that our results indicate two different CDT values for the same chain into two solvents. One would, however, expect the CDT values derived from thermoelasticity in acetone-swollen PEO and the ones from $[\eta]/T$ in acetone to agree within experimental error. The fact that they do not agree must be discussed in terms of the possibility of having intermolecular contributions to f_e even in a thermoelastic analysis performed at a constant volume. This possibility has been already explored by several workers[20,21] and, when present, would introduce an intermolecular contribution even in a quantity like the CDT, which should be strictly intramolecular in character.

For PEO chains, in particular, an intermolecular interaction energy varying with v_r at a constant volume seems to be very possible, owing to the tendency of PEO to aggregate in several solvents even at a very high degree of dilution.[22,23] The relatively high concentration of the networks studied (v_r = 0.8 used by Mark and Flory and v_r = 0.3 used by us) is certainly a factor favoring the formation of supermolecular structures, whose stretching behavior is not presently known. Intermolecular contributions of this nature can be reasonably assumed to play an important role. If this is the case, experimental values of CDT would give only an "apparent" measure of the temperature effect on single-chain dimensions. These, on the other hand, represent the only rather simplified situation with which present theory can deal. Conformational analysis of a polymer chain, based on an experimentally measured CDT value, through any of the presently known techniques, should therefore be regarded as a preliminary attempt only, necessarily to be discussed in the light of a much wider experimental basis.

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Elasticity Theory. I. Distribution Functions for Perfect Phantom Networks

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ABSTRACT: Distribution functions for chains, cross-links, and whole networks are obtained for networks composed of chains of a single length which are connected to one another by tetrafunctional cross-linkages, such that there are no free chain ends. The chains do not interact with one another except through the cross-links. Results are largely formal, save for the explicit demonstration that the formation of a perfect network results in chain shrinkage by a factor of 2 for perfect networks, as was shown by James. Graph theory is exploited to formulate the partition function for the perfect network, and by its means we show that the connectivity of the tetrafunctional network composed of μ chains can be defined in all details by specification of a $(\mu - 1)$-dimensional vector whose elements are the lengths of fundamental circuits. The calculation of the characteristic function for the radius of gyration of the network is carried to the penultimate stage; a later paper will deal with its evaluation. Two methods are used to solve the problem; the first considers the network as it exists, while in the second the formation of the network is stressed.

The influence of topological connectivity on the properties of macroscopic networks is considered in this paper. We do not purport to solve the problem of rubber elasticity; rather we consider a model for an elastic network which can be treated in some detail. With the aid of graph theory, it is possible to formulate the configuration integral for perfect phantom[1] networks in a particularly simple way.[2] The connectivity of graphs corresponding to networks can be expressed in terms of various matrices, and properties of these matrices give one some insight into the manner in which the connectivity influences properties.

We consider the main results of this paper to be (1) proof that chains in perfect phantom networks of any connectivity are contracted by a factor of 2,[2] on the average, from their unconstrained dimensions; (2) for networks composed of ν chains and $\mu = \nu/2$ cross-links, the network is completely defined by a $(\mu - 1)$-dimension vector; and (3) a formal result is obtained for the distribution function of the radius of gyration of a network, in which $\mu - 1$ normal modes of network oscillation are encountered.

The calculations follow closely the method used by Berlin and Kac[3] in their treatment of ferromagnetism, and by Fixman[4] in his calculation of the distribution function for a single chain. Dyson[5] has treated the similar problem of oscillations in a one-dimensional system of springs and masses. In several recent papers Edwards and Freed[6] have developed a powerful theory for elasticity which stresses the importance of topological constraints. Our treatment of the connectivity of the network (without entanglements) is compatible with that of Edwards and Freed. Simplicity in our approach is, however, accompanied by a concomitant preaverage over

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internal configurations of the polymer. A subsequent paper will show how this approximation can be avoided. Theories of elasticity have been recently reviewed by Dusek and Prins[7] and Mark.[8]

General Consideration of Graphs

The model for a perfect phantom network as used here is that of a network composed of Gaussian chains which interact with one another only through tetrafunctional network junctions. There are no chain ends. We may represent the connectivity of the network by means of a graph, in which edges represent chains and vertices represent cross-links. The graphs we wish to consider will in general be non-planar; *i.e.*, when drawn on the plane there are intersections of edges that are not vertices.

All graphs which represent tetrafunctional perfect phantom networks will possess at least one Euler circuit that passes through every edge of the graph once and only once. A necessary and sufficient condition that an Euler circuit exist on a connected graph is that all vertices be of even degree.[9] We may represent the Euler circuit as a circle, with half-vertices (or half-links) distributed uniformly on its circumference as shown in Figure 1. Let there be ν edges (chains), ν half-vertices (half-links), and $\mu = \nu/2$ vertices (cross-links). Pairs of half-links, labeled variously as i and j or $\mathcal{I}_k$ and $\mathcal{I}_k + \mathcal{C}_k$, will be joined by a chord in the circle graph if i and j coalesce to form a vertex in the network graph.

It is useful to associate a direction with each chord on the circle graph, so as to direct the chord from the lower to the higher index. Half-links are numbered from 1 to ν in a counterclockwise direction, and edges are labeled $\gamma_1, \gamma_2, \ldots, \gamma_\nu$, where edge γ_l connects half-vertex l to $l + 1$. Let the indices of the half-links that originate chords be labeled $\mathcal{I}_1, \mathcal{I}_2, \ldots, \mathcal{I}_\mu$; the corresponding termini will be labeled $\mathcal{I}_1 + \mathcal{C}_1, \mathcal{I}_2 + \mathcal{C}_2, \ldots, \mathcal{I}_\mu + \mathcal{C}_\mu$. Transformation from a circle graph to a network graph is the mapping

$$\mathcal{I}_m, \mathcal{I}_m + \mathcal{C}_m \longrightarrow m$$
$$\{\gamma\} \longrightarrow \{\gamma\}$$

That is half-vertices $\mathcal{I}_m$ and $\mathcal{I}_m + \mathcal{C}_m$ coalesce to form vertex m, while labels are carried along with the edges to which they belong. The number of edges in *fundamental* circuits is given by the set $\{\mathcal{C}\}$ of numbers $\mathcal{C}_1, \mathcal{C}_2, \ldots, \mathcal{C}_\mu$; in Appendix C it is shown that specification of $\mu - 1$ fundamental circuit lengths gives a total description of the network. Figure 2 depicts a small circle graph and the corresponding network graph. Consultation of this figure in subsequent steps will aid in establishing the correspondence between circle graphs, networks, and matrices.

The Kirchhoff Matrix[10]

The potential energy for a perfect phantom network is a quadratic form in the set of position vectors $\{\mathbf{R}\}$ of the μ cross-links, as was shown by James and Guth[11] Define the row vector $\tilde{\mathbf{R}}$, and corresponding column $\mathbf{R}$, by

$$\tilde{\mathbf{R}} = [x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_\mu, y_\mu, z_\mu] \quad (1)$$

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(11) H. M. James and E. Guth, *J. Chem. Phys.*, **11**, 455 (1943); **15**, 669 (1947).

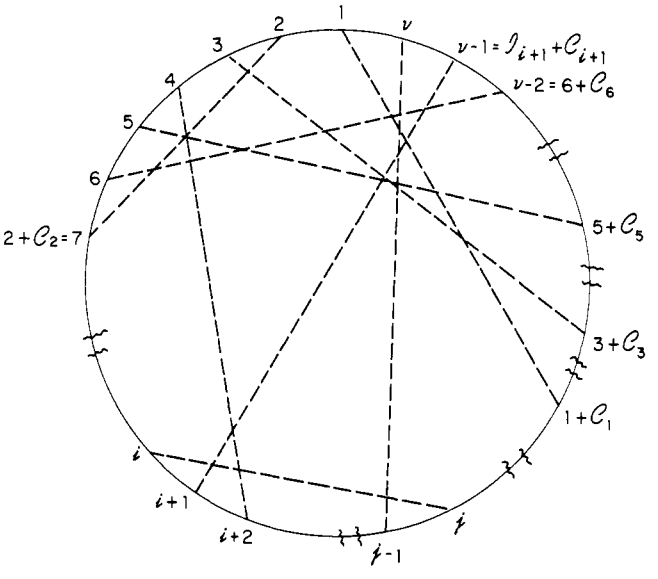

Figure 1. Circle graph that is equivalent to a network. Chains are located sequentially on the circumference with interposing half-links. If half-links i and j react with one another to form a cross-link, they are joined together by a chord. The termini of a chord are more conveniently labeled as $\mathcal{I}_k$ and $\mathcal{I}_k + \mathcal{C}_k$, where $\mathcal{C}_k$ is the number of chains between the two termini.

where x_i, y_i, and z_i are the x, y, and z coordinates of the ith cross-link. The potential energy $V\{\mathbf{R}\}$ will be given by

$$V\{\mathbf{R}\}/kT = \tilde{\mathbf{R}}(\mathbf{K}_\gamma \otimes \mathbf{E}_3)\mathbf{R} \quad (2)$$

The $\otimes$ operation is the direct product, which expands $\mathbf{K}_\gamma$ from $\mu \times \mu$ to $3\mu \times 3\mu$ so that x, y, and z coordinates are accommodated.

If there is a chain directly connecting cross-link i to cross-link j, and if this chain is labeled by the parameter γ_m, then the ij element of $\mathbf{K}_\gamma$ is given by

$$k_{ij} = k_{ji} = -\gamma_m(i - \gamma_m - j)$$
$$= 0 \ (i \quad j) \text{ or } (\subset i) \quad (3)$$

The diagram represents the connection consistent with the element; loops are given a weight of zero. Furthermore, let the diagonal elements k_{jj} be given by

$$k_{jj} = -\sum_{i=1}^{\mu} k_{ij} = -\sum_{i=1}^{\mu} k_{ji} \quad (4)$$

The matrix $\mathbf{K}_\gamma$ thus defined is known in graph theory as the variable Kirchoff matrix.[10] By use of eq 2 it yields the quadratic form

$$V\{\mathbf{R}\}/kT = \gamma_a(\mathbf{R}_1 - \mathbf{R}_2)^2 + \gamma_b(\mathbf{R}_1 - \mathbf{R}_3)^2 + \ldots + \gamma_j(\mathbf{R}_\mu - \mathbf{R}_k)^2 \quad (5)$$

The numbering scheme to be used for $\{\mathbf{R}\}$ and $\{\gamma\}$ has been completely general. We now consider a method of numbering graphs with particular properties (to be defined) which leads to some insight into the nature of the variable Kirchhoff matrix and even its spectrum. We first assume that there are no loops, *i.e.*, cross-links directly connected to themselves. Choose any cross-link in the network, and label it 1. Proceed from cross-link 1 (hereafter called vertex 1 to conform with graph theory usage) to any one of its neighbors *via* chain γ_1 (hereafter called edge γ_1), and label that vertex 2. Continue to travel from vertex to vertex, visiting each vertex once and only once, and label them in sequence 1, 2, 3, . . .,

$\mu - 1, \mu$; edges will be labeled $\gamma_1, \gamma_2, \ldots, \gamma_{\mu-1}, \gamma_\mu$, with γ_α joining α to $\alpha + 1$. The path thus defined is a Hamilton circuit[9,10] that visits each and every vertex once and only once. The requirement that there be a Hamilton circuit in the graph is used only in the present section. Not all fourvalent graphs that are permissible networks will possess Hamilton circuits.

The Hamilton circuit visits every vertex and half the edges. The last step returns to the path to the origin and completes the longest possible nonperiodic circuit in the graph. In order to complete the labeling of the edges, we now proceed on another Hamilton circuit, only this time we walk along each edge that was not labeled on the previous circuit; these edges will be labeled $\gamma_{\mu+1}, \gamma_{\mu+2}, \ldots, \gamma_\nu$. The second path will visit the labeled cross-links in a sequence that depends on the structure of the graph, but again it will return to the origin. For graphs that possess two consecutive Hamilton circuits there are only two possible secondary Hamilton circuits, since there are only two directions in which one may leave 1 to begin the second circuit. The two Hamilton circuits together constitute an Euler circuit which traverses each and every edge once and only once. We call the Euler path through the network that is composed of two consecutive Hamilton circuits the Hamilton–Euler path. (The circle graph for networks with Hamilton–Euler paths will be divided in two by a diameter joining 1 to $\mu + 1$ and all other chords cross this diameter.)

The Kirchhoff matrix **K** which describes the graph labeled as above is obtained from the variable Kirchhoff matrix when, for all m, $\gamma_m = \gamma$. Then

$$\gamma\mathbf{K} = \mathbf{K}_\gamma = \gamma \times \begin{bmatrix} 4 & -1 & 0 & 0 & \ldots & -1 & 0 & \ldots & 0 & -1 & & & -1 \\ -1 & 4 & -1 & 0 & \ldots & \ldots & -1 & 0 & \ldots & -1 & 0 & 0 & \\ 0 & -1 & 4 & -1 & 0 & \ldots & -1 & 0 & \ldots & -1 & 0 & 0 & \\ \cdot & & \cdot & & & & & & & & & \cdot & \\ \cdot & & & \cdot & & & & & & & & \cdot & \\ \cdot & & & & \cdot & & & & & & & -1 & \\ & & & & & \cdot & & & & & & \cdot & \\ 0 & & & & & & \cdot & & & & & \cdot & \\ & & & & & & & \cdot & & & & \cdot & \\ -1 & & & & & & & & \cdot & & & -1 & \\ & & & & & & & & & \cdot & & \cdot & \\ 0 & & & & & & & & & & \cdot & \cdot & \\ & & & & & & & & & & 4 & -1 & 0 \\ 0 & & & & & & & & & & -1 & 4 & -1 \\ -1 & & & & -1 & 0 & \ldots & 0 & -1 & 0 & -1 & 4 & \end{bmatrix} \quad (6)$$

The matrix **K** may be represented in terms of the symmetric circulant **A** defined by

$$a_{kl} = 2\delta_{kl} - \delta_{k,l+1} - \delta_{k,l-1} (\mathrm{mod}\ \mu) \quad (7)$$

and a permutation operator. The matrix representative of the permutation is **P** ($\mathbf{P}^{-1} = \tilde{\mathbf{P}}$); **P** contains a single nonzero element equal to unity in each column and row. Then

$$\mathbf{K} = \mathbf{A} + \tilde{\mathbf{P}}\mathbf{A}\mathbf{P} \quad (8)$$

The first factor is the Kirchhoff matrix for the primary Hamilton circuit; the term $\tilde{\mathbf{P}}\mathbf{A}\mathbf{P}$ is the Kirchhoff matrix for the secondary Hamilton circuit.

The Kirchhoff matrix and the variable Kirchhoff matrix both possess one zero eigenvalue corresponding to center of gravity motion of the network. That each possesses a zero eigenvalue may be demonstrated by adding all columns to the first in either **K** or $\mathbf{K}_\gamma$. The first column is then reduced to the null column. Inspection of eq 8 shows that there can be only one zero eigenvalue for **K**, since **A** has only one zero eigenvalue. (We believe that **K** has only one zero eigenvalue for any network, but a proof has not been found.) The eigenvalues $\lambda_l(\mathbf{A})$ of **A** are known to be

$$\lambda_l(\mathbf{A}) = 4 \sin^2 \pi l/\mu \quad (9)$$

and the transformation matrix **T** ($\mathbf{T}^{-1} = \tilde{\mathbf{T}} = \mathbf{T}$) which diagonalizes **A** has elements t_{ij} given by

$$t_{ij} = \mu^{-1/2}(\cos 2\pi ij/\mu + \sin 2\pi ij/\mu) \quad (10)$$

as was shown by Berlin and Kac.[3]

If the graph possessing a Hamilton–Euler circuit contains double edges, *i.e.*, the network contains pairs of chains joining pairs of cross-links, then **K** will contain the elements

$$\begin{bmatrix} \cdot & & & & \\ & \cdot & & & \\ & & -1 & 4 & -2 \\ & & -2 & 4 & -1 \\ & & & & \cdot \\ & & & & & \cdot \end{bmatrix}$$

Such occurrences will still conform to eq 8. However, if the graph contains loops, **K** will have elements

$$\begin{bmatrix} \cdot & & & & \\ & \cdot & & & \\ & & -1 & 4 & -1 \\ & & -1 & 2 & -1 \\ & & & -1 & 4 & -1 \\ & & & & & \cdot \\ & & & & & & \cdot \end{bmatrix}$$

where the row and column containing the factor 2 on the diagonal have zero entries everywhere except those shown. We then require a modified form of eq 8 to describe **K**. Let $\mathbf{P}'$ be a matrix obtained from **P** by replacement of some of the nonzero elements of **P** by zero. If the nth cross-link is joined to itself by a chain, then the nth column (row) of $\mathbf{P}'(\tilde{\mathbf{P}}')$ will be the null column (row). For graphs with loops and one Hamilton circuit we have

$$\mathbf{K} = \mathbf{A} + \tilde{\mathbf{P}}'\mathbf{A}\mathbf{P}' \quad (11)$$

so that the nth row and column of **K** will not have contributions from the second term.

The variable Kirchhoff matrix is a symmetric matrix that may be diagonalized by the unitary transformation

$$\mathbf{U}_\gamma\mathbf{K}_\gamma\tilde{\mathbf{U}}_\gamma = \mathbf{\Lambda}(\mathbf{K}_\gamma) \quad (12)$$

or, for the Kirchoff matrix

$$\mathbf{U}\mathbf{K}\tilde{\mathbf{U}} = \mathbf{\Lambda}(\mathbf{K}) \quad (13)$$

We now state two conjectures: (i) *the transformation matrix* **U** *is approximately equal to* **T** *defined by eq 10 and* (ii) *the spec-*

trum of K determined according to eq 13 is nondegenerate for random networks. Conjecture (ii) follows from consideration of the normal modes of the network as well as from (i). If we were to form the network from two circular chains, corresponding to the primary and secondary Hamilton circuits, selected modes of the two chains would add to one another. The normal modes of a single chain are doubly degenerate, but the additivity of modes is expected to remove the degeneracy. Alternatively, one may consider the oscillations in the fundamental circuits. Since there are $\mu - 1$ fundamental circuits and μ possible fundamental circuit lengths and since the wavelengths of the modes within a circuit are determined by the length of a circuit, it seems reasonable to expect little degeneracy in the spectrum. (We have been unable to relate the spectrum to circuit size except in a general way, *cf.* Appendix B.)

The first conjecture is based on the following simple approximation, valid for networks with Hamilton–Euler paths. Operate on **K** with

$$\tilde{\mathbf{T}}\mathbf{K}\mathbf{T} = \tilde{\mathbf{T}}\mathbf{A}\mathbf{T} + (\tilde{\mathbf{T}}\tilde{\mathbf{P}}\mathbf{T})(\tilde{\mathbf{T}}\mathbf{A}\mathbf{T})(\tilde{\mathbf{T}}\mathbf{P}\mathbf{T}) = \mathbf{\Lambda}(\mathbf{A}) + \tilde{\mathbf{P}}\mathbf{\Lambda}(\mathbf{A})\mathbf{P} \quad (14)$$

where

$$\mathbf{P} = \tilde{\mathbf{T}}\mathbf{P}\mathbf{T} = \mathbf{P} + \tilde{\mathbf{T}}[\mathbf{P}\mathbf{T} - \mathbf{T}\mathbf{P}] \quad (15)$$

The commutator has a random phase relative to $\tilde{\mathbf{T}}$ for a random network, and so the second term in eq 15 should be small relative to the first. Thus

$$\mathbf{P} \cong \mathbf{P}$$

$$\mathbf{U} \cong \mathbf{T}$$

and the eigenvalues of **K** are approximately

$$\lambda_l(\mathbf{K}) = 4(\sin^2 \pi l/\mu + \sin^2 \pi p_l/\mu) \quad (16)$$

where $\mathcal{P}_l$ is a random variable; $1 \leq \mathcal{P}_l \leq \mu$, $\mathcal{P}_\mu = \mu$. It is likely that the double degeneracy inherent in $\sin^2 \pi l/\mu$ is removed on addition of two such terms taken at random. Thus conjecture (ii) is supported. Preliminary Monte Carlo computer calculations also support conjecture (ii).

The Partition Function

The partition function for the network contained in an infinite volume is now easily obtained. The configuration integral Z may be written as

$$Z = \int_{-\infty}^{\infty} \cdots \int \exp[-\mathbf{R}(\mathbf{K}_\gamma \otimes \mathbf{E}_3)\mathbf{R}]\delta(\tilde{\mathbf{J}}\mathbf{R})\mathrm{d}\{\mathbf{R}\} \quad (17)$$

where $\tilde{\mathbf{J}}$ is a row of 1's; the δ function fixes the center of gravity of the network. Upon diagonalizing the quadratic form we obtain

$$Z = \int_{-\infty}^{\infty} \cdots \int \exp\{-\tilde{\mathbf{Q}}[\mathbf{\Lambda}(\mathbf{K}_\gamma) \otimes \mathbf{E}_3]\mathbf{Q}\}\, \mathrm{d}\{\mathbf{Q}_0\}\, \delta(\mathbf{q}_\nu)\mathrm{d}\mathbf{q}_\nu \quad (18)$$

where $\mathrm{d}\{\mathbf{Q}_0\}$ is the $3(\mu - 1)$-dimensional volume element obtained from $\mathrm{d}\{\mathbf{Q}\}$ by deletion of the volume element $\mathrm{d}\mathbf{q}_\nu$ corresponding to the zero eigenvalue of $\mathbf{\Lambda}_\gamma(\mathbf{K}_\gamma)$ and center of gravity motion. The Jacobian of a unitary transformation is unity. The column **Q** is obtained from **R** by the transformation

$$\begin{aligned} \mathbf{Q} &= \mathbf{U}_\gamma \mathbf{R} \\ \mathbf{R} &= \tilde{\mathbf{U}}_\gamma \mathbf{Q} \end{aligned} \quad (19)$$

Integration of eq 18 gives

$$Z = \pi^{3(\mu-1)/2}/|\mathbf{\Lambda}_0(\mathbf{K}_\gamma)|^{3/2} \quad (20)$$

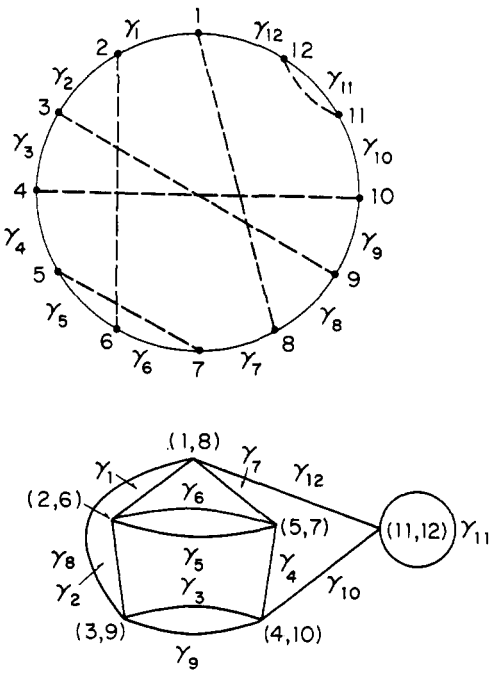

Figure 2. A labeled circle graph and its network. The mapping from the circle to the network is carried out by superimposing the termini of chords while maintaining the connectivity of the circle.

where the determinant $|\mathbf{\Lambda}_0(\mathbf{K}_\gamma)|$ of the matrix of eigenvalues of $\mathbf{\Lambda}(\mathbf{K}_\gamma)$ does not include the zero eigenvalue; the matrix $\mathbf{\Lambda}_0(\mathbf{K}_\gamma)$ is of order $(\mu - 1) \times (\mu - 1)$.

If all chains are the same length, we have

$$\begin{aligned} \tilde{\mathbf{R}}(\mathbf{K}_\gamma \otimes \mathbf{E}_3)\mathbf{R} &= \gamma\tilde{\mathbf{R}}(\mathbf{K} \otimes \mathbf{E}_3)\mathbf{R} \\ &= \gamma\tilde{\mathbf{Q}}[\mathbf{\Lambda}(\mathbf{K}) \otimes \mathbf{E}_3]\mathbf{Q} \end{aligned} \quad (21)$$

and

$$Z = (\pi/\gamma)^{3(\mu-1)/2}/|\mathbf{\Lambda}_0(\mathbf{K})|^{3/2} \quad (22)$$

We will have occasion to consider networks with chains of a single length, and explicit reference to the parent **K** will be omitted in such cases so that $\mathbf{\Lambda}_0 = \mathbf{\Lambda}_0(\mathbf{K})$.

Distribution of Chain Lengths

The mean-square displacement between cross-links that are directly connected by a chain in the network may be obtained from eq 22 when all chains contain the same number of bonds. The average $\langle r^2 \rangle_N$ we require is

$$\langle r^2 \rangle_N = \nu^{-1}[\langle(\mathbf{R}_1 - \mathbf{R}_2)^2\rangle + \langle(\mathbf{R}_2 - \mathbf{R}_3)^2\rangle + \ldots + \langle(\mathbf{R}_\mu - \mathbf{R}_1)^2\rangle + \langle(\mathbf{R}_1 - \mathbf{R}_j)^2\rangle + \ldots + \langle(\mathbf{R}_n - \mathbf{R}_1)^2\rangle] =$$

$$(\nu Z)^{-1}\int \cdots \int \tilde{\mathbf{R}}(\mathbf{K} \otimes \mathbf{E}_3)\mathbf{R} \exp[-\gamma\tilde{\mathbf{R}}(\mathbf{K} \otimes \mathbf{E}_3)\mathbf{R}]\delta(\tilde{\mathbf{J}}\mathbf{R})\mathrm{d}\{\mathbf{R}\} =$$

$$-\nu^{-1}\partial \ln Z/\partial\gamma = 3(\mu - 1)/2\nu\gamma \quad (23)$$

For a tetrafunctional network $\mu = \nu/2$. The parameter γ is related to the mean-square end-to-end displacement of a free chain, $\langle r^2 \rangle_0$, by

$$\gamma = 3/2\langle r^2 \rangle_0 \quad (24)$$

Thus

$$\langle r^2 \rangle_N = \langle r^2 \rangle_0/2 + 0(\nu^{-1}) \quad (25)$$

showing that chains in the network are contracted.[2]

The source of the contraction is easily understood, especially for networks with Hamilton–Euler paths. If only the

primary Hamilton circuit existed, the dimension between cross-links would be to $0(\nu^{-1})$, just $\langle r^2\rangle_0$. The force acting between nearest-neighbor half-links is delivered by a single chain for a large circle molecule. (The remainder of the circle contributes a negligible force of $0(\nu^{-1})$.) However, in the network the chains in the secondary Hamilton circuit must also deliver a force; junctions α and $\alpha + 1$ are attracted to one another not only by the chain joining them, but also by a multitude of other chains on paths through the rest of the network. That these other paths contribute, in effect, one addition chain between α and $\alpha + 1$ in the perfect network is perhaps surprising. One can draw small, redundant networks to convince oneself of the correctness of the result.

In a subsequent paper we will show that the general result for imperfect networks is

$$\langle r^2\rangle_N = \langle r^2\rangle_0/(2 - 1/C)$$

where C is the ratio of the number of cross-links to half the number of chain ends. Chain contraction is fundamental to syneresis, as has been demonstrated by Edwards and Freed[6] in their third paper.

Distribution of Cross-Links

The distribution of cross-links about the center of gravity of the network will now be considered. One may anticipate[2] that the distribution function is gaussian, and this we now prove. We require the probability $P_k(\varrho)d\varrho$ that cross-link k is in the volume element $d\varrho$ centered at ϱ. This probability can be formulated as

$$P_k(\varrho) = Z^{-1}\int\cdots\int \exp[-\tilde{\mathbf{R}}(\mathbf{K}_\gamma\otimes\mathbf{E}_3)\mathbf{R}]\delta(\varrho - \mathbf{R}_k)\delta(\tilde{\mathbf{J}}\mathbf{R})d\{\mathbf{R}\}$$

The integral may be solved by introducing the Fourier representation of the δ function.

$$\delta(\mathbf{r}) = (2\pi)^{-3}\int \exp(i\mathbf{k}\cdot\mathbf{r})d\mathbf{k}$$

In normal coordinates

$$\tilde{\mathbf{R}}(\mathbf{K}_\gamma\otimes\mathbf{E}_3)\mathbf{R} - i\mathbf{k}\cdot(\varrho - \mathbf{R}_k) = \tilde{\mathbf{Q}}[\mathbf{\Lambda}(\mathbf{K}_\gamma)\otimes\mathbf{E}_3]\mathbf{Q} - i\mathbf{k}\cdot(\varrho - \tilde{\mathbf{U}}_{\gamma,k}\mathbf{Q}) \quad (26)$$

where $\tilde{\mathbf{U}}_{\gamma,k}$ is the kth row of $\tilde{\mathbf{U}}_\gamma$. Upon separating $\mathbf{q}_\nu$ for the center of gravity, and completing the square in $\mathbf{Q}$ and then $\mathbf{k}$, the integration may be performed to obtain

$$P_k(\varrho) = \text{constant}\exp(-\varrho^2/\tilde{\mathbf{U}}_{k0}\mathbf{\Lambda}_0^{-1}(\mathbf{K}_\gamma)\mathbf{U}_{k0}) \quad (27)$$

in which $\tilde{\mathbf{U}}_{k0}$ is a row of dimension $1 \times (\mu - 1)$, obtained from $\tilde{\mathbf{U}}_{\gamma,k}$ by deletion of elements corresponding to the y and z coordinates of all $\mathbf{q}_l$, as well as the x component or $\mathbf{q}_\nu$. Let

$$\alpha_k = \tilde{\mathbf{U}}_{k0}\mathbf{\Lambda}_0^{-1}(\mathbf{K}_\gamma)\mathbf{U}_{k0}$$

so that the numbers of cross-links at ϱ in $d\varrho$, $N(\varrho)d\varrho$, may be expressed as

$$N(\varrho)d\varrho = \sum_{k=1}^{\mu}(\pi\alpha_k)^{-3/2}\exp(-\varrho^2/\alpha_k)d\varrho \quad (28)$$

Further simplification of this result requires consideration of the spectrum of $\mathbf{K}_\gamma$.

Distribution Function of the Radius of Gyration of the Network

For a sufficiently large number of cross-links and chains, the radius of gyration of the network will be obtained by summation of the squares of displacements from the center of gravity of cross-links alone. So long as the mean-square displacement between cross-links α and $\alpha + 1$ is much less than the radius of gyration of the network, it will be permissible to locate all of the mass of the chains at the network junctions. Then, the radius of gyration S^2 will be

$$S^2 = \mu^{-1}\tilde{\mathbf{R}}\mathbf{R} = \mu^{-1}\tilde{\mathbf{Q}}\mathbf{Q} \quad (29)$$

The probability $P(S^2)dS^2$ that the radius of gyration is between S^2 and $S^2 + dS^2$ may be formulated[4] as

$$P(S^2) = Z^{-1}\int\cdots\int \exp[-\tilde{\mathbf{R}}(\mathbf{K}_\gamma\otimes\mathbf{E}_3)\mathbf{R}] \times \delta(S^2 - \mu^{-1}\tilde{\mathbf{R}}\mathbf{R})\delta(\tilde{\mathbf{J}}\mathbf{R})d\{\mathbf{R}\}$$
$$= Z^{-1}\int\cdots\int \exp\{-\tilde{\mathbf{Q}}[\mathbf{\Lambda}(\mathbf{K}_\gamma)\otimes\mathbf{E}_3]\mathbf{Q}\} \times \delta(S^2 - \mu^{-1}\tilde{\mathbf{Q}}\mathbf{Q})\delta(\mathbf{q}_\nu)d\{\mathbf{Q}\} \quad (30)$$

Like previous integrals, eq 30 can be solved by using the Fourier representation of the δ function; we obtain

$$P(S^2) = (2\pi)^{-1}\int_{-\infty}^{\infty} e^{-ikS^2}|\mathbf{E} - ik\mu^{-1}\mathbf{\Lambda}_0^{-1}(\mathbf{K}_\gamma)|^{-3/2}dk \quad (31)$$

where $\mathbf{E}$ is the identity of order $(\mu - 1) \times (\mu - 1)$ and $i = \sqrt{-1}$. Further progress requires the eigenvalue spectrum of $\mathbf{K}_\gamma$. Comparison of eq 31 with the result of Fixman[4] for the distribution function for a chain leads us to conclude that $P(S^2)$ will be nongaussian.

The characteristic function $P_F(k)$ for the network is

$$P_F(k) = \prod_{l=1}^{\mu-1}[1 - ik/\mu\lambda_l(\gamma)]^{-3/2} \quad (32)$$

where the $\lambda_l(\gamma)$ are the nonzero eigenvalues of $\mathbf{K}_\gamma$. If all chains are the same length

$$\lambda_l(\gamma) = \gamma\lambda_l$$

with λ_l the nonzero eigenvalues of $\mathbf{K}$. Making use of the relation[4]

$$\ln P_F(k) = \sum_1^\infty(\xi_n/n!)(ik)^n \quad (33)$$

between $P_F(k)$ and the cumulants ξ_n of the distribution function, we obtain

$$\xi_n = [3(n-1)!/2(\mu\gamma)^n]\text{Tr}(\mathbf{\Lambda}_0^{-n}) \quad (34)$$

where $\text{Tr}(\mathbf{X})$ is the trace or spur of $\mathbf{X}$. Thus

$$\xi_1 = \langle S^2\rangle = ((3/2)\mu\gamma)\text{Tr}(\mathbf{V}_0^{-1}) = (2\langle r^2\rangle_0/\nu)\text{Tr}(\mathbf{\Lambda}_0^{-1})$$
$$\xi_2 = \langle S^4\rangle - \langle S^2\rangle^2 = (3/2\mu^2\gamma^2)\text{Tr}(\mathbf{\Lambda}_0^{-2}) = (8\langle r^2\rangle_0^2/3\nu^2)\text{Tr}(\mathbf{\Lambda}_0^{-2}), \text{ etc.}$$

It is interesting that eq 31 for the distribution function comprehends straight chains, circular chains, perfect networks, and imperfect networks. Differences among the four cases result from the different spectra of the Kirchhoff matrices.

To make the connection between the phantom model and real elastomers we assume that the mechanical radius of gyration R of the elastomer, is proportional to S. One defines R^2 as

$$R^2 = V^{-1}\int r^2dV$$

where r is the distance of a mass element from the center of gravity, and the integration is over the macroscopic volume V. Thus R^2 will obtain in the the strained state, and R_0^2 will be the mechanical radius of gyration in the unstrained state. The strained state of the network is assumed to correspond to a fluctuation state of the model; the free-energy change ΔG_{el} on stretching will be given by

$$\Delta G_{el} = k_BT\ln[P(S_0^2)/P(S^2)] \quad (35)$$

where S_0^2 is the most probable value of S^2, which corresponds to the unstrained state of the elastomer. In eq 35 k_B is Boltzmann's constant, and T is the absolute temperature. We will consider the ensemble of all networks shortly.

Nongaussian Chains

The calculations to this stage have been made for idealized, long chains. We wish to show in this section that, at least to first order, departures from Gaussian statistics can be included. The numbering scheme, matrix formulation, etc., remain applicable, but we use a different potential for interaction between cross-links. Following Flory,[12] let the distribution function $W(\mathbf{r})d\mathbf{r}$ of the end-to-end distance r of a single chain be given by

$$W(\mathbf{r})d\mathbf{r} = \text{constant}\exp(-\gamma r^2)[1 + a'r^2 + b'r^4 + \ldots]d\mathbf{r}$$

wherein constant, a', b', etc., are functions of the even moments of the distribution function. The partition function then assumes the form

$$Z_r = \text{constant}\int\cdots\int[1 + a\tilde{\mathbf{R}}(\mathbf{K}_\gamma\otimes\mathbf{E}_3)\mathbf{R} + \ldots] \exp[-\tilde{\mathbf{R}}(\mathbf{K}_\gamma\otimes\mathbf{E}_3)\mathbf{R}]\delta(\mathbf{JR})d\{\mathbf{R}\}$$

which is easily integrable[6] to give

$$Z_r = (\text{constant})Z[1 + (3a/2)(\mu - 1) + \ldots] \quad (36)$$

The free energy will be proportional to $(3a\nu/4)k_BT$ in first approximation, and there will exist an energetic contribution to the elastic equation of state which depends upon the temperature coefficients of the even moments of the end-to-end distance of the free chain.

An Alternate Approach

The formulation of the partition function for the network that we have considered was begun with a description of the potential energy of intact network. We now consider a different way of writing the configuration integral which makes use of the circle graphs, and which brings out several features of the network that are not obvious otherwise. This is accomplished by separating the backbone potential for the chains from the cross-linking condition. The formulation here is similar to methods used by Edwards and Freed[6] for introduction of constraints.

Let there be ν chains, all of the same length, attached to one another by half-links into a giant circle molecule, *cf.* Figure 1. The potential energy $V\{\mathbf{R}\}$ of the circle molecule depends upon the set $\{\mathbf{R}\}$ of position vectors of half-links $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_3$, . . ., $\mathbf{R}_\nu$. This potential energy may be written as

$$V\{\mathbf{R}\}/kT = \gamma[(\mathbf{R}_1 - \mathbf{R}_2)^2 + (\mathbf{R}_2 - \mathbf{R}_3)^2 + \ldots + (\mathbf{R}_{\nu-1} - \mathbf{R}_\nu)^2 + (\mathbf{R}_\nu - \mathbf{R}_1)^2] \quad (37)$$

if all chains between half-links have the same number of bonds. Define as before a row vector

$$\tilde{\mathbf{R}} = [\tilde{\mathbf{R}}_1\tilde{\mathbf{R}}_2\ldots\tilde{\mathbf{R}}_\nu] \quad (38)$$

where each $\tilde{\mathbf{R}}_i$ is a 1×3 vector with components x_i, y_i, z_i; the transposed column will be denoted by $\mathbf{R}$. The quadratic form, eq 37, is then

$$V\{\mathbf{R}\}/kT = \gamma\tilde{\mathbf{R}}(\mathbf{A}\otimes\mathbf{E}_3)\mathbf{R} \quad (39)$$

where $\mathbf{A}$ is the $\nu \times \nu$ version of the matrix defined in eq 7. That is

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

This matrix finds use in the theory of circular DNA; its properties are well characterized.[13] In particular, $\mathbf{A}$ is a symmetric circulant and is diagonalized by the transformation $\mathbf{\Lambda} = \mathbf{TA}\tilde{\mathbf{T}}$, where $\mathbf{T}$ (or its transpose $\tilde{\mathbf{T}} = \mathbf{T}^{-1}$) has elements t_{kl} given by (*cf.* eq 10)

$$t_{kl} = \nu^{-1/2}[\cos 2\pi kl/\nu + \sin 2\pi kl/\nu] \quad (40)$$

The eigenvalues λ_l which comprise $\mathbf{\Lambda}$ are

$$\lambda_l = 4\sin^2 \pi l/\nu \quad (41)$$

There is one zero eigenvalue, λ_ν, which corresponds to center of gravity motion of the chain. The other eigenvalues are doubly degenerate, save $\lambda_{\nu/2}$. Application of the transformation $\mathbf{T}$ sends $\{\mathbf{R}\}$ into a set of normal coordinates $\{\mathbf{Q}\}$, which may be represented as a $(1 \times 3\nu)$-dimensional column vector $\mathbf{Q}$ related to $\mathbf{R}$ by

$$\begin{aligned} \mathbf{Q} &= (\mathbf{T}\otimes\mathbf{E}_3)\mathbf{R} \\ \mathbf{R} &= (\tilde{\mathbf{T}}\otimes\mathbf{E}_3)\mathbf{Q} \end{aligned} \quad (42)$$

with transpose $\tilde{\mathbf{Q}} = \tilde{\mathbf{R}}(\tilde{\mathbf{T}}\otimes\mathbf{E}_3)$

The partition function can now be formulated. In the absence of cross-links, the circle molecule is described by the configuration integral

$$\int\ldots\int \exp[-\gamma\tilde{\mathbf{R}}(\mathbf{A}\otimes\mathbf{E}_3)\mathbf{R}]d\{\mathbf{R}\}$$

where $d\{\mathbf{R}\}$ is the 3ν-dimensional volume element $dx_1dy_1dz_1dx_2\ldots dy_\nu dz_\nu$. The cross-linkages are now imposed by insertion of an ordered product of δ functions which will ensure that half-link 1 is at the same location in space as half-link i, that 2 is located at j, that 3 is at k, etc. The structure of the ordered product of δ functions corresponds precisely to *one and only one* circle graph (see Figure 1). Now

$$Z = \int\ldots\int \exp[-\gamma\tilde{\mathbf{R}}\mathbf{AR}]\delta(\mathbf{R}_1 - \mathbf{R}_i)\delta(\mathbf{R}_2 - \mathbf{R}_j)\ldots \delta(\mathbf{R}_p - \mathbf{R}_q)d\{\mathbf{R}\} \quad (43)$$

where the sequence of indices of the position vectors with positive signs in the arguments of the δ functions runs in increasing order. The structure of this ordering will be apparent shortly.

To evaluate the integral we introduce the Fourier representation of the δ function, so that

$$Z = \int\ldots\int \exp[-\gamma\tilde{\mathbf{R}}(\mathbf{A}\otimes\mathbf{E}_3)\mathbf{R}] \exp[i\tilde{\mathbf{K}}(\mathbf{C}\otimes\mathbf{E}_3)\mathbf{R}]d\{\mathbf{R}\}\,d\{\tilde{\mathbf{K}}\} \quad (44)$$

(12) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969, pp 309–313.

(13) V. Bloomfield and B. H. Zimm, *J. Chem. Phys.*, **44**, 315 (1966).

where $\tilde{\mathbf{K}}$ is the $1 \times (3\nu/2)$ row composed of the wave vectors $\boldsymbol{\kappa}_l$

$$\tilde{\mathbf{K}} = [\tilde{\boldsymbol{\kappa}}_1\tilde{\boldsymbol{\kappa}}_2 \ldots \tilde{\boldsymbol{\kappa}}_{\nu/2}]$$

and $\tilde{\mathbf{C}}$ is the $(\nu/2) \times \nu$ cross-linking matrix (known in graph theory as the incidence matrix)

$$\tilde{\mathbf{C}} = \begin{bmatrix} 1 & 0 & 0 & 0 & -1 & 0 & 0 & \cdots & & & & & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & \cdots & 0 & -1 & 0 & \cdots & & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & \cdots & -1 & 0 & \cdots & & & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & \cdots & & & & & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & \cdots & 0 & -1 & 0 & \cdots & 0 \\ \vdots & & & & & & & & & & & & \vdots \\ \vdots & & & & & & & & & & & & -1 \\ \vdots & & & & & & & & & & & & \vdots \\ 0 & \cdots & & & & & 0 & 1 & 0 & \cdots & 0 & -1 & 0 & 0 \end{bmatrix} \quad (45)$$

The matrix $\tilde{\mathbf{C}}$ has a 1 *and* -1 in each row, and a 1 *or* -1 in each column. The ordering of the δ function ensures that there are only zero entries to the left of the diagonal running from the upper left corner to the middle of the last row in $\tilde{\mathbf{C}}$ for any network.

Upon introduction of the normal coordinates, the partition function becomes

$$Z = (2\pi)^{-3\nu/2} \int \cdots \int \exp\{-\gamma\tilde{\mathbf{Q}}[\boldsymbol{\Lambda}(\mathbf{A}) \otimes \mathbf{E}_3]\mathbf{Q} + i\tilde{\mathbf{K}}[(\tilde{\mathbf{C}}\tilde{\mathbf{T}}) \otimes \mathbf{E}_3]\mathbf{Q}\}\, d\{\mathbf{Q}\}\, d\{\boldsymbol{\kappa}\}\, \delta(\mathbf{q}_\nu) \quad (46)$$

The Jacobian is unity. The center of gravity coordinate $\mathbf{q}_\nu$, defined by

$$\mathbf{q}_\nu = \nu^{-1/2} \sum_{n=1}^{\nu} \mathbf{R}_n \quad (47)$$

is handled as before. The configuration integral may be evaluated by completing the square in the normal coordinates, with the result

$$Z = (\gamma/\pi)^{3/2}(\pi/\gamma)^{3\nu/4}/|\boldsymbol{\Lambda}_0|^{3/2}|\mathbf{G}_0|^{3/2} \quad (48)$$

Here $|\boldsymbol{\Lambda}_0| = |\boldsymbol{\Lambda}_0(\mathbf{A})|$ is the determinant of the $(\nu - 1) \times (\nu - 1)$ matrix $\boldsymbol{\Lambda}_0(\mathbf{A})$ obtained from $\boldsymbol{\Lambda}(\mathbf{A})$ by deletion of the last row and column which contain the zero eigenvalue. The determinant $|\mathbf{G}_0|$ of the matrix

$$\mathbf{G}_0 = \tilde{\mathbf{C}}\tilde{\mathbf{T}}_0\boldsymbol{\Lambda}_0^{-1}\mathbf{T}_0\mathbf{C} \quad (49)$$

depends upon the network structure and represents contributions to the partition function over and above those due to free chains. In eq 49, the matrix $\mathbf{T}_0$ is of dimension $(\nu - 1 \times \nu$ so as to be conformable with $\boldsymbol{\Lambda}_0^{-1}$; the last row of $\mathbf{T}$ is deleted to form $\mathbf{T}_0$. The structure of $\mathbf{G}_0$ is developed in Appendix B, while Appendix A is devoted to $\tilde{\mathbf{T}}_0\boldsymbol{\Lambda}_0^{-1}\mathbf{T}_0$ and similar matrices.

The distribution function of the radius of gyration of the network may be evaluated by the same method as before, *cf.* eq 31; we obtain

$$P(S^2) = (2\pi)^{-1} \int \exp(-i\kappa S^2)|\mathbf{E} - (i\kappa/\gamma\nu)\boldsymbol{\Lambda}_0^{-1}(\mathbf{A})|^{-3/2}|\mathbf{G}_0^{-1}\mathbf{G}_\xi|^{-3/2} d\kappa \quad (50)$$

The term involving $\boldsymbol{\Lambda}_0^{-1}(\mathbf{A})$ alone may be simplified[4] by the approximation

$$\prod_{l=1}^{\nu-1} [1 - i\kappa/4\gamma\nu \sin^2 \pi l/\nu]^{-3/2} \approx \prod_{l=1}^{\infty} (1 - i\kappa\nu/4\pi^2\gamma l^2)^{-3} = [\sin (i\kappa\nu/4\gamma)/(i\kappa\nu/4\gamma)]^{-3} \quad (51)$$

Were the network cross-links nonexistent, eq 51 would be the characteristic function for the giant circle molecule. (The characteristic function for a circle is the square of that for the linear chain because of degeneracy.) The influence of the network on the configuration of the giant circle molecule is contained in the term $|\mathbf{G}_0^{-1}\mathbf{G}_\xi|^{-3/2}$, where

$$\mathbf{G}_\xi = \tilde{\mathbf{C}}\tilde{\mathbf{T}}_0[\boldsymbol{\Lambda}_0(\mathbf{A}) - \xi^2\mathbf{E}]^{-1}\mathbf{T}_0\mathbf{C} \quad (52)$$

with

$$\xi^2 = i\kappa/\gamma\nu$$

We have not been able to obtain $\mathbf{G}_0^{-1}$ in simple form, and therefore we have not found a means to reduce $\mathbf{G}_0^{-1}\mathbf{G}_\xi$. This term can be expanded in powers of ξ^2, but the expansion is probably not convergent. The elements of $\mathbf{G}_\xi$ are calculated in Appendix B.

Graph Matrices

The incidence matrix $\mathbf{C}$ can be related to the Kirchhoff matrix $\mathbf{K}_\gamma$ in a straightforward way. We first note that, for any tetrafunctional network

$$\tilde{\mathbf{C}}\mathbf{C} = 2\mathbf{E}_{\nu/2} \quad (53)$$

where $\mathbf{E}_{\nu/2}$ is the identity of order $\nu/2$. Define the $\nu \times \nu$ matrix

$$\mathbf{A}_\gamma = \begin{bmatrix} \gamma_1 + \gamma_2 & -\gamma_1 & 0 & 0 & \cdots & 0 & -\gamma_\nu \\ -\gamma_1 & \gamma_1 + \gamma_2 & -\gamma_2 & 0 & \cdots & 0 & \\ 0 & -\gamma_2 & \gamma_2 + \gamma_3 & -\gamma_3 & \cdots & 0 & \\ \vdots & & & & & \vdots & \\ & & & & & 0 & \\ \vdots & & & \gamma_{\nu-2} + \gamma_{\nu-1} & & -\gamma_{\nu-1} & \\ -\gamma_\nu & 0 & \cdots & -\gamma_{\nu-1} & & \gamma_{\nu-1} + \gamma_\nu & \end{bmatrix} \quad (54)$$

which can be identified as the variable Kirchhoff matrix for the circle graph which represents the giant circle molecule. The edges of the circle are labeled serially and counterclockwise as in Figure 1, with γ_l connecting half-link l to $l + 1 \times$ (mod ν). Define also $|\mathbf{C}|$ as the matrix with elements $|c|_{kl} = |\mathbf{c}_{kl}|$; *i.e.*, the absolute value of the elements of $\mathbf{C}$. (There should be no confusion between the absolute value notation and the notion of determinate, since the determinant of $\mathbf{C}$ does not exist.) One can readily verify that

$$\mathbf{K}_\gamma = |\tilde{\mathbf{C}}|\mathbf{A}_\gamma|\mathbf{C}| \quad (55)$$

where $\mathbf{K}_\gamma$ is the variable Kirchhoff matrix for the graph with edges labeled as the edges in the circle graph and vertices labeled with the indices 1, 2, . . ., μ corresponding to the rows of $\mathbf{C}$. Here, as above, the graph is completely general except that all vertices are of degree 4, and of course $\mu = \nu/2$. Loops in the graph do not appear in $\mathbf{K}_\gamma$, even though the loop edge is labeled in $\mathbf{A}_\gamma$. The Kirchhoff matrix $\mathbf{K}$ with labels re-

moved is given by $\mathbf{K} = |\tilde{\mathbf{C}}|\mathbf{A}|\mathbf{C}|$. In Appendix C it is shown that $\mathbf{C}$ can be written in terms of a set of $\mu - 1$ fundamental circuits $\{\mathcal{C}\}$ of lengths $\mathcal{C}_1, \mathcal{C}_2, \ldots, \mathcal{C}_{\mu-1}$. Thus, the $\mu - 1$ nonzero eigenvalues of $\mathbf{K}$ will be functions of the set $\{\mathcal{C}\}$ of $\mu - 1$ circuit lengths. Diagonalization of $\mathbf{K}$ to obtain this dependence is a tantalizing prospect in addition to being extremely difficult.

Properties of Graphs and Ensembles

The matrices $\mathbf{G}_0$ and $\mathbf{K}$ which describe the networks composed of chains of the same length possess spectra which depend upon the connectivity of the network. Circle graphs and network graphs can be grouped into sets, such that members of each set represent one and only one distinct delabeled network graph. The eigenvalue matrices of the $\mathbf{G}_0$ or $\mathbf{K}$ for members of one of the sets cannot differ from one another by more than a permutation of the elements, even though the member matrices $\mathbf{C}$ differ substantially from one another. Thus, the number of networks of different connectivity is far less than the number[14]

$$(\nu - 1)(\nu - 3)(\nu - 5)\ldots 3\cdot 1 = \nu!/2^{\nu/2}(\nu/2)! \qquad (56)$$

of labeled circle graphs.

To show the way in which circle graphs become equivalent when reduced to network graphs, it is instructive to consider small networks composed of eight chains. If one draws these graphs, and combines whose which are obvious mirror images, rotations, and inversions, 17 sets of distinct delabeled circle graphs are obtained. On drawing network graphs for these, one finds that some of these sets yield equivalent delabeled network graphs. These ten distinct delabeled network graphs are shown in Figure 3. It is apparent that there is a distribution of graphs which could be described in terms of a distribution function. We wish to consider the formulation of such a function in this section.

The ultimate solution to this problem would be obtained if one were able to count all of the distinct delabeled network graphs by some algorithm. It is well known that trees can be counted using Polya's theory, but we have not been able to find any successful application of this counting theory to graphs that contain a large number of circuits. Perhaps we can hope that the circle graphs will lead to some insight into this problem of general importance.

To make this discussion more concrete than speculative, let each circle graph have equal *a priori* probability. The eigenvalue spectrum $f = f(\lambda)$ of $\mathbf{K}$ for a graph may be considered a functional parameter, and we seek the fraction $N(f)\delta f$ of graphs with spectra between f and $f + \delta f$. Since the distribution function of the radius of gyration depends only on the spectrum of $\mathbf{K}$, this definition seems adequate for present purposes. The partition function for the ensemble of networks[14] is

$$Z = \exp\int N(f) \ln Z(f)\delta f$$

Thus, the breadth of $N(f)\delta f$ is of fundamental importance. If $N(f)\delta f$ is sharply peaked, then, as is justified in statistical mechanics, the sum over all network structures may be replaced by the maximum term. If, on the other hand, the distribution is broad, then the sum over all networks must be computed. Since we have not been able to catalog larger networks than the small ones considered above, we avoid making a conjecture as to the nature of $N(f)\delta f$. Monte Carlo computer calculations might indicate the nature of this distribution function, and in addition would yield the spectra of $\mathbf{K}$ and $\mathbf{G}_0$. It appears possible to formulate $\mathbf{C}$ as a probability function; exposition of that treatment will be left to a later time.

(14) P. J. Flory, *J. Chem. Phys.*, **18**, 108 (1950).

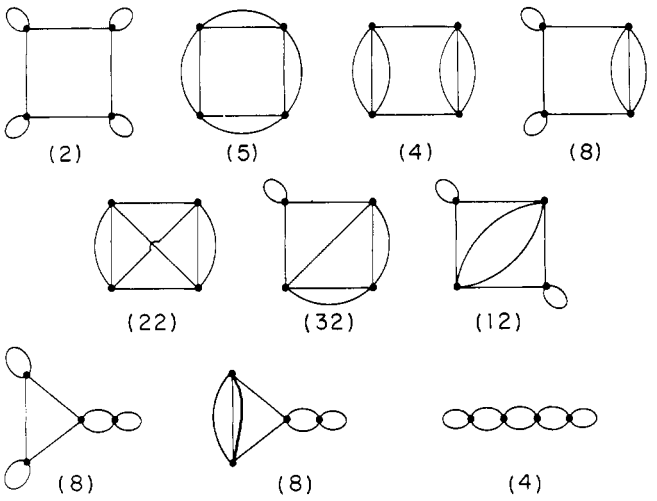

Figure 3. The distribution of four valent graphs of eight edges. The numbers refer to the number of circle graphs that yield each network. There are (7)(5)(3) = 105 circle graphs in all (see eq 56).

Discussion

The phantom model for elastomers can be treated in detail, and by identifying ΔG_{el} with $k_B T \ln [P(S_0^2)/P(S^2)]$ one can formulate a theory which avoids the use of constraints. The way in which the configurational entropy of a real elastomer is constrained by volume exclusion and entanglements, the former factor being possibly the more important, is of no concern.

The conjectured nongaussian behavior of the distribution function is sufficient to ensure that the elastic equation of state will contain contributions from terms other than $L_x^2 + L_y^2 + L_z^2$. Whether these additional terms bear any resemblance to the C_2 term will depend upon the nature of the spectrum of $\mathbf{K}$ or $\mathbf{G}_0$. Monte Carlo computer calculations of the spectra are in progress, and will be reported in another publication. Preliminary results of these calculations suggest that the distribution function of eigenvalues is linear, *i.e.*, the density is constant, for perfect networks. (Such behavior was found by James[2] for the simple cubic lattice.) As a consequence, $\langle S^2 \rangle \propto \ln \nu$ for networks without chain ends. We suspect that the *functional* dependence of $P(S^2)\mathrm{d}S^2$ on ν will depend upon the relative number of cross-links to chain ends. If this is the case, it seems likely that almost *any* result can be obtained for the elastic equation of state depending on the number of cross-links to primary chains. Volume exclusion in real elastomers prohibits the precipitous collapse of the network at high cross-link densities and intervenes in chain contraction; this effect might be more important than chain entanglements that act as additional cross-links.

At the gel point the eigenvalues λ_l of the Kirchhoff matrix are proportional to l^2, and there is an average of one cross-link per chain. We propose that at the syneresis point, $\lambda_l \propto l^{5/3}$. The cross-link density that gives this kind of spectrum will be considered elsewhere.

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Appendix A

The matrices that have been developed in the alternate method are composed of products of the type $\tilde{\mathbf{T}}_0\mathbf{M}_0^{-1}\mathbf{T}_0$. We will develop these product matrices in this appendix. All sums with which we deal can be approximated by known functions.

The matrix $\mathbf{G}_0$ which appears in the partition function is composed of the matrix

$$\mathbf{B} = \tilde{\mathbf{T}}_0\mathbf{\Lambda}_0^{-1}\mathbf{T}_0 \tag{A-1}$$

The elements b_{mn} of $\mathbf{B}$ are given by

$$b_{mn} = \frac{1}{4\nu}\sum_{l=1}^{\nu-1} \times \frac{(\cos 2\pi ml/\nu + \sin 2\pi ml/\nu)(\cos 2\pi ln/\nu + \sin 2\pi ln/\nu)}{\sin^2 \pi l/\nu} = \frac{1}{4\nu}\sum_{l=1}^{\nu-1}\frac{\cos 2\pi l(m-n)/\nu}{\sin^2 \pi l/\nu}$$

Here we note that b_{mn} depends only upon $|m-n|$, so

$$b_{mn} = b_{|m-n|} = b_t = \frac{1}{2\nu}\sum_{l=1}^{\nu/2}\frac{\cos 2\pi lt/\nu}{\sin^2 \pi l/\nu} \tag{A-2}$$

The last equation (A-2) may be summed by a lengthy calculation based on a recursion relation. The same result is obtained by transforming the sum to

$$b_t \cong \frac{\nu}{2\pi^2}\sum_{l=1}^{\infty}\frac{\cos 2\pi lt/\nu}{l^2} \tag{A-3}$$

This function is tabulated (Jolley);[15a] the result is

$$b_t = \frac{\nu}{12} - t(\nu - t)/2\nu \tag{A-4}$$

The exact result, obtained by the method described above, is $1/12\nu$ less than the right-hand side of eq A-4.

The matrices involved in the calculation of the distribution function have elements of the form

$$b_{mn}(\xi) = \frac{1}{\nu}\sum_{l=1}^{\nu-1}\frac{\cos 2\pi l(m-n)/\nu}{4\sin^2 \pi l/\nu - \xi^2} \tag{A-5}$$

This may be similarly reduced to

$$b_t(\xi) \cong \frac{\nu}{2\pi^2}\sum_{l=1}^{\infty}\frac{\cos 2\pi lt/\nu}{l^2 - (\xi\nu/2\pi)^2} \tag{A-6}$$

which yields (Jolley)[15b]

$$b_t(\xi) \cong \frac{1}{\nu\xi^2} - \frac{\cos[(t-\nu/2)\xi]}{2\xi\sin(\xi\nu/2)} \tag{A-7}$$

There are obviously many singularities of $b_{mn}(\xi)$, eq A-5, on the real axis, which do not coincide with the singularities of eq A-7. The approximate eq A-7 is well behaved in the neighborhood of $\xi = 0$, however, so there are no problems in handling the moments of the radius of gyration. One can be confident on physical grounds that there will not be difficulties from singularities of $b_t(\xi)$ which arise in the treatment of the distribution function.

Appendix B

The matrices which describe the network are of the form $\mathbf{G}_\xi = \tilde{\mathbf{C}}\mathbf{B}_\xi\mathbf{C}$, where the inner matrix $\mathbf{B}_\xi$ is always a symmetric circulant with elements given in Appendix A. Formation of $\mathbf{G}_\xi$ is somewhat cumbersome, in that a doubly subscripted indexing is essential. However, the structure of the network appears clearly in the end in terms of a set of fundamental circuits.

When premultiplying by $\tilde{\mathbf{C}}$, with elements $\tilde{c}_{km}$, and when postmultiplying by $\mathbf{C}$, one may use the Kronecker δ notation

$$\begin{aligned}\tilde{c}_{km} &= \delta_{g_k,m} - \delta_{g_k+e_k,m}\\ c_{nl} &= \delta_{n,g_l} - \delta_{n,g_l+e_l}\end{aligned} \tag{B-1}$$

Here g_k is the index (column number) of the $+1$ that appears in row k of $\tilde{\mathbf{C}}$ and $g_k + e_k$ is the column in which the -1 appears. The number of chains between the two half-links which form the kth cross-link is e_k when proceeding from g_k to $g_k + e_k$ in the counterclockwise direction and is $\nu - e_k$ when traveling in the clockwise direction.

Utilizing these definitions of $\tilde{\mathbf{C}}$ and $\mathbf{C}$, we obtain (with the dependence on ξ implicit in g_{kl} and b_{mn})

$$g_{kl} = \sum_{m,n=1}^{\nu}\tilde{c}_{km}b_{mn}c_{nl} = b_{g_k,g_l} + b_{g_k+e_k,g_l+e_l} - b_{g_k+e_k,g_l} - b_{g_k,g_l+e_l} \tag{B-2}$$

It will be recalled that $\mathbf{B}_\xi$ is a symmetric circulant, so that the matrix elements on the right-hand side of eq B-2 conform to a relation exemplified by

$$b_{g_k,g_l} = b_{|g_k-g_l|}$$

The elements of $\mathbf{G}_\xi$ clearly depend on the locations of four half-links on the circle molecule. Since $\mathbf{G}_\xi$ is symmetric, it suffices to consider $l > k$ when simplifying eq B-2. There are, however, three separate classes of matrix elements (four including the diagonal elements). Graphs of these three classes are depicted in Figure 4. For class i, eq B-2 and A-7 yield

$$2\xi\sin(\xi\nu/2)g_{kl}^{(i)} = -\cos[\xi(e_k + e_\beta - \nu/2)] - \cos[\xi(e_l + e_\beta - \nu/2)] + \cos[\xi(e_\beta - \nu/2)] + \cos[\xi(e_\alpha - \nu/2)] \tag{B-3}$$

where the e_l's are identified in Figure 4. Equation B-3 may be reduced to

$$g_{kl}^{(i)} = -\frac{\sin(e_k\xi/2)\sin(e_l\xi/2)\cos[(e_\alpha - e_\beta)\xi/2]}{(\xi/2)\sin(\nu\xi/2)} \tag{B-4}$$

The other two classes (ii and iii) of matrix elements are

$$g_{kl}^{(ii)} = -\frac{\sin[(\nu - e_k)\xi/2]\sin[(\nu - e_l - e_\alpha - e_\beta)\xi/2] + \sin(e_k\xi/2)\sin[(e_l - e_\alpha - e_\beta)\xi/2]}{2(\xi/2)\sin(\nu\xi/2)} \tag{B-5}$$

$$g_{kl}^{(iii)} = \frac{\sin[(\nu - e_k)\xi/2]\sin(e_l\xi/2)\cos[(e_\alpha - e_\beta)\xi/2]}{(\xi/2)\sin(\nu\xi/2)} \tag{B-6}$$

The diagonal elements of $\mathbf{G}_\xi$ may be obtained from either eq B-5 or B-6 by equating appropriate pairs of circuits. These elements are

$$g_{ll} = \frac{\sin(e_l\xi/2)\sin[(\nu - e_l)\xi/2]}{(\xi/2)\sin(\nu\xi/2)} \tag{B-7}$$

The class i diagram (see Figure 4) does not pass into the diagram which is associated with the diagonal matrix elements

(15) L. B. W. Jolley, "Summation of Series," Dover Publications, New York, N. Y., 1961, (a) #573; (b) #559.

given by eq B-7. This is due to the fact that as $\mathcal{C}_\alpha \to 0$ the graph passes from class i to class iii.

The graph matrix $\mathbf{G}_0$ obtained in the evaluation of the partition function has matrix elements which may be obtained from eq B-4–B-7 by computing the limit, as $\xi \to 0$, of g_{kl}. These elements are

$$\begin{aligned} g_{kl}^{(\mathrm{i})} &= -\mathcal{C}_k\mathcal{C}_l/\nu \\ g_{kl}^{(\mathrm{ii})} &= -\mathcal{C}_k\mathcal{C}_l/\nu + \mathcal{C}_\beta \\ g_{kl}^{(\mathrm{iii})} &= -\mathcal{C}_k\mathcal{C}_l/\nu + \mathcal{C}_l \\ g_{ll} &= \mathcal{C}_l(\nu - \mathcal{C}_l)/\nu \end{aligned} \tag{B-8}$$

The same elements may be obtained more directly from eq A-4 and B-2 with use of Figure 4. The specification of the matrices for a given network is now complete.

Appendix C

The incidence matrix $\mathbf{C}$ or $\tilde{\mathbf{C}}$ for the circle graph contains all information necessary to construct the network graph. From consideration of the incidence matrix it can be proved that there are $\mu - 1$ independent circuit lengths in fourvalent graphs of μ vertices.

Proof. Consider the incidence matrix $\tilde{\mathbf{C}}$ defined in eq 45 of the text. The first row contains $+1$ in element (1, 1) and -1 in element $(1, 1 + \mathcal{C}_1)$, where $\mathcal{C}_1$ is the number of edges in the circle graph between half-vertex 1 and its mate at the terminus of the chord drawn from 1. The first row of $\tilde{\mathbf{C}}$ can be constructed if one knows the value of $\mathcal{C}_1$. Given $\mathcal{C}_1$, the location of the $+1$ in row 2 of $\tilde{\mathbf{C}}$ is determined: it belongs in the first unoccupied column. For example, if $\mathcal{C}_1 = 1$, the first unoccupied column of $\tilde{\mathcal{C}}$ is column 3, and so $\tilde{c}_{23} = +1$. The column index of the -1 in row 2 will be $3 + \mathcal{C}_2$, and so specification of $\mathcal{C}_2$ locates it. If $\mathcal{C}_1 > 1$, then $\tilde{c}_{22} = +1$, and the -1 belongs to column $2 + \mathcal{C}_2$. Continuing in this fashion through all rows it can be seen that the sequence of integers $\mathcal{C}_1, \mathcal{C}_2, \mathcal{C}_3 \ldots, \mathcal{C}_{\mu-1}$ locates all elements in the incidence matrix, since in the last row there are only two possible positions for the $+1$ and -1, and the $+1$ must have a lower column index than the -1.

One may represent the incidence matrix as a vector

$$[\mathcal{C}_1, \mathcal{C}_2, \mathcal{C}_3, \ldots, \mathcal{C}_{\mu-1}]$$

of fundamental circuit lengths in a $(\mu - 1)$-dimensional space. Lattice points in this space represent directed fourvalent graphs, and graphs that differ only by permutations of numbering will be at different locations in this space. (The graphs are directed because edge γ_α connects α to $\alpha + 1$, and so each edge can be given a direction.)

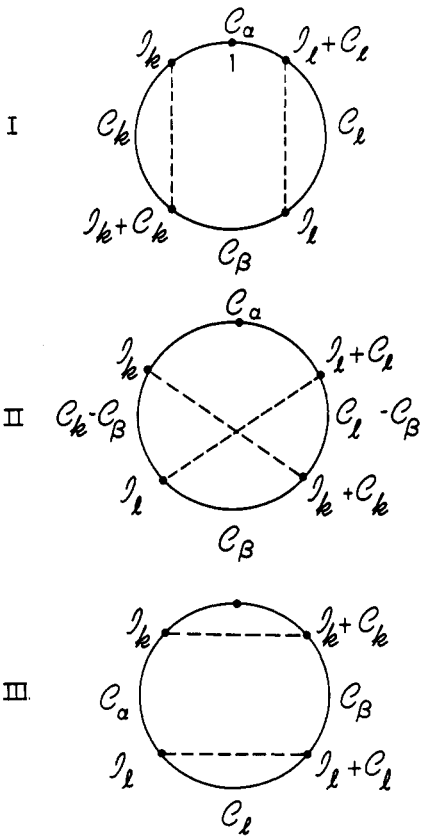

Figure 4. The three classes of connections for a pair of cross-links. Classes i and ii put two creases in the circle, and class ii puts in a fold.

A cyclic permutation of the circle graph, defined by $\alpha \to \alpha + 1 (\mathrm{mod}\ \nu)$, sends $[\mathcal{C}_1, \mathcal{C}_2, \ldots, \mathcal{C}_{\mu-1}, \mathcal{C}_\mu] \to [\nu - \mathcal{C}_\mu, \mathcal{C}_1, \mathcal{C}_2, \ldots, \mathcal{C}_{\mu-1}]$ if $\mathcal{C}_1 \neq \nu - 1$ or to $[\nu - \mathcal{C}_1, \mathcal{C}_2, \mathcal{C}_3, \ldots, \mathcal{C}_\mu]$ if $\mathcal{C}_1 = \nu - 1$. Thus it would appear that the vector

$$[\mathcal{C}_1(1 - \mathcal{C}_1/\nu), \mathcal{C}_2(1 - \mathcal{C}_2/\nu), \ldots, \mathcal{C}_{\mu-1}(1 - \mathcal{C}_{\mu-1}/\nu), \mathcal{C}_\mu(1 - \mathcal{C}_\mu/\nu)]$$

which has elements invariant to cyclic permutations, should describe nondirected, delabeled graphs. This vector is composed of the diagonal elements of $\mathbf{G}_0$ defined in Appendix B. Unfortunately, we have not been able to prove that this representation uniquely determines a circle graph, although we have not found examples where it is not unique.