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LETTER TO THE EDITOR

Internal transition in an infinitely long polymer chain

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Abstract. The existence of an internal transition (collapse) in a long polymer chain is investigated as follows: a chain of n segments is simulated by a self-avoiding walk of $n-1$ steps on a simple cubic lattice, an energy $-\epsilon$ being associated with each pair of neighbouring segments, and the distribution of the zeros of the partition function in the complex plane associated with the variable $x = \exp(\epsilon/kT)$ is studied for increasing n values. A tentative conclusion is that a line of roots cuts the real positive axis in $x_c \simeq 1{\cdot}74$ ($kT_c/\epsilon \simeq 1{\cdot}82$) in the limit $n \to \infty$, supporting the occurrence of a transition in this model.

The aim of this letter is to provide some further evidence for the occurrence of an internal transition in an infinitely long polymer chain as suggested by several recent works (Mazur and McCrackin 1968, McCrackin *et al* 1973, Domb 1974, Rapaport 1974, Massih and Moore 1975). Such a transition would correspond to a sudden collapse of the chain at a particular temperature T_c. The model considered here is very simple: the chain is simulated by a self-avoiding walk on a infinite lattice, each segment of the chain occupies one site exactly, no overlaps are allowed and each pair of non-consecutive segments occupying neighbouring sites contributes to the energy of the system by $-\epsilon$. The partition function of a finite chain of n segments (n-mer or self-avoiding walk of $n-1$ steps) is a polynomial of degree v_n in the variable $x = \exp(\epsilon/kT)$

$$Z_n(x) = \sum_0^{v_n} c_n(v)x^v \tag{1}$$

where $c_n(v)$ is the number of walks with v internal contacts and v_n is the maximum value of v; for a regular lattice of coordination number q, one obviously has $v_n < qn/2$.

The free energy of the chain *per segment*, given by

$$f_n(x)/kT = -n^{-1} \ln Z_n(x) \tag{2}$$

with x real and positive, may be conveniently rewritten in terms of the v_n roots $\{z_j\}$ of the equation $Z_n(z) = 0$; one has indeed

$$Z_n(x) \equiv c_n(0) \prod_1^{v_n} \left(1 - \frac{x}{z_j}\right) \tag{3}$$

and

$$f_n(x)/kT = -n^{-1} \ln c_n(0) - n^{-1} \sum_1^{v_n} \ln[1-(x/z_j)]. \tag{4}$$

As all coefficients $c_n(v)$ are real and non-negative, none of the roots z_j lies on the real positive axis of the complex z plane. As this is precisely the domain of variation of the physical variable x, $f_n(x)$ is analytic and no transition can occur, at least as long as n remains finite.

However, as the limit $n \to \infty$ is approached, a current situation is the formation of lines of roots in the z plane. If such a line of zeros crosses the positive real axis in some point x_c, then it is well known, since the fundamental work of Yang and Lee (1952), that the limiting function $f_\infty(x)$ is still analytic in both domains $0 < x < x_c$ and $x > x_c$, but that it presents some kind of singular behaviour in its derivatives at $x = x_c$ (transition point). Hence the very existence of a transition (as well as its location) can be inferred from the change with n of the root distribution within the z plane.

Here we shall limit ourselves to five-choice walks on the (three-dimensional) simple cubic lattice. The coefficients $c_n(v)$ were previously determined: (i) by exact counting for $n \leqslant 13$; and (ii) by a Monte Carlo sampling technique for $n \leqslant 40$ (Janssens and Bellemans 1975; up to $n = 31$ the sampling was based on 3×10^5 walks, but for higher n up to 40 only 2×10^3 walks were considered).

The roots corresponding to the exact data $n \leqslant 13$ are shown on figure 1 and there appears a rather neat tendency for them to build a regular contour around the origin which might well close on some point of the real positive axis as $n \to \infty$. The exploration of values of n larger than 13 requires some caution. As the corresponding $c_n(v)$ were estimated by means of a Monte Carlo sampling, they only lead to an approximate picture of the distribution of roots. The situation gets even worse for $n > 24$: indeed

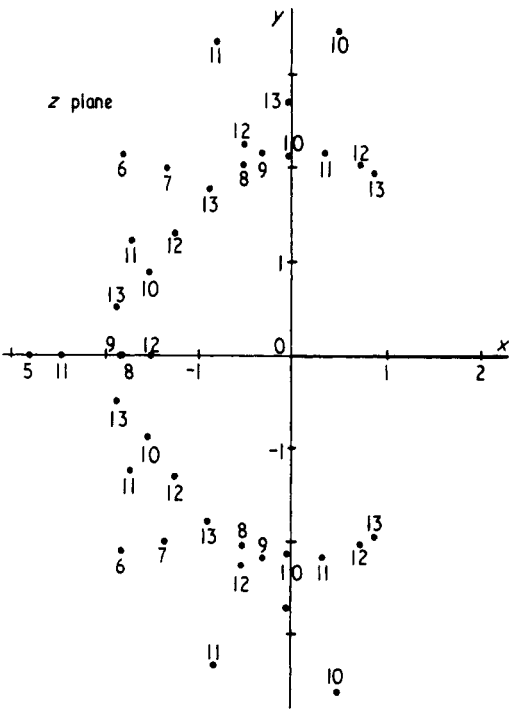

Figure 1. Distribution of the roots of $Z_n(x)$ for $n \leqslant 13$ (exact results). Note that some roots, lying too far away from the origin, have been omitted.

some $c_n(v)$ with v rather large are erroneously sampled as zero by the Monte Carlo program, because the corresponding configurations are relatively very improbable; hence even the total number of roots obtained is not quite correct in this case. We therefore limited our analysis to $n \leqslant 31$, considering the information available for larger n as not sufficiently accurate for the present purpose. (As a check we verified that for $n = 13$ the roots respectively obtained from the exact coefficients $c_{13}(v)$ and from their sampled values, were in excellent coincidence.)

The roots corresponding to Z_{23} and Z_{31} are plotted on figure 2 from which it appears that the tendency of the roots to build a contour around the origin is confirmed. On figure 3 we show the closest root to the positive x axis for all cases $n = 11$ to 31:

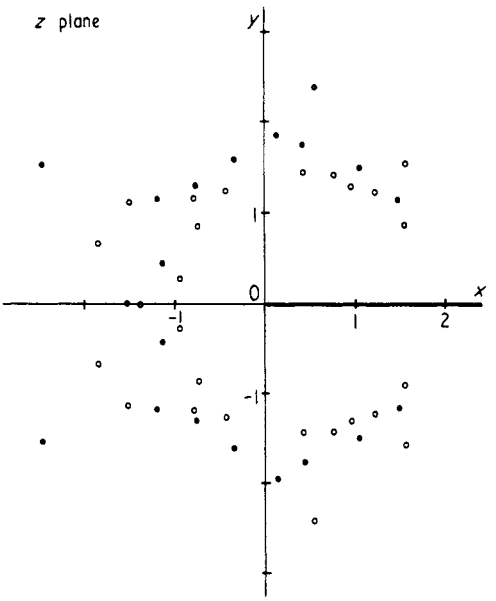

Figure 2. Distribution of the roots of Z_{23} and Z_{31} (Monte Carlo data). Note that two roots corresponding to $n = 23$ and one root corresponding to $n = 31$ have been omitted on account of their large distance from the origin. Full circles correspond to $n = 23$ and open circles to $n = 31$.

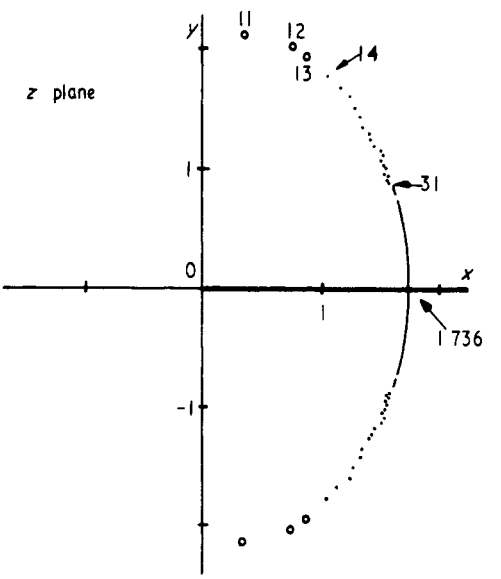

Figure 3. Closest root to the positive real axis for $11 \leqslant n \leqslant 31$. The full line corresponds to the least-squares fit of equation (5).

there is good evidence that, as the limit $n \to \infty$ is approached, a line of roots will cut this axis orthogonally near $x = 1{\cdot}7$. (Obviously values of x larger than one correspond to $\epsilon > 0$, ie the average force between neighbouring segments is attractive.) Assuming that the roots plotted on figure 3 roughly follow the parabolic curve

$$x = x_c - ay^2 \tag{5}$$

($z = x + iy$), a least-squares fit of the roots corresponding to $17 \leqslant n \leqslant 31$ yields

$$x_c = 1{\cdot}736 \pm 0{\cdot}012 \tag{6}$$

ie

$$kT_c/\epsilon = 1{\cdot}81 \pm 0{\cdot}02. \tag{7}$$

Although the quoted uncertainties may be somewhat too optimistic, the transition temperature T_c is undoubtedly much lower than the Θ temperature corresponding to the vanishing of the second virial coefficient of two interacting chains which was recently determined for this same model: $k\Theta/\epsilon = 3{\cdot}71 \pm 0{\cdot}01$ (Janssens and Bellemans 1975).

In principle the order of the transition follows from the (normalized) density of roots in x_c (Grossmann and Rosenhauer 1967) but no serious discussion of this matter can be carried out on the basis of the information available here. Figure 2 nevertheless suggests that the roots tend to be more or less uniformly distributed along the contour. Should this tendency be maintained in the limit $n \to \infty$, the density of roots in x_c would be finite and the transition would be a first-order one.

The extension of this work to other lattices is progressing. One of use (MJ) gratefully acknowledges the support of the Belgian IRSIA Institute.

References

Domb C 1974 *Polymer* **15** 259–62
Grossmann S and Rosenhauer W 1967 *Z. Phys.* **207** 138–52
Janssens M and Bellemans A 1975 *Macromolecules* submitted for publication
Mazur J and McCrackin F L 1968 *J. Chem. Phys.* **49** 648–65
McCrackin F L, Mazur J and Guttman C M 1973 *Macromolecules* **6** 859–71, 872–4
Massih A R and Moore M A 1975 *J. Phys.* A: *Math. Gen.* **8** 237–44
Rapaport D C 1974 *Macromolecules* **7** 64–6
Yang C N and Lee T D 1952 *Phys. Rev.* **87** 404–9, 410–19