Journal of Statistical Physics, Vol. 70, Nos. 3/4, 1993

Location of the Collapsed Phase for Two-Dimensional, Directed, Interacting Polymers

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Received July 17, 1992

By mapping a model for a directed polymer onto a novel polygon problem, we give a physically appealing proof for the location of the boundary of the collapsed phase in phase space, applicable also when interactions with a surface are included.

KEY WORDS: Polymers; phase transitions; statistical physics.

Models in which an interacting directed polymer is allowed to adsorb to a substrate have been the focus of much attention recently.(1–8) Essentially this has stemmed from the possibility of calculating analytical results for such models and the relative ease of numerical calculations relative to the isotropic case. These studies have advanced the understanding of dilute solutions of polymers in contact with a substrate where monomer–monomer interactions result in a collapse transition. The directed polymer problem appears to contain much of the physics of the isotropic case. Extended, collapsed, and bound phases are observed and the delineation of the phase diagram and calculation of associated exponents are of continuing interest. Exact calculations of the collapsed phase boundary in the monomer–monomer/surface interaction plane have been previously given; these calculations have relied on a conjecture relating to the position held by the collapsed phase in the full parameter space.(4,5,7) Igloi(6) presented an argument indicating that these conjectures were correct, based on a transfer formulation of the problem. In a recent paper Brak *et al.*(18) presented a proof for the location of the collapse transition in the bulk which did not contain such an assumption. In this communication we present a

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proof for the position of the boundary of the collapsed phase by mapping the system onto a novel polygon problem, giving a physically appealing and easily understood proof applicable also when a surface is present.

The model which has been most widely studied represents a polymer by a two-dimensional random walk on a square lattice which is directed, in the sense that steps in the negative x direction are not allowed, as shown in Fig. 1. The walk is allowed to gain an energy K for each visit to the adsorbing substrate and an energy J for every pair of nonconsecutive steps which fall in the same row, but adjacent columns.

The grand canonical partition function can be written

$$\mathscr{X} = \sum_{\text{walks}} \omega^L \kappa^l \tau^n \tag{1}$$

where ω is the step fugacity, $\kappa = \exp(-K/k_B T)$, and $\tau = \exp(-J/k_B T)$. Here L is the number of monomers in the walk, l the number of visits to the wall, and n the number of monomer–monomer interactions.

This model has the phase diagram in the (κ, τ) plane shown in Fig. 2 with ω adjusted to achieve the thermodynamic limit, where

$$\langle L \rangle = \frac{\partial \log \mathscr{X}}{\partial \log \omega} \tag{2}$$

the average number of monomers, diverges.

It is also interesting to consider the structure of the phase diagram in the (ω, τ) plane,(3,4) which is shown in Fig. 3 for the case $\kappa = 1$. The equation of the line bounding the collapsed phase in this plane is given

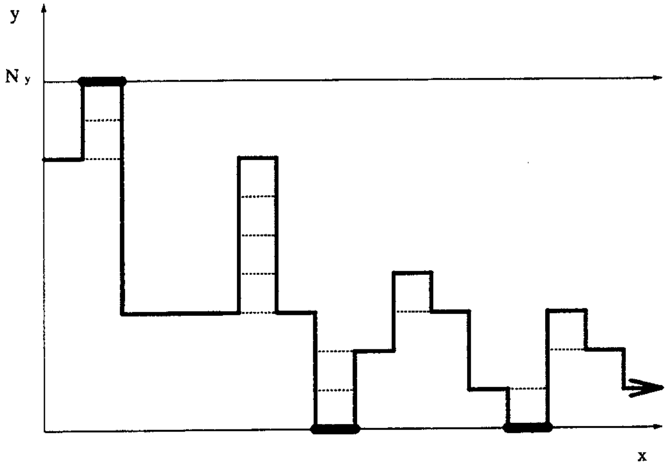

Fig. 1. A directed polymer confined to a lattice of width N_y. Monomer–monomer interactions J and monomer–surface interactions K are depicted by dotted and bold lines, respectively.

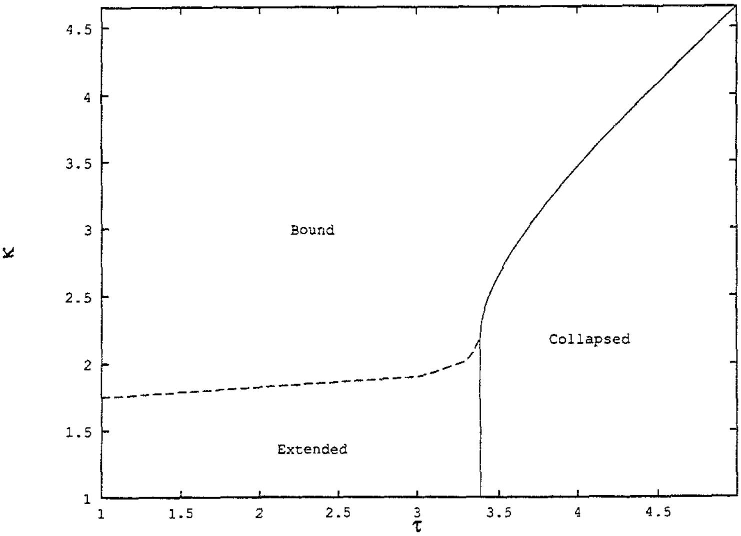

Fig. 2. The phase diagram of a directed polymer in the ($\kappa = \exp[-K/k_B T]$, $\tau = \exp[-J/k_B T]$) plane. The boundary between the extended and bound phases is based on the numerical results of Veal *et al.* [3] and is shown schematically. The boundary of the collapsed phase is an exact result [5, 6].

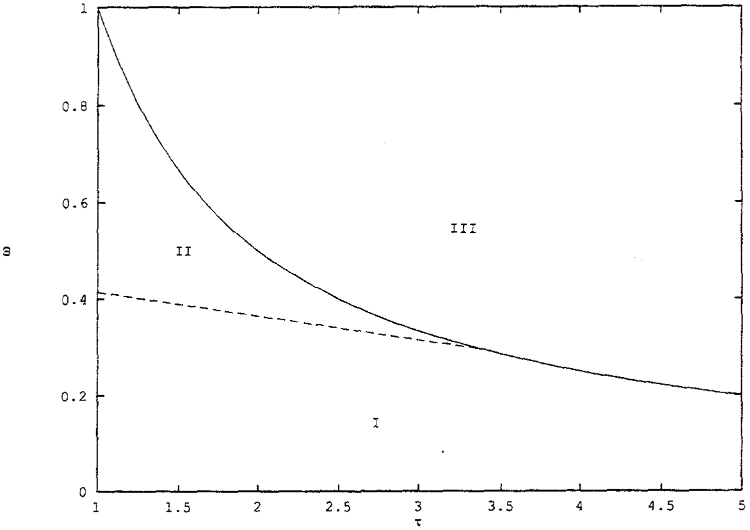

Fig. 3. Phase diagram in the (ω, τ) plane for $\kappa = 1$. The dotted line is schematic; the full line is $\omega\tau = 1$. In region I the polymer is finite; in region II it is infinite, but with zero density, and in region III it is infinite and space filling.

by $\omega\tau = 1$. This conclusion has been based on numerical and heuristic arguments. Brak *et al.*$^{(8)}$ have recently presented a rigorous proof of the location of this boundary for the case $\kappa = 1$. Here we present an alternative, more physical, proof.

If the smallest perimeter is drawn around the polymer so as to enclose all the steps of the walk and all the monomer–monomer interactions, as shown in Fig. 4, then the number of τ bonds is equal to the number of plaquettes enclosed. If we also associate a step with each plaquette, then the number of excess steps is equal to half the number of bonds in the enclosing perimeter. In this way the directed polymer model has been mapped onto a polygon model on a square lattice with an area fugacity of $\omega\tau$ and a perimeter fugacity of $\omega^{1/2}$. These polygons are similar to those studied by Fisher *et al.*,$^{(9)}$ although they are not self-avoiding, in that configurations in the directed polymer problem which consist of a column with no monomer–monomer interactions correspond to configurations in the polygon problem where the top and bottom edges touch. The mapping enables us to employ the elegant techniques used in the paper of Fisher *et al.*$^{(9)}$ to prove the location of the boundary of the collapsed phase.

Let $\nu_m(n)$ be the number of polygons with m edges and area n. Let

$$p_m = \sum_n \nu_m(n) \tag{3}$$

and define the area generating function

$$P_m(y) = \sum_n \nu_m(n)\, y^n \tag{4}$$

where $y = \omega\tau$ is the area fugacity for the polygon problem.

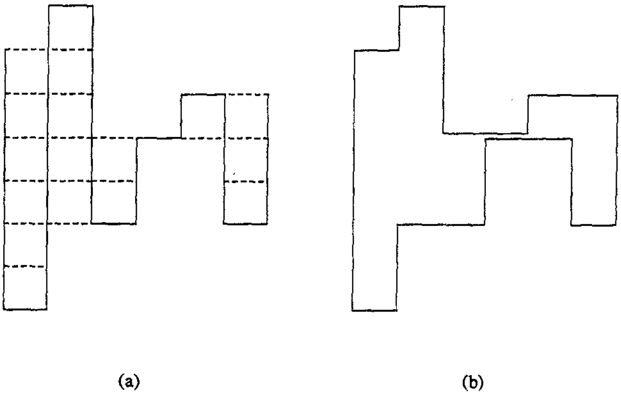
(a) (b)

Fig. 4. (a) A polymer configuration with the monomer–monomer interactions denoted by dotted lines. (b) The equivalent polygon.

Looking first at a fixed perimeter, it is apparent that the largest possible area which can be enclosed by a polygon is $m^2/16$ if m is divisible by 4, or $(m^2-4)/16$ otherwise. Since all the terms in $P_m(y)$ are nonnegative, $P_m(y)$ must be at least as large as any of them. Choosing the term corresponding to the largest area and considering $y>1$, this gives

$$\lim_{m\to\infty} m^{-2}\log P_m(y) \geqslant \frac{\log y}{16} \tag{5}$$

Similarly,

$$P_m(y) \leqslant p_m\, y^{m^2/16} \tag{6}$$

Since the polygons under investigation are a subset of all possible closed loops, p_m must be bounded above by the total number of random walks of length m, that is,

$$p_m \leqslant \exp(m\log q) \tag{7}$$

where q is the coordination number for the lattice, in this case 4. It follows from (5) and (6) that

$$\lim_{m\to\infty} m^{-2}\log P_m(y) = \frac{\log y}{16} \tag{8}$$

As the average area is given by

$$\langle n\rangle = \frac{\partial \log P_m(y)}{\partial \log y} \tag{9}$$

and since here the differentiation and limits commute,$^{(9)}$

$$\lim_{m\to\infty} m^{-2}\langle n\rangle = \frac{1}{16} \tag{10}$$

Hence, as long as $y>1$, the average area for the polygon model will diverge as the perimeter is taken to infinity. The area of the polygons maps into the number of monomer–monomer interactions in the polymer model and therefore this behavior corresponds to a polymer collapsing into a space-filling configuration.

If we now focus our attention on $y\leqslant 1$, we can easily see that $P_m(y)\leqslant p_m$. As before, $P_m(y)$ must be at least as large as any single term in the sum, in particular the term with the smallest area. In this case this is zero (as the polygons are not self-avoiding), that is,

$$P_m(y) \geqslant v_m(0) \tag{11}$$

As there is at least one configuration with zero area, $v_m(0)\geqslant 1$.

Since $p_m \leqslant \exp(4m)$, it follows immediately that

$$\lim_{m \to \infty} m^{-2} \log P_m(y) = 0 \tag{12}$$

Comparing Eqs. (8) and (12), it is immediately apparent that $\lim_{m \to \infty} m^{-2} \log P_m(y)$ is zero up to and including $y = \omega t = 1$ and then is nonzero for $y > 1$, showing that there is a phase transition at $\omega t = 1$.

We expect this argument to hold even when $\kappa \neq 1$, as the effect of the contact with the boundary will only enter along an edge, resulting in a change in the effective perimeter fugacity. The location of the transition is independent of this value, and hence will remain unaltered.

In this paper we have mapped a directed interacting polymer onto a new polygon model. In this way we have given a physically appealing proof for the position of the boundary of the collapsed phase.

ACKNOWLEDGMENTS

We should like to thank Prof. S. Whittington for helpful discussions and we acknowledge support from the SERC.

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Communicated by V. Privman