

Eternally green Flory theory

1. Effects of topological constraints on linked ring polymers in solvents of varying quality

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2. Circular Polycatenanes: Supramolecular Structures with Topologically Tunable Properties

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Flory theory is perhaps the simplest and the most successful theory computing non-trivial critical exponents in just one line. In its classical form, it treats linear polymers with self-avoidance. Why exactly it is so accurate is not entirely clear (at least to the present writer), despite some comments by De Gennes [1]. Original Flory theory is based on the minimization of the sum of two competing terms in free energy, one describing polymer elasticity and the other repulsion between monomers, and De Gennes makes an important point that both terms are inaccurate but one should not try to improve them, especially each of them separately.

Of course, these questions are purely academic, because classical self-avoidance is well described by the regular field theoretic machinery stemming from the $n = 0$ theorem [1].

Over the years, numerous modifications of Flory theory were developed in a variety of contexts, and more frequently than not they were also quite successful. Paraphrasing E.Wigner [2], we can talk of an “unreasonable effectiveness of Flory theory”. In many such applications, rigorous field theoretic treatment is not available. The first of the recommended papers, by Dehaghani et al, delivers one such example. It treats the so-called poly[n]catenane - a system consisting of many sequentially catenated polymeric rings, illustrated in the Figure 1. What would be the size (e.g., the gyration radius) of such an object, R ? Following quite directly the Flory prescription, Dehaghani et al minimize the free energy (in the units of $k_B T$)

$$F = F_{\text{elast}} + F_{\text{int}} , \text{ with } F_{\text{elast}} = \frac{R^2}{Na^2} , \text{ and } F_{\text{int}} = \frac{N^2 v}{R^3} . \quad (1)$$

The question is how to interpret parameters N , a , and v . Seemingly in contradiction with De Gennes, authors claim that good agreement with simulations is achieved by the following

“asymmetric improvement” of Flory theory. In the interaction term, they assume $N = nm$ the total number of monomers (see notation in the Fig. 1), and $v = b^3$ the excluded volume of one monomer, dictated by monomer length scale b . At the same time, in the entropic elasticity term they suggest to view N as the number of connected rings, $N = n$, while a as the size of one ring (and not the monomer scale), $a = bm^\nu$ (with $\nu \approx 3/5$ standard Flory exponent). Thus, the overall ansatz reads

$$F = \frac{R^2}{nm^{2\nu}b^2} + \frac{n^2m^2b^3}{R^3} \implies R \sim bn^{3/5}m^{16/25}. \quad (2)$$

This appears to work well with simulations. What some of us could think more logical, when excluded volume in the interaction term is taken to be the volume of one ring, $(bm^\nu)^3$, and the number of interacting units $N \rightarrow n$, does not work at all. Thus, Flory theory has hidden surprises.

Flory theory (and theory in general) aside, these poly[n]catenanes is a very interesting system. Unlike regular linear polymers, and similar to double stranded DNA or actin, these objects possess torsional rigidity - of purely topological origin. Second of the recommended papers, that by Tubiana et al, examined super-rings made of many interlocked rings. Because of torsional rigidity, these super-rings may form structures not unlike plectonemes familiar from closed circular DNA and, in general, they are the subject of all mathematical beauty of the famous Călugăreanu theorem (see also [3, 4]).

Writing this comment, I thought that Flory theory remains fresh, productive and puzzling for so many years, and this reminded me of the statement by Johann Wolfgang von Goethe, which seems a fitting end to this comment: “All theory is gray, my friend. But forever green is the tree of life” (“Grau, teurer Freund, ist alle Theorie, und Grün des Lebens goldner Baum”).

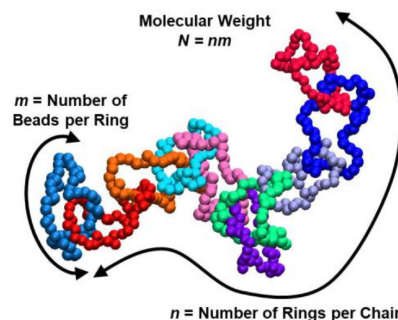


Figure 1: Cartoon of poly[n]catenane. Image copied from paper [3].

References

- [1] P.-G. de Gennes, “Scaling Concepts in Polymer Physics”, Cornell University Press, Ithaca, 1979.
- [2] E.P.Wigner, “The unreasonable effectiveness of mathematics in the natural sciences”, Communications on Pure and Applied Mathematics, 13, 1, 1960.
- [3] P.Rauscher, S.Rowan, J. de Pablo “Topological Effects in Isolated Poly[n]catenanes: Molecular Dynamics Simulations and Rouse Mode Analysis” ACS Macro Lett. 7, 938, 2018.
- [4] P.Rauscher, K.Schweizer, S.Rowan, and J. de Pablo “Thermodynamics and Structure of Poly[n]catenane Melts”, Macromolecules 53, 3390, 2020.