Exercise 05/06.05.2020

Gyration tensor of polymers

A polymer can be represented by a simple bead-spring model (see Figure 1). We[1] used the standard Kremer-Grest model (see the details in Addendum 1), built three different polymer topologies – a chain, a ring and a star polymer – and simulated them with the LAMMPS simulation package (http://lammps.sandia.gov).

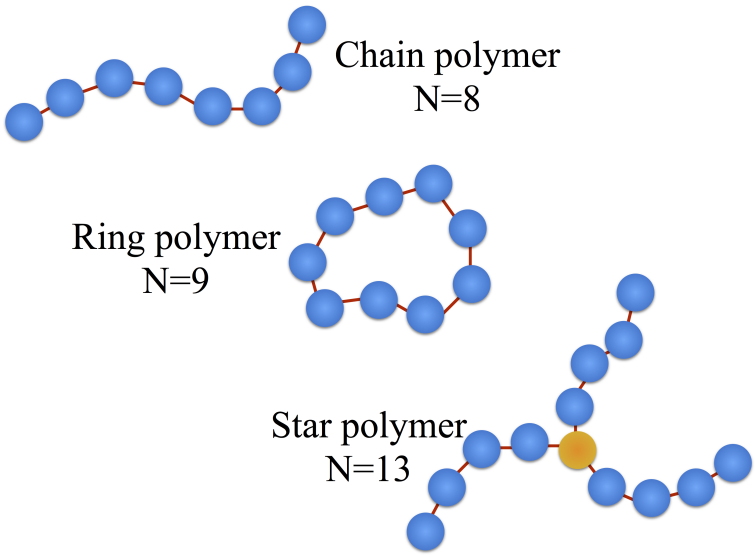

Figure 1: Polymers topologies.

The exercise consists in determining some of the parameters that characterize the shape of the different polymers: evaluate the gyration tensor and, from it, calculate the radius of gyration R_g, the asphericity b and the prolateness S^* (see Addendum 2).

List of tasks to be performed:

- Read the input data. The input files are named as "topology-stiffness.dat", where the topology is either "chain", "ring" or "star", while the stiffness parameter that determines the bending rigidity of the polymer is $0, 5, 10, 20$ or 50. Be aware that, the chain and ring polymers are composed by $N = 100$ monomers, while the star polymer is composed of f =50 arms, each consisting of $n = 100$ monomers, attached to a central monomer, thus resulting into $N = fn + 1 = 2501$ monomers in total. Also be aware that for each topology-stiffness combination a set of 100 independent polymer configurations is provided (the input file includes all of them, one after the other).

[1] credits to Dr. Emanuele Locatelli, Univ. Ass. at the University of Vienna

- Calculate the gyration tensor S
- Diagonalize the S matrix with the QR-algorithm and store the three eigenvalues
- Diagonalize the S matrix with a publicly available routine. You can try with the DGEEV routine of LAPACK or, for python users, numpy.linalg.eig. Compare the three eigenvalues with the ones obtained by your home-made diagonalization.
- Determine R_g, b and S^* and plot them as a function of the stiffness parameter. Check that
    1. on increasing the stiffness parameter κ, R_g increases within the range $R_g/\sigma \in [5, 25]$; at $\kappa = 0$, the star polymer has the largest R_g, while the R_gs of the chain and the ring polymers, initially relatively close to each other, become quite different on increasing the stiffness, as the ring has a more compact topology with respect to the chain
    2. the asphericity of the star polymer is around zero, while $b/R_g^2 \in [0, 1]$ for the chain and the ring polymers
    3. the prolateness of the star polymer is around zero, while $S^* \in [-0.2, 1.5]$ for the chain and the ring polymers; note that the chain becomes more and more prolate on increasing the stiffness, while the ring becomes eventually oblate.
- Perform a check on R_g by independently calculating it from the monomers positions.

Addendum 1

A bead-spring polymer consists of a sequence of beads (representing the monomers) whose specific interactions depend on the model chosen. When employing the Kremer-Grest model, the mutual interactions between all beads are given by the Weeks-Chandler-Anderson (WCA) potential

$$U_{\mathrm{WCA}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} + \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4} \right] & \text{for} \quad r < 2^{1/6}\sigma \\ 0 & \text{for} \quad r \geq 2^{1/6}\sigma \end{cases} \tag{1}$$

while bonded (consecutive) beads interact through the finite-extensible-non-linear spring (FENE) potential given by

$$U_{\mathrm{FENE}}(r) = \begin{cases} -\frac{KR_0^2}{2} \ln \left[1 - \left(\frac{r}{R_0}\right)^2 \right] & \text{for} \quad r < R_0 \\ \infty & \text{for} \quad r \geq R_0 \end{cases} \tag{2}$$

where ϵ is the characteristic energy of a bond, usually set equal to the thermal energy $\epsilon = k_B T = 1$ (where k_B is the Boltzmann constant), $\sigma = 1$ is the diameter of the beads usually set equal to one, R_0 is the maximum extent of a bond (set equal to $R_0 = 1.5\ \sigma$), and K is the spring constant (set equal to $K = 30\ \epsilon/\sigma^2$). Polymers of different bending rigidities can be obtained by adding a bending interaction defined by

$$U_{\mathrm{BEND}}(\theta) = \kappa(1 - \cos\theta) \tag{3}$$

where θ denotes the angle between subsequent bonds and κ is the stiffness parameter.
We simulated the Langevin dynamics of the different polymer topologies – a chain, a ring and star polymer – using the LAMMPS simulation package, for different bending rigidities, namely $\kappa = 0, 5, 10, 20$ and 50ϵ.

Addendum 2

Remember that the gyration tensor is defined by

$$S = \frac{1}{N}\sum_{i=1}^{N}(r_i^j - r_{\mathrm{cm}}^j)(r_i^k - r_{\mathrm{cm}}^k) \ \text{ for } \ j,k = 1,2,3 \tag{4}$$

where $r_i^{j,k}$ are the j,k-th Cartesian coordinates of the i-th monomer and $r_{\mathrm{cm}}^{j,k}$ are the j,k-th Cartesian coordinates of the center of mass of the polymer.
By properly diagonalizing the matrix S, we obtain

$$S = \begin{pmatrix} \lambda_x & 0 & 0 \\ 0 & \lambda_y & 0 \\ 0 & 0 & \lambda_z \end{pmatrix}$$

where $\lambda_x \leq \lambda_y \leq \lambda_z$.
We define the radius of gyration R_g as

$$\langle R_g^2 \rangle = \langle I_1 \rangle$$

the asphericity b as

$$\langle b \rangle = \left\langle \lambda_z - \frac{1}{2}(\lambda_x + \lambda_y) \right\rangle$$

and the prolateness S^* as

$$\langle S^* \rangle = \left\langle \frac{(3\lambda_x - I_1)(3\lambda_y - I_1)(3\lambda_z - I_1)}{I_1^3} \right\rangle$$

where $I_1 = \lambda_x + \lambda_y + \lambda_z$.

The radius of gyration can also calculated from the monomers positions as follows

$$\langle R_g^2 \rangle = \left\langle \frac{1}{N} \sum_{i=1}^{N} |\vec{r}_i - \vec{r}_{\mathrm{cm}}|^2 \right\rangle \tag{5}$$

where $\vec{r}_i$ is the position of the i-th monomer and $\vec{r}_{\mathrm{cm}}$ is the position of the center of mass of the polymer.
Note that all averages above are computed over all the independent configurations given.

Instructions

During the exercise a short protocol must be made and saved as `PROTOKOLL.txt` in the directory of the respective exercise day. The protocol is a simple ASCII text file that is created with a text editor with which you can also write your programs. The protocol must contain the following

1. Date, exercise number, group number, name(s) of the participating students
2. Time required for the tasks (approximately)
3. Name of the created files, the files must be located in the directory of the respective exercise day
4. The answers to any questions asked above
5. Possible problems or peculiarities, if they have occurred.