# Molecular theory of rubber elasticity

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Theories of rubber elasticity are reviewed and compared. Principal differences centre on the connection between the locations of network junctions and the macroscopic strain. Constraints on junctions imposed by surrounding chains have been postulated to be responsible for departures of experiments from the theory for idealized 'phantom' networks. Experimental evidence in support of theory developed using this hypothesis is discussed.

Molecular theories of rubber elasticity concur, in general, in yielding an elastic equation of state which, for simple elongation, takes the familiar form

$$f = \mathcal{F}(kT/L^0)(V/V^0)^{1/3}(\alpha - \alpha^{-2}) \quad (1)$$

where $f$ is the tensile force; $\mathcal{F}$ is a factor that depends on the constitution of the network; $L^0$ and $V^0$ are the length and the volume in the reference state in which the chains of the network assume a distribution of configurations coinciding with that for free, disconnected chains; and $\alpha = L/L_i$ is the extension ratio relative to the unstretched ($f = 0$) length $L_i$ at the prevailing volume $V$ of the strained material. Differences between various theories have centred on the value of $\mathcal{F}$. Experimental measurements, however, consistently demonstrate departures of the relationship of stress to strain from the form expressed by equation (1), which is common to most theories. It is the aim of this paper to clarify distinctions between theories falling in the two main categories in this field, and to direct attention to a recent theory which, in a sense, effects a compromise between earlier theories. It appears to account satisfactorily for the main feature of the elastic behaviour of rubber-like substances at equilibrium. The more conspicuous predictions of this theory are discussed below in relation to experimental evidence.

According to the first theories offered[1-6], the junctions of a rubber network may be considered to be firmly embedded in their surroundings. Hence, under strain they experience displacements like occlusions in a homogeneous isotropic medium; i.e., their displacements are affine in the macroscopic strain. The elastic free energy deduced for an 'affine network' that is subject to the foregoing constraint and that consists of Gaussian chains is[6,7].

$$\Delta A_{el} = \frac{1}{2}\nu_e kT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) - \mu_e kT \ln(\lambda_1\lambda_2\lambda_3) \quad (2)$$

where $\mu_e$ is the number of junctions, or crosslinkages, effectively embedded in the labyrinthine matrix of the surrounding network, $\nu_e$ is the number of chains connecting two such junctions and $\lambda_1, \lambda_2, \lambda_3$ are the principal extension ratios relative to the reference state specified above. The logarithmic term takes account of the dispersion of the junctions over the volume[6,7], which is proportional to $\lambda_1\lambda_2\lambda_3$. In perfect networks, i.e. networks free of chain ends or other defects, the definition of $\mu_e$, and hence of $\nu_e$ as well, are explicit. In imperfect networks these definitions are subject to the ambiguity of distinguishing between junctions that are constrained to occur in the environs of a given set of neighbouring chains and those that may undergo displacements therefrom under the influence of macroscopic deformation and thermal fluctuations.

The elastic free energy for an affine network, expressed by equation (2), yields equation (1) for the tensile force in uniaxial deformation with $\mathcal{F}$ therein equation to $\nu_e$.

The theory of James and Guth[8], representing an alternative approach to the treatment of rubber elasticity, proceeds from premises that avoid an arbitrary stipulation concerning the effect of the macroscopic strain on the locations of network junctions. Instead, the effect of the strain on the locations of the junctions, and hence on the configurations of the chains connecting them, is deduced from the model assumed. This model consists of a network of Gaussian chains connected in any arbitrary manner. The physical effect of the chains is assumed to be confined exclusively to the forces they exert on the junctions to which they are attached. This force for a Gaussian chain is proportional to the vector spanning the chain from one end to the other. The properties of the chains as material bodies that occupy space are dismissed, along with the integrity of their chemical structures. Thus, they may transect one another freely and, hence, are not restricted by neighbouring chains, through which they may move without restraint. 'Phantom network' is the designation applied to systems of hypothetical chains having these qualities[9].

It is important to observe that theories for both affine and phantom networks rest on the assumption that the stored elastic free energy resides within the chains. It is determined by the alteration of their configurations caused by the strain; interchain interactions make no contribution to the elastic free energy which, therefore, can be constructed as the sum of independent contributions from the individual chains*. The stated assumption is supported by theory and abundantly confirmed by experiments[9].

James and Guth[8] made the following deductions concern-

* Graessley[10,11] has identified interchain independence as the feature that characterizes a phantom network. According to this use of the term, all of the system here considered and, in close approximation, most real networks as well, would fall in the fictitious, or phantom, category. This usage departs from the original definition.

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ing the properties of Gaussian phantom networks: (i) the mean positions of their junctions are determined by the macroscopic dimensions, (ii) displacements of these mean positions are linear (i.e. affine) in the macroscopic strain, and (iii) fluctuations of the junctions from these mean positions are Gaussian and the magnitude of the fluctuations is invariant with strain.

The elastic free energy of a Gaussian phantom network is of the form[8,9]

$$\Delta A_{el} = \frac{1}{2} \xi kT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (3)$$

where $\xi$ is a parameter that characterizes the network structure. It follows that $\mathscr{F}$ in equation (1) is to be equated to $\xi$ in this case.

On the basis of arguments going beyond the James and Guth theory, the factor $\xi$ may be identified rigorously with the cycle rank of the network, i.e. with the number of independent circuits therein[9]. With $\xi$ thus defined, equation (1), with $\mathscr{F} = \xi$, and equation (3) hold for networks having junctions of any functionality, or mixture of functionalities, and of any degree or kind of imperfection. The parameter $\xi$ therefore subsumes all structural aspects of the network. It is calculable directly from the stoichiometry of the chemical constitution of the network, e.g. from the numbers of junctions of various functionalities and from the numbers of free ends of chains. Precarious distinctions between active vs. inactive junctions, or chains, and probabilistic calculations of the number of 'free' vs. 'active' chains or junctions are unnecessary. In fact, enumeration of chains, active and inactive alike, is superfluous. All this is circumvented by proceeding directly to the evaluation of $\xi$.

Since $\xi < \nu_e$, the force exerted by the phantom network is smaller than for its affine analogue. This is a consequence[9,13] of the fact that only the mean positions of the junctions are transformed by the strain in a phantom network, the fluctuations about these positions being unaffected by deformation[8], In an affine network, involvements with neighbouring chains are assumed, implicitly, to arrest fluctuations of junctions, causing them to undergo deformations that are linear in the strain. Hence, the chain vector distribution, comprising the convolution of mean values and fluctuations, is subject to affine transformation under strain.

For a perfect phantom network of functionality $\phi$[9,10,12]:

$$\xi = \nu(\phi - 2)/\phi \qquad (4)$$

where $\nu$ is the number of chains all of which are bounded by junctions at both ends in a perfect network. For perfect tri- and tetrafunctional networks, $\xi = \nu/3$ and $\nu/2$, respectively. Thus, for $\phi = 3$ and 4, respectively, the force $f$ assumes 1/3 and 1/2 of its value for a perfect affine network.

In real networks the dense interspersion of chains must restrict enormously (but not suppress completely!) the permissible configurational rearrangements of the chains. It is important to bear in mind, however, that it is the average over configuration space for an ensemble of networks that is relevant to the treatment of equilibrium properties rather than the time average for a given network. Whereas the magnitude of the partition function for the set of chains comprising the actual network is enormously reduced by the constraints imposed on them by their neighbours, averages over the ensemble of networks that may be formed in the interlinking process are unaffected. This follows at once from the randomness of the chemical process of network formation. Upon deformation of the ensemble of networks thus formed, however, the constraints imposed by the physical integrity of the chains and by their mutual volume exclusion may contribute to $\Delta A_{el}$, and hence to the stress.

The interactions of chains in a network are usually discussed in terms of discrete entanglements between pairs of chains. As a simple calculation shows, the space pervaded by a given chain may be shared by as many as a hundred or more other chains. By any acceptable definition of an entanglment, the given chain will be 'entangled' at least once with most of those that penetrate its spatial domain. Hence, each chain is subject to many entanglements all of which are more or less equivalent topologically. However, none of the profusion of entanglements in a typical network is equivalent to a chemical crosslinkage. Contacts between a pair of entangled chains are transitory and of short duration owing to the diffusion of segments and associated time-dependent changes of configuration. The locus of an entanglement, to the extent that it can be defined, is therefore variable; it may wander laterally along each of the chains involved.

It should be evident that the entanglements occurring in polymer networks cannot be equated to a set of enumerable crosslinkages. The supposition that one or two entanglements incident on a given chain can be singled out as elastically effective is an artifice without foundation in the structure and topology of polmer networks. These same criticisms apply to the entanglements invoked to explain the plateau modulus often exhibited by linear polmers under dynamic deformation within a certain range of frequency.

The configurations accessible to the network unquestionably are severely restricted by the copious interpenetration of the chains emanating from network junctions. Although these restraints, being random, cannot affect the ensemble average distribution in the state of reference, they must curtail the fluctuations which would occur in the corresponding phantom network. The restraints on fluctuations may be expected to depend on the strain; hence, they may contribute to the stress. We suggest therefore that the principal effects of the copious entanglements in polymer networks are manifested in their restrictions on fluctuations[9,13,14].

The junctions are the structural entities most vulnerable to these constraints. The chains pendant at a given junction must adopt configurations that are free of steric overlaps with the neighbouring chains with which they share the same region of space. Accommodation of a large fluctuation of the junction from its mean position entails configurational rearrangements of chains over a correspondingly large spatial domain. The number of eligible configurations for the system of chains is therefore smaller the greater the fluctuation of the junction. The fluctuations of junctions in a real network consequently must be restrained by the involvements of the chains attached to them with the many surrounding chains.

Thus, following the insights of Kuhn[2], we consider the fluctuations of junctions to be restricted by the entanglements of their pendant chains. At small deformations the displacements of junctions in the unswollen network consequently may conform more nearly to the traditional assumption[2,4–6] that they are affine in the macroscopic strain. Hence, equation (2) may afford a better approximation than equation (3), and $\mathscr{F} \approx \nu_e$ may be preferred over $\mathscr{F} = \xi$.

The configurational restraints on junctions are reasoned to diminish with elongation, and with dilation as well[13,14]. At high elongations or high degrees of swelling, therefore, $\mathscr{F}$ may approach $\xi$. It is this transition between extremes respresented by the 'affine' theory and the 'phantom' theory, respectively,

to which we attribute the well-known departures from the behaviour predicted by either theory alone, i.e. the observed departures from the form of the relationship of stress to uniaxial strain given by equation (1) with $\mathscr{F}$ treated as a constant, and by corresponding expressions for other types of strain. The 'transition' may involve a factor approaching 1/2 for a perfect tetrafunctional network ($\xi = \nu/2$).

In order to give quantitative expression to these ideas, we have represented the restrictions on junction fluctuations by domains of constraint[13]. These domains are conveniently taken to be Gaussian with respect to centres of action of the constraints. They may be otherwise represented if desired, with only minor effects on the results obtained[13]. That the displacements of the centres of constraint must be affine in the strain is self-evident. It is also apparent that the domains must be deformed by the strain in as much as they reflect the alteration of the surrounding network by the strain. This leads to the further assumption that the shapes of the domains of constraint, initially spherical, are affine in the strain.

With these assumptions, the elastic free energy is found to consist of two contributions, one $\Delta A_{ph}$ being that for the phantom network and the other $\Delta A_c$ arising from the constraints; i.e.,

$$\Delta A_{el} = \Delta A_{ph} + \Delta A_c \tag{5}$$

The latter term depends on the severity of the constraints. It is expressed[13] by the ratio $\kappa$ of the mean-square fluctuation of a junction about its mean position in the phantom network to the mean-square fluctuation allowed by the domain of constraint in the state of reference.

The stress likewise consists of two contributions. The tension in uniaxial strain is[13]:

$$f = f_{ph} + f_c = f_{ph}(1 + f_c/f_{ph}) \tag{6}$$

where

$$f_c/f_{ph} = (\mu_J/\xi)\,[\alpha K(\lambda_1^2) - \alpha^{-2}K(\lambda_2^2)]\,(\alpha - \alpha^{-2})^{-1} \tag{7}$$

and $\mu_J$ is the number of junctions subject to entanglement constraints; $\alpha$ is the extension ratio defined above,

$$\left.\begin{aligned}\lambda_1 &= \alpha(V/V^0)^{1/3}\\ \lambda_2 &= \alpha^{-1/2}(V/V^0)^{1/3}\end{aligned}\right\} \tag{8}$$

and

$$K(\lambda^2) = B\,[B(B+1)^{-1} + \kappa^{-1}(\lambda^2 B + B)\,(B + \kappa\lambda^{-2})^{-1}] \tag{9}$$

where

$$B = \kappa^2(\lambda^2 - 1)\,(\lambda^2 + \kappa)^{-2} \tag{10}$$

and

$$\dot{B} = B\,[(\lambda^2 - 1)^{-1} - 2\,(\lambda^2 + \kappa)^{-1}]\,\cdot \tag{11}$$

For a perfect network $\mu_J = \xi$. For imperfect networks $\mu_J$ may conceivably exceed $\xi$ somewhat.

If $\kappa = 0$, then $f_c = 0$ and the relations above revert to those for a phantom network. In the limit $\kappa \to \infty$ corresponding to complete suppression of junction fluctuations, $\Delta A_{el}$ reduces to equation (2). The stress–strain relationship converges likewise to that for the 'affine' network, i.e. to equation (1) with $\mathscr{F} = \nu$.

The theory briefly described succeeds in accounting for the fact that the reduced force $[f] = f(\alpha - \alpha^{-2})^{-1}$ decreases with extension. This decrease customarily is fitted to the Mooney–Rivlin equation according to which $[f]$ should be linear in $\alpha^{-1}$. This equation fails in compression ($\alpha < 1$) and for biaxial strains generally. According to the present theory, $f_c/f_{ph}$ (and hence $[f]$ as well) should reach a maximum value at small compressions ($\alpha \approx 0.8$), then decrease gradually with further compression. Experimental measurements support this prediction[15]. In fact, the theory approximates experimental measurements in poly(dimethyl siloxane) networks throughout a twenty-four-fold range in $\alpha$ embracing four-fold extension and six-fold compression[15].

The reduced force is predicted to decrease with swelling of the network as is invariable observed.

Finally, the theory accounts for a hitherto unexplained feature of the elastic free energy of dilation. According to experiments of Gee and coworkers[16] on natural rubber and of Yen and Eichinger[17] on siloxane and on poly(styrene-co-butadiene) networks the product $\lambda(\mu_1 - \mu_1)_{el}$ of the linear dilation $\lambda$ of the swollen network and the elastic contribution to the chemical potential of the diluent passes through a maximum with dilation, contrary to all previous theories. The present theory predicts such a maximum[18].

In view of the correspondence between predictions of this recent theory[13] and the principal features of the rleationships observed experimentally, there can be little doubt that constraints on fluctuations in real networks are responsible for departures from previous theories of rubber elasticity. The manner in which these constraints are incorporated into the present theory is arbitrary and intuitive rather than rigorous. Hence, strict quantitative agreement of this theory with experiment should not be expected. The complexities of the profusion of entanglements affecting the dense interspersion of chains discourage attempts to treat them accurately. It may be sufficient, however, to comprehend the physical principles governing the behaviour and properties of real networks in lieu of a more precise theory.

The issue remaining concerns the significance of the reduced force $[f_{ph}]$ for the phantom network deduced from experiments by application of the foregoing theory. Does $[f_{ph}]$ thus deduced from the relationship of stress to strain equal (approximately) the value calculated from the chemical structure (e.g. from the degree of crosslinking) according to equation (1), with $\mathscr{F} = \xi$? Or, is it necessary to postulate other constraints that have the effect of augmenting the effective number of crosslinkages?

As a procedural alternative, one may employ the Mooney–Rivlin plot as a basis for extrapolating data taken in uniaxial extension, the intercept being identified with $[f_{ph}]$. Discrepancies between this empirical procedure and the one above that relies on the approximate theory may be diminished by conducting the experiments on swollen networks, thus greatly diminishing the range of extrapolation of $[f]$.

Numerous experimental investigations have been carried out with the object of comparing the observed elastic modulus, or the reduced force, with predictions of theory. Results obtained have been reviewed by Falender, Yeh and Mark[19].

Poly(dimethyl siloxane) (PDMS) networks have been investigated most extensively. For tri- and tetrafunctional networks formed by end-linking hydroxyl-terminated linear PDMS, Mark and coworkers[20,21] found $\mathscr{F}/\nu \approx 0.27$ and 0.65, respectively, compared with the theoretical values of 1/3

and 1/2. For networks prepared by crosslinking vinylated PDMS, Falender *et al.*[19], found $\mathscr{F}/\nu \approx 0.59$ compared with a theoretical value of 0.53 calculated with allowance for variations in functionality about an average of $\bar{\phi} = 4$.

Results of Valles and Macosko[22] indicating values of this ratio greater than unity for end-linked siloxanes are questionable on the grounds that the shear moduli on which their results are based were determined dynamically. Although the shear stress was reported to be independent of shear rate, it is doubtful, on the basis of observations in static measurements on PDMS networks, that equilibrium was attained in their experiments.

Recently Wagner[23] has determined limiting values of the reduced forces for networks prepared by crosslinking PDMS photochemically in the presence of dicumyl peroxide. The degrees of crosslinking were determined by gas-phase chromatographic analysis of the hydrocarbons released by degradation of the polymer with molten potassium hydroxide[24]. Ratios $\mathscr{F}/\nu$ agree with the theoretical value, 0.5, within limits of ± 0.1 over a six-fold range of crosslinking.

Allen and coworkers[25] found $\mathscr{F}/\nu \approx 0.7$ for crosslinked polystyrene and a similar value for crosslinked poly(propylene oxide).

For a series of end-linked polybutadienes (PBD) with variable functionalities in the range $\phi = 4$ to 6 or higher, Kraus and Moczvgemba[26] found $\mathscr{F}/\nu = 0.64 \pm 0.15$ compared with theoretical ratios in the range 0.50 to 0.75. In apparent contradiction to these results, the measurements of Dossin and Graessley[11] on PBD networks crosslinked by electron beam radiation yield $\mathscr{F}/\nu \approx 1.8$–$3.5$. They deduced degrees of crosslinking from analysis of the gel point according to the theory of incipient network formation. Applicability of this theory requires the distribution of crosslinkages to be random. Clustering of the chemical events along 'spurs' of secondary elections produced by the primary election beam may conceivably have violated this condition, with the consequence that degrees of crosslinking in the final networks are underestimated.

The preponderance of the evidence available indicates that the reduced stress for rubber networks, when extrapolated to conditions such that the contribution of restraints on junctions becomes negligible, is in satisfactory agreement with network theory. It appears to be unnecessary therefore to postulate chain entanglements that augment the constraints imposed directly by permanent junctions of the covalent network.

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