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A semi-flexible attracting-segment model of three-dimensional polymer collapse

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HIGHLIGHTS

- Discussion on a three-dimensional semi-flexible AS model.
- Characterisation of one swollen and two collapsed phases.
- Characterisation of the transition between the phases.
- Discussion on the differences between two and three dimensional version of this model.

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ABSTRACT

Recently it has been shown that a two-dimensional model of self-attracting polymers based on attracting segments with the addition of stiffness displays three phases: a swollen phase, a globular, liquid-like phase, and an anisotropic crystal-like phase. Here, we consider the attracting segment model in three dimensions with the addition of stiffness. While we again identify a swollen and two distinct collapsed phases, we find that both collapsed phases are anisotropic, so that there is no phase in which the polymer resembles a disordered liquid drop. Moreover all the phase transitions are first order.

1. Introduction

An isolated polymer in solution undergoes a collapse transition from a swollen coil to a collapsed globule as the temperature is lowered and consequently the quality of the solvent is reduced. The canonical lattice model used to describe this scenario is the model of *Interacting Self-Avoiding Walks* (ISAW) on a regular lattice, such as the square or simple cubic lattice [1,2].

At high temperatures the self-avoiding walk is swollen, in that the fractal dimension of the walk d_f is less than the fractal dimension of simple random walks. The exponent $\nu = 1/d_f$ describes the scaling of the size of the walk, as measured for example by its radius of gyration, as a function of the length of the walk. It is known that $\nu = 3/4$ in two dimensions [3] and $\nu = 0.587597(7)$ in three dimensions [4].

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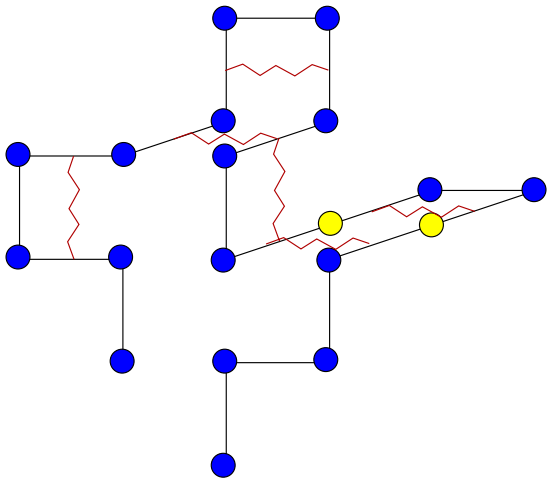

Fig. 1. A self-avoiding walk with the interactions of the attracting segment (AS) model shown as intertwined curves between bonds of the walk on opposite sides of the squares of the lattice. Also shown is an example of a stiffness segment pair which obtains a stiffness energy in our generalisation.

At low temperatures the self-avoiding walk is collapsed, in that the fractal dimension of the walk d_f is equal to the dimension d of the ambient space. The transition between the swollen coil and the collapsed globule happens at a particular temperature, called the θ-temperature.

In the standard description of the coil–globule transition, the transition is a tricritical point related to the $N \to 0$ limit of the φ^4–φ^6 O(N) field theory [5–7]; there is a second-order phase transition with a specific heat exponent conjectured to be $-1/3$ in two dimensions [8] and 0 in three dimensions with a logarithmic divergence of the specific heat. In two dimensions the fractal dimension of the walk is expected to be $d_f = 7/4$ [8] and $d_f = 2$ with logarithmic corrections in three dimensions.

The canonical model of interacting self-avoiding walks fits this scenario. In this model one expects the low-temperature state to be a liquid drop, i.e., the polymer is compact but disordered.

In stark contrast to this scenario, there is another simple interacting polymer model, the *Interacting Hydrogen-Bond* model (IHB) [9–11], where a pair of sites on the self-avoiding walk acquires a hydrogen-like bond potential if the sites are (non-consecutive) nearest neighbours, as in the ISAW model, and each site lies on a straight section of the walk. This model has been introduced in the context of biopolymers where hydrogen bonding plays an important role [12]. In contrast to ISAW, this model displays a first-order collapse transition in both two and three dimensions. Here, the low-temperature state is an anisotropic compact phase described as a polymer crystal.

Another model introduced to account for hydrogen bonding is the *Attracting Segments* model (AS) [13–15] (also known as 'interacting bonds'). It is a lattice model based on self-avoiding walks where an attractive potential is assigned to *bonds* of the walk that lie adjacent and parallel on the lattice (though not consecutive along the walk), see Fig. 1. On the square lattice, this model seems to have *two* phase transitions, one of which is identified as the θ-point [15].

If one introduces stiffness into the ISAW model, one arrives at the *semi-flexible* ISAW model [16–19]. In addition to the nearest-neighbour site interaction of ISAW, one introduces a stiffness energy associated with consecutive parallel bonds of the walk. This was studied on the cubic lattice by Bastolla and Grassberger [16], where it was shown that depending on the energetic weighting of straight segments one finds a single first-order transition from a swollen coil to a crystalline state for a strong energetic preference for straight segments, or a soft θ-transition from a swollen coil to a liquid globule, followed by a first-order transition to a crystalline state. In two dimensions, a similar scenario has been found [20], the main difference being that the transition between the globule and the frozen state becomes second-order.

The semi-flexible AS model, in which both straight segments and interacting segments carry an energy, as shown in Fig. 1, has been studied in two dimensions in Ref. [21], where it was found that it has a phase structure in common with the semi-flexible ISAW model.

In this paper, we discuss the semi-flexible AS model in three dimensions. While we again identify a swollen and two distinct collapsed phases, we find that both collapsed phases are anisotropic, so that there is no phase in which the polymer resembles a disordered liquid drop. The transitions between the swollen and each of the collapsed phases and between the two collapsed phases are first order. The three lines of transitions in parameter space meet at a triple point.

2. Our study

2.1. Semi-flexible attracting segments model

Our semi-flexible attracting segments model (semi-flexible AS model) is a self-avoiding walk on the simple cubic lattice, with self-interactions as in the AS model [13–15] and a stiffness (or equivalently bend energy) added. Specifically, the energy