NATIONAL TECHNICAL UNIVERSITY OF ATHENS
SCHOOL OF CHEMICAL ENGINEERING
EPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

POLYMER SCIENCE

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Computational Exercise

General Methodology for Estimating the Dimensions of Polymer Chains Based on Atomistic Monte Carlo Simulations of Single Unperturbed Chains

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SCOPE

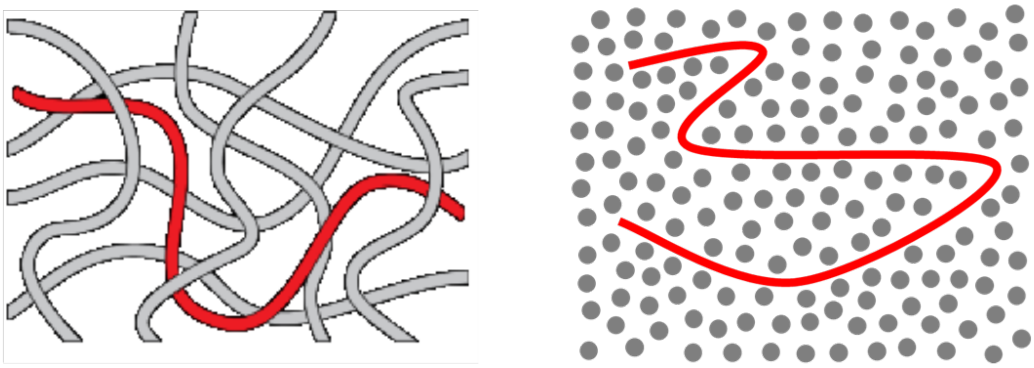
In this exercise we focus on the problem of estimating the conformational stiffness of unperturbed polymer chains of given chemical constitution via atomistic Monte Carlo simulations of single chains, using a detailed united atom force field for the representation of interactions.

THEORETICAL NOTE – CONFORMATIONS OF POLYMER CHAINS

A polymer chain can adopt a very large number of conformations. By conformation we mean an arrangement of the chain in space, which is determined by the relative positions of all its monomers and dictates the set of n bond vectors connecting neighboring atoms along its backbone. The conformations adopted by a polymer chain depend on three characteristics: (a) its stiffness, (b) interactions among its monomers, (c) interactions between the chain and its environment (other polymer chains in the case of a melt and/or solvent molecules in the case of a solution). In Figure 1 we see a schematic representation of conformations of a polymer chain (red curve) inside a polymer melt and inside a Θ-solution.

The dimensions of polymer chains, which are usually expressed through its mean squared end-to-end distance $\left\langle R^2 \right\rangle$ or its mean squared radius of gyration $\left\langle R_\mathrm{g}^2 \right\rangle$, and their conformational stiffness, which is usually quantified via Flory's characteristic ratio, C_∞, are related with a multitude of macroscopic properties which play an important role in the design of new polymeric materials and in the development of new coarse-grained models for these materials.

Both in the melt state and in a solvent under Θ conditions [see Figure 1(a), (b)] polymer chains behave as if they are free of nonlocal nonbonded interactions[1] between topologically distant segments along their backbones and subject only to local interactions.



(a) Polymer chain in a polymer melt **(b) Polymer chain in a Θ-solution**

Figure 1. Schematic representation of the conformation of a polymer chain in two different environments: (a) polymer melt; (b) Θ-solution.

This can be explained if one considers the constraints imposed on a chain by the surrounding chains in a melt, or by the surrounding solvent molecules in a Θ-solution. Under Θ-conditions, the tendency of the chain to swell in order to avoid nonlocal excluded volume interactions between topologically distant segments along its backbone is exactly compensated by a tendency to shrink in order to avoid unfavorable interactions between its segments and the surrounding solvent. Similarly, in a melt a chain has nothing to gain by swelling to avoid nonlocal excluded volume interactions, since, if it does so, it will encounter other chains which look like itself. Such chains in a melt or Θ solution are called **unperturbed**. In Figure 2 we see a representation of a single chain of polypropylene. The end-to-end distance vector **R**, the number of skeletal bonds n, and the equilibrium length of skeletal bonds l are marked in the figure.

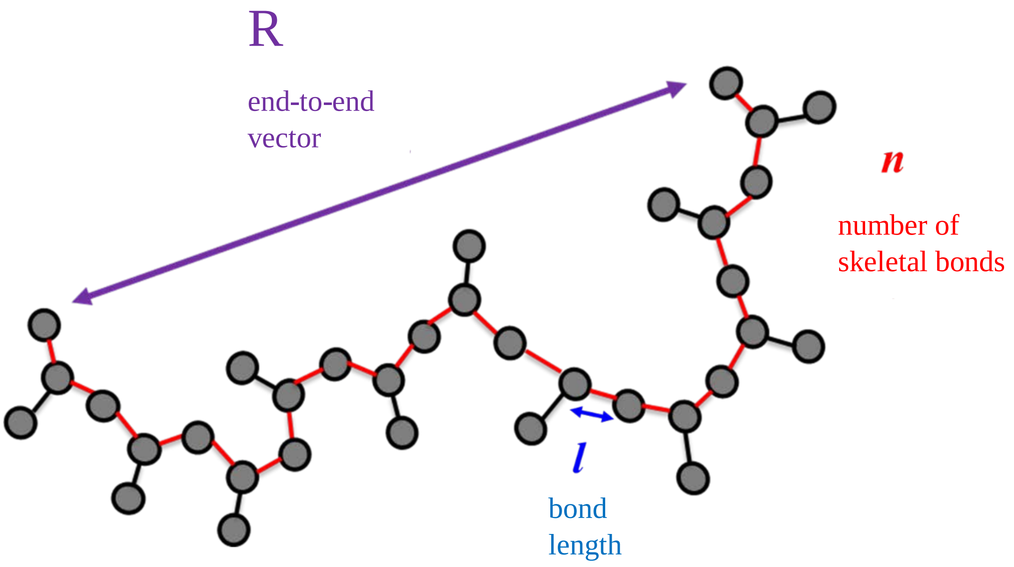


Figure 2. Schematic representation of a single chain of polypropylene, showing the end-to-end vector **R**, the number of skeletal (backbone) bonds n, and the skeletal bond length l.

The chains in an amorphous polymeric material (polymer melt, polymer glass) can be considered as unperturbed, to a very good approximation (Flory's random coil hypothesis) [2]. In a sufficiently long unperturbed chain, the mean squared end-to-end distance $\langle R^2 \rangle$ grows linearly with the number of skeletal bonds, n. Flory's characteristic ratio[1], C_∞, is defined as

$$C_\infty \equiv \lim_{n\to\infty} \frac{\langle R^2 \rangle}{n\, l^2} \tag{1}$$

where l^2 is the mean squared length of skeletal bonds. Moreover, in a sufficiently long unperturbed chain the mean squared end to end distance $\langle R^2 \rangle$ and the mean squared radius of gyration $\langle R_g^2 \rangle$ are related via the equation

$$\langle R_g^2 \rangle = \langle R^2 \rangle / 6 \tag{2}$$

The dimensions of polymer chains are related, *inter alia*, with viscoelastic properties such as the shear stress relaxation modulus $G(t)$ and the molar mass between entanglements M_e. Through theoretical semiempirical relations, the dimensions of polymer chains have been connected quantitatively to melt viscoelastic properties. These relations have been validated in important research studies such as those of Fetters et al.[3-5].

Experimentally, the stiffness and the dimensions of polymer chains can be estimated by two methods. The first is based on measurements of the intrinsic viscosity, $[\eta]$[6-8] . The second employs small angle neutron scattering (SANS) measurements[9-11].

The stiffness of unperturbed polymer chains can be predicted via the Rotational Isomeric State theory (RIS)[12-15]. In that theory, the calculation of $\langle R^2 \rangle$ and $\langle R_g^2 \rangle$ is based on a discretization of the space of different conformations that can be taken on by an unperturbed chain. Each skeletal bond is envisioned as capable of adopting a number of discrete torsional states, the torsion angle values attributed to these states and the relative free energies of pairs of states of successive bonds being determined by detailed atomistic conformational analysis of oligomeric analogues of the chain.

More recently, computations employing Monte Carlo sampling techniques and allowing for continuous variation of torsion angles have gained ground in relation to RIS model-based analytical calculations. For example, by analyzing well-equilibrated configurations of polymer melts obtained from connectivity-altering Monte Carlo simulations[16-20] one can readily compute $\langle R^2 \rangle$, $\langle R_g^2 \rangle$ and C_∞ in the melt state. These simulations take into account all interactions, inter- and intramolecular, bonded and nonbonded, local and nonlocal.

Obviously, atomistic simulations of single chains are much less computationally expensive than multichain simulations of the corresponding melts and would be preferable for the purpose of sampling uperturbed conformations and determining their spatial extent. Nevertheless, a problem arises in single chain simulations with the definition of local interactions. In other words, it is not obvious how, given the chemical constitution of a chain, one should define a range along the chain backbone within which all interactions can be considered local, such that sampling of single chains subject to these interactions only would yield a distribution of conformations representative of the melt state.

METHODOLOGY – SINGLE UNPERTURBED CHAIN MONTE CARLO ALGORITHM

The general methodology we will invoke in this computational exercise to estimate the dimensions and stiffness of unperturbed chains from their chemical constitution is based on conducting Monte Carlo simulations. These simulations are designed to sample the equilibrium distribution of conformations of a chain of given length *n* and chemical constitution at given temperature *T*[21,22]. In Figure 3 we present the general flow diagram of the algorithm we will use. Initially, we generate a starting conformation for the chain we wish to study.

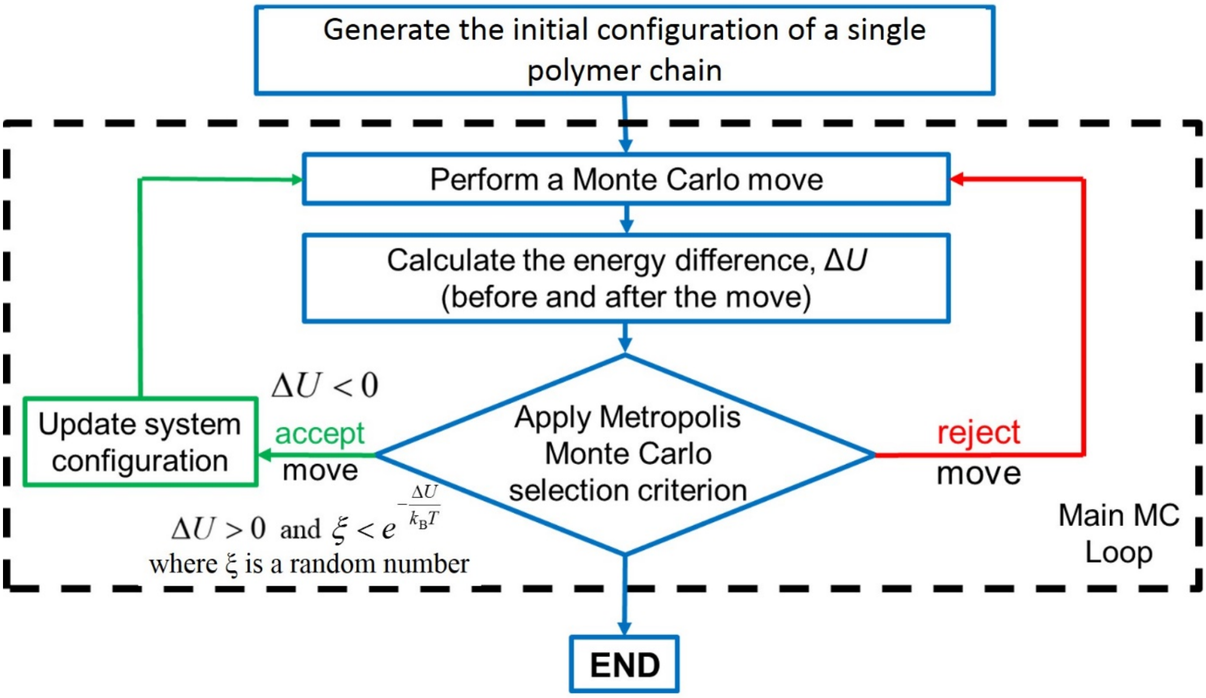
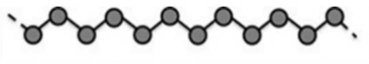


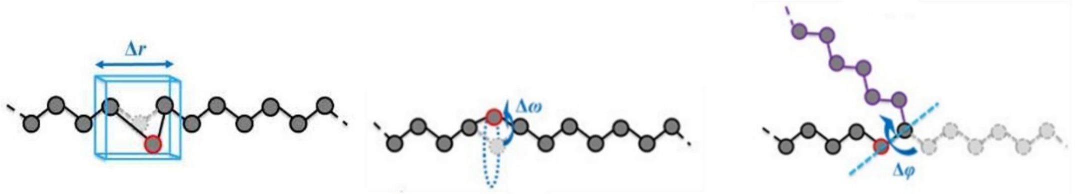
Figure 3. Flow diagram of the Monte Carlo algorithm to be used for sampling single chains.

Following the initial conformation generation, we enter the main loop of iterations of the algorithm. In each iteration we choose randomly one of the five Monte Carlo moves depicted in Figures 4 and 5. We implement the move, attempting a change in the conformation of the single chain, and we calculate the energy difference ΔU between the trial conformation and the old conformation according to a force field describing bonded and nonbonded interactions in the system. The trial conformation is accepted or rejected depending on the value of $\Delta U/(k_B T)$, with k_B being the Boltzmann constant, according to a typical Metropolis selection criterion, as shown in Figure 3. By repeating this procedure many times, we ultimately generate a large set of single-chain conformations representative of thermodynamic equilibrium of the sampled chain at temperature *T*. By taking averages of specific characteristics of the chain, such as the squared end-to-end distance, over all conformations in the set, we compute conformational properties, such as Flory's characteristic ratio.

The most important contribution of the methodology, however, is the computational scheme that has been developed for distinguishing between local and nonlocal interactions. This distinction is graphically represented in Figure 6.



(a) initial configuration

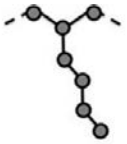


(b) single atom displacement (move atom)

(c) flip atom

(d) rotate strand (pivot)

Figure 4. The three Monte Carlo moves used for all polymer chains (linear or not). (a) initial configuration of the chain; (b) displacement of a single atom (move atom), during which an atom in the chain is randomly chosen and moved to a new position, picked from a uniform distribution within a cube of edge length Δr centered at the atom's initial position; (c) flip atom move, during which a randomly chosen atom in the chain is rotated by a randomly chosen angle $\Delta\omega$ around the axis connecting the atoms preceding and following it along the chain; (d) rotate strand (pivot) move, where an entire section of the polymer chain is chosen randomly and rotated around the bond connecting it to the rest of the chain by a randomly picked dihedral angle $\Delta\varphi$.



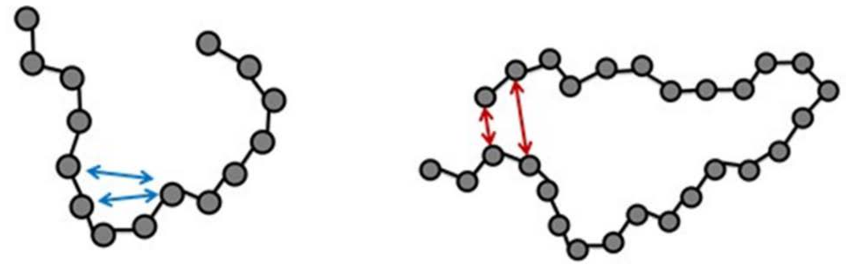
(a) initial configuration

(b) flip branch

(c) rotate branch

Figure 5. The two Monte Carlo moves designed especially for nonlinear (branched) chains: (a) initial configuration of the chain; (b) flip branch move, during which a branch of the chain is chosen randomly and rotated by a randomly chosen angle $\Delta\omega$ around an axis passing through the skeletal atom to which the branch is connected and drawn parallel to the line joining the skeletal atoms flanking the latter atom. (c) rotate branch move, during which a randomly chosen section of the branch is rotated around the bond connecting it to the rest of the chain by a randomly chosen angle $\Delta\varphi$.

By definition, an unperturbed chain is subject only to local interactions, such as those of Figure 6(a). If nonlocal nonbonded interactions are included in the Hamiltonian of a long isolated chain, then the chain will shrink, as most of these inreractions will be attractive. Thus, a single chain subject to all nonbonded interactions among its segments will no longer display the linear scaling between $\left\langle R^2 \right\rangle$ and n that is characteristic of unperturbed chains. Below a certain temperature the chain will collapse, taking the form of a globule, or it will crystallize[23]. As has been shown in many computational works, the Flory characteristic ratio, C_∞, depends in the range adopted for the calculation of local interactions. The question arises, how should this range be defined in simulations of a single polymer chain, such that the sampled conformations are representative of real unperturbed chains encountered in melts and Θ-solutions?



(a) local interactions (b) nonlocal interactions

Figure 6. Schematic representation of (a) local and (b) nonlocal interactions along a single chain.

In order to quantify the range of nonlocal interactions that should be included in the atomistic model of a single chain in order to sample unperturbed conformations representative of the melt state, we introduce a parameter, Δn_{pair}[21]. This parameter corresponds to the maximum topological distance along the chain backbone between electroneutral groups (usually structural units) within which nonbonded interactions (van der Waals and Coulomb) are active. The functional expressions used to represent these interactions are taken from the force field chosen to represent the polymer under study. Each atom in a given group i interacts with all atoms belonging to groups with indices $j \in \left[i - \Delta n_{\text{pair}}, i + \Delta n_{\text{pair}} \right]$ along the chain. The bigger Δn_{pair} is, the larger the range of nonlocal interactions that are taken into account. In order to determine an optimal value for the parameter Δn_{pair} for a chain of given chemical constitution, we compute the stiffness of the chain as a function of Δn_{pair}, as shown schematically in Figure 7 for polydimethylsiloxane (PDMS). The red broken ellipses in Figure 7 surround the electroneutral structural units with which the central structural unit i is allowed to interact for $\Delta n_{\text{pair}} = 2$. As already mentioned, the larger Δn_{pair} is, the larger the range of nonbonded interactions taken into account in sampling the chain. We observe that the chain stiffness is maximized for a specific value of the parameter Δn_{pair}. In the case of PDMS the maximum occurs for $\Delta n_{\text{pair}},= 2$. We assert that the optimal value for this parameter is the one for which the stiffness is maximized. The latter assertion constitutes an empirical criterion. Nevertheless, the values of characteristic ratios computed based on this criterion are in very good agreement with values extracted from well-equilibrated melt simulations employing the same force field parameters, as well as with measured experimental values.

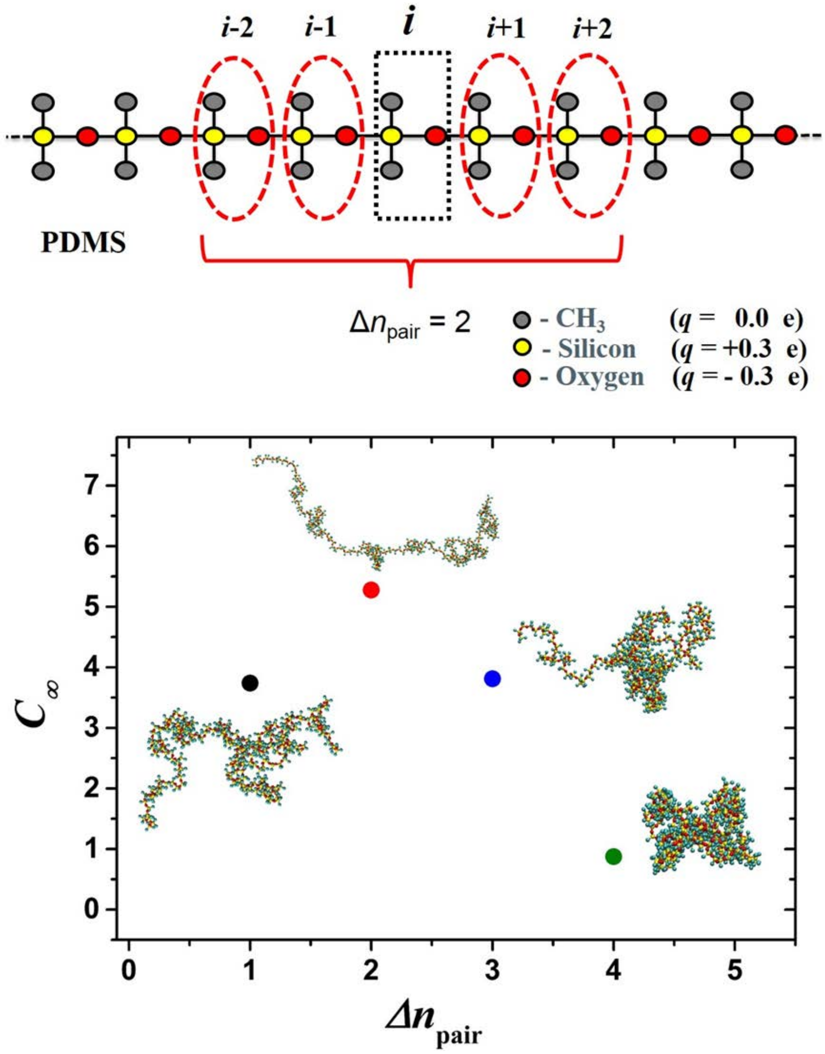


Figure 7. Schematic representation of a single unperturbed chain of polydimethylsiloxane. The red broken ellipses surround the neighboring electroneutral structural units with which the atoms of structural unit *i* are allowed to interact for $\Delta n_{\mathrm{pair}} = 2$. The plot presents the value of the estimated Flory characteristic ratio at equilibrium, C_{∞}, for various values of Δn_{pair} at a temperature of 298 K. Also presented are typical conformations of an atomistically represented PDMS chain for each of these values of Δn_{pair}. Clearly, for $\Delta n_{\mathrm{pair}} = 1$ the chains are not stiff enough because not enough local interactions are included in the model. On the other hand, for $\Delta n_{\mathrm{pair}} = 3$ and $\Delta n_{\mathrm{pair}} = 4$ the chains begin to collapse under the influence of attractive nonbonded interactions between topologically distant atoms. There is a clear maximum in stiffness for $\Delta n_{\mathrm{pair}} = 2$ and this is taken as the optimal value of Δn_{pair} for sampling unperturbed conformations of PDMS.

COMPUTATIONAL PART

In this computational exercise we will study the conformations adopted by single unperturbed chains of various molar masses for four polymers: Polyethylene (PE), isotactic polypropylene (*i*-PP), syndiotactic polypropylene (s-PP), and polydimethylsiloxane (PDMS). In Table 1 are presented the values of Δn_{pair} that are appropriate for sampling each of these chains in its unperturbed state and the mean values of bond lengths at equilibrium. Parameter ICoul is 1 if partial charges and electrostatic interactions are included in the force field used to describe a polymer and 0 if electrostatic interactions are absent from the model. Clearly, electrostatic interactions are important only in the case of PDMS.

Table 1. Recommended values of the parameters Δn_{pair} , of the mean skeletal bond lengths l, and of the parameter ICoul (parameter for the calculation of electrostatic interactions) for the polymers to be studied in this exercise at the temperatures indicated.

Polymer	T (K)	l (Å)	ICoul	Δn_{pair}
polyethylene (PE)	450	1.54	0	2
isotactic polypropylene (*i*-PP)	450	1.54	0	2
syndiotactic polypropylene (*s*-PP)	450	1.54	0	3
polydimethylsiloxane (PDMS)	298	1.64	1	2

In Table 2 are presented the recommended percentages of the five different types of attempted Monte Carlo moves for the different polymers.

Table 2. Recommended values of the relative frequencies of attempt (%) for the five different types of attempted Monte Carlo moves for each polymer

Polymer	Move Atom	Flip Atom	Rotate Strand	Rotate Branch	Flip Branch
PE	10.00	10.00	80.00	0.00	0.00
i-PP	10.00	10.00	70.00	0.00	10.00
s-PP	10.00	10.00	70.00	0.00	10.00
PDMS	10.00	10.00	70.00	0.00	10.00

In Table 3 are presented the equilibrium bond angles along the backbones of the four different polymers to be studied.

Table 3. Equilibrium bond angles along the backbones of the four different polymers to be studied

Angle	θ
$CH_2 – CH_2 – CH_2$	114.00^0
$CH – CH_2 – CH$	114.00^0
$CH_2 – CH – CH_2$	112.00^0
Si – O – Si	146.46^0
O – Si – O	107.82^0

For each of the four different polymers you are given eight (8) different initial conformations, which you must **equilibrate** by running the executable file *exercise.exe*, implementing the Monte Carlo algorithm that was outlined in the theoretical section. In order to run, the program needs two input files. The first is named *input.txt* and contains all the information necessary for the simulation, such as the total number of attempted Monte Carlo steps, the percentages of different attempted Monte Caro moves, the name of the file containing the initial conformation, etc. For each simulation run you conduct you will have to modify the contents of *input.txt* on the basis of the information provided in Table 1. The second input file contains the initial conformation of the polymer chain that will have to be equilibrated each time. For each polymer to be studied you are given 8 such files, which correspond to different chain lengths. The names of these files are of the form *polymer_n_number.txt*, where the number is indicative of the chain length, in skeletal bonds. (Attention: the exact number of skeletal bonds, *n*, will be printed out in the output file!). When the simulation is successfully completed, an output file will be produced, whose name is *output.txt*. This file contains the mean squared end-to-end distance, the mean squared radius of gyration, etc., as obtained from the simulation. Please note that the output file is generated in the same directory in which the executable finds itself. In case you wish to run a new simulation, after the first one is completed, you will have to move file *output.txt* to another location, so that the next simulation can start successfully. Further information concerning the execution of the algorithm can be found within the presentation *Instructions.pdf*. All files needed for solving the computational exercise are available at the following link:

http://comse.chemeng.ntua.gr/files/polymer_science/exercise_mar2021.zip

After completing your simulations and making sure all systems have equilibrated for all chemical constitutions and chain lengths, please answer the following questions:

1. Plot in a common diagram for all four polymers the dependence of the Flory characteristic ratio, C_n, as a function of the number of skeletal bonds n. Comment on the appearance of the resulting curves.

2. Estimate the Flory characteristic ratio of the four polymers in the limit of infinite chain length, C_∞, using a linear extrapolation method. Make a table showing the values of C_∞ for the different polymers you studied.

3. Which of the four different polymers exhibits the highest conformational stiffness and why?

4. Which of the four polymers is the most flexible and why?

5. Is there a difference in stiffness between isotactic and syndiotactic polypropylene? Interpret the effect of tacticity on the Flory characteristic ratio of these two polymers and comment on the consequences of chirality on the properties of polymers in general.

6. Calculate the Kuhn length, b_K, and the number of Kuhn segments per skeletal bond, N_K/n. for the four polymers. You may need Table 3 for this calculation. What is the physical meaning of these two quantities and how are they related to the stiffness of polymer chains?

7. Calculate the ratio of the mean squared end-to-end distance to the mean squared radius of gyration for the four polymers and plot it as a function of n in a common diagram. To what value does it converge and why?

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