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Ring polymers diffusing in a gel: Topology and dynamics

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Since the pioneering work of Edwards and de Gennes the dynamics of polymers in the melt has been understood using the tube and the reptation models. However, ring polymers continue to present a challenge to the theoretical community as the polymers lack of ends represents a severe topological constraint on the polymer configurations. This constraint is even more important when the rings are forced to diffuse through a gel. Polymers in the melt have often been compared with single chains diffusing trough a background of obstacles. However, a comprehensive description of dynamics of ring polymers moving in a gel is not yet available. We performed Molecular Dynamics simulations of a concentrated solution of un-knotted, un-linked 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. We observed some macroscopic similarity with the behavior of a pure melt of rings. This includes the crossover to globular state for long rings and the fact that loops have to travel many times their own size before reaching free diffusion $\langle \delta r_s^2 \rangle \sim t$. The novel aspect of this work is focused on the strategy employed to identify inter-ring penetrations. We take advantage of the ordered architecture of our gel to identify the inter-ring penetrations via linking of closed curves (Fig. (b)). Penetrations have always been conjectured to play an important role in solutions of rings, from the work of Klein in 1986 [1] to more recent studies [2], but they always proved very hard to observe and quantify. We report a method to unambiguously detect inter-ring penetrations and show that some of them 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 we ere able to simulate here. Finally, we compare the system to an evolving (directed) network of penetrating rings (Fig. (c)) and suggest that, in the limit of very long chains, a single 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 threading per chain grows linearly with the length of the rings, we conjecture that such topological glass is likely to emerge in the limit of very long rings.

References

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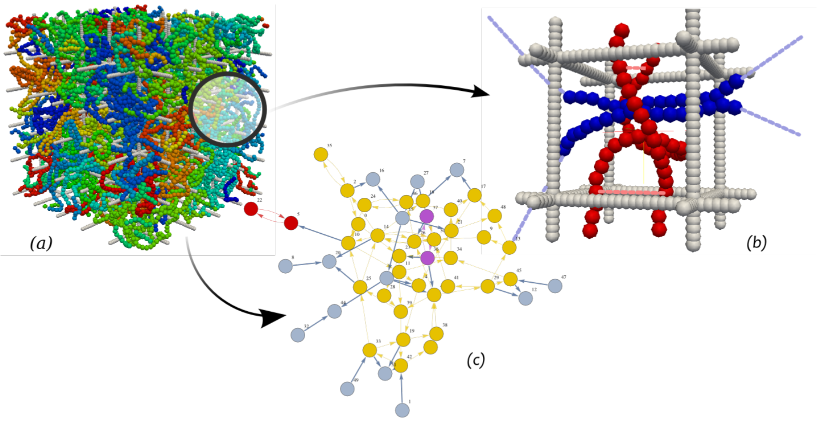

Figure 1: (a) Snapshot of our system. (b) Snapshot of a two chains configuration where the blue one is threading through the red one inside of one cubic lattice cell, bounded on the edges by gel polymer. Light red and light blue dotted lines indicate the asymptotic closure construction that we employ in order to identify threading, using a standard topological measure of contour linking. (c) Snapshot of the directed network of inter-penetrating rings. Notice the emergence of a spanning connected cluster (yellow), and smaller ones (red, purple).