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FINAL REPORT
"RINGEFF"
Effective interactions and correlations of ring polymers

PEOPLE
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Contents

1 Publishable summary

1.1 Introduction

Polymers and polymer composites play a key role in developing state-of-the-art, modern, technologically advanced and intelligent materials, as a result of their wide-ranging physical properties and the possibilities of modifying the same in mixtures (composites) with other ingredients. Polymers are also common in our lives as natural (wood and natural rubber) and synthetic (oil and natural gas) materials. In addition, the newest developments in biology and medicine focus on the study of such natural polymers as proteins, RNA and DNA. RNA and DNA are usually very long polymers (10^5 – 10^6 monomers), and are often found are in a knotted conformation, since the probability of a finding a knotted chain approaches unity when the length of the same goes to infinity [1]. These polymers can be open (linear polymers) or closed (both ends connected with one another, i.e., ring polymers) knotted or not. In all cases, the mathematical concept of *topology* and its significance for the physical properties comes into play. Proteins can display several topologies as well but, in this case, their length is not the reason why they could be knotted [2, 3] because they are smaller ($100 - -5000$ monomers). As a matter of fact, it is not clear at all why they are knotted or what are the properties/benefits of knotedness.

Analytical descriptions of the statistical mechanics of polymers with topological constraints are very complicated. This is due, mainly, to the difficulties in including topological constraints in the system's Hamiltonian. Consequently, numerical studies with computer simulations are the most common way to study this problem. Unfortunately, fully detailed computer simulations of big polymers, such as DNA or RNA, are difficult to perform due to limited computational power available. This problem can be overcome if **coarse-graining** techniques are considered. This procedure, based in scaling arguments of deGennes [5], achieves a bridging of the length scales from the microscopic to the mesoscopic one, and amounts to replacing the full, microscopic (monomers) degrees of freedom of the rings with either a single one (e.g., their center of mass) or a few ones in the language of the 'blobs', see figure 1.1. The main goal is to trace out the monomers and derive a mathematical object named *effective interaction* [6], $V_{\text{eff}}(r)$, where r denotes the separation between the centers of mass of two rings, see figure 1.2. It is suitable when the relevant motions take place at time scales that are longer than the ones involved in microscopic motions, and the length scales of interest are correspondingly longer than the size of microscopic movements. The scale that we are interested in is *mesoscopic*, i.e., of the order of the radius of gyration R_g, of a ring polymer. At this scale and for athermal solvents, the microscopic details of the rings should be immaterial, resulting thus in a *universal* effective interaction $V_{\text{eff}}(r) = k_{\text{B}}T f(x)$, where k_{B} is Boltzmann's constant, T is the absolute temperature and $x \equiv r/R_g$. The function $f(x)$ is thus independent of the degree of polymerization n, yet it does depend on the topology of the polymer; it has different forms for chains, unknotted or knotted rings.

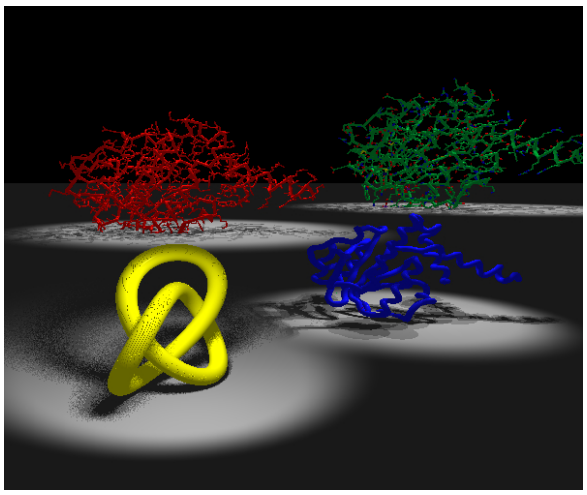

Figure 1.1: *Cross-grainned process for a real knotted protein named TrmH [4] (Protein Data Bank). From up to down: real protein;protein not consider kind of atoms;protein chain; and finally, topology of the chain (trefoil).*

The RINGEFF project was mainly focused on the role of topological constraints in coarse-graining methods. Our approach was fully computational and the simplest topologies were considered. The *results* obtained are *universal*, i.e., independent of microscopic polymer details, and they can be *applied in any field of polymer science* that needs computational simulations with topological constraints (drug design, chemistry, etc). In addition, new algorithms and techniques were developed from scratch to achieve these results.

1.2 Results and Conclusions

Within the RINGEFF-project, we obtained $V_{\text{eff}}(r)$ for different microscopic potentials (HS, LJ, LJ-24,6), polymer sizes (20-2000 monomers) and several topologies: Linear, ring, trefoil 3_1, and 5_1 topologies. We have thus been able to show that topology is a very important feature in polymer physics, at mesoscopic length scales (R_g) and at dilute/semi-dilute regimes, see figure 1.2. The feature observed in $V_{\text{eff}}(r)$ is independent of the microscopic potentials (microscopic details) that we considered. The $V_{\text{eff}}(r)$ calculated are valid up to the ring overlap concentration, see [7] for more deltais.

To extent the range of validity of coarse-graining, we also have increased the level of detail on this approximation applying the *"blob"* picture. In this framework, we have performed simulations with "soft potentials" preventing cross-linking, and obtained similar results with those from full monomeric resolution. This was the main goal in this project, since it reduces enormously the computational effort and, at the same time, include the ingredient of the topology in simulations. A key deliverable/achievement was the creation of a new algorithm to prevent crossing since we are dealing with "soft potentials", in which conservation of topology be satisfied [8]. In addition, during this project a very detailed analysis of the polymer shape was performed, to clarify the mass distribution of the polymer and to rationalize our results by treating rings as interpenetrating ellipsoids [9].

Finally, in RINGEFF we were able to analyze the interplay between topology and the solvent quality. This is a well known feature on linear chains but unexplored to-date with other topologies as ring, trefoil and 5_1 polymers. In this framework, we discovered that the more complicate is the topology, the lower the temperature at which the polymer achieves Gaussian statistics [10].

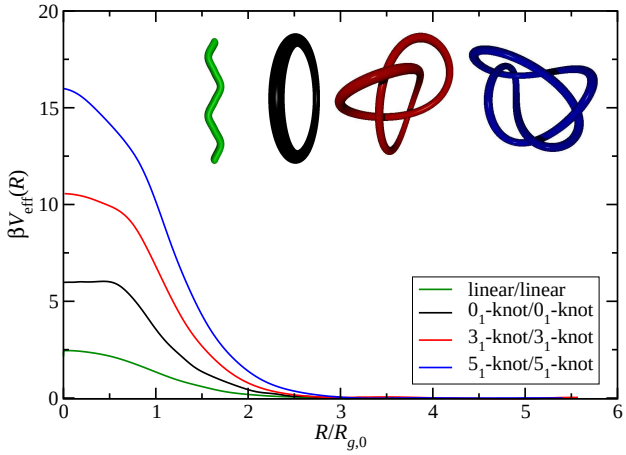

Figure 1.2: *Main plot: Comparison of the effective pair interaction potentials between the centers of mass of two linear, unknotted (0_1-knot), 3_1-knotted, and 5_1-knotted ring polymers with degree of polymerization $N = 100$, as indicated in the legend. Inset: analytically generated mathematical curves that demonstrate the linear, unknotted, 3_1-knot-, and 5_1-knot topologies (from left to right and color-coded as in the main plot).*

The RINGEFF project results could be applied in many fields of biology, medicine and new material design. They bring forward the ingredient of topology as an important property to take into account in, for example, DNA studies, knotted proteins and enzymology of DNA replication. In addition, the project put forward novel coarse-graining techniques with topology to simulate bigger scale systems, those necessary to design and studying of biology and medicine. Thereby, the benefits of this project could include many parts of the society, since biology and new materials science are two fundamental basis of the technological society of nowadays. At the same time, EU research have an step forward in a very unexplored field of polymers with topological constraints.

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