Master 2 Matière Condensée et Nanophysique: Internship projects

Self-assembled transient networks

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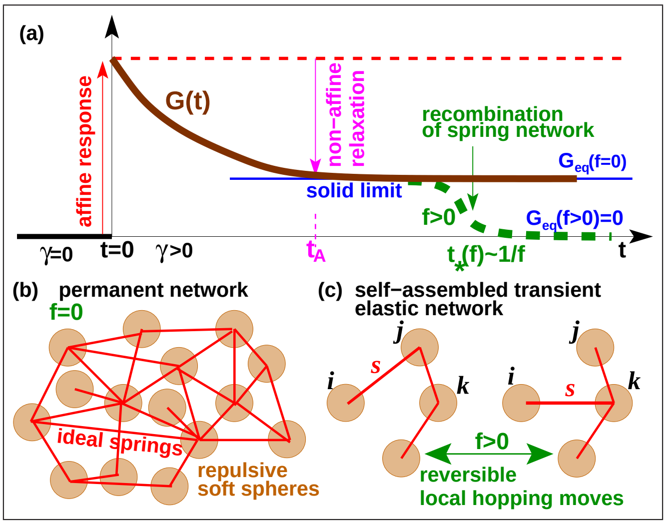
Research context:

Our research group is interested in the statistical physics of soft matter and the rheology of complex fluids with a particular emphasis on systems involving polymers [1]. Using simple coarse-grained models many fundamental and generic aspects of such systems can be investigated by means of Monte Carlo (MC) or molecular dynamics simulations [2,3]. One current research theme focuses on the linear elastic response of self-assembled transient polymer gels [1,4] and microemulsions bridged by so-called telechelic polymers [5,6]. A central rheological property characterizing the linear elastic response of such viscoelastic systems is the shear relaxation modulus $G(t)$ as sketched in panel (a) [1,6].

A simple computer model:

Amorphous solids may be modeled by repulsive beads connected randomly and permanently ($f = 0$) using ideal springs (panel (b)). At sufficiently high spring density $\rho_{\mathrm{sp}} > \rho_{\mathrm{p}}$ a *percolating* network [4] is formed. Thermodynamically this corresponds to a finite shear modulus $G_{\mathrm{eq}}(\rho_{\mathrm{sp}})$ as observed from the long-time limit of $G(t)$ [6]. As shown in panel (c), a simple model for self-assembled transient networks is obtained by reversibly bridging the beads assuming a finite recombination frequency f. This is done using local MC hopping moves subject to a Metropolis criterion [6].



Goal of project:

The main aim of the proposed numerical study combing both molecular dynamics and MC techniques is to characterize the ensemble averaged response modulus $G(t)$ for different f and ρ_{sp} and the corresponding equilibrium modulus $G_{\mathrm{eq}}(\rho_{\mathrm{sp}})$ for $f \to 0$. Using ensembles of $m = 100$ configurations we shall also attempt to compute the standard deviations $\delta G_{\mathrm{eq}}(\rho_{\mathrm{sp}})$, especially close to the percolation transition $\rho_{\mathrm{sp}} \approx \rho_{\mathrm{p}}$ where the relative fluctuations $\delta G_{\mathrm{eq}}/G_{\mathrm{eq}}$ could well be of order unity.

Required tasks and workflow:

1. Get acquainted to the existing simulation code;
2. Run one small test system and get $G(t)$ and G_{eq} using the linear response methods described in Ref. [2];
3. Generalize existing code by introducing an energy penalty ϵ_{sp} between springs bridging to the same bead;

4. Sample equilibrated configuration ensembles for different $(\rho_{\rm sp}, \epsilon_{\rm sp})$ at one high recombination frequency f and then at one much lower frequency;

5. Demonstrate that $G(t) \approx G_\star \exp(-t/t_\star)$ for $t_{\rm A} \ll t \ll t_\star(f) \sim 1/f$ with $G_\star$ being a finite plateau modulus, $t_{\rm A}$ a constant local time scale and $t_\star(f)$ the Maxwell relaxation time;

6. Show that $G_{\rm eq} = G_\star$ for all $(\rho_{\rm sp}, \epsilon_{\rm sp})$ by sampling quenched networks ($f = 0$);

7. Demonstrate that $G_{\rm eq}(\rho_{\rm sp})$ becomes finite above a critial density $\rho_{\rm p}$ where the largest cluster of connected springs percolates;

8. Verify that above percolation $G_{\rm eq}(\rho_{\rm sp}, \epsilon_{\rm sp}) \sim (\rho_{\rm sp} - \rho_{\rm p})^\alpha$ with $\alpha \approx 2$;

9. Preparation of internship report and talk.

References:

[1] M. Rubinstein and R.H. Colby, *Polymer Physics*, Oxford University Press (2003).

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[4] D. Stauffer and A. Aharony, *Introduction to percolation theory*, Taylor & Francis (1994).

[5] A. Zilman *et al.*, *Entropic Phase Separation in Polymer-Microemulsion Networks*, Phys. Rev. Lett. **91**, 015901 (2003).

[6] J. P. Wittmer, I. Kriuchevskyi, A. Cavallo and J. Baschnagel, *Shear-stress fluctuations in self-assembled transient elastic networks*, Phys. Rev. E **93**, 062611 (2016).

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