Draft for the thesis

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Summary Document for the draft of the Thesis.

Assembly of the network

The simulation methodology is based on [1] and [2], 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.

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.

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

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

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

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

[1] Nicoletta Gnan, Lorenzo Rovigatti, Maxime Bergman, and Emanuela Zaccarelli. In silico synthesis of microgel particles. *Macromolecules*, 50(21):8777–8786, November 2017. ISSN 0024-9297, 1520-5835. DOI: 10.1021/acs.macromol.7b01600

[2] Valerio Sorichetti, Andrea Ninarello, José Ruiz-Franco, Virginie Hugouvieux, Emanuela Zaccarelli, Cristian Micheletti, Walter Kob, and Lorenzo Rovigatti. Structure and elasticity of model disordered, polydisperse, and defect-free polymer networks. *The Journal of Chemical Physics*, 158(7):074905, February 2023. ISSN 0021-9606, 1089-7690. DOI: 10.1063/5.0134271

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,

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

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 .

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 . 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.

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,

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

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.

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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.

Processing the data

- Temperature
- Energy
- Pressure
- Stress

Pressure and Stress

Differences between the compute pressure and compute stress/atom.

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

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

Atom stress

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.

Theoretical framework

Brownian dynamics

Here explain the Langevin equation.

Stress

Introductory paragraph To characterize the behaviour of materials, constitutive relations serve as an input to the continuum theory...[3]

This derivation can be found in the apendix of[Admal and Tadmor, 2010][4]. Consider a system of N interacting particles with each particle position given by

$$\vec{r}_\alpha = \vec{r} + \vec{s}_\alpha, \tag{7}$$

where $\vec{r}$ is the position of the center of mass of the system and $\vec{s}_\alpha$ is the position of each point relative to the center of mass. Hence, we can express the momentum of each particle as

$$\vec{p}_\alpha = m_\alpha\left(\dot{\vec{r}} + \dot{\vec{s}}_\alpha\right) = m_\alpha\left(\dot{\vec{r}} + \vec{v}_\alpha^{\,\mathrm{rel}}\right). \tag{8}$$

Before starting the procedure, lets take into account that the center of mass of the system is given by

$$\vec{r} = \frac{\sum_\alpha m_\alpha \vec{s}_\alpha}{\sum_\alpha m_\alpha}, \tag{9}$$

and by replacing (7) in (8) we get the following relations, which will be used later,

$$\sum_\alpha m_\alpha \vec{r}_\alpha = \vec{0}, \quad \sum_\alpha m_\alpha \vec{v}_\alpha^{\,\mathrm{rel}} = \vec{0}. \tag{10}$$

Now we can start by computing the time derivative of tensorial product $\vec{r}_\alpha \otimes \vec{p}_\alpha$[5],

$$\frac{\mathrm{d}}{\mathrm{d}t}(\vec{r}_\alpha \otimes \vec{p}_\alpha) = \underbrace{\vec{v}_\alpha^{\,\mathrm{rel}} \otimes \vec{p}_\alpha}_{\text{Kinetic term}} + \underbrace{\vec{r}_\alpha \otimes \vec{f}_\alpha}_{\text{Virial term}}, \tag{11}$$

which is known as the *dynamical tensor virial theorem* and it is simply an alternative form to express the balance of linear momentum. This theorem becomes useful after making the assumption that there existis a time scale τ, which is short relative to macroscopic processes but long relative to the characteristic time of the particles in the system, over which the particles remain close to their original positions with bounded positions and velocities. Taking advantage of this property we can compute the time average of (11),

$$\frac{1}{\tau}\left(\vec{r}_\alpha \otimes \vec{p}_\alpha\right)\Big|_0^\tau = \overline{\vec{v}_\alpha^{\,\mathrm{rel}} \otimes \vec{p}_\alpha} + \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha}. \tag{12}$$

Assuming that $\vec{r}_\alpha \otimes \vec{p}_\alpha$ is bounded, and the time scales between microscopic and continuum processes are large enough, the term on the left-hand

[3] Capaz e ir introduciendo ideas del Clausius[**?**]

[4] Describe more if what is done in this article

[5] It is interesting to note that the tensorial product $\vec{r}_\alpha \otimes \vec{p}_\alpha$ has units of action and by tacking the time derivative we are dealing with terms that has units of energy.

side can be as small as desired by tacking τ sufficiently large and by summing over all particles we achieve the *tensor virial theorem*:

$$\overline{\mathbf{W}} = -2\overline{\mathbf{T}}, \tag{13}$$

where

$$\overline{\mathbf{W}} = \sum_{\alpha} \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha} \tag{14}$$

is the time-average virial tensor and

$$\overline{\mathbf{T}} = \frac{1}{2} \sum_{\alpha} \overline{\vec{v}_\alpha^{\,\mathrm{rel}} \otimes \vec{p}_\alpha} \tag{15}$$

is the time-average kinetic tensor. This expression for the tensor virial theorem applies equally to continuum systems that are not in macroscopic equilibrium as well as those that are at rest.

The assumption of the difference between the time scales allow us to simplify the relation by replacing (8) in (15), so that,

$$\overline{\mathbf{T}} = \frac{1}{2} \sum_{\alpha} m_\alpha \overline{\vec{v}_\alpha^{\,\mathrm{rel}} \otimes \vec{v}_\alpha^{\,\mathrm{rel}}} + \frac{1}{2} \left[\overline{\sum_{\alpha} m_\alpha \vec{v}_\alpha^{\,\mathrm{rel}}} \right] \otimes \dot{\vec{r}}, \tag{16}$$

which is not the simplification we expected, however, by the relations from (10), equation (16) simplifies to[6]

$$\overline{\mathbf{T}} = \frac{1}{2} \sum_{\alpha} m_\alpha \overline{\vec{v}_\alpha^{\,\mathrm{rel}} \otimes \vec{v}_\alpha^{\,\mathrm{rel}}}. \tag{17}$$

[6] No estoy muy seguro si incluir una discusión acerca del término cinético en la expresión del virial. Posiblemente un párrafo... posiblemente lo ponga en la interpretación del teorema. También, no se si ir metiendo interpretación durante la derivación o no, pero bueno.

On the other hand, instead of reducing the expression, we start to create the conection with the Cauchy stress tensor by distributing (14) into an internal and external contributions,

$$\overline{\mathbf{W}} = \underbrace{\sum_{\alpha} \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\,\mathrm{int}}}}_{\overline{\mathbf{W}}_{\mathrm{int}}} + \underbrace{\sum_{\alpha} \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\,\mathrm{ext}}}}_{\overline{\mathbf{W}}_{\mathrm{ext}}}. \tag{18}$$

The time-average internal virial tensor takes into account the interaction between particle α with the other particles in the system, meanwhile, the time-average external virial tensor considers the interaction with atoms outside the system, via a traction vector $\vec{t}$ and external fields acting on the system represented by $\rho\vec{b}$, where ρ is the mass density of it and $\vec{b}$ is the body force per unit mass applied by the external field. Therefore we can express the following,

$$\sum_{\alpha} \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\,\mathrm{ext}}} := \int_{\delta\Omega} \vec{\xi} \otimes \vec{t}\, dA + \int_{\Omega} \vec{\xi} \otimes \rho\vec{b}\, dV. \tag{19}$$

Where $\vec{\xi}$ is a position vector within the domain Ω occupied by the system of particles with a continuous closed surface $\delta\Omega$. Assuming that Ω is large enough to express the external forces acting on it in the form of the continuum traction vector $\vec{t}$.

With this we can substitute the traction vector with $\vec{t} = \boldsymbol{\sigma}\vec{n}$, where $\boldsymbol{\sigma}$ represent the Cauchy stress tensor and applying the divergence theorem in (19), we have

$$\overline{\mathbf{W}}_{\mathrm{ext}} = \int_{\Omega} \left[\vec{\xi} \otimes \rho\vec{b} + \mathrm{div}_{\vec{\xi}} \left(\vec{\xi} \otimes \boldsymbol{\sigma} \right) \right] dV = \int_{\Omega} \left[\boldsymbol{\sigma}^{\mathrm{T}} + \vec{\xi} \otimes \left(\mathrm{div}_{\vec{\xi}}\, \boldsymbol{\sigma} + \rho\vec{b} \right) \right] dV \tag{20}$$

Since we assume that we are under equilibrium conditions, the term $\text{div}_{\vec{\xi}}\boldsymbol{\sigma} + \rho\vec{b}$ is zero (20) it simplifies to

$$\overline{\mathbf{W}}_{\text{ext}} = V\boldsymbol{\sigma}^{\text{T}}. \tag{21}$$

By tacking into account that we integrate over the domain Ω we can say that we compute the spatial average of the Cauchy stress tensor,

$$\boldsymbol{\sigma}_{\text{av}} = \frac{1}{V}\int_{\Omega}\boldsymbol{\sigma}dV, \tag{22}$$

in which V is the volume of the domain Ω. Replacing (21) into (18), the tensor virial theorem (13) can be expressed as,

$$\sum_{\alpha}\overline{\vec{r}_{\alpha}\otimes\vec{f}_{\alpha}^{\text{int}}} + V\boldsymbol{\sigma}_{\text{av}}^{\text{T}} = -\sum_{\alpha} m_{\alpha}\overline{\vec{\upsilon}_{\alpha}^{\text{rel}}\otimes\vec{\upsilon}_{\alpha}^{\text{rel}}}. \tag{23}$$

Finally, solving for the Cauchy Stress tensor we get,

$$\boldsymbol{\sigma}_{\text{av}} = -\frac{1}{V}\left[\sum_{\alpha}\overline{\vec{f}_{\alpha}^{\text{int}}\otimes\vec{r}_{\alpha}} + \sum_{\alpha} m_{\alpha}\overline{\vec{\upsilon}_{\alpha}^{\text{rel}}\otimes\vec{\upsilon}_{\alpha}^{\text{rel}}}\right], \tag{24}$$

an expression that describe the macroscopic stress tensor in terms of microscopic variables[7].

To end the section it is important to show that (24) is symmetric. Therefore, we rewrite the internal force as the sum of forces between the particles,

$$\vec{f}_{\alpha}^{\text{int}} = \sum_{\beta_{\beta\neq\alpha}}\vec{f}_{\alpha\beta}, \tag{25}$$

and substituting (25) into (24), we have

$$\boldsymbol{\sigma}_{\text{av}} = -\frac{1}{V}\left[\sum_{\alpha,\beta_{\beta\neq\alpha}}\overline{\vec{f}_{\alpha\beta}\otimes\vec{r}_{\alpha}} + \sum_{\alpha} m_{\alpha}\overline{\vec{\upsilon}_{\alpha}^{\text{rel}}\otimes\vec{\upsilon}_{\alpha}^{\text{rel}}}\right]. \tag{26}$$

Due to the property $\vec{f}_{\alpha\beta} = -\vec{f}_{\beta\alpha}$ we obtain the following identity

$$\sum_{\alpha,\beta_{\beta\neq\alpha}}\vec{f}_{\alpha\beta}\otimes\vec{r}_{\alpha} = \frac{1}{2}\sum_{\alpha,\beta_{\beta\neq\alpha}}\left(\vec{f}_{\alpha\beta}\otimes\vec{r}_{\alpha} + \vec{f}_{\beta\alpha}\otimes\vec{r}_{\beta}\right) = \frac{1}{2}\sum_{\alpha,\beta_{\beta\neq\alpha}}\vec{f}_{\alpha\beta}\otimes\left(\vec{r}_{\alpha} - \vec{r}_{\beta}\right). \tag{27}$$

Therefore, by replacing the identity of (27) into (26), we have

$$\boldsymbol{\sigma}_{\text{av}} = -\frac{1}{V}\left[\frac{1}{2}\sum_{\alpha,\beta_{\beta\neq\alpha}}\overline{\vec{f}_{\alpha\beta}\otimes\left(\vec{r}_{\alpha} - \vec{r}_{\beta}\right)} + \sum_{\alpha} m_{\alpha}\overline{\vec{\upsilon}_{\alpha}^{\text{rel}}\otimes\vec{\upsilon}_{\alpha}^{\text{rel}}}\right], \tag{28}$$

expressed with indexical notation and using the eistein summation convention,

$$\sigma_{ij}^{\text{av}} = -\frac{1}{V}\left[\frac{1}{2}\sum_{\alpha,\beta_{\beta\neq\alpha}}\overline{f_i^{\alpha\beta}r_j^{\alpha} + f_i^{\beta\alpha}r_j^{\beta}} + \sum_{\alpha} m_{\alpha}\overline{\upsilon_i^{\alpha\ \text{rel}}\upsilon_j^{\alpha\text{rel}}}\right], \tag{29}$$

which is the same expression implemented in LAMMPS[Thompson et al., 2022].[8]

[7] It is important to acknowledge that several mathematical subtleties were not taken into consideration, however all the mathematical formality is adressed by Nikhil Chandra Admal and E. B. Tadmor in [Admal and Tadmor, 2010]

[8] No se si poner la referencia a la pagina de documentacionhttps://docs.lammps.org/compute_stress_atom.html

Virial Stress and Cauchy stress

Main articles for this section:

- On mechanical theorem application to heat
- The virial theorem and stress calculation in molecular dynamics
- General formulation of pressure and stress tensor for arbitrary many-body interaction potentials under periodic boundary conditions

The virial stress developed on the virial theorem of Clausis 1870 and Maxwell 1870 is

$$\sigma_{ij}^{V} = \frac{1}{V}\sum_{\alpha}\left[\frac{1}{2}\sum_{\beta=1}^{N}\left(R_i^{\beta} - R_i^{\alpha}\right)F_j^{\alpha\beta} - m^{\alpha}v_i^{\alpha}v_j^{\alpha}\right], \tag{30}$$

where (i, j) represents the directions x, y and z. β goes from 1 to N representing the neighbors of the particle with index α. Therefore, R_i^{α} is the position of the particle $alpha$ along the direction i, meanwhile $F_j^{\alpha\beta}$ is the force on particle α due to the interaction with particle β in the j direction. Finally, V is the total vovlume of the system, m^{α} is the mass of the particle α and v_i^{α} is the velocity of the particle α in direction i. It is important to acknowledge that the force $F_j^{\alpha\beta}$ is uniquely defined only for pair potentials and EAM type potentials.[9]

The virial stress calculated from molecular dynamics (MD) simulations has to be averaged voer time in order for it to be equivalent to the continuum Cauchy stress[Subramaniyan and Sun, 2008].

Viriral stress is indeed an atomistic definition for stress that is equivalent to the continuum Cauchy stress.

Molecular dynamics simulations are typically performed in the Eulerian reference frame[10] and hence will need to have velocity included in the stress definition.

[9] So…I need to check[Swenson, 1983] and[Tsai, 1979] to understand how we get that expression from the virial theorem. Also, I don't know what is the virial theorem

[10] I don't know what is the defference between the Langrangian framework and the Eulerian reference frame.

Pressure and stress relation

Pressure and stress are familiar physicla notions. Both refer to the force per unit area which two bodies in contact, or two parts of a single body separated by an imaginary plane, exert on one another. Both tensorial quantities[Tsai, 1979]. Under hydrostatic conditions, the relationship between external pressure and internal stress is particurlarly simple:

$$P = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}), \tag{31}$$

where $\sigma_{xx} = \sigma_{yy} = \sigma_{zz}$ and $\sigma_{xy} = \sigma_{yz} = \sigma_{zx} = 0$, that is, at equilibirum, the external pressure P is equal to the internal normal stress components and throught the system, the shear components being zero. Under these conditions, the external pressure may be calculated from the virial theorem:

$$PV = NkT - \frac{1}{3}\left\langle \sum_{i,j<1}^{N} \vec{r}_{ij} \cdot \frac{\partial \Phi_{ij}}{\partial r_{ij}} \right\rangle, \tag{32}$$

where V is the volume, N is the number of particles, T is the tmeperature of the system, k is the Boltzmann's constante, r_{ij} is the vector joining particles

i and j and Φ_{ij} is the interatomic potential between i and j. The angular brackets denote average over time[11].

The instantaneous internal stress ar a point is made up of two parts:

- The sum of the interatomic forces intercepted by a small area containing the point, averaged over the area.
- The momentum flux through this area during a time interval Δt

If an atom moves across the area, carrying momentum Δmv, then the area also "feels" a force equal to the momentum flux $\Delta mv/\Delta t$, and the force also contributes to the stress over the area in the interval Δt. The normal component of the sum of the forces gives the normal stress, and the in-plane component gives the tangential stress. The area may be either stationary or moving at a uniform velocity. It may also be at the boundary of the system.

The time averages of the instantaneous stress components then ive what may be called the "measured" stresses at the point.[Tsai, 1979]. ... This formulation is not new: Cauchy discussed the stress-strain relationship in a crystalline material from the viewpoint of "region of molecular activity" as early as 1828. ... The stress method applies equally to a system not in thermal equilibrium, because the temperature term does not appear explicitly in this formulation. ... the method of stress calculation may be applied locally, without requiring the system to be in equilibrium or even spatially homogeneous. ... it should be possible to use this method to obtain the stress distribution in a solid with a crack in it, whereas the virial method would be inapplicable in this case.

They show that the pressure calculated by the vrial method is actually the normal stress in the boundary planes. The stress method, on the other hand, can be used to calculated the stress not only in the boundary planes, but also in the interior planes.

The virial is defined as

$$\Upsilon = \sum_{i}^{N} \vec{r} \cdot \vec{F}_i, \tag{33}$$

[11] Is the same expression for the scalar pressure used by the compute pressure in lammps: documentation page.

Lammps implementation

Langevin Thermostat

compute stress/atom and pressure [12]

Virial contribution to the stress and pressure tensors[Thompson et al., 2009]. They find three ways of computing the virial contribution,

$$W(\vec{r}^N) = \sum_{k\in\vec{0}} \sum_{w=1}^{N_k} \vec{r}_w^k \cdot \vec{F}_w^k \tag{34}$$

$$W(\vec{r}^N) = \sum_{n\in Z^3} \sum_{i=1}^{N} \vec{r}_{i\vec{n}} \cdot \left(-\sum_{k\in\vec{0}} \frac{\mathrm{d}}{\mathrm{d}\vec{r}_{i\vec{n}}} u_k\left(\vec{r}^{N_k}\right) \right) \tag{35}$$

$$W(\vec{r}^N) = \sum_{n\in Z^3} \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i + \sum_{\vec{n}\in Z^3} \vec{\mathrm{Hn}} \cdot \sum_{i=1}^{N} \left(-\sum_{k\in\vec{0}} \frac{\mathrm{d}}{\mathrm{d}\vec{r}_{i\vec{n}}} u_k\left(\vec{r}^{N_k}\right) \right) \tag{36}$$

[12] Explain the scalar pressure, pressure tensor and stress tensor. Explain the relation between pressure and stress of the system.

[13]

[13] Skimming the equations (30) and that one, the virial term are similars. Need to check if they are equivalents.

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