Elasticity and Chain Dimensions in Gaussian Networks

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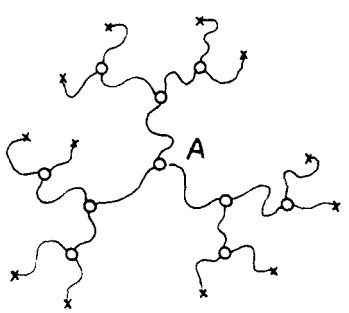
ABSTRACT: The free energy of deformation and the equilibrium dimensions of strands have been calculated for a network of Gaussian random coils. For networks without local loops, containing S elastically active strands and J elastically active junctions, the results are $\Delta A = (S - J)\,kT[([\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3]/2) - (J/S)\ln \alpha_x\alpha_y\alpha_z]$ and $\langle\langle r^2\rangle/\langle r^2\rangle_0\rangle_{eq} = J/S$. For perfect f-functional networks the coefficient on the logarithmic term is $2/f$, in agreement with an expression obtained some years ago by Flory. The equilibrium contraction ratio for perfect tetrafunctional networks is ½, in agreement with a suggestion by James and Guth and with the recent exact results of Eichinger.

Recently we developed an expression for the change in configurational free energy of random coil networks for constant volume deformation, based on the properties of ensembles of small sample networks.[1] The present paper extends this work to include changes in the network volume such as occur upon swelling with small molecule solvents. The aim is an equation of state for phantom networks[2] (those in which the constraints on configuration are provided only by the internal connections of the network itself) for use in extracting the contributions of network topology, such as chain entanglement, from the experimental behavior of real networks.[3] The various theories and controversies concerning the volume dependence of free energy in networks have been reviewed recently.[4-6]

In the earlier paper the entropy change for an ensemble of micronetworks, representative of the local connectivity pattern of the macroscopic network, was calculated. These micronetworks are composed of random coil (Gaussian) strands joining mobile junction points, and are anchored by a number of fixed points which move rigidly in response to any macroscopic deformation. The sketch shows an example of a third-order trifunctional micronetwork which has been built up around the central junction A.



The mobile junctions are denoted by circles and the peripheral fixed points by crosses. The example here is third order because each of the fixed points is three strands removed from the central junction. The micronetworks contain no closed loops (they are ring-free graphs or trees in Gordon's terminology[7]), which we believe correctly portrays the local connectivity pattern of most macroscopic networks. The distribution of fixed point positions was taken to be that corresponding to equilibrium for an ensemble of independent micronetworks of identical structure.[1]

The entropy change resulting from an affine displacement of the fixed points was found to be expressable as the sum of two contributions, one proportional to the number of strands in the micronetwork joining two mobile junctions, the other proportional to the number joining a fixed point and a mobile junction. Associations of the former with macroscopic networks, in which all junctions are mobile, leads to the following expression for the free energy of deformation ΔA for a macroscopic network with J elastically effective junctions[8,9] (junctions with three or more strands leading independently to the network) and S elastically effective strands (strands joining two elastically effective junctions):

$$A = (S - J)kT\left(\frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3}{2}\right) \qquad (1)$$

in which α_x, α_y, and α_z are the macroscopic stretch ratios along the principal strain directions. Since only volume preserving deformations were considered, the product $\alpha_x\alpha_y\alpha_z$ is unity. Also, since the micronetworks have no internal loops, the mean-square end-to-end distance of the strands $\langle r^2\rangle$ is the same as that for free strands, $\langle r^2\rangle_0$ (see below), so the reference state for determining α_x, α_y, and α_z in eq 1 is that for which $\langle r^2\rangle = \langle r^2\rangle_0$.

The same procedures can be followed in dealing with deformations which change the volume, at least to the point of establishing the response of a micronetwork ensemble. The final association with macroscopic network behavior is then made through an independent calculation of the equilibrium strand dimensions in phantom networks. Both calculations are carried out for networks with an arbitrary distribution of strand contour lengths.

Calculation of Averages

We will be calculating ensemble averages of the form:

$$\langle Q\rangle = \frac{\int \cdots \int Q \exp(-\tfrac{3}{2}Q)\mathrm{d}\mathbf{R}_1 \cdots \mathrm{d}\mathbf{R}_N}{\int \cdots \int \exp(-\tfrac{3}{2}Q)\mathrm{d}\mathbf{R}_1 \cdots \mathrm{d}\mathbf{R}_N} \qquad (2)$$

in which $\mathbf{R}_1, \ldots, \mathbf{R}_N$ are internal position vectors, $\mathrm{d}\mathbf{R}_i$ is the volume element, $\mathrm{d}x_i\mathrm{d}y_i\mathrm{d}z_i$, the integrals extend over all space, and Q is a quadratic function of the position vectors which is everywhere greater than zero (a positive-definite quadratic form). It is always possible to find a linear transformation of variables for such quadratic forms which converts them to a sum of squares in the new coordinates[10]

$$Q = \sum_{i=1}^{N}\sum_{j=1}^{N} \gamma_{ij}\mathbf{R}_i \cdot \mathbf{R}_j = \sum_{k=1}^{N} \lambda_k^2 \boldsymbol{\rho}_k \cdot \boldsymbol{\rho}_k \qquad (3)$$

in which the $\boldsymbol{\rho}_k$ ($k = 1, \ldots, N$) are the new coordinate vectors, and the eigenvalues of the transformation λ_k ($k = 1, \ldots, N$) are all real and nonzero. The integrals can then be written as in eq 4, in which Γ is the Jacobian of the linear transformation:

$$\mathrm{d}\mathbf{R}_1 \ldots \mathrm{d}\mathbf{R}_N = \Gamma d\boldsymbol{\rho}_1 \ldots d\boldsymbol{\rho}_N$$

$$\langle Q \rangle = \frac{\int \cdots \int \left(\sum_{k=1}^{N} \lambda_k^2 \rho_k \cdot \rho_k \right) \exp\left[-\frac{3}{2} \sum_{k=1}^{N} \lambda_k^2 \rho_k \cdot \rho_k \right] \Gamma d\rho_1 \ldots d\rho_N}{\int \cdots \int \exp\left[-\frac{3}{2} \sum_{k=1}^{N} \lambda_k^2 \rho_k \cdot \rho_k \right] \Gamma d\rho_1 \ldots d\rho_N} \tag{4}$$

$$\langle Q' \rangle = \frac{\int \cdots \int \sum_{k=1}^{N} \lambda_k^2 [\beta_x \rho_{k,x}^2 + \beta_y \rho_{k,y}^2 + \beta_z \rho_{k,z}^2] \exp\left[-\frac{3}{2} \sum_{k=1}^{N} \lambda_k^2 \rho_k \cdot \rho_k \right] d\rho_1 \ldots d\rho_N}{\int \cdots \int \exp\left[-\frac{3}{2} \lambda_k^2 \rho_k \cdot \rho_k \right] d\rho_1 \ldots d\rho_N} \tag{4a}$$

which is independent of the coordinates and therefore cancels from the equation for $\langle Q \rangle$. Term by term integration of eq 4 then leads immediately to the result in eq 5, irre-

$$\langle Q \rangle = N \tag{5}$$

spective of the individual values of λ_k. The usefulness of this result in the statistical mechanics of systems with quadratic interparticle potentials is well established.[11]

We can use the symmetry of the forms in eq 4 with respect to the three coordinate directions to develop a useful generalization of eq 5. Suppose that instead of eq 4 we wish to evaluate eq 4a, in which $\rho_{k,x}$, $\rho_{k,y}$, and $\rho_{k,z}$ are the respective components of ρ_k and the parameters β_x, β_y, and β_z are constants. Again, term by term integration leads to the result

$$\langle Q' \rangle = \frac{\beta_x + \beta_y + \beta_z}{3} N \tag{6}$$

Micronetwork Analysis with Volume Changes

Consider now an ensemble of loop-less micronetworks, each with S Gaussian strands, labeled $i = 1, \ldots, S$, joining J mobile junctions and F fixed points. The density of configurations available to strand i is proportional to $\exp\{-\frac{3}{2}(\mathbf{r}_i \cdot \mathbf{r}_i/\langle r_i^2 \rangle_0)\}$, $\mathbf{r}_i$ being the end-to-end vector of strand i and $\langle r_i^2 \rangle_0$ the mean-square end-to-end distance for the same strand as a free chain. Thus, the number of configurations available to micronetworks with specified positions of all junctions and fixed points is proportional to the product of the density of configurations for all strands, multiplied by the elemental volumes containing each of the fixed points and junctions (eq 7). The proportionality constant C' depends only on the number of strands and their contour length distribution, and is independent of the junction coordinates. One of the fixed points has been taken to be the origin of coordinates for each micronetwork. The positions of the remaining $F - 1$ fixed points are given by vectors drawn from this origin and labeled $\mathbf{R}_1, \ldots, \mathbf{R}_{F-1}$, while those of the mobile junctions are given by $\mathbf{R}_F, \ldots, \mathbf{R}_{F+J-1}$.

$$\delta\Omega' = C' \exp\left[-\frac{3}{2} \sum_{i=1}^{S} \frac{\mathbf{r}_i \cdot \mathbf{r}_i}{\langle r_i^2 \rangle_0} \right] \delta\mathbf{R}_1 \ldots \delta\mathbf{R}_{F-1} \delta\mathbf{R}_F \ldots \delta\mathbf{R}_{F+J-1} \tag{7}$$

The total number of configurations available to a micronetwork with a given set of internal fixed point coordinates $\mathbf{R}_1, \ldots, \mathbf{R}_{F-1}$ is the sum of contributions for all possible positions of the mobile junctions:

$$\delta\Omega = C' \left[\int \cdots \int \exp\left[-\frac{3}{2} \sum_{i=1}^{S} \frac{\mathbf{r}_i \cdot \mathbf{r}_i}{\langle r_i^2 \rangle_0} \right] \times d\mathbf{R}_F \ldots d\mathbf{R}_{F+J-1} \right] \delta\mathbf{R}_1 \ldots \delta\mathbf{R}_{F-1} \tag{8}$$

Now $\mathbf{r}_i$ is just the difference in the position vectors of the two junctions (or junction and fixed point) which are joined by strand i. It is therefore evident that $\sum_{i=1}^{S} \mathbf{r}_i \cdot \mathbf{r}_i/\langle r_i^2 \rangle_0$ is a quadratic function of the coordinates $\mathbf{R}_1, \ldots, \mathbf{R}_{F+J-1}$ and that it is also positive for all possible sets of the position vectors. It can therefore be transformed to form the required sum of squares

$$\sum_{k=1}^{F+J-1} \lambda_k^2 \rho_k \cdot \rho_k$$

We have in mind a particular procedure for converting to the sum of squares, namely the method of Lagrange applied first to the mobile junction coordinates and then to the fixed points. The method of Lagrange[10] proceeds by successive completion of squares. The terms remaining after each such completion contain only the variables left to be transformed. Thus, if we develop the transformation by completing the squares for the mobile junction coordinates first, then we can retain the association of the transformed coordinates $\rho_1, \ldots, \rho_{F-1}$ with the set of fixed point coordinates $\mathbf{R}_1, \ldots, \mathbf{R}_{F-1}$, as is needed in what follows.

After performing the indicated integrations over the J transformed mobile junction coordinates we arrive at

$$\delta\Omega = C \exp\left[-\frac{3}{2} \sum_{k=1}^{F-1} \lambda_k^2 \rho_k \cdot \rho_k \right] \delta\rho_1 \ldots \delta\rho_{F-1} \tag{9}$$

in which C is independent of the fixed point coordinates.

After deformation the internal coordinates of the fixed points are altered by the stretch ratios α_x, α_y, and α_z. Since the transformation of variables is linear, the transformed coordinates after deformation are altered by the same factors. The scalar products $\rho_k \cdot \rho_k$ become $\alpha_x^2 \rho_{k,x}^2 + \alpha_y^2 \rho_{k,y}^2 + \alpha_z^2 \rho_{k,z}^2$ after deformation, in which $\rho_{k,x}$, $\rho_{k,y}$, and $\rho_{k,z}$ are the respective components of ρ_k before deformation. The volume elements of $\delta\rho_i$ become $\alpha_x \alpha_y \alpha_z \delta\rho_i$. Thus, from the Boltzmann equation, the entropy of deformation for the micronetwork is

$$\Delta S(\rho_1, \ldots, \rho_{F-1}) = k \ln \frac{\delta\Omega(\text{deformed})}{\delta\Omega(\text{undeformed})}$$

or

$$\Delta S = -k \left[\frac{3}{2} \sum_{k=1}^{F-1} \lambda_k^2 [(\alpha_x^2 - 1)\rho_{k,x}^2 + (\alpha_y^2 - 1)\rho_{k,y}^2 + (\alpha_z^2 - 1)\rho_{k,z}^2] - \ln (\alpha_x \alpha_y \alpha_z)^{F-1} \right] \tag{10}$$

Since in the ensemble the probability of occurrence of any set of fixed point positions is taken to be proportional to the number of configurations available to a micronetwork with that set, the average entropy per micronetwork is

$$\Delta S = -k\left[\frac{3}{2}\frac{\int\cdots\int\sum_{k=1}^{F-1}\lambda_k^2[(\alpha_x^2-1)\rho_{k,x}^2+(\alpha_y^2-1)\rho_{k,y}^2+(\alpha_z^2-1)\rho_{k,z}^2]\exp\left\{-\frac{3}{2}\sum_{k=1}^{F-1}\lambda_k^2\boldsymbol{\rho}_k\cdot\boldsymbol{\rho}_k\right\}d\boldsymbol{\rho}_1\cdots d\boldsymbol{\rho}_{F-1}}{\int\cdots\int\exp\left\{-\frac{3}{2}\sum_{k=1}^{F-1}\lambda_k^2\boldsymbol{\rho}_k\cdot\boldsymbol{\rho}_k\right\}d\boldsymbol{\rho}_1\ldots d\boldsymbol{\rho}_k} - (F-1)\ln\alpha_x\alpha_y\alpha_z\right] \tag{11}$$

However, with eq 2–6 the first term on the right in brackets becomes simply

$$\left(\frac{\alpha_x^2+\alpha_y^2+\alpha_z^2-3}{2}\right)(F-1)$$

With entropy replaced by free energy, $\Delta A = -T\Delta S$, the free energy of deformation per micronetwork becomes finally:

$$\Delta A = (F-1)kT\left[\frac{\alpha_x^2+\alpha_y^2+\alpha_z^2-3}{2} - \ln\alpha_x\alpha_y\alpha_z\right] \tag{12}$$

The earlier paper dealt with constant volume deformations, $\ln\alpha_x\alpha_y\alpha_z$ being therefore equal to zero, and with a network reference state in which $(\langle r^2\rangle/\langle r^2\rangle_0)_{av}$, or $\langle\langle r^2\rangle/\langle r^2\rangle_0\rangle$, for the strands was equal to unity. The micronetworks were symmetrical in the sense that all fixed points were separated from the central network element (strand or junction) by the same number of strands. For such circumstances the number of fixed points and the number of strands are related through the junction functionality. The connection between micronetwork properties and those of macroscopic phantom networks was made merely by extracting the contribution of strands between mobile junctions, which is that given in eq 1. This procedure was justified by the fact that the contribution per strand between mobile junctions was independent of the size of the micronetwork.

It is unfortunately not possible to handle the logarithmic term in eq 12 in such a simple manner. The logarithmic term has to do with the change in available volume for the fixed point positions with an expansion or contraction of the micronetwork. For an ensemble of micronetworks the fixed points of each are established independently, and eq 12 applies. However, if these micronetworks are to be assembled to form a macroscopic network (by grouping fixed points into junctions), then the coefficient of the logarithmic term must be modified to reflect the retention of correlation in fixed point positions among micronetworks before and after deformation. Flory[12] dealt with this correlation contribution for networks composed of affinely deforming individual strands (which may be thought of as single-strand micronetworks with $F = 2$), and obtained the following expression for the free energy of a perfect f-function network with S strands

$$\Delta A = SkT\left[\frac{\alpha_x^2+\alpha_y^2+\alpha_z^2}{2} - \frac{2}{f}\ln\alpha_x\alpha_y\alpha_z\right] \tag{13}$$

We have so far not been able to extend Flory's calculation to larger micronetworks. However, as shown in the following section, it is possible to determine the coefficient of the logarithmic term in another way, namely from the dimensions of strands in phantom networks at equilibrium.

Equilibrium Dimensions of Network Strands

Consider the following extension of eq 1, including the logarithmic term of eq 13 but with a coefficient B to be determined.

$$\Delta A = (S-J)kT\left[\frac{\alpha_x^2+\alpha_y^2+\alpha_z^2-3}{2} - B\ln\alpha_x\alpha_y\alpha_z\right] \tag{14}$$

The equilibrium state is that for which ΔA is a minimum. If V_0 is the volume of the network in the reference state ($\langle\langle r^2\rangle/\langle r^2\rangle_0\rangle = 1$), and V is the volume in some isotropically deformed state, then $V/V_0 = \alpha^3$ and

$$\Delta A = 3(S-J)kT\left[\frac{\alpha^2-1}{2} - B\ln\alpha\right] \tag{15}$$

The value of α at the minimum of free energy is obtained from

$$\frac{\partial\Delta A}{\partial\alpha} = 3(S-J)kT\left(\alpha - \frac{B}{\alpha}\right) = 0 \tag{16}$$

from which

$$\alpha_{eq}^2 = B \tag{17}$$

The value of α_{eq}^2 can also be expressed microscopically:

$$\alpha_{eq}^2 = \left\langle\frac{\langle r^2\rangle}{\langle r^2\rangle_0}\right\rangle_{eq} \tag{18}$$

in which the average is calculated over all S elastically effective strands for an ensemble of macroscopic networks of identical structure:

$$\left\langle\frac{\langle r^2\rangle}{\langle r^2\rangle_0}\right\rangle_{eq} = \frac{1}{S}\sum_{i=1}^{S}\frac{\mathbf{r}_i\cdot\mathbf{r}_i}{\langle r_i^2\rangle_0} \tag{19}$$

As before, the individual strand vectors $\mathbf{r}_i$ are differences in position vectors of the two junctions connected by the strand, measured relative to some arbitrarily chosen junction as origin. Thus $\sum_{i=1}^{S} S\,\mathbf{r}_i\cdot\mathbf{r}_i/\langle r_i^2\rangle_0$ is a positive definite quadratic form involving $J-1$ junction vectors in the macroscopic network. The weighting factor for calculating the average dimensions is the number of configurations available to the network strands with the specified junction positions, which is

$$\delta\Omega = C''\exp\left[-\frac{3}{2}\sum_{i=1}^{S}\frac{\mathbf{r}_i\cdot\mathbf{r}_i}{\langle r_i^2\rangle_0}\right]\delta\mathbf{R}_1\ldots\delta\mathbf{R}_{J-1} \tag{20}$$

The average ratio of dimensions at equilibrium is therefore

$$\left\langle\frac{\langle r^2\rangle}{\langle r^2\rangle_0}\right\rangle_{eq} = \frac{1}{S}\frac{\int\cdots\int\left(\sum_{i=1}^{S}\frac{\mathbf{r}_i\cdot\mathbf{r}_i}{\langle r_i^2\rangle_0}\right)\exp\left[-\frac{3}{2}\sum_{i=1}^{S}\frac{\mathbf{r}_i\cdot\mathbf{r}_i}{\langle r_i^2\rangle_0}\right]d\mathbf{R}_1\ldots d\mathbf{R}_{J-1}}{\int\cdots\int\exp\left[-\frac{3}{2}\sum_{i=1}^{S}\frac{\mathbf{r}_i\cdot\mathbf{r}_i}{\langle r_1^2\rangle_0}\right]d\mathbf{R}_1\ldots d\mathbf{R}_{J-1}} \tag{21}$$

From eq 2–5 the ratio of integrals in eq 21 is simply $J - 1$. Thus,[15]

$$\left\langle \frac{\langle r^2 \rangle}{\langle r^2 \rangle_0} \right\rangle_{eq} = \frac{(J-1)}{S} \tag{22}$$

From eq 17 and 18, the coefficient B is $(J - 1)/S$, which is essentially J/S for a macroscopic network. Finally, the elastic free energy for an arbitrary macroscopic network with S elastically effective strands, J elastically effective junctions, and tree-like local connectivity is:

$$\Delta A = (S - J)kT\left[\frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3}{2} - \frac{J}{S}\ln \alpha_x\alpha_y\alpha_z\right] \tag{23}$$

The reference configuration for the network is that corresponding to free strand dimensions, or $\langle \langle r^2 \rangle / \langle r^2 \rangle_0 \rangle = 1$.

For networks in which all junctions have the same functionality f, the number of strands and junctions are related by $2S = Jf$, yielding for this special case

$$\alpha_{eq}^2 = \frac{2}{f} \tag{24}$$

and

$$\Delta A = \frac{f-2}{f} SkT\left[\frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3}{2} - \frac{2}{f}\ln \alpha_x\alpha_y\alpha_z\right] \tag{25}$$

The contraction factor for $f = 4$, $\alpha_{eq}^2 = \frac{1}{2}$, agrees with that inferred by James and Guth[13] and later derived by Eichinger[2] for tetrafunctional networks. The coefficient of the logarithmic term in eq 25 is that given by Flory (eq 13). The front factor on the entire expression, however, is smaller by the factor $(f - 2)/f$ or $\frac{1}{2}$ for the case of tetrafunctional networks.

All these results lead to the conclusion that the elastic properties of phantom Gaussian networks with locally tree-like connectivity are independent of strand length distribution, junction functionality distribution, and the detailed pattern of connectivity. Everything depends finally only on the total numbers of elastically active strands and elastically active junctions. It is also clear from eq 22 and 24 that the state of minimum free energy for the network corresponds to an average contraction of dimensions of the elastically effective strands, compared to their dimensions as free chains. How much of this contraction is actually obtained in real polymer networks till uncertain. For systems cross-linked in the undiluted state the amount of contraction actually obtained is likely to be small, and $\langle \langle r^2 \rangle / \langle r^2 \rangle_0 \rangle$ is probably very close to unity. It follows from eq 22 that intranetwork loops provide not only network elasticity but also the impetus for contraction. Aside from a presumably small fraction of intramolecular links,[14] there are no loops prior to the gel point and thus no driving force for coil contraction. Moreover, even beyond the gel point the vast majority of loops are almost certainly large scale and involve portions of many primary molecules. Thus, the configurational rearrangements required for contraction must be extremely slow and impeded as well by the interpenetration of strands from other loops in the network. Contraction could occur in networks formed in solution, however, since mobility is greater and since contraction could be brought about merely by the expelling of solvent. Such behavior probably accounts for the syneresis phenomenon which is sometimes observed in such systems at high cross-linking densities.[4,5]

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(15) Equation 22 is interesting in that it is applicable to any connected assembly of Gaussian strands, and not merely to large networks alone. Suppose J is the total number of points whose positions are needed to specify completely all end-to-end vectors of the S strands in the structure. For structure A below J is 8, S is 9, so $\langle \langle r^2 \rangle / \langle r^2 \rangle_0 \rangle_{eq}$ is $(8 - 1)/9$ = 7/9. Likewise for structure B, J is 2, S is 2 and $\langle \langle r^2 \rangle / \langle r^2 \rangle_0 \rangle_{eq} = (2 - 1)/2 = 1/2$. In general the positions of $S + 1$ points are needed to specify and end-to-end vectors of S strands in a connected array without loops. Thus, if J is the number of such points for a particular assembly, then $S + 1 - J$ must be the number of loops in that assembly. The average fractional contraction of strand dimensions at equilibrium, $\langle (\langle r^2 \rangle_0 - \langle r^2 \rangle) / \langle r^2 \rangle_0 \rangle_{eq}$, is therefore simply the ratio of loops to total strands, $(S - J + 1)/S$ or $1 - (J - 1)/S$. Some individual strands will of course be more contracted than others, depending on their participation in loops. In structure A for example, the dangling strands will have their free chain dimensions, while the loop participants will be more contracted than the average.