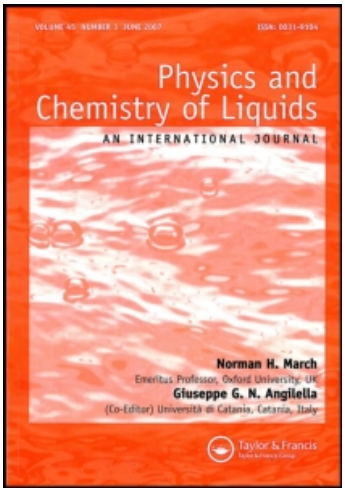

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Michael Falk[a]; George C. Marcotte[a]
[a] Atlantic Regional Laboratory, National Research Council of Canada, hali, Nova Scotia, Canada

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Molecular Size Distribution in Random Polyfunctional Condensation: The Combinatorial Factors†

MICHAEL FALK‡ and GEORGE C. MARCOTTE

Atlantic Regional Laboratory, National Research Council of Canada, Halifax, Nova Scotia, B3H 3Z1, Canada

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Several combinatorial factors entering into expressions for the distributions of molecular sizes in random polyfunctional condensations have been derived, including cases treated previously by Stockmayer and Flory. The simple method used in these derivations seems capable of extension to other related problems.

1 INTRODUCTION

More than thirty years ago Stockmayer[1] noted the formal and physical analogy between the process of condensation of saturated vapor to form a liquid and the reversible gelation which occurs during random polymerization of polyfunctional monomers. The similarity of vapor condensation and polymer gelation has since been successfully exploited by Gordon *et al.*[2] who described the process of saturation and precipitation of water in a dilute solution in benzene by means of the Flory-Stockmayer molecular size distribution expression, derived for a random polymerization process.[1,3] Recently, the condensation-gelation analogy has been explored still further by Cohen, Gibbs, and Fleming[4] who related Stockmayer's purely statistical independent variable α (corresponding to the extent of polymerization)

†NRCC No. 00000.

‡To whom correspondence should be addressed.

to the thermodynamic variables, temperature and density, used to describe vapor condensation. These authors' clarification of Stockmayer's analogy[4] is likely to bring about a wider use of the polymer-theory treatments of the Flory-Stockmayer type to problems related to liquid state, particularly in connection with the structure of liquid water.[5]

The distribution of molecular sizes in random processes of reversible polyfunctional polymerization (or condensation, for we will use these terms interchangeably) is therefore of some current interest. In deriving expressions for the most probable distribution of molecular sizes in the various possible types of such condensation, the most difficult part of the derivation is the evaluation of the combinatorial factor. Below we obtain several such factors by means of an elementary and, apparently, novel derivation which appears to be of fairly general applicability.

2 SELF-CONDENSATION OF IDENTICAL POLYFUNCTIONAL MONOMERS

Derivation of W_x

We shall first be concerned with the quantity W_x, defined as the number of ways in which x indistinguishable polyfunctional monomeric units (residues), each bearing f indistinguishable equivalent bonding sites, capable of forming inter-site bonds, can be combined into a "ringless x-mer", i.e. into a single polymeric molecule consisting of x residues and $x - 1$ bonds.

Consider a process of generation of a polymer, in which we start with a residue with its f sites "on trial". We proceed with a sequence of "successes" and "failures", where a success corresponds to a site being bonded while a failure corresponds to a site being non-bonded. Every failure removes one site while every success adds $f - 2$ new sites, as there are f new sites on the residue being added, but one new and one old site are used up in the bond. A ringless x-mer contains $x - 1$ bonds and $fx - 2x + 2$ non-bonded sites. Hence a sequence generating a ringless x-mer must consist of $x - 1$ successes and $fx - 2x + 2$ failures. The *total* number of distinct sequences of $x - 1$ successes and $fx - 2x + 2$ failures out of $(x - 1) + (fx - 2x + 2) = fx - x + 1$ trials is simply the binomial expression:

$$C_x = \binom{fx - x + 1}{x - 1} = \frac{(fx - x + 1)!}{(x - 1)!\,(fx - 2x + 2)!} \tag{1}$$

We see immediately that not all such sequences correspond to ways of generating an x-mer. For example, in the case of $f = 3$, $x = 2$, the sequence $- - + - -$ (where pluses denote successes, i.e. bonded sites, and minuses

denote failures, i.e. non-bonded sites) corresponds to one of the ways of generating a dimer, while the sequence $- - - + -$ does not, as the three failures at the beginning exhaust the available sites on the original residue. Clearly, a *proper* sequence generating an x-mer runs out of sites *at the end* of the sequence and not before.

We must derive the relation between the number of *proper* sequences generating an x-mer, W_x, and C_x, which is the *total* number of sequences of $x - 1$ successes and $fx - 2x + 2$ failures. To do this we consider an arbitrary sequence of $x - 1$ successes and $fx - 2x + 2$ failures, which may be illustrated by the sequence:

$$- - - - + - - - + + - - - - - - + - + - \qquad (2)$$

for which $f = 4$, $x = 6$, $x - 1 = 5$, and $fx - 2x + 2 = 14$. If we regard the sequence in (2) as cyclic, i.e. envisage the last element of the sequence to be followed immediately by the first element, then every success may be considered to be "neutralized" by $f - 2$ subsequent failures, with exactly f "unneutralized" failures being left over. These unneutralized failures are uniquely determined for any given sequence and may be discovered by the following bracketing procedure:

Bracket together every sub-sequence of a success followed immediately by $f - 2$ failures. Consider all symbols within brackets as neutralized and disregard them. Continue the bracketing process until the $x - 1$ successes have been uniquely bracketed with $(x - 1)(f - 2) = fx - 2x + 2 - f$ failures, and exactly f failures remain outside of all brackets

When applied to the sequence (2), the above procedure yields:

$$(-) -) \overset{*}{-} \overset{*}{-} (+ - -) \overset{*}{-} (+ (+ - -) - -) \overset{*}{-} (+ - (+ - \qquad (3)$$

where the $f = 4$ unneutralized failures, left outside of brackets, have been marked by asterisks. In the block of $fx - x + 1$ sequences generated by the cyclic permutations of an arbitrary sequence of $x - 1$ successes and $fx - 2x + 2$ failures there will be f sequences ending with one of the unneutralized failures. These sequences are all *proper*, because passing through any number of complete brackets has no net effect on the number of sites, so that we just run out of the original f sites at the fth encounter of an unneutralized failure, which is *at the end* of the sequence. On the other hand, the sequences ending with one of the symbols inside a bracket cannot be *proper*, because such a sequence must run out of the original f sites *before the end* of the sequence. Hence, in every such block there must be exactly f *proper* sequences out of a total of $fx - x + 1$. If f and $x - 1$ have a common factor, certain blocks of cyclically permuted sequences may split into several identical sub-blocks. In that case, in each such sub-block the ratio of *proper*

sequences to the total is also $f/(fx - x + 1)$. Therefore, the same fraction must also apply to the total set of C_x possible sequences, so that

$$W_x = \frac{f}{fx - x + 1} C_x = \frac{f(fx - x)!}{(x - 1)!\,(fx - 2x + 2)!}. \tag{4}$$

The expected number of ringless x-Mers N_x

We may now derive the limiting distribution expression for ringless x-mers in a system which initially contained N_0 monomeric units ($N_0 \to \infty$), and which had undergone a process of random bonding between pairs of sites until the fraction α of all sites became bonded. This regime corresponds to the *rings allowed* model defined and discussed in Ref. 6. The probability that any site encountered along the polymer is bonded or non-bonded must be α or $1 - \alpha$, respectively. As $x - 1$ bonded sites and $fx - 2x + 2$ non-bonded sites are encountered in the generation of an x-mer, the probability that a residue selected at random belongs to a ringless x-mer (neglecting the possibility of ring formation, which will be discussed in Section 4) must be

$$P_x = W_x\, \alpha^{x-1} (1 - \alpha)^{fx - 2x + 2}. \tag{5}$$

But P_x is also equal to the weight-fraction of x-mers in the system, $x N_x/N_0$, where N_x is the expected number of x-mers in the system. Thus

$$N_x = P_x N_0/x. \tag{6}$$

From (4), (5) and (6) we obtain

$$N_x = N_0 \frac{f(fx - x)!}{x!(fx - 2x + 2)!} \alpha^{x-1} (1 - \alpha)^{fx - 2x + 2} \tag{7}$$

which is the well-known Flory-Stockmayer expression.[1,3] Several alternative derivations of this equation have been reported,[7] but the simplicity of the present one makes it particularly suitable for extension to a variety of new cases, some examples of which are shown below.

3 SELF-CONDENSATION OF A MIXTURE OF POLYFUNCTIONAL MONOMERS

Derivation of W_j,x

We now consider a system which initially contains a mixture of n types of monomeric units (residues) which contain bonding sites of the same type and of equal reactivity. The number of such sites on the residue of the i-th type is f_i. The system undergoes random formation of inter-site bonds as before, until the fraction α of all sites have become bonded. A typical polymer will now contain x_i residues of the i-th type, and will be referred to as an x-mer,

where $\mathbf{x} = (x_1, x_2, \ldots, x_n)$. The detailed geometry and the internal relationships between the residues making up the x-mer will be disregarded. We wish to derive $W_{j,\mathbf{x}}$, the number of distinct ways of starting with a j-th type residue and generating a ringless $\mathbf{x}$-mer. In the generating process we must encounter x_i bonds to a residue of the i-th type ($i = 1,2, \ldots n; i \neq j$), $x_j = 1$ bonds to a residue of the j-th type, and

$$u = \Sigma x_i f_i - 2\Sigma x_i + 2 \tag{9}$$

non-bonded sites for a total of $\Sigma f_i x_i - \Sigma x_i + 1$ events or trials.† These events are of $n + 1$ types: n types of "successes", corresponding to the addition of one of the n types of residues, and a "failure", corresponding to a site being found non-bonded. The total number of distinct sequences of these events is now the multinomial expression

$$C_{j,\mathbf{x}} = \frac{(\Sigma f_i x_i - \Sigma x_i + 1)!}{(x_j - 1)! \prod_{i \neq j} x_i!\, u!} \tag{9}$$

with u given by Eq. 8 and the expression obtained representing a generalization of Eq. 1.

Again, not all of such sequences correspond to realizable ways of generating an $\mathbf{x}$-mer. The relation between $W_{j,\mathbf{x}}$ and $C_{j,\mathbf{x}}$ can be discovered by considering the block of sequences derived by cyclic permutations of an arbitrary sequence having the appropriate number of failures and successes of the various types. Every success of the i-th type can be considered to be neutralized by $f_i - 2$ subsequent failures. A bracketing procedure analogous to the one in the preceding section reveals exactly f_j unique unneutralized failures. Again, the necessary and sufficient condition for the sequence being "*proper*", i.e. corresponding to a feasible process of generation of an $\mathbf{x}$-mer, is that the sequence should end with such an unneutralized failure.

Consequently, the number of *proper* sequences in every block of $\Sigma f_i x_i - \Sigma x_i + 1$ cyclically related sequences is f_j, and the fraction of sequences which are *proper*, within each block and thus also for the complete set of sequences is

$$\frac{W_{j,\mathbf{x}}}{C_{j,\mathbf{x}}} = \frac{f_j}{\Sigma f_i x_i - \Sigma x_i + 1} \tag{10}$$

from which we obtain

$$W_{j,\mathbf{x}} = \frac{f_j (\Sigma f_i x_i - \Sigma x_i)!}{(x_j - 1)! \prod_{i \neq j} x_i! \, (\Sigma f_i x_i - 2\Sigma x_i + 2)!}. \tag{11}$$

Eqs. 10 and 11 are generalizations of Eq. 4.

†All sums (Σ) and products (Π) will be assumed to extend over $i = 1,2, \ldots, n$, unless otherwise indicated.

The expected number of ringless X-mers, N_x

From (11) we may derive the limiting distribution expression for x-mers without rings. If the system contained N_{0i} residues of type i, then, provided that the reaction has proceeded at random and that all $N_{oi} \to \infty$, the probability that a given site is bonded to a group on a residue of the i-th type must be

$$\alpha_i = \frac{f_i N_{0i}}{\Sigma f_i N_{oi}} \alpha$$

and the probability that it is unreacted must be $1 - \Sigma\alpha_i = 1 - \alpha$. Therefore, the probability that a residue of the j-th type, selected at random, belongs to an x-mer without rings is

$$P_{j,\mathbf{x}} = W_{j,\mathbf{x}}\, \alpha_j^{x_j - 1} \left(\prod_{i \neq j} \alpha_i^{x_i}\right)(1 - \alpha)^u. \tag{12}$$

But the expected number of ringless x-mers in this system, in analogy with Eq. 6 is

$$N_{\mathbf{x}} = P_{j,\mathbf{x}}\, N_{0j}/x_j. \tag{13}$$

Eliminating $P_{j,\mathbf{x}}$ from Eqs. 12 and 13, and substituting $W_{j,\mathbf{x}}$ from Eq. 11, we obtain:

$$N_{\mathbf{x}} = \frac{(\Sigma f_i x_i - \Sigma x_i)!\left[\Pi(f_i N_{0i})^{x_i}\right]\alpha^{\Sigma x_i - 1}(1 - \alpha)^{\Sigma f_i x_i - 2\Sigma x_i + 2}}{(\Pi x_i!)(\Sigma f_i x_i - 2\Sigma x_i + 2)!(\Sigma f_i N_{0i})^{\Sigma x_i - 1}}. \tag{14}$$

Eq. 14 represents the generalization of the Flory-Stockmayer expression (Eq. 7) for the polymerization of a mixture of n types of self-condensing monomer. The special case of $n = 2, f_1 = f$ and $f_2 = 2$ gives

$$N_{(x_1,x_2)} = \left(\frac{(fN_{01})^{x_1}(2N_{02})^{x_2}(fx_1 + x_2 - x_1)!}{(fN_{01} + 2N_{02})^{x_1 + x_2 - 1}\, x_1!\, x_2!(fx_1 - 2x_1 + 2)!}\right)\times$$

$$\left(\times\ \alpha^{x_1 + x_2 - 1}(1 - \alpha)^{fx_1 - 2x_1 + 2}\right. \tag{15}$$

which is equivalent to the expression given by Flory in Ref. 3, page 395.

4 CONDENSATION OF MONOMERS BEARING COMPLEMENTARY REACTIVE SITES

Derivation of W^A_{xy}

We now consider a system initially containing a mixture of monomers of two types, one which bears f_A bonding sites of type A and another which bears f_B bonding sites of type B. The system undergoes random formation of bonds of

type A ··· B, but not A ··· A or B ··· B. A representative ringless polymer, which we will call an x, y-mer, will contain x residues of type A, y residues of type B, and $x + y - 1$ A ··· B bonds. We wish to derive W^{A}_{xy}, the number of distinct ways of starting with a residue of type A and generating a ringless x, y-mer.

In the generating process we shall encounter y bonded A sites, designated $+$, and $f_A x - x - y + 1$ non-bonded A sites, designated $-$, for a total of $f_A x - x + 1$ events disposing of the sites of type A. The total number of distinct sequences of $f_A x - x + 1$ events of which y are of one type and the remaining ones are of another type is

$$\binom{f_A x - x + 1}{y} = \frac{(f_A x - x + 1)!}{y!(f_A x - x - y + 1)!}. \tag{16}$$

We shall also encounter $x - 1$ bonded B sites, designated $\pm$ and $f_B y - x - y + 1$ non-bonded B sites, designated $\mp$, for a total of $f_B y - y$ events disposing of the sites of type B. The total number of distinct sequences of $f_B y - y$ events, of which $x - 1$ are of one type and the remainder are of another type, is

$$\binom{f_B y - y}{x - 1} = \frac{(f_B y - y)!}{(x - 1)!\,(f_B y - y - x + 1)!}. \tag{17}$$

The complete sequence of events associated with the generation of an x, y-mer may be considered to be composed of a $(+, -)$ sequence combined with a $(\pm, \mp)$ sequence. Since at the start of the generation process we only have sites of type A on trial, and sites of type B only appear after an event of type $+$ (i.e. after an addition of a residue of type B, with $f_B - 1$ reactive sites on trial), a unique rule of the combination of the $(+, -)$ and $(\pm, \mp)$ sequences emerges: The combined sequence must begin with the non-underlined sequence, which continues until an event of type $+$ occurs. Each such event is then followed by $f_B - 1$ events taken consecutively from the underlined sequence. Since the underlined sequence has the length $f_B y - y = (f_B - 1)y$, and there are y events of type $+$, the total sequence is thus accounted for.

For example, in the case $f_A = 3, f_B = 4, x = y = 4$, the non-underlined sequence $- + - - + + - + -$ and the underlined sequence $\underline{- - + - - -}$ $\underline{+ + - - - -}$ would be uniquely combined into

$$- + \underline{- - +} - - + \underline{- - -} + \underline{+ + -} - + \underline{- - - -}. \tag{18}$$

The total number C^{A}_{xy} of sequences which have the required numbers of the four types of events for the generation of an x, y-mer starting with a residue of type A, and which follow our rule for combination, must be the double

binomial expression

$$C^{\wedge}_{xy} = \binom{f_A x - x + 1}{y} \times \binom{f_B y - y}{x - 1}. \tag{19}$$

As before, not all such combined sequences represent feasible ways of generating an x, y-mer. A *proper* combined sequence, corresponding to the generation of an x, y-mer, must run out of A sites at the last non-underlined event and out of B sites at the last underlined event and not before.

To derive the relation between the number of *proper* sequences, $W^{\wedge}_{xy}$, and the total number of sequences, $C^{\wedge}_{xy}$, we consider an arbitrary combined sequence such as the one in (18). If this sequence is considered cyclic, then each of the $x - 1$ events of type $\pm$ may be bracketed together with the following $f_A - 1$ non-underlined events, $+$ or $-$, ignoring any intervening events of type $\pm$ or any events previously enclosed in brackets. Applied to the sequence in (18) such bracketing procedure yields

$$(-)^{*} + \pm \pm (\pm - -)^{*} + \pm \pm \pm^{*} + (\pm (\pm \pm - +) \pm \square \pm -) \tag{20}$$

Such a procedure must always leave $(f_A x - x + 1) - (x - 1)(f_A - 1) = f_A$ non-underlined symbols, either $+$ or $-$, outside of the brackets; these are marked with asterisks in (20). Reasoning analogous to that in Section 2 shows that in a block of $f_A x - x + 1$ sequences generated by those cyclic permutations of an arbitrary sequence which start with one of the non-underlined symbols, the f_A sequences which start with a starred symbol are *proper*, while all the remaining sequences are *not proper*. Therefore the *proper* sequences constitute a fraction $f_A / f_A x - x + 1$ of every block and therefore also of the total set of $C^{\wedge}_{xy}$ possible combined sequences. Thus

$$\frac{W^{\wedge}_{xy}}{C^{\wedge}_{xy}} = \frac{f_A}{f_A x - x + 1}. \tag{21}$$

Inserting the value of $C^{\wedge}_{xy}$ from Eq. 19 we obtain

$$W^{\wedge}_{xy} = f_A \frac{(f_A x - x)!}{y!\,(f_A x - x - y + 1)!} \frac{(f_B y - y)!}{(x - 1)!\,(f_B y - y - x + 1)!}. \tag{22}$$

The expected number of x, y-mers, N_{xy}

We may now derive the limiting distribution expression for x, y-mers without rings. Suppose that the system contained initially N_{0A} monomers of type A and N_{0B} monomers of type B, and let $N_{0A} \to \infty$ and $N_{0B} \to \infty$. If the reaction has proceeded at random, with the fraction α_A of A sites and the fraction α_B of B sites having reacted, then the probability that a given site of type A has or has not reacted must be α_A or $1 - \alpha_A$, respectively. Similarly, the pro-

bability that a given site of type B has or has not reacted must be respectively α_B or $1 - \alpha_B$. Considerations of stoichiometry show that the quantities α_A and α_B are related by

$$f_A N_{0A} \alpha_A = f_B N_{0B} \alpha_B = \tfrac{1}{2}(f_A N_{0A} + f_B N_{0B})\alpha \tag{23}$$

where α may be defined as the fraction of all sites, of either type A or type B, which have reacted. The probability that a residue of type A, selected at random, belongs to an x, y-mer without rings is

$$P^A_{xy} = W^A_{xy} (\alpha_A)^y (1 - \alpha_A)^{f_A x - x - y + 1} (\alpha_B)^{x-1} (1 - \alpha_B)^{f_B y - y - x + 1}. \tag{24}$$

But the expected number of ringless x, y-mers in the system, by analogy with Eq. 6 is

$$N_{xy} = P^A_{xy} N_{0A}/x. \tag{25}$$

Combining Eqs. 21, 22, 23, and 24 we obtain

$$N_{xy} = \frac{2(f_A N_{0A} + f_B N_{0B})^{x+y-1}}{(2f_A N_{0A})^{y-1} (2f_B N_{0B})^{x-1}} \times \frac{(f_A x - x)!\,(f_B y - y)!}{y!\,(f_A x - x - y + 1)!\,x!\,(f_B y - y - x + 1)!} \times$$
$$\times \alpha^{x+y-1} (1 - \alpha_A)^{f_A x - x - y + 1} (1 - \alpha_B)^{f_B y - y - x + 1} \tag{26}$$

which is a special case of distribution equation presented by Stockmayer (Eq. 2 in Ref. 8) without proof.† It has since been derived by Whittle by means of generating functions.[9] The generalization to a mixture of several types of monomers bearing sites of type A and several types of monomers bearing sites of type B is straightforward.

4 RING-CONTAINING POLYMERS

Derivation of W_x

Finally, we return to the system of identical monomers described in Section 1 and consider $W_{x,k}$, the number of ways in which x indistinguishable residues, each bearing f indistinguishable reactive sites can be combined into an "x, k-mer", i.e. a single polymeric molecule containing x residues and k ring closures,‡ which implies the presence of $x - 1 + k$ bonds. The detailed in-

†Eq. 2 in Ref. 8 contains a printing error: the last term should be raised to the power n_j instead of m_j.

‡As has been stated in an earlier paper,[6] the number of ring closures corresponds to the *cyclomatic number* in graph theory.[10] The use of graph theory to describe multiatomic or multisegmented molecules has been advocated by Brostow[11,12] and Gordon[13,14] and their colleagues. It is possible that application of the more powerful graph-theoretical or generating-function techniques, outside the scope of the present elementary approach, could be used to obtain $W_{x,k}$ for $k > 1$.

ternal geometry of the x, k-mer will be disregarded. In the generation of an x, k-mer we shall encounter a sequence of three types of events: (i) success, i.e. the formation of an ordinary bond, (ii) failure, i.e. encountering a non-bonded site, and (iii) double failure, i.e. encountering an internal bond, which removes two reactive sites at once. These events must occur $x - 1$, $fx - 2x + 2 - 2k$, and k times, respectively, the total number of events in the sequence being $(x + 1) + (fx - 2x + 2 - 2k) + (k) = fx - x + 1 - k$.

The total number of distinct sequences of this type is given by the trinomial expression:

$$C_{x,k} = \binom{fx - x + 1 - k}{x - 1\ fx - 2x + 2 - 2k\ k} = \frac{(fx - x + 1 - k)!}{(x - 1)!\,(fx - 2x + 2 - 2k)!\,k!}. \tag{27}$$

As before, we observe that not all such sequences correspond to the generation of an x, k-mer. To derive the relation between $W_{x,k}$ and $C_{x,k}$ we consider the block of $fx - x - k + 1$ sequences derived by the cyclic permutations of an arbitrary sequence of $x - 1$ successes, $fx - 2x - 2k + 2$ failures and k double failures. Every success in the sequence can be considered to be neutralized by some combination of single and double failures adding up to the value $f - 2$. A bracketing procedure analogous to that described in section 1 would discover again for each sequence a unique set of unneutralized single and double failures adding up to the value f. (Any double failure "half-neutralized" in the bracketing procedure is subsequently counted as a single failure.)

While the total *value* of the unneutralized single and double failures must always be f, this can be variously made up by $f - 2d$ single failures and d double failures where d is any integer between 0 and $f/2$. As before, the necessary and sufficient condition that a sequence be proper is that it should end on an unneutralized failure (or an unneutralized or half-neutralized double failure). Therefore, the number of proper sequences in a block may be equal to $f, f - 1, \ldots f - l$, where the last case corresponds to the maximum number of unneutralized double failures, and l is the integral part of $f/2$ The relation of $W_{x,k}$ and $C_{x,k}$ must therefore be

$$\frac{W_{x,k}}{C_{x,k}} = \frac{\lambda_0 f + \lambda_1(f - 1) + \ldots + \lambda_l(f - l)}{fx - x - k + 1} \tag{28}$$

where $\sum_{i=0}^{l} \lambda_i = 1$ and the coefficients λ_i are proportional to the number of distinct cyclic blocks of sequences which yield $f - i$ "*proper*" sequences.

When $k = 0$, we observe that all blocks yield the same fraction $f/(fx - x +$

1) of proper sequences, so that $\lambda_0 = 1$, $\lambda_1 = \lambda_2 = \ldots 0$, and $W_{x,0}/C_{x,0} = f/(fx - x + 1)$.†

When $k = 1$ (and $f \geqq 3$) there will be two types of blocks and Eq. 28 becomes

$$\frac{W_{x,1}}{C_{x,1}} = \frac{\lambda_0 f + \lambda_1(f-1)}{fx - x}. \tag{29}$$

In order to calculate λ_0 and λ_1 we consider an arbitrary sequence of $x - 1$ successes and $fx - 2x + 1$ "non-successes" of which one is a double failure and $fx - 2x$ are single failures. If we treat all "non-successes" as single failures, a bracketing procedure can be applied as in Section 1. There will be found $(f-2)(x-1)$ non-successes within brackets, and $f - 1$ non-successes outside of brackets. If we now generate a set of $fx - 2x + 1$ sequences, each corresponding to placing the double failure in one of the non-success positions in the sequence, exactly $f - 1$ sequences in this set will have the double failure in one of the special positions *outside* of the brackets. Each of these $f - 1$ sequences will give rise to a block of cyclic permutations which will yield exactly $f - 1$ proper sequences, i.e. one per unneutralized failure. The remaining $(f-2)(x-1)$ sequences correspond to the double failure being placed in one of the positions *within* the brackets. These sequences contain an additional unneutralized failure (or a half-neutralized double failure) and therefore will yield blocks of cyclic permutations which yield one additional proper sequence for a total of f. Therefore, $\lambda_0 = (f-2)(x-1)/(fx - 2x + 1)$ and $\lambda_1 = (f-1)/(fx - 2x + 1)$. Substituting these values in Eq. 29, we obtain

$$\frac{W_{x,1}}{C_{x,1}} = \frac{f(f-2)(x-1) + (f-1)(f-1)}{(fx - x)(fx - 2x + 1)} = \frac{f(f-2)x + 1}{(fx - x)(fx - 2x + 1)}. \tag{30}$$

so that

$$W_{x,1} = \frac{[f(f-2)x + 1](fx - x - 1)!}{(x-1)!(fx - 2x + 1)!}. \tag{31}$$

Unfortunately, for $k > 1$ the combinatorial problem in deriving the λ's in Eq. 28 becomes rather complicated. We are left, however, with a lower and upper bound on $W_{x,k}$. Combining Eqs. 27 and 28, and noting that the numerator of Eq. 28 has the lower bound $f - l$ and the upper bound l, we obtain:

$$\frac{(f-l)(fx - x - k)!}{(x-1)!\,k!(fx - 2x + 2 - 2k)!} < W_{x,k} < \frac{f(fx - x - k)!}{(x-1)!\,k!(fx - 2x + 2 - 2k)!}. \tag{32}$$

†The quantities pertaining to ringless x-mers, $W_{x,0}$ and $C_{x,0}$, coincide with those designated respectively W_x and C_x in Section 2.

Since the upper and lower bound differ only by the factor $\frac{f}{f-1}$, which cannot be greater than two, the above inequality offers a potentially useful estimate of $W_{x,k}$.

THE EXPECTED NUMBER OF x,k-MERS, $N_{x,k}$

In order to derive the limiting distribution equation for polymers with rings we have to make some assumption about the relative probability of occurrence of ring-closures. For example, if the probability of a site being non-bonded is $1 - \alpha$, the probability of it being bonded is α. the probability that a site has reacted and has formed a ring is αp and the probability that it has reacted but has not formed a ring is $\alpha(1 - p)$, then, if we assume that all the above probabilities are independent of the size of the polymer† or its previous history, the probability $P_{x,k}$ that a residue selected at random belongs to an x, k-mer (which equals weight fraction of x, k-mers) must be

$$P_{x,k} = W_{x,k}(\alpha p)^k[\alpha(1 - p)]^{x-1}(1 - \alpha)^{fx-2x+2-2k} \tag{33}$$

For the expected number of x, k-mers, $N_{x,k}$, we obtain

$$N_{x,k} = \frac{N_0 P_{x,k}}{x} = N_0 \frac{W_{x,k}}{x} p^k (1 - p)^{x-1} \alpha^{x+k-1} (1 - \alpha)^{fx-2x+2-2k} \tag{34}$$

where the factor $W_{x,k}$ in Eqs. 33 and 34 is given within a factor of two by the inequality 32.

For a system which has condensed by random bond formation without restrictions, the probability p is of the order $1/N_0$. Thus, in the limit of $N_0 \to \infty$ we obtain the result that $P_{x,k} \to 0$ for any *finite* x, unless $k = 0$. This coincides with the deductions in Appendix I of Ref. 6.

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†This is, of course, a very drastic assumption. As discussed in Ref. 6. the model in which the probability of ring closure is independent of ring size corresponds to the situation in which inter-unit bonds impose no geometric restrictions. This may only be approached by those polymers which have highly flexible backbones.

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