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New results on a parity-dependent model of aggregation kinetics

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Abstract. A reaction kernel, $K(j,k) = K(k,j)$, is studied, for which the Smoluchowski equations of aggregation $\dot{c}_j = \frac{1}{2}\sum_{k,l=1}^{\infty} K(k,l)c_k c_l[\delta_{k+l,j} - \delta_{k,j} - \delta_{l,j}]$ can be solved. It takes only three values: $K(j,k) = K$ if j and k are both odd, $K(j,k) = L$ if j and k are both even and $K(j,k) = M$ if j and k have different parities. A considerable simplification over previous treatments is presented for the general case (K, L and M are three arbitrary positive numbers), and the time evolution of the concentrations is exhibited in completely explicit form for the (new) special case $L = 4M$. In another special case, $K = M$, the equation for the generating function of the concentrations can be reduced to quadratures; the analysis of this case, and of the general case, is postponed to a future paper.

1. Introduction

The kinetics of irreversible aggregation has been the object of much study, because of both the relevance of the subject for many systems of practical importance as well as for the interesting mathematical problems that arise in connection with it. Specifically, one is interested in the following process:

$$A_j + A_k \xrightarrow[K(j,k)]{} A_{j+k}. \tag{1}$$

Here A_j denotes an aggregate consisting of j fundamental units (monomers). The process described in (1) consists of two aggregates A_j and A_k sticking irreversibly to one another with a reaction rate $K(j,k)$ to form the larger aggregate A_{j+k}. If we assume that the probability of encounter between aggregates of sizes j and k is proportional to the product of the concentrations $c_j(t)$ and $c_k(t)$ of such aggregates, one is led to the following system of kinetic equations, called Smoluchowski equations, for these concentrations [1]:

$$\dot{c}_j = \frac{1}{2}\sum_{k,l=1}^{\infty} K(k,l)c_k c_l[\delta_{j,k+l} - \delta_{j,k} - \delta_{j,l}]. \tag{2}$$

Here and below we sometimes omit to indicate explicitly the dependence on the time t. The superscript dots denote, of course, derivatives with respect to t. The factor $\frac{1}{2}$ is conventional, to account for the double counting. The above equations are a set of coupled nonlinear ordinary

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differential equations (ODEs), which have a unique solution if positive initial conditions $c_j(0)$ are given, such that the moments

$$M_n(t) \equiv \sum_{j=1}^{\infty} j^n c_j(t) \tag{3}$$

are initially finite for *all* integers n [2]. Often, consideration is limited to the 'monodisperse' initial condition

$$c_j(0) = \delta_{j,1}. \tag{4}$$

We focus below on a slightly more general case. Note that a common factor in the initial conditions can always be absorbed by appropriately rescaling the concentrations and the time.

The equations given by (2) and (4) have only been solved for a few models. These include the 'bilinear' model

$$K(k,l) = A + B(k+l) + Ckl \tag{5}$$

where A, B and C are arbitrary constants (restricted to guarantee the positivity of $K(k,l)$ for all positive integer values of k and l) [3]. A second, 'exponential' model, solved recently [4], features the kernel

$$K(k,l) = 2 - q^k - q^l \tag{6}$$

where q is an arbitrary real number such that $0 \leqslant q < 1$. A third model was studied in [5] and [6]. Some asymptotic results were obtained and others conjectured using a generally accepted scaling theory. It features a kernel $K(j,k)$ which depends only on the parity of j and k:

$$\begin{aligned} &K(d,d) = K \qquad K(p,p) = L \\ &K(d,p) = K(p,d) = M \end{aligned} \tag{7}$$

where K, L and M are three positive constants and the arguments d respectively p run over the odd (*dispari*), and respectively even (*pari*) integers. One could replace one of these constants by unity by appropriately rescaling the time, but we shall not do so, in the interest of transparency.

The physical motivation for this model is somewhat unclear (see, however, [5] for a justification). It is nevertheless of interest, as some special cases are amenable to exact treatment. In fact, in [5], the case $M = 0$ was solved. While this is in fact a fairly straightforward result, it displayed some surprising features with respect to the generally accepted scaling theory [7, 8]. Indeed, in [5] it was suggested that this model was a counter-example to scaling, but it was then correctly pointed out in [9] that this was not really the case. Moreover, in [6], the case $M = (K + L)/2$ was solved and various asymptotic results were presented. In this paper we provide the complete solution of the problem in the special case

$$L = 4M. \tag{8}$$

To arrive at this result, we reduce the treatment of the Smoluchowski equations (2) with (7) to a simpler form than had been done hitherto, thereby opening the prospect of solving the general case (without any restriction on the three positive constants K, L and M, see (7)), at least in the sense of determining some exact asymptotic results. We also note that the generating function for the concentrations $c_j(t)$ in another special case, $K = M$, can be evaluated by quadratures. Further analysis of this second special case and of the general case will be presented separately.

Below we focus on the 'mono-bi-disperse' initial condition

$$c_j(0) = \alpha\delta_{j,1} + \frac{1-\alpha}{2}\delta_{j,2} \tag{9}$$

which entails that the total mass of the system (first moment) is unity:

$$M_1(t) = M_1(0) = \sum_{j=1}^{\infty} j c_j(t) = \sum_{j=1}^{\infty} j c_j(0) = 1. \tag{10}$$

The notation used here is the same as in (3), where the moments $M_n(t)$ are defined.

Of course, if $\alpha = 0$, only even aggregates are present and the model reduces (up to trivial modifications) to the original Smoluchowski model with a constant kernel, that is (5) with $B = C = 0$. The same, of course, happens for any initial condition if

$$K = L = M = A. \tag{11}$$

For the purpose of comparison, we end this introductory section by computing from the well known solution [3] for arbitrary initial conditions, the result of case (11) with initial conditions (9):

$$c_j(t) = \frac{4}{[2 + (1+\alpha)At]^2} \sum_{k=\max([j/2]-1,0)}^{j-1} \left[\frac{2At}{2 + (1+\alpha)At}\right]^k \times \binom{k+1}{2k - j + 2} \alpha^{2k-j+2} \left(\frac{1-\alpha}{2}\right)^{j-k-1}. \tag{12}$$

2. Reduction of the equations

In the following, we show how (2) with (7) can be reduced to a system of two nonlinear time-independent ODEs for functions related to the generating functions of the concentrations $c_j(t)$ with j odd and even. We define

$$D(\zeta, t) = \sum_{j=0}^{\infty} c_{2j+1}(t)\zeta^{2j+1} \qquad d(t) = D(1, t) = \sum_{j=0}^{\infty} c_{2j+1}(t) \tag{13}$$

$$P(\zeta, t) = \sum_{j=1}^{\infty} c_{2j}(t)\zeta^{2j} \qquad p(t) = P(1, t) = \sum_{j=1}^{\infty} c_{2j}(t). \tag{14}$$

One then finds from (2) and (7) that

$$\frac{\partial D}{\partial t}(\zeta, t) = MD(\zeta, t)P(\zeta, t) - D(\zeta, t)[Mp(t) + Kd(t)] \tag{15}$$

$$\frac{\partial P}{\partial t}(\zeta, t) = \frac{K}{2}[D(\zeta, t)]^2 + \frac{L}{2}[P(\zeta, t)]^2 - P(\zeta, t)[Lp(t) + Md(t)]. \tag{16}$$

Note that these are ODEs, rather than PDEs; the dependence of the solutions on ζ arises from the initial conditions, see below. Setting $\zeta = 1$ in these equations, and using (13), (14), one concludes that the functions $d(t)$ and $p(t)$ satisfy a closed set of equations:

$$\dot{p} = \frac{K}{2}d^2 - \frac{L}{2}p^2 - Mpd \tag{17}$$

$$\dot{d} = -Kd^2. \tag{18}$$

These equations are easily solved for $d(t)$ and $p(t)$, but we only need the former:

$$d(t) = \alpha/(1 + \alpha Kt). \tag{19}$$

To obtain this solution we used the initial condition

$$d(0) = \alpha \tag{20}$$

entailed by (9) and (13). We now note that the right-hand sides of the four ODEs (15)–(18) are homogeneous of degree two in the four dependent variables, so that one equation can be eliminated, keeping the three remaining ones autonomous by a time rescaling. We therefore set

$$\tilde{D}(\zeta,\theta) = D(\zeta,t)/d(t) \tag{21}$$
$$\tilde{P}(\zeta,\theta) = P(\zeta,t)/d(t) \tag{22}$$
$$\tilde{p}(\theta) = p(t)/d(t) \tag{23}$$

with

$$\dot{\theta}(t) = Kd(t) \tag{24}$$

entailing, see (19),

$$\theta(t) = \ln(1+\alpha K t) \qquad 1+\alpha K t = \mathrm{e}^{\theta}. \tag{25}$$

We thus get

$$K\frac{\partial \tilde{D}}{\partial\theta} = M\tilde{D}(\tilde{P}-\tilde{p}) \tag{26}$$
$$K\frac{\partial \tilde{P}}{\partial\theta} = \frac{K}{2}\tilde{D}^2 + \frac{L}{2}\tilde{P}^2 + [K-M-L\tilde{p}]\tilde{P} \tag{27}$$
$$K\tilde{p}' = -\frac{L}{2}\tilde{p}^2 + (K-M)\tilde{p} + \frac{K}{2}. \tag{28}$$

Here and below the prime denotes differentiation with respect to θ. These equations are supplemented by the following initial conditions, derived from (9) via (13), (14), (20)–(22):

$$\tilde{D}(\zeta,0) = \zeta \tag{29}$$
$$\tilde{P}(\zeta,0) = \frac{1-\alpha}{2\alpha}\zeta^2 \tag{30}$$
$$\tilde{p}(\theta) = \tilde{P}(1,0) = \frac{1-\alpha}{2\alpha}. \tag{31}$$

Since we will need this information below, from (26) we also compute the first derivative of $\tilde{D}(\zeta,\theta)$ at $\theta = 0$:

$$\left.\frac{\partial \tilde{D}(\zeta,\theta)}{\partial\theta}\right|_{\theta=0} = \frac{M}{K}[\tilde{P}(\zeta,0)-\tilde{p}(0)]\tilde{D}(\zeta,0) = \frac{M}{K}\frac{1-\alpha}{2\alpha}(\zeta^3-\zeta). \tag{32}$$

We now solve (26) for $\tilde{P}(\zeta,\theta)$,

$$\tilde{P}(\zeta,\theta) = \tilde{p}(\theta) + \frac{K}{M}\frac{\partial \ln \tilde{D}(\zeta,\theta)}{\partial\theta} \tag{33}$$

and we insert this expression in (27), obtaining, after some elementary computations,

$$\frac{\partial^2 \ln \tilde{D}}{\partial\theta^2} = \frac{M}{2K}(\tilde{D}^2-1) + \frac{L}{2M}\left(\frac{\partial \ln \tilde{D}}{\partial\theta}\right)^2 + \frac{K-M}{K}\frac{\partial \ln \tilde{D}}{\partial\theta}. \tag{34}$$

Remarkably, this second-order nonlinear ODE, which determines the dependence of $\tilde{D}(\zeta,\theta)$ on θ, is again *autonomous*, namely, the function $\tilde{p}(\theta)$ has completely dropped out (thanks to the nonlinear ODE it satisfies, see (28)). Let us moreover re-emphasize that (34) is an ODE rather than a PDE, the dependence of $\tilde{D}(\zeta,\theta)$ on ζ arising only from the initial conditions, see (29) and (32).

An additional simplification is achieved by the substitution

$$\tilde{D}(\zeta,\theta) = [F(\zeta,\theta)]^{-2M/L} \tag{35}$$

via which one obtains

$$F'' = aF' + b(F - F^c) \tag{36}$$

where

$$a = 1 - \frac{M}{K} \qquad b = \frac{L}{4K} \qquad c = 1 - \frac{4M}{L} \tag{37}$$

entailing, of course,

$$1 - a = b(1 - c). \tag{38}$$

Note that, in writing (36), we have used the notation introduced above (prime indicates differentiation with respect to θ), to emphasize that this differential equation is indeed an ODE.

The initial conditions for (36) are then given as follows:

$$F(\zeta,0) = [\tilde{D}(\zeta,0)]^{2/(c-1)} \tag{39}$$

$$\left.\frac{\partial F(\zeta,\theta)}{\partial\theta}\right|_{\theta=0} = \frac{2}{c-1}[\tilde{D}(\zeta,0)]^{(3-c)/(c-1)} \left.\frac{\partial \tilde{D}(\zeta,\theta)}{\partial\theta}\right|_{\theta=0}. \tag{40}$$

The transformation (35) is of course only applicable if $L \neq 0$. If $L = 0$, one sets, instead of (35),

$$\tilde{D}(\zeta,\theta) = \exp[F(\zeta,\theta)] \tag{41}$$

and thereby gets

$$F'' = aF' + \frac{1-a}{2}[\exp(2F) - 1] \tag{42}$$

with a defined by (37), and with the initial conditions

$$F(\zeta,0) = \ln[\tilde{D}(\zeta,0)] \tag{43}$$

$$\left.\frac{\partial F(\zeta,\theta)}{\partial\theta}\right|_{\theta=0} = [\tilde{D}(\zeta,0)]^{-1} \left.\frac{\partial \tilde{D}(\zeta,\theta)}{\partial\theta}\right|_{\theta=0}. \tag{44}$$

3. The special case $L = 4M$

In the case when $L = 4M$, entailing $c = 0$, see (37), (36) reduces to

$$F'' = b(F - 1) + (b - 1)F'. \tag{45}$$

This is a *linear autonomous* ODE, hence immediately solvable. To fix notation, note that this model has two free parameters: one that sets the overall timescale, which we chose to be K, and another dimensionless parameter, which we take to be b. To express the other quantities in those terms, we use (37), (38). To proceed, we need the initial conditions. We start with the most general initial conditions, specializing later to the 'mono-bi-disperse' case given in (9). We therefore define

$$\tilde{D}(\zeta,0) = \delta(\zeta) \qquad \tilde{P}(\zeta,0) = \pi(\zeta). \tag{46}$$

The initial conditions for $F(\zeta,\theta)$ then read (see (39), (40))

$$F(\zeta,0) = [\delta(\zeta)]^{-2} \tag{47}$$

$$\left.\frac{\partial F(\zeta,\theta)}{\partial\theta}\right|_{\theta=0} = -2b[\delta(\zeta)]^{-2}[\pi(\zeta) - \pi(1)]. \tag{48}$$

Hence (45) with (47) and (48) yield

$$F(\zeta,\theta) = 1 + \{[\delta(\zeta)]^2 - 1\}\beta_1(\theta) - 2d\,[\delta(\zeta)]^{-2}\,[\pi(\zeta) - \pi(1)]\beta_2(\theta). \tag{49}$$

Here $\beta_1(\theta)$ and $\beta_2(\theta)$ are defined as follows:

$$\beta_1(\theta) = \frac{b\mathrm{e}^{\theta} + \mathrm{e}^{-b\theta}}{b+1} = \frac{b(1+\alpha Kt) + (1+\alpha Kt)^{-b}}{b+1} \tag{50}$$

$$\beta_2(\theta) = \frac{\mathrm{e}^{\theta} - \mathrm{e}^{-b\theta}}{b+1} = \frac{1+\alpha Kt - (1+\alpha Kt)^{-b}}{b+1}. \tag{51}$$

From (35) and (49) one finds for $\tilde{D}(\zeta,\theta)$ the explicit expression

$$\tilde{D}(\zeta,\theta) = \frac{\delta(\zeta)}{[\beta_1(\theta) + 2b\pi(1)\beta_2(\theta)]^{1/2}}\left\{1 - \frac{2b\pi(\zeta)\beta_2(\theta) + [\beta_1(\theta) - 1][\delta(\zeta)]^2}{\beta_1(\theta) + 2b\pi(1)\beta_2(\theta)}\right\}. \tag{52}$$

This is too general to obtain a simple formula for the odd concentrations $c_{2j+1}(t)$, so we now specialize to the initial condition (9). This leads to the following expressions for $\delta(\zeta)$ and $\pi(\zeta)$, see (29), (30) and (46):

$$\delta(\zeta) = \zeta \tag{53}$$

$$\pi(\zeta) = \frac{1-\alpha}{2\alpha}\zeta^2. \tag{54}$$

From this one finally obtains, using (21), the expression

$$D(\zeta,t) = \frac{\alpha\zeta}{1+\alpha Kt}[s(t)]^{-1/2}\{1 - \zeta^2[1 - [s(t)]^{-1}]\}^{-1/2} \tag{55}$$

where $s(t)$ is given by

$$\begin{aligned} s(t) &= \beta_1(\theta) + \frac{b(1-\alpha)}{\alpha}\beta_2(\theta) \\ &= \frac{b}{\alpha(b+1)}(1+\alpha Kt) + \frac{(\alpha-1)b+\alpha}{\alpha(b+1)}(1+\alpha Kt)^{-b}. \end{aligned} \tag{56}$$

The motivation for introducing this function $s(t)$, see (55) and (56), will become clearer below.

Expansion in powers of ζ of the right-hand side of (55) yields immediately, via (13), the final result for the odd concentrations:

$$c_{2j+1}(t) = 2^{-2j}\binom{2j}{j}\frac{\alpha[s(t)]^{-1/2}}{1+\alpha Kt}\{1 - [s(t)]^{-1}\}^j. \tag{57}$$

Here and in what follows we use the standard notation for the combinatorial symbol so that

$$\binom{2j}{j} = \frac{(2j)!}{(j!)^2}. \tag{58}$$

To find the expression for $P(\zeta,t)$ we use (33), which yields, using (21) and (23),

$$\begin{aligned} P(\zeta,t) &= d(t)\tilde{p}(\theta) + \frac{d(t)}{b}\frac{\partial \ln \tilde{D}(\zeta,\theta)}{\partial\theta} \\ &= d(t)\tilde{p}(\theta) + \frac{1}{bK}\frac{\partial}{\partial t}\ln\left[\frac{D(\zeta,t)}{d(t)}\right] \end{aligned} \tag{59}$$

from which the following expression for $P(\zeta,t)$ is obtained:

$$P(\zeta,t) = \tilde{p}(\theta)d(t) + \frac{\dot{s}}{2bKs}\left\{-1 + \frac{\zeta^2}{2s[1 - \zeta^2(1 - s^{-1})]}\right\}. \tag{60}$$

From this, one finds by setting ζ to zero and noting that $P(0,t)$ must vanish as a result of (14), that

$$\tilde{p}(\theta) = \frac{\dot{s}(t)}{2bKs(t)d(t)} \tag{61}$$

hence

$$P(\zeta,t) = \frac{\dot{s}(t)\zeta^2}{2bK[s(t)]^2[1-\zeta^2(1-s^{-1})]}. \tag{62}$$

One then finds the result for the even concentrations by expanding in powers of ζ the right-hand side of this expression and comparing with (14):

$$c_{2j}(t) = \frac{\dot{s}(t)}{2bK[s(t)]^2}\{1-[s(t)]^{-1}\}^j. \tag{63}$$

Finally, we evaluate the moments $M_{n,d}(t)$ and $M_{n,p}(t)$ for the odd and even clusters, which we define as follows:

$$M_{n,d}(t) \equiv \sum_{j=0}^{\infty}(2j+1)^n c_{2j+1}(t) = \left(\zeta\frac{\partial}{\partial\zeta}\right)^n D(\zeta,t)\bigg|_{\zeta=1} \tag{64}$$

$$M_{n,p}(t) \equiv \sum_{j=1}^{\infty}(2j)^n c_{2j}(t) = \left(\zeta\frac{\partial}{\partial\zeta}\right)^n P(\zeta,t)\bigg|_{\zeta=1}. \tag{65}$$

These are easily obtained for small values of n using (55) and (60). In particular, for the zeroth moments, one finds

$$M_{0,d}(t) = d(t) = \frac{\alpha}{1+\alpha Kt} \tag{66}$$

$$M_{0,p}(t) = p(t) = \frac{\dot{s}(t)}{2bKs(t)} \tag{67}$$

while for the first moments one finds

$$M_{1,d}(t) = \frac{b}{b+1} + \frac{\alpha+(\alpha-1)b}{b+1}(1+\alpha Kt)^{-(b+1)} \tag{68}$$

$$M_{1,p}(t) = \frac{1}{b+1} - \frac{\alpha+(\alpha-1)b}{b+1}(1+\alpha Kt)^{-(b+1)}. \tag{69}$$

Likewise, for the second moments, one finds

$$M_{2,d}(t) = \frac{\alpha s(t)[3s(t)-2]}{1+\alpha Kt} \tag{70}$$

$$M_{2,p}(t) = \frac{[4s(t)-3]\dot{s}(t)}{bK}. \tag{71}$$

Let us end this section by emphasizing the neatness of the results we have displayed, which correspond to the 'mono-bi-disperse' initial conditions (9). Note in particular the two formulae, (57) and (63) together with (56), for the concentrations of the odd and even aggregates, which are much simpler than the corresponding formula for the constant kernel case, see (12).

4. Large-time and scaling behaviour of the system

Let us now discuss tersely the large-time behaviour of our system, (2) with (7)–(9). We consider first the behaviour of the concentrations as $t \to \infty$ for fixed j, and then we consider the behaviour, relevant for scaling, as both t and j diverge. In the following, in order to make the dependence of the results on the various rate constants fully explicit, we shall use both constants K and L (but never M), and the abbreviation $b = L/(4K)$ in the exponents only.

Let us start by noting that, as $t \to \infty$,

$$s(t) = \frac{KLt}{4K+L}[1 + (\alpha Kt)^{-1} + \mathrm{O}(t^{-2}) + \mathrm{O}(t^{-(b+1)})] \tag{72}$$

$$\dot{s}(t) = \frac{KL}{4K+L}[1 + \mathrm{O}(t^{-2}) + \mathrm{O}(t^{-(b+1)})]. \tag{73}$$

Here we have included two correction terms in the right-hand side, since either one might dominate, depending on the value of b, see (37).

It is then easily seen, from (57) and (63), that as $t \to \infty$ for fixed j,

$$c_{2j+1}(t) = 2^{-2j}\binom{2j}{j}\sqrt{\frac{4K+L}{L}}(Kt)^{-3/2}\left[1 - \left[\frac{3}{2} + \frac{(4K+L)\alpha j}{L}\right](\alpha Kt)^{-1} + \mathrm{O}(t^{-2}) + \mathrm{O}(t^{-(b+1)})\right] \tag{74}$$

$$c_{2j}(t) = \frac{2K(4K+L)}{L^2}(Kt)^{-2}\left[1 - \left[2 + \frac{(4K+L)\alpha j}{L}\right](\alpha Kt)^{-1} + \mathrm{O}(t^{-2}) + \mathrm{O}(t^{-(b+1)})\right]. \tag{75}$$

We thus see that, as usual, all concentrations go to zero as $t \to \infty$, but that, at large times, the odd concentrations dominate over the even ones at any given j. Indeed, as $t \to \infty$,

$$\frac{c_{2j+1}(t)}{c_{2j}(t)} = \frac{L}{2K}\left(1 + \frac{4K}{L}\right)^{-1/2} 2^{-2j}\binom{2j}{j}(Kt)^{1/2}[1 + (2\alpha Kt)^{-1} + \mathrm{O}(t^{-2}) + \mathrm{O}(t^{-(b+1)})]. \tag{76}$$

Note that this phenomenon is more pronounced if $L \gg K$: at first sight this finding might appear paradoxical, since if $L \gg K$ the even particles are more reactive than the odd ones, see (7), hence more even aggregates will be produced. However, in the limit we are considering now, namely that in which the aggregate size is kept fixed and the time goes to infinity, the dominant reaction in which A_j is involved is of the type $A_j + A_k \to A_{j+k}$ with $k \gg j$. Indeed, the total number of aggregates $d(t) + p(t)$ decays as $1/t$, whereas the total number of aggregates less than j is bounded from above by $4[D(1 - j^{-1}, t) + P(1 - j^{-1}, t)]$, which itself goes as $t^{-3/2}$. This bound follows from the general inequality

$$\sum_{k=1}^{j} a_k \leqslant 4\sum_{k=1}^{\infty} a_k(1 - j^{-1})^k \tag{77}$$

valid for any sequence of non-negative real numbers a_k and $j \geqslant 2$ a positive integer. However, it follows directly from (2) that, for j either odd or even, $\dot{c}_j/c_j$ contains two components: one which involves production of aggregates of size j and which is bounded by the number of aggregates of size less than j, and another which involves reaction of the aggregates of size j with arbitrary aggregates, leading to the disappearance of aggregates of odd size j. From these considerations, it is immediate that the latter reaction dominates in the regime we are now considering, so we understand that a greater reaction rate leads to a faster decay of aggregates of size j, as is indeed seen from (76).

It is also remarkable that the main terms in the right-hand sides of (74)–(76) are independent of the value of α (which we always assume to lie in the range $0 < \alpha \leqslant 1$); this is in agreement with a frequently made observation [7,8] that, at large times, the initial conditions are forgotten.

However, the analysis of the behaviour of the concentrations at large times and fixed j does not provide a complete picture of the behaviour of the system. This is already indicated by the large-time expressions of the first few moments of the odd and even concentrations; indeed, via (72), one easily gets, from (66)–(71), for $t \to \infty$,

$$M_{0,d} = (Kt)^{-1}[1 - (\alpha Kt)^{-1} + \mathrm{O}(t^{-2})] \tag{78}$$

$$M_{0,p} = 2(Lt)^{-1}[1 - (\alpha Kt)^{-1} + \mathrm{O}(t^{-2}) + \mathrm{O}(t^{-(b+1)})] \tag{79}$$

$$M_{0,d}/M_{0,p} = (L/2K)[1 + \mathrm{O}(t^{-2}) + \mathrm{O}(t^{-(b+1)})] \tag{80}$$

$$M_{1,d} = \left(1 + \frac{4K}{L}\right)^{-1}[1 + \mathrm{O}(t^{-(b+1)})] \tag{81}$$

$$M_{1,p} = \left(1 + \frac{4L}{K}\right)^{-1}[1 + \mathrm{O}(t^{-(b+1)})] \tag{82}$$

$$M_{1,d}/M_{1,p} = [L/(4K)][1 + \mathrm{O}(t^{-(b+1)})]. \tag{83}$$

We thus see that, as $t \to \infty$, the ratios of the first two moments of the odd and even concentrations tend to a constant. Indeed, it is easy to show (see the appendix) that as $t \to \infty$

$$M_{n,d}(t) = \frac{(2n)!}{2^n n!}\left(\frac{L}{4K + L}\right)^n (Kt)^{n-1}[1 + \mathrm{o}(1)] \tag{84}$$

$$M_{n,p}(t) = \frac{2^{n+1} n! K}{4K + L}\left(\frac{L}{4K + L}\right)^{n-1} (Kt)^{n-1}[1 + \mathrm{o}(1)]. \tag{85}$$

Note the strikingly simple expression for the ratio of these two moments:

$$\frac{M_{n,d}(t)}{M_{n,p}(t)} = 2^{-2n-1}\binom{2n}{n}\frac{L}{K}[1 + \mathrm{o}(1)] = \frac{1}{2\sqrt{\pi n}}\frac{L}{K}[1 + \mathrm{o}(1)] \tag{86}$$

where the last equality follows from Stirling's formula, see (91) below and, of course, only holds for large n. If we therefore measure the relative importance of the odd and even clusters via their contribution at large times to moments of high-order n, we find that the even clusters dominate the picture, whereas we had found exactly the opposite in the case of clusters of any fixed finite size, see (76). This is not surprising, since moments of order n are sensitive to the presence of clusters of size j with $j/s(t)$ of order n; see the remarks below on the scaling limit.

Next, to make contact with scaling theory, let us investigate the behaviour of the system in the scaling limit, namely when $t \to \infty$ and the index of the concentrations grows proportionately to the 'typical size' of the aggregates at time t,

$$j \approx xs(t) \approx xKLt/(4K + L) \tag{87}$$

see (72), with x fixed. In particular, let us evaluate in this limit (if it exists) the scaling function $\Phi(x)$, defined as the limit of $j^2 c_j(t)$ when both t and j converge with the ratio $x = (4K + L)j/(Lt)$ kept (approximately) fixed, namely with

$$j = \left[\left[\frac{KLtx}{4K + L}\right]\right] \tag{88}$$

where the symbol $[[y]]$ denotes the integer part of the real number y.

It is then easily seen that the limit in question *does not exist*, if the indices j are permitted to take both odd and even values. Indeed, as we now show, two *different* scaling functions must now be introduced, defined as follows:

$$\Phi_{d,p}(x) = \lim_{j\to\infty}[j^2 c_j(t)] \tag{89}$$

with j given by (88) and moreover required to be odd (*dispari*) for $\Phi_d(x)$ and even (*pari*) for $\Phi_p(x)$.

It is then easy to compute, from the exact expressions (57) and (63), the two scaling functions $\Phi_d(x)$ and $\Phi_p(x)$. Using the elementary fact that, in this limit (see (87)),

$$\lim_{t\to\infty} \{1 - [s(t)]^{-1}\}^j = \mathrm{e}^{-x} \tag{90}$$

as well as the following consequence of Stirling's formula:

$$2^{-2j} \binom{2j}{j} = \frac{1}{\sqrt{\pi j}}[1 + \mathrm{o}(1)] \tag{91}$$

we eventually find

$$\Phi_d(x) = \frac{L}{\sqrt{\pi}(4K + L)} x^{3/2} \mathrm{e}^{-x/2} \tag{92}$$

$$\Phi_p(x) = \frac{2K}{4K + L} x^2 \mathrm{e}^{-x/2}. \tag{93}$$

It is therefore seen that scaling is indeed obeyed when the limit is taken separately over the even and odd subsequences, but that the scaling function depends on the sequence chosen. Thus, the strict universality assumed in scaling theory fails, but some considerable generality is still found in the asymptotic behaviour. In particular, one finds independence from the initial conditions.

From scaling as stated in (92), (93) one can find the following heuristic argument for the large-time behaviour of the moments:

$$M_{n,\sigma}(t) \approx \sum_{j=1}^{\infty} j^{n-2} \Phi_\sigma[j/s(t)] \approx [s(t)]^{n-1} 2 \int_0^\infty \mathrm{d}\xi\, \xi^{n-2} \Phi_\sigma(\xi). \tag{94}$$

Here σ stands for either of the indices p or d and the sum in the second term covers the corresponding range of indices. Note the factor 2 due to the fact that the sum runs over half the integers in all cases. As is seen from the appendix, these relations are indeed satisfied.

5. Conclusions

To summarize, we have found a new special case of the parity-dependent constant kernel which can be solved in closed form. The solution can be given in somewhat implicit form for general initial conditions, but takes a simple explicit form for the case of the 'mono-bi-disperse' initial condition (9). Scaling properties are found to be somewhat unusual: the scaling limit is found to exist only if the limiting procedure is taken separately over the odd and even integers.

Finally, let us mention that the transformations shown here allow one to study the general scaling behaviour of the parity-dependent constant kernel model, at least for small values of the scaling parameter $j/s(t)$. This will be the object of a future publication.

Appendix

In the following, we prove the asymptotic forms for the moments $M_{n,d}(t)$ and $M_{n,p}(t)$ given in (84), (85). To this end we introduce a new variable z instead of ζ, defined as follows:

$$\zeta = \mathrm{e}^{z/s(t)}. \tag{95}$$

If one then introduces the transformed functions

$$\overline{D}(z, t) = D[\mathrm{e}^{z/s(t)}, t] \tag{96}$$

$$\overline{P}(z, t) = P[\mathrm{e}^{z/s(t)}, t] \tag{97}$$

one finds from (64), (65) immediately

$$M_{n,d}(t) = [s(t)]^n \left. \frac{\partial}{\partial z^n} \overline{D}(z,t) \right|_{z=0} \tag{98}$$

$$M_{n,p}(t) = [s(t)]^n \left. \frac{\partial}{\partial z^n} \overline{P}(z,t) \right|_{z=0} . \tag{99}$$

From (55) and (60) it is found that

$$\overline{D}(z,t) = \frac{\alpha}{1+\alpha K t} \left\{ 1 - 2z + \mathrm{O}\left[\frac{z^2}{s(t)} \right] \right\}^{-1/2} \tag{100}$$

$$\overline{P}(z,t) = \frac{\dot{s}(t)}{2bKs(t)} \left\{ 1 - 2z + \mathrm{O}\left[\frac{z^2}{s(t)} \right] \right\}^{-1} . \tag{101}$$

From these equations the asymptotic expressions (84) and (85) for the moments follow using (98) and (99).

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