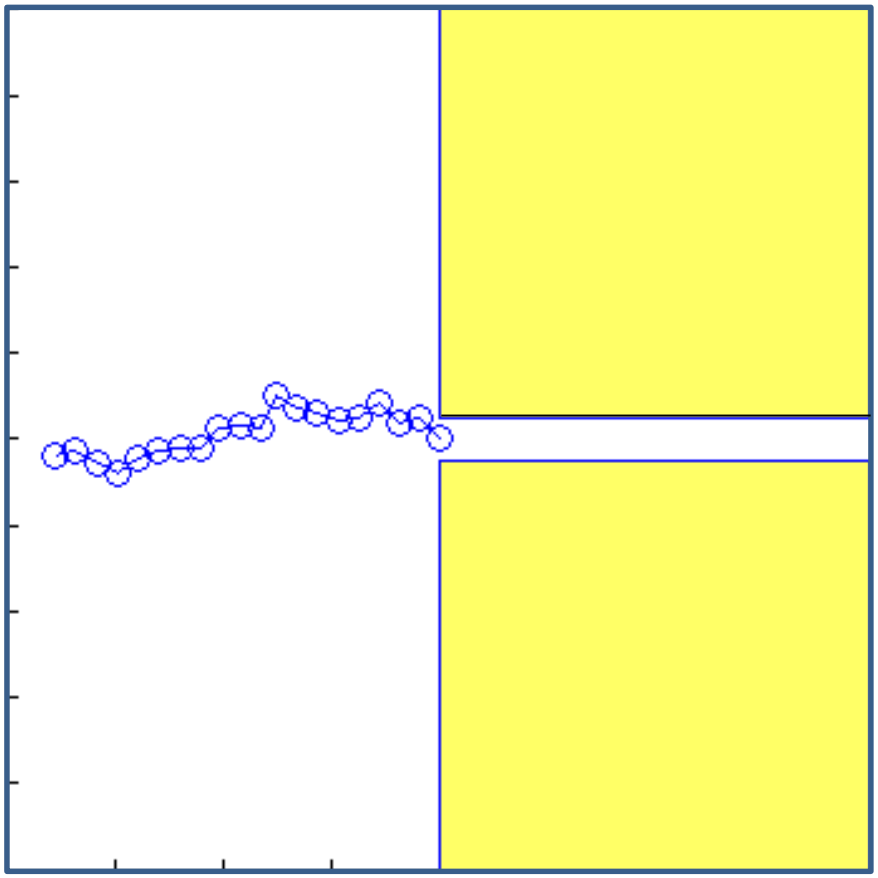


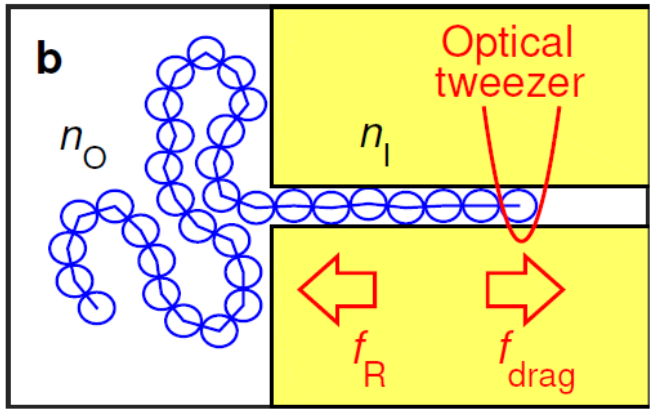
concentration c

activity coefficient r



Numerical experiments





Two ways to extract entropic forces:

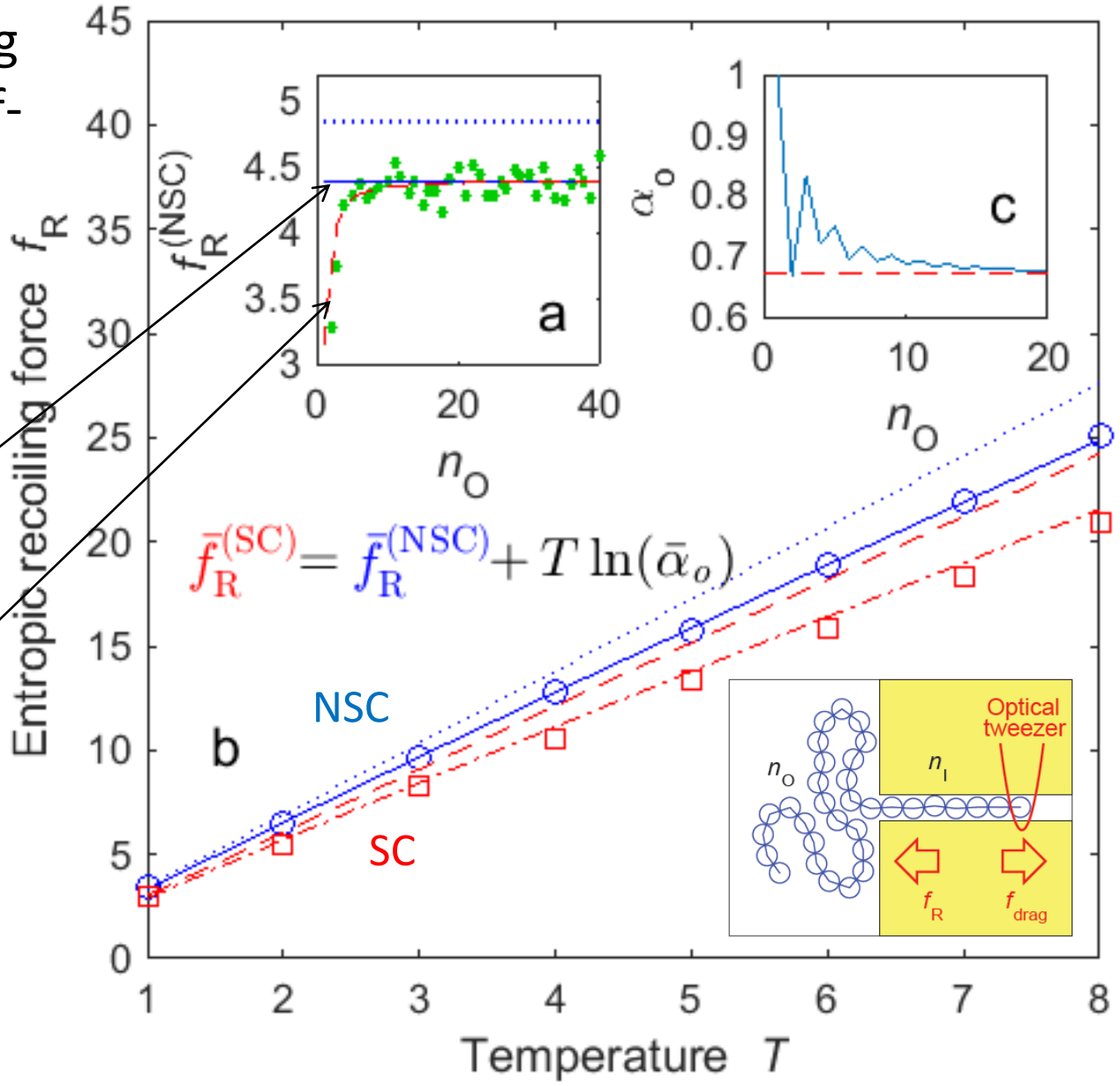
- Jarzynski equality
- Recursion formula (count microstates)

Force relation between different types of polymers

Pull non-self avoiding chains (NSC) and self-avoiding chains (SC) into a channel by an optical tweezer.

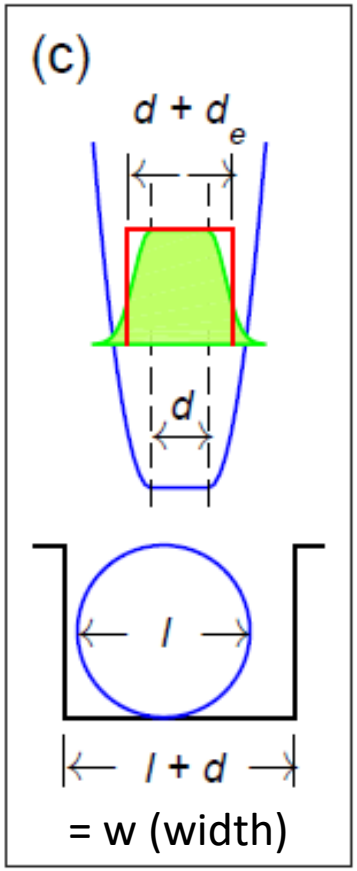
Recursion formula

Jarzynski equality



⊡ ⊙ exper. (JE)
--- theor. (RF)

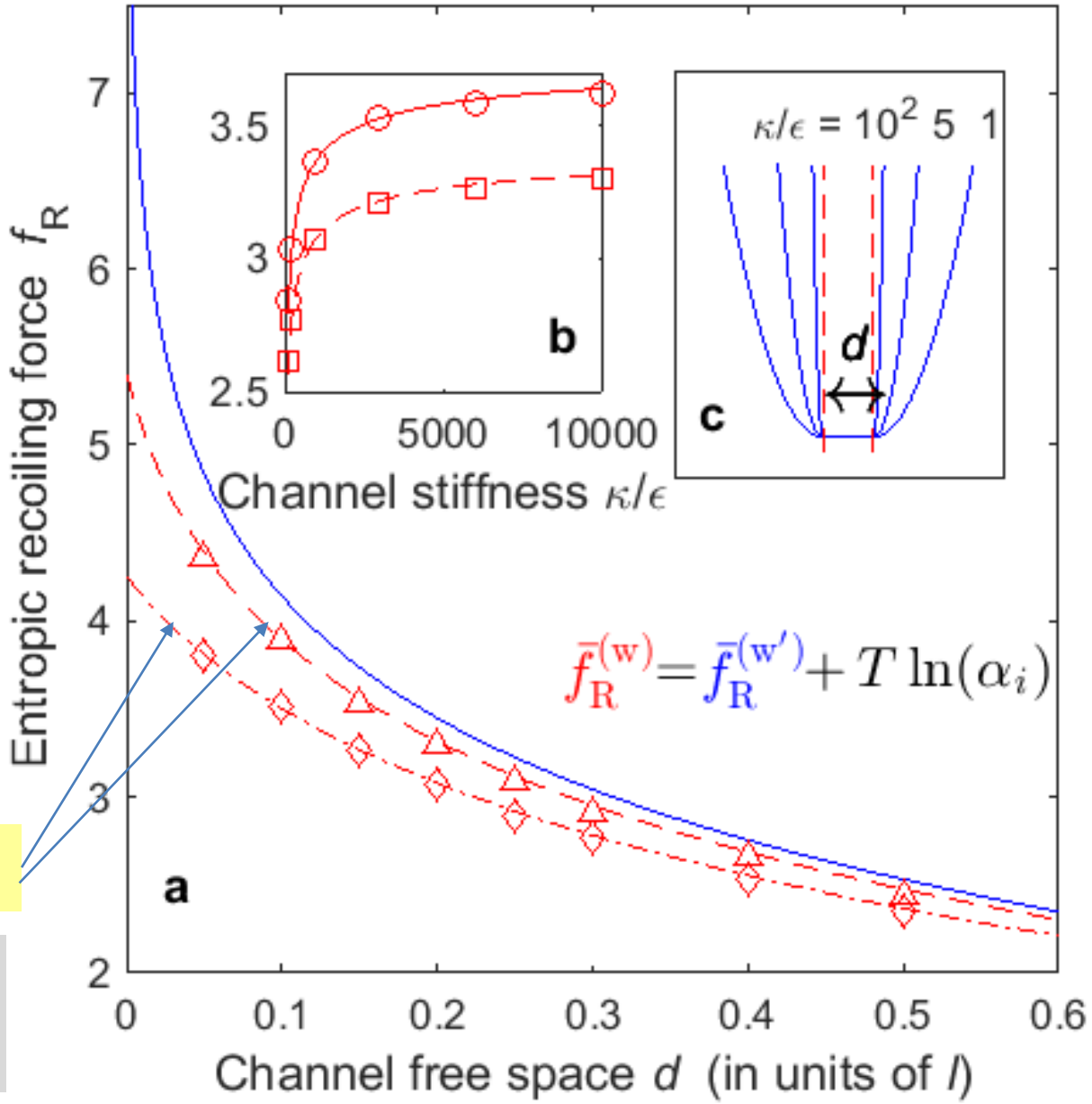
Force relation btw different channel widths & stiffnesses



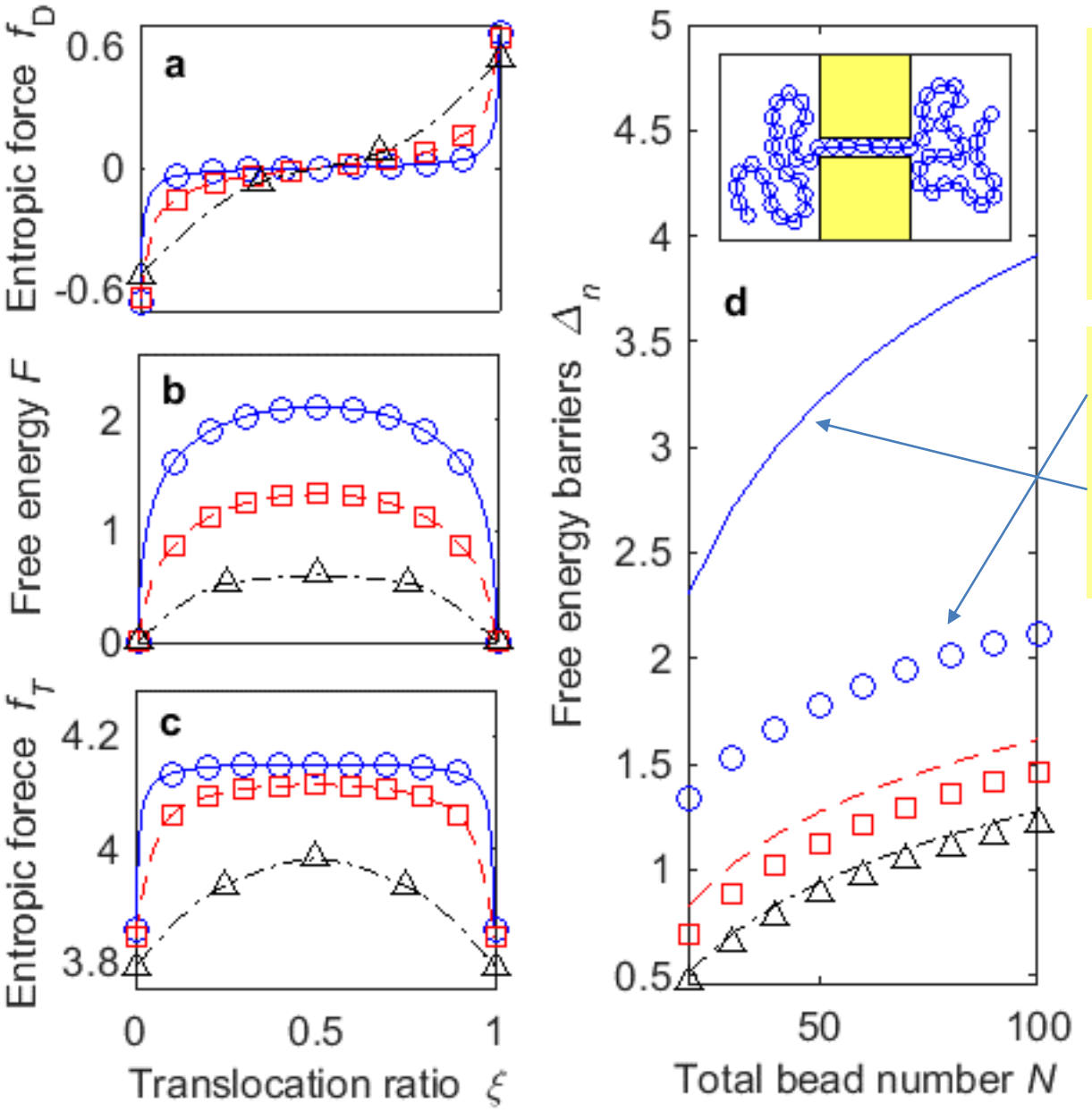
different stiffnesses

Δ ◊ exper. (JE)

_ _ _._._ theor. (RF)



Entropic drift & tension forces of tug-of-war



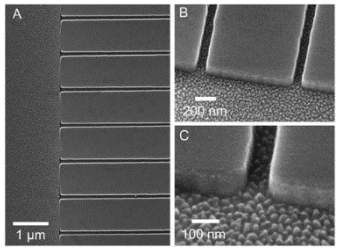
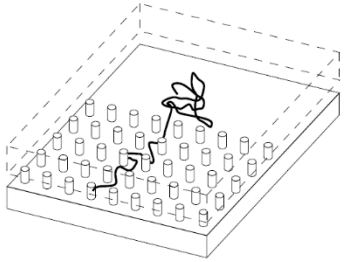
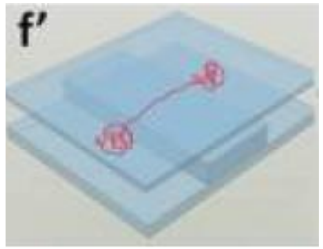
Entropic forces calculated by the RF coincide with our analytical formulas.

Our study reveals the overestimated traditional scaling approach.

In a, b, c, monomer number outside the channel N = **4**, **20**, **100**, $\xi = n_L / (N - n_l)$.

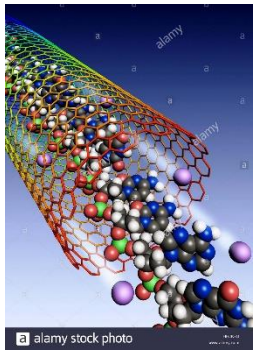
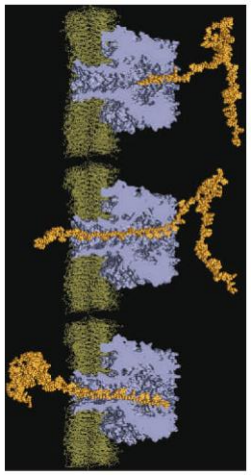
Applications

Comparison with existing experiments

experiments	Polymers & channel	f_R^{exp} (pN)	f_R^{theor} (pN)
	A dsDNA recoiling from a nano channel 90 nm wide, 100 nm deep. (Biophysical J.) Modeled by a strip of width 110 nm.	≈ 0.22	≈ 0.18
	A dsDNA recoiling from an array of nanopillars 35 nm in diameter with a center-to-center spacing of 160 nm, free space width 125 nm (Phys. Rev. Lett.) Modeled by a strip of width 125 nm.	≈ 0.04	≈ 0.12
	A dsDNA undergoing (i) a tug-of-war scenario and (ii) a recoiling-retraction scenario in a nanoslit of 110 nm in height (Nano Lett.) Modeled by a slit of height 110 nm.	≈ 0.30	≈ 0.28

A simple theory provides simultaneous consistency with several experimentally indirectly “measured” forces.

Predictions

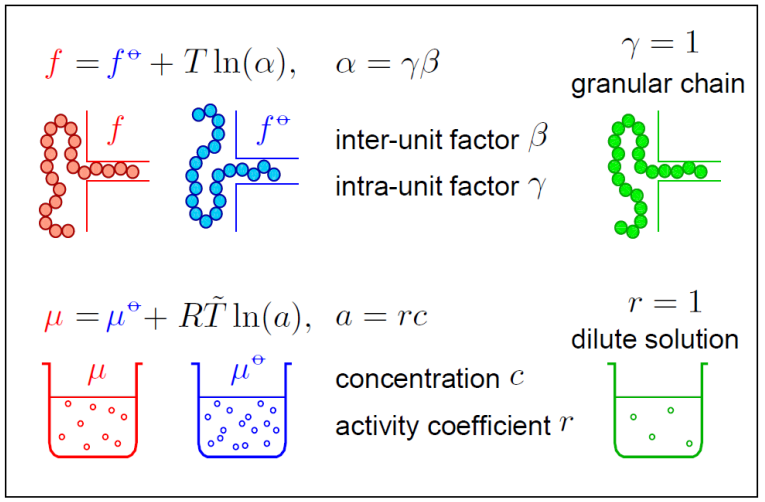
experiments	Polymers & channel	Entropic forces (pN)
	A ssDNA, partly confined in a 2D nanochannel or a 3D circular nanotube of width 1.6 nm. Modeled by an SC comprising beads of three nucleotide bases.	$f_R^{theor} \approx$ 11.32 (nanochannel) 21.76 (nanotube)
	A ssDNA oligomer threaded through an α-hemolysin (10 nm long, inner size 1.4 ~ 4.1 nm. Modeled by an NSC through a channel of the same width as the bead, with a hypothesized effective stiffness = $1 \sim 10^2$ pN/nm.	$f_T^{theor} \approx$ 1.47~14.09

General force scale: fN ~ pN

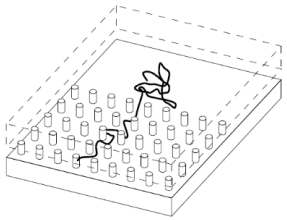
Upper bound seems to be ≈20 pN.

Summary

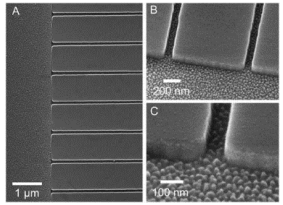
Theoretically
(mathematical equivalence)



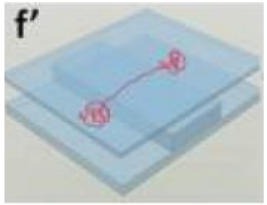
In practice
(justify pure entropic contributions in experimental measurements)



≈ 0.04 pN

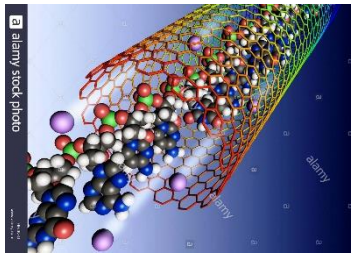


≈ 0.22 pN



≈ 0.17 ~ 0.51 pN

Upper bound of entropic forces in nature (≈20 pN)



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Hong-Qing Xie

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Chemical potential formalism for polymer entropic forces

Hong-Qing Xie[1] & Cheng-Hung Chang[1]