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Words words words
Hydrogels

A thesis presented by

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Acknowledgements

Total Thanks.

Thank..

Dedication

To ...

To ...

Abstract

In summary: More research is needed.

Contents

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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][Picchioni and Muljana, 2018].

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   A hydrogel is commonly describe as a material composed by a network of polymers chains that exhibits the abilitiy 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].[1]

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[1]the main difference with the microgels, is the size. Hydrogel is bulk, and microgelgel is particle.

The water absorption capacity, network stability of hydrogels, and the conformation of the network with polymer chains are attributable to crosslinking mechanisms[Priya et al., 2024, Ahmed, 2015]. Meanwhile, the polymer chains are predominantly composed with hydrophilic functional groups and can be modified to suit a variety of applications[Ahmed, 2015, Priya et al., 2024, Bustamante-Torres et al., 2021].

While the analysis of the impact of functional groups is important, the present project prioritizes the examination of mechanisms that are more pertinent to the mechanical response. The crosslinking mechanisms[2], in particular, are of particular interest, as they are responsible for resisting dissolution. This suggests that crosslinking mechanisms enable the network to undergo modification by external stimuli.

The subsequent sections will present the essential information to facilitate a comprehensive understanding of the crosslinking mechanisms, their relationship to the mechanical response, the reported mechanical response of hydrogels, and the correlation between rheology experiments and stress curves.

1.1.1 Crosslinking mechanisms

What a low hysteresis means in a hydrogel?

Intro to cross linking A crosslinker is a molecule that functions as a bridge between polymer chains, thereby facilitating the formation of an interconnected network. As previously suggested, it is pertinent to understand the mechanisms of crosslinking in order to gain insight into the correlation between these mechanisms and mechanical properties, such as elasticity, viscosity, solubility, glass transition temperature, strength, toughness, and melting point stiffness, swelling capacity, viscosity, and so forth[Priya et al., 2024]. The elements under consideration form stable bonds, which are comonly categorized into two main types: covalent (permanent) and physical (reversible)[Bustamante-Torres et al., 2021]. However, recent mechanisms, such as mechanical crosslinker mechanics, have been demostrated to form bridges due to the topology of the constituents of the hydrogel.

Figure 1.1: Image with the three different crosslinker mechanisms

Difference between physical and chemical bonds Although the concept of bonding is central to comprehending chemical structures and reactions. The criteria employed to characterize a chemical bond, its physical origin, and its nature remain subjects of debate[Kumar et al., 2021]. Consequently, establishing a precise distinction between "covalent" and "non-covalent" bonds remains challenging. Therefore, the description of crosslinker mechanisms is limited to the principal interactions reported in articles and the synthesis process, rather than focusing on the classification of interactions as "covalent" or "non-covalent", but rather as "reversible" or "irrevarsible". Also in

---

[2]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.

the recent work [Picchioni and Muljana, 2018] it is shown a "covalent" reversible network. Nonetheless, a general consensus exists that non-covalent bonds are, as a rule, recognized as being weaker than covalent bonds and it is widely accepted that a distinguishing characteristic between covalent and noncovalent bonds is the energy of interaction and equilibrium bond distance[Kumar et al., 2021, **?**].

Irreversible Cross-linking   In irreverisble cross-linked hydrogels, polymer chains are synthesized by chain growth polymerization, graft copolymerization, addition and condensation polymerization, ezymatic method, reactive functions groups and gamma and electron beam polymerization[Maitra and Shukla, /26/2014, Bustamante-Torres et al., 2021]. This types of crosslinking mechanisms exhibit a high degree of strength and stability, leading to a structural arrangement of interconnected polymer chains that is more robust and resistant to alterations in environmental conditions, such as temperature and pH[Maitra and Shukla, /26/2014].

Reversible Cross-linking   In reversible cross-linked hydrogels, polymer chains are held together by molecular entanglements or physicochemical interactions, including van der Waals forces, hydrogen bonds, hydrophobic interactions, charge condensation, crystallite formation, and supramolecular chemistry[Bustamante-Torres et al., 2021, Maitra and Shukla, /26/2014]. Some of the syhtesis methods for reverisble crosslinkin mechanisms are ionic interaction, crystallization, stereocomplex formation, hydrophobized polysaccharides, protein interaction, amphilic copolymers and hydrogen bond[Maitra and Shukla, /26/2014, Bustamante-Torres et al., 2021]. Furthermore, 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)[Picchioni and Muljana, 2018].

Mecanical bonds   As previously mentioned, a novel class of polymer architecture has recently emerged within the field of polymer science kwnon as mechanically interlocked polymers (MIPs). These polymers are distinguished by the presence of a mechanical bond, that is, a constraint of two (or more) molecular components in space without the formation of covalent bonds[Hart et al., 2021]. While these types of hydrogels exhibit substantial conformational flexibility while preserving a persistent spatial correlation between their components, their synthesis remains challenging.

1.1.2   Mechanical response of hydrogels

General mechanical properties of the croslsinking   Eventhough, physical crosslinking mechanisms are weaker than chemical ones, there numerous interactions contribute to complex behaviors. Meanwhile chemical crosslinking mechanisms are easier to control than physical crosslinking mechanisms because their preparation is independent of pH[Bustamante-Torres et al., 2021] and they are very brittle due to structural inhomogeneity and lack of energy dissipation[Xu et al., 2018].

Reversible crosslinking   The aforementioned interactions enable hydrogels to undergo structural changes without the rupture of any covalent bonds. Consequently, these materials exhibit enhance responsiveness to external stimuli, such as temperature, pH, or ionic strength. Additionally, hydrogels demonstrate high water sensitivity and thermal reversibility[Bustamante-Torres et al., 2021, Priya et al., 2024]. These materials are known to exhibit distinctive properties, including "self-healing" behavior, where the gel can reform after being broken. The lifespan of these hydrogels is brief, ranging from a few days to a maximum of a month, when maintained within physiological media.

Ir-reversible croslsinkg   Consequently, chemically cross-linked hydrogels generally exhibit greater mechanical strength and long-term stability. Furthermore, 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 due to the hydrophobic aggregation of the cross-linking agent[Bustamante-Torres et al., 2021]..

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].

Tunnable mechanical response with applications   Review of articles of applications

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.29,30[3]

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.34 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.35,36 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,39 they can adhere strongly to tissues to form protective barriers and bandages,40 and they can be delivered through spray applications to coat complex biological geometries.41

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.57 Interest in further developing the translational potential of hydrogels led 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).

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[3]Why the gelation in situ after injection is important?

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.57

Hybrid crosslinking hydrogels consist of covalent and noncovalent crosslinking[Xu et al., 2018]. The dynamic physical crosslinking could effectively dissipate energy via destruction and reorganization, and the chemical crosslinking could sustain skeleton construction [19,20][Xu et al., 2018].

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)[Picchioni and Muljana, 2018].

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[Picchioni and Muljana, 2018]. This can be achieved in principle through other weaker interactions, e.g., hydrogen bonding[Picchioni and Muljana, 2018].

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[Picchioni and Muljana, 2018]. 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[Picchioni and Muljana, 2018].

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 sotred 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[1] 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[2] to use the langevin dynamics mathematical framework.

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[1]Poner citas que desmuestrén que no es hipótesis, si no que se sabe
[2]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][3]. 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,

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

The friction constant γ[4] 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 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, $\vec{R}(t)$[5] is a "random force" subject to the following conditions

$$\left\langle \vec{R}(t) \right\rangle = 0$$

$$\left\langle \vec{R}(t)\vec{R}(t') \right\rangle = 2k_BT\gamma\delta\left(t - t'\right)$$

The no time correlation is equivalent to assuming that the viscoelastic relaxation of the solvent is very rapid with respect to solute motions[6].

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}[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:

$$\eta = \frac{V}{k_BT} \int_0^\infty \left\langle \sigma_{xy}(t)\sigma_{xy}(0) \right\rangle \mathrm{d}t$$

- 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

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[3]Para traer a colación la sensibilidad de la respuesta mecánica al parámetro de damp.

[4]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 $1/s$.

[5]No me acuerdo en donde está que se puede asumir que tiene distribución gaussiana.

[6]Grote land 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…[7]

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

$$\vec{r}_\alpha = \vec{r} + \vec{s}_\alpha, \tag{2.2}$$

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

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

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

$$\vec{r} = \frac{\sum_\alpha m_\alpha \vec{s}_\alpha}{\sum_\alpha m_\alpha}, \tag{2.4}$$

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

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

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

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

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 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 (2.6),

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

---

[7]Capaz e ir introduciendo ideas del Clausius[Clausius, 1870]

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

[9](Eventualmente pondré esto en párrafo) Notation: $\boldsymbol{\sigma}$ Tensor, $\vec{\sigma}$ vector, $\sigma_{i,j}$ tensor, $\overline{\sigma}$ time average,

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

$$\overline{\mathbf{W}} = -2\overline{\mathbf{T}}, \tag{2.8}$$

where

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

is the time-average virial tensor and

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

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,

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

which is not the simplification we expected, however, by the relations from (2.5), equation (2.11) simplifies to[11]

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

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,

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

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,

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

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

With this we can substitute the traction vector with $\vec{t} = \sigma\vec{n}$, where σ represent the Cauchy stress tensor and applying the divergence theorem in (2.14), we have

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

---

[11]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

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

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

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

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

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

Finally, solving for the Cauchy Stress tensor we get,

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

an expression that describe the macroscopic stress tensor in terms of microscopic variables[12].

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,

$$\vec{f}_{\alpha}^{\text{int}} = \sum_{\beta_{\beta\neq\alpha}}\vec{f}_{\alpha\beta}, \tag{2.20}$$

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

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

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

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

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

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

expressed with indexical notation and using the eistein summation convention,

$$\sigma_{ij}^{\text{av}} = -\frac{1}{V}\left[\frac{1}{2}\sum_{\alpha,\beta_{\beta\neq\alpha}}\overline{f_{i}^{\alpha\beta}r_{j}^{\alpha} + f_{i}^{\beta\alpha}r_{j}^{\beta}} + \sum_{\alpha}m_{\alpha}\overline{v_{i}^{\alpha\,\text{rel}}v_{j}^{\alpha\text{rel}}}\right], \tag{2.24}$$

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

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

[13]No se si poner la referencia a la pagina de documentacionhttps://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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