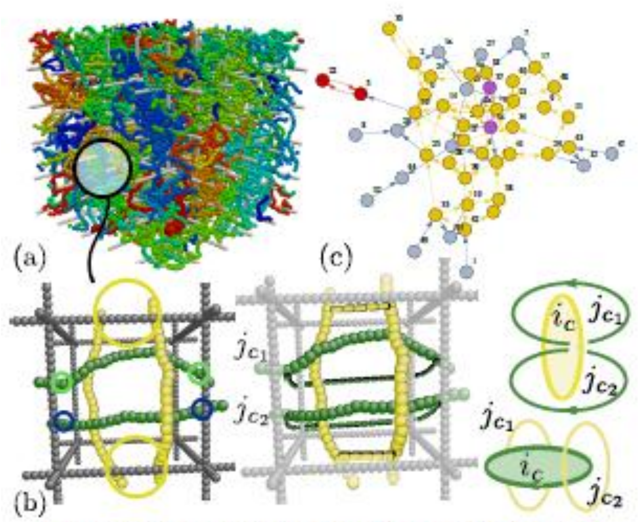
Threading dynamics of ring polymers in a gel

D Michieletto[1], D Marenduzzo[2], G P Alexander[1], E Orlandini[3] and M S Turner[1]

[1]Complexity Science DTC, University of Warwick, UK, [2]Department of Physics, University of Edinburgh, UK, [3]Department of Physics, University of Padua, Italy



(a) Snapshot of our system. (b) Snapshot of the threading of two chains indicating the closure construction that we employ for threading detection. (c) Snapshot of the directed network of inter-penetrating rings.

Ring polymers continue to present a challenge to the theoretical community as the polymers lack of ends represents a severe topological constraint on their conformations, especially when diffusing through a gel. In particular, threadings between rings have always been conjectured to play an important role in solutions of closed chains, from the work of Klein (Klein, Macromolecules 118 (1986)) to more recent ones (Halverson et al, J. Chem. Phys. 134 (2011)), but always proved very hard to detect and quantify. We performed large-scale Molecular Dynamics simulations of a concentrated solution of unknotted, unlinked rings in a background gel made up of a three dimensional cubic lattice of static polymer segments with lattice spacing equal to the chains Kuhn length (Fig. (a)), in order to detect inter-ring penetrations. We took advantage of the ordered architecture of our gel to unambiguously identify inter-ring threadings by measuring the linking of closed curves (Fig. (b)). We show that some of threadings have a life-time that is at least comparable to that of the longest relaxation time of the chains and argue that they may be much longer for longer chains than those we were able to simulate here. The achievement of an adequate description of inter-ring interactions could explain most of the confusion on the macroscopic properties of solutions of rings, where, on top of a fast diffusion, one can observe very long lived correlations. Finally, we compare our system to an evolving (directed) network of penetrating rings (Fig. (c)) and suggest that, in the limit of very long chains, a spanning connected component of threading rings may emerge, which would then exhibit very slow (glassy) dynamics at the scale of centre of mass motion for each chain, while retaining substantially unhindered motion at the level of individual chain segments. Having observed that the number of threadings per chain grows linearly with the length of the rings, we conjecture that such a topological glass is bound to emerge in the limit of very long rings.