# Gibbs and Helmholtz ensembles for flexible and semiflexible polymers with elastic bonds

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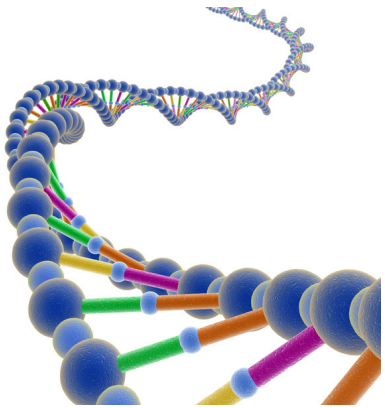
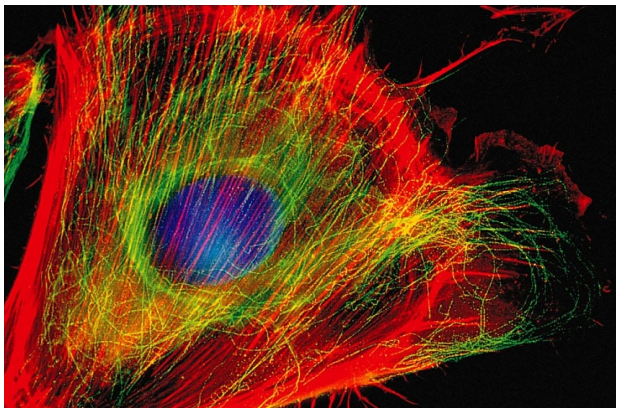
# Introduction to the problem

## Stretching experiments on arbitrarily long single polymer molecules

**Stretching experiments** on single **polymer** molecules of **arbitrary length** opened the way for studying the statistical mechanics of **finite systems** with relevant applications to structured materials of **biological interest**

Results of **stretching on DNA** have been found to be in **very good agreement** with **models**





These results suggested that the mechanical properties of DNA, and in particular its **flexibility** have a **relevant role in many biological processes**

This importance has attracted many theoretical physicists who produced several **models and relationships** to explain the experimental results

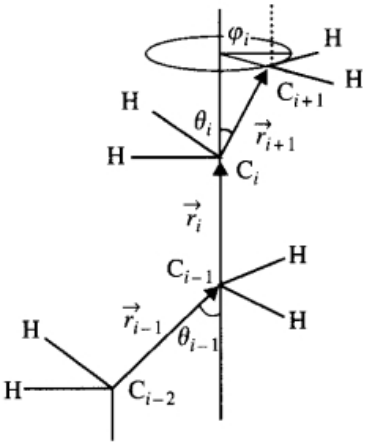
$\Rightarrow$ **understanding the force-extension relationship in polymers play an important role for the natural sciences**

# Models of polymers

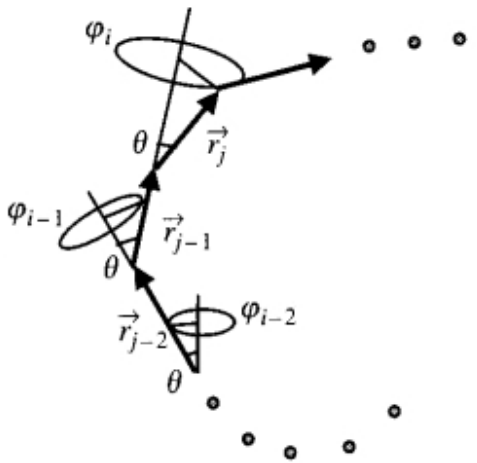
*Ideal chains: FJC, FRC, HRM*

## Freely-joined chain model (FJC)

- is the simplest model of a polymer
- **fixed length** polymer segments are linearly connected, and all **bond and torsion angles are equiprobable**
- the polymer can therefore be described by a simple random walk and ideal chain



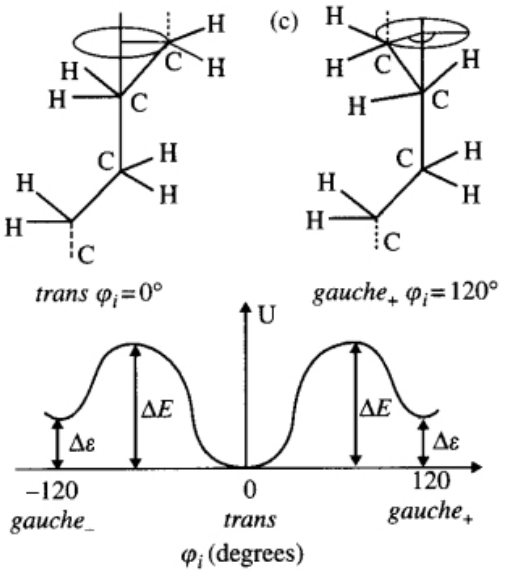

## Freely rotating chain model (FRC)




- takes into account that polymer segments make a **fixed angle** to neighbouring units because of specific chemical bonding
- under this fixed angle the segments are still free to rotate and all **torsion angles are equally likely**

## Hindered rotation model (HRM)

- the hindered rotation model assumes that
  the **torsion angle is hindered by a potential energy**
- this makes the probability of each torsion angle proportional to a **Boltzmann factor**

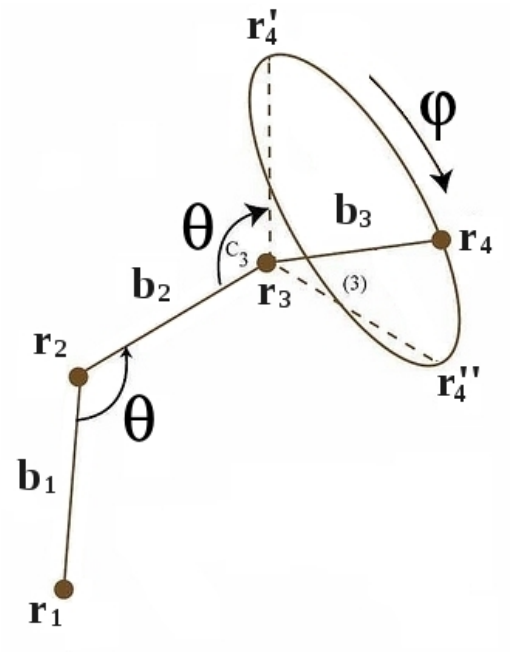


# Models adopted in literature

## FJC and WLC

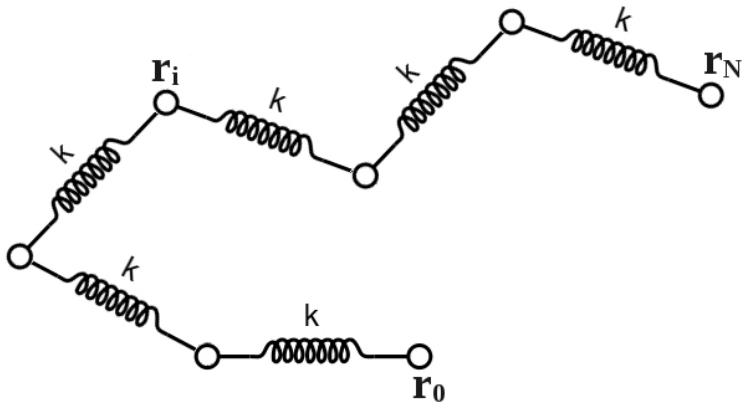
### *Models adopted in literature: polymer as an ideal chain*

- **freely jointed chain** (FJC) and **Worm-like chain** (WLC) are tipically studied [2]
- these models describe a wide range of experimental results on molecules of biological interest including **DNA**




### Two assumptions

- **Main assumption 1**: **inextensibility of the bond**
- **Main assumption 2**: **infinite number of monomers**



# Contributions to the problem

## Flexible and semiflexible polymers out from the thermodinamic limit

Our contribution deals with the thermoelastic response of a single chain **under stretching** with two specific features: the **extensibility of the bonds** between the monomers and the possibility to be **far from the thermodynamic limit** (arbitrary number of monomers) [1].

**Out of the thermodynamic limit**
**different boundary conditions applied yield to different constitutive equations**

- definition of **flexible** and **semiflexible** polymer **models**
- comparison between **different boundary conditions** $\Rightarrow$ **Helmholtz** and **Gibbs** ensembles
- characterisation of the **convergence to the thermodynamic limit** with **power laws** and **scaling exponent**

# Analytical approach: Statistical Mechanics foundation of polymers elasticity

## Definition of the problem

**Disordered polymers are too complex to be described using a deterministic method**

**$\Rightarrow$ Statistical approach is indeed mandatory**

### *Main definitions and hypotheses*

- A single monomer is characterized by **positions** $\bar{r}_i (i = 1, ..., N)$ and **momenta** $\bar{p}_i (i = 1, ..., N)$
- The hamiltonian of the system is: $H = \sum_{i=1}^{N} \bar{p}_i \cdot \bar{p}_i / 2m_i + V(\bar{r}_1, .., \bar{r}_N)$
- We consider the system in contact with a **thermal bath at temperature T**
- At thermal equilibrium, the **density probability** in the phase space is described by the Gibbs distribution:

$$\rho(q,p) = \frac{1}{Z} e^{-\frac{H(q,p)}{k_B T}}$$

where $Z = \iint_\Gamma e^{-\frac{H}{k_B T}} dqdp$ is the **partition function**.

# Original developement: analytical approach

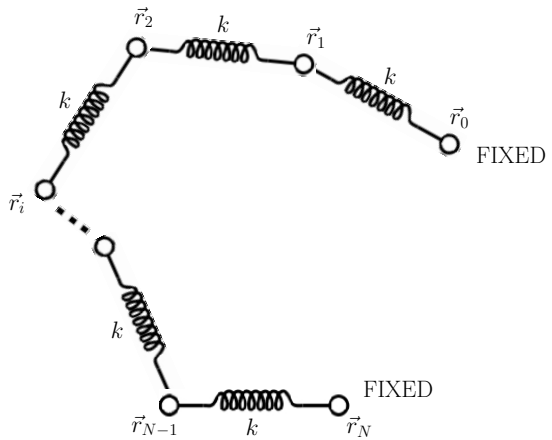
## Our goal

# OUR GOAL

Obtain the **thermodynamics** of the system starting from the above **Gibbs distribution**: two **dual approaches** are possible

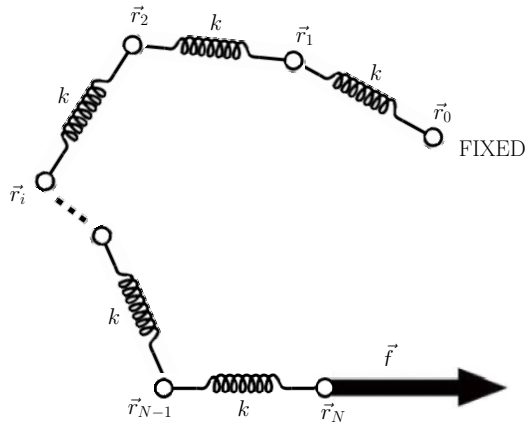
### *Helmholtz Ensemble*

- the positions of the **first monomer** $\bar{r}_0$ and of the **last monomer** $\bar{r}_N$ are **fixed**; the others monomers are free to move
- so we define $\bar{r} \equiv \bar{r}_N$ as a **macroscopic variable** (ideal gas into a given volume V)




### *Gibbs Ensemble*

- only the position of the **first monomer** $\bar{r}_0$ is **fixed** and the others are free to move
- a given **force** $\bar{f}$ is applied **to the last monomer**
- so we consider $\bar{f}$ as a **macroscopic variable** (gas constrained with a certain pressure $P$)




**In the thermodynamics limit (number of monomers $\to \infty$) the two ensembles are equivalent**

# Original developement: analytical approach

*Helmoltz and Gibbs ensemble*

## *Helmholtz Ensemble*

1. **Hypotheses**: $\bar{r}_0$ **fixed**, $\bar{r}_N$ and $\bar{p}_N = 0$ **fixed**
2. **Hamiltonian**:

$$H = H(\bar{r}_1, .., \bar{r}_N - 1, \bar{p}_1, .., \bar{p}_N - 1; \bar{r}_N)$$

3. **Partition function**:

$$Z_r = Z(\bar{r}, T) = \iint_\Gamma e^{-\frac{H(q,p,\bar{r})}{k_B T}} dqdp$$

4. **Equation of state**:

$$\bar{f} = \langle \frac{\partial H}{\partial \bar{r}_N} \rangle = -k_B T \frac{\partial}{\partial \bar{r}} ln Z_r(\bar{r}, T)$$

## *Gibbs Ensemble*

1. **Hypotheses**: $\bar{r}_0$ **fixed**, $\bar{f}$ **applied** to $\bar{r}_N$
2. **Augmented Hamiltonian**:

$$H = H(\bar{r}_1, ..., \bar{r}_N, \bar{p}_1, ..., \bar{p}_N) - \bar{f} \cdot \bar{r}_N$$

3. **Partition function**:

$$Z_f = Z(\bar{f}, T) = \iint_\Gamma e^{-\frac{H(q,p,\bar{f})}{k_B T}} dqdp$$

4. **Equation of state**:

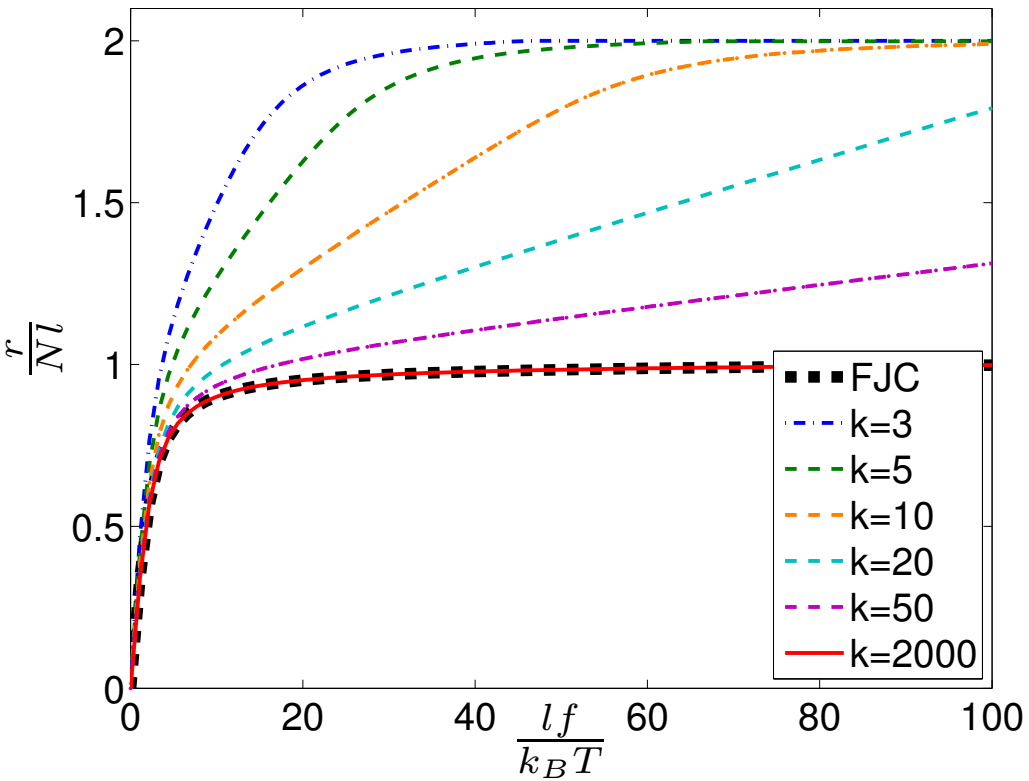
$$\bar{r} = -\langle \frac{\partial H}{\partial \bar{f}} \rangle = k_B T \frac{\partial}{\partial \bar{f}} ln Z_f(\bar{f}, T)$$

- we found an **analytic form of the partition function** $Z$ for each ensemble ($Z_r$, $Z_f$)
- we found the two **Laplace transforms** that allow us to switch between the two ensembles

# Original developement: analytical approach

*Results for the FJC, Gibbs and Helmholtz ensemble (thermodinamic limit)*

**Elongation vs. traction curve** for different values of the **spring constant**

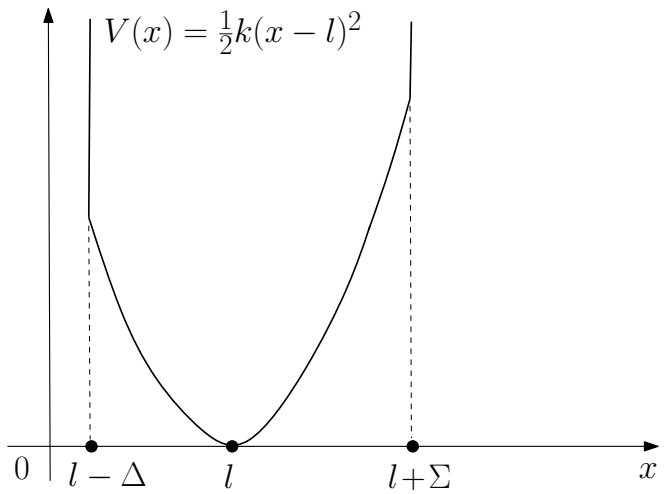



Temperature: $T = 293K$ **Semiflexible**

**FJC: stretching potential**

$\Rightarrow \frac{k_S}{2} \sum_{i=0}^{N-1} (\|\vec{r}_{i+1} - \vec{r}_i\| - l)^2$

***Gibbs Ensemble***




The elongation $r$ and the traction $f$ varying in the range $3 \leqslant k_S \leqslant 2000\ k_BT/m^2$.

**Three different regimes:**

1. very small applied force: **entropic zone**, linear relation: $r = Nl^2f/(3k_BT)$
2. **elastic region** characterized by a slope proportional to $k_S$
3. finally it is reached the **saturation** at the energy barrier $l + \Sigma$.

# Original developement: simulation approach

Montecarlo Simulations

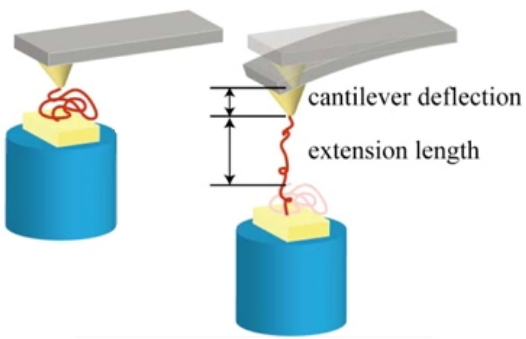
## Original simulation results

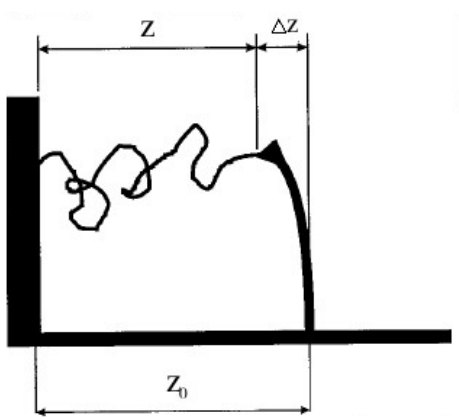
- **Gibbs case**: straightforwardly analytical/numerical results
- **Helmholtz case**: **much more difficult** to handle because of **numerical instabilities**

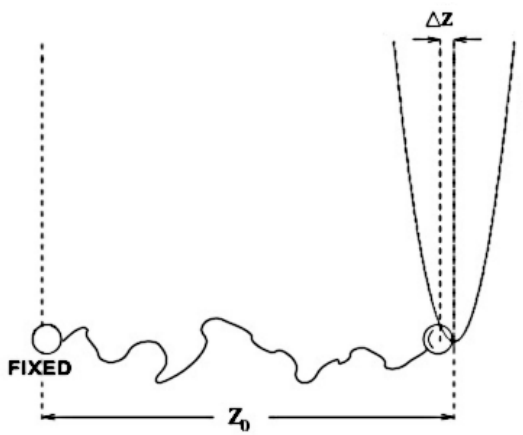
  $\Rightarrow$ a numerical approach can **bypass** such problems

**We developed a Metropolis Monte Carlo benchmark for the two ensembles**

we imposed the **stretching** of the polymer under a force provided by a **cantilever** [3] with a proper adjustable **elastic stiffness** $k_{trap}$



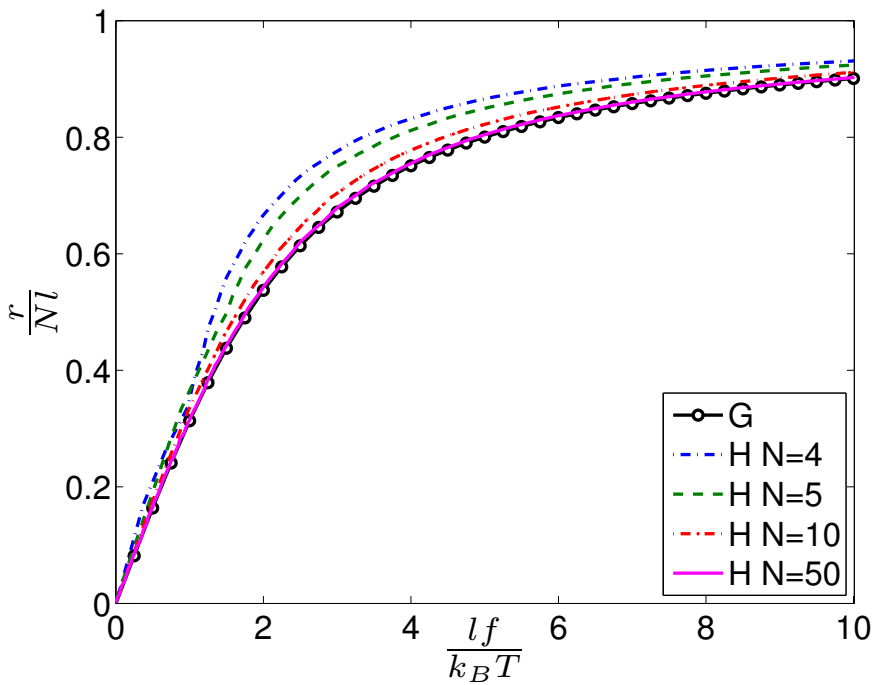

- **mean force** on the polymer: $\langle f \rangle = k_{trap} \langle \Delta z \rangle$
- **soft cantilever**: Gibbs ensemble ($k_{trap} = 0.01\ k_B T/m^2$)
- **stiff cantilever**: Helmholtz ensemble ($k_{trap} = 100\ k_B T/m^2$)

# Freely Jointed Chain

## Original results

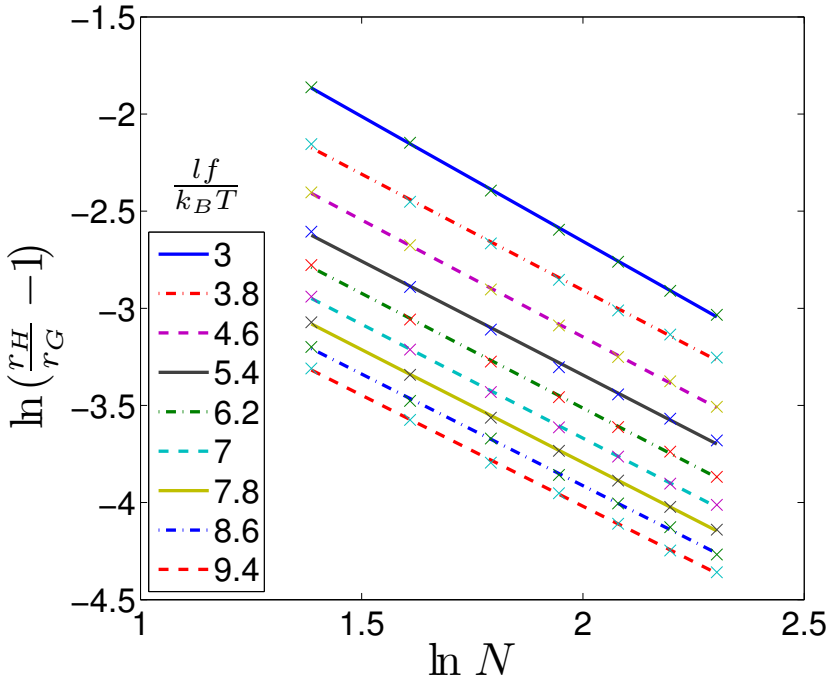
### Elastic response curves

- FJC $\Rightarrow k_S = 2000\, k_B T/m^2$
- Gibbs ensemble: **single curve** (independence of N)
- Helmholtz ensemble: **different curves** for different numbers of monomers




### Elongations comparison at a fixed force

- $\frac{r_H(N)}{r_G} = 1 + \frac{a}{N^\alpha}$
- each curve corresponds to a different value of the **normalized force**



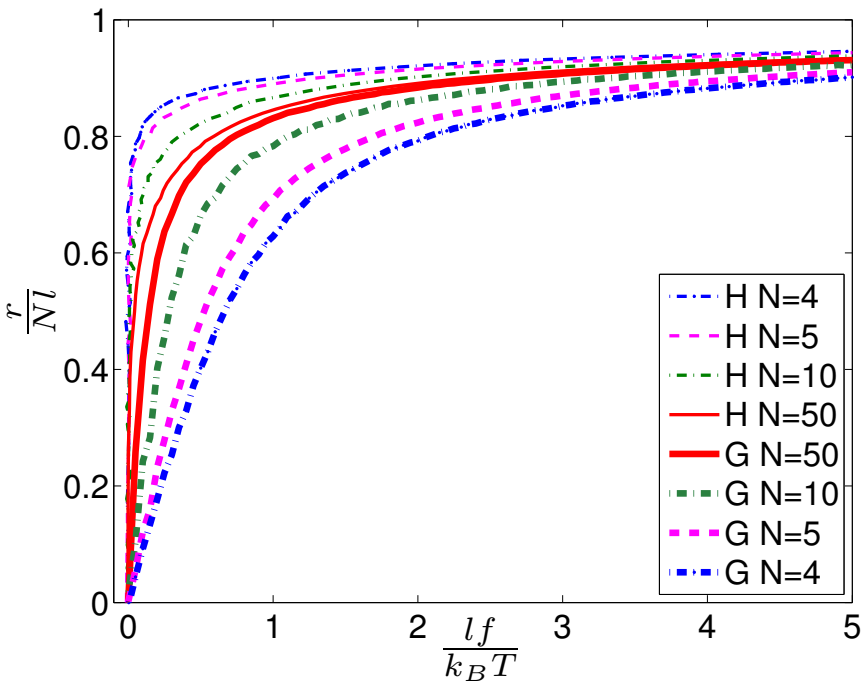

$\Rightarrow$ the **differences between the ensembles** are considerable for **short chains**!
Monte Carlo simulations are nicely fitted by the **power law** with $\alpha = 1.15 \pm 0.05$

# Worm Like Chain

## Original results

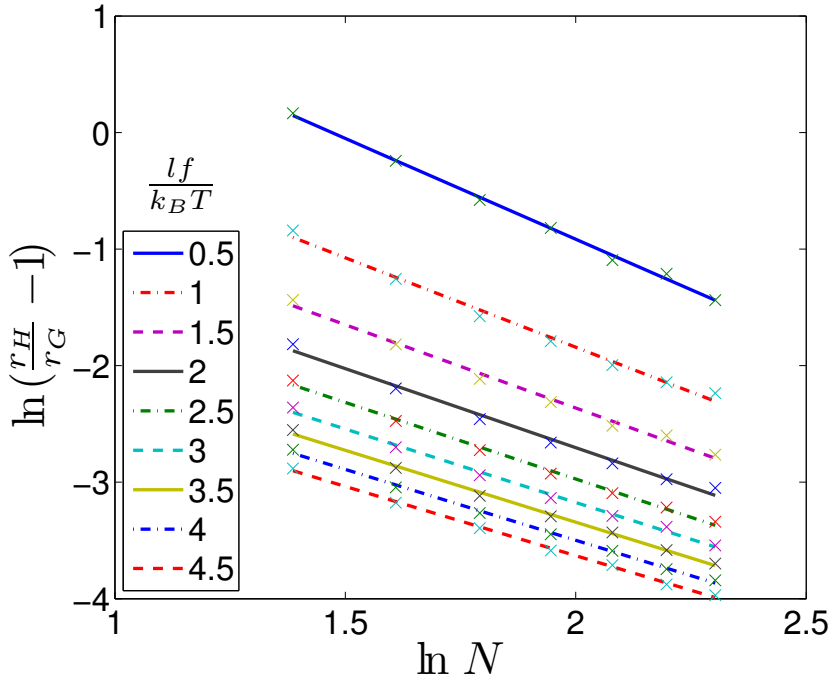
### Elastic response curves

- **WLC: bending potential** $\Rightarrow \frac{\kappa}{2}\sum_{i=1}^{N-1}\left(\vec{t}_{i+1}-\vec{t}_i\right)^2$
- $\Rightarrow k_S = 2000\ k_BT/m^2$ , $\kappa = 1\ k_BT$
- Gibbs ensemble: **different curves** for different numbers of monomers $\rightarrow$ dependence of N




### Elongations comparison at a fixed force

- $\frac{r_H(N)}{r_G(N)} = 1 + \frac{a}{N^\alpha}$
- $\alpha = 1.30 \pm 0.05$



# Comparison with literature

## Simulations details

# Marko and Siggia - Rosa et al.

### *Marko and Siggia interpolation formula [6]*

$$\frac{fl}{k_B T} = \frac{l}{L_p}\left[\frac{1}{4(1-\zeta)^2} - \frac{1}{4} + \zeta\right]$$

$\zeta = r/(Nl)$: polymer extension normalized to the contour length
$L_p = l\kappa/(k_B T)$:persistence length

**asymptotically** exact both in the **large- and small-force limits** of the continuous WLC model

### *Rosa et al. interpolation formula [7,8]*

For the **discrete version** of the WLC model, where finite size of the equilibrium length $l$ is accounted:

$$\begin{aligned}\frac{fl}{k_B T} &= \frac{2L_p}{l}\left[\sqrt{1+\left(\frac{l}{2L_p}\right)^2\frac{1}{(1-\zeta)^2}} - \sqrt{1+\left(\frac{l}{2L_p}\right)^2}\right] \\ &+ \left[3\frac{1-\mathcal{L}\left(\frac{L_p}{l}\right)}{1+\mathcal{L}\left(\frac{L_p}{l}\right)} - \frac{\frac{l}{2L_p}}{\sqrt{1+\left(\frac{l}{2L_p}\right)^2}}\right]\zeta\end{aligned}$$

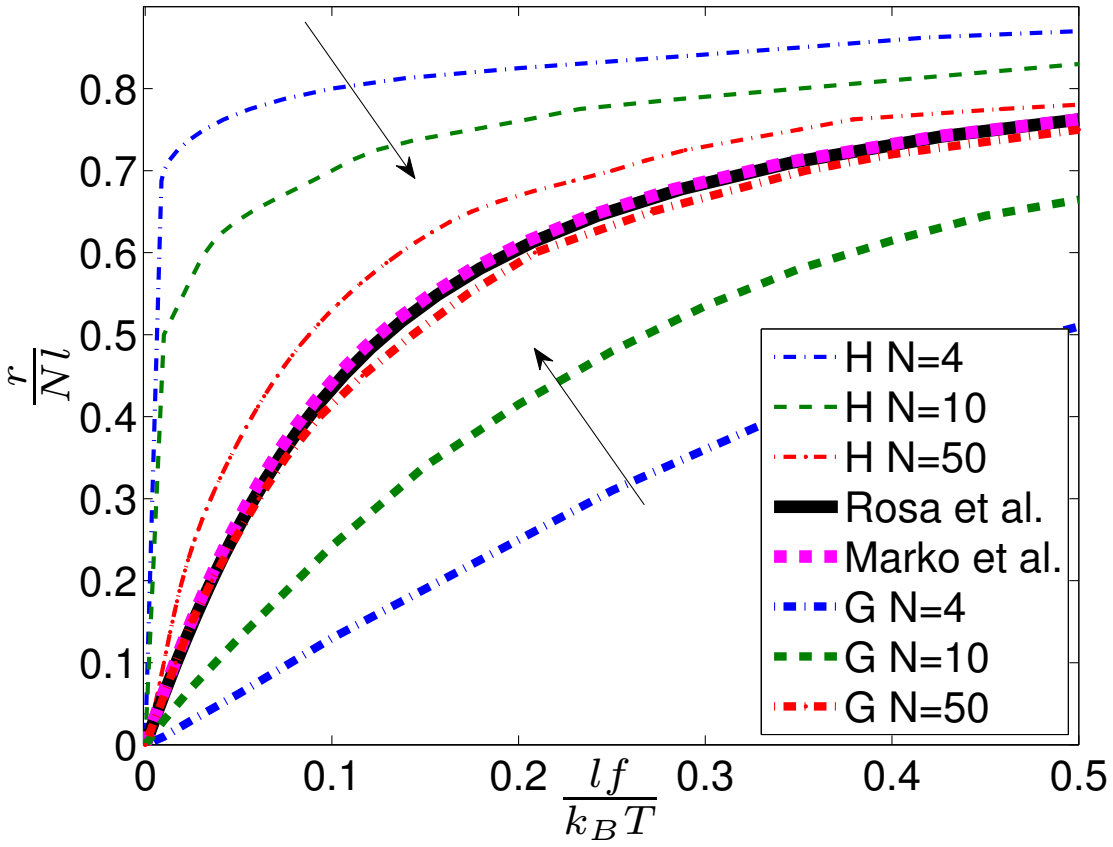
$\mathcal{L}(x) = \coth x - 1/x$ (Langevin function)

# Worm Like Chain: comparison with literature

## Original results

**MC vs analytical approximation**

- the analytical approximation curves are **contained** between the Gibbs and Helmholtz Monte Carlo solutions for $N$ **small**
- very good agreement with the behaviour of the WLC model at the **thermodynamic limit** ($N > 50$ in this case)



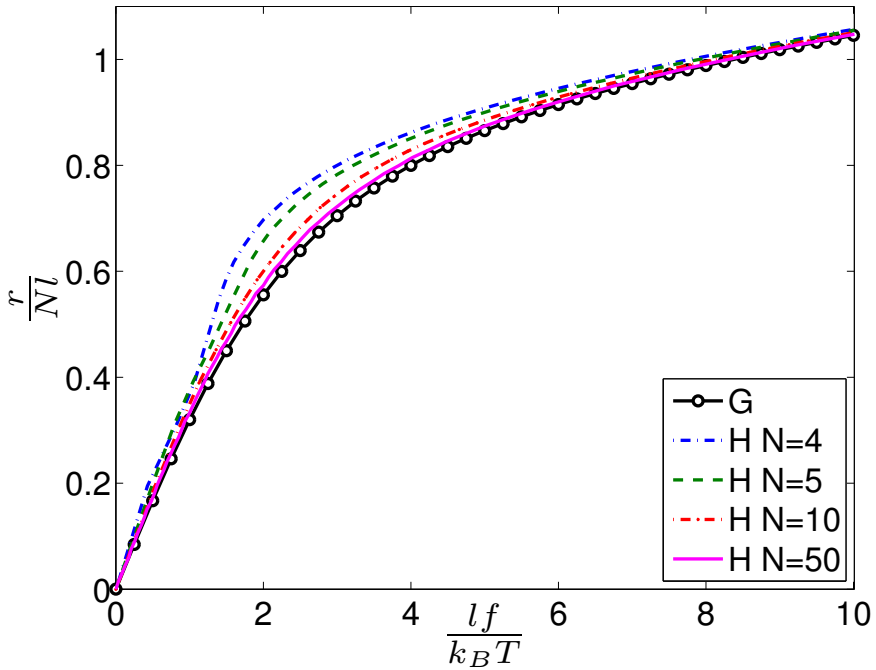
# Semiflexible Freely Jointed Chain

## Original results

**Main assumption** in both the standard FJC and WLC models: **inextensibility of the bonds** but when considering large forces **elasticity of chemical bonds** becomes important
$\rightarrow$ we set a **small value** for the elastic constant of the **spring** between the monomers
$\rightarrow$ from the pure FJC model to a **Gaussian-FJC model** (extensible bonds)

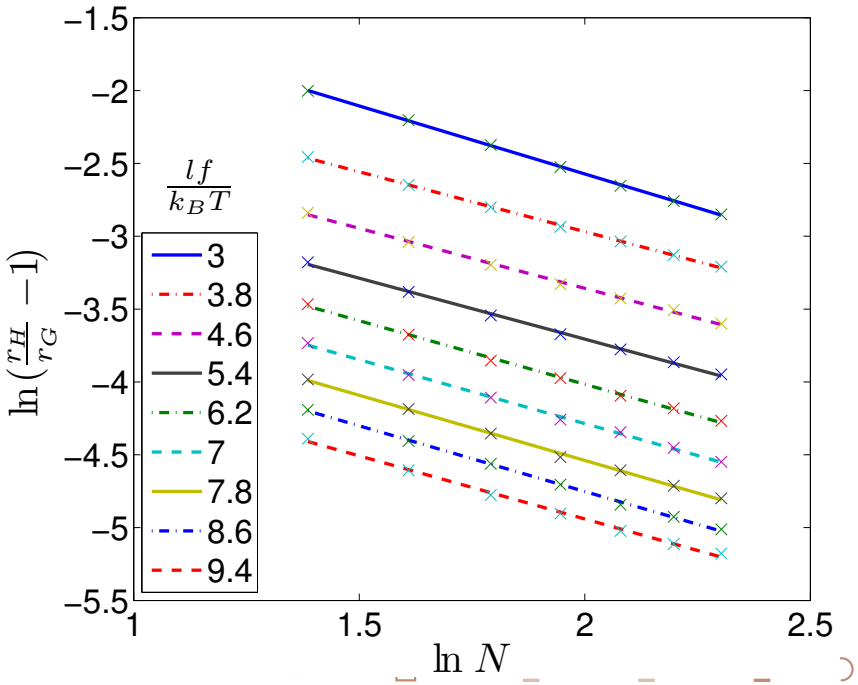
### Elastic response curves

- **stretching constant**: $k_S = 10\, k_B T/m^2$




### Elongations comparison at a fixed force

- $\frac{r_H(N)}{r_G} = 1 + \frac{a}{N^\alpha}$
- $\alpha = 0.80 \pm 0.05$

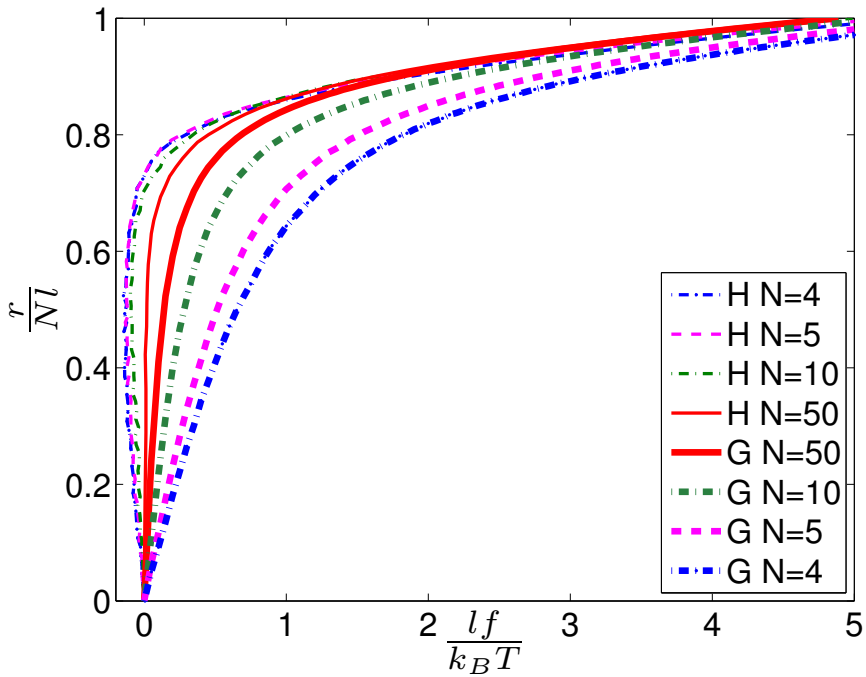


# Semiflexible Worm Like Chain

## Original results

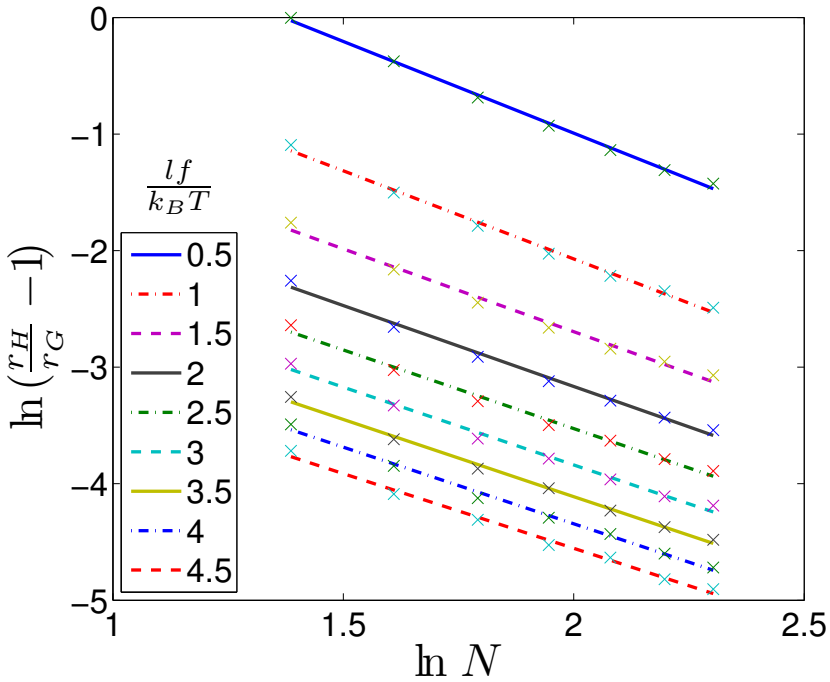
### Elastic response curves

- **stretching constant**: $k_S = 10\, k_B T/m^2$
- **bending constant**: $\kappa = 1\, k_B T$




### Elongations comparison at a fixed force

- $\frac{r_H(N)}{r_G(N)} = 1 + \frac{a}{N^\alpha}$
- $\alpha = 1.40 \pm 0.05$



# Conclusions and future work

## Analytical development and results

- **WE HAVE:**
  1. considered the **differences** in the **force-extension curves** between the Gibbs and Helmholtz ensembles
  2. explicitly **formulated flexible and semiflexible polymer models**, with and without extensible bonds

## Computational development and results

- **WE HAVE:**
  1. set a **workbench for molecular simulations**: Metroplolis Monte Carlo
  2. checked our previous theoric results by way of the **simulation feedback**
  3. proved that **different ensembles** lead to the **same results** when stretching a polymer chain if the number of monomers is large enough
  4. showed how the **convergence to the thermodynamic limit** upon increasing N follows a suitable **power law**

## Future works

- **WE PLAN TO:**
  1. extend the models to more complex, eventually with **nonlinear springs**
  2. consider models able to describe **conformational transitions** of a polymer chain
  3. study the statistical mechanics of flexible chains **immersed in a solvent**

# Bibliography



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