Polymer Simulations with

Pruned-Enriched Rosenbluth Method

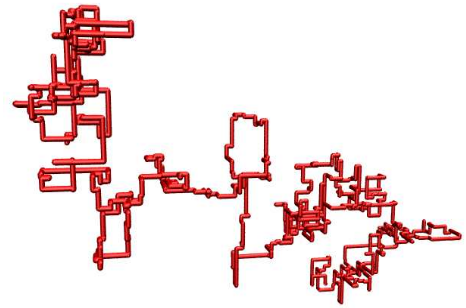
II

Hsiao-Ping Hsu

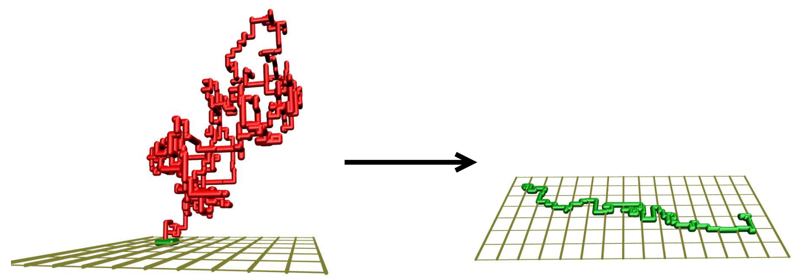
Institut für Physik, Johannes Gutenberg-Universität Mainz, Germany

Semiflexible chains

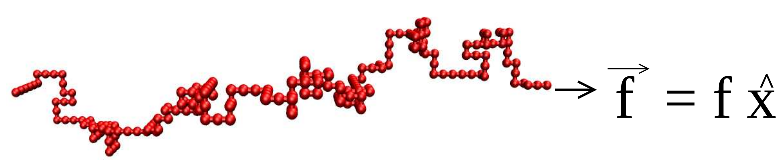
- Conformations of polymer chains in the bulk with variable stiffness



- Effect of chain stiffness on the adsorption transition of polymers



- Deformations of semiflexible chains under external stretching force



Semiflexible chains in bulk

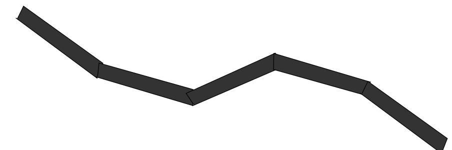
- How important is the excluded volume effect?
  - Biopolymers: dsDNA ($\ell_p \approx 50$nm), ssDNA ($\ell_p \approx 0.6$nm), ...

Semiflexible polymer chains

" $\stackrel{?}{=}$ "

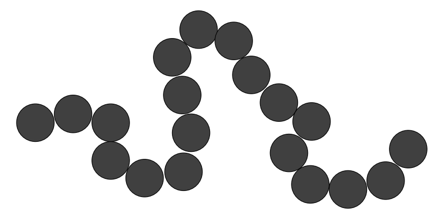
Worm−like chain model

(Kratky−Porod model)



dsDNA

(stiff chain)

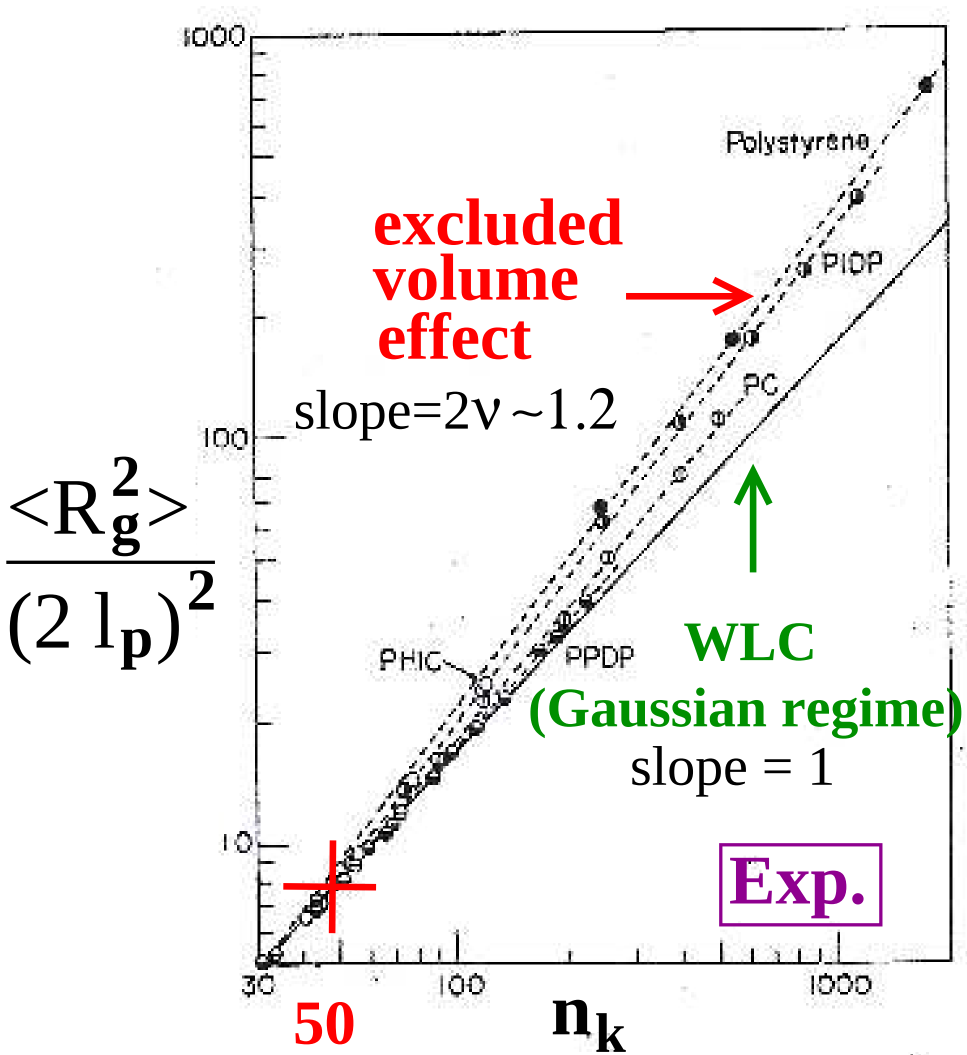


ssDNA

(flexible chain)

Semiflexible chains in bulk

- Experiment: different polymers with different stiffness



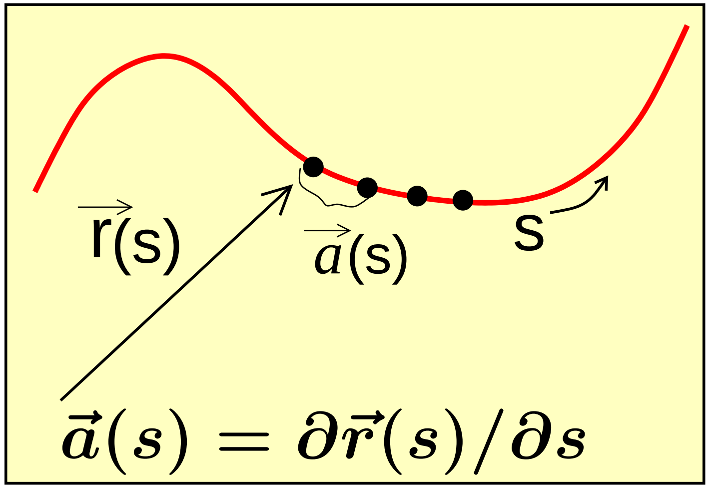
- R_g: radius of gyration
- ℓ_p: persistence length
- n_k: # of Kuhn segments,

$$n_k = L/(2\ell_p)$$

- L: contour length

Norisuye & Fuijta, Polymer J. 14,143 (1982)

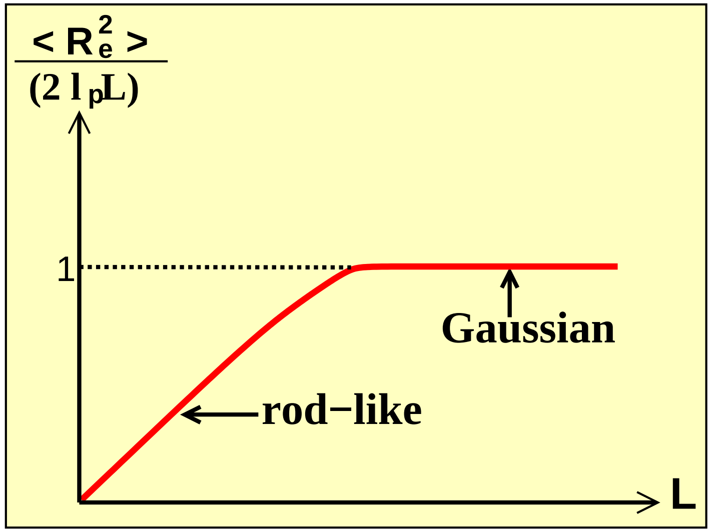
Worm-like chain model



- Orientational correlation function:
  $$\langle \vec{a}(s')\vec{a}(s'+s)\rangle \propto \exp(-s/\ell_p)$$
- Hamiltonian:
  $$\mathcal{H} = \frac{\ell_p k_B T}{2}\int_0^L ds \left(\frac{\partial^2 \vec{r}(s)}{\partial s^2}\right)^2$$
- End-to-end distance: $\vec{R}_e = \int_0^L \vec{a}(s)ds$

Question: Is neglect of excluded volume justified?

Worm-like chain model



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- End-to-end distance: $\vec{R}_e = \int_0^L \vec{a}(s)ds$
- Mean square end-to-end distance $\langle R_e^2\rangle$ ($= \langle \vec{R}_e \cdot \vec{R}_e\rangle$):

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

$$= \begin{cases} L/2\ell_p = (\ell_b N)/(2\ell_p) & \text{for } L \ll \ell_p \text{ (rod − like chain)} \\ 1 & \text{for } L \to \infty \text{ (Gaussian chain)} \end{cases}$$

Semiflexible SAW model

A semiflexible polymer chain under a good solvent condition

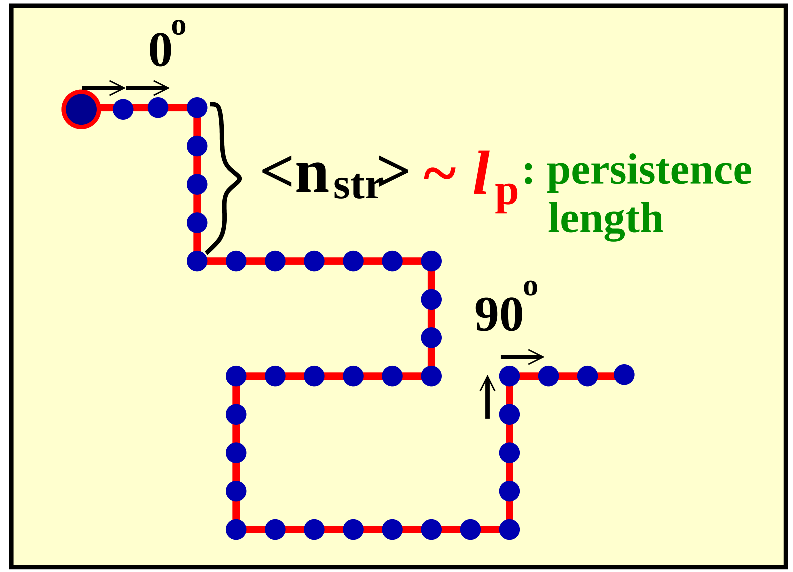
- Excluded volume effect

  $\Rightarrow$ Self-avoiding walk (SAW)

- Chain stiffness

  $\Rightarrow$ Bond-bending potential

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

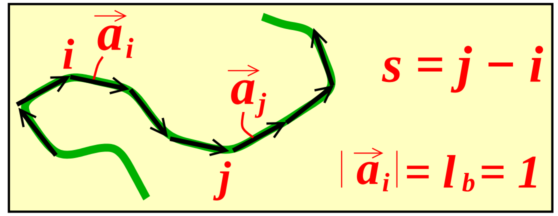


bending energy $\epsilon_b \uparrow$, stiffness $\uparrow$

on the square lattice $(d = 2)$ and simple cubic lattice $(d = 3)$

Persistence length ℓ_p

- Bond orientational correlation function:
  $\langle \cos\theta(s)\rangle = \langle \vec{a}_i \cdot \vec{a}_{j=i+s}\rangle / \ell_b^2$
  $\equiv \exp(-s\ell_b/\ell_p) \Rightarrow \ell_p/\ell_b$



[lattice spacing]

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

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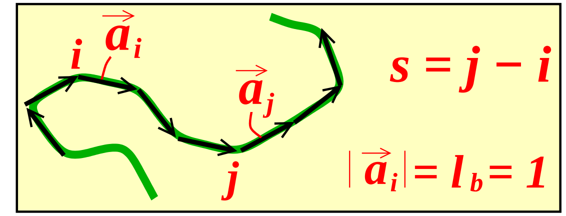

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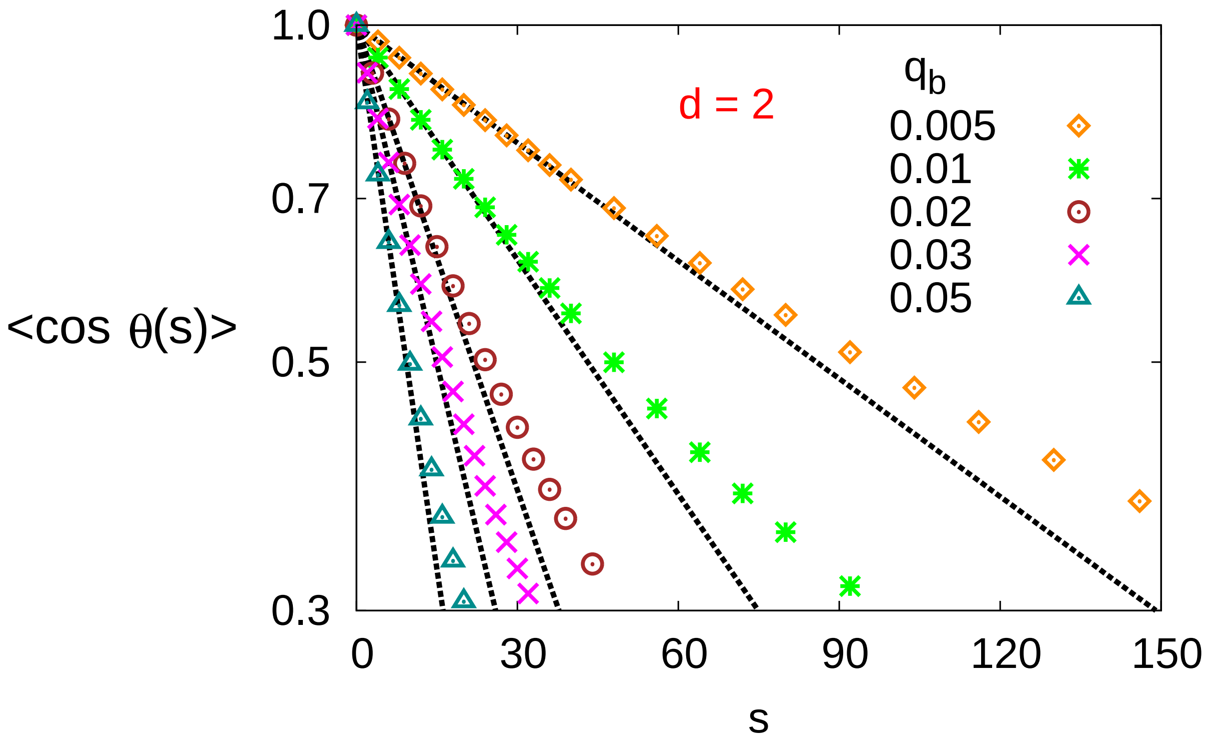

q_b	l_p (2D in bulk)	
0.005	124	stiff
0.01	62	
0.02	31	
0.03	21	
0.05	13	
0.1	8	
0.2	4	
0.4	2	
1.0	1	flexible

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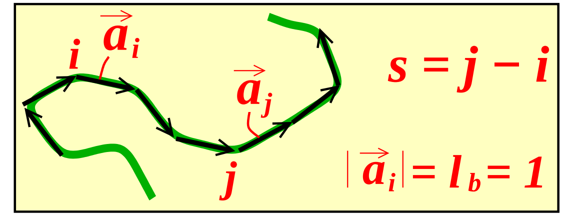

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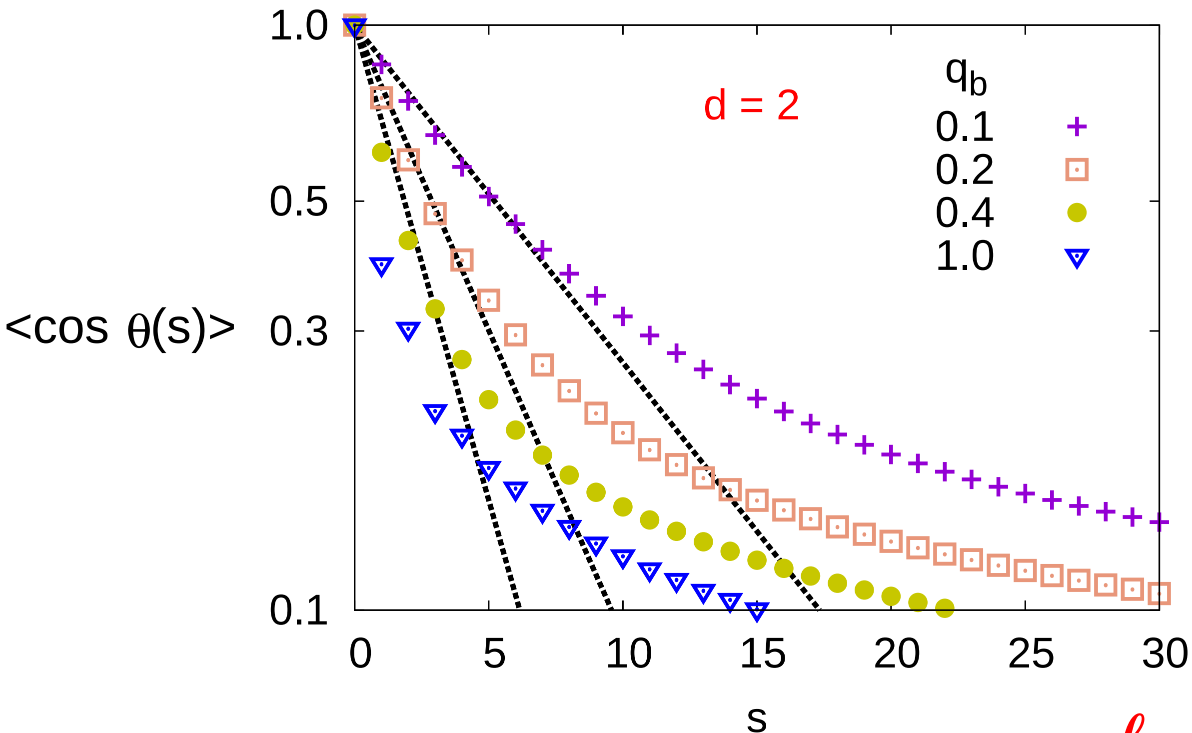

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$$\ell_p/\ell_b = -1/\ln\langle \cos\theta(s=1)\rangle$$

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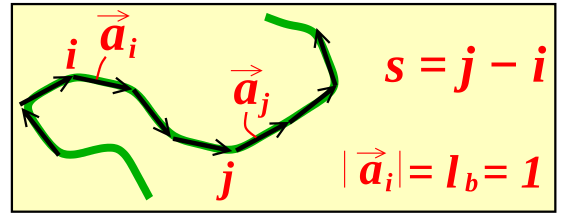

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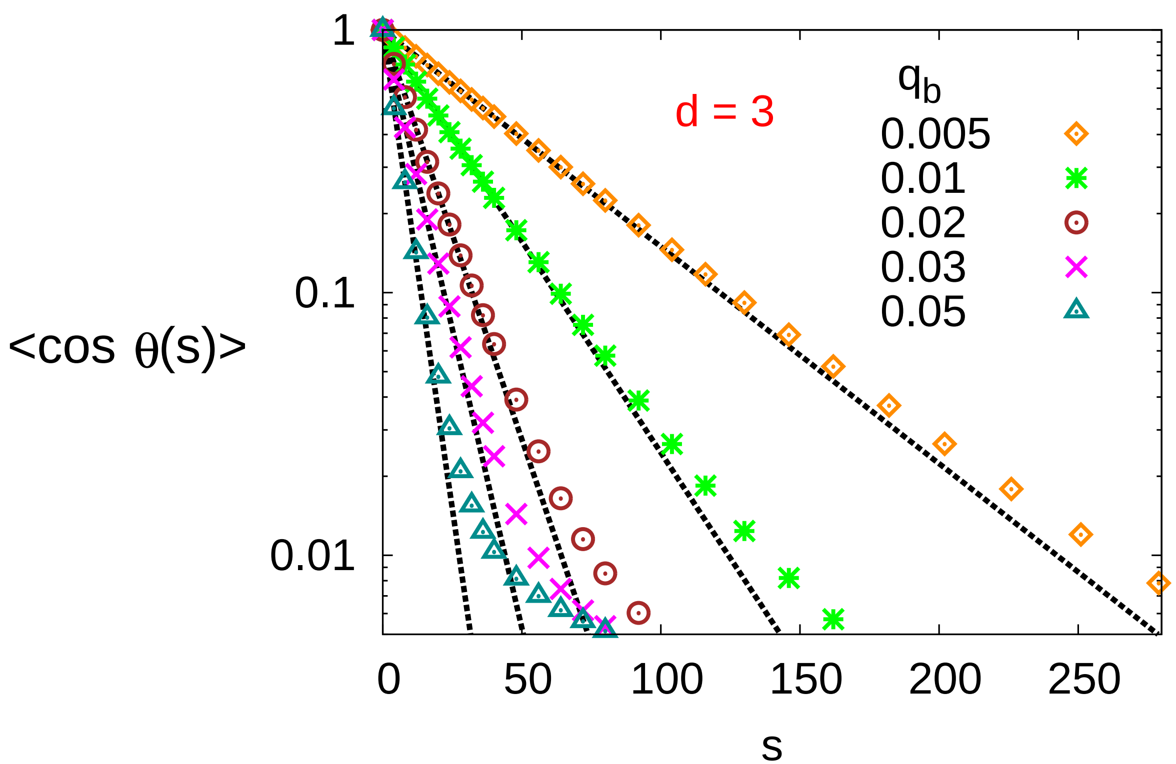

q_b	l_p (3D in bulk)	
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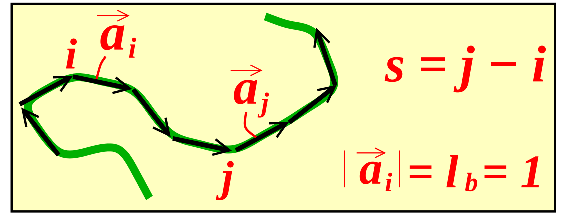

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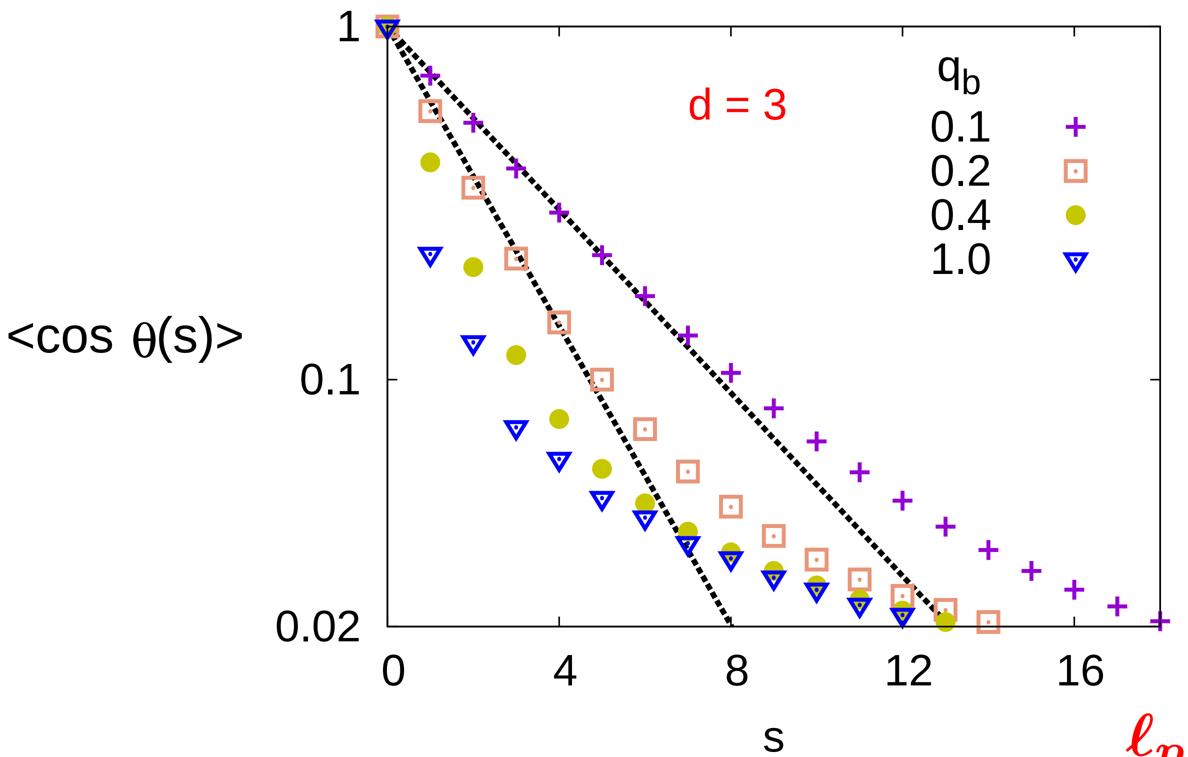

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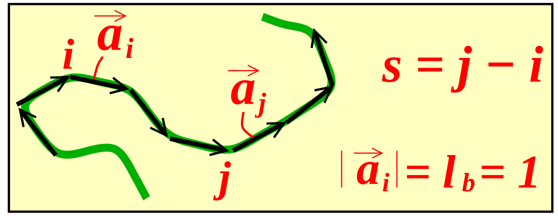
Bond orientational correlation function

- For rather flexible chains:

$$\langle \cos\theta(s)\rangle = \langle \vec{a}_i \cdot \vec{a}_{j=i+s}\rangle / \ell_b^2 \propto s^{-\beta}$$

$\beta = 2 - 2\nu$, ν: Flory exponent

Schäfer et al, J. Phys. A 32, 7875 (1999)



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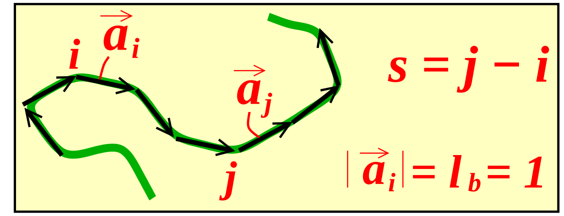

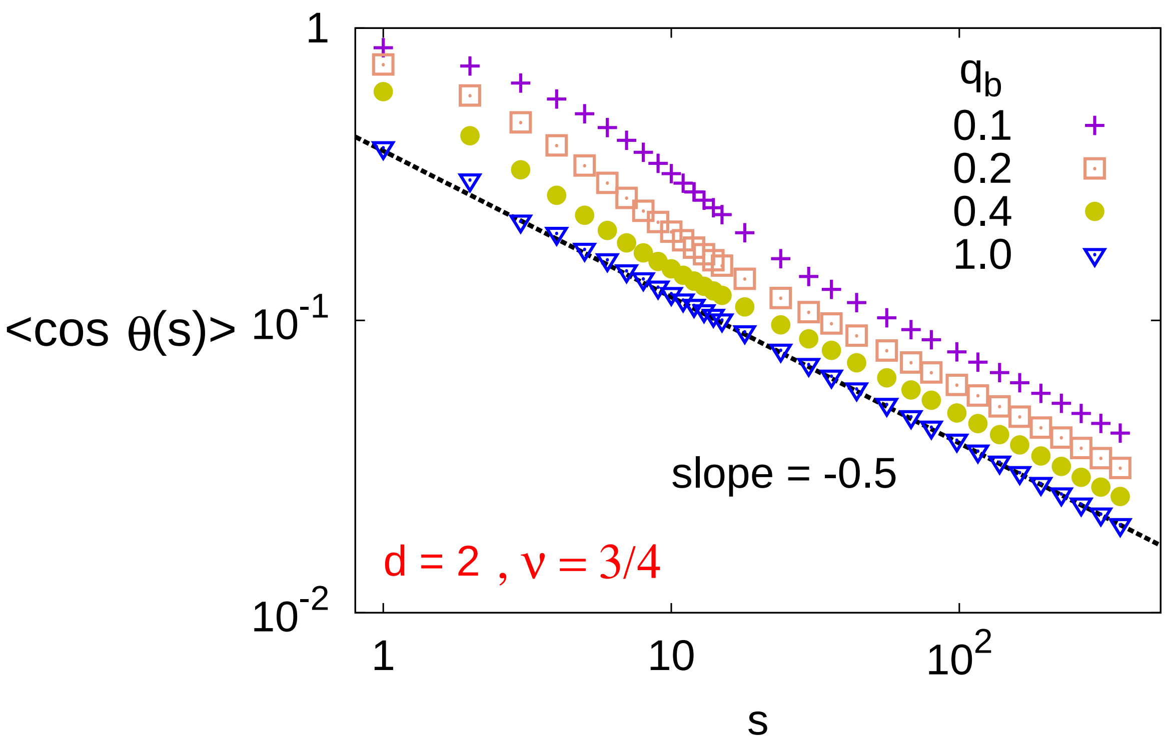

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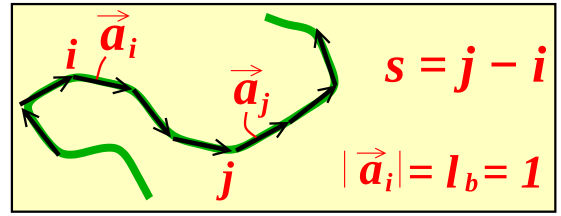

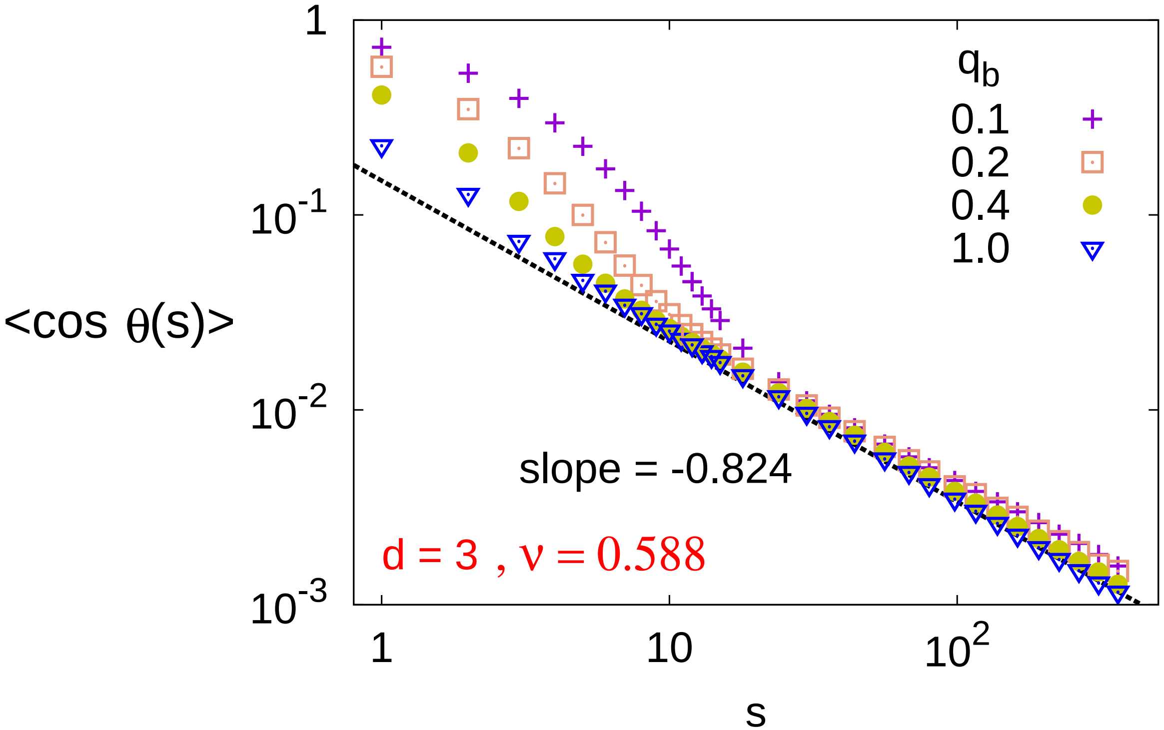

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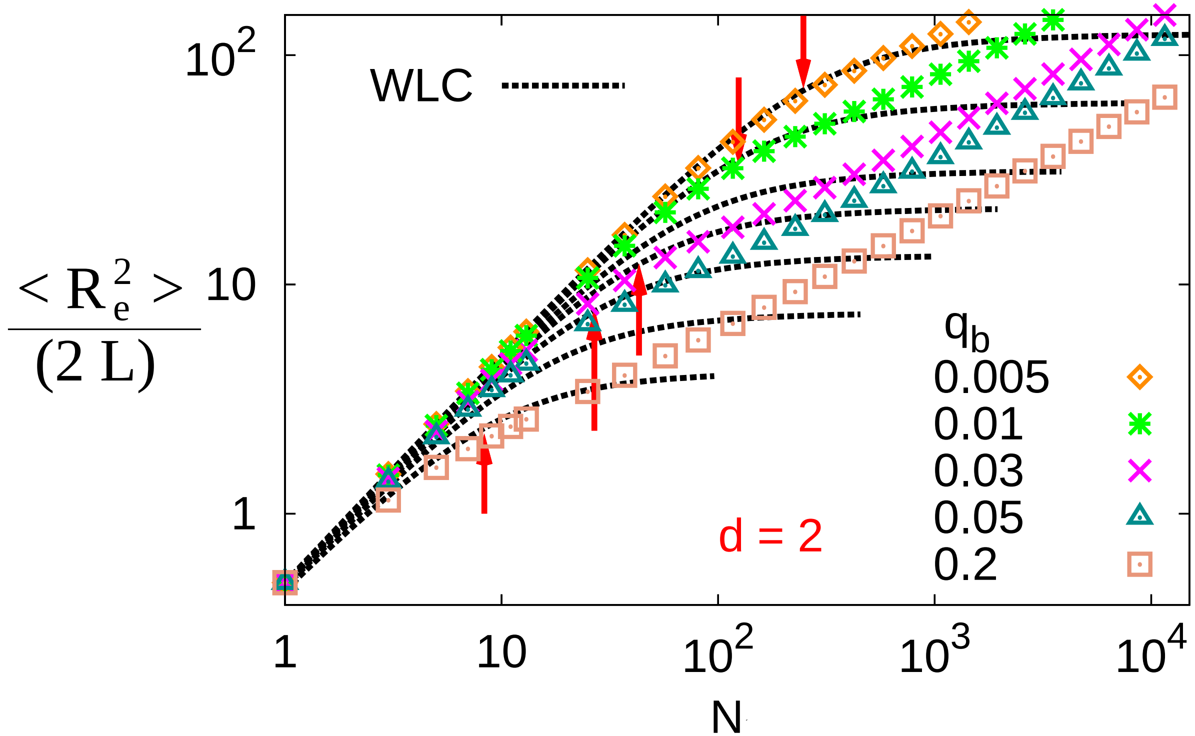
$2D$ semiflexible chains in bulk

- Mean square end-to-end distance $\langle R_e^2 \rangle$ $(= \langle (\sum_{j=1}^{N_b} \vec{a}_j)^2 \rangle)$:



crossover point ↓: $N_b^{\text{rod}}(q_b) = 2\ell_p/\ell_b$

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1.0	1	flexible

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

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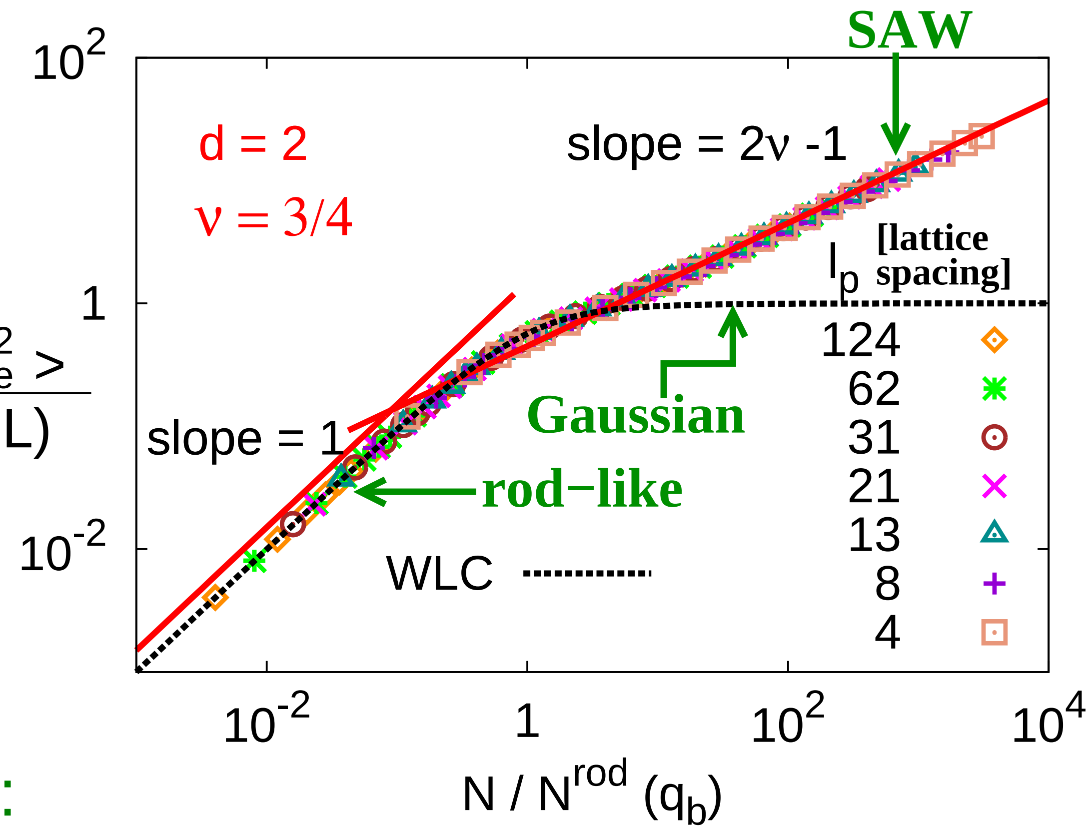

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WLC:

$$\frac{\langle R_e^2 \rangle}{2\ell_p L} = \begin{cases} L/2\ell_p = (\ell_b N)/(2\ell_p) & \text{for } L \ll \ell_p \text{ (rod − like chain)} \\ 1 & \text{for } L \to \infty \text{ (Gaussian chain)} \end{cases}$$

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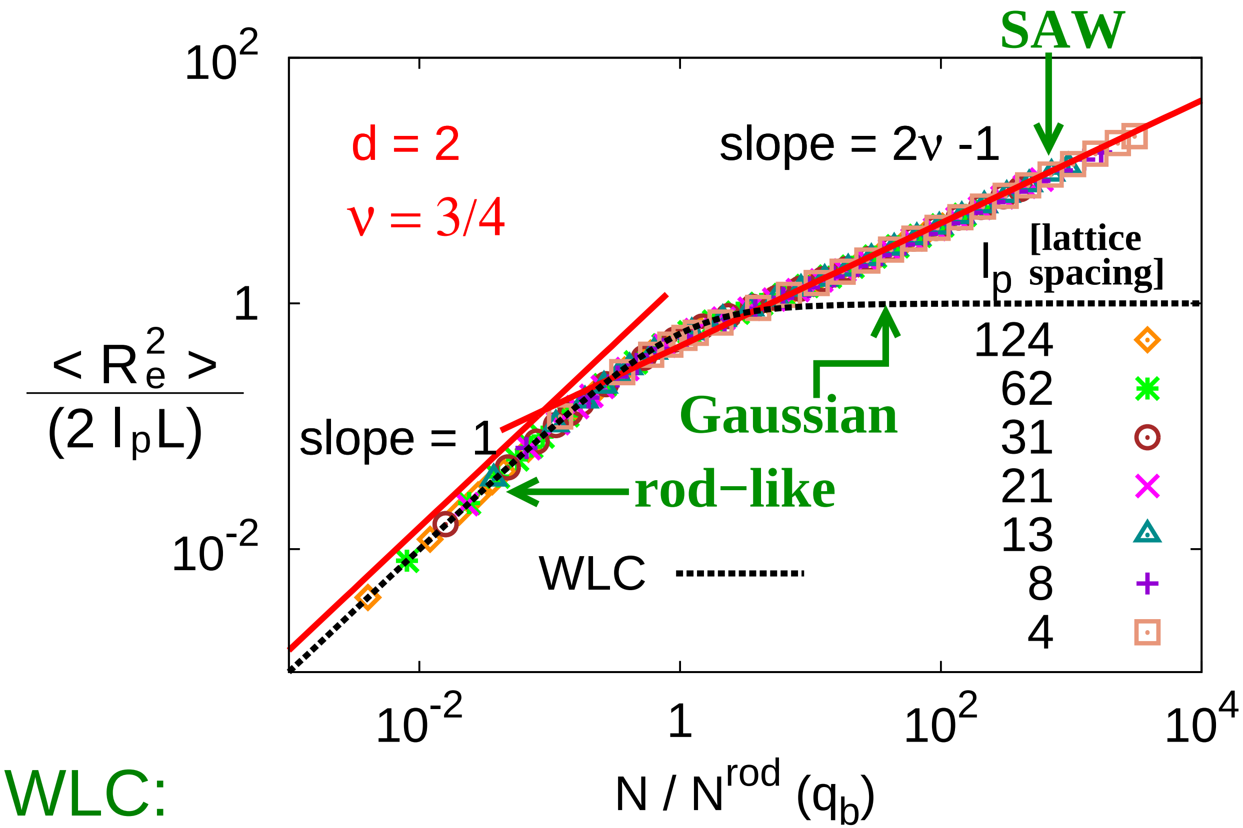

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WLC breaks down in d=2!

WLC:

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$3D$ semiflexible chains in bulk

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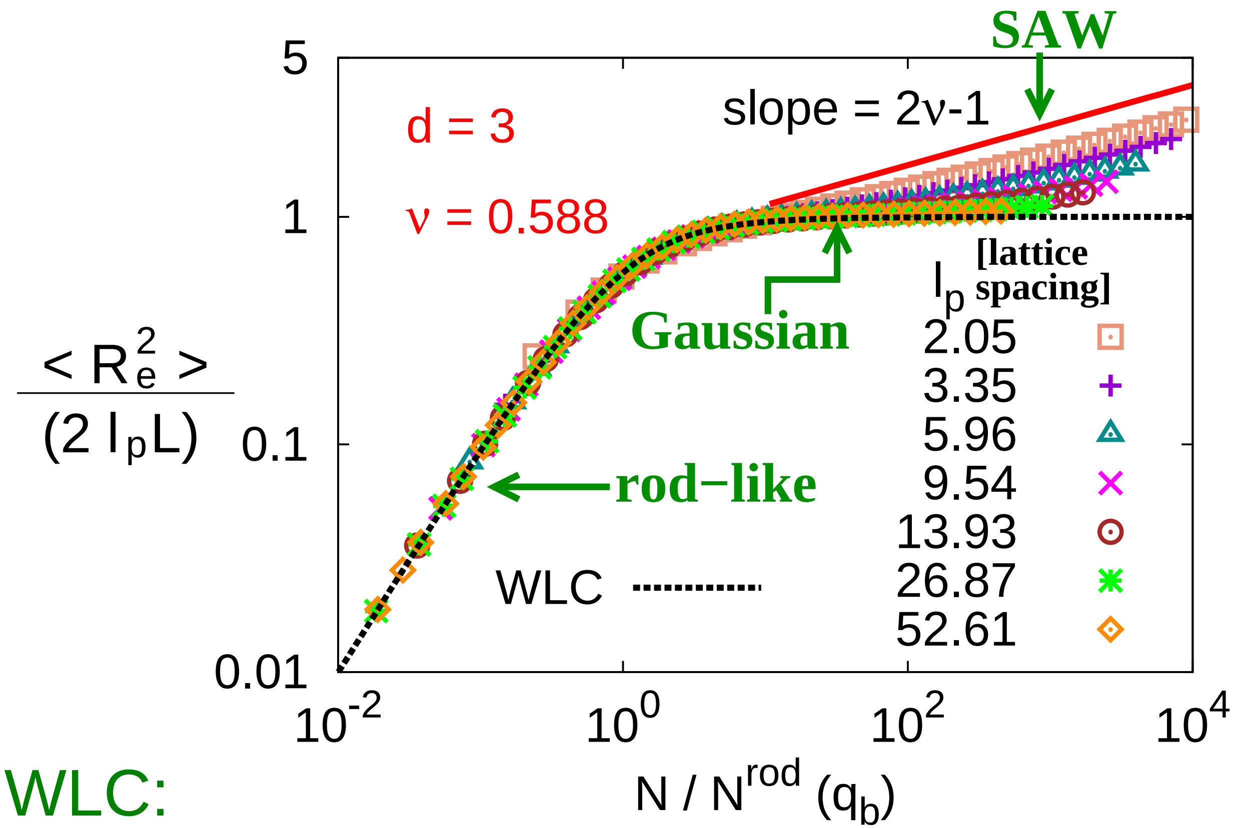

crossover point : $N^{\mathrm{rod}}(q_b) = 2\ell_p/\ell_b$

WLC:

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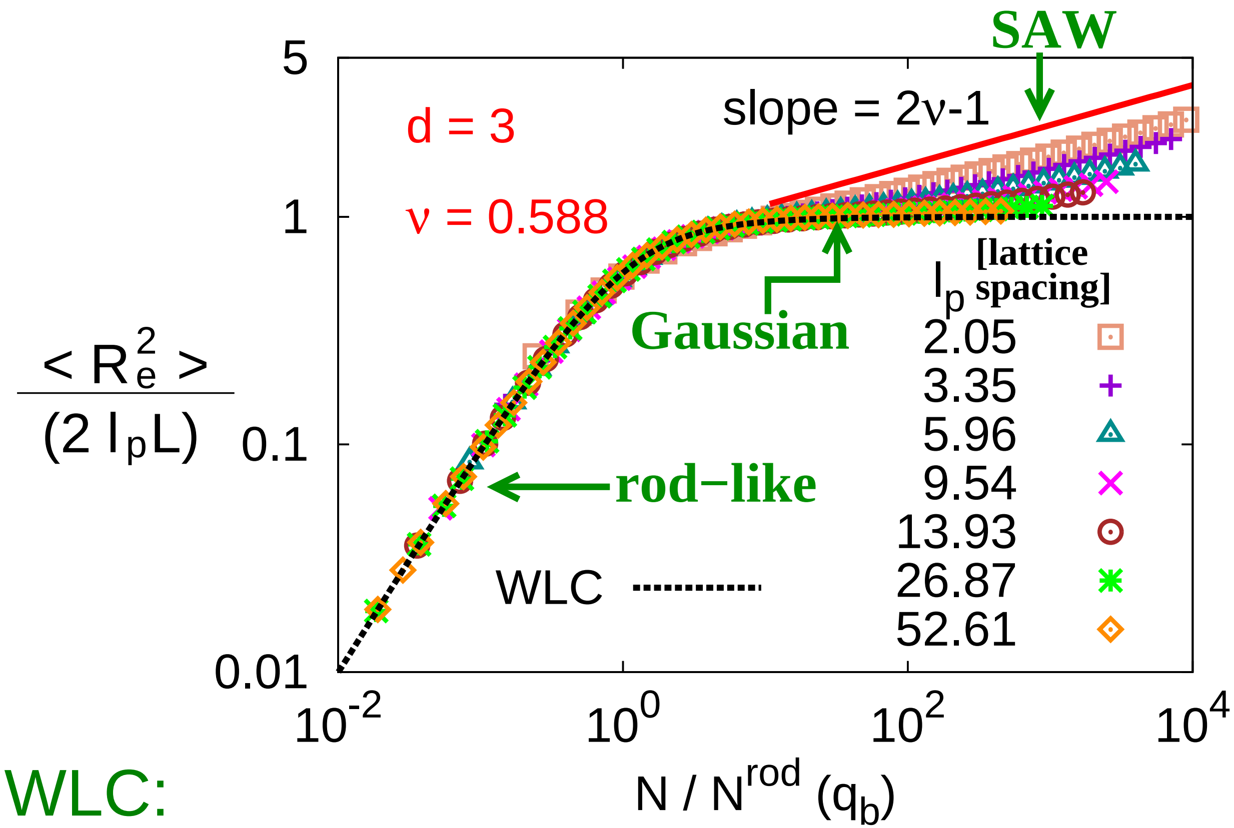

crossover point :
$N^{\text{rod}}(q_b) = 2\ell_p/\ell_b$

$3D$ WLC model works for stiff but very long chains, unlike $2D$

WLC:

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Flory-like theory for semiflexible chains

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

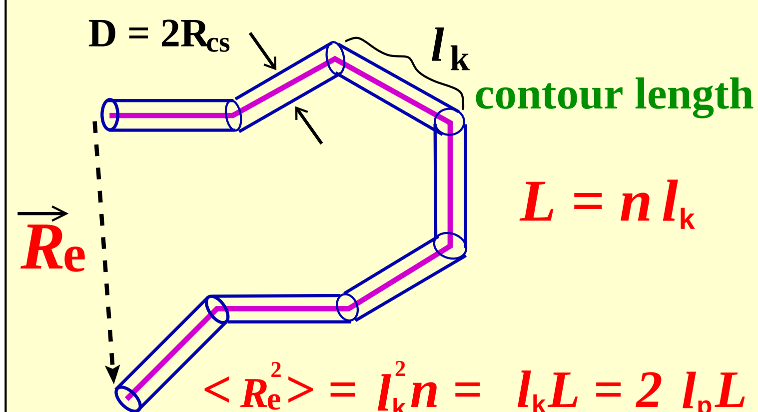
$$\Delta F \approx \frac{R_e^2}{\ell_K L}(\text{elastic energy}) + v_2 R_e^3 \left[\frac{L/\ell_K}{R_e^3}\right]^2 (\text{repulsive energy})$$

  - 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:

A chain with **n** units of Kuhn length l_k randomly linked:



[2nd virial coefficient · density]^2 · volume = $[v_2\rho^2]\, V$

$$v_2^{(d=2)} = \ell_k^2 v_2^{(d=3)} = \ell_K^2 D \;, \rho = \frac{n}{R_e^d} = \frac{L/\ell_K}{R_e^d} \;, V = R_e^d$$

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

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

- Minimizing ΔF with respect to R_e, i.e. $\partial \Delta F/\partial R_e = 0$:
  $\Rightarrow R_e \approx (v_2/\ell_K)^{1/5} L^{3/5} = (\ell_K D)^{1/5} (N\ell_b)^{3/5}$ (SAW)
- Upper bound of Gaussian chains ($R_e^2 = \ell_K L = \ell_K \ell_b N$):
  $\Rightarrow \Delta F \approx R_e^2/(\ell_K L) \sim 1$
  $v_2 R_e^3 \left[(L/\ell_K)/R_e^3\right]^2 < 1 \Rightarrow N < \ell_K^3/(\ell_b D^2) = N^*$
- Upper bound of Rod-like chains $R_e^2 = L^2 = N^2 \ell_b^2$:
  $R_e^2 = N^2 \ell_b^2 < \ell_K \ell_b N \Rightarrow N < \ell_K/\ell_b = 2\ell_p/\ell_b = N^{\text{rod}}$

Theoretical predictions

- Double crossover in $d = 3$:

$$R \approx L\,, \quad N < N^{\text{rod}} = \ell_k/\ell_b \quad (\text{rod} - \text{like chain})$$

$$R \approx (\ell_k L)^{1/2}\,, \quad N^{\text{rod}} < N < N^* \quad (\text{Gaussian coil})$$

$$R \approx (\ell_k D)^{1/5} L^{3/5}\,, \quad N > N^*\,(R > R^*) \quad (\text{SAW})$$

- Single crossover in $d = 2$:

$$R \approx L\,, \quad N < N^{\text{rod}} = \ell_k/\ell_b \quad (\text{rod} - \text{like chain})$$

$$R \approx (\ell_k)^{1/4} L^{3/4}\,, \quad N > N^{\text{rod}}\,(R > \ell_k) \quad (\text{SAW})$$

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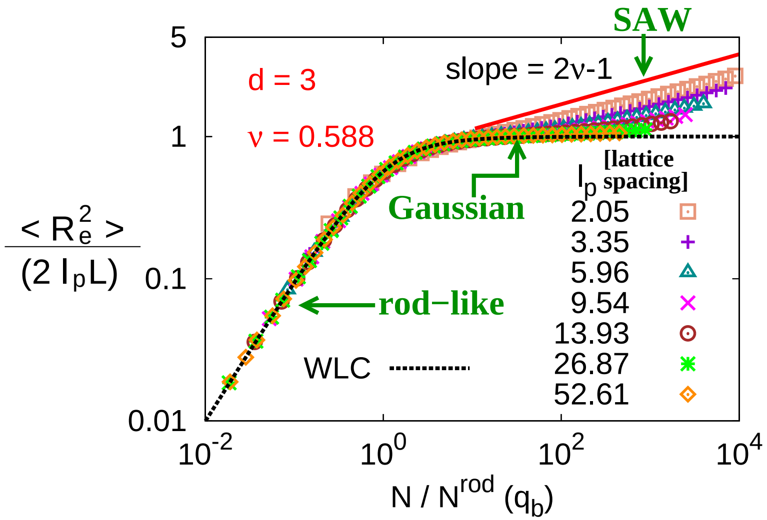

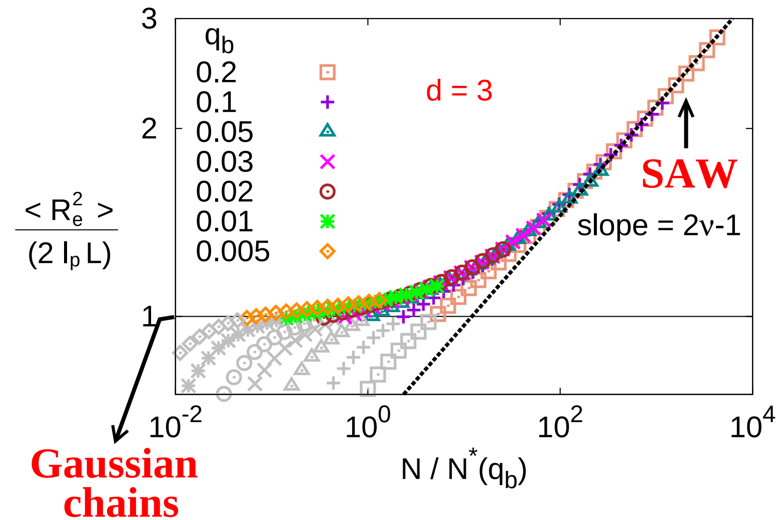

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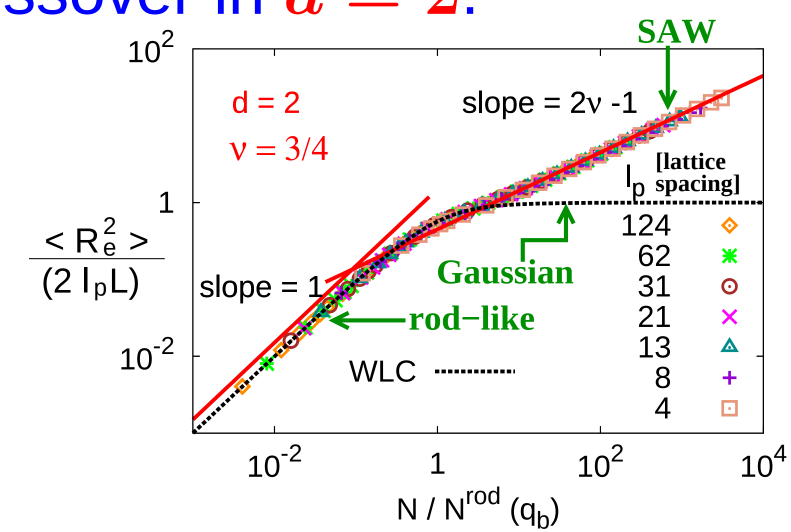
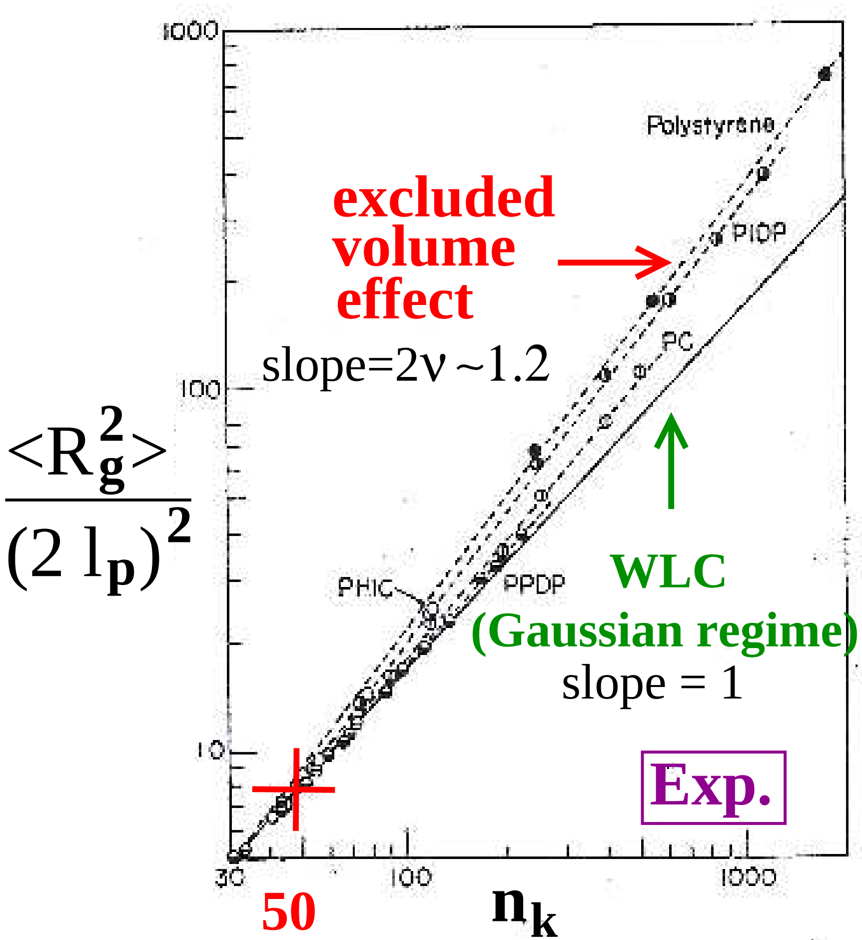


Verified !

Simulation vs. Experiment

- Mean square radius of gyration $\langle R_g^2 \rangle$:



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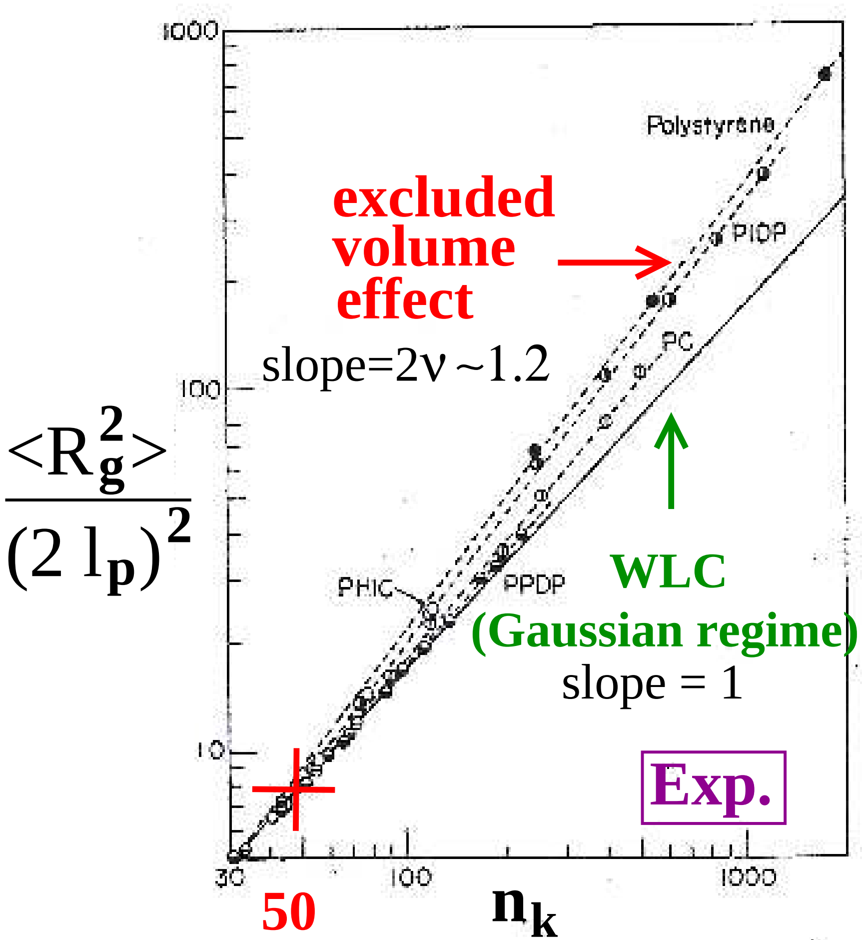
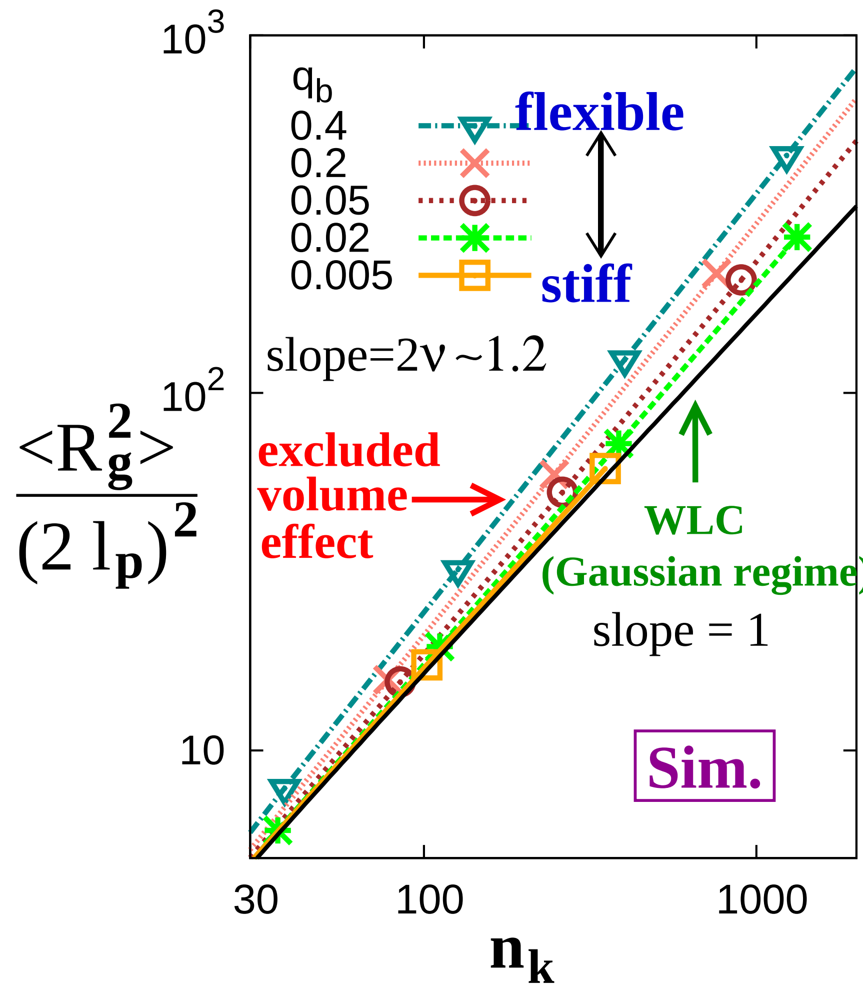


Norisuye & Fuijta, Polymer J. 14,143 (1982)



Hsu, Paul & Binder,
Macromol. Theory & Simul. 20, 510 (2011)

Structure factor $S(q)$

$$S(q) = \frac{1}{(N+1)^2} \left\langle \sum_{j=1}^{N+1} \sum_{k=1}^{N+1} \exp\left[i\vec{q} \cdot (\vec{r}_j - \vec{r}_k)\right] \right\rangle$$

- As $q \to 0$, $S(q) = 1 - \langle R_g^2 \rangle q^2/3 + \cdots$
  - Mean square gyration radius $\langle R_g^2 \rangle$:

$$\langle R_g^2 \rangle = \frac{\left\langle \sum_{j=1}^{N+1} \sum_{k=j+1}^{N+1} (\vec{r}_j - \vec{r}_k)^2 \right\rangle}{(N+1)^2}$$

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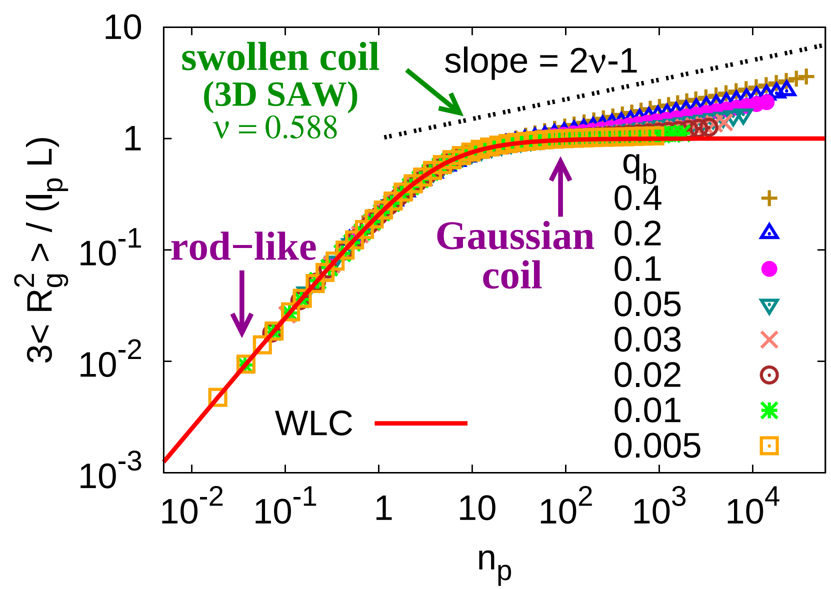
(stiff) $0.005 \le q_b \le 1.0$ (flexible)

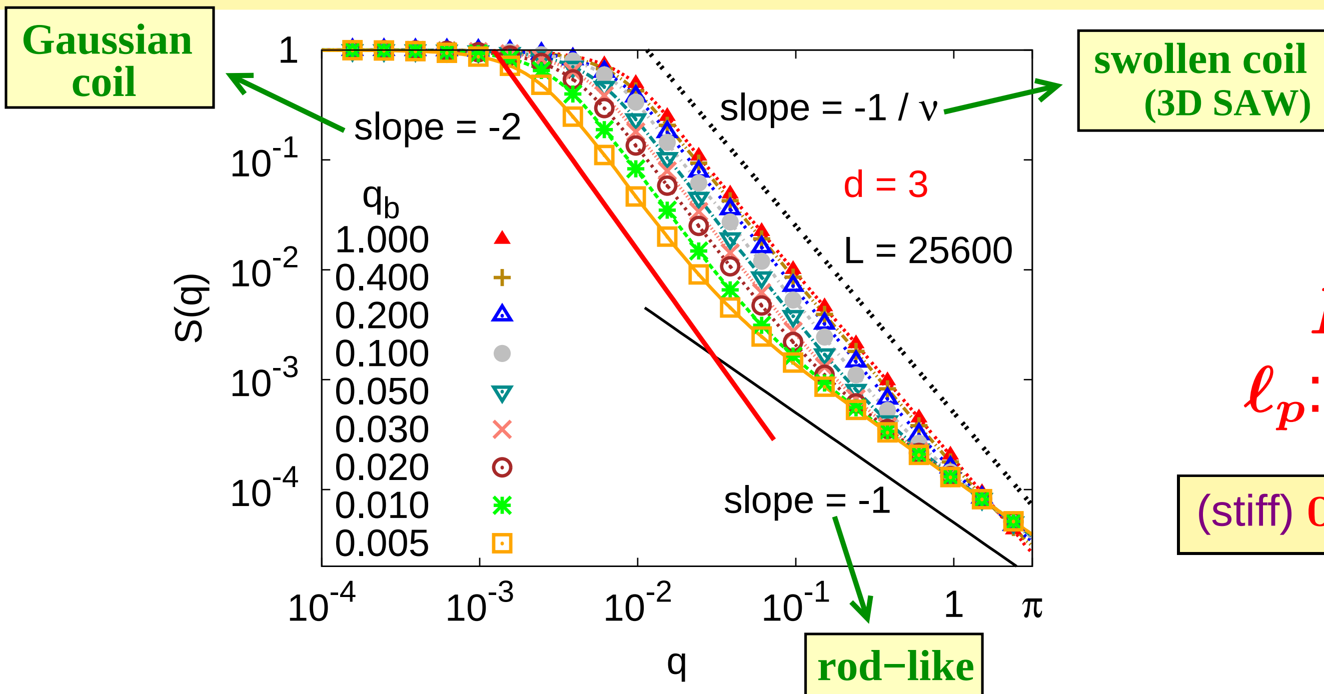


$$(L = N\ell_b = n_p\ell_p)$$

$$\frac{3\langle R_g^2\rangle}{\ell_p L} = 1 - \frac{3}{n_p} + \frac{6}{n_p^2} - \frac{6}{n_p^3}\left[1-\exp(-n_p)\right] \quad \text{(WLC)}$$

Benoit & Doty, J. Phys. Chem. 57, 958 (1953)

Simulation vs. Theory



$$L = n_p \ell_p$$

L: contour length

ℓ_p: persistence length

(stiff) $0.005 \le q_b \le 1.0$ (flexible)

- Rigid rod ($n_p < 1$):

$$S_{\rm rod}(q) = \frac{2}{qL}\left[\int_0^{qL} dx \frac{\sin x}{x} - \frac{1-\cos(qL)}{qL}\right],$$

$$S_{\rm rod}(q \to \infty) = \pi/(qL)$$

- Gaussian coil ($1 \ll n_p < n_p^* \ell_p$):

$$S_{\rm Debye}(q) = 2\frac{\exp(-X) - 1 + X}{X^2}, \quad X \equiv q^2 \langle R_g^2 \rangle$$

$S(q)$ of wormlike chains

- Exact solution by Stepanow:

$$S(q,n_p) = \frac{2}{n_p}\int_0^{n_p} ds_2 \int_0^{s_2} ds_1 \langle e^{iq[\vec{r}(s_2)-\vec{r}(s_1)]}\rangle\,, \;\; n_p = L/\ell_p$$

$$\vec{r}(s_2) - \vec{r}(s1) = \int_{s_1}^{s_2} ds \vec{t}(s)\,, \;\; \vec{t}(s) = \partial\vec{r}(s)/\partial s$$

Eur. Phys. J B 39, 499 (2004); J. Phys.: Condens. Matter 17, S1799 (2005)

- Approximation by Kholodenko:

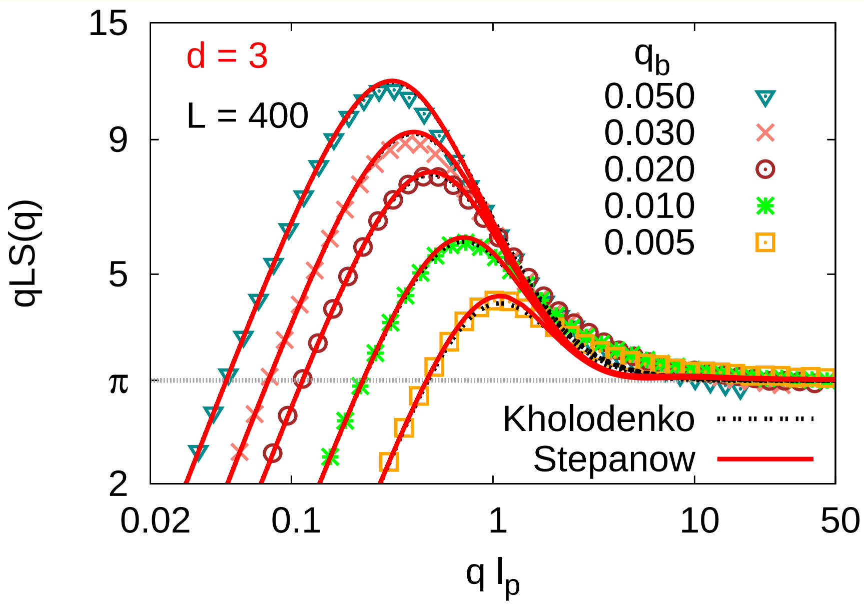
$$S(q) = \frac{2}{x}\left[I_1(x) - \frac{1}{x}I_2(x)\right]\,, \quad x = 3L/2\ell_p\,,$$

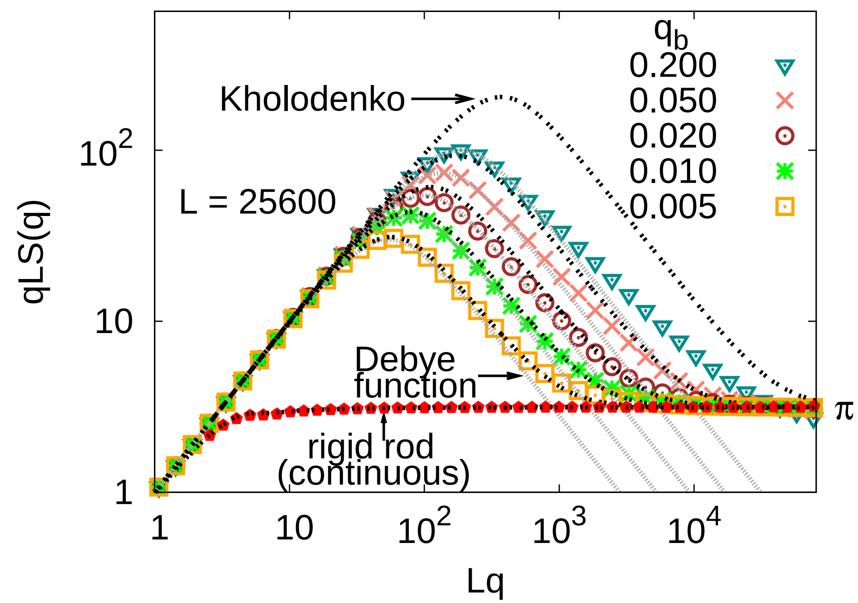
$$I_n(x) = \int_0^x dz\, z^{n-1} f(z)\,, \quad f(z) = \begin{cases} \frac{1}{E}\frac{\sinh(Ez)}{\sinh z}\,, & q \le 3/2\ell_p \\ \frac{1}{E'}\frac{\sin(E'z)}{\sinh z}\,, & q > 3/2\ell_p \end{cases}$$

$$E = [1-(2q\ell_p/3)^2]^{1/2}\,, \quad E' = [(2q\ell_p/3)^2 - 1]^{1/2}$$

Ann. Phys, 202, 186 (1990); Phys. Lett. A 178, 180 (1993); Macromolecules 26, 4179 (1993)

Kratky plot: $qLS(q)$ vs. Lq, ql_p





(stiff) $0.005 \leq q_b \leq 1.0$ (flexible)

- Rigid rod ($n_p = L/l_p < 1$):

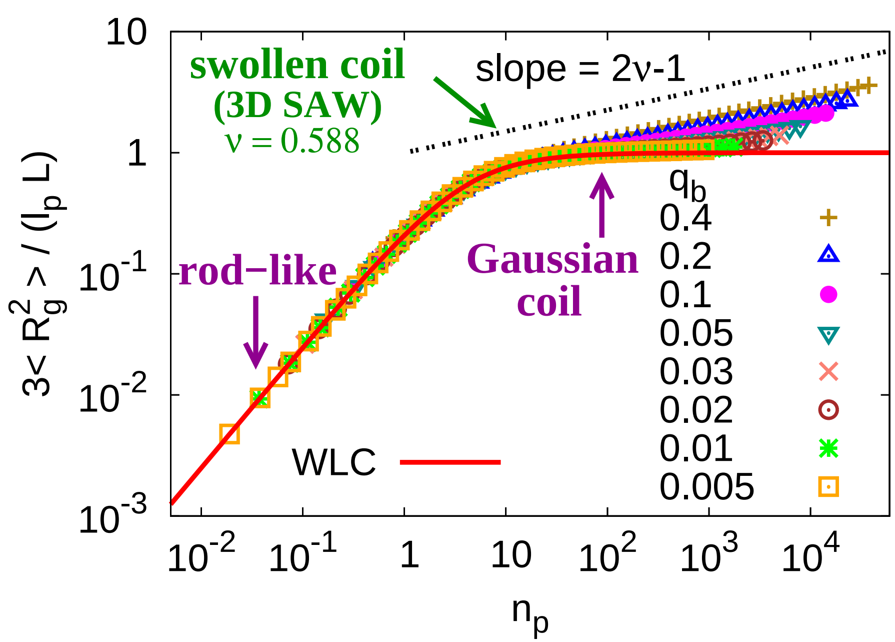
$$S_{\rm rod}(q) = \frac{2}{qL}\left[\int_0^{qL} dx \frac{\sin x}{x} - \frac{1-\cos(qL)}{qL}\right], \quad S_{\rm rod}(q \to \infty) = \pi/(qL)$$

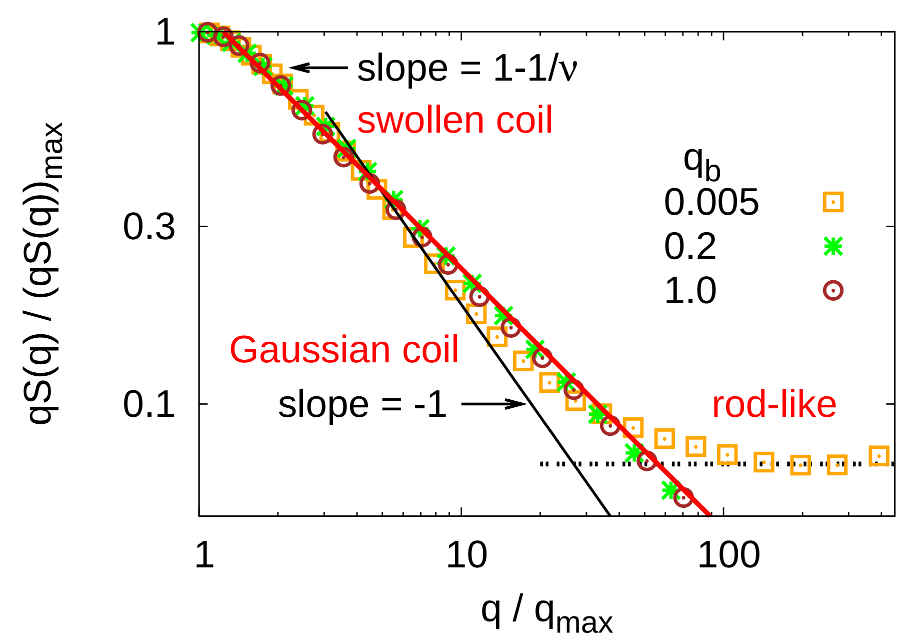
- Gaussian coil ($1 \ll n_p < n_p^* \ell_p$):

$$S_{\rm Debye}(q) = 2\frac{\exp(-X) - 1 + X}{X^2}, \quad X \equiv q^2 \langle R_g^2 \rangle$$

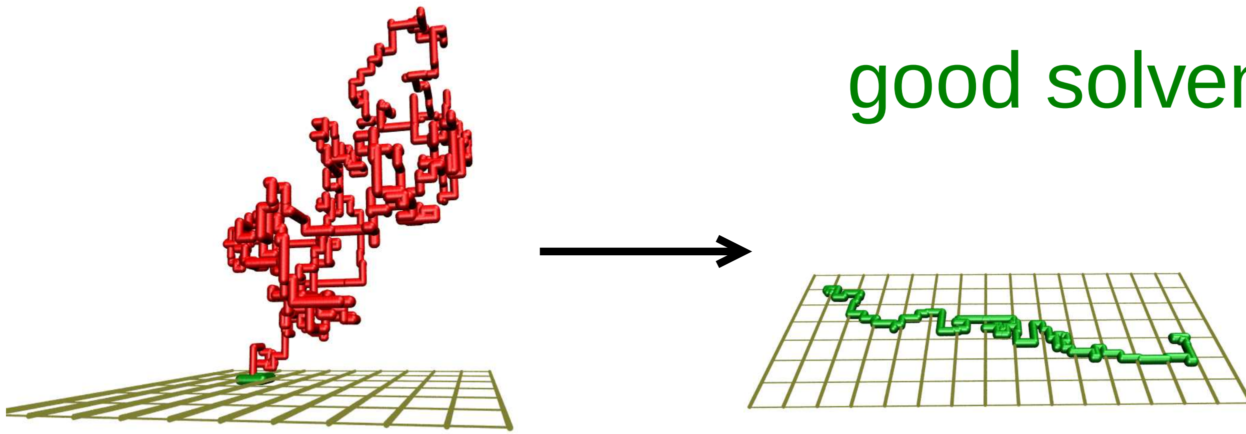
Crossover behavior

- Mean square gyration radius $\langle R_g^2 \rangle$:
  rod-like - Gaussian coil - swollen coil
- Structure factor $S(q)$:
  swollen coil - Gaussian coil - rod-like



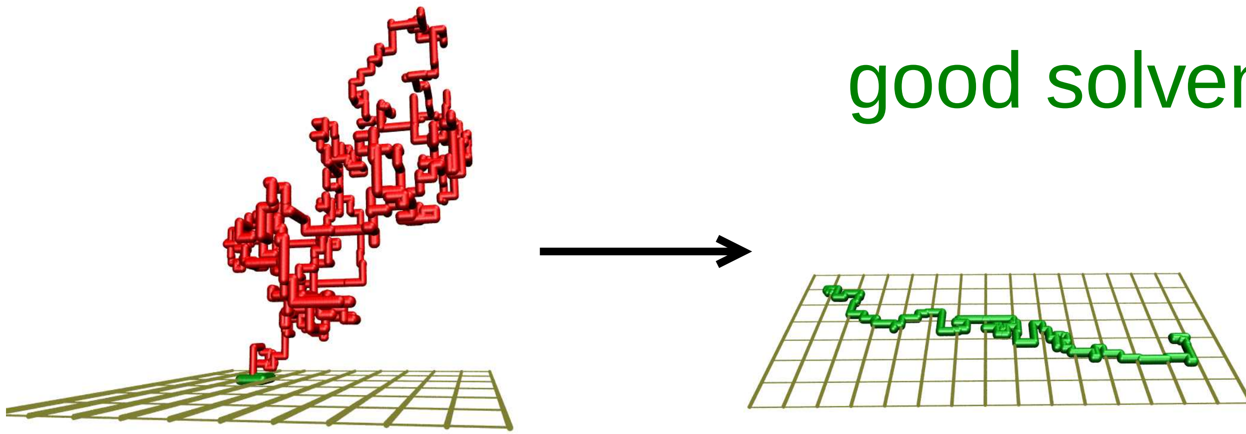


Effect of stiffness on the adsorption transition of single polymer chains



good solvent conditions

Effect of stiffness on the adsorption transition of single polymer chains



good solvent conditions

- A wide range of applications
- One of the challenging problems in statistical physics
- Intrinsic chain stiffness is a very important characteristic of most synthetic macromolecules and biopolymers

Questions?

- How important is the excluded volume effect on the conformational properties of adsorbed semiflexible chains?

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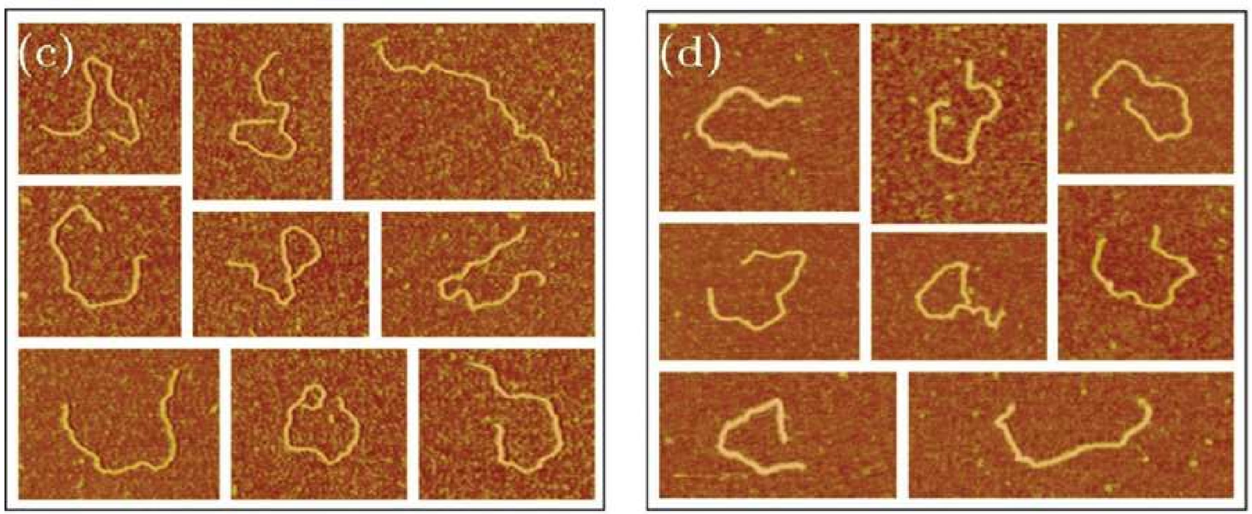
- How important is the excluded volume effect on the conformational properties of adsorbed semiflexible chains?
- Does it make sense to still use the worm-like chain (WLC) model in $d = 2$ dimensions?

DNA fragments on mica



Moukhtar et al., J. Phys. Chem. B 114, 5125 (2010)

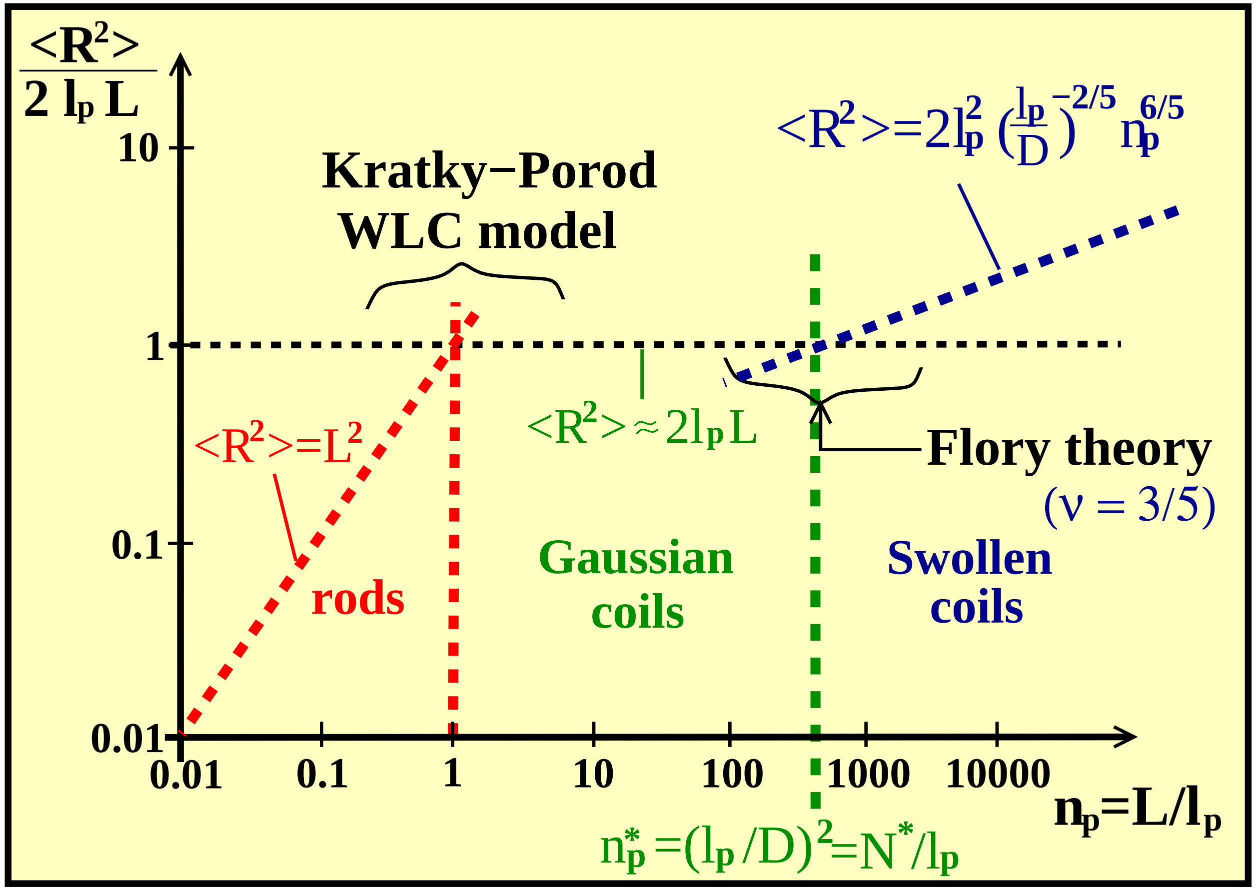
Questions?

- How important is the excluded volume effect on the conformational properties of adsorbed semiflexible chains?
- Does it make sense to still use the worm-like chain (WLC) model in $d = 2$ dimensions?
- Is the adsorption transition of first order or second order?

  - T. W. Burkhardt, J. Phys. A: Math. Gen. 26, L1157 (1993) $\Rightarrow$ first order
  - T. M. Birshtein et al., Biopolymers, 18, 1171 (1979)
    A. R. Khokhlov et al., Makromol. Chem. Theory Simul. 2, 151 (1993).
    $\Rightarrow$ second order
  - D. V. Kuznetsov et al., J. Phys. II (France), 7, 1287 (1997); J. Chem. Phys. 107, 4729 (1997); Macromolecules 31, 2679 (1998) $\Rightarrow$ first order, second order

Semiflexible chains in $d = 3$

- Mean square end-to-end distance $\langle R^2 \rangle$:



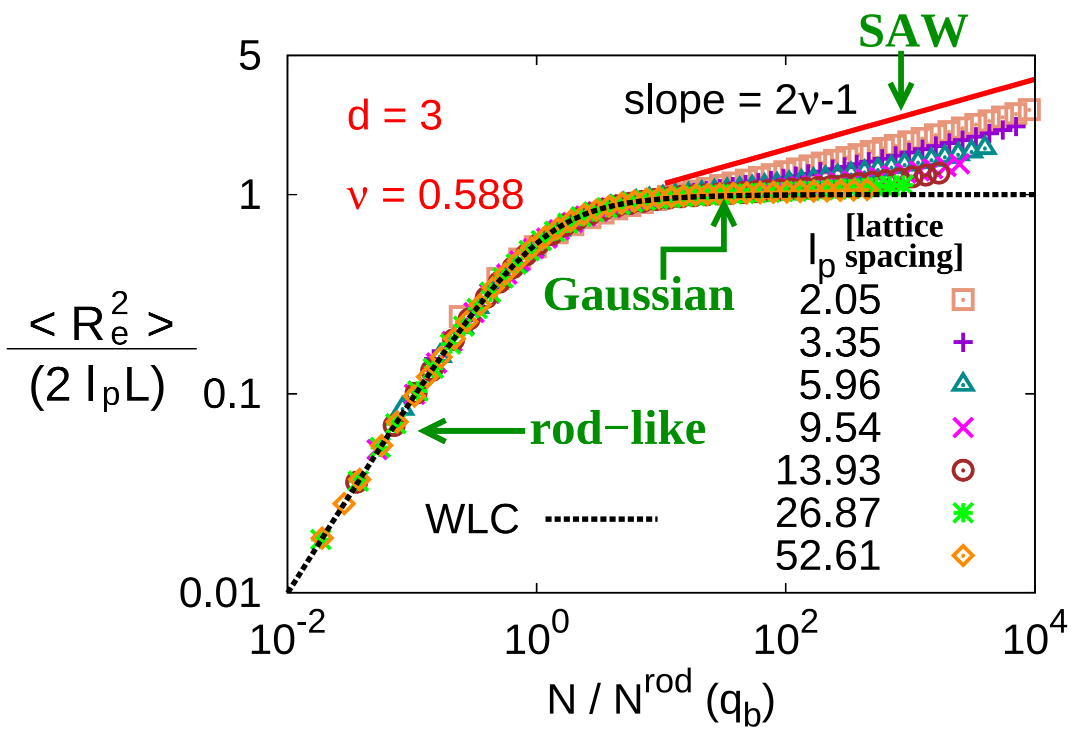
L: contour length
$L = N\ell_b, \ell_b = 1$

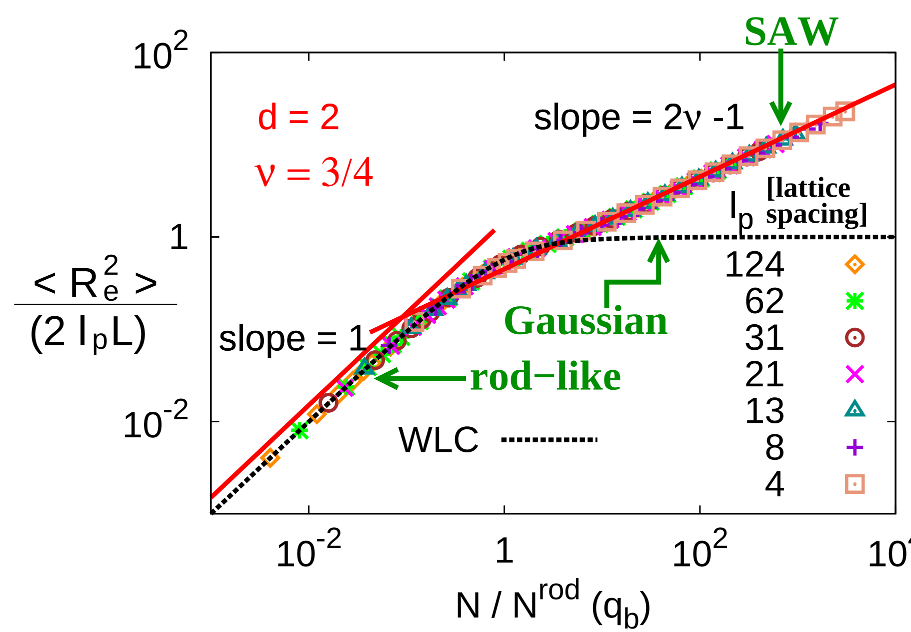
ℓ_p: persistence length

D: effective thickness

Semiflexible chains in $d = 3$

- Mean square end-to-end distance $\langle R^2 \rangle$:





$3D$ WLC model works for stiff but very long chains, unlike **$2D$**

Semiflexible chains in $d = 3$

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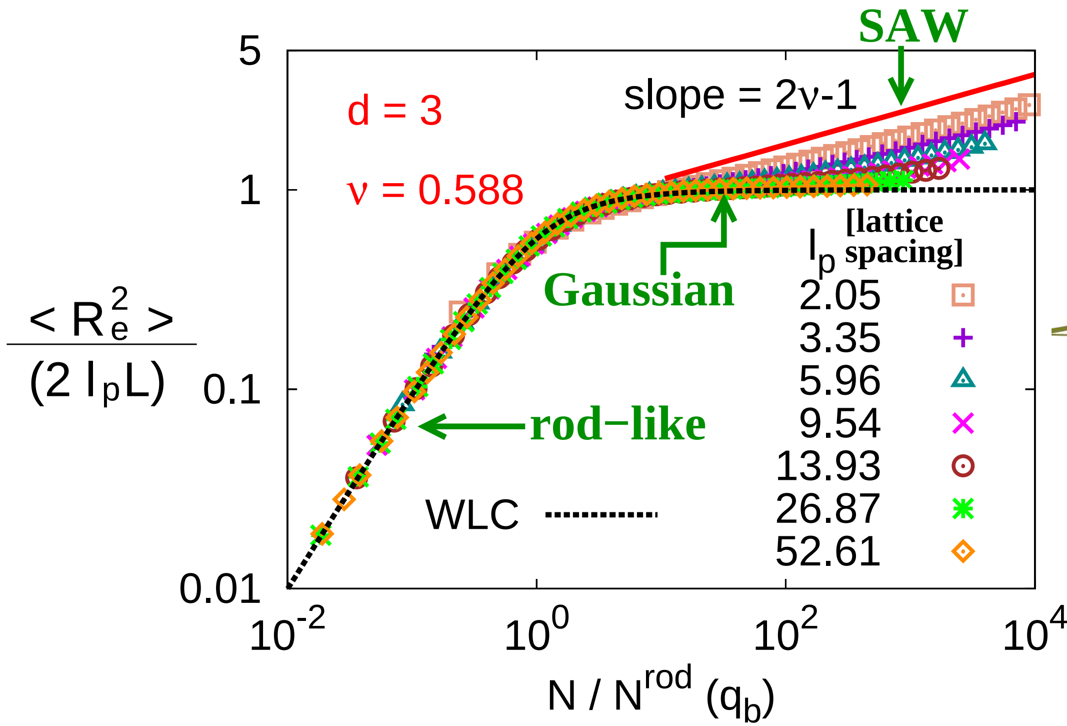
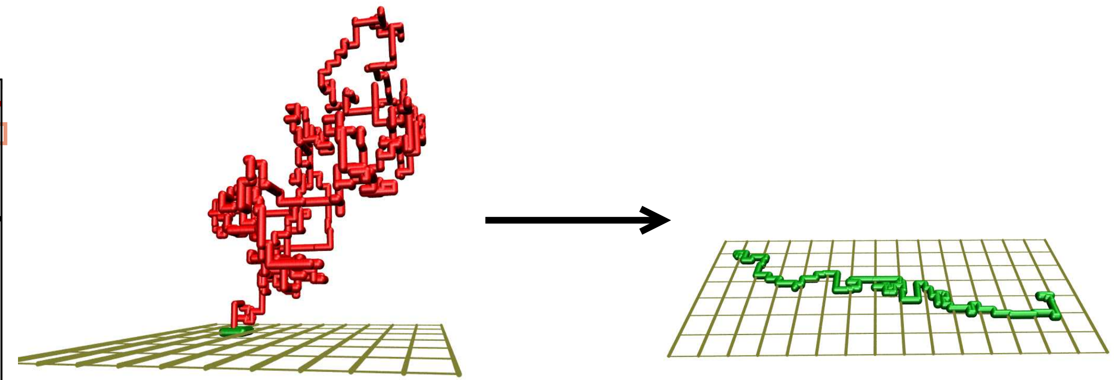
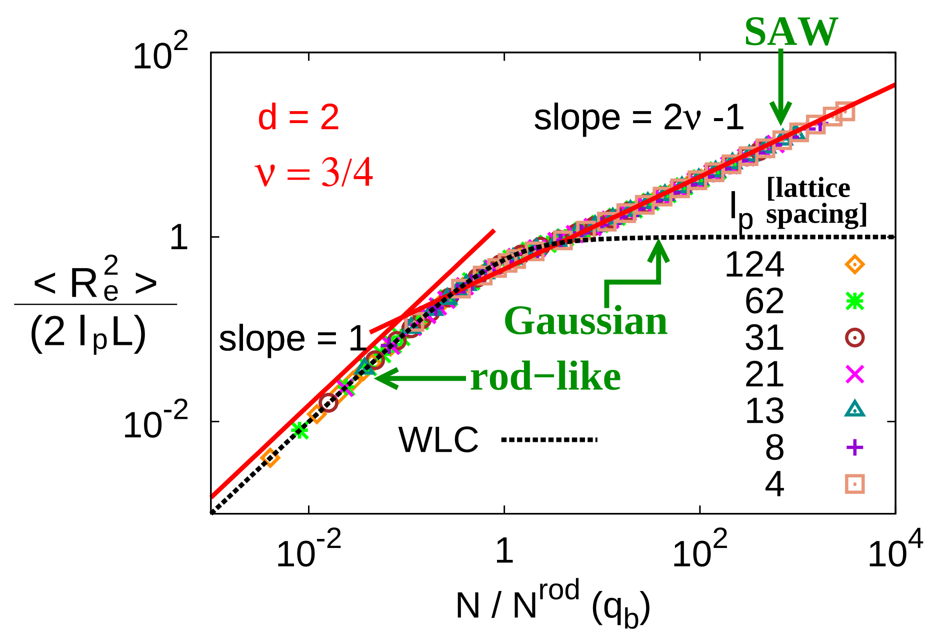






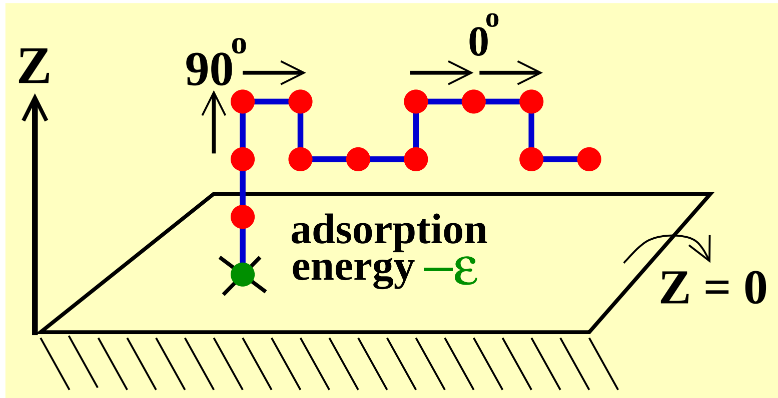
$3D$ WLC model works for stiff but very long chains, unlike $2D$

Model

Self-avoiding walk model on the simple cubic lattices in $d = 3$

- Bond-bending potential $U_{\text{bend}}(\theta) \Rightarrow$ flexibility of chains

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



bending energy $\epsilon_b \uparrow$, stiffness $\uparrow$

- Short-range contact adsorption potential:

$$U_{\text{ads}}(z_i) = \begin{cases} -\epsilon & z_i = 0 \\ 0 & z_i > 0 \end{cases}$$

$\epsilon > 0$ (attractive)

$\epsilon = 0$ (athermal)

(good solvent conditions) z_i: z-coordinate of the i^{th} monomer

- Partition sum:
  (a walk with N steps, N_{bend} local bends, N_s surface contacts)

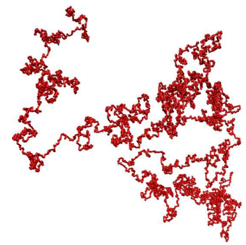
$$Z_{N,N_{\mathrm{bend}},N_s}(q_b) = \sum_{\mathrm{config.}} C_{N,N_{\mathrm{bend}},N_s} q_b^{N_{\mathrm{bend}}} q^{N_s}$$

  - $q_b = e^{-(\epsilon_b/k_B T)}$: bending factor
  - $q = e^{\epsilon/k_B T}$: adsorption factor

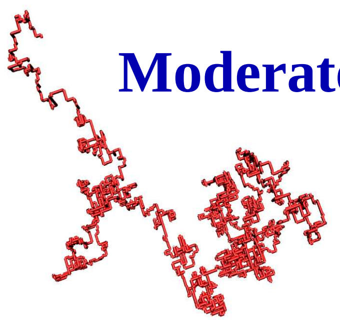
- Algorithm: PERM

Snapshots of semiflexible chains

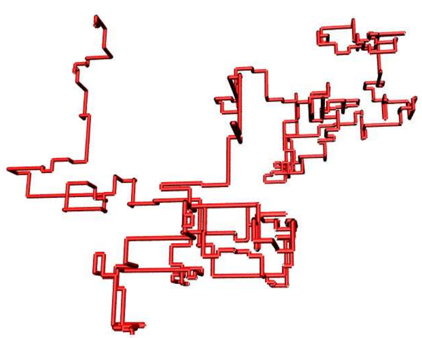
Flexible chain, $q_b = 0.4$



Moderately stiff chain, $q_b = 0.05$



Stiff chain, $q_b = 0.005$



q_b	l_p [lattice spaing]	
0.4	**1.13**	**flexible**
0.2	2.05	↑
0.1	3.35	
0.05	**5.96**	
0.03	9.54	
0.02	13.93	
0.01	26.87	↓
0.005	**52.61**	**stiff**

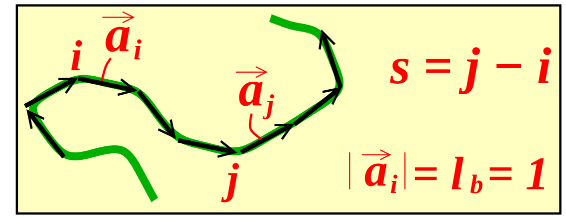
- q_b: bending factor
- ℓ_p: persistence length
- N: chain length

  $N = 25600 >> \mathcal{O}(10^2)$
  (previous simulations)

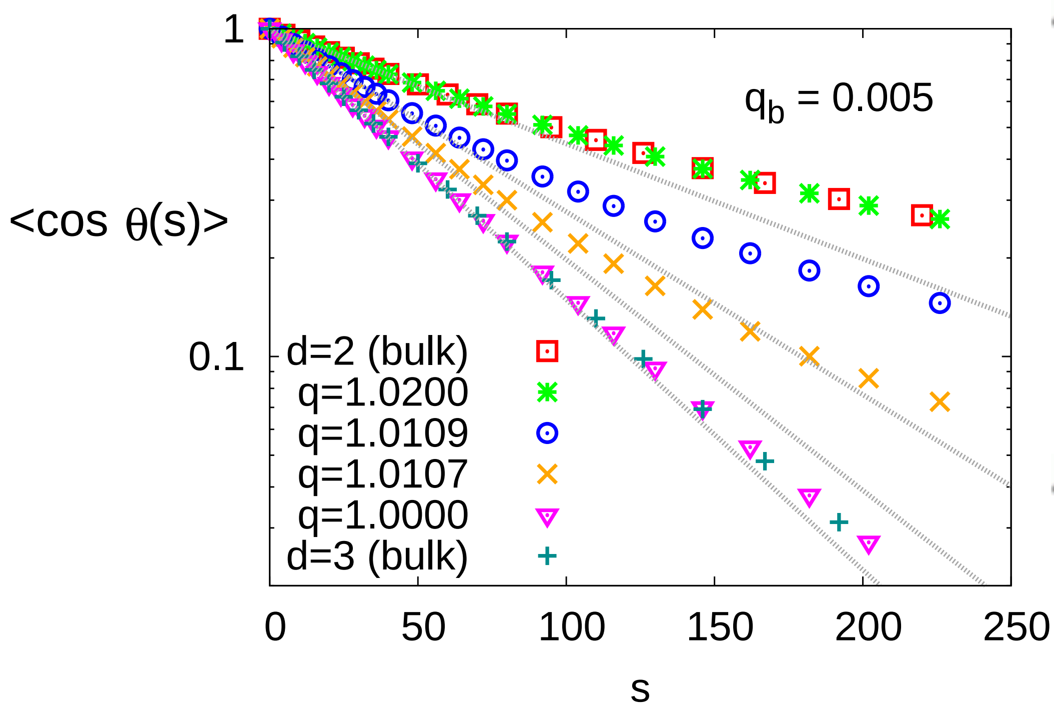
Persistence length ℓ_p

Standard definition:

- $\langle \cos\theta(s)\rangle = \exp(-s\ell_b/\ell_p) \Rightarrow \ell_p/\ell_b$



$s\ell_b$: contour length from monomer i to monomer j $(\ell_b = 1)$



- Semiflexible chains in bulk: $q_b = 0.005$
  - $\ell_p/\ell_b \approx 124$ in $d = 2$
  - $\ell_p/\ell_b \approx 53$ in $d = 3$
- Temperature $T(k_B/\epsilon) = 1/\ln q$

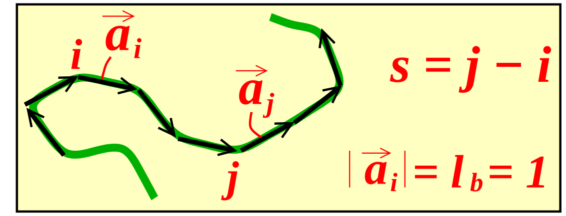
  adsorption energy $\epsilon = 1$

  Boltzmann constant $k_B = 1$

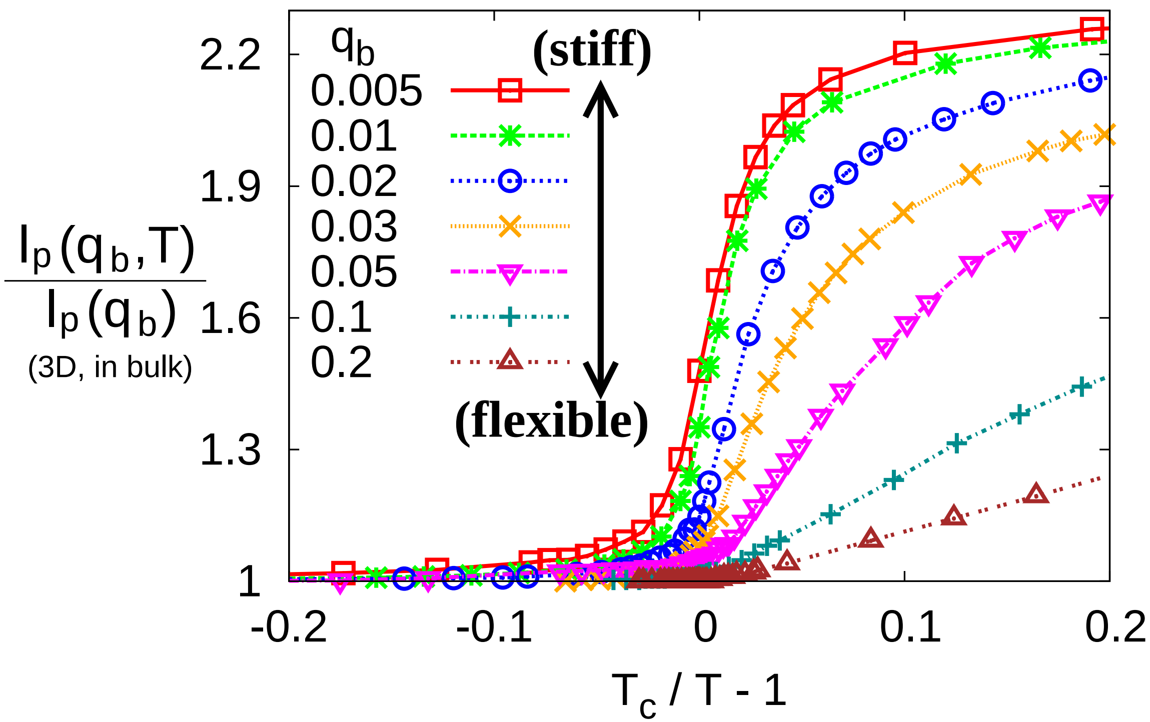
Persistence length ℓ_p

Standard definition:

- $\langle \cos\theta(s)\rangle = \exp(-s\ell_b/\ell_p) \Rightarrow \ell_p/\ell_b$



$s\ell_b$: contour length from monomer i to monomer j $(\ell_b = 1)$



— non−adsorbed ⟵ 0 ⟶ adsorbed —

T_c: transition point

$T > T_c$: non-adsorbed phase

$T < T_c$: adsorbed phase

$\Rightarrow$ Effective persistence length depends on the extent to which a chain is adsorbed

Adsorption transition of flexible chains

- Order parameter: $N_s/N \propto N^{\phi-1}$ at $T = T_c$ (critical point)

$$\frac{N_s}{N} \propto \begin{cases} \frac{1}{N} \mid \kappa \mid^{-1}, & \text{for } T > T_c \\ N^{\phi-1}, & \text{for } T = T_c \\ \kappa^{1/\phi-1}, & \text{for } T < T_c \end{cases} \qquad \kappa = T_c/T - 1$$

- Gyration Radius: $R^2_{g\perp}/R^2_{g\|} \sim const$ at $T = T_c$

$$R^2_{g\perp} \propto \begin{cases} N^{2\nu}, \\ \kappa^{-2\nu/\phi}, \end{cases} \qquad R^2_{g\|} \propto \begin{cases} N^{2\nu}, \ (3D\,SAW) & \text{for } T \geq T_c \\ \kappa^{2(\nu_2-\nu)/\phi} N^{2\nu_2}, \ (2D\,SAW) & \text{for } T < T_c \end{cases}$$

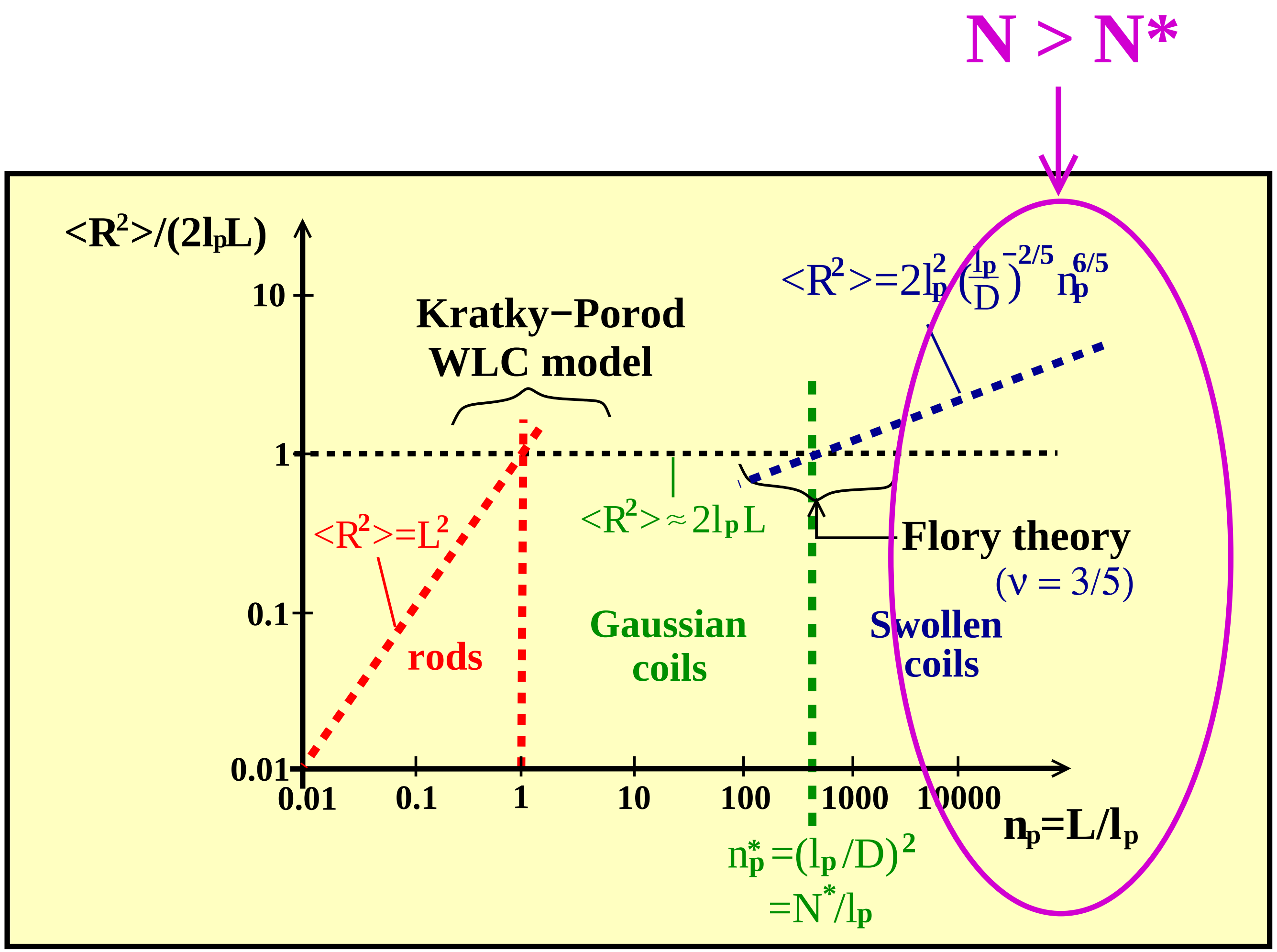
N: number of monomers, N_s: number of surface contact

ϵ: adsorption energy of a monomer, ϕ: crossover exponent

(non-adsorbed phase $\leftrightarrow$ adsorbed phase)

Determination of transition point

- Semiflexible chains of chain length $N > N^* \Rightarrow$ Swollen coils



Determination of transition point

- At $T = T_c$ ($q = q_c$) (In the thermodynamic limit $N \to \infty$):
  - Ratio between two gyration radius components:

$$R^2_{g\perp}(N)/R^2_{g||}(N) \sim const$$

  - Number of surface contacts: $N_s/N^\phi \sim const$

$$\phi_{\text{eff}}(N,q) = \ln[N_s(2N,q)/N_s(N/2,q)]/\ln 4$$
$$\approx \phi \quad \Rightarrow \text{crossover exponent}$$

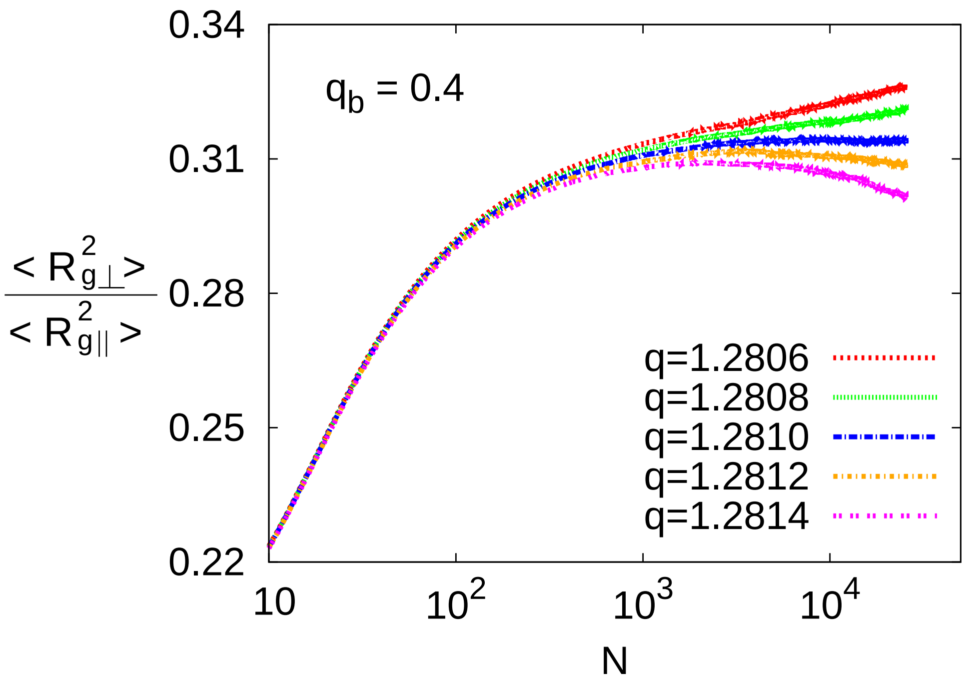
  - Partition sum: $Z_N(q,q_b) \propto \mu(q_b)^{-N} N^{\gamma_1^{sp}-1}$, μ: fugacity

$$\gamma^{(1)}_{1,\text{eff}}(N,q) = 1 + [4\ln Z_N - 3\ln Z_{N/3} - \ln Z_{3N}]/9$$
$$\gamma^{(2)}_{1,\text{eff}}(N,q) = 1 + \ln[Z_{2N}\mu^{3N/2}/Z_{N/2}]/\ln 4$$
$$\lim_{N\to\infty} \gamma^{(1)}_{1,\text{eff}} = \gamma^{(2)}_{1,\text{eff}} = \gamma_1^{sp} \quad \Rightarrow \text{surface entropic exponent}$$

Determination of $q_c = e^{\epsilon/k_B T_c}$

- Gyration Radius:

$R^2_{g\perp}/R^2_{g||} \sim const$



Flexible chains: $q_b = 0.4$

- Persistence length:

$\ell_p(q = 1) \approx 1.13$ lattice spacings

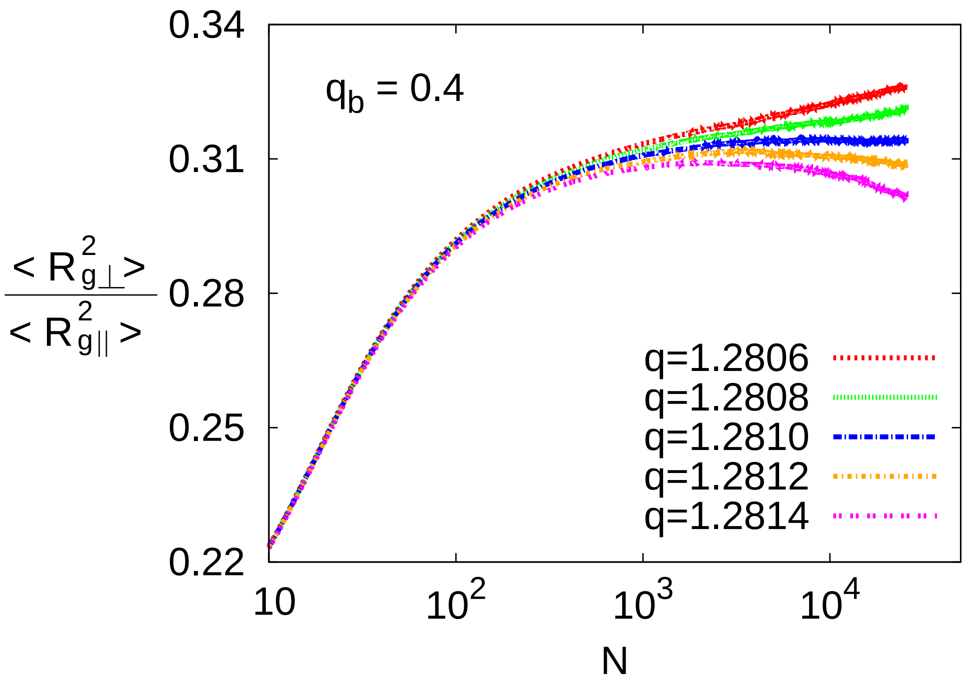
- Crossover point $N^* < 10$:

Gaussian chains $\leftrightarrow$ swollen coils

Determination of $q_c = e^{\epsilon/k_B T_c}$

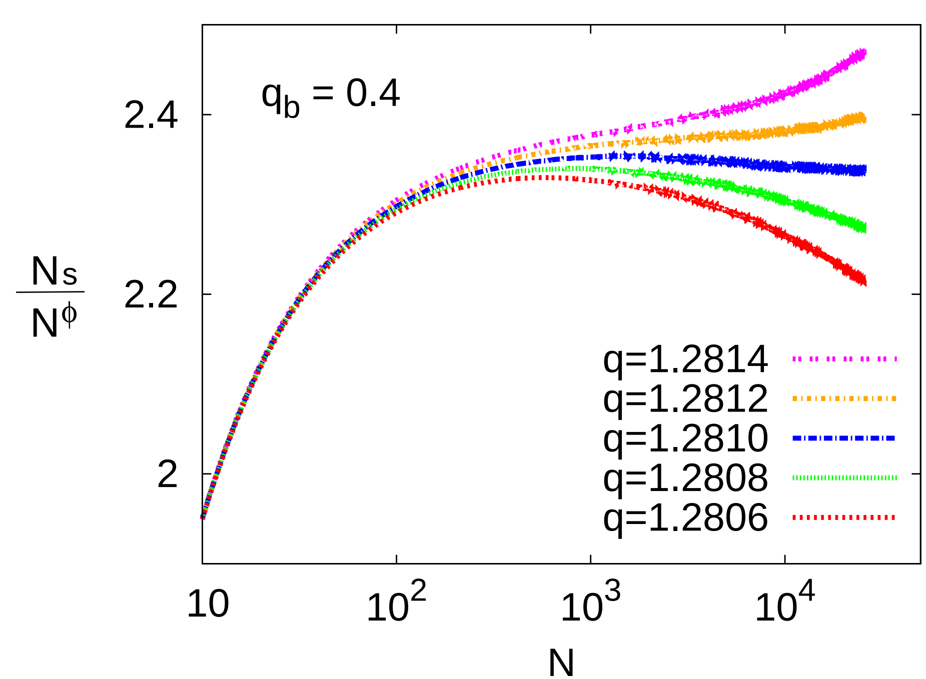
- Gyration Radius:

  $R^2_{g\perp}/R^2_{g||} \sim const$



- Order parameter:

  $N_s/N^\phi \sim const$



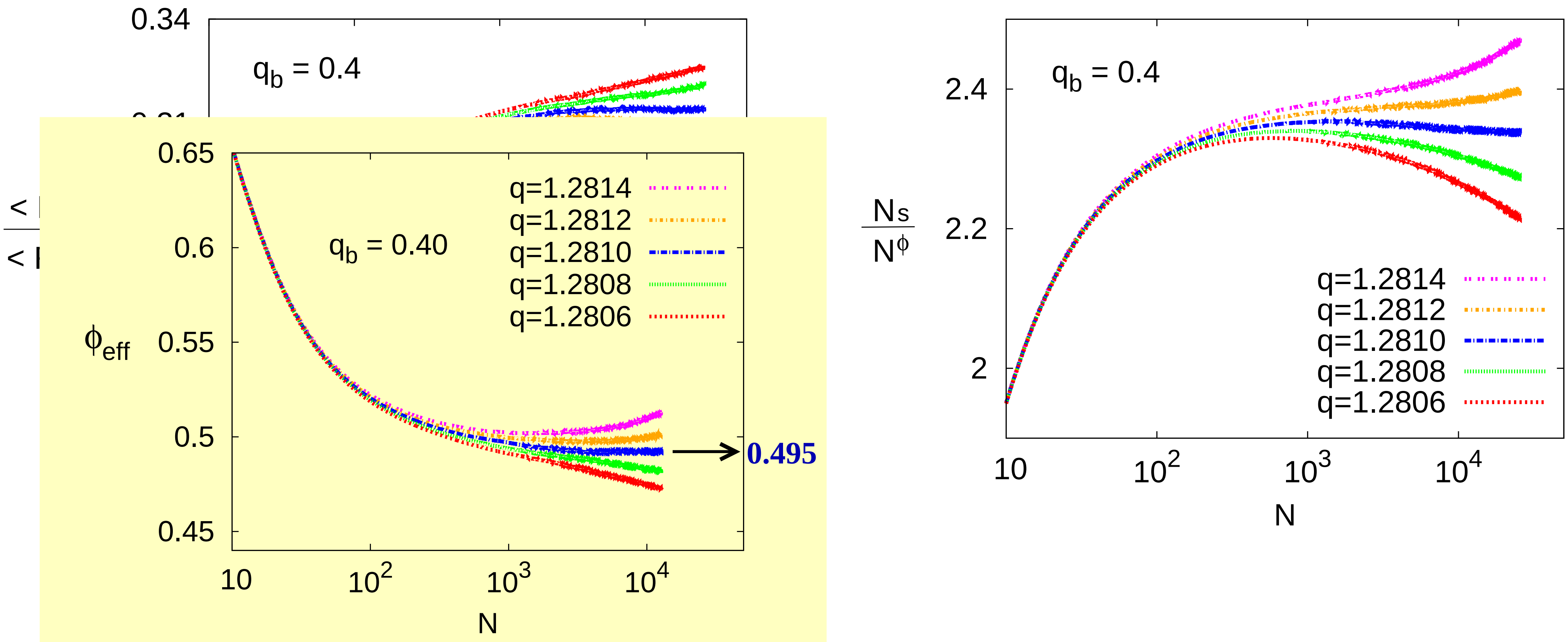
Determination of $q_c = e^{\epsilon/k_B T_c}$

- Gyration Radius:

  $R^2_{g\perp}/R^2_{g\|} \sim const$

- Order parameter:

  $N_s/N^{\phi} \sim const$



$$\left(\phi = \lim_{N\to\infty} \phi_{\text{eff}} = \frac{\ln(N_s(2N))/N_s(N))}{\ln 4} \approx const \text{ at } q = q_c\right)$$

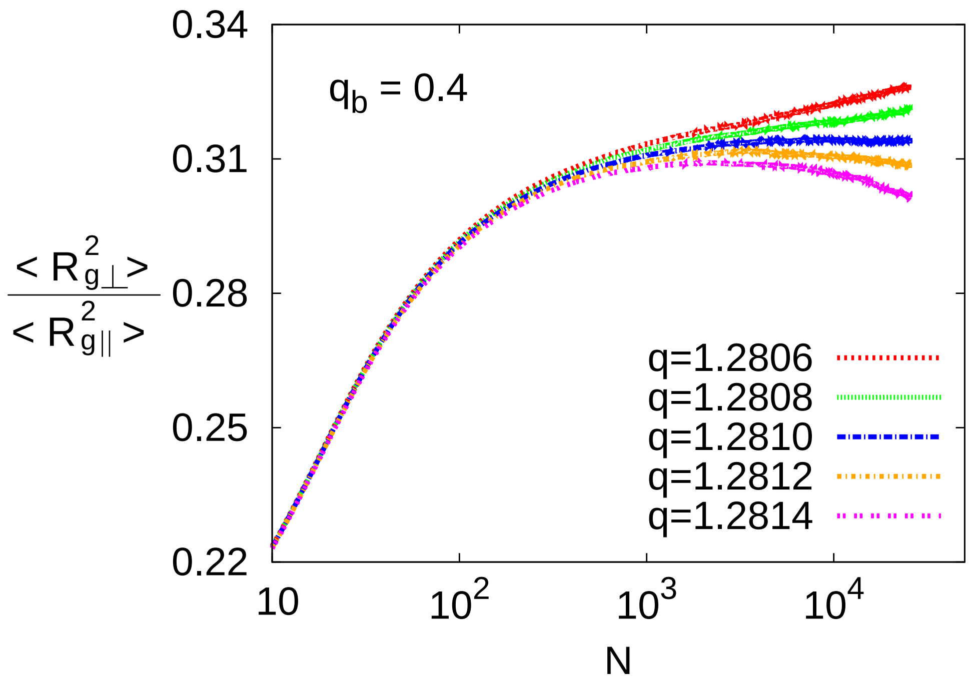
Determination of $q_c = e^{\epsilon/k_B T_c}$

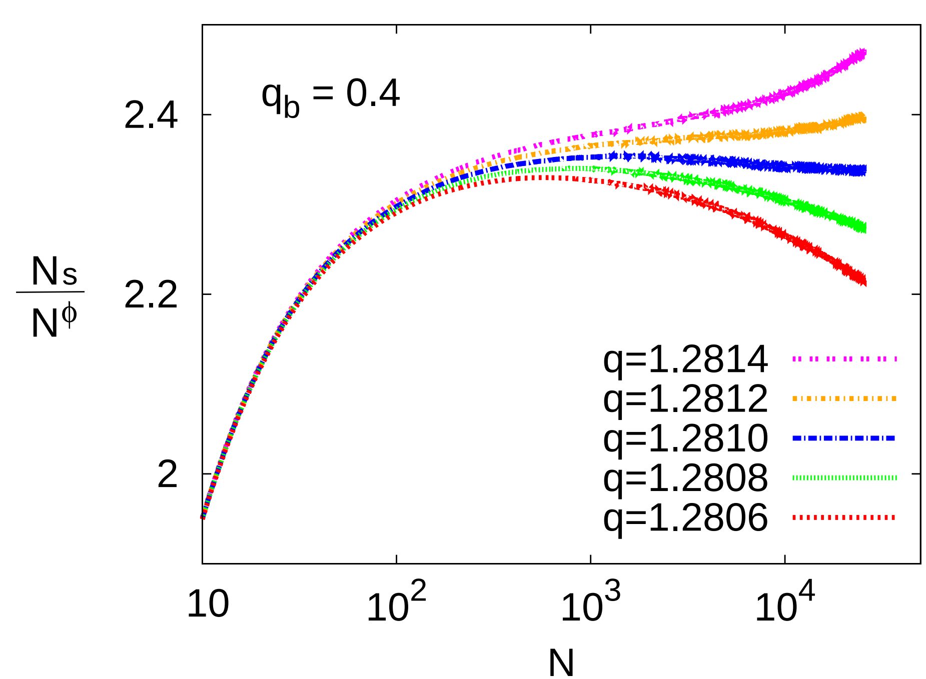
- Gyration Radius:

  $R^2_{g\perp}/R^2_{g||} \sim const$

- Order parameter:

  $N_s/N^{\phi} \sim const$



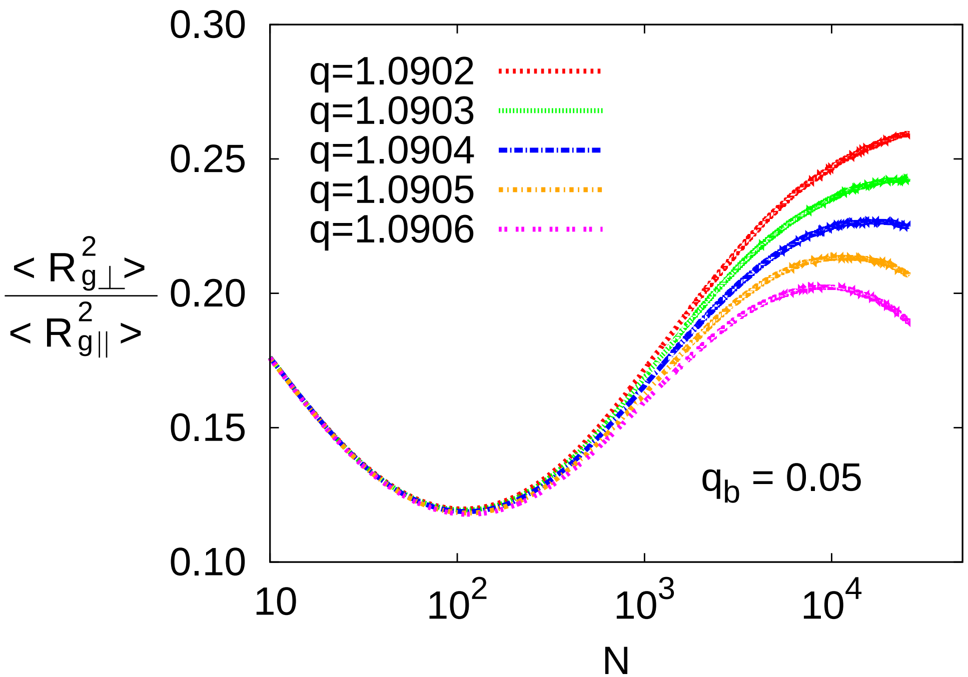


$\Rightarrow q_c = 1.2810(3)$, for $q_b = 0.4$

Determination of $q_c = e^{\epsilon/k_B T_c}$

- Gyration Radius:

$R^2_{g\perp}/R^2_{g||} \sim const$



Moderately stiff chains: $q_b = 0.05$

- Persistence length:

$\ell_p(q = 1) \approx 5.92$ lattice spacings

- Crossover point $N^* \approx 180$:

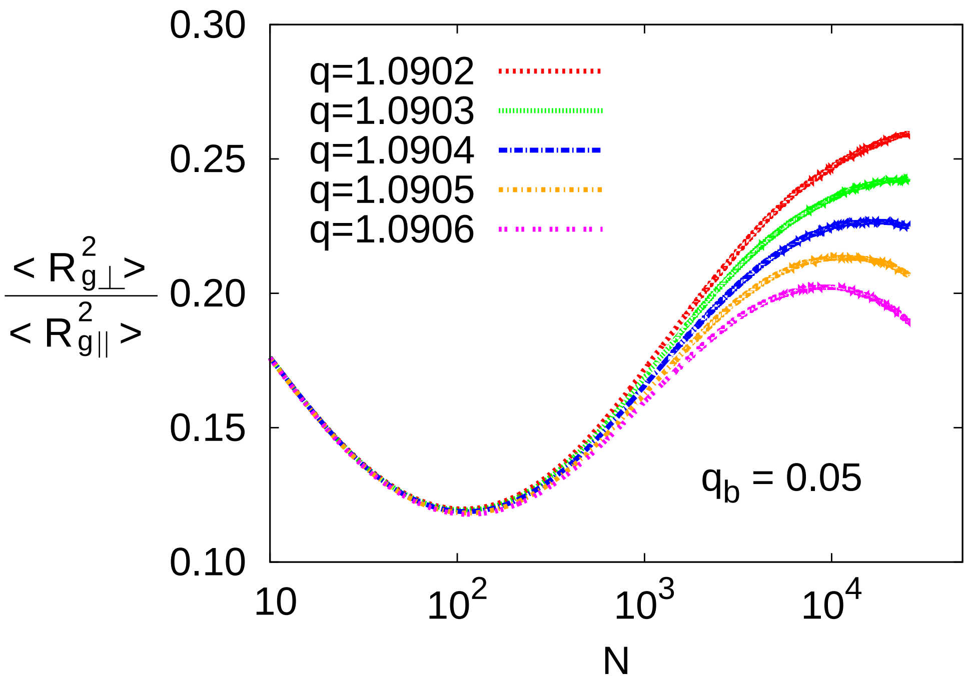
Gaussian chains $\leftrightarrow$ swollen coils

at $q = q_c(q_b = 0.4)$, $R^2_{g\perp}/R^2_{g||} \approx 0.32$

Determination of $q_c = e^{\epsilon/k_BT_c}$

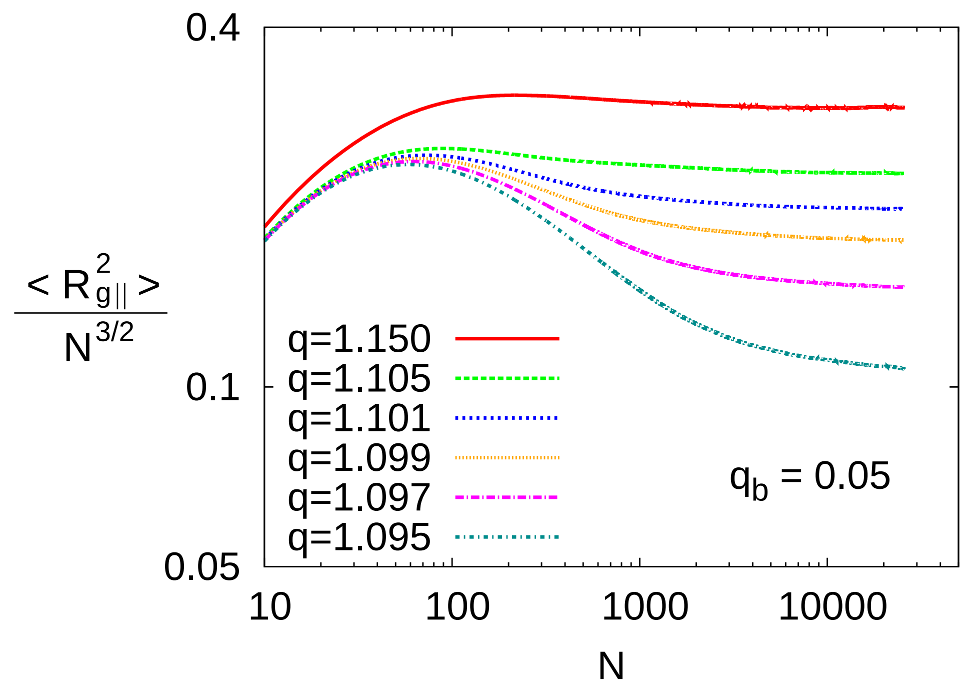
- Gyration Radius:

  $R^2_{g\perp}/R^2_{g||} \sim const$



- In the adsorbed regime, $q > q_c$ $(T < T_c)$:

  $R^2_{g||}/N^{2(\nu_2=3/4)} \sim const$



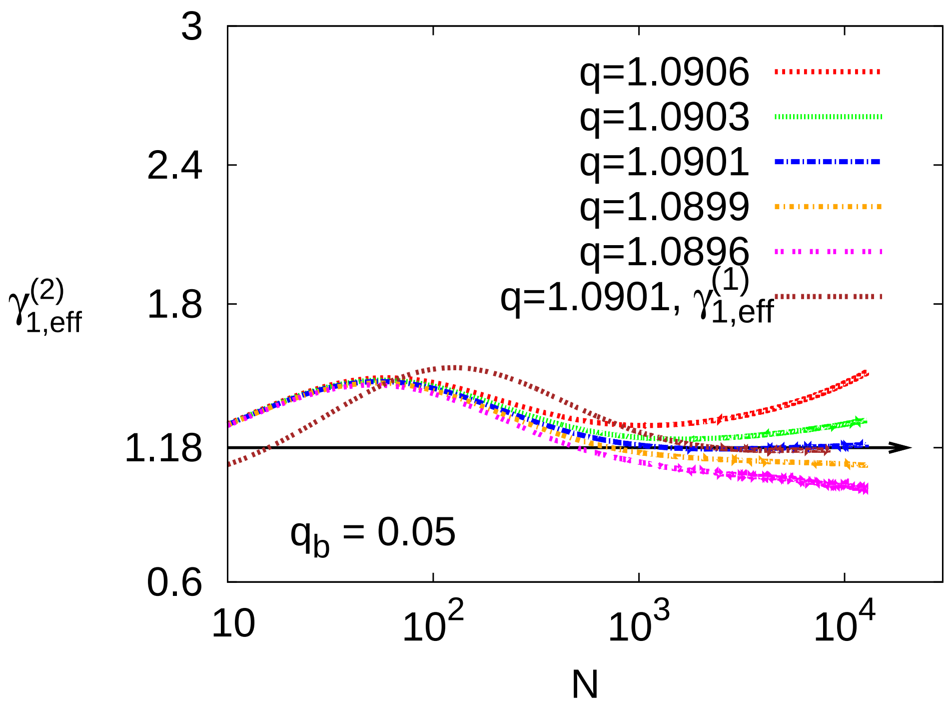
2D SAW

Determination of $q_c = e^{\epsilon/k_BT_c}$

- Effective surface entropic exponent:

$$\gamma^{(1)}_{1,\text{eff}} = 1 + \frac{4\ln Z_N - 3\ln Z_{N/3} - \ln Z_{3N}}{9}$$

$$\gamma^{(2)}_{1,\text{eff}} = 1 + \frac{\ln[Z_{2N}\mu^{3N/2}/Z_{N/2}]}{\ln 4}$$



$$\lim_{N\to\infty} \gamma^{(1)}_{1,\text{eff}} = \gamma^{(2)}_{1,\text{eff}} = \gamma^{sp}_1$$

$\Rightarrow q_c = 1.0901(3)$, for $q_b = 0.05$

Dependency between $\epsilon / k_B T_c$ and q_b

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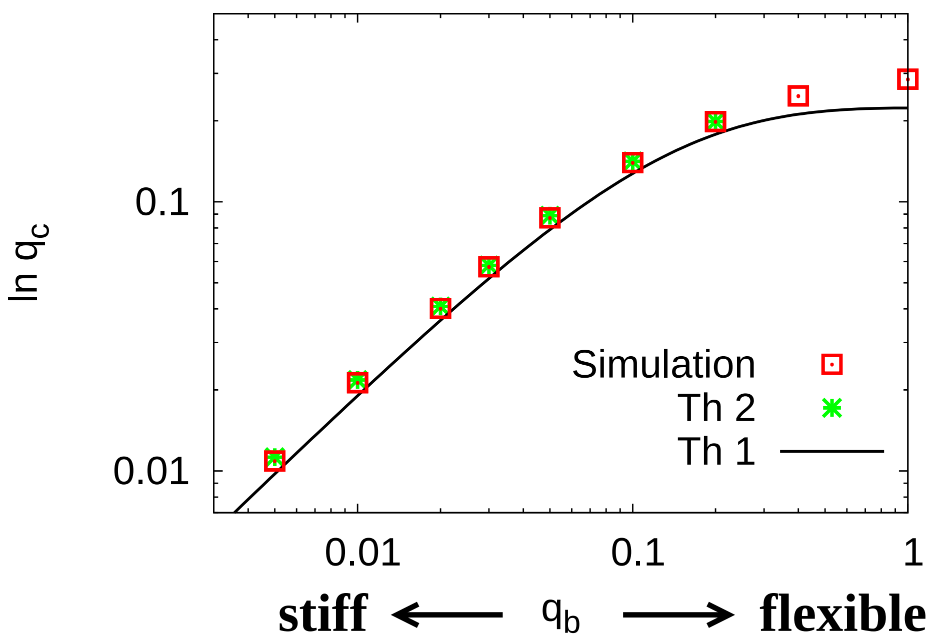
- Non-reversal random walks on the simple cubic lattice:

$$\frac{\epsilon}{k_B T_c} = \ln\left(\frac{2(4+q_b^{-1})}{(2+q_b^{-1}) + \left[(2+q_b^{-1})^2 + 16\right]^{1/2}}\right) \quad (\text{Th } 1)$$

Birshtein et. al., Biopoly. 18, 1171 (1979)



$$\frac{\epsilon}{k_B T_c} \propto \ln\left(\frac{2\ell_k + 2}{\ell_k + \sqrt{\ell_k^2 + 4}}\right) \quad (\text{Th } 2)$$

$\ell_k = 2\ell_P$: Kuhn length

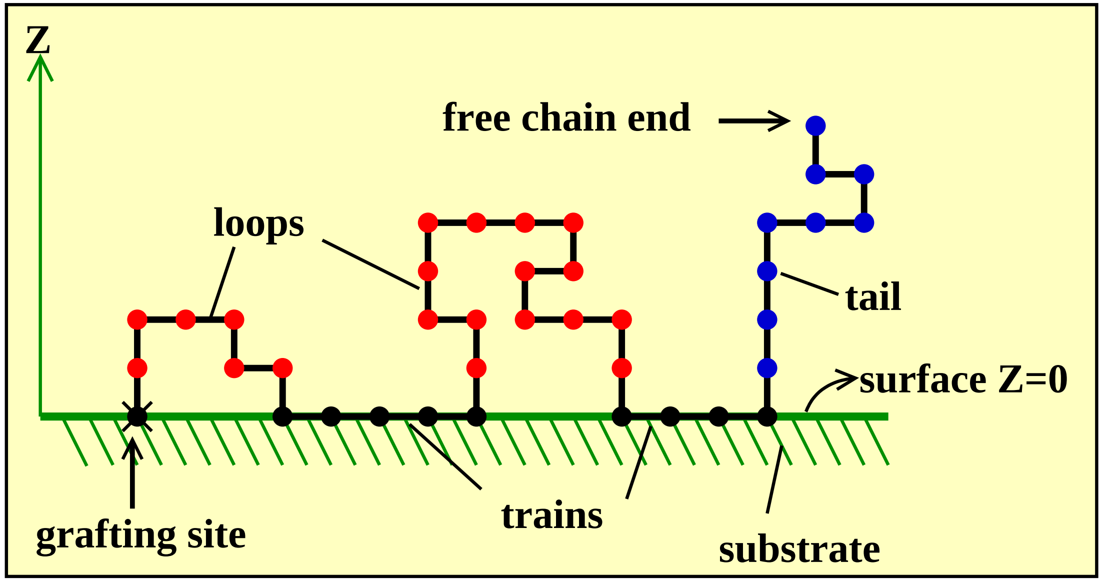
Linden et al., Macromolecules, 29, 1172 (1996)

critical adsorption energy:

$$\epsilon / k_B T_c = \ln q_c$$

Critical adsorption energy: $\epsilon / k_B T_c = \ln q_c \propto 1/\ell_p$, for large ℓ_p

Chain structures

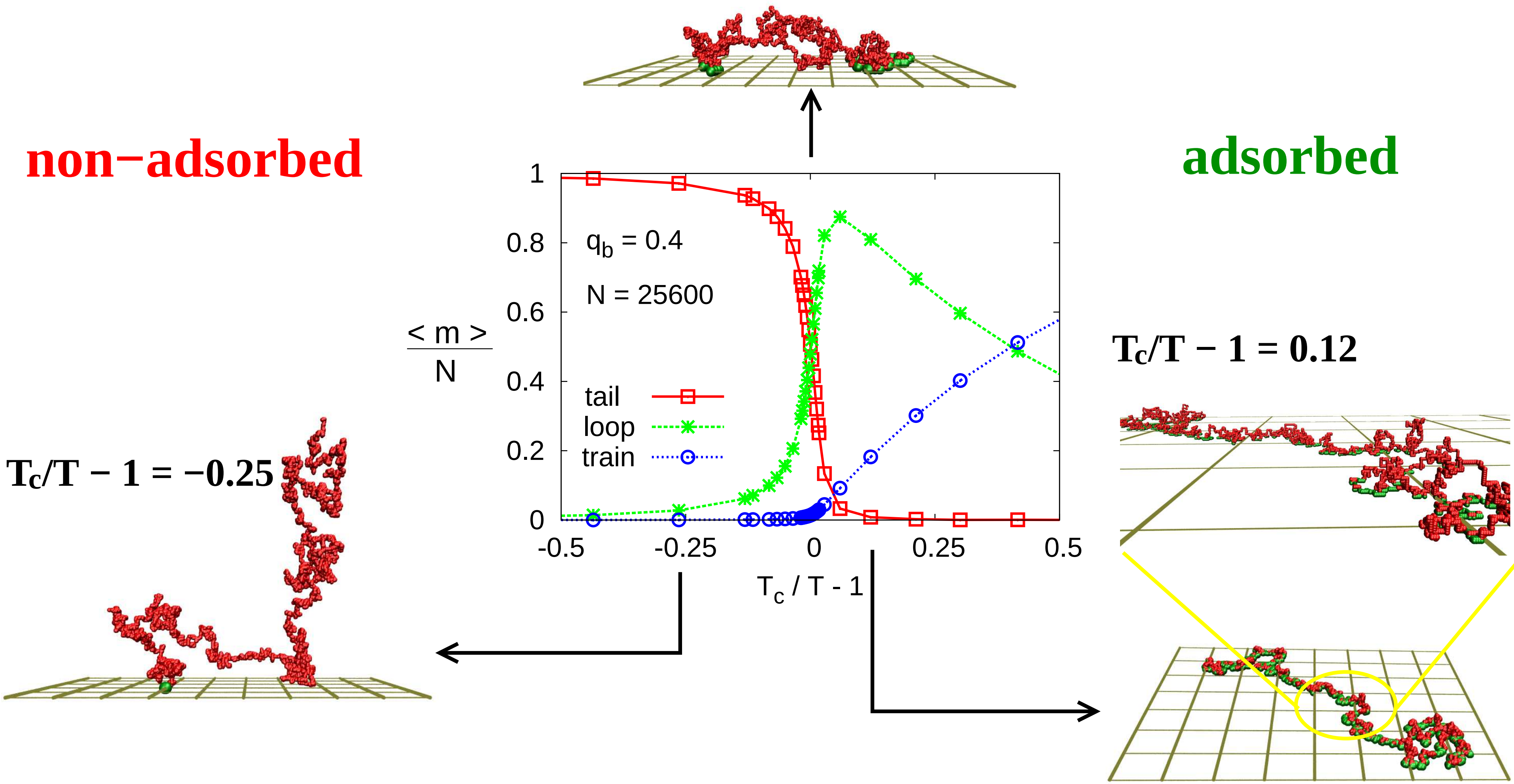


- Fraction of monomers in
  trains $\langle m_{\mathrm{train}} \rangle / N$, loops $\langle m_{\mathrm{loop}} \rangle / N$, tails $\langle m_{\mathrm{tail}} \rangle / N$
- Average lengths of
  trains $\langle l_{\mathrm{train}} \rangle$, loops $\langle l_{\mathrm{loop}} \rangle$, tails $\langle l_{\mathrm{tail}} \rangle$
- Average number of
  trains $\langle n_{\mathrm{train}} \rangle$, loops $\langle n_{\mathrm{loop}} \rangle$, tails $\langle n_{\mathrm{tail}} \rangle$

Flexible chains:

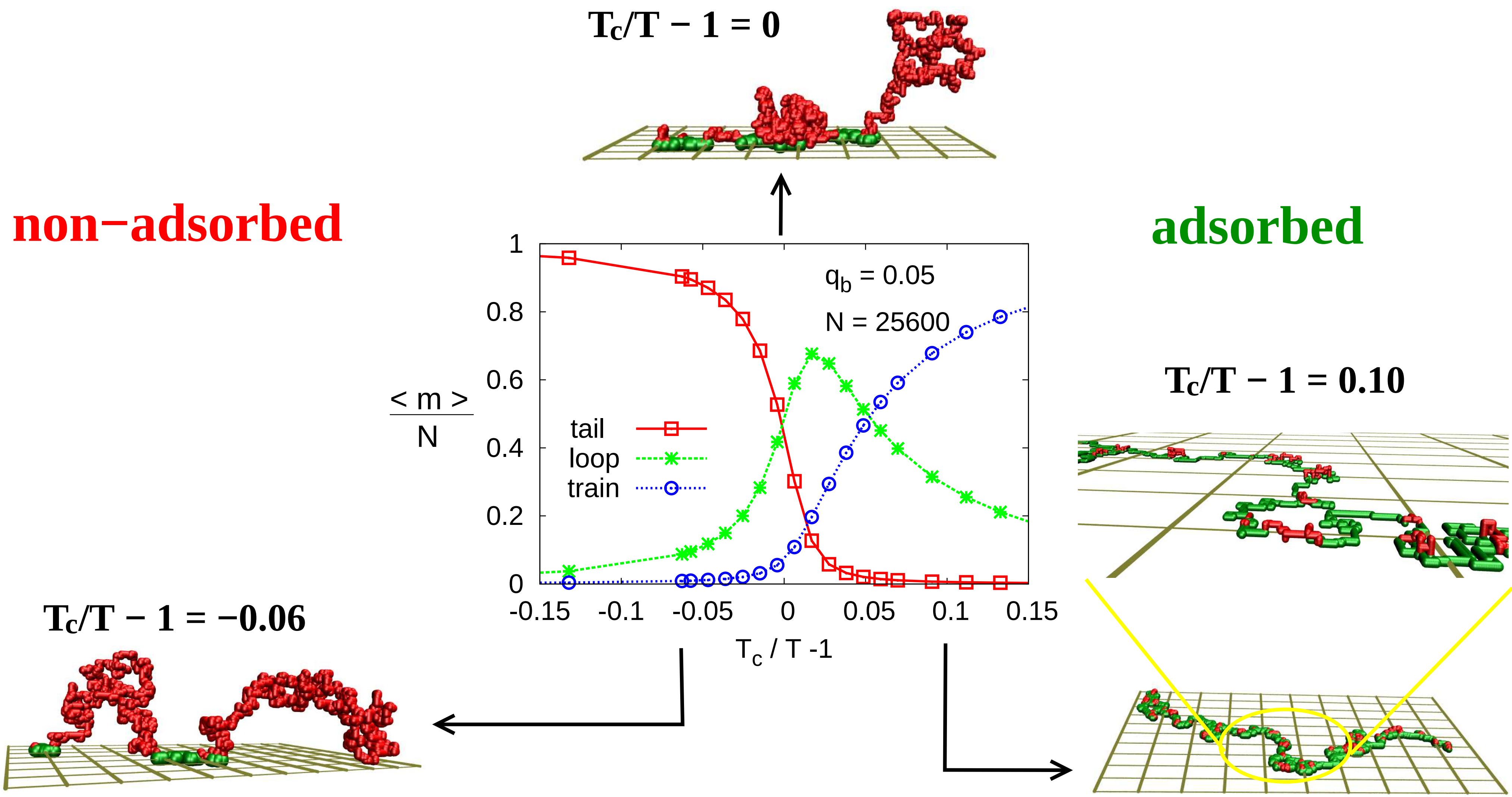
$$q_b = 0.4, \; \ell_p^{(3D)} = 1.13$$

$T_c/T - 1 = 0$



Moderately stiff chains:

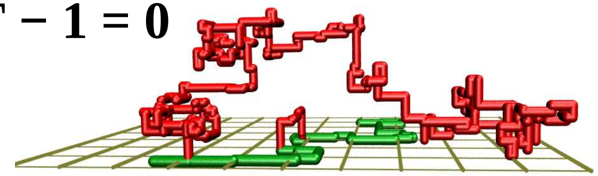
$$q_b = 0.05,\ \ell_p^{(3D)} = 5.96$$



Stiff chains:

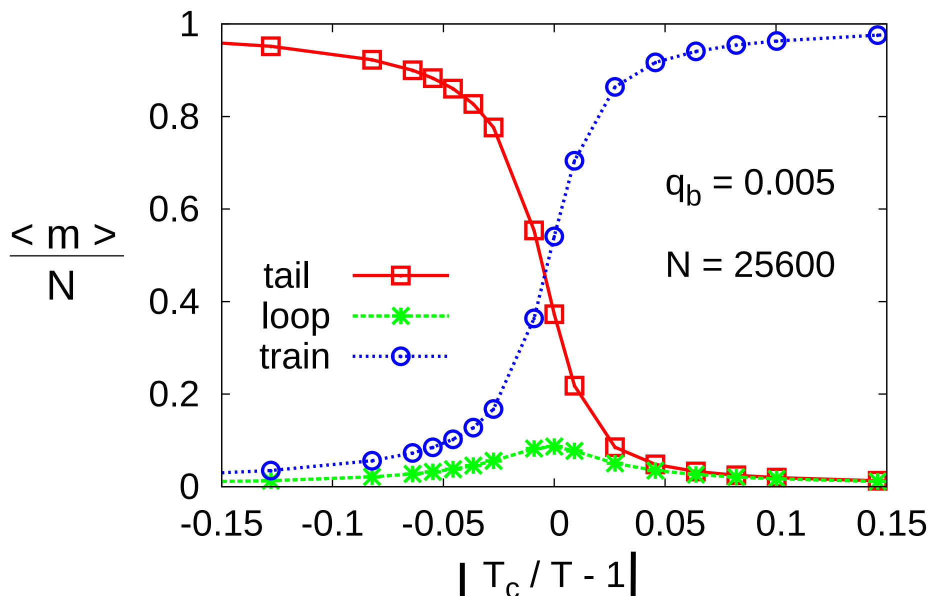
$$q_b = 0.005,\ \ell_p^{(3D)} = 52.61$$

$T_c/T - 1 = 0$

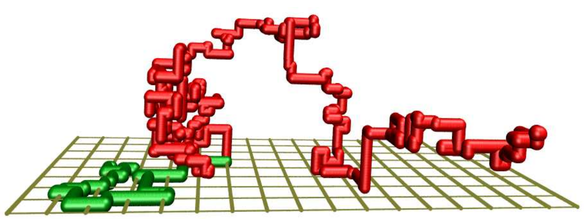


non−adsorbed

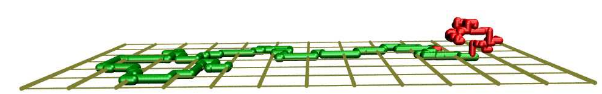
adsorbed



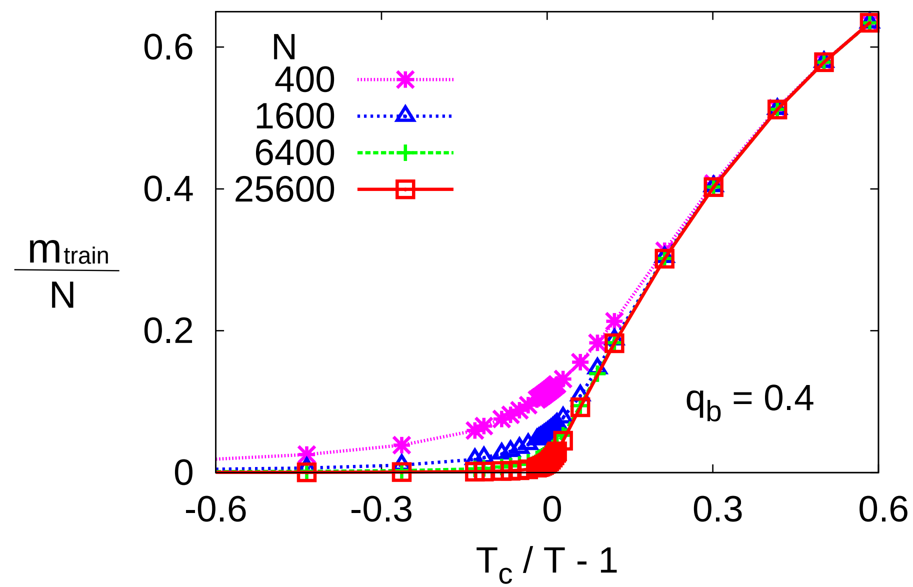
$T_c/T - 1 = -0.03$

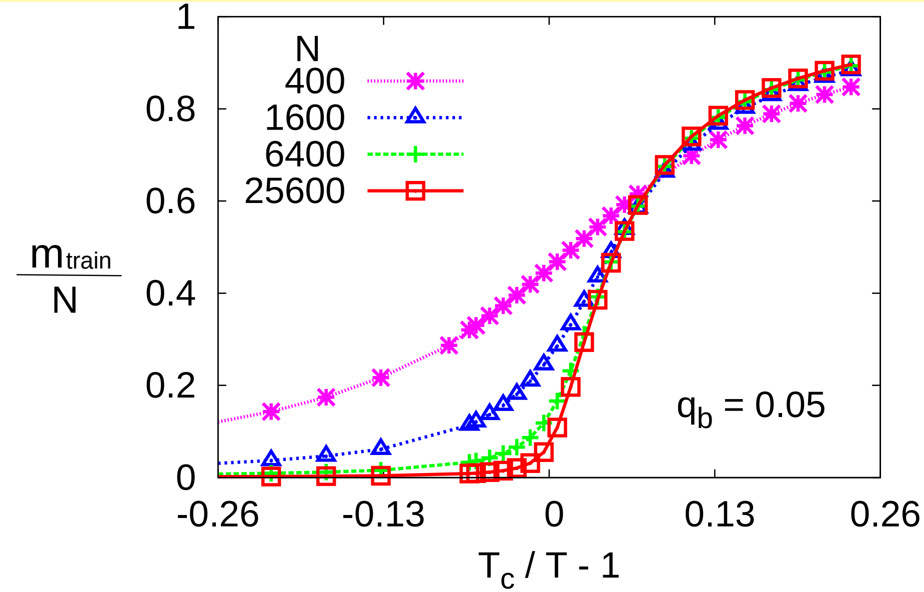


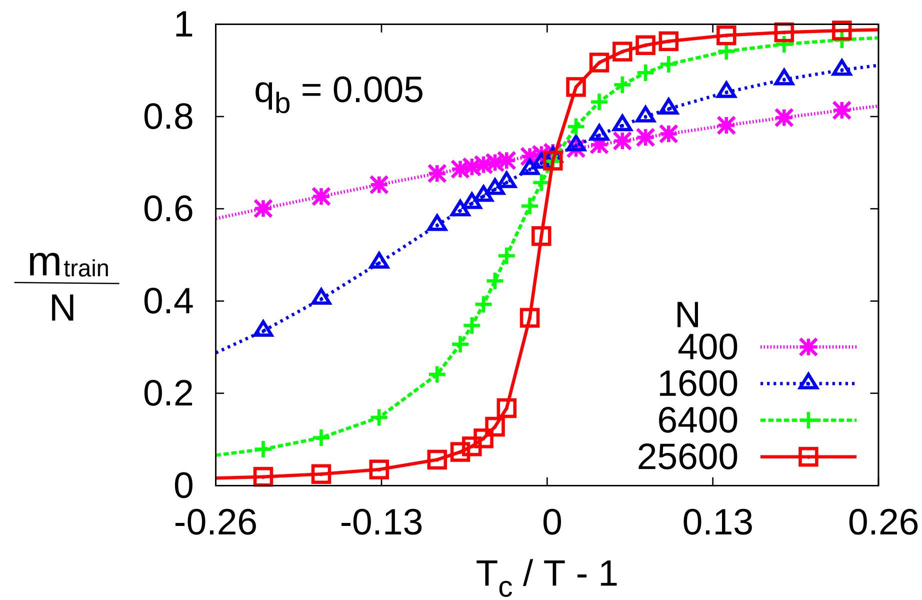
$T_c/T - 1 = 0.03$



Fraction of monomers in trains







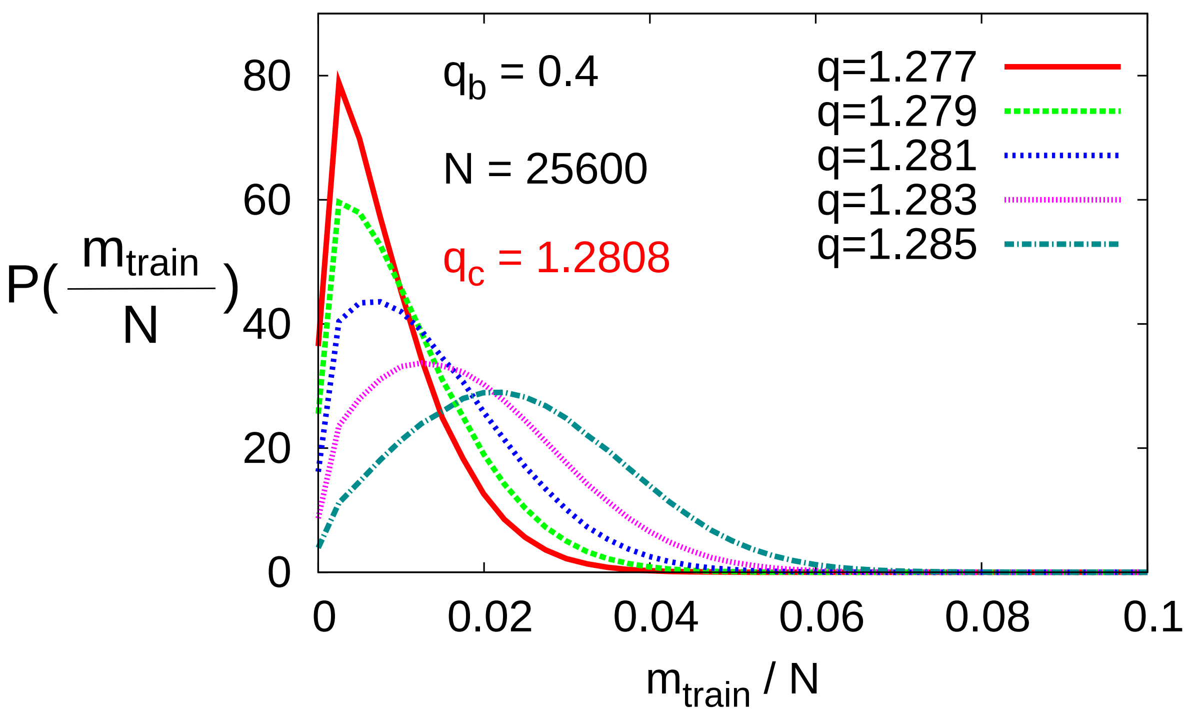
q_b	l_p
0.4	**1.13**
0.2	2.05
0.1	3.35
0.05	**5.96**
0.03	9.54
0.02	13.93
0.01	26.87
0.005	**52.61**

2nd order
flexible
↕
stiff
1st order

Distribution function $P(m_{\text{train}}/N)$

- Order parameter:
  Fraction of monomer surface contacts N_s/N
  $=$ Fraction of monomers in trains m_{train}/N

- Transition point: $q_c = \exp(\epsilon/k_B T_c)$



q_b	l_p	
0.4	**1.13**	**2nd order** flexible
0.2	2.05	
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0.005	52.61	stiff **1st order**

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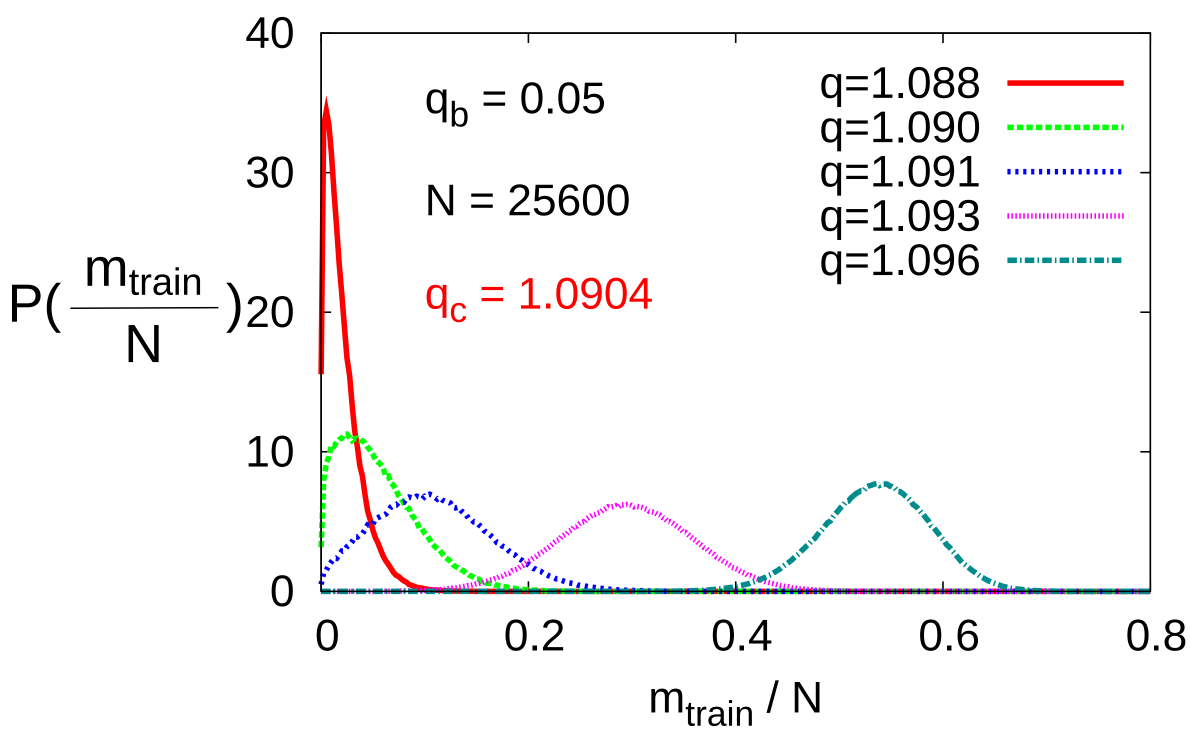

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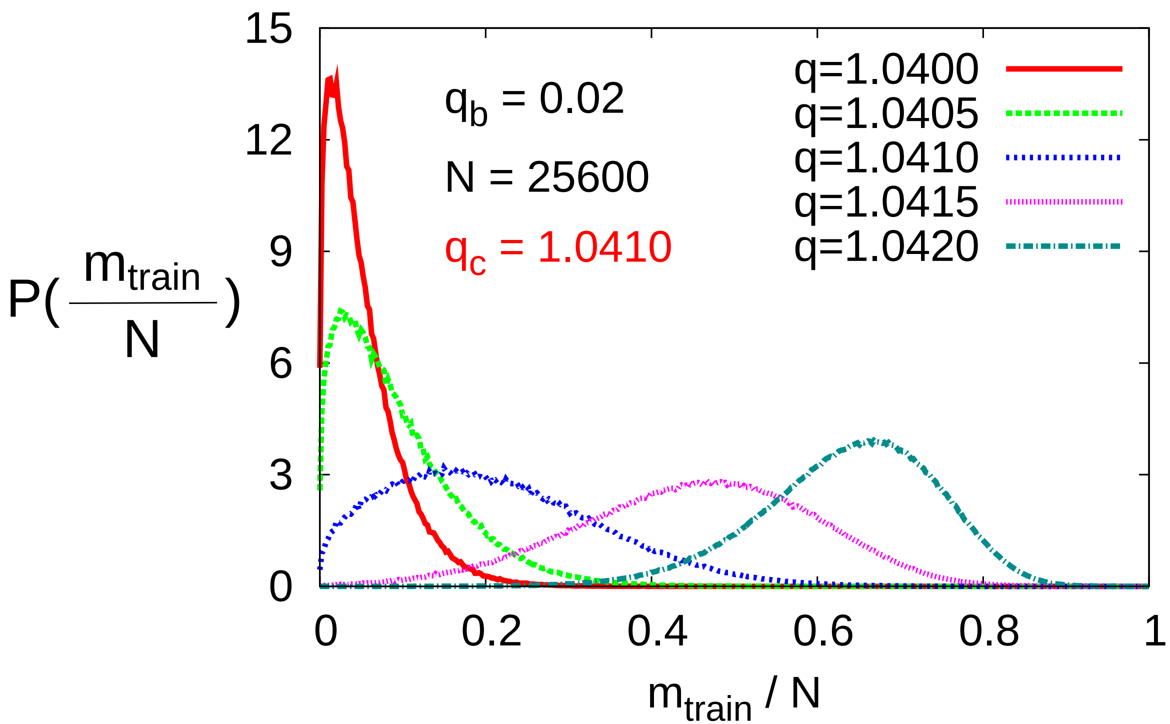

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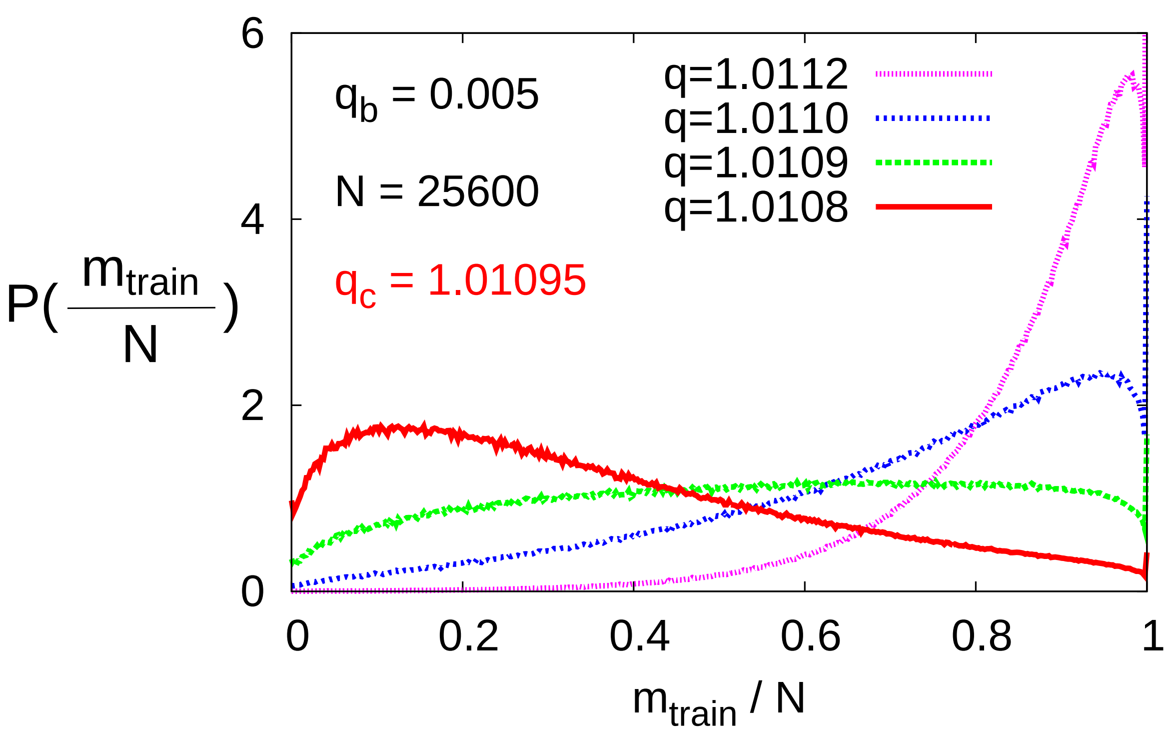

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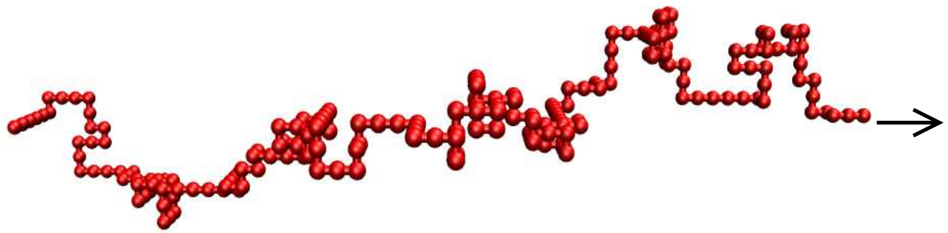
0.005	**52.61**	stiff
		1st order

Stretching semiflexible polymer chains

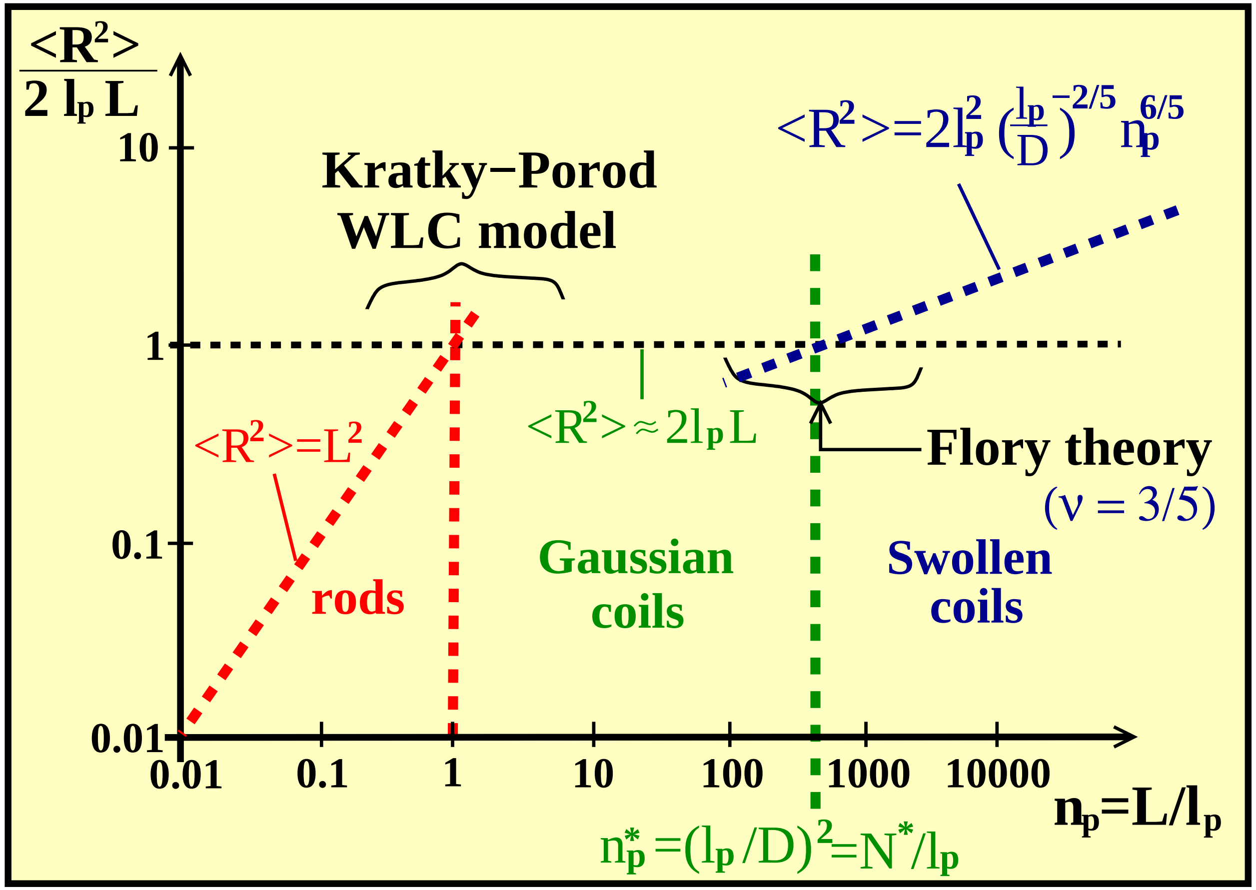


$\vec{f} = f\,\hat{x}$

- Experimental techniques of single molecule measurements: probing the tension-induced stretching of biological macromolecules
- Theoretical predictions of force-extension curves

Force-extension curves in $d = 3$

- Mean square end-to-end distance $\langle R^2 \rangle$:



L: contour length
$L = N\ell_b, \ell_b = 1$

ℓ_p: persistence length

D: effective thickness

for semiflexible chains in $d = 3$

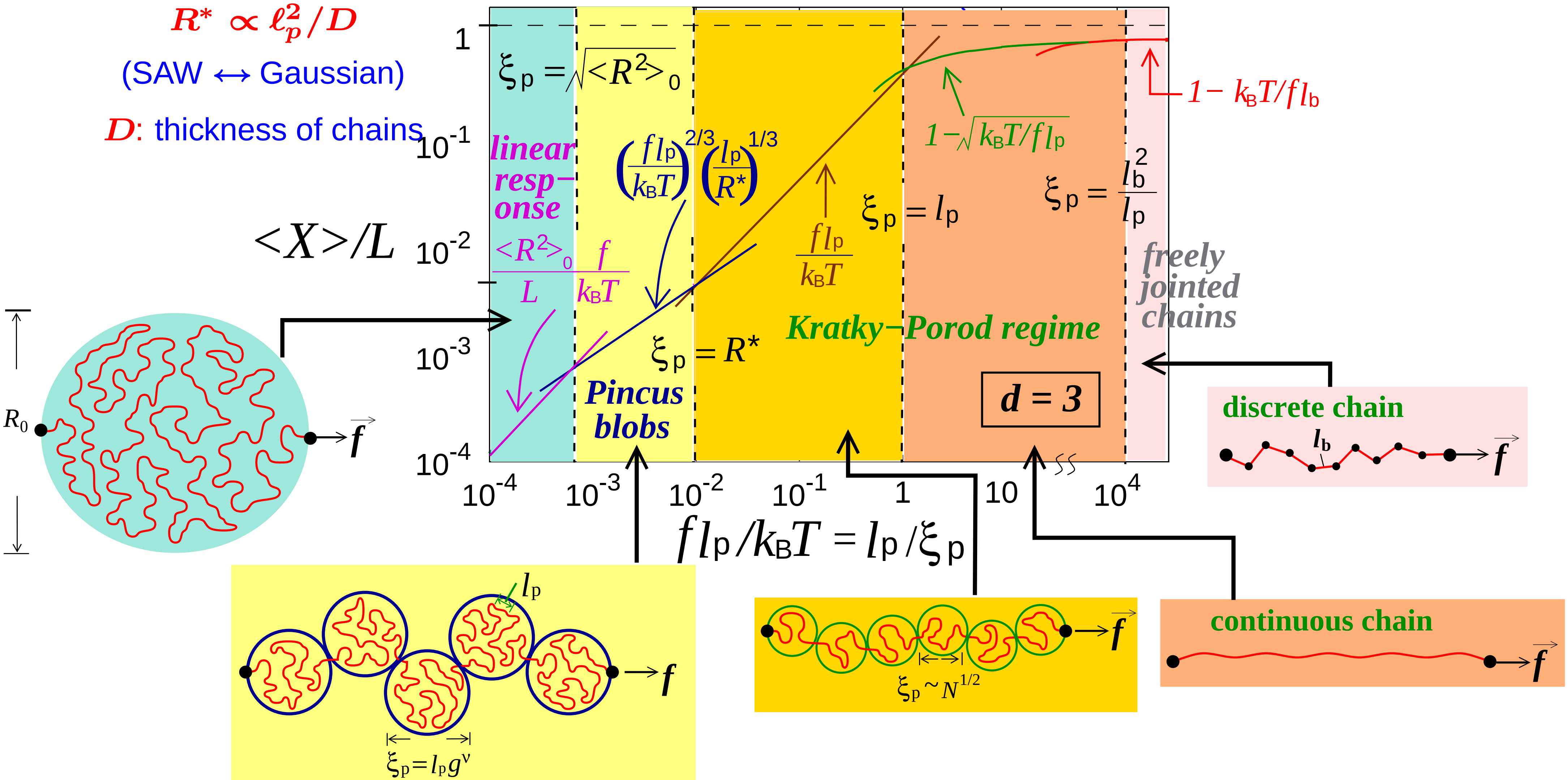
Force-extension curves in $d = 3$

$\xi_p = k_B T / f$: tensile length

$R^* \propto \ell_p^2 / D$

(SAW ↔ Gaussian)

D: thickness of chains



Hsu & Binder, J. Chem. Phys. 136, 024901 (2012)

Crossover scaling behavior

Force-extension curves: $C_y \frac{\langle X \rangle}{L}$ - $C_x \frac{f \ell_p}{k_B T}$

$\Rightarrow$ crossover point $(x_{cr}, y_{cr}) \sim (\mathcal{O}(1), \mathcal{O}(1))$

- Linear response ($\xi_p > \sqrt{\langle R^2 \rangle_0}$): $\frac{\langle X \rangle}{L} \approx \frac{\langle R^2 \rangle_0}{L} \frac{f}{k_B T}$
- Pincus blobs ($\sqrt{\langle R^2 \rangle_0} > \xi_p > R^* (= \ell_p^2 / D)$):

  $$\frac{\langle X \rangle}{L} \approx \left(\frac{f \ell_p}{k_B T} \right)^{2/3} \left(\frac{\ell_p}{R^*} \right)^{1/3}$$
- Kratky-Porod regime ($R^* > \xi_p > \ell_b^2 / \ell_p$):
  - $\frac{\langle X \rangle}{L} \approx (\frac{2}{3})(\frac{f \ell_p}{k_B T})$, small f ($R^* > \xi_p > \ell_p$)
  - $\frac{\langle X \rangle}{L} \approx 1 - \sqrt{\frac{k_B T}{4 f \ell_p}}$, large f ($\ell_p > \xi_p > \ell_b^2 / \ell_p$)
- Freely jointed chains ($\xi_p < \ell_b^2 / \ell_p$): $1 - \frac{k_B T}{f \ell_b}$

Crossover scaling behavior

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  > $R^* \approx \ell_p \approx \ell_b$ (SAW)
  > Kratky-Porod regime disappears

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  > $D \approx \ell_p$, $R^* \approx \ell_p$
  > Pincus blob regime takes over

- Kratky-Porod regime ($R^* > \xi_p > \ell_b^2 / \ell_p$):
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> $\langle R^2 \rangle_0 \approx R^{*2}$
> Pincus blob regime disappears

- Kratky-Porod regime ($R^* > \xi_p > \ell_b^2 / \ell_p$):
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- Freely jointed chains ($\xi_p < \ell_b^2 / \ell_p$): $1 - \frac{k_B T}{f \ell_b}$

Biased Semiflexible SAW model

- Excluded volume effect

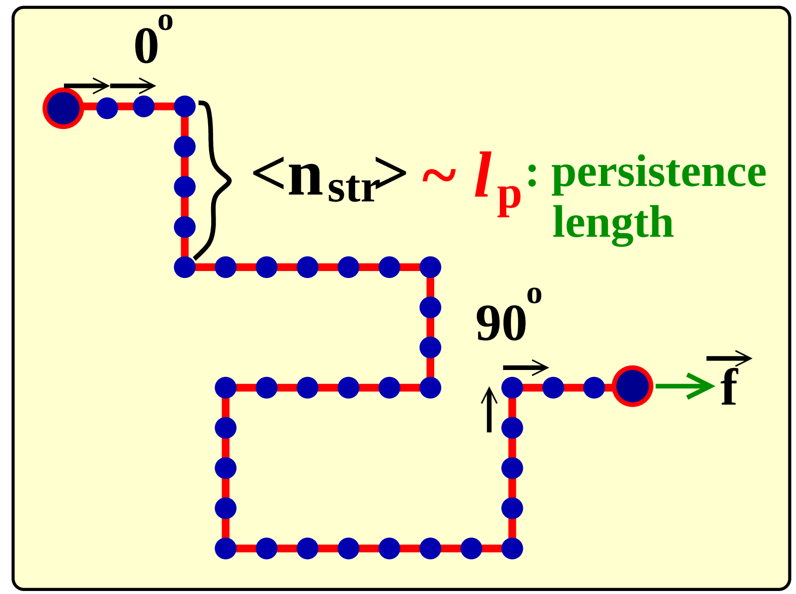
  $\Rightarrow$ Self-avoiding walk (SAW)

- Chain stiffness

  $\Rightarrow$ Bond-bending potential

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

  bending energy $\epsilon_b \uparrow$, stiffness $\uparrow$



- Deformation of chains

  $\Rightarrow$ Stretching force $\vec{f} = f\hat{x}$

on the simple cubic lattice $(d = 3)$

- Partition sum (a walk with N_b steps and N_{bend} local bends):

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

$q_b = e^{-(\varepsilon_b/k_BT)}$: bending factor, $b = e^{f/k_BT}$: stretching factor

X: end-to-end distance along $+x$-direction

$(X = x_{N+1} - x_1)$

- Algorithm: PERM

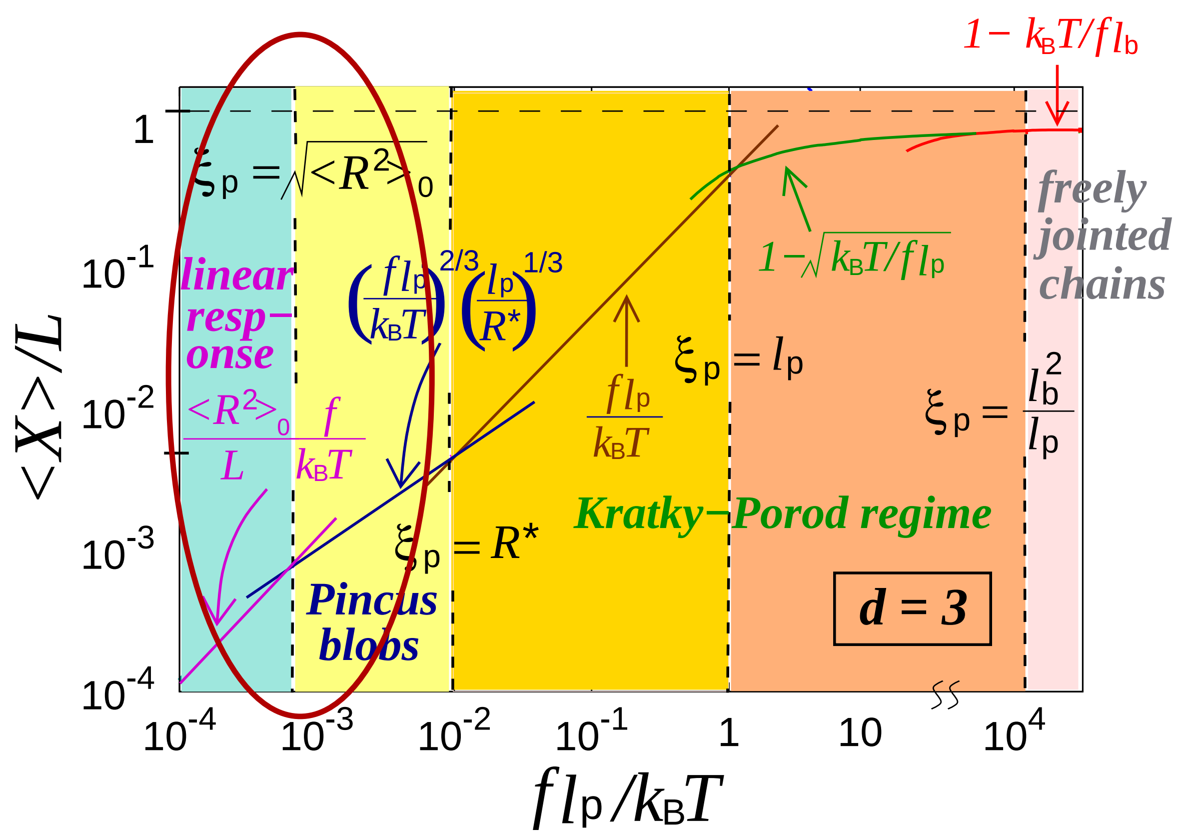
bias: $p_{+\hat{x}} : p_{-\hat{x}} : p_{\pm\hat{y}\,\text{or}\,\pm\hat{z}} = \sqrt{b} : \sqrt{1/b} : 1$

  - $0 \leq N_b \leq 25600$, short chain ↔ long chain
  - $0.005 \leq q_b \leq 1.0$, very stiff ↔ flexible (SAW)
  - $1 \leq b \leq 1.6$, no force ↔ strong force

q_b	l_p (3D in bulk)	
1.0	0.67	flexible
0.4	1.13	↑
0.2	1.81	
0.1	3.12	
0.05	5.70	
0.03	9.10	
0.02	13.35	
0.01	26.08	↓
0.005	51.52	stiff

Monte Carlo results in $d = 3$

- Linear response ⇔ Pincus blobs



$(x_{cr}, y_{cr}) \sim \mathcal{O}(1)$

⇒ scaling factors: $C_x = L^{3/5} l_b^{1/5} / l_p^{4/5}$, $C_y = L^{2/5}/(\ell_b \ell_p)^{1/5}$

Monte Carlo results in $d = 3$

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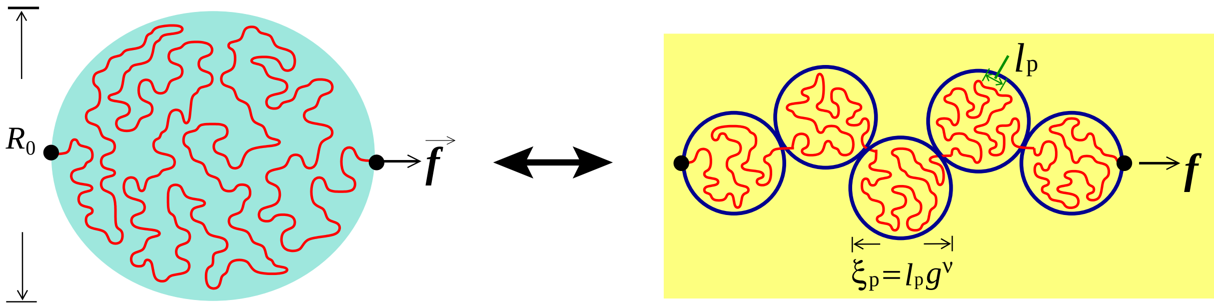

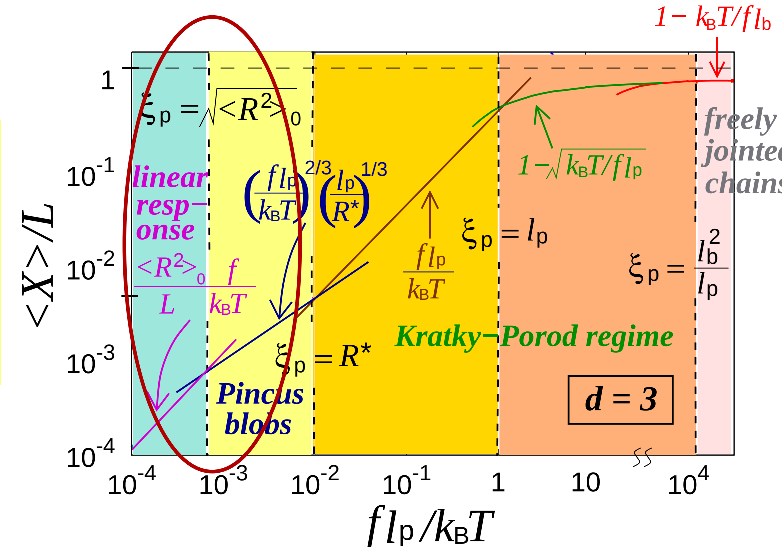

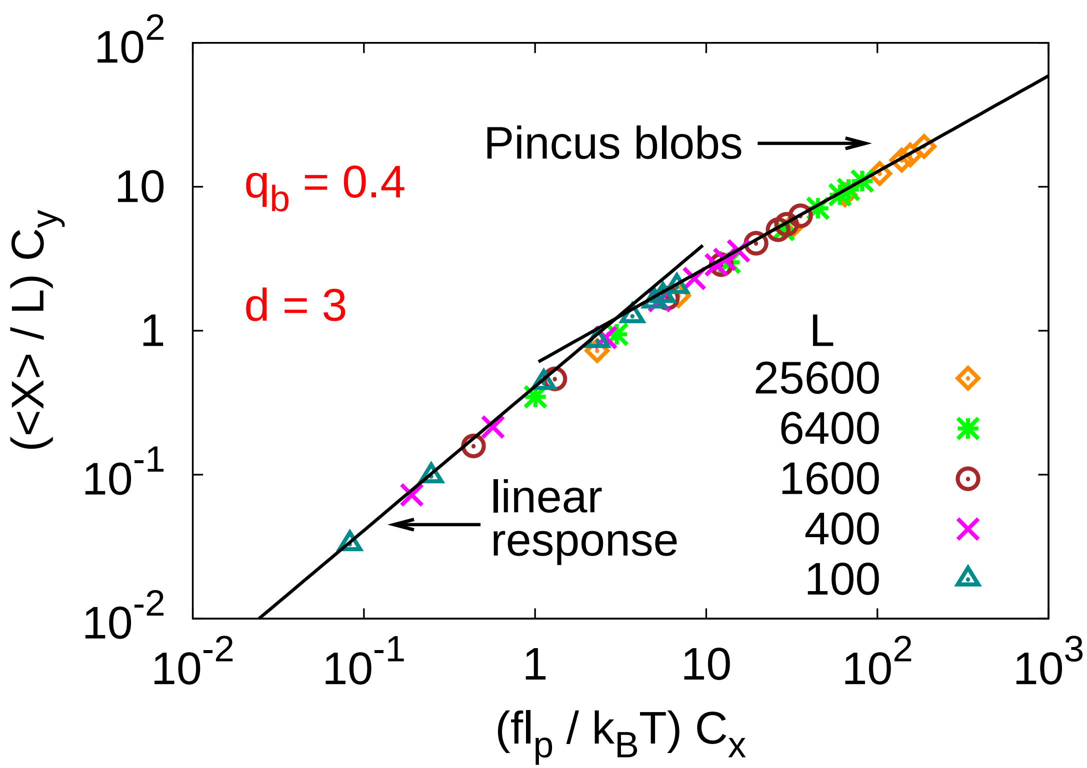

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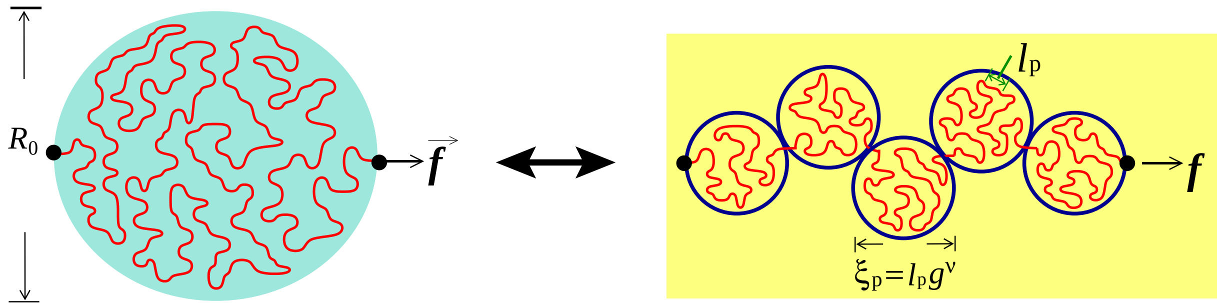

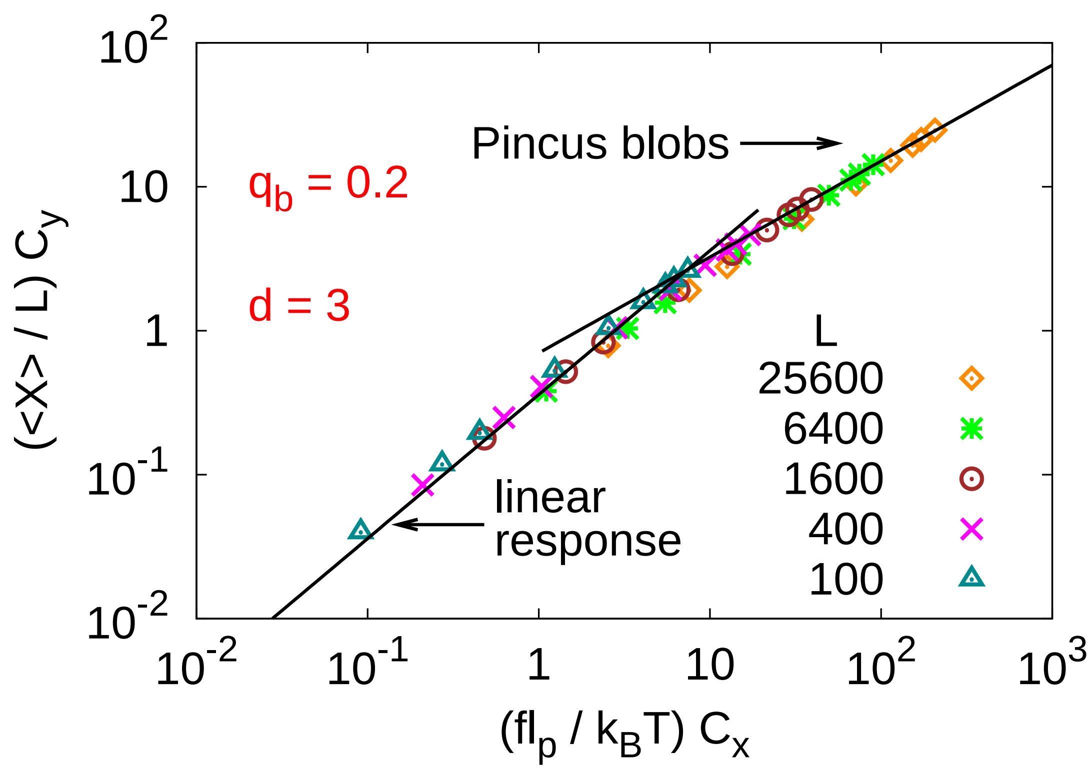

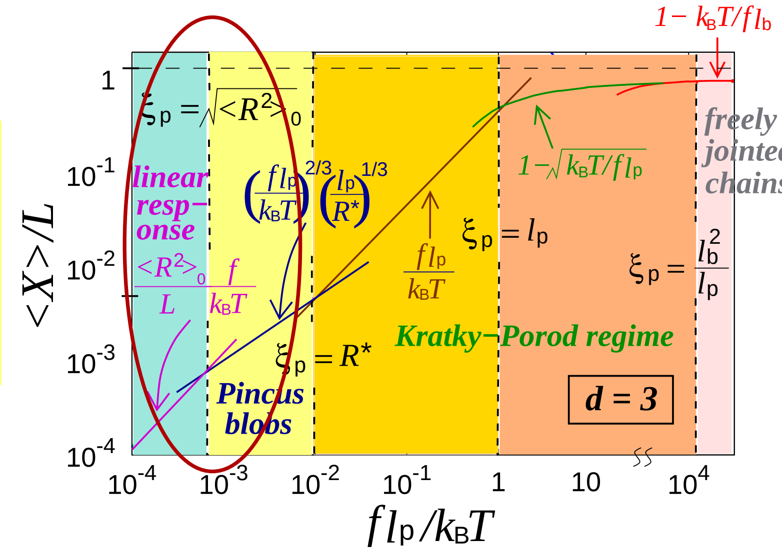

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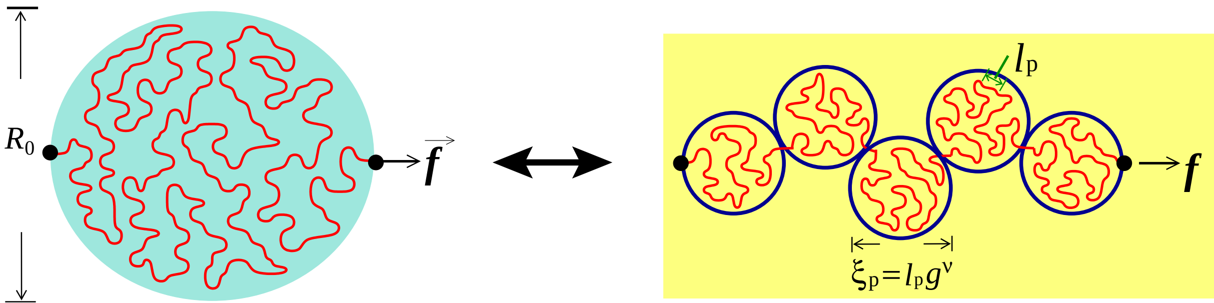

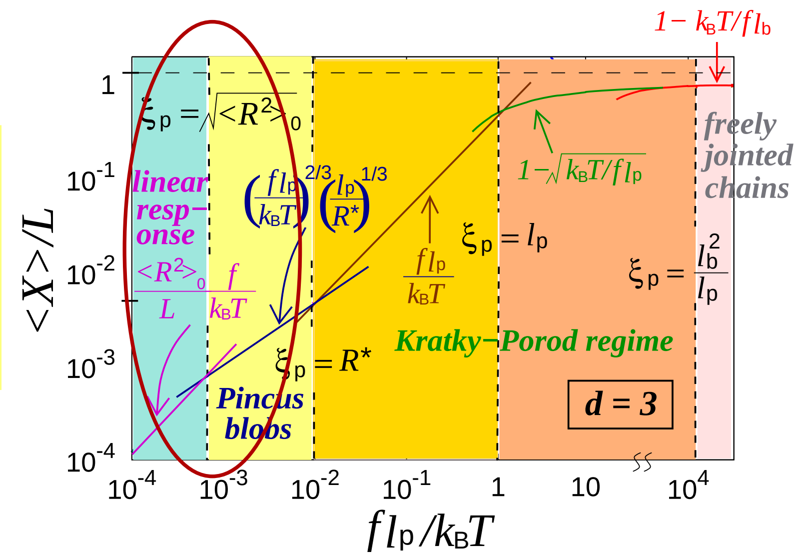

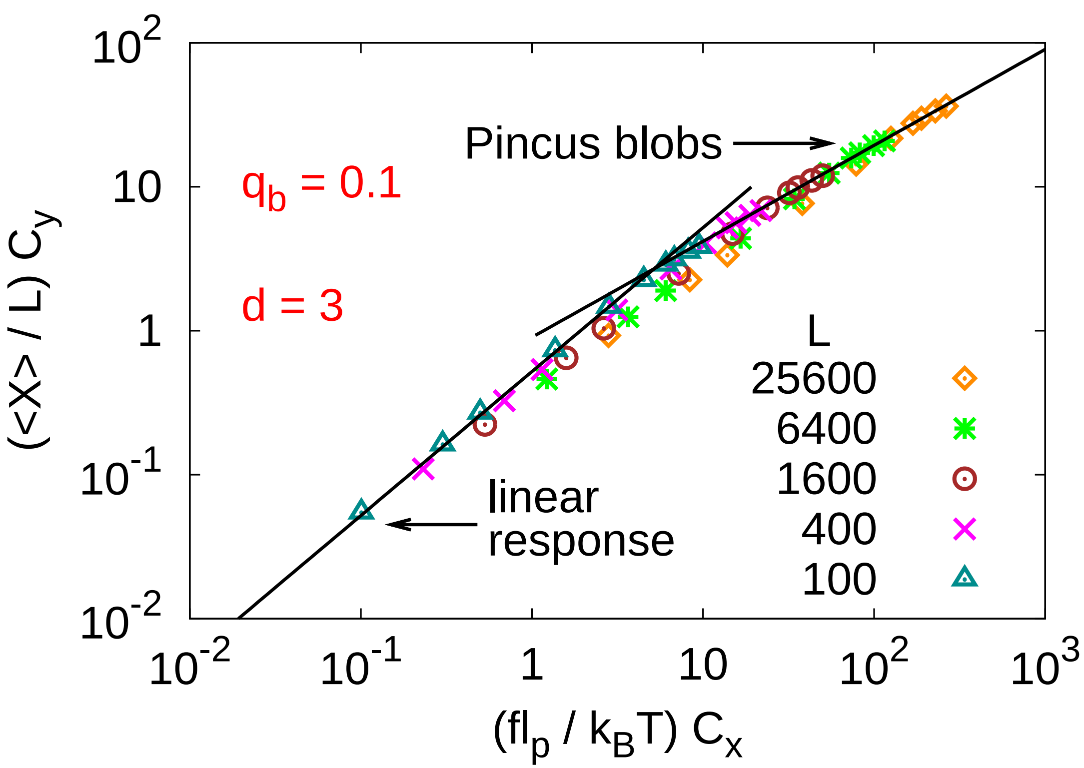

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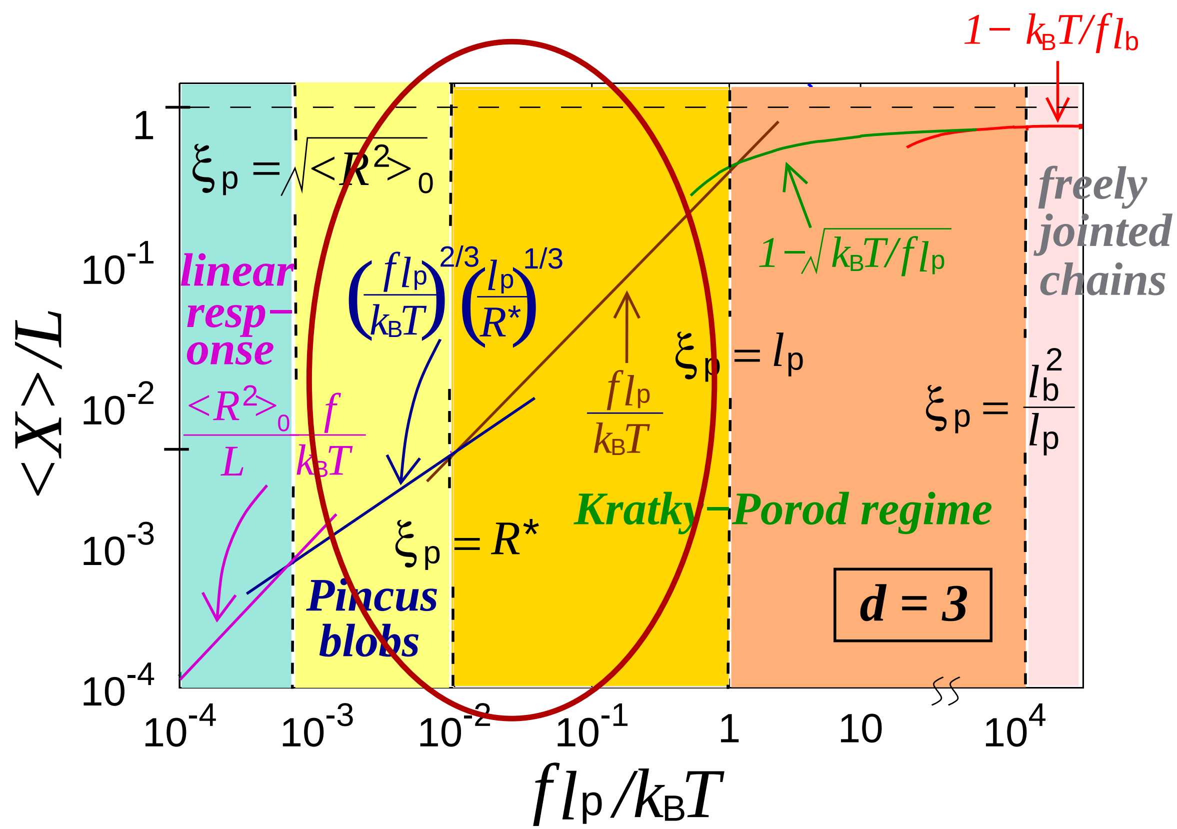
Monte Carlo results in $d = 3$

- Pincus blobs ⇔ Kratky-Porod (K-P) like regime



$(x_{\rm cr}, y_{\rm cr}) \sim \mathcal{O}(1) \Rightarrow$ scaling factors: $C_x = \ell_p/\ell_b$, $C_y = \ell_p/\ell_b$

Monte Carlo results in $d = 3$

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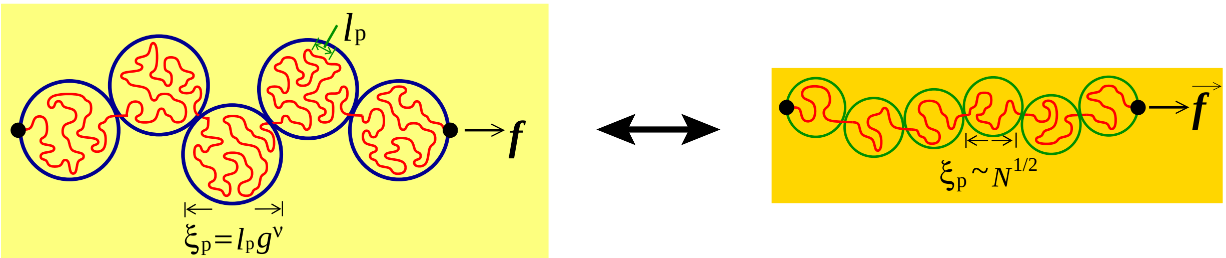

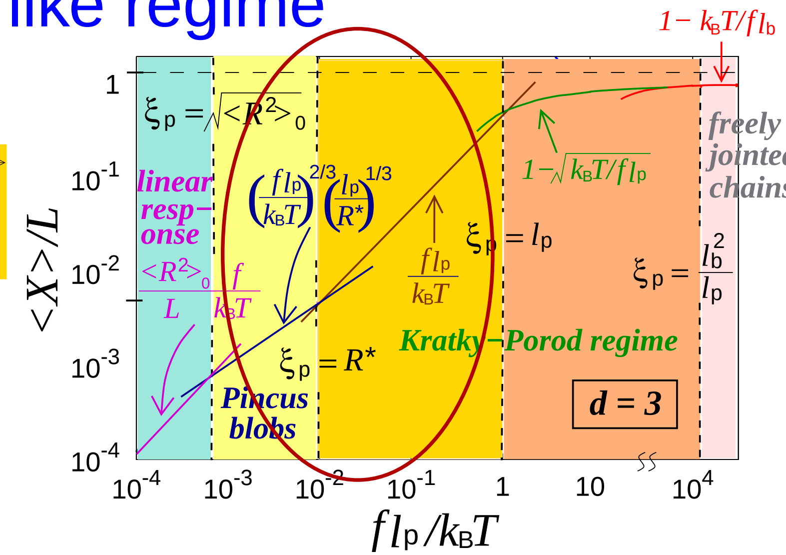

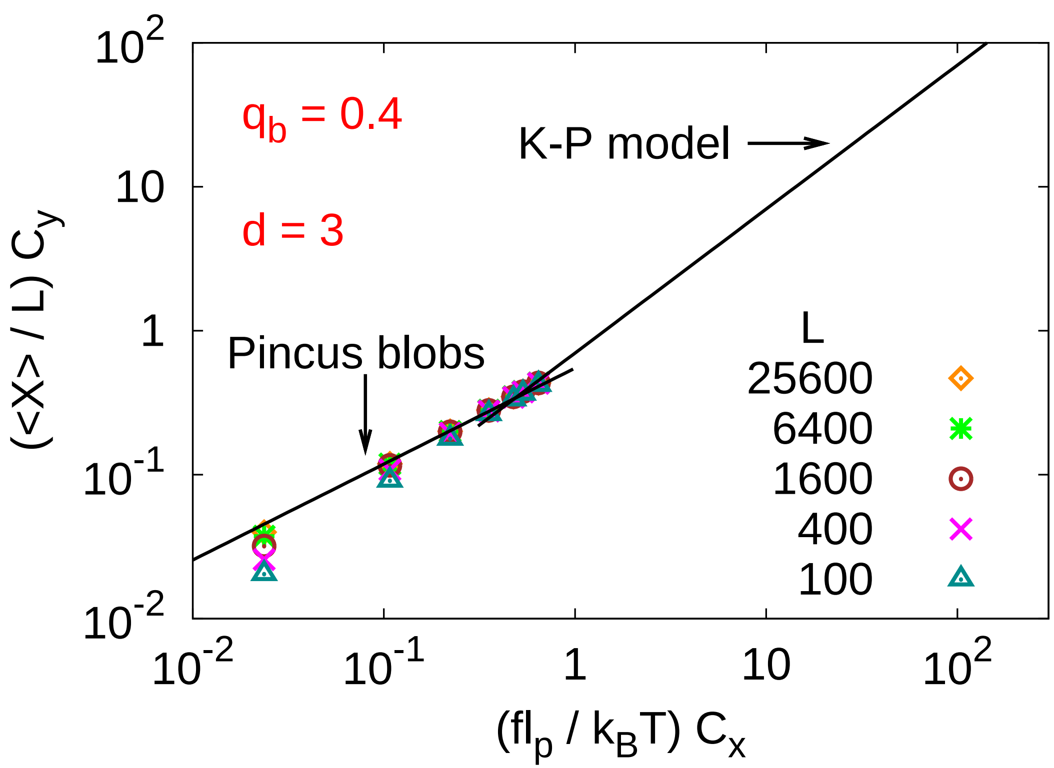

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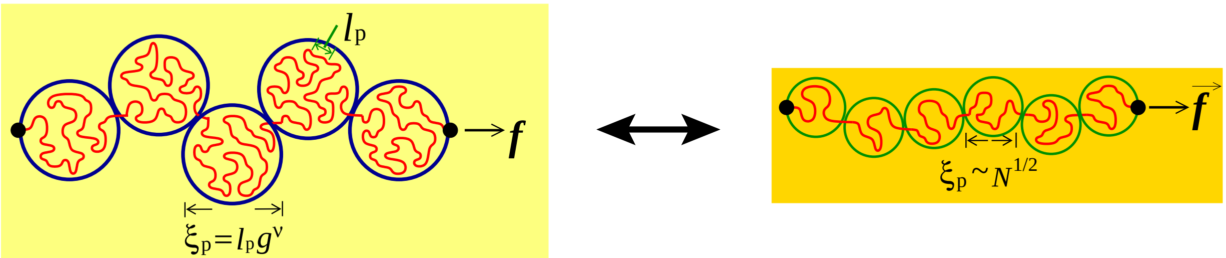

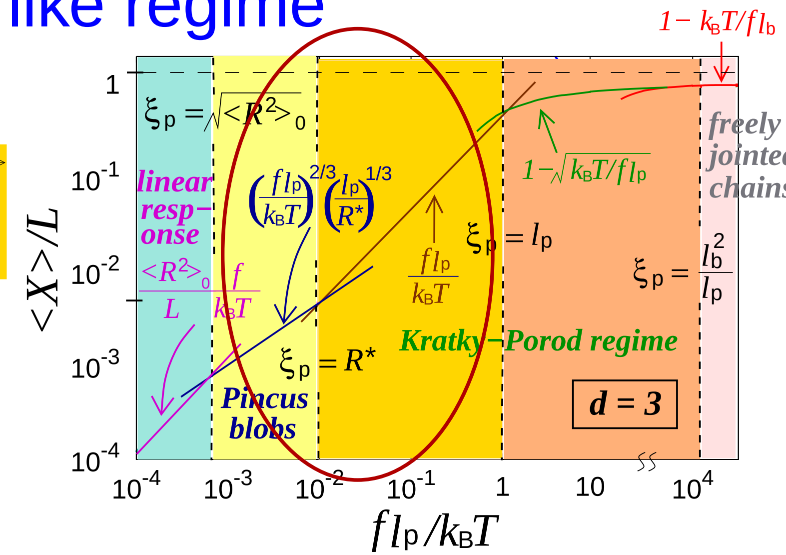

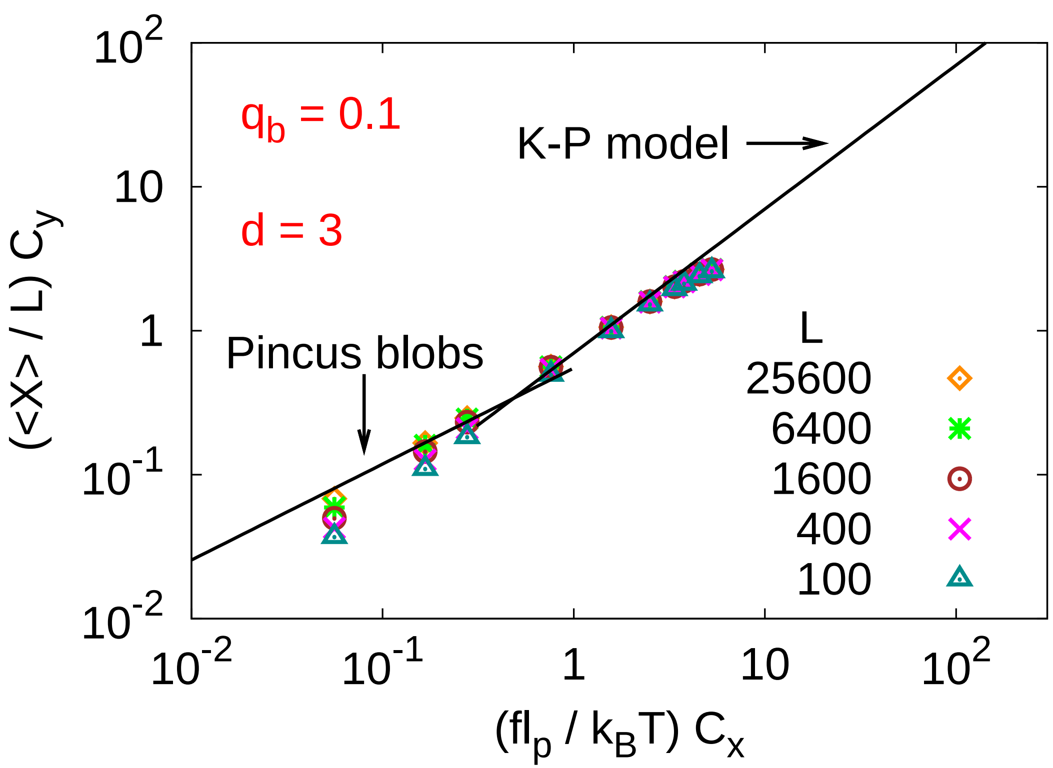

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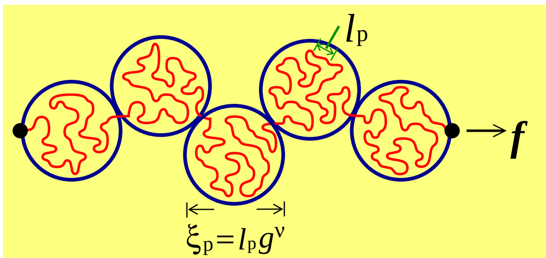

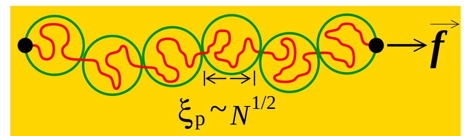

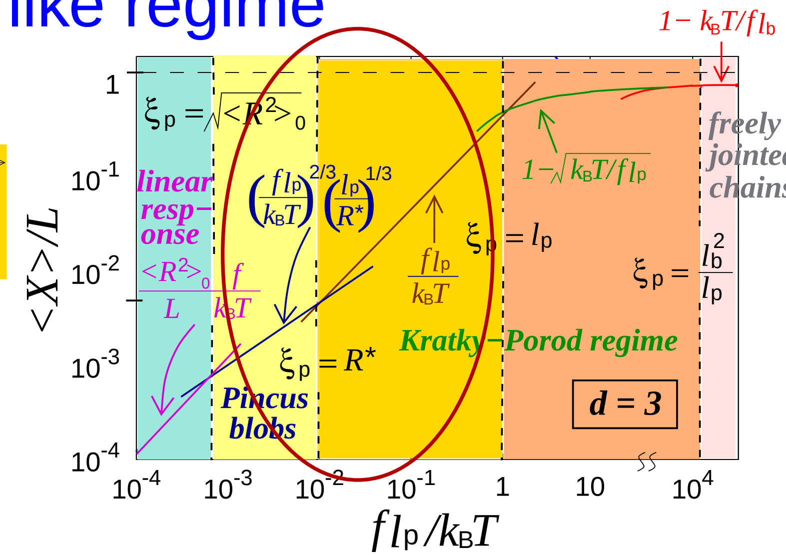

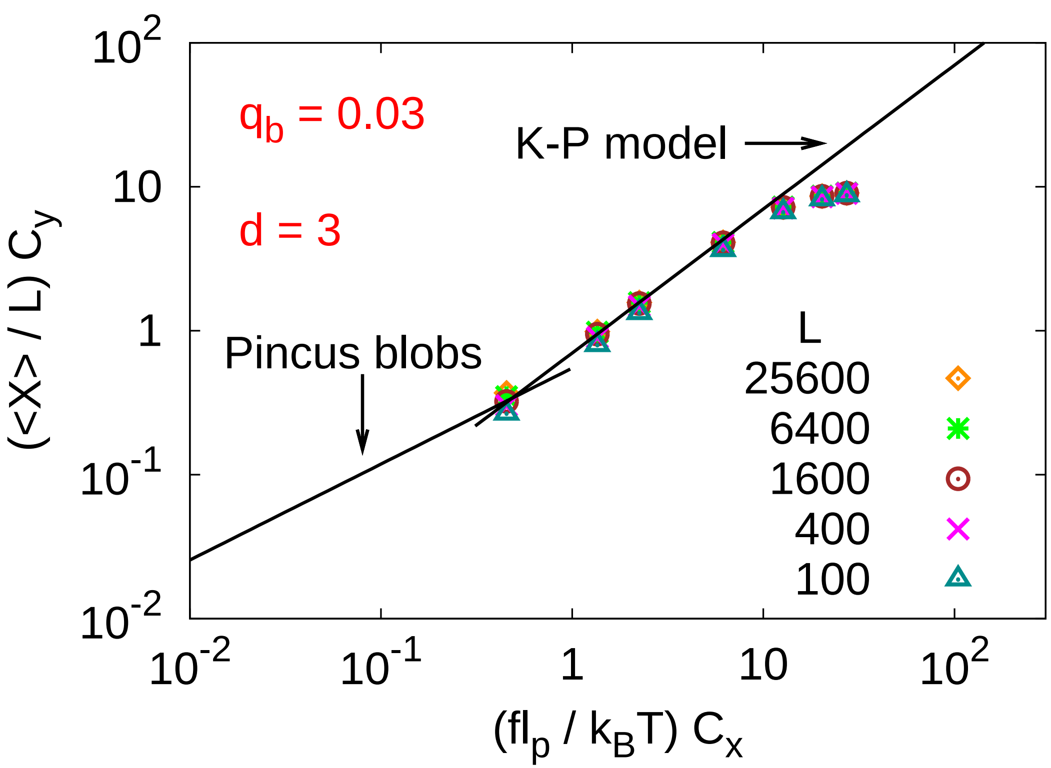

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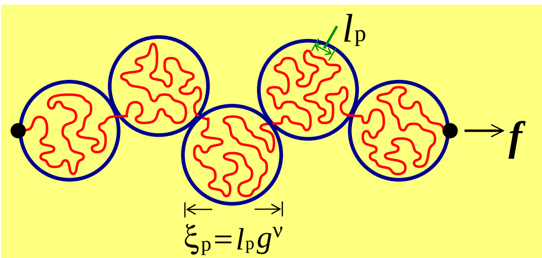

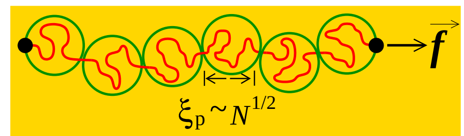

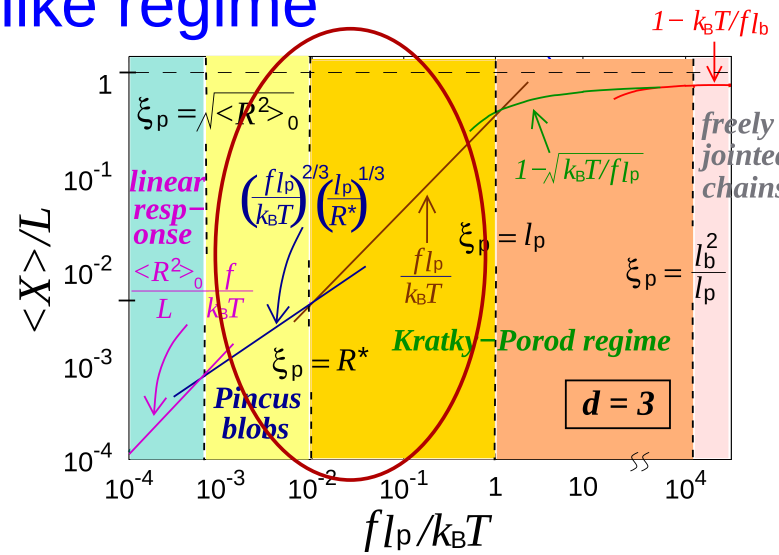

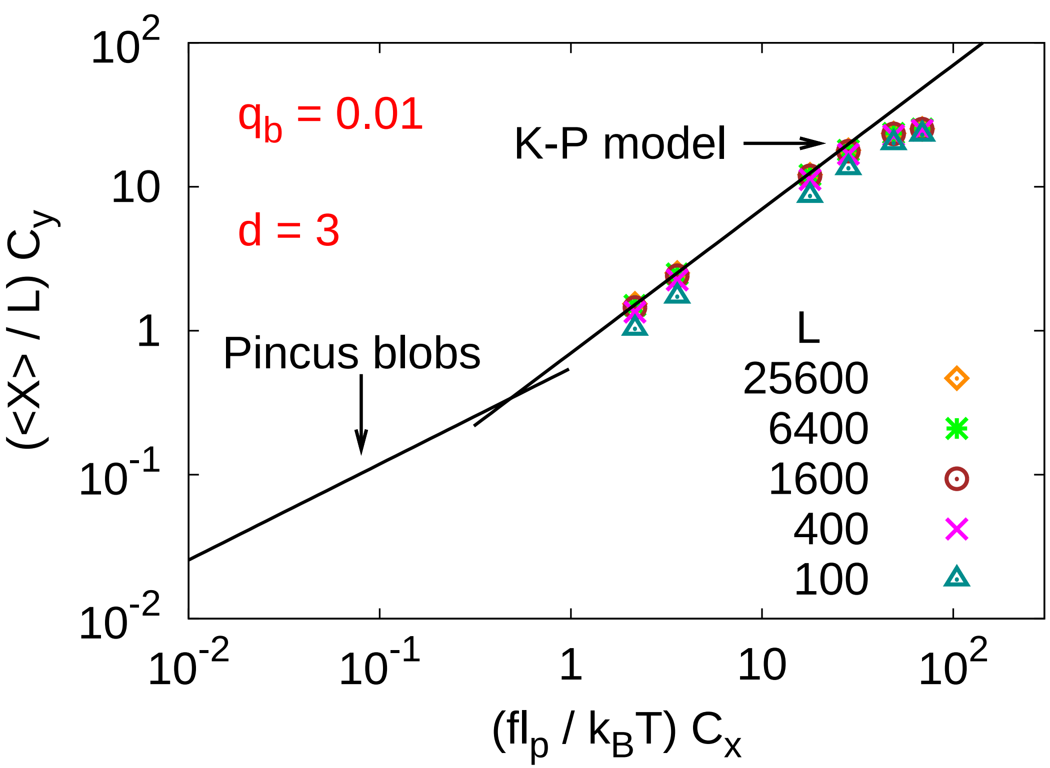

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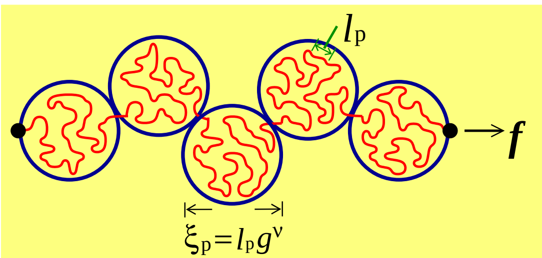

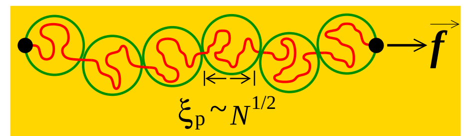

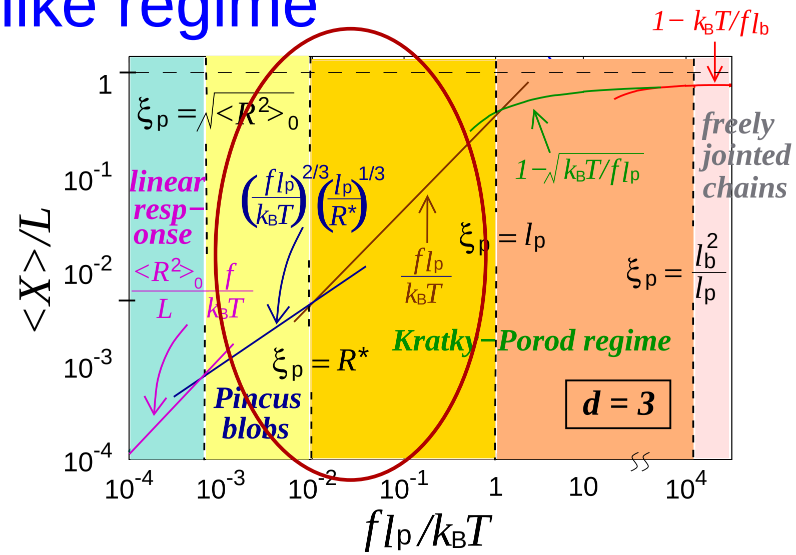

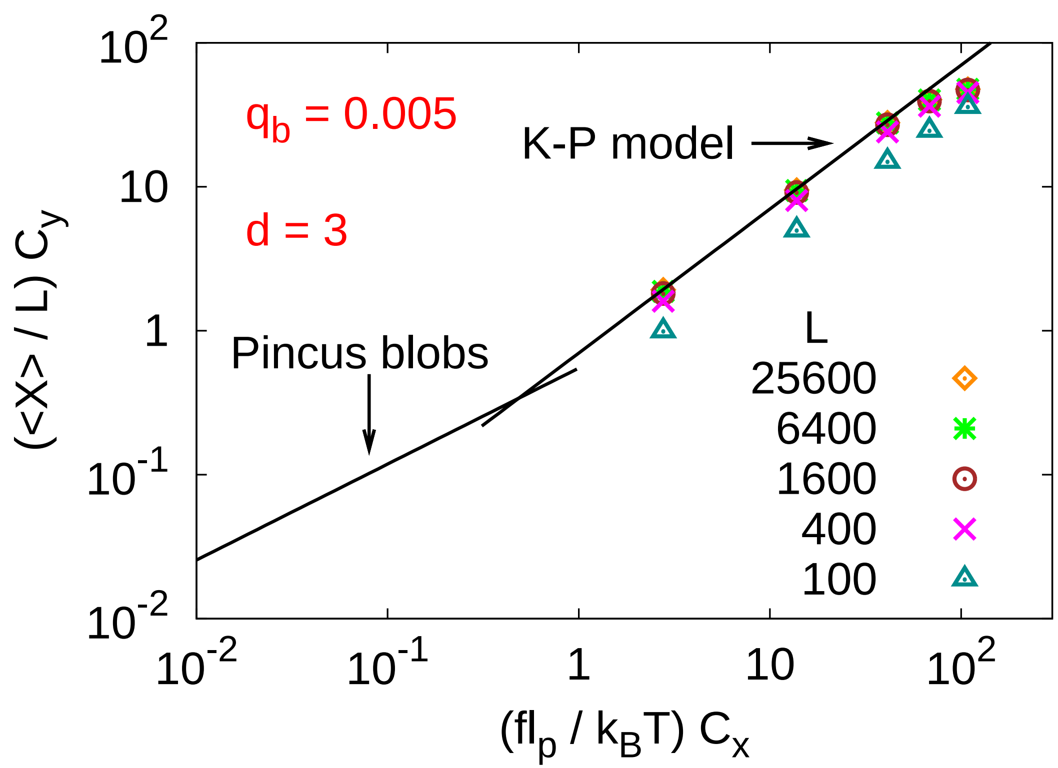

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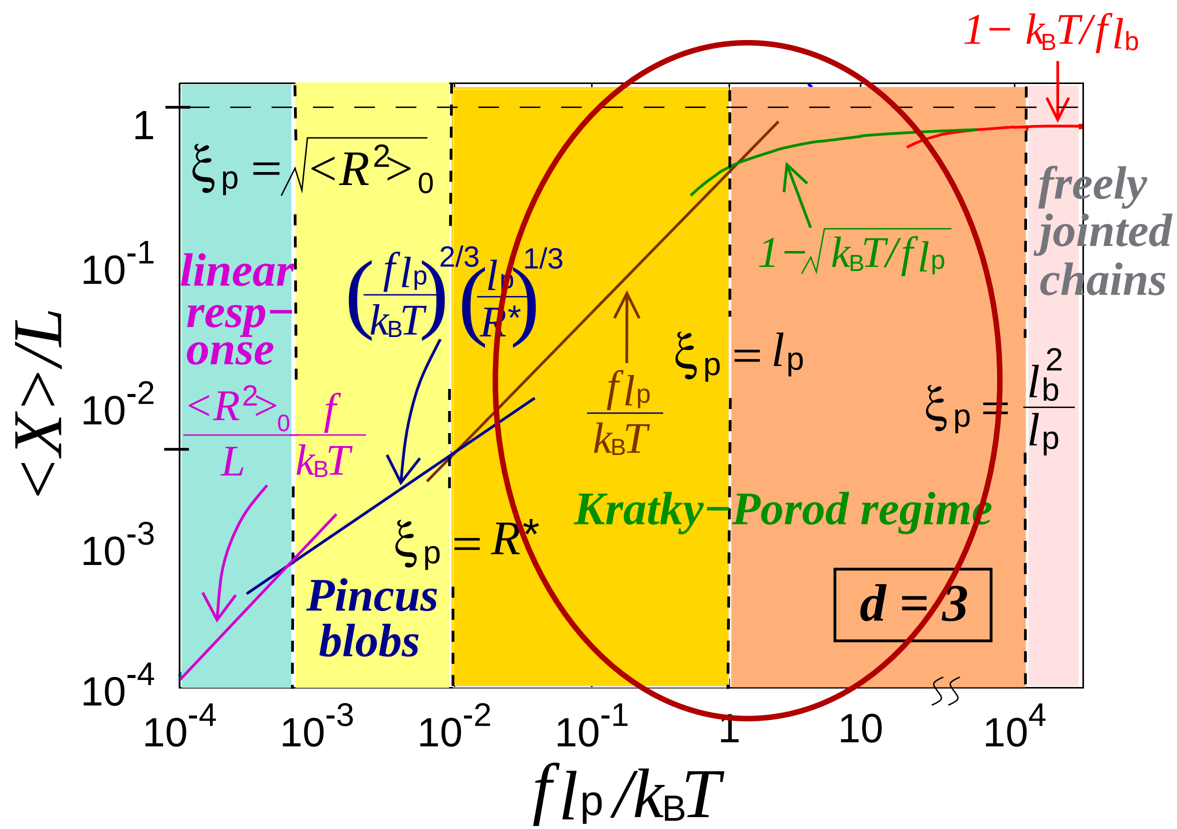

$(x_{\rm cr}, y_{\rm cr}) \sim \mathcal{O}(1) \Rightarrow$ scaling factors: $C_x = 1$, $C_y = 1$

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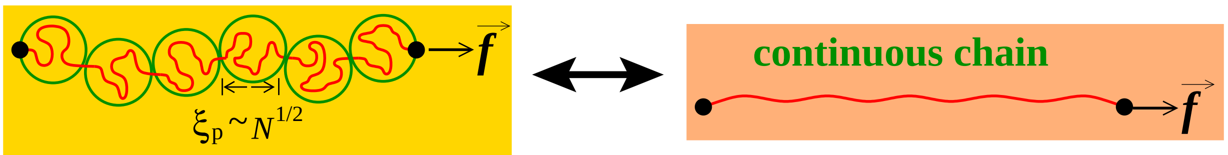

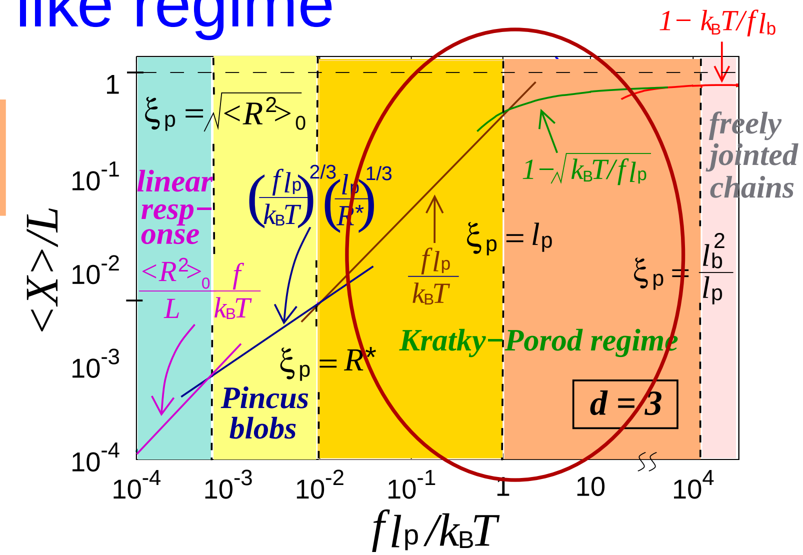

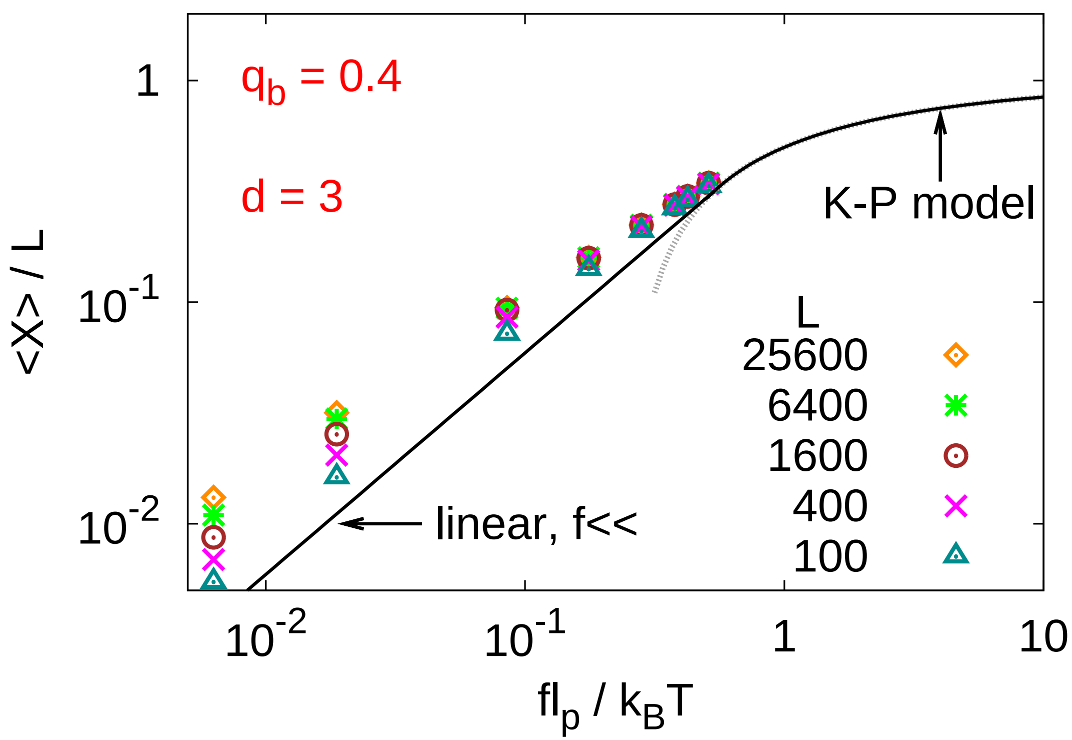

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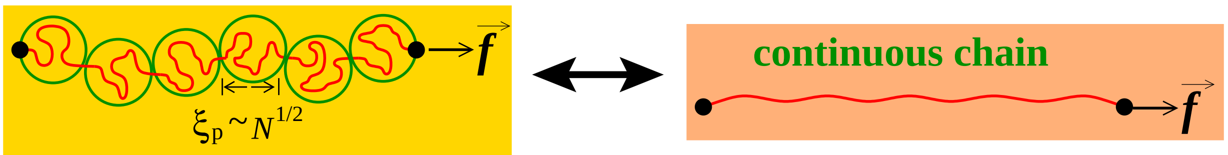

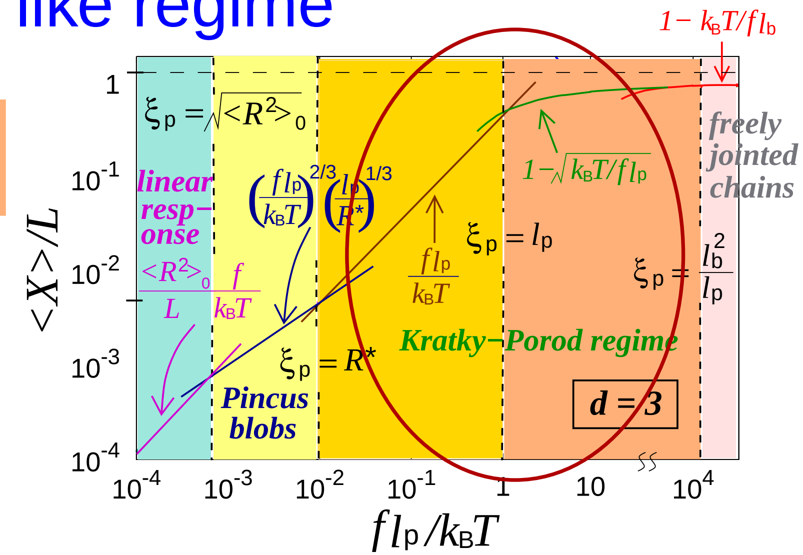

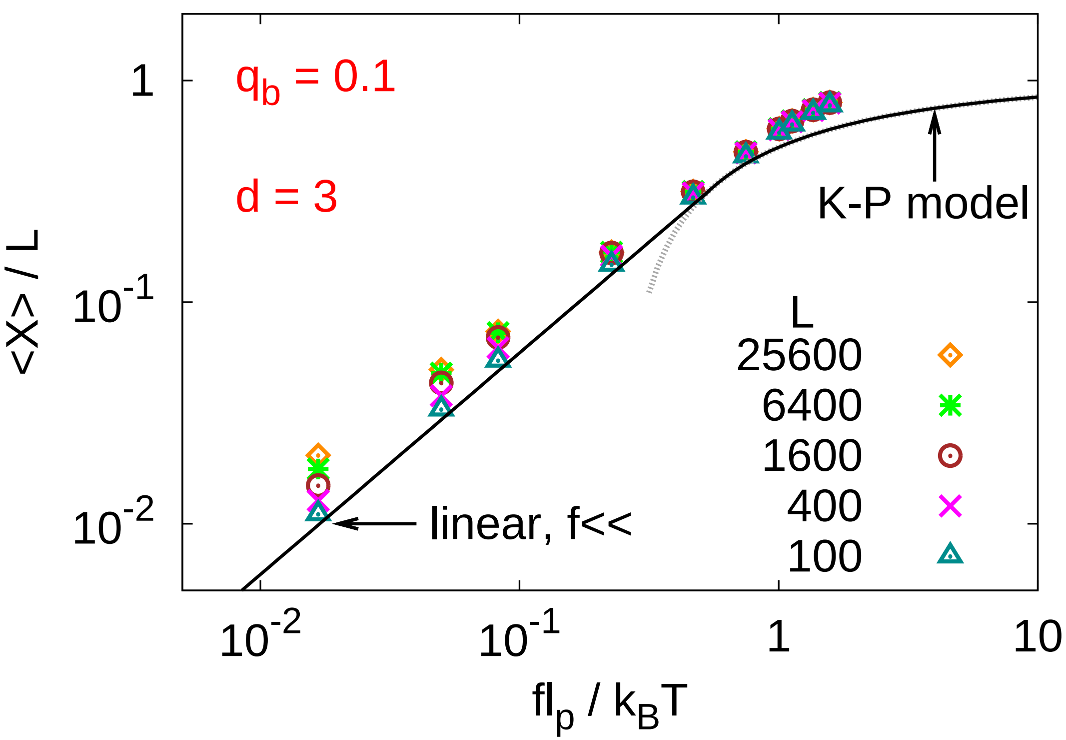

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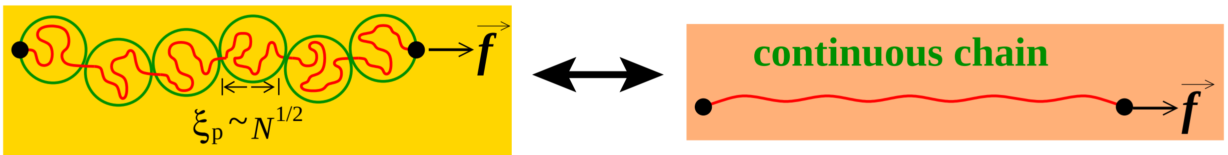

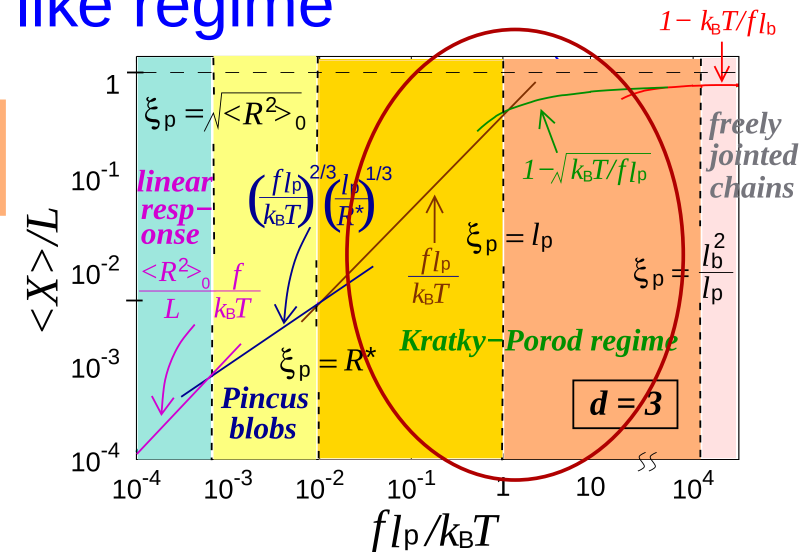

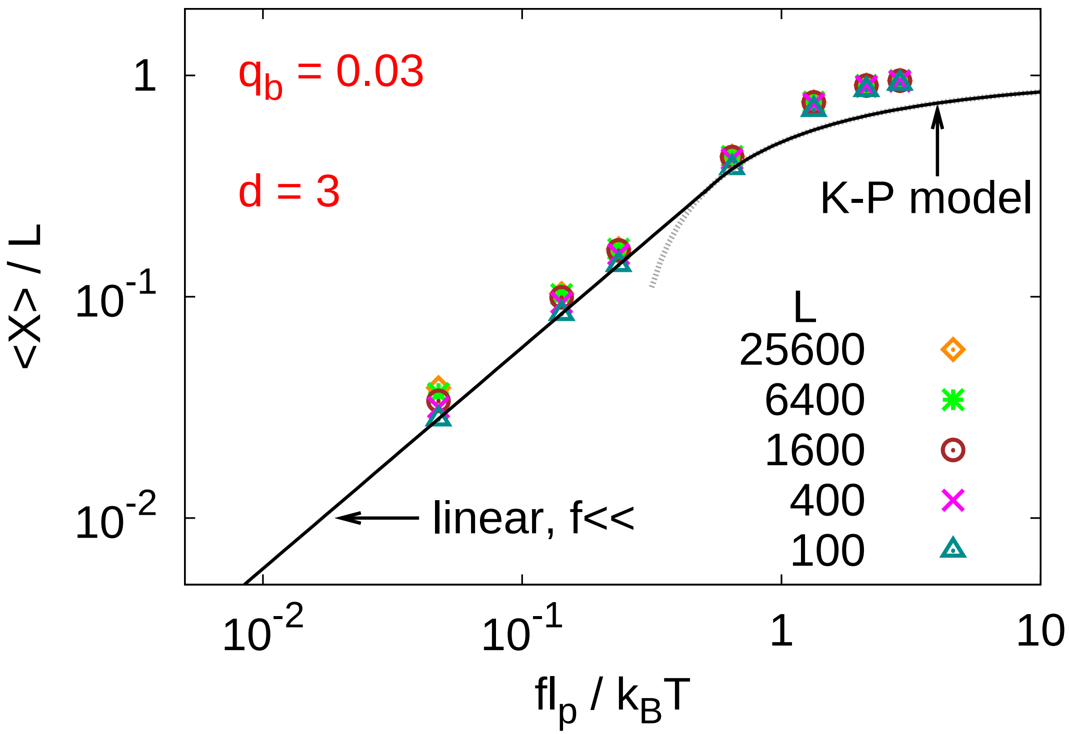

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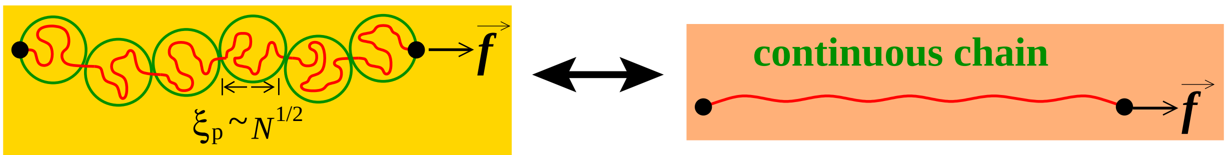

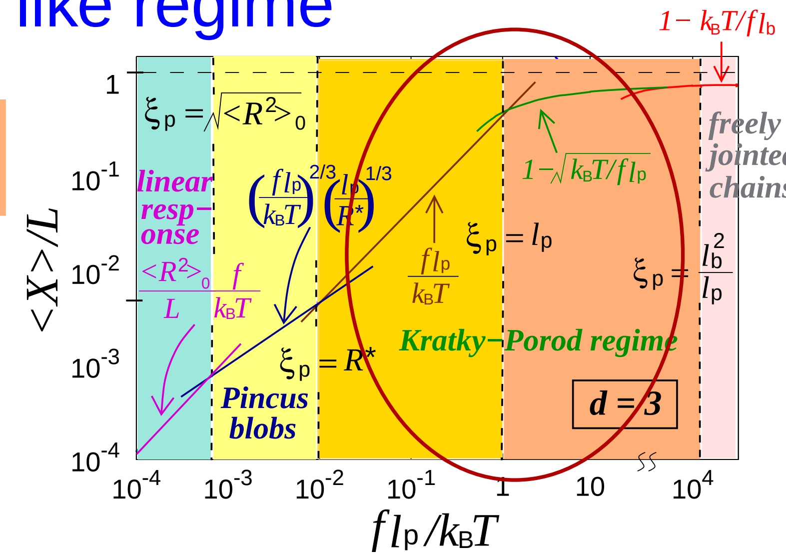

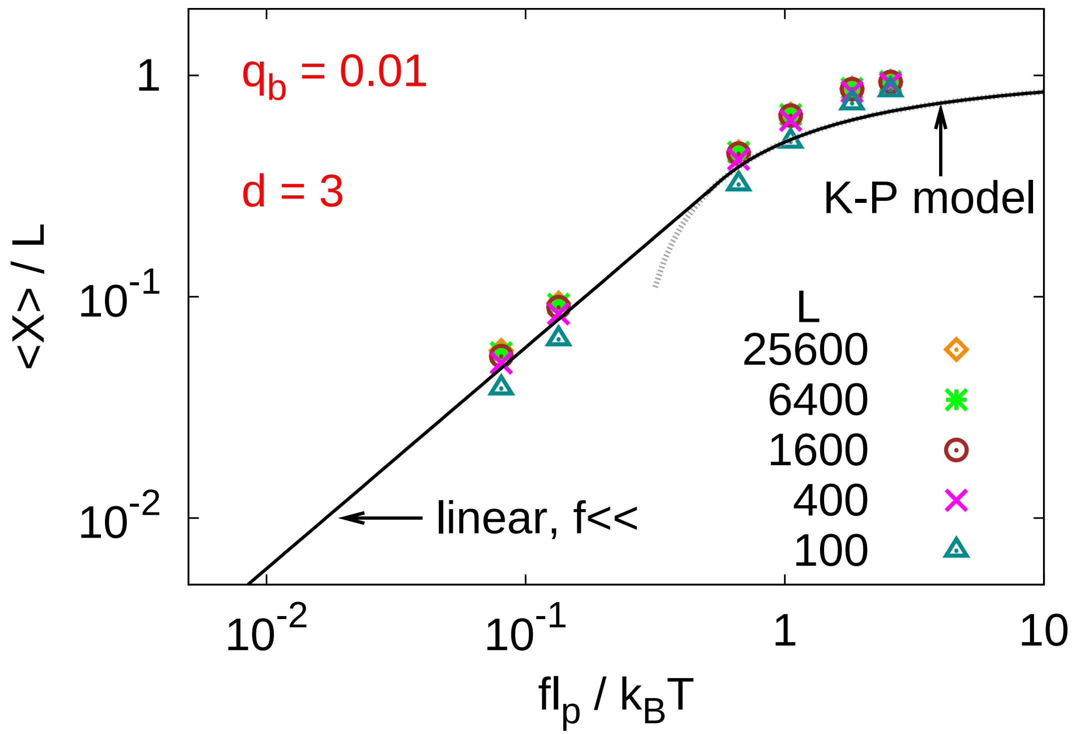

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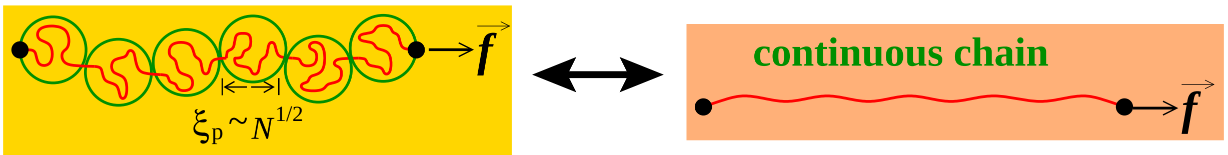

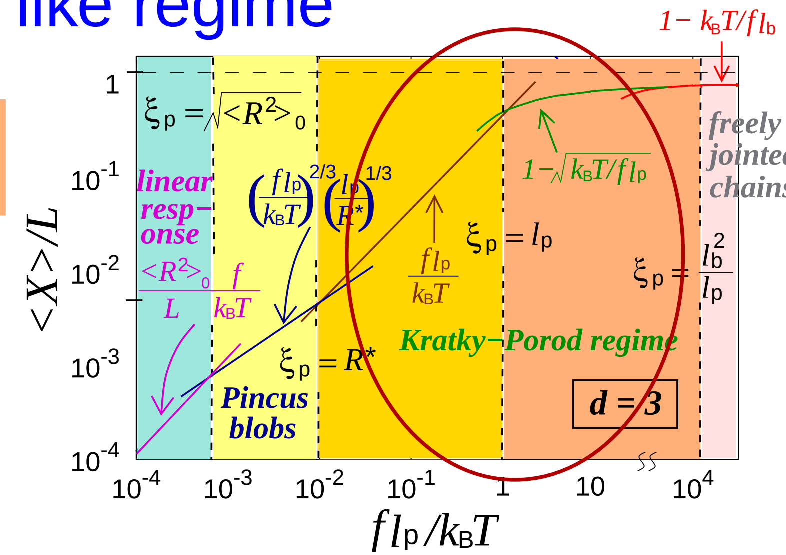

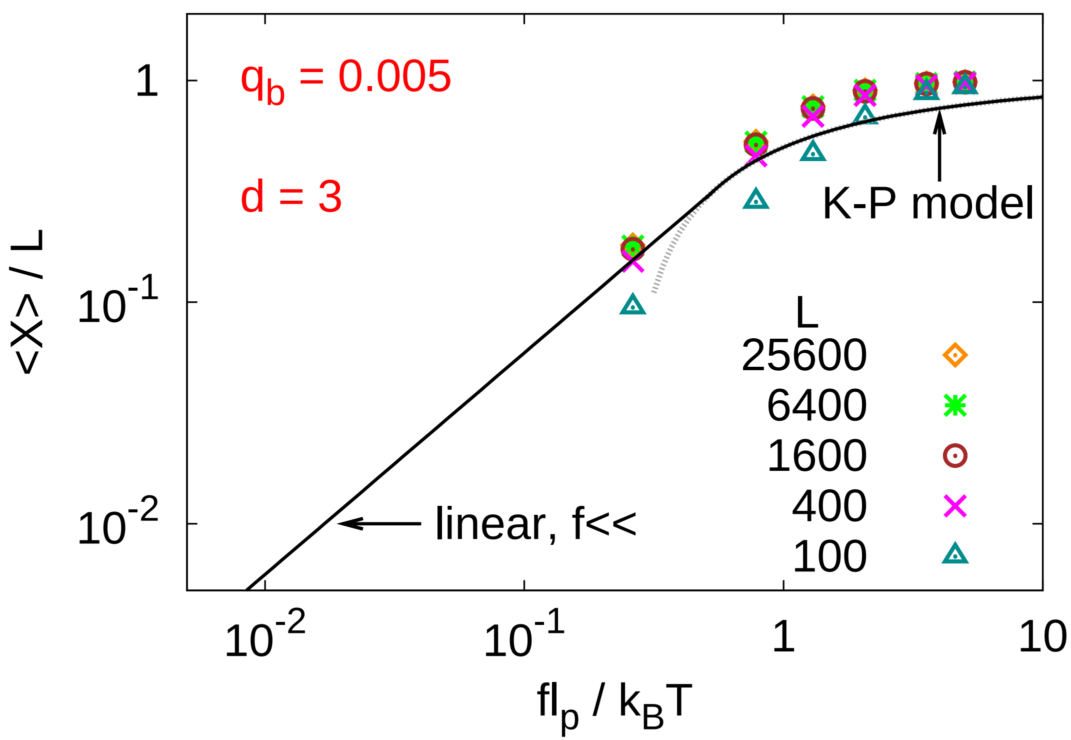

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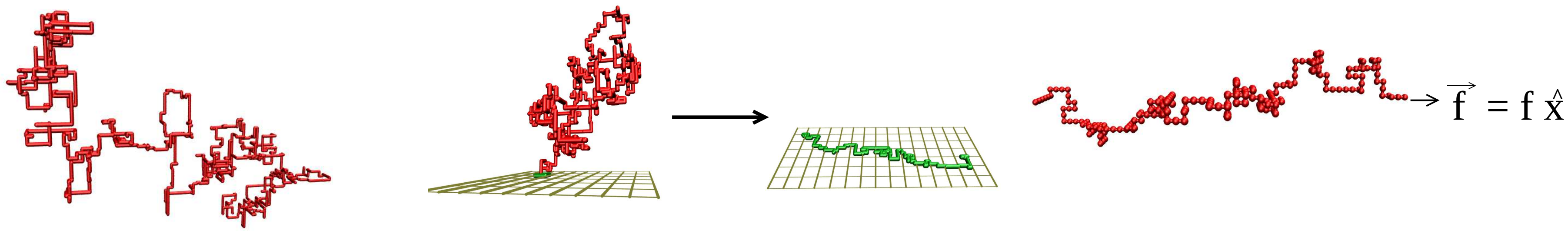
Summary



- Evidence for the importance of excluded volume effects
- Semiflexible polymer chains under good solvent conditions
  - The applicability of the Kratky-Porod model is tested
    breakdown in $d = 2$! (no intermediate Gaussian regime)
  - Theoretical predictions for the end-to-end distance R_e with using the Flory-like arguments are verified.
    - Rod-like - SAW (d=2)
    - Rod-like - Gaussian coils - SAW (d=3)

- Semiflexible chains adsorbed onto surface
  - Finite ℓ_p : simulation data $\Rightarrow$ continuous adsorption transition (critical adsorption energy $\epsilon/k_BT_c \sim 1/\ell_p$ for large ℓ_p)
  - In the rigid rod limit $\ell_p \to \infty$: adsorption transition is of 1st order
  - Much longer chain lengths $10^6 \leq N \leq 10^7$ are required
  - Theory for the analysis of crossovers is needed
- Stretching semiflexible polymer chains
  Theoretical predictions for the force-extension curves
  - linear response - Pincus blob - Kratky-Porod model - freely jointed chain