Structure and scaling analysis of stretched semiflexible polymer chains

Hsiao-Ping Hsu, Wolfgang Paul (Halle), Kurt Binder

Institut für Physik, Johannes Gutenberg-Universität Mainz, Germany

Motivation

- Semiflexible polymer chains vs.
  worm-like chain model (Kratky-Porod model)
  chain stiffness, excluded-volume effect
  - rod-like - SAW (d=2)
  - rod-like - Gaussian coil - SAW (d=3)
- Experimental techniques of single molecule measurements:
  tension-induced stretching of biological macromolecules,
  dsDNA ($\ell_p \approx 50$nm), ssDNA ($\ell_p \approx 0.6$nm), ...
- Stretching semiflexible chains
  $\Rightarrow$ force-extension curves
  theory $\leftrightarrow$ simulation

Worm-like chain model

Kratky-Porod model in the continuum limit (J. Colloid Sci., 4 35 (1949)):
(without considering the excluded volume interactions)

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

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

$$= \begin{cases} L^2 = (\ell_b N_b)^2 & \text{for } L \ll \ell_p \ (\text{rod}-\text{like chain}) \\ 2\ell_p L = \ell_k \ell_b N_b & \text{for } L \to \infty \ (\text{Gaussian chain}) \end{cases}$$

- $L = N_b \ell_b$: contour length
- N_b: number of monomers
- ℓ_b: bond length
- ℓ_p: persistence length

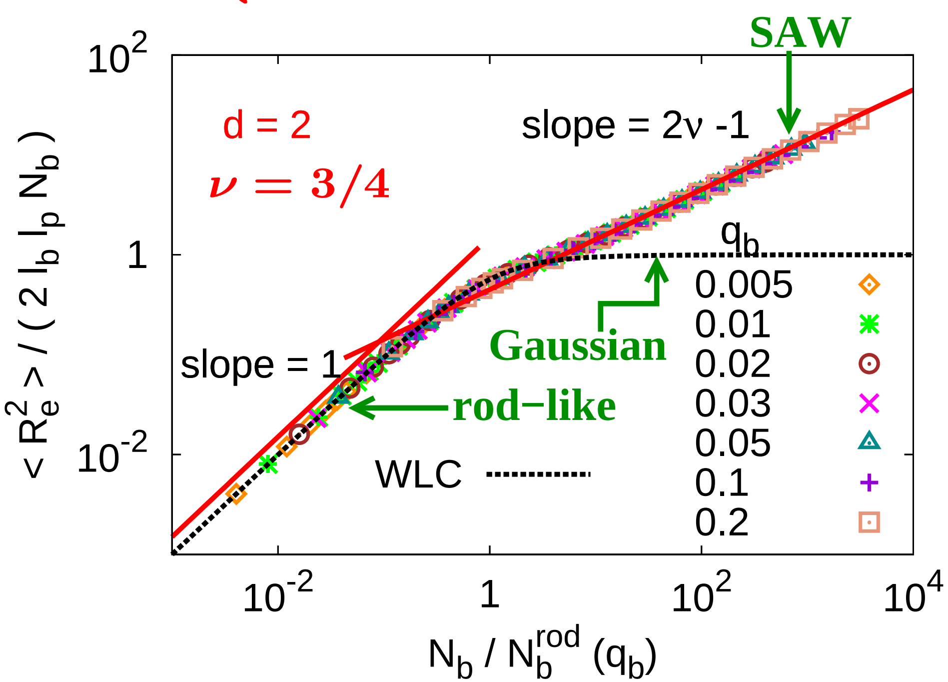
Simulation vs. Theory

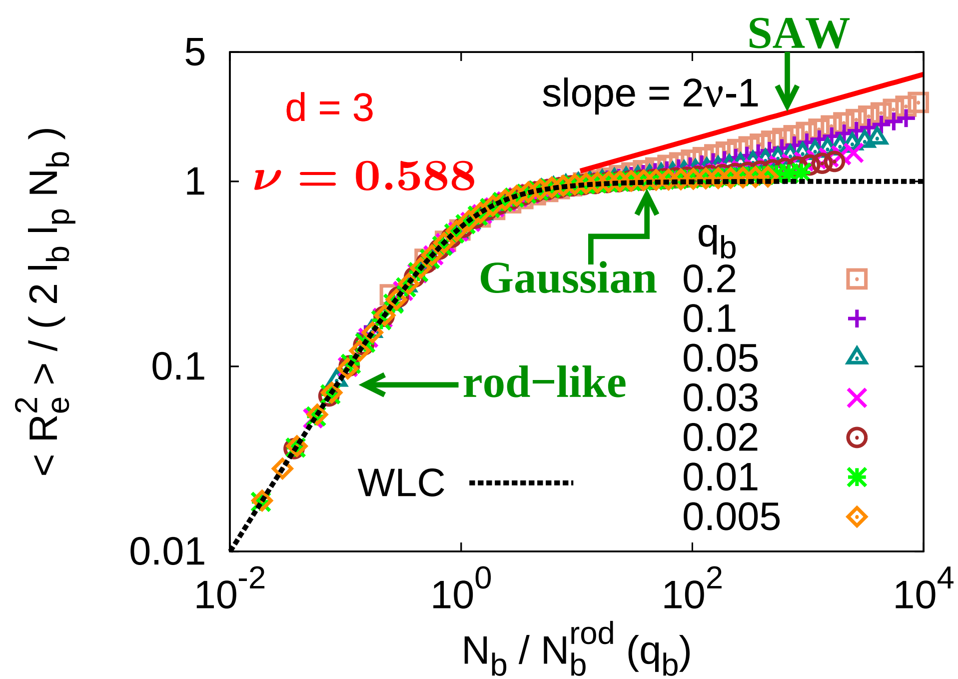
- Worm-like chain model (WLC):

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

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

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



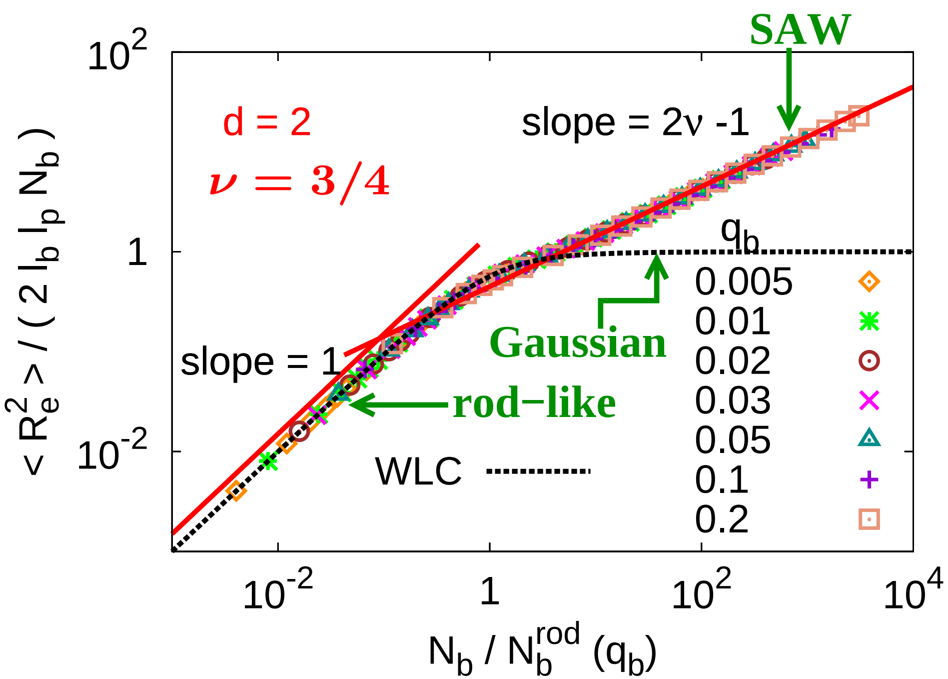


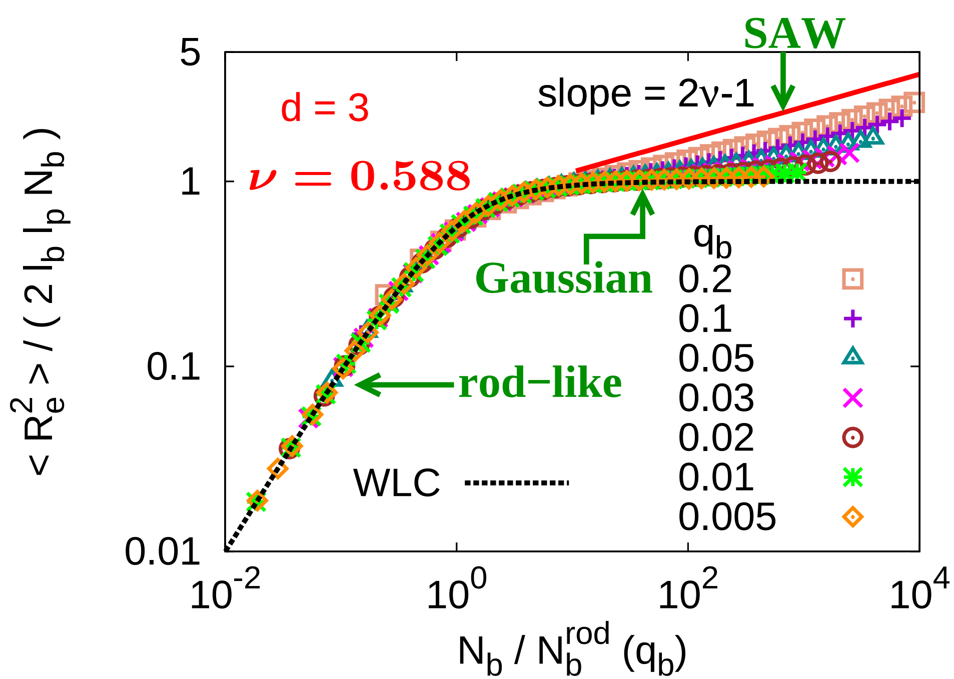
Simulation vs. Theory

- Flory-type free energy minimization arguments:

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

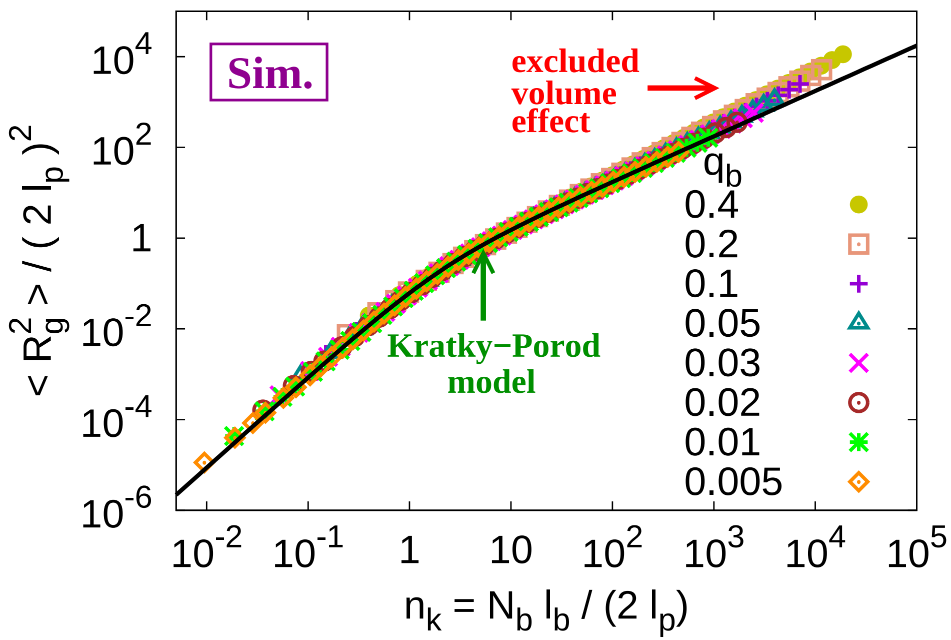
Netz & Andelman, Phys. Rep. 380, 1 (2003)

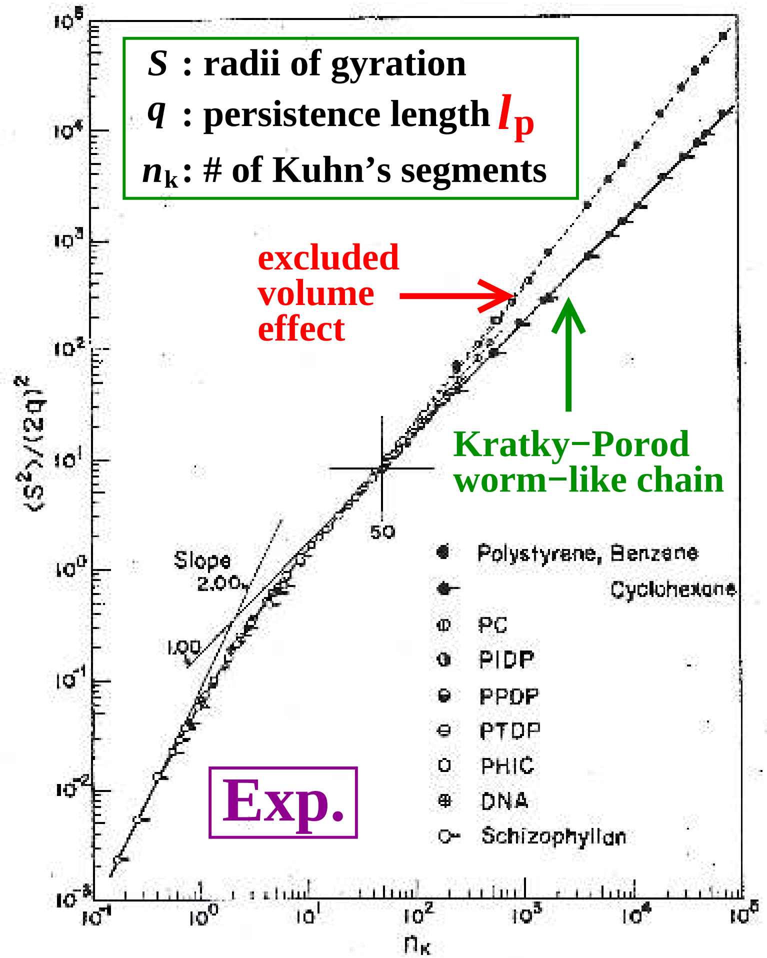




Simulation vs. Experiment

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





Hsu, Paul, & Binder

Europhys. Lett. 95, 68004 (2011); 92, 28003 (2010)

J. Phys. Chem. DOI:10.1021/jp204006z (2011)

Macromol. Theory & Simul. 20, 510 (2011)

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

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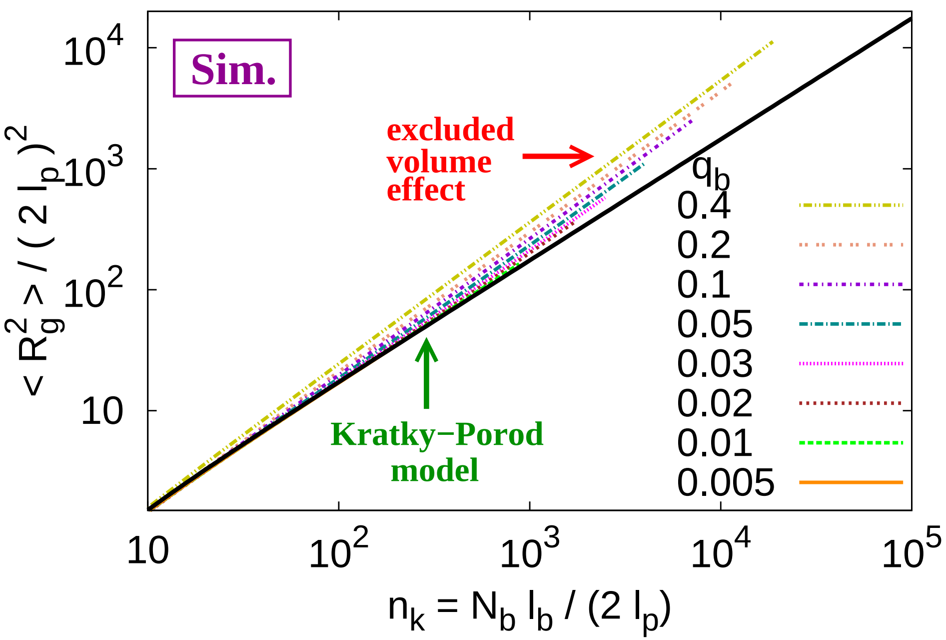

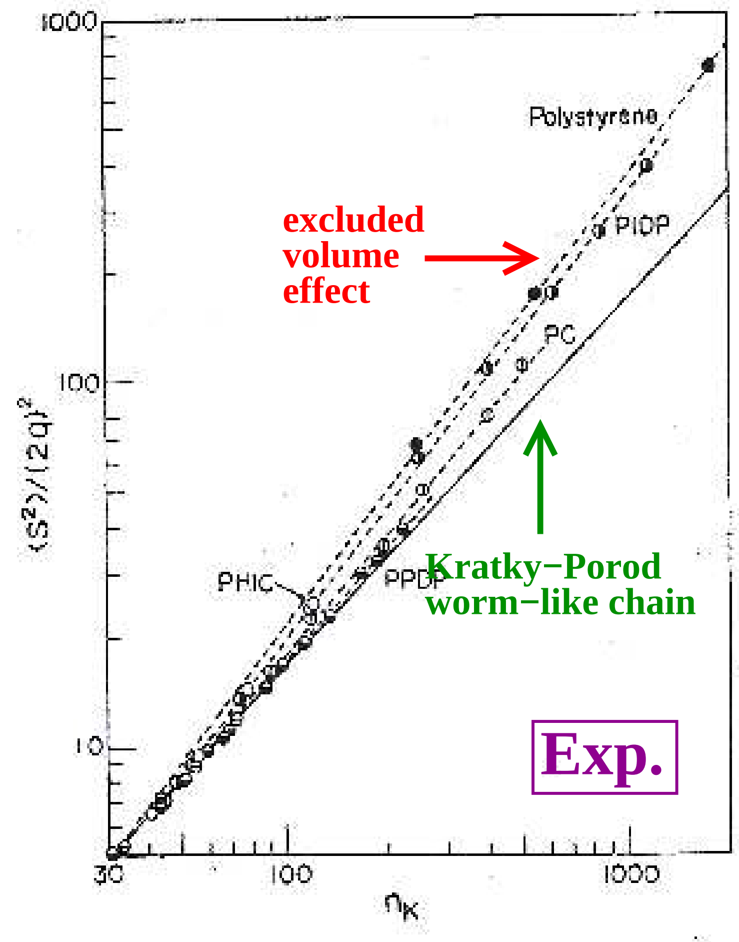

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Semiflexible SAW model

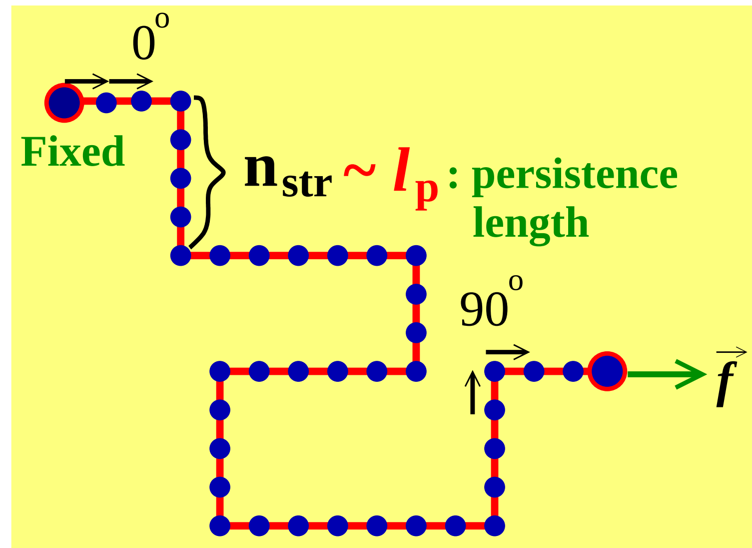
Self-avoiding walk model

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

- 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_{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

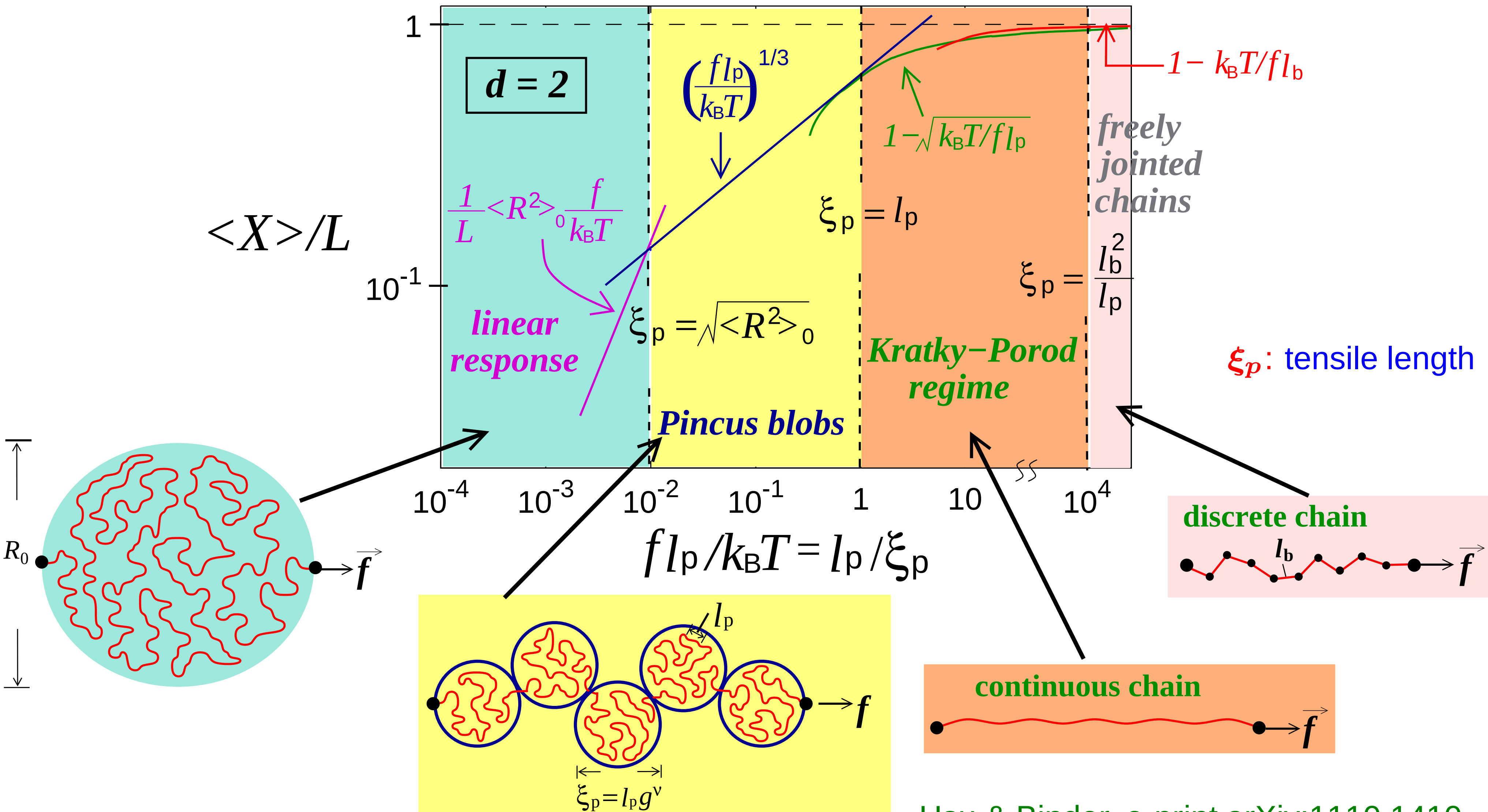
X: end-to-end distance along $+x$-direction ($X=x_{N_b}-x_0$)

- Algorithm: Pruned-Enriched Rosenbluth Method

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

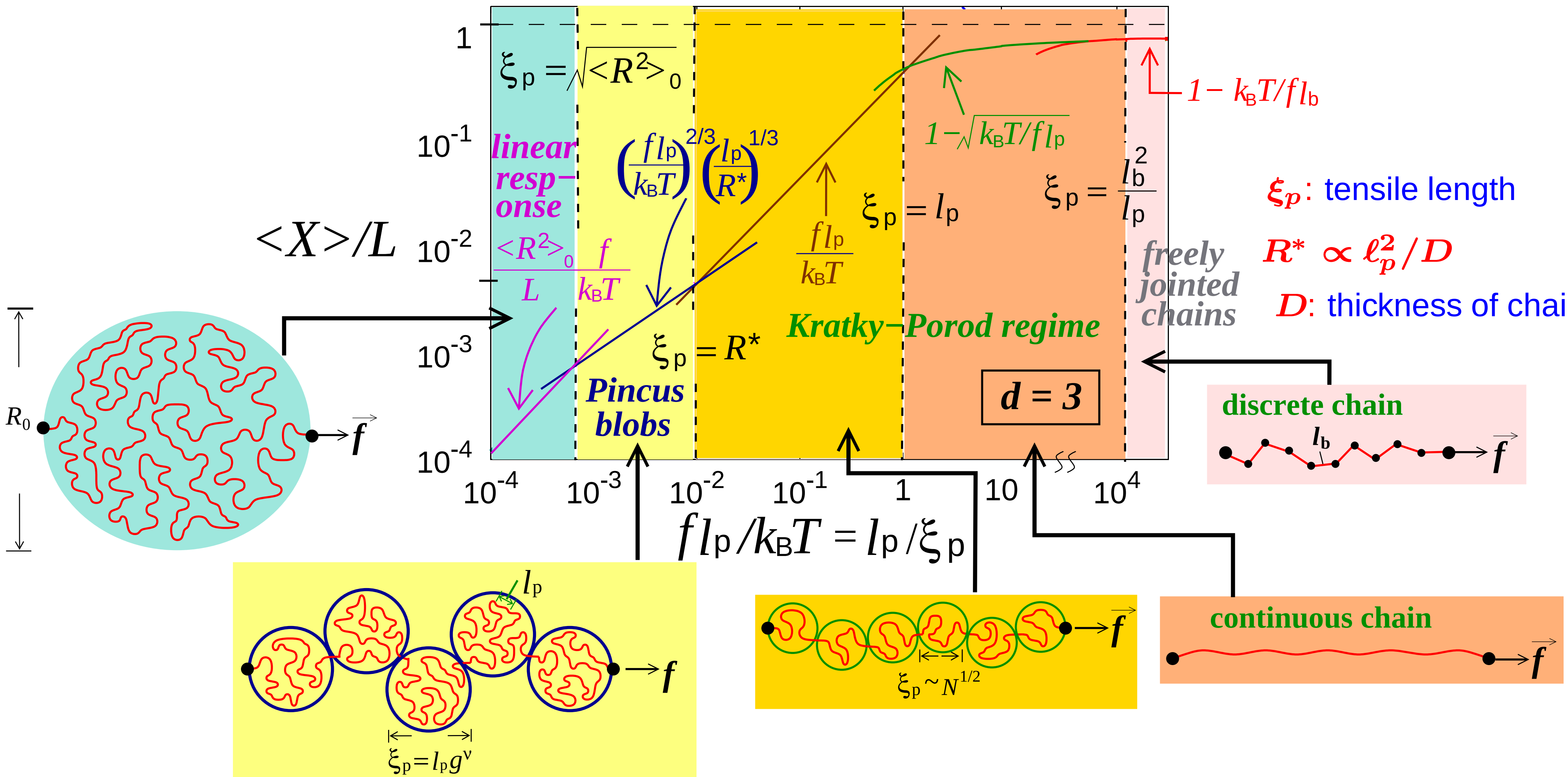
  - $0\le N_b\le 25600$, short chain $\leftrightarrow$ long chain
  - $0.005\le q_b\le 1.0$, very stiff $\leftrightarrow$ flexible (SAW)
  - $1\le b\le 1.6$, no force $\leftrightarrow$ strong force

Force-extension curves in $d = 2$



Hsu & Binder, e-print arXiv:1110.1410

Force-extension curves in $d = 3$



ξ_p: tensile length

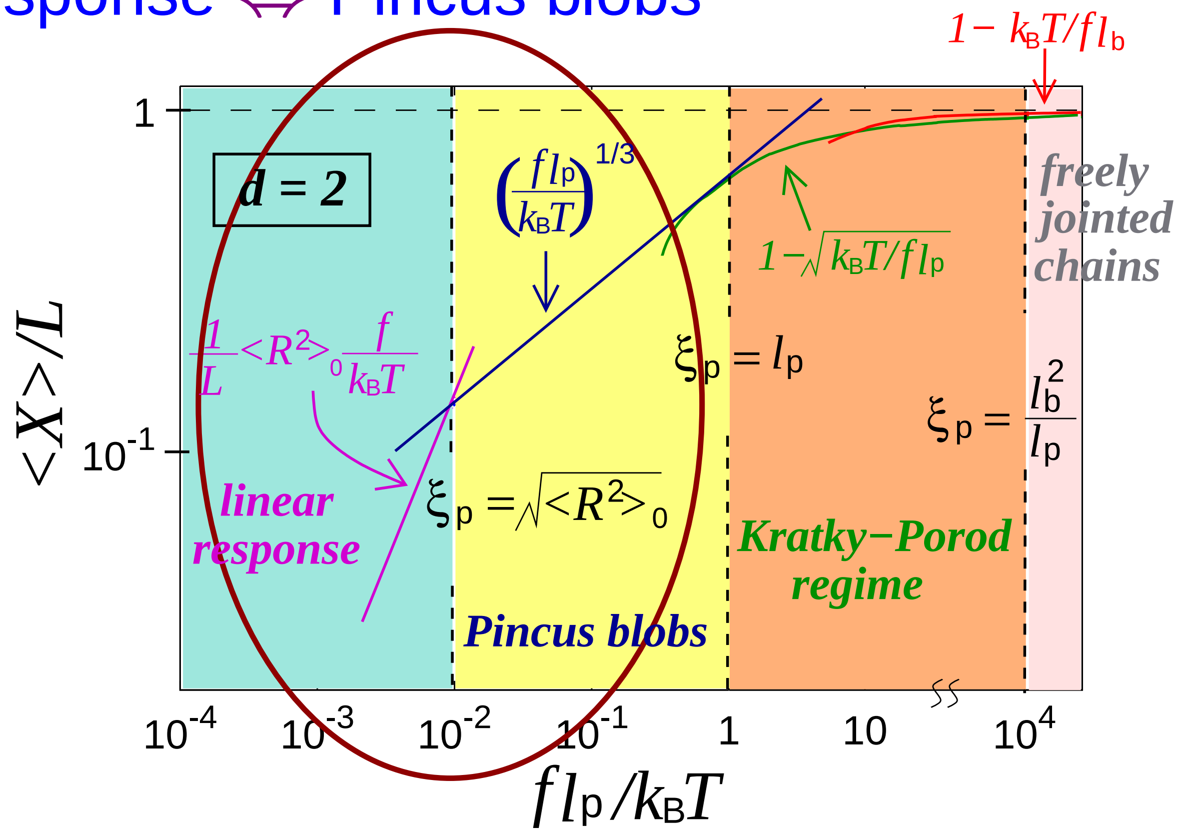
$R^* \propto \ell_p^2 / D$

D: thickness of chains

Hsu & Binder, e-print arXiv:1110.1410

Monte Carlo results in $d = 2$

- Linear response $\Leftrightarrow$ Pincus blobs



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

$\Rightarrow$ scaling factors: $C_x = (L/\ell_p)^{3/4}$, $C_y = (L/\ell_p)^{1/4}$

Monte Carlo results in $d = 2$

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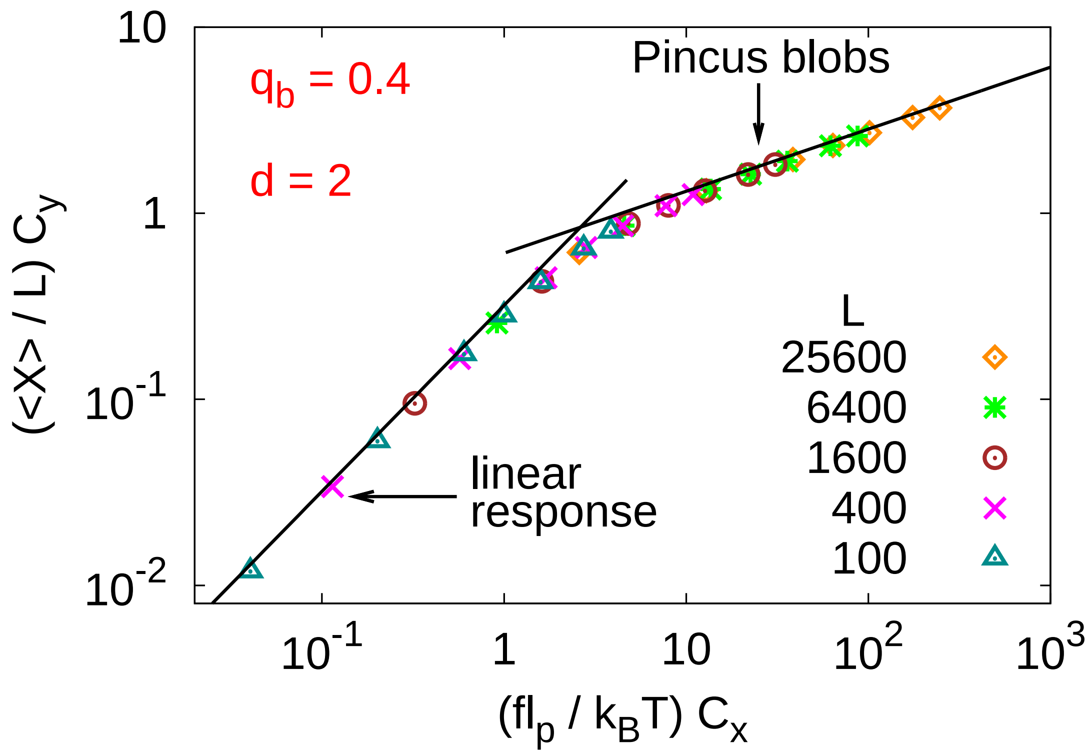

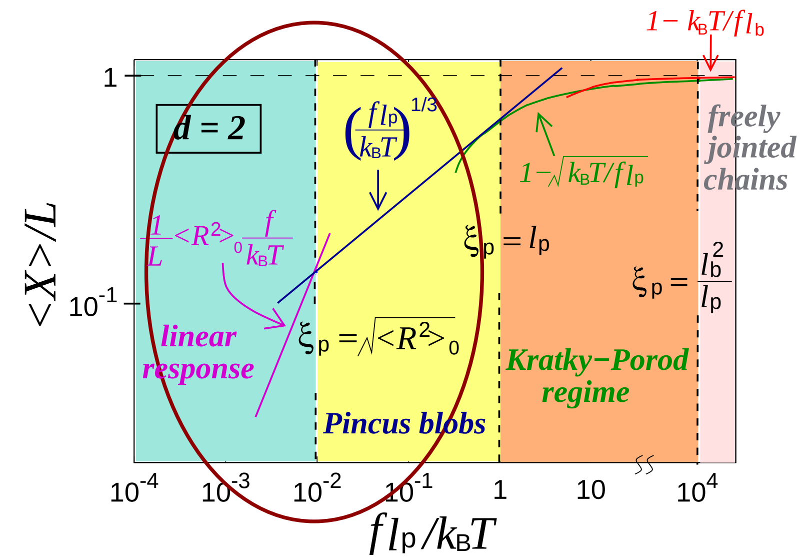

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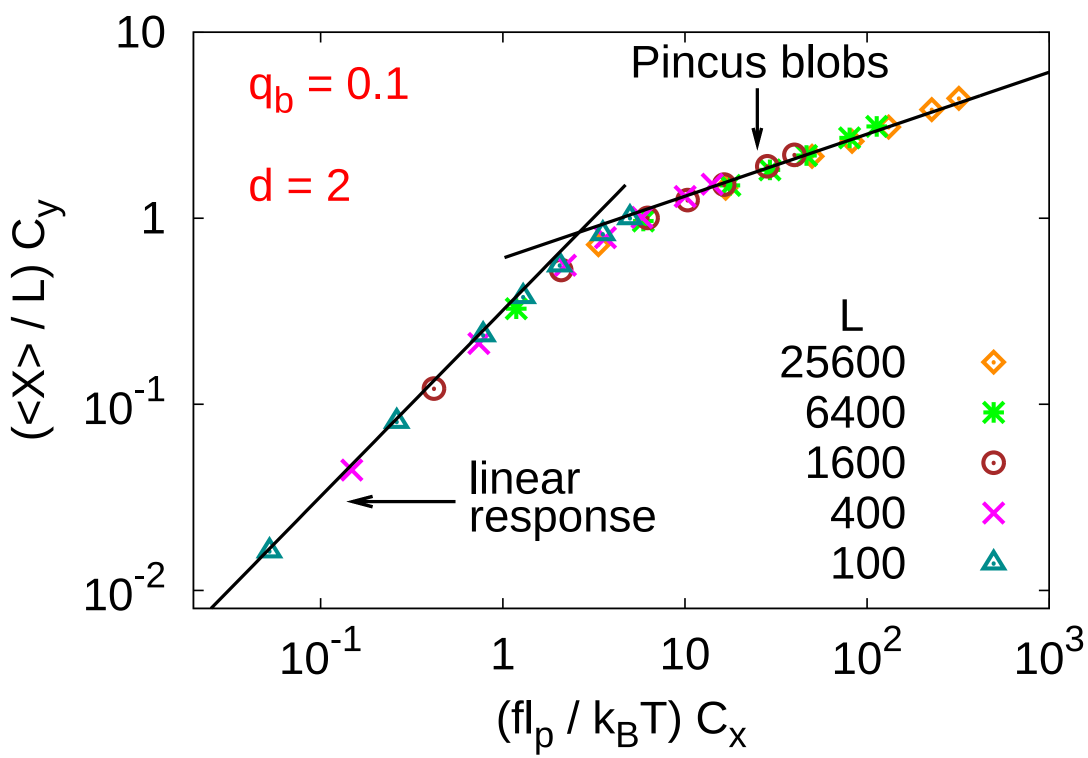

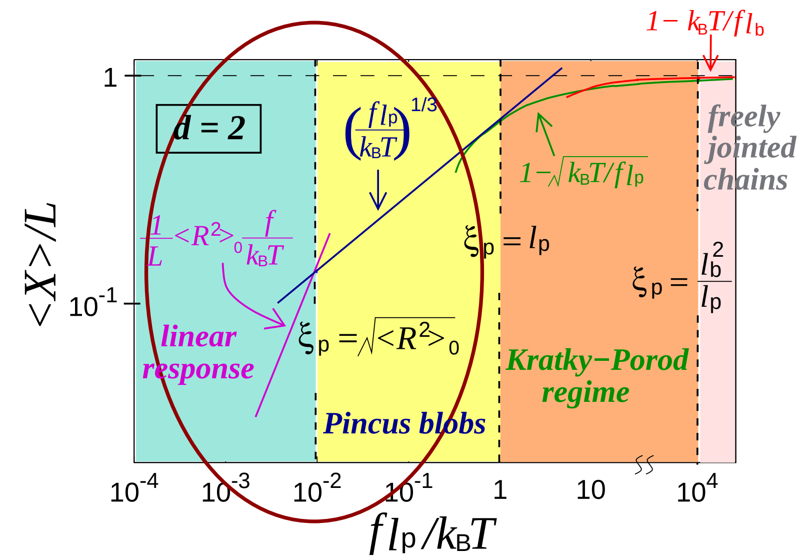

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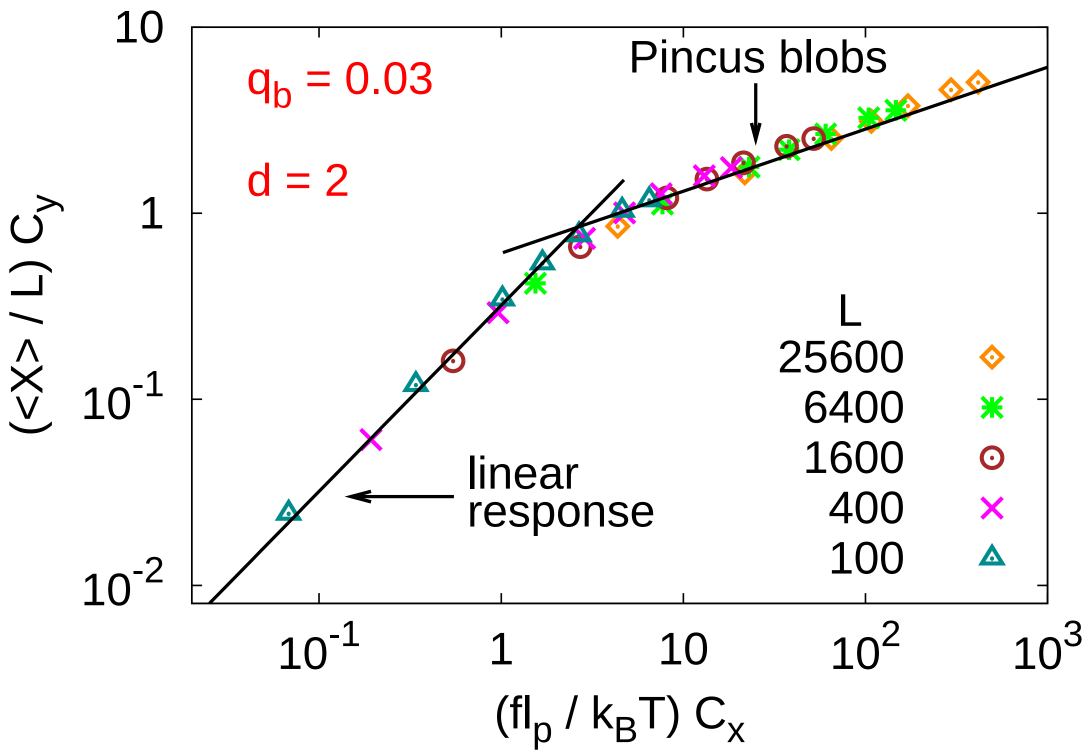

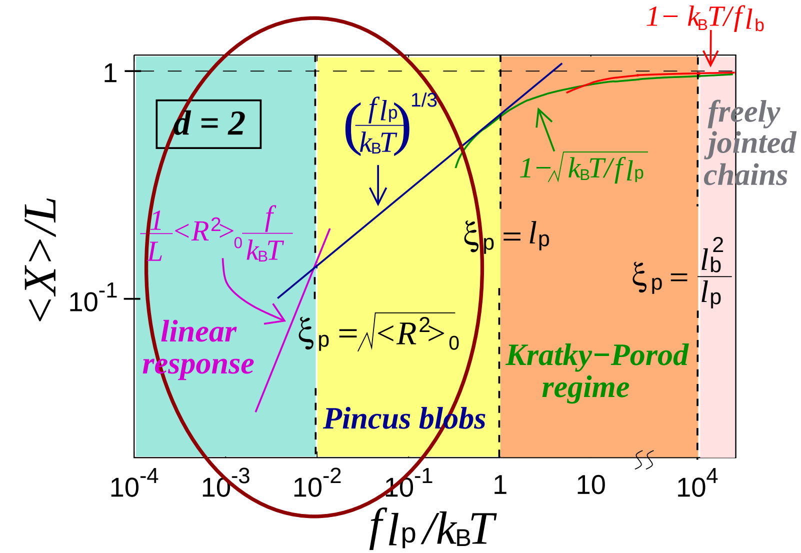

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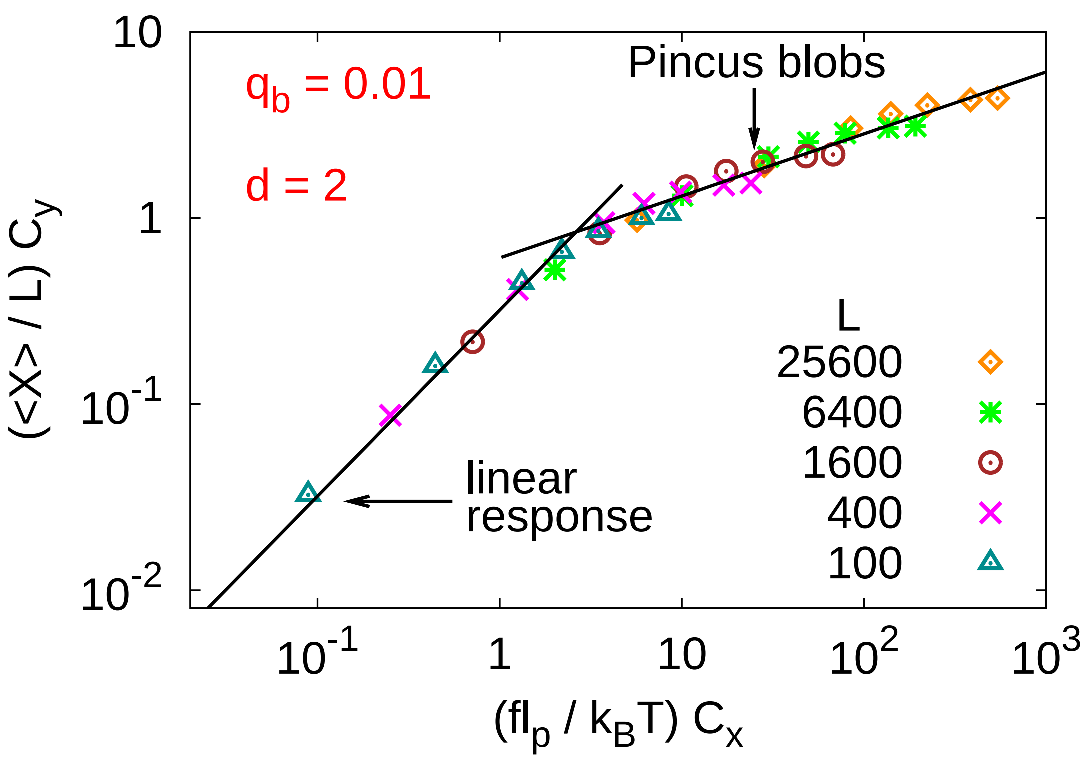

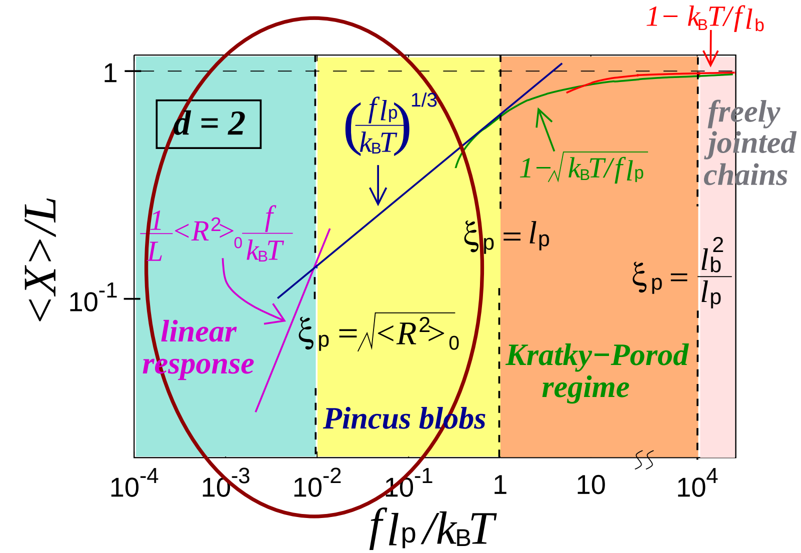

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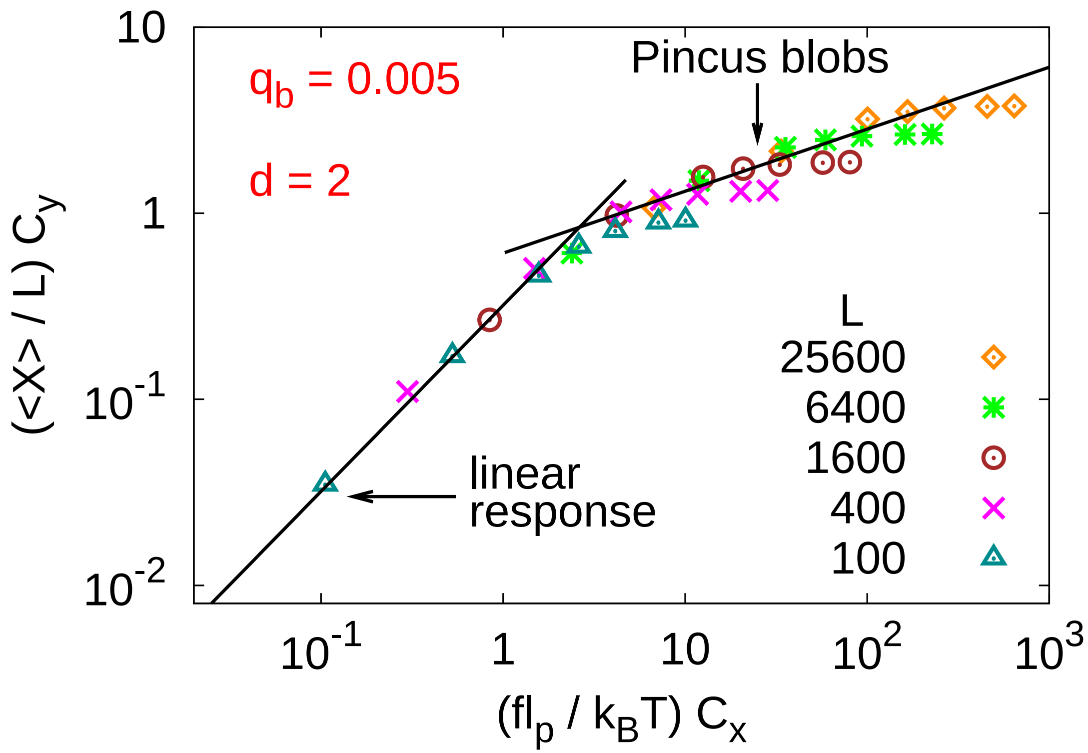

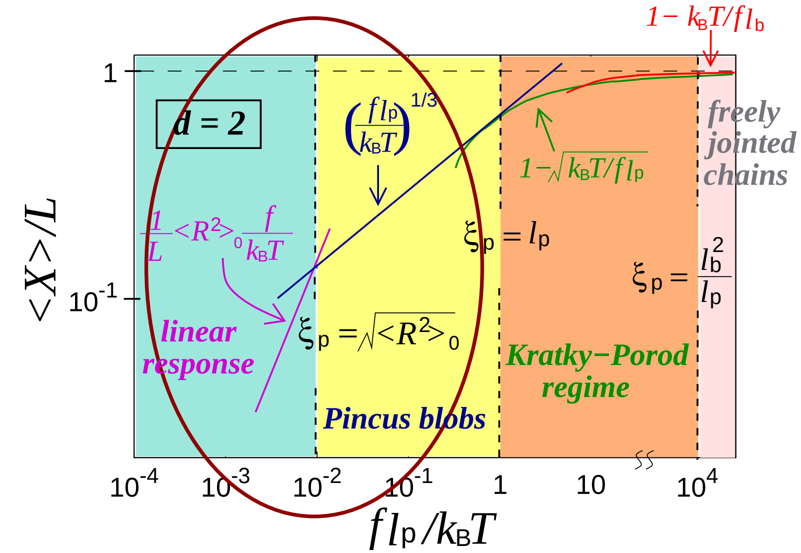

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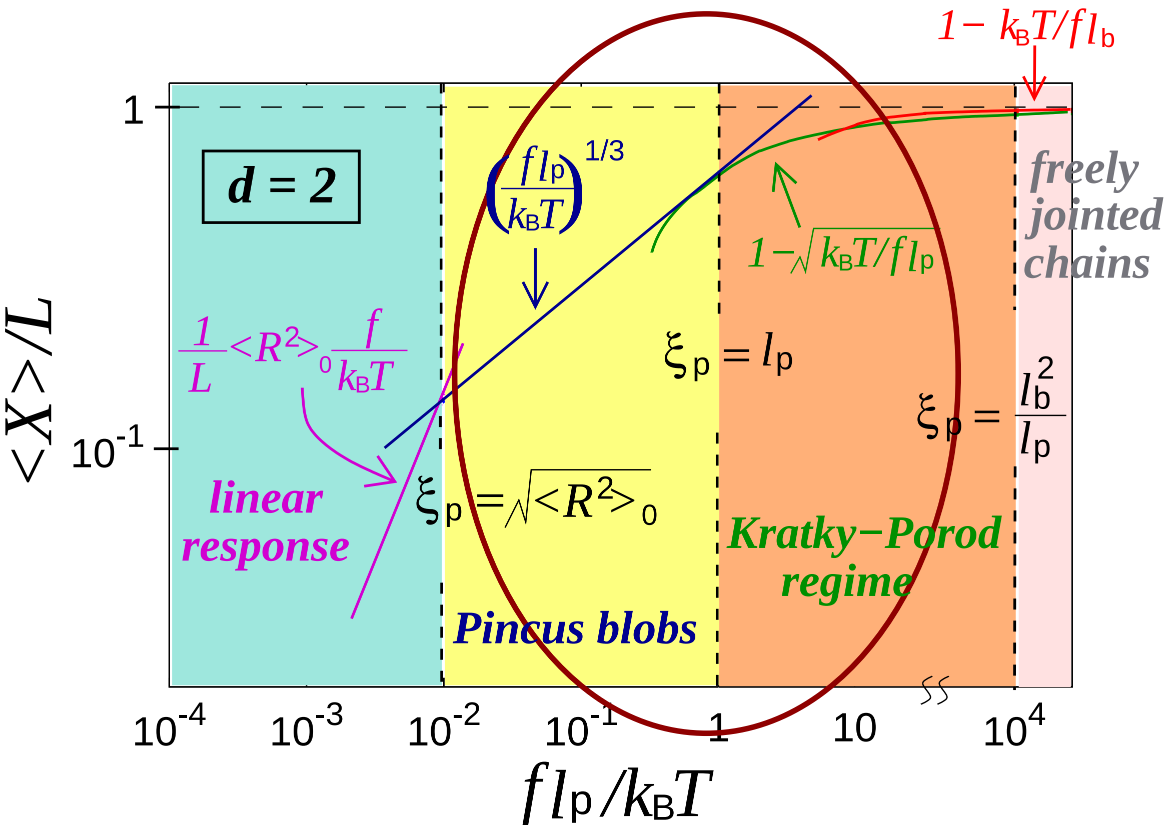
- Pincus blobs $\Leftrightarrow$ Kratky-Porod (K-P) like regime



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

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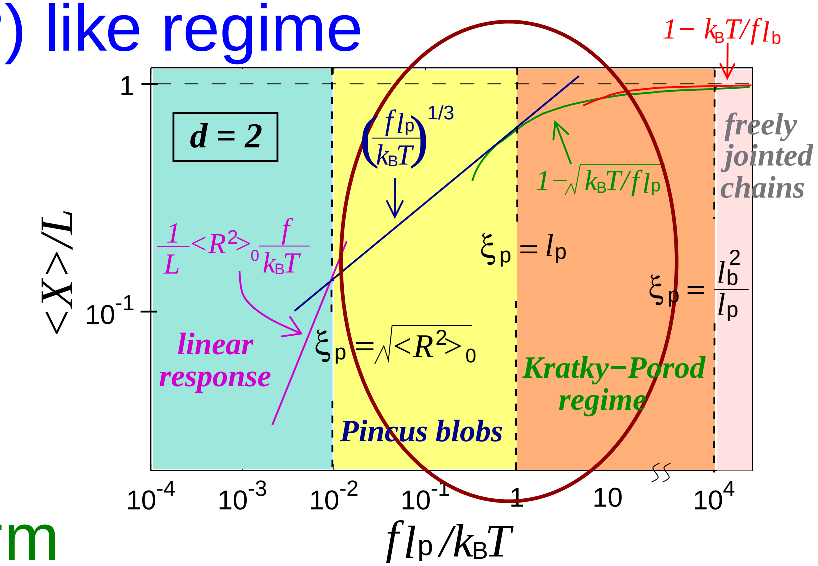

- Kratky-Porod model + a force term

$$\frac{f\ell_p}{k_BT} = \frac{3}{4}\frac{\langle X\rangle}{L} + \frac{1}{8(1-\langle X\rangle/L)^2} - \frac{1}{8}$$

$$\Rightarrow \frac{\langle X\rangle}{L} \approx \begin{cases} f\ell_p/k_BT & , \text{ small } f \\ 1 - 1/\sqrt{8f\ell_p/k_BT} & , \text{ large } f \end{cases}$$

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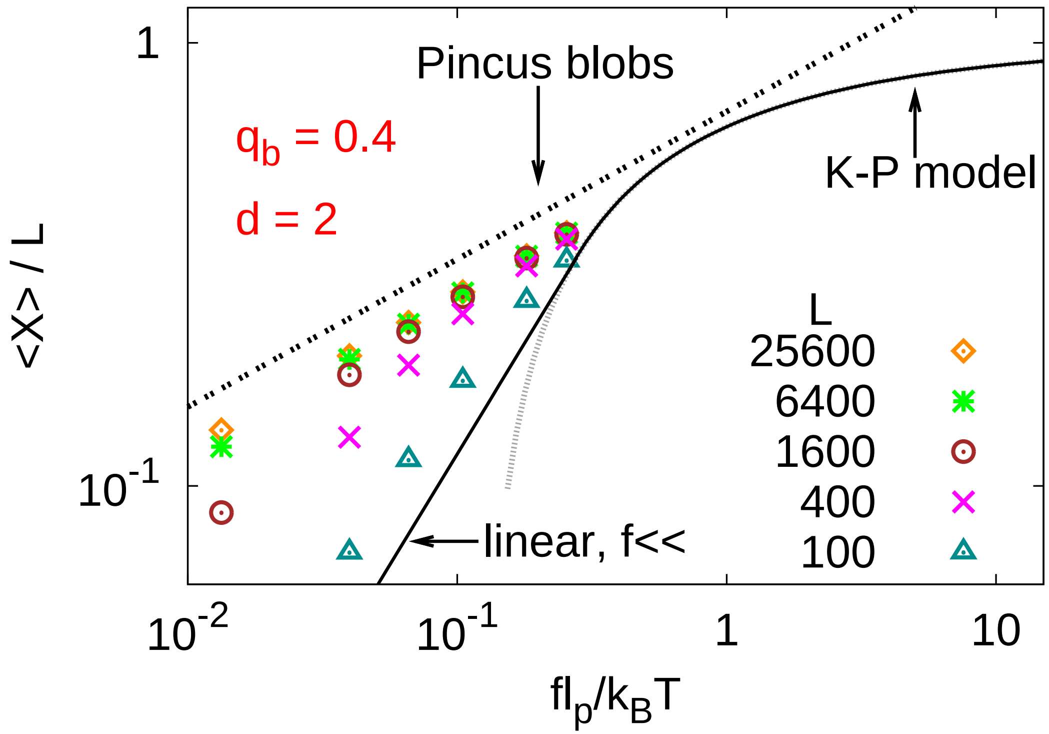

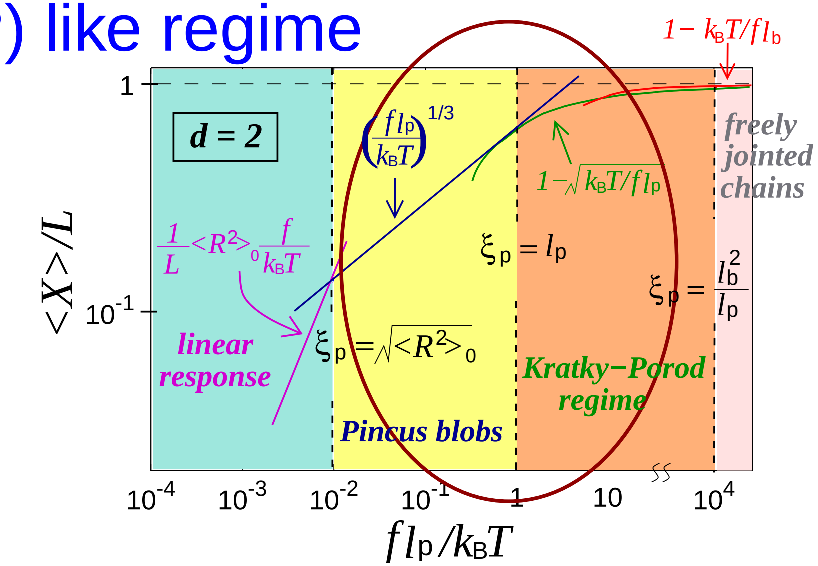

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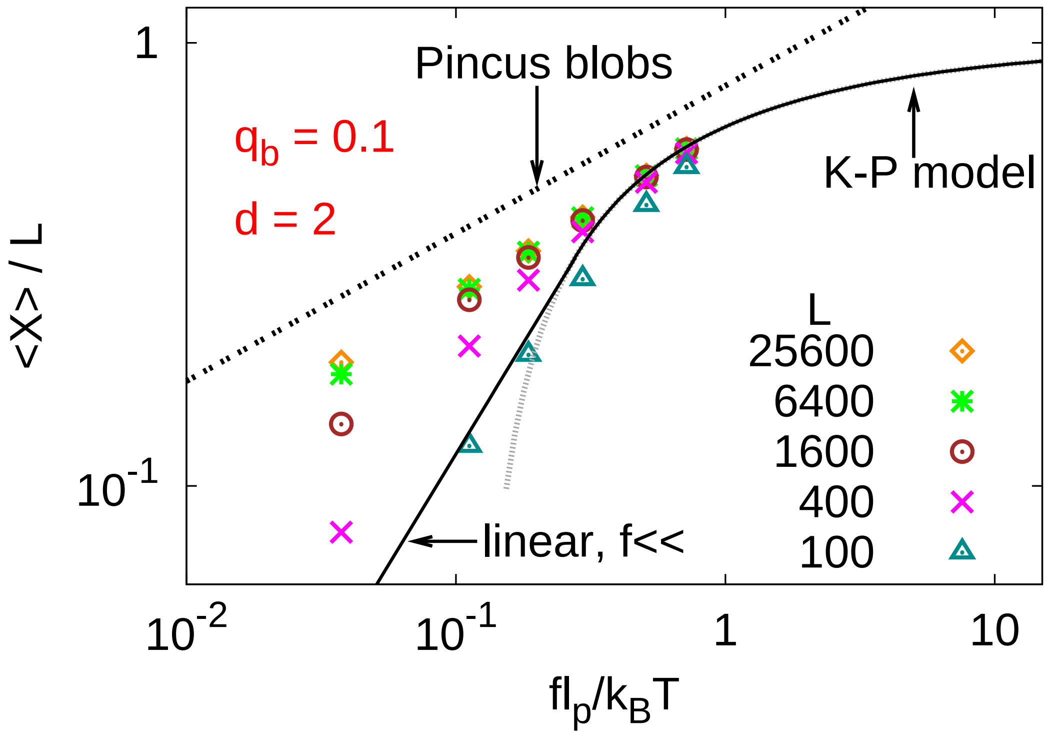

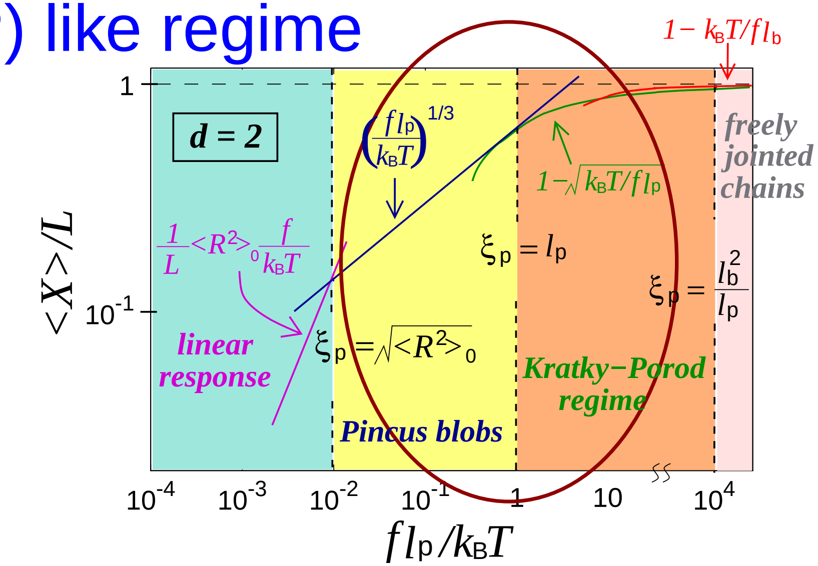

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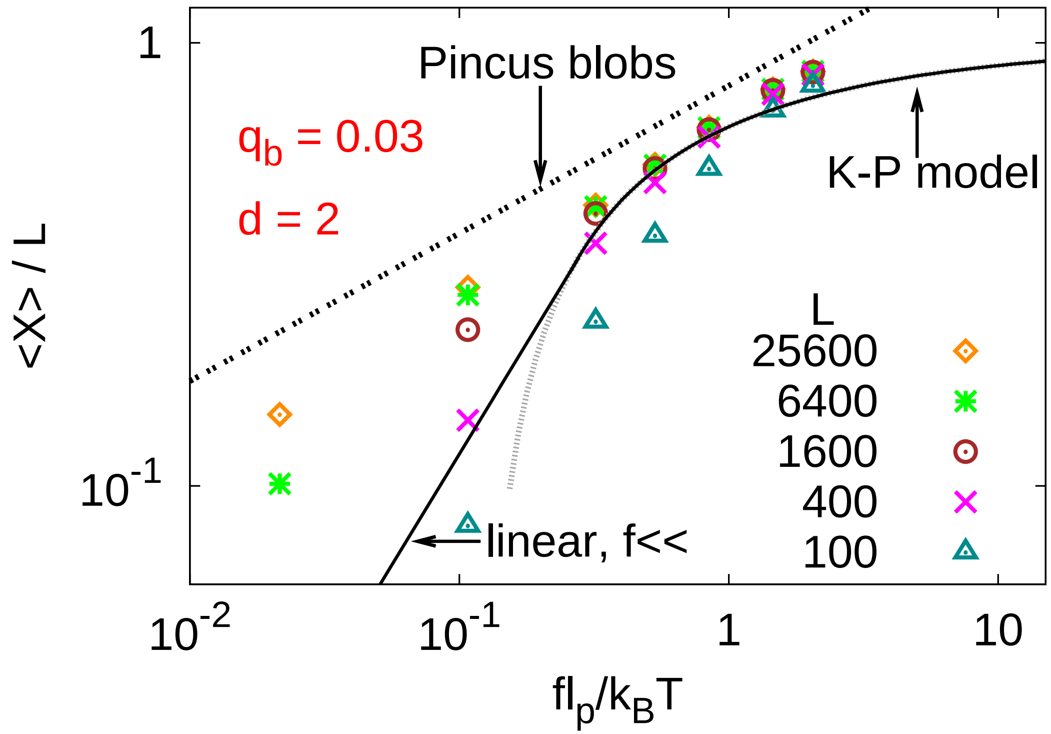

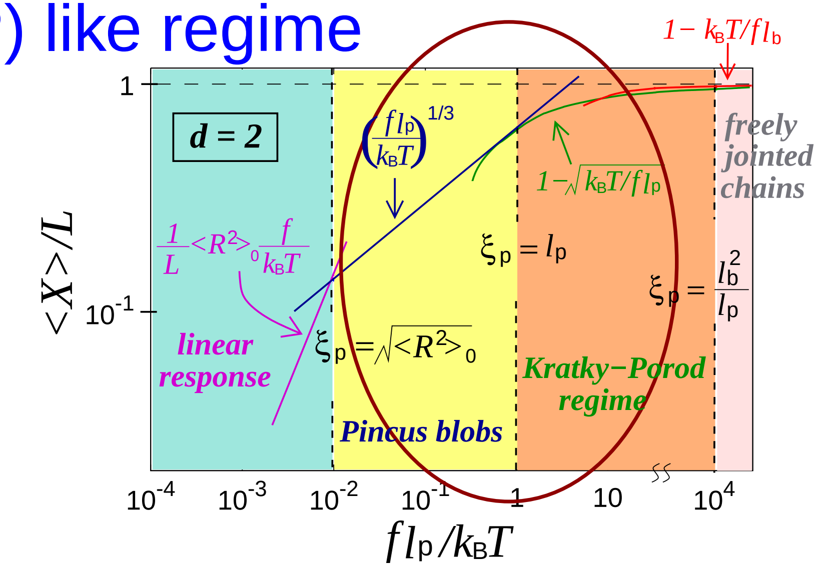

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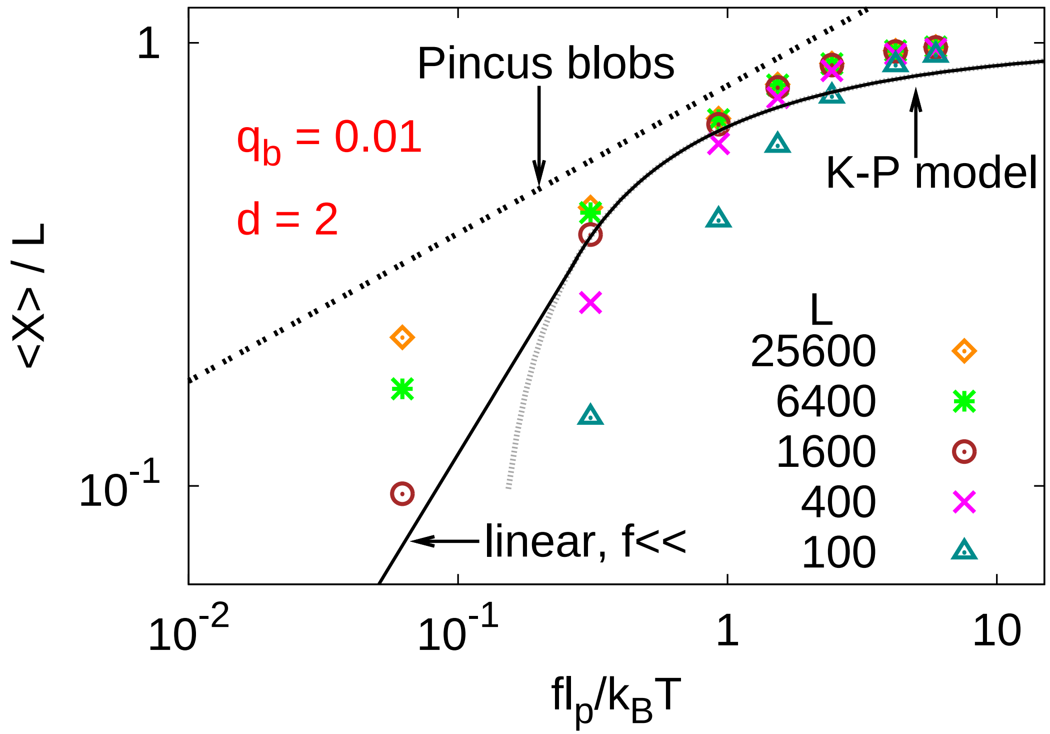

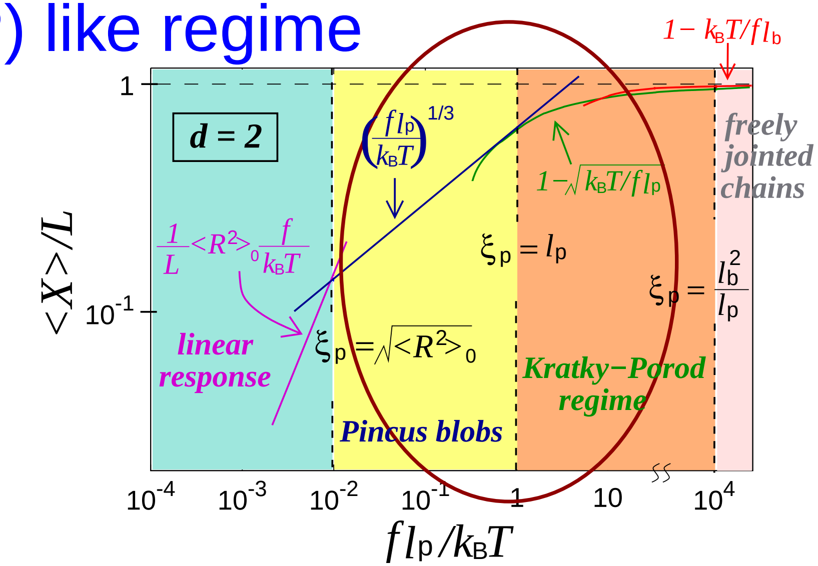

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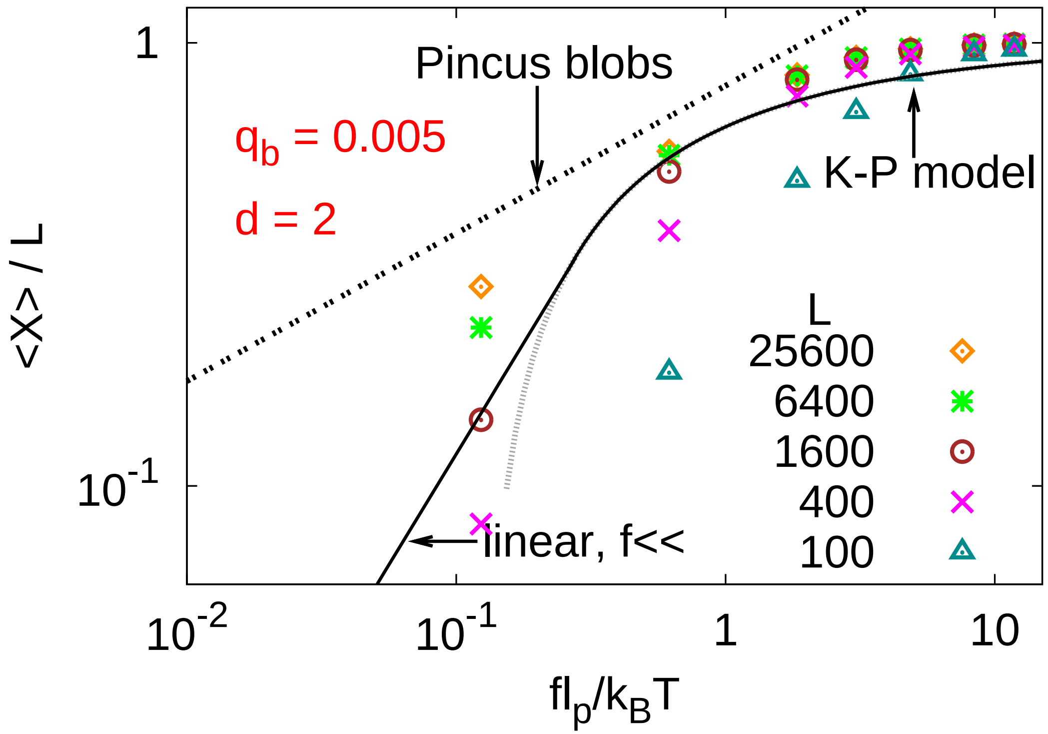

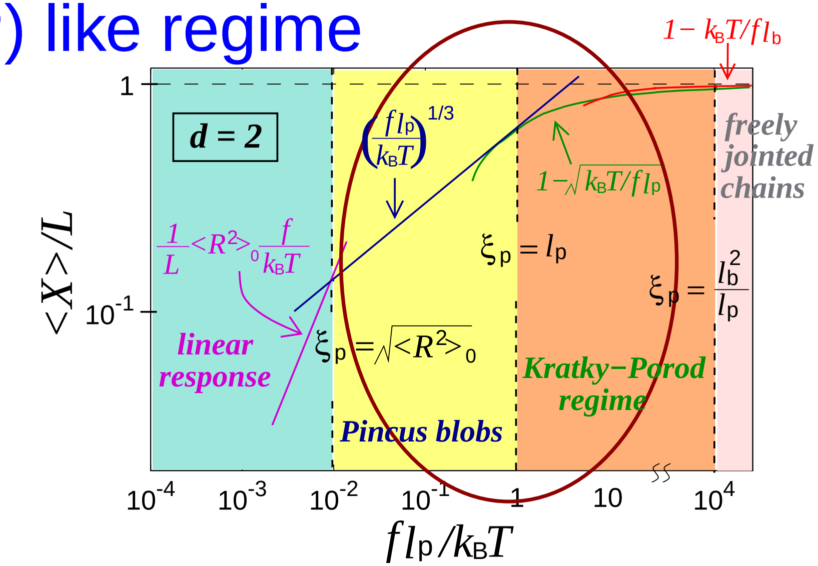

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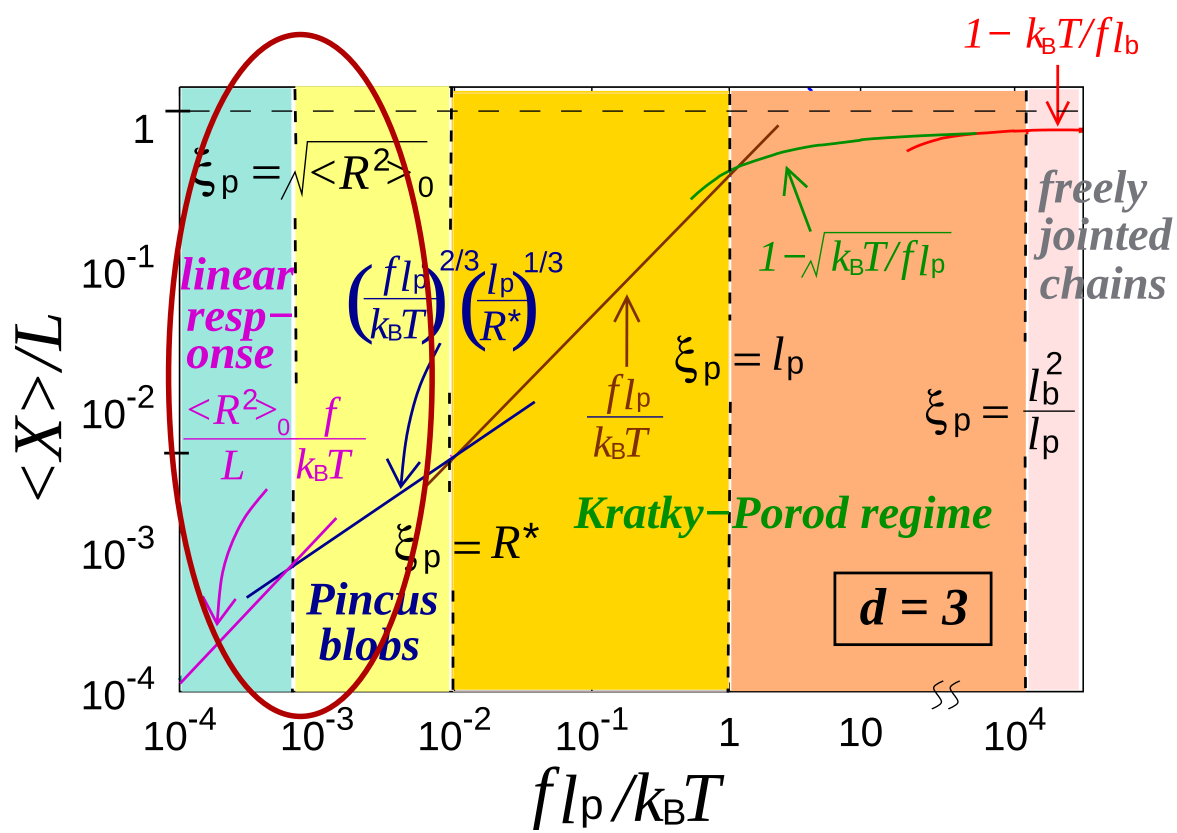

$(x_{cr}, y_{cr}) \sim \mathcal{O}(1)$

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

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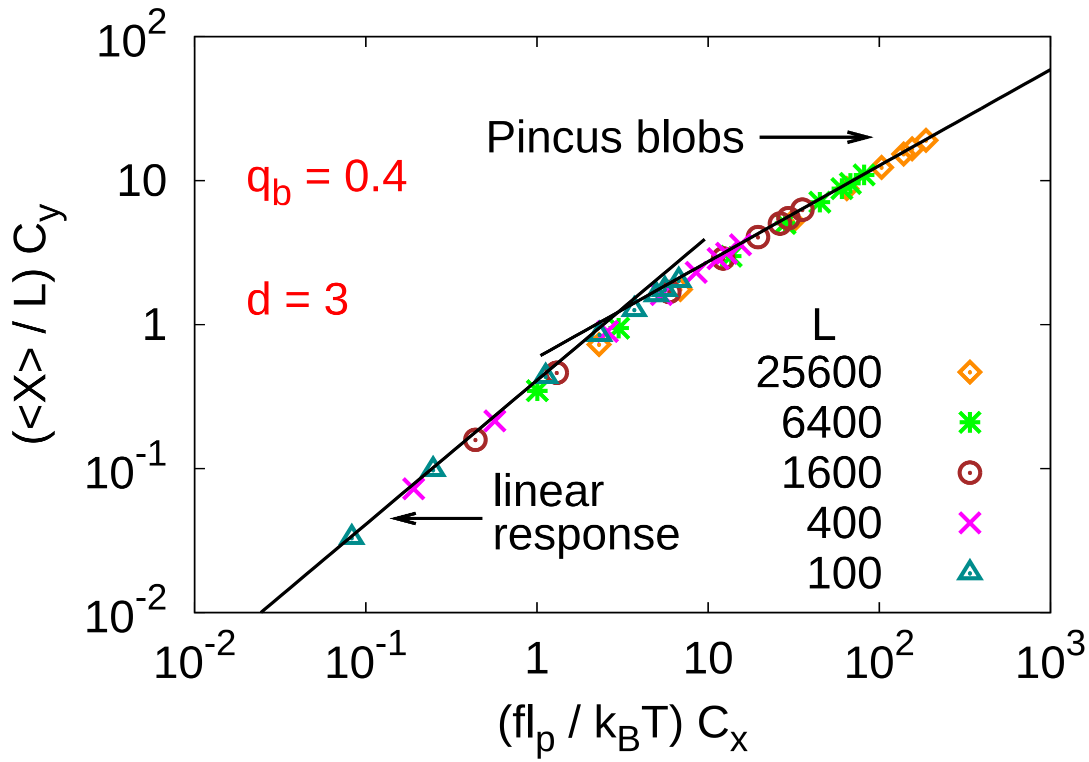

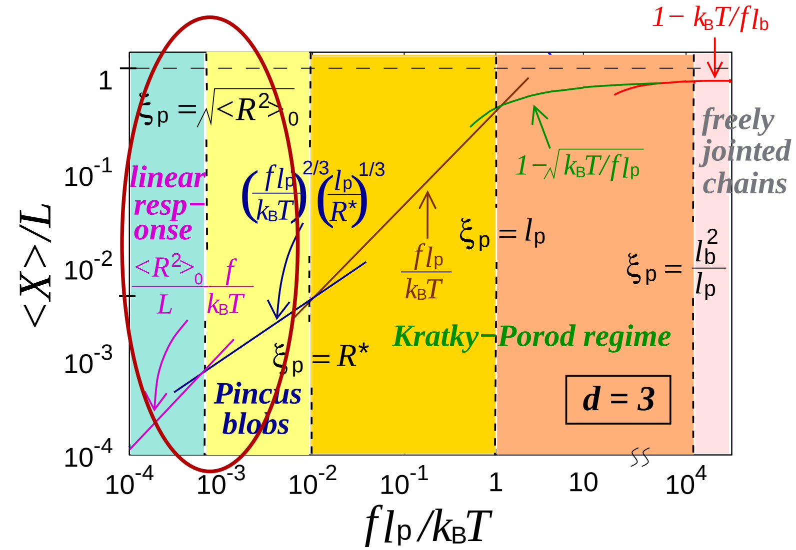

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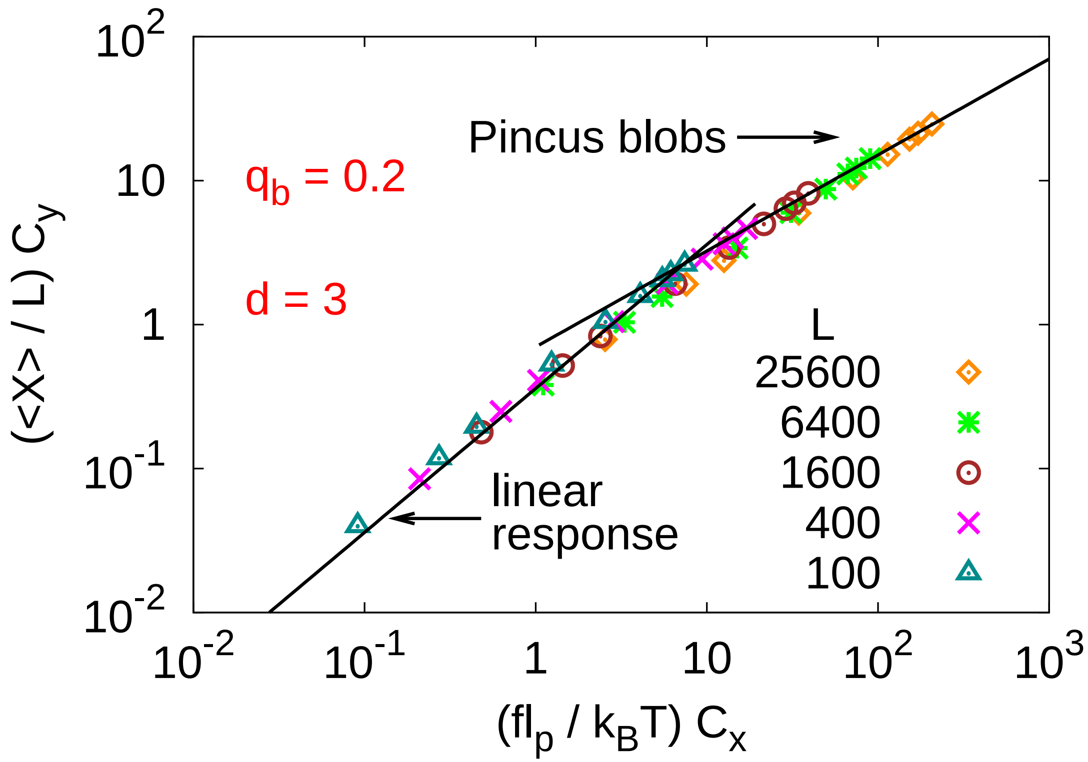

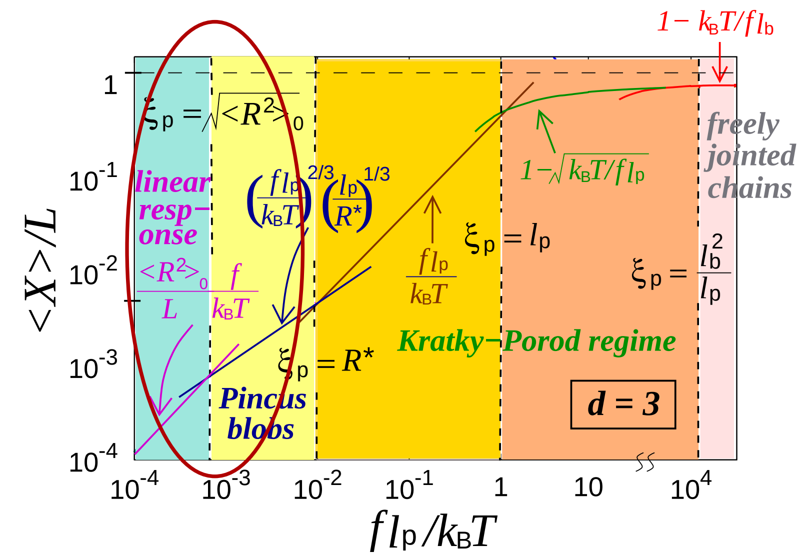

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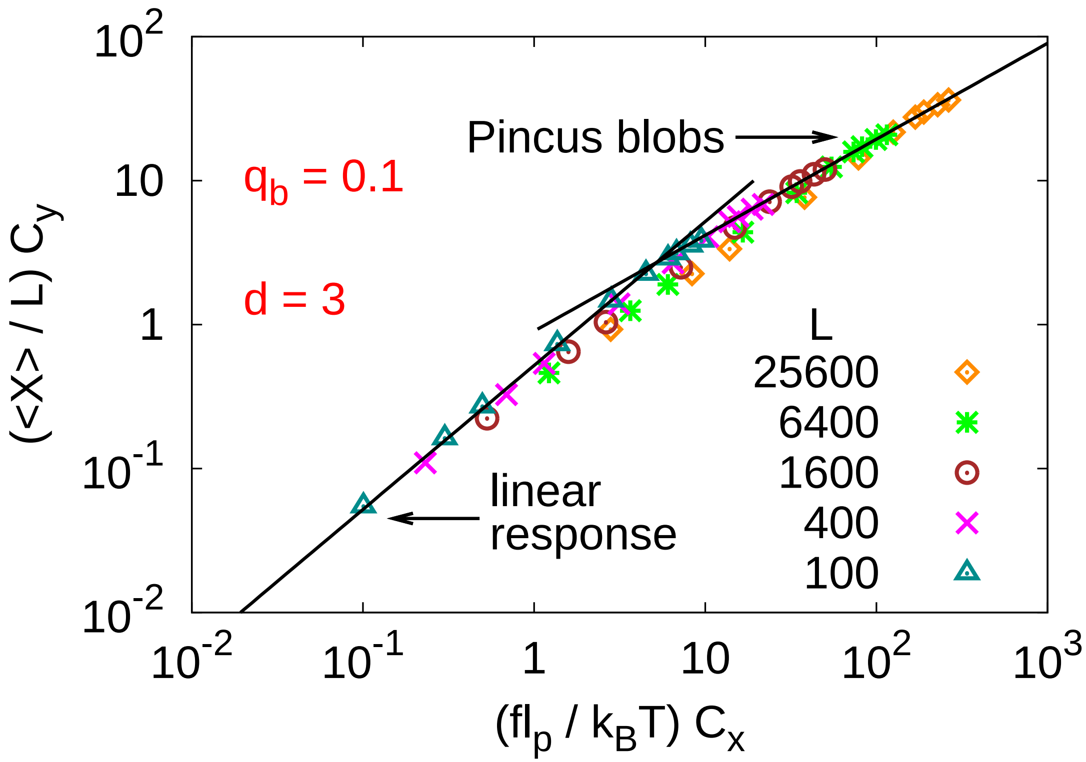

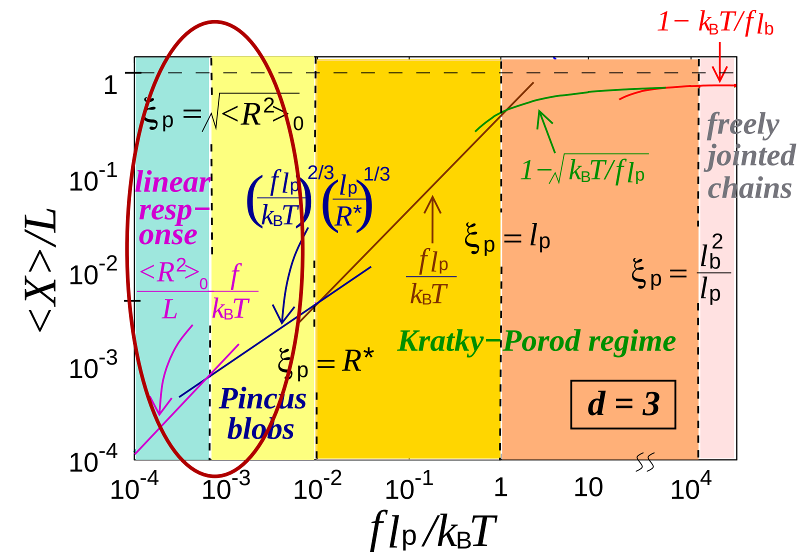

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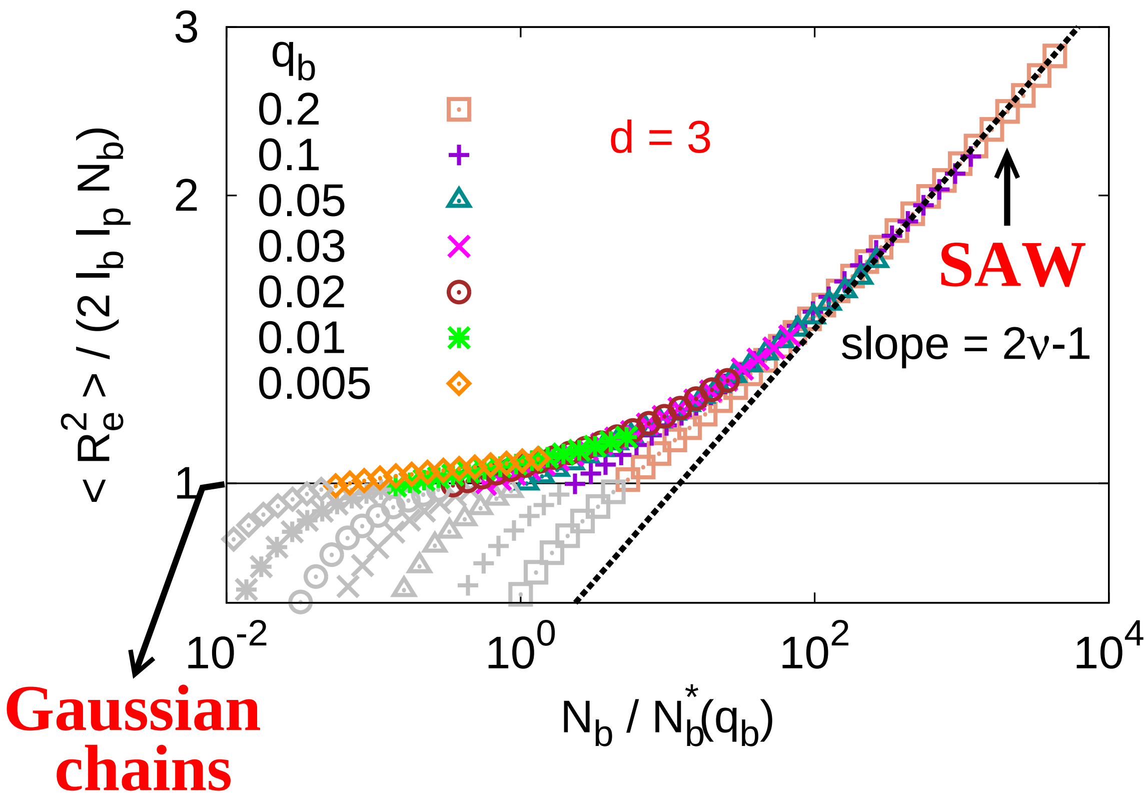

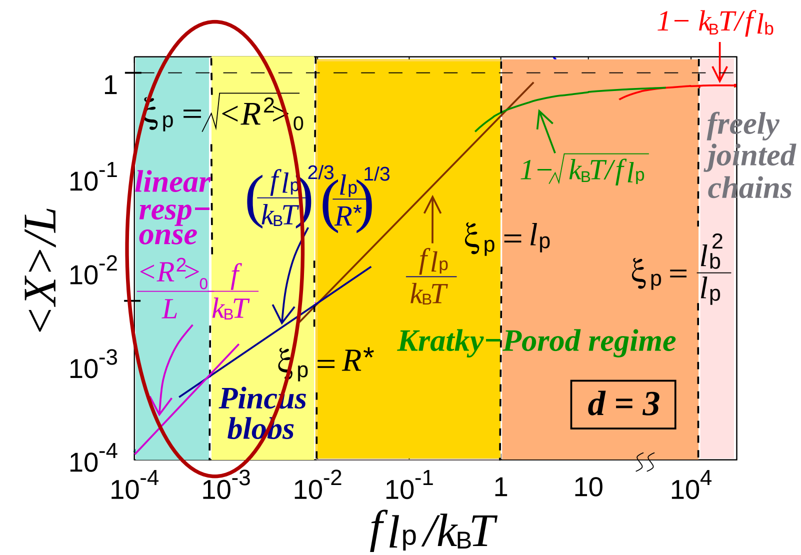

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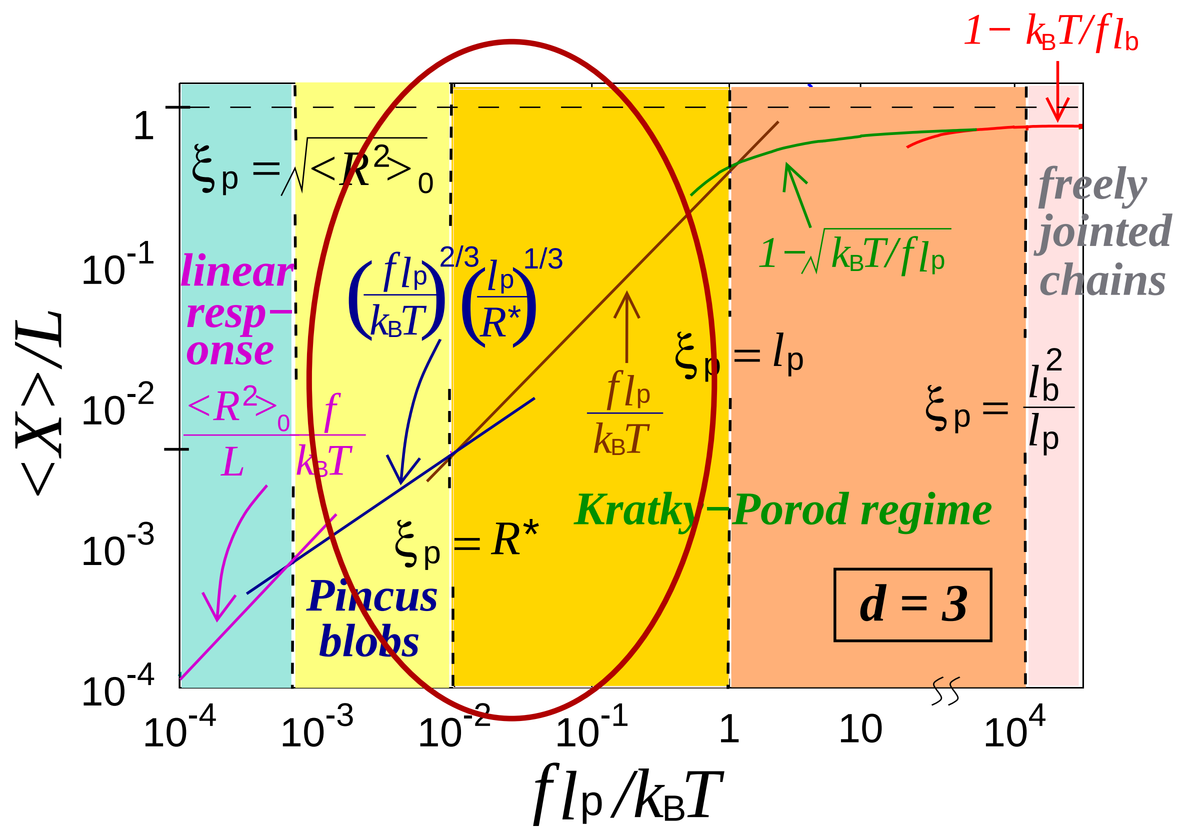

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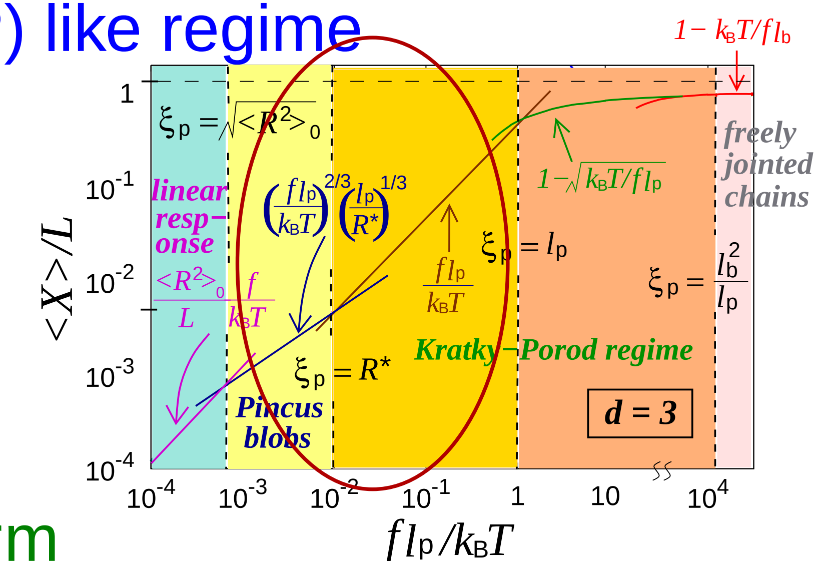

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$$\Rightarrow \frac{\langle X\rangle}{L} \approx \begin{cases} 2f\ell_p/3k_BT & , \text{ small } f \\ 1 - 1/\sqrt{4f\ell_p/k_BT} & , \text{ large } f \end{cases}$$

Monte Carlo results in $d = 3$

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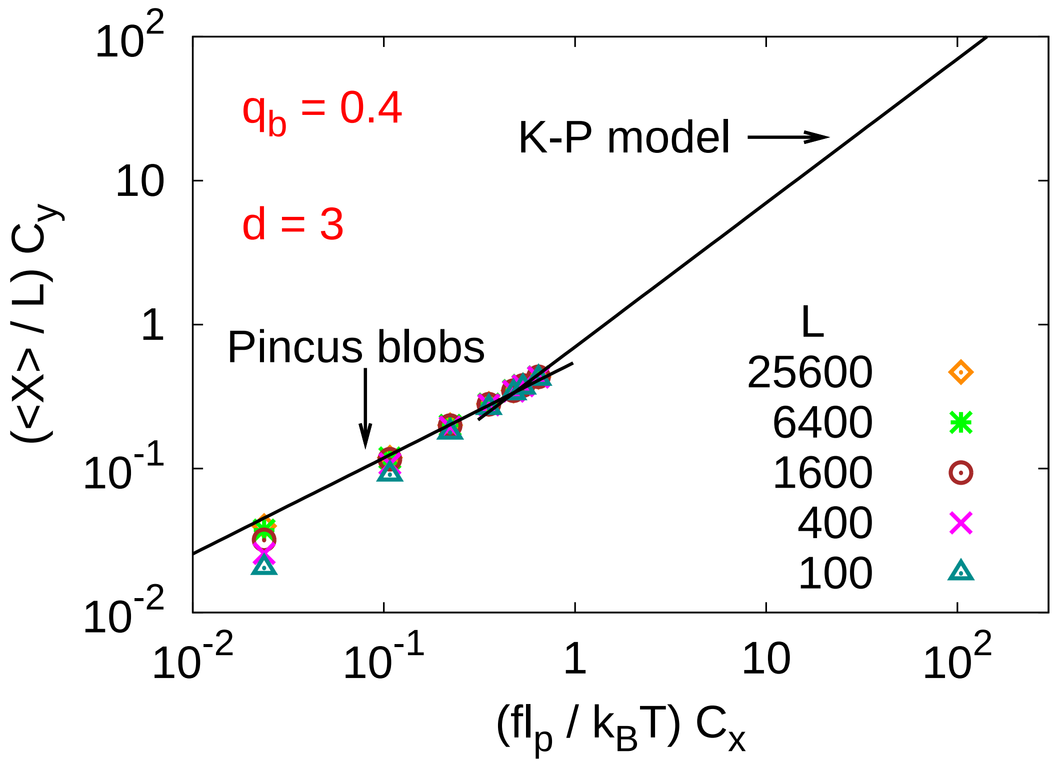

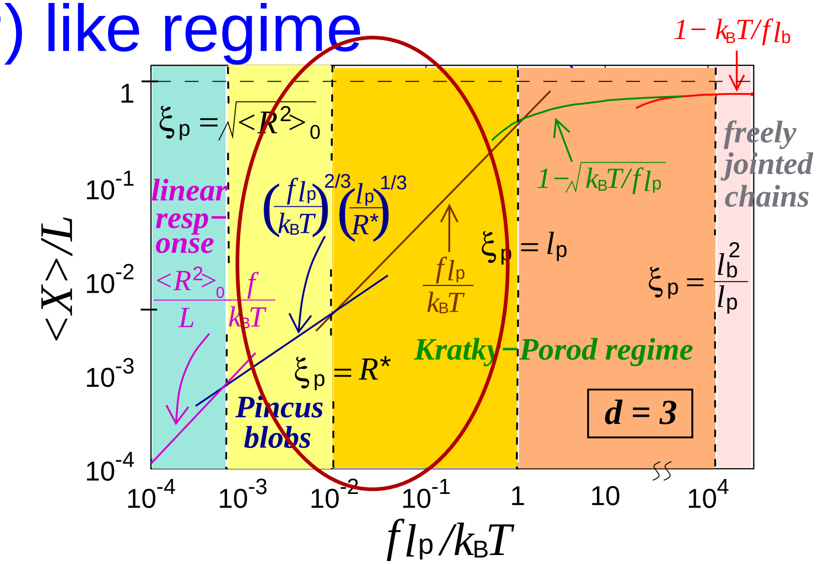

q_b	
0.4	flexible
0.2	
0.1	
0.05	
0.03	
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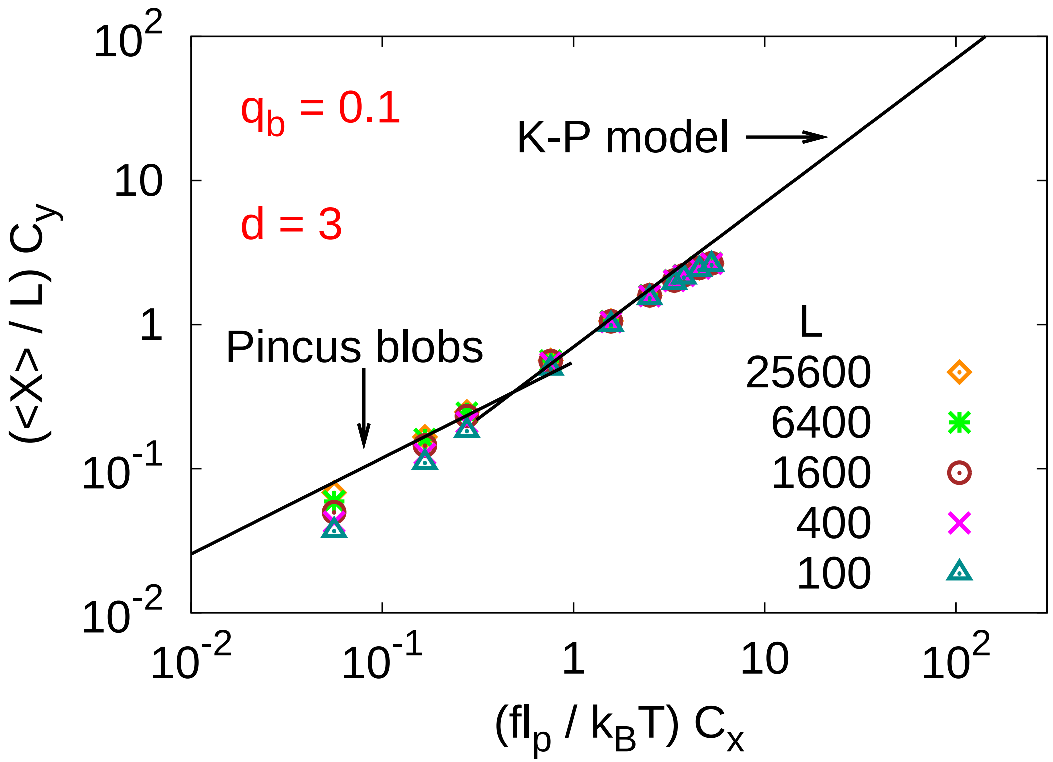

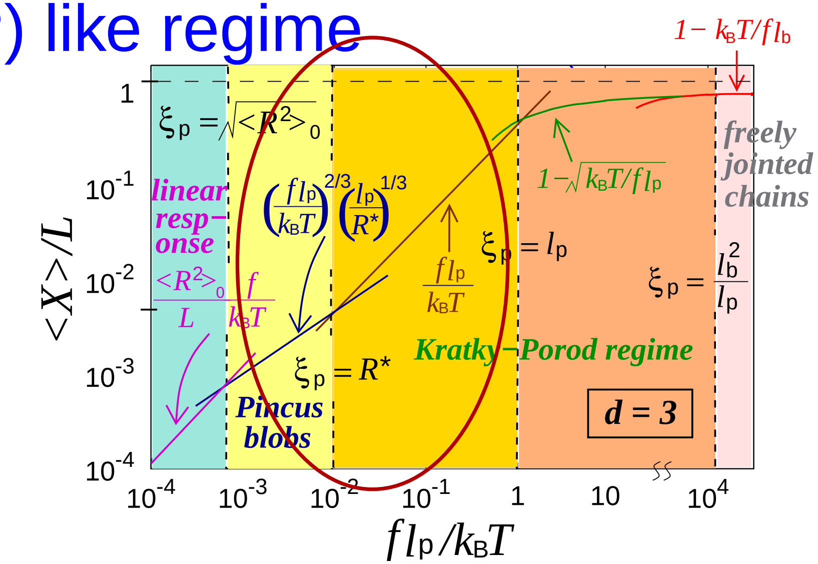

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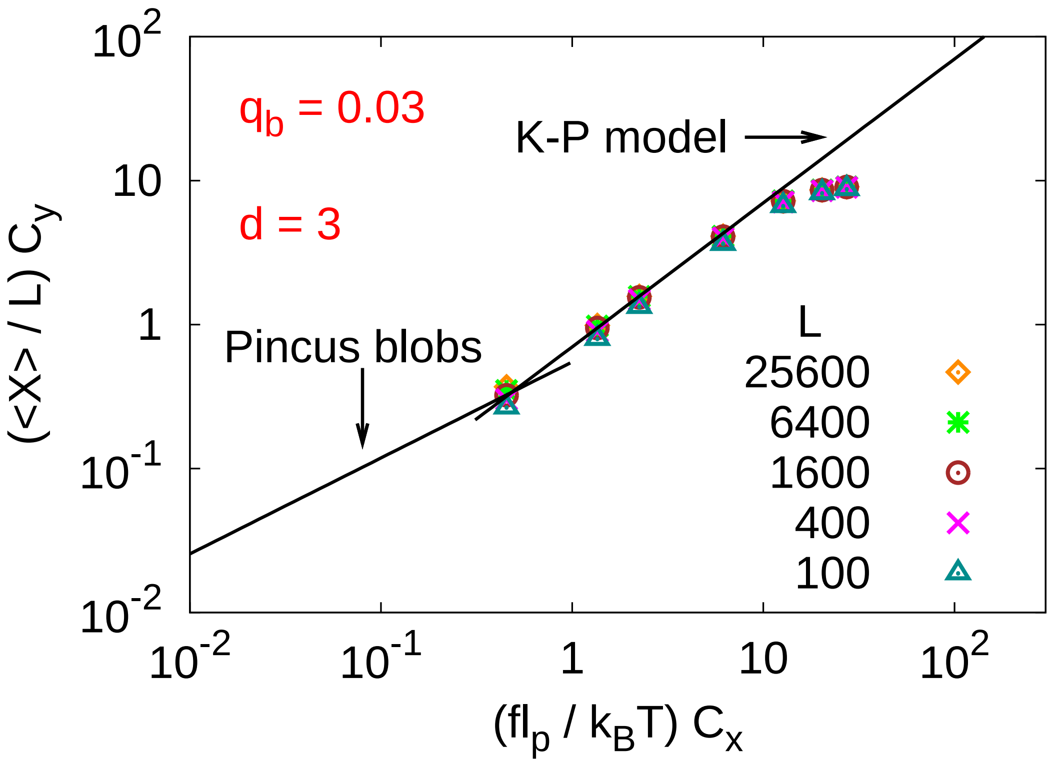

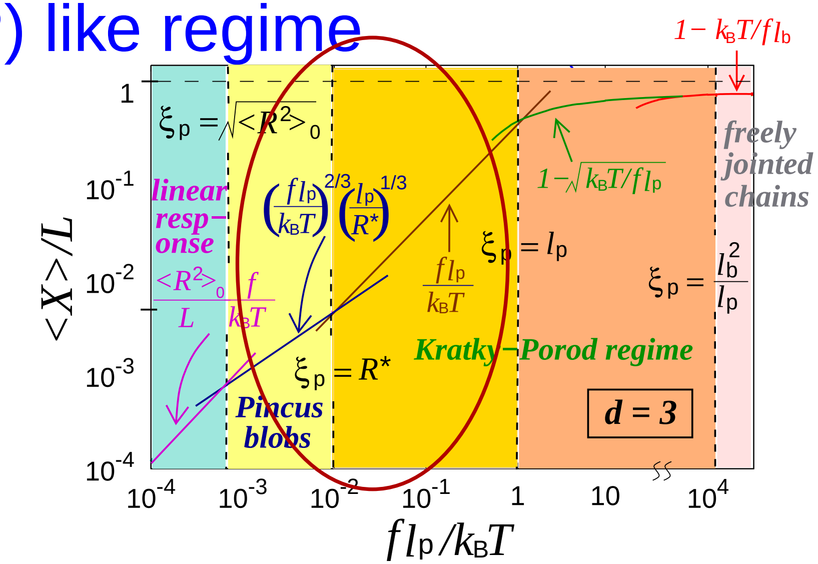

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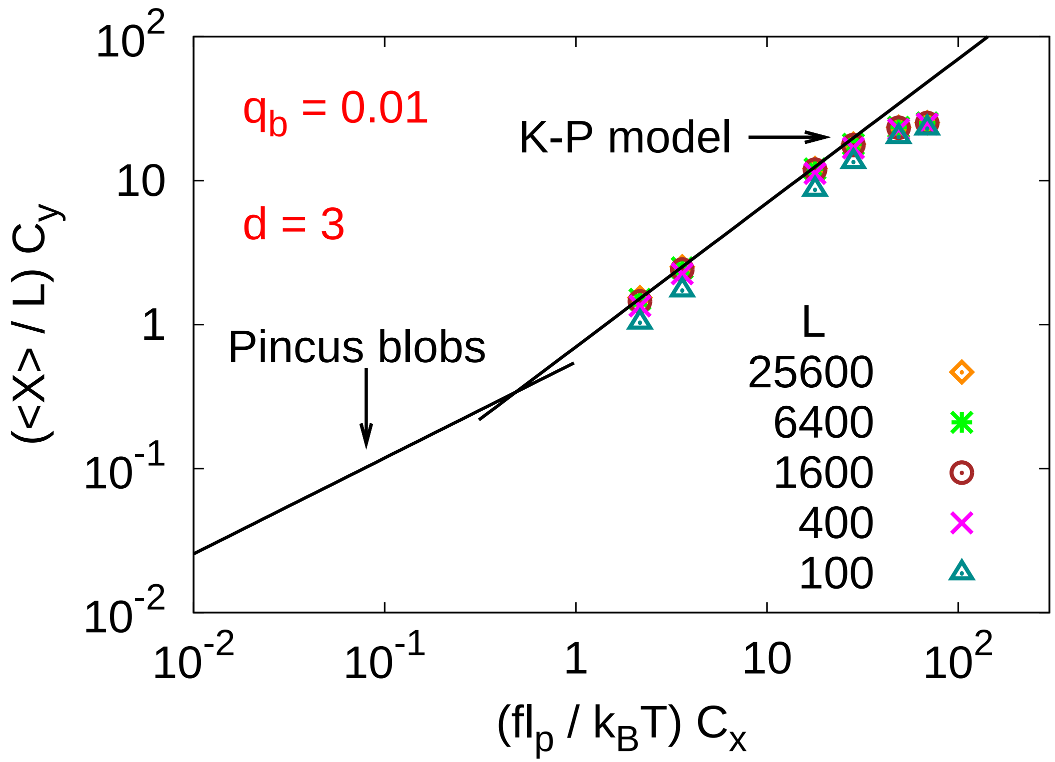

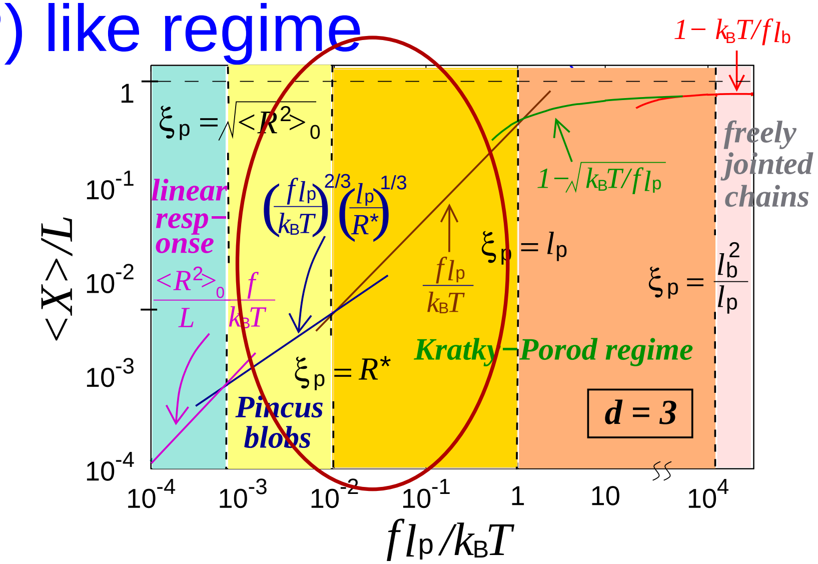

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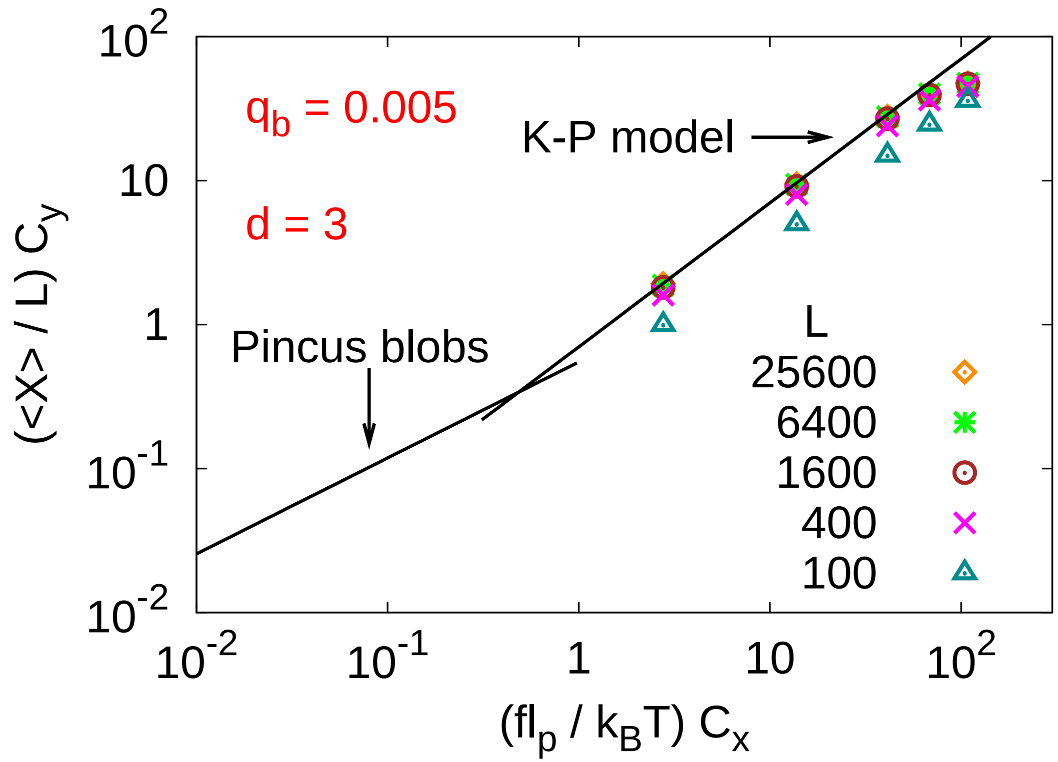

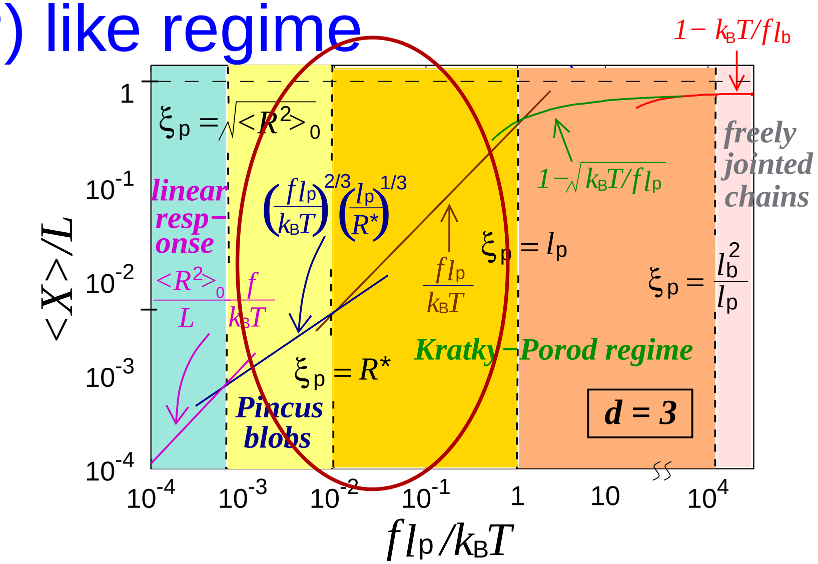

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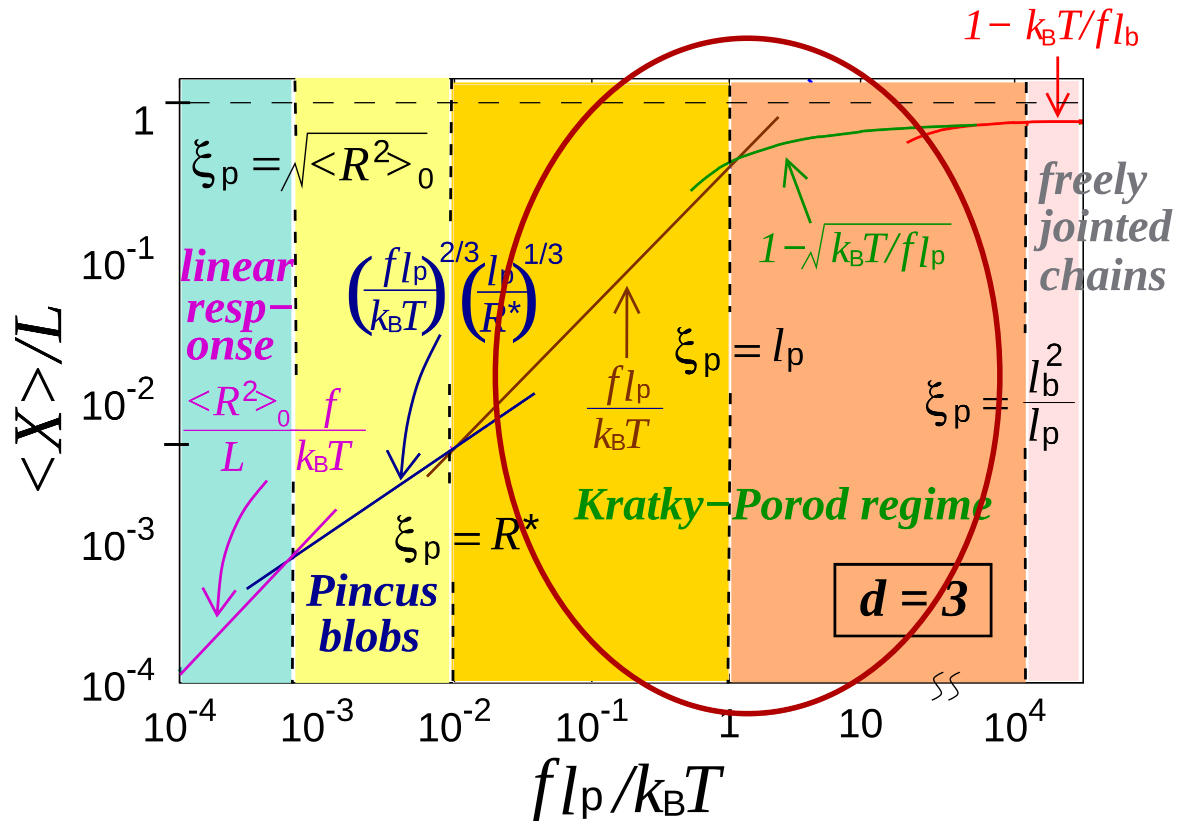

$(x_{\mathrm{cr}}, y_{\mathrm{cr}}) \sim \mathcal{O}(1) \Rightarrow$ scaling factors: $C_x = 1$, $C_y = 1$

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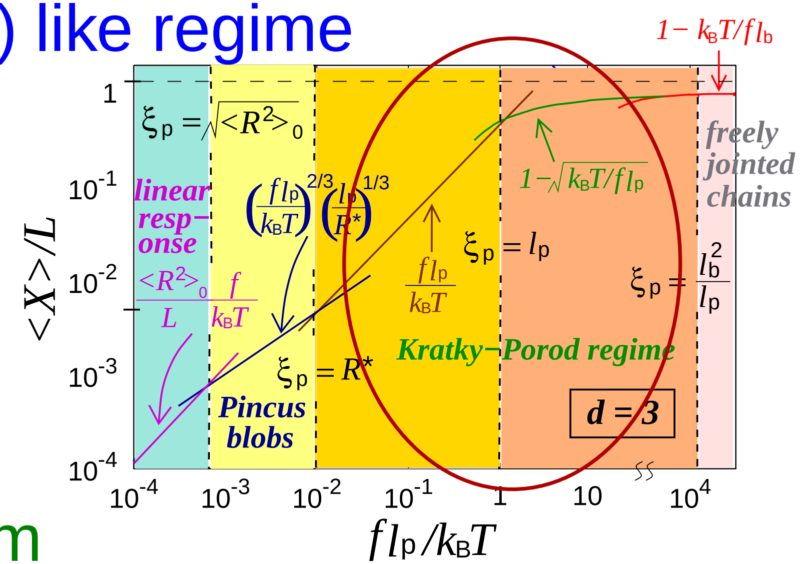


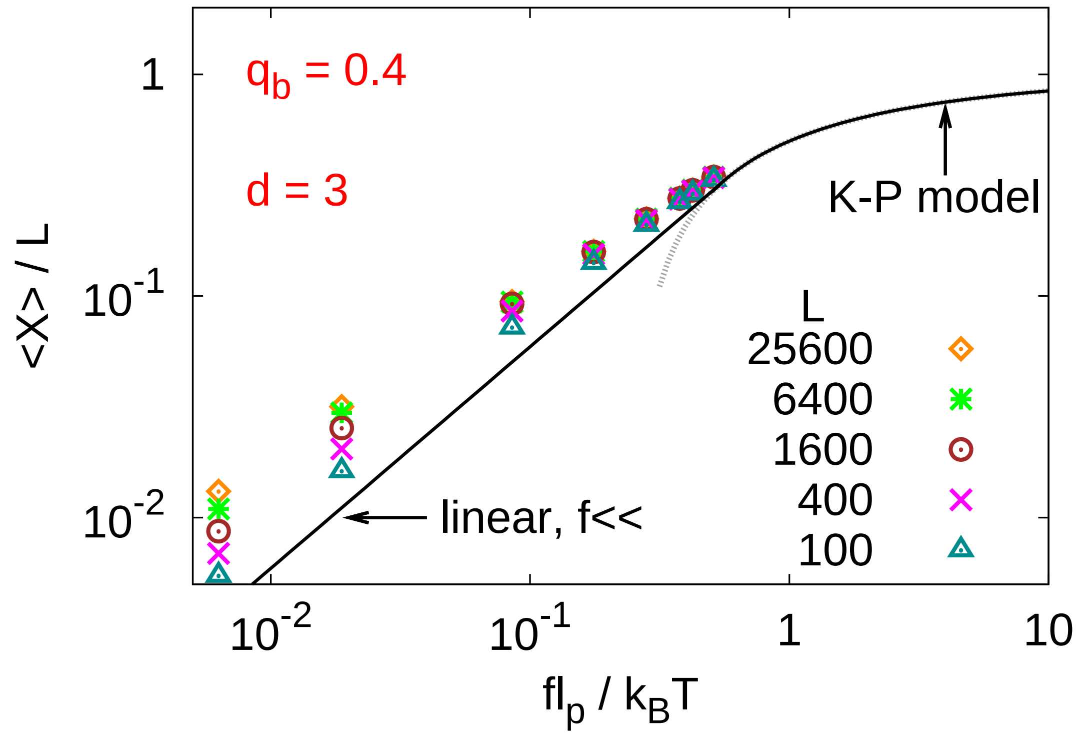
- Kratky-Porod model + a force term

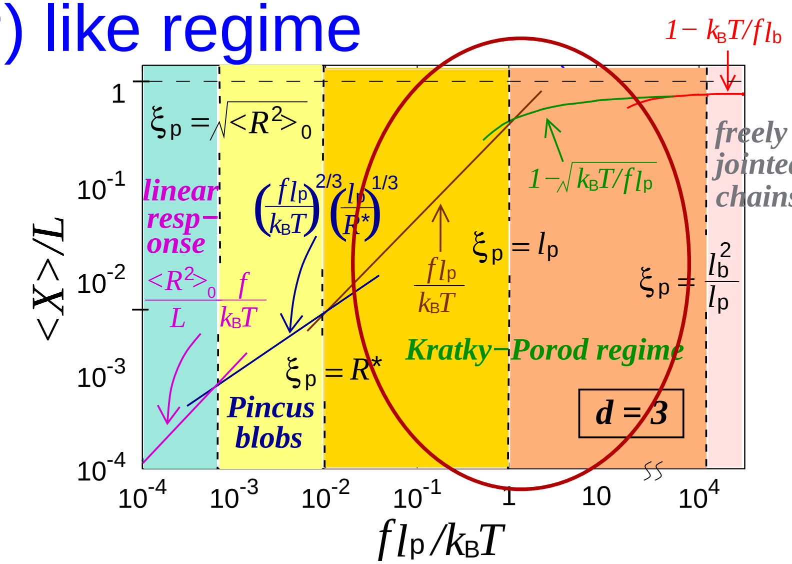
$$\frac{f\ell_p}{k_BT} = \frac{\langle X\rangle}{L} + \frac{1}{4(1-\langle X\rangle/L)^2} - \frac{1}{4}$$

$$\Rightarrow \frac{\langle X\rangle}{L} \approx \begin{cases} 2f\ell_p/3k_BT & , \text{ small } f \\ 1 - 1/\sqrt{4f\ell_p/k_BT} & , \text{ large } f \end{cases}$$

Monte Carlo results in $d = 3$

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





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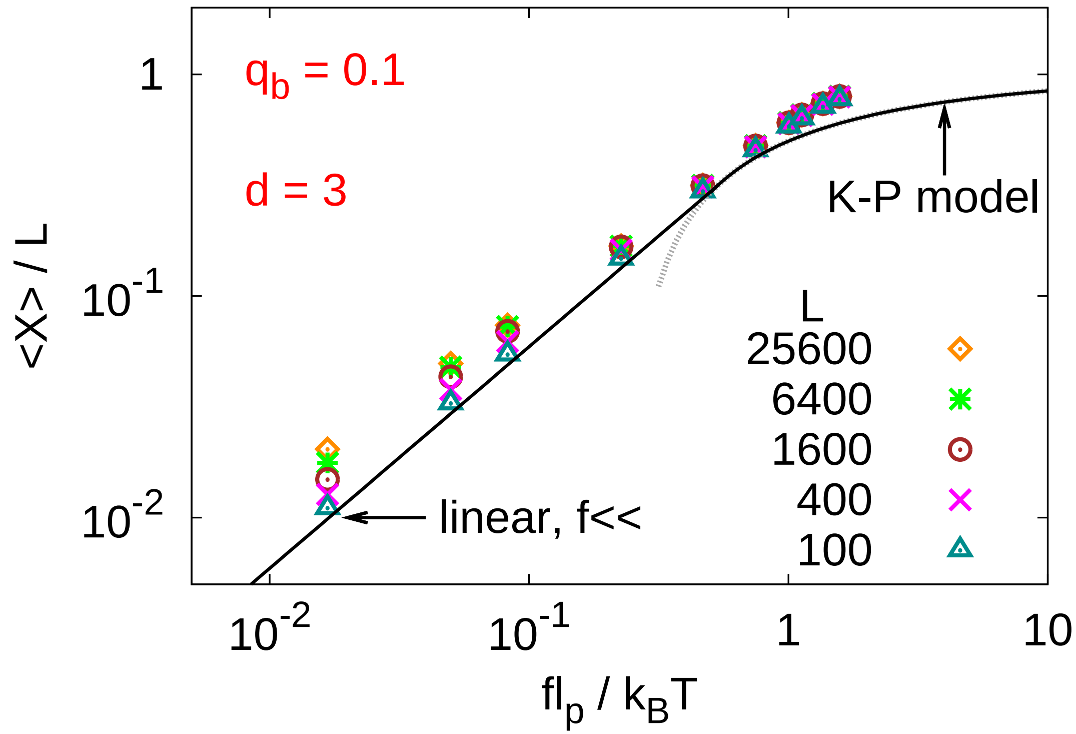

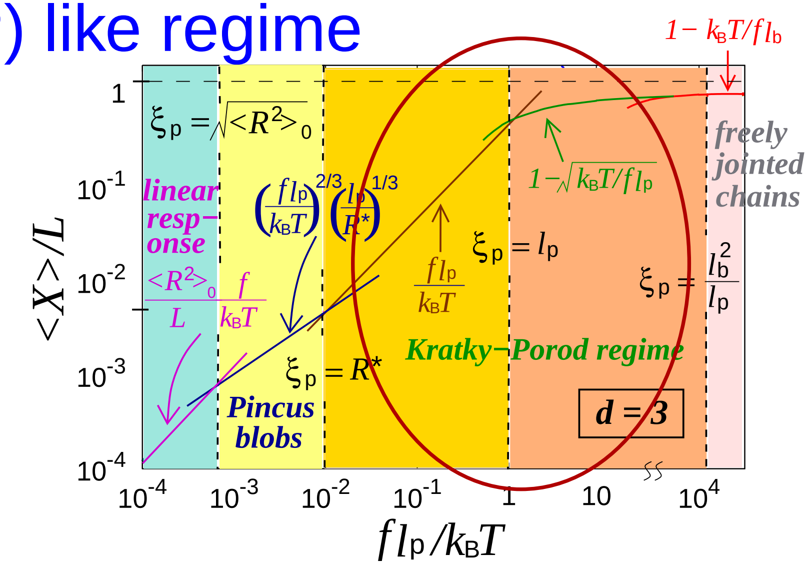

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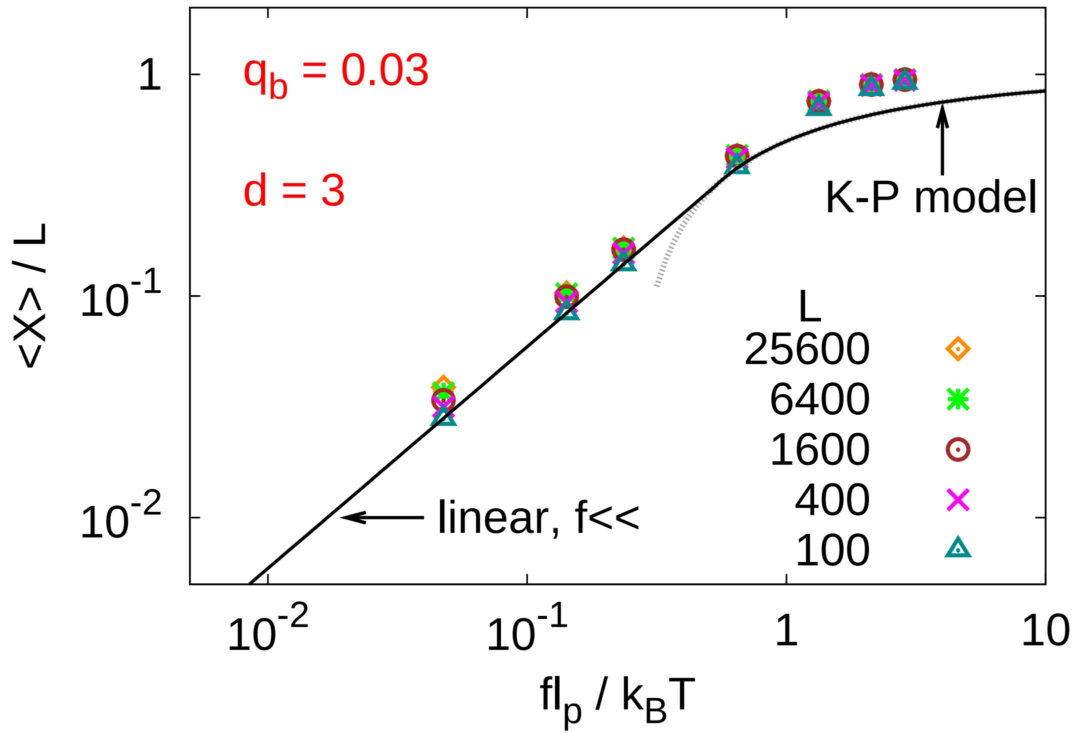

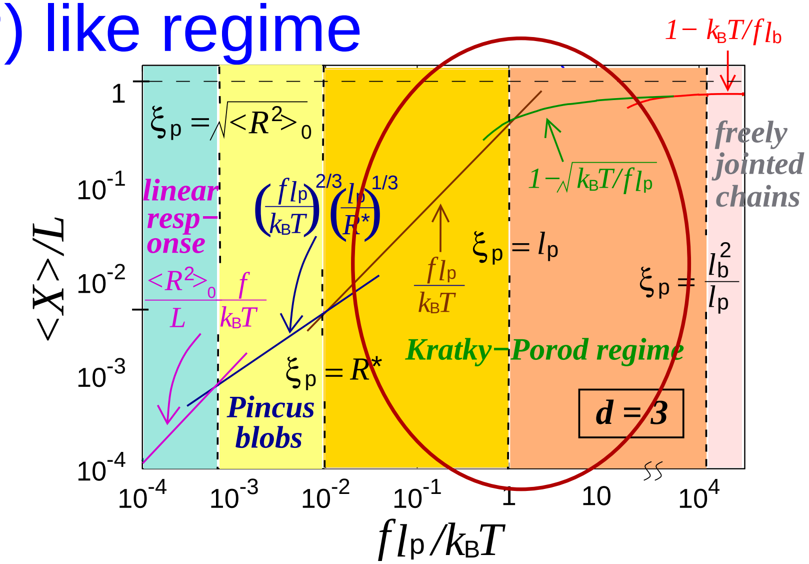

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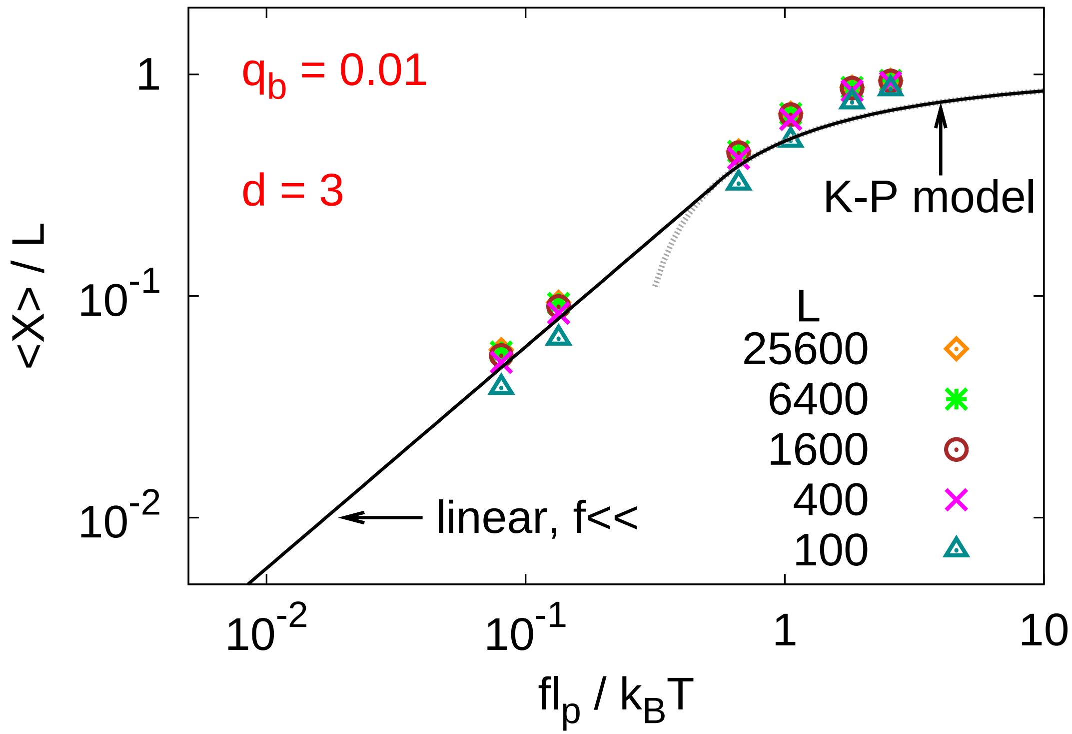

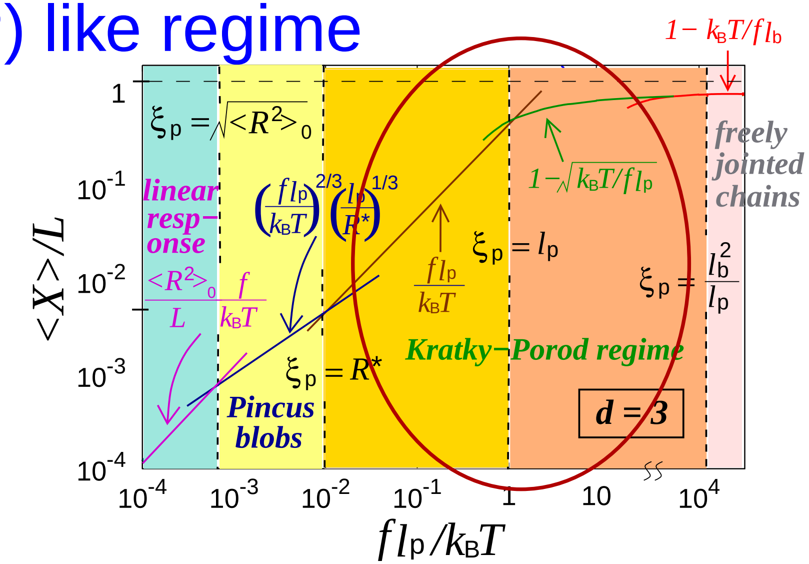

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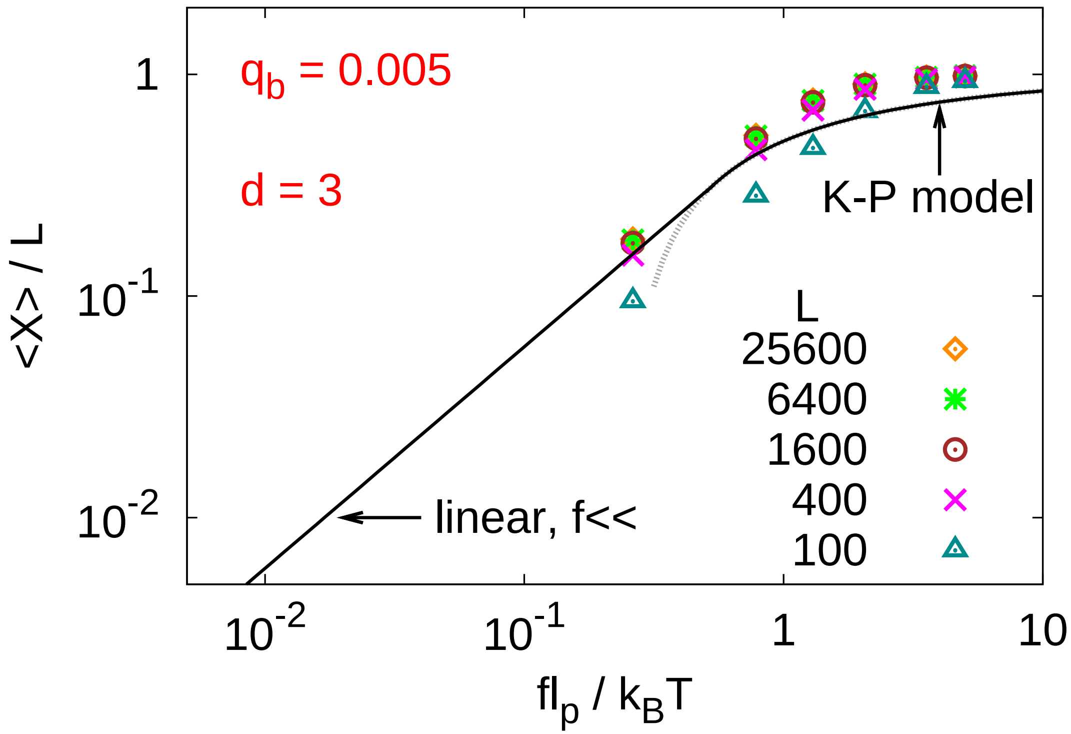

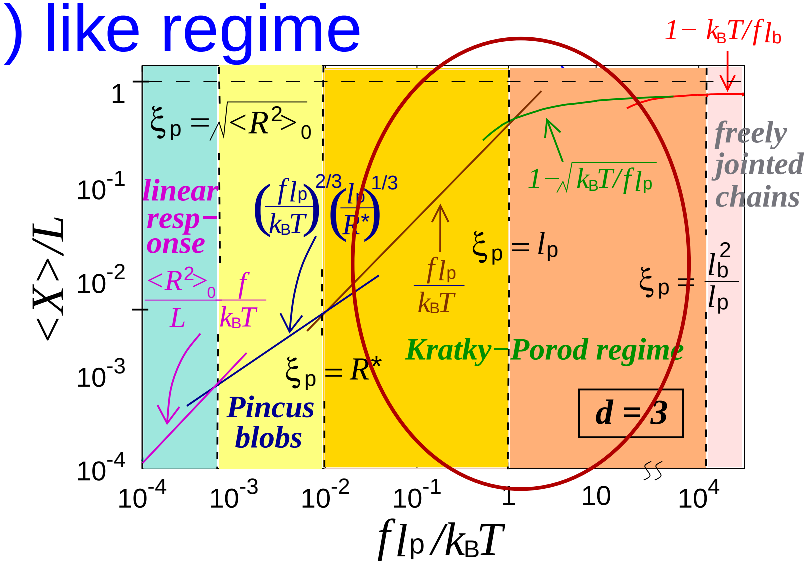

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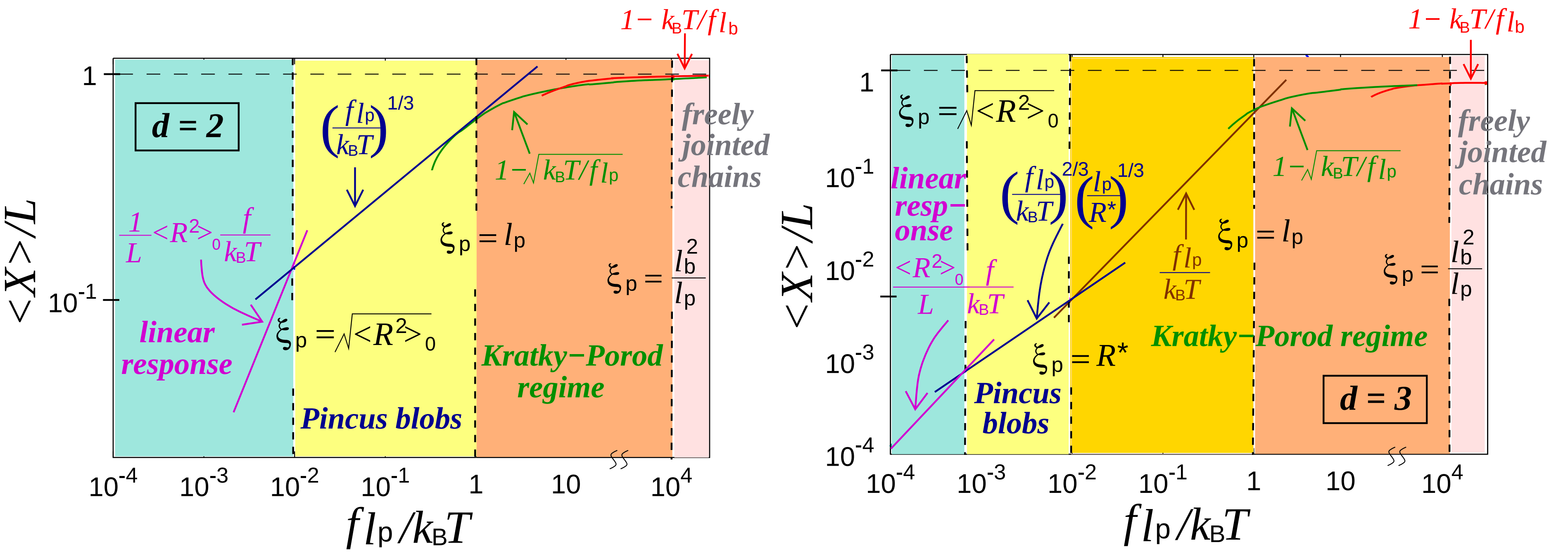
Conclusions



- Theoretical predictions (linear response - Pincus blob - Kratky-Porod model - freely jointed chain) for the force-extension curves are verified.
- Evidence for the importance of excluded volume effects