Polymer chain stiffness versus excluded volume: A Monte Carlo study of the crossover towards the wormlike chain model

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Motivation

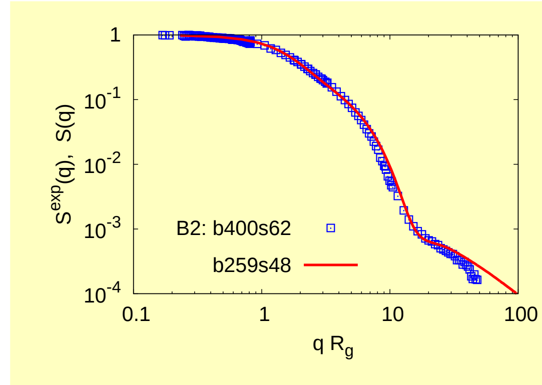
- Kratky-Porod worm-like chain model

  $\overset{?}{\Longrightarrow}$ Cylindrical bottle-brush polymers

control the local stiffness

simulation $\Leftrightarrow$ experiment

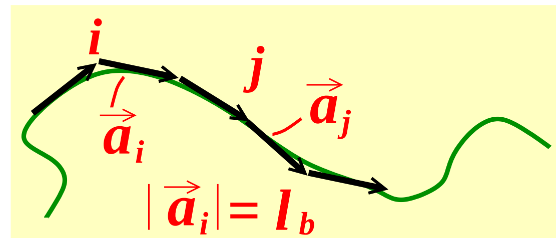
(Macromolecules 43, 1592 (2010))



- Examine the definition of persistence length ℓ_p

  $\Longrightarrow$ intrinsic stiffness of the backbone chain

  - Standard definition:



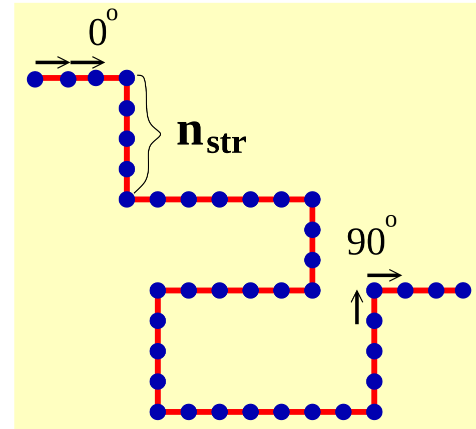
$$\langle \vec{a}_i \cdot \vec{a}_j \rangle / \ell_b^2 = \langle \cos \theta(s) \rangle = \exp(-s\ell_b/\ell_p)$$

  - Flory's local persistence length: $\ell_p(k) = \ell_b \langle \vec{a}_k \cdot \vec{R}_e / \mid \vec{a}_k \mid^2 \rangle$
  - New suggestion: $\langle R_e^2 \rangle = 2\ell_{p,R}\ell_b N_b^{2\nu}$

Semiflexible SAW model

Self-avoiding walk model + Bond-bending potential

on the simple cubic lattice



- Bending potential:

$$U_{\text{bend}}(\theta) = \varepsilon_b(1 - \cos\theta) = \begin{cases} 0 & \theta = 0^o \\ \varepsilon_b & \theta = 90^0 \end{cases}$$

- Partition sum (a walk with N_b steps and N_{bend} 90^0):

$$Z_{N_b}(q_b) = \sum_{\text{config.}} C_{N_b,N_{\text{bend}}} q_b^{N_{\text{bend}}}$$

$q_b = e^{-(U_{\text{bend}}/k_BT)} = e^{-(\varepsilon_b/k_BT)}$: Boltzmann factor

Grassberger, 1997

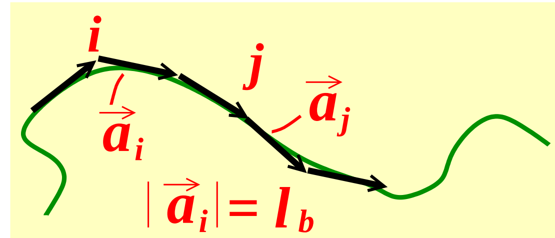
- Algorithm: Pruned-enriched Rosenbluth method (PERM)

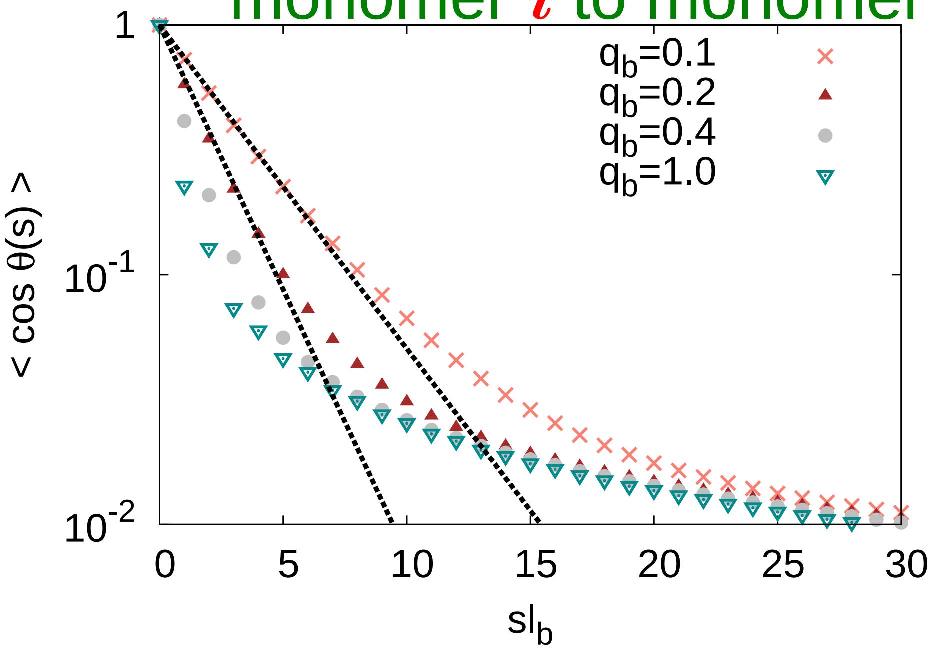
$0.005 \leq q_b \leq 1.0$, very stiff chain $\leftrightarrow$ flexible chain (SAW)

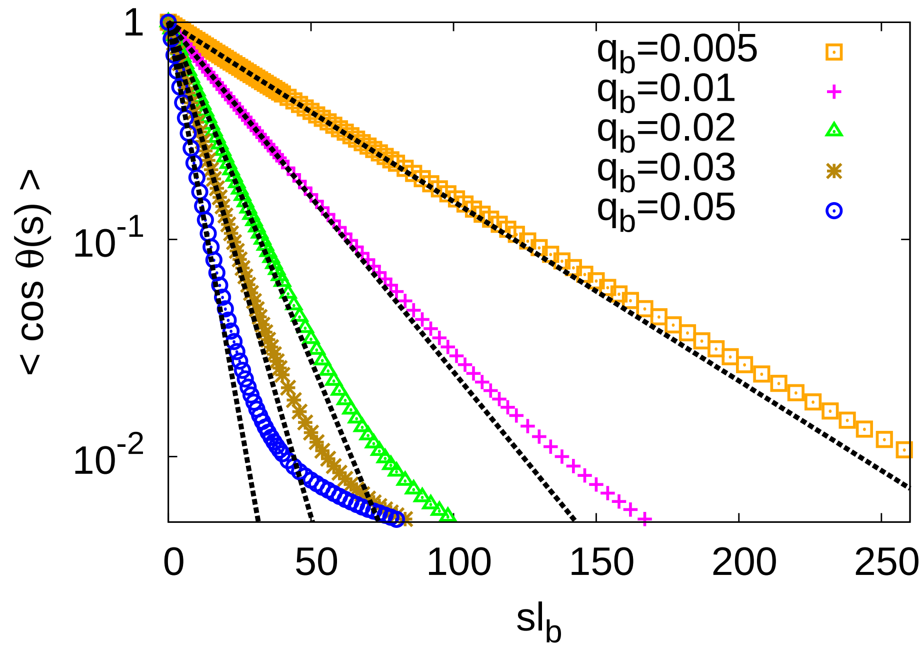
Persistence length ℓ_p

- Orientational correlation between bonds: $\langle \cos\theta(s)\rangle = \exp(-s\ell_b/\ell_p)$

  $s\ell_b$: contour length from monomer i to monomer j







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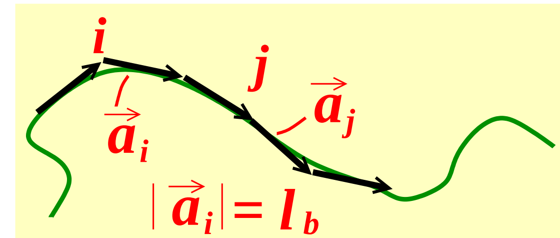

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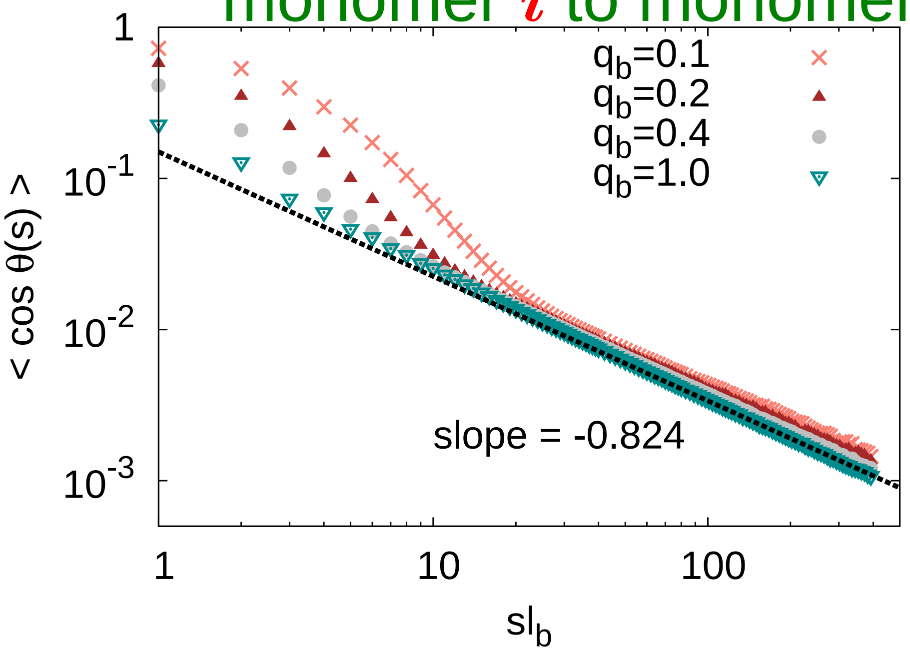
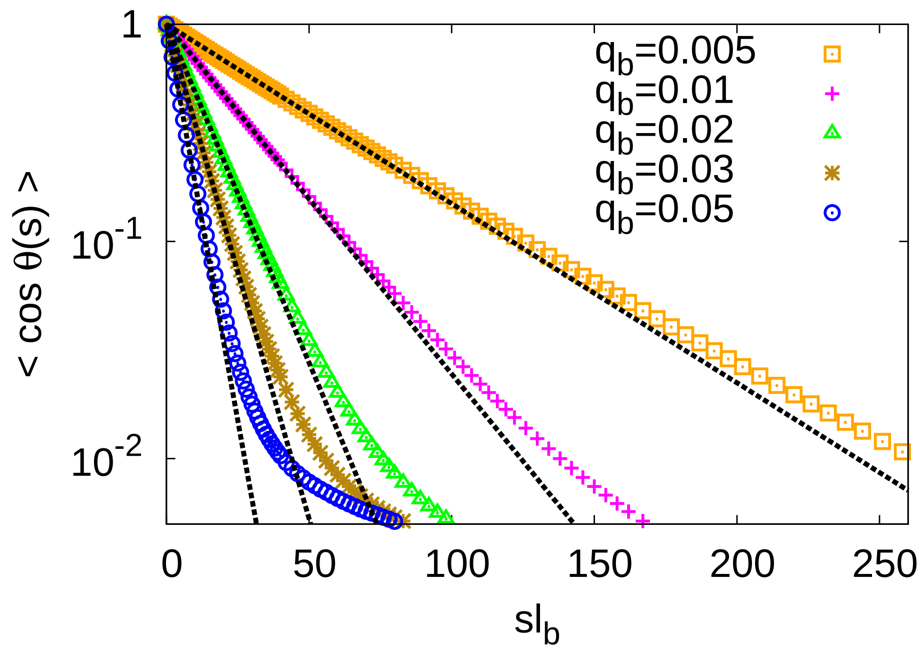




- $\langle \cos\theta(s) \rangle \propto s^{-\beta}$, $s^* < s \ll N_b$

  $\beta = 2 - 2\nu = 0.824$ (Schäfer et al. J. Phys. A: Math. Gen 32, 7875, (1999).)

Worm-like chain model

without considering the excluded volume interactions

- Kratky-Porod model in the continuum limit (J. Colloid Sci., 4 35 (1949)):

$$\langle R_e^2 \rangle = 2\ell_p L \left\{ 1 - \frac{\ell_p}{L}\left[1 - \exp(-L/\ell_p) \right] \right\}$$

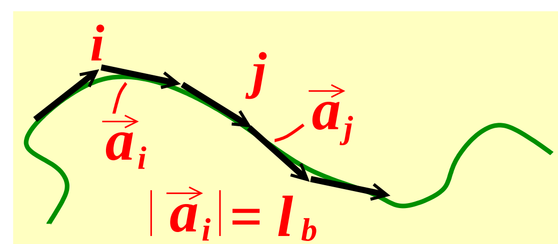
L: contour length $L = N_b \ell_b$

$$= \begin{cases} L^2 = (\ell_b N_b)^2 & \text{for } L \ll \ell_p \text{ (rod} - \text{like chain)} \\ 2\ell_p L = \ell_k \ell_b N_b & \text{for } L \to \infty \text{ (Gaussian chain)} \end{cases}$$

- Discrete worm-like chain (Winkler et. al., J. Chem. Phys. 101, 8119 (1994)):

$$\langle R_e^2 \rangle = N_b \ell_b^2 \left[\frac{1 + \langle \cos\theta \rangle}{1 - \langle \cos\theta \rangle} + \frac{2\langle \cos\theta \rangle}{N_b} \frac{\langle \cos\theta \rangle^{N_b} - 1}{(\langle \cos\theta \rangle - 1)^2} \right]$$

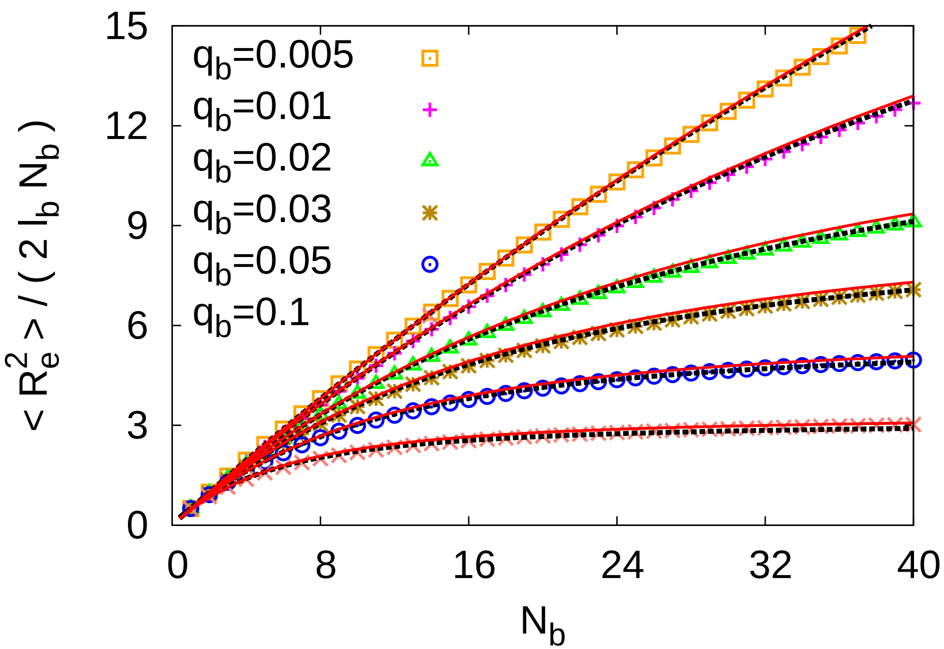
$$\langle \cos\theta \rangle = \langle \cos\theta(s = 1) \rangle$$

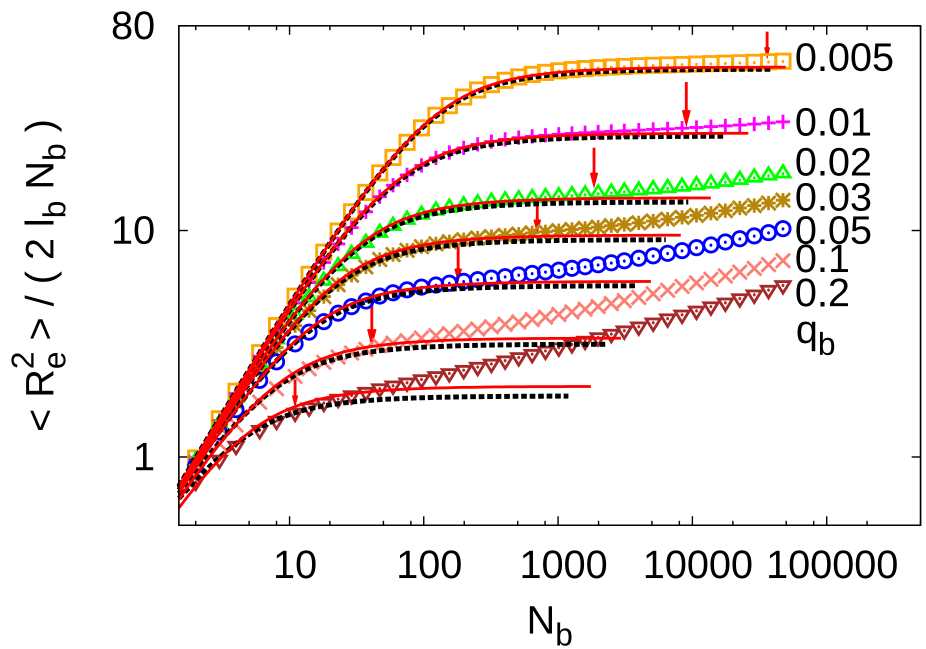


Simulation ⇔ Theory

- $\langle R_e^2 \rangle / (2\ell_b N_b)$ vs. N_b

rod-like chain ↔ Gaussian chain





continuous

discrete

worm−like chain model

↓ **N_b^* : crossover point**

(Gaussian chain <−> SAW)

Flory theory for semiflexible chains

- Effective free energy: Netz & Andelman, Phys. Rep. 380, 1 (2003)

$$\Delta F \approx \frac{R_e^2}{\ell_K L}\,(\text{elastic energy}) + \upsilon_2 R_e^3 \left[\frac{L/\ell_K}{R_e^3}\right]^2 (\text{repulsive energy})$$

  - Free Gaussian chain:

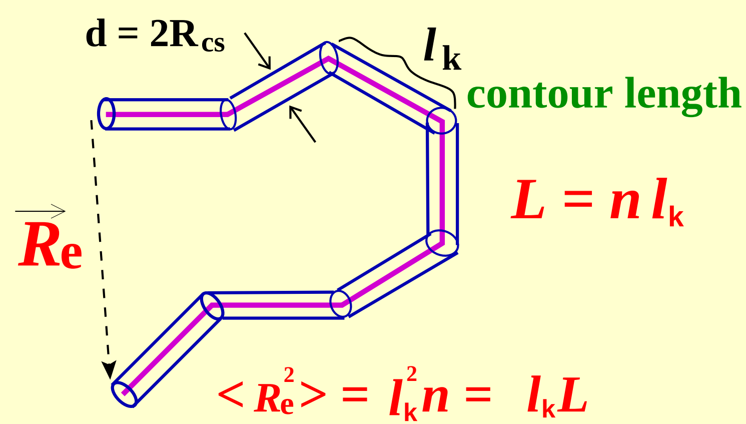
$$P(R_e) \sim \exp\left(-\frac{R_e^2}{2\langle R_e^2\rangle}\right) = \exp\left(-\frac{R_e^2}{2\ell_K L}\right)$$

  - Repulsive energy due to pairwise contacts:

    [2nd virial coefficient · density]² · volume = $[\upsilon_2\rho^2]\,V$

$$\upsilon_2 = \ell_K^2 d\ ,\ \rho = \frac{n}{R_e^3} = \frac{L/\ell_K}{R_e^3}\ ,\ V = R_e^3\ ,\ L_K = 2\ell_p$$

chain with n units of length l_k randomly linked:



Rod-like - Gaussian chain - SAW

(Rod-like chain) $\ell_K/\ell_b \ < N_b$ (Gaussian chain) $< \ N_b^*$ (SAW)

$$\text{Effective free energy}: \Delta F \approx \frac{R_e^2}{\ell_K L} + v_2 R_e^3 \left[\frac{L/\ell_K}{R_e^3}\right]^2$$

- Flory-type result, SAW:

  $\partial \Delta F / \partial R_e = 0$

  $\Rightarrow R_e \approx (v_2/\ell_K)^{1/5} L^{3/5} = (\ell_K d)^{1/5} (N_b \ell_b)^{3/5}$

- Gaussian chains:

  $\Delta F \approx R_e^2/(\ell_K L) \sim 1$, $R_e^2 = \ell_K L = \ell_K \ell_b N_b$

  $v_2 R_e^3 \left[(L/\ell_K)/R_e^3\right]^2 < 1 \Rightarrow N_b < \ell_K^3/(\ell_b d^2) = N_b^*$

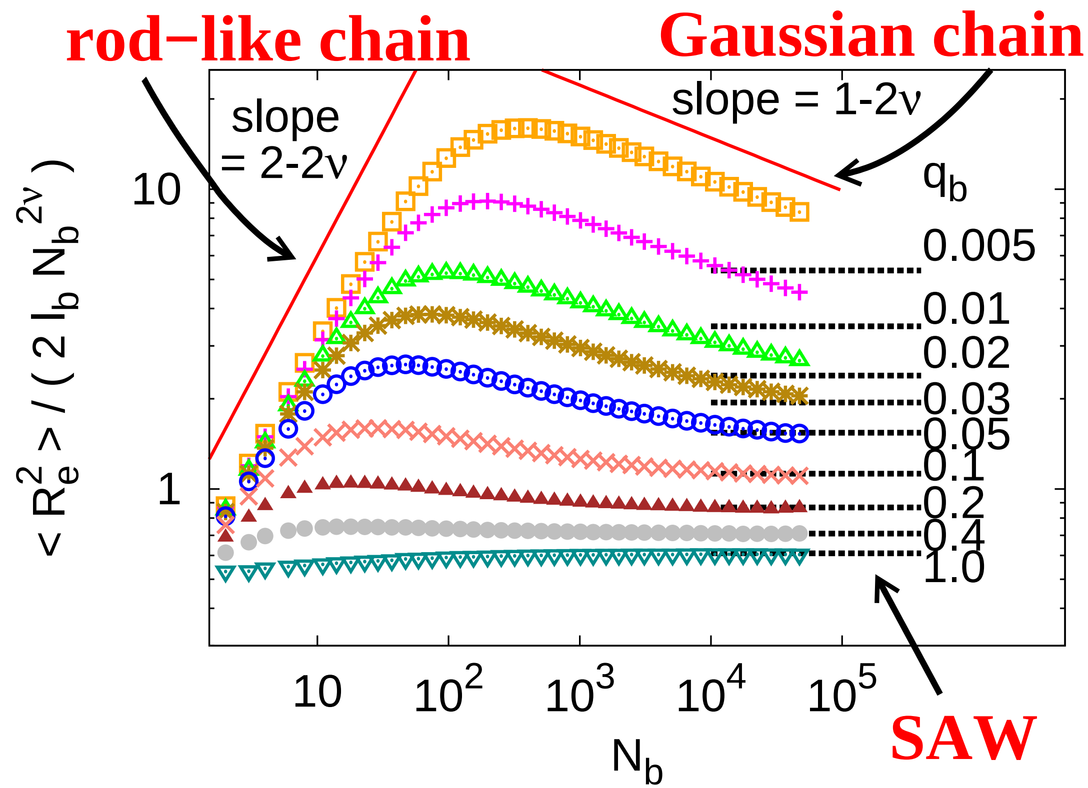
- Rod-like chains:

  $R_e^2 = L^2 = N_b^2 \ell_b^2 > \ell_K \ell_b N_b \Rightarrow N_b > \ell_K/\ell_b$

Evidence for the Netz-Andelman theory

- Semiflexible linear chains under good solvent conditions

$$\langle R_e^2 \rangle = 2\ell_{p,R}\ell_b N^{2\nu}, \quad \nu = 0.588$$



$$N_b = 50000\ !$$

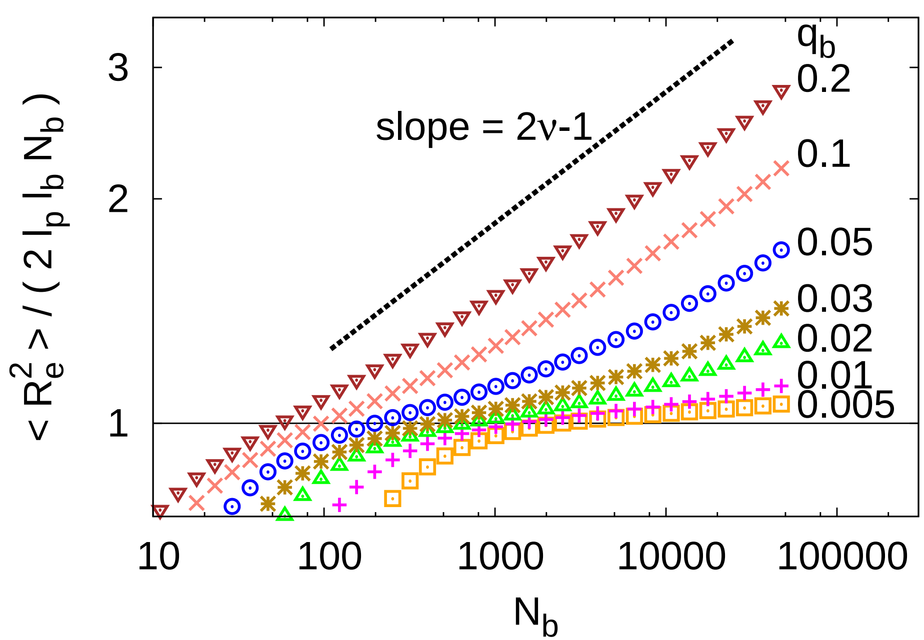
$\Rightarrow$ Netz-Andelman theory is useful for very stiff thin chains

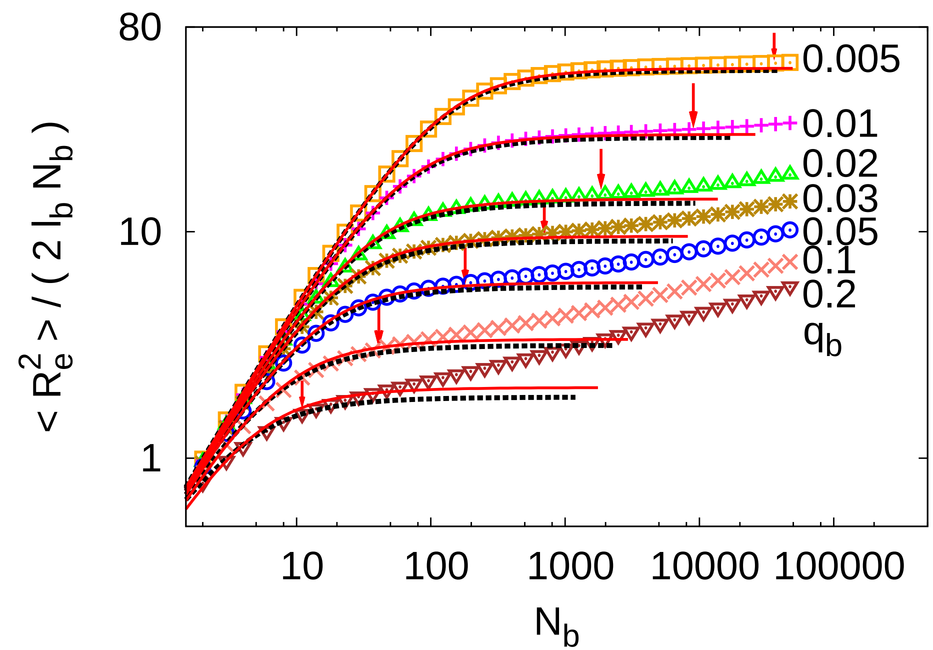
$$q_b \ll 1 \qquad \text{or} \qquad \ell_p \gg d$$

Crossover:

Gaussian chain $R_e^2 = 2\ell_p \ell_b N_b \Leftrightarrow R_e^2 = 2\ell_{p,R} \ell_b N_b^{2\nu}$ SAW

$\nu = 0.588$





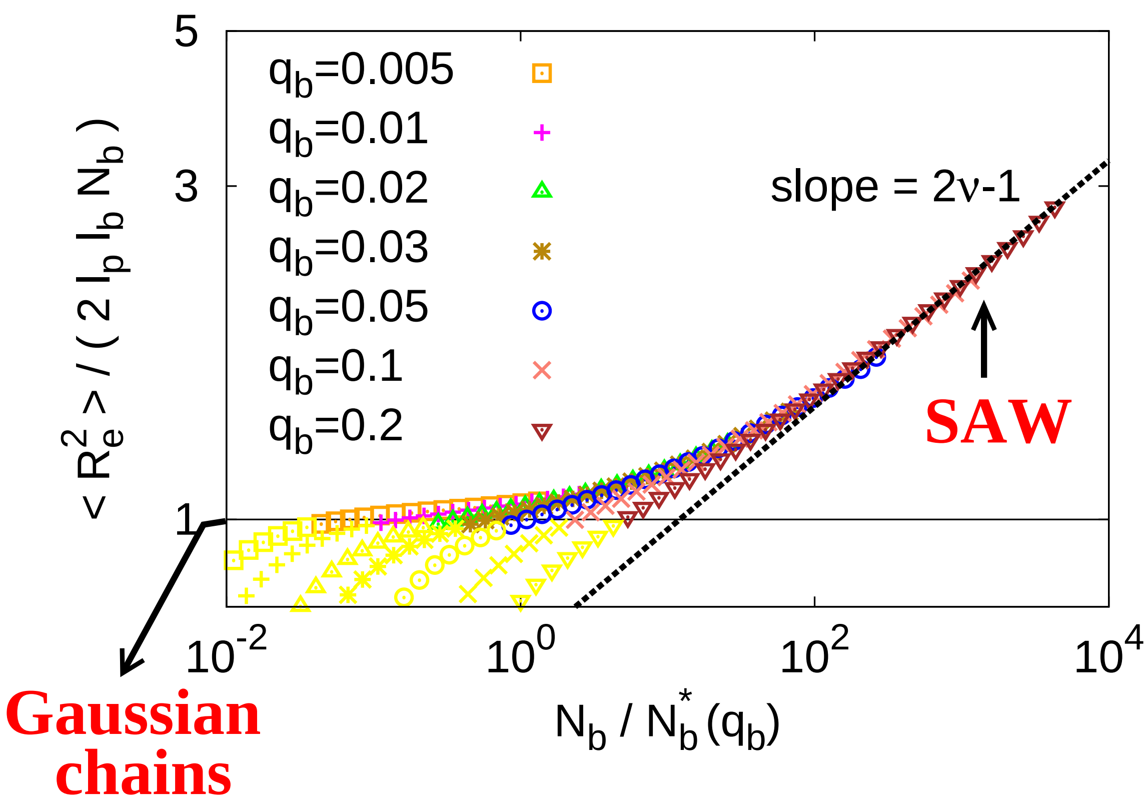
N_b^* : **crossover point**

(Gaussian chain <−> SAW)

Crossover:

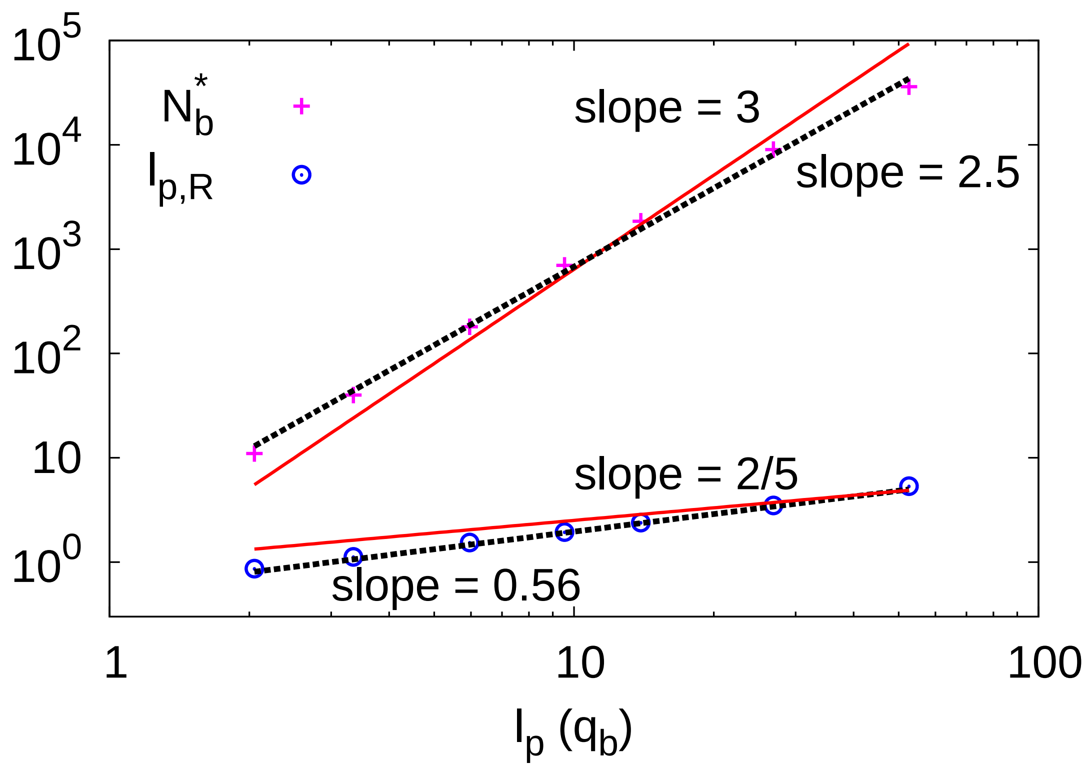
Gaussian chain $R_e^2 = 2\ell_p \ell_b N_b \Leftrightarrow R_e^2 = 2\ell_{p,R} \ell_b N_b^{2\nu}$ SAW

$\nu = 0.588$



$\ell_{p,R}$, N_b^* vs. ℓ_p

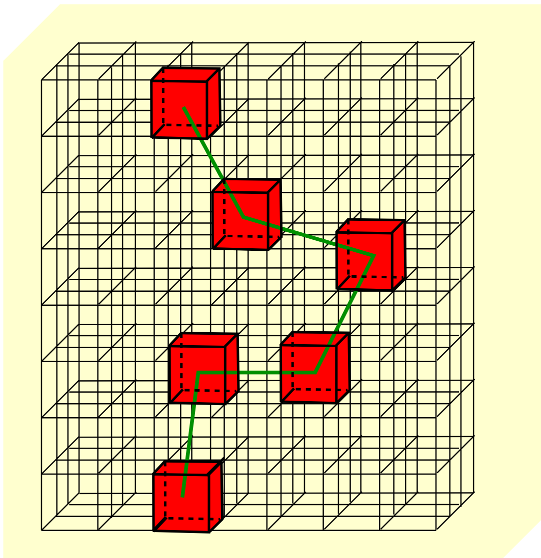
- Netz-Andelman theory $(\nu = 3/5)$:
  - $\ell_{p,R} \propto (\ell_p d)^{2/5}$
  - $N_b^* \propto {\ell_p}^3/(\ell_b d)^2$
- $\nu = 0.588$ (3DSAW)
  - $\ell_{p,R} \propto {\ell_p}^{0.56}$
  - $N_b^* \propto {\ell_p}^{2.5}$



Bottle-brush polymers

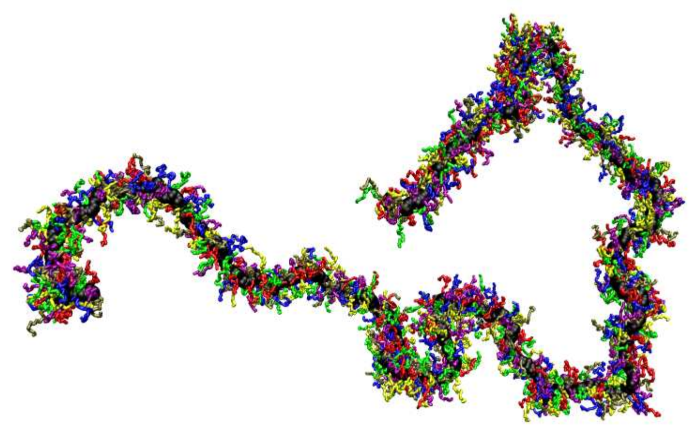
under good solvent conditions

- Bond-fluctuation model:



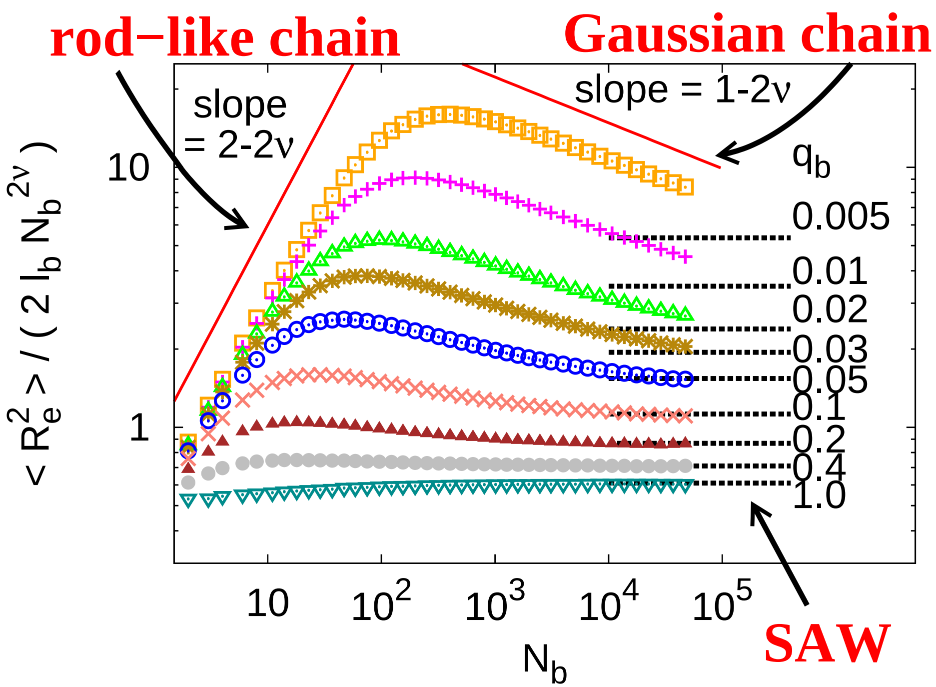
  - self-avoiding walks on a simple cubic lattice with bond constraints
  - 108 bond vectors $\vec{r}_b$ are from: [2,0,0], [2,1,0], [2,1,1], [2,2,1], [3,0,0], [3,1,0]
    $2 \le r_b \le \sqrt{10}$

- Backbone length $N_b = 1027$
  side chain length $N = 24$
  grafting density $\sigma = 1$

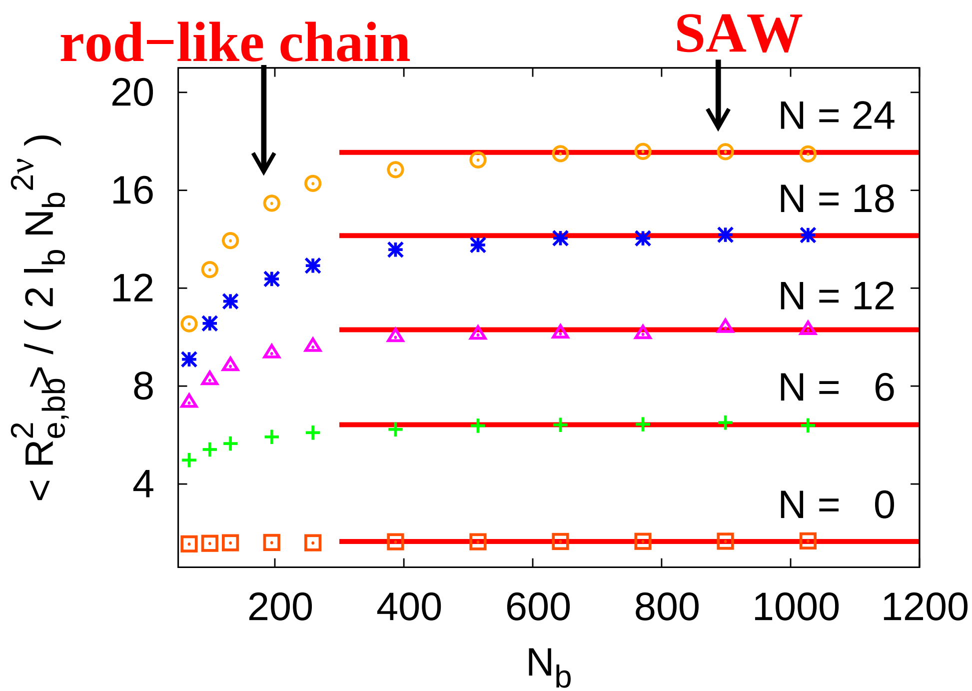


End-to-end distance R_e

- $\langle R_e^2 \rangle / (2\ell_b N_b^{2\nu})$ vs. N_b



semiflexible linear chains

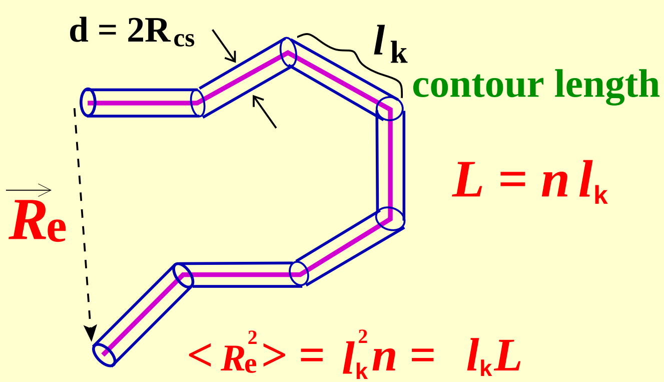


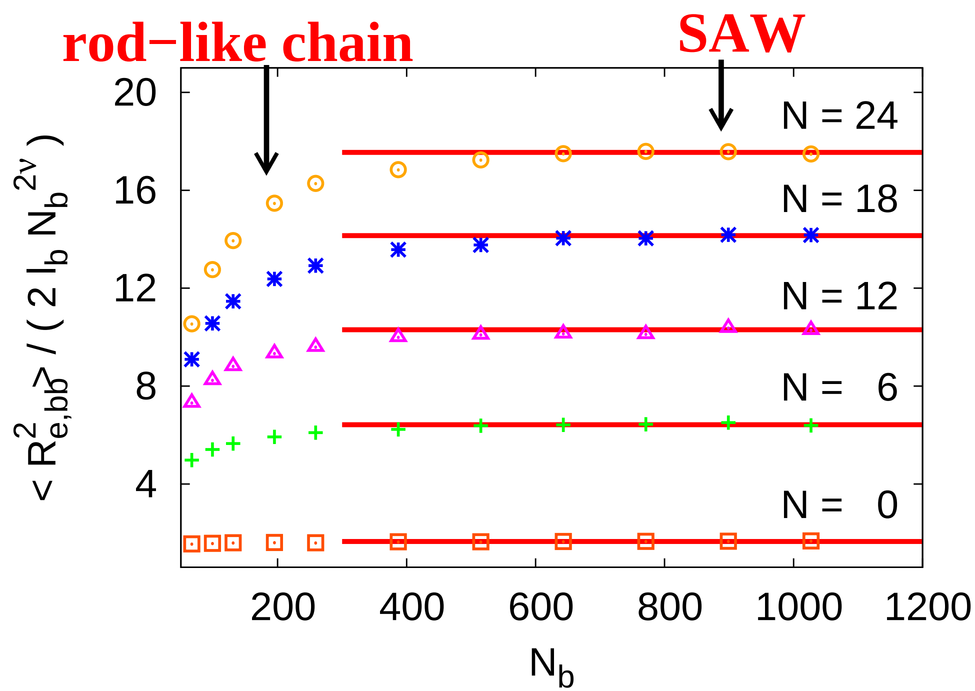
bottle-brush polymer

End-to-end distance R_e

- $\langle R_e^2 \rangle / (2\ell_b N_b^{2\nu})$ vs. N_b
- Gaussian regime: $\frac{\ell_K}{\ell_b} < N_b < \frac{\ell_K^3}{\ell_b d^2}\left(\frac{\ell_K}{d}\right)$
  (Netz-Andelman theory)

chain with n units of length l_k randomly linked:





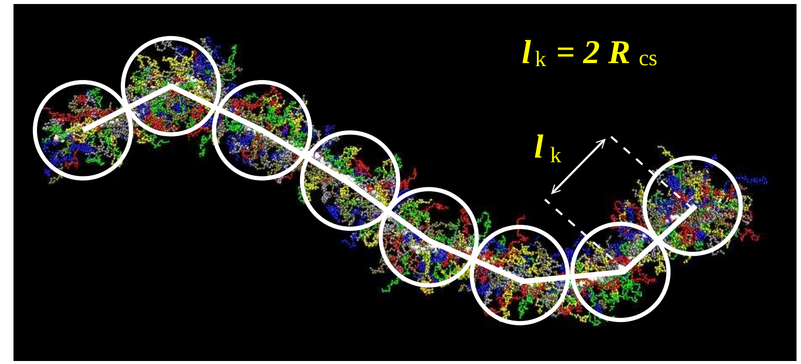
If $d = \ell_K$ effective beads

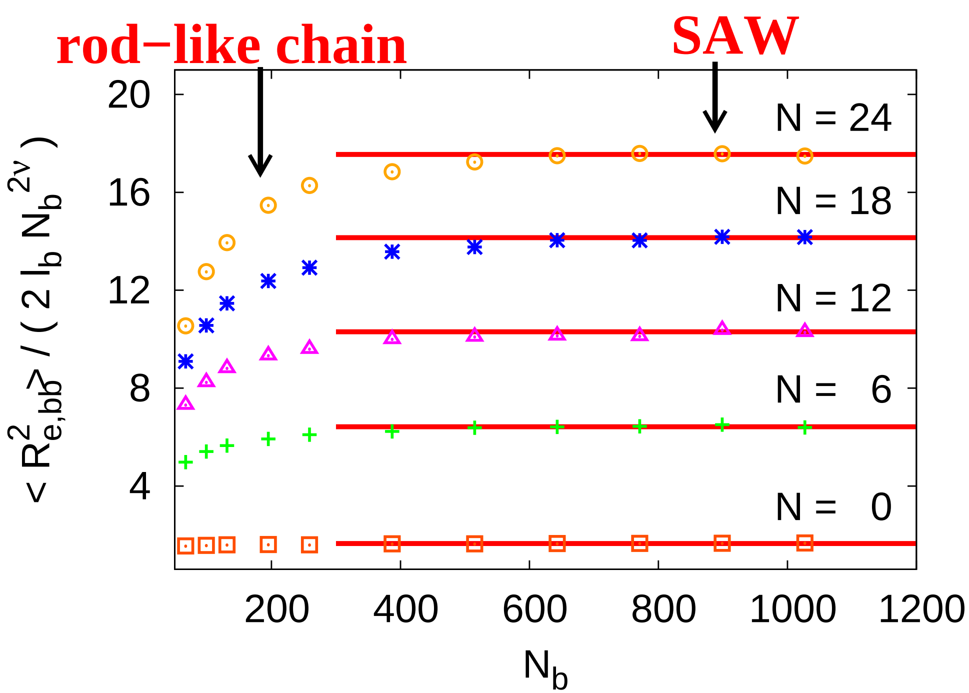
$\Rightarrow$ Gaussian regime is absent!

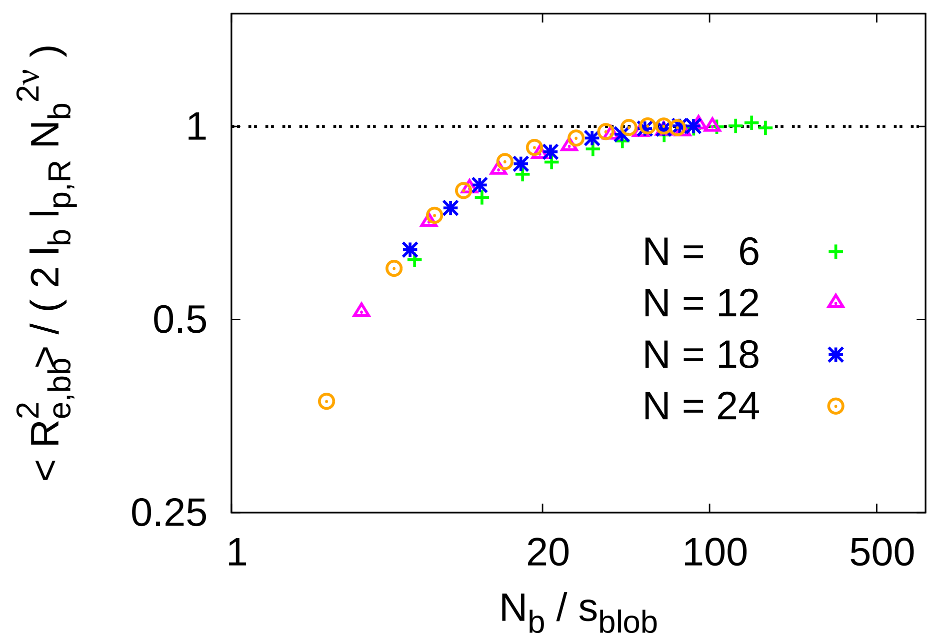
bottle-brush polymer

Coarse-grained view

- Mean square end-to-end distance $\langle R^2_{e,bb} \rangle = 2\ell_{p,R}\ell_b N_b^{2\nu}$
- Rescaling
  - $\langle R^2_{e,bb} \rangle \Rightarrow \langle R^2_{e,bb} \rangle / 2\ell_{p,R}\ell_b N_b^{2\nu}$
  - $N_b \Rightarrow N_b / s_{\text{blob}}$



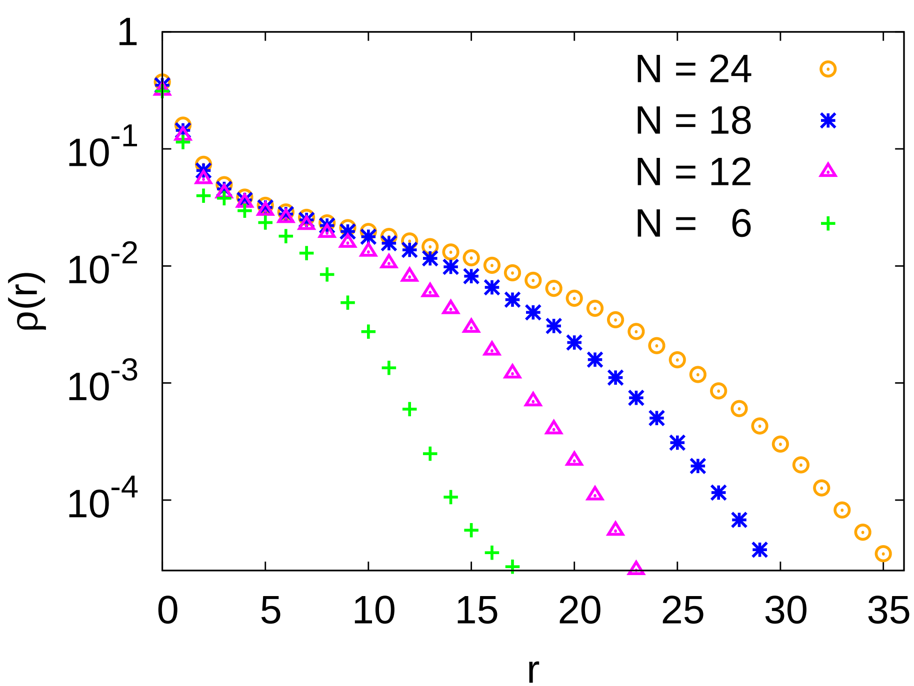


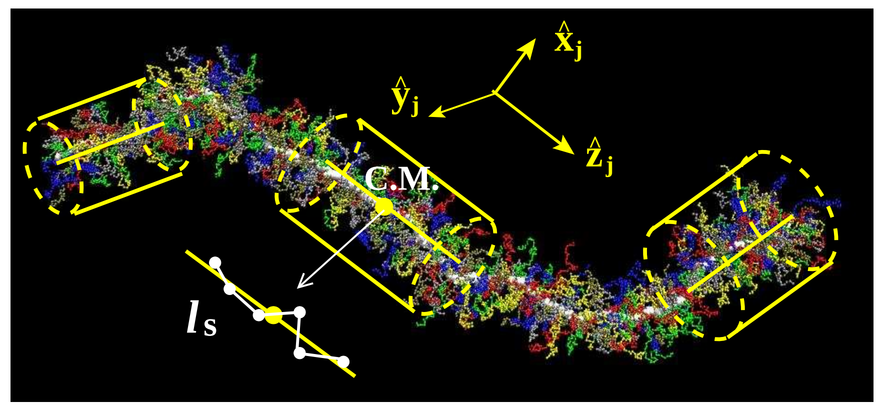


Blob chain length s_{blob}

- $\rho(r)$: radial monomer density profile

$\Rightarrow$ cross-sectional gyration radii $R_{cs}(N) = \left[\frac{\int r^3 dr \rho(r)}{\int r dr \rho(r)}\right]^{1/2}$





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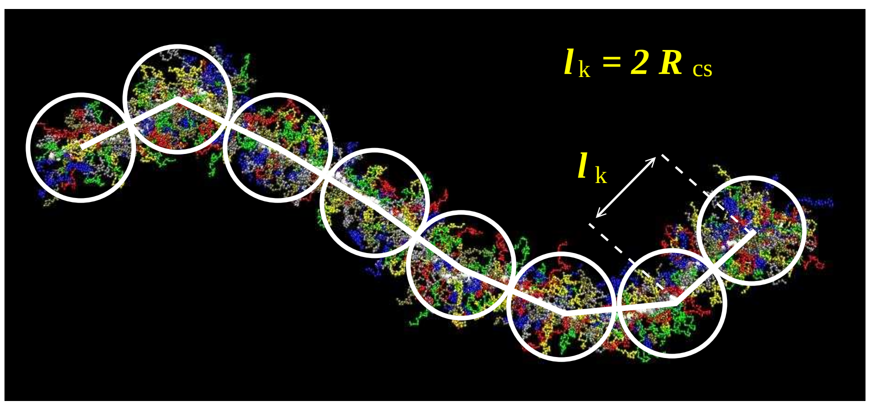
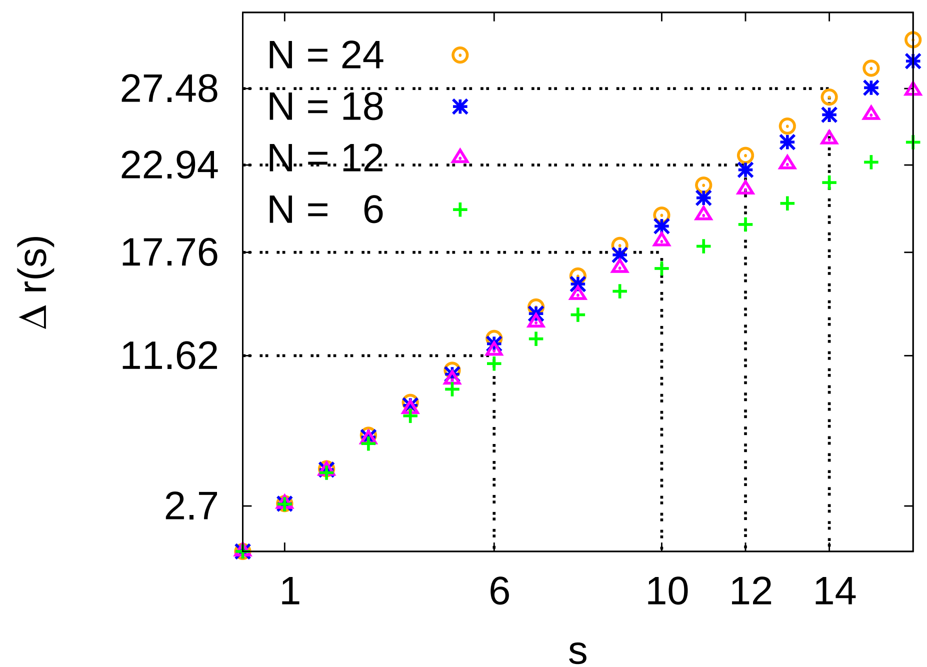
- $\Delta r(s)$: end-to-end distance of s subsequent monomers along the backbone

- $\Delta r(s = s_{\text{blob}}) = 2R_{\text{cs}}(N)$





Conclusions

- The Netz-Andelman theory for the semiflexible chains is verified (rod-like regime - Gaussian regime - SAW regime)
- The standard definition of persistence length, $\langle \cos \theta(s) \rangle \sim \exp(-s\ell_b/\ell_p)$ is of limited value i.e., apply only for Gaussian chains, not even for melts or chains at the Θ-point
- Bottle-brush polymers under good solvent conditions
  - Excluded volume effects remain important
  - Coarse-grained model exists - an effective bead-rod or bead-spring model of “blobs", $d = 2R_{cs}$
  - No pre-asymptotic Gaussian regime described by the Kratky-Porod worm-like chain model exists.

In two dimensions

Stiff polymers versus bottle-brush polymers

- Flory Theory

$$\Delta F \approx \frac{R_e^2}{\ell_K L}(\text{elastic energy}) + v_2 R_e^2 \left[\frac{L/\ell_K}{R_e^2}\right]^2 (\text{repulsive energy})$$

virial coefficient: $v_2 = \ell_K^2$ rather then $\ell_K d$

(all the shaded area is excluded for another stop of length ℓ_K)

  - minimize ΔF with respect to R_e:

    $\partial \Delta F / \partial R_e = 0 \Rightarrow R_e \approx (v_2/\ell_K)^{1/4} L^{3/4} = (\ell_K)^{1/4} (N_b \ell_b)^{3/4}$

  - find minimum length L where excluded volume is effective

    $\Rightarrow$ second term in ΔF of order unity, $R_e^2 = \ell_K L$

    $v(L/\ell_K)^2/(\ell_K L) = 1 \Rightarrow L^* = \ell_K^3/v_2 = \ell_K \Rightarrow$ rod-like chain

No preasymptotic Gaussian regime!

Bottle-brush polymers with a rigid backbone

- $\sigma = 2$: grafting density
  the comb polymer (SAW-model)
  fits an area $\sigma N_b N + N_b$
  $\Rightarrow$ rod-like chains

- $\sigma < \sigma_{\max} = 2$:
  every side chain only has an area $2N/\sigma$
  of rectangular shape $R_e \propto N$
  $\Rightarrow$ rod-like chains independent of σ,
  but $\langle R_{g,z}^2 \rangle \propto 1/\sigma$ independent of N!