Journal of Statistical Physics, Vol. 43, Nos. 1/2, 1986

Equilibrium Ring Formation in Polymer Solutions

John L. Spouge[1]

Received October 16, 1985

This paper delivers a flexible formalism for handling equilibrium ring formation. Based on graphical models of polymerization, it includes as special cases the Flory–Stockmayer RA_f model, the Flory A_fRB_g model, and Gordon's branching process formalism. When simple ring formation occurs in equireactive systems, it also includes the Jacobson–Stockmayer RA_2 and Hoeve RA_f models. The formalism is built from first principles in statistical mechanics and all assumptions are clearly stated. All parameters are given in terms of thermodynamic variables. With ring weights generalizing the Jacobson–Stockmayer Gaussian random walk, the formalism yields results for branching RA_f, A_fRB_g, and $RA_f - RB_g$ polymer models. Equireactivity then gives explicit solutions. The equireactive $RA_f - RB_g$ model compares favorably with data from gel-point vs. dilution experiments. With the exception of the Spanning Tree Approximation, graphical models of polymerization suffer from combinations of the following defects: equireactivity assumptions, restrictions to one type of monomer or bond, absence of rings, or absence of fused rings. This paper provides a promising "exact" approach to handling all of these problems simultaneously.

KEY WORDS: Flory RA_f model; random polycondensation; equilibrium ring formation.

1. INTRODUCTION

Flory's[1] RA_f model is the oldest paradigm of chemical polymerization. In the RA_f model, each monomer in a polymer has f functional groups of type A. The monomers react subject to three assumptions (see Fig. 1):

1. Functional groups of type A react with one another to form symmetric (A–A) bonds between the monomers.
2. Intramolecular reactions do not occur, so that only branched-chain (noncyclic) polymers are formed (i.e., polymers with rings are neglected).

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[1] Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

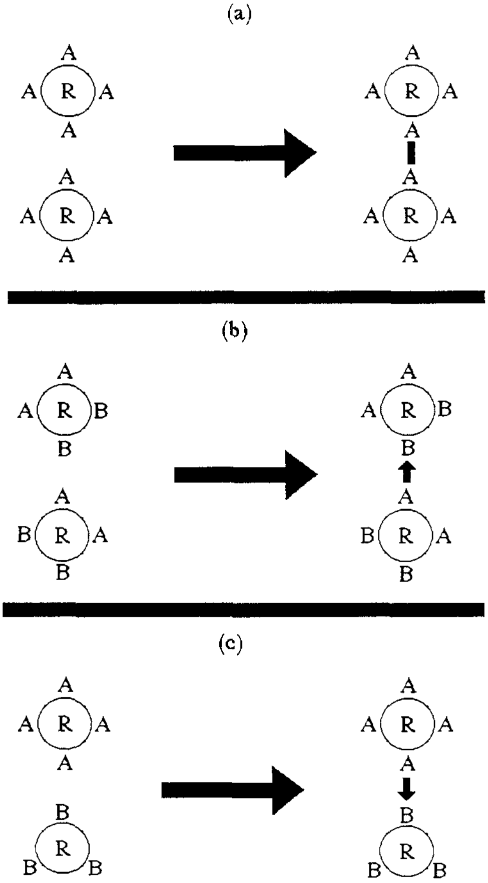


Fig. 1. (a) The RA_f model. This figure shows two RA_4 monomers combining to form a dimer. The bonds between monomers are of the symmetric A–A type. (b) The A_fRB_g model. This figure shows two A_2RB_2 monomers combining to form a dimer. The bonds between monomers are of the asymmetric A–B type. (c) The RA_f–RB_g model. This figure shows an RA_4 monomer combining with an RB_3 monomer to form a dimer. The bonds between monomers are of the asymmetric A–B type.

3. *Flory's Principle of Equireactivity*: Subject to conditions (1) and (2), all functional groups are equally reactive.

Let α, the extent of reaction, be the proportion of A groups which have reacted. Flory postulated that a gel corresponded to an infinite network. An infinite network occurs at the critical extent of reaction α_c:

$$(f-1)\alpha_c = 1 \tag{1.1}$$

By analogy with the chain reactions of neutron fission or gas explosion, Flory showed that the general criterion for an infinite network was this: if if one follows branches of the polymer, every reacted A group must, on average, lead to at least one other reacted A group. Since every reacted A group leads to $(f-1)$ other A groups and a proportion α of these have reacted, Eq. (1.1) follows.

By using a microcanonical ensemble, Stockmayer$^{(2)}$ showed that the sol distribution in the RA_f model was given by

$$x_i = \frac{w_i}{i!} \frac{\alpha^{i-1}(1-\alpha)^{fi-2i+2}}{f^{i-1}} \tag{1.2}$$

where x_i is the number fraction of $i$mers, polymers formed from i monomers. w_i, which is the number of ways of forming an $i$mer from its constituent monomers, equals

$$w_i = \frac{f^i(fi-i)!}{(fi-2i+2)!} \tag{1.3}$$

Cohen and Benedek$^{(3)}$ give a statistical mechanical basis for the RA_f model. Other elaborations of Flory's work include the size distribution for the ARB_g model$^{(1)}$ and the gel point and size distribution for the A_fRB_g model, $f \geqslant 2$, $g \geqslant 2$.$^{(4-6)}$ In the A_fRB_g models (see Fig. 1), each monomer has f functional groups of type A, g functional groups of type B, and A groups react with B groups to form *asymmetric* (A–B) bonds between the monomers. The A_fRB_g models are otherwise similar to the RA_f model.

The Principle of Equireactivity is applicable to several experimental systems. Experimental results for α_c are higher than the theoretical value predicted by Eq. (1.1). Flory$^{(1)}$ hypothesized that this was due to ring formation, which his theory neglected. With ring formation the reaction had to be driven further to produce the branching implied by Eq. (1.1). Equation (1.1), then, is really a lower bound for the critical extent of reaction.

Gordon$^{(7)}$ and Good$^{(8)}$ generalized the Flory–Stockmayer theory by making full use of branching processes, the formalism which describes chain reactions. This formalism makes Assumptions (1) and (2) of the RA_f model, but relaxes the Principle of Equireactivity and replaces it with

3′. *The First-Shell Substitution Effect (FSSE).* To explain this term, choose a monomer at random from the system. The number of monomers bonded to it has a well-defined probability distribution. In Flory's equireactive RA_f model, each group on the monomer reacts independently with probability α. The probability that a monomer chosen at random has i reacted functional groups is

$$p_i = \frac{f!}{i!\,(f-i)!}\,\alpha^i(1-\alpha)^{f-i} \tag{1.4}$$

In contrast to the Principle of Equireactivity, FSSE does not restrict p_i to a binomial form. FSSE does, however, assume that the monomers are bonded together at random, i.e., the number of bonds on a monomer does not influence the number of bonds on the monomers attached to it. The FSSE assumption, which is essentially a Markovian property, yields analytic solutions for the gel points and moments of the polymer distribution.

FSSE is a weaker assumption than the Principle of Equireactivity. For example, in the RA_3 model, it does not exclude the following steric effect: two reacted As might reduce the reactivity of the third A on a monomer.

Macken and Perelson(9) give a review of branching processes as applied to polymerization problems. Elaborations of the branching process formalism apply to the A_fRB_g model(10) and allow systems with multiple monomer and bond types.(11)

None of these models addresses the problem of ring formation, however. This had led to the application of other models to polymerization, notably percolation, scaling, and fractals.(12–14)

Attempts to include ring formation in Flory models are few: Jacobson, Beckmann, and Stockmayer(15,16) allowed for ring formation in linear RA_2 polymerizations and compared their model to experiment; Gordon and coworkers(17–19) introduced the Spanning Tree Approximation into the branching process formalism; and Hoeve(20) generalized the Jacobson–Stockmayer treatment to include simple rings in branching RA_f $(f \geqslant 3)$ polymers (see Fig. 2).

Hoeve's method treats the rings as another type of monomer, extends the Jacobson–Stockmayer statistical mechanical weighting for rings in RA_2 polymers, and then combines all monomers and rings at random.

Like Hoeve's paper, the body of this paper neglects fused rings, i.e., those rings which are not simple. "*Rings,*" *unless otherwise specified, refers to simple rings only.* Extension of this paper to fused rings is straightforward, though messy.

This paper generalizes Hoeve's by introducing structure into the polymers as follows: There are certain bonds which, when broken, disconnect the polymer. Call these bonds *articulation bonds.* When all articulation bonds are split, the polymer is broken into its constituent *units.* As Fig. 2 indicates, this description decomposes the polymer into a branched structure containing monomers and ringed units. We shall assume FSSE for

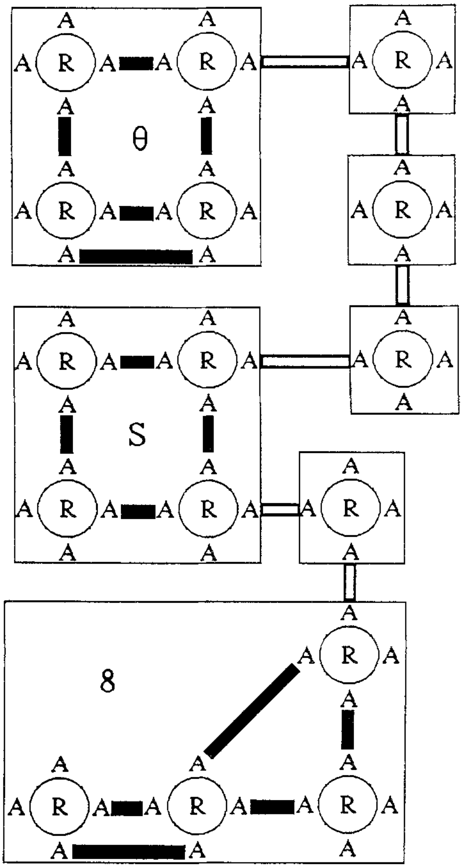


Fig. 2. This figure shows our basic description of polymer structure. There are certain bonds which, when broken, disconnect the polymer. These *articulation bonds* are hollow in Fig. 2. The pieces into which the polymer is broken are called *units*. The units are in boxes in Fig. 2. There are several types of units: they may be monomers; simple rings (marked by "S"); or complex rings such as θ rings (two triply bonded monomers with chains between) or 8 rings (two simple rings with a common quadruply bonded monomer). Even more complex rings are possible. The articulation bonds impose a tree structure on the polymer.

units (rather than just for monomers), so that *bonding between the units occurs at random*. The problem then is twofold: (1) determination of the frequency of each type of unit, and (2) calculation of the polymer distribution as the different units combine at random.

We refer to FSSE for units as the "Independence Assumption" (IA). This paper reserves the term "FSSE" for independence of monomers. "IA" seems a more appropriate term for independence of units because, as Gordon and Temple(21) point out, graphical theories of polymerization are analogous to ideal gas approximations in the thermodynamics of gases. As the molecules of an ideal gas are statistically independent, so are the units within our "ideal" graphical polymers.

The present paper confines its discourse to equilibrium, although the discussion speculates on kinetic extensions. The statistical mechanical approach taken gives all parameters in terms of thermodynamic variables. This has the advantage of allowing comparison between thermodynamic quantities for branched and linear polymers.

The progression of this paper is from weaker to more restrictive assumptions. Section 2 gives the statistical mechanics of any ideal theory of polymer solutions, while Section 3 gives the statistical mechanics of those theories employing the IA (which include those assuming FSSE). Between them, Sections 2 and 3 give the statistical mechanics of IA for multiple unit and bond types.

The progression is also from complexity to simplicity, from polymers to units to monomers to equireactivity. Section 2 hinges on a quantity called the polymer partition function, while Section 3 uses IA to relate the polymer partition function to a unit partition function. Section 4 then gives the unit partition function appropriate to rings in terms of a monomer partition function. For equireactive systems, the monomer partition function has a particularly simple form, and Section 5 solves the equireactive case for the RA_f, A_fRB_g, and RA_f–RB_g models. [The RA_f–RB_g model has both RA_f and RB_g monomers and only (A–B) bonds form between the monomers. See Fig. 1.] In Sections 4 and 5, the statistical mechanical weights for ring formation are based on random flights, but this is an arbitrary choice. As long as IA is retained, changing these weights according to the dictates of another theory is not difficult.

The formalism of Sections 2 and 3, though based on statistical mechanics, is essentially equivalent to the branching process formalism (Appendix A). The branching process formalism is not an efficient mathematical vehicle for our ring theory, because the probabilities it introduces [Eq. (1.4)] produce an inconvenient flood of normalizing factors (see Appendix A). The IA formalism of Sections 2 and 3 is superior when rings are present, the branching process formalism if they are not.

The RA_f, A_fRB_g, and RA_f–RB_g models provide examples of the IA formalism. Sections 3, 4, and 5 give a parallel development of each of these models. The development of the RA_f model is independent of the other two models. If the reader wishes, he can examine it alone on a first pass. I thought it better to collect all the common models into a single paper, rather than scatter them throughout the literature.

There has been some hope that introducing rings into the Flory theory might change its critical behavior. This critical behavior is the same as percolation on a Bethe lattice and yields the so-called classical critical exponents. Section 6 indicates that even if rings are accounted for, for theories based on IA, the critical exponents remain classical.

In statistical mechanical problems, combinatorics are usually done with the canonical partition function. To avoid cumbrous formulas in Sections 2 and 3, however, grand partition functions handle much of the combinatorics in this paper. As a result, IA and the ideal gas analogies lead to somewhat unusual combinatorial proofs. The reader who feels uncomfortable with such "proofs" should recall that they are merely plausibility arguments for the equations. The justification of such proofs rests on agreement with experiment or previously accepted theories.

Accordingly, Section 7 briefly compares our theory with experiment. The appendices also indicate the equivalence of the present approach to the following theories: (A) the branching process formalism;(7) (B) the thermodynamics of the equireactive Flory RA_f model;(3) (C) rings in equireactive linear RA_2 polymers;(15) and (D) simple rings in equireactive branched RA_f polymers.(20)

2. IDEAL SOLUTION STATISTICAL MECHANICS

[Please note that this section overburdens the mnemonic value of the letter "P" (polymer, pressure, partition function, etc.). I ask the reader's forbearance in noting the differences in case and style between the various Ps, most of which appear only in this section.]

There are two approaches to the statistical mechanics of polymer solutions. The first uses lattice statistics; the second uses ideality assumptions to introduce mathematical independence amongst the molecules in solution. Because the first approach is usually longer and requires approximations,(2) and because the simplest approximations lead to results identical to ideal theories,(22) we adopt the ideality approach.

This approach treats the solution as a mixture of ideal gases. We examine the following grand canonical ensemble: consider a fixed volume V in equilibrium with an infinite bath at temperature T. The volume freely exchanges material and energy with the bath. The bath contains a polymer solution composed of a solvent S and several types of polymer, which we index by Π. Let μ_Π be the chemical potential of polymers of type Π (Πmers).

Assume momentarily for the sake of argument that the volume V contains only one species of ideal gas molecule with molecular canonical partition function Z. [In this paper, Z with various subscripts will always denote canonical partition functions. For such Z, implicitly, $Z = Z(T, V)$.]

If μ is the chemical potential of a single ideal gas molecule, then, in a slight abuse of terminology, we call $[\exp(\beta\mu)Z]$ the molecular grand partition function. This abuse of terminology is unambiguous and is very useful later on. The grand partition function of the gas in V^(23)^ is

$$\Xi = \sum_{i=1}^{\infty} \frac{[\exp(\beta\mu)Z]^i}{i!} = \exp[\exp(\beta\mu)Z] \tag{2.1}$$

where $\beta = (kT)^{-1}$ and k is Boltzmann's constant. There may be any number i of molecules in V, hence the summation. Because the gas is ideal, the molecules are independent, so the molecular grand partition functions are multiplicative. $i!$ appears in the denominator because the molecules are interchangeable under quantum statistics.

Under the ideality approximation, the molecules in a polymer solution are treated as independent ideal gases. The grand partition function for the polymer sol phase is therefore the product of the grand partition functions for the solvent and polymer molecules:(23)

$$\Xi = \exp\left[\exp(\beta\mu_S)\, Z_S + \sum_{(\Pi)} \exp(\beta\mu_\Pi)\, Z_\Pi\right] \tag{2.2}$$

where Z_S is the canonical partition function for a solvent molecule, and μ_S, its chemical potential. Z_Π and μ_Π are the corresponding values for a Πmer and the sum is over all polymer types Π. For reasons given in the Discussion, *we consider only pregelation polymer systems in this paper*, so the gel does not appear in Eq. (2.2).

The principle that the grand partition function for a system composed of independent particles is the product of the grand partition functions for the particles will be used in a somewhat unusual context in Section 3.

The grand potential of the volume V is

$$\begin{aligned} \Omega &= pV = -kT \ln \Xi \\ &= -kT\left[\exp(\beta\mu_S)\, Z_S + \sum_{(\Pi)} \exp(\beta\mu_\Pi)\, Z_\Pi\right] \end{aligned} \tag{2.3}$$

The first two equalities are standard formulas.(23)

All thermodynamic quantities relating to the polymers can be calculated by means of the *polymer grand partition function*

$$\mathbf{P} = \sum_{(\Pi)} \exp(\beta\mu_\Pi)\, Z_\Pi \tag{2.4}$$

[Again, the (ab)use of the term "polymer grand partition function" is similar to the use of "molecular grand partition function" following Eq. (2.1).] For example, note the standard formula$^{(23)}$

$$d\Omega = -S\,dT - p\,dV - \sum N\,d\mu \tag{2.5}$$

S is the entropy of the system; p is its pressure; N is the number of particles of a certain type in the system, μ the corresponding chemical potential; and the sum is over all types of particles in the system.

Therefore the total number of Πmers in V is

$$\begin{aligned} N_\Pi &= -(\partial\Omega/\partial\mu_\Pi)_{T,V,\mu\neq\mu_\Pi} \\ &= kT(\partial\mathbf{P}/\partial\mu_\Pi)_{T,V,\mu\neq\mu_\Pi} = \exp(\beta\mu_\Pi)\,Z_\Pi \end{aligned} \tag{2.6}$$

where the partial derivative is taken in Eq. (2.4) with T, V, and all chemical potentials except μ_Π held constant.

Hereafter we make the assumption of *spatial homogeneity*: all canonical partition functions Z have a volume-independent part z satisfying $zV = Z$. Also, unless otherwise indicated, *lower cases will indicate the intensive quantities corresponding to extensive variables* (e.g., $nV = N$, $zV = Z$, etc.). Equations (2.4) and (2.6) have obvious lower-case (intensive) analogs.

For example, let $\mathbf{p} = \mathbf{P}/V$ be the *intensive polymer grand partition function.* Equations (2.4) and (2.6) implicitly show that the terms of $\mathbf{p}$ are the concentrations n_Π of Πmers in V. Terms of intensive grand partition functions like $\mathbf{p}$ typically have interpretations as concentrations. In $\mathbf{p}$, the terms corresponding to Πmers are marked with the factor $\exp(\beta\mu_\Pi)$. These facts are used several times throughout the rest of this paper.

Let $\mathbf{M}$ index the types of monomers composing a Πmer, $j_{\mathbf{M}\Pi}$ be the number of monomers of type $\mathbf{M}$ ($\mathbf{M}$ monomers) in a Πmer, and $\mu_\mathbf{M}$ be the chemical free energy of an $\mathbf{M}$ monomer. Equation (2.6) becomes practical when combined with

$$\mu_\Pi = \sum_{(\mathbf{M})} j_{\mathbf{M}\Pi}\mu_\mathbf{M} \tag{2.7}$$

Equation (2.7) states that the reaction forming the Πmer from its constituent monomers is in equilibrium: the chemical free energies of the reactants and products are equal.$^{(24)}$

Equations (2.4), (2.7), and the fact that $z = Z/V$ is independent of both V and the chemical potentials μ_Π shows

$$\begin{aligned} kT\left(\frac{\partial\mathbf{p}}{\partial\mu_\mathbf{M}}\right)_{T,\mu\neq\mu_\mathbf{M}} &= kT\frac{d\mathbf{p}}{d\mu_\mathbf{M}} = \sum_{(\Pi)} j_{\mathbf{M}\Pi}\exp(\beta\mu_\Pi)\,z_\Pi \\ &= \sum_{(\Pi)} j_{\mathbf{M}\Pi}n_\Pi = n_\mathbf{M} \end{aligned} \tag{2.8}$$

i.e., the operator $kT\,d/d\mu_{\mathbf{M}}$ acting on $\mathbf{p}$ gives the $\mathbf{M}$ monomer concentration. These equations, one for each monomer-type $\mathbf{M}$, implicity yield the chemical potential of the different monomer types in terms of the monomer concentrations.

In Eq. (2.8), we have expressed $\mathbf{p}$ as a function of T and the chemical potentials $\mu_{\mathbf{M}}$. The total derivative notation is convenient and will be used throughout the rest of this paper whenever partial derivatives of $\mathbf{p}$ are taken. Under those circumstances, it always has the same force as the partial derivative in Eq. (2.8).

Let $m_{\mathbf{M}}$ and m_{Π} be the relative molecular masses of $\mathbf{M}$ monomers and Πmers, respectively. Applying the following operator to $\mathbf{p}$ yields the ith moment of the polymer concentrations

$$\begin{aligned} M_i &= \sum_{(\Pi)} m_{\Pi}^{i} n_{\Pi} = \sum_{(\Pi)} \left[\sum_{(\mathbf{M})} j_{\mathbf{M}\Pi} m_{\mathbf{M}} \right]^{i} n_{\Pi} \\ &= \left[kT \sum_{(\mathbf{M})} m_{\mathbf{M}} \frac{d}{d\mu_{\mathbf{M}}} \right]^{i} \mathbf{p} \end{aligned} \tag{2.9}$$

[Note the total derivatives; cf. Eq. (2.8).]

The molecular weight averages MW_n, MW_w, etc., are ratios of the moments, e.g., $MW_n = M_1/M_0$, $MW_w = M_2/M_1$, etc. The average degrees of polymerization DP_n, DP_w, etc., are the same ratios with all $m_{\mathbf{M}}$s set to 1.(25)

With IA, the next section turns Eq. (2.8) [and (2.9)] into a practical method for computing polymer statistics.

3. STATISTICAL MECHANICS OF THE INDEPENDENCE ASSUMPTION

The equations of Section 2 hold in any mean-field theory of the sol phase at equilibrium. We shall use IA (the Independence Assumption) to relate several intensive grand partition functions to $\mathbf{u}$, the intensive grand partition function for the units. These relationships determine $\mathbf{p}$ when $\mathbf{u}$ is known. From $\mathbf{p}$, the methods of Section 2 can then calculate the statistics of the polymer distribution.

For the rest of this paper, all the grand partition functions will be intensive (e.g., $\mathbf{p}$ where $\mathbf{p}V = \mathbf{P}$). Bold lower case Roman letters $\boldsymbol{l}$, $\mathbf{p}$, $\mathbf{u}$, etc., denote intensive grand partition functions. Because of frequent usage, these are referred to as "partition functions" without further qualification. Bold upper case Roman letters will now denote indexes, e.g., $\mathbf{L}$ for bonds (mnemonically, "links," as we require the partition function $\mathbf{b}$ elsewhere), $\mathbf{U}$ for units, etc.

As shown in Fig. 2, the articulation bonds decompose the polymers into their constituent units. Let **U** index of the different types of units. Let $\mu_{\mathbf{U}}$ be the chemical free energy of units of type **U** (**U** units) and $j_{\mathbf{MU}}$ be the number of **M** monomers in a **U** unit. Then

$$\mu_{\mathbf{U}} = \sum_{(\mathbf{M})} j_{\mathbf{MU}} \mu_{\mathbf{M}} \tag{3.1}$$

Like Eq. (2.7), Eq. (3.1) is merely a statement that the reaction forming **U** from its constituent monomers is in equilibrium: the chemical free energies of the reactants and the products are equal.

Let **L** index the different types of bonds, denoted by lower case Roman letters a, b, c, etc. Define the *conjugate* of an a bond, an a^* bond, to be an a bond as viewed from the opposite end. For example, in the $A_f RB_g$ model, if an a bond is an $(A\text{–}B)$ bond as viewed from the reacted A group (in the direction of the arrows in Fig. 1), then an a^* bond is an $(A\text{–}B)$ bond as viewed from the reacted B group (against the direction of the arrows in Fig. 1). Obviously $(a^*)^* = a$, for any type of bond. We allow the possibility of symmetric bonds, e.g., if an a bond is an $(A\text{–}A)$ bond in the RA_f model, then a bonds viewed from both ends are the same: $a^* = a$.

This notation allows great flexibility: one type of functional group may react with several other types of functional groups, or one type of bond may appear in several chemically dissimilar positions [e.g., (1 → 4) and (1 → 6) glycosidic linkages in starches]. In such cases, we merely give the bonds we wish to distinguish different labels.

Let $z_{\mathbf{U};i,j,k,\ldots}$ be the intensive canonical partition funtion of a unit **U** which gives rise to i a bonds, j b bonds, k c bonds, etc. (see Fig. 3). Let **a** be the (*implicity, intensive grand*) partition function for the polymer part attached to the other end of the a bond (similarly **b**, **c**, etc.). Two major assumptions enter here: (1) unambiguous specification of "the polymer part" requires the tree structure introduced by the articulation bonds and (2) IA guarantees that **a** is statistically independent of the particular a bond under observation. We call **a** the *a bond partition function*; generically, **a**, **b**, **c**, etc., are *bond-type partition functions*. The bonds represented here are articulation bonds, not bonds between monomers within the units; the reader should keep this in mind.

The *unit partition function* **u**, representing the states of a polymer attached to a unit, is

$$\mathbf{u} = \sum_{(\mathbf{U})} \exp(\beta\mu_{\mathbf{U}}) \sum_{(i,j,k,\ldots)} z_{\mathbf{U};i,j,k,\ldots} \mathbf{a}^i \mathbf{b}^j \mathbf{c}^k \cdots \tag{3.2}$$

In Eq. (3.2), we have expressed **u** as a function of $\mu_{\mathbf{M}}$ [note Eq. (3.1)],

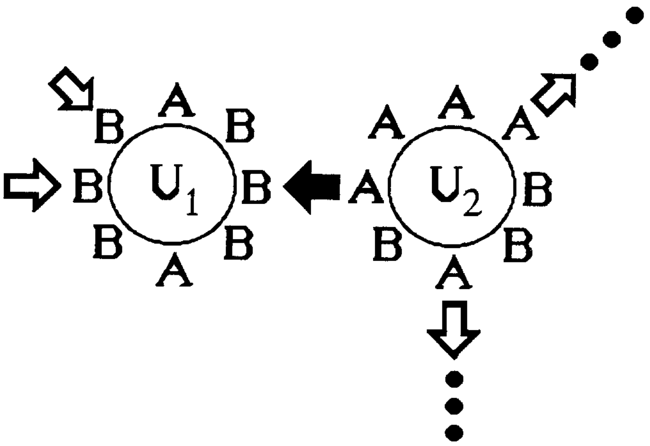


Fig. 3. U_1 and U_2 are units (see Fig. 2) in a system with A–B bonds [see Figs. 1(b) and (c)]. The bonds here are asymmetric and this is indicated by an arrow going from A groups to B groups. For the purposes of the text, the solid bond is an a^* bond when viewed from B to A, or an a bond when viewed from A to B. The solid bond is the incoming bond to the polymer part attached to U_1 through U_2. U_2 is the initial unit of this polymer part which, as the dots indicate, continues on past the bonds on U_2.

$z_{\mathrm{U};i,j,k,\ldots}(T)$, and $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$,... . We use this expression for $\mathbf{u}$ throughout the rest of the paper, particularly when we take partial derivatives of $\mathbf{u}$.

This use of grand partition functions is somewhat unusual. Equation (3.2) expresses the combinatorics of the present problem correctly, however. Fix a unit in space (see U_1 in Fig. 3), hence the *intensive* grand partition function. The initial unit may be one of several types U, hence the first summation. The factor $\exp(\beta\mu_{\mathrm{U}})$ accounts for the chemical potential of the unit. The unit may give rise to any number i of a bonds, any number j of b bonds, etc., hence the second summation. The factor $z_{\mathrm{U};i,j,k,\ldots}$ accounts for the states of the unit under the prescribed conditions. The bonds arising from the initial unit are again fixed in space, so the final factors $\mathbf{a}^i\mathbf{b}^j\mathbf{c}^k\cdots$ are *intensive* grand partition functions, and account for the chemical potentials and states of the polymer parts attached to the unit through the bonds.

To explain Eq. (3.2) further, let us, like Jacobson and Stockmayer,(15) introduce the convenient fiction of a small bond volume v_s confining any two reacted functional groups. v_s never appears in our equations, so for convenience we take this fictional quantity to be the same for all bonds. When the intensive canonical partition function $z_{\mathrm{U};i,j,k,\ldots}$ is written out in full, its terms define position in the bond volume v_s for each reacted group on the initial unit (U_1 in Fig. 3). The same is true for the partition functions **a**, **b**, **c**, etc., which represent polymer parts attached to the initial unit. Except for the bond volume it shares with the initial unit, each polymer part is independent of the initial unit and the other polymer parts. In fact, if each polymer part is viewed relative to its bond volume, IA guarantees that everything *is* independent of everything else. Hence, in this "ideal gas" approximation of polymerization, because the polymers are systems composed of independent units, partition functions like **a**, **b**, **c**, etc., are multiplicative, just as the grand partition functions in Eqs. (2.1) and (2.2) were. The form of Eq. (3.2) is the consequence of this independence.

The next equation uses the full force of IA: the bond-type partition functions **a**, **b**, **c**, etc., are given by

$$\begin{aligned}\mathbf{a}^* &= \sum_{(\mathrm{U})} \exp(\beta\mu_{\mathrm{U}}) \sum_{(i,j,k,\ldots)} z_{\mathrm{U};i,j,k,\ldots}\, i\mathbf{a}^{i-1}\mathbf{b}^j\mathbf{c}^k\cdots \\ &= \frac{\partial\mathbf{u}}{\partial\mathbf{a}}\end{aligned} \tag{3.3}$$

with one equation for each bond type (directed bonds appear in two of these equations on the left, once as a^* and once as a).

Equation (3.3) expresses $\mathbf{a}^*$ as a function of the chemical potentials μ_{M}, the intensive canonical partition functions $z_{\mathrm{U};i,j,k,\ldots}(T)$, and bond-type partition functions **a**, **b**, **c**,... . Here and throughout the rest of the paper we adopt the following convention: partial derivatives of **u** are taken with **u** given by Eq. (3.2); all variables not appearing in the denominator of the partial derivative are held constant. We shall frequently use Eq. (3.3) to take derivatives of **a**, **b**, **c**, etc., by the chain rule.

The justification for Eq. (3.3) is the following: $\mathbf{a}^*$ is the partition function of the polymer part on the end of an a^* bond. Call the a^* bond the incoming bond to the polymer part (see Fig. 3). Examine the initial unit U_2 on the incoming bond. By IA, the initial unit is statistically identical to any other unit. Hence Eqs. (3.2) and (3.3) are identical until the bond-type partition functions **a**, **b**, **c**, etc., are considered. The factor $z_{\mathrm{U};i,j,k,\ldots}$ corresponds to an initial **U** unit giving rise to i a bonds, j b bonds, etc. Any of the i a bonds on such a unit could be the incoming a^* bond. Multiplying $z_{\mathrm{U};i,j,k,\ldots}$ by i accounts for this extra multiplicity of states. Since one of the i a bonds is also the incoming a^* bond, it does not contribute to the polymer part on the end of that incoming bond. Lowering the power of **a** by one in the factor $\mathbf{a}^i\mathbf{b}^j\mathbf{c}^k\cdots$ of Eq. (3.2) accounts for this. The operator $\partial/\partial\mathbf{a}$ takes each factor $\mathbf{a}^i$ in Eq. (3.2), multiplies it by i and lowers the power of **a** by one. Equation (3.3) follows.

Like the unit partition function of Eq. (3.1), we may define a *bond par-*

tition function, representing the states of a polymer attached to an articulation bond

$$\boldsymbol{l} = 1/2 \sum_{(\mathbf{L})} \mathbf{a}\mathbf{a}^* \tag{3.4}$$

(**b** is needed later; mnemonically, $\boldsymbol{l}$ for "link").

Consider a bond volume fixed in space ($\boldsymbol{l}$ is intensive). The bond may be of any type, hence the summation of **a** over the bond indexes **L**. There are two ends to any a bond: from one end it is an a bond, from the other end it is an a^* bond. **a** and **a*** are the partition functions of these two polymer parts relative to the common bond volume. If a bonds are asymmetric ($a \neq a^*$), then the a bond is counted twice in the sum of Eq. (3.4), once as an a bond and once as an a^* bond, and the factor 1/2 corrects for that. If, however, a bonds are symmetric ($a = a^*$), then the a bond term appears only once in the sum of Eq. (3.4), but the factor of 1/2 then accounts for the symmetry of a bonding. In the ideal gas analogy, the factor of 1/2 is necessary only if the two independent particles (polymer parts) composing the system (polymer) are statistically identical.

The simple but crucial observation which bypasses the need for the branching process formalism is this: because the units and articulation bonds provide a tree structure for the polymers (see Fig. 2), *every polymer contains exactly one more unit than articulation bond.* Equation (3.2), being the partition function for units, weights each polymer by the number of units the polymer contains. Equation (3.4), being the partition function for articulation bonds, weights each polymer by the number of articulation bonds the polymer contains. To restate, recall the terms of (intensive grand) partition functions can be interpreted as concentrations [see Eq. (2.6) et seq.]. Each term in Eq. (2.4) for **p** gives the concentration of a polymer; the term corresponding to a polymer with u units appears u times in **u**, since terms of **u** correspond to polymers attached to a unit in a specific state; similarly the same term appears $(u-1)$ times in $\boldsymbol{l}$, giving the total concentration of articulation bonds in the polymer. (The individual terms of the bond partition function even give the concentrations of the different types of articulation bonds. Section 4 uses this to give the extents of reaction for functional groups.)

The intensive polymer grand partition function is therefore the difference of Eqs. (3.2) and (3.4)

$$\mathbf{p} = \mathbf{u} - \boldsymbol{l} \tag{3.5}$$

Whittle[26,27] is the first to point out this generating function relationship. By the results in Section 2, Eqs. (3.3)–(3.5) effectively give the polymer statistics once **u** is determined.

Equations (3.4) and (3.5) allow a useful restatement of Eq. (2.8)

$$
\begin{aligned}
n_{\mathrm{M}} &= kT\frac{d\mathbf{p}}{d\mu_{\mathrm{M}}}\\
&= kT\left\{\frac{\partial \mathbf{u}}{\partial \mu_{\mathrm{M}}} + \sum_{(\mathbf{L})}\frac{\partial \mathbf{u}}{\partial \mathbf{a}}\frac{\partial \mathbf{a}}{\partial \mu_{\mathrm{M}}} - \sum_{(\mathbf{L})}\mathbf{a}^{*}\frac{\partial \mathbf{a}}{\partial \mu_{\mathrm{M}}}\right\}\\
&= kT\frac{\partial \mathbf{u}}{\partial \mu_{\mathrm{M}}}
\end{aligned}
\tag{3.6}
$$

Equation (3.3) was used to carry out the partial differentiation and the derivative of Eq. (3.4) was symmetrized.

$kT\,d/d\mu_{\mathrm{M}}$ operating on Eq. (3.3) yields a gelation criterion:

$$
kT\frac{d\mathbf{a}^{*}}{d\mu_{\mathrm{M}}} = kT\frac{\partial^{2}\mathbf{u}}{\partial \mathbf{a}\,\partial \mu_{\mathrm{M}}} + \sum_{(\mathbf{b}\in \mathbf{L})}\frac{\partial^{2}\mathbf{u}}{\partial \mathbf{a}\,\partial \mathbf{b}}\,kT\frac{\partial \mathbf{b}}{\partial \mu_{\mathrm{M}}}
\tag{3.7a}
$$

or in matrix notation

$$
\mathbf{J}\left[kT\frac{d\mathbf{a}^{*}}{d\mu_{\mathrm{M}}}\right] = \left[kT\frac{\partial^{2}\mathbf{u}}{\partial \mathbf{a}\,\partial \mu_{\mathrm{M}}}\right]
\tag{3.7b}
$$

The total derivative has the same force as in Eq. (2.8). Equation (3.7) is a set of linear simultaneous equations for $\{kT\,d\mathbf{a}^{*}/d\mu_{\mathrm{M}}\}$ over all the bond types $\mathbf{a}^{*}\in \mathrm{L}$. These equations have a unique finite solution unless

$$
\Delta = \det \mathbf{J} = \det\left[\delta_{a^{*}b} - \frac{\partial^{2}\mathbf{u}}{\partial \mathbf{a}\,\partial \mathbf{b}}\right] = 0
\tag{3.8}
$$

where $\delta_{a^{*}b} = 1$, $a^{*} = b$; $\delta_{a^{*}b} = 0$, otherwise. The rows and columns of the determinant are indexed by a and b, and, according to our convention, the partial derivatives are taken with all chemical potentials and bond-type partition functions except **a** and **b** held constant.

Since $\mathbf{a}^{*}$ is the partition function of the polymer part on the end of an a^{*} bond [see Eq. (3.3) et seq.], the left side of Eq. (3.7a) is the concentration of **M** monomers in the polymer part on the end of an a^{*} bond [cf. Eq. (3.6)]. At least one such concentration on the left side of Eqs. (3.7a) diverges if Eq. (3.8) is satisfied. Hence Eq. (3.8) is a gelation criterion.

Equation (3.8) is a necessary, though not sufficient condition for gelation, however. The necessary and sufficient condition is that the matrix **J** have at least one zero eigenvalue, the remaining eigenvalues positive (i.e., **J** is nonnegative definite). Examine Eq. (3.2): if there are no articulation bonds in the system ($\mathbf{a} = \mathbf{b} = \mathbf{c} = \cdots = 0$), **J** is the identity matrix (all eigenvalues 1). As bonds form, solutions $kT\,d\mathbf{a}/d\mu_{\mathrm{M}}$ of Eq. (3.7) remain finite until at least one of the eigenvalues of **J** becomes 0. By continuity, the remaining eigenvalues must be either positive or zero.

By Eq. (2.9), the 0th moment of the polymer concentrations, the total polymer concentration, is the numerical value of the polymer partition function **p**. The first moment of the polymer concentrations is a linear combination of the monomer concentrations given in Eq. (3.6). Higher moments are more difficult to obtain, but if there is only one bond type, the second moment is relatively easily obtained. We handle three cases: (A) symmetric (A–A) bonding, one monomer type; (B) asymmetric (A–B) bonding, one monomer type; and (C) asymmetric (A–B) bonding, two monomer types. In Case (C), the first monomer type has only A groups and bonds only to the second monomer type, which has only B groups.

In Cases (A) and (B), let the relative molecular mass of the monomer be m and its chemical potential be μ. Likewise in Case (C), except we subscript m and μ by **A** and **B** for the monomers with A and B groups, respectively. We shall frequently refer to the lists of equations which follow.

Case A: One Type of Monomer, *A*–*A* Bonding

Denote (A–A) bonds by a and the a bond partition function by **a**. Since a bonds are symmetric, Eq. (3.3) becomes

$$\mathbf{a}=\frac{\partial \mathbf{u}}{\partial \mathbf{a}} \tag{3A.1}$$

In Eq. (3.4), the bond-partition function $\boldsymbol{l}$ is a single term $\frac{1}{2}\mathbf{a}^2$. By Eq. (3.6), the monomer concentration is

$$n=kT\left(\frac{\partial \mathbf{p}}{\partial \mu}\right)_T=kT\frac{d\mathbf{p}}{d\mu}=kT\frac{\partial \mathbf{u}}{\partial \mu} \tag{3A.2}$$

The 0th moment of the polymer concentrations is given by the polymer partition function

$$\mathbf{p}=\mathbf{u}-\tfrac{1}{2}\mathbf{a}^2 \tag{3A.3}$$

To obtain the second moment of the polymer concentrations, we need the following preliminary result

$$\begin{aligned}\frac{d\mathbf{a}}{d\mu}&=\frac{\partial^2\mathbf{u}}{\partial \mathbf{a}\,\partial \mu}+\frac{\partial^2\mathbf{u}}{\partial \mathbf{a}^2}\frac{d\mathbf{a}}{d\mu}\\ &=\Delta^{-1}\frac{\partial^2\mathbf{u}}{\partial \mathbf{a}\,\partial \mu}\end{aligned} \tag{3A.4}$$

where

$$\Delta = 1 - \frac{\partial^2 \mathbf{u}}{\partial \mathbf{a}^2} \tag{3A.5}$$

[The total derivative in Eq. (3A.4) has the same meaning as it did in Eq. (3A.2).] Differentiating Eq. (3A.1) with respect to μ yields the first equality of Eq. (3A.4); solving for the left side of Eq. (3A.4) then yields the second equality.

Δ is the Δ of Eq. (3.8), so $\Delta = 0$ at the gel point (necessary and sufficient in this case). Equation (2.9) for the second moment now gives

$$\begin{aligned} M_2 &= \left[kTm \frac{d}{d\mu} \right]^2 \mathbf{p} = (mkT)^2 \frac{d}{d\mu} \frac{\partial \mathbf{u}}{\partial \mu} \\ &= (mkT)^2 \left(\frac{\partial^2 \mathbf{u}}{\partial \mu^2} + \frac{\partial^2 \mathbf{u}}{\partial \mathbf{a}\, \partial \mu} \frac{d\mathbf{a}}{d\mu} \right) \\ &= (mkT)^2 \left[\frac{\partial^2 \mathbf{u}}{\partial \mu^2} + \Delta^{-1} \left(\frac{\partial^2 \mathbf{u}}{\partial \mathbf{a}\, \partial \mu} \right)^2 \right] \end{aligned} \tag{3A.6}$$

[For partial derivatives, $\mathbf{u}$ is expressed according to Eq. (3.2), so the chain rule must be used to eliminate the intermediate parameter $\mathbf{a}$.] Equation (3A.2) yields the second equality. According to Eqs. (3A.4)–(3A.6), M_2 blows up at the gel point, as of course it should.

These equations give all the polymer statistics of interest in terms of the unit partition function $\mathbf{u}$ and its derivatives. Sections 4 and 5 give $\mathbf{u}$ for insertion into the formulas of this and the following subsections.

Case B: One Type of Monomer, *A–B* Bonding

Call $(A\text{–}B)$ bonds as viewed from the A group a bonds, and from the B group, b bonds. Of course, $\mathbf{a}^* = \mathbf{b}$ and $\mathbf{b}^* = \mathbf{a}$. Equation (3.3) becomes

$$\mathbf{b} = \frac{\partial \mathbf{u}}{\partial \mathbf{a}} \tag{3B.1}$$

A similar equation with $\mathbf{a}$ and $\mathbf{b}$ reversed also holds. In Eq. (3.4), the bond-partition function $\boldsymbol{l} = \frac{1}{2}(\mathbf{a}\mathbf{a}^* + \mathbf{b}\mathbf{b}^*) = \mathbf{a}\mathbf{b}$. Equation (3A.2) continues to describe the monomer concentration.

The 0th moment of the polymer concentrations is given by the polymer partition function

$$\mathbf{p} = \mathbf{u} - \mathbf{a}\mathbf{b} \tag{3B.2}$$

To obtain the second moment of the polymer concentrations, we differentiate Eqs. (3B.1) [as we did in Eq. (3.7)] to obtain the following

$$\begin{aligned}\frac{d\mathbf{a}}{d\mu}&=\frac{\partial^2\mathbf{u}}{\partial\mathbf{b}\,\partial\mu}+\frac{\partial^2\mathbf{u}}{\partial\mathbf{b}\,\partial\mathbf{a}}\frac{d\mathbf{a}}{d\mu}+\frac{\partial^2\mathbf{u}}{\partial\mathbf{b}^2}\frac{d\mathbf{b}}{d\mu}\\ \frac{d\mathbf{b}}{d\mu}&=\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mu}+\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}^2}\frac{d\mathbf{a}}{d\mu}+\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mathbf{b}}\frac{d\mathbf{b}}{d\mu}\end{aligned}\tag{3B.3}$$

Considered as a simultaneous equation in $d\mathbf{a}/d\mu$ and $d\mathbf{b}/d\mu$, Eq. (3B.3) has a matrix $\mathbf{J}$ whose determinant is

$$\Delta=\left(1-\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mathbf{b}}\right)^2-\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}^2}\frac{\partial^2\mathbf{u}}{\partial\mathbf{b}^2}\tag{3B.4}$$

Δ is the Δ of Eq. (3.8), so $\Delta=0$ at the gel point (necessary condition). Equation (2.9) for the second moment now gives

$$\begin{aligned}M_2&=\left[kTm\frac{d}{d\mu}\right]^2\mathbf{p}=(mkT)^2\frac{d}{d\mu}\frac{\partial\mathbf{u}}{\partial\mu}\\ &=(mkT)^2\left(\frac{\partial^2\mathbf{u}}{\partial\mu^2}+\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mu}\frac{d\mathbf{a}}{d\mu}+\frac{\partial^2\mathbf{u}}{\partial\mathbf{b}\,\partial\mu}\frac{d\mathbf{b}}{d\mu}\right)\\ &=(mkT)^2\left\{\frac{\partial^2\mathbf{u}}{\partial\mu^2}+\Delta^{-1}\left[\left(\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mu}\right)^2\frac{\partial^2\mathbf{u}}{\partial^2\mathbf{b}}\right.\right.\\ &\qquad\left.\left.+2\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mu}\frac{\partial^2\mathbf{u}}{\partial\mathbf{b}\,\partial\mu}\left(1-\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mathbf{b}}\right)+\left(\frac{\partial^2\mathbf{u}}{\partial\mathbf{b}\,\partial\mu}\right)^2\frac{\partial^2\mathbf{u}}{\partial^2\mathbf{a}}\right]\right\}\end{aligned}\tag{3B.5}$$

[As in Section 3A, for partial derivatives, $\mathbf{u}$ is expressed according to Eq. (3.2), so the chain rule is used to eliminate the intermediate parameters $\mathbf{a}$ and $\mathbf{b}$.] Solving Eq. (3B.3) by Cramer's rule gives $d\mathbf{a}/d\mu$ and $d\mathbf{b}/d\mu$ in Eq. (3B.5). Again, the polymer statistics are determined by $\mathbf{u}$.

The necessary and sufficient condition for a gel point given after Eq. (3.8) becomes

$$1=\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mathbf{b}}+\left(\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}^2}\frac{\partial^2\mathbf{u}}{\partial\mathbf{b}^2}\right)^{1/2}\tag{3B.6}$$

Equation (3B.6) is a consequence of the following trivial theorem: $\mathbf{J}=[a_{ij}]_{2\times 2}$ is nonnegative definite with a zero eigenvalue if $a_{11}\geqslant 0$ and $\det\mathbf{J}=0$.

Case C: Two Types of Monomer, *A*–*B* Bonding

We call the monomers bearing A groups **A** monomers, and those bearing B groups **B** monomers. Equation (3B.1) and its reverse with **a** and **b** interchanged continue to give the bond-type partition functions. In Eq. (3.4), the bond-partition function still satisfies $\mathbf{l}=\mathbf{ab}$. By Eq. (3.6) the **A**-monomer concentration is

$$n_{\mathrm{A}}=kT\frac{d\mathbf{p}}{d\mu_{\mathrm{A}}}=kT\frac{\partial\mathbf{u}}{\partial\mu_{\mathrm{A}}} \tag{3C.1}$$

and similarly for the **B**-monomer concentrations. [Out of harmless convenience, we retain the total derivative notation. It has the same force as the partial derivative notation in Eq. (3.6), however.]

The 0th moment of the polymer concentrations is given by the polymer partition function **p**. **p** has the same form as in Eq. (3B.2).

Δ in Eq. (3B.4) and the gelation criterion Eq. (3B.6) remain unchanged. The second moment of the polymer concentrations can be calculated as in Section 3B by differentiating Eqs. (3B.1), first with respect to μ_{A} and then with respect to μ_{B} to obtain analogs of Eqs. (3B.3). Equation (2.9) gives

$$M_2=\left[kT\left(m_{\mathrm{A}}\frac{d}{d\mu_{\mathrm{A}}}+m_{\mathrm{B}}\frac{d}{d\mu_{\mathrm{B}}}\right)\right]^2\mathbf{p} \tag{3C.2}$$

Recall that the operator $d/d\mu_{\mathrm{A}}=\partial/\partial\mu_{\mathrm{A}}+\partial\mathbf{a}/\partial\mu_{\mathrm{A}}\,d/\partial\mathbf{a}+\partial\mathbf{b}/\partial\mu_{\mathrm{B}}\,d/\partial\mathbf{b}$ (and similarly for $d/d\mu_{\mathrm{B}}$). After some messy algebra like that producing Eq. (3B.5), Eqs. (3.6) and the analogs of Eq. (3B.3) give

$$\begin{aligned}M_2=(kT)^2\Bigg\{&m_{\mathrm{A}}^2\frac{\partial^2\mathbf{u}}{\partial\mu_{\mathrm{A}}^2}+2m_{\mathrm{A}}m_{\mathrm{B}}\frac{\partial^2\mathbf{u}}{\partial\mu_{\mathrm{A}}\,\partial\mu_{\mathrm{B}}}+m_{\mathrm{B}}^2\frac{\partial^2\mathbf{u}}{\partial\mu_{\mathrm{B}}^2}\\&+\Delta^{-1}\Bigg[\left(m_{\mathrm{A}}\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mu_{\mathrm{A}}}+m_{\mathrm{B}}\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mu_{\mathrm{B}}}\right)^2\frac{\partial^2\mathbf{u}}{\partial^2\mathbf{b}}\\&+2\left(m_{\mathrm{A}}\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mu_{\mathrm{A}}}+m_{\mathrm{B}}\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mu_{\mathrm{B}}}\right)\left(m_{\mathrm{A}}\frac{\partial^2\mathbf{u}}{\partial\mathbf{b}\,\partial\mu_{\mathrm{A}}}+m_{\mathrm{B}}\frac{\partial^2\mathbf{u}}{\partial\mathbf{b}\,\partial\mu_{\mathrm{B}}}\right)\left(1-\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mathbf{b}}\right)\\&+\left(m_{\mathrm{A}}\frac{\partial^2\mathbf{u}}{\partial\mathbf{b}\,\partial\mu_{\mathrm{A}}}+m_{\mathrm{B}}\frac{\partial^2\mathbf{u}}{\partial\mathbf{b}\,\partial\mu_{\mathrm{B}}}\right)^2\frac{\partial^2\mathbf{u}}{\partial^2\mathbf{a}}\Bigg]\Bigg\}\end{aligned} \tag{3C.3}$$

Not surprisingly, this is Eq. (3B.5) with the operator $m_{\mathrm{A}}\,\partial/\partial\mu_{\mathrm{A}}+m_{\mathrm{B}}\,\partial/\partial\mu_{\mathrm{B}}$ replacing $m\,\partial/\partial\mu$. Again, calculation of the polymer statistics reduces to determination of the unit partition function **u**.

4. RANDOM-FLIGHT RINGS IN BRANCHED POLYMERS

Jacobson and Stockmayer$^{(15)}$ gave weights for ring formation in linear RA_2 polymers. Hoeve$^{(20)}$ applied those weights to ring formation in branched RA_f ($f \geqslant 3$) polymers. For monomers, this section extends those results from equireactivity to FSSE. Note, however, that the formalism in Section 3 can handle arbitrary ring weights, not just the random-flight weights presented here.

This section extends the ring weights for the three cases handled by Jacobson and Stockmayer to FSSE in branched polymers. The three case are (see Fig. 1): (A) systems containing RA_f monomers with (A–A) bonding; (B) systems containing A_fRB_g monomers with (A–B) bonding; and (C) systems containing both RA_f and RB_g monomers with (A–B) bonding. Like Jacobson and Stockmayer, we make extensive use of the Truesdell functions,$^{(28)}$

$$\varphi(x, s) = \sum_{j=1}^{\infty} \frac{x^j}{j^s} \tag{4.1}$$

If a polymer chain is formed by several links $\mathbf{L}$ joined end to end, the probability density (i.e., probability per unit volume) of the two ends coinciding is

$$\left[d\Big/\left(2\pi \sum b_{\mathrm{L}}^2\right)\right]^{d/2} \tag{4.2}$$

Here d is the (Euclidean) dimension in which the random walk takes place, and the sum is of the squares of the lengths b_{L} of the links $\mathbf{L}$ in the polymer chain. This expression makes

(1) *The Random Flight Assumption.*$^{(29,30)}$ The polymer chains are freely jointed so that the polymer configuration is a random walk; and

(2) *The Gaussian Approximation.*$^{(31,32)}$ The number of steps that the walk takes is large enough that the distribution of one end of the walk relative to the other is approximately a Gaussian (i.e., multivariate normal) distribution.

We now consider the separate cases.

Case A: RA_f Monomers, A–A Bonding

Let us call a unit which is a monomer a *monomer unit* and one which is a ring a *ring unit*. If the number of monomers in the ring is j, let us call the ring unit a *j ring*.

Let μ be the chemical potential of the single type of monomer in the system, z_i be the canonical partition function of a monomer unit giving rise to i bonds, and let $\mathbf{a}$ be the partition function of the polymer part on the end of an $(A\text{–}A)$ bond. By analogy with Eq. (3.2), the partition function for a monomer unit is

$$\mathbf{m} = \exp(\beta\mu) \sum_{i=0}^{f} z_i \mathbf{a}^i \tag{4A.1}$$

For this system, the partition function for a j ring is

$$\mathbf{j} = \mathbf{m}_2^j (2j)^{-1} p_j \tag{4A.2}$$

We use $\mathbf{m}_1$, $\mathbf{m}_2$, $\mathbf{m}_3$, etc., to denote the first, second, third, etc., partial derivatives of $\mathbf{m}$ with respect to $\mathbf{a}$. p_j is the probability density of closure for a ring composed of j monomers.

Figure 4 gives the interpretation of Eq. (4A.2). Consider the j monomers from which the ring will be formed. I claim that $\mathbf{m}_2$ is the partition function for any one of these monomers. (It is *not* $\mathbf{m}$ because the monomers are no longer independent units, they will be part of a single ring unit.)

Assume that the number of reacted groups i on a particular monomer has been specified. Paint one reacted functional group on this monomer black and one red. The black and red groups will attach this monomer to other monomers within the ring unit rather than to other units. Hence these groups no longer form articulation bonds. The black and red groups can be chosen in $i(i-1)$ ways. These specify extra states that z_i does not account for. Hence, instead of partition function $[\exp(\beta\mu)\, z_i \mathbf{a}^i]$, a ring monomer has partition function $[\exp(\beta\mu)\, i(i-1)\, z_i \mathbf{a}^{i-2}]$. The operator producing $[\exp(\beta\mu)\, i(i-1)\, z_i \mathbf{a}^{i-2}]$ from $[\exp(\beta\mu)\, z_i \mathbf{a}^i]$ is double differentiation, so the partition function for the monomer is $\mathbf{m}_2$. [This is an echo of the argument producing the right side of Eq. (3.3).] Since there are j monomers in the ring, this gives the first factor in Eq. (4A.2).

We now form a j chain (Fig. 4b) from the monomers. Note that the two end groups of the chain are reacted groups. There are $j!$ ways of arranging the monomers in positions $1, 2, 3 \cdots j$ of the j chain. We bond the black functional group of position i to the red functional group of position $i+1$, $i = 1, 2, 3 \cdots (j-1)$. We then divide by $j!$ to account for the indistinguishability of the monomers under quantum statistics, so the factor $j!$ never appears in Eq. (4A.2). The chain is now oriented from an initial red functional group at one end to a terminal black group at the other.

We now close the oriented j chain into a j ring. There are j distinct orderings of the monomers within the oriented j chain which produce the

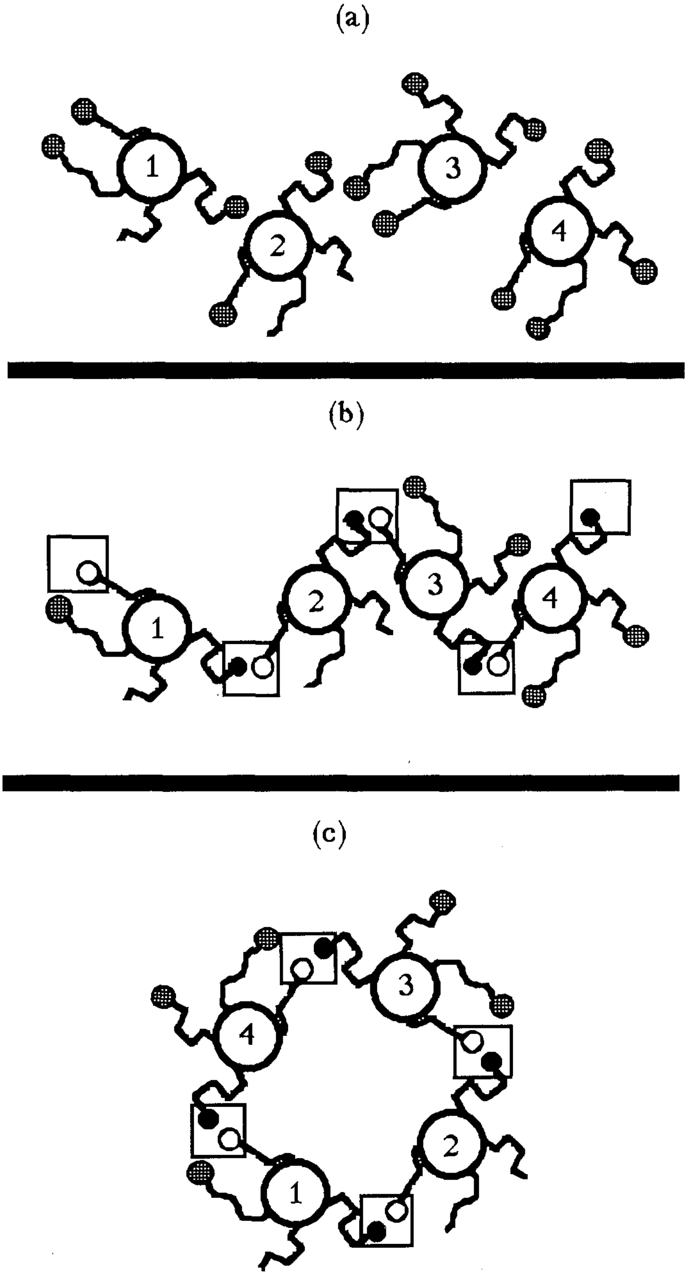


Fig. 4. This figure gives the derivation of the ring weights. We start in Fig. 4(a) with four RA_4 monomers. Their reacted groups are indicated by gray circles; the remaining functional groups are unreacted. On each monomer, we color one reacted functional group red and one black. They react red to black in Fig. 4(b) to form a chain with an initial red group and a terminal black group. In Fig. 4(c), the final stage, the bond volumes of the initial and terminal groups are identified.

same monomer order within the j ring (these may be found by breaking any of the j bonds in the j ring that the j chain produces). In addition, changing the j chain orientation by interchanging red and black does not affect the j ring produced. Hence division by $2j$ in Eq. (4A.2) reflects ring symmetries.

p_j in Eq. (4A.2) accounts for the entropy of closing the random walk. As in Section 3, denote the bond volume by v_s. Consider the partition function for the chain in Fig. 4: there is a factor v_s^{2j} implicit in it. This factor positions the $2j$ ring-forming functional groups within their respective bond volumes. If the chain closes to form a ring, factors v_s^{2j-1} still occur, but the terminal black functional group must return to the bond volume v_s belonging to the initial red functional group. When v_s is small, to a good approximation this occurs with probability $v_s p_j$, where p_j is the probability density of the j-monomer random walk returning to origin.

According to Eq. (4.2), p_j for the Gaussian walk in this situation is[15,33]

$$p_j = j^{-3/2} b^{-3} [3/(2\pi v)]^{3/2} \tag{4A.3}$$

Here v is the number of links between functional groups in a monomer and b is the "average" link length.

Equation (4A.3) *assumes that the random walks between any two functional groups in a monomer are equivalent.* In linear RA_2 monomers (where the monomers have only two functional groups), this is a trivial assumption. In RA_f monomers with $f \geqslant 3$, absence of this assumption poses difficult combinatorial problems.

In summary, the first factor $\mathbf{m}_2^j$ in Eq. (4A.2) gives the monomer partition functions within a ring; the derivatives occur because ring formation consumes two functional groups per monomer; the second factor gives the symmetry factor for ring formation; while the third factor accounts for random walk closure of the ring.

There is a very useful way of looking at Eq. (4A.2). In RA_f polymerizations, $\mathbf{m}_2^j$ is a partition function which gives the concentration of j chains separating a pair of reacted A groups. (Recall that the j chains are as in Fig. 4b and have two reacted functional groups on the end.) Again, the partition function is *not* $\mathbf{m}^j$: we must specify which A groups join the monomers together; the pair of A groups on the end also require specification. Likewise, $\mathbf{j}$ is the partition function giving the concentration of j rings. Hence $(2j)^{-1} p_j$ gives the relative frequency of j-ring to j-chain configurations. The Jacobson and Stockmayer[15] analysis of RA_2 polymerization is a special case of the present theory (see Appendix C). Hence it must likewise give $(2j)^{-1} p_j$ as the relative frequency of j-ring to

j-chain configurations. Equation (4A.2) is therefore quite consistent with the Jacobson–Stockmayer analysis.

Let

$$R = b^{-3}[3/(2\pi\nu)]^{3/2} \tag{4A.4}$$

The unit partition function is therefore

$$\mathbf{u} = \mathbf{m} + \sum_{j=1}^{\infty} \mathbf{j} = \mathbf{m} + \tfrac{1}{2}R\varphi(\mathbf{m}_2, \tfrac{5}{2}) \tag{4A.5}$$

Both Jacobson and Stockmayer$^{(15)}$ and Hoeve$^{(20)}$ use p to denote the total extent of reaction of A groups and α to denote the extent of reaction of A groups in the chain fraction. (The latter provided a convenient intermediate parameter in their theories, but is unnecessary in ours.) In this paper, p_A *denotes the total extent of reaction of A groups*:

$$fnp_A = \mathbf{a}^2 + R\varphi(\mathbf{m}_2, \tfrac{3}{2}) \tag{4A.6}$$

The first term on the right is twice the a-bond partition function [see comments following Eq. (3A.1)]. As stated before Eq. (3.5), $\frac{1}{2}\mathbf{a}^2$ is the concentration of articulation (A–A) bonds. Hence the concentration of reacted A groups forming articulation bonds is $\mathbf{a}^2$. The second term on the right represents reacted A groups forming the ring units: formation of every j ring consumes $2j$ groups. Hence, in Eq. (4A.5), $\frac{1}{2}R\mathbf{m}_2^j j^{-5/2}$ (representing the concentration of j rings) is multiplied by $2j$. The right side of Eq. (4A.6) therefore represents the total concentration of reacted A groups. The left is the total concentration of A groups (fn), multiplied by the proportion of A groups which have reacted. Hence the two sides of Eq. (4A.6) are equal.

The two terms on the right of Eq. (4A.6) can be interpreted separately as belonging to articulation bonds and ring units. Such interpretations are used several times in the Appendixes to generate the results of previous theories.

In Case A, Eqs. (4A.5) and (4A.6), in conjunction with Section 3A, constitute a formal solution to the problem of simple rings. Section 3A requires various partial derivatives of $\mathbf{u}$: the following are typical examples of the derivatives:

$$\frac{\partial \mathbf{u}}{\partial \mu} = \beta[\mathbf{m} + \tfrac{1}{2}R\varphi(\mathbf{m}_2, \tfrac{3}{2})] \tag{4A.7}$$

Compare Eqs. (4A.7) and (4A.5) for $\mathbf{u}$ and its derivative. $\mathbf{m}$ [Eq. (4A.1)], containing the factor $e^{\beta\mu}$, is multiplied by β, as is the Truesdell term of $\mathbf{u}$;

because the Truesdell function contains *powers* of $e^{\beta\mu}$, $\partial/\partial\mu$ lowers the order of the Truesdell function from $\frac{5}{2}$ to $\frac{3}{2}$.

$$\frac{\partial \mathbf{u}}{\partial \mathbf{a}} = \mathbf{m}_1 + \tfrac{1}{2}R\frac{\mathbf{m}_3}{\mathbf{m}_2}\,\varphi(\mathbf{m}_2, \tfrac{3}{2}) \tag{4A.8}$$

This equation gives a typical pattern for differentiation of Truesdell functions with respect to **a**. The differentiation lowers their order by one and premultiplies them by the factor shown.

The equations of this subsection, though constituting a formal solution to the problem of simple rings, seem to be intractable to computer solution in their present form. When the Principle of Equireactivity holds, however, new parameters allow computer solution of the equations. Section 5 carries this solution out.

Because of the computational intractability of the general equations, we only give the unit partition function and extents of reaction specific to the next two subsections. These unit partition functions and their derivatives [which are similar to Eqs. (4A.7) and (4A.8)] can then be substituted into the equations of Section 3.

Case B: A_fRB_g Monomers, A–B Bonding

In this and the following subsection, we mainly quote results since they are analogous to the first subsection. The partition function for a monomer unit is

$$\mathbf{m} = \exp(\beta\mu) \sum_{\substack{i=0,f\\ j=0,g}} z_{i,j}\mathbf{a}^i\mathbf{b}^j \tag{4B.1}$$

Here $z_{i,j}$ is the canonical partition function of a monomer unit having i reacted A groups and j reacted B groups; **a** is the bond-type partition function for the polymer part on the end of an A–B bond, as viewed from the A group; similarly **b**, as viewed from the B group.

The partition function for a j ring is

$$\mathbf{j} = \mathbf{m}_{11}^j\, j^{-1} p_j \tag{4B.2}$$

$\mathbf{m}_{11}$ is the second partial derivative of **m**, once with respect to **a** and once with respect to **b**. $\mathbf{m}_{12}$ represents the third partial of **m**, once with respect to **a** and twice with respect to **b**, and so forth.

The first factor in Eq. (4B.2) gives the monomer partition functions within the ring; the partial derivatives occur because ring formation consumes two functional groups per monomer, one of type A, the other of type B {if a monomer has i reacted A groups and j reacted B groups, then the monomer-unit partition function term $\exp(\beta\mu)\, z_{i,j}\mathbf{a}^i\mathbf{b}^j$ is replaced by $ij\exp(\beta\mu)\, z_{i,j}\mathbf{a}^{i-1}\mathbf{b}^{j-1} = \partial^2/\partial\mathbf{a}\,\partial\mathbf{b}[\exp(\beta\mu)\, z_{i,j}\mathbf{a}^i\mathbf{b}^j]$ in the ring}; the second factor gives the symmetry factor for forming the ring (the *directed A–B* bonds remove the factor of two present in the previous case, because the bonds now orient the ring); while the third factor accounts for random walk closure of the ring.

In this case, the probability density for return to origin is

$$p_j = j^{-3/2} b^{-3} [3/(2\pi v)]^{3/2} \tag{4B.3}$$

Again v is the number of links between functional groups in a monomer and b is the "average" link length. Equation (4B.3), like Eq. (4A.3), assumes that the random walks between any two functional groups in a monomer are equivalent.

We define R as before

$$R = b^{-3} [3/(2\pi v)]^{3/2} \tag{4B.4}$$

In this case, the unit partition function is

$$\mathbf{u} = \mathbf{m} + \sum_{j=1}^{\infty} \mathbf{j} = \mathbf{m} + R\varphi(\mathbf{m}_{11}, \tfrac{5}{2}) \tag{4B.5}$$

The extents of reaction p_A for A groups and p_B for B groups satisfy

$$fnp_A = \mathbf{ab} + R\varphi(\mathbf{m}_{11}, 3/2) = gnp_B \tag{4B.6}$$

The first term in the middle is the bond partition function [see comments following Eq. (3B.1)]. As stated following Eq. (3.4), **ab** is the concentration of articulation (A–B)-bonds. Hence the concentration of reacted A groups forming articulation bonds is **ab**. The second term in the numerator represents reacted A groups forming the ring units: formation of every j ring consumes j A groups. Hence, in Eq. (4B.5), $R\mathbf{m}_{11}^{j} j^{-5/2}$ (representing the concentration of j rings) is multiplied by j. The middle of Eq. (4B.6) therefore represents the total concentration of reacted A groups, which is the same as the left side of Eq. (4B.6). The second equality follows because the concentration of reacted A groups must equal the concentration of reacted B groups, since every A group reacts with exactly one B group.

Case C: RA_f and RB_g Monomers, *A–B* Bonding

Once again, we mainly quote results. Let **A** index an RA_f monomer and **B**, an RB_g monomer. Let the partition functions for RA_f and RB_g monomer units be

$$\mathbf{m}_{\mathrm{A}} = \exp(\beta\mu_{\mathrm{A}}) \sum_{i=0}^{f} z_{\mathrm{A}i}\mathbf{a}^{i} \qquad (4\mathrm{C}.1\mathrm{a})$$

$$\mathbf{m}_{\mathrm{B}} = \exp(\beta\mu_{\mathrm{B}}) \sum_{i=0}^{g} z_{\mathrm{B}i}\mathbf{b}^{i} \qquad (4\mathrm{C}.1\mathrm{b})$$

Because of *A–B* bonding, every ring unit contains equal numbers of RA_f and RB_g monomers. *We call rings containing j* **A** *monomers and j* **B** *monomers j rings. In Case C, j rings contain a total of* 2*j monomers.* The *j*-ring partition function is

$$\mathbf{j} = \mathbf{m}_{\mathrm{A}2}^{j}\mathbf{m}_{\mathrm{B}2}^{j}(2j)^{-1}p_j \qquad (4\mathrm{C}.2)$$

The first factor in Eq. (4C.2) gives the monomer partition functions within a ring for the RA_f monomers, the second for the RB_g monomers. $\mathbf{m}_{\mathrm{A}2}$ is the second partial derivative of $\mathbf{m}_{\mathrm{A}}$ with respect to **a**; $\mathbf{m}_{\mathrm{B}2}$ is the second partial derivative of $\mathbf{m}_{\mathrm{B}}$ with respect to **b**. As in Section 4A, the double derivatives occur because ring formation consumes two functional groups per monomer. The second factor gives the symmetry factor for forming the ring. (There is a factor of two as in Section 4A. The *A–B* bonds, though directed, do *not* orient the ring in this case: they occur in oppositely directed apirs.) The third factor accounts for random walk closure of the ring. In this case, the probability density for return to origin is

$$p_j = j^{-3/2}\{3/[2\pi(v_{\mathrm{A}}b_{\mathrm{A}}^2 + v_{\mathrm{B}}b_{\mathrm{B}}^2)]\}^{3/2} \qquad (4\mathrm{C}.3)$$

Here v_{A} is the number of links between the groups on the **A** monomers; v_{B} the corresponding number for **B** monomers. b_{A} and b_{B} are the corresponding average link lengths. Equation (4C.3) assumes that the random walks between any two *A* groups on an **A** monomer are equivalent, and likewise for *B* groups on **B** monomers.

We define

$$R = \{3/[2\pi(v_{\mathrm{A}}b_{\mathrm{A}}^2 + v_{\mathrm{B}}b_{\mathrm{B}}^2]\}^{3/2} \qquad (4\mathrm{C}.4)$$

The unit partition function is

$$\begin{aligned}\mathbf{u} &= \mathbf{m}_{\mathrm{A}} + \mathbf{m}_{\mathrm{B}} + \sum_{j=1}^{\infty} \mathbf{j} \\ &= \mathbf{m}_{\mathrm{A}} + \mathbf{m}_{\mathrm{B}} + \tfrac{1}{2}R\varphi(\mathbf{m}_{\mathrm{A}2}\mathbf{m}_{\mathrm{B}2}, \tfrac{5}{2}) \qquad (4\mathrm{C}.5)\end{aligned}$$

If n_{A} and n_{B} are the concentrations of **A** and **B** monomers, respectively, then the extents of reaction p_A for A groups and p_B for B groups satisfy

$$fn_{\mathrm{A}}\, p_A = \mathbf{ab} + R\varphi(\mathbf{m}_{\mathrm{A}2}\mathbf{m}_{\mathrm{B}2}, \tfrac{3}{2}) = gn_{\mathrm{B}}\, p_B \tag{4C.6}$$

The first term in the middle is the bond partition function [see comments following Eq. (3B.1)]. As in Section 4B, the concentration of reacted A groups forming articulation bonds is **ab**. The second term in the middle represents reacted A groups forming the ring units: formation of every j ring consumes $2j$ A groups (there are j **A** monomers in the j ring, each of which contributes two reacted A groups). Hence, in Eq. (4C.5), $\frac{1}{2}R\mathbf{m}_{\mathrm{A}2}^{j}\mathbf{m}_{\mathrm{B}2}^{j}\, j^{-5/2}$ (representing the concentration of j rings) is multiplied by $2j$. The middle of Eq. (4C.6) therefore represents the total concentration of reacted A groups, which is the same as the left side of Eq. (4C.6). As in Eq. (4B.6), the second equality follows because the concentration of reacted A groups must equal the concentration of reacted B groups.

5. EQUIREACTIVE RING FORMATION

This section gives a practical method for computer solution of Section 4 when the Principle of Equireactivity holds. In each case, we can represent the zero and second moments and the extent of reaction in terms of a free parameter [$\mathbf{m}_2$ in Cases A and C; $\mathbf{m}_{11}$ in Case B]. Varying the free parameter gives the relationship between the moments and the extent of reaction. The gel point criterion fixes the free parameter and gives the critical extent of reaction as a function of the ring parameter

$$r = R/n \tag{5.1}$$

n is the total monomer concentration. [In Case C, $n = n_{\mathrm{A}} + n_{\mathrm{B}}$.] The larger r is, the greater the tendency to ring formation. In our analysis, r and n [or r, n_{A}, and n_{B} in Case C] are independent variables.

The relevant equations, being too long, are not given explicitly. Instead, the subsections give **u** and its partial derivatives for substitution into Section 3. This method is effective for computer programming. Section 5D comments on the computer results.

Case A: Equireactive RA_f Monomers, A–A Bonding

In this subsection, we assume a single RA_f monomer type, symmetric (A–A) bonds, and equireactivity:

$$\mathbf{m} = e^{\beta\mu} z_0 (1 + e^{-\beta\varepsilon/2}\mathbf{a})^f \tag{5A.1}$$

μ is the chemical potential of a monomer. z_0 is the intensive canonical partition function an unreacted monomer. ε is the standard free energy change occurring when two specified functional groups react.(3) (ε denotes the free energy because the $A_f RB_g$ model usurps the more common g.) ε includes contributions both from mean-field reorientation of solvent molecules and from polymer bond energy and entropy. It also includes entropy costs from localization of the two functional groups. $\varepsilon/2$ is therefore the standard free energy change due to reaction of either of the functional groups. **a** is, as usual, the partition function for the polymer part on the end of an A–A bond. The binomial form of Eq. (5A.1) reflects the independent equireactivity of the f functional groups on a monomer in the Flory RA_f model.

The reparametrization allowing solution of the equireactive case hinges on the introduction of

$$s = e^{\beta\varepsilon}(1 + e^{-\beta\varepsilon/2}\mathbf{a})^2\,\mathbf{m}_2/n \tag{5A.2}$$

(Recall that $\mathbf{m}_2$ is the second partial of **m** with respect to **a**.) All the partials of **m** with respect to **a** can be expressed in terms of $\mathbf{m}_2$ and s:

$$\begin{aligned} \mathbf{m}n^{-1} &= s/[f(f-1)] \\ \mathbf{m}_1 n^{-1/2} &= (\mathbf{m}_2 s)^{1/2}/(f-1) \\ \mathbf{m}_3 n^{1/2} &= (f-2)\,\mathbf{m}_2(\mathbf{m}_2/s)^{1/2} \\ \mathbf{m}_4 n &= (f-2)(f-3)\,\mathbf{m}_2^2/s \end{aligned} \tag{5A.3}$$

The factors of n ensure that the right sides of Eqs. (5A.3) are nondimensional.

After division by n, Eq. (3A.2) and (4A.7) for the monomer concentration become

$$1 = s/[f(f-1)] + \tfrac{1}{2}r\varphi(\mathbf{m}_2, \tfrac{3}{2}) \tag{5A.4}$$

s is therefore a known function of $\mathbf{m}_2$.

u in Eq. (4A.5) and its partials are given by

$$\begin{aligned} \mathbf{u}n^{-1} &= s/[f(f-1)] + \tfrac{1}{2}r\varphi(\mathbf{m}_2, \tfrac{5}{2}) \\ \frac{\partial \mathbf{u}}{\partial \mathbf{a}} n^{-1/2} &= [(\mathbf{m}_2/s)^{1/2}/(f-1)][s + \tfrac{1}{2}r(f-1)(f-2)\,\varphi(\mathbf{m}_2, \tfrac{3}{2})] \\ \frac{\partial^2 \mathbf{u}}{\partial \mathbf{a}^2} &= (\mathbf{m}_2/s)\{s + \tfrac{1}{2}r(f-2)[(f-2)\,\varphi(\mathbf{m}_2, \tfrac{1}{2}) - \varphi(\mathbf{m}_2, \tfrac{3}{2})]\} \end{aligned} \tag{5A.5}$$

$\partial/\partial\mu$ multiplies these expressions by β and lowers the order of the Truesdell functions by 1 [see Eq. (4A.7) et seq.]. This allows calculation of any of the partials of Section 3.

Case B: Equireactive A_fRB_g Monomers, A–B Bonding

In this subsection, we assume a single A_fRB_g monomer type, asymmetric (A–B) bonds, and equireactivity

$$\mathbf{m} = e^{\beta\mu} z_0 (1 + e^{-\beta\varepsilon/2}\mathbf{a})^f (1 + e^{-\beta\varepsilon/2}\mathbf{b})^g \tag{5B.1}$$

μ, z_0, and ε have interpretations as in Eq. (5A.1). **a** and **b** have their usual interpretations as bond-type partition functions. The binomial form of Eq. (5B.1) reflects the independent equireactivity of the f A groups and g B groups on a monomer in the A_fRB_g model.

The reparametrization allowing solution of this case is

$$\begin{aligned} s_a &= e^{\beta\varepsilon}(1 + e^{-\beta\varepsilon/2}\mathbf{a})^2\, \mathbf{m}_{11}/n \\ s_b &= e^{\beta\varepsilon}(1 + e^{-\beta\varepsilon/2}\mathbf{b})^2\, \mathbf{m}_{11}/n \\ s &= e^{\beta\varepsilon}(1 + e^{-\beta\varepsilon/2}\mathbf{a})(1 + e^{-\beta\varepsilon/2}\mathbf{b})\, \mathbf{m}_{11}/n = (s_a s_b)^{1/2} \end{aligned} \tag{5B.2}$$

(Recall that $\mathbf{m}_{11}$ is the second partial of **m**, once with respect to **a**, and once with respect to **b**.) s_a and s_b serve as intermediate parameters which will be eliminated in favor of s. All the partials of **m** can be expressed in terms of $\mathbf{m}_{11}$ and these parameters

$$\begin{aligned} \mathbf{m} n^{-1} &= s/(fg) \\ \mathbf{m}_{10} n^{-1/2} &= (s/s_a)^{1/2} (\mathbf{m}_{11} s)^{1/2}/g \\ \mathbf{m}_{20} &= (s/s_a)\, \mathbf{m}_{11}(f-1)/g \\ \mathbf{m}_{21} n^{1/2} &= (s/s_a)^{1/2}(f-1)\, \mathbf{m}_{11}(\mathbf{m}_{11}/s)^{1/2} \\ \mathbf{m}_{22} n &= (f-1)(g-1)\, \mathbf{m}_{11}^2/s \\ \mathbf{m}_{31} n &= (s/s_a)(f-1)(f-2)\, \mathbf{m}_{11}^2/s \end{aligned} \tag{5B.3}$$

The right sides of Eqs. (5B.3) are again nondimensional. The remaining partials we require can be obtained from Eqs. (5B.3) by interchanging (f, s_a) and (g, s_b). The intermediate parameters s_a and s_b disappear in the formulas of Section 3 because of the identity $(s/s_a)(s/s_b) = 1$. Equations (5B.3) have been written in a form facilitating this cancellation and initial factors of (s/s_a) and (s/s_b) need not be programmed into a computer.

After division by n, Eqs. (3A.2) and (4B.5) for the monomer concentration become

$$1 = s/(fg) + r\varphi(\mathbf{m}_{11}, \tfrac{3}{2}) \tag{5B.4}$$

s is therefore a known function of $\mathbf{m}_{11}$.

$\mathbf{u}$ in Eq. (4B.5) and its partials are given by

$$\begin{aligned}
\mathbf{u}n^{-1} &= s/(fg) + r\varphi(\mathbf{m}_{11}, \tfrac{5}{2}) \\
\frac{\partial \mathbf{u}}{\partial \mathbf{a}} n^{-1/2} &= (s/s_a)^{1/2}[(\mathbf{m}_{11}/s)^{1/2}/g] \\
&\quad \cdot \{s + r(f-1)\, g\varphi(\mathbf{m}_{11}, \tfrac{3}{2})\} \\
\frac{\partial^2 \mathbf{u}}{\partial \mathbf{a}^2} &= (s/s_a)(\mathbf{m}_{11}/s)[(f-1)/g] \\
&\quad \cdot \{s + rg[(f-1)\,\varphi(\mathbf{m}_{11}, \tfrac{1}{2}) - \varphi(\mathbf{m}_{11}, \tfrac{3}{2})]\} \\
\frac{\partial^2 \mathbf{u}}{\partial \mathbf{a}\,\partial \mathbf{b}} &= (\mathbf{m}_{11}/s)\{s + r(f-1)(g-1)\,\varphi(\mathbf{m}_{11}, \tfrac{1}{2})\}
\end{aligned} \tag{5B.5}$$

Interchange of $(f, s_a, \mathbf{a})$ and $(g, s_b, \mathbf{b})$ gives the remaining partials with respect to $\mathbf{a}$ and $\mathbf{b}$. $\partial/\partial\mu$ multiplies these expressions by β and lowers the order of the Truesdell functions by 1 [see Eq. (4A.7) et seq.] as before, yielding the remaining partials of Section 3.

Case C: Equireactive RA_f–RB_g Monomers, A–B Bonding

In this subsection, we assume two monomer types, **A** (RA_f) and **B** (RB_g), asymmetric (A–B) bonds between them, and equireactivity:

$$\mathbf{m}_{\mathrm{A}} = \exp(\beta\mu_{\mathrm{A}})\, z_{\mathrm{A}0}(1 + e^{-\beta\varepsilon/2}\mathbf{a})^f \tag{5C.1a}$$

$$\mathbf{m}_{\mathrm{B}} = \exp(\beta\mu_{\mathrm{B}})\, z_{\mathrm{B}0}(1 + e^{-\beta\varepsilon/2}\mathbf{b})^g \tag{5C.1b}$$

μ, z_0, and ε have interpretations as in Eq. (5A.1). In this case, $\mathbf{m}$, μ, and z_0 have subscripts reflecting the two monomer types. $\mathbf{a}$ and $\mathbf{b}$ have their usual interpretations as bond-type partition functions. The binomial form of Eqs. (5C.1) reflects the independent equireactivity of the functional groups in the RA_f–RB_g model.

Define

$$n = n_{\mathrm{A}} + n_{\mathrm{B}}, \qquad x_{\mathrm{A}} = n_{\mathrm{A}}/n, \qquad x_{\mathrm{B}} = n_{\mathrm{B}}/n$$

n is the total monomer concentration, and x_{A} and x_{B} are the number fractions of monomers of type **A** and **B**, respectively.

The reparametrization allowing solution of this case is

$$\begin{aligned} s_{\mathrm{A}} &= e^{\beta\varepsilon}(1+e^{-\beta\varepsilon/2}\mathbf{a})^2\,\mathbf{m}_{\mathrm{A}2}/n \\ s_{\mathrm{B}} &= e^{\beta\varepsilon}(1+e^{-\beta\varepsilon/2}\mathbf{b})^2\,\mathbf{m}_{\mathrm{B}2}/n \end{aligned} \tag{5C.2}$$

We also define

$$\mathbf{m}_2 = \mathbf{m}_{\mathrm{A}2}\mathbf{m}_{\mathrm{B}2} \tag{5C.3}$$

$\mathbf{m}_{\mathrm{A}2}$ and $\mathbf{m}_{\mathrm{B}2}$ serve as intermediate parameters which will be eliminated in favor of $\mathbf{m}_2$. All the partials of $\mathbf{m}$ can be expressed in terms of $\mathbf{m}_{\mathrm{A}2}$, $\mathbf{m}_{\mathrm{B}2}$, and the parameters in Eq. (5C.2). These equations have the same form as Eqs. (5A.3), with one set for **A** monomers and one set for **B** monomers. In Eqs. (5A.3) replacing $\mathbf{m}$ by $\mathbf{m}_{\mathrm{A}}$ and s by s_{A} yields the equations for **A** monomers; replacing $\mathbf{m}$ by $\mathbf{m}_{\mathrm{B}}$, s by s_{B}, and f by g, yields the equations for **B** monomers. n remains unchanged (and hence unsubscripted in the two sets of equations).

The intermediate parameters $\mathbf{m}_{\mathrm{A}2}$ and $\mathbf{m}_{\mathrm{B}2}$ disappear in the formulas of Section 3 because of the Eq. (5C.3).

After division by n, Eqs. (3C.1) and (4C.5) for the monomer concentrations become

$$x_{\mathrm{A}} = s_{\mathrm{A}}/[f(f-1)] + \tfrac{1}{2}r\varphi(\mathbf{m}_2, \tfrac{3}{2}) \tag{5C.4a}$$

$$x_{\mathrm{B}} = s_{\mathrm{B}}/[g(g-1)] + \tfrac{1}{2}r\varphi(\mathbf{m}_2, \tfrac{3}{2}) \tag{5C.4b}$$

s_{A} and s_{B} are therefore known functions of $\mathbf{m}_2$.

$\mathbf{u}$ in Eq. (4C.5) and its partials are given by

$$\begin{aligned} \mathbf{u}n^{-1} &= s_{\mathrm{A}}/[f(f-1)] + s_{\mathrm{B}}/[g(g-1)] + \tfrac{1}{2}r\varphi(\mathbf{m}_2, \tfrac{5}{2}) \\ \frac{\partial\mathbf{u}}{\partial\mathbf{a}}n^{-1/2} &= (\mathbf{m}_{\mathrm{A}2}^{1/2}/\mathbf{m}_2^{1/4})[(\mathbf{m}_2^{1/2}/s_{\mathrm{A}})^{1/2}/(f-1)] \\ &\quad\cdot\{s_{\mathrm{A}} + \tfrac{1}{2}r(f-1)(f-2)\,\varphi(\mathbf{m}_2, \tfrac{3}{2})\} \\ \frac{\partial^2\mathbf{u}}{\partial\mathbf{a}^2} &= (\mathbf{m}_{\mathrm{A}2}/\mathbf{m}_2^{1/2})(\mathbf{m}_2^{1/2}/s_{\mathrm{A}}) \\ &\quad\cdot\{s_{\mathrm{A}} + \tfrac{1}{2}r(f-2)[(f-2)\,\varphi(\mathbf{m}_2, \tfrac{1}{2}) - \varphi(\mathbf{m}_2, \tfrac{3}{2})]\} \\ \frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mathbf{b}} &= [\mathbf{m}_2^{1/2}/(s_{\mathrm{A}}s_{\mathrm{B}})^{1/2}]\,\tfrac{1}{2}r(f-2)(g-2)\,\varphi(\mathbf{m}_2, \tfrac{1}{2}) \end{aligned} \tag{5C.5}$$

interchange of $(f, s_{\mathrm{A}}, \mathbf{a}, \mathbf{m}_{\mathrm{A}2})$ and $(g, s_{\mathrm{B}}, \mathbf{b}, \mathbf{m}_{\mathrm{B}2})$ gives the remaining partials with respect to **a** and **b**. The intermediate parameters $\mathbf{m}_{\mathrm{A}2}$ and $\mathbf{m}_{\mathrm{B}2}$

disappear in the formulas of Section 3 because of the identity $\mathbf{m}_{A2}\mathbf{m}_{B2}/\mathbf{m}_2 = 1$. Equations (5C.5) have been written in a form facilitating this cancellation, so that the first factor of $\partial\mathbf{u}/\partial\mathbf{a}$ and $\partial^2\mathbf{u}/\partial\mathbf{a}^2$ (and similarly, the first factor of $\partial\mathbf{u}/\partial\mathbf{b}$ and $\partial^2\mathbf{u}/\partial\mathbf{b}^2$) need not be programmed into a computer. As before, $\partial/\partial\mu_A$ and $\partial/\partial\mu_B$ both multiply these expressions by β and lower the order of the Truesdell functions by 1 [see Eq. (4A.7) et seq.], *except*: both $\partial/\partial\mathbf{a}$ and $\partial/\partial\mu_A$ annihilate the second term $\mathbf{m}_B$ of $\mathbf{u}$ [Eq. (4C.5)] and its derivatives (and similarly, $\partial/\partial\mathbf{b}$ and $\partial/\partial\mu_B$ annihilate the first term $\mathbf{m}_A$ and its derivatives. Note the single-term form of $\partial^2\mathbf{u}/\partial\mathbf{a}\,\partial\mathbf{b}$ above). For example, compare $\partial\mathbf{u}/\partial\mathbf{a}$ to the single-term form of

$$\frac{\partial^2\mathbf{u}}{\partial\mathbf{a}\,\partial\mu_\mathbf{B}}\,n^{-1/2} = (\mathbf{m}_{\mathbf{A}2}^{1/2}/\mathbf{m}_2^{1/4})(\mathbf{m}_2^{1/2}/s_\mathbf{A})^{1/2}$$

$$\cdot\,\tfrac{1}{2}r(f-2)\,\varphi(\mathbf{m}_2, \tfrac{1}{2})$$

This gives the remaining partials of Section 3C.

D: Computer Results

Results appear in Fig. 5. In order to introduce common scales for the moment graphs in Cases A and B, we graph the ordinates M_0/n and nm^2/M_2 against p_A. The scaling factors n and nm^2 are the values M_0 and M_2 assume if $p_A = 0$. The ordinates therefore always lie in the interval [0, 1]. In Case C, the ordinates are M_0/n and $(n_A m_A^2 + n_B m_B^2)/M_2$. Because M_1 is a constant [see Eqs. (2.8) and (2.9)], and because $MW_n = M_1/M_0$ and $MW_w = M_2/M_1$, the moment graphs are similar to corresponding ones for molecular weight averages.

Similarly, in the graphs of critical extents of reaction p_{Ac} vs. ring parameter r, the ordinate is the relative gel point

$$\rho(p_{Ac}) = (p_{Ac0}^{-1} - p_{Ac}^{-1})/(p_{Ac0}^{-1} - 1) \tag{5D.1}$$

p_{Ac0} is the critical extent of reaction when the ring parameter $r = 0$ [and is given by Eq. (1.1) for Flory's RA_f model]. $\rho(p_{Ac}) = 0$ at $r = 0$ and increases as the critical extent of reaction p_{Ac} increases. Physically, the maximum value $\rho(p_{Ac})$ may assume is 1, since critical extents of reaction p_{Ac} may not exceed 1. $\rho(p_{Ac})$ measures the change in p_{Ac} due to the presence of rings.

Analytic results in Appendixes E and F for $r = 0$ and $r = \infty$ provided computing checks. Experimental ring parameters r are typically between 0.1 and 3.0. As Eqs. (4A.4), (4B.4), and (4C.4) indicate, r increases if the random walk between groups on the same monomer is made shorter. r also increases with increasing dilution.

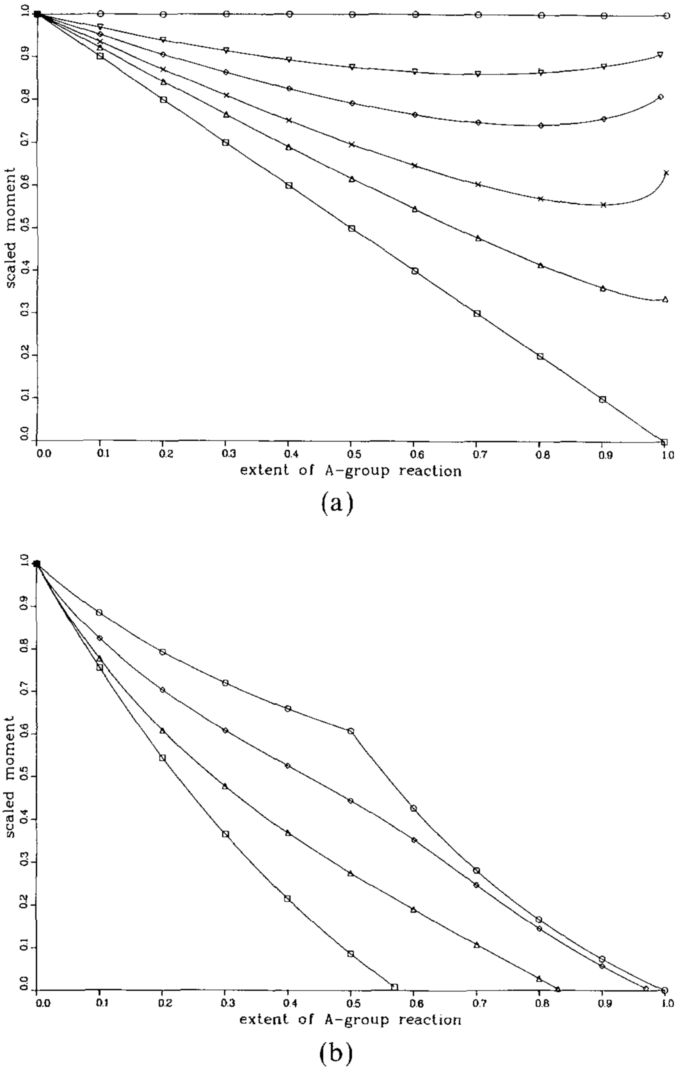
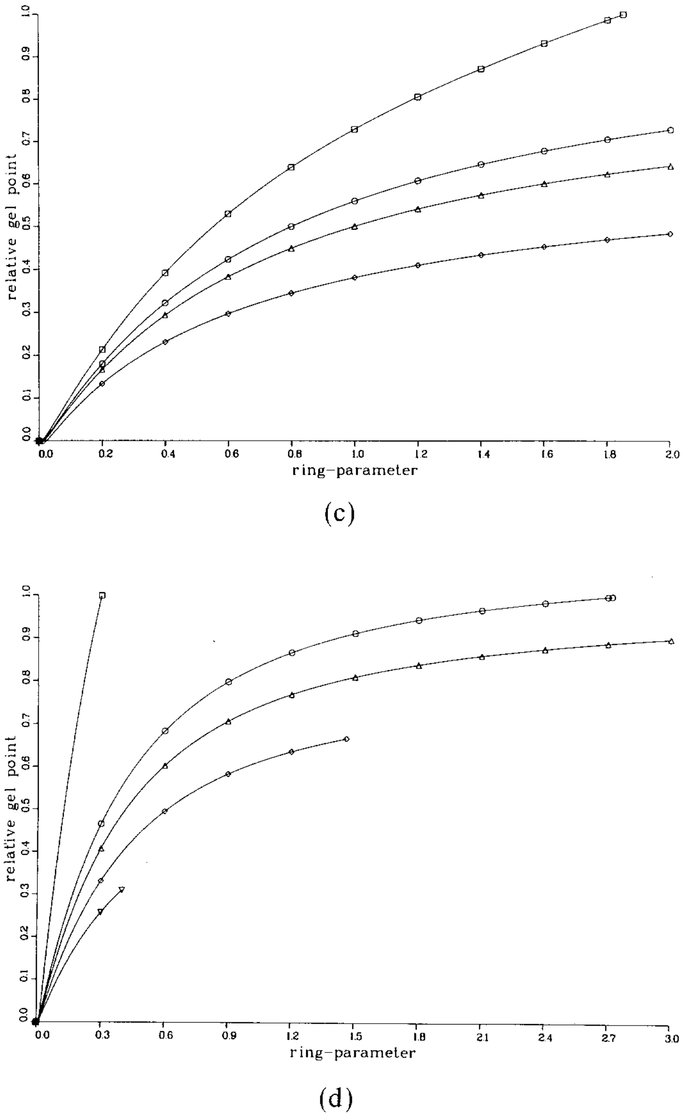


Fig. 5. (a) M_0/n vs. p_A for an RA_2 system. The curves have different ring parameters r: 0.0 (box), 0.5 (pyramid), 1.0 (cross), 2.0 (diamond), 4.0 (wedge), and ∞ (octagon). (b) $(n_A m_A^2 + n_B m_B^2)/M_2$ vs. p_A for an RA_2–RB_4 system in which $x_A = \frac{2}{3}$ and $x_B = \frac{1}{3}$, so that concentrations of A groups and B groups are equal and $p_A = p_B$. The relative molecular masses of the species are $m_A = 146$ and $m_B = 136$. The curves have different ring parameters r: 0.0 (box), 1.0 (pyramid), 10.0 (diamond), and ∞ (octagon). (c) $\rho(p_{Ac})$ vs. r for RA_f systems. The curves are for f equaling: 3 (box), 4 (octagon), 5 (pyramid), and ∞ (diamond). (d) $\rho(p_{Ac})$ vs. r for RA_4–RB_2 systems. The curves are for different number fractions x_A of RA_4 monomers equaling: 0.2 (box), 0.3 (octagon), $\frac{1}{3}$ (pyramid), 0.4 (diamond), and 0.5 (wedge).



(c)

(d)

Fig. 5 (*continued*)

The text following also gives physical interpretations for $r = \infty$. These provide some intuitive background for more realistic values of r. *Recall that the interpretations and graphs are limited by our restriction to simple rings.* The discussion speculates on the absence of this restriction.

Figure 5(a) graphs M_0/n vs. p_A for RA_2 polymer systems. The r values, from bottom to top, are $r = 0.0$, 0.5, 1.0, 2.0, 4.0, and ∞. (Jacobson and Stockmayer(15) also investigated this case theoretically. See Appendix C.) For $r = 0$ (no rings), the graph is linear because all reactions are intermolecular: every extra bond joins two more polymers together. This behavior is typical of M_0/n when $r = 0$. For $r = \infty$ (infinite tendency to ring formation), there is no branching: all polymers are monomeric, i.e., either monomers or 1 rings. As p_{Ac} increases, more and more monomers react with themselves, but $M_0/n = 1$ remains the same.

The remaining curves show the unusual feature of this graph: M_0/n is not necessarily a decreasing function of p_A. The ARB and RA_2–RB_2 models also display this behavior. For all these models, nm^2/M_2 behaves similarly. This behavior occurs because r, the ratio of j rings to j chains [see Eq. (4A.3) et seq.], is fixed. As p_A increases, the concentration of the larger chains initially increases, but finally monomers are driven into the smaller rings in order to consume functional groups. Since the j ring to j chain ratio is constant, this implies a decrease in the moments, as shown in Figure 5A. This behavior does not occur for monomers other than RA_2, ARB, and RA_2–RB_2: other types of monomers can branch out of simple rings in order to consume functional groups.

Figure 5(b) graphs $(n_{\mathrm{A}} m_{\mathrm{A}}^2 + n_{\mathrm{B}} m_{\mathrm{B}}^2)/M_2$ vs. p_A for an RA_2–RB_4 model. Here $x_{\mathrm{A}} = \frac{2}{3}$ and $x_{\mathrm{B}} = \frac{1}{3}$ (concentrations of A and B groups are equal). $m_{\mathrm{A}} = 146$ and $m_{\mathrm{B}} = 136$ (chosen because these are the relative molecular masses for adipic and pentaerythritol, respectively, an actual RA_2–RB_4 system). The r values, from bottom to top, are $r = 0.0$, 1.0, 10.0, and ∞. The curves intersect the x axis at the gel points ($M_2 = \infty$), e.g., $p_{Ac} = 3^{-1/2} = 0.577\cdots$ for $r = 0$.

The curve for $r = \infty$ is typical: the portion left of the cusp represents formation of 1 rings from monomers. For an RA_f–RB_g model, 1 rings are dimeric, one **A** monomer and one **B** monomer, so 1 rings contribute to the moments in RA_2–RB_4 models. At the cusp, the 1 rings are saturated, so the polymers start to form articulation bonds. As the reader can verify, articulation occurs if $f \geqslant 3$, $g \geqslant 3$; if $f = 2$, $g \geqslant 3$ and $x_{\mathrm{A}} > x_{\mathrm{B}}$; or (by interchange) if $f > 3$, $g = 2$ and $x_{\mathrm{A}} < x_{\mathrm{B}}$.

A cusp occurs for A_fRB_g models if $f \geqslant 2$, $g \geqslant 2$. For A_fRB_g models, the left portion of the curve before the cusp is constant at 1 because 1 rings are monomeric in A_fRB_g models.

Gelation occurs only at $p_{Ac} = 1$ because each 1 ring has two unreacted

B groups available for articulation bonds, so the 1 rings cannot branch. Hence the 1 rings must be joined end-to-end to form an infinite network. This occurs only at complete reaction $p_{Ac} = 1$. In general, if sufficient branching from 1 rings can produce gelation, $p_{Ac} < 1$; if not, then gelation does not occur. The reader can work out the various cases if he wishes; Appendix E gives some analytic results.

Figure 5(c) gives the relative gel point $\rho(p_{Ac})$ vs. r for RA_f models, $f = 3$, 4, 5, and ∞, from top to bottom. Figure 5(c) displays unexpected behavior at the origin. The presence of rings initially lowers the gel point (!). This can be verified analytically for the RA_f model and is due to a singularity of the Truesdell function $\varphi(x, \frac{5}{2})$ at $x = 1$. This singularity is a negative power of $\ln x$ and rapidly becomes negligible away from $x = 1$.

Hence rings, if very infrequent, stabilize large aggregates and aid gelation. If more frequent, they uselessly consume functional groups. I have not detected this effect numerically in the other models, nor have I bothered to verify it analytically in those cases. The result is purely theoretical. Even in the RA_f case, the ring parameters required (<0.02) are too small to be achieved experimentally and the perturbation of the gel point (0.1%) is likewise too small for experimental detection.

The RA_3 model in Figure 5(c) shows a critical dilution $r \cong 1.85$, beyond which gelation cannot occur. In the RA_3 model, a 1 ring has only a single unreacted A group available for articulation bonding. Hence, in this model, the 1 rings terminate polymer branches and a critical dilution occurs. For the similar reasons, the RA_3–RB_2 (or symmetrically, RA_2–RB_3) model is the only other model which *always* displays a critical dilution, although, as described below, depending on the relative concentrations of the species, some other RA_f–RB_g models also do so.

Figure 5(d) displays behavior more typical of the RA_f–RB_2 (or RA_2–RB_g) models. The curves graph relative gel points $\rho(p_{Ac})$ vs. ring parameter r, for the RA_4–RB_2 model. The values of the A monomer number fraction x_{A} are, from top to bottom, 0.2, 0.3, $\frac{1}{3}$, 0.4, and 0.5. $x_{\mathrm{A}} = \frac{1}{3}$ for equal concentrations of A and B groups. At this equimolar x_{A}, there is no critical dilution and the curve continues out to $r = \infty$. At other x_{A}'s, for large enough r, the minority functional group is consumed in rings before gelation occurs and the curves stop. For $x_{\mathrm{A}} = 0.2$ and 0.3, the minority A groups are consumed in rings and the absence of A groups limits gelation at $p_{Ac} = 1$. For $x_{\mathrm{A}} = 0.4$ and 0.5, the minority B groups are consumed and limit gelation at $p_{Bc} = 1$. In the latter cases, the graphs stop at the corresponding values of p_{Ac}. There is never a critical dilution for RA_f–RB_g models when $f \geqslant 3$ and $g \geqslant 3$.

This concludes the discussion of the numerical results. The discussion points out that some of the results are artifacts of our restriction to simple rings. We now turn out attention to critical behavior of models making the IA assumption.

6. CRITICAL BEHAVIOR

Models involving the IA are equivalent to percolation processes on Bethe lattices. Not surprisingly from this perspective, IA models have the same (classical) critical exponents. The only Bethe lattice results I know are for percolation on a finite number of vertex types.(34) Since rings come in an infinite number of sizes (corresponding to an infinite number of vertex types), it seems worthwhile to produce the critical exponents in the context of the present theory. There has been some hope that introducing rings into the Flory theory might change the critical exponents. The present section dashes that hope in the context of IA models.

We shall confine our attention to Case A in Section 4: a single monomer type bonded by a single symmetric (A–A) bond type and no equireactivity assumptions. (Of course, this does not exclude the possibility that the monomers can form ring units.) The general observations in this section probably hold for more elaborate situations. Equations (3A.1), (3A.2), and the gelation criterion $\Delta = 0$ from Eq. (3A.5) are the basis of the exposition.

In order to streamline the determination of the critical exponents, we introduce some notation. For any quantity q, define q_c to be its critical value, and define d_- and $d_\pm$ to be the operators

$$d_- q = q_c - q \qquad \text{and} \qquad d_\pm q = |q - q_c| \tag{6.1}$$

The differences are assumed to be infinitesimals. (By analogy, we could define another operator: $d_+ q = q - q_c$, but we shall not use it in this paper.) The symbol $\sim$ will denote asymptotic proportionality (the ratio of the two sides approaches a finite constant); $\approx$, asymptotic equality (the ratio of the two sides approaches unity).

For the case under consideration, our quantities are expressed as functions of variables μ and $\mathbf{a}$. We shall use μ as the independent order parameter. The operator d_- obeys

$$d_- \approx \partial/\partial\mu \cdot d_- \mu + \partial/\partial\mathbf{a} \cdot d_- \mathbf{a} \sim d_- \mathbf{a} \tag{6.2}$$

The final asymptotic proportionality holds only if $d_- \mathbf{a}$ on the right side of Eq. (6.2) blows up. To determine $d_- \mathbf{a}$, we apply the first part of Eq. (6.2) to Eq. (3A.1):

$$d_- \mathbf{a} = \frac{\partial^2 \mathbf{u}}{\partial\mathbf{a}\,\partial\mu} d_- \mu + \frac{\partial^2 \mathbf{u}}{\partial\mathbf{a}^2} d_- \mathbf{a} \tag{6.3}$$

If we solve Eq. (6.3) for $d_-\mathbf{a}$, $\Delta\, d_-\mathbf{a}$ appears on the left side of Eq. (6.3), where Δ is defined in Eq. (3A.5). To get the asymptotic behavior of Δ, we see

$$\begin{aligned}\Delta = 1 - \frac{\partial^2 \mathbf{u}}{\partial \mathbf{a}^2} &= \left(\frac{\partial^2 \mathbf{u}}{\partial \mathbf{a}^2}\right)_{\mathrm{c}} - \frac{\partial^2 \mathbf{u}}{\partial \mathbf{a}^2} \\ &\sim d_-\mathbf{a} \end{aligned} \tag{6.4}$$

by Eq. (6.2). Hence Eq. (6.3) implies

$$(d_-\mathbf{a})^2 \sim d_-\mu \tag{6.5}$$

Equation (6.5), (6.2) (with d_- acting on n), and (3A.2) give the following asymptotic equalities:

$$(d_-\mu)^{1/2} \sim d_-\mathbf{a} \sim d_- n \sim \frac{d^2\mathbf{p}}{d\mu^2}\, d_-\mu \tag{6.6}$$

Equations (2.4) and (2.7) imply that $\mathbf{p}$ has the form

$$\mathbf{p} = \sum_{i=1}^{\infty} \exp(i\beta\mu)\, z_i \tag{6.7}$$

$z_i = z_i(T)$ is the intensive canonical partition function for an $i$mer. As Eqs. (2.4)–(2.6) indicate, the terms of $\mathbf{p}$ give the concentrations of the $i$mers. We denote these by n_i.

Hendriks et al.$^{(35)}$ note the following result:

If $g(x) = \sum r_j e^{jx}$ has a singularity $(-x)^\rho$ ($\rho \neq 1, 2, 3,\ldots$), then r_j has the following asymptotic behavior

$$g(x) \approx (-x)^\rho \quad \leftrightarrow \quad r_j \approx j^{-\rho-1}/\Gamma(-\rho)$$

Equation (6.6) gives

$$i^2 z_i \sim i^{-1/2} \Rightarrow z_i \sim i^{-5/2} \tag{6.8}$$

Hence $\{n_i\}$ obeys the scaling law

$$n_i \sim i^{-5/2} \exp[-i\omega(d_-\mu)^2] \tag{6.9}$$

where ω is a complicated but determinable positive constant.

This is an example of the general scaling law$^{(12)}$

$$n_i \sim i^{-\tau}\Psi[i(d_\pm \mu)^{1/\sigma}] \tag{6.10}$$

Under this general scaling law, the exponents $\tau = \frac{5}{2}$ and $\sigma = \frac{1}{2}$ in Eq. (6.9) are sufficient to determine any other critical exponent.$^{(12)}$ These values are the so-called classical exponents characterizing critical percolation on a Bethe lattice.

7. COMPARISON TO EXPERIMENT

Table I gives gel point data$^{(36)}$ for a mixture of adipic acid $[(CH_2CH_2COOH)_2 = RA_2]$ and pentaerythritol $[C(CH_2OH)_4 = RB_4]$ at various dilutions in dimethoxytetraethylene glycol. The concentrations of the carboxyl and alcohol groups are equal, i.e., the number fraction of adipic acid is $x_A = \frac{2}{3}$ and of pentaerythritol, $x_B = \frac{1}{3}$. V is the volume of the mixture plus solvent; V_0 is the corresponding volume of the mixture in the absence of the solvent. The relative molecular mass of the mixture is $(\frac{2}{3})146 + (\frac{1}{3})136 = 142.7$ g/mol. The specific volume of the undiluted mixture is 0.813 cm^3/g, giving a concentration of $n = 5.19$ monomers nm^{-3}.

Figure 6 shows a fit of theory ($r = 0.115$ at the undiluted concentration) to data. Substitution into Eqs. (5.1) and (4C.4) gives

$$vb^2 = v_A b_A^2 + v_B b_B^2 = 0.673 \text{ nm}^2 \tag{7.1}$$

$v = v_A + v_B = 11$ is the total number of links in a 1 ring and b is the net "effective" link length. Equation (7.1) yields

$$b = 0.247 \text{ nm} \tag{7.2}$$

The discussion comments on Fig. 6 and the result of Eq. (7.2).

Table I. Effect of Dilution on the Gel Point[a]

% Solvent	V/V_0	$p_{Ac} = p_{Bc}$
0	1.00	0.631
0	1.00	0.630
21.1	1.36	0.640
21.3	1.36	0.641
31.7	1.63	0.658
40.6	1.92	0.671
49.7	2.34	0.689
53.8	2.57	0.709
66.1	3.27	0.831

[a] Specific volume of undiluted adipic acid-pentaerythritol = 0.813 cm^3/g. Specific volume of dimethoxytetraethylene glycol solvent = 1.10 cm^3/g. V_0 = undiluted volume of mixture; V = volume in solvent.

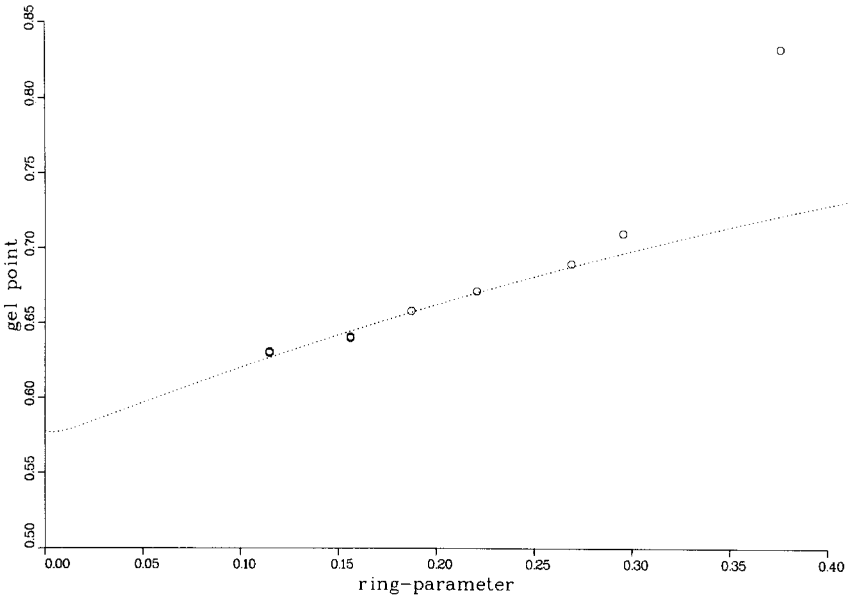


Fig. 6. p_{Ac} vs. r for an adipic acid-pentaerythritol (RA_2–RB_4) mixture diluted in dimethoxytetraethylene glycol. $x_A = \frac{2}{3}$ and $x_B = \frac{1}{3}$, yielding equimolar concentrations of A and B groups, so that $p_{Ac} = p_{Bc}$. The octagons are experimental data from Table I and the dotted curve is a theoretical fit with $r = 0.115$ for the undiluted mixture.

8. DISCUSSION

This paper delivers a flexible ring formalism. Rings introduce great problems of notation and description. Accordingly, Sections 2 and 3 develop the polymer partition function for notation and the unit partition function for description (Fig. 2). The basic assumptions in this development are: (1) ideality of the polymer solution (to get the polymer grand partition function); (2) spatial homogeneity [to get the (intensive) polymer (grand) partition function]; and (3) the Independence Assumption (IA) (to get the unit partition function). IA, as Gordon(21) points out, is really an ideal gas approximation for polymers. This observation is not a casual one, as cluster expansions(37) can relax both assumptions (1) and (3). IA cluster expansions are equivalent to higher-shell substitution effects(38) and can approximate excluded-volume effects. Inclusion of excluded-volume effects by considering chain (as well as ring) units is also a possibility.

Notation and description now aside, the rings are given statistical weights. Section 4A does this by extending the Jacobson–Stockmayer(15) random-flight ring weights from linear to branching polymers. The extension chosen makes the relative frequency of chain to ring configurations

[Figs. 4(b) and 4(c)] the same for both linear and branching polymers. The ring formalism can handle other ring weights, but this choice is a natural one.(20) The ring weights could probably be improved.

Section 5 solves the equireactive cases for the RA_f, A_fRB_g, and RA_f–RB_g models. Computer solution requires a reparametrization of the problem. This reparametrization may generalize to nonequireactivity.

The only units this paper allows are monomers and simple rings. Those units generate terms in the unit partition functions of Section 4. In Section 5 the nondimensionalized monomer terms contain the factor r^0, and, the simple ring terms, r^1. Higher powers of the ring parameter r correspond to more complex rings, e.g., r^2 terms (which I have in hand) correspond to θ and 8 rings (Fig. 1). Hence the unit partition functions given are really expansions in r, truncated at the term corresponding to simple rings. The last two points in Table I and Fig. 6 may be showing truncation effects, since high dilutions at those points favor nonsimple rings.

In Section 7, the effective link length $b = 0.247$ nm is too small.(16,18,33) (The link length could also have been adjusted for fixed bond angles and correlations between the azimuthal angles of the bonds.(17)) The experiment cannot, however, be considered a definitive test of the theory (nonequireactivity, non-Gaussian random walks, etc.) and, despite this, b is still reasonably close to the expected range of 0.3–0.4 nm. This is an encouraging result.

Section 6 on critical behavior raises some very interesting issues. For example, exactly what idealized problem was solved? Given the assumptions of the discussion's first paragraph and the truncation of the unit partition function, we solved ring formation "exactly" if there are enough rod shaped links in a monomer to provide Gaussian random walks. Up to any fixed size of polymer, the links can dodge the excluded volume issue by being sufficiently thin.

From this perspective, the Malthusian paradox(39) in branching processes results from an improper interchange of limits. (Our theory is equivalent to the branching processes: see Appendix A.) The Malthusian paradox is that space, which grows cubically with linear dimension, cannot contain the branching process gel, which grows exponentially with the linear dimension. In the branching process gel, no finite thinness of link can compensate for the excluded volume effects. The branching process theory must first put "infinitely thin" links into arbitrarily large polymers. Those polymers then become the "infinitely large" gel. A theory of the gel phase may have to *start* with the "infinitely large" gel to cope with the problem of excluded volume. If this is so, the classical exponents of Section 6 may have no bearing on polymeric criticality.

Despite this, the gel point in Section 3 is a good theoretical estimate (Fig. 6), because it represents a saturation of the sol capacity for monomers;(3) higher monomer concentrations must be absorbed by a gel. This is a statement about sols and not about gels, so the reservations in the preceding paragraph are inapplicable.

This paper was careful to consider only the sol phase [Eq. (2.2) et seq.]. If, however, the chemical potential of the gel phase monomers were known, Eq. (2.8) could be used in reverse: since equilibrium chemical potential is independent of phase,(24) the concentration of sol phase monomers can be calculated from the chemical potential of gel phase monomers. The statistics of the gel phase would then determine monomer concentrations in the sol. This paper can accommodate all possible chemical potentials in the gel: these form a continuum,(40) not just a Flory/Stockmayer(41) dichotomy.

Despite the foregoing tentative reservations about applicability outside the sol phase, the branching process formalism has been used to calculate mechanical properties of gels.(42) Appendix A relates the unit partition function of the ring formalism to the probability generating function of the branching process formalism. Branching processes, if correct in the gel phase, should be very much improved by inclusion of rings. This inclusion is now a very attractive possibility.

Though this paper restricted itself to equilibrium, the description of units and articulation bonds implicit in Fig. 2 is applicable even to kinetic polymerization. An obvious question: can then methods of this paper handle ring kinetics?

As a simplest case, consider irreversible polymerization for equireactive RA_2 model. If c_j is the concentration of j chains [j monomers in a chain, but *without the reacted end groups of Figure* 4(b)], and n_j is the concentration of j rings, then the time derivatives of c_j and n_j obey(33)

$$\begin{aligned} \dot{c}_j &= \tfrac{1}{2}k_\alpha \sum_{m+n=j} c_m c_n - k_\alpha c_j \sum_{n=1}^{\infty} c_n - k_\sigma c_j j^{-3/2} \\ \dot{n}_j &= -k_\sigma c_j j^{-3/2} \end{aligned} \tag{8.1}$$

k_α is the rate constant for reaction of a pair of A groups, and k_σ is the rate constant for monomeric ring closure. The factor of $j^{-3/2}$ appears because, as an idealization, Gaussian random walks close the rings. The terms of the first equation have physical interpretations: (1) reaction of an m chain and an n chain $(m+n=j)$ produces a j chain; (2) reaction of a j chain with anything else removes a j chain; and (3) end-group reaction changes a j chain into a j ring.

The methods of Appendix C show that FSSE restricts the form of c_j and n_j in RA_2 ring formation. No expressions of those forms provide exact solutions of Eq. (8.1). Though approximations are possible, no idealization of the kinetic problem has an exact solution satisfying FSSE. *A fortiori*, the basic assumptions of this paper are excluded.

ACKNOWLEDGMENTS

I thank Walter Stockmayer for providing the data in Table I. This work was supported by the U.S. Department of Energy.

APPENDIX A. EQUIVALENCE TO BRANCHING PROCESSES

The branching process formalism is based on probability generating functions (p.g.f.'s). The terms of the unit p.g.f. give the probability of finding a unit of a particular type in a particular state. Equation (1.4) gives such a probability: the unit p.g.f. in the case described would be

$$U(A) = \sum_{i=0}^{f} p_i A^i = \sum_{i=0}^{f} \binom{f}{i} \alpha^i (1-\alpha)^{f-i} A^i = (1-\alpha+\alpha A)^f \qquad \text{(A.1)}$$

A is a marker variable whose exponent gives the number of reacted A groups on a unit. In the notation of Section 3, if we call $(A\text{–}A)$ bonds a bonds, the exponent also equals the number of outgoing a bonds on the unit. In other words, A is also the marker variable for outgoing a bonds. Probability generating functions like Eq. (A.1) must satisfy the normalizing condition $P(1) = 1$: the total probability sums to 1.

In the general case, when the unit partition function is given by Eq. (3.2), the unit p.g.f. is

$$U(A, B, C,...) = \frac{\mathbf{u}(A\mathbf{a}, B\mathbf{b}, C\mathbf{c},...)}{\mathbf{u}(\mathbf{a}, \mathbf{b}, \mathbf{c},...)} \qquad \text{(A.2)}$$

where the dependence of $\mathbf{u}$ on $\mathbf{a}, \mathbf{b}, \mathbf{c},...$ has been written explicitly. $\mathbf{u}(A\mathbf{a}, B\mathbf{b}, C\mathbf{c},...)$ is the value of $\mathbf{u}$ when $A\mathbf{a}$ replaces $\mathbf{a}$, $B\mathbf{b}$ replaces $\mathbf{b}$, $C\mathbf{c}$ replaces $\mathbf{c}$, etc. Equations (3.3) give the numerical values of $\mathbf{a}, \mathbf{b}, \mathbf{c},...$. The terms of $U(A, B, C,...)$, given by Eqs. (3.2) and (A.2), represent the probability of choosing a random unit and finding it in a particular state. A is the marker variable for outgoing a bonds, B for outgoing b bonds, etc. The presence of $\mathbf{u}(\mathbf{a}, \mathbf{b}, \mathbf{c},...)$ in the denominator ensures that U satisfies the normalizing condition $U(1, 1, 1,...) = 1$.

The a^* bond p.g.f. (for a unit on the end of a a^* bond) should likewise be $\mathbf{a}^*$, the a^*-bond partition function, appropriately normalized. If we denote the a^* bond p.g.f. by A^*, then Eq. (3.3) implies

$$\mathbf{a}^* = \frac{(\partial\mathbf{u}/\partial\mathbf{a})(A\mathbf{a}, B\mathbf{b}, C\mathbf{c},...)}{\partial\mathbf{u}/\partial\mathbf{a}(\mathbf{a}, \mathbf{b}, \mathbf{c},...)} \qquad \text{(A.3)}$$

where the dependence of $\partial\mathbf{u}/\partial\mathbf{a}$ on $\mathbf{a}, \mathbf{b}, \mathbf{c},\ldots$ has been written explicitly. $(\partial\mathbf{u}/\partial\mathbf{a})(A\mathbf{a}, B\mathbf{b}, C\mathbf{c},\ldots)$ is the value of $\partial\mathbf{u}/\partial\mathbf{a}$ when $A\mathbf{a}$ replaces $\mathbf{a}$, $B\mathbf{b}$ replaces $\mathbf{b}$, $C\mathbf{c}$ replaces $\mathbf{c}$, etc. Equations (A.2) and (A.3) imply

$$A^* = \frac{(\partial U/\partial A)(A, B, C,\ldots)}{(\partial U/\partial A)(1, 1, 1,\ldots)} \tag{A.4}$$

This is the universal consistency condition of Gordon and Malcolm,(43) also noted by Whittle.(26)

Equation (A.4) is the mathematical springboard for the branching process formalism [cf. Ref. 11, Eqs. (4) and (5)]. In the present context, the unit and bond p.g.f.'s are renormalized unit and bond-type partition functions. Branching processes are therefore equivalent to the formalism in Section 3.

APPENDIX B. STATISTICAL MECHANICS OF THE FLORY RA_f MODEL

In this appendix, we assume a single RA_f monomer type, symmetric $(A\text{–}A)$ bonds, equireactivity, and no rings:

$$\mathbf{u} = e^{\beta\mu} z_0 (1 + e^{-\beta\varepsilon/2}\mathbf{a})^f \tag{B.1}$$

Compare Eq. (B.1) to Eqs. (5A.1) and (4A.5). Absence of additional terms in the unit partition function $\mathbf{u}$ implies that monomers are the only units in the system, i.e., $R = 0$ (no rings). ε corresponds to the free energy g in the Cohen–Benedek(3) notation.

Equations (3.3) and (3.5) become

$$\mathbf{a} = f e^{-\beta\varepsilon/2} e^{\beta\mu} z_0 (1 + e^{-\beta\varepsilon/2}\mathbf{a})^{f-1} \tag{B.2}$$

$$\mathbf{p} = \mathbf{u} - \tfrac{1}{2}\mathbf{a}^2 \tag{B.3}$$

We require a version of the Lagrange expansion:(44)

If $\mathbf{a} = e^{\beta\mu} g(\mathbf{a})$, then

$$f(\mathbf{a}) = f(0) + \sum_{i=1}^{\infty} \frac{d^{i-1}}{d\mathbf{a}^{i-1}} \{f'(\mathbf{a})[g(\mathbf{a})]^i\}_{\mathbf{a}=0}\, e^{i\beta\mu} \tag{B.4}$$

where $\{\cdot\}_{\mathbf{a}=0}$ indicates evaluation at $\mathbf{a} = 0$.

Applying the expansion to Eqs. (B.1)–(B.3) yields

$$\mathbf{p} = \sum_{i=1}^{\infty} e^{i\beta\mu} \frac{w_i}{i!} z_0^i e^{-(i-1)\beta\varepsilon} \tag{B.5}$$

where $\{w_i\}$ are as in Eq. (1.2).

Since $e^{\beta\mu}$ marks polymers which are monomers [Eq. (2.4)], the free monomer concentration is the first term of Eq. (B.5):

$$n_1 = e^{\beta\mu} w_1 z_0 = e^{\beta\mu} z_0 \tag{B.6}$$

Back substitution into Eq. (B.5) gives

$$\mathbf{p} = \sum_{i=1}^{\infty} \frac{w_i}{i!} e^{-(i-1)\beta\varepsilon} n_1^i \tag{B.7}$$

a result in accord with Eq. (II-15) of Cohen and Benedek.$^{(3)}$

Equations (3A.2), (B.1), and)B.2) give the total monomer concentration:

$$n = f^{-1}\mathbf{a}(e^{\beta\varepsilon/2} + \mathbf{a}) \tag{B.8}$$

Equations (B.8) and (4A.6) give the extent of reaction

$$\alpha = \mathbf{a}/(e^{\beta\varepsilon/2} + \mathbf{a}) \tag{B.9}$$

Eliminating **a** from the last two equations yields

$$\alpha/(1-\alpha)^2 = fne^{-\beta\varepsilon} \tag{B.10}$$

a result identical with Cohen and Benedek's Eq. (II-17b).

Finally, the criticality condition $\Delta = 0$ from Eq. (3A.5) becomes

$$\mathbf{a} = (f-2)^{-1} e^{\beta\varepsilon/2} \tag{B.11}$$

which, when substituted into Eq. (B.8) agrees with Cohen and Benedek's Eq. (IV-15b).

It is interesting to compare Cohen and Benedek's canonical ensemble approach [their Eq. (II-1)] to the grand canonical ensemble approach of Eq. (2.2). The two approaches lead to equivalent results in the equireactive case without rings.

APPENDIX C. EQUIVALENCE TO THE JACOBSON–STOCKMAYER MODEL

In this section, we assume equireactive RA_2 monomers:

$$\mathbf{m} = e^{\beta\mu} z_0 (1 + e^{-\beta\varepsilon/2}\mathbf{a})^2 \tag{C.1}$$

m is the monomer-unit partition function. Unlike **u** in Appendix B, **m** is *not* the unit partition function because there are rings in the system.

Section 4A gives the appropriate description of ring formation in this system. Note that

$$\mathbf{m}_2 = 2e^{\beta\mu} z_0 e^{-\beta\varepsilon} \tag{C.2}$$

Equation (4A.5) gives the unit partition function

$$\mathbf{u} = \mathbf{m} + \tfrac{1}{2} R\varphi(\mathbf{m}_2, \tfrac{5}{2}) \tag{C.3}$$

Equations (3.3), (C.2), and solution of the resulting equation for $\mathbf{a}$ yield

$$\begin{aligned} \mathbf{a} &= 2e^{-\beta\varepsilon/2} e^{\beta\mu} z_0 (1 + e^{-\beta\varepsilon/2}\mathbf{a}) \\ &= e^{\beta\varepsilon/2}\mathbf{m}_2/(1 - \mathbf{m}_2) \end{aligned} \tag{C.4}$$

Equations (3A.3) and (C.3) give the polymer partition function

$$\mathbf{p} = \mathbf{m} - \tfrac{1}{2}\mathbf{a}^2 + \tfrac{1}{2} R\varphi(\mathbf{m}_2, \tfrac{5}{2}) \tag{C.5}$$

When the monomers are bifunctional, all polymers are either chains or isolated ring units: only chains can contain articulation bonds. Hence the first two terms in the polymer partition function represent chains and the third represents rings.

Consider the ring term in the polymer partition function. Because of Eq. (3.1), the chemical potential of a j ring is

$$\mu_j = j\mu \tag{C.6}$$

Equation (2.6) and accompanying remarks justify the following. In Eq. (C.5), $\exp(j\beta\mu) = \exp(\beta\mu_j)$ appearing in the Truesdell term $\frac{1}{2} R\mathbf{m}_2^j j^{-5/2}$ marks the j-ring contribution to $\mathbf{p}$. The concentration of j rings in the system is

$$n_j = \tfrac{1}{2} R\mathbf{m}_2^j j^{-5/2} \tag{C.7}$$

Similar considerations apply to the first two terms of $\mathbf{p}$,

$$\begin{aligned} \mathbf{m} - \tfrac{1}{2}\mathbf{a}^2 &= \tfrac{1}{2}e^{\beta\varepsilon}\mathbf{m}_2(1 - \mathbf{m}_2)^{-2} - \tfrac{1}{2}e^{\beta\varepsilon}\mathbf{m}_2^2(1 - \mathbf{m}_2)^{-2} \\ &= \tfrac{1}{2}e^{\beta\varepsilon}\mathbf{m}_2(1 - \mathbf{m}_2)^{-1} \end{aligned} \tag{C.8}$$

Expand Eq. (C.8) in powers of $\mathbf{m}_2$. $\exp(j\beta\mu)$ now marks the j-chain contribution in the first two terms of $\mathbf{p}$, so the concentration of j chains in the system is

$$c_j = \tfrac{1}{2}e^{\beta\varepsilon}\mathbf{m}_2^j \tag{C.9}$$

These results agree with those of Jacobson and Stockmayer(15) if we identify our notation with theirs (their B is our $\frac{1}{2}R$):

$$A/V \leftrightarrow \tfrac{1}{2}e^{\beta\varepsilon} \tag{C.10}$$

$$x \leftrightarrow \mathbf{m}_2 \tag{C.11}$$

The Jacobson–Stockmayer notation appears on the left.

In order to compare this appendix with the next one, consider a bond in a j ring. The relative weight(20) for this bond being closed versus open is the ratio of j rings to j chains, times j, the number of bonds in a j ring:

$$\frac{j\mathbf{n}_j}{\mathbf{c}_j} = Re^{-\beta\varepsilon} j^{-3/2} \tag{C.12}$$

APPENDIX D. EQUIVALENCE TO HOEVE'S MODEL

The assumptions of Section 5A [equireactive RA_f monomers, symmetric (A–A) bonds, and simple rings] are equivalent to Hoeve's(20) assumptions.

We need a multivariable version of the Lagrange Expansion:(11)

If $\mathbf{a} = \sum_{j=0}^{\infty} x_j g_j(\mathbf{a})$, then the coefficient of $\prod_{j=0}^{\infty} x_j^{u_j}$ in $f(\mathbf{a})$ is the coefficient of $\mathbf{a}^{u-1}$ in

$$\frac{(u-1)!}{\prod_{j=0}^{\infty} u_j!} f'(\mathbf{a}) \prod_{j=0}^{\infty} [g_j(\mathbf{a})]^{u_j} \tag{D.1}$$

where $u = \sum u_j$. (Interpret both 0! and 0^0 as 1.)

In Eqs. (3A.1) and (4A.8), multiply the first term $\mathbf{m}_1$ by a marker variable x_0 representing monomer units, and the term

$$\tfrac{1}{2}R(\mathbf{m}_3/\mathbf{m}_2)\,\mathbf{m}_2^j\, j^{-3/2}$$

by a marker variable x_j representing j rings.

We expand the bond partition function $\frac{1}{2}\mathbf{a}^2$ to get the polymer concentrations. By the remarks following Eq. (3.4), the terms of $\frac{1}{2}\mathbf{a}^2$ are the polymer concentrations multiplied by $(u-1)$, where u is the number of units in a polymer. Because the marker variable x_j represents j rings, the coefficient of $\prod x_j^{u_j}$ in $\frac{1}{2}\mathbf{a}^2$ is $n\{u_j\}$, the concentration of polymers containing u_0 monomer units and u_j j rings, times $(u-1)$, where $u = \sum u_j$ is the number of units in a $\{u_j\}$ polymer.

By using Eqs. (3A.1) and (4A.8) to take the Lagrange Expansion of $\frac{1}{2}\mathbf{a}^2$, the coefficient of $\prod x_j^{u_j}$ in $\frac{1}{2}\mathbf{a}^2$ is the coefficient of $\mathbf{a}^{u-1}$ in

$$\left[(u-1)!\Big/\prod_{j=0}^{\infty} u_j!\right]\mathbf{a}[fe^{-\beta\varepsilon/2}e^{\beta\mu}z_0(1+e^{-\beta\varepsilon/2}\mathbf{a})^{f-1}]^{u_0}$$

$$\cdot\prod_{j=1}^{\infty}\{\tfrac{1}{2}Re^{j\beta\mu}[f(f-1)(f-2)\,e^{-3\beta\varepsilon/2}z_0(1+e^{-\beta\varepsilon/2}\mathbf{a})^{f-3}]$$

$$\cdot[f(f-1)\,e^{-\beta\varepsilon}z_0(1+e^{-\beta\varepsilon/2}\mathbf{a})^{f-2}]^{j-1}\,j^{-3/2}\}^{u_j}$$

$$=\left[(u-1)!\Big/\prod_{j=0}^{\infty} u_j!\right][fe^{-\beta\varepsilon/2}e^{\beta\mu}z_0]^{u_0}$$

$$\cdot\prod_{j=1}^{\infty}\{\tfrac{1}{2}Re^{j\beta\mu}[f(f-1)(f-2)\,e^{-3\beta\varepsilon/2}z_0]$$

$$\cdot[f(f-1)\,e^{-\beta\varepsilon}z_0]^{j-1}\,j^{-3/2}\}^{u_j}$$

$$\cdot\mathbf{a}(1+e^{-\beta\varepsilon/2}\mathbf{a})^{(f-1)u_0+\sum_{j=1}^{\infty}[(f-2)(j-1)u_j+(f-3)u_j]}$$

Taking the coefficient of $\mathbf{a}^{u-1}$ and dividing it by $(u-1)$ gives

$$=\left[e^{\beta\varepsilon}\Big/\prod_{j=0}^{\infty} u_j!\right][fe^{\beta\mu}z_0e^{-\beta\varepsilon}]^{u_0}$$

$$\cdot\prod_{j=1}^{\infty}\{(f-2)\,j\,\tfrac{1}{2}Re^{-\beta\varepsilon}[f(f-1)\,e^{\beta\mu}z_0e^{-\beta\varepsilon}]^{j}\,j^{-5/2}\}^{u_j}$$

$$\cdot\frac{[fu_0-u_0+(f-2)\sum_{j=1}^{\infty}ju_j-\sum_{j=1}^{\infty}u_j]!}{[fu_0-2u_0+(f-2)\sum_{j=1}^{\infty}ju_j-2\sum_{j=1}^{\infty}u_j+2]!} \tag{D.2}$$

These results agree with Hoeve's, if we identify our notation with his:

$$m_j \leftrightarrow u_j \tag{D.3}$$

$$A \leftrightarrow e^{\beta\varepsilon} \tag{D.4}$$

$$x \leftrightarrow e^{\beta\mu}z_0e^{-\beta\varepsilon} \tag{D.5}$$

$$y_j \leftrightarrow \tfrac{1}{2}Re^{-\beta\varepsilon}[f(f-1)x]^j\,j^{-5/2} \tag{D.6}$$

Hoeve's notation is on the left. In his paper$^{(20)}$ (but in our notation), Hoeve's Eqs. (5) and (11) identify $Re^{-\beta\varepsilon}j^{-3/2}$ as the relative weight for ring closure in a j ring. [Corresponding to the factor $\frac{1}{2}Re^{-\beta\varepsilon}$ in Eq. (D.6).] This agrees with the result for RA_2 monomers at the end of Appendix C and demonstrates that our approach compares systems of bifunctional and multifunctional polymers directly.

APPENDIX E. LIMITING RESULTS FOR $r=0$

Setting $r=0$ in Section 5 gives the following results:

Case A. Equireactive RA_f Monomers, $r=0$

Equation (5A.4) gives $s=f(f-1)$, so Eqs. (4A.5), (4A.6), (5A.5), and (3A.1) yield

$$\mathbf{m}_2=(f-1)\,p_A \tag{EA.1}$$

Equations (3A.1), (3A.3), (3A.5), (3A.6), (4A.5), (5A.3), and (5A.5) yield

$$M_0/n=1-\tfrac{1}{2}f\mathbf{m}_2/(f-1) \tag{EA.2}$$

$$\Delta=1-\mathbf{m}_2 \tag{EA.3}$$

$$M_2/(nm^2)=1+\Delta^{-1}f\mathbf{m}_2/(f-1) \tag{EA.4}$$

Case B. Equireactive A_fRB_g Monomers, $r=0$

Equation (5B.4) gives $s=fg$, so Eqs. (4B.5), (4B.6), (5B.5), and (3B.1) yield

$$\mathbf{m}_{11}=fp_A=gp_B \tag{EB.1}$$

Equations (3B.1), (3B.2), (3B.4), (3B.5), (4B.5), (5B.3), and (5B.5) yield

$$M_0/n=1-\mathbf{m}_{11} \tag{EB.2}$$

$$\Delta=(1-\mathbf{m}_{11})^2-(f-1)(g-1)\,\mathbf{m}_{11}^2/(fg) \tag{EB.3}$$

$$M_2/(nm^2)=1+\Delta^{-1}\mathbf{m}_{11}[2fg-(f+g)\,\mathbf{m}_{11}]/(fg) \tag{EB.4}$$

Case C. Equireactive RA_f–RB_g Monomers, $r=0$

Equations (5C.4) give $s_{\mathrm{A}}=f(f-1)\,x_{\mathrm{A}}$ and $s_{\mathrm{B}}=g(g-1)\,x_{\mathrm{B}}$, so Eqs. (4C.5), (4C.6), (5C.3), (5C.5), and (3B.1) yield

$$\mathbf{m}_2=(f-1)(g-1)\,fx_{\mathrm{A}}\,p_A^2/(gx_{\mathrm{B}}) \tag{EC.1}$$

Equations (3B.1), (3B.2), (3B.4), (3C.3), (4C.5), (5A.3), and (5C.5) yield

$$M_0/n=1-fx_{\mathrm{A}}\,p_A \tag{EC.2}$$

$$\Delta=1-\mathbf{m}_2 \tag{EC.3}$$

$$\begin{aligned}M_2/n&=m_{\mathrm{A}}^2x_{\mathrm{A}}+m_{\mathrm{B}}^2x_{\mathrm{B}}\\&\quad+\Delta^{-1}fx_{\mathrm{A}}\,p_A[2m_{\mathrm{A}}m_{\mathrm{B}}+m_{\mathrm{A}}^2(g-1)\,p_B+m_{\mathrm{B}}^2(f-1)\,p_A]\end{aligned} \tag{EC.4}$$

For the last equation, note Eq. (5C.5): $fx_{\mathrm{A}}\,p_A=gx_{\mathrm{B}}\,p_B$.

APPENDIX F. LIMITING RESULTS FOR $r = \infty$

Let $r \to \infty$ in Eqs. (5A.4), (5B.4), and (5C.4). Since the left sides of these equations remain finite, the argument of φ must tend to 0 in each case. Analytic solution is then possible because $\varphi(x, s) \approx x$ as $x \to 0$, regardless of the Truesdell order s. ($\approx$ is asymptotic equality, as usual.) Replacing $\varphi(x, s)$ by x is done without further explanation in all the following cases.

Section 5D gives the physical interpretation of these results.

Case A. Equireactive RA_f Monomers, $r = \infty$

Equation (5A.4) gives rise to two cases: either $s \approx s_0 = 0$, or $s \approx s_0 > 0$.

(a) $s \approx s_0 > 0$. This corresponds to all polymers being monomers or 1 rings. Equations (4A.6), (5A.5), and (3A.1) yield

$$fp_A \approx r\mathbf{m}_2 \tag{FA.1}$$

Equation (4A.6) shows that all polymers remain monomeric while $fp_A \leqslant 2$. Equations (3A.1), (3A.3), (3A.5), (3A.6), (4A.5), (5A.3), and (5A.5) yield

$$M_0/n \approx 1 \tag{FA.2}$$

$$\Delta \approx 1 \tag{FA.3}$$

$$M_2/(nm^2) \approx 1 \tag{FA.4}$$

(a) $s \approx s_0 = 0$. Articulation bonds have started to form. Equation (5A.4) shows that $\frac{1}{2}r\mathbf{m}_2 \approx 1$. Equations (4A.6), (5A.5), and (3A.1) yield

$$fp_A = (f-2)^2(\mathbf{m}_2/s) + 2 \tag{FA.5}$$

Note that now $fp_A > 2$. Equations (3A.1), (3A.3), (3A.5), (3A.6), (4A.5), (5A.3), and yield

$$M_0/n \approx 2 - \tfrac{1}{2}fp_A \tag{FA.6}$$

$$\Delta \approx 1 - (fp_A - 2)(f-3)/(f-2) \tag{FA.7}$$

$$M_2/(nm^2) \approx 1 - \Delta^{-1}(fp_A - 2) \tag{FA.8}$$

Case B. Equireactive A_fRB_g Monomers, $r = \infty$

Equation (5B.4) gives rise to two cases: either $s \approx s_0 = 0$, or $s \approx s_0 > 0$.

(a) $s \approx s_0 > 0$. This corresponds to all polymers being monomers or 1 rings. Equations (4B.6), (5B.5), and (3B.1) yield

$$fp_A = gp_B \approx r\mathbf{m}_{11} \tag{FB.1}$$

Equation (4B.6) shows that all polymers remain monomeric while $fp_A \leqslant 1$. Equations (3B.1), (3B.2), (3B.4), (3B.5), (4B.5), (5B.3), and (5B.5) yield

$$M_0/n \approx 1 \tag{FB.2}$$

$$\Delta \approx 1 \tag{FB.3}$$

$$M_2/(nm^2) \approx 1 \tag{FB.4}$$

(a) $s \approx s_0 = 0$. Articulation bonds have started to form. Equation (5B.4) shows that $r\mathbf{m}_{11} \approx 1$. Equations (4B.6), (5B.5), and (3B.1) yield

$$fp_A = gp_B \approx (f-1)(g-1)(\mathbf{m}_{11}/s) + 1 \tag{FB.5}$$

Note that now $fp_A > 1$. Equations (3B.1), (3B.2), (3B.4), (3B.5), (4B.5), (5B.3), and (5B.5) yield

$$M_0/n \approx 2 - fp_A \tag{FB.6}$$

$$\Delta \approx (2 - fp_A)^2 - (1 - fp_A)^2(f-2)(g-2)/[(f-1)(g-1)] \tag{FB.7}$$

$$M_2/(nm^2) \approx 1 + \Delta^{-1}(fp_A - 1)\{2 - (fp_A - 1)(f+g-2)/[(f-1)(g-1)]\} \tag{FB.8}$$

Case C. Equireactive RA_f–RB_g Monomers, $r = \infty$

Without loss of generality, assume $x_\mathbf{B} \leqslant x_\mathbf{A}$. Equation (5C.4) gives rise to two cases: either $s_\mathbf{A} \geqslant s_\mathbf{B} \approx s_0 = 0$, or $s_\mathbf{B} \approx s_0 > 0$.

(a) $s_\mathbf{B} \approx s_0 > 0$. This corresponds to all polymers being monomers or 1 rings. Equations (4C.6), (5C.5), (5C.3), and (3B.1) yield

$$fp_A x_\mathbf{A} = gp_B x_\mathbf{B} \approx r\mathbf{m}_2 \tag{FC.1}$$

Equations (4C.6) and (5C.4b) show that all polymers remain monomers or 1 rings while $gp_B \leqslant 2$. Equations (3B.1), (3B.2), (3B.4), (3C.3), (4C.5), (5A.3), and (5C.5) yield

$$M_0/n \approx 1 - \tfrac{1}{2} fp_A x_\mathbf{A} \tag{FC.2}$$

$$\Delta \approx 1 \tag{FC.3}$$

$$M_2/n \approx m_\mathbf{A}^2 x_\mathbf{A} + m_\mathbf{A} m_\mathbf{B} f x_\mathbf{A} p_A + m_\mathbf{B}^2 x_\mathbf{B} \tag{FC.4}$$

(a) $s_\mathbf{B} \approx s_0 = 0$. Articulation bonds have started to form. Equations (5C.4) show that $\tfrac{1}{2} r\mathbf{m}_2 \approx x_\mathbf{B}$, $s_\mathbf{A} = f(f-1)(x_\mathbf{A} - x_\mathbf{B})$. Equations (4C.6), (5C.5), (5C.3), and (3B.1) yield

$$fp_A x_\mathbf{A} = gp_B x_\mathbf{B} \approx [\mathbf{m}_2/(s_\mathbf{A} s_\mathbf{B})]^{1/2}(f x_\mathbf{A} - 2x_\mathbf{B})(g-2)\, x_\mathbf{B} + 2x_\mathbf{B} \tag{FC.5}$$

Note that now $gp_B > 2$. Equations (3B.1), (3B.2), (3B.4), (3C.3), (4C.5), (5A.3), and (5C.5) yield

$$M_0/n \approx 1 + x_{\mathrm{B}} - f x_{\mathrm{A}} p_A \tag{FC.6}$$

$$\Delta \approx [1-(f-2)\delta]^2 - \delta^2[s_{\mathrm{A}} + (f-3)(g-3)\,x_{\mathrm{B}}](g-3)/[(g-2)\,x_{\mathrm{B}}] \tag{FC.7}$$

where

$$\delta = (f x_{\mathrm{A}} p_{\mathrm{A}} - 2x_{\mathrm{B}})/(f x_{\mathrm{A}} - 2x_{\mathrm{B}})$$

Finally

$$\begin{aligned} M_2/n \approx{} & m_{\mathrm{A}}^2 x_{\mathrm{A}} + 2m_{\mathrm{A}} m_{\mathrm{B}} x_{\mathrm{B}} + m_{\mathrm{B}}^2 x_{\mathrm{B}} \\ & + \Delta^{-1}\{\delta^2[m_{\mathrm{A}}(f x_{\mathrm{A}} - 2x_{\mathrm{B}}) + m_{\mathrm{B}}(f-2)\,x_{\mathrm{B}}]^2(g-3)/[(g-2)\,x_{\mathrm{B}}] \\ & + 2\delta(m_{\mathrm{A}} + m_{\mathrm{B}})[m_{\mathrm{A}}(f x_{\mathrm{A}} - 2x_{\mathrm{B}}) + m_{\mathrm{B}}(f-2)\,x_{\mathrm{B}}][1-(f-2)\delta] \\ & + \delta^2(m_{\mathrm{A}} + m_{\mathrm{B}})^2[s_{\mathrm{A}} + (f-3)(g-3)\,x_{\mathrm{B}}]\} \end{aligned} \tag{FC.8}$$

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