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Abstract

In this paper we consider some systems of ordinary differential equations which are related to coagulation-fragmentation processes. In particular, we obtain explicit solutions of such systems which involve certain coefficients obtained by solving a suitable algebraic recurrence relation. The coefficients are derived in two relevant cases: the high-functionality limit and the Flory-Stockmayer model. The solutions thus obtained are polydisperse (that is, is different from zero for all n) and may exhibit monotonically increasing or decreasing total mass. We also solve a monodisperse case (where μ_n is different from zero but is equal to zero for all $n > 1$) in the high-functionality limit. In contrast to the previous result, the corresponding solution is now shown to display a sol-gel transition when the total initial mass is larger than one, but not when such mass is less than or equal to one.

Keywords

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REMARKS ON ACCESSIBLE STEADY STATES FOR SOME COAGULATION-FRAGMENTATION SYSTEMS

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ABSTRACT. In this paper we consider some systems of ordinary differential equations which are related to coagulation-fragmentation processes. In particular, we obtain explicit solutions $\{c_k(t)\}$ of such systems which involve certain coefficients obtained by solving a suitable algebraic recurrence relation. The coefficients are derived in two relevant cases: the high-functionality limit and the Flory-Stockmayer model. The solutions thus obtained are polydisperse (that is, $c_k(0)$ is different from zero for all $k \geq 1$) and may exhibit monotonically increasing or decreasing total mass. We also solve a monodisperse case (where $c_1(0)$ is different from zero but $c_k(0)$ is equal to zero for all $k \geq 2$) in the high-functionality limit. In contrast to the previous result, the corresponding solution is now shown to display a sol-gel transition when the total initial mass is larger than one, but not when such mass is less than or equal to one.

1. Introduction. This note is concerned with some infinite systems of coupled ordinary differential equations related to classical models of polymer formation. More precisely, we are interested in the way equilibrium distributions may be characterized and arrived at. Before describing our results in detail, it may be worth recalling some relevant background information.

The problem of understanding how large structures form from an initial given distribution of their elementary components has deserved a great deal of attention in several physical contexts. Arguably, the earliest mathematical model proposed to shed light into this question was given by Smoluchowski [24, 5]. His description of coagulation of colloidal particles in a solution can be summarized as follows. Let $c_k(t)$ denote the concentration of aggregates or clusters made up of k ($k \geq 1$) identical individual particles (or monomers) at time $t \geq 0$. Assuming a number of hypotheses on the physical mechanism of coagulation, namely, (a) that monomers

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are functionally identical, (b) that k -aggregates (or k -mers) undergo identical Brownian motion, and (c) that k -mers coalesce whenever they are close enough to each other, Smoluchowski's analysis [24] led to the system of ordinary differential equations

$$\dot{c}_k = \frac{1}{2} \sum_{i+j=k} a_{ij} c_i c_j - \sum_{j \geq 1} a_{kj} c_k c_j \quad (k \geq 1) \quad (1)$$

with a particularly simple choice of the coagulation coefficients

$$a_{ij} = \text{constant} \quad (i, j \geq 1). \quad (2)$$

After some rescaling, (1), (2) can be rewritten as

$$\dot{c}_k = \sum_{i+j=k} c_i c_j - 2 \sum_{j \geq 1} c_k c_j \quad (k \geq 1). \quad (3)$$

It turns out that (3) can be solved assuming the monodisperse initial distribution $c_k(0) = \mu \delta_{1k}$ ($k \geq 1$), where $\mu > 0$ and δ is the usual Kronecker delta. The solution is given by

$$c_1(t) = \frac{\mu}{(1 + \mu t)^2}, \quad c_k(t) = \frac{(\mu t)^{k-1}}{(1 + \mu t)^{k+1}} \quad (k \geq 2).$$

Note that for $k \geq 2$, $c_k(t)$ first peaks to a maximum but eventually decays to zero as t goes to infinity.

Interest in aggregation processes was particularly enhanced by the flowering of polymer theory associated with, among others, the names of P. J. Flory and W. Stockmayer in the years following 1940. In particular, in a series of classical papers [11, 12, 13], Flory presented what was later called the RA_f model of polymer formation. According to this model, each functional unit of a polymer is considered to have a number f (f a positive integer) of functional groups of a given type A. These units react among themselves subject to the following conditions: (a) functional groups may link with one another to form bonds among the units, (b) intramolecular reactions do not occur, so that only branched-chain, noncyclic polymers can be formed, and (c) all unrelated functional groups are equally active.

The analysis introduced by Flory, and which was subsequently developed by Stockmayer [26], allowed to obtain the most probable distribution of molecular sizes for a chosen extent of reaction. This was done by maximizing the function

$$\Omega(c_k) = N! \prod_{k \geq 1} \left(\frac{w_k}{k!} \right)^{c_k} \frac{1}{c_k!}$$

for fixed values of $M = \sum_{k \geq 1} k c_k$ and $N = \sum_{k \geq 1} c_k$. Note that $\Omega(c_k)$ represents the total number of ways in which N units may be formed into c_1 monomers, c_2 dimers, ..., c_k k -mers, etc. On the other hand, w_k denotes the number of ways in which k units may form a k -mer, assuming as before that intramolecular reactions do not occur. In [26, Appendix A] Stockmayer computed $\{w_k\}$ by means of a combinatorial argument, thus obtaining

$$w_k = \frac{f^k (fk - k)!}{(fk - 2k + 2)!} \quad (k \geq 1). \quad (4)$$

This formula was instrumental in deriving information on a number of aspects, including the possible onset of a sol-gel transition. This was characterized by the formation of "infinitely large molecules (to be understood as molecules having dimensions of an order of magnitude approaching that of the containing vessel) which

are insoluble and do not contribute back to the reaction" [11]. After deriving a size-distribution law, Stockmayer [26, Appendix A] observed that up to some extent of reaction, the distribution law "may be derived from a set of differential equations describing the kinetic process," namely, (1) with the choice of coefficients

$$a_{ij} = r_i r_j, \quad r_j = (f - 2)j + 2 \quad (i, j \geq 1) \quad (5)$$

and some integer $f \geq 3$ (the so-called Flory-Stockmayer coefficients). For later reference it is worth to include here the following limit version of (5) (usually called the high-functionality case):

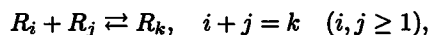
$$a_{ij} = ij \quad (i, j \geq 1). \quad (6)$$

It was soon realized, however, that coagulation kinetics as given by (1) only admits trivial equilibrium distributions, i.e., $\lim_{t \rightarrow \infty} c_k(t) = 0$ for all $k \geq 1$. In other words, additional terms have to be added to (1) for nontrivial steady states to exist. A natural way to do this is to consider

$$\dot{c}_k = \frac{1}{2} \sum_{i+j=k} (a_{ij} c_i c_j - b_{ij} c_{i+j}) - \sum_{j \geq 1} (a_{kj} c_k c_j - b_{kj} c_{k+j}) \quad (k \geq 1). \quad (7)$$

In addition to the coagulation rates $\{a_{ij}\}$, (7) also includes the fragmentation coefficients $\{b_{ij}\}$. In this system, the second (respectively, the fourth) term on the right corresponds to the removal (respectively, to the production) of k -mers by breakage of k -clusters into smaller units (respectively, by splitting of $(k + j)$ -clusters into smaller units). Note that only binary events (encounters or splittings) are taken into account in (1) or (7).

It should be emphasized that the coefficients $\{a_{ij}\}$ and $\{b_{ij}\}$ cannot be selected independently. For instance, it is customary to assume that a detailed balance condition holds [27, 6, 8]. Roughly speaking, this can be thought of as asserting that we consider the global, reversible process as a sequence of reactions of the form



each of which should be in equilibrium. For instance, it may be required that as time increases the number of k -mers lost to i -mers and j -mers ($i + j = k$) through fragmentation is exactly balanced by the number of k -mers formed by coagulation of i -mers and j -mers [6, 8]. This detailed balance condition can be recast in the form

$$\frac{a_{ij}}{b_{ij}} = \lim_{t \rightarrow \infty} \frac{c_{i+j}(t)}{c_i(t) c_j(t)} \quad (i, j \geq 1). \quad (8)$$

For a nontrivial steady state $\{\alpha_k\}$ of (7) this reads

$$b_{ij} \alpha_{i+j} = a_{ij} \alpha_i \alpha_j \quad (i, j \geq 1). \quad (9)$$

An immediate consequence of (9) is the following: for any sequence of positive numbers $\{\alpha_k\}$ and for any given set of coagulation coefficients $\{a_{ij}\}$, we may select the fragmentation rates $\{b_{ij}\}$ as in (9) so that the sequence $\{\alpha_k\}$ becomes a nontrivial steady state of (7).

From these remarks we may wonder whether such steady states are accessible, that is, whether nontrivial solutions $\{c_k(t)\}$ of (7) exist such that $\lim_{t \rightarrow \infty} c_k(t) = \alpha_k$ for all $k \geq 1$. Moreover, it seems natural to select steady states that represent meaningful equilibrium distributions and are therefore derived by suitable combinatorial or thermodynamical arguments. We shall return to this last point at the end of Section 3.

In addition to (9), a so-called normalization condition is often required [6, 8], whereby the total fragmentation rate has to be proportional to the number of bonds:

$$\frac{1}{2} \sum_{i+j=k} b_{ij} = \lambda(k-1) \quad (k \geq 1). \quad (10)$$

The positive constant λ is called the fragmentation strength of the process under consideration. The analysis in [6] shows that λ is a function of the free energy of bond formation, which is assumed to be equal for any bond in the system.

Let us now describe the contents of this work. In Section 2 we gather some preliminary results concerning explicit solutions of irreversible models of the form (1) for particular choices of the coagulation rates $\{a_{ij}\}$. In Section 3 we show that for a large class of coagulation coefficients and under the assumption that the detailed balance condition (9) holds, accessible steady states are provided by the solutions of a suitable recurrence relation. We then discuss the nature of these equilibrium states. For the Flory-Stockmayer and high-functionality cases, we derive explicit formulas for the solutions of this recurrence relation. We also show the existence of a continuum of polydisperse initial conditions of the form $c_k(0) = c_{0k} > 0$ ($k \geq 1$) for which the corresponding solution $\{c_k(t)\}$ converges monotonically to equilibrium distributions, and whose total mass $\sum_{k \geq 1} kc_k(t)$ increases or decreases in time. Finally, in Section 4 we give a sufficient condition for the existence of a phase transition for (7), (6), (9) starting from a monodisperse initial distribution. This will be accomplished by a transformation that allows us to go back and forth from the irreversible model (1) to the reversible model (7) under a different balance condition that in particular implies (9) for equilibrium distributions.

We conclude this section by noting that coagulation-fragmentation models different from (1) or (7) have been considered in the literature (see, for instance, [21, 22, 23, 14]). Particular attention has been paid to continuous models, where integral interaction terms (which reduce to (1) or (7) for Dirac mass type kernels) are introduced in the corresponding balance equations. We shall not pursue that subject here but refer the reader instead to [1, 2, 9, 17, 10] and the references therein for further information. We also refer to [7] for an account of existence results for irreversible equations, as well as a discussion of a finite-dimensional version of the corresponding process. The case where spatial inhomogeneities are considered has also been subject of considerable interest; please refer to [4, 3, 16] and their references for more details.

2. Preliminary results. In this section we gather some material concerning explicit solutions of kinetic models which will be useful for later purposes. The idea of solving (1) in a recursive way plays a key role in McLeod's seminal work [20] on the irreversible model in the high-functionality limit. More precisely, consider (1), (6) with monodisperse initial conditions

$$c_k(0) = \delta_{1k} \quad (k \geq 1). \quad (11)$$

McLeod [20] proved that for $0 \leq t \leq 1$, the problem under consideration has a unique solution $\{c_k(t)\}$ which preserves mass, i.e.,

$$M(t) = \sum_{k \geq 1} kc_k(t) = 1 \quad (0 \leq t \leq 1). \quad (12)$$

Furthermore, this solution can be written explicitly as

$$c_k(t) = \frac{k^{k-3}e^{-k}}{(k-1)!} t^{k-1} e^{k(1-t)} \quad (k \geq 1). \quad (13)$$

However, (12) was shown to break down for $t > 1$ and so (13) no longer provides a solution for such times.

Continuation beyond the critical time $t = 1$ was later achieved by Leyvraz and Tschudi [19]. They showed that the sequence $\{c_k(t)\}$ defined by

$$c_k(t) = \frac{k^{k-3}e^{-k}}{(k-1)!} t^{k-1} e^{k(1-t)} \text{ for } 0 \leq t \leq 1, \quad c_k(t) = \frac{k^{k-3}e^{-k}}{(k-1)!} \frac{1}{t} \text{ for } t > 1 \quad (14)$$

for all $k \geq 1$ is a solution of (1), (6), (11) which exhibits a sol-gel transition at the gelation time $t = 1$. By this we mean that the mass $M(t)$ is not preserved when $t > 1$, i.e.,

$$M(t) = 1 \text{ for } 0 \leq t \leq 1, \quad M(t) = \frac{1}{t} \text{ for } t > 1.$$

Actually, the analysis in [19] reveals that a sol-gel transition also occurs if (11) is replaced by $c_k(0) = \mu \delta_{1k}$ ($k \geq 1$) for any $\mu > 0$; the corresponding gelation time is then $t = t_\mu = \mu^{-1}$.

The post-gel solution given in (14) for $t > 1$ was generalized by Leyvraz [18] as follows. Let the coagulation rates in (1) be given by

$$a_{ij} = r_i r_j \quad (i, j \geq 1), \quad r_j > r_1 > 0 \quad (j \geq 2), \quad \lim_{j \rightarrow \infty} \frac{1}{r_j} = 0. \quad (15)$$

Note that (5) and (6) satisfy (15). Setting

$$c_k(t) = \frac{\alpha_k}{t} \quad (k \geq 1), \quad (16)$$

we see that $\{c_k(t)\}$ is a solution of (1), (15) provided $\{\alpha_k\}$ satisfies the recurrence relation

$$\alpha_k = r_k \alpha_k \sum_{j \geq 1} r_j \alpha_j - \frac{1}{2} \sum_{i+j=k} r_i r_j \alpha_i \alpha_j \quad (k \geq 1). \quad (17)$$

It was shown in [18] that (17) has a nontrivial, positive solution $\{\alpha_k\}$ whenever (15) is satisfied, and that $\sum_{k \geq 1} k \alpha_k$ is convergent. Thus, (1), (15) admits a solution of the form (16) under the given assumptions on the coagulation rates. For later reference we point out that setting $k = 1$ in (17) yields

$$\sum_{j \geq 1} r_j \alpha_j = \frac{1}{r_1} \quad (18)$$

so that (17) can be rewritten as

$$\frac{1}{2} \sum_{i+j=k} \frac{r_i r_j \alpha_i \alpha_j}{\alpha_{i+j}} = \frac{r_k}{r_1} - 1 \quad (k \geq 1). \quad (19)$$

Hence, the sequence $\{\alpha_k\}$ is a solution of (17) if and only if it is a solution of (18), (19).

3. On accessible steady states from polydisperse conditions and explicit solutions of a related recursion relation. Here we provide a link between accessible steady states of (7) under the detailed balance assumption (9) and solutions to Leyvraz's recurrence relation (17). We also derive explicit solutions to this recurrence relation for certain choices of the coagulation coefficients. Our first result is the following theorem:

Theorem 1. *The problem (7), (15), (9) has a solution of the form*

$$c_k(t) = \alpha_k u(t) \quad (k \geq 1),$$

where $\{\alpha_k\}$ satisfies (17) and $u(t)$ is the solution of the logistic equation

$$\dot{u} = u(1 - u), \quad u(0) = u_0 > 0.$$

If $0 < u_0 < 1$ (respectively, $u_0 > 1$), then $c_k(t)$ and $M(t) = \sum_{k \geq 1} kc_k(t)$ increase (respectively, decrease) in time and satisfy

$$\lim_{t \rightarrow \infty} c_k(t) = \alpha_k \quad (k \geq 1), \quad \lim_{t \rightarrow \infty} M(t) = \sum_{k \geq 1} k\alpha_k.$$

Proof. A straightforward computation gives

$$\begin{aligned} & \frac{1}{2} \sum_{i+j=k} (a_{ij}c_i c_j - b_{ij}c_{i+j}) - \sum_{j \geq 1} (a_{kj}c_k c_j - b_{kj}c_{k+j}) - \dot{c}_k \\ &= \frac{1}{2} \sum_{i+j=k} \left(r_i r_j \alpha_i \alpha_j u^2 - \frac{r_i r_j \alpha_i \alpha_j}{\alpha_{i+j}} \alpha_{i+j} u \right) \\ & \quad - \sum_{j \geq 1} \left(r_k r_j \alpha_k \alpha_j u^2 - \frac{r_k r_j \alpha_k \alpha_j}{\alpha_{k+j}} \alpha_{k+j} u \right) - \alpha_k u(1 - u). \end{aligned}$$

The right-hand side can be simplified to

$$\begin{aligned} &= \left(\frac{1}{2} \sum_{i+j=k} r_i r_j \alpha_i \alpha_j - r_k \alpha_k \sum_{j \geq 1} r_j \alpha_j + \alpha_k \right) u^2 \\ & \quad + \left(-\frac{1}{2} \sum_{i+j=k} r_i r_j \alpha_i \alpha_j + r_k \alpha_k \sum_{j \geq 1} r_j \alpha_j - \alpha_k \right) u = 0. \end{aligned}$$

The monotonicity and asymptotic behavior follow from a standard analysis of the logistic equation. \square

We remark that the fragmentation rates in Theorem 1 were chosen so as to satisfy the detailed balance assumption (9), so it follows that $\{\alpha_k\}$ is a stationary solution of (7). Moreover, in view of the properties of the logistic function $u(t)$, this steady-state solution is dynamically accessible by means of the flow associated with (7). However, for the normalization condition (10) to be satisfied as well with the same choice of fragmentation rates, we see from (19) that $\{r_k\}$ has to be of the form $r_k = Ak + B$ ($k \geq 1$), where $A > 0$ and $B \geq 0$. In such case we have $\lambda = A(A+B)^{-1}$. Note that $\lambda = f^{-1}(f-2)$ in the Flory-Stockmayer case (5) while $\lambda = 1$ in the high-functionality case (6).

In the following theorem we derive explicit expressions for $\{\alpha_k\}$ when the coagulation rates are given by (6) ($A = 1, B = 0$) and (5) ($A = f - 2, B = 2$).

Theorem 2.

(i) If $\{a_{ij}\}$ is given in (6), then the solution of (17) is

$$\alpha_k = \frac{k^{k-3}e^{-k}}{(k-1)!} \quad (k \geq 1). \quad (20)$$

Moreover, we have

$$\sum_{k \geq 1} k\alpha_k = 1, \quad \sum_{k \geq 1} \alpha_k = \frac{1}{2}. \quad (21)$$

(ii) If $\{a_{ij}\}$ is given in (5), then the solution of (17) is

$$\alpha_k = \frac{(f-2)^{1-k}}{f} \left(\frac{f-2}{f-1}\right)^{f-k-k} \frac{(fk-k)!}{k!(fk-2k+2)!} \quad (k \geq 1). \quad (22)$$

Moreover, we have

$$\sum_{k \geq 1} [(f-2)k+2]\alpha_k = \frac{1}{f}, \quad \sum_{k \geq 1} k\alpha_k = \frac{f-1}{f^2(f-2)}, \quad \sum_{k \geq 1} \alpha_k = \frac{1}{2f^2}. \quad (23)$$

Proof. Let $r_j = Aj + B$ in (17). Rearranging terms yields

$$\begin{aligned} \lambda(1-k)\alpha_k = & -\frac{A^2}{2} \sum_{i+j=k} ij\alpha_i\alpha_j - \frac{AB}{2} \sum_{i+j=k} i\alpha_i\alpha_j \\ & - \frac{AB}{2} \sum_{i+j=k} \alpha_i j\alpha_j - \frac{B^2}{2} \sum_{i+j=k} \alpha_i\alpha_j \quad (k \geq 1), \end{aligned} \quad (24)$$

where $\lambda = A(A+B)^{-1}$. Define the generating function

$$F(z) = \sum_{k \geq 1} \alpha_k e^{-kz} \quad (z \geq 0).$$

Multiplying (24) by e^{-kz} and summing over all k , we obtain the ordinary differential equation

$$(AF' - BF)^2 + 2\lambda(F' + F) = 0, \quad (25)$$

where $'$ denotes differentiation with respect to z .

Introduce the two functions

$$G = -AF' + BF, \quad H = F' + F, \quad (26)$$

which can be viewed as a linear system for the unknowns F' and F . The solution to this linear system is

$$-(A+B)F' = G - BH, \quad -(A+B)F = -AH - G. \quad (27)$$

In terms of G and H , (25) and (27) can be expressed as

$$G^2 + 2\lambda H = 0, \quad -AH' - G' = G - BH. \quad (28)$$

Eliminating H in (28) and decomposing into partial fractions gives us

$$\left(\frac{1}{G} - \frac{2A+B}{2\lambda+BG}\right)G' = -1. \quad (29)$$

Recalling (18), this equation is to be solved under the condition

$$G(0) = -AF'(0) + BF(0) = \sum_{k \geq 1} r_k \alpha_k = \frac{1}{A+B}. \quad (30)$$

By standard uniqueness results, (29), (30) has a unique solution (at least locally at $z = 0$) so that we expect $\{\alpha_k\}$ to be the unique solution of (17) satisfying (18).

To proceed further, we consider two cases: $B = 0$ and $B > 0$. Suppose first that $B = 0$. Then $\lambda = 1$ and (29) simplifies to

$$\left(\frac{1}{G} - A\right) G' = -1.$$

Integrating with respect to z gives

$$G = e^{-z}\Phi(G), \quad \Phi(G) = Ke^{AG}, \quad (31)$$

where K is an arbitrary constant of integration. From (30) we get $K = (Ae)^{-1}$. Applying Lagrange's Inversion Theorem [15] to (31), we have

$$G(z) = \sum_{k \geq 1} D_{\eta}^{k-1}[\Phi(\eta)]^k \Big|_{\eta=0} \frac{e^{-kz}}{k!} = \sum_{k \geq 1} \frac{k^{k-1} e^{-k}}{Ak!} e^{-kz}. \quad (32)$$

But from the first equation of (26) we also have $G(z) = \sum_{k \geq 1} Ak\alpha_k e^{-kz}$. Equating coefficients with (32) and setting $A = 1$ gives (20). From (30) we get $G(0) = A^{-1}$ while from the first equation in (28) we have $H(0) = -2^{-1}A^{-2}$, whence $F'(0) = -A^{-2}$ and $F(0) = 2^{-1}A^{-2}$ from (27). We obtain (21) upon setting $A = 1$.

Now suppose that $B > 0$. Integrating (29) with respect to z , we obtain

$$G = e^{-z}\Phi(G), \quad \Phi(G) = K(2\lambda + BG)^{(2A+B)/B}, \quad (33)$$

where K is an arbitrary constant of integration. Applying Lagrange's Inversion Theorem to (33), and using the first equation in (26), we have

$$G(z) = \sum_{k \geq 1} D_{\eta}^{k-1}[\Phi(\eta)]^k \Big|_{\eta=0} \frac{e^{-kz}}{k!} = \sum_{k \geq 1} (Ak + B)\alpha_k e^{-kz}, \quad (34)$$

from which $\{\alpha_k\}$ follows upon equating coefficients. In the case when the coefficients are of Flory-Stockmayer type we specify $A = f - 2$ and $B = 2$ so that

$$G(0) = \frac{1}{f}, \quad \lambda = \frac{f-2}{f}, \quad K = \frac{f^{f-2}}{(2f-2)^{f-1}},$$

and

$$\Phi(G) = \frac{f^{f-2}}{(2f-2)^{f-1}} \left[\frac{2(f-2)}{f} + 2G \right]^{f-1}.$$

A straightforward calculation gives

$$\begin{aligned} D_{\eta}^{k-1}[\Phi(\eta)]^k \Big|_{\eta=0} &= \frac{f^{fk-2k}}{(2f-2)^{fk-k}} \frac{(fk-k)!}{(fk-2k+1)!} \left[\frac{2(f-2)}{f} \right]^{fk-2k+1} 2^{k-1} \\ &= \frac{(f-2)^{fk-2k+1}}{f(f-1)^{fk-k}} \frac{(fk-k)!}{(fk-2k+1)!} \\ &= \frac{(f-2)^{1-k}}{f} \left(\frac{f-2}{f-1} \right)^{fk-k} \frac{(fk-k)!}{(fk-2k+1)!}. \end{aligned}$$

Substituting in the second term of (34) and comparing coefficients with the third gives (22). The first equation in (23) follows from the fact $G(0) = f^{-1}$. We can compute $H(0)$ from the first equation in (28) to get $H(0) = -[2f(f-2)]^{-1}$. From (27) we obtain

$$F'(0) = -\frac{f-1}{f^2(f-2)}, \quad F(0) = \frac{1}{2f^2}.$$

Thus the second and third equations in (23) can readily be verified. \square

The results of this section can be summarized as follows. Theorem 1 shows the existence of a solution $\{c_k(t)\}$ of (7) with product-type coagulation rates (15), fragmentation coefficients as given in (9), and with polydisperse initial conditions. This solution is "semi-explicit" since we still need to solve the recursion relation (17) for $\{\alpha_k\}$ (assuming of course that we are also interested in finding explicit solutions). At any rate, the existence of $\{\alpha_k\}$ was already shown by Leyvraz [18]. However, in the high-functionality and Flory-Stockmayer cases, Theorem 2 gives us the explicit analytical expressions for $\{\alpha_k\}$. In fact, the proof of Theorem 2 tells us how to find $\{\alpha_k\}$ when $r_k = Ak + B$ ($k \geq 1$) with B not necessarily zero, while the explicit results given in [19] were only for the case $B = 0$.

One may wonder if equilibrium states for a given process can be determined from first principles. Consider an aggregation process characterized by a family of coagulation coefficients $\{a_{ij}\}$. Building up on Stockmayer's work leading to (4), Spouge [25] noticed that if we denote by w_k the number of ways of forming a k -mer from k distinguishable units with distinguishable functional groups, then $\{w_k\}$ is related to $\{a_{ij}\}$ by the relation

$$w_1 = 1, \quad (k-1) \frac{w_k}{k!} = \frac{1}{2} \sum_{i+j=k} a_{ij} \frac{w_i}{i!} \frac{w_j}{j!} \quad (k \geq 2). \quad (35)$$

As discussed in [25], it is possible to solve (35) explicitly in the bilinear case

$$a_{ij} = A + B(i+j) + Cij \quad (i, j \geq 1), \quad (36)$$

where $A, B, C \geq 0$. In particular, it was shown that $w_k = k^{k-2}$ ($k \geq 1$) when $\{a_{ij}\}$ is given by (6), while $\{w_k\}$ satisfies (4) when $\{a_{ij}\}$ is given by (5).

It has been observed by several authors [25, 8] that (4) gives rise to stationary states of (7) which arise from equilibrium distributions for reversible processes satisfying (9) and (10). To verify this, let λ and q be arbitrary positive numbers for the moment. Then on setting

$$w_k = \frac{k! \alpha_k}{\lambda q^k} \quad (k \geq 1), \quad (37)$$

where $\{w_k\}$ satisfies (4), we can readily see that

$$\lambda(k-1)\alpha_k = \frac{1}{2} \sum_{i+j=k} r_i r_j \alpha_i \alpha_j, \quad r_j = (f-2)j + 2, \quad (i, j, k \geq 1). \quad (38)$$

This equation reduces to (19) if we choose $\lambda = f^{-1}(f-2)$. As mentioned in the last paragraph of Section 2, for $\{\alpha_k\}$ to be a solution of (17) we must choose q such that

$$\sum_{k \geq 1} r_k \alpha_k = \lambda \sum_{k \geq 1} \frac{r_k w_k}{k!} q^k = \frac{1}{f}.$$

From (22) we see that

$$q = \frac{1}{f(f-2)} \left(\frac{f-2}{f-1} \right)^{f-1}.$$

With these choices for λ and q , it follows that $\{\alpha_k\}$ is a solution of the recursion relation (17). In addition, if $\{b_{ij}\}$ is chosen so as to satisfy (9), then $\{\alpha_k\}$ is a stationary state of (7).

4. Reversible and irreversible processes: phase transitions from monodisperse conditions. In this section we show that a phase transition can occur in the system with fragmentation (7) under monodisperse initial conditions. To accomplish this, we first derive a relation between the irreversible model (1) and the reversible model (7) when a detailed balance condition similar to (8) is imposed.

Let $\{c_k(t)\}$ be a solution of (7) and suppose that for any $i, j \geq 1$, the function

$$v(t) = \frac{a_{ij}c_i(t)c_j(t)}{b_{ij}c_{i+j}(t)} \tag{39}$$

is independent of the indices i and j for all $t > 0$. Note that this assumption implies (9) for an accessible steady state $\{\alpha_k\}$ of (7). Using (39) we can rewrite (7) as

$$\left(1 - \frac{1}{v}\right)^{-1} \dot{c}_k = \frac{1}{2} \sum_{i+j=k} a_{ij}c_i c_j - \sum_{j \geq 1} a_{kj}c_k c_j \quad (k \geq 1).$$

Defining

$$\tau = \int_0^t \left[1 - \frac{1}{v(s)}\right] ds, \quad \tilde{c}_k(\tau) = c_k(t) \quad (k \geq 1),$$

we obtain

$$\tilde{c}'_k = \frac{1}{2} \sum_{i+j=k} a_{ij}\tilde{c}_i\tilde{c}_j - \sum_{j \geq 1} a_{kj}\tilde{c}_k\tilde{c}_j \quad (k \geq 1), \tag{40}$$

which corresponds to the irreversible model (1). Here, ' denotes differentiation with respect to τ . Conversely, if $\{\tilde{c}_k(\tau)\}$ solves (40) and (39) holds, then we may retrace our steps and define a new time scale $t = t(\tau)$ through the relation

$$\frac{d\tau}{dt} = 1 - \frac{b_{ij}\tilde{c}_{i+j}(\tau)}{a_{ij}\tilde{c}_i(\tau)\tilde{c}_j(\tau)} \tag{41}$$

so that $c_k(t) = \tilde{c}_k(\tau)$ is a solution of (7). We can now state the following theorem:

Theorem 3. Consider (7), (6), (9) with monodisperse initial conditions

$$c_k(0) = \mu\delta_{1k} \quad (k \geq 1), \tag{42}$$

and assume that $\{\alpha_k\}$ satisfies (20). Let

$$u(t) = \frac{e^t}{e^t - 1}, \quad t_\mu = \ln \frac{\mu}{\mu - 1} \quad (\mu > 1).$$

(i) If $\mu > 1$ then the sequence $\{c_k(t)\}$ defined by

$$c_k(t) = \alpha_k [u(t)]^{1-k} \left[\mu e^{1-\mu/u(t)} \right]^k \quad \text{for } 0 \leq t \leq t_\mu, \quad c_k(t) = \alpha_k u(t) \quad \text{for } t > t_\mu \tag{43}$$

for all $k \geq 1$ is a solution of the problem under consideration. Moreover, $M(t) = \sum_{k \geq 1} kc_k(t)$ satisfies

$$M(t) = \mu \quad \text{for } 0 \leq t \leq t_\mu, \quad M(t) = u(t) \quad \text{for } t > t_\mu, \tag{44}$$

and $\lim_{t \rightarrow \infty} c_k(t) = \alpha_k$ for all $k \geq 1$.

(ii) If $0 < \mu \leq 1$, then the sequence $\{c_k(t)\}$ defined by

$$c_k(t) = \alpha_k [u(t)]^{1-k} \left[\mu e^{1-\mu/u(t)} \right]^k \quad (k \geq 1) \tag{45}$$

is a solution of the problem under consideration for all $t \geq 0$. Moreover,

$$M(t) = \sum_{k \geq 1} kc_k(t) = \mu \tag{46}$$

for all $t \geq 0$ and $\lim_{t \rightarrow \infty} c_k(t) = \alpha_k (\mu e^{1-\mu})^k$ for all $k \geq 1$.

Proof. Consider the solution obtained by Leyvraz and Tschudi [19] for the problem (40), (6) under monodisperse initial conditions $\tilde{c}_k(0) = \mu \delta_{1k}$ for all $k \geq 1$:

$$\tilde{c}_k(\tau) = \frac{\alpha_k}{\tau} [\mu \tau e^{(1-\mu)\tau}]^k \text{ for } 0 \leq \tau \leq \tau_\mu, \quad \tilde{c}_k(\tau) = \frac{\alpha_k}{\tau} \text{ for } \tau > \tau_\mu, \quad (47)$$

where $\tau_\mu = \mu^{-1}$. Note that this solution can be expressed in the form $\tilde{c}_k(\tau) = \alpha_k \tau^{-1} [\Psi(\tau)]^k$ where $\Psi(\tau) = \mu \tau e^{1-\mu\tau}$ for $0 \leq \tau \leq \tau_\mu$ and $\Psi(\tau) = 1$ for $\tau > \tau_\mu$. In addition, this solution satisfies

$$\sum_{k \geq 1} k \tilde{c}_k(\tau) = \mu \text{ for } 0 \leq \tau \leq \tau_\mu, \quad \sum_{k \geq 1} k \tilde{c}_k(\tau) = \frac{1}{\tau} \text{ for } \tau > \tau_\mu. \quad (48)$$

From (41) we see that $d\tau/dt = 1 - \tau$. Imposing the condition that $\tau(0) = 0$, an integration yields

$$\tau = 1 - e^{-t}, \text{ or equivalently, } e^{-t} = 1 - \tau. \quad (49)$$

For $\mu > 1$ the gelation time τ_μ is transformed into t_μ via (49). Recalling that $\tilde{c}_k(\tau) = c_k(t)$, a direct substitution transforms (47) and (48) into (43) and (44), respectively. As $t \rightarrow \infty$ we have from (49) that $\tau \rightarrow 1^-$ and the second equation in (47) has to be used since the first one is valid only until $\tau = \tau_\mu$, which is strictly less than one by assumption. Hence $c_k(t)$ tends to α_k as $t \rightarrow \infty$ for all $k \geq 1$.

On the other hand, for $0 < \mu \leq 1$, the first part of (47) is valid for $0 \leq \tau \leq 1 \leq \tau_\mu$ and thus (49) holds for all $t \geq 0$. Substituting $\tilde{c}_k(\tau) = c_k(t)$ in the first equation of (47) gives (45), while the first equation in (48) yields (46), both valid for $t \geq 0$. The condition $t \rightarrow \infty$ is equivalent to $\tau \rightarrow 1^-$ in the first equation of (47) so that $c_k(t)$ tends to $\alpha_k (\mu e^{1-\mu})^k$ as $t \rightarrow \infty$ for all $k \geq 1$. \square

The results of this section can be summarized as follows. First we considered the problem of when the irreversible model (1) and the reversible model (7) are equivalent. It turns out that they are equivalent when (39) holds. Moreover, (39) implies the usual balance condition (9). Next we considered the irreversible model (1) with coagulation rates of the high-functionality type and with monodisperse initial conditions depending on a parameter μ . The solution to this problem is provided by the solution of Leyvraz and Tschudi [19]. It was also verified that (39) holds in this case. With the same coagulation rates and initial conditions, and with the fragmentation coefficients given by (9), we obtained an equivalent reversible model. The results of Theorem 3 showed that when $\mu > 1$, sol-gel transition also occurs in the reversible model. However, when $0 < \mu \leq 1$, we found a solution of the reversible model whose total mass is preserved throughout so gelation does not occur. For each μ we also obtained the asymptotic values of the solution and total mass.

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