Probing Swollen Polymer Structure with Single-Molecule Elasticity Experiments

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Overview

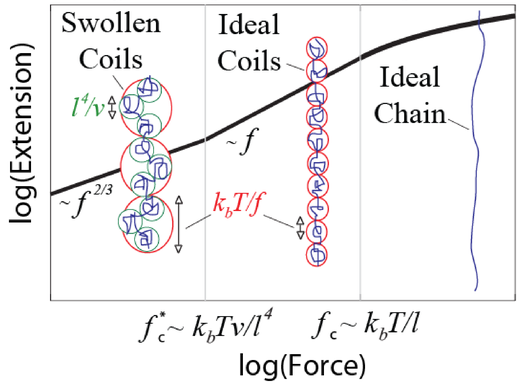
Goal: Investigate low-force elasticity of polymers to reveal structural information at zero force

Motivation: Reconciling polymer physics with single-molecule elasticity measurements; investigating polymer structure in solution for understanding biological systems (nucleic acids, proteins) and technological applications (synthetic polymer synthesis, characterization)

Method: Single molecule force-extension measurements with multiplexed magnetic tweezers [4] on flexible polymers: (i) chemically-denatured ssDNA, (ii) synthetic PEG with magnetic tweezers, and (iii) base-stacking poly(dA)

Results: 1. First observation of universal power-law elasticity at low force
charges on denatured ssDNA give it monomers that are roughly spherical; Kuhn length $l \sim [1:1]^{1/2}$ and varies strongly in 2:1 salt [1-3]
2. PEG has slender monomers revealing an 'Ideal Coils' elastic regime
3. Poly(dA)'s base-stacking appears as a 'marginal solvent' exponent

Scaling theory: flexible polymers swell at low forces



Previous experiments exert forces too large to observe swelling:

$$f \gtrsim 0.1 \text{ pN}$$

Many experiments use dsDNA:

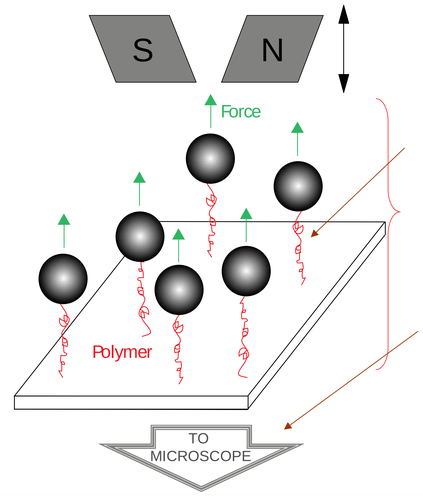
$$l_{ds} \approx 100 \text{ nm}$$

→ dsDNA cannot loop under forces greater than

$$k_bT/l_{ds} \approx 0.05 \text{ pN}$$

To see swelling behavior we need to pull on flexible polymers with small forces

Magnetic tweezers access sub-pN forces



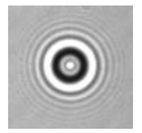
Magnets induce force; moving magnets far from sample allows access to sub-pN forces

Functionalized polymers tether paramagnetic beads

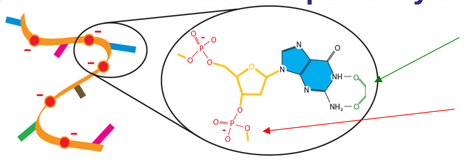
Many tethered beads manipulated and tracked in parallel [4]

Video tracking gives (x, y, z) of bead and force f applied to polymers

Bead image

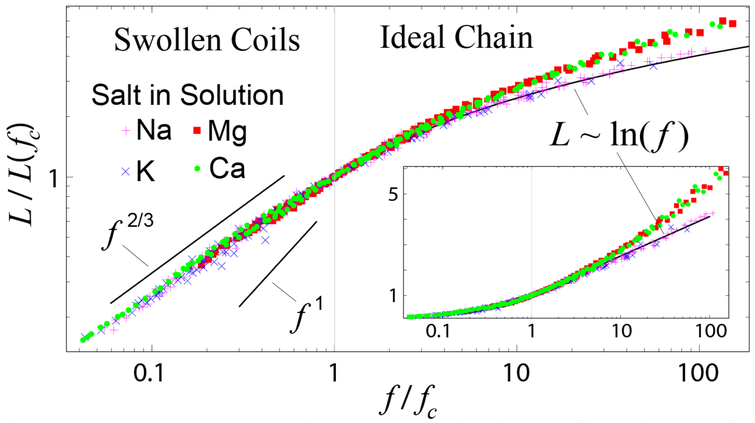


(i) Denatured ssDNA is perfectly self-avoiding

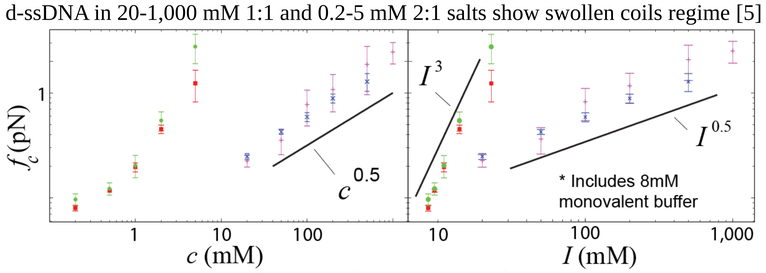


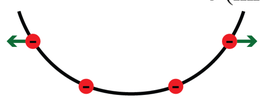
Denatured with glyoxal to prevent hairpins [6]

Charged, flexible sugar-phosphate backbone



d-ssDNA in 20-1,000 mM 1:1 and 0.2-5 mM 2:1 salts show swollen coils regime [5]

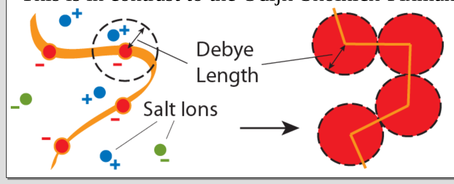




Charged polymers stiffened by e-static repulsion between monomers, and thus have salt-dependent Kuhn lengths

We measure $l \sim k_bT/f_c \sim [1:1]^{-0.51\pm0.04}$

This is in contrast to the Odijk-Skolnick-Fixman Theory which predicts $l \sim [1:1]^{-1}$ [7,8]

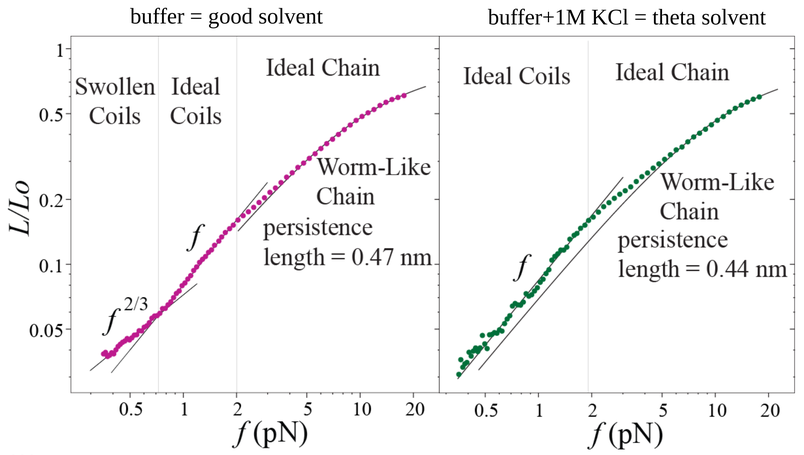


Kuhn Length and Diameter of statistical monomers scales with Debye Length:

Spherical Monomers $v \sim l^3$

No Ideal Coils Regime!

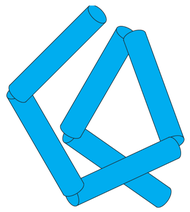
(ii) PEG has an ideal coil regime



We measure:

Contour Length	Kuhn length	Excluded volume	High-f persis. length
$Lo \approx 570$ nm	$l \sim 1.1$ nm	$v \sim 0.2$ nm^3	$p \approx 0.47$ nm

all with a single pulling expt. on a single polymer



PEG monomers are uncharged, and therefore the diameter of their statistical monomers is limited by their steric size:

Cylindrical Monomers $v < l^3$

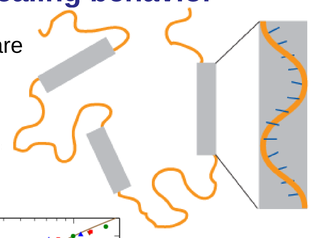
Ideal Coils Regime Appears!

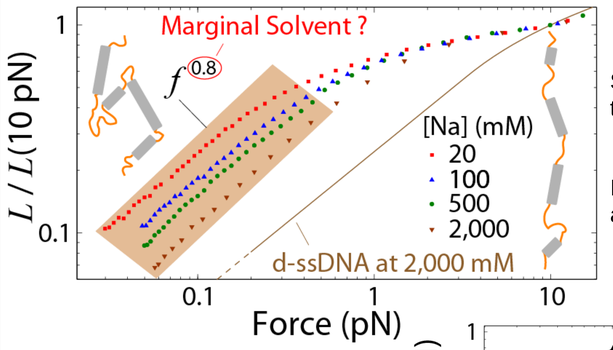
(iii) PolydA shows intermediate scaling behavior

Adenine bases tend to stack; stacked bases are stiffer than unstacked bases

Base-stacking is weakly cooperative [9]

At low force we have a statistical copolymer of stacked and unstacked domains

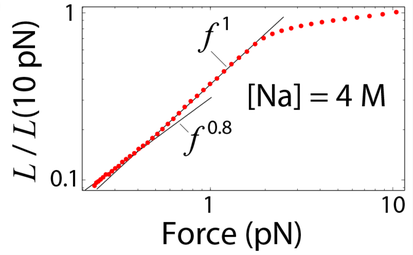




Significantly stiffer than d-ssDNA

Intermediate scaling at low force

At higher salt an 'Ideal Coil' -like linear scaling regime forms at intermediate forces, pushing the marginal scaling regime to only the lowest forces



Summary

1. Flexible polymers, low forces permit access to universal elastic regimes in single-molecule polymer experiments permitting estimate of microscopic polymer properties.
2. ssDNA has isotropic repulsive monomer-monomer interactions due to electrostatics causing monomers to appear spherical and excluded volume to swell the polymer immediately upon coiling
3. PEG has more cylindrical monomers, permitting the polymer to coil without swelling
4. polydA reveals an intermediate scaling exponent at low force indicative of base-stacking domains interspersed by random coil domains

References

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