

# ON THE TOROIDAL AND CRYSTALLINE GLOBULES IN DILUTE HOMOPOLYMER SOLUTIONS

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Conformational transitions of semi-flexible polymers have been of considerable interest for analytical studies [1, 2] and computer simulations [3, 4] recently. It is well known that folding of a sufficiently stiff chain results in formation of a torus. Importantly, the transitions coil-to-torus and torus-to-globule are discontinuous, and thus there are associated regions of metastability. This results in a rather complex kinetic picture of expansion or folding, essentially dependent on the quench depth [5].

Here we study the conformational states of semi-flexible and stiff homopolymers in infinitely dilute solutions by means of the Gaussian variational theory [6] and Monte Carlo simulation in continuous space [7].

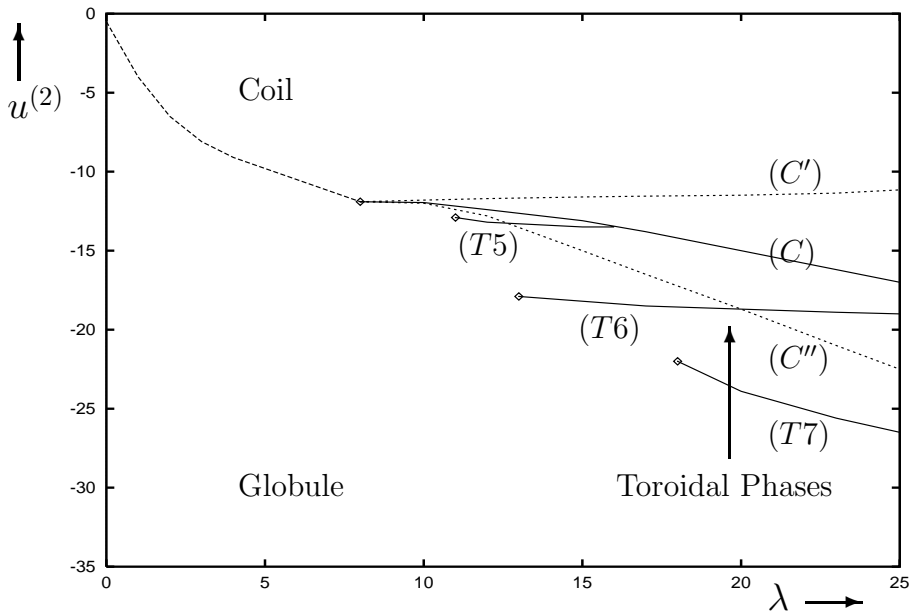


Figure 1. Phase diagram of the stiff homopolymer in terms of the stiffness,  $\lambda$ , and the second virial coefficient,  $u^{(2)}$ , for  $N = 100$ . Here (C) is the collapse transition curve, and (T5)-(T7) are toroidal states with the winding number  $\mathcal{N}_w = 5, 6, 7$ .

The phase diagram of the stiff homopolymer obtained from the Gaussian variational method is presented in Figure 1. It is found to contain phases of the coil, where monomer attraction is insufficient to form compact states, the globule in the region of either a low stiffness or a strong monomer attraction, and a number of toroidal phases characterised by distinct winding number  $\mathcal{N}_w$ . The collapse transition changes its behaviour from continuous to discontinuous starting from some value of the stiffness. The globule of a semi-flexible polymer (see Figure 2a) is different in the local structure from that of the flexible homopolymer, although global scaling characteristics are the same for both cases. The toroidal phases (see Figure 2b) lie in the intermediate region in  $u^{(2)}$  starting from some critical values of the stiffness parameter. The transition curves separating such states from each other, as well as from the coil and the spherical globule, all correspond to discontinuous transitions and terminate in critical points. For a given sufficiently large degree of polymerisation  $N$  there exist a certain number of different toroidal states, which grows with  $N$  approximately linearly. The existence of the toroidal states

has been also confirmed by off-lattice Monte Carlo simulation for the similar model of local stiffness. In addition, hairpin conformations with abrupt U-turns corresponding to metastable states have been observed (see Figure 2c). These appear as nonequilibrium intermediaries during kinetics of folding.

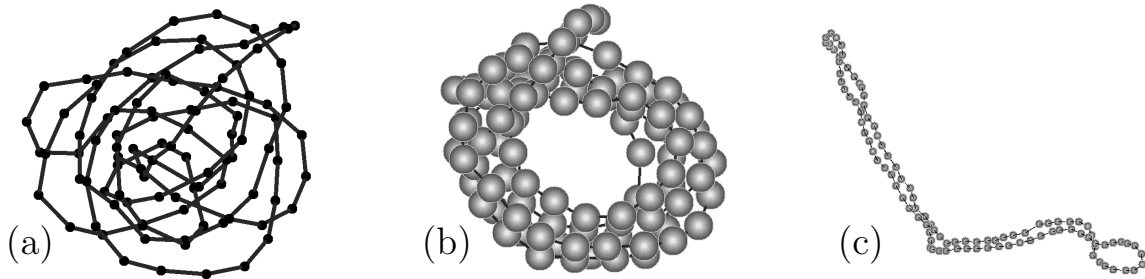


Figure 2. Snapshots of typical conformations of the stiff homopolymer with  $N = 100$ . Figures (a)-(c) correspond to the globule of a semi-flexible homopolymer, the toroidal globule and a “hairpin” kinetic state respectively.

We believe that the existence of the toroidal states is pretty much related to the choice of the bending energy as the square of the local curvature of the chain. Indeed, such a choice is natural for representing the persistent flexibility of polymers. This mechanism of flexibility is dominant for many helical or rather stiff chains such as DNA. The rotational-isomeric flexibility due to rotation around carbon-carbon and other bonds is also very important for many polymers. For representing this mechanism of flexibility a model with discrete bending angles is more appropriate. Such models, however, possess crystalline solid-like states [3] instead of toroidal ones.

We find crystalline structures present in our Monte Carlo simulation even for a flexible homopolymer at sufficiently low temperatures. The transition of a liquid-like globule to a solid crystalline globule is discontinuous and results in a significant change of the pair monomer correlation function. The correlation function has characteristic peaks at separations equal to  $dn$ , where  $d$  is the excluded volume diameter and  $n = 1, 2, \dots$  for the liquid state, while at separations equal to  $d\sqrt{n}$  for the solid state. Moreover, the different-time correlation functions exhibit extremely slow dynamics for the crystalline globule.

## References

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