Structure of bottle-brush polymers in solutions: a Monte Carlo study

Hsiao-Ping Hsu, Wolfgang Paul, and Kurt Binder

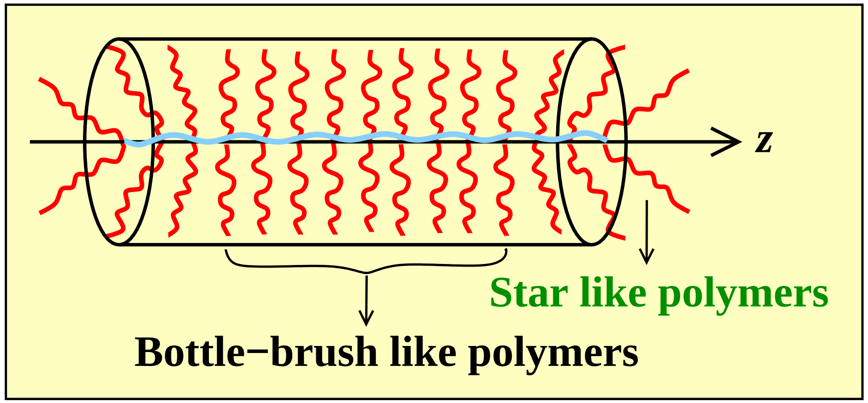
Institut für Physik, Johannes Gutenberg-Universität Mainz

D-55099 Mainz, Staudinger Weg 7, Germany

Outline

Bottle-brush polymers:

- Comb copolymers with high grafting densities of side chains



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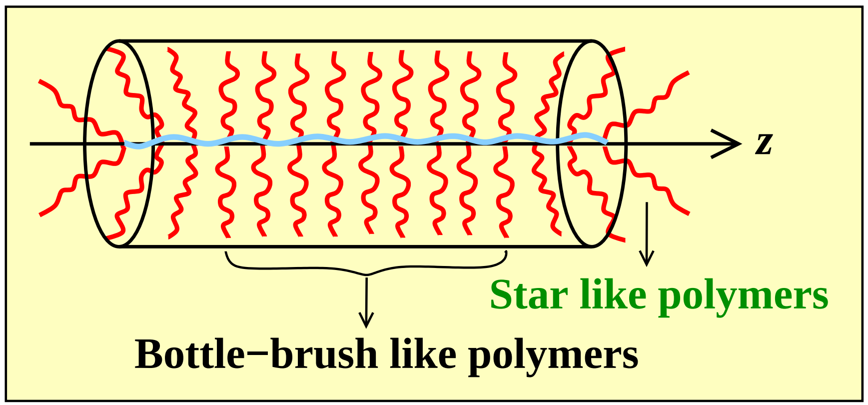
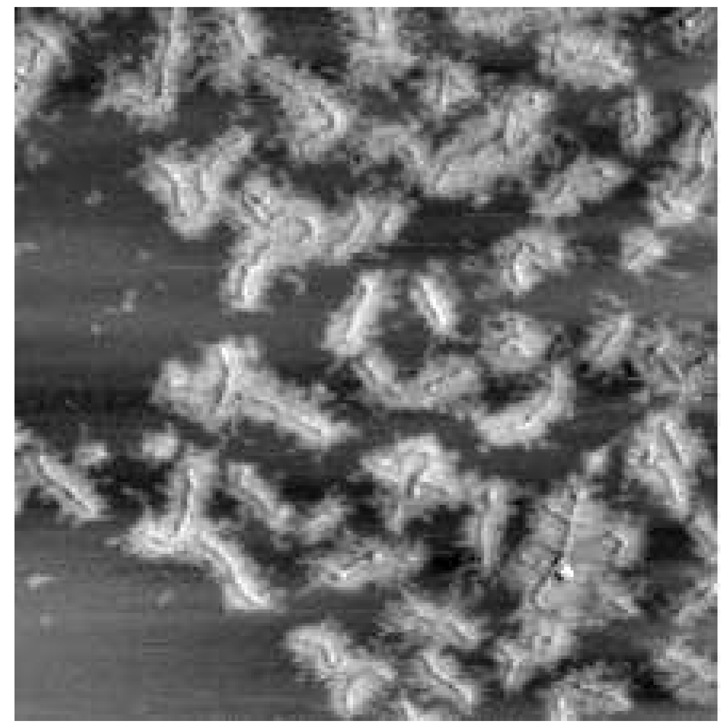
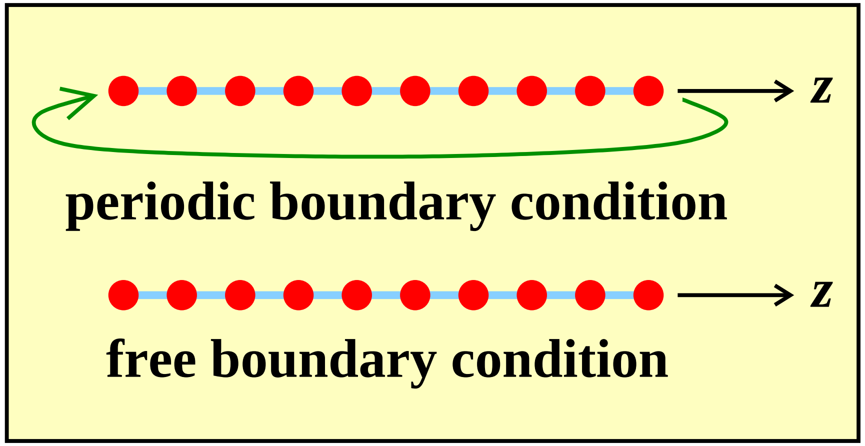


- Properties
  - Solvent quality, PH, or temperature



Prof. Schmidt / Univ. Mainz

- Monte Carlo simulations $\Rightarrow$ structure and conformation
  straight rigid backbones (p.b.c & f.b.c.),
  flexible side chains



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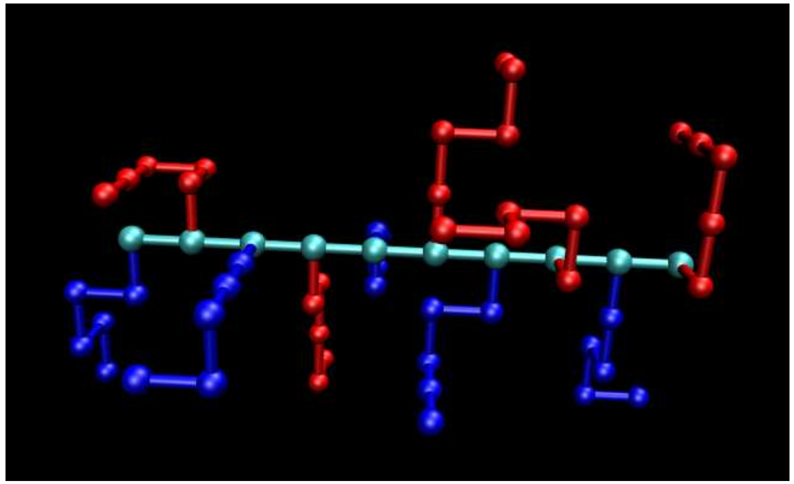


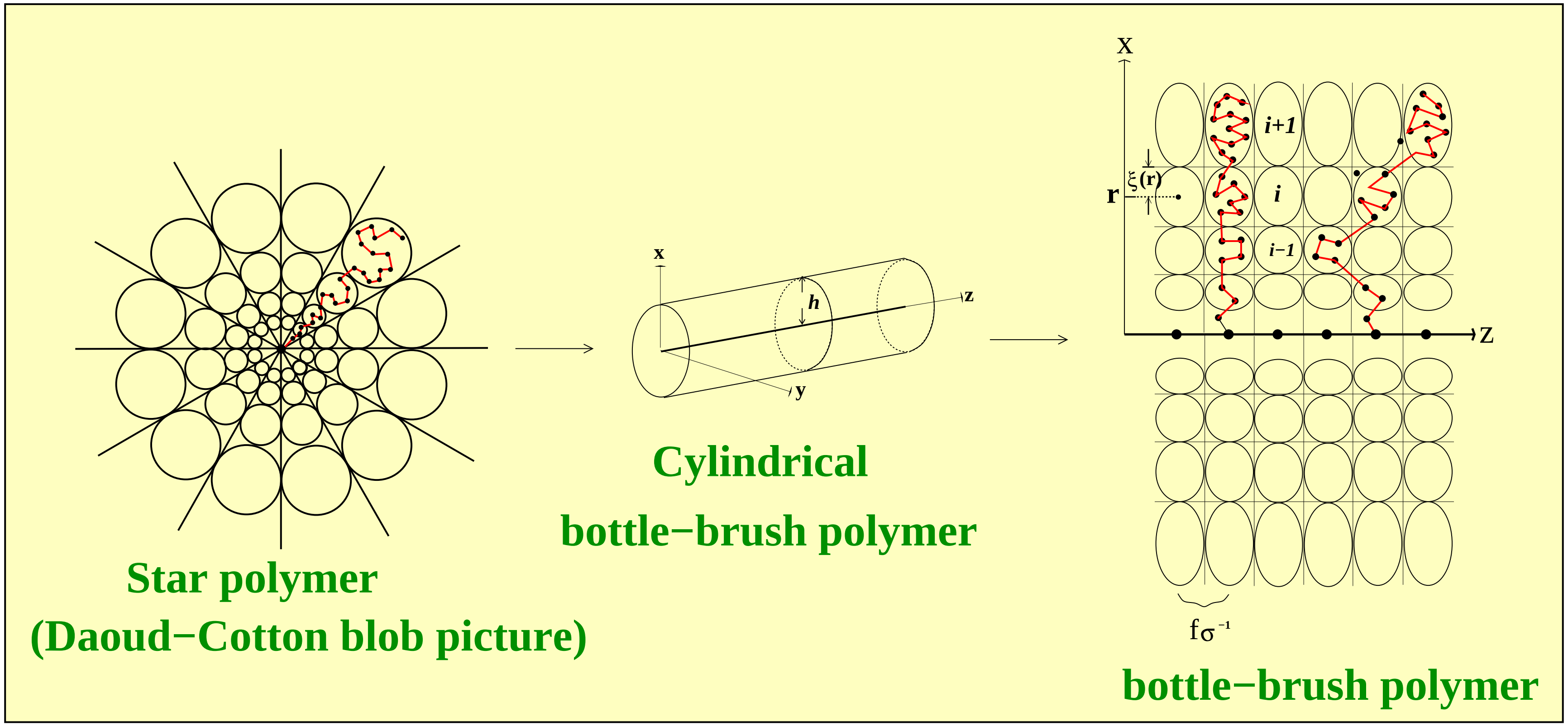
  - Coarse-grained model:
    self-avoiding walks on
    a simple cubic lattice
  - Good and Theta solvents:
    excluded volume effect,
    attractions between non-bonded monomers
  - Pruned-enriched Rosenbluth method

    Grassberger, Phys. Rev. E56, 3682 (1997)

    Hsu, Paul & Binder, Macromol. Theory Simul., 16, 660 (2007)

Theory

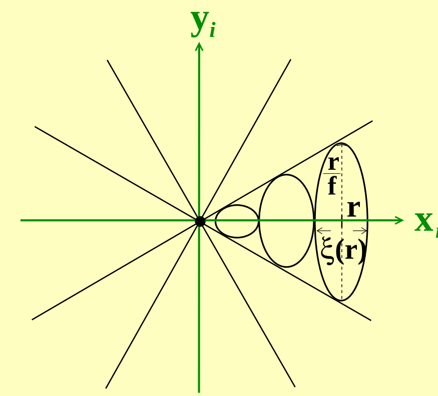
- Blob pictures of polymers in a good solvent



Star polymer
(Daoud−Cotton blob picture)

Scaling predictions

Hsu, Paul, & Binder, Macromol. Theory & Simul. 16, 660 (2007)



Bottle−brush polymer
(blob picture)

- Height of the bottle brush:

  $$h \propto \sigma^{(1-\nu_3)/(1+\nu_3)} N^{2\nu_3/(1+\nu_3)}$$

  Murat & Grest, Macromolecules, 24, 704 (1991)

- Gyration radii:

  $R_{gx} \propto \sigma^{(1-\nu_3)/(1+\nu_3)} N^{2\nu_3/(1+\nu_3)}$ (radial x-direction)

  $R_{gy} \propto \sigma^{(2\nu_3-1)/(2\nu_3+2)} N^{3\nu_3/(2\nu_3+2)}$ (tangential y-direction)

  $R_{gz} \propto \sigma^{(2\nu_3+1)/(2\nu_3+2)} N^{\nu_3/[2(1+\nu_3)]}$ (axial z-direction)

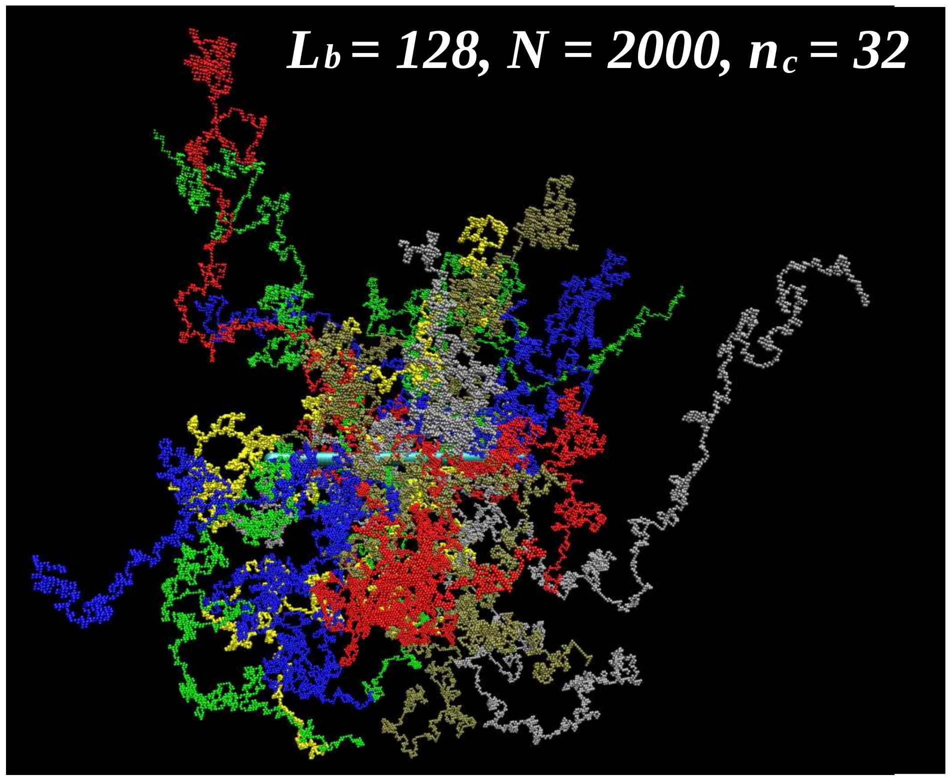
- Density of monomers in the radial direction:

  $$\rho(r) \propto (r/\sigma)^{\delta}, \quad \delta = \frac{1-3\nu_3}{2\nu_3} \sim -0.65, \qquad \nu_3 \approx 0.588$$

  Wijmans & Zhulina, Macromolecules 26, 7214 (1993)

Snapshot: $N_{tot} = 64128$

- Backbone length $L_b = 128$ (p.b.c.), side chain length $N = 2000$, number of side chains $n_c = 32$, grafting density $\sigma = \frac{n_c}{L_b} = 1/4$

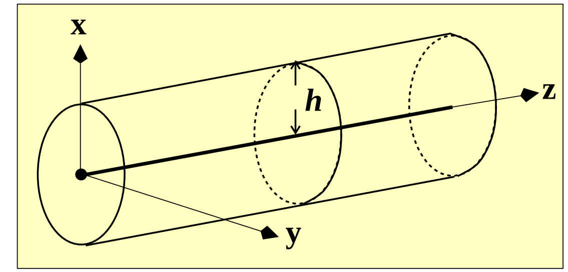


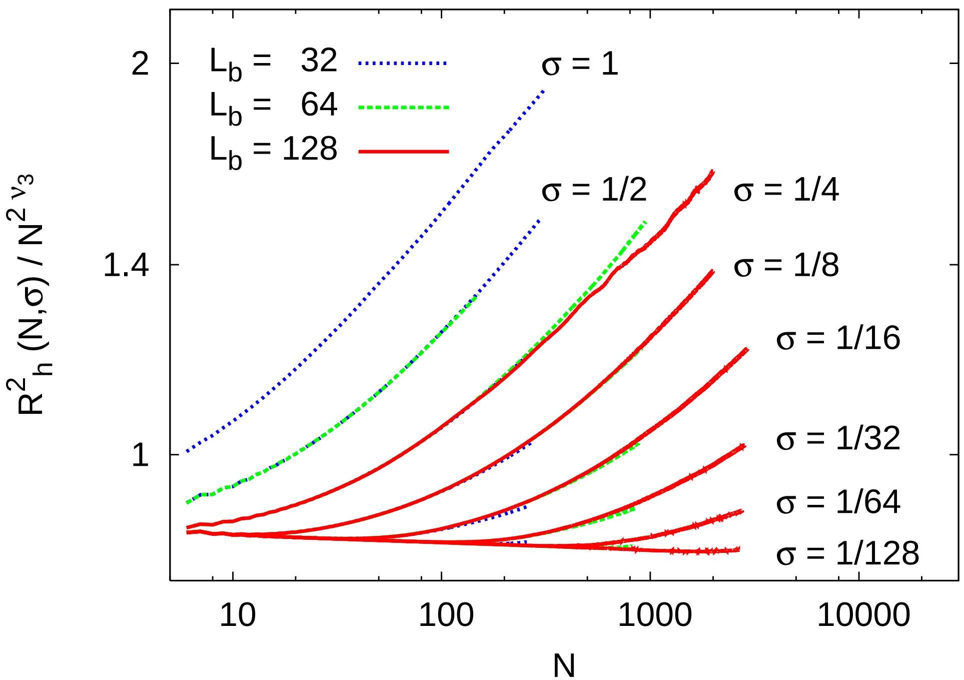
Mean square height $R_h^2(N,\sigma)$

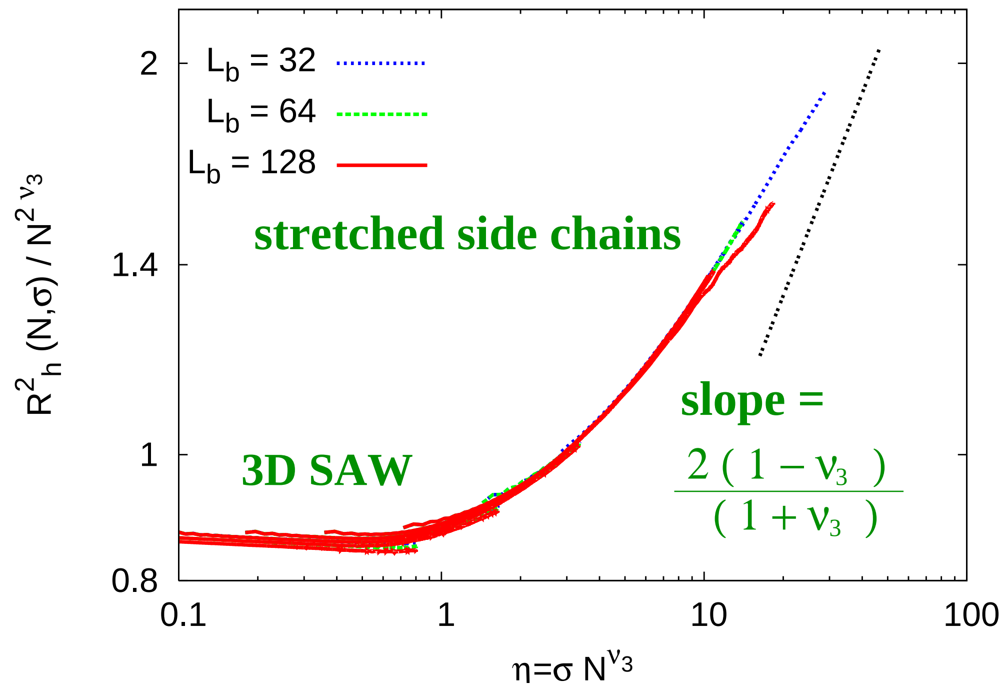
- Cross-over scaling ansatz:

$$R_h^2(N,\sigma) = N^{2\nu_3}\tilde{R}^2(\eta = \sigma N^{\nu_3})$$

$$\tilde{R}^2(\eta) = \begin{cases} 1 & , \quad \eta \to 0 \\ \eta^{\frac{2(1-\nu_3)}{(1+\nu_3)}} & , \quad \eta \to \infty \end{cases}$$

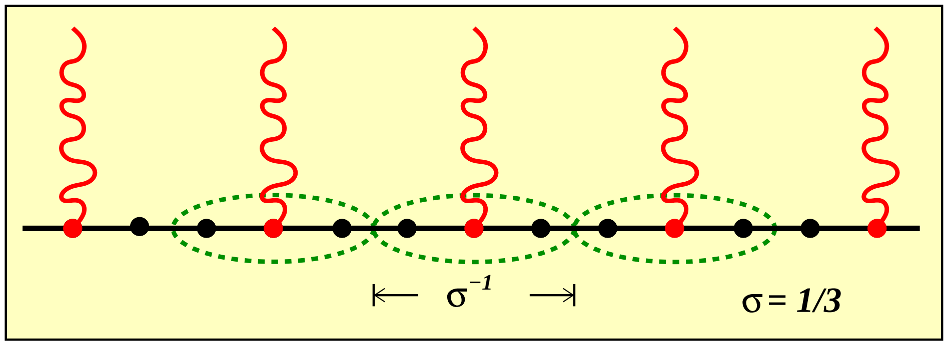


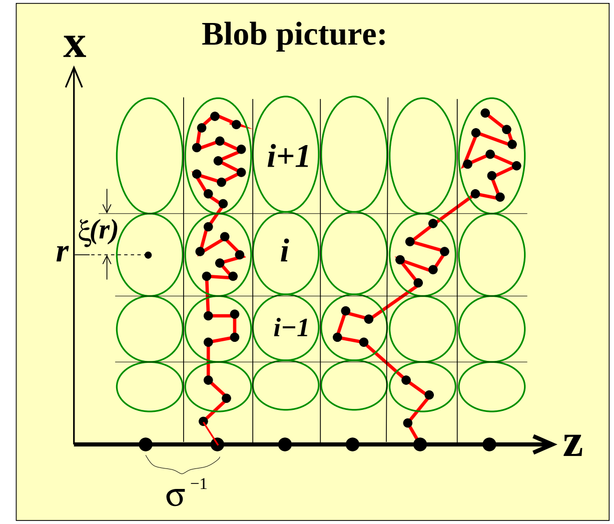




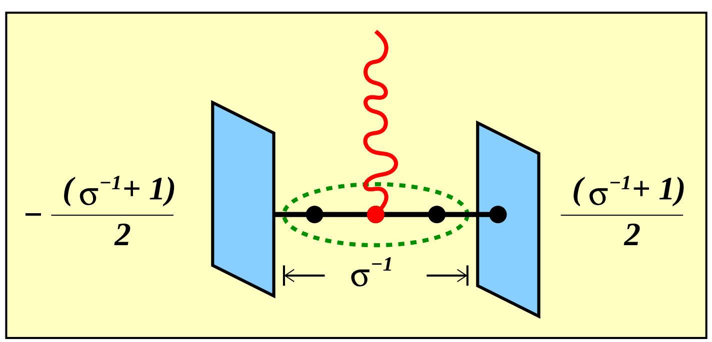
Quasi-2D SAW?

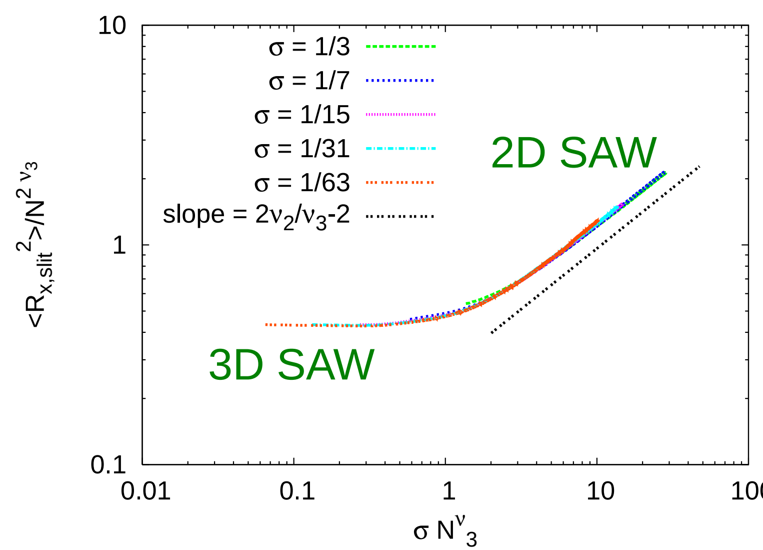
- Side chains of bottle-brush polymers:





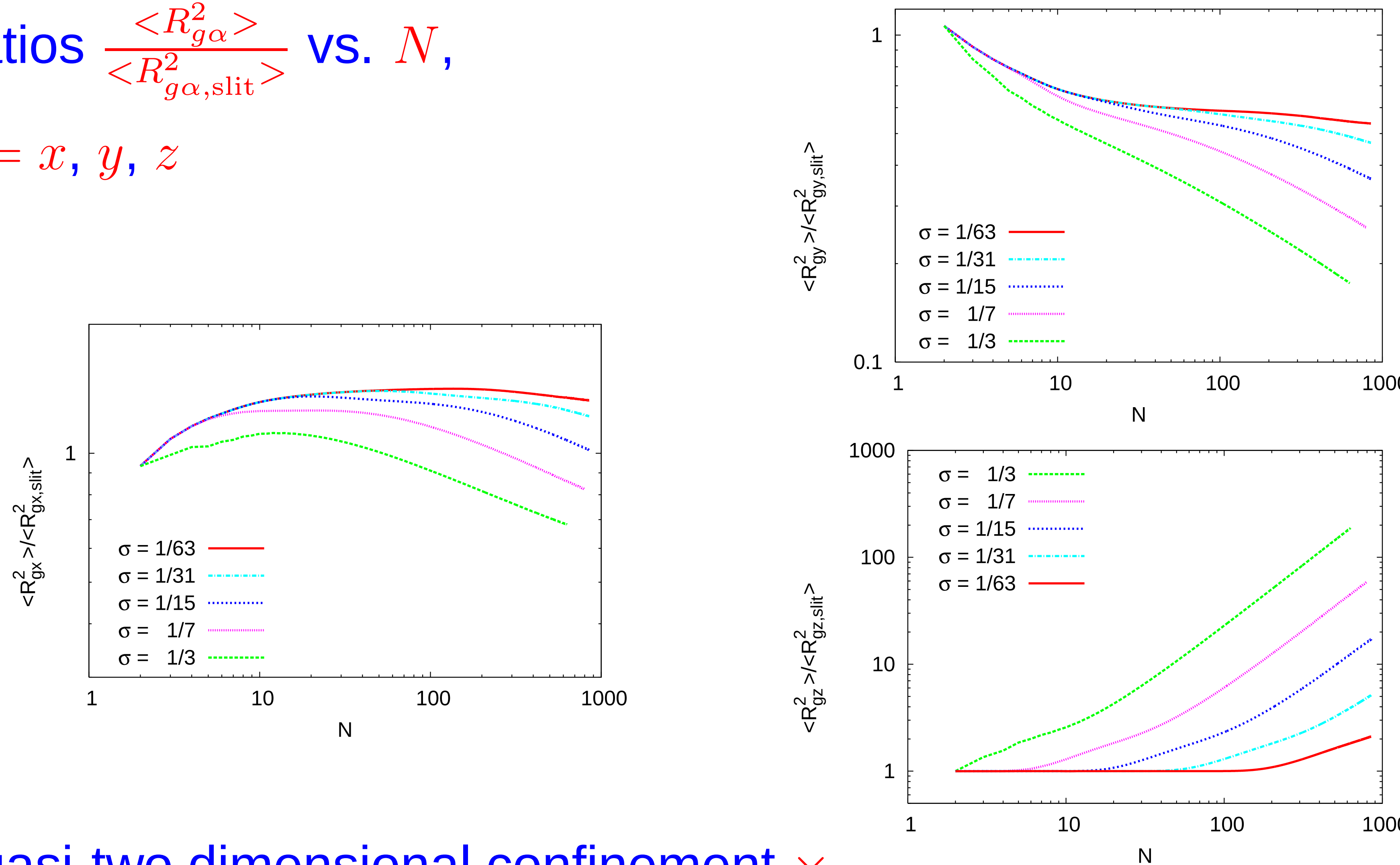
- A Single chain confined in a slit:





- Ratios $\frac{<R^2_{g\alpha}>}{<R^2_{g\alpha,\text{slit}}>}$ vs. N,

  $\alpha = x,\ y,\ z$

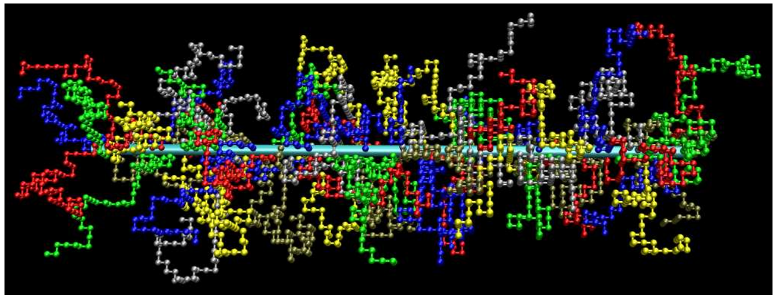


- Quasi-two dimensional confinement ×

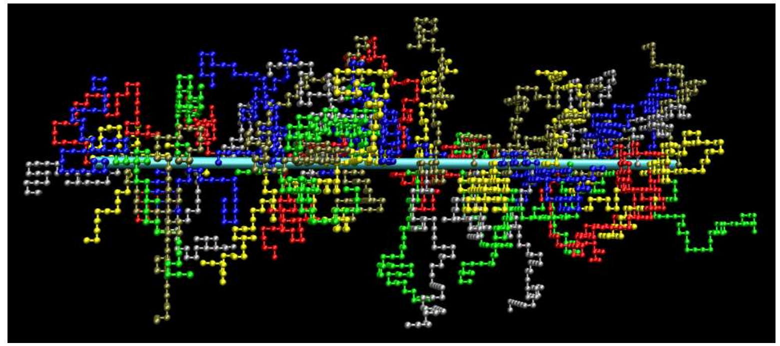
Snapshots

Bottle-brush polymers with $L_b = 64$, $N = 50$, $\sigma = 1$

- Good solvents:

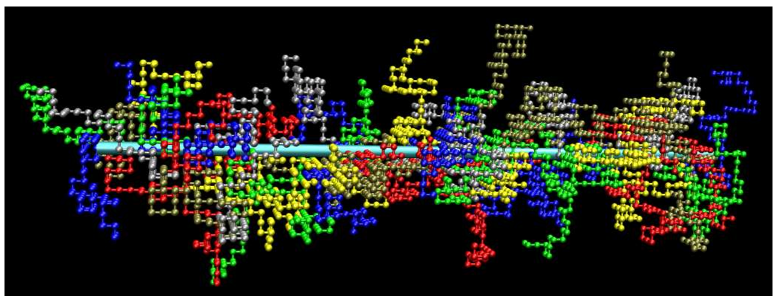


(f.b.c.)

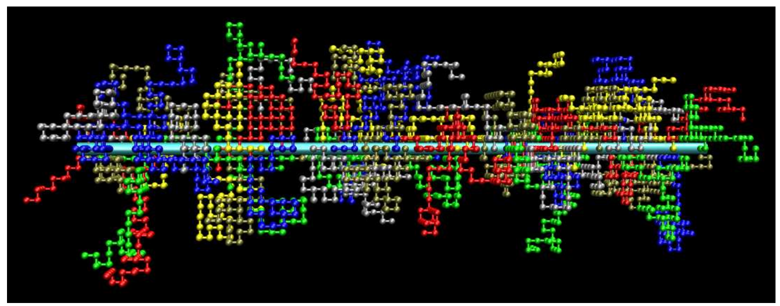


(p.b.c.)

- Theta solvents:



(f.b.c.)

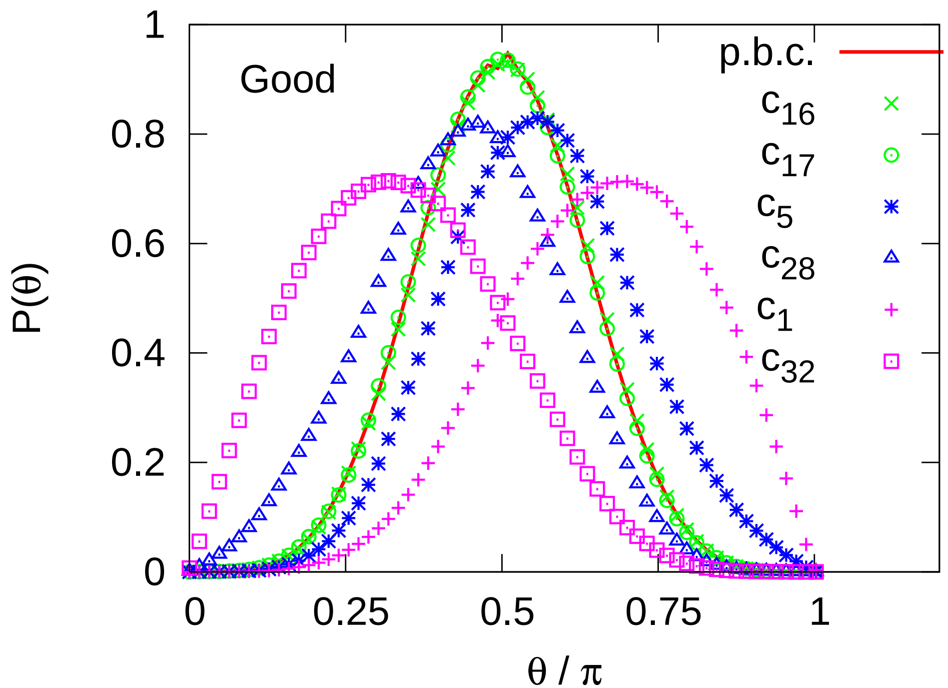


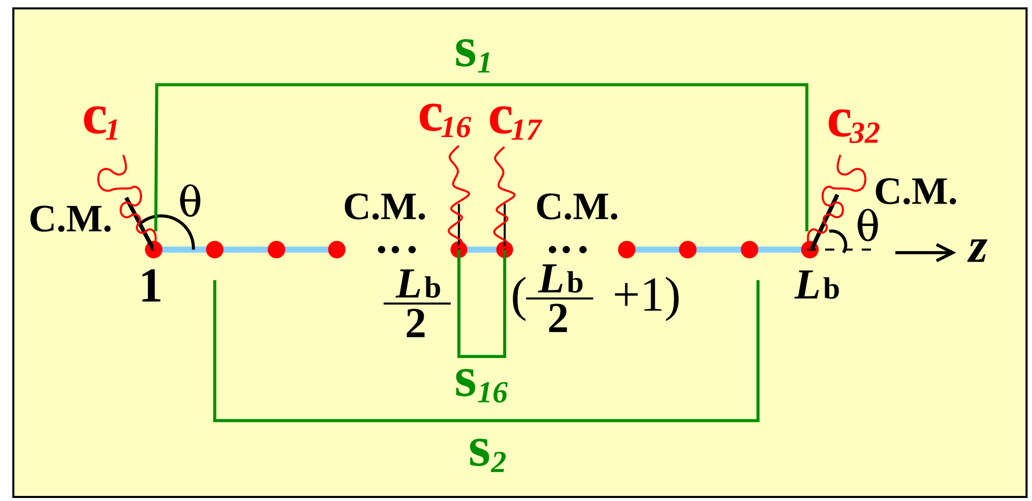
(p.b.c).

$L_b = 32, N = 50, \sigma = 1$

- Distribution function $P(\theta)$ vs. θ

  θ : angle between the vectors towards the center of mass (C.M.) of each side chain and the direction of backbone





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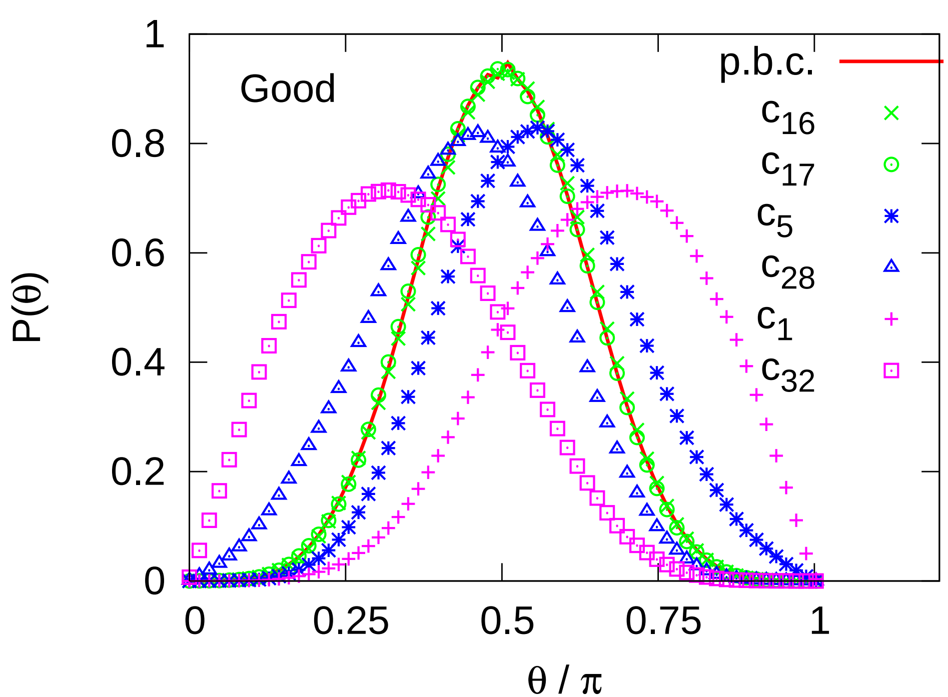
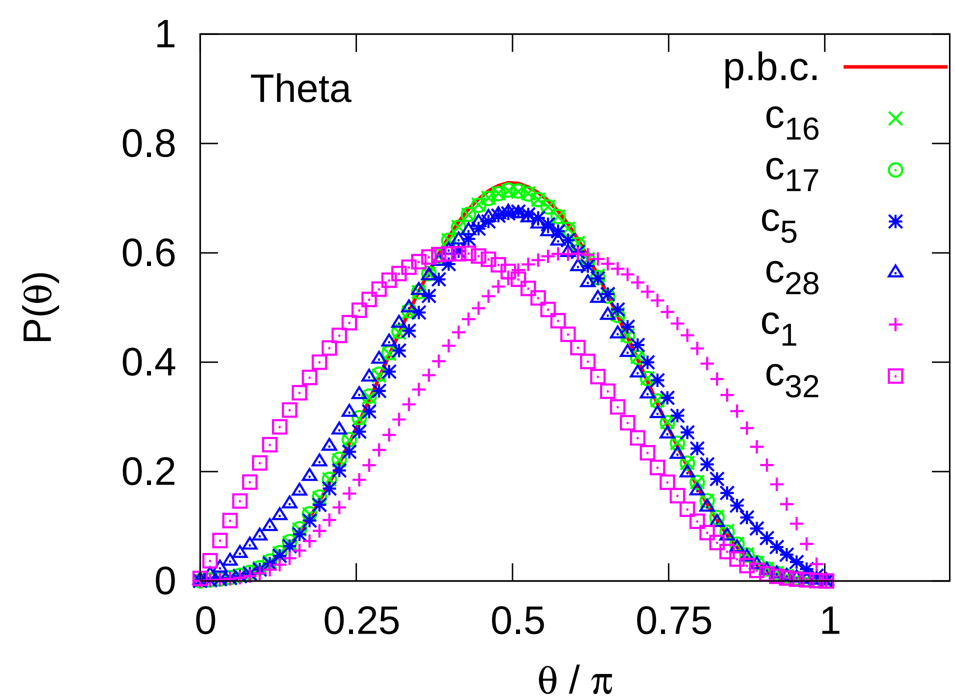


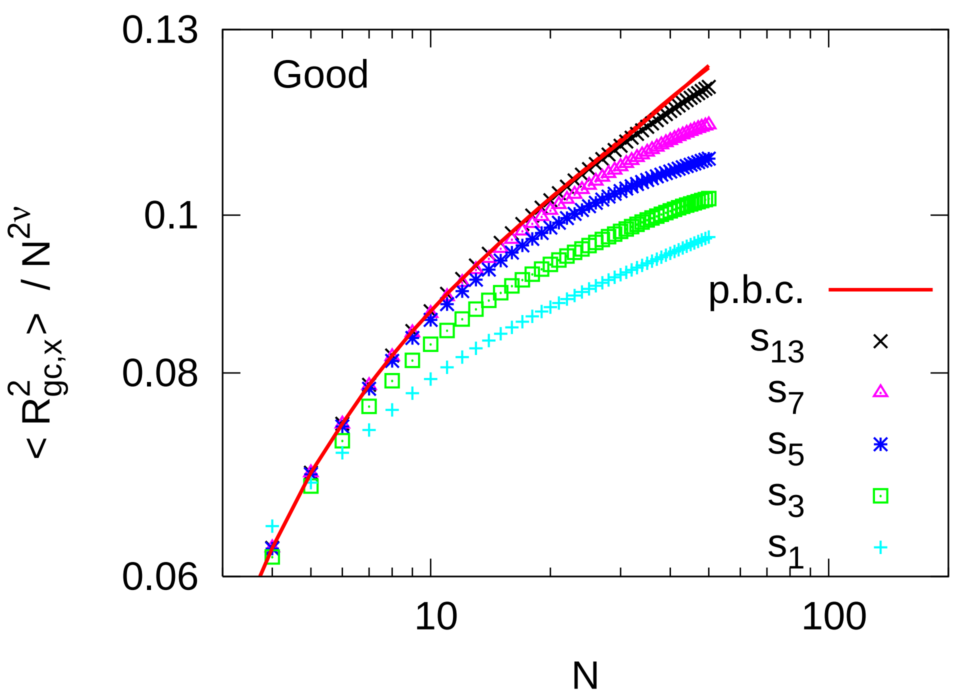


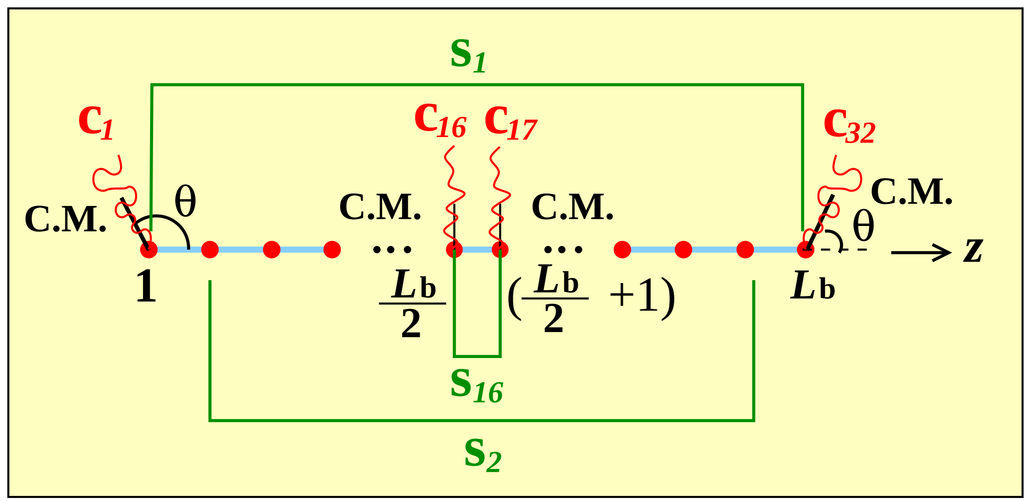
$L_b = 32, N = 50, \sigma = 1$

- Rescaled mean square gyration radii of the side chains

  $< R^2_{gc,x} > /N^{2\nu}$ vs. N, $\nu = 0.588$

  (along the radial direction)





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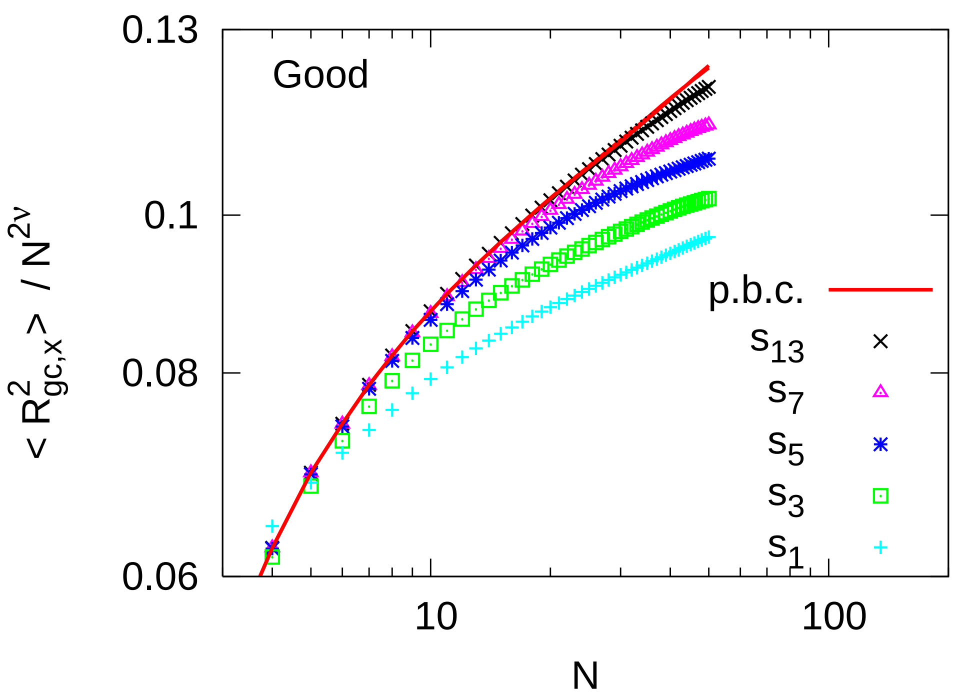

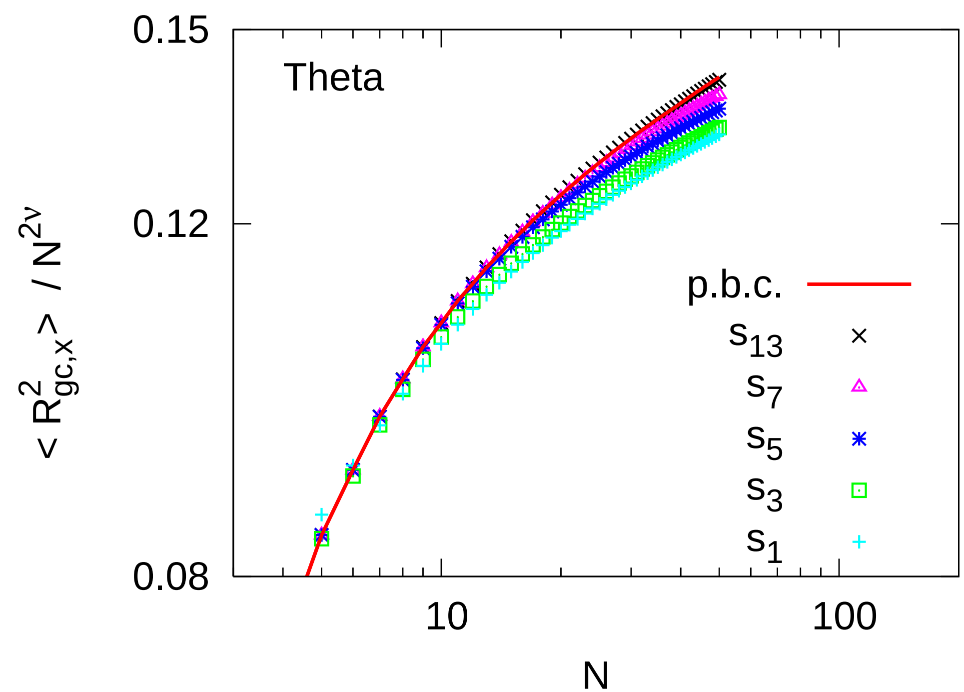

$L_b = 32$, $N = 50$, $\sigma = 1$

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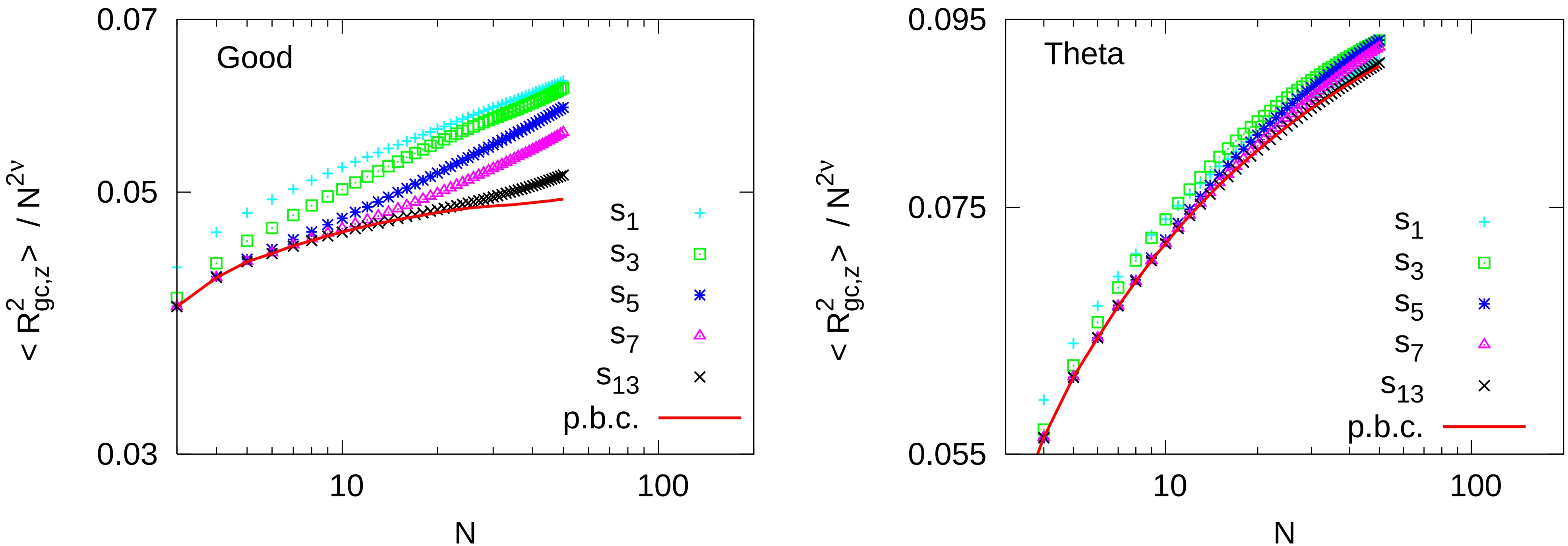
  $< R^2_{gc,z} > / N^{2\nu}$ vs. N, $\quad \nu = 0.588$

  (along the backbone direction)



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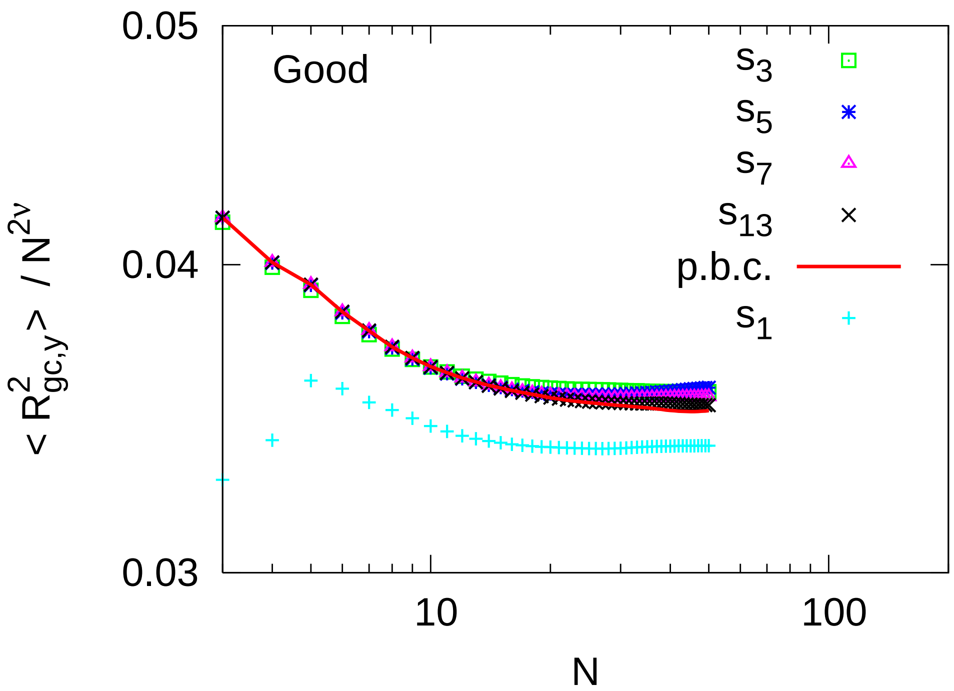
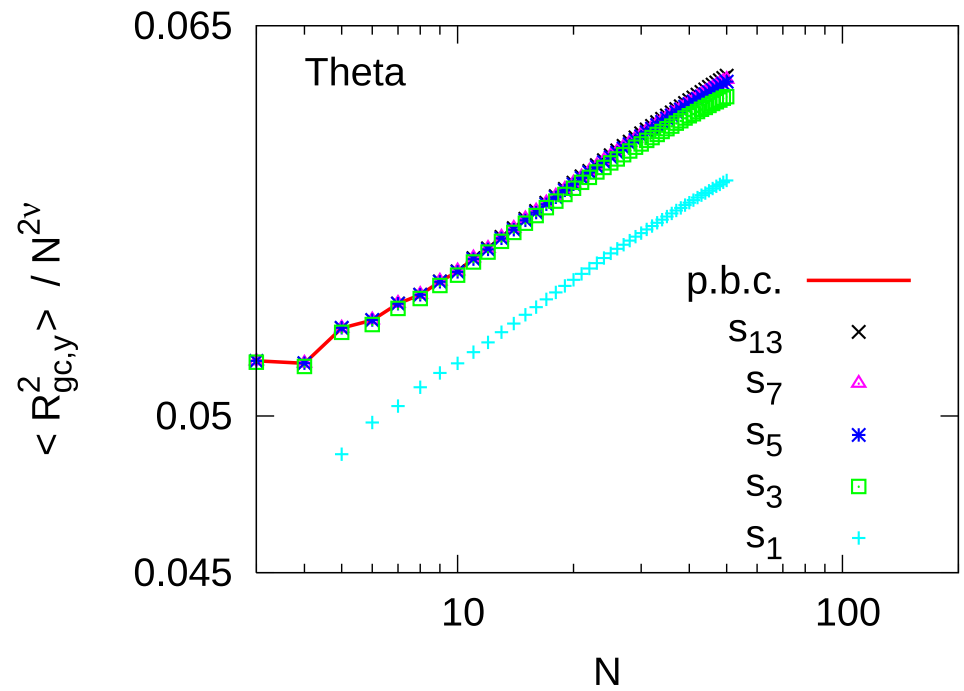
- Rescaled mean square gyration radii of the side chains

  $< R^2_{gc,y} > /N^{2\nu}$ vs. N, $\nu = 0.588$

  (along the tangential direction)



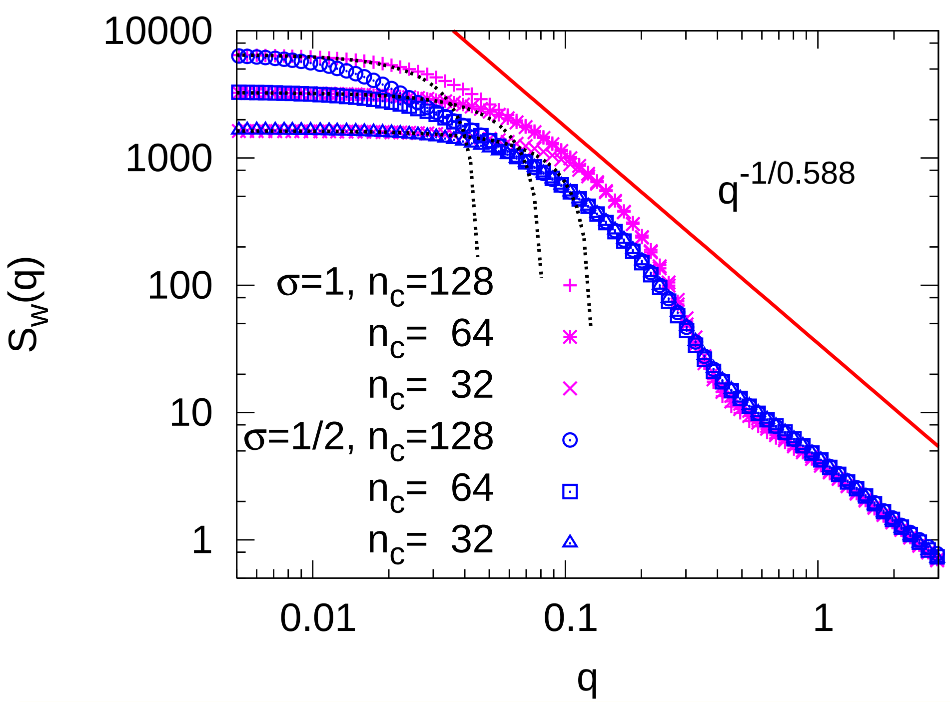


Scattering functions $S_w(q)$

The total scattering function 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)



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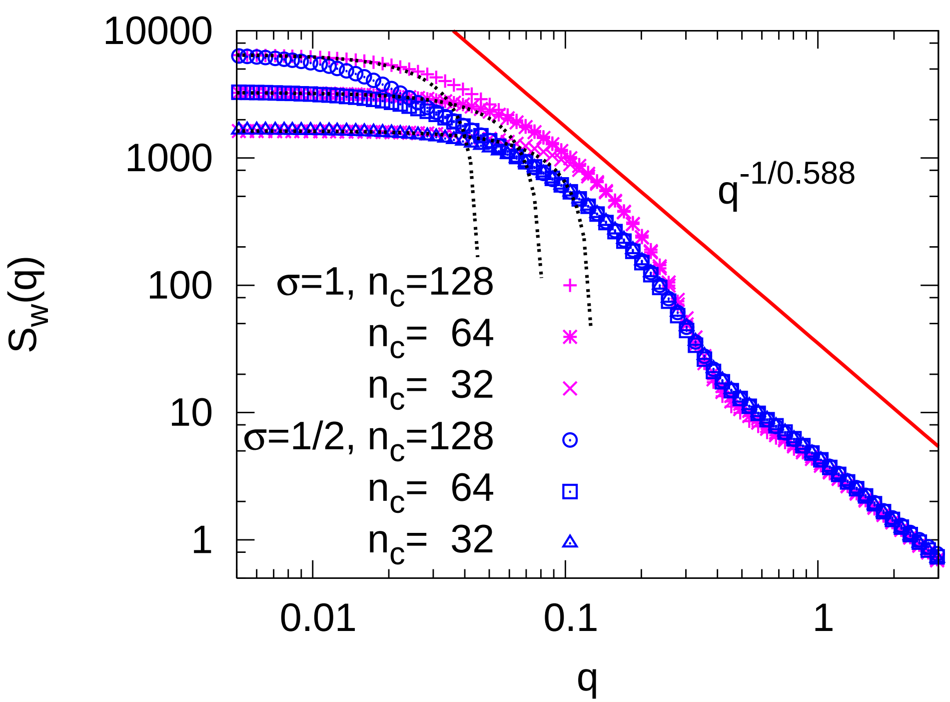

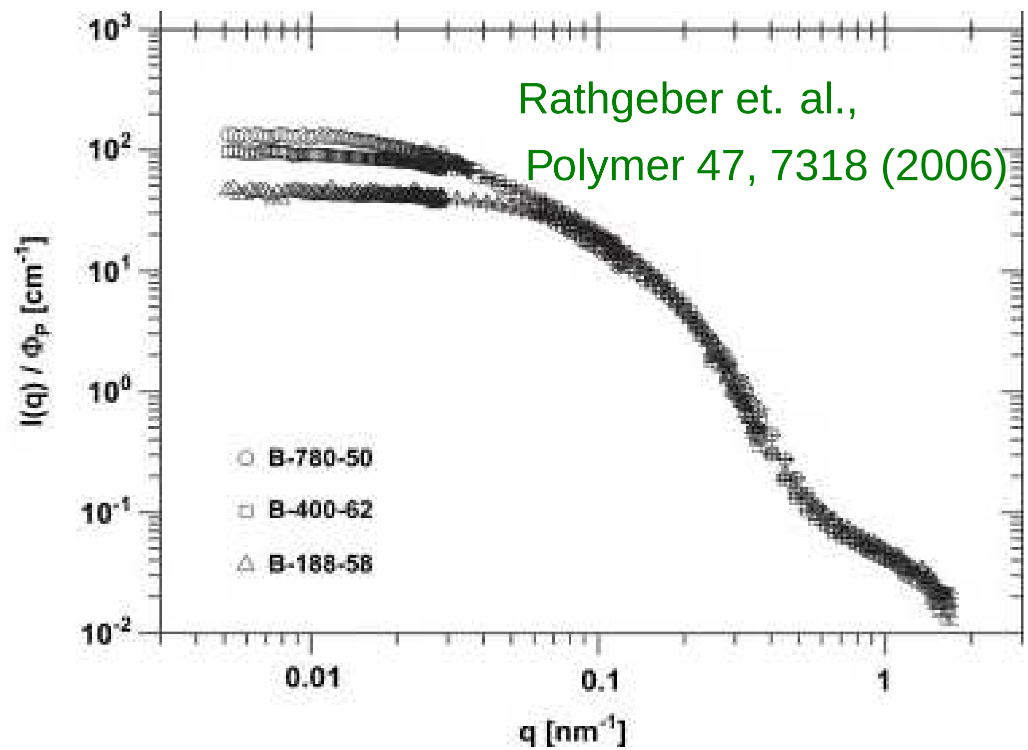

Rathgeber et. al., Polymer 47, 7318 (2006)

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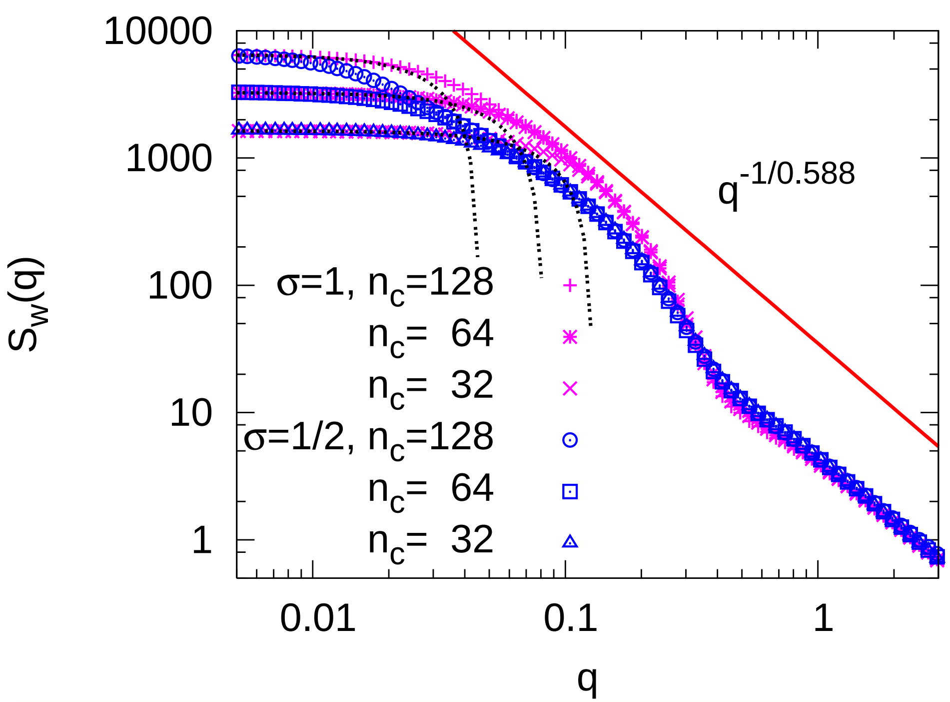


- small q: $S_w(q) \approx \mathcal{N}_{tot}[1 - q < R_g^2 > /3]$
- intermediate q-value: ?
- large q $(q \geq 0.5)$: $S_w(q) \propto q^{-1/\nu}$, $\nu = 0.588$ (flexible chains)

Cross section structure factor $S_{\text{xs}}(q)$

- Assuming (experimental data analysis)

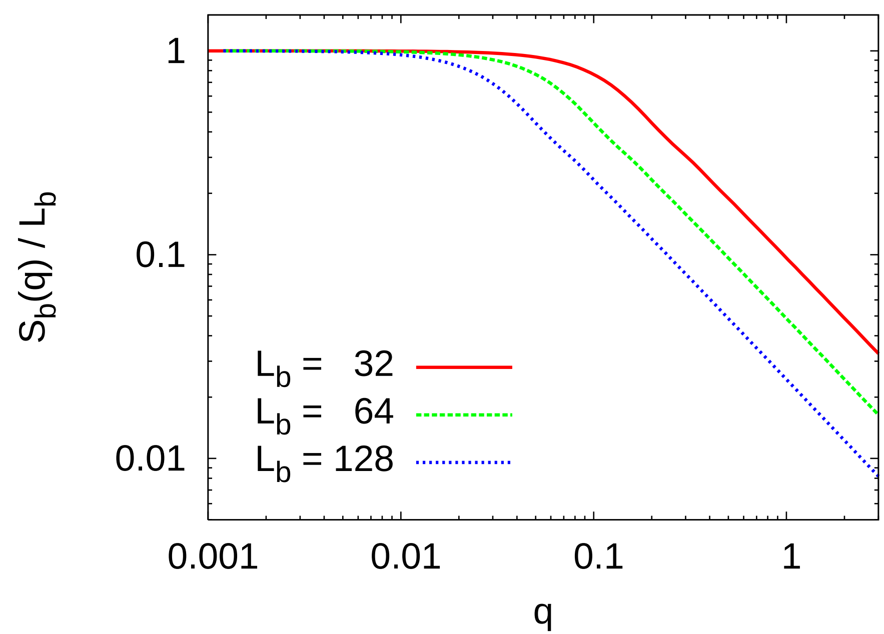
$$S_w(q) \equiv S_b(q) S_{\text{xs}}(q)$$

worm−like micelles ✓

bottle−brush polymers ?

- $S_b(q)$: scattering function of the rigid backbone

$$S_b(q) = \frac{1}{L_b} \sum_{i=1}^{L_b} \sum_{j=1}^{L_b} \frac{\sin(q \mid j-i \mid)}{q \mid j-i \mid} = -1 + \frac{2}{L_b} \sum_{k=0}^{L_b-1} (L_b - k) \frac{\sin(qk)}{qk}$$



$S_{\rm xs}(q)$ and $\rho_{\rm xs}(r)$

- Cross sectional scattering $S_{\rm xs}(q)$:

$$S_{\rm xs}(q) = \frac{\mid \int_0^\infty dr r \rho_{\rm xs}(r) J_0(qr) \mid^2}{\mid \int_0^\infty dr r \rho_{\rm xs}(r) \mid^2}$$

2-d Fourier transform,

neglecting corrections in $\rho_{\rm xs}(r)$ fluctuations

- Radial density distribution $\rho_{\rm xs}(r)$:

$$\rho_{\rm xs}(r) = \frac{1}{2\pi} \int_0^\infty [S_{\rm xs}(q)]^{1/2} J_0(qr) q dq$$

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

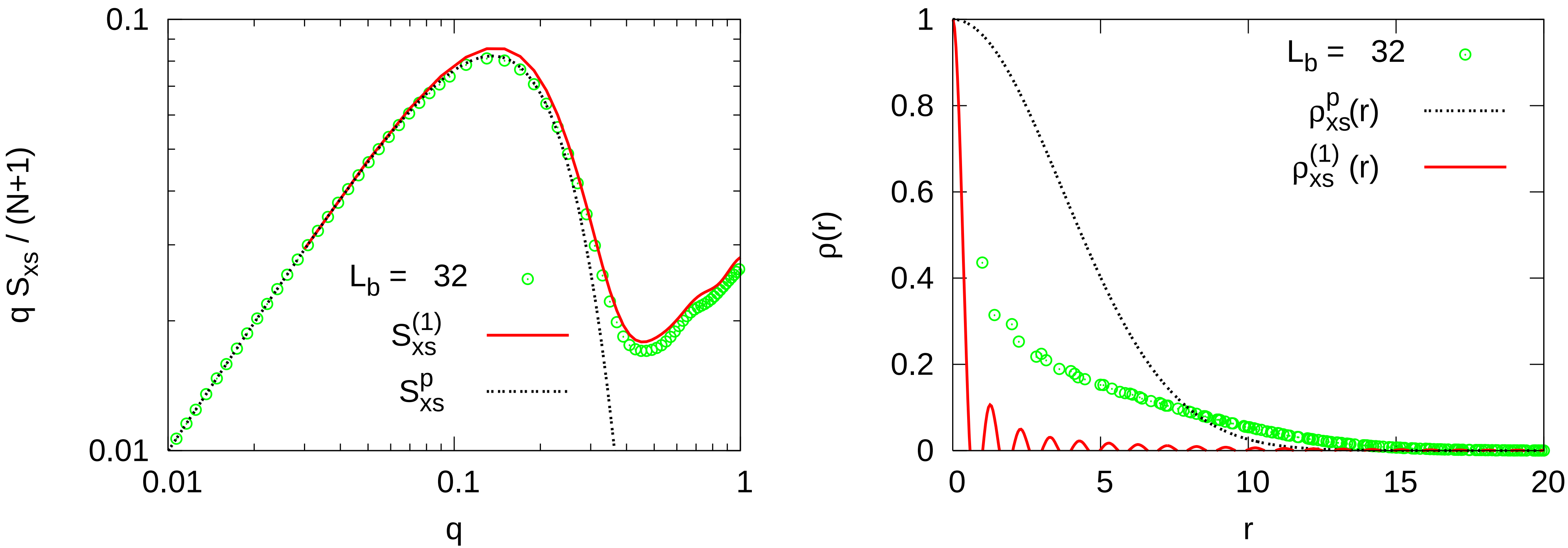
$S_{\mathrm{xs}}(q) \leftrightarrow \rho_{\mathrm{xs}}(r)$

- Assumption of $S_{\mathrm{xs}}(q)$:

Zhang et. al., Macromolecules 39, 237 (2007).

$$S_{\mathrm{xs}}^{p} = \left[\frac{2J_1(qR_c)}{qR_c}\exp(-q^2 s^2/2)\right]^2 \rightarrow \rho_{\mathrm{xs}}^{p}(r)$$

- MC results of $S_{\mathrm{xs}}(q \leq 1.0) \rightarrow \rho_{\mathrm{xs}}^{(1)}(r) \rightarrow S_{\mathrm{xs}}^{(1)}(q)$

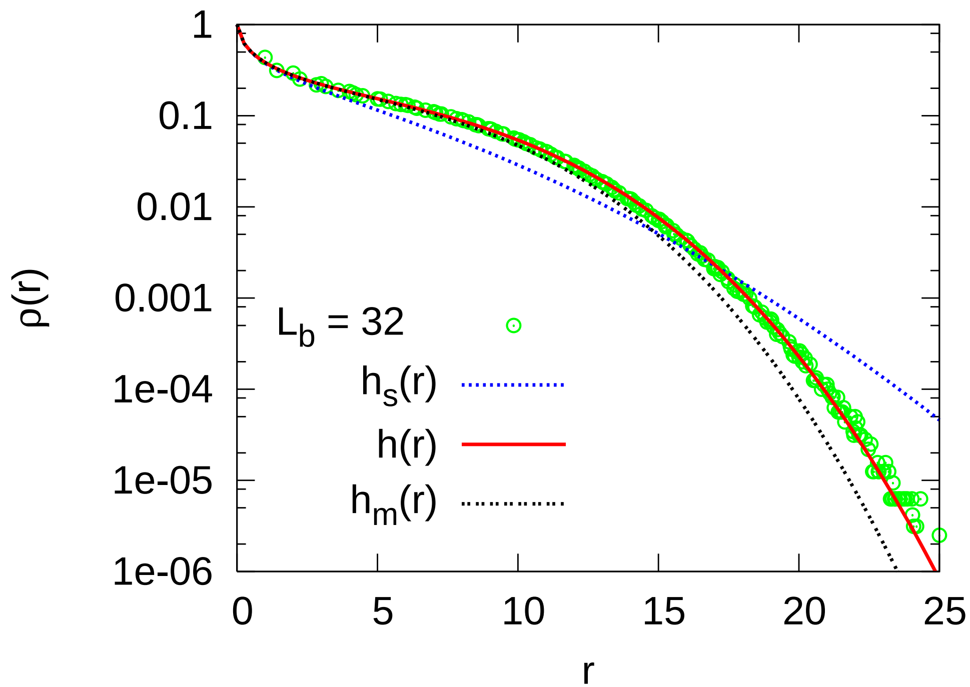


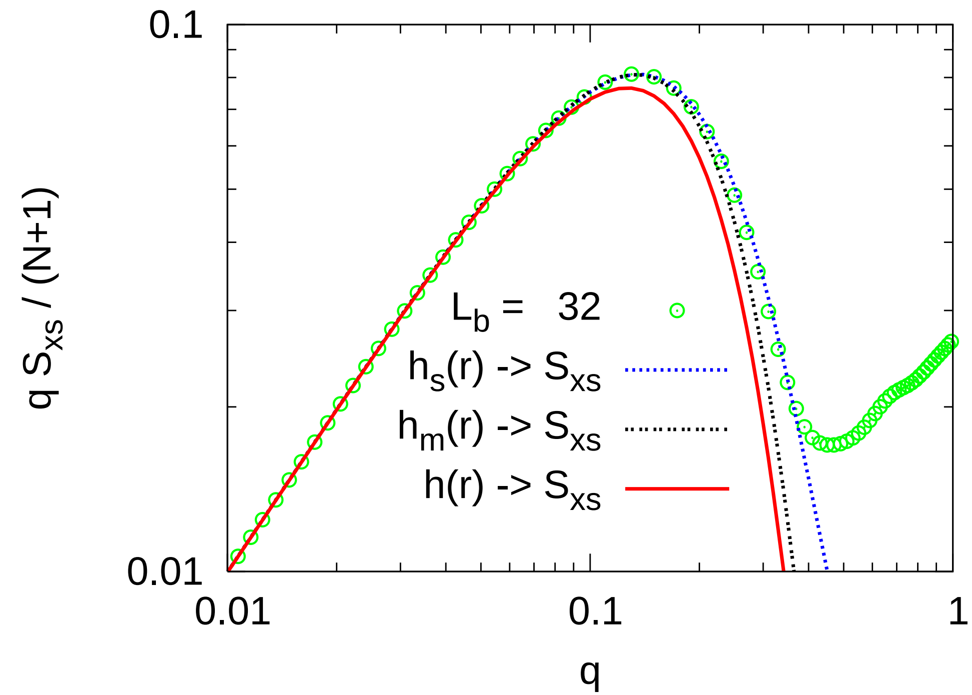
$\rho(r) \leftrightarrow S_{\mathrm{xs}}(q)$

- The fitting function $h(r)$: Hsu, Paul & Binder, arXiv:0808.1485 (2008)

$$h(r) = \frac{\sigma}{1+(r/r_1)^{x_1}} \exp[-(r/r_2)^{x_2}] \to S_{\mathrm{xs}}(q)$$

scaling prediction: $\rho(r) \sim r^{-0.65} \Rightarrow x_1 = 0.65$





Summary

- Generalization of the blob picture to cylindrical bottle-brush polymers.
- Scaling regime barely reachable in simulation and not relevant for experimental side chain lengths
  cross-over: 3D SAW $\Rightarrow$ 3D weak stretched side chains
  (no evidence for the quasi-2d picture)
- Geometrical characteristics of individual side chains
- Phenomenological models for Exp. (invalid)
- A new fitting function $h(r)$ for radial density distribution $\rho(r)$
  $\Rightarrow$ Scattering function $S_{\rm xs}(q)$