tions; in considering these data it should be recalled that a value of 5–10 represents a reasonable likely maximum for $x$ in experimental measurements. Clearly, relatively low radiation doses ($D/D_g$) need to be employed for reasonably accurate estimates to be made of molar mass averages and hence of radiation chemical yields. Measurements of molar size averages in the pregel region should therefore be confined to the region $D < 0.4D_g$, a restriction that necessitates high accuracy and/or the collection of adequate numbers of experimental measurements. If the data are being obtained by equilibrium sedimentation, particular care is required in the extrapolations used for determination of true average molar masses from measured values of $\bar{M}_w(D)^{app}$ and $\bar{M}_z(D)^{app}$, since their dependences on rotor speed become progressively more pronounced with increasing radiation dose $D$ due to the greater polydispersity of the sample.[17]

## Conclusions

1. Numerical solution of Saito's integro-differential equation for chain scission[10] by a "marching" method has been shown to give correct molecular size distributions.
2. Analytical expressions have been developed for the dose dependence of $\bar{M}_w$ and $\bar{M}_z$ for an initial Schulz–Zimm system undergoing cross-linking only.
3. An analytical solution for simultaneous scission and cross-linking of an initial Schulz–Zimm molecular size distribution is presented, but complexity of some of the terms seems likely to restrict its use.
4. Combination of "marching" solutions for scission and cross-linking has permitted evaluation of weight distributions by a multicycle procedure in which the total dose is considered to comprise a series of dose increments. This method of calculating distributions is shown to be superior to the single step procedure used previously.
5. Measurements of solution properties of irradiated polymers should be restricted to doses such that $D < 0.4D_g$ if values of $\bar{M}_w(D)$ and $\bar{M}_z(D)$ are to be compared with theoretical values calculated from analytical expressions.

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# The Elastic Free Energy of Dilation of a Network

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ABSTRACT: The elastic contribution $(\mu_1 - \mu_1{}^0)_{el}$ to the chemical potential of the diluent in a swollen network is treated according to recent theory which takes account of constraints on junctions in real networks. The quantity $\lambda(\mu_1 - \mu_1{}^0)_{el}$, where $\lambda$ is the linear expansion ratio, exhibits a maximum with increase in $\lambda$ in qualitative agreement with experimental measurements, but contrary to previous theories. The premise that the free energy of a swollen network is additive in the contributions from mixing and elastic deformation is supported by the comparison of experiment with theory.

Recently Yen and Eichinger[1] reported experiments comparing the small difference between the activity of the diluent in a swollen network and in a solution of the linear polymer at the same concentration. They investigated poly(dimethylsiloxane) (PDMS) swollen with benzene and poly(styrene-*co*-butadiene) using benzene and *n*-heptane, respectively, as diluents in separate series of experiments. Similar experiments were carried out a number of years ago by Gee, Herbert, and Roberts[2] using natural rubber and benzene. Yen and Eichinger confirmed the earlier work of Gee et al. showing the contribution of the network to the chemical potential of the diluent to be at variance with conventional theories of rubber elasticity. Specifically, the product of this elastic contribution $(\mu_1 - \mu_1{}^0)_{el}$ to the chemical potential of the diluent and the linear dilation ratio $\lambda$ passes through a maximum with concentration, according to the carefully executed investigations cited. Network theories examined by these authors predict either constancy of this product or increases that are essentially monotonic with concentration.

Yen and Eichinger[1] concurred with the opinion of Gee, Herbert, and Roberts[2] that the results cast doubt on a major premise of the theory of swelling of networks, namely the hypothesis that the elastic and mixing free energies are separable. Expression of the free energy of such a system as the sum of two terms, one arising from the intermolecular forces of short-range operating between neighboring species (chain units and solvent molecules, if the latter are present) and the other from deformation of the network, underlies theories of rubber elasticity as well as of swelling.

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Yen and Eichenger[1] did not compare their results with a more recent theory[3,4] of rubber elasticity, according to which the fluctuations of network junctions are restricted in a manner dependent on the strain, including the volumetric dilation. Fluctuations of the junctions cause the deformation of the network chains to be nonaffine in the macroscopic strain.[5] According to this theory,[3,4] the fluctuations of the junctions are restricted by the interspersion of their pendant chains with other members of the network. The resulting configurational restraints are reasoned to diminish with increase in strain, including isotropic dilation. As is shown below, this theory appears to be unique in accounting, qualitatively at least, for the peculiar dependence of the elastic contribution to the chemical potential of the diluent demonstrated by the experiments cited above.

## Theory

Taking the contribution of the network to the free energy to be separable from, and therefore additive with, the intermolecular free energy, we express the Helmholtz free energy of the system as follows[6]

$$\Delta A = \Delta A_{\mathrm{M}} + \Delta A_{\mathrm{el}} \tag{1}$$

The intermolecular term is designated by the subscript "M", denoting "mixing", inasmuch as compositional changes are of immediate concern rather than changes pertaining to the equation of state at fixed chemical content.[6]

The chains pendant at a given junction must necessarily adopt configurations that are free of spatial overlaps with the neighboring chains with which they share the same region of space. According to the theory put forward recently,[3,4] fluctuations of junctions about their mean positions are restricted on this account. A large fluctuation entails configurational rearrangements of chains occupying a greater region of space. Hence, the number of eligible configurations is expected to be smaller the greater the displacement of the junction from its preferred location in relation to its neighbors. In contrast to the transitory entanglements often postulated to account for the time-dependent behavior of polymers, the restrictions here considered depend upon the totality of configurations accessible to the system, and hence are operative at equilibrium.

The elastic free energy derived on this basis can be resolved into two terms as follows[3]

$$\Delta A_{\mathrm{el}} = \Delta A_{\mathrm{ph}} + \Delta A_{\mathrm{c}} \tag{2}$$

The first term, $\Delta A_{\mathrm{ph}}$, is the contribution of the corresponding phantom network in which the chains are devoid of all material properties other than the forces they deliver on the junctions to which they are attached. The second term, $\Delta A_{\mathrm{c}}$, arises from the aforementioned restrictions on junctions of the real network and the resulting restraints on the fluctuations of junctions about their mean positions. For a network of Gaussian chains[5,7]

$$\Delta A_{\mathrm{ph}} = \tfrac{1}{2}\xi kT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{3}$$

where $\lambda_1$, $\lambda_2$, and $\lambda_3$ are the principal extension ratios relative to the state of reference and $\xi$ is the cycle rank of the network,[5] i.e., the number of cuts required to reduce the network to a tree having no closed circuits. Thus, $\xi$ is the number of independent circuits in the network.

Equation 3 is general. It holds for any network regardless of its functionality and degree of imperfection. In the specific case of a perfect network having $\mu_{\mathrm{J}}$ junctions of functionality $\phi$,

$$\xi = \mu_{\mathrm{J}}(\phi - 2)/2 \tag{4}$$

For a perfect tetrafunctional network, $\xi = \mu_{\mathrm{J}}$.

The second term in eq 2 depends on the number $\mu_{\mathrm{J}}$ of junctions subject to the restraints imposed by neighboring chains, on the strain expressed by $\lambda_1$, $\lambda_2$, and $\lambda_3$, and on the parameter $\kappa$ that specifies the severity of the restraints. According to the theory,[3] this term is given by

$$\Delta A_{\mathrm{c}} = \tfrac{1}{2}\mu_{\mathrm{J}}kT \sum_{t=1-3} [B_t - \ln(B_t + 1) + D_t - \ln(D_t + 1)] \tag{5}$$

where

$$B_t = \kappa^2(\lambda_t^2 - 1)(\lambda_t^2 + \kappa)^{-2} \tag{6}$$

and

$$D_t = \lambda_t^2\kappa^{-1}B_t \tag{7}$$

These relationships are derived on the assumption that the restraints imposed by neighbors on the junctions are Gaussian functions of the fluctuations and that the domains of constraint undergo deformations that are affine in the strain. On this basis, the a priori probability of a fluctuation $\Delta\mathbf{s}$ of a junction from the center of its domain of constraint by neighbors, in the absence of influences of the network on the junction, is given by

$$\mathcal{P}(\Delta\mathbf{s}) = (\text{constant}) \exp[-\kappa\rho(\Delta\mathbf{s})^{\mathrm{T}}(\lambda\lambda^{\mathrm{T}})^{-1}\Delta\mathbf{s}] \tag{8}$$

where $(\Delta\mathbf{s})^{\mathrm{T}}$ is the transpose of the column vector $\Delta\mathbf{s}$ expressing the displacement of the junction from the center of its domain of constraint, and $\rho = 3/2\langle(\Delta R)^2\rangle$ is the parameter that characterizes the (Gaussian) fluctuations $\Delta\mathbf{R}$ of the junctions from their mean positions in the phantom network. In the reference state, where $\lambda\lambda^{\mathrm{T}}$ equals the identity, $\langle(\Delta s)^2\rangle_0 = 3/2\kappa\rho$, according to eq 8. It follows that

$$\kappa = \langle(\Delta R)^2\rangle / \langle(\Delta s)^2\rangle_0 \tag{9}$$

i.e., $\kappa$ is the ratio of the mean square fluctuation of a junction in the phantom network to the mean square fluctuation that the constraints by neighbors would allow, in the state of reference, if influences due to the connectivity of the network were somehow eliminated, e.g., if the forces exerted by chains of the phantom network were nullified. Thus, $\kappa$ measures the severity of constraints exerted by neighboring chains relative to those imposed by the network of phantom chains.

The elastic contribution of the network to the chemical potential of the diluent under conditions of isotropic swelling such that the volume is $V = \lambda^3V^0$, where $V^0$ is the volume in the state of reference, is given by

$$(\mu_1 - \mu_1^0)_{\mathrm{el}} = (\partial\Delta A_{\mathrm{el}}/\partial\lambda)_{\mathrm{T}}(\partial\lambda/\partial n_1)_{\mathrm{T}} \tag{10}$$

where $\lambda = \lambda_1 = \lambda_2 = \lambda_3$, and $n_1$ is the number of molecules of diluent in the swollen network. Inasmuch as $V = \lambda^3V^0$, evaluation of the last coefficient in eq 10 yields

$$(\mu_1 - \mu_1^0)_{\mathrm{el}} = (\mathrm{v}_1/3V^{2/3}V^{0^{1/3}})(\partial\Delta A_{\mathrm{el}}/\partial\lambda)_{\mathrm{T}} \tag{11}$$

where $\mathrm{v}_1$ is the molar volume of the diluent, or more precisely its partial molar volume.

The result obtained by evaluation of the derivative in eq 11, according to eq 2, 3, and 5, can be written

$$(\mu_1 - \mu_1^0)_{\mathrm{el}}/RT = (\mathrm{v}_1/V^0)\lambda^{-1}[\xi + \mu_{\mathrm{J}}K(\lambda)] \tag{12}$$

where

$$K(\lambda) \equiv \dot{B}/(1 + B^{-1}) + \dot{D}/(1 + D^{-1}) \tag{13}$$

with

$$\dot{B} \equiv \partial B/\partial(\lambda^2) \qquad (14)$$

and

$$\dot{D} \equiv \partial D/\partial(\lambda^2) \qquad (15)$$

If $a_1^{\mathrm{N}}$ is the activity of the diluent in the network and $a_1^{\mathrm{L}}$ is its activity in the uncross-linked polymer at the same concentration, then eq 12 may be replaced by

$$\Delta(\ln a_1) \equiv \ln (a_1^{\mathrm{N}}/a_1^{\mathrm{L}}) = (\xi \mathrm{v}_1/V^0\lambda)[1 + (\mu_{\mathrm{J}}/\xi)K(\lambda)] \qquad (16)$$

The volume fraction of polymer in the swollen network is $v_2 = V_{\mathrm{N}}/V$, where $V_{\mathrm{N}}$ is the volume of the neat network in the absence of diluent and $V$ is the volume of the swollen network. In general, $V^0$ may depart from $V_{\mathrm{N}}$. This will be true especially if the network is formed in the presence of an arbitrary quantity of diluent. Accordingly, we relate $\lambda$ to $V$, and hence to the degree of swelling, as follows:

$$\lambda = (V_{\mathrm{N}}/V^0)^{1/3}v_2^{-1/3} = (v_2^0/v_2)^{1/3} = (v_2^0)^{1/3}\alpha_{\mathrm{s}} \qquad (17)$$

where $v_2^0$ is the volume fraction of polymer in the state (isotropic) of reference of volume $V^0$ such that $\langle r^2 \rangle$ for the network chains matches the value $\langle r^2 \rangle_0$ for the free unperturbed chains,[6] and $\alpha_{\mathrm{s}} = v_2^{-1/3}$ is the linear dilation specifically due to dilution by the diluent. Ordinarily, $V^0$ may be identified with the volume at which the network was formed. If, however, the temperature of the experiment differs from the temperature prevailing at formation of the network, then $V^0$ must be corrected to conform with the change of $\langle r^2 \rangle_0$ with temperature.[6]

In the case of a phantom network, for which $\kappa = 0$, the function $K(\lambda)$ is zero for all $\lambda$. Hence, $\lambda\Delta(\ln a_1)$ should be a constant for a given network, independent of the dilation. For an "affine" network in which fluctuations of junctions are suppressed $K(\lambda) = 1 - \lambda^{-2}$.[3] If, further, we take $\mu_{\mathrm{J}}/\xi = 1$, then eq 16 reduces in this case to

$$\Delta(\ln a_1)_{\mathrm{el}} = 2\xi(\mathrm{v}_1/V^0)\lambda^{-1}(1 - 1/2\lambda^2) \qquad (18)$$

Thus, for the affine network, with its junctions firmly embedded in their surroundings, $\lambda\Delta(\ln a_1)_{\mathrm{el}}$ should increase monotonically with $\lambda^2$. The familiar Mooney–Rivlin empirical expression for the free energy yields a similar dependence of $\lambda\Delta(\ln a_1)_{\mathrm{el}}$ on swelling. As Yen and Eichinger[1] point out, none of these relationships accounts for the maxima exhibited by experimental values of this quantity plotted against $\lambda^2$. Calculations based on the theory here adapted to isotropic swelling are presented below.

Before turning to the calculations, it is opportune to examine briefly the manner in which the constraints on junctions due to their encumbrances by neighhboring chains have been introduced above. Their representation by the three-dimensional Gaussian function, eq 8, is quite arbitrary, to be sure. However, the precise form of the distribution chosen to represent $\mathcal{P}(\Delta\mathbf{s})$ is of little importance. The corresponding analysis[8] carried out using a square-well potential, within which well $\mathcal{P}(\Delta\mathbf{s})$ is constant and beyond which it is zero, leads to results qualitatively similar to those based on eq 8 and summarized above.

The dependence of the domain of constraint on the strain is important, however. This dependence can be altered conveniently by expressing the a priori probability of a displacement $\Delta x_t$ from the center of constraint in the direction of the $t$ axis as follows:[3]

$$\mathcal{P}(\Delta x_t) = (\text{constant}) \exp[-\kappa p \lambda_t^{-p}(\Delta x_t)^2] \qquad (19)$$

where $p$ is subject to arbitrary specification. For $p = 2$, this equation is equivalent to eq 8 for one dimension measured along a principal axis of the strain. A larger $p$ renders the range of fluctuations more steeply dependent on the strain.

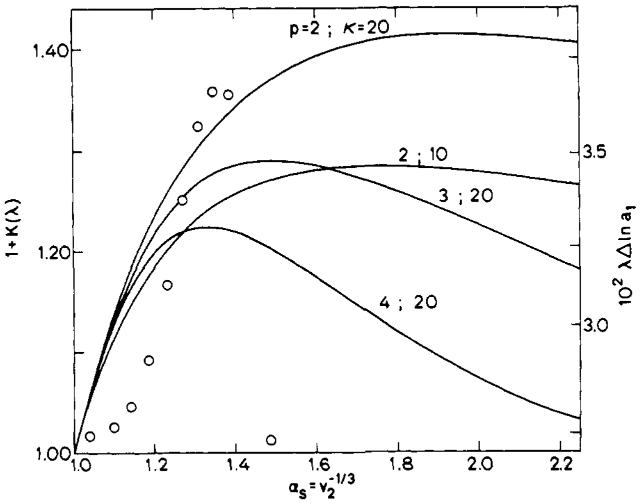

**Figure 1.** The factor $1 + K(\lambda)$, to which $\lambda(\mu_1 - \mu^0)_{\mathrm{el}}$ is proportional (see eq 12 and 16) when $\mu_{\mathrm{J}} = \xi$, plotted against the linear dilation ratio $\alpha_{\mathrm{s}}$ for networks formed in the unswollen state (hence, $v_2^0 = 1$ and $\lambda = \alpha_{\mathrm{s}}$). Values of $p$ and $\kappa$ are included with each curve. The points represent smoothed experimental results of Gee, Herbert, and Roberts[2] for rubber–benzene expressed as the product of $\lambda$ and the relative enhancement $\Delta \ln a_1$ of the activity of the diluent due to the network (see right-hand ordinate scale).

Generalization of eq 6 and 7, for positive integral values of $p$ not necessarily equal to 2, is achieved by adoption of the following definitions of $B$ and $D$:

$$B = \kappa^2(\lambda^2 - 1)(\lambda^p + \kappa)^{-2} \qquad (20)$$

$$D = \lambda^p\kappa^{-1}B \qquad (21)$$

the index $t$ being omitted. Other relations above hold without additional alterations.

## Results of Calculations

Calculations have been carried out for values of the parameters $\kappa$ and $p$ falling within the range that optimizes agreement between theory and experiments on the stress in uniaxial deformation.[3,4,9] The number $\mu_{\mathrm{J}}$ of junctions whose fluctuations are affected by constraints of neighboring chains was set equal to the cycle rank $\xi$ of the network. Calculations are presented in Figure 1 for networks prepared in the absence of diluent and, hence, for which $v_2^0 \equiv V_{\mathrm{N}}/V^0 = 1$. The elastic contribution to the chemical potential is proportional to $1 + K(\lambda)$, the quantity plotted on the ordinate, according to eq 16 with $\mu_{\mathrm{J}} = \xi$. The increase in $\ln a_1$ by the combined effects of the network is likewise proportional to this quantity, according to eq 16. For $v_2^0 = 1$, the linear dilation $\lambda$ relative to the state of reference equals $\alpha_{\mathrm{s}}$ plotted on the abscissa. Values of the parameters $p$ and $\kappa$ are indicated with each curve in Figure 1.

Curves calculated according to eq 12–15 and 20–21 (or eq 6 and 7 for $p = 2$) invariably display maxima. This feature is manifested for a range of parameters extending well beyond those used in the illustrative calculations shown in Figure 1. The location of the maximum and its magnitude vary with $\kappa$ and $p$, as the curves in this figure demonstrate, but its occurrence in consequence of constraints on junctions that diminish with dilation is virtually universal. The physical basis for this feature is at once apparent.

The points shown as open circles in Figure 1 are smoothed results published by Gee, Herbert, and Roberts[2]

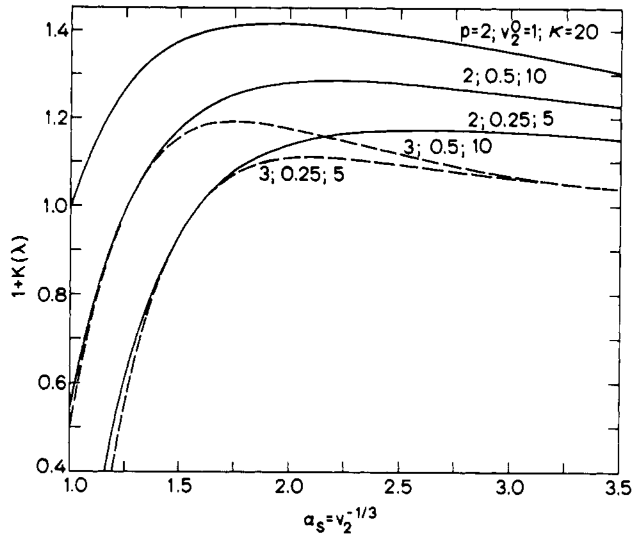

**Figure 2.** Calculations of $1 + K(\lambda)$ for networks formed at volume fractions $v_2^0 < 1$. Values of $p$, $v_2^0$, and $\kappa$ are given with each curve.

for the system natural rubber–benzene. The experiments require high precision and the values for $\Delta \ln a_1$ are subject to large errors. The point for the largest value of $\alpha_s$ is for equilibrium swelling in liquid benzene. The activity for the linear polymer at this concentration was not measured but was estimated from the interaction parameter $\chi$ for this system. Consequently, this point is susceptible to large vitiation by inaccuracy in $\chi$ and in particular by its change with concentration. Experimental inaccuracies notwithstanding, the occurrence of a maximum in $\chi\Delta \ln a_1$ is indicated. Its location and magnitude are consistent with calculations based on theory for values of the parameters ($\kappa$ = 10–20 and $p$ = 2–3) indicated by experiments relating stress to strain for typical rubbers.[3,9,10]

Yen and Eichinger[1] observed a much larger maximum in $\lambda\Delta \ln a_1$ for PDMS with benzene. It occurred at somewhat smaller dilations in the vicinity of $\alpha_s = 1.2_5$. The maxima for poly(styrene-*co*-butadiene) with benzene and with *n*-heptane are not well defined by their experiments, but they are indicated to be somewhat smaller than that depicted in Figure 1 for rubber–benzene. They occur in the neighborhood of $\alpha_s$ = 1.25–1.5. Hence, the results of Yen and Eichinger for these latter systems appear to be more nearly in accord with the theory than their results for PDMS–benzene.

The calculations in Figure 2 illustrate the effect of formation of the network in solution, whereby $v_2^0 < 1$. Values of $p$, $v_2^0$, and $\kappa$ are noted with each curve. The uppermost curve, taken from Figure 1 for $v_2^0 = 1$, is shown for comparison. Values chosen for $\kappa$ have been adjusted in proportion to $v_2^0$ on the grounds that one may expect $\kappa$ to depend on the degree of interpenetration of the domains pervaded by the junctions and the pendant chains attached to each of them. The degree of interpenetration[5] should decrease proportionately to $v_2^0$ for a given degree of cross-linking.

For $v_2^0 < 1$, $K(\lambda)$ is negative for $\alpha_s < (v_2^0)^{-1/3}$, i.e., for $\lambda < 1$; see eq 17. In this range, where the network is compressed relative to its reference state, constraints on junctions tending to render their displacements under strain more nearly affine in the strain encourage dilation and the concomitant swelling. At dilations for which $\alpha_s > (v_2^0)^{-1/3}$, $K(\lambda)$ again becomes positive. The maximum in $1 + K(\lambda)$ is broadened and much reduced. It very nearly vanishes if the network is formed at large dilutions (small $v_2^0$).

An increase in $\kappa$ at given $v_2^0$, according to calculations not presented, has the effect of enhancing both the decrease in $K(\lambda)$ for $\alpha_s < (v_2^0)^{-1/3}$ and its increase for $\alpha_s > (v_2^0)^{-1/3}$. The curve remains comparatively flat at large $\alpha_s$, however.

Experimental results with which to compare the calculations for networks characterized by $v_2^0 < 1$ are not available. The striking effect of altering the topology of the network in this manner is nevertheless of interest.

## Conclusions

The inevitable approximations of theory offered in an effort to account for the complexities of restrictions on junction fluctuations on the one hand and the considerable experimental difficulties confronting accurate evaluation of the elastic contribution to the chemical potential on the other may preclude quantitative correlations between theory and experiment. The comparisons presented nevertheless indicate qualitative correspondence. This is manifested most strikingly in the persistence of the maxima in Figure 1, prediction of which appears to be unique to the present theory. More importantly, inferences that these maxima cast doubt on the validity of the basic premise of theories of rubber elasticity and swelling, namely the premise that elastic and mixing contributions to the free energy are additive, are shown to be groundless by the analysis presented.

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