

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

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abstract

Recently it has been shown that a two-dimensional model of self-attracting polymers based on attracting segments displays two phase transitions, a ϕ -like collapse between swollen polymers and a globular state and another between the globular state and a polymer crystal. On the other hand, the canonical model based on attracting monomers on lattice sites displays only one: the standard tricritical ϕ collapse transition. Here we consider the attracting segment model with the addition of stiffness and show that it displays the same phases as the canonical model.

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1. Introduction

The canonical description of the thermodynamic states of an isolated polymer has a reference high temperature disordered state known as the 'swollen coil' or 'extended state' which is described by the $N \rightarrow 0$ of the magnetic $O(N)$ model and correspondingly by the $N \rightarrow 0$ of the ϕ^4 $O(N)$ field theory [1]. The lattice model of self-avoiding walks is a good model of this situation where in both two and three dimensions the fractal dimension of the polymer d_f is less than the dimension of space and also less than the fractal dimension of simple random walks (which is 2). The values of $d_f \rightarrow 1$, where ν is the exponent describing the scaling of the radius of gyration of the polymer with its length, are $\nu=3/4$ in two dimensions [2] and $\nu=1/2$ in three dimensions, have been well studied [3]. It is expected that if the temperature is lowered then the polymer will undergo a collapse at one particular temperature, called the θ -temperature. At temperatures lower than the θ -temperature the fractal dimension of the polymer attains that of space, that is $d_f \rightarrow d$. The standard description of the collapse transition is a tricritical point related to the $N \rightarrow 0$ limit of the ϕ^4 $O(N)$ field theory [4–6]. Thermodynamically this implies that there is a second-order phase transition on lowering the temperature: the specific heat exponent α is conjectured to be $\alpha=1/3$ in two dimensions [7] and 0 in three dimensions with a logarithmic divergence of the specific heat. In two dimensions the fractal dimension of the polymer is expected to be $d_f \rightarrow 7/4$ [7]. The low temperature state has been likened to a liquid drop; it is compact but disordered [8]. The corresponding lattice model which displays this collapse θ -transition is the *Interacting Self-Avoiding Walk* model (ISAW) [9,10] where an attractive potential is associated with pairs of sites of the walk adjacent on the lattice though not consecutive along the walk. The ISAW model is the canonical model of polymer collapse.

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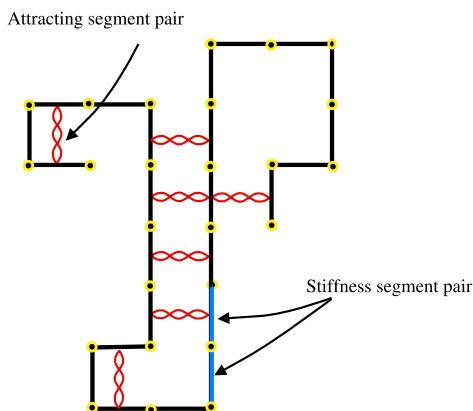


Fig. 1. A self-avoiding walk with the interactions of the attracting segment (AS) model shown as intertwined curves between bonds of the walk on opposite sides of the squares of the lattice. Also shown is an example of a stiffness segment pair which obtains a stiffness energy in our generalisation.

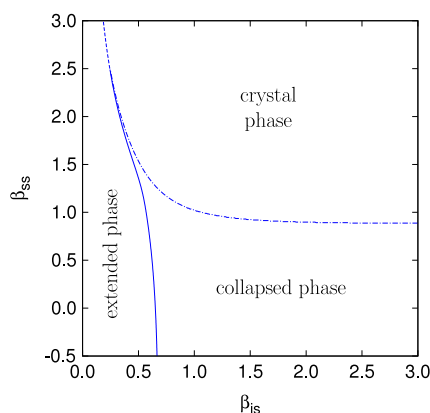


Fig. 2. Estimated phase diagram for the square lattice semi-flexible ISAW model where β_{is} is proportional to the energy of nearest-neighbour interactions and β_{ss} is proportional to the energy of stiffness.

More recently two other simple models of a single polymer have been studied. These have been introduced in the context of biopolymers where hydrogen bonding plays an important role [11], and the interacting residua lie on partially straight segments of the chain. The first one, the *Interacting Hydrogen Bond* model (IHB) [12–14], modifies the ISAW model such that 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 displays, in contrast to ISAW, a single collapse transition which is *first order* in both two and three dimensions. Here the low temperature state is an anisotropic ordered compact phase that is described as a polymer crystal.

The second model introduced to account for hydrogen bonding is the *Attracting Segments* model (AS) [15–17] (also known as ‘interacting bonds’). It is a lattice model based upon 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. This model has been less extensively studied on regular lattices – it has been studied on the square lattice [17] – though two phase transitions have been identified, one of which is identified as the θ -point.

Crucially, there is a different modification of the ISAW model that displays two phase transitions for a range of parameters, namely the *semi-flexible* ISAW model [18–21]. Here two energies are included: the nearest-neighbour site interaction of the ISAW model and also a stiffness energy associated with consecutive parallel bonds of the walk (equivalently, a bending energy for bends in the walk). This has been studied on the cubic lattice by Bastolla and Grassberger [18]. They showed that when there is a strong energetic preference for straight segments, this model undergoes a single first-order transition from the excluded-volume high temperature state to a crystalline state. On the other hand, if there is only a weak preference for straight segments, the polymer undergoes two phase transitions. On lowering the temperature the polymers undergoes a θ -point transition to the liquid globule followed at a lower temperature by a first-order transition to the frozen crystalline phase. Recent work [22] on the semi-flexible ISAW model on the square lattice displays a similar phase diagram (see Fig. 2) though the transition between the globule and the frozen state has been seen to be second order.

It would seem reasonable to conjecture that the phases and phase transitions seen in the semi-flexible ISAW model are essentially those seen in both the IHB model and the AS model. On the other hand the addition of stiffness to the

IHB model has been seen to change little of the behaviour of that model [22]. Importantly, the IHB model was recently extended [23,24] to a hybrid model (IHB-INH) that includes both the hydrogen-like bond interactions and non-hydrogen-like bond interactions, with separate energy parameters. When the non-hydrogen bonding energy is set to zero the IHB model is recovered. If both energies are set to be the same value then the ISAW *without stiffness* is recovered. For large values of the ratio of the interaction strength of hydrogen bonds to non-hydrogen bonds it was found that a polymer will undergo a single first-order phase transition from a swollen coil at high temperatures to a folded crystalline state at low temperatures. On the other hand, for any ratio of these interaction energies less than or equal to one there is a single γ -like transition from a swollen coil to a liquid droplet-like globular phase. For intermediate ratios two transitions can occur, so that the polymer first undergoes a γ -like transition on lowering the temperature, followed by a second transition to the crystalline state. In three dimensions it was found that this second transition is first order, while in two dimensions they found that it is probably second order with a divergent specific heat. In other words, by adding an energy to both the hydrogen-like and non-hydrogen-like interactions a phase diagram similar to the one for the semi-flexible ISAW is found. We note that the IHB model has been generalised on the cubic lattice in such a way that two different crystalline phases were observed [14].

Here we bring together some of the pieces of this puzzle by studying the AS model in the presence of stiffness on the square lattice. We concentrate our study in two dimensions where only one type of crystalline phase has been observed.

2. Our study

2.1. Semi-flexible attracting segments model

Our semi-flexible attracting segments model (semi-flexible AS model) is a simple self-avoiding walk on square lattice, with self-interactions as in the AS model [15–17] and a stiffness (or equivalently bend energy) added. Specifically, the energy of a single chain (walk) consists of two contributions (see Fig. 1): the energy ϵ_{as} for each attracting segment pair, being a pair of occupied bonds of the lattice that are adjacent and parallel on the lattice and not consecutive along the walk; and an energy ϵ_{ss} for each stiffness segment pair, being a pair of bonds consecutive along the walk that are parallel. A walk configuration γ_n of length n has total energy

$$E_{\gamma_n} = \epsilon_{as} m_{as}(\gamma_n) + \epsilon_{ss} m_{ss}(\gamma_n) \quad (2.1)$$

where m_{as} denote the number of attracting segment pairs and m_{ss} denotes the number of stiffness segment pairs. The partition function is defined then as

$$Z_n = \sum_{\gamma_n} e^{-\beta E_{\gamma_n}} = \sum_{m_{as}, m_{ss}} C_{n, m_{as}, m_{ss}} e^{-\beta \epsilon_{as} m_{as} - \beta \epsilon_{ss} m_{ss}} \quad (2.2)$$

where $\beta \epsilon_{as} = \epsilon_{as} / k_B T$ and $\beta \epsilon_{ss} = \epsilon_{ss} / k_B T$ for temperature T and Boltzmann constant k_B . $C_{n, m_{as}, m_{ss}}$ is the density of states, which we have estimated by means of Monte Carlo simulations.

2.2. Simulations

On the square lattice we performed simulations using the FlatPERM algorithm [25], estimating the density of states up to lengths for $n \leq 128$ over the two parameters m_{as} and m_{ss} . We have also estimated the end-to-end distance as a measure of the size of the polymer: this enables us to estimate the fractal dimension of the polymer via estimation of the exponent ν . We are unable to reliably estimate the entropic exponent γ . The density of states allows us to calculate the internal energy and the specific heat, or equivalently, the mean values and the fluctuations of m_{as} and m_{ss} , respectively. This allows to locate phase transitions through the possible divergences in the specific heat. To detect orientational order, we estimated the *anisotropy parameter* [18]. In two dimensions, denoting the number of bonds parallel to the x -, and y -axes by n_x and n_y , respectively, we define

$$D = 1 - \frac{\min(n_x, n_y)}{\max(n_x, n_y)} \quad (2.3)$$

to be the anisotropy parameter. In a system without orientational order, this quantity tends to zero as the system size increases. A non-zero limiting value less than one of this quantity indicates weak orientational order with n_{min} / n_{max} , while a limiting value of one indicates strong orientational order, where $n_{max} = n_{min}$.

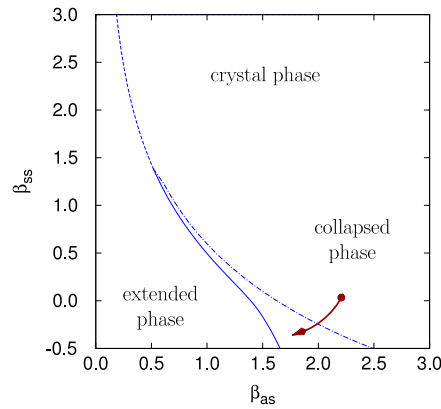


Fig. 3. Phase boundaries based upon data at length 128. The boundaries were found by looking for the maximum in fluctuation in the number of a_s contacts (the left boundary) and the number of ss segments (the right boundary).

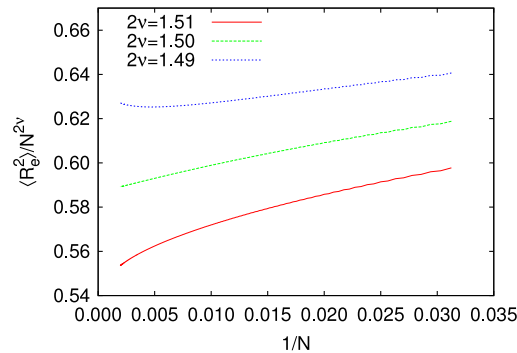


Fig. 4. The end-to-end distance $\langle R_g^2 \rangle$ divided by N^2 for the extended phase in 2d, for $\beta_{as}/\beta_{ss} \in [0.5; 1.0]$. We used three different values of β_{ss} centred around the expected 0.75.

2.3. Results

Fig. 3 shows the peak positions of the fluctuations in m_{as} and m_{ss} at length 128 from simulations on the square lattice. It is clear from shorter lengths that some of these peaks are asymptotically diverging. We therefore have a finite size approximation to a phase diagram in this figure. While the collapsed phase seems to be small on this diagram, it is thermodynamically stable. Except for small shifts in the location of the transition lines, we do not expect any significant changes to the phase diagram in the thermodynamic limit.

To characterise the possible phases in each region we have considered the scaling of the end-to-end distance. For small β_{as} we find that the exponent is close to $3/4$: specifically we find $d_f \approx 1.33$ for $\beta_{as}/\beta_{ss} \in [0.5; 1.0]$ (see Fig. 4).

On the other side of the first curve separating small β_{as} from larger β_{as} we find that d_f is close to 2 no matter how large β_{as} becomes: at points β_{as}/β_{ss} being $1.8; 0.5; 2.3; 0.5$ and $3.0; 0.5$ we find $d_f \approx 2.00$ (see Fig. 5). Hence the two phases to the right of the leftmost curve are dense.

To distinguish the two low temperature phases we have measured the anisotropy parameter. We find that the anisotropy parameter is tending to zero for values of β_{as} smaller than the right boundary and tending towards one for values of β_{as} larger than the right boundary. That is, it tends to zero in the swollen and globular phases and one in the crystal phase. In Fig. 6 we show the anisotropy parameter at fixed $\beta_{ss} \approx 1.5$ and at fixed $\beta_{as} \approx 2.0$ plotted for three different polymer lengths. There are stronger corrections to scaling in the globule-to-crystal transition evident.

We therefore surmise that for high temperatures the polymer is in the swollen phase, while at intermediate temperatures the polymer may be in a globular state, and for low enough temperatures always enters the anisotropic crystalline state. One can compare the finite size phase diagram that we have to that of the semi-flexible ISAW model [18,22], see Fig. 2. Apart from a shift of boundaries, so that for $\beta_{ss} \approx 0$ there is only one phase transition, the two diagrams are remarkably similar.

Let us now focus on positive β_{ss} where straight segments of the walk are favoured. For definiteness let us consider $\beta_{ss} \approx 1.5$. From Fig. 3 we expect to see a single phase transition on varying β_{as} from the swollen phase at low β_{as} to the crystalline state at large β_{as} . This is indeed what we observe when considering the fluctuations in m_{as} . Fig. 7 shows the fluctuations of m_{as} scaled by N^2 (proportional to the specific heat per monomer divided by a factor of length) plotted against a scaling β_{as} : they display a single point at which this quantity converges, indicating a strong first-order-like divergence in

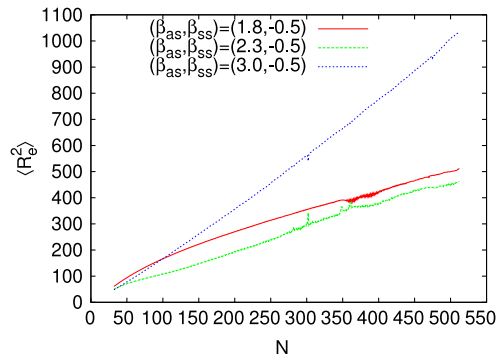


Fig. 5. The curves show the behaviour of the end-to-end distance at three points, $1.8; -0.5$, $2.3; -0.5$ and $3.0; -0.5$, in the phase diagram. These are expected to cover both the collapsed 'globule' phase and the crystal phases. In all three cases we observe linear scaling with the length, which is in good agreement with theory prediction that $\langle R_g^2 \rangle \propto N^{0.5}$ in two dimensions.

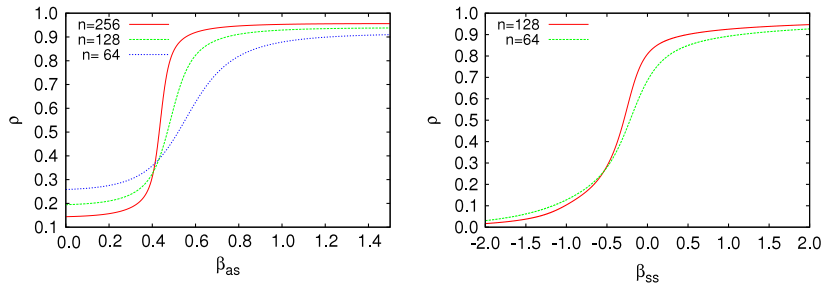


Fig. 6. The anisotropy parameter ρ for $\beta_{ss} = 1.5$ (left) and $\beta_{ss} = 2.0$ (right) for polymer lengths $n = 64, 128$ and 256 . For $\beta_{ss} = 1.5$ it is converging to 0 for small β_{as} and to 1 for large β_{as} , changing over roughly at $\beta_{as} \approx 0.4$. For $\beta_{ss} = 2.0$ it is converging to 0 for small β_{ss} and to 1 for large β_{ss} , changing over roughly at $\beta_{ss} \approx 0.5$.

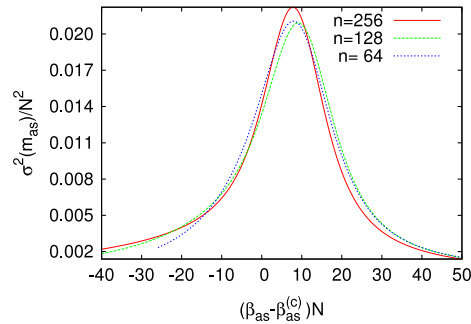


Fig. 7. A plot of the fluctuations per monomer divided by N in the number of attracting segment contacts (β_{as}) at $\beta_{ss} = 1.5$ with the horizontal axis scaled as $(\beta_{as} - \beta_{as}^{(c)})/N$. We have used $\beta_{ss}^{(c)} = 0.424$. Shown are lengths 64, 128 and 256.

the specific heat per monomer. This is in accord the nature of the swollen-to-crystal transition in the semi-flexible ISAW model [18,26]: it is first order.

We now examine negative β_{ss} , where turns in the walk are favoured. Having identified the phases here to be swollen and globular in nature we may expect that the associated transition should be in the universality class of the θ -point [7] with its specific heat signature being weak ($\alpha < 0$). Let us refer to this transition point as $\beta_{as}^*, \beta_{ss}^*$. It is difficult to see a transition with a convergent specific heat singularity at the lengths considered here. Our data indicates a weak second-order-like transition, certainly not first order, with the transition clearly weakening with length. Corrections-to-scaling do not allow an exponent analysis.

Finally we have tried to examine the globule-to-crystal transition that occurs for large enough β_{as} on varying β_{ss} , or for some range of β_{ss} about zero at large negative values of β_{as} (larger than $\beta_{as}^*, \beta_{ss}^*$). In the semi-flexible ISAW model the globule-to-crystal transition [22] has been found to be second order. This transition between low temperature phases has yet to be carefully characterised and the simulations here did not shed further light on it.

It is also instructive to consider the phase diagram of the extended interacting hydrogen bonding model [23]. While the different type of parameters make comparisons indirect, we note that the same phases occur and same phase transitions

as the two semi-flexible models discussed in two dimensions. This supports the idea that regardless of how stiffness is introduced in the interacting polymer model, these three phases will occur in an appropriate parameter space. To make this conclusion more concrete one can realise that by enlarging the parameter space of concern in the manner considered in [16] the ISAW model, the IHB and the AS models are all specialisations of a more general model. Now we have seen that with the addition of a further stiffness parameter the general phase structure of the more general model should still contain these three phases and phases transition discussed above.

While the previous arguments focus on the general phase structure, it is worth noting that details of the phase diagram depend sensitively on how attraction and stiffness is incorporated into the lattice model. For example, while stiffness does not significantly affect the location of the β -transition in the semi-flexible ISAW model, stiffness enhances the occurrence of neighbouring attracting segments in the semi-flexible AS model. This leads to the globule-coil transition occurring at increasing values of κ as κ_{ss} decreases, as shown by our simulations, see Fig. 3.

In this article we have analysed the semi-flexible attracting segments model of polymer collapse in two dimensions and shown that it has a phase structure in common with the standard model of semi-flexible ISAW which interacts via nearest-neighbour occupied sites. This phase structure is also in common with extended hydrogen bonded polymer models in two dimensions. In future work it would be interesting to consider the three-dimensional case and understand the connection to the work on various $O(n)$ models of polymer collapse [27,28].

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