INSTITUTO TECNOLÓGICO Y DE ESTUDIOS SUPERIORES DE MONTERREY

CAMPUS MONTERREY

Some title that will have the word Hydrogels

BY

Me

A DISSERTATION
SUBMITTED TO THE MNT GRADUATE PROGRAM
AND THE COMMITTEE OF GRADUATE STUDIES OF
TECNOLOGICO DE MONTERREY
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

the same as Leo, I'll check later

MONTERREY, NUEVO LEÓN, MÉXICO , MAY 2003

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THE COMMITTEE MEMBERS HEREBY RECOMMEND THE THESIS PRESENTED BY **RUBEN MORALES-MENÉNDEZ** TO BE ACCEPTED AS A PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN INTELLIGENT SYSTEMS

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Monterrey, NL México, May 2003

External Advisors Acknowledgements

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I would like to thank ...

Nando de Freitas

I would like to thank ...

Acknowledgements

I would like to thank

Thank..

Dedication

To ...

To ...

Abstract

Fault diagnosis is ...

Contents

List of Tables

List of Figures

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.

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

1.1 Context

[1]

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

Tunnable mechanical response with applications Review of articles of applications

Why computers and not rheometers? Explain[2] how in silico experiments can help to understand the relation between the network and the mechanical response.

[1] State of art?
[2] that Tec didn't pay the bills for a lab.

Chapter 2

Theoretical framework

2.1 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 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].[1] The water absorption capacity and network stability of hydrogels can be controlled by crosslinking mechanisms, which involves forming covalent or non-covalent bonds between polymer chains[2][Priya et al., 2024, Ahmed, 2015]. On the other hand, hydrogels are generally prepared based on hydrophilic monomers that can reulate the properties for specific applications[Ahmed, 2015, Priya et al., 2024].

Transtition to talk about crosslink Furthermore, crosslinking affects various physical properties of the hydrogel, such as elasticity, viscosity, solubility, glass transition temperature, strength, toughness, and melting point[Priya et al., 2024].

Since we are interested in the mechanical response of the material, our focus will be in the crosslinking mechanisms.

Crosslinking is another essential process that can be controlled and intentionally modified using ionizing radiations[Priya et al., 2024].

Crosslinking involves the formation of chemical bonds between polymer chains, creating a three-dimensional network structure[Priya et al., 2024].

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

[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.

Difference between physical and chemical bonds I have the intuition that the basic difference is the energy required for braking in given conditions.

Physical 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. Unlike chemical cross-linking, physical cross-linking is 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. They may exhibit unique properties, such as "self-healing" behaviour, where the gel can reform after being broken. The hydrogels prepared by these interactions are uniquely physical gels and have high water sensitivity and thermal reversibility. 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. Therefore, in this form, hydrogels are used when a short-term drug release is required.

Chemical 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 network of interconnected polymer chains. The cross-links are typically formed through chemical reactions, such as polymerization or cross-linking agent-induced reactions. The presence of covalent bonds makes the hydrogel structure more robust and resistant to changes in environmental conditions, such as temperature and pH. 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.

Mecanical 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.

2.2 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].

2.3 Molecular dynamics

- Langevin equation
- Velocity Verlet

2.3.1 Brownian 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[3] 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[4] to use the langevin dynamics mathematical framework.

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][5]. 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[6] 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, $\vec{R}(t)$[7] is a "random force"subject to the following conditions

$$\left\langle \vec{R}(t) \right\rangle = 0$$
$$\left\langle \vec{R}(t)\vec{R}(t') \right\rangle = 2k_B T\gamma\delta\left(t - t'\right)$$

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

[4] Supongo que eventualmente justificaré la desición.

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

[6] 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 $1/s$.

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

The no time correlation is equivalent to assuming that the viscoelastic relaxation of the solvent is very rapid with respect to solute motions[8].

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:

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

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

2.4 Mechanical response

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

2.4.1 Stress

Introductory paragraph To characterize the behaviour of materials, constitutive relations serve as an input to the continuum theory...[9]

This derivation can be found in the apendix of[Admal and Tadmor, 2010][10].[11] 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

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

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,

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

[8]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]

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

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

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

Now we can start by computing the time derivative of tensorial product $\vec{r}_\alpha \otimes \vec{p}_\alpha$[12],

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

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),

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

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

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

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,

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

which is not the simplification we expected, however, by the relations from (2.5), equation (2.11) simplifies to[13]

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

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,

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

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

[12] 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.

[13] 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.

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

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

Since we assume that we are under equilibrium conditions, the term $\text{div}_{\vec{\xi}}\boldsymbol{\sigma} + \rho\vec{b}$ 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,

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

Finally, solving for the Cauchy Stress tensor we get,

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

an expression that describe the macroscopic stress tensor in terms of microscopic variables[14].

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

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

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

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

[14]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]

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

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

expressed with indexical notation and using the eistein summation convention,

$$\sigma_{ij}^{\mathrm{av}} = -\frac{1}{V}\left[\frac{1}{2}\sum_{\alpha,\beta_{\beta\neq\alpha}} \overline{f_i^{\alpha\beta} r_j^{\alpha} + f_i^{\beta\alpha} r_j^{\beta}} + \sum_{\alpha} m_{\alpha}\overline{\upsilon_i^{\alpha\ \mathrm{rel}}\upsilon_j^{\alpha\mathrm{rel}}}\right], \tag{2.24}$$

which is the same expression implemented in LAMMPS[Thompson et al., 2022].[15]

[15]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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