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Study of polymer crystals under deformation via MD simulation

- **An internship chosen and practiced by:**
  Aaron WANDHAMMER & Asma SOUFI
- **Under the supervision of:**
  DR Hendrik MEYER

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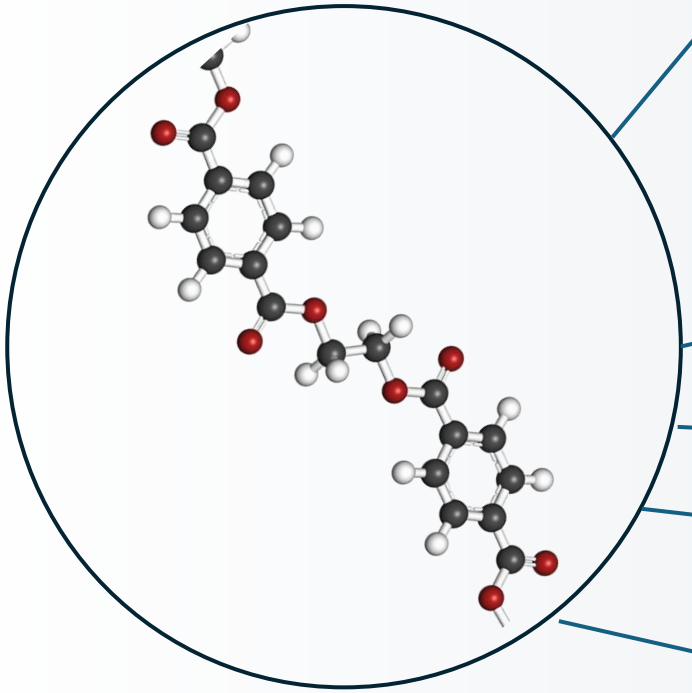
1. **Introduction :** what is a polymer and its applications
   Methodology :
   1. Defining the model
   2. Brief definition of software tools
   3. Algorithms for MD simulation
2. **Results :**
   1. Melting process
   2. Deformation process
3. **Conclusion / Outlook**

What is a Polymer



Natural polymers : DNA, Silk, Wool, Protein

Medical Applications

Food Containers

Electronics Devices

Paints

METHODOLOGY

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MD Simulation Process

Input

Structure/Topology

- Molecular Description
- Initial positions 'r' and velocities 'v'

Force Field- Potential Functions

- Excluded Volume Potential
- Connectivity Potential
- Angular interaction Potential

Compute Forces

Updates 'r' and 'v'

Repeat for n steps

Integration of Newton's equations of motion + Thermostat and Barostat (Nosé-Hoover]

Output

- New Positions
- Forces
- Energies
- Temperature
- Pressure

Etc

Verlet Algorithm : Integration method

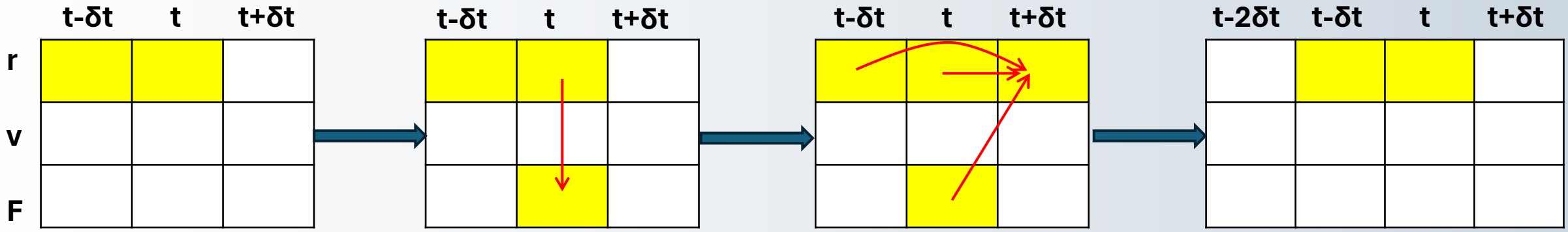
The basic idea is to write two third-order Taylor expansions for the positions, one forward and one backward in time :

$$r(t+\delta t) = r(t) + v(t)\delta t + 1/2\, a(t)\delta t^2$$
$$r(t-\delta t) = r(t) - v(t)\delta t + 1/2\, a(t)\delta t^2$$

And by summing this two equations, we obtain :

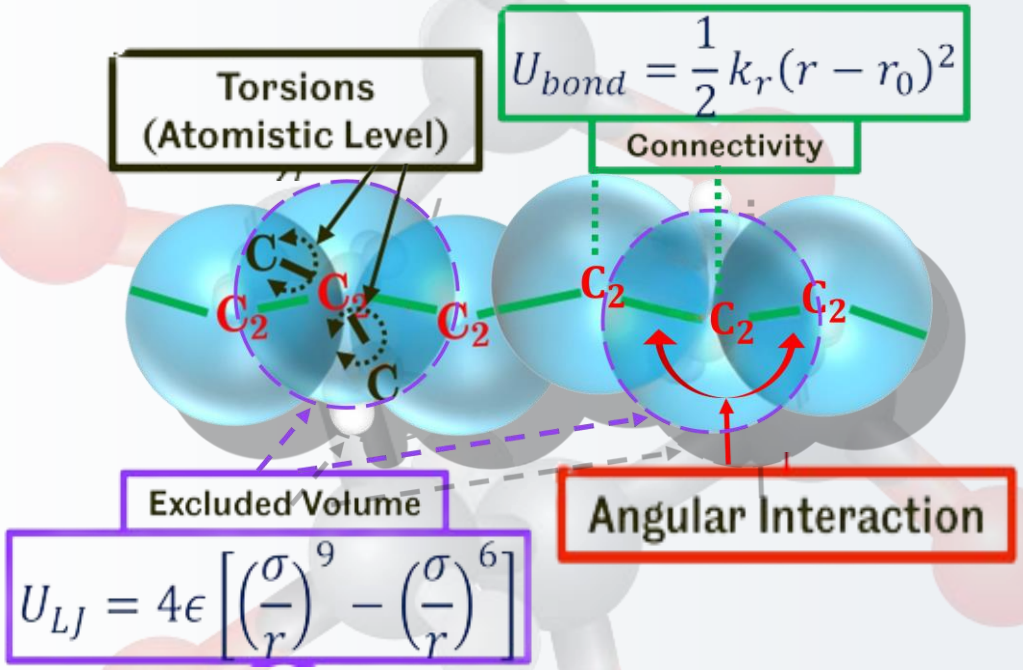
$$r(t+\delta t) = 2r(t) + r(t-\delta t) + a(t)\delta t^2$$

The Verlet algorithm uses positions and accelerations at time t and the positions from time t-δt to calculate new positions at time t+δt. The Verlet algorithm uses no explicit velocities .

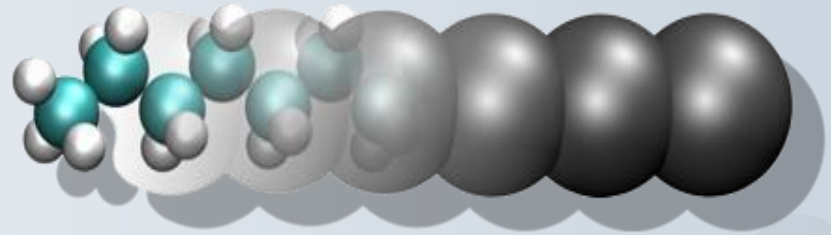


Defining the model

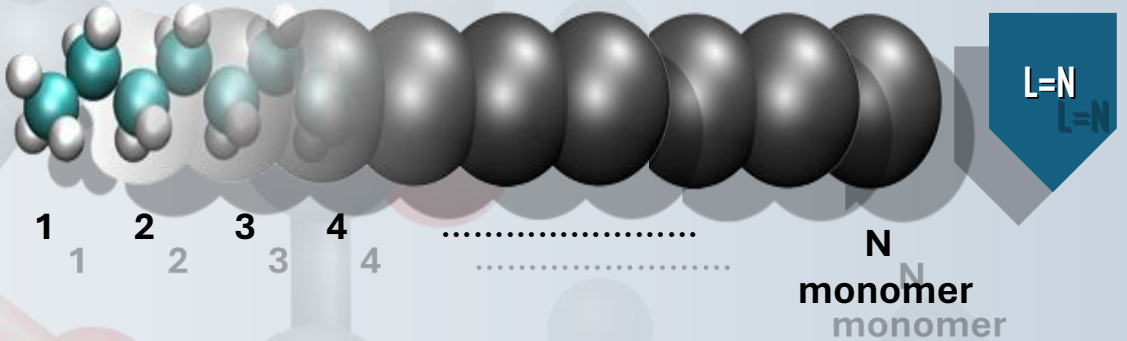
Force Field- Potential Functions



CG- United Monomer



Configurations with different length « L » chain



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Simulated Thermodynamic properties

For the simulation, we determined the thermodynamic properties, Temperature and Pressure as following:

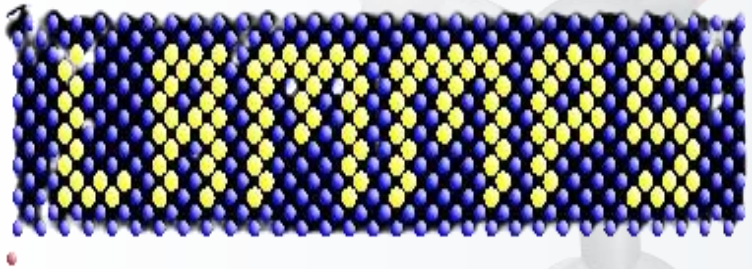
$$k_B T = \frac{\langle 2K \rangle}{f}$$

$$P = \rho k_B T + \frac{1}{dV} \left\langle \sum_{i<j} f(r_{ij}) \, . \, r_{ij} \right\rangle$$

Nosé Hoover Thermostat/Barostat

It is a mechanism for controlling temperature and pressure, ensuring that calculated thermodynamic properties (such as temperature and pressure) are maintained at target values: introduce a new degree of freedom that plays the role of heat bath

Brief description for used software



LARGE ATOMIC/MOLECULAR MASSIVELY PARALLEL SIMULATOR

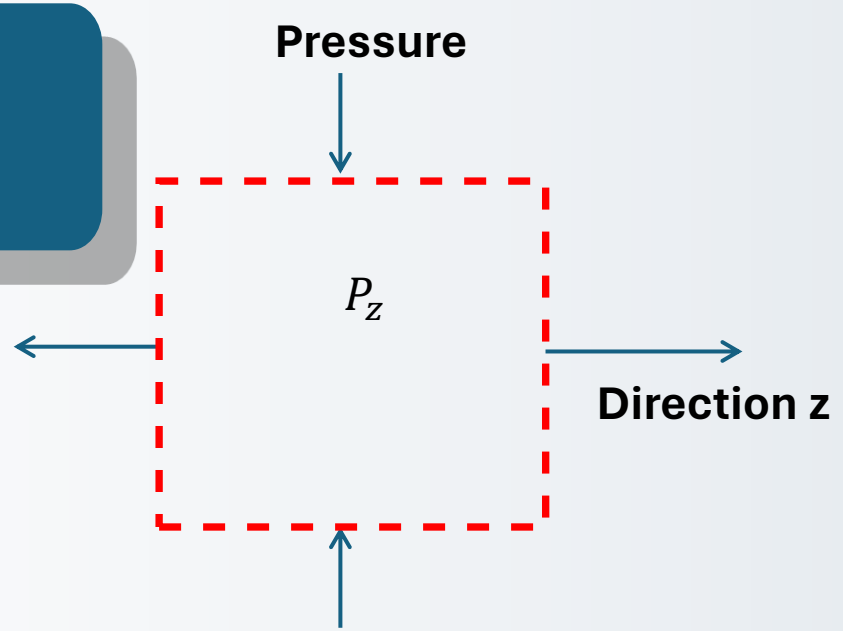
- Performs molecular dynamics (MD)
- Large Systems (Atomic/Polyatomic/granular...etc)
- Parallel execution for using multiple no of processors
- Solves the fondamental dynamic formula F=ma
- Use Force Fields to describe interaction between models

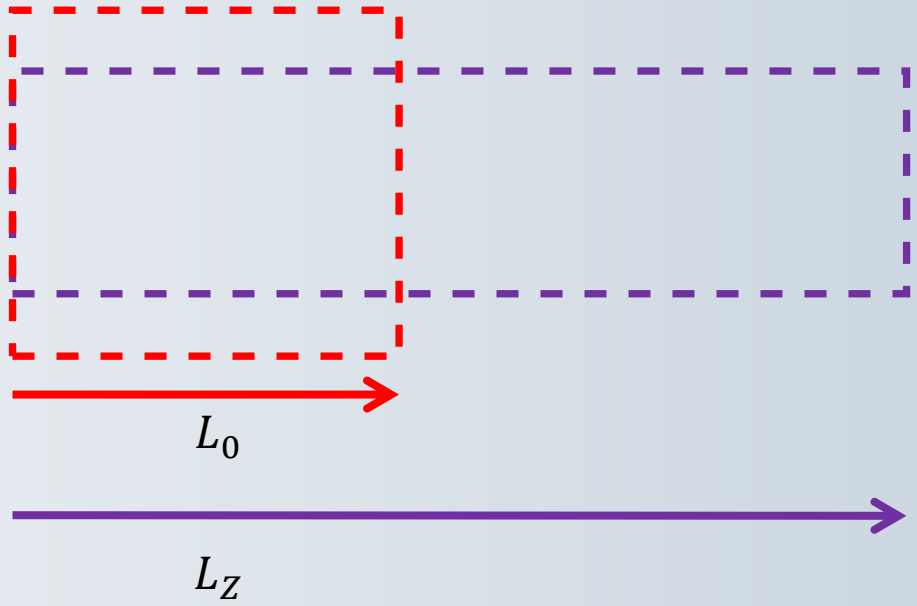
VMD

Post Process : Visualization using output data

Deformation Process

Schematic view of Deformation





Mechanical response parameters:

True Stress : $P_0 - P_z$; Response of the system to strain, relative change of internal pressure

True Strain : $\log(L_z/L_0)$; Relative elongation of the material/box

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RESULTS

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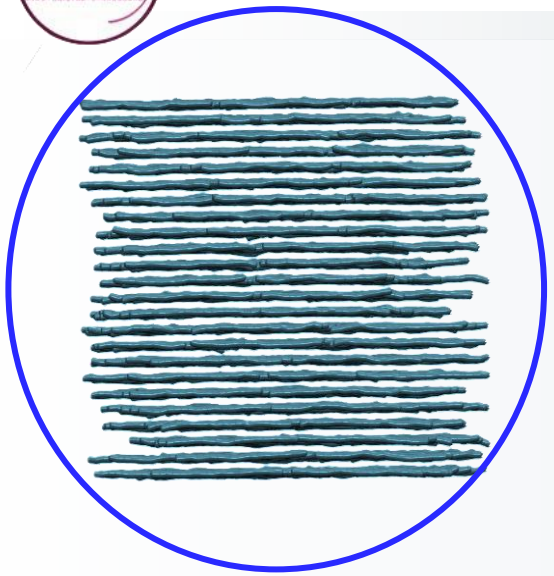
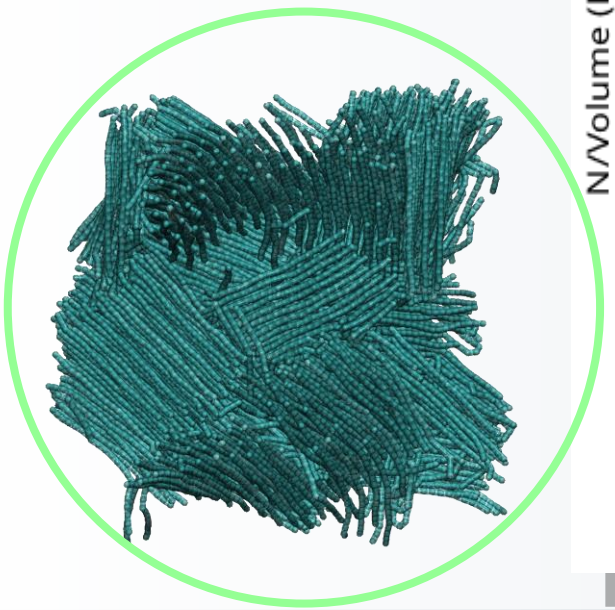
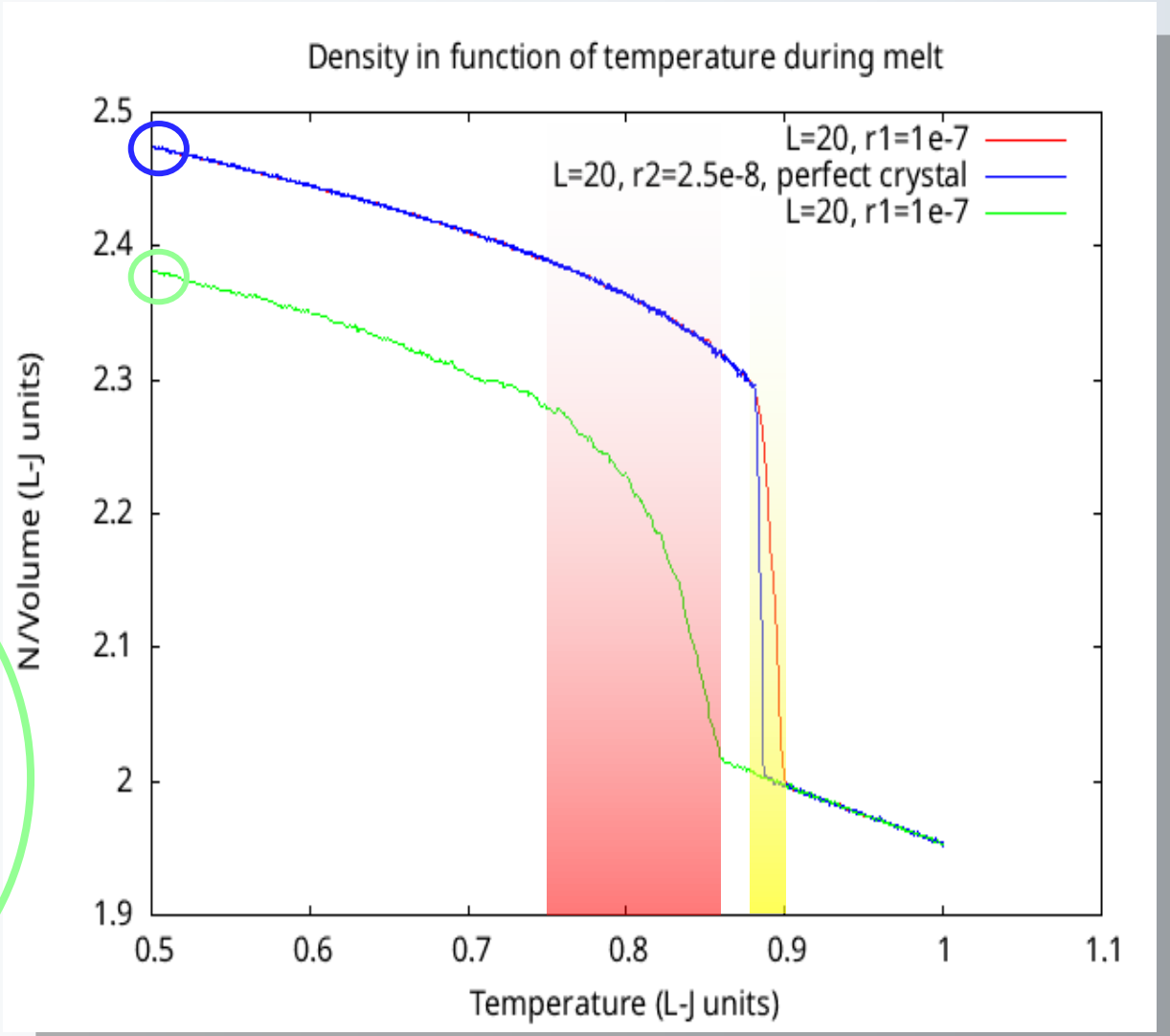
Melting Process : First Characterization







Phase Transition Identification(Crystallinity and Morphology)

Perfect system

Highest density at low Temperature.
Sharp/sudden density decrease at Melting point.

Semicrystalline system

Lowest density at low Temperature.
gradual density decrease at Melting point.

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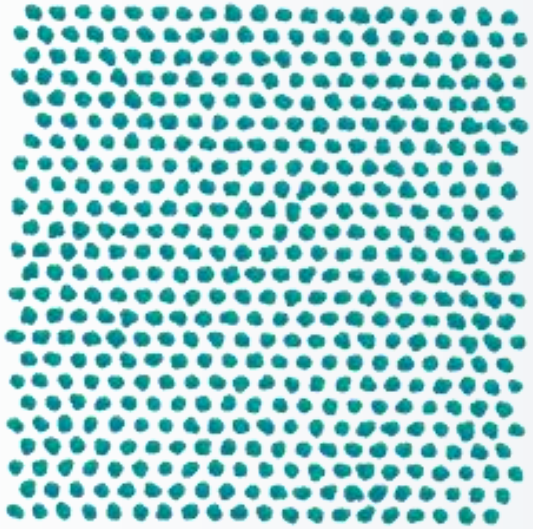
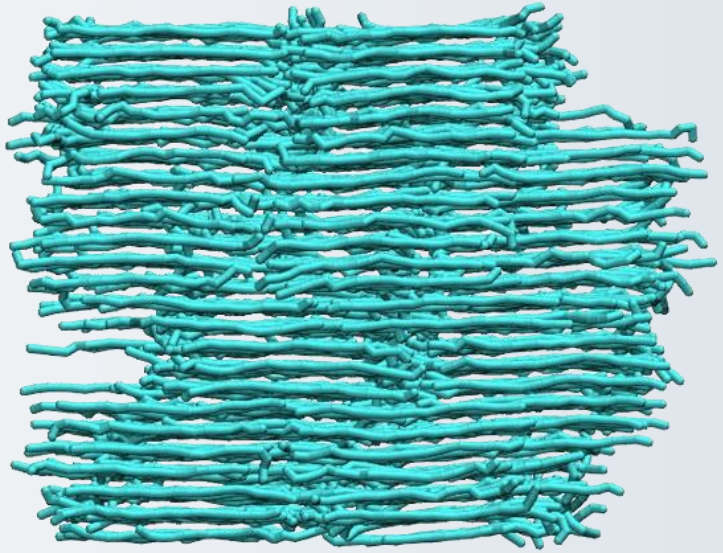
Melting Process Analysis: Visualization

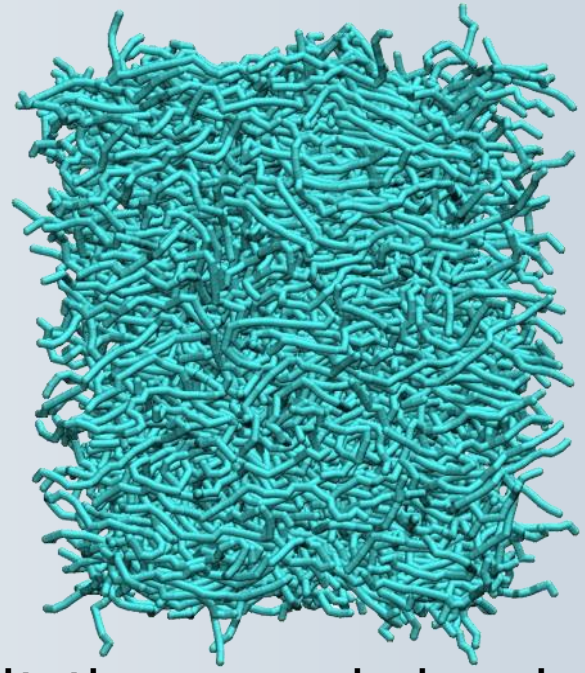
Perfect system



Solid state: as initial state, the polymer is in crystalline structure That is hexagonal, where the chains are ordered and Oriented in the direction Z



Phase transition: we can still notice some ordered domains built in 2 columns and that are attached by amorphous domains



Liquid state: we can clearly see that all chains polymers are disordered and oriented to different directions due to high Temperature above the critical point.

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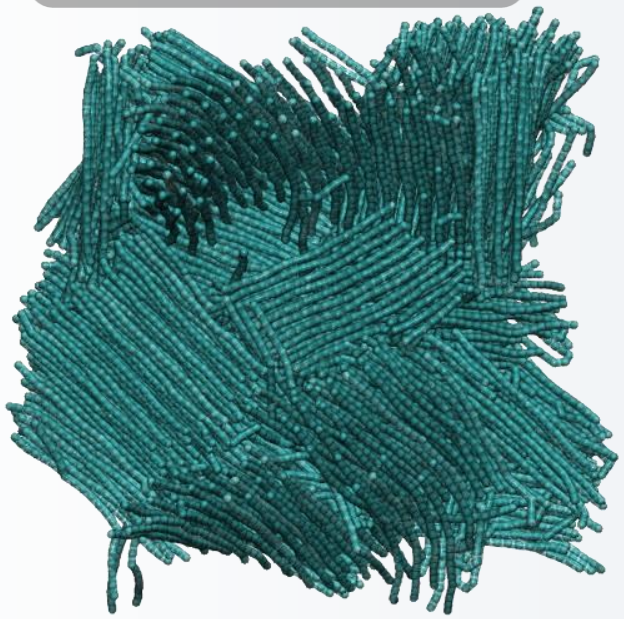
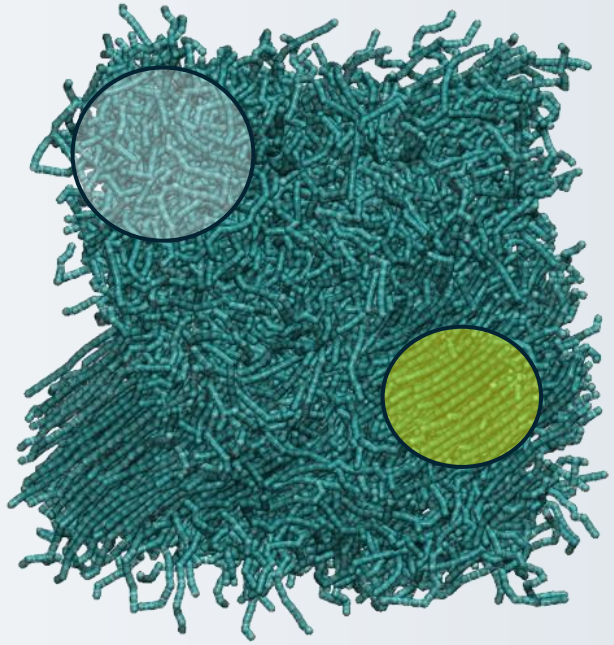
Melting Process Analysis: Visualization

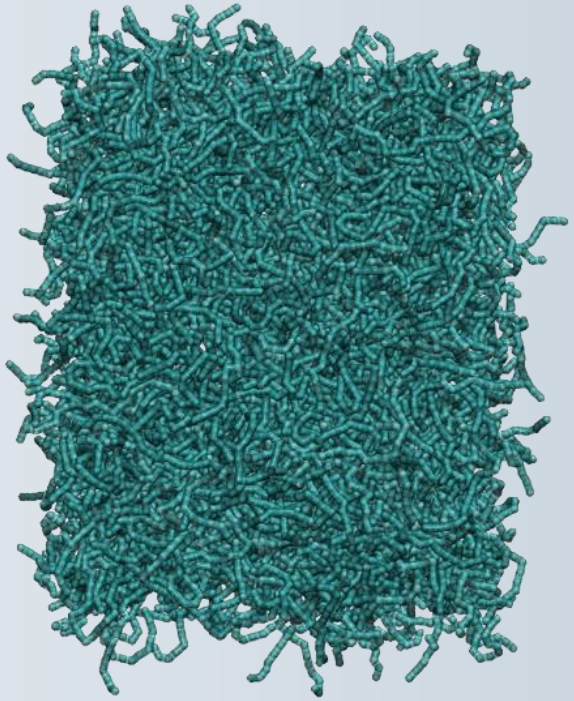
Semicrystalline system



Solid state: as initial state, it looks like a packet of ordered domains with differente orientation direction.



Phase transition: some ordered domains are remained but there's a manifestation of structure instability which mentions amorphous behavior in some region



Liquid state: this state means a lack in crystalline structure, where the chains are arranged randomly and without a predictable,repeating pattern.

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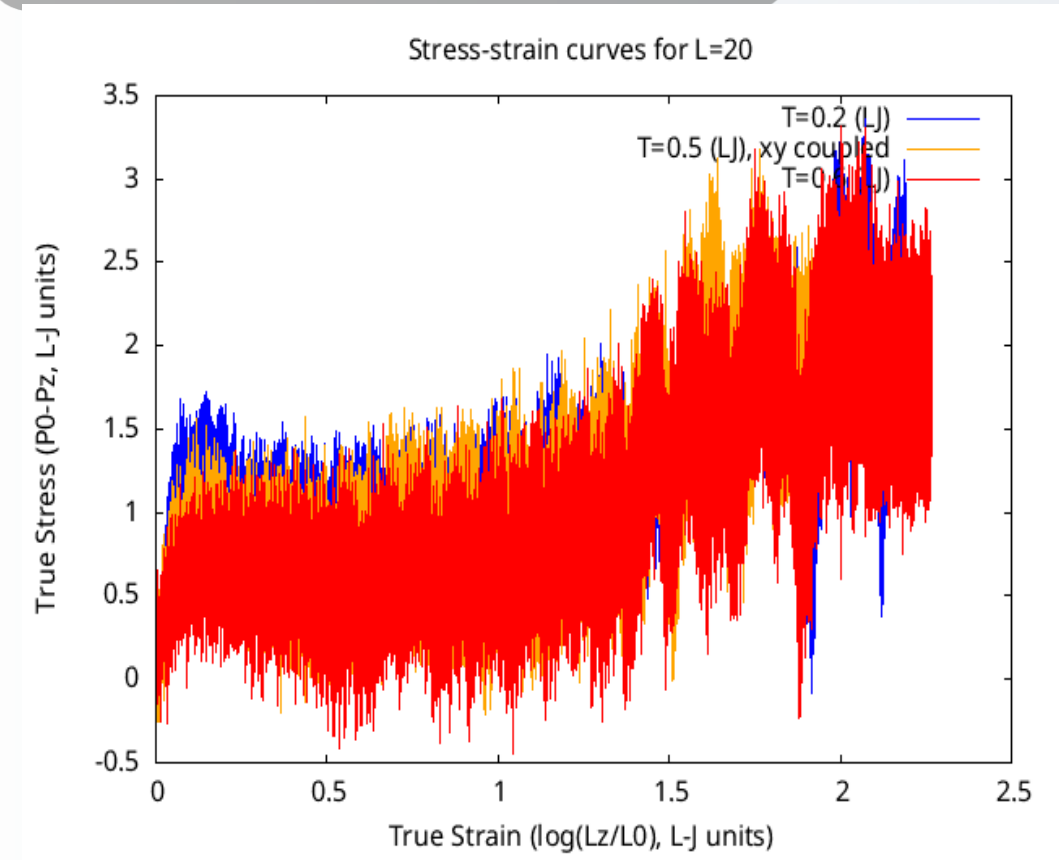
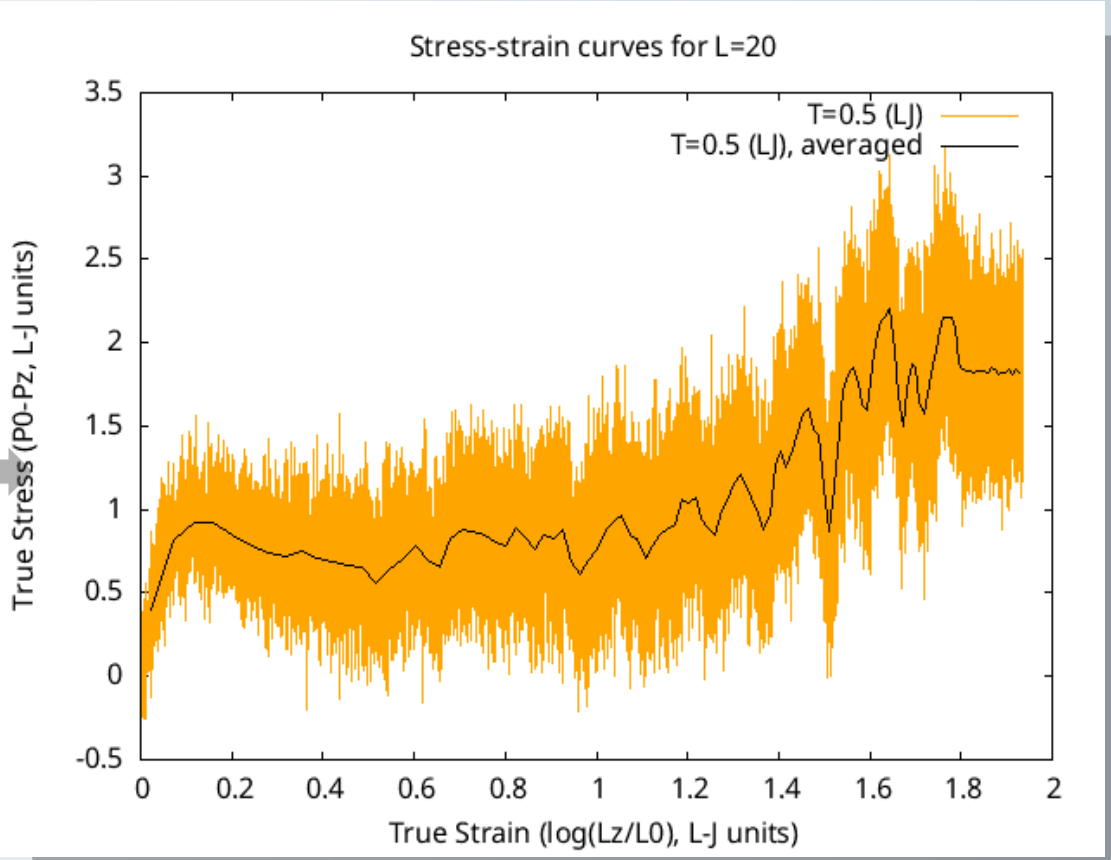
Deformation Process Analysis

Semicrystalline system with Length Chain L=20





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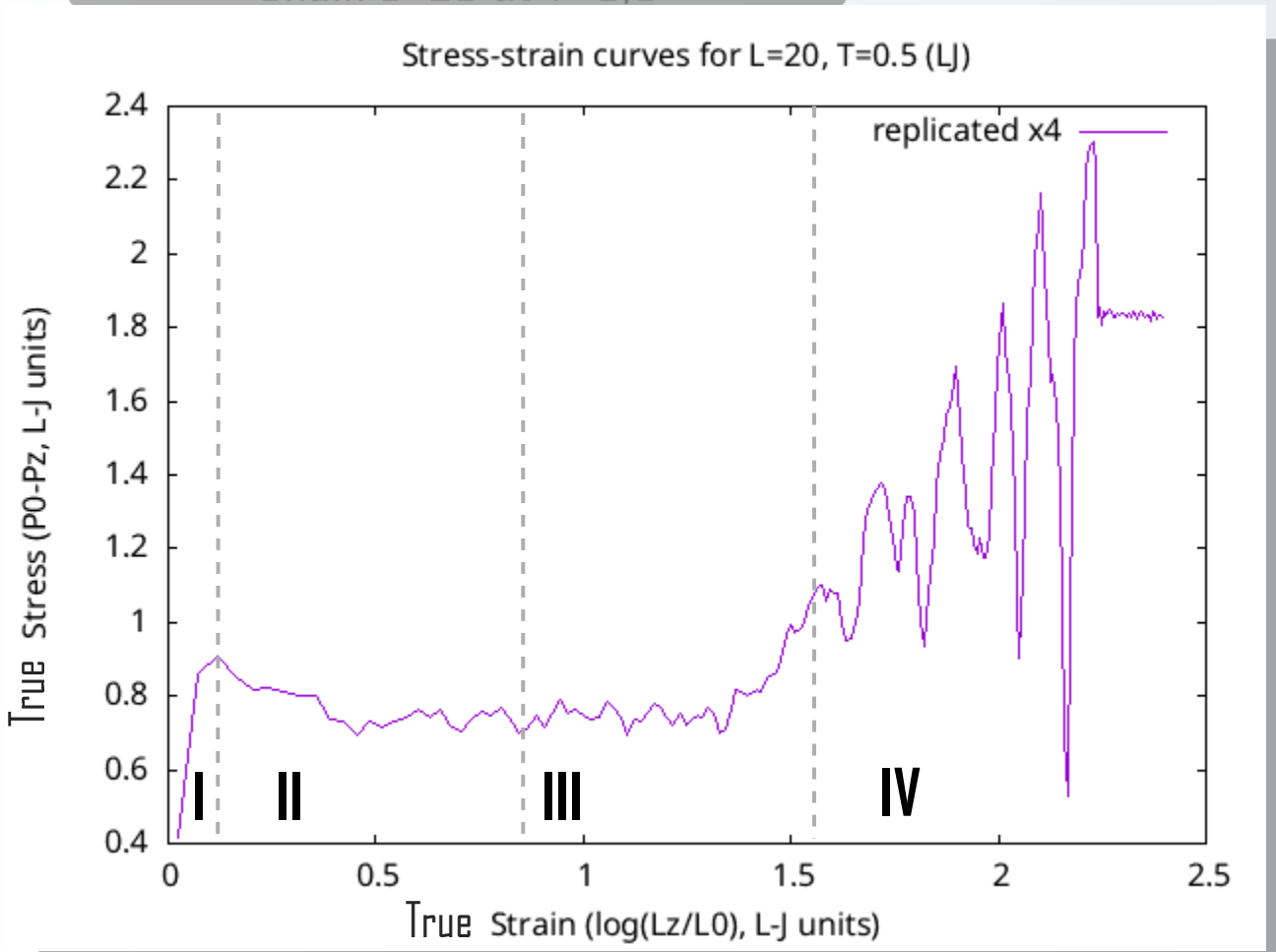
Deformation Process Analysis

Semicrystalline system with Length Chain L=20 at T=0,5



4 different types of behavior/regime for all temperature :

I. Elastic : For small strain, linear behaviour

II. Strain-softening : Beyond the elastic regime, depending on the parameters (Temperature, the length of the polymers, ...) , the stress is either constant with the strain or decrease with the strain

III. Strain-hardening : Beyond the strain-softening regime, the stress increases with the strain (weak for short chains)

IV. IV. Strain-hardening + oscillations : Apparition of oscillations of increasing amplitudes for high strain, before failure.

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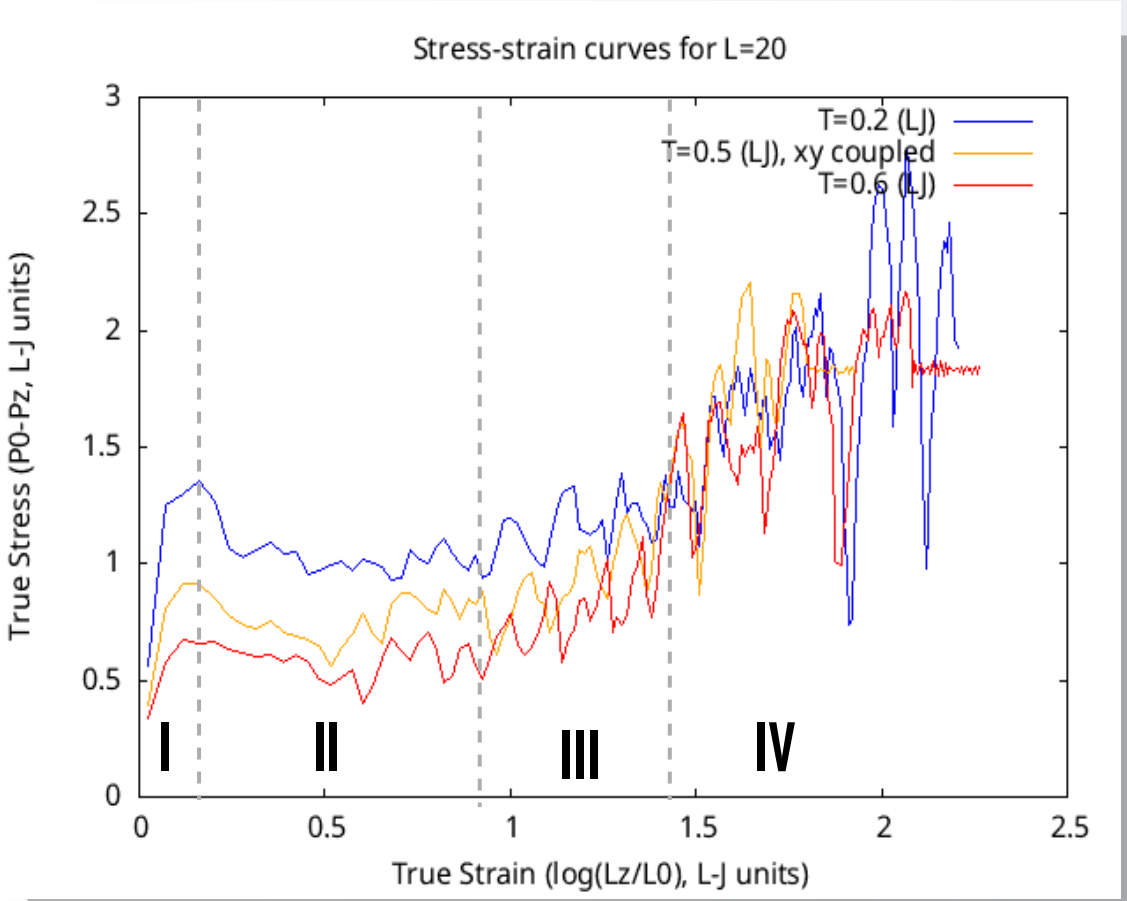
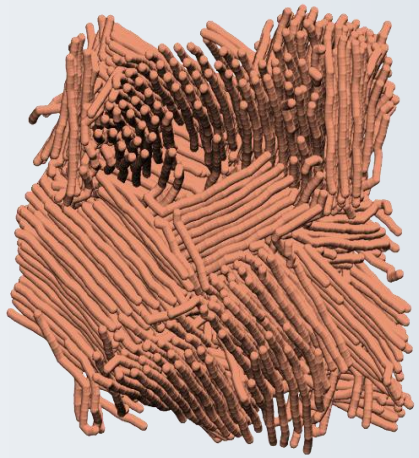
Deformation Process Analysis

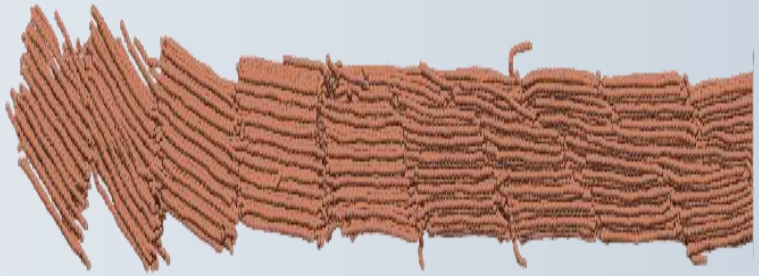
Semicrystalline system with Length Chain L=20



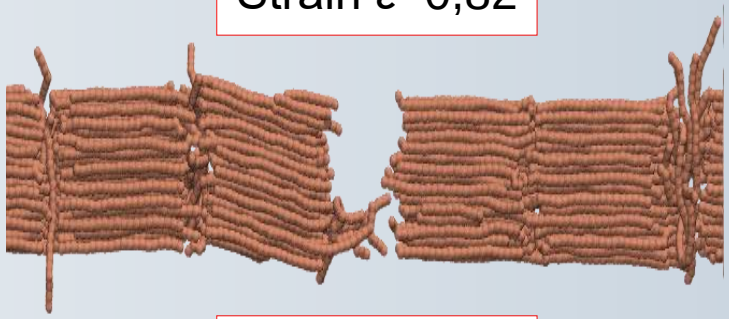
I. Elastic
II. Strain-softening
III. Strain-hardening
IV. Strain-hardening + oscillations



Strain ε=0



Strain ε=0,82



Strain ε=2,21

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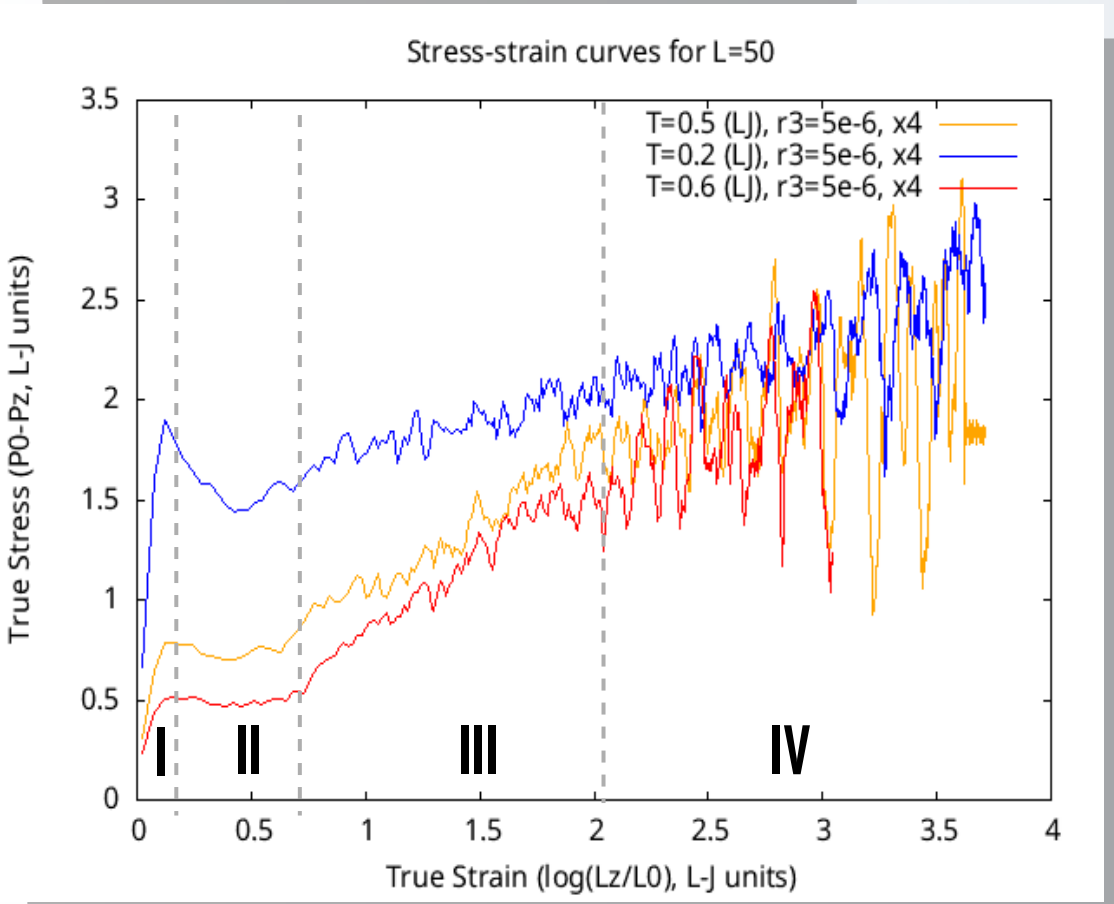
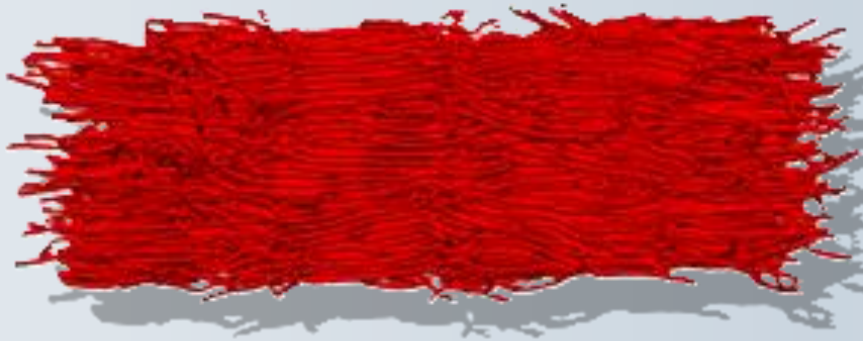
Deformation Process Analysis

Semicrystalline system with Length Chain L=50 and different T



I. Elastic
II. Strain-softening
III. Strain-hardening
IV. Strain-hardening + oscillations

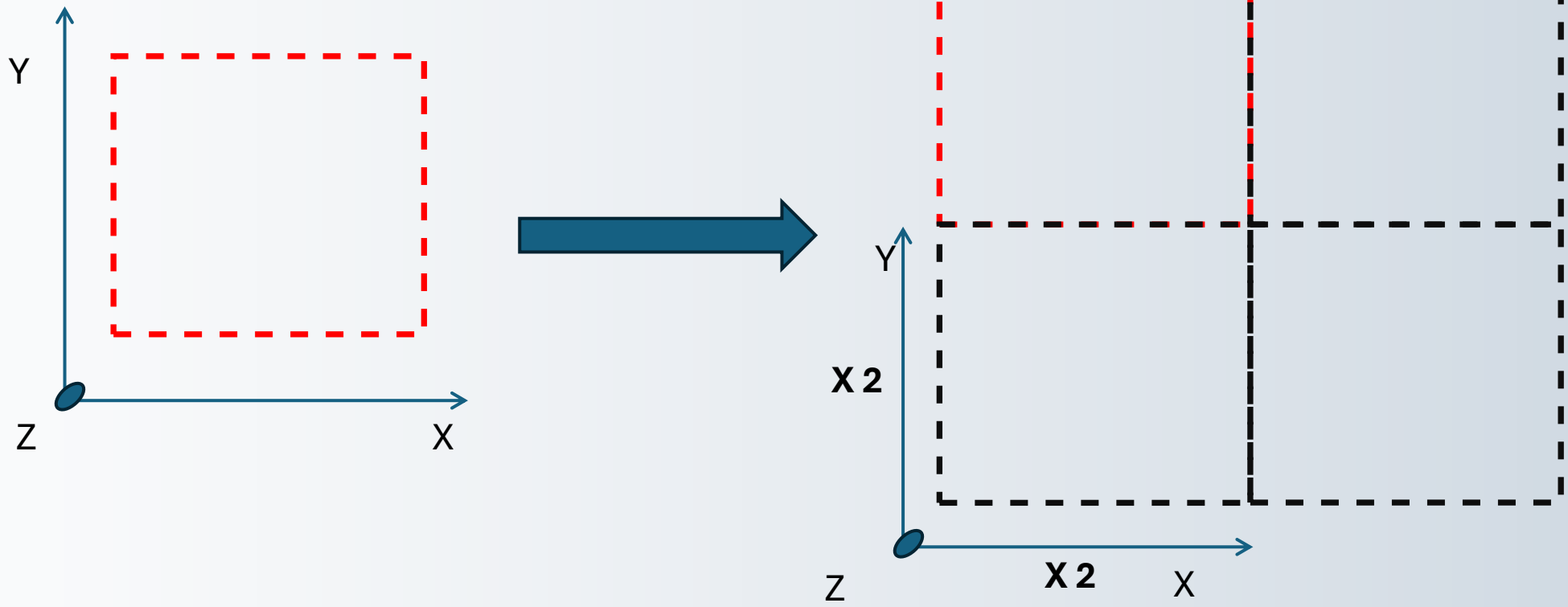
Strain ε=0



Strain ε=1,2

Deformation Process

Replicated Systems



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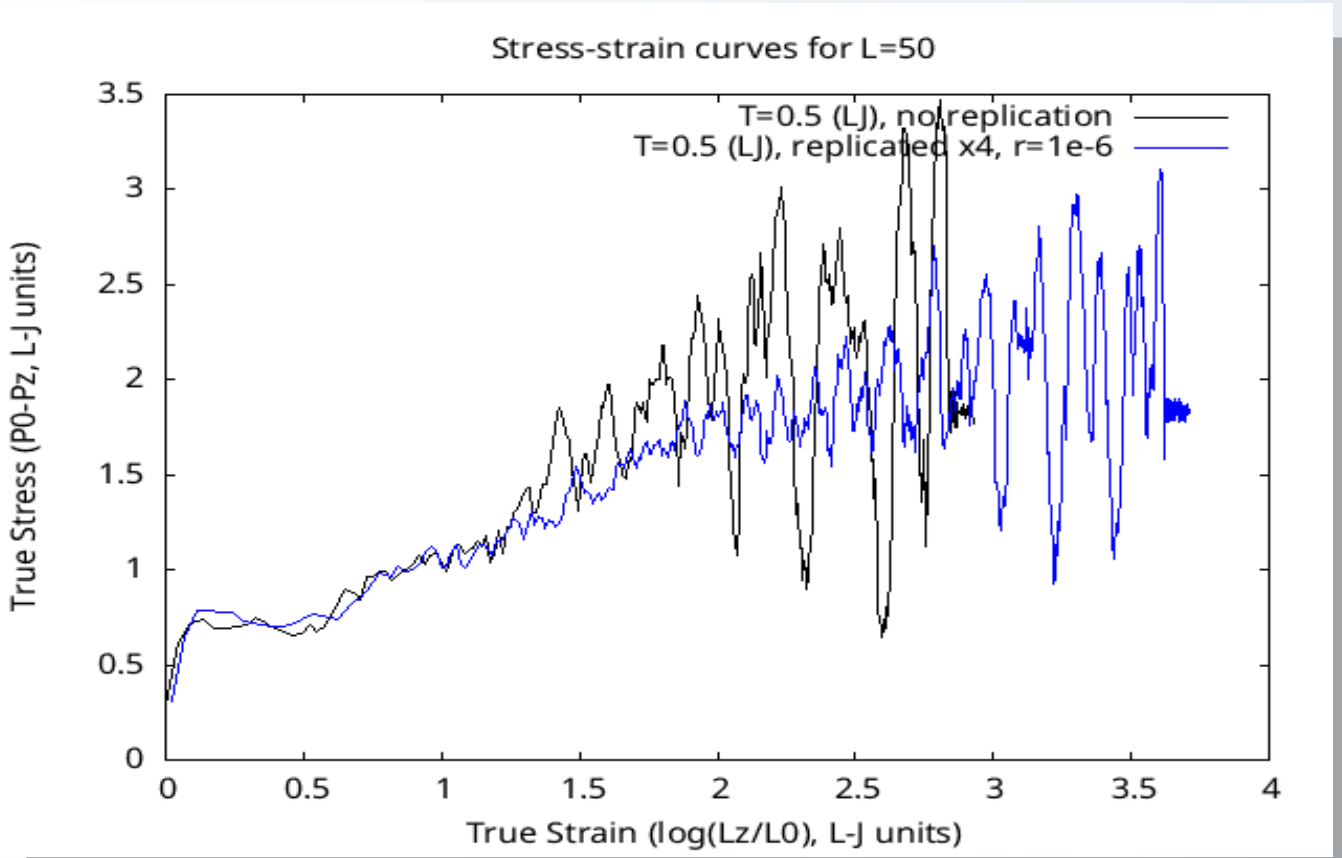
Deformation Process Analysis

Differences in behavior for non replicated- replicated systems



The non-replicated system presents those oscillations way before the replicated one, with a higher amplitude, and breaks for smaller strain.

This can be explained by the fact that those oscillations appear due to the rearrangement of the polymers inside the box, it is a numerical artefact due to the finite volume of the simulation box:

With the replicated systems, we can consider more polymers inside the box, thus explaining why the oscillations appear later.

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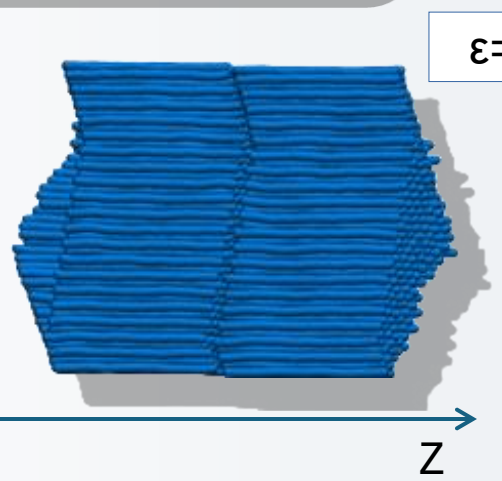
Deformation Process Analysis

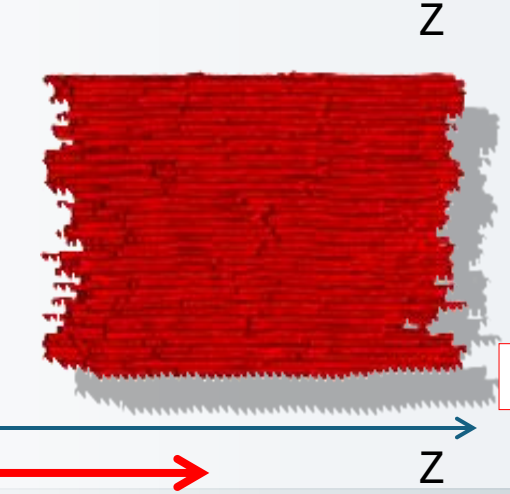
Perfect Crystal under deformation in different directions

Deformation direction



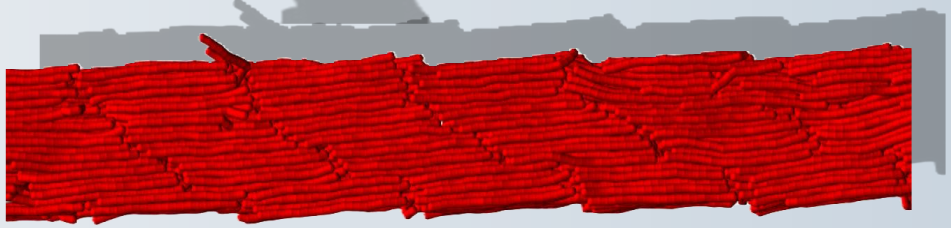
ε=0

ε=1.4



Deformation direction

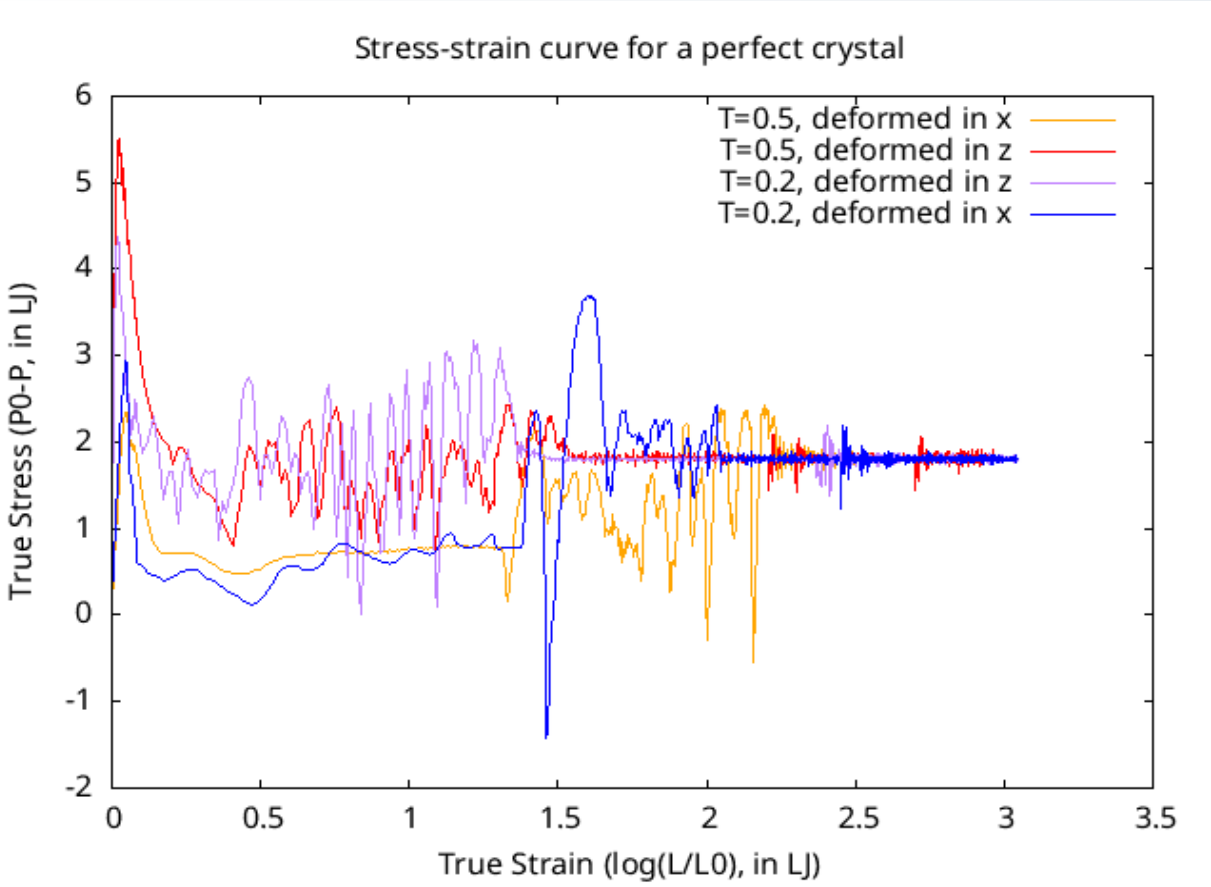
ε=0



ε=1.5

Deformation Process Analysis

Perfect Crystal under deformation in different directions



Two different behavior for the different directions of deformations :

- In z direction, right after the spike, the stress starts to oscillate, meaning that the polymers rearrange themselves in lamellae, before eventually breaking.

- In x direction, after the spike the stress remains approximatively constant for a long period of strain where the polymers rearranges, aligning themselves in this direction. When most polymers are aligned in the z direction, the stress start to oscillate before failure.

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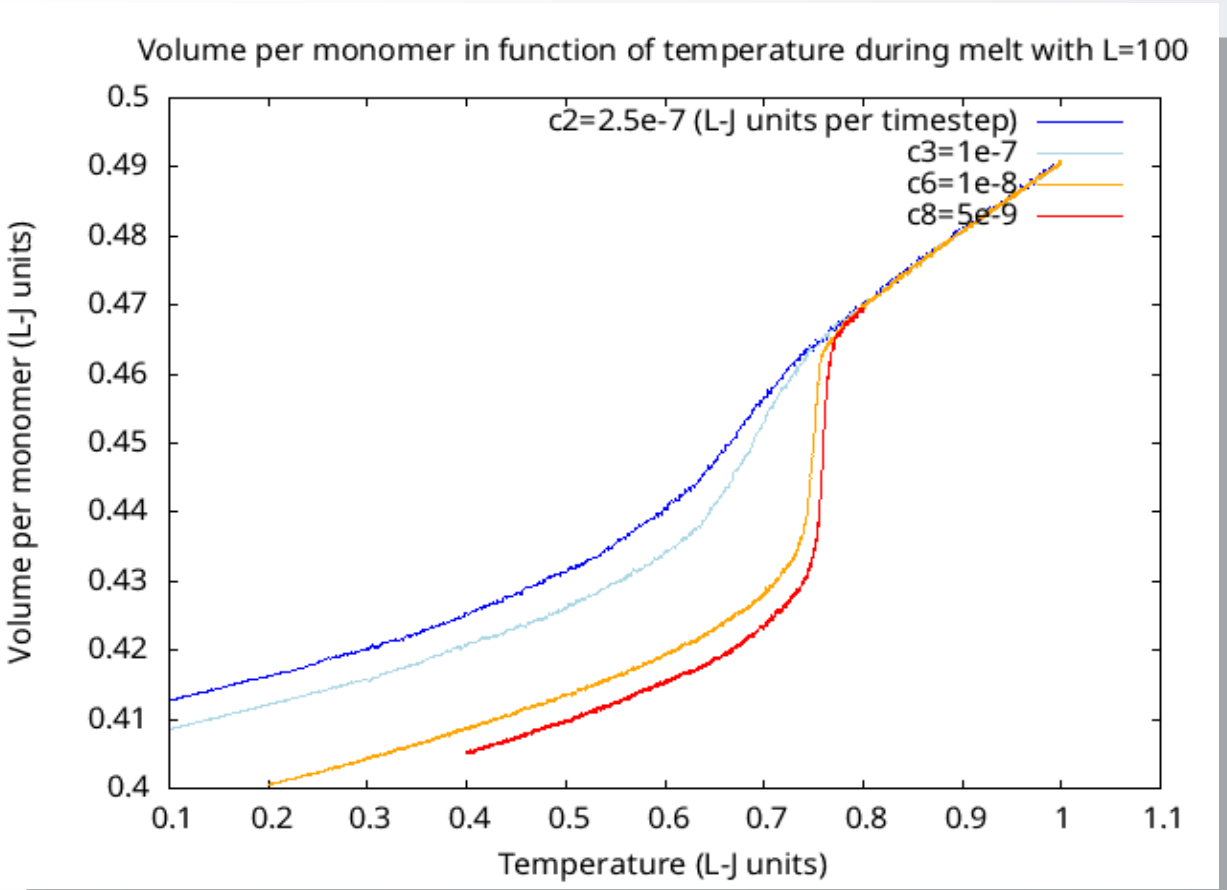
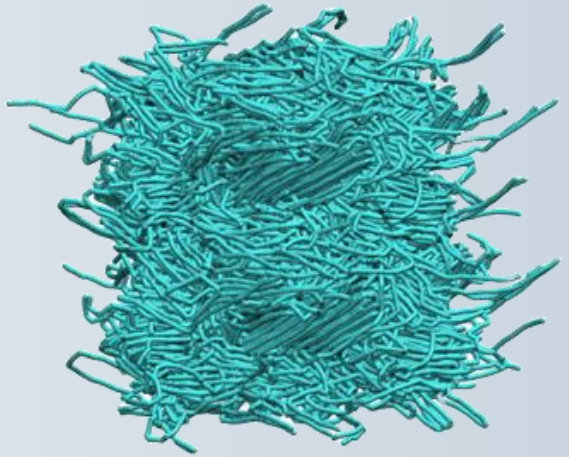
Deformation Process Analysis

Obtained different Crystallinities with different cooling rates

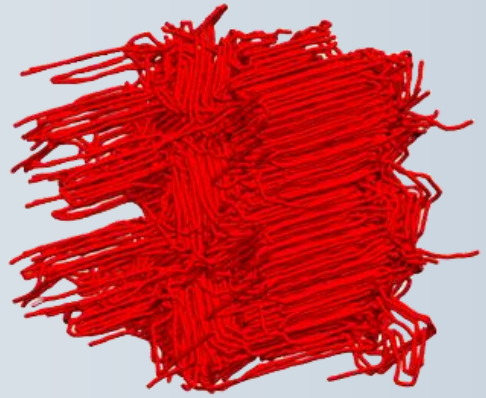


Initial configuration for the highest cooling rate (c2)



Initial configuration for an high cooling rate (c3)

Initial configuration for a small cooling rate (c6)



Initial configuration for the smallest cooling rate (c8)

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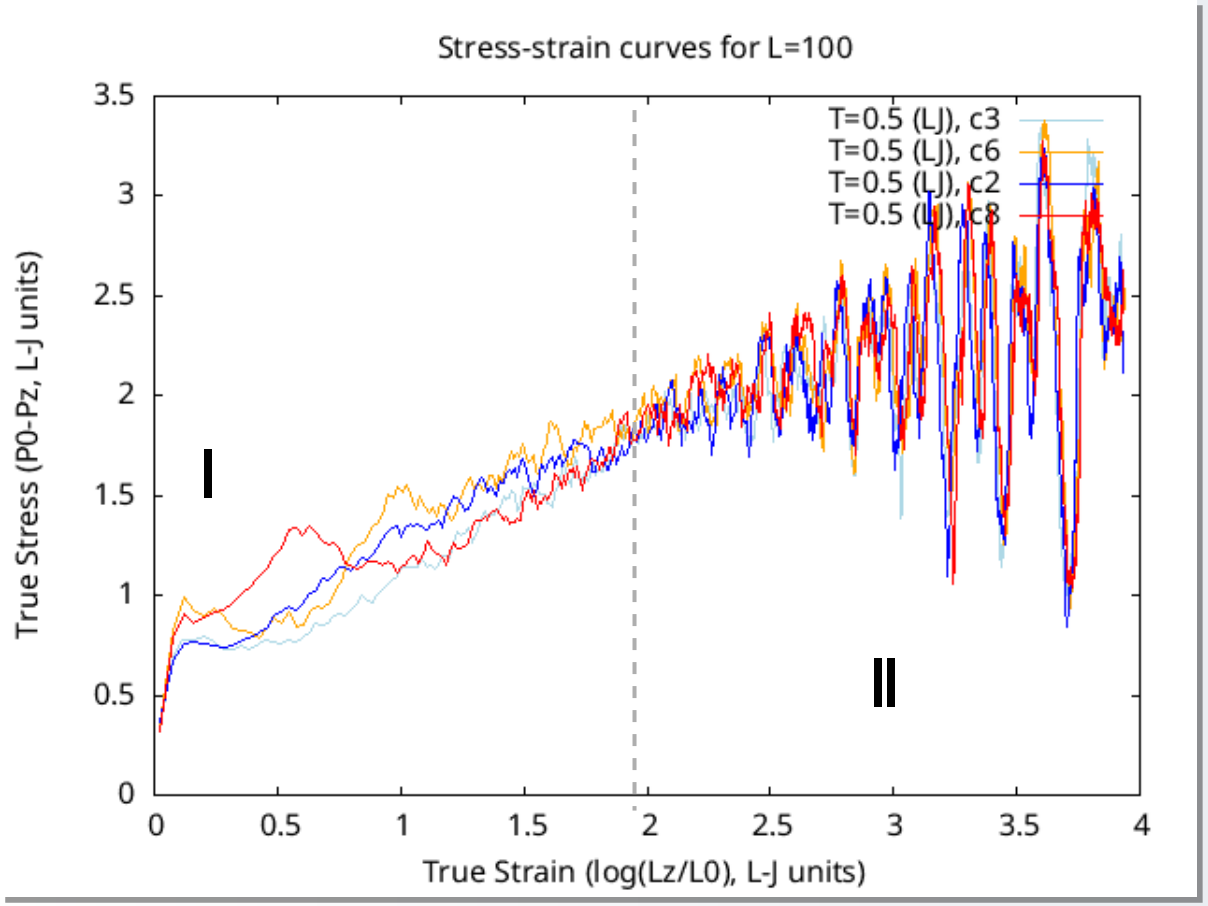
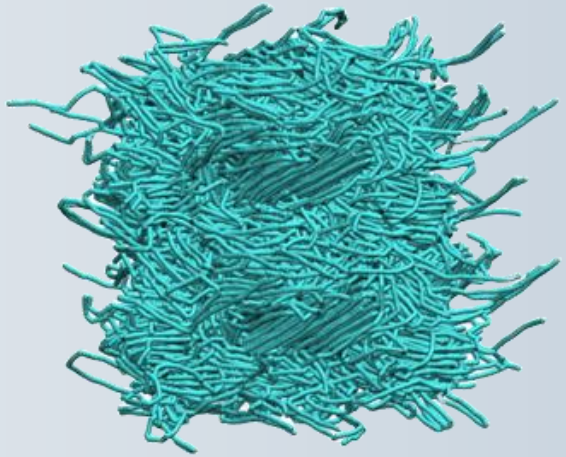
Deformation Process Analysis

Differences in behavior for different initial configurations at T=0,5

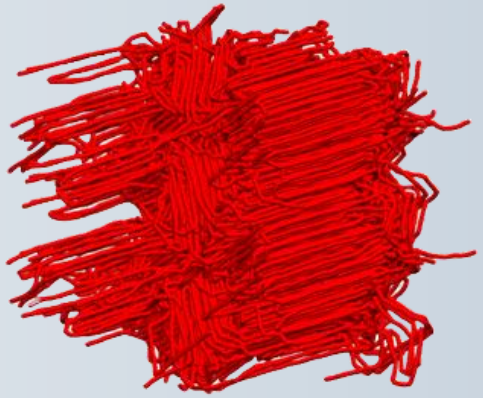


Initial configuration for the highest cooling rate (c2)



Initial configuration for an high cooling rate (c3)

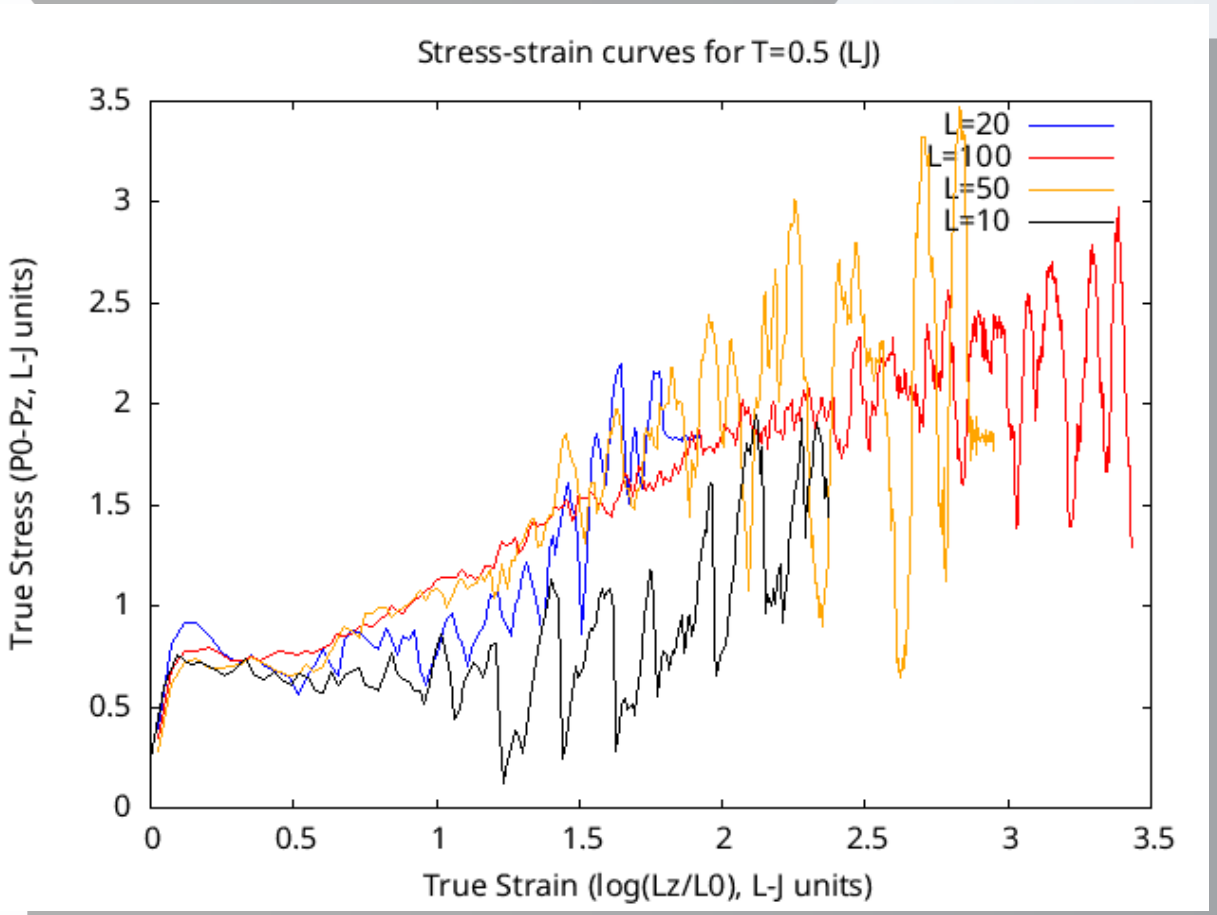
Initial configuration for a small cooling rate (c6)



Initial configuration for the smallest cooling rate (c8)

Deformation Process Analysis

Differences in behavior for different chain length at T=0.5



1. For larger chain length, the 3rd regime (strain-hardening) seems to go to higher strains than for smaller ones.

2. In the strain-softening regime, systems with the smallest chains present a decrease in stress relative to strain, whereas for larger chains, the stress remains somewhat constant.

3. The longer the chains are, the more chance there is that chains becomes entangled at some point, increasing the stress.

4. The larger the chains are, the more the system can sustain strain before failure.

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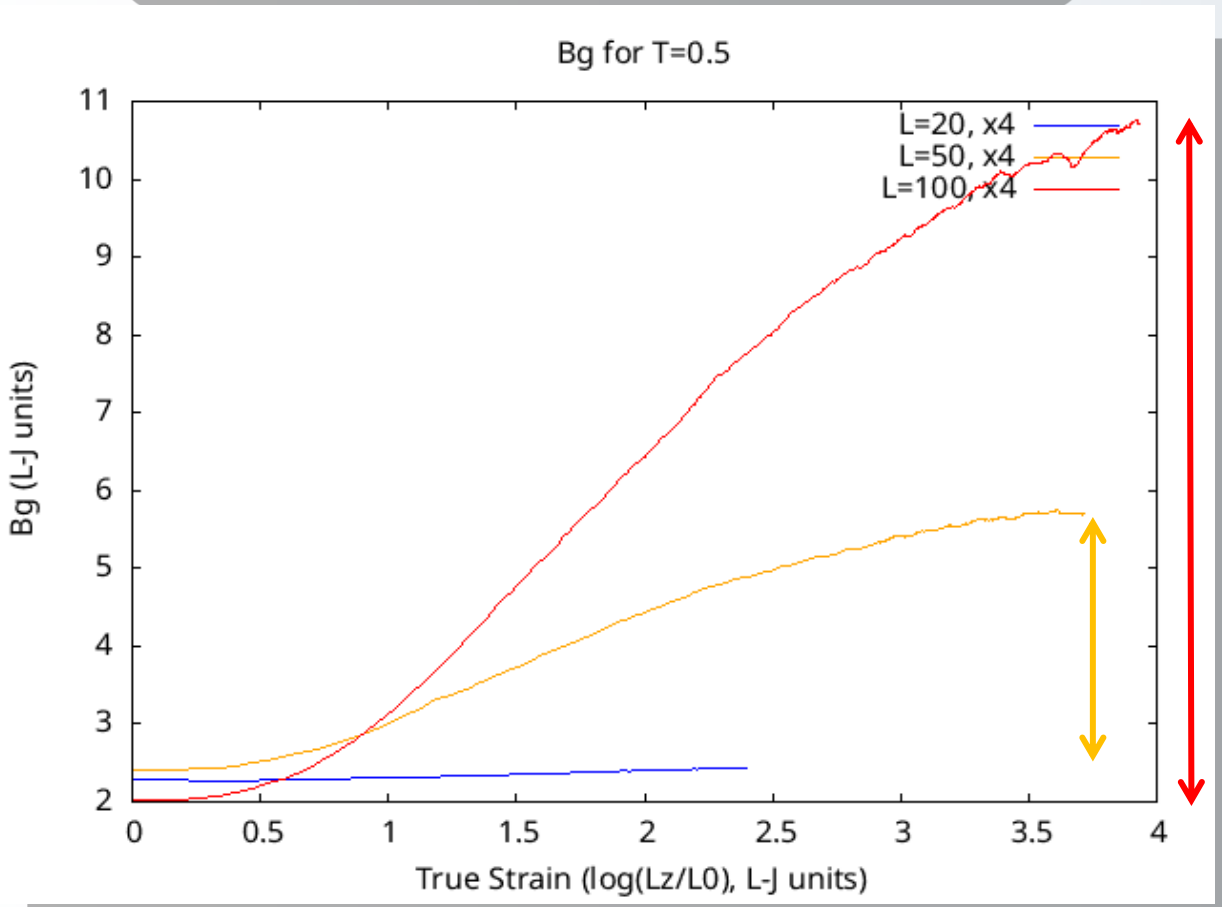
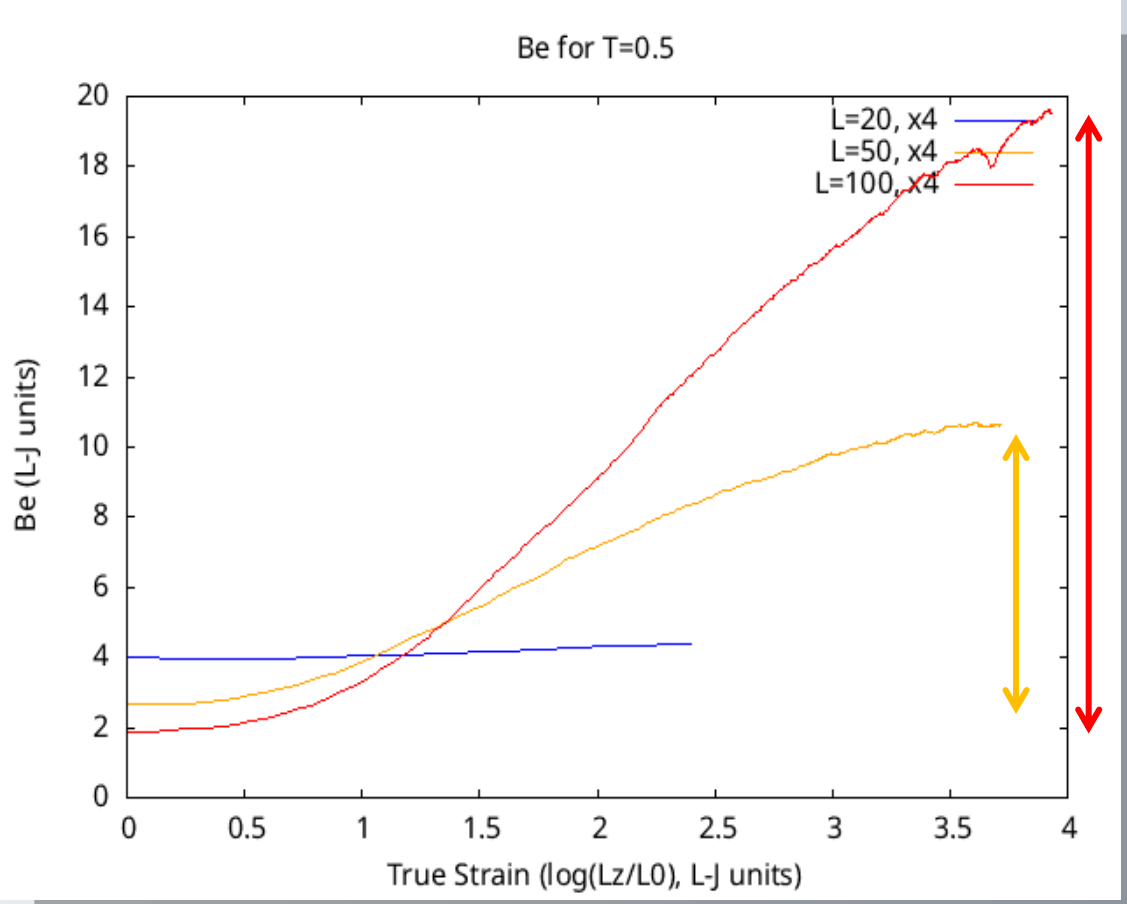
Conformation during deformation

Giration radius Rg and end-to-end distance Re for different chain length at T=0.5

$Bg=6*(Rg^2)/L$

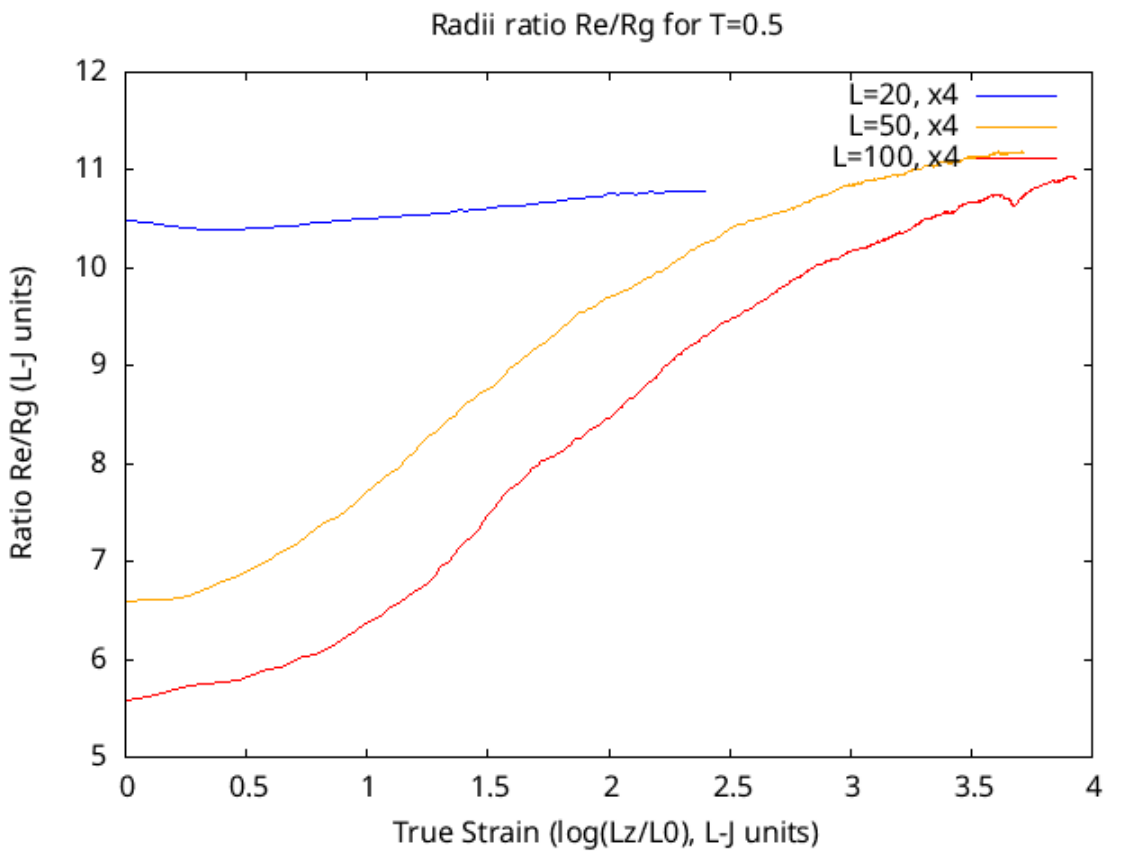
$Be=(Re^2)/L$





What is a Polymer

Ratio $< R_e^2 > / < R_g^2 >$ at T=0.5 (LJ) for different length



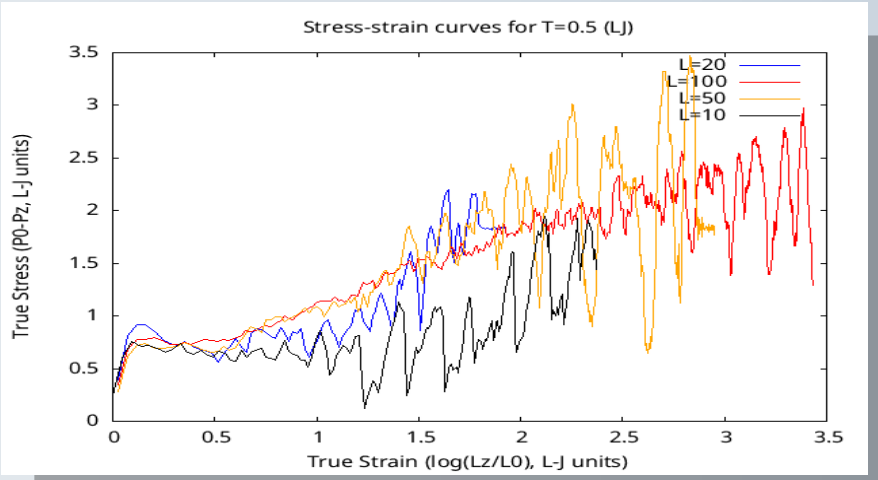
Small chain ⇒ constant ratio
(Chains are already stretched in the initial configuration)

End of deformation ⇒ Approximative ratio value ~11.
(Perfectly straight polymer has a ratio value of 12)

Larger chain ⇒ ratio valu is below value 6.
(Which is the reference to Gaussian ideal polymers)

Conclusion

- Study of polymer crystals under deformation via MD simulation
- Identify 4 regimes in the Stress strain curves
- Comparison of Crystalline and semicrystalline Polymers
- Chain length Dependance



Further studies :

- Quantification of order parameters

(Orientational order and structure factor)