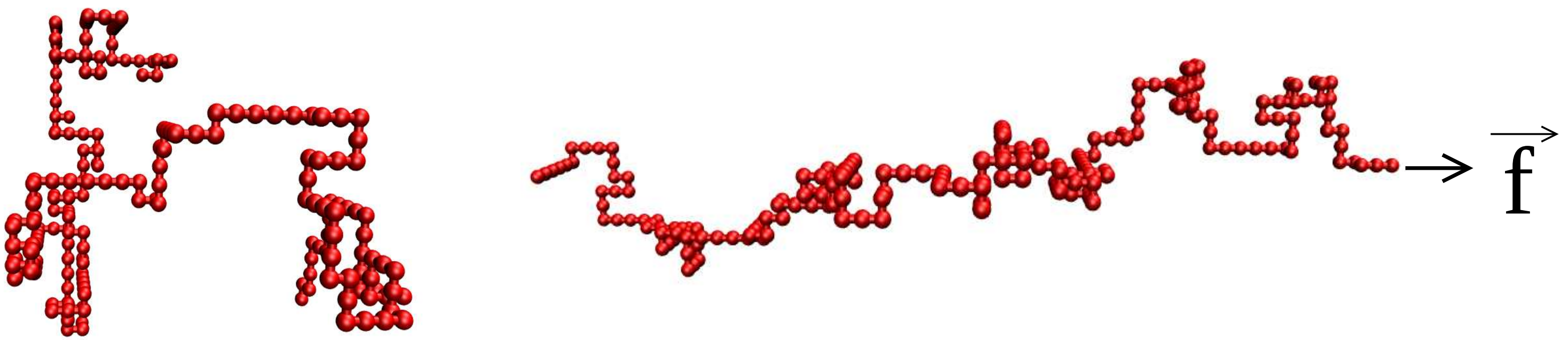
Scattering function of semiflexible polymer chains under good solvent conditions



Hsiao-Ping Hsu, Wolfgang Paul, and Kurt Binder

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Motivation

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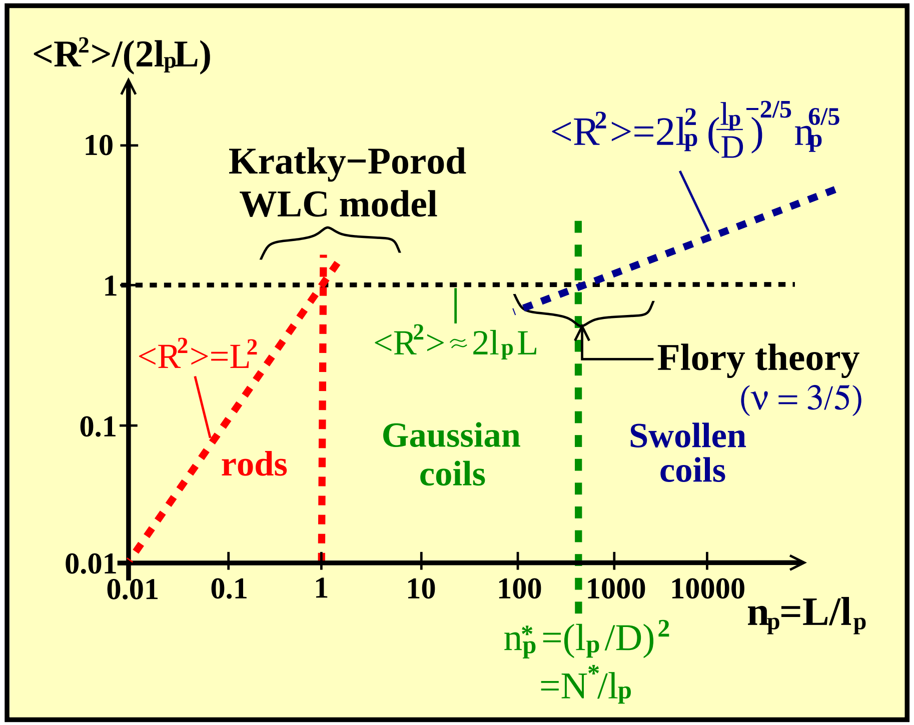
- Mean square end-to-end distance:



Hsu, Wolfgang, Binder

EPL 92, 28003 (2010)

JCP 136, 024901 (2012)

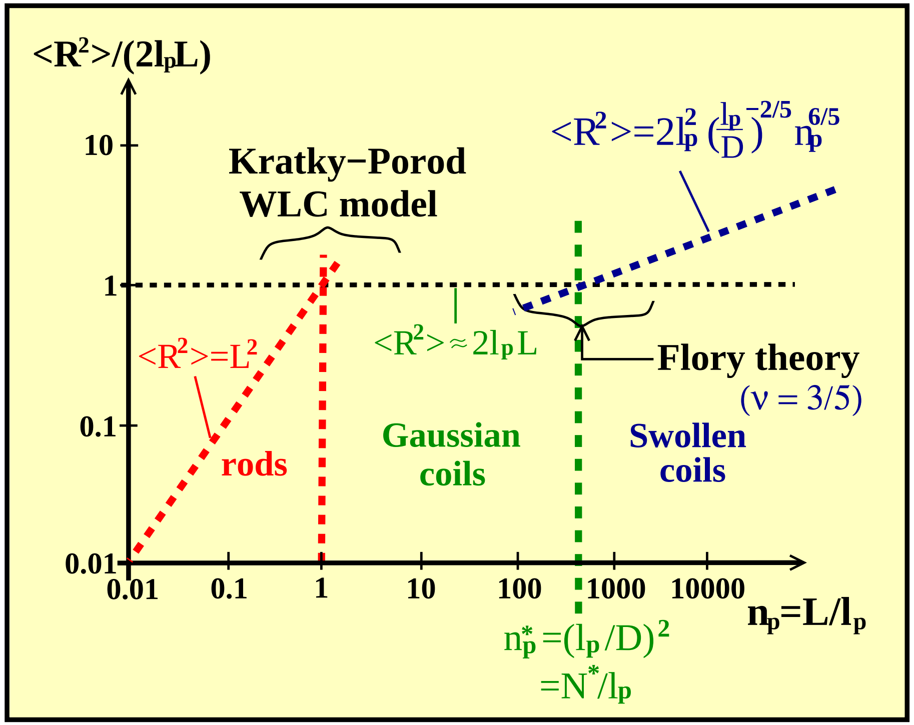
$L = N = n_p\ell_p = N$: contour length, ℓ_p: persistence length

D: effective thickness (cross-section diameter)

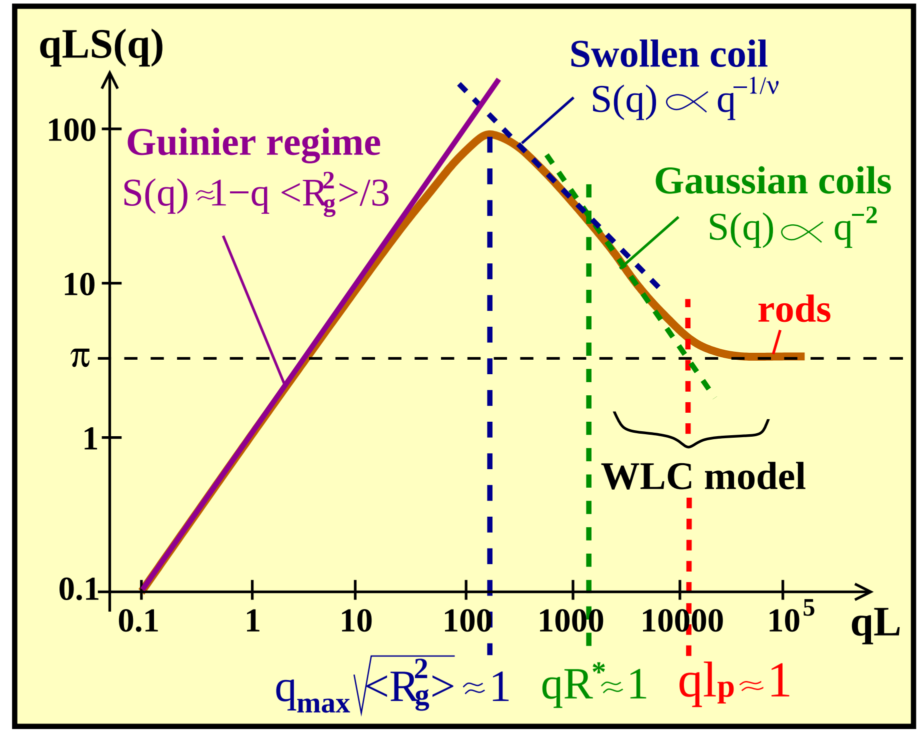
"=" strength of excluded volume interaction

Motivation

- Mean square end-to-end distance:



- Structure factor $S(q)$:



$L = N = n_p \ell_p = N$: contour length, ℓ_p: persistence length

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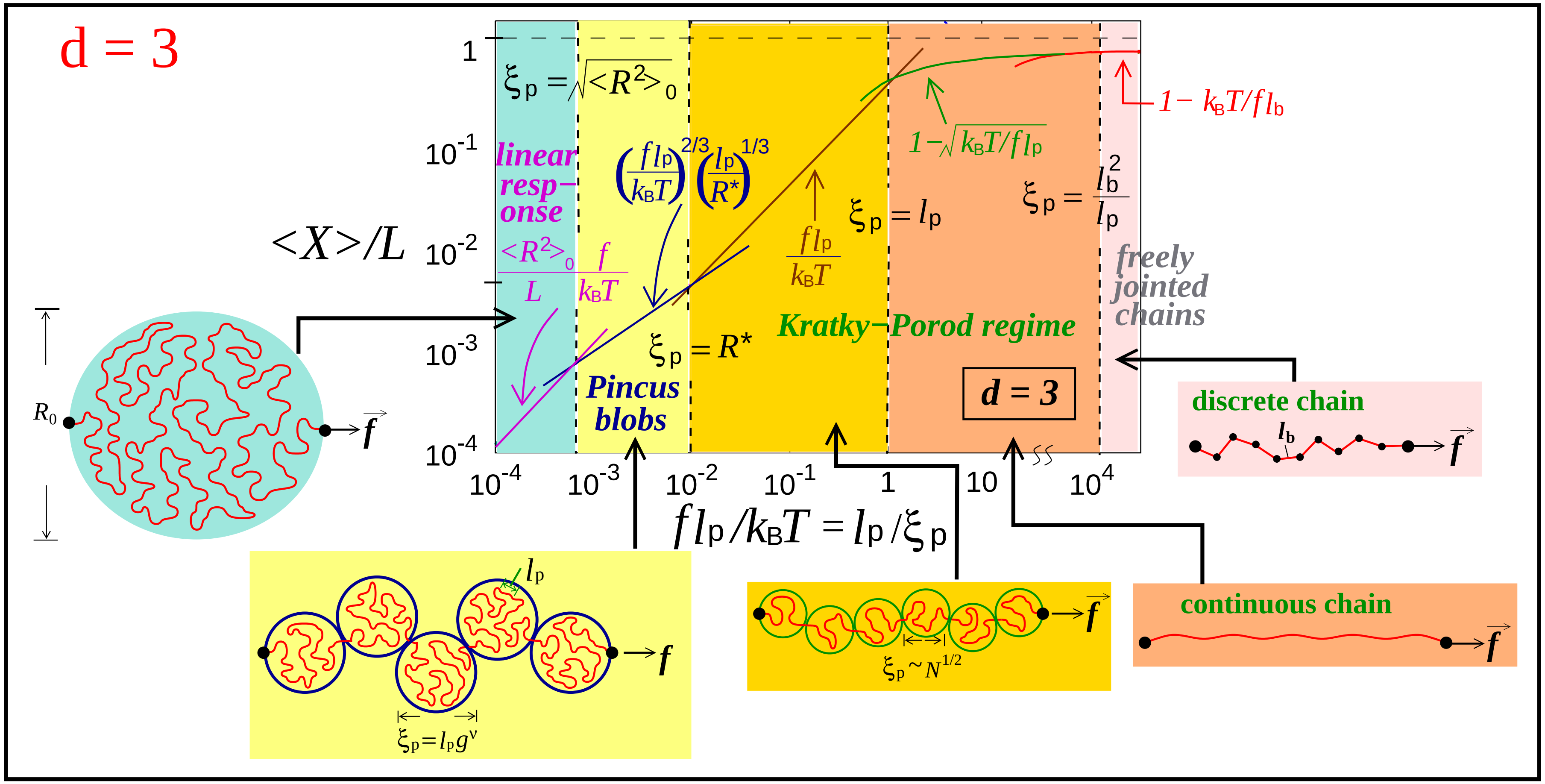
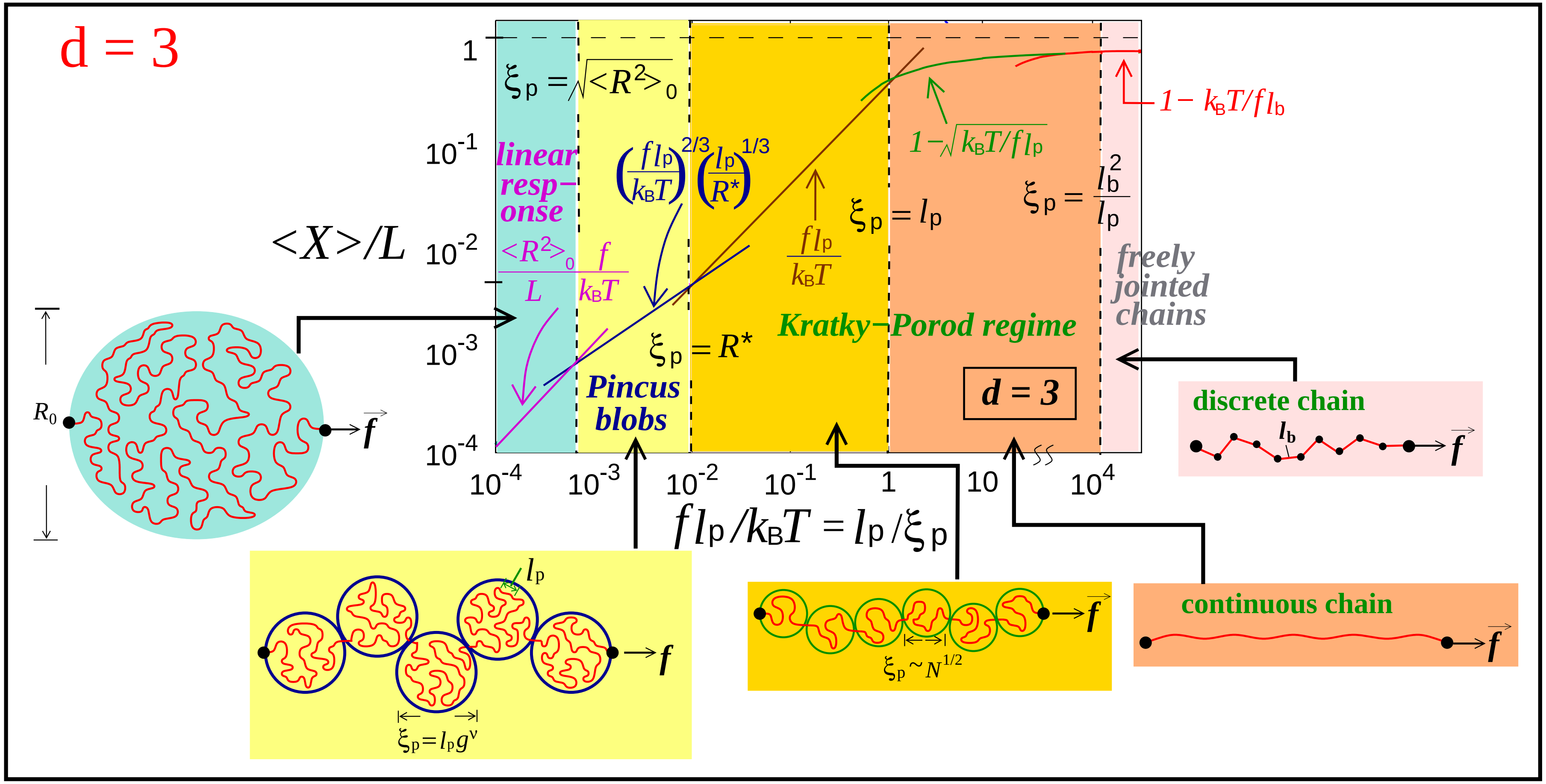
Force-extension curves:



$\boldsymbol{X}$: chain extension, $\boldsymbol{f}$: force, $\boldsymbol{\xi_p = k_B T / f}$: tensile length

Force-extension curves:



$\boldsymbol{X}$: chain extension, $\boldsymbol{f}$: force, $\boldsymbol{\xi_p = k_B T / f}$: tensile length

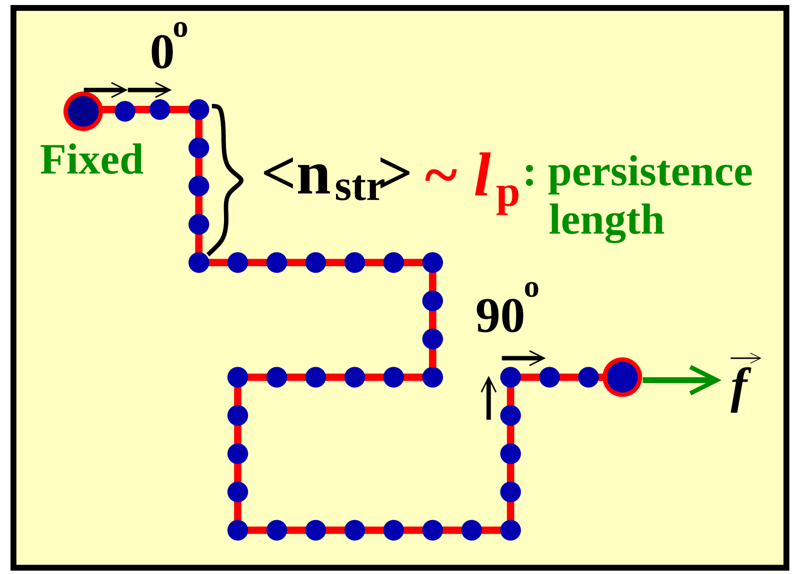
$\Rightarrow$ Structure of stretched semiflexible chains

Semiflexible SAW model

Self-avoiding walk model on the simple cubic lattice in $d =)$

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

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



- Stretching force $\vec{f} = f\hat{x}$
  $\Rightarrow$ deformation of chains

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

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

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

X: end-to-end distance along $+x$-direction ($X = x_{N_b} - x_0$)

- Algorithm: Pruned-Enriched Rosenbluth Method

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

Hsu & Grassberger, J. Stat. Phys. 144, 597 (2011), (review)

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

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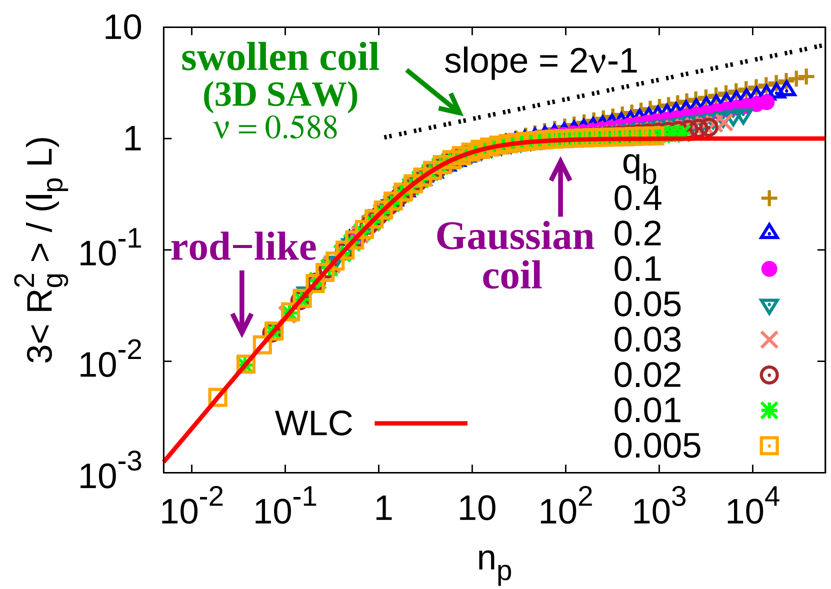
$$(L = N\ell_b = n_p \ell_p)$$

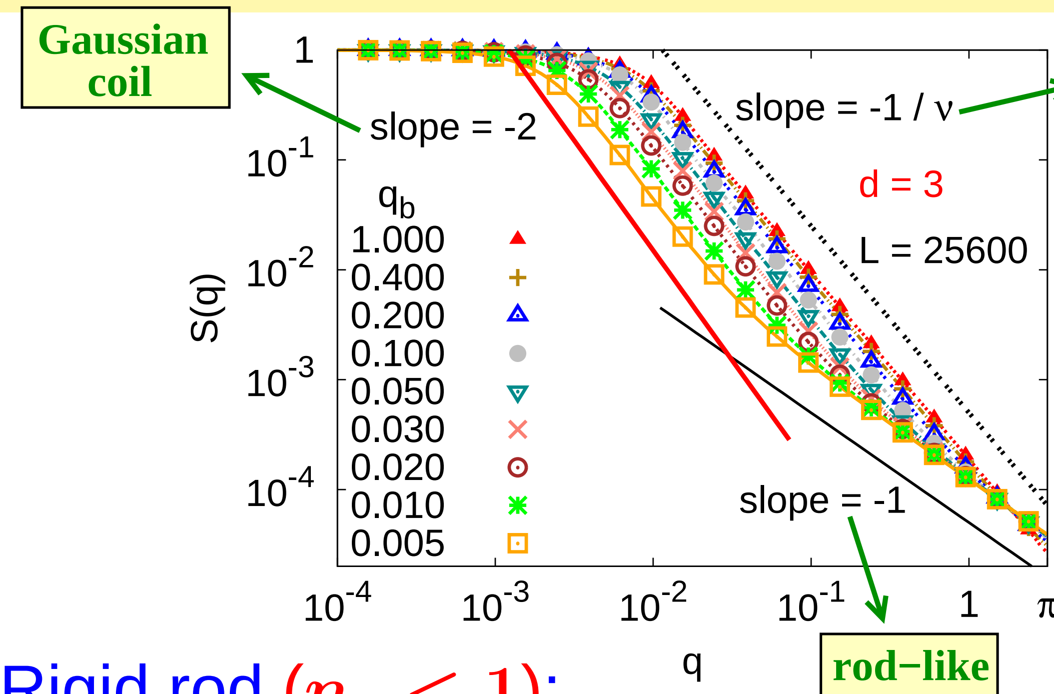
(stiff) $0.005 \leq q_b \leq 1.0$ (flexible)



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

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

Simulation vs. Theory



$L = n_p \ell_p$

L: contour length

ℓ_p: persistence length

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

- Rigid rod $(n_p < 1)$:

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

- 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:

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

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

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

- Approximation by Kholodenko:

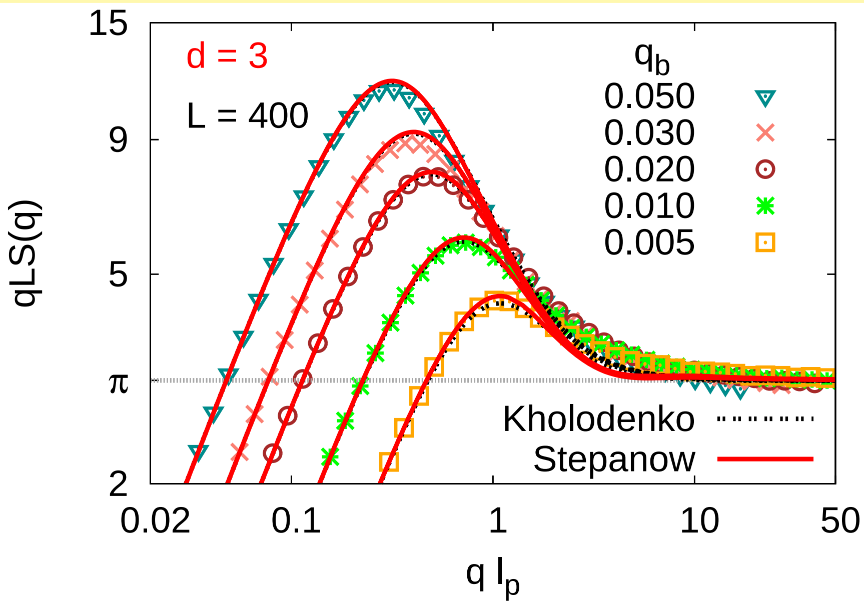
$$S(q) = \frac{2}{x}\left[I_1(x) - \frac{1}{x}I_2(x)\right]\,, \quad x = 3L/2\ell_p\,,$$

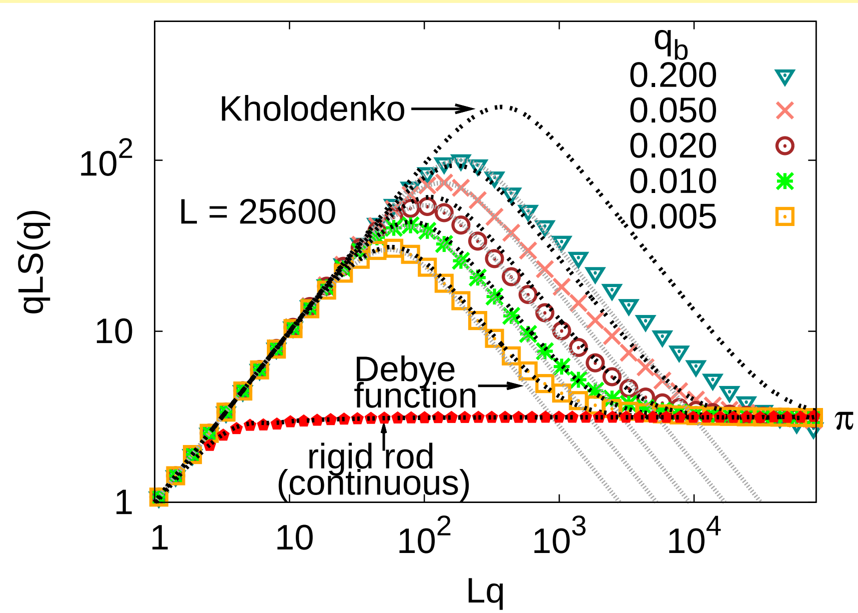
$$I_n(x) = \int_0^x dz\, z^{n-1} f(z)\,, \quad f(z) = \begin{cases} \frac{1}{E}\frac{\sinh(Ez)}{\sinh z}\,, & q \leq 3/2\ell_p \\ \frac{1}{E'}\frac{\sin(E'z)}{\sinh z}\,, & q > 3/2\ell_p \end{cases}$$

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

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

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





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

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

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

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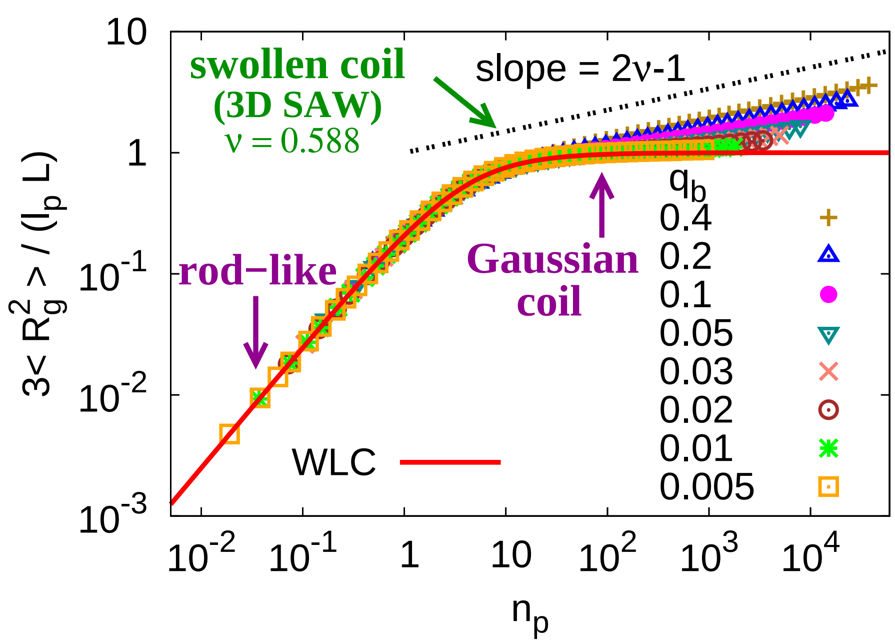
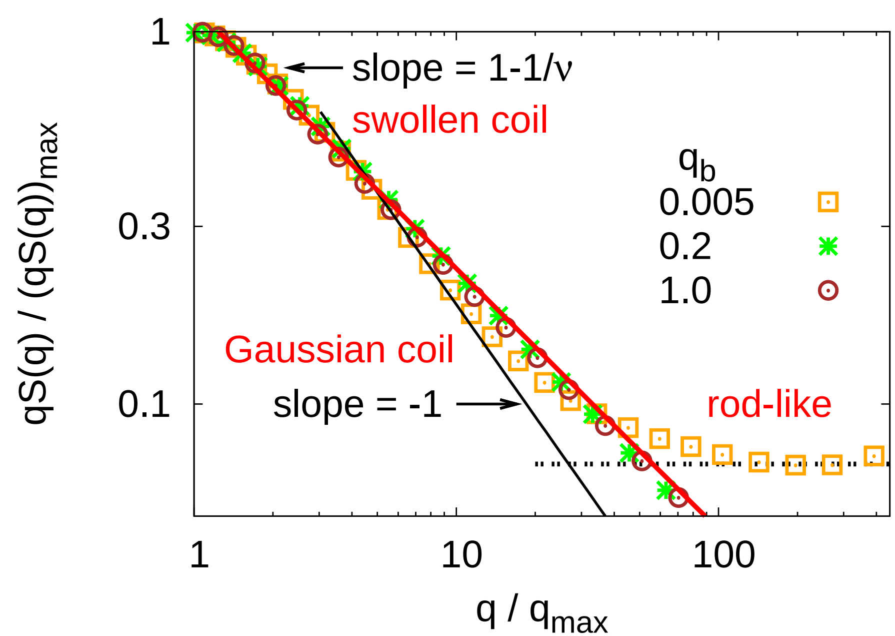
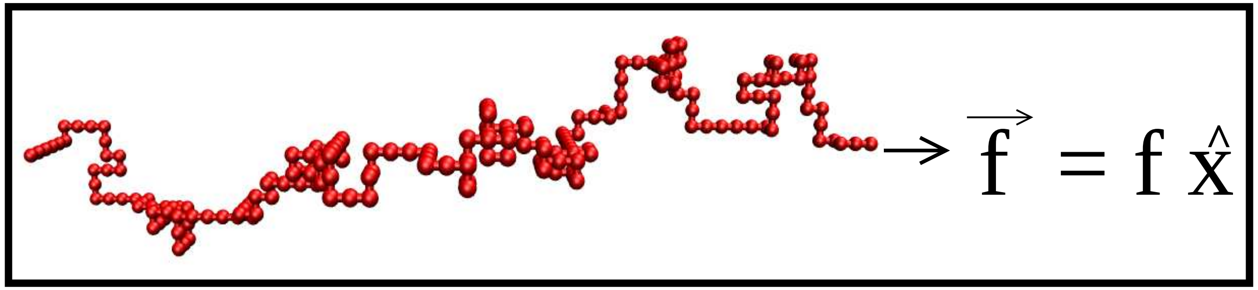
Crossover behavior: $\langle R_g^2 \rangle$, $S(q)$

- 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





Stretched semiflexible chains



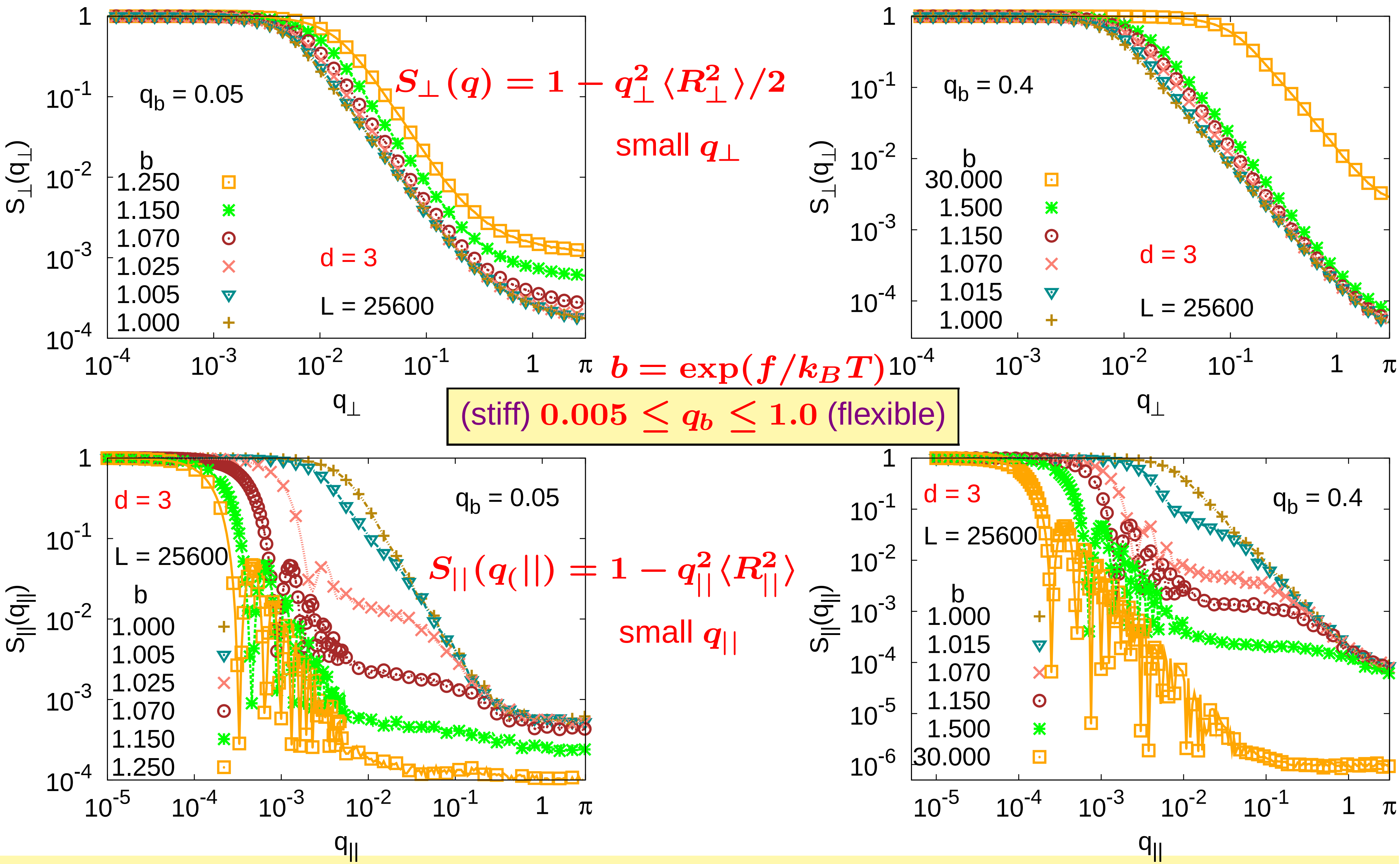
- Structure factor $S(q) \Rightarrow S_{||}(q_{||}),\ S_{\perp}(q_{\perp})$

$$S_{||}(q_{||}) = \frac{1}{(N+1)^2}\left\{ \langle \left[\sum_{j=1}^{N+1} \sin(q_{||} x_j) \right]^2 \rangle + \langle \left[\sum_{j=1}^{N+1} \cos(q_{||} x_j) \right]^2 \rangle \right\}$$

$$S_{\perp}(q_{\perp}) = \frac{1}{(N+1)^2}\left\{ \langle \left[\sum_{j=1}^{N+1} \sin(q_{\perp} \cdot \vec{\rho}_j) \right]^2 \rangle + \langle \left[\sum_{j=1}^{N+1} \cos(q_{\perp} \cdot \vec{\rho}_j) \right]^2 \rangle \right\}$$

$$\vec{r}_j = (x_j, y_j, z_j) = (x_j, \vec{\rho}_j)$$

Structure factors $S_{||}(q_{||}), S_\perp(q_\perp)$

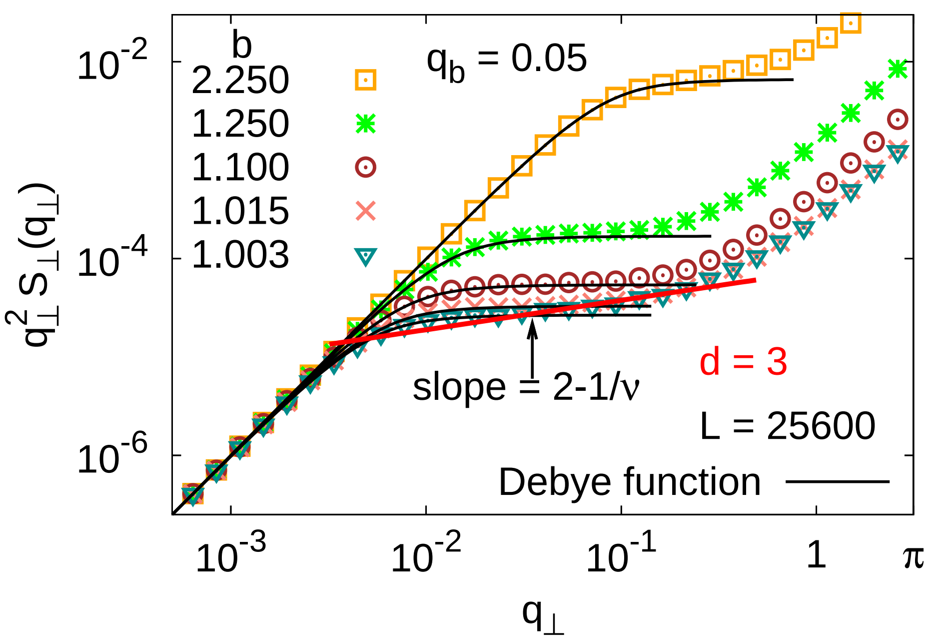


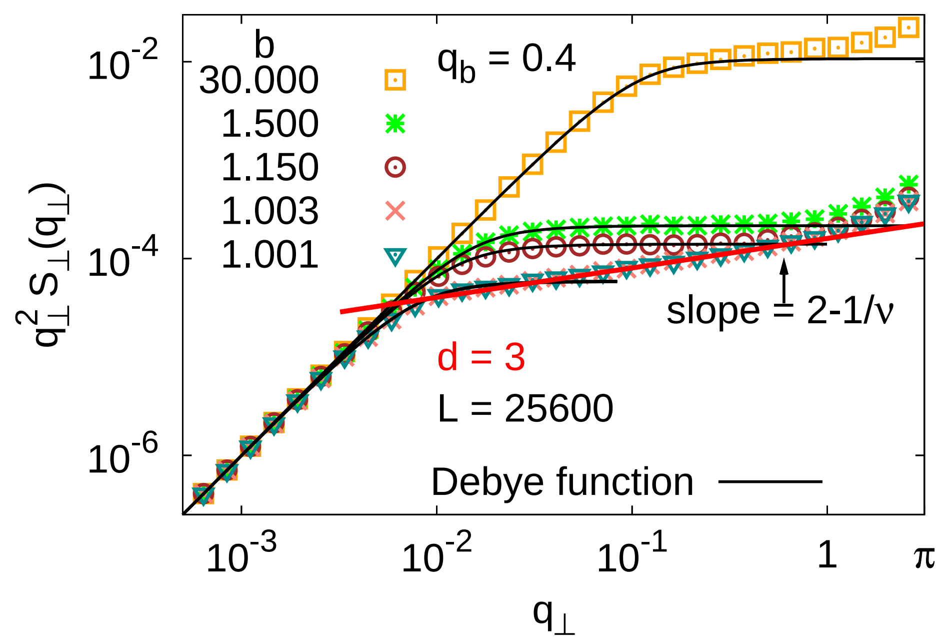
$q_\perp^2 S_\perp(q_\perp)$ vs. $q_\perp$

- Gaussian chains under stretch $\vec{f} = f\hat{x}$: $q_\perp = \sqrt{q_y^2 + q_z^2}$

$$S_\perp^{\rm Debye}(q_\perp) = 2\frac{\exp(-X_\perp) - 1 + X_\perp}{X_\perp^2}\,, \quad X_\perp = \frac{3}{2} q_\perp^2 \langle R_{g,\perp}^2 \rangle$$

$q^2 S(q) \approx 4/(3\langle R_{g,\perp}^2\rangle)$ as $q \gg 1$



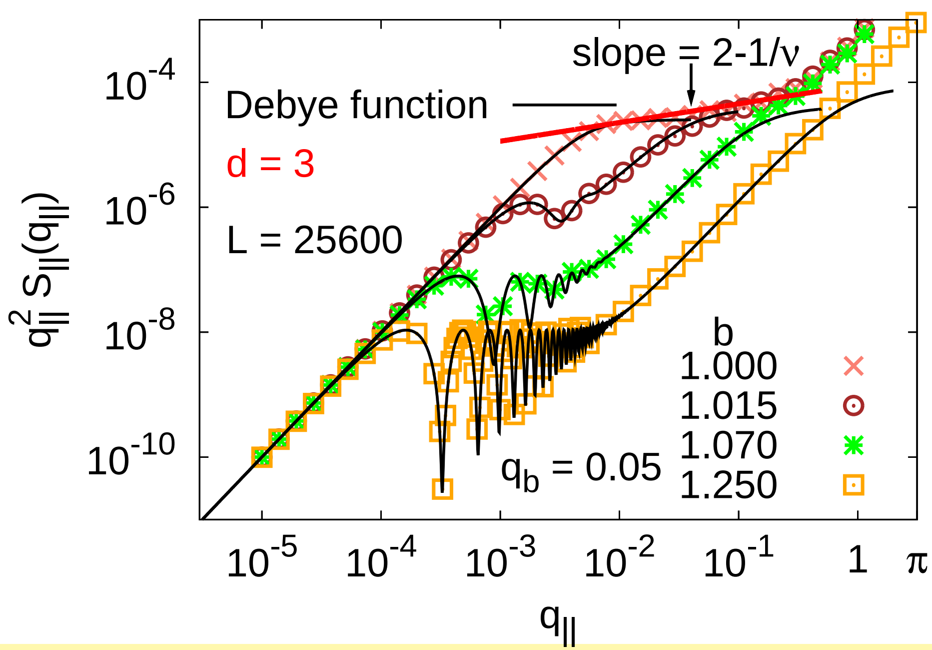


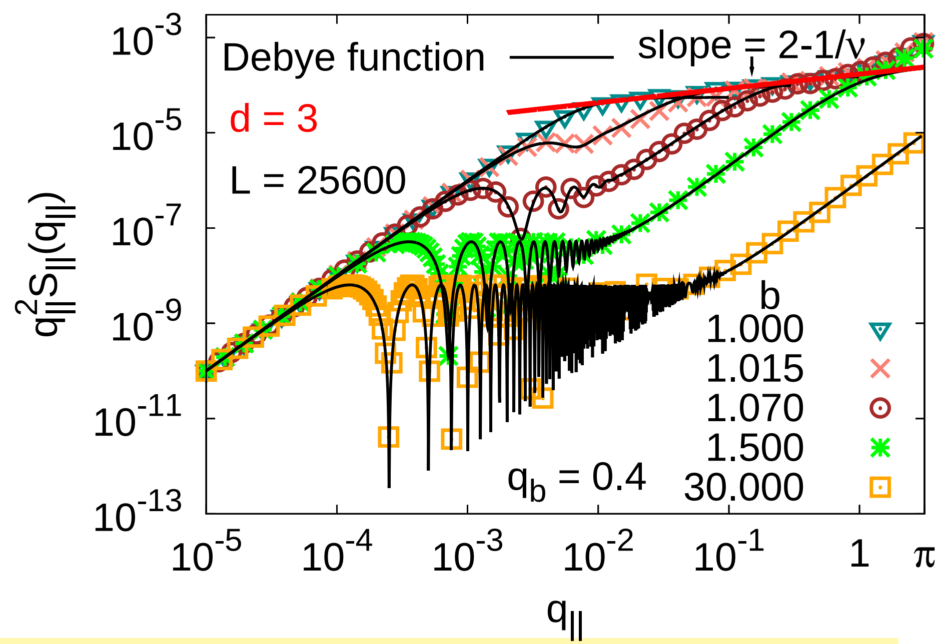
$q_{||}^2 S_{||}(q)$ vs. $q_{||}$

- Gaussian chains under stretch $\vec{f} = f\hat{x}$: $\quad q_{||} = q_x$

$$S_{||}^{\text{Debye}}(q_{||}) = 2Re\left\{\frac{\exp(-X_{||}) - 1 + X_{||}}{X_{||}^2}\right\}, X_{||} = q_{||}^2\frac{\langle X^2\rangle - \langle X\rangle^2}{2} + iq_{||}\langle X\rangle$$

$$q_{||}^2 S_{||}^{\max}(q_{||}) \approx \frac{4}{\langle X\rangle^2}, \qquad q_{||}\langle X\rangle = (2m+1)\pi\,, \;\; m = 0, 1, \ldots,$$





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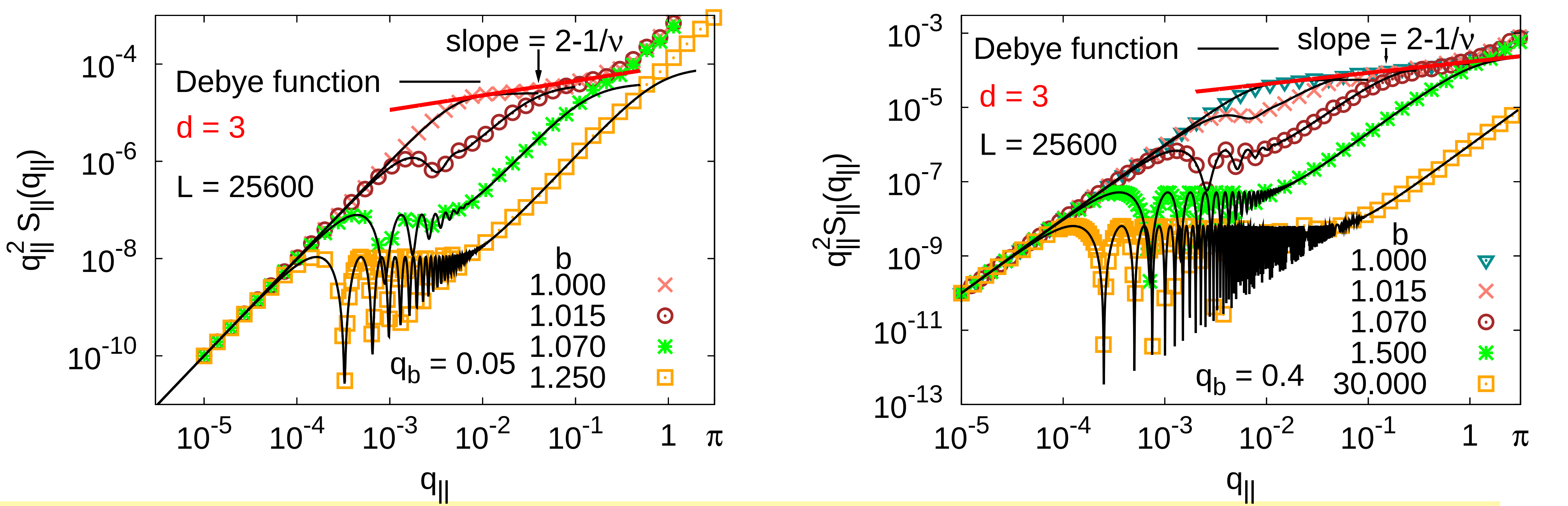
"=" a harmonic one-dimensional “crystal” of length $Na = \langle X\rangle$



Conclusions

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- Unstretched semiflexible chains
  - Theoretically predicted crossover behavior for the mean square gyration radius $\langle R_g^2 \rangle$ and the structure factor $S(q)$ are verified
  - The applicability of the Kratky-Porod worm-like chain model to describe the structure factor $S(q)$ is tested
- Stretched semiflexible chains
  - The anisotropy of the structure factor $(S_\perp(q_\perp))$, $S_{||}(q_{||}))$ is well described by the modified Debye function
  - The oscillatory behavior of $S_{||}(q_{||}) \Rightarrow$ a string of elastically coupled particles

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