

INSTITUTO TECNOLÓGICO Y DE ESTUDIOS SUPERIORES DE  
MONTERREY  
CAMPUS MONTERREY



Words words words  
Hydrogels

A thesis presented by

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INSTITUTO TECNOLÓGICO Y DE ESTUDIOS SUPERIORES DE  
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# Acknowledgements

Total Thanks.

Thank..

# Dedication

To ...

To ...

# Abstract

In summary: More research is needed.

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# Chapter 1

## Introduction

**Curiosity/phenomenology** Paragraph that will tell the reader that hydrogels are cool.

**Applications/Market size of the applications sectors** If the previous paragraph does not convince the reader, well my last hope is that money does.

Besides, because of such a wide variety of response triggers, hydrogels can serve as sensors or actuators or can be utilized in controlled drug delivery systems, biosensors, tissue engineering scaffolds, and others [20], because of their biomimetic properties and multi functionalities [21][Bustamante-Torres et al., 2021].

In particular, biomedical applications are very popular and include cell culture [5], wound dressing and healing [2,6], drug delivery [2,7,8], tissue engineering scaffolds [9], bone repair [10], and cartilage regeneration [11][?].

**Description of the Thesis** What the reader will find in each chapter and section.

**Why computers and not rheometers?** Explain how in silico experiments can help to understand the relation between the network and the mechanical response.

### 1.1 State of the art: Hydrogels

- Characteristics
- Descriptions
- Synthesis techniques
- Cross-linking (Bond breaking)

**General description of a hydrogel** We can describe a hydrogel as networks formed by cross-linked polymer chains that exhibits the ability to swell and retain a significant fraction of water within its structure, but will not dissolve in water[Ahmed, 2015, Ahmed et al., 2025, Priya et al., 2024, Bustamante-Torres et al., 2021].<sup>1</sup> The water absorption capacity and network stability of hydrogels can be controlled by crosslinking mechanisms, which

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<sup>1</sup>the main difference with the microgels, is the size. Hydrogel is bulk, and microgel is particle.

involves forming covalent or non-covalent bonds between polymer chains<sup>2</sup>[Priya et al., 2024, Ahmed, 2015]. On the other hand, hydrogels are generally prepared based on hydrophilic monomers that can regulate the properties for specific applications[Ahmed, 2015, Priya et al., 2024].

Hydrogels are composed of hydrophilic functional groups which explains the ability to absorb water, while their resistance to dissolution is related with the crosslinking mechanisms between the network chains[Bustamante-Torres et al., 2021]. Although the analysis of the impact of functional groups it is interesting enough, in this project we focus on the mechanisms that are more relevant to the mechanical response, and, since the crosslinking mechanisms is responsible to the resistance to dissolution, we can say that the crosslinking mechanisms allow the network to be modified by external stimuli.

In the next sections it is shown the necessary information to have a general idea of the crosslinking mechanisms, the relation of those mechanisms with the mechanical response, the reported mechanical response of hydrogels and the relation between the rheology experiments with stress curves.

### 1.1.1 Crosslinking mechanisms

A crosslinker is a molecule that serves as a bridge between polymer chains allowing to form an interconnected network. These elements form stable bonds which are commonly categorized in two main types: covalent (permanent) and physical (reversible), however, there are recent mechanisms, such as mechanical crosslinker mechanics in which the bridge is due to the topology of the constituents of the hydrogel.

Therefore, these mechanisms can be thought as the principal responsible for the mechanical properties.

A crosslinker is a molecular agent that functions by bridging polymer chains to form a networked structure, thereby transforming individual macromolecules into an interconnected matrix. The integration of crosslinkers within these materials confers a number of advantageous properties, including enhanced mechanical integrity, dimensional stability, and tailored responsiveness.

This is achieved by facilitating the formation of stable bonds, which can be categorized into two main types: covalent (permanent) and physical (reversible). Examples of these bonds include hydrogen bonds and host-guest interactions, found in hydrogels, elastomers, and coatings, respectively.

These elements function as molecular "staples," determining critical properties such as stiffness, swelling capacity, and resilience by restricting chain mobility while enabling stimuli-triggered reconfiguration (e.g., temperature/pH-triggered gel-sol transitions).

The selection of crosslinker (e.g., glutaraldehyde for permanent networks, cyclodextrin for slide-ring gels) is instrumental in dictating the material's functionality in a myriad of applications, ranging from drug delivery to wearable electronics.

The crosslinking mechanism can be thought as a cohesion force that

Crosslinking mechanisms play a significant role; consequently, they frequently function as a classification parameter. Typically, hydrogels are classified into two categories: physically cross-linked hydrogels and chemically cross-linked hydrogels [14], which obtain different properties based on each synthesis[Bustamante-Torres et al., 2021].

The cohesion forces that allow the cross-linking of the polymer have a covalent character, and other forces such as electrostatic, hydrophobic, dipole-dipole interactions, or hydrogen bonds intervene [11–13][Bustamante-Torres et al., 2021].

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<sup>2</sup>The hydrogels are prepared using different methods like chemical cross-linking of monomers, physical cross-linking using temperature or pH changes, and blending of natural or synthetic polymers.

Similarly, hydrophilic polymers can be cross-linked through chemical bonds, leading to the formation of hydrogels, which are materials that have attracted particular attention in the biomedical field [17][Bustamante-Torres et al., 2021].

**Transition to talk about crosslink** A general correlation exists between the mechanical properties<sup>3</sup> of the hydrogel and its crosslinking mechanisms. The incorporation of crosslinkers results in an increase in the molecular weight of the polymer chains, thereby limiting their translational movement and decreasing their solubility, and augment the interactions between the polymer chains[Priya et al., 2024]. Since we are interested in the mechanical response of the material, our focus in this section is to explore the crosslinking mechanisms in hydrogels.

**Difference between physical and chemical bonds** Crosslinking mechanisms involves the formation of *bonds*<sup>4</sup> between polymer chains that can be reversible or irreversible. Confusingly referred as *physical cross-linking* and *chemical cross-linking*. Sentences about the energy difference to break those bonds. I have the intuition that the basic difference is the energy required for braking in given conditions.

Moreover, since the hydrogel has covalent crosslinking, it can return to its original state after unloading[?].

It was also found that the energy dissipation of HGel with a low chemical crosslinking density was dependent on the hydrophobic interaction at the initial deformation stage[?]<sup>5</sup>. Molecular chains between two chemical crosslinking points were crimped and curled, and therefore the physical crosslinking would play a major role for energy dissipation.

As a result, we can conclude that at initial deformation state the physical crosslinking would play the major role of energy dissipation, whereas the chemical and physical crosslinking would work synergistically in large deformation dissipated more energy to enhance mechanical strength of HGel[?]. The mechanical property of H-Gel was also affected by the ratio of MBA, AAm, HMA and core-shell LPs[?].

**Reversible Cross-linking** [Priya et al., 2024] In physically cross-linked hydrogels, the interactions between polymer chains are not covalent but rather based on physical interactions. These interactions can include hydrogen bonding, van der Waals forces, hydrophobic interactions, or coordination bonds and are reversible under certain conditions, which means that the hydrogel can undergo structural changes without breaking any covalent bonds. This characteristic makes physically cross-linked hydrogels more responsive to external stimuli like temperature, pH, or ionic strength and have high water sensitivity and thermal reversibility. They may exhibit unique properties, such as “self-healing” behaviour, where the gel can reform after being broken. These kinds of hydrogel have a short lifespan, in the range of a few days to a maximum of a month, in the physiological media.

Hydrogels can be cross-linked through physical or reversible networks, which hold them together by molecular entanglements or physicochemical interactions such as hydrogen bonds, hydrophobic interactions, charge condensation, or supramolecular chemistry[Bustamante-Torres et al., 2021]. The interactions that occur in this type of hydrogels are weak[Bustamante-Torres et al., 2021]. However, they are numerous and contribute to the presence of complex behaviors[Bustamante-Torres et al., 2021]. Since the interactions depend significantly on external stimuli (pH, ionic strength, the composition of the solvent, or the temperature), they allow hydrogels to be highly versatile concerning the environment, unlike covalently bonded materials[Bustamante-Torres et al., 2021].

<sup>3</sup>Such as elasticity, viscosity, solubility, glass transition temperature, strength, toughness, and melting point[Priya et al., 2024]

<sup>4</sup>I'm not very sure to use this word.

<sup>5</sup>Pascals has the same units as the “dissipation” energy, “dissipation” energy is the area under the loading and unloading curves.

Crystallization (This crystallization process includes crystal nucleation and crystal growth) Amphiphilic Copolymers (amphiphilic copolymers can aggregate in water to form micelles and hydrogels in which the hydrophobic segments of the polymer self-assemble [40][Bustamante-Torres et al., 2021], Cross-linking is thought to occur by hydrophobic interactions [41]) Hydrogel Cross-linking by charge interactions Cross-linking (or de-crosslinking) can be achieved in situ by pH changes that cause ionization or protonation of ionic functional groups and cause gelation[Bustamante-Torres et al., 2021]. Interaction by Hydrogen Bonds Hydrogen bonding interactions can be used to produce hydrogels in vitro by freeze-thaw cycles. Stereo-Complexing Stereo-complexing refers to the interactions between polymeric chains, or small molecules, of the same chemical composition but different stereochemistry. Protein interaction Cross-linking by protein interactions can be accomplished through the use of genetically engineered proteins or antigen–antibody interactions[Bustamante-Torres et al., 2021].

**Irreversible Cross-linking** [Priya et al., 2024] In chemically cross-linked hydrogels, covalent bonds form between the polymer chains. These covalent bonds are strong and stable, resulting in a 3D structure of interconnected polymer chains more robust and resistant to changes in environmental conditions, such as temperature and pH. The cross-links are typically formed through chemical reactions, such as polymerization or cross-linking agent-induced reactions. As a result, chemically cross-linked hydrogels generally exhibit greater mechanical strength and long-term stability.

Chemically crosslinked hydrogels are easier to control as compared to physical hydrogels as their preparation method and applications are not dependent on their pH.

This preparation of hydrogel networks is easy to control when compared to physical hydrogels as their preparation and the applications they are used for are not dependent on their pH.

Hydrogels are called chemical or permanent when they consist of covalently crosslinked networks. It generally contains regions of the high cross-linking density and low degree of swelling (clusters), dispersed in the regions of the low cross-linking density and high swelling index. The presence of these clusters is due to the hydrophobic aggregation of the cross-linking agent[Bustamante-Torres et al., 2021].

Graft Copolymerization and Irradiation Crosslinking This method allows radiation to act on the polymer matrix, inducing the formation of reactive sites that may interact with a molecule to be grafted, initiating a free radical polymerization process [80]. Reactive function groups These are covalent reactions between the functional groups of the polymers (mainly -OH, -COOH, -NH<sub>2</sub>) that provide solubility to water-soluble polymers [99,100]. Enzymatic Method Cross-linking of the hydrogel occurs under mild conditions without the need for the use of low molecular weight compounds (monomers, initiators, cross-linking agents), irradiation, or prior polymer functionalization to favor its cross-linking [31,119]. Enzymes often exhibit a high degree of substrate specificity, potentially avoiding side reactions during cross-linking.

the conventional hydrogels crosslinked by chemical bonds are very brittle due to intrinsic structural inhomogeneity and lacking effective energy dissipation mechanism[?].

**Mechanical bonds** [Hart et al., 2021] A key feature that controls the properties of a polymeric material is its architecture. Beyond the conventional linear polymer, architectures such as branched, cyclic, bottlebrush, star and block copolymers have expanded the property profile of polymeric materials and offered opportunities for polymer research and applications. Recently, the polymer field has seen the emergence of a new class of polymer architecture: mechanically interlocked polymers (MIPs), which are polymers that include a mechanical bond. Mechanical bond is when two (or more) molecular components are constrained in space without being covalently bonded together. Mechanically interlocked molecules (MIMs) possess large conformational freedom while maintaining a permanent

spatial association between the components<sup>1–4</sup>. Conceptually, there are a myriad of ways the mechanical bond can be incorporated into polymer architectures (Fig. 1), and these unique and varied structures can enable property profiles that have never been seen before.

**Network-mechanical response relation** Introduce the idea of how by understanding the network we can manipulate/control the mechanical response.

The research of hydrophilic polymers has been complex because the physical properties of solubility or swellability depend on different factors, such as the type of polymer, molecular weight, the ratio of polar groups, and degree of cross-linking[Bustamante-Torres et al., 2021]. High molecular weight and a high degree of cross-linking will reduce the hydrophilicity of the molecule [18,19][Bustamante-Torres et al., 2021].

**Tunable mechanical response with applications** Review of articles of applications

### 1.1.2 Mechanical response of hydrogels

Just describe the phenomena and say that it depends on the structure and so on.

**Viscoelasticity**

**Yield stress**

**Shear thinning**

**Transition to talk about printing hydrogels** [Correa et al., 2021] Subsequent work developed safer cross-linking mechanisms, which began a trend toward triggering gelation in situ after injection, providing a minimally invasive way of administering hydrogels to practically any organ or tissue.<sup>29,30<sup>6</sup></sup>

Unlike earlier hydrogels that relied on covalent cross-links, some of these hydrogels have self-healing properties and possess mechanical properties akin to native tissue, capable of countering natural forces and stresses of a body in motion. More recently, shear-thinning hydrogels were developed that are formed through dynamic and reversible cross-linking.<sup>34</sup> For example, physical hydrogels use noncovalent interactions (e.g., supramolecular chemistries) between soluble building blocks in order to self-assemble into a dynamic, reversibly cross-linked network.<sup>35,36</sup> These “dynamic hydrogels” assembled through reversible cross-links afford the unique property of being injectable even after having formed a gel, due to their shear-thinning and selfhealing behaviors. Current research on dynamic hydrogels has revealed novel and useful capabilities that have opened new frontiers for this technology.

For example, they can stabilize delicate protein and cellular cargoes to combat pharmaceutical cold-chain limitations,<sup>39</sup> they can adhere strongly to tissues to form protective barriers and bandages,<sup>40</sup> and they can be delivered through spray applications to coat complex biological geometries.<sup>41</sup>

static covalent cross-links ultimately introduced translational challenges for clinical implementation, since traditional covalent gels require invasive surgical implantation to access nonsuperficial tissues. Additionally, new manufacturing processes, such as 3D printing, require dynamic rheological properties during processing, disqualifying the use of traditional covalent hydrogels.<sup>57</sup> Interest in further developing the translational potential of hydrogels led

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<sup>6</sup>Why the gelation in situ after injection is important?

to innovative methods to implant them through minimally invasive means, of which the most clinically relevant is injection through a needle or catheter (Figure 3).

static covalent cross-links ultimately introduced translational challenges for clinical implementation, since traditional covalent gels require invasive surgical implantation to access nonsuperficial tissues. Additionally, new manufacturing processes, such as 3D printing, require dynamic rheological properties during processing, disqualifying the use of traditional covalent hydrogels.<sup>57</sup>

Hybrid crosslinking hydrogels consist of covalent and noncovalent crosslinking[?]. The dynamic physical crosslinking could effectively dissipate energy via destruction and reorganization, and the chemical crosslinking could sustain skeleton construction [19,20][?].

The molecular reversibility can be actually achieved in two different ways: either by making use of equilibrium reactions (e.g., the Diels-Alder one) or through dynamic exchange reactions (e.g., reaction of an excess amino groups with epoxide ones)[?].

The general idea is that the use of dynamic covalent bonds allows the polymeric network to adjust itself as a result of an external stimulus[?]. This can be achieved in principle through other weaker interactions, e.g., hydrogen bonding[?].

the use of covalent bonds displays two distinct and clear advantages [25]. In first instance, the network is still covalently linked, which renders it quite robust against small random fluctuations in environmental conditions such as temperature. Furthermore, exchange reactions such as the one of an amine with an imine are often kinetically controlled by the use of catalysts. In turn, this allows the possibility to freeze the network conformation (by slowing the kinetics) when desired[?]. The general concept behind the use of reversible interactions for the hydrogel polymeric chains is the (reversible) network disruption with immediate release of any loading (Figure 3).

Reversible bonds can be incorporated along the backbone (red circles) or at the crosslinking point (green triangles). The network, when subjected to an appropriate external stimulus, can then break at the crosslinking point (route A) or along the backbone (route B). This generates network fragments that can be quite different in terms of chemical structure even if in both cases the loading (blue circles) will be released. As a result of the network disruption, the load is released as the polymeric chains become soluble and not able anymore to entrap the load[?].

### 1.1.3 Rheology/stress

Main review:[Gu et al., 2020, Sheiko and Dobrynin, 2019]

**Bridge of the experiments and interpretation** Hysteresis curves to get the stored energy and the dissipated energy.

**Name some network structures** The correlation between the structure with the hysteresis loops

**Link to mechanical response** Same as before.

**What if we can change the structure on command and in real time?** Bridge to crosslinkers.

**How crosslinking affects the mechanical response** Crosslinking is another essential process that can be controlled and intentionally modified using ionizing radiations[Priya et al., 2024].

# Chapter 2

## Theoretical framework

### 2.1 Soft colloids

**Argument** Why we can use a simulation protocol for microgels to modeled hydrogels?

- Why we can model hydrogels as Soft colloids?
- Idea of patchy particles and insterpretaion of interaction rules
- teaser of simulation experiments

Hydrophilic gels that are usually referred to as hydrogels are networks of polymer chains that are sometimes found as colloidal gels in which water is the dispersion medium [1][Ahmed, 2015].

### 2.2 Molecular dynamics

- Langevin equation
- Velocity Verlet

#### 2.2.1 Langevin dynamics

From a general point of view there are two types of methods to make a quatitative description of systems: one focused on simulating dynamics at the microscale, and the other dedicated to deriving or establishing evolutionary equations at the macroscale[Wang et al., 2025]. Since we assume that the a microgel's mechanical response derives from its internal structure<sup>1</sup> we choose to simulate the dynamics at the microscale. Additionally, by treating the microgel as a colloid, permits applying Brownian motion theory to model its response under shear deformation. Finally, there are two commonly used mathematical frameworks to model the Brownian motion, the continuous time random walk (CTRW) model and the Langevin equation[Wang et al., 2025], in this work we decided<sup>2</sup> to use the langevin dynamics mathematical framework.

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<sup>1</sup>Poner citas que desmuestren que no es hipótesis, si no que se sabe

<sup>2</sup>Supongo que eventualmente justificaré la desición.

This is because, the solid phase of the colloid has a large mass and will change their momenta after many collisions with the solvent 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[Thijssen, 2007] and Langevin theory takes advantage of this difference in time scale to 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[Pastor, 1994]. 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 brownian particle and another linked to the frequent collisions that the brownian particle suffers with particles of the bath[Hansen and McDonald, 2006]<sup>3</sup>. Therefore, two terms are used to create a mathematical representation of the solvent: a frictional force proportional to the velocity of the brownian particle and a fluctuating force. Hence,

$$m \frac{d\vec{v}(t)}{dt} = \vec{F}(t) - m\gamma\vec{v}(t) + \vec{R}(t). \quad (2.1)$$

The friction constant  $\gamma$ <sup>4</sup> parametrises the effect of solvent damping and activation and is commonly referred to as the collision frequency in the simulation literature, even though formally a Langevin description implies that the solute suffers an infinite number of collisions with infinitesimally small momentum transfer. Also, the fact that the second term is not a function of the position of any of the particles involves the neglect of hydrodynamic interaction or spatial correlation in the friction kernel spatial correlation in the friction kernel[Pastor, 1994]. On the other hand,  $\vec{R}(t)$ <sup>5</sup> is a “random force”subject to the following conditions

$$\begin{aligned} \langle \vec{R}(t) \rangle &= 0 \\ \langle \vec{R}(t) \vec{R}(t') \rangle &= 2k_B T \gamma \delta(t - t') \end{aligned}$$

The no time correlation is equivalent to assuming that the viscoelastic relaxation of the solvent is very rapid with respect to solute motions<sup>6</sup>.

In comparing the results of Langevin dynamics with those of other stochastic methods [28-31], the relevant variable is the velocity relaxation time,  $\tau_v$  which equals  $\gamma^{-1}$ [Pastor, 1994] The Langevin equation improves conformational sampling over standard molecular dynamics[Paquet and Viktor, 2015].

- 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.

## 2.2.2 Velocity Verlet

### Overview of the method

<sup>3</sup>Para traer a colación la sensibilidad de la respuesta mecánica al parámetro de damp.

<sup>4</sup>Cuidado con las unidades. Hacer análisis dimensional, porque por la condición de correlación en  $R$ ,  $\gamma$  ocupa tener unidades de masa entre tiempo, pero en la ecuación, solo ocupa unidades de  $1/s$ .

<sup>5</sup>No me acuerdo en donde está que se puede asumir que tiene distribución gaussiana.

<sup>6</sup>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.[Pastor, 1994]



## Characteristics of the method

## 2.3 Mechanical response

- Macroscopic Stress (Cauchy)
- Microscopic Stress (PhD Thesis of pointwise fields )

### 2.3.1 Stress

**Introductory paragraph** To characterize the behaviour of materials, constitutive relations serve as an input to the continuum theory. . . <sup>7</sup>

This derivation can be found in the appendix of [Admal and Tadmor, 2010]<sup>8,9</sup>. Consider a system of  $N$  interacting particles with each particle position given by

$$\vec{r}_\alpha = \vec{r} + \vec{s}_\alpha, \quad (2.2)$$

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

$$\vec{p}_\alpha = m_\alpha (\dot{\vec{r}} + \dot{\vec{s}}_\alpha) = m_\alpha (\dot{\vec{r}} + \vec{v}_\alpha^{\text{rel}}). \quad (2.3)$$

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

$$\vec{r} = \frac{\sum_\alpha m_\alpha \vec{s}_\alpha}{\sum_\alpha m_\alpha}, \quad (2.4)$$

and by replacing (2.2) in (2.3) we get the following relations, which will be used later,

$$\sum_\alpha m_\alpha \vec{r}_\alpha = \vec{0}, \quad \sum_\alpha m_\alpha \vec{v}_\alpha^{\text{rel}} = \vec{0}. \quad (2.5)$$

Now we can start by computing the time derivative of tensorial product  $\vec{r}_\alpha \otimes \vec{p}_\alpha$ <sup>10</sup>,

$$\frac{d}{dt}(\vec{r}_\alpha \otimes \vec{p}_\alpha) = \underbrace{\vec{v}_\alpha^{\text{rel}} \otimes \vec{p}_\alpha}_{\text{Kinetic term}} + \underbrace{\vec{r}_\alpha \otimes \vec{f}_\alpha}_{\text{Virial term}}, \quad (2.6)$$

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 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 (2.6),

$$\frac{1}{\tau} (\vec{r}_\alpha \otimes \vec{p}_\alpha) \Big|_0^\tau = \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{p}_\alpha} + \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha}. \quad (2.7)$$

<sup>7</sup>Capaz e ir introduciendo ideas del Clausius[Clausius, 1870]

<sup>8</sup>Describe more if what is done in this article

<sup>9</sup>(Eventualmente pondré esto en párrafo) Notation:  $\sigma$  Tensor,  $\vec{\sigma}$  vector,  $\sigma_{i,j}$  tensor,  $\bar{\sigma}$  time average,

<sup>10</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.

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*:

$$\overline{\mathbf{W}} = -2\overline{\mathbf{T}}, \quad (2.8)$$

where

$$\overline{\mathbf{W}} = \sum_{\alpha} \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha} \quad (2.9)$$

is the time-average virial tensor and

$$\overline{\mathbf{T}} = \frac{1}{2} \sum_{\alpha} \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{p}_\alpha} \quad (2.10)$$

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 (2.3) in (2.10), so that,

$$\overline{\mathbf{T}} = \frac{1}{2} \sum_{\alpha} m_{\alpha} \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{v}_\alpha^{\text{rel}}} + \frac{1}{2} \left[ \sum_{\alpha} m_{\alpha} \overline{\vec{v}_\alpha^{\text{rel}}} \right] \otimes \dot{\vec{r}}, \quad (2.11)$$

which is not the simplification we expected, however, by the relations from (2.5), equation (2.11) simplifies to<sup>11</sup>

$$\overline{\mathbf{T}} = \frac{1}{2} \sum_{\alpha} m_{\alpha} \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{v}_\alpha^{\text{rel}}}. \quad (2.12)$$

On the other hand, instead of reducing the expression, we start to create the conection with the Cauchy stress tensor by distributing (2.9) into an internal and external contributions,

$$\overline{\mathbf{W}} = \underbrace{\sum_{\alpha} \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\text{int}}}}_{\overline{\mathbf{W}}_{\text{int}}} + \underbrace{\sum_{\alpha} \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\text{ext}}}}_{\overline{\mathbf{W}}_{\text{ext}}}. \quad (2.13)$$

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,

$$\sum_{\alpha} \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\text{ext}}} := \int_{\delta\Omega} \vec{\xi} \otimes \vec{t} dA + \int_{\Omega} \vec{\xi} \otimes \rho \vec{b} dV. \quad (2.14)$$

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  $\vec{t} = \sigma \vec{n}$ , where  $\sigma$  represent the Cauchy stress tensor and applying the divergence theorem in (2.14), we have

$$\overline{\mathbf{W}}_{\text{ext}} = \int_{\Omega} \left[ \vec{\xi} \otimes \rho \vec{b} + \text{div}_{\vec{\xi}} \left( \vec{\xi} \otimes \sigma \right) \right] dV = \int_{\Omega} \left[ \sigma^T + \vec{\xi} \otimes \left( \text{div}_{\vec{\xi}} \sigma + \rho \vec{b} \right) \right] dV \quad (2.15)$$

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<sup>11</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.

Since we assume that we are under equilibrium conditions, the term  $\text{div}_{\xi} \boldsymbol{\sigma} + \rho \vec{b}$  is zero (2.15) it simplifies to

$$\overline{\mathbf{W}}_{\text{ext}} = V \boldsymbol{\sigma}^T. \quad (2.16)$$

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

$$\boldsymbol{\sigma}_{\text{av}} = \frac{1}{V} \int_{\Omega} \boldsymbol{\sigma} dV, \quad (2.17)$$

in which  $V$  is the volume of the domain  $\Omega$ . Replacing (2.16) into (2.13), the tensor virial theorem (2.8) can be expressed as,

$$\sum_{\alpha} \overline{\vec{r}_{\alpha} \otimes \vec{f}_{\alpha}^{\text{int}}} + V \boldsymbol{\sigma}_{\text{av}}^T = - \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}}. \quad (2.18)$$

Finally, solving for the Cauchy Stress tensor we get,

$$\boldsymbol{\sigma}_{\text{av}} = -\frac{1}{V} \left[ \sum_{\alpha} \overline{\vec{f}_{\alpha}^{\text{int}} \otimes \vec{r}_{\alpha}} + \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}} \right], \quad (2.19)$$

an expression that describe the macroscopic stress tensor in terms of microscopic variables<sup>12</sup>.

To end the section it is important to show that (2.19) is symmetric. Therefore, we rewrite the internal force as the sum of forces between the particles,

$$\vec{f}_{\alpha}^{\text{int}} = \sum_{\beta \neq \alpha} \vec{f}_{\alpha\beta}, \quad (2.20)$$

and substituting (2.20) into (2.19), we have

$$\boldsymbol{\sigma}_{\text{av}} = -\frac{1}{V} \left[ \sum_{\alpha, \beta \neq \alpha} \overline{\vec{f}_{\alpha\beta} \otimes \vec{r}_{\alpha}} + \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}} \right]. \quad (2.21)$$

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

$$\sum_{\alpha, \beta \neq \alpha} \vec{f}_{\alpha\beta} \otimes \vec{r}_{\alpha} = \frac{1}{2} \sum_{\alpha, \beta \neq \alpha} \left( \vec{f}_{\alpha\beta} \otimes \vec{r}_{\alpha} + \vec{f}_{\beta\alpha} \otimes \vec{r}_{\beta} \right) = \frac{1}{2} \sum_{\alpha, \beta \neq \alpha} \vec{f}_{\alpha\beta} \otimes (\vec{r}_{\alpha} - \vec{r}_{\beta}). \quad (2.22)$$

Therefore, by replacing the identity of (2.22) into (2.21), we have

$$\boldsymbol{\sigma}_{\text{av}} = -\frac{1}{V} \left[ \frac{1}{2} \sum_{\alpha, \beta \neq \alpha} \overline{\vec{f}_{\alpha\beta} \otimes (\vec{r}_{\alpha} - \vec{r}_{\beta})} + \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\text{rel}} \otimes \vec{v}_{\alpha}^{\text{rel}}} \right], \quad (2.23)$$

expressed with indexical notation and using the eistein summation convention,

$$\sigma_{ij}^{\text{av}} = -\frac{1}{V} \left[ \frac{1}{2} \sum_{\alpha, \beta \neq \alpha} \overline{f_i^{\alpha\beta} r_j^{\alpha} + f_i^{\beta\alpha} r_j^{\beta}} + \sum_{\alpha} m_{\alpha} \overline{v_i^{\alpha \text{ rel}} v_j^{\alpha \text{ rel}}} \right], \quad (2.24)$$

which is the same expression implemented in LAMMPS[Thompson et al., 2022].<sup>13</sup>

<sup>12</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]

<sup>13</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)

## **Chapter 3**

# **Numerical Experiments**

### **3.1 Simulation protocol**

### **3.2 Results**

## **Chapter 4**

# **Conclusion**

- What we achieve
- Future work

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## Curriculum Vitae

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