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Macrocyclization Equilibria. 1. Theory

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Abstract: The Jacobson–Stockmayer theory of cyclization equilibria $R_1\text{–}M_x\text{–}R_2 \rightleftarrows \text{c-}M_x + R_1\text{–}R_2$ where c-M_x is the cyclic x-mer comprising $n = \nu x$ bonds is elaborated to take account of restrictions on the directions of the bonds joined in ring closure. On the assumption that bonds formed are equivalent to those broken, the equilibrium constant is $K_x = W(\mathbf{0})[2\Gamma_0(1)]/\sigma_{cx}N_A$ where $W(\mathbf{r})$ is the probability density function for the n-bond chain vector $\mathbf{r}$; $\Gamma_0(\gamma)$ is the probability distribution, when $\mathbf{r} = \mathbf{0}$, of $\gamma \equiv \cos \Delta\theta$, $\Delta\theta$ being the angle between a hypothetical bond $n + 1$ and bond 1; σ_{cx} is the symmetry number of the ring; and N_A is Avogadro's number. $\Gamma_0(1)$ may be expanded in averaged Legendre polynomials, $\langle P_k \rangle_{r=0}$, with argument $\gamma_{r=0}$. The averaged polynomials are expanded in the quantities $\langle P_k r^{2p} \rangle$, which can be evaluated by Monte Carlo methods applied to appropriate rotational isomeric state models; alternatively they may be expanded in moments $\langle \gamma^m r^{2p} \rangle$, lower ones of which can be computed by matrix generator techniques. Calculations for various chains with $10 < n < 50$ invariably yield $2\Gamma_0(1) < 1$, indicating unfavorable correlations between the directions of terminal bonds. These calculations are consistent with the low values of K_x generally observed in this range, sometimes with a minimum at $n = 10$ to 25. The asymmetry of the distribution $W(\mathbf{r})$, as manifested in the persistence vector $\mathbf{a} \equiv \langle \mathbf{r} \rangle$, in conjunction with the necessity for bond n to approach atom 0 from a direction opposed to vector $\mathbf{a}$ provides a qualitative explanation for this well established pattern of behavior of K_x for cyclic homologues. Calculations for hypothetical chains with acute bond angles yield $2\Gamma_0(1) > 1$ in confirmation of the foregoing explanation. The preferential formation of small rings ($n = 5$ to 8) is explicable conversely by favorable directional correlations in conformations for which $r \approx \mathbf{0}$.

Primary Formulations

Consider the cyclization process

$$\text{-}M_x\text{-} \rightleftarrows \text{c-}M_x \qquad (1)$$

where -M_x- is a chain molecule comprising a sequence of x repeating units and c-M_x is the corresponding cyclic compound. The repeating unit may, for example, be -CH_2-, -CH_2CH_2O-, or most notably -$Si(CH_3)_2O$-. The x-meric acyclic reactant -M_x- may be a bifunctional species X-M_x-Y from which the by-product XY is eliminated in process 1. For our purposes it is advantageous to regard it as a biradical, as the representation above implies, even though the occurrence of the biradical may be hypothetical.

The corresponding combination reaction between two acyclic species may be represented by

$$\text{-}M_x\text{-} + \text{-}M_y\text{-} \rightleftarrows \text{-}M_{x+y}\text{-} \qquad (2)$$

or by

$$X\text{-}M_x\text{-}Y + X\text{-}M_y\text{-}Y \rightleftarrows X\text{-}M_{x+y}\text{-}Y + XY \qquad (2')$$

The bond forming processes in (1) and (2) are assumed to be identical. By comparing these two processes, the one involving cyclization and the other combination, we may educe the effects of constraints associated with formation of the cyclic species. Specifically, subtraction of (2) from (1) gives

$$\text{-}M_{x+y}\text{-} \rightleftarrows \text{-}M_y\text{-} + \text{c-}M_x \qquad (3)$$

This equilibrium is governed by the *cyclization constant*[1-3]

$$K_x = K_1/K_2 = [\text{-}M_y\text{-}][\text{c-}M_x]/[\text{-}M_{x+y}\text{-}] \qquad (4)$$

The nature of the terminal groups, expressed noncommittally by dashes, obviously is immaterial. What matters is that the unspecified terminal groups in the species -M_y- and -M_{x+y}- be chemically equivalent. Then K_x measures the propensity for cyclization. It equates to the concentration of the cyclic compound when the concentrations of -M_y- and -M_{x+y}- are equal.

The foregoing scheme is applicable to cyclization processes in general. It is readily adapted to the treatment of chain $\rightleftarrows$ ring equilibria in polymeric systems. Then process 3 is construed as the abstraction of a cyclic species comprising x units from a longer chain of $x + y$ units. The establishment of this equilibrium inevitably will be accompanied by equilibration between various linear species. The concentration of the linear species of size y is then proportional to $p^{y-1}(1 - p)$, where p is the extent of reaction for the acyclic molecules,[1] i.e., the ratio of interunit bonds formed to the total number of such bonds that may be formed according to the processes 2 or 2′.

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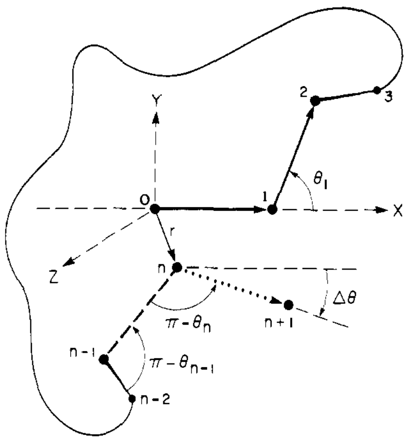

Figure 1. Acyclic segment of n atoms, 0 through $n-1$, in a conformation approaching the requirements for cyclization. See text for details.

Hence,

$$K_x = [\text{c-M}_x]p^{-x} \tag{5}$$

a relationship due to Jacobson and Stockmayer.[1] In the limit of high extents of reaction, where $p^x \approx 1$ and the average degree of polymerization (y) is large, this reduces to the simple equality[1]

$$K_x = [\text{c-M}_x] \tag{5'}$$

The acyclic x-meric segment from which the ring is formed comprises $n = \nu x$ chain atoms joined by $n-1$ bonds, ν being the number of chain atoms per repeat unit. The atoms of the segment are numbered 0 to $n-1$, as in Figure 1. The bonds are indexed 1 to $n-1$, with bond i connecting atoms $i-1$ and i. The angles between consecutive bond vectors are denoted by θ_1, etc., as indicated in Figure 1. These are the supplements of the conventional bond angles, π-θ. The conformation of the x-meric acyclic segment is specified by rotations $\varphi_2, \varphi_3, \ldots, \varphi_{n-2}$ about the $n-3$ internal bonds. Formation of the ring involves establishment of bond n between atoms 0 and $n-1$. In Figure 1 this anticipated bond is shown dashed; it joins atom $n-1$ with a hypothetical atom n. According to the scheme represented in this figure, ring closure involves coalescence of atom n with the initial atom 0. A hypothetical bond $n+1$, shown dotted in Figure 1, is appended for reasons that will be apparent below.

Closure of the sequence of $n-1$ bonds to form the n-membered cyclic molecule is contingent upon fulfillment of three conditions: (i) atom $n-1$ must be situated at a distance from atom 0 equal to the length of anticipated bond n, i.e., the vector $\mathbf{r}_{n-1}$ spanning atoms 0 to $n-1$ must be of the required length; (ii) the direction of this vector with respect to bond vectors 1 and $n-1$ must yield acceptable bond angles π-θ_{n-1} and π-θ_n at atoms $n-1$ and n (or 0), respectively, within tolerable limits; and (iii) the conformation specified by torsional angles $\varphi_1, \varphi_2, \ldots, \varphi_n$, properly weighted according to its probability of occurrence with due regard for torsional strain, must be acceptable.

Our procedure is to generate a sequence of $n+1$ bonds on the basis of a rotational isomeric state (RIS) scheme[3-6] appropriate to the chain considered. For the fulfillment of conditions (i) and (ii) it is required that the vector $\mathbf{r}_n \equiv \mathbf{r}$ that spans bonds 1 through n (see Figure 1) must vanish within a volume element $\delta\mathbf{r}$ and that the hypothetical bond $n+1$ must be parallel to bond 1 within acceptable limits. Compliance with the stipulation $\mathbf{r} \approx \mathbf{0}$ assures that condition (i) is fulfilled. At the same time, the correct valence angle at atom $n-1$ is guaranteed by the employment of the proper value of θ_{n-1} in the RIS procedure.[3,6] Condition (ii) as it relates to θ_n further requires that γ, defined by $\gamma \equiv \cos\Delta\theta$, where $\Delta\theta$ is the angle between hypothetical bond $n+1$ and bond 1, must fall within the range $1-\delta\gamma$ to 1.

Bond lengths and bond angles are assigned their normal values in the RIS generation of a conformation of the sequence of $n+1$ bonds. The conformation is specified by torsional angles φ_2 to φ_n, inclusive. These are assigned discrete values, suitably chosen in order to optimize the representation of the conformational characteristics of the real chain by the RIS model.[21] In the process of generating these conformations, each of them is accorded a probability of occurrence proportional to its statistical weight, the latter being determined by the combination of rotational states $\{\varphi\}$ for the given conformation. It follows that the procedure fulfills condition (iii) above as it pertains to bonds 2 to n. The conformation of bond 1, determined by the mutual orientations of bonds 2 and n, is not comprehended by the procedure described. Hence, the acceptability of the conformation imposed on bond 1 must be separately considered if full compliance with condition (iii) is to be required.

Elaborating the Jacobson-Stockmayer[1] theory to include conditions of angle compliance,[2,3] we express the molar standard-state free-energy change for reaction 1 as follows:

$$\Delta G^0_{(1)} = \Delta G^* - RT\ln\left\{[W(\mathbf{0})\delta\mathbf{r}][\Gamma_0(1)\delta\gamma] \times \left[\sum_{\eta}\Phi_{0,1}(\varphi_\eta)\delta\varphi_\eta\right](\sigma_a/\sigma_{cx})\right\} \tag{6}$$

where $W(\mathbf{r})$ is the probability of the value $\mathbf{r}$ for the end-to-end vector per unit volume, and $\delta\mathbf{r}$ is the admissible departure from $\mathbf{r} = \mathbf{0}$ for the formation of the required bond; $\gamma \equiv \cos\Delta\theta$ and, hence, $\mathrm{d}\gamma = -\sin(\Delta\theta)\,\mathrm{d}(\Delta\theta) = -(2\pi)^{-1}\,\mathrm{d}\omega$ is the measure of increment of solid angle; $\Gamma_\mathbf{r}(\gamma)\delta\gamma$ is the probability that γ assumes the specified value within the range $\delta\gamma$, with $\mathbf{r}$ having the value denoted by subscript; $\Phi_{\mathbf{r},\gamma}(\varphi_\eta)\delta\varphi_\eta$ is the probability of a torsional angle φ_η for bond 1, within the permissible range $\delta\varphi_\eta$, when r and γ assume the values denoted by subscripts; the summation includes the several admissible conformations indexed by η; σ_a and σ_{cx} are symmetry numbers for the acyclic chain and for the cyclic x-mer, respectively; and ΔG^* is a function of temperature that expresses the molar free energy change for bond formation when the reacting partners have been juxtaposed in the manner stipulated.

For the corresponding intermolecular reaction 2, all values of γ and φ are equally probable; i.e., $\Gamma_0(\gamma) = 1/2$ for $-1 \leq \gamma \leq 1$ and $\Phi_{0,1}(\varphi) = 1/2\pi$ for $0 \leq \varphi \leq 2\pi$. Hence, the molar standard free energy change is

$$\Delta G^0_{(2)} = \Delta G^* - RT\ln\left[N_A\sigma_a\delta\mathbf{r}(\delta\gamma/2)(\textstyle\sum\delta\varphi_\eta/2\pi)\right] \tag{7}$$

where N_A is Avogadro's number and all species are in their standard states at concentrations of one mole per unit volume. The geometrical constraints $\delta\mathbf{r}$, $\delta\gamma$, and $\delta\varphi_\eta$ and the free energy of bonding ΔG^* are assumed to be the same as for the cyclization process. Inasmuch as the bonds formed are equivalent, these assumptions should hold accurately, except for small rings that may be subject to bond angle and/or torsional strain. Cyclic compounds of this latter description are beyond the scope of the present treatment.

By combination of eq 6 and 7, we obtain

$$\Delta G^0_{(3)} = -RT\ln\left[2W(\mathbf{0})\Gamma_0(1)\bar{\Phi}_0/\sigma_{cx}N_A\right] \tag{8}$$

where

$$\bar{\Phi}_0 = 2\pi\textstyle\sum\Phi_{0,1}(\varphi_\eta)\delta\varphi_\eta/\sum\delta\varphi_\eta \tag{9}$$

measures the probability of compliance of the torsion angle φ for bond 1 with the requirements for an acceptable conformation relative to this probability for the corresponding acyclic union. It follows from eq 8 that the cyclization equilibrium constant is given by

$$K_x \equiv K_{(3)} = 2W(\mathbf{0})\Gamma_0(1)\overline{\Phi}_0/\sigma_{cx}N_A \tag{10}$$

Consider the set of conformations for the x-meric sequence that meet the distance requirement $\mathbf{r} = \mathbf{0}$ within $\delta\mathbf{r}$. If among these conformations the direction of hypothetical bond $n + 1$ is distributed at random relative to bond 1, i.e., if the directions of these two bonds are uncorrelated when the distance requirement is met, then the probability density of γ is uniform over the interval $-1 \leq \gamma \leq 1$. It follows that $\Gamma_0(\gamma) = \frac{1}{2}$ for all admissible values of γ, and in particular for $\gamma = 1$, when the directions of bonds 1 and $n + 1$ are uncorrelated. The torsional requirements for bond 1 in the ring formed by closure should be less stringent than the directional constraints. Hence, if the length (and "flexibility") of the sequence suffices to suppress directional correlations, the vanishing of torsional correlations for bond 1 in those conformations for which $\mathbf{r} \approx \mathbf{0}$ and $\gamma \approx 1$ seems assured. Then, $\Phi_{0,1}(\varphi) = 1/2\pi$ for all φ, and $\overline{\Phi}_0 = 1$. When these conditions are fulfilled, the cyclization equilibrium constant simplifies to

$$K_x = W(\mathbf{0})/\sigma_{cx}N_A \tag{11}$$

Under the further assumption that the density distribution function $W(\mathbf{r})$ is Gaussian, one obtains[1-3]

$$K_x = (3/2\pi\langle r_n^2\rangle)^{3/2}/\sigma_{cx}N_A \tag{12}$$

where $\langle r_n^2\rangle$ is the mean-square end-to-end length of the random x-meric sequence comprising $n = \nu x$ skeletal bonds, ν being the number of such bonds per repeating unit. If $\langle r_n^2\rangle$ is taken to be proportional to n, which is legitimate only for sufficiently long chains[3] (and in absence of effects of excluded volume[7,8]), then

$$K_x = (3/2\pi C_\infty l^2)^{3/2}/n^{3/2}\sigma_{cx}N_A \tag{13}$$

where C_∞ is the limiting value of the characteristic ratio, i.e., $C_\infty = \lim_{n\to\infty}(\langle r^2\rangle_0/nl^2)$, l being the bond length. The subscript 0 denotes absence of perturbations due to excluded volume or other effects.

Equation 13 is a restatement of Jacobson and Stockmayer's result.[1] It expresses the limiting form for very large n or x. Since, as they pointed out, the symmetry number σ_{cx} is proportional to x (e.g., for polysiloxanes it is $2x$) and therefore to n, the cyclization constant is asymptotically proportional to $n^{-5/2}$. To recapitulate, the approximations underlying this relationship are as follows: (1) the neglect of angle correlations leading to eq 11; (2) the assumption that $W(\mathbf{r})$ is Gaussian, which leads to eq 12; and finally (3) expression of $\langle r_n^2\rangle$ as linear in n. All of these approximations must fail as n decreases.

Experimental cyclization constants K_x for poly(dimethylsiloxane)[7-9] (PDMS) extending up to rings with $x = 202$ units, or $n = 404$ bonds, appear to converge to values only ca. 10 to 25% below those calculated according to eq 12 or 13 for $x > 75$ units. This confirmation of the Jacobson–Stockmayer theory is achieved without benefit of adjustable parameters.[2,3,8,9] As the ring size is diminished, the ratio of observed to calculated values of K_x decreases; it passes through a minimum at $x = 12$. At $x = 10$–12 the observed K_x are only about one-fourth of the values calculated; see Figure 2 of the following paper.[10] As x decreases below ten units, the observed K_x increase rapidly; for $4 \leq x \leq 6$ they exceed predictions of eq 12 from values of $\langle r_x^2\rangle$ calculated according to RIS theory.[3,11] For the tetrameric ring ($x = 4$) of eight atoms, this being the ring of the smallest size that can be formed without bond-angle strain (the bond angles being 110° and ca. 143° at Si and at O, respectively), K_x is about twice the value predicted by eq 12.

This pattern of the cyclization constants within a series of homologues is duplicated, qualitatively, in a number of other series of bifunctional compounds. In some instances the effects are much more pronounced than in the cyclic PDMS homologues. If, in a series of organic aliphatic condensates, the cyclic compound of the minimum size that is strain free comprises $n = 5$ to 7 members, the observed cyclization constant may exceed the value calculated according to eq 12 by an order of magnitude or more, the cyclic compound being the only product of condensation even in absence of a diluent. Usually K_x decreases rapidly with increase in n. The tendency to cyclize often passes through a minimum for x (or for n) approximately twice the optimum size in a series of homologues, as was shown many years ago by Stoll and Rouvé[12] and by Carothers and coworkers.[13] In the vicinity of the minimum, K_x may depart from the value calculated according to eq 12 to an even greater degree[12] than for the PDMS series (see Figure 2 of the following paper[10]). Such observations are widespread, of long-standing, and generally well known. Explanations have been wanting.

The pronounced propensity to form small rings of the favored size finds ready explanation in the analysis of directional requirements, as we have pointed out previously.[2,3] This is a consequence of the fact that fulfillment of the distance requirement $\mathbf{r} \approx \mathbf{0}$ when n approximates the minimum size permitting ring closure without bond angle strain virtually assures that directional requirements are met as well. For a tetrahedrally bonded, five-membered ring the closed conformation for which $\mathbf{r} = \mathbf{0}$ is very nearly planar; it is unique, and free of appreciable bond angle strain. In the case of the homologous six-membered sequence, preference for bond staggering yields $\mathbf{r} \approx \mathbf{0}$ in only two conformations. These are the chair forms in which the bond formed by closure assumes either the g^+ or the g^- conformation. Thus, an acceptable bond angle is a concomitant of closure ($r = 0$) for these small rings. For the tetrahedrally bonded six-membered ring, absence of torsional strain is assured as well, provided that staggered conformations are dominant to the virtual exclusion of all others.

It follows that $\Gamma_0(1)\delta\gamma$ may approach unity for these small rings. Hence, $2\Gamma_0(1)$ conceivably may approach $1/\delta\gamma$. The magnitude of $\delta\gamma$ is difficult to estimate. A value of $2\Gamma_0(1)$ much greater than unity is clearly indicated, however. Simultaneously, $\overline{\Phi}_0$ will exceed unity if, as in the case of the tetrahedral six-membered ring or in the eight-membered PDMS ring, bond staggering prevails. Both factors enhance K_x according to eq 10. On the other hand, such short sequences are decidedly non-Gaussian, and $W(\mathbf{0})$ may be lowered substantially on this account. The enhanced formation of small rings indicates that the former factors outweigh the latter, and this is in accordance with expectation.

Previously, the suggestion has been made that the minimum in $K_x(\text{obsd})/K_x(\text{calcd})$ for rings of intermediate size is a consequence of unfavorable bond directions for closed conformations.[2] In this paper and the two[10,14] that follow we investigate the role of the bond direction factor $2\Gamma_0(1)$ in eq 10, and at the same time examine $W(\mathbf{0})$ and its departure from the Gaussian probability density at $\mathbf{r} = \mathbf{0}$. Rings for which x (or n) exceeds the value where K_x exhibits a minimum are of primary concern. The torsional factor is ignored on the grounds that its effect probably is small for the large rings here considered. Accordingly, we replace eq 10 by

$$K_x = 2W(\mathbf{0})\Gamma_0(1)/\sigma_{cx}N_A \tag{14}$$

The Direction Correlation Factor. Theory

It is expedient to expand the direction correlation distribution $\Gamma_{\mathbf{r}}(\gamma)$ in the Legendre polynomials $P_k(\gamma)$; i.e., we let

$$\Gamma_{\mathbf{r}}(\gamma) = \sum_{k=0}^{\infty} A_{k,\mathbf{r}}P_k(\gamma) \tag{15}$$

Evaluation of the coefficients $A_{k,\mathbf{r}}$ by appeal to the orthogonality of these polynomials in conjunction with the normalization condition

$$\int_{-1}^{1} \Gamma_{\mathbf{r}}(\gamma)\,\mathrm{d}\gamma = 1$$

yields

$$2\Gamma_{\mathbf{r}}(\gamma) = \sum_{k=0}^{\infty} (2k+1)\langle P_k\rangle_{\mathbf{r}} P_k(\gamma) \tag{16}$$

where the $\langle P_k\rangle_{\mathbf{r}}$ are averages of the polynomials over all configurations having the specified value of $\mathbf{r}$, i.e.

$$\langle P_k\rangle_{\mathbf{r}} = \int_{-1}^{1} P_k(\gamma)\Gamma_{\mathbf{r}}(\gamma)\,\mathrm{d}\gamma \tag{17}$$

In terms of the moments

$$\langle \gamma^m\rangle_{\mathbf{r}} = \int_{-1}^{1} \gamma^m \Gamma_{\mathbf{r}}(\gamma)\,\mathrm{d}\gamma$$

the averaged polynomials are

$$\begin{gathered}\langle P_0\rangle_{\mathbf{r}} = 1\\ \langle P_1\rangle_{\mathbf{r}} = \langle\gamma\rangle_{\mathbf{r}}\\ \langle P_2\rangle_{\mathbf{r}} = \tfrac{1}{2}(3\langle\gamma^2\rangle_{\mathbf{r}} - 1)\\ \langle P_3\rangle_{\mathbf{r}} = \tfrac{1}{4}(10\langle\gamma^3\rangle_{\mathbf{r}} - 6\langle\gamma\rangle_{\mathbf{r}})\\ \text{etc.}\end{gathered} \tag{18}$$

In the circumstances of immediate interest, $\mathbf{r} = \mathbf{0}$ and $\gamma = 1$ giving

$$2\Gamma_{\mathbf{0}}(1) = \sum_{k=0}^{\infty} (2k+1)\langle P_k\rangle_{\mathbf{r}=0} \tag{19}$$

If the distribution of directions of bond $n+1$ relative to bond 1 is random, all terms beyond the first (unity) vanish in eq 19. If the distribution function $\Gamma_{\mathbf{0}}(\gamma)$ is linear in γ, only the first two terms in eq 19 are nonzero; if it is quadratic in γ, the first three polynomials suffice; and so forth.

The averaged polynomials defined by eq 17 are given alternatively by

$$\langle P_k\rangle_{\mathbf{r}} = \tilde{Z}_{\mathbf{r}}^{-1} \int_{\mathbf{r}} \cdots \int P_k(\gamma)\exp(-E\{\mathbf{l}\}/kT)\,\mathrm{d}\{\mathbf{l}\}/\mathrm{d}\mathbf{r} \tag{20}$$

where $\{\mathbf{l}\}$ is the set of all skeletal bond vectors 1 to $n+1$, and the integrations include all configuration space $\{\mathbf{l}\}$ in which the chain vector spanning bonds 1 to n conforms to its specified value $\mathbf{r}$. The configuration integral subject to the same condition is

$$\tilde{Z}_{\mathbf{r}} = \int_{\mathbf{r}} \cdots \int \exp(-E\{\mathbf{l}\}/kT)\,\mathrm{d}\{\mathbf{l}\}/\mathrm{d}\mathbf{r} \tag{21}$$

Fourier inversion (see Appendix A) allows $\langle P_k\rangle_{\mathbf{r}}$ to be expressed as a series in powers of $r^2/\langle r^2\rangle$ with coefficients determined by $\langle P_k r^{2p}\rangle$ where $p = 0, 1, 2, \ldots,$ and $\langle\,\rangle$ denotes the average without restriction on $\mathbf{r}$. Specifically for $r = 0$, the result is

$$\langle P_k\rangle_{r=0} = (\tilde{Z}_{r=0}/Z)^{-1}(3/2\pi\langle r^2\rangle)^{3/2}\Big[f_{k;0} - \tfrac{3}{2}f_{k;2} + \left(\frac{3}{2}\right)^2\frac{1}{2!}f_{k;4} - \left(\frac{3}{2}\right)^3\frac{1}{3!}f_{k;6} + \ldots\Big] \tag{22}$$

where

$$\begin{gathered}f_{k;0} = \langle P_k\rangle\\ f_{k;2} = \frac{\langle P_k r^2\rangle}{\langle r^2\rangle} - \langle P_k\rangle\\ f_{k;4} = \frac{\langle P_k r^4\rangle}{\langle r^2\rangle^2} - \frac{10}{3}\frac{\langle P_k r^2\rangle}{\langle r^2\rangle} + \frac{5}{3}\langle P_k\rangle\\ f_{k;6} = \frac{\langle P_k r^6\rangle}{\langle r^2\rangle^3} - 7\frac{\langle P_k r^4\rangle}{\langle r^2\rangle^2} + \frac{35}{3}\frac{\langle P_k r^2\rangle}{\langle r^2\rangle} - \frac{35}{9}\langle P_k\rangle\\ \text{etc.}\end{gathered} \tag{23}$$

In eq 23, $\langle P_k\rangle$. $\langle P_k r^2\rangle$, etc., denote averages over all configurations regardless of $\mathbf{r}$, and Z is the configuration integral likewise without restriction on $\mathbf{r}$. The numerical coefficient of the ith term in $f_{k;2p}$ is given by

$$(2p+1)!/(-6)^{i-1}(i-1)!(2p-2i+3)!$$

The density distribution of vector $\mathbf{r}$ is given by[3,4]

$$W(\mathbf{r}) = \tilde{Z}_{\mathbf{r}}/Z \tag{24}$$

The ratio of partition functions appearing in eq 22 is the density $W(\mathbf{0})$ at $\mathbf{r} = \mathbf{0}$.

In the approximation that $W(\mathbf{r})$ is Gaussian, $\tilde{Z}_{r=0}/Z = W(\mathbf{0}) \approx (3/2\pi\langle r^2\rangle)^{3/2}$. The approximation can be improved,[15] in principle to any desired degree, by replacing $(\tilde{Z}_{r=0}/Z)^{-1}(3/2\pi\langle r^2\rangle)^{3/2}$ in eq 22 by the reciprocal of the Hermite series $\mathcal{H}(\mathbf{r})$ which for $\mathbf{r} = \mathbf{0}$ is

$$\mathcal{H}(0) = 1 + 3\cdot 5g_4 + 3\cdot 5\cdot 7g_6 + \ldots \tag{25}$$

where

$$\begin{gathered}g_4 = -(1/2^3)(1 - 3\langle r^4\rangle/5\langle r^2\rangle^2)\\ g_6 = -(1/2^3\cdot 3!)[3(1 - 3\langle r^4\rangle/5\langle r^2\rangle^2) - (1 - 3^2\langle r^6\rangle/5\cdot 7\cdot\langle r^2\rangle^3)]\\ \text{etc.}\end{gathered} \tag{26}$$

(see ref 3 or 6). Then

$$\langle P_k\rangle_{r=0} = [\mathcal{H}(0)]^{-1}\Big[f_{k;0} - \frac{3}{2}f_{k;2} + \frac{3^2}{2^3}f_{k;4} - \frac{3^2}{2^4}f_{k;6} + \ldots\Big] \tag{27}$$

The quantities $\langle P_k r^{2p}\rangle$ required for the evaluation of the coefficients $f_{k;2s}$ may be estimated in good approximation by resort to Monte Carlo methods[16] using conditional probabilities deduced from a suitable rotational isomeric state scheme for analysis of the configurational statistics.[3] In order to avoid accumulation of errors in the several moments, it is preferable to take the average over the entire polynomial $f_{k;2s}$ defined in eq 23. The sum in eq 22 and 27, truncated at the desired term, can be averaged likewise as a whole. In this way $\langle P_k\rangle_{r=0}$ is obtained directly. The calculation of $2\Gamma_{\mathbf{0}}(1)$ may be carried out similarly.

Alternatively, the quantities $\langle P_k r^{2p}\rangle$ can be evaluated from the moments $\langle\gamma^m r^{2p}\rangle$. where $m = k, k-2$, etc., these moments being combined according to the definitions of the Legendre polynomials, as given in eq 18 but without restriction on $\mathbf{r}$. Thus, for example,

$$\langle P_3 r^{2p}\rangle = \tfrac{1}{4}(10\langle\gamma^3 r^{2p}\rangle - 6\langle\gamma r^{2p}\rangle)$$

The moments $\langle\gamma^m r^{2p}\rangle$ may be computed by the exact matrix multiplication methods developed for implementation of the RIS scheme (see Appendix to the following paper[10]). The generator matrices required for these calculations become excessively large for $p > 2$, however.

Results of Exploratory Calculations and Discussion

The simplest model chain to be considered consists of a succession of identical bonds joined at identical angles with rotation about each bond represented by three states of equal

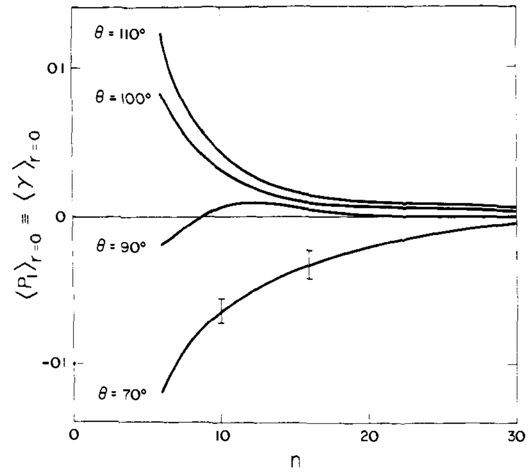

Figure 2. Averaged Legendre polynomials of the first order, $\langle P_1\rangle_{r=0}$, for chains of identical bonds joined at identical angles θ, with equally weighted, neighbor-independent rotational states at torsional angles 0°,±120°. Calculations were carried out according to eq 27 truncated at $f_{1;6}$ and with $\mathcal{H}(0) = 1$ using Monte Carlo methods as described in the text. Bond angle supplements θ are indicated with each curve.

weight at torsional angles $\varphi = 0$, 120, and $-120°$ measured from trans. The repeat unit spans one skeletal bond and all units are identical. Rotations about the various bonds are taken to be mutually independent; i.e., for this model each bond rotational state is accorded a statistical weight of unity without regard for the states of neighboring bonds. It follows that $\langle \sin \varphi\rangle = \langle \cos \varphi\rangle = 0$, and hence that $\langle r^2\rangle$ and $\langle P_1\rangle \equiv \langle\gamma\rangle$ (without restriction on **r**) coincide with values for the corresponding chain with free rotation. The correspondence does not hold for higher moments, however.

Conformations of model chains comprising n bonds were assigned on the basis of sets of n computer-generated random numbers, the state of each bond being identified with an equal interval of the numerical range in keeping with the stipulation above. The quantities $f_{1;0} \ldots f_{1;6}$ were calculated according to eq 23 for each chain thus generated. It was expedient to compute the second moment $\langle r^2\rangle$ required by these polynomials using exact algebraic methods[3,6] instead of relying on Monte Carlo chains for this purpose. Substitution of the $f_{1;2s}$ thus evaluated in eq 27 yielded P_1 at $\mathbf{r} = \mathbf{0}$ for the given Monte Carlo chain. Averages for 8000 Monte Carlo chains at every integral value of n in the range 6–30 were identified with the corresponding configurational average $\langle P_1\rangle_{r=0} \equiv \langle\gamma\rangle_{r=0}$, the series according to eq 27 being truncated at the term in $f_{1;6}$; the Hermite series was replaced by unity, as for a Gaussian distribution $W(\mathbf{r})$. Results of these calculations are summarized in Figure 2 where $\langle P_1\rangle_{r=0}$ is plotted against the number n of bonds in the chain. The respective curves represent data for the several values of the valence angle supplement θ indicated with each curve. For $\theta = 70°$, the probable error for an individual point is indicated. Error bars are virtually the same for other values of θ.

The trend of $\langle P_1\rangle_{r=0} \equiv \langle\gamma\rangle_{r=0}$ toward negative values of increasing magnitude with decrease in n illustrated by the $\theta = 70°$ curve in Figure 2 appears to be general for $\theta < 90°$ on the basis of numerous computations for various model chains and for real ones as represented in the RIS scheme. Some of these computations are presented below (see Figure 5) and in the following papers.[10,14] The implication that $2\Gamma_0(1)$ falls below unity for chains of this class is confirmed by calculations of higher averaged Legendre polynomials, $\langle P_k\rangle_{r=0}$. Their contributions to $2\Gamma_0(1)$ appear to be considerably smaller than that of $\langle P_1\rangle_{r=0} = \langle\gamma\rangle_{r=0}$ in all cases investigated with $\theta < 90°$, very small values of n excepted. They vanish rapidly with n, however. Thus, an adverse directional correlation appears to be general for realistic bond angles.

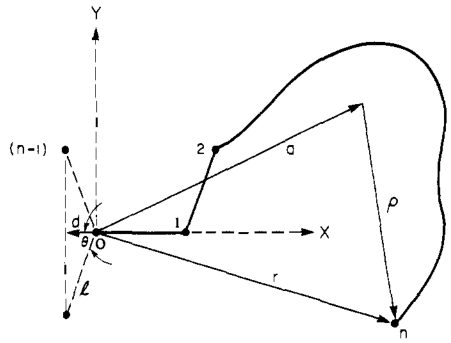

Figure 3. Schematic representation of a chain of n atoms. See text for details.

For $\theta > 90°$, the trend of $\langle\gamma\rangle_{r=0}$ is positive with decreasing n; see Figure 2. This observation is believed to be general also, although it is supported by fewer computations.

The behavior of $\langle P_1\rangle_{r=0} \equiv \langle\gamma\rangle_{r=0}$ with n briefly described and illustrated in Figure 2 led us to the following hypothesis, best explained by reference to Figure 3. The fixed bond angle θ imposes correlations between successive bonds. In real chains these are enhanced and perpetuated over greater ranges by hindrances to rotation and usually by strong neighbor dependences of these hindrances also. If one chooses an internal frame of reference affixed to the first two bonds of the chain, then the distribution of chain vector **r** is found to be highly asymmetric for a chain of finite length ($n < \sim 50$).[16-18] This asymmetry is manifested most notably in the *persistence vector*[6,19] **a** defined as the average of **r** over all configurations of the chain, averaging being performed in the internal reference frame defined by bonds 1 and 2; see Figure 3. For chains with $\theta \approx 70°$, the projection of **a** on the direction of the first bond (the X axis in Figure 1) is positive and may be fairly large; usually it is several times the bond length.[16-18] To meet the distance requirement for ring closure, a configuration must, in a manner of speaking, overcome its natural tendency to proceed toward the neighborhood of the terminus of **a**. An immediate consequence is a marked diminution in the density $W(\mathbf{0})$ of chain vectors with $\mathbf{r} \approx \mathbf{0}$. This density may fall substantially below predictions for a spherical Gaussian distribution centered at the zeroth atom. The equilibrium constant K_x may be lowered appreciably on this account.

With reference to fulfillment of the direction condition, we observe that most of those configurations meeting the condition $\mathbf{r}_n \equiv \mathbf{r} = \mathbf{0}$ will approach the origin from the direction of **a**. Stated more exactly, for those configurations for which $\mathbf{r} \approx \mathbf{0}$ the angle θ between the positive directions of bond vectors $\mathbf{l}_n$ and **a** will more frequently be obtuse than acute. The projection of **a** on $\mathbf{l}_1$ being positive, the direction of bond n relative to bond 1 when $\mathbf{r} \approx \mathbf{0}$ tends therefore to be unfavorable for ring closure. Thus, the asymmetry of the distribution of configurations about atom 0 disfavors the rearward approach required for ring closure at an acceptable bond angle.

We thus arrive at a qualitative explanation for adverse directional correlations when $\theta < 90°$. In order to develop this hypothesis in quantitative terms, we observe that atom $n - 1$ must occur on the perimeter of the base of a cone with axis collinear with the X axis (see Figure 3) and with generators of the required length and direction for ring closure. The height of the cone is $d = l \cos \theta$. Thus, the chain vector $\mathbf{r}_{n-1}$ is required to have a component $-d$ along the X axis.

Ignoring the difference between the distributions W_{n-1} and W_n for bonds $n - 1$ and n, respectively, we consider the distribution $W_a(\rho)$ of vectors $\rho = \mathbf{r} - \mathbf{a}$ for the chain of n bonds about the terminus of **a**.[16,20] We take $W_a(-\mathbf{a} - \mathbf{d})$ as an ap-

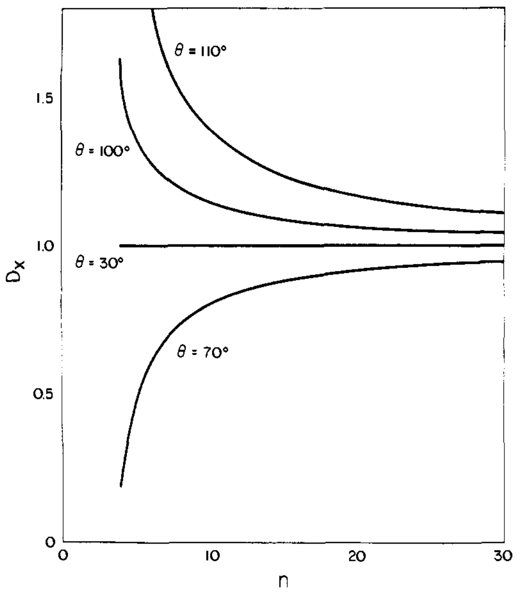

Figure 4. The approximate directional correlation index D_x according to eq 29 for the simple chains represented in Figure 2.

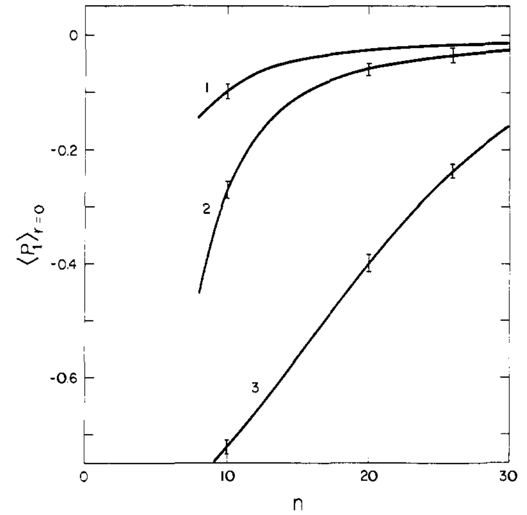

Figure 5. Averaged Legendre polynomials of the first order, with $r = 0$, for three model chains with rotational states at 0 and ±120°. (1) Independent and equally weighted conformations, all angles $\theta = 70°$. (2) Independent and equally weighted conformations with alternating angles, $\theta = 70$ and 40°. (3) Chain with $\theta = 70°$ and nonequivalent, interdependent rotational states as specified by the statistical weight parameters $\sigma = 0.5$ and $\omega = 0$, see text. Calculations were carried out according to eq 27 truncated at $f_{1;6}$ and eq 25 truncated at g_4.

proximation to the required mean density over the perimeter. In order to abstract the angular factor from the distance requirement, we compare this density with its counterpart $W_a(-\mathbf{a} + \mathbf{d})$ on the opposite side of the origin. On this basis, the ratio

$$D_x = W_a(-\mathbf{a} - \mathbf{d})/W_a(-\mathbf{a} + \mathbf{d}) \qquad (28)$$

should provide an approximate measure of the directional factor for the chain with x units or n bonds.

For our purposes it will suffice to approximate $W_a(\rho)$ by the three-dimensional Gaussian distribution

$$W_a(\rho) = (\mathrm{Const}) \exp[-(1/2)\rho^{\mathrm{T}}\langle\rho\rho^{\mathrm{T}}\rangle^{-1}\rho] \qquad (29)$$

where ρ^{T} is the transpose of ρ and $\langle\rho\rho^{\mathrm{T}}\rangle$ is the second moment tensor averaged over all configurations of the chain.[6,20] (The distinction between this anisotropic Gaussian distribution about the terminus of $\mathbf{a}$ and the conventional *spherical* Gaussian about atom 0 is important.) Substitution in eq 28 gives

$$D_x = \exp(-2\mathbf{a}^{\mathrm{T}}\langle\rho\rho^{\mathrm{T}}\rangle^{-1}\mathbf{d}) \qquad (30)$$

The persistence vector $\mathbf{a}$ and the second moment tensor $\langle\rho\rho^{\mathrm{T}}\rangle$ averaged in the same reference frame (see above) are readily calculated by methods given previously.[6,17,21]

Results of calculations of D_x carried out in this manner for the model chains treated above are shown in Figure 4. The anticipated adverse ($D_x < 1$) and favorable ($D_x > 1$) correlations for $\theta < 90°$ and for $\theta > 90°$, respectively, are confirmed.

In Figure 5 we show values of $\langle P_1\rangle_{r=0} \equiv \langle\gamma\rangle_{r=0}$ calculated for three model chains: (1) the threefold, equally weighted chain treated above, with $\theta = 70°$; (2) the chain with alternating angle supplements $\theta = 70$ and 40° (resembling PDMS in this respect), likewise with three, equally weighted states for each bond; and (3) the simple chain with $\theta = 70°$ and gauche (±120°) states weighted by the factor $\sigma = 0.5$ relative to a weight of unity for trans, the $g^{\pm}g^{\mp}$ combinations being excluded ($\omega = 0$; see ref 3). The lattermost chain resembles polymethylene. For models 1 and 2, 15 000 Monte Carlo chains were generated with the rotational state of each bond assigned an equal range of random numbers. For model 3, 25 000 chains were generated, the random number ranges being apportioned according to the conditional probabilities calculated by RIS methods described previously.[3,16] The averaged quantities $\langle P_1\rangle_{r=0}$ were calculated as described above using eq 27 with $\mathcal{H}(0)$ calculated according to eq 25 truncated at g_4; see eq 26. The probable error for an individual point is indicated at several values of n in Figure 5.

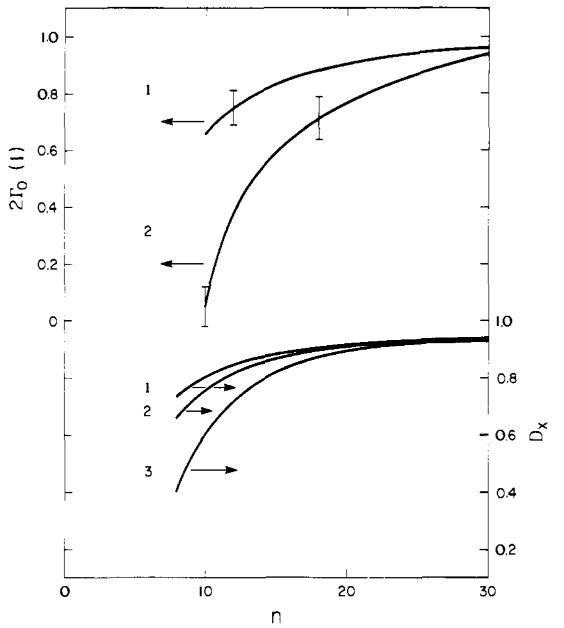

Figure 6. The directional correlation index D_x and correlation factor $2\Gamma_0(1)$ for the model chains represented in Figure 5. The latter quantities were calculated according to eq 19 truncated at $k = 5$ from moments taken as averages from sets of 15 000 Monte Carlo chains.

Reduction of θ to 40° at alternate bonds reduces $\langle P_1\rangle_{r=0} \equiv \langle\gamma\rangle_{r=0}$ as expected; compare curves 1 and 2 in Figure 5. The reduced incidence of gauche states and the neighbor correlations between states of neighboring bonds, implicit in suppression of $g^{\pm}g^{\mp}$ pairs, lowers $\langle\gamma\rangle_{r=0}$ markedly (curve 3) relative to its value for the equally weighted chain (curve 1) having the same number of bonds.

In the upper part of Figure 6 we show $2\Gamma_0(1)$ calculated according to eq 19 for model chains 1 and 2. Averaged Legendre polynomials $\langle P_k \rangle_{r=0}$ were evaluated up to and including that for $k = 5$. The moments $\langle P_2 \rangle_{r=0} \ldots \langle P_5 \rangle_{r=0}$ that are required for this purpose, in addition to $\langle P_1 \rangle_{r=0}$ shown in Figure 5, were evaluated in the manner described above, the series in eq 27 being truncated at $f_{k;6}$ in each instance. The implications of the first moments $\langle P_1 \rangle_{r=0} \equiv \langle \gamma \rangle_{r=0}$ and their dependence on n as shown in Figure 5 are confirmed in Figure 6. Results of similar calculations for chains of kind (3) are not shown since $f_{k;6}$ is large for $k > 2$, being on the order of 0.5; hence, truncation of eq 27 at this term is premature. These calculations indicated however that $2\Gamma_0(1)$ for chain (3) is substantially lower than for the other two model chains.

Also shown in Figure 6 are values of D_x calculated as set forth above. The correspondence between this index and $2\Gamma_0(1)$ is not quantitative. Nevertheless, it supports the hypothesis offered above in explanation of the consistently unfavorable correlations between directions of the terminal bonds at ring closure ($r \approx 0$) when $\theta < 90°$.

Applications of the theory presented in this paper are demonstrated in the two articles[10,14] that follow. There we treat cyclization in each of two series of polymer homologues, namely, PDMS[10] and poly(aminocaproamide).[14] Convergences of the series in eq 27 and 19 are examined in greater detail in these two papers.

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Appendix

Fourier transformation of eq 20 gives

$$F_k(\mathbf{q}) = \int \tilde{Z}_{\mathbf{r}} \langle P_k \rangle_{\mathbf{r}} \exp(i\mathbf{q} \cdot \mathbf{r})\, \mathrm{d}\mathbf{r} \tag{A1}$$

or, from eq 24

$$F_k(\mathbf{q}) = Z \int W(\mathbf{r}) \langle P_k \rangle_{\mathbf{r}} \exp(i\mathbf{q} \cdot \mathbf{r})\, \mathrm{d}\mathbf{r} \tag{A2}$$

Let $\mathbf{r}$ be specified in a reference frame external to the chain. Then $W(\mathbf{r})$ and $\langle P_k \rangle_{\mathbf{r}}$, being averages over all bond vectors $\mathbf{l}$, depend only on the magnitude r of vector $\mathbf{r}$, and eq A2 reduces to

$$F_k(\mathbf{q}) = Z \int_0^\infty W(r) \langle P_k \rangle_r (qr)^{-1} \sin(qr) 4\pi r^2\, \mathrm{d}r$$

Series expansion of sin (qr) and integration gives

$$F_k(\mathbf{q}) = Z \left[\langle P_k \rangle - \frac{1}{3!} \langle P_k r^2 \rangle q^2 + \frac{1}{5!} \langle P_k r^4 \rangle q^4 - \ldots \right] \tag{A3}$$

Division of this equation by $\exp(q^2 \langle r^2 \rangle / 6)$ and multiplication by the series expansion of this exponential yields

$$F_k(\mathbf{q}) = Z \exp(-q^2 \langle r^2 \rangle / 6) \times \left\{ f_{k;0} - \frac{\langle r^2 \rangle}{3!} f_{k;2} q^2 + \frac{\langle r^2 \rangle^2}{5!} f_{k;4} q^4 - \ldots \right\} \tag{A4}$$

where $f_{k;0}, f_{k;2}$, etc., are defined by eq 23.

Fourier inversion of eq A4 gives

$$\tilde{Z}_{\mathbf{r}} \langle P_k \rangle_{\mathbf{r}} = (2\pi)^{-3} \int F_k(\mathbf{q}) \exp(-i\mathbf{q} \cdot \mathbf{r})\, \mathrm{d}\mathbf{q} = (2\pi^2)^{-1} \int_0^\infty F_k(\mathbf{q}) (qr)^{-1} \sin(qr) q^2\, \mathrm{d}q$$

Substitution from eq A4, series expansion of sin (qr), and integration in series leads to the result

$$\begin{aligned} \langle P_k \rangle_{\mathbf{r}} = (\tilde{Z}_{\mathbf{r}}/Z)^{-1} (3/2\pi \langle r^2 \rangle)^{3/2} \Bigg\{ \Bigg[& f_{k;0} - \frac{3}{2} f_{k;2} + \frac{3^2}{2^2 \cdot 2!} f_{k;4} - \frac{3^3}{2^3 \cdot 3!} f_{k;6} + \ldots \Bigg] - \frac{3}{2} \Bigg[f_{k;0} - \frac{5}{2} f_{k;2} \\ & + \frac{7 \cdot 3}{2^3} f_{k;4} - \frac{9 \cdot 3}{2^4} f_{k;6} + \ldots \Bigg] \frac{r^2}{\langle r^2 \rangle} + \frac{3^2}{2^2 \cdot 2!} \Bigg[f_{k;0} \\ & - \frac{7}{2} f_{k;2} + \frac{9 \cdot 7 \cdot 3}{2^3 \cdot 5} f_{k;4} - \ldots \Bigg] \frac{r^4}{\langle r^2 \rangle^2} - \ldots \Bigg\} \end{aligned} \tag{A5}$$

which for $r = 0$ reduces to eq 22.

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