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Numerical studies of collapsing polymers

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Abstract. The behaviour of a polymer dissolved in a poor solvent is studied using the self-interacting self-avoiding walk model. The properties of short polymers are generated by exact enumeration methods and the results extrapolated to large systems. Evidence supporting the existence of a phase transition is obtained. The exponents governing the length dependence of the partition function and moments of the distribution functions appear to be temperature dependent.

1. Introduction

The self-avoiding walk on a lattice has long been regarded as a simple model for a polymer chain in dilute solution (Domb 1969). If attractive interactions between points on the walk which lie on neighbouring lattice sites are incorporated, then the model represents a polymer dissolved in a poor solvent with a tendency to collapse from a loosely coiled, random high-temperature state to a compact, ordered low-temperature state. A collapse of this kind may well be marked by a phase transition.

A model of this nature has sufficient physical content to enable it, in principle, to provide answers to the following questions. Is there a phase transition and, if there is, what is its nature? How do the exponents governing various aspects of the behaviour depend on temperature, or are they temperature independent? What is the nature of the ordered state? Answers to such questions would have to be qualified by the fact that the polymer is embedded in a lattice, although the difference between the close-packed lattice and continuum cases may well be small.

Aside from mean-field type polymer theories and cluster expansions (e.g. Yamakawa 1971), none of which have produced answers to the above questions, the problem can be studied using Monte Carlo and exact enumeration techniques. Monte Carlo (Mazur and McCrackin 1968, McCrackin *et al* 1973) operates on chains ranging in length up to about 1000 units, but, under certain circumstances, in particular at low temperatures, its ability to adequately sample the chain configuration space is severely limited. Exact enumeration, on the other hand, predicts the behaviour exactly, but due to the exponential growth rate of the number of possible configurations, it is only capable of dealing with short chains—up to 10–20 units, depending on the underlying lattice. The two techniques complement one another and, despite the considerable difference in the size of system studied, the results generally agree remarkably well.

In the absence of an analytic solution to the polymer problem Massih and Moore (1975) studied the related problem of embedding a chain in a lattice, allowing sites to be visited more than once but edges only once. Their solution was confined to a

generalization of the Bethe lattice, the triangular cactus tree, and displayed a phase transition. Subsequent calculations for the conventional self-avoiding walk polymer model for a class of generalized Bethe lattices are due to Morita (1976). In these calculations the chain is found to undergo a second-order phase transition at a finite temperature; at the transition point the specific heat experiences a jump discontinuity, and the mean end-to-end distance is continuous but its derivative not.

The relevance of these results, applying as they do only to tree-like lattices, to the problem of a polymer on a regular lattice is not obvious. The connectivity and dimensionality of the underlying lattice play important roles in determining the nature of the phase transition, as evidenced by the Ising model which exhibits mean-field behaviour on tree-like lattices, and it is only when a regular lattice is employed that the physically interesting non-classical behaviour appears (Domb 1960). Furthermore, the behaviour of the polymer below the transition as predicted by these calculations appears unrealistic; the chain locks into its ground-state configuration at the transition point and shows no subsequent temperature dependence. Such artificial behaviour can be attributed to the restricted connectivity of tree-like lattices and need not be expected to occur on a regular lattice.

Studies of the critical behaviour of lattice spin systems led to the proposal of the universality hypothesis for critical exponents (Kadanoff 1971, Griffiths 1971). If this hypothesis is extended to cover the polymer problem it predicts that the exponents governing length dependence of the polymer behaviour should, in the long-chain limit, be temperature independent, except possibly at the transition point where a sudden change of value may occur (Domb 1974). Nagle (1974), on the other hand, draws a distinction between the kinds of interaction present in spin systems and those of the polymer problem, and argues that the strong spatial correlations in the latter reduce the likelihood that universality is applicable. At the present time there is no firm evidence either way; even the numerical results presented in the body of this article fail to resolve the issue.

An alternative approach to the problem is through the renormalization group. Burch and Moore (1976) have used this method, supplemented by additional approximations, to predict a specific heat which diverges at the transition point. Though their work requires assuming the existence of a Θ point, a feature whose existence is doubtful (McCrackin *et al* 1973, Rapaport 1974a), their conclusions support the exact enumeration results (§ 4).

In this paper we discuss the properties of lattice embedded polymers with attractive interactions. The exact enumeration data upon which the analysis is based, and the techniques employed, were described in an earlier paper (Rapaport 1976, to be referred to as I) which dealt with the corresponding problem for repulsive interactions. Both chain and ring polymers are described; in general the ring results are of poorer quality than those of the chains and, consequently, the emphasis is on the latter. The results described here all apply to the FCC lattice.

2. Data generation

The partition function of a polymer chain of $n + 1$ units, or a ring of n units, embedded in a regular lattice, can be written as

$$c_n(\theta) = \sum_{m \geq 0} c_{nm} e^{m\theta} \quad (2.1)$$

where $\theta = J/k_B T$, and $-J$ is the strength of interaction between non-adjacent polymer units which approach to nearest-neighbour separation (I). For the attractive forces considered here $J > 0$. The coefficients c_{nm} are the numbers of n -link chains or rings with m nearest-neighbour pairs. In the limit $\theta = 0$, (2.1) reduces to the number of n -step self-avoiding walks (chains) or the number of returns to the origin of an n -step walk (rings), the properties of which have been extensively studied (Domb 1969).

The moments of the chain end-to-end distance distribution have the form (I)

$$R_n^p(\theta) = c_n(\theta)^{-1} \sum_{m \geq 0} \sum_r c_{nm}(r) e^{m\theta} \quad (2.2)$$

The moments of the distribution of distances between the polymer units and the centre of mass, $S_n^p(\theta)$, for both chains and rings, can be similarly expressed.

The coefficients needed to generate the $c_n(\theta)$ polynomials and the $p = 2$ R and S moments as far as $n = 9$ (chains) and $n = 12$ (rings) for the FCC lattice were tabulated in I. They are obtained by straightforward exhaustive enumeration of the possible chain and ring configurations.

The thermodynamic properties of the polymer are obtained from the mean number of nearest-neighbour pairs of units, per link,

$$g_n(\theta) = \langle m \rangle = (nc_n(\theta))^{-1} \sum_{m \geq 0} mc_{nm} e^{m\theta} = n^{-1} \frac{\partial}{\partial \theta} \ln c_n(\theta).$$

The internal energy per link is then $-Jg_n(\theta)$. The fluctuation in $\langle m \rangle$ is given by

$$h_n(\theta) = \langle m^2 \rangle - \langle m \rangle^2 = n^{-1} \frac{\partial^2}{\partial \theta^2} \ln c_n(\theta)$$

and the specific heat per link is just $k_B \theta^2 h_n(\theta)$. The quantity $h_n(\theta)$ will subsequently be referred to as the specific heat.

The thermodynamic and configurational properties at low temperatures are dominated by the high-order coefficients in (2.1) and (2.2). Inspection of the tabulated coefficients in I reveals that if only the highest-order coefficients (corresponding to the $\theta \rightarrow \infty$ limit) are retained, the values of both c_n and the moments vary irregularly with n , as opposed to the smooth behaviour at $\theta = 0$. This irregular behaviour is due to finite size effects; much larger n -values must be reached before geometrical constraints will allow a compact configuration to form. As will become apparent in the sequel, the presence of these irregular high-order terms is felt even at relatively small values of θ .

3. Configurational properties

Using the methods described in I we have analysed the n -dependence of the moments $R_n^p(\theta)$ and $S_n^p(\theta)$ for a range of positive values of θ . As was the case in the earlier work, the most important quantity is the exponent $\gamma(\theta)$ characterizing the large- n behaviour:

$$R_n^2(\theta) \sim r_0(\theta) n^{\gamma(\theta)} \quad \theta \geq 0, \quad (3.1)$$

with analogous forms for $S_n^2(\theta)$ and the higher-order moments. In the high-temperature limit ($\theta = 0$) (3.1) reduces to the familiar self-avoiding walk result with $\gamma(0) = 6/5$ for both $R_n^2(0)$ and $S_n^2(0)$. At zero temperature ($\theta = \infty$) the polymer exists in the collapsed state and one would expect that $\gamma(\infty) = 2/3$; in other words, the mean

end-to-end distance and radius of gyration are proportional to the radius of the collapsed polymer.

At intermediate values of θ there are two types of behaviour consistent with (3.1): one is that $\gamma(\theta)$ varies continuously with θ , the other that the exponent is constant in both the high- and low-temperature phases with an abrupt jump in value at the transition point. The former suggests a steady growth of ordered regions along the polymer as the temperature is lowered, the latter a sudden collapse into the ordered state at the transition point. A third possibility is that (3.1) is incorrect over part or all of the range (excluding $\theta = 0$), however no extrapolation methods exist for handling behaviour which cannot be described by (3.1) (e.g. an essential singularity).

The exponent $\gamma(\theta)$ is obtained by fitting the R -moment data to the relation (I)

$$\frac{R_{n+1}^2(\theta)}{R_n^2(\theta)} \simeq 1 + \frac{\gamma(\theta)}{n} + O(n^{-2}) \quad (3.2)$$

and similarly for the S moment. A precondition for obtaining reasonable estimates of $\gamma(\theta)$ is that the ratios R_{n+1}^2/R_n^2 rapidly converge to unity. For example, linear extrapolation of the $\theta = 0$ R -moment ratios against $1/n$ yields a limiting value which differs from unity by only 0.1%; for $\theta = 0.18$ the difference is approximately 1%. This deviation, small though it is, is capable of producing a relative error in $\gamma(\theta)$ an order of magnitude larger.

Estimates for $\gamma(\theta)$ have been obtained by the Neville table method (an extension of equation (3.2) to higher order, see I); the results for the $p = 2$ chain moments appear in tables 1 and 2. For both R and S moments the exponent appears to decrease gradually as θ increases, and at the same time the convergence of the Neville table becomes

Table 1. Neville table estimates of the exponent $\gamma(\theta)$ obtained from the chain moment $R_n^2(\theta)$, for various θ . The corresponding Monte Carlo (MC) results are also shown.

	n	k				MC
		0	1	2	3	
$\theta = 0$	6	1.212	1.206	1.194	1.189	1.192
	7	1.211	1.204	1.200	1.208	
	8	1.210	1.203	1.198	1.196	
$\theta = 0.05$	6	1.175	1.163	1.148	1.136	1.153
	7	1.173	1.162	1.157	1.170	
	8	1.172	1.161	1.158	1.160	
$\theta = 0.10$	6	1.133	1.109	1.085	1.060	1.098
	7	1.129	1.104	1.092	1.103	
	8	1.125	1.102	1.094	1.097	
$\theta = 0.11$	6	1.124	1.097	1.070	1.042	1.073
	7	1.119	1.091	1.076	1.085	
	8	1.115	1.088	1.078	1.080	
$\theta = 0.12$	6	1.114	1.084	1.054	1.022	1.023
	7	1.109	1.077	1.059	1.066	
	8	1.104	1.073	1.060	1.062	

Table 2. Estimates of $\gamma(\theta)$ obtained from the chain moment $S_n^2(\theta)$. The Monte Carlo (MC) results are also shown.

	<i>n</i>	<i>k</i>				MC
		0	1	2	3	
$\theta = 0$						1.186
	6	1.090	1.192	1.210	1.209	
	7	1.106	1.198	1.216	1.223	
	8	1.118	1.203	1.215	1.214	
$\theta = 0.05$						1.154
	6	1.060	1.150	1.164	1.156	
	7	1.074	1.156	1.170	1.178	
	8	1.084	1.160	1.171	1.172	
$\theta = 0.10$						1.102
	6	1.026	1.101	1.105	1.087	
	7	1.037	1.103	1.107	1.110	
	8	1.046	1.104	1.107	1.107	
$\theta = 0.11$						1.075
	6	1.019	1.090	1.092	1.072	
	7	1.029	1.091	1.092	1.093	
	8	1.037	1.091	1.092	1.091	
$\theta = 0.12$						1.027
	6	1.012	1.079	1.078	1.055	
	7	1.021	1.078	1.077	1.075	
	8	1.028	1.078	1.075	1.073	

poorer. Also given in the tables are the exponents obtained by Monte Carlo studies (McCrackin *et al* 1973); there no extrapolation proved necessary, as the exponents were found by measuring the gradients of the straight line obtained after plotting each moment against *n* on a log-log scale.

The exponent estimates provided by the different methods agree with one another as far as $\theta = 0.11$, but above this the Monte Carlo estimates change more rapidly than those of exact enumeration. For $\theta > 0.125$ the Monte Carlo results can no longer be fitted to a straight line and no exponent estimates are possible. Over the range of θ for which exponents can be obtained the values of $\gamma(\theta)$ for both *R* and *S* moments appear almost equal and, as was the case for repulsive interactions (I), this suggests that irrespective of the correct asymptotic behaviour the limiting *n*-dependence of both kinds of moment are the same. Similar results, though of lower quality, are obtained for the ring *S* moments.

The close agreement between the exact enumeration and Monte Carlo exponent results is a strong argument in favour of a θ -dependent exponent. The former method involves chains of up to *n* = 9, the latter up to *n* = 1000, a difference of two orders of magnitude! Although experience with lattice spin systems has shown that exponents normally obey universality, there is no convincing reason why polymers must do likewise. Furthermore, even one of the spin systems, the exactly soluble eight-vertex model (Baxter 1971), does not obey universality, and dimensional arguments have been given (Kadanoff and Wegner 1971) to explain the breakdown.

Nevertheless, if one has good reason to believe that universality should apply then a possible explanation for the spurious θ -dependence of the exponents is to be found in I. Briefly stated it is that (3.1) is only the leading-order term in an expansion involving

decreasing powers of n (and perhaps other more complicated n -dependent forms). As θ increases these corrections become increasingly important, and true asymptotic behaviour only appears at much larger values of n . Hence the quality of extrapolation based on a fixed n will decrease with increasing θ . In the case of the Monte Carlo results which also yield θ -dependent exponents, it may be possible to attribute the behaviour to the inability of the method to sample the entire configuration space of the polymer. Although the Monte Carlo method proved highly successful in the non-interacting self-avoiding walk problem, the presence of attractive forces may make it difficult for the Monte Carlo generator to access certain regions of configuration space and the final results will consequently be biased. Now that exact results are available for tree-like lattices it may well prove possible to test this observation.

The exact calculations on the generalized Bethe lattices predict a constant exponent, $\gamma(\theta) = 2$, for the end-to-end distance above the transition (Morita 1976). It is not obvious what bearing this has on the regular lattice under investigation since tree-like lattices are effectively infinite dimensional, in the sense that the number of neighbours of a given site grows exponentially with distance rather than as some power of the distance.

The dependence of $S_n^2(\theta)$ on θ for fixed n is shown in figure 1. The curves are similar in form to those for much longer chains obtained by Monte Carlo methods (McCrackin *et al* 1973, results given only for simple cubic lattice) and suggest that the infinite chain has either an inflection point or a jump discontinuity at some value of θ . The density distribution of the polymer is closely related to the S moments; an inflection point would indicate a continuous density variation as seen in second-order phase transitions, whereas a jump discontinuity suggests a transition of first order. Similar behaviour is observed to occur in the R moments.

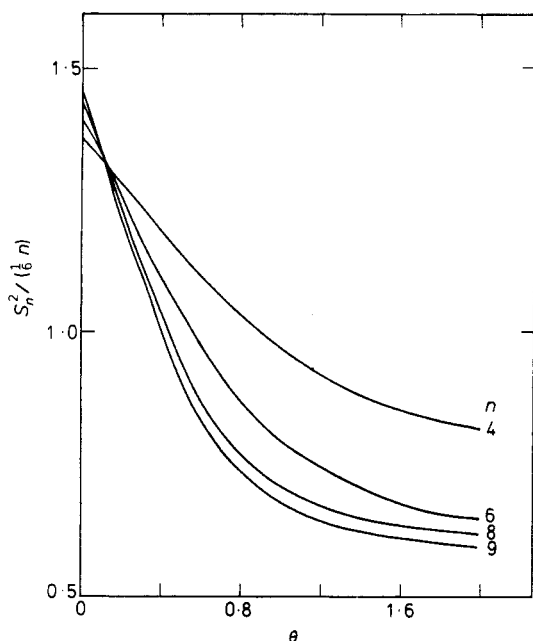


Figure 1. Plot of the chain mean-square radius of gyration $S_n^2(\theta)$, divided by the random-walk value $n/6$, against n . Note the crossover just below $\theta = 0.2$; in the $\theta \rightarrow \infty$ limit a jump or inflection point may develop in this region.

The low-temperature nature of $\gamma(\theta)$ cannot be deduced from available exact enumeration or Monte Carlo data; in the former case this is due to the finite size irregularities mentioned in § 2, in the latter the problem is one of inadequate sampling.

4. Thermodynamic properties

In the limiting case $\theta = 0$ the partition function reduces to the number of self-avoiding walks, or returns to the origin, whose asymptotic behaviour is (Domb 1969)

$$c_n \sim c_0 \mu^n n^\alpha.$$

For non-zero θ this generalizes to

$$c_n(\theta) \sim c_0(\theta) \mu(\theta)^n n^{\alpha(\theta)}. \quad (4.1)$$

The analysis for $\theta < 0$ (I) yielded results consistent with (4.1); $\mu(\theta)$ decreased as $|\theta|$ increased reflecting an increased 'effective' excluded volume, and the exponent $\alpha(\theta)$ remained almost constant.

The results of a similar analysis for $\theta > 0$ appear in figure 2 and table 3. The chain and ring $\mu(\theta)$ estimates obtained by linear extrapolation are seen to lie fairly close

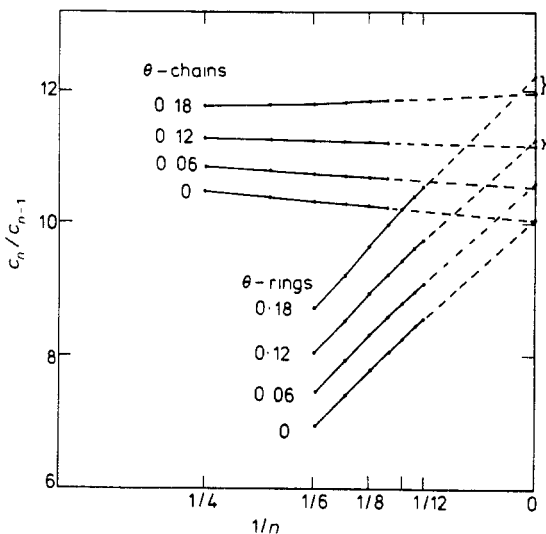


Figure 2. Estimation of $\mu(\theta)$ from the partition function. In each case the broken line is the linear extrapolation based on the final pair of points.

Table 3. Chain and ring estimates of $\mu(\theta)$ and $\alpha(\theta)$ obtained using linear extrapolation.

θ	$\mu_{\text{ch}}(\theta)$	$\mu_{\text{ri}}(\theta)$	$\alpha_{\text{ch}}(\theta)$	$\alpha_{\text{ri}}(\theta)$
0	10.03	10.05	0.170	-1.78
0.03	10.27	10.27	0.149	-1.71
0.06	10.53	10.54	0.121	-1.66
0.12	11.16	11.24	0.039	-1.61
0.18	11.97	12.21	-0.089	-1.65

together; if the residual curvature of the plots is taken into account by performing a Neville table analysis the agreement is slightly improved. This suggests the assertion that over the range of θ studied the chain and ring $\mu(\theta)$ values are identical. The statement was previously proposed for $\theta < 0$ (I), and is known to be exact for $\theta = 0$. The exponent $\alpha(\theta)$ appears to vary with θ (table 3), but in view of the discussion in § 3 a constant exponent still remains a possibility.

When plotted as a function of θ , the mean number of nearest-neighbour pairs, $g_n(\theta)$, shows a rapid increase in value as θ decreases towards zero (the slope of the curves is given by $h_n(\theta)$ —see below). Complete collapse, in the sense that most polymer units are surrounded by the maximum number of nearest neighbours, is not possible for small n , and the growth of $g_n(\theta)$ must be gradual. However, in the limit $n \rightarrow \infty$ the behaviour of $g_n(\theta)$ may well be similar to that proposed for the moments (§ 3), namely an inflection point or discontinuity at the transition point.

The form of the specific heat $h_n(\theta)$ is a more revealing indicator of the behaviour as $n \rightarrow \infty$. The function is plotted in figure 3 for various chain lengths. The maximum

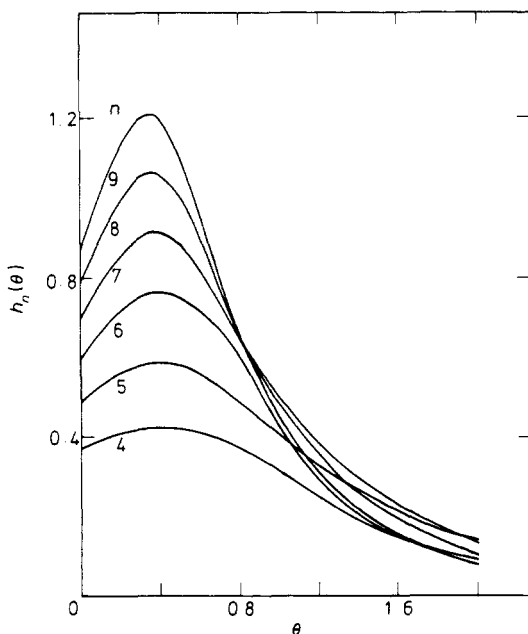


Figure 3. Chain specific heat $h_n(\theta)$ against θ .

values attained by $h_n(\theta)$ are seen to increase with n ; when the maxima are plotted against $\ln n$ they are seen to diverge more rapidly than $\ln n$ (Rapaport 1974b). In the case of the two-dimensional Ising model a similar trend in the specific heat leads to a divergence in the infinite limit (Ferdinand and Fisher 1969). Results taken from Monte Carlo studies (Mazur and McCrackin 1968) show that the trend established by the short chains persists to much higher values of n , and one is led to conclude that the specific heat of the infinite chain diverges at the transition point. Qualified confirmation of this statement is obtained from approximate renormalization group calculations (Burch and Moore 1976).

An alternative approach to the polymer phase transition problem is through a study of the distribution of the zeros of the partition function in the complex temperature plane. Let $\eta = \exp \theta$; the partition function polynomial (2.1) is then

$$c_n(\eta) = \sum_m c_{nm} \eta^m = c_n(\eta = 0) \prod_m \left(1 - \frac{\eta}{\eta_m^0} \right)$$

where $\{\eta_m^0\}$ is the set of complex zeros of $c_n(\eta)$. Since all the coefficients c_{nm} are positive none of the zeros can lie on the positive real axis and the thermodynamic properties of finite chains are analytic functions of temperature. However, as $n \rightarrow \infty$ a subset of the zeros may well form a continuous curve which intersects the real axis, and this would lead to singularities in the free energy derivatives. The detailed nature of these singularities is determined by the density of zeros in the neighbourhood of the intersection point (Abe 1967).

The zeros of $c_n(\eta)$ are shown in figure 4. Only the first quadrant is displayed since the distribution of zeros is symmetric about the real axis, and the zeros with negative

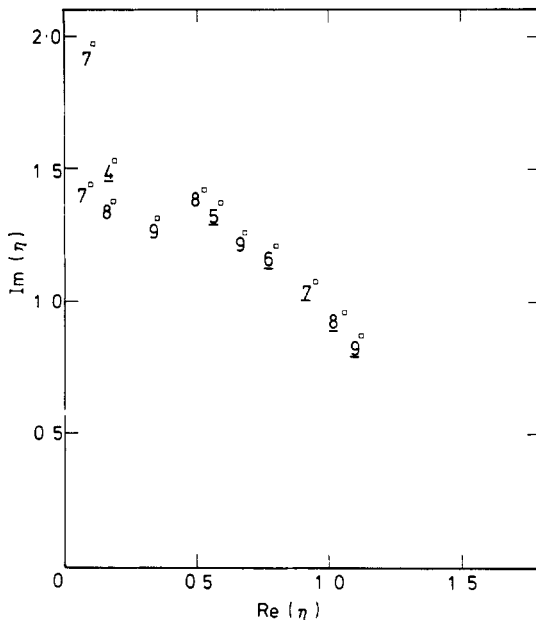


Figure 4. Chain partition function zeros. The pattern is symmetric about the real axis, and zeros with negative real parts are omitted. The zero closest to the real axis for each value of n is underlined.

real parts are not relevant. The closest zeros to the real axis for each value of n are seen to lie on a fairly smooth trajectory. Finsky *et al* (1975) have made an analogous study for the simple cubic lattice using both exact and Monte Carlo methods. The Monte Carlo results strongly suggest that the zeros lie on a continuous curve and it proved possible to estimate where the curve crossed the real axis. The exact enumeration results, however, cannot be fitted to a smooth curve with any reasonable degree of confidence; instead we will compare the results with the specific heat analysis presented earlier.

In table 4 the values $\theta_R = \ln \eta_R$, where η_R is the distance from the origin of the zero closest to the real axis, are listed together with θ_M , the locations of the corresponding specific heat maxima. The difference between the two sets of values is small, for $n = 9$ they differ by less than 2%. This suggests that the apparent divergence of the specific heat is closely related to the gradual approach of the zeros to the real axis.

Table 4. Comparison of the logarithm of the distance from the origin of the closest partition function zero to the real axis (θ_R) with the θ -value at which the specific heat maximum occurs (θ_M), for chains.

n	θ_R	θ_M
6	0.373	0.405
7	0.363	0.379
8	0.357	0.356
9	0.347	0.342

A rough extrapolation of the θ_M values yields a limiting value of 0.2. If θ_M and θ_R eventually coincide then one would expect the intersection of the curve of zeros with the real axis to occur somewhere between $\eta = 1.2$ and 1.3. From figure 4 this appears to be a likely possibility.

The corresponding results for the rings are less clear. The partition function zeros appear to lie along two trajectories, and the ring specific heats indicate a limiting θ_M value very close to zero. These results may well be due to finite size effects which, for given n , are more pronounced for rings than for chains.

5. Review

Exact enumeration methods have been used in an attempt to study the properties of the self-interacting polymer model. The exponents governing the length dependence of the partition function and moments do not appear to be temperature independent. The moment exponent estimates, $\gamma(\theta)$, agree with those obtained in the Monte Carlo study; in both cases the deviation of $\gamma(\theta)$ from the $\theta = 0$ value of 6/5 is not confined to the transition region ($\theta \approx 0.2$) but is noticeable as soon as θ departs from zero. Thus, unlike the polymer with repulsive interactions where a case could be made favouring constant exponents (1), the attractively interacting system does not appear to obey universality. Of course the possibility that both methods are unable to handle the problem remains, but the close agreement between the results render this unlikely.

The results indicate that a phase transition characterized by a divergent specific heat occurs when the chain switches between its collapsed and expanded states. The existence of this transition gains further support from the exact solution on the generalized Bethe lattices and the renormalization group calculations.

In regard to the low-temperature behaviour, neither exact nor Monte Carlo methods have succeeded in throwing light on the problem. The Bethe-type lattice calculations reveal a chain which remains locked in a fixed configuration on the low-temperature side of the transition. For a regular lattice however, analogy with the picture of clusters of ordered and disordered spins in the Ising model (Fisher 1967)

suggests a scheme whereby the polymer collapse is only partial at non-zero temperatures; the polymer contains both ordered and disordered sections (Lifshitz 1969), and the ordered sections gradually increase in size and coalesce as temperature is reduced.

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