

Analytic solutions to Smoluchowski's coagulation equation: a combinatorial interpretation

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1985 J. Phys. A: Math. Gen. 18 3063

(<http://iopscience.iop.org/0305-4470/18/15/028>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 31/05/2010 at 09:11

Please note that [terms and conditions apply](#).

Analytic solutions to Smoluchowski's coagulation equation: a combinatorial interpretation†

John L Spouge

Theoretical Biology and Biophysics, Group T-10, Mail Stop K710, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Received 28 March 1985

Abstract. Many analytic solutions of the polydisperse coagulation equation

$$\frac{dx_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij}x_i x_j - x_k \sum_{j=1}^{\infty} K_{kj}x_j$$

$$x_k(0) = \xi_k \geq 0 \quad \xi_k \text{ arbitrary}$$

have combinatorial interpretations. The interpretations are based on random polycondensation models from polymer chemistry. The notion of chemical bonding inherent in these polymer models introduces additional mathematical structure. This structure allows combinatorial interpretation of the coagulation solutions when the coagulation kernel is bilinear:

$$K_{ij} = A + B(i+j) + Cij.$$

The Smoluchowski coagulation equations are the infinite system

$$\frac{dx_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij}x_i x_j - x_k \sum_{i=1}^{\infty} K_{ik}x_i$$

$$x_k(0) = \xi_k \geq 0 \quad k = 1, 2, 3, \dots \quad (1)$$

(von Smoluchowski 1916). Equation (1) has the following physical interpretation: consider a fixed volume V containing a large number of moving particles. These particles we call *units*. These units vary in mass, but all masses are integral multiples of some fundamental mass. We scale the mass units to make fundamental mass one. At $t = 0$, the units begin to clump irreversibly (coagulate). The clumps formed we call polymers; a polymer of mass k we call a k -mer; in particular, a k -mer unit is a unit of mass k . (Polymer chemistry provides a convenient terminology, but the applications of equation (1) are in fact much broader.) $x_k(t)$ is the concentration of k -mers in V at time t , ξ_k is the (initial) concentration of k -mer units in V , $K_{ij} = K_{ji}$ is the rate constant for coagulation of i -mers and j -mers.

K_{ij} is called the coagulation kernel. The coagulation equation (1) gives the rate of change of k -mer concentration as the sum of two terms representing:

- (1) k -mer formation from coagulation of smaller masses, and
- (2) k -mer disappearance by coagulation with other masses.

† Work completed under the auspices of the United States Department of Energy.

Units of volume are usually chosen to normalise the initial mass concentration to unity:

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

This paper restricts itself to the bilinear kernels,

$$K_{ij} = A + B(i + j) + Cij \tag{3}$$

where A , B and C are arbitrary constants.

One expects conservation of mass to hold:

$$\sum_{k=1}^{\infty} kx_k(t) = \sum_{k=1}^{\infty} k\xi_k = 1. \tag{4}$$

Multiply equation (1) by k , then sum over $k = 1, 2, 3, \dots$. For the bilinear kernels, the series on the right are absolutely convergent when $\sum k^2x_k(t)$ is, and they have algebraic sum zero. The expression on the left is the derivative of equation (4), which is therefore constant.

In fact, for $C \neq 0$, $\sum k^2x_k(t)$ diverges at a finite time, t_c , when an infinite aggregate (or gel) forms. After t_c , the total mass $\sum kx_k(t)$ diminishes as the gel traps more and more mass (McLeod 1962, Drake 1972). Post-gel ($t > t_c$) solutions for equation (1), although known (Ziff and Still 1980, Ernst *et al* 1984), will not be considered in this paper.

Let

$$s_k = b + ak. \tag{5}$$

Ziff *et al* (1984) give the following transformation linking two solutions

$$\text{(Model I)} \quad k_{ij} = s_i s_j = b^2 + ab(i + j) + a^2 ij \tag{6a}$$

$$\text{(Model II)} \quad K_{ij} = s_{i+j} = b + a(i + j) \tag{6b}$$

of the coagulation equation (1). Let $\{c_k(t)\}$ be the solutions $\{x_k(t)\}$ for model I and $\{n_k(t)\}$ be the solutions for model II. Then the gel time for model I satisfies

$$\frac{1}{t_c} = a \sum_{k=1}^{\infty} k s_k c_k(0). \tag{7}$$

If the initial conditions of the two models are linked by

$$n_k(0) = t_c a s_k c_k(0), \tag{8}$$

then the solutions are related by

$$n_k(t) = e^{-at} t_c a s_k c_k(t_c(1 - e^{-at})). \tag{9}$$

The transformation maps the pre-gel interval $[0, t_c)$ of model I onto the interval $[0, \infty)$ of model II (which does not gel).

Note that the kernels of equation (6) are special cases of bilinear kernels (3) that Spouge (1983a) solves as follows. Let

$$\mu = \mu(t) = \sum_{k=1}^{\infty} x_k(t). \tag{10}$$

Then for $t < t_c$, summing equation (1) over $k = 1, 2, 3, \dots$ yields

$$\begin{aligned} d\mu/dt &= -\frac{1}{2}(A\mu^2 + 2B\mu + C) \triangleq -\frac{1}{2}D(\mu) \\ \mu(0) &\triangleq \mu_0. \end{aligned} \tag{11}$$

(\triangleq denotes a definition.) Let $\{\xi_{ku}: u = 1, 2, \dots, k; k = 1, 2, 3, \dots\}$ satisfy the (computationally practical) recursion

$$\begin{aligned} \xi_{k1} &= \xi_k \quad k = 1, 2, 3, \dots \\ (u-1)\xi_{ku} &= \sum_{i+j=k} \sum_{r+s=u} \frac{K_{ij}}{D(\mu_0)} \xi_{ir}\xi_{js} \quad u = 2, 3, \dots, k \end{aligned} \tag{12}$$

where $i = 1, 2, \dots, k-1$ and $r = 1, 2, \dots, u-1$. Then, for $t < t_c$,

$$x_k(t) = \sum_{u=1}^k x_{ku}(t) \tag{13}$$

where

$$x_{ku}(t) = \xi_{ku}(\mu_0 - \mu)^{u-1} \frac{D(\mu)}{D(\mu_0)} \begin{cases} \exp[(\mu - \mu_0 - \frac{1}{2}Ct)k] & A = 0 \\ \left[\frac{D(\mu)}{D(\mu_0)} \right]^{(B/A)k} \exp\left[\left(-\frac{AC - B^2}{A} \right) kt \right] & A \neq 0. \end{cases} \tag{14}$$

Spouge (1983a) gives these equations for a continuous mass spectrum (equation (14a) of that paper should read $x(\mu - 1)$ rather than $x\mu$). In that paper, μ_0 was normalised to be one. Here the normalisation is not possible because the fundamental mass fixes the units of mass. The table of Spouge (1983a) gives solutions of equation (11) subject to $\mu_0 = 1$; trivial manipulation of that table gives table 1 here.

This paper demonstrates that equations (7)-(9) and (10)-(14) have forms dictated by combinatorial considerations. The demonstration requires knowledge of the Flory

Table 1. Solutions of $d\mu/dt = -\frac{1}{2}(A\mu^2 + 2B\mu + C)$, $\mu(0) = \mu_0$, $\mu_{\pm} = [-B \pm (B^2 - AC)^{1/2}]/A$, $\alpha = -B/A$, $\gamma = (AC - B^2)^{1/2}/A$.

Cases	t	μ
$C = 0, B = 0$	$\frac{2}{A} \frac{\mu_0 - \mu}{\mu_0 \mu}$	$\frac{2\mu_0}{A\mu_0 t + 2}$
$C = 0, B \neq 0$	$\frac{1}{B} \ln\left(\frac{A\mu + 2B}{A\mu_0 + 2B} \frac{\mu_0}{\mu}\right)$	$\frac{2B\mu_0}{(A\mu_0 + 2B)e^{Bt} - A}$
$C \neq 0, A = 0, B = 0$	$\frac{2}{C}(\mu_0 - \mu)$	$\frac{2\mu_0 - Ct}{2}$
$C \neq 0, A = 0, B \neq 0$	$\frac{1}{B} \ln\left(\frac{2B\mu_0 + C}{2B\mu + C}\right)$	$\frac{(2B\mu_0 + C)e^{-Bt} - C}{2B}$
$C \neq 0, A \neq 0, B^2 = AC$	$\frac{2A(\mu_0 - \mu)}{(A\mu + B)(A\mu_0 + B)}$	$\frac{2A\mu_0 - B(A\mu_0 + B)t}{A[2 + (A\mu_0 + B)t]}$
$C \neq 0, A \neq 0, B^2 > AC$	$\frac{2}{A(\mu_+ - \mu_-)} \ln\left(\frac{\mu_0 - \mu_+}{\mu - \mu_+} \frac{\mu - \mu_-}{\mu_0 - \mu_-}\right)$	$\mu_+ + \frac{(\mu_+ - \mu_-)(\mu_0 - \mu_+)}{(\mu_0 - \mu_-) \exp[A(\mu_+ - \mu_-)t/2] - (\mu_0 - \mu_+)}$
$C \neq 0, A \neq 0, B^2 < AC$	$\frac{2}{A\gamma} \left(\tan^{-1} \frac{\mu_0 - \alpha}{\gamma} - \tan^{-1} \frac{\mu - \alpha}{\gamma} \right)$	$\alpha + \gamma \frac{\mu_0 - \alpha - \gamma \tan(A\gamma t/2)}{\gamma + (\mu_0 - \alpha) \tan(A\gamma t/2)}$

(1941) polymer models, RA_f (solved by Stockmayer (1943)) and A_gRB_{f-g} (solved by Flory (1952) for $g = 1$, and Spouge (1983b, c) for general g).

In the RA_f polymer model, each monomer has f functional groups of the type A (see figure 1). The monomers react subject to three conditions.

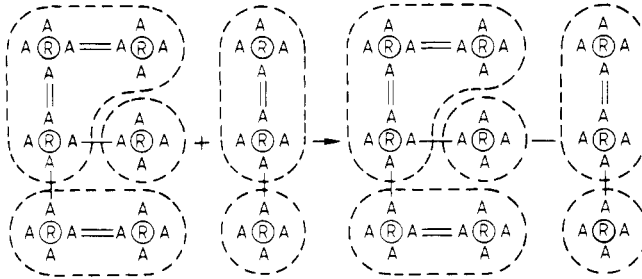


Figure 1. This figure shows two RA_4 polymers, a 6-mer, and a 3-mer reacting to form a 9-mer. The broken curves encircle the original units that formed the polymers, and double lines indicate bonds present at $t = 0$. Single lines indicate bonds that have formed after $t = 0$. The 6-mer contains 3 units, so it is a 3-unit 6-mer.

- (i) functional groups of the type A react with one another to form bonds between the monomers,
- (ii) intramolecular reactions do not occur (so that only branched-chain (non-cyclic) polymers are formed), and
- (iii) Flory's principle of equireactivity: subject to conditions (i) and (ii), all unreacted functional groups are equally likely to react; i.e., reaction takes place at random.

The A_gRB_{f-g} polymer model is similar, except that each monomer has g functional groups of the type A, $f - g$ of the type B, and condition (i) is replaced by

- (i): functional groups of the type A react with those of the type B to form bonds between the monomers.

For these two models the coagulation kernels are

(RA_f model)

$$K_{ij} = [2 + (f - 2)i][2 + (f - 2)j] \tag{15a}$$

(A_gRB_{f-g} model)

$$K_{ij} = [1 + (f - g - 1)i][1 + (g - 1)j] + [1 + (g - 1)i][1 + (f - g - 1)j]. \tag{15b}$$

Proof. In the RA_f model, an i -mer has fi functional groups. The number of bonds equals $i - 1$ because the polymers are branched-chain (condition (iii)). The number of functional groups consumed by bonding is $2(i - 1)$, so each i -mer has $fi - 2(i - 2) = 2 + (f - 2)i$ unreacted functional groups. Equation (15a) gives the number of ways an i -mer can react with a j -mer. Within an irrelevant constant of proportionality (which can be absorbed into the time scale of equation (1)), this is K_{ij} .

Similarly, for the A_gRB_{f-g} model, each i -mer has $(f - g)i - (i - 1) = 1 + (f - g - 1)i$ unreacted B groups and $gi - (i - 1) = 1 + (g - 1)i$ unreacted A groups. A similar calculation for j -mers yields the K_{ij} of equation (15b). For $g = 1$,

(ARB_{f-1} model)

$$K_{ij} = 2 + (f-2)(i+j). \tag{15c}$$

Note that the kernels of equations (15) are all bilinear (equation (3)). In addition (as noted by Ziff *et al* 1984), equations (15a) and (15c) are special cases of equations (6a) and (6b) with $a = f-2$ and $b = 2$. Figure 2 gives the combinatorial interpretation behind the transformation of equations (8) and (9).

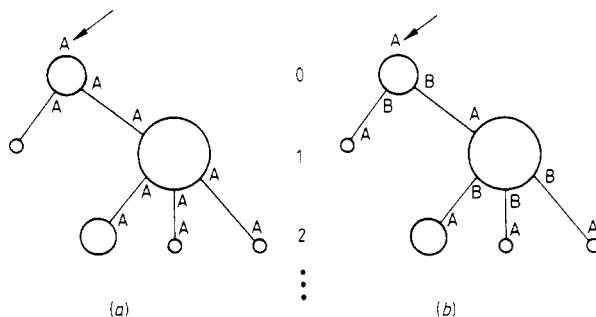


Figure 2. The arrow indicates a random unreacted A group. Since the polymers lack rings, they may be represented as family trees, where the different circle sizes represent the different unit sizes. (a) shows an RA_f polymer, while (b) shows the corresponding ARB_{f-1} polymer. The text shows that the recursive structure of the generations 0, 1, 2, ... in the family tree forces correspondence between the polymer models.

Let the concentrations of the initial units be given by equation (8), where $\{c_k(t)\}$ represents the RA_f model and $\{n_k(t)\}$ the ARB_{f-1} model. Equation (8) guarantees that the probability that a random A group belongs to a k -mer unit,

$$s_k c_k(0) \left(\sum_{k=1}^{\infty} s_k c_k(0) \right)^{-1} = n_k(0) \left(\sum_{k=1}^{\infty} n_k(0) \right)^{-1} \tag{16}$$

is the same for both models. (In the RA_f model, s_k is the number of unreacted A groups on a k -mer.) The existence of k -mer units ($k > 1$) implies that some functional groups have already reacted at $t = 0$. Call the other functional groups virgin groups. As time progresses, the virgin groups react. At any time t , let α , the extent of reaction, be the proportion of virgin A groups that have reacted in the RA_f system and the proportion of virgin B groups that have reacted in the ARB_{f-1} system. (The time t yielding a fixed α differs for the two systems.) Let us compare the RA_f and ARB_{f-1} models at fixed α .

Pick a random unreacted A group from the system. The probability that this belongs to a k -mer in either model is

$$\frac{s_k c_k(\alpha)}{\sum_{k=1}^{\infty} s_k c_k(\alpha)} = \frac{n_k(\alpha)}{\sum_{k=1}^{\infty} n_k(\alpha)}. \tag{17}$$

Figure 2 proves the equality as follows.

The probability that the unreacted A group belongs to a k -mer unit is the same for both models (equation (16)). Because of equireactivity, the remaining functional groups on the unit have reacted independently of one another with probability α . In both RA_f and ARB_{f-1} , these reacted functional groups lead to a random reacted A

group. The probability that the reacted A group belongs to a k -mer unit is the same for both models (equation (16)), etc. Continuing recursively, we find that equation (16) is sufficient to enforce equation (17).

Equation (17) gives the form for equation (9). Clearly, if t is the time for the extent of reaction α in the ARB _{$f-1$} model, $t_c(1 - e^{-at})$ is the time for the same extent of reaction in the RA _{f} model. This change of parameter, as well as determination of the sums in equation (17), will not be done explicitly since it is combinatorially uninformative.

Likewise, equations (10)–(14) have a combinatorial interpretation. As the units coagulate, a particle can be characterised by its mass and by the number of units it contains. As Spouge (1983a) points out, $x_{ku}(t)$ is the concentration at time t of k -mers which are composed of u units (call these u -unit k -mers). Equation (13) states that each k -mer contains u units, $u = 1, 2, \dots, k$.

In the Flory polymer models, because of equireactivity, bonds have formed randomly between the units. For a fixed extent of reaction α , *it does not matter whether these bonds were formed reversibly or irreversibly, they are still formed at random.* (van Dongen and Ernst (1984) exploit this fact to solve a version of equation (1) allowing fragmentation.) We can regard the polymerisation process as an equilibrium system and use the principle of detailed balance (Lewis 1925, Kelly 1978):

$$(u-1)x_{ku}(t) = \kappa(t) \sum_{i+j=k} \sum_{r+s=u} K_{ij}x_{ir}(t)x_{js}(t) \quad u = 2, 3, \dots, k. \quad (18)$$

The left side is proportional to the rate at which random bonds are broken in u -unit k -mers. Since the units maintain their integrity in the equilibrium analogy (only virgin groups react at random in the kinetic formulation), only the $u-1$ bonds between the u units can break (see figure 1). The sums on the right are proportional to the rate at which random bonds are formed to produce u -unit k -mers. $\kappa(t)$ is the constant of proportionality giving the appropriate extent of reaction α .

Since k -mer units, being units, are never formed in the kinetic formulation, but only disappear by coagulation with other polymers,

$$\begin{aligned} \frac{dx_{k1}}{dt} &= -x_{k1} \sum_{i=1}^{\infty} K_{ik}x_i = -x_{k1} \sum_{i=1}^{\infty} [A + B(i+k) + Cik]x_i \\ &= -x_{k1}(A\mu + B + (B\mu + C)k). \end{aligned} \quad (19)$$

Because $\mu(t)$ is known (equation (11)), and because $x_{k1}(0) = \xi_k$ (i.e., at $t=0$, all particles are units), this yields equation (14) for $u=1$, which we write as

$$x_{k1}(t) \triangleq \xi_{k1}g(t)f^k(t). \quad (20)$$

Comparing equations (12) and (18) and noting equation (20) shows

$$x_{ku}(t) = \xi_{ku}[\kappa(t)D(\mu_0)g(t)]^{u-1}g(t)f^k(t) \triangleq \xi_{ku}h^{u-1}(t)g(t)f^k(t). \quad (21)$$

$h(t)$ is most easily determined by substituting equation (21) into

$$\frac{dx_{ku}}{dt} = \frac{1}{2} \sum_{i+j=k} \sum_{r+s=u} K_{ij}x_{ir}x_{js} - x_{ku} \sum_{i=1}^{\infty} K_{ik}x_i. \quad (22)$$

Equation (22), which keeps track of u -unit k -mers, is analogous to equation (1). Simplifying equation (22) as we did equation (19) and substituting equation (2), determines $h(t)$ and yields equation (14) for $x_{ku}(t)$.

Many analytic solutions of the coagulation equation can be related to the Flory models of polymerisation and, as such, have forms dictated by combinatorial considerations. It would be interesting to know if analytic solutions of related equations (e.g., Leyvraz 1985) have similar interpretations.

Acknowledgments

This work was supported by the United States Department of Energy.

I would like to thank Peter van Dongen and David Covell for useful discussions.

References

- Drake R L 1972 *J. Atmos. Sci.* **29** 537
Ernst M H, Ziff R M and Hendriks E M 1984 *J. Coll. Interface Sci.* **97** 266
Flory P J 1941 *J. Am. Chem. Soc.* **63** 3083, 3091, 3096
— 1952 *Principles of Polymer Chemistry* (Ithaca: Cornell University Press)
Kelly F P 1978 *Reversibility and Stochastic Networks* (New York: Wiley)
Lewis G N 1925 *Proc. Natl. Acad. Sci. USA* **11** 179
Leyvraz F 1985 *J. Phys. A: Math. Gen.* **18** 321
McLeod J B 1962 *Quart. J. Math. Oxford Ser. (2)* **13** 119, 193
Spouge J L 1983a *J. Phys. A: Math. Gen.* **16** 3127
— 1983b *Macromolecules* **16** 121
— 1983c *J. Stat. Phys.* **31** 363
Stockmayer W H 1943 *J. Chem. Phys.* **11** 45
van Dongen P J C and Ernst M H 1984 *J. Stat. Phys.* **37** 301
von Smoluchowski M 1916 *Z. Phys.* **17** 557, 585
Ziff R M, Ernst M H and Hendriks E M 1984 *J. Coll. Interface Sci.* **100** 220
Ziff R M and Still G 1980 *J. Chem. Phys.* **73** 3492