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Exploration of mechanical responses of Hydrogels via numerical simulation.

This is the subtitle

Masters thesis

September 23, 2025

Supervisor	Antonio	their job
Cosupervisor	Claudia	also their job
Jury members	jury 1	jobs
	jury 2	...

Francisco Javier Vazquez Tavares, *Exploration of mechanical responses of
Hydrogels via numerical simulation.*, This is the subtitle, September 23, 2025.

For my homies

Abstract

This thesis explores the theoretical framework necessary for analysing computational simulations of the mechanical response of a network under shear deformation. This network is modelled on a hydrophilic polymeric network based on a PNIPAM microgel protocol. The protocol has been implemented in LAMMPS to take advantage of the parallelisation of the velocity Verlet algorithm and Langevin dynamics. We found that...

Acknowledgements

... Thanks to Tec and SECHIT for the economical support. ...

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1 *Introduction*

I found it quite intriguing to explore how materials react mechanically from first principles, and I devoted two years to this research, with the possibility of extending it further. Despite the financial constraints and significant computational resources required to solve quantum mechanical systems, we have implemented a feasible computational methodology to investigate the correlation between molecular geometrical structure and mechanical response. In addition, the computational methodology is based on a numeric protocol that replicates the polymeric network of PNIPAM microgels, which are a size-tunable hydrogel. After a brief literature review has revealed the extensive range of applications for hydrogels in various fields. And a thorough review of the existing literature has revealed a lack of consensus on the precise “origin” of the mechanical response exhibited by hydrogels.

In this regard, the key objective of the thesis is to explore a computational methodology for identifying parameters that represent the main properties of the polymeric network. These parameters can then be coupled into constitutive relations to predict the mechanical response of a simplified polymeric network. To that end, we have established the following specific objectives:

- ◇ Replicate the numeric protocol.
- ◇ Adapt the protocol to create a more general network.
- ◇ Apply shear deformation to the network.
- ◇ Characterize the network before and after shear.
- ◇ Analyze the parameters of the network under different shear conditions and different network parameters.

We expect that the parameter analysis will assist us in selecting a parameter or a combination of parameters to couple them into a constitutive equation. It is important to clarify that the definition of the constitutive equation or the mathematical procedure/proposal are not within the scope of this thesis. The objective is to identify a relation between network characteristics and mechanical response.

In the following section, we will explore the applications of hydrogels identified during the literature review. We will also introduce the main characteristics of

the mechanical response in general terms. The subsequent theoretical framework chapter begins by explaining how to quantify the properties of the material and how to apply numerical simulations to analyze the system. Finally, we closed with the analysis of the numerical solutions chapter and the conclusion of this work.

1.1 *Why Hydrogels?*

While the numerical protocol was initially developed for a specific polymeric network, we modified it to represent a more simplified case that resembles a broader group of polymeric networks. These polymeric networks are collectively referred to as hydrogels. Hydrogels are composed primarily of hydrophilic monomers, which are biocompatible, making them suitable for medical applications. In general terms, hydrogels exhibit visco-elastic and visco-plastic mechanical responses. The material's viscoelasticity response makes it suitable for use in shock absorption, vibration damping, and biological tissue mimicry. Meanwhile, the viscoplasticity response makes the material suitable for energy dissipation.

1.1.1 *Applications*

Medical applications Drug delivery, emergency therapy, corneal tissue, bone tissue, tissue healing.

Environmental applications Remediation to sensing in wastewater, heavy metal removal, selective recovery, nutrient retention.

Smart materials promising sensors and actuators with graphene, photoresponsive hydrogels, stimuli-responsive injectable hydrogels, future flexible smart devices, future regenerative medicine, human-machine integration.

1.1.2 *Mechanical response*

The origin of the mechanical properties of hydrogels from first principles remains incompletely understood due to the complex multi-scale nature of these materials. One of the main reasons is that hydrogels consist of heterogeneous, often disordered polymer networks swollen with water, where molecular interactions

(covalent bonds, physical crosslinks, entanglements, and solvent–polymer interactions) collectively determine macroscopic elasticity and viscoelasticity. Accurately bridging atomic-scale forces and chemical bond dynamics to bulk mechanical behavior involves coupling nonlinear polymer physics, solvent effects, and dynamic crosslink kinetics. This presents a significant challenge to current theoretical and computational models. Furthermore, spatial heterogeneity, network defects, and time-dependent rearrangements complicate deriving constitutive relations purely from fundamental physics, necessitating multiscale approaches and approximations.

2 *Theoretical Framework*

2.1 *Hydrogels*

Introduction From bibliographic review, we can say that a hydrogel is a polymeric network that has the capacity of swelling[cites]. Some examples are, polyacrylamide, sodium polyacrylate, Poly(vinyl alcohol), Poly(ethylene glycol), Poly(hydroxyethyl methacrylate), agarose, alginate, gelatin, pectin, starch, cellulose-based networks, protein networks, among others. In order to try to understand (some of) the properties of the hydrogels, we are going to explore what is a polymeric network and what is the capacity of swelling.

In general terms, a polymeric network is a three dimensional structure formed by long polymer chains that are interconnected. Meanwhile, the swellability is defined as the capacity to absorb significant amounts of a solvent without dissolving, resulting in an increase volume. Since the swellability is a “capacity” of the network, we are going to start by exploring what is a polymeric structure.

2.1.1 *Polymeric networks*

Introduction From a structural perspective, polymer networks consist of network “junctions”, which consist of three or more strands connected by a mechanism. This mechanism is commonly refer as “crosslink” and can be describe through physical interactions or covalent bonds. On the other hand, we recall that a polymer is a macromolecule composed by monomers that are covalently bondend together forming a strand. Monomers can possess specific functional groups or reactive sites, which determine the manner in which monomers bind together. This, in turn, influences the structural and property characteristics of the resulting polymer. Part of the swelling capacity can be explained by the type of monomers in the network, meanwhile the structural frameworks allows to explain the mechanical response and the swelling.

Swellability The capacity for substantial solvent absorption and expansion of hydrogels is attributable to the expansion of the network due to osmotic pressure and the hydrophilic functional groups of the monomers that constitute hydrogels. Some of the key hydrophilic groups are, hydroxyl group, amide group, carboxylate anion, ether group. The hydrophilic phenomenon, from a chemical perspective, occurs when molecules possess polar or charged functional groups that spontaneously form hydrogen bonds or electrostatic interactions with water, enabling water to diffuse over the surface. Nevertheless, the network's integrity remains intact due to the crosslink mechanism.

Crosslink The underlying principles of crosslink mechanism are the physical interactions and covalent bonds. However it is important to acknowledge that, for example, given sufficiently strong and static physical interactions, physical networks can behave identically to covalent bonded networks; alternatively, the incorporation of mechanisms for covalent bond exchange can result in chemical networks that exhibit adaptable mechanical properties regulated by external stimuli [cite]. Consequently, an emphasis on bond strengths and exchange rates provides more informative insights for accurately inferring the properties of hydrogels.

With this understanding, a covalent bond is defined as a specific type of chemical bond that occurs when two atoms share one or more pairs of electrons. On the other hand, a physical interaction is defined as a non-covalent force that describes how atoms, ions, or molecules attract or repel each other without forming new chemical entities. The covalent bond is the result of quantum mechanical interactions between atomic orbitals. In these interactions, shared electrons occupy a molecular orbital that extends over both atoms. In contrast, physical interactions are attributed to electrostatic, van der Waals, or dipole forces, arising from the redistribution of electron density and the consequent energy alterations between particles.

Now we can dive into the different types of polymer networks and the different types of crosslink mechanisms. After that, then we are going to spend some paragraphs into explore the ideas of mechanical response through constitutive relations. In order to end with the mechanical response of hydrogels and some connections with the polymeric network.

2.1.2 *Types of polymeric networks: Gels*

Introduction In general terms a polymeric network can be divided into one of four major classes: thermosets, thermoplastics, elastomers, and gels. Thermosets are rigid, covalently bonded polymer networks with high modulus, which are insoluble and degrade rather than melt upon heating. In contrast, thermoplastics are held together by strong physical interactions, allowing them to be remolded and recycled when heated. Elastomers are soft, deformable with covalent networks used above their glass transition temperature, capable of large reversible extensions. Finally, gels are liquid-swollen networks, either covalent or physical interactions, that are soft and highly deformable.

Gels In detail, a gel is a three-dimensional, crosslinked polymer network formed by physical or chemical crosslinks, which serve to trap the solvent molecules via intermolecular interactions, including hydrogen bonding and osmotic forces. This process prevents the fluid from flowing freely. This results in a material with both solid and liquid characteristics—elasticity from the polymer network and fluidity from the entrapped solvent. This description resembles that of a hydrogel. The hydrogel, however, is a specific type of gel in which the solvent is water and the polymers are hydrophilic.

Gel point The classification of a polymer network as a gel is characterized by the formation of a continuous, system-spanning (infinite) network through the process of polymerization or crosslinking mechanisms. This phenomenon is indicative of the percolation* of the polymeric network. And it is known as the gel point. At this point, the polymer chains become sufficiently interconnected through crosslinks to create a macroscopic network that spans the entire volume, causing the material to gain elasticity and lose fluidity, transitioning† it from a viscous liquid (sol) to a solid-like gel.

Finally, it must be mentioned that not all polymer networks can achieve a gel point. To reach this point requires sufficient network connectivity due to enough reactive sites and a high enough crosslinking density. For instance, linear, unbranched, or insufficiently crosslinked polymers remain soluble and do not gel.

*In physics, percolation describes the emergence of large-scale connectivity in disordered systems. On the other hand, mathematically, is the study of cluster formation in a random graph or lattice when sites or bonds are occupied with a given probability.

†This transition is a percolation threshold where the molecular weight and network correlation length diverge.

2.1.3 *Crosslink mechanisms*

Intro According to the literature, the most common classification is typically as physical or covalent hydrogels. In regards to the main crosslink mechanism present in the polymeric network. However, it is important to note that, although the crosslink mechanism plays a significant role in network integrity, it is not the sole mechanism that can adequately describe the mechanical response in terms of network structure. In this regard, three primary crosslink mechanisms can be identified: covalent, physical interactions, and mechanical*.

*No estoy seguro si hablar de técnicas de sintetización o si explicar mejor los mecanismos de bond exchange en redes covalentes y en redes físicas.

Covalent Crosslinking Polymer chains are linked by covalent bonds, which are typically formed through free-radical polymerization, click chemistry, or UV-induced reactions. This results in a static, stable, and robust network with high mechanical strength and low reversibility. However, when dynamic covalent chemistry is applied, it can allow bond exchange and self-healing properties.

Physical Crosslinking Polymer chains are held together by non-covalent interactions, including hydrogen bonding, ionic interactions, hydrophobic associations, and van der Waals forces. Given the possibility of bond exchange under normal conditions, the network is dynamic. Therefore, they tend to be softer and less mechanically robust in comparison to covalently crosslinked hydrogels. Finally, these networks are reversible, enabling self-healing, shape-memory, and stimuli-responsive behaviors.

Mechanical Crosslinking Finally, these types of crosslinked networks are held together by physical entanglements or interpenetrating polymer chains. Examples include double-network hydrogels, slide-ring gels, and highly entangled architectures. This provides toughness and elasticity properties by dissipating energy through chain movement and entanglement.

2.1.4 *Reverible networks*

Intro Another common classification in literature is to categorize the polymeric network as reversible or irreversible. It is a common association that networks with physical crosslink mechanisms are reversible, while covalently crosslinked

networks are irreversible. However, regardless of the crosslink mechanism, the network can be shown to be reversible.

Physical networks The interactions can spontaneously break and reform due to thermal fluctuations or changes in the microenvironment, such as pH, ionic strength, temperature. When external stress or energy disturbs the network, some physical bonds dissociate. Free chain segments then seek new partners, allowing dynamic rejoining at different sites. This ongoing exchange can lead to self-healing, viscoelastic behavior, and adaptability of the hydrogel. The equilibrium and kinetics of bond formation/dissociation can be tuned by controlling the physical interactions.

Covalent networks In “dynamic” covalent bonds, such as imine, boronate ester, thioester, disulfide, and transesterification, the network has the capacity to break and reform via chemical equilibrium. This process is driven by external stimuli, including temperature, pH, or catalysts. The external stimuli facilitate the exchange of polymer chains at crosslinked points through either associative or dissociative mechanisms. The associative mechanism occurs when new bonds form before old bonds break. In contrast, the dissociative mechanism occurs when old bonds break before new bonds form. The exchange of polymer chains enables the material to exhibit self-healing, stress relaxation, and shape adaptability while maintaining the mechanical strength provided by covalent bonds to the network. Finally, it is important to note that the energy barrier for exchange, bond stability, and stimulus-dependence govern the rate and reversibility of the process.

2.2 *Mechanical response*

The concept of a material’s mechanical response describes the relationship between the deformation of a material and the applied stress and/or shear rate. Nevertheless, this relationship can be described from a macroscopic scale and also from a microscopic scale. At the macroscopic level, the description captures the effective mechanical response as a continuum property. At the microscopic level, it provides insights into the origin of the mechanical response and how structural features at small scales control the macroscopic response. In this section, we will delve into the various descriptions and explore the quantification of this relationship.

In the following methodology, we will couple the macroscopic and microscopic scale: We employ the macroscopic constitutive relations; however, the stress tensor is defined from the microscopic scale.

Constitutive relations The relationship between deformation and stress is expressed through a constitutive equation. This equation is a mathematical tool that quantifies the relationship. It is used to predict or model material behavior, as reflected by empirical observations. Additionally, these equations can be defined from both the microscopic and microscopic scale. These two scales are linked through the implementation of averaging or homogenization procedures. However, there is a difference in interpretation and application. These issues will be addressed in the following sections.

Tensors Before proceeding, it is necessary to know the quantitative representation of stress and strain. Both quantities are mathematically represented as second-rank tensors, which can be algebraically expressed as a $n \times n$ matrix. Furthermore, it is important to interpret tensors as a generalization of scalars, vectors, and matrices to describe physical quantities which depend on direction and coordinate system, yet follow specific transformation rules under changes of coordinates. Allowing to quantify not just the magnitude but also orientation and how the physical quantity acts along different directions in space. In summary, the tensor enables the capture of multidirectional physical properties that remain constant under coordinate changes*. Keeping this in mind, we can proceed with a description of the strain tensor. The stress tensor will be defined until the microscopic section, together with the relation to the microscopic-macroscopic relation. This is due to the scope of the thesis.

*Quiero poner una imagen de como se ve el tensor y así con proyecciones en el plano cartesiano

Strain In physics, the deformation of a material relative to its original shape under applied forces is quantified by the relative displacement between points in the material. This measure is represented by the dimensionless strain tensor (eqn (2.1)). This quantification tool enables the description of normal strain, such as elongation or compression, through the use of diagonal terms, and shear strain via off-diagonal terms.

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (2.1)$$

This mathematical representation is only valid for infinitesimal small deformations. Where u_i are the component of the displacement vector field and x_j are the spatial coordinates.

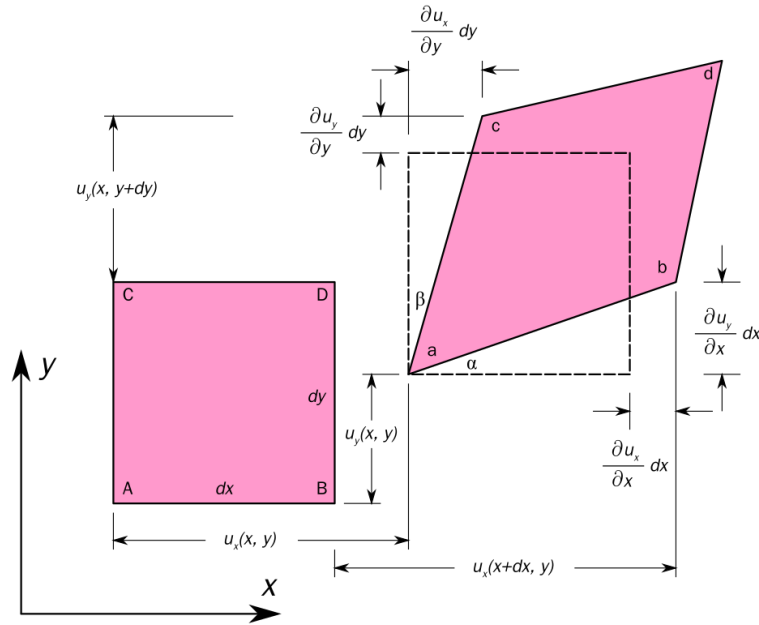


Figure 2.1. Strain representation Wikipedia

(Add the derivation of the book?)

2.2.1 Macroscopic description

Now that we know how to quantify strain, we can quantify the four main mechanical responses, elastic, plastic, viscoelastic, and viscoplastic. In a broad sense, the elastic relation is when the material returns to its original shape after load removal. In contrast, the plastic deformation is a permanent deformation once stress exceeds a yield threshold σ_y . Furthermore, the viscoelastic response is time-dependent combining the elastic and viscous behaviour. Finally, the viscoplastic, combines the irreversible plastic strain with a rate-dependent viscous effects.

Elastic relation An elastic deformation is when the material returns to its original configuration once the stress is removed. The quantification of this response is

given by a linear equation (equation (2.2)), with a proportionality constant known as elastic modulus or Young's modulus. The equation (2.2) is interpreted as the stiffness, that is how the material resists deformation. Some examples of this type of deformation are the stretching of a metal spring within its elastic limit or the compression of a rubber ball.

$$\sigma = E\epsilon \quad (2.2)$$

$$\sigma_{ij} = C_{ijkl}\epsilon_{kl} \quad (2.3)$$

Plastic relation In contrast, a plastic deformation is when the material has an irreversible change in the shape or size. It is generally accepted that a material first enters an elastic regime and then reaches a yield point. After this point, the deformation is irreversible. The quantification of the plastic relation (eqn (2.4)) typically links stress and plastic strain as a function of the current stress and internal variables. This is valid when the deformation goes beyond the yield stress and the specific algebraic expression is dictated by the material's properties.

$$\epsilon_p = f(\sigma, \text{Internal variables}), \quad \sigma > \sigma_y. \quad (2.4)$$

It is important to acknowledge that the definition of yield stress is also dependent on the material and the loading conditions. For this reason, there are many yield criteria developed for different materials and conditions, such as Drucker-Prager, Mohr-Coulomb, Von Mises or Tresca criterion. The two most common yield criteria are the Von Mises and Tresca criterion. The von Mises yield criterion it is commonly used for ductile materials. It is base on the energy associated with shape change. This is defined by a critical value (as shown in the equation (2.5)) in terms of the distortional energy or equivalent shear stress and independent of hydrostatic pressure. On the other hand, the Tresca yield criterion is a max-shear based criterion. It is based on the yield strength in simple tension (see equation (2.6)).

Von Mises Criterion

$$\sigma_y = \sqrt{\frac{3}{2} \mathbf{s} : \mathbf{s}} \quad (2.5)$$

where \mathbf{s} is the deviatoric stress tensor.

Tresca criterion

$$\sigma_y = \max(|\sigma_1 - \sigma_2|, |\sigma_2 - \sigma_3|, |\sigma_3 - \sigma_1|) \quad (2.6)$$

where $\sigma_1, \sigma_2, \sigma_3$ are the principal stresses.

Viscoelastic relation A viscoelastic deformation is defined as the process by which a material partially “stores” elastic energy and partially dissipates energy. The quantification of the relation is by relating the instantaneous stress, strain and a time-dependent relaxation modulus (equation (2.7)). This relationship also enables the description and modeling of memory effects and rate dependence, which are commonly observed in polymers, biological tissues, and certain soft solids.

Not sure if I want to explain more the relaxation modulus.

The following equation is the generalized expression of the Maxwell or Kelvin-Voigt model:

$$\sigma(t) = \int_0^t G(t - \tau) \frac{d}{d\tau} \epsilon(\tau) d\tau. \quad (2.7)$$

Where τ is a dummy variable and $G(t)$ is the time-dependent relaxation modulus.

Viscoplastic relation Finally, a viscoplastic is to describe when a material flows plastically like a viscous fluid under stress beyond the yield stress. The quantification is determined by a function of strain rate, stress, yield stress, and internal variables (see equation (2.8)). As with the plastic relation, the specific algebraic expression is dictated by the material’s properties. However, this relationship is used to describe materials that initially respond as solids below the yield stress but flow like viscous fluids once yielding occurs.

Add examples of specific constitutive equations

$$\dot{\epsilon}_p = f(\sigma, \sigma_y, \dot{\epsilon}, \text{Internal variables}) \quad (2.8)$$

2.2.2 Microscopic description

Stress In continuum mechanics and physics, the measure of internal forces distributed within a material that arise in response to external loads is referred as stress. As before, this measure is represented by a second-order tensor with units of $\text{kg m}^{-1} \text{s}^{-2}$. The mathematical representation of the stress tensor is given by the Cauchy stress tensor, which relates a traction vector \vec{T} acting on a surface \vec{n} with the stress tensor σ , equation (??).

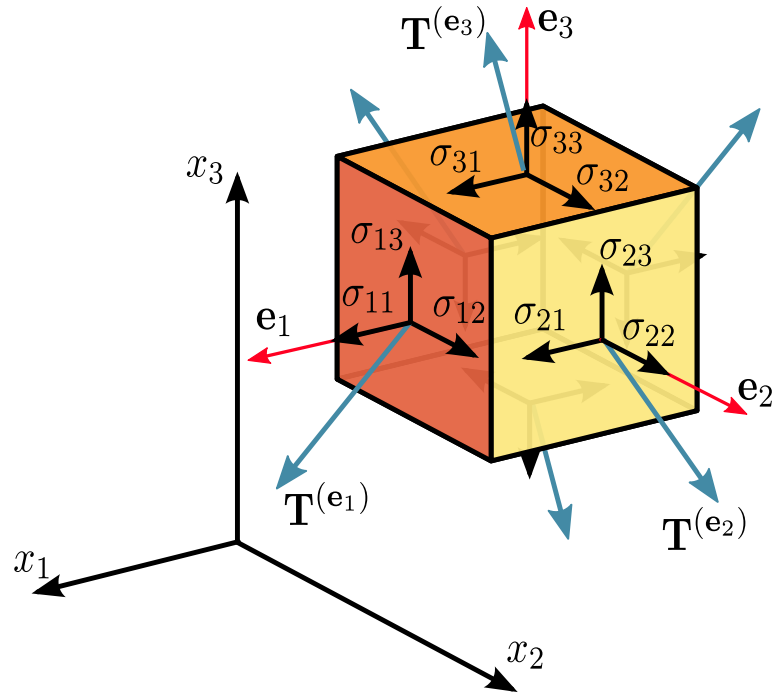


Figure 2.2. Stress tensor wikipedia

Macro-Micro realltion From a microscopic scale, the stress tensor describes the instantaneous local force from atomic interactions and momentum flux. As

a consequence of the scale, the tensor fluctuates strongly due to thermal motion, position and local arrangement of atoms. The bridge between the microscopic description and the macroscopic scale is a spacial and statistical averaging of the microscopic stress over a region much larger than atomic dimensions*.

$$\sigma_{ij}^{\text{macro}} = \lim_{V \rightarrow \infty} \langle \sigma_{ij}^{\text{micro}} \rangle$$

Elastic regime In the case of an elastic deformation, the force applied to the material is largely retained. This is due to the stretching of the distance between the particles. The particles' displacement is minimal, with no effect on bond integrity. This is generally understood to mean that the material stores potential energy that is released during unloading.

Plastic regime [†] In the context of plastic deformation, the phenomenon is often described as dislocation and crystal defects in crystalline materials. However, given that the material under consideration is a polymeric network, plastic deformation is more likely to involve the rupture of crosslinks between chains and the sliding or stretching of individual chains beyond their reversible limit. In the scenario of networks with physical entanglements, chains have the potential to slip past another, thereby overcoming energy barriers and irreversibly reorganizing the networks' topology. In the cases of bond rupture, the crosslink density can be reduced or the polymeric chain can be broken.

[†] Here it is important the idea of reversibility and stuff about self healing

Viscoelastic regime For this type of mechanical response, the network undergoes an elastic deformation. However, during the elastic deformation process, the network may undergo changes in configuration due to polymer sliding or crosslinking reconfiguration. During these changes, the interaction between polymer chains causes an energy dissipation process, resulting in a viscous response and a time dependency. This time dependency is commonly known as *stress relaxation*, which refers to the time-dependent decrease in stress under a constant, maintained strain.

Viscoplastic regime The viscoplastic response is comparable to the viscoelastic response because it integrates plastic deformation with an energy dissipation process. The most significant distinction is that, in contrast to the elastic process of network sliding or crosslink reconfiguration, the polymeric network undergoes

bond breakage. Additionally, the disentanglement of chains is a significant phenomenon that plays a crucial role in energy dissipation. Furthermore, the response is contingent on the time scale. The reconfiguration of the network is determined by the relaxation time following bond breakage and crosslinking reconfiguration. Finally, similar to the plastic deformation, the viscoplastic deformation occurs after a yielding point, in which the deformation of the network structure is permanent.

2.2.3 Literature review: Hydrogel's Mechanical response

Well, I guess that I need to read papers and stuff.

2.2.4 Bridge of macro to micro stress tensor

Molecular stress is equivalent to continuum stress After exploring the constitutive equations and the main mechanisms related to the main mechanical responses observed in hydrogels, we will demonstrate the validity of the methodology of molecular dynamics to analyze the mechanical response via numerical solutions. This will be achieved by showing the equivalence between the macro-stress tensor and the micro-stress tensor. This mathematical derivation that links the macro-stress tensor with the micro-stress tensor is addressed in the appendix of [1].*

*(Eventualmente pondré esto en párrafo) Notation: σ Tensor, $\vec{\sigma}$ vector, $\sigma_{i,j}$ tensor, $\bar{\sigma}$ time average,

Derivation Consider a system of N interacting particles with each particle position given by

$$\vec{r}_\alpha = \vec{r} + \vec{s}_\alpha, \quad (2.9)$$

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

$$\vec{p}_\alpha = m_\alpha (\dot{\vec{r}} + \dot{\vec{s}}_\alpha) = m_\alpha (\dot{\vec{r}} + \vec{v}_\alpha^{\text{rel}}). \quad (2.10)$$

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

$$\vec{r} = \frac{\sum_\alpha m_\alpha \vec{s}_\alpha}{\sum_\alpha m_\alpha}, \quad (2.11)$$

and by replacing (2.9) in (2.10) we get the following relations, which will be used later,

$$\sum_{\alpha} m_{\alpha} \vec{r}_{\alpha} = \vec{0}, \quad \sum_{\alpha} m_{\alpha} \vec{v}_{\alpha}^{\text{rel}} = \vec{0}. \quad (2.12)$$

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

$$\frac{d}{dt}(\vec{r}_{\alpha} \otimes \vec{p}_{\alpha}) = \underbrace{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{p}_{\alpha}}_{\text{Kinetic term}} + \underbrace{\vec{r}_{\alpha} \otimes \vec{f}_{\alpha}}_{\text{Virial term}}, \quad (2.13)$$

*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.

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 (2.13),

$$\frac{1}{\tau}(\vec{r}_{\alpha} \otimes \vec{p}_{\alpha}) \Big|_0^{\tau} = \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{p}_{\alpha}} + \overline{\vec{r}_{\alpha} \otimes \vec{f}_{\alpha}}. \quad (2.14)$$

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 τ sufficiently large and by summing over all particles we achieve the *tensor virial theorem*:

$$\overline{\mathbf{W}} = -2\overline{\mathbf{T}}, \quad (2.15)$$

where

$$\overline{\mathbf{W}} = \sum_{\alpha} \overline{\vec{r}_{\alpha} \otimes \vec{f}_{\alpha}} \quad (2.16)$$

is the time-average virial tensor and

$$\overline{\mathbf{T}} = \frac{1}{2} \sum_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{p}_{\alpha}} \quad (2.17)$$

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 (2.10) in (2.17), so that,

$$\bar{\mathbf{T}} = \frac{1}{2} \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}} + \frac{1}{2} \left[\overline{\sum_{\alpha} m_{\alpha} \vec{v}_{\alpha}^{\text{rel}}} \right] \otimes \dot{\vec{r}}, \quad (2.18)$$

which is not the simplification we expected, however, by the relations from (2.12), equation (2.18) simplifies to*

$$\bar{\mathbf{T}} = \frac{1}{2} \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}}. \quad (2.19)$$

On the other hand, instead of reducing the expression, we start to create the conection with the Cauchy stress tensor by distributing (2.16) into an internal and external contributions,

$$\bar{\mathbf{W}} = \underbrace{\sum_{\alpha} \overline{\vec{r}_{\alpha} \otimes \vec{f}_{\alpha}^{\text{int}}}}_{\bar{\mathbf{W}}_{\text{int}}} + \underbrace{\sum_{\alpha} \overline{\vec{r}_{\alpha} \otimes \vec{f}_{\alpha}^{\text{ext}}}}_{\bar{\mathbf{W}}_{\text{ext}}}. \quad (2.20)$$

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,

$$\sum_{\alpha} \overline{\vec{r}_{\alpha} \otimes \vec{f}_{\alpha}^{\text{ext}}} := \int_{\delta\Omega} \vec{\xi} \otimes \vec{t} dA + \int_{\Omega} \vec{\xi} \otimes \rho \vec{b} dV. \quad (2.21)$$

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

*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.

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 $\vec{t} = \sigma \vec{n}$, where σ represent the Cauchy stress tensor and applying the divergence theorem in (2.21), we have

$$\bar{\mathbf{W}}_{\text{ext}} = \int_{\Omega} \left[\vec{\xi} \otimes \rho \vec{b} + \text{div}_{\vec{\xi}} \left(\vec{\xi} \otimes \sigma \right) \right] dV = \int_{\Omega} \left[\sigma^T + \vec{\xi} \otimes \left(\text{div}_{\vec{\xi}} \sigma + \rho \vec{b} \right) \right] dV \quad (2.22)$$

Since we assume that we are under equilibrium conditions, the term $\text{div}_{\vec{\xi}} \sigma + \rho \vec{b}$ is zero (2.22) it simplifies to

$$\bar{\mathbf{W}}_{\text{ext}} = V \sigma^T. \quad (2.23)$$

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,

$$\sigma_{\text{av}} = \frac{1}{V} \int_{\Omega} \sigma dV, \quad (2.24)$$

in which V is the volume of the domain Ω . Replacing (2.23) into (2.20), the tensor virial theorem (2.15) can be expressed as,

$$\sum_{\alpha} \overline{\vec{r}_{\alpha} \otimes \vec{f}_{\alpha}^{\text{int}}} + V \sigma_{\text{av}}^T = - \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}}. \quad (2.25)$$

Finally, solving for the Cauchy Stress tensor we get,

$$\sigma_{\text{av}} = -\frac{1}{V} \left[\sum_{\alpha} \overline{\vec{f}_{\alpha}^{\text{int}} \otimes \vec{r}_{\alpha}} + \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}} \right], \quad (2.26)$$

an expression that describe the macroscopic stress tensor in terms of microscopic variables*.

To end the section it is important to show that (2.26) is symmetric. Therefore, we rewrite the internal force as the sum of forces between the particles,

$$\vec{f}_{\alpha}^{\text{int}} = \sum_{\beta \neq \alpha} \vec{f}_{\alpha\beta}, \quad (2.27)$$

*It is important to acknowledge that several mathematical subtleties were not taken into consideration, however all the mathematical formality is adresssed by Nikhil Chandra Admal and E. B. Tadmor in [1]

and substituting (2.27) into (2.26), we have

$$\sigma_{av} = -\frac{1}{V} \left[\sum_{\alpha, \beta \neq \alpha} \overline{\vec{f}_{\alpha\beta} \otimes \vec{r}_\alpha} + \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}} \right]. \quad (2.28)$$

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

$$\sum_{\alpha, \beta \neq \alpha} \vec{f}_{\alpha\beta} \otimes \vec{r}_\alpha = \frac{1}{2} \sum_{\alpha, \beta \neq \alpha} \left(\vec{f}_{\alpha\beta} \otimes \vec{r}_\alpha + \vec{f}_{\beta\alpha} \otimes \vec{r}_\beta \right) = \frac{1}{2} \sum_{\alpha, \beta \neq \alpha} \vec{f}_{\alpha\beta} \otimes (\vec{r}_\alpha - \vec{r}_\beta). \quad (2.29)$$

Therefore, by replacing the identity of (2.29) into (2.28), we have

$$\sigma_{av} = -\frac{1}{V} \left[\frac{1}{2} \sum_{\alpha, \beta \neq \alpha} \overline{\vec{f}_{\alpha\beta} \otimes (\vec{r}_\alpha - \vec{r}_\beta)} + \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}} \right], \quad (2.30)$$

expressed with indexical notation and using the eistein summation convention,

$$\sigma_{ij}^{\text{av}} = -\frac{1}{V} \left[\frac{1}{2} \sum_{\alpha, \beta \neq \alpha} \overline{f_i^{\alpha\beta} r_j^\alpha + f_i^{\beta\alpha} r_j^\beta} + \sum_{\alpha} m_{\alpha} \overline{v_i^{\alpha \text{ rel}} v_j^{\alpha \text{ rel}}} \right], \quad (2.31)$$

*No se si poner la referencia a la pagina de documentacion

which is the same expression implemented in LAMMPS[7].*

This allows us to quantify the relationship between network properties and the macroscopic Cauchy stress tensor. As a result, we can begin to explore which molecular process dominates each deformation regime.

2.3 Molecular dynamics

In this section, we present the mathematical tools, also known as molecular dynamics (MD), employed to simulate the polymeric network. Molecular dynamics is a widely used method for analyzing the mechanical responses of polymeric networks because it provides detailed insight into structure-property relationships. This is due to its ability to represent atomic-level interactions via Newtonian mechanics, enabling the modeling of different crosslinking mechanisms, polymer chain con-

figurations, time-dependent deformations, and others. First, we will introduce the concept of colloids. Then, we will describe Langevin dynamics and explain how to solve them using the Velocity Verlet algorithm.

2.3.1 Colloids

We have explored the concepts of how a hydrogel can be understood as a polymeric network and how that helps to gain insight into the mechanical response and the different mechanical responses. Now it is essential to introduce the concept of colloid to integrate the mathematical tools with the hydrogel representation as a polymeric network.

Colloids A colloid is a heterogeneous mixture of two substances in different matter states and in different ratio. It is commonly describe that one of the substance is dispersed into the other substance. The disparsed substance it is commonly denoted as disparsed phase, while the other substance is denoted as the continuous phase. The average size of the scattered phase's spots ranges from 1 nanometer to 1 micrometer.

This definition enables the classification of the material into the following eight categories: foam, solid foam, aerosol, emulsion, gel, aerosol (solid), sol and solid sol. As outlined in the table 2.1. Naturally, our primary objective is to represent the hydrogel as a gel.

Name of Colloid	Disparsed Phase	Continuous Phase	Examples
Foam	Gas	Liquid	Whipped cream, froth
Solid Foam	Gas	Solid	Pumice, styrofoam
Aerosol	Liquid	Gas	Fog, mist
Emulsion	Liquid	Liquid	Milk, mayonnaise
Gel	Liquid	Solid	Jelly, cheese
Aerosol (solid)	Solid	Gas	Smoke, airborne dust
Sol	Solid	Liquid	Paint, ink
Solid sol	Solid	Solid	Coloured glass, alloys

Table 2.1. This is a table

The hydrogel can be understood as a mixture of water in the liquid state and a polymer network in the solid state. Furthermore, the polymeric network typically exhibits a porosity ranging from 5 to 20 nanometers, however they can be tuned to reach the micron-scale size. This porosity enables the representation of the water as the dispersed phase, while the polymeric network is represented as the continuous phase. Therefore, the hydrogel can be modelled as a colloid.

2.3.2 *Langevin dynamics*

Now that we know that we can model a hydrogel as a colloid, we can start applying mathematical tools to create a quantitative description of the material. Langevin dynamics is an excellent framework for representing this system, as it couples the pairwise interactions of the polymers with an efficient representation of the interaction of the water with the polymer, and the dissipation of energy due that results from the water-polymer interaction. It is important to note that this mathematical representation models an infinitesimal particle. Therefore, a methodology is required that couples the infinitesimal particle with a polymer network. The following methodology will be outlined following a description of the Langevin equation and the Velocity Verlet algorithm, in order to facilitate the process of storytelling.

Taking into account the colloidal representation of the hydrogel, the Langevin theory takes advantage of the densities of the solid and liquid phases. Since the solid phase of the colloid has a large mass, it will change their momenta after many collisions with the water molecules and the picture which emerges is that of the heavy particles forming a system with a much longer time scale than the solvent molecules[6]. This time scale difference can be used to our favour in the sense that we can eliminate the details of the degrees of freedom of the solvent particles and represent their effect by stochastic and dissipative forces allowing longer simulations that would be impossible if the solvent were explicitly included[4].

However, the representation of the solvent by a stochastic and dissipative force, introduce the problem of characterize two very different timescales. One associated with the slow relaxation of the initial velocity of the particle and another linked to the frequent collisions that the particle suffers with particles of the bath[2]*.

*Para traer a colación la sensibilidad de la respuesta mecánica al parámetro de damp.

Therefore, two terms are used to create a mathematical representation of the solvent: a frictional force proportional to the velocity of the particle and a fluctuating force.

By considering newtonian mechanics and the previous discussion, the Langevin dynamics are mathematically represented by the following differential equation,

$$m \frac{d\vec{v}(t)}{dt} = \vec{F}(t) - m\gamma\vec{v}(t) + \vec{R}(t). \quad (2.32)$$

The term in the left-hand side of the equation denotes the change of momentum of the particle. The first term on the right-hand side of the equation represents the force due to the interaction of the particle with other particles. The second term couples the dissipation of energy of the particle due to its interaction with the solvent. Finally, the third term takes into account the exchange of momenta with the solvent.

The friction constant γ^* parametrises the effect of solvent damping and activa-

*Cuidado con las unidades. Hacer análisis dimensional, porque por la condición de correlación en R , γ ocupa tener unidades de masa entre tiempo, pero en la ecuación, solo ocupa unidades de $1/s$.

On the other hand, the term $\vec{R}(t)^\dagger$ is a “random force” subject to the following conditions

†No me acuerdo en donde está que se puede asumir que tiene distribución gaussiana.

$$\langle \vec{R}(t) \rangle = 0 \quad (2.33)$$

$$\langle \vec{R}(t)\vec{R}(t') \rangle = 2k_B T \gamma \delta(t - t') \quad (2.34)$$

The no time correlation is equivalent to assuming that the viscoelastic relaxation of the solvent is very rapid with respect to solute motions[‡].

‡Grote and Hynes [26] have investigated this assumption for motions involving barrier crossing and have found that while it is seriously in error for passage over sharp barriers (such as 12 recombination); it is quite adequate for conformational transitions such as might be found in polymer motions.[4]

In comparing the results of Langevin dynamics with those of other stochastic methods [28-31], the relevant variable is the velocity relaxation time, τ_v which equals γ^{-1} [4] The Langevin equation improves conformational sampling over standard molecular dynamics[3].

- ◊ Hablar acerca de que la fuerza aleatoria puede tener distribución gaussiana, pero no necesariamente.
- ◊ hablar de la ecuación de Green-Kubo:

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle dt$$

- ◊ No se que tanto hablar de la idea de correlación y su aplicación en estos temas.

2.3.3 Velocity Verlet

Intro The core concept of the Velocity Verlet algorithm is to update particle positions and velocities using both current and predicted accelerations, ensuring time-reversibility and energy conservation over long simulations. In systems governed by Langevin dynamics, the algorithm can incorporate random forces consistent with the fluctuation-dissipation theorem to simulate physically realistic Brownian motion.

From a mathematical point of view, this algorithm is a second-order integrator for ordinary differential equations. Furthermore, from a computational perspective, Velocity Verlet is an explicit algorithm, easy to implement, and efficient in terms of memory usage. It requires only the positions, velocities, and accelerations from the previous timestep. Which allows efficient parallelization and eliminates the need for additional memory allocations per step.

```

Nt ← Simulation steps;
r ← Initial positions;
v ← Initial velocities;
while N ≤ Nt do
    v(t + ½Δt) ← v(t) + ½a(t)Δt;
    r(t + Δt) ← r(t) + v(t + ½Δt)Δt;
    a(t + Δt) ← -∇U(r(t + Δt));
    v(t + Δt) ← v(t + ½Δt) + ½a(t + Δt)Δt;
end

```

Algorithm 1: Velocity Verlet algorithm

3 *Patchy particle scheme for hydrophilic polymeric networks*

Now that we have covered the theoretical framework, we can delve into the numerical tools that will help us find relations between the polymeric network and the mechanical response. First, we will describe the patchy particle scheme for simulating PNIPAM cross-linked networks. Then, we will describe the numerical simulation protocol. Next, we will introduce the LAMMPS package and explain how it can be used to simulate these systems. Finally, we will present and analyze the simulation results.

3.1 *Simulation protocol*

One of the microgels that has been the focus of significant research is the type that is based on PNIPAM cross-linked networks. In the article *In silico Synthesis of Microgel Particles*, the authors present a flexible numerical protocol capable of designing individual microgel particles based on PNIPAM cross-linked networks. This protocol can generate particles with properties comparable to the experimental ones. In this project, we employ a similar protocol to explore its versatility and identify a numerical tool that can facilitate connections between network configuration and mechanical response.

Our primary focus is on creating networks without spherical confinement and without mimicking the swelling behavior of PNIPAM microgels with temperature. Therefore, the central strategy involves the implementation of a binary mixture of patchy particles to generate a disordered polymeric network structure, followed by the application of shear deformation. The primary benefit of this protocol is that previous numerical efforts in microgel modeling have predominantly concentrated on unrealistic networks consisting of chains of equivalent length, frequently establishing cross-linked connections on crystalline lattice regions or where closed polymer networks are assembled by directly integrating randomly dispersed cross-linkers with polymer chains.

3.1.1 *Patchy particles representation*

A patchy particle can be defined as a sphere with radius r containing n spheres of radius $l < r$ on its surface. The smaller spheres are typically referred to as “patches” and the number of patches is often referred to as “functionality”. The center of the patches can be placed on the surface of the central particle. However, it can also be modified to be at a point inside the enclosed volume of the main particle.

The implementation of patchy particles as monomers and crosslinkers is a highly effective strategy. This is due to the fact that it facilitates the integration of the infinitesimal representation by the Langevin dynamics with a particle that possesses volume and functionality. The functionality representation is important because it allows for the representation of the monomer and cross-linker molecules that can form a polymeric network. However, it is important to recognize that the geometry of the monomers and functional groups is assumed to be spherical.

Finally, to define the volume of the particle, a repulsive pairwise interaction is defined between the central particles. Meanwhile, to the formation of a polymeric network is facilitated by an attractive pairwise interaction defined between patches. Because this model is designed to simulate the final network, not the synthesis process, the pairwise interaction between central particles and patches is not defined.

3.1.2 *Description of the system*

Interaction potentials We start by describing the interaction potentials between patchy particles. The interaction between the central particles is modeled with a Weeks-Chandler-Andersen repulsive potential,

$$U_{WCA}(r_{i,j}) = \begin{cases} 4\epsilon_{i,j} \left[\left(\frac{\sigma}{r_{i,j}} \right)^{12} - \left(\frac{\sigma}{r_{i,j}} \right)^6 \right] + \epsilon_{i,j}, & r_{i,j} \in [0, 2^{1/6}\sigma], \\ 0, & r_{i,j} > 2^{1/6}\sigma \end{cases}, \quad (3.1)$$

where $r_{i,j}$ is the distance between the center of the central particles, σ is the diameter of the particles and $\varepsilon_{i,j}$ is the energy of the interaction. On the other hand, the patch-patch interaction is modeled with an attractive potential,

$$U_{\text{patchy}}(r_{\mu\nu}) = \begin{cases} 2\varepsilon_{\mu\nu} \left(\frac{\sigma_p^4}{2r_{\mu\nu}^4} - 1 \right) \exp \left[\frac{\sigma_p}{(r_{\mu\nu} - r_c)} + 2 \right], & r_{\mu\nu} \in [0, r_c], \\ 0, & r_{\mu\nu} > r_c, \end{cases} \quad (3.2)$$

where $r_{\mu\nu}$ is the distance between two patches, σ_p is the diameter of the patches, r_c is the cut distance of interaction set to $1.5\sigma_p$ and $\varepsilon_{\mu,\nu}$ is the interaction energy between the patches. This potential can be interpreted as a reversible interaction.

It is important to say that if we let the polymeric network form with only those potentials, the patches are going to form cluster of more than 2 patches, which is not desirable since this will mean that every single monomer can be a crosslinker*. Hence, the interaction between patches is complemented by a three-body repulsive potential, defined in terms of (3.2), 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[5].

$$U_{\text{swap}}(r_{l,m}, r_{l,n}) = w \sum_{l,m,n} \varepsilon_{m,n} U_3(r_{l,m}) U_3(r_{l,n}), \quad r_{l,n} \in [0, r_c], \quad (3.3)$$

where

$$U_3(r) = \begin{cases} 1 & r \in [0, r_{\min}], \\ -U_{\text{patchy}}(r)/\varepsilon_{m,n}, & r \in [r_{\min}, r_c] \end{cases}. \quad (3.4)$$

The sum in (3.3) 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 $\varepsilon_{m,n}$ 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 (3.2), *i.e.* $\varepsilon_{m,n} \equiv |U_{\text{patchy}}(r_{\min})|$. Finally, the energy of interaction between crosslinker patches ($\varepsilon_{\mu^i, \mu^i}$) are set to 0 to allow only crosslinker-monomer and monomer-monomer bonding (figure ??).

Physical Parameters Particle size, box length, packing fraction, temperature.

Deformation protocol Constant shear rate, vary shear rate between simulations. First goes the assembly protocol then the shear deformation. Go beyond the elastic limit to see what's up.

3.2 *LAMMPS*

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) is a highly flexible, open-source molecular dynamics software solution used for simulating atomic, molecular, and mesoscale systems. And is widely recognized for its extensibility, complete documentation, and active support in scientific communities focused on materials modeling and molecular simulation. It is designed to efficiently model materials science, chemistry, and physics problems by enabling large-scale simulations on parallel computing architectures. Furthermore, its parallelized structure allows efficient computation of large or complex systems, and supports integration with other computational tools and machine learning methods.

To define a simulation with this software we need to create an input script. This input script is defined as a series of lines, with each line beginning with a command name and followed by one or more arguments separated by whitespace. The program incorporates programming commands that define variables, perform conditional tests, execute loops, or invoke shell commands to launch an external program. The input script is parsed and executed one line at a time. This feature allows a single script to run a simulation in stages, alter one or more parameters between stages, or run a series of independent simulations where the entire system is reinitialized multiple times.

Implementation About tables and the general script.

- ◇ table command
- ◇ langevin command
- ◇ threebody command
- ◇ boundary command

Not sure if I need to describe almost line by line the scripts.

3.2.1 *Three-body potential*

How was defined the table potential into lammmps, the projections and that stuff.

3.3 *Results*

So.. The results and stuff

3.3.1 *Mechanical response*

Strain stress graph

3.3.2 *Network analysis*

I guess that figures of the final network and parameter of order or size of porous or whatever.

4 *Conclusion*

We conclude that we have a conclusion in two years.

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