Entanglement in non-concatenated ring polymers

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Abstract

Polymer melts and solutions are composed by many macromolecules of varying architectures, which we can see as mathematical curves in space. The entanglement of these macromolecules is related to the mechanical properties of the material. In simulations, in order to avoid boundary effects, Periodic Boundary Conditions (PBC) are used. The periodic linking number is a measure of pairwise entanglement of chains in a system employing PBC. Closed chains with zero pairwise linking can form higher order entanglement that is not detected by the periodic linking number. In this work, using the periodic linking number and properties of the Gauss linking integral for open curves, we provide a method to detect such entanglement.

Introduction

Physical systems that are filamentary, that is threadlike in structure, can experience entanglement. A solution of macromolecules like DNA or polymers is one such example that is susceptible to entanglement. Specifically, we identify entanglement in terms of linking and knotting which can be described with tools from topology. In this sense, a knot (or link) is one or more simple closed curves in space. They are classified with respect to their complexity by topological invariants, like knot polynomials. The phenomena of linking/knotting can have mechanical consequences and influence both the physical properties and function of a macromolecule.

We created a script to calculate measures of entanglement of chains in a polymer melt. We looked at observations obtained from molecular dynamics simulations, employing periodic boundary conditions: a collection of 1600 rings, 400 monomers in length each from (2)

Measures of Entanglement

Finite form of Gauss linking integral:
L is the Gauss linking integral, considering two polygonal curves, consisting of edges $e_i = 1, \dots, n; r_j, j = 1, \dots \mathrm{m}$ then

$$\mathrm{L}(l_1, l_2) = \sum_{i=1}^{n} \sum_{j=1}^{m} L(e_i, r_j)$$

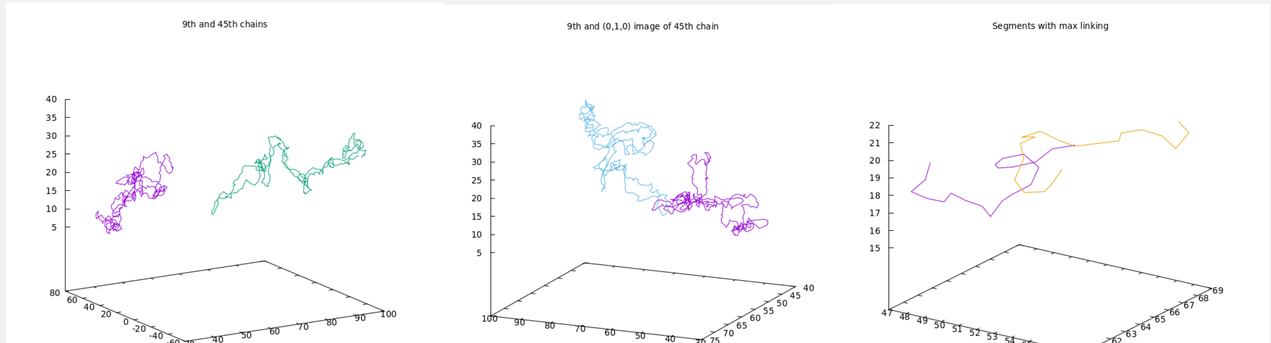
Local Periodic Linking Number: (LKP)
The linking number between any two "free chains" of a periodic system. This is a summation of the linking numbers between a minimal unfolding, or representation, and an all intersecting images, or copies, of a second free chain.

$$LK_p(I, J) = \sum_{1 \le v \le k} L(I_u, J_v); I_u = \text{minimal unfolding of image}$$

Segmented Linking:
Calculation of linking number between any two arbitrary segments of any two given free chains I, J_v where v denotes a translation vector. The length of the segment can be passed as a function parameter.

Results

We analyzed data provided from (2) and computed measures of entanglement via a C++ script for the 9th and 45th rings (out of the collection of 1600).
We were able to calculate the LKP of this pair and further determined the segmented linking between the 9th chain and all images of the 45th.



Conclusions

The figures above are plots of our rings and segments responsible for linking. Our first plot is a plot of the two rings in question from our collection. The second is identical with the exception that the second ring has been translated by $(0, l, 0)$; We can see that the two intersect. This image was responsible for the largest linking value in context with all other images. The furthest right plot is the segment pair that produces the largest linking value.
The method utilized is computationally intensive but can be implemented to determine the entanglement of any pair of rings in a collection. In addition, the segments of rings which produce larger values for linking can be easily determined to located components responsible for more linking. Upon successive calculations, we saw that small segments could often have a larger effect on entanglement than larger segments.

References

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