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Embeddable random networks: method

B.E. Eichinger

Department of Chemistry, University of Washington, P.O. Box 351700, Seattle, WA 98118-1700, USA

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This paper is dedicated with admiration to Prof James E. Mark on the occasion of his 70th birthday

Abstract

The random networks that are formed in typical elastomer cure or cross-linking reactions obey the statistics of local chemical reactions, but it is the long-range, and not the local, properties of the structures that determine their desirable material properties. Properties such as the gel point and cycle rank are determined by the global structure of a network. Forging a connection between local statistics and global structure has been a challenging problem. Tracking the evolution of random structures during the course of cross-linking reactions has been the object of a considerable body of theoretical research. However, much of this research has ignored the space-filling requirements of the resulting statistically branched structures. As especially emphasized by Gordon and co-workers, the chemical structures that are formed in typical cross-linking reactions can be understood within the context of graph theory. However, a pure mathematical graph has no metrical information, which means that any information on the embedding of the graph in three-space will be impossible to infer from the graph alone. Here it is shown that one can introduce physically meaningful metrical information on the graph structure by imposing a spatial distribution of cross-links and chains from the beginning. This ensures that the resulting statistical networks are capable of being embedded in the space of that generates the distribution.

Keywords: Gelation; Network statistics; Graph theory

1. Introduction

A polymer network consists of molecules or chains that are bonded together by cross-linkages into a larger structure. Depending on the application, the resulting branched structures may consist of many chains, yet fall short of being macroscopic. Dendrimers, microgels, and hyperbranched polymers are interesting examples of branched molecules of this class. Some of these molecules may be a preliminary stage on the way to formation of a truly macroscopic network. Except for dendrimers, these structures share a common structural feature—the pattern of their connectivity or topology cannot be predicted except by statistical means.

The language of mathematical graph theory provides a convenient description of network structure, and further allows one to borrow results from the mathematical literature for application to the chemical problem. The correspondence is well known: chains are the edges of a graph and the cross-links are its vertices. A graph is a set of vertices, $\mathbf{V}=\{v_1, v_2,\ldots,v_\mu\}$, together with an incidence relation,

$$\mathbf{E}=\begin{Bmatrix} v_{i_1} & v_{j_1} & \cdots & v_{\nu_1} \\ v_{i_2} & v_{j_2} & \cdots & v_{\nu_2} \end{Bmatrix}$$

that associates the vertices in pairs. (Chain ends are counted as vertices in this mapping.) It is not difficult to convince oneself that this abstract information suffices to describe the basic topology of any network. However, the physical problem may also require associated information to be relayed with the graph, such as the molecular weights of the chains/edges, the chemical structure of the chains and cross-links, the length or length distribution of the chains, and so on. It is not difficult to append information of this sort to a graph of a given structure, so as to describe its chemistry in as much detail as desired.

The basic insight into the structure of networks was provided by Flory [1] in his seminal discovery that the gel condition could be determined very simply by asking for the expected number of chains that emanate from a randomly selected cross-link that is connected to a chain. When this number of continuing chains equals or exceeds unity, there is a finite probability that a path of chains will continue to infinity. This suffices to define the gel point. His elegant

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calculation introduced the salient features of the graphical structure of a network, and in one figure [1] he further planted the seed for what was to become the powerful application of cascade theory to branching processes by Gordon and co-workers [2,3].

This theory of network formation, in which the structures are first approximated as acyclic trees, has been elaborated and improved upon in scores of publications. Notable is the work of Stockmayer [4,5], Gordon [2,3], Dusek [6–8], Stepto [9,10], Miller and Macosko [11], and others too numerous to mention. One of the principle themes of the later work has been to correct the theory for the formation of cycles, which at the very least, lead to 'wasted reactions' with subsequent delay of the gel point. However, the corrections that have been offered to date have generally not included the whole array of cycles that can form, and many treatments do not attempt to count the number of cycles of all sizes that can form. This is a formidable task, but one which would give a complete solution to the network structure problem if it were to be solved.

A principle deficiency in the branching theory, regardless of its formulation, is implicit in the graph used to represent the physical system. It is that no metrical information is inherent in the statistical model. To develop the statistical description of networks that include cycles, one needs this metric information—the probability for formation of a closed cycle depends critically on the embedding of the model system in an ambient space, most usually the three-dimensional Euclidean space $\mathbf{R}^3$. This is precisely the reason for performing computer simulations—the embedding of the cross-links and chains in space can be imposed in a physically meaningful way to influence the formation of cyclics [12–16].

In this paper, an attempt is made to formulate a statistical model that captures this embedding without the intervention of computer modeling. It proceeds by using the essential features of branching or cascade theory—that one can associate a network structure with a directed graph (digraph) with an embedding that depends on metrical distance rather than graphical path length. This solves one problem, but naturally opens up several others. Hopefully the method will prove useful.

2. Review of branching theory

The statistical problem in branching or cascade theory is best described with a rooted tree. A tree is a graph with no circuits, i.e. in a connected tree there is a single, unique, shortest path from every vertex to every other vertex. A rooted tree has one distinguished vertex called the root. Given a tree, potentially infinite in size, select a root vertex near the center of the structure. This vertex has at most F edges emanating from it, and may have fewer. A vertex that is connected to the root by k edges is said to be a member of the kth generation. Consider the case where all vertices represent identical chemical cross-linkages, so that all vertices have the same maximum degree F. Let the expected number of edges connected to the root be αF. The vertices at the ends of this first generation of edges can generate $\alpha(F-1)$ edges, those in turn are capable of generating $\alpha(F-1)$ edges, and so on. The ratio of the number of vertices in the $(i+1)$st generation to those in the ith is $\alpha(F-1)$. When this number equals or exceeds unity (for all i), there is a finite probability that a path to infinity exists. This is the Flory gel point [1].

The number of edges, $|E|_N$, in the tree of N generations is easily seen to be

$$|E|_N = \alpha F + \alpha F[\alpha(F-1)] + \alpha F[\alpha(F-1)]^2 + \cdots + \alpha F[\alpha(F-1)]^{N-1} = \alpha F \frac{[\alpha(F-1)]^N - 1}{[\alpha(F-1)] - 1} \quad (1)$$

$$\lim_{N \to \infty} |E|_N = \frac{\alpha F}{1 - \alpha(F-1)}, \text{ for } \alpha(F-1) < 1$$

Just at the gel point, $\alpha(F-1)=1$, there is a linear growth in the number of edges with the number of generations. However, if $\alpha(F-1)>1$, there is an exponential explosion in the number of vertices. Clearly, just past the gel point the trees that conform to these statistics cannot be embedded in $\mathbf{R}^3$ with a physically realistic density of chains and cross-links.

The number of vertices in the last generation is the last term in the sum, and the total number of vertices in the tree is just one more than the number of edges, giving the ratio of the number of vertices in generation N to the total number of vertices as

$$1 - \frac{1}{[\alpha(F-1)]}$$

for large N. For a 3-valent tree, e.g. $\alpha=1$ and $F=3$, all vertices except those in the last generation have three neighboring vertices, and fully one half of the vertices are in the last generation, and it gets worse as the junction functionality increases.

Cyclization has to be invoked to attenuate the growth of statistically branched structures. A chain that closes a cycle clearly cannot generate off-spring in the next generation, which obviously reduces the number of edges that can be emerge from that generation. Several theories to incorporate cyclization in one or another approximation have been formulated. One of the earliest of these treatments in the context of Cascade Theory was made by Dusek, Gordon, and Ross-Murphy [3]; much later is the work of Dušek et al. [6] who treat hyperbranched molecules where only one ring can form. The theory of Ahmed, Rolfes, and Stepto [10,17] accounts for cycles of any size, but does not provide

information on the length of the cycles that are formed. The work of Lang, Goritz, and co-workers [18–20] utilizes both analytical theory and computer simulations to investigate the probability of cyclization, and furthermore reports the distribution of cycle sizes.

The statistical theory aside, Flory pointed out long ago that in a typical elastomer there is very little correlation between the spatial neighbors and topological neighbors of a given cross-link. This follows easily from a simple calculation of the average number of cross-links that lie within the average volume pervaded by a single chain, given the typical stoichiometry of cured elastomers. However, if one considers cross-links that are separated by a great distance in the elastomer, it must surely be the case that, on the average, the shortest path of chains from one to the other traverses a number of chains that grows in proportion to the distance of separation between the cross-links. That is, at large spatial separations, the correlation between spatial distance and topological distance (number of generations) grows stronger. The expected number of topological neighbors at a large distance r from a given cross-link is therefore expected to grow as the volume of a spherical shell of radius r. This implies that the exponential growth of the branching theory must be completely suppressed and replaced by polynomial growth. This is very difficult, if not impossible, to do with a treatment that is based on branching statistics. This problem has motivated development of computer models [12,21,22] that incorporate spatial information, i.e. begin with an embedding of chains and cross-links in $\mathbf{R}^3$, and which allow for the formation of networks while obeying physically realistic embedding principles. Here an analytical treatment is presented that complements the computer simulations.

3. Basic constructions

The critical feature of branching theory that makes it so effective is that it is based on directed graphs (conveniently called digraphs), i.e. graphs with a direction assigned to each edge. This assignment is implicit in the sequence of generations—each edge can be assigned a direction from the parent to the off-spring. Happily, this feature can be retained in graphs embedded in $\mathbf{R}^\delta$ by directing edges out from a root vertex, conveniently chosen to lie near the geometrical center of the structure, such that the edge that connects two vertices that are at distances r_1 and r_2 from the root are joined by an edge that is directed from $\min(r_1, r_2)$ to $\max(r_1, r_2)$. This notion, combined with generating functions borrowed from cascade theory, provide tools that enable several statements to be made about the statistics of embedded graphs.

Consider an ensemble of digraphs, each containing μ vertices and ν edges in a volume V. The mean density of vertices is $m=\mu/V$, and ultimately it will be assumed that the local density of vertices is independent of position. Given a root near the geometrical center of the graph, let the number of vertices in a volume element at a distance r from the root be $M(\mathbf{r})\mathrm{d}\mathbf{r}$, so that the number in the spherical shell, $\mathbf{S}_r$, a distance r from the root is $M(\mathbf{r})4\pi r^2\mathrm{d}r = M(r)4\pi r^2\mathrm{d}r$. (At this point it may be noted that the entire treatment can be generalized to spaces of any dimension δ, not necessarily integral. However, the discussion will be restricted to $\delta=3$.) This set of vertices is further subdivided into those with in-degree k and total degree or valence f, denoted $M_k^f(r)$. The vertices model cross-linkages that can be attached to a maximum of F chains; a given vertex may be attached to $f<F$ edges owing to incomplete chemical reaction.

Define three additional probability distribution functions. First, $W(\mathbf{r})\mathrm{d}\mathbf{r}$ is the a priori probability distribution of the end-to-end vector of a chain in the network. To keep the nomenclature from becoming too burdensome, we will take all chains to have the same molecular weight. Further let $P(r)$ be the probability that a chain that has one end in the spherical shell a distance r from the root has its other end in the ball $\mathbf{B}_r^3$. (The ball $\mathbf{B}_r^3$ is the inside of the sphere of radius r.) Then $Q(r)=1-P(r)$ is the probability that the other end lies in the complement of $\mathbf{B}_r^3$, denoted by $\mathbf{R}^3/\mathbf{B}_r^3$. In other words, select vertex at random at a distance r from the root. The probability that an edge connected to it will be directed inward is $P(r)$, and the probability that it will be directed outward is $Q(r)$. Let p be the probability that an edge is attached to one of the F functions of the vertex, and $q=1-p$ is then the probability that the function has not reacted. The edges attached to a given vertex are assumed to be uncorrelated. The generating function for configurations at a vertex selected at random, $\bar{g}(r)^F$, is just

$$\bar{g}(r)^F = \{p[P(r)+Q(r)]+q\}^F \tag{2a}$$

Written out, this is

$$\bar{g}(r)^F = \sum_{f=0}^{F}\binom{F}{f}p^f[P(r)+Q(r)]^f q^{F-f}$$

$$= \sum_{f=0}^{F}\sum_{k=0}^{f}\binom{F}{f}\binom{f}{k}p^f P(r)^k Q(r)^{f-k}q^{F-f} \tag{2b}$$

The terms containing p^f give the total probability that a vertex will have f edges attached (degree f), and the term with $p^f P(r)^k$ is the probability that a vertex has simultaneously total degree f and in-degree k. Thus,

$$M_k^f(r) = \left(\frac{\mu}{V}\right)\binom{F}{f}\binom{f}{k}p^f P(r)^k Q(r)^{f-k}q^{F-f} \tag{2c}$$

which treats all chains and reactive sites on cross-linkages as distinguishable.

The immediately appealing feature of this construction is that a vertex in $\mathbf{S}_r$ that has in-degree $k=2$ looks like it closes a cycle! This is so because the other ends of the two directed edges that are incident on this vertex originate in a smaller volume, and those are attached to edges that themselves

originate in a smaller volume, and so on, until the edges are found that are attached to the same vertex. Unfortunately, the in-degree $k \geq 2$ vertices do not, in general, count circuits because, at the very least, there are secondary roots in $\mathbf{B}_r^3$ that may have all but one edge lying in the $\mathbf{R}_3/\mathbf{B}_r^3$. Fig. 1 shows a configuration on the left with closure of a circuit, while on the right is a configuration where an in-directed edge in $\mathbf{S}_r$ is attached to a vertex that has zero in-degree. While the vertex in $\mathbf{S}_r$ might be a member of a circuit, it is not the critical link that closes the circuit like the vertex on the left does. This observation suggests a further definition.

There are four classes of vertices that distinguish themselves as being important in the analysis. The first class consists of those vertices that have no attached edges. This class is denoted by C_E, the subscript denoting empty. Class C_I has in-degree zero; vertices in this class comprise the root and all secondary roots (such as on the right in Fig. 1). Class C_T has out-degree zero. A vertex in this class has no paths into $\mathbb{R}^3/\mathbb{B}_r^3$. Finally, all other vertices are in class C_C; they have in-degree at least one and out-degree at least one. Vertices of this class are the basis for a Flory calculation of the gel point.

The generating functions for the various classes of vertices are easy to write down.

The generating function for all vertices except those that are unreacted is

$$g^F(r) = \{p[P(r) + Q(r)] + q\}^F - q^F \tag{3}$$

and all others are derived from this one by inspection. As before, terms in these functions containing p^f give the probability that a vertex selected at random in $\mathbf{S}_r$ has f edges attached.

Generating functions (gf) for higher order clusters are likewise straightforward to write down. The gf for two vertices connected by a chain (Fig. 2), is

$$g^{F-1}(r_1)pW(|r_1 - r_2|)pg^{F-1}(r_2) \tag{4}$$

without regard for the relative magnitudes of r_1 and r_2. In this equation, the factor $g^{F-1}(r_1)pW(|r_1 - r_2|)$ is the a priori probability of finding a vertex in the spherical shell at r_1 with at least one edge attached with probability p; the edge gets the $W(|r_1 - r_2|)$ factor, and the final $pg^{F-1}(r_2)$ component is the probability that the distinguished edge is attached to another vertex of any complexion. It should be clear that one may construct a catalog of clusters similar to that of Walasek and Ziabicki [23].

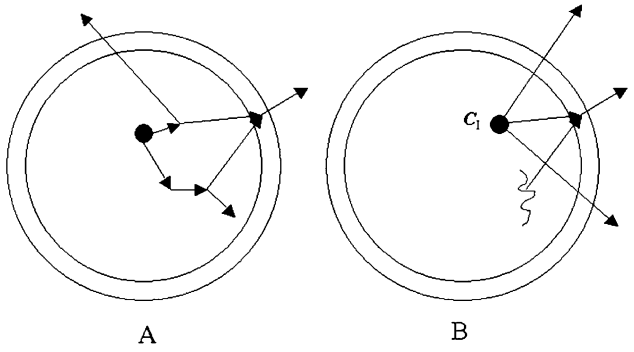

Fig. 1. The graphical fragment A (left) has a vertex in the shell at r, and this vertex closes a cycle. On the right (part B) the vertex in the shell is directly connected to a vertex of C_I, and hence does not close a circuit. However, this vertex could belong to a cycle that is closed by a vertex in a larger shell.

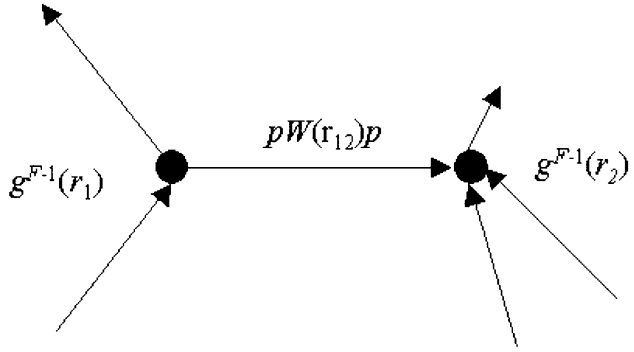

Fig. 2. Illustrating construction of the generating function for a cluster of two vertices connected by a chain. The figure is drawn for $r_{12} = r_2 - r_1 > 0$.

4. Edge statistics

One would like to know something about the distribution of edges in addition to what is provided by the gf for vertices. One statistic that is relatively easy to construct is the incremental flux of edges through $\mathbf{S}_r$. Let $N(r)$ be the number of edge vectors that impinge on $\mathbf{S}_r$, while $N(r + \delta r)$ is the number that emerge from $\mathbf{S}_r$. Let the total out-degree of vertices in $\mathbf{S}_r$ be $E_0(r)$, and the in-degree be $E_i(r)$. It is clear that the there are edge vectors that pass unaffected through $\mathbf{S}_r$, some that terminate there, and some that originate there. The increment in edge vectors from $\mathbf{S}_r$ is

$$N(r + \delta r) - N(r) = [E_0(r) - E_i(r)]\delta r \tag{5}$$

The expected out-degree and in-degree are given by

$$E_0(r)/[4\pi r^2(\mu/V)] = \left(\partial \bar{g}(s,t,r)^F/\partial t\right)|_{s=t=1}$$

$$= FpQ(r)\bar{g}(s,t,r)^{F-1} = FpQ(r)$$

and

$$E_i(r)/[4\pi r^2(\mu/V)] = \left(\partial \bar{g}(s,t,r)^F/\partial s\right)|_{s=t=1}$$

$$= FpP(r)\bar{g}(s,t,r)^{F-1} = FpP(r)$$

where the augmented gf

$$\bar{g}(s,t,r)^F = \{p[sP(r) + tQ(r)] + q\}^F \tag{6}$$

has been constructed to facilitate calculations. This gives

$$N(r + \delta r) - N(r) = 4\pi r^2(\mu/V)pF(1 - 2P(r))\delta r \tag{7}$$

and with use of the asymptotics of $P(r)$ for large r from the Appendix A, one finds

$$\frac{\mathrm{d}N(r)}{\mathrm{d}r} \sim 4\left(\frac{\pi}{\gamma}\right)^{1/2}\left(\frac{\mu}{V}\right)Fr$$

so that

$$\Delta N(r) \sim 2\left(\frac{\pi}{\gamma}\right)^{1/2}\left(\frac{\mu}{V}\right)Fr^2 \tag{8}$$

for the increment in the number of chains passing through a large spherical shell at r owing to the cross-links that are present in the shell. This is a consistency check, if nothing else, showing that the cross-links in any sufficiently large shell maintain the flux of chains that are required to fill physical space. Eq. (7) will be interesting to study for small r, which is not pursued here.

5. Gel point

The statistics that we are considering here encompass both sol and gel. If one reaches into the ensemble of structures that obey these statistics to select a single cross-link, the probability that it will be part of the gel depends ultimately upon the entire long-range structure of the connected component of which it is a part. Thus, if one happened to grab a vertex from the class C_I, it may well happen that this vertex is attached to the gel. However, the presence of a gel is decided by the paths away from this vertex, e.g. the selected vertex must be connected to a vertex from C_C to even be considered a viable candidate to be part of the gel. The critical issue establishing the presence of a gel is the occurrence of a connected path containing vertices of class C_C.

Thus one may imitate Flory [1] and ask for the expected number of edges that emerge from vertices in the shell $\mathbf{S}_r$ that are subsequently connected to vertices that are farther from the origin.

The construction of the expectation value, $E_\mathrm{C}(r)$, of the number of edges per vertex that are connected at both ends to vertices in class C_C proceeds as follows. The a priori probability for selecting a vertex of class C_C in $\mathbf{S}_r$ is just the gf $g^f_\mathrm{C}(r)$ from Table 1. However, to get the conditional probability that the out-vectors, the $Q(r)$ factors, are connected to vertices in C_C located anywhere in $\mathbf{R}^3/\mathbf{B}^3_r$, the $Q(r)$ factors must be changed to

$$\hat{Q}(r) = \int_{\mathbf{R}^3/\mathbf{B}^3_r} W(\mathbf{r}'-\mathbf{r})p[g^{F-1}_\mathrm{C}(r') + g^{F-1}_\mathrm{I}(r')]\mathrm{d}\mathbf{r}' \tag{9}$$

The two g factors arise because there are $F-1$ functions that remain on the cross-link that terminates the chain, and the configuration of these can be of either class C_C or C_I.

The expectation value that we seek is readily derived from the function

$$\hat{g}^F_\mathrm{C}(t,r) = \{p[P(r)+t\hat{Q}(r)]+q\}^F - \{pt\hat{Q}(r)+q\}^F - \{pP(r)+q\}^F + q^F \tag{10}$$

by differentiation with respect to the auxiliary counting variable t to get

$$E_\mathrm{C}(r) = Fp\hat{Q}\{[p(P+\hat{Q})+q]^{F-1} - (p\hat{Q}+q)^{F-1}\} \tag{11}$$

Now, the presence of gel is determined by the long-range connectivity of the network, so we may calculate this expectation value for $r>\rho$, where ρ is sufficiently large so that the $P(r)\approx 1/2$ to any required degree of accuracy. (Carving out the sphere of radius ρ corresponds physically to the space occupied by the ball of a falling ball viscometer, for example.)

First we need to evaluate $\hat{Q}$ for large r. Modification of Eq. (9) above for $r>\rho$, gives

$$\begin{aligned}\hat{Q} &= Qp[g^{F-1}_\mathrm{C}(r>\rho) + g^{F-1}_\mathrm{I}(r>\rho)] \\ &= Qp\{[p(P+Q)+q]^{F-1} - (pQ+q)^{F-1}\} \\ &= \frac{1}{2}p\left[1-\left(1-\frac{p}{2}\right)\right]^{F-1}\end{aligned} \tag{12}$$

since $P=Q=1/2$ in this limit. The equations are now sufficiently complicated that numerical solutions are recommended. Fig. 3 shows the results from a simple numerical evaluation of these equations. Plotted is the expected number of edges that connect a vertex of class C_C in a given shell far from the origin with another vertex of the same class that is farther from the origin. When the expectation value exceeds one, the Flory gelation condition is met.

It is seen from the figure that networks with maximum functionality three do not meet the Flory gelation condition. It should not be inferred that the method is faulty because of this. Rather, the calculation that has been done is only a first approximation to the gel point. In particular, paths that backtrack from a vertex in a shell to pick up a vertex of class

Table 1
Generating functions for the four classes of crosslinks

Class	Generating function
C_E	$g^F_E = q^F$
C_I	$g^F_I(r) = \{pQ(r)+q\}^F - q^F$
C_T	$g^F_T(r) = \{pP(r)+q\}^F - q^F$
C_C	$g^F_C(r) = g^F(r) - g^F_I(r) - g^F_T(r)$

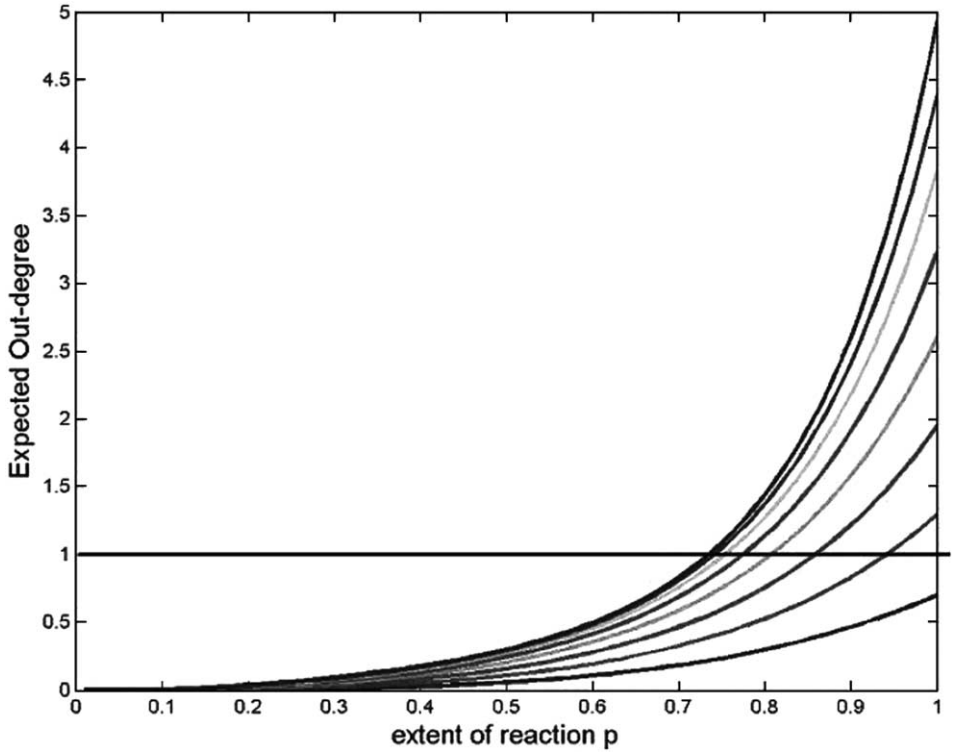

Fig. 3. Expected number of chains that are capable of sustaining network growth when cross-links have maximum functionality three (lowest curve) to ten (upper curves). The horizontal line at 1 denotes the Flory criterion; where the curves cross the line is the gel point from the first approximation as described in the text.

C_I, whose out-vectors then contribute to the flux of chains through the shell, can contribute substantially for small F, and these have not been included in the above calculation (Fig. 1 right). The calculation of the expected number of edges that contribute for clusters of this sort will require evaluation of integrals of the form

$$\int_{\mathbf{B}_r^3} W(\mathbf{r}-\mathbf{r}')\mathrm{d}\mathbf{r}' \prod_{j=1}^{f} \int_{\mathbf{R}^3/\mathbf{B}_r^3} W(\mathbf{r}'-\mathbf{r}_j)\mathrm{d}\mathbf{r}_j$$

which are slightly more challenging than that of the Appendix A. However, it appears that these are tractable, and will be considered in future work.

6. Conclusions

An initial foray has been made into the theory of embedded networks in this presentation, but it appears that the general treatment is capable of giving far deeper insights into network structure. It has been shown that some non-trivial statistics of networks can be calculated with the method, including an estimate of the gel point. Further elaboration of the method promises to be rewarding.

Appendix A

The calculation of the $P(r)$ factor that appears throughout the equations is straightforward for Gaussian chains and is included here for completeness. Expressed succinctly, the probability that a chain has one end on the sphere $\mathbf{S}_r^2$ and the other anywhere in the ball $\mathbf{B}_r^3 = B$ is

$$P(r) = \int_B W(\mathbf{r}-\mathbf{r}')\mathrm{d}\mathbf{r}' \tag{A1}$$

The probability distribution for the end-to-end vector for a Gaussian chain is the traditional

$$W(\mathbf{r})\mathrm{d}\mathbf{r} = \left(\frac{\gamma}{\pi}\right)^{3/2} \exp(-\gamma r^2)\mathrm{d}\mathbf{r}; \quad \gamma = \frac{3}{2\langle r^2\rangle_0} \tag{A2}$$

with $\langle r^2\rangle_0$ being the unperturbed mean square end-to-end distance.

The integral is easily done to yield the exact expression

$$P(r) = \frac{1}{2}\left\{\mathrm{erf}(2\gamma^{1/2}r) - \frac{1}{(\pi\gamma)^{1/2}r}[1-\exp(-4\gamma r^2)]\right\} \tag{A3a}$$

For small r, expansion of the error function gives

$$P(r) = 2\left(\frac{\gamma}{\pi}\right)^{3/2} V(B_r^3) + \cdots$$

The first term is just twice as large at the probability for

finding the end-to-end vector within $V(B_r^3)$ given one end at the origin, as is deduced directly from $W(\mathbf{r})\mathrm{d}\mathbf{r}$. The eccentricity of our configuration is responsible for the factor of two.

For large r an asymptotic expansion is needed, suggesting that the error function be converted to its complement, to give

$$P(r) = \frac{1}{2}\left\{1 - \frac{1}{(\pi\gamma)^{1/2}r} - \mathrm{erfc}(2\gamma^{1/2}r) + \frac{\exp(-4\gamma r^2)}{(\pi\gamma)^{1/2}r}\right\} \tag{A3b}$$

For large r only the first two terms are important. But for completeness, the asymptotic expansion for erfc gives

$$P(r) \sim \frac{1}{2} - \frac{1}{2(\pi\gamma)^{1/2}r} + \frac{\exp(-4\gamma r^2)}{2(\pi\gamma)^{1/2}r} + \cdots \tag{A4}$$

which tends to 1/2 as $r \to \infty$, as it must. For any r, $Q(r) = 1 - P(r)$.

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