θ Region of a Polymer Chain

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ABSTRACT: Exact enumeration methods have been used in the study of the self-interacting, self-avoiding lattice walk model of a polymer chain, with particular emphasis on the θ point at which the effects of interaction and volume exclusion are supposed to cancel. θ temperature estimates for short chains computed from the partition function and the moments of the end-point separation have been extrapolated to infinite chain length. The extrapolated results, some of which fail to converge satisfactorily, do not point to the existence of a unique θ point, but suggest a relatively broad range of θ temperatures.

For many years it has been accepted practice to regard the random walk as a useful model of an isolated polymer chain in dilute solution. On account of its Markovian nature this model is readily treated by analytical methods, and easily generalized to allow for various kinds of interaction between neighboring units along the chain.[1] Such a model is obviously oversimplified in that it neglects both the long-range correlations introduced by the requirement that no two chain units can share the same location in space—the excluded volume property, and the interaction between widely separated units along the chain which happen to approach each other in particular spatial configurations.

To facilitate the incorporation of these features into the model the chain is assumed to be embedded in a regular two- or three-dimensional lattice, with each unit occupying a lattice site, and the links between adjacent units corresponding to the bonds between nearest-neighbor sites. The excluded volume property becomes the prohibition against any two chain units occupying the same site. This is the well-known self-avoiding walk problem, which, though practically unassailable by analytical means, has been extensively studied by both Monte Carlo and exact enumeration methods, and a great deal is known about its behavior.[2] The results point to the lattice independence of many of the properties (foremost among them the exponent γ describing the asymptotic length dependence of the mean-square end-point separation: $R_n{}^2 = \langle r^2 \rangle_n \sim n^\gamma$, $n \rightarrow \infty$) for a given lattice dimensionality. Recent Monte Carlo studies[3] indicate that off-lattice walks may show the same behavior (this issue has yet to be finally resolved, see, *e.g.*, ref 4), providing further justification for concentrating on the computationally simpler lattice problem.

The actual interaction between the chain units in solution, presumably of short range only, is represented in this picture by a constant force J which acts only between units lying on adjacent lattice sites, irrespective of their separation measured along the chain, and is otherwise zero. If the force is attractive (J negative) the chain contracts as the temperature is reduced, and we are faced with the possibility of a phase transition between the loosely coiled state and an ordered, tightly coiled configuration (evidence for this will be presented elsewhere). Furthermore, there will be a certain temperature at which the effects of excluded volume and interaction "cancel," and the system appears to be merely a random chain. This temperature has become known as the θ point,[5] though there is no *a priori* reason why each characteristic of the chain (moments of the mean-square end-point separation, moments of gyration, etc.) should not have its own θ temperature, perhaps all lying within a relatively narrow interval, perhaps not. The θ point concept has proved useful in the interpretation of experimental results, for it is only in the absence of long-range correlations that the system is Markovian and amenable to treatment by exact analytic methods.

The self-avoiding walk with interactions has been the subject of only a limited amount of study, both by Monte Carlo methods,[6] and by a preliminary exact enumeration investigation based on very limited data.[7] We have extended considerably the exact enumeration studies, and in this, the first of a series of articles on the subject, report on those results which are related to the θ point concept.

Calculation. The partition function of a chain of $n + 1$ units—*i.e.*, an n-step walk (or chain)—at temperature T is

$$c_n(\theta) = \sum_{m \geq 0} c_{nm} e^{m\theta} \tag{1}$$

where $\theta = -J/k_BT$ (k_B is the Boltzmann constant), and c_{nm} is the number of n-step chains with m nearest-neighbor pairs of units not adjacent along the chain. The upper limit of the summation is the maximum number of pairs which can be formed, and depends both on the lattice type and on n. Once the form of the partition function is known the thermodynamic properties (internal energy, specific heat, entropy) follow by differentiation. For $\theta = 0$, $c_n(\theta)$ reduces to the total number of n-step self-avoiding walks.

The mean-square end-point separation and its higher order moments are defined as

$$R_n{}^p(\theta) = c_n(\theta)^{-1} \sum_{m \geq 0} \sum_r r^p c_{nm}(r) e^{m\theta} \tag{2}$$

where $c_{nm}(r)$ is the number of n-step, m pair chains with end-point separation r. The mean-square radius of gyration and its moments can be defined in a similar manner.

The method of exact enumeration involves the generation of all possible walks for small values of n, the evaluation of the quantities of interest, and finally the extrapolation of the results to $n = \infty$. There has been a certain amount of controversy over the validity of the extrapolation to infinite chains; however the method has proved its reliability in the study of magnetic spin systems,[8] and when used for the ordinary self-avoiding walk problem yields results consistent with Monte Carlo estimates based on much longer walks.[2]

The number of walks grows exponentially with n, and the enumeration of all but the shortest walks must be performed by computer. The problem has been programmed

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(1) P. J. Flory, "Statistical Mechanics of Chain Molecules," Wiley, New York, N. Y., 1969.

(2) C. Domb, *Advan. Chem. Phys.*, **15**, 229 (1969).

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(8) C. Domb, *Advan. Phys.*, **19**, 339 (1970).

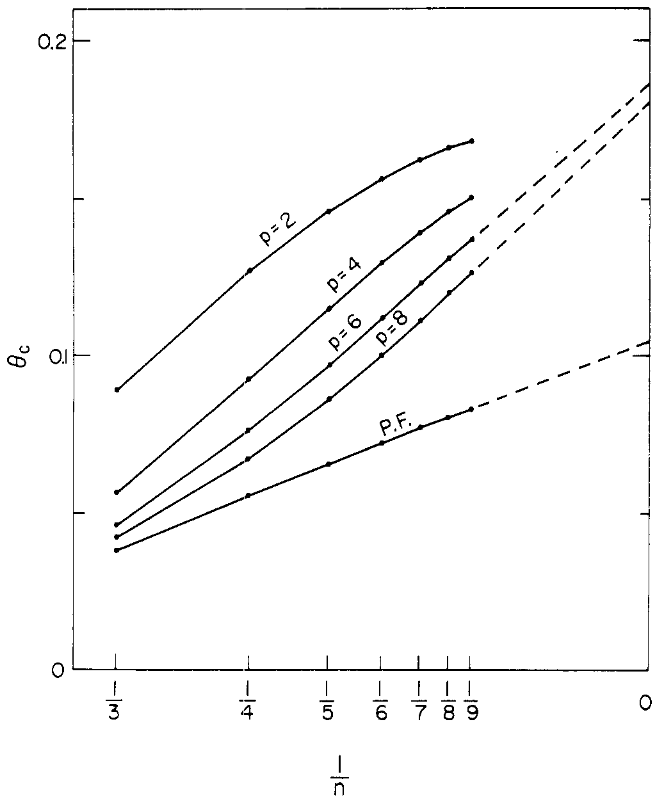

Figure 1. Plots of the θ_c estimates from the endpoint distribution moments and partition function (*i.e.*, the solutions to eq 3 and 4) *vs.* $1/n$. For the $p = 6$ and 8 moments and the partition function the results have been extrapolated linearly to $n = \infty$. In the case of the moments the validity of the extrapolations is uncertain (see Table I and text).

Table I
Extrapolated Estimates of θ_c Obtained from the pth Moment of the End-Point Separation (p = 2, 4, 6, and 8) Using the Neville Table Method

n	$k^a = 0$	1	2	3
		$p = 2$		
4	**0.1271**			
5	**0.1462**	0.2227		
6	**0.1568**	0.2101	0.1851	
7	**0.1630**	0.1998	0.1740	0.1592
8	**0.1666**	0.1919	0.1681	0.1583
9	**0.1687**	0.1858	0.1647	0.1578
		$p = 4$		
4	**0.0923**			
5	**0.1149**	0.2054		
6	0.1296	0.2030	0.1981	
7	0.1394	0.1982	0.1863	0.1706
8	0.1461	0.1933	0.1787	0.1661
9	0.1509	0.1889	0.1734	0.1629
		$p = 6$		
4	0.0760			
5	0.0971	0.1814		
6	0.1122	0.1879	0.2009	
7	0.1232	0.1892	0.1924	0.1811
8	0.1313	0.1883	0.1856	0.1743
9	0.1375	0.1865	0.1801	0.1690
		$p = 8$		
4	0.0675			
5	0.0863	0.1611		
6	0.1005	0.1720	0.1938	
7	0.1116	0.1776	0.1917	0.1890
8	0.1201	0.1802	0.1879	0.1816
9	0.1269	0.1810	0.1837	0.1753

[a] The $k = 0$ column contains the actual values of θ_c and the k = 1, 2, 3 columns contain the extrapolants from the linear, quadratic, and cubic polynomials in $1/n$.

and a complete enumeration of all walks up to $n = 9$ on the face-centered cubic lattice has been undertaken. The task of the program is to compute the numbers $c_{nm}(r)$, or the equivalent for the radius of gyration. (Although there are some 1.7×10^9 nine-step walks, the taking into account of lattice symmetry reduces this enumeration problem considerably.) These numbers are then used in equations of forms (1) and (2) to yield expressions for the thermodynamic quantities, the endpoint distribution, etc., of the n-step chains. Work is currently in progress on extending the study to include other lattices and the complete results will be published later. Here we concentrate on results which bear directly on the θ point.

We define the θ point of a given quantity (*e.g.*, a moment) as that value θ_c of θ for which the quantity has the same value as the random walk with no immediate reversals on the same lattice (*i.e.*, a walk in which self-intersections other than immediate reversals are permitted). The no-reversal random walk generating function is known,[9] and it is a simple matter to compute the moments of the end-point separation $\bar{R}_n^p$. For given n and p, θ_c is then the solution of the equation

$$R_n^p(\theta_c) = \bar{R}_n^p \tag{3}$$

and is readily obtained by standard numerical techniques.

A further estimate of θ_c is the solution of

$$c_n(\theta_c) = q(q-1)^{n-1} = \bar{c}_n \tag{4}$$

where q is the lattice coordination number and $\bar{c}_n$ is, of course, the number of n-step no-reversal walks. The reasoning behind eq 4 is that in the limit $n \rightarrow \infty$, $c_n(\theta_c) \sim \mu(\theta_c)^n$, where, by analogy with the random case, $\mu(\theta)$ is the "effective" coordination number. The limiting form of (4) is then just $\mu(\theta_c) = q - 1$.

Once the θ_c values for the short chains have been computed some method is required for extrapolating to the infinite chain limit. There are a number of well-tested extrapolation techniques in use in other branches of statistical physics—notably in the field of critical phenomena.[10] The simplest technique which can be applied to the polymer problem amounts to a linear extrapolation against $1/n$ of the n-step chain results to the $n = \infty$ limit. The so-called Neville table method, which we shall describe below, is an obvious generalization of this technique. Other methods are also in use (*e.g.*, Padé approximants), but these are generally successful only when data are available for larger n values than is the case here.

Results

Figure 1 shows the values of θ_c obtained by solving eq 3 plotted against $1/n$ for chains of length 3-9 with p = 2, 4, 6, and 8. The θ_c values computed from eq 4 are also shown. In the case of the partition function and the sixth and eighth moments, at first sight it would appear reasonable to extrapolate linearly against $1/n$ to $n = \infty$. For p = 2 and 4 such extrapolation is clearly unwarranted.

A more general means of extrapolation is the Neville table method. First the points are fitted, $k + 1$ at a time, to a kth degree polynomial of the form $a_{k0} + a_{k1}/n + \cdots + a_{kk}/n^k$ (Lagrange interpolation); the coefficient a_{k0} is then the result of extrapolating to $n = \infty$. ($k = 1$ corresponds to the linear extrapolation of Figure 1.) The θ_c es-

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[9] C. Domb and M. E. Fisher, *Proc. Cambridge Phil. Soc.*, **54**, 48 (1958).

[10] D. L. Hunter and G. A. Baker, Jr., *Phys. Rev.*, **B7**, 3346 (1973).

Table II
Extrapolated Estimates of θ_c from the Partition Function

n	$k = 0$	1	2	3
4	0.05565			
5	0.06586	0.1067		
6	0.07249	0.1057	0.1037	
7	0.07713	0.1050	0.1033	0.1029
8	0.08058	0.1047	0.1037	0.1043
9	0.08324	0.1045	0.1040	0.1046

timates obtained in this manner from the moments are displayed in Table I, and those from the partition function in Table II. The $k = 0$ columns contain the actual θ_c values for the chains.

The extrapolated θ_c estimates from the partition function apparently settle down very quickly and suggest a final value $\theta_c = 0.104$. The estimates yielded by the moments, however, are still drifting slowly, and it is only the linear extrapolant which seems to improve with increasing p. The higher order extrapolants for the moments (*i.e.*, the $k = 2$ and 3 columns of Table I) suggest the possibility that the extrapolated θ_c values ought really to increase with p. This would mean that the linear extrapolations for $p = 6$ and perhaps even $p = 8$ in Figure 1 are premature. On the other hand, it must be remembered that higher order extrapolants increasingly reflect the behavior of shorter chains where the end effects are more significant. The net result is that the slow convergence of the extrapolants prevents reliable estimation of θ_c for the infinite chain moments; this is very different from the partition function analysis (Table II) where consistent estimates are obtained for all orders of extrapolation.

It appears likely that the final θ_c estimates will lie within the range approximately 0.15–0.18, which is well separated from that of the partition function. But on the basis of this analysis alone the problem of whether the different moments of the infinite chain have the same θ_c or, if this is not the case, the p dependence of θ_c, cannot be resolved.

These results reflect the obvious. For short chains a quantity such as the end-point distribution function (and its moments) is far more sensitive to a variation in chain length than the thermodynamic quantities. The latter depend only on the total number of nearest-neighbor pairs, and not on the manner in which they are distributed along the chain. The end-point distribution does in a sense reflect the distribution of nearest-neighbor pairs and, consequently, longer chains are needed for the limiting behavior to become apparent.

We conclude with a comparison with θ_c estimates obtained from Monte Carlo studies.[6] The θ_c for the partition function, essentially obtained by fitting the Monte Carlo data to the limiting form of (4), was found to be slightly greater than 0.1, close to our extrapolated estimate of 0.104. The estimate $\theta_c = 0.14$ was obtained from the Monte Carlo data on the second moment of the end-point distribution by searching for that value of θ for which the data best fitted the limiting form of (3); *i.e.*, $R_n^2(\theta_c) \sim n$, where $\gamma = 1 -$ the Markovian value. It could be argued that the Neville table for $p = 2$ is converging to a limit in the vicinity of 0.14, but this is by no means certain.

Summary

The results obtained by the exact enumeration method suggest that there exists an extended temperature interval over which different properties of the model polymer chain adopt the values appropriate to the random, no-reversal chain. However, the analysis is unable to determine whether the different moments of the end-point distribution share the same θ temperature in the infinite chain limit. The apparent lack of a unique θ point (as defined by eq 3 and 4) should not come as a surprise—it would perhaps be more surprising if the cancellation of the effects of excluded volume and attractive interaction on different properties were to occur at exactly the same temperature. Studies of polymer chains on other lattices and, possibly, chains with other kinds of interactions, may well provide further insight into the nature of the θ region.

Acknowledgments. The author is grateful to Dr. J. Mazur for helpful discussion. This work has been supported in part by the B. de Rothschild Foundation.

Thermodynamic Properties of Moderately Concentrated Solutions of Poly(dimethylsiloxane) in *n*-Alkanes

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ABSTRACT: The interaction parameter χ for solutions of poly(dimethylsiloxane) (PDMS) in *n*-alkanes has been determined through osmotic pressure measurements over the concentration range of 5–30 wt %. The free volume theory derived by Delmas and his coworkers fairly well explains the dependence of χ_1, which is the extrapolated value of χ to zero concentration, on temperature and the chain length of solvent. However, the agreement between lower critical solution temperatures estimated by the theory and the observed ones is poor for the solutions of PDMS in comparison with that for the solutions of polyisobutylene in *n*-alkanes. For the solutions of PDMS in *n*-octane and *n*-nonane, the temperature and concentration dependency of χ was examined by the aid of Flory's theory. A method for the derivation of the parameters in his theory was proposed. A good agreement of the theory with the experiment was obtained by the method proposed for the solution of PDMS in *n*-nonane.

Recently, free volume theories of polymer solution thermodynamics have attracted the notice of many investigators, since they semiquantitatively explain various phenomena which have not been interpreted by the traditional theories. Patterson and his coworkers applied Prigogine's theory[2a] to polymer solutions and discussed the lower critical solution temperature.[2b,3] Flory also proposed a free volume theory[4,5] which yields somewhat different

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