LETTER TO THE EDITOR

Collapse transition in a simple polymer model: exact results

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Abstract. We calculate the exact values of the thermodynamic parameters at the collapse transition of a directed polymer with attractive nearest-neighbour interactions.

In a recent letter [1], the polymer collapse (coil–globule) transition was modelled by a directed self-avoiding walk with attractive nearest-neighbour interactions. Numerical results were obtained for this model, which led to a conjecture for the exact values of the thermodynamic parameters at the collapse transition. In this letter we prove that the result is indeed exact.

We consider the polymer in figure 1 on an infinite lattice; the polymer is directed in that steps in the negative x direction are forbidden. Hence, the position of the polymer in column i, n_i, is single-valued and is given by the height of the directed bond from a fixed reference level. We consider the statistical properties of an ensemble of polymer chain conformations at a given chemical potential, μ, which controls the average chain length [2]. Interactions are introduced through an attractive energy, $-J$, between bonds which occupy the same row in adjacent columns (see figure 1).
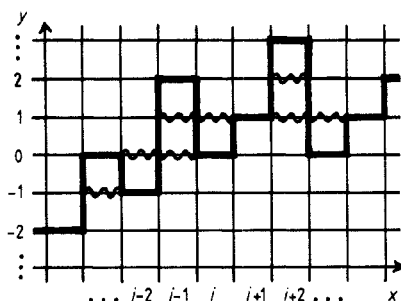

Figure 1. A polymer directed along the x axis. Monomer–monomer interactions are represented by wavy lines.

The grand canonical energy of a particular polymer configuration with L_x steps in the x direction is

$$-E\left(\{u_i\}\right) = \mu \left(|u_1| + |u_{L_x+1}|\right)/2 + \sum_{i=1}^{L_x} [\mu \ell_i + J m_i] \tag{1}$$

where $u_i = (n_{i-1} - n_i)$ is the height difference between neighbouring columns and both ℓ_i and m_i are functions of u_i as follows:

$$\ell_i = 1 + (|u_i| + |u_{i+1}|)/2 \tag{2}$$

and

$$m_i = \begin{cases} \min(|u_i|, |u_{i+1}|) & \text{if } u_i u_{i+1} \le 0 \\ 0 & \text{otherwise.} \end{cases} \tag{3}$$

Note that u_1 and u_{L_x+1} fix the positions of the ends of the polymer chain. The partition function for all walks with L_x steps can be written

$$\mathcal{Z}_{L_x} = \sum_{\{u_i\}} \exp\left[-E(\{u_i\})/k_B T\right] \tag{4}$$

where the summation is over all polymer configurations given by the set of all possible integer values $\{u_i : i = 1, \ldots, L_x\}$. Defining a transfer matrix, $\mathbf{T}$, by

$$\mathbf{T}(u_i, u_{i+1}) = \exp\left[(\mu \ell_i + J m_i)/k_B T\right] \tag{5}$$

the partition function, (4), can be rewritten as the trace of the L_xth power of $\mathbf{T}$,

$$\mathcal{Z}_{L_x} = \sum_{\{u_1, u_{L_x+1}\}} \psi(u_1) \mathbf{T}^{L_x} \psi(u_{L_x+1}) \tag{6}$$

where

$$\psi(u_i) = \exp\left[(\mu |u_i|)/2k_B T\right]. \tag{7}$$

As usual, the trace is dominated by the largest eigenvalue of $\mathbf{T}$, λ_0, for large L_x and

$$\mathcal{Z}_{L_x} \sim (\lambda_0)^{L_x} \qquad \text{as } L_x \to \infty. \tag{8}$$

Summing over L_x gives the grand partition function for all walks on the lattice,

$$\mathcal{Z} = \sum_{L_x=0}^{\infty} \mathcal{Z}_{L_x} = \sum_{\text{walks}} \omega^L \tau^M \tag{9}$$

where $\omega = \exp(\mu/k_B T)$, $\tau = \exp(J/k_B T)$, L is the total length of the walk and M is the number of nearest-neighbour interactions.

The grand potential for the polymer is defined by

$$\Omega(\mu, J) = -k_B T \ln \mathcal{Z} = -\mu \langle L \rangle - J \langle M \rangle \tag{10}$$

where $\langle \ldots \rangle$ denotes the thermodynamic average of a quantity. As $\lambda_0 \to 1^-$, the grand potential diverges and (substituting the form (8) into the sum (9))

$$\Omega \sim k_B T \ln\left[1 - \lambda_0(\omega, \tau)\right] \qquad \text{as } \lambda_0 \to 1^-. \tag{11}$$

Physically, this is associated with the divergence of the average length of the polymer, $\langle L \rangle$. If $\lambda_0 (\omega, \tau)$ approaches 1 continuously as ω is varied at a fixed value of τ, we can define a critical value of ω, $\omega^\star (\tau)$, by

$$\lambda_0 [\omega^\star (\tau)] = 1. \tag{12}$$

The numerical results presented in [1] suggested that the polymer model has a line of critical values, $\omega^\star (\tau)$, up to a *tricritical* point found at

$$(\omega^\star, \tau^\star) = (0.295\,5977, 3.382\,976). \tag{13}$$

Above the tricritical point, $\tau > \tau^\star$, a phase transition to a collapsed phase was observed for $\omega' (\tau) = \tau^{-1}$, as ω was varied. Our aim here is to explain this observation and derive the exact values of $(\omega^\star, \tau^\star)$ analytically.

For $\tau = 1$, the largest eigenvalue is known to be [2]

$$\lambda_0 = \omega \left(\frac{1 + \omega}{1 - \omega} \right) \tag{14}$$

from which it follows immediately that

$$\omega^\star (\tau = 1) = \sqrt{2} - 1 = 0.4142\ldots \tag{15}$$

and [3]

$$\langle |u_i| \rangle = 1 \qquad \text{at } \omega^\star (\tau = 1). \tag{16}$$

In the basis specified by our model, the eigenvectors of the transfer matrix are of the form

$$\phi (u_i) = t^{|u_i|} \tag{17}$$

with $t = \omega^{1/2}$ for the eigenvector, ϕ_0, associated with λ_0. The square of the elements of this eigenvector, $\phi_0^2 (u_i)$, give the probabilities of finding particular height differences between neighbouring columns. From (17), we see that the probability vanishes as $u_i \to \infty$ for $\omega < 1$. Hence, a characteristic length for transverse fluctuations of the polymer chain can be defined as

$$\xi_y = - (\ln \omega)^{-1} \tag{18}$$

when $\tau = 1$. It is also possible to calculate the largest eigenvalue for $J/k_{\mathrm{B}}T \ll 1$;

$$\lambda_0 \left(\frac{J}{k_{\mathrm{B}}T} \right) \simeq \omega \left(\frac{1 + \omega}{1 - \omega} \right) + \frac{J}{k_{\mathrm{B}}T} \left[\frac{2\omega^3}{(1 - \omega^2)^2} \right] + \mathcal{O} \left[\left(\frac{J}{k_{\mathrm{B}}T} \right)^2 \right]. \tag{19}$$

From the results (16) and (19), we find that

$$\frac{\langle M \rangle}{\langle L \rangle} = \frac{\sqrt{2} - 1}{4} = 0.1035\ldots \qquad \text{at } \omega^\star (\tau = 1). \tag{20}$$
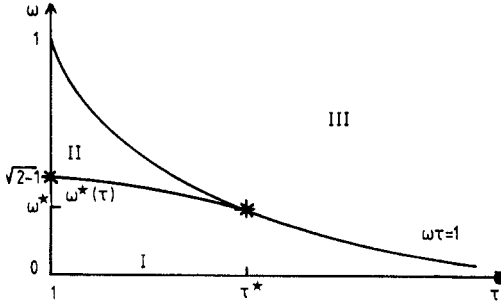
Figure 2. Schematic phase diagram for the directed polymer. In region I the average length of the polymer chain is finite, in region II it has infinite length but zero density and in region III the density is finite. The coordinates of the points marked by a cross can be calculated exactly.

The numerical results presented in [1] showed that $\omega^\star(\tau)$ decreases with increasing τ, as shown schematically in figure 2. The other pertinent curve in figure 2 is $\omega\tau = 1$, which corresponds to a stronger singularity in the grand potential. Physically, it corresponds to a transition above which the grand potential is extensive. In region I of figure 2, $\lambda_0 < 1$ and the average length of the polymer is finite. On approaching $\omega^\star$, the average length diverges and in region II it is infinite, with $1 < \lambda_0 < \infty$. However, the density of monomers on the lattice is zero in both regions I and II.

In region III, the density of monomers is finite and λ_0 scales exponentially with the width of the lattice, N_y, if the model is defined on a series of strips of finite width. On increasing ω at fixed $\tau > \tau^\star$, a transition takes place from the finite-length polymer region I to the dense polymer region III. This will occur at $\omega'(\tau)$ defined by

$$\omega'(\tau) = \tau^{-1} \qquad \text{for } \tau > \tau^\star. \tag{21}$$

This condition can be understood physically by noticing that $\omega\tau$ is an *effective* fugacity for monomers with nearest-neighbour bonds. Since, for $\omega\tau > 1$, the free energy is dominated by contributions from polymer configurations containing a macroscopic (extensive) number of nearest-neighbour bonds, a transition is expected across $\omega\tau = 1$.

At the collapse transition, both the average length of the polymer chain, $\langle L \rangle$, and the average number of nearest-neighbour bonds, $\langle M \rangle$, become macroscopic; that is, both $\langle L \rangle / V$ and $\langle M \rangle / V$ become non-vanishing in the infinite volume limit, $V \to \infty$. This must occur at a *tricritical* point, $(\omega^\star, \tau^\star)$, located at the intersection of the lines $\omega^\star(\tau)$ and $\omega\tau = 1$. Thus, $(\omega^\star, \tau^\star)$ is defined by

$$\omega^\star \tau^\star = 1 \qquad \text{and} \qquad \lambda_0(\omega^\star, \tau^\star) = 1. \tag{22}$$

Substituting $\omega = \tau^{-1}$ in the transfer matrix, its structure simplifies, allowing once again an analytic treatment. The eigenvectors of $\mathbf{T}$ are of the form

$$\phi(u_i) = e^{iku_i} \tag{23}$$

with the maximum eigenvalue occurring for $k = 0$:

$$\lambda_0 = \omega\left(1 + 2\sum_{j=1}^{\infty} \omega^{j/2}\right) = \omega\left(\frac{1 + \omega^{1/2}}{1 - \omega^{1/2}}\right). \tag{24}$$

Hence,

$$\omega^\star = \tfrac{1}{9}\left[\left(17 + 3\sqrt{3}\sqrt{11}\right)^{1/3} + \left(17 - 3\sqrt{3}\sqrt{11}\right)^{1/3} - 1\right]^2 = 0.295\,597\,74\ldots \tag{25}$$

with

$$\tau^\star = (\omega^\star)^{-1} = 3.382\,9757\ldots \tag{26}$$

in agreement with the numerical calculations. From the largest eigenvector, we see that all height differences are degenerate along $\omega\tau = 1$ (that is, the probability density is uniform).

The numerical study in [1] also considered the transitions that occur in the presence of adsorbing surfaces. A *multicritical* point, where adsorption and collapse transitions occur simultaneously, was identified at $(\omega^\star, \tau^\star, \kappa^\star)$, where $\omega^\star$ and $\tau^\star$ are given by equations (25) and (26) and $\kappa^\star$ is the critical value of the relevant Boltzmann factor for the surface binding potential. For $\tau = 1$, the phase boundary between bound and unbound polymer phases is

$$\kappa\,(1 - \omega) = 1 \tag{27}$$

[2, 3]. For the tricritical point, we expect the phase boundary to be given by

$$\kappa\left(1 - \omega^{1/2}\right) = 1 \tag{28}$$

which gives the exact value at the multicritical point,

$$\kappa^\star = \left[1 - (\omega^\star)^{1/2}\right]^{-1} = 2.191\,4878\ldots \tag{29}$$

in agreement with the numerical calculations.

This study was motivated by Dr J O Indekeu's conjecture for the exact values of the parameters at the collapse–adsorption transition (equations (25), (26) and (29)). We would like to thank Dr Indekeu and Dr D B Abraham for helpful discussions and suggestions which have stimulated phases of this work.

Note added in proof. In collaboration with D P Foster (Oxford) we have now *proved* that the phase boundary in the (κ, τ) plane between the bound and collapsed phases is given exactly by

$$\kappa = \tfrac{1}{2}\left\{(\tau + 1) + \left[(\tau + 1)^2 - 4\tau^2(\tau - 1)^{-1}\right]^{1/2}\right\} \qquad \kappa > \kappa^\star$$

and that between the collapsed and unbound phases by

$$\tau = \tau^\star \qquad \kappa < \kappa^\star.$$

These results have been obtained independently by F Igloi (Koln).

References

[1] Veal A R, Yeomans J M and Jug G 1990 *J. Phys. A: Math. Gen.* **23** L109
[2] Privman V and Švrakić N M 1989 Directed models of polymers, interfaces and clusters: scaling and finite-size properties *Lecture Notes in Physics* **338** (Berlin: Springer)
[3] Forgacs G, Privman V and Frisch H L 1989 *J. Chem. Phys.* **90** 3339