

A Transformation Linking Two Models of Coagulation

ROBERT M. ZIFF,¹ M. H. ERNST, AND E. M. HENDRIKS

*Department of Chemical Engineering, The University of Michigan, Ann Arbor, Michigan 48109 and
Institute for Theoretical Physics, State University of Utrecht, 3508 TA Utrecht, The Netherlands*

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It is shown that a given solution to Smoluchowski's coagulation equation with the kernel $K_{ij} = (ai + b)(aj + b)$ can be directly transformed to obtain a solution to the same equation with $K_{ij} = a(i + j) + b$.

The evolution of the distribution of particle size, in systems where coagulation or agglomeration takes place, is described by Smoluchowski's coagulation equation,

$$dc_k/dt = \frac{1}{2} \sum_{i+j=k} K_{ij}c_i c_j - c_k \sum_j K_{kj}c_j \quad [1]$$

where $c_k(t)$ is the cluster size distribution and K_{ij} are the rate constants of the coagulation process. (Unless otherwise indicated, sums are over all positive integers.) Complete, explicit solutions to [1] have been found only when K_{ij} is given by 1, $i + j$, ij , and their linear combinations (1). In this paper, we show that two classes of soluble models, with $K_{ij} = (ai + b)(aj + b) = s_i s_j$ (model I), and $K_{ij} = ai + aj + b = s_{i+j}$ (model II), are closely related, such that a given solution of one model can be directly transformed into a solution of the other ($s_k \equiv ak + b$). These two models are directly applicable to two systems of condensation polymerization. In the following, we give a derivation of this transformation and apply it to some special examples. We also discuss the generalization to continuum models.

The total mass or number of structural units, $\sum kc_k(t)$, remains constant, unless ge-

lation (infinite cluster growth) occurs. For those K_{ij} where gelation occurs, mass conservation is valid only up to the onset of gelation, at time t_c , and the solution past the gel point requires special considerations (2, 3). In model I gelation occurs in a finite time (as shown below); however, the post-gel solution will not be of concern here since only the behavior for $t < t_c$ is relevant for the transformation.

Let $c_k(t)$ be a solution model I, described by the coagulation equation

$$dc_k/dt = \frac{1}{2} \sum_{i+j=k} s_i s_j c_i c_j - s_k c_k \sum_j s_j c_j \quad [2]$$

for a given initial condition $c_k(0)$. To make the transformation we multiply [2] by s_k and introduce $\tilde{c}_k \equiv s_k c_k$, with the result

$$d\tilde{c}_k/dt = \frac{1}{2} \sum_{i+j=k} s_{i+j} \tilde{c}_i \tilde{c}_j - \tilde{c}_k s_k \sum_j \tilde{c}_j. \quad [3]$$

We can recast the RHS of [3] in the form of the coagulation equation for model II, with $K_{ij} = s_{i+j}$, by writing $s_k = s_{k+j} - aj$. We thus find

$$\begin{aligned} \frac{d\tilde{c}_k}{dt} - a\tilde{c}_k \sum_j j\tilde{c}_j \\ = \frac{1}{2} \sum_{i+j=k} s_{i+j} \tilde{c}_i \tilde{c}_j - \tilde{c}_k \sum_{j=1}^{\infty} s_{k+j} \tilde{c}_j. \quad [4] \end{aligned}$$

¹ To whom correspondence should be sent.

Multiplying [2] by ks_k and summing over k , we find that the quantity $m(t)$, defined by

$$m(t) = a \sum_k k \tilde{c}_k(t) = a \sum_k ks_k c_k(t) \quad [5]$$

satisfies

$$dm/dt = m^2$$

or

$$m(t) = (t_c - t)^{-1} \quad [6]$$

valid for $t < t_c$. The point t_c , where m diverges, marks the onset of gelation for this model. The value of t_c is determined by the initial condition as

$$1/t_c = a \sum_k k \tilde{c}_k(0) = a \sum_k ks_k c_k(0) \quad [7]$$

which is a combination of the first and second moments of c_k .

On the account of [6] the LHS of [4] may be written as $m(d/dt)(\tilde{c}_k/m)$. As the next step we introduce new variables $c_k^*(\tau) = \tilde{c}_k(t)/m(t)$ and $d\tau = m(t)dt$, which allows us to write [4] in the form

$$dc_k^*/d\tau = \frac{1}{2} \sum_{i+j=k} s_{i+j} c_i^* c_j^* - c_k^* \sum_j s_{k+j} c_j^* \quad [8]$$

where $c_k^*(\tau)$ is seen to satisfy the coagulation equation for model II. Integration of $d\tau = mdt$ with $\tau(0) = 0$ yields

$$t = t_c(1 - e^{-\tau}) \quad [9]$$

and

$$c_k^*(\tau) = \tilde{c}_k(t)/m(t) = t_c e^{-\tau} s_k c_k(t_c(1 - e^{-\tau})). \quad [10]$$

The total mass in the new model is given by

$$\sum_k kc_k^*(\tau) = 1/a \quad [11]$$

on account of [9], [10], and [6]. The mass can be made equal to any value of rescaling τ and $c_k^*(\tau)$. Following standard convention, we choose the mass to be unity, and thus rescale as

$$n_k(\tau) \equiv ac_k^*(a\tau). \quad [12]$$

This completes the transformation.

In summary, to transform a solution $c_k(t)$ of model I to a solution $n_k(t)$ of model II, we have found

$$n_k(t) = a(ak + b)t_c e^{-at} c_k(t_c(1 - e^{-at})). \quad [13]$$

The initial conditions of these two solutions are related by

$$n_k(0) = a(ak + b)t_c c_k(0) \quad [14]$$

and the mass in model II is normalized to unity:

$$\sum_k kn_k(t) = 1. \quad [15]$$

It follows, especially, that a solution for a monodisperse initial condition in one model is transformed into a solution for a monodisperse initial condition of the other. The quantity t_c in the above transformation is determined from the initial distribution in model I by [7]. To transform model II to model I we invert [13], to find

$$c_k(t) = \frac{n_k[-(1/a) \ln(1 - t/t_c)]}{a(ak + b)(t_c - t)} \quad [16]$$

where the initial conditions are still related by [14]. To find t_c we set the total mass of system I equal to unity, $\sum kc_k(0) = 1$. Then it follows directly from [14]:

$$t_c = \sum_k kn_k(0)/[a(ak + b)]. \quad [17]$$

In model II, t_c does not mark any singularity, but only represents a parameter of the transformation based upon the initial behavior of $n_k(0)$. The time interval $0 < t < t_c$ in model I is mapped to the interval $0 < t < \infty$ in model II, so that the pre-gel solution of the former is stretched to a complete solution to latter, with the singular (gel) point moved to $t = \infty$. In the reverse transformation, the entire solution of model II is compressed to the pre-gel solution of model I.

Now we consider some examples and applications. The polymerization of f -functional branched monomers, RA_f (where f is an integer larger than unity) is described by the

coagulation equation with $K_{ij} = [(f-2)i + 2] \cdot [(f-2)j + 2]$ (4-7), and the solution for a monodisperse initial condition, $c_k(0) = \delta_{k1}$, is given by

$$c_k(t) = \frac{f(fk-k)!}{(fk-2k+2)!} \frac{(ft)^{k-1}}{k!(1+ft)^{(f-1)k+1}} \quad [18]$$

where $t_c = 1/f(f-2)$ (which follows from [7]). Applying the transformation with $a = (f-2)$ and $b = 2$, we find

$$n_k(t) = \frac{e^{-(f-2)t}(fk-k)!}{(fk-2k+1)!k!} \left(\frac{1-e^{-(f-2)t}}{f-2} \right)^{k-1} \times \left(1 + \frac{1-e^{-(f-2)t}}{f-2} \right)^{-1-(f-1)k} \quad [19]$$

for the solution with $K_{ij} = (f-2)(i+j) + 2$ and monodisperse initial conditions, $n_k(0) = \delta_{k1}$, which describes the polymerization of ARB_{f-1} branched molecules (4-8).

As another example, consider the solution for $K_{ij} = ij$, again for monodisperse initial conditions:

$$c_k(t) = t^{k-1} e^{-kt} k^{k-2} / k! \quad [20]$$

Applying [13], we find

$$n_k(t) = e^{-t}(1-e^{-t})^{k-1} \times \exp(-k(1-e^{-t}))k^{k-1}/k! \quad [21]$$

as the solution for $K_{ij} = i+j$ with monodisperse initial conditions.

The transformation may be used to extend to the model $K_{ij} = i+j$ the many known results for the model ij (2, 3). For example, as $t \uparrow t_c = 1/M_2(0)$, the asymptotic behavior of c_k for large k is given by (3)

$$c_k \simeq (2\pi\mu t_c^3)^{-1/2} k^{-5/2} \times \exp[-k(t-t_c)^2/2\mu t_c^3] \quad [22]$$

where $\mu = M_3(0)$ and $M_n = \sum k^n c_k$, and M_1 is assumed to be 1. This is valid in the limit $k \rightarrow \infty$, $t \uparrow t_c$ with $k(t-t_c)^2$ fixed. Note that [22] depends only upon M_1 , M_2 , and M_3 of the initial distribution. Applying [13] and [14], we find

$$n_k(t) \simeq (B/\pi)^{1/2} k^{-3/2} e^{-t} \exp[-Bke^{-2t}] \quad [23]$$

with

$$B^{-1} = 2 \sum k^2 n_k(0) \quad [24]$$

for the large k - and t -behavior of the size distribution in the model $K_{ij} = i+j$ (9, 10). This result is valid in the coupled limit of $k \rightarrow \infty$ and $t \rightarrow \infty$ with ke^{-2t} constant.

The transformation may be extended to the case of continuous variables, where Smoluchowski's equation is written in integral form. Here, because the size variable, x , can also be scaled, one can choose units so that two initial moments are arbitrarily given. We assume units are chosen such that $M_1(0) = M_2(0) = 1$. Let the size distribution $c(x, t)$ be the solution for a transition kernel $K(x, y) = xy$ (model I) and $n(x, t)$ be a solution for the kernel $K(x, y) = x+y$ (model II). The analog of [13] becomes, for general initial conditions:

$$n(x, t) = e^{-t} x c(x, (1-e^{-t})). \quad [25]$$

Note that $t_c = 1$ because of the choice $M_2 = 1$. If we apply the transformation [25] to the closed form solution of the model $K(x, y) = xy$ (11):

$$c(x, t) = e^{-(1+t)x} I_1(2x\sqrt{t}) / (x^2\sqrt{t}) \quad [26]$$

corresponding to the initial condition $xc(x, 0) = e^{-x}$, then we find the solution for the model $K(x, y) = x+y$ (12):

$$n(x, t) = x^{-1}(1-e^{-t})^{-1/2} e^{-t} \times \exp[-x(2-e^{-t})] I_1[2x(1-e^{-t})^{1/2}] \quad [27]$$

corresponding to the initial condition $n(x, 0) = e^{-x}$. The transformation may also be applied to the infinite-series solutions of I and II given in Refs. (1, 13).

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