LETTER TO THE EDITOR

Polymer coil–globule transition by real space renormalisation

Giancarlo Jug

Theory and Computational Science Group, AFRC-IFRN, Colney Lane, Norwich NR4 7UA, UK

Abstract. A simple real space renormalisation scheme is proposed for the statistics of the polymer coil–globule transition in two dimensions. This approach describes the coil, θ point and globular states of the macromolecule within a single two-parameter transformation. Results from a small-cell calculation include the θ-point size exponent, $\nu_\theta = 0.494$, and crossover exponent $\phi = 0.486$.

There has been extensive interest during the last decade in the theoretical study of the coil–globule transition in a polymer molecule in solution as induced by the change from a good to a poor solvent (see, e.g., Sanchez 1979, Saleur 1986 and references therein). Since in actual experiments on polymer solutions demixing often replaces macromolecular collapse, a partial motivation for these studies lies in the analogy between the coil–globule transition and the folding/unfolding of globular proteins (Moore 1977, Volkenstein 1977, Obukhov 1986). In the case of a protein molecule, the folding transition, which partly determines the biological functionality of the molecule, is induced by the aggregation tendency of the solvophobic residues in the primary structure of the chain (Dill 1985). A drastic simplification, but a necessary first step in the understanding of the folding transition, is therefore the situation where all monomers have the same affinity with the solvent. In this case, there is general agreement that the collapse to a globular state can be modelled by a change in the sign of the monomer–monomer excluded volume interaction as the temperature is lowered below the Flory compensation point θ, for example (de Gennes 1979). The presence of repulsive three- and higher-body interactions prevents collapse of the chain to unphysically high densities.

This line of thought has led to a description of the coil–globule transition in terms of a crossover phenomenon formally related to that occurring in a magnetic system near its tricritical point (de Gennes 1975, 1978, 1979, Stephen 1975). There are, in principle, three ranges in temperature (or other variable driving the transition), with the molecule's size ξ behaving asymptotically as:

$$\xi \sim N^{\nu_{SAW}} \qquad \text{for} \quad T > \theta$$

$$\xi \sim N^{\nu_\theta} \qquad \text{at} \quad T = \theta$$

$$\xi \sim N^{\nu_G} \qquad \text{for} \quad T < \theta$$

with a smooth interpolation between the high-temperature (coil or self-avoiding walk, SAW) and low-temperature (globular, G) regimes. Analytically, this can be expressed

in terms of a scaling form for $\xi(N, T)$:

$$\xi = N^{\nu_\theta}F(wN^\phi) \tag{1}$$

where N is the polymerisation index, $w \sim T - \theta$ is the strength of the monomer–monomer short-ranged interaction and $F(x)$ and ϕ are the crossover function and exponent, respectively, such that for $x > 0$ (SAW phase) ξ diverges with an exponent ν_{SAW}, whilst for $x < 0$ (G phase) ξ diverges with a new exponent ν_G ($= 1/d$ for a dense space-filling molecule). Since in $d = 3$ the exponents ν_θ and ϕ take up classical values, the novel situation arises in two dimensions, where the evaluation of these exponents has been the subject of intense theoretical investigations following the experimental work of Villanove and Rondelez (1980) on polymer monolayers.

In this letter I will introduce a novel lattice approach to the polymer coil–globule transition in two dimensions, giving some estimates for the exponents ν_θ and ϕ. However, the main purpose of this work is to provide a simple, yet efficient, statistical treatment that can be implemented to study more realistic models of protein conformational phase transitions in the bulk as well as at interfaces, where the connection with the functionality of cell membrane proteins can be achieved. The model I propose is a lattice random walk consisting of $N \gg 1$ steps where suitable constraints are imposed. In the coil phase only configurations that are self-avoiding walks are accepted, whilst in the globular phase only configurations with two (but not three or more) monomer contacts are considered. In figure 1 examples of SAW and G configurations are given, and one can see that, for the same N, more compact structures are achieved in the latter case.
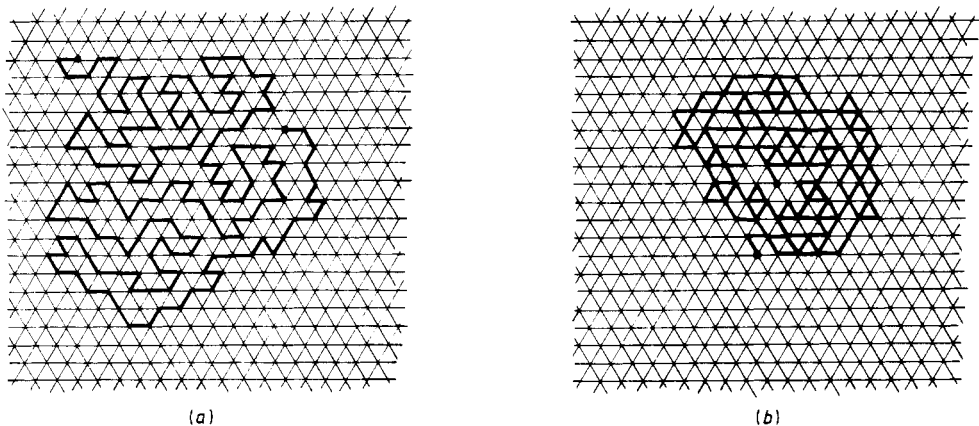
(a)   (b)

Figure 1. Examples of self-avoiding (a) and globular (b) configurations on the triangular lattice. Both configurations have $N = 150$ links.

In order to solve the model asymptotically for $N \to \infty$, I will employ a real space cell renormalisation scheme that has the advantage of simplicity and efficiency. It is easy to convince oneself that self-avoiding and self-attracting walks can be easily accommodated on small cells of the triangular lattice. In one approach (Family 1980, Redner and Reynolds 1981) one considers all configurations starting from a chosen site of the cell (e.g. a corner) and spanning the cell in at least one chosen direction. Figure 2 shows the bare and renormalised cells employed in this work, with a rescaling factor $b = 2$. Following Redner and Reynolds (1981), I introduce a monomer fugacity
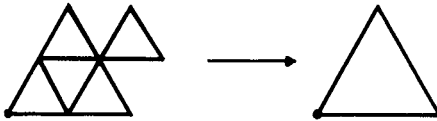
Figure 2. Bare and renormalised cells used in this work.

K and a cell partition function $Z(K)$ enumerating all possible SAW or G spanning configurations:

$$Z(K) = \sum_{n}^{\{cell\}} a_n K^n$$

where a_n is the total number of n-step configurations. A recursion relation $K' = K'(K)$ is generated by imposing that the cell partition function is conserved in the renormalisation process:

$$Z'(K') = Z(K).$$

A number of uncontrolled approximations is introduced in this way (for a partial discussion see the articles in Burkhardt and van Leeuwen (1982)). However, improvement on mean-field theory results is generally expected and the asymptotic properties of the polymer chain are obtained from the relevant fixed point $K = K' = K^*$ of the recursion relation through

$$\mu = 1/K^*$$

$$\nu = \ln b / \ln \lambda \qquad \lambda = dK'/dK|_{K^*} \tag{2}$$

where $\mu = \lim_{n \to \infty} (a_n / a_{n-1})$ is the effective lattice connectivity of the polymer chain. For the present cell, figure 2, one has

$$Z_{SAW}(K) = K^2 + 6K^3 + 17K^4 + 15K^5 + 4K^6 \tag{3}$$

for SAW configurations (figure 3) and

$$Z_G(K) = Z_{G1}(K) + Z_{G2}(K) + Z_{G3}(K) + Z_{G4}(K)$$

$$Z_{G1}(K) = 2K^5 + 16K^6 + 20K^7 + 10K^8$$

$$Z_{G2}(K) = K^6 + 6K^7 + 14K^8 + 9K^9 \tag{4}$$

$$Z_{G3}(K) = 2K^9$$

$$Z_{G4}(K) = K^9$$

for G configurations (figure 4). It should be noticed that globular cell configurations are such that at least one possible site in the cell hosts a monomer–monomer contact.
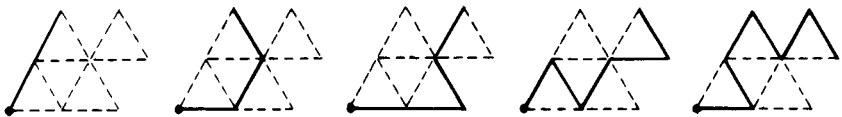

Figure 3. Some of the configurations contributing to $Z_{SAW}(K)$.

Figure 4. Some of the configurations contributing to $Z_G(K)$.

An exceedingly dense molecule will result if all sites are imposed to host such contacts. In (4), $Z_{GM}(K)$ refers to globular cell configurations containing M contacts. The renormalised partition functions are:

$$Z'_{SAW}(K') = K' + 2K'^2$$
$$Z'_G(K') = K' + 2K'^2 + K'^3. \tag{5}$$

Using the relations of (2), the following results are obtained:

SAW phase: $K^* = 0.318$, $\mu = 3.146$, $\lambda = 2.413$, $\nu = 0.787$

G phase: $K^* = 0.558$, $\mu = 1.790$, $\lambda = 3.915$, $\nu = 0.508$.

The SAW exponent $\nu_{SAW} = 0.787$ should be compared with the (conjectured) exact value $\nu_{SAW} = \frac{3}{4}$ (Nienhuis 1982). A comparable direct decimation approach on the triangular lattice (Napiorkowski *et al* 1979) yields $\mu_{SAW} = 4.828$ and $\nu_{SAW} = 0.708$. The results for the G phase represent new estimates; the exponent $\nu_G = 0.508$ is an approximation for the compactness exponent $\nu_G = 1/d = \frac{1}{2}$, which is believed to be exact for dense polymer globules (Duplantier 1986a).

In order to study the θ point and the coil–globule transition, it is now convenient to set up a two-parameter renormalisation recursion relation by introducing a variable f, $0 \leqslant f \leqslant 1$, representing the probability that one of the possible sites in the cell is the host of a monomer–monomer contact. The variable f may depend on temperature through $\exp(-E/kT)$, where $E < 0$ is the relative attraction energy between two monomers. The special values $f = 0$ and $f = 1$ will then represent the high- and low-temperature regimes, respectively, whilst the θ point will correspond to an intermediate value f_θ, so that, near the θ point, one has $w \sim f_\theta - f$ in (1). The full cell partition function is now:

$$Z(K|f) = (1-f)^4 Z_{SAW}(K) + Z_G(K|f)$$
$$Z_G(K|f) = f Z_{G1}(K) + f^2 Z_{G2}(K) + f^3 Z_{G3}(K) + f^4 Z_{G4}(K) \tag{6}$$

for the bare cell and

$$Z'(K'|f') = (1-f')Z'_{SAW}(K') + f' Z'_G(K') \tag{7}$$

for the renormalised cell. A renormalisation recursion relation for f can be defined by asserting that only bare cell configurations with at least one f site contribute to the renormalised cell f' site. There is a configurational weight $f^M(1-f)^{4-M}$ and a normalisation in order to preserve the probabilistic nature of f and f':

$$f' = \left(\sum_M f^M (1-f)^{4-M} Z_{GM}(K) \right)$$

$$\times \left((1-f)^4 Z_{SAW}(K) + \sum_M f^M (1-f)^{4-M} Z_{GM}(K) \right)^{-1}. \tag{8}$$

Equations (6)–(8) guarantee that the coil and globule recursion relations are recovered in the $f = 0$ and $f = 1$ limits. These equations, together with (3)–(5), give rise to a two-parameter recursion relation $K' = K'(K, f)$, $f' = f'(K, f)$, and generate the flow given in figure 5. There are three relevant fixed points, those with $f^* = 0$ and $f^* = 1$ corresponding to the SAW and G phases, respectively. The third fixed point is to be
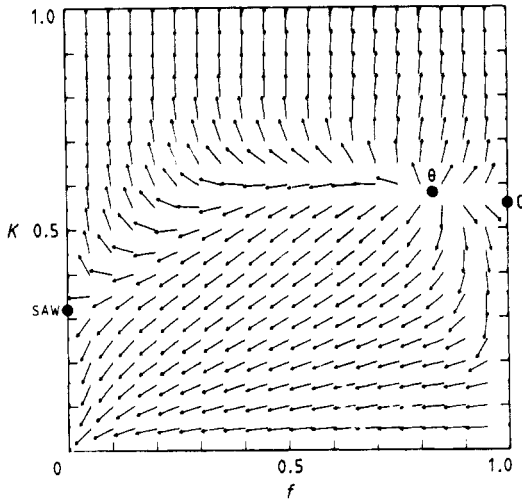
Figure 5. Global flow diagram of the two-parameter recursion relation.

identified with the θ multicritical point and is unstable in all directions. Its parameters are as follows:

$$\theta \text{ point:} \qquad f^* = 0.828, \quad K^* = 0.582, \quad \mu = 1.717, \quad \lambda_1 = 4.069,$$

$$\lambda_2 = 1.977, \quad \nu = 0.494.$$

The crossover exponent is therefore given by

$$\phi = \ln \lambda_2 / \ln \lambda_1 = 0.486$$

where λ_1 and λ_2 are the eigenvalues of the linearised recursion relation matrix $\partial(K', f')/\partial(K, f)$ evaluated at the θ fixed point. The present estimates for ν_θ and ϕ are to be compared with the results of a number of different approaches. A two-loop ε expansion yields (de Gennes 1975, Stephen and McCauley 1973, Stephen 1975)

$$\nu_\theta = \tfrac{1}{2} + \tfrac{2}{363}\varepsilon^2 = 0.505$$

$$\phi = \tfrac{1}{2} + \tfrac{3}{22}\varepsilon = 0.636$$

for $\varepsilon = 3 - d = 1$ (see also Kholodenko and Freed 1984a, b, Duplantier 1982, 1986b). Extrapolation of exact finite-size estimates gives $\nu_\theta = 0.55 \pm 0.01$ (Derrida and Saleur 1985) and $\phi = 0.48 \pm 0.07$ (Saleur 1986). Series expansion estimates include $\nu_\theta = 0.503 \pm 0.01$ (Ishinabe 1985) and $\nu_\theta = 0.535 \pm 0.025$ and $\phi = 0.64 \pm 0.05$ (Privman 1986). Numerical simulation studies (Baumgärtner 1982, Tobochnik *et al* 1982) yield similar values. A conjecture (Jan *et al* 1986) identifies ν_θ with the exponent of the infinitely growing SAW, $\nu_{\text{IGSAW}} = 0.567 \pm 0.003 \simeq \tfrac{4}{7}$ (Kremer and Lyklema 1985). Also, experiments on polymer monolayers (Villanove and Rondelez 1980) lead to $\nu_\theta = 0.56 \pm 0.01$ (see also Duplantier *et al* 1986). Therefore, the present small-cell real space calculation does well in predicting the correct phase diagram and the value of the θ crossover exponent ϕ. However, the situation for μ_θ and ν_θ is less satisfactory, since one should have $\mu_\theta > \mu_G$ and $\nu_\theta > \nu_G$. It is likely that better estimates will arise from larger cell calculations.

   In conclusion, I have proposed a novel lattice model for the statistics of the polymer coil–globule transition. The model gives reasonable results in two dimensions and is

simple enough for extension to three dimensions and to inhomogeneous environments and polymer composition.

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