A New Scaling Form for the Collapsed Polymer Phase

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Abstract

By studying the finite length scaling of a self–interacting partially directed self avoiding walks we have verified a new scaling form for the collapsed phase of self avoiding walks problems. We suggest therefore that this should hold in polymer systems.

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Many different approaches have been applied to the study of polymeric solutions. The properties of an isolated polymer chain are of significant importance here and lattice statistical mechanics has provided one model based upon self-avoiding walks with nearest-neighbour monomer–monomer interactions (ISAW) that has been widely studied in this context [1, 2]. In the physical dimensions $d$ of two and three, this model demonstrates three different behaviours or phases. At high temperatures the self-avoidance constraint causes effective excluded volume interactions which favour extended (over the average purely random walk) configurations. There exists a critical point which is believed to model the $\theta$–point of polymer systems and at low temperatures a collapsed phase dominated by globule–like configurations persists. The radius of gyration $R_G(L)$ describing the average size of configurations as a function of the walk length $L$ behaves as

$$R_G \sim AL^\nu$$

with $\nu$ taking on different values in the three phases and in different dimensions. In particular, in the collapsed phase it has been fairly well established that the configurations are compact and $\nu = 1/d$. The study of the ISAW model has been focussed on the infinite temperature or free SAW and the $\theta$–point where $d_f = 1/\nu$, the fractal dimension of the objects, takes on non–trivial values.

The asymptotic behaviour of the partition function for ISAWs at high and $\theta$–temperatures has been assumed to take on the following form

$$Q_L \sim q_0 \mu^L L^{\gamma -1}$$

where $\log \mu(T)$ is proportional to the temperature dependent free energy, and which has been conjectured as applying to real polymer chains [3, 4]. However, the question of the existence of $\gamma$ at low temperatures has not been answered [1] and the lack of theoretic work has not encouraged the study of the low temperature behaviour of ISAWs. The above form for the partition function implies that the large $L$ corrections to the free energy are logarithmic.

It would seem natural to ask whether a surface tension term may be appropriate at low temperatures when the polymer is in a compact configuration. Hence, we conjecture

$$Q_L \sim q_0 \mu_0^L \mu_1^L \mu^{L\sigma} L^{\gamma -1}$$

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as a likely form for the partition function in the collapsed phase of ISAWs. Here \( \log \mu_1(T) \) is proportional to a temperature dependent surface free energy while \( \sigma \) is a constant which should be close to 1/2 in two dimensions and close to 2/3 in three since the surface of a compact object in \( d \) dimensions is \( d - 1 \) and \( \sigma \) would then be \( (d - 1)/d \). It is not clear however whether self-avoidance constraint may not lead to a smaller value of \( \sigma \), that is the fractal dimension of the ‘surface’ is lowered. The above form should hold for dilute polymer systems in a poor solvent/or at a low temperature including chains, rings and branched molecules.

The above form has historical precedent in the cluster partition functions that occur in the droplet model of condensation. Some time ago Fisher and collaborators [5, 6] developed a theory of condensation in an attempt to understand the low temperature behaviour of a fluid system that undergoes a first order transition. This involved considering the partition function for clusters of molecules separately. One might consider, rather intuitively, the clustering of molecules in a fluid system as analogous to the collapsing of polymer systems. This analogy is most simply contemplated by considering site animals, that are models for branched polymers together with, say, Ising model clusters. Then the collapsed phase of the ISAW model is clearly a candidate for the existence of this extra correction term. There also exist simple site animal problems [7] and a special subset of walks, known as spiralling [8], in two dimensions where the form of the partition function contains only the \( \mu_1(T) \) term (with \( \sigma = 1/2 \)); these problems are non-interacting however.

To study the validity of this conjecture we have examined the system of partially directed interacting SAWs in two dimensions and computed series up to walks of length 6000. We have found strong evidence for the existence of \( \sigma \) and a value very close to 1/2 (see figure 1). We have also identified the low temperature value of \( \gamma \) to be approximately 1/4. The partition function was calculated over a range of fixed temperatures and the form (3) was compared to the result. Firstly, assuming the existence of only \( \sigma \) and not necessarily \( \gamma \) gives \( \sigma = 0.498 \pm 0.003 \) over the range of temperatures in figure 1 (we have avoided the critical and zero temperature regions for the usual reasons). Next, given the complete form (3) and assuming a value of \( \sigma \) equal to 1/2, a stable value of \( \mu_1(T) < 1 \) could be found to between 7 and 10 figure accuracy depending on the temperature. Also, a convergent value of \( \gamma - 1 \) was found for each temperature (see figure 2) and this being a constant \((-0.7500) \) within 0.02%. 

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With the most sophisticated fit (taking account of higher terms in a conjectured expansion of the free energy) a higher accuracy is achieved with \( \gamma = 0.250000 \pm 0.000005 \) being able to be inferred (A longer account of this work will be included in a complete study of the finite length scaling of this model [9]). We point out that while an exact solution for the generating function has been found in the generalised canonical ensemble [10, 11] the standard connection between the generalised and canonical ensemble breaks down at low temperatures [12] and this is the reason for the necessity of enumerations. It would be interesting in this context to further examine these conditions in an attempt to extend them. The interacting partially directed SAW model is a variant of the ISAW model that allows only steps in the positive \( x \)-direction. This model seems to possess all the richness of the full model and it would be of great interest to see whether the exponent \( \sigma \) exists for interacting self avoiding walks and whether its value is indeed 1/2.

The introduction of \( \mu_1(T) \) allows the definition of another critical point exponent \( \chi \) since \( \mu_1(T) \) approaches 1 as the temperature is increased towards the \( \theta \) point. That is,

\[
|1 - \mu_1(T)| \sim |T - T_c|^\chi
\]

In the Fisher droplet model this exponent is always 1. Our enumerations and (tri–)critical scaling theory [13] give a value of 3/4 for this exponent implying a non–trivial extension of the Fisher model to tricritical points.

In conclusion, the interacting partially directed SAW model has been studied at low temperatures by means of extremely long series and provides good evidence for a scaling form similar to the one Fisher used to describe the essential singularity of a first order transition. The interacting partially directed SAW system hence gives a realisation of the droplet model. Moreover, it is reasonable to conjecture that the form (3) should be valid in the collapsed phase of SAWs and for dilute polymer solutions at low temperatures which they model. The new correction term can be understood as a surface energy contribution to the asymptotic free energy. We hope this conjecture will stimulate field theoretic and other methods of analysis to investigate the collapsed phase of ISAWs.
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References


Figure Captions

Figure 1. Estimates for the exponent $\sigma$ plotted against a suitable scaling variable for a range of temperatures, found from the calculated partition function. The temperatures are, from top to bottom, $T/T_c = 0.29, 0.34, 0.41, 0.50, 0.61, 0.72, 0.825$. These estimates do not take into account the logarithmic correction of the $\gamma$ term.

Figure 2. Estimates for the exponent $\gamma - 1$ fitting the calculated partition function to the full form (3). Again these cover the same range of temperatures as in Figure 1. from top to bottom (on the left hand side). Fitting these curves with 3rd and 4th order polynomials in $L^{-1/2}$ produces remarkably stable results.