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Effect of Segment–Segment Association on Chain Dimensions

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ABSTRACT: When clusters each consisting of m repeat units form in bulk polymer or polymer solution, as do ion pairs in ionomers, there is an increase in chain dimensions. Dimensions in this work are characterized by an expansion factor α, where $\alpha^2 = \langle L^2 \rangle / \langle L^2 \rangle_0$, the ratio of mean-square end-to-end distance between the neighboring units along the chain backbone that participate in cluster formation to the analogous value in the absence of cluster formation. Statistical considerations show that, as long as $\alpha \leq 2$, $\alpha^2 - 1 = \phi m^{2/3} f^{1/2} [1 + \psi (v_2 f)^{2/3}]$. The dimensionless factor ϕ is equal to $(CN_A)^{-2/3} M_0^{-1/3} (2\kappa)^{-1}$, where C is concentration, N_A is Avogadro's number, M_0 is the molecular weight of a repeat unit, and κ is the proportionality factor between the unperturbed mean-square end-to-end distance and the molecular weight. The dimensionless factor ψ is determined by the geometry of the clusters. It is equal to 0.770 for spheres and increases with increasing asymmetry of the clusters; f and v_2 are the fraction of repeat units participating in cluster formation and the volume fraction of polymer. Statistical thermodynamics is used to predict α and m for clusters of simple geometry. For lamellar clusters, it was found that $m^{1/2} = (\theta_2/4A)\{1 + [1 - 16A(1 - \ln C\bar{v}f)/\theta_2{}^2]^{1/2}\}$, where $A = (\alpha^4 - \alpha^2 + 1)/\alpha^2$, θ_2 is a dimensionless measure of the surface energy of a cluster, and $\bar{v}$ is the specific volume of the polymer.

Introduction

In a recent publication, Earnest, Higgins, Handlin, and MacKnight[2] showed that clustering of ionic groups in sulfonate ionomers is accompanied by an increase in the mean radius of gyration of the polymer chains. Indeed, they reported that chain extension increased monotonically with increasing ion content. Although this observation is clearly of great importance in understanding the nature of ionomers, its implications are far broader in scope. The results of these experiments imply that other polymer systems in which there is extensive chain overlap and where there are loci of strong interaction distributed along the chain backbone may demonstrate greater chain dimensions than in the absence of such loci. Other such systems include solutions of ionomers and aqueous solutions of polymer containing a small percent of hydrophobic groups (either as repeat units or units pendent to the chain).

In this paper, we present a statistical mechanical treatment of the effect of segment–segment association on the dimensions of polymer molecules. We restrict the discussion to molecules that are sufficiently flexible to be described as random flight chains. For solutions, we will assume that the polymer concentration is sufficiently large that the system can be described as a uniform distribution of polymer repeat units throughout the solution. That is, equal elements of volume that are large compared to the volume of a repeat unit but no larger than the hydrodynamic volume of entire chains contain equal numbers of repeat units. This condition is met if there is sufficient overlap of the repeat units of any given chain with those of its neighbors. The criterion[3] for chain overlap is $C[\eta] > 1.0$. If $C[\eta] > 10.0$, there is such extensive chain overlap that polymer solutions are on the borderline of being entangled (see Figures 4 and 5 of ref 3). The theory developed in this paper is only correct insofar as the assumption of uniform density of repeat units holds. Considering the criterion for chain overlap,[3] we can say that if $10 \geq C[\eta] \geq 1.0$, the uniform segment density model is a good approximation and that if $C[\eta] > 10$, it is a precise description of a solution.

Model and General Approach

The aim of the following analysis is to compare the conformational statistics of an assembly of linear, flexible polymer molecules that have localized sites for polymer–polymer interaction along the chain backbone (interacting molecules) with the conformational statistics of an assembly of hypothetical reference molecules. The reference molecules are defined as being identical with the interacting molecules in every respect except that they do not have the loci of strong interaction. The conformational statistics of the two assemblies would be different, and the difference would depend upon the nature of the loci of strong interaction. If, for example, we consider a solution of a copolymer of ethylene and a small amount of acrylic acid in a nonpolar solvent, carboxyl–carboxyl hydrogen bond formation would be a strong driving force for dimerization of the carboxylic acid groups. If, on the other hand, we consider an aqueous solution of a copolymer prepared from mostly the sodium salt of acrylic acid and a small amount of an olefin, the olefin repeat units could form clusters of 2, 3, 4, or possibly many more units through hydrophobic bonding. Eisenberg[4] has presented strong arguments for cluster formation in ionomers in the solid state. Whether or not the interacting repeat units are limited to dimerization or can associate to form large clusters would play an important role in the analysis of the conformational statistics of the assembly.

In relating the theoretical treatment to experiment, we could choose the interacting molecules to be, for example, those of an ionomer prepared from polystyrene by sulfonating a small fraction of the pendent phenyl groups and neutralizing the sulfonic acid groups. A melt or solution of such an ionomer would interact strongly through ion pair association at loci along the chain backbone.[2] We could, then, compare the conformational statistics of an assembly of such ionomer molecules with the statistics of an identical assembly of polystyrene molecules. It is important to note, however, that the assembly of polystyrene molecules would only serve as a good approximation to the reference polymer since the reference polymer is defined as the ionomer stripped of the ionic forces associated with the ion pairs and not the ionomer stripped of the molecular volume and van der Waals forces associated with its sulfonate salt groups. Nonetheless, considering the assembly of polystyrene molecules as the reference polymer would be justified if the fraction of sulfonated phenyl groups in the polystyrene ionomer were sufficiently small.

The theory developed here applies only to polymer melts or solutions at concentrations greater than the critical concentration for chain overlap.[3] We thus include only solutions that can be modeled, at least to a very good first approximation, as having a uniform distribution of repeat

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units throughout the entire volume occupied by the solution. For both melts and solutions considered in this paper the mean-square end-to-end distance of monodisperse reference chains is directly proportional to their molecular weight.[5] This implies that the reference polymer chains demonstrate Gaussian statistics. In the analysis to follow, we will refer to the lengths of chain connecting interacting repeat units as subchains; f will be the fraction of the repeat units involved in cluster formation.

To make the analysis tractable, we introduce four approximations: (1) Interacting repeat units are equally spaced along the chain backbone. (2) Gaussian statistics apply to the subchains connecting interacting groups as well as to entire molecules. (3) Every cluster contains the same number of repeat units. (4) Each cluster is formed only from those repeat units which would be the m nearest neighbors in the absence of cluster formation. Approximation 4 is equivalent to specifying that the clusters of m repeat units are formed in such a way as to minimize the deviation from the equilibrium statistics of the reference chains and thus minimize the free energy of cluster formation.

Approximation 2 restricts the theory to real polymer systems for which $f \leq 0.05$. This would correspond to subchains of at least 20 noninteracting repeat units, which should correspond to chains reasonably well approximated by Gaussian behavior.[6]

We begin the analysis by first considering a solution or melt of the reference chains at thermodynamic equilibrium. The assembly of reference chains would have well-defined distributions of radii of gyration, end-to-end distances, etc. We replace the reference chains by an identical assembly of interacting chains, but the assembly of interacting chains is to be distributed in every respect as the assembly of reference chains. It is then imagined that the interacting chains are allowed to come to a new equilibrium through cluster formation, with clusters forming from nearest-neighbor interacting repeat units. We first determine the effect of this cluster formation on the mean-square end-to-end distance between interacting repeat units and thus on the mean-square end-to-end distance of the assembly of molecules. Rubber elasticity theory then supplies the entropy change ΔS_r due to end-to-end extension of the chain molecules. To this must be added ΔS_a, the loss in entropy associated with confining repeat units to aggregates (or clusters) when they could otherwise be located quite independently anywhere in the solution or bulk polymer. This second entropy term has an analogue in the dimerization, trimerization, etc. of small-molecule species. To these entropy effects will then be added a van Laar energy of association (or cluster formation), ΔE. This term is written as an energy but could include a local entropy contribution and would be better interpreted as a free energy.

The free energy of association, or cluster formation, is thus written

$$\Delta G = \Delta E - T\Delta S_a - T\Delta S_r \tag{1}$$

It will be assumed that there is no change in volume of the system with cluster formation so that ΔG represents both Helmholtz and Gibbs free energies.

This paper will deal with one special case of the more general theory—sufficiently strong loci of interaction that *every* interacting repeat unit is involved in cluster formation. For this special case f is equal to the fraction of repeat units of the interacting polymer that carry loci of interaction. This restriction, along with approximations 1–4 given above, and a model for ΔE imply that the only degree of freedom in calculating ΔG is then the number of repeat units in each cluster, m. The value of m that minimizes ΔG is assumed to be that which is observed experimentally. The analysis then gives $\langle L^2\rangle/\langle L^2\rangle_0$, the ratio of mean-square end-to-end distances of the subchains connecting repeat units in clusters to that of the subchains of the hypothetical reference molecules, and m as functions of ΔE.

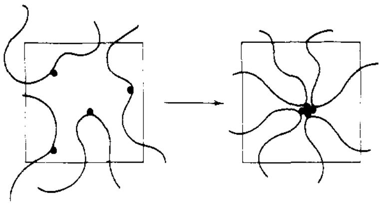

Figure 1. Formation of a cluster of four repeat units from a central repeat unit and its three nearest neighbors.

Cluster Formation and ΔS_r

Analysis of the effect of cluster formation on chain statistics requires a measure of the distance interacting segments move from their (otherwise) equilibrium positions in cluster formation. To develop such a measure, we will assume that after cluster formation, each cluster will lie somewhere in the unit cell of a cubic lattice of dimension l. The volume assigned to each cluster, $\delta V = l^3$, will thus be assumed to have been occupied by the m nearest neighbor interacting groups before they associated to form a cluster. By the definition of δV, it follows that

$$\delta V = M_0 m / C N_A f = l^3 \tag{2}$$

where M_0 is the molecular weight of a repeat unit, f is the fraction of repeat units involved in cluster formation, and N_A is Avogadro's number. Formation of a cluster of four repeat units is shown in Figure 1.

Discrete probabilities are used to initiate the analysis. In the absence of cluster formation, the probability that the x component of a subchain vector lies in an interval δx about a value x is given by

$$W_0(x)\delta x = \frac{\beta}{\pi^{1/2}} e^{-\beta^2 x^2} \delta x \tag{3}$$

The Gaussian parameter characterizing the end-to-end distance vector of reference molecules of n subchains is $\beta/n^{1/2}$. Identical distributions functions can be written for the y and z directions.

The value of the dimensionless product βl determines much about the nature of the problem and its solution. For example, it determines the probability that the two ends of any given subchain occupy the same lattice volume. If $\beta l \ll 1$, it is clear that one can assume that every subchain has its two ends in different lattice volumes, whereas if βl is of order unity, one must account for the likelihood that both ends of any subchain occupy the same lattice volume. In addition, another consequence of the condition $\beta l \ll 1$ greatly simplifies the analysis of the effect of cluster formation on the mean-square end-to-end distance of the subchains. Consider one end of a subchain before cluster formation. Since we can locate the lattice anywhere in space, it is obvious that the distribution function for locating the first end of the subchain is constant everywhere within its lattice volume. In addition, if $\beta l \ll 1$ the distribution function $W_0(x)$ would vary only negligibly over a distance equal to l, and the probability distribution for locating the second end of the subchain would also be (essentially) constant everywhere within its lattice volume. This does not imply, of course, that the constant probability would be the same for all lattice volumes in which

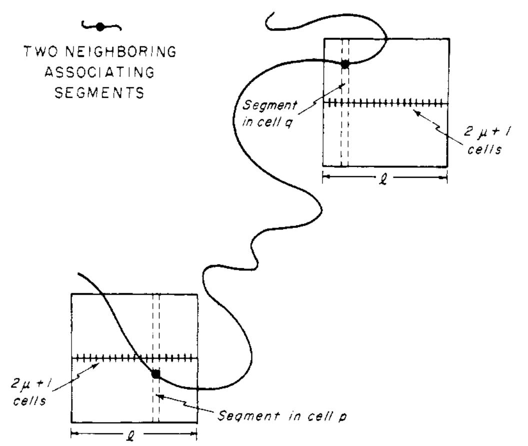

Figure 2. Side view of two lattice volumes containing neighboring repeat units which participate in cluster formation.

the second end of the subchain might fall.

The assumption that there is a constant probability of locating any end of any subchain anywhere within the lattice volume it occupies is essential to the development presented in this section. In principle, therefore, the conclusions are valid only in the limit as $\beta l \rightarrow 0$. In practice, however, the results are valid up to a surprisingly large value of βl. The Appendix gives a more general analysis of the effect of cluster formation on the mean-square end-to-end distance of the subchains. It is shown that the small-βl analysis is quantitatively correct as long as $\beta l \leq 1$, less than 5% in error if $1 < \beta l < 1.75$, and less than 10% in error if $1.75 < \beta l < 2$.

Since the problem is initiated in a discrete probability space, the x axis of each lattice volume is divided into $2\mu + 1 = s$ cells of length $l/(2\mu + 1)$. Before the two ends of any subchain enter into cluster formation they will be found in certain lattice volumes, and according to the model described above, they remain in their respective lattice volumes after cluster formation. If $\beta l \ll 1$, it would be equally likely to find the x component of either end in any cell within their lattice volumes before cluster formation. It might be added that since we are considering the case where $\beta l \ll 1$, it would be highly unlikely to find both ends of a subchain in the same lattice volume.

Determining the effect of cluster formation on the x component of the mean-square end-to-end distance vectors of the subchains is a two-step process. We first imagine that the x component of one end of each subchain of the assembly is shifted into cell p and the x component of the other end into cell q of their respective lattice volumes regardless of which cells they fall in before the shift. This shifting of subchain ends will clearly change the distribution function for the x component of the end-to-end distance vectors and its mean-square value. The new mean-square value will be denoted as $\langle x^2\rangle'$, with the prime indicating that this value applies to some arbitrarily fixed pair of cells p and q. In the next step, we account for the fact that every pair of subchain ends is not fixed in cells p and q within clusters. To proceed further, then, we assume that either end of any subchain selected at random would have an equal probability of being anywhere within a cluster; values of $\langle x^2\rangle'$ must thus be averaged over all p and q that fall within a cluster to determine $\langle x^2\rangle$, the mean-square x component of the end-to-end distance vector after cluster formation. It is clear that although $\langle x^2\rangle'$ is independent of the cluster model, $\langle x^2\rangle$ will depend upon the cluster geometry.

Determining how p, q, and l fix $\langle x^2\rangle'$ proceeds as follows: Since it is equally probable that the first end of a subchain is in any one of the $2\mu + 1$ cells before it is fixed in cell p, there are exactly $2\mu + 1$ equally probable shifts that could place it in that cell. The distances of these shifts measured in cell lengths are $(\mu + p)$, $(\mu - 1 + p)$, $(\mu - 2 + p)$, ..., (0), ..., $(-\mu + 2 + p)$, $(-\mu + 1 + p)$, and $(-\mu + p)$. Likewise there are exactly $2\mu + 1$ equally probable shifts of the second end that could have placed it in cell q. The distances of these shifts measured in cell lengths are $(\mu + q)$, $(\mu - 1 + q)$, $(\mu - 2 + q)$, ..., (0), ..., $(-\mu + 2 + q)$, $(-\mu + 1 + q)$, and $(-\mu + q)$. Any pair of shifts of the two ends that are not equal will change the x component of the end-to-end distance vector of the subchain. There are a total of $(2\mu + 1)^2$ combinations of shifts. For example, if the first end is shifted by $(\mu + p)$ and the second end by $(\mu + q)$, the change in the x component of the end-to-end distance vector is $(p - q)$ cell lengths. The $(2\mu + 1)^2$ equally probable changes in the x component of the end-to-end distance vectors are tabulated in matrix form below:

$$\begin{array}{lllll}
(p-q) & (1+p-q) & \cdots & (2\mu-1+p-q) & (2\mu+p-q) \\
(-1+p-q) & (p-q) & \cdots & (2\mu-2+p-q) & (2\mu-1+p-q) \\
(-2+p-q) & (-1+p-q) & \cdots & (2\mu-3+p-q) & (2\mu-2+p-q) \\
\cdots & \cdots & \cdots & \cdots & \cdots
\end{array}$$

There are s diagonal terms in the above matrix, and each is associated with a shift of $(p - q)$ cell lengths; $s - 1$ terms are associated with a shift of $(1 + p - q)$ and $s - 1$ terms associated with a shift of $(-1 + p - q)$ cell lengths; $s - 2$ terms are associated with a shift of $(2 + p - q)$ and $s - 2$ terms associated with a shift of $(-2 + p - q)$ cell lengths; etc.

If eq 3 describes the distribution of the x component of the vector before the end points are fixed at p and q, the distribution after the end points are fixed is the following sum of s^2 shifted Gaussians:

$$\begin{aligned}W(x) = \frac{\beta^{1/2}}{\pi^{1/2}s^2}[&se^{-\beta^2(x+\nu d)^2} + (s-1)e^{-\beta^2(x+d+\nu d)^2} + \\ &(s-2)e^{-\beta^2(x+2d+\nu d)^2} + \ldots + e^{-\beta^2(x+sd+\nu d)^2} + \\ (s-1)e^{-\beta^2(x-d+\nu d)^2} &+ (s-2)e^{-\beta^2(x-2d+\nu d)^2} + \ldots + e^{-\beta^2(x-sd+\nu d)^2}]\end{aligned} \tag{4}$$

where

$$\nu = p - q \tag{5}$$

$$d = l/s \tag{6}$$

After the ends of the assembly of subchains are fixed in cells p and q, the mean-square value of the x component of their end-to-end distance vector is given by

$$\langle x^2\rangle' = \int_{-\infty}^{+\infty} x^2 W(x)\,\mathrm{d}x \tag{7}$$

Substituting eq 4 into eq 7 and integrating gives

$$\begin{aligned}\langle x^2\rangle' &= \frac{1}{s^2}[s^2\langle x^2\rangle_0 + sd^2\nu^2 + (s-1)d^2(1+\nu)^2 + \\ &(s-2)d^2(2+\nu)^2 + \ldots + d^2(s+\nu)^2 + (s-1)d^2(1-\nu)^2 + \\ &\qquad (s-2)d^2(2-\nu)^2 + \ldots + d^2(s-\nu)^2] \\ &= \langle x^2\rangle_0 + \frac{d^2}{s^2}[s\nu^2 + 2(s-1)(1+\nu^2) + 2(s-2) \times \\ &\qquad (2^2+\nu^2) + 2(s-3)(3^2+\nu^2) + \ldots + 2(s^2+\nu^2)]\end{aligned} \tag{8}$$

where

$$\langle x^2\rangle_0 = \int_{-\infty}^{+\infty} x^2 W_0(x)\,\mathrm{d}x = (2\beta^2)^{-1} \tag{9}$$

Since $d = l/s$, the sum in eq 8 becomes an integral as $s \rightarrow \infty$. In taking the limit, however, we require p and q to remain proportional to s. The ratio $r = (p - q)/s$ is thus a constant and the final result is

$$\langle x^2\rangle' = \langle x^2\rangle_0 + \frac{l^2}{6}(1 + 6r^2) \qquad (10)$$

The two ends of all subchains would not have their x components fixed in cells p and q respectively within their lattice volumes. Indeed, it was assumed they were distributed at random throughout the volume of the clusters. To account for this distribution of subchain ends within the clusters, we first consider all the clusters to be of the same shape and to have the same orientation on the lattice. We then examine the x-axis projections of chords passing through the clusters. In view of the above assumption, it would then be equally probable that subchain ends that lie on a given chord would be located anywhere along its length. Given two chords, then, one can easily calculate the mean-square value of r for all of the subchains with one end on the first chord and the other end on the second. We will designate that mean-square as $\langle r^2\rangle'$. Then, however, one must average over all possible pairs of chords associated with fixed cluster orientations and all possible cluster orientations to obtain $\langle r^2\rangle$. Once obtained, however, $\langle x^2\rangle$ can be written

$$\langle x^2\rangle = \langle x^2\rangle_0 + \frac{l^2}{6}(1 + 6\langle r^2\rangle) \qquad (11)$$

Analysis of complex cluster shapes with random orientation is beyond the scope of this paper. We will, however, consider simple cases that illustrate general behavior. For simplicity, only clusters of some symmetry will be considered. For the analysis the origin of the coordinate system will be taken at the center of the clusters. Because of cluster symmetry, we can write

$$\begin{aligned} P_1(x_1) &= \frac{1}{\zeta} \qquad \text{if } -\frac{\zeta}{2} \le x_1 \le \frac{\zeta}{2} \\ &= 0 \qquad \text{otherwise} \end{aligned} \qquad (12a)$$

$$\begin{aligned} P_2(x_2) &= \frac{1}{\xi} \qquad \text{if } -\frac{\xi}{2} \le x_2 \le \frac{\xi}{2} \\ &= 0 \qquad \text{otherwise} \end{aligned} \qquad (12b)$$

where $P_1(x_1)$ is the probability distribution for finding one end of a subchain on chord one of length ζ and $P_2(x_2)$ is the probability distribution for finding the other end of the subchain on chord two of length ξ. For all subchains with their two ends located on chords of length ζ and ξ we can then write

$$\langle r^2\rangle' = \frac{1}{l^2}\int_{-\zeta/2}^{+\zeta/2}\int_{-\xi/2}^{+\xi/2}\frac{(x_1 - x_2)^2}{\zeta\xi}\,\mathrm{d}x_1\,\mathrm{d}x_2 = \frac{\zeta^2 + \xi^2}{12l^2} \qquad (13)$$

The simplest cluster geometry would be cubic clusters aligned with their edges parallel to the lattice. For that example

$$\langle r^2\rangle = \langle r^2\rangle' = a^2/6 \qquad (14a)$$

where

$$a = \zeta/l = \xi/l \qquad (14b)$$

For this case

$$\langle x^2\rangle = \langle x^2\rangle_0 + \frac{l^2}{6}[1 + a^2] \qquad (15)$$

and

$$\langle L^2\rangle = \langle L^2\rangle_0 + \frac{l^2}{2}[1 + a^2] \qquad (16)$$

If we let v_2 be the volume fraction of polymer and M_0/f the molecular weight of the subchains, we can write

$$\langle L^2\rangle_0 = \kappa M_0/f \qquad (17)$$

where κ is the proportionality constant between the mean-square end-to-end distance and the molecular weight and

$$a^2 = (v_2 f)^{2/3} \qquad (18)$$

(assuming no change in volume on cluster formation)

$$\alpha^2 = \langle L^2\rangle/\langle L^2\rangle_0 \qquad (19)$$

The result is

$$\alpha^2 = 1 + \left(\frac{m}{CN_\mathrm{A}}\right)^{2/3}\left(\frac{f}{M_0}\right)^{1/3}\frac{1}{2\kappa}[1 + (v_2 f)^{2/3}] \qquad (20)$$

(oriented, cubic clusters)

It should be noted that the term $(v_2 f)^{2/3}$ need not be included if $v_2 \ll 1$. Even in bulk polymer it contributes less than 5% to the term in square brackets if $f < 0.01$.

In general, the clusters would not be cubic, and even if they were, they could not be assumed to be aligned with a hypothetical lattice system except in the case of highly oriented material. More realistic models would be those in which the clusters would either be spherical or have some well-defined shape and oriented at random.

The next simplest cluster model is spherical clusters of radius R. The probability of a chord parallel to the x axis passing through the sphere, $P_3(y,z)$, is

$$\begin{aligned} P_3(y,z) &= 1/\pi R^2 \qquad \text{if } y^2 + z^2 \le R^2 \\ &= 0 \qquad \text{otherwise} \end{aligned} \qquad (21a)$$

and the length of a chord is $2(r^2 - y^2 - z^2)^{1/2}$. Averaging $\langle r^2\rangle'$ over all possible pairs of chords gives

$$\langle r^2\rangle = \int\int\int\int P_3(y_1,z_1)P_3(y_2,z_2)\rho(y_1,z_1,y_2,z_2)\,\mathrm{d}y_1\,\mathrm{d}z_1\,\mathrm{d}y_2\,\mathrm{d}z_2 \qquad (21b)$$

where $\rho(y_1,z_1,y_2,z_2)$ is $\langle r^2\rangle'$ for a pair of chords passing through the sphere and is a function of y_1, z_1, y_2, and z_2. In this example, chord lengths ζ and ξ in eq 13 are replaced by $2(R^2 - y_1^2 - z_1^2)^{1/2}$ and $2(R^2 - y_2^2 - z_2^2)^{1/2}$, respectively. Substituting this expression for $\rho(y_1,z_1,y_2,z_2)$ into eq 21b and integrating gives

$$\langle r^2\rangle = R^2/3l^2 \qquad (22)$$

Given this expression for $\langle r^2\rangle$, eq 20 can be modified to apply to spheres by replacing $(v_2 f)^{2/3}$ by $2(3/4\pi)^{2/3}(v_2 f)^{2/3} = 0.770(v_2 f)^{2/3}$.

Integrating over all orientations of other shapes gives results not expressible in simple closed form. But to illustrate the effect of shape, one can assume that the clusters are oriented with their axes pointing only along the three orthogonal axes of the lattice system, with all three orientations being equally probable. For example, consider a rectangular solid with three orthogonal dimensions L, L, and D. It is easy to show that

$$\langle r^2\rangle = \tfrac{1}{18}(2L^2 + D^2) \qquad (23)$$

For this example the term $(v_2 f)^{2/3}$ in eq 20 is replaced by

$$[(2q^2 + 1)/3q^{4/3}](v_2 f)^{2/3} \qquad (24)$$

where

$$q = L/D \qquad (25)$$

To express the general case, it is thus convenient to replace the term $(v_2 f)^{2/3}$ in eq 20 by $\psi(v_2 f)^{2/3}$, where the value of ψ depends upon the shape of the cluster. In the last example if $q = 10$, $\psi = 3.09$ and if $q = 0.1$, $\psi = 7.33$.

In summary, then, we write

$$\alpha^2 = 1 + \left(\frac{m}{CN_A}\right)^{2/3}\left(\frac{f}{M_0}\right)^{1/3}\left(\frac{1}{2\kappa}\right)[1 + \psi(v_2f)^{2/3}] \quad (26)$$

where ψ is a measure of the symmetry of the clusters. It increases from a value from 0.770 for spheres to substantially larger values for highly asymmetric clusters. It is convenient, however, to express eq 26 in the simplified form

$$Z = \phi m^{2/3} f^{1/3}[1 + \psi(v_2f)^{2/3}] \quad (27)$$

where

$$Z = \alpha^2 - 1$$

$$\phi = (CN_A)^{-2/3}(M_0)^{-1/3}(2\kappa)^{-1} \quad (28)$$

Equation 4 indicates that the distribution of vector lengths between neighboring segments that are associated in clusters is non-Gaussian. Nonetheless we will take the equation of rubber elasticity[7] as a first approximation to ΔS_r. The result is

$$\Delta S_r = -\frac{3CfR}{2M_0}[Z - \ln(1 + Z)] \quad (29)$$

Entropy of Localization

Segment–segment association decreases the entropy of the system in a way quite independent of the rubber elasticity effect discussed above. In the absence of association, the segments are independent of one another and could exist anywhere within the volume of the system (consistent with the chain structure of the molecules). Upon association, however, some of the segments are constrained to remain as dimers, trimers, tetramers, etc., reducing the number of complexions available to the system. This is not unlike the decrease in entropy associated with dimerization or trimerization of small-molecule species.

The argument leading to an estimation of this entropy effect, ΔS_a, is most easily framed in terms of a disaggregation process. We will imagine that the aggregates, or clusters, are distributed on a lattice as described above. Each lattice volume is divided into $\mathcal{N}_1$ cells. The volume of a cell equals that of a repeat unit; i.e.

$$\mathcal{N}_1 = \delta V/v_0 = m/C\bar{v}f \quad (30)$$

where v_0 is the molecular volume of a repeat unit and $\bar{v}$ is the specific volume of the polymer. Each cluster thus has $\mathcal{N}_1/m$ available locations within the lattice volume. Upon disaggregation of one cluster, the m repeat units in the given lattice volume can be distributed on $\mathcal{N}_1$ locations. If Ω_{a1} and Ω_{b1} are the number of complexions available to the given cell volume before and after disaggregation, we can write

$$\Omega_{a1} = \mathcal{N}_1/m \quad (31)$$

$$\Omega_{b1} = \mathcal{N}_1(\mathcal{N} - 1)(\mathcal{N} - 2)...(\mathcal{N}_1 + 1 - m) \quad (32a)$$

Or, if $\mathcal{N}_1 \gg m$, eq 32a can be rewritten

$$\Omega_{b1} = \mathcal{N}_1{}^m \quad (32b)$$

with negligible error.

It is important to note, however, that eq 32a and 32b hold only if we assume that the m repeat units are still constrained to remain in their original lattice volumes after disaggregation. As long as the neighboring lattice volumes all contain clusters, the disaggregated chains would be locked into a network and would thus have a limited range of mobility and could not diffuse beyond their original lattice volumes.

After the first cluster has been disaggregated, the new equilibrium state of the system is one in which the remaining clusters would each be located in new lattice volumes, slightly larger than the original. The new lattice volumes would contain $\mathcal{N}_2$ cells each where

$$\mathcal{N}_2 = \mathcal{N}_1 N_c/(N_c - 1) \quad (33)$$

where N_c is the number of clusters per unit volume before disaggregation and is equal to CfN_A/mM_0. Corresponding numbers of complexions before and after disaggregating the second cluster would be

$$\Omega_{a2} = \mathcal{N}_2/m \quad (34)$$

$$\Omega_{b2} = \mathcal{N}_2{}^m \quad (35)$$

We thus imagine the disaggregation process to proceed stepwise, with the equilibrium lattice volume containing the clusters increasing each time a cluster is disaggregated. It thus follows that the number of cells per lattice volume after $p - 1$ clusters have been disaggregated, $\mathcal{N}_p$, is given by

$$\mathcal{N}_p = \mathcal{N}_1 \frac{N_c}{N_c - p} \quad (36)$$

For every cluster disaggregated there will be an element of entropy change δS_p, where

$$\delta S_p = k \ln \frac{\mathcal{N}_p{}^m}{\mathcal{N}_p/m} \quad (37)$$

The entropy of disaggregation, which is just $-\Delta S_a$, is given by

$$-\Delta S_a = \sum_{p=0}^{N_c} \delta S_p \quad (38)$$

or

$$\Delta S_a = -\int_{p=0}^{N_c} k \ln (m\mathcal{N}_p{}^{m-1})\, dp \quad (39)$$

when the sum is replaced by an integral. The final result can be written

$$\Delta S_a = \frac{RCf}{M_0}\left[\frac{m-1}{m}\ln\left(\frac{C\bar{v}f}{m}\right) - \frac{(m-1) + \ln m}{m}\right] \quad (40)$$

Strong Interactions

The form of the energy interaction term, ΔE, will depend upon the geometry of the clusters. We will consider only two geometries—spherical and lamellar.

For the spherical case ΔE will consist of two contributions—bulk energies of interaction and surface energies of interaction. Since the number of segments in the bulk is proportional to R^3 and the number of surface interactions is proportional to R^2, we can write

$$\frac{\Delta E}{RT} = -mN_c\left[\theta_1{}^s - \frac{\theta_2{}^s}{m^{1/3}}\right] \quad (41)$$

where $\theta_1{}^s$ and $\theta_2{}^s$ are dimensionless energies characterizing bulk and surface interactions, respectively.

It is possible to be more definitive in modeling ΔE for a lamellar cluster. For simplicity, we will assume that the lamellae are formed from building blocks as shown in Figure 3. Each lamella has two sheets of segments with ν^2 segments in each sheet. It follows that $m = 2\nu^2$. Since this model is appropriate for ionomers, we will assume that the building blocks represent sulfonate or carboxylate ion

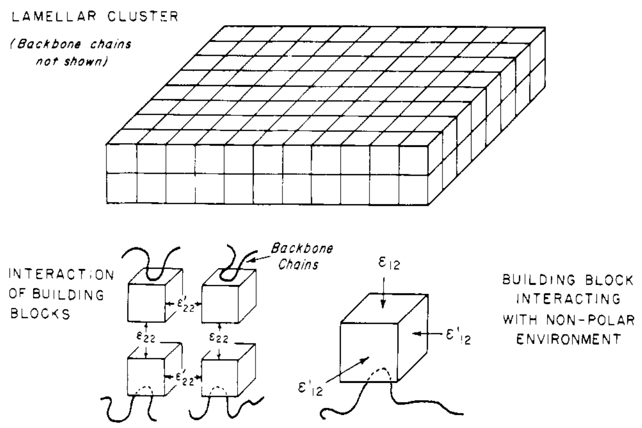

Figure 3. Simplified picture of a lamellar cluster indicating directions of energies of interaction. For clarity, backbone chains connected to top and bottom of the cluster are now shown.

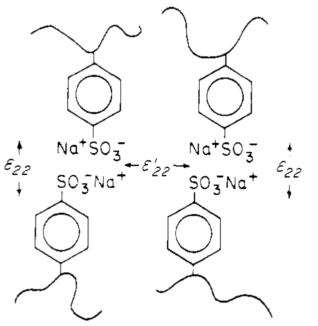

Figure 4. Possible interactions between sodium sulfonate ion pairs.

pairs (with corresponding cations) as shown in Figure 4. Consequently, two different energies of interaction between the ionic groups are required in describing the formation of a lamella. For example, the sodium sulfonate ion pair can interact end-to-end by a strong electrostatic interaction as shown in Figure 4. The segment pairs can then interact laterally to form the lamella; the second interaction energy could well be somewhat weaker—possibly demonstrating a value intermediate between electrostatic and van der Waals interactions. Indeed, one could even expect the end-on and lateral interactions between the polar groups and the nonpolar continuum to be different.

Using this model for interactions in lamellar clusters, we can write

$$\Delta E = N_c\nu^2[\epsilon_{22} + \epsilon_{11} - 2\epsilon_{12} + 4(\epsilon_{22}' + \epsilon_{11} - 2\epsilon_{12}')] - \nu[4(\epsilon_{22}' + \epsilon_{11} - 2\epsilon_{12}')] \quad (42)$$

where ϵ_{11} is the energy of interaction of nonpolar continuum with nonpolar continuum, ϵ_{22} is the end-on interaction energy of two ion pairs, ϵ_{22}' is the lateral interaction energy of two polar groups (assuming ion pairs had already joined as segment pairs), ϵ_{12} is the end-on interaction energy of ion pair with nonpolar continuum, and ϵ_{12}' is the lateral interaction of polar group and nonpolar continuum. Equation 41 is conveniently recast in the form

$$\frac{\Delta E}{RT} = -mN_c\left[\theta_1^l - \frac{\theta_2^l}{m^{1/2}}\right] \quad (43a)$$

$$\frac{\Delta E}{RT} = -\frac{Cf}{M_0}\left[\theta_1^l - \frac{\theta_2^l}{m^{1/2}}\right] \quad (43b)$$

$$\theta_1^l = \frac{-1}{2kT}[\epsilon_{22} + \epsilon_{11} - 2\epsilon_{12} + 4(\epsilon_{22}' + \epsilon_{11}' - 2\epsilon_{12}')] \quad (44)$$

$$\theta_2^l = \frac{-2(2^{1/2})}{kT}[\epsilon_{22}' + \epsilon_{11}' - 2\epsilon_{12}'] \quad (45)$$

In order to include both models for cluster geometry, we will write

$$\frac{\Delta G}{RT} = \frac{Cf}{M_0}\left\{-\left(\theta_1 - \frac{\theta_2}{m^b}\right) - \frac{m-1}{m}\ln\left(\frac{C\bar{v}f}{m}\right) + \frac{(m-1)+\ln m}{m} + \frac{3}{2}[Z - \ln(1+Z)]\right\} \quad (46)$$

where b equals $^1/_3$ for spherical clusters and $^1/_2$ for lamellar clusters.

The value of m that minimizes $\Delta G/RT$ will be taken as the observed value for the system. Differentiating eq 46 with respect to m and setting the result equal to zero gives

$$-\frac{b\theta_2}{m^{b+1}} + \frac{1}{m} + \frac{1}{m^2}[1 - \ln(C\bar{v}f)] + \frac{Z^2}{m(1+Z)} = 0 \quad (47)$$

In the case of spherical clusters, m can be determined as a function of θ_2 by solution of a cubic equation. Since the physical significance of the solution is obscured by the complex analytical expression for the roots of a cubic equation, this example is best studied by a computer analysis of eq 27 and 47. That problem will not be pursued here. For lamellar clusters, however, eq 47 gives the following simple expession for $m^{1/2}$:

$$m^{1/2} = \frac{\theta_2}{4A}\left\{1 + \left[1 - \frac{16A[1 - \ln(Cv_2f)]}{\theta_2^2}\right]^{1/2}\right\} \quad (48)$$

where

$$A = \frac{1 + Z + Z^2}{1 + Z} \quad (49)$$

Equations 27, 48, and 49 can be solved to give Z (or α) and m as a function of f.

Discussion

The simplest example among the cluster models described in the previous section is the case for which θ_1 is large enough to ensure that all interacting groups participate in dimer formation but for which there is negligible driving force for formation of larger clusters from the dimers. The latter condition is ensured if $\theta_2 \le 0$ in the models for spherical and lamellar clusters. No detailed thermodynamics of cluster formation need be considered for this simplest example, and setting $m = 2$ in eq 27 gives Z as a function of f.

If we consider dimer formation in bulk polymer, v_2 is equal to unity. If we take a typical value of ϕ, say $^1/_3$, and set $\psi = 1$, eq 27 becomes

$$Z = 0.529f^{1/3}(1 + f^{2/3}) \quad (50)$$

For $f = 0.001$, 0.01, and 0.05, $Z = 0.053$, 0.192, and 0.221. These chain extensions correspond to $\alpha = 1.026$, 1.092, and 1.105 or about 3, 9, and 10%. These chain extensions would, for example, apply to poly(styrenesulfonic acid) containing 0.1, 1.0, and 5.0 mol % sulfonic acid repeat units as long as all of the sulfonated repeat units are dimerized by acid–acid hydrogen bonds and none of the hydrogen-bonded pairs associate to form larger clusters.

If $\theta_2 > 0$ (for the models presented in the previous section), the equilibrium state may contain clusters of more than two interacting repeat units. Only the case of lamellar clusters will be considered here. An important feature of the analysis for lamellar clusters is that eq 48 gives real values for m only if

$$16A[1 - \ln(C\bar{v}f)]/\theta_2^2 \le 1 \quad (51)$$

Table I
Critical Values of *f*, *Z*, and *m* for the Lamellar Model

θ_2	f_c	Z_c	m_c
6	0.541	0.404	1.61
7	0.184	0.446	2.36
8	0.0705	0.360	3.33
9	0.0230	0.280	4.50
10	6.52×10^{-3}	0.209	5.82
11	1.63×10^{-3}	0.149	7.86
12	3.65×10^{-4}	0.102	8.83

In addition, eq 46 indicates that unless the above inequality is satisfied, the minimum value of ΔG is given for $m = 2$ (it was assumed that θ_1 was large enough to ensure that $m \geq 2$). These relationships imply that for each value of θ_2, there is a minimum value of *f* below which clusters of $m > 2$ will not form. This critical value of *f*, denoted as f_c, is given by

$$C\bar{v}f_c = e^{1-\theta_2^2/16A_c} \tag{52}$$

where A_c is the value of *A* at f_c. The number of repeat units per cluster at f_c is denoted by m_c. To a first approximation, A_c can be set equal to 1.0 in eq 51. It is, however, easy to solve eq 27, 48, and 51 simultaneously for f_c, Z_c, and m_c. The results for several values of θ_2 for bulk polymer are given in Table I. Parameters ϕ and ψ were set equal to typical values of 0.333 and 1.00, respectively.

Since *m* was treated as a continuous variable in minimizing ΔG, it is unlikely that any computed value of *m* would be a whole number, even though at the outset we assumed that each cluster consisted of the same (whole) number of segments. Considering the various approximations and assumptions used in the development of the theory, it would be pointless to restrict the solution to whole-number values of *m* that minimize ΔG. Furthermore, each cluster in real systems might not be made up of the same number of repeat units. In that case, *m* given by the theory would be interpreted as the average number of repeat units per cluster.

Table I indicates that for $\theta_2 = 6$ and 7 (corresponding to energies of about 3.6 and 4.2 kcal/mol at room temperature) no clusters of $m > 2$ form unless *f* is greater than values for which the theory applies. Since the theory is suspect at 18 mol % and totally inapplicable at 54 mol % interacting repeat units, it is not clear just how large *f* must be before dimers associate into clusters. From the quantitative standpoint, however, it is clear that for such small energies of interaction, no clusters of $m > 2$ will form in polymer unless there is a substantial fraction of interacting repeat units. Theory predicts that $\theta_2 = 8$–9 (energies of 4.8–5.4 kcal/mol at room temperature) represents the borderline for formation of clusters of $m > 2$ for polymer of, say, 10 mol % or less interacting repeat units. For $\theta_2 > 10$ (energies greater than 6.0 kcal/mol at room temperature), clusters of $m > 2$ form in polymer with fractions of interacting repeat units over the entire range of experimental interest.

It is important to remember that the values of m_c listed in Table I represent the number of repeat units per cluster for polymer chains with just a large enough fraction of interacting repeat units to effect formation of clusters of $m > 2$. Table II gives both *m* and *Z* for bulk polymer as functions of *f* for $f > f_c$ for $\theta_2 = 10$, 12, and 15. Comparison of the two tables shows that $m > m_c$ if $f > f_c$. The important feature shown in Table II is, however, that the change in *m* over the entire range of *f* for which the theory applies is not great—only about 30% for $\theta_2 = 15$ over a decade and a half in *f*. It is interesting, however, that *m* can demonstrate a maximum within the range of *f* of experimental interest. The expansion factor increases monotonically with *f*.

Table II
Repeat Units per Cluster and *Z* as Functions of Fraction of Interacting Repeat Units for Stronger Interaction Energies

θ_2	*f*	*m*	*Z*
10	0.007	6.55	0.231
	0.010	7.93	0.299
	0.020	8.93	0.418
	0.030	9.07	0.494
	0.040	9.03	0.552
	0.050	8.94	0.601
12	0.001	14.3	0.199
	0.002	15.6	0.267
	0.003	16.0	0.312
	0.004	16.2	0.347
	0.005	16.2	0.375
	0.006	16.1	0.400
	0.008	16.0	0.441
	0.010	15.9	0.475
	0.020	15.0	0.592
	0.030	14.4	0.671
	0.040	13.8	0.732
	0.050	13.3	0.783
15	0.001	31.6	0.336
	0.002	30.4	0.416
	0.003	29.5	0.469
	0.004	28.8	0.509
	0.006	27.5	0.570
	0.008	26.5	0.617
	0.010	25.8	0.656
	0.020	23.1	0.788
	0.030	21.4	0.877
	0.040	20.2	0.945
	0.050	19.3	1.002

Finally, we note that eq 48 places an upper bound on the number of repeat units in lamellar clusters. As θ_2 gets large we note that *m* approaches but is always less than $(\theta_2/2A)^2$.

Acknowledgment. I express my gratitude to members of the Department of Chemical Engineering and Chemical Technology of Imperial College for their hospitality and assistance during my leave at their institution. In addition, I acknowledge the many stimulating discussions with W. J. MacKnight, who suggested that the relationship between cluster formation and chain dimensions in ionomers might be a challenging theoretical problem. Finally, I thank Mr. Soonyong Hong for doing the computer evaluation of eq A-13.

Appendix. A General Analysis of the Effect of Localizing Subchain Ends on Mean-Square End-to-End Distances

In this development, we will take special account of the possibility that before cluster formation, the two ends of a subchain may occupy the same lattice volume, nearest-neighbor lattice volumes, next-nearest-neighbor lattice volumes, etc. Since, however, each orthogonal component of the end-to-end distance vector of a subchain behaves independently, we need consider only a one-dimensional problem. We thus need to take into account only whether the *x* components of the two subchain ends occupy the same one-dimensional lattice interval, nearest-neighbor lattice intervals, etc. where the intervals of length *l* are laid out along the *x* axis. As before, each lattice interval is divided up into $2\mu + 1 = s$ cells. Also as before, we will be concerned with the effect on the mean square of the *x* component of the subchain vectors when one end is fixed in cell *p* and the other in cell *q*. It is important to re-

Table A-1
Values of R_i and u_i for Gaussian Quadrature with 2–5 Ordinate-Abscissa Pairs

K	i	u_i	R_i
2	±1	0.288675	$^1/_2$
3	0	0	$^4/_9$
	±1	0.387298	$^5/_{18}$
4	±1	0.169991	0.326073
	±2	0.430568	0.173927
5	0	0	$^{64}/_{225}$
	±1	0.269235	0.239314
	±2	0.453090	0.118463

member, however, that the x components of the two ends are fixed in cells p and q within whatever lattice intervals they happen to occupy before they are fixed since the model does not provide for the interacting groups to cross lattice boundaries upon cluster formation. In this development, however, there are no assumptions made about the magnitude of βl.

Those subchains for which both ends occupy the same lattice interval before they are fixed in cells p and q will have the x component of their end-to-end distance vectors equal to $(p - q)l/s$ after they are fixed. Those subchains which, before their ends are fixed, have the x component of one end in a given lattice interval and the other end in the nth lattice interval to the right would have the x component of their end-to-end distance vector equal to $(p - q + ns)l/s$ after the ends are fixed. Those subchains for which the second end is in the nth lattice interval to the left would have the x component of their end-to-end distance vector equal to $(p - q - ns)l/s$. In this development, then, it is convenient to let n run from $-\infty$ to $+\infty$, with negative values of n implying that the second end is in a lattice volume to the left of the first end.

If the x component of one end of a subchain is in the ith cell of the lattice interval it occupies, the probability that the other end is in the same lattice interval, $f_0^{(i)}$, is given by

$$f_0^{(i)} = \int_{-(i-1)l/s}^{[1-(i-1)/s]l} W_0(x)\,\mathrm{d}x \tag{A-1}$$

where the subscript zero on $f_0^{(i)}$ implies that both ends fall within the same lattice interval. If the x component of one end of a subchain is in the ith cell of a given lattice interval, the probability that the other end is in the nth lattice interval to the right, $f_n^{(i)}$, is given by

$$f_n^{(i)} = \int_{[n-(i-1)/s]l}^{[n+1-(i-1)/s]l} W_0(x)\,\mathrm{d}x \tag{A-2}$$

By taking negative values of n, eq A-2 gives the probability of finding the second end of the subchain in the $(-n)$th lattice interval to the left of that occupied by the first end when the first end is in cell i.

Since the probability that the first end of a subchain in any cell is equal to s^{-1}, the probability distribution for the x component of the end-to-end vectors of the subchains after an end is fixed in cell p and the other end in cell q, regardless of what lattice interval the two ends occupy, is written

$$W(x) = \frac{1}{s}\sum_{i=1}^{s}\sum_{n=-\infty}^{+\infty} f_n^{(i)}\delta[x - (p - q + ns)l/s] \tag{A-3}$$

We note that $W(x)$ is normalized since

$$\int_{-\infty}^{+\infty} W(x)\,\mathrm{d}x = \frac{1}{s}\sum_{i=1}^{s}\sum_{n=-\infty}^{+\infty}\int_{[n-(i-1)/s]l}^{[n+1-(i-1)/s]l} W_0(x)\,\mathrm{d}x = \frac{1}{s}\sum_{i=1}^{s}\int_{-\infty}^{+\infty} W_0(x)\,\mathrm{d}x = 1 \tag{A-4}$$

The mean square of the x component of the end-to-end vectors of the subchains after the ends are fixed is

$$\langle x^2\rangle' = \sum_{n=-\infty}^{+\infty}\sum_{i=1}^{s} s^{-1}f_n^{(i)}\int_{-\infty}^{+\infty}\delta[x - (p - q + ns)l/s]x^2\,\mathrm{d}x = l^2\sum_{n=-\infty}^{+\infty}\sum_{i=1}^{s} s^{-1}[r^2 + n^2]f_n^{(i)} \tag{A-5}$$

where

$$r = (p - q)/s \tag{A-6}$$

As in the body of this paper, the prime on $\langle x^2\rangle'$ implies that this mean-square distance applies only when the ends of each subchain are fixed in cells p and q.

Later in the development, we will let the cell size approach zero and s approach infinity. Since r is the relative positions of the two ends of a subchain along the x axis of their respective lattice volumes, it remains fixed as $s \to \infty$.

The integrals of eq A-1 cannot be expressed in closed form. This difficulty can be circumvented, however, by applying Gauss' technique of numerical quadrature.[8] Gauss developed this method to give the most accurate possible numerical integration utilizing a given number of values of the integrand. Values of the independent variable where the integrand is to be evaluated are determined by the range of integration and the number of values of the integrand to be used. It is especially interesting that the values of the independent variable where the integrand is to be evaluated are not equally spaced and that the end points of the range of integration are never used. The Gaussian quadrature is best illustrated by transforming to an independent variable u such that the range of integration is $-^1/_2 \to +^1/_2$. Gauss' technique then expresses the integral over any function $g(u)$ as

$$\int_{-1/2}^{+1/2} g(u)\,\mathrm{d}u = R_1 g(u_1) + R_2 g(u)_2 + \ldots + R_K g(u_K) \tag{A-7}$$

The values of R_j and u_j are completely determined by K, the number of ordinate–abscissa pairs taken. The u's are symmetrically placed with respect to the midpoint of the range of integration and the R's are the same for each symmetric pair of u's. Examples are given in Table A-1. The numerical integration can be made as accurate as desired by taking K sufficiently large. It also turns out that

$$R_1 + R_2 + R_3 + \ldots + R_K = 1$$

$$R_1u_1 + R_2u_2 + \ldots + R_Ku_K = 0$$

$$R_1u_1^2 + R_2u_2^2 + \ldots + R_Ku_K^2 = \frac{1}{3 \times 2^2} = \frac{1}{12}$$

$$R_1u_1^3 + R_2u_2^3 + \ldots + R_Ku_K^3 = 0$$

$$R_1u_1^4 + R_2u_2^4 + \ldots + R_Ku_K^4 = \frac{1}{5 \times 2^4} = \frac{1}{80} \tag{A-8}$$

Using this technique to evaluate $f_n^{(i)}$, one finds

$$f_n^{(i)} = \frac{\beta l}{\pi^{1/2}}\sum_{j=1}^{K} R_j e^{-\beta^2 l^2[n+1/2+u_j-(i-1)/s]} \tag{A-9}$$

where the approximation can be made as exact as one pleases by taking K sufficiently large.

In the next step of the development, we evaluate $\sum_{i=1}^{s} s^{-1}f_n^{(i)}$, but since we can go to the continuum limit by letting the cell size approach zero and s approach infinity, the sum becomes an integral

$$\sum_{i=1}^{s} s^{-1} f_n^{(i)} = \frac{\beta l}{\pi^{1/2}} \sum_{j=1}^{K} R_j \int_0^1 e^{-\beta^2 l^2 (n+1/2+u_j-\xi)^2}\, \mathrm{d}\xi \qquad \text{as } s \to \infty \tag{A-10}$$

Applying the Gaussian quadrature a second time gives

$$\sum_{i=1}^{s} s^{-1} f_n^{(i)} = \frac{\beta l}{\pi^{1/2}} \sum_{j=1}^{K} \sum_{k=1}^{K} R_j R_k e^{-\beta^2 l^2 (n+u_{jk})^2} \qquad \text{as } s \to \infty \tag{A-11}$$

where

$$u_{jk} = u_j - u_k \tag{A-12}$$

Substituting eq A-11 into eq A-5 and letting $s \to \infty$ gives

$$\langle x^2 \rangle' = \frac{\beta l^3}{\pi^{1/2}} \sum_{j=1}^{K} \sum_{k=1}^{K} R_j R_k \sum_{n=-\infty}^{+\infty} (r^2 + n^2) e^{-\beta^2 l^2 (n+u_{jk})^2} \tag{A-13}$$

As long as the summation over n can be adequately approximated by an integral, eq A-13 can be written

$$\langle x^2 \rangle' = \frac{\beta l^3}{\pi^{1/2}} \sum_{j=1}^{K} \sum_{k=1}^{K} R_i R_j \left[r^2 \left(\frac{\pi^{1/2}}{\beta l} \right) + \left(\frac{\pi^{1/2}}{2\beta^3 l^3} \right) + u_{jk}^{\,2} \left(\frac{\pi^{1/2}}{\beta l} \right) \right] \tag{A-14}$$

The summation of eq A-14 can be evaluated by using the relationship of eq A-8, and the result is

$$\begin{aligned} \langle x^2 \rangle' &= \frac{1}{2\beta^2} + \frac{l^2}{6}(1 + 6r^2) \\ &= \langle x^2 \rangle_0 + \frac{l^2}{6}(1 + 6r^2) \end{aligned} \tag{A-15}$$

Equation A-15 is identical with eq 10. Since the Gaussian quadrature becomes exact as $K \to \infty$ and since eq A-15 is independent of K, no error was introduced by introducing the numerical integrations *as long as* the summations over n in eq A-13 can be replaced by integrals with negligible error. Indeed the limitations on the substitution of integrals for summations define the limitations on the applicability of eq A-15.

In setting these limitations, we note that the errors will be greater in approximating $\sum n^2 \exp[-\beta^2 l^2 (n + u_{jk})^2]$ by an integral than for approximating the analogous summation without the factor n^2. Furthermore, it can be shown that $|u_{jk}| < 1$. As a test of the limit of applicability of eq A-15, we thus examine the circumstances under which the following approximation is an accurate one

$$\sum_{n=-\infty}^{+\infty} n^2 e^{-\beta^2 l^2 (n+h)^2} \cong \int_{-\infty}^{+\infty} n^2 e^{-\beta^2 l^2 (n+h)^2}\, \mathrm{d}n \tag{A-16}$$

for $0 \le h \le 1$. By evaluating the summations and comparing with the value of the integrals, one finds that if $\beta l = 0.7$, the integral is about 0.05% greater than the sum; if $\beta l = 1$, the integral is never more than 0.20% greater than the sum; if $\beta l = 1.2$, the integral is never more than 2.6% greater than the sum; and if $\beta l = 1.3$, the integral is never more than 6.2% greater than the sum. Since we have examined the accuracy of the least accurate terms on the right-hand side of eq A-14, eq A-15 must give $\langle x^2 \rangle'$ to at least the same accuracy. We conclude, then, that eq A-15 is essentially exact as long as $\beta l \le 1$.

Finally, as an additional check on the range over which eq A-15 applies, the summations in eq A-13 were performed on a digital computer. The results verified the conclusion that eq A-15 is essentially exact for $\beta l \le 1$. In addition, however, the computer analysis demonstrated that eq A-15 is less than 5% in error if $1 \le \beta l \le 1.75$ and less than 10% in error if $1.75 < \beta l \le 2.0$. As a consequence, the mathematical treatment in the body of this paper is exact up to values of $Z \le 0.33$, good to at least 5% if $0.33 < Z \le 1.0$, and good to at least 10% if $1.0 < Z < 1.33$. It is thus clear that deviations between theory and experiment would have their origins in the limitations of the model and not in the mathematical analysis.

We close by noting that the computer evaluation of the summations in eq A-13 provides the basis for extending the theory to larger values of βl. This is necessary if the theory is to be extended to solutions. That material will be given in a subsequent publication.

Note Added in Proof: The distribution functions given in eq 4 and A-3 are incomplete. As written, they imply that a value of $\nu = p - q$ (or $r = \nu/s$), either positive or negative, defines the conformational statistics of the assembly of subchains. The distributions thus have nonzero odd moments. In reality, for any value of $|\nu|$ there would be equal numbers of subchains with positive values of ν and negative values of ν. The true distributions would thus be the sum of two equally weighted functions of the types shown in eq 4 and A-3, one as written and one with ν replaced by $-\nu$. Introducing these more complete forms for $W(x)$ would, of course, have no effect on the rest of the development.

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