

# Dynamics of self-threading ring polymers in a gel: Supplementary Information

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## Molecular Dynamics Simulation Details

We model the ring polymers using a standard bead-spring semi-flexible model based on the Kremer Grest<sup>1</sup> model. Every bead in our simulation interacts via a shifted Lennard-Jones potential with a cut-off  $r_c = 2^{1/6}\sigma$ . The gel is itself made of beads which partially overlap in order to preserve the topological status of the ring polymer, *i.e.* unlinked from the gel. The beads in the gel interact only with the beads forming the polymers via the same shifted Lennard-Jones potential. The beads forming the gel are not treated in the dynamics, meaning that the background structure is fixed and static at all times. Nearest neighbour beads along the ring polymers interact via a finitely extensible non-linear elastic (FENE) potential. The non-linear chain's flexibility is then introduced by an angular potential. The total intra-chain potential is therefore given by the following Hamiltonian:

$$H_{intra} = \sum_{i=1}^M \left[ U_{FENE}(i, i+1) + U_b(i, i+1, i+2) \right] + \sum_{i=1}^{M-1} \sum_{j=i+1}^M U_{LJ}(i, j) \quad (1)$$

where  $M$  is the number of beads in the ring and the terms with  $i > M$  represent those interactions needed to join the ends of the polymer in a ring fashion, *i.e.* a modulo- $M$  indexing is implicitly assumed to take into account the ring periodicity. Each monomer has nominal size  $\sigma$  and position  $r_i$ , while the distance between two monomers  $i$  and  $j$  is given by  $d_{i,j} = |r_i - r_j|$ . The finitely extensible non-linear elastic potential is of the form:

$$U_{FENE}(i, i+1) = -\frac{k}{2} R_0^2 \ln \left[ 1 - \left( \frac{d_{i,i+1}}{R_0} \right)^2 \right]$$

for  $d_{i,i+1} < R_0$  and  $U_{FENE}(i, i+1) = \infty$ , otherwise;  $R_0 = 1.5\sigma$ ,  $k = 30 \epsilon/\sigma^2$  and the thermal energy  $k_B T$  is set to  $\epsilon$ . The

bending energy, or stiffness term, takes the standard Kratky-Porod form (discretized worm-like chain):

$$U_b(i, i+1, i+2) = \frac{k_B T \xi_p}{\sigma} \left[ 1 - \frac{d_{i,i+1} \cdot d_{i+1,i+2}}{d_{i,i+1} d_{i+1,i+2}} \right]$$

where  $\xi_p$  is the persistence length of the chain which is fixed at  $5\sigma$ . Polymers are significantly bent by thermal fluctuations at contour lengths larger than the Kuhn length  $l_k = 2\xi_p$ . Here, the persistence length  $\xi_p$  is always assumed to be much smaller than the total length of the chain, so that the chains resemble a flexible polymer, rather than a rigid rod. The 'cut and shifted' Lennard-Jones potential takes the following form:

$$U_{LJ}(i, j) = 4\epsilon \left[ \left( \frac{\sigma}{d_{i,j}} \right)^{12} - \left( \frac{\sigma}{d_{i,j}} \right)^6 + 1/4 \right]$$

for  $d_{i,j} < 2^{1/6}\sigma$  and  $U_{LJ}(i, j) = 0$ , otherwise. The same potential is also used to regulate all the pair interactions between monomers belonging to the chain and the fixed mesh. The chain-mesh Hamiltonian is:

$$H_{chain-mesh} = \sum_{k=1}^{M_{gel}} \sum_{i=1}^M U_{LJ}(k, i) \quad (2)$$

the index  $i$  runs over the beads in the chain and  $k$  runs over the beads forming the mesh. The bead mass is  $m$  and the friction acting on each bead is set to  $\xi/m = \tau_{LJ}^{-1}$ . The integration is performed in the over-damped limit of the Langevin equation using Verlet algorithm with time step  $\Delta t = 0.01 \tau_{LJ}$ , as in previous works<sup>2,3</sup>. The ring is initialised outside the mesh in a easily parametrisable fashion. Initially, a short run is performed where instead of the Lennard-Jones potential, we employ a soft repulsive potential between bonded beads with energy  $E_s = 40\epsilon$  and cutoff  $r_s = 2^{1/6}\sigma$ . In this way we gently push the bonded monomers apart and avoid numerical blow ups. After this short run, the soft potential is replaced by the Lennard-Jones potential described above. At this point we drag the polymer inside the mesh by applying an external force on some of the monomers. Once the ring is completely contained in the gel we adapt the simulation box in order to perfectly fit the size of the gel and test the ring topology. If the ring is in a unknotted state we proceed with the equilibration run.

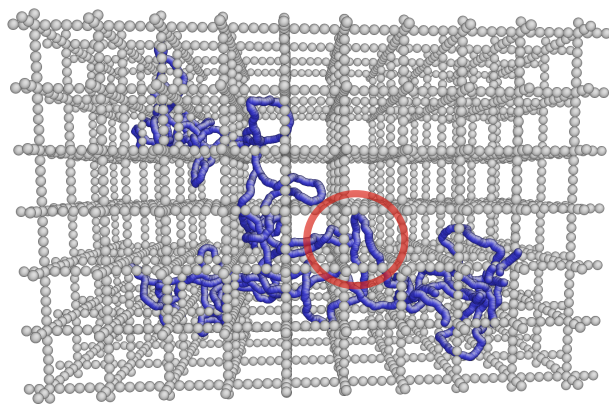
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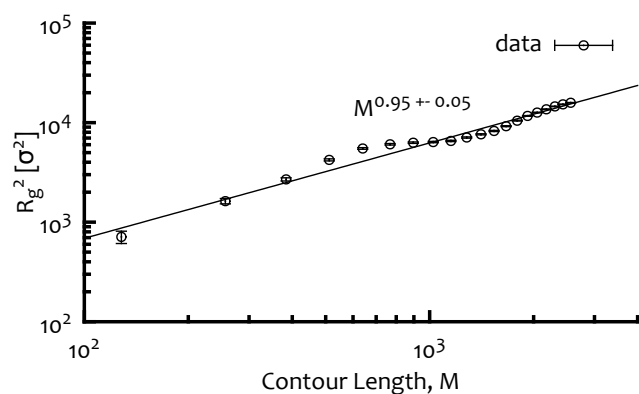
## Equilibrium Configuration

The presence of the gel with lattice spacing comparable with the polymer Kuhn length forces the chain to spread across multiple unit cells. The equilibrium configuration resembles that assumed by a lattice animal (see Fig. 1).



**Fig. 1** Equilibrium configuration of the ring polymer in gel. The shape resembles that of a lattice animal. Highlighted in red, two segments of the chain which are about to self-thread. The gel structure is here thinned for clarity.

In order to study the scaling of the gyration radius of the polymer we compute  $R_g^2$  of portions (much longer than the Kuhn length) of the chain. Our findings are shown in Fig. 2. We report a scaling law  $R_g^2 \sim M^{0.95 \pm 0.05}$  that is in agreement with the values of  $\nu$  found in the main text.



**Fig. 2** Radius of gyration squared  $R_g^2$  for different contour lengths, averaged over different starting points along the chain. The fit suggests values of the entropic exponent  $\nu$  in agreement with those found by the Kinetic Monte Carlo approach described in the main text.

## References

- 1 K. Kremer and G. S. Grest, *The Journal of Chemical Physics*, 1990, **92**, 5057.
- 2 J. D. Halverson, W. B. Lee, G. S. Grest, A. Y. Grosberg and K. Kremer, *The Journal of chemical physics*, 2011, **134**, 204904.
- 3 J. D. Halverson, W. B. Lee, G. S. Grest, A. Y. Grosberg and K. Kremer, *J. Chem. Phys.*, 2011, **134**, 204905.