

AN EXAMPLE OF THE MONTECARLO SIMULATIONS: THE LANGEVIN DYNAMICS

Objectives

After completing the reading of this chapter, you will be able to:

Construct a polymer chain.

Devising a simple MC simulation program for a polymer chain.

Calculate the end-to-end vector and the radius of gyration of a polymer chain.

Verify the constancy of the bond segment vector, a key requirement of any polymer chain under equilibrium.

Visualize the motion of the polymer chain through a series of snapshots.

Keywords

Polymer chain, Harmonic potential, Langevin dynamics, End-to-end vector, Radius of gyration, Bond segment vector.

Introduction

A polymer is a substance comprising of many repetitive structural units. Examples of polymeric substances are abundant around us. The nonmetallic parts of your computer are made from phenol-formaldehyde polymers, the body of the ball point pen you use is made from polyethylene, all synthetic clothes are made through polymerization processes of suitable raw materials, the disposable plastic cutlery you use for eating food are polymeric substances. In biological context, essentially all biological macromolecules *e.g.*, proteins, lipids, polysaccharides are polymeric. Many of the household items (buckets, mugs, milk cans, vegetable baskets etc) are also made from polymeric substances.

A simple model for a linear polymer

As polymers comprise of monomers, modeling the polymers may be simplified by choosing appropriate definition and properties of the monomers. To illustrate the point, let us consider a

linear polymer, polyethylene, $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$, as an example. Here, we may consider CH_3 and CH_2 as united atom groups (or ‘beads’) connected through bonds (with known force constants). The bonds actually behave as ‘springs’ allowing small stretching and compression due to vibrational motion. Thus, simply put, a linear polymer (like polyethylene) is modeled as a ‘bead-spring chain’.

In the bead-spring chain, the bead particles interact through a harmonic potential (known as the Fraenkel potential). For the sake of simplicity, we neglect the bond angle bending and dihedral torsional modes of the chain. The Fraenkel potential has the form

$$U_{\text{Fraenkel}}(r) = \frac{H_F}{2}(r - b_0)^2 \quad (29.1)$$

where, H_F is the force constant and b_0 is the equilibrium bead-bead distance.

The Langevin equation is the most appropriate equation of motion of the beads of the chain. In the Langevin dynamics method, motion of each bead i of the chain is dictated by a total force \mathbf{F}_i^T on the bead, which comprises of force arising from potential, frictional force and a random force.

$$\mathbf{F}_i^T = m \ddot{\mathbf{r}}_i = \mathbf{F}_i^C + \mathbf{F}_i^F + \mathbf{F}_i^R \quad (29.2)$$

where, m is the mass of the bead. The force arising from the chosen Fraenkel potential are included in \mathbf{F}_i^C . The frictional force acting on the bead is, $\mathbf{F}_i^F = -\xi \mathbf{v}_i$, where \mathbf{v}_i is the velocity of the bead and ξ is the friction coefficient. The friction coefficient ξ is related to the fluctuations of the random force \mathbf{F}_i^R through the fluctuation-dissipation theorem [See “*Statistical Mechanics*” by D. A. McQuarrie, Harper and Row, New York; 1976].

$$\langle \mathbf{F}_i^R(t) \rangle = 0 \quad (29.3a)$$

$$\langle \mathbf{F}_i^R(t) \cdot \mathbf{F}_j^R(t') \rangle = 6k_B T \xi \delta_{ij} \delta(t - t') \quad (29.3b)$$

The temperature T of the system is maintained through eq. (29.3), and k_B is the Boltzmann constant. In the Monte Carlo simulation of the Langevin equation of a polymer chain, we replace the continuous time variable with a small time step Δt . If the position of the i th bead at time step t is denoted by $\mathbf{r}_i(t)$, the simulation form of the Langevin equation for the bead can be written as,

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \frac{d^2}{2k_B T} \mathbf{F}_i^T(t) + \mathbf{d}_i(t) \quad (29.4)$$

where, $\mathbf{F}_i^T(t)$ is the total force on the i th bead arising out of the interaction potential. The random step vector $\mathbf{d}_i(t)$ is characterized by the two moments,

$$\langle \mathbf{d}_i(t) \rangle = 0 \quad (29.5a)$$

$$\langle \mathbf{d}_i(t) \mathbf{d}_j(t') \rangle = d^2 \mathbf{I} \delta_{ij} \delta(t-t') \quad (29.5b)$$

where, \mathbf{I} is an unit tensor. The random displacement d , and time step Δt , are related through the diffusion constant D , of the chain.

$$d^2 = 2D\Delta t = \frac{2k_B T \Delta t}{\xi} \quad (29.6)$$

It is to be noted that in eq. (29.4) and (29.6), mass of the bead does not appear explicitly as it does in eq. (29.2); but the bead mass is implicit in the friction coefficient as, $\xi = \frac{k_B T}{D} = m\gamma$, where γ is the collision frequency [See “*Molecular Modelling: Principles and Applications*”, by A. R. Leach, Second edition, Pearson Education Limited, Essex; 2001].

The Langevin dynamics method is therefore a special Monte Carlo method, since the positions of the particles are implicitly decided by random numbers (see eqs. 29.4-29.6).

Properties of interest in simulating a linear polymer

Any polymer chain is characterized by several properties, viz., the end-to-end distance, its radius of gyration and the bond-segment distance. We define these quantities below.

End-to-end distance

An ideal polymer chain is a freely-jointed chain of N monomers. If the positions of the monomers are (r_1, r_2, \dots, r_N) , then the end-to-end vector, \vec{R} may be defined as

$$\vec{R} = (\vec{r}_N - \vec{r}_1) \quad (29.7)$$

The end-to-end distance, R is the norm of the end-to-end vector, \vec{R} .

$$R^2 = |\vec{R} \cdot \vec{R}| \quad (29.8a)$$

$$R = \sqrt{R^2} \quad (29.8b)$$

The two ends of the polymer chain are never coincident, even if the chain forms a coil under special conditions (like changing a solvent, changing temperature etc). The magnitude of the end-to-end distance, R is always taken to be “statistically averaged” in real systems. In the simulations, R^2 is easily evaluated from the position coordinates of the end monomers, from which R can be easily calculated.

Radius of gyration

The radius of gyration, R_g of the polymer chain is defined through its square,

$$R_g^2 = \frac{1}{N} \sum_{i=1}^N (r_i - r_{\text{com}})^2 \quad (29.9)$$

$$\text{Thus, } R_g = \sqrt{R_g^2} \quad (29.10)$$

where r_i are the position coordinates of the i th monomer and r_{com} are the coordinates of the centre-of-mass of the chain. During the motion of the chain, one can calculate r_{com} and consequently, R_g^2 and R_g can be easily evaluated.

Bond segment distance

The bond segment distance in a polymer chain is a representative of the so-called Kuhn segment or Rouse segment of the chain. The bond segment distance is calculated through its square,

$$\langle b^2 \rangle = \frac{1}{N-1} \sum_{i=1}^{N-1} (r_{i+1} - r_i)^2 \quad (29.11)$$

$$\text{So that, } b = \sqrt{\langle b^2 \rangle} \quad (29.12)$$

This quantity is very important and its magnitude must not change in all equilibrium simulations.

Throughout this chapter, we report the results using the following units: length in terms of the bead diameter σ and time as the Monte Carlo steps.

Simulation of the linear polymer

For the sake of simplicity, we illustrate the Langevin dynamics simulation by considering a single chain of $N = 20$ beads. Initial configuration of the chain of N beads has been generated as follows. Taking the first bead as the seed (placed arbitrarily at the origin), coordinates (x_i, y_i, z_i) of the successive beads are generated using $(x_i = x_{i-1} + \sigma \sin \theta \cos \phi; y_i = y_{i-1} + \sigma \sin \theta \sin \phi; z_i = z_{i-1} + \sigma \cos \theta; \text{ for } i = 2, 3, \dots, N)$; angles θ and ϕ are obtained from, $\theta = \pi * qq$ and $\phi = 2\pi * ff$ respectively, where qq and ff are two random numbers generated for each bead. Consecutive inter-bead distances are matched with σ , before accepting the coordinates of the new bead to build the chain. Figure 29.1 represents the initial configuration of the chain.

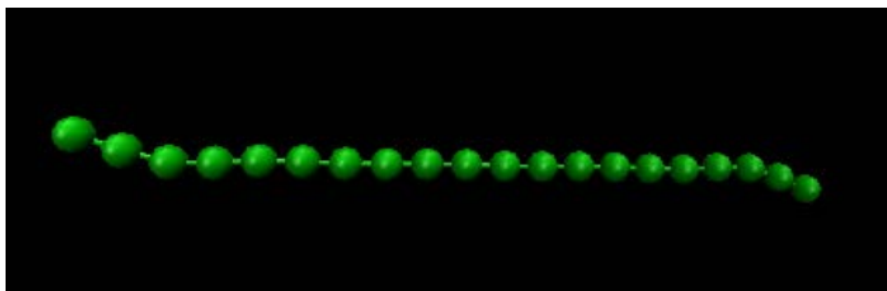


Figure 29.1: Initial configuration of a 20-beads chain.

This chain is acted upon by the Fraenkel potential only [eq. (29.1)] and its motion is followed for 10^5 MC steps. During the simulation, the square of end-to-end vector R^2 and the square of the radius of gyration R_g^2 are calculated along with the square of the average bond-segment distance $\langle b^2 \rangle$.

Results

Square of the end-to-end vector R^2 , square of the radius of gyration R_g^2 and square of the average bond-segment distance $\langle b^2 \rangle$.

Figures 29.2, 29.3 and 29.4 present the variations of the square of the end-to-end vector R^2 , square of the radius of gyration R_g^2 and square of the average bond-segment distance $\langle b^2 \rangle$, respectively, with time steps of the MC simulation.

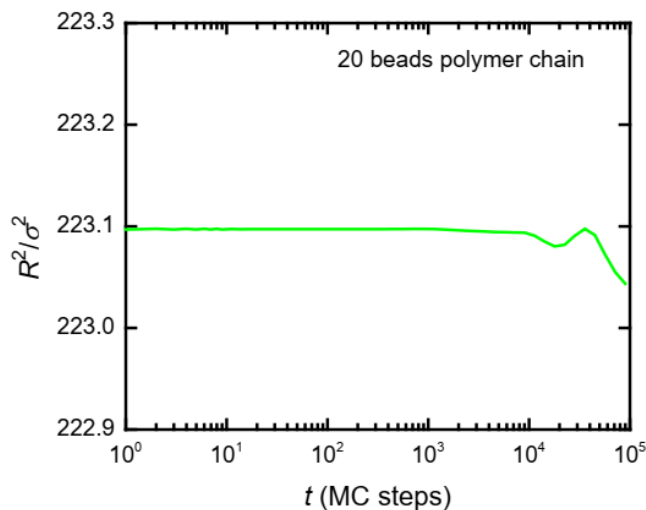


Figure 29.2: Variation of the square of the end-to-end vector, R^2 of the 20 beads polymer chain.

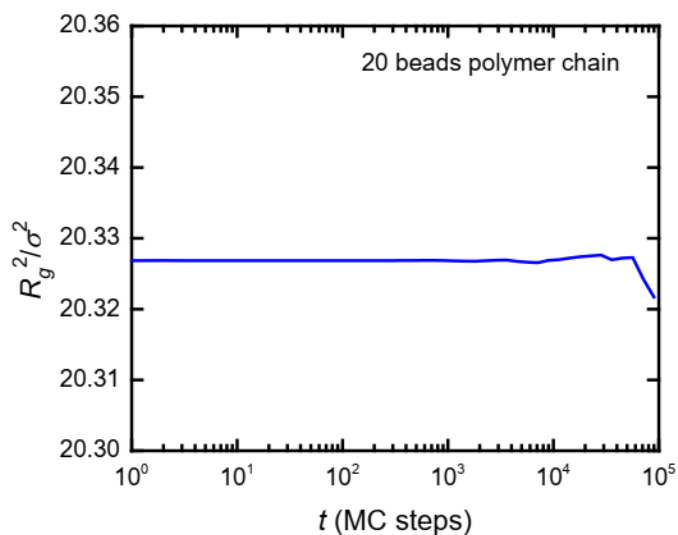


Figure 29.3: Variation of the square of the radius of gyration, R_g^2 of the 20 beads polymer chain.

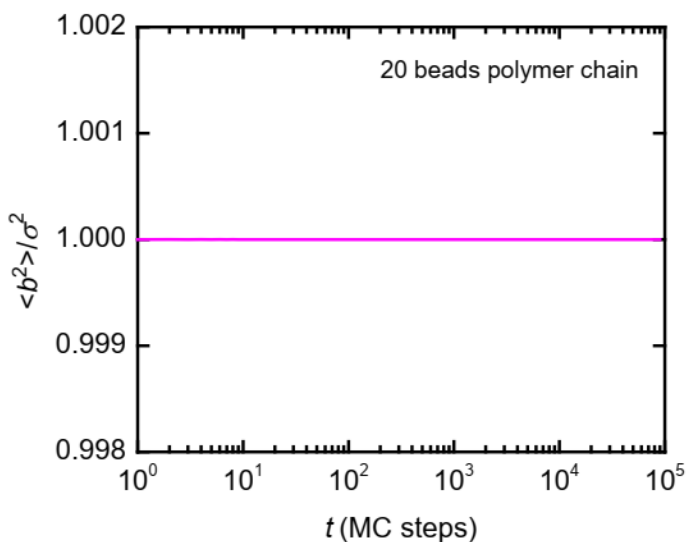


Figure 29.4: Variation of the square of the average bond segment distance, $\langle b^2 \rangle$ of the 20 beads polymer chain. Note the constancy of $\langle b^2 \rangle$.

As the R^2 and R_g^2 are equilibrium properties of the polymer chain, these are expected to change very little with time. The slight variations seen in Figs 29.2 and 29.3, after ca. 2×10^4 MC steps are indications of the chain to start coiling. In the case of the square of the average bond-segment distance $\langle b^2 \rangle$, the magnitude should not change at all and this is what is revealed in Fig. 29.4.