Statistical Mechanics of Random-Flight Chains. IV. Size and Shape Parameters of Cyclic, Star-like, and Comb-like Chains[1]

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ABSTRACT: As an extension of our previous work, the moments of the distribution for a linear combination Q of random orthogonal components of the square radius S^2 and the moments of the shape distribution are calculated for three types of nonlinear macromolecules: rings, irregular star molecules, and regular comb molecules. The molecular structure has a marked effect upon the shape of the macromolecule. The introduction of either ring closures or branch points into a linear molecule decreases noticeably its originally high asymmetry. Thus the shape parameter seems to be a useful second variable, in addition to the mean-square radius $\langle S^2 \rangle$, for the discussion of dilute solution properties of linear and nonlinear flexible macromolecules.

In our recent papers[2a] an attempt has been made to characterize the instantaneous state of a particular linear random-flight chain molecule by more parameters than just its size. For this purpose, we used the three principal orthogonal components $0 \leq L_1^2 \leq L_2^2 \leq L_3^2$ of its square radius S^2 obtained by decomposing S^2 along the principal axes of inertia of the chain ($L_1^2 + L_2^2 + L_3^2 = S^2$). The principal components L_k^2 determine the size and the shape of an ellipsoid which is equivalent, as regards its inertial properties, to our chain and they can be thus considered as the shape parameters of the chain as well. With time, the flexible molecule can assume many different conformations and therefore its shape must be described in terms of a three-dimensional shape distribution function $W(L_1^2,L_2^2,L_3^2)$ or, more conveniently, in terms of statistical moments $\langle L_1^{2u}L_2^{2v}L_3^{2w} \rangle$ around zero of the shape distribution, where u, v and w are nonnegative integers. The results showed that in average the shape of a linear chain is highly asymmetrical, with the ratios of the mean square principal components $\langle L_3^2 \rangle : \langle L_2^2 \rangle : \langle L_1^2 \rangle \simeq 12:2.7:1$. Since there is some indication[2b] that the shape factor may be important for the experimentally observable quantities (*e.g.*, the second virial coefficient), it is worthy to gain some information on the shape of nonlinear macromolecules as well. Intuitively, it is expected that with an increasing number of restrictions imposed on the chain structure, such as branch points and/or ring closures, the shape of the macromolecule will become more symmetrical. The shape factor might help to explain the differences between the dilute solution properties of linear and nonlinear molecules which have customarily been discussed in terms of the parameter g so far.[3] It has long been recognized[4] and recently reminded again[5] that this single parameter g, the ratio of the mean-square radii of nonlinear and linear macromolecules, cannot be expected to account for all of the observed effects.

In this paper we present results of some studies of the shape characteristics of ring, star and comb macromolecules, as compared to our recent data on linear chains. Information on the shape distribution is obtained by both analytical and numerical methods. The detailed description of these methods can be found in our previous work.[2a]

(1) Part of this material was presented at the International Symposium on Macromolecules, Helsinki, July 2-7, 1972. For part III, see K. Šolc, *Macromolecules*, **5**, 705 (1972).
(2) (a) K. Šolc and W. H. Stockmayer, *J. Chem. Phys.*, **54**, 2756 (1971); *ibid.*, **55**, 335 (1971). (b) W. Gobush, K. Šolc, and W. H. Stockmayer, to be published.
(3) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).
(4) W. H. Stockmayer and M. Fixman, *Ann. N. Y. Acad. Sci.*, **57**, 334 (1953).
(5) E. F. Casassa and G. C. Berry, *Polym. Prepr. Amer. Chem. Soc., Div. Polym. Chem.*, **12**, No. 2, 19 (1971).

Analytical Method

It is difficult to find the information on the *principal* component distribution, $W(L_1^2,L_2^2,L_3^2)$, of random-flight chains directly. We chose rather an indirect way, with the advantage of obtaining simultaneously data on the distribution of *random* orthogonal components X_{kk} of the square radius ($X_{11} + X_{22} + X_{33} = S^2$).[6] Using the generating function method described by Coriell and Jackson,[7] it is relatively easy to calculate the moments $\langle Q^n \rangle$ for chains with various structures of the quantity Q defined as a linear combination of random orthogonal components X_{kk}

$$Q \equiv \sum_{k=1}^{3} C_k X_{kk} \tag{1}$$

On the other hand, it is also possible to derive relations for the moments $\langle q^n \rangle$ of the analogously defined quantity q for an ensemble of equivalent ellipsoids with some principal axes distribution $W^*(L_1^2,L_2^2,L_3^2)$. The moments $\langle q^n \rangle$ for such ensemble can be expressed[2a] in terms of principal component moments $\langle L_1^{2u}L_2^{2v}L_3^{2w} \rangle^*$ of the ellipsoid distribution $W^*(L_1^2,L_2^2,L_3^2)$. Obviously, if the moments $\langle Q^n \rangle$ were equal to $\langle q^n \rangle$ for all n and all possible combinations of C_k coefficients of eq 1, then the distribution $W^*(L_1^2,L_2^2,L_3^2)$ would describe exactly the shape distribution of random-flight chains. Thus, by putting $\langle q^n \rangle$ equal to $\langle Q^n \rangle$ and solving the resulting sets of linear equations, the average moments of the principal component distribution of the random-flight chains can be found. The method used for linear chains has now been generalized to flexible molecules of any definite topological structure and can be applied, provided we are able to solve the resulting determinant.

The first step is to formulate the probability of a specified conformation of the chain. Let the molecule have N beads, each of unit mass, and for convenience fix the zeroth bead at the origin of an orthogonal coordinate system. The coordinates of the remaining $N - 1$ beads are denoted by $\mathbf{x}^{(m)}$, $m = 1, 2, \ldots, N - 1$. Then, with neglect of both short- and long-range interactions and with the assumption of a gaussian bond-length distribution

$$p(\mathbf{x}^{(m)} - \mathbf{x}^{(m-1)}) = (2\pi\sigma^2/3)^{-3/2} \exp[-(3/2\sigma^2)(\mathbf{x}^{(m)} - \mathbf{x}^{(m-1)})^2] \tag{2}$$

(6) As opposed to the principal components L_k^2, the random components X_{kk} of the mean-square radius are obtained by decomposing S^2 along the orthogonal coordinate axes x_k which bear no special relation to the principal axes of the chain; the mutual orientation of the two sets of axes is random. The values of X_{11}, X_{22}, and X_{33} vary with changing orientation of the chain even if its shape (characterized by L_k^2) is being kept constant.
(7) S. R. Coriell and J. L. Jackson, *J. Math. Phys.*, **8**, 1276 (1967).

the conformation probability distribution function can be written as

$$P(\mathbf{x}^{(1)},\mathbf{x}^{(2)},\ldots,^{(N-1)}) = \text{const}(2\pi\sigma^2/3)^{-3(N-1)/2}\exp[-(3/\sigma^2)\sum_{k=1}^{3}\mathbf{y}_k{}^T\mathbf{V}\mathbf{y}_k] \quad (3)$$

$-\frac{1}{2}$ to the (n,m) and (m,n) elements of $\mathbf{V}$. The size of the symmetrical matrix $\mathbf{V}$ is $(N-1)\times(N-1)$ since only $N-1$ freely moving beads have to be considered. Obviously one topological structure can be represented by many different matrices, depending upon the way of numbering the beads, and it is only the matter of convenience which way is chosen.

The symmetrical tensor of random orthogonal components X_{kl} of the square radius, referred to our coordinate system, is given by

Here σ^2 is the mean square bond length and $\mathbf{y}_k$ is the $(N-1)$-dimensional vector of the kth coordinates of the beads, $\mathbf{y}_k \equiv \mathbf{x}_k{}^{(1)}, \mathbf{x}_k{}^{(2)}, \ldots, \mathbf{x}_k{}^{(N-1)}$. The normalization constant can be determined by integration over all coordinates: *e.g.*, for chains without any rings, const = 1, for chains containing one ring of N_r bonds, const = $N_r{}^{3/2}$, etc. The matrix $\mathbf{V}$ can be set up easily for any definite structure without painful consideration of the individual bond probabilities p of eq 2 by observing the following rules. Designate the $N-1$ freely moving beads of the macromolecule by integers from 1 to $N-1$, preferably in a way which results in a convenient form of the matrix $\mathbf{V}$. Then the matrix $\mathbf{V}$ is made up of two kinds of contributions. (1) Each bond attached to the nth bead contributes $\frac{1}{2}$ to the (n,n) element in the main diagonal of $\mathbf{V}$ (*e.g.*, an end bead is represented by $\frac{1}{2}$, beads in the linear part of the chain by 1 and n-functional branch points by $n/2$). (2) A bond connecting the nth and the mth beads contributes

$$X_{kl} = N^{-1}\sum_m[(\mathbf{x}_k{}^{(m)} - N^{-1}\sum_j \mathbf{x}_k{}^{(j)})\times(\mathbf{x}_l{}^{(m)} - N^{-1}\sum_j \mathbf{x}_l{}^{(j)})] = N^{-1}\mathbf{y}_k{}^T\mathbf{G}\mathbf{y}_l \quad (4)$$

where $k,l = 1, 2, 3$ and $G_{ij} = \delta_{ij} - N^{-1}$.

Now the distribution function $P(Q)$ of the linear combination of random orthogonal components of S^2 for a particular type of chain can be calculated from eq 1, 3, and 4 by means of the Dirac δ function, $\delta(x)$, as an integral over all bead coordinates $\mathbf{x}^{(m)}$ (or $\mathbf{y}_k$)

$$P(Q) = \text{const}(2\pi\sigma^2/3)^{-3(N-1)/2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp[-(3/\sigma^2)\sum_k \mathbf{y}_k{}^T\mathbf{V}\mathbf{y}_k]\times\delta(Q - \sum_k C_k X_{kk})\prod_k d\mathbf{y}_k \quad (5)$$

After introducing the Fourier representation of the δ function, the expression can be partially integrated with the result

$$P(Q) = \text{const}(2\pi)^{-1}2^{-3(N-1)/2}\int_{-\infty}^{\infty}\exp(i\lambda Q)\mathrm{d}\lambda\prod_k|A_k|^{-1/2} \quad (6)$$

where

$$\mathbf{A}_k = \mathbf{V} + iC_k\lambda'\mathbf{G} \quad (6a)$$

and λ' is the reduced integration variable, $\lambda' = \lambda\sigma^2/3N$. The final integration over λ has usually to be carried out numerically.[7,8] Only for some specially defined Q's [such that $C_1 = C_2$ and sign$(C_3) \neq$ sign(C_1)] the analytical integration can be performed in the complex plane and the distribution function $P(Q)$ expressed as a sum of $N-1$ terms.[2a] Thus, for instance, the distribution of the sum of two random orthogonal components, $X_{11} + X_{22}$, is available analytically for all topological structures of the chain. There is only one exception to this general rule we are aware of: for rings with odd number of bonds, a simple analytical integration in the complex plane is always possible and the distribution function $P(Q)$ is accessible regardless of the choice of coefficients C_k.[9]

(8) H. Fujita and T. Norisuye, *J. Chem. Phys.*, **52**, 1115 (1970).

Table I
Relative Deviation of the Reduced Mean-Square Radius from the Limiting Value for $N\to\infty$, $\Delta \equiv (\langle S^2\rangle_{r,N} - \langle S^2\rangle_{r,\infty})/\langle S^2\rangle_{r,\infty}$, as the Function of the Chain Length N for a Linear Chain ($f = 1$) and for Stars with Four ($f = 4$) and Eight ($f = 8$) Branches

	Δ in %		
$N-1$	$f=1$	$f=4$	$f=8$
24	−0.160	6.66	21.5
40	−0.059	4.19	13.5
80	−0.015	2.17	6.94
160	−0.004	1.10	3.52
240	−0.002	0.74	2.36

For the calculation of shape parameters rather the moments $\langle Q^n\rangle$ than the distribution $P(Q)$ itself are needed. They are obtained by differentiation of the characteristic function $K(\lambda)$ of the distribution $P(Q)$.[10] For our purpose, it is convenient to decompose the characteristic function into a product, $K(\lambda) = K_1(\lambda)K_2(\lambda)K_3(\lambda)$, where from eq 6 we have

$$K_k(\lambda) = \text{const}^{1/3}2^{-(N-1)/2}|A_k|^{-1/2} \quad (7)$$

Denoting the reduced mth derivative of $K_k(\lambda)$ at $\lambda = 0$ by $K^{(m)}$ (which is independent of the subscript k)

$$K^{(m)} = (3N^2)^{-m}\left.\frac{\partial^m K_k}{\partial(i\lambda' C_k)^m}\right|_{\lambda=0} \quad (8)$$

we can write the first three reduced moments of $P(Q)$ distribution in terms of $K^{(m)}$ as

$$\begin{aligned}\langle Q\rangle_r &= -3\langle C\rangle K^{(1)}\\ \langle Q^2\rangle_r &= 3[\langle C^2\rangle K^{(2)} + 2\langle CC\rangle(K^{(1)})^2]\\ \langle Q^3\rangle_r &= -3[\langle C^3\rangle K^{(3)} + 6\langle C^2C\rangle K^{(1)}K^{(2)} + 2\langle CCC\rangle(K^{(1)})^3]\end{aligned} \quad (9)$$

where the reduced moments are defined as $\langle Q^n\rangle_r \equiv \langle Q^n\rangle(N\sigma^2)^{-n}$ and the averages of the C coefficients are

$$\langle C^uC^vC^w\rangle = (1/6)(\langle C_1{}^uC_2{}^vC_3{}^w\rangle + \langle C_1{}^uC_3{}^vC_2{}^w\rangle + \langle C_2{}^uC_1{}^vC_3{}^w\rangle + \langle C_2{}^uC_3{}^vC_1{}^w\rangle + \langle C_3{}^uC_1{}^vC_2{}^w\rangle + \langle C_3{}^uC_2{}^vC_1{}^w\rangle) \quad (10)$$

We note that due to the random orientation of the macromolecules with respect to the coordinate axes, the moments $\langle Q^n\rangle_r$ depend only on the averages $\langle C^uC^vC^w\rangle$ rather than on the individual products of the constants C_k.

The derivation of relations between the average moments of the *principal* component distribution $W(L_1{}^2,L_2{}^2,L_3{}^2)$ for the chain macromolecules and the derivatives of the characteristic function $K^{(m)}$ follows closely the way outlined previously[2a] and does not need to be reproduced here in detail. Equation 25 of ref 2a gives the nth moment $\langle q^n\rangle$ of the $P(q)$ distribution for an ensemble of ellipsoids, in terms of the principal component moments

(9) K. Šolc, *Macromolecules*, **5**, 705 (1972).

(10) H. Cramér, "Mathematical Methods of Statistics," Princeton Univ. Press, Princeton, N. J., 1958, Chapter 11.

$\langle L_1^{2u}L_2^{2v}L_3^{2w}\rangle$ and of the coefficients C_k defining the quantity q analogously to eq 1. If the ensemble is to represent correctly the shape distribution of random-flight chains, $\langle q^n\rangle$ has to be equal to $\langle Q^n\rangle$ regardless of the particular choice of the coefficients C_k. Thus, each term of eq 9 for $\langle Q^n\rangle$ has to be equal to the corresponding term in the rearranged eq 25, ref 2a, for $\langle q^n\rangle$. In this way, a set of n linear equations is obtained for each n relating the nth order derivatives of the characteristic function to the n different average moments of the nth order of the principal component distribution. By solving the sets of equations up to $n = 3$, the following relations for the average principal component moments were obtained

$$\begin{aligned}
\langle L^2\rangle_r &= -K^{(1)}\\
\langle L^4\rangle_r &= 2K^{(2)} - (K^{(1)})^2\\
\langle L^2L^2\rangle_r &= {}^1/_2[3(K^{(1)})^2 - K^{(2)}]\\
\langle L^6\rangle_r &= {}^1/_4[9K^{(1)}K^{(2)} - 11K^{(3)} - 2(K^{(1)})^3]\\
\langle L^4L^2\rangle_r &= {}^1/_8[3K^{(3)} + 6(K^{(1)})^3 - 17K^{(1)}K^{(2)}]\\
\langle L^2L^2L^2\rangle_r &= {}^1/_4[9K^{(1)}K^{(2)} - K^{(3)} - 12(K^{(1)})^3]
\end{aligned} \tag{11}$$

The average moments $\langle L^{2u}L^{2v}L^{2w}\rangle$ are defined by analogy to the average coefficients $\langle C^uC^vC^w\rangle$ (eq 10), *e.g.*, $\langle L^2L^2\rangle = 3^{-1}(\langle L_1^2L_2^2\rangle + \langle L_1^2L_3^2\rangle + \langle L_2^2L_3^2\rangle)$, etc., and their reduction is identical with that of $\langle Q^n\rangle$ moments (eq 9).

The problem of calculating the moments $\langle Q^n\rangle$ and $\langle L^{2u}L^{2v}L^{2w}\rangle$ for chain molecules of any definite topological structure has thus been reduced to solving the determinant of the matrix **A** (eq 6a). Additional operations require only the differentiation (eq 7 and 8) and substitution of the results in eq 9 and 11, respectively. The determinants for rings, stars and combs are solved in the Appendix. In the following we give a brief account of our results. For finite N, the results are given in terms of the derivatives of the characteristic function $K^{(m)}$, and any of the specific relations for the moments $\langle Q^n\rangle$ and $\langle L^{2u}L^{2v}L^{2w}\rangle$ can be arrived at easily by using eq 9 and 11. Only in some special cases the explicit relations are given and discussed. For $C_1 = C_2 = C_3 = 1$ the relations for the first moment $\langle Q\rangle$ yield the mean-square radius $\langle S^2\rangle$ as the function of the chain length N. In the limit for $N \to \infty$, these results reduce to the well known relations which have been obtained earlier by different methods.[3,11-14]

Rings

The derivatives of the characteristic function for rings are obtained from eq 7, 8, and A13

$$\begin{aligned}
6^2K^{(1)} &= -(1 - N^{-2})\\
6^3K^{(2)} &= (1/30)(1 - N^{-2})[10(1 - N^{-2}) - 3(1 - 9N^{-2})]\\
6^4K^{(3)} &= -(1/420)(1 - N^{-2})[70(1 - N^{-2})^2 - 42(1 - N^{-2})(1 - 9N^{-2}) + 3(1 - 9N^{-2})(1 - 25N^{-2})]
\end{aligned} \tag{12}$$

Using now eq 9, we have, *e.g.*, the following relations for the moments of the square radius distribution

$$\begin{aligned}
\langle S^2\rangle_r &= (1/12)(1 - N^{-2})\\
\langle S^4\rangle_r &= (1/2160)(17 - 10N^{-2} - 7N^{-4})\\
\langle S^6\rangle_r &= (1/544320)(457 + 357N^{-2} - 357N^{-4} - 457N^{-6})
\end{aligned} \tag{13}$$

Comparing eq 13 with the results for linear chains,[2a,7] we note that the well-known relation $\langle S^2\rangle_{\text{ring},N} = ({}^1/_2) \times \langle S^2\rangle_{\text{linear},N}$, derived for large N by Kramers[11] and by Zimm and Stockmayer,[3] holds exactly for any length of the chain. Also in the limit for $N \to \infty$, the variance of the square radius distribution, $\langle S^4\rangle - \langle S^2\rangle^2$, for a ring chain is just ${}^1/_8$th of the variance for a linear chain; hence the S^2 distribution for cycles is much narrower than for linear chains.[9] The shape of ring molecules is less asymmetrical than the shape of linear chains, as follows from comparison of the average principal component moments for both types of chains

$$\begin{aligned}
&\text{Rings, } N \longrightarrow \infty\\
&\qquad \langle L^4\rangle:\langle L^2L^2\rangle = 9:4\\
&\qquad \langle L^6\rangle:\langle L^4L^2\rangle:\langle L^2L^2L^2\rangle = 163:43:18\\
&\text{Linear chains, } N \longrightarrow \infty \text{ [2a]}\\
&\qquad \langle L^4\rangle:\langle L^2L^2\rangle = 13:3\\
&\qquad \langle L^6\rangle:\langle L^4L^2\rangle:\langle L^2L^2L^2\rangle = 379:39:9
\end{aligned} \tag{14}$$

Stars

For irregular star-like macromolecules composed of f branches, the lengths of which are denoted by N_j, $j = 1, 2, \ldots f$, the derivatives $K^{(m)}$ are obtained from eq (A19)

$$\begin{aligned}
6K^{(1)} &= -\Lambda_1\\
6^2K^{(2)} &= 3\Lambda_1^2 - 2\Lambda_2\\
6^3K^{(3)} &= -15\Lambda_1^3 + 18\Lambda_1\Lambda_2 - 4\Lambda_3
\end{aligned} \tag{15}$$

where the quantities Λ_k are defined in terms of the reduced moments λ_l of the branch-length distribution

$$\lambda_l = (\Sigma_j N_j^l)(\Sigma_m N_m)^{-l} \tag{16}$$

and the parameter $\nu = \Sigma_m N_m = N - 1$

$$\begin{aligned}
3\Lambda_1 &= -(\nu/N)^3(2\lambda_3 - 3\lambda_2 - 3\nu^{-1} - 2\nu^{-2})\\
15\Lambda_2 &= (\nu/N)^5[16\lambda_5 - 20\lambda_3\lambda_2 - 10\lambda_4 + 15\lambda_2^2 + 5\nu^{-1}(6\lambda_4 - 3\lambda_2^2 - 8\lambda_3 + 6\lambda_2) + 5\nu^{-2}(4\lambda_3 - 6\lambda_2 + 3) - 5\nu^{-3} - 6\nu^{-4}]\\
105\Lambda_3 &= -(\nu/N)^7[272\lambda_7 - 336\lambda_5\lambda_2 - 140\lambda_4\lambda_3 + 210\lambda_3\lambda_2^2 - 112\lambda_6 + 210\lambda_4\lambda_2 - 105\lambda_2^3 + 7\nu^{-1}(120\lambda_6 - 120\lambda_4\lambda_2 - 40\lambda_3^2 + 30\lambda_2^3 - 96\lambda_5 + 120\lambda_3\lambda_2 + 30\lambda_4 - 45\lambda_2^2) + 7\nu^{-2}(164\lambda_5 - 160\lambda_3\lambda_2 - 170\lambda_4 + 120\lambda_2^2 + 90\lambda_3 - 45\lambda_2) + 35\nu^{-3}(24\lambda_4 - 12\lambda_2^2 - 32\lambda_3 + 24\lambda_2 - 3) + 7\nu^{-4}(44\lambda_3 - 66\lambda_2 + 30) - 28\nu^{-5} - 48\nu^{-6}]
\end{aligned} \tag{17}$$

The moments λ_k do not change with a proportional increase in the length of all f branches; such growth of the molecular weight affects only the parameter ν. Perhaps it is interesting to note that stars approach the asymptotic behavior for $N \to \infty$ much slower and with an opposite trend than the linear and cyclic molecules do. For instance, in the expression for $\langle S^2\rangle_r$ the correction term for finite chain length is negative and proportional to N^{-2} for both rings and linear chains (*cf.* eq 13), while it is positive and contains also the linear term N^{-1} in the case of stars (*cf.*

(11) H. A. Kramers, *J. Chem. Phys.*, **14**, 415 (1946).
(12) T. A. Orofino, *Polymer*, **2**, 305 (1961).
(13) M. Kurata and M. Fukatsu, *J. Chem. Phys.*, **41**, 2934 (1964).
(14) W. C. Forsman, *Macromolecules*, **1**, 343 (1968).

Table II
Some Reduced Moments of the Shape Distribution $W(L_1^2,L_2^2,L_3^2)$ for Chains of Different Structures[a]

	$\langle L^2\rangle_r \cdot 10^2$		$\langle L^4\rangle_r \cdot 10^4$		$\langle L^2L^2\rangle_r \cdot 10^4$		$\langle L_3^2\rangle:\langle L_2^2\rangle:\langle L_1^2\rangle$
	b	*c*	*b*	*c*	*b*	*c*	*c*
Linear	5.55	5.40	80.2	75.4	18.5	17.7	11.8:2.69:1
Rings	2.78	2.85	13.9	14.6	6.16	6.21	6.5:2.35:1
Stars							
$f = 3$	4.34	4.32	37.9	37.2	14.0	13.9	8.47:2.83:1
$f = 4$	3.50	3.47	21.3	20.7	9.98	9.92	6.22:2.56:1
$f = 6$	2.51	2.52	9.28	9.32	5.54	5.59	4.35:2.09:1
$f = 8$	1.95	1.95	5.16	5.07	3.49	3.48	3.46:1.91:1
Combs							
$m = 10, n = 30$	2.84	2.84	13.8	13.6	6.65	6.69	5.29:2.18:1
$m = 20, n = 20$	3.46	3.41	25.7	25.1	8.54	8.29	7.42:2.21:1
$m = 30, n = 10$	4.36	4.26	47.2	44.3	12.0	11.7	9.90:2.46:1

[a] The number of beads in each chain is $N = 241$ (except for rings where $N = 50$). The parameters f, m, and n characterizing the structures are defined in the text. [b] Calculated from analytical relations (eq 11, 12, 15–17, 19). [c] Obtained by Monte Carlo method using an ensemble of 2000 chains (except for rings where the size of the ensemble was 100 chains).

eq 9 and 15–17)

$$\langle S^2\rangle_r = (\nu/N)^3(\tfrac{1}{2}\lambda_2 - \tfrac{1}{3}\lambda_3 + \tfrac{1}{2}\nu^{-1} + \tfrac{1}{3}\nu^{-2})$$

In Table I there are the percentage deviations of $\langle S^2\rangle_r$ from the limiting value for $N \to \infty$ for a linear chain and regular stars with four and eight branches in dependence upon the number of beads N in the molecule. The slow convergence for stars cannot be explained by the fact that a linear branch of a star is f times shorter than the total number of bonds in the molecule; *e.g.*, the deviation for eight-branch star with $N = 240$ is +2.36% while that of a linear molecule with $N = 30$ is −0.11%, *i.e.*, it is much smaller and of the opposite sign.

The special case of a regular star molecule with f branches, each of them consisting of n bonds, is obtained easily from eq 15 and 17 by substitutions $\lambda_l = f^{1-l}$ and $\nu = nf$. For instance, in the limit for the branch length n increasing to infinity, the moments $\langle S^{2k}\rangle_r$ and the ratios of the average principal moments are simply

$$\begin{aligned}
\langle S^2\rangle_r &= (1/6f)(3 - 2f^{-1}) \\
\langle S^4\rangle_r &= (1/540f^2)(135 - 120f^{-1} + 4f^{-2}) \\
\langle S^6\rangle_r &= (1/68040f^3)(8505 - 5670f^{-1} - \\
&\qquad 2772f^{-2} + 568f^{-3}) \qquad (18) \\
\langle L^4\rangle:\langle L^2L^2\rangle &= \\
&\quad (45 + 60f^{-1} - 92f^{-2}):(45 - 90f^{-1} + 48f^{-2}) \\
\langle L^6\rangle:\langle L^4L^2\rangle:\langle L^2L^2L^2\rangle &= \\
&\quad (945 + 5670f^{-1} + 252f^{-2} - 6488f^{-3}): \\
&\quad (945 - 630f^{-1} - 2268f^{-2} + 1992f^{-3}): \\
&\quad (945 - 3780f^{-1} + 5292f^{-2} - 2448f^{-3})
\end{aligned}$$

It is apparent from eq 18 that with the number of branches f increasing from 1 or 2 (which corresponds to a linear chain), the distribution of the reduced mean-square radius $\langle S^2\rangle_r$ becomes sharper and the molecules more symmetrical. In the hypothetical limit of $f \to \infty$ the molecular shape would attain spherical symmetry.

Combs

The structure of regular comb-like macromolecules is characterized by three parameters m, n, and f. The molecule consists of a linear chain of mf bonds with f side chains, each of n bonds, attached to the linear backbone in regular intervals (at the mth bead, $2m$th bead, ..., fmth bead). The total number of beads in the chain is $N = 1 + f(m + n)$. In this case the explicit relations for the derivatives $K^{(j)}$ become too complicated and it is more convenient to express them in terms of auxiliary functions defined below. In order to simplify the notation we also introduce an additional structural parameter $g = m + n$. From eq A32 we have

$$\begin{aligned}
-6N^2K^{(1)} &= (f - 1)D_{n1} + N^{-1}B_1 \\
6^2N^4K^{(2)} &= (f - 1)[(f + 1)\times \\
&\quad D_{n1}^2 + 2N^{-1}D_{n1}B_1 - 2D_{n2}] + 3N^{-2}B_1^2 - 2N^{-1}B_2 \\
-6^3N^6K^{(3)} &= (f - 1)\{(f + 1)[(f + 3)D_{n1}^3 + \qquad (19) \\
&\quad 3N^{-1}D_{n1}^2B_1 - 6D_{n2}D_{n1}] + 9N^{-2}D_{n1}B_1^2 - \\
&\quad 6N^{-1}(D_{n1}B_2 + D_{n2}B_1) + 4D_{n3}\} + 15N^{-3}B_1^3 - \\
&\quad 18N^{-2}B_1B_2 + 4N^{-1}B_3
\end{aligned}$$

where

$$\begin{aligned}
B_1 &= (U_{g-1,1} - D_{n1} - D_{m-1,1})V_{f-1} + D_{n1}V_f + \\
&\quad (U_{g-1} - 1)V_{f-1,1} + V_{f1} \\
B_2 &= (U_{g-1,2} - D_{n2} - 2D_{n1}D_{m-1,1} - D_{m-1,2})V_{f-1} + \\
&\quad 2(U_{g-1,1} - D_{n1} - D_{m-1,1})V_{f-1,1} + \\
&\quad (U_{g-1} - 1)V_{f-1,2} + D_{n2}V_f + 2D_{n1}V_{f1} + V_{f2} \\
B_3 &= (U_{g-1,3} - D_{n3} - 3D_{n2}D_{m-1,1} - 3D_{n1}D_{m-1,2} - \\
&\quad D_{m-1,3})V_{f-1} + 3(U_{g-1,2} - D_{n2} - 2D_{n1}D_{m-1,1} - \\
&\quad D_{m-1,2})V_{f-1,1} + 3(U_{g-1,1} - D_{n1} - D_{m-1,1})V_{f-1,2} + \\
&\quad (U_{g-1} - 1)V_{f-1,3} + D_{n3}V_f + 3D_{n2}V_{f1} + 3D_{n1}V_{f2} + V_{f3} \\
V_f &= U_f \\
V_{f1} &= \tfrac{1}{2}U_{f1}Y_1 \\
V_{f2} &= \tfrac{1}{2}U_{f1}Y_2 + \tfrac{1}{4}U_{f2}Y_1^2 \\
V_{f3} &= \tfrac{1}{2}U_{f1}Y_3 + \tfrac{3}{4}U_{f2}Y_1Y_2 + \tfrac{1}{8}U_{f3}Y_1^3 \\
Y_1 &= D_{m-1,1} + D_{g1} - D_{n1} \\
Y_2 &= D_{m-1,2} + D_{g2} - D_{n2} - 2D_{n1}(D_{g1} - D_{n1}) \\
Y_3 &= D_{m-1,3} + D_{g3} - D_{n3} - 3(D_{g2}D_{n1} + D_{g1}D_{n2}) + \\
&\quad 6D_{n1}(D_{n2} + D_{n1}D_{g1} - D_{n1}^2) \\
D_{jk} &= U_{jk} - U_{j-1,k} \\
U_j &= j + 1 \\
U_{jk} &= 2\cdot 4\cdot 6\cdots(2k)\binom{j + k + 1}{2k + 1}, \quad k > 0
\end{aligned}$$

For $f = 1$ or for $n = 0$ the results reduce to those for a linear chain, for $m = 0$ they yield the relations for a regular star with f branches, each of n bonds, and for $f = 2$ the results are identical with the relations obtained for a star

with three branches, consisting of m, n, and $(m + n)$ bonds.

Keeping m and n constant and increasing f, the shape becomes more and more asymmetrical. In the limit for $f \rightarrow \infty$ it is identical with that of a linear molecule, independently of m and n (unless $m = 0$), since the effect of the infinitely long chain backbone prevails over the effect of finite side chains. However, the moments of S^2 distribution as well as the individual principal component moments do depend upon m and n, as can be seen from the derivatives

$$\left.\begin{aligned} K^{(1)} &= -(m/g)/18 \\ K^{(2)} &= (m/g)^2/180 \\ K^{(3)} &= -61(m/g)^3/68{,}040 \end{aligned}\right\} \text{ for } f \longrightarrow \infty \qquad (20)$$

Monte Carlo Method

For the investigation of the effect of branching on the average molecular parameters of macromolecules, it is convenient to generate several chain structures simultaneously avoiding thus the repetition of common procedures. For this purpose linear subchains of an appropriate length M are successively generated, their contributions to the tensor of random orthogonal components $\mathbf{X}$ are calculated, and then they are interconnected in several different ways to yield chains of several desired structures. Our data for random-flight chains with nine different structures (linear, four stars, and four combs) on simple cubic six-choice lattice were obtained simultaneously, using subchains of ten bonds each. The generation of each subchain starts at the origin of its y coordinate system. If the kth coordinate of the mth bead of the lth subchain generated is denoted by $y_{kl}{}^{(m)}$, then the only important parameters, as regards the subchain's contribution to $\mathbf{X}$, are

$$\begin{aligned} \kappa_k{}^l &\equiv \sum_{m=1}^{M} y_{kl}{}^{(m)} \\ \kappa_{jk}{}^l &\equiv \sum_{m=1}^{M} y_{jl}{}^{(m)} y_{kl}{}^{(m)} \end{aligned} \qquad (21)$$

and the coordinates $y_{kl}{}^{M}$ of its last bead, where M is the number of bonds in the subchain. Using this notation, we can write the sums appearing in eq 4 for $\mathbf{X}$ as

$$\sum_{m=1}^{N-1} x_k{}^{(m)} = \sum_{l=1}^{t} (\kappa_k{}^l + M\eta_k{}^l) \qquad (22)$$

$$\sum_{m=1}^{N-1} x_j{}^{(m)} x_k{}^{(m)} = \sum_{l=1}^{t} (\kappa_{jk}{}^l + \kappa_j{}^l \eta_k{}^l + \kappa_k{}^l \eta_j{}^l + M\eta_j{}^l \eta_k{}^l) \qquad (23)$$

where t is the number of subchains in the macromolecule, $t = (N - 1)/M$, and $\eta_k{}^l$ is the kth coordinate of the first bead of the lth subchain, referred however to the real x-coordinate system of the particular macromolecule. The quantities κ are obviously independent of the chain structure and, once calculated, they may be used for any chains which can be composed from generated subchains. The way of linking the subchains together affects only the parameters η. There are many ways to build up the chain of a particular structure from t created subchains; this multitude of options could be used to increase the size of the investigated ensemble. Two possible definitions of η are illustrated by two examples

Linear molecule

$$\eta_k{}^l = \sum_{i=1}^{l-1} y_{ki}{}^{(M)}$$

Regular star (f branches of n bonds each)

$$\eta_k{}^{jn+l} = \sum_{i=1}^{l-1} y_{k,jn+i}{}^{(M)} \qquad (24)$$

where $j = 0, 1, \cdots, f - 1$, and $l = 1,2, \cdots, n$.

The generation of rings is more difficult and has to be done separately since we have to ensure that the loop closes after the desired number of steps. This can be achieved by reevaluating at each step the probability of proceeding in each of the six directions available. On the simple cubic lattice, the number of ways to get from the lattice point t_1, t_2, t_3 back to the origin in j steps is

$$\Omega_j(t_1,t_2,t_3) = \sum_{|j_k|} j![j_1!j_2!j_3!(j_1 + |t_1|)!(j_2 + |t_2|)!(j_3 + |t_3|)!]^{-1} \qquad (25)$$

$$j_1 + j_2 + j_3 = {}^1/_2(j - |t_1| - |t_2| - |t_3|) \qquad (25a)$$

where the sum extends over all combinations of nonnegative integers j_k satisfying the condition shown in eq 25a. The desired probabilities can now be found as the ratios; *e.g.*, if the cycle is to be closed at the origin in j steps, the probabilities of making a step in the 1 direction back to and away from origin, respectively, are

$$\begin{aligned} P_j{}^{1\leftarrow}(t_1,t_2,t_3) &= \Omega_{j-1}(t_1 - \epsilon,t_2,t_3)/\Omega_j(t_1,t_2,t_3) \\ P_j{}^{1\rightarrow}(t_1,t_2,t_3) &= \Omega_{j-1}(t_1 + \epsilon,t_2,t_3)/\Omega_j(t_1,t_2,t_3) \end{aligned} \qquad (26)$$

where $\epsilon = t_1/|t_1|$. For the actual computation, it is convenient to store the terms of the sum (eq 25) in a matrix $\mathbf{T}_{j_1 j_2}$ (note that j_3 is determined by eq 25a). For each step made, the set of "new" $\mathbf{T}_{j_1 j_2}$ elements can be obtained from the set of "old" $\mathbf{T}_{j_1 j_2}$ elements by simple multiplication, as follows from eq 25. At the start of random walk, the size of the matrix $\mathbf{T}$ is $({}^1/_2)N$; with each step made away from the origin, however, the size decreases by one. It is not necessary to keep track of all of the elements of $\mathbf{T}$, since some of them are vanishingly small and their contribution to the sum (25) can be neglected. However, with proceeding random walk the boundary of the significant terms in $\mathbf{T}$ is gradually changing and has to be rechecked periodically. For our chains with $N = 50$, we neglected all elements of $\mathbf{T}$ smaller than 10^{-6} × the largest elements of $\mathbf{T}$, and the reinvestigation of the boundary was made after each five steps. The generation of cycles is very time-consuming despite of taking all possible precautions. Thus, using the described methods, a typical run generating 25 cyclic chains of 50 bonds each would take approximately the same time as the generation of 300 chains of 9 different linear and branched structures of 240 bonds each.

The principal axes for each chain generated were obtained by diagonalizing its matrix $\mathbf{X}$ (eq 4) using the same method as previously.[2a]

The shape of the random-flight chains, as expressed by the ratios of the mean square principal components $\langle L_3{}^2\rangle:\langle L_2{}^2\rangle:\langle L_1{}^2\rangle$, seems to be even more sensitive than the mean square radius $\langle S^2\rangle$ to the nonrandomness of pseudorandom numbers generated by the computer. The earlier data[2a] obtained by Dartmouth College GE-635 computer on 2000 linear chains of 50 bonds each on simple cubic lattice, showing an error of only 0.16% in $\langle S^2\rangle$, yielded the ratio $\langle L_3{}^2\rangle:\langle L_1{}^2\rangle \simeq 11.8:1$. Surprisingly, using the Burroughs 5500 computer we obtained for 1500 chains of 240 bonds a much higher ratio 13.5:1 and an unreasonably high mean-square radius $\langle S^2\rangle_r \simeq 0.180$ (an error of ~8.2%). A closer examination proved that the pseudorandom number generator provided for Basic by Burroughs is highly unsuitable for generating the lattice chains. In a series of ten runs, each of which generated 100 linear

chains of 50 bonds, the third random component $\langle X_{33} \rangle$ was consistently lower than the average $\langle S^2 \rangle/3$ while the second component $\langle X_{22} \rangle$ was in all but one (*i.e.*, in nine) cases higher than $\langle S^2 \rangle/3$. The obvious consequence of this preference for the direction 2 as compared to the direction 3 is then the observed more elongated shape of the generated chain. This failure in performance occurred despite the fact that the pseudorandom number generator satisfied the commonly used randomness criteria. Since the effect of such systematic deviations from randomness is cumulative, it becomes more serious in longer chains. Probably this effect might be considerably suppressed by allowing the generated subchains to reorient and mirror randomly in one of 48 possible ways before interconnecting them in a macromolecule; however, we have not investigated this option. Our results indicate that a very efficient way of checking the quality of a pseudorandom number generator is simply to generate self-intersecting linear random-flight cubic lattice chains of N beads and to compare the obtained ensemble averages $\langle X_{kk} \rangle$ with their analytical values, $\langle X_{kk} \rangle = (1 - N^{-2})/18$. It can be shown that both results should be identical despite the fact that the Monte Carlo method employs steps of constant length and allows only six possible orientations, while the analytical method with Gaussian step-length distribution works in a continuous space. (This is, however, not true for higher moments $\langle X_{kk}{}^n \rangle$, $n > 1$.)

The results given in Table II were obtained on the Dartmouth College GE-635 computer by the above-described methods. GE-635 seems to produce the opposite distortion, though to a much lesser extent than B5500. The data for 2000 chains of 240 bonds in Table II were obtained in four separate runs in all of which, with increasing "linear" character (asymmetry) of the chain structure, there was an increase in negative deviations of homogeneous average moments $\langle L^2 \rangle$ and $\langle L^4 \rangle$ from the analytical values. Also the earlier data[2a] on chains with 100 bonds showed a negative deviation. Nevertheless, the reasonable agreement between the analytical and Monte Carlo average moments indicates that the ratios of principal component moments are fairly accurate.

The change in the structure of a chain results in a considerable change of its shape parameters. Any cycles and/or branch points present in the molecule increase its symmetry. Thus the closing of a ring decreases the ratio $\langle L_3^2 \rangle : \langle L_1^2 \rangle$ roughly by a factor of two, as compared to a linear chain. The star molecule with three branches is the only structure with the ratio $\langle L_2^2 \rangle : \langle L_1^2 \rangle$ slightly higher than that of a linear chain, probably due to the third branch sticking out on the average "perpendicularly" to the direction of the first two branches at the branch point. With increasing number of branches, the star molecule becomes more symmetrical; *e.g.*, for $f = 4$, its shape corresponds approximately to that of a ring molecule, although its size $\langle S^2 \rangle$ is by ~25% larger than that of the cyclic chain. The spherical limit for $f \to \infty$, however, is approached slowly; a star molecule with $f = 8$ still shows a noticeable asymmetry. With constant f and g, the shape of a comb-macromolecule changes smoothly with increasing m as could be anticipated, approaching the asymmetric shape of the linear chain.

The brief data presented in Table II are intended as an illustration of the effect of ring formation and branching upon the shape of macromolecules. It appears that the asymmetry cannot be attributed to the connectivity of random-flight chains. On the contrary, it is rather the *lack* of connectivity (each bead is connected only to its two immediate neighbors and does not interact with other beads at all) which causes the high asymmetry of linear chains. Under such conditions, the effect of the stochastic nature of random-flight chains becomes predominant, and since only very few of the immense number of conformations available are spherically symmetrical, the average shape is considerably asymmetrical. With an increasing number of constraints imposed on the chain in the form of loops and branch points, the beads are losing their freedom to move, the number of asymmetrical conformations available is decreasing and the shape is becoming more symmetric. A highly branched molecule has to be almost isotropic.

The documented dependence of the average shape of a macromolecule on its structure is so significant that the shape factor might be a useful parameter for discussing the solution properties of polymers with various molecular structures.

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Appendix

The generating function method[7] seems to be most powerful for solving the determinants characterizing random-flight chains. The elements of an eigenvector **H** of the matrix **A** obviously have to satisfy the equation

$$\Sigma_l A_{kl} H_l = \xi H_k \qquad k = 1, 2, \cdots, N-1 \qquad \text{(A1)}$$

where ξ is the eigenvalue of the matrix **A**. In general, the relation for the generating function $f(x)$ of the elements of an eigenvector

$$f(x) = \sum_{k=1}^{N-1} H_k x^k \qquad \text{(A2)}$$

can be found from eq A1; it is apparent that by multiplying eq A1 by x^k and summation over k, the expression $\xi f(x)$ is reproduced on the right-hand side. After identification of the individual elements of the eigenvector, the $(N-1)$-th degree polynomial in ξ for the $N-1$ eigenvalues of the matrix **A** (which is proportional to its characteristic polynomial) can be set up. If this polynomial is written in the form

$$\prod_{i=}^{N-1} (d_i \xi - b_i) = 0 \qquad \text{(A3)}$$

then the eigenvalues of **A** are $\xi_i = b_i/d_i$, and the determinant

$$|A| = \prod_{i=1}^{N-1} (b_i/d_i) = b/d \qquad \text{(A4)}$$

can be calculated as the ratio of the absolute term to the coefficient of ξ^{N-1} in the polynomial (A3). The detailed description of the method can be found in ref 7.

In order to reduce the number of subscripts displayed in the equations, the subscript k of eq 6a is omitted in next paragraphs. The often used arguments $1 + i\lambda'C$ and $1 + i\lambda'C - \xi$ of Chebyshev polynomials of the second kind are abbreviated as t and τ, respectively, *i.e.*, $U_m(t) \equiv U_m(1 + i\lambda'C)$ and $U_m(\tau) \equiv U_m(1 + i\lambda'C - \xi)$. The symbol Ξ_m denotes the sum of Chebyshev polynomials

$$\Xi_m(t) \equiv \sum_{l=0}^{m} U_l(t)$$

The difference of two consecutive Chebyshev polynomials will be written as D, *i.e.*, $D_m(t) \equiv U_m(t) - U_{m-1}(t)$.

Rings

For cycles, the matrix **V** is identical to one of the matri-

ces investigated by Rutherford[15]

$$V_{ml} = \delta_{ml} - 1/2(\delta_{m,l+1} + \delta_{m,l-1}) \quad \text{(A5)}$$

The resulting matrix **A** is highly symmetrical and it can be expected to possess similar symmetry properties as **V** with well-known eigenvalues. In analogy to **V**, it is assumed that the odd eigenvectors of **A** are symmetric whereas the even ones are antisymmetrical. Since in both cases there are only $[N/2]$ elements with different absolute values, where $[N/2]$ denotes the integer value of $N/2$, the generating function of an eigenvector can be written as

$$f(x) = \sum_{k=1}^{\nu_1} H_k x^k + \tfrac{1}{2}\delta H_\nu x^\nu \quad \text{(A6)}$$

where $\nu_1 \equiv [(N-1)/2]$, $\nu \equiv N/2$, $\delta = 0$ for N odd and $\delta = 1$ for N even. From eq 6a, A1, A5, and A6 we get the generating function explicitly as

$$f(x) = x[H_1 + x^{\nu_1}(H_{\nu_1}x - H_{\nu_1+1}) + \tfrac{1}{2}\delta x^\nu(H_\nu x + H_\nu x^{-1} - H_{\nu+1} - H_{\nu-1})] - (i\lambda' C/N)(\sum_{l=1}^{N-1} H_l)(\delta x^\nu + 2\sum_{l=1}^{\nu_1} x^l)](x^2 - 2x\tau + 1)^{-1} \quad \text{(A7)}$$

Symmetrical eigenvectors are obtained from eq A7 by using the normalization condition

$$\sum_{l=1}^{N-1} H_l = 1$$

Independently of whether N is even or odd, the eq A7 with eq A6 yields for $x = 1$ the first element

$$H_1 = \xi - (i\lambda' C/N) \quad \text{(A8a)}$$

The rest of the elements is obtained by expanding the denominator of eq A7 in terms of Chebyshev polynomials and comparing the terms on both sides of the equation

$$H_k = H_1 U_{k-1}(\tau) - 2(i\lambda' C/N)\,\Xi_{k-2}(\tau) \quad \text{(A8b)}$$

The characteristic polynomial can now be set up by substituting H_k from eq A8 back into the normalization condition. Finally, the contribution to $|A|$ made by symmetric eigenvectors is found by means of eq A4

$$|A|_s = 2^{1-\nu}N^{-1}(2 + i\lambda' C)\,U_{\nu-1}(t) \quad N \text{ even}$$
$$= 2^{-\nu_1}N^{-1}[U_{\nu_1}(t) + U_{\nu_1-1}(t)] \quad N \text{ odd} \quad \text{(A9)}$$

The antisymmetrical eigenvectors have to satisfy the condition

$$\sum_{l=1}^{N-1} H_l = 0$$

From here, the elements are identified as

$$H_m = H_1 U_{m-1}(\tau) \quad \text{(A10)}$$

where $H_1 = 2(\xi - i\lambda' C) - (2 - \delta)H_{\nu 1}$, and their contribution to the determinant $|A|$ is

$$|A|_a = 2^{-\nu_1}[U_{\nu_1}(t) + (1 - \delta)U_{\nu_1-1}(t)] \quad \text{(A11)}$$

The determinant $|A|$ is then equal to the product $|A|_s|A|_a$

$$|A| = 2^{-(N-2)}N^{-1}(2 + i\lambda' C)U_{\nu-1}^2(t) \quad N \text{ even}$$
$$2^{-(N-1)}N^{-1}[U_{\nu_1}(t) + U_{\nu_1-1}(t)]^2 \quad N \text{ odd} \quad \text{(A12)}$$

Transcribed in terms of goniometric functions, both expressions turn out to be identical

$$|A| = 2^{-(N-1)}N^{-1}\sin^2(N\theta/2)\,\sin^{-2}(\theta/2) \quad \text{(A13)}$$

where $\cos\theta = 1 + i\lambda' C$.

Stars

For star molecules, the most convenient way of designating the beads is to number consecutively the beads of one branch after another (always starting at the center of the molecule which is fixed at the origin). Then, the matrix **V** for a molecule composed of f branches with N_m bonds, $m = 1, 2, \ldots, f$, can be separated into $f \times f$ submatrices $\mathbf{v}_{mn}$. Since there is no direct interaction among the beads belonging to different branches, only the submatrices on the main diagonal of **V** are nonzero matrices

$$(\mathbf{v}_{mn})_{jl} = \delta_{mn}[\delta_{jl} - 1/2(\delta_{j,l+1} + \delta_{j,l-1} + \delta_{j,N_m}\delta_{l,N_m})] \quad \text{(A14)}$$

Correspondingly to **V**, also the matrix **A** and its eigenvectors **H** can be partitioned in submatrices $\mathbf{a}_{mn}$ and subeigenvectors $\mathbf{h}_m$, respectively [*e.g.*, $(\mathbf{h}_m)_l$ corresponds to an **H** element with the subscript

$$l + \sum_{n=1}^{m-1} N_n]$$

Equation A1 for the eigenvalues ξ can now be written in the form

$$\Sigma_{n,l}(\mathbf{a}_{mn})_{kl}(\mathbf{h}_n)_l = \xi(\mathbf{h}_m)_k \quad \text{(A15)}$$

The generating function of the mth subeigenvector, defined here as

$$f_m(x) = \sum_{j=1}^{N_m} (\mathbf{h}_m)_j x^j \quad \text{(A16)}$$

turns out to be identical with that of a linear chain with N_m bonds (see eq 13 of ref 7) and yields for $(\mathbf{h}_m)_j$ the relation

$$(\mathbf{h}_m)_j = 2[(\xi - i\lambda' C)\Omega_m + i\lambda' C(N_m/N)]U_{j-1}(\tau) - 2(i\lambda' C/N)\Xi_{j-2}(\tau) \quad \text{(A17)}$$

where

$$\Omega_m = \sum_{l=1}^{N_m} (\mathbf{h}_m)_l \quad \text{(A17a)}$$

By summing eq A17 over j and using eq A17a, a linear equation for Ω_m is recovered

$$\Omega_m[U_{N_m}(\tau) - U_{N_m-1}(\tau)] = (2i\lambda' C/N)[N_m\,\Xi_{N_m-1}(\tau) - \sum_{j=1}^{N_m} \Xi_{j-2}(\tau)] \quad \text{(A18)}$$

Finally, by using the normalization condition

$$\sum_{m=1}^{f} \Omega_m = 1$$

the characteristic polynomial of **A** is obtained and the determinant $|A|$ found

$$|A| = 2^{-(N-1)}N^{-1}\{\prod_{m=1}^{f}[U_{N_m}(t) - U_{N_m-1}(t)] + \sum_{m=1}^{f} U_{N_m-1}(t) \prod_{\substack{l=1 \\ l\neq m}}^{f} [U_{N_l}(t) - U_{N_l-1}(t)]\} \quad \text{(A19)}$$

In the special case of a regular star molecule with $N_m = n = \text{const}$, eq A19 reduces to the simple form

$$|A| = 2^{-(N-1)}N^{-1}[U_n(t) - U_{n-1}(t)]^{f-1}[U_n(t) + (f-1)U_{n-1}(t)] \quad \text{(A20)}$$

(15) D. E. Rutherford, *Proc. Roy. Soc. Edinburgh, Sect. A*, **63**, 232 (1952).

Combs

For the purpose of our calculation, the comb molecule may be thought of as being formed by regular addition of f submolecules, each of g bonds, in such a way that the first bead of each submolecule is attached to the mth bead of the preceding one. Alternately, we can state that the chain backbone of fm bonds bears f side chains, each of n bonds ($m + n = g$), attached in regular intervals. The beads are numbered consecutively in one submolecule after another. Here the matrix $\mathbf{V}$ can be divided into $f \times f$ square submatrices $\mathbf{v}_{ij}$, each of size $g \times g$. The size of $\mathbf{V}$ is again $(N-1) \times (N-1)$, where $N = 1 + fg$. Only the submatrices in the main diagonal of $\mathbf{V}$

$$(\mathbf{v}_{jj})_{kl} = \delta_{kl}[1 + {}^1/_2(\delta_{km} - \delta_{km}\delta_{jf} - \delta_{kg})] - {}^1/_2(\delta_{k,l+1} + \delta_{k,l-1}) \quad \text{(A21)}$$

and their immediate neighbors

$$(\mathbf{v}_{j,j+1})_{kl} = -{}^1/_2\,\delta_{km}\delta_{l1}$$
$$(\mathbf{v}_{j,j-1})_{kl} = -{}^1/_2\delta_{k1}\delta_{lm} \quad \text{(A22)}$$

are nonzero matrices. The set of equations for the eigenvalues ξ is again applied in the form analogous to eq A15. The definition of the generating function for a subeigenvector is rather arbitrary; we chose the generating function corresponding to the jth submolecule in the form

$$f_j(x) = \sum_{k=1}^{g}(\mathbf{h}_j)_k x^{(j-1)m+k} \qquad j = 1, 2, \ldots, f \quad \text{(A23)}$$

where the power of x depends upon the "distance" (measured by the number of bonds) of the corresponding bead from the zeroth bead of the comb. With this definition, $f_j(x)$ is obtained from eq A21 and A22 in the form shown in eq A24 where $\psi \equiv \Sigma_{il}(\mathbf{h}_i)_l$. By the standard method of expanding the denominator of eq A24 and comparing the right-hand side of eq A23 and A24, a relation is obtained for $(\mathbf{h}_j)_k$

$$f_j(x) = x^{m(j-1)+1}\{[(\mathbf{h}_j)_1 - (\mathbf{h}_{j-1})_m x] + x^m[(\mathbf{h}_j)_m(1-\delta_{jf}) - (\mathbf{h}_{j+1})_1] + (\mathbf{h}_j)_g x^g(x-1) - 2(i\lambda' C/N)\psi \sum_{k=1}^{g} x^k\}[x^2 - 2x\tau + 1]^{-1} \quad \text{(A24)}$$

$$(\mathbf{h}_j)_k = (\mathbf{h}_j)_1 U_{k-1}(\tau) - 2(i\lambda' C/N)\psi\,\Xi_{k-2}(\tau) + [(\mathbf{h}_j)_m(1-\delta_{jf}) - (\mathbf{h}_{j+1})_1]U_{k-m-1}(\tau) - (\mathbf{h}_{j-})_m U_{k-2}(\tau) \quad \text{(A25)}$$

Owing to the presence of the freely moving branch points, the individual subvectors $\mathbf{h}_j$ of a comb macromolecule are not separated in eq A25. Of special importance here are the first and the mth element of each subvector, physically corresponding to the formation of a branch point, and they have to be determined first of all. There are two linear equations relating these two elements: the first one is obtained from eq A25 by putting $k = m$; the second one is obtained by comparing eq A24, written for $x = 1$, with the eq A25 summed over k. They can be solved, yielding an equation for the first element $(\mathbf{h}_{j+1})_1$ and a recurrent relation for the mth element $(\mathbf{h}_{j+1})_m$

$$(\mathbf{h}_{j+1})_1 = [(\mathbf{h}_{j+1})_m + (\mathbf{h}_j)_m U_{m-2} + 2(i\lambda' C/N)\psi\,\Xi_{m-2}]U_{m-1}{}^{-1} \quad \text{(A26)}$$

$$(\mathbf{h}_{j+1})_m = E(\mathbf{h}_j)_m + F(\mathbf{h}_{j-1})_m + H \quad \text{(A27)}$$

$j = 1, 2, \ldots, f-1$

$$E \equiv D_{m-1} + (D_g/D_n)$$
$$F \equiv (U_{m-2}D_g - U_{m-1}D_{g-1})/D_n = -1$$
$$H \equiv 2(i\lambda' C/N)\psi\{[(D_g/D_n) - 1]\Xi_{m-2} - (U_{m-1}U_{g-1}/D_n)\} \quad \text{(A27a)}$$

where the argument of the functions U_k, D_k, and Ξ_k is τ. Finally the repeated application of the recurrence formula A27 leads to an explicit expression for the mth element

$$(\mathbf{h}_{j+1})_m = (\mathbf{h}_1)_m \sum_{k=0}^{[j/2]}(-1)^k\binom{j-k}{k}E^{j-2k} + H\sum_{l=0}^{j-1}\sum_{k=0}^{\min(l,\,j-1-l)}(-1)^k\binom{l}{k}E^{l-k} \quad \text{(A28a)}$$

Recalling the definition of Chebyshev polynomials of the second kind

$$U_j(x) = \sum_{k=0}^{[j/2]}(-1)^k\binom{j-k}{k}(2x)^{j-2k}$$

it is also observed that the sum of the mth elements, which will be needed later, can be written in the simple form

$$\sum_{j=1}^{l}(\mathbf{h}_j)_m = \sum_{k=0}^{l-1}[(\mathbf{h}_1)_m + (l-1-k)H]U_k(E/2) \quad \text{(A28b)}$$

where $E/2$ (defined by eq A27a) is the argument of the Chebyshev polynomial U_k.

The characteristic polynomial of the matrix $\mathbf{A}$ for combs can now be obtained by summing the eq A25 over the subscripts j and k and applying the normalization condition $\psi = 1$

$$[\Xi_{n-1} - \Xi_{g-2} + (1 + U_{m-2})(\Xi_{g-1} - \Xi_{n-1})U_{m-1}{}^{-1}] \times \sum_{j=1}^{f-1}(\mathbf{h}_j)_m + (\Xi_{g-1} - \Xi_{n-1})U_{m-1}{}^{-1} \times [(\mathbf{h}_f)_m + 2f(i\lambda' C/N)\,\Xi_{m-2}] + (\mathbf{h}_1)_1\Xi_{n-1} - 2f(i\lambda' C/N)[\sum_{j=0}^{g-2}(g-1-j)U_j] - 1 = 0 \quad \text{(A29)}$$

Upon substitution of eq A28 into eq A29 we note that the order of the characteristic polynomial is too low, which is the consequence of the denominator $D_n(\tau)$ present in E as defined by eq A27a. Therefore eq A29 has to be multiplied by $D_n{}^{f-1}(\tau)$, to bring its order to the needed fg. Also, it is not immediately clear whether some of the terms of eq A29 are divisible by $U_{m-1}(\tau)$ as required by the presence of the denominators $U_{m-1}{}^{-1}(\tau)$ in it. For this reason, it is necessary to multiply temporarily the eq A29 by $U_{m-1}(\tau)$. This means that instead of working with the characteristic polynomial

$$\prod_{j=1}^{fg}(\xi d_j - b_j) = 0 \quad \text{(A30)}$$

(*cf.* eq A3 and A4), we use the polynomial

$$\prod_{j=1}^{fg}(\xi d_j - b_j)\prod_{k=1}^{m-1}(\xi d_k{}^* - b_k{}^*) = 0 \quad \text{(A31)}$$

where the second product is identically equal to $U_{m-1}(\tau)$. The sought determinant $|A|$ will then be calculated as the ratio $|A| = (b'/d')/(b^*/d^*)$, where b' and d' are the absolute term and the coefficient of the term ξ^{fg+m-1} of eq A31 (*i.e.*, of eq A29 multiplied by $D_n{}^{f-1}(\tau)U_{m-1}(\tau)$, and b^* and d^* are the absolute term and the coefficient of the term ξ^{m-1} of $U_{m-1}(\tau)$, respectively. After some tedious calculation the determinant is found to be

$$|A| = 2^{-(N-1)}N^{-1}D_n{}^{f-1}[D_n U_f(E/2) + (U_{g-1} - D_n D_{m-1})U_{f-1}(E/2)] \quad \text{(A32)}$$

with E defined in eq A27a. The argument of all functions except U_f and U_{f-1} in eq A32 is $t \equiv 1 + i\lambda' C$.