Laboratoire Interdisciplinaire Carnot de Bourgogne

PRACTICAL WORK – SOFT MATTER

Numerical simulations of ideal chain model of polymer

Dr. Adrien Nicolaï & Pr. Patrick Senet

Laboratoire Interdisciplinaire Carnot de Bourgogne
ICB UMR CNRS 6303
icb.u-bourgogne.fr

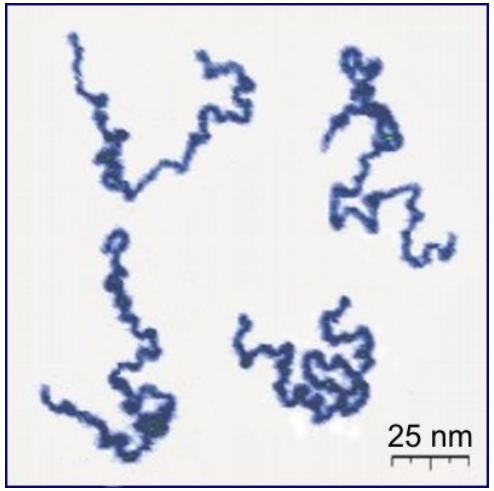
Presentation

Theoretical lecture: Pr. SENET

Practical work: Dr. NICOLAÏ

2h Exercise + 4h Practical

Grade: 50% *theoretical exam* + 50% *practical work*



Location: computer room D102

GRADE: Report of 4 pages MAX about practical work – template of research paper

DEADLINE: Friday January 12th, 2024 – 6 PM

Introduction

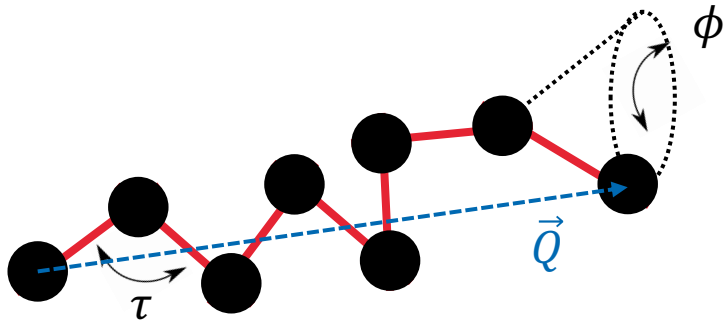
Numerical simulations of ideal chain model of polymer using PYTHON

The **freely-jointed chain** (FJC) model consist of a chain of bonds: the orientation of the different bonds is completely uncorrelated and no direction is preferred.

2 parameters: number of bonds N and bond length b
($N+1$ monomers; no exlcuded volume = "phantom" chains)

- One measure of extent: $\langle Q^2 \rangle = Nb^2 + \sum_{i \neq j}^{N} b^2 \langle cos\theta_{ij} \rangle$

There is no correlation between the segments: angle between 2 bond vectors $\theta_{ij}\ (= 180 - \tau_{ij})$ can have all values -> $\langle cos\theta_{ij} \rangle = 0$



i.e. the bond angle τ [0,180] and torsion angle ϕ [0,360] can have any value

Mean square **end-to-end distance** $\langle Q^2 \rangle = Nb^2$

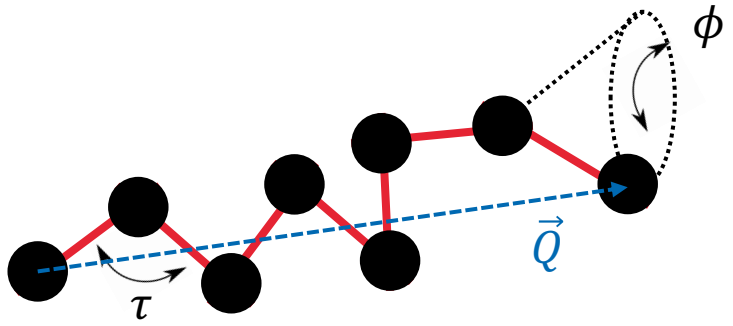
see chapter 2 of theoretical lectures for demonstration

Introduction

Numerical simulations of ideal chain model of polymer using PYTHON

The **freely-jointed chain** (FJC) model consist of a chain of bonds: the orientation of the different bonds is completely uncorrelated and no direction is preferred.

2 parameters: number of bonds N and bond length b
($N+1$ monomers; no exlcuded volume = "phantom" chains)



i.e. the bond angle τ [0,180] and torsion angle ϕ [0,360] can have any value

- One measure of extent: $\langle Q^2 \rangle = Nb^2 + \sum_{i \neq j}^{N} b^2 \langle cos\theta_{ij} \rangle$

- Probability distribution **end-to-end distance** $\mathrm{P}(\vec{Q}) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} exp\left(-\frac{3Q^2}{2Nb^2}\right)$
$N \to \infty$

see chapter 2 of theoretical lectures for demonstration

Introduction

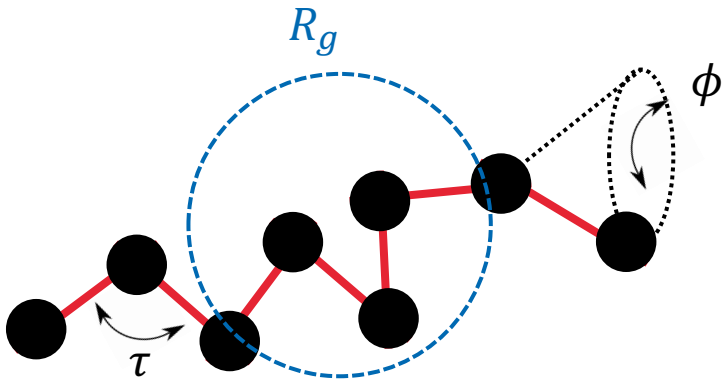
Numerical simulations of ideal chain model of polymer using PYTHON

- Another measure of extent R_g: radius of gyration
  (accounts for the position of all monomers)

$$R_g^2 = \frac{1}{N}\sum_{i=0}^{N}\left(\vec{R}_i - \vec{R}_{cm}\right)^2$$

$\vec{R}_i$: position of monomer i

$$\vec{R}_{cm} = \frac{1}{N}\sum_{i=0}^{N}\vec{R}_i$$: position of center of mass



i.e. the bond angle τ [0,180] and torsion angle ϕ [0,360] can have any value

Mean square radius of gyration $\langle R_g^2 \rangle = \frac{Nb^2}{6} (N \to \infty)$

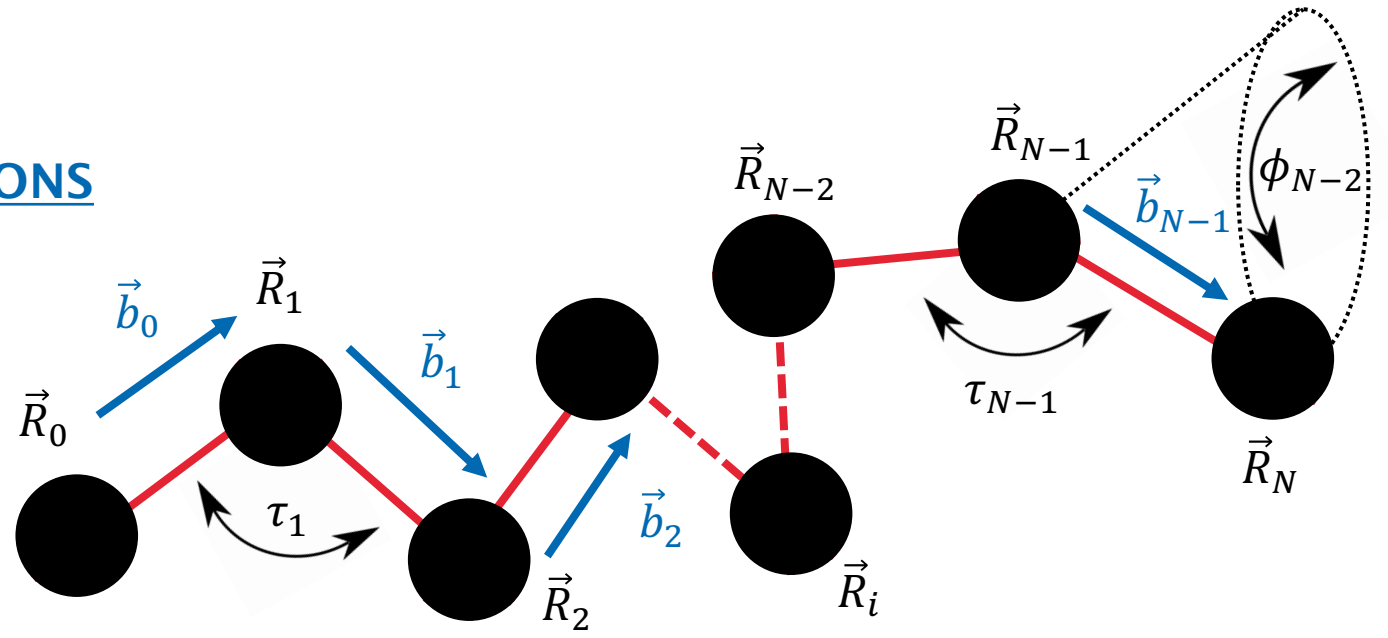
see chapter 2 of theoretical lectures for demonstration

Simulations

Numerical simulations of ideal chain model of polymer using PYTHON

Modelling of polymer conformation using FJC model

NOTATIONS



- $N+1$ monomers $\vec{R}$
- N bonds $\vec{b}$
- $N-1$ bond angles τ
- $N-2$ dihedral angles ϕ

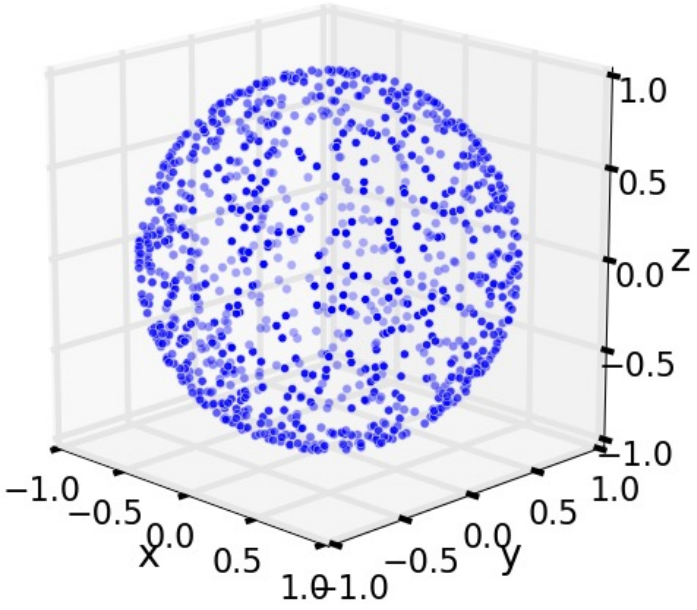
Algorithm

Numerical simulations of ideal chain model of polymer using PYTHON

- Define parameters: b, N and T
- For t = 1 -> T
  - Generate N bond vectors $\vec{b}$

    generate uniformly distributed numbers in the cube $[-1,1]^3$ and ignore any points that are further than a unit distance r from the origin. This will ensure a uniform distribution in the region $r \leq 1$. Next, normalize each random vector to have unit norm so that the vector retains its direction but is extended to the sphere of unit radius. As each vector within the region $r \leq 1$ has a random direction, these points will be uniformly distributed on a sphere of radius 1.

  - Compute N+1 monomers coordinates $\overrightarrow{R_{i+1}} = \overrightarrow{R_i} + \vec{b}$

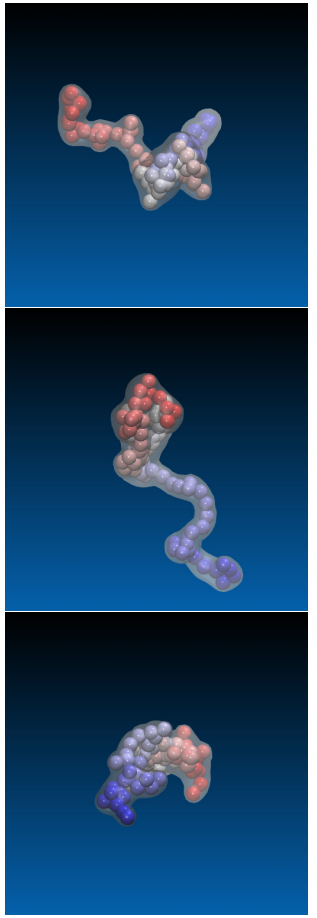


- OUTPUT: xyz trajectory file (https://en.wikipedia.org/wiki/XYZ_file_format)

Python script

See *script_FJC_simulation_STUDENT.ipynb*

Jupyter Notebook

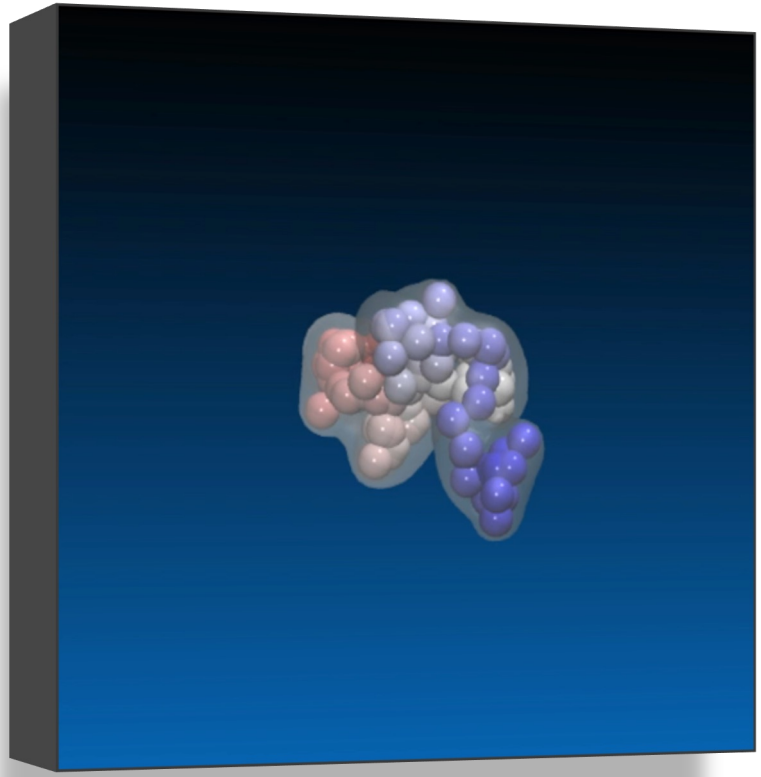


Exercise

Numerical simulations of ideal chain model of polymer using PYTHON

Exercise:

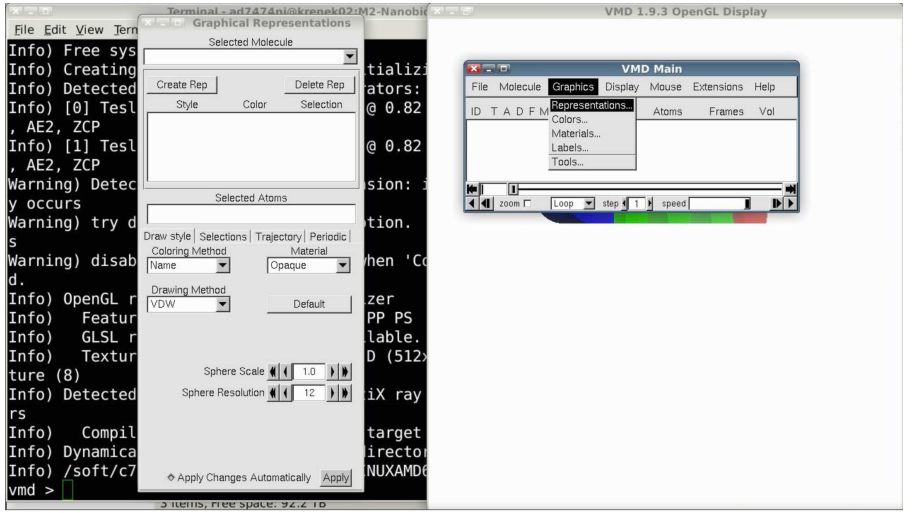
1) *Generate T=1000 conformations of the polymer (N = 100)*
2) *Visualize the structures using VMD software*
3) *Compute and plot time series of METRICS Q & R_g*
4) *Compute $\langle Q^2 \rangle$ & $\langle R_g^2 \rangle$*
5) *Compare numerically with theoretical values*



Visualization

VMD

1. Load the file *polymer.xyz* (File -> New Molecule -> Browse…-> Load)
2. Go to Graphics -> Representation
3. Select Coloring Method = Index and Drawing Method = VDW
4. Select Material Glossy
5. Change Sphere Resolution to 50
6. Go to File -> Render…
7. Select Tachyon (internal, in-memory rendering)
8. Define filename and click on Start Rendering to generate an image of the screen



Practical work

- **<u>GOAL</u>: verified numerically the 4 following theoretical results**

1

- Mean square end-to-end distance $\langle Q^2 \rangle = Nb^2$

- Mean square radius of gyration $\langle R_g^2 \rangle = \frac{Nb^2}{6} (N \to \infty)$

} for $N = 10 \dots 1000$

2

- Probability distribution end-to-end distance $\mathrm{P}(Q) = 4\pi Q^2 \left(\frac{3}{2\pi N b^2}\right)^{3/2} exp\left(-\frac{3Q^2}{2Nb^2}\right)$ for $N = 100$

- Singular behavior $\mathrm{P}(Q) = \frac{Q}{2b^2}$ for $N = 2$

+ study of the influence of T + comparison with theory (estimation of errors)

Practical work

Numerical simulations of ideal chain model of polymer using PYTHON

3 - Structure factor $I(k) = \sum_{i=0}^{N}\sum_{j=0}^{N}\left\langle \frac{\sin(k\|\overrightarrow{R_i} - \overrightarrow{R_j}\|)}{k\|\overrightarrow{R_i} - \overrightarrow{R_j}\|} \right\rangle$ for $N = 100$

- Comparison with Guinier approximation $I(k) = (N+1)^2\left[1 - \frac{(kR_g)^2}{3}\right]$

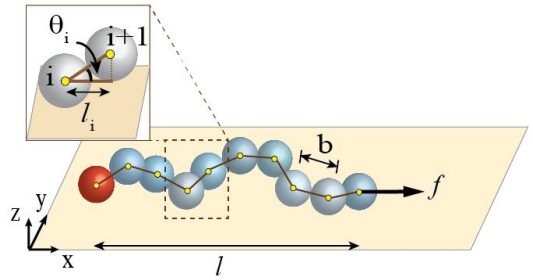
+ estimation of Rg from I(k) + error

Practical work

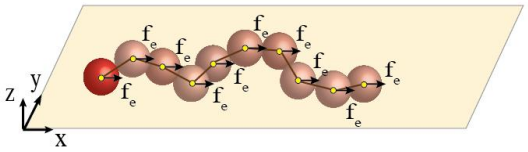
- **TO GO FURTHER:**

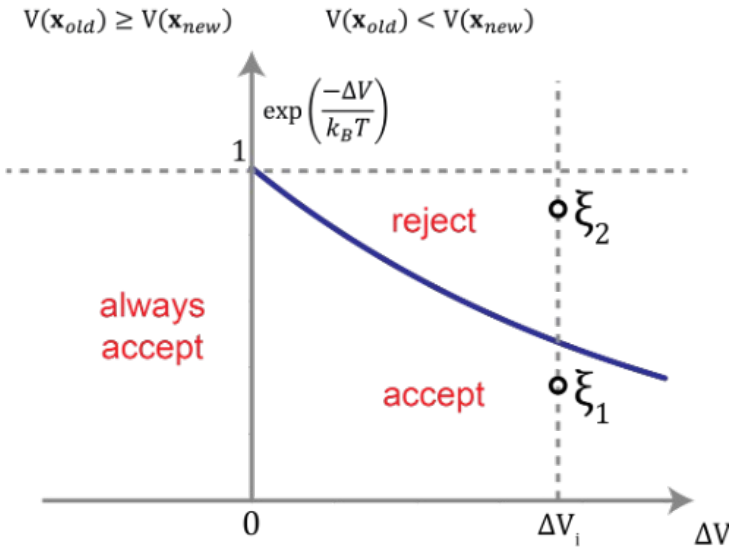
Consider a force F along the cartesian X direction and a temperature T. Compute the force-extension curve as a function of the force F applied using a Metropolis Monte-Carlo algorithm.

A



B





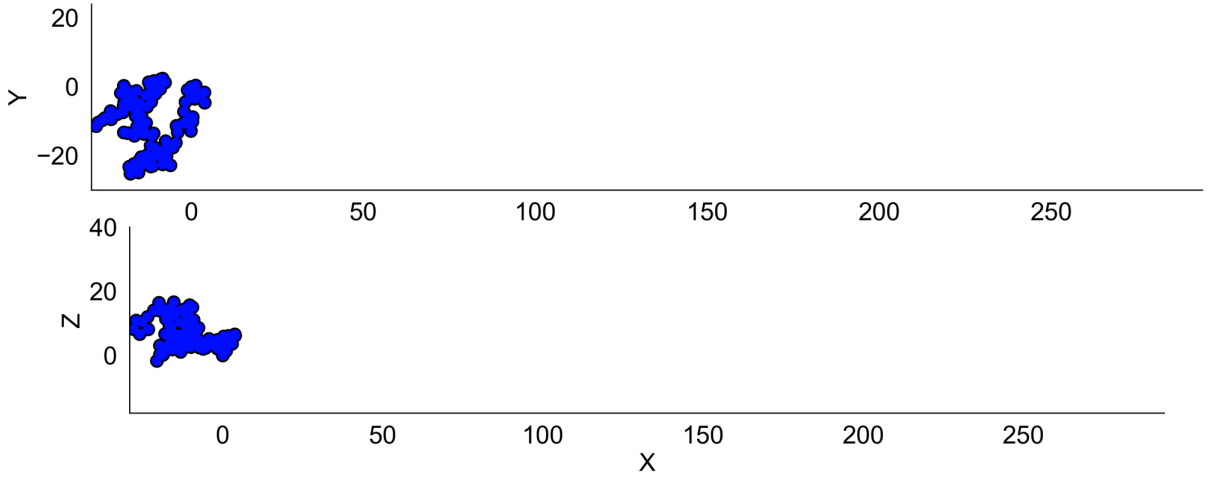
Algorithm

- Create a structure of FJC polymer (t=0)
- Define a force along x: F = [Fx,0,0]
- Compute potential energy $V = -\vec{F}.\vec{Q}$
- Modify randomly one bond vector
- Compute the new potential energy
- Use Metropolis MC to accept or reject the move
- Iterate over T conformations
- Compute Q(T) = extension

Practical work

- **TO GO FURTHER:**

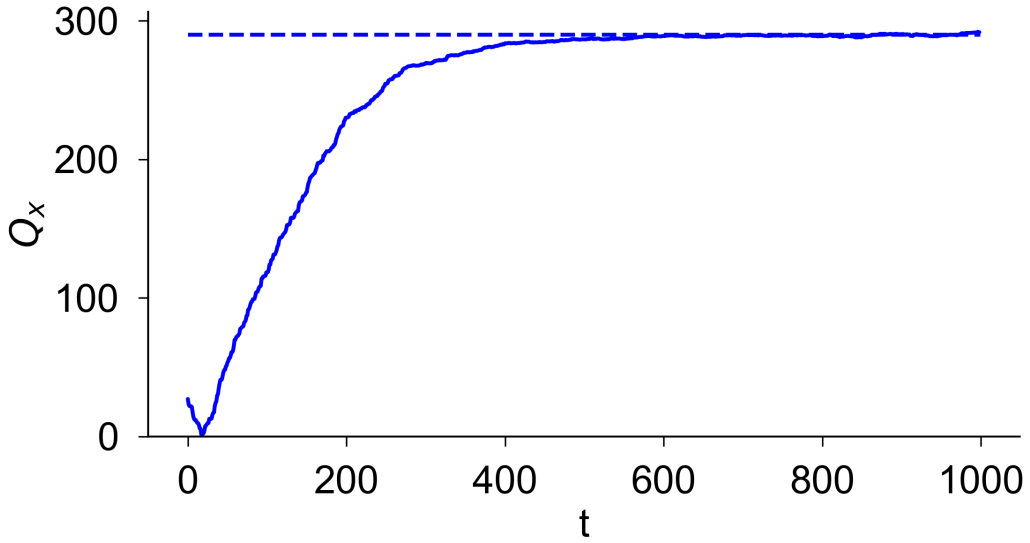
Consider a force F along the cartesian X direction and a temperature T. Compute the force-extension curve as a function of the force F applied using a Metropolis Monte-Carlo algorithm.

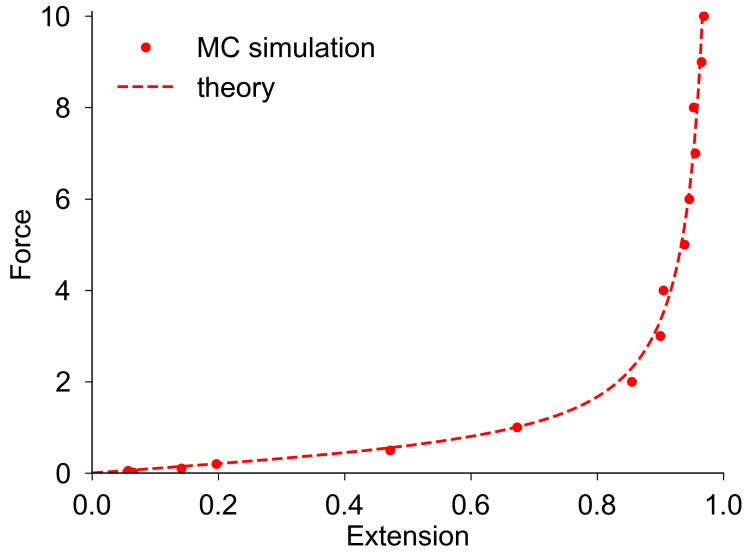


Practical work

- **TO GO FURTHER:**

Consider a force F along the cartesian X direction and a temperature T. Compute the force-extension curve as a function of the force F applied using a Metropolis Monte-Carlo algorithm.



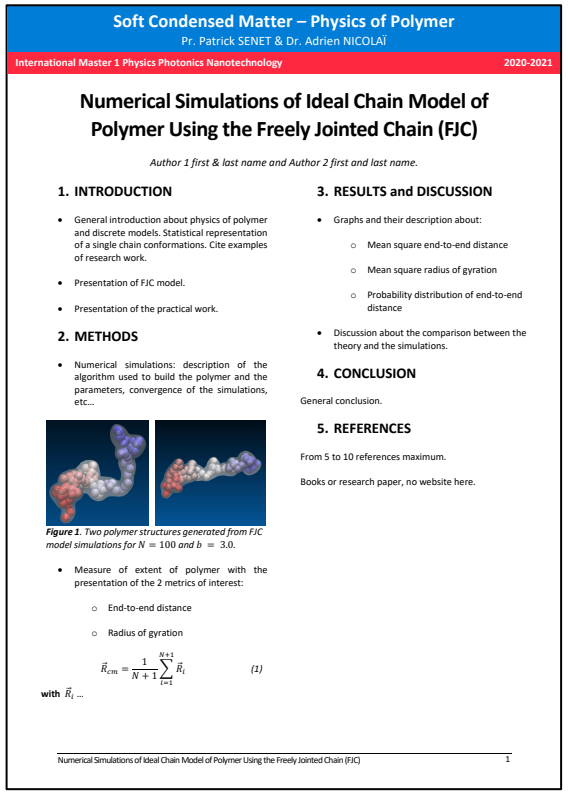


$$|\vec{Q}.\overrightarrow{u_x}| = Nb\left[\coth(\alpha) - \frac{1}{\alpha}\right], \alpha = \frac{Fb}{k_B T}$$

Practical work

- **Write a report following the template provided to you as a research paper**

  - INTRODUCTION
  - METHODS
  - RESULTS and DISCUSSION
  - CONCLUSION
  - REFERENCES



Soft Condensed Matter – Physics of Polymer

Pr. Patrick SENET & Dr. Adrien NICOLAÏ

International Master 1 Physics Photonics Nanotechnology 2020-2021

Numerical Simulations of Ideal Chain Model of Polymer Using the Freely Jointed Chain (FJC)

Author 1 first & last name and Author 2 first and last name.

1. INTRODUCTION

- General introduction about physics of polymer and discrete models. Statistical representation of a single chain conformations. Cite examples of research work.
- Presentation of FJC model.
- Presentation of the practical work.

2. METHODS

- Numerical simulations: description of the algorithm used to build the polymer and the parameters, convergence of the simulations, etc...

***Figure 1**. Two polymer structures generated from FJC model simulations for $N = 100$ and $b = 3.0$.*

- Measure of extent of polymer with the presentation of the 2 metrics of interest:
  - End-to-end distance
  - Radius of gyration

$$\vec{R}_{cm} = \frac{1}{N+1}\sum_{i=1}^{N+1}\vec{R}_i \qquad (1)$$

with $\vec{R}_i$ ...

3. RESULTS and DISCUSSION

- Graphs and their description about:
  - Mean square end-to-end distance
  - Mean square radius of gyration
  - Probability distribution of end-to-end distance
- Discussion about the comparison between the theory and the simulations.

4. CONCLUSION

General conclusion.

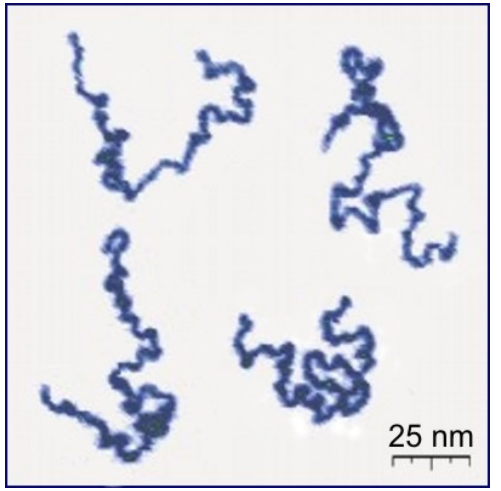
5. REFERENCES

From 5 to 10 references maximum.

Books or research paper, no website here.

Numerical Simulations of Ideal Chain Model of Polymer Using the Freely Jointed Chain (FJC) 1

VERY STRICT INSTRUCTIONS ABOUT CONTENTS AND FORMATTING !



Laboratoire Interdisciplinaire Carnot de Bourgogne

END

adrien.nicolai@u-bourgogne.fr