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Lattice polymers with two competing collapse interactions

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Abstract
We study a generalized model of self-avoiding trails, containing two different types of interaction (nearest-neighbour contacts and multiply visited sites), using computer simulations. This model contains various previously studied models as special cases. We find that the strong collapse transition induced by multiply-visited sites is a singular point in the phase diagram and corresponds to a higher order multi-critical point separating a line of weak second-order transitions from a line of first-order transitions.

Keywords: polymer collapse, lattice polymers, self-avoiding trails, self-avoiding walks, theta point
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(Some figures may appear in colour only in the online journal)

1. Introduction

1.1. The polymer collapse transition

There are various statistical mechanical models of the polymer collapse phase transition [1, 2]. However, there are two basic elements in each of the models: on the one hand, the configurations of the polymer have some type of so-called excluded volume, that implies molecules are separate in space, and on the other hand the configurations have an attractive force between different parts of the polymer, that drives the transition. On lattices, both self-avoiding walks (SAW), where different sites of walk avoid being on the same site of the lattice, and self-avoiding trails (SAT), which are walks that can share sites though not bonds of the lattice, have been used as the configuration space for collapse models. The attractive

force has been modelled both by adding energies for shared sites and also via so-called nearest-neighbour contacts, where sites adjacent on the lattice not joined by a step of the walk are given an energy. When SAW are coupled with nearest-neighbour interactions the canonical ISAW model is reproduced (see [2] for a review), while when trails are coupled with site interactions the ISAT model [3] is reproduced. Despite what one might expect from the principle of universality the collapse of these models appears to behave differently [4–6].

A recent study [7] considered self-avoiding trails interacting via nearest-neighbour contacts (INNSAT) as a hybrid of the two models. Evidence from computer simulations showed that the collapse transition in INNSAT is different from the collapse transition in ISAT, which is a strong second-order transition, but similar to ISAW which is predicted to be a weak second-order transition where the specific heat converges at the transition. In ISAW collapse one needs to consider the third derivative of the free energy to see a divergent quantity and then only weakly divergent. It was also found that the low-temperature phase of the two trail-collapse models differ substantially: the phase associated with multiply visited site interactions is fully dense in the thermodynamic limit (as shown in [8]). The low-temperature phase associated with nearest-neighbour contacts wasn't fully dense as is believed to be the case for interacting SAW [24].

1.2. Magnetic systems

The properties of lattice polymers are also related to those of magnetic systems near their critical point [2]. More precisely, SAW configurations appear as the diagrams of the high-temperature expansion of an $O(n)$ magnetic system when taking the formal limit of zero components ($n \to 0$), and their scaling exponents can be obtained from the $O(n)$ critical point. In this mapping the collapse transition corresponds to a tri-critical point of the magnetic system and one would hope to obtain the critical exponents for the polymer collapse transition from the ones of this tri-critical point.

Various authors [9–13] have studied critical and tri-critical $O(n)$ spin systems. For a special choice of the model on the honeycomb lattice, exact results were obtained in [9] for two cases: a critical point and a special point governing the low-temperature phase. When $n \to 0$ these two cases become the *dilute* and *dense* polymer phase. The dilute and dense phases were also found along two branches of a square-lattice $O(n)$ model [10, 11] together with two different branches describing the critical behaviour that occurs when $O(n)$ and Ising degrees of freedom on the square lattice display a joint critical point.

On the other hand, Duplantier and Saleur in 1987 [14] realized that, on the honeycomb lattice, an self-interaction for SAW could be obtained by introducing vacancies, hexagonal faces that the SAW is not allowed to touch. Using this observation they could obtain a set of critical exponents for the polymer collapse transition which have been subsequently found to correctly describe the collapse in the ISAW model (see the extensive list of references in [15] for example). We will refer to the universality class of this critical point as the 'θ-point'. An exact description has now been proposed [12, 13] for the tri-critical $O(n)$ model in two dimensions as a function of n.

When it comes to ISAT the scenario is much less clear, in particular it not obvious how the change of topology caused by the presence of crossings affects the above picture. The description in terms of height model and Coulomb Gas allows one to consider the presence of crossings only as a perturbation (see [16] for a review of these methods). The exponent associated to loop crossings is the same as that of cubic symmetry breaking, which is known to be irrelevant in the critical $O(n)$ phase, but it has been observed [17] that this is not true in the low-temperature phase, where the introduction of crossings is a relevant operator which

leads to a different universality class. This is generically referred to as the *Goldstone phase* and it is believed [13, 17] to be described by the intersecting loop model proposed in [18, 19] and since called the Brauer model [20].

The relevance of crossings at the collapse point is not clear. While the cubic perturbation is still believed to be relevant at the tri-critical $O(n)$ point [13], a recent numerical study [7] seems to indicate that the Duplantier and Saleur universality class is stable in the presence of crossings, at least with respect to the cross-over and length-scale exponents.

Very recently Nahum *et al* [21] published a study of loop models with crossings. Their analysis is based on a replica limit of the σ model on real projective space $\mathbb{RP}^{m-1}$. They give a field theoretic description of the ISAT which explains the phase diagram found numerically in [22] and suggests that the ISAT collapse transition is an infinite-order multi-critical point.

1.3. A model with competing interactions

In this paper we consider a polymer model of SAT with both multiply visited site and nearest-neighbour interactions. This model generalises ISAT and INNSAT. It also contains in a limiting case the ISAW model, when the Boltzmann weight associated with multiply visited sites is sent to zero.

We study the model via computer simulations using the flatPERM algorithm, and so extend the study of INNSAT in [7]. We point out that this model has been studied some time ago by Wu and Bradley [23] via real-space renormalization, which predicted a tetra-critical point separating the ISAT and ISAW collapse points. In contrast, we find that there is likely to be the ISAT collapsed point itself, that separates a line of first-order transitions from ISAW-like weaker θ-point type transitions.

In section 2 we define the model introduced by Wu and Bradley. In section 3, we present the results of our simulational studies and deduce a conjectured phase diagram. We end by summarising our conclusions in section 5.

2. The Wu–Bradley model

A model of interacting SAT with both nearest-neighbour interaction and site interactions can be defined as follows. Consider the set of bond-avoiding paths $\mathcal{T}_n$ of length n. Given a SAT $\psi_n \in \mathcal{T}_n$, we associate an energy $-\varepsilon_t$ every time the path visits the same site more than once, as in ISAT. Additionally, we define a *contact* whenever there is a pair of sites that are neighbours on the lattice but not consecutive on the walk, as in ISAW. We associate an energy $-\varepsilon_c$ with each contact.

For each configuration $\psi_n \in \mathcal{T}_n$ we count the number $m_t(\psi_n)$ of doubly visited sites and $m_c(\psi_n)$ of contacts; see figure 1. Hence we associate with each configuration a Boltzmann weight $\tau^{m_t(\psi_n)}\omega^{m_c(\psi_n)}$ where $\tau = \exp(\beta\varepsilon_t)$, $\omega = \exp(\beta\varepsilon_c)$, and β is the inverse temperature $1/k_BT$. The partition function of the model is given by

$$Z_n(\tau, \omega) = \sum_{\psi_n \in \mathcal{T}_n} \tau^{m_t(\psi_n)}\omega^{m_c(\psi_n)}. \tag{2.1}$$

The probability of a configuration ψ_n is then

$$p(\psi_n; \tau, \omega) = \frac{\tau^{m_t(\psi_n)}\omega^{m_c(\psi_n)}}{Z_n(\tau, \omega)}. \tag{2.2}$$

The average of any quantity Q over the ensemble set of paths $\mathcal{T}_n$ is given generically by

$$\langle Q\rangle(n; \tau, \omega) = \sum_{\psi_n \in \mathcal{T}_n} Q(\psi_n)\, p(\psi_n; \tau, \omega). \tag{2.3}$$

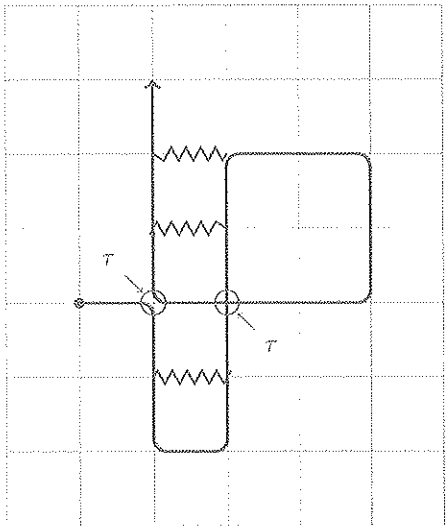

Figure 1. An example of a configuration for the two interaction model, with $m_c = 3$ (as there are three nearest-neighbour contacts illustrated via zigzag (red) lines) and $m_t = 2$ (as there are two doubly visited sites). The trail can visit a site of the lattice twice by 'touching' and by 'crossing' itself. Note that there is no contact between the second and the seventh visited site of the walk, even though these are non-consecutive nearest-neighbour sites, as both sites are visited consecutively by a different segment of the trail.

In particular, we can define the average number of doubly visited sites per site and their respective fluctuations as

$$u^{(t)} = \frac{\langle m_t \rangle}{n} \quad \text{and} \quad c^{(t)} = \frac{\langle m_t^2 \rangle - \langle m_t \rangle^2}{n}. \tag{2.4}$$

One can also consider the average number of contacts of the trail and their fluctuations

$$u^{(c)} = \frac{\langle m_c \rangle}{n} \quad \text{and} \quad c^{(c)} = \frac{\langle m_c^2 \rangle - \langle m_c \rangle^2}{n}. \tag{2.5}$$

This model interpolates between three previously studied models; when we set $\omega = 1$ the model reduces to the ISAT model. It should be noted that an important observation [8, 25] for ISAT is that the low temperature phase is maximally dense. On the square lattice this implies that if one considers the proportion of the sites on the trail that are at lattice sites which are not doubly occupied via

$$p_n = \frac{n - 2\langle m_t \rangle}{n}, \tag{2.6}$$

then it is expected that

$$p_n \to 0 \quad \text{as} \quad n \to \infty. \tag{2.7}$$

Very recently the ISAT model has been studied in the context of a loop model with crossings [21], where it has been suggested that the ISAT collapse point is an infinite-order multi-critical point described by the $O(n \to 1)$ sigma model studied in [17].

If otherwise we set $\tau = 0$ doubly visited sites are excluded and the model reduces to the ISAW model. Finally if we set $\tau = 1$ it becomes the INNSAT model studied in [7]. One would think that the presence of crossings would affect the universality class of the collapse

transition (e.g. as portrayed in [21]) but in [7] it was shown that the INNSAT model has a collapse transition in the same universality class as ISAW, that is the θ-point.

3. Numerical results

We began by simulating the full two parameter space by using the flatPERM algorithm [26] which is a flat histogram version of the Pruned and Enriched Rosenbluth Method (PERM) developed in [27]. For the PERM algorithm, at each iteration a polymer configurations is generated kinetically (which is to say that each growth step is selected at random from all possible growth steps) along with a weight factor to correct the sample bias. At each growth step, configuration with very high weight relative to other configurations of the same size are enriched (duplicated) while configuration with low weight or that cannot be grown any further are pruned (discarded). Despite introducing a correlation between each iteration, this simple mechanism greatly improves the algorithm efficiency. A single iteration is then concluded when all configurations have been pruned and the total number of samples generated during each iteration depends on the specificity of the problem at hand and on the details of the enriching/pruning strategy. FlatPERM extends this method by cleverly choosing the enrichment and pruning steps to generate for each polymer size n a quasi-flat histogram in some chosen micro-canonical quantities $\mathbf{k} = (k_1, k_2, \ldots, k_\ell)$ and producing an estimate $W_{n,\mathbf{k}}$ of the total weight of the walks of length n at fixed values of $\mathbf{k}$. From the total weight one can access physical quantities over a broad range of temperatures through a simple weighted average, e.g.

$$\langle \mathcal{O} \rangle_n(\tau) = \frac{\sum_{\mathbf{k}} \mathcal{O}_{n,\mathbf{k}} \left(\prod_j \tau_j^{k_j} \right) W_{n,\mathbf{k}}}{\sum_{\mathbf{k}} \left(\prod_j \tau_j^{k_j} \right) W_{n,\mathbf{k}}}. \tag{3.1}$$

The quantities k_j may be any subset of the physical parameters of the model. To study the full two parameter phase space we set $(k_1, k_2) = (m_t, m_c)$ and $(\tau_1, \tau_2) = (\tau, \omega)$.

We have first simulated the model using the full two-parameter flatPERM algorithm up to length $n = 256$, running 4.4×10^6 iterations, and collecting 2.3×10^{11} samples at the maximum length. To obtain a landscape of possible phase transitions, we plot the largest eigenvalue of the matrix of second derivatives of the free energy with respect to τ and ω (measuring the strength of the fluctuations and covariance in m_t and m_c) at length $n = 256$ on the left-hand side of figure 2.

We expect the ISAT transition to be somewhat shifted away from $(\omega, \tau) = (1, 3)$ due to considering a finite-size ensemble. If one considers the vertical line $\omega = 1$, one notices that the maximal eigenvalue peaks at a value of τ somewhat greater than 3. We remind that the phase transition for $\omega = 1$ is a strong second-order phase transition where the specific heat diverges with an exponent 0.68(5). For $\omega < 1$, there exists a line of even stronger peaks that join with the peak at $\omega = 1$, from which one can infer that there exists a strong phase transition on varying τ for each $\omega < 1$. This is borne out by finite-size scaling analysis. Specifically, we have studied the model when $\omega = 0.5$: for this value of ω we have simulated the model using a one-parameter flatPERM algorithm up to length $n = 1024$, running 7.9×10^6 iterations, and collecting 2.7×10^{10} samples at the maximum length. We find that the specific heat divergence is commensurate with a first-order transition with a linear divergence. To test this assumption of a first-order transition, we consider the distribution of the number of contacts for various values of τ near the peak of the specific heat. Figure 3 shows a clear bimodal distribution, confirming the first-order character of the transition.

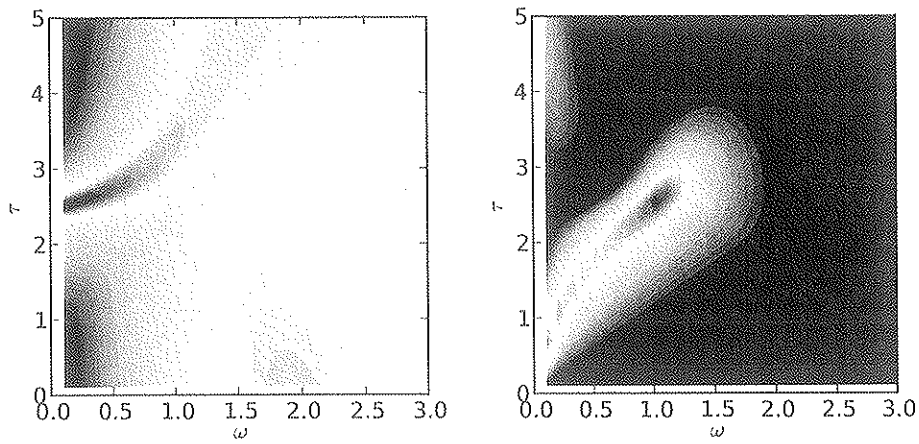

Figure 2. Left: density plot of the logarithm of the largest eigenvalue $\lambda_{\max}$ of the matrix of second derivatives of the free energy with respect to τ and ω at length 256. Right: density plot of the ratio $\lambda_{\min}/\lambda_{\max}$ of the eigenvalues of the matrix of second derivatives of the free energy with respect to τ and ω at length 256.

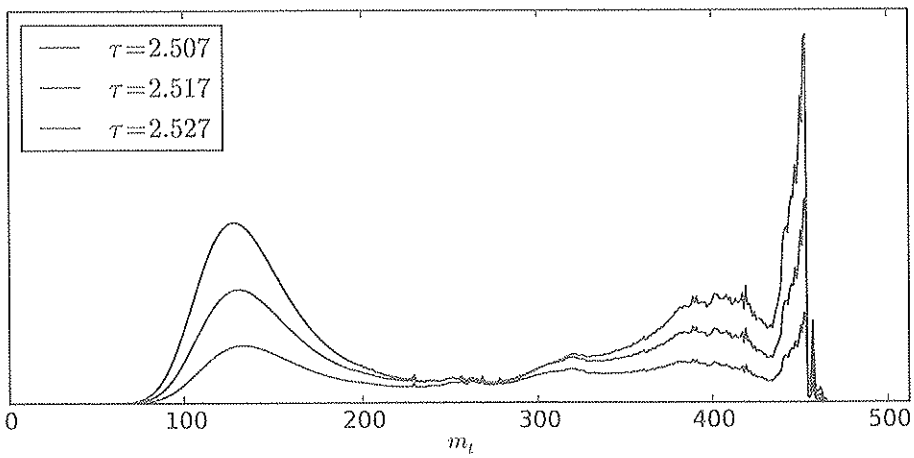

Figure 3. Distribution of the number of contacts for various τ at fixed $\omega = 0.5$.

It is hence likely that there exists a line of first-order phase transitions at values of τ near 3 for each value of $\omega \lesssim 1$. We will return to the question of whether the line of first-order transitions extends all the way to $\omega = 1$ below.

Returning to our two-parameter data, let us first note that when $\tau = 0$ our model is the ISAW model and hence there is a weak θ-like transition at $(\omega, \tau) = (\omega_c, 0)$ with $\omega_c \sim 1.94$ (see [15] and references therein for recent estimates of ω_c), which is reflected in the density plot by a broad peak near $\omega = 2$ on varying ω when $\tau = 0$. A line of such weak peaks extends to larger values of τ. When $\tau = 1$, the model becomes the previously studied INNSAT [7], which also demonstrated a weak θ-like transition with exponent estimates encompassing ISAW values. We thus conjecture that the entire line lies in the θ-universality class.

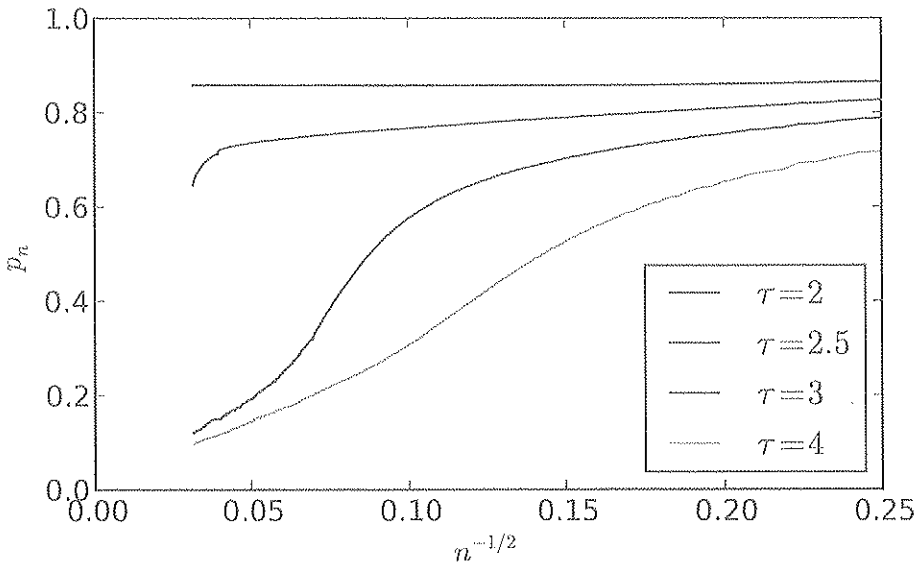

Figure 4. Plots of p_n, the proportion of steps that visit singly occupied sites at fixed $\omega = 0.5$ and $\tau = 2.0$, 2.5, 3.0, and 4.0 (from top to bottom), versus $n^{-1/2}$. The scale $n^{1/2}$ is the natural scale for the border of a dense configuration.

Now if the suggestion that the ISAT collapse corresponds to an infinite-order multi-critical point [21] is correct, it is then natural and simplest to conjecture that the line of first-order transitions meets with the line of θ-like transitions at that point.

We obtain an indication of where the two lines might join by considering the ratio between the two eigenvalues of the covariance matrix $H_{ij} = \partial^2_{ij} \log Z_n$ where $i, j \in \{\omega, \tau\}$. This is based on the heuristic argument that the component $\tau\tau$ (respectively $\omega\omega$) is the specific heat associated to multiply visited sites (nearest-neighbour contacts) and will dominate the spectrum when the transition is driven by this interaction. When the two eigenvalues coincide is then argued to indicate the presence of a higher order critical point. The density plot of the eigenvalue ratio is shown on the right-hand side of figure 2. One clearly observes a unique point close to the ISAT collapse point, where the two eigenvalues have the same magnitude.

Considering again the density plot of the largest eigenvalue, the line of peaks that is associated with first-order transitions for $\omega < 1$ and that meets the ISAT critical point for $\omega = 1$ extends to higher values of ω. This implies some type of phase transition at low temperatures. To understand what this transition might be, we now consider the low temperature phases for fixed values of ω and τ. When $\omega = 1$, an analysis of the ISAT model has previously shown that the low temperature phase is *maximally dense* with the proportion p_n of sites on the trail that are not doubly occupied going to zero in the thermodynamic limit of infinite length [8, 25]. Here we plot the same quantity for various temperatures when $\omega = 0.5$ in figure 4. At low values of τ the quantity p_n converges to a non-zero value while for larger values p_n seems to converge to zero within error, with a transition visible around $\tau \approx 2.5$.

To illustrate the nature of the polymer around the transition, we present some typical configurations with specified numbers of contacts that have been generated in a simulation at $\omega = 0.5$. These can be seen in figure 5. Not only do these configurations illustrate the nature of the low-temperature phase where the number of contacts is large (see the configuration with $m_t = 452$), but they also clearly demonstrate the first-order nature of the collapse,

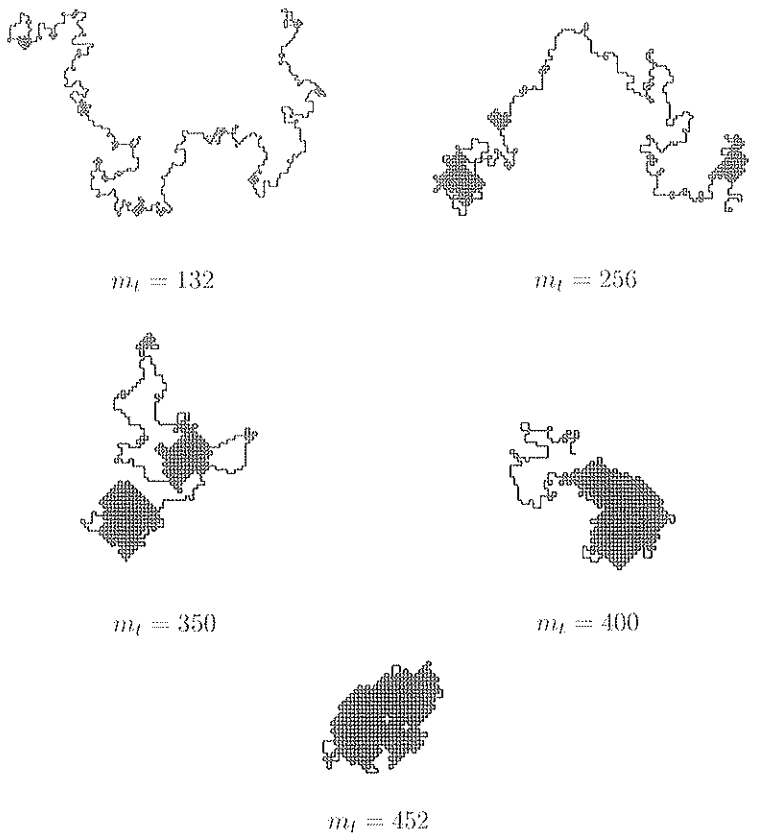

Figure 5. Typical configurations of 1024-step walks with specified numbers m_t of contacts, that have been generated in a simulation at $\omega = 0.5$. The values of m_t have been chosen such as to cover the whole range of the histogram in figure 3. The configurations illustrate the co-existence of fully dense and swollen parts of the polymer, demonstrating the first-order nature of the transition.

as we observe co-existence of fully dense and swollen parts of the polymer for smaller values of m_t.

Now let us consider low temperatures for fixed values of τ. In our previous work on INNSAT [7], when $\tau = 1$ the quantity p_n was seen to converge to a non-zero value regardless of temperature: see figure 7 in [7]. This phase is unambiguously of a different nature as that for large τ at fixed ω. We can therefore conclude that the line of peaks for large values of ω and τ in the largest eigenvalue plot is associated with a transition between these two low temperature phases: one being maximally dense and the other not. We have not investigated this transition here but an analysis of a transition between similar phases [28] leads us to conjecture that it is second order.

The entire phase diagram in the ω, τ-quadrant is therefore split into three phases we already know: the swollen high-temperature phase in the lower-left corner, a low-temperature globular phase of the ISAW model on the right (as determined in [7]), and the low-temperature maximally dense phase of the ISAT model in the top left. We then have two critical lines and

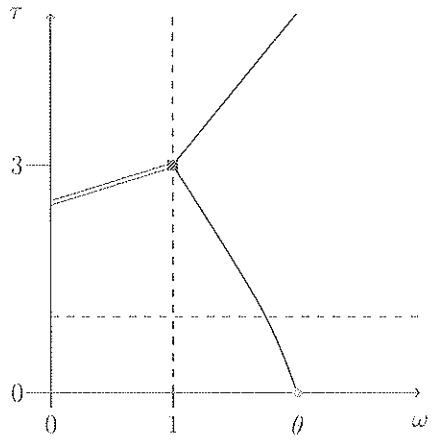

Figure 6. Proposed phase diagram. The double-line indicates a line of first-order transitions. The horizontal and vertical dashed lines are respectively the ISAT and INNSAT model, the ISAW model corresponds to the axis $\tau = 0$. The red square and the green circle correspond respectively to the ISAT collapse point and the ISAW θ-point.

one first order line joining together at the multi-critical point located at $(\omega, \tau) = (1, 3)$ that separates these phases. Putting all this information together gives us the conjectured phase diagram in figure 6.

4. Conclusions

We investigated a two-parameter model of polymer collapse that has competing interactions, first studied by Wu and Bradley [23], and contains three previously investigated models of polymer collapse, namely ISAT, ISAW and INNSAT, as specializations.

We find that the phase diagram for the Wu–Bradley model contains three phases: a swollen phase and two collapsed phases, one of which is maximally dense. The corresponding three phase boundaries, two of which are second order and one of which is first order, meet seemingly at the collapse point of the ISAT model, and is in agreement with the suggestion in [21] that the ISAT transition is an higher order multi-critical point. The second-order phase transition line between the swollen and not maximally dense collapsed phase contains the transitions in the ISAW and INNSAT models, which we conjecture to be a line of θ-like transitions.

We can conjecture that the two collapsed phases belong to the $O(n \to 0)$ Goldstone phase [17, 21], due to the presence of crossings. It is an open question whether the divergence of these two phases can be related to the appearance of a type of Ising order, as portrayed in [21]. More work needs to be done to elucidate the nature of these phases, and to resolve the transition between them. At present, this seems to be out of reach of available algorithms.

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