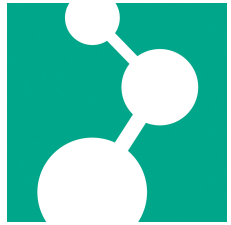


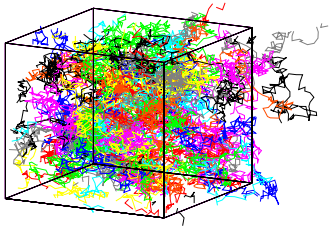
Lattice Monte Carlo Simulations of Polymer Melts

Hsiao-Ping Hsu

Max-Planck-Institut für Polymerforschung, Mainz, Germany

Motivations

- How to generate nearly equilibrated initial melt configurations? (based on the bond fluctuation model)



Polymer melts: Bead-spring model in the continuum

1. Generate Gaussian chains (switch off the excluded volume interactions) and arrange these chains randomly in a simulation box

2. Switch on gradually the excluded volume interactions
   $\Rightarrow$ chain deformation (self-screening, correlation hole effects)

Auhl et al., J. Chem. Phys. 119, 12718 (2003).

Moreira et al. unpublished (2014)

Motivations

- How to generate nearly equilibrated initial melt configurations? (based on the bond fluctuation model)
  Test the pre-packing strategy
  before the excluded volume interactions is switched on

Polymer melts: Bead-spring model in the continuum

1. Generate Gaussian chains (switch off the excluded volume interactions) and arrange these chains randomly in a simulation box

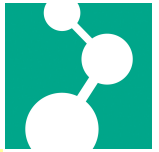
   Solution: Pre-packing $\Rightarrow$ reduce the local density fluctuation (rearrange Gaussian chains in the box)

2. Switch on gradually the excluded volume interactions
   $\Rightarrow$ chain deformation (self-screening, correlation hole effects)

Auhl et al., J. Chem. Phys. 119, 12718 (2003).

Moreira et al. unpublished (2014)

Motivations



- How to generate nearly equilibrated initial melt configurations? (based on the bond fluctuation model)
  Test the pre-packing strategy
  before the excluded volume interactions is switched on
- Check the effects of chain stiffness on the conformations of polymer chains in a melt non-Gaussian corrections

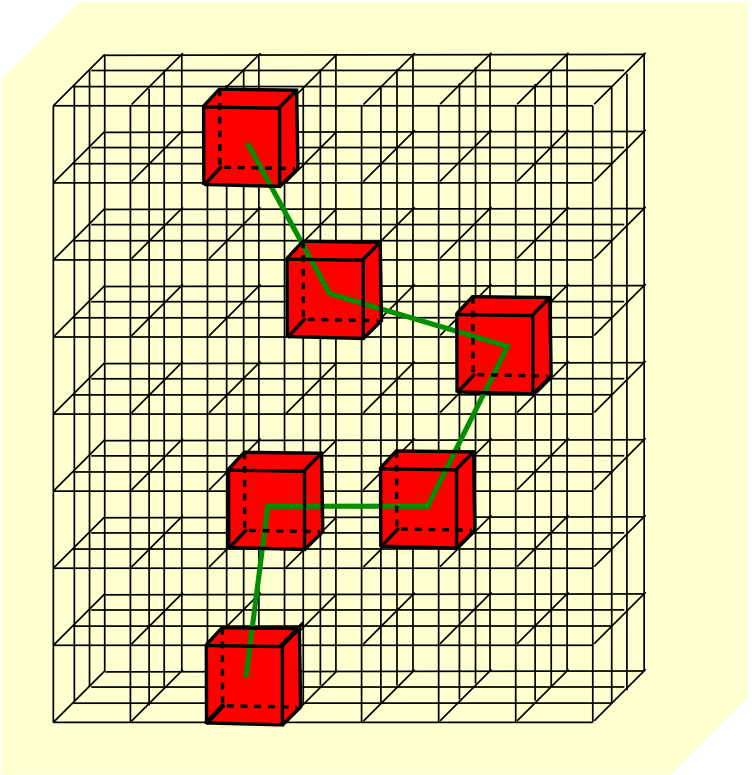
Why polymer chains in a melt are not random walks

J. P. Wittmer et al., EPL 77, 56003 (2007)

"The deviations (from ideality) come from the interplay of chain connectivity and the incompressibility of the melt, leading to an effective repulsion between chain segments of all size" $R^2(s) = b_e^2(s - c_s/\sqrt{s})$

Flory ideality hypothesis (1949): "Chains in a melt are (nearly) ideal"
intrachain "=" interchain excluded volume interactions $R^2(s) = b_e^2 s$

Bond fluctuation model (BFM)



- 3D SAWs on a simple cubic lattice with bond constraints
- 108 bond vectors $\vec{b}$ are from:

  $\{(\pm 2, \ 0, \ 0), (\pm 2, \pm 1, \ 0),$
  $(\pm 2, \pm 1, \pm 1), (\pm 2, \pm 2, \pm 1),$
  $(\pm 3, \ 0, \ 0), (\pm 3, \pm 1, \ 0)\}$

  including all permutations

  $$2 \leq | \vec{b} | \leq \sqrt{10}$$

- 87 bond angles

Carmesin & Kremer, Macromolecules 21, 2819 (1988)
Wittmann & Kremer, Comp. Phys. Commun. 61, 309 (1990)
Deutsch & Binder, J. Chem. Phys. 94, 2294 (1991)
Paul et al., J. Phys. II 1, 37 (1991)

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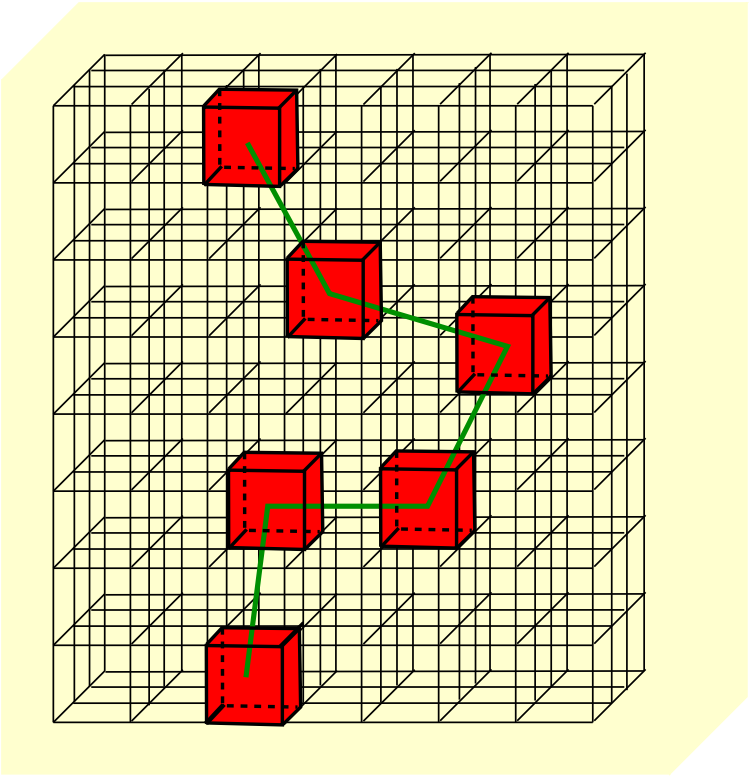

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  including all permutations

  $$2 \leq |\ \vec{b}\ | \leq \sqrt{10}$$

- 87 bond angles

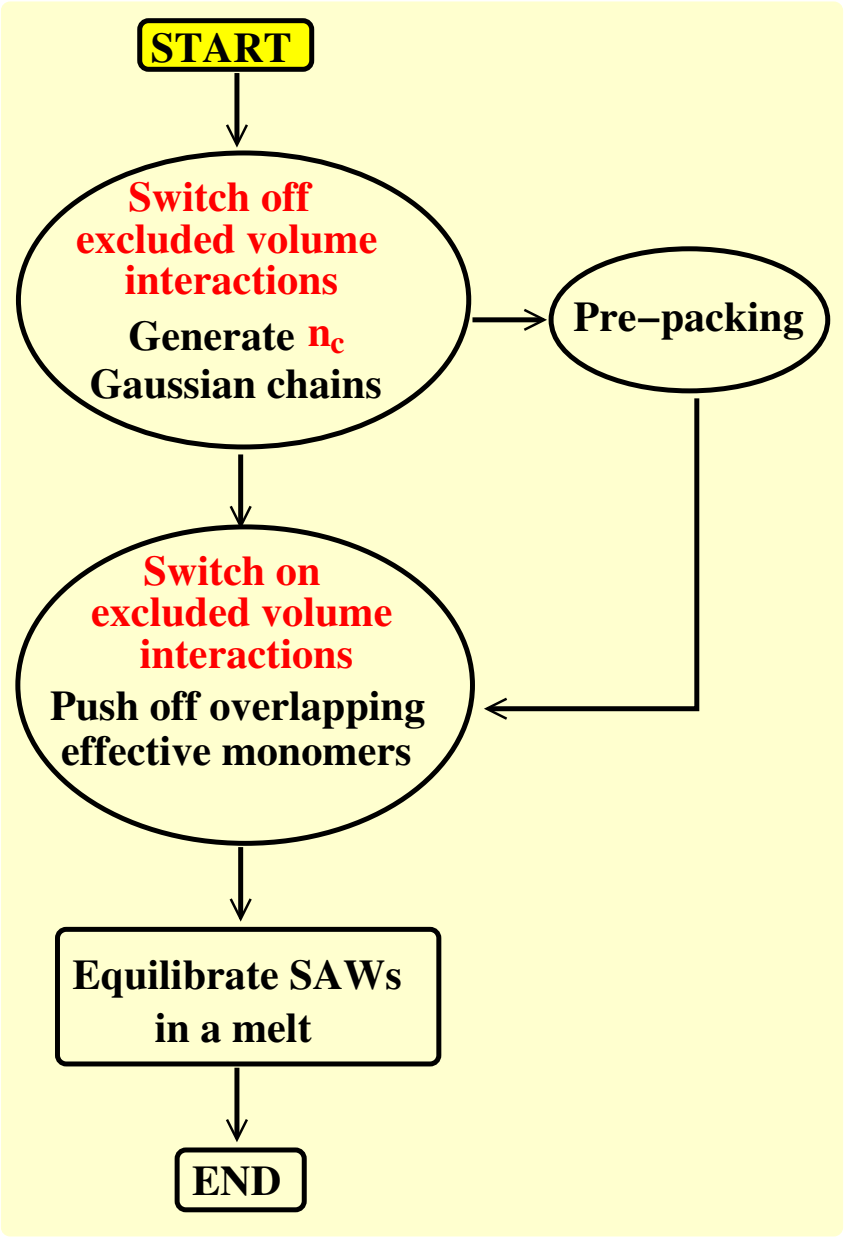
Linear polymers in a melt

"=" 3D SAWs based on the BFM at a volume fraction $\phi = 0.5$

Simulation techniques

Set up the system

- Lattice size:
  $V = L^3 = 128^3$ (periodic b.c.)
- Monomer density:
  $\rho = \phi/8 = 0.5/8 = N_{\mathrm{tot}}/L^3$
- Total number of monomers:
  $N_{\mathrm{tot}} = n_c N = 131072 \approx 10^5$
  n_c: # of chains
  N: # of monomers per chain
- Bond bending potential:
  $U_b = \varepsilon_b(1 - \cos\theta)$
  (chain stiffness)

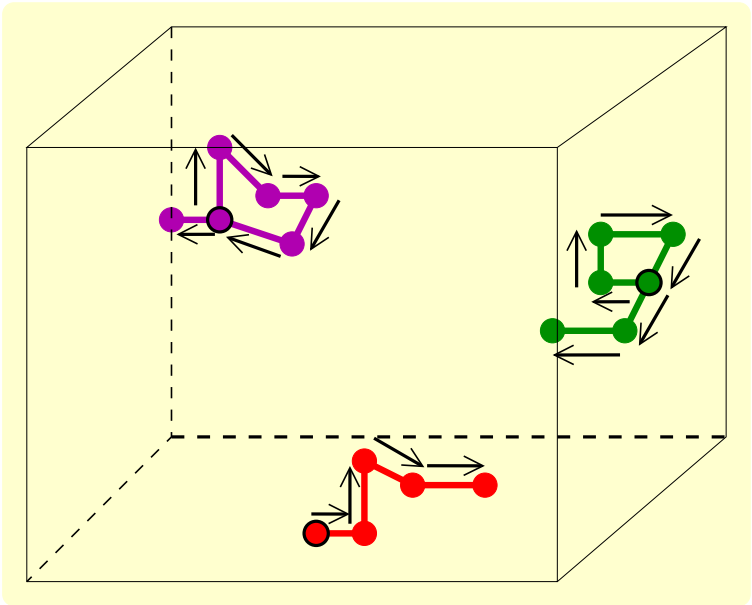


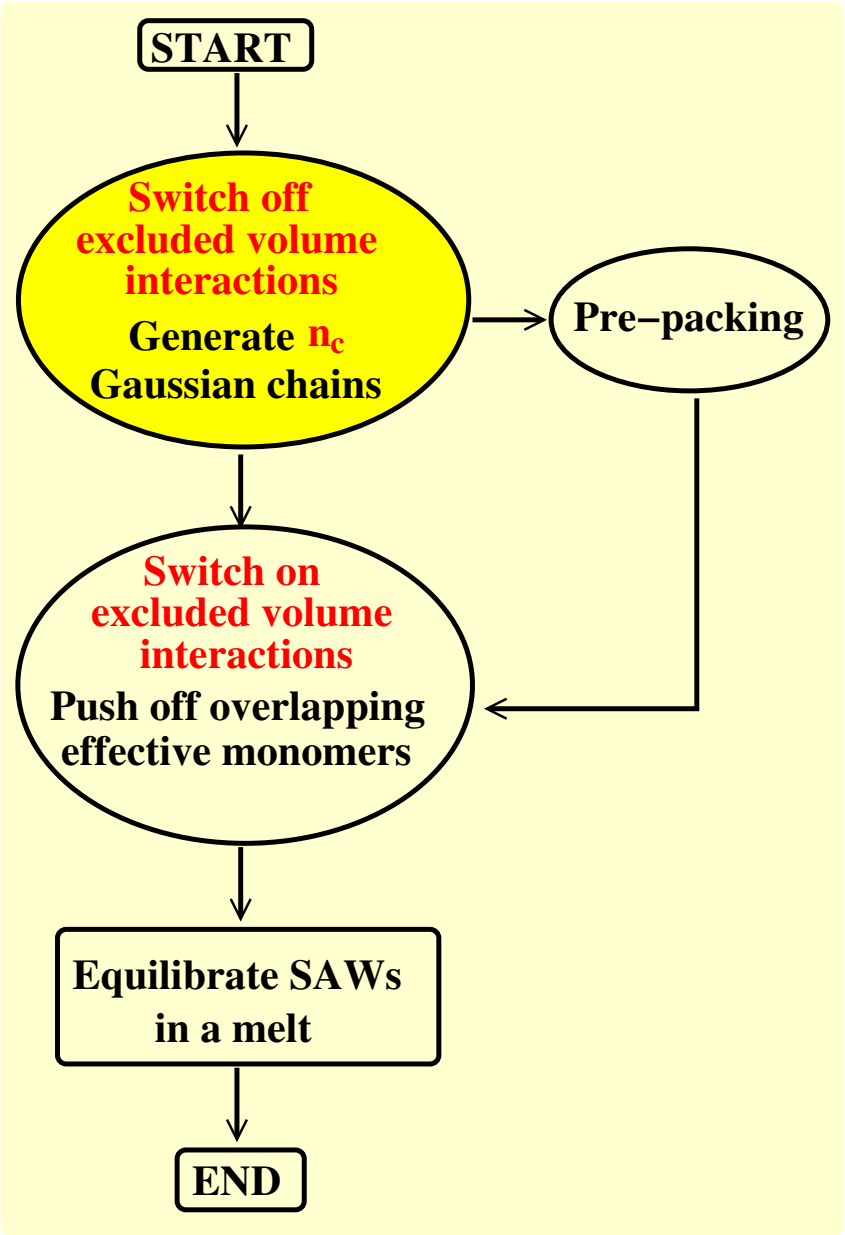
Simulation techniques

Generate n_c NRRWs of size N

- Chain growth algorithm:

  Polymer chains are built like non-reversal random walks (NRRWs) by adding one monomer at each step until all n_c chains reaching the required size N





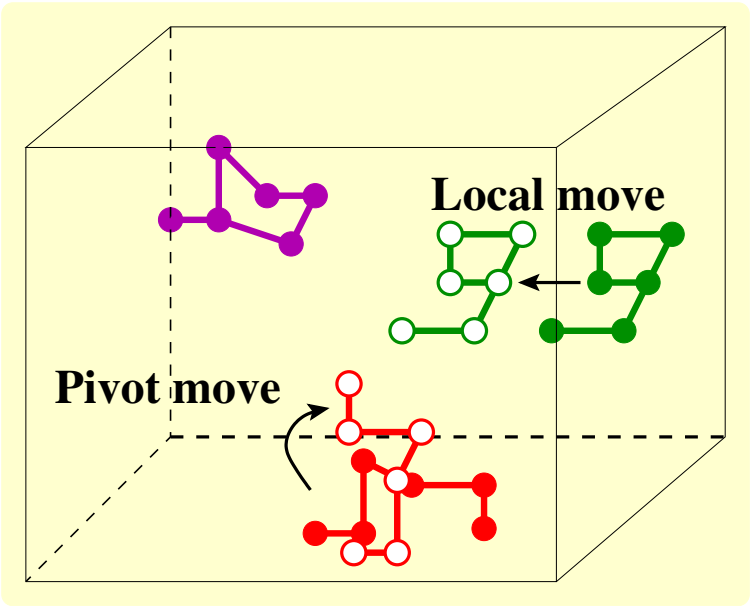
Simulation techniques

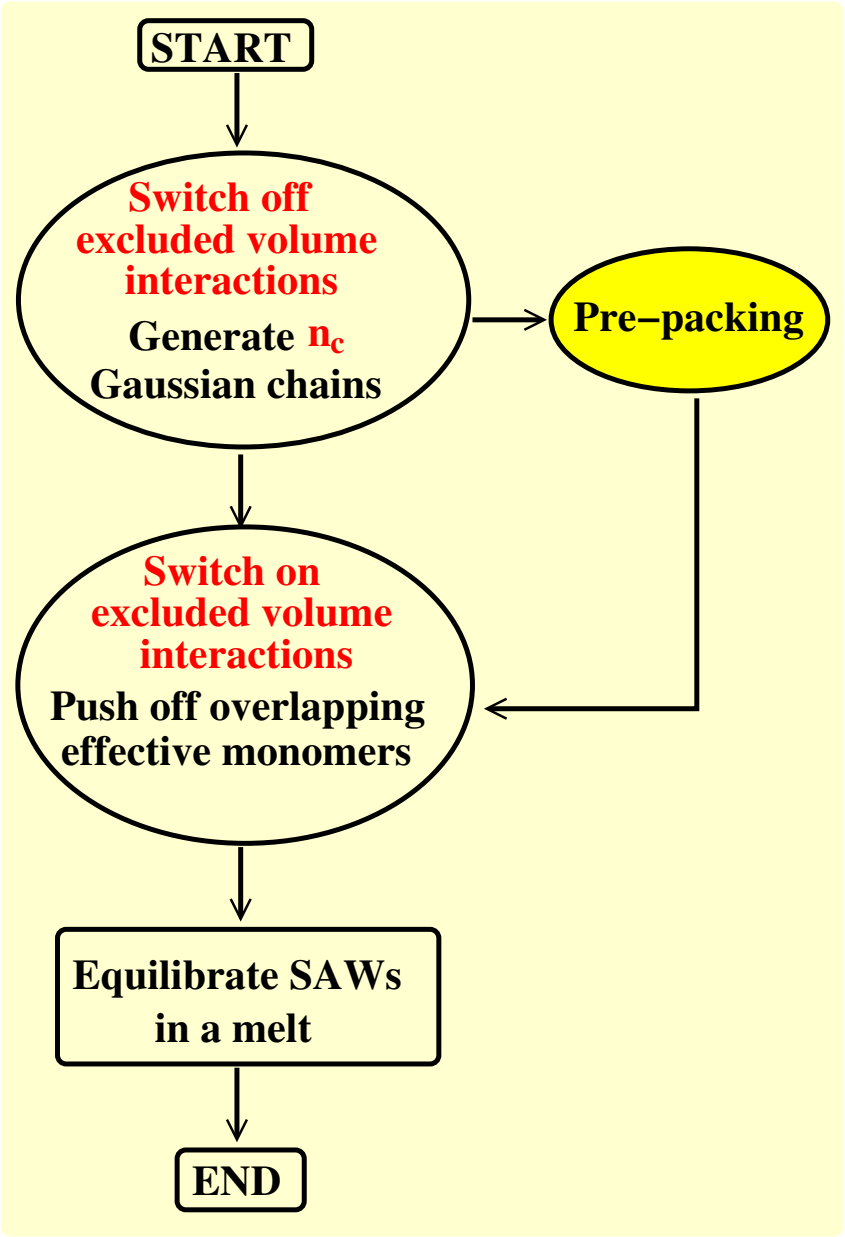
Pre-packing:

keep chain structures (NRRWs)

rearrange chains

- Monte Carlo moves:
  Local 26 moves, Pivot moves
  (pivot point: center of mass)





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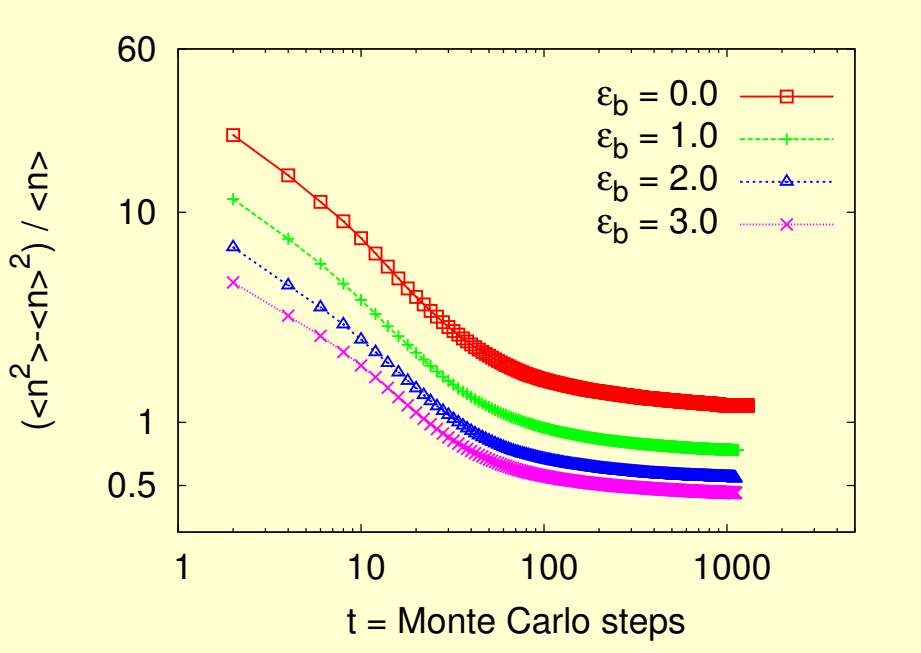
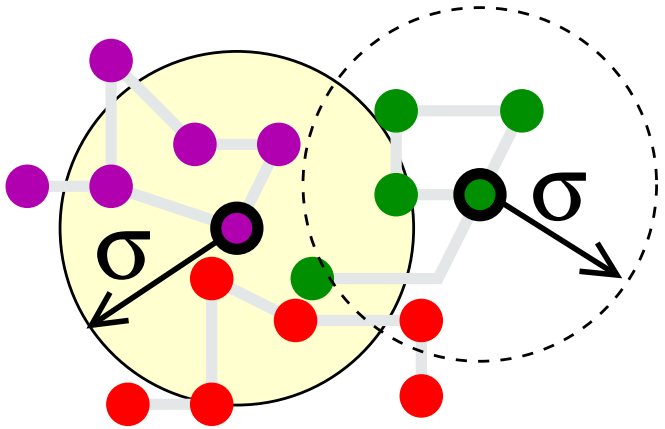


- Monte Carlo moves:
  Local 26 moves, Pivot moves
  (pivot point: center of mass)
- Cost function:
  average local density fluctuation

$$U(\sigma) = \langle n(\sigma)^2 \rangle - \langle n(\sigma) \rangle^2$$

$$= \frac{1}{N_{\rm tot}} \sum_{i=1}^{N_{\rm tot}} n_i^2(\sigma) - \left(\frac{1}{N_{\rm tot}} \sum_{i=1}^{N_{\rm tot}} n_i(\sigma) \right)^2$$

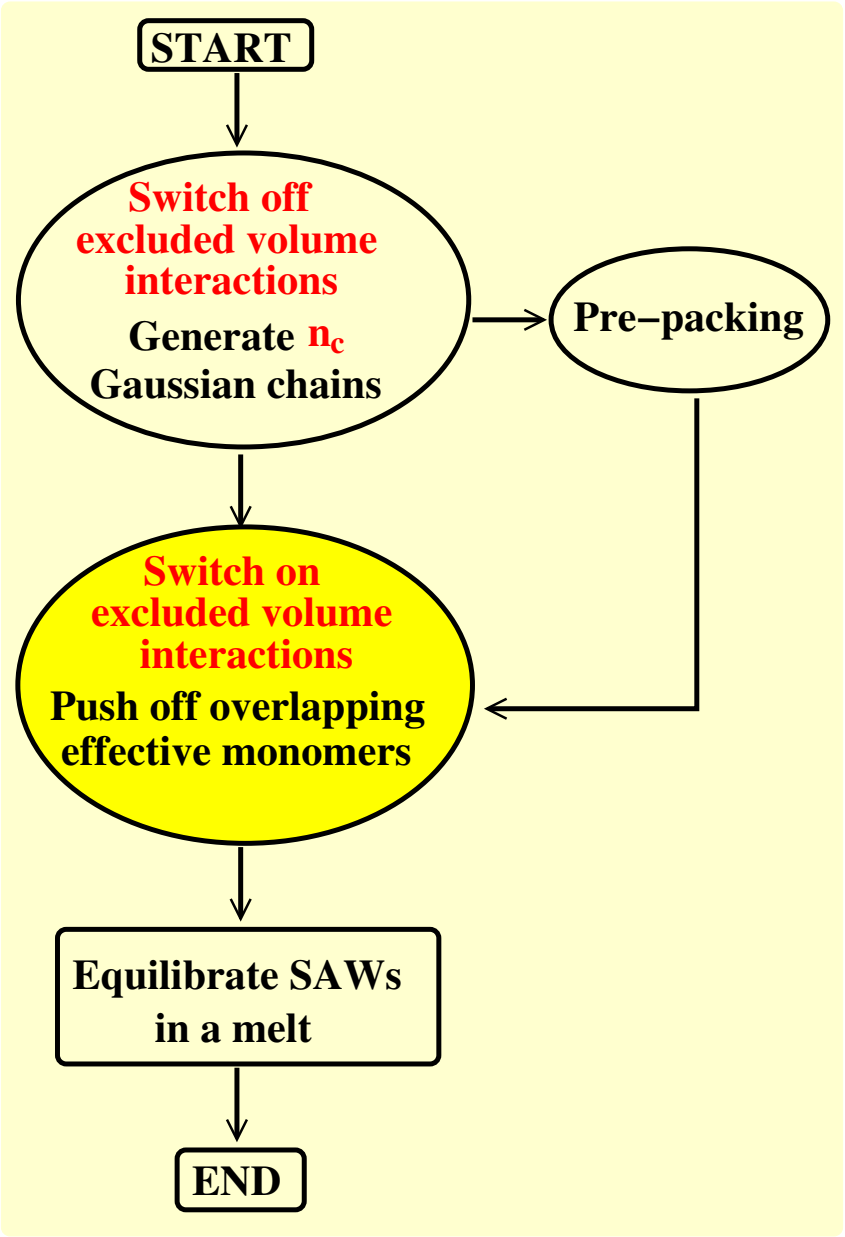
$$n_i(\sigma) = \sum_{j=1, j \neq i}^{N_{\rm tot}} H(\sigma - r_{ij}) \,, \; H(x) = \begin{cases} 0 \,, \text{ for } x < 0 \\ 1 \,, \text{ for } x \geq 0 \end{cases}$$



Simulation techniques

Push off
overlapping effective monomers
blocking the same lattice sites

- Monte Carlo moves:
  Local 26 moves
  Slithering snake moves
- Criterion:
  - Bond constraints
  - Chain stiffness
    $\exp(-\Delta U_b) > r$
    $0 < r < 1$, random number
    $\Delta N_{\text{over}} < 0$



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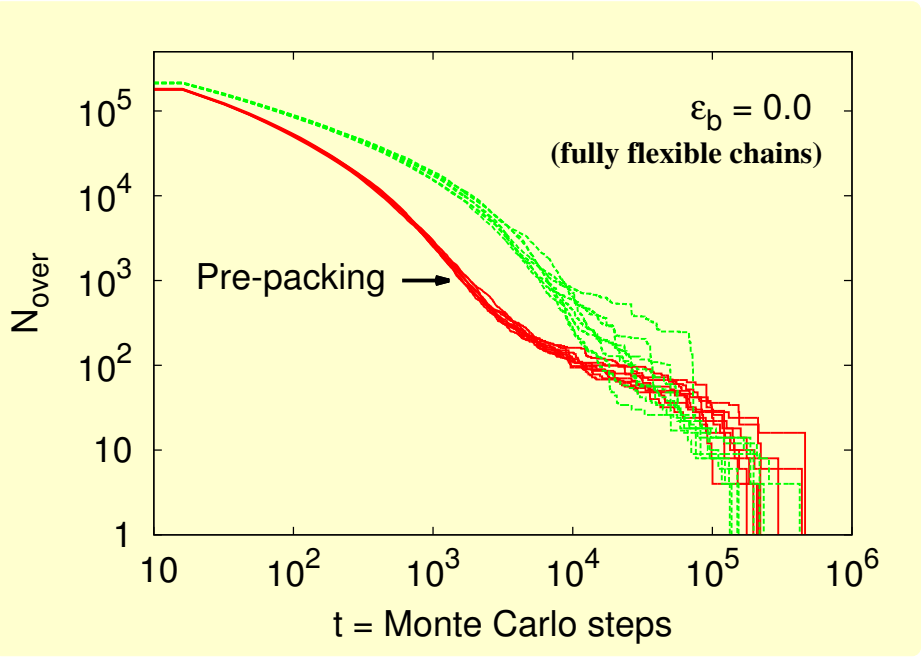
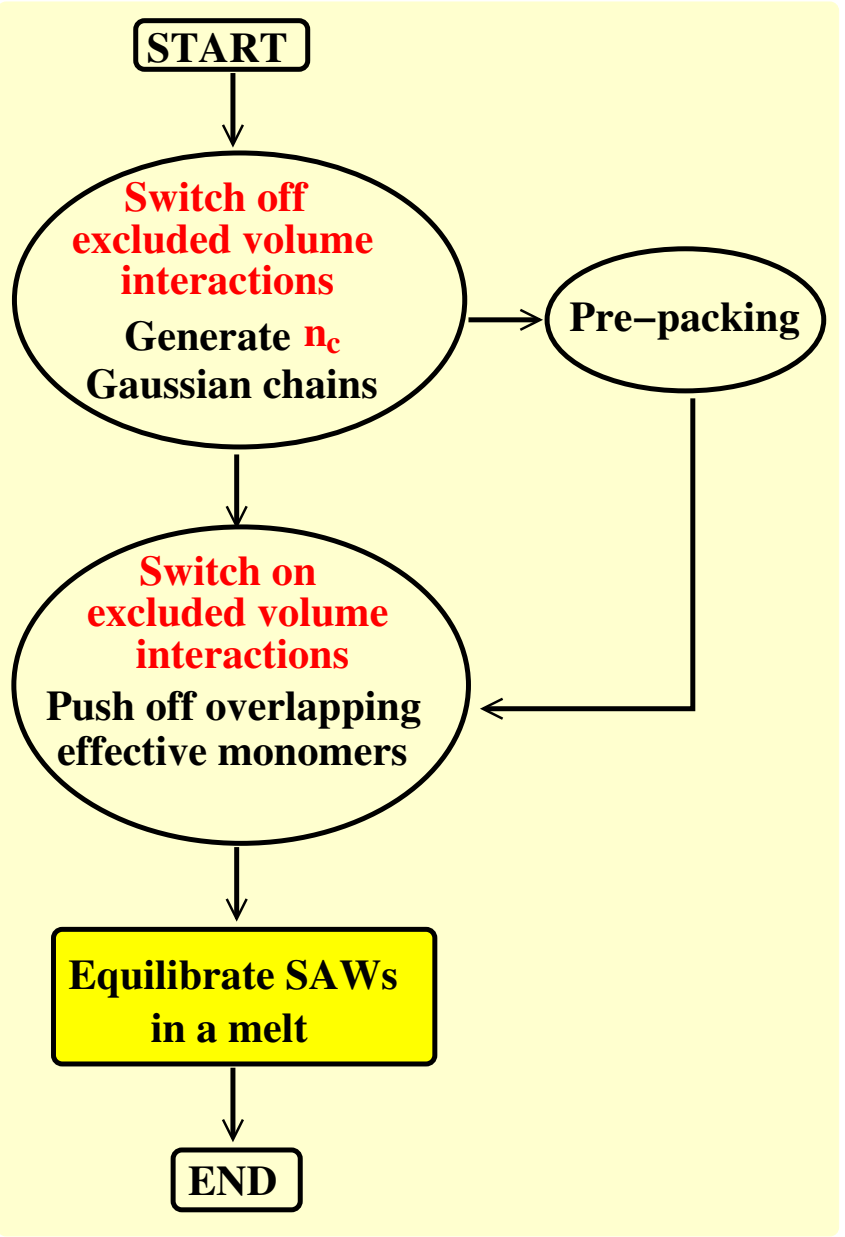


NRRWs ($N_{\text{over}} > 0$) $\Rightarrow$ SAWs ($N_{\text{over}} = 0$)

Simulation techniques

- Monte Carlo moves:
  - Local 26 moves
  - slithering snake moves
  - pivot moves:
    48 symmetric operators
    (no change, rotation by 90^o,
    180^o, reflections, inversions)
- Criterion:
  - Bond constraints
  - Chain stiffness
    $\exp(-\Delta U_b) > r$
    $0 < r < 1$, random number
  - Self- and mutual-avoidance



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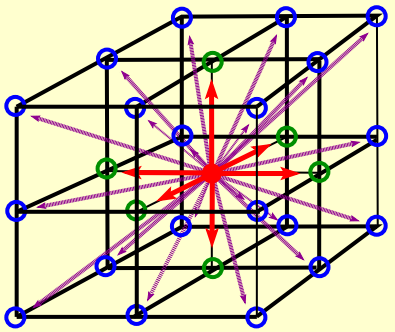
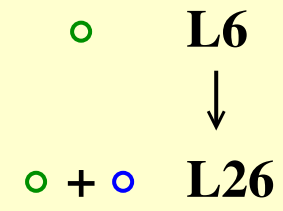
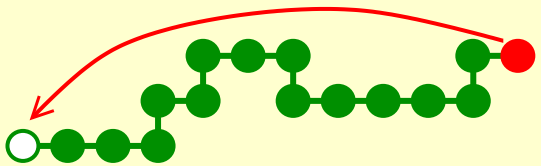
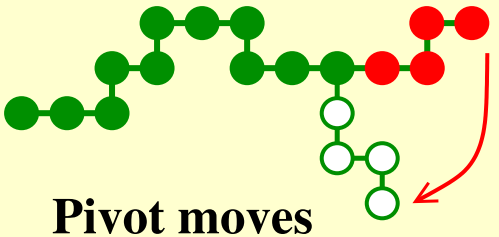






Slithering snake moves

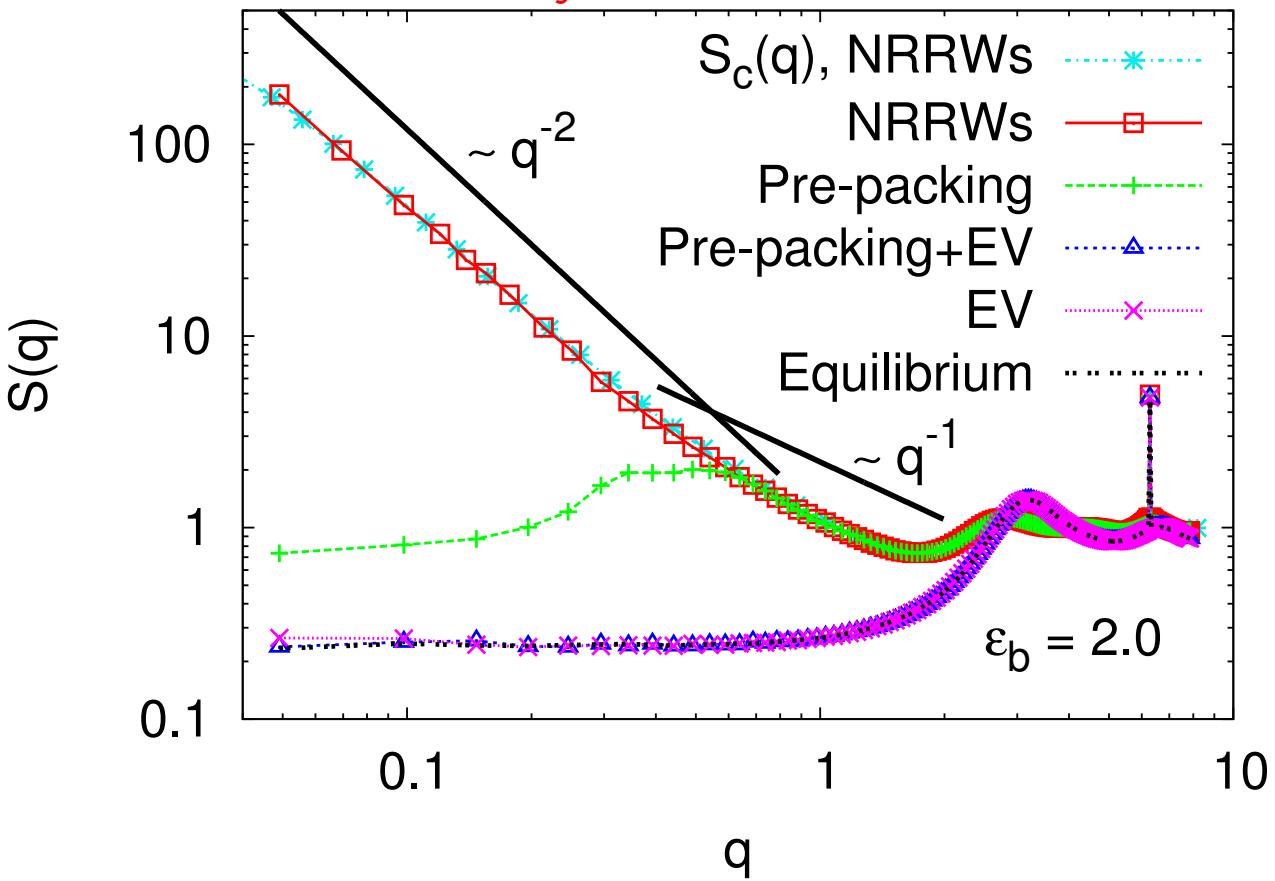


Pivot moves

Collective structure factor $S(q)$

- Representing the conformations of the whole polymer system at different stages

$$S(q) = \frac{1}{N_{\mathrm{tot}}} \left\langle \sum_{i=0}^{N_{\mathrm{tot}}} \sum_{j=0}^{\mathrm{N_tot}} \exp(i\vec{q} \cdot [\vec{r}_i - \vec{r}_j]) \right\rangle$$

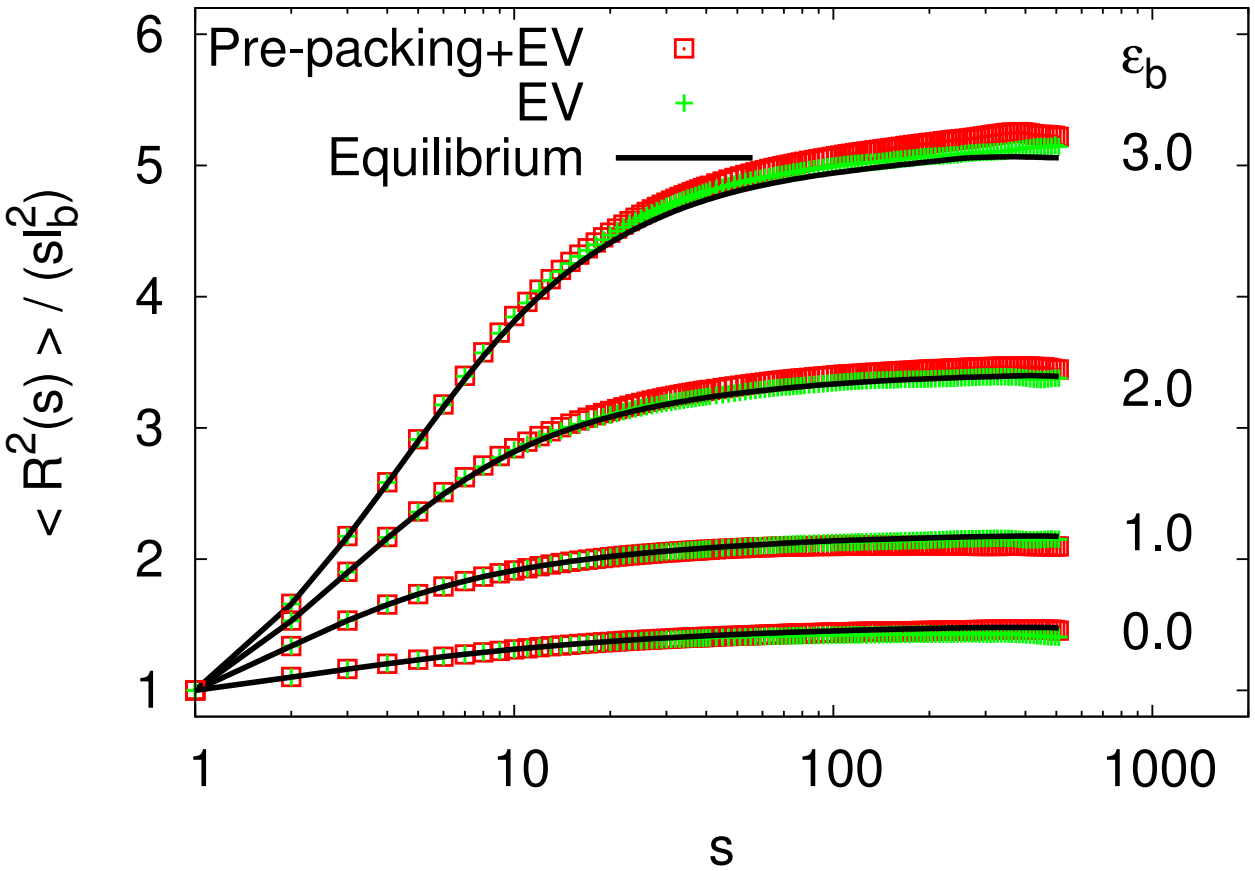


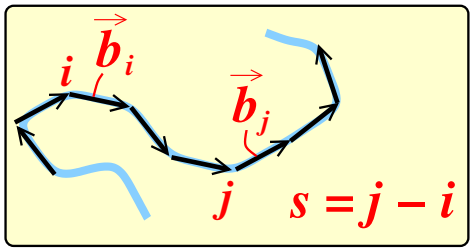
ε_b	l_p [lattice spacing]
0.0	1.18
1.0	2.52
2.0	4.30
3.0	6.60

Mean square internal distance $R(s)$

- Initial configurations of SAWs

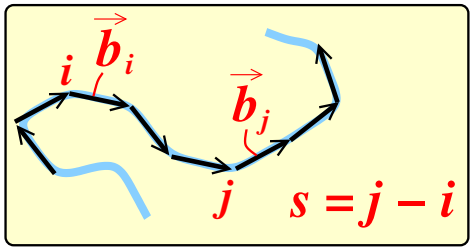
$$\langle R^2(s) \rangle = \left\langle \frac{1}{n_c} \sum_{n=1}^{n_c} \left[\frac{1}{N-s} \sum_{j=1}^{N-s} (\vec{r}_{n,j} - \vec{r}_{n,j+s})^2 \right] \right\rangle$$

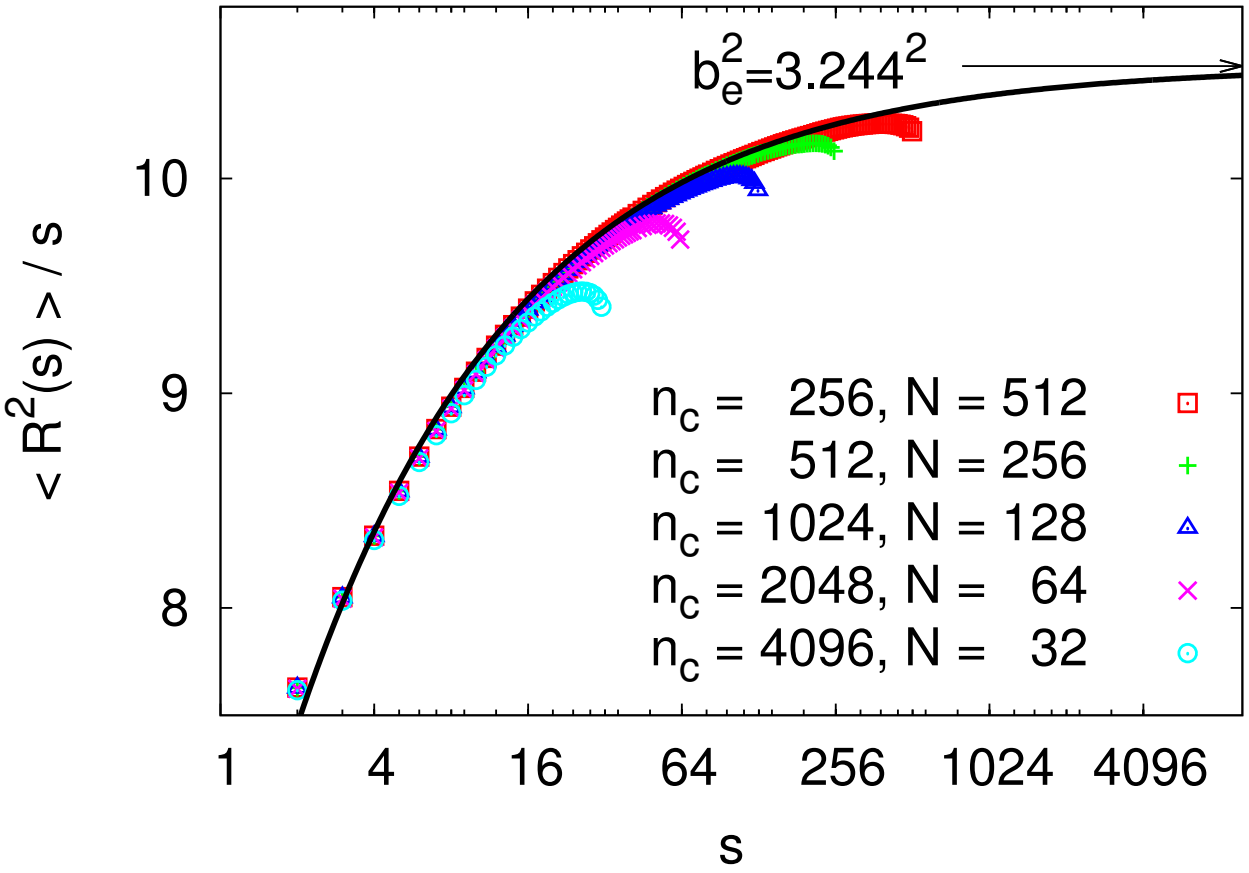




Mean square internal distance $R(s)$

- Fully flexible chains in a melt





Theoretical prediction:

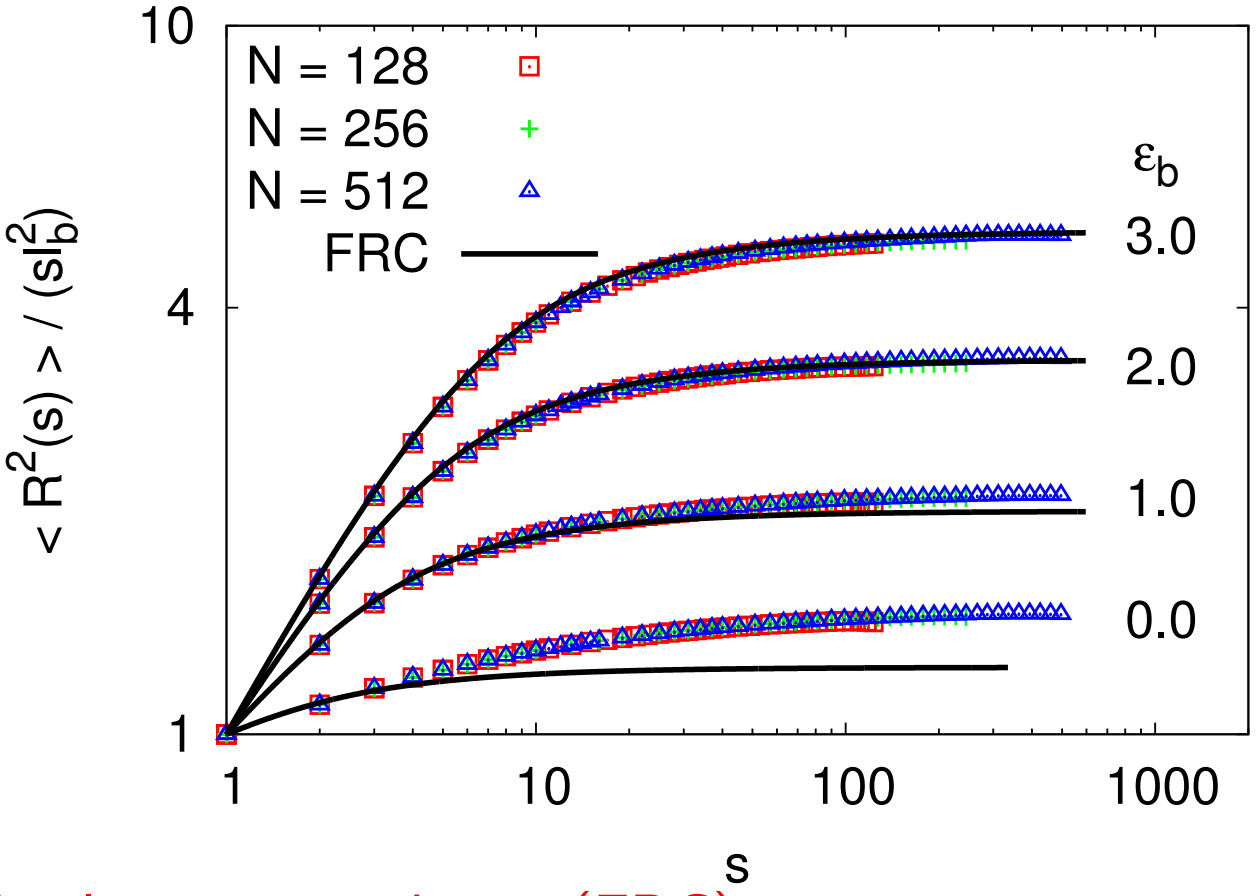
$$R^2(s)/s = b_e^2(1 - c_s/\sqrt{s}) \qquad \text{for} \quad 1 \ll s \ll N$$

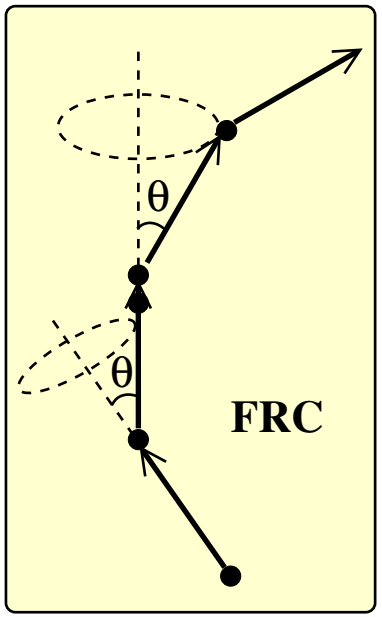
$$(b_e = 3.244,\ c_s = 0.412)$$

Wittmer et al., Phys. Rev. E 76, 011803 (2007)

Mean square internal distance $R(s)$

- Fully flexible and semi-flexible chains in a melt





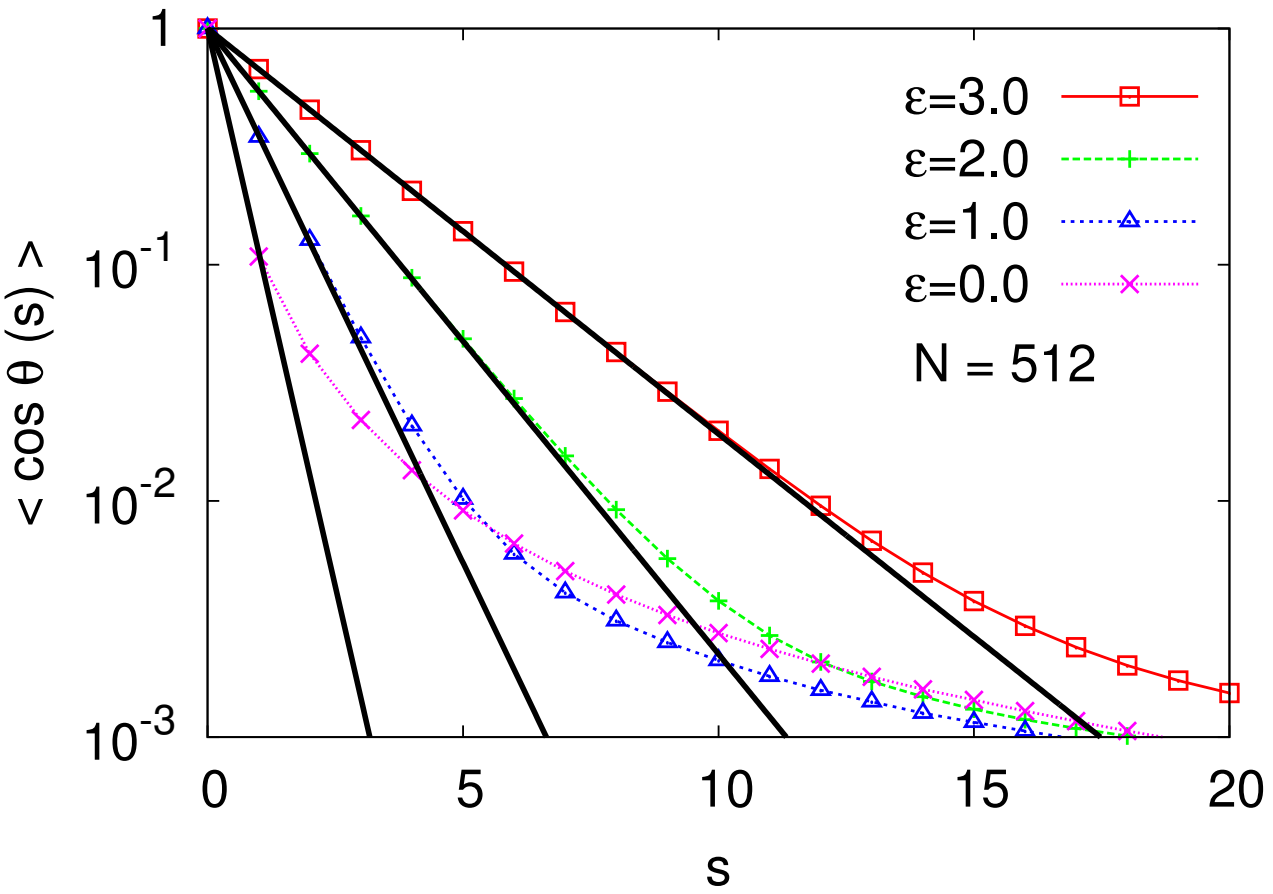
Freely rotating chains (FRC):

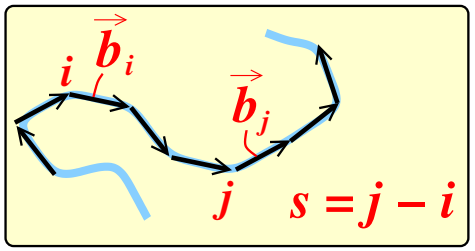
$$R^2(s)/s = \ell_b^2 \left(\frac{1 + \langle \cos\theta \rangle}{1 - \langle \cos\theta \rangle} - \frac{2\langle \cos\theta \rangle (1 - \langle \cos\theta \rangle^s)}{s(1 - \langle \cos\theta \rangle)^2} \right)$$

Persistence length ℓ_p

- Bond-bond orientational correlation function:

$$\langle \cos\theta \rangle \propto \exp(-s\ell_b/\ell_p)\,, \quad \text{(Gaussian chains)}$$



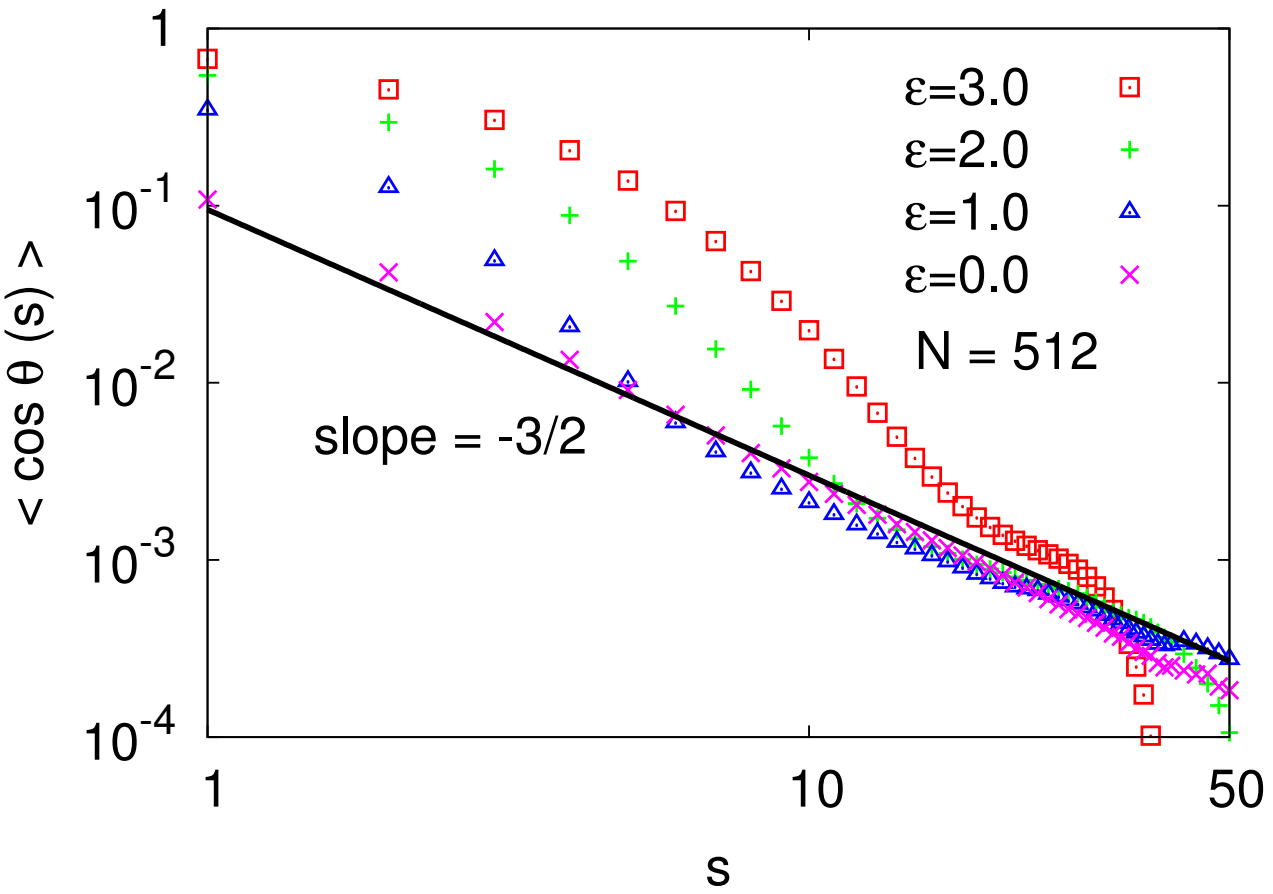


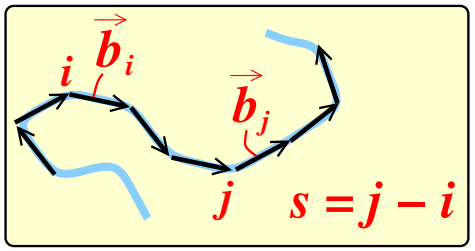
ε_b	l_p	l_b [lattice spacing]
0.0	1.18	2.63
1.0	2.52	2.62
2.0	4.30	2.62
3.0	6.60	2.61

Persistence length ℓ_p

- Bond-bond orientational correlation function:

$$\langle \cos\theta \rangle \propto s^{-3/2}\,, s^* < s < N \qquad (\text{dense melts}\,,\ \Theta\,\text{point})$$





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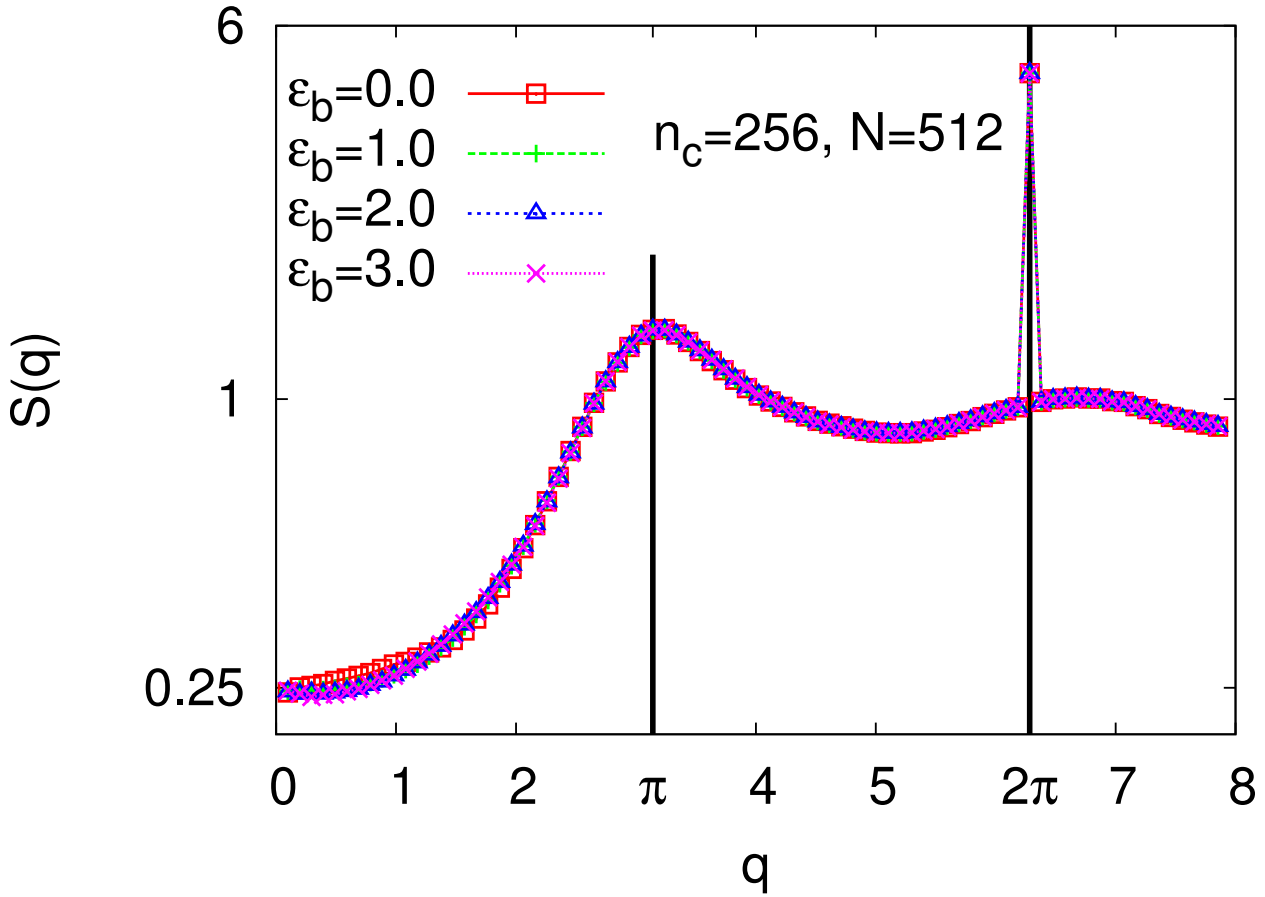
Collective structure factor $S(q)$

- The scattering from polymer melts in equilibrium



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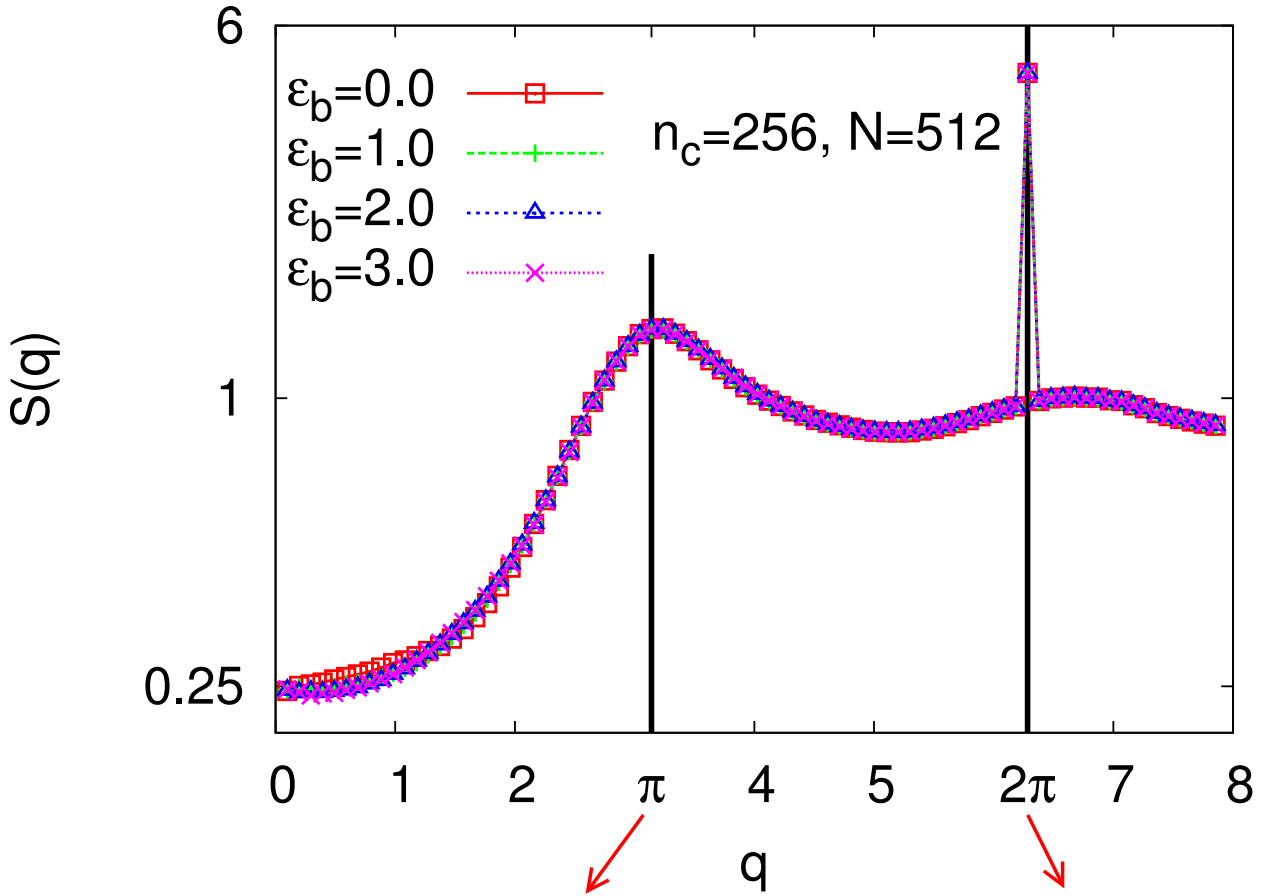
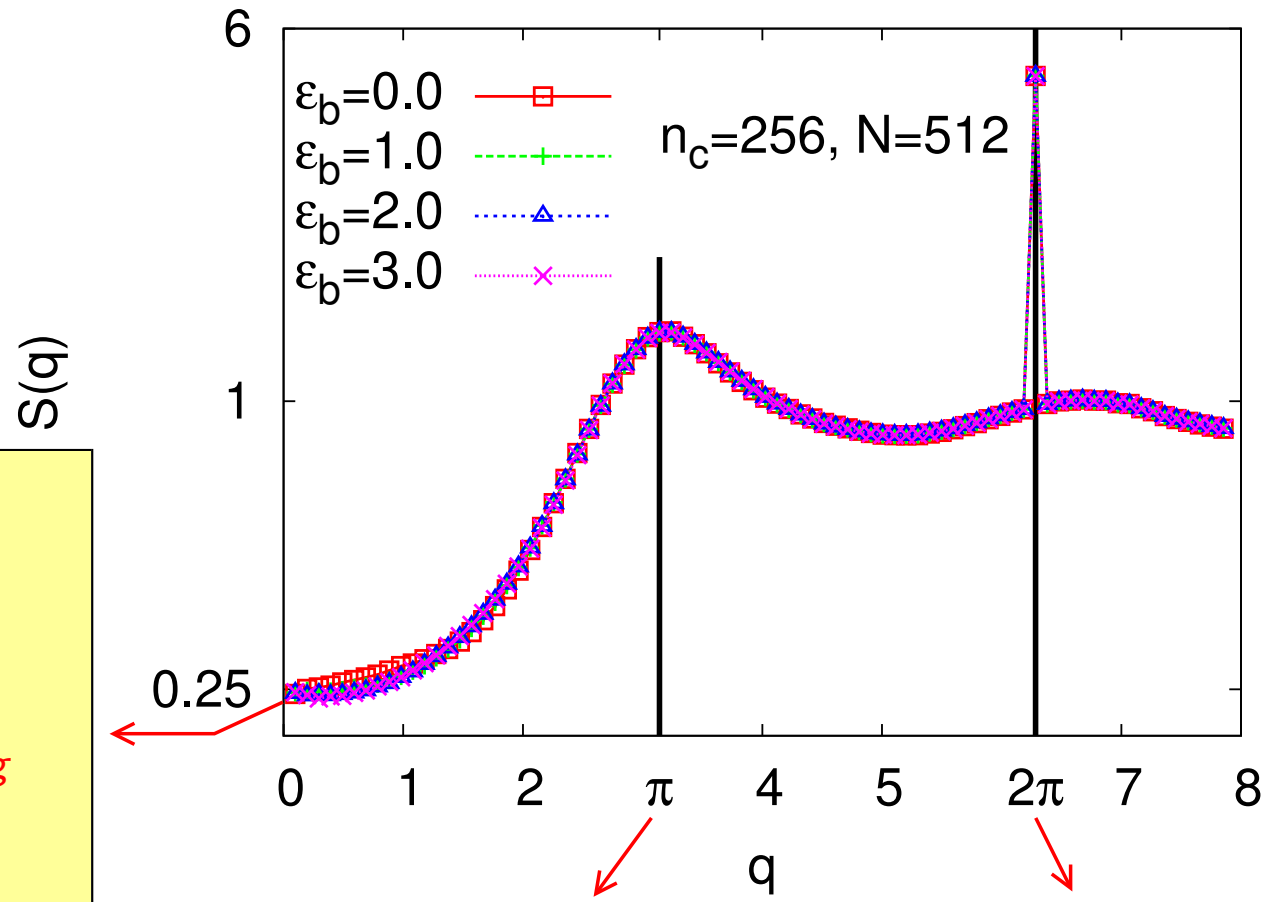


Mean inter-particle distance
$\approx$ 2 [lattice spacings]

Bragg peak

Collective structure factor $S(q)$

- The scattering from polymer melts in equilibrium



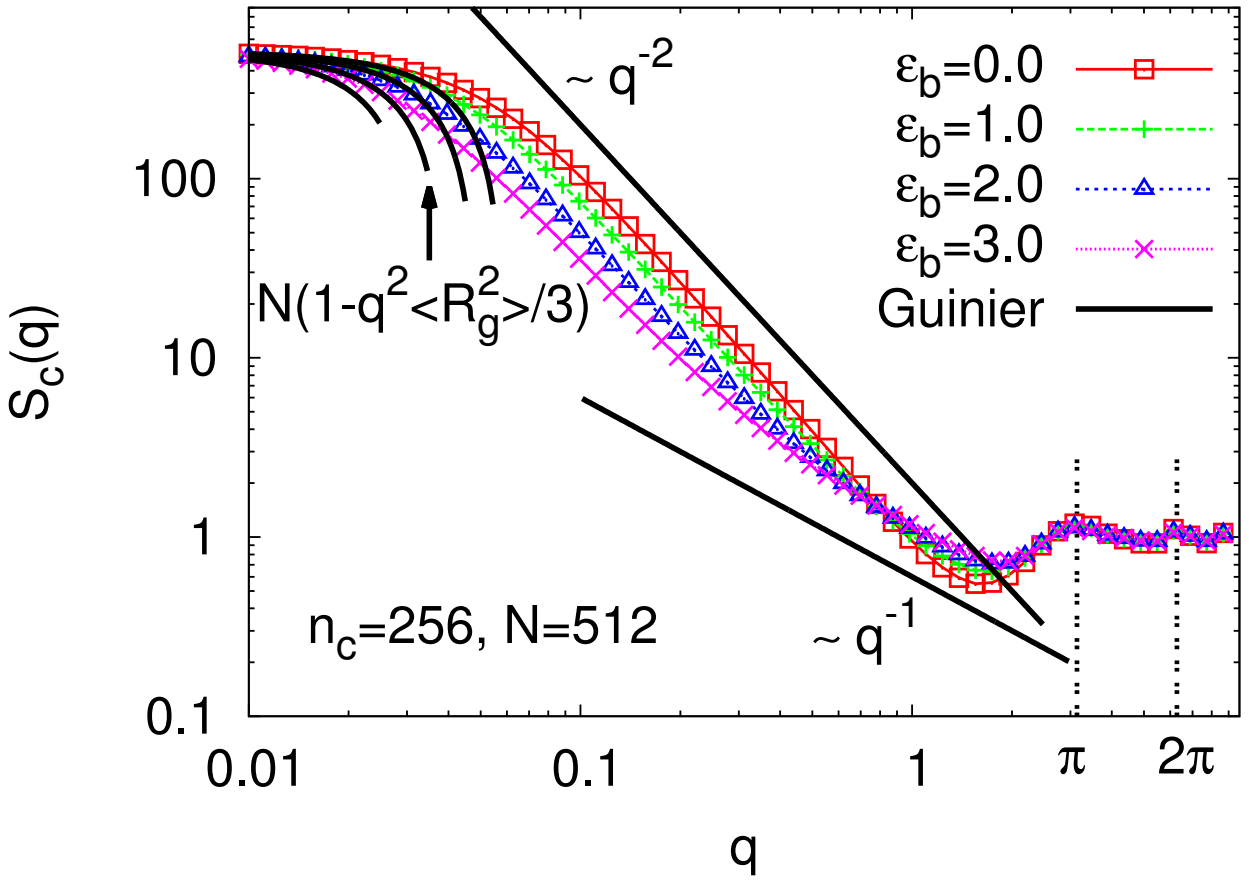
"Dimensionless compressibility"
$\lim_{q\to 0} S(q) = \rho k_B T \kappa_T = C_g$
$\kappa_T \equiv -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial p}\right)_T$
(isothermal compressibility)

Mean inter-particle distance ≈ 2 [lattice spacings]

Bragg peak

Structure factor $S_c(q)$

- The scattering from single chains in a melt in equilibrium

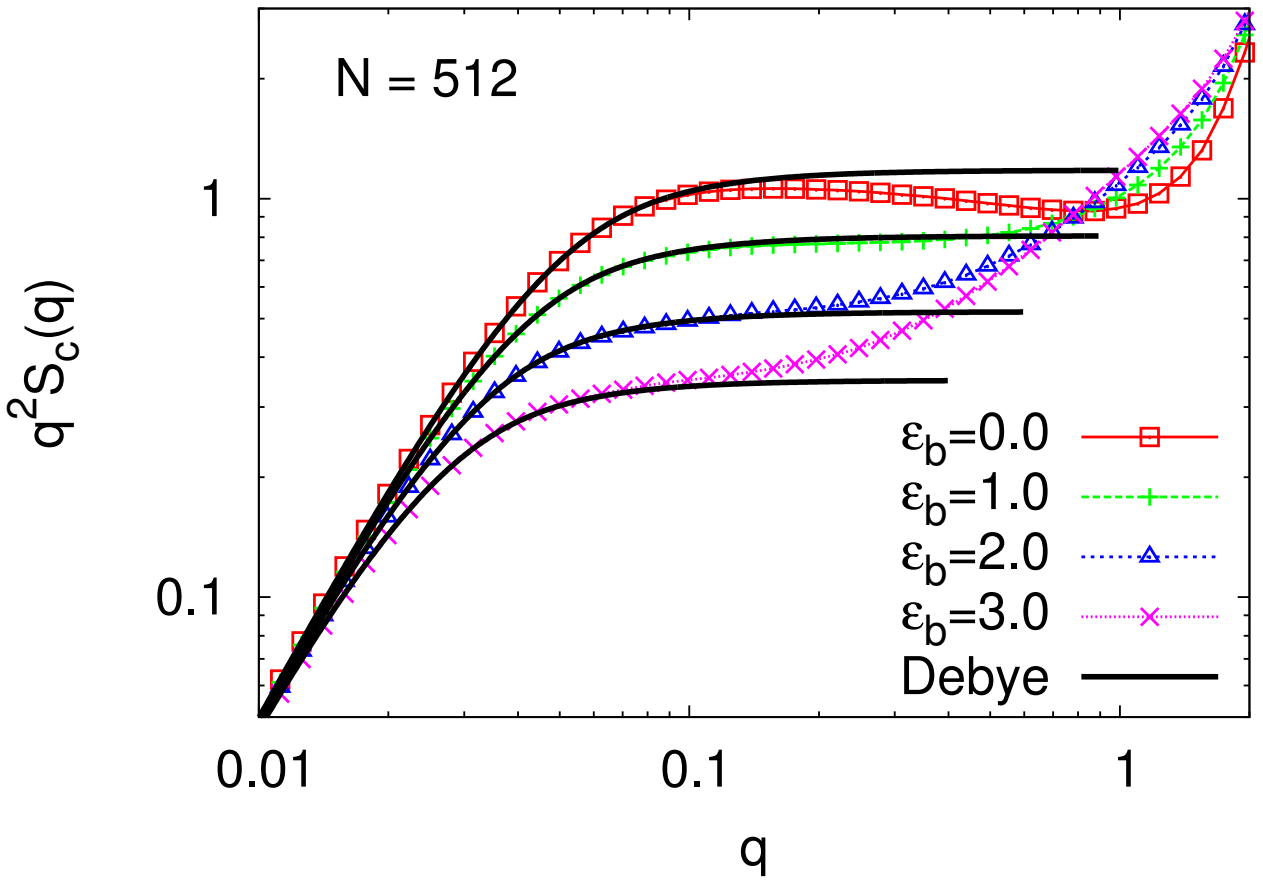


- Gaussian coils: (ideal chains) $S(q) \sim q^{-2}$
- Rigid-rod: $S(q) \sim q^{-1}$

Kratky-plot: $q^2 S_c(q)$ vs. q

Debye function describes the scattering from Gaussian chains

$$S_{\mathrm{Debye}}(q) = \frac{2}{\eta}\left(1 - \frac{1}{\eta} + \frac{\exp(-\eta)}{\eta}\right) \qquad \text{with} \qquad \eta = q^2 \langle R_g^2 \rangle$$



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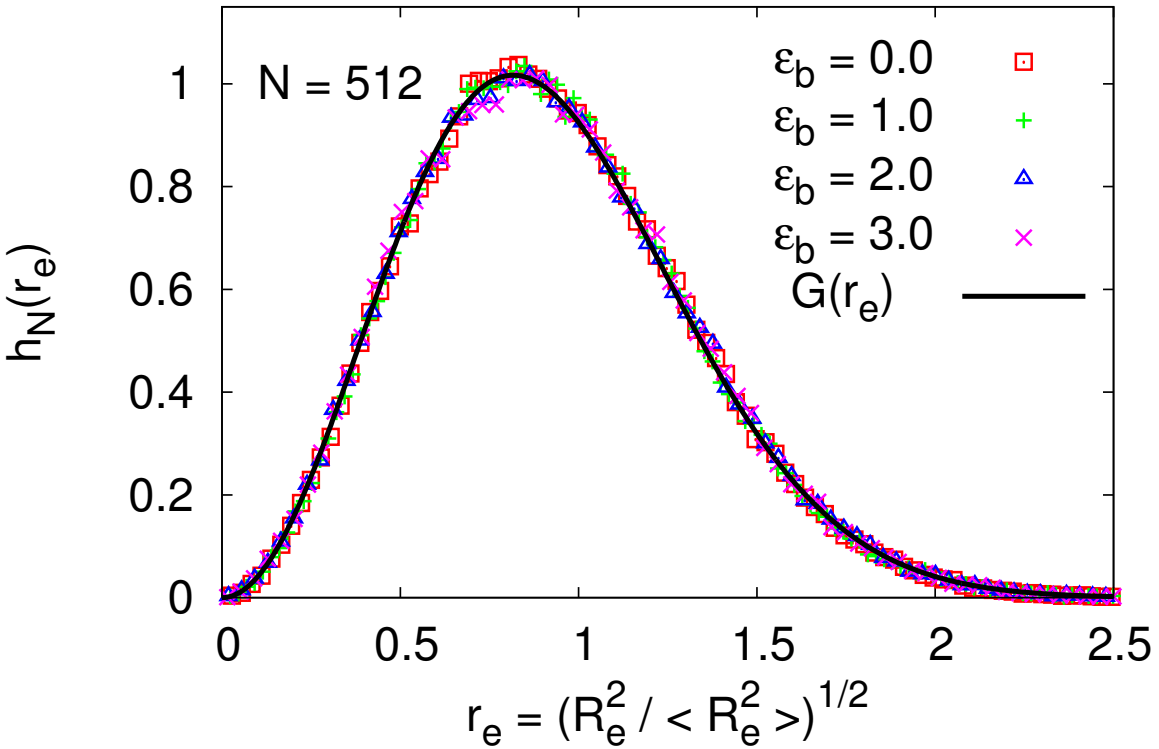
Probability distribution of R_e

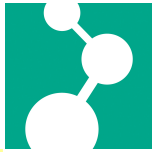
$P(\vec{R}_e)$ obeys the Gaussian distribution for ideal chains

$$P_N\left(\vec{R}_e\right) = \left(\frac{3}{2\pi N \ell_b^2}\right)^{3/2} \exp\left(-\frac{3R_e}{2N\ell_b^2}\right), \qquad \int_0^\infty 4\pi R_e^2 P_N(\vec{R}_e) dR_e = 1$$



$$\Rightarrow G(r_e) = 4\pi r_e^2 \left(\frac{3}{2\pi}\right)^{3/2} \exp\left(-\frac{3r_e^2}{2}\right) \text{“}=\text{”} h_N(r_e)$$ normalized histogram

Conclusion



- Pre-packing strategy:

  bead-spring model $\rightarrow$ bond fluctuation model

  $\Rightarrow$ efficient for preparing quasi-equilibrium configurations of large polymer systems (marginally incomplete elimination of excluded volume violations is allowed)

- The deviations from Gaussian statistics found for fully flexible chains in a melt is confirmed

- Conformational properties of semiflexible polymer chains in a melt are investigated in detail

  $\Rightarrow$ check the effect of chain stiffness for the non-Gaussian corrections

Acknowledgments

- Prof. Dr. Kurt Binder
  Johannes Gutenberg-Universität Mainz
- Prof. Dr. Kurt Kremer, Dr. Livia Moreira
  Max-Planck-Initut für Polymerforschung, Mainz
- Prof. Dr. Wolfgang Paul
  Martin-Luther-Universität Halle-Wittenberg
- Computational resources:
  - The John von Neumann-Institut für Computing (NIC), Jülich
  - The Rechenzentrum Garching (RZG), the supercomputer center of the Max Planck Society

Thank You!