

Solutions and critical times for the monodisperse coagulation equation when $a_{ij}=A + B(i + j) + Cij$

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

1983 J. Phys. A: Math. Gen. 16 767

(<http://iopscience.iop.org/0305-4470/16/4/014>)

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 30/05/2010 at 17:03

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

Solutions and critical times for the monodisperse coagulation equation when $a_{ij} = A + B(i + j) + Cij$

John L Spouge

Trinity College, Oxford OX1 3BH, England

Received 13 September 1982

Abstract. This paper shows that if $a_{ij} = A + B(i + j) + Cij$, the solutions of Smoluchowski's coagulation equation (monodisperse case)

$$dx_k/dt = -x_k \sum_{i=1}^{\infty} a_{ik}x_i + \frac{1}{2} \sum_{i=1}^{k-1} a_{i,(k-i)}x_ix_{k-i}, \quad k = 1, 2, 3, \dots,$$

$$x_1(0) = 1, x_2(0) = x_3(0) = \dots = 0, \tag{1}$$

can be expressed as equilibrium distributions conditioned on a deterministically changing (and known) parameter. A partial converse is also given. Because the equilibrium distributions are already known, this effectively solves (1) for the given a_{ij} . If $C \neq 0$, then there is a finite critical time $t = t_c$ when the moments of the right of (1) cease to converge. We find t_c for all the given a_{ij} .

1. Introduction

In 1916, Smoluchowski modelled colloidal coagulation with an infinite set of differential equations. Those equations generalise to the so-called coagulation equation:

$$dx_k/dt = -x_k \sum_{i=1}^{\infty} a_{ik}x_i + \frac{1}{2} \sum_{i=1}^{k-1} a_{i,(k-i)}x_ix_{k-i}, \quad k = 1, 2, 3, \dots,$$

$$x_1(0) = 1, x_2(0) = x_3(0) = \dots = 0. \tag{1}$$

Equation (1) has this interpretation: consider a suspension of randomly diffusing identical particles (called units). At time $t = 0$, the units start to clump irreversibly (coagulate) when they meet. Call the clusters so formed polymers. (Polymer chemistry is the best-developed paradigm for the process. We adopt its terminology for convenience, but do not imply that applications of (1) are restricted to polymer chemistry.) Call a polymer of k units a k -mer. Then

$x_k = x_k(t)$ = the concentration of k -mers at time t (normalised so that the initial concentration of units, $x_1(0)$, is 1).

The boundary conditions in (1) state that initially all particles are units. This is the so-called monodisperse case. We do not consider the polydisperse case (initial particles of varying size) in this paper.

$a_{ij} = a_{ji}$ = the rate constant for aggregation of i -mers and j -mers.

This is the coagulation kernel. The coagulation equation (1) gives the rate of change of the k -mer concentration with respect to time as the sum of two terms: the first is the rate of k -mer coagulation with other particles, causing k -mer disappearance; the

second is the rate at which k -mers form from the coagulation of smaller particles (the factor of $\frac{1}{2}$ ensures that each such coagulation is counted once).

Smoluchowski (1916) solved the system (1) for equal a_{ij} 's (i.e. when all polymer pairs clump at the same rate, regardless of size).

Drake's (1972a) thorough review of coagulation gave explicit solutions of the coagulation equation (polydisperse case) for the kernels

$$a_{ij} = A + B(i + j) + Cij, \quad C = 0 \quad \text{or} \quad B^2 = AC. \quad (2)$$

These solutions contained the monodisperse cases as specialisations. Drake also stated that he 'was able to write down a 'formal series' for the solution . . . for arbitrary A , B and C '. He goes on to say: 'the formal series appears to have no practical value'. Note, however, that Drake was seeking solutions for the polydisperse case of coagulation.

In fact, we shall show that the solutions for the coagulation equation (monodisperse case) when the kernel is bilinear (without restriction)

$$a_{ij} = A + B(i + j) + Cij \quad (3)$$

are known. We shall also give critical times for the bilinear kernels. To explain this term, note that (1) implies conservation of units:

$$\sum_{k=1}^{\infty} kx_k(t) = \sum_{k=1}^{\infty} kx_k(0) = 1. \quad (4)$$

(Multiply (1) by k , then sum over all k . For the bilinear kernels, the series obtained on the right are absolutely convergent when $\sum k^2 x_k(t)$ is, and have algebraic sum zero. The expression obtained on the left is the derivative of (4), hence (4) must be constant.)

This constancy is preserved up to the critical time t_c , when an infinite aggregate (called a gel in polymer chemistry) forms. After t_c , the left side of (4) diminishes to zero, because the gel traps more and more units. (For bilinear kernels, gel formation corresponds to divergence of the second moment of $x_k(t)$, i.e. $\sum k^2 x_k(t)$. See Drake 1972b, Ziff 1980.)

We obtain our results by relating the solutions of the monodisperse coagulation equation to equilibrium distributions. As in Stockmayer (1943) and Spouge (1982, 1983) we condition the equilibrium distributions on the separation of the system, which is

$$\mu = \mu(t) = \sum_{k=1}^{\infty} x_k(t) \quad (5)$$

the total polymer concentration at time t . (Stockmayer (1943) used a different, but equivalent parameter.) Summing (1) over k yields

$$d\mu/dt = -\frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} a_{ij} x_i x_j, \quad t < t_c. \quad (6)$$

For the bilinear kernels (3), equations (4), (5) and (6) give

$$d\mu/dt = -\frac{1}{2}(A\mu^2 + 2B\mu + C). \quad (7)$$

Hence, for the bilinear kernels (3), this equation parametrises time by total polymer concentration μ .

2. Equilibrium models

This section generalises some combinatoric results in Spouge (1982, 1983) which applied only to chemical polymers. The results here apply to more general aggregation processes. Consider a *reversible* aggregation process



where R_k represents a k -mer. In this section, x_k is the k -mer concentration at equilibrium.

When applied to the system of reactions (8), the principle of detailed balance (Whittle 1965) states: if the system (8) is in equilibrium, then each reaction is also in equilibrium. Let the forward rate of reaction (8) be a_{ij} , and let the rate of k -mer break-up be b_k . By considering reactions (8) for fixed k and summing over $i = 1, 2, \dots, (k - 1)$, the principle of detailed balance gives

$$b_k x_k = \sum_{i+j=k} a_{ij} x_i x_j, \quad k = 2, 3, 4, \dots \quad (9)$$

For many models of aggregation, the reactions (8) represent creation/destruction of a bond. For such models, k -mers have $(k - 1)$ bonds, and if the rate of k -mer break-up is proportional to the number of bonds, (9) becomes

$$2(k - 1)\kappa x_k = \sum_{i+j=k} a_{ij} x_i x_j \quad (10)$$

where κ is a constant, as yet undetermined.

In order to solve (10), we introduce the generating function

$$Z = \sum_{k=1}^{\infty} (w_k/k!) e^{-\beta k} \quad (11)$$

where $w_1 = 1$ and the constants $\{w_k/k!\}$ ($k = 1, 2, 3, \dots$) satisfy (10) with $\kappa = 1$ when they replace $\{x_k\}$. (The factorial appears in order to agree with previous notation.)

The solution of (10) is

$$x_k = \kappa (w_k/k!) e^{-\beta k} \quad (12)$$

where β is an arbitrary constant. If we condition the $\{x_k\}$ on the total polymer concentration μ (see equation (5)), then

$$x_k = (\mu/Z)(w_k/k!) e^{-\beta k}. \quad (13)$$

If, in addition, the x_k are normalised so that the total concentration of units is 1 (see equation (4)), then

$$Z = -\mu Z' \quad (14)$$

where Z' , Z'' etc denote successive derivatives of Z with respect to β .

The moments of x_k are

$$\sum_{k=1}^{\infty} k^n x_k = \mu (Z^{(n)}/Z)(-1)^n. \quad (15)$$

We now restrict the discussion to the bilinear kernels (3). For these kernels, recursion (10) for $w_k/k!$ becomes

$$2(k-1)\frac{w_k}{k!} = \sum_{i+j=k} [A+B(i+j)+Cij]\frac{w_i}{i!}\frac{w_j}{j!}. \tag{16}$$

Multiplying (16) by $e^{-\beta k}$ and summing over k gives

$$2(-Z' - Z) = AZ^2 - 2BZZ' + C(Z')^2. \tag{17}$$

Equations (17) and (14) imply

$$Z = 2\mu(1-\mu)/(A\mu^2 + 2B\mu + C), \tag{18}$$

$$Z' = -2(1-\mu)/(A\mu^2 + 2B\mu + C). \tag{19}$$

Differentiating (17) and substituting (18) and (19) gives

$$Z'' = \frac{2(1-\mu)}{A\mu^2 + 2B\mu + C} \frac{-A\mu^2 + 2A\mu + 2B + C}{(A + 2B)\mu^2 + 2C\mu - C}. \tag{20}$$

Having summarised the equilibrium models, we now relate them to the solutions of the coagulation equation (monodisperse case).

3. Solution of the coagulation equation

This section gives a tedious algebraic verification of:

Theorem 1. For the bilinear kernels (3), and for those kernels only, the monodisperse coagulation equation (1) has the solution $\{x_k\}$ of equations (10)–(14), where equation (7) gives the total polymer concentration μ as a function of time for $t < t_c$.

This theorem states: only for the bilinear kernels are distributions (1) equal to equilibrium distributions conditioned on total polymer concentration μ .

Proof. Consider first the bilinear kernels (3). Divide equation (1) by x_k and consider the first term of the right side:

$$-\sum_{i=1}^{\infty} a_{ik}x_i = -\sum_{i=1}^{\infty} [A+B(i+k)+Cik]x_i = k(-B\mu - C) + (-A\mu - B) \tag{21}$$

(see equations (4) and (5)).

The second term of the right side becomes

$$\frac{1}{x_k} \frac{1}{2} \sum_{i+j=k} a_{ij}x_i x_j = (k-1)\frac{\mu}{Z} = (k-1)\frac{A\mu^2 + 2B\mu + C}{2(1-\mu)} \tag{22}$$

(see equations (10), (12), (13) and (18)).

To get the left side of (1), we differentiate (14) with respect to μ to obtain

$$\frac{d\beta}{d\mu} = \frac{-Z'}{Z' + \mu Z''} = \frac{(A + 2B)\mu^2 + 2C\mu - C}{(A\mu^2 + 2B\mu + C)(1-\mu)} \tag{23}$$

(see equations (19) and (20)).

Differentiate (13) with respect to μ to get

$$\frac{1}{x_k} \frac{dx_k}{d\mu} = \frac{1}{\mu} - \frac{Z'}{Z} \frac{d\beta}{d\mu} - k \frac{d\beta}{d\mu}. \tag{24}$$

Therefore

$$\frac{1}{x_k} \frac{dx_k}{dt} = \frac{1}{x_k} \frac{dx_k}{d\mu} \frac{d\mu}{dt} = \frac{k[(A + 2B)\mu^2 + 2C\mu - C] + [A\mu^2 - 2A\mu - (2B + C)]}{2(1 - \mu)} \tag{25}$$

(see equations (24), (14), (23) and (7)).

The sum of (21) and (22) equals (25), which demonstrates satisfaction of (1) for the bilinear kernels (3).

To demonstrate that satisfaction occurs *only* when the kernel is bilinear, note that (22) and (24) (hence (25)) are linear functions of k , no matter what the kernel is. Satisfaction of (1) implies that (21) (the difference of (25) and (22)) must also be a linear function of k . For $t < t_c$, equation (21) converges absolutely, so we may take second differences with respect to k inside the summation on the left side:

$$\sum_{i=1}^{\infty} (\Delta^2 a_{ik}) x_i = 0 \quad \text{for all } \mu \tag{26}$$

(second differences of linear functions are 0). Because this is a power series in $e^{-\beta}$ (see (13))

$$\Delta^2 a_{ik} = 0 \quad \text{for all } i. \tag{27}$$

Hence a_{ik} is a linear function of k . Since $a_{ij} = a_{ji}$, a_{ij} must have the symmetric bilinear form (3).

Since Spouge (1982) summarises the equilibrium solutions for bilinear kernels (2), $C = 0$ or $B^2 = AC$, and Spouge (1983) gives the solutions for the remaining bilinear kernels, this theorem is tantamount to solving the monodisperse coagulation equation for all bilinear kernels.

The next section gives the critical times t_c for all bilinear kernels.

4. Critical times for bilinear kernels

As noted after equation (4), the second moment of x_k diverges at the critical time t_c . Because of equation (15), this implies that Z'' diverges. This occurs when μ equals the critical separation

$$\begin{aligned} \mu_c &= \frac{-C + [C(A + 2B + C)]^{1/2}}{A + 2B}, & A + 2B \neq 0, \\ &= \frac{1}{2}, & A + 2B = 0, \end{aligned} \tag{28}$$

since this is the only positive root of the denominator of (20).

To obtain the critical times, we solve (7) by separating the variables and substitute μ_c for μ .

The results are summarised in table 1 ('ln' denotes a natural logarithm). To my knowledge, the critical time for $C \neq 0$, $B^2 = AC$ is the only one previously published (Leyvraz and Tschudi 1981). After conversion of notation, that result agrees with table 1.

Table 1. Critical times t_c . For all bilinear kernels $a_{ij} = A + B(t + j) + Cij$

$$\mu_c = \frac{-C + [C(A + 2B + C)]^{1/2}}{A + 2B}, A + 2B \neq 0 \left\{ \begin{array}{l} d\mu \\ dt \end{array} \right. = -\frac{1}{2}(A\mu^2 + 2B\mu + C)$$

$$\mu_c = \frac{1}{2}, A + 2B = 0$$

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

Column 1 of table 1 gives the cases for the integration of (7). Column 2 gives the solution of (7) in each case (t as a function of μ). In the cases $C \neq 0$, $A \neq 0$, $B^2 \geq AC$, the intermediate values μ_+ , μ_- , α and γ simplify the form of the solution. t_c is the value of t when μ_c (equation (28)) replaces μ . Simplification of the resulting expression, where applicable, appears in column 3 (under ' t_c '). Column 4 gives μ as a function of t .

Acknowledgment

This work was supported by a Fellowship of the Medical Research Council of Canada.

References

- Drake R L 1972a in *Topics in current aerosol research, International reviews in aerosol physics and chemistry* vol 2, ed G M Hidy and J R Brock (Oxford: Pergamon)
— 1972b *J. Atmos. Sci.* **29** 537
Leyvraz F and Tschudi H R 1981 *J. Phys. A: Math. Gen.* **14** 3389
Smoluchowski M von 1916 *Z. Phys.* **17** 557, 585
Spouge J L 1982 *Macromolecules* **15** Nov-Dec to be published
— 1983 *J. Stat. Phys.* submitted
Stockmayer W H 1943 *J. Chem. Phys.* **11** 45
Whittle P 1965 *Proc. Camb. Phil. Soc.* **61** 475
Ziff R M 1980 *J. Stat. Phys.* **23** 241