Draft for the thesis

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Summary Document for the draft of the Thesis.

Introduction

Acknowledge

Objectives

Justification

Description of the micro-gel

- What is a microgel

- Connection with colloids

- Link to brownian dynamics

——— Connecting Elasticity and Effective Interactions of Neutral Microgels: The Validity of the Hertzian Model[Rovigatti et al., 2019]

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Stress localization, stiffening, and yielding in a model colloidal gel[Colombo and Del Gado, 2014]

Colloidal gels, which can form in suspensions of colloidal particles in the presence of attractive effective interactions, are particularly appealing as materials whose functions can be in principle designed at the level of the nanoscale (particle) components

In colloidal suspensions, gels can form even in extremely dilute systems via aggregation of the particles into a rich variety of network structures that can be suitably tuned by changing the solid volume fraction, the physico-chemical environment, or the processing conditions. Hence, these handles could be used to design a specific complex mechanical response in addition to the selected nano-particle properties

Colloidal gels are typically very soft, but the variety of microstructures may lead to an equal variety in the mechanics

The microstructural complexity may also enable adjustments of the mechanical response to the external deformation. Soft gels can be in principle made to yield relatively easily, but in certain cases, a significant strain hardening has been observed before yielding finally occurs

The yielding of colloidal gels, due to breaking and reorganization of the network structure, can be accompanied by strong inhomogeneity of stresses and strains throughout the material[1]

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Polymer Networks: From Plastics and Gels to Porous Frameworks[Gu et al., 2020]

When bifunctional molecules are linked together, linear macromolecules, or "linear polymers," with high molecular weights can form. Analogously,

[1] Pos hay otros fenómenos que llevan a yielding

when molecules with functionality greater than two are linked together, three-dimensional (3D) macromolecules, or "polymer networks," with very high (classically referred to as "infinite"[1,2]) molecular weights can form. Early organic chemists referred to polymerization, the process used to form linear and 3D polymers, as a "chemical combination involving the operation of primary valence forces," further stating that "the term polymer should not be used (as it frequently is by physical and inorganic chemists) to name loose or vaguely defined molecular aggregates."[1] Similarly, Wallace Carothers defined polymerization as, "any chemical combination of a number of similar molecules to form a single molecule."[1] These notions either implicitly or explicitly defined polymers as being composed of strongly (covalently) bonded constituents. Today, however, it is widely accepted that linear polymers and polymer networks can be constructed from covalent and/ or non-covalent bonds; indeed, the full spectrum of bonding interactions, reaction mechanisms, and chemical compositions (e.g., organic, inorganic, biological) can be leveraged to design fascinating new polymer networks with exceptional properties.

From a structural perspective, polymer networks are composed of network "junctions" (in some cases, these can also be referred to as "crosslinks", defined as a bond that links one strand to another), which have three or more groups (the exact "branch functionality" we refer to as f) emanating from a core, connected together by f "strands." Strands can be linear polymer chains, flexible short molecules, rigid struts/ linkers, etc. As noted above, junctions and strands in polymer networks can be linked together via physical interactions (e.g., van der Waals interactions, hydrophobic interactions, Coulombic interactions, metalligand coordination) or covalent bonds. Hence, polymer networks are conventionally classified as "physical" (supramolecular) or "chemical" (covalent) networks. It should be noted that this classification does not always accurately reflect material properties; bond strengths and exchange rates are much more informative. For example, given sufficiently strong and static physical interactions, physical networks can behave identically to chemical networks; alternatively, the incorporation of mechanisms for covalent bond exchange can result in chemical networks that exhibit adaptable mechanical properties regulated by external stimuli. Thus, the properties of polymer networks can vary widely depending on the composition of the junctions and strands as well as the formation and use conditions. With this broad view in mind, nearly all polymer networks, regardless of their colloquial name, structure, properties, etc. can generally be divided into one of four major classes: thermosets, thermoplastics, elastomers, and gels.

Gels are polymer networks constructed from either covalent or supramolecular bonds that are swollen in liquid media such as water or organic solvents. The network structure ensures that the liquid is held within the material. Gels are usually very soft (Young s moduli of 103–104 Pa) but are often capable of undergoing relatively large deformation. Examples of gels include gelatin, fibrin, and polyacrylamide hydrogel.

As perhaps the most important, useful, and broadly studied class of materials from theoretical, academic, and industrial perspectives, polymer networks can have many unique properties, including elasticity, tunable

mechanical strength, porosity, and swellability. These properties and others have led to numerous applications of polymer networks in everyday life, such as adhesives, cosmetics, sorbents, membranes, rubber products, coating materials, and food packaging. Moreover, as recent developments have imparted unconventional properties (e.g., malleability, self-healing, conductivity, ultra-high permanent porosity, enhanced crystallinity, and stimuli-responsiveness) into polymer networks, they continue to hold great promise in advanced applications including drug delivery systems,[3] tissue engineering scaffolds,[4] soft actuators,[5] gas storage,[6] catalysis,[6–8] and electronic materials.[9] Thus, though polymer networks have been widely studied for more than a century, there are features of their structure that have only recently been leveraged to impart new properties; an even deeper understanding is needed to realize the next-generation of functional, and ideally sustainable, polymer networks.

In this review, we introduce key concepts related to the formation, characterization, and properties of polymer networks. Our goal is to provide newcomers to the field with broad and up-to-date knowledge that can serve as a starting point for more detailed investigations of topics of interest. Major focus is devoted to polymer network structure, which includes both chemical and topological aspects. Additionally, several types of recently developed polymer networks with exceptional properties are highlighted.

Theoretical framework

Description of the microgel

Description of the microgel as a colloid to introduce the langevin methodology.

"The dynamics of a macromolecular system is entirely determined by the potential $U(rN)$ associated with the process. For computational and practical reasons, this potential is virtually always an approximation of the real physical potential[2]."[Paquet and Viktor, 2015]

[2] Those potentials are explained in the following section?
Would be better to describe the parameters in the implementation and the model here?

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.

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

[4] 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 sys-

tem 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,

$$m\frac{\mathrm{d}\vec{v}(t)}{\mathrm{d}t} = \vec{F}(t) - m\gamma\vec{v}(t) + \vec{R}(t). \qquad (1)$$

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

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

[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 $1/s$.

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

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

[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].

[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]

- 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.

Stress

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

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

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

$$\vec{r}_\alpha = \vec{r} + \vec{s}_\alpha, \tag{2}$$

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

$$\vec{p}_\alpha = m_\alpha\left(\dot{\vec{r}} + \dot{\vec{s}}_\alpha\right) = m_\alpha\left(\dot{\vec{r}} + \vec{v}_\alpha^{\text{rel}}\right). \tag{3}$$

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

$$\vec{r} = \frac{\sum_\alpha m_\alpha \vec{s}_\alpha}{\sum_\alpha m_\alpha}, \tag{4}$$

and by replacing (2) in (3) we get the following relations, which will be used later,

$$\sum_\alpha m_\alpha \vec{r}_\alpha = \vec{0}, \quad \sum_\alpha m_\alpha \vec{v}_\alpha^{\text{rel}} = \vec{0}. \tag{5}$$

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

$$\frac{\mathrm{d}}{\mathrm{d}t}(\vec{r}_\alpha \otimes \vec{p}_\alpha) = \underbrace{\vec{v}_\alpha^{\text{rel}} \otimes \vec{p}_\alpha}_{\text{Kinetic term}} + \underbrace{\vec{r}_\alpha \otimes \vec{f}_\alpha}_{\text{Virial term}}, \tag{6}$$

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 (6),

$$\frac{1}{\tau}(\vec{r}_\alpha \otimes \vec{p}_\alpha)\bigg|_0^\tau = \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{p}_\alpha} + \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha}. \tag{7}$$

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*:

$$\overline{\mathbf{W}} = -2\overline{\mathbf{T}}, \tag{8}$$

where

$$\overline{\mathbf{W}} = \sum_\alpha \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha} \tag{9}$$

is the time-average virial tensor and

$$\overline{\mathbf{T}} = \frac{1}{2}\sum_\alpha \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{p}_\alpha} \tag{10}$$

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.

[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,

[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.

The assumption of the difference between the time scales allow us to simplify the relation by replacing (3) in (10), so that,

$$\overline{\mathbf{T}} = \frac{1}{2} \sum_\alpha m_\alpha \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{v}_\alpha^{\text{rel}}} + \frac{1}{2} \left[\overline{\sum_\alpha m_\alpha \vec{v}_\alpha^{\text{rel}}} \right] \otimes \dot{\vec{r}}, \qquad (11)$$

which is not the simplification we expected, however, by the relations from (5), equation (11) simplifies to[13]

$$\overline{\mathbf{T}} = \frac{1}{2} \sum_\alpha m_\alpha \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{v}_\alpha^{\text{rel}}}. \qquad (12)$$

On the other hand, instead of reducing the expression, we start to create the conection with the Cauchy stress tensor by distributing (9) into an internal and external contributions,

$$\overline{\mathbf{W}} = \underbrace{\sum_\alpha \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\text{int}}}}_{\overline{\mathbf{W}}_{\text{int}}} + \underbrace{\sum_\alpha \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\text{ext}}}}_{\overline{\mathbf{W}}_{\text{ext}}}. \qquad (13)$$

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,

$$\sum_\alpha \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\text{ext}}} := \int_{\delta\Omega} \vec{\xi} \otimes \vec{t} \, dA + \int_\Omega \vec{\xi} \otimes \rho \vec{b} \, dV. \qquad (14)$$

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 (14), we have

$$\overline{\mathbf{W}}_{\text{ext}} = \int_\Omega \left[\vec{\xi} \otimes \rho\vec{b} + \text{div}_{\vec{\xi}} \left(\vec{\xi} \otimes \boldsymbol{\sigma} \right) \right] dV = \int_\Omega \left[\boldsymbol{\sigma}^{\text{T}} + \vec{\xi} \otimes \left(\text{div}_{\vec{\xi}} \, \boldsymbol{\sigma} + \rho\vec{b} \right) \right] dV$$
$$(15)$$

Since we assume that we are under equilibrium conditions, the term $\text{div}_{\vec{\xi}} \, \boldsymbol{\sigma} + \rho\vec{b}$ is zero (15) it simplifies to

$$\overline{\mathbf{W}}_{\text{ext}} = V \boldsymbol{\sigma}^{\text{T}}. \qquad (16)$$

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,

$$\boldsymbol{\sigma}_{\text{av}} = \frac{1}{V} \int_\Omega \boldsymbol{\sigma} \, dV, \qquad (17)$$

in which V is the volume of the domain Ω. Replacing (16) into (13), the tensor virial theorem (8) can be expressed as,

$$\sum_\alpha \overline{\vec{r}_\alpha \otimes \vec{f}_\alpha^{\text{int}}} + V \boldsymbol{\sigma}_{\text{av}}^{\text{T}} = -\sum_\alpha m_\alpha \overline{\vec{v}_\alpha^{\text{rel}} \otimes \vec{v}_\alpha^{\text{rel}}}. \qquad (18)$$

[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.

Finally, solving for the Cauchy Stress tensor we get,

$$\boldsymbol{\sigma}_{\mathrm{av}} = -\frac{1}{V} \left[\sum_{\alpha} \overline{\vec{f}_{\alpha}^{\mathrm{int}} \otimes \vec{r}_{\alpha}} + \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\mathrm{rel}} \otimes \vec{v}_{\alpha}^{\mathrm{rel}}} \right], \qquad (19)$$

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

To end the section it is important to show that (19) is symmetric. Therefore, we rewrite the internal force as the sum of forces between the particles,

$$\vec{f}_{\alpha}^{\mathrm{int}} = \sum_{\substack{\beta \\ \beta \neq \alpha}} \vec{f}_{\alpha\beta}, \qquad (20)$$

and substituting (20) into (19), we have

$$\boldsymbol{\sigma}_{\mathrm{av}} = -\frac{1}{V} \left[\sum_{\substack{\alpha,\beta \\ \beta \neq \alpha}} \overline{\vec{f}_{\alpha\beta} \otimes \vec{r}_{\alpha}} + \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\mathrm{rel}} \otimes \vec{v}_{\alpha}^{\mathrm{rel}}} \right]. \qquad (21)$$

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

$$\sum_{\substack{\alpha,\beta \\ \beta \neq \alpha}} \vec{f}_{\alpha\beta} \otimes \vec{r}_{\alpha} = \frac{1}{2} \sum_{\substack{\alpha,\beta \\ \beta \neq \alpha}} \left(\vec{f}_{\alpha\beta} \otimes \vec{r}_{\alpha} + \vec{f}_{\beta\alpha} \otimes \vec{r}_{\beta} \right) = \frac{1}{2} \sum_{\substack{\alpha,\beta \\ \beta \neq \alpha}} \vec{f}_{\alpha\beta} \otimes \left(\vec{r}_{\alpha} - \vec{r}_{\beta} \right). \qquad (22)$$

Therefore, by replacing the identity of (22) into (21), we have

$$\boldsymbol{\sigma}_{\mathrm{av}} = -\frac{1}{V} \left[\frac{1}{2} \sum_{\substack{\alpha,\beta \\ \beta \neq \alpha}} \overline{\vec{f}_{\alpha\beta} \otimes \left(\vec{r}_{\alpha} - \vec{r}_{\beta} \right)} + \sum_{\alpha} m_{\alpha} \overline{\vec{v}_{\alpha}^{\mathrm{rel}} \otimes \vec{v}_{\alpha}^{\mathrm{rel}}} \right], \qquad (23)$$

expressed with indexical notation and using the eistein summation convention,

$$\sigma_{ij}^{\mathrm{av}} = -\frac{1}{V} \left[\frac{1}{2} \sum_{\substack{\alpha,\beta \\ \beta \neq \alpha}} \overline{f_i^{\alpha\beta} r_j^{\alpha} + f_i^{\beta\alpha} r_j^{\beta}} + \sum_{\alpha} m_{\alpha} \overline{v_i^{\alpha\,\mathrm{rel}} v_j^{\alpha\mathrm{rel}}} \right], \qquad (24)$$

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

Computational Implementation

General description

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

[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]

[15] No se si poner la referencia a la pagina de documentacionhttps://docs.lammps.org/compute_stress_atom.html

- $\vec{r}_i$: Position of Crosslinker central particle

- $\vec{r}_j$: Position of Monomer central particle

- $\{\vec{r}_{\mu}^i\}$ Set of positions of the patches in the crosslinker patchy particle

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

$$U_{WCA}(r_{i,j}) = \begin{cases} 4\varepsilon_{i,j}\left[\left(\frac{\sigma}{r_{i,j}}\right)^{12} - \left(\frac{\sigma}{r_{i,j}}\right)^{6}\right] + \varepsilon_{i,j}, & r_{i,j} \in [0, 2^{1/6}\sigma], \\ 0, & r_{i,j} > 2^{1/6}\sigma \end{cases} \quad , \quad (25)$$

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 interacton. The patch-patch interaction is modeled with an attractive potential,

$$U_{\text{patchy}}(r_{\mu\upsilon}) = \begin{cases} 2\varepsilon_{\mu\upsilon}\left(\frac{\sigma_p^4}{2r_{\mu\upsilon}^4} - 1\right)\exp\left[\frac{\sigma_p}{(r_{\mu\upsilon}-r_c)} + 2\right], & r_{\mu\upsilon} \in [0, r_c], \\ 0, & r_{\mu,\upsilon} > r_c, \end{cases} \quad (26)$$

where $r_{\mu\upsilon}$ 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 $\varepsilon_{\mu,\upsilon}$ is the interaction energy between the patches. Moreover, the interaction between patches is complemented by a three-body repulsive potential, defined in terms of (26), that provides an efficient bond-swapping mechanism making possible to easily equilibrate the system at extremely low temperatures, while at the same time, reataining the single-bond-per-patch condition[Sciortino, 2017],

$$U_{\text{swap}}(r_{l,m}, r_{l,n}) = w \sum_{l,m,n} \varepsilon_{m,n} U_3(r_{l,m}) U_3(r_{l,n}), \quad r_{l,n} \in [0, r_c], \quad (27)$$

where

$$U_3(r) = \begin{cases} 1 & r \in [0, r_{\min}], \\ -U_{\text{patchy}}(r)/\varepsilon_{m,n}, & r \in [r_{\min}, r_c] \end{cases} \quad . \quad (28)$$

The sum in (27) 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 tuned 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 (26), $i.e.$ $\varepsilon_{m,n} \equiv \left|U_{\text{patchy}}(r_{\min})\right|$. 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 2).

Assembly of the network

We perform molecular dynamics (MD) simulations at fixed temperature $T = kBT/\varepsilon = 0.05$, where kB is the Boltzmann constant. Thanks to such a low temperature, the system tends to maximize the number of bonds. In addition, owing to the bondswapping mechanism, the system is able to continuously restructure itself, until the large majority of possible bonds are formed. It is important to said that the main difference between the articles cited and the implementation in this htesis are the absence of FENE bonds and the swelling potential.
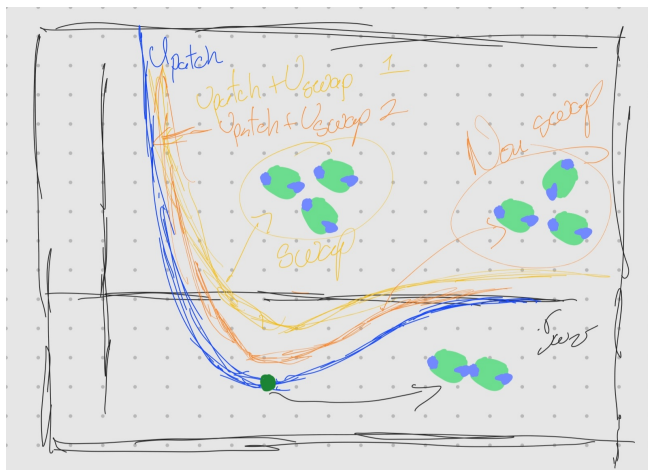
Figure 1: La idea de la figura es poner el pontecial de interacción entre paches y ver el efecto del pontecial de 3 cuerpos cuando $w = 1$ y cuando $w \gg 1$.
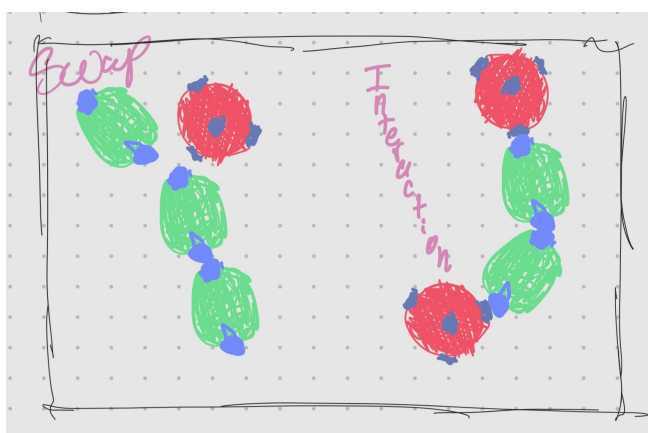

Figure 2: La idea de esta es mostrar las posibles configuraciones (monomero-monomero, monomero-crosslinker y un poco de pontecial de 3 cuerpos)

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