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Expansion of a Polymer Chain in a Θ Solvent: The Screened-Interaction Model

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ABSTRACT: The model develops the assumption that in the Θ state the chain self-repulsion due to the covolume is exactly balanced by a free energy attraction influenced by the solvent (Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303). It is shown that if the balance is exact for two atoms remote along the chain, the interaction between closer atoms is repulsive because the maximum of the a priori probability for their distance r tends to concentrate in the covolume-forbidden region around $r = 0$. As a consequence, an expansion over the ideal size of the phantom chain appears, which develops in a range roughly between 10 and 1000 chain atoms, and asymptotically tends to a constant value for large molecular weights. Considering a realistic estimate of the van der Waals size of the chain atoms and assuming a Gaussian distribution for their mutual distance, with a suitable lower cutoff to account for the non-Gaussian behavior of short-chain sections ($\lesssim$40–60 skeletal atoms), the resulting mean-square expansion is about 5%, 20%, and 30% for polyethylene, atactic polystyrene, and isotactic polypropylene, respectively.

The Model

Several years ago in a fundamental paper[1] Flory showed that the free energy A of a dissolved polymer molecule may be expressed as follows:

$$(A - A_0)/k_BT = \tfrac{3}{2}(\alpha^2 - 1) - 3 \ln \alpha + a_2(\alpha) \qquad (1)$$

where A_0 is the free energy of the ideal phantom chain, α is the degree of expansion assumed as uniform, and $a_2(\alpha)$, proportional to α^{-3}, is essentially the second virial term; i.e., it depends on the probability of pairwise contacts between chain atoms. Both in a Θ solution and in the melt the a_2 term vanishes and the chain behaves ideally, i.e., $\alpha = 1$; however, while in the molten state this result proceeds from the mixing entropy of very long chains tending to zero, it is quite a different matter for an ideal solution, where a small, positive solvent–polymer energy interaction exactly compensates the negative entropic term.[1,2] The resulting situation may also be viewed in terms of polymer segment–segment interactions alone, neglecting explicit reference to the solvent, by stating that the expansion effect due to the intrinsic volume of the chain is balanced by the (solvent influenced) attraction between the polymer segments.[2]

In the present paper we will further develop the logical implications of the above picture. It was shown recently through a perturbative approach applied to the expanded chain configurations (thereby ignoring higher order correlations among intrachain contacts) that $a_2(\alpha)$ may be expressed as[3]

$$a_2(\alpha) = \sum_{k<m}\sum a_2\{k,m\} = \beta \sum_{k<m}\sum W_{km}(0) \qquad (2)$$

where $W_{km}(\mathbf{r})$ is the probability density for the vector distance r between the kth and the mth chain atoms and β is the excluded volume parameter. It should be stressed that we refer to the actual probability for the real chain—as opposed to that for the unperturbed, phantom chain—which opens the way to a self-consistent type of configurational description.[3] A more general formulation of the above result is

$$a_2(\alpha) = \sum_{k<m}\sum \int_V e(\mathbf{r}) W_{km}(\mathbf{r})\ \mathrm{d}^3\mathbf{r} \qquad (3)$$

where $k_BTe(\mathbf{r})$ is the effective interaction free energy function between two chain atoms;[4] this is sufficiently short-ranged for many purposes that $e(\mathbf{r}) \simeq \beta\delta(\mathbf{r})$ ($\delta(\mathbf{r})$ is the Dirac δ function in three dimensions), so that eq 2 is recovered. In terms of the classical perturbative approach (see, in particular, eq 13.1 and 13.2 of ref 4) the effective potential function $e(\mathbf{r})$ may be written as

$$e(\mathbf{r}) = 1 - \exp(-w(\mathbf{r})/k_BT)\ (= -\chi(r)) \qquad (4)$$

where $w(\mathbf{r})$ represents the actual potential for a pairwise interaction. Such a potential will be considered as effectively renormalized to include the higher order interactions involving atoms in the vicinity of those two on which the pairwise interaction is based, according to the ideas of Khokhlov.[5]

It will be useful henceforth to distinguish two contributions within the function $e(\mathbf{r})$, respectively corresponding to the *covolume* and to the *solvent interaction* effect. While the former merely prohibits the spatial self-interference of the chain, the latter effect accounts for the free energy difference between a polymer self-contact and the polymer–solvent interactions that would take place in its absence. Since here we assume the size of the solvent molecules to be small, an interaction will be regarded as localized around any chain atom in a region of space of about the same size as that of a statistical segment of the polymer. Accordingly, for two chain atoms at a distance r we have

$$e(\mathbf{r}) = e_c(\mathbf{r}) + e_{si}(\mathbf{r}) \qquad (5)$$

Although both the covolume (e_c) and the solvent-interaction (e_{si}) functions are short-ranged, the latter obviously survives at larger r's; since it is related with the dis-

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placement of solvent molecules from being in contact with the chain, it will be positive or negative, depending on whether the solvent is good or poor, respectively. Defining the integral value and the second moment of the two functions as

$$\upsilon_{\mathrm{c}} = \int_V e_{\mathrm{c}}(\mathbf{r})\ \mathrm{d}^3\mathbf{r}; \qquad \upsilon_{\mathrm{si}} = \int_V e_{\mathrm{si}}(\mathbf{r})\ \mathrm{d}^3\mathbf{r} \tag{6}$$

$$\langle r_{\mathrm{c}}^2\rangle = \int_V r^2 e_{\mathrm{c}}(\mathbf{r})\ \mathrm{d}^3\mathbf{r}/\upsilon_{\mathrm{c}}; \qquad \langle r_{\mathrm{si}}^2\rangle = \int_V r^2 e_{\mathrm{si}}(\mathbf{r})\ \mathrm{d}^3\mathbf{r}/\upsilon_{\mathrm{si}}$$

with

$$\langle r_{\mathrm{si}}^2\rangle > \langle r_{\mathrm{c}}^2\rangle \tag{7}$$

we will confine our attention to the particular case in which the integral value of $e(\mathbf{r})$ vanishes, i.e.

$$\beta = \upsilon_{\mathrm{c}} + \upsilon_{\mathrm{si}} = 0 \tag{8}$$

It should be remarked that Edwards already adopted an analogous distinction between attractive and repulsive components reaching a balance at a polymer's ideal state.[6] However, he deals with concentrated solutions or melts, with the consequence that in his case $e_{\mathrm{si}}(\mathbf{r})$ is long-ranged and the results are basically different from ours. We shall further comment on this point in the discussion.

Let us now proceed to evaluate the general term of the sum in eq 3. We shall adopt the Gaussian approximation, deferring to the next section the analysis of its range of validity. Replacing the two indices k and m in eq 3 with a single index k applying to their difference, we have

$$a_2[k] = \int_V e(\mathbf{r}) W_k(\mathbf{r})\ \mathrm{d}^3\mathbf{r} = \left(\frac{3}{2\pi\langle r_k^2\rangle}\right)^{3/2} \int_V [e_{\mathrm{c}}(\mathbf{r}) + e_{\mathrm{si}}(\mathbf{r})] \exp(-3r^2/2\langle r_k^2\rangle)\ \mathrm{d}^3\mathbf{r} \tag{9}$$

Since $\langle r_k^2\rangle$ is usually much larger than both $\langle r_{\mathrm{c}}^2\rangle$ and $\langle r_{\mathrm{si}}^2\rangle$, the exponential may be expanded as a power series truncated after the second term, and in view of eq 6–8

$$a_2[k] = (3/2)^{5/2}\pi^{-3/2}\upsilon_{\mathrm{c}}(\langle r_{\mathrm{si}}^2\rangle - \langle r_{\mathrm{c}}^2\rangle)\langle r_k^2\rangle^{-5/2}\ (>0) \tag{10}$$

(It should be noticed that if $\beta \neq 0$, i.e., $T \neq \Theta$, the leading term of $a_2[k]$ would be proportional to $\langle r_k^2\rangle^{-3/2}$.) We will now introduce the expansion of $\langle r_k^2\rangle$ in Fourier modes:[3]

$$\langle r_k^2\rangle = \frac{l^2}{N}\sum_{\{q\}} C(q)\tilde{\alpha}^2(q) \sin^2(qk/2)/\sin^2(q/2) \tag{11}$$

$$\{q\} = 0, \pm 2\pi/N, \pm 4\pi/N, ..., \pm\pi$$

where l and N respectively are the length and the number of skeletal bonds. As for the generalized characteristic ratio $C(q)$[7]

$$C(q) = \langle\tilde{\mathbf{l}}(q)\cdot\tilde{\mathbf{l}}(-q)\rangle_0/Nl^2 \tag{12}$$

$$\tilde{\mathbf{l}}(q) = \sum_{k=1}^{N}\mathbf{l}(k)e^{iqk}$$

where $\mathbf{l}(k)$ is the general chain-bond vector and $\tilde{\alpha}^2(q)$ is the expansion ratio of $\langle\tilde{\mathbf{l}}(q)\cdot\tilde{\mathbf{l}}(-q)\rangle$ over its unperturbed value (denoted by a subscript zero). In other words, we now abandon the assumption of a uniform expansion of the chain, implicit in eq 1, proceeding henceforth to consider all the configurational degrees of freedom of the chain. In view of (3) and (10), eq 1 reduces to

$$(A - A_0)/k_{\mathrm{B}}T = \sum_{\{q\}}[(3/2)(\tilde{\alpha}^2(q) - 1) - 3\ln\tilde{\alpha}(q)] + K_0\sum_{k=\bar{k}}^{N}(N-k)\langle r_k^2\rangle^{-5/2} \tag{13}$$

where

$$K_0 = \frac{3}{2}\left(\frac{3}{2\pi}\right)^{3/2}\upsilon_{\mathrm{c}}(\langle r_{\mathrm{si}}^2\rangle - \langle r_{\mathrm{c}}^2\rangle) \tag{14}$$

and $\bar{k}$ is the lower limit of the intrachain bond separation below which interatomic space interference is forbidden on account of stereochemical constraints and conformational interactions between adjacent monomeric units.[3]

Differentiating eq 13 with respect to $\tilde{\alpha}(q)$, remembering (1), and equating to zero, we get the integral equation for the unknown function $\tilde{\alpha}(q)$ (cf. eq 18 of ref 3 by analogy)

$$\tilde{\alpha}^2(q) = 1\Big/\left\{1 - {}^5\!/_3 K_0 l^2 C(q) \times (\sin(q/2))^{-2}\int_{\bar{k}}^{N}\mathrm{d}k\ (1 - k/N)\sin^2(qk/2)\langle r_k^2\rangle^{-7/2}\right\} \tag{15}$$

Since the maximum value of both $\sin^2(qk/2)/\sin^2(q/2)$ and $C(q)$ is at $q = 0$ for any k, it is apparent that $\tilde{\alpha}^2(q)$ will also be largest at $q = 0$. Consequently, we will now concentrate for a while on $\tilde{\alpha}^2(0)$, i.e., the square expansion factor of the end-to-end distance $|\tilde{\mathbf{l}}(0)|$ (see eq 12), assuming at first that it tends to a finite limit for any N. From eq 11, replacing $\tilde{\alpha}^2(q)$ and $C(q)$ with $\tilde{\alpha}^2(0)$ and $C(0)$, respectively, an asymptotic, upper bound limit of $\langle r_k^2\rangle$ is, for large k,

$$\langle r_k^2\rangle_{\lim} = kC(0)\tilde{\alpha}^2(0)l^2 \tag{16}$$

$$\lim_{k\to\infty}\langle r_k^2\rangle = \langle r_k^2\rangle_{\lim} \tag{16'}$$

Substitution of this expression into eq 15 with $q = 0$ gives the approximate equation

$$\tilde{\alpha}^7(0) - \tilde{\alpha}^5(0) \simeq {}^{10}\!/_3(K/\bar{k}^{1/2})(1 - (\bar{k}/N)^{1/2})^2 \tag{17}$$

where

$$K = K_0/(C(0)^{2.5}l^5) \tag{18}$$

thus confirming the existence of an asymptotic limit of $\tilde{\alpha}(0)$ as $N \to \infty$. Overestimation of $\langle r_k^2\rangle$ by $\langle r_k^2\rangle_{\lim}$ is especially large for small k's; therefore, although the functional form of eq 17 should be roughly correct, the lower cutoff $\bar{k}$ should be replaced by a suitable effective parameter. This conclusion is confirmed by our numerical solution of the integral equation (15) for different values of the parameters K_0 and $\bar{k}$ (with $N \gg \bar{k}$), obtained following the same iterative procedure as done in a previous work.[3] According to the results reported in Figure 1, the square expansion factor $\alpha^2(k)$ between kth neighboring chain atoms, defined as

$$\alpha^2(k) = \langle r_k^2\rangle/\langle r_k^2\rangle_0 \tag{19}$$

(where the subscript zero refers to the phantom chain, i.e., $\tilde{\alpha}^2(q) \equiv 1$ in eq 11), changes with k ($>\bar{k}$) in about the same way as expected from eq 17 for the mean-square extension of a chain with $k = N$ atoms. In particular, for $K/\bar{k}^{1/2} \ll 1$

$$\alpha^2(k) \simeq 1 + K(A/\bar{k}^{1/2} - B/k^{1/2}) \tag{20}$$

the constants A and B being of order unity. Also, from the above it is easy to show that $\alpha^2(k)$ tends to $\tilde{\alpha}^2(0)$ for $k \to \infty$ as a monotonously increasing function.

Numerical Results and Discussion

We have shown that if the interaction energy screening is perfectly balanced for two atoms remote along the chain sequence, the same interaction between two closer atoms should be slightly repulsive. In fact, the maximum of the a priori probability for their distance r tends to concentrate in the covolume-forbidden region around $r = 0$. Let us now proceed to the basic question, i.e., to assess in quantitative

Table I[a]
Parameters Characterizing Polyethylene (PE), Isotactic Polypropylene (PP), and Atactic Polystyrene (PS)

	a	b	c	$C(0)$	$\bar{k}$	v_c, Å^3	d, Å	$\langle r_{si}^2 \rangle$, Å^2	$\langle r_c^2 \rangle$, Å^2	K_0, Å^5	K
PE	0.0949	0.9840	0.4670	6.4	40	23.1[b]	4.43[b]	19.62	9.81	112.0	0.125
PP	0.1275	0.9682	0.4906	4.5	28	37.1[c]	5.39[c]	29.05	14.52	266.6	0.716
PS	0.0887	0.9883	0.4180	8.0	50	76.9[d]	7.33[c]	53.73	26.86	1021.7	0.650

[a] $C(q) = a/(1 - b\cos q) + c$ (ref 7); l (C–C bond length) = 1.54 Å; $\bar{k}$ = minimum number of chain bonds for an intramolecular contact; v_c = (volume of crystalline unit cell)/(number of skeletal atoms/unit cell); d = minimum distance between chain axes in the crystalline state; $\langle r_{si}^2 \rangle = d^2$; $\langle r_c^2 \rangle = d^2/2$; $K_0 = (3/2)(3/2\pi)^{3/2} v_c(\langle r_{si}^2 \rangle - \langle r_c^2 \rangle)$; $K = K_0/(C^{2.5}(0)l^5)$. [b] Reference 12. [c] Reference 13. [d] Reference 14.

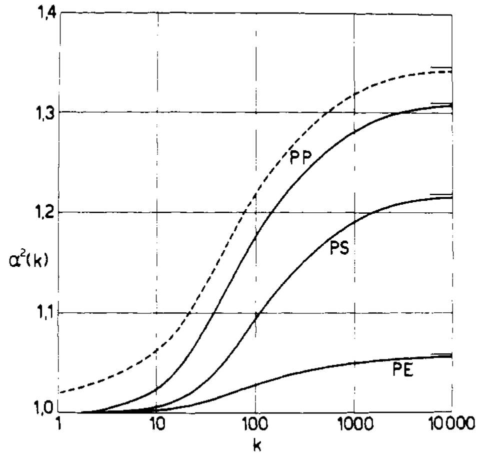

Figure 1. Square expansion factor $\alpha^2(k)$ between chain atoms separated by k bonds (see eq 19). PP, PS, and PE respectively stand for isotactic polypropylene, atactic polystyrene, and polyethylene. In the first case the curve obtained without imposing the bond-length constraint (see eq 26) is also reported as a dashed line. Horizontal bars close to k = 10 000 indicate the asymptotic value $\bar{\alpha}^2(0)$ (see eq 16). The chains are assumed as infinitely long ($N \rightarrow \infty$).

terms how much the currently accepted results should be modified, in view of the related expansion. First of all, it is apparent that no basic change in the definition of the Θ state is required, as long as the equality $\beta = v_c + v_{si} = 0$ still implies $\langle r_N^2 \rangle / Nl^2$ = constant for large N. However, the constant itself should not be exactly identified with the characteristic ratio $C(0)$ of an ideal polymer chain devoid of intrinsic volume, the configurational behavior of which is solely determined by its local stereochemical structure and first-neighboring conformational interactions (ideal phantom chain).[8]

To obtain an approximate estimate of the expansion effect due to the screened-interaction potentials, we will take into consideration polyethylene (PE), isotactic polypropylene (PP), and atactic polystyrene (PS) as fairly typical examples of chains with different flexibility and bulkiness, the unperturbed dimensions of which have been subjected to several experimental investigations.[9] Let us preliminarily discuss the range of validity of the Gaussian law for $W_k(\mathbf{r})$ (see eq 9), bearing in mind that only the small values of r ($\lesssim$10 Å) are important in the present context. Flory and co-workers[10,11] carried out detailed investigations on the probability distribution of the end-to-end vector of polyethylene and poly(dimethylsiloxane) chains of different length. For the sake of comparison, we will translate their radial distribution function $W(r)$ into $4\pi r^2 \bar{W}_k(\mathbf{r})$, where $\bar{W}_k(\mathbf{r})$ is a spherically averaged density probability, directly comparable with our $W_k(\mathbf{r})$ (eq 2–9). Expanding $\bar{W}_k(\mathbf{r})$ into an even-power series (b_{0k} and $b_{ik} > 0$)

$$\bar{W}_k(\mathbf{r}) = b_{0k} - b_{1k}r^2 + b_{2k}r^4 + \ldots =$$
$$b_{0k}\exp(-b_{1k}r^2/b_{0k}) + \text{terms with } r^4 \text{ and higher powers} \tag{21}$$

the excluded volume coefficient $a_2[k]$ (see eq 9) reduces to

$$a_2[k] = b_{1k}(\langle r_{si}^2 \rangle - \langle r_c^2 \rangle)v_c \tag{22}$$

since for our practical purposes the terms depending on r^4 and higher powers may be neglected. We carried out a numerical analysis of the radial distributions $4\pi r^2 \cdot \bar{W}_k(\mathbf{r})$ obtained by Yoon and Flory for PE chains with k = 10, 20, and 40 skeletal bonds, in the range $0 < r < 7$ Å (Figures 22–24 of ref 10). Both the Monte Carlo and the Gaussian profiles are well represented by polynomials truncated after the b_{2k} term (see eq 21); the resulting ratios between the Monte Carlo and the Gaussian values of b_{1k} are ~0, ~0.4, and ~0.8 for k = 10, 20, and 40, respectively. Otherwise said, the terms with k = 10, 20, and 40 appearing in the free energy expression (13) should be reduced by these respective factors; within our simplified scheme, we decided to account approximately for this effect by choosing for polyethylene a lower cutoff $\bar{k}$ equal to 40. As for PP and PS, the corresponding figure was modified according to an inverse dependence on the length of the statistical segment, i.e., on $C(0)$ (see Table I).

Proceeding to evaluate the constant K_0 (see eq 14), we have chosen the following criteria to evaluate the parameters v_c, $\langle r_{si}^2 \rangle$, and $\langle r_c^2 \rangle$. As for v_c, it will merely be identified with the intrinsic volume to be attributed on the average to each chain atom and its substituted groups; namely, considering the polymer crystal structure as our reference state,[12-14] v_c will be given by the unit cell volume divided by the number of skeletal atoms comprised therein (see Table I). (It should be noted that here we are referring to isotactic polystyrene, the structural data of which are roughly extended to the atactic polymer.) However, it is to be pointed out that some overestimate of v_c may be entailed in this picture, because eq 1 and 2 rest on the implicit assumption that pairwise contacts are independent events; i.e., any correlation among them is ignored within the present approximation.[3] In fact, the occurrence of one contact makes additional contacts involving adjacent atoms more probable, and their consequent clustering should reduce the proportion of the forbidden configurations below the level implicit in the present picture. Let us now label with d the shortest distance between chain axes in the crystalline state. To the extent that it should roughly correspond to the distance between the skeletal atoms of two contacting segments at their van der Waals optimum separation, we will identify $\langle r_{si}^2 \rangle$ with d^2. Also, $\langle r_c^2 \rangle$ will be merely equated to the mean-square radius of gyration of a cylinder with radius d, i.e., $d^2/2$. In conclusion

$$\langle r_{si}^2 \rangle - \langle r_c^2 \rangle \simeq d^2 - d^2/2 = d^2/2 \tag{23}$$

(We remark that this estimate may be presumed as too small, to the extent that two-chain segments in solution are conformationally unsuitable to give a crystalline-like packing, which may somehow compensate the previous overestimate of v_c.) As expected, the resulting value of K_0

is much larger for PP and PS than for PE (see Table I). More important, the related adimensional parameter K (see eq 17 and 18) is of order unity in the two former cases, thus suggesting a significant asymptotic expansion, i.e., $\tilde{\alpha}^2(0) - 1 > 0.1$. In fact, the values of K would be 0.43 and 0.37 for PP and PS, if the respective, average experimental figures of C_∞ (i.e., $\sim$5.5 and 10[9]) were substituted for $C(0)$ in eq 18. On the other hand, considering the relationship

$$C_\infty = \lim_{N\to\infty} (\langle r_N^2 \rangle / N l^2) = C(0)\tilde{\alpha}^2(0) \tag{24}$$

which may be derived from eq 12, the corresponding expansion would make $C(0)$ smaller than C_∞, and K would be further enhanced. We have avoided the self-entanglement of the problem by first choosing a value of $C(0)$ that gives the experimental characteristic ratio after accounting for the expansion. The functions $C(q)$ adopted by us were derived from those previously evaluated for polyethylene[7] through the approximate analytical form

$$C(q) = [a/(1 - b \cos q)] + c \tag{25}$$

the parameters of which (see Table I) are fitted on (i) the value chosen for $C(0)$, (ii) the assumption that the peak half-width $\Delta q_{1/2}$ is inversely proportional to $C(0)$,[7b] and (iii) the normalization requirement

$$\frac{1}{2\pi}\int_{-\pi}^{+\pi} C(q)\, dq = 1 \tag{26}$$

The above equation amounts to the constraint that the C–C bond length in the unperturbed state is equal to l, as may be verified from eq 11 after putting $k = 1$ and $\tilde{\alpha}^2(q) \equiv 1$ and changing the sum into the integral. This also suggests that the fixed-bond-length constraint may be introduced into our formalism by merely adding a term $\mu(\sum_q C(q)\tilde{\alpha}^2(q) - N)$ to the free energy (see eq 13); after differentiation the integral equation (15) contains an extra term $+(2/3\mu)C(q)$ in the denominator, and the Lagrange multiplier μ is then obtained by imposing $\sum_q C(q)\tilde{\alpha}^2(q) = N$. Obviously enough, the iterative procedure to evaluate $\tilde{\alpha}(q)$ from eq 15[3] has been extended by us to include μ as well. Besides, for the sake of simplicity we have considered the infinite chain limit (i.e., $N \to \infty$).

The results of $\alpha^2(k)$ vs. k (see eq 19) are reported in Figure 1 for the three polymers. While in all the cases the bond-length constraint has been applied, the curve corresponding to no constraint is also reported for polypropylene; as may be seen, the difference between the values of $\alpha^2(k)$ is about 0.035 and is almost constant through the whole k range. (In the other two cases the expansion is smaller, and this difference is also proportionately smaller.) For $k = 1000$ about 90% of the asymptotic expansion is reached, and most of its change is localized in the interval $10 < k < 1000$. Hopefully, diffraction experiments should be able to detect this effect. In particular, considering that the ratio $\langle r_k^2 \rangle / k l^2$ should not increase appreciably for the ideal, phantom chain beyond $k > 100$,[8] the range $100 < k < 1000$ should be particularly informative (i.e., roughly $0.02 < Q$ $(=4\pi \sin(\theta/2)/\lambda) < 0.07$ Å^{-1}). In fact, here the expansion should lead to a Q^{-n} behavior of the equilibrium structure factor $S(Q)$, n being smaller than the value of 2 that is to be expected for the ideal chain.[16] Quite obviously, the smallest expansion is obtained with the thin polyethylene macromolecule. The extreme case of a thin chain could be represented by poly(tetrafluoroethylene), which has no bulky side groups and a very long statistical segment ($C_\infty \approx 30$[17]); the calculated asymptotic expansion would be around 1%.

The computed characteristic ratios $C_\infty = C(0)\tilde{\alpha}^2(0)$ are 6.7, 5.9, and 9.8 for PE, PP, and PS, respectively, in reasonable agreement with experiment.[9] It should be noted that a change in $C(0)$ for the strongly expanded isotactic polypropylene would imply a smaller change in C_∞, because the resulting $\tilde{\alpha}^2(0)$ tends to compensate the difference; as an example, if $C(0)$ is varied from 4.5 to 4.0, C_∞ changes from 5.9 to 5.6. This suggests that with polymer chains not particularly extended and carrying bulky side groups (e.g., poly(α-olefins) in general), the experimental value of C_∞ might be influenced to a relatively minor degree by the iso-, syndio-, or atactic stereochemical structure, in spite of possible differences in $C(0)$. This indeed appears not to be inconsistent with the experimental data (see ref 9; see also Table II of ref 15 and references reported therein).

It should be stressed that the self-consistent method used here is an approximation, the implications of which are difficult to control. However, comparison between the power-law exponents of $\alpha^2(k)$ and of $p(k)$ (probability of contact between atoms separated by k bonds) as obtained with the present and with exact field theoretical methods appears to be good.[3] As a further remark, although third-order and higher order contacts have been explicitly ignored, the screened-interaction repulsion has some analogy with that postulated for the third-virial term.[18–22] In particular, from field theoretical methods Stephen[20] obtains $\alpha^2 = 1 + A/\ln N$ for an N-atom chain at the Θ point, with a logarithmically small expansion. More recently, Duplantier[21] gets $\alpha^2 = \rho(1 - A/\ln N)$, where ρ (>1) depends on the three-body interactions. This result is qualitatively in good agreement with the conclusions of the present study, although deriving from a different physical origin. Webman, Lebowitz, and Kalos[22] investigate by Monte Carlo methods the collapse of a polymer chain at $T < \Theta$ by using interatomic potentials with both a repulsive and an attractive component, in analogy with the present approach; they also find an expansion of $\langle r_N^2 \rangle$ at the Θ temperature. While we shall discuss these conclusions in more detail in a following paper on polymer collapse,[23] here we may point out that our results also implicitly indicate that the effective Θ temperature appears to decrease for short chains. Formal comparison of the screened-interaction effect with the third-virial term may be carried out in the mean-field approximation. As explicitly pointed out by de Gennes,[18] the latter term would be given in eq 1 by a positive addendum independent of N and proportional to α^{-6}. The corresponding screened-interaction term may be obtained after dividing both members of eq 17 by α^6 (where $\alpha \equiv \tilde{\alpha}(0)$) and then integrating over α and comparing with eq 1; the resulting term is also independent of N (for $N \to \infty$) but is proportional to α^{-5}. However, it should be pointed out that at $T < \Theta$, in the region of incipient collapse, the average compression degree α may only be attributed to pairs of atoms separated by a number of bonds of order N at least. This introduces a dependence as $\alpha^{-5}N^{-1/2}$ into the screened-interaction term, thus creating a resistance against collapse that increases with $N^{-1/2}$, unlike the case of the three-body interactions.[23]

It should be concluded that the present approach obviously needs further refining in addition to comparison with experiment. The contact probability between atoms relatively close along the chain sequence ($k \simeq \bar{k}$) should be more closely investigated, and more accurate criteria to evaluate v_c, $\langle r_c^2 \rangle$, and $\langle r_{si}^2 \rangle$ could perhaps be established (cf. eq 6).

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A Theoretical Basis for Viscoelastic Relaxation of Elastomers in the Long-Time Limit[†]

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ABSTRACT: A molecular interpretation of the viscoelastic behavior of elastomers at long times is developed. This interpretation is based on a model consisting of dangling chain ends (branches) in a cross-linked network with topological constraints (entanglements). We make use of results by de Gennes for the reptation of a single branched chain with topological constraints. We then sum over contributions to the relaxation modulus from a distribution of branch lengths. The distribution function for chain branches was obtained by assuming that the network was formed from primary molecules due to a random cross-linking process. This leads to a relaxation modulus having power law dependence on time as in the empirical Chasset and Thirion equation. The theory also predicts that the parameters in the Chasset and Thirion equation have a cross-link density dependence which is consistent with available experimental data on natural rubber. Furthermore, the present treatment predicts that relaxation curves of different cross-link density are approximately superposable along the log time axis. The shift factor is predicted to have power law dependence on cross-link density, as observed experimentally by Plazek. Finally, the present theory predicts that the Plazek exponent (x) for the shift factor is approximately related to the Chasset and Thirion exponent (m) for the relaxation modulus ($x \sim 2/m$) in a manner consistent with available experimental data.

Introduction

It is well-known[1,2] that elastomers undergo extremely long-term relaxation processes as seen in stress relaxation and creep experiments. Furthermore, the time required to achieve equilibrium decreases dramatically as the cross-link density increases. Ferry has suggested[2] that the molecular mechanism responsible for this long-term process is the diffusion of chain branches (dangling ends) in the presence of entanglements. Recently, de Gennes[3] analyzed the reptation of branched polymers in the presence of topological constraints. We feel that this approach may provide a molecular basis for certain empirical relationships which describe the viscoelastic behavior of elastomers in the terminal relaxation region. The purpose of this paper, therefore, is to compare these existing empirical observations with the predictions of the theories for reptation of branched chains.

Phenomenological Observations

Typical stress relaxation behavior[1] of elastomers at long times is shown in Figure 1 for natural rubber. Chasset and Thirion[1] recognized that an excellent representation of this data is given by

$$E(T) = E_\infty[1 + (t/\tau_0)^{-m}] \tag{1}$$

for large times t, where $E(t)$ is the isothermal relaxation modulus. E_∞ is the equilibrium modulus, and m and τ_0 are material parameters. This relationship holds for temperatures below which no chemical reaction or degradation occurs during the experiment. In most systems the exponent m is approximately 0.1. A similar expression also holds for the time dependence of the creep compliance.[2] Equation 1 is an excellent representation of data for many systems and is sometimes used for estimating the equilibrium modulus E_∞ from stress relaxation experiments.

The relaxation behavior is strongly dependent on temperature and cross-link density. Plazek[4] and Dickie and Ferry[5] observed that viscoelastic curves at fixed cross-link

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