Lab 5 : Polymers

MSE-421 Statistical Mechanics

Contents

Objectives:

1. **How does temperature alter the shape of polymers?**
2. **Study the coil-globule transition and obtain the crossover temperature**
3. **Estimate the Flory exponent and characterize the polymer**

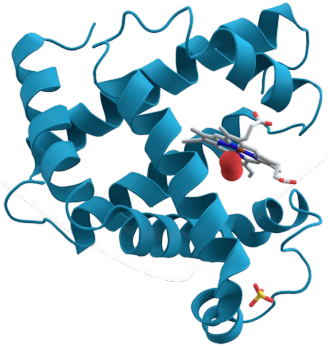
Deadlines:

- **Lab04 (Liquids) : Wednesday, 29 May 2024, 03:00**
- **Lab05 (Polymers) : Tuesday, 4 June 2024, 03:00**

Polymers in everyday life

Polyisoprene

Teflon



Proteins
(myoglobin)

Polyester

Polyethylene

Polymers

Staudinger (1920) : Macromolecular Hypothesis

“Polymers are molecules made of covalently bonded elementary units, called monomers.

Staudinger, H. (1920), Über Polymerisation. Ber. dtsch. Chem. Ges. A/B, 53: 1073-1085 (in German)

(Nobel Prize in Chemistry 1953)

IUPAC Recommended Term

polymer

A substance composed of macromolecules.

PAC, 1996, 68, 2287. (Glossary of basic terms in polymer science (IUPAC Recommendations 1996)) on page 2289

More info at: https://doi.org/10.1351/goldbook.P04735 *Official IUPAC Definition*

https://en.wikipedia.org/wiki/Polymer

Flory Theory of a polymer chain

Established by Paul J. Flory (Nobel Prize in Chemistry, 1974)

Paul J. Flory – Nobel Lecture. NobelPrize.org. Nobel Prize Outreach AB 2024. Thu. 23 May 2024.

The theory lies lies on the assumption that we can consider a real polymer chain as composed of two components:

1. **An ideal (no interactions) chain (entropic contribution)**
2. **A dilute 'gas' of monomers (energetic contribution)**

For a real polymer chain, monomer-monomer and monomer-solvent interactions are considered.

Scaling "law"

$$R_g \sim bN^{\nu}$$

Ideal polymer chain

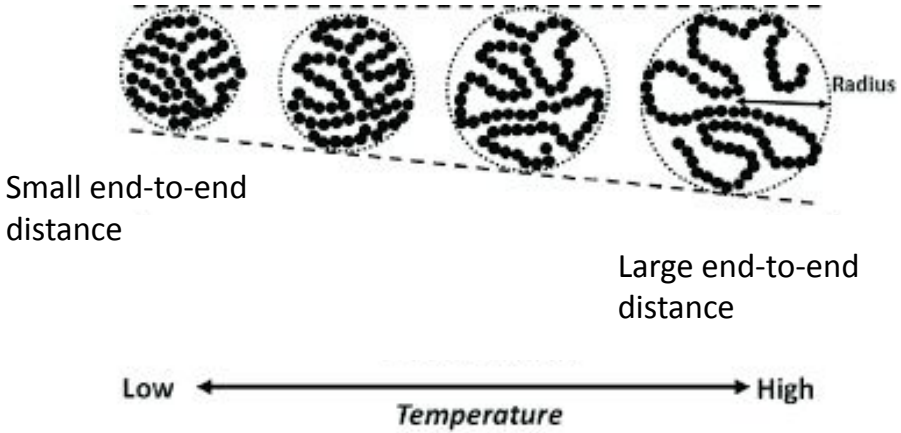
$$\nu = 1/2$$

Coil-globule thermodynamic transition

Of great importance in biology : such transitions are observed in proteins and DNA

J. Chem. Phys. 102, 6595–6602 (1995)

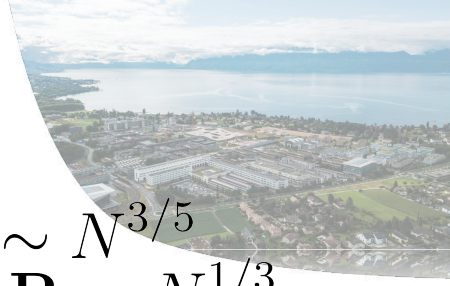
Study the average end-to-end distance as a function of T.



Transition (theta) point -> Ideal chain

M. W. Tibbitt, Lecture 6: Real polymer chains – Flory theory (2019)

Polymer in a solvent and scaling laws

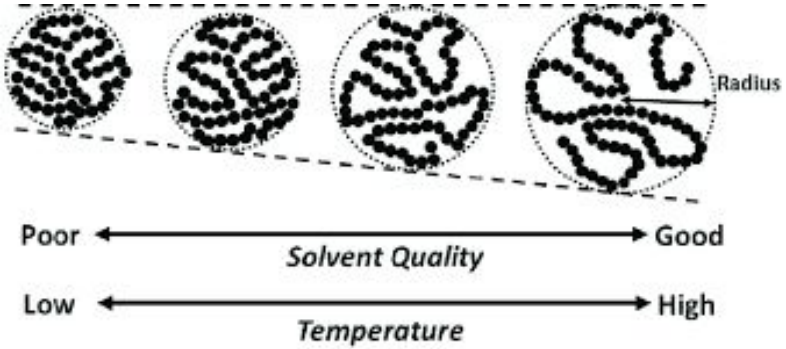


- **Good solvent : A solvent in which a polymer expands** $\mathbf{R} \sim N^{3/5}$
- **Poor solvent : A solvent in which the polymer collapses** $\mathbf{R} \sim N^{1/3}$
- **theta solvents : A solvent in which a polymer acts like an ideal chain**

$$\mathbf{R} \sim N^{1/2}$$

(Random walk)

inter-monomer and solvent-chain interactions cancel each other



$$\mathbf{R} = \mathbf{r}_N - \mathbf{r}_1$$

M. W. Tibbitt, Lecture 6: Real polymer chains – Flory theory (2019)

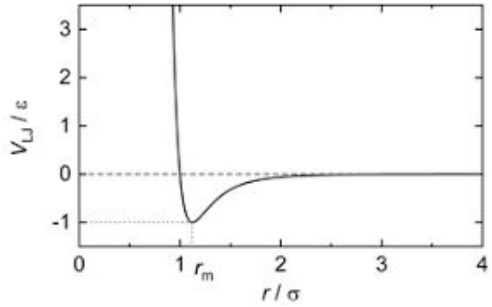
Lab 5

Our physical system:

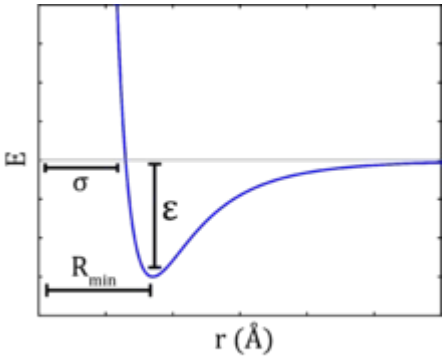
- **Single chain in vacuum**
- **100 identical monomers**
- **Monomers are linked by a harmonic potential**

$$V_N(\{\mathbf{r}_i\}) = \frac{1}{2}k\sum_j |\mathbf{r}_{j+1} - \mathbf{r}_j|^2$$

- **Lennard-Jones interaction between monomers**



$$V_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



Lab 5

Study the shape of polymer chains for the following temperature values

$$T \in \{0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.4\}\,(\text{LJ units})$$

$$T = \frac{k_B T\,(\text{in K})}{\epsilon}$$

Study coil-glubole transition and determine crossover temperature.

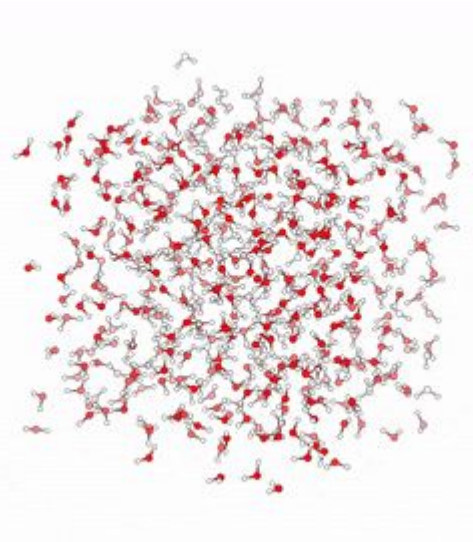
For a given temperature value $T = 4.4$, extract the Flory exponent.

$$N \in \{75, 100, 150\}$$

Molecular Dynamics

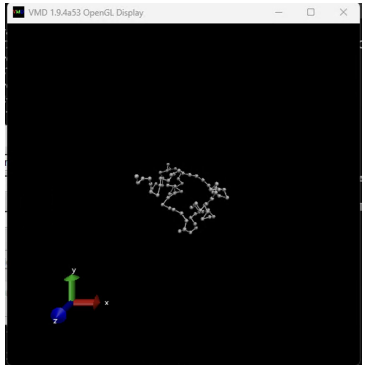
“MD is the science of simulating motion of a system of particles according to Newton's classical equations of motion”

(“Pursuing Laplace’s Vision on Modern Computers | SpringerLink” by Schlick T.)



You will not have to implement anything!

→ We will use the software Visual Molecular Dynamics

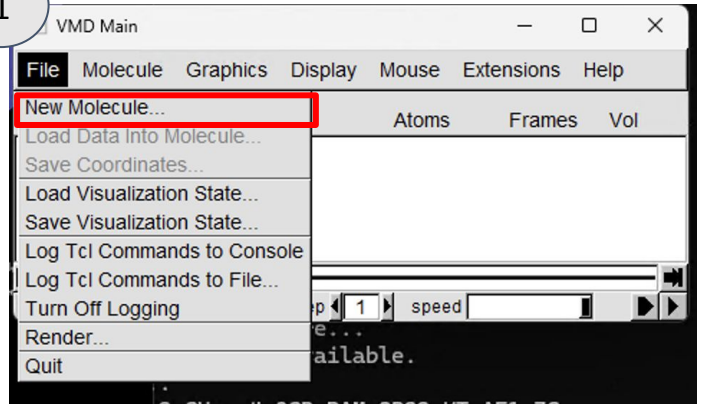


VMD
Visual Molecular Dynamics

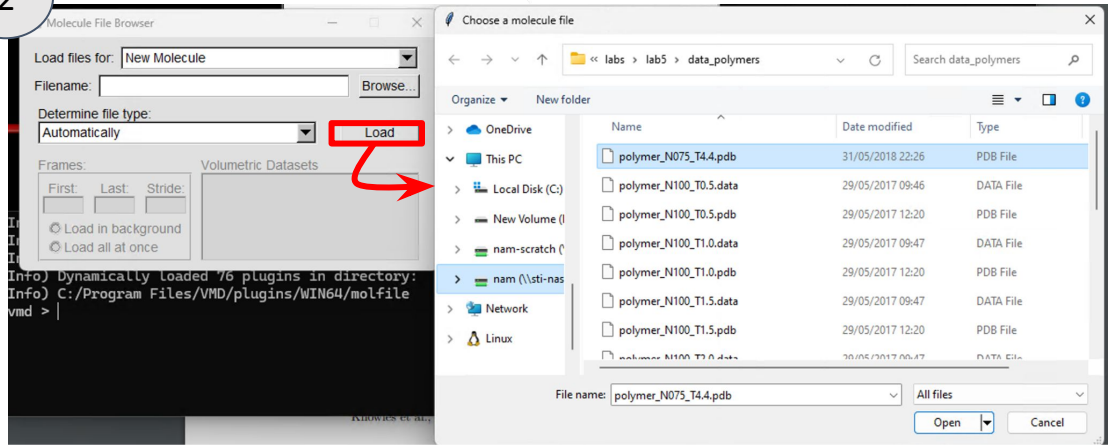
VMD / Load a molecule

Open VMD + load a molecule (.pdb extension) from data_polymers/

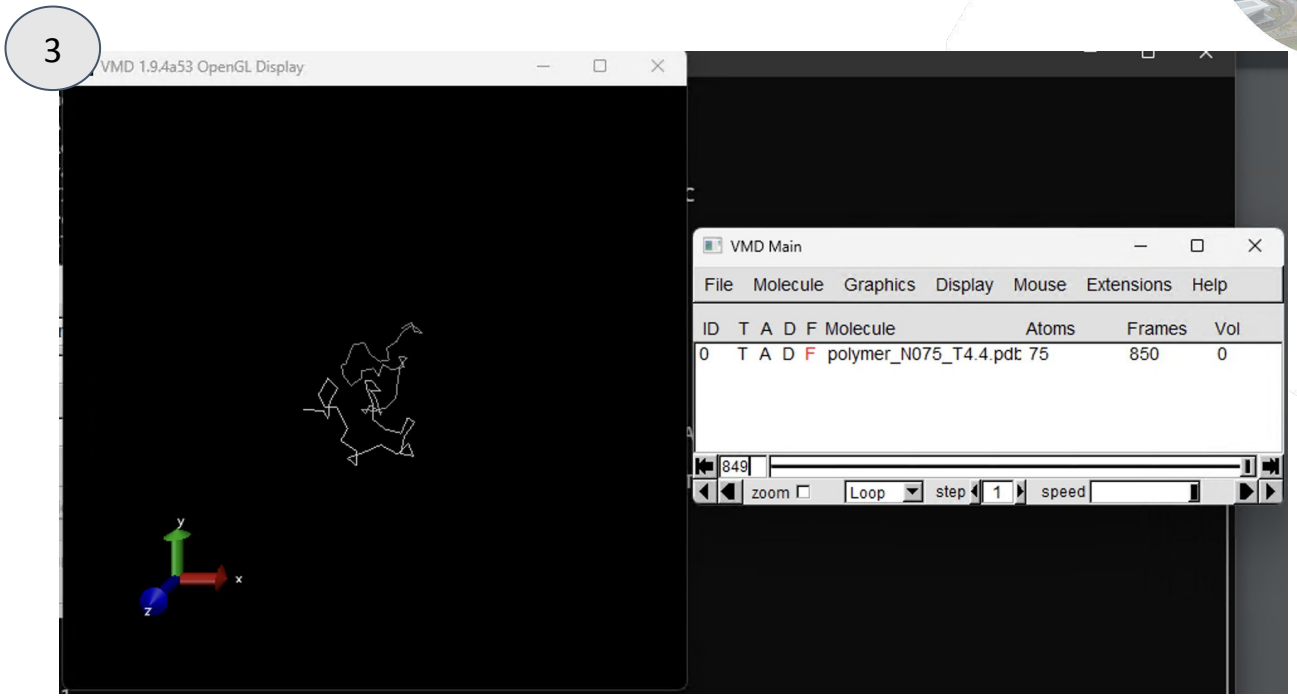
1



2

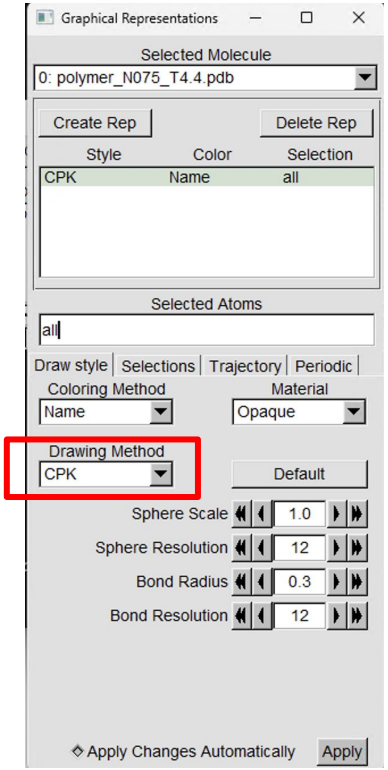


VMD / Load a molecule

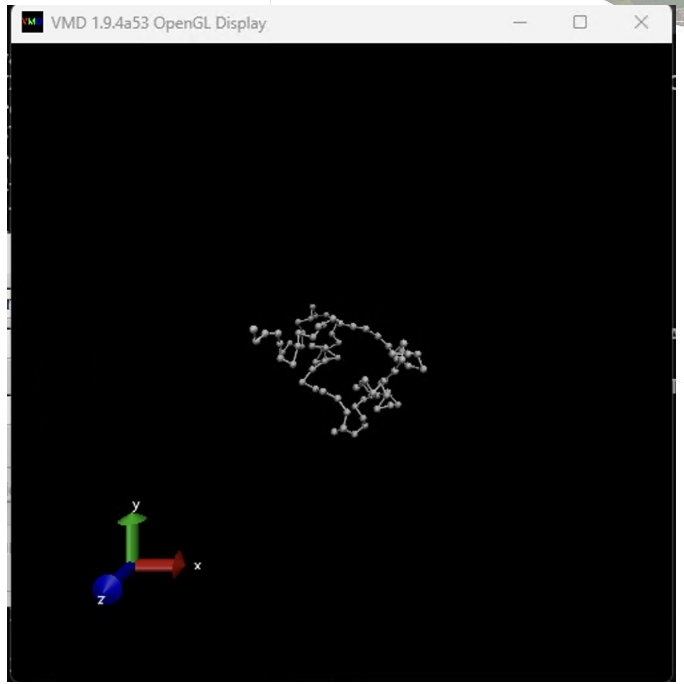


VMD / How to make beads visible

From Graphics -> Representations



Choose CPK in Drawing Method

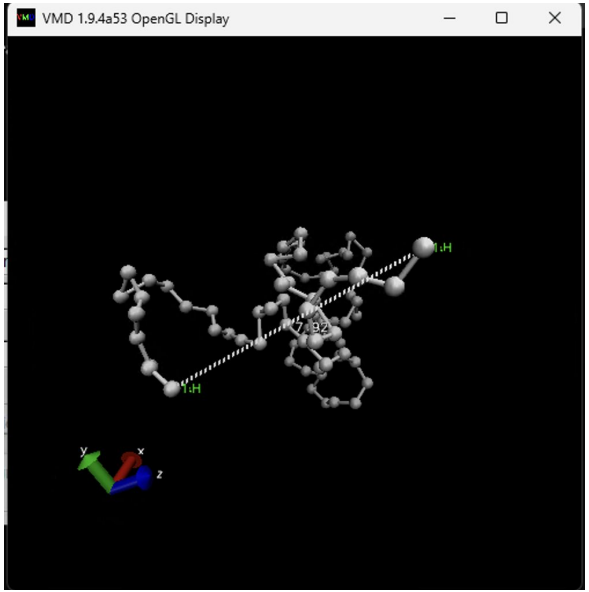


VMD / How to choose end-to-end distance

Use Mouse -> Scale Mode to zoom in

Use Mouse -> Rotate Mode to rotate the structure

Use Mouse -> Label -> Bonds to choose end points of a bond



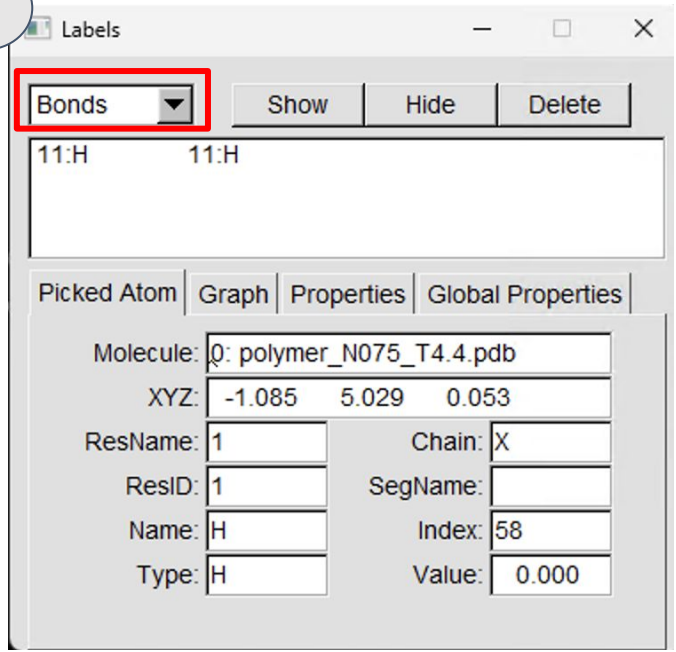
For our polymer, we can define the end-to-end distance

VMD / Time evolution of end-to-end distance

Use Graphics -> Labels

Choose Bonds here

1



2