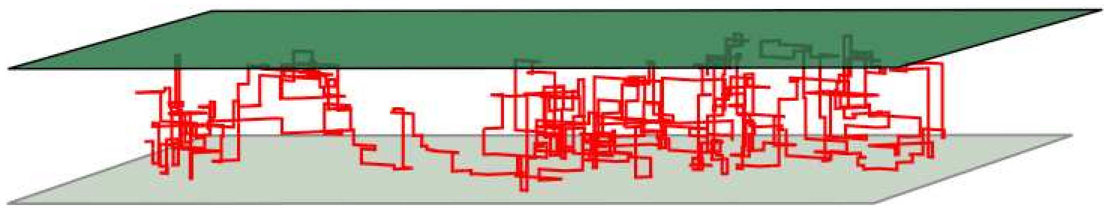
Confined semiflexible chains in a good solvent: A Monte Carlo test of scaling concepts



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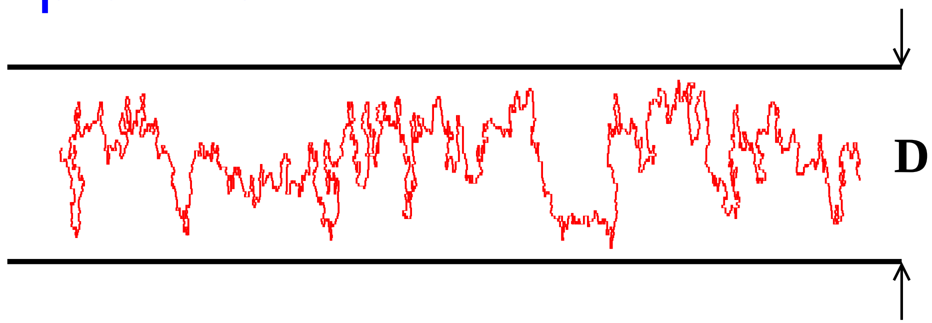
Polymers in confining geometries

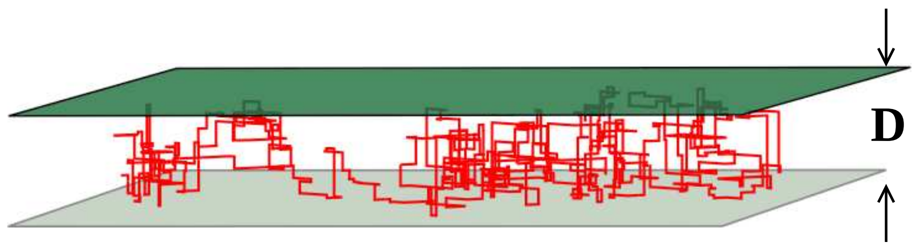
- A strip of width D:



(nanoslit)

$d = 2 \longrightarrow d = 1$

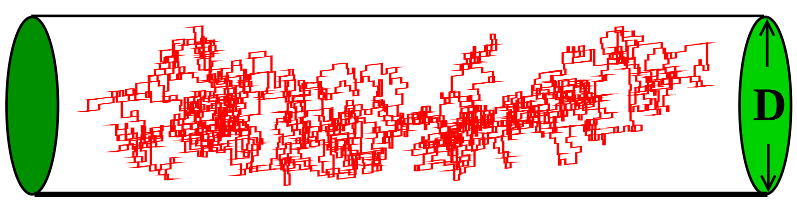
- Two parallel hard walls separated by a distance D:



(nanoslit)

$d = 3 \longrightarrow d = 2$

- A tube of diameter D:



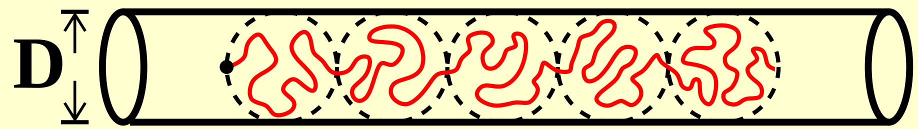
(nanochannel)

$d = 3 \longrightarrow d = 1$

Theoretical predictions (flexible $\longrightarrow$ stiff)

Daoud – de Gennes regime:

J. Phys. (Paris) 38, 85 (1977)



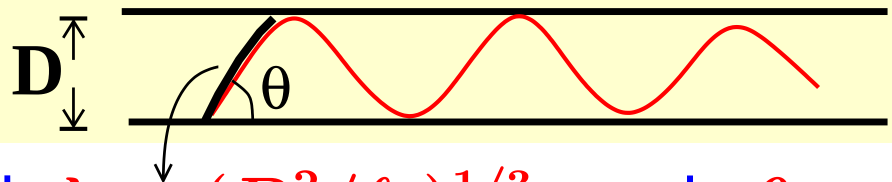
$D >> l_p$

free energy: $\Delta F/k_BT = D^{-5/3}\ell_p^{1/3}$ ℓ_p: persistence length

end-to-end distance: $R_{||} = L\ell_p^{1/3}D^{-2/3}$

Odijk regime:

Macromolecules, 16, 1340 (1983)



$D < l_p$

deflection length $\lambda = (D^2/\ell_p)^{1/3}$, angle $\theta \approx D/\lambda \approx (D/\ell_p)^{1/3}$

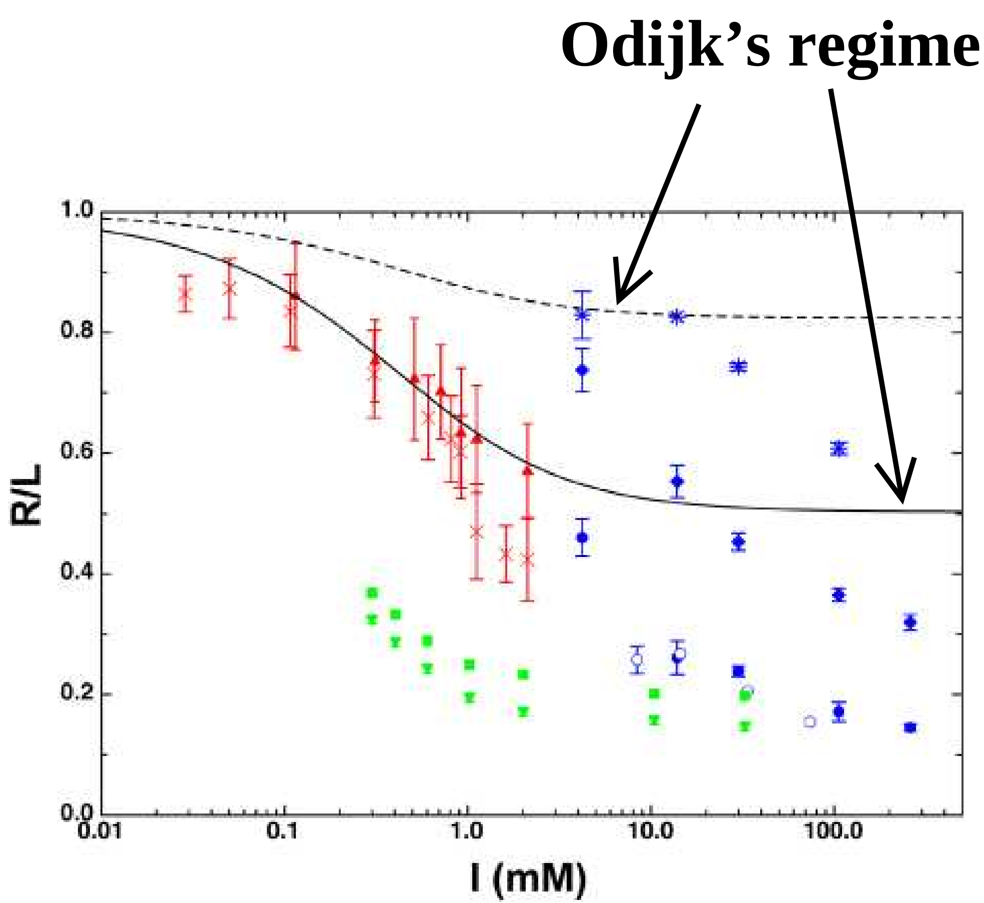
The Kratky-Porod model: $\mathcal{H}_{KP}\{\vec{r}(s)\} = \frac{k}{2}\int_0^L ds \left(\frac{\partial^2 \vec{r}}{\partial s^2}\right)^2$

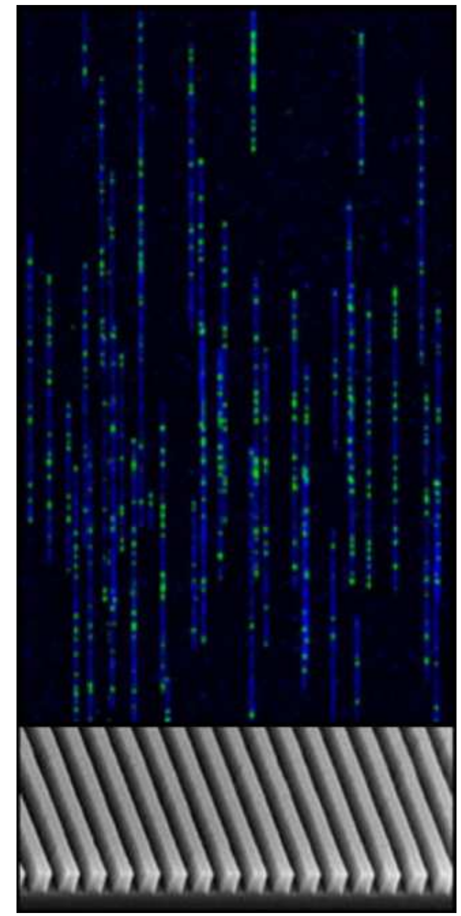
$\Rightarrow$ free energy: $\Delta F/k_BT \sim L/\ell_p^{1/3}D^{2/3}$, $L \geq \ell_p$

end-to-end distance: $R_{||} = L\cos(\theta) = L(1 - A(D/\ell_p)^{2/3})$

DNA confined in nanochannel (Exp)

- Extension R/L vs. ionic-strength I



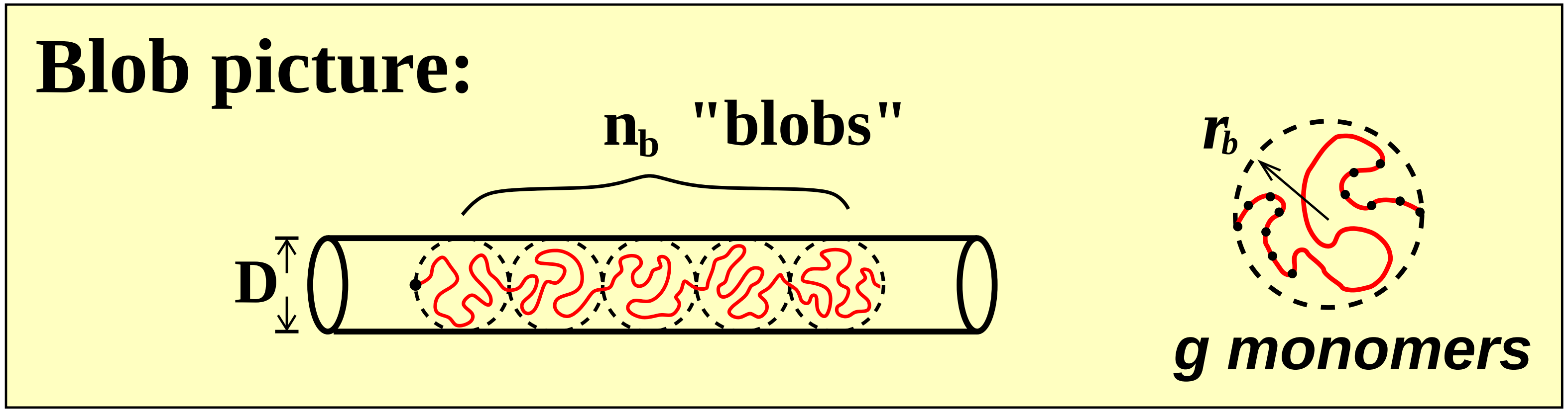


DNA confined in imprinted nanochannel arrays

Reisner et al. Rep. Prog. 75, 106601 (2012)

Daoud - de Gennes blob theory

- Flexible polymer chains of size N confined in a tube



- Total number of monomers: $N = g n_b$ ℓ_b: bond length
- End-to-end distance: $R_{||} = n_b(2r_b) = n_b D$ || tube

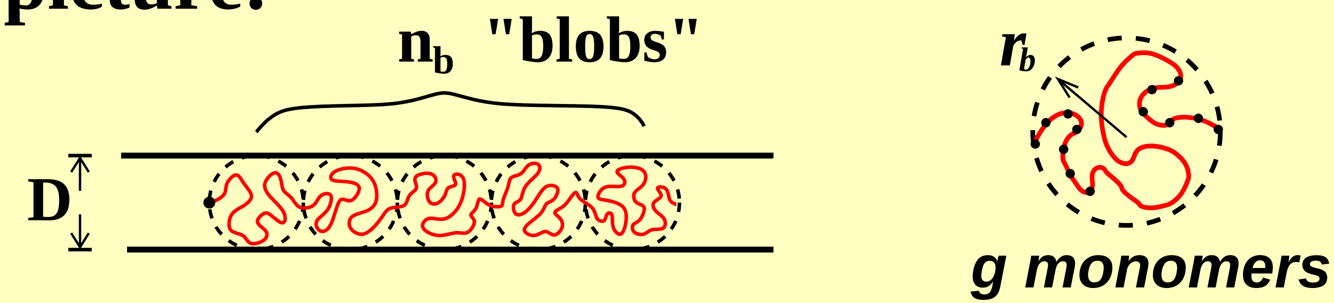
  within a blob, $D = \ell_b g^\nu = 2r_b$, $\nu = 3/5$ (Flory, 3DSAW)

  $\Rightarrow R_{||} = N\ell_b(D/\ell_b)^{1-1/\nu}$
- Free energy: $\Delta F = n_b[k_B T] = N/g = N(D/\ell_b)^{-1/\nu}$

Daoud - de Gennes blob theory

- Flexible polymer chains of size N confined in a strip

Blob picture:



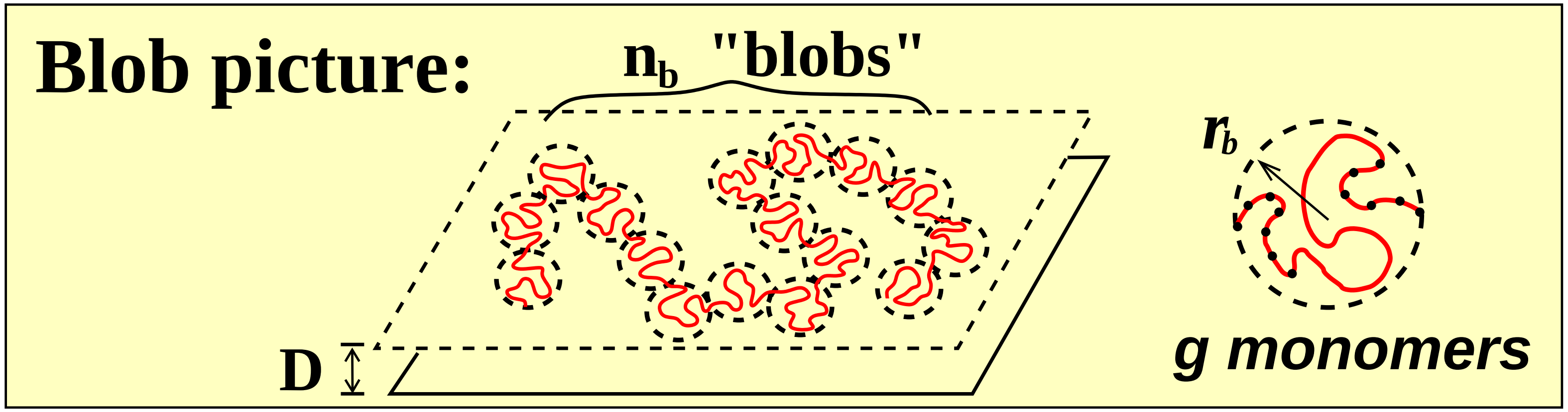
- Total number of monomers: $N = g n_b$ $\qquad \ell_b$: bond length
- End-to-end distance: $R_{||} = n_b(2r_b) = n_b D$ $\qquad$ || strip

  within a blob, $D = \ell_b g^{\nu} = 2r_b \;,\;\; \nu = 3/4$ (Flory, 2DSAW)

  $\Rightarrow R_{||} = N\ell_b (D/\ell_b)^{1-1/\nu}$
- Free energy: $\Delta F = n_b[k_B T] = N/g = N(D/\ell_b)^{-1/\nu}$

Daoud - de Gennes blob theory

- Flexible polymer chains of size N confined in a slit



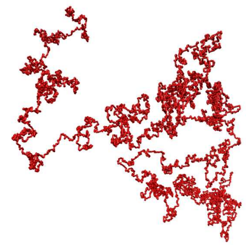
- Total number of monomers: $N = gn_b$ ℓ_b: bond length
- End-to-end distance: $R_{||} = n_b(2r_b) = n_b{}^{3/4}D$ || walls

  within a blob, $D = \ell_b g^\nu = 2r_b$, $\nu = 3/5$ (Flory, 3DSAW)

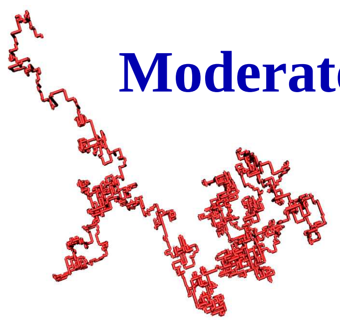
  $\Rightarrow R_{||} = N^{3/4}\ell_b(D/\ell_b)^{1-3/4\nu} \approx \ell_b N^{3/4}(D/\ell_b)^{-1/4}$
- Free energy: $\delta F = n_b[k_B T] = N/g = N(D/\ell_b)^{-1/\nu}$

Snapshots of 3D semiflexible chains

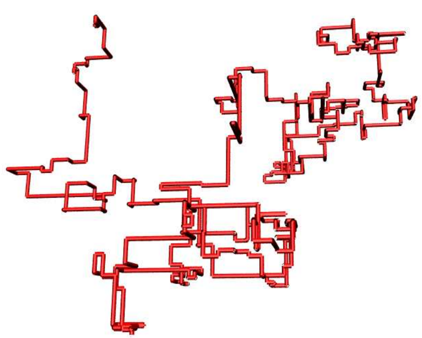
Flexible chain, $q_b = 0.4$



Moderately stiff chain, $q_b = 0.05$



Stiff chain, $q_b = 0.005$



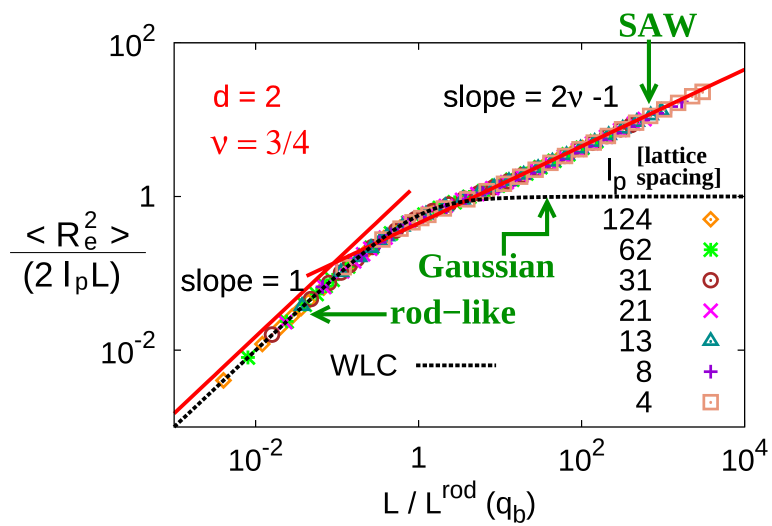
q_b	l_p [lattice spacing]	
0.4	**1.13**	**flexible**
0.2	2.05	↑
0.1	3.35	
0.05	**5.96**	
0.03	9.54	
0.02	13.93	
0.01	26.87	↓
0.005	**52.61**	**stiff**

- q_b: bending factor
- ℓ_p: persistence length
- L: contour length, $L = N\ell_b$

$\ell_p\,, L \leftrightarrow D$ (confinement constraint) ?

Semiflexible chains in bulk

- Single crossover (rod-like - SAW) in $d = 2$:

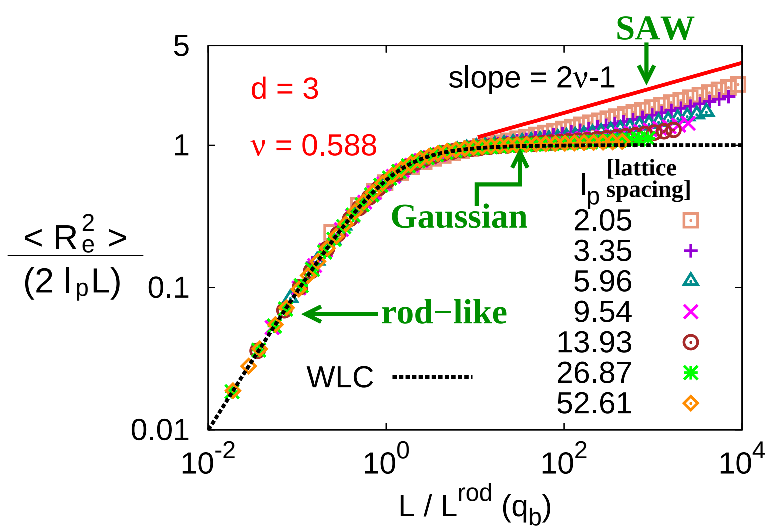


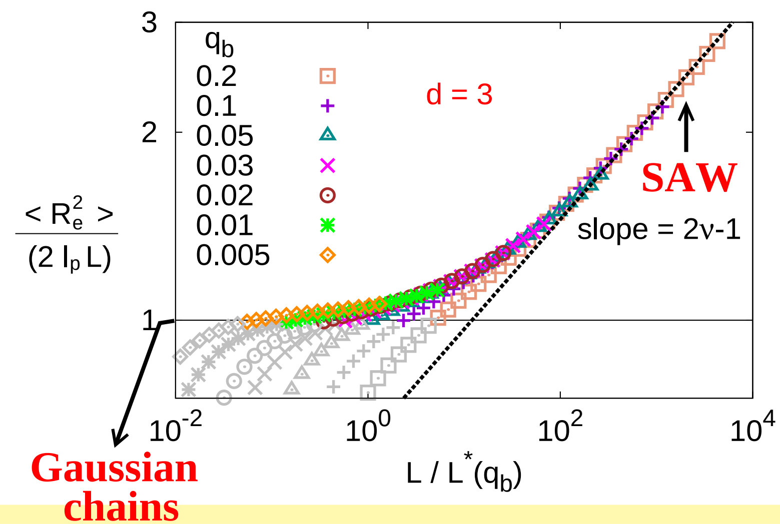
theoretical predictions:

$$L^{\text{rod}} = \ell_p$$

$$L^* = \ell_P^3/\ell_b^2$$

- Double crossover (rod-like - Gaussian - SAW) in $d = 3$:





Semiflexible SAW model with PERM

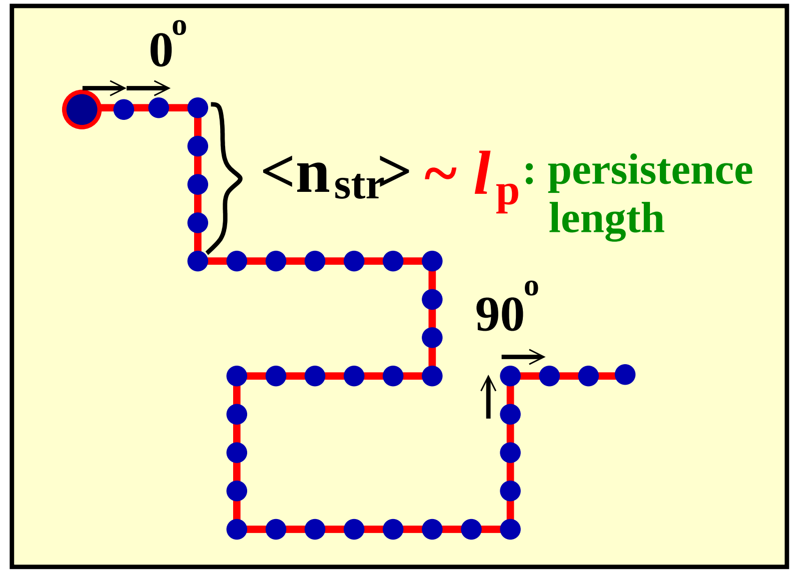
A semiflexible polymer chain in a good solvent

- Excluded volume effect $\Rightarrow$ Self-avoiding walk (SAW)
- Chain stiffness

  $\Rightarrow$ Bond-bending potential

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

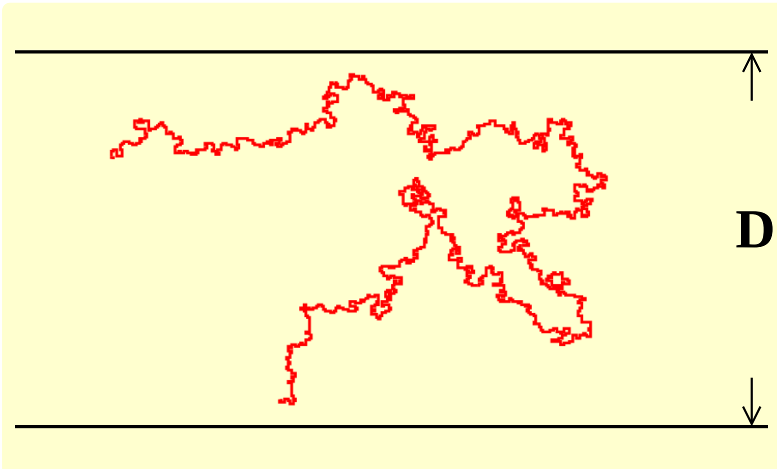
  bending energy $\epsilon_b \uparrow$, stiffness $\uparrow$



- Partition sum: $Z_{N,N_{\text{bend}}} = \sum_{config.} C_{N,N_{\text{bend}}} q_b^{N_{\text{bend}}}$

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

Flexible chains confined in a strip

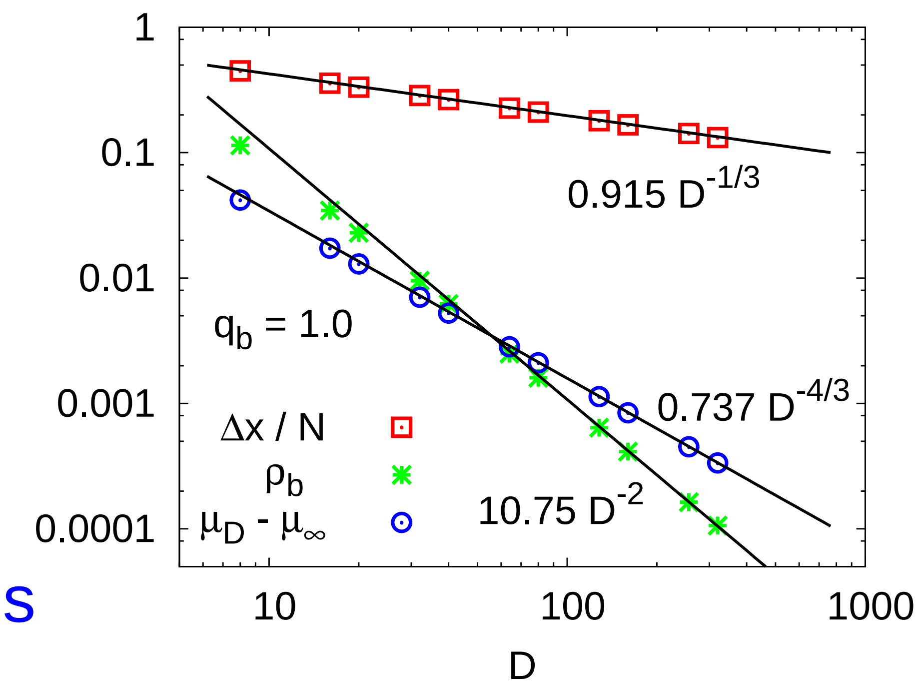


strip width: $8 \leq D \leq 320$

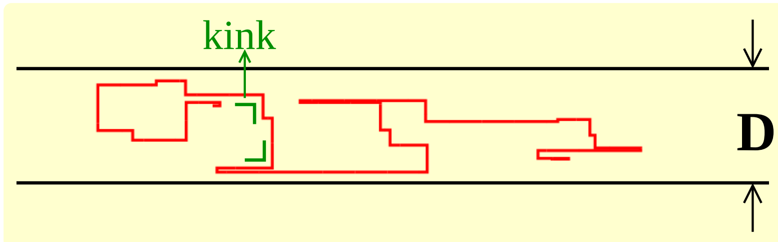
chain length: $N \leq 128\,000$

Hsu & Grassberger, Eur. Phys. J. B 36, 209 (2003)

- Scaling predictions:
  - Fugacity per monomer
    $\mu_D - \mu_\infty \approx 0.737 D^{-4/3}$
  - End-to-end distance
    $\langle \Delta x \rangle / N \approx 0.915 D^{-1/3}$
  - Monomer density on the walls
    $\rho_b \approx 10.75 D^{-2}$



Semiflexible chains confined in a strip



strip width: $8 \leq D \leq 320$

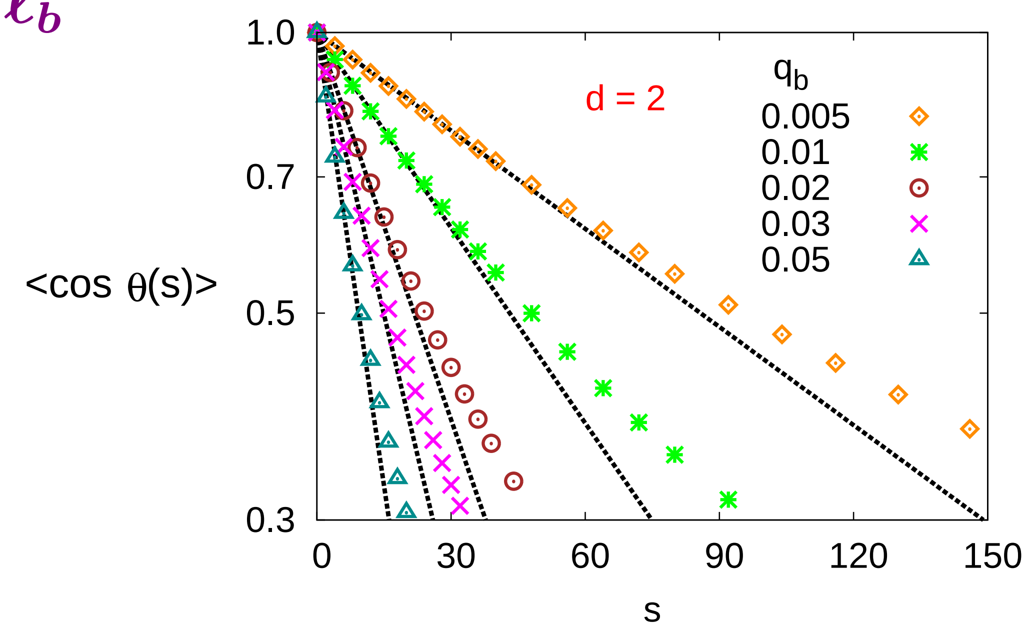
chain length: $N \leq 128\,000$

effective persistence length: $\ell_p(D)$

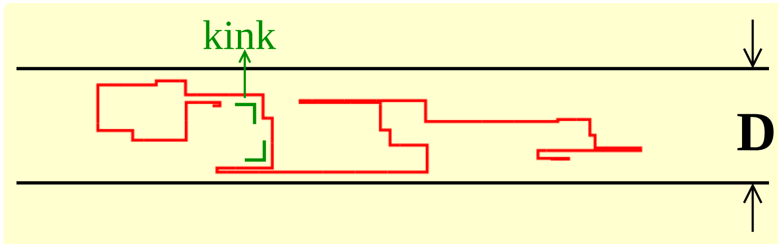
- Bond orientational correlation function:

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

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**



Semiflexible chains confined in a strip



strip width: $8 \leq D \leq 320$

chain length: $N \leq 128\,000$

effective persistence length: $\ell_p(D)$

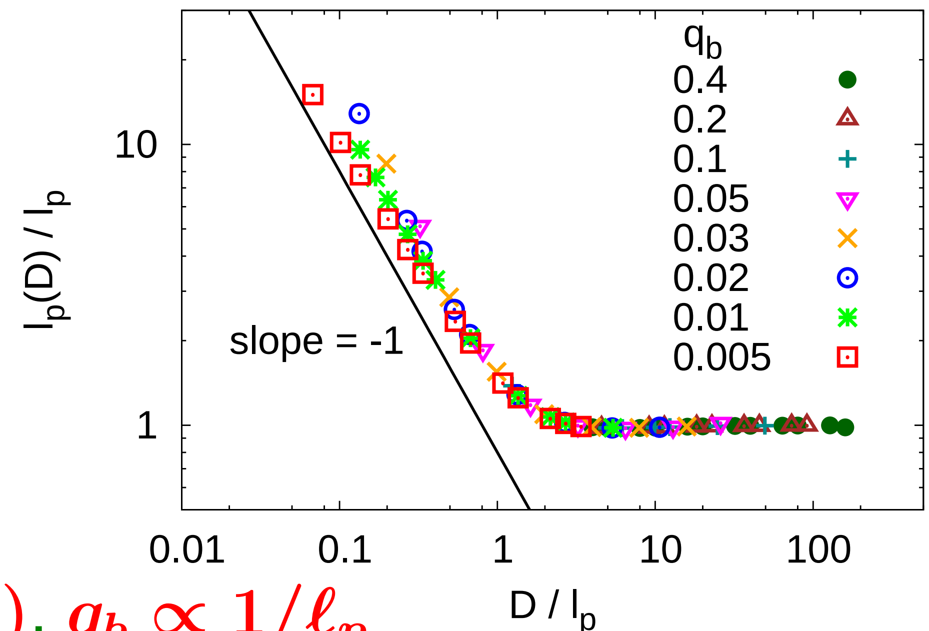
- Scaling hypothesis for $\ell_p(D)$ ($\ell_p(D) \rightarrow \ell_p$ as $D \rightarrow \infty$)

$$\ell_p(D) = \ell_p \tilde{P}(\eta = D/\ell_p)$$

with

$$\tilde{P}(\eta) = \begin{cases} 1 & \text{for } \eta \gg 1 \\ c/\eta & \text{for } \eta \ll 1 \end{cases}$$

c: constant



Each 90^o kink contributes

a factor $q_b = \exp(-\epsilon_b/k_B T)$, $q_b \propto 1/\ell_p$

$\ell_p(D) \propto \ell_p^2$, $D \ll \ell_p$

Scaling predictions (flexible $\longrightarrow$ stiff)

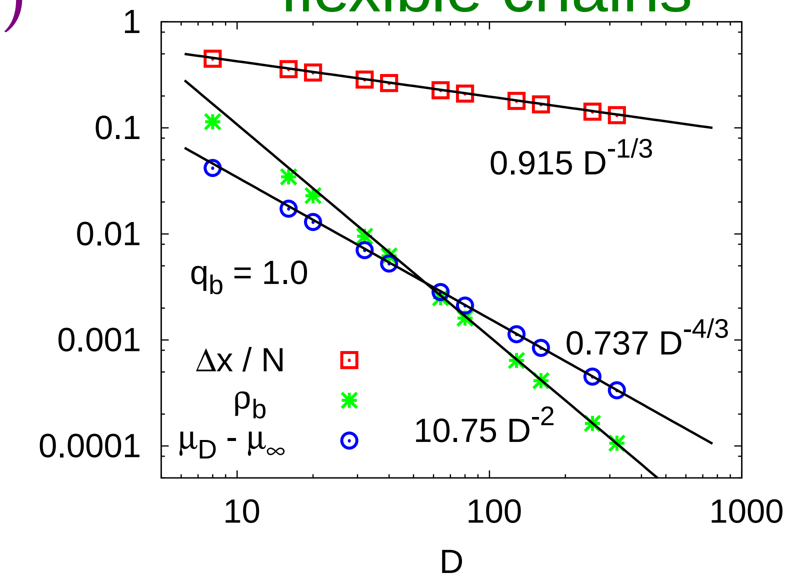
- Fugacity per monomer $(\eta = D/\ell_p)$

  $$[\mu_D(q_b) - \mu_\infty(q_b)]\ell_p \sim \eta^{-4/3}$$

- Free energy per monomer

  $$F(q_b, D) = \ell_p^{-1} \tilde{F}(\eta)$$
  $$= -\frac{1}{N} \ln \frac{Z_N(q_b, D)}{Z_N(q, \infty)}$$

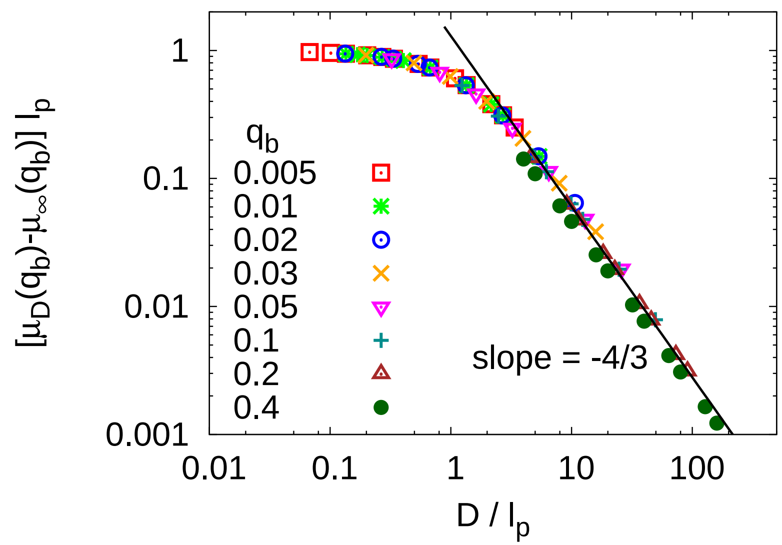
flexible chains



Scaling laws of the partition sum Z_N
in the thermodynamic limit $N \rightarrow \infty$

- $Z_N(q_b) \sim \mu_\infty(q_b)^{-N} N^{\gamma-1}$ (in bulk)

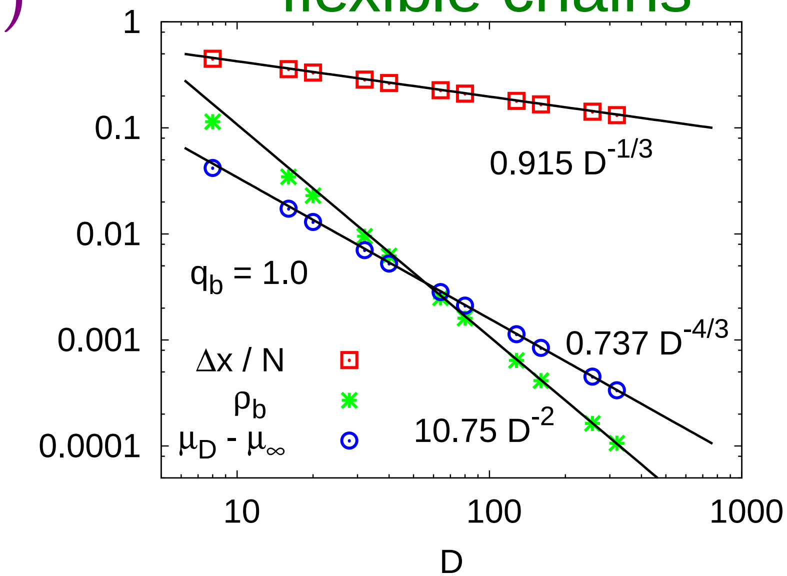
  the entropic exponent $\gamma = 43/32$
- $Z_N(q_b, D) \sim \mu(q_b, D)^{-N}$ (in strip)

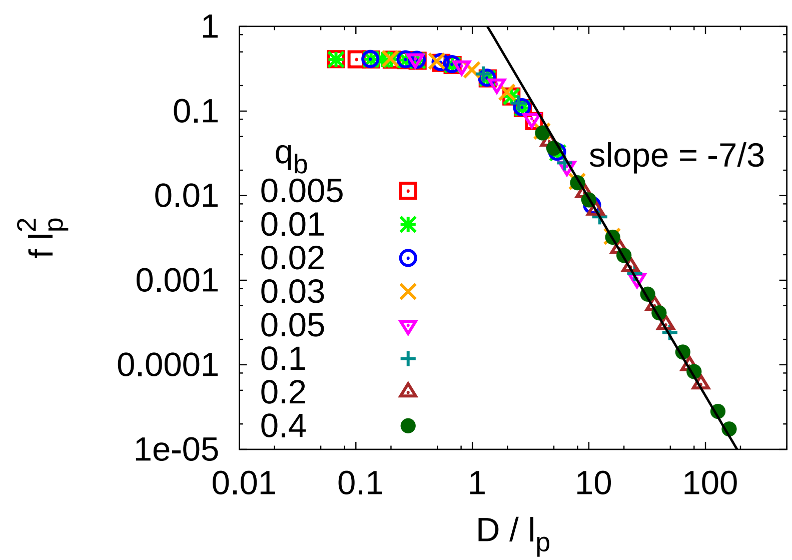


Scaling predictions (flexible $\longrightarrow$ stiff)

- Fugacity per monomer $(\eta = D/\ell_p)$
  $[\mu_D(q_b) - \mu_\infty(q_b)]\ell_p \sim \eta^{-4/3}$
- Free energy per monomer
  $F(q_b, D) = \ell_p^{-1}\tilde{F}(\eta)$
- Force per monomer
  $f = \frac{\partial F}{\partial D} = \ell_p^{-2}\tilde{F}_f(\eta)$,
  $\tilde{F}_f(\eta \gg 1) \propto \eta^{-7/3}$

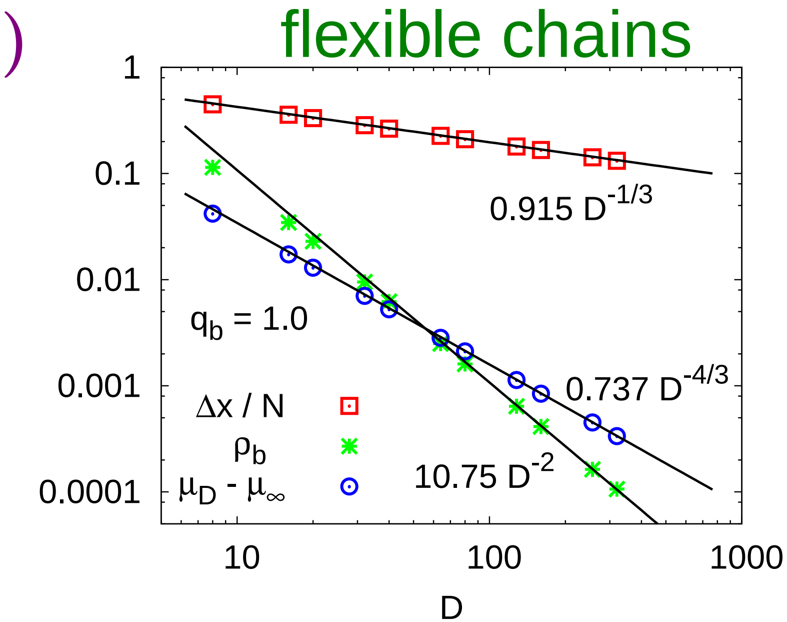
flexible chains

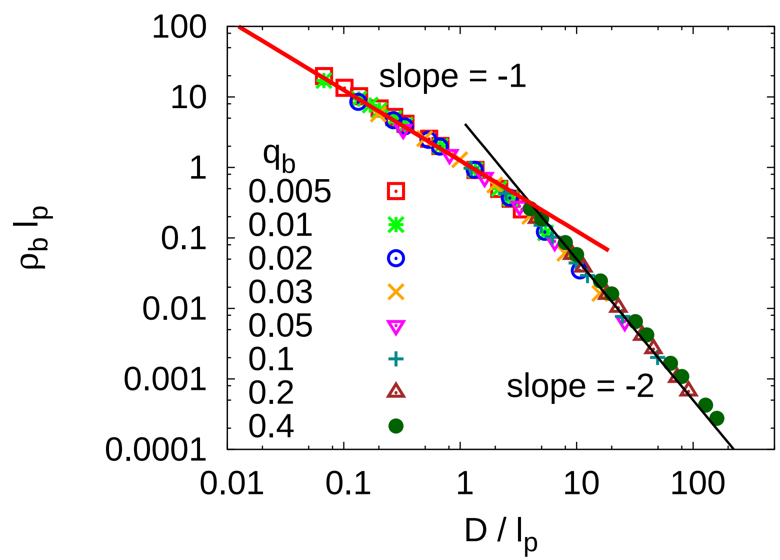




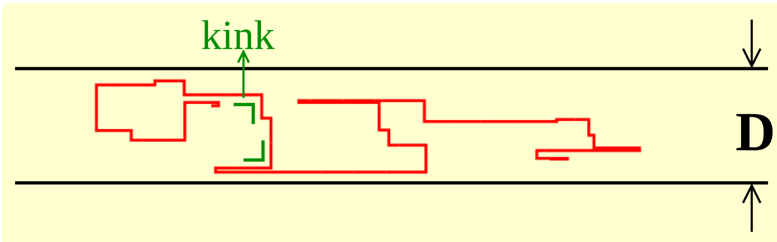
Scaling predictions (flexible $\longrightarrow$ stiff)

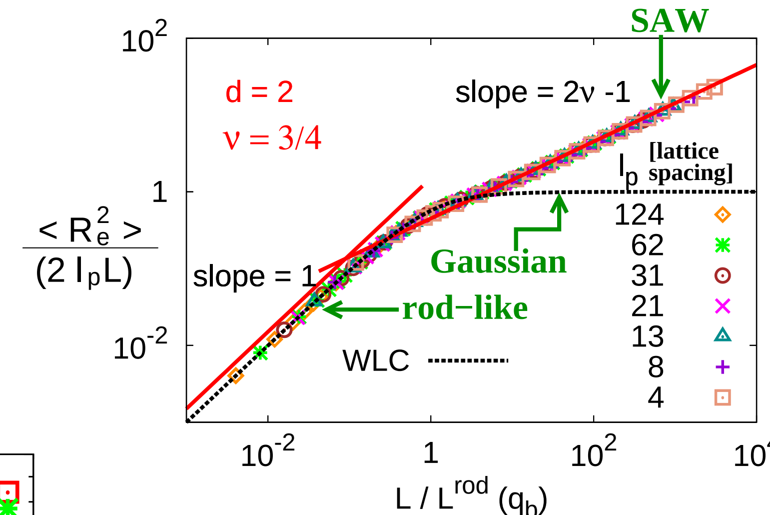
- Fugacity per monomer $(\eta = D/\ell_p)$
  $$[\mu_D(q_b) - \mu_\infty(q_b)]\ell_p \sim \eta^{-4/3}$$
- Free energy per monomer
  $$F(q_b, D) = \ell_p^{-1}\tilde{F}(\eta)$$
- Force per monomer
  $$f = \frac{\partial F}{\partial D} = \ell_p^{-2}\tilde{F}_f(\eta),$$
  $$\tilde{F}_f(\eta \gg 1) \propto \eta^{-7/3}$$
- End-to-end distance
  $$\langle \Delta x \rangle = N\tilde{X}(\eta),\ \tilde{X} \propto \eta^{-1/3}$$
- Monomer density on the walls
  $$\rho_b = \frac{N f \ell_p}{\langle \delta x \rangle} = \ell_p^{-1}\tilde{F}_\rho(\eta),$$
  $$\tilde{F}_\rho(\eta \gg 1) \propto \eta^{-2}$$

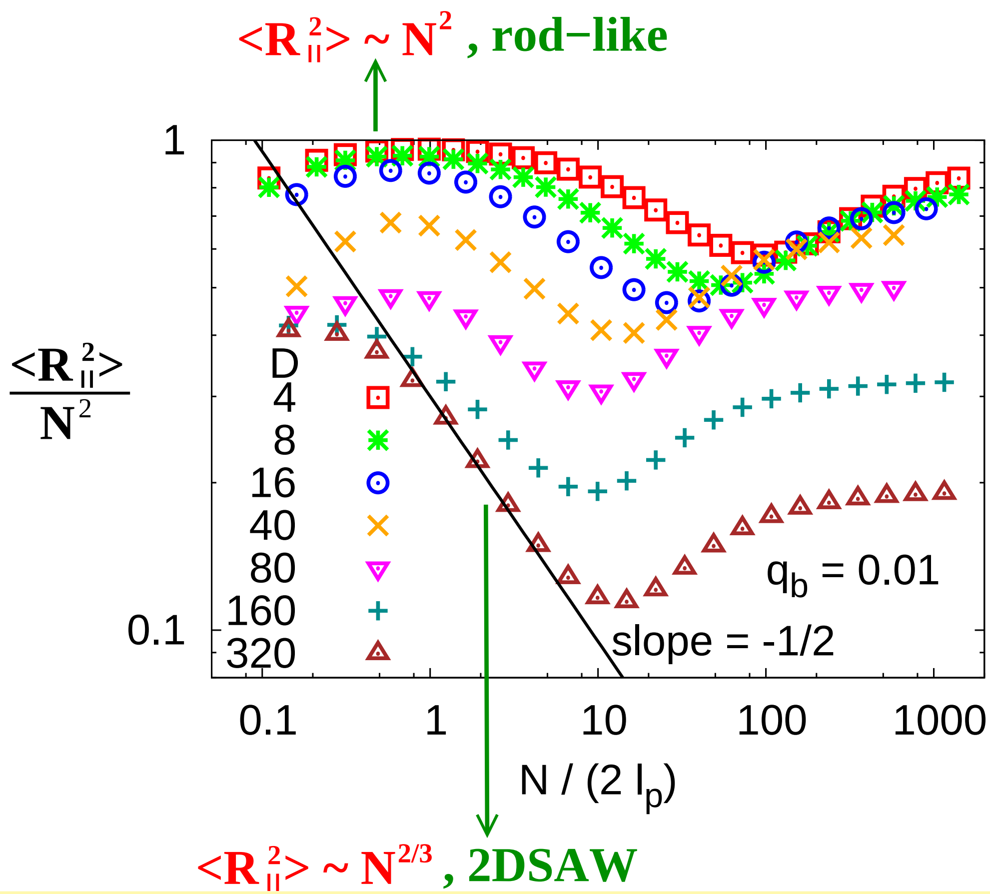




End-to-end distance || walls







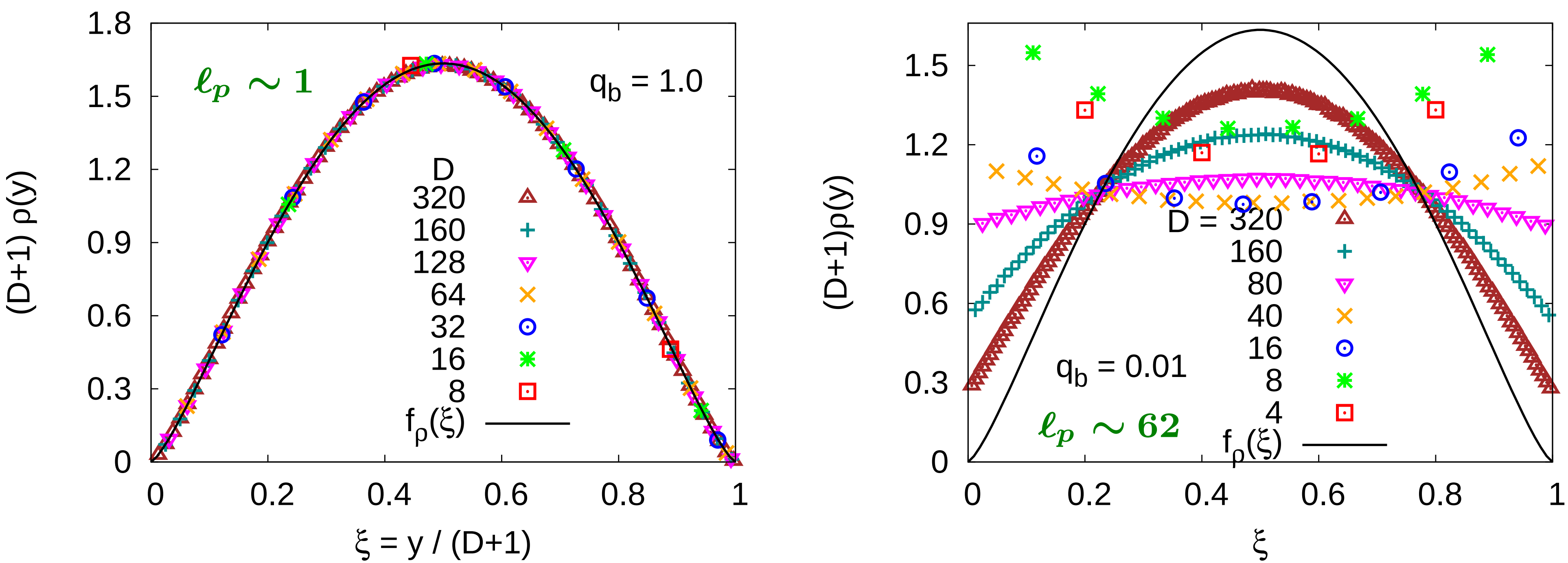
$\ell_p \approx 62$

Monomer density profiles

- Scaling prediction: *Eisenriegler et al., J. Chem. Phys. 77, 6269 (1982)*

$$\rho(y) = \frac{1}{D+1} f_\rho(\xi) \equiv \frac{1}{D+1} A[\xi(1-\xi]^{4/3}, \;\; \xi = y/(D+1)$$

$A = 10.38$, *Hsu & Grassberger, Eur. Phys. J. B 36, 209 (2003)*



3D semiflexible chains confined in a slit

- Scaling predictions (in bulk):

  $R \approx L \equiv N\ell_b,\ L < \ell_p$ (rod-like)

  $R \approx (\ell_p L)^{1/2},\ \ell_p < L < \ell_p^3/\ell_b^2$ (Gaussian)

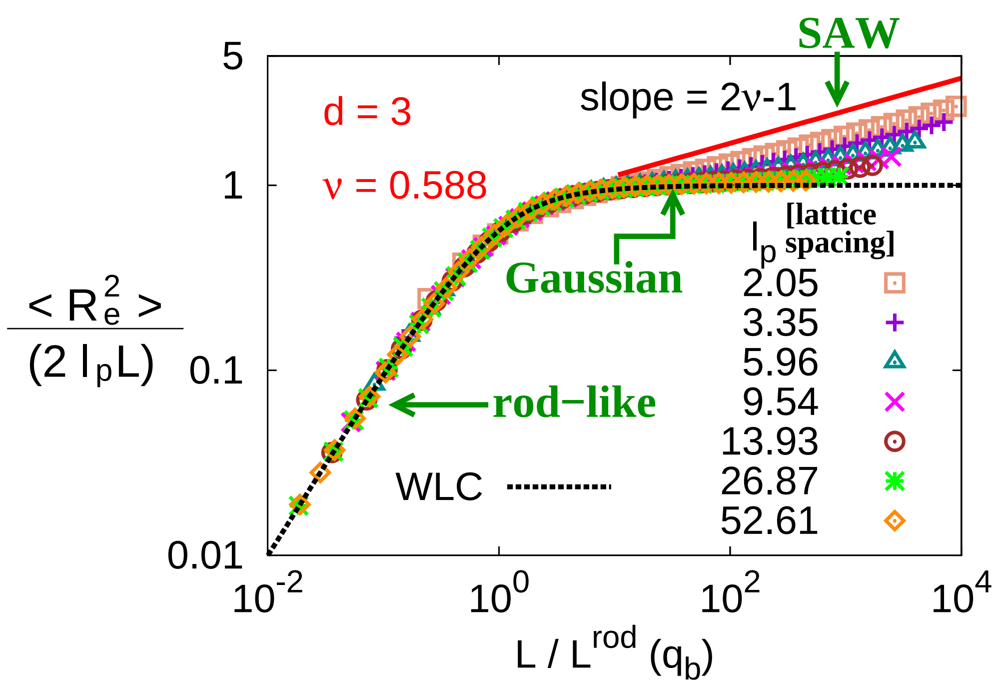
  $R \approx (\ell_p \ell_b)^{1/5} L^{3/5},\ L > \ell_p^3/\ell_b^2$ (SAW-like)

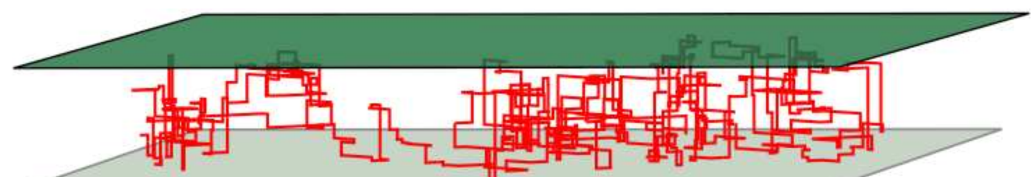
Cross-over point

(Gaussian $\leftrightarrow$ SAW)

$$L^* = \ell_P^3/\ell_b^2$$

$$R^* = \ell_p^2/\ell_b$$





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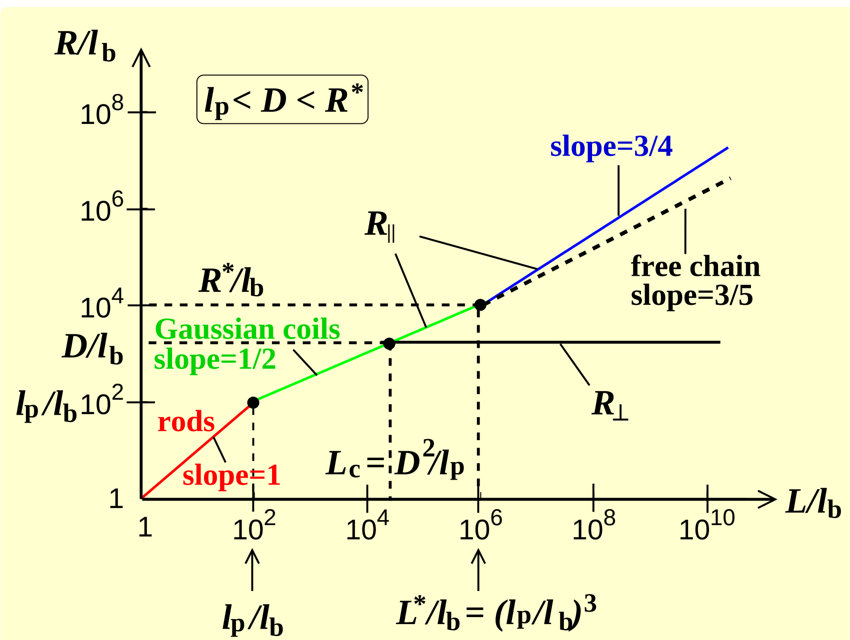
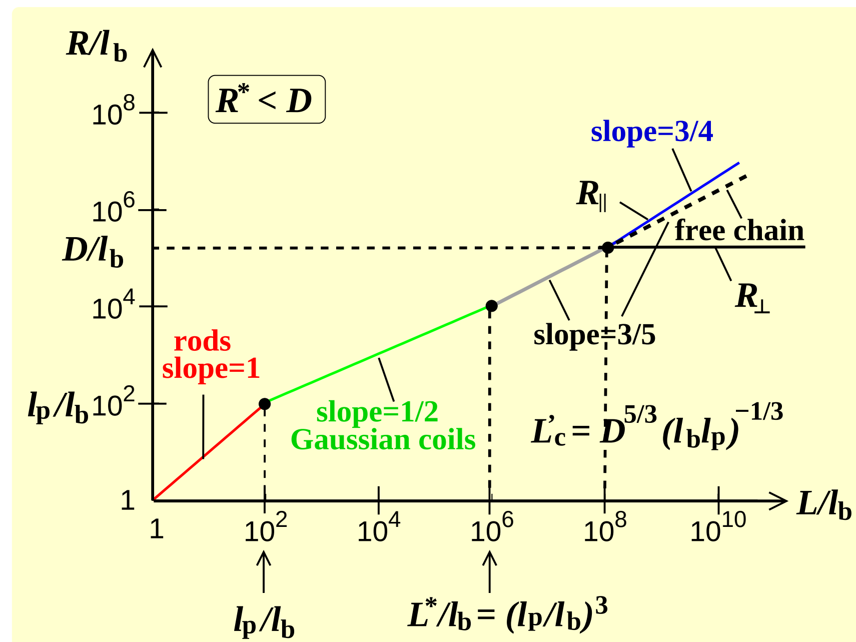
> Cross-over point
> (Gaussian $\leftrightarrow$ SAW)
> $L^* = \ell_P^3/\ell_b^2$
> $R^* = \ell_p^2/\ell_b$

- Scaling predictions (in slit):



Confined Gaussian chains



Confined SAW-like chains

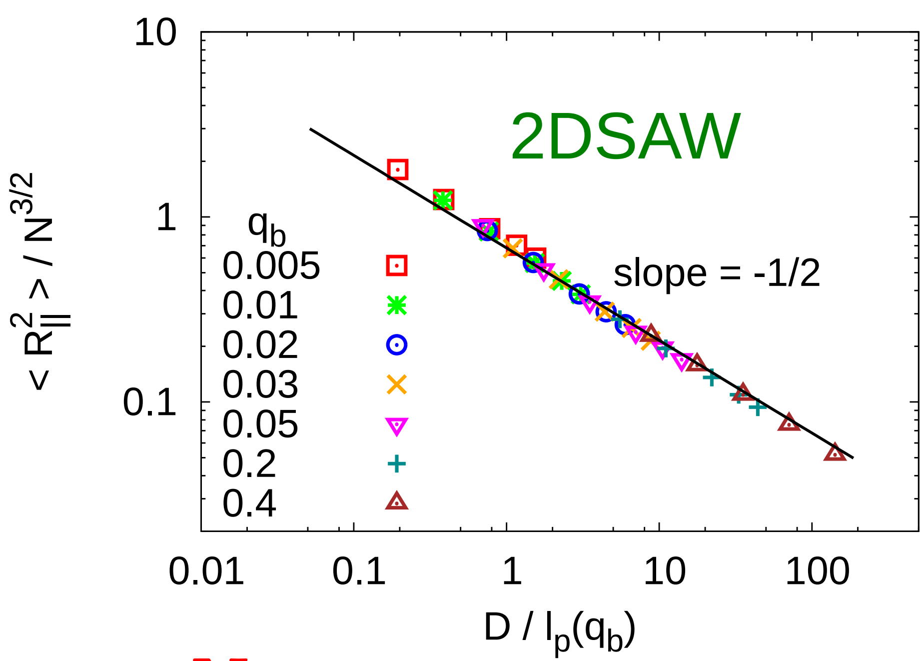
End-to-end distance || walls ($L = N\ell_b \gg L^*$)

- Confined Gaussian chains ($\ell_p < D < R^*$):

$$R_{||}^2 = (R^*)^2 n_{\text{blob}}^{3/2} = \ell_b^{5/2} \ell_p^{-1/2} N^{3/2}$$

- Confined SAW-like chains ($D > R^*$):

$$R_{||}^2 = D^2 n_{\text{blob}}^{3/2} = \ell_b^2 (D/\ell_p)^{-1/2} N^{3/2}$$



$N \to \infty$

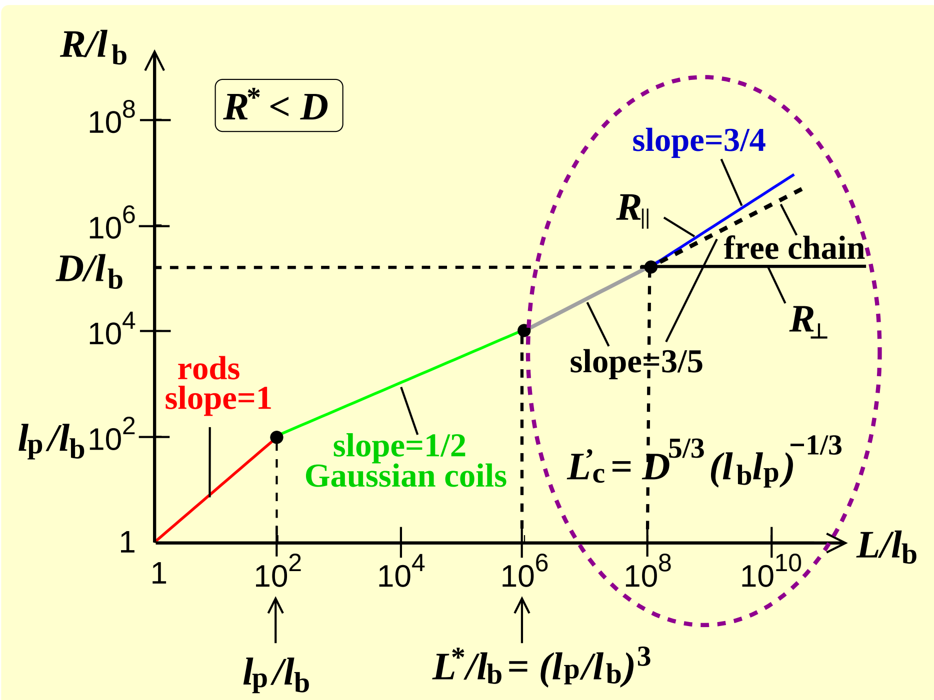
q_b	l_p (3D in bulk)	
0.005	51.52	stiff
0.01	26.08	↑
0.02	13.35	
0.03	9.10	
0.05	5.70	
0.1	3.12	
0.2	1.81	
0.4	1.13	↓
1.0	0.67	flexible

End-to-end distance ||, ⊥ walls ($L > L^*$)

- Free semiflexible chains: $R \approx (\ell_p \ell_b)^{1/5} (N \ell_b)^{\nu=3/5}$
- Confined semiflexible chains

  $R_{||}^2, R_{\perp}^2 \sim \ell_p^{2/5} N^{2\nu}$ (3DSAW)

  $\leftrightarrow R_{||}^2 \sim \ell_p^{1/2} N^{3/2} D^{-1/2} \ell_b^2$ (2DSAW), $\quad \leftrightarrow R_{\perp}^2 \sim D^2$



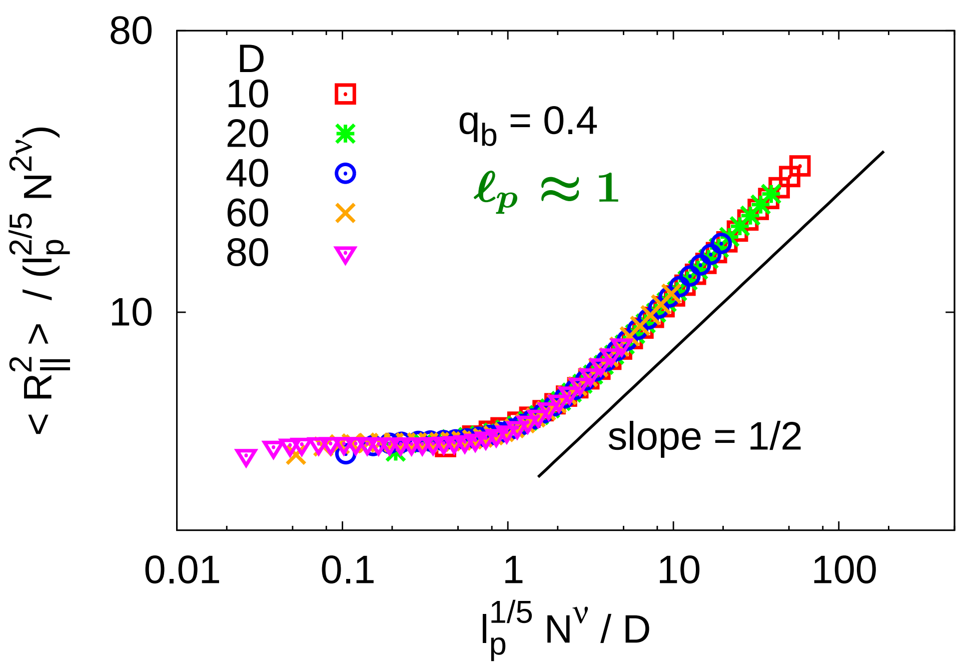
At the crossover point:
$N^{3/5}/D \sim \ell_p^{-1/5}$

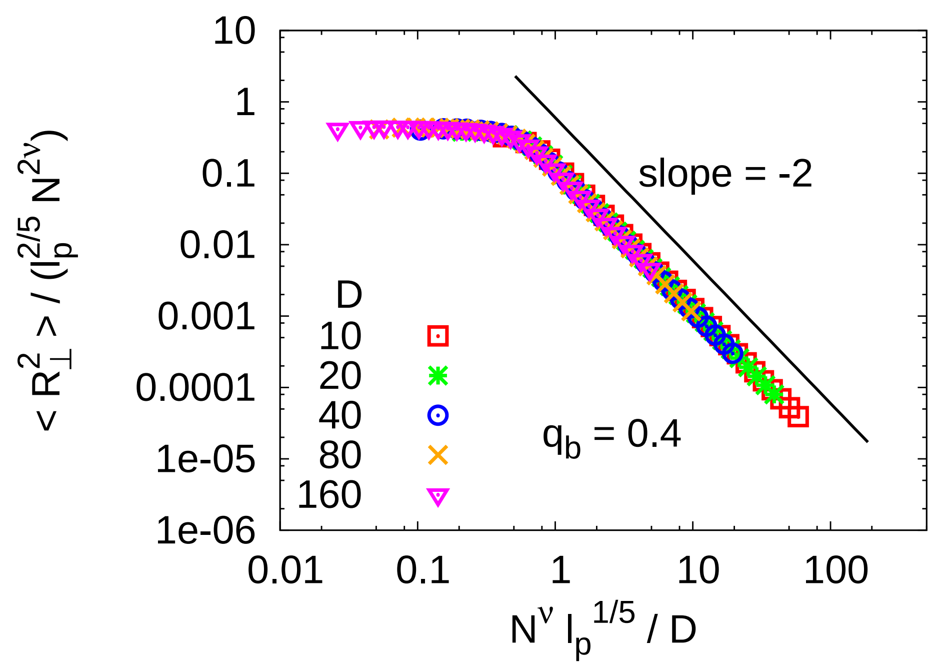
End-to-end distance $||$, $\perp$ walls ($L > L^*$)

- Free semiflexible chains: $R \approx (\ell_p \ell_b)^{1/5} (N\ell_b)^{\nu=3/5}$
- Confined semiflexible chains

$R_{||}^2, R_{\perp}^2 \sim \ell_p^{2/5} N^{2\nu}$ (3DSAW)

$\leftrightarrow R_{||}^2 \sim \ell_p^{1/2} N^{3/2} D^{-1/2} \ell_b^2$ (2DSAW), $\leftrightarrow R_{\perp}^2 \sim D^2$



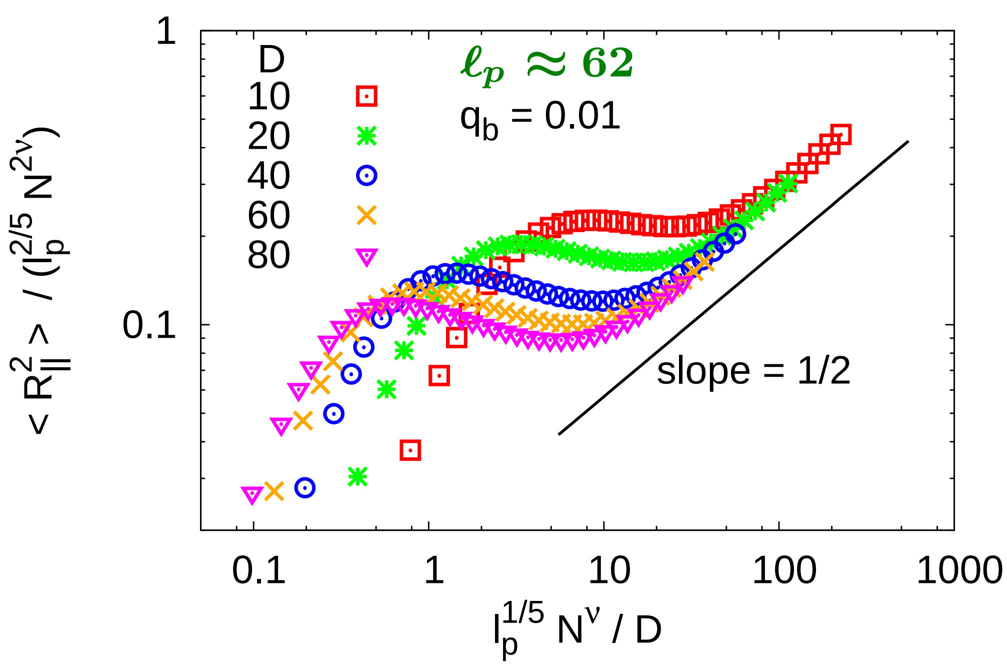


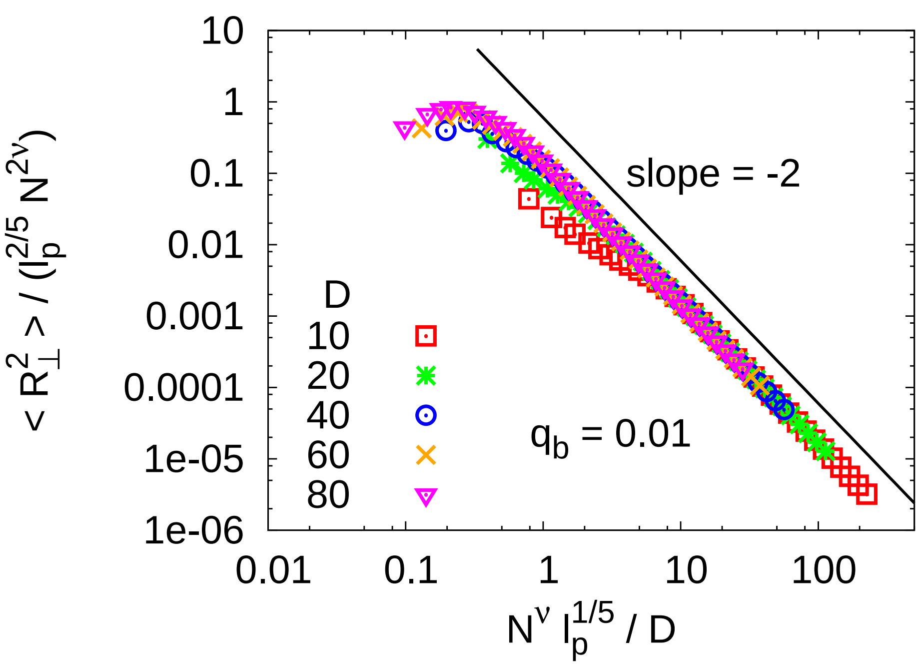
End-to-end distance ||, ⊥ walls ($L > L^*$)

- Free semiflexible chains: $R \approx (\ell_p \ell_b)^{1/5} (N\ell_b)^{\nu=3/5}$
- Confined semiflexible chains

$R_{||}^2$, $R_{\perp}^2 \sim \ell_p^{2/5} N^{2\nu}$ (3DSAW)

$\leftrightarrow R_{||}^2 \sim \ell_p^{1/2} N^{3/2} D^{-1/2} \ell_b^2$ (2DSAW), $\leftrightarrow R_{\perp}^2 \sim D^2$



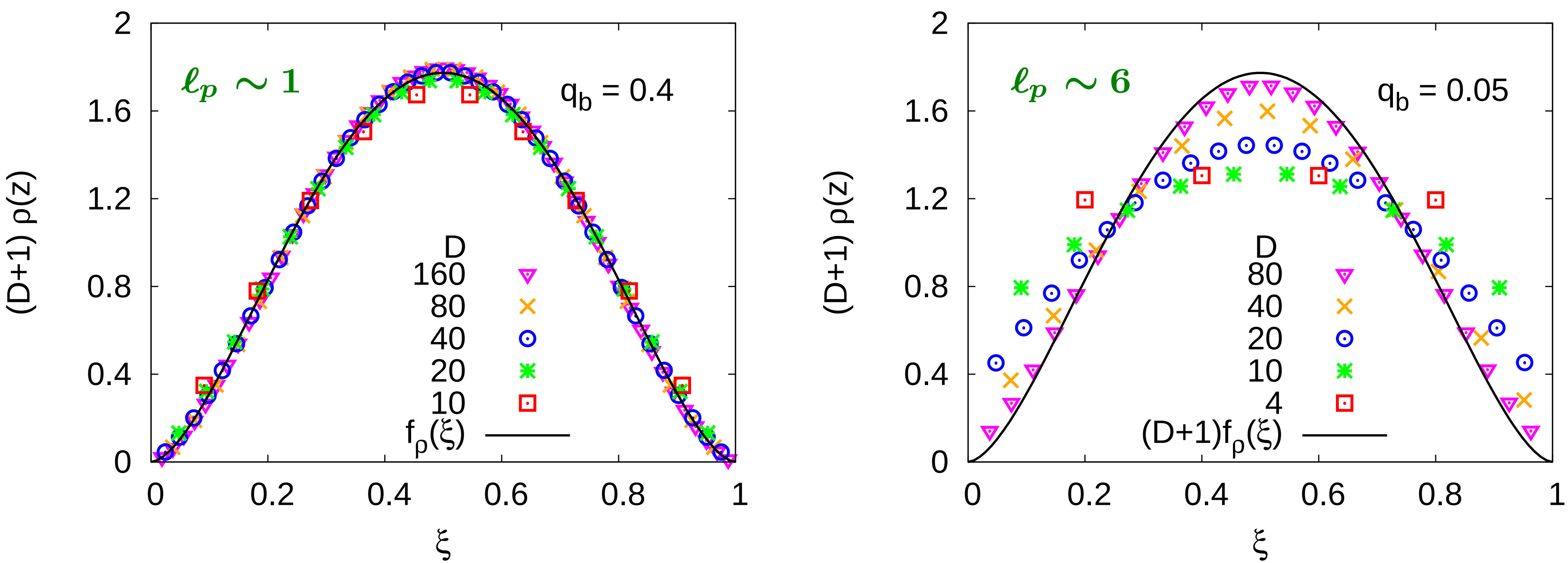


Monomer density profiles

- Scaling prediction: *Eisenriegler et al., J. Chem. Phys. 77, 6269 (1982)*

$$\rho(z) = \frac{1}{D+1} f_\rho(\xi) \equiv \frac{1}{D+1} A[\xi(1-\xi]^{4/3}, \;\; \xi = z/(D+1)$$

$A = 18.74$, *Hsu & Grassberger, J. Chem. Phys. 120, 2034 (2004)*



Conclusions

- Under weak confinement $D \gg \ell_p$:
  the Daoud - de Gennes scaling predictions are verified
- Under strong confinement $D \leq \ell_p$: strong deviations from the predictions based on Kratky-Porod worm-like chain model
- Odijk's deflection length plays no role for semiflexible polymers with discrete bond angles
- Monte Carlo test of scaling concepts $\Rightarrow$ interpretation of future experimental studies

References: Soft Matter **9***, 10512 (2013), Macromolecules* **46***, 8017 (2013)*

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