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Review

Configuration Statistics of Gaussian Molecules

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ABSTRACT: The theory of the distribution function of the radius of gyration of a Gaussian molecule is discussed from a general standpoint, applicable to any molecule regardless of topology or connectivity. The treatment is based upon elementary graph theory and a few theorems on singular matrices, both of which are developed in the text.

The theory of the distribution function of the radius of gyration of the linear chain was presented by Fixman[1] in 1962. Since that time several papers have appeared in which this theory has been applied to various types of molecules. This review is intended to clarify the relationships between these papers with a coherent and comprehensive point of view. It is a study of the statistical mechanics of the quadratic potential.

The theory of the spatial dimensions of linear chains has reached a high state of development, as evidenced in the rotational isomeric state (RIS) theory.[2] Considerable progress has been made in applying this theory to branched molecules as well.[3] Nevertheless, the cruder Gaussian representation of the backbone potential continues to be of interest in polymer theory, mainly because the means do not yet exist to apply RIS theory to several fundamental problems. It is not apparent that the RIS scheme can be applied to volume exclusion, to dynamics in the low frequency range, or to configurations of molecules with interdependent circuits. The Gaussian model, on the other hand, has been readily applied to these problems, and it has yielded surprisingly accurate results in many cases.

If one attempts to translate theories for the linear chain to branched or otherwise reticulated molecules, the first problem that must be mastered is the description of molecular connectivity. When stripped of details, a molecule can be represented by points and lines. At one extreme these represent atoms and covalent bonds, and at the other they represent fictional elements that collectively mimic the mechanical properties of a real molecule. A diagrammatic representation of either structure is a graph, and the methods of graph theory provide a coherent framework both for codifying structures and for formulating suitable potential energies.

Use is made of the theories of both graphs and generalized matrix inverses to explore the distribution function of the radius of gyration of Gaussian molecules. Other aspects of these molecules receiving attention are viscoelasticity, the expansion factor, and the distribution function of the inertial tensor. An effort has been made to keep the content general and self-contained, so that the reader will have available the tools necessary both to comprehend and to apply the methods to any molecule of interest.

We begin with definitions and conventions for nomenclature. Following this, several matrix and graph theorems are developed before launching into the main problems: the configuration integral, the distribution function of the radius of gyration, and the calculation of the characteristic function. A section containing several examples and computational tricks follows, and anyone intent on calculating the properties of reticulated molecules should find some labor-saving devices there. Finally, there is a short discussion of some problems that arise in interpretation of the solution properties of polymers.

Definitions

As mentioned, two mathematical objects prove to be extremely useful for discussing a Gaussian molecule: they are a graph and a generalized inverse. Before displaying the applicable theory of these devices it may be helpful to collect together a set of basic notational conventions and definitions.[4,5]

A Gaussian molecule is a molecule represented as a

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collection of n beads labeled with the numerals 1 through n, the beads being fastened together with at least $n - 1$ Hookean springs. Let the spatial configuration of the beads be specified by the $3n$ dimensional vector $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n)$, and let the spring constant of the bond joining beads i and j be $kT\gamma_{ij} = 3kT/2\langle l_{ij}^2\rangle$, where $\langle l_{ij}^2\rangle$ is the mean-square extension of the spring. The potential of mean force $V(\mathbf{R})$ of the molecule is given by

$$V(\mathbf{R}) = kT\sum_{i-j}\gamma_{ij}(\mathbf{r}_i - \mathbf{r}_j)^2 \qquad (1a)$$

where the sum runs over all bonds directly connecting a pair of beads, as indicated by the index of summation $i - j$. This model was devised by Rouse[6] for the linear chain, and it has been applied to other specific molecules to be discussed.

A graph is a set $\{\mathbf{V},\mathbf{E}\}$ of labeled vertices v_i, $1 \le i \le |\mathbf{V}|$, and labeled edges e_j, $1 \le j \le |\mathbf{E}|$, together with an incidence relation associating each e_j with a pair, not necessarily different, of vertices. The number of vertices will be denoted by $|\mathbf{V}| = n$, and the number of edges (cardinality of the set $\mathbf{E}$) is $|\mathbf{E}|$. A connected graph is a pictorial representation of a Gaussian molecule; the synonymous pairs of words (vertex, bead) and (edge, bond) identify the graph and the molecule.

A connected graph is a graph in which every vertex can be reached from all others on a path of edges.

The degree of vertex v_i is denoted by δ_i and is equal to the number of edges attached by v_i.

A regular graph is a connected graph in which every vertex has degree $\delta_i = \delta$.

A directed graph is a graph with a direction assigned to every edge. This is also called a digraph.

A general graph might contain multiple edges joining pairs of vertices, loops, circuits, and a distribution of vertex degrees.

A tree is a connected graph in which there is a unique path from all v_i to all v_j. A tree has no circuits.

A spanning tree contains all of the vertices of a graph and a subset of its edges.

A rooted tree is a tree with one vertex uniquely identified as the root.

A reduced graph is obtained from a general graph by deletion of all vertices of degree $\delta_i = 2$; the intervening edges are fused and labeled with the number of deleted vertices.

An incidence matrix is a $|\mathbf{V}| \times |\mathbf{E}|$ matrix $\mathbf{C}$ consisting of 0, +1, and −1. If edge e_j in a digraph is directed from v_l to v_k, the jth column of $\mathbf{C}$ consists of +1 and −1 in the kth and lth rows, respectively; all other elements of the column are null.

An adjacency matrix is a symmetric $|\mathbf{V}| \times |\mathbf{V}|$ matrix $\mathbf{A}$ whose i,j element $a_{ij} = a_{ji}$ is the number of edges joining vertices v_i and v_j in an undirected graph.

A variable adjacency matrix is an adjacency matrix in which a_{ij} is a label or function associated with the edge(s) joining v_i and v_j.

A Kirchhoff matrix is a $|\mathbf{V}| \times |\mathbf{V}|$ matrix $\mathbf{K} = \Delta - \mathbf{A}$, where $\Delta = \mathrm{Diag}(\delta_i)$ is a diagonal matrix of vertex degrees.

A Petrie matrix is an $m \times n$ matrix $\mathbf{P}$ of zeroes and ones in which the unit elements occur consecutively in columns.

A configuration space is a $3|\mathbf{V}|$ dimensional space represented variously as $\mathbf{R}^{3n}$, as a $3 \times n$ matrix $\mathbf{R}$, or as a $1 \times 3n$ vector $\mathbf{r}$. The elements of $\mathbf{R}$ or $\mathbf{r}$ locate the beads of a Gaussian molecule in three-dimensional space. (The generalization to m dimensional spaces is readily inferred in all that follows.)

The spectral density is the number of eigenvalues λ_i of a matrix that lie between λ and $\lambda + d\lambda$ and is denoted by $g(\lambda)\, d\lambda$.

The distribution function is used in two senses: as the distribution function of the radius of gyration $\mathbf{P}(s)\, ds$ giving the probability that a molecule has a radius of gyration between s and $s + ds$ or alternatively as the cumulative distribution function $M(\lambda)$ related to $g(\lambda)$ by $dM(\lambda) = g(\lambda)\, d\lambda$.

$\mathrm{Tr}(\mathbf{X})$ is the trace of the $n \times n$ matrix $\mathbf{X} = (x_{ij})$;

$$\mathrm{Tr}(\mathbf{X}) = \sum_{i=1}^{n} x_{ii}$$

$\mathrm{Det}(\mathbf{X})$ is the determinant of the square matrix $\mathbf{X}$; at times it is denoted by $|\mathbf{X}|$.

$\mathrm{Rk}(\mathbf{X})$ is the rank of an $m \times n$ matrix $\mathbf{X}$, that is, the maximal number of linearly independent rows or columns of $\mathbf{X}$.

The direct product is denoted by $\mathbf{A} \otimes \mathbf{B} = (a_{ij}b_{kl})$. If $\mathbf{A}$ is $m_1 \times n_1$ and $\mathbf{B}$ is $m_2 \times n_2$, the direct product is of the order $m_1m_2 \times n_1n_2$.

The transpose is denoted by $\mathbf{X}'$, where $\mathbf{X} = (x_{ij})$ and $\mathbf{X}' = (x_{ji})$.

$\mathbf{1}_n$ is the identity matrix of rank n. When the context is clear the subscript will be supressed.

$\mathbf{J}_n$ is a $1 \times n$ row vector; $\mathbf{J}_n = (1, 1, ..., 1)$.

$\mathbf{U}_n$ is an $n \times n$ matrix of ones; $\mathbf{U}_n = \mathbf{J}'_n\mathbf{J}_n$.

$\mathbf{e}_i$ is a unit vector in the direction of the ith coordinate axis;

$$\mathbf{J}_n = \sum_{i=1}^{n} \mathbf{e}_i;\ \mathbf{1}_n = (\mathbf{e}'_1, \mathbf{e}'_2, ..., \mathbf{e}'_n)$$

Theorems

There are several matrix and a few integration theorems which are essential to the development of our subject; they are provided in this section together with proofs where the latter are sufficiently simple.

Theorem 1, T1: define two $m \times n$ matrices $\mathbf{W}$ and $\mathbf{Z}$, an $m \times m$ matrix $\mathbf{A}$, and an $n \times n$ matrix $\mathbf{B}$, related by

$$\mathbf{W} = \mathbf{AZB}$$

If the row form $\mathbf{Z}_r$ of $\mathbf{Z}$ is written as

$$\mathbf{Z}_r = (z_{11}, z_{12}, ..., z_{1n}, z_{21}, ..., z_{2n}, ..., z_{m1}, ..., z_{mn})$$

then

$$\mathbf{W}_r = \mathbf{Z}_r(\mathbf{A}' \otimes \mathbf{B})$$

as may be shown by direct construction.

Theorem 2, T2: a real symmetric matrix $\mathbf{A}$ is diagonalized by an orthogonal transformation matrix $\mathbf{T}$ according to

$$\mathbf{TAT}' = \Lambda = \mathrm{Diag}(\lambda_i)$$

The orthogonal matrix $\mathbf{T}$ satisfies $\mathbf{TT}' = \mathbf{T}'\mathbf{T} = \mathbf{1}$, and $\mathrm{Det}(\mathbf{TT}') = \mathrm{Det}(\mathbf{T})\,\mathrm{Det}(\mathbf{T}') = [\mathrm{Det}(\mathbf{T})]^2 = 1$, so that $\mathrm{Det}(\mathbf{T}) = \pm 1$. The theorem is established by Wilkinson.[7] It is always possible to choose $\mathrm{Det}(\mathbf{T}) = +1$. Let $\mathbf{E} = \mathrm{Diag}(\pm 1)$; clearly

$$\mathbf{ETAT}'\mathbf{E}' = \mathbf{T}_1\mathbf{AT}'_1 = \mathbf{E}\Lambda\mathbf{E}' = \mathbf{E}\Lambda\mathbf{E}' = \Lambda$$

If $\mathrm{Det}(\mathbf{T}) = -1$, choose $\mathrm{Det}(\mathbf{E}) = -1$, so that $\mathrm{Det}(\mathbf{T}_1) = +1$. Since $\mathbf{T}_1\mathbf{T}'_1 = \mathbf{ETT}'\mathbf{E}' = \mathbf{EE}' = \mathbf{1}$, $\mathbf{T}_1$ is orthogonal.

Theorem 3, T3: any $m \times n$ real matrix $\mathbf{Z}$ may be represented as

$$\mathbf{Z} = \mathbf{T}'_m \begin{bmatrix} \Gamma & 0 \\ 0 & 0 \end{bmatrix} \mathbf{T}_n$$

where $\mathbf{T}_m(\mathbf{T}_n)$ is orthogonal and of rank $m(n)$, and $\Gamma =$

Diag(γ_i); Rk(Γ) = Rk(**Z**), since the rank of a product of matrices such as these is the minimal rank of the factors. This is known as the Autonne, Eckart, Young theorem and is proved by Ben-Israel and Greville[8] for complex **Z**.

Theorem 4, T4: the Moore–Penrose or genearlized inverse $\mathbf{Z}^+$ of a real matrix **Z** is uniquely given by the four conditions[9]

$$\mathbf{ZZ^+Z} = \mathbf{Z} \quad \text{(i)}$$

$$\mathbf{Z^+ZZ^+} = \mathbf{Z^+} \quad \text{(ii)}$$

$$(\mathbf{ZZ^+})' = \mathbf{ZZ^+} \quad \text{(iii)}$$

$$(\mathbf{Z^+Z})' = \mathbf{Z^+Z} \quad \text{(iv)}$$

If **Z** is nonsingular, $\mathbf{Z}^+ = \mathbf{Z}^{-1}$ trivially satisfies all four conditions. Several corollaries follow directly from T2–T4.

Corollary 1, C1: the generalized inverse of **Z** given in T3 is

$$Z^+ = T'_n \begin{bmatrix} \Gamma^{-1} & 0 \\ 0 & 0 \end{bmatrix} T_m$$

The proof is had by showing that the four conditions of T4 are satisified. We have

$$ZZ^+ = T'_m \begin{bmatrix} \Gamma & 0 \\ 0 & 0 \end{bmatrix} T_n T'_n \begin{bmatrix} \Gamma^{-1} & 0 \\ 0 & 0 \end{bmatrix} T_m$$

$$= T'_m \begin{bmatrix} 1_r & 0 \\ 0 & 0 \end{bmatrix} T_m$$

where r = Rk(**Z**) = Rk(Γ). Similarly,

$$Z^+Z = T'_n \begin{bmatrix} 1_r & 0 \\ 0 & 0 \end{bmatrix} T_n$$

from which conditions iii and iv are seen to hold. Finally

$$(ZZ^+)Z = Z(Z^+Z) = T'_m \begin{bmatrix} \Gamma & 0 \\ 0 & 0 \end{bmatrix} T_n T'_n \begin{bmatrix} 1_r & 0 \\ 0 & 0 \end{bmatrix} T_n$$

$$= T'_m \begin{bmatrix} \Gamma & 0 \\ 0 & 0 \end{bmatrix} T_n = Z$$

satisfies condition i, and ii is demonstrated by similar manipulations.

Corollary 2, C2: the eigenvalues γ_i of **Z** in T3 and C1 may be taken to be the positive square roots of the eigenvalues λ_i of **ZZ′**. Since $\mathbf{T}_n$ in T3 may be multiplied from the left by $\mathbf{E}_n$ without changing its orthogonality, the signs of the γ_i may be changed at will. Secondly,

$$ZZ' = T'_m \begin{bmatrix} \Gamma^2 & 0 \\ 0 & 0 \end{bmatrix} T_m, \quad T_m ZZ' T'_m = \begin{bmatrix} \Lambda_r & 0 \\ 0 & 0 \end{bmatrix}$$

follows directly from T3. Thus, $\Gamma^2 = \Lambda_r$, where Λ_r is the diagonal matrix (evidently positive definite) of nonzero eigenvalues of **ZZ′**. We also have

$$Z'Z = T'_n \begin{bmatrix} \Gamma^2 & 0 \\ 0 & 0 \end{bmatrix} T_n$$

showing that the nonzero eigenvalues of **Z′Z** are identically the same as those of **ZZ′**.

Theorem 5, T5: the Kirchhoff matrix $\mathbf{K} = (k_{ij})$ of a graph **G** is defined to be the matrix of the quadratic form

$$\sum_{i-j}(\mathbf{r}_i - \mathbf{r}_j)^2 = \mathrm{Tr}(\mathbf{RKR}')$$

If bonds of the molecule differ, the elements of **K** carry the labels γ_{ij} of the bonds. Let the Greek indices run from 1 to 3 and the Roman from 1 to n, then

$$(\mathbf{r}_i - \mathbf{r}_j)^2 = \sum_{\alpha=1}^{3} (x_{\alpha i} - x_{\alpha j})^2$$

where

$$\mathbf{r}_i = (x_{\alpha i}),\ 1 \le \alpha \le 3$$

and

$$\mathrm{Tr}(\mathbf{RKR}') = \sum_{\alpha}\sum_{i}\sum_{j} x_{\alpha i} k_{ij} x_{\alpha j}$$

The matrix **K** is given by **K** = **CC′**, where **C** is the incidence matrix of the digraph obtained by orienting the edges of **G** in any arbitrary manner. This is easily seen to be true, since the $3 \times |\mathbf{E}|$ matrix of bond vectors $(x_{\alpha i} - x_{\alpha j}) = \mathbf{b}$ can be constructed from the $3 \times |\mathbf{V}|$ matrix of bead position vectors by **b** = **RC**. Hence,

$$\sum_{i-j}(\mathbf{r}_i - \mathbf{r}_j)^2 = \mathrm{Tr}(\mathbf{bb}') = \mathrm{Tr}(\mathbf{RCC'R}') = \mathrm{Tr}(\mathbf{RKR}')$$

The matrix **C′C** ≠ **K** and has no special significance[10,11] even though its nontrivial eigenvalues are those of **CC′** = **K** as C2 shows and even though **C′C** is recognizable as the Rouse matrix for a linear chain of $n - 1$ beads.[10]

Theorem 6, T6: the rank of **K**, Rk(**K**), = $|\mathbf{V}| - p$, where p is the number of connected components of the graph **G**. This theorem was understood by Kirchhoff;[12] more recently Bryant[13] has supplied a simple proof. It is clear that Rk(**C**) = Rk(**K**) and that **Rk**(**C**) is no larger than $|\mathbf{V}| - 1$ since **JC** = 0. In essence, if the graph has two components, **C** can be partitioned into

$$\begin{bmatrix} C_1 & 0 \\ 0 & C_2 \end{bmatrix}$$

by a permutation of rows and columns, where C_1 and C_2 have rank $|\mathbf{V}_1| - 1$ and $|\mathbf{V}_2| - 1$, respectively, with $|\mathbf{V}| = |\mathbf{V}_1| + |\mathbf{V}_2|$.

Corollary 3, C3: the Kirchhoff matrix constructed from **CC′** has the properties ascribed to it in the definition. The ith row of **C** has as many ±1 elements as there are edges attached to v_i; k_{ii} is therefore equal to δ_i. The elements k_{ij} are nonzero for $i \neq j$ only if the ith row of **C** contains nonzero elements coinciding with nonzero elements in the jth column of **C′**. Since $i \neq j$, this will be true only when v_i and v_j share an edge, and since a direction has been assigned to each edge the contribution to k_{ij} is (−1)(+1) = −1. The contributions from multiple edges are additive.

Corollary 4, C4: the eigenvalues λ_i of **K** lie in the interval

$$0 \le \lambda_i \le 2\delta_{\max}$$

where $\delta_{\max}$ is the maximal degree (functionality) of the vertex set **V**. This is a simple application of Gerschgorin's theorem.[14] The maximum eigenvalue $\lambda_{\max}$ of **K** is bounded from below by[15]

$$\lambda_{\max} \ge \max_{i \neq j} [(k_{ii} - k_{jj})^2 + 4k_{ij}^2]^{1/2}$$

The Kirchhoff matrix of a connected graph of n vertices has exactly one zero eigenvalue; the corresponding right eigenvector is $|\mathbf{V}|^{-1/2}\mathbf{J}' = n^{-1/2}\mathbf{J}'$. The right eigenvectors of **K** constitute one of the matrices in the subset of the orthogonal group with structure $\mathbf{T}'_n = (n^{-1/2}\mathbf{J}', \mathbf{t}')$ where $\mathbf{t}'$ is of order $n \times (n - 1)$.

Corollary 5, C5: the Kirchhoff matrix of a connected graph of n vertices can always be written as

$$\mathbf{K} = \mathbf{T'\Lambda T} = \mathbf{t'}\Lambda_{n-1}\mathbf{t}$$

where $\mathrm{Rk}(\Lambda_{n-1}) = n - 1$. The generalized inverse $\mathbf{K}^+$ of $\mathbf{K}$ is

$$\mathbf{K}^+ = \mathbf{t}'\Lambda^{-1}{}_{n-1}\mathbf{t}$$

Note that $\mathbf{t}$ defined in C4 satisfies

$$\mathbf{T}'_n\mathbf{T}_n = n^{-1}\mathbf{J}'\mathbf{J} + \mathbf{t}'\mathbf{t} = \mathbf{1}_n$$

$$\mathbf{t}'\mathbf{t} = \mathbf{1}_n - n^{-1}\mathbf{U}$$

and

$$\mathbf{T}_n\mathbf{T}'_n = \begin{bmatrix} n^{-1/2}\mathbf{J} \\ \mathbf{t} \end{bmatrix} [n^{-1/2}\mathbf{J}', \mathbf{t}'] = \begin{bmatrix} 1 & n^{-1/2}\mathbf{J}\mathbf{t}' \\ n^{-1/2}\mathbf{t}\mathbf{J}' & \mathbf{t}\mathbf{t}' \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & \mathbf{1}_{n-1} \end{bmatrix}$$

so that $\mathbf{J}\mathbf{t}' = 0$, $\mathbf{t}\mathbf{t}' = \mathbf{1}_{n-1}$. Hence,

$$\mathbf{K}\mathbf{K}^+ = \mathbf{K}^+\mathbf{K} = \mathbf{t}'\mathbf{t} = \mathbf{1}_n - n^{-1}\mathbf{U}$$

and the rest follows from T4. Since $\mathbf{t}\mathbf{J}' = 0$, it is also true that

$$\mathbf{K}^+\mathbf{J}' = 0$$

The last two conditions on $\mathbf{K}^+$ plus $(\mathbf{K}^+)' = \mathbf{K}^+$ suffice to construct $\mathbf{K}^+$ directly from $\mathbf{K}$ without diagonalization, at least in simple cases.

Corollary 6, C6: define the matrix $\mathbf{K}$ as

$$\mathbf{K} = \begin{bmatrix} \delta_1 & -\mathbf{l}_1 \\ -\mathbf{l}'_1 & \mathbf{K}_1 \end{bmatrix}$$

where δ_1 is the valence (degree) of v_1 and $\mathbf{l}_1$ is a row vector of order $1 \times (n-1)$ containing nonzero entries in columns j if v_1 is connected to v_j. An inverse $\mathbf{K}^*$ satisfying conditions i and ii of T4 is given by[16]

$$\mathbf{K}^* = \begin{bmatrix} 0 & 0 \\ 0 & \mathbf{K}_1^{-1} \end{bmatrix}$$

as may be verified directly. It is assumed here that $\mathrm{Rk}(\mathbf{K}) = n - 1$, so that $\mathrm{Det}(\mathbf{K}_1) \neq 0$ and hence that $\mathbf{K}_1^{-1}$ is the usual inverse. Demonstration of (i) and (ii) makes use of the fact that $\delta_1 - \mathbf{l}_1\mathbf{K}_1^{-1}\mathbf{l}'_1 = 0$, which necessarily follows from $\mathrm{Det}(\mathbf{K}) = 0$ and $\mathrm{Det}(\mathbf{K}_1) \neq 0$.

Also define $\mathbf{E}_g = \mathbf{1} - n^{-1}\mathbf{U} = \mathbf{t}'\mathbf{t}$ as in C5. Then

$$\mathbf{K}^+(\mathbf{K}\mathbf{K}^*\mathbf{K})\mathbf{K}^+ = \mathbf{K}^+\mathbf{K}\mathbf{K}^+$$

gives

$$\mathbf{K}^+ = \mathbf{E}_g\mathbf{K}^*\mathbf{E}_g$$

with the use of condition ii and C5. This corollary provides a very effective means to calculate $\mathbf{K}^+$ directly when the structure of the graph allows a relatively simple calculation of $\mathbf{K}_1^{-1}$.

Corollary 7, C7: the generalized inverse $\mathbf{C}^+$ of $\mathbf{C}$ is $\mathbf{C}'\mathbf{K}^+$. For the proof use T4 and C5; the second condition is illustrated as

$$\mathbf{C}\mathbf{C}^+ = \mathbf{C}\mathbf{C}'\mathbf{K}^+ = \mathbf{K}\mathbf{K}^+ = \mathbf{K}^+\mathbf{K} = \mathbf{1} - n^{-1}\mathbf{U}$$

$$\mathbf{C}^+(\mathbf{C}\mathbf{C}^+) = \mathbf{C}'\mathbf{K}^+(\mathbf{K}\mathbf{K}^+) = \mathbf{C}'(\mathbf{K}^+\mathbf{K}\mathbf{K}^+) = \mathbf{C}'\mathbf{K}^+ = \mathbf{C}^+$$

Theorem 7, T7: a set of vectors $\Delta\mathbf{R} = (\mathbf{r}_i - \mathbf{r}_{i+1})$ can be constructed from $\mathbf{R}$ by

$$\Delta\mathbf{R} = \mathbf{R}\mathbf{C}_1$$

where $\mathbf{C}_1$, of order $n \times (n-1)$, has the structure

$$\mathbf{C}_1 = \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \\ -1 & 1 & & & \cdot \\ 0 & -1 & & & \cdot \\ \cdot & 0 & & & \cdot \\ \cdot & \cdot & & & \cdot \\ \cdot & \cdot & & & \cdot \\ \cdot & \cdot & & & 1 \\ 0 & 0 & \cdots & 0 & -1 \end{bmatrix}$$

For the linear chain, $\Delta\mathbf{R}$ is just the set of bond vectors, and for other molecules, it is simply a set of interbead vectors that may or may not be bonds. Any $\mathbf{r}_i - \mathbf{r}_j$ can be obtained as

$$\mathbf{r}_i - \mathbf{r}_j = \sum_{k=i}^{j-1}(\mathbf{r}_k - \mathbf{r}_{k+1}) = \Delta\mathbf{R}\begin{bmatrix} 0 \\ \mathbf{J}_{j-i-1} \\ 0 \end{bmatrix}$$

A $3 \times |\mathbf{E}|$ array $\mathbf{b}$ of these vectors is constructed by

$$\mathbf{b} = \Delta\mathbf{R}\mathbf{P}$$

where $\mathbf{P}$ is a Petrie matrix.[17] The quadratic potential is proportional to $\mathrm{Tr}(\mathbf{b}\mathbf{b}')$ if all bonds have the same mean-square displacement, so that

$$\mathrm{Tr}(\mathbf{b}\mathbf{b}') = \mathrm{Tr}(\mathbf{R}\mathbf{C}_1\mathbf{P}\mathbf{P}'\mathbf{C}'_1\mathbf{R}') = \mathrm{Tr}(\mathbf{R}\mathbf{K}\mathbf{R}')$$

showing that

$$\mathbf{K} = \mathbf{C}_1\mathbf{P}\mathbf{P}'\mathbf{C}'_1$$

If one makes the choice of a bond vector frame $\mathbf{R}^{3(n-1)}$ rather than a bead vector frame $\mathbf{R}^{3n}$, then $\mathbf{P}\mathbf{P}'$ substitutes for $\mathbf{K}$.[17-30] However, if the molecule contains circuits, the bead vector frame is preferred, since in this case $\mathbf{P}\mathbf{P}'$ is much more difficult to construct than is $\mathbf{K}$. (The point is that one can simply look at the graph representing any molecule and immediately construct $\mathbf{K}$.) On the other hand, if the molecule is a tree, $\mathbf{P}\mathbf{P}' = \mathbf{1}_{n-1}$ if $\mathbf{b}$ is defined properly. Other complications to be discussed later enter into calculations in the bond vector frame, which lends an overall preference to $\mathbf{R}^{3n}$.

A few additional observations are worthy of note at this point. In many cases it is not necessary to obtain the four-condition inverse of $\mathbf{K}$. Frequently it suffices to construct a two- or three-condition inverse, i.e., an inverse satisfying only two or three of the Penrose conditions in T4, which differs from $\mathbf{K}^+$ by constant columns or rows. Second, one can construct an Abelian group from all powers (over the complex field $\mathbf{z}$) of $\mathbf{K}$, where $\mathbf{K}^z = \mathbf{t}'\Lambda^z{}_{n-1}\mathbf{t}$, $z \in \mathbf{z}$. Finally, the generalized inverse is implicit in the Wang-Uhlenbeck theorem,[1,31] although it was not originally recognized as such.

Theorem 8, T8. The last theorem of this section concerns integration over a subspace of $\mathbf{R}^{3n}$. Let the volume element of $\mathbf{R}^{3n}$ be denoted by $\mathrm{d}\mathbf{R}$, and let $\mathrm{d}\sigma$ be the volume element of a subspace σ^m of dimension m of $\mathbf{R}^{3n}$. Then an integration of $f(R)$ over the complement of σ^m is a function of the coordinates σ of σ^m and is denoted by

$$h(\sigma) = \int_{\mathbf{R}^{3n-m}} f(\mathbf{R})\, \mathrm{d}\mathbf{R}/\mathrm{d}\sigma$$

The same result is obtained in another way. Let $\sigma = \phi(\mathbf{R})$, where ϕ is a vector (or scalar) valued function mapping $\mathbf{R}^{3n}$ onto the subspace σ^m. An integration over $\mathbf{R}^{3n}$ which leaves σ invariant may be written as

$$\hat{h}(\sigma) = \int_{\mathbf{R}^{3n}} \delta(\sigma - \phi(\mathbf{R}))f(\mathbf{R})\, \mathrm{d}\mathbf{R}$$

where $\delta(\sigma - \phi(\mathbf{R}))$ denotes a product of Dirac delta functions, one for each component of σ. That the two integrals

are identical follows immediately from

$$\int_{\mathbf{R}^{3n}} \delta(\sigma - \phi(\mathbf{R}))f(\mathbf{R})\, d\mathbf{R} = \int_{\sigma^m} \delta(\sigma - \phi(\mathbf{R}))\, d\sigma \int_{\mathbf{R}^{3n-m}} f(\mathbf{R})\, d\mathbf{R}/d\sigma = \int_{\sigma^m} \delta(\sigma - \phi(\mathbf{R}))h(\phi(\mathbf{R}))\, d\sigma = h(\sigma)$$

A few additional theorems will be used in the subsequent derivations; they have not been included in this section because they are deemed to be well known.

Configuration Integral

The configurational integral is primarily required for normalization of the distribution functions to be calculated later. In itself, the free energy of a Gaussian molecule probably has little significance. Greater significance can be attached to the free energy of one molecule relative to a standard, say the linear chain with the same number of beads. Such a comparison of relative statistical weights may be assumed to incur at least partial cancellation of the errors inherent in the application of a crude model to a real system.

In all that follows, the molecule has but one type of bond. If a distribution of bond types is desired, the mth column of the incidence matrix $\mathbf{C}$ must be multiplied by $\gamma_m^{1/2} = \gamma_{ij}^{1/2}$, presuming that the mth bond, which connects vertices i and j, is characterized by $\gamma_{ij} = 3/2\langle l^2_{ij}\rangle$. Thus, in general

$$\mathbf{V}(\mathbf{R}) = kT[\mathrm{Tr}(\mathbf{RC}\gamma\mathbf{C}'\mathbf{R}')] \tag{1b}$$

where $\gamma = \mathrm{Diag}(\gamma_m)$ and $\mathrm{Rk}(\gamma) = |\mathbf{E}|$. Henceforth, $\gamma = \gamma\mathbf{1}$, the graph has only one component, and

$$\mathbf{V}(\mathbf{R}) = kT\gamma[\mathrm{Tr}(\mathbf{RCC}'\mathbf{R}')] = kT\gamma[\mathrm{Tr}(\mathbf{RKR}')] \tag{1c}$$

The Kirchhoff matrix for a connected molecule has one and only one zero eigenvalue. Because of this, $\mathbf{V}(\mathbf{R})$ is a function of $3(n-1)$ coordinates only; let σ denote the remaining three coordinates. The configuration integral Z is given by

$$Z = \int_{\mathbf{R}^{3(n-1)}} \exp[-\gamma(\mathrm{Tr}(\mathbf{RKR}'))]\, d\mathbf{R}/d\sigma \tag{2}$$

First choose $d\sigma = d\mathbf{r}_i$, where $\mathbf{r}_i$ is the column vector locating v_i, and then set $\mathbf{r}_i = 0$ in the potential. This corresponds to choosing a coordinate frame centered on v_i and co-moving with it. Since $\mathbf{r}_i$ does not appear in the potential, neither do the elements $k_{il} = k_{li}$. Deletion of $\mathbf{r}_i$ from $\mathbf{R}$ yields $\mathbf{R}_i$ and $\mathbf{K}$ condenses to $\mathbf{K}_i$ on striking the ith row and column; the orders of $\mathbf{R}_i$ and $\mathbf{K}_i$ are $3 \times (n-1)$ and $(n-1) \times (n-1)$, respectively. If $\mathbf{x}$ is any 3×1 vector, $\mathbf{R} \rightarrow \mathbf{R} + \mathbf{xJ}$ leaves the potential invariant since $\mathbf{JK} = 0$. The configuration integral is thus independent of the origin of coordinates and now becomes

$$Z = \int_{\mathbf{R}^{3(n-1)}} \exp[-\gamma(\mathrm{Tr}(\mathbf{R}_i\mathbf{K}_i\mathbf{R}_i))]\, d\mathbf{R}_i \tag{3}$$

Define the normal coordinates $\mathbf{Q} = \mathbf{R}_i\mathbf{T}$, $\mathbf{TT}' = 1$, where $\mathbf{T}'\mathbf{K}_i\mathbf{T} = \tilde{\Lambda}_i$. Since $\mathrm{Det}(\mathbf{T}) = 1$ by T2, the Jacobian of the transformation is unity. Now apply T1 to $1_3\mathbf{Q}\tilde{\Lambda}_i \rightarrow \mathbf{Q}_r$ $(1_3 \otimes \tilde{\Lambda}_i)$ and $(1_3\mathbf{Q}1_{n-1})' \rightarrow [\mathbf{Q}_r(1_3 \otimes 1_{n-1})]' = (1_3 \otimes 1_{n-1})\mathbf{Q}_r'$ to yield

$$Z = \int_{\mathbf{R}^{3(n-1)}} \exp[-\gamma\mathbf{Q}_r(1_3 \otimes \tilde{\Lambda}_{n-1})\mathbf{Q}_r']\, d\mathbf{Q}_r \tag{4}$$

with the use of the direct product theorem, $(\mathbf{A} \otimes \mathbf{B})(\mathbf{C} \otimes \mathbf{D}) = (\mathbf{AC}) \otimes (\mathbf{BD})$. The integral is now simply a product of $3(n-1)$ Gaussian integrals over the real line and gives

$$Z = (\pi/\gamma)^{3(n-1)/2}|\tilde{\Lambda}_i|^{-3/2} = (\pi/\gamma)^{3(n-1)/2}|\mathbf{K}_i|^{-3/2} \tag{5a}$$

where the last form with $|\mathbf{K}_i| = \mathrm{Det}(\mathbf{K}_i)$ follows on undoing the transformation to normal coordinates. $\mathrm{Det}(\mathbf{K}_i) \neq 0$ because $\mathrm{Rk}(\mathbf{K}) = n-1$, and $\mathbf{K}_i$ is of order $(n-1) \times (n-1)$.

Since Z is independent of the origin of coordinates, it has been proved that

$$\mathrm{Det}(\mathbf{K}_1) = \mathrm{Det}(\mathbf{K}_i), \qquad 2 \leq i \leq n$$

To get yet another representation of Z, choose the origin of coordinates at the center of mass (cm) defined by $\sigma = n^{-1}\mathbf{RJ}'$. Apply a normal coordinate transformation to $\mathbf{R} = \mathbf{QT}'$, where now $\mathbf{T}$ satisfies the conditions of C4. The zero eigenvalue belongs to the coordinates $\mathbf{q}_n = n^{-1/2}\mathbf{RJ}' = n^{1/2}\sigma$; the volume element $d\mathbf{R}/d\sigma \rightarrow n^{3/2}\, d\mathbf{Q}/d\mathbf{q}_n$. Thus

$$Z = (\pi/\gamma)^{3(n-1)/2}\, n^{3/2}|\Lambda_{n-1}|^{-3/2} \tag{5b}$$

by the same arguments leading to eq 5a. Here $|\Lambda_{n-1}| = \mathrm{Det}(\Lambda_{n-1})$ is the determinant of nonzero eigenvalues of $\mathbf{K}$. Comparison of eq 5a and 5b gives the following theorem.

Theorem 9, T9: the value of the determinant of the order $(n-1) \times (n-1)$ matrix $\mathbf{K}_i$ obtained by deletion of the ith row and column of $\mathbf{K}$ is independent of i and is related to the determinant of the matrix Λ_{n-1} of nonzero eigenvalues of $\mathbf{K}$ by

$$\mathrm{Det}(\mathbf{K}_i) = n^{-1}\, \mathrm{Det}(\Lambda_{n-1})$$

It is not difficult to prove[13] that $\mathrm{Det}(\mathbf{K}_i)$ is the number of spanning trees of the graph described by $\mathbf{K}$ that are rooted at v_i (apply the Binet–Cauchy theorem to $\mathbf{K}_i = \mathbf{C}_i\mathbf{C}_i'$).

One can immediately apply T9 to interesting cases: (a) tree, including the linear chain, $\mathrm{Det}(\mathbf{K}_i) = 1$ since there is only one specifically rooted spanning tree on any given unrooted tree; (b) circular chain, $\mathrm{Det}(\mathbf{K}_i) = n$, since the spanning tree rooted on v_1 may have a left branch terminating on any v_j, $1 \leq j \leq n$, while the right branch terminates on v_{j+1}, $n+1 \equiv 1 \pmod n$; and (c) network, the previous examples demonstrate that $\mathrm{Det}(\mathbf{K}_i) > 1$ for any molecule with one or more circuits; if Z_N and Z_L denote the configuration integrals for a net and for a linear chain, respectively, both with the same $|\mathbf{V}| = n$, then $Z_N/Z_L < 1$, and the free energy of the net is larger than that of the corresponding linear chain and is all the larger the more circuits it comprises. This generalizes the Jacobson–Stockmayer ring weighting factors[32] to molecules containing an arbitrary number of circuits.

The potential may also be expressed in a form suitable for dealing with the distribution function of the gyration tensor.[33-40] Apply T3 to $\mathbf{R}$, remembering that $\mathrm{Rk}(\mathbf{R}) = 3$, to obtain

$$\mathrm{Tr}(\mathbf{RKR}') = n[\mathrm{Tr}(\mathbf{T}_3'\mathbf{S}^{1/2}\mathbf{t}_{3,n}\mathbf{K}\mathbf{t}_{3,n}'\mathbf{S}^{1/2}\mathbf{T}_3)] = n[\mathrm{Tr}(\mathbf{St}_{3,n}\mathbf{K}\mathbf{t}_{n,3})] \tag{6}$$

the last form arising from the invariance of the trace to cyclic permutations. Here $n^{1/2}\mathbf{S}^{1/2} = \mathrm{Diag}(n^{1/2}S_i^{1/2})$ are the eigenvalues of $\mathbf{R}$; in the center of mass and principal axes frame $\mathbf{S}$ is the gyration tensor of the molecule, distinguished from the inertial tensor by the fact that the inertial tensor[41] in the same frame is $\mathrm{Diag}(n(s^2 - S_i))$ if all beads have unit mass. In eq 6 $\mathbf{t}_{3,n}$ is the first three rows of the orthogonal matrix $\mathbf{T}_n$ as required by T3 (which diagonalizes $\mathbf{R}$ but not $\mathbf{K}$). It is apparent that $s^2 = \mathrm{Tr}(\mathbf{S})$.

Distribution Functions

The restriction of the configuration integral to the subspace complementary to the radius of gyration yields the probability distribution $\mathbf{W}(s)\, ds$ of s. The integrations

are most conveniently performed for $\mathbf{P}(s^2)\,ds^2$, and since

$$\mathbf{P}(s^2)\,ds^2 = 2s\mathbf{P}(s^2)\,ds = \mathbf{W}(s)\,ds$$

no loss of generality results from computation of the latter distribution. Define

$$s^2 = n^{-1}[\mathrm{Tr}(\mathbf{RR}')] - \sigma^2$$

where σ^2 is the square of the vector from the origin of coordinates to the cm of the molecule. In this frame $\mathbf{R} = \mathbf{R}_c + \sigma\mathbf{J}$, where $\mathbf{R}_c\mathbf{J}' = 0$, and

$$s^2 = n^{-1}(\mathrm{Tr}[(\mathbf{R}_c + \sigma\mathbf{J})(\mathbf{R}_c' + \mathbf{J}'\sigma')]) - \sigma^2 = n^{-1}[\mathrm{Tr}(\mathbf{R}_c\mathbf{R}_c' + n\sigma\sigma')] - \sigma^2 = n^{-1}[\mathrm{Tr}(\mathbf{R}_c\mathbf{R}_c')] \quad (7)$$

If the origin coincides with the cm of the molecule, simplifications occur.

In the bond vector frame, the expression for s_2 is more complicated. By T7, $\Delta\mathbf{R} = \mathbf{RC}_1$ comprises the set of bond vectors for a linear chain, which is momentarily our exclusive concern. This equation can be inverted by use of the theory of the generalized inverse[42] if there exists a $\mathbf{C}_1^{(i)}$ satisfying only condition (i) of T4 such that

$$\Delta\mathbf{R}\mathbf{C}_1^{(i)}\mathbf{C}_1 = \Delta\mathbf{R} \quad (8)$$

Since $\Delta\mathbf{R}$ consists of linearly independent vectors, this can only be true if $\mathbf{C}_1^{(i)}\mathbf{C}_1 = \mathbf{1}_{n-1}$. This left inverse of $\mathbf{C}_1$ is the Petrie matrix

$$\mathbf{P}_1 = \mathbf{C}_1^{(i)} = \begin{bmatrix} 1 & 0 & 0 & \cdot & \cdots & 0 & 0 \\ 1 & 1 & 0 & \cdot & \cdots & 0 & 0 \\ 1 & 1 & 1 & 0 & \cdots & 0 & 0 \\ & & & & & & \\ & & & & & 0 & \\ 1 & 1 & \cdot & \cdot & \cdots & 1 & 0 \end{bmatrix}, \quad \mathbf{P}_1\mathbf{C}_1 = \mathbf{1}_{n-1} \quad (9)$$

as may be verified directly.[43] The solution[42] of the inverse problem is

$$\mathbf{R} = (\Delta\mathbf{R})\mathbf{P}_1 + \mathbf{Y}(\mathbf{1}_n - \mathbf{C}_1\mathbf{P}_1) \quad (10a)$$

where $\mathbf{Y}$ is any $3 \times n$ matrix. But

$$\mathbf{1}_n - \mathbf{C}_1\mathbf{P}_1 = \begin{bmatrix} 0 \\ -\mathbf{J} \end{bmatrix}$$

by construction, so

$$\mathbf{R} = (\Delta\mathbf{R})\mathbf{P}_1 + \mathbf{yJ} \quad (10b)$$

where $\mathbf{y}$ is the last column of $\mathbf{Y}$ to within the sign. The cm coordinates are given by $\mathbf{R} = \mathbf{R}_c + \sigma\mathbf{J}$, so that

$$\mathbf{R}_c = (\Delta\mathbf{R})\mathbf{P}_1 + (\mathbf{y} - \sigma)\mathbf{J}$$

where

$$\mathbf{R}_c\mathbf{J}' = (\Delta\mathbf{R})\mathbf{P}_1\mathbf{J}' + n(\mathbf{Y} - \sigma) = 0$$

$$\mathbf{y} - \sigma = -n^{-1}(\Delta\mathbf{R})\mathbf{P}_1\mathbf{J}'$$

and finally

$$\mathbf{R}_c = (\Delta\mathbf{R})\mathbf{P}_1(\mathbf{1}_n - n^{-1}\mathbf{U}) \quad (11)$$

In the bond vector frame

$$s^2 = n^{-1}(\mathrm{Tr}[(\Delta\mathbf{R})\mathbf{P}_1(\mathbf{1}_n - n^{-1}\mathbf{U})\mathbf{P}_1'(\Delta\mathbf{R})']) \quad (12)$$

since $\mathbf{1}_n - n^{-1}\mathbf{U}$ is idempotent.

The matrix $\mathbf{P}_1(\mathbf{1}_n - n^{-1}\mathbf{U})\mathbf{P}_1'$ is dense (meaning that most of the elements are nonzero). Consequently, the bead vector frame is much to be preferred for treatment of the radius of gyration, where all the matrices ($\mathbf{K}$ for the potential and $\mathbf{1}_n$ for s^2) are sparse. For molecules more complicated than the linear chair just discussed, the matrix standing in place of $\mathbf{P}_1(1 - n^{-1}\mathbf{U})\mathbf{P}_1'$ is less transparent, but it can be constructed by use of the above method. Select $n - 1$ linearly independent columns from $\mathbf{C}$ to constitute $\mathbf{C}_1$. The left inverse $\mathbf{C}_1^{(i)}$ exists by virtue of T3 and C1, and the remainder of the construction follows the above plan. Henceforth, the bond vector frame is set aside, and the general development is resumed.

The distribution function for s^2 is now evaluated[1] as

$$\mathbf{P}(s^2)\,ds^2 = Z^{-1}\,ds^2 \int_{\mathbf{R}^{3(n-1)}} \delta(s^2 - n^{-1}[\mathrm{Tr}(\mathbf{R}_c\mathbf{R}_c')]) \times \exp[-\gamma[\mathrm{Tr}(\mathbf{R}_c\mathbf{K}\mathbf{R}_c')]]\,d\mathbf{R}_c \quad (13)$$

where $d\mathbf{R}_c = d\mathbf{R}/d\sigma$. The Fourier representation of the delta function gives

$$\mathbf{P}(s^2)\,ds^2 = (2\pi Z)^{-1}\,ds^2 \int \exp(i\beta s^2) \exp[-\gamma(\mathrm{Tr}(\mathbf{R}_c(\mathbf{K} + \xi\mathbf{1})\mathbf{R}_c'))]\,d\mathbf{R}_c\,d\beta$$

where $\xi = i\beta/\gamma n$. Transformation to normal coordinates $\mathbf{Q}$ according to C4 yields

$$\mathbf{P}(s^2)\,ds^2 = (2\pi Z)^{-1}\,ds^2 \int \exp(i\beta s^2) \exp[-\gamma(\mathrm{Tr}(\mathbf{Q}(\Lambda_{n-1} + \xi\mathbf{1}_{n-1})\mathbf{Q}'))]\,d\mathbf{Q}\,d\beta \quad (14)$$

Since $\mathbf{R}_c\mathbf{J}' = 0$, the cm coordinates vanish from the potential and from $d\mathbf{Q}$. (The factor of $n^{3/2}$ which accompanies the transformation has been absorbed into Z^{-1}.) Application of T1 followed by integration over $d\mathbf{Q}$ in eq 14 and simplification yields the crucial result of the paper.

Theorem 10, T10: integration of eq 14 yields

$$\mathbf{P}(s^2)\,ds^2 = (ds^2/2\pi) \int_{-\infty}^{\infty} \exp(i\beta s^2)[\mathrm{Det}(\mathbf{1}_{n-1} + \xi\Lambda_{n-1}^{-1})]^{-3/2}\,d\beta \quad (15a)$$

$$\xi = i\beta/\gamma n$$

which is the general solution for $\mathbf{P}(s^2)$ for any molecule which is unperturbed by volume exclusion.

Unfortunately, eq 15a cannot be integrated until the eigenvalues are specified. The singularities of the integrand occur on the positive imaginary axis at $\beta = i\gamma n\lambda_l$, $1 \le l \le n - 1$, and are branch points or poles of order $3m$, the latter occurring for $2m$-fold degenerate eigenvalues. In certain cases, i.e., for large linear chains[1,44] and for circular chains,[45] the integral can be done by use of the residue theorem. Otherwise one must resort to numerical integration of eq 15a.

The symmetry of $\mathbf{D}(\beta) = [\mathrm{Det}(\mathbf{1}_{n-1} + (i\beta/\gamma n)\Lambda_{n-1}^{-1})]^{-3/2}$ ensures that $\mathbf{P}(s^2)$ is real.[46] Since the complex conjugate satisfies $\bar{\mathbf{D}}(\beta) = \mathbf{D}(-\beta)$, one can put

$$\mathbf{D}(\beta) = \mathbf{D}_r(\beta) + i\mathbf{D}_i(\beta) = [\mathbf{D}(\beta) + \mathbf{D}(-\beta)]/2 + i[\mathbf{D}(\beta) - \mathbf{D}(-\beta)]/2$$

to see that $\mathbf{D}_r(\beta) = \mathbf{D}_r(-\beta)$, and $\mathbf{D}_i(\beta) = -\mathbf{D}_i(-\beta)$. Only the symmetric part of the integrand of eq 15a contributes, so that

$$\mathbf{P}(s^2) = \pi^{-1} \int_0^{\infty} [\mathbf{D}_r(\beta) \cos \beta s^2 - \mathbf{D}_i(\beta) \sin \beta s^2]\,d\beta \quad (15b)$$

which can be evaluated numerically.[24-30,46-48]

Other distribution functions of interest are those giving the joint probability of several vectors that are linear combinations of the bead vectors. Let $\sigma = \mathbf{R}_c\mathbf{F}$, where $\mathbf{F}$ is an $n \times m$ matrix with constant elements comprising the coefficients f_{jk} of the linear forms

$$\sigma_{\alpha k} = \sum_{j=1}^{n} x_{\alpha j} f_{jk},\ 1 \le k \le m,\ 1 \le \alpha \le 3$$

The probability distribution of σ is obtained as

$$\mathbf{P}(\sigma)\,d\sigma = d\sigma Z^{-1}\int \delta(\sigma - \mathbf{R}_c\mathbf{F})\exp[-\gamma(\mathrm{Tr}(\mathbf{R}_c\mathbf{K}\mathbf{R}_c'))]\,d\mathbf{R}_c \tag{16}$$

by the conventions of T8. Let β be a $3 \times m$ matrix of real variables; the usual procedure gives

$$\mathbf{P}(\sigma) = [(2\pi)^{3m}Z]^{-1}\int \exp[i(\mathrm{Tr}(\sigma\beta'))]\exp[-\gamma[\mathrm{Tr}(\mathbf{R}_c\mathbf{K}\mathbf{R}_c' + i\gamma^{-1}\mathbf{R}_c\mathbf{F}\beta')]]\,d\mathbf{R}_c\,d\beta$$

Introduce normal coordinates $(0,\mathbf{Q}) = \mathbf{R}_c(n^{-1/2}\mathbf{J}',\mathbf{t}')$, and by C5 obtain

$$\mathbf{P}(\sigma) = [(2\pi)^{3m}Z]^{-1}\int \exp[i(\mathrm{Tr}(\sigma\beta'))]\exp[-\gamma(\mathrm{Tr}(\mathbf{Q}\Lambda_{n-1}\mathbf{Q}' + i\gamma^{-1}\mathbf{Q}\mathbf{t}\mathbf{F}\beta'))]\,d\mathbf{Q}\,d\beta$$

Complete the square in the second exponential [by the transformation $\mathbf{Q} = \mathbf{V} - (i/2\gamma)\beta\mathbf{F}'\mathbf{t}'\Lambda_{n-1}^{-1}$] to yield

$$\mathbf{P}(\sigma) = [(2\pi)^{3m}Z]^{-1}\int \exp[i(\mathrm{Tr}(\sigma\beta'))]\exp[-\gamma(\mathrm{Tr}(\mathbf{V}\Lambda_{n-1}\mathbf{V}' + (1/4\gamma^2)\beta\mathbf{F}'\mathbf{K}^+\mathbf{F}\beta'))]\,d\mathbf{V}\,d\beta$$

with the use of C5. Integrate over V, complete the square in β, and integrate over β to yield the following result.

Theorem 11, T11: the distribution function of $\sigma = \mathbf{R}_c\mathbf{F}$ is given by

$$\mathbf{P}(\sigma)\,d\sigma = (\gamma/\pi)^{3m/2}|\mathbf{F}'\mathbf{K}^+\mathbf{F}|^{-3/2}\exp[-\gamma(\mathrm{Tr}(\sigma(\mathbf{F}'\mathbf{K}^+\mathbf{F})^{-1}\sigma'))]\,d\sigma$$

It is of course required that $\mathrm{Rk}(\mathbf{F}) = m \le n - 1$ for the inverse $(\mathbf{F}'\mathbf{K}^+\mathbf{F})^{-1}$ and $\mathrm{Det}(\mathbf{F}'\mathbf{K}^+\mathbf{F})$ to exist. Theorem 11 is nothing other than the Wang–Uhlenbeck theorem.[31]

The remaining distribution function to be mentioned here is that of the gyration tensor, and at that I simply advise the interested reader to consult the literature[33-40] to see how this much more difficult problem is tackled.

Characteristic Function

The Fourier integral, eq 15a, gives $\mathbf{P}(s^2)\,ds^2$ in terms of the characteristic function $\mathbf{D}(\beta)$, and we can now add Theorem 12, T12: the generating function of the moments of s^2 is given by

$$\begin{aligned}\langle\exp(-as^2)\rangle_0 &= \int_0^\infty e^{-as^2}\mathbf{P}(s^2)\,ds^2 \\ &= [\mathrm{Det}(\mathbf{1}_{n-1} + (a/\gamma n)\Lambda_{n-1}^{-1})]^{-3/2} \\ &= [(a/\gamma n)\,\mathrm{Det}(\Lambda_{n-1})/\mathrm{Det}(\mathbf{K} + (a/\gamma n)\mathbf{1}_n)]^{3/2}\end{aligned}$$

The last part is easily proved:

$$\begin{aligned}\mathrm{Det}(1_{n-1} + \xi\Lambda_{n-1}^{-1}) &= \mathrm{Det}(\Lambda_{n-1}^{-1})\,\mathrm{Det}(\Lambda_{n-1} + \xi 1_{n-1}) \\ &= \mathrm{Det}\begin{bmatrix}\Lambda_{n-1} + \xi 1_{n-1} & 0 \\ 0 & \xi\end{bmatrix}[\xi\,\mathrm{Det}(\Lambda_{n-1})]^{-1} \\ &= \mathrm{Det}(\mathbf{K} + \xi 1_n)/\xi\,\mathrm{Det}(\Lambda_{n-1})\end{aligned}$$

For the first part:

$$\int_0^\infty e^{-as^2}\mathbf{P}(s^2)\,ds^2 = (2\pi)^{-1}\int_0^\infty\int_{-\infty}^\infty e^{-(a-i\beta)s^2}\mathbf{D}(\beta)\,d\beta\,ds^2 = (i/2\pi)\int_{-\infty}^\infty \frac{\mathbf{D}(\beta)}{\beta + ia}\,d\beta$$

$$a > 0$$

on interchange of the order of integrations. The pole at $\beta = -ia$ is encircled by closing the contour in the lower half-plane. Only one singularity is enclosed, since those of $\mathbf{D}(\beta)$ are on the upper half-plane. The integrand is well behaved since $\mathbf{D}(\beta) \to |\beta|^{-3(n-1)/2}$ as $|\beta| \to \infty$. The residue theorem gives $\langle\exp(-as^2)\rangle_0 = \mathbf{D}(-ia)$.

The moments of s^2 must be extracted from the cumulants since the product representation of $\mathbf{D}(-ia)$ is difficult to handle. In exponential form

$$\mathbf{D}(-ia) = \prod_{j=1}^{n-1}(1 + a/\gamma n\lambda_j)^{-3/2} = \exp[-(3/2)\sum_{j=1}^{n-1}\ln(1 + a/\gamma n\lambda_j)] = \exp[(3/2)\sum_{j=1}^{n-1}\sum_{p=1}^{\infty}(-a/\gamma n)^p\lambda_j^{-p}/p]$$

$$\langle\exp(-as^2)\rangle_0 = \exp[(3/2)\sum_{p=1}^{\infty}[(-a/\gamma n)^p/p](\mathrm{Tr}(\Lambda_{n-1}^{-p}))] \tag{17}$$

Expansion of both sides of eq 17 and comparison of coefficients of a^m gives

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = n^{-1}(\mathrm{Tr}(\Lambda_{n-1}^{-1})) = n^{-1}(\mathrm{Tr}(\mathbf{K}^+)) \tag{18a}$$

$$(\langle s^4\rangle_0 - \langle s^2\rangle_0^2)/\langle l^2\rangle_0^2 = (2/3n^2)(\mathrm{Tr}(\Lambda_{n-1}^{-2})) = (2/3n^2)(\mathrm{Tr}[(\mathbf{K}^+)^2]) \tag{19a}$$

and so on.

Another expression for $\langle s^2\rangle_0$ can be obtained from the Lagrange and Wang–Uhlenbeck theorems. The Lagrange theorem[2,49] gives

$$\langle s^2\rangle = n^{-2}\sum_{i<j}\langle(\mathbf{r}_i - \mathbf{r}_j)^2\rangle$$

and T11, the Wang–Uhlenbeck theorem, yields

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = n^{-2}\sum_{i<j}(k_{ii}^+ + k_{jj}^+ - 2k_{ij}^+) \tag{18b}$$

upon computing $\langle(\mathbf{r}_i - \mathbf{r}_j)^2\rangle_0$. In this application of T11, $\mathbf{F}'$ = (0,0, ..., 1,0, ..., 0,–1,0, ..., 0), where the +1(–1) occurs in column $i(j)$. Define $\mathbf{C}_c$ to be the incidence matrix for the complete regular graph, i.e., the graph on n vertices with every vertex connected to every other. The rows of $\mathbf{C}_c$ consist of all possible $\mathbf{F}'$ (to within an inconsequential sign), and since there are $n_p = n(n-1)/2$ pairs of vertices $\mathbf{C}_c$ is of order $n \times n_p$. The Kirchhoff matrix $\mathbf{K}_c$ for the complete graph is clearly

$$\mathbf{K}_c = \mathbf{C}_c\mathbf{C}_c' = n\mathbf{1} - \mathbf{U} = n\mathbf{E}_g \tag{20}$$

The sum in eq 18b is just

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = n^{-2}(\mathrm{Tr}(\mathbf{C}_c'\mathbf{K}^+\mathbf{C}_c)) \tag{18c}$$

as is readily seen from the structure of $\mathbf{C}_c'\mathbf{K}^+\mathbf{C}_c$. But

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = n^{-2}(\mathrm{Tr}(\mathbf{K}^+\mathbf{C}_c\mathbf{C}_c')) = n^{-1}(\mathrm{Tr}(\mathbf{K}^+\mathbf{E}_g)) = n^{-1}(\mathrm{Tr}(\mathbf{K}^+)) \tag{18d}$$

which is identical with eq 18a.

If the molecule is very large a continuous distribution of eigenvalues is appropriate. Let $x = j/n$, $n^{-1} \to dx$ and $\lambda_j \to \lambda(x)$, so that

$$\mathbf{D}(-ia) = \exp\left[-(3n/2)\int_{1/n}^{1-1/n}\ln(1 + a/\gamma n\lambda(x))\omega(x)\,dx\right]$$

where $\omega(x)$ is the degeneracy of $\lambda(x)$. A change of variables from x to λ yields

$$\mathbf{D}(-ia) = \exp\left[-(3n/2)\int_{\lambda_1}^{\lambda_{n-1}}\ln(1 + a/\gamma n\lambda)g(\lambda)\,d\lambda\right] \tag{21}$$

where $g(\lambda) = \omega(x)(d\lambda/dx)^{-1}$ is the density of eigenvalues, and $\lambda_1 = \min(\lambda_j)$ and $\lambda_{n-1} = \max(\lambda_j)$. We thus have alternative expressions for the moments:

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = \int_{\lambda_1}^{\lambda_{n-1}} \lambda^{-1} g(\lambda)\, d\lambda \qquad (18e)$$

$$(\langle s^4\rangle_0 - \langle s^2\rangle_0{}^2)/\langle l^2\rangle_0{}^2 = (2/3n)\int_{\lambda_1}^{\lambda_{n-1}} \lambda^{-2} g(\lambda)\, d\lambda \qquad (19b)$$

and so on. One must expect that the uncritical passage to the continuum contained in eq 21 will at times be incorrect. This is apparently the case when $g(\lambda)$ is singular and is perhaps worrisome for other pathologies of $g(\lambda)$.[50]

The theory of the viscoelasticity of molecules in either the free-draining[51] or screened[52] limits proceeds simply, according to the methods of Rouse[6] and Zimm,[51] to give relaxation times inversely proportional to the nonzero eigenvalues of **K**. Let $\tau_j = \alpha/\lambda_j$, where α = (constant)$f\cdot\langle l^2\rangle_0/kT$, where f is the friction factor for a bead (all beads are here assumed to have the same friction factor), and kT has the usual significance. The stress relaxation modulus[53] is given by

$$\mathbf{G}(t) = \sum_j \mathbf{G}_j \exp(-t/\tau_j) = \mathbf{G}_0 \sum_j \exp(-t/\tau_j)$$

for a discrete spectrum, the last form resulting when $\mathbf{G}_0 = \mathbf{G}_j$ for all j. One can express $\mathbf{G}(t)$ in terms of the spectral density by

$$\mathbf{G}(t) = n\mathbf{G}_0 \int_{\lambda_1}^{\lambda_{n-1}} \exp(-\lambda t/\alpha) g(\lambda)\, d\lambda \qquad (22a)$$

and then in terms of $\tau = \alpha/\lambda$ by

$$\mathbf{G}(t) = n\mathbf{G}_0 \int_{-\infty}^{\infty} \exp(-t/\tau)(\alpha/\tau) g(\alpha/\tau)\, d \ln \tau \qquad (22b)$$

where $g(\lambda)$ is assumed to vanish outside the interval $\lambda_1 \leq \lambda \leq \lambda_{n-1}$. Equation 22b may be compared with the usual formulation[53]

$$\mathbf{G}(t) = \int_{-\infty}^{\infty} \exp(-t/\tau)\mathbf{H}(\tau)\, d \ln \tau$$

in terms of the contribution $\mathbf{H}(\tau)\, d \ln \tau$ to the stress relaxation from processes relaxing between $\ln \tau$ and $\ln \tau + d \ln \tau$, to give

$$\mathbf{H}(\tau) = \mathbf{H}(\alpha/\lambda) = n\mathbf{G}_0 \lambda g(\lambda) \qquad (23)$$

This intimate relation between viscoelasticity and the equilibrium distribution functions naturally arises from the underlying quadratic potential.

The spectral density $g(\lambda)\, d\lambda$ can be evaluated[54] as

$$g(\lambda) = (1/\pi n) \lim_{\epsilon \to 0_+} \operatorname{Im} \frac{d}{d\lambda} \operatorname{Det}(\lambda - i\epsilon - \mathbf{K}) \qquad (24)$$

where n is large so that the contribution from the zero eigenvalue of **K** is negligible. Equation 24 is useful if the molecule possesses sufficient regularity to render the derivative and limiting process tractable.

Evaluation of Matrices and Functions

The construction of $\mathbf{K}^+$ can be accomplished directly without inversion in some cases, as mentioned in C5. Linear equations for the matrix elements of $\mathbf{K}^\# = (\mathbf{K}^\#)'$ can be constructed from $\mathbf{K}^\#\mathbf{K} = \mathbf{K}\mathbf{K}^\# = 1 - n^{-1}\mathbf{U}$, and these can sometimes be solved upon setting $k_{11}{}^\# = 0$. The four-condition inverse $\mathbf{K}^+$ is obtained as $\mathbf{K}^+ = \mathbf{K}^\# + a\mathbf{U}$, where a is chosen so that $\mathbf{K}^+\mathbf{J}' = 0$. This procedure works for the linear and circular chain but is difficult to apply for more complicated molecules.

The most direct method for producing $\mathbf{K}^+$ for simple molecules is to use C6. Inverses of two $m \times m$ tridiagonal matrices occur in many cases, and for convenience they are given here:

$$\mathbf{A}_1 = \begin{bmatrix} 2 & -1 & 0 & \cdot & \cdot & \cdot & 0 \\ -1 & 2 & -1 & 0 & & & \cdot \\ 0 & -1 & 2 & -1 & \cdot & \cdot & \cdot \\ \cdot & 0 & & & 0 & \cdot & \\ \cdot & & & & -1 & 0 & \\ \cdot & & & -1 & 2 & -1 & \\ 0 & \cdot & \cdot & \cdot & 0 & -1 & 1 \end{bmatrix};$$

$$\mathbf{A}_1{}^{-1} = [a_{1,ij}{}^{-1}];\ a_{1,ij}{}^{-1} = \min(i,j) \qquad (25)$$

$$\mathbf{A}_2 = \mathbf{A}_1 + \operatorname{Diag}(0, 0, \ldots, 0, 1);\ \mathbf{A}_2{}^{-1} = [a_{2,ij}{}^{-1}];$$

$$a_{2,ij}{}^{-1} = \min(i,j) - ij/(m+1) \qquad (26)$$

The generalized inverse $\mathbf{K}^+$ for the linear chain of n beads is given by

$$\mathbf{K}^+ = \mathbf{E}_g \begin{bmatrix} 0 & 0 \\ 0 & \mathbf{A}_1{}^{-1} \end{bmatrix} \mathbf{E}_g = \mathbf{E}_g \mathbf{K}^* \mathbf{E}_g$$

and application of eq 18d yields

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = n^{-1}(\operatorname{Tr}(\mathbf{E}_g\mathbf{K}^*\mathbf{E}_g)) = n^{-1}(\operatorname{Tr}(\mathbf{K}^*\mathbf{E}_g)) = n^{-1}(\operatorname{Tr}(\mathbf{A}_1{}^{-1})) - n^{-2}\mathbf{J}_{n-1}\mathbf{A}_1{}^{-1}\mathbf{J}_{n-1}{}' = n^{-1}[n(n-1)/2] - n^{-2}[n(n-1)(2n-1)/6] = (n/6)(1 - 1/n^2) \qquad (27)$$

For the circular chain $\mathbf{K}^*$ is given in terms of $\mathbf{A}_2{}^{-1}$, and one can verify[45] that

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = (n/12)(1 - 1/n^2) \qquad (28)$$

As a last example of these calculations consider a v-branch star with arms of m_i beads, $1 \leq i \leq v$; $\mathbf{K}^*$ is a direct sum of v matrices of the type $\mathbf{A}_1{}^{-1}$, each of order $m_i \times m_i$. The mean-square radius of gyration is easily obtained from eq 27 upon inspecting the structure of the direct sum and is

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = n^{-1}\sum_{i=1}^{v}[m_i(m_i-1)/2 - n^{-1}m_i(m_i-1)(2m_i-1)/6] \qquad (29a)$$

where

$$n = 1 + \sum_{i=1}^{v} m_i$$

If all chains are the same length, and $m = m_i \gg 1$, eq 29a simplifies to

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = (m/2)(1 - 2/3v) \qquad (29b)$$

and the ratio g of $\langle s^2\rangle_0$ for the star to $\langle s^2\rangle_0$ for the linear chain with the same number of beads is

$$g = (3 - 2/v)/v \qquad (30)$$

For more highly ramified molecules that are yet represented as trees, the method of Zimm and Stockmayer[55,56] is to be preferred over that just described for the calculation of $\langle s^2\rangle_0$. Advantages in the matrix formulation become fully evident upon consideration of the characteristic function and higher moments of s^2, especially for molecules with circuits.

Upon application of T12 to the calculation of the characteristic function $\mathbf{D}(\beta)$ for a variety of molecules, one makes frequent use of two determinants:

$$\operatorname{Det}(\mathbf{A}_1 + \xi 1) = \mathbf{V}_m(\cos\theta) = \frac{\cos(m + 1/2)\theta}{\cos\theta/2},\ \xi = -2 + 2\cos\theta \qquad (31)$$

$$\mathrm{Det}(\mathbf{A}_2 + \xi\mathbf{1}) = \mathbf{U}_m(\cos\theta) = \frac{\sin(m+1)\theta}{\sin\theta}, \quad \xi = -2 + 2\cos\theta \quad (32)$$

The angle θ is in general complex. The following identities may be verified by elementary trigonometry or by use of recurrence relations for Chebyshev polynomials:

$$\mathbf{V}_m = 2\cos\theta\mathbf{V}_{m-1} - \mathbf{V}_{m-2} \quad (33a)$$

$$\mathbf{U}_m = 2\cos\theta\mathbf{U}_{m-1} - \mathbf{U}_{m-2} \quad (33b)$$

$$\mathbf{U}_m - \mathbf{U}_{m-1} = \mathbf{V}_m \quad (33c)$$

$$\mathbf{V}_m - \mathbf{V}_{m-1} = \xi\mathbf{U}_{m-1} \quad (33d)$$

$$\mathbf{V}_{p+1}\mathbf{V}_q - \mathbf{V}_p\mathbf{V}_{q-1} = \xi\mathbf{U}_{p+q} \quad (33e)$$

Given a molecular graph it is not difficult to construct the characteristic function. If the molecule does not contain any v_i with $\delta_i > 2$, select one vertex as the root and label this vertex v_1; if the molecule has μ vertices with $\delta_i > 2$, label these multifunctional junctions with $v_1, v_2, \ldots, v_\mu$, preferably in a natural rather than a random sequence. The following algorithm has been given before[57] and is included here for completeness: (1) Construct the $\mu \times \mu$ matrix $\mathrm{Diag}(\delta_i + \xi)$. (ii) Subtract $\mathbf{U}_{m-1}/\mathbf{U}_m$ from the α, α and β, β elements and subtract $1/\mathbf{U}_m$ from the α, β and β, α elements if a chain of m beads ($m + 1$ bonds) joins vertices v_α and v_β. (iii) Subtract $\mathbf{V}_{m-1}/\mathbf{V}_m$ from the α, α element if a dangling (one free end) chain of m beads (m bonds) is jointed to v_α. (iv) Subtract $2(1 + \mathbf{U}_{m-1})/\mathbf{U}_m$ from the α, α element if a loop of m beads ($m + 1$ bonds) is attached to v_α. (v) Multiply the determinant of the variable Kirchhoff matrix (for the reduced graph) that has just been constructed by

$$\prod_i \mathbf{V}_{m_i} \prod_j \mathbf{U}_{m_j}$$

where there is one $\mathbf{V}_{m_i}(\mathbf{U}_{m_j})$ for each monovalent (bivalent) chain of $m_i(m_j)$ beads in the molecule.

In the above, the arguments of $\mathbf{U}_m$ and $\mathbf{V}_m$ are both $\cos\theta = 1 + \xi/2$. It should also be mentioned that if two or more chains attach to a pair of vertices their contributions are additive.

The algorithm may be applied to the linear chain, where one end has been selected as the root. We have

$$\xi^{-1}\,\mathrm{Det}(\mathbf{K} + \xi\mathbf{1}) = (1 + \xi - \mathbf{V}_{n-2}/\mathbf{V}_{n-1})\mathbf{V}_{n-1}/\xi = ((2+\xi)\mathbf{V}_{n-1} - \mathbf{V}_{n-2} - \mathbf{V}_{n-1})/\xi = \mathbf{U}_{n-1} \quad (34)$$

by use of eq 33a and 33d. It is unnecessary to compute $\mathrm{Det}(\Lambda_{n-1})$, since $\mathbf{D}(0) = 1$ suffices to provide the normalization. Hence[1,45,46]

$$\mathbf{D}(\beta) = \left(\frac{\sin n\theta}{n\sin\theta}\right)^{-3/2}, \qquad \cos\theta = 1 + i\beta/2\gamma n \quad (35)$$

is the characteristic function for the linear chain. Similarly, for the circular chain[45]

$$\xi^{-1}\,\mathrm{Det}(\mathbf{K} + \xi\mathbf{1}) = [2 + \xi - 2(1 + \mathbf{U}_{n-2})/\mathbf{U}_{n-1}]\mathbf{U}_{n-1}/\xi = (\mathbf{U}_n - \mathbf{U}_{n-2} - 2)/\xi = (\mathbf{V}_n + \mathbf{V}_{n-1} - 2)/\xi = \left[\frac{\sin n\theta/2}{\sin\theta/2}\right]^2$$

and

$$\mathbf{D}(\beta) = \left[\frac{\sin n\theta/2}{n\sin\theta/2}\right]^{-3}, \qquad \cos\theta = 1 + i\beta/2\gamma n \quad (36)$$

The v-branch star with uniform arms is neatly summarized in[26-30,35,58]

$$\xi^{-1}\,\mathrm{Det}(\mathbf{K} + \xi\mathbf{1}) = (v + \xi - v\mathbf{V}_{m-1}/\mathbf{V}_m)\mathbf{V}_m{}^v/\xi = [(v-2)\xi\mathbf{U}_{m-1} + \mathbf{V}_{m+1} - \mathbf{V}_{m-1}]\mathbf{V}_m{}^{v-1}/\xi = [(v-1)\mathbf{V}_{m-1} + \mathbf{U}_m]\mathbf{V}_m{}^{v-1}$$

so that finally

$$\mathbf{D}(\beta) = [(v\mathbf{U}_{m-1} + \mathbf{V}_m)\mathbf{V}_m{}^{v-1}/(1 + vm)]^{-3/2} \quad (37)$$

The reader is encouraged to extend this list of known characteristic functions by calculating $\mathbf{D}(\beta)$ for molecules shaped like 8 and γ. Combs are of considerable importance for the representation of graft copolymers; the intricate calculation of their characteristic functions has been achieved by Šolc.[35] Another interesting molecule is the regular tree of m generations, which can also be called a finite Bethe lattice. All junctions have valence v except for those of the mth generation, which have valence 1. The determinant

$$\xi^{-1}\,\mathrm{Det}(\mathbf{K} + \xi\mathbf{1}) = \prod_{k=1}^{m} \mathbf{B}_k{}^{\alpha_k} \quad (38a)$$

where

$$\mathbf{B}_k = (v-1)^{k/2}\mathbf{U}_k - (v-1)^{(k+1)/2}\mathbf{U}_{k-1}, \qquad 1 \le k \le m$$

$$\mathbf{B}_k = (v-1)^{m/2}(\mathbf{U}_m - (v-1)^{-1}\mathbf{U}_{m-2}) - (v-1)^{(m+1)/2}(\mathbf{U}_{m-1} - (v-1)^{-1}\mathbf{U}_{m-3}), \qquad k = m \quad (38b)$$

and

$$\alpha_k = 1, \qquad k = m$$

$$\alpha_k = v - 1, \qquad k = m - 1 \quad (38c)$$

$$\alpha_k = v(v-1)^{m-2-k}(v-2), \qquad k < m - 1$$

In this case as before $\mathbf{U}_k = \mathbf{U}_k(\cos\theta)$, but now

$$\cos\theta = (v + \xi)/2(v-1)^{1/2} \quad (38d)$$

and the total number of junctions is $[v(v-1)^{m-1} - 2]/(v-2)$. (The calculation is done by writing $\mathbf{K}$ in block tridiagonal form, where the off-diagonal blocks are of order $1 \times v$, $v \times v(v-1)$, $v(v-1) \times v(v-1)^2$, etc. Elementary row or column operations beginning with the last yields a continued fraction representation of $\mathrm{Det}(\mathbf{K} + \xi\mathbf{1})$, which can then be simplified to the form given.[59])

Finally, the spectrum of $\mathbf{K}$ for an infinitely large and randomly selected regular graph of degree v has been obtained by McKay.[60] He finds

$$g(\lambda) = \frac{v[\lambda(2v-\lambda) - (v-2)^2]^{1/2}}{2\pi\lambda(2v-\lambda)}, \qquad v - 2(v-1)^{1/2} \le \lambda \le v + 2(v-1)^{1/2} \quad (39a)$$

$$g(\lambda) = 0, \qquad \text{otherwise} \quad (39b)$$

(For $v = 2$ this spectral density reduces correctly to that for a large circular chain.) The determinant required for $\mathbf{D}(\beta)$ is obtained as

$$\xi^{-1}\,\mathrm{Det}(\mathbf{K} + \xi\mathbf{1}) = \prod_{k=1}^{n-1}(\lambda_k + \xi) = \exp\left(n\int \ln(\xi + \lambda)g(\lambda)\,d\lambda\right)$$

by arguments similar to those leading to eq 21. A change

of variables to $\lambda = v - 2(v-1)^{1/2}\cos\omega$ gives

$$\int \ln(\xi+\lambda)g(\lambda)\,d\lambda = \frac{v}{2\pi}\int_0^{\pi} \frac{\ln(\xi + v - 2(v-1)^{1/2}\cos\omega)\sin^2\omega\,d\omega}{[(v-2)/2(v-1)^{1/2}]^2 + \sin^2\omega} \quad (40)$$

The integral can be computed to within a complex constant by evaluating

$$\int \ln(\xi+\lambda)g(\lambda)\,d\lambda = \int d\xi \int \frac{g(\lambda)}{\xi+\lambda}\,d\lambda$$

and the constant can be fixed by demanding that $\mathbf{D}(0) = 1$. This procedure, together with series expansion, or direct evaluation of eq 18e, gives

$$\langle s^2\rangle_0/\langle l^2\rangle_0 = (v-1)/v(v-2) \quad (41)$$

The integration in eq 40 is somewhat tedious, and the resulting equation is lengthy, so it is not displayed here.

The integral in eq 40 has recently been evaluated directly by B. D. McKay for ξ lying outside the interval where $g(\lambda) \neq 0$. His result will yield the number of spanning trees on regular random graphs provided the passage to the integral is justified.

It may have been noticed that the mean square radius of gyration in eq 41 is unphysical in the extreme; it is a manifestation of the now well known collapse of Gaussian networks. However, it is necessary to qualify eq 39–41 as unphysical from the beginning. McKay's theory, which is the first real advance in understanding the properties of large random nets, is based upon the fact (discovered independently by McKay[60] and Wormald[61]) that the number of circuits C_k of k edges in large random graphs is independent of the number of vertices. Any real net is constrained at the time of formation so as to favor the linking of spatial neighbors. In the set of all graphs, those which are constrained are incommensurate with those that are not. To make physically realistic nets one must introduce spatial constraints at the time of formation. Computer calculations based upon this principle will soon be published; it suffices here to note that the spectral density of $\mathbf{K}$ is weighted heavily on small eigenvalues for $v < 5$ and that the minimum nonzero eigenvalue goes to zero as $n^{-0.40}$ as $n \to \infty$ for all v. This tempers the collapse but does not prevent it.

The above mentioned characteristic functions that reduce to standard special functions are of interest primarily because they hasten numerical computations. Evaluation of $\mathbf{P}(s^2)\,ds^2$ is usually accomplished by numerical integration, the exceptions to date being for the linear and circular chains, in the hands of Fujita and Norisuye[44] and Šolc,[45] respectively. The results of numerical quadrature can usually be expressed by a function of the form[47,48]

$$\langle s^2\rangle_0\mathbf{P}(t)\,dt = A[1+\exp(a/t^{\beta})]^{-1}t^{(3\omega_1/2)-1}\exp(-n\gamma\lambda_1\langle s^2\rangle_0 t)\,dt \quad (42)$$

where $t = s^2/\langle s^2\rangle_0$, ω_1 is the degeneracy of the minimum nonzero eigenvalue λ_1, and a and β are fitted parameters. The constant A normalizes the function and is not independent of other parameters. If eq 42 has any merit it is in accuracy and in the relative ease of manipulation in applications. For example, if $\mathbf{D}(\beta)$ is a simple function, the numerical quadrature in eq 15b can be done with a small computer by standard interpolation methods for only a few values of t in the range 0.8–1.2, and eq 42 is certainly not difficult to evaluate for various values of A, a, and β so as to fit the results of the quadratures.

The molecules for which distribution functions $\mathbf{P}(s^2)\,ds^2$ have been evaluated to date are (1) linear, (2) circular, (3) stars, and (4) random regular nets. The general feature that has emerged is that $\mathbf{P}(t)\,dt$ tends to become narrower as the complexity of the molecule increases. The mean square radius of gyration $\langle s^2\rangle_0/\langle l^2\rangle_0$ seems never to exceed the diameter[5] of the molecular graph and may be much smaller if the molecule has many circuits. The density of small eigenvalues of $\mathbf{K}$ must be large if $\langle s^2\rangle_0$ is to assume large values. For linear and circular chains the spectral density varies as $\lambda^{-1/2}$ for small λ (in the large n limit); for random regular nets there are no small eigenvalues. The presence of small eigenvalues implies that the molecule has long relaxation and retardation times.

Applications

The distribution functions that have been discussed form the basis for further elaboration to experimental observables. For example, the scattering function is the Fourier transform of the pair correlation function, and by T11 both functions are determined by the elements of the generalized inverse of $\mathbf{K}$. This applies, of course, only to Θ conditions. If excluded volume interactions perturb the pair distribution in a way that the simple scaling $\langle s^2\rangle = \alpha^2\langle s^2\rangle_0$ does not encompass, then the difficulties for analysis mount rapidly.

The excluded volume expansion factor $\alpha^2 = \langle s^2\rangle/\langle s^2\rangle_0$ can be calculated by the following relatively simple method. First-order perturbation theory gives[62-64]

$$\alpha^2 - 1 = \frac{X(\gamma/\pi)^{3/2}\langle l^2\rangle_0}{n\langle s^2\rangle_0}\sum_{i<j} g_{ij}^{-5/2}h_{ij} \quad (43)$$

where

$$g_{ij} = k_{ii}^{+} + k_{jj}^{+} - 2k_{ij}^{+}$$
$$h_{ij} = k_{ii}^{2+} + k_{jj}^{2+} - 2k_{ij}^{2+} \quad (44)$$

with elements k_{ij}^{+} from the generalized inverse $\mathbf{K}^{+}$ and k_{ij}^{2+} from the square $(\mathbf{K}^{+})^2$. The binary cluster integral X is defined by Fixman[62] and is evaluated by Yamakawa[63] so as to be compatible with Flory's theory. If one now uses the Flory–Fisk[65] theory to formulate

$$\alpha^2 = \frac{\int_0^{\infty} s^2\mathbf{P}(s^2)\exp(-A/s^3)\,ds^2}{\langle s^2\rangle_0\int_0^{\infty}\mathbf{P}(s^2)\exp(-A/s^3)\,ds^2} \quad (45)$$

with the constant A fixed by means of eq 43, then α^2 can be determined numerically for all values of X and n. In eq 45 the unperturbed distribution function $\mathbf{P}(s^2)\,ds^2$ may be represented by eq 42 for ease of numerical evaluation.

Use of the Gaussian model for other types of calculations is straightforward. The hydrodynamic radius in the nondraining limit is determined by[63,65]

$$\sum_{i<j}\langle|\mathbf{r}_i - \mathbf{r}_j|^{-1}\rangle = \sum_{i<j} 2(\gamma/\pi g_{ij})^{1/2}$$

with the use of T11 and the definition of g_{ij} in eq 44. In the Zimm theory of dynamics[51] the full $\mathbf{H}$ matrix with off-diagonal elements proportional to $g_{ij}^{-1/2}$ is required, and the Rouse–Zimm matrix is replaced by the Kirchhoff matrix $\mathbf{K}$. Clearly, the whole of linear chain theory generalizes upon replacing the Rouse–Zimm matrix by its generalization, the Kirchhoff matrix.

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