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An exactly solvable model for externally controlled coagulation

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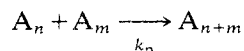
Abstract. We consider a system of coagulating monomers together with an external source of monomer with arbitrary production rate $p(t)$. The moments $M_k(t) = \sum_{n=1}^{\infty} n^k \nu_n(t)$, where $\nu_n(t)$ is the concentration of n -mer at time t (and therefore also the weight and z average of the system), are obtained exactly as a function of $p(t)$. The special case where the external source is the conversion of a substrate molecule to a monomer is discussed in more detail. If $p(t)$ is an exponential, the concentrations $\nu_n(t)$ can actually be evaluated by a simple contour integral.

Consider a system consisting only of molecules (monomers) capable of reacting irreversibly to form larger molecules (polymers). Suppose further that the polymers similarly react with each other and that the reaction constants between two polymers are independent of size.

The kinetic behaviour of this system has been studied by Smoluchowski (1916) with regard to coagulation of colloidal suspensions. In connection with polymerisation processes such a model as well as more elaborate ones have been extensively investigated (see, for example, Tompa 1976, Peebles 1971).

It is the object of this paper to study the case where monomers are produced according to some definite law by a given external source. An important case would be monomer production by catalytic conversion of another molecule otherwise not involved in the polymerisation process. We discuss this later in more detail.

Let us denote the n -mer molecule by A_n . The polymerisation process can then be described as follows:



where k_p is the polymerisation rate constant and is assumed to be independent of either n or m . A few remarks about the assumptions involved are in order.

(i) We assume the reaction to be irreversible, i.e. dissociation of a molecule into smaller components is disregarded.

(ii) We assume no mechanisms terminating the polymerisation process. This means that molecules will keep growing without limit as time increases, which is clearly unrealistic for the late stages of such a reaction.

(iii) The constancy of k_p might be derived from the assumption that the molecules grow without branching, having only two reactive sites. This would involve the further assumption that cyclisation can be neglected. Since we are already restricted by (ii) to the early stages of the reaction, such a neglect may not be so serious. It must, however,

be emphasised that we only require k_p to be constant. In the theory of colloidal suspensions this is usually justified by a compensation of two effects: the increase of the collision cross section for large aggregates and the decrease of their diffusion constants.

Let us now introduce some notation:

$\nu_n(t)$: concentration of n -mers at time t .

$p(t)$: rate of monomer production at time t .

$P(t) = \int_0^t p(u) du$: total production of monomer by the external source since time 0.

We rescale the time as follows:

$$\tau = k_p t$$

to obtain the equations:

$$\begin{aligned} \nu_1' &= P' - \nu_1 \sum_{k=1}^{\infty} \nu_k \\ \nu_n' &= \frac{1}{2} \sum_{k=1}^{n-1} \nu_k \nu_{n-k} - \nu_n \sum_{k=1}^{\infty} \nu_k \quad (n \geq 2) \\ \nu_n(0) &= 0 \quad (n \geq 1) \end{aligned}$$

where the prime denotes differentiation with respect to τ . We now define:

$$\begin{aligned} S(\tau) &= \sum_{k=1}^{\infty} \nu_k(\tau) \\ \sigma(z; \tau) &= \sum_{k=1}^{\infty} \nu_k(\tau) z^k \\ \phi(z; \tau) &= \sigma(z; \tau) - S(\tau) \end{aligned}$$

for which the following equations hold:

$$\begin{aligned} S' &= P' - \frac{1}{2} S^2 \quad S(0) = 0 \\ \frac{\partial \sigma}{\partial \tau}(z; \tau) &= z P' + \frac{1}{2} \sigma^2(z; \tau) - S(\tau) \sigma(z; \tau) \quad \sigma(z; 0) = 0. \end{aligned}$$

The first equation is obtained by summing all the equations for ν_n , and the second can be verified using the definition and comparing the coefficients of z^n .

It follows that

$$\begin{aligned} \frac{\partial \phi}{\partial \tau}(z; \tau) &= (z-1) P' + \frac{1}{2} \phi^2(z; \tau) \quad (1) \\ \phi(z; 0) &= 0. \end{aligned}$$

We wish to obtain quantities of the type:

$$M_k(\tau) = \sum_{n=1}^{\infty} n^k \nu_n(\tau).$$

It is clear that we can obtain them as linear combinations of $\partial \phi / \partial z(1, \tau), \dots, \partial^k \phi / \partial z^k(1, \tau)$. Therefore we make the ansatz:

$$\phi(z; \tau) = \sum_{k=1}^{\infty} \frac{m_k(\tau)}{k!} (z-1)^k$$

since $\phi(1, \tau) = 0$. With (1) we get

$$\begin{aligned}
 m_1(\tau) &= P(\tau) \\
 m_2(\tau) &= \int_0^\tau P^2(u) \, du \\
 m_3(\tau) &= 3 \int_0^\tau du P(u) \int_0^u du' P^2(u')
 \end{aligned}$$

and generally:

$$m_n(\tau) = \frac{1}{2} \sum_{k=1}^{n-1} \binom{n}{k} \int_0^\tau du m_k(u) m_{n-k}(u).$$

It follows that

$$\begin{aligned}
 M_1(\tau) &= m_1(\tau) = P(\tau) \\
 M_2(\tau) &= m_1(\tau) + m_2(\tau) = P(\tau) + \int_0^\tau P^2(u) \, du \tag{2} \\
 M_3(\tau) &= m_3(\tau) + 3m_2(\tau) + m_1(\tau) \\
 &= 3 \int_0^\tau du \left[P^2(u) + P(u) \int_0^u du' P^2(u') \right] + P(\tau)
 \end{aligned}$$

which give the number, weight and z average of the system as a function of time.

As to the concentrations $\nu_n(\tau)$ it does not appear possible to give such simple formulae for their evaluation. Clearly

$$\nu_n(\tau) = \sum_{k=n}^{\infty} \frac{(-1)^{k-n}}{k!(k-n)!} m_k(\tau). \tag{3}$$

However, the evaluation of $m_k(\tau)$ for large k , whether numerical or analytical, is utterly impracticable. Equation (3) is therefore only useful for τ such that $m_k(\tau)$ decreases very rapidly with k . A more practicable way would be to solve (1) exactly for the given function $P(\tau)$ and then to use the formula

$$\nu_n(\tau) = \frac{1}{2\pi i} \oint_C \frac{\phi(z; \tau)}{z^{n+1}} \, dz \tag{4}$$

where C is any contour enclosing the origin; the problem of solving (1) exactly, however, cannot be solved for a general function $P(\tau)$ but must be considered for each particular case separately.

This research was motivated by static light scattering experiments (done by the group of Professor W Känzig at the ETH-Zürich) measuring the intensity of light scattered by a solution of fibrinogen and thrombin. Fibrinogen is converted by thrombin into fibrin which in turn coagulates. In this case monomer is produced by conversion of an otherwise inert molecule S . We have:

$$P(\tau) = \nu_S(0) - \nu_S(\tau)$$

where $\nu_S(\tau)$ denotes the concentration of S at time τ .

In the Born approximation the scattered light intensity measures the second moment of the concentrations of the scatterers (see, for example, Berne and Pecora

1976). Since the molecule S also contributes to the scattered light intensity we must add $\nu_S(\tau)$ to the expression (2) for $M_2(\tau)$. This gives:

$$\tilde{M}_2(\tau) = M_2(\tau) + \nu_S(\tau) = \nu_S(0) + \int_0^\tau P^2(u) du.$$

If for small times $P(\tau) = O(\tau^\gamma)$ then clearly:

$$\tilde{M}_2(\tau) - \tilde{M}_2(0) = O(\tau^{2\gamma+1}).$$

This agrees nicely with a 'time lag' observed in static light scattering experiments. For an illustration see, for example, figure 1.

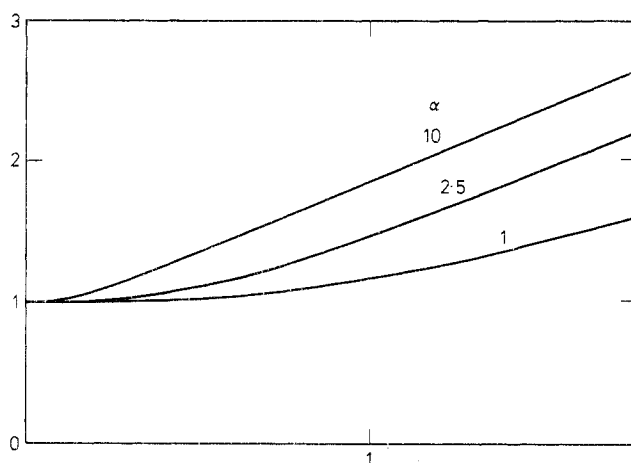
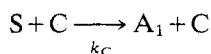


Figure 1. Plot of the function $\tilde{M}_2(\tau)$ with $P(\tau) = 1 - e^{-\alpha\tau}$ for different values of α .

If the conversion takes place through the following catalytic reaction:



we have

$$\nu'_S = -k_C \nu_C \nu_S / k_p$$

where the catalyser concentration ν_C is a constant. Therefore

$$\nu_S(\tau) = \nu_S(0) \exp(-\alpha\tau) \quad (\alpha = k_C \nu_C / k_p).$$

Equation (1) can then be solved by standard methods (see, for example, Kamke 1956) yielding:

$$\phi(z; \tau) = \alpha \lambda e^{-\alpha\tau/2} \frac{K_1(\lambda) I_1(\lambda e^{-\alpha\tau/2}) - I_1(\lambda) K_1(\lambda e^{-\alpha\tau/2})}{K_1(\lambda) I_0(\lambda e^{-\alpha\tau/2}) + I_1(\lambda) K_0(\lambda e^{-\alpha\tau/2})}$$

where $\lambda = (2\nu_S(0)(1-z)/\alpha)^{1/2}$. K and I are modified Bessel functions in the notation of Abramowitz and Stegun (1964). We have, however, not succeeded in evaluating (4) analytically, even in this simplest case.

Summarising, it may be said that, if the rate of monomer production is known as a function of time, it is fairly straightforward to compute the lowest moments of the

concentration distribution. For higher moments integrations in higher and higher dimensions become necessary, so that the evaluation becomes prohibitively difficult. The same applies to the functions $\nu_n(\tau)$ unless $P(\tau)$ be so simple that equation (1) can be solved analytically, as is the case for $\nu_S(\tau) = \exp(-\alpha\tau)$.

In the fibrinogen–thrombin system described above, however, the Born approximation is not applicable except to the very smallest clusters. It is not complicated to account for the finite size of the scatterers but this would go beyond the scope of this paper. It is furthermore doubtful whether the initial assumptions of our model would hold in this case. We therefore do not attempt a comparison with experimental results.

Acknowledgments

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