TEMPERATURE DEPENDENCE OF THE CONFIGURATIONAL FREE ENERGY OF A BRANCHED POLYMER

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Abstract

We consider a lattice model of branched polymers in dilute solution in which the polymer is modelled as an animal, weakly embeddable in the (simple cubic) lattice. In order to model the effect on the thermodynamic properties of changing the temperature or the quality of the solvent, we include an energy associated with the number of near-neighbour contacts between pairs of vertices of the animals. We show that the configurational free energy of the animal is a continuous function of the temperature and derive rigorous upper and lower bounds on the temperature dependence of the free energy. Finally, we comment on similarities between these results and corresponding ones for a model in which the energy is associated with the cyclomatic index of the animal.

1. Introduction

Self-avoiding walks on a regular lattice form a convenient model for the configurational properties of a linear polymer molecule in dilute solution in a good solvent. If near-neighbour interactions are weighted with a suitable Boltzmann factor, the (infinite) walk is thought to undergo a transition which models the internal transition in a polymer brought about by the dominance of attractive forces between monomers at low temperatures. This transition has been studied theoretically for many years [1–7].

Lattice animals serve as a corresponding model for the configurational properties of randomly branched polymers in dilute solution in a good solvent. As the solvent quality decreases, branched polymers are expected to become more compact and a collapse transition, analogous to that in linear polymers, is expected to occur. This transition has been examined using lattice animal models and a variety of approaches [8–11]. The models studied by these authors are formulated using different language, but can all be expressed in terms of a cycle fugacity as the driving force for collapse [12]. One can think of this as associating an energy with every (elementary)

cycle so that the overall energy is proportional to the cyclomatic index. If this energy is attractive, this could lead to a collapse phenomenon since animals with many cycles will be more compact than those with few cycles (see also the important related paper by Dhar [13], which proves that there is a collapse transition in a directed animal model).

A model closer to that used for linear polymers is one in which interactions are introduced between pairs of vertices of the animal which are not incident on the same edge of the animal. If these interactions are sufficiently strong, it seems that a collapse transition may occur.

In a previous paper [14], we derived rigorous results about the form of the configurational free energy for a model with a cycle fugacity, but corresponding rigorous results for the near-neighbour interaction model are not available. In this paper, we supply some of these results; a more detailed analysis is in preparation. In section 2, we discuss the problem of lattice animals with no energy terms and recall some key rigorous results. In section 3, we define what we mean by a near-neighbour interaction model and prove some theorems that establish the continuity of the configurational free energy. We derive bounds on the temperature dependence of the free energy, both for attractive and repulsive near-neighbour interactions. In section 4, we compare the near-neighbour interaction and cycle fugacity models and show that there are similarities in the behaviour of the limiting free energy as the appropriate fugacity varies. Finally, in section 5, we point out a number of open questions in this area.

2. Lattice animals

We shall consider the d-dimensional hypercubic lattice, although we shall be primarily concerned with the simple cubic lattice in three dimensions (and occasionally the square lattice in two dimensions). We shall need to consider two kinds of animals embeddable in these lattices. A *bond animal* is a connected sub-graph of the lattice and a *site animal* is a connected section-graph of the lattice. In a bond animal, two vertices which are neighbours on the lattice may or may not be incident on a common edge but, in a site animal, if two vertices of the animal are neighbours on the lattice, then they are automatically joined by an edge. Sometimes we say that a bond animal is *weakly embeddable* in the lattice and that a site animal is *strongly embeddable* in the lattice. We ask for the number of bond animals with n sites where two animals are considered distinct if they cannot be superimposed by translation. Let this number be a_n. It is easy to see that, on the square lattice, $a_1 = 1$, $a_2 = 2$, $a_3 = 6$ and $a_4 = 23$. Similarly, we can ask for the number (A_n) of site animals with n sites. On the square lattice, $A_1 = 1$, $A_2 = 2$, $A_3 = 6$ and $A_4 = 19$.

An animal consists of a set of vertices (with integer coordinates in $\mathbb{R}^d$) and we define the *top vertex* and *bottom vertex* using lexicographic ordering. We can concatenate an animal with n vertices with an animal with m vertices by translating such that the

top vertex of one animal is one lattice space away from the bottom vertex of the other. By adding an edge joining these two vertices, we obtain an animal with $n+m$ vertices, but not all animals with $n+m$ vertices can be obtained in this way. This gives rise to the super-multiplicative inequality

$$a_{n+m} \geq a_n a_m, \tag{2.1}$$

with a similar relation for A_n. It can be shown [15,16] that $a_n^{1/n}$ is bounded above and this, together with (2.1), is enough to show that

$$\sup_{n>0} n^{-1} \log a_n = \lim_{n\to\infty} n^{-1} \log a_n = \log \lambda \tag{2.2}$$

and, using similar arguments, that

$$\sup_{n>0} n^{-1} \log A_n = \lim_{n\to\infty} n^{-1} \log A_n = \log \Lambda. \tag{2.3}$$

Since every site animal is a bond animal (i.e. $A_n \leq a_n$), it is clear that $\Lambda \leq \lambda$ and in fact, it can be shown that [16]

$$\Lambda < \lambda. \tag{2.4}$$

Although the exact values of the "growth constants" λ and Λ are not known, accurate numerical estimates are available [17,18].

3. The near-neighbour interaction model

We write $a_n(b)$ for the number of distinct (up to translation) bond animals with n vertices and with b near-neighbour contacts, i.e. pairs of vertices which are unit distance apart but which are not incident on a common edge.

In order to investigate the thermodynamics of this model, we shall be interested in the behaviour of the partition function

$$Z_n(\beta) = \sum_b a_n(b) \exp(\beta b) \tag{3.1}$$

and of

$$G(\beta) = \lim_{n\to\infty} n^{-1} \log Z_n(\beta), \tag{3.2}$$

which, apart from a change in sign, is a reduced limiting free energy per vertex.

We first consider the maximum possible number of near-neighbour contacts $b_{\max}(n)$. The average valence of a vertex of a tree is $2 - (2/n)$ so, since the coordination number of the d-dimensional hypercube lattice is $2d$, we have

$$b_{\max}(n) \leq \left(2d-2+\frac{2}{n}\right)\frac{n}{2} = (d-1)n+1. \tag{3.3}$$

A pair of animals can be concatenated by translating so that the top vertex of one is unit distance from the bottom vertex of the other and adding an edge to join these two vertices. Because of the definitions of top and bottom vertices, this does not introduce new near-neighbour contacts, so that

$$a_{n_1}(b_1)a_{n_2}(b_2) \leq a_{n_1+n_2}(b_1+b_2). \tag{3.4}$$

Multiplying by $\exp[\beta(b_1+b_2)]$ and summing over b_1 and b_2 gives

$$Z_{n_1}(\beta)Z_{n_2}(\beta) \leq (d-1)(n_1+n_2)(1+o(1))Z_{n_1+n_2}(\beta), \tag{3.5}$$

and from (3.5) it is easy to show the existence of the limit

$$\lim_{n\to\infty} n^{-1}\log Z_n(\beta) \equiv G(\beta). \tag{3.6}$$

To prove that $G(\beta)$ is convex (and therefore continuous), it is sufficient to show that

$$\tfrac{1}{2}[G(\beta_1)+G(\beta_2)] \geq G([\beta_1+\beta_2]/2). \tag{3.7}$$

This follows immediately from

$$\begin{aligned} Z_n(\beta_1)Z_n(\beta_2) &= \sum_{b_1} a_n(b_1)\exp(\beta_1 b_1)\sum_{b_2} a_n(b_2)\exp(\beta_2 b_2) \\ &\geq \left(\sum_b a_n(b)\exp[(\beta_1+\beta_2)b/2]\right)^2 \\ &= Z_n\left(\frac{\beta_1}{2}+\frac{\beta_2}{2}\right)^2 \end{aligned} \tag{3.8}$$

on taking logarithms, dividing by n and letting $n\to\infty$.

Next, we identify $G(0)$. Since

$$\sum_b a_n(b) = a_n, \tag{3.9}$$

clearly

$$G(0) = \lim_{n\to\infty} n^{-1}\log\sum_b a_n(b) = \log\lambda. \tag{3.10}$$

For real values of β, we have

$$Z_n(\beta) = \sum_b a_n(b) \exp(\beta b) \geq a_n(0), \tag{3.11}$$

but $a_n(0) = A_n$ so that

$$G(\beta) \geq \lim_{n \to \infty} n^{-1} \log a_n(0) = \log \Lambda. \tag{3.12}$$

Clearly, since $Z_n(\beta)$ is non-decreasing, $G(\beta) \leq G(0)$ for $\beta \leq 0$ but, at least for large negative β, we can derive a much stronger upper bound. We consider a bond animal with n vertices and b near-neighbour contacts. If we add the b edges needed to reduce the number of near-neighbour contacts to zero, we obtain a site animal with n vertices. The resulting site animal could have many different bond animals as precursors, and we can bound the number of precursors by noticing that we could remove b edges from the site animal in at most $\binom{dn}{b}$ ways. Hence,

$$a_n(b) \leq \binom{dn}{b} a_n(0), \tag{3.13}$$

so that

$$Z_n(\beta) \leq a_n(0)(1 + \exp \beta)^{dn}, \tag{3.14}$$

and hence

$$G(\beta) \leq \log \Lambda + d \log(1 + \exp \beta). \tag{3.15}$$

Now, letting $\beta \to -\infty$ in (3.15), together with (3.12), gives

$$\lim_{\beta \to -\infty} G(\beta) = \log \Lambda. \tag{3.16}$$

We now derive bounds for $\beta \geq 0$. Since

$$Z_n(\beta) \leq \exp(\beta b_{\max}) \sum_b a_n(b), \tag{3.17}$$

we have

$$G(\beta) \leq (d-1)\beta + \log \lambda \tag{3.18}$$

and

$$\limsup_{\beta \to \infty} \beta^{-1} G(\beta) \leq (d-1). \tag{3.19}$$

Clearly, $G(\beta) \geq \log \lambda$ for all positive β and, in addition,

$$Z_n(\beta) \geq a_n(b_{\max}) \exp(\beta b_{\max}). \tag{3.20}$$

We can obtain a lower bound on $b_{\max}$ by considering Hamiltonian walks which, together with (3.3), establishes that $b_{\max} = (d-1)n + o(n)$. This, and the fact that $a_n(b_{\max})$ is non-negative, establish that

$$\lim_{\beta \to \infty} \frac{G(\beta)}{\beta} = (d-1). \tag{3.21}$$

In two dimensions we can do a little better, since $a_n(b_{\max})$ is bounded below by the number of (undirected) Hamiltonian walks on the square lattice, which is in turn bounded below by the corresponding number on the Manhattan lattice. Using Kasteleyn's exact result [19] for these walks, we obtain

$$G(\beta) \geq \frac{G}{\pi} + (d-1)\beta, \tag{3.22}$$

for all real β, where G is Catalan's constant $G = 0.9159\ldots$. In three dimensions, we can stack up a set of Hamiltonian circuits on copies of the square lattice with Manhattan orientations, and suitably connect these layers to form a compact walk on the simple cubic lattice. The net effect of this is that (3.22) is also valid in three dimensions. This argument can then be repeated in higher dimensions so that (3.22) is valid for all d.

4. Comparison of models

In this section, we compare the general form of the results for two models of the thermodynamics of branched polymers in dilute solution, especially as a function of temperature or solvent quality. In order to look at phenomena such as collapse, the model needs to incorporate a driving force which will reduce the dimensions of the branched polymer as the temperature is increased. In the model discussed in section 3, this is accomplished by incorporating an attractive interaction between non-bonded near-neighbour pairs of vertices. An alternative idea [11, 14] is to favour animals with many cycles at low temperature. This is accomplished by considering the number $a_n^0(c)$ of bond animals with n vertices and c independent cycles, and examining the behaviour of the partition function

$$Q_n(\beta) = \sum_c a_n^0(c) \exp(\beta c) \tag{4.1}$$

and

$$F(\beta) = \lim_{n \to \infty} n^{-1} \log Q_n(\beta). \tag{4.2}$$

We have analysed this model in some detail elsewhere [14] and we summarize some of our results here in order to make a comparison with the work described in section 3. Some key results from [14] are:

(a) $F(\beta)$ is a convex, continuous, strictly increasing function;

(b) $F(0) = \log \lambda$;

(c) for $\beta \leq 0$

$$\log \lambda^0 < F(\beta) \leq \min[\log \lambda, \log \lambda^0 + (d-1)\log(1+\exp\beta)], \tag{4.3}$$

where λ^0 is the growth constant for bond trees, known to be strictly less than λ [14,16];

(d) $\lim_{\beta \to -\infty} F(\beta) = \log \lambda^0$;

(e) for $\beta \geq 0$

$$\max[\log \lambda, (d-1)\beta] \leq F(\beta) \leq \log \lambda + (d-1)\beta; \tag{4.4}$$

(f) $\lim_{\beta \to \infty} F(\beta)/\beta = d-1$.

It is clear that there are strong similarities between the two models. The primary difference is in fact the lower bound for $\beta \leq 0$ and the corresponding value of the $\beta \to -\infty$ limit. One would therefore expect both models to be equally useful in describing the general thermodynamic properties of dilute solutions of branched polymers.

5. Some open questions

In this final section, we point out a number of important questions which deserve attention. There can be little doubt that the most important of these is the existence of a collapse transition. That is, is $G(\beta)$ an analytic function of β? If not, can we say anything about the nature and location of the singular point(s)? This seems to be a very difficult question and we have no results which bear on it. Of course, we expect that $G(\beta)$ will be analytic for $\beta \leq 0$ and that there will be just one singular point for $\beta > 0$.

For $\beta \leq 0$, our results seem reasonably satisfactory. However, for $\beta > 0$ a number of interesting questions remain. We know that $G(\beta)$ is asymptotic to a line with gradient $d-1$. Can we establish the value of the intercept of this line? If not, can we at least improve our current upper and lower bounds on this intercept? This is equivalent to asking for the limiting entropy of the compact phase. We have shown that the compact phase in the near-neighbour interaction model has non-zero limiting entropy. This is in sharp contrast with the cycles model where, by extending the arguments of [14], we can show that the limiting entropy in the compact phase is zero.

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