

# Draft for the thesis

Francisco Vazquez-Tavares

July 7, 2025

**Summary** Document for the draft of the Thesis.

## Introduction

## Acknowledge

## Objectives

## Justification

## 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...<sup>1</sup>

This derivation can be found in the appendix of [Admal and Tadmor, 2010]<sup>2</sup>. Consider a system of  $N$  interacting particles with each particle position given by

$$\vec{r}_\alpha = \vec{r} + \vec{s}_\alpha, \quad (1)$$

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

$$\vec{p}_\alpha = m_\alpha (\dot{\vec{r}} + \dot{\vec{s}}_\alpha) = m_\alpha (\dot{\vec{r}} + \vec{v}_\alpha^{\text{rel}}). \quad (2)$$

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

$$\vec{r} = \frac{\sum_\alpha m_\alpha \vec{s}_\alpha}{\sum_\alpha m_\alpha}, \quad (3)$$

and by replacing (1) in (2) we get the following relations, which will be used later,

$$\sum_\alpha m_\alpha \vec{r}_\alpha = \vec{0}, \quad \sum_\alpha m_\alpha \vec{v}_\alpha^{\text{rel}} = \vec{0}. \quad (4)$$

Now we can start by computing the time derivative of tensorial product  $\vec{r}_\alpha \otimes \vec{p}_\alpha$ <sup>3</sup>,

$$\frac{d}{dt}(\vec{r}_\alpha \otimes \vec{p}_\alpha) = \underbrace{\vec{v}_\alpha^{\text{rel}} \otimes \vec{p}_\alpha}_{\text{Kinetic term}} + \underbrace{\vec{r}_\alpha \otimes \vec{f}_\alpha}_{\text{Virial term}}, \quad (5)$$

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  $\tau$ , which is short relative to macroscopic processes but long relative to the

<sup>1</sup> Capaz e ir introduciendo ideas del Clausius[Clausius, 1870]

<sup>2</sup> Describe more if what is done in this article

<sup>3</sup> 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.

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 (5),

$$\frac{1}{\tau}(\vec{r}_\alpha \otimes \vec{p}_\alpha) \Big|_0^\tau = \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{p}_\alpha} + \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha}. \quad (6)$$

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

$$\overline{\mathbf{W}} = -2\overline{\mathbf{T}}, \quad (7)$$

where

$$\overline{\mathbf{W}} = \sum_{\alpha} \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha} \quad (8)$$

is the time-average virial tensor and

$$\overline{\mathbf{T}} = \frac{1}{2} \sum_{\alpha} \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{p}_\alpha} \quad (9)$$

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 (2) in (9), so that,

$$\overline{\mathbf{T}} = \frac{1}{2} \sum_{\alpha} m_{\alpha} \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{v}_\alpha^{\text{rel}}} + \frac{1}{2} \left[ \sum_{\alpha} m_{\alpha} \overline{\vec{v}_\alpha^{\text{rel}}} \right] \otimes \dot{\vec{r}}, \quad (10)$$

which is not the simplification we expected, however, by the relations from (4), equation (10) simplifies to<sup>4</sup>

$$\overline{\mathbf{T}} = \frac{1}{2} \sum_{\alpha} m_{\alpha} \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{v}_\alpha^{\text{rel}}}. \quad (11)$$

On the other hand, instead of reducing the expression, we start to create the conection with the Cauchy stress tensor by distributing (8) into an internal and external contributions,

$$\overline{\mathbf{W}} = \underbrace{\sum_{\alpha} \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\text{int}}}}_{\overline{\mathbf{W}}_{\text{int}}} + \underbrace{\sum_{\alpha} \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\text{ext}}}}_{\overline{\mathbf{W}}_{\text{ext}}}. \quad (12)$$

The time-average internal virial tensor takes into account the interaction between particle  $\alpha$  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  $\rho$  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,

$$\sum_{\alpha} \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\text{ext}}} := \int_{\delta\Omega} \vec{\xi} \otimes \vec{t} dA + \int_{\Omega} \vec{\xi} \otimes \rho \vec{b} dV. \quad (13)$$

<sup>4</sup> 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.

Where  $\vec{\xi}$  is a position vector within the domain  $\Omega$  occupied by the system of particles with a continuous closed surface  $\delta\Omega$ . Assuming that  $\Omega$  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 (13), we have

$$\overline{\mathbf{W}}_{\text{ext}} = \int_{\Omega} \left[ \vec{\xi} \otimes \rho \vec{b} + \text{div}_{\vec{\xi}} \left( \vec{\xi} \otimes \boldsymbol{\sigma} \right) \right] dV = \int_{\Omega} \left[ \boldsymbol{\sigma}^T + \vec{\xi} \otimes \left( \text{div}_{\vec{\xi}} \boldsymbol{\sigma} + \rho \vec{b} \right) \right] dV \quad (14)$$

Since we assume that we are under equilibrium conditions, the term  $\text{div}_{\vec{\xi}} \boldsymbol{\sigma} + \rho \vec{b}$  is zero (14) it simplifies to

$$\overline{\mathbf{W}}_{\text{ext}} = V \boldsymbol{\sigma}^T. \quad (15)$$

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

$$\boldsymbol{\sigma}_{\text{av}} = \frac{1}{V} \int_{\Omega} \boldsymbol{\sigma} dV, \quad (16)$$

in which  $V$  is the volume of the domain  $\Omega$ . Replacing (15) into (12), the tensor virial theorem (7) can be expressed as,

$$\sum_{\alpha} \overline{\vec{r}_{\alpha} \otimes \vec{f}_{\alpha}^{\text{int}}} + V \boldsymbol{\sigma}_{\text{av}}^T = - \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}}. \quad (17)$$

Finally, solving for the Cauchy Stress tensor we get,

$$\boldsymbol{\sigma}_{\text{av}} = -\frac{1}{V} \left[ \sum_{\alpha} \overline{\vec{f}_{\alpha}^{\text{int}} \otimes \vec{r}_{\alpha}} + \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}} \right], \quad (18)$$

an expression that describe the macroscopic stress tensor in terms of microscopic variables<sup>5</sup>.

To end the section it is important to show that (18) is symmetric. Therefore, we rewrite the internal force as the sum of forces between the particles,

$$\vec{f}_{\alpha}^{\text{int}} = \sum_{\beta \neq \alpha} \vec{f}_{\alpha\beta}, \quad (19)$$

and substituting (19) into (18), we have

$$\boldsymbol{\sigma}_{\text{av}} = -\frac{1}{V} \left[ \sum_{\alpha, \beta \neq \alpha} \overline{\vec{f}_{\alpha\beta} \otimes \vec{r}_{\alpha}} + \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}} \right]. \quad (20)$$

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

$$\sum_{\alpha, \beta \neq \alpha} \vec{f}_{\alpha\beta} \otimes \vec{r}_{\alpha} = \frac{1}{2} \sum_{\alpha, \beta \neq \alpha} \left( \vec{f}_{\alpha\beta} \otimes \vec{r}_{\alpha} + \vec{f}_{\beta\alpha} \otimes \vec{r}_{\beta} \right) = \frac{1}{2} \sum_{\alpha, \beta \neq \alpha} \vec{f}_{\alpha\beta} \otimes (\vec{r}_{\alpha} - \vec{r}_{\beta}). \quad (21)$$

Therefore, by replacing the identity of (21) into (20), we have

$$\boldsymbol{\sigma}_{\text{av}} = -\frac{1}{V} \left[ \frac{1}{2} \sum_{\alpha, \beta \neq \alpha} \overline{\vec{f}_{\alpha\beta} \otimes (\vec{r}_{\alpha} - \vec{r}_{\beta})} + \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}} \right], \quad (22)$$

<sup>5</sup> It is important to acknowledge that several mathematical subtleties were not taken into consideration, however all the mathematical formality is addressed by Nikhil Chandra Admal and E. B. Tadmor in [Admal and Tadmor, 2010]

expressed with indexical notation and using the eistein summation convention,

$$\sigma_{ij}^{\text{av}} = -\frac{1}{V} \left[ \frac{1}{2} \sum_{\alpha, \beta \neq \alpha} \overline{f_i^{\alpha\beta} r_j^\alpha + f_i^{\beta\alpha} r_j^\beta} + \sum_{\alpha} m_{\alpha} \overline{v_i^{\alpha \text{rel}} v_j^{\alpha \text{rel}}} \right], \quad (23)$$

which is the same expression implemented in LAMMPS[Thompson et al., 2022].<sup>6</sup>

<sup>6</sup> No se si poner la referencia a la pagina de documentacion [https://docs.lammps.org/compute\\_stress\\_atom.html](https://docs.lammps.org/compute_stress_atom.html)

## Computational Implementation

### General description

The simulation methodology is based on the work presented in[Gnan et al., 2017] and[Sorichetti et al., 2023], with the objective of create a representative polymer structure of a microgel and characterize the mechanical response under shear deformation. This methodology creates the structure by using a mixture of two types of patchy particles. The patchy particles are spheres of identical size and mass decorated by patches to represent interaction sites. One type represent a *Crosslinker* and is define by 1 central particle with 4 patches placed at the vertices of a circumscribed tetrahedron. The other one represent a *Monomer* define by 1 central particle and 2 patches placed at the poles.

The interaction between the central particles is modeled with a Weeks-Chandler-Andersen repulsive potential,

$$U_{WCA}(r_{i,j}) = \begin{cases} 4\epsilon_{i,j} \left[ \left( \frac{\sigma}{r_{i,j}} \right)^{12} - \left( \frac{\sigma}{r_{i,j}} \right)^6 \right] + \epsilon_{i,j}, & r_{i,j} \in [0, 2^{1/6}\sigma], \\ 0, & r_{i,j} > 2^{1/6}\sigma \end{cases}, \quad (24)$$

where  $r_{i,j}$  is the distance between the center of the central particles,  $\sigma$  is the diameter of the particles and  $\epsilon_{i,j}$  is the energy of the interacton. The patch-patch interaction is modeled with an attractive potential,

$$U_{\text{patchy}}(r_{\mu v}) = \begin{cases} 2\epsilon_{\mu v} \left( \frac{\sigma_p^4}{2r_{\mu v}^4} - 1 \right) \exp \left[ \frac{\sigma_p}{(r_{\mu v} - r_c)} + 2 \right], & r_{\mu v} \in [0, r_c], \\ 0, & r_{\mu, v} > r_c, \end{cases} \quad (25)$$

where  $r_{\mu v}$  is the distance between two patches,  $\sigma_p$  is the diameter of the patches,  $r_c$  is the cut distance of interaction set to  $1.5\sigma_p$  and  $\epsilon_{\mu, v}$  is the interaction energy between the patches. Moreover, the interaction between patches is complemented by a three-body repulsive potential, defined in terms of (25), that provides an efficient bond-swapping mechanism making possible to easily equilibrate the system at extremely low temperatures, while at the same time, retaining the single-bond-per-patch condition[Sciortino, 2017],

$$U_{\text{swap}}(r_{l,m}, r_{l,n}) = w \sum_{l,m,n} \epsilon_{m,n} U_3(r_{l,m}) U_3(r_{l,n}), \quad r_{l,n} \in [0, r_c], \quad (26)$$

where

$$U_3(r) = \begin{cases} 1 & r \in [0, r_{\min}], \\ -U_{\text{patchy}}(r)/\epsilon_{m,n}, & r \in [r_{\min}, r_c] \end{cases}. \quad (27)$$

- $\vec{r}_i$ : Position of Crosslinker central particle
- $\vec{r}_j$ : Position of Monomer central particle
- $\{\vec{r}_\mu^i\}$  Set of positions of the patches in the crosslinker patchy particle
- $\{\vec{r}_v^j\}$  Set of positions of the patches in the monomer patchy particle

The sum in (26) runs over all triples of bonded patches (patch  $l$  bonded both with  $m$  and  $n$ ).  $r_{l,m}$  and  $r_{l,n}$  are the distances between the reference patch and the other two patches. The parameter  $\epsilon_{m,n}$  is the energy of repulsion and  $w$  is used to tune the swapping ( $w = 1$ ) and non-swapping bonds ( $w \gg 1$ ). The cut off distance  $r_c$  is the same as in the potential of interaction between patches, meanwhile the minimum distance  $r_{\min}$  is the distance at the minimum of (25), i.e.  $\epsilon_{m,n} \equiv |U_{\text{patchy}}(r_{\min})|$ . Finally, the energy of interaction between crosslinker patches ( $\epsilon_{\mu^i, \mu^i}$ ) are set to 0 to allow only crosslinker-monomer and monomer-monomer bonding (figure 2).

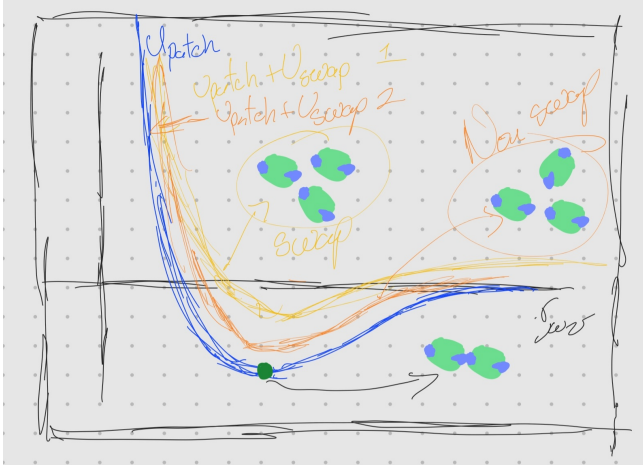


Figure 1: La idea de la figura es poner el potencial de interacción entre patches y ver el efecto del potencial de 3 cuerpos cuando  $w = 1$  y cuando  $w \gg 1$ .

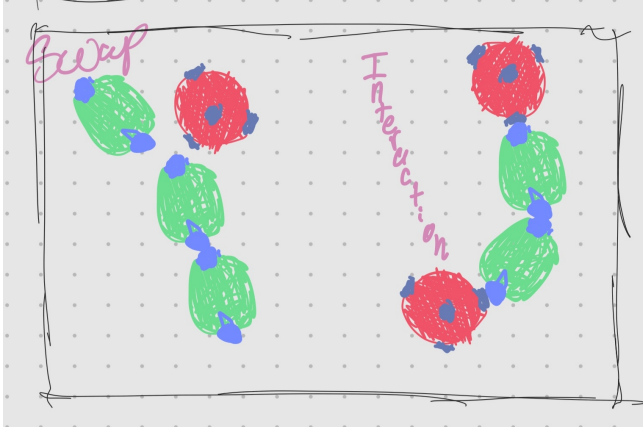


Figure 2: La idea de esta es mostrar las posibles configuraciones (monomero-monomero, monomero-crosslinker y un poco de potencial de 3 cuerpos)

Once we defined the interactions between the particles in the system, we define a simulation protocol divided in the following processes, assembly and shear. Which are going to be described in detail in the following sections.

After the assembly process, the structure is analysed to see if the structure percolates or not and verify if there are only binary patch-interactions, otherwise we checked the implementation of the potentials or the parameters. Once the hydro-gel structure meets the requirements we start with the shear process and monitored the temperature and energy to see if the simulation was converging. Once those tests are done, the mechanical response was analyzed through the components of the stress tensor and structure characterization.

### *Assembly of the network*

We perform molecular dynamics (MD) simulations at fixed temperature  $T = kBT / \epsilon = 0.05$ , where  $kB$  is the Boltzmann constant. Thanks to such a low temperature, the system tends to maximize the number of bonds. In addition, owing to the bondswapping mechanism, the system is able to continuously restructure itself, until the large majority of possible bonds are formed.

It is important to say that the main difference between the articles cited and the implementation are the absence of FENE bonds and the swelling potential.

because part of the exploration is to analyze what happens in the deformation if the interactions between crosslinker and monomer can swap.

### *References*

- Nikhil Chandra Admal and E. B. Tadmor. A unified interpretation of stress in molecular systems. *Journal of Elasticity*, 100(1):63–143, June 2010. ISSN 1573-2681. DOI: 10.1007/s10659-010-9249-6.
- R. Clausius. Xvi on a mechanical theorem applicable to heat. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 40(265):122–127, August 1870. ISSN 1941-5982, 1941-5990. DOI: 10.1080/14786447008640370.
- 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.
- Francesco Sciortino. Three-body potential for simulating bond swaps in molecular dynamics. *The European Physical Journal E*, 40(1):3, January 2017. ISSN 1292-8941, 1292-895X. DOI: 10.1140/epje/i2017-11496-5.
- Valerio Sorichetti, Andrea Ninarello, José M. Ruiz-Franco, Virginie Hugouvieux, Walter Kob, Emanuela Zaccarelli, and Lorenzo Rovigatti. Effect of chain polydispersity on the elasticity of disordered polymer networks. *Macromolecules*, 54(8):3769–3779, April 2021. ISSN 0024-9297, 1520-5835. DOI: 10.1021/acs.macromol.1c00176.
- 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.
- Arun K. Subramaniyan and C.T. Sun. Continuum interpretation of virial stress in molecular simulations. *International Journal of Solids and Structures*, 45(14–15):4340–4346, July 2008. ISSN 00207683. DOI: 10.1016/j.ijsolstr.2008.03.016. URL <https://linkinghub.elsevier.com/retrieve/pii/S0020768308001248>.

- Robert J. Swenson. Comments on virial theorems for bounded systems. *American Journal of Physics*, 51(10):940–942, October 1983. ISSN 0002-9505, 1943-2909. DOI: 10.1119/1.13390. URL <https://pubs.aip.org/ajp/article/51/10/940/1052035/Comments-on-virial-theorems-for-bounded-systems>.
- A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott, and S. J. Plimpton. LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Comp. Phys. Comm.*, 271:108171, 2022. DOI: 10.1016/j.cpc.2021.108171.
- Aidan P. Thompson, Steven J. Plimpton, and William Mattson. General formulation of pressure and stress tensor for arbitrary many-body interaction potentials under periodic boundary conditions. *The Journal of Chemical Physics*, 131(15):154107, October 2009. ISSN 0021-9606, 1089-7690. DOI: 10.1063/1.3245303. URL <https://pubs.aip.org/jcp/article/131/15/154107/316893/General-formulation-of-pressure-and-stress-tensor>.
- D. H. Tsai. The virial theorem and stress calculation in molecular dynamics. *The Journal of Chemical Physics*, 70(3):1375–1382, February 1979. ISSN 0021-9606, 1089-7690. DOI: 10.1063/1.437577. URL <https://pubs.aip.org/jcp/article/70/3/1375/89129/The-virial-theorem-and-stress-calculation-in>.