Exact solution of a coagulation equation with removal term

1984 J. Phys. A: Math. Gen. 17 2299

(http://iopscience.iop.org/0305-4470/17/11/024)

J. Phys. A: Math. Gen. 17 (1984) 2299–2303. Printed in Great Britain

Exact solution of a coagulation equation with removal term

E M Hendriks

Institut für Theoretische Physik, Universität zu Köln, Zülpicher Str. 77, D-5000, Köln 41, West Germany

Received 13 February 1984

Abstract. Smoluchowski's coagulation equation with coagulation rate $K_{ij} \propto ij$ for the process $A_i + A_j \to A_{i+j}$ is solved in the presence of a removal term of the general form $-a(t)c_k - b(t)kc_k$. The solution for the monomer initial condition has the same k-dependence as in the case without sinks, but for $b > b_0 > 0$ the solution never reaches the gelation transition.

1. Introduction

In recent years, Smoluchowski's coagulation equation

$$\dot{c}_k = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j=1}^{\infty} K_{kj} c_j \tag{1}$$

describing the time evolution of the size distribution $c_k(t)$ in coagulating or polymerising systems has been extensively studied. The coagulation rate for the clustering process $A_i + A_j \to A_{i+j}$ equals K_{ij}.

For high enough rates, the solution of (1) describes a phase transition (gelation), signalled by the divergence of some moment of the size distribution at a definite (critical) point. This happens e.g. when $K_{ij} = s_i s_j$, with $s_k \sim k^{\omega}$ $(k \to \infty)$, iff $\omega > \frac{1}{2}$ (Leyvraz and Tschudi 1981, Hendriks *et al* 1983). Although equation (1) describes a kind of mean field theory, spatial fluctuations being neglected, for $\omega \neq 1$ non-classical critical exponents are found.

Polymerising systems with f-functional monomeric units in the non-cyclic approximation are modelled by the choice $s_k = (f-2)k + 2$ (Stockmayer 1943, 1944, Ziff and Stell 1980). The solution of (1) for the monomer initial condition $c_k(0) = \delta_{k1}$ is then equivalent to the Flory–Stockmayer classical theory of gelation, at least in the sol phase $(t < t_c)$. The critical point is at $t = t_c = [f(f-2)]^{-1}$ (Ziff and Stell 1980) and is characterised by classical, critical exponents.

In the high functionality limit, $f \to \infty$, one may use $f^2 t$ as a new time variable and K_{ij} reduces to ij. The solution of the resulting equation contains the full gelation transition. This case lends itself as an instructive example, as the mathematics is not too technical, and the solution has been analysed in great detail (Ziff *et al* 1983). Also, experiments have been performed at high functionality (von Schulthess *et al* 1980). We quote the solution for the monomer initial condition valid in the sol phase $(t \leq t_c = 1)$ (Stockmayer 1944)

$$c_k(t) = (kt)^{k-1} \, e^{-kt}/kk!. \tag{2}$$

0305-4470/84/112299+05$02.25

The solution of (1) in the gel phase ($t \geq t_c$) equals $c_k(t_c)/t$ (Leyvraz and Tschudi 1982, Ziff *et al* 1983). It describes a situation without sol–gel interaction. If one insists on (2) being valid also in the gel phase, then (1) has to be modified past the gel point through the addition of a term $(\Sigma_{j=1}^{\infty} jc_j - 1)kc_k$. The factor inside the brackets is to be interpreted as the negative of the gel fraction $G(t)$ (Ziff *et al* 1983).

In this paper we derive the exact solution of equation (1) with $K_{ij} = ij$ in the presence of a removal (sink) term of the general form:

$$S = -a(t)c_k - b(t)kc_k \tag{3}$$

in which a and b are arbitrary functions of time. The term $-ac_k$ arises when material is allowed to flow out of the system at a steady rate, through a leak or a pipe. The term $-bkc_k$ describes a removal process that acts more effectively for larger clusters. Such a term arises when, e.g. already at $t = 0$, gel is present in a polymerising system. For coagulation, the structure of removal terms corresponding to various processes have been given by Crump and Seinfeld (1981). It is of interest to investigate the effect of such terms on properties of the solution, such as critical exponents, the occurrence of gelation and so on. When also a source is present, there is the possibility of a steady state. Criteria on the asymptotic behaviour of K_{ij} and the source and sink terms, to ensure the existence of such a steady state, have been derived (Crump and Seinfeld 1982, White 1982). For $\omega = 1$, source dependent critical exponents have been found (Hendriks and Ziff 1984).

In the present case, with $K_{ij} = ij$ and (3) describing the removal process, an explicit form of solution can be found. It will follow that when $b(t) > b_0 > 0$, the solution never reaches the phase transition, the removal process being too strong.

2. The solution

The equation to be studied reads:

$$\dot{c}_k = \tfrac{1}{2} \sum_{i+j=k} ijc_ic_j - kc_k \sum_{j=1}^{\infty} jc_j - ac_k - bkc_k \tag{4}$$

in which a and b are arbitrary, given, non-negative functions of time. The solution can be constructed with the help of the generating function:

$$f(x, t) = \sum_{k=1}^{\infty} kc_k \, \mathrm{e}^{kx}. \tag{5}$$

The actual derivation is given in the appendix. For the monomer initial condition, $c_k(0) = \delta_{k1}$, the result can be written in the form

$$c_k(t) = \Gamma(t)[\zeta(t)]^k(k^{k-2}/k!) \tag{6}$$

which has the same k-dependence as equation (2), the solution valid in the absence of removal terms. For $k \to \infty$ it takes the asymptotic form:

$$c_k(t) \simeq (2\pi)^{-1/2}\Gamma(t)\, \mathrm{e}^{kx_0(t)}k^{-5/2} \qquad (k \to \infty) \tag{7}$$

the same kind of behaviour as is found in the classical Flory–Stockmayer theory of gelation or in random percolation on a Bethe lattice. The quantity $x_0(t)$ (≤ 0) represents the time dependent position of the leftmost singularity of $f(x, t)$. Only when $x_0(t) = 0$

at some point, the solution describes gelation. The time dependent functions $\Gamma(t)$ and $\zeta(t)$ depend on the functions $a(t)$ and $b(t)$, in a complicated manner:

$$\Gamma(t) = \mathrm{e}^{-A(t)} \Big/ \int_0^t \exp(-A(t'))\,\mathrm{d}t' \tag{8}$$

with $A(t) \equiv \int_0^t a(t')\,\mathrm{d}t'$, and

$$\zeta(t) = \int_0^t \exp(-A(t'))\,\mathrm{d}t' \Big/ \exp\left(\int_0^t (M(t') + b(t'))\,\mathrm{d}t'\right) \tag{9}$$

in which $M(t)$ is the (sol) mass present in the system:

$$M(t) = f(0, t) = \sum_{k=1}^{\infty} k c_k(t). \tag{10}$$

An explicit form of $M(t)$ in terms of a and b cannot be given, but rather a differential equation that it satisfies which using the variables $\mu \equiv \mathrm{e}^A M$ and $\tau \equiv \int_0^t \exp(-A(t'))\,\mathrm{d}t'$ attains the form

$$\dot{\mu} = \mu(\dot{\mu}\tau - b). \tag{11}$$

If one is interested in the precise time evolution of the $c_k(t)$, (11) may be solved numerically, with the initial condition $\mu(0) = 1$.

3. Discussion of the solution

As has been mentioned, solution (7) has, as far as the k-dependence is concerned, the same structure as in the classical theory of gelation. Does it also describe a gelation transition? To answer this question, we consider the mean cluster size, or the second moment of the size distribution:

$$M_2(t) = \sum_{k=1}^{\infty} k^2 c_k(t) = f_x(0, t) \tag{12}$$

which can be calculated from the solution (see appendix):

$$M_2(t) = M\left(1 - M\,\mathrm{e}^{A(t)} \int_0^t \mathrm{e}^{-A(t')}\,\mathrm{d}t'\right)^{-1} = \mathrm{e}^{-A}\mu(1 - \mu\tau)^{-1}. \tag{13}$$

Gelation would happen at a point for which $\mu(t)\tau(t) = 1$, since then the second moment diverges. However, for $b > b_0 > 0$ this is impossible, as follows directly from (11), which leads to an inconsistency if one assumes $\mu(t)\tau(t) = 1$ at some value of t.

Alternatively, one may consider the motion of the singularity $x_0(t)$. It follows from (6), with the help of the ratio test, that $\mathrm{e}^{x_0} = \zeta\,\mathrm{e}^{-1}$ and hence from (9) and the definitions of μ and τ we have

$$x_0(t) = \mu\tau - 1 + \log(\mu\tau). \tag{14}$$

Gelation corresponds to $x_0(t)$ hitting the origin, for which it is necessary that $\mu(t)\tau(t) = 1$. This shows that no moment diverges at all if $b > b_0 > 0$.

Thus, the sink term $-bkc_k$ causes the solution to stay away from the gelation transition. For the same reason, when in the absence of sources and sinks (11) the gel is allowed to interact with the sol which corresponds to adding a term of the form

$-bkc_k$ the size distribution has an algebraic tail $k^{-5/2}$ only *at* the critical point t_c exactly, whereas beyond t_c it is again dominated by exponential decay, as in (7).

For $b > b_0 > 0$, the singularity $x_0(t)$ moves from $x_0 = \infty$ at $t = 0$ towards a minimum value and then back to $x_0 = \infty$ again. Its precise motion depends on $a(t)$ and $b(t)$ via the solution of (11).

For $b = 0$, the solution (6) reduces to (2) with t simply replaced by τ. This case need not be analysed, as it is fully equivalent to (1) with $K_{ij} = ij$, the solution of which has been treated in detail (Ziff *et al* 1983). The sink term can be transformed away by passing to τ as the new time variable. For the monomer initial condition, the critical point now lies at the solution of the equation $\tau(t) = \int_0^t \exp(-A(t'))\,dt' = 1$, which only exists if $\tau(\infty) > 1$, i.e. when the removal process is not too strong.

Appendix

We derive the solution of (4). It follows from (4) that the generating function, (5), satisfies a nonlinear partial differential equation:

$$f_t = ff_x - (M + b)f_x - af \tag{A1}$$

in which M depends on f itself

$$M(t) = f(0, t) = \sum_{k=1}^{\infty} kc_k. \tag{A2}$$

We treat M first as an arbitrary function and later require the solution to satisfy (A2). The inverse function $X(f, t)$, defined by the relation $X(f(x, t), t) = x$ satisfies

$$X_t - afX_f = -f + M + b. \tag{A3}$$

This is a linear PDE and can be solved using the method of characteristics. The solution, in terms of an arbitrary function $F(u)$, can be written as

$$e^x = F(f\,e^{A(t)}) \exp\left(\int_0^t dt'\,(M(t') + b(t') - f\,e^{A(t)-A(t')})\right) \tag{A4}$$

with $A(t) \equiv \int_0^t a(t')\,dt'$. This determines $f(x, t)$ implicitly. The sol mass $M(t)$ follows from (A4) by putting $x = 0$, and requiring (A2) to hold. For the monomer initial condition, $c_k(0) = \delta_{k1}$, one has $f(x, 0) = e^x$, hence $F(u) = u$. The solution then reduces to

$$e^x = f \exp\left(A(t) + \int_0^t dt'\,(M(t') + b(t') - f\,e^{A(t)-A(t')})\right) \tag{A5}$$

and the consistency relation equation (A2) implies

$$1 = M(t) \exp\left(A(t) + \int_0^t dt'(M(t') + b(t') - M(t)\,e^{A(t)-A(t')})\right). \tag{A6}$$

Differentiating this with respect to t yields a differential equation for M, which using the variables $\mu = e^A M$ and $\tau = \int_0^t e^{-A(t')}\,dt'$ becomes (11). The explicit form (6) can be obtained as follows. We introduce auxiliary quantities F_1, F_2 and z as

$$F_1 \equiv \exp\left(A(t) + \int_0^t (M(t') + b(t'))\,dt'\right) \tag{A7}$$

$$F_2 \equiv e^{A(t)} \int_0^t \exp(-A(t'))\,dt' \tag{A8}$$

$$z = e^x \tag{A9}$$

such that the solution equation (A5) can be written as

$$z = fF_1\, e^{-fF_2}. \tag{A10}$$

The fact that f is the generating function of the quantities kc_k implies

$$c_k = \frac{1}{2\pi i k} \oint \frac{dz\, f(z)}{z^{k+1}} \tag{A11}$$

in which the integration path is a closed contour around $z = 0$. This remains so if we change to the new integration variable $\zeta = fF_2$, where f is related to z via (A10). One finds

$$\begin{aligned} c_k &= \frac{1}{2\pi i k F_2}\left(\frac{F_2}{F_1}\right)^k \oint d\zeta\, (\zeta c^{-\zeta})^k (1-\zeta) \\ &= \frac{1}{F_2}\left(\frac{F_2}{F_1}\right)^k \frac{k^{k-2}}{k!} \end{aligned} \tag{A12}$$

which completes the derivation of equation (6). Expression (13) for $M_2(t)$ follows from differentiating (A5) with respect to x and substituting $x = 0$, using (A6).

References

Crump J G and Seinfeld J H 1980 *J. Coll. Interf. Sci.* **90** 2
—— 1981 *J. Aerosol Sci.* **12** 405
Hendriks E M, Ernst M H and Ziff R M 1983 *J. Stat. Phys.* **31** 519
Hendriks E M and Ziff R M 1984 *Preprint* Cologne
Leyvraz F and Tschudi H R 1981 *J. Phys. A: Math. Gen.* **14** 3389
—— 1982 *J. Phys. A: Math. Gen.* **15** 1951
Stockmayer W H 1943 *J. Chem. Phys.* **11** 45
—— 1944 *J. Chem. Phys.* **12** 125
von Schulthess G K, Benedek G B and de Blois R W 1980 *Macromolecules* **13** 940
White W H 1982 *J. Coll. Interf. Sci.* **87** 204
Ziff R M 1980 *J. Stat. Phys.* **23** 241
Ziff R M, Ernst M H and Hendriks E M 1983 *J. Phys. A: Math. Gen.* **16** 519
Ziff R M and Stell G 1980 *J. Chem. Phys.* **73** 3492