Statistiãne lastnosti polielektrolitov

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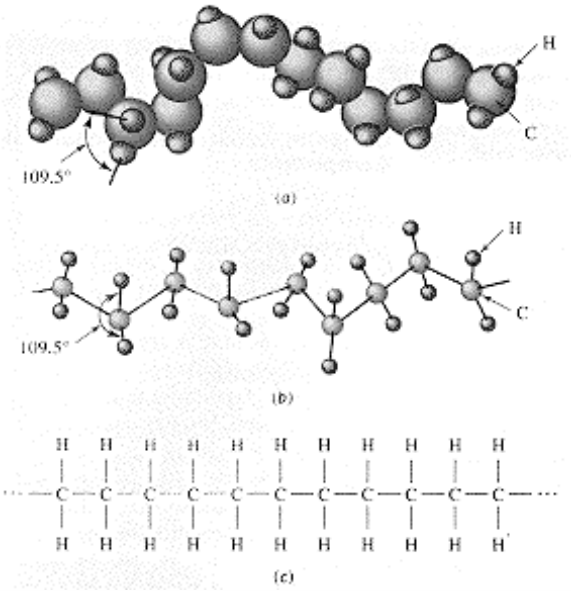
Zgodovina polimerov

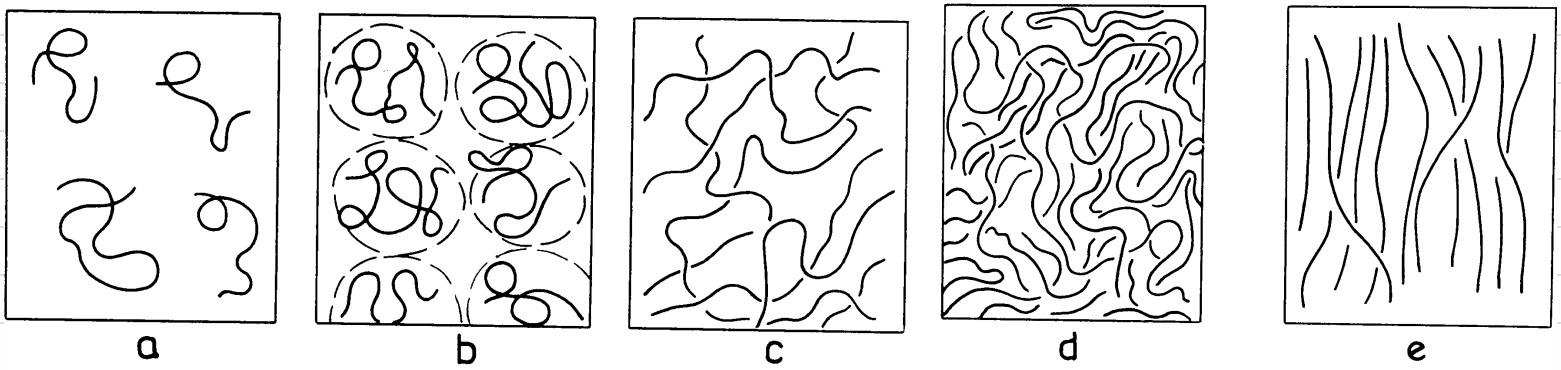
- H. Staudinger, 1920
- P. Flory
- W. Kuhn
- T. Odijk, 1970

Kemiãna struktura polimerov

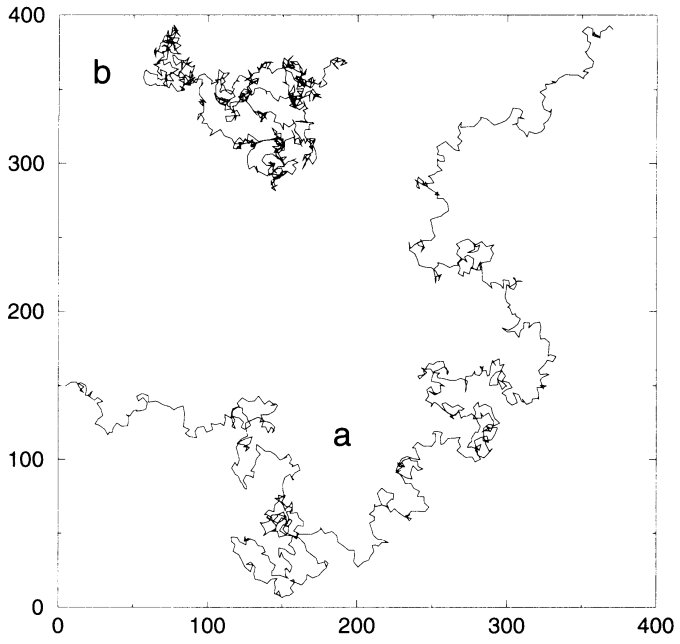
- Veliko monomerov

  $N \approx 10^2 - 10^4$
- Polietilen $[CH_2]_n$
- DNA, $N \approx 10^9$
- Raztopine





Nakljuãni sprehod



- Oddaljenost

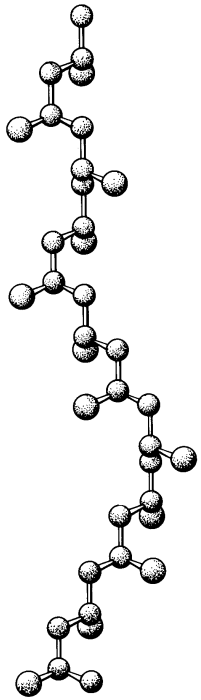
$$\vec{R}_N = \sum_{i=0}^{N} \vec{r}_i$$

- Nekoreliranost

$$< \vec{r}_i \cdot \vec{r}_j >= \ddot{a}_{i,j} b^2$$

- Povpreãje

$$< \vec{R}_N^2 >= \sum_{i,j=0}^{N} < \vec{r}_i \cdot \vec{r}_j > = Nb^2 = Lb$$

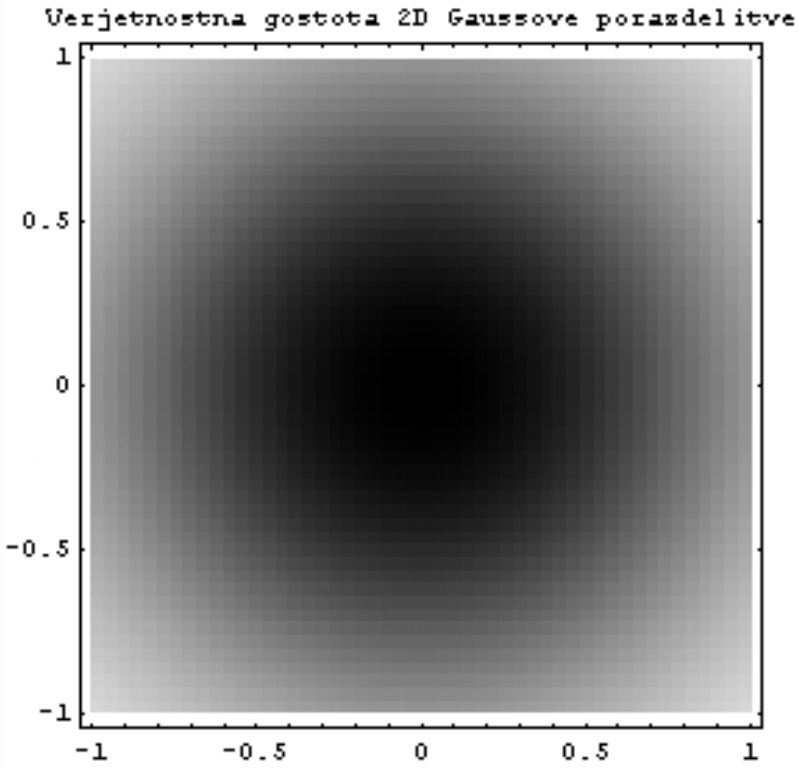


Univerzalnost

- Polimeri
- Brownovo gibanje

$$< \vec{R}_N^2(t) >= Dt$$

Porazdelitev dolĬin



- Porazdelitev dolĬin

$$\Psi(\vec{R}_i) = Ae^{-\frac{3\vec{R}_i^2}{2Nb^2}}$$

$$< \vec{R}^2 >= Nb^2$$

- Entropija

  Iz $S = k_B \log \Psi$ dobim

$$\Delta S = -\frac{3}{2} k_B T \frac{R^2}{Nb^2}$$

Polimeri - Lp

- Elastiãna energija

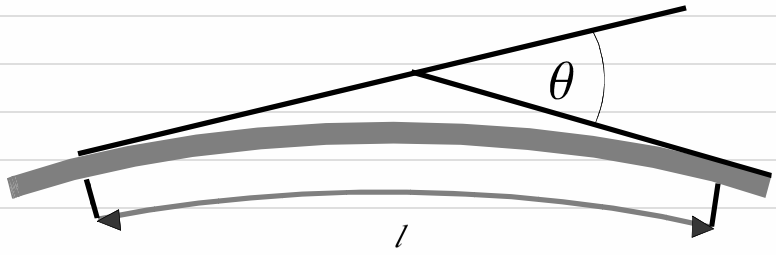
$$W = W_0 + \frac{a}{2}\int\left(\frac{d\theta}{dl}\right)^2 dl$$

- S pomoãjo Boltzmannove porazdelitve $w \propto e^{-\Delta W / k_B T}$

  izraãunam $< \cos\theta >= e^{-l/L_p}$

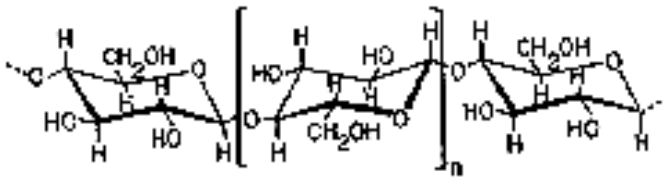
- Persistenãna dolÏina

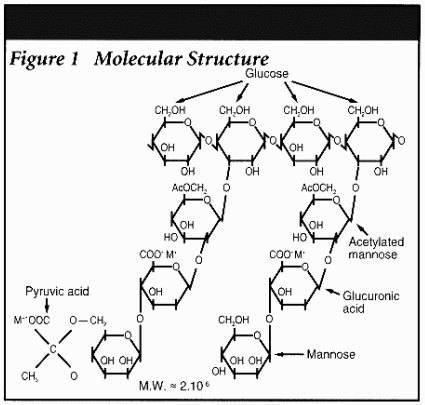
$$L_p = \frac{a}{k_B T}$$



L_p pri razliãnih polimerih

POLIMER	Lp	OPIS
Schizofilan	200nm	Trojna vija
Xantan	120nm	V hamburgerjih
DNA	50nm	Dvojna vija
Celuloza	17nm	Papir





Polimeri - R^2

- Povpreãni kvadrat odmika

$$< \vec{R}_N^2 >= 2LL_p - 2L_p(1 - \exp\frac{-L}{L_p})$$

- Limite
  - velike Lp

$$< \vec{R}_N^2 >= L^2(1 - \frac{L}{3L_p})$$

ravna palica

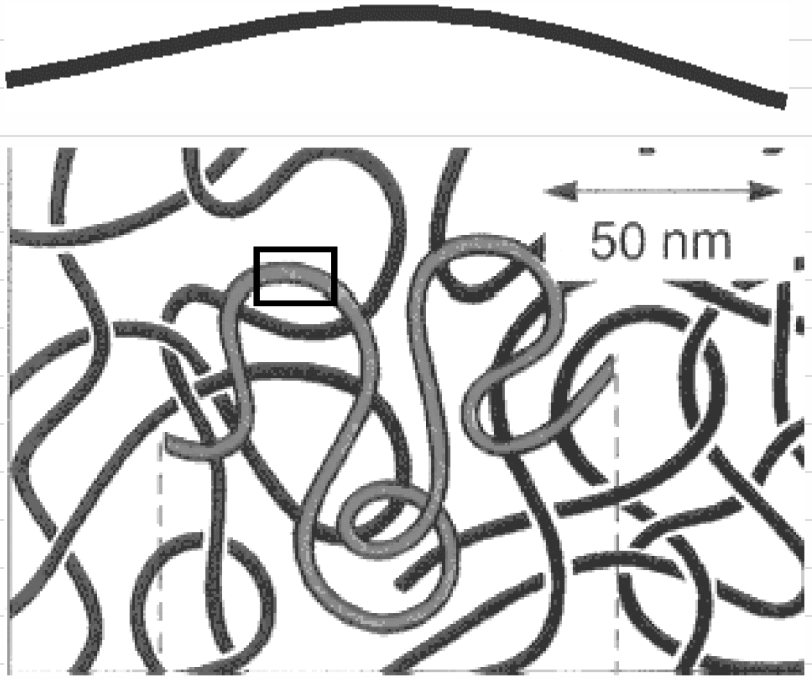
  - male Lp

$$< \vec{R}_N^2 >= 2LL_p$$

nakljuãni sprehod

  - Kuhnova dolÏina

$$b = 2L_p$$



Polielektroliti - potencial

- Coulombov potencial

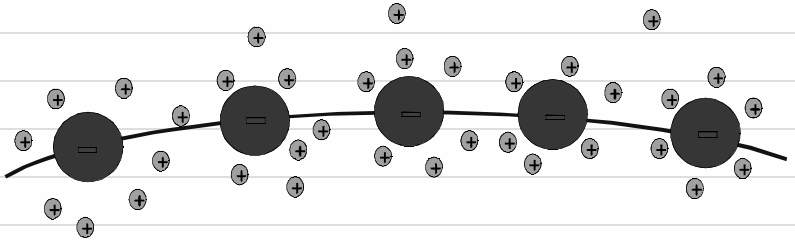
$$U = \frac{e^2}{4\pi\varepsilon\varepsilon_0}\frac{1}{r}$$

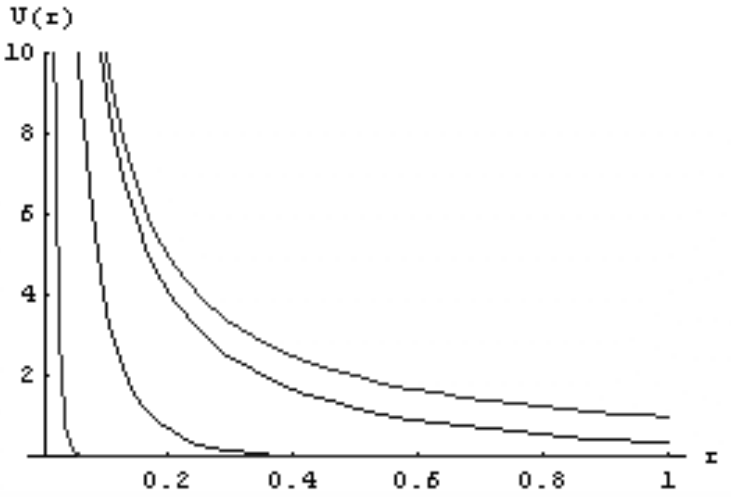
- Debye-Hückelov potencial

$$U = \frac{e^2}{4\pi\varepsilon\varepsilon_0}\frac{\exp(-\kappa r)}{r}$$

konstanta senãenja

$$\kappa^2 = \frac{2\rho_0 e_0^2}{\varepsilon\varepsilon_0 k_B T}$$





Skalirni zakoni (1)

- I‰ãem skalirni koeficient y

$$< R > \propto N^{\nu} \propto L^{\nu}$$

- Notranjo energijo prevedem na integral

$$W = \frac{1}{2}\int\int dl_1 dl_2 U(|\vec{r}(l_1) - \vec{r}(l_2)|)$$

- Coulombov potencial

$$W \approx \frac{e^2}{8\pi\varepsilon\varepsilon_0}\frac{L^2}{R}$$

minimaliziram F

$$F = W - TS$$

$$F \approx \alpha\frac{L^2}{R} + \beta\frac{R^2}{L}$$

dobim

$$R \propto L$$

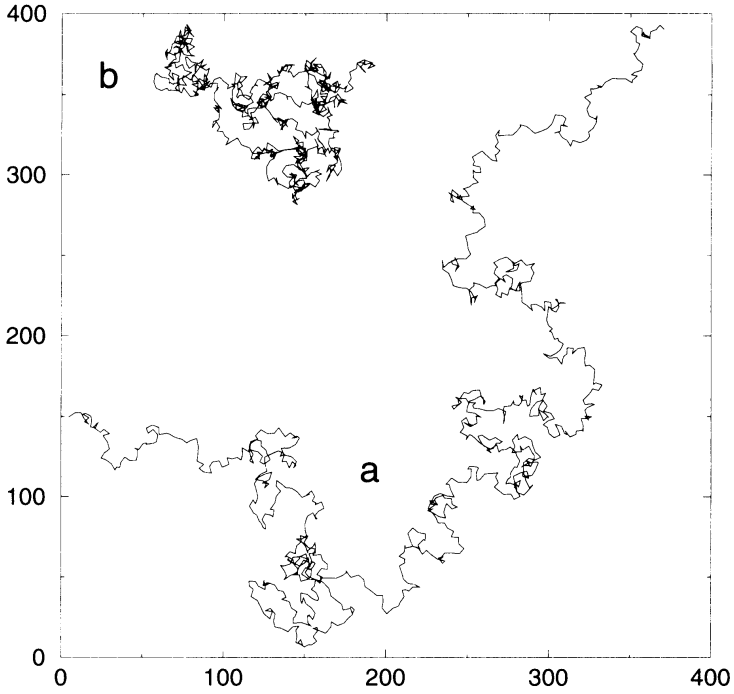
Skalirni zakoni (2)

- Efekt izkljuãenega volumna

z minimizacijo F dobim

$$R \propto L^{3/5}$$

Flory



Elektrostatiãna L_p

- Izraãunam obliko polielektrolita, kot da ne bi bil nabit

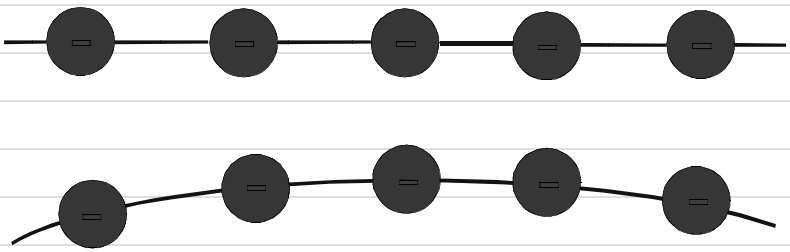
$$\Delta F_C = \Delta F_P + U_{el}$$

Skupna persistenãna dolÏina se poveãa

$$L_S = L_{el} + L_P$$

Eletrostatiãna persistenãna dolÏina

$$L_{el} = \frac{\lambda_B}{4\kappa^2 A^2}$$



- Rezultati

ravna palica

$$< \vec{R}_N^2 >= L^2\left(1 - \frac{L}{3(L_p + L_{el})}\right)$$

naključni sprehod ??

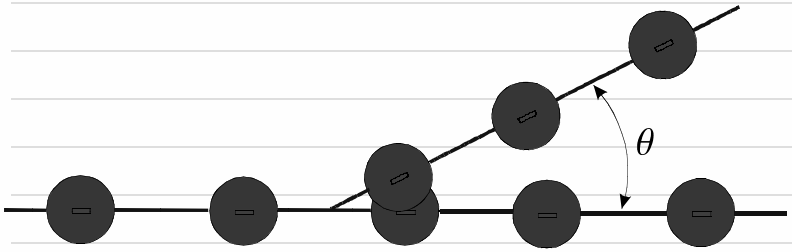
$$< \vec{R}^2 >= 2L(L_p + L_{el})$$

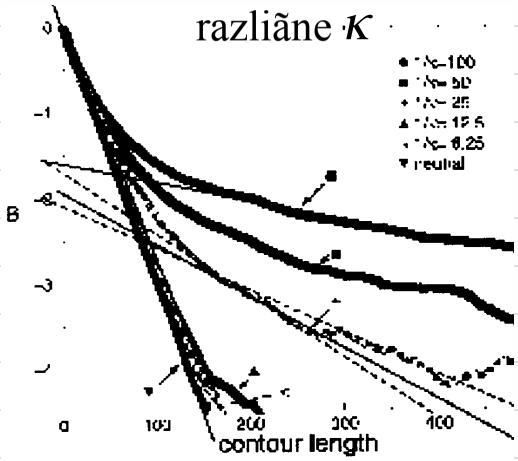
Numeriãne simulacije (Monte Carlo)

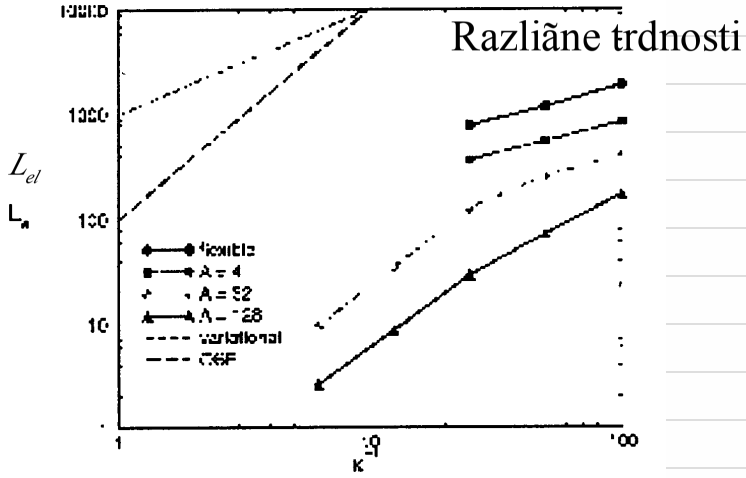
- Izberem si zaãetno obliko verige
- Izberem si pivotirni korak
- âe je
  - $\Delta W < 0$ spremembo sprejmem
  - $\Delta W > 0$ spremembo sprejmem

  z verjetnostjo $e^{-\frac{\Delta W}{k_B T}}$

$$< \cos\vartheta >= e^{-L/L_S}$$

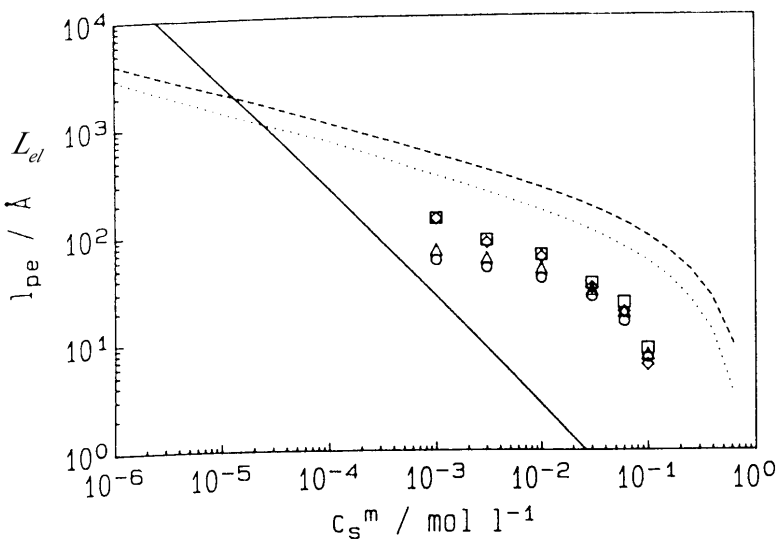


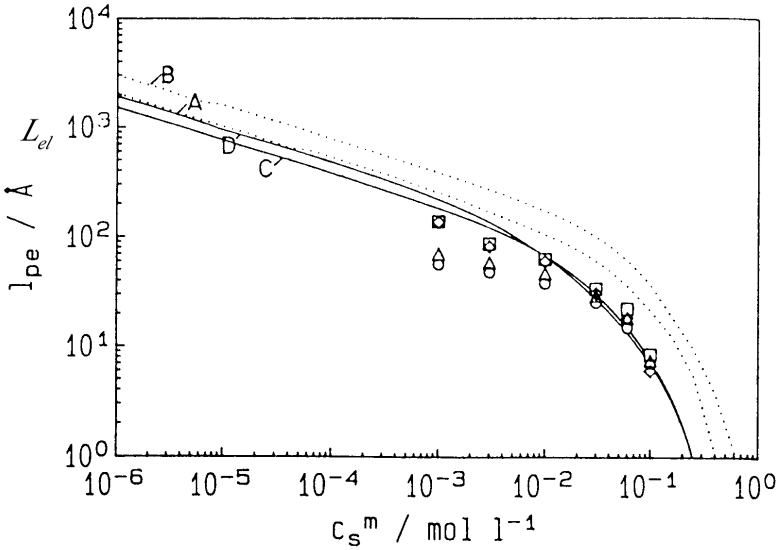




Meritve

- Svetlobno sipanje
- Primerjava meritev (toãke), simulacije (ãrtkano) in teorije (polna ãrta)
- Odijk $L_{el} \propto \kappa^{-2} \propto c^{-1}$





Zakljuãek

- Polimeri
  - opi‰emo jih z enim parametrom (persistenãno dolÏino)
- Polielektroliti
  - opis z enim parametrom ni veã primeren
- Simulacije & meritve