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Configurational properties of polymers in a good solvent

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Abstract. Self-interacting, self-avoiding polymer chains and rings are generated on the FCC lattice by exact enumeration. The effect of the 'good' solvent is represented by a short-range repulsive interaction between pairs of polymer units. The partition function and the moments of the end-to-end distance and mass distributions are extrapolated to obtain the limiting behaviour at various temperatures. Difficulties encountered in determining the exponents and their temperature dependence are discussed.

1. Introduction

The self-avoiding walk, or chain, on a lattice has been extensively studied as a model of a single polymer chain in dilute solution. The model has turned out to be insoluble by analytic means, but exact enumeration and Monte Carlo studies have provided what is generally regarded as a reliable picture of the configurational properties (Domb 1969). The self-avoiding condition, according to which a lattice site cannot be occupied by more than a single chain unit, is used to simulate the excluded volume of the individual units. Any additional interactions apart from this hard core are omitted from the model.

The neglected interactions fall into two groups: (i) forces between neighbouring units (e.g., bond torsion), and (ii) the interaction between non-neighbouring units whose strength depends on their spatial separation but not on the distance between them as measured along the chain backbone. Forces belonging to type (i) have been explored in detail, but only in the absence of excluded volume in order to facilitate analytic treatment (Flory 1969). The justification for neglecting excluded volume in these studies is that the polymer is assumed to be at its Θ-temperature where the excluded volume effect is approximately cancelled by the (in this case) attractive force of type (ii).

Looked at from a statistical mechanical standpoint type (ii) forces are the more interesting of the two; because they are non-Markovian they are capable of producing a qualitative change in behaviour, similar in nature to the change produced in the random walk when excluded volume is introduced. Type (i) forces, on the other hand, do not destroy the Markovian structure and the exponents governing asymptotic behaviour remain unchanged; the same is true if, for example, immediate reversals are prohibited in the random walk. Only the type (ii) force is discussed here.

Contributions to the type (ii) interaction between pairs of units arise from polymer–polymer, polymer–solvent and solvent–solvent forces. Depending on the relative strengths of the three components, the resultant interaction may be of either sign. If negative, polymer–solvent contacts are favoured, then the typical chain configuration will be more open than if only excluded volume is present—the chain is in a 'good'

solvent. A particular case of the good solvent is the athermal solution; the effective interaction is zero and the usual self-avoiding picture applies. If the effective force is positive the chain tends to contract and the solvent is said to be 'poor'. A chain in a poor solvent should undergo a phase transition and collapse into an ordered state at sufficiently low temperature. Similar behaviour may be expected from ring polymers.

In this paper we study the properties of isolated chain and ring polymers in a good solvent; the poor solvent behaviour is reserved for a subsequent article. The models used are the self-avoiding chain and the ring embedded in a lattice, with interactions occurring between non-neighbouring units when they appear on adjacent lattice sites. Exact enumeration methods are used to exhaustively generate the possible configurations of relatively small systems (§ 2) and the results are extrapolated to produce estimates of the asymptotic forms of the configurational properties (§ 3). The relation between the inadequate convergence of some of the numerical results and the perturbation expansion approach to the problem is discussed in § 4. Frequent reference is made to the results obtained in a study of the non-interacting case (Rapaport 1975 to be referred to as I).

2. Chain and ring generation

Consider a self-avoiding chain of $n+1$ units located on the sites of a regular lattice and joined together by n links. Adjacent units along the chain are located on neighbouring sites. Between each pair of non-adjacent units which, in a particular embedding, lie on neighbouring lattice sites, there is an interaction of constant strength $-J$. The chain partition function at a temperature T has the form

$$c_n(\eta) = \sum_{m \geqslant 0} c_{nm} \eta^m \tag{2.1}$$

where $\eta = \exp \theta$, $\theta = J/k_B T$, and c_{nm} is the number of (n, m) embeddings, i.e., the number of n-link chains having m nearest-neighbour pairs of units. $c_n(\eta)$ is a finite polynomial in η whose degree depends both on the value of n and the lattice type. In the non-interacting or high temperature limit ($\eta = 1$), $c_n(1)$ becomes c_n, the number of n-step self-avoiding walks. The other limiting case is $\eta = 0$ ($T = 0$), which corresponds to double excluded volume—no nearest-neighbour pairs.

The partition function of an n-link ring can also be written in the form (2.1). For $\eta = 1$ it reduces to u_n—the number of returns to the origin of the n-step self-avoiding walk (self-avoiding except for the endpoints). Subscripts will be used to distinguish between the chain and ring quantities where necessary.

The moments of the chain end-to end distance distribution are defined as

$$R_n^p(\eta) = c_n(\eta)^{-1} \sum_{m \geqslant 0} \sum_r r^p c_{nm}(r) \eta^m \tag{2.2}$$

where $c_{nm}(r)$ is the number of (n, m) configurations whose endpoint separation is r (the links are taken to have unit length). Similarly, the moments of the distribution of distances from the centre of mass of the polymer are

$$S_n^p(\eta) = c_n(\eta)^{-1} \sum_{m \geqslant 0} \sum_s s^p c_{nm}(s) \eta^m \tag{2.3}$$

for both chains and rings, with $c_{nm}(s)$ the number of (n, m) configurations whose units are a mean square distance s^2 from the centre of mass.

The exact enumeration procedure for an n-link polymer involves the computer evaluation of the coefficients $c_{nm}(r)$ and/or $c_{nm}(s)$ for all allowed values of m, r and s. The partition function coefficients follow from

$$c_{nm} = \sum_r c_{nm}(r) = \sum_s c_{nm}(s).$$

The computational techniques were outlined in I, and amount to a full evaluation of the possible configurations, using lattice symmetry and careful programming to reduce the computation time to a minimum. The output of the calculation consists of the partition function expressed in polynomial form (2.1) and the R or S moments as ratios of two such polynomials (2.2, 2.3). Lists of the coefficients required to construct the partition function and $p = 2$ moments as functions of η appear in the appendix.

Only the face-centred cubic (FCC) lattice is considered in this work; extensive studies, both exact and Monte Carlo, of the non-interacting case on other three-dimensional lattices (Domb 1969) indicate that many of the limiting properties are lattice independent, but that larger systems must be studied to obtain results of comparable quality to the FCC. It would seem reasonable to presume that the same will prove true for the interacting case.

For non-interacting FCC chains and rings, $c_n(1)$ is known to $n = 12$ and 14 respectively (Martin *et al* 1967, Sykes *et al* 1972b), and the chain moments $R_n^p(1)$ to $n = 10$ (McKenzie 1973). In order to extend the calculations this far, special techniques, 'counting theorems', have been developed to keep computational effort at a tolerable level; these techniques are not readily applied when $\eta \neq 1$ and the highest n values attained are consequently smaller. For $S_n^p(1)$ no special methods exist and, prior to the present study, direct enumeration had produced values of $S_{n,\mathrm{ch}}^2(1)$ as far as $n = 7$ (Domb and Hioe 1969). In the present work the partition function and moments have been generated to $n = 9$ and 12 for chains and rings respectively. The moments $S_n^p(1)$ for non-interacting chains and rings were discussed in detail in I.

3. Analysis of results

A number of methods are available for extrapolating the small-n results to obtain the limiting behaviour of large systems (Hunter and Baker 1973); the choice of how sophisticated a method can be used is determined by the amount of data avilable. In studies of systems such as the two-dimensional Ising model, closed form results exist which can be used to corroborate the predictions of the numerical analysis. Backed up by these successes one proceeds with greater confidence to study similar systems for which no analytic results are available. Comparison of exact and extrapolated results also reveals some of the shortcomings of the numerical method (see § 4).

3.1. Partition function

The numerical analysis of chains and rings with $\eta = 1$ yields

$$c_n \sim c_0 \mu^n n^{1/6} \qquad u_n \sim u_0 \mu^n n^{-7/4} \tag{3.1}$$

in three dimensions (c_0 and u_0 are constants), and for the FCC lattice $\mu = 10{\cdot}035$ (Domb 1969, Sykes *et al* 1972a). These results are in accord with one of the few available

rigorous results, namely that

$$c_n \sim \mu^n f(n), \qquad u_n \sim \mu^n g(n). \tag{3.2}$$

Bounds have been established for the unspecified functions $f(n)$ and $g(n)$—they offer no aid to the numerical extrapolator, and the same value of μ applies both to chains and rings (Hammersley 1964, discussion of paper by Domb), The analysis was carried out for the simple cubic lattice only, but (3.2) should also apply to the FCC and other regular lattices. Clearly the asymptotic forms (3.1) represent only the dominant terms in an infinite series of descending powers of n (possibly including logarithmic terms, etc), but the available data are insufficient to determine the higher order contributions.

The obvious generalization of (3.1) to the interacting chain or ring is

$$c_n(\eta) \sim c_0(\eta)\mu(\eta)^n n^{\alpha(\eta)} \qquad \eta \leqslant 1. \tag{3.3}$$

No rigorous results have been established for $\eta \neq 1$, and the suitability, or otherwise, of (3.3) must be determined by the numerical studies alone. Before we turn to a discussion of the numerical analysis, a brief word about the expected η-dependence of the exponent α is in order. If one accepts the universality hypothesis (Griffiths 1970, Kadanoff 1971) and its obvious extension to polymers, namely that the exponents governing the large-n behaviour (which are the analogues of critical indices in spin systems) should depend on gross features such as symmetry and dimensionality, but not on details such as temperature, then α should be independent of η for $\eta \leqslant 1$. It remains to be seen whether the numerical results support this claim.

According to (3.3), the ratios of successive $c_n(\eta)$ should have the form

$$\frac{c_n(\eta)}{c_{n-1}(\eta)} \approx \mu(\eta)\left(1+\frac{\alpha(\eta)}{n}+\mathrm{O}(n^{-2})\right). \tag{3.4}$$

If the higher order terms in (3.4) are relatively small, linear extrapolation of the ratios against $1/n$ should yield a sequence of converging estimates for $\mu(\eta)$. In figure 1 chain and ring ratios are plotted against $1/n$ for various η and, where the plots are sufficiently smooth, the line between the last pair of points has been continued to $1/n = 0$. Higher order extrapolation is also possible; for this (3.4) is modified to include further powers of $1/n$:

$$\frac{c_n(\eta)}{c_{n-1}(\eta)} \approx \mu(\eta)\left(1+\frac{a_1(\eta)}{n}+\ldots+\frac{a_k(\eta)}{n^k}+\mathrm{O}(n^{-k-1})\right). \tag{3.5}$$

Sets of $k+1$ successive ratios (using the coefficients $c_{n-k-1}, \ldots c_n$) are used to derive estimates of $\mu(\eta)$ for given k and various n. The results of the polynomial fit are given in tables 1 and 2; this form of presentation is known as the Neville table. The $k = 0$ column contains the ratios themselves, and the $k = 1$ values are the linear extrapolants of figure 1.

In figure 1 the chain $\mu(\eta)$ estimates are well converged over the entire range of η, but the ring values appear overestimated by the linear extrapolation for $\eta < 1$. These observations are confirmed by the Neville tables. Thus, although the graph suggests a 5% difference between $\mu_{\mathrm{ch}}(\eta)$ and $\mu_{\mathrm{ri}}(\eta)$ for $\eta = 0{\cdot}4$ and $0{\cdot}8$, the higher order analysis points to values much closer together. For $\eta = 0$ rings, simple extrapolation is not possible because of the oscillations, but the general trend is towards the corresponding

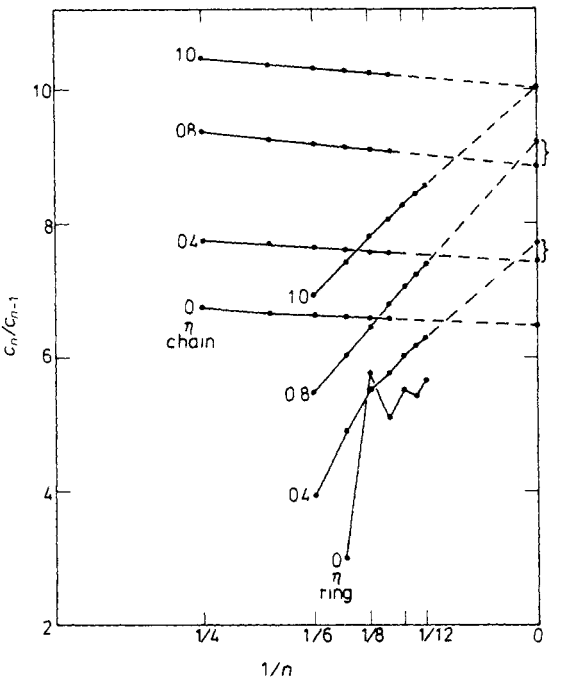

Figure 1. Estimation of $\mu(\eta)$ from the partition function for various η. The linear extrapolation is a continuation of the line joining the final pair of points in each case.

Table 1. Neville table estimates of $\mu(\eta)$ for chains.

	n \ k	0	1	2	3
$\eta = 0$					
	7	6·606	6·461	6·323	5·452
	8	6·590	6·481	6·544	6·912
	9	6·577	6·466	6·414	6·154
$\eta = 0{\cdot}4$					
	7	7·606	7·417	7·404	7·406
	8	7·584	7·423	7·444	7·509
	9	7·566	7·425	7·430	7·403
$\eta = 0{\cdot}6$					
	7	8·271	8·043	8·074	8·006
	8	8·244	8·049	8·069	8·061
	9	8·222	8·054	8·069	8·069
$\eta = 0{\cdot}8$					
	7	9·126	8·842	8·897	8·845
	8	9·092	8·854	8·891	8·882
	9	9·066	8·862	8·889	8·886
$\eta = 1{\cdot}0$					
	7	10·276	10·031	10·054	10·041
	8	10·246	10·032	10·034	10·000
	9	10·222	10·032	10·035	10·037

Table 2. Neville table estimates of $\mu(\eta)$ for rings. Entries omitted show too much scatter. Compare with table 1.

	n \ k	0	1	2	3
$\eta = 0$					
	10	5·508	9·337	—	—
	11	5·416	4·499	—	—
	12	5·652	8·249	—	—
$\eta = 0{\cdot}4$					
	10	6·022	8·363	11·38	—
	11	6·167	7·617	4·261	—
	12	6·295	7·707	8·152	—
$\eta = 0{\cdot}6$					
	10	6·395	8·948	8·052	11·00
	11	6·599	8·638	7·246	5·096
	12	6·754	8·459	7·563	8·512
$\eta = 0{\cdot}8$					
	10	7·030	9·322	9·170	9·163
	11	7·233	9·271	9·043	8·704
	12	7·398	9·205	8·878	8·383
$\eta = 1{\cdot}0$					
	10	8·264	10·103	9·813	11·046
	11	8·428	10·071	9·928	10·233
	12	8·563	10·054	9·971	10·101

chain value. The results can therefore be taken to support the relation

$$\mu_{ch}(\eta) = \mu_{ri}(\eta), \qquad \eta \leqslant 1$$

a natural extension of the rigorous $\eta = 1$ result (3.2).

Estimates of the exponent $\alpha(\eta)$ can in principle be derived from (3.4) once $\mu(\eta)$ is known. However, the value is very sensitive to the choice of μ and a small relative error in μ produces a relative change in α larger by an order of magnitude. Table 3 contains estimates of $\alpha(\eta)$; the numbers in parentheses are the values of $\mu(\eta)$ which, when substituted into (3.4), give $\alpha_{ch}(\eta) = 1/6$. The results suggest a constant exponent $\alpha_{ch}(\eta) = 1/6$ for $\eta < 1$. The ring values are more widely spread, but in view of the inadequate convergence of $\mu_{ri}(\eta)$ the results are consistent with $\alpha_{ri}(\eta) = -7/4$. Overall, the analysis suggests an η-independent exponent α, in agreement with the

Table 3. Chain and ring exponents $\alpha(\eta)$. The same $\mu(\eta)$ estimates are used for both and are taken from the linear extrapolants of table 1. The μ-values in parentheses give $\alpha_{ch}(\eta) = 1/6$ when substituted back into equation (3.4).

η	$\mu_{ch}(\eta)$		$\alpha_{ch}(\eta)$	$\alpha_{ri}(\eta)$
0	6·47	(6·46)	0·149	−1·52
0·2	6·91	(6·90)	0·155	−1·71
0·4	7·42	(7·43)	0·177	−1·82
0·6	8·06	(8·07)	0·181	−1·94
0·8	8·86	(8·90)	0·209	−1·98
1·0	10·03	(10·04)	0·172	−1·76

universality prediction. A similar conclusion for chains only was proposed by Fisher and Hiley (1961) based on very limited data.

3.2. R moments

Exact numeration and Monte Carlo treatment of three-dimensional chains leads to the conclusion

$$R_n^2(1) \sim r_0 n^{6/5}. \tag{3.6}$$

(Domb 1969). Unlike the partition function, there is no rigorous confirmation of (3.6). The generalization to the interacting case is

$$R_n^2(\eta) \sim r_0(\eta) n^{\gamma(\eta)} \qquad \eta \leqslant 1. \tag{3.7}$$

Here, as with the partition function, universality predicts a constant exponent. From (3.7)

$$\frac{R_{n+1}^2(\eta)}{R_n^2(\eta)} \approx 1 + \frac{\gamma(\eta)}{n} + O(n^{-2}). \tag{3.8}$$

Equation (3.8) differs from (3.4) in that the extrapolation is now effectively against $1/(n-1)$ rather than $1/n$. This change is found to yield better results in the linear analysis, but because the difference is $O(n^{-2})$ the higher order extrapolations are not significantly altered. The quality of the exponent estimates depends on how rapidly the moment ratio (3.8) tends to unity as $n \to \infty$; linear extrapolation of (3.8) gives limiting values ranging from 0·999 for $\eta = 1$ to 0·982 for $\eta = 0$.

Estimates of γ are obtained by rearranging (3.8):

$$\chi_n(\eta) = n\left(\frac{R_{n+1}^2(\eta)}{R_n^2(\eta)} - 1\right) \approx \gamma(\eta) + O(n^{-1}). \tag{3.9}$$

The results are plotted in figure 2; the Neville table obtained by fitting $\chi_n(\eta)$ to a kth degree polynomial in $1/n$ appears in table 4. The results should be compared with those for $\eta = 1$ (I, McKenzie 1973). The downward curvature of the graphed ratios, taken together with the Neville table, provide support for the universality prediction $\gamma_{ch}(\eta) = 6/5$ for $\eta \leqslant 1$. For the particular case $\eta = 0$, similar estimates were recently obtained for the tetrahedral and body-centred cubic lattices (Torrie and Whittington 1975).

3.3. S moments

The limiting behaviour $S_{n,ch}^2(1) \sim s_0 n^{6/5}$ is predicted by both exact enumeration (I) and Monte Carlo studies (McCrackin *et al* 1973). Exponent estimates for $\eta < 1$ are obtained in the same manner as before and appear in figure 3 and table 5. The drift away from unity of the extrapolated moment ratios is similar to that of the R moments.

The graphed results suggest $\gamma_{ch}(\eta) \approx 1{\cdot}3$ for $\eta < 1$. While the Neville table clearly shows that this is an overestimate, it also indicates that the progress towards 6/5 is very slow. The only Monte Carlo results available for $\eta < 1$ are on the simple cubic lattice (McCrackin *et al* 1973) and even then only for the case $\eta = 0$; the value given is $\gamma_{ch}(0) = 1{\cdot}25$.

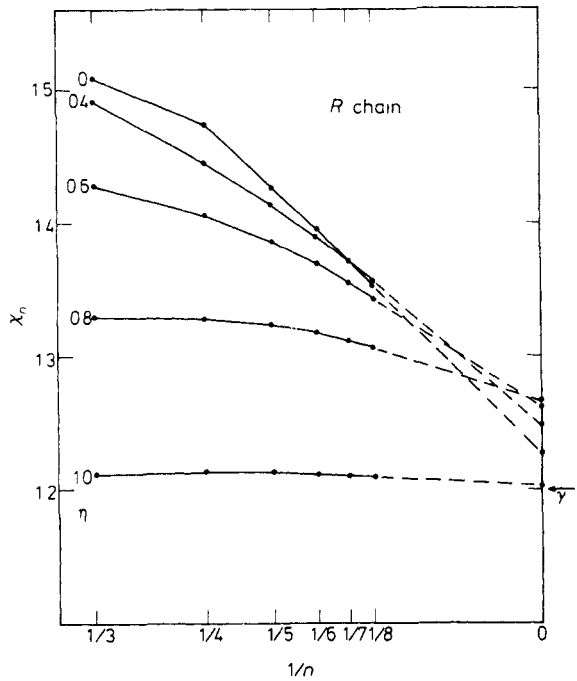

Figure 2. Chain R moments: estimation of $\gamma(\eta)$ for various η. χ_n is defined in equation (3.9), and as $n \to \infty$, $\chi_n(\eta) \to \gamma(\eta)$.

Table 4. Chain R moments: estimates of $\gamma(\eta)$.

	n \ k	0	1	2	3
$\eta = 0$					
	6	1·396	1·251	1·287	1·545
	7	1·371	1·219	1·141	0·946
	8	1·353	1·227	1·251	1·434
$\eta = 0{\cdot}4$					
	6	1·390	1·273	1·249	1·244
	7	1·371	1·258	1·218	1·178
	8	1·356	1·248	1·220	1·222
$\eta = 0{\cdot}8$					
	6	1·318	1·287	1·257	1·250
	7	1·312	1·275	1·246	1·232
	8	1·306	1·266	1·238	1·224

The behaviour of $S^2_{n,\mathrm{ri}}(1)$ is similar to $S^2_{n,\mathrm{ch}}(1)$ (I), though not as well converged. For $\eta < 1$ the ring exponent analysis (figure 4) is unable to predict $\gamma_{\mathrm{ri}}(\eta)$; the Neville table is of no help in this case.

3.4. Higher moments and reduced moments

Analysis of higher chain and ring moments for $\eta = 1$ (I) indicates that they have the form (3.6) but with exponent $\gamma_p = p\gamma/2$ ($\gamma = 6/5$). We have studied the $p = 4$ and 6 R

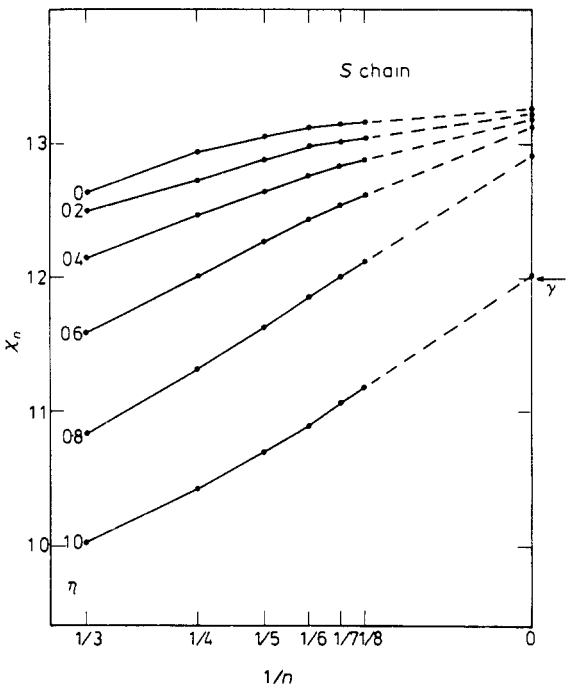

Figure 3. Chain S moments: estimation of $\gamma(\eta)$.

Table 5. Chain S moments: estimates of $\gamma(\eta)$.

	n \ k	0	1	2	3
$\eta = 0$					
	6	1·312	1·349	1·352	1·408
	7	1·315	1·330	1·280	1·184
	8	1·316	1·327	1·318	1·381
$\eta = 0{\cdot}4$					
	6	1·277	1·336	1·330	1·321
	8	1·284	1·328	1·307	1·276
	8	1·289	1·320	1·297	1·280
$\eta = 0{\cdot}8$					
	6	1·185	1·294	1·303	1·297
	7	1·201	1·293	1·292	1·279
	8	1·212	1·291	1·283	1·267

and S moments for $\eta < 1$; the convergence of the results decreases with increasing p, but suggests that $\gamma_p(\eta) \approx p\gamma(\eta)/2$ with the value of $\gamma(\eta)$ as obtained from the corresponding $p = 2$ moment.

If the higher moments do have exponents of this form, where $\gamma(\eta)$ may or may not be a constant, then the reduced moments $\bar{M}_n^p = M_n^p/(M_n^2)^{p/2}$ should approach finite limits as $n \to \infty$. As a typical example we give the Neville table for the reduced chain moment $\bar{R}_n^4(\eta)$ in table 6. The table displays a persistent upward drift as k, the order of

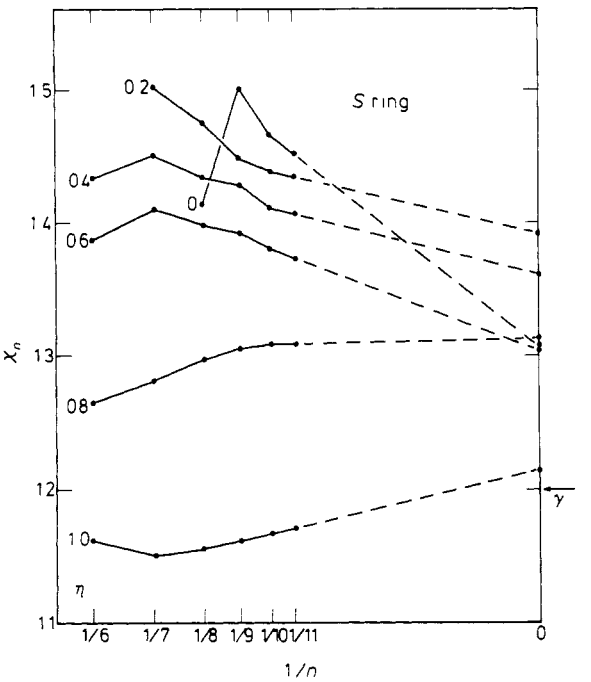

Figure 4. Ring S moments: estimation of $\gamma(\eta)$.

Table 6. Extrapolated estimates of the reduced moment $\bar{R}_n^4(\eta)$.

	n \ k	0	1	2	3
$\eta = 0$					
	7	1·192	1·321	1·381	1·394
	8	1·211	1·343	1·410	1·459
	9	1·228	1·359	1·416	1·427
$\eta = 0{\cdot}4$					
	7	1·231	1·318	1·370	1·397
	8	1·244	1·336	1·389	1·420
	9	1·256	1·351	1·402	1·430
$\eta = 0{\cdot}8$					
	7	1·313	1·368	1·387	1·405
	8	1·321	1·375	1·399	1·417
	9	1·328	1·383	1·408	1·427

extrapolation, is increased; the same is true for $\bar{R}_n^4(1)$ (McKenzie 1973), and for the other reduced R and S moments.

The explanation for the Neville table drift is the neglect of significant corrections to the asymptotic behaviour of the moments. One expects the typical form of the leading terms to be

$$M_n^2(\eta) \sim m_0(\eta) n^{6/5} + m_1(\eta) n + \ldots, \tag{3.10}$$

so that

$$\bar{M}_n^4(\eta) \approx \bar{m}_0(\eta) + \bar{m}_1(\eta) n^{-\sigma} + O(n^{-2\sigma}). \tag{3.11}$$

If $\sigma \simeq 1$, the technique of fitting to a polynomial in $1/n$ ought to yield good results. However, it follows from (3.10) that the correct value is $\sigma = 1/5$, so it is hardly surprising that the Neville table fails to converge. With the limited quantity of data available, it does not appear possible to utilize the result (3.11) in order to improve the convergence.

The η-dependence of the moment ratios $R^2_{n,\mathrm{ch}}/S^2_{n,\mathrm{ch}}$ and $S^2_{n,\mathrm{ch}}/S^2_{n,\mathrm{rl}}$ has also been studied. The corresponding $\eta = 1$ results were given in I. For the chain ratio the curvature of the plots against $1/n$ increases as $\eta \to 0$, with a steadily increasing limiting value. The limit at $\eta = 0$ (nearest-neighbour approach forbidden) is about 7·0, well below the rigid linear chain value of 12. The data for the mixed ratio show poor convergence for $\eta < 1$.

4. Perturbation approach

Overall, the convergence of the extrapolations proves to be best in the non-interacting ($\eta = 1$ or $\theta = 0$) case, for each of the properties investigated. The results become progressively worse as $\eta \to 0$ ($\theta \to -\infty$), some properties more rapidly so than others. Similar variations in the quality of extrapolated results have been encountered in a number of other studies (e.g., the Ising model with non-magnetic impurities, Rapaport 1972) and seem to arise whenever an additional variable (in this example the impurity concentration) is introduced into a system being studied by series methods. The variations are usually attributed to the numerical techniques seeing not the correct asymptotic form, but rather a modified form dominated by a set of confluent singularities which appear when the extra variable is treated by perturbation methods. This represents a limitation of the numerical analysis which is not readily overcome, unless sufficient *a priori* information about the structure of the expansion is made available.

As a concrete example of this effect, consider the chain partition function $c_n(\theta)$—now regarded as a function of θ. We define the generating function

$$C(\theta, x) = \sum_{n \geqslant 0} c_n(\theta) x^n. \tag{4.1}$$

For the purposes of this discussion assume that the form (3.3) with a constant exponent α characterizes the asymptotic behaviour; the singular part of (4.1) can be evaluated by taking only the dominant asymptotic contribution for each n and ignoring the early terms of the series which do not contribute to the singularity:

$$C(\theta, x) \sim c_0(\theta)(1 - \mu(\theta)x)^{-\alpha - 1}. \tag{4.2}$$

This summation is only valid in the neighbourhood of the singularity, i.e., for $\mu(\theta)x \approx 1$, but this is of course the region the numerical analysis attempts to explore. The singularity (4.2) and the asymptotic form of $c_n(\theta)$ are related through Darboux's theorem (Ninham 1963).

It is reasonable to expect that $\mu(\theta)$ can be expanded as a Taylor series about $\theta = 0$. Equation (4.2) can then be developed as a series in ascending powers of $\theta/(1 - \mu x)$:

$$C(\theta, x) \sim C_0(1 - \mu x)^{-\alpha - 1} + C_1 \theta (1 - \mu x)^{-\alpha - 2} + \ldots \tag{4.3}$$

where $\mu \equiv \mu(\theta = 0)$. Only the most strongly singular term (as $\mu x \to 1$) has been retained in (4.3) at each order of θ. Expanding $\exp \theta$ in (4.1) and rearranging also yields an expansion in θ; since $c_n(\theta)$ can be written as

$$c_n(\theta) = \sum_{t \geq 0} g_{nt} \theta^t$$

the generating function becomes

$$C(\theta, x) = \sum_{t \geq 0} G_t(x) \theta^t \tag{4.4}$$

with

$$G_t(x) = \sum_n g_{nt} x^n.$$

Matching powers of θ between (4.3) and (4.4) yields the dominant singularity of each function $G_t(x)$,

$$G_t(x) \sim C_t (1 - \mu x)^{-\alpha - 1 - t},$$

or equivalently,

$$g_{nt} \sim C_t \mu^t n^{\alpha + t}. \tag{4.5}$$

Numerical verification of (4.5) has been attempted. The results of a Neville table study of g_{nt} appear in table 7. Note that for $t = 0$, g_{n0} is just $c_n(0)$. While it is apparent from the tables that the various estimates are all heading in the general direction of the self-avoiding value $\mu = 10{\cdot}035$, they have not yet achieved convergence. Exponent estimates are consequently unobtainable, and the validity of (4.5) cannot be confirmed.

In the annealed impurity Ising model, behaviour analogous to that of (4.5) was predicted for the susceptibility and confirmed by numerical analysis. Series extrapolation for various impurity concentrations (the analogue of θ) produced the correct location of the shifted critical temperature (the analogue of $\mu(\theta)$), but the exponent estimates were found to be incorrect by an amount which increased with concentration.

Table 7. Neville table estimates of μ using the coefficients g_{nt}.

	n \ k	0	1	2
$t = 1$				
	7	12·757	8·302	11·299
	8	12·271	8·871	10·576
	9	11·929	9·195	10·330
$t = 2$				
	7	15·200	6·078	13·597
	8	14·232	7·450	11·569
	9	13·562	8·204	10·842
$t = 3$				
	7	18·104	1·895	19·587
	8	16·462	4·966	14·178
	9	15·358	6·530	12·004

The explanation given for these spurious results should also apply to the polymer analysis: the analysis effectively sees only the early terms in a series of singularities of form (4.3) and, though this is adequate for numerical estimation of $\mu(\theta)$, the more sensitive exponent is hidden beneath the complex structure of the series.

From this analysis, it is apparent that a perturbation expansion approach to the polymer problem, namely the exact calculation (via some diagrammatic method) of terms up to a given order in θ, will not predict the exponent correctly. This point is reinforced by a further Ising model example. Consider the ferromagnetic system in a weak magnetic field H. The partition function is known to be non-singular and yet the terms of a perturbation expansion in H diverge increasingly strongly at the $H=0$ critical temperature. A full resummation of the expansion must lead to the non-singular behaviour (Domb and Hunter 1965), but this is not a result which could be deduced from just a few terms of the expansion. Additional information, in this case the fact that there is no singularity for $H \neq 0$, is required to complete the analysis.

5. Summary

We have used exact enumeration methods to study the behaviour of self-interacting polymer chains and rings on the FCC lattice. The emphasis has been on the asymptotic n-dependence, and extrapolation techniques have been used to examine the limiting behaviour for values of η corresponding to a repulsive interaction between neighbouring units. In several cases the exponent extrapolations do not converge adequately and, though the universality hypothesis remains consistent with the results, it cannot in general be established convincingly. On the basis of the discussion of § 4, the slow convergence of the exponent analyses is not unexpected, nor is it easily overcome.

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Appendix. Partition functions and moments

The partition functions of both chains and rings have the general form (2.1). The coefficients c_{nm} appear in tables A1 and A2; note that the chain coefficients have been divided by 12 (the lattice coordination number) and the ring coefficients by $2n$ (the symmetry number of the corresponding polygon).

In order to list the R and S moments, we rewrite (2.2, 2.3) as

$$M_n^p(\eta) = c_n(\eta)^{-1} \sum_{m \geqslant 0} M_{nm}^p \eta^m$$

with

$$M_{nm}^p = \sum_r r^p c_{nm}(r)$$

for the R moments, etc. The coefficients M_{nm}^2 for the various moments are tabulated in tables A3–5; the values have again been divided by 12 or $2n$.

Table A1. Chain partition function coefficients c_{nm} (/12). For each n the values are given as a sequence of pairs $m:c_{nm}$.

$n=3$							
	0:	47	1:	42	2:	24	3: 4
$n=4$							
	0:	317	1:	376	2:	292	3: 144
	4:	96					
$n=5$							
	0:	2109	1:	3218	2:	2936	3: 2000
	4:	1420	5:	712	6:	296	7: 20
$n=6$							
	0:	13983	1:	25756	2:	28488	3: 21816
	4:	17972	5:	11124	6:	6964	7: 3856
	8:	824	9:	360			
$n=7$							
	0:	92371	1:	199668	2:	253634	3: 231098
	4:	195268	5:	146516	6:	99148	7: 65936
	8:	37108	9:	19336	10:	5132	11: 2464
$n=8$							
	0:	608761	1:	1509368	2:	2167128	3: 2230300
	4:	2074630	5:	1678204	6:	1276332	7: 903760
	8:	593836	9:	389056	10:	221496	11: 92200
	12:	48808	13:	14208			
$n=9$							
	0:	4003587	1:	11197520	2:	17911722	3: 20530626
	4:	20584696	5:	18283276	6:	14876516	7: 11455256
	8:	8145780	9:	5666660	10:	3782448	11: 2332604
	12:	1321632	13:	624100	14:	318832	15: 106784
	16:	5788					

Table A2. Ring partition function coefficients c_{nm} (/2n).

$n=5$							
	0:	0	1:	24	2:	72	3: 72
$n=6$							
	0:	28	1:	6	2:	168	3: 272
	4:	288	5:	192	6:	16	
$n=7$							
	0:	72	1:	360	2:	120	3: 960
	4:	1320	5:	1464	6:	1296	7: 384
	8:	192					
$n=8$							
	0:	363	1:	1176	2:	3102	3: 1776
	4:	5352	5:	7032	6:	7764	7: 8052
	8:	4788	9:	1776	10:	888	
$n=9$							
	0:	1640	1:	6072	2:	12840	3: 22888
	4:	19728	5:	32904	6:	40360	7: 45216
	8:	46896	9:	37632	10:	18816	11: 12288
	12:	4096					
$n=10$							
	0:	8130	1:	32136	2:	68772	3: 116178
	4:	170868	5:	174480	6:	227304	7: 251976
	8:	275568	9:	289176	10:	257208	11: 178224
	12:	99984	13:	63816	14:	25932	15: 1668

Table A2—continued.

$n = 11$							
	0:	40032	1:	170640	2:	403560	3: 664176
	4:	1000608	5:	1305480	6:	1409424	7: 1659816
	8:	1736376	9:	1788576	10:	1837824	11: 1722024
	12:	1381272	13:	953880	14:	552672	15: 382896
	16:	126816	17:	37152			
$n = 12$							
	0:	207423	1:	923028	2:	2303292	3: 4173932
	4:	6102579	5:	8366220	6:	10226534	7: 11090688
	8:	12353616	9:	12649688	10:	12559644	11: 12310452
	12:	11716380	13:	10057224	14:	7833588	15: 5126984
	16:	3530376	17:	2100552	18:	843788	19: 298176
	20:	32784					

Table A3. Chain R moment coefficients M^2_{nm} (/12).

$n = 3$							
	0:	247	1:	122	2:	36	3: 4
$n = 4$							
	0:	2504	1:	2020	2:	1016	3: 324
	4:	148					
$n = 5$							
	0:	22797	1:	25698	2:	17772	3: 8300
	4:	4664	5:	1592	6:	468	7: 24
$n = 6$							
	0:	194240	1:	280924	2:	246144	3: 147740
	4:	95308	5:	45444	6:	21516	7: 9152
	8:	1504	9:	592			
$n = 7$							
	0:	1581763	1:	2793796	2:	2933434	3: 2159394
	4:	1538756	5:	918052	6:	501844	7: 269712
	8:	113292	9:	52296	10:	10996	11: 5032
$n = 8$							
	0:	12466252	1:	26006424	2:	31736596	3: 27364628
	4:	21690904	5:	14843668	6:	9361816	7: 5577332
	8:	2938120	9:	1619768	10:	741176	11: 274840
	12:	124440	13:	31496			
$n = 9$							
	0:	95852463	1:	230595664	2:	320068290	3: 315207014
	4:	274539364	5:	210290280	6:	147320656	7: 97151992
	8:	58385220	9:	34681312	10:	19242276	11: 9936348
	12:	4961752	13:	2059336	14:	890480	15: 254212
	16:	12568					

Table A4. Chain S moment coefficients M^2_{nm} (/12).

$n = 3$							
	0:	41·2500000000	1:	26·0000000000	2:	11·2500000000	3: 1·50000000000
$n = 4$							
	0:	395·440000000	1:	362·720000000	2:	218·560000000	3: 91·5200000000
	4:	48·9600000000					

Table A4—continued.

$n=5$							
0:	3481·91666666	1:	4300·94444444	2:	3228·66666666	3:	1816·55555555
4:	1124·77777777	5:	475·777777777	6:	172·666666666	7:	10·0000000000
$n=6$							
0:	29110·2040816	1:	44876·7346938	2:	41965·3061224	3:	27495·4285714
4:	19586·0408163	5:	10545·8775510	6:	5807·83673469	7:	2844·57142857
8:	550·530612244	9:	220·408163265				
$n=7$							
0:	234358·687500	1:	434132·375000	2:	477047·937500	3:	377350·250000
4:	282389·875000	5:	185086·000000	6:	111107·812500	7:	65990·1250000
8:	33286·3750000	9:	15922·1250000	19:	3861·00000000	11:	1754·75000000
$n=8$							
0:	1834606·41975	1:	3969415·55555	2:	5014703·20987	3:	4549689·18518
4:	3781837·48148	5:	2726828·29629	6:	1848661·03703	7:	1176974·51851
8:	693900·246913	9:	416189·728395	10:	215787·358024	11:	83917·9259259
12:	41527·2098765	13:	11286·9135802				
$n=9$							
0:	14050622·4700	1:	34785317·6000	2:	49610092·4600	3:	50769129·9400
4:	45907899·3600	5:	36741780·8000	6:	26988677·1600	7:	18785775·5200
8:	12084184·9600	9:	7675615·68000	10:	4675112·68000	11:	2663760·92000
12:	1405973·12000	13:	621320·200000	14:	299028·800000	15:	93909·0400000
16:	4919·80000000						

Table A5. Ring S moment coefficients M^2_{nm} $(/2n)$.

$n=5$							
0:	0·00000000000	1:	15·3600000000	2:	45·1200000000	3:	36·4800000000
$n=6$							
0:	25·6666666666	1:	5·50000000000	2:	132·666666666	3:	212·000000000
4:	192·666666666	5:	112·000000000	6:	8·00000000000		
$n=7$							
0:	79·8367346938	1:	380·081632653	2:	120·000000000	3:	896·326530612
4:	1208·81632653	5:	1206·85714285	6:	959·020408163	7:	256·653061224
8:	117·551020408						
$n=8$							
0:	500·062500000	1:	1472·25000000	2:	3726·37500000	3:	1974·37500000
4:	5789·62500000	5:	7376·43750000	6:	7588·12500000	7:	7171·12500000
8:	3928·87500000	9:	1333·87500000	10:	633·750000000		
$n=9$							
0:	2658·37037037	1:	9291·25925925	2:	17870·8148148	3:	30708·7407407
4:	24804·4444444	5:	40145·4814814	6:	47881·7777777	7:	50772·1481481
8:	49014·5185185	9:	36367·7037037	10:	16972·4444444	11:	10434·3703703
12:	3256·88888888						
$n=10$							
0:	15375·1800000	1:	56478·4800000	2:	114695·160000	3:	179026:260000
4:	252991·920000	5:	245298·960000	6:	307975·920000	7:	332227·200000
8:	349223·520000	9:	345570·960000	10:	287866·800000	11:	186922·560000
12:	98673·8400000	13:	59874·6000000	14:	22843·9200000	15:	1417·80000000
$n=11$							
0:	86808·7933884	1:	346048·264462	2:	764446·214876	3:	1197063·27272
4:	1695556·95867	5:	2117606·67768	6:	2188209·91735	7:	2480695·33884
8:	2513508·09917	9:	2512841·85124	10:	2468742·74380	11:	2186056·06611
12:	1656050·57851	13:	1081805·35537	14:	594572·033057	15:	391357·487603
16:	121730·380165	17:	34795·6363636				

Table A5—continued.

$n = 12$							
0:	509164·416666	1:	2122566·58333	2:	4878293·00000	3:	8498685·75000
4:	11847706·8333	5:	15445716·3333	6:	18077035·5833	7:	18823320·7500
8:	20224779·1666	9:	20011931·9166	10:	19295537·0000	11:	18288322·1666
12:	16615085·3333	13:	13565657·3333	14:	10039903·6666	15:	6245775·00000
16:	4124339·50000	17:	2318518·50000	18:	882453·666666	19:	303392·333333
20:	31418·0000000						

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