

LETTER TO THE EDITOR

Collapse of two-dimensional linear polymers: a transfer matrix calculation of the exponent ν_t

B Derrida and H Saleur

SPT, CEN Saclay, F-91191 Gif-sur-Yvette, France

Received 27 August 1985

Abstract. Using a transfer matrix technique and finite size scaling, we calculate the exponent ν_t of two-dimensional polymers at the θ point. We find $\nu_t = 0.55 \pm 0.01$ by two slightly different calculations on the square lattice. This value is compared with those which had been previously proposed in the literature.

The collapse of linear polymers has been a subject of constant interest in polymer physics for many years. By varying the temperature or the solvent composition of a polymer solution, one can observe the precipitation of a polymer aggregate (Flory 1966), or the collapse of single polymer chains (Nishio *et al* 1979), if the solution is dilute enough. This effect is due to the competition between repulsive interactions which dominate in the good solvent regime, and attractive interactions which are induced by the solvent and make the chains collapse in the poor solvent regime (de Gennes 1979).

This collapse transition has been mainly studied in the three dimensional case. Exact enumerations on lattice models (Rapaport 1974, 1977), Monte Carlo simulations (Webman *et al* 1981) and various mean field type approximations (Lifschitz *et al* 1978 and references therein) have given controversial results. In 1975 de Gennes suggested that the transition could be described as the tricritical point of a zero component magnetic spin model. The scaling behaviours predicted by this analogy were investigated by Monte Carlo methods (Kremer *et al* 1982). The logarithmic corrections which are present because $D = 3$ is the upper critical dimension have been calculated by field theory methods (Stephen 1975, Duplantier 1982). The collapse of 2D linear polymers is of more recent interest (Villanove and Rondelez 1980, Tobochnick *et al* 1982).

In this work, we study the properties of a self-avoiding walk (SAW) (a walk which does not visit any site more than once) on a regular two-dimensional (square) lattice. By definition of the model, the energy of a configuration \mathcal{C} of the walk is $-B(\mathcal{C})$, where $B(\mathcal{C})$ is the number of pairs of neighbouring sites on the lattice which are visited by the walk. Thus the Boltzmann factor associated to a configuration \mathcal{C} is just $\exp(B(\mathcal{C})/T)$. The self-avoiding constraint represents the excluded volume effect, as usual, whilst the energy $-B(\mathcal{C})$ represents the attractive forces between monomers. The simplest geometrical quantity one can study is the average size $\langle \mathbf{R}^2 \rangle_N$ of a chain of N steps, which is defined by

$$\langle \mathbf{R}^2 \rangle_N = \sum_{\mathcal{C}} (\mathbf{R}(\mathcal{C}))^2 \exp(B(\mathcal{C})/T) \left(\sum_{\mathcal{C}} \exp(B(\mathcal{C})/T) \right)^{-1} \quad (1)$$

where in (1), the sums run over all the configurations \mathcal{C} of the walk and $\mathbf{R}(\mathcal{C})$ is the

end-to-end distance of the chain in configuration \mathcal{C} . For long chains ($N \rightarrow \infty$), one expects that the average size $\langle \mathbf{R}^2 \rangle_N$ increases like a power law with the length of the chain, that is

$$\langle \mathbf{R}^2 \rangle_N \sim N^{2\nu}. \quad (2)$$

At infinite temperature, the energies of configurations play no role, the problem reduces to the usual SAW problem and therefore $\nu = \nu_{\text{SAW}}$ ($= 3/4$ in dimension 2). When one lowers the temperature, one expects a phase transition at a critical temperature θ where ν jumps. Below that temperature θ , the chain is collapsed. Therefore, we can write,

$$\nu = \begin{cases} \nu_{\text{SAW}} & \text{for } T > \theta \\ \nu_t & \text{for } T = \theta \\ 1/d = 1/2 & \text{for } T < \theta. \end{cases} \quad (3)$$

The purpose of the present work is to determine both θ and ν_t using finite-size scaling.

Our approach is very similar to the one which was used to study the collapse of branched polymers (Derrida and Herrmann 1983). We start by calculating exactly, using a transfer matrix method, the properties of a very long walk ($N \rightarrow \infty$) on a strip of finite width n . We then obtain estimations of the temperature θ and of the exponent ν_t using finite-size scaling.

We will not describe here the technical details which were used to construct transfer matrices; these have been explained in Klein (1980), Derrida (1981), Derrida and Herrmann (1983) and the generalisation of the method to the model studied here is straightforward. The basic quantity that we calculate using transfer matrices is a length $\xi_n(x, T)$, which is defined in the following way. If we call $\omega_{OR}(N, B)$ the number of SAWs of N steps and of energy $-B$ whose ends are at O and R , one can define the correlation function $G_{OR}(x, T)$ by

$$G_{OR}(x, T) \sim \sum_{N, B} x^N \exp(B/T) \omega_{OR}(N, B). \quad (4)$$

When one considers the model on a strip of width n , the behaviour of $G_{OR}(x, T)$ for large $|R|$ is given by the first eigenvalue $\lambda_n(x, T)$ of the transfer matrix

$$\begin{aligned} G_{OR}(x, T) &\sim [\lambda_n(x, T)]^{|R|} \\ &= \exp(-|R|/\xi_n(x, T)) \end{aligned} \quad (5)$$

and this defines the length $\xi_n(x, T)$. From the knowledge of $\xi_n(x, T)$, one can calculate the average end-to-end distance $\langle |R| \rangle$ of a walk of N steps in the limit $N \rightarrow \infty$ (Derrida and Herrmann 1983), that is

$$\lim_{N \rightarrow \infty} (N/\langle |R| \rangle) = n \rho_n(T), \quad (6)$$

where $\rho_n(T)$ is the density of the walk on the strip and is given by

$$\rho_n(T) = \frac{1}{n} \frac{\partial \log \lambda_n(\tilde{x}(T), T)}{\partial \log x}, \quad (7)$$

where in (7) the derivative has to be calculated at the point $\tilde{x}(T)$ defined by

$$\lambda_n(\tilde{x}(T), T) = 1. \quad (8)$$

Let us now see how, from the knowledge of $\rho_n(T)$ and $\xi_n(x, T)$, one can extract estimations for θ and ν_t .

In the neighbourhood of the θ temperature, one expects the following finite-size scaling (valid for $n \gg 1$ and $T - \theta \ll 1$) for the density

$$\rho_n(T) \sim n^{1/\nu_t - 2} F[(T - \theta)n^{\phi_t/\nu_t}] \quad (9)$$

where $F(0)$ is a constant.

In figure 1, we have plotted $X_n(T)$ against $\beta = 1/T$, where X_n is defined by

$$[X_n(T)]^{-1} = \frac{\log(\rho_{n+2}(T)/\rho_n(T))}{\log[(n+2)/n]} + 2. \quad (10)$$

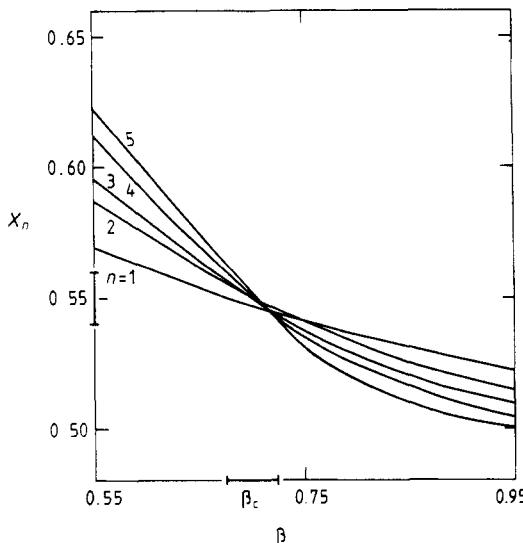


Figure 1. Plot of X_n (see formula (10)) against β . For large n , the curves should intersect at (β_c, ν_t) . Our estimates, with their error bars, are indicated in formula (11).

The densities were calculated for strips with periodic boundary conditions on a square lattice. If formula (9) is valid even for rather narrow widths, one expects that the curves for different n will cross at $\beta_c = \theta^{-1}$ and that the value of X_n at the intersection will give ν_t . Because of parity effects, we could only compare size n and size $n+2$ (see equation (10)). In figure 1, we see that the curves cross rather well and we estimate that their intersection is

$$\beta_c^{-1} = \theta = 1.42 \pm 0.04 \quad \text{and} \quad \nu_t = 0.55 \pm 0.01. \quad (11)$$

A slightly different way of finding θ and ν_t consists in doing a two strip renormalisation (see § 4 of Derrida and Herrmann 1983). We first calculate the value $\tilde{x}(T)$ given by the phenomenological renormalisation

$$(1/n)\xi_n(\tilde{x}(T), T) = [1/(n+2)]\xi_{n+2}(\tilde{x}(T), T) \quad (12)$$

and then we estimate ν for each temperature using

$$\nu^{-1} = \frac{\log(\xi'_{n+2}(\tilde{x}, T)/\xi'_n(\tilde{x}, T))}{\log[(n+2)/n]} - 1, \quad (13)$$

where ξ'_n denotes the derivative of ξ_n with respect to x . Here again, for parity reasons, we compare only sizes n and $n+2$. In figure 2, we plot ν obtained by this method against β . As in the case of branched polymers (figure 7 of Derrida and Herrmann 1983) the curves intersect almost at the same point, and the estimations of ν_t and θ are in agreement with (11).

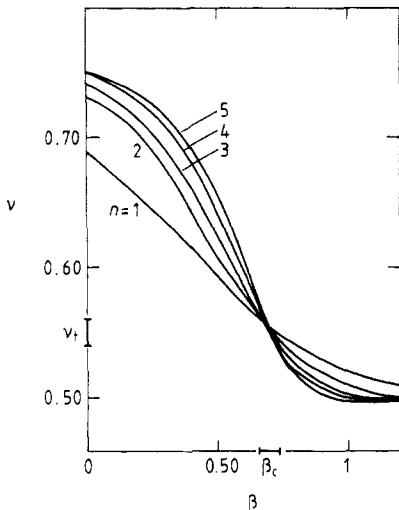


Figure 2. Plot of the exponent ν obtained by a two strip renormalisation with sizes n and $n+2$ (formula (13)). When n increases, this exponent converges to the SAW value $\nu = 3/4$ for $T > \theta$ ($\beta < \beta_c$) and to the collapse value $\nu = 1/2$ for $T < \theta$ ($\beta > \beta_c$). At the temperature θ it gives ν_t .

We did similar calculations for strips parallel to the diagonal direction of the square lattice (and also for the hexagonal and triangular lattices). In these cases, the parity effects are even stronger. We found two different intersections: one for odd widths and another one for even widths. However, these two intersections were rather close and were both compatible with the error bars given in (11).

Let us now compare our results with those which have already been proposed in the literature. Using a Monte Carlo method for the same model, Baumgartner (1982) has obtained $\nu_t = 0.505$ and $\theta = 1.31 \pm 0.06$. This value of ν_t disagrees with ours. We think that the main reason for this discrepancy is that the reptation method does not efficiently sample the compact configurations, which are the most important ones in the low temperature phase. Moreover, in Monte Carlo simulations, one studies finite chains and some surface effects might be present, like the ones which were observed for branched polymers (Dickman and Schieve 1984). These surface effects are always eliminated in the transfer matrix calculations since the length of the chain is always very large.

A recent conjecture (Coniglio *et al* 1985) identifies the exponent ν_t with the expansion exponent $\nu = 0.567 \pm 0.003$ of the IGSAW (Kremer and Lyklema 1984). This value is much closer to our result (11) although it seems slightly too high. We think that the present accuracy of their results and of ours is not sufficient to rule out that the collapse transition exponent ν_t might be the same as the IGSAW exponent.

Two values of ν_t were also predicted using field theory approaches. The value 0.505 (de Gennes 1975) using the ϵ expansion ($\epsilon = 3 - d$) of Stephen and McCauley

(1973), which can be recovered in a direct polymer approach (Duplantier 1985), seems much too low, probably because one does not know enough terms in the ϵ expansion or because the expansion could break down before $\epsilon = 1$. Kholodenko and Freed (1984) did a different calculation which gave $\nu_t = 0.55$. This is in much better agreement with (11). However, in their calculation, they also predict a value of the crossover exponent ϕ_t and our preliminary results again using transfer matrices seem to disagree with theirs.

Lastly, the experiments on 2D polymer monolayers (Villanove and Rondelez 1980) gave $\nu_t = 0.56 \pm 0.01$ which is in good agreement with our calculation.

Like in the case of branched polymers, we also tried to make more sophisticated renormalisations (Derrida and Herrmann 1983, Beale 1984) using three widths, or using the second eigenvalue of the transfer matrix. These calculations which worked rather well for branched polymers did not allow us to extract θ or ν in a conclusive way for linear polymers. We think that the main difference between the two problems is that the low temperature phase is more complicated in the case of linear polymers: there is a zero temperature entropy since the problem reduces in this limit to the problem of Hamiltonian walks. This zero temperature entropy is very reminiscent of frustrated systems and it would be interesting to see whether the collapse transition could be seen as a kind of spin glass transition. In the future, we hope to study the properties of this low temperature phase more carefully.

We would like to thank B Duplantier, H J Herrmann, J L Lebowitz and N Jan for useful discussions.

References

Baumgartner A 1982 *J. Physique* **43** 1407
 Beale P D 1984 *J. Phys. A: Math. Gen.* **17** L335
 Coniglio A, Jan N, Majid I and Stanley H E 1985 *Preprint*
 de Gennes 1975 *J. Physique Lett.* **36** L55
 —— 1979 *Scaling concepts in polymer physics* (New York: Cornell University Press)
 Derrida B 1981 *J. Phys. A: Math. Gen.* **14** L5
 Derrida B and Herrmann H J 1983 *J. Physique* **44** 1365
 Dickman R and Schieve W C 1984 *J. Physique* **45** 1727
 Duplantier B 1982 *J. Physique* **43** 991
 —— 1985 in preparation
 Flory P J 1966 *Principles of polymer chemistry* (New York: Cornell University Press)
 Kholodenko A L and Freed K F 1984 *J. Chem. Phys.* **80** 900
 Klein D J 1980 *J. Stat. Phys.* **23** 561
 Kremer K, Baumgartner A and Binder K 1982 *J. Phys. A: Math. Gen.* **15** 2879
 Kremer K and Lyklema J W 1985 *J. Phys. A: Math. Gen.* **18** 1511
 Lifschitz I M, Grosberg A Yu and Khokhlov A R 1978 *Rev. Mod. Phys.* **50** 683
 Rapaport D C 1974 *Phys. Lett.* **48A** 339
 —— 1977 *J. Phys. A: Math. Gen.* **10** 637
 Stephen M J 1975 *Phys. Lett.* **53A** 363
 Stephen M J and McCauley J L 1973 *Phys. Lett.* **44A** 89
 Nishio I, Sun S T, Swislow G and Tanaka T 1979 *Nature* **281** 208
 Tobochnik J, Webman I, Lebowitz J L and Kalos M H 1982 *Macromolecules* **15** 549
 Villanove R and Rondelez F 1980 *Phys. Rev. Lett.* **45** 1502
 Webman I, Lebowitz J L and Kalos M H 1981 *Macromolecules* **14** 1495