

Draft for the thesis

Francisco Vazquez-Tavares

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Summary Document for the draft of the Thesis.

Introduction

Acknowledge

Objectives

Justification

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 potential¹.”[Paquet and Viktor, 2015]

¹ 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 quantitative 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 structure² 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 decided³ to use the langevin dynamics mathematical framework.

² Poner citas que desmuestren que no es hipótesis, si no que se sabe

³ Supongo que eventualmente justificaré la decisión.

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]⁴. Therefore, two terms are used to create a mathematical representation of the solvent: a frictional force proportional to the velocity of the brownian particle and a fluctuating force. Hence,

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

The friction constant γ ⁵ 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, $\vec{R}(t)$ ⁶ is a “random force”subject to the following conditions

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

The no time correlation is equivalent to assuming that the viscoelastic relaxation of the solvent is very rapid with respect to solute motions⁷.

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:

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

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

References

- Nikhil Chandra Admal and E. B. Tadmor. A unified interpretation of stress in molecular systems. *Journal of Elasticity*, 100(1):63–143, June 2010. ISSN 1573-2681. DOI: 10.1007/s10659-010-9249-6.
- R. Clausius. Xvi on a mechanical theorem applicable to heat. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 40(265):122–127, August 1870. ISSN 1941-5982, 1941-5990. DOI: 10.1080/14786447008640370.

⁴ Para traer a colación la sensibilidad de la respuesta mecánica al parámetro de damp.

⁵ 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 $1/s$.

⁶ No me acuerdo en donde está que se puede asumir que tiene distribución gaussiana.

⁷ Grote and Hynes [26] have investigated this assumption for motions involving barrier crossing and have found that while it is seriously in error for passage over sharp barriers (such as 12 recombination); it is quite adequate for conformational transitions such as might be found in polymer motions.[Pastor, 1994]

- Nicoletta Gnan, Lorenzo Rovigatti, Maxime Bergman, and Emanuela Zaccarelli. In silico synthesis of microgel particles. *Macromolecules*, 50(21):8777–8786, November 2017. ISSN 0024-9297, 1520-5835. DOI: 10.1021/acs.macromol.7b01600.
- Jean Pierre Hansen and Ian R. McDonald. *Theory of simple liquids*. Elsevier Academic Press, 2006.
- Jing-Tao Lü, Bing-Zhong Hu, Per Hedegård, and Mads Brandbyge. Semi-classical generalized langevin equation for equilibrium and nonequilibrium molecular dynamics simulation. *Progress in Surface Science*, 94(1):21–40, February 2019. ISSN 0079-6816. DOI: 10.1016/j.progsurf.2018.07.002.
- Eric Paquet and Herna L. Viktor. Molecular dynamics, monte carlo simulations, and langevin dynamics: A computational review. *BioMed Research International*, 2015:183918, 2015. ISSN 2314-6133. DOI: 10.1155/2015/183918.
- Giorgio Parisi. *Statistical field theory*. Addison Wesley, 1988.
- R. W. Pastor. Techniques and applications of langevin dynamics simulations. In G. R. Luckhurst and C. A. Veracini, editors, *The Molecular Dynamics of Liquid Crystals*, pages 85–138. Springer Netherlands, Dordrecht, 1994. ISBN 978-94-011-1168-3. DOI: 10.1007/978-94-011-1168-3₅.
- Francesco Sciortino. Three-body potential for simulating bond swaps in molecular dynamics. *The European Physical Journal E*, 40(1):3, January 2017. ISSN 1292-8941, 1292-895X. DOI: 10.1140/epje/i2017-11496-5.
- Valerio Sorichetti, Andrea Ninarello, José M. Ruiz-Franco, Virginie Hugouvieux, Walter Kob, Emanuela Zaccarelli, and Lorenzo Rovigatti. Effect of chain polydispersity on the elasticity of disordered polymer networks. *Macromolecules*, 54(8):3769–3779, apr 2021. ISSN 0024-9297, 1520-5835. DOI: 10.1021/acs.macromol.1c00176.
- Valerio Sorichetti, Andrea Ninarello, José Ruiz-Franco, Virginie Hugouvieux, Emanuela Zaccarelli, Cristian Micheletti, Walter Kob, and Lorenzo Rovigatti. Structure and elasticity of model disordered, polydisperse, and defect-free polymer networks. *The Journal of Chemical Physics*, 158(7):074905, feb 2023. ISSN 0021-9606, 1089-7690. DOI: 10.1063/5.0134271.
- Arun K. Subramaniyan and C.T. Sun. Continuum interpretation of virial stress in molecular simulations. *International Journal of Solids and Structures*, 45(14–15):4340–4346, July 2008. ISSN 00207683. DOI: 10.1016/j.ijsolstr.2008.03.016. URL <https://linkinghub.elsevier.com/retrieve/pii/S0020768308001248>.
- Robert J. Swenson. Comments on virial theorems for bounded systems. *American Journal of Physics*, 51(10):940–942, October 1983. ISSN 0002-9505, 1943-2909. DOI: 10.1119/1.13390. URL <https://pubs.aip.org/ajp/article/51/10/940/1052035/Comments-on-virial-theorems-for-bounded-systems>.

Johannes M. M. H. Thijssen. *Computational physics*. Cambridge University Press, 2007.

A. P. Thompson, H. M. Aktulga, R. Berger, D. S. Bolintineanu, W. M. Brown, P. S. Crozier, P. J. in 't Veld, A. Kohlmeyer, S. G. Moore, T. D. Nguyen, R. Shan, M. J. Stevens, J. Tranchida, C. Trott, and S. J. Plimpton. LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Comp. Phys. Comm.*, 271: 108171, 2022. DOI: 10.1016/j.cpc.2021.108171.

Aidan P. Thompson, Steven J. Plimpton, and William Mattson. General formulation of pressure and stress tensor for arbitrary many-body interaction potentials under periodic boundary conditions. *The Journal of Chemical Physics*, 131(15):154107, October 2009. ISSN 0021-9606, 1089-7690. DOI: 10.1063/1.3245303. URL <https://pubs.aip.org/jcp/article/131/15/154107/316893/General-formulation-of-pressure-and-stress-tensor>.

D. H. Tsai. The virial theorem and stress calculation in molecular dynamics. *The Journal of Chemical Physics*, 70(3):1375–1382, February 1979. ISSN 0021-9606, 1089-7690. DOI: 10.1063/1.437577. URL <https://pubs.aip.org/jcp/article/70/3/1375/89129/The-virial-theorem-and-stress-calculation-in>.

Heng Wang, Xuhao Li, Lijing Zhao, and Weihua Deng. Multiscale modeling and simulation for anomalous and nonergodic dynamics: From statistics to mathematics. *Fundamental Research*, January 2025. ISSN 2667-3258. DOI: 10.1016/j.fmre.2024.12.024.