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Polymers and Random Graphs: Asymptotic Equivalence to Branching Processes

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In 1974, Falk and Thomas did a computer simulation of Flory's Equireactive RA_f Polymer model, rings forbidden and rings allowed. Asymptotically, the Rings Forbidden model tended to Stockmayer's RA_f distribution (in which the sol distribution "sticks" after gelation), while the Rings Allowed model tended to the Flory version of the RA_f distribution. In 1965, Whittle introduced the Tree and Pseudomultigraph models. We show that these random graphs generalize the Falk and Thomas models by incorporating first-shell substitution effects. Moreover, asymptotically the Tree model displays postgelation "sticking." Hence this phenomenon results from the absence of rings and occurs independently of equireactivity. We also show that the Pseudomultigraph model is asymptotically identical to the Branching Process model introduced by Gordon in 1962. This provides a possible basis for the Branching Process model in standard statistical mechanics.

KEY WORDS: RA_f; polymer; rings allowed and forbidden; branching processes; random graphs.

1. INTRODUCTION

Flory's[1] RA_f model is the best-known model of chemical polymerization. In this model, each monomer has f functional groups of type A. The A's react with one another to bind the monomers together (see Fig. 1a). Making two assumptions:

1. intramolecular reaction does not occur, and
2. subject to (1), any pair of A's is equally likely to react (the Principle of Equireactivity),

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Flory[2–4] showed that an infinite polymer (or gel) formed only when $f \geqq 3$ and

$$\alpha \geqq \alpha_c = (f-1)^{-1} \tag{1}$$

α, the extent of reaction, is the probability that a random A group has reacted; α_c is its critical value.

Stockmayer[5] showed that the weight fraction of n-mers (i.e., the proportion of monomers in polymers of size n) is

$$w_n = n \frac{f(fn-n)!}{(fn-2n+2)!\, n!} \alpha^{n-1}(1-\alpha)^{fn-2n+2} \tag{2}$$

Stockmayer's derivation (using a statistical mechanical microcanonical ensemble) implied that Eq. (2) holds only for $\alpha \leqq \alpha_c$ and that for $\alpha > \alpha_c$, the n-mer distribution "sticks," i.e., the weight fractions maintain the same proportions to each other as they had at $\alpha = \alpha_c$, but their total decreases, implying a net loss of sol (finite polymer) to the gel.

Flory[6] disputed this interpretation and said that Eq. (2) held for all α. Because $\sum w_n < 1$ for $\alpha > \alpha_c$, the sol again loses mass to the gel, but the Flory gel mass differs from the mass predicted by Stockmayer.

Falk and Thomas[7] did a computer simulation to clarify the assumptions underlying the Flory and Stockmayer interpretations (see

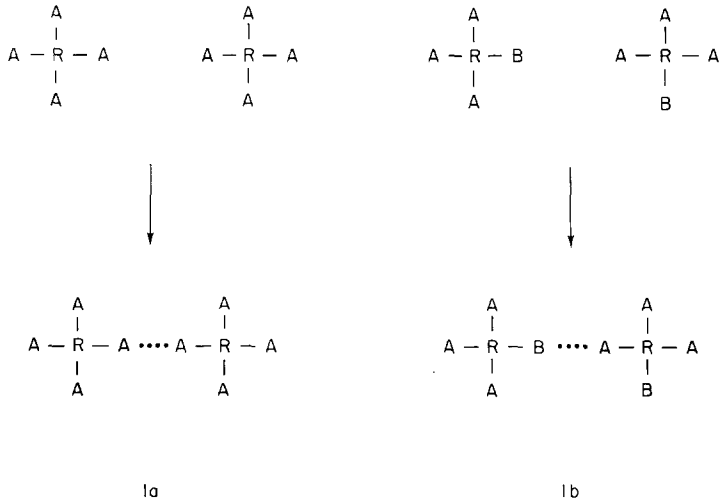


Fig. 1. Figure 1a shows two RA_4 monomers reacting to form a dimer. Figure 1b shows the same situation for the Flory A_3RB Model. The A_fRB_g model is like the RA_f model except each monomer has f A's and g B's, and A's react only with B's and vice versa.

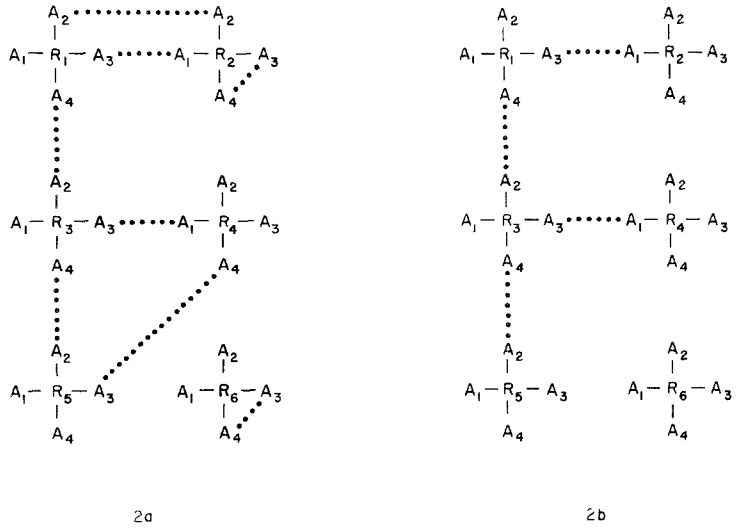
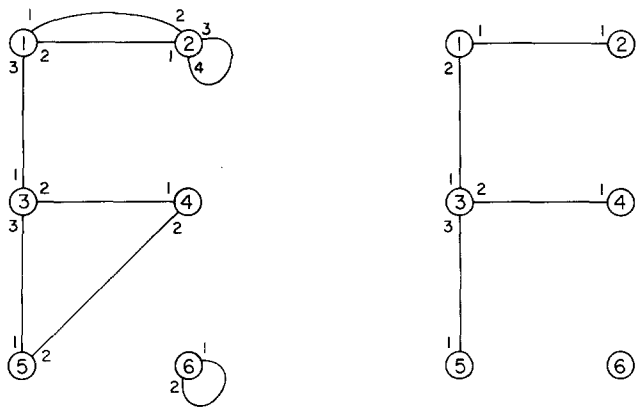


Fig. 2. Figure 2 shows the two Falk and Thomas simulations. To accord with classical statistics (in which monomers and functional groups, though chemically identical, are distinguishable), the monomers (R) and functional groups (A) on each monomer have been given a distinguishing subscript. Figure 2a shows the Rings Allowed model, in which intramolecular reaction is permitted; Fig. 2b shows the Rings Forbidden model, in which intramolecular reaction is forbidden.

Fig. 2). In the Rings Forbidden model, $N\,\mathrm{RA}_f$ monomers were bonded by joining pairs of A's stepwise at random, and those bonds resulting in intramolecular reaction were rejected. As $N \to \infty$, the polymer distribution conformed to Stockmayer's interpretation. Donoghue and Gibbs[8–10] later confirmed the asymptotic result analytically.

In the Rings Allowed model, Falk and Thomas duplicated the above simulation, except that intramolecular reaction was not rejected. As $N \to \infty$, the polymer distribution conformed to Flory's interpretation. Asymptotically, only the gel contained rings because two A's in a finite polymer have an infinitesimal chance of reacting. Donoghue[11] later confirmed Flory's gel statistics by duplicating this simulation. I[12] have since verified these results analytically.

My verification used techniques from Whittle's[13–18] results on random pseudomultigraphs (see Fig. 3 for terminology from Harary's[19] book on graph theory). Whittle's model is equivalent to the following scheme (Spouge[20]): consider N-pseudomultigraphs (i.e., pseudomultigraphs on N vertices). Without further reference, any graph is labeled, ordered, and possibly unconnected unless otherwise mentioned. Assign a weight U_G to an



3a 3b

Fig. 3. Figure 3 shows Whittle's Pseudomultigraph (Fig. 3a) and Tree (Fig. 3b) models. The realizations shown correspond to the Falk and Thomas realizations in Fig. 2 for the equireactive $\{H_j\}$ of Eq. (6).

General Terminology: (We use the term "graph" to denote any graphical object, e.g., tree or pseudomultigraph.) The *vertices* of the graphs are circles, numbered to show that the graphs are *labeled*. Edges (which we shall call *bonds* to emphasize the chemical application) join the vertices. The half-edges are numbered near each vertex to show that the graphs are *ordered*. The graphs in Fig. 3 are *undirected*; the graphs would be *directed* if every bond had an arrow to indicate its directedness. (This would be like the directedness of an A–B bond in the A_fRB_g model of Fig. 1b.)

Graphical Partition: The *degree* of a vertex is the number of bonds emanating from it (e.g., the degrees of vertices 2 and 3 in Fig. 3a are 4 and 3). We use H_j as a *marker-variable* for a vertex of degree j. The product $H_2^3H_3^2H_4$ is a list of vertex degrees in Fig. 3a; this is the *partition* of Fig. 3a. The partition of Fig. 3b is $H_0H_1^3H_2H_3$.

Components: In both Figs. 3a and 3b, vertices 1–5 form a component because they are *connected*. The singleton vertices 6 are also components.

Pseudomultigraphs are graphs which may have *loops* (e.g., like that bonding vertex 6 to itself in Fig. 3a), *multiple bonds* (e.g., like those joining vertices 1 and 2 in Fig. 3a), or *cycles* (e.g., like those formed by bonds joining vertices 3–5 in Fig. 3a). Fig. 3b might be considered a special type of pseudomultigraph lacking these features.

Conventions in This Paper: All graphs in this paper are labeled, ordered, and undirected. Unless otherwise specified, pseudomultigraphs may be unconnected. A graph with k vertices is called a k-graph, e.g., k-component, k-pseudomultigraph.

Trees: The components of Fig. 3b have no loops, multiple bonds, or cycles. They are therefore *trees*. Note that a k-tree has $(k-1)$ bonds. Fig. 3b is a collection of trees, also called a *forest*.

Consider the 5-tree in Fig. 3b. Choosing a vertex, e.g., vertex 3, to be the *root* makes it a *rooted tree*. Likewise, choosing a bond, e.g., the bond between vertices 1 and 3, to be the *root-bond* makes it a *bond-rooted tree*. Splitting the root-bond in half then divides the bond-rooted tree into 2 *link-trees*. Consider the link-tree consisting of vertices 3–5. The half-edge 1 of vertex 3 is the *link* and vertex 3 is the *link-vertex*.

N-pseudomultigraph G as follows (see Fig. 3a): if G has partition $\prod H_j^{n_j}$ and B bonds

$$U_G = \prod H_j^{n_j} \beta^B \tag{3}$$

where $\{H_j\}$ and β are preassigned non-negative numbers. We select G from N-pseudomultigraphs with probability

$$P(G) = U_G \Big/ \sum_{(G)} U_G = U_G / U_N \tag{4}$$

where U_N is the sum of the weights of all N-pseudomultigraphs.

In Eq. (3), $\{n_j\}$ satisfy the following constraints:

$$\sum_{j=0}^{\infty} n_j = N \tag{5a}$$

$$\sum_{j=0}^{\infty} j n_j = 2B \tag{5b}$$

so that β^B in Eq. (3) could be absorbed into $\prod H_j^{n_j}$ by rescaling $\{H_j\}$. It is useful, however, to regard $\{H_j\}$ as entropy factors intrinsic to the vertices, and β as an energy factor controlling the extent of bonding within the pseudomultigraphs.

Whittle's Tree model is similarly constructed (see Fig. 3b) except that the components of the graph are trees rather than connected pseudomultigraphs. Weights are assigned as in Eqs. (3) and (4) and constraints (5a) and (5b) continue to hold.

Comparis of Figs. 2 and 3 shows that the Falk and Thomas models are equivalent to Whittle's models when

$$\begin{aligned} H_j &= \frac{f!}{j!(f-j)!}, \qquad j = 0, 1, 2, \ldots, f \\ &= 0 \qquad \text{otherwise} \end{aligned} \tag{6}$$

if the number of bonds is fixed at

$$B = \frac{f\alpha}{2} N \tag{7}$$

(This is the number of bonds in Fig. 2 if the extent of reaction there is α.) The value of H_j is equivalent to selecting j of the f A's on a monomer. The ordering in Whittle's models then corresponds to a unique realization in the

Falk and Thomas models. (Compare, e.g., Figs. 2 and 3) If U_N and G in Eq. (4) are restricted to graphs on N vertices with B bonds, with B given by Eq. (7), Eq. (4) gives the probabilities corresponding to the Falk and Thomas models.

The fixed bond version [Eq. (7)] of Whittle's models is introduced to indicate a connection between these models and standard polymer chemistry models. Having done this, *we now consider only those Whittle models that use β instead of B.* Such models (Pseudomultigraph and Tree), described near Eqs. (3)–(5), are random graphs on a fixed number of vertices that *allow the bonding (B) to vary.*

From the discussion of Eqs. (6) and (7), the Rings Allowed model and the Pseudomultigraph model are equivalent in the equireactive case. The Equireactive Pseudomultigraph model [Eq. (6)] obviously generalizes (general H_j), while the Rings Allowed model finds an asymptotic generalization in the Branching Process model of Gordon[22] and Good.[23] Gordon introduced this model to account for the First Shell Substitution Effect [see, e.g., Gordon and Ross-Murphy[24]]: due to steric effects, the bonding of an A is influenced by the bonding of other A's on the same unit. One might well expect the Pseudomultigraph model with general H_j to be asymptotically equivalent to the Branching Process model.

We also know that the Equireactive Tree model [Eq. (6)] is equivalent to the Rings Forbidden model. In turn, the latter is asymptotically equivalent to the Stockmayer RA_f model in which the sol distribution "sticks" after gelation. One might expect the general Tree model to "stick" after gelation as well.

Before showing these expectations to be correct, we require some standard results which follow.

2. GRAPHICAL PRELIMINARIES

The first thing we require is an efficient enumeration of ordered, labeled trees by partition. To this end we introduce

$$H(y) = \sum_{j=0}^{\infty} H_j y^j \tag{8}$$

where H_j is the weight assigned to a vertex of degree j. For this section only, $\beta = 1$.

Let l_k be the sum of the weights of ordered, labeled link k-trees (see Fig. 3) when $\beta = 1$. Then

$$l_k = \sum_{j=1}^{\infty} jH_j \left(\sum \frac{k!}{k_1!\, k_2! \cdots k_{j-1}!} l_{k_1} l_{k_2} \cdots l_{k_{j-1}} \right) \tag{9}$$

where the second sum is over all solutions of

$$k_1 + k_2 + \cdots + k_{j-1} = k - 1 \tag{10}$$

where $\{k_i\}$ are positive integers. The proof: any link tree has a link-vertex of degree $j(H_j)$ which gives rise to $(j-1)$ link trees. Because of ordering, there are j choices for the link and the $(j-1)$ link-trees are distinguishable. Because of labeling, the $(k-1)$ vertices on the link-trees must be allocated (also there are k possible labels for the link-vertex), hence the multinomial coefficient after the second sum.

Equations (9) and (10) imply

$$y \triangleq L(x) \triangleq \sum_{k=1}^{\infty} l_k \frac{x^k}{k!} = \sum_{j=1}^{\infty} j H_j x \left(\sum_{k=1}^{\infty} l_k \frac{x^k}{k!} \right)^{j-1} = xH'L(x) = xH'(y) \tag{11}$$

($\triangleq$ denotes a definition.)

If t_k is the sum of the weights of ordered, labeled k-trees, then the corresponding sum for rooted trees is kt_k, since every k-tree can be rooted on any of its k vertices. The generating function for rooted trees,

$$R(x) \triangleq \sum_{k=1}^{\infty} k t_k \frac{x^k}{k!} = x \sum_{j=0}^{\infty} H_j y^j = xH(y) \tag{12}$$

since every rooted tree consists of a root (x) of degree $j(H_j)$ attached to j link-trees (y^j). A cautious reader can verify Eq. (12) through a recursion similar to Eq. (9).

Likewise, the generating function for trees,

$$T(x) \triangleq \sum_{k=1}^{\infty} t_k \frac{x^k}{k!} = xH(y) - \frac{1}{2} y^2 \tag{13}$$

Equation (13) is formally verified by dividing Eq. (12) by x and integrating. Integrating $H(y)$ by parts and applying Eq. (11) yields Eq. (13). Equation (13) also has a combinatoric interpretation: $xH(y)$ is the generating function for rooted trees (kt_k) while $\frac{1}{2} y^2$ is the generating function for bond-rooted trees, since each bond-rooted tree is essentially an unordered pair of link-trees. The weight of bond-rooted k-trees is $(k-1)\, t_k$ since a tree can be bond-rooted on any of its bonds. $T(x)$ is the difference of these two generating functions since $t_k = kt_k - (k-1)\, t_k$.

Gordon's Branching Process model is similar to the enumeration of tree weights. For ease of comparison, the presentation given here is a graph theoretic one, although replacement of graph-theoretic terms (e.g., "monomer" instead of "vertex") allows a chemical interpretation. In the model, there are an infinite number of vertices. p_j is the probability that a random vertex is of degree j. The vertices are bonded into trees "at random" [a notion defined after Eq. (15)].

Let

$$P(x) \triangleq \sum_{j=0}^{\infty} p_j x^j \tag{14}$$

If λ_k is the probability that a link-tree has k vertices, then

$$\lambda_k = \sum_{j=1}^{\infty} \frac{jp_j}{P'(1)} \sum \lambda_{k_1} \lambda_{k_2} \cdots \lambda_{k_{j-1}} \tag{15}$$

where the second sum ranges over the set of values given in Eq. (10).

Proof. The probability that a link leads to a vertex of degree j is the *a priori* probability (p_j) times the vertex degree (j) (a vertex of high degree is more likely to be at the end of a "random' link). Division by $P'(1) = \sum jp_j$ normalizes jp_j into a probability. The second sum gives the probability that the $(j-1)$ link-trees from the link-vertex have $(k-1)$ vertices between them [see Eq. (10)]. Equation (15) implies

$$\eta \triangleq \sum_{k=1}^{\infty} \lambda_k x^k = x \frac{P'(\eta)}{P'(1)} \tag{16}$$

Let w_k (the weight-fraction in chemical terminology) be the proportion of vertices in trees with k vertices. Then

$$W(x) \triangleq \sum_{k=1}^{\infty} w_k x^k = x \sum_{j=0}^{\infty} p_j \eta^j = xP(\eta) \tag{17}$$

Proof. The vertex (x) has degree $j(p_j)$ and gives rise to j link-trees (η^j); cf. Eq. (12).

Gordon *et al.*[25] give a rigorous derivation of Eqs. (15)–(17). These equations complete our preliminaries. The next section proves the asymptotic equivalence of Whittle's Pseudomultigraph model to Gordon's Branching Process model.

3. THE PSEUDOMULTIGRAPH MODEL

Consider the Pseudomultigraph model (Fig. 3a) on N vertices with variable bond number; weights are given by Eq. (3). The sum of the weights of pseudomultigraphs with B bonds and partition $\prod H_j^{n_j}$ is

$$U_{NB}\left\{\prod H_j^{n_j}\right\} = \frac{N!}{\prod n_j!} \frac{(2B)!}{2^B B!} \prod H_j^{n_j} \beta^B \tag{18}$$

where $\{n_j\}$ satisfy Eqs. (5).

Proof. Label the vertices 1, 2,..., N. Assign a degree to each vertex $(N!/\prod n_j!)$. If vertex 1 has degree j, make j copies of 1, i.e.: $1_1, 1_2,..., 1_j$, to represent half-edge ordering. There are now $2B$ numbers. Permute them $[(2B)!]$ and pair the numbers, starting from the beginning of the sequence [i.e., pair position $(2k-1)$ with $2k$, $k=1, 2,..., B$]. Join the pseudomultigraph half-edges in accordance with the sequence pairing. This overcounts the distinct pseudomultigraphs by a factor $2^B B!$ since the order within number-pairs is immaterial (2^B) as is the order of the pairs themselves $(B!)$. The remaining factors of Eq. (17) give the weight of any one of the pseudomultigraphs.

The $(2B)$th moment of the standard normal distribution is

$$\frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} e^{-x^2/2} x^{2B}\, dx = \frac{(2B)!}{2^B B!} \tag{19}$$

Substitution in Eq. (18) followed by summation over all $\{n_j\}$ satisfying Eq. (5b) shows that

$$\begin{aligned} U_N &= \sum_{(\sum n_j = N)} U_{NB} \left\{ \prod H_j^{n_j} \right\} = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} e^{-x^2/2} H^N(x\sqrt{\beta})\, dx \\ &= \frac{1}{(2\pi\beta)^{1/2}} \int_{-\infty}^{\infty} e^{-x^2/2\beta} H^N(x)\, dx \end{aligned} \tag{20}$$

We are interested in U_N as $N \to \infty$.
Set

$$\beta = (bN)^{-1} \tag{21}$$

Scaling β this way (with b constant) maintains the average number of bonds per vertex constant (as we shall demonstrate). Equation (21) makes U_N an integral to which the saddle-point method applies [see, e.g., Pólya and Szegö[26], p. 96]. The essence of this method is that

$$I \triangleq \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} g(x) \exp Nf(x)\, dx \sim g(\xi)[-Nf'(\xi)]^{-1/2} \exp Nf(\xi) \tag{22}$$

where ξ is the value of x maximizing f (assumed unique) and $\sim$ indicates that the ratio of the two sides approaches 1 as $N \to \infty$. The heuristic for Eq. (22) is straightforward: expand $f(x)$ in the integral in a Taylor series about $x = \xi$ up to $(x-\xi)^2$, noting $f'(\xi) = 0$. Extract the last two factors in Eq. (22) from the integral. The result is the expectation of $g(X)$, where X is a

normally distributed random variable with expectation ξ and variance $[-Nf''(\xi)]^{-1/2}$. As $N \to \infty$, the distribution concentrates at ξ, so $E[g(X)] \to g(\xi)$, the first factor in Eq. (22).

With Eq. (21), the integral in Eq. (20) has the form of Eq. (22) with

$$g(x) = \beta^{-1/2}$$
$$f(x) = -\tfrac{1}{2}bx^2 + \ln H(x) \tag{23}$$

If $f(s)$ has a unique, positive maximum s,

$$f'(s) = -bs + \frac{H'(s)}{H(s)} = 0 \tag{24}$$

The hypothesis holds for many "physical" $\{H_j\}$, e.g., the equireactive ones in Eq. (6). The expected proportion of vertices of degree j is

$$p_j = \frac{1}{N}\frac{H_j}{U_N}\frac{\partial U_N}{\partial H_j} = \frac{1}{U_N}\sum_{(G)}\frac{1}{N}H_j\frac{\partial U_G}{\partial H_j} \tag{25}$$

Proof. Note Eq. (3) for U_G. $H_j \partial U_G/\partial H_j$ multiplies the weight U_G by the number of vertices of degree j in G and $1/N$ normalizes this to a proportion. Because U_N is the sum of the weights U_G, the factor $1/U_N$ normalizes the weights into probabilities, and Eq. (25) holds. Using Eqs. (20) and (25) yields

$$p_j \sim \frac{H_j s^j}{H(s)} \qquad \text{as} \quad N \to \infty \tag{26}$$

since $\partial U_N/\partial H_j$ multiplies the integrand of Eq. (20) by $[N/H(x)]\,\partial H(x)/\partial H_j = Nx^j/H(x)$. Expressing Eq. (25) as a ratio of two integrals and applying the saddle-point formula Eq. (22) yields Eq. (26). Therefore

$$P(x) \triangleq \sum_{j=0}^{\infty} p_j x^j \sim \frac{H(sx)}{H(s)} \qquad \text{as} \quad N \to \infty \tag{27}$$

where $\sim$ indicates asymptotic equality of coefficients of x^j, $j = 0, 1, \ldots$. Relating this to the Branching Process model requires an expression for w_k [cf. Eq. (17)], the expected proportion of vertices in connected k-pseudomultigraphs. If $m_k(G)$ is the number of k-components of G,

$$w_k \triangleq \sum_{(G)} \frac{km_k(G)}{N}\frac{U_G}{U_N} = \frac{k}{N}\frac{N!}{(N-k)!\,k!}c_k\frac{U_{N-k}}{U_N} \tag{28}$$

where c_k is the sum of the weights of connected k-pseudomultigraphs (i.e., the analog of U_N for *connected* pseudomultigraphs).

Proof of the Second Equality. Cancel the factor $k/(NU_N)$ from both sides. What remains on the left has a combinatoric interpretation: it is the total weight of constructing a pseudomultigraph on N vertices, then coloring one of its k-components black. This equals the weight of choosing k of the N vertices to be black, constructing the black k-component, then constructing a pseudomultigraph from the remaining $(N-k)$ vertices. [It is also possible to give a formal proof of Eq. (28) by differentiating Eq. (36) with respect to c_k.]

Fix k and let $N \to \infty$. Since $\beta = (bN)^{-1}$, b fixed, the terms of highest order in c_k are those belonging to trees, since amongst the k-components these have the smallest number of bonds. Hence

$$c_k \sim t_k \beta^{k-1} \qquad \text{as} \quad N \to \infty \tag{29}$$

where t_k [as in Eqs. (11)–(13)] is the sum of the weights of k-trees for $\beta = 1$ and general $\{H_j\}$. Also

$$\frac{U_{N-k}}{U_N} \sim H^{-k}(s) \qquad \text{as} \quad N \to \infty \tag{30}$$

since the integrals for U_{N-k} and U_N are identical [Eq. (20)], except for an extra factor $H^{-k}(x)$ in the U_{N-k} integrand.

Therefore Eqs. (28)–(30) give

$$w_k \sim b \frac{kt_k}{k!} [bH(s)]^{-k} \qquad \text{as} \quad N \to \infty \tag{31}$$

Comparing this expression with Eqs. (11) and (12) shows

$$W(x) \triangleq \sum_{k=1}^{\infty} w_k x^k \sim b \frac{x}{bH(s)} H(y) = x \frac{H(y)}{H(s)} \tag{32}$$

where

$$y = \frac{x}{bH(s)} H'(y) = xs \frac{H'(y)}{H'(s)} \tag{33}$$

the second equality following from Eq. (24). Comparison of Eqs. (27), (32), and (33) with Eqs. (16) and (17) (using the dummy variable $y = s\eta$) demonstrates the asymptotic equivalence of the Pseudomultigraph model to the Branching Process model.

We now examine the Tree model.

4. THE TREE MODEL

This model is like the Pseudomultigraph model except that all graph components are trees. Tree weights are given by Eq. (29), which is now an exact, rather than asymptotic, equality. Comparison with Eqs. (11)–(13) shows

$$C(x) \triangleq \sum_{k=1}^{\infty} c_k \frac{x^k}{k!} = \beta^{-1} T(x\beta) = xH(y) - \frac{1}{2\beta} y^2 \tag{34}$$

where

$$y = x\beta H'(y) \tag{35}$$

If U_N is the sum of weights for N-forests, Percus[27], p. 52 (see also Whittle[18]), shows

$$U(x) \triangleq \sum_{N=0}^{\infty} U_N \frac{x^N}{N!} = 1 + \sum_{k=1}^{\infty} \frac{C^k(x)}{k!} = \exp C(x) \tag{36}$$

Heuristic. Every forest decomposes into k trees and $C^k(x)$ is the generating function for ordered k-tuples of trees. $1/k!$ removes the ordering. [Comparing coefficients of x^N on both sides of Eq. (36) gives a combinatoric proof.]

Extracting the coefficient of x^N from both sides of Eq. (36) by the Cauchy residue theorem yields

$$\frac{U_N}{N!} = \frac{1}{2\pi i} \int_{\Gamma} \frac{\exp C(x)\, dx}{x^N} \frac{dx}{x} \tag{37}$$

where Γ denotes integration around a contour take counterclockwise about the origin. Change variables as in Eq. (35):

$$\frac{U_N}{N!} = \frac{1}{2\pi i} \int_{\Gamma} \exp Ng(y) \frac{H'(y) - yH''(y)}{H'(y)} \frac{dy}{y} \tag{38}$$

where

$$g(y) = b \frac{yH(y)}{H'(y)} - \frac{1}{2} y^2 + \ln \frac{\beta H'(y)}{y} \tag{39}$$

$$g'(y) = [byH(y) - H'(y)] \frac{H'(y) - yH''(y)}{yH'(y)^2} \tag{40}$$

$g'(y)$ has two roots: s, satisfying Eq. (24), and σ, satisfying

$$H'(\sigma) = \sigma H''(\sigma) \tag{41}$$

To apply the saddle-point method, deform the contour Γ to pass through the *minimum* ζ of $g(y)$ on the positive reals. Since Γ is perpendicular to the real axis at ζ, $|g(y)|$ takes a local *maximum* on Γ at ζ. Moreover, Γ can usually be further deformed to make the local maximum a global maximum. This can be done for the equireactive $\{H_j\}$ of Eq. (6).

The hypotheses in the remainder of this section apply to the equireactive $\{H_j\}$ and to some other $\{H_j\}$ as well. The remainder of this section is certainly false for Whittle's[15] "unchemical" Cosh model $[H(x) = \cosh x]$ because $H_1 = 0$. It may also fail for some "chemical" $\{H_j\}$ as well. In the remainder, "*if*" denotes a hypothesis, holding for equireactive $\{H_j\}$, requiring verification for general $\{H_j\}$.

If $H_1 \neq 0$ [so the integrand of Eq. (38) does not have an essential singularity at $y = 0$], and *if* the real minimum ζ of $g(y)$ is unique, the variable y in Eq. (38) may be transformed, $y = \zeta + iu$, to produce an integral to which the saddle-point method, Eq. (22), may be applied. If $\zeta = s$, application is immediate. If $\zeta = \sigma$, the integrand of Eq. (38) zeroes at $y = \sigma$; an integration by parts [one part being $\exp Ng(y) \cdot g'(y)$] eliminates the zero to allow application.

In either case,

$$\frac{U_{N-k}}{(N-k)!} \Big/ \frac{U_N}{N!} \sim \left[\frac{\zeta}{\beta H'(\zeta)}\right]^k \tag{42}$$

since the integrands from Eq. (37) differ only by a factor of x^k, given by Eq. (35).

Substitution of Eqs. (42) and Eq. (29) (now exact) into Eq. (28) gives

$$w_k \sim b \frac{kt_k}{k!} \left[\frac{\zeta}{H'(\zeta)}\right]^k \tag{43}$$

Comparison with Eqs. (11) and (12) shows

$$W(x) \triangleq \sum_{k=1}^{\infty} w_k x^k \sim b \frac{x\zeta}{H'(\zeta)} H(y) \tag{44}$$

where

$$y = \frac{x\zeta}{H'(\zeta)} H'(y) \tag{45}$$

For $\zeta = s$ [satisfying Eq. (24)], Eqs. (44) and (45) are identical to Eqs. (32) and (33), indicating identical (pre-gel) distributions for the Pseudomultigraph and Tree models (a result known to Whittle[15]). For $\zeta = \sigma$ (postgel), the

saddle-point condition Eq. (41) does not involve b. Eq. (44) then shows that the weight-fractions for the general Tree model "stick" as b changes.

For the equireactive $\{H_j\}$, the positive real minimum ζ is either s or σ, whichever critical point is the closer to the origin. As β increases with N fixed (decreasing b and increasing the bonding), s moves away from the origin and ceases to be the relevant saddle-point when it crosses σ at gelation. Donoghue[10] demonstrates this behavior for the equireactive $\{H_j\}$, although we have now shown this behavior to be a more general phenomenon.

5. DISCUSSION

We have shown [despite my initial impression to the contrary, Spouge,[28] Discussion and Summary] that Whittle's Tree and Pseudomultigraph models generalize the Falk and Thomas Rings Forbidden and Rings Allowed models, respectively, by incorporating first-shell substitution effects.

The Tree model displays the postgel "sticking" found in the Stockmayer interpretation of Flory's RA_f model, while the Pseudomultigraph model is asymptotically equivalent to Gordon's Branching Process model.

The Pseudomultigraph model chosen (fixed vertex number N, variable bonding B regulated by an energy factor β) is like a statistical mechanical canonical ensemble. It provides a standard statistical mechanical basis for the Branching Process model as a thermodynamic limit.

In a rigorous canonical ensemble treatment, error estimates for saddle-point integrals [Eq. (22)] are required. For equireactive $\{H_j\}$, Watson's lemma[29] will provide such error control for our integrals [Eqs. (20) and (38)]. A rigorous general analysis of our integrals is difficult because the behavior of relevant saddle-points can be quite diverse [cf. Whittle's[15] Cosh model].

Grand canonical treatments often bypass such difficulties. This method fails for the Pseudomultigraph model because the grand partition function always diverges.[15] [Multiply Eq. (20) by $v^N/N!$ and sum over N. The result diverges for all v.]

Directed graphs provide a means for analysis of Flory's[1] A_fRB_g model (see Fig. 1b), an object of recent interest [Spouge[30–32], Van Dongen and Ernst[33],[34]]. Generalization of this paper to directedness and to multiple particle types is possible. In this respect, it is likely that Whittle's[17] results for pseudomultigraphs on multiple-type vertices are asymptotic to this author's[28] results on Branching Process models for multiple particle types.

There are clearly many problems remaining open.

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