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Dimension and Shape of Model Chains as a Function of Their Intermolecular Separation[1]

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ABSTRACT: In the course of investigations concerning the pair distribution function $G(R)$ of Monte-Carlo-generated cubic lattice model chains, the variation of the squared radius of gyration, s^2, and the squared end-to-end distance, h^2, with intermolecular distance R has been studied for isolated pairs of chains (each chain covering 50 lattice points) for athermal as well as for Θ conditions. Coming from infinite R, s^2 first decreases and, after passing a minimum, finally for $R \rightarrow 0$ increases to ca. 1.2 times the value at infinite R, $\langle s^2 \rangle_0$. Splitting s^2 into its components parallel and perpendicular to the axis connecting the centers of mass of the two chains, $s^2_{\parallel}$ and $s^2_{\perp}$, reveals that the decrease in s^2 at moderate approach is caused by $s^2_{\parallel}$, which qualitatively shows the same behavior as s^2, however, in a much more pronounced manner, while $s^2_{\perp}$ rises continuously with progressive approach until at $R \rightarrow 0$ $s^2_{\parallel}$ and $s^2_{\perp}$ flow together. At very large R Θ chains exhibit an additional small maximum in s^2 and $s^2_{\parallel}$ and a small minimum in $s^2_{\perp}$. With incipient approach, Θ chains therefore, on average, have the shape of weakly prolate ellipsoids which on decreasing separation transforms into that of oblate ellipsoids until the coils exhibit uniformly expanded dimensions in the limit of $R \rightarrow 0$. On the other hand, when coming from infinite R, athermal chains start with the stage of oblate ellipsoids, finally also being uniformly expanded for vanishing R. Similar results have been obtained for h^2. By summation of the deviations of s^2 and h^2 from their values at infinite separation over all intermolecular separations, the coefficients of the dependence of average dimensions on concentration in the limit of infinite dilution are accessible. These coefficients are negative for athermal chains and turn out to be positive for Θ chains.

Small-angle neutron-scattering experiments[2,3] as well as Monte-Carlo calculations on multiple chain systems[4-7] have established that for athermal polymer solutions the chain dimensions (i.e., radius of gyration, end-to-end distance) decrease with increasing concentration and, furthermore, on proceeding to pure polymer the chain dimensions may well approach the "unperturbed dimensions".[2,3,5-7] Thus these methods have given support to the predictions put forward by Flory,[8] according to which the chain dimensions in bulk polymer should be the same as those at infinite dilution in a Θ solvent. On the other hand, similar Monte-Carlo calculations carried out for multiple chain systems in their Θ state[9] have shown that in this case the chain dimensions at low concentrations *increase* with polymer concentration and, after having passed through a maximum value, also tend to return to the dimensions characteristic for isolated chains under Θ conditions (i.e., in this case to the *same* dimensions which are exhibited at infinite dilution).

Nothing at all, however, is known about the mechanism according to which all of these changes in chain dimensions are effectuated, i.e., how shape and size of the polymer chains vary with their intermolecular separation. As (average) intermolecular separation (between nearest neighbors) and polymer concentration for sure are anticorrelated quantitites, such knowledge certainly not only would give deeper insight into the secondary phenomena which accompany the interaction of chain molecules, but also should contribute to the understanding of the differences in the low concentration behavior of athermal and Θ chains.

Fortunately there exists a rather simple way to obtain such an insight. In a recent communication we have described a method for evaluating the low concentration limit of the pair distribution function of four-way cubic lattice chains.[10] This method, which easily can be adapted to any other type of lattice or off-lattice chains, is not restricted to athermal systems, but can be extended to chains, too, in which additionally allowance is made for finite segment–segment interactions between two nonsuccessive segments which happen to lie on neighboring sites of the lattice (or, more generally, occupy neighboring positions in space). In the course of this procedure equilibrated ensembles of ν chains (ν = 100–300) consisting of 50 segments each were produced by a modified Metropolis-Monte-Carlo process, and all N possible pairs of chains, which can be picked out of the ensembles ($(\nu - 1)(\nu/2) \equiv N$), were placed into the same lattice at all significant intermolecular separations R, R being chosen to point into one of the directions of the three main axes of the lattice. (Other choices, e.g., R directed into the direction of the plane or space diagonals, lead to substantially equal results.) The value of the pair distribution function for a certain intermolecular distance R, $G(R)$, then is obtained as the average of the Boltzmann factor of all pair configurations for this value of R,

$$G(R) = \frac{1}{N}\sum_{j=1}^{i-1}\sum_{i=1}^{\nu} e^{-E_{ij}/k\mathrm{T}} \equiv \frac{1}{N}\sum_{i\neq j} e^{-E_{ij}/kT} = e^{-U(R)/kT} \quad (1)$$

E_{ij} being the intermolecular interaction energy within a specific pair ij, and $U(R)$ being the pair potential describing the *average* interaction within an isolated pair at intermolecular distance R. Due to the choice of the segment–segment interaction potential $\epsilon(r)$ ($r = 0$, $\epsilon = \infty$; $r = 1$, $\epsilon = \phi kT$, $r > 1$, $\epsilon = 0$; r is the segment–segment distance) the application of the superposition principle (the Boltzmann factor for chain–chain interaction is evaluated as the product of the Boltzmann factors of all segment–segment interactions between segments of different chains) automatically makes the intermolecular Boltzmann factor $e^{-E_{ij}/kT}$ zero when there is at least one overlap between the two chains forming the pair (one pair of segments from different chains for which r equals zero). As a consequence only pairs free of overlaps (compatible pairs) can contribute to the double sum in eq 1. The Boltzmann factor for such a compatible pair, which is uniquely determined by the number of intermolecular segment–segment contacts n_{ij}, then is simply $e^{-n_{ij}\phi}$. Accordingly, eq 1 can be written

$$G(R) = \frac{1}{N}\sum_{i\neq j} e^{-n_{ij}\phi} \text{ (compatible pairs)} \quad (1a)$$

For athermal chains, for which $\phi = 0$, $G(R)$ degenerates to the fraction of pair configurations which are compatible.

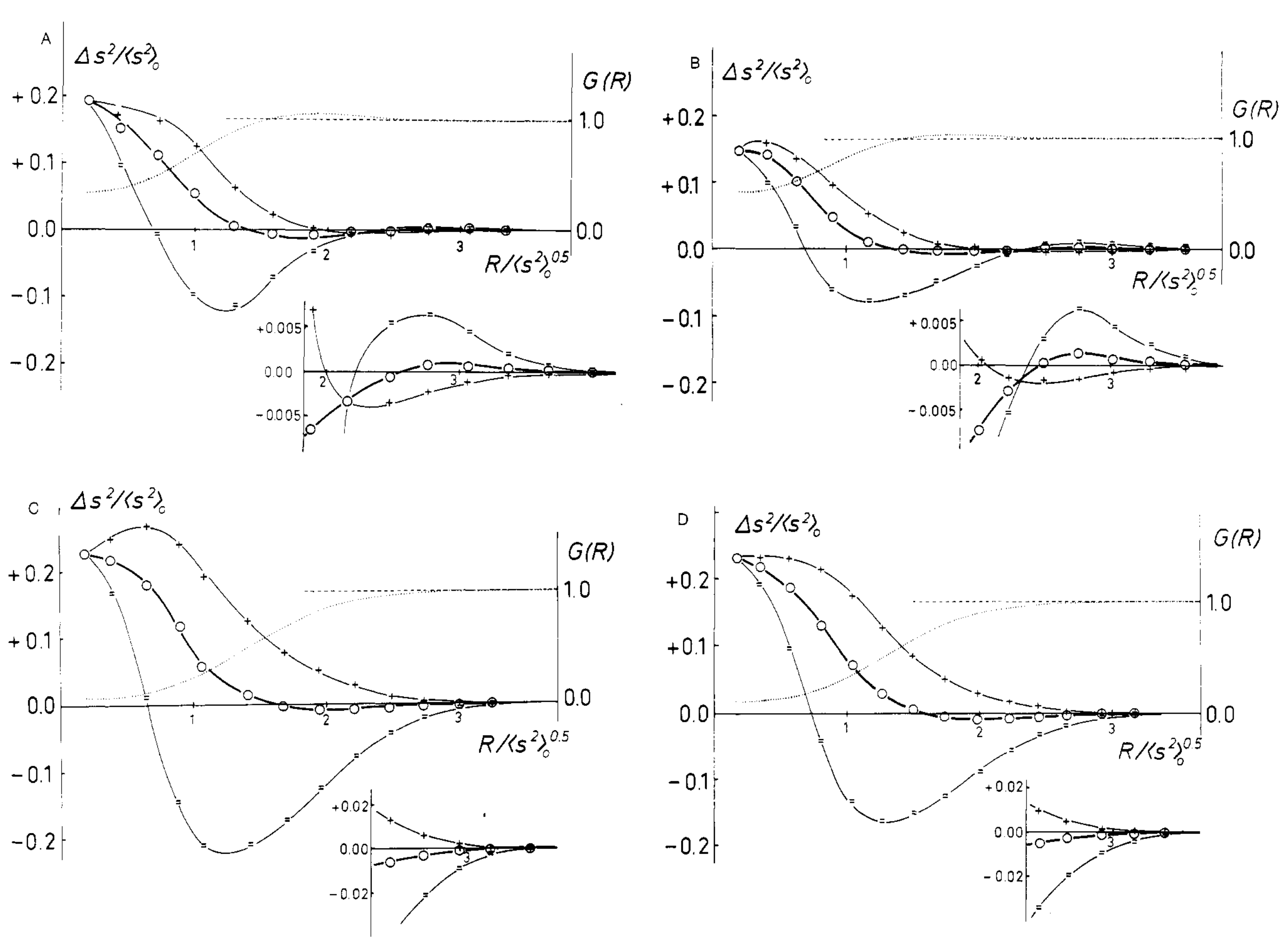

Figure 1. Left scale: deviation of the squared radius of gyration (○) and its component parallel (=) and perpendicular (+) to the axis connecting the centers of mass from and relative to their values at infinite separations as a function of (reduced) separation of centers of mass $R/\langle s^2\rangle_0^{0.5}$ for isolated pairs of cubic lattice model chains. The insert gives part of the curves on an enlarged ordinate scale. Right scale: pair distribution function $G(R)$ (dotted curve) of the system. (A) Four-way cubic lattice chains, Θ conditions; $\langle s^2\rangle_0 = 11.41$. (B) Five-way cubic lattice chains, Θ conditions; $\langle s^2\rangle_0 = 14.21$. (C) Four-way cubic lattice chains, athermal conditions; $\langle s^2\rangle_0 = 14.33$. (D) Five-way cubic lattice chains, athermal conditions; $\langle s^2\rangle_0 = 17.93$.

At this stage of the calculations the squared dimensions (squared radius of gyration, s^2, squared end-to-end distance, h^2) of the chains which form compatible pair configurations at a given R simply have to be registered.

The average values, which are characteristic for a certain intermolecular separation, can be calculated according to

$$s^2(R) = \frac{\frac{1}{2}\sum\limits_{i\neq j}(s_i^2 + s_j^2)e^{-E_{ij}/kT}}{\sum\limits_{i\neq j} e^{-E_{ij}/kT}} = \frac{\frac{1}{2}\sum\limits_{i\neq j}(s_i^2 + s_j^2)e^{-n_{ij}\phi}}{\sum\limits_{i\neq j} e^{-n_{ij}\phi}} \qquad (2)$$

$$h^2(R) = \frac{\frac{1}{2}\sum\limits_{i\neq j}(h_i^2 + h_j^2)e^{-E_{ij}/kT}}{\sum\limits_{i\neq j} e^{-E_{ij}/kT}} = \frac{\sum\limits_{i\neq j}(h_i^2 + h_j^2)e^{-n_{ij}\phi}}{\sum\limits_{i\neq j} e^{-n_{ij}\phi}} \qquad (3)$$

with the summations in the last expression of eq 2 and 3 to be extended over compatible pairs only.

According to the method chosen for the construction of the ensembles, the chains are already represented in the ensembles with their correct probability of occurrence; only the Boltzmann factor corresponding to the intermolecular energy enters into the calculations of the average dimensions of the pairs. $s^2(R)$ and $h^2(R)$ will represent the change in size which occurs on variation of intermolecular separation. In order to get information on the change in shape, too, the changes occurring in size have to be split into those taking place in the direction of the axes connecting the centers of mass of the two chains ($s^2_{\parallel}$, $h^2_{\parallel}$) and those at right angles to this direction ($s^2_{\perp}$, $h^2_{\perp}$). As there are two main axes perpendicular to the axes connecting the centers of mass, $s^2_{\perp}$ has double the weight of $s^2_{\parallel}$, i.e.,

$$s^2 = 2s^2_{\perp} + s^2_{\parallel} \qquad (4)$$

Results

Calculations have been carried out for athermal ($\phi = 0$) and Θ chains ($\phi = -0.265$) of the four-way as well as the five-way cubic lattice type, each chain consisting of 50 segments (i.e., covering 50 lattice points). As five-way lattice chains have a less tightly coiled structure compared to four-way chains, the effect of different coil tightness on size and shape also can be studied.

The results are represented in Figure 1A–D as the deviations of $s^2(R)$ from and relative to the value of s^2 at infinite separation, $\Delta s^2/\langle s^2\rangle_0$, as a function of intermolecular distance R. These figures also contain the pair distribution function $G(R)$ for the same system. In Figure 2 as an example the dependence of the analogous quantity referring to the squared end-to-end distance, $\Delta h^2/\langle h^2\rangle_0$, on the separation between the two centers of mass, R, is shown.

Size Factors. In principle, the behavior can be characterized in the following way.

Θ Chains. The overall dimensions (s^2, h^2), when coming from infinite separations ($\langle s^2\rangle_0$, $\langle h^2\rangle_0$), first increase very slightly (by 0.2% at most at $R \approx 2.8\langle s^2\rangle_0^{1/2}$) then decrease until a minimum (at $R \approx 1.8\langle s^2\rangle_0^{1/2}$) is reached, corre-

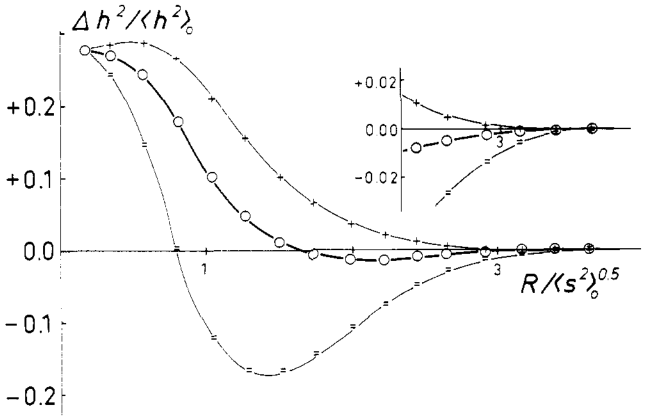

Figure 2. Deviation of the squared end-to-end distance (○) and its component parallel (=) and perpendicular (+) to the axis connecting the centers of mass from and relative to their values at infinite separation as a function of (reduced) separation between centers of mass $R/\langle s^2\rangle_0^{0.5}$ for isolated pairs of five-way cubic lattice chains under athermal conditions ($\langle s^2\rangle_0 = 17.93$, $\langle h^2\rangle_0 = 110.81$; same ensemble as in Figure 1D). The insert gives part of the curve on an enlarged ordinate scale.

sponding to values which are ~1% lower than the average of the isolated chains at infinite separation. Further decrease of R leads to a marked increase of s^2 and h^2 (15–25% relative to infinite separation) at the lowest values of R.

Athermal Chains. The outer range with slightly increased dimensions to be found for Θ chains is missing here. Coming from infinite R, dimensions first decrease with incipient intermolecular interaction. After passing through a minimum (1–1.5% reduction of squared dimensions at $R \approx 2\langle s^2\rangle_0^{1/2}$) dimensions strongly increase, finally exceeding their values at infinite separation, $\langle s^2\rangle_0$ and $\langle h^2\rangle_0$, by 20–30%.

Independent of thermodynamic conditions (athermal or Θ chains), in general, the squared end-to-end distance is the more susceptible quantity. In most cases the effects on s^2 are markedly lower than those on h^2. Surprisingly, however, there is little difference between the extents to which the dimensions of four-way and five-way cubic lattice chains are affected by intermolecular separation.

Shape Factors. By splitting Δs^2 ($\equiv s^2(R) - \langle s^2\rangle_0$) and Δh^2 ($\equiv h^2(R) - \langle h^2\rangle_0$) into its components parallel ($\Delta s^2_{\parallel}$, $\Delta h^2_{\parallel}$) and orthogonal ($\Delta s^2_{\perp}$, $\Delta h^2_{\perp}$) to R ($\Delta s^2 = 2\Delta s^2_{\perp} + \Delta s^2_{\parallel}$) we can see that it is the parallel component which is primarily responsible for all size and shape changes.

Θ Systems. In principle, except for quantitative aspects, the parallel components show a dependence on R similar to that of the overall quantitites, the shift of squared dimensions at the maximum at large separations and at the minimum, however, being larger by one order of magnitude (ca. +0.7% and ca. −8%, respectively). Because the difference between parallel and orthogonal components vanishes for vanishing R, the relative increase in dimensions for $R \rightarrow 0$ will be the same for the overall quantities and their components. Except for this inner range, where accordingly orthogonal and parallel components flow together, the orthogonal components behave contrary to the parallel component, i.e., coming from infinite separation they first pass through a minimum before they increase to the value characteristic for zero intermolecular separation.

Athermal Systems. Similar to what has been observed for s^2 and h^2, the maxima of s^2 and $h^2_{\parallel}$ at large values of R, which appear in the Θ systems when coming from infinite separations, do not appear in this case: beginning interaction (decreasing R) causes parallel components to decrease and orthogonal components to increase. While this continues with decreasing R for the orthogonal components, the parallel components pass through a minimum and finally approach the orthogonal components at vanishing R at markedly increased dimensions.

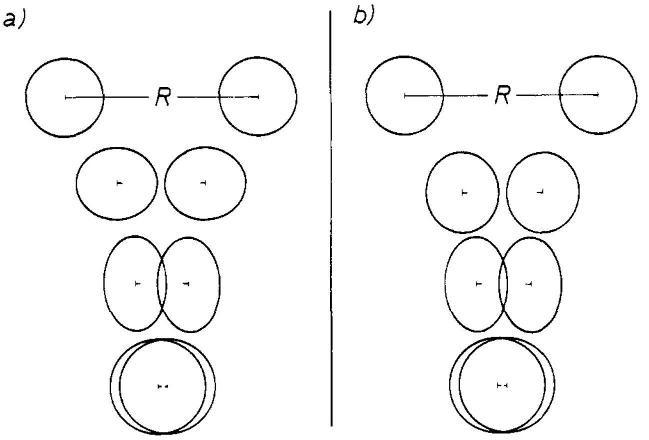

Figure 3. Schematic representation (not true to scale) of the change in size and shape within an isolated pair of chains on variation of separation: (a) Θ system; (b) athermal system.

Again the changes in h^2 are more pronounced than those in s^2 and the data do not depend significantly on the lattice type for athermal as well as for Θ chains.

The overall changes in both shape and size with intermolecular separation are schematically represented in Figure 3 for athermal as well as for Θ conditions.

Discussion

The size behavior is best understood when considered as the outcome of the changes in the orthogonal and parallel components produced by intermolecular interaction.

Θ Systems. Bearing in mind that for Θ systems the interaction on approach of the chains at larger R is an attractive one,[11] it is conceivable that the primary effect due to the attraction operative between the two members of the pair is an increase in the parallel component. This is accompanied by a reduction in the orthogonal components which effect a partial (but not total) compensation, so that a weak net increase in overall dimensions results, the average shape of the chains in this case being best described as that of an weakly prolate ellipsoid. On further approach of the two macromolecules, when the potential turns to positive (repulsive), the chains are squeezed (compressed) in the direction of the vector of their intermolecular distance. Again there is some counteraction (dilatation) by the components at a right angle so that the net result is an oblate ellipsoid with decreased overall dimensions. However, there seems to be a limit in the squeezing process; further reduction of intermolecular separation finally is accompanied by a steep increase of the parallel component which continuously approaches the (increased) values of the orthogonal ones, so that as a final result (at $R \rightarrow 0$) the chains could be looked at as uniformly expanded. This means that small intermolecular separations are accomplished preferentially with chain structures of low compactness.

Athermal Chains. Due to the absence of attractive interaction, the state of prolate ellipsoids does not appear here. Coming from infinity, incipient interaction, which is repulsive in type, directly leads to oblate ellipsoids with decreased overall dimensions which on further approach of the macromolecules change to apparently uniformly expanded particles with no component being preferred to the other in their average shape, as has been already de-

Table I

Limiting Slopes, k_s and k_h, Characterizing the Dependence of $\Delta s^2/\langle s^2\rangle_0$ and $\Delta h^2/\langle h^2\rangle_0$, Respectively, of Cubic Lattice Chains (50 Segments) on the Fraction of Occupied Lattice Sites φ at Vanishing Concentration ($\varphi \to 0$)

	k_s[a]	k_s[b]	k_h[a]	k_h[b]
four-way, Θ system	0.10 ± 0.03		0.13 ± 0.07	
five-way, Θ system	0.16 ± 0.02	0.21 ± 0.02	0.18 ± 0.05	0.21 ± 0.04
four-way, athermal system	−0.35 ± 0.03		−0.44 ± 0.02	
five-way, athermal system	−0.38 ± 0.02	−0.42 ± 0.03	−0.48 ± 0.03	−0.50 ± 0.04

[a] Calculated according to eq 6a and 6b, respectively. [b] Data taken from Monte-Carlo simulation of multiple chain systems.[6,13]

scribed for Θ chains. The larger effects exhibited by $h^2(R)/\langle h^2\rangle_0$ (relative to $s^2(R)/\langle s^2\rangle_0$) can be explained by the broader distribution of h^2 values in the ensemble compared to the s^2 distribution. Preferential removal at one wing of the distribution therefore causes the average of the rest, which forms the compatible pairs, to be shifted to a larger extent for $h^2(R)/\langle h^2\rangle_0$ than for $s^2(R)/\langle s^2\rangle_0$.

Relationship of $s^2(R)$ and $h^2(R)$ to Concentration Dependence of Chain Dimensions

In a theoretical treatment of the concentration dependence of chain dimensions,[12] a method is given for the calculation of the variation of chain dimensions with concentration in the limit of vanishing polymer concentration from the pair distribution function $G(R)$ and the chain dimensions as a function of intermolecular separation, e.g., $s^2(R)$ or $h^2(R)$, respectively. According to this concept, the overall change in chain dimensions at a certain overall particle density $\bar{\rho}$ can be envisaged as the sum of all changes occurring simultaneously at all intermolecular separations R, weighted with the actual particle density $\rho(R)$ at these R values

$$\Delta s^2(\bar{\rho}) = 4\pi \int_0^\infty \rho(R) R^2 (s^2(R) - \langle s^2\rangle_0)\, \mathrm{d}R \qquad (5)$$

As $G(R) = \rho(R)/\bar{\rho}$ and the volume fraction φ of the polymer chains is connected to $\bar{\rho}$ by $\varphi = \bar{\rho} n v_1$ (n = the number of segments per chain, v_1 = the volume of one segment; in our model $v_1 \equiv 1$) and replacing integration by summation, this can be transformed into

$$\frac{\Delta s^2(\varphi)}{\langle s^2\rangle_0} = \frac{4\pi}{n} \sum_{R=0}^{\infty} R^2 G(R) \frac{\Delta s^2(R)}{\langle s^2\rangle_0} \varphi \equiv k_s \varphi \qquad (6a)$$

where k_s, due to the fact that $G(R)$ as well as $\Delta s^2(R)$ refer to isolated pairs, now is the limiting ($\varphi \to 0$) coefficient characterizing the variation of relative chain dimensions with the volume fraction φ. A fully analogous equation also holds for $\Delta h^2(\rho)$.

$$\frac{\Delta h(\varphi)}{\langle h^2\rangle_0} = \frac{4\pi}{n} \sum_{R=0}^{\infty} R^2 G(R) \frac{\Delta h^2(R)}{\langle h^2\rangle_0} \varphi \equiv k_h \varphi \qquad (6b)$$

Table I shows the data obtained for these limiting coefficients k_s and k_h for four-way and five-way cubic lattice chains estimated according to eq 6a and 6b. For five-way cubic lattice chains these quantities can be directly compared to the corresponding values which are obtained from the investigation of the concentration dependence of the squared dimensions by Monte-Carlo simulation of multiple chain systems.[6,13]

It should be recalled that the ensembles used in our calculations are not very large (100–300) so that not every detail in the statistics of chain size and shape can be equally well represented within the ensemble. Considering further that Δs^2 or Δh^2 change their sign (once in the case of athermal chains, even twice in the case of Θ chains) so that the resulting sum will be made up out of positive and negative contributions, which are of comparable order of magnitude, comparatively small errors due to imperfect statistics may induce a relatively large scatter of the quantities k_s and k_h calculated for an ensemble, especially for the Θ systems. Taken all together, however, the agreement of the values calculated according to eq 6a and 6b with the limiting slopes obtained from multiple chain systems is very satisfactory. Above all, in spite of all of the scatter, the limiting slopes obtained for Θ systems turn out to be positive, thus again adding to the arguments against the existing theories, which unanimously predict a zero concentration dependence of chain dimensions for Θ systems.[14]

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(11) $G(R) = \exp\{-U(R)/kT\}$; accordingly $G(R) > 1$ corresponds to a negative (attractive) pair potential $U(R)$, whereas there is net repulsion ($U(R) > 0$) when $G(R) < 1$.

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