Universität Freiburg – Institut für Physik
Applied Theoretical Physics
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Exercise 11 for '*Computational Physics - Material Science*', SoSe 2021
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Please provide a well documented submission of your solution. Your submission should include

- A pdf file containing the solution to the questions with the corresponding equations that are implemented in your codes. Figures must contain axis titles with corresponding units and a caption.
- The source code should be commented, and the equations given in the pdf file have to be referenced in the source code.
- There is no need to provide the trajectory files.
- In case your code is not working properly, please provide a description of the debugging attempts you did.

Exercise 11.1: Modelling single polymer chains

We consider a linear polymer chain made of $(N+1)$ beads A_i. A simple way to model such a system is to assume (i) that beads i and $i+1$ are bonded, and (ii) beads i and j interact though a LJ potential when A_i and A_j are not consecutive beads. The energetic part of the Hamiltonian, U, (leading to the 'force field') for such a description is thus:

$$U = \frac{1}{2} \sum_{i \in bonds} k_{bond}(r_i - r_0)^2 + \frac{1}{2} \sum_i \sum_{j=i+2} U_{LJ}(r_{ij})$$

where (r_0, k_{bond}) are the bond length and the spring constant, respectively. The non-bonded interactions between between beads i and j are defined with the LJ potential, and its associated set of parameter (σ, ϵ).
In polymer physics, the mean-square end-to-end distance can be defined as:

$$\langle r_{ee}^2 \rangle = \left\langle \sum_{i=1}^{N} \mathbf{r_i} \sum_{j=1}^{N} \mathbf{r_j} \right\rangle$$

where $\mathbf{r_i}$ represents the bond vector connecting monomer i and $i+1$.

The objective of this exercise is to model, using a coarse-grain approach, the structure of ideal and real polymer chains, and to recover some of the scaling laws of polymer physics.

a) Starting with the canonical ensemble as implemented on sheet #10, setup a linear polymer chain made of $(N+1) = 51$ beads connected by $N = 50$ bonds described by the force field defined above. Assuming no LJ interactions between beads ($\epsilon = 0$), simluate the trajectory of the polymer chain at $T = 300$ K during 200000 time steps (the first 5000 time steps

being used to equilibrate the temperature). Calculate and plot the end-to-end distance distribution as a probability function $P(r_{ee})$. Compare your result with the analytical solution obtained for the FJC model $\left(P(r_{ee}) = 4\pi r_{ee}^2 \left(\frac{3}{2\pi N r_0^2}\right)^{3/2} exp\left(-\frac{3r_{ee}^2}{2Nr_0^2}\right)\right)$. Provide an ovito snapshot of the polymer chain obtained after 10^6 time steps. *(To simplify the implementation, the initial configuration can be at the center of a cubic box with dimensions much larger than the polymer chain.)*

b) Perform the same simulation than in (a), but now with $N \in (30, 70, 90, 110)$. For each configuration, calculate $\sqrt{< r_{ee}^2 >}$. Plot $\sqrt{< r_{ee}^2 >}$ versus N. Assuming $\sqrt{< r_{ee}^2 >} = N^{\nu} r_0$, what is the magnitude of the exponent ν you obtained by fitting such a functional form to your data? How does it compared with the theoretical scaling obtained for the FJC model?

c) Perform the same simulation and analysis than in (a) and (b), but now with $\epsilon = 0.1$ and 1 $k_B T$. Plot $\sqrt{< r_{ee}^2 >}$ versus N. What is now the value of the exponent ν? To which solvent types can these LJ interactions be associated?

Numerical values of quantities to be used:

quantity	value (units)
k_B	1.38×10^{-23} (m^2 kg s^{-2} K^{-1})
ϵ	k_BT
σ	3.2×10^{-10} (m)
r_0	3.2×10^{-10} (m)
k_{bond}	1058 (kCal/mol/$\mathring{A}^2$)
T_d	300 (K)
mass	2.56×10^{-26} (kg)
Δt	0.5×10^{-15} (s)