Distribution functions for Gaussian molecules. II. Reduction of the Kirchhoff matrix for large molecules

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Distribution functions for Gaussian molecules. II. Reduction of the Kirchhoff matrix for large molecules

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The eigenvalues of the Kirchhoff matrix for a molecule consisting of m chains and μ multifunctional junctions can be calculated from a reduced matrix of dimension $\mu \times \mu$. Many of the eigenvalues for complicated molecules can be obtained exactly, and the remainder are accessible by numerical methods. We find small eigenvalues for trifunctional networks which can be associated with very slowly relaxing oscillations in gels. In addition, networks have μ high frequency modes, which are located in unique regions of the spectrum.

I. INTRODUCTION

Calculation of the distribution function of the radius of gyration of an arbitrary Gaussian molecule depends upon the eigenvalue spectrum of the Kirchhoff matrix that describes the molecular connectivity.[1-5] The same is true of the distribution function of the inertial tensor.[5-8] The distribution functions of the radius of gyration described in the previous paper[9] (hereafter referred to as I) were all done for relatively small molecules, consisting of no more than $n \cong 60$ nodes or beads. For relatively small values of n, the distribution functions for linear and circular chains and for stars with only a few branches have essentially converged to the asymptotic limit. The same can be said for networks, provided it is recognized that the computations in I have been done without regard for interjunction chains. Thus, if the molecule of interest is not too complex, its Kirchhoff matrix may be generated directly in the computer; matrix diagonalization followed by numerical quadrature yields its distribution function without exhausting computer resources.

For molecules of high complexity this cannot be done. For illustrative purposes, suppose that one is interested in random nets of 50 four-valent nodes connected to one another by $100 = 50 \times 4/2$ chains of 50 nodes each. Presumably, these are sufficiently long chains and large number of multifunctional junctions to approach the asymptotic limit. Altogether, there are 5050 nodes, requiring about 12.7×10^6 storage locations for the Kirchhoff matrix alone. Since our aim is to understand the properties of networks, including interjunction chains, it is clearly necessary to reduce the Kirchhoff matrix to manageable size. The method by which this can be accomplished will be described here.

II. CONSTRUCTION OF THE KIRCHHOFF MATRIX

The chains in a complex molecule are either bonded at both ends to multifunctional junctions, as is indicated in Fig. 1(a), or are bonded only at one end, as in Fig. 1(b). The nodes of these chains have valence, or functionality $f \leq 2$. The remaining nodes in the molecule have functionality $f > 2$. Label the multifunctional junctions with the numbers $1, 2, \ldots, \mu$ in any order. Next, label the nodes on a-type chains in sequential order, but without restrictions on the order of the chains. Finally, label the nodes on b-type chains from the junctions to the free ends. The last label will be N, and there are $N - \mu$ beads on chains.

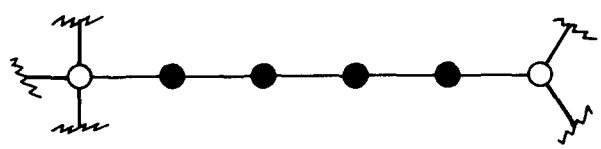
With this labelling scheme, the Kirchhoff matrix $\mathbf{K}$ is written in the block form ($\mathbf{C}'$ is the transpose of $\mathbf{C}$)

$$\mathbf{K} = \begin{bmatrix} \mathbf{F} & -\mathbf{C}_2 & -\mathbf{C}_1 \\ -\mathbf{C}_2' & \mathbf{A} & 0 \\ -\mathbf{C}_1' & 0 & \mathbf{B} \end{bmatrix}$$

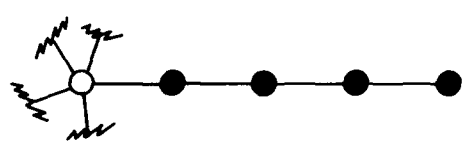
where the blocks are described as follows:

A: A direct sum of matrices $\mathbf{A}(n_i)$, $1 \leq i \leq N_a$, where n_i is the number of vertices on the ith chain of type a; there are N_a chains of this type. Each matrix has the structure

$$\mathbf{A}(n_i) = \begin{bmatrix} 2 & -1 & 0 & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ -1 & 2 & -1 & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ 0 & -1 & 2 & -1 & 0 & \cdot & \cdot & \cdot & 0 \\ \vdots & & & & & & & & \vdots \\ & & & & \cdot & \cdot & -1 & 2 & -1 \\ 0 & \cdot & \cdot & \cdot & \cdot & \cdot & 0 & -1 & 2 \end{bmatrix},$$



a



b

FIG. 1. Subgraphs illustrating the two types of chains found in networks. Type a chains are connected to multifunction junctions at both ends. This class includes loops. Type b chains are attached at only one end.

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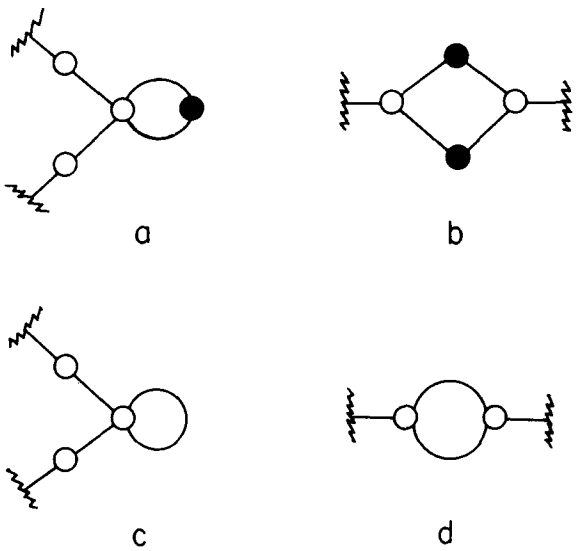

FIG. 2. Structures allowed in the algorithm are a and b. Structures c and d are disallowed, not because they cannot be accommodated, but because they are deemed physically unrealistic.

and by itself is not a Kirchhoff matrix, since the sums of elements in the first and last rows are not zero. The dimension of $\mathbf{A}(n_i)$ is $n_i \times n_i$.

B: The direct sum of matrices $\mathbf{B}(n_j)$, $1 \leq j \leq N_b$, where n_j is the number of nodes on the jth chain (N_b chains in all) of type b. Each of these matrices has a form like $\mathbf{A}(n_i)$, except that the last diagonal element is 1 instead of 2.

$\mathbf{C}_1$: This is a vectorlike sum of matrices whose role is to connect b-type chains to multifunctional junctions. There is a single nonzero element of unity in the first column of each of the $\mu \times n_j$ submatrices of

$$\mathbf{C}_1 = [\mathbf{C}(n_1), \mathbf{C}(n_2), \ldots, \mathbf{C}(n_{N_b})].$$

The $\mathbf{C}(n_j)$ conform with $\mathbf{F}$ (number of rows) and with $\mathbf{B}(n_j)$ (number of columns).

$\mathbf{C}_2$: Constructed like $\mathbf{C}_1$, except that each of the $\mathbf{C}(n_i)$ has two nonzero elements; there is a 1 in both the first and last columns which serves to connect both ends of an a-type chain to the appropriate junctions.

F: The diagonal elements of this matrix are the integral values of the functionality of each of the $f > 2$ vertices. Most of the off-diagonal elements of $\mathbf{F}$ will be zero. That is, the α,β element of $\mathbf{F}$ may equal -1 only if two multiple junctions are directly connected by a single bond.

The matrix $\mathbf{K}$ constructed in this fashion describes a molecule with no double edges or loops consisting of a single bond. Since the intention is to represent the structure of a real molecule in the Gaussian approximation as accurately as possible, it seems that such defect structures should be excluded. The scheme described encompasses graphs such as Figs. 2(a) and 2(b), but excludes Figs. 2(c) and 2(d). (Structures of type 2c simply reduce f by two, and those of type 2d can be handled by placing -2 in the α,β element of F. These are trivial elaborations which need not be of further concern.)

III. THE SECULAR EQUATION

To simplify the following discussion, let $[\mathbf{C}_2, \mathbf{C}_1] = \mathbf{C}$ and

$$\mathbf{A} = \begin{bmatrix} \mathbf{A} & 0 \\ 0 & \mathbf{B} \end{bmatrix},$$

so that

$$\mathbf{K} = \begin{bmatrix} \mathbf{F} & -\mathbf{C} \\ -\mathbf{C}' & \mathbf{A} \end{bmatrix}.$$

The eigenvalues λ_l, $1 \leq l \leq N$ of $\mathbf{K}$ are the solutions of the determinantal equation

$$|\mathbf{K} - \lambda \mathbf{1}_N| = 0, \tag{1}$$

where $\mathbf{1}_N$ is the identity of rank N. Let $\mathbf{F}_\lambda = \mathbf{F} - \lambda \mathbf{1}_\mu$ and $\mathbf{A}_\lambda = \mathbf{A} - \lambda \mathbf{1}_{N-\mu}$. It is easily seen that,

$$|\mathbf{K} - \lambda \mathbf{1}_N| = \begin{bmatrix} \mathbf{F}_\lambda & -\mathbf{C} \\ -\mathbf{C}' & \mathbf{A}_\lambda \end{bmatrix} = \left| \begin{bmatrix} 1 & \mathbf{C}\mathbf{A}_\lambda^{-1} \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{F}_\lambda & -\mathbf{C} \\ -\mathbf{C}' & \mathbf{A}_\lambda \end{bmatrix} \right|,$$

$$= \begin{vmatrix} \mathbf{F}_\lambda - \mathbf{C}\mathbf{A}_\lambda^{-1}\mathbf{C}' & 0 \\ -\mathbf{C}' & \mathbf{A}_\lambda \end{vmatrix} = |\mathbf{F}_\lambda - \mathbf{C}\mathbf{A}_\lambda^{-1}\mathbf{C}'|\,|\mathbf{A}_\lambda| = 0, \tag{2}$$

since $\mathbf{A}_\lambda$ is nonsingular for at least some values of λ (as will be shown), and can therefore be inverted. Hence, the $N \times N$ determinant has been reduced to a product of a $\mu \times \mu$ determinant $|\mathbf{F}_\lambda - \mathbf{C}\mathbf{A}_\lambda^{-1}\mathbf{C}'|$ with

$$|\mathbf{A}_\lambda| = \prod_i |\mathbf{A}_\lambda(n_i)| \prod_j |\mathbf{B}_\lambda(n_j)|. \tag{3}$$

All that remains to be done in a formal sense is to invert $\mathbf{A}_\lambda$ and compute its determinant as Eq. (3) indicates. The constituent determinants in Eq. (3) will be considered first. Expansion of the determinant

$$A_n = |\mathbf{A}_\lambda(n)| = |\mathbf{A}(n) - \lambda \mathbf{1}_n|$$

$$= \begin{vmatrix} 2-\lambda & -1 & 0 & \cdot & \cdot & 0 \\ -1 & 2-\lambda & -1 & & & \cdot \\ 0 & -1 & & & & 0 \\ & & & & 2-\lambda & -1 \\ 0 & 0 & \cdot & \cdot & -1 & 2-\lambda \end{vmatrix},$$

by the first row gives

$$A_n = (2-\lambda)A_{n-1} - A_{n-2}, \tag{4}$$

with $A_0 = 1$, $A_1 = 2 - \lambda$. The solution of this recurrence relation is

$$A_n = \sin(n+1)\theta/\sin\theta, \qquad \lambda = 4\sin^2\theta/2. \tag{5}$$

This function is otherwise known as the Chebyshev polynomial $U_n(\cos\theta)$. Similar treatment of $B_n = |\mathbf{B}_\lambda(n)|$ gives

$$B_n = (2-\lambda)B_{n-1} - B_{n-2}, \tag{6}$$

with $B_0 = 1$, $B_1 = 1 - \lambda$. The solution of Eq. (6) is

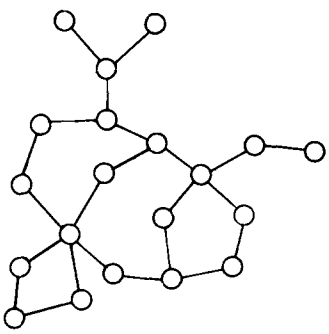

FIG. 3. A general graph containing doubly connected nodes, loops, circuits, and dangling ends.

$$B_n = \cos(n+\tfrac{1}{2})\theta/\cos\theta/2\,, \qquad \lambda = 4\sin^2\theta/2\,. \tag{7}$$

If $\theta = l\pi/(n+1)$, A_n vanishes, and if $\theta = (2l+1)\pi/(2n+1)$, B_n vanishes, where l is an integer; for these values of θ the matrix $\mathbf{A}_\lambda$ cannot be inverted. However, for all other θ the inverse does exist, and it is always possible to approach singular points after inversion.

The inverses of $\mathbf{A}_\lambda(n_i)$ and $\mathbf{B}_\lambda(n_j)$ are not required, since one need only compute

$$\mathbf{C}\mathbf{A}_\lambda^{-1}\mathbf{C}' = \sum_i \mathbf{C}_2(n_i)\mathbf{A}_\lambda^{-1}(n_i)\mathbf{C}_2'(n_i) + \sum_j \mathbf{C}_1(n_j)\mathbf{B}_\lambda^{-1}(n_j)\mathbf{C}_1'(n_j)\,, \tag{8}$$

owing to the structure of $\mathbf{C}$ and $\mathbf{A}_\lambda$. The elements $c_{\alpha\beta}$ of $\mathbf{C}_2(n_i)$ may be written,

$$c_{\alpha\beta} = \delta_{\sigma\alpha}\delta_{1\beta} + \delta_{\rho\alpha}\delta_{n\beta}\,, \tag{9}$$

where σ is the label of the $f>2$ vertex attached to the front end (vertex 1) of chain i, and ρ is the label of that attached to the back end (vertex n_i). The elements of

$$[\mathbf{C}_2(n_i)\mathbf{A}_\lambda^{-1}(n_i)\mathbf{C}_2'(n_i)]_{\alpha\beta} = \delta_{\sigma\alpha}(\delta_{\sigma\beta}a_{11}^{-1} + \delta_{\rho\beta}a_{1n}^{-1}) + \delta_{\rho\alpha}(\delta_{\sigma\beta}a_{n1}^{-1} + \delta_{\rho\beta}a_{nn}^{-1})\,, \tag{10a}$$

where a_{ij}^{-1} is the i,j element of $\mathbf{A}_\lambda^{-1}(n_i)$. There are only four nonzero elements in the matrix, and they are located at the intersections of rows and columns σ and ρ.

The inverse elements a_{ij}^{-1} are easily obtained as the ratio of the cofactor of a_{ij} to the determinant A_n. They are given by

$$\begin{aligned} a_{11}^{-1} &= a_{nn}^{-1} = A_{n-1}/A_n = \sin n\theta/\sin(n+1)\theta\,, \\ a_{1n}^{-1} &= a_{n1}^{-1} = 1/A_n = \sin\theta/\sin(n+1)\theta\,. \end{aligned} \tag{10b}$$

Eq. (10a) includes the case of a loop, such as in Fig. 2(a). There is a single nonzero element on the diagonal at location σ,σ with value $2(a_{11}^{-1} + a_{1n}^{-1})$ for these structures.

A similar treatment of the terms involving $\mathbf{B}_\lambda^{-1}(n_j)$ in Eq. (8) gives

$$[\mathbf{C}_1(n_j)\mathbf{B}_\lambda^{-1}(n_j)\mathbf{C}_1'(n_j)]_{\alpha\beta} = \delta_{\sigma\alpha}\delta_{\sigma\beta}b_{11}^{-1}\,, \tag{11a}$$

where the free-ended chain is attached to node σ. These matrices contain a single nonzero element on the diagonal at σ,σ with value

$$b_{11}^{-1} = \cos(n-1/2)\theta/\cos(n+1/2)\theta\,. \tag{11b}$$

All the ingredients are now available to construct the reduced Kirchhoff matrix $\mathbf{F}_\lambda - \mathbf{C}\mathbf{A}_\lambda^{-1}\mathbf{C}'$. The simple rules for doing so are contained in the next section.

IV. ALGORITHM

Consider the graph shown in Fig. 3 to represent a Gaussian molecule in all details. It consists of $\mu = 4$ multifunctional junctions of various valencies, as well as connecting chains of various structure. The determinant for solution of the eigenvalue problem is formulated in general as follows; the example may be consulted for visualization of the steps.

(i) Construct the graph with all $f>2$ vertices labelled from 1 to μ.

(ii) Construct a $\mu\times\mu$ matrix of zeros.

(iii) Enter $f_\sigma - 4\sin^2\theta/2$ in the diagonal σ,σ position for all σ, $1\leq\sigma\leq\mu$, where f_σ is the functionality of node σ.

(iv) Subtract $\sin n_i\theta/\sin(n_i+1)\theta$, where θ is given by Eq. (5), from the σ,σ element if σ is connected to a chain of n_i beads which is also connected to node ρ. Note that the ρ,ρ element will subsequently receive the same decrement.

(v) Subtract $\cos(n_j-1/2)\theta/\cos(n_j+1/2)\theta$ from the σ,σ element if a free-ended chain of n_j beads is connected to vertex σ.

(vi) Subtract $2(\sin\theta+\sin n_i\theta)/\sin(n_i+1)\theta$ from the σ,σ element for each loop of n_i nodes attached to σ.

(vii) Subtract $\sin\theta/\sin(n_i+1)\theta$ from the σ,ρ and ρ,σ elements if nodes σ and ρ are directly connected by a chain of n_i beads. Note that if $n_i=0$, the entry is -1 as is proper for nodes connected by a single Gaussian bond. If two chains connect the same nodes, terms for each will be subtracted from the σ,ρ and ρ,σ elements.

The determinant of the matrix generated by this simple algorithm must then be multiplied by Eq. (3), and the roots of the resulting polynomial of order N in λ must be found. Care must be taken to find all complex roots of the polynomial in θ, which correspond to $\lambda>4$.

V. ILLUSTRATIONS

A. Stars

The simplest nontrivial application of the procedure described above is to calculation of the eigenvalues of the Kirchhoff matrix for an f-branch star with all arms containing the same number n of nodes. The algorithm gives

$$[f-\lambda - f\cos(n-1/2)\theta/\cos(n+1/2)\theta] \times[\cos(n+1/2)\theta/\cos(\theta/2)]^f = 0\,, \tag{12a}$$

or

$$[(f-4\sin^2\theta/2)\cos(n+1/2)\theta - f\cos(n-1/2)\theta] \times[\cos(n+1/2)\theta]^{f-1} = 0\,. \tag{12b}$$

(Some care must be exercised in simplifying equations of this type to insure that the resulting polynomial is of order N in λ.) As is readily seen from Eq. (12b), there

are n eigenvalues that are $f-1$ fold degenerate. They are given by

$$(n+1/2)\theta_l = (l-1/2)\pi\,, \qquad 1 \le l \le n\,,$$

or

$$\lambda_l = 4\sin^2(l-1/2)\pi/(2n+1)\,. \tag{13a}$$

This confirms the computer calculations reported in I. The remaining $(fn+1)-n(f-1)=n+1$ eigenvalues are solutions of

$$f[\cos(n+1/2)\theta - \cos(n-1/2)\theta] = 4\sin^2\theta/2\cos(n+1/2)\theta\,, \tag{14a}$$

which simplifies to

$$f-1 = -\sin(n+1)\theta/\sin n\theta\,. \tag{14b}$$

It is apparent that $\lambda=0$ is a solution of Eq. (14a), so that there are n nonzero solutions of Eq. (14b).

In the trivial case $f=2$, the solutions of Eq. (14b) are

$$\lambda_l = 4\sin^2 l\pi/(2n+1)\,. \tag{13b}$$

This example corresponds to a linear chain of $N=2n+1$ beads. The eigenvalues are in this case known to be

$$\lambda_k = 4\sin^2\pi k/2N\,.$$

Equation (13a) corresponds to odd k, and Eq. (13b) corresponds to even k. For $f>2$, Eq. (14b) seems not to possess simple analytical solutions. The equation is equivalent to that derived earlier by Šolc [Eq. (A20) of Ref. 8]. Accurate solutions may be found by numerical methods. Approximate solutions may be obtained for large n, since, in this case, $n\theta_l = l\pi - \phi/n$, where ϕ is of order unity. For $1 \le l < n$, we find $\lambda_l = 4\sin^2\pi l/2n$ to terms of $0(1/n^2)$, and $\lambda_n = f^2/(f-1)$ since $\theta_n = \pi - il\ln(f-1)$. These results are in complete accord with computer calculations reported in I.

B. Perfect random nets

By a perfect random net we mean a network in which all junctions have functionality f and are connected to one another by chains of the same number of nodes n without loops, double edges or free ends. The algorithm in this case yields

$$\mathbf{F}_\lambda - \mathbf{C}\mathbf{A}_\lambda^{-1}\mathbf{C}' = [f(1-\sin n\theta/\sin(n+1)\theta) - \lambda]\mathbf{1}_\mu - (\sin\theta/\sin(n+1)\theta)\mathscr{A}\,, \tag{15}$$

where $\mathscr{A}$ is the adjacency matrix for the graph of f-functional nodes alone. There is a $+1$ in element σ,ρ of $\mathscr{A}$ if σ and ρ are directly connected by a chain.

Note that when $\lambda=0$, Eq. (16) reduces to

$$\mathbf{F}_0 - \mathbf{C}\mathbf{A}_0^{-1}\mathbf{C}' = (n+1)^{-1}(f\mathbf{1}_\mu - \mathscr{A})\,, \tag{16}$$

which is just the James–Guth[10,11] matrix to within a factor of $3/2\langle l^2\rangle_0$. The statement is evidently true for all networks, regardless of the distribution of chain lengths, or of the presence of loops and free ends, as inspection of the algorithm shows.

Since $\mathscr{A}$ in Eq. (15) is a symmetric matrix, it is diagonalized by a rotation to yield the secular equation

$$\prod_{\sigma=1}^{\mu}\{f[1-\sin n\theta/\sin(n+1)\theta] - 4\sin^2\theta/2 - \xi_\sigma\sin\theta/\sin(n+1)\theta\}(\sin(n+1)\theta/\sin\theta)^{\mu f/2} = 0\,, \tag{17a}$$

or

$$f[\sin(n+1)\theta - \sin n\theta] - 4\sin^2(\theta/2)\sin(n+1)\theta - \xi_\sigma\sin\theta = 0\,, \qquad 1 \le \sigma \le \mu\,, \tag{17b}$$

and

$$[\sin(n+1)\theta]^{\mu(f-2)/2} = 0\,, \tag{17c}$$

where the ξ_σ are the eigenvalues of $\mathscr{A}$. It is easily seen that the Kirchhoff matrices considered in I correspond to $f\mathbf{1}_\mu - \mathscr{A}$, so that the eigenvalues found there are simply $f-\xi_\sigma = \kappa_\sigma$.

From Eq. (17c), one finds that there are n eigenvalues,

$$\lambda_l = 4\sin^2\pi l/2(n+1)\,, \qquad 1 \le l \le n\,, \tag{18}$$

each with high degeneracy $\mu(f-2)/2$. The remaining polynomials, Eq. (17b), are each of order $n+1$, and there are μ equations, giving a total of $\mu(n+1)+n\mu(f-2)/2 = \mu(1+nf/2)$ eigenvalues. (There are μ junctions and $\mu f/2$ chains each of n nodes.) It is interesting to note that of the total number of eigenvalues, the fraction $(1-2/f)(1+2/nf)$ of them are obtained very simply from Eq. (17c). Equation (17b) simplifies to

$$\cos(n+3/2)\theta + (f-1)\cos(n+1/2)\theta - \xi_\sigma\cos\theta/2 = 0\,, \tag{17d}$$

from which it can be seen that the zero eigenvalue belongs to the equation with $\kappa_1 = f-\xi_1 = 0$.

Solutions of Eq. (17d) may be approached by assuming that $n\theta$ is a small number. In first approximation, we find $n\theta = (2\kappa_\sigma/f)^{1/2}$. From the results of I, it is clear that $n\theta$ will be small only for $f=3$, and then only for the smallest eigenvalues κ_σ. Thus, for $f>3$, there are no eigenvalues of order less than $1/n^2$. The mean square dimensions of an $f \ge 4$ perfect random net will not be of order greater than the dimensions of a single chain.[12,13] For $f=3$, there are eigenvalues of order $1/\mu n^2$ which correspond to Jello modes with long relaxation times. The behavior of $f=3$ random nets is quite distinct from the whole class of $f>3$ nets. Further analysis of Eq. (17d) is quite difficult in general, but it is not difficult to see that, as n becomes large, there is one complex root $\theta = \pi - il\ln(f-1)$ for each ξ_σ. Thus, there will be μ degenerate eigenvalues $\lambda = f^2/(f-1)$ for large n. In general, there will be μ eigenvalues $\lambda = f_\sigma^2/(f_\sigma - 1)$ if there is a distribution of functionality. Since there are only μ eigenvalues $\lambda > 4$, they must be associated with high frequency vibrations of the junctions. Rowland and Labun[14] have found just such modes from proton spin–lattice relaxation times in polybutadiene. The lower frequency intrachain modes are related to Eq. (18), and the remaining $n\mu - 1$ modes will be related to oscillations of chains and circuits. We will return to solutions of Eq. (17d) at a later time.

VI. CONCLUSION

Although the number of illustrative examples has been limited, it will not be difficult for the interested reader

to apply the method to molecules of interest if their structure is sufficiently regular. It is clear that, if there is a distribution of chain lengths and many f-functional nodes in the molecule, the computations become very difficult. Degeneracy of eigenvalues will be lifted in proportion to the breadth of the distribution. Diagonalization of the adjacency matrix with variable elements will be very time consuming if the molecule does not possess sufficient regularity to write a recurrence relation for the $\mu \times \mu$ dimensional determinant in terms of lower order determinants. (Combs can be treated by use of a recurrence relation.[8]) These observations suggest that experience first be gained on uniform chain-length molecules before addressing the more difficult cases.

The advantage of the reduction discussed here is that it applies to all molecules. Other techniques, such as those based upon generating functions,[8] work admirably well if the molecule is sufficiently regular, but fail if any element of randomness is introduced into the problem. Furthermore, the algorithm can be programmed once for all applications.

ACKNOWLEDGMENTS

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