LETTER TO THE EDITOR

General model for collapse in lattice animals

S Flesia†, D S Gaunt†, C E Soteros‡ and S G Whittington§

† Department of Physics, King's College, Strand, London WC2R 2LS, UK
‡ Department of Mathematics and Statistics, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0W0
§ Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Abstract. We consider a two-variable model for collapse in a lattice model of a branched polymer in a dilute solution. We model the polymer as a lattice animal with two fugacities, one corresponding to monomer–monomer interactions and the other to interactions between monomers and solvent. We investigate the nature of the phase diagram for this model and show that it contains three branches. We estimate the values of the crossover exponent ϕ along these branches and discuss the relationship to one-variable models. In particular, we show that one point on the phase boundary is related to a percolation transition.

The collapse transition in branched polymers in dilute solution has been studied theoretically by a number of authors, using a variety of different models. The transition from an expanded to a collapsed state can be driven by a cycle fugacity (Derrida and Herrmann 1983, Dickman and Shieve 1984, 1986, Lam 1987, 1988, Chang and Shapir 1988, Madras *et al* 1990, Vanderzande 1992), by a contact fugacity (Madras *et al* 1990, Gaunt and Flesia 1991, Flesia and Gaunt 1992) or by a solvent fugacity (Flesia 1992). Physically we expect both the interaction between pairs of monomers, and the interaction between monomers and solvent to be important and, in this paper, we introduce a two-variable model which explicitly includes both of these terms. In principle this idea can be applied both to trees and to animals but we concentrate on the animal problem because the phase diagram has a richer structure. Because of Euler's relation, there is a connection between the numbers of monomer–monomer contacts, monomer–solvent contacts, and cycles, so that this two-variable model can be re-expressed in terms of any pair of these quantities. Euler's relation also allows the model to be related to the weak and strong embedding versions of the above one-variable models.

We focus on the square lattice though many of our results are more generally applicable. Consider a lattice animal, weakly embedded in the square lattice, with n vertices, e edges and with cyclomatic index c. We define a *contact* as a pair of nearest-neighbour occupied vertices not directly connected by an occupied edge. Similarly we define a *solvent contact* as an edge which joins a vertex of the animal to a neighbouring unoccupied vertex. If the number of contacts is k and the number of solvent contacts is s, then (using Euler's relation)

$$s = 2n + 2 - 2c - 2k. \tag{1}$$

We define the canonical partition function

$$Z_n(\beta_1, \beta_2) = \sum_{s,k} a_n(s,k) e^{\beta_1 s + \beta_2 k} \tag{2}$$

where $a_n(s,k)$ is the number of animals with n vertices, s solvent contacts and k contacts. It can be shown that the limiting reduced free energy

$$F(\beta_1, \beta_2) = \lim_{n \to \infty} n^{-1} \log Z_n(\beta_1, \beta_2) \tag{3}$$

exists and is a convex function of β_1 and β_2. Moreover, $F(\beta_1, \beta_2)$ is monotone increasing and continuous.

This model is related to several one-variable models. Clearly, setting $\beta_1 = 0$ gives the contact model, and setting $\beta_2 = 0$ gives the solvent model. In addition, it follows from (1) that the line $\beta_2 = 2\beta_1$ corresponds to the cycle model. Consequently we expect transitions for a positive value of β_2 when $\beta_1 = 0$, for a negative value of β_1 when $\beta_2 = 0$ and for a negative value of β_1 (and also a negative value of β_2, of course) when $\beta_2 = 2\beta_1$.

It is also possible to relate the model to percolation, and this yields a singular point along a particular curve in the (β_1, β_2) plane. For a fixed origin on the lattice, we define $P_n(p)$ as the probability that the cluster containing the origin consists of n vertices, at edge occupation probability p. Then

$$P_n(p) = n \sum_{e,s,k} a_{n,e,s,k} p^e (1-p)^{s+k} \tag{4}$$

where $a_{n,e,s,k}$ is the number of clusters with n vertices, e edges, s solvent contacts and k contacts. Using Euler's relation and summing over e

$$P_n(p) = n p^{2n} \sum_{s,k} a_n(s,k) p^{-s/2-k} (1-p)^{s+k}$$
$$= n p^{2n} Z_n(\beta_1, \beta_2) \tag{5}$$

where $e^{\beta_1} = (1-p)/\sqrt{p}$ and $e^{\beta_2} = (1-p)/p$. These equations define parametrically a curve in the (β_1, β_2) plane along which the lattice animal problem is isomorphic to the edge percolation problem. We call this the *percolation curve*.

The decay of the cluster size distribution $P_n(p)$ is well understood, and the behaviour above and below the percolation threshold p_c is quite different (see e.g. Grimmett 1989). For $p < p_c$

$$\lim_{n \to \infty} n^{-1} \log P_n(p) < 0 \tag{6}$$

while for $p > p_c$

$$\lim_{n \to \infty} n^{-1} \log P_n(p) = 0. \tag{7}$$

These results show that the free energy $F(\beta_1, \beta_2)$ is non-analytic along the percolation curve at $\beta_1 = \log[(1-p_c)/\sqrt{p_c}] = -\frac{1}{2}\log 2$ and $\beta_2 = \log[(1-p_c)/p_c] = 0$. This argument determines one point on the phase boundary. Since this point is on the β_1 axis it corresponds to the solvent model.

We now use series analysis techniques to investigate the phase diagram. Using the exact enumeration data given in Madras *et al* (1990) we have computed $Z_n(\beta_1, \beta_2)$ for $n \leqslant 19$. For fixed β_1, or for fixed β_2 we calculate the fluctuations per site in k, i.e. $(\langle k^2 \rangle - \langle k \rangle^2)/n$ and in s, i.e. $(\langle s^2 \rangle - \langle s \rangle^2)/n$. At fixed positive β_1 the fluctuations in s and in k show pronounced peaks at the same value of β_2 (see figure 1(a)) indicating a transition from the expanded to collapsed region as β_2 increases. At moderately large negative values of β_2 the fluctuations in s show a sharp peak as β_1 increases, but there is no evidence of a peak in the fluctuations in k. Similarly, at moderately large negative values of β_1, there is a peak in the fluctuations in k as β_2 increases, but there is no peak in the fluctuations in s (see figure 1(b)). We interpret these results as implying the existence of three phases, separated by three phase boundaries, meeting at the triple point, as shown schematically in figure 2. One phase (E) is expanded and the other two are compact, with small numbers of solvent contacts. However, in the compact phase (C_k), corresponding to positive or small negative values of β_2, the clusters have large numbers of contacts, while in the compact phase (C_c), corresponding to more negative values of β_2, the clusters have large numbers of cycles, and the transition between these phases reflects the exchange of cycles for contacts.
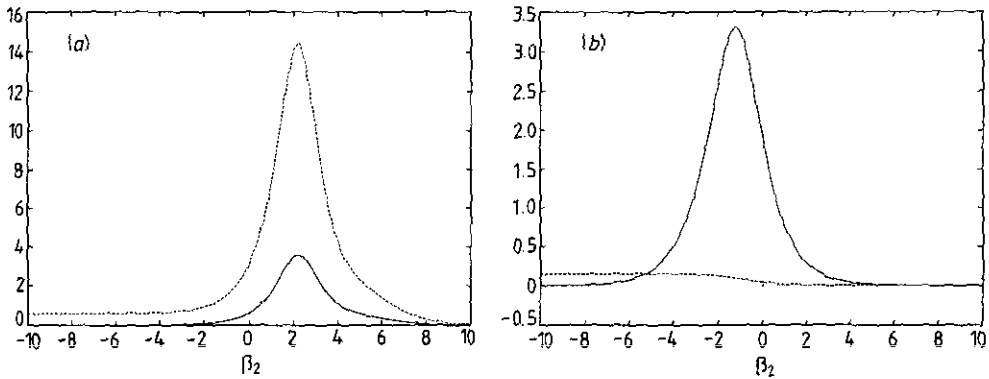

Figure 1. Fluctuations in k (full line) and in s (dashed line) for $n = 19$ as a function of β_2 for (a) fixed $\beta_1 = 1$ and (b) fixed $\beta_1 = -4$.
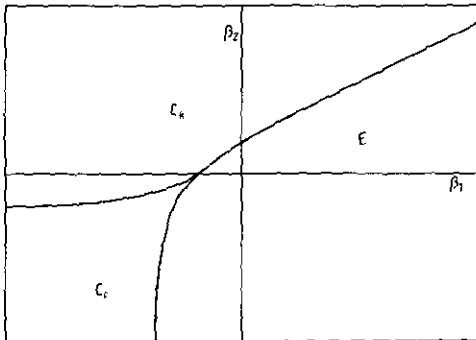

Figure 2. Sketch of the phase diagram in the (β_1, β_2) plane.

We expect three different values of the crossover exponent ϕ, one corresponding to each of the three branches of the coexistence curve. We have estimated the

numerical values of ϕ, along the three coexistence curves and find $\phi(E-C_k) = 0.60 \pm 0.03$, $\phi(E-C_c) = 0.66 \pm 0.03$ and $\phi(C_c-C_k) = 0.6 \pm 0.1$. The error bars for these estimates of ϕ overlap and we cannot rule out the possibility of a common value of ϕ.

The general shapes of the coexistence curves can also be obtained from the numerical results. The phase boundary between E and C_k appears to be asymptotic to a line with gradient 2. For β_1 and β_2 both large and positive we expect the clusters to have few cycles and to behave essentially as trees. It is not difficult to show that the phase boundary in a two-variable model for trees is a straight line with gradient 2 (Flesia 1992). Similarly, the phase boundary between E and C_c appears to be asymptotic to a line with infinite slope, and that between C_c and C_k seems to be asymptotic to a line with slope close to zero. Along the phase boundary between E and C_c, the clusters will be dominated by strong embeddings as $\beta_2 \rightarrow -\infty$. In this limit the number of contacts will be zero and there is a mapping between the cycle model and the solvent model (for strong embeddings) (Flesia 1992). Hence, we expect the critical temperature, in this limit, to be related to the critical temperature of the cycle model for strong embeddings (which is in agreement with our estimate), and we expect the crossover exponent along this branch to be the same as that for the cycle model for strong embeddings (Derrida and Herrmann 1983, Vanderzande 1992). In two dimensions the value of the crossover exponent for the cycle model for strong embeddings is thought to be 2/3 (Derrida and Herrmann 1983, Vanderzande 1992) and this is consistent with our numerical estimate.

For trees there is no phase corresponding to C_c and for the cycle model in strongly embedded animals there is no phase corresponding to C_k. In both trees and strongly embedded animals there is a relation between s and either k or c which leads to a very simple phase diagram. However, the phase diagram for this two-variable model is quite rich. This will be investigated in more detail in a subsequent publication where we shall give a more precise numerical determination of the phase diagram.

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