Register Polymeerkundige

RPK- B Polymer physics 2022

Paul van der Schoot
TU Eindhoven/ Utrecht University

Jasper van der Gucht
Wageningen University

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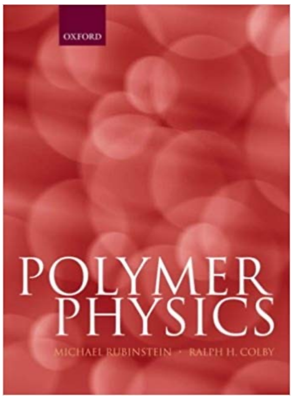
PTN

PROGRAMME
RPK-B 2022
POLYMER PHYSICS

Register Polymeerkundige

30 September 2022	**Polymer Physics – Introduction** Prof.dr.ir. Jasper van der Gucht (WUR) Dr. Wouter G. Ellenbroek (TU/e)
07 October JB	**Polymer Physics – Introduction** Prof.dr.ir. Jasper van der Gucht (WUR) Dr. Wouter G. Ellenbroek (TU/e)
14 October JB	**Polymers at Interfaces** Prof.dr.ir. Frans Leermakers (WUR)
	Polymer Depletion Interactions Prof.dr. Remco Tuinier (TU/e)
21 October	**Supramolecular Polymers** Prof.dr.ir. Jasper van der Gucht (WUR)
	Self-healing Polymers Dr. Santiago J. Garcia Espallargas (TUD)
28 October	**Liquid Crystalline Polymers** Prof.dr. Steven J. Picken (TUD)
	Polymer Networks Dr. Eduardo Mendes (TUD)
04 November	**Polyelectrolytes** Prof.dr. Christian Holm (University of Stuttgart - Germany)
11 November	**Polymer Dynamics** Prof.dr. Daniel Read (University of Leeds - UK)
18 November	**Polymer Characterization** Prof.dr.ir. Ilja Voets (TU/e)
25 November	**Block Copolymers** Dr. Giuseppe Portale (RuG)
02 December	**Glass Transition in Polymers** Dr. Alexey Lyulin (TU/e)
16 December	**Exam RPK-B** (open book) 13:00 – 16:00 hrs NH Hotel Utrecht
27 January 2023	**Re-sit exam RPK-B** (open book) 13:00 – 16:00 hrs NH Hotel Utrecht



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Exam

- Relevant sections from Rubinstein & Colby (detailed study guide will follow)
- Slides plus additional materials
- Exam consists of 12-13 questions, 5 of which need to be answered
- More detailed information will follow!

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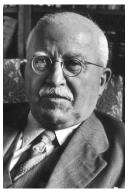
A brief history of polymer physics

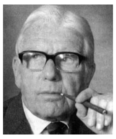
Macromolecular hypothesis **(1920)**



Herman Staudinger
Nobel Prize Chemistry 1953

Experimental support **(1920-1930)**

Wallace Carothers
Synthesis of well-defined polymers



Herman Mark
X-ray diffraction of polymers

Foundations of polymer physics **(1930-1960)**

Paul Flory
Nobel Prize Chemistry 1974

- Polymer sizes (Kuhn)
- Chain statistics (Flory)
- Thermodynamics (Flory-Huggins)
- Gelation (Flory-Stockmayer)
- Rubber elasticity (Kuhn, James, Guth)
- Dynamics (Rouse, Zimm)

Modern polymer physics **(1960-1980)**

Pierre-Gilles de Gennes
Nobel Prize Physics 1991

- Scaling approach for polymer solutions (de Gennes, des Cloizeaux)
- Tube model, reptation (Edwards, de Gennes, Doi)

Current polymer physics

- Block copolymers
- Associating polymers
- Crystallization
- Glass transition
- Liquid-crystalline polymers
- Charged polymers
- Conducting polymers
- Biological polymers
- Ultra-tough polymers
- Self-healing polymers
- Supramolecular polymers
- Polymer-covered surfaces
- ......

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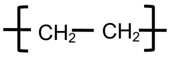
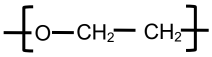
Types of polymers

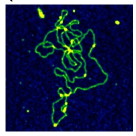
Polyethylene



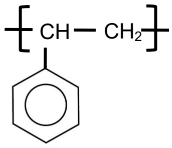
Polyethylene oxide



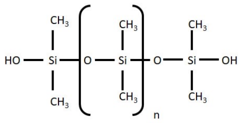
Nucleic acids (DNA / RNA)

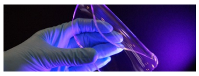


Polystyrene

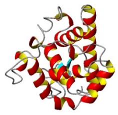


Polydimethylsiloxane

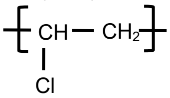




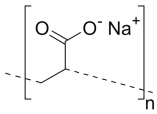
Proteins



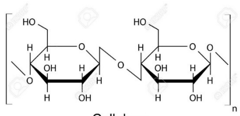
Polyvinylchloride



Polyacrylate



Polysaccharides



Cellulose

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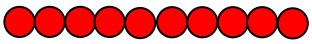
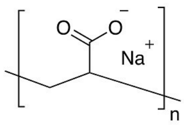
Types of polymers

Homopolymer

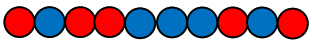


Polyelectrolyte

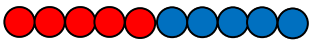


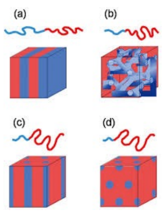
Christian Holm, 4/11

Random copolymer



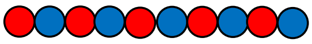
Block copolymer





Giuseppe Portale, 25/11

Alternating copolymer



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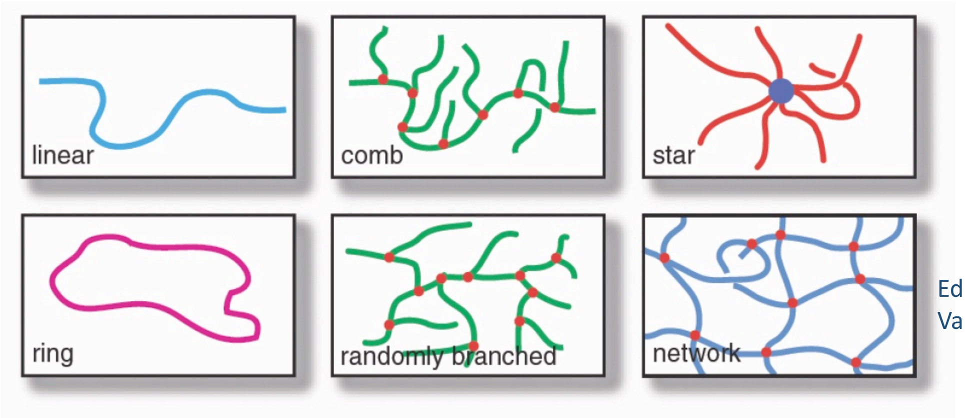
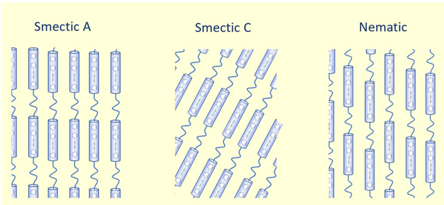
Polymer architecture



Eduardo Mendes, 28/10
Van der Gucht 21/10



Liquid crystalline polymers
Picken 28/10

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Polymer properties depend on:

- Chemical composition of the chain
- Degree of polymerization/ molar mass:
- Flexibility of the chain
- Architecture
- Homo/copolymer

$$M = nM_{mon}$$

Polymer physics: describe properties in terms of length, bending stiffness, interactions

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Introductory lectures: day 1 and 2

Chapters 1-5 Rubinstein & Colby

- Week 1:
  - Polymer conformations; simple chain models
  - Radius of gyration, end-point distribution
  - Single chain elasticity

  - Excluded volume
  - Collapse and swelling
  - Scaling concepts

- Week 2:
  - Polymer solutions and mixtures: Flory Huggins theory
  - Chi parameter
  - Osmotic pressure, phase separation

  - Overlap concentration
  - Semidilute solutions, melts
  - Scaling concepts

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Energy scales

Thermal energy: $kT \approx 4.1 \cdot 10^{-21}\mathrm{J}$ or $2.5\ \mathrm{kJ/mol}$

Covalent bond: $\sim 350\ \mathrm{kJ/mol}$ or $140\ kT$

Bending energy: $\sim kT$

Non-covalent interactions: $\ll kT$ to $\gg kT$

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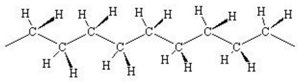
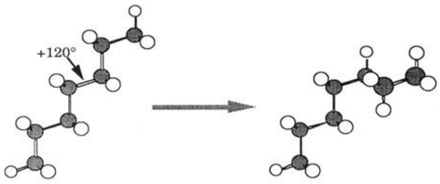
Conformation of polymers

Conformation = stereostructure of the molecule defined by its sequence of bonds and torsion angles





Average conformation depends on:
- Chain flexibility
- Degree of polymerization
- Interactions between monomers
- Interactions with surroundings

Examples of different random coil conformations

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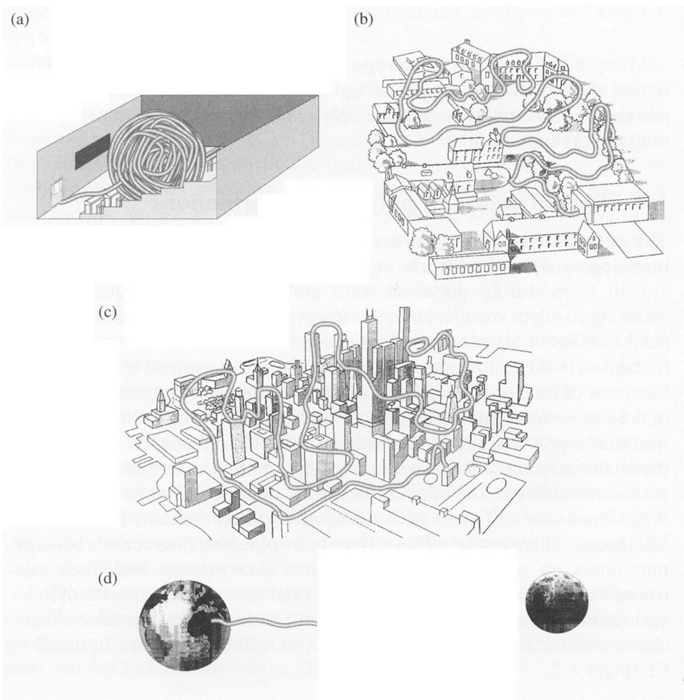
Polymer of 10^{10} bonds, with bond length 1 cm



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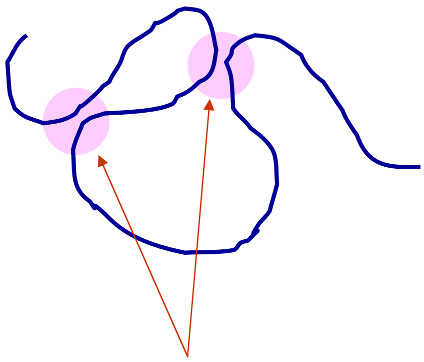
Ideal versus real chains



These interactions are ignored in the ideal chain model → Justified under **theta conditions** and in **polymer melts**

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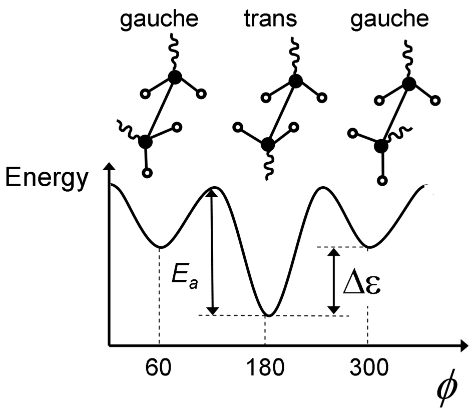
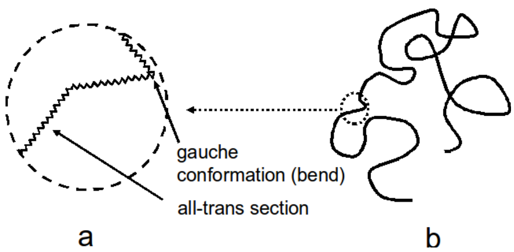
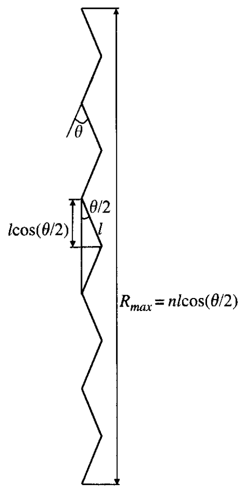
Chain flexibility







All-trans state

$\Delta\varepsilon$: determines relative probability of trans and gauche

E_a: determines dynamics of conformational changes

(Polethylene: $\Delta\varepsilon \approx 0.8\ kT$)

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Polymer models

- **Freely jointed chain**
- Freely rotating chain (**exercise**)
- **Wormlike chain**
- Hindered rotation model
- Rotational isomeric state model
- **Kuhn model**
- ..

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Characteristic ratios and Kuhn length of several polymers

Table 2.1 Characteristic ratios, Kuhn lengths, and molar masses of Kuhn monomers for common polymers

Polymer	Structure	C_∞	b (Å)	ρ ($\mathrm{g\,cm^{-3}}$)	M_0 ($\mathrm{g\,mol^{-1}}$)
1,4-Polyisoprene (PI)	$-(CH_2CH{=}CHCH(CH_3))-$	4.6	8.2	0.830	113
1,4-Polybutadiene (PB)	$-(CH_2CH{=}CHCH_2)-$	5.3	9.6	0.826	105
Polypropylene (PP)	$-(CH_2CH_2(CH_3))-$	5.9	11	0.791	180
Poly(ethylene oxide) (PEO)	$-(CH_2CH_2O)-$	6.7	11	1.064	137
Poly(dimethyl siloxane) (PDMS)	$-(OSi(CH_3)_2)-$	6.8	13	0.895	381
Polyethylene (PE)	$-(CH_2CH_2)-$	7.4	14	0.784	150
Poly(methyl methacrylate) (PMMA)	$-(CH_2C(CH_3)(COOCH_3))-$	9.0	17	1.13	655
Atactic polystyrene (PS)	$-(CH_2CHC_6H_5)-$	9.5	18	0.969	720

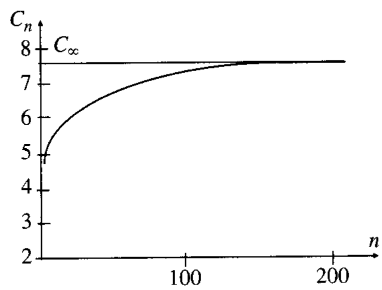

Fig. 2.4
Flory's characteristic ratio C_n saturates at C_∞ for long chains.

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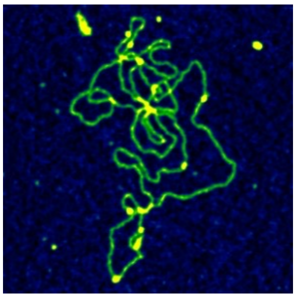
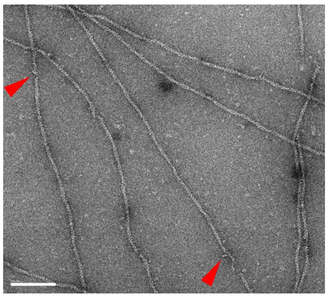
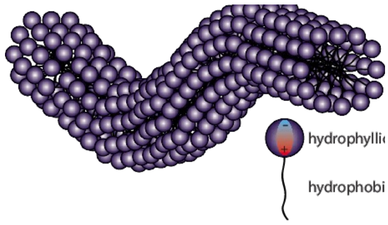
Wormlike chains



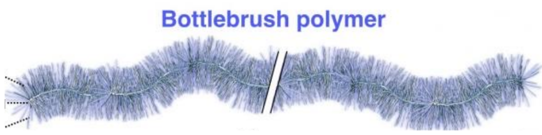
DNA



Protein filament



Wormlike micelle



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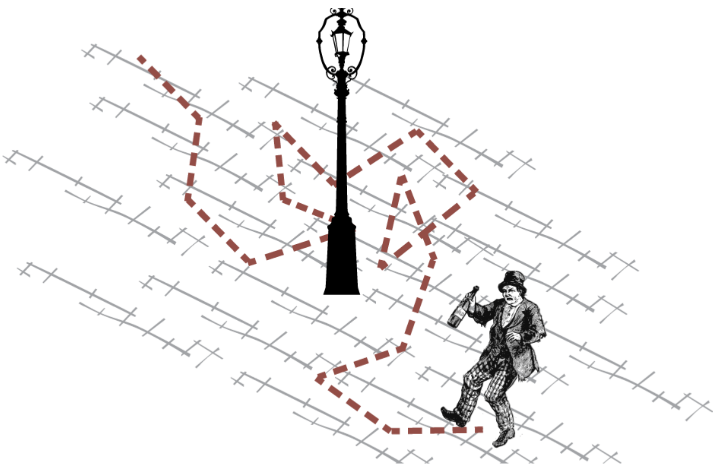
Random walk



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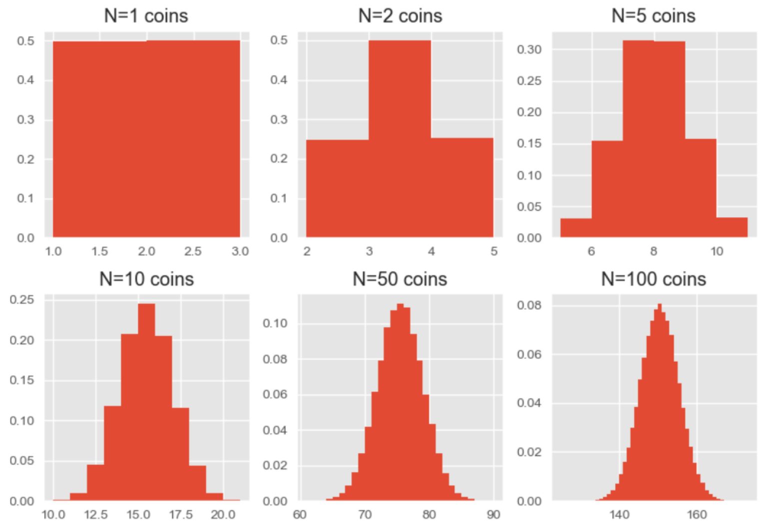
Central limit theorem



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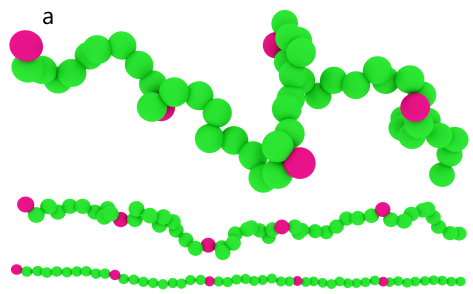
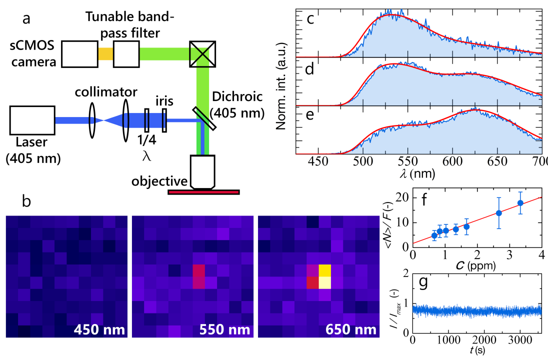
Polymer as force sensor





T. van de Laar, H. Schuurman, P. van der Scheer, J.M. van Doorn, J. van der Gucht, J.Sprakel, Chem, 4 (2018), 269 .

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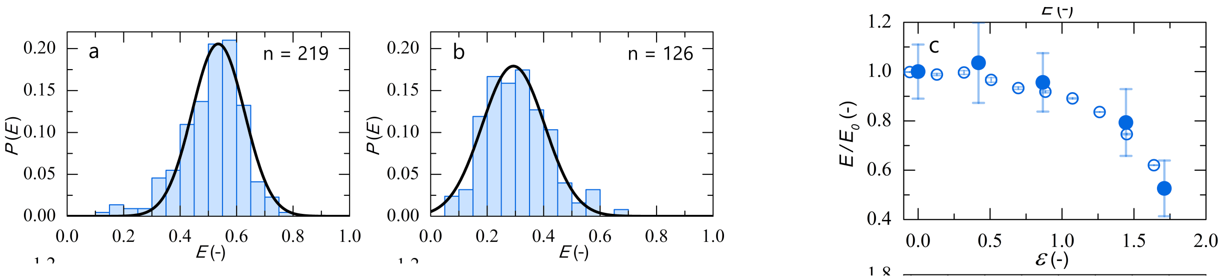
Polymer as force sensor




RESOURCE
Voor iedereen van Wageningen University & Research

WETENSCHAP - 19 JANUARI 2018

WUR-onderzoekers meten kleinste kracht ooit

tekst: Tessa Louwerens

Onderzoekers van de leerstoelgroep Physical Chemistry and Soft Matter hebben een methode ontwikkeld om ultrakleine krachten te meten aan één enkel molecuul. Het is de kleinste kracht die ooit gemeten is. Wetenschappers kunnen met deze metingen inzicht krijgen in allerlei biologische processen, zoals de groei van planten. Ook kan de methode worden gebruikt bij het ontwikkelen van zelf-reparerend materiaal voor ruimteschepen.

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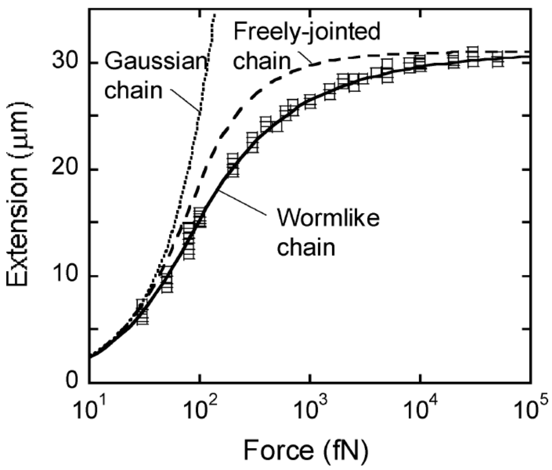
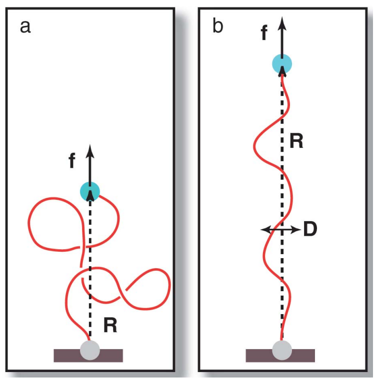
Force-extension curve for DNA





Optical tweezer experiment

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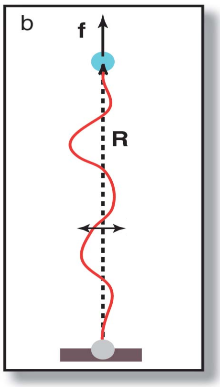
Stretching a freely-jointed chain



$$U = -\vec{f} \cdot \vec{R} = -\vec{f} \cdot \sum_{i=1}^{N} \vec{b}_i$$

$$P(\{\vec{b}_i\}) \sim e^{-\beta U} = \prod_{i=1}^{N} e^{\beta \vec{f} \cdot \vec{b}_i}$$ with $\beta = 1/kT$

$$\langle \vec{b}_i \rangle = \frac{\int_{|\vec{b}|=b} \vec{b} e^{\beta \vec{f} \cdot \vec{b}} \, d\vec{b}}{\int_{|\vec{b}|=b} e^{\beta \vec{f} \cdot \vec{b}} \, d\vec{b}}$$ integration over spherical shell with radius b

$$= b \left[\coth(\gamma) - \frac{1}{\gamma} \right] \frac{\vec{f}}{f}$$ with $\gamma = fb/kT$

$$R = N \langle b_i \rangle = Nb \left[\coth(\gamma) - \frac{1}{\gamma} \right]$$

$$\coth x = \frac{e^x + e^{-x}}{e^x - e^{-x}}$$

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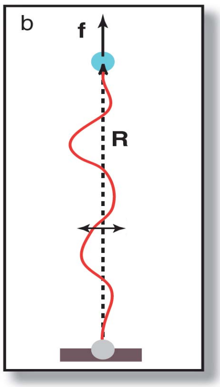
Stretching a freely-jointed chain



$$R = Nb \left[\coth(\gamma) - \frac{1}{\gamma} \right]$$ with $\gamma = fb/kT$

$$\gamma \ll 1: \quad R = Nb \frac{\gamma}{3} = \frac{Nb^2 f}{3kT}$$

$$\gamma \gg 1: \quad R = Nb \left[1 - \frac{1}{\gamma} \right] \text{ or } f = \frac{kT}{b \left[1 - \frac{R}{R_{max}} \right]}$$

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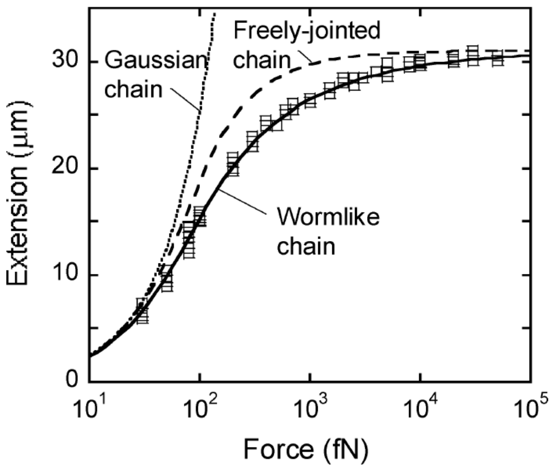

Freely jointed chain

$$\mathrm{R} = \mathrm{N}b\left[\coth(\gamma) - \frac{1}{\gamma}\right] \quad \text{with } \gamma = fb/kT$$

Wormlike chain (Marko-Siggia)

$$\mathrm{f} \approx \frac{kT}{2b}\left[\frac{R_{max}^2}{(R_{max}-R)^2} - 1 + \frac{4R}{R_{max}}\right]$$

(accurate approximation)

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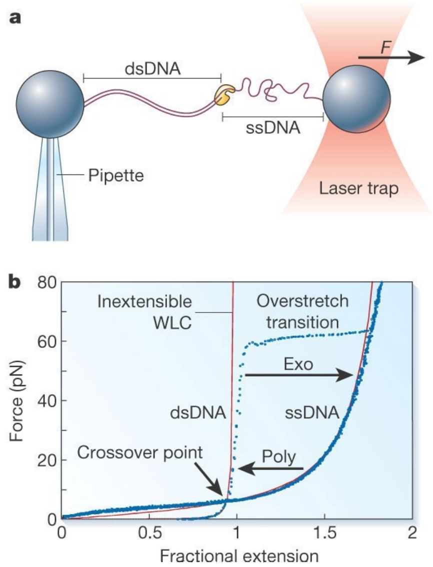
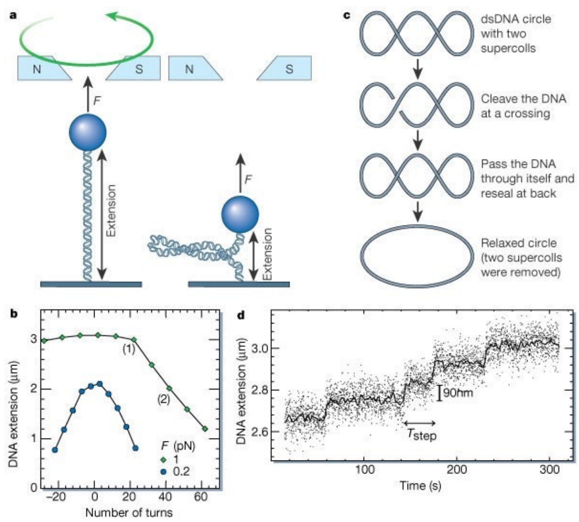
Single molecule DNA experiments

DNA replication by polymerase



Topoisomerase activity



See Bustamante et al. Nature 2003

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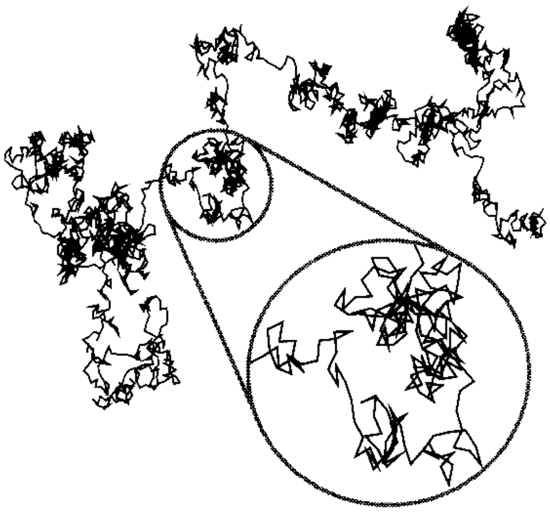
Structure of an ideal polymer chain



Structure can be measured with scattering (SAXS, SANS)

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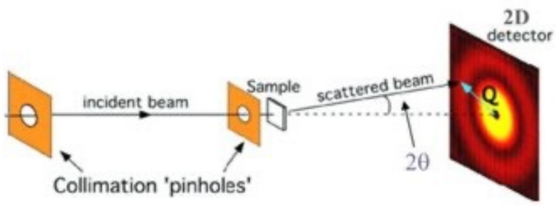
Xray-scattering



Lecture Ilja Voets

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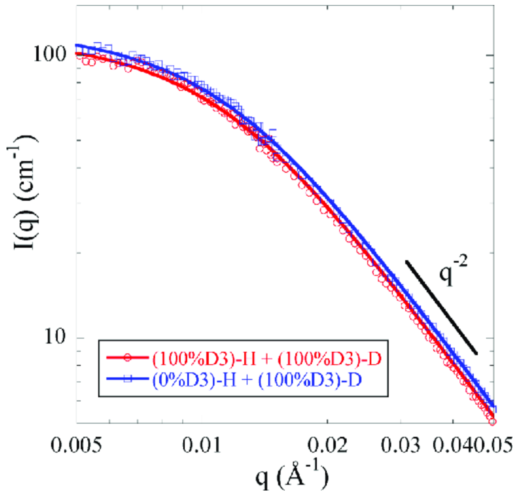
Form factor single chains



Single chain form factor:

$$P(q) = \frac{2}{(qR_g)^4}\left[e^{-(qR_g)^2} - 1 + (qR_g)^2\right]$$

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