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Chain Expansion in the Θ State

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ABSTRACT: The conformation of a polymer chain with N ($\gg 1$) skeletal atoms in the Θ state is investigated by considering the two-atom repulsions arising from mere prohibition of their space overlap (screened interactions) in addition to the classical two- and three-atom interactions. The free energy due to the screened interactions depends on $\langle r^2\rangle^{-5/2}$ instead of $\langle r^2\rangle^{-3/2}$ as for the classical two-atom interactions, $\langle r^2\rangle$ being the mean-square interatomic distance. Unlike the long-range two- and three-body interactions, the screened interactions are of a medium-range type; in addition, they cannot be simply absorbed in the effective segment length for a finite linear chain. The Gaussian approximation is used and a series expansion is adopted for the mean-square distances whose coefficients are evaluated through a self-consistent optimization of the free energy. The Θ temperature is obtained from the vanishing of the second virial coefficient through an appropriate treatment of the intramolecular free energies. For a real hydrocarbon chain like atactic polystyrene the expansion ratio $\alpha^2(N) = \langle r^2(N)\rangle / \langle r^2(N)\rangle_{\text{(phantom chain)}}$, where $\langle r^2(N)\rangle$ is the mean-square length, is accurately expressed as $\bar{\alpha}^2(1 - \Delta/\sqrt{N})$, $\bar{\alpha}^2$ being about 1.20 and Δ of order unity; this result is overwhelmingly due to the screened interactions, the classical two- and three-body interactions playing a minor role. Both the N dependence and (approximately) the figures for $\bar{\alpha}^2$ and Δ are in agreement with Monte Carlo results obtained by Bruns from chains placed on a regular lattice (*Macromolecules* **1989**, *22*, 2829); a substantial agreement is also observed with experimental results reported by Konishi et al. for atactic polystyrene chains of relatively low molecular weight (*Macromolecules* **1990**, *23*, 290). The logarithmic terms predicted for $\alpha^2(N)$ by the renormalization group approach in the long-chain limit are also commented upon.

Introduction

It is well-known that, for a given polymer/solvent pair, a temperature may be reached at which interactions between different chains essentially disappear by mutual cancellation. This is denoted as the Θ temperature and is the analogue of the Boyle temperature for a real gas.[1] Since the interactions only depend on the nature of the interacting atoms under given conditions, absence of forces between atoms of *different* chains must be accompanied by a similar absence of forces *within* a given chain; this concept is expressed by stating that at the Θ temperature we have the *unperturbed state* of the chain.[1,2] Accordingly, the resulting picture is somehow similar to that to be expected for an ideal chain wherein the constituent atoms are completely insensitive to one another. It should be remembered, though, that such a lack of intramolecular interactions is due to a balance of long-range attractive and repulsive interactions and also that it is by no means complete. First of all, interactions at short range, namely between atoms separated by about 10–15 covalent bonds or less, in no way may be suppressed by any choice of solvent or temperature. These interactions are strictly associated with a relatively small set of highly probable local conformations, producing strong spatial correlation among neighboring atoms. Second, although the hard-core repulsion between any two atoms, no matter how widely separated in the topological sense, may be somehow balanced by attraction at suitable distances, the fact remains that they cannot overlap in space (covolume requirement). We shall define as the *phantom chain* the ideal model in which the covolume requirement is neglected except for the shortest range interactions.[2] This model, in which correlation between adjacent skeletal rotations plays an essential role, is frequently regarded as a sufficiently accurate description of the real unperturbed chain.[2]

In the phantom chain all the mean-square interatomic distances may be exactly evaluated through the generalized characteristic ratio $C(q)$, proportional to the mean-square amplitude of the Fourier configurational components along the chain contour; in turn, $C(q)$ may be obtained through conformational–statistical analysis.[3] When the number k of chemical bonds separating two chain atoms exceeds some limit, of order 100 for several hydrocarbon polymers, their mean-square distance gradually approaches the dependence $kC(0)l^2$, where l is the bond length. This simple result, reminiscent of the random-walk chain, indicates that the chain portion separating the two atoms comprises essentially uncorrelated segments (statistical segments) the length of which is $\approx lC(0)$. In turn, the number of conformations available to the chain portion is very large, no high-probability conformational subset existing which predominates over the whole; consequently, we may apply the Gaussian statistics to the mean-square distances.[4] In the following, we shall assume that the chain length exceeds the previously indicated limit, so that identification of $C(q)$ with the constant value $C(0)$ is effectively permitted. While $C(0)$ may be denoted as the phantom-chain characteristic ratio, we will show that it may be significantly lower than the actual characteristic ratio C_∞ of the real chain, owing to its nonphantom character.[5,6]

In the present paper the results of a statistical–conformational investigation of real polymer chains in their unperturbed, or Θ, state will be reported. Actually, this problem has been the subject of considerable debate in recent years.[7–18] Of the several issues at stake, here we point out in particular the two following ones: (i) whether approaches based on the usual two- and three-body interaction model predict expansion or contraction with respect to the ideal phantom chain, for varying chain lengths; (ii) whether or not significant repulsive forces not reducible to the usual two- and three-body interactions exist,[5,6] which may significantly expand the chain beyond the phantom size, thus possibly explaining the Monte Carlo results obtained by Mazur and McCrackin[14] and, especially, by Bruns.[15] We will show that the second issue appears to be intimately entangled with the first one. In particular, the basic result of the present paper is that the "screened interactions" effect, namely the residual repul-

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sion arising from the lack of coincidence between the repulsive and the attractive range between two atoms—the former spanning interatomic distances r smaller than the van der Waals value r_{vdW}, the latter $r > r_{\mathrm{vdW}}$[5,16]—appears to override the attraction predicted for unperturbed chains by considering two- and three-body interactions only.[11-13] The present study is based on the Gaussian approximation, namely on the a priori assumption that the mean-square distance between any two atoms is Gaussian. The actual value of the mean-square distances will be obtained after a suitable minimization of the free energy, considering all interatomic interactions and using the same Fourier configurational representation that leads to $C(q)$.[3-6] It should be noted that in principle the real probability distribution is not necessarily of the Gaussian type, because it results from a weighted average of distributions over the different contact graphs of the chain, each of which is Gaussian.[17] However, due to the relative weakness of the interactions at the Θ temperature, the Gaussian approximation appears to be quite adequate, under normal circumstances. Only in the case of chains reaching an extremely large length, renormalization group results (see in particular the work by Stephen,[8] Cherayil et al.,[11] and Duplantier[9,18]) suggest a correction to the mean-square end-to-end distance which reaches its asymptotic limit as $(\ln N)^{-1}$, N being the number of chain atoms, and which is not encompassed except marginally by our analysis. The quantitative relevance of this logarithmic term will be discussed at the end of the section dealing with the chain deformation at $T = \Theta$.

Starting from the model description, we shall propose a new procedure to obtain the Θ temperature for linear chains by differentiation of the *intra*molecular free energy. At this temperature, the chain deformation with respect to the phantom chain model will be evaluated by a self-consistent procedure. The results will be compared with those from Monte Carlo calculations,[14,15] as well as with recent experimental data on unperturbed polystyrene. We will also briefly comment on the values of the Θ temperature expected for linear chains of varying length and those predicted for regular star polymers. A general discussion will follow.

Model

For the sake of simplicity, we shall consider first a bead-and-spring model, with $(n + 1)$ beads and n ($\gg 1$) bonds of mean-square length ℓ^2. In the purely phantom state with no intramolecular interactions, the mean-square end-to-end distance is $n\ell^2$, as expected for an n-step random walk. Since $NC(0)l^2$ is the corresponding mean-square distance of an unperturbed phantom chain with N chemical bonds of length l, which only experiences stereochemical interactions in the shortest range (<5–15 bonds),[2,3] we may state the correspondence

$$n = N \qquad \ell^2 = C(0)l^2 \tag{1}$$

$C(0)$ being the phantom chain characteristic ratio. In other words, to the extent that we are only interested in specifying the mean-square distances, our bead-and-spring model will consist of $N (\cong N + 1)$ beads (=atoms), provided the effective bond length is $\ell = l\sqrt{C(0)}$. (It should be stressed that the bead-and-spring model does not have the same contour length as the phantom chain, so that ℓ is not to be understood as the statistical segment length.) The unperturbed real chain will be obtained after long- and medium-range interactions are introduced, as discussed in the following. The interatomic distances will be assumed to retain the Gaussian distribution, although their mean-square values will generally differ from the random-walk expectation.

The long-range interactions include the classical two- and three-body interactions. Let us consider atoms A, B, C, ... within the same chain, with mean-square distances $\langle r^2{}_{\mathrm{AB}}\rangle$, $\langle r^2{}_{\mathrm{AC}}\rangle$, $\langle r^2{}_{\mathrm{BC}}\rangle$, ... In $k_{\mathrm{B}}T$ units, each atom pair contributes to the free energy a two-body term

$$a_2(\mathrm{A, B}) = \beta\left(\frac{3}{2\pi\langle r^2{}_{\mathrm{AB}}\rangle}\right)^{3/2} \tag{2}$$

whereas each atom triple gives a three-body term

$$a_3(\mathrm{A, B, C}) = \bar{y}\left(\frac{3}{2\pi}\right)^3[f(\langle r^2{}_{\mathrm{AB}}\rangle,\langle r^2{}_{\mathrm{BC}}\rangle,\langle r^2{}_{\mathrm{AC}}\rangle)]^{-3/2} \tag{3}$$

In these equations, β is the binary cluster integral, $\bar{y}$ is the three-body interaction parameter, and $f(x,y,z)$ is given by

$$f(x,y,z) = {}^1/_2(xy + yz + xz) - {}^1/_4(x^2 + y^2 + z^2) \tag{4}$$

In turn, $f^{-3/2}$ is proportional to the probability of the three-atom contact. It may be shown that the requirement $f(x,y,z) > 0$ implies that the root-mean-square distances between A, B, and C must fulfill the same inequalities as the edge lengths of a triangle (chain connectivity requirement).[6,19] At the Θ state an important simplification arises. Let A, B, and C follow along the chain sequence and k, k_1, and $(k + k_1)$ be the numbers of chain bonds separating the pairs (AB), (BC), and (AC), respectively. Letting

$$\langle r^2{}_{\mathrm{AC}}\rangle = \langle r^2(k + k_1)\rangle = \langle r^2(k)\rangle + \langle r^2(k_1)\rangle + \delta(k,k_1) \tag{5}$$

the function f reduces to

$$f(\langle r^2{}_{\mathrm{AC}}\rangle,\langle r^2{}_{\mathrm{BC}}\rangle,\langle r^2{}_{\mathrm{AC}}\rangle) = \langle r^2(k)\rangle\langle r^2(k_1)\rangle - \delta^2(k,k_1)/4 \cong \langle r(k)\rangle\langle r^2(k_1)\rangle \tag{6}$$

where the last approximate equality is justified because in the Θ state $\delta(k,k_1)$ is small compared with $\langle r^2(k)\rangle$ and $\langle r^2(k_1)\rangle$, reducing to zero in the phantom chain limit. It is not difficult to check that the related inaccuracy is smaller than the admissible error in the present context. In the vicinity of the Θ temperature, $\bar{y}$ may be regarded as a positive constant, whereas β is defined as

$$\beta = \int_v[1 - \exp(-w(\mathbf{r})/k_{\mathrm{B}}T)]\,\mathrm{d}^3\mathbf{r} \tag{7}$$

where the effective interatomic potential $w(\mathbf{r})$ is assumed of the Lennard-Jones type (see Figure 1); it should be noted that $w(\mathbf{r})$ embodies the effect of the solvent. Unlike $\bar{y}$, β is strongly temperature-dependent in the vicinity of Θ. Denoting as Θ_{ph} the phantom chain Θ temperature giving $\beta(\Theta_{\mathrm{ph}}) = 0$, in which case we have the ideal phantom chain if no other interaction exists, we shall take

$$\beta = \tau_{\mathrm{ph}}B(2\pi\ell^2/3)^{3/2} \qquad \tau_{\mathrm{ph}} = (T - \Theta_{\mathrm{ph}})/T \tag{8}$$

The pure number B is proportional to the volume effectively occupied by one chain atom. If β is zero or positive, in the infinite chain limit the repulsive effect due to the a_2 and a_3 terms leads to the well-known dependence of the mean-square chain size as $N^{2\nu}$, $2\nu \cong 1.2$. If β is so negative that the contraction effect of the a_2 terms is overwhelming, in the same limit the mean-square chain size is $\propto N^{2/3}$. As a third possibility, β may be slightly negative, so that the opposite effects of the a_2 and a_3 terms are exactly compensated, and we are at the Θ temperature, the mean-square chain size being $\propto N$. The effective parameter controlling contraction or expansion of the whole chain is $\beta_{\mathrm{eff}}\sqrt{N}$, wherein $\beta_{\mathrm{eff}} = \beta + \sigma_3$,[6] σ_3 being the three-body correction to the bare interaction parameter

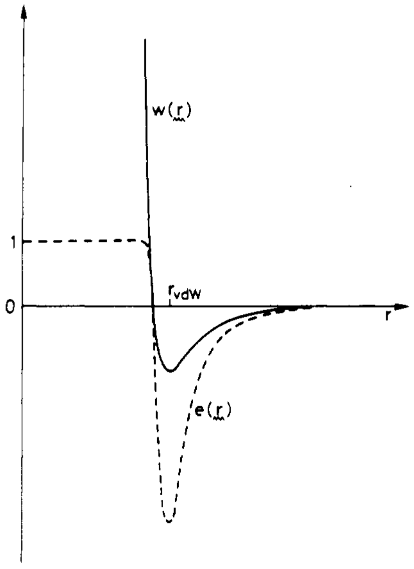

Figure 1. Interatomic potential $w(\mathbf{r})$ as a function of interatomic distance $r = |\mathbf{r}|$ (solid line). The effective potential $e(\mathbf{r}) = 1 - \exp(-w(\mathbf{r})/k_BT)$ corresponding to the integrand in eq 7 is also shown (dashed line); the temperature is chosen so that the positive and negative areas under $e(\mathbf{r})$ cancel ($\beta = 0$).

β. We see that the long-range interactions determine the so-called tricritical behavior of the polymer dilute solution at the Θ point,[7] in the thermodynamic limit $N \to \infty$. It should be noted that since the Θ state is attained for $\beta_{\text{eff}} = 0$ (see the following), use of eq 8 implies also a somewhat subtle rescaling of B to take into account those three-body interactions in which two of the three atoms are close along the chain sequence.

Let us now briefly discuss the medium-range, or screened, interactions. We give at first the result: even for β equal to zero or negative, the interaction potential between atoms A and B within the same chain comprises a repulsive contribution of the form

$$a_{2S}(\mathrm{A,B}) = K_0\langle r^2_{\mathrm{AB}}\rangle^{-5/2} \qquad K_0 \propto v_c\langle\Delta^2 r\rangle \tag{9}$$

which adds to $a_2(\mathrm{A,B})$ (see eq 2). v_c is the effective volume per chain atom, $\langle\Delta^2 r\rangle$ is the mean-square chain thickness, and K_0 may be regarded as independent from temperature.[5,6,16] The physical origin of a_{2S} resides in that, if $\langle r^2_{\mathrm{AB}}\rangle$ is finite, the *effective* binary integral for the atom pair must be evaluated by introducing a probability weight $\propto \exp(-3r^2/2\langle r^2_{\mathrm{AB}}\rangle)$ inside the integral of eq 7. This new factor makes the contribution of the repulsive volume at low $|\mathbf{r}|$ *larger* than that of the attractive volume at high $|\mathbf{r}|$ (see Figure 1) even if $\beta = 0$, so that we have a net positive result $\propto \langle r^2_{\mathrm{AB}}\rangle^{-5/2}$. Otherwise said, in spite of the attractive region surrounding and screening the hard-core repulsion, the resulting screened interaction remains repulsive, although milder than the classical two-body repulsion $\propto \langle r^2_{\mathrm{AB}}\rangle^{-3/2}$. The resulting effect progressively expands a typical hydrocarbon chain beyond the phantom size, up to an interatomic separation of a few thousand chain bonds, after which it reaches an asymptotic limit.[5,6] This fact, together with the absence of substantial changes induced upon the tricritical behavior of infinitely long chains around the Θ point, justifies the definition of *medium-range* interactions for the screened interactions. It was shown that these interactions may become important in resisting chain collapse at $T < \Theta$, where most interatomic distances become very small.[16,19]

From a previous study of the screened interaction effect in the infinite, unperturbed chain,[5] the resulting mean-square distance between two atoms separated by k bonds was given by

$$\langle r^2(k)\rangle \cong \langle r^2(k)\rangle_{\text{ph}}\bar{\alpha}^2[1 - \Delta/\sqrt{k}] \tag{10}$$

where $\langle r^2(k)\rangle_{\text{ph}} = k\ell^2$ is the phantom chain value, $\bar{\alpha}^2$ (>1) is the asymptotic expansion limit, and Δ is a suitable positive parameter. Since a basically similar law also applies to the residual effect of the two- and three-body interactions around the Θ point, logarithmic corrections excepted (see the following), we shall use eq 10 as a perturbative starting point to the conformational analysis at the Θ state. The parameters in eq 10 will be obtained after a self-consistent optimization of the chain free energy, according to a well-established procedure.[5,6,19] The whole approach may be regarded as a second-order perturbation analysis, if the first-order level is assumed to coincide with the mere determination of $\bar{\alpha}^2$ in eq 10, disregarding Δ. For simplicity, we shall focus our analysis on the mean-square end-to-end distance $\langle r^2(N)\rangle$, assuming the uniform conformational behavior given by eq 10 throughout the chain. Since no confusion may arise in this context, no suffix is adopted here to denote the Θ state.

Θ Temperature

The unperturbed, or Θ, temperature of a polymer/solvent pair is defined as the one at which the second virial coefficient A_2 vanishes. In turn, A_2 may be expressed as[17]

$$A_2 = -(N_{\mathrm{Av}}/2VM^2)\int[W(1,2) - W(1)W(2)]\,\mathrm{d}(1,2) \tag{11}$$

N_{Av}, V, and M being, respectively, Avogadro's number, the volume of the solution, and the polymer molar mass, whereas $W(1)$, $W(2)$, and $W(1,2)$ are the Boltzmann statistical weights of chain 1, of chain 2, and of the ensemble of both chains, respectively. The integral is performed over all the configurational coordinates—external as well as internal—of the two chains and may be expressed as

$$\int[W(1,2) - W(1)W(2)]\,\mathrm{d}(1,2) = V^2[Z(1,2) - Z(1)Z(2)] = V^2(\exp[-\mathcal{A}(1,2)] - \exp[-\mathcal{A}(1) - \mathcal{A}(2)]) \tag{12}$$

where the Z's and the $\mathcal{A}$'s are the configurational partition functions and the Helmholtz free energies in k_BT units, respectively. From eqs 11 and 12 we have

$$A_2 = -C(\exp[-\mathcal{A}_{\text{inter}}(1,2)] - 1)$$
$$\mathcal{A}_{\text{inter}}(1,2) = \mathcal{A}(1,2) - \mathcal{A}(1) - \mathcal{A}(2)$$
$$C = (N_{\mathrm{Av}}V/2M^2)\exp[-\mathcal{A}(1) - \mathcal{A}(2)] \tag{13}$$

$\mathcal{A}_{\text{inter}}(1,2)$ is the intermolecular free energy. In the vicinity of the Θ temperature and assuming at first that we only have two-atom interactions, from eqs 20.11–20.17 of Yamakawa's book[17] we get

$$\mathcal{A}_{\text{inter}}(1,2) = (N^2\beta/v_c)[1 - \beta P_2/N^2 + \beta^2 P_3/N^4 \ldots] \tag{14}$$

where N and β were already introduced in eqs 1, 7, and 8, whereas P_2, P_3 ... are proportional to the probabilities of having simultaneous contacts between 2, 3, ... pairs of atoms. Equation 14 provides a useful normalization constant for the interaction free energy because we get

$$[\partial\mathcal{A}_{\mathrm{inter}}(1,2)/\partial\beta]_{\beta\to 0} = N^2/v_c \qquad (15)$$

In the same limit $\beta \to 0$ we also have, from Yamakawa's eq 20.11–20.14

$$C_{\beta\to 0} = N_{\mathrm{Av}}v_c/2M^2 \qquad (16)$$

which completes the normalization constants needed for A_2. From eq 13 we see that the equation $A_2 = 0$ is satisfied when $\mathcal{A}_{\mathrm{inter}}(1,2) = 0$, which may also be taken as the condition determining the Θ temperature.

The single-chain free energy $\mathcal{A}$ will be written as a sum of an elastic component $\mathcal{A}_{\mathrm{el}}$ and an intramolecular interactions contribution $\mathcal{A}_{\mathrm{intram}}$:

$$\mathcal{A} = \mathcal{A}_{\mathrm{el}} + \mathcal{A}_{\mathrm{intram}} \qquad (17)$$

While the former component is purely configurational, i.e., entropic, the latter arises from the interatomic contacts within the chain.[6,19] In the following section we show that $\mathcal{A}_{\mathrm{inter}}(1,2)$ may be obtained from suitable differentiation of $\mathcal{A}_{\mathrm{intram}}$.

Intermolecular Free Energy

Within the Gaussian approach, at the Θ temperature the intramolecular free energy of the N-bond chain with a cutoff $\bar{k}$ is given by (in k_BT units)

$$\mathcal{A}_{\mathrm{intram}}(N,\bar{k}) = \mathcal{A}_2 + \mathcal{A}_3 + \mathcal{A}_{2\mathrm{S}} \qquad (18)$$

where (see eqs 1–9)

$$\mathcal{A}_2 = \sum\sum\nolimits_{\mathrm{A<B}} a_2(\mathrm{A,B}) = \bar{\tau}_{\mathrm{ph}}B \int_{\bar{k}}^{N} (N-k)\frac{\mathrm{d}k}{J(k)^{3/2}}$$

$$\mathcal{A}_3 = \sum\sum\sum\nolimits_{\mathrm{A<B<C}} a_3(\mathrm{A,B,C}) = K_1\int_{\bar{k}}^{N-\bar{k}}\frac{\mathrm{d}k}{J(k)^{3/2}}\int_{\bar{k}}^{N-k}\frac{(N-k-k_1)\,\mathrm{d}k_1}{J(k_1)^{3/2}} \qquad (19)$$

$$\mathcal{A}_{2\mathrm{S}} = \sum\sum\nolimits_{\mathrm{A<B}} a_{2\mathrm{S}}(\mathrm{A,B}) = K\int_{\bar{k}}^{N}(N-k)\frac{\mathrm{d}k}{J(k)^{5/2}}$$

$$J(k) = \langle r^2(k)\rangle/\ell^2 \qquad \bar{\tau}_{\mathrm{ph}} = (\Theta - \Theta_{\mathrm{ph}})/\Theta \qquad (20)$$

The bar over τ_{ph} indicates $T = \Theta$ (see eq 8).

In eqs 19 and 20 the sums are extended to all the atom pairs and triples, the atoms A, B, C, ... following in the order along the chain. The other symbols are defined as (see eqs 3 and 9)

$$K_1 = \bar{y}(3/2\pi\ell^2)^3 \qquad K = K_0/\ell^5 \qquad (21)$$

In these equations $\bar{\tau}_{\mathrm{ph}}B$, K_1, and K are all adimensional constants respectively specifying the two-body, the three-body, and the screened interactions. Differentiating both sides of eq 18 with respect to $\bar{k}$, remembering eqs 19 and 20, we get

$$\partial\mathcal{A}_{\mathrm{intram}}(N,\bar{k})/\partial\bar{k} = -\frac{N-\bar{k}}{J(\bar{k})^{3/2}}[\bar{\tau}_{\mathrm{ph}}B + K/J(\bar{k})] - \frac{2K_1}{J(\bar{k})^{3/2}}\int_{\bar{k}}^{N-\bar{k}}\frac{N-k-\bar{k}}{J(k)^{3/2}}\,\mathrm{d}k \qquad (22)$$

This result has an interesting interpretation in terms of intermolecular interactions. Let us consider Figure 2, showing the diagram of two interacting chains 1 and 2, each comprising $(N-\bar{k})$ atoms, where the interactions are of the two- and three-body type, respectively A...B and A...B...C. It is possible to see that the right-hand side of eq 22 gives, apart from the sign, the free energy of interaction between the general atom of one chain and the $(N-\bar{k})$ atoms of the other chain, provided we assume that the mean-square distance between interacting atoms A and B on different chains is the same as between atoms separated by $\bar{k}$ bonds on the same chain. The factor 2 accompanying K_1 in the right-hand side of eq 22 accounts for the double choice inherent with the three-body contact, namely with atom A on chain 2 and atoms B and C on chain 1 or vice versa (see Figure 2). From eq 22 the interaction free energy $\mathcal{A}_{\mathrm{inter}}(1,2)$ defined in eq 13 may be obtained after the following steps. First, the chain considered in eq 22 must comprise $(N+\bar{k})$ atoms, instead of N, to produce the correct interaction multiplicity; accordingly, we must replace N with $(N+\bar{k})$ in eq 22. Second, the result must be further multiplied by N, because there are effectively N atoms on chain 2 to interact with chain 1. Third, the A...B contact probability, equal to $v_c/[2\pi\ell^2J(\bar{k})/3]^{3/2} = p_1$ in eq 22, must be replaced by $v_c/V = p$, where $p \ll p_1$ because the solution diameter $V^{1/3}$ is much larger than the root-mean-square average distance A...B in Figure 1:

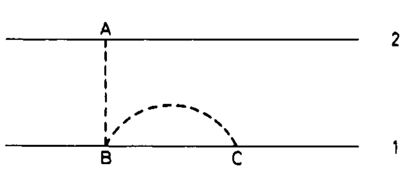

Figure 2. Diagram of interactions between chains 1 and 2. Two-body interactions are given by A...B and three-body interactions by A...B...C. Point A may be on chain 2 and points B and C on chain 1, as in this figure, or vice versa.

$$V^{1/3} \gg \ell J(\bar{k})^{1/2} \qquad (23)$$

This replacement is simply achieved by substituting $J(\bar{k})$ with $3V^{2/3}/(2\pi\ell^2)$ in eq 22, which effectively cancels the term with K relative to the others, because V is arbitrarily large. Consequently, *only the terms deriving from $\mathcal{A}_2$ and $\mathcal{A}_3$ will survive*. Finally, we must remember that $\mathcal{A}_{\mathrm{inter}}(1,2)$ is defined after the external coordinates[17] have been normalized out, which amounts to multiplying again the result by V/v_c. As a result, the factor V disappears and we have

$$\mathcal{A}_{\mathrm{inter}}(1,2|N,\bar{k}) = (N/v_c)[2\pi\ell^2J(\bar{k})/3]^{3/2}G(N+\bar{k},\bar{k}) = 0 \qquad (24)$$

where

$$G(N,\bar{k}) = -\partial[\mathcal{A}_2(N,\bar{k}) + \mathcal{A}_3(N,\bar{k})]/\partial\bar{k} = J(\bar{k})^{-3/2}\left[(N-\bar{k})\bar{\tau}_{\mathrm{ph}}B + 2K_1\int_{\bar{k}}^{N-\bar{k}}\frac{N-k-\bar{k}}{J(k)^{3/2}}\,\mathrm{d}k\right] \qquad (25)$$

In the above equations the dependence of the quantities from N and $\bar{k}$ is stated explicitly. By setting $K_1 = 0$, we see that the result for $\mathcal{A}_{\mathrm{inter}}(1,2)$ is consistent with eq 15, remembering that $\tau_{\mathrm{ph}}B(2\pi\ell^2/3)^{3/2} = \beta$ (see eq 8).

An important feature emerges from analysis of eqs 22, 24, and 25, namely the screened interaction free energy $\mathcal{A}_{2\mathrm{S}}$ does not contribute explicitly to $\mathcal{A}_{\mathrm{inter}}(1,2)$, therefore to the second-virial coefficient A_2 (see eq 13).[20] This result is due to the power dependence $a_{2\mathrm{S}}(\mathrm{A,B}) \propto \langle r^2_{\mathrm{AB}}\rangle^{-u}$, the exponent u being larger than that appearing both in $a_2(\mathrm{A,B})$ and in $a_3(\mathrm{A,B,C})$ (5/2 instead of 3/2, see eqs 2, 3, 6, and 9). Otherwise said, at the Θ temperature no screened interaction arises between two atoms on different chains, because their mean-square distance is so large as to render the effective value of their binary cluster integral vanishing (see Figure 1). On the other hand, the screened interactions affect indirectly $\mathcal{A}_{\text{inter}}(1,2)$, and therefore the actual Θ temperature, by modifying $J(k)$ in eq 25, and hence the contact probability between the two atoms on the same chain in the evaluation of the three-body interactions. Moreover, we shall see that the *intramolecular expansion* induced by the screened interactions is by no means negligible, which is not surprising if we consider that they are not balanced by three-body terms at the Θ state, unlike the two-body interactions.

As a general comment, it should be stressed that the procedure leading to eq 24 is based on the assumption that no conformational effects are to be expected as a result of interactions between chains, which is basically correct in the vicinity of the Θ temperature. Furthermore, it is only valid if the probability of a three-body contact ($\propto f^{-3/2}$, see eq 4) may be effectively factorized as in eq 6, which, strictly speaking, is also only valid for linear chains close to the Θ temperature. We shall comment later on the relevance of this point for star polymers.

Chain Deformation at $T = \Theta$

According to eqs 13, 24, and 25, the requirement $A_2 = 0$ to be obeyed at $T = \Theta$ reduces to $\mathcal{A}_{\text{inter}}(1,2) = 0$, which in turn is a function of $J(k) = \langle r^2(k)\rangle/\ell^2$. Remembering that $J(k)$ reduces to k in the unperturbed phantom state, in the second-order approximation approach we have, from eq 10

$$J(k) \cong \bar{\alpha}^2(1 - \Delta/\sqrt{k})k \qquad J^p(k) \cong \bar{\alpha}^{2p}(1 - p\Delta/\sqrt{k})k^p \tag{26}$$

where $\Delta/\sqrt{k}$ is taken as small compared to unity and $\bar{\alpha}^2$ (>1) is the asymptotic square expansion factor of the interatomic distances. From eqs 24–26 we have

$$\mathcal{A}_{\text{inter}}(1,2) = (N^2/v_{\text{c}})(2\pi\ell^2/3)^{3/2}\{\bar{\tau}_{\text{ph}}B + 2K_1\bar{\alpha}^{-3}[2\bar{k}^{-1/2} - 4N^{-1/2} + 2\bar{k}^{1/2}N^{-1} + {}^3/_2\Delta\bar{k}^{-1} - {}^3/_2\Delta N^{-1}(1 + \ln(N/\bar{k}))]\} = 0 \tag{27}$$

or

$$\bar{\tau}_{\text{ph}} = -(4K_1/B\sqrt{\bar{k}}\alpha^3)\{[1 - (\bar{k}/N)^{1/2}]^2 + {}^3/_4\Delta\sqrt{\bar{k}}[\bar{k}^{-1} - N^{-1}(1 + \ln(N/\bar{k}))]\} \tag{27$'$}$$

From this result we see that the Θ temperature is shifted from the phantom value Θ_{ph} by an amount depending on N (we remind the reader that $\bar{\tau}_{\text{ph}} = (\Theta - \Theta_{\text{ph}})/\Theta$; see eq 20)

$$\Theta(N) \cong \Theta_{\text{ph}}[1 + \bar{\tau}_{\text{ph}}(N)] \cong \Theta_\infty + (\text{constant})/\sqrt{N} \tag{27$''$}$$

considering that $\bar{\tau}_{\text{ph}} \ll 1$. Θ_∞ is $\Theta(N \to \infty)$ and depends not only on the ratio K_1/B between the coefficients of the three- and two-body contributions but also on Δ, which in turn depends on the strength of the screened interaction as a second-order effect:

$$\Theta_\infty = \Theta_{\text{ph}}\left[1 - \frac{4K_1}{B\sqrt{\bar{k}}\bar{\alpha}^3}\left(1 + \frac{3}{4}\frac{\Delta}{\sqrt{\bar{k}}}\right)\right] \tag{27$'''$}$$

Neglecting the small contribution depending on Δ, eq 27$'$ reduces to eq 32$'$ of ref 19. It is also possible to check that eqs 27–27$'''$ reduce to the result obtained by Cherayil et al.[11,21] within a perturbative cutoff calculation and also by Duplantier[18], if we put $\bar{\alpha}^2 = 1$, $\Delta = 0$.

To obtain the strain parameters $\bar{\alpha}^2$ and Δ, we shall concentrate on the square strain ratio of the end-to-end distance, namely

$$\alpha^2(N) = \langle r^2(N)\rangle/\langle r^2(N)\rangle_{\text{ph}} = J(N)/N \tag{28}$$

Let us reiterate that the average expansion with respect to the phantom state between any two atoms is taken to be a unique function of their bond separation, regardless of whether they are chain ends or not (uniform approximation). Accordingly, from eq 26 $\alpha^2(N)$ is

$$\alpha^2(N) \cong \bar{\alpha}^2(1 - \Delta/\sqrt{N}) \tag{29}$$

In turn, the uniform approximation corresponds to the Fourier representation based on the "periodic chain",[6] where the statistically orthogonal vectors $\tilde{\mathbf{l}}(q)$ are given by

$$\tilde{\mathbf{l}}(q) = \sum_{h=1}^{N}\mathbf{l}(h)e^{iqh} \qquad \{q\} = 0, \pm2\pi/n, \pm4\pi/N, ..., \pm\pi$$

$$\langle\tilde{\mathbf{l}}(q)\cdot\tilde{\mathbf{l}}(q')\rangle = N\ell^2\tilde{\alpha}^2(q)\,\Delta(q + q') \qquad (\tilde{\alpha}^2{}_{\text{ph}}(q) \equiv 1) \tag{30}$$

In eq 30 $\mathbf{l}(h)$ is the general bond vector, brackets denote configurational average, and Δ stands for the Kronecker delta. Knowledge of all the $\tilde{\alpha}^2(q)$ enables us to evaluate $\langle r^2(k)\rangle$[6]

$$\langle r^2(k)\rangle = \ell^2N^{-1}\sum_{\{q\}}\tilde{\alpha}^2(q)\sin^2(qk/2)/\sin^2(q/2) \tag{31}$$

which in turn leads to $\mathcal{A}_2$, $\mathcal{A}_3$, and $\mathcal{A}_{2\text{S}}$ (see eqs 19 and 20). The elastic free energy $\mathcal{A}_{\text{el}}$ is also given by the $\tilde{\alpha}^2(q)$'s

$$\mathcal{A}_{\text{el}} = {}^3/_2\sum_{\{q\}}[\tilde{\alpha}^2(q) - 1 - \ln\tilde{\alpha}^2(q)] \tag{32}$$

so that the free energy $\mathcal{A} = \mathcal{A}_{\text{el}} + \mathcal{A}_2 + \mathcal{A}_3 + \mathcal{A}_{2\text{S}}$ may be constructed (see eqs 17–20) and we write the equilibrium equations $\partial\mathcal{A}/\partial\tilde{\alpha}^2(q) = 0$ for the unknowns $\tilde{\alpha}^2(q)$.[19] Since from eq 30 the end-to-end vector $\mathbf{r}(N) = \sum_h\mathbf{l}(h)$ is given by $\tilde{\mathbf{l}}(0)$, $\alpha^2(N)$ reduces to $\tilde{\alpha}^2(q = 0)$ for an N-bond chain, and therefore we shall focus our attention on the derivation of $\tilde{\alpha}^2(0)$. From $\partial\mathcal{A}/\partial\tilde{\alpha}^2(0) = 0$, we have

$$\tilde{\alpha}^2(0) = \alpha^2(N) = \left\{1 - N^{-1}\int_{\bar{k}}^{N-\bar{k}}\mathrm{d}k\frac{k^2}{J(k)^{5/2}}\left[J(\bar{k})^{3/2}G(N + \bar{k} - k, \bar{k}) + \frac{5}{3}\frac{K}{J(k)}(N - k)\right]\right\}^{-1} \tag{33}$$

where $G(N,\bar{k})$ is defined in eq 25. Using eq 26 for $J(k)$ and eq 27$'$ for $\bar{\tau}_{\text{ph}}B$, excluding terms of order N^{-1} or smaller, we get ($T = \Theta$)

$$\alpha^2(N) = [1 + A + BN^{-1/2} + CN^{-1/2}\ln(N/\bar{k})]^{-1} \tag{34}$$

where

$$A = -\frac{K}{\bar{\alpha}^7}\left(\frac{10}{3\sqrt{\bar{k}}} + \frac{35}{6}\frac{\Delta}{\bar{k}}\right) + \frac{K_1}{\bar{\alpha}^8}\left(4\pi - \frac{32}{3}\right)$$

$$B = \frac{20}{3}\frac{K}{\bar{\alpha}^7} + \frac{K_1}{\bar{\alpha}^8}\left(\Delta(52\ln 2 - 30) - \frac{8}{3}\sqrt{\bar{k}}\right)$$

$$C = 2K_1\Delta/\bar{\alpha}^8 \tag{35}$$

Comparison of eq 34 with eq 29 shows that, neglecting the

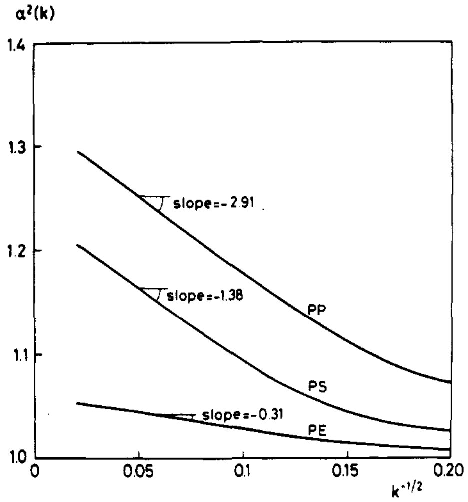

Figure 3. Square expansion factor $\alpha^2(k) = \langle r^2(k)\rangle / \langle r^2(k)\rangle_{\rm ph}$ for atoms separated by k bonds within an unperturbed infinite chain plotted vs $k^{-1/2}$ (from ref 5). The suffix ph indicates the phantom chain (see text). PP stands for isotactic polypropylene, PS for atactic polystyrene, and PE for polyethylene; short-range correlation between rotational states is accounted for. The slopes ($=-\bar{\alpha}^2\Delta$, see text) of the linear portions are also reported. The plots are interrupted for $k^{-1/2} < 2 \times 10^{-2}$ because of insufficient accuracy of the original results;[5] recent calculations show that the linear dependence extends to $k^{-1/2} \to 0$ (see text).

logarithmic term and regarding both A and $B/\sqrt{N}$ as small compared with unity

$$\bar{\alpha}^2 \cong 1/(1 + A) \qquad \Delta \cong B/(1 + A) \tag{36}$$

which may be regarded as a system of two equations in the unknowns $\bar{\alpha}$ and Δ. Applying these results to atactic polystyrene as a realistic example and using the same parameters adopted in refs 5, 6, 16, and 19, i.e., $K = 0.65$, $K_1 = 10^{-3}$, and $\bar{k} = 50$, we have

$$A = -(0.306 + 0.076\Delta)\bar{\alpha}^{-7} + 0.002\bar{\alpha}^{-8}$$

$$B = 4.333\bar{\alpha}^{-7} - (0.019 - 0.006\Delta)\bar{\alpha}^{-8}$$

$$C = 0.002\Delta\bar{\alpha}^{-8} \tag{37}$$

Setting $C \cong 0$, through eq 36 we get $\bar{\alpha}^2 = 1.27$ and $\Delta = 2.4$. These figures are in rough agreement with the results $\bar{\alpha}^2 = 1.22$ and $\Delta' = 1.1$ from self-consistent calculations of $\alpha^2(k)$ reported in Figure 3 after ref (5) (curve labeled as PS), using the equation $\alpha^2(k) = J(k)/k = \bar{\alpha}^2(1 - \Delta'/\sqrt{k})$ in analogy with eq 29. In the same figure we also show the analogous curves calculated for the infinite unperturbed chains of isotactic polypropylene (PP) and polyethylene (PE);[5] as it may be seen, the plots are interrupted at low values of $k^{-1/2}$, where the numerical accuracy accepted in ref 5 is insufficient to show that the linearity persists in the limit $k^{-1/2} \to 0$, as we have now fully confirmed by recent numerical results. Actually, unlike the present study, the joint effect of $\mathcal{A}_2$ and $\mathcal{A}_3$ was totally disregarded in ref 5, thus putting $K_1 = 0$. (This is consistent with the fact that the two- and three-body interactions cancel exactly in the infinite unperturbed chain; see in the following.) However, it should be stressed that even the present results for finite chains would change very little by setting $K_1 = 0$, as the contribution deriving from $\mathcal{A}_{2S}$ is about in the ratio 300:1 to that from $\mathcal{A}_2 + \mathcal{A}_3$ for both coefficients A and B. Concerning C, its relative weight is negligible no matter how large is N. The most significant source of the discrepancy between the results of Δ in this work and Δ' in ref 5 (see Figure 3) is due to the fact that the two quantities have a slightly different meaning.

In fact, eq 37 applies to the end-to-end distances of *finite* chains with N bonds, unlike ref 5, where the infinite chain is treated and the expansion is evaluated for all the internal distances. If we consider that (i) $\alpha^2(k)$ for the infinite chain is larger than $\alpha^2(N)$ with $N = k$, because in the infinite chain a k-bond segment is also expanded as a result of repulsions involving atoms outside the segment itself,[22] and (ii) both $\alpha^2(k)$ and $\alpha^2(N)$ tend to the same limit $\bar{\alpha}^2$ for k and $N \to \infty$, we conclude that the rate of increase of $\alpha^2(k)$ with k, i.e., Δ' from Figure 3, is *smaller* than that of $\alpha^2(N)$ with N, i.e., Δ from eq 37.

We point out that the terms comprising the factor $\bar{\alpha}^{-7}$, i.e., the leading ones in eq 37, derive from the screened interaction free energy $\mathcal{A}_{2S}$ and produce a significant chain expansion that goes to an asymptotic limit with increasing N. In the hypothetical case $K = 0$, i.e., $\mathcal{A}_{2S} = 0$, only the residual contribution from $(\mathcal{A}_2 + \mathcal{A}_3)$ is left (terms with factor $\bar{\alpha}^{-8}$ in eq 37). It is interesting to remark that *in this case we would have a chain contraction*, because $\bar{\alpha}^2 = 0.998$, $\Delta = -0.019$, and the ratio B/C is around 500, so that the logarithmic term turns out to be negligible even in the absence of the screened interactions. Even if K were to be changed by a factor up to, say, 10, the $\bar{\alpha}^{-8}$ terms would only change by the same factor, with no important consequence on the conclusions.

In an interesting study recently published, on the basis of Monte Carlo calculations Bruns shows that a self-avoiding unperturbed chain placed on a regular lattice does indeed follow eq 29 for sufficiently large N's.[15] Bruns simulates the unperturbed state through the requirement $A_2 = 0$ by applying an attractive potential to all nonbonded atom pairs placed on adjacent lattice sites and considers both a cubic and a diamond lattice. He compares his Monte Carlo results with the mean-square end-to-end distances evaluated in a RIS scheme where only the smallest rings are forbidden and the only attractive interactions taken into consideration are those between atoms separated by three and five bonds in the cubic lattice and in the diamond lattice case, respectively. Therefore

$$\alpha^2(N) = \langle r^2(N)\rangle_{\rm Monte\ Carlo} / \langle r^2(N)\rangle_{\rm RIS} \tag{38}$$

For sufficiently large N's, Bruns' results are in excellent agreement with eq 29 with $\bar{\alpha}^2 = 1.43$ and $\Delta = 1.2$ for the cubic lattice and $\bar{\alpha}^2 = 1.18$ and $\Delta = 1.0$ for the diamond lattice. Using the equation for K (see eqs 9 and 21)

$$K = \pi(3/2\pi)^{5/2} v_{\rm c} \langle \Delta^2 r\rangle / [C(0) l^2]^{5/2} \tag{39}$$

we may roughly equate the average volume per chain atom $v_{\rm c}$ with the volume associated with a single lattice point ($v_{\rm c} = l^3$ and $v_{\rm c} = 8l^3/(3\sqrt{3})$ for the cubic and diamond cases, respectively), the mean-square chain thickness $\langle \Delta^2 r\rangle$ with l^2, or the lattice squared bond length, and the characteristic ratio $C(0)$ with

$$C(0) = \lim_{N\to\infty} [\langle r^2(N)\rangle_{\rm RIS} / N l^2] \tag{40}$$

Taking $C(0) = 1.18$ and $C(0) = 2.06$ from Figure 2 or ref 15, we get $K = 0.33$ and $K = 0.13$ for the cubic lattice and the diamond lattice, respectively. From the approximate eq 17 of ref 5, where $\bar{\alpha}^2(0) = \bar{\alpha}^2$, we get

$$\bar{\alpha}^7 - \bar{\alpha}^5 \cong {}^{10}/_{3} K/\sqrt{\bar{k}} \tag{41}$$

and taking $\bar{k} = 4$ and 6 for the cubic lattice and the diamond lattice, we get the respective values $\bar{\alpha}^2 = 1.29$ and $\bar{\alpha}^2 = 1.13$ for the two cases. Although these figures are somehow smaller than those [1.43 (cubic) and 1.18 (diamond)]

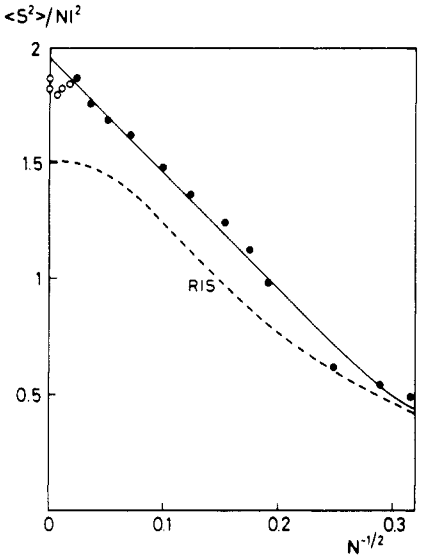

Figure 4. Experimental mean-square radius of gyration $\langle S^2\rangle$ of polystyrene samples, with (average) number N of chain atoms, corrected for the mean-square thickness[23] and plotted as $\langle S^2\rangle/Nl^2$ ($l \equiv l_{C\text{-}C}$) vs $N^{-1/2}$. (Solid circles) Small-angle X-ray scattering;[23] (open circles) small-angle light scattering.[23,27] In either case, monodisperse ($M_w/M_n < 1.1$) atactic polystyrene in cyclohexane at $\Theta = 34.5$ °C was used. The solid line is the best-fitting straight line through the points. The dashed curve shows the RIS calculation[23] with parameters taken from ref 24.

derived from Bruns' results,[15] the ratio between the differential expansions $[\tilde{\alpha}^2{}_{\text{cubic}} - 1]/[\tilde{\alpha}^2{}_{\text{diamond}} - 1]$ is well reproduced. We believe the discrepancy to be due to the inherent difficulty of deriving reliable values for v_c, $\langle \Delta^2 r\rangle$, and $\bar{k}$ from the geometry of the lattice model. In this connection, we point out that the numerical Monte Carlo results obtained by Mazur and McCrackin for the cubic lattice with no bond reversal appear to be very close to Bruns' in the limit $N \to \infty$, although these authors do not explicitly report[14] the N dependence of $\tilde{\alpha}^2$.

The present theoretical results may also explain the recent experimental measurements[23] of the mean-square radii of gyration $\langle S^2\rangle$ from low molecular weight atactic polystyrene ($578 \le M_w \le 97\,300$) in the unperturbed state. The ratio $\langle S^2\rangle/Nl^2$, already corrected in ref 23 for the chain mean-square thickness, is shown in Figure 4 as a function of $N^{-1/2}$ in comparison with the results of a RIS calculation carried out with the parameters originally proposed by Yoon et al.[24] It is noteworthy that a linear dependence is indeed observable from the experimental data, whereas it is absent in the RIS plot, which levels off much earlier (about one decade) with increasing N. The linear dependence of $\langle S^2\rangle$ from $N^{-1/2}$ is also predicted by our approach and provides an experimental determination of the parameter Δ. In fact, using for simplicity eq 10 for all values of k and remembering eq 1, we get

$$\langle S^2\rangle = N^{-2}\int_0^N (N-k)\langle r^2(k)\rangle\,\mathrm{d}k = N\frac{C(0)l^2}{6}\tilde{\alpha}^2\left(1 - \frac{8}{5}\frac{\Delta}{\sqrt{N}}\right) \tag{42}$$

from Figure 4, we have $C(0)\tilde{\alpha}^2 = 11.7$ and $\Delta = 1.49$. Considering that $\langle S^2\rangle$ is the average of all the interatomic distances within the chain, the resulting figure for Δ falls nicely between the value 1.1 for internal portions of an infinite chain[5] and the value 2.4 obtained for the end-to-end distance of finite chains in the present paper.

A remark concerning the quantitative aspects of the logarithmic correction predicted by the renormalization group approaches of Cherayil et al.[11] and Freed[13] and of Duplantier[9,18] is in order. The approach of the former group gives[11]

$$\alpha^2(N) = 1 - 1.900K_1/[1 + 44\pi K_1 \ln (N/\bar{k})] \tag{43}$$

where our symbols are used; we point out that $1.900 = 4\pi - 32/3$ (see eq 35). We see that the predicted contraction is in agreement with our calculations for $K = 0$ if we disregard the logarithmic term in comparison with unity in eq 43.[11,13] Moreover, Cherayil et al.[11] suggest a value $K_1 = 0.001$ from comparison of their analytical results with simulations on the face-centered cubic lattice, which produces a correction of the same amount as found by us for polystyrene [$\alpha^2(N) = 1 - 0.0019 \cong 0.998$]. The result by Duplantier[9,18] is different insofar as a contraction result similar to eq 43 only holds if the logarithmic term is around unity, being followed by an asymptotic expansion for $44\pi K_1 \ln (N/\bar{k}) \gg 1$. Stephen's result is still different in that it predicts a logarithmic expansion for any N range.[8]

The above quantitative comparisons are consistent with the conclusion that most high molecular weight polymers are probably not seriously affected by the logarithmic correction.

Generalized Interatomic Interactions

From eqs 17, 20, and 32 we obtained the stationary condition $\partial\mathcal{A}/\partial\tilde{\alpha}^2(0) = 0$, $\mathcal{A} = \mathcal{A}_{\text{el}} + \mathcal{A}_{\text{intram}}$. The resulting equation may be expressed as

$$\left\{\left(1 - \frac{1}{\tilde{\alpha}^2(0)}\right)\right\} + \left\{-N^{-1}\int_{\bar{k}}^{N} \mathrm{d}k\,\frac{k^2}{J(k)^{5/2}}\left[J(\bar{k})^{3/2}G(N + \bar{k} - k, \bar{k}) + \frac{5}{3}\frac{K}{J(k)}(N-k)\right]\right\} = 0 \tag{44}$$

where G is defined in eq 25 and the terms within the first and within the second braces respectively correspond to $\partial\mathcal{A}_{\text{el}}/\partial\tilde{\alpha}^2(0)$ and $\partial\mathcal{A}_{\text{intram}}/\partial\tilde{\alpha}^2(0)$. They will be denoted as the *generalized* elastic and intramolecular interactions, respectively. In turn, the latter may be expressed as a sum of terms over all the atom pairs

$$\partial\mathcal{A}_{\text{intram}}/\partial\tilde{\alpha}^2(0) = -\frac{3}{2}\int_{\bar{k}}^{N}(N-k)\Phi(k)\,\mathrm{d}k \tag{45}$$

where

$$\Phi(k) = \Phi_1(k) + \Phi_2(k) = N^{-1}\frac{k^2}{J(k)^{5/2}}\left[\frac{J(\bar{k})^{3/2}}{(N-k)}G(N + \bar{k} - k, \bar{k}) + \frac{5}{3}\frac{K}{J(k)}\right] \tag{45$'$}$$

$\Phi(k)$ may be regarded as the generalized intramolecular interaction between each pair of chain atoms separated by k bonds, a positive sign denoting repulsion. It is obtained as the sum of two contributions, of which $\Phi_1(k)$ is due to the two- and three-body interactions (with factor G) and $\Phi_2(k)$ is due to the screened interactions (with factor K). In view of eq 25 the former contribution is given by

$$\Phi_1(k) = N^{-1}\frac{k^2}{J(k)^{5/2}}\left[\bar{\tau}_{\text{ph}}B + 2K_1\int_{\bar{k}}^{N-k}\left(1 - \frac{k_1}{N-k}\right)\frac{\mathrm{d}k_1}{J(k_1)^{3/2}}\right] \tag{46}$$

Since at $T = \Theta$ $J(k)$ is very close to k, the last integral is largest for $k = 0$. On the other hand, at $T = \Theta$ $\Phi_1(0)$ is zero in view of eqs 24 and 45′. Consequently, for $k > 0$, $\Phi_1(k)$

is always negative, which means that in the unperturbed state *the sum of the two- and three-body generalized interactions is always attractive for any atom pair*, within the Gaussian approximation, although tending to zero for $k \rightarrow 0$. As a result, if we disregarded the screened interactions, the unperturbed chain would contract with respect to the phantom chain, or random-walk chain, model. Conversely, $\Phi_2(k)$ is always positive, since the repulsive screened interactions do not have an attractive counterpart.

From comparison of eq 19 with eq 46 we have the following identity ($N - \bar{k} \cong N$):

$$N\int_{\bar{k}}^{N}(N-k)\frac{J(k)}{k^2}\Phi_1(k)\,\mathrm{d}k = \mathcal{A}_2 + 2\mathcal{A}_3 \qquad (47)$$

On the other hand, inspection of eq 45′, where $J(k) \cong k$, shows that $\Phi_1(k)$ decreases very slowly with increasing k, thus remaining very close to zero for the range of k giving a significant contribution to the integral in eq 47. As a consequence, the Θ point may be approximately given by the vanishing of the integral in eq 47, i.e., by the following approximate equation

$$\mathcal{A}_2 + 2\mathcal{A}_3 \cong 0 \qquad (48)$$

which may be shown to be equivalent to eq 27 within terms of order N^{-1} inside the braces. In principle, eq 48 should be only applicable to linear chains or to branched chains, provided their interactions are given by a suitable sum of contributions from linear portions. Actually, in a recent paper we showed that for regular star polymers the only contributions not falling in that category—namely the three-body interactions among atoms placed on three different arms—may be neglected because they are of order N^{-1} relative to the largest term.[25] Denoting with Θ_∞ the common value of the Θ temperature for an infinitely large regular star with any number of arms, we have [N (total number of chain atoms) $\gg 1$]

$$\Theta(N,f) \cong \Theta_\infty - \varphi\chi(f)N^{-1/2}$$

$$\chi(f) = \sqrt{f}\,[f(2-\sqrt{2}) + \sqrt{2} - 4] \qquad (49)$$

where f is the number of equal arms emanating from a common junction and φ is a constant that may be derived from eq 27, assuming the linear chain as a special star polymer with $f = 1$ or 2. The interesting feature of eq 49 is that $\Theta(N,f)$ *decreases* with increasing N if $f \leq 4$, whereas it *increases* with N if $f > 4$, due to the larger relative weight of the three-body interactions with larger f.[25] It should be added that eq 49 was first obtained by Cherayil et al. within the cutoff calculation scheme.[21]

Concluding Remarks

The Θ state of an N-bond chain is defined by the vanishing of the second-virial coefficient A_2 or, equivalently, of the free energy $\mathcal{A}_{\text{inter}}(1,2)$ resulting from interaction between two identical chains. We have shown in the present paper that for linear chains $\mathcal{A}_{\text{inter}}(1,2)$ may be obtained from a purely *intra*molecular analysis after differentiating the sum of the attractive two-body and repulsive three-body chain free energies with respect to the lower cutoff interatomic separation (see eqs 19, 22, and 24). Under these conditions, the intramolecular two- and three-body interactions between topologically adjacent atoms cancel exactly, but for remote atoms the attraction prevails and the chain would experience a contraction, if no other interaction terms were to exist (see eq 45′ and following considerations). However, *the effective value of the binary potential cannot be the same for all the atom pairs*. Even if the binary potential is zero or negative for two atoms with a large average distance, as it happens with atoms belonging to different chains, its effective value becomes large and positive for topologically adjacent atoms with a small mean-square distance $\langle r^2 \rangle$. The additional, repulsive contribution arises from imperfect screening of the hard-core repulsion by the van der Waals type attraction and is proportional to $\langle r^2 \rangle^{-5/2}$ (screened interactions, see eq 9).[5] It should be mentioned in this context that Martin,[26] considering explicitly an interatomic potential similar to that shown in Figure 1, arrived at similar conclusions by predicting an asymptotically finite expansion of the chain with respect to the phantom state. Incidentally, it is noteworthy that he finds an explicit, linear dependence of the second virial coefficient on the finite width of the interatomic potential. This is in contrast with that given by us in eq 24; in fact, we expect an *indirect* (i.e., second-order) dependence, to the extent that the screened interactions affect the three-body contribution by modifying the contact probability between atoms on the same chain.

Our second-order perturbation analysis shows that in a real hydrocarbon polymer chain the expansion produced by the screened interactions overwhelms the weak attraction produced by the classical two- and three-body forces. As a result, the mean-square end-to-end distance of an N-bond chain experiences an expansion $\alpha^2(N)$ over the phantom-state value approximately given by $\alpha^2(N) = \bar{\alpha}^2(1 - \Delta/\sqrt{N})$, where $\bar{\alpha}^2$ is in the range 1.20–1.35 for atactic polystyrene and isotactic polypropylene after a realistic estimate of the parameters. These conclusions appear to offer a clear interpretation of the recent Monte Carlo calculations carried out by Bruns on self-avoiding lattice walks,[15] although the evaluation of the real chain parameters fitting Bruns' lattice models is inevitably approximate. The present $\alpha^2(N)$ expansion law was already somewhat implicit in the conclusions of a previous study on the unperturbed infinite chain, where N is to be interpreted as the number of bonds separating two chain atoms.[5]

This investigation is based on the Gaussian approximation. The previously mentioned $\alpha^2(N)$ law is regarded as a truncated series expansion, and the strain parameters $\bar{\alpha}^2$ and Δ are derived from a self-consistent approach by which the free energy being optimized applies to the configuration of the actual chain, not of the ideal phantom chain. The strain parameters depend on both the screened interactions (see terms with coefficient K in eq 35) and on the two- and three-body interactions (see terms with coefficient K_1 in eq 35), according to an intimately mixed dependence. In this connection, we point out that a logarithmic expansion is hidden in the results of eqs 34–37. If the logarithmic term of eq 34 is not neglected, then we have $\Delta \cong [B + C \ln (N/\bar{k})]/(1 + A)$ in eq 36, which in turn would produce a logarithm in the expression of A, therefore of $\bar{\alpha}^2 = (1 + A)^{-1}$.

It is worth pointing out that the screened interactions potential producing the $N^{-1/2}$ effect found by Bruns[15] is in no way derivable from the classical long-range two- and three-body interactions, being originated by an entirely independent source. On the other hand, an energy contribution depending on $N^{-1/2}$ might also be expected from the four-body interactions,[7] which might suggest some connection with Bruns' results.[15] However, considering that the three-body effect is quantitatively very small for a typical polymer like polystyrene, it can be concluded that the four-body interactions should be even smaller.

Accordingly, we believe that they should be ruled out as a significant source of the $N^{-1/2}$ effect.

As a final remark, the characteristic ratio of the real unperturbed chain is, after the present analysis

$$C_\infty = \lim_{N\to\infty} [\langle r^2(N)\rangle / Nl^2] = \bar{\alpha}^2 C(0) \qquad (50)$$

therefore being larger than that of the corresponding phantom chain. In the typical case of atactic polystyrene,[5,6] the relative increase amounts to more than 20%. As a consequence, the effect of the screened interactions on a very long chain may be included in the effective segment length if this is rescaled by the factor $\bar{\alpha}^2$.

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