Coarse graining

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1 Credits

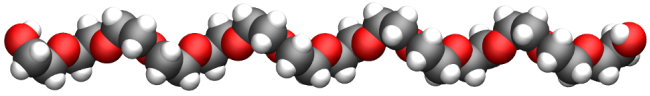
Special thanks to Wouter G. Ellenbroek for the *Simulation tetraPEG gelation* part of the tutorial. LAMMPS is a classical molecular dynamics code with a focus on materials modeling. The acronym stands for Large-scale Atomic/Molecular Massively Parallel Simulator. [1, 2]. LAMMPS is a free and Open Source software maintained by researchers at the Sandia National Laboratories and Temple University (US). The LAMMPS input files and scripts in the first part of the workshop were set up by Massimiliano Paesani and partially rely on the details provided in `https://lammpstutorials.github.io/sphinx/build/html/tutorials/level2/polymer-in-water.html`. The second part of the workshop is based on the work of Chiara Raffaelli on hybrid hydrogels [3]. For visualization and post-processing we primarily use Ovito, available through `https://www.ovito.org` and developed by Alexander Stukowski [4].

2 Installation instructions

Install Ovito Basic from `https://www.ovito.org`.

The simulations themselves are provided in a self-contained IPython notebook intended to be run in Google Colab. Only a web browser is needed for this to work.

3 Introduction



PEG (polyethylene glycol) polymers are synthetic polymers that consist of repeating units of ethylene oxide. The physical characteristics of PEG polymers vary depending on the molecular weight, which is determined by the number of repeating units of ethylene oxide in the polymer chain. PEG polymers are water-soluble, biocompatible, and have low toxicity, making them widely used in various applications, such as pharmaceuticals, cosmetics, and food. They can be used to improve the solubility and bioavailability of poorly soluble drugs. They are generally considered safe for use in humans and animals, but their safety profile depends on the specific molecular weight, concentration, and use. Simulating PEG polymers can be a great way to determine quantitative conformations conformations, lengths, and stability for their real- life applications. The goal of the workshop is to understand the advantages and disadvantages of coarse-grained simulations. For this, we will first simulate a PEG polymer consisting of ten repeating units of ethylene oxide in explicit water and vacuum. We will stretch the polymer and compute the end-to-end distance.

Next, we will simulate the formation of tetraPEG hydrogels [5] out of two types of 4-arm PEG star polymers. Each type has all four arms functionalized with an endgroup that can react with an endgroup of the other type to make a covalent bond (e.g. the azide-alkyne click reaction). These gels form easily and homogeneously at low concentrations. For this we will use a coarse-grained bead-spring model with 10 beads per arm, such that each star consists of 41 beads in total, including the star center. The beads interact with a repulsive Weeks-Chandler-Andersen (WCA) potential [6] and the star is in implicit solvent.

4 Part 1: PEG polymer in vacuum

Typically in a simulation, we follow a protocol as below

- prepare the topology of the system (here, a PEG 10-mer)
- build the simulation box and add water molecules
- add neutralizing counterions and optionally adjust the ion concentration to match experiments
- minimize the potential energy of the system
- equilibrate the system
- perform production runs
- analyze the data

In view of time, for the all-atom simulations here, you will only perform the last two steps. For this

- Download the input files from: `https://github.com/ilieim/TCCM`
- Go to Google Colab
- Go to File → Open Notebook → Github
- type ilieim and select TCCM
- pick *Tutorial*
- run all the cells

5 Part 2: Gelation of star polymers

The protocol can be summarized as follows:

1. Place `Nstars` star polymers of each type randomly in a simulation box.
2. Set repulsive WCA interactions between all beads (polymers in good solvent), harmonic bonds between neighboring beads, and a Langevin thermostat.
3. Minimize the potential energy.
4. Compress the simulation box during a short MD run to reach the desired polymer concentration.
5. Equilibrate for 20,000 steps.
6. Activate the `bond/create` fix to enable formation of bonds between two end beads of opposite type.
7. Run gelation for 200,000 steps.

The concentration is entered in units of 1 wt%, although the precise value needs to be taken with a grain of salt because the conversion between LJ units and physical units contains some inexact assumptions. For the arm lenghts employed here, simulating at 8 wt% gives decent results.

5.1 Running a simulation

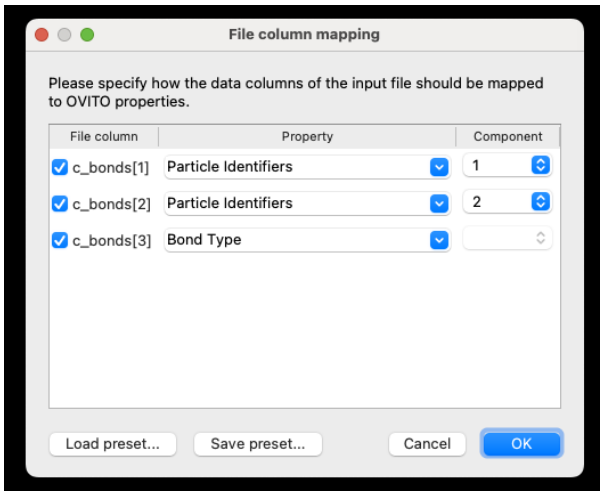
The section *Running Gelation Simulations* contains a cell for setting the parameters of the next run and a cell for executing the run. The latter takes 30 seconds and ends with an automatically initiated download of a zip file containing the results of the simulation.

The default run uses `Nstars=8` and a concentration of 8 wt%. These parameters can obviously be varied. To keep things simple these are the only two that can be varied easily. Other modifications require more work[1].

6 Ovito

To work with Ovito, unzip the data you wish to visualize. Start Ovito (or open a "New Program Window" if it was already running). The way Ovito works if you have dynamic bonds is as follows:

1. "Load File"
2. "Load File" $\Longrightarrow$ Select both the file `gelation_initial_topology_XXX.dat` and the file `gelation_trajectory_XXX.bin`. At this point you could already play a movie but it will not draw the dynamic bonds because it lacks information on those.
3. Ovito has a default size for drawing the particles that may be too large for good visibility. In the overview of the data pipeline on the right hand side of your screen, click "Particles" and then modify the "Standard radius" below to a smaller value. 0.3 works well. This only needs to be done once.
4. Again in the overview of the data pipeline in the top right, use "Add modification" $\Longrightarrow$ "Load trajectory".
5. Ovito will ask you to open a trajectory file. This should be done in the "Trajectory Source" panel in the bottom right (which has another "Load File" icon).Use this to open the file `gelation_bondinfo_XXX.dump`. Ovito will ask you what the contents of this file represent. Answer as follows:



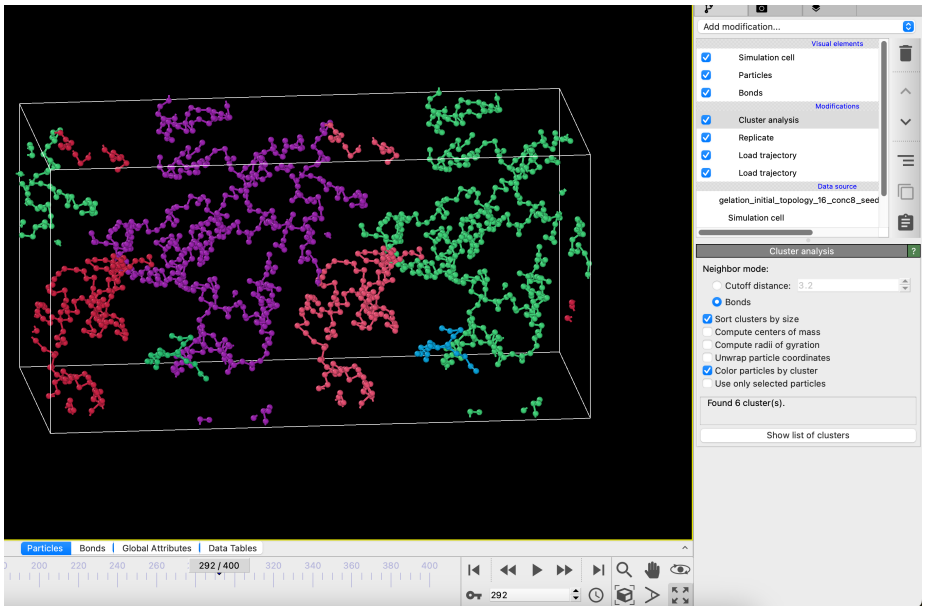
[1]For example, if you want to vary the arm length, you'll need to generate appropriate molecule files and modify the `create_lammps_dict` function.

Note that your answer to the File column mapping dialog is retained by Ovito so you will only need to do this once if future bondinfo files use the same column definition.

6. Click the Play button at the bottom of the window to see the result, or drag the frame selector. If the graphics are choppy it may help to swap the two "Load Trajectory" modifications in the pipeline editor (top right) so that the one for the bondinfo file is on top.

7. Explore the "Cluster Analysis" and "Replicate" modifications. Make sure they are listed above the "Load Trajectory" modifications. If using both "Cluster Analysis" and "Replicate" at the same time the result depends on the order in which you place them.

The final result could look something like this (depending on the settings for the final two added modifications):



Finally if you want to create a movie, go to "Rendering" tab next to the "Pipelines" tab. Most default settings are fine. Don't forget to check the "Save to file" box and choose a filename (recommended format: mp4).

7 What to do?

What to do depends on your interests... vary the concentration, the system size, the arm length, play around with Ovito. Check the difference between the two systems.

References

[1] Steve Plimpton. "Fast parallel algorithms for short-range molecular dynamics". In: *J. Comp. Phys.* 117.1 (1995), pp. 1–19.

[2] Aidan P. Thompson, H. Metin Aktulga, Richard Berger, Dan S. Bolintineanu, W. Michael Brown, Paul S. Crozier, Pieter J. in 't Veld, Axel Kohlmeyer, Stan G. Moore, Trung Dac Nguyen, Ray Shan, Mark J. Stevens, Julien Tranchida, Christian Trott, and Steven J. Plimpton. "LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales". In: *Computer Physics Communications* 271 (Feb. 2022), p. 108171. DOI: 10.1016/j.cpc.2021.108171.

[3] Chiara Raffaelli and Wouter G Ellenbroek. "Stress relaxation in tunable gels". In: *Soft Matter* (2021). Publisher: Royal Society of Chemistry. DOI: 10.1039/D1SM00091H.

[4] Alexander Stukowski. "Visualization and analysis of atomistic simulation data with OVITO–the Open Visualization Tool". In: *Modelling and Simulation in Materials Science and Engineering* 18.1 (Dec. 2009), p. 015012.

[5] Takamasa Sakai, Takuro Matsunaga, Yuji Yamamoto, Chika Ito, Ryo Yoshida, Shigeki Suzuki, Nobuo Sasaki, Mitsuhiro Shibayama, and Ung-Il Chung. "Design and Fabrication of a High-Strength Hydrogel with Ideally Homogeneous Network Structure from Tetrahedron-like Macromonomers". In: *Macromolecules* 41.14 (July 2008), pp. 5379–5384. ISSN: 0024-9297. DOI: 10.1021/ma800476x.

[6] John D. Weeks, David Chandler, and Hans C. Andersen. "Role of repulsive forces in determining the equilibrium structure of simple liquids". In: *The Journal of Chemical Physics* 54.12 (June 1971), pp. 5237–5247. ISSN: 00219606. DOI: 10.1063/1.1674820.