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# Kinetics of Polymerization

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It is shown that three basic models of the Flory–Stockmayer theory of polymerization may all be described directly by means of a kinetic rate equation of a form first discussed by Smoluchowski, and correspond to the three known classes of solutions to this equation. The kinetics of gelation are discussed from the rate equation; the nature of both the Flory and the Stockmayer gelation theories is shown, and a new model of gelation is proposed. Some new solutions to Smoluchowski's equation are given in an appendix.

**KEY WORDS**: Kinetics of polymerization; kinetics of gelation; gelation; polymerization; condensation polymerization; Flory–Stockmayer theory; Smoluchowski's coagulation equation; coagulation.

## 1. INTRODUCTION

Condensation polymerization is the process of polymer formation by the continual and universal linking of elemental chemical units. The progress of this process is characterized by the size distribution function, whose evolution may be predicted theoretically either by the statistical method of Flory(1) and Stockmayer,(2),[2] or alternatively as the solution of a kinetic rate equation, as first shown by Dostal and Raff.(3) In the present paper, we will sketch both of these methods of solution for three basic polymer models, showing that the two methods are equivalent. We will also discuss the gelation transition, unifying both the Flory and the Stockmayer models of gelation, and obtain for the first time the kinetics of gel formation. The kinetic description of these polymer problems turns out to be formally equivalent to the kinetics

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[2] Note that in Ref. 2, as well as those of Ref. 1, the molecular weight distributions rather than the concentrations are discussed.

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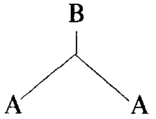
of colloidal clustering and droplet growth, as first discussed by Smoluchowski,(4),[3] and this analogy will also be discussed.

The basic chemical monomers from which the polymers are formed will be called *units*. Those of the first polymer model which we will examine may be represented schematically as

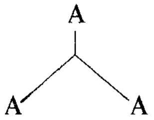
A–B (I)

where A and B represent active areas on the molecule, often called functional groups, with the property that only a free A and free B may bind together. Units of the second model may be represented as



(II)

where the free A's and B's have the same reactive property as in the previous case, but because of the two A ends on each unit, networks or trees may form. Units of the third model may be represented as



(III)

and these A's have the property that they may react and bind to each other. We assume two commonly made simplifying assumptions concerning the growth of polymers from these units(1,2):

(i) The polymers cannot bond with themselves, or cross-link.

(ii) The reactivity of a free group is independent of the size of the polymer to which it is attached.

The first assumption implies that closed rings or cycles cannot form, so that polymers of the first type will form linear chains and not rings, and those of sizes $v_k(t)$, defined as the concentration ($\equiv$number per unit volume) of $k$-mers, where a $k$-mer is a polymer composed of $k$ units in any configuration. dation, breakup, or termination.

The problem is to find, for each model, the time-dependent distribution of sizes $v_k(t)$, defined as the concentration ($\equiv$number per unit volume) of $k$-mers, where a $k$-mer is a polymer composed of $k$ units in any configuration. We assume that at $t = 0$ the system is monodisperse and consists only of monomers, and choose the unit of volume so that the concentration of these monomers is unity. Thus we take

$$v_k(0) = \begin{cases} 1 & k = 1 \\ 0 & k > 1 \end{cases} \tag{1}$$

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[3] An account of this work is given in Ref. 5.

as the initial condition. Note that the conservation of mass, or of total units, implies, for all time, that

$$\sum_{k=1}^{\infty} k v_k = 1 \tag{2}$$

The solution by the Flory–Stockmayer method is based upon the idea, whose validity follows from assumption (ii), that the bonding process may be thought of as a random process, such that, at each point in time, an independent probability $p$ determines whether or not an individual group has been reacted. This number $p$ will equal the total fraction of such groups bonded at that time, and thus represent the extent of the reaction. Then $v_k$ is found as the most probable distribution consistent with the value of $p$. Its determination entails an examination of all possible configurations of polymers, a combinatorial problem which would not be soluble in general without making assumption (i). The Flory–Stockmayer theory is by nature static, as its basic variable is not time but the parameter $p$, although the time dependence of $p$ may ultimately be determined, and the complete time dependence of $v_k(t)$ may be found.

To derive a kinetic rate equation of polymerization, consider the dynamic process that takes place: As fragments of polymers come into contact, chemical bonds are made between the free groups at a constant rate, by virtue of assumption (ii). This constant may be taken to be unity by an appropriate choice of time units. The rate (per unit volume) at which $i$-mers and $j$-mers react to form $(i+j)$-mers is given by the number of possible reactions per unit volume between free groups, which is equal to the product of the concentrations of the two polymers $v_i$ and $v_j$ multiplied by the number of possible ways a single $i$-mer and a single $j$-mer may join, denoted by $K_{ij}$. In short, the rate at which $i$-mers and $j$-mers combine to form $(i+j)$-mers is given by $K_{ij}v_iv_j$.[4] Because the concentration of $k$-mers is increased by all reactions between $i$-mers and $j$-mers such that $i+j=k$, and reduced by reactions between $k$-mers and all the rest, the development of $v_k$ is described by the equation

$$\frac{dv_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij} v_i v_j - v_k \sum_{j=1} K_{kj} v_j \tag{3}$$

This is a generalized form of Smoluchowski's equation. It represents an infinite set of nonlinear differential equations for each given matrix $K_{ij}$. Note that there is no spatial dependence in this equation, as the second assumption effectively implies that the polymers are randomly and homo-

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[4] The rate that $i$-mers combine with each other is assumed to be $\frac{1}{2}K_{ii}{v_i}^2$.

geneously distributed in space and the system is infinite. By multiplying Eq. (3) by $k$ and summing over all $k$, one can evidently verify that $(d/dt)\sum kv_k = 0$ and therefore that mass is conserved, as is expressed by Eq. (2), for a general $K_{ij}$ (although later we will find some exceptions to this). In the following sections, we will derive the appropriate $K_{ij}$ for each of the three models and show that the Flory–Stockmayer results, with the proper time dependence of $p$, also satisfy Eq. (3), subject to the initial conditions (1).

The coagulation problem considered by Smoluchowski$^{(4)}$ concerns the formation of clusters in a system of suspended particles. These particles are assumed to be in some specified kind of motion, such as Brownian motion, which brings them in contact with each other, at which time they may stick together, or agglomerate. A $k$-mer is defined as a cluster comprised of $k$ basic particles or units of mass. (This is a discrete version of the problem, which is the case, for example, for a system that is initially monodisperse.) $K_{ij}$ is now a collision matrix which reflects the mechanism of particle motion and tendency for adhesion, such that $K_{ij}v_iv_j$ is the rate per unit volume that $i$-mers and $j$-mers combine with each other to form $(i+j)$-mers (see footnote 4). Implicit in this is the assumption that these colloidal particles are randomly and homogeneously distributed in space for all time. The evolution of the distribution $v_k$ will be described by Smoluchowski's equation (3). In all studies of Smoluchowski's equation only three classes of exact solutions have been found,[5] or more precisely, solutions for three classes of collision matrices. We will show that these classes correspond to the three polymer models considered here, which are also the three basic types studied by Flory and Stockmayer. It may be noted that in the literature of coagulation physics, these particular collision matrices which allow an exact solution represent only approximations to physical processes of interest, and it has not been generally appreciated that physical models exist which precisely correspond to these matrices, as these polymer models do. In the Appendix we discuss some new classes of solutions to Smoluchowski's equation and their implications for the general question of the conditions for a gelation transition to occur.

## 2. MODEL I

Flory's solution for this model goes as follows: After reacting for some period of time, the system will be composed of linear polymers of varying length $k$, $k = 1, 2, 3, \ldots$, and will be described by a parameter $p$ defined as the fraction of $A$ groups that are bonded. This $p$ is also equal to the concentration of bonded A's, by virtue of the chosen unit of volume implicit

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[5] For a general review, see Ref. 6.

in Eq. (1) or (2). In this model, $p$ will also be the fraction, probability, and concentration of bonded B's, since there is one B for each A. Choose a free A in this "frozen" system; the probability $P_k$ that it is at the end of a $k$-mer is given by

$$P_k = p^{k-1}(1-p) \tag{4}$$

since a $k$-mer contains exactly $k-1$ bonds. The concentration of $k$-mers $v_k$ is found by multiplying $P_k$ by the concentration of free A's, which is $1-p$. This gives Flory's result$^{(1)}$ that for linear polymers,

$$v_k = p^{k-1}(1-p)^2 \tag{5}$$

One can easily verify that (5) satisfies the conservation law (2) and also that the probabilities $P_k$ are properly normalized,

$$\sum_{k=1}^{\infty} P_k = 1 \tag{6}$$

To find the time dependence of this solution, observe that assumption (ii) implies that the rate of reaction is proportional to the concentration of free A's multiplied by the concentration of free B's, both equal to $1-p$. Then, assuming that the time has been scaled to make the constant of proportionality unity, the differential equation for $1-p$ is

$$\frac{d}{dt}(1-p) = -(1-p)^2 \tag{7}$$

The right-hand side is negative because each reaction decreases the population of free ends. The solution to Eq. (7), consistent with (1), is

$$p = 1/(1+t) \tag{8}$$

Thus $p$ increases monotonically in time from zero to one, and Eqs. (5) and (7) give the complete time-dependent solution of this problem. Its general properties are as follows: The concentration of monomers $v_1$ decreases monotonically in time from its value 1 at $t = 0$, and for large times it approaches $1/t^2$. The concentrations of all other $k$-mers grow from zero linearly, peak at $t = (k-1)/2$, and then decay again to zero, eventually as $1/t^2$. Thus the peaks occur sequentially at each half unit of time. Each curve peaks and decays in succession as the average size of the polymer increases.

One can easily verify that $v_k(t)$ given by Eqs. (5) and (8) satisfies Smoluchowski's equation. The matrix $K_{ij}$, for all $i$ and $j$, is just equal to 2, as each of these linear polymers has a single A end and a single B end, and so there are always just two ways the polymers can combine. One can also *derive* the solution directly from the rate equation, with the aid of a generating function of the distribution,(7),6 or simply by successive solution, as was done by Smoluchowski.(4) Smoluchowski was considering the coagulation of colloidal particles, in which the mechanism of collision is dominated by Brownian motion. Smoluchowski showed that the collision matrix for this mechanism is proportional to $2 + (i/j)^{1/3} + (j/i)^{1/3}$, and for $i/j \approx 1$ this is well approximated by a constant. The solution of $v_k(t)$ from (3) in connection with the linear polymerization problem was first done by Dostal and Raff,(3) who also showed that (3) is equivalent to the probabilistic approach. A model for the antigen–antibody response mechanism has been shown to be mathematically analogous to this linear polymer model by Perelson,(8) who has discussed this mechanism using both approaches.

## 3. MODEL II

Because the basic units in this model have two A ends, treelike polymers may form, such as in the example of a 4-mer shown in Fig. 1. Flory's solution for the $v_k$ goes as follows: Suppose that, at a given frozen point in time, a certain fraction $p$ of the A's have reacted. The concentration of reacted A's will be $2p$, because there are two A's on each unit and there is one unit per unit volume on the average. The fraction of reacted B's will be $2p$, because there are half as many B's as A's, and their concentration will also be $2p$. Choose a free B in the system; the probability that it is at the top of a tree, as in Fig. 1, consisting of exactly $k$ units (or, in other words, attached to a $k$-mer) is given by

$$P_k = p^{k-1}(1-p)^{k+1}N_k \tag{9}$$

The first two factors express the probability of there being $k-1$ A–B bonds and $k+1$ free A's, and $N_k$ gives the number of possible ways of com-

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[6] In Ref. 7, a continuous distribution was considered, in which case the generating function is replaced by the Laplace transform.

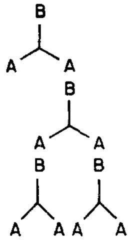

Fig. 1. An example of one possible 4-mer of model II. Note that there are five free A groups and one free B group.

bining these $k$ units. The distribution $\nu_k$ is found by multiplying $P_k$ by the concentration of free B's,$^{(1,2)}$

$$\nu_k = (1 - 2p)p^{k-1}(1 - p)^{k+1}N_k \tag{10}$$

An explicit expression for $N_k$ may be found as follows.[7] Since the $k - 1$ units of a $k$-mer which are below the "top" unit (see Fig. 1) may be partitioned between the two A ends of the top unit in $k - 1$ ways, $N_k$ satisfies the recursion relation

$$N_k = \sum_{i=0}^{k-1} N_i N_{k-1-i} \tag{11}$$

where we define $N_0 \equiv 1$. Then the generating function $g(z)$ defined by

$$g(z) \equiv \sum_{k=1}^{\infty} z^k N_k \tag{12}$$

satisfies the quadratic equation

$$g = z(1 + g)^2 \tag{13}$$

whose solution gives

$$g(z) = \frac{1 - 2z - (1 - 4z)^{1/2}}{2z} = \sum_{k=1}^{\infty} z^k \frac{(2k)!}{k!\,(k+1)!} \tag{14}$$

Thus,

$$N_k = \frac{(2k)!}{k!\,(k+1)!} \tag{15}$$

The time development of $p$ may be found by the same reasoning as used in the previous example. The concentration of free B's, $1 - 2p$, decreases at a rate proportional to its product with the concentration of free A's, $2(1 - p)$:

$$\frac{d}{dt}(1 - 2p) = -(1 - 2p)2(1 - p) \tag{16}$$

and the solution of this equation gives

$$p = (e^t - 1)/(2e^t - 1) \tag{17}$$

(Of course the same result follows from the differential equation for the decrease of free A's.) As $t$ varies from 0 to $\infty$, $p$ increases monotonically from zero to 1/2; $p$ cannot go beyond 1/2 because when $p = 1/2$ there are no more free B's. As in the previous model, each curve successively peaks and decays, but here the process goes faster and faster as

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[7] This is similar to the method of Flory, Ref. 9. Compare Ref. 2.

larger polymers are formed, as is reflected by the time at which $\nu_k$ peaks, which is given by $\frac{1}{2}\ln(k+1)/2$.

Note that $P_k$ and $\nu_k$ are properly normalized only when $p \leqslant 1/2$:

$$\sum_{k=1}^{\infty} P_k = \begin{cases} 1, & p \leqslant 1/2 \\ [(1-p)/p]^2, & p > 1/2 \end{cases} \tag{18}$$

$$\sum_{k=1}^{\infty} k\nu_k = \begin{cases} 1, & p < 1/2 \\ -[(1-p)/p]^2, & p > 1/2 \end{cases} \tag{19}$$

These results may be proved from Eqs. (12)–(15) by letting $z = p(1-p)$.[8] Although, as we have noted, there is no physical significance of Eq. (19) for $p > 1/2$ in the polymer problem, $P_k$ and Eq. (18) retain their meaning for all $p$ in the context of the construction we used to build (stochastically) the polymer trees in the derivation of $P_k$ given by Eq. (9). When $p > 1/2$, Eq. (18) implies that there is a nonzero probability that an infinite cluster is attached to the free B, given by

$$1 - [(1-p)/p]^2 \tag{20}$$

This varies from 0 to 1 as $p$ increases from 1/2 to 1. That construction is a representation of a branching process where, at each generation, either zero or two branches occur, with probability $1-p$ and $p$, respectively. This same branching process describes the reproduction of a line of amoebas, and also a chain reaction in uranium, with each unit representing the splitting of an individual amoeba or atom. Let $p$ be the probability that an amoeba, for example, survives to reproduction (splitting) age; then $P_k$ of Eq. (9) gives the probability that a given amoeba has exactly $k+1$ descendants, and Eq. (15) gives the probability that it has an infinite number of descendants, when $p > 1/2$. Here the branched tree represents the entire history of the amoeba line or the uranium chain reaction, and may contain many, or even an infinite number, of generations, while in the related polymer problem the "tree" represents just one polymer at a single instant in time. Indeed, the study of the descendants of an individual is the problem (called the Galton–Watson problem) that led to the development of branching theory.[9]

In this model, an $i$-mer has one free A end and $i+1$ free B's, and may combine with a $j$-mer either by attaching one of its B's to the latter's free A, which it can do in $i+1$ ways, or by attaching its one free A to the $j$-mer's free B's—in $j+1$ ways. Therefore $K_{ij}$ should be $i+j+2$. To verify that $\nu_k(t)$

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[8] Flory gives a simple way to derive these results for $p > 1/2$ from those for $p < 1/2$. See Ref. 1, Ch. 9.

[9] See, for example, Feller.(10) Note that branching theory (and thus polymerization) is also related to the so-called percolation problem; see, for example, Frisch and Hammersley.(11)

given by Eqs. (10) and (17) satisfies Smoluchowski's equation, the relation

$$\sum \nu_k = 1 - 2p \tag{21}$$

and also the normalization requirement (19) (both only valid for $p \leqslant 1/2$) are useful. One finds that the time part of $\nu_k$ cancels, and remaining is the identity

$$(k-1)N_k = \frac{1}{2} \sum_{i+j=k} (i+j+2)N_iN_j \tag{22}$$

which is satisfied by the $N_k$ of (15), since (22) implies for the generating function (12) the differential equation

$$g' - g = g(g + g') \tag{23}$$

where $g' \equiv z\, dg/dz$, whose solution [consistent with $N(1) = 1$] is identical to Eq. (13).

The solution to Smoluchowski's equation for a slightly different matrix $K_{ij}$, namely with $K_{ij} = i + j$, has been previously found by Golovin(12) and Scott(13),[10] in the study of shear coagulation of colloids—that is, coagulation when the fluid in which the particles are suspended is in perfect shear flow. The actual collision matrix for this problem (e.g., Ref. 15) is given by $(i^{1/3} + j^{1/3})^3$, which they approximated by $i + j$ so that the equations are solvable. The solution for $K_{ij} = i + j$ is quite similar to the solution for $i + j + 2$ in that, for example, the peaks of the concentration curves retain their logarithmic spacing.

Note that this model may be generalized to include any number $n$ of A ends on each unit. Both the probabilistic and kinetic methods may be generalized to find the solution, which is qualitatively the same as the case for $n = 2$. The collision matrix for the general model is given by $K_{ij} = (n-1)(i+j) + 2$.

## 4. MODEL III

The units of this model also form trees, as a consequence of the assumption that cross-linking is prohibited. This assumption is perhaps less realistic here than in the other models, for in this model reactive ends are all of the same type and have many opportunities to bond with each other. (Later, however, we will allow for some cross-linking to take place in the gelled state.) Again, let $p$ be equal to the fraction of reacted A's. The *concentration* of such A's will be $3p$, and the concentration of free A's will be $3(1-p)$, because there are three A ends on each unit and one unit per unit volume,

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[10] Note that the solution for $K_{ij} = i + j - 1$ is given by Lushkinov.(14)

on the average. Flory calculated the $v_k$ by observing that at a given point in time in a system of these polymers the probability that any randomly chosen free A end is a part of a $k$-mer is simply given by the $P_k$ of Eq. (9), because in a $k$-mer there are $k - 1$ A–A bonds and $k + 1$ free A's besides the one singled out, and because the number of configurations is given by the same combinatorial factor $N(k)$. Then $v_k$ is found by multiplying $P_k$ by the concentration of free A's, $3(1 - p)$, and dividing by the number of free A's on a single $k$-mer, $k + 2$, so that each configuration is counted only once. This gives

$$v_k = \frac{3(1-p)P_k}{k+2} = 3(1-p)^{k+2}p^{k-1}\frac{(2k)!}{k!\,(k+2)!} \tag{24}$$

The time development of $p$ follows from the differential equation for the concentration of free A's:

$$\frac{d}{dt}3(1-p) = -[3(1-p)]^2 \tag{25}$$

whose solution consistent with Eq. (1) is given by

$$p = 3t/(1+3t) \tag{26}$$

As time goes from zero to infinity, this $p$ increases monotonically from zero to one, and the functions $v_k(t)$ given by Eqs. (24) and (26) successively peak and then decay to zero. However, the time at which $v_k$ reaches its maximum is given by $t = 1/3 - 1/(k+2)$, so that by $t = 1/3$ (when $p = 1/2$) all the curves will have reached their peak and they will all actually be decreasing! This abnormal behavior is accompanied by the apparently incorrect normalization of $v_k$ when $p > 1/2$:

$$\sum k v_k = \begin{cases} 1, & p \leqslant 1/2 \\ [(1-p)/p]^3, & p > 1/2 \end{cases} \tag{27}$$

Also, at $p = 1/2$ the second moment of $v_k$ (which is equal to the mean of the mass distribution) becomes infinite:

$$\sum k^2 v_k = \begin{cases} \dfrac{1+p}{1-2p} = \dfrac{1+6t}{1-3t}, & p < 1/2 \\ \left(\dfrac{1-p}{p}\right)^3 \dfrac{2-p}{2p-1}, & p > 1/2 \end{cases} \tag{28}$$

The proofs of these expressions follow from Eq. (14).

Next, consider the kinetic equation for this model. Since an $i$-mer has $i + 2$ free A's, any of which may join with any of the $j + 2$ free A's on a

$j$-mer, $K_{ij}$ is equal to $(i+2)(j+2)$. The infinite sum in the second ("loss") term of Smoluchowski's equation (3) is now given by

$$\sum (j+2)\nu_j = \begin{cases} 3(1-p), & p \leqslant 1/2 \\ 3p[(1-p)/p]^3, & p > 1/2 \end{cases} \tag{29}$$

where we have used Eqs. (9), (18), (24), and (27). One finds that (3) is satisfied by $\nu_k(t)$ given by (24) and (26) only for $t < 1/3$. Note that the identity (22) is used in this proof also. For $t > 1/3$, the $\nu_k$ do not satisfy (3), and in fact one can show that there is no $p(t)$ such that $\nu_k(p)$ of the form (24) is a solution to (3).

Before finding consistent solutions past $t = 1/3$, we will investigate what is happening at the instant 1/3. We can assume that the above solution is valid up to and including that time.

The partial sum

$$-\frac{d}{dt}\sum_{k=1}^{L} k\nu_k \tag{30}$$

represents the rate (per unit volume) that units that were formerly part of polymers of size less than or equal to $L$ are becoming parts of polymers whose size is greater than $L$—thus the flux past size $L$. Using (24) and (26) to calculate $d\nu_k/dt$, we find that (30) is given by

$$\frac{1+6t}{t(1+3t)}\sum_{1}^{L} k\nu_k - \frac{1-3t}{t(1+3t)}\sum_{1}^{L} k^2\nu_k \tag{31}$$

Letting $L \to \infty$, (30) gives the rate at which units attach to an *infinite* polymer. When $t < 1/3$, this rate is zero, for the two sums above become just the first and second moments, and using (27) and (28), we see that those two terms cancel. However, when $t = 1/3$, then second term above is zero for each $L$, and when $L \to \infty$ we get the value 9/2 from the first term. Thus,

$$\lim_{L\to\infty} -\frac{d}{dt}\sum_{k=1}^{\infty} k\nu_k = \begin{cases} 0, & t < 1/3 \\ \frac{9}{2}, & t = 1/3 \end{cases} \tag{32}$$

The behavior at $t = 1/3$ marks the beginnings of the formation of a polymer of infinite size—a gel. At the next instant in time, some gel will exist, and $\sum k\nu_k$ will be less than unity. The latter sum represents only finite-sized polymers, which we identify with the sol. The difference $1 - \sum k\nu_k$ gives the concentration of units which belong to the gel, and its time derivative is the rate of gel growth, as given by (32). Note that the *concentration* $\nu$ of the infinite-size polymers must always be zero, even when a gel is present; this is why the gel does not contribute to any of the sums over $\nu_k$ above.

The gel growth (32) can also be derived in a parallel way from

Smoluchowski's equation directly, multiplying (3) by $k$ and summing over all $k$. Again, at the instant $t = 1/3$, the limit $L \to \infty$ must be taken very carefully because there appears the divergent sum $\sum k^2 \nu_k$. Thus, mass conservation (2) is not a universal consequence of Smoluchowski's equation.

The gelation rate is a discontinuous function of time. One way to represent this is by distribution of free A's in the system. In the sol, the concentration of free A groups is given by

$$[\mathrm{A_{free}(sol)}] = \sum_{k=1}^{\infty} (k+2)\nu_k \tag{33}$$

because each $k$-mer has $k + 2$ free A groups. An expression for this sum is given by (29). When $t < 1/3$, (33) satisfies the differential equation

$$\frac{d}{dt}[\mathrm{A_{free}(sol)}] = -[\mathrm{A_{free}(sol)}]^2 \tag{34}$$

which is identical to (25). When $t = 1/3$, we have the coupled equations

$$\frac{d}{dt}[\mathrm{A_{free}(sol)}] = -[\mathrm{A_{free}(sol)}]^2 - \tfrac{9}{2} \tag{35}$$

$$\frac{d}{dt}[\mathrm{A_{free}(gel)}] = \tfrac{9}{2} \tag{36}$$

These follow from (32), also using the fact that on the average there is one free A for each unit in the gel when it is first forming. The 9/2 term reflects the formation of gel by cascading growth.

Thus, for $t > 1/3$, we found that the solution (24)–(26) does not satisfy Smoluchowski's equation. It is not obvious whether the solution is wrong or the equation is wrong, for when a gel forms, we have seen that infinite sums may give some unexpected results. We will find both the correct solution to Eq. (3) and also the appropriate equation for the solution (24)–(26) and reveal the meaning of each. We will then propose a third equation and solution completely consistent with the assumption of no cross-linking. The kinetic equations will all be of the following form:

$$\frac{\partial \nu_k}{\partial t} = \frac{1}{2} \sum_{i+j=k} (i+2)(j+2)\nu_i \nu_j - (k+2)\nu_k X \tag{37}$$

$X$ represents an expression for the total concentration of free A groups with which the sol polymers are allowed to react, and depends upon the way in which the gel is assumed to react.

### 4.1. Stockmayer's Solution

Suppose that the gel cannot interact with the sol, so that the sol polymers can only interact with themselves. Then the quantity $X$ above will equal $[\mathrm{A}_{\mathrm{free}}(\mathrm{sol})]$:

$$X = \sum (j + 2)\nu_j \tag{38}$$

and in this case Smoluchowski's equation is unchanged by the presence of a gel. It follows that $[\mathrm{A}_{\mathrm{free}}(\mathrm{sol})]$ satisfies the closed equation (34) for all time, and shows that the sol reacts always with itself only. The solution of Smoluchowski's equation (3) for $t > 1/3$ that matches the solution (24)–(26) at $t = 1/3$ with continuous value and first derivative [so that Eq. (3) is also satisfied at the point $t = 1/3$] is found to be simply

$$\nu_k(t) = \nu_k(1/3)[2/(9t - 1)] \tag{39}$$

Here, all the concentration curves, as well as all their moments that are finite, diminish in the same way from their values at $t = 1/3$. During this time, the nature of the sol does not change—for example, the fraction of A's that are bonded remains fixed at 1/2 for all time—except that the sol is disappearing, since

$$\sum k\nu_k = \begin{cases} 1, & t \leqslant 1/3 \\ 2/(9t - 1), & t > 1/3 \end{cases} \tag{40}$$

[Note that the results in Eqs. (27)–(29) for $p > 1/2$ do not apply for this solution.] This apparent loss of mass is again due to the formation of a gel, containing units at a concentration

$$1 - \sum k\nu_k = \frac{9t - 3}{9t - 1} \tag{41}$$

(for $t \geqslant 1/3$). Equation (32) shows that there is a continuous cascading process in which matter is lost to infinity for all $t > 1/3$. The time derivative of (38), which is 9/2, matches the rate of gel growth found from Eq. (32).

As this is formed, it does not, by assumption, incorporate any more finite polymers, and so one may assume anything about the intramolecular reactions in the gel without affecting the properties of the sol or the amount of gel which is present. For example, if one assumes that the gel cannot cross-link, then the fraction of its A ends that are reacted remains fixed at 2/3 no matter how much gel exists. On the other hand, if one allows cross-linking, then that fraction would approach unity—in which case the gel would be completely cross-linked and would have no free ends to react. This would provide one possible explanation of the gel's inability to react with the sol, especially if the cross-linking occurs very quickly. Another situation in which the gel would effectively be inactive is one in which spatial homogeneity is broken and the gel forms in separated regions of space where its interaction with the rest will only be a surface term which is insignificant in an infinite system. Note that the overall fraction of A's that are bonded now depends on the assumptions made concerning the gel, and therefore the quantity $p$ is not as useful a quantity here. It is better to think of two values of $p$, one for the sol ($=1/2$) and another for the gel (depending upon its properties). The overall $p$ is then a linear combination of these two. This is reminiscent of a first-order phase transition, in which many properties are linear combinations of those representing each phase.

This solution found here for $t > 1/3$ was originally derived by Stockmayer,$^{(2)}$ who showed that it represents the most probable distribution for a fixed $\sum v_k$ and $\sum k v_k$, assuming that the gel is not cross-linked. He also compared this to Flory's solution and revealed the nature of each in regard to cross-linking. Although he wrote a kinetic equation for this problem, identical with Eq. (3) with $K_{ij} = (i + 2)(j + 2)$, and showed that the solution for $t < 1/3$ is given by (24)–(26), he did not solve the equation for $t > 1/3$ and did not discuss the time dependence of this part of the solution.

### 4.2. Flory's Solution

Flory considered that $v_k$ given by Eq. (24) is still valid when $1/2 < p \leqslant 1$, with the apparent deficiency of units,

$$1 - \sum k v_k = 1 - \left(\frac{1-p}{p}\right)^3 \tag{42}$$

representing the concentration of units in the gel. The parameter $p$ in this solution is still interpreted as the overall fraction of reacted A's, even when a gel is present. These $v_k$ satisfy (37) if $X$ is taken to be

$$X = 3(1 - p) \tag{43}$$

for all $p$, and $p(z)$ is given by (26). This $X$ may be compared with the value given by Smoluchowski's equation, in (29). According to the interpretation of $p$ in this solution, $X$ represents the total concentration of free A groups $[\mathrm{A}_{\mathrm{free}}(\mathrm{sol})] + [\mathrm{A}_{\mathrm{free}}(\mathrm{gel})]$, and so the sol polymers react with both the gel and sol.

We can show the nature of this solution by writing separate differential equations for $[\mathrm{A}_{\mathrm{free}}(\mathrm{sol})]$ defined by (33) and $[\mathrm{A}_{\mathrm{free}}(\mathrm{gel})]$:

$$\frac{d}{dt}[\mathrm{A}_{\mathrm{free}}(\mathrm{sol})] = -[\mathrm{A}_{\mathrm{free}}(\mathrm{sol})]^2 - [\mathrm{A}_{\mathrm{free}}(\mathrm{gel})] \sum (k+2)^2 v_k \tag{44}$$

$$\frac{d}{dt}[\mathrm{A_{free}(gel)}] = -[\mathrm{A_{free}(gel)}]^2 - [\mathrm{A_{free}(gel)}]\sum k(k+2)\nu_k \tag{45}$$

The first equation follows from Eq. (37), with $X = [\mathrm{A_{free}(sol)}] + [\mathrm{A_{free}(gel)}]$, by multiplying it with $k + 2$ and summing over all $k$, and the second follows using the fact that the sum $[\mathrm{A_{free}(sol)}] + [\mathrm{A_{free}(gel)}] = 3(1 - p)$ satisfies the differential equation (25) for all time. Thus we have separated those free A's that belong to finite polymers from those of the gel. The second term in each of these equations accounts for the reaction of finite polymers with the condensate, for, when a $k$-mer and a gel combine, which occurs at a rate $(k + 2)\nu_k[\mathrm{A_{free}(gel)}]$, the number of unreacted A's (per unit volume) lost to $[\mathrm{A_{free}(sol)}]$ is $k + 2$, and the number added to $[\mathrm{A_{free}(gel)}]$ is $k$. (This can easily be seen by making a sketch of such a reaction.) The first term in Eq. (44) represents the reaction of free A's when finite polymers bond together. Likewise, the first term in Eq. (45) represents the reaction of the free A's on the gel among themselves—that is, cross-linking in the gel.[11]

The existence of cross-linking can be inferred from the nature of the gel itself, for in the gel the *fraction* of the A's that are free is given by

$$\frac{[\mathrm{A_{free}(gel)}]}{3(1 - \sum k\nu_k)} = \frac{p(1-p)}{p^2 - p + 1} \tag{46}$$

and, when $p > 1/2$, this is always less than 1/3, while in a $k$-mer that has no cross-links that fraction is given by $(k + 1)/3k$ and is always greater than 1/3. The difference between (46) and 1/3 represents the degree of cross-linking.

In Eqs. (44) and (45), the sol and gel are shown to be like two systems which interact with each other only in proportion to the amount of gel present. There is no cascading growth of gel when $t > 1/3$. At the instant $t = 1/3$, Eqs. (44) and (45) are ambiguous, for as they stand the last terms of each are products of $[\mathrm{A_{free}(gel)}]$, which is zero, and the second moment, which is infinite. At $t = 1/3$, one must refer to Eqs. (35) and (36), which express the instantaneous occurrence of cascading.

## 4.3. A Third Solution

Consider a system where the A groups belonging to the gel may react with those in the sol polymers, as in the previous model, but where now

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[11] Flory's solution of polymerization has been criticized by Stockmayer(2) and also by Pis'men and Kuchanov(16) as being erroneous in that the gelation appears in an arbitrary way. We disagree with this view, since we have shown that Flory's solution represents definite and explicit assumptions concerning the reactivities of the sol and gel, as expressed in Eqs. (44) and (45). Note that Pis'men and Kuchanov showed (using a rate equation) that the transformation from a sol to a gel can be made while allowing some degree of cross-linking within individual polymers even before gelation occurs. This leads to a smoothing out of the transition.

the gel may not cross-link, just as the polymers in the sol are assumed not to cross-link. Here $X$ will equal $[\mathrm{A}_{\text{free}}(\text{sol})] + [\mathrm{A}_{\text{free}}(\text{gel})]$, where the former is given by (33) and the latter by

$$[\mathrm{A}_{\text{free}}(\text{gel})] = 1 - \sum k v_k \tag{47}$$

since, in an un-cross-linked gel, the concentration of free A groups will equal the concentration of units. Thus,

$$X = 1 + 2 \sum v_k \tag{48}$$

It follows from Eqs. (37) and (48) that $[\mathrm{A}_{\text{free}}(\text{sol})]$ and $[\mathrm{A}_{\text{free}}(\text{gel})]$ satisfy

$$\frac{d}{dt}[\mathrm{A}_{\text{free}}(\text{sol})] = -[\mathrm{A}_{\text{free}}(\text{sol})]^2 - [\mathrm{A}_{\text{free}}(\text{gel})] \sum (k+2)^2 v_k \tag{49}$$

$$\frac{d}{dt}[\mathrm{A}_{\text{free}}(\text{gel})] = -[\mathrm{A}_{\text{free}}(\text{gel})] \sum k(k+2) v_k \tag{50}$$

for $t > 1/3$. These are identical to Eqs. (44)–(45) except for the absence of the term which represents intramolecular bonding of the gel. The solution of Eqs. (37) and (48) for $v_k(t)$ is of the form

$$v_k = f(q)[q(1-q)]^k \frac{(2k)!}{k!\,(k+2)!} \tag{51}$$

where $q$ is some function of time. This is similar in form to $v_k(p)$ given by (24). Note that $q$ has no probabilistic significance here. The determination of $f(q)$ and then $q(t)$ requires the solution of a nonlinear differential equation. Although we have not been able to solve that equation in a closed form, we have found the approximate result, valid for large $t$, that

$$v_k \approx 3e^{-t}[e^{-t}(1-e^{-t})]^k \frac{(2k)!}{k!\,(k+2)!} \tag{52}$$

so that these functions decay exponentially in time. This behavior may be deduced from (37) and (48) directly, which, when the $v_k$ are small, just reduce to

$$\frac{d}{dt} v_k \approx -(k+2) v_k \tag{53}$$

The term on the right-hand side comes from the constant term in $X$, which represents a constant supply of free A's for the sol polymers to react with, and produces an exponential decay of the sol.

## 5. CONCLUSIONS AND FURTHER REMARKS

We have found that the kinetics of the three polymer models are described by (3) with the matrix $K_{ij}$ given by

$$K_{ij}=\begin{cases} 2 & \text{(I)} \quad (54a) \\ i+j+2 & \text{(II)} \quad (54b) \\ (i+2)(j+2) & \text{(III)} \quad (54c) \end{cases}$$

respectively. Only the first model and the third model (in the ungelled state) were previously studied by this approach, in the works referenced above. The real advantage of reexpressing the polymerization problem in terms of a rate equation is especially apparent in the third polymer system, where an explicit solution of the gelation kinetics was found. The three models of gelation discussed here are described by Eq. (37), in which $X$, which represents the expression for the total concentration of free A ends with which the sol polymers may react, is given by

$$X=\begin{cases} \sum (k+2)v_k & \text{(Stockmayer)} \quad (55a) \\ 3(1-p) & \text{(Flory)} \quad (55b) \\ 1+2\sum k v_k & \quad (55c) \end{cases}$$

respectively. Note that in Flory's model of gelation, $X$ is expressed not in terms of $v_k$, but instead in terms of the probabilistic parameter $p$, so Eqs. (37) and (55b) do not really represent a closed kinetic equation for $v_k$. The solutions for the three gelation processes may be compared by considering the loss of sol in each:

$$-\sum k\dot{v}_k=\begin{cases} -2/(9t-1) & \text{(Stockmayer)} \quad (56a) \\ -1/t^2 & \text{(Flory)} \quad (56b) \\ \sim -e^{-t} & \quad (56c) \end{cases}$$

In Stockmayer's solution, the sol polymers may not react with free groups on the gel and the gel is formed by a continuation of the cascading process for all time. In Flory's solution, the sol is allowed to react with the gel and so the gelation occurs at a faster rate, even though the cascading process stops after $t = 1/3$. The assumption behind this solution, that the fraction of reacted A ends is always equal to $p$, implies that the gel itself must cross-link. In this third solution presented here we do not allow this cross-linking to occur, and because the concentration of free groups on the gel does not diminish in this way, the conversion of sol into gel occurs the fastest of all. In this model, the cascading also stops immediately after $t = 1/3$.

The formation of a gel implies that the conservation of mass as is expressed in Eq. (2) is no longer obeyed. This can happen in Stockmayer's solution because $\sum k^2 v_k$ is infinite for all $t > 1/3$, in which case Eq. (2) does not follow from (3). Although in the second and third solutions $\sum k^2 v_k$ is finite for $t > 1/3$, the rate equation itself has been modified according to (55b) and (55c) such that (2) does not follow.

That Smoluchowski's equation has singular solutions was first shown, in connection with the coagulation problem, by McLeod.(7) He considered the collision matrix $K_{ij} = ij$, for which the solution is qualitatively very similar to the one for $K_{ij} = (i + 2)(j + 2)$ as given here. Note that McLeod chose this matrix for the purpose of proving a general theorem on the existence of solutions rather than for a particular physical model. He did not discuss the solution past the singular point. Solutions to Smoluchowski's equation have been found only for collision matrices which are linear combinations of 1, $i + j$, and $ij$, as we have noted, and these solutions show singular behavior whenever $K_{ij}$ contains the term $ij$. One may ask the question: What are the general conditions on $K_{ij}$ such that the solution to Smoluchowski's equation is singular? We have made a conjecture on these conditions based upon the discovery of an enlarged class of solutions to Smoluchowski's equation, given in the Appendix. These are only partial solutions in that for each $K_{ij}$ only a certain single moment can be found, yet this is enough to say whether the solution becomes singular in a finite period of time. For this entire class of solutions, which includes all the previously known solutions, we find that a singularity develops (no matter what the initial conditions) for all $K_{ij}$ in which the diagonal behavior grows faster than $i$—that is, when $d$, defined by

$$K_{ii} \sim \text{const} \times i^d \tag{57}$$

for $i \to \infty$, is greater than 1. When $d \leqslant 1$, the solution is regular. Although there may be pathological forms of $K_{ij}$ for which the solutions do not fall in this simple classification, (57) is probably a valid criterion for determining whether a solution is singular for all $K_{ij}$ of physical interest, since the $K_{ij}$ of physical processes are generally well behaved functions of $i$ and $j$ similar in form to the $K_{ij}$ for which we have found exact solutions.

Are there any coagulation problems which satisfy (57) and therefore show singular behavior? It seems that for all commonly discussed problems, $d < 1$. However, for an infinite system of gravitationally attracting, randomly distributed particles with a Maxwellian velocity distribution, the collision matrix is the sum of the free flight matrix and a matrix proportional to

$$K_{ij} = (ij)^{1/2}(i + j)^{1/2}(i^{1/3} + j^{1/3}) \tag{58}$$

Here $d = 11/6$ and a singular growth should occur. This may possibly have some cosmological implications.

An example for which $i = 1$, which should exhibit transitional behavior like the case $K_{ij} = i + j$ or $\cancel{i} + \cancel{j} + 2$, is given by the problem of coagulating particles imbedded in a shear flow,⁽¹⁵⁾ for which $K_{ij}$ is proportional to $(i^{1/3} + j^{1/3})^3$. In the earliest papers on the subject of coagulation, Smoluchowski⁽⁴⁾ described an experiment of Paine⁽¹⁸⁾ in which this coagulation process was produced by "moderate stirring" of a fluid. At a delayed point in time, he observed a sudden production of very large clusters, just as one would expect from the solution described above.

## APPENDIX

In this appendix we will derive some new solutions to Smoluchowski's equation. These solutions will be expressed in terms of a single moment of the distribution. We define the *nth* moment $M_n$ by

$$M_n = \sum_{k=1}^{\infty} k^n \nu_k \tag{A1}$$

First, we note the behavior of the $M_n$ of the three models discussed in the text. In models I and II, where the solution is always regular, all $M_n$ are positive, finite, monotonic functions of time, decreasing for $n < 1$ and increasing for $n > 1$. In model III, however, $M_2$ becomes infinite at $t = 1/3$ according to (28):

$$M_2 = \frac{1 + 6t}{1 - 3t} \tag{A2}$$

valid for $t \leqslant 1/3$, while $M_0$, which is given by

$$M_0 = \frac{1 - (3/2)t}{1 + 3t} \tag{A3}$$

according to (26), (27), and (29) (valid for $t \leqslant 1/3$), shows no irregularities at $t = 1/3$. However, it eventually behaves unphysically as a consequence of the gelation transition, for if (A3) is considered for times beyond $t = 1/3$, one sees that at $t = 2/3$ it goes to zero and then goes negative. Thus, looking only at (A3), one can deduce that the complete solution $\nu_k(t)$ which (A3) represents must cease to be valid at some point in time before $t = 2/3$, at which time a nonanalytic transition to another solution must take place. Note that it is not the $M_0$ of the actual solution which becomes negative, but the extension or analytic continuation of $M_0$ of the initial distribution, beyond the gel point, and neither is (A3) the $M_0$ of any of the actual solutions of gelation. One can show that all the $M_n$ of model III for $n \geqslant 2$ become infinite at $t = 1/3$, and all $M_n$ for $n \leqslant 0$ become zero at some $t > 1/3$.

To analyze the nature of the new solutions, we will assume that the relation between the behavior of the moments and gelation holds in general. Thus, if the $M_n$ we find turns out to be finite and positive for all time, we will assume that the entire solution is regular, while if $M_n \to \infty$ at some time for $n > 1$ or $M_n \to 0$ at some time for $n < 1$, we will consider that a gelation transition occurs at some (unknown) time.

Now, it follows from (3) that $M_n$ satisfies[12]

$$\frac{dM_n}{dt} = \frac{1}{2} \sum_{i,j=1}^{\infty} [(i+j)^n - i^n - j^n] v_i v_j K_{ij} \tag{A4}$$

where the double sum on $i$ and $j$ is unrestricted. Since we are only interested in the solution for the times preceding the gelation transition, we need not question the validity of the interchange of summations which is required to derive (A4), and we can also assume that $M_1 = 1$. We can choose three expressions for $K_{ij}$ which make (A4) a closed equation:

(i) Let

$$K_{ij} = \frac{Aij}{(i+j)^n - i^n - j^n} \tag{A5}$$

where $A$ is a constant, and $n$ may be thought of as a parameter, $n \neq 1$, and not necessarily integral. For example, when $n = 0$, 2, and 3, we have

$$n = 0: \qquad K_{ij} = -Aij \tag{A6}$$

$$n = 2: \qquad K_{ij} = A/2 \tag{A7}$$

$$n = 3: \qquad K_{ij} = A/3(i+j) \tag{A8}$$

Since $K_{ij}$ must be nonnegative, it follows that

$$\begin{aligned} A < 0 \quad &\text{when} \quad n < 1 \\ A > 0 \quad &\text{when} \quad n > 1 \end{aligned} \tag{A9}$$

For this class of $K_{ij}$, (A4) becomes

$$\frac{dM_n}{dt} = \frac{A}{2} \sum_{i,j=1}^{\infty} ij v_i v_j = \frac{A}{2} {M_1}^2 = \frac{A}{2} \tag{A10}$$

and so $M_n$ is given by

$$M_n(t) = M_n(0) + At/2 \tag{A11}$$

for an arbitrary initial distribution $M_n(0)$. Thus, for each value of the param-

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[12] This formula appears in Drake.(6)

eter $n$, we generate a unique $K_{ij}$ by (A5), for which the $n$th moment of the solution of Smoluchowski's equation is given by (A11). For each $K_{ij}$ we can only find one moment of the distribution, so the solution is incomplete. Yet one moment is enough to determine whether a gelation transition occurs, by using our criteria discussed above. When $A < 0$, the solution (A11) goes to zero in a finite amount of time, and by (A9), we conclude that all $K_{ij}$ of (A5) with $n < 1$ lead to singular behavior, while all $K_{ij}$ with $n > 1$ give regular solutions to Smoluchowski's equation.

(ii) In this case, we let

$$K_{ij} = A \frac{i^n j + i j^n}{(i+j)^n - i^n - j^n} \tag{A12}$$

($n \neq 1$). For example,

$$n = 0: \quad K_{ij} = -A(i+j) \tag{A13}$$

$$n = 2: \quad K_{ij} = A(i+j)/2 \tag{A14}$$

$$n = 3: \quad K_{ij} = A(i^2+j^2)/3(i+j) \tag{A15}$$

Again, $A$ must be positive or negative according to (A9). Equation (A4) gives

$$dM_n/dt = AM_n M_1 \tag{A16}$$

or

$$M_n(t) = M_n(0)e^{At} \tag{A17}$$

For all values of $n$ this solution is regular for all finite times, and so we conclude that none of these $K_{ij}$ leads to gelation.

(iii) Let

$$K_{ij} = \frac{A i^n j^n}{(i+j)^n - i^n - j^n} \tag{A18}$$

($n \neq 1$). For example,

$$n = 0: \quad K_{ij} = -A \tag{A19}$$

$$n = 2: \quad K_{ij} = Aij/2 \tag{A20}$$

$$n = 3: \quad K_{ij} = Ai^2j^2/3(i+j) \tag{A21}$$

The sign of $A$ is given by (A9) since $K_{ij} \geqslant 0$. Equation (A4) becomes

$$dM_n/dt = A[M_n]^2 \tag{A22}$$

or

$$M_n(t) = M_n(0)/[1 - AM_n(0)t] \tag{A23}$$

In this example, a singularity occurs at a positive time if and only if $A > 0$, or when $n > 1$.

These solutions may be further classified according to the asymptotic behavior of the collision matrices. In Eq. (57) we define the diagonal exponent $d$, and for the three classes of $K_{ij}$ considered above, $d$ is given by

$$d = \begin{cases} 2 - n & \text{(i)} \\ 1 & \text{(ii)} \\ n & \text{(iii)} \end{cases} \tag{A24}$$

Compiling all our results, we find that gelation always corresponds to those forms of $K_{ij}$ considered here in which $d > 1$, and regular solutions correspond to the forms of $K_{ij}$ in which $d \leqslant 1$. This is our result, which we propose should apply to a very large class of $K_{ij}$, perhaps including all the common ones of physical interest.

Thus we have found three classes of $K_{ij}$ for which solutions to (A4) can be obtained. What the $K_{ij}$ of each of these classes have in common is the form of the expression of a certain moment. These solutions include the $M_0$ and $M_2$ of the three fundamental forms of $K_{ij}$: 1, $i+j$, $ij$, which are similar to those discussed in the text, and for which the entire solution is known. In a sense, the new solutions can be thought of as generalizations of the fundamental ones. Note that (A4) can actually be solved with $K_{ij}$ equal to a linear combination of (A5), (A12), and (A18); the solution for $M_n$ is formally equivalent to a solution found by Drake(6) for $M_2$ when $K_{ij} = A + B(i+j) + Cij$—the case of $n = 2$. Note also that the procedure we used can be generalized to develop closed equations for $(d/dt)[\sum f(k)v_k]$ for any weight function $f(k)$, and thus giving rise to even larger classes of $K_{ij}$ for which Smoluchowski's equation has closed solutions.[13]

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[13] Note that even larger classes of $K_{ij}$ can be devised such that Eq. (3) or (A4) allows a "solution" for some moments, or perhaps some $v_k$, in terms of a basic moment such as $M_0$, which, however, cannot be determined. One such solution has been discussed by Lushkinov(14); see also Lushkinov and Piskanov.(15)

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