Surface critical exponents for models of polymer collapse and adsorption: the universality of the Theta and Theta ' points

LETTER TO THE EDITOR

Surface critical exponents for models of polymer collapse and adsorption: the universality of the Θ and Θ' points.

D P Foster†, E Orlandini‡ and M C Tesi‡

† Theoretical Physics, University of Oxford, 1 Keble Road, Oxford, UK
‡ Dipartimento di Fisica, Università di Bologna, INFN Sezione di Bologna, Bologna, Italy

Abstract. The surface critical exponents are estimated both in ordinary and in special regimes from exact series expansions of up to 28 terms for a model of the Θ point. They are found to be in agreement with those derived for the Θ' point, confirming the conjecture that the Θ and Θ' points lie in the same universality class. Some essential features of the phase diagram for a self-interacting, self-avoiding polymer in solution are also calculated to a higher degree of accuracy than previously obtained.

Polymer adsorption on a substrate has received considerable attention not only because of its intrinsic merit as a problem in statistical mechanics [1], but also because of its relevance for technological processes such as the stabilization of colloidal dispersions used in paints, pharmaceuticals and foodstuffs [2].

Such problems, in the context of statistical mechanics, can be seen as surface critical phenomena and are now fairly well understood when they occur alone [3–6]. Adsorption occurs at a multicritical point which corresponds to the special transition of magnetic systems. In $d = 2$ the critical exponents have been calculated exactly [5].

The situation is not so clear, on the other hand, when the possibility of collapse is introduced. A self-avoiding random walk with attractive nearest-neighbour interactions between non-consecutively visited sites shows a critical Θ temperature [7] above which it behaves as a polymer in a good solution and below which it behaves like a compact globule (fractal dimension $D = d$). The Θ point separating these two regimes is again multicritical [8] and in $d = 2$ still constitutes a big challenge in statistical mechanics.

An alternative model, the so-called Θ' model, was proposed [9,10] and conjectured to be in the same universality class as the usual Θ model [10]. Using a version of this model in which the self-interaction was introduced by annealed percolation vacancies on an hexagonal lattice, bulk and ordinary surface exponents were either found exactly or conjectured, on the basis of Coulomb gas and conformal invariance methods [10]. While the bulk exponents were in agreement with those reported for more traditional Θ-point models [11,12], the surface exponents were in clear disagreement [13,14]; this gave rise to a long standing debate as to whether the Θ and Θ' multicritical points belong to the same universality class [15–18].

In a recent letter Vanderzande *et al* [19] demonstrated that the surface exponents obtained for the Θ' model correspond not to the ordinary transition but to the special

one. They also estimated the surface exponent, γ_1, at the ordinary transition for the Θ' model, using methods of exact enumeration, and found that this is in agreement with the best estimates for such an exponent in the Θ model†. This led them to confirm that the Θ and Θ' points do lie in the same universality class.

In this letter we compute the surface critical exponents both at the ordinary and, for the first time, special Θ points. The determination of these exponents stands as a crucial test of the universality class of the Θ point and we shall demonstrate that the values obtained are in very close agreement with those calculated for the Θ' point. In the accurate determination of the special exponents it is crucial to have a very precise knowledge of the location in phase space of the special Θ point. We were able to locate not only the special point, but also the phase boundary between the extended and collapsed polymer phases to a much greater accuracy than previously obtained by transfer matrix techniques [14].

The Θ-point model studied consisted of a self-avoiding walk on a square lattice in the infinite half-plane which was allowed to gain an energy K for every step on the boundary and an energy J for every pair of nearest-neighbour non-consecutively visited sites (see figure 1).
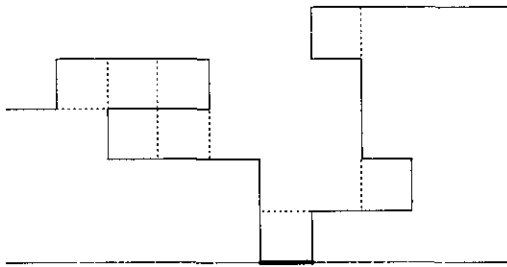

Figure 1. An isotropic polymer on the half-plane. Polymer interactions with the surface are represented by a heavy solid line, and monomer–monomer interactions by a dotted line.

We can define the following canonical partition functions:

$$Z_N^\alpha = \sum_{i,j} C_N^\alpha(i,j)\kappa^i \tau^j \tag{1}$$

where $C_N^\alpha(i,j)$ are the number of walks of length N with i steps at the boundary and j nearest-neighbour interactions, $\kappa = \exp(K/kT)$ and $\tau = \exp(J/kT)$. $\alpha = 1$ denotes that the walks have the additional restriction that the first site visited lies in the boundary whereas $\alpha = 11$ indicates that not only the first site but also the last site visited lies in the boundary.

We can also define the thermal average of the square radius of gyration for walks of N steps starting on the surface by

† For the ordinary Θ' point γ_1 can be obtained exactly using diagrammatic and Coulomb gas arguments. (Stella; private communication)

$$\langle R_N^2 \rangle = \frac{1}{Z_N^\alpha} \sum_{i,j} R_N^2(i,j) \kappa^i \tau^j \tag{2}$$

where $R_N^2(i,j)$ represents the sum of the square radius of gyration of all N-step walks having exactly i nearest-neighbour pairs and j adsorbed steps. The coefficients $C_N^1(i,j)$, $C_N^{11}(i,j)$ and R_N^2 were calculated using exact enumeration of all the allowed walks on the square lattice consistent with self-avoidance and exclusion from the lower half-plane for values of N up to and including 28.

The square average radius of gyration is expected to have a strong N dependence given by

$$\langle R_N^2 \rangle \sim N^{2\nu} \tag{3}$$

defining the critical exponent ν. As the critical exponent thus defined is independent of the α chosen and the number of configurations for $\alpha = 11$ is much smaller than for $\alpha = 1$ we chose to calculate only the radius of gyration for polymer configurations with one end fixed, being more asymptotic for a given length of polymer. The surface critical exponents, γ_1 and γ_{11}, are defined by

$$Z_N^\alpha \sim \mu^N N^{\gamma_\alpha - 1} \tag{4}$$

where μ is the effective connectivity constant.

There are various methods to analyse the coefficients C_N and R_N^2 to extract information about the exponents. In this work we used three different methods; Padé analysis [20], differential approximants [21,22] and direct log–log calculation [23].

If we define the grand canonical partition function by

$$\mathcal{Z}^\alpha = \sum_{N=0}^{\infty} \omega^N Z_N^\alpha \tag{5}$$

where ω is the step fugacity, then we can see that

$$\mathcal{Z}^\alpha = (1 - \omega\mu)^{-\gamma_\alpha} \tag{6}$$

and that it diverges when ω reaches a critical value $\omega_c = 1/\mu$. At this value the length of the polymer described by the grand canonical partition function also diverges and so this value of ω corresponds to the thermodynamic limit.

In practice we do not know $\mathcal{Z}$ but an approximation to it given by a partial sum up to some maximum polymer length. Both the methods of Padé analysis and that of differential approximants were used to investigate these truncated series and to provide estimates of both ω_c and γ_α.

The exponent ν may be calculated in an analogous way by constructing the relevant generating function. Here, on the other hand, the quantity analogous to ω_c is clearly 1, enabling a better approximation for ν than for γ_α as the location of the pole is known exactly.

An alternative method for computing the exponents is by direct log–log calculation [23] from equations (3) and (4). A series of approximations for ν and γ_α may be obtained directly

$$2\nu^{N,m} = \frac{\log(R_N^2/R_{N-m}^2)}{\log(N/(N-m))} \tag{7}$$

$$\gamma_\alpha^{N,m} = \frac{\log(Z_N^\alpha/Z_{N-m}^\alpha) - m\log(\mu)}{\log(N/(N-m))} + 1. \tag{8}$$

Due to the large parity effects in polymer problems of this sort it is usual to choose $m = 2$ and from now on we shall drop the m index from the approximations to the exponents. To calculate the γ_α exponents we require a knowledge of μ, the connectivity constant; alternatively we may calculate the difference between γ_1 and γ_{11} [20, 22], from the series, which then removes the necessity to know μ. Assuming that μ is a constant in κ while we are in one of the de-adsorbed phases then, using enumeration data for interacting walks in the full-plane, we can calculate also the quantity $\gamma - \gamma_\alpha$ from the equation

$$\gamma - \gamma_\alpha = \frac{\log(Z_N Z_{N-2}^\alpha/Z_{N-2} Z_N^\alpha)}{\log(N/(N-2))} \tag{9}$$

where Z_N is defined analogously to Z_N^α, but without the presence of a surface. This assumption seems to hold to a surprisingly high degree even for walks in the length range considered.

The location of the bulk Θ point was determined from the intersections of successive approximations to ν in the limit as $N \to \infty$. It is expected that these intersections, if they exist, are natural locators of multicritical points due to the crossover effects associated with them. It is tempting to utilize this method even in a situation in which an additional interaction with the boundary is present. In this case, though, we find that the method becomes very imprecise and that the phase boundary between the collapsed and extended phases shows considerable uncertainty in τ as κ is increased. The value of ν calculated from these intersections also fluctuates quite badly.

As we know that the value of ν should remain a constant up to and including the special transition, we may use the value exactly known at the ordinary Θ point [10] and substitue it into equation (3) to determine the position of the phase boundary. This method applied to the ordinary Θ point using Padé approximants gives an improved value for τ^* of

$$\tau^* = 1.93 \pm 0.03. \tag{10}$$

In spite of the uncertainty in the τ direction, there is a more systematic settlement as the length of the walks considered increases, consistent with the assumption that the phase boundary between the extended and collapsed phases is a straight line at a fixed value of τ. The special Θ point, corresponding to the end of the Θ line, is detected around $\kappa^* = 2.1$. While this is not an accurate enough method for determining the position of the special point to enable a precise calculation of critical exponents, it does provide a benchmark by which to compare the results of other methods.

Another method to locate the special point is to calculate estimates of ω_c as a function of κ at τ^*; if the phase boundary between the collapsed and extended

phases is truly straight then we would not expect ω to have a dependence on $\kappa < \kappa^*$ except for finite size corrections. Indeed we find that, using both methods of Padé analysis and differential approximants, ω remains fairly constant until some value of κ at which stage it falls consistently as a function of κ, indicating the presence of an adsorbed phase. As ω is expected to remain constant as a function of κ below the adsorption transition for all values of τ, this method may be used to compute the entire adsorbed phase boundary. Both Padé analysis and the method of differential approximants were used and checked against the known location of the adsorption transition for $\tau = 1$ where they were in close agreement, and were consistent with each other elsewhere. The important factor, therefore, in the accurate determination of the location of the special point is a good estimate of the ordinary Θ point. Both methods of differential approximants and of Padé analysis gave the location of the special point as

$$\tau^* = 1.93 \pm 0.03 \tag{11}$$

$$\kappa^* = 2.15 \pm 0.05 \tag{12}$$

$$\omega_c = 0.3113 \pm 0.0005 \tag{13}$$

A more systematic method for the calculation of the adsorbed phase boundary, based on equation (9), is to look for intersections in successive approximations for $\gamma - \gamma_1$, see figure 2, in the same spirit used above for ν intersections, analysing odd and even N approximations separately. We found that the location of the adsorption for $\tau = 1$ is at $\kappa = 2.044 \pm 0.002$, with a corresponding value of $\gamma_1^{sp} = 1.460 \pm 0.004$, in excellent agreement with the work of Guim and Burkhart [6], and the location of the special Θ point in agreement with the values quoted above. The phase diagram obtained using this method is shown in figure 3. The method becomes less selective in determining the phase boundary beyond the Θ point and therefore the collapsed–adsorbed phase boundary should be considered schematic.
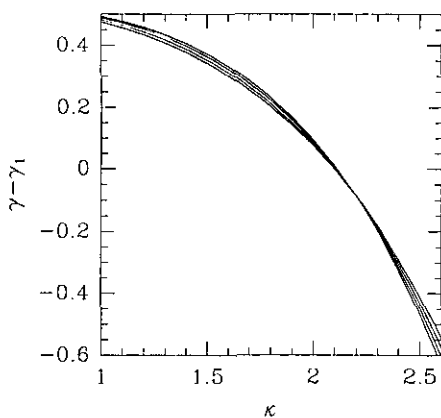

Figure 2. $\gamma - \gamma_1$ versus κ for $\tau = 1.93$ showing intersections at the adsorption transition.

At the special Θ point we may also define a surface crossover exponent, ϕ_s defined by [24]
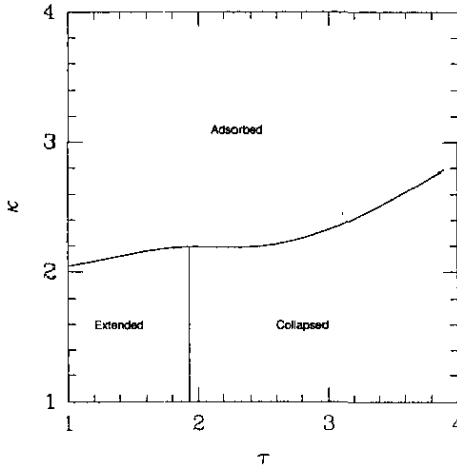
$$\langle N_s \rangle \sim N^{\phi_s} \tag{14}$$

Figure 3. The phase diagram in the κ–τ plane, the collapsed–adsorbed phase boundary being schematic.

where N_s is the number of steps in the surface, calculated for walks contributing to the coefficients C_N^1, and is given by

$$\langle N_s \rangle = \kappa \frac{\partial \log Z_N^1}{\partial \kappa}. \tag{15}$$

Computing the residues of the logarithmic derivative with respect to ω of Z^1 and Z^{11} both at the ordinary and special points and evaluating (15) at the special point we obtain values for the exponents given by

$$\gamma_1^{\text{ord}} = 0.57 \pm 0.02 \tag{16}$$
$$\gamma_{11}^{\text{ord}} = -0.55 \pm 0.05 \tag{17}$$
$$\gamma_1^{\text{sp}} = 1.14 \pm 0.05 \tag{18}$$
$$\gamma_{11}^{\text{sp}} = 0.56 \pm 0.08 \tag{19}$$
$$\phi_s = 0.4 \pm 0.05 \tag{20}$$

These compare favourably with the exponents calculated for the Θ' model, whose special point exponents are given exactly as $\gamma_1 = 8/7$, $\gamma_{11} = 4/7$ and $\phi_s = 8/21$ [16], whereas at the ordinary point they agree with previously reported results.

Summarizing, we studied a model for self-avoiding self-interacting polymers (the Θ-point model) in presence of an adsorbing wall and we estimated the ordinary and special surface critical exponents from data obtained by exact enumeration. On the square lattice we have been able to obtain up to 28 steps in the series, a good improvement with respect to previous calculations, taking advantage of all possible symmetries present in the model considered.

The resulting series were carefully analysed using various different methods such as Padé analysis, differential approximants and direct calculation, in order to obtain as precisely as possible the location, in parameter space, of the multicritical point corresponding to the special Θ transition, and its critical exponents. The special

surface Θ exponents constitute strong evidence that the Θ and Θ' models do in fact belong to the same universality class.

The results obtained and the methods used clearly indicate that the boundary between the extended and collapsed phases is straight, in disagreement with the conjecture of a temperature shift at the special Θ point due to surface stabilization of the collapsed phase [25].

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