How random are knots in polymers?
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Knots as a Topological Order Parameter for Semiflexible Polymers
Phys. Rev. Lett. **116**, 128301 (2016)
arXiv:1506.07376
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How knots in polymers are formed and to what extent there are specific selection rules has been a matter of extensive research. This is not only an interesting topic by itself, but also is of relevance to protein folding and conformation. Some years ago Kardar and coworkes[1, 2] studied knotted polymers subject to a variety of constraints. These constraints usually lead to rather tight knots. For instance, when a chain is put under oscillatory external tension, like transverse oscillations of a skipping rope, not only the knot might be pulled tight, it might also be localized in a specific way[3]. At the same time the appearance of specific knots has been viewed as a random process, originating from the fact that for standard (self avoiding) walks each accessible conformation should have the very same probability. There have been many studies on the statistics of knotted ring polymers searching for the chain length dependence of different classes of knots. While this applies to homopolymers, the question of encoding specific conformations, i.e. specific knots in this case, into the sequence of the chain is of immediate relevance to protein folding[4]. How complex is such a code, or how many letters does one need etc. Even more so this eventually also holds for the pathway of folding, which would be needed for (bio-)physical processes. To enhance the knotting probability it seems sufficient to add a few adhesive sites along the backbone of the chain[5]. However this does not yet say anything a priori about the type of knot. Parallel to that, extensive simulation studies on the collapse transition of semi-flexible polymers have been performed, displaying coiled, collapsed, crystallized, frozen, bent, hairpin and toroidal conformations, depending on details of the interactions such as the ratio of bond length versus range of effective attractions etc.[6]. While this still applies to simple homopolymers, the situation for proteins of course is much more complicated. Virnau et al.[7] scanned the whole Protein Data Bank (http://www.pdb.org) and identified 36 different proteins forming relatively simple knots, none of which has more than five crossings. A very recent work [8] suggests that randomly sequenced HP polymers have a higher probability to form knots than proteins (somehow it seems that evolution tries to avoid knotted proteins[9]).

In this context I find it interesting that Marenz and Janke[10] recently found a new kind of pseudo phase for semi-flexible bead-stick homopolymers. 'Pseudo' refers to the fact that the phases depend on the size of the polymer. The 'phase diagram' is best characterized by specific distinct thermodynamically stable (or quasi stable because of the finite size of the systems) knots, depending on chain length, chain stiffness and temperature. The transition into different knots displays further interesting aspects. Detailed microcanonical simulations revealed that different conformations can have the same energy, thus the thermodynamic stability of the specific knots is determined by the density of states of a specific topology compared to other states, which is directly accessible by such simulation protocols. We

generally intend to investigate soft matter problems on the level of rather generic properties. This still rather simple example shows, that one has to keep the interplay of systems specific and generic aspects in mind and that finite size effects might lead to interesting, qualitatively different properties.

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