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# Two- and Three-Body Interactions in the Θ State: Linear and Star Polymers

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ABSTRACT: The conformation of linear and star polymers is studied at the Θ temperature, determined by the vanishing of the second virial coefficient. This is achieved through exact compensation of intermolecular two-body attractions and three-body repulsions. The analogous compensation within the molecule is not complete, leaving in the star residual three-body repulsions because of a larger multiplicity. The resulting expansion is mostly concentrated in the core region. Its effect on the overall polymer size is discussed in terms of the topological ratio $g = \langle S^2 \rangle_{\text{star}} / \langle S^2 \rangle_{\text{lin}}$, $\langle S^2 \rangle$ being the mean-square radius of gyration. The calculated $g$ values are in good agreement with experiment, and the observed nonuniversality of $g$ is naturally explained. On the other hand, the molecular weight dependence of $g$ apparently differs from that suggested by the (limited) experimental results available, and the expansion of the hydrodynamic radius is less than observed. Possible reasons for this discrepancy are briefly proposed.

## Introduction

Regular star polymers may be viewed as a benchmark for theories of polymer conformation and dynamics by providing a further variable in addition to molecular weight and temperature, namely, the polymer topology, or, more specifically, the number of arms $f$.[1-3] In particular, the Θ state of star polymers, defined by the vanishing of the second virial coefficient $A_2$,[4] provides a stringent test of the relative importance of different intra- and intermolecular interactions. Let us denote as "phantom" polymer the hypothetical polymer devoid of any intramolecular interaction beyond, possibly, the short-range stereochemical interactions;[2,5] for such a polymer the two-body interactions vanish identically at the temperature $\Theta_{\text{ph}}$. The phantom polymer has a random-walk conformation, wherein the stereochemical details are effectively absorbed in the mean-square step length $l^2$. Recent experimental results show that, in the Θ state, stars with $f \gtrsim 9$ display quite a larger size than is expected for the phantom polymer, unlike linear and lightly branched polymers.[6-12] Since two-body interactions are basically cancelled at $T = \Theta$, this experimental finding suggests that residual many-body interactions become relevant for such stars because of the overcrowded core. Furthermore, the very existence of many-body, and in particular of three-body, *inter*molecular interactions does explain the relatively large depression of the actual Θ temperature of stars compared to that of linear chains.[8,10,11] Theory shows that Θ is depressed from the value $\Theta_{\text{ph}}$, the difference $\Theta_{\text{ph}} - \Theta$ being larger the larger is the number of arms and/or the smaller is the molecular weight, although in the asymptotic limit a value $\Theta_\infty$ ($<\Theta_{\text{ph}}$) is reached independent of the number of arms.[2,13,14] The Θ-point is achieved through a finely-tuned compensation of long-range *inter*molecular two- and three-body interactions, the former being attractive and temperature-dependent and the latter repulsive and temperature-independent. Analogous *intra*molecular interactions do exist, although it was recently shown that in a linear polymer they achieve a virtually complete compensation.[15] Therefore, in the long-chain limit the random-walk model does apply, whereas shorter-range interactions are relevant for finite chains.[3,16] However, this compensation need not be complete in the case of stars because certain intramolecular many-body interactions have no intermolecular counterpart due to the star topology: we are referring, in particular, to the three-body repulsions among atoms on three different arms.

In the present paper we study the Θ state of regular stars having up to 18 arms considering both two- and three-body interactions, in the assumption that the latter are the most important many-body interactions. In other words, a detailed treatment of higher-order terms should be explicitly included only for larger star functionalities. The model adopted is an equivalent bead-and-spring polymer; the lower cutoff to intramolecular interactions[2] shall be put equal to 1 for simplicity in the present coarse-grained and discrete model, since each spring connecting adjacent beads represents a number of chemical bonds on the order of a few tens. Furthermore, in the following beads and springs will be designated for convenience as atoms and bonds. Assuming a Gaussian distribution of the interatomic distances within a Fourier configurational description,[5] the polymer conformation is obtained by self-consistent minimization of the intramolecular free energy $\mathcal{A}$ formed by an elastic and by an intramolecular term. The elastic term, $\mathcal{A}_{\text{el}}$, has an entropic origin and correctly accounts for all the relevant degrees of freedom of the molecule.[17] Furthermore, it satisfies the constraint of preserving the correct bond length under both expansion and contraction for large enough molecular weight.[18] It is therefore implicit in the present approach that we do not assume any affine deformation of the polymer with respect to the phantom polymer. The intramolecular free energy consists of the above-discussed long-range two- and three-body terms, $\mathcal{A}_2$ and $\mathcal{A}_3$, although in the final section we shall also discuss briefly shorter-range interactions arising from the finite width of the interatomic potential:[2,5,16] the interatomic hard-core repulsion is screened in part by solvent-induced attraction, but the cancellation is not complete, whence the name "screened interactions".[16] The resulting net potential leaves a repulsive effect even at the Θ temperature. Since these temperature-independent interactions do not modify the asymptotic proportionality between the mean-square radius of gyration and the molecular weight, they were denoted as medium-range interactions.[5] The attractive two-body term $\mathcal{A}_2$ is given by the sum of the contributions of all the atom pairs ($h$, $j$), each being proportional to the probability density of contact between the two atoms, $p_{hj}$, and to the temperature shift $\Theta - \Theta_{\text{ph}}$. On the other hand, the repulsive term $\mathcal{A}_3$

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is taken as temperature-independent and is given by a sum over all the atom triplets $(h, j, k)$ of the corresponding probability densities $p_{hjk}$. It should be noted that $p_{hjk}$ *does not factorize* in the product $p_{hj} \cdot p_{jk}$ for any combination of the indices $(h, j, k)$ even within the Gaussian approximation *because of the polymer connectivity*;[5] it does so only in the very special case of the random-walk phantom polymer *if the three atoms belong to one or two arms*, whereas the factorizability breaks down anyway if the atoms belong to three arms. It must be stressed that in the above $\Theta$ is determined *via* the criterion $A_2 = 0$ by the mutual compensation of intermolecular two- and three-body interactions. Since the latter necessarily involve two atoms on the same molecule, evaluation of this contribution, hence of the $\Theta$ temperature, implies knowledge of the actual chain conformation.[15] Therefore, $\Theta$ must be optimized together with the chain conformation to achieve a logically consistent theory.

## Mathematical Approach

**1. Normal Modes and the Average Polymer Dimensions.** Let us consider a regular star with $N + 1$ total atoms and $f$ equal arms, each comprising $N/f$ atoms sequentially numbered from zero at the branch point to $N/f$ at the free end. We denote by $\mathbf{l}^{(r)}(h)$ the $h$th bond vector on the $r$th arm connecting atoms $h - 1$ and $h$ and oriented in the direction of the latter atom. The generic polymer conformation, specified by a given set of these $N$ bond vectors, may be conveniently decomposed into an equivalent set of $N$ statistically independent vectors, i.e., the normal modes. We point out, incidentally, that the latter are the same normal modes that are required in polymer dynamics.[5,18] The normal modes of the star belong to two groups with different multiplicities because of the star symmetry and are given by the Fourier modes[2,19]

$$\tilde{\mathbf{l}}(q_{2m}) = f^{-1/2}C\sum_{h=1}^{N/f}[\sum_{r=1}^{f}\mathbf{l}^{(r)}(h)] \sin [q_{2m}(h - 1/2)] \qquad \text{(antisymmetrical modes)}$$

$$\tilde{\mathbf{l}}(q_{2m-1}) = f^{-1/2}C\sum_{h=1}^{N/f}[\sum_{r=1}^{f}\mathbf{l}^{(r)}(h)e^{ir\varphi}] \cos [q_{2m-1}(h - 1/2)] \qquad \text{(symmetrical modes)} \quad (1)$$

$$m = 1, 2, ..., N/f$$

$$q_p = \pi p/(2N/f + 1); \quad \varphi = 2\pi/f; \quad C = 2/(2N/f + 1)^{1/2}$$

The former modes have a unit multiplicity since they are given by an antisymmetrical linear combination of the bond vectors on all the arms, whereas the latter are formed by symmetrical linear combinations of bond vectors on one arm and on each of the other $f - 1$ arms.[19] Correspondingly, these modes repeat $f - 1$ times with factors $e^{irv\varphi}$, $v = 1, 2, ..., f - 1$. However, since their mean-square values are equal and independent of $v$, we may simply consider the modes with $v = 1$ as in eq 1 with a multiplicity $f - 1$.[19,20]

The orthogonality between the modes is expressed as

$$\langle \tilde{\mathbf{l}}(q_{2m}) \cdot \tilde{\mathbf{l}}(q_{2n}) \rangle = l^2 \alpha_m{}^2 \delta_{mn}$$

$$\langle \tilde{\mathbf{l}}^*(q_{2m-1}) \cdot \tilde{\mathbf{l}}(q_{2n-1}) \rangle = l^2 \beta_m{}^2 \delta_{mn} \qquad (2)$$

the cross terms being anyway orthogonal by symmetry; $\alpha_m{}^2$ and $\beta_m{}^2$ are the strain ratios of the mean-square amplitudes of the modes with respect to the phantom polymer. In principle, these normal modes apply rigorously under the assumption of (i) conformational uniformity and (ii) short-range correlation.[5,19] These conditions are strictly met only by the phantom polymer but apply also to a polymer of sufficiently large molecular weight in the $\Theta$ state, because long-range interactions basically cancel each other and medium-range interactions (the screened interactions) die off quickly enough. (Incidentally, it was also shown that even in a good solvent the Fourier modes do form a satisfactory basis for the true normal modes, at least within the crossover regime of excluded volume.[19]) Since the normal modes are formed by a combination of (mostly) independent bond vectors, the Central Limit Theorem guarantees that they follow a Gaussian distribution. This result permits us to get the configurational, or elastic, free energy $\mathcal{A}_{\text{el}}$. In $k_{\text{B}}T$ units, we have[2,19]

$$\mathcal{A}_{\text{el}} = (3/2) \sum_{m=1}^{N/f} \{\alpha_m{}^2 - 1 - \ln \alpha_m{}^2 + (f - 1)[\beta_m{}^2 - 1 - \ln \beta_m{}^2]\} \quad (3)$$

where the different mode multiplicities are explicitly indicated.

In terms of the strain ratios of the Fourier modes, the mean-square distance between atoms $h$ and $j$ on arms $r$ and $s$ is given by[19]

$$\langle r^2(h,j) \rangle_{rs} = (l^2/f) \sum_{m=1}^{N/f} \{(a^{(m)}{}_{hj})^2 \alpha_m{}^2 + [(f - 1)(b^{(m)}{}_{hj})^2 + 2f(1 - \delta_{rs})b^{(m)}{}_{0h}b^{(m)}{}_{0j}]\beta_m{}^2\} \quad (4)$$

where

$$a^{(m)}{}_{hj} = C \sin [q_{2m}(j + h)/2] \sin [q_{2m}(j - h)/2]/\sin (q_{2m}/2)$$

$$b^{(m)}{}_{hj} = C \cos [q_{2m-1}(j + h)/2] \sin [q_{2m-1}(j - h)/2]/\sin (q_{2m-1}/2) \quad (4')$$

the $C$ constant and the Fourier coordinate $q_p$ ($p = 2m$ or $2m - 1$) being given in eq 1. Using $\alpha_m{}^2 \equiv \beta_m{}^2 \equiv 1$ in the above equation, we recover the phantom polymer results $\langle r^2(h,j) \rangle = |h - j|l^2$ for atoms on the same arm ($r = s$) and $\langle r^2(h,j) \rangle = (h + j)l^2$ for atoms on different arms ($r \neq s$).

The mean-square radius of gyration can also be expressed through the strain ratios of the normal modes as

$$\langle S^2 \rangle = [2(N + 1)^2]^{-1}\sum_{h}\sum_{j}\langle r^2(h,j) \rangle = l^2[4(N + 1)]^{-1} \times \sum_{m=1}^{N/f}\left[\frac{\alpha_m{}^2}{\sin^2 (q_{2m}/2)}\left(1 + \frac{2 - f}{N + 1}\right) + (f - 1)\frac{\beta_m{}^2}{\sin^2 (q_{2m-1}/2)}\right] \quad (5)$$

whereas the hydrodynamic radius $R_{\text{H}}$ is given by

$$R_{\text{H}}{}^{-1} = (N + 1)^{-2}\sum_{h}\sum_{j}\langle r^{-1}(h,j) \rangle, \quad \langle r^{-1}(h,j) \rangle = [6/\pi\langle r^2(h,j) \rangle]^{1/2} \quad (5')$$

within the usual Kirkwood approximation.[4,5]

**2. Intramolecular Free Energy and the Self-Consistent Equations at the Θ Temperature.** Let us first give the two- and three-body intramolecular probability density of contact. We remind that, as stated in the Introduction, the corresponding free-energy contributions $\mathcal{A}_2$ and $\mathcal{A}_3$ are proportional to the sums over all the atoms pairs and triplets of these probability densities.

As a consequence of the Gaussian distribution of the Fourier modes and of their orthogonality, the joint distribution function of the $\tilde{l}(q_p)$'s is Gaussian too, if we neglect quartic terms in the exponential; in turn, this implies a Gaussian distribution of the interatomic distances.[5] Therefore, the intramolecular probability density of contact between the two atoms $h$ and $j$ is given by

$$p_{hj} \sim \langle r^2(h,j)\rangle^{-3/2} \qquad (6^{\rm I})$$

and that among the three atoms $h$, $j$, and $k$ by[21]

$$p_{hjk} \sim {\Psi_{hjk}}^{-3/2} \qquad (6^{\rm II})$$

where

$$\Psi_{hjk} \equiv \Psi\{\langle r^2(h,j)\rangle/l^2, \langle r^2(j,k)\rangle/l^2, \langle r^2(h,k)\rangle/l^2\} \qquad (6^{\rm III})$$

and

$$\Psi(x,y,z) = \frac{1}{2}(xy + xz + yz) - \frac{1}{4}(x^2 + y^2 + z^2) \qquad (6^{\rm IV})$$

$\langle r^2(h,j)\rangle$, etc., standing for the mean-square distance between atoms either on one or on two arms. Note that the requirement $\Psi > 0$ in eq $6^{\rm II}$ is equivalent to the inequality which must be satisfied by the three sides of a triangle with vertices $h$, $j$, and $k$; therefore, it is consistent with the connectivity requirement among the three atoms. Defining

$$\Delta = (2l^2)^{-1}\{\langle r^2(h,k)\rangle - \langle r^2(h,j)\rangle - \langle r^2(j,k)\rangle\} \qquad (7)$$

we may also write, in complete generality

$$\Psi_{hjk} = \frac{1}{l^4}\langle r^2(h,j)\rangle\langle r^2(j,k)\rangle - \Delta^2 \qquad (8)$$

If the triplet of atoms $h$, $j$, and $k$ is ordered along this topological sequence either on one or on two arms, we have $\Delta \equiv 0$ in the special case of the phantom polymer. This means that the contact probability among the three atoms $h$, $j$, and $k$ factorizes into the product of the contact probabilities among the pairs $(h, j)$ and $(j, k)$. This property does not hold in general, although in the Θ state we expect for such triplets Δ to be much smaller than any mean-square distance entering its definition.

With the inclusion of the screened interactions for completeness, the intramolecular free energy is given by,[2,5,16] in $k_{\rm D}T$ units

$$\mathcal{A}_{\rm intra} = \mathcal{A}_2 + \mathcal{A}_{2\rm s} + \mathcal{A}_3 \qquad (9)$$

$$\mathcal{A}_2 = \tau_{\rm ph}B\sum_{h<j}\sum[\langle r^2(h,j)\rangle/l^2]^{-3/2} \qquad (10)$$

$$\mathcal{A}_{2\rm s} = K\sum_{h<j}\sum[\langle r^2(h,j)\rangle/l^2]^{-5/2} \qquad (11)$$

$$\mathcal{A}_3 = K_1\sum_{h<j<k}\sum\sum{\Psi_{hjk}}^{-3/2} \qquad (12)$$

the double or triple sums being performed over all the different pairs or triplets of atoms in the molecule each counted only once. In eq 10 the quantity $\tau_{\rm ph}B$ is proportional to the binary cluster integral[4] and determines the strength of the long-range two-body interactions,[15] the adimensional parameter $B$ is proportional to the effective covolume per skeletal atom and

$$\tau_{\rm ph} = (T - \Theta_{\rm ph})/T \qquad (13)$$

$\Theta_{\rm ph}$ being the Θ temperature of the phantom polymer. Furthermore, $K$ and $K_1$ in eqs 11 and 12 are the parameters giving the strength of the screened interactions and of the three-body interactions, respectively; they are taken as temperature-independent and positive, thus indicating the repulsive nature of the corresponding interactions.

The polymer conformation in the Θ state is obtained through self-consistent minimization of the overall free energy

$$\mathcal{A} = \mathcal{A}_{\rm el} + \mathcal{A}_{\rm intra} \qquad (14)$$

using for the reduced temperature $\tau_{\rm ph}$ the value that makes the second virial coefficient $A_2 = 0$, say $\bar{\tau}_{\rm ph}$. The latter condition is equivalent to the requirement $\mathcal{A}_{\rm inter} = 0$, where $\mathcal{A}_{\rm inter}$ is the interaction free energy *between two different molecules*. $\mathcal{A}_{\rm inter}$ depends only on the long-range interactions, since the solution volume is always much larger than the volume pervaded by each molecule and the screened interactions are negligible because of their medium-range nature. Therefore, the interaction free energy per skeletal atom of one molecule is[2,15]

$$\mathcal{A}_{\rm inter} \sim (N+1)\tau_{\rm ph}B + 2K_1\sum_{h<j}\sum[\langle r^2(h,j)\rangle/l^2]^{-3/2} \qquad (15)$$

The terms on the right-hand side arise respectively from the two- and the three-body interactions with all the atoms of the other molecule, the coefficient 2 being due to the same interactions wherein the two polymers are interchanged. Note that at the temperature $T = \Theta_{\rm ph}$ we have $\tau_{\rm ph} = 0$ and $\mathcal{A}_{\rm inter}$ is positive because of the sign of $K_1$, so that the surviving long-range interactions are repulsive. In other words, at $T = \Theta_{\rm ph}$ the polymer is in a good solvent.

The Θ temperature is given by the vanishing of $\mathcal{A}_{\rm inter}$, which leads to the equation[13,15]

$$\bar{\tau}_{\rm ph}B = -2\frac{K_1}{N+1}\sum_{h<j}\sum[\langle r^2(h,j)\rangle/l^2]^{-3/2} \qquad (16)$$

where

$$\bar{\tau}_{\rm ph} = (\Theta - \Theta_{\rm ph})/\Theta \qquad (16')$$

Incidentally, from these equations we see that indeed $\Theta < \Theta_{\rm ph}$.

Going back to the polymer conformation, we may now carry out the minimization of the free energy in eqs 14, 3, and 9–12 by setting $\partial\mathcal{A}/\partial{\alpha_m}^2 = 0$ and $\partial\mathcal{A}/\partial{\beta_m}^2 = 0$, after replacing $\tau_{\rm ph}B$ in eq 10 with $\bar{\tau}_{\rm ph}B$ as determined through eq 16. We get

$$1/\alpha_m^{\,2} = 1 - l^5 f^{-1} \sum\sum_{h<j} \langle r^2(h,j)\rangle^{-5/2} ({a^{(m)}}_{hj})^2 \times \left[\bar{\tau}_{\mathrm{ph}}B + \frac{5}{3}\frac{Kl^2}{\langle r^2(h,j)\rangle}\right] - K_1 \sum\sum\sum_{h<j<k} {\Psi_{hjk}}^{-5/2} \frac{\partial \Psi_{hjk}}{\partial {\alpha_m}^2} \qquad (17^{\mathrm{I}})$$

$$1/\beta_m^{\,2} = 1 - l^5 f^{-1} \sum\sum_{h<j} \langle r^2(h,j)\rangle^{-5/2} \times \left[({b^{(m)}}_{hj})^2 + \frac{2f}{f-1}(1-\delta_{\mathrm{rs}}){b^{(m)}}_{0h}{b^{(m)}}_{0j}\right] \times \left[\bar{\tau}_{\mathrm{ph}}B + \frac{5}{3}\frac{Kl^2}{\langle r^2(h,j)\rangle}\right] - \frac{K_1}{f-1} \sum\sum\sum_{h<j<k} {\Psi_{hjk}}^{-5/2} \frac{\partial \Psi_{hjk}}{\partial {\beta_m}^2} \qquad (17^{\mathrm{II}})$$

where $f \neq 1$,

$$\frac{\partial \Psi_{hjk}}{\partial {\alpha_m}^2} = f^{-1}\{({a^{(m)}}_{hj})^2[\langle r^2(j,k)\rangle/l^2 + \Delta] + ({a^{(m)}}_{jk})^2[\langle r^2(h,j)\rangle/l^2 + \Delta] - ({a^{(m)}}_{hk})^2\Delta\} \qquad (17^{\mathrm{III}})$$

$$\frac{\partial \Psi_{hjk}}{\partial {\beta_m}^2} = \frac{f-1}{f}\left\{\left[({b^{(m)}}_{hj})^2 + \frac{2f}{f-1}(1-\delta_{rs}){b^{(m)}}_{0h}{b^{(m)}}_{0j}\right] \times [\langle r^2(j,k)\rangle/l^2 + \Delta] + \left[({b^{(m)}}_{jk})^2 + \frac{2f}{f-1}(1-\delta_{rs}){b^{(m)}}_{0j}{b^{(m)}}_{0k}\right][\langle r^2(h,j)\rangle/l^2 + \Delta] - \left[({b^{(m)}}_{hk})^2 + \frac{2f}{f-1}(1-\delta_{rs}){b^{(m)}}_{0h}{b^{(m)}}_{0k}\right]\Delta\right\} \qquad (17^{\mathrm{IV}})$$

In the above, each Kronecker delta $\delta_{rs}$ applies to the pairs of atoms $(h, j)$, $(j, k)$, or $(h, k)$ indicated by the subscript of the terms ${b^{(m)}}_{0h}{b^{(m)}}_{0j}$, etc., accompanying it, depending on whether they belong to the same arm ($r = s$) or to two different arms ($r \neq s$). Equations 4 and 17 form a set of coupled equations to be solved self-consistently.

## Numerical Procedure

The coupled equations (4 and 17), together with eq 16 for the $\bar{\tau}_{\mathrm{ph}}B$ parameter, were solved through a numerical iterative procedure[3,16,19] neglecting the screened interactions by setting $K = 0$ in eqs 11 and 17. To put it otherwise, we consider the expansion effect due to the finite width of the interatomic potential in the asymptotic limit, where the polymer deformation is affine and independent of the number of arms and may be considered as absorbed into an effective, renormalized segment length.[3] As for the three-body interactions, we chose for $K_1$ the value $2 \times 10^{-3}$, equal to the value giving the best fit to experimental results of the collapse of linear polystyrene in a poor solvent,[2] although we also varied somewhat this parameter to study its influence. The iterative procedure was carried out as follows. We start with the phantom polymer strain ratios $\alpha_m^{\,2} \equiv \beta_m^{\,2} \equiv 1$, thus getting $\langle r^2(h,j)\rangle = |h - j|l^2$ for atoms on the same arm (see eq 4; $r = s$) or $\langle r^2(h,j)\rangle = (h + j)l^2$ for atoms on different arms ($r \neq s$). We then insert these mean-square distances in eq 17 and, using the $\bar{\tau}_{\mathrm{ph}}B$ value obtained through eq (16) with the same $\langle r^2(h,j)\rangle$'s, we get an improved set of $\alpha_m^{\,2}$'s and $\beta_m^{\,2}$'s, wherefrom the new mean-square distances are calculated, and so forth. The procedure is repeated until the strain ratios, hence the $\langle r^2(h,j)\rangle$'s and $\bar{\tau}_{\mathrm{ph}}B$, do not change any more from one cycle to the next, thus indicating self-consistency among the results. Calculations were carried out for the linear chain with $f = 2$ and for 6-, 12-, and 18-arm stars with arm lengths $N/f$ up to 400 atoms, where a linear extrapolation to $N \to \infty$ could be safely made (see later). With this procedure, the computer time increases as $(N/f)^4$, thus becoming soon prohibitively large even though convergence is relatively fast (the number of cycles required to achieve stability in at least the third decimal place of the strain ratios was 4–6 depending on $f$ and on the value of $K_1$ if the screened interactions are ignored): a typical CPU time on an IBM 3090 VF computer was about 50 min per iteration cycle at the intermediate arm length of $N/f = 200$. However, since we are mainly interested in the most collective modes only, which determine the overall polymer size, we chose to optimize only the modes with $m \leq 50$ (see eqs 1 and 17), of course taking into account *all* the two- and three-body interactions, whereas the modes with $m > 50$ were constrained to a unit value. In this way, the computer time increase "only" as $(N/f)^3$. This approximation is entirely adequate, since (i) the sum over the modes yielding $\langle S^2\rangle$ in eq 5 converges quickly because the importance of the modes decreases with increasing $q_p$ as $q_p^{-2}$ ($p = 2m$ or $2m - 1$; see eq 1) and (ii) a comparison with complete calculations carried out at intermediate $N/f$ shows that the errors entailed by this procedure are throughout less than 0.5% on $\alpha_m^{\,2}$ and $\beta_m^{\,2}$ for $m > 50$ (i.e., for those strain ratios constrained to unity) and less than 0.1% both on the modes with $m \leq 50$ and on $\langle S^2\rangle$.

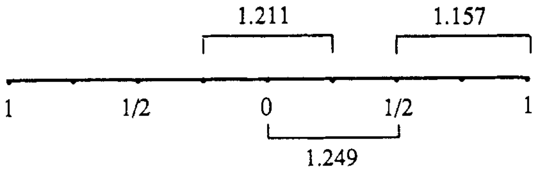
A few calculations were also performed with the full eqs 17 adopting the value $K = 0.09$ for the screened interactions parameter as derived for atactic polystyrene in previous work.[3,16] These medium-range interactions mostly affect relatively local modes, while tending to a constant value for collective modes.[3] Since the latter are precisely the modes mostly influenced by the residual long-range three-body interactions, the interplay of these effects requires the simultaneous optimization of most, if not all, the strain ratios of the normal modes. Furthermore, the number of cycles in the iterative procedure becomes at least twice as large; for these reasons, only a few exploratory calculations were performed with the full equations (17) in order to determine the general behavior (see the final section).

## Results and Discussion

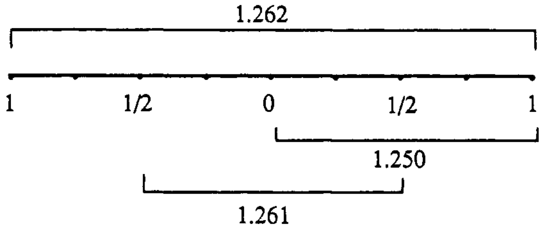
**1. Interatomic Distances.** Let us first consider the interatomic distances in the star. The following scheme reports some typical values of $\alpha_{hj}^{\,2}$, where

$$\alpha_{hj}^{\,2} = \langle r^2(h,j)\rangle/\langle r^2(h,j)\rangle_{\mathrm{ph}} \qquad (18)$$

between atoms located in different positions at the fixed topological separation of $(1/2)(N/f)$ bonds (i.e., half the arm length) in an 18-arm star with $N/f = 200$ bonds per arm.



Only two arms are depicted for clarity; the horizontal axis is numbered as $h/(N/f)$ in either direction from the branch point labeled as zero. As a general result, we see that the expansion of a given strand is smaller near the free ends of the arms and larger in the vicinity of the star core but largest whenever one of the strand ends coincides with the branch point. This finding is analogous to that obtained for stars in a good solvent[19] and is related with the loss of correlation in the initial directions of the arms as they emanate from the branch point. In this way, a compromise is achieved between two opposite requirements: the intraarm repulsions are best relieved, while no excessive interarm repulsions are generated. The expansion of a strand of atoms increases with its length, although reaching a limiting value at large topological separation for a given $f$. For the same star as considered before, we have the following $\alpha_{hj}^2$ values:



The upper value refers to the mean-square distance between atoms at the free ends of two arms with a topological separation of $2N/f$ bonds, whereas the lower values give the expansion of the mean-square distances between atoms separated by $N/f$ bonds either on one arm or symmetrically across the branch point (note that the former value is the expansion coefficient of the mean-square arm length). Again, strands close to one arm end experience a smaller deformation compared to those in the star interior. For a comparison, in the above example the expansion factor of the mean-square radius of gyration, defined as

$$\alpha_S^2 = \langle S^2\rangle / \langle S^2\rangle_{\mathrm{ph}} \tag{19}$$

is $\alpha_S^2 = 1.257$, slightly less than the expansion of the farthest atoms. In the limit $N \rightarrow \infty$, we expect this difference to become negligible. (Concerning $\langle S^2\rangle_{\mathrm{ph}}$, we remind everyone that here the phantom polymer is treated as a discrete polymer with no intramolecular interactions by setting $K_1$, hence $\bar{\tau}_{\mathrm{ph}}B$, equal to zero.[3])

**2. Radius of Gyration.** As for the overall polymer size, we report in Figure 1 the expansion factor $\alpha_S^2$ as a function of $N^{-1/2}$. This plot yields straight lines in most of the range for all the stars considered here (for 12- and 18-arm stars, terms in $N^{-1}$ are nonnegligible and a small curvature is present at large $N^{-1/2}$), and the present results can be easily extrapolated to the limit $N \rightarrow \infty$ (dotted lines). Within a $K_1$ figure of the same order as that used here, the residual three-body interactions are essentially a small perturbation over the phantom polymer in the case of lightly-branched stars: thus, we checked that for the 6-arm star the difference $\alpha_S^2 - 1$ is proportional to $K_1$, whereas for the 12- and 18-arm stars this proportionality is increasingly less accurate because of higher-order terms.

The fundamental result shown by Figure 1 is that the star undergoes an $f$-dependent expansion even in the asymptotic limit, unlike that found in the presence of the screened interactions only.[3] As anticipated, the attractive two-body interactions within the star due to the lowering of the Θ temperature with respect to $\Theta_{\mathrm{ph}}$ cancel a large share of the repulsive three-body interactions involving atoms on one or two arms, but the three-body interactions among atoms on three different arms are inherently noncompensated. The multiplicity of these interactions increases quickly with $f$, being given by $f(f-1)(f-2)$, so as to yield an asymptotic finite expansion dependent on $f$, even though they become weaker and weaker as the atoms are farther away from the branch point. On the other hand, the linear polymer has no such interactions, and it is slightly *contracted* with respect to the phantom chain.[13,15] The contraction is largest at the chain ends, since some three-body interactions are missing as compared to internal atoms because of the lack of outer atoms.

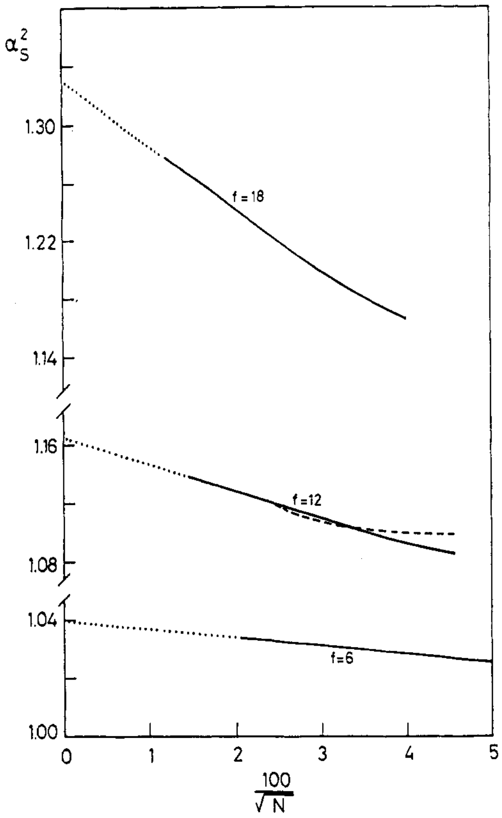


**Figure 1.** Expansion factor $\alpha_S^2 = \langle S^2\rangle/\langle S^2\rangle_{\mathrm{ph}}$ vs $N^{-1/2}$ for 6-, 12-, and 18-arm stars (note the different scales on the vertical axis). The solid curves show the numerical results obtained with three-body repulsions only, neglecting the screened interactions (see text); the dotted lines show the linear extrapolation to the asymptotic values. The results of the calculations with inclusion of the screened interactions are shown with the dashed curve.

It is anyway a very small effect, amounting to less than 0.1% for the mean-square end-to-end distance and to about half that value for the mean-square radius of gyration for any molecular weight.[22] Therefore, in the linear chain $\alpha_S^2$ can be safely equated to 1 throughout.

The topological index $g$ is often employed to characterize the degree of compactness of a star polymer compared to the linear chain with the same molecular weight at the corresponding Θ temperatures. The $g$ index is defined as

$$g = \langle S^2\rangle_{\mathrm{star}} / \langle S^2\rangle_{\mathrm{lin}} \tag{20}$$

Remembering eq 19, we may also write

$$g = g_{\mathrm{ph}} \frac{\alpha_{S,\mathrm{star}}^{\;2}}{\alpha_{S,\mathrm{lin}}^{\;2}} \tag{20$'$}$$

where $g_{\mathrm{ph}}$ is the $g$ ratio of the phantom polymer. For a discrete collection of beads as considered here, $g_{\mathrm{ph}}$ is given by[3]

$$g_{\mathrm{ph}} = \frac{N/f + 1}{(N+1)(N+2)} \left[ \frac{N}{f}(3f-2) + 2 \right] \tag{21}$$

which reduces to the familiar result[23]

$$g_{\mathrm{ph},\infty} = (3f-2)/f^2 \tag{21$'$}$$

for $N \rightarrow \infty$. Since for the linear chain $\alpha_S^2 = 1$ to a very good approximation, as said before, $\alpha_{S,\mathrm{star}}^2$ provides also the relative increase of the $g$ index over the phantom polymer value. In the limit $N \rightarrow \infty$, this increase in quite small for the 6-arm star (about 4%), whereas it is more substantial for the 12-arm (~17%) and for the 18-arm star (~33%). The asymptotic $g$ values obtained from eq 20$'$ and Figure 1 are collected in Table I in comparison

**Table I**
**Θ Expansion of Star Polymers**

*g* Ratio: $g = \langle S^2\rangle_{\mathrm{star}}/\langle S^2\rangle_{\mathrm{lin}}$

| $f$ | phantom polymer[a] | present work | PS[b] | PIP[c] | MC[d] | scaling theory[e] |
|---|---|---|---|---|---|---|
| 6 | 0.444 | 0.462 | 0.46[6] | 0.46[7] | 0.48 | 0.469 |
| 12 | 0.236 | 0.275 | 0.276[9,10] | 0.33[8] | 0.28 | 0.332 |
| 18 | 0.160 | 0.213 | 0.228[9,10] | 0.29[11] | | 0.271 |

*h* Ratio: $h = R_{\mathrm{H,star}}/R_{\mathrm{H,lin}}$

| $f$ | phantom polymer[f] | present work | PS[b] | MC[g] |
|---|---|---|---|---|
| 6 | 0.798 | 0.809 | 0.89[29] | 0.89 |
| 12 | 0.623 | 0.665 | 0.81[9]<br>0.75[10] | 0.82 |
| 18 | 0.528 | 0.598 | 0.76[9]<br>0.71[10] | 0.73 |

[a] From eq 21′.[23] [b] Atactic polystyrene in cyclohexane at 34.5 °C. [c] Polyisoprene in dioxane at 34 °C. [d] Monte Carlo simulations on a lattice (see text), Θ-point criterion $\langle S^2\rangle \sim N$.[24] [e] From the equation $g = 1.15f^{-1/2}$, as fitted to PIP results.[25] [f] From eq 25.[28] [g] Monte Carlo simulations with a Lennard-Jones potential whose energy parameter reproduces the Θ state via the criterion $\langle S^2\rangle \sim N$.[30]

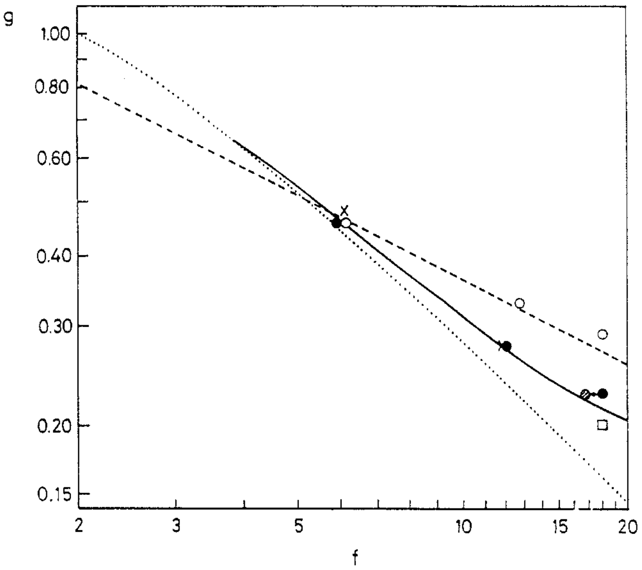


**Figure 2.** Topological ratio $g = \langle S^2\rangle_{\mathrm{star}}/\langle S^2\rangle_{\mathrm{lin}}$ plotted as a function of the arm number $f$. The present results, valid for atactic polystyrene, are shown with the solid curve. The dotted curve shows the phantom polymer result $g_{\mathrm{ph},\infty} = (3f - 2)/f^2$ and the dashed curve the scaling prediction, fitted to polyisoprene, $g = 1.15f^{-1/2}$ (see text). The other symbols are the experimental results from atactic polystyrene[6,9,10] (filled circles), from polyisoprene[7,8,11] (open circles), from polybutadiene[12] (open square), and from Monte Carlo simulations[24] (crosses). For the polystyrene star having nominally 18 arms, the hatched circle reports the observed $g$ value shifted to the experimental average value $f = 16.8$[9] (see text).

with some experimental results[6-11] and with Monte Carlo simulations,[24] as well as with results from scaling theory.[25] The same values, with a few others,[12] are also shown in a plot of $g$ vs $f$ in Figure 2. The agreement of the present results with experiment is very good in the case of atactic polystyrene (PS),[6,9,10] a small discrepancy being present only in the case of the 18-arm star. However, it must be noted that some polydispersity in the arm number was present in these samples due to an incomplete reaction of the preformed arms with the 18 functional sites of the linking agent. Thus, the average value of $f$ was determined to be actually 16.8.[9] Using the latter figure instead of the nominal value of 18, the corresponding point shifts to the hatched circle in Figure 2, in even better agreement with our result. It is noteworthy that polystyrene is the polymer on which the $K_1$ parameter adopted here was adjusted through a fit with an entirely different kind of experiment, namely, poor-solvent collapse of linear chains.[2] On the other hand, 12- and 18-arm polyisoprene (PIP)[7,8,11] display larger $g$ values than PS (see Table I), whereas a few data from other polymers yield smaller figures, such as 0.20 as reported for 18-arm polybutadiene.[12] This scatter in the topological $g$ index points to a nonuniversality of the Θ state, as already suggested.[1] This nonuniversality is due to the residual three-body interactions that introduce the polymer-dependent parameter $K_1$ in addition to the reduced temperature and the effective mean-square segment length $l^2$ considered in two-parameter theories.[4] Theoretical evaluation of $K_1$ is rather difficult and even its qualitative trend in different polymers is not obvious, since it depends on the volume-to-length ratio of the statistical segment[5] (more precisely, $K_1 \sim (v_c/l^3)^2$, $v_c$ being the effective covolume per skeletal atom).

Monte Carlo simulations on a lattice yield a satisfactory agreement with experiments on PS stars,[24] but their accuracy is difficult to assess. First of all, it is not clear if the nonuniversality of the Θ point can be reproduced. In fact, simulation results on self-avoiding polymers with a suitable attractive potential do suggest that the effective segment length depends on the chosen lattice but also that its value cancels identically when ratios between linear and star polymers are considered, such as in the $g$ ratio, thus yielding a universal behavior.[26] Furthermore, the Θ-point criterion often adopted is that some typical mean-square polymer size (such as the arm length) is proportional to the number of bonds it encompasses.[24,26] This criterion is different from that currently adopted of a vanishing of $A_2$.[4] Although the two should be equivalent in the $N \to \infty$ limit, it is interesting to note that Monte Carlo simulations adopting the latter criterion give slightly smaller $g$ values for lightly branched polymers ($f \leq 6$).[27] It would be of interest to extend these simulations to more heavily branched stars as a test of the two approaches. As for the scaling theory, it assumes explicitly that the arms are stretched out in the core region because of space-filling requirements.[25] The star is therefore described in terms of shells of concentrated, semidilute and dilute solutions, moving radially outward from the branch point, and this leads to the scaling relationship

$$g = 1.15f^{-1/2} \tag{22}$$

where the numerical coefficient is fitted to the PIP experimental results.[25] (Interestingly, the same scaling relationship can be obtained through a modified Flory theory with inclusion of three-body interactions.[1]) The corresponding values are reported in Table I and in Figure 2. We note however that unlike the present approach scaling theory appears to be justified on theoretical grounds only for heavily branched polymers; furthermore, the scaling law itself is not consistent with PS results, which require a larger negative exponent (see Figure 2 and ref 9).

**3. Hydrodynamic Radius.** In the case of the hydrodynamic radius, we obtain a smaller expansion than for the radius of gyration. The corresponding strain ratio $\alpha_{\mathrm{H}}$, defined as

$$\alpha_{\mathrm{H}} = R_{\mathrm{H}}/R_{\mathrm{H,ph}} \tag{23}$$

plotted as a function of $N^{-1/2}$ gives straight lines at large $N$. The inequality $\alpha_{\mathrm{H}} < \alpha_{\mathrm{S}}$ holds throughout, as it could be expected from the pattern of the intramolecular distances discussed above. In fact, $R_{\mathrm{H}}$ is more influenced than $\langle S^2\rangle$ by the short-range distances, as may be seen by comparison of the defining equations (5). The topological ratio $h$ is given by

$$h = R_{\mathrm{H,star}}/R_{\mathrm{H,lin}} \tag{24}$$

and, in analogy with the $g$ ratio, it may be written as

$$h = h_{\mathrm{ph}}(\alpha_{\mathrm{H,star}}/\alpha_{\mathrm{H,lin}}) \tag{24'}$$

In turn, $h_{\mathrm{ph}}$ is given by a simple equation only in the $N \rightarrow \infty$ limit:[28]

$$h_{\mathrm{ph},\infty} = \frac{f^{1/2}}{2 - f + (f-1)\sqrt{2}} \tag{25}$$

The asymptotic values of $h$ obtained in the present work are reported in Table I together with $h_{\mathrm{ph},\infty}$ in comparison with experimental data from atactic polystyrene (PS)[9,10,29] and with Monte Carlo simulations.[30] The increase of $h$ above the phantom polymer value is definitely much smaller than indicated by experiments, even though we should note that the latter data are quite scarce and show a significant scatter.[9,10] On the other hand, Monte Carlo simulations are in good agreement with the PS data.[30] This is due to a more accurate description of the polymer diffusion than that used to derive eq 5′, which makes recourse to the preaveraging approximation for the hydrodynamic interaction[4,5] (see also ref 1 for a brief but lucid discussion of this issue). However, one could also speculate that these simulations point also to some conformational inadequacy of the present model at short interatomic distances, particularly in the core region.

## Concluding Remarks. The Effect of Medium-Range Interactions

In the present paper we study the effect of long-range two- and three-body interactions in linear and star polymers at the Θ point. We use a self-consistent procedure involving minimization of the intramolecular free energy with respect to all the relevant degrees of freedom. The present approach is therefore basically different from that of Cherayil, Douglas, and Freed,[13] who tackled the same problem using the method of the cutoff regularization in the continuum chain limit. However, it should be stressed that their results were obtained perturbatively to the first order in the three-body parameter and therefore apply only to lightly-branched polymers ($f < 9$).

Both the experimentally observed nonuniversality of the $g$ ratio (see eq 20) and its increase over the random-walk phantom polymer prediction are quantitatively explained by residual three-body repulsions involving in particular three atoms on three different arms. These interactions have a greater importance the larger is the arm number $f$ and cannot be compensated through attractive interactions caused by the downward shift of the Θ temperature that is required to make the second virial coefficient $A_2$ equal to zero. Concerning the mean-square radius of gyration and the related topological index $g$, the agreement of the present calculations with experimental results is particularly good for polystyrene stars (see Table I and Figure 2). We stress that the $K_1$ parameter of the three-body interactions adopted here was determined independently through a fit with an entirely different kind of experimental data on linear polystyrene.[2] For other polymers, $K_1$ must be adjusted in a nontrivial way, leading to nonuniversality in the Θ-point behavior[1] (see also Table I).

On the other hand, other results obtained in this paper appear to be less satisfactory. (i) First of all, the topological index $h$, related to the hydrodynamic radii of the star and of the linear polymer through eq 24, turns out to be larger than expected for phantom polymers, but not as much as the (scarce) experimental data suggest. According to recent Monte Carlo simulations,[30] the discrepancy should be mostly attributed to shortcomings in the current treatment of the hydrodynamic interaction, in particular the preaveraging approximation which appears to be more serious in star polymers than it does in linear chains. Furthermore, the relatively high density in the core region suggests the possibility of some intramolecular hydrodynamic screening, while specific conformational peculiarities in the core region cannot be ruled out. (ii) In the second place, the molecular-weight dependence of the $g$ ratio (or equivalently of $\alpha_S{}^2$; see Figure 1) has the opposite behavior than is found experimentally. More specifically, we see from eq 21 and Figure 1 that $g$ should *increase* with molecular weight, whereas it was reported to *decrease* to the asymptotic limit in the case of 12-arm polystyrene stars.[10] On the other hand, a few data on 12-arm polyethylene stars with a relatively low molecular weight suggest an essentially constant value of $g$.[31]

Concerning point ii, we note that in a recent work dealing with lightly-branched stars[3] we studied the effect of the screened interactions arising from the finite width of the interatomic potential (or, in other words, from the finite thickness of the polymer backbone). The basic result was that $g$ should indeed decrease to the asymptotic value $g_{\mathrm{ph},\infty}$ (see eq 21′) with increasing molecular weight. The combined effect of the three-body and of the screened interactions is expected to be simply additive, as a first approximation, so that the expansion factor $\alpha_S{}^2$ (see eq 19) should be roughly given by the product of the corresponding factors due to either interaction alone. In fact, the screened interactions arise from a medium-range potential, so that the resulting asymptotic expansion is independent of $f$ and is approached more quickly with $N$ than that due to long-range three-body repulsions. Therefore, the latter are the dominant factor at large $N$ and the $g$ ratio is expected to be the same as that reported in Table I and in Figure 2. Conversely, at small $N$ some interplay of the two repulsive interactions may come into play and the factorizability of $\alpha_S{}^2$ may be inaccurate.

We therefore carried out also a few exploratory calculations on the 12-arm star considering both the medium-range screened interactions and the long-range two- and three-body interactions (see the full eq 17 and the Numerical Procedure section). The numerical results are shown in Figure 1 (dashed curve) as $\alpha_{S,\mathrm{star}}{}^2/\alpha_{S,\mathrm{lin}}{}^2$ for a comparison with the calculations accounting only for the three-body interactions (we remind everyone that in this case $\alpha_{S,\mathrm{lin}}{}^2 \equiv 1$ to a very good degree, so that in either case the values reported in the figure yield also $g/g_{\mathrm{ph}}$; see eq 20′). Indeed, it turns out that $\alpha_S{}^2$ may be factorized in the separate contributions at large $N$, although following a more complicated pattern at small $N$. Since the expansion factor due to the screened interactions tends rather quickly to an asymptotic constant value *that is the same for the linear and the star polymer*,[3] as said before, the ratio $\alpha_{S,\mathrm{star}}{}^2/\alpha_{S,\mathrm{lin}}{}^2$ obtained with the full calculation merges at large $N$ with the results obtained with the residual three-body interactions alone (compare the dashed and the solid lines in Figure 1). Therefore, the asymptotic $g$ values previously discussed (Table I and Figure 2) do not change, as expected. At smaller $N$, the results are determined by a rather intricate interplay of effects qualitatively sketched in the following. First of all, the interatomic distances undergo a larger expansion because of the extra repulsive potential. This extra expansion decreases $|\bar{\tau}_{\mathrm{ph}}B|$; see eq 16: in other words, any two atoms are kept farther apart, so that their intramolecular contact is less likely; the same is true for the intermolecular three-body interactions. From the intramolecular viewpoint, a decrease in $|\bar{\tau}_{\mathrm{ph}}B|$ weakens the two-body long-range attractions, which compensate the three-body repulsions less effectively. However, these are weakened too, because the further expansion of the star decreases also the three-body probability density of contact (see eqs 6), whereas the screened interactions are not affected directly by the change in $\bar{\tau}_{\mathrm{ph}}B$. Because of their medium-range nature, the latter are most effective at relatively small $N$. On the other hand, in the linear chain at the $\Theta$ point the residual three-body interactions are vanishingly small, being balanced almost exactly by the two-body attractions, and the screened interactions are the only repulsive potential actually left. In conclusion, in the case of linear and of lightly-branched polymers ($f < 6$) the three-body repulsions may be neglected to a very good approximation for any $N$, whereas their contribution is the dominant factor in heavily-branched polymers for large enough $N$.

As a final comment, we note that the three-body repulsions account satisfactorily for the asymptotic values of the $g$ ratio in the $\Theta$ state, including its nonuniversality, but not for its molecular-weight dependence. Since the latter was experimentally determined only on 12-arm polystyrene and polyethylene stars that show a different behavior,[10,31] it would be interesting to have data from different polymers, as well as from more heavily-branched stars as a test of nonuniversality in this respect too.

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