Draft for the thesis

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July 9, 2025

Summary Document for the draft of the Thesis.

Introduction

Acknowledge

Objectives

Justification

Theoretical framework

Theory of simple liquids Computational Physics

Most realistic physical systems are tractable only in a model, in which the interesting features of the system are highlighted and in which the less relevant parts are either eliminated or treated in an approximate way.

In this spirit we have for example eliminated molecular degrees of freedom by considering (parts of) molecules to be rigid. Another example of this approach is the Langevin dynamics technique.

Consider a solution containing polymers or ions which are much heavier than the solvent molecules. As the kinetic energy is on average divided equally over the degrees of freedom, the ions or polymers will move much more slowly than the solvent molecules. Moreover, because of their large mass, they will change their momenta only 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. This difference in time scale can be employed to eliminate the details of the degrees of freedom of the solvent particles and represent their effect by forces that can be treated in a simple way. This process can be carried out analytically through a projection procedure (see chapter 9 of Ref. [11] and references therein) but here we shall sketch the method in a heuristic way.

How can we model the effect of the solvent particles without taking into account their degrees of freedom explicitly? When a heavy particle is moving through the solvent, it will encounter more solvent particles at the front than at the back. Therefore, the collisions with the solvent particles will on average have the effect of a friction force proportional and opposite to the velocity of the heavy particle. This suggests the following equation of motion for the heavy particle:

[11] J. P. Hansen and I. R. McDonald, Theory of Simple Liquids 2nd edn. New York, Academic Press, 1986.

To make the model more realistic we must include the rapid variations in the force due to the frequent collisions with solvent particles on top of the coarse-grained friction force. We then arrive at the following equation:

where R(t) is a 'random force'. Again, the time correlations present in

the fluid should show up in this force, but they are neglected once more and the force is subject to the following conditions

Its basis is the stochastic theory used by Langevin to describe the brownian motion of a large and massive particle in a bath of particles that are much smaller and lighter than itself. The problem is characterised by 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. Langevin assumed that the force acting on the brownian particle consists of two parts: a systematic, frictional force proportional to the velocity u(t), but acting in the opposite sense, and a randomly fluctuating force, R(t), which arises from collisions with surrounding particles.

Brownian dynamics

Brief explanation of what is Brwonian motion, what is trying to represent/model, how this can modeld the microgel.

Even though there are different mathematical representations that describes the brownian motion, we use the langevin equation[1] described with increments of Wiener process,

$$\begin{cases} \mathrm{d}r = v\,\mathrm{d}t \\ \mathrm{d}v = -\frac{\gamma}{m}v\,\mathrm{d}t - \frac{1}{m}\nabla U(r)\,\mathrm{d}t + \sqrt{\frac{2\gamma k_B T}{m}}\mathrm{d}W_t \end{cases}. \tag{1}$$

The Wiener process has the correlation property of $\langle \mathrm{d}W_i \mathrm{d}W_j \rangle = \delta_{ij}\mathrm{d}t$. γ represent the viscosity of the implicity medium, k_B is the Boltzmann constant and T the tempereture of the system.[2]

formullations of the Langeving equation[3], we choose to described the brownian motion using

Here explain the Langevin equation.

Stress

Introductory paragraph   To characterize the behaviour of materials, constitutive relations serve as an input to the continuum theory...[4]

This derivation can be found in the apendix of[Admal and Tadmor, 2010][5].[6] 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

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

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,

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

[1] No se que más decir a parte de "porque está implementado en lammps", jsjs

[2] En lammps está cómo

$$F_c - \frac{m}{\mathrm{damp}}v + \propto \sqrt{\frac{k_B T m}{\mathrm{d}t\,\mathrm{damp}}}$$

[3] No estoy muy seguro si decir el resto de formalismos

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

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

[6] (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 $\vec{r}_\alpha \otimes \vec{p}_\alpha$[7],

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

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),

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

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.

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

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

which is not the simplification we expected, however, by the relations from (5), equation (11) simplifies to[8]

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

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,

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

The time-average internal virial tensor takes into account the interaction between particle α with the other particles in the system, meanwhile, the

[7] 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.

[8] 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.

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,

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

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

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

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

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

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,

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

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

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

Finally, solving for the Cauchy Stress tensor we get,

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

an expression that describe the macroscopic stress tensor in terms of microscopic variables[9].

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,

$$\vec{f}_\alpha^{\text{int}} = \sum_{\substack{\beta \\ \beta \neq \alpha}} \vec{f}_{\alpha\beta}, \tag{20}$$

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

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

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

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

[9] 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 (22) into (21), we have

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

expressed with indexical notation and using the eistein summation convention,

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

which is the same expression implemented in LAMMPS[Thompson et al., 2022].[10]

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

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.

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

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

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],

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

- $\vec{r}_i$: 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

- $\{\vec{r}_\upsilon^j\}$ Set of positions of the patches in the monomer patchy particle

where

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

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.* $\varepsilon_{m,n} \equiv |U_{\text{patchy}}(r_{\min})|$. Finally, the energy of interaction between crosslinker patches ($\varepsilon_{\mu^i,\mu^i}$) are set to 0 to allow only crosslinker-monomer and monomer-monomer bonding (figure 2).
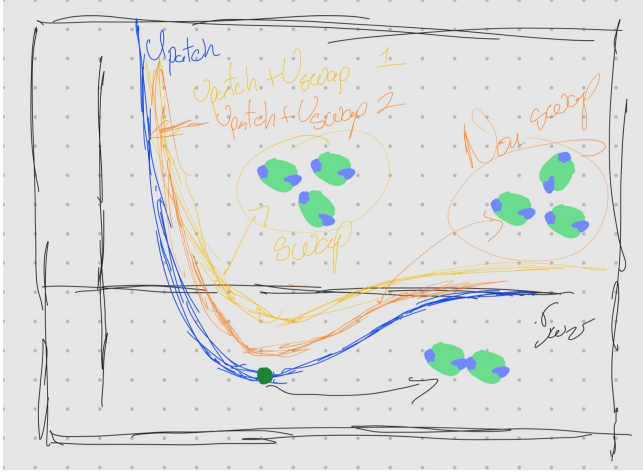

Figure 1: La idea de la figura es poner el pontecial de interacción entre paches y ver el efecto del pontecial de 3 cuerpos cuando $w = 1$ y cuando $w \gg 1$.
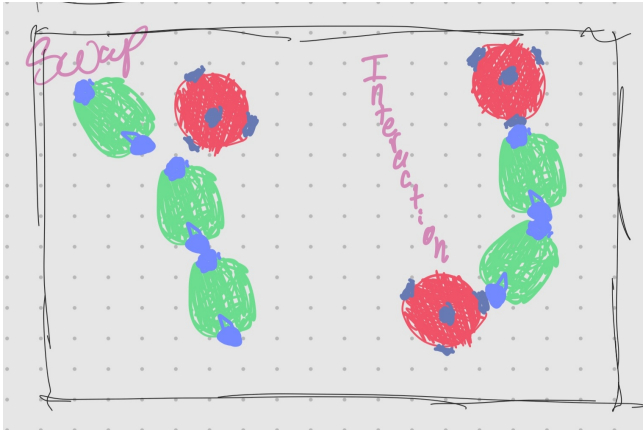

Figure 2: La idea de esta es mostrar las posibles configuraciones (monomero-monomero, monomero-crosslinker y un poco de pontecial de 3 cuerpos)

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.

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