Seeking Topological Glasses

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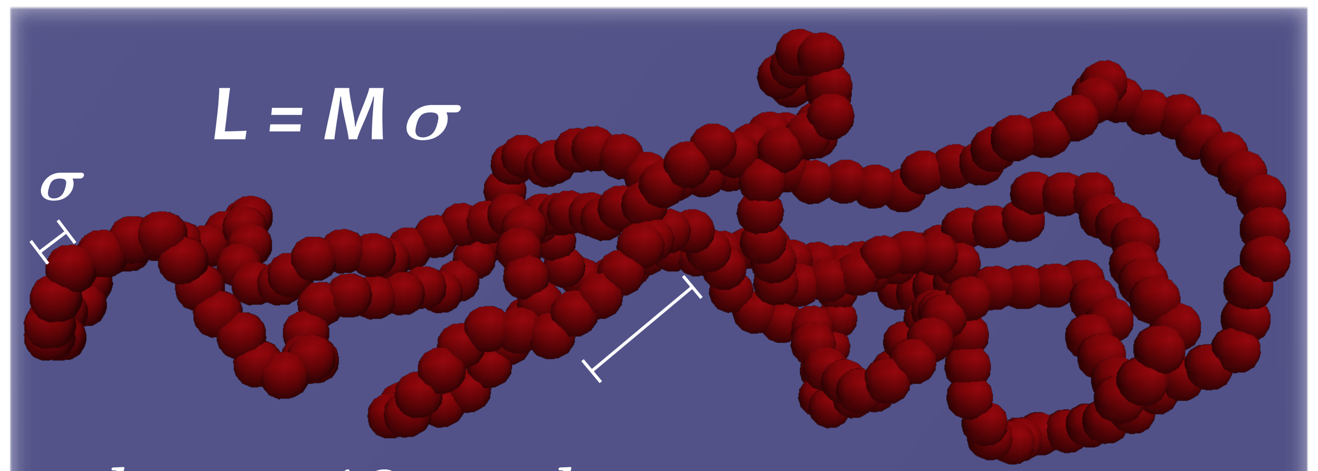
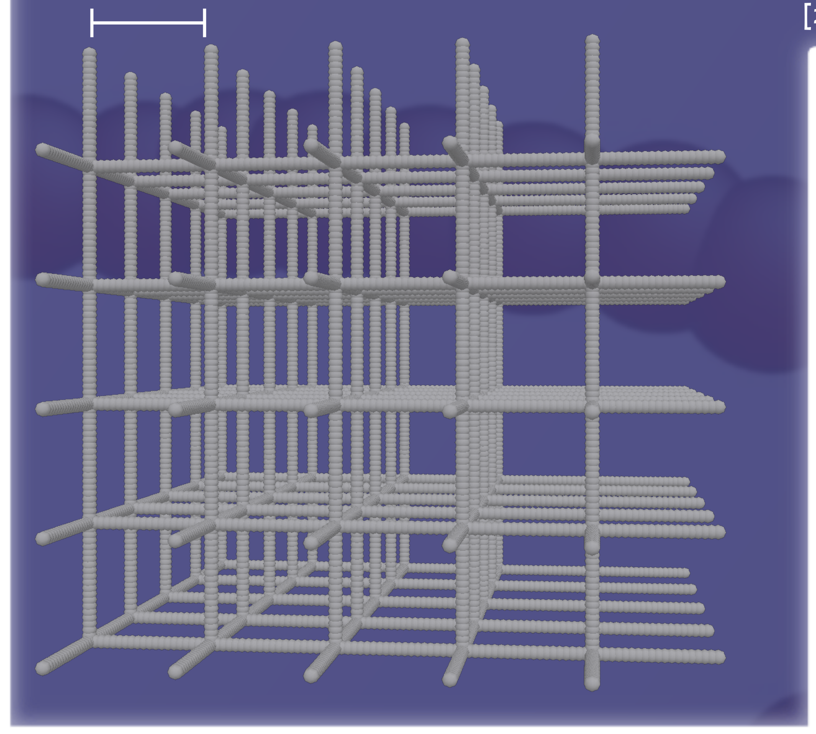
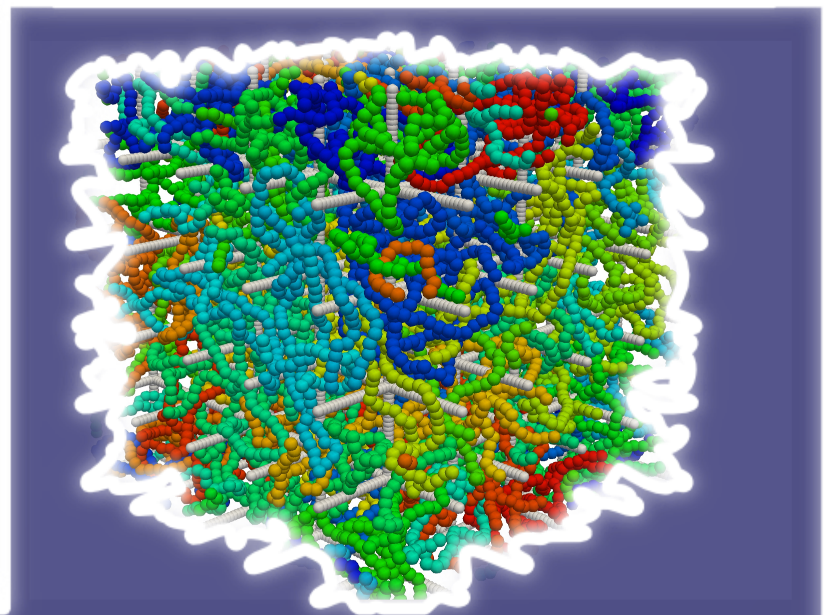
The System

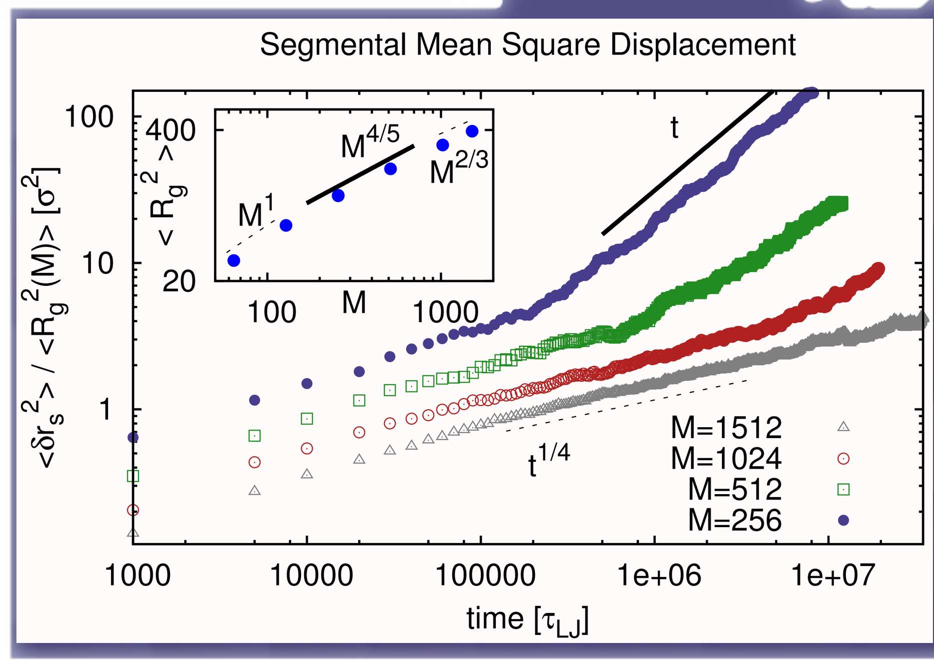


$l_{box} = 10\sigma = l_{Kuhn}$



[1] LAMMPS, http://lammps.sandia.gov
[2] Kremer, Grest. J. Chem. Phys. 92 (1990)





Above a snapshot of the rings diffusing through the gel (pictured on the left). The segmental MSD shows the regimes observed in [4]. R_g (inset) appears to follow three distinct scaling regimes [3].

[3] Halverson et al. J. Chem. Phys. 134, 204904 (2011)
[4] Halverson et al. J. Chem. Phys. 134, 204905 (2011)

Threading and Linking

Each Ring is closed, in turn, by joining every pair of intersections along the faces of the box b.

This ring is labelled with i_b in Eq. (1). The other strands beloging to j are treated as linear chains the ends of which are joined far away from the box.

The Threading number $Th(i,j)$ is then half of the sum over all the unit cubes of the lattice. $Th(i,j)$ is assured to be a natural number since for each thread, two links are needed.

$$2\langle Th(i,j)\rangle = \left\langle \sum_{b=1}^{B} \sum_{j_b}^{N_s(b,j)} Lk(i_b, j_b) \right\rangle \quad (1)$$

B is the total number of unit boxes in the system and $N_s(b,j)$ the number of strands in b belonging to j.

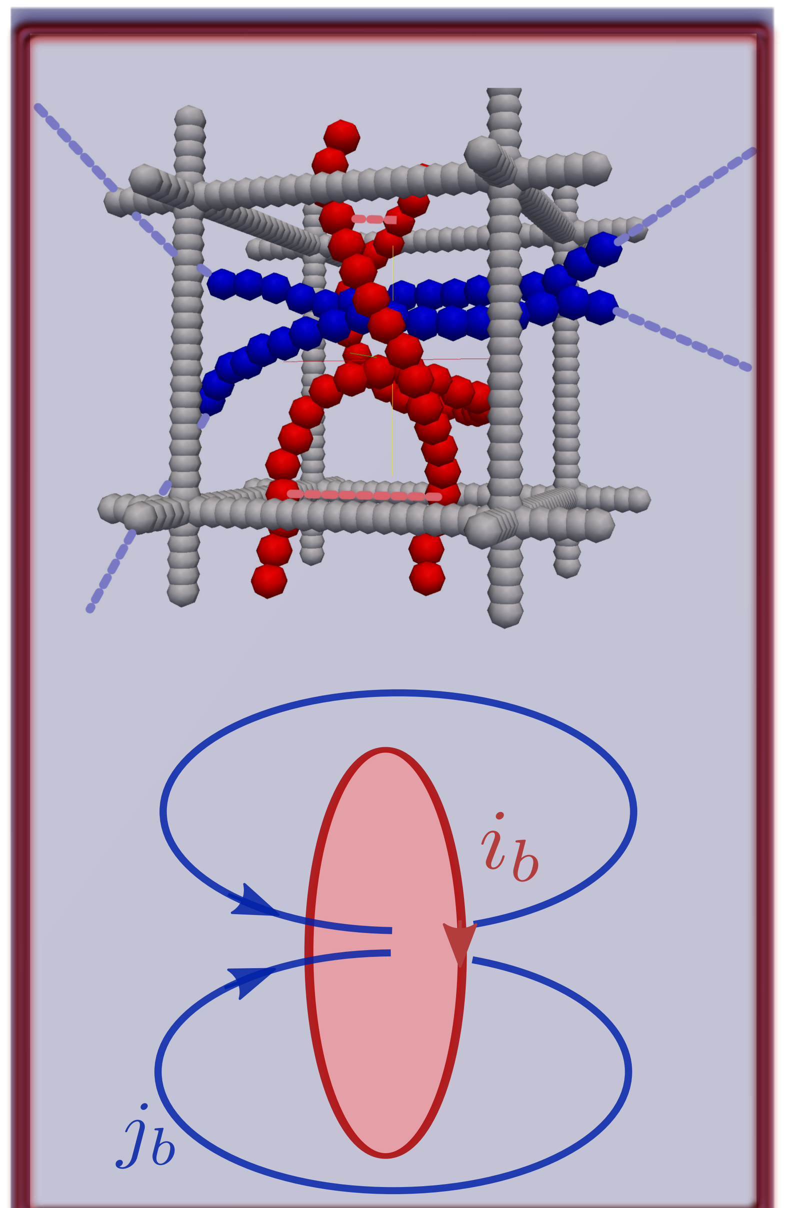


Figure 1. Procedure to identify threadings occurring inside a unit box. The red ring is "closed" at the intersections with the faces of the box. While the blue strands are joined far away from the unit box.

Results

The time correlation between threadings can be studied using Eq.(2).

$$P_p(t) = \mathcal{N} \langle p(i,j;t_0) p(i,j;t_0+t) \rangle_{i,j,t_0} \quad (2)$$

$\mathcal{N}$ is the normalisation and $p(i,j;t)$ is 1 if ring j is threading i at time t.

We observe that $P_p(t)$ decays slower for longer chains, meaning Long-Lived Threadings. The plateau for large t's represents the Background Threading Probability, and can be used to retrieve p_{th}, the Local Threading Probability, via a Mean-Field argument, as in Eq. (3).

$$P_p(t \to \infty) = N_{sb} p_{th} \simeq N_v^2 p_{th} / B \quad (3)$$

N_{sb} is the number of shared boxes of two randomly chosen rings, N_v the number of cells visited on average by a single ring and B the total number of cells.

In Fig. (3) the Number of Threadings per Chain is found to Increase Linearly with the length M. In the inset the local threading p_{th} is observed to be independent from M in the long chains regime.

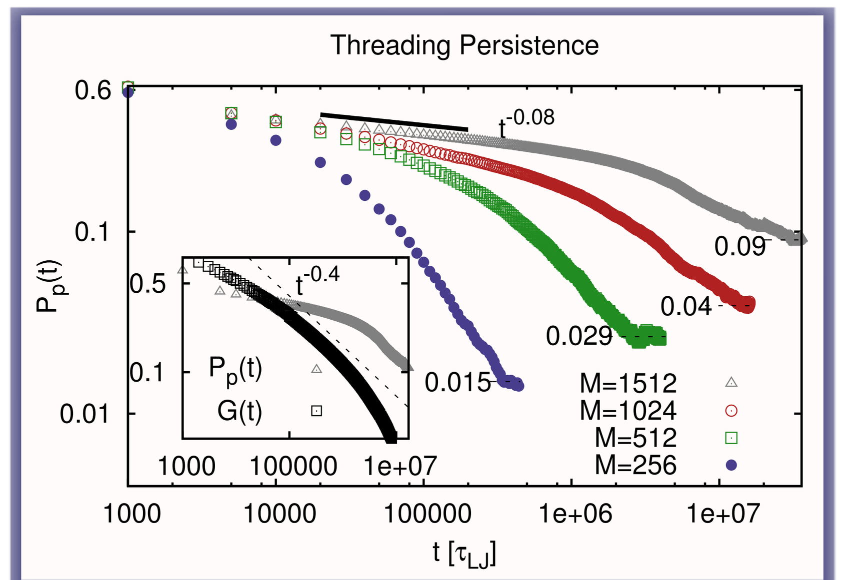


Figure 2. Threading persistence $P_p(t)$ as defined in Eq. (2) for different values of the chains length M. In the inset the Threading Persistence is compared with the stress realxation modulus $G(t)$ which is found to decay as in past experimental works[5].

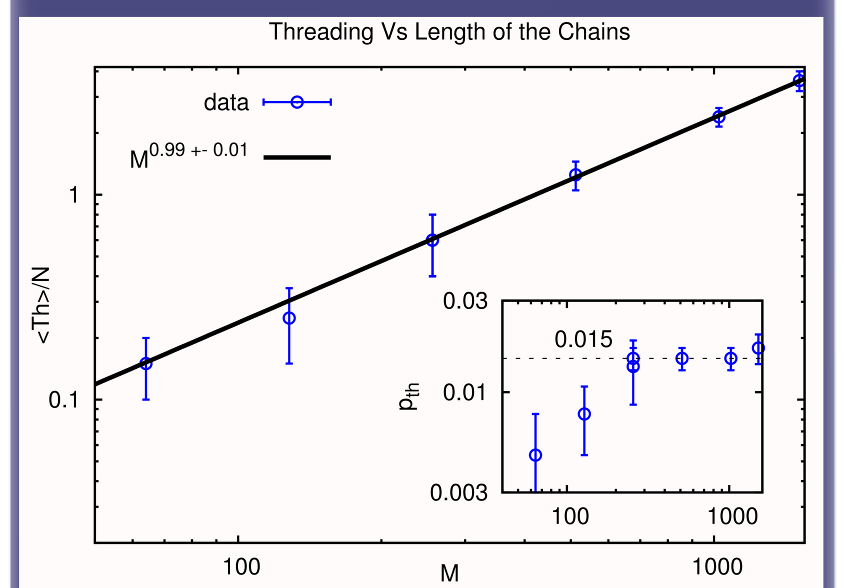


Figure 3. The Number of Threadings per chain, as a function of the chain length M, shows a linear increase. In the inset the Local Probability of Threading is plotted as a function of the length M.

[5] Kapnistos et al. Nature Materials 7 (2008)

Conclusions

Our results clearly indicate the existence of threadings in solutions of rings, as hypothesised in [5] and [6].

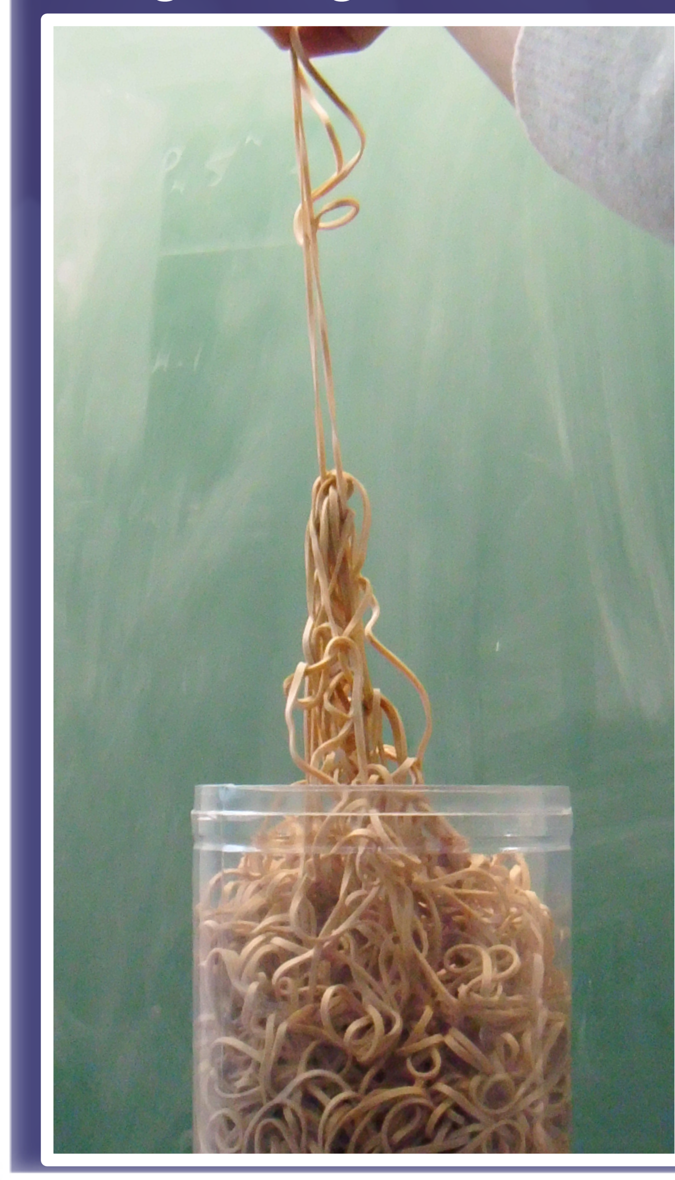
They suggest the emergence (at very large M) of a big large Cluster of Threading Rings. Such configuration would lead to a Topological Glass, with intermediate properties between those of vulcanised and liquid polymeric material.

The scaling of R_g and MSD match with those in melts of rings in [3] and [4].

Our next project is to generalise models describing loops diffusing through a lattice of obstacles to the case where they can be wound around the obstacles, or pins, which get then removed at later times.

[6] Klein. Macromolecules 118,33 (1986)

Pulling the Ring....out of the Hat



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