The Graph-like State of Matter. 9. Statistical Thermodynamics of Dilute Polymer Solutions†

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ABSTRACT: The pathway to the properties of dilute polymer solutions through the range of two-parameter theories is redirected with the aid of combinatorial algebra. The Fixman perturbational partition function for finite chains is transformed into the convergent classical Gibbs form, thus removing the restriction to the vicinity of the theta state. The Möbius inversion and inclusion/exclusion technique, whose power has recently been emphasised by G.-C. Rota, allows the classical form to be exploited, but work by several mathematicians, physicists, and chemists supplies necessary ingredients. The non-Markovian properties of Pólya lattice walks, a problem of great mathematical beauty, enter the physical theory only at the very end and in simplified form. The parameters in the partition function are calibrated from scattering measurements and related to theories, initiated by Dvoretsky and Erdös, of self-intersecting walks. The central limit theorem of probability theory here provides the key. Finally, the theories and experimental results on *covalent* cyclization, especially by Allen, Edwards, Walsh, and Burgess, are integrated with the graph-theoretical analysis of *temporary* contact-pair formation. Briefly, then, for the purposes of physical as distinct from the mathematical theory, the so-called excluded volume can be "re-included" in an almost Markovian theory by the combinatorial principle of inclusion/exclusion. Further developments are likely to center on integrating into dilute solution theory, the analysis of the nature of contact potentials, pursued successfully in semidilute solutions by Huggins.

(I) Introduction

Huggins[1] and Flory[2] offered their pioneering lattice-type theory of the thermodynamics of semidilute polymer solutions in 1941. Ever since, it has seemed important to extend the range of thermodynamic theories to the very dilute concentration range, where coils are well separated from each other. The so-called two-parameter theories[3] evolved ways of dealing with configurational properties of isolated chains in solvents good, bad, or indifferent. However, a usable partition function for such systems, which would allow configurational properties to be integrated with other equilibrium properties in a general framework of statistical mechanics, has as far as we are aware eluded theoreticians.

This conundrum has been dominated by the excluded volume problem, which Flory[4] put on the map in the early days of polymer science. Between 1954 and 1960, progress was reviewed by polymer scientists on three occasions (Wall and Hiller,[5] Hermans,[6] and Casassa[7]; see also Stockmayer[8]). Apart from citing these reviews in 1963, Hammersley[9] mentioned that scores of papers had already been devoted to the excluded volume, and he added some qualitative theorems on the underlying model of nonintersecting (Pólya) walks on lattice graphs, such as that of the cubic or hypercubic lattice.

The problem is elusive, because of the non-Markovian behavior of such excursions. At the Science Research Council Rencontre[10] on Applications of Combinatorial Mathematics at Aberdeen in 1975, Paul Erdös stressed the great beauty of the mathematical problem, toward whose solution several theoretical physicists had meanwhile made important contributions, for instance Edwards,[11] Domb,[12] and de Gennes.[13]

As regards thermodynamic aspects, however, the perturbation treatment of volume exclusion in polymer chains, inaugurated by Teramoto[14] and by Fixman,[15] and extended by Yamakawa and Tanaka,[16] led to divergence troubles (see IIb below) of a series of terms with alternating signs.

The structure of these series, examined by heuristic methods in a previous paper of this series, leads to the conclusion that an application of combinatorial methods based on the principle of inclusion/exclusion, or, more generally, on Möbius inversion, might usefully be applied. Moreover, some recent mathematical literature underlines the timeliness of exploring such combinatorial patterns. Gian-Carlo Rota, in particular, has been publishing a series of papers, often with distinguished co-authors, which fully justifies its running title: On the Foundations of Combinatorial Theory (some of the results are found in his recent book[17]). It is significant that the series started[18] with the sentence: "One of the most useful principles of enumeration in discrete probability and combinatorial theory is the celebrated *principle of inclusion–exclusion.*" The principle is then set in the wide framework of the inversion of the Möbius function of a partially ordered set as a fundamental principle of enumeration (see also ref. 19). Like the later parts of Rota's series, his first paper is no doubt a potential gold mine for theoretical physicists and chemists. Little more than just the basic notions of these combinatorial techniques, however, are required to make the modest progress in the context of solution thermodynamics which is recorded here, namely (a) to dispose unambiguously of the question, repeatedly examined from different viewpoints,[20–24] of the source of the divergence difficulties, and more importantly (b) to arrive at a usable partition function for an isolated chain in solution. Indeed, once this is done, it is not hard to disguise the connection of the problem with the classical Möbius[25] function, by expressing the few lines of theory simply as an exercise in ordinary matrix inversion. While the combinatorics required is simple, recent work by mathematicians, physicists, and chemists has proved very beneficial in the practical implementation of our program. First, this program involved the shifting of the main burden of the physical theory from the non-Markovian to Markovian aspects of lattice walks, where the work initiated by Dvoretsky and Erdös[26] on self-intersecting walks, and its recent development by Spitzer[27] and Flatto,[28] has proved invaluable (see section IVc below). Second, the theoretical calculations and chemical experiments by Edwards, Allen, and co-workers[29] have provided us very useful ingredients to reinforce the present work (see section IV4).

(II) Combinatorial Relation between the Gibbs and Fixman Forms of the Partition Function

The schematization of a polymer chain as a string of n beads, with pairs of beads in mutual contact to form contact pairs, is illustrated in Figure 1. The counting of the configurations available to a chain will be facilitated by the familiar

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† Affectionately dedicated to Professor M. L. Huggins, on the occasion of his 80th birthday.

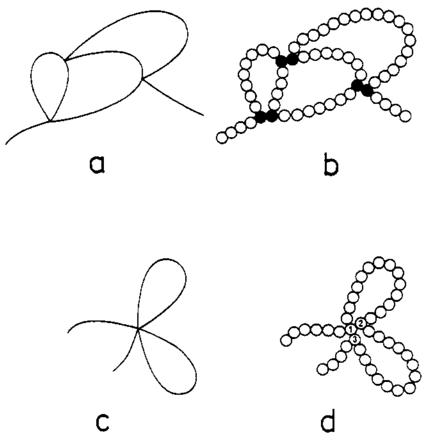

Figure 1. The chain graph (a) corresponds to bead model (b) for a polymer chain, which here features three contact pairs (black beads). The chain graph (c) illustrates a multiple (here, a triple) intersection, corresponding to bead model (d). The walker returns twice to the bead marked 1 to form the two contact pairs (2,1) and (3,1), in accordance with variant (ii) of section IVb. In variant (iii), there would be a third contact pair (2,3).

one-to-one correspondence between chain configurations and lattice walks (Figure 2). One end bead of the chain is placed at the origin of, say, the diamond lattice, and successive beads then mark other points on the lattice visited by the "walker".

Not surprisingly, the enumeration of configurations of a chain with a *given* m contact pairs is easier, if no bias is allowed for or against the presence of additional contact pairs. Thus various theories, e.g., self-consistent field calculations[30] or the Wang–Uhlenbeck theorem as generalized by Fixman,[15] lead naturally to the number (or mean-square dimensions) of chains which have at least m, say, contact pairs but may have more, with an overcounting procedure explained as follows. The theories lead in the first place to the number N_{mj} of configurations which share at least a specified set, labeled as the jth, of m contact pairs, but may have more. Summation over all j then arrives at a number N_m which heavily overcounts any given configuration: instead of being counted once, it is counted $\binom{\psi}{m}$ times, where ψ is the number of contact pairs of the given configuration. The overcount is corrected subsequently by the terms in an alternating series (see below).

The canonical Gibbs form of the partition function arises naturally as a function of the number n_m of configurations which have *exactly* m contact pairs, where each set of exactly m contact pairs is included once in the count. The connection between N_{mj} and n_m is furnished by a simple combinatorial lemma, which reads (for a maximum number $P(n)$ of contact pairs):

$$N_m = \sum_j N_{mj} = \binom{m}{m} n_m + \binom{m+1}{m} n_{m+1} + \ldots + \binom{P(n)}{m} n_{P(n)} \qquad (1)$$

whose proof follows immediately from the definitions. Of course, if the set of configurations is replaced by any set of objects, and the set of contact pairs possessed by a configuration is replaced by any set of properties, the combinatorial interpretation of eq 1 is suitably generalized.

The canonical configurational partition function Z for a chain of n units (e.g., on a lattice) is written thus:

$$Z(n) = \sum_{m=0}^{P(n)} n_m(n) e^{-mE/kT} \qquad (2)$$

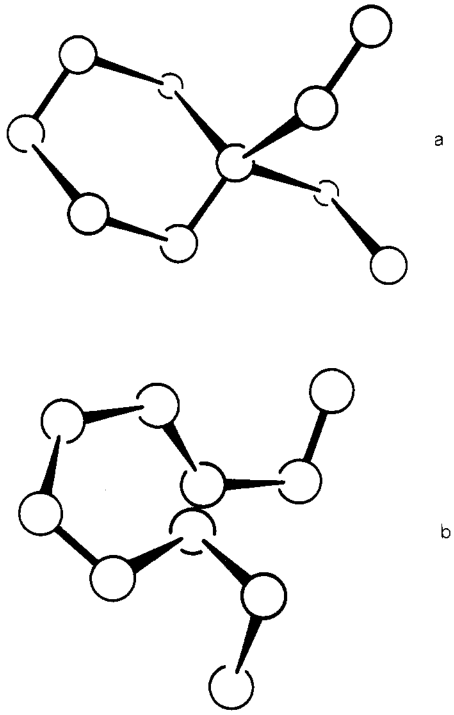

Figure 2. The transformation of an intersection in part of a walk (on a diamond lattice, not shown) in the diagram a into a contact pair in diagram b by moving the two congruent beads apart to form a contact pair in violation of the lattice condition.

where $n_m(n)$ is the number (or measure) of distinct chain configurations with exactly m contact pairs and E is the energy of a contact pair.

Write

$$Z(n) = \sum_{m=0} n_m(n)[1 - (1 - e^{-E/kT})]^m \qquad (3)$$

and expand in powers of $(1 - \exp(-E/kT))$. Then

$$Z(n) = \sum[-(1 - e^{-E/kT})]^m \left[\binom{m}{m} n_m + \binom{m+1}{m} n_{m+1} + \ldots + \binom{P(n)}{m} n_{P(n)} \right] \qquad (4)$$

$$Z(n) = \sum_{m=0}^{P(n)} [-(1 - e^{-E/kT})]^m \sum_j N_{mj}(n) \qquad (5)$$

where the passage from (4) to (5) applies the lemma. Any partition function such as (2) is algebraically equivalent to a form such as (5) with alternating signs. For small E, and defining

$$\beta \equiv E/kT \qquad (6)$$

we discover the discrete form of the partition function of Fixman[15]

$$Z(n) = \sum_{m=0}^{P(n)} (-\beta)^m \sum_j N_{mj} \qquad (7)$$

In order to put the present work in perspective with the long history of the two-parameter theories, the comparison of the two forms (eq 2 and 7) of the partition function is pursued under a number of headings: (2a) The passage from discrete to continuum models, which have been preferred in the past; (2b) the problem of divergence of the partition function in the continuum models based on eq 7; (2c) the comparison of perturbation solutions with exact solutions and the appropriate reference state about which perturbations are considered.

(a) From Discrete to Continuum Models. The discrete lattice model leads directly by algebra from the canonical form (eq 2) to the Fixman form (eq 7), viz., to an expansion in powers of a *small* variable β, with coefficients which count the number of relevant configurations. The classical expansion in terms of Boltzmann weights and degeneracies (eq 2) is abandoned in (5) in favor of a Taylor expansion in the variable $-(1 - \exp(-E/kT))$, denoted as χ by Fixman[15] and by Yamakawa.[3] We saw that in the discrete lattice treatment χ is replaced (eq 5) by β in the perturbation approximation ($E \ll kT$). However, in the continuum treatment, the summation over N_{mj} in (5) or (7) is replaced by integration. This integration involves $3m$ space coordinates and changes the status of the dimensionless variable β to the volume β^*, i.e., the statistical excluded volume parameter or binary cluster integral. The most straightforward way of making this transition from the simple discrete model to the physically less appropriate and inevitably more complicated continuum approximation uses the following steps:

$$\sum_{m=0}^{P(n)} [-(1 - e^{-E/kT})]^m \sum_j N_{mj}(n) / \sum_m \sum_j N_{mj}(n)$$

$$\approx \sum_{m=0}^{P(n)} \sum_j \int \cdots \int N_{mj}^*(n; r_1, r_2, \ldots, r_m) \times [-(1 - e^{-E(r)/kT})]^m \left(\prod_{i=1}^{m} 4\pi r_i^{\,2} \right) \mathrm{d}r \qquad (8)$$

where N_{mj}^* on the right is the normalized probability density of configurations for which the jth set of m specified contacts lies in the range r_1 to $r_1 + \mathrm{d}r_1$, r_2 to $r_2 + \mathrm{d}r_2, \ldots$, etc. We assume a pairwise additive radially symmetric potential function $E(r)$, sufficiently sharply peaked near the origin $r = 0$ and identical for each contact pair so that for the values of the integrand which contribute significantly, N_{mj}^* can be taken as the constant value $N_{mj}^*(n;\ r_1 = 0,\ r_2 = 0, \ldots, r_m = 0)$. Factoring this out of the integral gives the normalized continuum Fixman[15] form of the partition function:

$$Z^* = Z / \sum_m \sum_j N_{mj} \approx \sum_{m=0}^{P(n)} (-\beta^*)^m \times \sum_j N_{mj}^*(n; r_1 = 0, r_2 = 0, \ldots, r_m = 0) \qquad (9)$$

where the binary cluster integral has been evaluated as

$$\beta^* = \int_0^\infty (1 - e^{-E(r)/kT}) 4\pi r^2 \, \mathrm{d}r \qquad (10)$$

In passing from (8) to (9), we have accepted the necessary factorization into m equal integrals but have avoided a delta-function notation.

(b) The Divergence Problem. The discrete formulation shows clearly the source of the trouble. During the algebraic transformation, from eq 2 to 5, the coefficients are regrouped and weighted with additional large coefficients (eq 4) which amount to a heavy alternate overcounting and subsequent overcorrection (alternating signs in eq 5). By such means we can easily render the convergent series

$$1 + \tfrac{1}{2} + \tfrac{1}{4} + \tfrac{1}{8} \ldots$$

divergent, say:

$$1 + 10(\tfrac{1}{2}) - 10 + 100(\tfrac{1}{4}) - 100 + 1000(\tfrac{1}{8}) - 1000 \ldots$$

Although Z for finite chains, with the finite number $P(n)$ of possible contact pairs, exists, it is not in practice easily amenable to the calculation of statistical averages. The perturbation theory took:

$$N_m \sim A_m n^{m/2} \qquad (11)$$

The factor $n^{1/2}$ could then be combined with β^* and some other constants to produce a variable

$$z = (3/2\pi b^2)^{3/2} \beta^* n^{1/2} \qquad (12)$$

On this postulate, Z^* becomes a power series with alternating signs and rapidly increasing coefficients A_m in z. It is now well known that in reality A_m does not become independent of n and that several of the A_m (e.g., A_1, A_2) diverge as $n \to \infty$. Accordingly, the series expansion of Z^* in powers of z is not an asymptotic expansion[31] for the partition function of a long polymer chain. It is undefined (meaningless) in the limit $n \to \infty$. Oono[23] remarked that interchange of the limits $z \to 0$ and $n \to \infty$ is not necessarily allowed.

If the configurational expansion ratio α^2 is found by expanding the ratio of the two appropriate formal power series as a new power series in z:

$$\alpha^2 = \frac{1}{nb^2} \frac{\sum_m (-\beta^*)^m \sum_j N_{mj}^* \overline{R}_m^{\,2}}{\sum_m (-\beta^*)^m \sum_j N_{mj}^*} = 1 + c_1 z + c_2 z^2 + \ldots \qquad (13)$$

where $\overline{R}_m^{\,2}$ is defined formally in eq 28, the heuristic result is probably much happier. Edwards[21] claimed that this series in $c_m z^m$ for α^2 was indeed an asymptotic series for $n \to \infty$ but that its higher terms were of little use.

Aronowitz and Eichinger[20] thought that divergence of the partition function was traceable to a different cause from that suggested above, namely from the inclusion in the count of configurations of multiple contacts to a given bead, and specifically to multiple contacts between given pairs of beads. However, Gordon and Tutte[32] showed how these terms are eliminated from the count in the Petrie matrix formalism, simply by restricting the count to staggered Petrie matrices, as defined by them. This is essential since the Wang–Uhlenbeck[15] theorem is not applicable to graphs with more than one link between a given contact pair, so that we must not allow the graph-theoretical formalism to include such cases. Even when these configurations were specifically excluded, it was deduced[20] from computer results for short chains ($n \sim 6$) that the radius of convergence of the partition function was $O(n^{-1/2})$, i.e., it goes to 0 as $n \to \infty$.

(c) Reference States: Perturbation and Exact Solution. Fixman's perturbation model was based on a chain composed of Gaussian subchains. Since the junction points of subchains are prevented from coinciding in the space in which the chain is embedded, the reference state obeyed this "excluded volume" prescription; perturbation then gave access to information on contributions from configurations violating this prescription through the effects of any single contact pair, of any two contact pairs, or three, but higher terms in the perturbation series were too complicated to evaluate. (The partition function was also asymptotically nonexistent, see IIb above.) The difficulty resided in the non-Markovian behavior of the reference chain without contacts, a model closely similar to that of nonintersecting walks on a lattice.

(III) Random Walks on Lattice Graphs

We turn to the lattice walk variant in preference to the Gaussian subchain variant of the excluded volume problem, a choice now often made. When non-Markovian behavior of a statistical model causes trouble, it often pays[33] to concentrate on Markovian aspects of the same model, in the hope that the major features of the physical situation can be mapped into these easily handled aspects. Completely random lattice walks do have self-intersections. Instead of "forbidding" these, it is fruitful to interpret a self-intersection of a lattice walk as a contact pair, as illustrated by passing from Figure 2a to Figure 2b. An intersection of the formal walk on the lattice graph is then interpreted as a local violation of the lattice condition when the graph is embedded in an Euclidian space of three dimensions. (The contact pair in Figure 2b may look unrealistic, because in solution a pair of polymer units in contact will be separated by a distance *larger* than a chemical bond, represented by the lattice spacing. It is nevertheless drawn much shorter, purely for convenience of illustration. What matters is that, at the cost of an energetic penalty, each intersection in the lattice walk is mapped one-to-one into a local violation of the lattice condition, see section X.)

It is shown in the next section that the number of intersections in a three-dimensional lattice walk of n steps tends to normality and behaves in Markovian fashion. The mean number $\mu_0(n)$ of the Gaussian distribution of the number of intersections will represent our reference state applicable to the theta state. At the cost of separating the physical theory from the beautiful mathematical problem of nonintersecting random walks, the old reference state, clearly implicit in the classical perturbation treatment of a chain without contact pairs, moves out of the range of states which contribute significantly to the thermodynamics.

(IV) The Theory of Transient Random Lattice Walks

(a) Local Constraints on Randomness. The requisite theory for the Markovian aspects of transient lattice walks (in which the walker visits a given point at most a finite number of times as $n \to \infty$) is unaffected by the restriction that he may never backtrack immediately along a step just completed. This restriction turns the truly random walk on the diamond lattice, with four choices at each step, into the three-choice variant corresponding to constant (tetrahedral) bond angles. Walks on graphs of lattices of >2 dimensions are transient and those for ≤2 dimensions are recurrent.[34]

(b) Counting of Contact Pairs. The number of self-intersections on the walker's path could be dissected into contact *pairs* in three ways, viz., by charging a fixed energy penalty for: (i) each lattice point visited more than once by the walker, or (ii) each return visit to any point already visited, or (iii) each of the $i(i-1)/2$ pairs of interactions implied in each i-fold self-intersection.

In the limit $n \to \infty$ of the Markovian theory, the three variants merely produce calculable changes in the value of the parameter ρ introduced below, which is of no consequence in testing the theory. In the experimental range of chain lengths, differences could be more substantial but are probably largely covered by the non-Markovian correction made in section VIII. Intersections of multiplicity greater than 4 are very rare. Beads 2 and 3 in Figure 1d illustrate the notion that each pair of beads represented in the multiple intersection need not behave like a contact in three-dimensional space, so that variant (iii) overestimates the contact number and energy penalty. Variant (ii) is adopted as the most reasonable, leading to a maximum number of $n-1$ contacts in a chain of length n (an exceedingly unlikely event).

(c) The Central Limit Theorem. The set of random lattice walks of $2n$ steps is, in an obvious sense, merely the Cartesian square of the set of such walks of n steps, namely by starting a second walk of n steps at the end point of a first walk of n steps. The self-intersections can be classified into those involving only the first n steps, those involving only the second n steps, and finally intersections of the second n-step walk with the first. It follows from recent mathematical theory (see eq 15, 17, and 20 below) that for walks on three-dimensional lattice graphs the last category, the cross-intersections between the first half and the second half of a walk, can be neglected asymptotically for long walks. This is equivalent to Markovian behavior and the applicability of the central limit theorem for the distribution of the number of intersections, which then takes the form

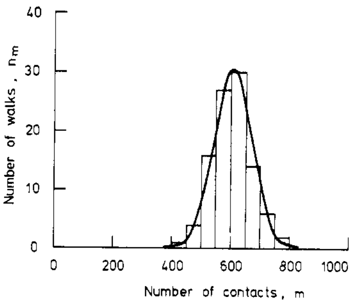

Figure 3. Computer-generated histogram for 100 three-choice random walks of length 5000 steps on a diamond lattice and optimum fit to a Gaussian probability density.

$$n_m(n) \sim (\text{constant})e^{-[(m-\mu_0(n))^2/2\sigma_0{}^2(n)]} \qquad (14)$$

with the mean and standard deviation becoming proportional to the number n of steps, i.e., the chain length:

$$\mu_0(n) = \rho n + o(n) \qquad (15)$$

where the constant ρ is identified in eq 19 below, and

$$\sigma_0{}^2(n) = c_\sigma n + o(n) \qquad (16)$$

where c_σ is a constant for a given lattice graph.

A typical display of the approach to Gaussian form (eq 14) is shown by the computer-generated histogram in Figure 3 for 100 walks of length 5×10^3 on the diamond lattice. Figure 4 presents conventional type plots to estimate the constants μ_0 and $\sigma_0{}^2$ by extrapolation of $n \to \infty$ for the diamond and cubic lattices.

For a rigorous justification we use the notation and results in the recent paper by Flatto,[28] embodying work acknowledged to earlier workers. The range R_n of a walk of n steps is the number of distinct points visited. This concept was initiated in the seminal paper by Dvoretsky and Erdös.[26] From our method of counting (variant (ii) above), we have for the number of intersections:

$$m = n - R_n + 1 \qquad (17)$$

Spitzer et al.[27] showed that for transient walks

$$\lim_{n\to\infty} R_n/n = \epsilon \qquad \text{(almost surely)} \qquad (18)$$

where ϵ is called the escape probability for the given lattice graph.

Accordingly

$$\lim_{n\to\infty} m/n = 1 - \epsilon \equiv \rho \qquad \text{(almost surely)} \qquad (19)$$

where ρ is the probability of at least one return to any given point previously visited already (no matter how often). Flatto[28] remarks the implication

$$\lim_{n\to\infty} E(R_n)/n = \epsilon \qquad (20)$$

and accordingly, using eq 17 we recover (15).

The following interpretation is directly obvious: the mean number of contacts approaches asymptotically the number of steps n, times the probability that the walker returns at least once more to any given visited point. But from the last equation the applicability of the central limit theorem follows, leading to the Gaussian form of eq 14 for the density distribution of m about μ_0.

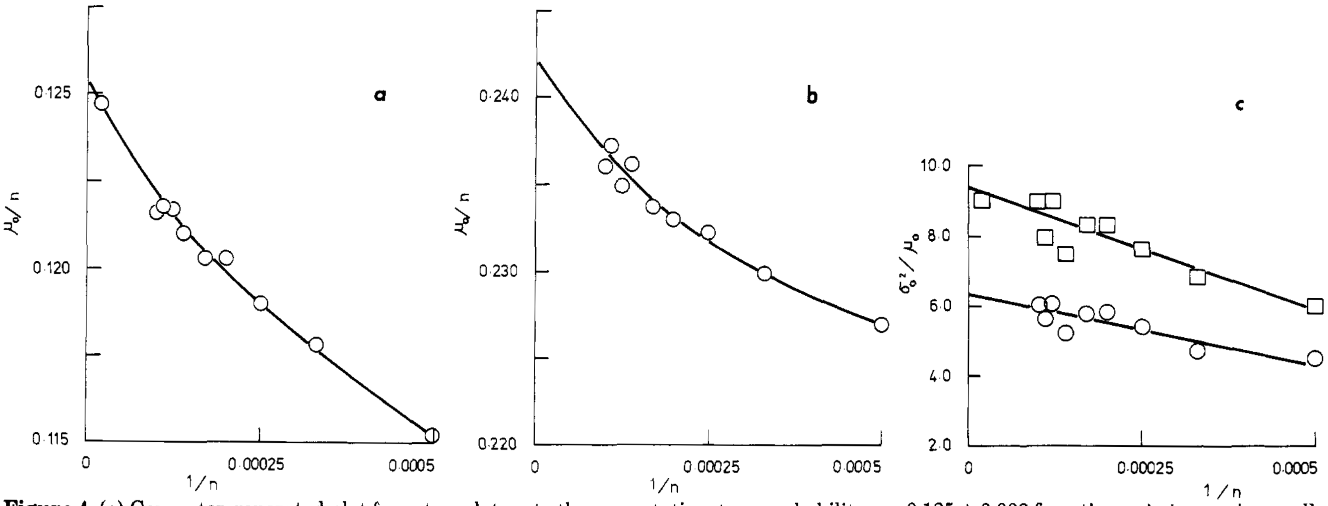

Figure 4. (a) Computer-generated plot for extrapolation to the asymptotic return probability $\rho = 0.125 \pm 0.003$ for a three-choice random walk on the diamond lattice as the number of steps $n \to \infty$. The expectation μ_0 of the Gaussian (cf. Figure 3) is seen to be rather slow to approach the asymptotic form of eq 21. (b) Same as a, but for four-choice cubic lattice (bond angle of 90°). (c) Extrapolation plot ratio of variance to mean for three-choice random walks on diamond (top plot) and four-choice cubic lattice (bottom plot). The evident correlation of scatter in the two plots is an artifact due to their sharing a common seed for the pseudo-random-number generator.

(V) Statistical Averages in Dilute Polymer Solution

In order to generalize the treatment given in section II for partition functions to the case of the calculation of physical averages, we write eq 1 in matrix form. All matrices will be implied to be of order P, where P, the maximum number of contact pairs contemplated, may now be taken as $n - 1$ (see section IVb).

In matrix form, eq 1 reads

$$\mathbf{N} = [P]\mathbf{n} \qquad (21)$$

with the vectors

$$\mathbf{N}^{\mathrm{T}} \equiv [N_0, N_1, N_2, \ldots] \qquad (22)$$

$$\mathbf{n}^{\mathrm{T}} \equiv [n_0, n_1, n_2, \ldots] \qquad (23)$$

(where T means transposition), and the matrix:

$$[P] \equiv \begin{bmatrix} \binom{0}{0} & \binom{1}{0} & \binom{2}{0} & \binom{3}{0} & \cdots \\ 0 & \binom{1}{1} & \binom{2}{1} & \binom{3}{1} & \cdots \\ 0 & 0 & \binom{2}{2} & \binom{3}{2} & \cdots \\ 0 & 0 & 0 & \binom{3}{3} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \equiv \begin{bmatrix} 1 & 1 & 1 & 1 & \cdots \\ 0 & 1 & 2 & 3 & \cdots \\ 0 & 0 & 1 & 3 & \cdots \\ 0 & 0 & 0 & 1 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \qquad (24)$$

Now Pascal's triangle has the following pretty matrix inversion property:

$$[P]^{-1} \equiv \begin{bmatrix} \binom{0}{0} & \binom{1}{0} & \binom{2}{0} & \binom{3}{0} & \cdots \\ 0 & \binom{1}{1} & \binom{2}{1} & \binom{3}{1} & \cdots \\ 0 & 0 & \binom{2}{2} & \binom{3}{2} & \cdots \\ 0 & 0 & 0 & \binom{3}{3} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix}^{-1} = \begin{bmatrix} +\binom{0}{0} & -\binom{1}{0} & +\binom{2}{0} & -\binom{3}{0} & +\cdots \\ 0 & +\binom{1}{1} & -\binom{2}{1} & +\binom{3}{1} & -\cdots \\ 0 & 0 & +\binom{2}{2} & -\binom{3}{2} & +\cdots \\ 0 & 0 & 0 & +\binom{3}{3} & -\cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix} \qquad (25)$$

This solves the problem of finding n in terms of N:

$$\mathbf{n} = [P]^{-1}\mathbf{N} \qquad (26)$$

The first of the equations summarized in (26), for n_0 in terms $\mathbf{N}$, is precisely the equation which expresses the principle of inclusion and exclusion, which is thus generalized in (26) to the Möbius inversion for our problem (see section I). If r_m denotes a physical property for chains with precisely m contact pairs, then that property is found for a dilute solution thus:

$$r = \sum_m n_m r_m e^{-\beta m} \Big/ \sum_m n_m e^{-\beta m} \qquad (27)$$

The property of greatest interest is probably the mean-square radius, say $\bar{r}_m{}^2$. Since n_m is known to be asymptotically

Gaussian (eq 14), and β is a parameter to be adjusted, all is available on the right of (27), except how $\bar{r}_m{}^2$ varies with m. The same Möbius inversion procedure is again useful. We define a mean-square radius $\overline{R}_m{}^2$ which is related to $\bar{r}_m{}^2$ in the same way as N_m is related to n_m and

$$N_m\overline{R}_m{}^2 \equiv \sum_j N_{mj}\overline{R}_{mj}{}^2 \tag{28}$$

where j labels the jth way of choosing m contact pairs among the n beads of a chain. $\overline{R}_{mj}{}^2$ is the mean square radius of lattice walks which have at least this given set of m intersections but may have more, just as N_{mj} is the number of such walks. Among the four sets of quantities n_m, $\bar{r}_m{}^2$, N_m, $\overline{R}_m{}^2$, it turns out that n_m and $\overline{R}_m{}^2$ are the ones readily accessible. While we have no direct approach to $\bar{r}_m{}^2$, of which the special case $\bar{r}_0{}^2$ represents the classical excluded volume problem, we shall present six methods for evaluating $\overline{R}_m{}^2$, four from recent work in the literature. These six methods amply agree within the limits required for rationalizing data on the light scattering of dilute polymer solutions, or their thermodynamic properties in general, using the standard statistical mechanics of eq 27. Define the diagonal matrices

$$[\overline{R}^2] = \mathrm{diag}\{\overline{R}_0{}^2, \overline{R}_1{}^2, \ldots\} \tag{29}$$

and

$$[\bar{r}^2] = \mathrm{diag}\{r_0{}^2, r_1{}^2, \ldots\} \tag{30}$$

Then $N_m\overline{R}_m{}^2$ (cf. eq 28) is the mth component of the vector $[\overline{R}^2]\mathbf{N}$, and, from its definition, we use the same combinatorial principles as underly eq 21, to transform as follows (cf. eq 44 below):

$$[\overline{R}^2]\mathbf{N} = [P][\bar{r}^2]\mathbf{n} \tag{31}$$

so that the problem of finding $\bar{r}_m{}^2$ is solved with the aid of (21):

$$[\bar{r}^2]\mathbf{n} = [P]^{-1}[\overline{R}^2][P]\mathbf{n} \tag{32}$$

or in component form:

$$\bar{r}_m{}^2 = \frac{1}{n_m}\sum_{i=m}^{n-1}\binom{i}{i-m}(-1)^{m+i}\,\overline{R}_i{}^2\sum_{j=1}^{n-1}\binom{j}{j-i}n_j \tag{33}$$

Asymptotically, as $n \to \infty$, the behavior of this violently oscillating series is undefined just like (7). But in applications to physical measurements of eq 27, this misbehavior is damped out by the Gaussian weights n_m and above the theta point in addition by the Boltzmann weights exp $-\beta m$. Defining the vector

$$\mathbf{B}^{\mathrm{T}} = \{e^{-0\beta}, e^{-1\beta}, e^{-2\beta}, \ldots\} \tag{34}$$

we may write eq 27 for the mean-square radius in matrix form

$$\bar{r}^2 = \mathbf{B}^{\mathrm{T}}[\bar{r}^2]\mathbf{n}/\mathbf{B}^{\mathrm{T}}\mathbf{n} = \mathbf{B}^{\mathrm{T}}[P]^{-1}[\overline{R}^2][P]\mathbf{n}/\mathbf{B}^{\mathrm{T}}\mathbf{n} \tag{35}$$

where the last equality has used eq 31, which solves our problem (cf. section VII)

(VI) Six Approaches to the Estimation of $\overline{R}_m{}^2$

For random lattice walks, the mean-square radius is asymptotically proportional to the mean-square end-to-end distance, which in general is easier to calculate. Expansion ratios of walks in the presence of an intersegment potential for root-mean-square end-to-end distances and for mean-square radii are taken in much of the literature as asymptotically equal for practical purposes; the point is discussed in refs 3 and 35. We shall make this approximation in what follows by putting the mean-square radius $\bar{r}_m{}^2$ equal to one-sixth of the end-to-end distance.

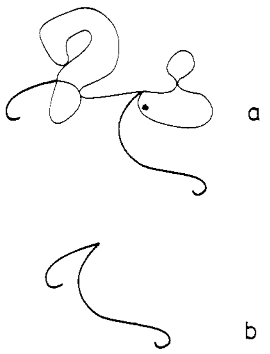

Figure 5. Contraction of chain graph (a), known to have $m = 5$ specified contacts, to its two end pieces, joined to form the chain graph (b). For convenience, no other contacts have been shown besides the five which are supposed to be specified.

(1) The mean-square radius $\overline{R}_m{}^2$ may be estimated by the following lower bound for the corresponding mean-square end-to-end distance. Consider the graph of a lattice walk known to have *at least* a given set of m contacts (Figure 5a). Submit to *elementary contraction* all lines (bonds) except those in the two terminal sections of the chain (Figure 5b). (Elementary contraction of a line means its deletion, the two points on which it was incident being identified.) The contracted graph 3 of Figure 5b represents an unrestricted random lattice walk, whose mean-square length is asymptotically equal to νb^2, where ν is the number of its bonds and b the bond length. It remains to find the average over ν for all choices of the $2m$ beads out of n (the chain length) for making m contacts. If these beads are chosen *at random* along the chain then the mean number of bonds of the contracted chain, comprising the terminal sections of the original uncontracted chain, is given thus:

$$\langle\nu\rangle = n/(m + 1/2) \qquad (m = 1, 2, \ldots) \tag{36}$$

$$\langle\nu\rangle = n/(m + 1) \qquad (\text{trivially, for } m = 0) \tag{37}$$

Since the mean value μ_0 of the asymptotically Gaussian m distribution is large (eq 15), we may smooth (36) and (37) by taking (37) to be valid for all m, so that

$$\overline{R}_m{}^2 = b^2\nu/6 = b^2n/6(m + 1) \tag{38}$$

We have good reason to guess that $\overline{R}_m{}^2 > b^2n/6(m + 1)$ since the elementary contraction process is bound to reduce the value of $\overline{R}_m{}^2$. In greater physical detail, the $2m$ beads for pairing into m contacts should not have been picked at random along the chain graph, but each such set chosen should be weighted by the number of configurational microstates it represents, i.e., the number of distinct lattice walks it can be mapped into. Since intuitively these weights favor more extended chains, the conclusion that for large n

$$\overline{R}_m{}^2 \geqslant b^2n/6(m + 1) \tag{39}$$

is a strong conjecture. Note that the solution is graph theoretical (one-dimensional) and leans on the dimensionality of the embedding space only through the first equality of (38) which is true for random walks embedded in spaces of any number of dimensions. The next three estimates will lead to the equality in (39).

(2) The second method even disconnects the graph into (zero-dimensional) point segments moving under a potential which leads to Gaussian segment–density distribution. Unfortunately it is difficult to obtain results for $m > 1$, but $\overline{R}_1{}^2 = b^2n/12$ in agreement with (38) is readily obtained. This is, of course, an application of a general method due to Flory and explained in his first textbook.[4]

To derive this expression we make use of the notation and equation of Tompa.[36] His eq 4.132 relates the free-energy change when two molecules approach each other until the distances between their centers of mass is a:

$$\Delta F(a) = kTX(\exp(-3a^2/4\bar{r}^2))$$

with X given by $2(\alpha^2 - 1)$ (his eq 4.137). Putting $a = 0$ and identifying the two segment distributions reduces both the number of segments and the symmetry number by a factor 2, giving simply

$$\Delta F = 2kT(\alpha^2 - 1) \qquad (40)$$

which is thus the configurational free energy of an isolated polymer chain, to an approximation to be refined later.

Now writing the mean-square radius as a ratio of the power series in the parameter z (eq 13) and truncating after the first term in the numerator and denominator leads to

$$\alpha^2 = (1 + b_1z)/(1 + a_1z) \equiv (1 + b_1z)/Z \qquad (41)$$

With the denominator the configurational partition function Z, we attempt to reconstruct eq 40. The appropriate partition function is given by (40), strictly only for α^2 independent of T, thus:

$$Z \approx 1 - 2(\alpha^2 - 1) \qquad (42)$$

and we require to find the constant ratio b_1/a_1 which satisfies (41) and (42), as $z \to 0$. This ratio is simply seen to be ½. But we have:

$$\bar{R}_1{}^2 = \frac{b^2n}{6}\frac{b_1}{a_1}$$

as a special case of eq 43, explained below, so that $\bar{R}_1{}^2 = b^2n/12$ in agreement with (38) for $m = 1$.

(3) The third method is based on a preceding paper in this series.[24] An explicit but heuristic evaluation of the coefficients a_m and b_m (eq 13) of the Fixman formula for α^2 was derived from simple combinatorial arguments. We thus find from eq 34 and 35 in that paper that $b_m/a_m = 1/(m + 1)$, so that

$$\bar{R}_m{}^2 = \bar{R}_0{}^2b_m/a_m = b^2n/6(m + 1) \qquad (43)$$

(cf. eq 39). Both b_m and a_m were[24] heuristically "pre-averaged" values. Individually, the b_m and a_m values were unrealistic as approximations because their *leading terms* disappeared in the course of pre-averaging. Nevertheless, the ratio b_m/a_m is probably quite realistic, since re-expansion (eq 13) of the ratio of the two series as a new power series gave the first three coefficients jointly in rather fair agreement with literature evaluations of the same perturbation series by heuristic methods based on the continuum approach. Equation 43 is *not*, however, merely a perturbation result. Since the potential (Boltzmann) weights have cancelled from the ratio, its validity as a fair estimate is not restricted to the close vicinity of the theta state. Equation 43 is obtained for random walks in any number of dimensions from the "pre-averaging" of powers of the Petrie intersection determinant I practiced in the original paper. The coefficient a_m is proportional to $I^{(d/2)+1}$ and b_m to $I^{d/2}$, where d is the dimensionality of the embedding space of the chain graph. Thus b_m/a_m is invariant under changes in d, the solution being essentially graph theoretical.

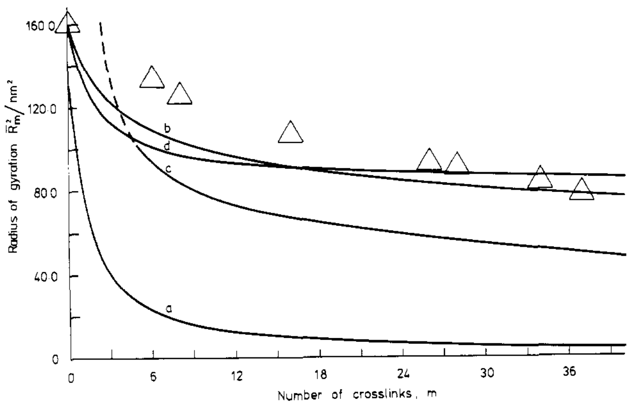

Figure 6. Effect of random cyclization on chain dimensions. Triangles, experimental points of Allen et al.;[29] for curves a, b, c, d see text.

(4) There is little doubt that the fourth method, being based on the self-consistent field perturbation method, and within a three-dimensional continuum framework, is the one that will most commend itself to physicists. We refer to the elegant theory for estimating $\bar{R}_m{}^2$ by Edwards et al.[30] and their subsequent *experimental* testing of the theory.[29] They were concerned with the mean-square radii of homodisperse chains "cyclized" by inserting at random m permanent covalent bonds into the chain of n repeat units. We now see how this procedure makes accessible to experimental investigation the same mean-square radius $\bar{R}_m{}^2$ which features in principle (cf. method 3) as the ratio of the mth terms in the numerator and denominator respectively of Fixman's perturbation series for α^2, eq 13. To show this as clearly as possible, we solve the component form of eq 31 and use (21) to obtain

$$\bar{R}_m{}^2 = \frac{n_m\bar{r}_m{}^2 + n_{m+1}\bar{r}_{m+1}{}^2\binom{m+1}{1} + n_{m+2}\bar{r}_{m+2}{}^2\binom{m+2}{2} + \ldots}{n_m + n_{m+1}\binom{m+1}{1} + n_{m+2}\binom{m+2}{2} + \ldots} \qquad (44)$$

In the "cyclized ensemble" of chains, each chain has at least m permanent (covalent) contacts and may have any number ($i \leqslant n - m - 1$) of temporary contact pairs. We neglect any differences in the conformations accessible to a chain of $m + 1$ contacts resulting from the nature (i.e., permanent or temporary) of a given contact pair. A permanent contact nevertheless represents a different (packet of) quantum state(s) from a temporary one. Then eq 44 follows from the first axiom of statistical mechanics: *each quantum state is equally weighted.* Accordingly, a given conformation of $m + 1$ contacts, of which exactly i are temporary, has a weight of $\binom{m+1}{i}$, the number of distinct ways in which the temporary ones can be chosen.

The insertion of m covalent links to cyclize a linear chain will be strictly "at random" when eq 44 applies. If many active units are first built into the chain at random, and $2m$ of them, chosen at random, subsequently paired to produce the cycles according to the dynamics of intramolecular collisions, this random pairing will produce a cyclized ensemble with $\bar{R}_m{}^2$ given very nearly by (44); the approximation would seem to be exact, if the permanency of pairing arose instantaneously in every chain, at a time when it happened to have $\geqslant m$ temporary contact pairs. Edwards et al[29,30] found from their SCF theory:

$$\bar{R}_m{}^2 \sim n/(m + 1) \qquad (45)$$

(5) We turn to the method of finding $\bar{R}_m{}^2$ by experiment. The only data available were obtained by Edwards et al.[29] from polystyrene containing a proportion (ca. 4%) of chloromethylated units of which a selection were covalently paired by diisocyanate. Their data of $\bar{R}_m{}^2$ vs. m from light scattering are shown in Figure 6. The plot according to eq 45 (Figure 6,

plot a) strongly deviates from the experimental data in the direction of the inequality in eq 39. The empirical equation

$$\overline{R}_m{}^2 \sim n/(m+1)^{1/5} \tag{46}$$

is seen to fit the data quite reasonably (plot b). Edwards and co-workers were rightly led to improve the SCF model equation (eq 45). They did so by introduction of parameters depending on physical refinements such as the finite thickness of the chain and the length of the covalent chains used to link the members of each contact pair; this corrected theory leads to plot c.

(6) Our sixth method of approach shows, however, that a good part of the required correction results (plot d) already from carrying out the purely graph-theoretical calculation (cf. methods 6-1 and 6-2 above) more accurately by refining inequality 39, without attending to effects thus such as chain thickness, arising from a three-dimensional space in which the chain can be embedded.

Plot d was calculated from Monte-Carlo computations of the mean-square radius of long chains (10^9) constrained to have at least m contacts pre-selected at random. These calculations will be described and analyzed in greater detail elsewhere. The following description aims to show why plot d may safely be accepted as an estimate for $\overline{R}_m{}^2$.

It is well known that for tree-like molecules $\overline{R}_0{}^2$ is proportional to the mean length (number of bonds) taken over all paths in the molecule, there being a unique path from any bead i to any bead j. A computer approach to $\overline{R}_m{}^2$ of randomly cyclized chains modifies this method of evaluation by three approximations: (a) A sample of 100 cyclized molecules of $n = 10^9$ beads is constructed by selecting m contact pairs at random among the n beads to simulate the pre-assigned chemical cross-links of Allen et al.[29] For each such molecule $\overline{R}_0{}^2$ is constructed as follows and the results are averaged. (b) Instead of finding the mean of all $n(n-1)/2$ paths in each n-bead molecule, the mean is estimated from a small sample of D ($\approx$1000) suitably weighted paths between randomly chosen pairs (i,j) of beads. The formula employed:

$$\overline{R}_0{}^2 = \frac{1}{nD}\sum_{k=1}^{D}(n-l_k)l_k$$

is valid for a linear uncyclized chain,[37] when l_k is the length of the unique path linking the kth pair of beads chosen. (c) Since in the presence of cycles the path may not be unique, a unique path is *constructed* for the kth selected pair (i,j) say, as follows. A continuous path is traced along the beads from i in a direction chosen at random at the start, until the first bead i' is encountered which is a member of a contact pair. Similarly a path is traced from j to the first encountered j' belonging to a contact pair. The shortest path from i' to j' is found by a minimum-path algorithm.[38] The length l_k is then taken as that of the path i–i'–j'–j (provided no bead on that path occurs more than once; otherwise the attempt is rejected).

(VII) Möbius Inversion from "Cyclized" to Uncyclized (Linear) Chains

We recall our strategy of estimating $\overline{R}_m{}^2$ for insertion in (29) to form the matrix $[\overline{R}^2]$, and hence calculate via eq 35 the mean-square radius $\overline{r}^2$ of long, isolated polymer chains in a solvent, when the interactions are characterized by the potential β (cf. eq 34). A diversity of crude theories have led to $\overline{R}_m{}^2$ being proportional to $1/(m+1)$ (see eq 38, 43, and 45), while experiments or refined theory led to results more closely fitted by proportionality of $\overline{R}_m{}^2$ to some function like $1/(m+1)^{1/5}$ (eq 46), as shown in plots b, c, and a of Figure 6. It turns out below that even such substantial variations in the functional form of $\overline{R}_m{}^2$ lead, via the Möbius-type inversion formulas of eq 35, to changes in $\overline{r}^2$ which are negligible, when reasonable adjustments have been made in the parameter(s) involved.

Equation 43 obtained as a first approximation to $\overline{R}_m{}^2$ by four different approaches above gives a specially simple functional form for $\overline{r}_m{}^2$. Inserting eq 43 in 29 and eq 39 in 35, we obtain (using eq 24 and 25) in component form.

$$\alpha^2 \equiv 6\overline{r}^2/b^2n = \sum_{m=0} n_m(n)\sum_{t=0}^{m}\sum_{p=0}^{t} e^{-p\beta} \times \binom{m}{t}\binom{t}{p}(-1)^{t-p}\frac{1}{t+1}\Big/\sum_{m=0}^{\infty} n_m(n)e^{-\beta m} \tag{47}$$

The summations over t and p are found combinatorially by the trinomial expansion:

$$(e^{-\beta}-1+x^{-1})^m \equiv \sum_{t=0}^{m}\sum_{p=0}^{t}\frac{m!}{p!(t-p)!(m-t)!}e^{-p\beta}(-1)^{t-p}x^{-m+t} \tag{48}$$

Multiply both sides by x^m, collect factorials into binomial coefficients, and integrate over x from 0 to 1:

$$\sum_{t=0}^{m}\sum_{p=0}^{t} e^{-p\beta}\binom{m}{t}\binom{t}{p}(-1)^{t-p}\frac{1}{t+1} = \int_0^1 (1-x(1-e^{-\beta}))^m\,\mathrm{d}x = (1-e^{-(m+1)\beta})/(1-e^{-\beta})(m+1) \tag{49}$$

Substituting this result in (47) yields

$$\alpha^2 = \sum_{m=0}^{\infty} n_m \frac{1+e^{-\beta}+e^{-2\beta}+\ldots+e^{-m\beta}}{m+1}\Big/\sum_{m=0}^{\infty} n_m e^{-\beta m} \tag{50}$$

Note that for the normal distribution n_m (eq 14), with asymptotic behavior according to (15) and (16), the ith moment of the distribution becomes asymptotically equal to $\mu_0{}^i$. Expanding the exponentials in the numerator and denominator of (49) produces series expansions in terms of these moments which are easily summed, so that

$$\alpha^2 = (e^{\mu_0(n)\beta}-1)/\mu_0(n)\beta \qquad (n \to \infty) \tag{51}$$
$$= (e^{\rho n\beta}-1)/\rho n\beta$$

Before discussing this solution we generalize it thus:

$$\alpha^2 = \sum_{m=0}^{\infty} n_m(n)\sum_{t=0}^{m}\sum_{p=0}^{t} e^{-p\beta}\binom{m}{t}\binom{t}{p} \times (-1)^{t-p}\frac{1}{(t+1)^q}\Big/\sum_{m=0}^{\infty} n_m(n)e^{-\beta m} \tag{52}$$

to introduce an empirical exponent, such as $q = 1/5$ in eq 48, in place of $q = 1$ in eq 43 and 47 (and cf. Figure 6d). The summations over t and p are now reducible to a single integral as an excellent approximation. In (48), substitute $\exp(\Theta)$ for x, multiply both sides by $(\Theta^{q-1}e^{-(m+1)\Theta}/\Gamma(q)$, and integrate over Θ from 0 to infinity:

$$\sum_{t=0}^{m}\sum_{p=0}^{t} e^{-p\beta}\binom{m}{t}\binom{t}{p}(-1)^{t-p}\frac{1}{(t+1)^q} = \frac{1}{\Gamma(q)}\int_0^{\infty} e^{-\Theta}\,[1-(1-e^{-\beta})e^{-\Theta}]^m\Theta^{q-1}\,\mathrm{d}\Theta, \qquad 0 < q < 1 \tag{53}$$

When the right-hand side of eq 53 is substituted in the numerator of eq 51, α^2 is still easily evaluated by computer for all interesting values of q in the stated range and for sufficiently large n to ensure that eq 14 is acceptable.

Equation 51 shows at a glance that the elusive beauty of the mathematical Pólya walk problem remains inviolate. The limit $\beta \to \infty$ purports to cause an absurd exponential explosion of the chain diameter. This is understandable, because in this limit we are overstraining the central limit theorem underlying eq 14. For $\beta \to \infty$, eq 51 does indeed reduce to the expansion ratio for the chains in the fraction n_0 (cf. eq 50) devoid of contacts. But the central limit results of eq 14, while correctly indicating that n_0 is an inconceivably small number (cf. Figure 3), do not tell us correctly *how* this quantity tends to zero. This point is covered by (central limit) theorem 3, p 443, in Renyi's textbook.[39]

The theorem does, however, deal very precisely with the statistics of chains which have numbers of contacts close to the peak value μ_0. Applications of eq 51 to scattering data cover a range of μ values, i.e., mean number of contacts, which differ (see section IX) by less that $\pm\sigma_0$ from the value μ_0 in the reference state at T_Θ. Equation 51 does, therefore, provide a solution to the physical problem.

For the asymptotic contact number distribution (eq 14), the configurational partition function (eq 2) becomes

$$Z = e^{-\mu_0\beta+0.5\sigma_0{}^2\beta^2}\left[(2\pi\sigma_0{}^2)^{-1/2}\sum_{m=0}^{\infty} e^{-(m-(\mu_0-\beta\sigma_0{}^2))^2/2\sigma_0{}^2}\right] \tag{54}$$

For

$$\beta < (\mu_0 - 4\sigma_0)/\sigma_0{}^2 \tag{55}$$

an inequality satisfied for all but rather short chains, Z reduces as an excellent approximation to

$$Z \approx e^{-\mu_0\beta+0.5\sigma_0{}^2\beta^2} \tag{56}$$

The configurational enthalpy relative to the theta state is found by inserting (56) in (27) with $r_m = mE$ to be

$$\Delta H_{\text{conf}} = \mu_0 E - (\sigma_0{}^2E^2/RT) \tag{57}$$

The potential of mean force is expanded in a Taylor series:

$$\beta kT \equiv c_1[(T - T_\Theta)/T_\Theta] + c_2[(T - T_\Theta)/T_\Theta]^2 + \ldots \tag{58}$$

This mirrors the usual treatment[3] of the cluster integral β^*, to which β is proportional near T_Θ, if it is small and sharply peaked. Note that ΔH_{conf} according to (57) is an extensive property, proportional (eq 15 and 16) to chain length n, as befits the Markovian model, whose limits have now been reached.

(VIII) The Non-Markovian Element

An isolated lattice violation will incur a *small* energy penalty, since it can be accommodated by small rotations of bonds in a cycle away from their energy minima (cf. Figure 2). When a large number of lattice violations occur in the neighborhood of a point in the three-dimensional embedding space, β for each violation may become appreciable. We postulate that β is proportional to the average polymer concentration $\bar{c}$ in the coil volume. The a posteriori nature of the postulated adjustment in β, and the crude average procedure it implies, are encouraged by the sharpness of the Gaussian probability distribution for the number m of contacts, which is displayed inside the summation in the partition function of eq 56. Putting $c_2 = 0$ in (58) the postulate may be written:

$$c_1 = kb^3\bar{c} \tag{59}$$

where the proportionality constant k has dimensions of energy. The average concentration $\bar{c}$ is found by the familiar approximation:

$$\bar{c} = n/\alpha^3(\bar{r}^2)^{3/2} = 3^{3/2}/\alpha^3 n^{1/2} b^3 \tag{60}$$

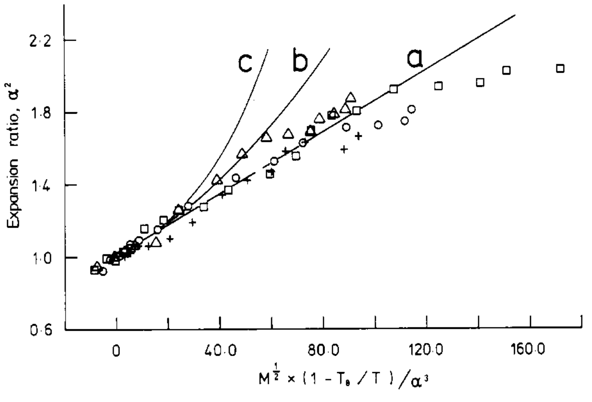

Figure 7. α^2 as a function of $M^{1/2}(1 - T_\Theta/T)/\alpha^3$. Curves a, b, and c represent eq 61, 51, and 52 ($q = 1/5$), respectively, with β given by eq 58 with $C_2 = 0$ and C_1 adjusted to the initial slope of the Berry data. The samples are polystyrenes[41] of molecular weights 0.622×10^6 (in decalin-4, +), 1.05×10^6 (in decalin-2, △), 1.56×10^6 (in decalin-1, 2, ○), 4.4×10^6 (in decalin 2, □). For further details of solvents see ref 41.

Expanding (51) and truncating to

$$\alpha^2 \approx 1 + {}^1\!/_2\mu_0\beta = 1 + {}^1\!/_2\rho n\beta \tag{61}$$

(cf. eq 15) we substitute (58), truncated at the linear term, and use (59) and (60) to find

$$\alpha^5 - \alpha^3 = (3^{3/2}/2)k\rho n^{1/2}(T - T_\Theta)/kTT_\Theta \tag{62}$$

This is precisely Flory's very successful equation,[40] but for the interpretation of the constants. In this graph-like state treatment, we have not dissociated the chain into point segments so as to create osmotic forces which notionally balance the elastic forces in the connected chain, nor, of course, have we estimated the proportionality constant k.

(IX) Discussion

The re-casting of the dilute solution model with the help of Möbius inversion has achieved the first purpose, to derive eq 62, long known to serve experimental scattering data well, in a form directly linked to a convergent partition function. In fact, eq 61 shows that the expansion ratio is governed by $\mu_0\beta$, which also completely determines the partition function Z, eq 56, as T_Θ is approached ($\beta \to 0$). At temperatures removed from T_Θ, we also need the small term $\sigma_0{}^2\beta^2/2$ in Z, but this is merely $(\mu_0\beta)^2\cdot(\sigma_0{}^2/2\mu_0{}^2)$, where the factor $(\mu_0\beta)^2$ is again found from scattering measurements (eq 61), while the small factor $(\sigma_0{}^2/2\mu_0{}^2)$ can be estimated from the statistics of lattice walks (Figures 4c and 4a,b). Of course, the equations derived are rather simple: the configurational enthalpy (eq 57) is almost exactly the energy E per contact times the mean number μ_0 of contacts per chain at T_Θ, with a small correction for the variance to console us.

The second purpose of re-casting stems from the hope that a good foundation for so naive a theory should point the way to further refinements. (For a review of recent approaches see, for example, ref 41.) Which of the several truncated series entering jointly into these foundations will bear the addition of a further term, without doing violence to statistical significance, that is often the question facing the refiner of a theory. It is from this viewpoint that we fit once again the well-known scattering data of Berry[42] on polystyrene/decalin. We emphasize that our motive is not to improve upon the fit of these data in comparison with classical variants, most of which fit more than adequately in relation to the inevitable experimental error.

Figure 7 shows a plot, suggested by Berry, of α^2 against a quantity proportional to the "potential" β, assumed to be given by eq 58 with $c_2 = 0$, plus eq 59 and 60. Thus the Flory equation becomes (eq 61) a straight line (marked a). Plot b represents eq 51 in place of (61), and plot c represents eq 52,

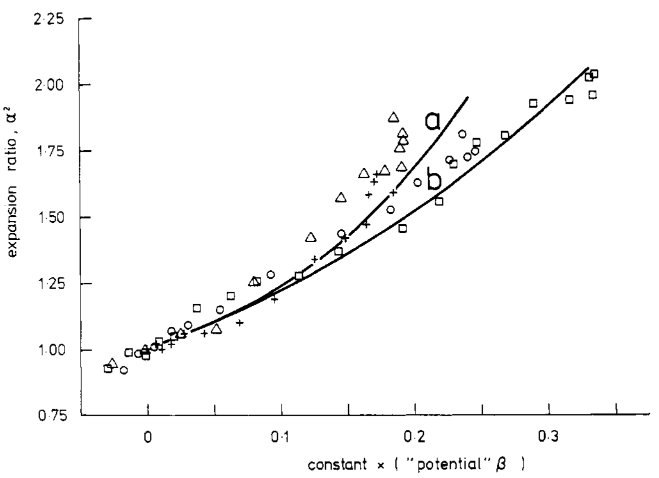

Figure 8. α^2 plotted against the "potential" β. Curves a and b represent eq 52 and 51, respectively, with β given by eq 58 ($C_2/C_1 = -1.4$). Polymer samples are identified in Figure 7.

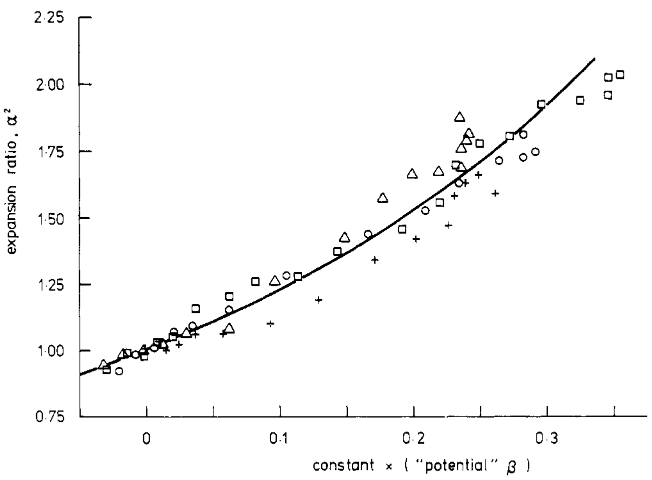

Figure 9. α^2 as a function of the "potential" β. The curve represents eq 51 with β given by eq 58 ($C_2/C_1 = -1.3$) and containing stiff-chain correction factors (see Figure 10).

with $q = 1/5$ as suggested by eq 46. All three plots are adjusted to the same initial slope at T_Θ, the point (0,1), and fit equally well over a range of between 10 and 30 °C around T_Θ, depending on molecular weight. This range of validity would exceed the legitimate aspirations of a perturbation, but these are not merely perturbation theories. The elegant theory of Flory,[8,40] plot a, fits much better than b, and c fits less well still, though it seemed the best bet from the viewpoint of our input into the theory (Figure 6). It is, however, unsafe to conclude that physical factors neglected in deriving (52), or the special case (51), dictate the truncation of these series at their linear terms, as tentatively practiced in eq 61.

The data points at high molecular weights do not fit any of the three plots at high temperatures. This may reflect corresponding-state effects which foreshadow the approach of the Rowlinson[43,44] (LCST) point $T_\Theta{}'$. It is reasonable to model such an effect by inclusion of the square term shown in eq 58, so that the present theory is well adapted to testing this conjecture. Introducing the resulting square term in (62), this generalized Flory-type equation can readily fit the Berry data, which amounts to straightening out the curvature apparent in the trend of the experimental points in Figure 7. The optimal ratio of c_2/c_1 would be ca. −0.94, leading to $T_\Theta{}' = 320$ °C (neglecting any cubic or higher terms in (58)!). We prefer to show the fittings in Figure 8 of the data to the untruncated versions of our theory, i.e., eq 52–53 to give plot a and eq 51 to give plot b. These were produced by adjustment in the parameter c_1, plot a to attempt the best fit of all the data and b to fit specifically the highest molecular weight (squares). The ratio c_2/c_1 for both plots was taken as −1.4, leading to $T_\Theta{}' = 221$ °C.[51]

(1) The Finite-Chain Effect. The deviations in Figure 8 are noticeably systematic, reflecting the molecular weights of the samples. The theory is now sufficiently refined to take into account the lack of attainment of asymptotic statistics, viz., the finite-chain effect. The rather slow convergence is apparent in the scales along the $(1/n)$ axes of Figures 4a and 4b, where the resultant finite-chain effect on μ_0 (cf. eq 61) has the right sign to reduce the scatter of the data in Figure 8 but is still quite insufficient in magnitude. However, Figure 4 is based on flexible chains with fixed bond angles, without allowance for short-range interactions which stiffen the chain. Pending the necessary computation, we here (Figure 9) allow for this stiffening, which reduces the factor ρ in eq 62 in terms of shortening all the chains by a constant factor (ca 200), see Figure 10. The fit in Figure 9 is everywhere within the experimental error inevitably contained even in Berry's data,[42] nor are deviations noticeably systematic. Accordingly, for the moment our theory grinds to a halt. The parameter ρ, a fundamental quantity introduced by Pólya into the theory of random walks, does now appear to be well adapted to model effects of chain stiffness and the finite-chain effects in polymer science.

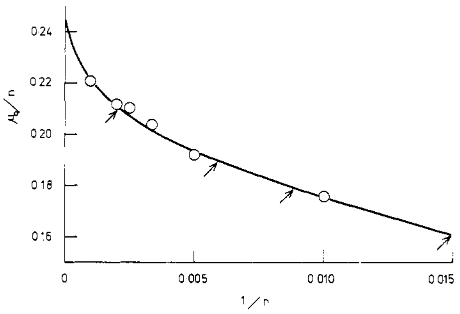

Figure 10. Figure 4b extended to include shorter lattice walks. Arrows indicate tentative μ_0 values to correct eq 51 for chain stiffness, as applied in Figure 9.

(X) Conclusions

(a) The Physical Assumptions Reviewed. The simplifications made for arriving at a partition function, consistent with scattering measurements, are of little significance. The concept of lattice violation, crudely schematized in Figure 2, needs no refinement, when we look back on the use made of it. We could equally well follow the conventional strict lattice structure, excluding intersections by an infinite potential, and placing instead our small penalty $\exp(-\beta)$ upon nearest-neighbor contacts on the lattice. In that case (a) Markovian behavior, and the Gaussian distribution of the number n_m of these contacts is still valid. Such walks on graphs of three-dimensional lattices are a fortiori transient; the central limit theorem applies a fortiori, too. (b) The only other part of the statistical theory to check is the behavior of $\overline{R}_m{}^2$. The introduction of contact pairs between nearest neighbors on the lattice, rather than between intersections, does not affect the functional form of $\overline{R}_m{}^2$ enough to upset the final results, since we saw that the change from the form $\overline{R}_m{}^2 \propto (m+1)^{-1}$ to $\overline{R}_m{}^2 \propto (m+1)^{-1/5}$ leaves the fit to the data little affected (cf. the correction for *long* cross-links by Edwards et al.[29]).

The values of β deduced from the fits in Figures 7–9 are small, viz., $\beta \equiv E/kT < 0.1$. Also the average number $\mu_0 - \mu$ of contacts lost by chain expansion is small, in the range from 2 to 20, and always $<\sigma_0$. This makes the approximation $\bar{R}_m{}^2$ = (end-to-end vector)^2/6 reasonable throughout the temperature range. These assertions are checked as follows: from (61) we find $\beta = 2(\alpha^2 - 1)/\mu_0$ and from (54) $\mu_0 - \mu = \beta\sigma_0{}^2$. The appropriate values of μ_0 and $\sigma_0{}^2$ are clear from Figures 3, 4, and 10 and of α^2 from Figures 7–9.

(b) Relation to the Virial Expansion. We believe the right approach to connect dilute and semidilute regimes was offered by Stockmayer and co-workers[45] through what has been called the bridging theory.[46] The present work was in large measure motivated by the obvious need to formulate a partition function for the statistical fraction of isolated chains, which features in applications of the bridging theory to phase equilibria, so as to free ourselves from the piecemeal ascent through the virial series. It is hoped to extend the present work to improvements in the bridging theory and to a better formulation of the virial series which, in principle, that theory already contains. The whole shape of our present theory in the sub-T_Θ range (cf. Figure 9), and its relation to the so-called collapse transition, is postponed to a future report. Beyond that, further developments are likely to center on integrating into dilute solution theory the analysis of the nature of contact potentials, pursued successfully in semidilute solutions by Huggins.[47]

(c). Mathematical Postcript. The Markovian theory has enabled us to operate directly in a conceptual three-dimensional embedding space. In contrast, the renormalization group approach perturbs a four-dimensional model and then descends to three dimensions by a long extrapolation. Flatto's work is concerned to explore extensions even down to two dimensions. He proves that for such (*recurrent*) random walks of n steps the number of points visited at least once, and at most p times, has variance, not of order n as for transient walks, but of order $n^2 \log \log n/\log^5 n$ for all p. In these circumstances, the central limit theorem is unlikely to be helpful for graphs of two-dimensional lattices.

The matrix algebra of eq 25–33 implements the inversion from the Möbius function to the Riemann function[18,19] for the set of contact pairs of a chain graph, partially ordered by containment of subsets. Containment of subgraphs was the partial ordering relation used recently to rationalize molecular additivity schemes by Möbius inversion.[48] That work, like the present, centered on eliminating troubles due to the omission of terms by truncation or otherwise. More sophisticated partial orderings have been exploited elsewhere in statistical mechanics, e.g., by Nettleton and Green.[49] In polymer science, probably the first use of Möbius inversion was made by Menefee and Peticolas.[50]

A glance at Rota's work on cultivating anew the modern extensions of the Möbius function of 1837, or at Flatto's review and extension of random-walk theory, shows that the present work exploits only the most elementary results. The cost to physical theory in general of the not infrequent neglect of, or delay in, applying the work of pure mathematicians and statisticians, should cause concern.

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References and Notes

(1) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N.Y. Acad. Sci.*, **41**, 1 (1942); *J. Am. Chem. Soc.*, **64**, 1712 (1942).

(2) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(3) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971.

(4) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.

(5) E. T. Wall and L. A. Hiller, *Annu. Rev. Phys. Chem.*, **5**, 267 (1954).

(6) J. J. Hermans, *Annu. Rev. Phys. Chem.*, **8**, 179 (1957).

(7) E. F. Casassa, *Annu. Rev. Phys. Chem.*, **11**, 477 (1960).

(8) W. H. Stockmayer, *Makromol. Chem.*, **35**, 54 (1960).

(9) J. M. Hammersley, *Sankhya, Indian J. Stat. A*, **25**, 29, 269 (1963).

(10) M. Gordon and H. N. V. Temperley, *Chem. Br.*, **12**, 51 (1976).

(11) S. F. Edwards, *Proc. Phys. Soc., London*, **85**, 613 (1965).

(12) C. Domb, *J. Chem. Phys.*, **38**, 2957 (1963).

(13) P. G. de Gennes, *Phys. Lett. A*, **38**, 339 (1972).

(14) E. Teramoto, *Busseiron Kenkyu*, **39**, 1 (1951); **40**, 18 (1951).

(15) M. Fixman, *J. Chem. Phys.*, **23**, 1656 (1955).

(16) H. Yamakawa and G. Tanaka, *J. Chem. Phys.*, **47**, 3991 (1967).

(17) G.-C. Rota, "Finite Operator Calculus", Academic Press, New York, N.Y., 1975.

(18) G.-C. Rota, *Z. Wahrscheinlichkeitstheorie*, **2**, 340 (1964).

(19) C. Berge, "Principle of Combinatorics", Academic Press, New York, N.Y., 1971.

(20) S. Aronowitz and B. E. Eichinger, *Macromolecules*, **9**, 377 (1976).

(21) S. F. Edwards, *J. Phys. A: Math., Nucl. Gen.*, **8**, 1171 (1975).

(22) C. Domb and G. S. Joyce, *J. Phys. Chem.*, **5**, 956 (1972).

(23) Y. Oono, *J. Phys. Soc. Jpn.*, **39**, 25 (1975), *ibid.*, **41**, 787 (1976).

(24) M. Gordon, S. B. Ross-Murphy, and H. Suzuki, Abstracts of the 23rd Meeting of the Society of Polymer Science, Japan, Vol. 2, 1974, p 362; *Eur. Polym. J.*, **12**, 733 (1976).

(25) A. F. Möbius, *J. Reine Angew. Math.*, **9**, 105 (1832).

(26) A. Dvoretsky and P. Erdös, Proceedings of the 2nd Berkeley Symposium on Stochastic Processes, University of California, Press, Berkeley, Calif., 1950.

(27) F. Spitzer, "Principles of Random Walk", Van Nostrand, Princeton, N.J., 1964.

(28) L. Flatto, *Ann. Prob.*, **4**, 229 (1976).

(29) G. Allen, J. Burgess, S. F. Edwards, and D. J. Walsh, *Proc. R. Soc. London, Ser. A*, **334**, 453, 465, 477 (1973).

(30) S. F. Edwards and K. F. Freed, *J. Phys. C*, **3**, 739, 750, 760 (1970).

(31) A. Erdélyi, "Asymptotic Expansions", Dover Publications, New York, N.Y., 1956.

(32) M. Gordon and W. T. Tutte, *Proc. Cambridge Philos. Soc.*, **75**, 155 (1975).

(33) M. Gordon and T. G. Parker, *Proc. R. Soc. Edinburgh, Sect. A*, **69**, 181 (1970–1971).

(34) E. F. Beckenbach, "Applied Combinatorial Mathematics", Wiley, New York, N.Y., 1964, p 101.

(35) F. T. Wall and J. J. Erpenbeck, *J. Chem. Phys.*, **30**, 634 (1959).

(36) H. Tompa, "Polymer Solutions", Butterworths, London, 1956.

(37) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).

(38) R. W. Floyd, "CACM Algorithm 97", ACM, New York, N.Y., 1976.

(39) A. Renyi, "Probability Theory", North Holland Publishing Co., Amsterdam and London, 1970.

(40) P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

(41) E. F. Casassa, *J. Polym. Sci., Polym. Symp.*, **No. 54**, 53–83 (1976).

(42) G. C. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).

(43) D. Patterson and G. Delmas, *Trans. Faraday Soc.*, **65**, 708 (1969).

(44) B. E. Eichinger, *J. Chem. Phys.*, **53**, 561 (1970).

(45) R. Koningsveld, W. H. Stockmayer, J. W. Kennedy, and L. A. Kleintjens, *Macromolecules*, **7**, 73 (1974); L. A. Kleintjens, R. Koningsveld, and W. H. Stockmayer, *Br. Polym. J.*, in press.

(46) M. Gordon, P. A. Irvine, and J. W. Kennedy, *J. Polym. Sci., Polym. Symp.*, in press.

(47) M. Huggins, *J. Phys. Chem.*, **80**, 1317 (1976).

(48) J. W. Kennedy, M. Gordon, J. Essam, and P. Whittle, *J. Chem. Soc., Faraday Trans. 2*, **73**, 1289 (1977).

(49) R. E. Nettleton and M. S. Green, *J. Res. Natl. Bur. Stand. Sect. B*, **64b**, 41 (1960).

(50) E. Menefee and W. L. Peticolas, *J. Chem. Phys.*, **35**, 946 (1961).

(51) **Note added in proof:** We thank Professor J. M. G. Cowie of the University of Stirling, Scotland, for investigating a solution of polystyrene ($M = 2 \times 10^6$) in decalin (≈38% trans). It did not show phase separation up to 320 K. He comments that, if the LCST can be detected in this system at all, it is extremely high.