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A NOTE ON THE KINETIC EQUATIONS OF COAGULATION

M. SLEMROD

Dedicated to John Nohel on the
occasion of his sixty-fifth birthday.

ABSTRACT. This paper provides a new derivation of the Leyvraz and Tschudi solution [**1**] of the discrete Smoluchowski-Flory-Stockmayer equations of coagulation.

0. Introduction. Models of cluster growth appear in a wide variety of applications. One well-known example is the Smoluchowski-Flory-Stockmayer theory of gelation where it was found that all concentrations decrease in time and the quantity representing mass density is conserved for only a finite time after which it decreases [**1, 2**]. A related example is provided by Perelson [**3**] who uses Smoluchowski's rate equation as a model for the growth of an antigen-antibody aggregate.

The models themselves are coupled infinite systems of ordinary differential equations (in the discrete case) or a single integro-differential equation (in the continuous case). In this note I reconsider the classical Smoluchowski-Flory-Stockmayer discrete equations and derive their solution via a simple summation identity. This approach provides a shorter derivation of the result given earlier by Leyvraz and Tschudi [**1**].

1. The equations. Let $c_j(t) \geq 0$, $j = 1, 2, \ldots$, denote the expected number of clusters consisting of j particles per unit of volume. The

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discrete coagulation-fragmentation equations are

$$\dot{c}_j = \frac{1}{2}\sum_{k=1}^{j-1}[a_{j-k,k}, c_{j-k}c_k - b_{j-k,k}c_j] - \sum_{k=1}^{\infty}[a_{j,k}c_jc_k - b_{j,k}c_{j+k}] \tag{1.1}$$

for $j = 1, 2, \ldots$. The coagulation rate $a_{j,k}$ and fragmentation rates $b_{j,k}$ are nonnegative constants with $a_{j,k} = a_{k,j}$, $b_{j,k} = b_{k,j}$. The continuous version of (1.1) may be found in the paper of Barrow [**4**] and is given by

$$\begin{aligned} \frac{\partial c}{\partial t}(j,t) = &\int_0^j [a(j-k,k)c(j-k,t)c(k,t) - b(j-k,k)c(j,t)]\,dk \\ &- \int_0^{\infty} [a(j,k)c(j,t)c(k,t) - b(j,k)c(j+k,t)]\,dk. \end{aligned} \tag{1.2}$$

In (1.2), $a(j,k)$, $b(j,k)$ are symmetric nonnegative kernels. Existence of solutions to (1.1) is discussed in the papers of Spouge [**5**], White [**6**] and, most recently, Ball and Carr [**7**]. Unfortunately, these papers do not apply to the Smoluchowski-Flory-Stockmayer theory described below. Existence of solutions to the continuous model has been given by Aizenman and Bak [**8**] under rather stringent conditions on the kernels a, b. In the case $a(j,k) = A + B(i+j) + Cij$, $b(j,k) = \lambda$, Barrow [**4**] solved the moment equation for the total number of clusters $\int_0^{\infty} c(k,t)\,dk$ and showed that the kinetic equation admits a nontrivial stationary solution only when $B = C = 0$, $\lambda \neq 0$.

In this note I consider (1.1) in the case of Smoluchowski's pure coagulation equations for which $b_{jk} \equiv 0$. Furthermore, I restrict myself to the special case $a_{jk} = jk$, so that (1.1) becomes the Smoluchowski-Flory-Stockmayer system

$$\dot{c}_j = \frac{1}{2}\sum_{k=1}^{j-1}(j-k)kc_{j-k}c_k - jc_j\sum_{k=1}^{\infty}kc_k. \tag{1.3}$$

For simplicity, the initial data is assumed to be monodisperse, i.e.,

$$c_1(0) = 1, \quad c_j(0) = 0, \quad 2 \leq j < \infty. \tag{1.4}$$

A solution for (1.3), (1.4) for $0 \leq t \leq 1$ was given by McLeod [**9**] by the following straightforward procedure: Formally, (1.1), in general, and

(1.3), in particular, conserve the total density $\rho(t) \doteq \sum_{k=1}^{\infty} kc_k(t)$. If density is indeed conserved, $\rho(t) = \rho(0) = 1$, one may solve (1.3) by solving the simpler system

$$\dot{c}_j = \frac{1}{2}\sum_{k=1}^{j-1}(j-k)kc_{j-k}c_k - jc_j, \tag{1.5}$$

recursively. This yields the formula

$$c_j(t) = \frac{j^{j-3}}{(j-1)!}t^{j-1}\exp(-jt), \quad j = 1, 2, \dots . \tag{1.6}$$

However, as noted by McLeod, the desired conservation of density of (1.6) breaks down for $t > 1$, and, hence, (1.6) is no longer a valid solution past the critical "gelation" time $t = 1$.

The resolution of the problem was provided by Leyvraz and Tschudi [**1**] who solved (1.3), (1.4) for all $t \geq 0$ by setting $\rho(t) = \sum_{k=1}^{\infty} kc_k(t)$, $\phi_j(t) = jc_j(t)\exp(j\int_0^t \rho(\tau)\,d\tau)$, and $G(z,t) = \sum_{k=1}^{\infty}\phi_k(t)z^k$. A straightforward computation shows that the generating function G satisfies the quasilinear hyperbolic partial differential equation

$$\frac{\partial G}{\partial t} = zG\,\frac{\partial G}{\partial z}, \quad 0 \leq z \leq 1,\ t > 0, \tag{1.7}$$

with initial data

$$G(z,0) = z. \tag{1.8}$$

Equation (1.7) may be integrated via the method of characteristics to obtain $G(z,t)$ from which one may recover $\phi_j(t)$, $j = 1, \dots$, and finally $c_j(t)$. The end result is that Leyvraz and Tschudi obtained that, while (1.6) is indeed valid for $0 \leq t \leq 1$, for $t > 1$, $c_j(t)$ should be given by

$$c_j(t) = \frac{j^{j-3}e^{-j}1}{(j-1)!t}, \quad t \geq 1. \tag{1.9}$$

In this case the density $\rho(t)$ satisfies

$$\begin{aligned} \rho(t) &= 1, \quad 0 \leq t \leq 1 \\ \rho(t) &= \frac{1}{t}, \quad 1 \leq t < \infty, \end{aligned} \tag{1.10}$$

indicating a decrease in density after the critical gelation time $t = 1$.

In the next section I give another derivation of (1.6), (1.9) which makes no recourse to the generating function. In fact, a careful reading of McLeod's paper shows that he had almost computed the correct post-gel solution in Section 3 of [**9**]. Unfortunately, as he was not searching for density decreasing solutions, he did not take full advantage of his formula to obtain (1.9) for $t \geq 1$.

2. The solution. As in Section 1, define the density $\rho(t) = \sum_{k=1}^{\infty} kc_k(t)$ so that (1.3) becomes

$$\dot{c}_j = \frac{1}{2}\sum_{k=1}^{j-1}(j-k)kc_{j-k}c_k - \rho(t)jc_j \tag{2.1}$$

or, alternatively, with

$$\phi_j(t) = \exp\left(j\int_0^t \rho(\tau)\,d\tau\right)c_j(t),$$

we see

$$\dot{\phi}_j = \frac{1}{2}\sum_{k=1}^{j-1}(j-k)k\phi_{j-k}\phi_k \tag{2.2}$$

with (1.4) implying

$$\phi_j(0) = 1, \quad \phi_j(0) = 0, \quad 2 \leq j < \infty. \tag{2.3}$$

Now solve (2.2), (2.3) recursively to obtain

$$\phi_j(t) = \frac{j^{j-3}}{(j-1)!}t^{j-1};$$

hence,

$$c_j(t) = \frac{j^{j-3}t^{j-1}}{(j-1)!}\exp\left(-j\int_0^t \rho(\tau)\,d\tau\right). \tag{2.4}$$

But, by definition, $\rho(t) = \sum_{k=1}^{\infty} jc_j(t)$ so that $\rho(t)$ must satisfy the equation

$$\rho(t) = \sum_{j=1}^{\infty} \frac{j^{j-2}t^{j-1}}{(j-1)!} \exp\left(-j\int_0^t \rho(\tau)\,d\tau\right)$$

or, equivalently,

$$t\rho(t) = \sum_{j=1}^{\infty} \frac{j^{j-1}(t\exp(-\int_0^t \rho(\tau)\,d\tau))^j}{j!}. \tag{2.5}$$

Next note the relevant identity

$$\sum_{j=1}^{\infty} \frac{j^{j-1}(xe^{-x})^j}{j!} = x, \quad 0 \le x \le 1, \tag{2.6}$$

which may be found in the collection of Jolley [**10**, p. 24, Series 130]. The interval of convergence $0 \le x \le 1$ is not noted by Jolley but is easily obtained by ratio test for $0 \le x < 1$ and Stirling's formula at $x = 1$. In fact, this is proven in the paper of McLeod [**9**].

For the moment assume

$$t\exp\left(-\int_0^t \rho(\tau)\,d\tau\right) \le e^{-1}, \quad \text{for all } t > 0, \tag{2.7}$$

and let $x(t)$ be that value x, $0 \le x(t) \le 1$, which satisfies the equation

$$x(t)\exp(-x(t)) = t\exp\left(-\int_0^t \rho(\tau)\,d\tau\right). \tag{2.8}$$

As the graph of xe^{-x} is monotone increasing for $0 \le x \le 1$ and monotone decreasing for $1 \le x$ with a maximum e^{-1} at $x = 1$, (2.7) will imply a solution of (2.8) and $x(t)$ can always be uniquely found. Thus (2.5), (2.6) imply

$$t\rho(t) = x(t). \tag{2.9}$$

Equations (2.8), (2.9) provide two equations in the two unknowns $x(t), \rho(t)$ for all $t > 0$. Now substitute the $x(t) = t\rho(t)$ from (2.9) into (2.8) to obtain

$$\rho(t)\exp(-t\rho(t)) = \exp\left(-\int_0^t \rho(t)\,d\tau\right), \quad t > 0, \tag{2.10}$$

and, hence,

$$\log \rho(t) - t\rho(t) = -\int_0^t \rho(t)\, d\tau. \tag{2.11}$$

At points of differentiability of $\rho(t)$, differentiate (2.11) to see that $\rho(t)$ satisfies

$$\left(\frac{1}{\rho(t)} - t\right) \dot{\rho}(t) = 0, \tag{2.12}$$

where recall of the initial data is given by

$$\rho(0) = 1. \tag{2.13}$$

For $0 \leq t < 1$, the solution of (2.12), (2.13) is $\rho(t) = 1$ and (2.7) is satisfied. For $1 < t$, a choice must be made between a function satisfying $\dot{\rho}(t) = 0$ (which, for continuous $\rho(t)$, would mean $\rho(t) = 1$) and $\rho(t) = 1/t$. If $\rho(t) = 1$ is chosen, then (2.9) becomes $t = x(t)$, i.e., $x(t) > 1$ which contradicts the definition of $x(t)$. This necessitates the choice $\rho(t) = 1/t$ which yields $x(t) = 1$ and also satisfies (2.7). Enforcing continuity at $t = 1$ yields

$$\begin{aligned} \rho(t) &= 1, \quad 0 \leq t \leq 1, \\ &\frac{1}{t}, \quad 1 < t, \end{aligned} \tag{2.14}$$

as the solution of (2.10). Finally, substitute (2.14) into (2.9). This yields the Leyvraz and Tschudi solution

$$\begin{aligned} c_j(t) &= \frac{j^{j-3} t^{j-1} \exp(-jt)}{(j-1)!}, \quad 0 \leq t \leq 1, \\ &= \frac{j^{j-3} e^{-j}}{(j-1)!} \frac{1}{t}, \quad 1 < t, \end{aligned} \tag{2.15}$$

$j = 1, 2, \ldots$.

3. Remarks. One may ask what is the point of the above exercise if the only result was to obtain a known formula. I would suggest that what should be emphasized is the approach based on deriving equation (2.5). Hence, the problem became one of looking for a *fixed point* ρ of the nonlinear integral equation (2.5). Of course, the ability to solve (2.5) in explicit simple form is, to some extent, luck. However, it may be that other problems involving cluster dynamics and gelation in both the discrete and continuous cases can also be converted into similar fixed point problems where the existence of a fixed point $\rho(t)$ in an appropriate function space yields the relevant solution.

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Center for Mathematical Sciences, University of Wisconsin, Madison, WI 53706