Stretching a freely-jointed chain with two-level hinges

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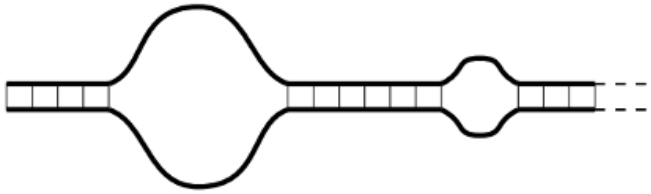
Overview

- Motivation - Background
- Model
- Recursion relation for arbitrary N
- Casimir force
- Landau (mean field) theory
- Generating function approach
- Summary - Outlook

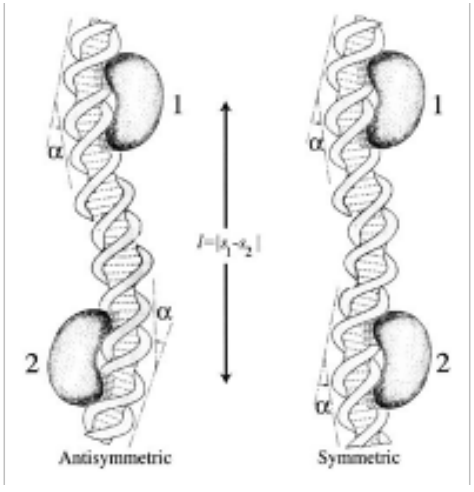
Motivation - Background

DNA denaturation bubbles



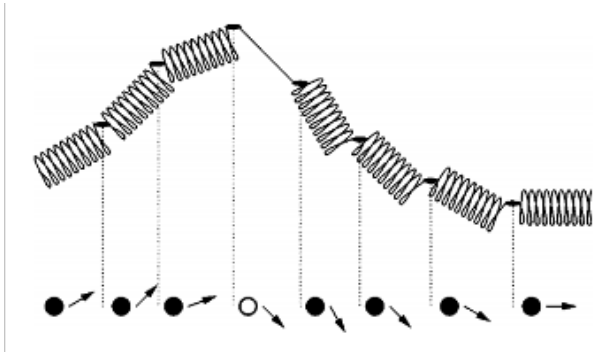
Y. Kafri *et al.* PRL (2000)

DNA-binding proteins



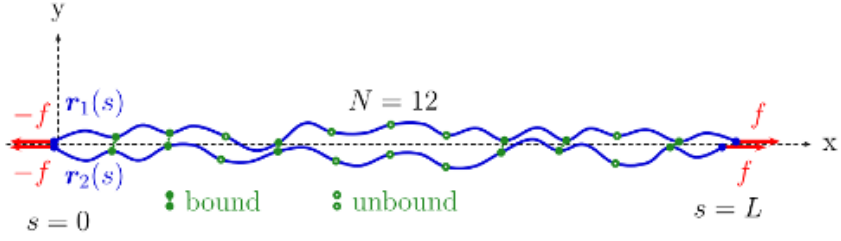
J. Rudnick *et al.* Biophys. J. (1999)

Helix-Coil transition in polypeptides



A. Levine *et al.* PRE (2005)

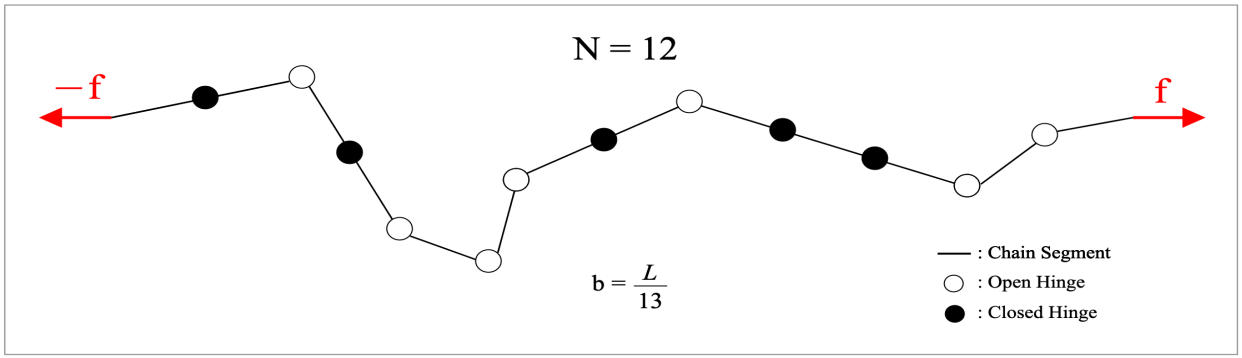
Cross-linked F-Actin filaments



P. Benetatos *et al.* New J. Phys. (2014)

Model: reversible Freely Jointed Chain (rFJC)

What all the above systems have in common is the presence of two reversible local microstates which differ in bending stiffness. We seek a minimal theoretical model in order to understand the underlying physics.



N is the total number of hinges, b is the rod length, $(N+1)b = L$ is the total contour length. Closing a hinge lowers its energy by ϵ.

(Similar to [Tamashiro and Pincus, PRE (2021)] but without cooperativity and [Reinecker *et al.*, Colloid Polym Sci (1995)] but in the Gibbs ensemble.)

Model: reversible Freely Jointed Chain (rFJC)

Partition function

In the Gibbs (fixed tension) ensemble, the partition function reads

$$\mathcal{Z} = \prod_{i=1}^{N} \sum_{n_i=0}^{1} \int d\Omega_i \exp\left(\frac{fb\cos\theta_i}{k_B T}\right) v(n_i) \times \int d\Omega_{N+1} \exp\left(\frac{fb\cos\theta_{N+1}}{k_B T}\right) ,$$

where

$$\begin{aligned} v(n_i) &= \exp\left(\frac{n_i \epsilon}{k_B T}\right) \frac{1}{\sin\theta_i} \delta(\theta_i - \theta_{i+1}) \delta(\phi_i - \phi_{i+1}) , \\ &\quad \text{for} \quad n_i = 1, \\ &= 1, \quad \text{for} \quad n_i = 0 \end{aligned}$$

and $d\Omega_i = \sin\theta_i d\theta_i d\phi_i$

Recursion relation for N reversible hinges

If we define

$$g(n) := \mathrm{e}^{(n-1)\epsilon} 4\pi \frac{\sinh(nf)}{nf},$$

we obtain

$$\begin{aligned} \mathcal{Z}(N) &= \mathcal{Z}(N-1)g(1) + \mathcal{Z}(N-2)g(2) + \mathcal{Z}(N-3)g(3) \\ &\quad + \ldots + \mathcal{Z}(1)g(N-1) + \mathcal{Z}(0)g(N) \\ &\quad + \mathcal{Z}(-1)g(N+1) \end{aligned}$$

for $N \geq 1$, where $\mathcal{Z}(0) = g(1)$ and $\mathcal{Z}(-1) = 1$.

(Useful for exact numerical calculations.)

We obtain the force-extension relation from $\langle z \rangle = \dfrac{\partial \ln(\mathcal{Z}(N))}{\partial f}$ and the mean occupation number (fraction of closed hinges) from $\langle n \rangle = \dfrac{1}{N} \dfrac{\partial \ln(\mathcal{Z}(N))}{\partial \epsilon}$. (We assume $k_B T = 1$ and $b = 1$.)

Fluctuation-mediated (Casimir) force

The entropic change in the Gibbs free energy of a uFJC due to the presence of two closed hinges (adsorbed ligands) at sites i and $j > i+1$ is

$$\begin{aligned}\Delta G(i|j>i+1) &= -2\ln\left[\frac{4\pi\sinh(2f)}{2f}\right] \\ &\quad +4\ln\left[\frac{4\pi\sinh(f)}{f}\right]\end{aligned}$$

The corresponding change if the two closed hinges are located at i and $i+1$ is

$$\begin{aligned}\Delta G(i|i+1) &= -\ln\left[\frac{4\pi\sinh(3f)}{3f}\right] \\ &\quad +3\ln\left[\frac{4\pi\sinh(f)}{f}\right]\end{aligned}$$

We can show that the difference is always

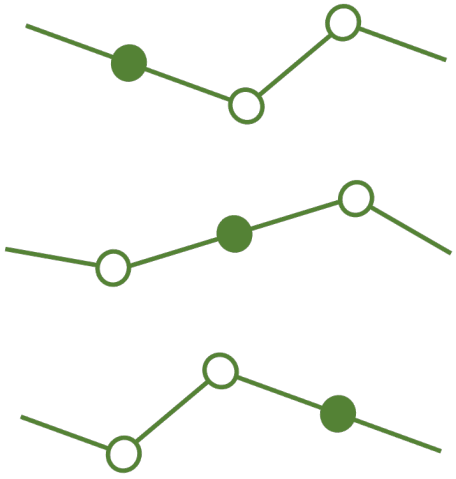
$$\Delta G(i|i+1) - \Delta G(i|j>i+1) < 0\ ,$$

which implies a nearest-neighbour (short range) Casimir attraction. As such, it is incapable of driving a phase transition in our $1d$ system.

Similar for a wormlike chain with fluctuating bending stiffness [Levine *et al.*, PRE, (2013)].

Membranes are different [Pincus *et al.*, Biophys. J., (1994)].

Mean field approach - Gibbs ensemble



rFJC with b

$(N = 3,\ N_c = 1, \mathrm{L} = 4\mathrm{b})$

uFJC with $\tilde{b} \equiv \frac{(N+1)b}{N+1-N_c}$

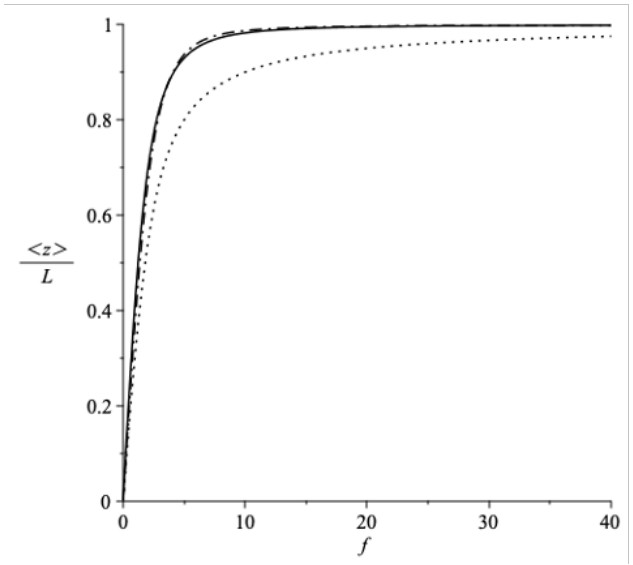
$(\tilde{b} = \frac{4}{3}b,\ L = 4b)$

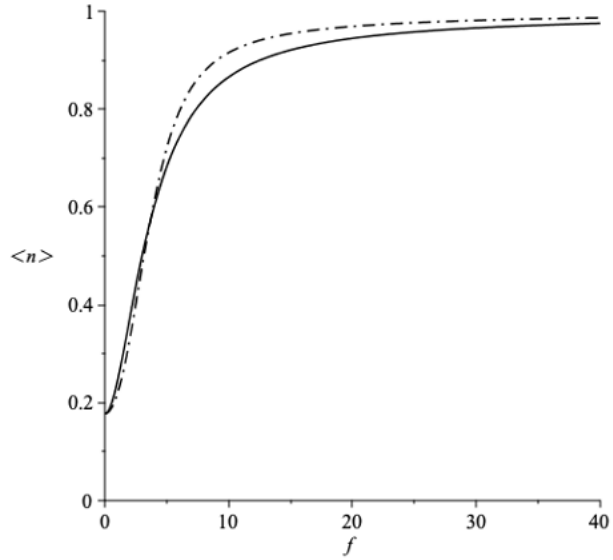
$$\mathcal{Z}(N) \approx \sum_{N_c=0}^{N} \binom{N}{N_c} \mathrm{e}^{N_c \epsilon} \left[\frac{4\pi \sinh(f\tilde{b})}{f\tilde{b}} \right]^{N+1-N_c}$$

cf. for the uFJC, $\mathcal{Z}(N) = \left(\frac{4\pi \sinh(fb)}{fb} \right)^{N+1}$

Mean field approach - Gibbs ensemble

Force-extension relation, mean occupation number





Force-extension relation for $N = 19$, $\epsilon = 1$, $k_B T = 1$, and $b = 1$.

Solid line: exact (recursion relation)

Dash-dotted: mean field approximation

Dotted: uFJC (for comparison)

Mean occupation number as a function of the tension for $N = 19$, $\epsilon = 1$, $k_B T = 1$, and $b = 1$.

Solid line: exact (recursion relation)

Dash-dotted: mean field approximation

Mean field approach - Gibbs ensemble

Landau Gibbs free energy

For $N \gg 1$, we use the Stirling approximation and replace the sum by the dominant term which corresponds to $N_c = nN$.

n plays the role of an order parameter.

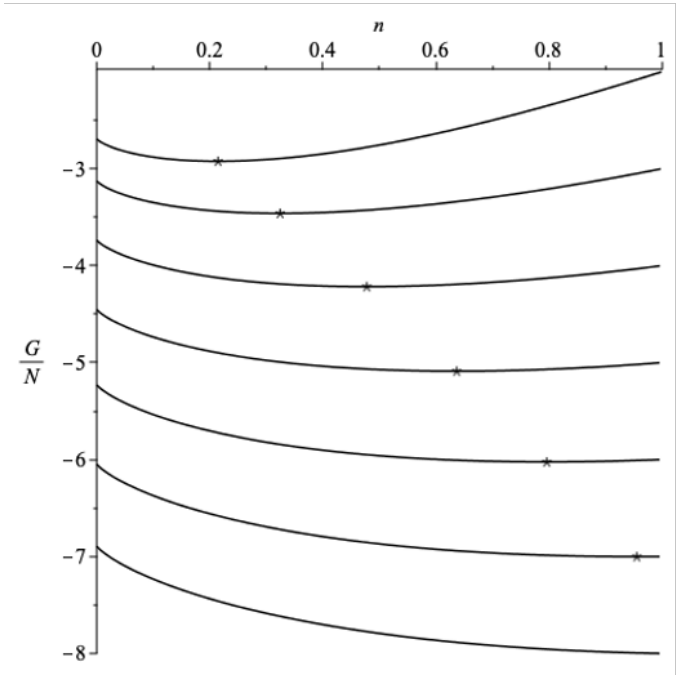
The resulting Gibbs free energy per link reads

$$\begin{aligned} \frac{G}{N} \quad \approx \quad & -\epsilon n + [n \ln(n) + (1-n)\ln(1-n)] \\ & -(1-n)\ln\left[\frac{4\pi(1-n)\sinh(fb/(1-n))}{fb}\right] \end{aligned}$$

The first term is the contribution from the activation energy, the second term is the contribution from the mixing entropy in the realisations of closed hinges, and the last term is related to the tensile energy of the stretched chain.

Mean field approach - Gibbs ensemble

Landau Gibbs free energy



The **Landau Gibbs** free energy per link as a function of n for $\epsilon = 1$ and $f = 1, 2, 3, 4, 5, 6, 7$ (from top to bottom). We assume $k_B T = 1$ and $b = 1$. At a "critical" force, $n_{\min}$ continuously reaches 1.

??Phase transition??

Mean field approach - Helmholtz ensemble

Landau Helmholtz free energy

The mean field free energy in the Helmholtz (fixed extension) ensemble was calculated by [Reineker *et al.*, Colloid Polym Sci (1995)],

$$\mathcal{Z}_H \propto \sum_{N_c=0}^{N} \binom{N}{N_c} (N_c+1)^{3/2} \mathrm{e}^{N_c \epsilon}$$
$$\times \exp\left\{ -(N+1-N_c)\left[\mathcal{L}^{-1}\left(\frac{z}{L}\right)\frac{z}{L} - \ln\left(\frac{\sinh\left(\mathcal{L}^{-1}\left(\frac{z}{L}\right)\right)}{\mathcal{L}^{-1}\left(\frac{z}{L}\right)}\right)\right]\right\},$$

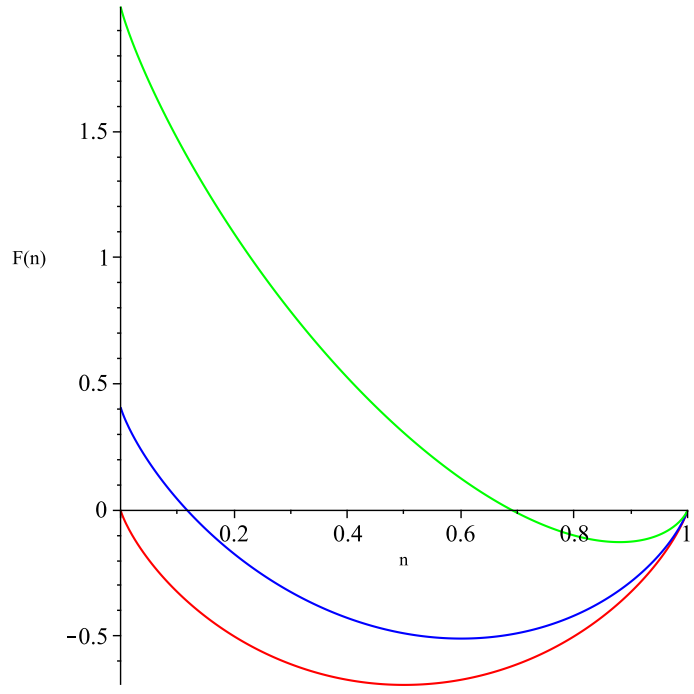
where, in this case, the independent control parameter is the strain z/L, and $\mathcal{L}^{-1}(x)$ stands for the inverse Langevin function.

As before, we can obtain the Landau free energy per link in the Helmholtz ensemble,

$$\begin{aligned}\frac{F}{N} &\approx -\epsilon n + [n\ln(n) + (1-n)\ln(1-n)] \\ &+ (1-n)\mathcal{L}^{-1}\left(\frac{z}{L}\right)\frac{z}{L} - (1-n)\ln\left(\frac{\sinh\left(\mathcal{L}^{-1}\left(\frac{z}{L}\right)\right)}{\mathcal{L}^{-1}\left(\frac{z}{L}\right)}\right)\end{aligned}$$

Mean field approach - Helmholtz ensemble

Landau Helmholtz free energy



The Landau Helmholtz free energy per link as a function of n for $\epsilon = 1$ and $z/L = 0.01, 0.5, 0.9$ (red, blue, green, respectively). We assume $k_B T = 1$ and $b = 1$. In this case, $n_{\min}$ is always strictly within the range $0 < n_{\min} < 1$.

No phase transition! Ensemble inequivalence!

Generating function method (Necklace model)

The generating function method (necklace model) is used in order to yield exact results in the thermodynamic limit and to determine whether a phase transition exists. The chain is viewed as a sequence of flexible blocks (coil-like with all hinges open, **A**) and stiff blocks (rod-like with all hinges closed, **B**). The end points are always rods (of length b). The statistical weight of a coil of size n (number of elementary rods) is

$$Q_n^A = \left(\frac{4\pi \sinh(f))}{f}\right)^n$$

and that of a rod of size n is

$$Q_n^B = \frac{4\pi \sinh(nf))}{nf} \exp\left((n-1)\epsilon\right)$$

grand partition function reads

$$W(p) = W_B + W_B W_A W_B + W_B W_A W_B W_A W_B + \cdots,$$

where

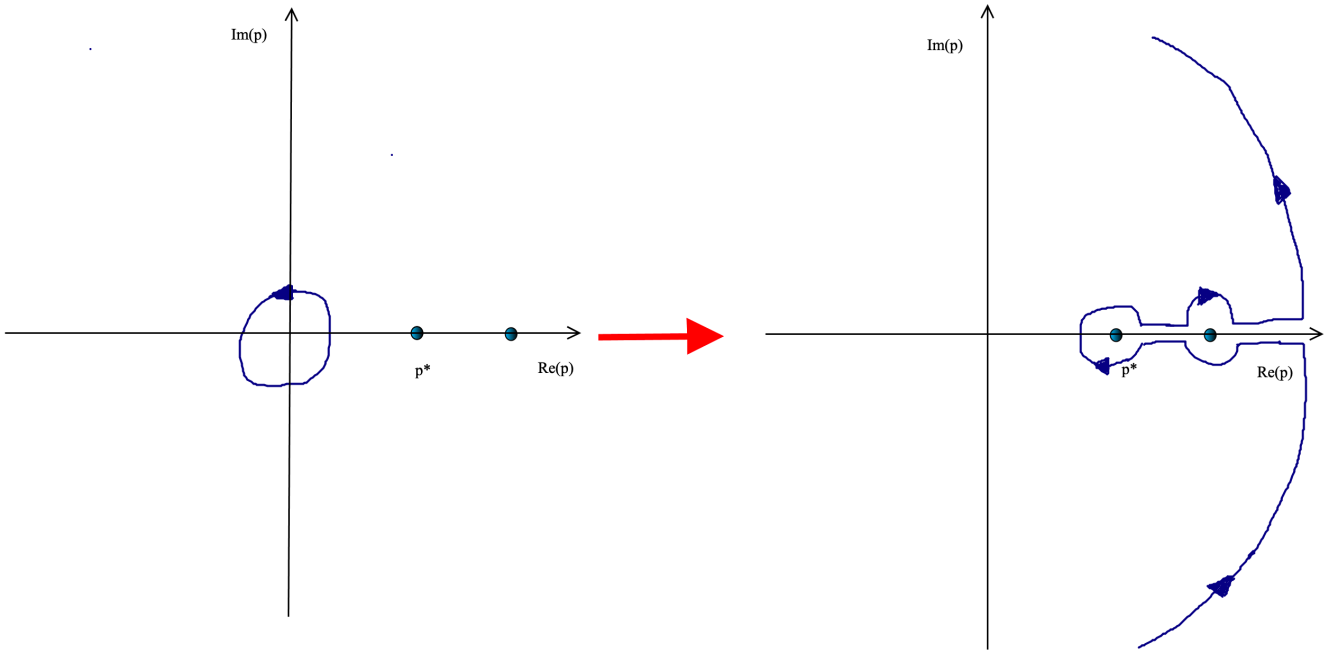
$$W_A(p) = \sum_{n=1}^{\infty} Q_n^A p^n$$

and

$$W_B(p) = \sum_{n=1}^{\infty} Q_n^B p^n$$

Generating function method - Background

(Darwin & Fowler, Lifson, Poland & Scheraga, Fisher, Kafri-Mukamel-Peliti, Kardar, *et al.*)



We can view p as a complex variable. From the Cauchy theorem, $\mathcal{Z}(N) = \frac{1}{2\pi i} \oint W(p) p^{-N-1} dp$, where the contour encloses the origin, but no singularity of $W(p)$.

In the thermodynamic limit, $N \gg 1$, the real positive singularity closest to the origin, p^*, dominates and $\mathcal{Z}(N) \approx -Res(W(p^*)) p^{*-N-1}$, which implies for the Gibbs free energy density $\lim_{N\to\infty} \frac{G(N)}{N} = k_B T \ln(p^*)$

Generating function method - Lack of a phase transition

For sufficiently small p, $W(p)$ can be written as

$$W(p) = \frac{W_B(p)}{1 - W_A(p)W_B(p)}$$

The behavior of the rFJC at the thermodynamic limit is determined by the smallest positive singularity of $W(p)$. $W_A(p)$ has a singularity at p_A where it diverges. Similarly, $W_B(p)$ has a singularity at p_B. The smallest positive singularity of $W(p)$ is the root of the equation

$$\frac{1}{W_A(p)} = W_B(p),$$

$p = p^*$, which lies in the interval $0 < p < \min\{p_A, p_B\}$.

- Since the crossing point of the two curves, $\frac{1}{W_A(p)}$ and $W_B(p)$ **changes smoothly by varying the control parameters** of our system (f, ϵ, T), with the change being entirely analytic, we conclude that **there is no phase transition in the rFJC.**

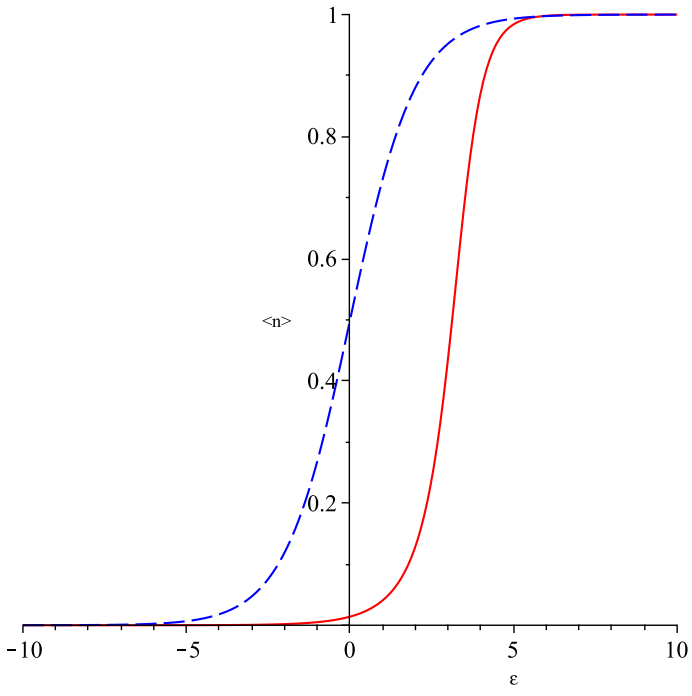
Generating function method - Linear response

The linear compliance $D := \frac{1}{L}\left(\frac{\partial \langle z \rangle}{\partial f}\right)\Big|_{f=0}$ as a function of ϵ is obtained by expanding p^* to quadratic order in f,

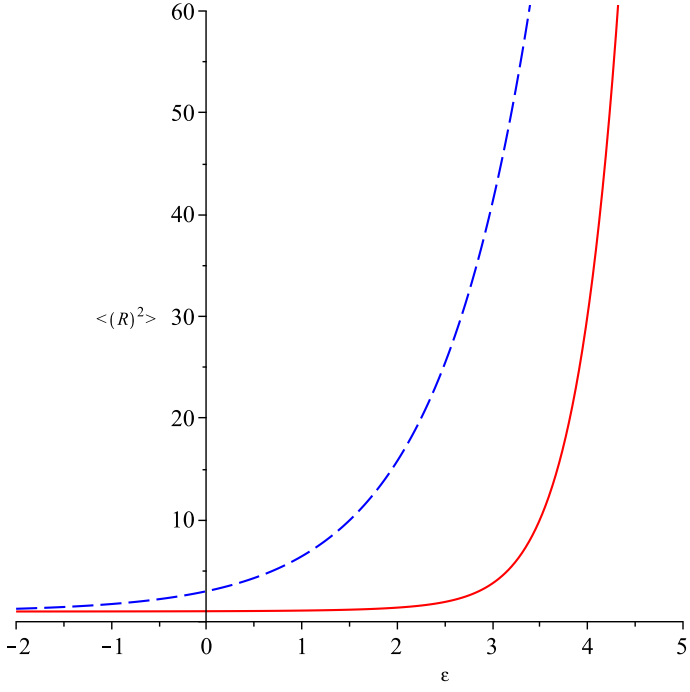
$$\begin{aligned} D &\approx \frac{1}{3} + \frac{2-\sqrt{5}}{3\pi(\sqrt{5}-5)} \exp(\epsilon) \quad \text{for} \quad \exp(\epsilon) \ll 1 \\ &\approx \frac{\exp(2\epsilon)}{24\pi^2} \quad \text{for} \quad \exp(\epsilon) \gg 1 \end{aligned}$$

- The linear compliance D of the rFJC **is always greater** than that of the uFJC $\left(D > \frac{1}{3}\frac{b}{k_b T}\right)$.
- From linear response theory, $\langle R^2 \rangle := \langle (\mathbf{R}(L) - \mathbf{R}(0))^2 \rangle_{f=0} = 3DL \Longrightarrow$ **the free (un-stretched) rFJC has a larger effective Kuhn length** in comparison with the uFJC ($\langle R^2 \rangle = L$).

Generating function method - free chain ($f = 0$)



Modified Langmuir isotherm for the free rFJC compared to the usual Langmuir isotherm (dashed line). We assume $k_B T = 1$.



The ratio of the mean square end-to-end distance of a free (unstretched) rFJC over the mean square end-to-end distance of the uFJC (taken as unit) as a function of the energy ϵ (we assume $k_B T = 1$). The dashed line is the mean field approximation of [Reiniker *et al.*, Colloid Polym Sci (1995)].

Generating function method - strong stretching

($f \gg k_B T/b$)

The Gibbs free energy per link in the strong stretching limit is

$$\ln(p^*) \approx -f - \epsilon - \exp\left(-\frac{f^2 \mathrm{e}^{2\epsilon}}{(2\pi)^2}\right)$$

By taking the appropriate derivatives, we obtain

- the force-extension relation,

$$\frac{\langle z \rangle}{L} = 1 - \frac{fb\ \mathrm{e}^{2\epsilon/(k_B T)}}{2\pi^2 k_B T} \exp\left(-\frac{(fb)^2\ \mathrm{e}^{2\epsilon/(k_B T)}}{(2\pi k_B T)^2}\right) \quad (cf.\ \ 1 - \frac{k_B T}{fb} \ \text{ for the uFJC!})$$

- and the mean occupation number,

$$\langle n \rangle = 1 - \frac{(fb)^2\ \mathrm{e}^{2\epsilon/(k_B T)}}{2\pi^2 (k_B T)^2} \exp\left(-\frac{(fb)^2\ \mathrm{e}^{2\epsilon/(k_B T)}}{(2\pi k_B T)^2}\right)$$

Conclusions - Outlook

- The mean fraction of closed hinges increases with increasing tension.
- Even though there is no sharp phase transition as we increase the force, there are two regimes:
  1. At weak tension, the chain swells and is more compliant than its usual counterpart.
  2. At strong tension, the chain straightens a lot and is much less compliant than its usual counterpart. This is a drastic (qualitative) change in the response.
- Ensemble (Gibbs *vs* Helmholtz) inequivalence and breakdown of the mean field approximation (strong fluctuations).
- Explicit calculation of fluctuations?

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