Statistical Mechanics of Random Coil Networks

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ABSTRACT: The free energy of deformation for random coil networks has been determined from the properties of ensembles of small sample networks, called micronetworks. According to these calculations, the front factor g in the theory of rubber elasticity depends on the functionality f of the network junctions: $g = (f - 2)/f$. Thus, g is ⅓ for trifunctional networks, ½ for tetrafunctional networks, and approaches the classical value of unity only in the limit of high junction functionality. The results confirm an earlier suggestion of Duiser and Staverman that, regardless of junction point functionality, the modulus of a perfect network is proportional to $\nu - n$, ν being the concentration of network strands and n the concentration of network junctions.

The kinetic theory of rubber elasticity rests on a number of premises. The strands comprising the network are assumed to behave as random coils, the displacements of the mean junction positions are assumed to be affine (*i.e.*, in proportion to changes in the macroscopic dimensions), and the free energy change of the network upon deformation is assumed to be the simple sum of contributions from changes in the distribution of configurations of individual strands. Finally, the set of configurations available to individual strands is assumed to depend only upon the mean displacement of their chain ends and to be independent of those of neighboring strands for all states of deformation. Such networks of "phantom" strands are predicted theoretically to behave as neo-Hookean solids. For constant volume homogeneous deformations, the free energy of deformation per unit volume, or stored energy function, is of the form

$$\Delta F = g\frac{\nu kT}{2}\frac{\langle r^2\rangle}{\langle r^2\rangle_0}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \qquad (1)$$

in which $\langle r^2\rangle$ is the mean-square end-to-end distance of the strands in the undeformed network, $\langle r^2\rangle_0$ is the same quantity for the strands with junction points removed (free strands), kT is the Boltzmann factor, α_x, α_y, and α_z are the macroscopic stretch ratios of the network along the x, y, and z principal strain axes ($\alpha_x\alpha_y\alpha_z = 1$ for a constant volume deformation), ν is the number of strands per unit volume of network, and g is a factor which is unity in all the early theories.[1-3] Somewhat different values for g have been reported in recent theories.[4-6] Other differences among investigators are not related to g directly, but, rather, to inferences drawn about changes in chain dimensions as the network is formed.[7,8]

The conflicts regarding g are annoying, not only because they concern the foundations of an otherwise attractive and successful molecular theory, but also because they prevent an unequivocal separation of chemical network contributions from other contributions, such as chain entanglement, to the observed properties of real networks. In an attempt to resolve these difficulties we have reexamined the problem. Based on the properties of ensembles of small sample networks, termed here micronetworks, an expression for g has been obtained which depends on network junction functionality. In networks with tetrafunctional junctions g is ½, for example, while in networks with trifunctional junctions g is ⅓.

We were led to this work in particular by a result obtained by Duiser and Staverman.[4] They calculated the entropy of deformation contributed by the strands radiating from a central f-functional junction point in an equal-strand network (all strands of the same contour length). All junction points except the central junction were taken to be anchored in the solid and to move with deformation in proportion to the changes in macroscopic dimensions. The central junction was left free to occupy any position. The instantaneous coordinates of the central junction are x_p, y_p, and z_p, relative to a Cartesian coordinate system fixed in space with arbitrary origin but with axes aligned along the principal strain directions. The fixed points, with coordinates $x_1, y_1, z_1; x_2, y_2, z_2; \ldots$; and x_f, y_f, z_f, move strictly in an affine manner with the macroscopic displacements, becoming $\alpha_x x_1, \ldots, \alpha_z z_f$ after deformation. For a collection of such network elements, with $\langle r^2\rangle = \langle r^2\rangle_0$, and the number of strands per element equal to f, Duiser and Staverman obtain an expression which is equivalent to

$$\Delta F = \frac{f-1}{f}\frac{\nu kT}{2}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \qquad (2)$$

whereas the theories which assume an affine displacement of all strand junctions yield

$$\Delta F = \frac{\nu kT}{2}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \qquad (3)$$

From a further argument based on the successive release of each junction in the network, maintaining adjacent junctions fixed, Duiser and Staverman go on to infer a value of $g = (f - 2)/f$ for a network in which all junctions are mobile. Since they did not display their averaging procedure over all possible fixed point positions in detail, it seemed important to verify the calculations. However, that their results are indeed correct, insofar as eq 2 is concerned, is shown by the following analysis. We display the calculations in somewhat greater detail than necessary because the analysis of more elaborate micronetworks follows a similar procedure.

Properties of Micronetwork Ensembles

Let $\Omega(x_1, \ldots, z_f)$ be the number of distinguishable configurations of the f-functional network element shown for a given set of f fixed point positions. For Gaussian strands, following Duiser and Staverman

$$\Omega(x_1, \ldots, z_f) = \iiint_{-\infty}^{\infty} C \exp\{-\beta^2\sum_{i=1}^{f}[(x_i - x_p)^2 + (y_i - y_p)^2 + (z_i - z_p)^2]\}dx_p dy_p dz_p \qquad (4)$$

and after integration

$$\Omega(x_1, \ldots, z_f) = C\left(\frac{\pi}{f\beta^2}\right)^{3/2}\exp\{-\beta^2[X^2 + Y^2 + Z^2]\} \qquad (5)$$

where C is a normalizing constant which is independent of deformation, $\beta^2 = \frac{3}{2}\langle r^2\rangle_0$ is the same for all strands, and

$$X^2 = \sum_{i=1}^{f} x_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} x_i\right)^2$$
$$Y^2 = \sum_{i=1}^{f} y_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} y_i\right)^2 \quad (6)$$
$$Z^2 = \sum_{i=1}^{f} z_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f} z_i\right)^2$$

in the rest state.

From the Boltzmann relation

$$\Delta S = k \ln \frac{\Omega(\alpha_x x_1, \ldots, \alpha_z z_f)}{\Omega(x_1, \ldots, z_f)} \quad (7)$$

the contribution to the entropy of deformation by network elements with the particular set of fixed junction positions chosen is

$$\Delta S(x_1, \ldots, z_f) = -k\beta^2[(\alpha_x^2 - 1)X^2 + (\alpha_y^2 - 1)Y^2 + (\alpha_z^2 - 1)Z^2] \quad (8)$$

To obtain the entropy change for a collection of N_0 f-functional network elements in a system of volume V, the contributions of all possible fixed point arrangements must be summed. Let $N(x_1, \ldots, z_f)dx_1 \ldots dz_f$ be the number of f-functional network elements in the system with fixed point coordinates in the range $x_1, x_1 + dx_1; \ldots; z_f, z_f + dz_f$. The points are fixed while the system is at equilibrium, so the frequency of any set of fixed point positions is taken to be proportional to the number of distinguishable configurations available to an f-functional element with those positions. Thus

$$N(x_1, \ldots, z_f)dx_1 \ldots dz_f = N_0 \frac{\Omega(x_1, \ldots, z_f)dx_1 \ldots dz_f}{\int_{-L}^{L} \ldots \int_{-L}^{L} \Omega(x_1, \ldots, z_f)dx_1 \ldots dz_f} \quad (9)$$

in which for convenience we have taken the original network to be a cube of edge length $2L$, the origin of coordinates at the center of the cube and the strain axes normal to the faces of the cube.

From eq 8 above, and having divided by the sample volume to obtain the entropy change per unit volume, we obtain

$$\Delta S = k\beta^2 \frac{N_0}{V}[\alpha_x^2 + \alpha_y^2 + \alpha_z^3 - 3]\overline{X^2} \quad (10)$$

in which

$$\overline{X^2} = \frac{\int_{-L}^{L} \ldots \int_{-L}^{L} X^2 \exp\{-\beta^2 X^2\}dx_1 \ldots dx_f}{\int_{-L}^{L} \ldots \int_{-L}^{L} \exp\{-\beta^2 X^2\}dx_1 \ldots dx_f} \quad (11)$$

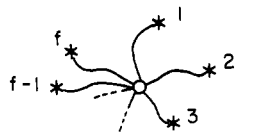

Figure 1. First-order f-functional micronetwork. The circle represents a mobile junction, and the crosses represent fixed junctions.

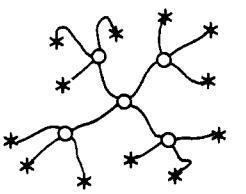

Figure 2. Second-order tetrafunctional micronetwork.

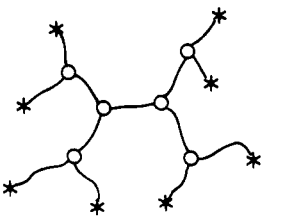

Figure 3. Second-order trifunctional micronetwork around strand A.

and the isotropy of the undeformed network ($\overline{X^2} = \overline{Y^2} = \overline{Z^2}$) has been used to eliminate $\overline{Y^2}$ and $\overline{Z^2}$.

From among the f integration variables, one can be taken as an external coordinate which serves merely to locate the position in space of a particular f-functional micronetwork. The remaining $f - 1$ variables are then internal coordinates, measuring relative positions of the fixed points. Integration over the external coordinate yields $2L$, which appears in both numerator and denominator and cancels. Integration over the remaining $f - 1$ internal coordinates may be taken from $-\infty$ to ∞ since the internal dimensions of most elements are small compared to L. Thus, eq 12 is obtained in which x_f has been chosen to be the external coordinate, and $\xi_i = x_i - x_f$.

The function X^2 is a quadratic form which can be expressed as $X^2 = b_{ij}\xi_i\xi_j$, in which the b_{ij} ($i = 1, \ldots, f - 1; j = 1, \ldots, f - 1$) are components of a symmetric matrix. A linear transformation of variables $\xi_i = \sum_{j=1}^{f-1} a_{ij}v_j$ can be used to eliminate the cross products in X^2, leading to the form $X^2 = \sum_{i=1}^{f-1} \lambda_i^2 v_i^2$ after transformation. The λ_i ($i = 1, 2, \ldots, f - 1$) are the eigenvalues of the matrix **b**. The result of this change of integration variables is eq 13 in which

$$\overline{X^2} = \frac{\int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \left[\sum_{i=1}^{f-1} \xi_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f-1} \xi_i\right)^2\right] \exp\left\{-\beta^2\left[\sum_{i=1}^{f-1} \xi_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f-1} \xi_i\right)^2\right]\right\} d\xi_1 \ldots d\xi_{f-1}}{\int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \exp\left\{-\beta^2\left[\sum_{i=1}^{f-1} \xi_i^2 - \frac{1}{f}\left(\sum_{i=1}^{f-1} \xi_i\right)\right]\right\} d\xi_1 \ldots d\xi_{f-1}} \quad (12)$$

$$\overline{X^2} = \frac{\int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \left(\sum_{i=1}^{f-1} \lambda_i^2 v_i^2\right) \exp\left\{-\beta^2 \sum_{i=1}^{j-1} \lambda_i^2 v_i^2\right\} J dv_1 \ldots dv_{f-1}}{\int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \exp\left\{-\beta^2 \sum_{i=1}^{j-1} \lambda_i^2 v_i^2\right\} J dv_1 \ldots dv_{f-1}} \quad (13)$$

J is the Jacobean of the transformation, a term which is nonzero if none of the λ_i is zero and which factors out of the integrals as a constant for any linear transformation. Direct integration then yields

$$\overline{X^2} = (f - 1)/2\beta^2 \tag{14}$$

Substitution in eq 10 yields

$$\Delta S = -\frac{kN_0(f-1)}{2V}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \tag{15}$$

With $\Delta F = -T\Delta S$ and $\nu = fN_0/V$, this equation reduces to eq 2. It should be noted that the result does not depend at all on the magnitude of the eigenvalues, as long as all are nonzero, but only on their number. This fortunate simplification applies also to more complex micronetworks and enables us to evaluate their properties with practically no additional labor.

Consider the micronetwork in Figure 2, in which the fixed points are more remotely connected to the central element. In this example of tetrafunctional linking there are five mobile junction points and 12 fixed points. Labeling the fixed junctions 1, . . . , 12 and the mobile points 13, . . . , 17 we find, in terms of x coordinates only

$$\Omega(x_1, \ldots, x_{12}) = C\left(\frac{\pi}{4\beta^2}\right)^2\left(\frac{\pi}{3\beta^2}\right)^{1/2}\exp\{-\beta X^2\} \tag{16}$$

in which

$$X^2 = \sum_{i=1}^{12} x_i^2 - \frac{1}{4}[(x_1 + x_2 + x_3)^2 + (x_4 + x_5 + x_6)^2 + (x_7 + x_8 + x_9)^2 + (x_{10} + x_{11} + x_{12})^2] \tag{17}$$

By application of the previous procedures, we arrive at finally

$$\Delta F = \frac{11}{16}\frac{\nu kT}{2}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \tag{18}$$

in which the "11" is one less than the number of 12 fixed points in the element, and "16" is the number of strands in the element.

The same reasoning appears to be applicable to any micronetwork. The number of fixed points in a jth order tetrafunctional micronetwork (of which Figure 1 with $f = 4$ is first order and Figure 2 is second order) is $4 \times 3^{j-1}$. There is one external coordinate for each micronetwork and therefore $4 \times 3^{j-1} - 1$ internal coordinates. The number of strands in a jth order tetrafunctional micronetwork is $2(3^j - 1)$. Hence the free energy of deformation for an ensemble of jth order tetrafunctional micronetworks, assuming the eigenvalues for X^2 expressed in internal coordinates are all nonzero, is

$$\Delta F = \frac{4 \times 3^{j-1} - 1}{2(3^j - 1)}\frac{\nu kT}{2}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \tag{19}$$

As j increases, the fixed points (those which are compelled to move affinely) become more remote in their connections with the central portions of the micronetwork. As j tends to infinity the response corresponds to that of an ensemble of micronetworks in which only very remote portions are compelled to move in an affine manner. In the limit

$$\lim_{j\to\infty}\left[\frac{4 \times 3^{j-1} - 1}{2(3^j - 1)}\right] = \tfrac{2}{3} \tag{20}$$

for tetrafunctional micronetworks.

This result is easily generalized to f-functional networks. For a f-functional, j-order micronetwork the number of strands is $N_j(f)$, and

$$N_j(f) = \frac{f}{f-2}[(f-1)^j - 1] \tag{21}$$

The corresponding number of fixed points is $P_j(f)$, and

$$P_j(f) = f(f-1)^{j-1} \tag{22}$$

The number of internal coordinates for any such micronetwork is $P_j(f) - 1$, and the ratio $R_j(f) = (P_j(f) - 1)/N_j(f)$ governs the free energy of deformation

$$\Delta F_j(f) = R_j(f)\frac{\nu kT}{2}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \tag{23}$$

The limiting value for an f-functional ensemble is therefore

$$R_\infty(f) = \lim_{j\to\infty} R_j(f) = \frac{f-2}{f-1} \tag{24}$$

in which, for example, $R_\infty(4) = \frac{2}{3}$ and $R_\infty(3) = \frac{1}{2}$. Only in the case of very large functionalities does $R_j(f)$ approach the classical value of 1.0. Note, however, that $R_\infty(f)$ is not the same as the front factor g for a macroscopic network. The fraction of fixed points in a real macroscopic network is vanishingly small, while in micronetworks the fraction remains appreciable even as $j \to \infty$. Nevertheless, a value of g can be determined from $R_\infty(f)$ as will be shown later.

The micronetworks considered above were built up around a central junction. They can also be constructed around a central strand. It is clear that the same analysis carries through as before and that $N_j'(f)$ and $P_j'(f)$, the numbers of strands and fixed points in these micronetworks, are obtainable from the previous $N_j(f)$ and $P_j(f)$.

$$N_j'(f) = 2\left[\frac{f-1}{f}N_{j-1}(f)\right] + 1 \tag{25}$$

$$P_j'(f) = 2\frac{f-1}{f}P_{j-1}(f) \tag{26}$$

The ratio $R_j'(f) = (P_j'(f) - 1)/N_j'(f)$ for these micronetworks is therefore

$$R_j'(f) = \frac{2(f-1)^{j-1} - 1}{2[(f-1)/(f-2)][(f-1)^{j-1} - 1] + 1} \tag{27}$$

An ensemble of first-order micronetworks here corresponds to a collection of independent strands with end points which are compelled to move affinely, and for which $R_1'(f) = 1$. This seems to reconcile the difference noted earlier between the results of Wall[1] and Flory[3] and those of Duiser and Staverman.[5] Within the context of the theory presented here, both DS and WF deduced the elastic properties of a macroscopic network from an analysis of first-order micronetworks, the DS result from a central junction, first-order micronetwork, and the WF result from a central strand, first-order micronetwork. Both types of micronetworks approach the same limiting behavior as the order tends to infinity (eq 24), and lead to the same values of g (see below).

None of the micronetworks considered contain closed loops, which is certainly not the case in real networks. Each such loop involving mobile junctions would increase the number of strands, while leaving the number of fixed points unchanged. Thus, it appears that closed loops would tend to reduce the effective value of $R_j(f)$. Consideration of closed loops would require a detailed analysis dealing with the physical structure of real networks. In any case we do not believe that corrections for closed loop formation would alter the results appreciably, for the following reason. It is not required that there be no loops in the entire system, but merely that most junctions (or strands) be connected through their first few orders without redundancy (closed loops). We are only seeking to remove the junctions which are constrained to move in an affine manner sufficiently far from strands near the center of the micronetwork that the contribution of the latter to the modulus no longer changes

if the constraints become still more remote. With tetrafunctional strands $R_3(4)$ is already 0.673 . . . , compared to the limiting value $R_\infty(4) = 0.666$ . . . . Thus the existence of *large-scale* loops, of which there must be many in real networks,[9] should not alter these results appreciably.

The consideration of configurations available to a connected network of strands, rather than to the strands independently, parallels very closely the earlier analysis of James.[10] However, he was concerned with the configurations available to a network of macroscopic dimensions, in which the fixed points lay only on the surface. Because of this latter stipulation the mathematics became unwieldly and the limiting behavior was not obtainable. The viewpoint here differs in that we consider the properties of micronetworks which remain small compared to the dimensions of the sample, although still containing many strands. The frequency of occurrence for positions of fixed points which anchor micronetworks to the sample is taken to correspond to the equilibrium distribution of the corresponding strand end positions in the macroscopic network. Properties are then calculated for an ensemble of such independent micronetworks, each of which is of sufficiently high order that the contribution per strand has already reached a limiting value. The method used here turns out to resemble in some ways the graph theory approach of Eichinger.[8] The results seem quite different, perhaps because the network topologies differ.

Evaluation of the Front Factor

We have thus far avoided associating $R_\infty(f)$ (or $R_\infty'(f)$) with g for a macroscopic network, since even in high-order micronetworks the number of strands with fixed ends in any micronetwork remains a large proportion of the total. Each fixed point corresponds to a strand with one end fixed and the other attached to a mobile junction. Thus the number of strands with one fixed end is $P_j(f)$, the number with both ends attached to mobile junctions is $N_j(f) - P_j(f)$, and the fraction of strands with one end fixed $F_j(f)$ is $P_j(f)/N_j(f)$. It turns out that, with eq 21 and 22, $R_j(f)$ can be expressed simply in terms of the fractions of the two types of strands

$$R_j(f) = \frac{f-1}{f} F_j(f) + \frac{f-2}{f}[1 - F_j(f)] \quad (28)$$

This result confirms the inference drawn by Duiser and Staverman from the behavior of first-order micronetworks only, namely that, regardless of micronetwork order, the contribution to the modulus of each strand bounded by mobile junctions is $(f-2)/f$, while that for strands in which one end is compelled to move affinely is $(f-1)/f$. In the macroscopic network all strands have two mobile junctions (except possibly those attached to the boundary), and hence the modulus contribution per strand is

$$g = (f-2)/f \quad (29)$$

Although the calculations so far only deal with micronetworks in which all strands have the same contour length (β^2 is the same for all strands), the procedure is clearly applicable to statistically formed networks, and in particular to the case of random cross-linking. Intermediate steps are more complicated, of course, since one must consider the distribution of strand contours as well, but the results are the same as given here for regular networks. That is to say, the value of g inferred from the properties of sufficiently high-order micronetworks depends only on the functionality of the network junctions. In this respect the results agree with the discussion of Flory and Wall,[11] although differing in regard to the value of g obtained.

The free energy of deformation can also be expressed in terms of $n(f)$, the concentration of junction points per unit volume, since $\nu = fn(f)/2$.

$$\Delta F = \frac{(f-2)n(f)}{2}\frac{kT}{2}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \quad (30)$$

In cases where junctions of different functionalities are present, $(f-2)n(f)$ is replaced by $\sum_{f=3}^{\infty}(f-2)n(f)$.

In random tetrafunctional cross-linking, elastically active network junctions are those cross-links for which at least three of the four strands radiating from the cross-link lead independently to the gel. Langley[12,13] has shown how to calculate the concentration of cross-links with three and four strands leading to the gel, $n(3)$ and $n(4)$ respectively, from the statistics of cross-linking. The resulting expression for the free energy of deformation is therefore

$$\Delta F = \frac{n(3) + 2n(4)}{2}\frac{kT}{2}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \quad (31)$$

The concentration of elastically effective strands, ν, is $(3n(3) + 4n(4)/2$, so the effective value of g for such networks is

$$\bar{g} = (2 - r)/(4 - r) \quad (32)$$

in which r is $n_3/(n_3 + n_4)$, the fraction of effective network junctions in the system which have three strands leading to gel. Thus, since r is a function of cross-linking density ($r = 1$ at the gel point and $r = 0$ in the limit of high cross-link density), the value of $\bar{g}$ should vary with cross-link density, in contrast with predictions of the early theories.

All these properties follow at once from a principle which was first suggested by Duiser and Staverman, and which we have deduced here from the properties of micronetworks of arbitrary order; the effective number of network strands per unit volume, ν^*, is equal to the concentration of strands joining elastically active junctions, ν, minus the total concentration of elastically effective junctions, n, irrespective of functionality.

$$\Delta F = \frac{\nu^* kT}{2}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) = \frac{(\nu - n)kT}{2}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \quad (33)$$

So far we have assumed that all the eigenvalues of the required transformation (to arrive at the analogy of eq 13 for any micronetwork) are nonzero. Stated slightly differently, we have assumed that the eigenvalues of the transformation which diagonalizes the quadratic form

$$Q_j(f) = \sum_{i=1}^{i=P} x_i^2 - \frac{1}{f}\sum_{i=1}^{(P/f)-1}\left(\sum_{k=1}^{i-1} x_{(f-1)i+k}\right)^2 \quad (34)$$

(in which $P = P_j(f)$) include one and only one eigenvalue equal to zero. Equation 34 is the general expression for X^2, which is given in eq 6 and eq 17 for two special cases. The zero eigenvalue may be eliminated by choosing one coordinate as an external coordinate (by the substitution $\xi_i = x_i - x_1$ ($i = 2, \ldots, P_j(f)$) for example), and it is assumed that there are no others. This assumption seems reasonable on physical grounds, since it implies only that the internal coordinates of the fixed points are linearly independent, but we have been unable to find a proof.

Summary

The front factor g in the theory of rubber elasticity has been calculated from the properties of an ensemble of sample networks, called micronetworks. The value obtained depends only upon the functionality of the network junctions:

$g(f) = (f - 2)/f$. This result differs from those of a number of previous theories, for which g was found to be unity and independent of network connectivity. It confirms the inference of Duiser and Staverman, drawn from the behavior of first-order micronetworks, and agrees with the value $g = \frac{1}{2}$ obtained by Edwards for the case of networks formed by random tetrafunctional cross-linking.

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Harmonically Bound Particle Model for Quasi-Elastic Light Scattering by Gels

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ABSTRACT: The intensity fluctuations of the scattered light in time reflect the dynamics of the scattering entities. In the case of a gel, the initial amplitude of the intensity autocorrelation function has been found to be greatly reduced compared to that of its "sol" state. The initial amplitude seems to correlate with the constraint imposed on the motion of a macromolecule in its "gel" state. Assuming each macromolecule in the "gel" state to behave as a harmonically bound particle executing independent Brownian motion about a stationary mean, and including the presence of additional static scattering due to spatial structuring of the Rayleigh scatterers, the intenstiy autocorrelation function is derived. Three physical parameters may then be deduced from autocorrelation measurements, *i.e.*, a chain elastic constant which can be related to the equilibrium storage or shear modulus, the conventional diffusion coefficient or frictional constant, and the fraction of static scattering in addition to that prescribed by Rayleigh scattering. Quantitative measurements were done on polyacrylamide gels. The equilibrium storage moduli deduced from light scattering experiments were compared with those determined by unilateral compression measurements.

It has been observed that the initial amplitude of the normalized intensity autocorrelation function of the scattered light, *i.e.*, $g^{(2)}(0)$, is drastically reduced going from the "sol" to the "gel" state for actin–heavymeromyosin complexes[1] and agarose.[2] For freely diffusing particles, the normalized intensity autocorrelation function may be written as[3]

$$g^{(2)}(\tau) = 1 + |g^{(1)}(\tau)|^2 = 1 + \exp(-2DK^2\tau) \quad (1)$$

where $g^{(1)}(\tau)$ represents the normalized autocorrelation function of the optical field; D is the translational diffusional coefficient; K is the amplitude of the scattering vector, $(4\pi\eta_0/\lambda_0) \sin \theta/2$, where η_0 is equal to the refractive index of the scattering medium, λ_0 is the wavelength of the incident light in vacuum and θ is the scattering angle, and τ is the delay time.

Hence, the theoretical value of $g^{(2)}(0)$ from eq 1 is 2 for any scattered optical field that is Gaussian with zero mean. However, measured estimators of $g^{(2)}(\tau)$ are limited by incomplete spatial coherence at the detector so that experimentally, an instrument constant, α, should be included in eq 1 and in practice, $0 < \alpha < 1$.

$$g^{(2)}(\tau) - 1 = \alpha \exp(-2DK^2\tau) \quad (2)$$

α can be determined from measurements on polystyrene latex spheres or similar monodisperse free diffusing particles. Consequently, if $g^{(2)}(0) - 1$ for a scattering system is observed to be significantly less than α, as is the case for our measurements on gels so far, it may be concluded that the representation $g^{(1)}(\tau) = e^{-\Gamma\tau}$ is inadequate.

Carlson and Fraser[1] have proposed a simple modl for scattering molecules in the gel state which assumes each molecule as harmonically bound and executing Brownian motion. A collection of such identical, independent harmonically bound particles, each executing Brownian motion about a stationary mean position, is considered to be a simple model for a gel. It is reasonable to expect the gel particles, *i.e.*, the macromolecular chains, to execute only limited motions about a stationary mean, with the "harmonic" constraint provided by its closely packed neighbors. In the case of covalently cross-linked gels, the cross-links themselves may also affect the motions of the chains. Tanaka, Hocker, and Benedek[4] have developed a continuum theory for gels that makes no provision for the large static scattering due to spatial correlation of the Rayleigh scatterers which is usually observed in gels. In this paper, we present a revised version of the theory proposed by Carlson and Fraser and an experimental test of it. A sample of our experimental data was also fitted with an equation conforming to the continuum theory but with an added provision for the static scattering. The results are discussed in the last section.