

# Journal

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# 2024

## July

Jul. 16, 2024 — Tuesday

About Voronoi tessellation and characterization techniques in softmatter. In the article Yang, Zou, and Yu (2002)

They analyse a system with 5000 particles and vary the radius from 100 to 0.1 m and analyse the number of edges for each polyhedron face, number of faces for each polyhedron face, perimeter, area of a polyhedron face and perimeter, area and volume of a polyhedron. In a nutshell, they said that the topological and metric properties of Voronoi polyhedra are quantified as a function of particles size and packing density. Edges, vertices, volume, area in terms of the particle size and packing fraction. According to the results of the article, the average face number decreases when the particle size and packing density decreases. The distributions of face number and edges become broader and more asymmetric. On the other hand, the average perimeter and area of polyhedra increases and the distributions of polyhedron surface area and volume become more flat and can be described by the log-normal distribution. Finally, the average sphericity coefficient of Voronoi Polyhedra varies with packing density. [The sphericity,  $\Psi$ , of an object is the ratio of the surface area of a sphere with the same volume to the object's surface area  $\Psi = \pi^{1/3} (6V_p)^{2/3} / A_p$ ].

They mention the following laws: Aboav-Weaire's law and Lewis's law.

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In the article Lazar, Lu, and Rycroft 2022 in the section of Stability they state that: When geometric quantities are used for classification purposes, thresholds for the range of possible values must be chosen, on the other hand, topological ones can change abruptly under small perturbations of particle coordinates.

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How we can relate the topological and metric properties with reological properties?

Relation between the interatomic interaction with the geometric properties. I think that there is a relation between the superficial area of the voronoi faces with pressure between two particles.

Thinking about the Lennard-Jones potential in three dimensions, it creates an sphere of potential. It can be computed the pressure in a plane that intersect that sphere.

I think that, that relation, between the potential and the intersecte plane, will help to create a connection between reological properties and structural stuff.

$$\vec{P}_{VC} = -\frac{d}{dr}LJ(r)|_{r \in R^2} \frac{1}{A_{VC}} \hat{e}_r,$$

where  $A_{VC}$  is the area of the shared plane between two voronoi cells and the force is evaluated at that plane. The VC indicates, "Voronoi Cell".

Now, this has the same units of the stress tensor.

To introduce the direction of the plane into the pressure, we take dot product with the spherical coordinate system, and then multiply by the normal vector of the plane,

$$\vec{P}_{plane} = [\vec{P}_{VC} \cdot (\hat{e}_r, \hat{e}_\phi, \hat{e}_\theta)] \hat{n}_{plane}$$

Create an histogram of the normal vector. Histogram of the dot product between the normal vector with the cartesian reference.

The better way to analyse the macro characteristics is an histogram.

About packing density: Using the volumen of voronoi polyhedra. It can be said that a system is jammed, when the mean of the volumens of the voronoi polyhedra tends to a minimum.

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About the simulations. 50 simulations with 500 patchy particles took 24 hrs. This is 500 Monomers and Crosslinker. All of them has 50 CL and 450 MO, hence, 200 patches for the 50 CL and 900 patches for MO, hence, 1600 particles in total.

I have no idea how to improve the time of the simulation. Each simulation takes between 27-28 mins.

★ Jul. 17, 2024 — Wednesday

Key point of the reunion:

- Start the script for shear deformation
- Keep in mind to vary the following parameters:
  1. Cross-Linker concentration
  2. Size of the box (Packing density)
  3. The energy of the Patch-Patch interaction.
- Analyze the density distribution of the voronoi parameters
- Make an animation, where the color of the particle represents the volume of the voronoi cell and share the script.
- Hint: Directores

About the idea of the normal vector: They do not see a great future.

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The deformation script is done, basically I copy the code from Felipe.

### Jul. 19, 2024 — Friday

Yesterday I finish the scripts for the shear deformation and investigate some papers that help me to understand what I'm trying to do for the thesis project.

I found the article by Sheiko and Dobrynin [2019](#) and here are some "main" points:

- Materials response to deformation is expressed by a stress-strain curve measured at controlled strain rate and temperature.
- A set of stress-strain curves constitute the "mechanical phenotype".
- The dependency of those curves help us to understand the molecular relaxation processes, such as conformational transformation, bond scission and molecule displacement.
- In the article, they classify a material, based on their stress-strain curves, in three categories: Thermoplastics, Biological networks and Synthetic network.
- Feature of interest for the article: Firmness is the stiffness enhancement in response to deformation and is one of nature's defense mechanisms preventing accidental organ rupture.
- Solid thermoplastics, the mechanical properties are predominantly controlled by molecular interactions.
- Elastomers, the mechanical properties are controlled by the changes in the system configuration, by unravelling network strands at nearly constant mass density.
- A network architecture is defined by: Connectivity, dimensions and flexibility of network strands.
- The weak dependence on chemical compositions helps to manipulate the mechanical response.
- In the article they focus on the Shear modulus.
- Topological defects: Chain entanglements, dangling chain ends, loops, multiple strands and side chains.
- Search of definitions:
  1. Shear modulus:
  2. Cross-link functionality:
  3. Degree of polymerization: Number of monomeric units (MO and CL)
  4. Kuhn length: A theoretical treatment, developed by Werner Kuhn, in which a real polymer chain is considered as a collection of  $N$  Kuhn segments each with a Kuhn length  $b$ . Each Kuhn segment can be thought of as if they are freely jointed with each other.
- The softness at small deformations is manipulated by changing the cross-link density.
- Linear chain Networks
  - The cross-link density is THE control parameter

- The Young's modulus can be tune by introducing loops and dangles.
  - Modify the junctions can controll the network topology
  - The cross-link functionality can be increased by adding dendrimes, colloidal particles and microphase domains.
  - Their equilibrium characteristics are mostly determined by the degree of polymerization of the chemical network strand.
  - Strand entanglements can create a loweer limit for the shear modulus and upper limit for the elongation-at-break.
  - Softness can be achieved by solvent swelling.
  - Swelling leads to strand extensions and therefore firmness enhacement.
- Dual Networks
    - Networks with permanent cross-links and dynamic cross-links.
    - Permamnent cross-link are responsible for elastic properties and sample shape
    - Dynamic cross-link regulate energy dissipation and strain-rate response.
    - Dynamic networks depen on strain rate, permanent network does not depend on strain rate.
    - At higher rates, physical cross-links do not have enough time to break and behave as permanent cross-links, resulting in high modulus and strength.
    - **To characterize the dynamic mechanical properties of the dual networks at small deformations, evolution of the stress relaxation Young's modulus  $E(t)$  during uniaxial extension at a constant temperature is calculated by using a linear viscoelasticity approximation.**
  - Network with Brush-Like strands: I didn't read it with detail, beacuse it is out of my scope/comprehension/interest at the moment. It will be great to read it with more knowledge in the area.

Need to check Dealy and Larson 2006 for more information about polymer structures and their characterization.

Now, in the sense, that the curve of strain-stress is essential to characterize the material, I search in lammps how to compute the stres and strin in the simulation. What I found is an page where there explain how to [Calculate elastic constants](#) and according to that page, the elastic constants (strain and stress) are related as follows:

$$s_{ij} = C_{ijkl} e_{kl},$$

where the repeates indices impley summation.  $s_{ij}$  are the elemnts of the symmetric stress tensor,  $e_{kl}$  are the elements of the symmetric strain tensor and  $C_{ijkl}$  are the elemnts of the fourth rank tensor of elastic constants.

Then, they state that the elastic constant can be computed at *zero temperature* or *finite temperature* and metiond the following methods for doing it in LAMMPS,

- At zero temperature

1. The  $C_{ijkl}$  are estimated by deforming the simulation box in one of the six directions using `change_box` command. Then compute the changes in the stress tensor.

- At finite temperature

1. Exploit the relation between elastic constants, stress fluctuations, and the Born matrix. Ray and Rahman 1984
2. Measure the change in average stress tensor in an NVT simulations when the cell volume undergoes a finite deformation.
3. Sample the triclinic cell fluctuations that occur in an NPT simulation.

Finally, in the article Clavier et al. 2017 a nice review of the advantages and disadvantages of all of these methods is provided.

So the next week I will check those articles and the examples scripts in lammmps.

Possibly, during the weekend's I transfer old entries of multiple daily log in Obsidian, notebooks, Git and Discord.

### Jul. 22, 2024 — Monday

Today I check the examples scripts from [Calculate elastic constants](#), specifically the *Zero temperature* and *Born\_Matrix* examples. I understood the methodology. The scripts create a set of particles, then minimize the system and save that state. Then, a set of 12 deformations are applied, a pair of deformation per basis: xx, yy, zz, xz, yz, xy, with positive and negative sign, to change the direction. Then, the stress and pressure tensors are used to compute the strain tensor.

In the *zero temperature* scheme, this is the end of the simulation, meanwhile, this procedure is repeated thru an interval of time for the *Born\_Matrix* example.

I want to apply that methodology to characterize the hydrogel, but first, the scripts need to be converted from reduced units to real units. Also, I want/need to understand the relations between stress-strain parameters, pressure, stress, the derivatives of the potential energy with stress and strain. Furthermore, I need to seek information about an order parameter to propose.

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Taking into account, that temperature is the mean of the velocity of system of particles, we can create a vague relation between the "structure" and the temperature. Assuming that a solid or fluid has more bonds between particles than a gas, a gas has a greater temperature than the others. However, how can we establish a range of temperature or a temperature in which occurs a transition between solid, to liquid to gas.

If we think that the temperature is a mean, hence we can use the standard deviation as a tool to identify a transition. When the standard deviation of the temperature is localized, then it is in a state, but when the standard deviation is broader, we can stipulate that is happening a phase transition.

Now, here are few points that need to be clarified:

- The temperature is a mean of the particle velocities in a system. To analyze the standard deviation of the temperature, that means to take into account  $N$  systems at constant number of particles, volume and energy (NVE).

- The other points I don't remember because I take another line of thought.

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About viscosity, temperature and rheological properties.

The viscosity, temperature and rheological properties are consequence of the composition of the material. The temperature is more related with the internal velocity of the particles, meanwhile, the viscosity and rheological properties are more related with the relative position between particles.

I understand the structure of the material, as the relative position of the particles between them, hence, the viscosity and the rheological properties are observables of the structure of the material. On the other hand, the temperature is an observable of the velocity of the particles.

It is important to take into account, that the velocity of the particles is affected by the position of the particles and the position of the particles is affected by the velocity of them. Hence, we can use the three of them to state phase changes.

In a broad sense, the temperature will help to differentiate between solids and liquid with gases. The viscosity between solids and gases with liquids and rheological properties between liquids and gases with solids.

Now, with all that in mind, How we can relate those properties with specific structures? That a set of parameters will help to know that a material has chains in "U" or will form vesicles or chains.

To be honest, I infer that to respond that, we also need to take into account the compounds and the electronic properties of their compounds. Because, that will help to connect the macro with the micro properties.

About Pressure. Pressure is an external variable. Pressure is the change of momentum over time per area. Now, the temperature is the expected value of the kinetic energy, which is related with the momentum of the particles. So pressure, will help to understand the change of properties through time.

The pressure will help to observe the change of temperature over time. This is, because the temperature is directly related with the velocity and mass, such as the momentum. However, the mass is assumed to be constant, even in deformation, there is no change in mass, only in the surface area at constant volume. So, when the temperature changes, then the pressure registers that change in time, because the velocity changes.

However, under deformation, the area also changes, hence, the pressure changes.

Now I need more basic information about SoftMatter stuff, hence I will watch the following videos:

[Kent State 2020 course on Statistical Mechanics of SoftMatter](#)

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some stuff of definitions:

- Shear Strain: The engineering shear strain ( $\gamma_{xy}$ ) is defined as the change in angle between lines  $\vec{AC}$  and  $\vec{AB}$ .
- Shear stress (often denoted by  $\tau$ ) is the component of stress coplanar with a material cross section.
- In materials science, shear modulus or modulus of rigidity, denoted by  $G$ , or sometimes  $S$  or  $\mu$ , is a measure of the elastic shear stiffness of a material and is defined as the ratio of shear stress to the shear strain.

- Young's modulus  $E$  describes the material's strain response to uniaxial stress in the direction of this stress (like pulling on the ends of a wire or putting a weight on top of a column, with the wire getting longer and the column losing height),
- The Poisson's ratio  $\nu$  describes the response in the directions orthogonal to this uniaxial stress (the wire getting thinner and the column thicker),
- The bulk modulus  $K$  describes the material's response to (uniform) hydrostatic pressure (like the pressure at the bottom of the ocean or a deep swimming pool),
- The shear modulus  $G$  describes the material's response to shear stress (like cutting it with dull scissors).

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#### Recomendtions of Dr. Tensor, jsjs

- Statistical Physics, A Guenault (Chapman and Hall)
- Introductory Statistical Mechanics, DS Betts and RE Turner (Addison Wesley)
- Introductory statistical Mechanics, Bowley and Sanchez (Oxford)
- Introduction to Statistical Physics, K Huang (Taylor and Francis)
- Statistical Mechanics: A Survival Guide, A. M. Glazer and J. S. Wark (Oxford University Press)

Other references: [Statistical Physics, Daijiro Yoshioka](#), [Introduction to the Theory of Soft Matter, Jonathan V. Selinger](#)

#### ★ Jul. 24, 2024 — Wednesday

#### Important points of the reunion:

- We are more interested in the curve behaviour.
- Changes in the code: Flip yes, remap x
- Graphs
  - Shear rate vs pressure
  - Sheare rate vs stress
- Oscillatory rheology.
- To charetirize the elastic regime.
- Change shear rate and then viscosity.
- Viscosity in dough.



- Then search for yield stress.
- To see the elastic limit.
- For further simulation: Change the shear rate: Do not let the system to relax.
- Experimentally, not necessarily you are in a stationary state.
- First we are going to center in the macroscopic properties.
- Daniel Bonn.

## August

### Aug. 05, 2024 — Monday

Last week I was on vacation.

Important changes: I added the `nve` fix to create Brownian Dynamics Other stuff: The pressure command gives the components of the stress tensor of a collection of atoms.

Stuff about tensors: [What is a fourth rank tensor Answer N](#) In layman's terms, what is a Tensor Field?

About fluctuations in Stress in Young's Modulus: [LAMMPS forum](#). Basically: They use moving average over the `ave/time` command in lammps to smooth the curves.

Some stuff to take into account:

- `fix nvt/sllod`

Observations/questions: The strain-rate vs stress curves means that the stress at each strain rate is the final stress of the deformation or is like an average of a steady state?

The strain vs stress curves means that the stress at each strain is the final stress or the average of the stress?

When the deformation is applied, there is a strain, which is the ratio of the initial position with the final position of the deformation. You can create that deformation at different rhythms, hence the strain-rate/strain vs stress curves.

For me, those kinds of graphs makes sense if the stress at each strain is the average with the standard deviation of the deformation process at a constant strain-rate.

Now... in LAMMPS the pressure command gives a 6 elements for the stress tensor, so... I need to take the dot product with that? I guess, because in all articles they report a scalar. Also, makes sense to report the stress tensor component that is parallel to the deformation.

Idea for Thesis keywords?: Characterization of hydrogels *In silico*

Need to finish the reading of the Entropy based fingerprint for local crystalline order article.

Next articles to read:

- Importance of many-body correlations in glass transition: An example from polydisperse hard spheres
- Enhancing Entropy and Enthalpy Fluctuations to Drive Crystallization in Atomistic Simulations

- Well-Tempered Metadynamics: A Smoothly Converging and Tunable Free-Energy Method
- Escaping free-energy minima

So... this is interesting. How a deformation can start a phase transition-

### Aug. 06, 2024 — Tuesday

Entropy based fingerprint for local crystalline order Metadynamics to enhance the probability of inducing the crystal formation un an accessible computer time. Metadynamics relies on the identification of appropriate collective variables. They found that enthalpy and an approximate expression for entropy based on the two body correlation function, were useful collective variables in this constext. The main thing is that Enthalpy and entropy are global properties and in order to be able to use them as local parmters we have to project them onto each atom.

The pair correlation function accounts for about 90% of the configurational entropy, and is given by,

$$S_2 = -2\pi\rho k_B \int_0^\infty [g(r)\ln g(r) - g(r) + 1] r^2 dr,$$

$\rho$  is the system's density, and  $g(r)$  is the radial distribution function.

The projection on atom  $i$  can be achieved using the xpression:

$$s_s^i = -2\pi\rho k_B \int_0^{r_m} [g_m^i(r)\ln g_m^i(r) - g_m^i(r) + 1] r^2 dr.$$

The radial distribution function is defined as

$$g_m^i(r) = \frac{1}{4\pi\rho r^2} \sum_j \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(r-r_j)^2}{2\sigma^2}\right],$$

$j$  are the neighbors of atom  $i$ ,  $r_{ij}$  is the distance between atoms  $i, j$ , and  $\sigma$  is a broadening parameter.  $\sigma$  shall be so small such that  $g_m(r) \approx g(r)$ , yet large enough for the derivatives relative to the atomic positions to be manageable.

To distinct the distributions more clearly, they define an average local entropy:

$$\bar{s}_s^i = \frac{\sum_j s_s^j f(r_{ij}) + s_s^i}{\sum_j f(r_{ij}) + 1}$$

,  $j$  runs over the neighbors of atom  $i$  and  $f(r_{ij})$  is a switching function with cutoff  $r_a$ :

$$f(r_{ij}) = \frac{1 - (r_{ij}/r_a)^N}{1 - (r_{ij}/r_a)^M},$$

$N = 6, M = 12$ .

$\bar{s}_s$  is the entropy fingerprint. The ability to distinguish sharply between solid-like and liquid-like molecules depend on a wise choice of the parameters  $r_m$  and  $r_a$ . As  $r_m$  is increased the difference between liquid and solid more and more evident. By increasing  $r_a$  eventually the locality of the entropy finger print is lost.

The entropy fingerprint is able to distinguish liquid-like from solid-like atomic environments and is best achieved if we accompany the definition of local entropy with a measure of local enthalpy.

To distinguish between the phases, it is needed to calculate the joint probability distribution of the enthalpy and entropy fingerprints ( $P(\bar{S}_H, \bar{S}_S)$ ).

About the simulations

So... the assembly still works and has been upgraded. However, the deformation simulation still breaks :). I decrement the time step and improve a little bit: instead of breaking at 600 steps, it breaks at 20 000 steps.

Need to search another technique in LAMMPS for the shear deformation.

Hoover thermostat vs Langevin thermostat Damping in Langevin thermostat

So ... I change the Langevin thermostat for a Hoover-Nose thermostat, and the simulation does not longer break.

So... new changes in the shear rate, gamma delta and other stuff improves the simulation.

### Aug. 07, 2024 — Wednesday

So ... the Langevin implementation is still breaking, but the nvt integration works.

In the Langevin thermostat, when I increment the damp parameter, it helps to create more iterations, but eventually it breaks due to missing particles. With the nvt assembly, the velocities of the particles go crazy.

So... I change the shear rate, because I think that I'm trying to force some results. I want to see a slow deformation. Also, due to the change of units, my intuition can not be trusted.

So, I will stop to force results, follow the recommendations of the documentation and change the rate of deformation and the maximum strain.

The next step, is to create the graph of the stress components over time. Then I want to add the computes of the entropy and enthalpy.

Well, it's like magic. As expected, I reduce the shear rate, and the velocities of the particles slow down and the clusters are preserved. At higher shear rates, the velocities of the particles go high, and the clusters are no longer preserved.

Now, taking that into account, the number of clusters will help to now if there is a reconfiguration of the system or no. Also, when the number of clusters decrease at a faster rate, we can say that is in a liquid phase or something like that.

Maybe it will be wise to see how to calculate the elastic constants.

### ★ Aug. 08, 2024 — Thursday

In the reunion Toño and Caludia said that the Langevin and nve commands are correct and start checking at my code. Then, Toño change the integration command nve to nverigid and the simulation didn't break.

### Aug. 09, 2024 — Friday

Now that the simulations are properly coded, it is time to change the parameters.

The command *deform* with the *erate* keyword it adds a relative fraction of the total box length each time step.

The parameters that we are going to change are:

- Shear rate
- Number of CrossLinkers

I have some doubts about the damp parameter of the Langevin thermostat. Because, it is always said that it represent a viscosity and the medium, hence, the rheological properties of the simulation will change, so... it will be interesting how the properties changes with the damp parameter.

Well, also, the main objective is that we want to connect the macroscopic response with the structural properties of the chain.

For that, It will be nice to change the mass of the system, to see if the behaviour changes or not.

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Understanding the response of Polyethylene glycol diacrylate Hydrogel Networks: A statistical Mechanics-Based Framework article.

To derive a microstructurally motivated and energy-based model that captures the three essential features that enable deformation in PEGDA hydrogels:

- Entropic contribution of the PEG chains
- Deformation of rods
- Mechanical PA-PA interactions.

The resume of the relations are: We demonstrate that in the limit of short PEG chains and long PA rods, the behavior is governed by PA-PA interactions, which we attribute to the mechanical restrictions due to the high density grafting of PEG chains to the PA cores. In the case of long PEG chains and short PA rods, the hydrogel behaves entropically due to the deformation of the PEG chains.

Those are the main ideas that I was interested. The advantage or the characteristic of that polymer is that is a brush like, such that, we can define a system of coordinate around the principal chain, and then consider the transformation of the that system of coordinates after the compression.

Read: A microscopically motivated model for the swelling-induced drastic softening of hydrogen-bond dominated biopolymer networks.

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