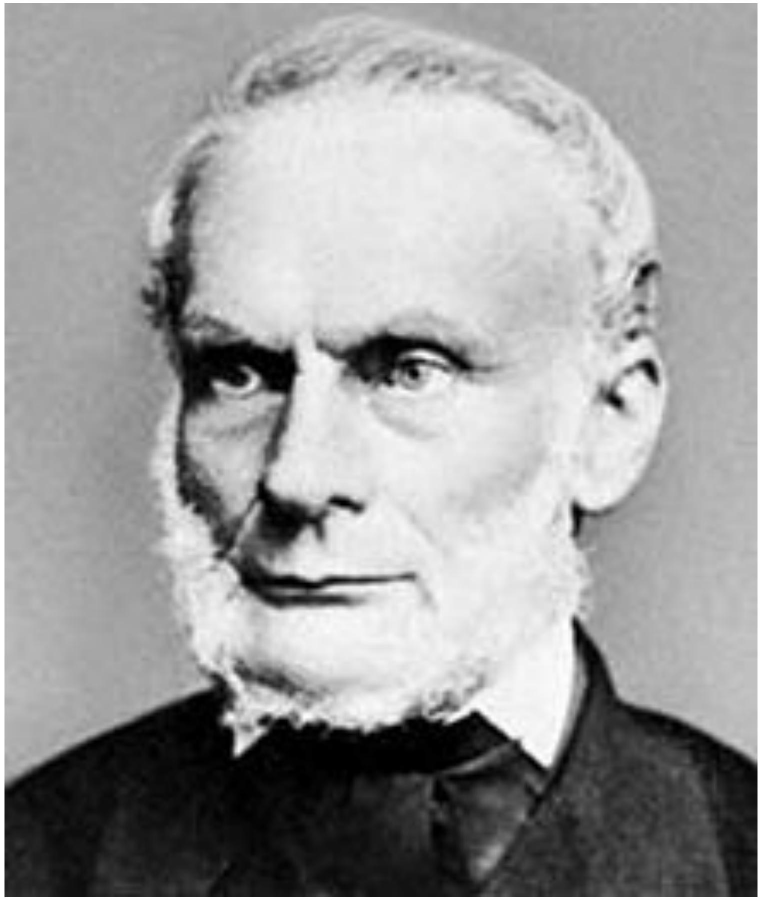
Entropy, temperature, free energy, and entropic forces

Chia-Fu Chou@2010

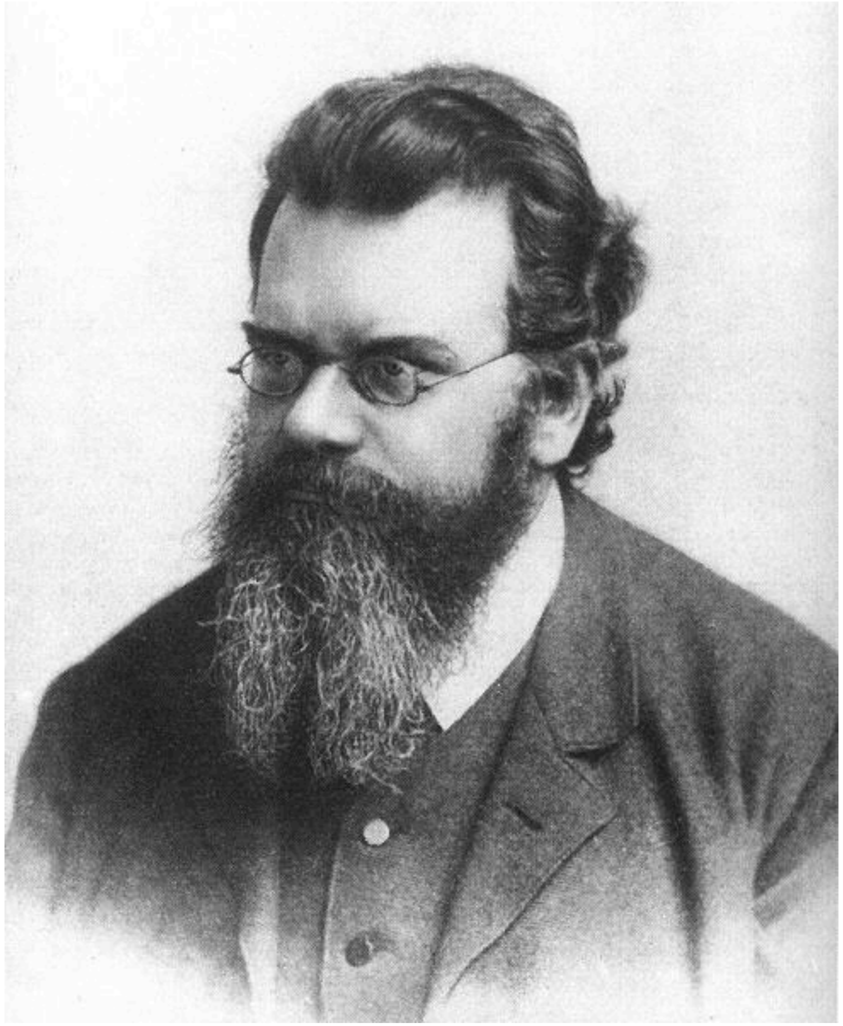
Rudolf Clausius, originator of the concept of entropy @ 1865



The term entropy was coined in 1865 by Rudolf Clausius based on the Greek εντροπία [entropía], a turning toward, from εν- [en-] (in) and τροπή [tropē] (turn, conversion).

Ice melting in a warm room is a common example of increasing entropy, described in 1862 by Rudolf Clausius as an increase in the desegregation of the molecules of the body of ice.

Ludwig Eduard Boltzmann (1844-1906)




S = k. log W
LVDWIG
BOLTZMANN
1844 - 1906
HENRIETTE
BOLTZMANN
1854 - 1938
DR PHIL. PAULA
BOLTZMANN
GEB. CHIARI
1891 - 1977
ARTHUR
BOLTZMANN
1881 - 1952
LVDWIG
BOLTZMANN
1925 - 1943
GEFALLEN BEI SMOLENSK

Laws of thermodynamics

0th law of thermodynamics: If two thermodynamic systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with each other.

1st law of thermodynamics: Energy can be neither created nor destroyed. It can only change forms.
In any process in an isolated system, the total energy remains the same.

$$dU = TdS - pdV$$

TdS=δQ and pdV=δW.

δQ=dU+δW

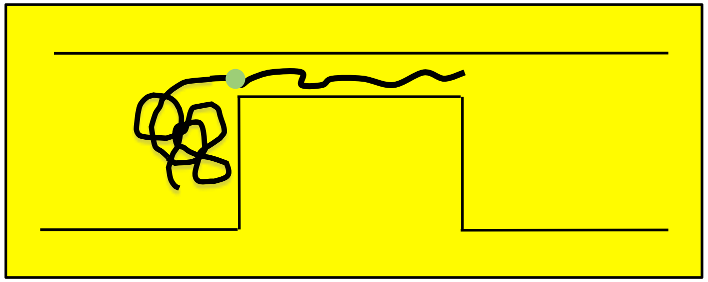
2nd law of thermodynamics: dS≥0

$$S = k_{\mathrm{B}} \ln \Omega \,.$$

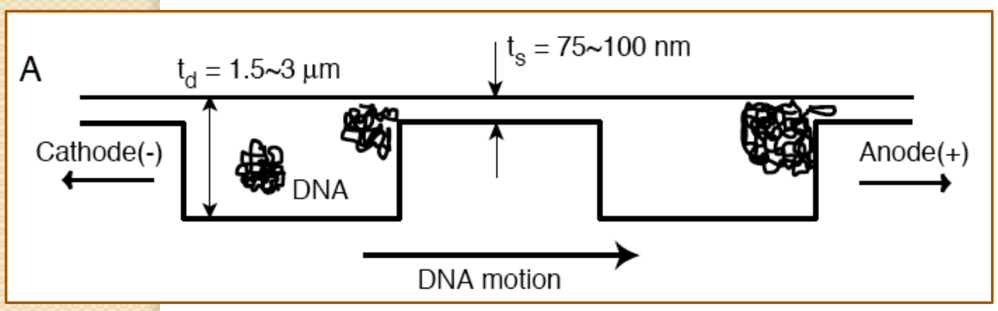
3rd law of thermodynamics: S → 0, as T → 0.

Micro- to Nanofluidic Interface

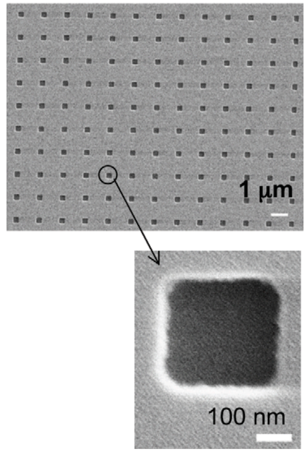
(1) Entropic barrier

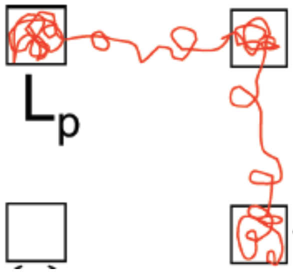


Nanoseparators
J. Han et al., Science 2000

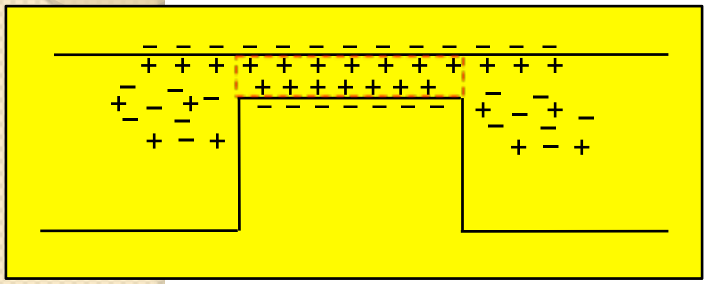


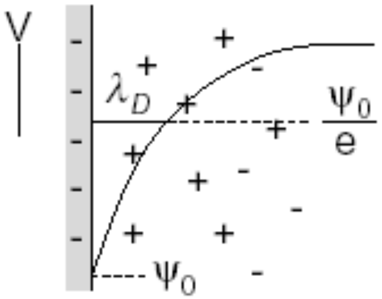
Digital DNA
Reisner et al., PNAS 2009





(2) Debye layer overlapping



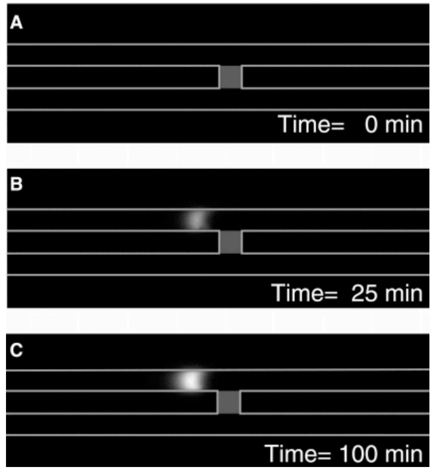


$$\lambda_D = \sqrt{\frac{\varepsilon RT}{2F^2 c}}$$

Conc / M	λ_D / nm
10^{-5}	100
10^{-4}	30
10^{-3}	10
10^{-2}	3
10^{-1}	1

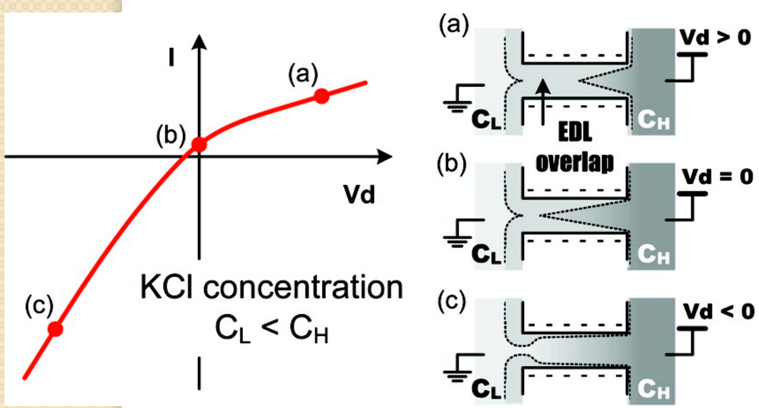
Nanoconcentrators

Wang et al., Anal. Chem. 2005



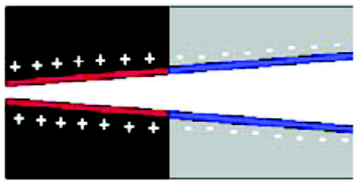
Rectified Ion Transport

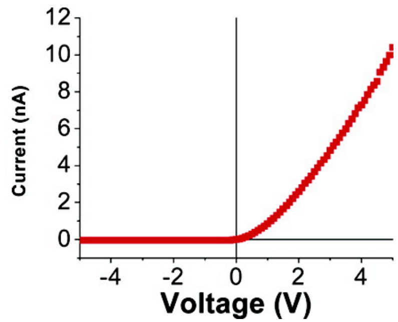
Cheng & Guo, Nano Lett. 2007



Nanofluidic diode

Vlassiouk and Siwy, Nano Lett. 2007

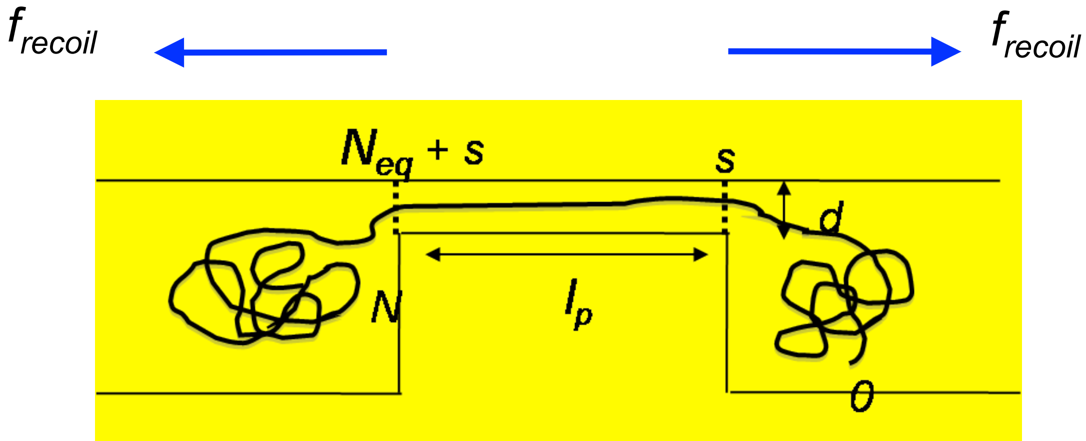




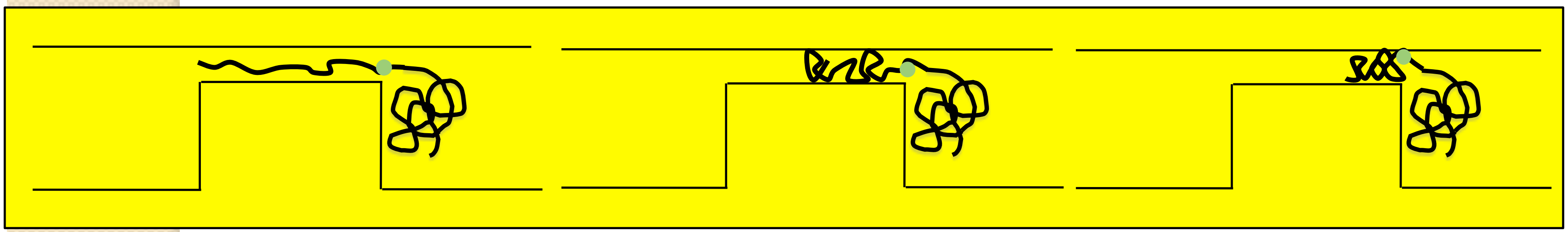
Single molecule tug-of-war of DNA

Understanding the entropic forces acting on the DNA

$$F = U - TS;\ f = -grad(F) = T\,grad(S)$$

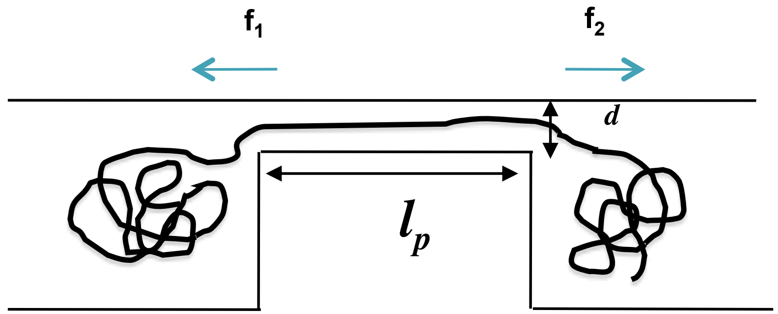


DNA retraction by entropic recoiling from nano- to microchannel



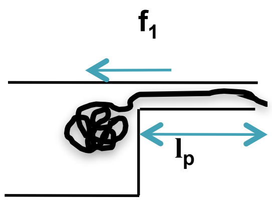
What is to be verified?

(1)



F	Free energy
l_p	projected length of polymer inside the channel
f	force

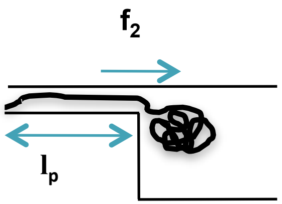
❖ **What do we expect?**



$$F(l_p) \propto l_p$$

(Burkhardt et al., J.Phys A, 1997)

(cylindrical tube diameter (D) << persistence length (P))



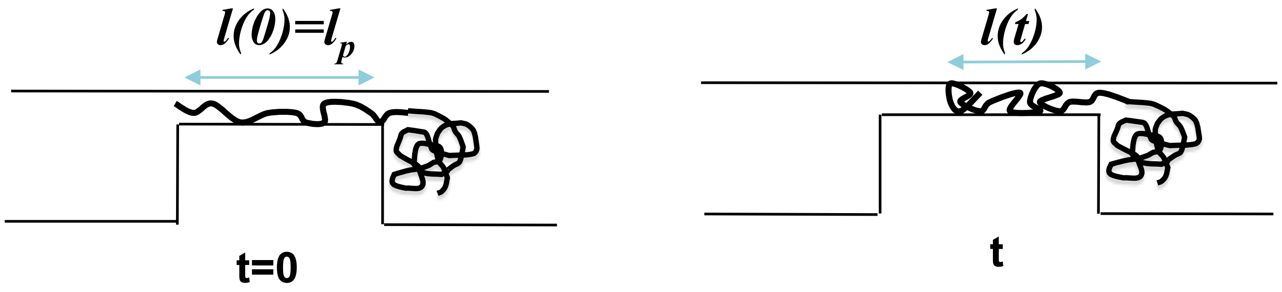
Recoiling force $f = dF/dl$

is l_p independence $f_1 \cong f_2$

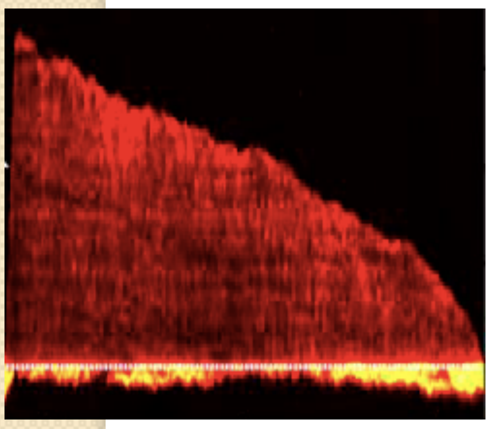
(Turner et al., PRL 2002)

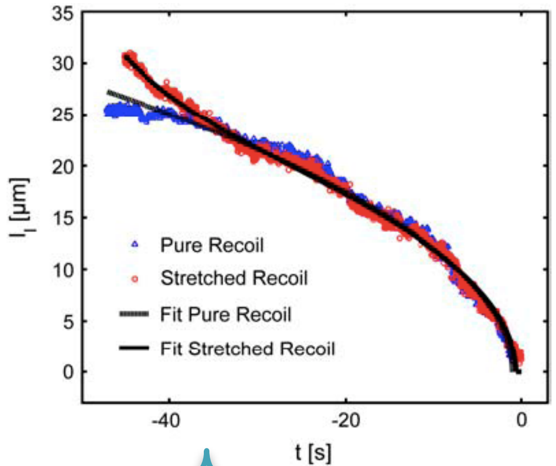
Motivation

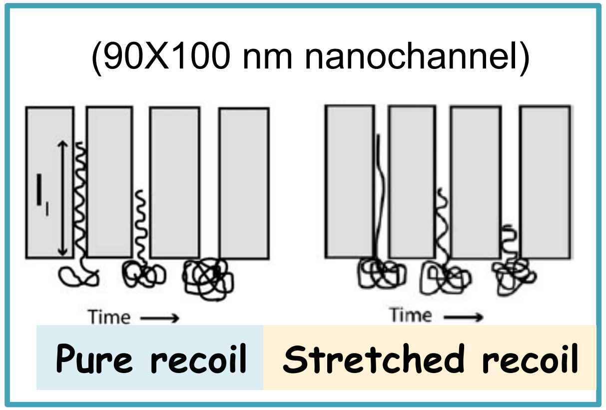
(2)



❖ What do we expect?







$$l(t) = \left[1 + \left(l_p\sqrt{\frac{\rho}{2 f t_f}} - 1\right)e^{-t/\tau}\right]\sqrt{-\frac{2f}{\rho}\left(t - t_f\right)}$$

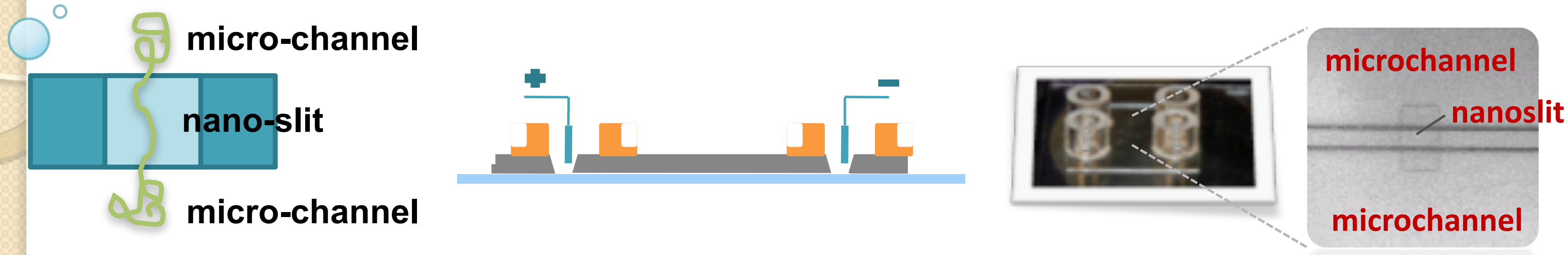
~ phenomenological formula.

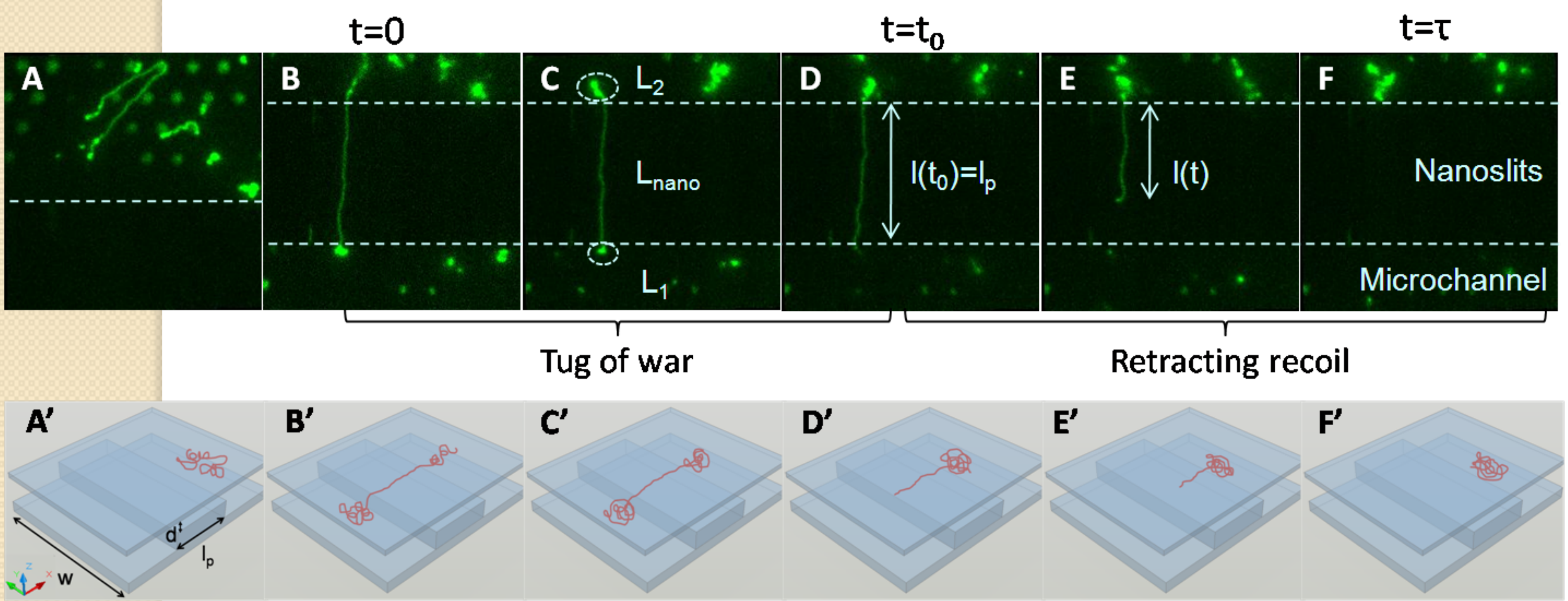
ρ	Drag coefficient per unit extended length
t_f	translocation time

Estimated recoiling force ~ 200 fN

(Mannion et al, Biophys. J.,90,4538 2006)

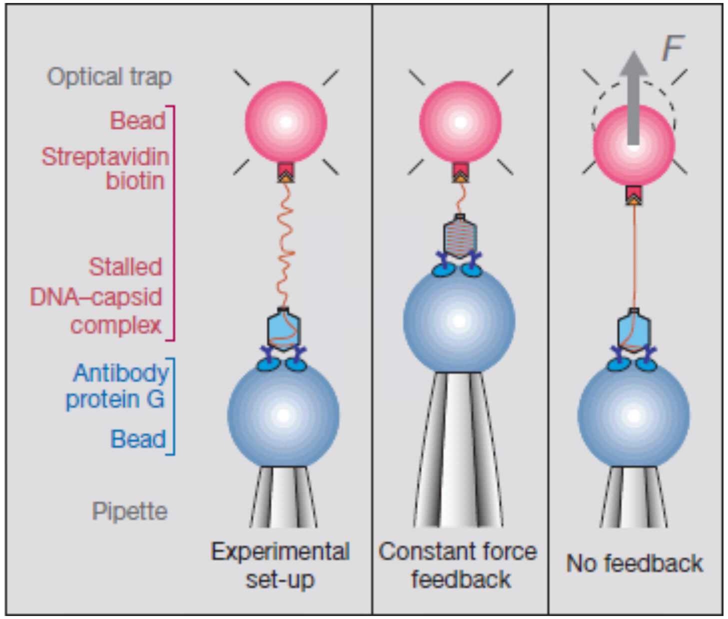
DNA tug-of-war through a nanoslit

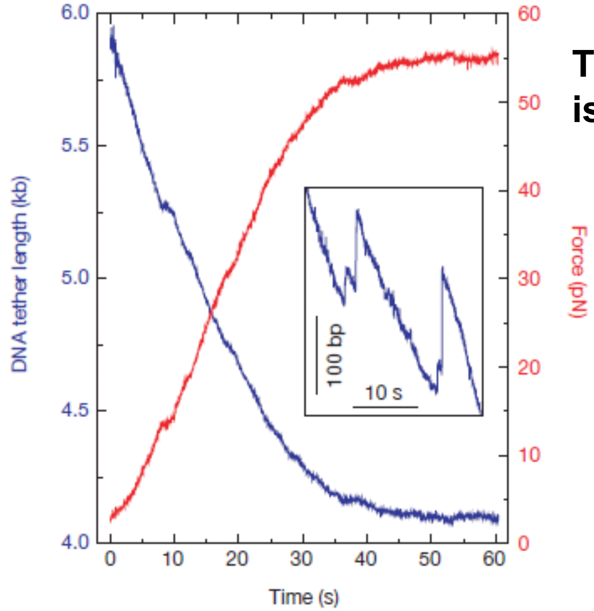




Discussion

Bacteriophage φ29 packages its 6.6 μm long, double-stranded DNA into 42 X 54 nm capsid.





The highest force is 55 pN.

There are *entropic*, *electrostatic* and *bending* energies of DNA which need to be overcomed to package the DNA to near-crystalline density.

Comparing to our results, the entropic recoiling force of 50 nm nanoslits is around 1 pN.

Smith *et al.*, Nature 413, 748 (2001)

Nanopore Single-molecule sequencing

Proc. Natl. Acad. Sci. USA
Vol. 93, pp. 13770–13773, November 1996
Biophysics

Characterization of individual polynucleotide molecules using a membrane channel

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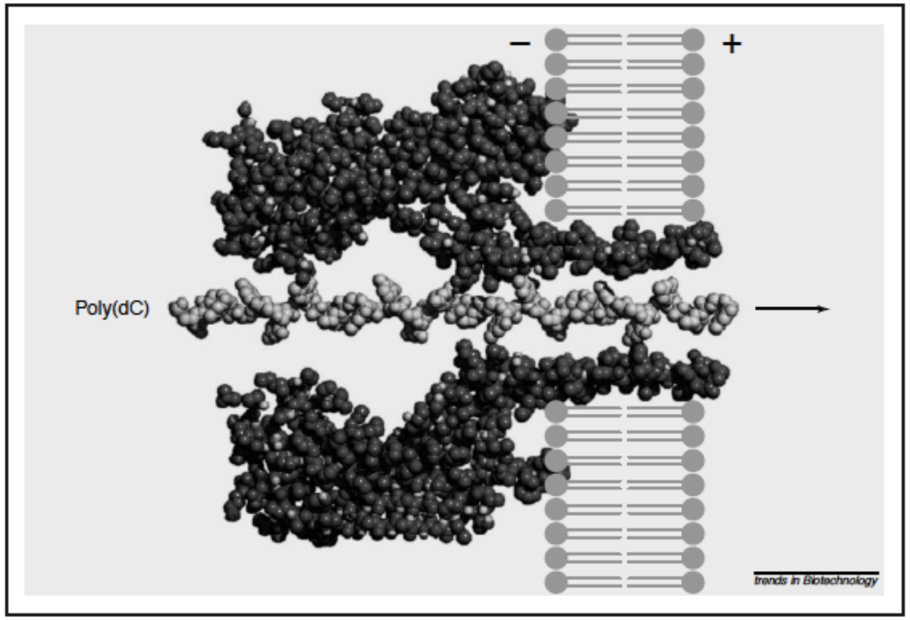
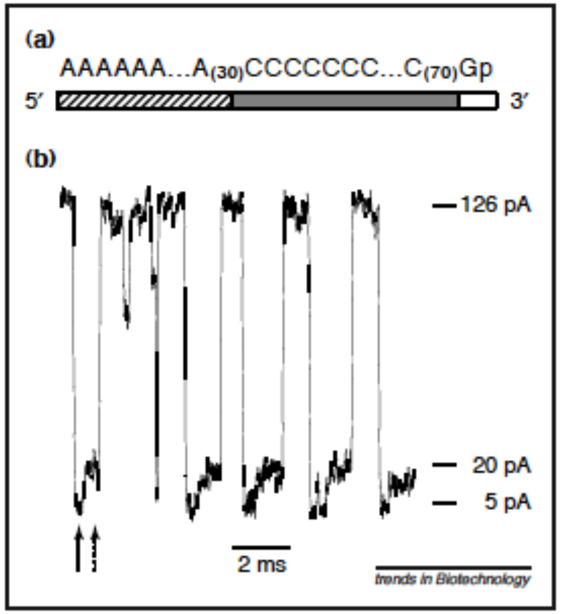
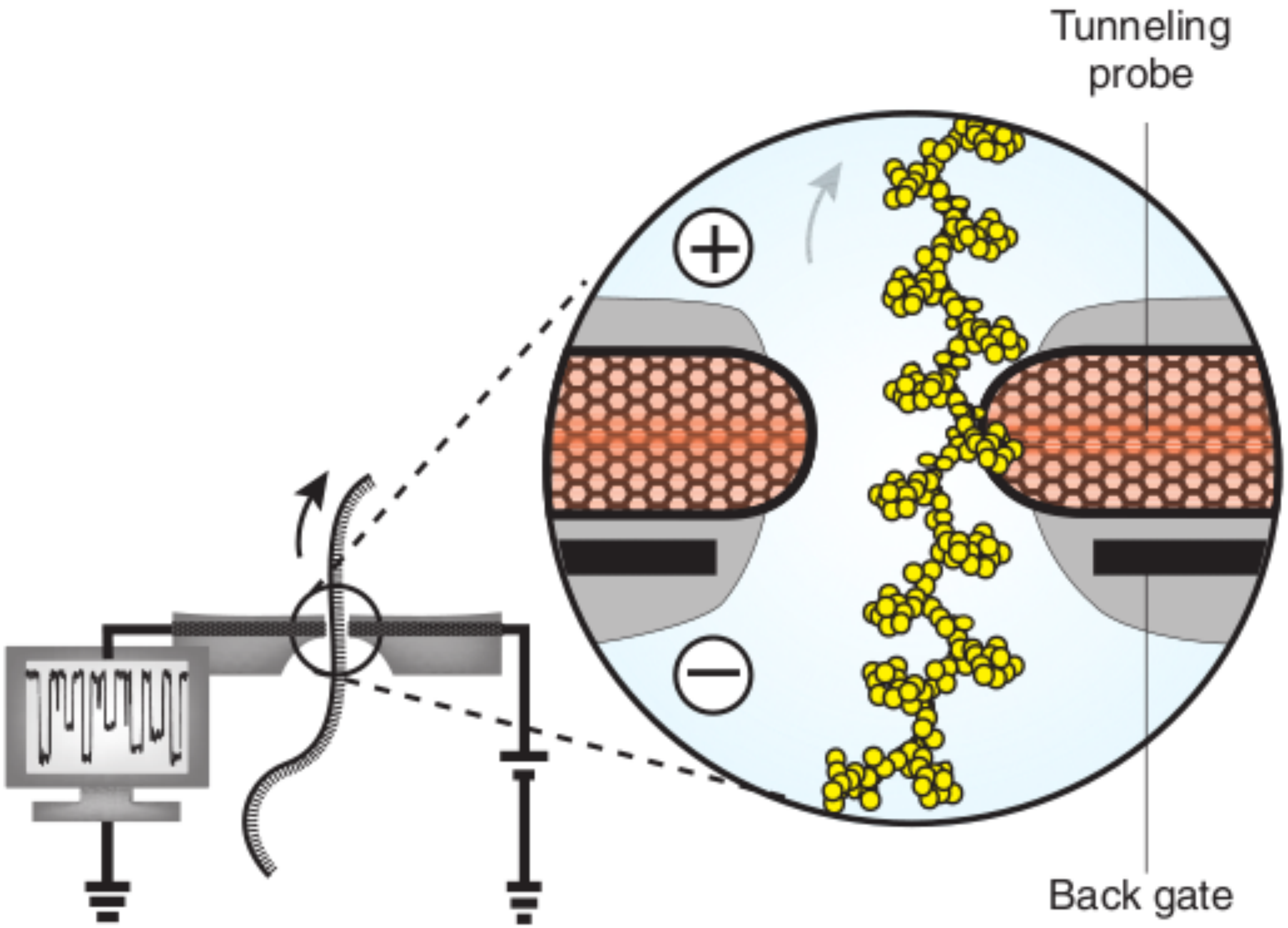
Contributed by Daniel Branton, September 5, 1996

A single α-hemolysin channel (Ø =2.5 nm) embedded in a lipid bilayer



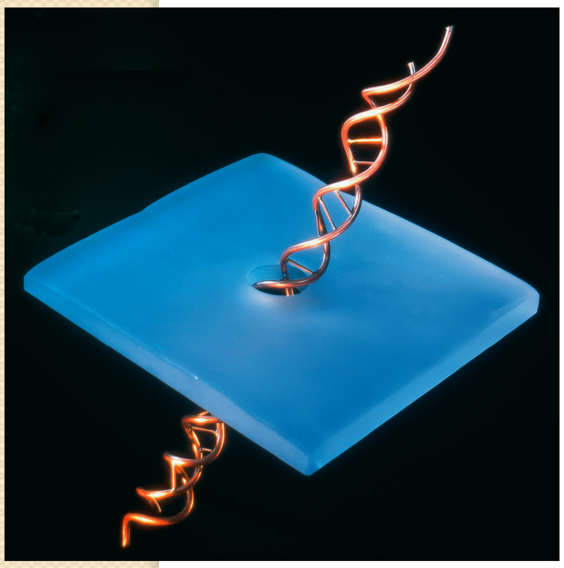


Solid State Nanopore DNA Sequencing

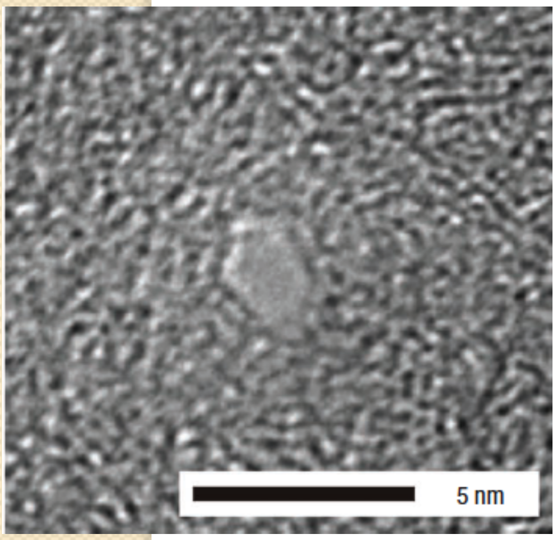


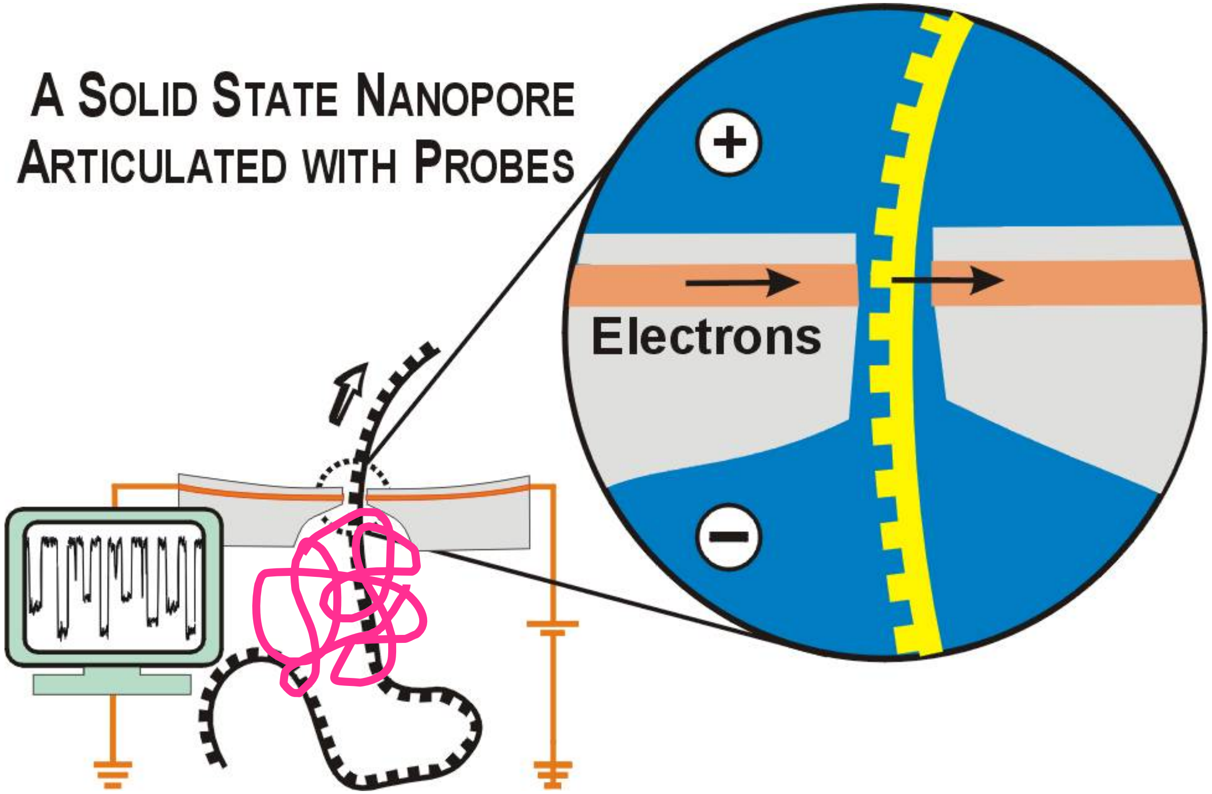
Nature Biotechnology 10, 1145 (2008)

Nanopore single-molecule sequencing



Dekker group, Nat. Mater. 2003





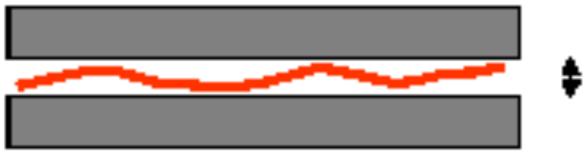
D. Branton, J. Golovchenko, Harvard

Polymer dynamics in confined nanoenvironment

DNA is stretched in small channels because the energy to form a loop is greater than kT

$$W_{loop} = \pi k_B T \frac{L_p}{R}$$

$2R = 2\mu m$ $\quad W_{loop} \approx 0.15 k_B T < k_B T$



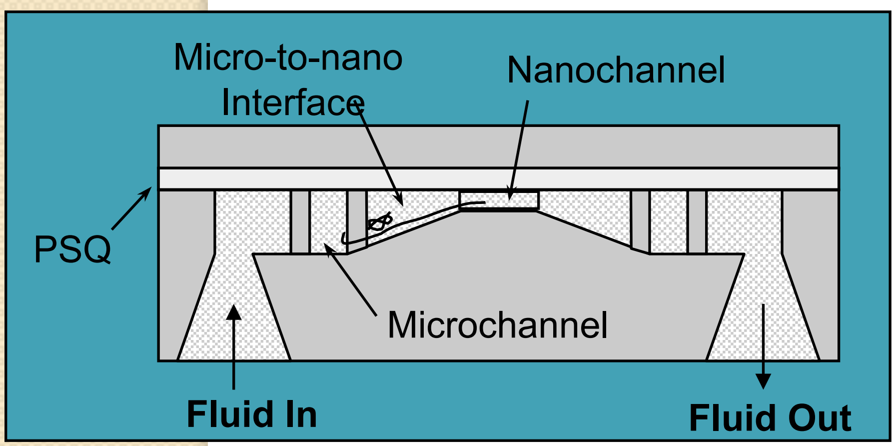
$2R = 0.1\mu m$ $\quad W_{loop} \approx 3 k_B T > k_B T$

For DNA the persistence length L_p=50nm

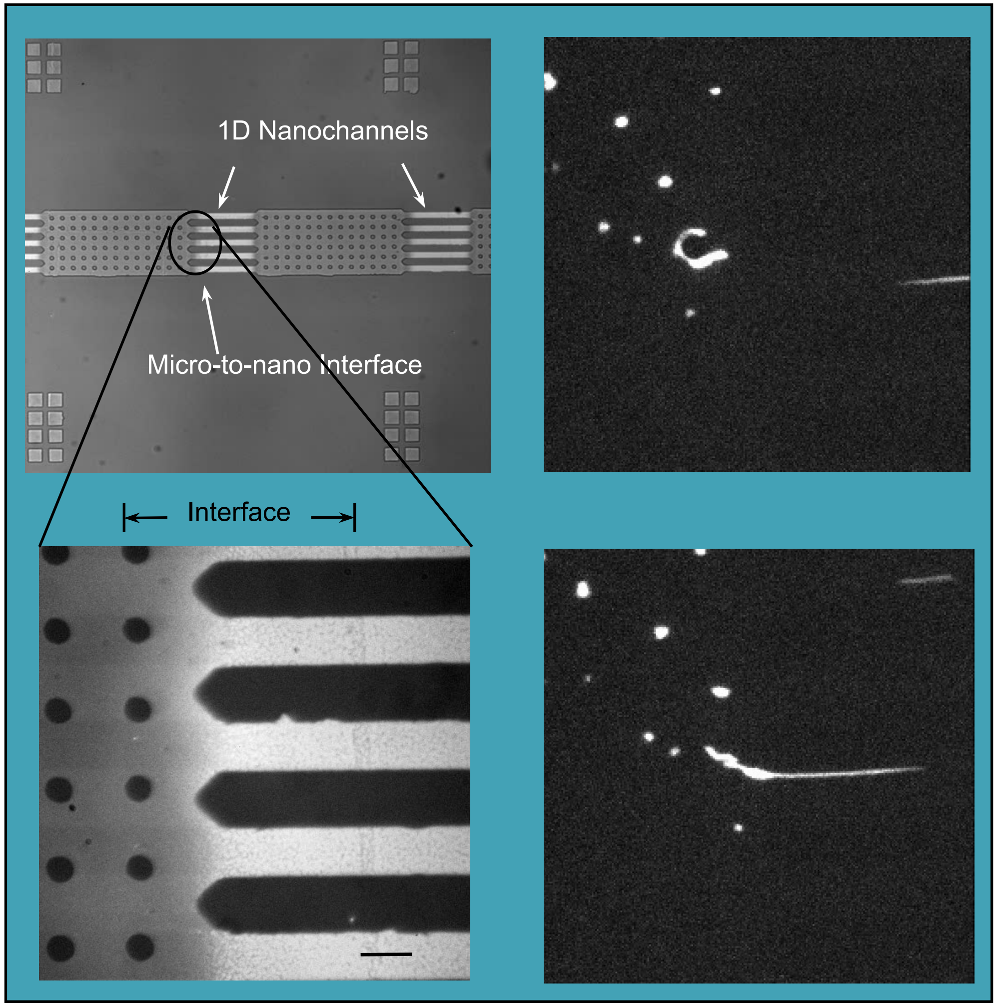
J. Tegenfeldt

World-micro-nano interfacing

→ **Continuous reduction of entropy**



Gu, Gupta, Chou *et al. Lab Chip*, 7, 1198 (2007)



DNA strands going up the ramp in the interfaced area (movie)

Exercise 2

- In entropic recoiling at a micro-nanofluidic interface, how does one derive the retraction length with a sqrt(t) dependence?

(Turner, Craighead et al., PRL 2002)

(Mannion et al, Biophys. J.,90,4538 2006)

- How is the temperature determined in a Bose-Einstein condensate?