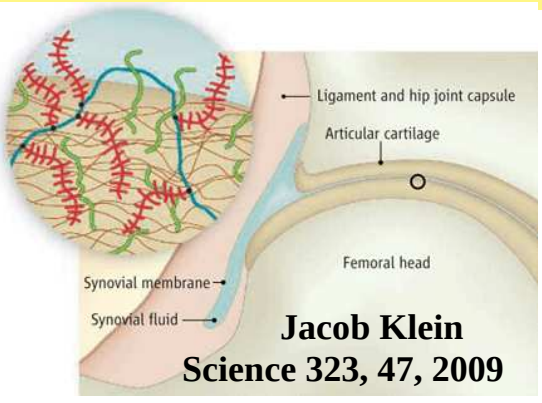
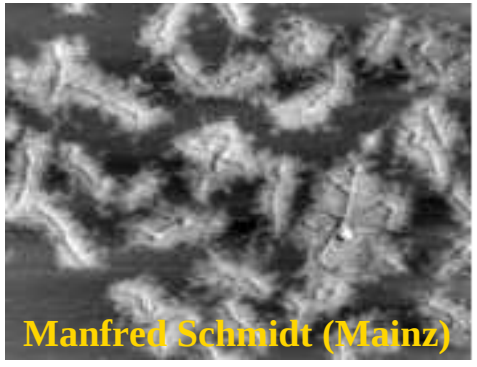


Jacob Klein
Science 323, 47, 2009


Manfred Schmidt (Mainz)

Structure Analysis of Bottle-Brush Polymers: Simulation and Experiment

Hsiao-Ping Hsu

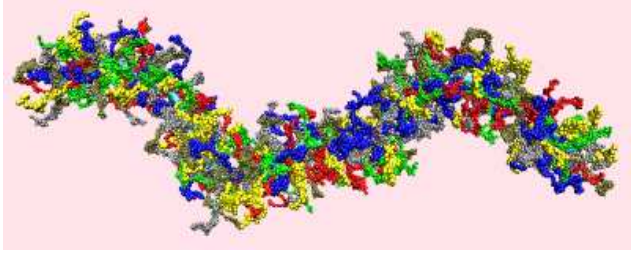

http://www.blueberryforest.com

Institut für Physik, Johannes Gutenberg-Universität Mainz, Germany

with

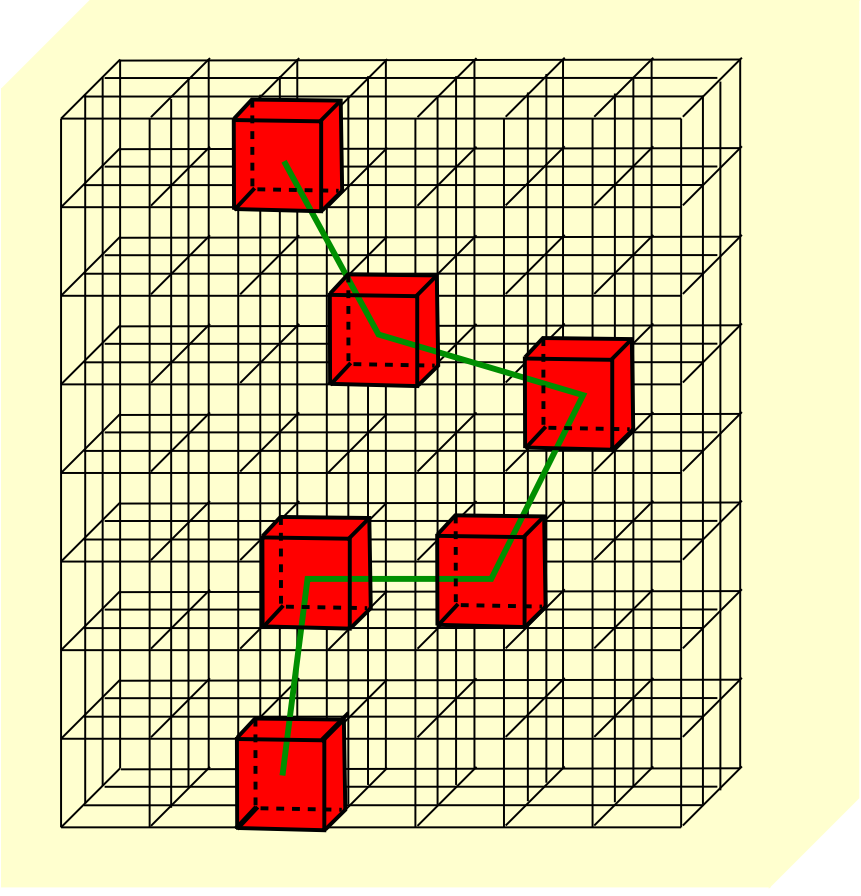
Wolfgang Paul (Mainz, Halle)

Silke Rathgeber, Kurt Binder (Mainz)



Model and Algorithm

- Bond fluctuation model:

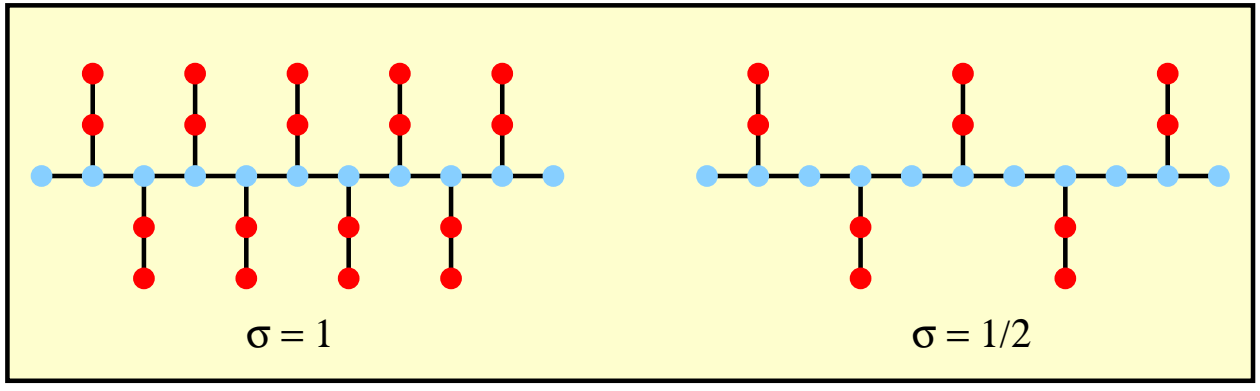


- self-avoiding walks on
  a simple cubic lattice
  with bond constraints
- 108 bond vectors $\vec{r}_b$ are from:
  [2,0,0], [2,1,0], [2,1,1],
  [2,2,1], [3,0,0], [3,1,0]

$$2 \leq r_b \leq \sqrt{10}$$

linear polymer chain $\Rightarrow$ bottle-brush polymer

- Geometry of bottle-brush polymers:



$N_{\mathrm{tot}} = N_b + n_c N$: total # of monomers

$N_b = [(n_c - 1)/\sigma + 1] + 2$: monomers in a backbone

N: monomers in a side chain

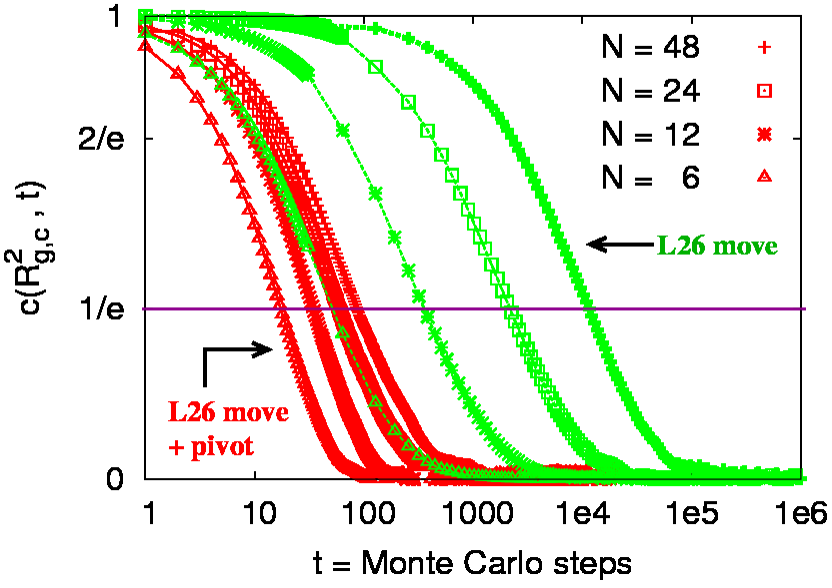
n_c: # of side chains, σ: grafting density

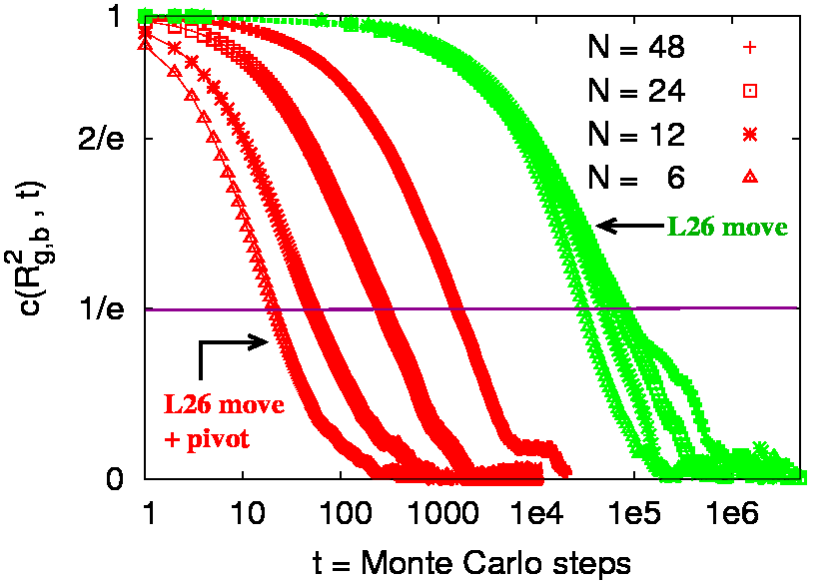
- Algorithm:

L26 move, pivot algorithm

Autocorrelation functions $c(A,t)$

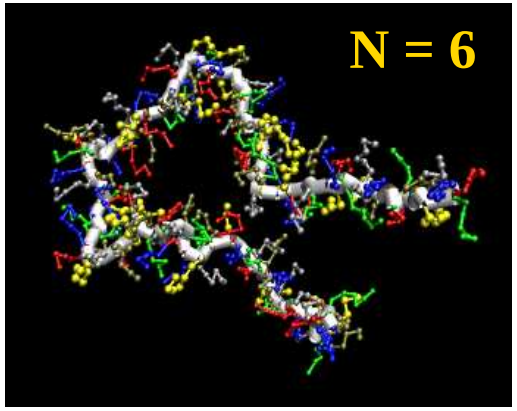
$$c(A,t) = \frac{< A(t_0)A(t_0+t) > - < A(t_0) >< A(t+t_0) >}{< A(t_0)^2 > - < A(t_0) >^2} .$$

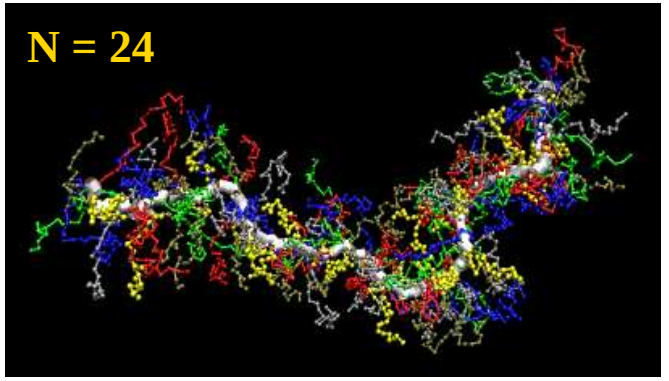


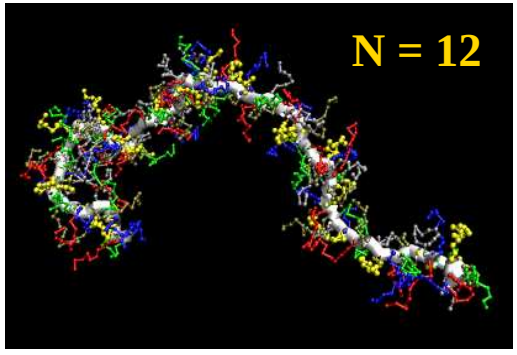


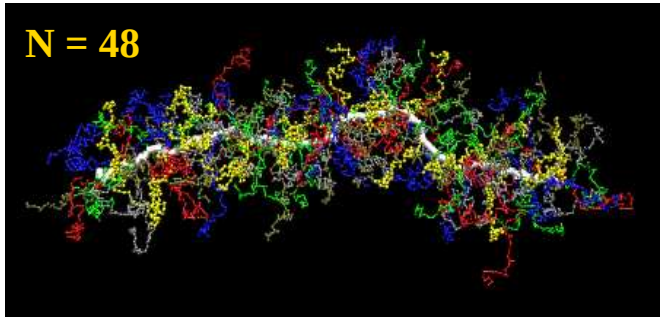
- $A = R^2_{g,c}$: square radius of gyration of side chain monomers
- $A = R^2_{g,b}$: square radius of gyration of backbone monomers

Snapshots: $N_b = 131, \sigma = 1$





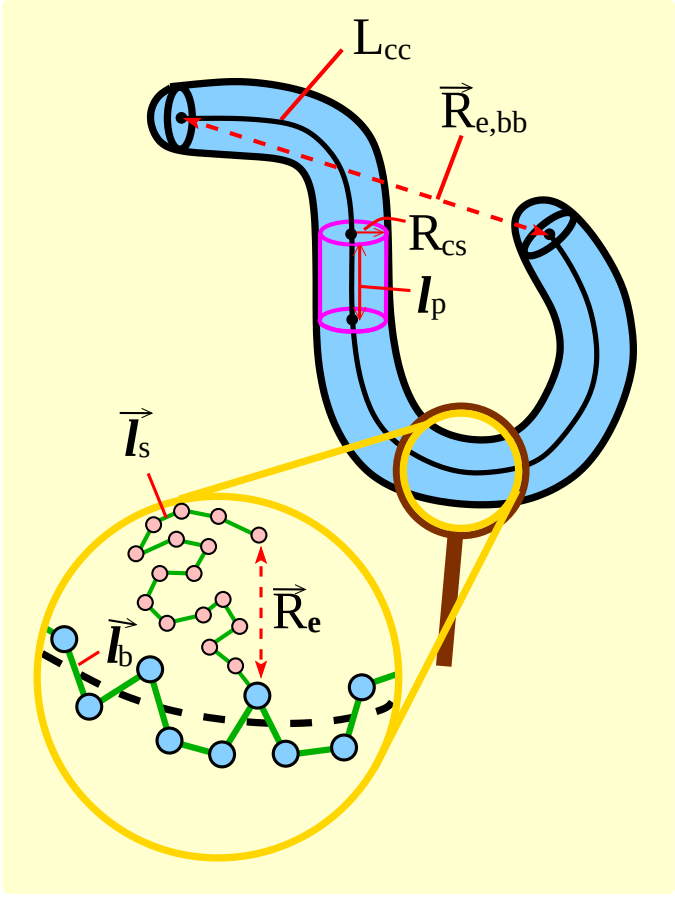




- backbone chain length N_b, side chain length N
- grafting density $\sigma \sim n_c/N_b$ (n_c: number of side chains)
- solvent quality: temperature, PH, ... (good solvent)

Structural characterization

Coarse-grained description of a bottle-brush polymer as a flexible spheocylinder:



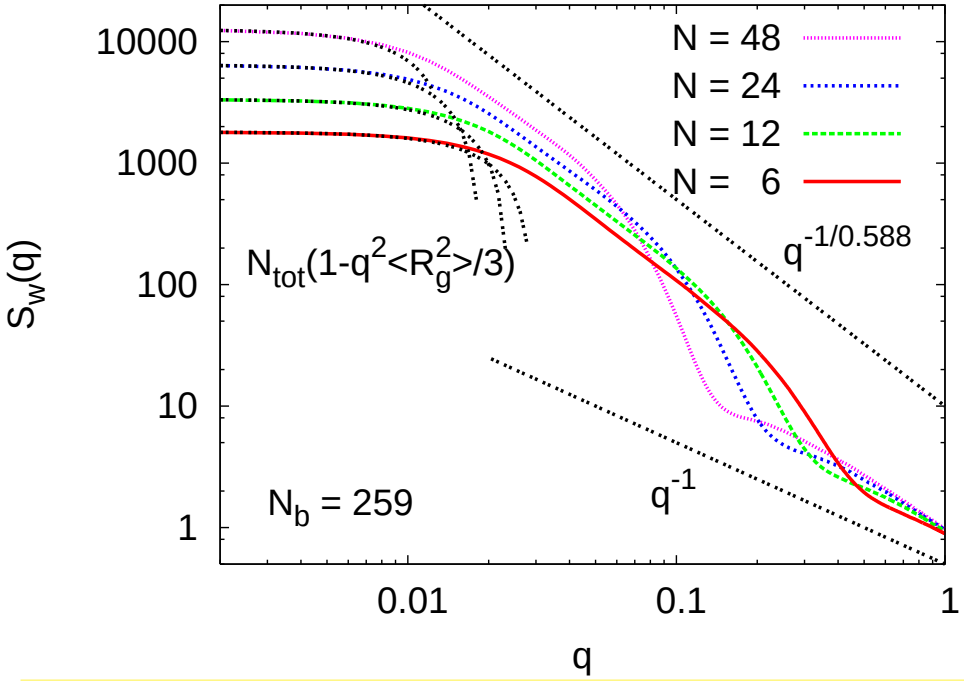
- L_{cc}: length of the axes of the cylinder
- $\vec{R}_{e,bb}$: end-to-end vector of the backbone chain
- R_{cs}: cross-sectional radius
- ℓ_p: persistence length
- $\vec{R}_e$: end-to-end vector of the side chain
- $\vec{\ell}_s$: bond vector connecting monomers in the side chains
- $\vec{\ell}_b$: bond vector connecting monomers in the backbone chain

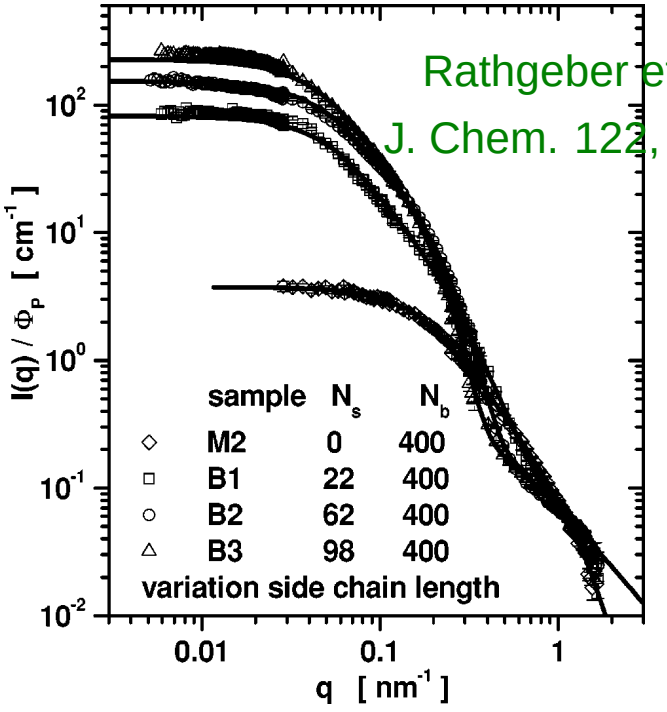
Structure factor $S_w(q)$

The structure factor for the bottle-brush polymers

$$S_w(q) = \frac{1}{\mathcal{N}_{tot}} \sum_{i=1}^{\mathcal{N}_{tot}} \sum_{j=1}^{\mathcal{N}_{tot}} < c(\vec{r}_i) c(\vec{r}_j) > \frac{\sin(q \mid \vec{r}_i - \vec{r}_j \mid)}{q \mid \vec{r}_i - \vec{r}_j \mid}$$

$c(\vec{r}_i) = 1$ (0) if $\vec{r}_i$ is occupied (unoccupied)





Rathgeber et. al.,
J. Chem. 122, 124904 (2005)

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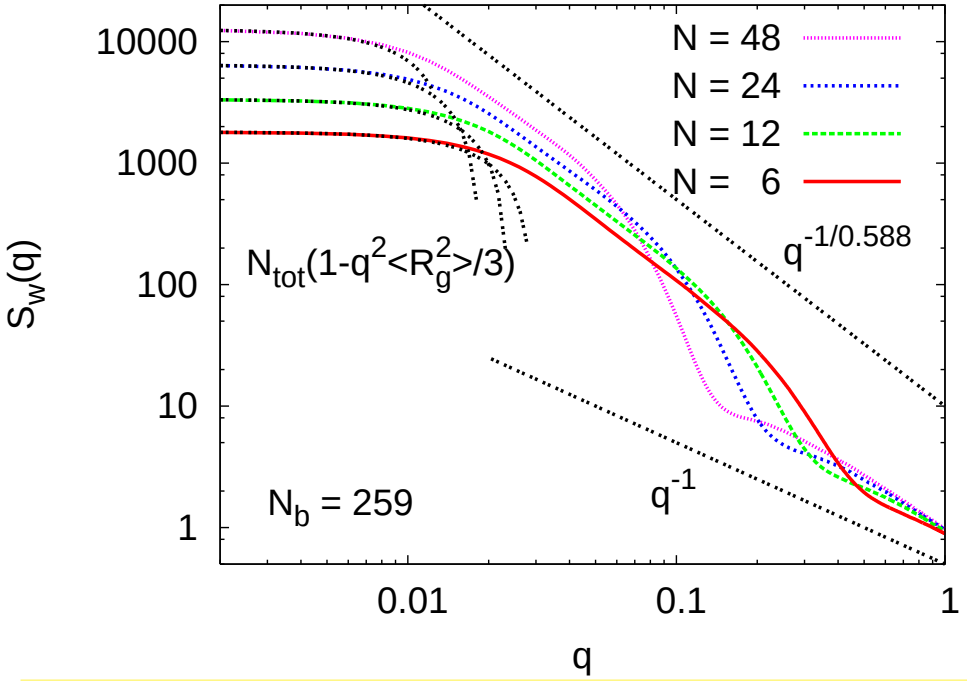
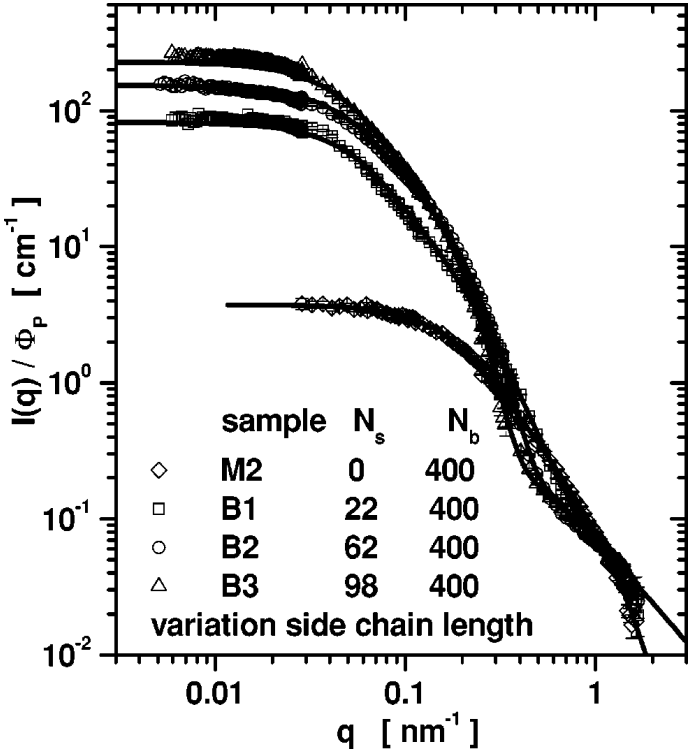


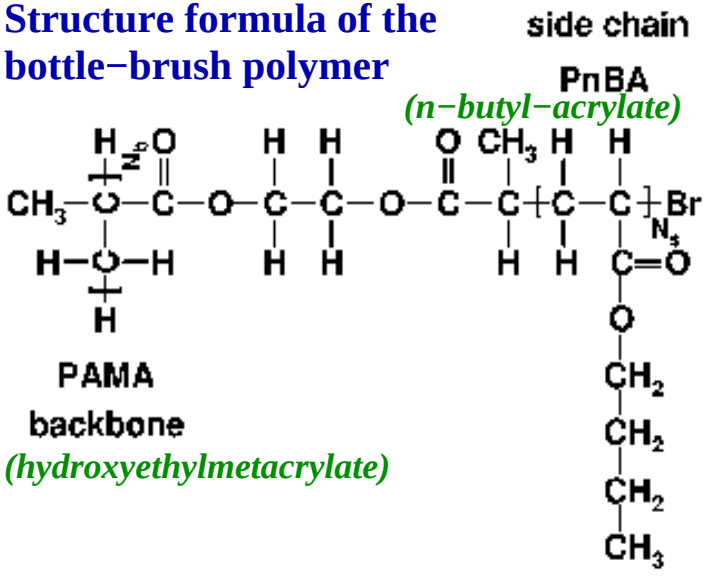
- small q (Guinier regime):
  $S_w(q) \approx \mathcal{N}_{tot}[1 - q^2 < R^2_{g,bb} > /3]$
- intermediate q-value:
  $S_w(q) \propto q^{-1/\nu}, \nu = 0.588$
- large q: almost rigid segments

- Experimental results: ($\sigma \approx 1$, good solvent)

(Rathgeber et. al., J. Chem. 122, 124904 (2005))



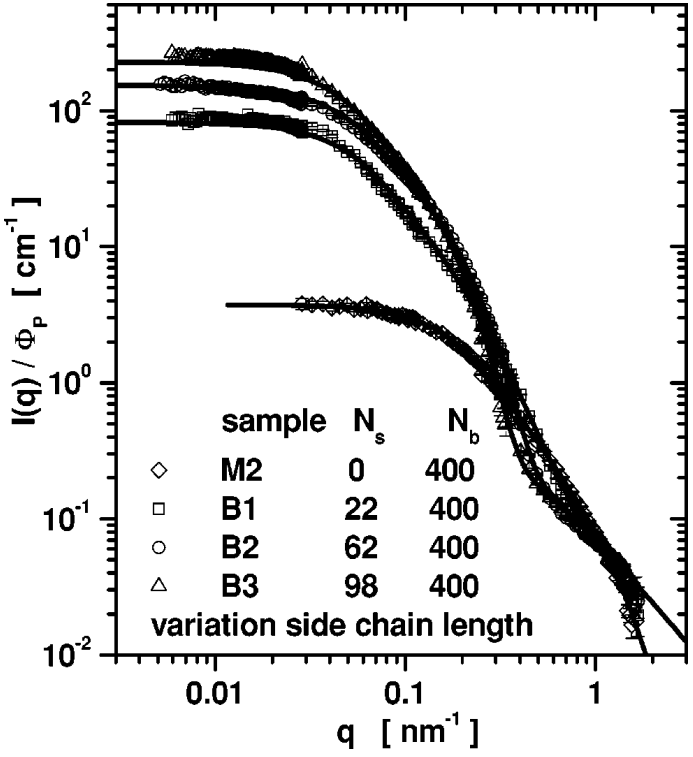
Structure formula of the bottle−brush polymer



- Techniques: static light scattering, small angle neutron scattering, x-ray scattering

- Experimental results: ($\sigma \approx 1$, good solvent)

(Rathgeber et. al., J. Chem. 122, 124904 (2005))

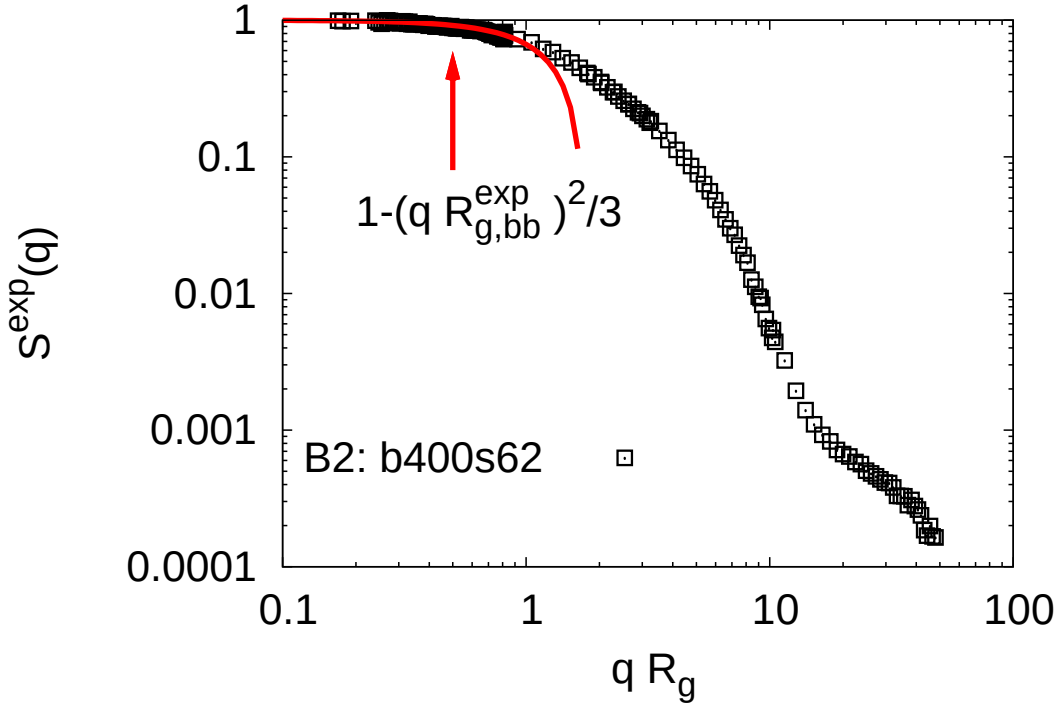


	Backbone chain length	Side chain length
Exp	(N_b^{exp}	N^{exp})
Simulation	(N_b	N)

- Techniques: static light scattering, small angle neutron scattering, x-ray scattering

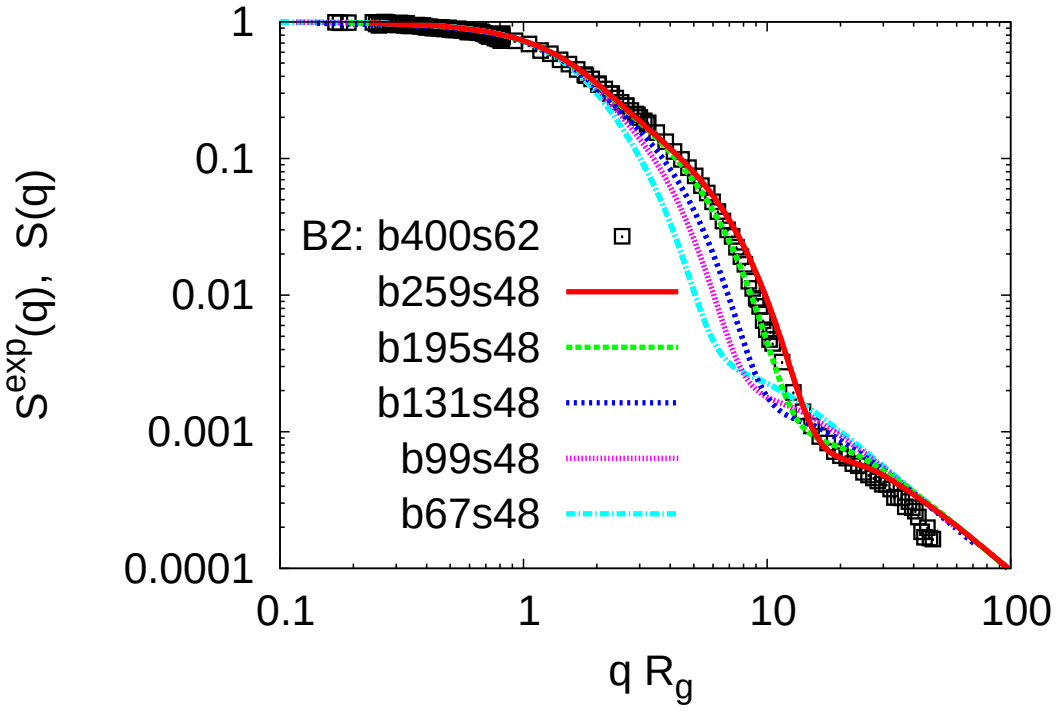
Exp. and sim.: $S(q)$

- $S^{\mathrm{exp}}(q \to 0) = 1$
- $q \to qR$, $R_{g,bb}^{\mathrm{exp}} \approx 30.5$ nm (Guinier formula)



$$R_g = \langle R_g^2 \rangle^{1/2}$$

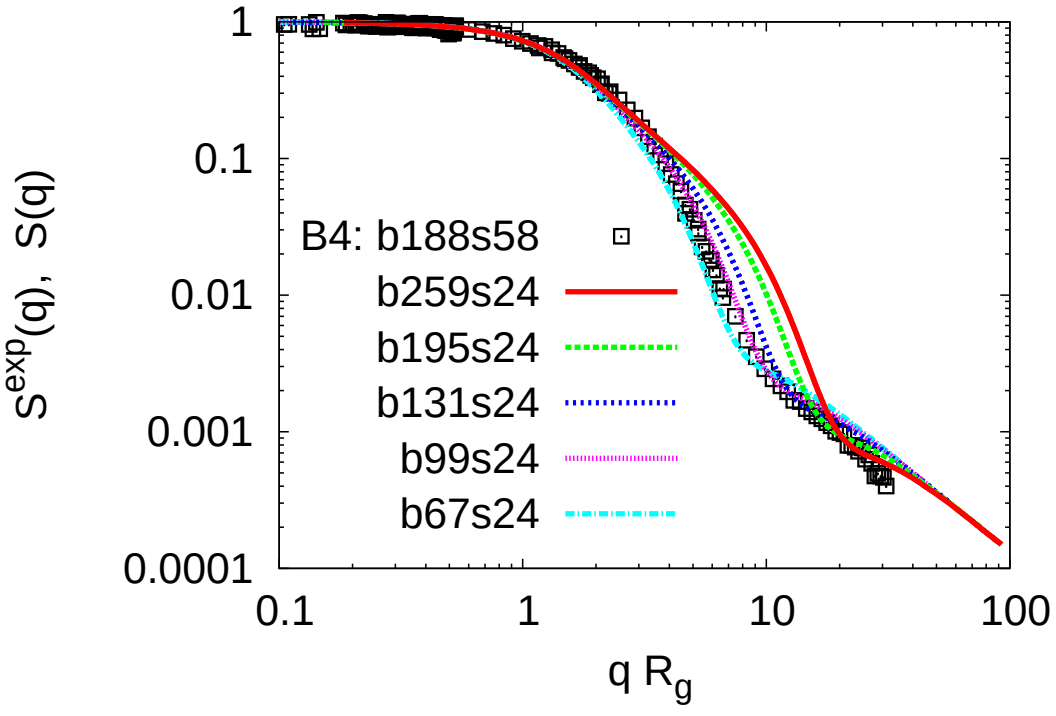
Exp. and sim.: $S(q)$



- Exp. (b400s62): $N_b = 400$, $N = 62$, $R_{g,bb}^{\mathrm{exp}} = 30.5$ nm
- Sim. (b259s48): $N_b = 259$, $N = 48$, $R_{g,bb} = 115.8$ lattice spacing

$\Rightarrow$ 1 nm $\approx$ 3.79 lattice spacing

Exp. and sim.: $S(q)$



- Exp. (b188s58): $N_b = 188$, $N = 58$, $R_{g,bb}^{\mathrm{exp}} = 21$ nm
- Sim. (b99s24): $N_b = 99$, $N = 24$, $R_{g,bb} = 46.94$ lattice spacing

$\Rightarrow$ 1 nm $\approx$ 2.235 lattice spacing

Radial density profile $\rho_{cs}(r)$

Assumptions in the analysis of experimental data:

- Gaussian profile: $\rho_{cs}(r) \propto \exp(-r^2/\langle R^2_{g,cs}\rangle)$

  $\langle R^2_{g,cs}\rangle = 2\pi \int_0^\infty r dr \rho_{cs}(r) r^2$, $2\pi \int_0^\infty r dr \rho_{cs}(r) = 1$

- Decoupling approximations for the scattering data:

  $$S_w(q) \approx S_b(q) S_{cs}(q)$$

  - Scattering function of the backbone $S_b(q)$:

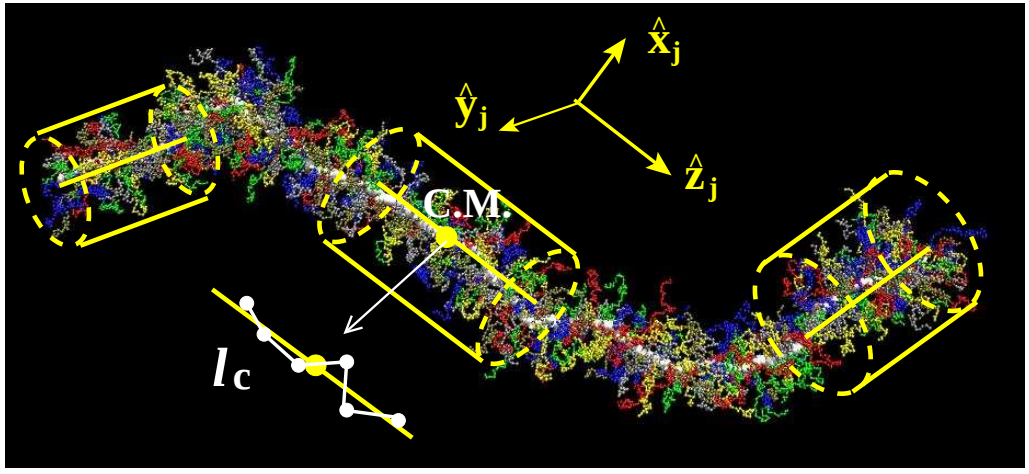
    $S_b(q) = [1 - \chi(q)] S_{\text{SAW chain}}(q) + \chi(q) S_{\text{rod}}(q)$

  - Cross sectional scattering $S_{cs}(q)$:

    $S_{cs}(q) = [2\pi \int_0^\infty dr r \rho_{cs}(r) J_0(qr)]^2$

    $J_0(r)$: the zeroth order Bessel function

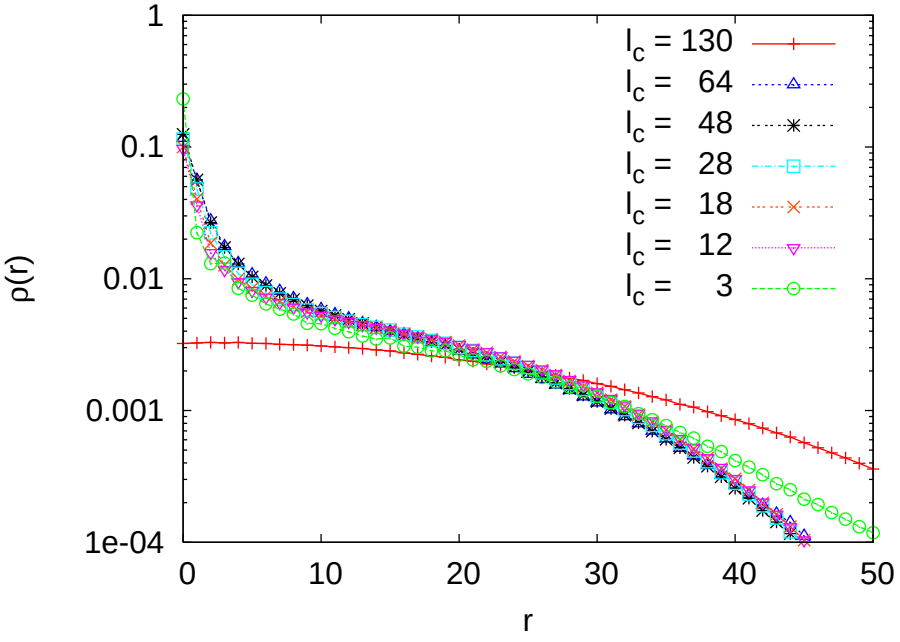
Simulations: $\rho(r)$



backbone:
undulating line

- On a coarse-grained scale $l_c \Rightarrow$ cylindrical-like object (straight rigid backbone of $l_c + 1$ monomers)
  - direction $\hat{z} = \frac{1}{l_c} \sum_i^{l_c} \hat{e}_i$ going through C.M.
  - length: $R_e^c = \| \vec{r}_{n+l_c} - \vec{r}_n \|$
  - Monomers located within this cylinder segment are counted

$$\rho(r) = \frac{1}{n_s}\left\langle \sum_{j=1}^{n_s} \rho_j(r) \right\rangle \ , \ n_s = \frac{N_b}{\ell_c}$$



$$(N_b = 131, N = 48)$$

- For each cylindrical-like object j:

  $\rho_j(r) = \frac{N(r)}{N_r}$, $\sum_r N(r) = N$

  $N(r)$: # of monomers in the interval $[r, r + dr]$

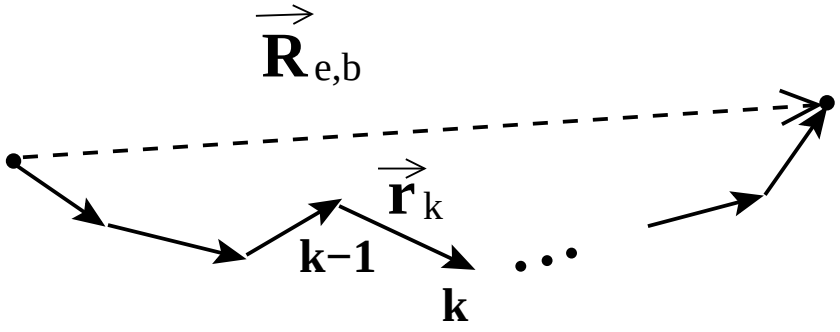
  N_r: # of lattice sites (x_j, y_j) satisfying the constraint $r^2 = x_j^2 + y_j^2$

$\Rightarrow \ell_c \sim \ell_p$ (persistence length)

Persistence length of backbone

- $l_p^{(k)}$: the projection of the end-to-end vector, $\vec{R}_{e,b}$, on the segment vector $\vec{r}_k$:

$$l_p^{(k)} = \left\langle \frac{\vec{r}_k}{\mid \vec{r}_k \mid} \cdot \vec{R}_{e,b} \right\rangle$$



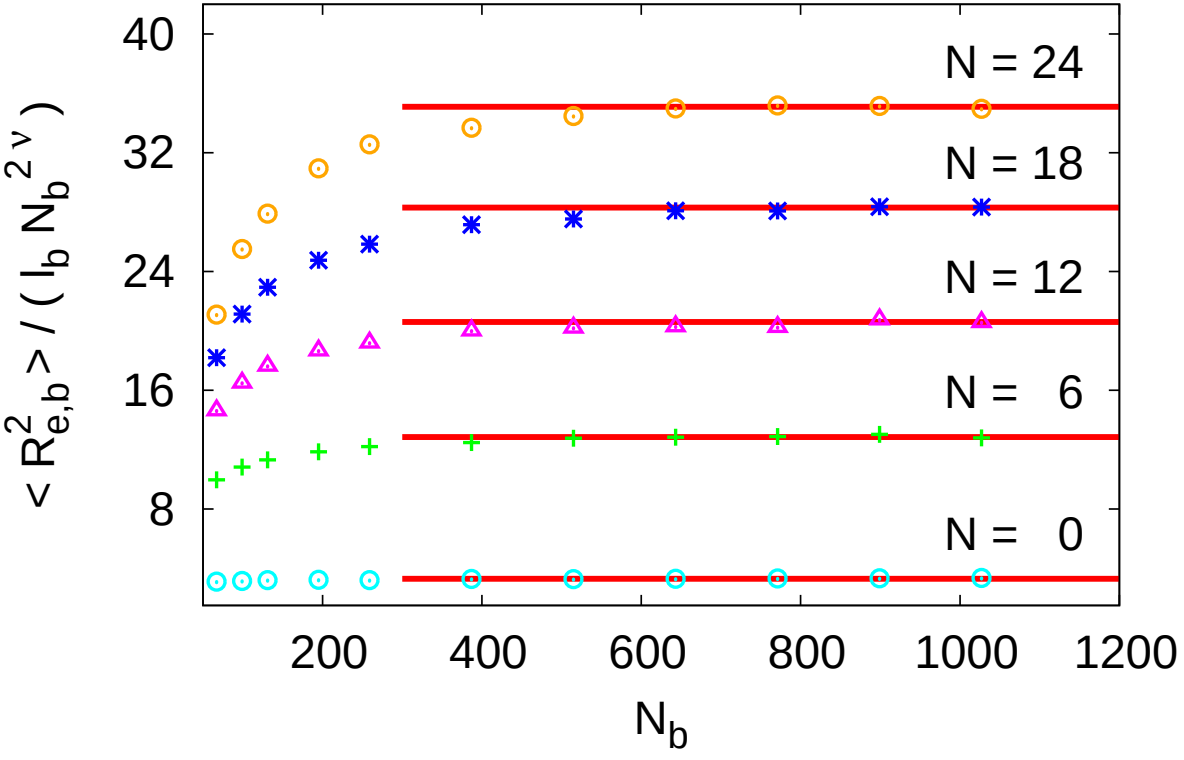
- l_s: the length over which correlations in the direction of the tangent are lost.

$$< \cos\theta(s) > \; = \; \left\langle \frac{1}{N_b - 1 - s} \sum_{i=1}^{N_b - 1 - s} \vec{u}_i \cdot \vec{u}_{i+s} \right\rangle \; , \vec{u}_i = \frac{\vec{r}_i}{\mid \vec{r}_i \mid}$$

$$\sim \; e^{-s/l_s} \; (\mathrm{worm-like\,chain})$$

Persistence length ℓ_p:

- Scaling law of mean square end-to-end distance of the back-bone: $R^2_{e,b}(N) = 2\ell_p \ell_b N_b^{2\nu}$ as $N_b \to \infty$

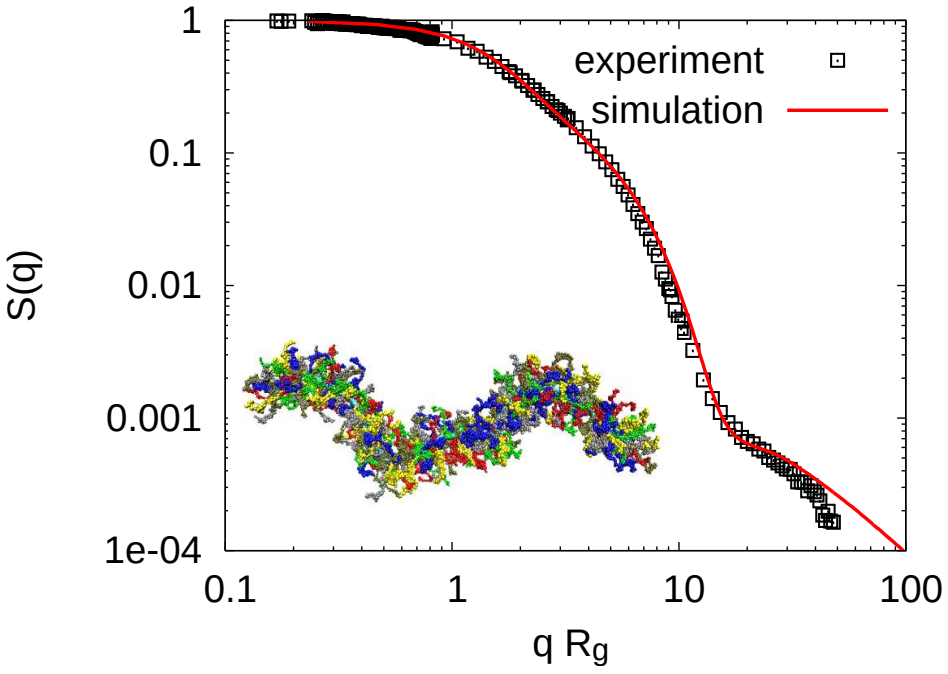


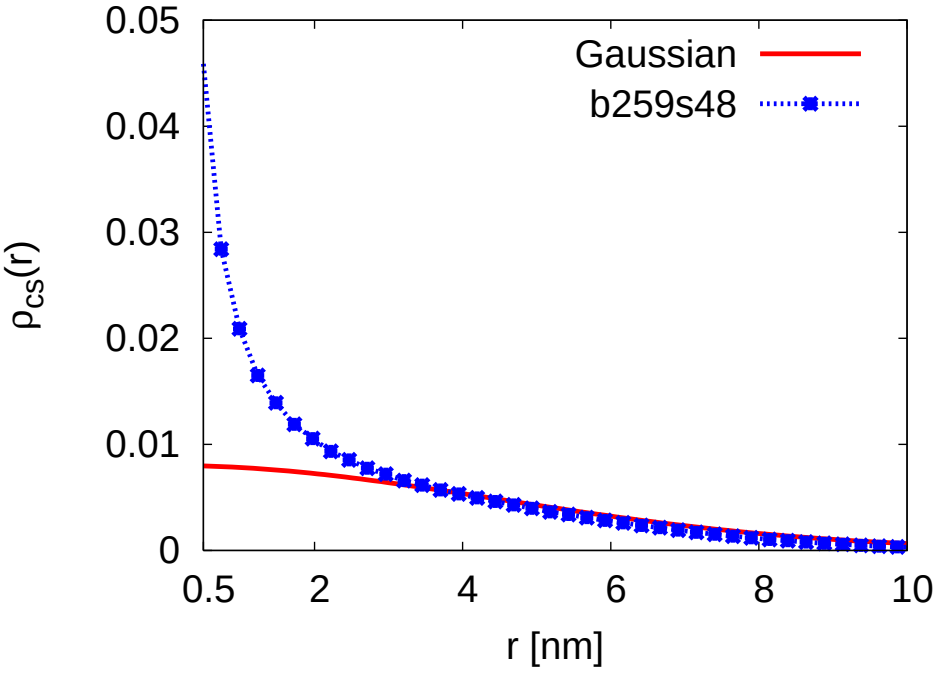
N: side chain length

$\nu \approx 0.588$ (3D SAW)

$\Rightarrow$ Local intrinsic stiffness of the backbone of bottle-brush polymer

Exp. and Sim.: $S(q)$, $\rho_{\mathrm{cs}}(r)$, $R_{g,\mathrm{cs}}$





- Experiment ($N_b = 400$, $N = 62$): $R_{g,\mathrm{cs}} = 6.30$ nm
- Simulation ($N = 259$, $N = 48$): $R_{g,\mathrm{cs}} = 5.04$ nm

JOHANNES GUTENBERG UNIVERSITÄT MAINZ

References:

- "*How to Define Variation of Physical Properties Normal to an Undulating One-Dimensional Object*", phys. rev. lett. 103, 198301 (2009).
- "*Characteristic Length Scales and Radial Monomer Density Profiles of Molecular Bottle-Brushes: Simulation and Experiment*", preprint (2009).
- "*Standard Definitions of Persistence Length Do Not Describe the Local "Intrinsic" Stiffness of Real Polymer Chains*", preprint (2009).

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