Topological structure and macroscopic behaviour of permanently crosslinked polymer systems

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The problems of description and derivation of the topological structure of crosslinked polymers are briefly discussed. An approximate phenomenological description based on one-, or many-junction distribution functions is proposed, and macroscopic properties of crosslinked systems are expressed through such functions. A detailed structure of a random, quasi-equilibrium tetrafunctional system is derived.

It was realized many years ago that the important physical properties of crosslinked polymers should depend on the topological structure, i.e. on the way in which chain macromolecules are linked together in network junctions. Flory[1], Tobolsky[2], Case[3], Scanlan[4], Mullins and Thomas[5], and others, discussed the effects of free-end chains on rubber elasticity, gelation conditions and other features of the macroscopic behaviour of polymer networks. The early models emphasized only selected aspects of the topological structure, such as overall concentration of free-end chains, or distribution of junctions with various numbers of free-end chains or loops, and neglected other possible structures. The author, after several attempts at building such limited models[6,7], arrived at more general formulations, taking into account all topologically admissible types of network junctions[8]. This paper reviews briefly the general problems of description and determination of network structure, and introduces a simple method of treating the topological structure of tetrafunctional networks in terms of the one-junction distribution function.

FORMATION OF PERMANENT NETWORKS: STRUCTURE AND MACROSCOPIC BEHAVIOUR

The general philosophy of the approach used in these studies is based on the postulate that there exists a unique relation between molecular structure of the system, $\underset{\sim}{\xi}$, and its macroscopic behaviour, $\underset{\sim}{M}$

$$\underset{\sim}{\xi} \Rightarrow \underset{\sim}{M};\ \underset{\sim}{M} = \underset{\sim}{M}(\underset{\sim}{\xi}) \tag{1}$$

Consider some formation conditions, F, which can result in different structures $\underset{\sim}{\xi}_1, \underset{\sim}{\xi}_2, \ldots, \underset{\sim}{\xi}_i$, each structure giving rise to some, generally different sets of macroscopic properties $\underset{\sim}{M}_1 = \underset{\sim}{M}(\underset{\sim}{\xi}_1), \underset{\sim}{M}_2 = \underset{\sim}{M}(\underset{\sim}{\xi}_2), \ldots, \underset{\sim}{M}_i = \underset{\sim}{M}(\underset{\sim}{\xi}_i)$ (*Figure 1*).

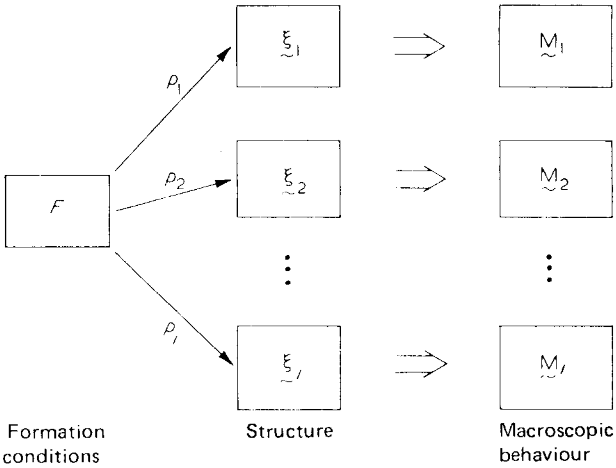

Figure 1 Network formation conditions (F); the resulting structures ($\underset{\sim}{\xi}_i$) and macroscopic behaviour of permanently crosslinked systems ($\underset{\sim}{M}_i$). p_i are frequencies (or probabilities) of formation individual structures $\underset{\sim}{\xi}_i$

Equation (1) results from the definition of the permanently crosslinked system as a system with fixed constraints (junctions) formed in an irreversible thermodynamic process. Since, by definition, a junction (crosslink) once formed cannot dissociate, there is no way in which structures $\underset{\sim}{M}_i$ could control the formation process, or interact one with another. Consequently, the macrosopic behaviour of any particular structure $\underset{\sim}{\xi}_j$ produced in the formation process is determined by that, and only that structure, rather than being affected by other structures $\underset{\sim}{\xi}_j, j \neq i$, which could have been, but have not been, produced.

A different approach was used by Deam and Edwards[9] who represented the macroscopic properties $\underset{\sim}{M}$ as a weighted-average of $\underset{\sim}{M}_i$ related to various structures $\underset{\sim}{\xi}_i$ with the probabilities p_i of formation of individual structures as statistical weights.

$$\underset{\sim}{M} = \sum_i p_i \underset{\sim}{M}_i(\underset{\sim}{\xi}_i) \tag{2}$$

Although the previous formulation (equation 1) seems to be better justified theoretically, equation (2) may appear more useful when experimentally observed properties are

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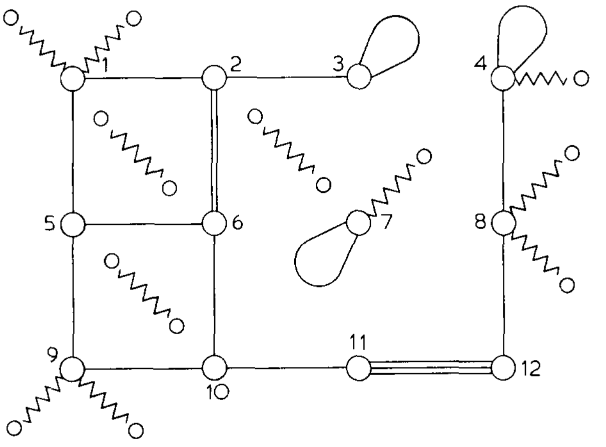

Figure 2 Crosslinked system composed of 12 junctions. Connection matrix L_{ij} see equation (3)

analysed, but the particular structure of the network is unknown.

TOPOLOGICAL STRUCTURE OF CROSSLINKED SYSTEMS

Two aspects of the structure of crosslinked systems should be discussed separately – connections of junctions via polymer chains, and chain entanglement.

The structure of connections in a system containing N_j junctions with maximum functionality, s, and N_c chains, can be described completely by a square symmetric matrix $(N_j + 1) \times (N_j + 1)$. *Figure 2* presents a scheme for a simple system composed of $N_j = 12$ tetrafunctional junctions ($s = 4$), and corresponding connection matrix L_{ij} given by equation (3)

$$L_{ij} = \begin{array}{c|ccccccccccccc}
 & 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\
\hline
0 & 3 & 2 & 0 & 1 & 1 & 0 & 0 & 1 & 2 & 2 & 1 & 0 & 0 \\
1 & 2 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
2 & 0 & 1 & 0 & 1 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 \\
3 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
4 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
5 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 \\
6 & 0 & 0 & 2 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
7 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
8 & 2 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
9 & 2 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
10 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 1 & 0 \\
11 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 3 \\
12 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 3 & 0
\end{array} \tag{3}$$

It should be noted that L_{00} denotes the number of chains in the system which are not attached to any junction; the diagonal components L_{ii} indicate loops attached to junction i; $L_{ij} = L_{ji}$ $(i \neq j)$ describe the number of network chains spanning different junctions i and j. The components L_{i0} describe the number of free-end chains attached to junction i. Naturally, all components are limited so that:

$$\left.\begin{array}{ll}
L_{ij} = 0, 1, \ldots, s & \text{for } i \neq j \\
L_{ii} = 0, 1, \ldots, s/2 & \\
L_{00} = 0, 1, 2, \ldots, N_c &
\end{array}\right\} \tag{4}$$

The total number of various types of chains in the system can easily be expressed by L_{ij}, viz.: the number of uncrosslinked chains in the system, U, reads

$$U = L_{00} \tag{5}$$

the number of free-end chains, F

$$F = \sum_{j=1}^{N_j} L_{j0} \tag{6}$$

the number of loops, L

$$L = \sum_{i=1}^{N_j} L_{ii} \tag{7}$$

the number of chains spanning different junctions, C

$$C = \sum_{i=1}^{N_j} \sum_{j>i}^{N_j} L_{ij} \tag{8}$$

and the total number of chains, N_c

$$N_c = \sum_{i=0}^{N_j} \sum_{j>i}^{N_j} L_{ij} + U \tag{9}$$

Naturally, the number of functionalities occupied by chains at the ith junction cannot exceed s, i.e.:

$$2L_{ii} + \sum_{j=0}^{N_j} L_{ij} \leqq s \tag{10}$$

Consequently, the number of voids, V, i.e. unsaturated functionalities, results from the balance

$$V = s N_j - 2L - 2C - F \tag{11}$$

The matrix L_{ij} characterizes the topological structure as far as connections of junctions are concerned.

The problem of entanglement is more difficult. Formally, one could introduce another square matrix $N_c \times N_c$, whose components E_{ij} would characterize the state of entanglement ($E_{ij} > 0$) or non-entanglement ($E_{ij} = 0$) for each pair of network chains (i, j). For calculation of E_{ij} one could use an approach similar to Prager–Frisch integrals[10] or Edwards' invariants[11] (see *Figure 3*). However, the adequate formalism for many entangled chains in three-dimensional space has not been developed yet, and the theory of macroscopic effects introduced by chain entanglement is not well advanced. Therefore we will confine our considerations to the problems of connections.

The connection matrix L_{ij} containing the complete information about the topological structure of the system can be compared with the list of all positions and impulses for

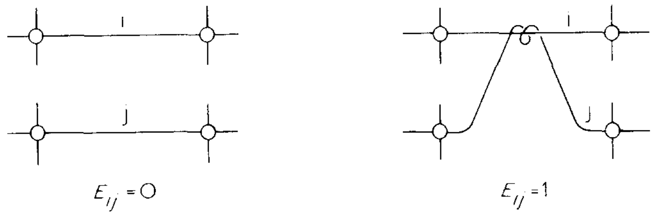

Figure 3 Unentangled (a) and entangled (b) pair of network chains (*i*, *j*).

N particles in statistical mechanics. For evident reasons, as in statistical mechanics, the problem must be reduced to simpler terms with few variables, if it is to be employed in any tractable calculations.

For this purpose we will first introduce a one-junction distribution, n_k, an analogue of a one-particle distribution function $f^1(\underset{\sim}{q}, \underset{\sim}{p})$ in statistical mechanics. Like f^1, n_k can be obtained by summation (replacing integration in the case of f^1) of many-particle distributions. n_k is defined as the probability that a junction in the system has a configuration *k*, or as a fraction of *k*-type junctions. Unlike position and impulse distribution $f^1(\underset{\sim}{q}, \underset{\sim}{p})$ in statistical mechanics, n_k is a function of a discrete variable *k*. For given maximum functionality of junctions, *s*, there exists a finite number of topologically distinct junctions, which determines values of the variable *k*. We have discussed this problem in a recent paper[8] showing that this number is approximately proportional to the third power of *s*. To distinguish all configurations of an *s*-functional junction, it is convenient to introduce the concept of structural elements which are attached in different combinations to such a junction[8]. Uncrosslinked chains, free-end chains and loops result in a natural way from the (00), (0*i*) and (*ii*) components of the connection matrix L_{ij}. It is convenient to complete this list by introducing voids, *V*, i.e. unsaturated functionalities, (equation 11) and to split the connections between pairs of different junctions, *C*, (equation 8) into separate classes of singlets, *S*, doublets, *D*, triplets, *T*, etc. up to *s*-multiplets, *Ms*, i.e. multiple connections between the same pair of junctions. In terms of the components of L_{ij}, a singlet corresponds to $L_{ij} = 1$, a doublet to $L_{ij} = 2$, etc. Structural elements appearing in tetrafunctional systems ($s = 4$) are shown in *Figure 4*. It should be noted that individual structural elements are not topologically equivalent, as they occupy different numbers of functionalities of a single junction: unattached chains – 0, free-end chains, singlets and voids – 1, loops and doublets – 2, *n*-multiplets–*n*, i.e. the number equal to the corresponding L_{ij} value. Consequently, the total number of chains *C* spanning pairs of junctions, *C*, (equation 8) can be presented as the sum:

$$C = S + 2D + 3T + \ldots\ldots s \cdot Ms \tag{12}$$

where *Ms* is an *s*-fold multiplet.

For a tetrafunctional junction there exist 34 admissible combinations of the 7 structural elements *F*, *V*, *S*, *L*, *D*, *T*, *Q*. Uncrosslinked chains *U*, do not affect the structure of junctions, but they enter the equations of balance, and play some role in the macroscopic behaviour.

For tetrafunctional systems, (*Figure 5*) $n_k(k = 0, 1, 2, \ldots, 33)$ provides the one-junction distribution function which can be used for determining the observable physical characteristics. In a similar way a two-junction distribution function n_{kl} can be introduced emphasizing correlations between pairs of adjacent junctions; a three-junction function can then be added n_{klm}, etc.

JUNCTION DISTRIBUTION AND MACROSCOPIC CHARACTERISTICS

The physical characteristics of a crosslinked system such as the average contraction coefficient of network chains $A = \langle h^2_{\text{net}}\rangle/\langle h^2_0\rangle$, modulus of elasticity, *G*, gel–sol ratio, critical crosslink density for gelation, etc., can be derived from the topological structure of the network via junction distribution functions. The total number of network chains attached to junctions, $N_c - U$, requires only the knowledge of the one-junction function, n_k:

$$N_c - U = \sum_k n_k u_k \tag{13}$$

where u_k are contributions introduced by combinations of structural elements present in the *k*-type junctions. Clearly, voids contribute 0 chains, singlets ½, free-end chains, loops and doublets 1 chain, triplets and quadruplets 3/2 and 2 chains, respectively. Using the codes shown in *Figure 5*, the coefficient u_k for $k = 0$ (junction s^4 with four singlets) will be $u_0 = 2$, that for $k = 6$ (junction *sfl* with one loop, one singlet and one free-end chain), $u_6 = 5/2$, etc.

Other physical characteristics require information about higher order distribution functions either directly, or indirectly through network continuity parameters. To determine the number of junctions contained in the unextractable gel fraction, critical gelation conditions, the number of elastically effective chains and junctions, and the average contraction of networks chains, we need to know the probability *p* that a path issuing from some junction will lead to infinity (boundary of the macroscopic sample) without being terminated. The approximate method yielding such information is based on the theory of cascade processes[12] which yields for the extinction probability, $e = 1 - p$, the equation:

$$e \sum_{m=1}^{s} m\,\tilde{n}^{(m)} = \sum_{m=1}^{s} m\,\tilde{n}^{(m)} e^{m-1} \tag{14}$$

where $\tilde{n}^{(m)}$ is the fraction of junctions from which *m* paths issue to *m* other junctions. $\tilde{n}^{(m)}$ are sums of selected groups

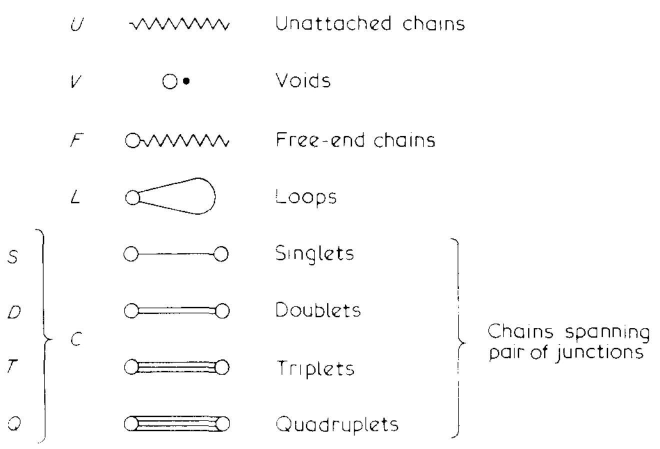

Figure 4 Formal elements of network structure

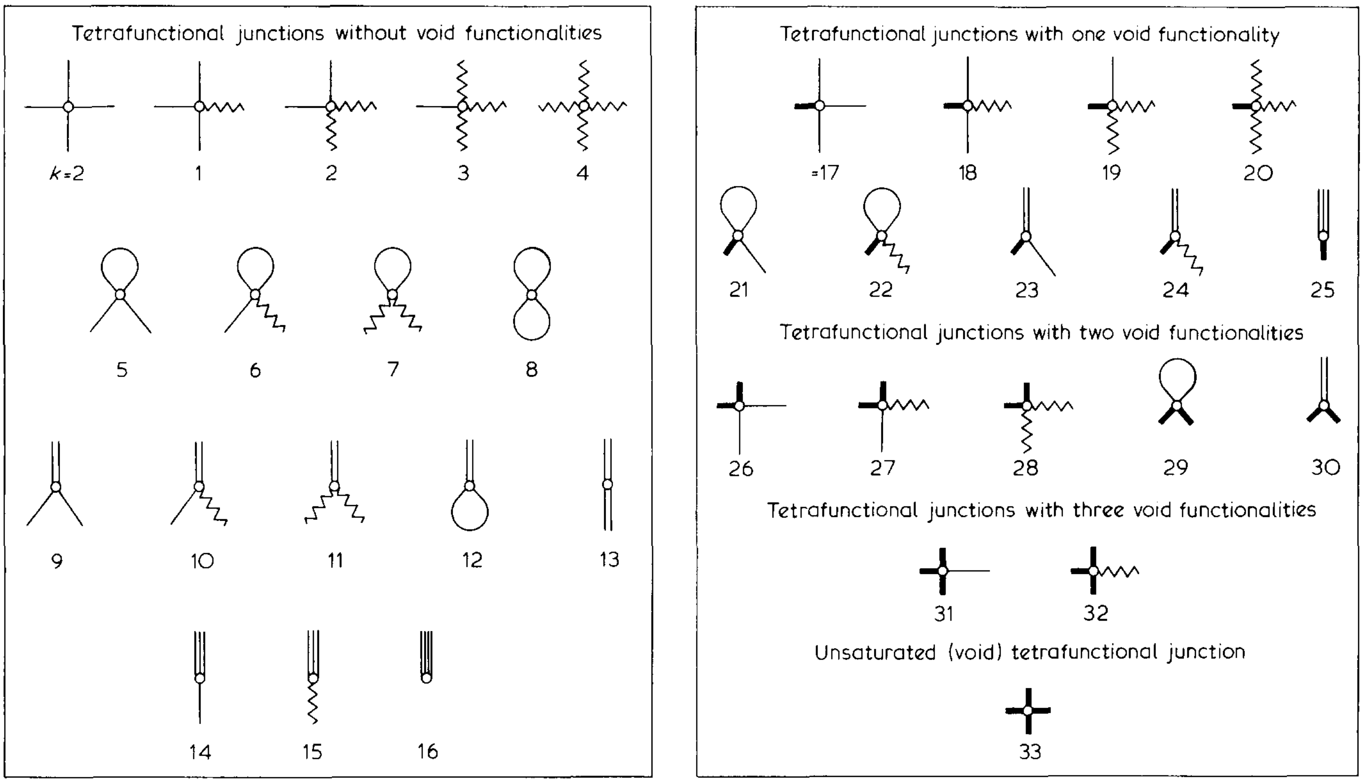

Figure 5 Topologically admissible types of tetrafunctional junctions

of various junctions, n_k; e.g. for tetrafunctional systems (see *Figure 5*)

$$\left.\begin{aligned}&\tilde{n}^{(4)} = n_0 \qquad \text{(junctions } s^4 \text{ with four singlets)}\\&\tilde{n}^{(3)} = n_1 + n_9 + n_{17} \text{ (junctions } s^3f,\ s^2d \text{ and } s^3v)\\&\tilde{n}^{(2)} = n_3 + n_5 + n_{10} + n_{13} + n_{14} + n_{18} + n_{23} + n_{25}\\&\quad \text{etc} \ldots\end{aligned}\right\} \tag{15}$$

The cascade model, based on a Markovian process, neglects correlations between structures of different junctions, implicitly assuming the higher distribution functions to be of the cluster form:

$$\left.\begin{aligned}&n_{kl} = n_k n_l\\&n_{klm} = n_k n_l n_m\\&\text{etc} \ldots\end{aligned}\right\} \tag{16}$$

Presently there does not exist any reliable method of calculation of path continuity using a non-Markovian theory allowing for the correlation of junctions.

Having obtained the extinction probability, e, we can calculate the critical condition for gelation[8]:

$$e > 1 \Longleftrightarrow \tilde{n}^{(1)} < \sum_{k=1,}^{s-2} \sum_{m=k+2}^{s} m\,\tilde{n}^{(m)} \tag{17}$$

the fraction of elastically effective junctions $N_{j,eff}/N_j$, i.e. junctions from which at least 3 independent paths lead to boundaries of the system:

$$N_{j,eff}/N_j = \sum_{m=3}^{s} \sum_{k=3}^{m} \tilde{n}^{(m)} \binom{m}{k} (1-e)^k e^{m-k}, \tag{18}$$

and the fraction of junctions contained in the inextractable part of the system, gel

$$N_{j,\mathrm{gel}}/N_j = \sum_{k=1}^{s} \tilde{n}^{(k)}(1 - e^k) \tag{19}$$

The modulus of elasticity, controlled by the number of elastically effective chains, $N_{c,eff}$:

$$G = N_{c,eff} kT A_{eff} \tag{20}$$

reduces to a simple formula when the contraction coefficient for the effective chains, A_{eff}, is expressed by the number of elastically effective chains, $N_{c,eff}$ and junctions, $N_{j,eff}$ (refs 8 and 13):

$$A_{eff} = \langle h^2_{\mathrm{net}} \rangle / \langle h^2_0 \rangle = (N_{j,eff} - 1)/N_{c,eff} \cong N_{j,eff}/N_{c,eff} \tag{21}$$

yielding:

$$G = N_{j,eff} kT \tag{22}$$

All these characteristics can be evaluated for any system for which the one-junction distribution function, n_k, is known, and the correlations between junctions are neglected.

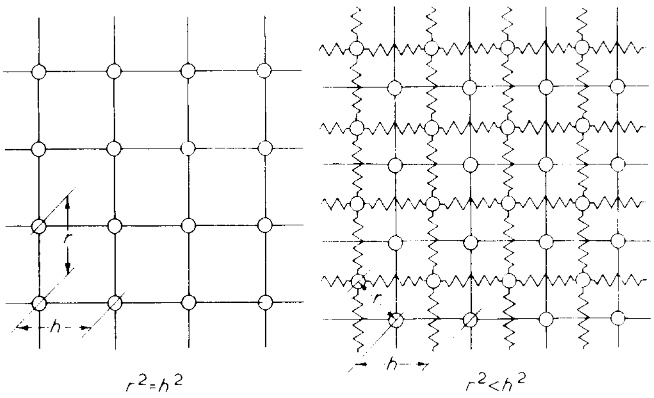

Figure 6 Two systems composed of network chains with the same average end-to-end distance *h*, but different densities of crosslinks. (a) Simple network, $\langle r^2\rangle = \langle h^2\rangle$, $f = 1$; (b) interpenetrating system composed of two superposed networks $\langle r^2\rangle < \langle h^2\rangle$, $f > 1$

POSSIBLE SOURCES OF INFORMATION ABOUT JUNCTION DISTRIBUTION

The analogy between junction distribution functions n_k, $n_{kl}, \ldots$ on the one hand, and one-, two- and many-particle distribution functions $f^1(\utilde{q}, \utilde{p}), f^2(\utilde{q}_1, \utilde{q}_2, \utilde{p}_1, \utilde{p}_2), \ldots$ in statistical mechanics on the other, is limited. Unlike $f^N(\utilde{q}, \utilde{p})$, the distribution of junctions in a permanent network is static, and the configuration of any chosen junction does not change with time. The statistical nature of such distributions concerns stochastic properties of the formation process, rather than the statistical behaviour of the configurations of junctions once formed. Therefore, the distribution functions cannot be derived from any conservation laws, such as the Liouville equation and the resulting YKBBG hierarchy.

The most natural source of information about the topological structure of permanently crosslinked systems should be provided by the kinetics of crosslinking. Following the early works of Flory[14] and Stockmayer[15], many attempts have been made to derive information about network structure from kinetic considerations (see ref 16 for a review). Most of these theories were based on cascade, or branching-tree processes, and neglected correlations between junctions produced in consecutive generations. So far, kinetic considerations have not brought about any complete one-junction distribution function n_k, to say nothing about functions of higher order. It seems, however, that the continuously developing theory of crosslinking kinetics together with the development of more realistic non-Markovian stochastic models can contribute to future progress in this field.

Another approach attempted for deriving network structure is thermodynamic optimization, i.e. minimization of the free energy of network formation, *F*, with respect to structure:

$$\utilde{\xi}_{\mathrm{opt}}: \quad F(\utilde{\xi}_{\mathrm{opt}}) = \text{Minimum} \tag{23}$$

Following the early scheme by Flory[17], Ziabicki and Klonowski solved equation (23), calculating the 'thermodynamically most probable' distribution of tetrafunctional junctions with zero, one, two, three and four free-end chains[6]. It should be noted, however, that thermodynamic optimization is not justified for the topological features of permanently crosslinked systems; crosslinking is an irreversible process and results in the formation of fixed crosslinks which are not in equilibrium. So, thermodynamic optimization of the positions of junctions in the space of chain contours is lacking in physical sense. Alternatively, some features related to chain conformation can reasonably be discussed in quasi-equilibrium terms if there is a mechanism for responding to the introduction of crosslinks. Such a characteristic is the chain contraction factor *A*, calculated independently by Graessley[18], Walasek[8,13] and others, from the equilibrium considerations concerning a system of chains with fixed constraints (junctions). For Gaussian chains of any contour lengths this leads to:

$$A = \langle h^2_{\mathrm{net}}\rangle / \langle h^2_0\rangle = (N_j - 1)/N_c \tag{24}$$

The contraction factor *A* depends only on the number of degrees of freedom represented by network junctions, N_j. For a tree-like system (no closed loops of any order) the number of chains, $N_c = N_j - 1$ and *A* reduces to unity:

$$A = 1 \tag{24a}$$

For ideal networks with all functionalities saturated by singlets spanning different junctions, $N_c = sN_j/2$, and:

$$A = 2/s \tag{24b}$$

Equilibrium chain dimensions $\langle h^2_{\mathrm{net}}\rangle$ calculated from thermodynamic considerations indicate also that the most probable structure formed in a concentrated polymer is an interpenetrating system of many networks. The interpenetration, or 'connectivity' factor *f* introduced in one of our papers[6]:

$$f = \langle h^2_{\mathrm{net}}\rangle / \langle r^2\rangle \tag{25}$$

calculated from the thermodynamically optimized chain end-to-end distance, and the average square junction-to-junction distance $\langle r^2\rangle$ related to concentration of crosslinks in unit volume N_j/V_0:

$$\langle r^2\rangle = a(N_j/V_0)^{-2/3} \tag{26}$$

(*a* is a dimensionless geometric constant), with equations (24) and (26), reduces to:

$$f = \langle h^2_0\rangle\,(A/a)(N_j/V_0)^{2/3} \tag{27}$$

Except for very short network chains (small $\langle h^2_0\rangle$) and very dilute systems (small N_j/V_0), the connectivity factor *f* is larger than unity, indicating a high degree of interpenetration. $f = 1$ corresponds to a simple network, and $f < 1$ indicates that formation of a coherent network structure requires the extension of chains beyond the 'thermodynamically optimum' length $A\langle h^2_0\rangle$. *Figure 6* presents schematically a simple ($f = 1$) and an interpenetrating network ($f > 1$).

Another justifiable application of the thermodynamic approach is provided by the calculation of the relative concentration of loops, singlets, and higher multiplets from the equilibrium conformation of chains. This approach was used by Stockmayer and Weil[19], and later by Helfand and Tonelli[20] for the calculation of intramolecular loops; the modification will be described later in this paper.

Last, but not least, the fractions of junctions with different configurations of topological elements, n_k, can be considered as phenomenological parameters to be determined experimentally. In principle, fractions of various pairs, n_{kl}, triads, n_{klm}, etc, can also be considered in this manner. However, for tetrafunctional systems, the number of parameters n_k is 34, and that of admissible pairs, n_{kl}, is 139, which considerably exceeds the present experimental possibilities. Experiment can yield the sol–gel ratio, modulus of elasticity (or the fraction of elastically effective junctions, $N_{j,eff}$), and equilibrium swelling coefficient. In some cases, chemical analysis, the balance of reacting groups, or crosslinking agent can provide additional information, totalling 3–5 independent equations. Consequently, any tractable model should be reduced to the above number of parameters. In the next two sections we will present such a model, based on the gradual reduction of the one-junction distribution, n_k, using two assumptions: randomness, and quasi-equilibrium conformation of network chains.

RANDOM TETRAFUNCTIONAL SYSTEMS

To reduce the number of parameters required for the description of the topological structure we shall introduce the model of a random system, assuming that the probabilities of functionalities in a given junction to be saturated by various structural elements are independent of each other, and proportional to the concentration of such elements in the system. For each structural element we will introduce a dimensionless characteristic equal to the fraction of junction functionalities occupied by such elements, or the probability that a functionality chosen at random is saturated by the particular element. Since the total number of functionalities in a tetrafunctional system with N_j junctions is $4N_j$, these probabilities read:

$v = V/4N_j$ for voids,
$f = F/4N_j$ for free-end chains,
$l = L/2N_j$ for loops,
$s = S/2N_j$ for singlets,
$d = D/N_j$ for doublets,
$t = 3T/2N_j$ for triplets,
and $q = 2Q/N_j$ for quadruplets

Naturally, the above fractions sum up to unity:

$$v + f + l + s + d + t + q = 1 \tag{28}$$

The assumption of randomness leads naturally to the junction distribution function in the multinomial form:

$$n_k = C_k v^{\alpha} f^{\beta} l^{\gamma} s^{\delta} d^{\epsilon} t^{\sigma} q^{\mu} \tag{29}$$

where n_k and the exponents satisfy the following normalization conditions

$$\sum_k n_k = 1 \tag{30}$$

$$\alpha + \beta + \delta + 2(\gamma + \epsilon) + 3\sigma + 4\mu = 4 \tag{31}$$

The coefficients C_k for all admissible types of junctions (*Figure 4*) should be calculated from the combinatorials. Since the individual structural elements are not topologically equivalent – some of them occupy jointly 4 (quadruplet), 3 (triplet), or 2 functionalities of a junction (doublet, loop), C_k are not simple numerical coefficients, but they depend also on the sums of functionalities occupied by monofunctional ($\Sigma = v + f + s$), bifunctional ($\Delta = l + d$) and trifunctional elements (t). The derivation of C_k is not difficult but lengthy. The details will be published separately. Here we will report only the results for two different cases: (a) crosslinking by connection of chains with reacting end-groups to a tetrafunctional crosslinking agent; and (b) crosslinking by intersection of long chains with bifunctional bridges. Both these cases are presented schematically in *Figure 7*.

Case (a) corresponds to systems, which, like polyurethane elastomers, are formed from a linear polymer with reactive end-groups, A, combined with a low-molecular, s-functional crosslinking agent RB_s. In such a case, all combinations of structural elements (for $s = 4$: 34 combinations indicated in *Figure 4*) can be formed. Also the apparently nonphysical combination $k = 33$, (v^4 = a junction with all void functionalities) represents a sensible structural feature – a crosslinking agent RB_4 to which no chains have been attached. In the process involving a large excess of crosslinking agent, such 'junctions' can quite often be formed. They do not contribute to network properties explicitly, but implicitly affect (through normalization conditions, equations 30 and 31) the concentration of elastically effective junctions and macroscopic behaviour of the system. The general formula for the fraction of k-type junctions, i.e. one with α voids, β free-end chains, γ loops, δ singlets, ϵ doublets, σ triplets, and μ quadruplets reads[21]:

$$n_k = \frac{2!(4/3)^{\sigma}(\alpha + \beta + \delta)!(\Sigma - t/3)^{2(1-\sigma-\mu)-(\gamma+\epsilon)}}{(2-\gamma-\epsilon)!\alpha!\beta!\gamma!\delta!\epsilon!(\Sigma + \Delta - t/3)^{1-\sigma-\mu}} \times v^{\alpha} f^{\beta} l^{\gamma} s^{\delta} d^{\epsilon} t^{\sigma} q^{\mu} \tag{32}$$

where the individual exponents can assume the following values:

$$\begin{aligned} &\alpha, \beta, \delta \in \{0, 1, 2, 3, 4\} \\ &\gamma, \delta \in \{0, 1, 2\} \\ &\sigma, \mu \in \{0, 1\} \end{aligned} \tag{33}$$

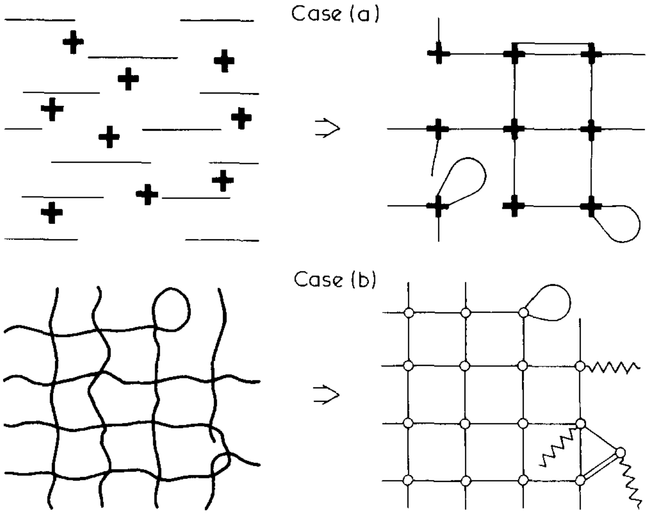

Figure 7 Scheme for two different processes of crosslinking. (a) End-to-end linking of short chains with the aid of tetrafunctional crosslinking agent. (b) Crosslinking by intersection of long chains

and the normalization equations (28) and (31) apply. For instance, for $k = 0$ (junction s^4 with four singlets), equation (32) reduces to:

$$n_0 = [(\Sigma + \Delta - t/3)]s^4 \tag{34a}$$

and for $k = 9$ (junction s^2d with two singlets and one doublet)

$$n_9 = 2[(\Sigma - t/3)/(\Sigma + \Delta - t/3)]s^2d \tag{35a}$$

etc.

Case (b) describes the formation of networks from long chains with reacting groups A distributed along their contours, and linked directly (bonds A–A) or with the aid of a bifunctional crosslinking agent –B– (bridges A–B–A). Radiation crosslinking is an example of the first process, and vulcanization of rubber is an example of the latter.

Crosslinking by 'intersections', as case (b) is sometimes called, does not allow the production of all the types of tetrafunctional junctions shown in *Figure 4*. First, no triplets, or quadruplets can be formed: $t \equiv 0$, $q \equiv 0$. Second, no junctions with voids appear in the topological pattern. 'Voids', i.e. unsaturated reactive groups, A, always exist in the system, but they do not contribute any information to the topological structure of the system nor do they affect its properties. Therefore we will neglect all junctions with voids, putting $v \equiv 0$. Finally, there is no way in which junctions with two loops ($k = 8; l^2$) can be formed, though combinations with a single loop ($k = 5, s^2l; k = 6, sfl; k = 7, f^2l$; and $k = 12, dl$) can all be realized. This introduces some asymmetry in the combinatorial calculation of the distribution function n_k (ref 21). The result reads:

$$n_k = \frac{2^\gamma[\epsilon + \frac{1}{2}(\beta + \delta)]!(\beta + \delta)!(\Sigma + d - l)^{1-\gamma}}{[\frac{1}{2}(\beta + \delta)]!\beta!\delta!\epsilon!(\Sigma + d)^{2-\gamma}\Sigma^{\beta+\gamma+\delta+\epsilon-2}} \times f^\beta l^\gamma s^\delta d^\epsilon \tag{36}$$

with

$$\beta, \delta \in \{0, 1, 2, 3, 4\}$$
$$\epsilon \in \{0, 1, 2\} \tag{37}$$
$$\gamma \in \{0, 1\}$$

and the normalization conditions:

$$\left.\begin{aligned} \beta + \delta + 2(\epsilon + \gamma) &= 4 \\ f + s + d + l &= 1 \end{aligned}\right\} \tag{38}$$

Consider the two examples discussed above for case (a). For $k = 0$ (junction s^4) we obtain now:

$$n_0 = [(\Sigma + d - l)/(\Sigma)^2]s^4 \tag{34b}$$

and for $k = 9$ (junction s^2d)

$$n_9 = 2[(\Sigma + d - l)/\Sigma]s^2d \tag{35b}$$

The results (34b, 35b) differ from those obtained for the previous case (equations 34a and 35a).

Equations (32) and (36) describe a one-junction distribution function n_k for random systems formed respectively by end-to-end linking [case (a)] or intersections [case (b)]. 33 original variables n_k (34 less the normalization condition equation 30) have been reduced to normalized fractions of individual structural elements $v, f, l, s, \ldots, q$. This makes 6 parameters for case (a) (7 structural parameters less normalization condition equation 28) and only 3 parameters for case (b).

Macroscopic properties of random crosslinked systems can be expressed as functions of concentrations of structural elements, and used for the evaluation of experimental data. There is also a possibility of further reducing the number of parameters by assuming the quasi-equilibrium conformation of polymer chains at the instant of crosslinking, and by using chemical group analysis.

QUASI-EQUILIBRIUM CONFORMATION OF LINEAR CHAINS AND THE FRACTION OF STRUCTURAL ELEMENTS

The approach originally proposed by Stockmayer and Weil[19] is based on the assumption that at the instant of introducing a crosslink, macromolecules exhibit equilibrium conformations, so that the resulting distribution of crosslinks corresponds to the equilibrium distribution of temporary contacts between macromolecules. This idea used by other authors[19,20] for the calculation of the concentration of intramolecular loops has been exploited, with some modification, in our studies.

Instead of asking about the absolute concentration of loops, doublets, triplets and quadruplets, we will compare two possible situations, say, formation of a singlet, or a loop, two singlets, or a doublet, and consider the relative probability of the above events yielding the ratios l/s, d/s, etc. Consider the two situations shown in *Figure 8*.

A network chain with a molecular weight M issues from the junction i and can either be linked to one of the other junctions surrounding i to form a singlet (*Figure 8a*), or return to i forming a loop (*Figure 8b*). If N_j junctions are randomly distributed in the volume V_0, the probability that the end of the chain will find one of the junctions contained in the spherical shell with radius h and thickness dh is:

$$dP(s) = (N_j\delta v/V_0)4\pi W(h)h^2dh \tag{39}$$

and the total probability of its being attached to any other junction:

$$P(s) = 4\pi(N_j\delta v/V_0)\int_0^\infty W(h)h^2dh = (N_j\delta v/V_0) \tag{40}$$

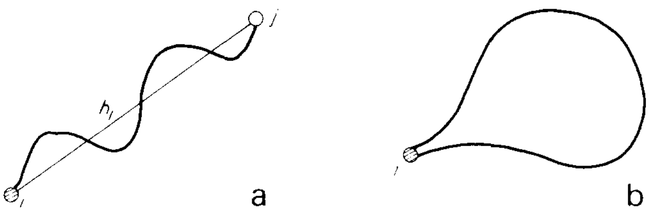

Figure 8 Comparison of two different situations controlled by conformation: (a) formation of a singlet with end-to-end distance h_i; (b) formation of a loop ($h_i = 0$)

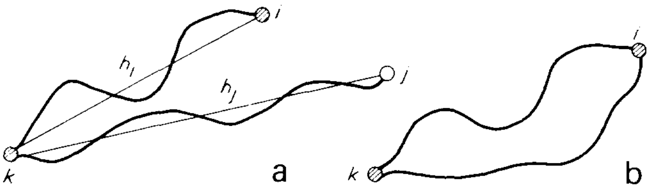

Figure 9 Comparison of two different situations controlled by conformation: (a) formation of two singlets with end-to-end distances h_i and h_j; (b) formation of a doublet with end-to-end distance h_i

where δv is the molecular volume occupied by a single junction and $W(h)$ is the end-to-end probability density. Alternatively, the probability that the chain returns to its origin at i and forms a loop (*Figure 8b*) reads:

$$P(l) = W(0)\delta v \tag{41}$$

It can be noted that $P(s)$ is proportional to junction density N_j/V_0, but independent of the statistical properties of the chain: the function $W(h)$ appears in equation (40) as the normalization integral. On the other hand, $P(l)$ does not depend on N_j/V_0 but is controlled by density at $h = 0$. For a given chain with molecular weight M, the relative probability that a loop will be formed instead of a singlet reads:

$$l/s = P(l)/P(s) = W(0)V_0/N_j \tag{42}$$

and is inversely proportional to the volume concentration of junctions in the system. For a Gaussian end-to-end distribution, equation (42) reduces to:

$$l/s = (3/2\pi)^{3/2}(V_0/N_j)(\langle h_0^2\rangle)^{-3/2} \tag{43}$$

Thus the relative number of loops in the system increases when network chains are short[22] but flexible (small values of $\langle h_0^2\rangle$), and the crosslink density in unit volume is small. Formation of networks in dilute systems (high V_0) naturally stimulates loop formation[22]. For a polydisperse system of network chains, the loop ratio l/s changes with the $-3/2$ moment of the molecular weight distribution function $f(M)$:

$$l/s \sim \langle M^{-3/2}\rangle = \int f(M)M^{-3/2}\mathrm{d}M \tag{44}$$

Comparing the situation of two singlets (one with the end-to-end distance h_i, the other with h_j) with that of a doublet with $h = h_i$ (*Figures 9a* and *9b*) one obtains the relative probability[21]:

$$P(d)/P(s) = d/s = 4\pi \int_0^\infty W_i(h_i)W_j(h_i)h_i^2\mathrm{d}h_i \cdot (V_0/N_j) \tag{45}$$

which for Gaussian statistics reduces to:

$$d/s = (3/2\pi)^{3/2}(V_0/N_j)(\langle h_i^2\rangle + \langle h_j^2\rangle)^{-3/2} \tag{46}$$

and for identical molecular weights ($\langle h_i^2\rangle = \langle h_{ji}^2\rangle$) differs only by a numerical factor from the expression for l/s (equation 43) but for polydisperse systems exhibits a more complex relation with molecular weight distribution:

$$d/s = \langle[(M_i + M_j)^{-3/2}]\rangle = \int\int f(M_i)f(M_j)\,[M_i + M_j]^{-3/2} \times \mathrm{d}M_i\mathrm{d}M_j \tag{47}$$

The relative probability of doublets is of the same order of magnitude as that of loops, and taking one structure into consideration we cannot neglect the other.

Similar considerations, described in detail elsewhere[21] yield for the remaining two ratios for network chains (i, j, k) and (i, j, k, m):

$$(t/s)_{jk} = 4\pi \int_0^\infty W_i(h_i)W_j(h_i)W_k(h_i)h_i^2\mathrm{d}h_i(V_0/N_j)^2 \tag{48}$$

$$(q/s)_{jkm} = 4\pi \int_0^\infty W_i(h_i)W_j(h_i)W_k(h_i)W_m(h_i)h_i^2 \bullet \mathrm{d}h_i(V_0/N_j)^3 \tag{49}$$

It can be noted that the relative probability of triplets and quadruplets depends on higher powers of the dilution ratio (V_0/N_j) and can play a significant role only when the volume concentration of junctions is very low. After averaging over molecular weight distribution $f(M)$, even more complex moments appear in equations (48) and (49) viz.:

$$\int\int\int f(M_1)f(M_2)f(M_3)\left[\sum_{i=1}^{3}\sum_{j>i}^{3} M_iM_j\right]^{-3/2} \bullet \mathrm{d}M_1\mathrm{d}M_2\mathrm{d}M_3 \tag{50}$$

and

$$\int\int\int\int f(M_1)f(M_2)f(M_3)f(M_4)\left[\sum_{i=1}^{4}\sum_{j>i}^{4}\sum_{k>j}^{4} M_iM_jM_k\right]^{-3/2} \bullet \mathrm{d}M_1\mathrm{d}M_2\mathrm{d}M_3\mathrm{d}M_4 \tag{51}$$

Equations (42), (45), (48) and (49) reduce topological variables to the concentration of voids, free-end chains and singlets, one of them being determined by the normalization condition. The additional information required is the number concentration of junctions, and the molecular weights of network chains.

For monodisperse, or slightly polydisperse systems, all four ratios l/s, d/s, t/s and q/s can be presented as functions of a single variable $Z = [3/2\pi\langle h_0^2\rangle]^{3/2}(V_0/N_j)$, viz.:

$$\left.\begin{aligned} l/s &= Z \\ d/s &= 2^{-3/2}Z \\ t/s &= 3^{-3/2}Z^2 \\ q/s &= 4^{-3/2}Z^3 \end{aligned}\right\} \tag{52}$$

The individual fractions calculated from equations (52) are plotted vs. Z in *Figure 10*. All the fractions increase monotonically with various powers of Z, thus determining the range in which their appearance becomes important. Simple transformations reduce the parameter Z to the form:

$$Z = (3m^*N_{\mathrm{Av}}/2\pi a)^{3/2}M^{-3/2}X^{-1}v_p^{-1}\rho^{-1} \tag{53}$$

where m^* is molecular mass per unit contour length, N_{Av} is Avogadro's number, a is the length of the statistical chain segment, M is the molecular weight of the network chain, X is the number of crosslinks per unit mass of the polymer, v_p is the volume fraction of polymer and ρ is the polymer density.

Unlike (N_j/V_0), X is insensitive to the dilution affecting v_p. Such a separation of physically significant parameters facilitates the discussion of various crosslinking processes in terms of structure.

When the network is formed from short chains of molecular weight M_0 by end-to-end linking [case (a)], the gradual introduction of crosslinks (an increase of X) leads to a reduction of the parameter Z and consequently to the reduction of the concentration of loops, doublets, triplets and quadruplets. In this case, Z is inversely proportional to X and so are the relative concentrations of loops and doublets. The slope of Z vs. X^{-1} is the higher, the shorter the network chains ($Z \sim M^{-3/2}$).

On the other hand, when crosslinking is the result of intersection [case (b)], the resulting molecular weight of network chains M decreases with increasing crosslink density X. At high enough values of X, $M \sim X^{-1}$, and one obtains Z proportional to $X^{1/2}$. With increasing density of crosslinks, X, the concentration of loops, doublets, etc., slowly increases. This result is independent of the original molecular weight of the uncrosslinked polymer, M_0. The effect of dilution is similar in two cases: the parameter Z and the related concentrations of loops, doublets, etc. is inversely proportional to volume fraction of polymer in the state of crosslinking, v_p, or higher powers of v_p.

CONCLUSIONS

The phenomenological model of a permanently crosslinked system based on the one-junction distribution function, n_k, involves a number of parameters which should be determined from experimental data. This number being rather high (17 for trifunctional systems[8], 34 for tetrafunctional ones), the model should be further simplified by assuming a random, multinomial distribution of structural elements in individual junctions. This reduces the model to 6 independent parameters in the case of end-to-end linking, and 3 independent parameters for networks obtained from long-chain macromolecules by intersection of their contours. The assumption of a quasi-equilibrium conformation of polymer chains at the instant of crosslinking allows for a further reduction in the number of variables, and calculation of the relative concentration of loops, doublets, triplets and quadruplets. Ultimately we arrive at the models with 2–3 parameters which can be derived from the experimentally available information.

Crosslinking by end-to-end connection, and crosslinking by the intersection of long chains, generally produces different structures, and the concentration of loops, doublets, triplets and quadruplets changes with crosslink density X in different ways: it decreases with X^{-1} in the case of end-to-end linking, and increases as $X^{1/2}$ for crosslinking by intersection. This fact, and the relations derived between topological structure on the one hand, and the initial molecular weight, M_0, chain stiffness, polymer concentration on the other one, indicates that formation conditions can be used to control the resulting topological structure and the related physical behaviour of networks.

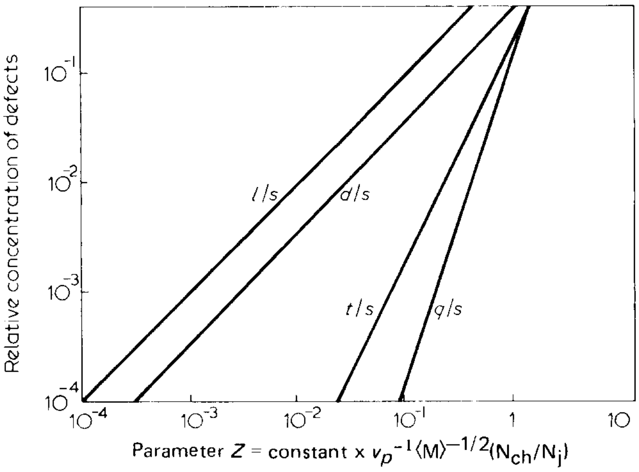

Figure 10 The ratios of loops (l/s), doublets (d/s), triplets (t/s) and quadruplets (q/s) to singlets plotted vs. parameter Z = constant x $(V_0/N_j)\langle h_0^2\rangle^{-3/2}$

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