Extrapolation Solution for Conformational Characteristics of Random Copolymers

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ABSTRACT: The use of the rotational isomeric model for random copolymers poses serious mathematical difficulties in the evaluation of the statistical average over the random monomer sequences along the chain. These difficulties have led to the use of Monte Carlo simulations to effect these averages. A random variable method is combined here with the replica "trick" for the configurational free energy and with the $n \to 0$ "trick" for averages such as the characteristic ratio to provide an analytic solution for the average over the random monomer sequences. If the problem begins with a ν-state rotational isomeric model, our averaged results involve the calculation of a set of $2\nu^n$-dimensional (for the free energy) and $10\nu^{n+1}$-dimensional (for the characteristic ratio) rotational isomeric type problems. The random copolymer results are to be obtained as the limit that $n \to 0$. A set of numerical procedures is introduced to perform the $n \to 0$ extrapolation. The first involves a propagation method to exploit information concerning how the properties of the copolymer system change with small changes, say, in the relative concentration of one monomer type. The second involves an iterative extrapolation–interpolation scheme. The methods are tested by calculations for a chain composed of stereoisomers for which Monte Carlo data are available. The method appears to provide very good results when the individual extrapolation steps can be made close to linear, while large uncertainties are introduced for nonlinear extrapolations. The Monte Carlo simulations also experience large statistical errors in this case. An independent test of the random variable method is provided also by consideration of random L-alanine–glycine copolymers with independent bond rotations.

I. Introduction

A great deal of experimental information has been gained concerning the conformational statistics of synthetic homopolymers under ideal conditions where only short-range steric interactions need be treated. Random copolymers, where the monomer sequencing is controlled by kinetic or biological considerations, have been subjected to far less study.[1,11-15] These copolymers are of considerable technological importance (e.g., ethylene–propylene polymers as oil additives) and naturally arise in biological systems.[16] For example, polysaccharides, fatty acids, etc. can be reproduced biologically by the same general types of catalytic step-by-step elongation in solvent[16] that is used to generate the synthetic copolymers. Synthetic polynucleotides are utilized as models for understanding the more complicated DNA, RNA, and proteins. A major goal is to provide a relationship between the physical properties of these random copolymers and the characteristics of the individual monomer units and the probability distribution for their sequencing along the chain.

It is the random arrangement of the monomers along the chain which produces the major impediment to a theoretical description of the conformational statistics of random copolymers. In principle, it is necessary to calculate the conformational characteristics for each possible monomer sequence and *then* to perform the average over the distribution of monomers along the chain.[1] The mathematical complexity of this task has led to the introduction of severe mathematical approximations. The simplest involves the calculation of the conformational characteristics of a chain of "averaged" monomer units, using the same techniques as for homopolymers. Thus, for instance, if the monomer distribution is totally random (a Bernoullian distribution) with probability p of monomers of type A and $1 - p$ for type B, the property X having X_A and X_B for the two monomer types is replaced by its average $\bar{X} = pX + (1 - p)X_B$ and homopolymer calculations are applied by using $\bar{X}$. Flory already notes that this approach is valid only for rather special cases of independent rotational potentials.[1] However, this averaging provides only a crude approximation when the bond rotations become interdependent. In these latter cases Monte Carlo methods have been utilized to perform the proper averages over the allowed chain sequences.[1,11-14]

Here we show how the use of the so-called replica trick[3] and the $n \to 0$ limiting methods[4-6] can provide an analytic representation of the properly averaged properties of random copolymers. The final results are obtained in terms of an extrapolation procedure in which series of rotational isomeric model-type calculations are performed with matrices of higher and higher dimensionalities. The final desired result for the random copolymer is obtained in the limit of an extrapolation to zero-dimensional matrices. Such methods have been used in the past to consider the description of rubber elasticity,[3] polymer excluded volume,[4,6] random alloys,[5,7] and percolation problems.[8] The general theory is illustrated for the cases of the configurational free energy and the characteristic ratio as these provide examples of the two basic types of methods utilized. The calculation of other configurational properties of interest follows along similar lines as either one of these two.

Explicit numerical calculations are provided for the case of the characteristic ratio, which appears to be the most technically complicated within the $n \to 0$ limiting methods. Comparison is made with Monte Carlo calculations for a model of random copolymer composed of optical isomers as presented in the book by Flory.[1] The large dimensionality of the required matrices forces the $n \to 0$ extrapolation to be performed with relatively few points, on the order of 4 only for the characteristic ratio. Extrapolation is rather straightforward when the input points enable the use of linear- or near-linear-type extrapolation procedures.

Section II outlines the theory of the $n \to 0$ extrapolation method for the configurational free energy, while that for the characteristic ratio is given in section III. The validity of the random variable method, which is an essential ingredient of the theory, is checked by consideration of a Bernoullian-type random L-alanine–glycine copolymer with independent bond rotations. The numerical calculations for this case are presented in the Appendix. Sections II

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and III extend these random variable formalisms to the case when bond rotations are interdependent and $n \to 0$ methods are necessary to provide analytical "solutions". The Appendix also provides the generalization to the case of Markovian copolymers.

Section IV describes the propagation method to calculate the properties of the random copolymer for the case of a very small concentration of one of the components. The extrapolation methods are described in section V, where we describe a numerical algorithm involving a combination of extrapolation and interpolation which is designed in such a way that each extrapolation step is kept as close to linear as possible. We believe that the ability to use a nearly linear type of extrapolation is possible when the statistical ensemble of random copolymer sequences provides quantities which are not greatly fluctuating over the random copolymer sequence distribution. However, when the fluctuation of these properties becomes large, e.g., in the case of a type of phase transition, the $n \to 0$ extrapolation appears to be rather nonlinear and its results become less reliable. The Monte Carlo calculations have also been found to be poorly convergent under the same set of circumstances. Additional input data for the $n \to 0$ extrapolation are provided by the exactly calculable quantities associated with the nonrandom cases of the individual homopolymers. A simple propagation formula enables us to compute analytically properties of the random copolymers for the case of low concentrations of one of the components by using some data for the pure homopolymers along with input data for the $n \to 0$ method. When employed for very low concentrations, the propagation method provides certain important input data for the $n \to 0$ extrapolation procedure applied for nonzero concentrations. A comparison between the $n \to 0$ limiting procedure and the Monte Carlo calculations is presented in section VI.

II. Calculation of the Configurational Free Energy

Within the rotational isomeric model the definition of the configurational free energy F for the homopolymer is written in the form

$$-\beta F = \ln \mathbf{J}^* \mathbf{u}^N \mathbf{J} \tag{2.1}$$

where, as described by Flory,[1] $\mathbf{J}^*$ is a ν-dimensional row vector with elements $J^*_i = \delta_{i1}$, while $\mathbf{J}$ is a ν-dimensional column vector with elements $J_i = 1$ for $i = 1, ..., \nu$; $\mathbf{u}$ is a $\nu \times \nu$-dimensional matrix, composed of statistical weights according to the nearest-neighbor rotational isomeric model and $\beta = (kT)^{-1}$.

For the random copolymer we introduce a series of random variables c_i such that

$$\begin{aligned} c_i^{\mathrm{A}} &= 1 \quad \text{if monomer } i \text{ is A type} \\ &= 0 \quad \text{if monomer } i \text{ is B type} \end{aligned} \tag{2.2}$$

$$\begin{aligned} c_i^{\mathrm{B}} &= 0 \quad \text{if monomer is A type} \\ &= 1 \quad \text{if monomer is B type} \end{aligned} \tag{2.3}$$

These random variables satisfy the equations[2]

$$\begin{aligned} c_i^{\mathrm{A}} + c_i^{\mathrm{B}} &= 1 \qquad (c_i^{\mathrm{A}})^2 = c_i^{\mathrm{A}} \\ (c_i^{\mathrm{B}})^2 &= c_i^{\mathrm{B}} \qquad c_i^{\mathrm{A}} c_i^{\mathrm{B}} = 0 \end{aligned} \tag{2.4}$$

For illustrative purposes we consider a two-component system, but the techniques are readily generalized to the case of many components. The average over the monomer sequence distribution is designated as $\langle \cdots \rangle_c$ so that if p is the fraction of monomer type A within the chain, then

$$\langle c_i^{\mathrm{A}} \rangle_c = p \qquad \langle c_i^{\mathrm{B}} \rangle_c = 1 - p \qquad \langle 1 \rangle = 1 \tag{2.5}$$

where $0 \le p \le 1$. The general methods are illustrated here for the case of the Bernoullian distribution, but they can immediately be extended to the case of a Markovian distribution of monomers along the chain (see Appendix). This generalization is used in section VI.

Random matrices $\bar{\mathbf{u}}_i$ can be defined by using (2.2) to (2.4) as

$$\bar{\mathbf{u}}_i = \mathbf{u}^{\mathrm{AA}} c_{i-1}^{\mathrm{A}} c_i^{\mathrm{A}} + \mathbf{u}^{\mathrm{AB}} c_{i-1}^{\mathrm{B}} c_i^{\mathrm{A}} + \mathbf{u}^{\mathrm{BA}} c_{i-1}^{\mathrm{A}} c_i^{\mathrm{B}} + \mathbf{u}^{\mathrm{BB}} c_{i-1}^{\mathrm{B}} c_i^{\mathrm{B}} \tag{2.6}$$

The random $\bar{\mathbf{u}}_i$ play the same role as the statistical matrices in the nonrandom case (2.1). Here $\mathbf{u}^{\mathrm{AA}}$, $\mathbf{u}^{\mathrm{AB}}$, $\mathbf{u}^{\mathrm{BA}}$, and $\mathbf{u}^{\mathrm{BB}}$ are the statistical matrices associated with a succession of AA-, AB-, BA-, and BB-type bonds, respectively.

Whereas the simple expression (2.1) can be evaluated through direct matrix multiplication, or equivalently by finding the eigenvalues of the matrix $\mathbf{u}$, for the random copolymer case it is necessary to evaluate the average of the function of random variables $\{c_i^{\mathrm{A}}, c_i^{\mathrm{B}}\}$ over the random sequence distribution in the chain. Therefore, the ensemble-averaged configurational free energy is given by[1]

$$-\beta F = \langle \ln \mathbf{J}^* \prod_{i=1}^{N} \bar{\mathbf{u}}_i \mathbf{J} \rangle_c \equiv \langle \ln Z(c_i^{\mathrm{A}}, c_i^{\mathrm{B}}) \rangle_c \tag{2.7}$$

where the dependence on the set of random variables c_i^{A} and c_i^{B} has been explicitly noted. Equation 2.7 cannot be directly evaluated analytically as it stands because of the complexity of the average over the random variables c_i^{A} and c_i^{B}. The replica trick,[3] however, enables us to convert (2.7) to a limiting expression in which the individual terms are readily calculated analytically. The identity

$$\ln x = \lim_{n \to 0} \frac{x^n - 1}{n} \tag{2.8}$$

enables us to transform (2.7) into the expression

$$-\beta F = \lim_{n \to 0} \frac{\langle (\mathbf{J}^* \prod_{i=1}^{N} \bar{\mathbf{u}}_i \mathbf{J})^n \rangle_c - 1}{n} \tag{2.9}$$

Note that the quantity $\mathbf{J}^* \prod_{i=1}^{N} \bar{\mathbf{u}}_i \mathbf{J}$ in (2.9) is just some real number for each chain sequence. We can evaluate the average over the random chain sequences in (2.9) when n is a positive integer. This is now shown in detail.

Consider the property of direct products of matrices

$$(\mathbf{A} \otimes \mathbf{B})(\mathbf{C} \otimes \mathbf{D}) = \mathbf{AC} \otimes \mathbf{BD} \tag{2.10}$$

where if A, B, C, or D are just numbers, the symbol $\otimes$ is just a simple multiplication. For integers n the n-fold product in (2.9) can be explicitly written as a product of n factors; i.e.

$$(\mathbf{J}^* \prod_{i=1}^{N} \bar{\mathbf{u}}_i \mathbf{J})^n = (\mathbf{J}^* \prod_{i=1}^{N} \bar{\mathbf{u}}_i \mathbf{J}) \ldots (\mathbf{J}^* \prod_{i=1}^{N} \bar{\mathbf{u}}_i \mathbf{J}) \tag{2.11}$$

Using the general definition (2.10), one can express formula 2.11 in direct product form as

$$(\mathbf{J}^* \prod_{i=1}^{N} \bar{\mathbf{u}}_i \mathbf{J})^n = \mathbf{J}^* \otimes \ldots \otimes \mathbf{J}^* \prod_{i=1}^{N} (\prod_{j=1}^{n} \otimes \bar{\mathbf{u}}_{ij}) \mathbf{J} \otimes \ldots \otimes \mathbf{J} \tag{2.12}$$

where $\mathbf{J}^* \otimes \ldots \otimes \mathbf{J}^*$ and $\mathbf{J} \otimes \ldots \otimes \mathbf{J}$ are n-fold direct products of $\mathbf{J}^*$ and $\mathbf{J}$, respectively, and we have used the notation $\prod_{j=1}^{n} \otimes \bar{\mathbf{u}}_{ij} \equiv \bar{\mathbf{u}}_i \otimes \ldots \otimes \bar{\mathbf{u}}_i$ as shorthand for the n-fold direct product of $\bar{\mathbf{u}}_i$ matrices. The properties of the random variables $\{c_i^{\mathrm{A}}, c_i^{\mathrm{B}}\}$ described in (2.4) enable this direct product to be converted to

$$\prod_{j=1}^{n}\otimes \bar{\mathbf{u}}_{ij} = \prod_{j=1}^{n}\otimes \mathbf{u}^{AA}c_{i-1}{}^{A}c_i{}^{A} + \prod_{j=1}^{n}\otimes \mathbf{u}^{AB}c_{i-1}{}^{B}c_i{}^{A} + \prod_{j=1}^{n}\otimes \mathbf{u}^{BA}c_{i-1}{}^{A}c_i{}^{B} + \prod_{j=1}^{n}\otimes \mathbf{u}^{BB}c_{i-1}{}^{B}c_i{}^{B} \quad (2.13)$$

where again the n-fold direct product matrices are written as

$$\prod_{j=1}^{n}\otimes \mathbf{u}^{mq} \equiv \mathbf{u}^{mq}\otimes \ldots \otimes \mathbf{u}^{mq}; \qquad m, q \in \{A, B\}$$

Let us now introduce the matrices $\prod_{j=1}^{n}\otimes \mathbf{u}^{mq} = \mathbf{U}^{mq}$, so that (2.13) may be reexpressed as

$$\prod_{j=1}^{n}\otimes \bar{\mathbf{u}}_{ij} = \mathbf{U}^{AA}c_{i-1}{}^{A}c_i{}^{A} + \mathbf{U}^{AB}c_{i-1}{}^{B}c_i{}^{A} + \mathbf{U}^{BA}c_{i-1}{}^{A}c_i{}^{B} + \mathbf{U}^{BB}c_{i-1}{}^{B}c_i{}^{B} \quad (2.14)$$

It is convenient to represent (2.14) in the supermatrix form as

$$\prod_{j=1}^{n}\otimes \bar{\mathbf{u}}_{ij} \equiv \mathbf{U}_i = (c_{i-1}{}^{A}c_{i-1}{}^{B})\begin{pmatrix}\mathbf{U}^{AA} & \mathbf{U}^{AB}\\ \mathbf{U}^{BA} & \mathbf{U}^{BB}\end{pmatrix}\begin{pmatrix}c_i{}^{A}\\ c_i{}^{B}\end{pmatrix} \quad (2.15)$$

Note that the matrices $\mathbf{U}_i$ depend on the index n, but for notational simplicity this dependence is not explicitly indicated.

The product of statistical matrices $\bar{\mathbf{u}}_i$ in (2.12) can be rewritten with the aid of (2.13) to (2.15) in the matrix form[2] involving the random variables $\{c_i{}^{A}, c_i{}^{B}\}$ as

$$\prod_{i=1}^{N}\mathbf{U}_i = (c_0{}^{A}c_0{}^{B})\mathbf{U}\left[\prod_{i=2}^{N}\begin{pmatrix}c_i{}^{A} & 0\\ 0 & c_i{}^{B}\end{pmatrix}\mathbf{U}\right]\begin{pmatrix}c_N{}^{A}\\ c_N{}^{B}\end{pmatrix} \quad (2.16)$$

The averaging procedure follows, according to (2.5), as

$$\left\langle\prod_{i=1}^{N}\mathbf{U}_i\right\rangle_c = (p, 1-p)\mathbf{U}\left[\begin{pmatrix}p & 0\\ 0 & 1-p\end{pmatrix}\mathbf{U}\right]^{(N-1)}\begin{pmatrix}p\\ 1-p\end{pmatrix}$$

$$= (1, 1)[\mathbf{U}_p]^{N}\begin{pmatrix}p\\ 1-p\end{pmatrix} \quad (2.17)$$

where $\mathbf{U}$ and $\mathbf{U}_p$ are given by

$$\mathbf{U} = \begin{pmatrix}\mathbf{U}^{AA} & \mathbf{U}^{AB}\\ \mathbf{U}^{BA} & \mathbf{U}^{BB}\end{pmatrix} \quad (2.17a)$$

$$\mathbf{U}_p = \begin{pmatrix}p\mathbf{U}^{AA} & p\mathbf{U}^{AB}\\ (1-p)\mathbf{U}^{BA} & (1-p)\mathbf{U}^{BB}\end{pmatrix} \quad (2.17b)$$

It is convenient to introduce the $2\nu^n$-dimensional row and column vectors $\mathscr{J}^*$ and $\mathscr{J}$, respectively, with the definitions

$$\mathscr{J}^*_i = \delta_{i,1} + \delta_{i,\nu^n+1} \qquad i = 1, \ldots, 2\nu^n$$

$$\mathscr{J}_i = p \qquad i = 1, \ldots, \nu^n$$
$$= 1-p \qquad i = \nu^n+1, \ldots, 2\nu^n \quad (2.18)$$

so that the final expression (2.9) for the free energy can be written as

$$-\beta F = \lim_{n\to 0}\frac{\{\mathscr{J}^*\mathbf{U}_p{}^{N}\mathscr{J}\} - 1}{n} \quad (2.19)$$

The index n enters into the matrices $\mathscr{J}^*$, $\mathscr{J}$, and $\mathbf{U}$ through the dimensionality of these matrices. Hence, (2.19) is of the form of a standard-type rotational isomeric calculation; however, it now involves matrices of dimensionality $2\nu^n$ instead of the ν-dimensional matrices for the homopolymer cases. The problem then involves the calculation of the largest eigenvalues of the matrix

$$\mathbf{U}_p = \left|\left|\begin{matrix}p\mathbf{U}^{AA} & p\mathbf{U}^{AB}\\ (1-p)\mathbf{U}^{BA} & (1-p)\mathbf{U}^{BB}\end{matrix}\right|\right| \quad (2.20)$$

whose dimensionality is $2\nu^n$, $n = 1, 2, 3, \ldots$. For low values of n it is also rather simple to compute directly the product $\mathscr{J}^*\mathbf{U}_p{}^{N}\mathscr{J}$ for $n = 1, 2, 3, \ldots$. Once this is done, it is necessary to attempt to extrapolate the results obtained for $n = 1, 2, 3, \ldots$ to the value $n = 0$. Because the quantity $\mathscr{J}^*\mathbf{U}_p{}^{N}\mathscr{J}$ is in practice a rather large number, it is not advisable directly to extrapolate to $n = 0$ the function

$$F(n) = \frac{1}{n}(\mathscr{J}^*\mathbf{U}_p{}^{N}\mathscr{J} - 1) \quad (2.21)$$

Alternatives involve the extrapolation of $\log F(n)$ or the use of the expression

$$\log x = \log y + \lim_{n\to 0}\frac{(x/y)^n - 1}{n}$$

where y is a suitable normalization factor to keep $\langle(x/y)^n\rangle_c$ of order unity.

The $n \to 0$ extrapolation appears to be algebraically simpler for the free energy than for other configurational properties of the chain. The other cases are now illustrated by choosing the characteristic ratio.

III. Characteristic Ratio

The homopolymer characteristic ratio can be calculated as[1]

$$C_N = \frac{\langle R^2\rangle}{Nl^2} = 1 + \frac{1}{2^{-1}Nl^2Z}\mathbf{J}^*[\mathbf{E}_\nu \quad 0 \quad 0]\mathscr{T}_1{}^{(N-1)}\begin{bmatrix}0\\ \mathbf{E}_\nu\otimes \mathbf{m}\\ \mathbf{E}_\nu\end{bmatrix}\mathbf{J} \quad (3.1)$$

where Z, $\mathbf{J}^*$, and $\mathbf{J}$ are the same as in (2.1), while the other matrices in (3.1) are defined by

$$\mathscr{T}_1 = \begin{bmatrix}\mathbf{u} & (\mathbf{u}\otimes \mathbf{m}^{T})\|\mathbf{T}\| & 0\\ 0 & (\mathbf{u}\otimes \mathbf{E}_3)\|\mathbf{T}\| & \mathbf{u}\otimes \mathbf{m}\\ 0 & 0 & \mathbf{u}\end{bmatrix} \quad (3.2)$$

$$\|\mathbf{T}\| = \begin{pmatrix}\mathbf{T}_1 & & 0\\ & \ddots & \\ 0 & & \mathbf{T}_\nu\end{pmatrix} \quad (3.3)$$

$$\mathbf{T}_i = \begin{bmatrix}\cos\theta_i & \sin\theta_i & 0\\ \sin\theta_i\cos\phi_i & -\cos\theta_i\cos\phi_i & \sin\phi_i\\ \sin\theta_i\sin\phi_i & -\cos\theta_i\sin\phi_i & -\cos\phi_i\end{bmatrix} \quad (3.4)$$

where

$$\mathbf{m} = \begin{pmatrix}l\\ 0\\ 0\end{pmatrix}$$

$\mathbf{E}_\nu$ is just unit matrix dimensionality ν, l is the effective bond length, and $\mathbf{u}$ is the same matrix as in (2.1). These results are simply formally generalized to the random copolymer case by introducing the random variables $\{c_i{}^{A}, c_i{}^{B}\}$ again so that in analogy with (2.6) we have the random $\mathbf{F}$ matrices

$$\bar{\mathscr{T}}_i = \mathscr{T}^{AA}c_{i-1}{}^{A}c_i{}^{A} + \mathscr{T}^{AB}c_{i-1}{}^{B}c_i{}^{A} + \mathscr{T}^{BA}c_{i-1}{}^{A}c_i{}^{B} + \mathscr{T}^{BB}c_{i-1}{}^{B}c_i{}^{B} \quad (3.5)$$

Hence, the characteristic ratio for the random copolymer can be written as the average over random monomer sequence distributions along the chain as

$$C_N = 1 + \frac{2}{N}\left\langle \frac{1}{l^2 Z} \mathrm{J}^*[\mathrm{E}_\nu \quad 0 \quad 0] \prod_{i=1}^{N-1} \mathcal{T}_i \begin{bmatrix} 0 \\ \mathrm{E}_\nu \otimes \mathrm{m} \\ \mathrm{E}_\nu \end{bmatrix} \mathrm{J} \right\rangle_c \tag{3.6}$$

where $Z = Z(c_i^A, c_i^B)$ in the denominator of (3.6) is the partition function with the identical monomer sequence that appears in the numerator of (3.6). This feature introduces the severe mathematical complexity to the problem. Other functions of the random variables $\{c_i^A, c_i^B\}$ pose the same difficulty in performing the average because of the existence of the random variables $\{c_i^A, c_i^B\}$ in both the numerator and the denominator. It can readily be verified that there is no straightforward way to replace the denominator by some other random function which would enable an analytic calculation of the averages over the random variables $\{c_i\}$. Instead, we introduce the simple identity

$$\frac{N}{D} = \lim_{n \to 0} N D^{n-1}$$

which forms the basis of the $n \to 0$ limiting method. Given this simple identity, (3.6) can be rewritten in the limiting form of

$$C_N = 1 + \frac{2}{l_{\mathrm{eff}}^2 N} \lim_{n \to 0} \langle (\mathbf{J}_E^* \prod_{i=1}^{N-1} \tilde{\mathcal{T}}_i \mathbf{J}_E)(\mathbf{J}^* \prod_{i=1}^{N-1} \bar{\mathbf{u}}_i \mathbf{J})^{n-1} \rangle_c \tag{3.7}$$

where the matrices $\mathbf{J}_E^*$ and $\mathbf{J}_E$ are row and column matrices, respectively, with components

$$\mathrm{J}_E^* = \mathrm{J}^*[\mathrm{E}_\nu \quad 0 \quad 0]$$
$$\mathrm{J}_E = \begin{bmatrix} 0 \\ \mathrm{E}_\nu \otimes \mathrm{m} \\ \mathrm{E}_\nu \end{bmatrix} \mathrm{J} \tag{3.7a}$$

and the quantity l_{eff} is defined as

$$l_{\mathrm{eff}}^2 = p(l^{\mathrm{AA}})^2 + (1-p)(l^{\mathrm{AB}})^2 + p(1-p)[(l^{\mathrm{AB}})^2 + (l^{\mathrm{BA}})^2] \tag{3.7b}$$

Other more general cases are readily considered as necessary.

We now demonstrate that for n equal to positive integers the expression (3.7) can be analytically averaged over the random monomer sequence distribution. Following the methods in (2.11) to (2.19), we may rewrite (3.7) in the form of

$$C_N = 1 + \frac{2}{l_{\mathrm{eff}}^2 N} \lim_{n \to 0} \mathcal{J}^* \hat{\mathcal{F}}^{(N-1)} \mathcal{J} \tag{3.8}$$

where the matrices $\mathcal{J}^*$ and $\mathcal{J}$ are written as

$$\mathcal{J}^* = \left[\underbrace{\mathrm{J}^* \otimes \cdots \otimes \mathrm{J}^*}_{n}\right] \left\{ \left[(1,1) \otimes [\mathrm{E}_\nu \quad 0 \quad 0]\right] \otimes \underbrace{\mathrm{E}_\nu \otimes \cdots \otimes \mathrm{E}_\nu}_{n-1} \right\} \tag{3.9a}$$

$$\mathcal{J} = \left\{ \left[\begin{pmatrix} p \\ 1-p \end{pmatrix} \otimes \begin{pmatrix} 0 \\ \mathrm{E}_\nu \otimes \mathrm{m}_{\mathrm{eff}} \\ \mathrm{E}_\nu \end{pmatrix} \right] \otimes \underbrace{\mathrm{E}_\nu \otimes \cdots \otimes \mathrm{E}_\nu}_{n-1} \right\} \left[\underbrace{\mathrm{J} \otimes \cdots \otimes \mathrm{J}}_{n} \right] \tag{3.9b}$$

$$\hat{\mathcal{F}} = \begin{pmatrix} p\hat{\mathcal{F}}^{\mathrm{AA}} & p\hat{\mathcal{F}}^{\mathrm{AB}} \\ (1-p)\hat{\mathcal{F}}^{\mathrm{BA}} & (1-p)\hat{\mathcal{F}}^{\mathrm{BB}} \end{pmatrix} \tag{3.9c}$$

and the $\hat{\mathbf{F}}$ matrices are defined by the direct product involving $n-1$ $\mathbf{U}$ factors as

$$\hat{\mathcal{F}}^{\mathrm{mq}} = \mathcal{F}^{\mathrm{mq}} \otimes \mathbf{u}^{\mathrm{mq}} \otimes \ldots \otimes \mathbf{u}^{\mathrm{mq}}; \qquad \mathrm{m, q} \in \{\mathrm{A, B}\}$$

Thus, the description of the characteristic ratio of the random copolymer reduces to the calculation of the quantity

$$\varphi(n) = \mathcal{J}^* \hat{\mathcal{F}}^{(N-1)} \mathcal{J} \tag{3.10}$$

where $n = 1, 2, 3, \ldots$ can readily be calculated by matrix multiplication, and extrapolation must be performed to $n \to 0$. Because the quantities $\varphi(n)$ become numerically very large, it is convenient to extrapolate $\log \varphi(n)$ instead. Since the matrices in (3.10) are of dimensionality $10\nu^{n+1}$, the case of n equaling about 4 or 5 is the largest which is practical to calculate. This implies the use of an extrapolation with few input points. It is, therefore, useful in addition to utilize information that has already been obtained concerning the chain conformation statistics at some monomer concentration p to enable its estimation at some value $p + \delta p$ where δp is sufficiently small. This propagation approach provides some guidelines for the extrapolation procedure.

IV. Propagation Method

The previous two sections developed methods which are based on an extrapolation procedure $n \to 0$. Because the calculation of the functions $\varphi(n)$ and $F(n)$ can in practice only be made for a few values of n, there is a certain uncertainty with regard to the possible extrapolation procedure, especially if the extrapolation is essentially nonlinear. These extrapolation methods are described in the next section. Here, however, we discuss an alternative propagation method which provides important input to the extrapolation method. Although this propagation method is very restrictive in its applicability, it provides important supplementary information to the extrapolation method.

Consider first the calculation of $\langle \ln Z(c_i^A, c_i^B) \rangle_c$. It is clear that when the concentration of A-type monomers p equals 0 or 1, the exact results can be readily evaluated according to (2.1), so that we have, for example,

$$F(p = 0) \equiv \ln Z(0) \tag{4.1}$$

with a similar equation for $p = 1$. The notation in (4.1) and (2.21) should not be confused. However, since this section never introduces the variable n, no confusion should arise. Consider now the case of p sufficiently small in some sense. For such p we may write the expression

$$F(p) = \langle \ln Z(p) \rangle_c = \langle \ln Z(p) + \ln Z(0) - \ln Z(0) \rangle_c = \ln Z(0) + \langle \ln [Z(p)/Z(0)] \rangle_c \tag{4.2}$$

Here the p in $Z(p)$ has to be understood in the symbolic sense as a function of the random variables $\{c_i^A, c_i^B\}$. For $p \to 0$ we assume that $Z(p)$ is comparable to $Z(0)$. Using the formula

$$\ln x = (x-1) - \frac{(x-1)^2}{2} + \frac{(x-1)^3}{3} - \frac{(x-1)^4}{4} + \ldots \qquad 0 < x \leq 2 \tag{4.3}$$

one may reexpress eq 4.2 as

$$F(p) = \ln Z(0) + \frac{\langle Z(p) \rangle_c}{Z(0)} - 1 - \frac{1}{2}\left(\frac{\langle Z^2(p) \rangle_c}{Z^2(0)} - 2\frac{\langle Z(p) \rangle_c}{Z(0)} + 1 \right) + \ldots \tag{4.4}$$

It is always possible to choose p sufficiently small that the

series in (4.4) is rapidly converging. Defining the quantity $Z_1 = \exp[F(p)]$, it is possible to attempt to evaluate $F(p + \delta p)$ from the expansion

$$F(p + \delta p) = F(p) + \frac{\langle Z(p + \delta p)\rangle_c}{Z_1} - 1 - \frac{1}{2}\left(\frac{\langle Z^2(p + \delta p)\rangle_c}{Z_1^2} - 2\frac{\langle Z(p + \delta p)\rangle_c}{Z_1} - 1\right) + \ldots \quad (4.5)$$

where the notation δp is used to represent a sufficiently small quantity. Hence, given the knowledge of $F(p)$, the propagation method (4.5) may be used to obtain $F(p + \delta p)$, etc. It should be noted that in order to perform such calculations it is necessary to evaluate the expression $(\mathcal{J}^*\mathbf{U}_p{}^N\mathcal{J})^n \equiv \langle Z^n(p)\rangle_c$, which is already calculated by use of formulas 2.19 and 2.21.

Consider now the case of the characteristic ratio. Here we must evaluate quantities which may be written in the symbolic form

$$R(p) = \langle N(p)/Z(p)\rangle_c \quad (4.6)$$

where $N(p)$ is a symbolic for all the quantities in the numerator of eq 3.6. Equation 4.6 may be expressed as

$$R(p) = \langle N(p) \exp\{-\ln Z(p)\}\rangle_c \quad (4.7)$$

Again, for $p = 0$ eq 4.6 reduces to that for the homopolymer

$$R(0) = N(0)/Z(0) \quad (4.8)$$

which is exactly solvable. For $p \neq 0$ the general expression (4.7) is equivalently given by

$$R(p) = \langle N(p) \exp\{-\ln Z(p) + \ln Z(0) - \ln Z(0)\}\rangle_c = \left\langle \frac{N(p)}{Z(0)} \exp\left\{-\ln \frac{Z(p)}{Z(0)}\right\}\right\rangle_c \quad (4.9)$$

Using formula 4.3 for p sufficiently small, one can expand the exponent to yield

$$R(p) = \left\langle \frac{N(p)}{Z(0)} \exp\left\{-\left(\frac{Z(p)}{Z(0)} - 1\right) - \frac{1}{2}\left(\frac{Z(p)}{Z(0)} - 1\right)^2 + \ldots\right\}\right\rangle_c = \frac{5}{2}\frac{\langle N(p)\rangle_c}{Z(0)} - 2\frac{\langle N(p)Z(p)\rangle_c}{Z^2(0)} + \frac{1}{2}\frac{\langle N(p)Z^2(p)\rangle_c}{Z^3(0)} \quad (4.10)$$

Note that the moments in the numerator of (4.10) are just the values of $\varphi(n)$ for $n = 1, 2, \ldots$, which have been evaluated in section III. The expansions (4.5) and (4.10) should only be considered for sufficiently small p and perhaps only in an asymptotic sense; i.e., the series may not provide better results by systematically increasing the number of terms in the expansion.

Assume we somehow know the quantity $R(p)$ with some accuracy and we wish to determine $R(p + \delta p)$ from it. Evidently, the expression

$$R(p + \delta p) = \langle N(p + \delta p) \exp\{-\ln Z(p + \delta p) + \ln Z(p) - \ln Z(p)\}\rangle_c \quad (4.11)$$

is now complicated beyond that in (4.2) and (4.5) because of the presence of the functions $N(p + \delta p)$ inside the $\langle\cdots\rangle_c$.

We may, however, consider the quantity

$$R(p + \delta p) = \langle N(p + \delta p) \exp\{-\ln Z(p + \delta p) + \ln \langle Z(\bar{p})\rangle_c - \ln \langle Z(\bar{p})\rangle_c\}\rangle_c \quad (4.12)$$

where $\langle Z(\bar{p})\rangle_c$ is evaluated for some concentration $\bar{p}$ within the range of $(p, p + \delta p)$. Such a substitution is quite arbitrary so that we can attempt to employ other convenient numbers than $\langle Z(\bar{p})\rangle_c$ which provide a small expansion parameter. This appears to be more readily possible in the low- and high-concentration limits. Fortunately, these are the limits that are needed to provide input for the extrapolation method.

V. Extrapolation Method

The ultimate success of the $n \to 0$ method for describing the configurational statistics of random copolymers essentially rests upon the ability to perform the $n \to 0$ extrapolation. At first sight it may appear as if it is hopeless to attempt to extrapolate values of a function known only for $n = 1$, 2, 3, and 4, say, to obtain the value at $n = 0$ unless the extrapolation is a simple linear form. The extrapolation procedure described here, in effect, attempts to have the extrapolation as nearly linear as possible in each iterative step of the extrapolation process. In addition, essential information concerning the p dependence of various properties is incorporated to provide certain guidelines for the extrapolation procedure. When the extrapolation departs significantly from a local linear-type extrapolation, the accuracy of the method deteriorates. There is then a strong sensitivity to the choice of the extrapolation step. In the example described in section VI the Monte Carlo calculations in these cases appear also to have a large statistical error. Thus, a comparison of Monte Carlo and $n \to 0$ limit methods suggests that a near-linear-type extrapolation procedure results from a statistical ensemble in which the dispersion in the property of interest is fairly narrow. On the other hand, when the dispersion is very large or when the distribution of properties among the different random monomer sequences along the chain becomes strongly bimodal, the $n \to 0$ extrapolation procedure becomes highly nonlinear, and the Monte Carlo statistics become more slowly convergent. Hence, a consideration of the nature of the extrapolation procedure can provide guidelines as to the distribution in the properties of the members of the random ensemble of monomer sequences in the copolymer.

We begin with a situation in which the data points $y(n)$ for $n = 1$, 2, 3, and 4 are equally spaced from each other along n. We can then use the extrapolation procedure to obtain the function y at a point $n + \eta$ given its values at $n + 1$, $n + 2$, etc. The extrapolation can be used to go to increasing or decreasing values of n, but here we only have need for the case decreasing values for n. The full function is designated as $y(x)$, with x a continuous variable. The general extrapolation formula is based on the use of the numerical Taylor series[9]

$$y(x + \eta) = y(x) + \eta\Delta^{(1)}y(x) + \frac{1}{2!}\eta(\eta - 1)\Delta^{(2)}y(x) + \frac{1}{3!}\eta(\eta - 1)(\eta - 2)\Delta^{(3)}y(x) + \ldots \quad (5.1)$$

Here $\eta = (x - x_0)h^{-1}$, where h is the distance between the given numerical points (in our case $h = 1$, $x_0 = 1$)

$$\Delta^{(1)}y(x) = y(x + 1) - y(x)$$

$$\Delta^{(2)}y(x) = \Delta^{(1)}y(x + 1) - \Delta^{(1)}y(x) \quad \text{etc.}$$

If the terms $\Delta^{(2)}$, $\Delta^{(3)}$, etc. are negligible in comparison to the first two terms on the right side of (5.1), then the extrapolation procedure over the step length η is a linear one and can be carried out with reliability. Hence, it would be natural to require that succeeding terms in the numerical Taylor series expansion provide smaller and smaller contributions.

We begin the extrapolation procedure by having the points, say, at $x = 1$, 2, 3, and 4; then, for a suitable value of η discussed below, (5.1) can be used to obtain the value

of y at the point $x = 1 + \eta$ (note that η is negative). It is possible then to use a form of the numerical Taylor series for the case where points are no longer equally spaced. However, we choose instead to utilize an approach which attempts to "improve" our knowledge of the function $y(x)$ in the range span of the available points. Now, we can utilize the extrapolated value at the point $n = 1 + \eta$ to provide a fifth input point for an interpolation utilizing, for example, the Lagrange polynomial given by the formula[9]

$$p(x) = \sum_{i=1}^{N} y_i f_i(x) \tag{5.2}$$

where the function f_i is defined by

$$f_i(x) = [(x - x_1)(x - x_2)...(x - x_{i-1})(x - x_{i+1})...(x - x_N)]/ [(x_i - x_1)(x_i - x_2)...(x_i - x_{i-1})(x_i - x_{i+1})...(x_i - x_N)] \tag{5.2a}$$

The Lagrange polynomial (5.2) can then be used with the input data at $x = 1$, 2, 3, and 4 and $x = 1 + \eta$ to interpolate the function $y(x)$ to obtain interpolated values at the points $x = 2 + \eta$, $3 + \eta$, and $4 + \eta$. Then, given these *equally spaced* point values of the function y at $x = n + \eta$, for $n = 1$, 2, 3, and 4, these points can be substituted again in the numerical Taylor series (5.1) to obtain an extrapolated value at $x = 1 + 2\eta$ etc. (It is, of course, possible to use a variable step length, but for simplicity we maintain a constant one. Perhaps greater accuracy can be obtained in the future by utilization of a variable step size routine.)

Having obtained the extrapolated value of $y(1 + 2\eta)$, we now have an additional point $y(1 + 2\eta)$ to add to further "improve" the Lagrange polynomial (5.2). Hence, after N extrapolated points, there are $4 + N$ input points in the Lagrange polynomial (5.2). (The numerical calculations in the next section use four input points, but in calculations of, say, the configurational free energy, more input points could be generated because of the lower dimensionality of the required matrices, and, of course, the above discussion is suitably modified for this case.)

We have found in our calculations of section VI that if the initial (e.g., four point) Lagrange polynomial is not "improved" as we perform the extrapolation, then the final extrapolated results are physically meaningless. It suggests that the combined use of the extrapolation and interpolation formulas (5.1) and (5.2), respectively, provide a much better fitting function to the original limited data.

It is clear that the extrapolated results should depend on a proper choice of the extrapolation step η. The numerical Taylor series expansion requires that η be sufficiently small. However, if η is chosen to be too small, too many points are required to extrapolate all the way to $x = 0$; then the possible numerical errors accumulate. As noted previously in this section, an optimal situation occurs when the ratios of succeeding terms in (5.1) are progressively smaller. However, beyond the first-order correction, the relative ratios of succeeding terms

$$R_1 = \left|\frac{(\eta - 1)\Delta^{(2)}y(x)}{2\Delta^{(1)}y(x)}\right| \tag{5.3a}$$

$$R_2 = \left|\frac{(\eta - 2)\Delta^{(3)}y(x)}{3\Delta^{(2)}y(x)}\right| \tag{5.3b}$$

are practically independent of the step size η, provided that this step size is small, as it is always the case. Hence, the only step-dependent ratio is the leading one

$$R_0 = \left|\frac{\eta\Delta^{(1)}y(x)}{y(x)}\right| \tag{5.4}$$

When it is impossible to choose R_0 much larger than R_1 and R_2 for a given η, we have found that it is reasonable to demand that the value of R_0 should be comparable to that of R_1 and R_2, giving the bounding relation $R_0 \in (R_1, R_2)$. This serves as one crude criterion for the choice of the step length η. In addition, we utilize information from the propagation method of section IV to provide another more sophisticated criterion.

Consider now the expansion (5.1) for the particular concentration p which is now explicitly indicated. Assume that we have performed N steps in the extrapolation and interpolation procedure described above. Let $y_{N,p}$ be the Nth extrapolated value for the concentration p. Then, the next extrapolated point according to (5.1) is given by the formula

$$y_{N+1,p} = y_{N,p} - \eta_p\Delta^{(1)}y_{N,p} + \tfrac{1}{2}\eta_p(\eta_p + 1)\Delta^{(2)}y_{N,p} - \tfrac{1}{6}\eta_p(\eta_p + 1)(\eta_p + 2)\Delta^{(3)}y_{N,p} + ... \tag{5.5}$$

where the negative sign of η has been utilized so that η_p is the absolute value of the step length used for the concentration p. Using (5.5) as an iterative procedure, we may express everything in an iterative form

$$y_{N+1,p} = y_{0,p} - \eta_p\sum_{i=1}^{1/\eta_p}\Delta^{(1)}y_{i,p} + \tfrac{1}{2}\eta_p(\eta_p + 1)\sum_{i=1}^{1/\eta_p}\Delta^{(2)}y_{i,p} - \tfrac{1}{6}\eta_p(\eta_p + 1)(\eta_p + 2)\sum_{i=1}^{1/\eta_p}\Delta^{(3)}y_{i,p} + ... \tag{5.6}$$

Consider the analogous iterative expression for a nearby concentration $p + \delta p$. We can write the analogous formula

$$y_{N+1,p+\delta p} = y_{0,p+\delta p} - \eta_{p+\delta p}\sum_{i=1}^{1/\eta_{p+\delta p}}\Delta^{(1)}y_{i,p+\delta p} + ... \tag{5.7}$$

For small enough δp the approximate derivative with respect to p is given by the quantity k according to

$$y_{N+1,p} - y_{N+1,p+\delta p} \equiv k\delta p = y_{0,p} - y_{0,p+\delta p} + \eta_{p+\delta p}\sum_{i=1}^{1/\eta_{p+\delta p}}\Delta^{(1)}y_{i,p+\delta p} - \eta_p\sum_{i=1}^{1/\eta_p}\Delta^{(1)}y_{i,p} + ... \tag{5.8}$$

Since δp is taken to be rather small, the step size at concentration $p + \delta p$ is written as a small correction to that at p

$$\eta_{p+\delta p} = \eta_p + \delta\eta \tag{5.9}$$

Then, combining (5.8) and (5.9) yields the approximation

$$k\delta p \approx \Delta^{(0)}y_{0,p} + \eta_p\sum_{i=1}^{1/\eta_p}(\Delta^{(1)}y_{i,p+\delta p} - \Delta^{(1)}y_{i,p}) + \delta\eta\sum_{i=1}^{1/\eta_{p+\delta p}}\Delta^{(1)}y_{i,p} + ... \tag{5.10}$$

where k is some as yet unknown proportionality coefficient. The value of k can be estimated as follows: Given a value of k taken from propagation data, an estimate of $\eta_{p+\delta p}$ can be obtained (see below) and hence $y_{N,p+\delta p}$ can be obtained, also enabling the calculation of k. It turns out that the final results for the numerical data in section VI are fairly insensitive to the value of k. (There k is found to be of the order of unity due to the slow variation of η_p with p). In order to provide estimates of the quantity $\delta\eta$, we introduce upper bounds to the differences in (5.10) as follows: Let

$$\Delta^{(1)}y_{i,p+\delta p} \leq \Delta^{(1)}{}_{p+\delta p}$$
$$\Delta^{(1)}y_{i,p} \leq \Delta^{(1)}{}_{p} \tag{5.11}$$

define upper estimates for the magnitude of the various differences (usually the initial first differences are taken). Then we obtain from (5.10) and (5.11) the estimate for $\delta\eta$ as

$$\delta\eta \simeq \pm\left[\frac{\eta_p}{\Delta^{(1)}{}_p}\left|k\delta p - \Delta^{(0)}y_{0,p}\right| + \eta_p\left|1 - \frac{\Delta^{(1)}{}_{p+\delta p}}{\Delta^{(1)}{}_p}\right|\right] \quad (5.12)$$

Because of the use of absolute values and upper estimates, the signs in (5.12) are undetermined and both should be tried. In general, the higher differences $\Delta^{(2)}$ etc. should be utilized, but again, in our numerical example of section VI these have found to be of negligible importance.

Given the methods for estimation of $\delta\eta$ for a change in probability δp, it is still necessary to establish the initial values of η for the very small (or large) concentrations p. This input information is obtained from the propagation method of section IV, which provides estimates of η_p for concentrations δp and $1 - \delta p$ from the respective exactly known limits $p = 0$ and 1. Given these propagation estimates, step lengths $\eta_{\delta p}$ and $\eta_{1-\delta p}$ can be adjusted to reproduce the results of the propagation method by extrapolation–interpolation. Then the definition of (5.12) for the change in step length with a change in p is utilized to enable a determination of the extrapolation step length for nearby concentrations $p + \delta p$. By beginning the procedure at both known limits of $p = 0$ and $p = 1$ and by successively working toward the center ($p = 0.5$), we can establish whether the extrapolation from both extreme ends meets to provide a common estimation at $p = 0.5$. The processes beginning with $p = 0$ and $p = 1$ utilized both choices of sign in (5.12), starting from both ends at $p = 0$ and $p = 1$. Thus, propagating from $p = 0$, there is one calculated curve using the upper sign and one curve using the lower sign, while propagating from $p = 1$, there are likewise two curves. One pair of curves (either + from one side and – from the other side, or vice versa) may join or come close to joining at the center (p = 0.5), indicating a consistent extrapolation–propagation.

Since $\delta\eta$ is by definition supposed to be small, it is only changed in the process of changing concentration if the projected value of $\delta\eta$ from (5.12) is rather large, say, or the order of $|\delta\eta|/\eta_p \sim 0.1$. If the projected change is smaller than that, it is usually left as 0.

The net result of this process is a fairly sophisticated extrapolation scheme which on the surface appears to begin only with a very limited number of data points for any concentration point p. However, it is clear that information is utilized for the known values of $p = 0$ and $p = 1$ as well as for the concentration dependence of the quantities of interest for all previously calculated concentrations p. Nevertheless, the verification that this extrapolation procedure is adequate to "squeeze out" the required $n \to 0$ limiting values must be determined by consideration of numerical examples, to which we now turn.

VI. Numerical Example and Discussion

Appendix I shows how the random variable $\{c_i\}$ formalism can be easily extended to the case of a chain with a Markovian monomer sequence distribution. The results are readily transferred here for the interdependent bond rotation case. In the case of the characteristic ratio C_N, for instance, the matrix (3.9c) is simply replaced by

$$\hat{\mathcal{J}}' = \begin{pmatrix} p_A{}^A\hat{\mathcal{J}}^{AA} & p_A{}^B\hat{\mathcal{J}}^{AB} \\ p_B{}^A\hat{\mathcal{J}}^{BA} & p_B{}^B\hat{\mathcal{J}}^{BB} \end{pmatrix} \quad (6.1)$$

where $p_u{}^m$ (m, u = A, B) are the corresponding conditional probabilities defined in the Appendix. In addition, $l_{eff}{}^2$ of (3.7c) is replaced by the quantity

$$l_{eff}{}^2 = p_{AA}(l^{AA})^2 + p_{AB}(l^{AB})^2 + p_{BA}(l_{BA})^2 + p_{BB}(l^{BB})^2 \quad (6.2)$$

where $p_{mu} = p_u{}^m p_u$ and p_u is the monomer probability defined in (2.5).

These preliminaries enable us to discuss a numerical example described in the classic book of Flory.[1] The model involves a polymer chain composed of a random sequence of d and l asymmetric vinyl units. This model provides a serious test of the $n \to 0$ limiting methods for several reasons. The chain with a random combination of isotactic and syndiotactic segments exhibits a helix–coil phase transition when the concentration of isotactic segments approaches unity. In this case the characteristic ratio C_N exhibits large fluctuations as a function of monomer sequences and tends toward infinity in the limit of a purely isotactic chain because it steadily approaches the helical conformation. This feature of the model represents an extreme and difficult case for the $n \to 0$ limit methods. However, it also precludes the use of the propagation method beginning from the purely syndiotactic chain. We believe that the negative aspect of this latter difficulty with the model is overshadowed by the positive tests provided by the former difficulty.

We now proceed to describe in more detail the model and Monte Carlo calculations. The repulsions between the sterically interacting groups alter the positions of the rotational minima so that individual residue positions become explicitly asymmetric with respect to the planar "all-trans" configuration. Hence, by varying the polymerization conditions, it is possible to generate more "right" or "left" chains in the sense reviewed by Flory. Technologically, however, an equal probability to have "right" or "left" chains is generated, but biologically only one preferential orientation is often found. Therefore, it is interesting to have information about both types of molecules separately. Our method enables us separately to consider these different cases.

Flory reviews Monte Carlo calculations for the above-described type of chains, which yield only an average over "right"- and "left"-type chains. $w_{iso} = w$ is the probability independent of position along the chain that the kth unit of the chain is isotactic (l or d) if its predecessor is also isotactic (l or d, respectively). This definition of w automatically implies $w_{syn} = 1 - w$.

The Monte Carlo calculations employ a random number procedure to generate random d,l monomer sequences as follows: For a set of molecules, each consisting of x units, a set of ordered $x - 1$ random numbers ranging from 0 to 1 is produced. Those numbers within each set which are less than or equal to w are taken to specify an isotactic dyad in which the d or l character of one unit is perpetuated in the subsequent one. Those numbers exceeding w denote syndiotactic dyads in which the d,l character of a subunit is opposite to its predecessor along the chain.

It is necessary to consider the relationship between the conditional probability w and the full probability p for having, say, an l subunit at the kth place. The latter is just the sum of the probabilities for ll and dl pairs which give

$$p = pw + (1 - p)(1 - w) \quad (6.3)$$

Equation 6.3 implies (since $w \neq 1$ in general) that

$$p = \tfrac{1}{2} \quad (6.3a)$$

The result (6.3a) is physically very clear. For each chain, starting with an l unit, there is its "mirror image", or dual,

Table I
Statistical Weight Matrices for the Vinyl Chain[a]

$$u_d' = \begin{bmatrix} 1 & 1 & 0.05 \\ 1 & 1 & 0 \\ 1 & 0 & 0.05 \end{bmatrix} \qquad u_{dd}'' = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$u_l' = \begin{bmatrix} 1 & 0.05 & 1 \\ 1 & 0.05 & 0 \\ 1 & 0 & 1 \end{bmatrix} \qquad u_{ll}'' = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

$$u_{dl}'' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad u_{ld}'' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

[a] The parameters ω, τ, τ', and η are taken in accordance with those given for the Monte Carlo data; see pp 234–237 of ref 1.

Table II
Values of the Function $\log \varphi(n)$ for the Case When the Chain Starts with l Subunits

	n			
w	1	2	3	4
0	23.95969	44.50897	65.05825	
0.2	22.78477	42.47676	62.27469	82.15962
0.5	20.53386	38.47875	56.81359	75.43595
0.6	19.50878	36.6660	54.36255	72.44378
0.8	16.49490	31.38188	47.2820	63.86133
0.9	13.84365	26.700	41.01363	56.27931
1.0	6.225	8.2225	10.2225	

which begins with a d unit. Therefore, the monomer sequence average has a mixture of representatives from both sets taken with equal weights. The previous discussion emphasizes that the sequence of dyads ll, dd, ld, and dl types in the numerator of (3.1) must be identical with that in the denominator, i.e., in the Z function. Note also that chains with x dyads have $N = 2x$ skeletal bonds. Input data for the vinyl copolymer involve $l_{\text{eff}}^2 = 2.3409$ Å, which corresponds to a C bond length equal to 1.53 Å. The C–C–C bond angle is 112°, which corresponds to $\theta = 68°$. The ϕ angles are taken for the undistorted case of $\phi_1 = 0°$, $\phi_2 = 120°$, $\phi_3 = -120°$, but other distorted values may be considered similarly. In view of distinct dl and ld transfer matrices this, nevertheless, yields some difference between "right" (starting with d) and "left" (starting with l) molecules. For completeness, data for all relevant matrices are presented in Table I. Given these data, the model requires the use of the matrix

$$\hat{\mathcal{F}}' = \begin{pmatrix} w\hat{\mathcal{F}}_{ll} & (1-w)\hat{\mathcal{F}}_{ld} \\ (1-w)\hat{\mathcal{F}}_{dl} & w\hat{\mathcal{F}}_{dd} \end{pmatrix} \qquad (6.4)$$

where the conditional probabilities in (6.1) are expressed in terms of w. In addition, the value $p = {}^1/_2$ must be used in (3.9b). "Left" and "right" chains, respectively, can be separated by use of the column vectors

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

in (3.9b); then the final average may use

$$\begin{pmatrix} p \\ 1-p \end{pmatrix} = \begin{pmatrix} {}^1/_2 \\ {}^1/_2 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The qualitative behavior of C_N as a function of w is independent of N in the limit of large N for Gaussian chains. Hence, the computation time has been shortened by considering a set of polymers composed of 100 subunits (or 200 bonds). Differences may appear from the Monte Carlo calculations ($N = 400$) in the limit $w \simeq 1$ because of the non-Gaussian character of the helical chains in this limit.

Table III
Values of the Function $\log \varphi(n)$ for Chains Starting with d Subunits

	n			
w	1	2	3	4
0	23.95975	44.5090	65.0583	
0.2	22.78473	42.47672	62.27465	82.15956
0.4	21.38910	39.99840	58.88090	77.97178
0.5	20.53339	38.47874	56.81358	75.43594
0.6	19.50878	36.6660	54.36256	72.44378
0.8	16.49490	31.38187	47.28199	63.96133
0.9	13.84377	26.7010	41.01364	56.27930
1.0	6.1363	8.1363	10.1963	

Table IV
Values of the Function $\log \varphi(n)$ for Chains Starting with l Subunits Used as Inputs for Propagation-Extrapolation Methods

	n			
w	1	2	3	4
0.0	23.35975	44.5090	65.0583	
0.05	23.67346	44.02593	64.40025	84.79366
0.1	23.3859	43.530	63.7210	83.95178
0.15	23.09081	43.01516	63.01409	83.07551
0.2	22.78473	42.47672	62.274647	82.15956
0.25	22.46476	41.9110	61.4980	81.19835
0.5	20.5339	38.47874	56.81358	75.43594
0.75	17.43221	33.02213	49.47421	66.51143
0.85	15.34312	29.36023	44.58112	60.59631
0.3	13.84377	26.7010	41.01364	56.27930
0.95	11.652	22.6880	35.5620	49.6341
0.975	9.93747	19.346656	30.89572	43.8576
1.0	6.1963	8.1963	10.1963	

Table V
Some Values of the Function $F(n = 1) + 1 = \mathcal{J}^* U_{w_{\text{iso}}}^N \mathcal{J}$ Needed for the Propagation Continuation

w_{iso}	$F(n = 1) + 1$
0	3.54225×10^{20}
0.05	2.09596×10^{20}
0.1	1.20082×10^{20}
0.15	6.63798×10^{19}
0.2	3.52590×10^{19}
0.95	1.597569×10^{8}
1.0	99.0

Table VI
Some Values of $\Delta^{(k)}y_w^{(1)}$ Needed for Step Correction Estimates ($y = \log \varphi(n)$)

w	$\Delta^{(1)}y_w^{(1)}$	$\Delta^{(2)}y_w^{(1)}$	$\Delta^{(3)}y_w^{(1)}$
0.1	20.144	0.047	−0.007
0.25	19.44624	0.14076	−0.02726
0.5	17.9448	0.39	−0.10264
0.75	15.590	0.8620	−0.2766
0.85	14.017	1.204	−0.409
0.9	12.856	1.4572	−0.505
0.95	11.046	1.818	−0.610

Our $n \to 0$ computational method produces the results summarized in Tables II–VII. The calculations exhibit good qualitative and in most cases quantitative agreement with the Monte Carlo data. Comparison of Tables II and III shows almost no difference between the corresponding data for "left" and "right" chains. This arises because of the initial choice of $\Delta\phi = 0$. This, however, would no longer be true when $\Delta\phi \neq 0$. The two cases are presented separately only to demonstrate how they may be studied individually in the general case. Because the $\Delta\phi = 0$ results are practically the same for the d and l cases, one of them is (see Table IV) used for the extrapolation–propagation

Table VII
Comparative Data for the Calculation of Characteristic Ratio C_N

w	step η	C_N extrap	C_N prop	C_N Monte Carlo	comments
0		11.9367		10.2	linear extrapolation; step size independent
0.1	−0.025	134.149	8.618	8.3-9.8	step size −0.025 is unreasonable;
	−0.05	11.380			step −0.06 is optimal and was
	−0.06	10.1725			chosen as initial correct step
	−0.01	9.45607			
0.25	−0.06	8.0399	5.736	7.5-8	choice of step −0.06 from (5.12)
0.5	−0.05	7.02877		7.5-8.5	choice of steps −0.05 and −0.045
	−0.045	7.165579			from (5.12)
	−0.04				
0.75	−0.035	7.32629		10-12	choice of both steps from (5.12)
	−0.03	9.061			
0.85	−0.03	8.10852		15-17	choice of −0.028 and −0.025 from
	−0.028	9.5873			(5.12); average C_N extrap =
	−0.025	25.0696			17.32847
0.9	−0.025	19.936		19-23	
0.95	−0.025	21.22409	divergent	28-38	choice of step −0.02 from (5.12)
	−0.023	43.4782			
	−0.020	40.3585			
1.0		67.7865			linear extrapolation; step size independent

procedure. Table IV shows that data for $w = 0$ and $w = 1$ exhibit a clear linear dependence of the form $a + \alpha b$, so that the term with $n = 4$ is unnecessary. The values of w in Table IV are chosen to coincide with those given in Flory's book.[1] Tables V and VI contain additional calculated data for the propagation and extrapolation methods. The propagation method employs three terms in the logarithmic expansion (6.3). The estimate $\ln \langle Z(w) \rangle$ is used for the denominator (see formula 4.13). *The propagation method by itself may be sufficient for calculating the free energy* (see formulas 4.4 and 4.5), but Table VII shows that it can be employed for the characteristic ratio only for the rather small values of w ($w \lesssim 0.1$).

The data in Table VI exhibit increasing deviations from linearity as w increases. This feature suggests the existence of large fluctuations in the characteristic ratio for individual random monomer sequences with this value of w. The fluctuations are also reflected by larger statistical errors in the Monte Carlo calculations for these values of w. The large nonlinearity of the extrapolation and the fluctuations inducing them are demonstrated explicitly in Table VII, where for $w = 0.85$ and 0.95 slight changes in the step length η produce large shifts, and hence uncertainties, in the extrapolated result. Another reflection of the singular behavior for $w \to 1$ is the divergence of the three-term propagation expansion for C_N in the neighborhood of $w = 0.95$. The propagation method for $w = 0.975$, using the data in Table IV, gives a divergent result also.

The $n \to 0$ extrapolation method appears to produce reasonably reliable results when combined with the propagation method for small w if the extrapolation is fairly linear over the extrapolation step length η. This situation prevails for $w \lesssim 0.5$ and probably results from having the distribution of characteristic ratios over the ensemble of random monomer sequences be a fairly narrow one. For $w > 0.5$ the distribution probably becomes rather broad; the extrapolation becomes more nonlinear with larger errors and the Monte Carlo calculations also exhibit larger statistical errors. We believe these features to be general aspects of the $n \to 0$ extrapolation procedure. Other model examples with well-defined characteristic ratios for $w = 0$ *and* $w = 1$ (or $p = 0$ *and* $p = 1$) would have the benefit of enabling the extrapolation–propagation procedure to begin at the exactly known $w = 0$ and $w = 1$ (or $p = 0$ and $p = 1$) limits, working toward $w = {}^1/_2$ (or

Table VIII
Parameters of G^{ij} Matrices for the L-Alanine-Glycine System[a]

		G^{AA}		
1.0	0.49	0.19	0.6	0.0
0.0	0.49	0.19	0.6	1.0
0.0	−0.1	−0.58	0.22	0.0
0.0	0.66	−0.27	−0.27	0.0
0.0	0.0	0.0	0.0	1.0
		G^{AB}		
1.0	0.49	0.19	0.6	0.0
0.0	0.49	0.19	0.6	1.0
0.0	−1.0	−0.58	0.22	0.0
0.0	0.66	−0.27	−0.27	0.0
0.0	0.0	0.0	0.0	1.0
		G^{BA}		
1.0	0.33	−0.11	0.0	0.0
0.0	0.33	−0.11	0.0	1.0
0.0	−0.16	−0.34	0.0	0.0
0.0	0.0	0.0	−0.11	0.0
0.0	0.0	0.0	0.0	1.0
		G^{BB}		
1.0	0.33	−0.11	0.0	0.0
0.0	0.33	−0.11	0.0	1.0
0.0	−0.16	−0.34	0.0	0.0
0.0	0.0	0.0	−0.11	0.0
0.0	0.0	0.0	0.0	1.0

[a] A designates L-alanine and B, glycine. G^{ij} matrices as calculated by Whittington for his Monte Carlo calculations from the T matrices given by Miller et al.[10]

Table IX
Comparison between Monte Carlo Calculations[a] and Direct Calculations According to Eq A.6

p(L-alanine)	$C_{100}^{MC\,a}$	C_{100}^{exact}	$C_{\infty}^{MC\,a,b}$	$C_{\infty}^{MC\,a,c}$	C_{1000}^{exact}
0.1	2.1053	2.1160	2.1354	2.1290	2.1177
0.2	2.2223	2.2256	2.2665	2.2598	2.2333
0.3	2.3848	2.3886	2.4009	2.3918	2.3990
0.6	2.6048	2.6129	2.6212	2.6385	2.6277
0.5	2.9490	2.9187	2.9194	2.9664	2.9407
0.6	3.3795	3.390	3.3301	3.4454	3.3730
0.7	4.0248	3.9315	4.0280	4.1209	3.9866
0.8	4.9018	4.8048	5.0355	5.1385	4.9900
0.9	6.2271	6.1883	6.3403	6.4592	6.3699

[a] Monte Carlo calculations of Whittington. [b] Extrapolated C_{∞} based on C_{30}^{MC} and C_{100}^{MC}. [c] Extrapolated C_{∞} based on C_{30}^{MC} and C_{100}^{MC}.

$p = {}^1/_2$). The degree to which these two curves join at w (or p) = ${}^1/_2$ is another measure of the internal consistency of the method.

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Appendix

We can readily generalize the random variable method to Markovian copolymers. For this purpose it is useful to define the conditional probabilities

$$\begin{aligned} p_A{}^A &= p_{AA}/p_A \qquad p_B{}^A = p_{AB}/p_B \\ p_A{}^B &= p_{BA}/p_A \qquad p_B{}^B = p_{BB}/p_B \end{aligned} \tag{A.1}$$

having i = {A or B} upper index if i is specified (by lower index on p) and also the quantities $p^{\alpha\beta} = p_{\alpha\beta}p_\alpha p_\beta$ for $\alpha\beta$ = {A, B}. Then we may introduce the random matrix

$$U_i' = p^{AA}u^{AA}c_{i-1}{}^A c_i{}^A + p^{AB}u^{AB}c_{i-1}{}^A c_i{}^B + p^{BA}u^{BA}c_{i-1}{}^B c_i{}^A + p^{BB}u^{BB}c_{i-1}{}^B c_i{}^B =$$

$$(c_{i-1}{}^A c_{i-1}{}^B)U^{(M)}\begin{pmatrix} c_i{}^A \\ c_i{}^B \end{pmatrix} \tag{A.2}$$

with the "doubly conditional" probabilities $p^{\alpha\beta}$ as the c_ic_{i-1} terms eventually introduce the monomer probabilities. Following the same steps as in (2.16) and (2.17), with U_i' and $U^{(M)}$ instead of unprimed quantities, we readily find that the monomer sequence average of $\prod_{i=1}^N U_i'$ is

$$\left\langle \prod_{i=1}^N U_i' \right\rangle = (1, 1)[U^{(M)}]^N \begin{pmatrix} p \\ 1-p \end{pmatrix} \tag{A.3}$$

with $U^{(M)}$ readily obtained as

$$U^{(M)} = \begin{pmatrix} pp^{AA}u^{AA} & pp^{AB}u^{AB} \\ (1-p)p^{BA}u^{BA} & (1-p)p^{BB}u^{BB} \end{pmatrix} = \begin{pmatrix} p_A{}^A u^{AA} & p_A{}^B u^{AB} \\ p_B{}^A u^{BA} & p_B{}^B u^{BB} \end{pmatrix} \tag{A.4}$$

The leftmost factor in (A.3) sets the probability for the last monomer on the chain (the Nth); then each factor of $U^{(M)}$ contains the conditional probabilities for successive monomer units $i + 1$ given the already specified i. The quantity l^2 must now be written as in (6.2).

The validity of random variable method is independently tested for the Bernoullian type of copolymer L-alanine–glycine with independent bond rotations. In this case the transformation matrices between adjacent monomers are still composition dependent. But unlike the general case, now it is possible to perform the C-averaging independently for both numerator and denominator. This yields great simplifications. In particular, we may start now from the basic formula[1,11-14] (compare to 3.1)

$$C_N = \frac{\langle R_N{}^2\rangle}{Nl^2} = 1 + \frac{2}{Nl^2}(1 \;\; 0 \;\; 0 \;\; 0 \;\; 0)\prod_{i=1}^{N-1} G_i \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 1 \end{pmatrix} \tag{A.5}$$

where

$$G_i = \begin{pmatrix} 1 & l_i\langle T_i\rangle & 0 \\ 0 & \langle T\rangle & l_i \\ 0 & 0 & 0 \end{pmatrix} \tag{A.5a}$$

and

$$\langle T_i\rangle = \int\int\int d\psi\, d\chi\, d\varphi\, T_i(\varphi,\chi,\psi) \times \exp\{-\beta E(\varphi,\psi,\chi)\} / \int\int\int d\psi\, d\chi\, d\varphi \exp\{-\beta E(\varphi,\psi,\chi)\} \tag{A.5b}$$

Introduction of random c_i numbers, like in (2.6), immediately yields for random copolymer

$$\langle C_N\rangle_c = 1 + \frac{2}{Nl^2}\mathcal{J}^*[L^{(p)}]^{N-1}\mathcal{J} \tag{A.6}$$

where

$$\mathcal{J}^* = (1 \;\; 0 \;\; 0 \;\; 0 \;\; 0 \;\; 1 \;\; 0 \;\; 0 \;\; 0 \;\; 0) \quad \text{(row vector)}$$

$$\mathcal{J} = (0 \;\; p \;\; 0 \;\; 0 \;\; p \;\; 0 \;\; (1-p) \;\; 0 \;\; 0 \;\; (1-p)) \quad \text{(column vector)} \tag{A.6a}$$

and

$$L^{(p)} = \begin{pmatrix} pG^{AA} & pG^{AB} \\ (1-p)G^{BA} & (1-p)G^{BB} \end{pmatrix} \tag{A.6b}$$

The Monte Carlo data for the L-alanine–glycine system were provided by Whittington.[2] He uses an ensemble of random copolymers, each of 100 units having an effective step length $|\mathbf{l}_i| = 1$. The numerical vs. Monte Carlo results presented in the Table IX serve as a nice illustration of the use of random variable methods. Table VIII provides supplemental information regarding to this case. Additional information can be found in ref 11–14.

References and Notes

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