THEORY OF ELASTICITY WITHOUT ENTANGLEMENTS

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ABSTRACT

A comprehensive statistical mechanical theory for elastic networks is developed on a basis which neglects the interaction between network atoms and superficial constraints. The strain is calculated from the molecular configuration by means of the gyration tensor. The probability distribution of the latter quantity may be evaluated from an appropriately modified configuration integral. Terms in this integral are conveniently manipulated with use of the incidence matrix for the complete star graph representative of all possible interactions between atoms. The last formal step entails averaging thermodynamic functions over all internal connectivities that might be formed under a given set of external constraints. Finally, an illustrative calculation is performed for the Gaussian model with excluded volume interaction; entanglements are not included in the model.

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1. INTRODUCTION

The formal theory of high elasticity to be presented here is developed from beginning concepts to final averages. It is applicable to all elastic materials regardless of chemical structure. Specific calculations on a particular model are made to exhibit the manner in which the configuration integral is handled; the model does not include entanglements. The aim of the discussion is to show that it is possible to develop a theory for elastomers which avoids, or at least makes explicit, all approximations to the fundamental relations between the strain and molecular configuration, including network connectivity.

The subject is developed in four stages. We first choose a particularly simple way for dealing with the mechanical coupling between the elastomer and the stress applicators. This is not done without approximation; but it can be argued that in the thermodynamic limit the error entailed on ignoring the interaction energy between the system (elastomer) and surroundings (stress applicators and thermal bath) is negligible. Next it will be shown that the general thermodynamic stress–strain relation is reducible to a form which is appropriate if the elastic free energy is a function of the radius of gyration of the network. Here a new view of affine deformations emerges. Following this is a section on the formulation of the configuration integral; graphs and matrices which are useful and important aids for organizing terms in and computing the value of the configuration integral are introduced there.

At the last stage of the formal theory the methods for computing ensemble averages are discussed. Finally, the techniques of the third section are applied to the quadrature of the configuration integral for a model network consisting of Gaussian chains which interact with one another via a short-range repulsive force. The integrations can be carried to the penultimate stage, at which point it becomes necessary to diagonalize random sparse matrices.

2. GENERAL CONSIDERATIONS

Elastomers, to be effective as mechanical devices, must be constrained only over a small fraction of their surface. Let $S(\mathbf{r})$ be the bounding surfaces of the stress-applying devices. The discontinuous surface-specifying function $S(\mathbf{r})$ is considered to depend parametrically upon the space point $\mathbf{r}$ in the laboratory reference frame. Now consider the set of volumes $V_i[\mathbf{r}, S(\mathbf{r})]$, $1 \leqslant i \leqslant \infty$, bounded by continuous surfaces, all of which include $S(\mathbf{r})$, as depicted in *Figure 1*. Further, let the measure of volume $\mu(V_i) \leqslant \mu(V_{i+1})$, so that the set consists of a sequence of increasingly large volumes. The limit of this set, V_∞, is the volume available to the elastomer. Whether the network occupies a large or a small portion of this volume is determined by internal forces.

The potential energy of the system of N atoms, or groups of atoms, is $V(\{\mathbf{R}\})$, which depends upon the set $\{\mathbf{R}\}$ of atomic positions. The configuration integral Z is given by
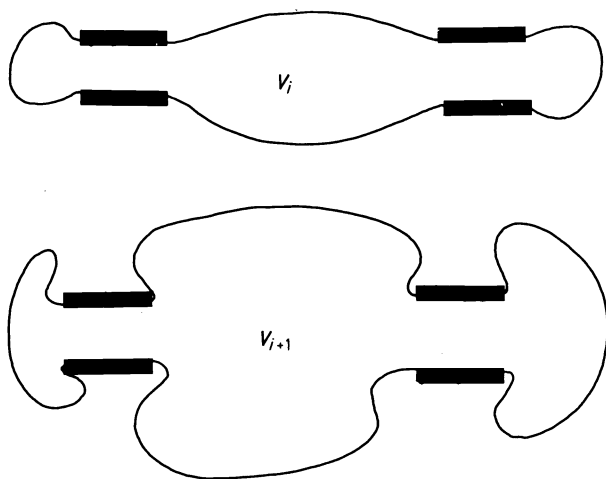

Figure 1. A representation of the set of volumes V_i which are available to network atoms. The heavy bars represent fixed external constraining devices. The volume over which integrals must be performed is V_∞, a volume of infinite measure but one which is partially bounded by the fixed surfaces indicated

$$Z = \int_{V_\infty} \cdots \int \exp\left[-\beta V(\{\mathbf{R}\})\right] d\{\mathbf{R}\} \tag{1}$$

where $\beta = 1/kT$, and the integrations extend over the entire domain V_∞. The potential $V(\{\mathbf{R}\})$ includes terms representing the interaction between the atoms comprising the restraining device, i.e. $S(\mathbf{r})$, and the elastomer.

We now state the main assertion of this section:

In the thermodynamic limit of large systems the energy of interaction between network atoms and constraining surface atoms may be taken to be a negligible fraction of the interaction energy of network atoms themselves. Likewise, the bounding surface $S(\mathbf{r})$ is taken to be a negligible fraction of the total surface area of the elastomer.

This assumption is motivated by: (1) the difficulty of restraining surface atoms in any rigorous manner (the method of James and Guth[1] has been criticized repeatedly in this respect[2, 3]); (2) the reluctance to admit that it is necessary to compute the configuration integral for all conceivable or useful constraints. Freed[3] has previously pointed out the importance of the thermo-dynamic limit.

The volume V_∞ has now become all of space with no restrictions. However, by un-restricting the volume in which to place the elastomer we have created new problems. Since the volume is infinite, the configuration integral diverges even for connected networks, owing to the centre of gravity (c.g.) motion. This is easily circumvented by choosing a coordinate system which is co-moving with the c.g., and this in turn is accomplished by inserting the delta function $\delta(\Sigma_{i=1}^{N} \mathbf{r}_i)$ in the configuration integral, so that equation (1) becomes

$$Z = \int_{-\infty}^{\infty} \cdots \int \delta\left(\sum_{i=1}^{N} \mathbf{r}_i\right) \exp\left[-\beta V(\{\mathbf{R}\})\right] d\{\mathbf{R}\} \tag{2}$$

Here we have taken all atomic groups to be identical, with the ith group located at $\mathbf{r}_i$. Elaboration to account for individual atom positions in the delta function is easily accomplished by taking the argument of this func-tion to be

$$\sum_i m_i \mathbf{r}_i / \sum_i m_i$$

where m_i is the mass of atom i. For simplicity, however, we will henceforth deal exclusively with generic networks composed of N identical groups. The reader should have no difficulty in applying the equations to two or more types of groups or even to individual atoms as may be appropriate. However, it is worth noting that the general properties of elastomers are relatively insensitive to chemical composition, and our preoccupation at this stage with general descriptions is convenient, not shortsighted.

The second problem which is raised on passing from equation (1) to equation (2) is that the obvious means for introducing the strain have

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disappeared. It will be necessary to augment equation (2) so as to obtain information of one kind or another which relates to the macroscopic configuration in space. We now turn to the question of what kind of information is required of the configuration integral.

3. STRESS–STRAIN RELATION

The fluctuation theory which is to be offered here has its basis in the work of Wall and Flory.

The definition of strain which we shall use dates to the time of the mathematician Cauchy. Main features of the development may be found in monographs devoted to continuum mechanics and elasticity[4, 5].

Let the infinitesimal distance ds_0 between two material points in the unstrained body be given by

$$ds_0^2 = h_{\alpha\beta}dy^\alpha dy^\beta \tag{3}$$

where dy^α is the component of the displacement along the αth coordinate axis. The tensor $h_{\alpha\beta}$ is the metric for the space, and is determined by the intrinsic geometry of the medium. (The summation convention is used throughout.) The similar displacement ds^2 between the same two points in the strained state is

$$ds^2 = g_{\alpha\beta}dx^\alpha dx^\beta \tag{4}$$

where $g_{\alpha\beta}$ is the metric tensor of this state, and the dx^α are the new natural coordinates. These new coordinates are related to the old by

$$dx^\alpha = (\partial x^\alpha/\partial y^\mu)\,dy^\mu$$
$$= \lambda_{.\mu}^\alpha dy^\mu \tag{5}$$

where $\lambda_{.\mu}^\alpha$ is the deformation gradient tensor. Substitution from equation (5) into equation (4) and subtraction of equation (3) gives

$$ds^2 - ds_0^2 = (g_{\mu\nu}\lambda_\alpha^\mu\lambda_\beta^\nu - h_{\alpha\beta})\,dy^\alpha\,dy^\beta$$
$$= 2\eta_{\alpha\beta}\,dy^\alpha\,dy^\beta \tag{6}$$

where $\eta_{\alpha\beta}$ is in hydrodynamics the Lagrangian strain tensor; it is related to the Eulerian strain $\varepsilon_{\alpha\beta}$ by

$$\eta_{\alpha\beta} = \varepsilon_{\mu\nu}\lambda_\alpha^\mu\lambda_\beta^\nu \tag{7}$$

(The Lagrangian and Eulerian strains are functions of the coordinates of the undeformed and deformed states, respectively.)

Analysis[4] of the (virtual) work accompanying deformation gives the symmetric stress tensor $T_0^{\alpha\beta}$ referred to the undeformed state as

$$T_0^{\alpha\beta} = \rho(\partial\hat{A}/\partial\eta_{\alpha\beta})_T \tag{8}$$

where ρ is the mass density and $\hat{A}$ is the (Helmholtz) free energy per unit mass. This free energy is, properly speaking, a point function, i.e. it may vary from point to point in the medium. Yet, statistical mechanics does not pro-

vide the means for calculation of the free energy per unit mass, except in the trivial sense of the total free energy divided by the total mass. This is only the second of such difficulties in connecting continuum mechanics to statistical mechanics. (The first is in the definition of strain, where it is necessary to be more precise in specification of distances. We cannot be referring to displacements between instantaneous atomic positions, for these microscopic coordinates fluctuate rapidly even in the equilibrium state. Instead, a point of the continuum must be understood to refer to the c.g. of large collections of atoms which nonetheless occupy only a very small volume.) In order for us to be able to calculate the stress, the elastomer is taken to be homogeneous, so that equation (8) becomes

$$T_0^{\alpha\beta} = V^{-1}(\partial A/\partial \eta_{\alpha\beta})_T \tag{9}$$

where A is the total free energy and V is the total volume for the particular state of strain at which the derivative is evaluated.

The combined first and second laws are written in terms of the free energy as

$$\mathrm{d}A = -S\,\mathrm{d}T + VT_0^{\alpha\beta}\,\mathrm{d}\eta_{\alpha\beta} \tag{10}$$

We will later return to this equation for ensemble averaging.

More convenient than $T_0^{\alpha\beta}$ is the stress $T^{\alpha\beta}$ referred to the coordinate system of the stressed state. Owing to the tensor character of $T_0^{\alpha\beta}$, we immediately have

$$
\begin{aligned}
T^{\alpha\beta} &= (\partial x^\alpha/\partial y^\mu)(\partial x^\beta/\partial y^\nu)\,T_0^{\mu\nu} \\
&= \lambda_\mu^\alpha \lambda_\nu^\beta T_0^{\mu\nu} \\
&= V^{-1}\lambda_\mu^\alpha \lambda_\nu^\beta (\partial A/\partial \eta_{\mu\nu})_T
\end{aligned}
\tag{11}
$$

The free energy, and the strain, are ultimately dependent upon the whole collection $\{\mathbf{R}\}$ of atomic coordinates. To establish the connection between the two, we now introduce a tensor $S^{\alpha\beta}$ which is defined by

$$S^{\alpha\beta} = N^{-1}\sum_{i=1}^{N} x_i^\alpha x_i^\beta \tag{12}$$

which will be called the 'gyration tensor'[6]. The sum on i is over all groups comprising the material, and the x_i^α are the coordinates of the ith group referred to a coordinate system co-moving with the c.g. of the network. The coordinates x_i^α of the atomic group i in the deformed state will certainly be affinely connected to the coordinates in the undeformed state y_i^α by

$$
\begin{aligned}
x_i^\alpha &= (\partial x_i^\alpha/\partial y_i^\mu)y_i^\mu \\
&= \lambda_{\mu:i}^\alpha y_i^\mu
\end{aligned}
\tag{13}
$$

if the deformation is infinitesimal in the continuum sense. It may be that atoms interchange relative positions on such a deformation, but individual atoms must follow a mean classical path that is continuous and differentiable,

and equation (13) holds for all i. Since this is the case, equation (12) becomes

$$S^{\alpha\beta} = N^{-1} \sum_{i=1}^{N} \lambda^{\alpha}_{\mu:i} \lambda^{\beta}_{\nu:i} y^{\mu}_i y^{\nu}_i \qquad (14)$$

and the *average* deformation gradient may be defined by

$$S^{\alpha\beta} = \lambda^{\alpha}_{\mu} \lambda^{\beta}_{\nu} S^{\mu\nu}_0 \qquad (15)$$

where

$$S^{\mu\nu}_0 = N^{-1} \sum_{i=1}^{N} y^{\mu}_i y^{\nu}_i \qquad (16)$$

This quantity $\lambda^{\alpha}_{\mu} \lambda^{\beta}_{\nu}$ is what is required in the stress–strain relation (equation 11) for the homogeneous medium; the atomic $\lambda^{\alpha}_{\mu:i}$ are not meaningful in continuum mechanics.

It is seen that questions concerning whether or not a deformation is affine are moot. The proper connection between molecules and the continuum demands that the strain be defined as an average, and deformations in the continuum can always be taken to be affine.

Inspection of the strain tensor, as defined in equation (6), suggests the formation of

$$g_{\alpha\beta} S^{\alpha\beta} - h_{\mu\nu} S^{\mu\nu}_0 = (g_{\alpha\beta} \lambda^{\alpha}_{\mu} \lambda^{\beta}_{\nu} - h_{\mu\nu}) S^{\mu\nu}_0$$

$$S^2 - S^2_0 = 2\eta_{\mu\nu} S^{\mu\nu}_0 \qquad (17)$$

Here S^2, or S^2_0 in the undeformed state, is just the trace of $S^{\alpha\beta}$, i.e. the squared radius of gyration in the sense common to polymer chain configuration theory, if the coordinate system is Cartesian. The same identification may be made in the general curvilinear case.

Equation (17) now will be used to simplify the stress–strain relation (equation 11). First, it is seen from equation (17) that

$$(\partial A/\partial \eta_{\mu\nu})_T = (\partial A/\partial S^2)_T (\partial S^2/\partial \eta_{\mu\nu}) \qquad (18)$$

and, hence, that

$$T^{\alpha\beta} = (2/V)\lambda^{\alpha}_{\mu} \lambda^{\beta}_{\nu} S^{\mu\nu}_0 (\partial A/\partial S^2)_T$$

$$= (2/V) S^{\alpha\beta} (\partial A/\partial S^2)_T \qquad (19)$$

since the undeformed state is independent of $\eta_{\mu\nu}$. This particular version of the stress–strain relation is of importance for the actual calculation of the elastic free energy. The fact that A could be calculated as a function of S^2 alone, is a simplification, especially since one may make use of the same mathematical techniques for whole networks as have been used for single chains. However, it must be admitted that the free energy may not be a function of the radius of gyration alone, especially if Šolc's work[6] is considered. In fact, equation (19) may be used to prove that the elastic free energy cannot be a function of S^2 alone. If equation (19) were correct, then an asymmetrical body could not sustain a uniform dilation in the presence of a hydrostatic pressure. Such a contention is untenable, and so equation (19) is not a

sufficient description of the equation of state. However, an alternative and exact version of the stress–strain relation is easily obtained if the strain is taken in the principal axes, for which $S^{\alpha\beta} \to S^{\alpha\alpha} = \lambda_\alpha^2 S_0^{\alpha\alpha}$; then

$$t^\alpha = (2/V)S^{\alpha\alpha}(\partial A/\partial S^{\alpha\alpha}) \qquad \text{(no sum)} \qquad (20)$$

and we consider $A = A(S^{11}, S^{22}, S^{33})$. (It is also possible to obtain the stress in terms of the invariants of λ_μ^α, or $S^{\alpha\beta}$, as Rivlin has shown[7].) The virtue of equations (19) and/or (20) is that they make a direct connection to our next subject.

4. CONFIGURATION INTEGRAL

Gyration tensor

The above considerations suggest that equation (2) may be modified to

$$Z(S^2)\,dS^2 = dS^2 \int \ldots \int \delta\left(S^2 - N^{-1} \sum_{i=1}^N \mathbf{r}_i^2\right)\delta\left(\sum_{i=1}^N \mathbf{r}\right)$$

$$\times \exp\left[-\beta V(\{\mathbf{R}\})\right]\,d\{\mathbf{R}\} \qquad (21)$$

for use with equation (19), or to

$$Z(S^{\alpha\beta})\prod_{\alpha \leqslant \beta} dS^{\alpha\beta} = \prod_{\alpha \leqslant \beta} dS^{\alpha\beta}\int\ldots\int \prod_{\alpha \leqslant \beta} \delta\left(S^{\alpha\beta} - N^{-1}\sum_{i=1}^N x_i^\alpha x_i^\beta\right)$$

$$\times \delta\left(\sum_{i=1}^N \mathbf{r}_i\right)\exp\left[-\beta V(\{\mathbf{R}\})\right]\,d\{\mathbf{R}\} \qquad (22)$$

for application of equation (20). In the former approximation, the intrinsic coordinate system is not rigidly fixed to the origin, but instead may rotate and as a consequence the network is rotationally averaged. Hence, equation (21) should only be considered for spherically symmetric bodies. However, equation (22) is so difficult to handle that equations (21) and (19) offer the best opportunity for calculations, and may be generally applied with the understanding that they are approximations.

(The situation with elasticity is here parallel to single-chain configuration theory. For many years the distribution function of the radius of gyration was considered to be a satisfactory description of the chain statistics. It is only since Šolc[6] showed how to handle the gyration tensor and that the tensor is not spherically symmetric that there has been concern for the anisotropy of the distribution.)

As a demonstration of the inherent difficulties of equation (22), but also as a beginning on the integral, we will show how the gyration tensor can be handled. First note that

$$\prod_{\alpha \leqslant \beta} \delta\left(S^{\alpha\beta} - N^{-1}\sum_{i=1}^N x_i^\alpha x_i^\beta\right) = (2\pi)^{-6}\int\ldots\int \exp\left[i\sum_{\alpha \leqslant \beta} k_{\alpha\beta}S^{\alpha\beta}\right.$$

$$\left. - i\sum_{\alpha \leqslant \beta} k_{\alpha\beta}N^{-1}\sum_{i=1}^N x_i^\alpha x_i^\beta\right]d\mathbf{k} \qquad (23)$$

where the volume element $d\mathbf{k} = dk_{11}dk_{22}dk_{33}dk_{12}dk_{13}dk_{23}$. The gyration

tensor is symmetric, so that the matrix of wave vectors

$$
\mathbf{k} = \begin{bmatrix} k_{11} & k_{12} & k_{13} \\ k_{12} & k_{22} & k_{23} \\ k_{13} & k_{23} & k_{33} \end{bmatrix} \tag{24}
$$

has only six independent components. The matrix $\mathbf{k}$ may be rendered in polar form by

$$
\mathbf{k} = \mathbf{M}\boldsymbol{\kappa}\mathbf{M}' \tag{25}
$$

where $\boldsymbol{\kappa}$ is diagonal $[\kappa_1, \kappa_2, \kappa_3]$ and $\mathbf{M}$ (transpose $\mathbf{M}'$) is the $O(3)$ rotation matrix dependent upon the three Euler angles θ, ϕ and ψ. The rotation matrix $\mathbf{M} = \mathbf{CBA}$, where $\mathbf{C} = \mathbf{C}(\psi)$, $\mathbf{B} = \mathbf{B}(\phi)$ and $\mathbf{A} = \mathbf{A}(\theta)$ are rotations in two dimensions. We require the Jacobian of the transformation from $d\mathbf{k}$ to $d\kappa_1 d\kappa_2 d\kappa_3 d\theta d\phi d\psi$. (In the principal axes of $S^{\alpha\beta}$ there are only three independent components of $S^{\alpha\beta}$, which allows integrations over angles to be performed separately.)

The Jacobian is easily obtained[8]. We make use of the fact that in an n-dimensional real space the invariant $ds^2 = g_{\alpha\beta} dx^\alpha dx^\beta$ has an associated invariant volume element $\sqrt{g}\, dx$, where g is $\det(g_{\alpha\beta})$. The invariant ds^2 in $\mathbf{k}$-space is conveniently taken to be $\mathrm{Tr}\,(d\mathbf{k}d\mathbf{k})$, and the volume element is $8^{\frac{1}{2}}$ larger than that appearing in equation (23). Now, from equation (25),

$$
d\mathbf{k} = (d\mathbf{M})\boldsymbol{\kappa}\mathbf{M}' + \mathbf{M}(d\boldsymbol{\kappa})\mathbf{M}' + \mathbf{M}\boldsymbol{\kappa}(d\mathbf{M}') \tag{26}
$$

or

$$
\mathbf{M}'\, d\mathbf{k}\,\mathbf{M} = (\delta\mathbf{M})\boldsymbol{\kappa} - \boldsymbol{\kappa}(\delta\mathbf{M}) + d\boldsymbol{\kappa} \tag{27}
$$

where $\delta\mathbf{M} = \mathbf{M}'d\mathbf{M}$ is antisymmetric. In equation (27) we have made use of the fact that $\mathbf{M}'\mathbf{M} = \mathbf{E}_3$ (the identity of dimension 3×3) and $(d\mathbf{M})\mathbf{M}' = -\delta\mathbf{M}$. From equation (27) we have

$$
\mathrm{Tr}\,(d\mathbf{k}d\mathbf{k}) = \mathrm{Tr}\,(d\boldsymbol{\kappa}d\boldsymbol{\kappa}) + \mathrm{Tr}\,\{[(\delta\mathbf{M})\boldsymbol{\kappa} - \boldsymbol{\kappa}(\delta\mathbf{M})][(\delta\mathbf{M})\boldsymbol{\kappa} - \boldsymbol{\kappa}(\delta\mathbf{M})]\} \tag{28}
$$

Identification of terms on the right-hand side of this equation with the matrix $g_{\alpha\beta}$ in variables $d\kappa_i$ and δm_i ($i = 1, 2, 3$), the latter of which are functions of $d\theta$, $d\phi$ and $d\psi$, and subsequent transformation, via another Jacobian, from δm_i to the Euler angles, gives

$$
d\mathbf{k} = \prod_{i > j} |\kappa_i - \kappa_j|\, d\kappa_1\, d\kappa_2\, d\kappa_3\, d\theta\, \sin\phi\, d\phi\, d\psi \tag{29}
$$

Finally, the $k_{\alpha\beta}$ may be obtained as functions of the κ_i and angles by direct calculation from equation (25).

The reader might now profitably consult Šolc[6] to see how the angle integrations are accomplished in terms of beta functions. This is not the place to give the very complicated result of those integrations. Suffice it to say that further pursuit of the exact theory does not at this date look very promising, and so we are obliged to reconsider equation (21), which is practically tractable. Regardless of which function one chooses to calculate, the remaining comments of this section apply to both.

Potential energy and matrices

The potential energy of the system $V(\{\mathbf{R}\})$ is separable into two parts as

$$V(\{\mathbf{R}\}) = V_b(\{\mathbf{R}\}) + V_{\bar{b}}(\{\mathbf{R}\}) \tag{30}$$

representing, respectively, the total potentials for bonded (b) and non-bonded ($\bar{b}$) interactions. As is usual, we assume that the potentials depend upon the directed distance between atoms (or groups of atoms), so that V_b and $V_{\bar{b}}$ are in fact functions of the set of $N(N-1)/2$ vectors $\mathbf{r}_i - \mathbf{r}_j$. (Added body forces $\mathbf{X}$ will contribute to the potential terms of the type $\mathbf{X} \cdot \mathbf{r}_i$. We exclude from further consideration this elaboration.)

It is generally certain that the bond potential is not determined completely by near-neighbour interactions. For instance, the potential energy of a real chain depends upon bond lengths, bond angles, dihedral angles[9] and perhaps higher-order bond correlations. Such terms could be represented in the potential by appropriate combinations of $(\mathbf{r}_i - \mathbf{r}_{i+1}) \cdot (\mathbf{r}_i - \mathbf{r}_{i+1})$, $(\mathbf{r}_i - \mathbf{r}_{i+1}) \cdot (\mathbf{r}_{i+1} - \mathbf{r}_{i+2})$, $(\mathbf{r}_i - \mathbf{r}_{i+1}) \cdot (\mathbf{r}_{i+2} - \mathbf{r}_{i+3})$ and $(\mathbf{r}_i - \mathbf{r}_{i+1})$, $(\mathbf{r}_{i+k} - \mathbf{r}_{i+k+1})$, respectively. The non-bonded interactions will be taken to be pairwise additive.

It is now convenient to organize the construction of the various $\mathbf{r}_i - \mathbf{r}_j$. To this end, define[10] the $N(N-1)/2 \times N$ matrix

$$C' = \begin{bmatrix}
1 & -1 & 0 & 0 & \cdot & \cdot & \cdot & 0 \\
1 & 0 & -1 & 0 & \cdot & \cdot & \cdot & 0 \\
\cdot & & & & & & & \cdot \\
\cdot & & & & & & & \cdot \\
1 & 0 & \cdot & \cdot & \cdot & \cdot & 0 & -1 \\
0 & 1 & -1 & 0 & \cdot & \cdot & \cdot & 0 \\
0 & 1 & 0 & -1 & 0 & \cdot & \cdot & 0 \\
\cdot & & & & & & & \cdot \\
0 & \cdot & \cdot & \cdot & 1 & \cdot & -1 & 0 \\
\cdot & & & & & & & \cdot \\
0 & \cdot & \cdot & \cdot & \cdot & 0 & 1 & -1
\end{bmatrix} \tag{31}$$

and the $1 \times 3N$ row vector

$$\mathbf{R}' = [\mathbf{X}', \mathbf{Y}', \mathbf{Z}'] \tag{32}$$

where, for example,

$$\mathbf{X}' = [x_1, x_2, \ldots, x_N] \tag{33}$$

Here, and in the following, $\mathbf{A}'$ denotes the transpose of $\mathbf{A}$. The operation

$$(\mathbf{E}_3 \otimes C')\mathbf{R}$$

where $\otimes$ denotes the direct product, creates a $3N(N-1)/2 \times 1$ vector which consists of all possible pairs $\mathbf{r}_i - \mathbf{r}_j$. Some of these vectors determine the potential for bonded interactions V_b, and the remainder belong to $V_{\bar{b}}$. A given $\mathbf{r}_i - \mathbf{r}_j$ belongs to either V_b or $V_{\bar{b}}$, but not to both, if we are dealing with real atoms. However, it may be that a particular model, e.g. the Gaussian chain with volume exclusion, requires some of the $\mathbf{r}_i - \mathbf{r}_j$ to appear in both V_b and $V_{\bar{b}}$.

The matrix C' is the incidence matrix[10] of an associated graph, the 'complete star on the circle', which is depicted in *Figure 2* for a small system consisting of $N = 11$ atomic groups, alternatively called vertices or nodes in the terminology of graph theory. The chords on the circle should be considered to be directed from the (lower-indexed) node for which the $+1$ appears in the m, i element of C' to the (higher-indexed) node for which the -1 appears in the m, j element of C'. That is, the vector $\mathbf{r}_i - \mathbf{r}_j$ is the mth $[\bmod N(N-1)/2]$ row of $(\mathbf{E}_3 \otimes C')\mathbf{R}$. Furthermore, the chords are of one or another type, depending upon whether the adjoined pair of nodes belongs to V_b or to $V_{\bar{b}}$. Such indications on *Figure 2* would spoil a pretty graph, and so the graphical representation of differences between chords is deferred to the section on illustrative calculations.
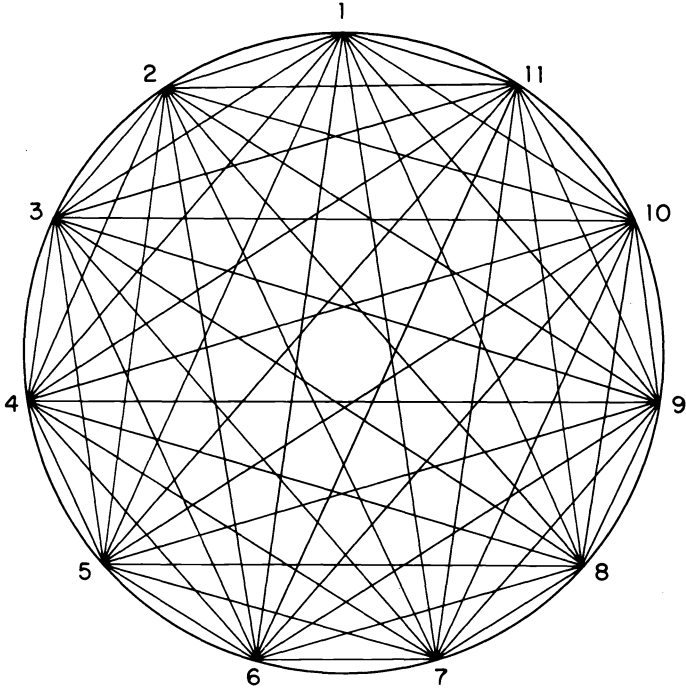

Figure 2. The complete star on a circle of eleven vertices

Those terms of $(\mathbf{E}_3 \otimes C')\mathbf{R}$ which belong to V_b are claimed by the operation

$$[\mathbf{E}_3 \otimes (\mathbf{J}'_b C')]\mathbf{R}$$

where

$$120 \quad \mathbf{J}'_b = \begin{bmatrix} 1 & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ 0 & 0 & 1 & 0 & \cdot & \cdot & 0 \\ \cdot & & & & & & \cdot \\ \cdot & & & & & & \cdot \\ 0 & \cdot & \cdot & \cdot & 0 & 1 & 0 \\ \cdot & & & & & & \cdot \\ 0 & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{bmatrix} \quad (34)$$

is an $M \times N(N-1)/2$ matrix consisting of rows containing a single non-zero element equal to unity. Here M is the total number of $\mathbf{r}_i - \mathbf{r}_j$ terms required for specification of V_b. The remaining atomic distances required in $V_{\bar{b}}$ are generated by

$$[\mathbf{E}_3 \otimes (J_{\bar{b}}^r C')]\mathbf{R}$$

where $J_{\bar{b}}^r$ contains all rows of the identity of order $N(N-1)/2$ that are not found in $\mathbf{J}_b$. In other words,

$$\begin{bmatrix} J_b' \\ J_{\bar{b}}' \end{bmatrix} P = \mathbf{E}_{N(N-1)/2} \tag{35}$$

where P is a permutation.

The matrix C' has completeness properties, which, added to the fundamental character of the vectors $\mathbf{r}_i - \mathbf{r}_j$, suggest it above other matrices for primary consideration as the tool for construction of the configuration integral. The first such property is

$$N^{-1}CC' = \mathbf{E}_N - N^{-1}\mathbf{U} \tag{36}$$

where $\mathbf{U}$ is an $N \times N$ matrix, all elements of which are unity. This relation is easily seen to be true by direct construction, and has been algebraically proved[10] for N prime. In operations involving C, equation (36) acts as a *generalized* identity. For example,

$$(N^{-1}CC')C = (\mathbf{E}_N - N^{-1}\mathbf{U})C = C \tag{37a}$$

and

$$C'(N^{-1}CC') = C'(\mathbf{E}_N - N^{-1}\mathbf{U}) = C' \tag{37b}$$

for $\mathbf{U}C = \mathbf{O}$ and $C'\mathbf{U} = \mathbf{O}$, since $C(C')$ contains a $+1$ and -1 in each column (row).

In addition, we may construct an Abelian group from C. Let $\mathbf{A}$ be an $N \times N$ matrix which possesses the properties

$$\left. \begin{array}{l} \mathbf{A}\mathbf{U} = \mathbf{U}\mathbf{A} = \mathbf{O} \\[4pt] \mathbf{A}^{-1}\mathbf{U} = \mathbf{U}\mathbf{A}^{-1} = \mathbf{O} \\[4pt] \mathbf{A}\mathbf{A}^{-1} = \mathbf{E}_N + \text{const. }\mathbf{U} \end{array} \right\} \tag{38}$$

These conditions are similar to those required of the generalized, or Moore–Penrose, inverse[11]. The matrices

$$\mathbf{G}^{(n)} = N^{-n-1}C'\mathbf{A}^n C; \ -\infty \leqslant n \leqslant \infty \tag{39}$$

form an Abelian group. This statement has been proved[10], and will not be completely proved here. However, one aspect of the group property is easily demonstrated:

$$\begin{aligned} \mathbf{G}^{(m)}\mathbf{G}^{(n)} &= N^{-(m+n+2)}(C'\mathbf{A}^m C)(C'\mathbf{A}^n C) \\ &= N^{-(m+n-1)}C'\mathbf{A}^m(\mathbf{E}_N - N^{-1}\mathbf{U})\mathbf{A}^n C \\ &= N^{-(m+n-1)}C'\mathbf{A}^{m+n}C = \mathbf{G}^{(m+n)} \end{aligned} \tag{40}$$

With this background material we will later return to $S^{\alpha\beta}$ and the configuration integral, so as to obtain formulas for a model system which depend only upon the $\mathbf{r}_i - \mathbf{r}_j$. It is first interesting to note that we may obtain the generalization of Lagrange's theorem very quickly. From equation (22) the scalar function

$$\sum_{\alpha \leqslant \beta} k_{\alpha\beta} N^{-1} \sum_{i=1}^{N} x_i^{\alpha} x_i^{\beta} = N^{-1} \mathbf{R}'(\bar{\mathbf{k}} \otimes E_N)\mathbf{R} \tag{41}$$

where $\bar{\mathbf{k}}$ has off-diagonal elements which are just half those of $\mathbf{k}$. Now make use of equation (36) with $\mathbf{X}'\mathbf{U} = \mathbf{Y}'\mathbf{U} = \mathbf{Z}'\mathbf{U} = 0$, to obtain

$$N^{-1}\mathbf{R}'(\bar{\mathbf{k}} \otimes E_N)\mathbf{R} = N^{-2}\mathbf{R}'(\bar{\mathbf{k}} \otimes CC')\mathbf{R}$$

$$= N^{-2}\mathbf{R}'(\mathbf{E}_3 \otimes C)(\bar{\mathbf{k}} \otimes E)(\mathbf{E}_3 \otimes C')\mathbf{R} \tag{42}$$

Here we have used the theorem on direct products, and the unlabelled $\mathbf{E}$ is of order $N(N - 1)/2$. The result, equation (42), is easily seen to be Lagrange's theorem if $\bar{\mathbf{k}} = \mathbf{E}_3$.

The utility of the matrices which have been introduced depends ultimately upon the form of the potential energy. That is, if the potentials are such as to allow representations in simple functions of matrices so that integrals can be computed, then what has been laid out in this section will be computationally useful. If, on the other hand, potentials are so complex as to defy such representation, then we have only obtained a superfluous accounting procedure, and other devices will have to be used for calculations. There is, however, at least one model, i.e. the Gaussian, for which these matrices are extremely useful. We will apply the results of this section to Gaussian chains after considering the last formality.

5. ENSEMBLE AVERAGES

The stress–strain relation, and other thermodynamic relations, must be averaged over the ensemble of all possible internal constraints or connectivities. However, at the time of network formation, the polymer is subject to a set $\{i\}$ of initial conditions, or constraints, which influence the averaging procedure. Such conditions might include the nature of the crosslinking reagent, a container of particular shape, a diluent, etc., which act so as to form networks of a particular structure. To put the influence of these constraints in another way, they act so as to select networks non-randomly from the ensemble of all possible networks.

The mathematical description of the type of averaging required has already been made by Edwards and Freed[3, 12]. The notation here is somewhat different from theirs. Let $P(\{C\}|\{i\})$ be the conditional probability for forming a network with a specified connectivity, denoted by $\{C\}$, given that a set $\{i\}$ of conditions prevailed at the time of cure. Since the network that is formed is immutable, if elastic limits are not met, it is the free energy that must be averaged, and not the partition function. The effect of averaging the partition function is to allow the crosslinks to scramble during strain. Thus, if $X(\{C\})$ is a thermodynamic function which depends upon the internal constraints

$\{C\}$, we must form

$$\langle X \rangle = \sum_{\{C\}} P(\{C\}|\{i\})X(\{C\}) \tag{43}$$

It will be noted that $\langle X \rangle$ is dependent upon the initial constraints; in this way a rubber band remembers that it is a band, and does not become a ball.

The fundamental thermodynamic relation (10) is averaged as

$$d\langle A \rangle = -\langle S \rangle \, dT + \langle V T_0^{\alpha\beta} \rangle \, d\eta_{\alpha\beta} \tag{44}$$

The volume must be included in the averaging, since it fluctuates owing to the absence of a container. The strain is not averaged, since the free energy $\langle A \rangle$ refers to a *particular* state of strain as specified by $S^{\alpha\beta}$. This is somewhat clearer on inspection of equations (10) and (19), which become, respectively,

$$\langle V T_0^{\alpha\beta} \rangle = (\partial \langle A \rangle / \partial \eta_{\alpha\beta})_T \tag{45}$$

and

$$\langle V T^{\alpha\beta} \rangle = 2 S^{\alpha\beta} (\partial \langle A \rangle / \partial S^2)_T \tag{46}$$

Finally, the complete equation (20) is averaged to

$$\langle V t^\alpha \rangle = 2 S^{\alpha\alpha} (\partial \langle A \rangle / \partial S^{\alpha\alpha})_T \quad \text{(no sum)} \tag{47}$$

We expect that $S_0^{\alpha\beta}$ is fixed by the initial conditions, and, hence, members of the ensemble over $\{C\}$ must all be characterized by the same $S_0^{\alpha\beta}$.

For practical purposes, the average of the product on the left-hand side of equation (47) may be approximated as the product of averages; it is anticipated that fluctuations in the volume are small. Thus

$$\langle t^\alpha \rangle \cong (2/\langle V \rangle) S^{\alpha\alpha} (\partial \langle A \rangle / \partial S^{\alpha\alpha})_T \tag{48}$$

which is construed to be essentially exact.

If the free energy is a function of S^2 only, then the most probable value of S^2 occurs where $(\partial \langle A \rangle / \partial S^2)_T = 0$. This state is free from stress, and presumably occurs at $S^2 > 0$. In fact, this simple condition alone is sufficient to show that theories which give only a Gaussian form to $Z(S^2)$, and, hence, only the $\lambda - 1/\lambda^2$ strain function for uniaxial stretch, are in need of modification[13].

Further analysis of equation (46) in the case of a uniform hydrostatic pressure is instructive. First, take the principal axes of $S^{\alpha\beta}$, and, hence, of $\langle T^{\alpha\beta} \rangle$, so that

$$t^x = \langle T^{xx} \rangle = (2/\langle V \rangle) S^{xx} (\partial \langle A \rangle / \partial S^2)_T \tag{49}$$

with similar equations for y- and z-components. This equation can be shown to conform to standard thermodynamics if the material is taken to be spherical or cubical. Then $S^{xx} = S^{yy} = S^{zz}$, and $t^x = t^y = t^z = -p$. However, the general case works out as easily. Define

$$\langle p \rangle = -(\tfrac{1}{3}) g_{\alpha\beta} \langle T^{\alpha\beta} \rangle = -(\tfrac{2}{3} \langle V \rangle) S^2 (\partial \langle A \rangle / \partial S^2)_T \tag{50}$$

where use has been made of equation (17). Alternatively, equation (50) is

$$\langle p \rangle = -(\tfrac{2}{3} \langle V \rangle)(\partial \langle A \rangle / \partial \ln S^2)_T$$
$$= -(\tfrac{2}{3} \langle V \rangle)(\partial \langle A \rangle / \partial \langle V \rangle)_T (\partial \langle V \rangle / \partial \ln S^2) \tag{51}$$

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Dimensional analysis alone gives

$$\langle p \rangle = -(\partial\langle A \rangle/\partial\langle V \rangle)_T \tag{52}$$

Further use of equation (51) may be made to calculate the Gibbs free energy $\langle G \rangle$ by

$$\langle G \rangle = \langle A \rangle + \langle pV \rangle \cong \langle A \rangle + \langle p \rangle\langle V \rangle$$
$$= \langle A \rangle - (\tfrac{2}{3})(\partial\langle A \rangle/\partial \ln S^2)_T \tag{53}$$

where the latter expression can be obtained exactly by similar reasoning from equation (46).

A final comment on averaging may be directed to the problem of network reformation or other historical phenomena. Let $\{C_j\}$ be the set of internal constraints present at time t_j $(0 \leqslant j \leqslant \infty)$, and for convenience take $\{C_0\} = \{i\}$, where the latter set has been previously defined as the initial external constraints (at time t_0 the external constraints are translated into internal constraints by the crosslinking reaction, if it is instantaneous). Then $P(\{C_{j+1}\}|\{C_j\})$ represents the probability for transition from $\{C_j\}$ to $\{C_{j+1}\}$ during the time interval $t_j \to t_{j+1}$. The condition of the network at time t_n is then obtained as

$$P(\{C_n\}|\{i\}) = \sum_{\{C_1\}}\sum_{\{C_2\}}\cdots\sum_{\{C_{n-1}\}}\prod_{j=0}^{n-1} P(\{C_{j+1}\}|\{C_j\}) \tag{54}$$

The probability may be represented by an exponential, and the temporal grain made small to give

$$P(\{C_T\}|\{i\}) = \int\cdots\int \exp\left[-\int_0^T F(t)\,dt\right]\prod d\{C_t\} \tag{55}$$

a functional integral[3]. Further pursuit of such a theory would take us far afield of the present discussion. The interested reader should consult the work of Edwards and Freed[3, 12] to see how the theory of elasticity is developed by use of the devices exemplified by equation (55).

6. THE GAUSSIAN MODEL

The procedure described in section 4 will now be applied to the calculation of the configuration integral for a bead–spring network of given connectivity, in which the beads repel one another on close contact. The probability for finding a pair of beads separated by $\mathbf{r}_{ij}$ is

$$\exp[-\gamma\mathbf{r}_{ij}^2] \tag{56}$$

if the beads are directly connected by a spring. Here $\gamma = 3/2\langle l^2 \rangle_0$, where $\langle l^2 \rangle_0$ is the unperturbed mean square step length. In addition, the beads repel one another in pairs by a potential given by

$$\exp[-\beta V(\mathbf{r}_{kl})] = 1 - \alpha\exp[-\psi\mathbf{r}_{kl}^2] \tag{57}$$

where α and ψ are parameters to be specified later.

[The potential (57) has been chosen for the following reasons: (1) if

$\alpha = X(\psi/\pi)^{\frac{1}{2}}$, and if we take $\psi \to \infty$ at the end of the calculation, the δ-function pseudo-potential devised by Fixman is recovered; (2) if alternatively $\alpha = 1$, then $\exp[-\beta V(\mathbf{r}_{kl})] = 0$ at $\mathbf{r}_{kl} = 0$, and $1 - \exp[-\beta V(\mathbf{r}_{kl})]$ is positive semi-definite and is normalizable to $(\pi/\psi)^{\frac{1}{2}} = X$; (3) it is easily integrated, and possesses the above generality. However, the potential is only a gross approximation, and should not be considered in any other light. Yet it is at least as good as, if not better than, other approximate potentials that have been used for the polymer excluded volume problem to date.]

There exist at least two ways to introduce crosslinks. In one method, the set of N groups is taken to represent the network as it exists in the cross-linked state. Then the function $\exp[-\gamma \mathbf{R}'(E_3 \otimes \mathbf{A})\mathbf{R}]$ contains all terms necessary to describe the product of probabilities (equation 56) for primary chain bonds as well as for bonds introduced by crosslinks. Here $\mathbf{A} = C\mathbf{J}_b\mathbf{J}_b'C'$, and $\mathbf{J}_b'$ selects rows from C' which correspond to both nearest neighbours and far-distant strangers in the complete star. The integrals over $\{\mathbf{R}\}$ may be computed formally with this representation, as Forsman and co-workers[14] have shown more recently than James and Guth[1], who first devised this representation. However, the eigenvalues of $\mathbf{A}$ are required for progress beyond formality, and $\mathbf{A}$ is not easy to diagonalize. Furthermore, the alternative to be discussed shortly allows us to use the properties of C discussed in section 4 to some advantage. Nevertheless, this is the direct route, and possesses the advantage of simplicity. It is easy to see, for example, that the network consists of as many disjoint pieces as there are zero eigenvalues of $\mathbf{A}$.
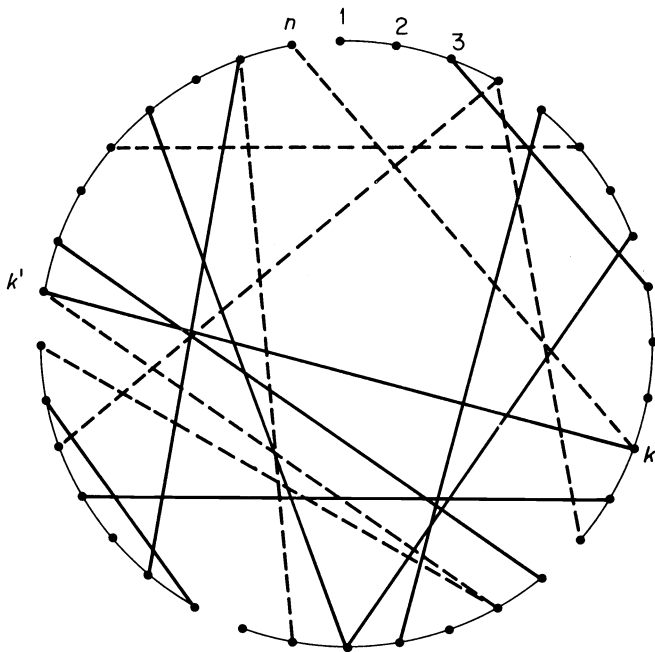

Figure 3. A representation of one term in cluster expansion of the configuration integral. The circle, with breaks, is the set of primary chains; the solid and dashed chords represent crosslinks and excluded volume interactions, respectively

The zero eigenvalues correspond to the c.g. motion of the pieces. A connected network is described by a matrix $\mathbf{A}$ containing a single zero eigenvalue.

An alternative method for introducing crosslinks has been presented elsewhere[15]. In that scheme the crosslinks were represented by δ-functions, which constrain specified pairs of beads to occupy the same volume elements. Calculation of the configuration integral for a network composed of a multitude of primary chains with such a representation requires special treatment of the c.g. of each chain, and the formulas are rather lengthy. For illustrative purposes, the representation originated by James and Guth is to be preferred for calculations on networks with defects. In effect, a multitude of difficulties are formally delayed to the ultimate quadrature, and in any case, this is as far as the theory can yet be taken.

The configuration integral (equation 22) is now

$$Z(S^{\alpha\beta}) \prod_{\alpha \leqslant \beta} dS^{\alpha\beta} = \prod_{\alpha \leqslant \beta} dS^{\alpha\beta} \int \cdots \int \prod_{\alpha \leqslant \beta} \delta(S^{\alpha\beta} - N^{-1}\Sigma x_i^\alpha x_i^\beta) \prod_\alpha \delta(\Sigma x_i^\alpha)$$
$$\times \exp[-\gamma \mathbf{R}'(\mathbf{E}_3 \otimes \mathbf{A})\mathbf{R}] \prod_{k<l} [1 - \alpha \exp(-\psi \mathbf{r}_{kl}^2)] \, d\{\mathbf{R}\} \qquad (58)$$

in which it is assumed that the spectrum of $\mathbf{A}$ contains a single zero. To save some space, the volume element in the gyration tensor space is henceforth deleted. The product of excluded volume factors is expanded in powers of α to obtain

$$Z(S^{\alpha\beta}) = \sum_{p=0}^{N} \alpha^p \int \cdots \int \prod_{\alpha \leqslant \beta} \delta(S^{\alpha\beta} - N^{-1} \Sigma x_i^\alpha x_i^\beta) \prod_\alpha \delta(\Sigma x_i^\alpha)$$
$$\times \exp[-\gamma \mathbf{R}'(\mathbf{E}_3 \otimes \mathbf{A})\mathbf{R}] \Sigma^{(p)} \exp[-\psi \mathbf{R}'(\mathbf{E}_3 \otimes \mathbf{B}_p)\mathbf{R}] \, d\{\mathbf{R}\} \qquad (59)$$

where $\Sigma^{(p)}$ is a sum over all circle graphs consisting of p distinct chords. A graph associated with one such term in equation (54) is shown in *Figure 3*. The matrix is

$$\mathbf{B}_p = C \mathbf{J}_p \mathbf{J}_p' C'$$

in which $\mathbf{J}_p'$ contains only p non-zero rows corresponding to the p chords in the circle graph. The sum $\Sigma^{(p)}$ may be stated as the sum over all $\mathbf{J}_p$. The upper limit on the sum over integers p is left unspecified.

The integration over $\{\mathbf{R}\}$ in equation (59) is effected by transforming to normal coordinates, with concomitant diagonalization of both $\bar{\mathbf{k}}$ (see equation 41) and $\gamma \mathbf{A} + \psi \mathbf{B}_p$ to obtain

$$Z(S^{\alpha\beta}) = (\pi/\gamma)^{3(N-1)/2} \sum_{p=0}^{L} \alpha^p \int \cdots \int \exp(i\bar{k}_{\alpha\beta}S^{\alpha\beta})\Sigma^{(p)} |\Xi_p|^{-\frac{1}{2}}$$
$$\times \left(\prod_{\mu > \nu} |\kappa_\mu - \kappa_\nu| \right) d\kappa \, d\Omega \qquad (60)$$

where $|\Xi_p|$ denotes the determinant of

$$\Xi_p = \mathbf{E}_3 \otimes \Lambda_p - (i/\gamma N)\kappa \otimes \mathbf{E}_{N-1} \qquad (61)$$

and Λ_p is the matrix (of dimension $N-1$) of non-zero eigenvalues of

$\mathbf{A} + \psi\gamma^{-1}\mathbf{B}_p$. In equation (60) $d\Omega = d\theta \sin\phi \, d\psi$, with the angles defined on the intervals $0 \leqslant \theta \leqslant 2\pi$, $0 \leqslant \phi \leqslant \pi$, $0 \leqslant \psi \leqslant 2\pi$, and $d\mathbf{\kappa} = d\kappa_1 \, d\kappa_2 \, d\kappa_3$. (There is a trivial factor of 2^3 associated with the change of basis for $\bar{\mathbf{k}}$ as well as $(2\pi)^{-6}$ which are discarded in proceeding from equation (59) to equation (60).)

If only the S^2-dependence of Z is desired, equation (21) may be integrated to

$$Z(S^2) = (\pi/\gamma)^{3(N-1)/2} \sum_{p=0}^{N} \alpha^p \int \exp(ikS^2)\Sigma^{(p)}|\mathbf{\Phi}_p|^{-\frac{3}{2}} \, dk \qquad (62)$$

where

$$\mathbf{\Phi}_p = \Lambda_p - (ik/\gamma N)\mathbf{E}_{N-1} \qquad (63)$$

These equations are seen to be equivalent to the result of Coriell and Jackson[16] for a single chain without volume exclusion. For reduction to this case, take $\alpha = 0$; the matrix $\mathbf{A}$ is defined as the usual Rouse matrix, and the non-zero eigenvalues of $\mathbf{A}$, i.e. Λ_0, are $4\sin^2 \pi l/2N$. Circular chains have been done by Šolc[17].

Further progress with the theory to completion of the quadratures is very difficult. The spectrum of $\mathbf{A} + \psi\gamma^{-1}\mathbf{B}_p$ is required for all $\mathbf{B}_p$, and final averages as specified in section 5 require the spectra of all $\mathbf{A}$. Any approximations in the latter averaging have to be handled with some care, so as to avoid pre-averaging. However, there is reason to believe, especially from the work of Gordon and collaborators[18], that calculation of the determinants is not an insurmountable problem, and that spectra of even relatively small random networks contain most, if not all, of the information necessary to extrapolate to very large N.

The quick method of calculation which has been demonstrated here does not allow use of the group properties of C that were discussed in section 4. The alternative route, mentioned above and used for the excluded volume problem[10], takes the quadratures into wave space, where the order of matrices CAC' is reversed to $C'BC$. Products of matrices of this form are readily computed by use of the group property, and, because of this, the alternative representation may be more useful for actual calculations. It has been our purpose here to show how far the theory can be taken, and to point out the essential ingredients needed to complete the last steps; other methods of calculation are equivalent to the one demonstrated.

The fact that sums over the excluded volume contributions are calculated differently from the sum over connectivity is the result of our neglect of entanglements. A more complete and accurate theory which incorporates entanglements would place these two aspects of the configuration integral on more equal footing. Entanglements certainly act so as to restrict the neighbours of a given segment to an elite few; segments are confined to a much smaller region of real space, and the network to a smaller phase space, than the above theory would allow. Whether a soft Gaussian cluster function is adequate to describe such containment is a question which deserves investigation.

ACKNOWLEDGEMENT

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