Simulations documentation

Francisco Javier Vázquez Tavares

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1 Assembly of the network

The simulation methodology is based on [Gnan et al., 2017] and [Sorichetti et al., 2023], with the objective of create a representative polymer structure of a hydro-gel and characterize its rheological properties. This methodology creates the desire structure by creating an interaction between two types of patchy particles. One type of patchy particle represent a Crosslinker and is define with 5 particles, one at the center and the rest are placed in the vertices of a tetrahedron that circumscribes the center particle. The other type of patchy particle represent a Monomer and is define with 3 particles, one at the center and the rest are placed at the poles of the center particle with an 180 degrees between them. Prior to describe with detail the methodology, it is important mention that to from now on I will refer to the center particle of the Crosslinker patchy particle as "CL" and the particles around CL as "PA". Naturally, the center particle of the Monomer patchy particle as "MO" and the particles around MO as "PB".

The proposed methodology to create hydro-gels considers that the geometry of the position of the PA and PB are the same in all the patchy particles and does not change during the simulation. Also, takes into account the following interactions: CL$\longleftrightarrow$MO, PA$\longleftrightarrow$PB, PB$\longleftrightarrow$PB. The CL$\longleftrightarrow$MO interaction is repulsive, and the PA$\longleftrightarrow$PB, PB$\longleftrightarrow$PB interactions are attractive.

There are 3 principal models.

1.1 Potentials

The potentials that describes the interactions mentioned above are a WCA and a threebodody potential. The threbody helps to swap interaction between patchy particles and the WCA to add repulsive behaviour of CL and MO.

$$U_{WCA}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \varepsilon, \quad r \in [0, 2^{1/6}\sigma] \tag{1}$$

$$U_{\text{patchy}}\left(r_{\mu\upsilon}\right) = 2\varepsilon_{\mu\upsilon}\left(\frac{\sigma_p^4}{2r_{\mu\upsilon}^4} - 1\right)\exp\left[\frac{\sigma_p}{\left(r_{\mu\upsilon} - r_c\right)} + 2\right], \quad r_{\mu\upsilon} \in [0, r_c] \tag{2}$$

$$U_{\text{swap}}(r) = w\sum_{\lambda,\mu,\upsilon}\varepsilon_{\mu\upsilon}U_3\left(r_{\lambda,\mu}\right)U_3\left(r_{\lambda,\upsilon}\right), \quad r_{\mu\upsilon} \in [0, r_c] \tag{3}$$

$$U_3 = -U_{\text{patchy}}(r)/\varepsilon_{\mu\upsilon}, \quad r_{\mu\upsilon} \in [0, r_c] \tag{4}$$

1.2 Tables

To use those potentials in LAMMPS we need to declare the force at a given distance. Hence, the gradient in polar coordinates is computed, $\nabla = \partial_r\hat{r} + 1/r\partial_\theta$, $\vec{F} = -\nabla U$.

$$\vec{F}_{\text{WCA}}(r) = -\frac{\varepsilon}{r}\left[24\left(\frac{\sigma}{r}\right)^{6} - 48\left(\frac{\sigma}{r}\right)^{12}\right], \quad r \in \left[0, 2^{1/6}\sigma\right] \tag{5}$$

$$\vec{F}_{\text{patchy}}(r) = -\left\{-\frac{\varepsilon\sigma_p}{r^5(r-r_c)^2}\left[4r_c^2\sigma_p^3 + \sigma_p^3(\sigma_p - 8r_c)r - 2r^5 + 4r^2\sigma_p^3\right]\exp\left[\frac{\sigma_p}{r - r_c} + 2\right]\right\}, \quad r_{\mu\upsilon} \in [0, r_c] \tag{6}$$

For the force of the swap mechanism, we analyze that is computed using a chain rule,

$$U_{\text{swap}}(r)$$

1.3 LAMMPS implementation

We use reduce units, Lennard-Jones units.

To create the patchy particles, the `zero` bond style is used. The reason to use this, is because bond forces and energies are not computed, but the geometry of bond pairs is accessible to other commands (Ref).

The pair styles used in the simulation are: `hybrid/overlay`, `zero`, `lj/cut`, `table` and `threebody/table`. The `hybrid/overlay` style is used because superimposed multiple potentials in an additive fashion (Ref). The rest of pair styles are to implement the potentials described in 1.1.

The length of the box is set, such that the desire Monomers and Cross-Linkers can be spawn. The mass of the patches are set to be the half mass of the CL and MO.

The `pair_coeff` commands where set to accomplish the simulation describe in 2. With respect the `create_atoms` command, the *overlap* keyword was assign to a value of the diameter of CL and MO.

Then, the `rigid/small` fix command is used to create the Monomers and Cross-Linkers particles. This is because, this command is typucally best for a system with large number of small rigid bodiesRef.

The `neighbor` command was set of type bin with a value of 1.8 and the `neigh_modify` command with the exclude keyword was added to save needless computation due to the rigid bodies (Ref).

Then, a Langevin thermostat is used with a velocity-Verlet time integration algorithm to perform Brownian dynamics with the commands `fix lagevin` and `fix nve`. The Langevin thermostat is implemented to models an interaction with a background implicit solvent, in this case water. Meanwhile, the `fix nve` help to create a system trajectory consistent with the microcanonical ensemble, in which the number of particles, volume and energy remains constant.

finally, multiple `computes` are used to get the potential, kinetic and total energies, temperature and voronoi analysis.

1.4 Packing fraction

To approximate a desire packing fraction in the simulation we consider that the packing fraction represent the ratio between the volume of the particle with respect the total volume of the simulation box,

$$\phi = \frac{V_{\text{particles}}}{V_{\text{box}}}.$$

Since, the packing fraction and the volume of the particles are defined, we compute for the volume of the simulation box, and then assume that the simulation box is a cube.

We use a “ghost” particle to compute the approximate volume, due to easier calcalculations.

We assume a sphere of $r_{\text{CP}} + r_{\text{patch}}$ and compute the volume of that "ghost" sphere.

$$V_{\text{ghost}} = \frac{3}{4}\pi(r_{\text{CP}} + r_{\text{patch}})^3$$

considering that $r_{\text{CP}} = 0.5, r_{\text{patch}} = 0.2$, the volume is,

$$\begin{aligned} V_{\text{ghost}} &= \frac{3}{4}\pi(0.7)^3 \\ &= 0.8. \end{aligned}$$

Now, to compute the dimensions of the simulation box,

$$\begin{aligned} V_{\text{box}} &= \frac{V_{\text{particles}}}{\phi} \\ &= \frac{0.8}{\phi} \\ \frac{V_{\text{box}}}{3} &= \frac{1}{3}\frac{0.8}{\phi} \\ L &= \frac{0.8}{3\phi} \end{aligned}$$

2 Shear deformation

We want to apply a shear deformation in one direction and try to find connections between the structure an there rheological properties.

The main rheological properties to measure are: stress, and hopefully yield stress.

2.1 LAMMPS implementation

We use reduce units, Lennard-Jones units.

To create the patchy particles, the `zero` bond style is used. The reason to use this, is because bond forces and energies are not computed, but the geometry of bond pairs is accessible to other commands (Ref).

The pair styles used in the simulation are: `hybrid/overlay`, `zero`, `lj/cut`, `table` and `threebody/table`. The `hybrid/overlay` style is used because superimposed multiple potentials in an additive fashion (Ref). The rest of pair styles are to implement the potentials described in 1.1.

The length of the box is set, such that the desire Monomers and Cross-Linkers can be spawn. The mass of the patches are set to be the half mass of the CL and MO.

The `pair_coeff` commands where set to accomplish the simulation describe in 2. With respect the `create_atoms` command, the *overlap* keyword was assign to a value of the diameter of CL and MO.

Then, the `rigid/small` fix command is used to create the Monomers and Cross-Linkers particles. This is because, this command is typucally best for a system with large number of small rigid bodiesRef.

The `neighbor` command was set of type bin with a value of 1.8 and the `neigh_modify` command with the exclude keyword was added to save needless computation due to the rigid bodies (Ref).

Then, a Nose/Hoover thermostat is used with a time integration algorithm to perform non-equilibrium Molecular dynamics with the command `fix nvt/sllod`. This command is implemented because this thermostat is used for a simulation box that is changing size and/or shape, creating a "streaming" velocity. This position-dependent streaming velocity is subtracted from each atom's actual velocity to yield a thermal velocity which is used for temperature computation and thermostatting (Ref).

To introduce the shear deformation the `fix deform` command is used with the *erate* keyword and remap *v* and flip yes.

finally, multiple `computes` are used to get the potential, kinetic and total energies, temperature and voronoi analysis.

3 Processing the data

- Temperature
- Energy
- Pressure
- Stress

3.1 Pressure and Stress

Differences between the compute pressure and compute stress/atom.

3.1.1 Pressure

The **scalar** pressure is computed as follows,

$$P = \frac{Nk_BT}{V} + \frac{1}{Vd}\sum_{i=1}^{N}\vec{r}_i \cdot \vec{f}_i.$$

The pressure **tensor** is computed as follows

$$P_{e_i,e_j} = \frac{1}{V}\sum i = 1^N m_i v_{i_{e_i}} v_{i_{e_j}} + \frac{1}{V}\sum_{i=1}^{N}{}' r_{e_i i} f_i.$$

3.1.2 Atom stress

3.1.3 Relation between pressure and stress

$$p = -\frac{1}{dV}\sum_{i=1}^{N}\mathrm{Tr}(\sigma_i)$$

where d is the dimension of the simulation, $d = 3$, V is the volume of the simulation box. σ_i is the stress per atom calculation.

From the results we do not get the exact behaviour between the stress and pressure, but the difference is constant and small, indicating that are equivalent.

Bibliography

[Gnan et al., 2017] Gnan, N., Rovigatti, L., Bergman, M., and Zaccarelli, E. (2017). *In Silico* Synthesis of Microgel Particles. *Macromolecules*, 50(21):8777–8786.

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