Orientation-Dependent Interactions in Polymer Systems. 1. Segmental Orientation in Weakly Deformed Systems

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ABSTRACT: The effects of orientation-dependent interactions on the segmental orientation in weakly deformed polymer systems were reexamined on the basis of lattice theories and gas-of-rods theories. Both the freely jointed chain and the wormlike chain were considered as polymer models. It was shown in a somewhat general fashion that the orientation-dependent excluded-volume effect or packing effect could give rise to a considerable amount of excess orientation over that predicted in the absence of such an effect. For a dry system of freely jointed chains comprising rodlike segments of axial ratio 2, for example, the relative excess orientation was estimated to range roughly from 30 to 100%, depending on the theories. This value of the axial ratio seems to approximate the flexibilities of common vinyl polymers, and in this context, the volume effect would never be a minor one even for the "flexible" class of polymers. The nature of and the differences among the various statistical models were discussed in some detail.

Previously,[1] we discussed the segmental orientation in weakly deformed polymer systems using the cubic-lattice model of Di Marzio[2] and obtained the indication that the excluded-volume effect or the packing effect could lead to values of segmental orientation in a dry system 50-100% larger than those predicted by the "gaslike theory" that neglects the volume effect. This simple model, even though sufficient to suggest the importance of such a phenomenon, included no parameter with which to correlate the model with real polymers. Accordingly, the reality of the predicted effect was not very clear, particularly for systems of highly flexible polymers. This is also the case with the molecular dynamical simulation study of Gao and Weiner,[3] which also suggests a strong volume effect on segmental orientation.

Recently, Erman et al.[4] adopted a Flory-type lattice model[5] to estimate the amount of segmental orientation in a network of freely jointed chains. This model includes the axial ratio x of the rodlike segment as a flexibility parameter. Their results are qualitatively similar to ours but predict much less extra orientation than the values noted above, especially when the chain length is short. Their conclusion is that the volume-effect contributions to orientation would be of minor importance for flexible polymers with $x \leq 3$.[4] This theory is significant for clearly showing the role of chain flexibilities. The conclusion, however, should be viewed with reserve, since their theory, too, is based on a particular model, the accuracy of which is still unclear. Insofar as dilute solutions are concerned, lattice models are known to highly underestimate the excluded-volume effect, as compared with the Onsager-type models.[6]

In the absence of theories proven to be reliably applicable to both dilute and dense systems, it will be important now to make clear how much difference can result by adopting different models available to date. This is the main topic to be dealt with in this work. For simplicity, we confine the discussion here to systems only weakly deformed by an external force field. Both the freely jointed chain and the wormlike chain[7] are considered as polymer models. Several versions of the lattice model and of the Onsager model are used to estimate the orientation-dependent packing entropy. The nature of and the differences among the models will be discussed in some detail. The effects of the orientation-dependent dispersion forces[8,9] will also be incorporated into the theory, just for the sake of generality.

Theoretical Formulation

We consider an incompressible system containing N long freely jointed chains each comprising m rodlike segments of length b, hence the total length of the chain, L, being

$$L = mb \quad (m \gg 1) \tag{1}$$

Systems of wormlike chains will be discussed later (see the Discussion section). The system may or may not be cross-linked.[10] Let us assume that the system is deformed by an external force so that the a priori distribution density of segment vector $\mathbf{b}$ becomes $f^*(\mathbf{b})$ with

$$\int f^*(\mathbf{b})\, \mathrm{d}\Omega = 1 \tag{2}$$

where Ω is the space angle. f^* denotes the equilibrium distribution that would be attained in the absence of any intersegmental interactions, i.e., in the *gaslike* system. Hereafter an asterisk shall denote the gaslike system. The distribution, $f(\mathbf{b})$, in the *actual* system with interactions can be different from f^*. It can be easily shown that the excess orientational entropy ΔS_o of the actual system over that of the gaslike system is

$$\Delta S_o/k = Nm \int f \ln (f^*/f)\, \mathrm{d}\Omega \tag{3}$$

where k is the Boltzmann constant.[11] The excess free energy ΔF over that of the gaslike system may be written as

$$\Delta F/T = E_o/T - (S_p + \Delta S_o) \tag{4}$$

where T is the temperature; E_o and S_p are the orientation-dependent terms of internal energy and packing (combinatorial) entropy, respectively, both being assumed to be functions of the overall distribution f. Minimization of ΔF with respect to f yields the equilibrium distribution that would realize, as a function of the external deformation f^*. This is the problem to be considered.

Even though rigorous analyses are possible in most cases, we choose, for simplicity, the following trial distributions, errors associated with this particular choice being trivial for the present purpose

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$$f^*(\theta) = I^* \exp(\beta^* \cos^2 \theta) \qquad (5)$$

$$f(\theta) = I \exp[(\beta^* + \beta) \cos^2 \theta] \qquad (6)$$

where θ is the angle from the reference direction, I^* and I are constants determined by eq 2 and the like, and β^* and β are parameters characterizing degrees of orientation. For $\beta = 0$, eq 6 reduces to eq 5, as it should be. The order parameter η defined by

$$\eta = (3/2)\langle \cos^2 \theta \rangle - (1/2) \qquad (7)$$

is related to β^* and β through

$$\langle \cos^2 \theta \rangle = \int f(\theta) \cos^2 \theta \, d\Omega \qquad (8)$$

To obtain η^*, replace f by f^*.

For small orientations (small β^* and β), eqs 5 and 6 are expanded around $\beta^* = \beta = 0$, and the integrations in eqs 2, 3, 8, and the like are performed to yield

$$\Delta S_o/k = -(2/45)Nm\beta^2 \qquad (9)$$

$$\eta^* = (2/15)\beta^* \qquad (10)$$

$$\eta = (2/15)(\beta^* + \beta) \qquad (11)$$

Equation 9 shows that ΔS_o is independent of β^* or the external deformation when it is small.[1] Elimination of β and β^* from eqs 9–11 gives

$$\Delta S_o/k = -(5/2)Nm(\eta - \eta^*)^2 \qquad (12)$$

In what follows, we try to give the remaining terms in eq 4 as a function of η using several of the representative models devised so far. Some versions of those models will be described in the Discussion section.

Packing Entropy S_p. According to the Onsager model,[6] the S_p of a system containing sufficiently long freely jointed chains may be given by[7]

$$S_p/k = (\pi/4)cNmb^2D\rho \qquad (13)$$

Here c and D are the number density and diameter, respectively, of the segment, and ρ is defined by

$$\rho = 1 - (4/\pi)\langle|\sin \theta_{ij}|\rangle_{i,j} \qquad (14)$$

where θ_{ij} is the angle between segments i and j, and $\langle\ \rangle_{i,j}$ denotes the mean over all i and j. For small ρ (small β), eq 14 can be approximated by[12]

$$\rho = (5/8)\eta^2 \qquad (15)$$

Thus we have

$$S_p/k = (5/8)Nmx\phi\eta^2 \quad \text{(O-model)} \qquad (16)$$

where $x = b/D$ is the segmental axial ratio, and $\phi = (\pi/4)bD^2c$ is the (core) volume fraction of polymer.

The second model considered here is the lattice model of Flory.[5] In this notation, the S_p for this model reads[5b]

$$S_p/k = (Nmx/\phi)[\mu\phi + (1 - \mu\phi) \ln (1 - \mu\phi)] \qquad (17)$$

$$\mu = 1 - (4/\pi)\langle|\sin \theta|\rangle \qquad (18)$$

For small μ, eq 18 with eq 6 gives

$$\mu = (1/12)(\beta^* + \beta) \qquad (19)$$

and eq 17 with eqs 10, 11, and 19 gives

$$S_p/k = (25/128)Nmx\phi\eta^2 \quad \text{(F-model)} \qquad (20)$$

The third model is also a lattice model. This model assumes that a fraction p of the "bonds" lies in the direction X of the Cartesian coordinate XYZ and a fraction $(1 - p)/2$ lies in each of the directions Y and Z. For sufficiently long chains ($mx \gg 1$), this model gives (see Appendix I)

$$S_p = (Nmx/\phi)\{(1 - p\phi) \ln (1 - p\phi) + 2[1 - (1 - p)\phi/2] \ln [1 - (1 - p)\phi/2]\} \qquad (21)$$

It is simple to give p by

$$p = \langle \cos^2 \theta \rangle \qquad (22)$$

For small orientations ($p \sim 1/3$), eq 21 with eqs 7 and 22 yields

$$S_p/k = \phi(3 - \phi)^{-1}Nmx\eta^2 \quad \text{(D-model)} \qquad (23)$$

Equation 21 was originally derived by Di Marzio,[1,2] and we will term eq 23 the "D-model". Needless to say, the axial ratio x and the volume fraction ϕ appearing in the above lattice equations are measured with the size of the lattice site as reference.[5]

Energy Term E_o. Maier and Saupe[8] have developed a theory on the orientation-dependent dispersion forces between molecules with anisotropic polarizabilities. Later it was slightly modified by Flory and Ronca,[9] whose result suggests an E_o of the form

$$E_o/k = -Nmx\phi B\eta^2 \qquad (24)$$

where B corresponds to Flory–Ronca's $T^*/2$. We have reinterpreted their $\tilde{V}^{-1}$ as the (core) volume fraction ϕ. Here we adopt eq 24.

Equilibrium Orientation. With eqs 12, 16, 20, 23, and 24, eq 4 is written in the general form

$$\Delta F/(NmxkT) = -\phi\eta^2(g + B/T) + (5/2x)(\eta - \eta^*)^2 \qquad (25)$$

$$g = 5/8 \quad \text{(O-model)} \qquad (26a)$$

$$g = 25/128 \quad \text{(F-model)} \qquad (26b)$$

$$g = (3 - \phi)^{-1} \quad \text{(D-model)} \qquad (26c)$$

The minimization of eq 25, $(\partial\Delta F/\partial\eta)_{T,V} = 0$, yields

$$\begin{aligned} G &\equiv (\eta - \eta^*)/\eta^* \\ &= (H - 1)^{-1} \qquad (27) \end{aligned}$$

with

$$H = [(2/5)x\phi(g + B/T)]^{-1} \qquad (28)$$

G denotes the relative excess orientation with the gaslike system as reference.

Discussion

Using the cubic-lattice model of Di Marzio, we had estimated the relative excess orientation to amount to 100% in a weakly deformed dry system.[1] That treatment was based on the same expression of S_p as used here (eq 21), while the orientational entropy ΔS_o was calculated on the basis of the number of bonds. This would correspond to a freely jointed chain with $x = 1$. Real polymers may be characterized by larger x, and if so, the previous estimate can still be too low. On the other hand, the orientational distribution $f(\mathbf{b})$ previously assumed was such that f was nonzero only along the three axes of the lattice, which clearly is an oversimplification leading to an overestimation of excess orientation. On these accounts, the previous estimate is highly qualitative. Before discussing these results, we wish to make somewhat clearer the significance and limitations of the models.

Onsager-Type Models. The Onsager model is known to describe with fair accuracy the nematic–isotropic transitions of solutions of long straight rods.[13] The model was extended by Khokhlov and Semenov[7] to solutions of freely jointed chains and of wormlike chains.[14] In this extension, it is required that the axial ratio of the segment, x, or that per persistence length, x_p, be large enough. Perhaps this requirement is not too strict (unless one deals with very dilute solutions where the excluded-volume effect between highly coiled macromolecules prevents the segments from randomly contacting each other[15,16]). This view comes from the realization of the orientation-dependent excluded-volume effect being essentially of a local nature, arising from direct contacts of limited portions of molecules. A major part of the effect should be caused by the directions of the tangential vectors of molecules at the contact point, and the chain configuration should be of minor importance. The situation should be analogous to the fact that the second virial coefficient A_2 of a flexible chain is, to the first-order perturbation approximation, equivalent to the A_2 of a straight rod of the same size.[16] We also note that the lattice models devised so far are independent of chain flexibility. For example, eqs 20 and 23 show that $S_p \sim mx = L/D$, being independent of x (see also Appendix I). The S_p of the O-model, eq 16, takes the same form.

A more serious matter with the O-model concerns its applicability to dense systems, for the Onsager theory is based on A_2 only. Several attempts have been made to modify the theory for enhanced applicabilities.[13,17–19] All those theories suggest a g factor (eq 26) of the form (see, e.g., eq A-13)

$$g = (5/8)h(\phi) \tag{29}$$

where h is an increasing function of ϕ such that $h = 1$ for $\phi = 0$ and $h \to \infty$ for $\phi \to 1$, the degree of the singularity near $\phi = 1$ strongly depending on the models. It may be mentioned that, among the Onsager-type theories, which are theories of the "gas" of rodlike molecules, the O-model provides the most modest estimation of excess orientation. Kimura,[12] who applied the Onsager model to an analysis of the thermotropic liquid-crystalline behavior of low-mass compounds, suggested the reality of the model in a semiquantitative sense at least.

Lattice Models. The F- and D-models, being lattice models, are formally applicable to both solutions and neat fluids. The F-model gives a g value about 1/3 of that of the O-model, while the D-model gives an intermediate value between them, for all ϕ. The difference between the F- and D-models comes from different approximations used in counting the number of ways to pack molecules in the lattice. The models themselves are essentially the same. In this regard, some confusion seems to prevail. Examination of the Flory counting process[5] shows that it is equivalent to saying that a fraction μ (eq 18) of bonds lies in the preferred direction X and the rest, $1 - \mu$, lies in directions Y and Z normal to X. Following Di Marzio,[2] but disregarding steps along Y and Z, we obtain the Flory result. That is, eq 17 is obtained from the Di Marzio eq 21 by setting $p = \mu$ but neglecting the second term in braces, which derives from steps along Y and Z. (Note that in eq 21 the factor $p\phi$ associated with the first term has been canceled with the factor $(1 - p)\phi$ associated with the second.) With the second term in braces incorporated in the F-model, its g value is increased by 50% for $\phi = 0$, becoming virtually identical with that of the D-model.

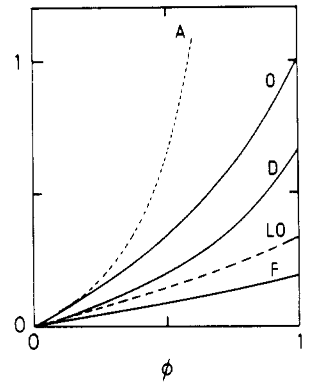

Figure 1. Relative excess orientation G as a function of polymer volume fraction ϕ for a weakly deformed freely jointed chain system with $x = 2$, predicted by the O-, D-, and F-models (eq 26), the LO-model (eq 30), and the A-model (eqs 30 and A-13). The energetic contribution B is assumed to be zero (see eqs 27 and 28).

The remaining small difference is due to different definitions of bond fractions, i.e., p vs μ, both being rather arbitrary. In Appendix I, we have formulated a lattice model that does not require defining a preferred direction and is tentatively termed the "lattice-version-of-Onsager" model (LO-model). This model gives g exactly half that of the O-model (eq A-11 with eq 15):

$$g = 5/16 \quad \text{(LO-model)} \tag{30}$$

Axial Ratio of Freely Jointed Chain Segment. Insofar as configurational properties such as mean-square end-to-end length $\langle r^2 \rangle_0$ are concerned, the freely jointed chain as well as the wormlike chain will well describe real chains of sufficient length. In his discussion on the nematic–isotropic transitions of semirigid chains, Flory suggests the use of the axial ratio x_K of the Kuhn segment, which may be estimated with[20]

$$x_K = (\langle r^2 \rangle_0 / M)(N_A \rho' M/L)^{1/2} \tag{31}$$

where M and ρ' are the molecular weight and density, respectively, of the polymer. Molten polyethylene (PE), for example, is roughly characterized by[21] $\langle r^2 \rangle_0 / M = 0.011$ nm^2, $\rho' = 1.0$ g cm^{-3}, and $M/L = 110$ nm^{-1}, for which we have $x_K = 2.8$. It will probably be inaccurate to use this value for the x in our discussion, for PE and most other flexible polymers will not be well described by the freely jointed chain (nor by the wormlike chain, see below) with the characteristic parameters adjusted by dimensional considerations. The estimation of ΔS_0, hence x, should be based on realistic polymer models.[22,23] According to Volkenstein,[23] vinyl polymers are somewhat more flexible, typically, by several tens of percent, from the electrooptical point of view than from the dimensional point of view. With this in mind, an x value of about 2 may not be too unrealistic for typical flexible polymers. A similar x value has been suggested by Erman et al.[4a]

Comparison of Numerical Results. In Figure 1, the relative excess orientation G (eq 27) is plotted as a function of ϕ for the case with zero internal energy ($B = 0$) and $x = 2$. The figure shows that G increases with increasing ϕ, values at $\phi = 1$ being 0.19 (F), 0.33 (LO), 0.67 (D), and 1.0 (O). The F-model, which gives the smallest G, still predicts about a 20% excess orientation in the dry state. In our notation, the result of Erman et al.,[4a] who used a slightly modified Flory lattice to treat a cross-linked system, is given (in the long-chain, small-deformation limit) by

$$H = 12.8/(x\phi) - 0.166 \quad \text{(eq 50, ref 4a)} \tag{32}$$

This is practically the same as the relation $H = 12.8/(x\phi)$

obtained here (eq 28 with eq 26b and $B = 0$). These authors state that the relative excess orientation never exceeds 15% for $x \leq 3$ in the dry state.[4a,b] It should be noted that this statement is correct for the simulated case with finite segment number m (the result for $m = 20$ is given in the paper[4a]). In the long-chain, small-deformation limit with which we are conerned here, their model gives a G value of 0.32 for $\phi = 1$ and $x = 3$ (eq 32).

Lattice theories are a liquidlike theory and intrinsically underestimate volume effects compared with Onsager-type theories of gas. Despite the considerable success of the Onsager-type theories in describing the lyotropic liquid crystals of long straight or nearly straight molecules,[13,24] we do not see any definite reason why gas theories[25] are to be preferred over liquid theories. The Onsager-type theories might owe their success, at least in part, to the usually large difference in characteristic size, e.g., diameter, between polymer and solvent molecules. A need is apparent for more experimental and theoretical work before we are able to discuss model proprieties. At this stage, we can only suggest that the LO-model, which seems to include less arbitrariness than other lattice models, may possibly be viewed as providing a measure of the lower limit of G. The upper limit could be measured by the O-model. In this regard, the D-model might not be too unreasonable in a practical sense.

The analysis given so far does indicate nonminor volume effects on segmental orientation. The Maier–Saupe-type interactions ($B > 0$) can bring about enhanced orientations (see eq 28). The effects of such an interaction have been discussed by Jarry and Monnerie,[26] whose result for weak deformations takes the same form as eqs 27 and 28 with $x = \phi = 1$ and $g = 0$ (their U corresponds to our $2B/T$, see eq 16 in ref 26; see also Doi and Watanabe[27]).

Finally we make a brief comment on systems of wormlike chains. As stated in Appendix II, the relative excess orientation G of these systems may be given by eq 27 with

$$H = [(4/15)x_p\phi(g + B/T)]^{-1} \tag{33}$$

where x_p is the axial ratio of the chain segment of a unit persistence length. From the dimensional point of view, x_p is related to the axial ratio x of the freely jointed chain by $x_p = x/2$, in the long-chain limit.[22] On the other hand, comparison of eqs 28 and 33 shows that to obtain the same value of H or G, x_p has to be $3x/2$. This means that the wormlike chain is orientationally much more flexible (hard to orient) than it is dimensionally.[14] The argument already given suggests that the orientational flexibilities of real (flexible) polymers will be somewhere between those of these two models. Particular care should be taken in correlating these idealized models with real chains.[20,28]

To summarize, the conclusion of Erman et al. should be reversed. The excess orientation could be much larger than what they have estimated on the basis of the particular model of the Flory type.

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Appendix I. Consideration on Lattice Models

Consider a lattice with a total of N_0 sites, in which N chains are being packed. A chain is divided into n submolecules each of the same size as a lattice site; hence, the number of bonds per chain is $n - 1$. The correspondence to the freely jointed chain defined in the text is

$$n = mx \tag{A-1}$$

The directions of the bonds within the same chain may or may not be correlated with each other: chain rigidity does not enter the theoretical formulation, as is commonly the case with the lattice models devised so far.[2,5]

After r chains have been packed, the probability of the first submolecule of the $(r + 1)$th chain being successfully placed in the lattice is

$$Q_{0,r+1} = (N_0 - rn)/N_0 \tag{A-2}$$

The probability Q_{r+1} of the first and subsequent steps being successful will depend on the "obstruction factor" σ_i

$$\sigma_i = \langle|\sin\theta_{ij}|\rangle_j \tag{A-3}$$

where θ_{ij} is the angle between the bond (step) i in question and a bond j already present in the system, and $\langle\ \rangle_j$ denotes the mean over all j. Following the conventional arguments,[2,5] we give Q_{r+1} by

$$Q_{r+1} = \frac{N_0 - rn}{N_0 - r(n-1)(1-\sigma_i)} \tag{A-4}$$

The total number of ways to pack N chains is proportional to

$$\Omega = \prod_{r=1}^{N}\prod_i [Q_{0,r}Q_r^{\,p_i(n-1)}] \tag{A-5}$$

where p_i is the fraction of bonds in the ith direction. The orientation-dependent terms S_p of the packing entropy are obtained from $k \ln \Omega$

$$S_p/k = N_0\sum_i [p_i/(1-\sigma_i)](A_i \ln A_i) \tag{A-6}$$

$$A_i = 1 - \phi(1 - n^{-1})(1 - \sigma_i) \tag{A-7}$$

where $\phi = Nn/N_0$ is the polymer volume fraction.

For the cubic lattice XYZ, it holds that $p_i = 1 - \sigma_i$, and we recover eq 21 by setting $p_X = p$, $p_Y = p_Z = (1 - p)/2$, $n^{-1} = 0$, and $N_0 = Nmx/\phi$ (eq A-1). More generally, eq A-6 with $p_i = 1 - \sigma_i$ reduces to the Di Marzio equation derived for a general lattice with a coordination number z (eq 6 in ref 2). That equation, however, predicts a trivial orientation dependence of S_p for large z. This is due to the complete discreteness of the lattice and is perhaps unrealistic in such a limit.

Preaveraging σ_i in eqs A-6 and -7 such that

$$\sigma = \sum_i p_i\sigma_i = \langle|\sin\theta_{ij}|\rangle_{ij} \tag{A-8}$$

and assuming that bonds can a priori take all directions in space, we obtain

$$S_p/k = (N_0/\rho)(A \ln A) \tag{A-9}$$

$$A = 1 - \phi(1 - n^{-1})\rho \tag{A-10}$$

with ρ defined by eq 14. To derive eqs A-9 and A-10, we have multiplied σ by a factor $(\pi/4)^{-1}$ so that $S_p = 0$ in the isotropic state.[5b] The preaveraging approximation is fully justified for small ρ and/or small ϕ. For small ρ and large n, eq A-9 with eqs A-1 and A-10 reads

$$S_p/k = (1/2)Nmx\phi\rho \tag{A-11}$$

which gives eq 30.

Similarity of the derivation process of eq A-9 to that of the Onsager equation will be evident. In this connection, it may be interesting to refer to one of the equations derived by Alben,[18] who applied the idea of the lattice theory to the packing problem in continuous space (hence, his theory is a gas theory,[25] not a liquid theory). In this notation, Alben's result for a system containing *mN long* rods may be written as

$$S_p = -2Nmx\rho[1 + \phi^{-1} \ln (1 - \phi)] \qquad \text{(A-12)}$$

Referring to eq 15, we see that this model is different from the O-model by a factor

$$h = -2\phi^{-2}[\phi + \ln (1 - \phi)] \quad \text{(A-model)} \qquad \text{(A-13)}$$

which is the very factor appearing in eq 29.

Appendix II. Systems of Wormlike Chains

According to Khokhlov and Semenov,[7] the entropy s of a wormlike chain characterized by a total length L, a persistance length b_p, and an orientational distribution density $f(\theta)$ is given by

$$s/k = (L/8b_p) \int f^{-1}(\partial f/\partial\theta)^2 \, d\Omega \qquad \text{(A-14)}$$

For a distribution of the form $f \sim \exp(\beta \cos^2 \theta)$ with a small β (see the text), eq 29 gives

$$s/k = -(L/15b_p)\beta^2 \qquad \text{(A-15)}$$

The excess entropy ΔS_0 of a system containing N such chains should also be independent of an applied external (small) deformation, as in the system of freely jointed chains. Thus, ΔS_0 for the trial distributions, eqs 5 and 6, may be given by

$$\begin{aligned} \Delta S_0/k &= -(L/15b_p)N\beta^2 \\ &= -(15/4)Nm_p(\eta - \eta^*)^2 \qquad \text{(A-16)} \end{aligned}$$

where $m_p = L/b_p$ denotes the number of segments with the persistence length as reference. As suggested in the text, S_p as well as E_0 may be considered, at least to a first approximation, as independent of chain configuration. Hence, all other equations relevant to the freely jointed chain are valid, if we reinterpret m as m_p and x as $x_p = b_p/D$. This gives eq 33.

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(10) For a cross-linked system, the chain is defined as the portion of the network between cross-links. Because we are concerned here with weakly deformed chains, the following discussion is free from the existence of cross-links.[1]
(11) The number of ways, W, to distribute m rods among r solid-angle elements, each of size $4\pi/r$, is

$$W = m! \prod_{i=1}^{r} (f_i^{*m_i}/m_i!)$$

where m_i is the number of rods in the ith element ($\sum m_i = m$), and f_i^* is the a priori probability that a rod falls in the ith element. Writing $f_i = m_i/m$ and using the Stirling approximation, we have

$$\ln W = m \sum_{i=1}^{r} f_i \ln (f_i^*/f_i)$$

which is equivalent to eq 3. For a uniform a priori distribution, $f^* = (4\pi)^{-1}$, eq 3 reduces to the familiar relation for an externally undeformed system.[6,7] Previously[1] ΔS_0 was written as ΔS.
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