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A new solvable model of aggregation kinetics

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Abstract. A new reaction kernel, $K(j,k) = 2-q^j-q^k$ with $0 < q < 1$, is introduced, 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. The time evolution of the concentrations $c_j(t)$ and of their moments $M_n(t) = \sum_{j=1}^{\infty} j^n c_j(t)$ is analysed. The $c_j(t)$ decay at large times as $t^{-(2-q^j)}$ in striking contrast to the behaviour of the constant kernel $K(j,k) = 2$, for which $c_j(t)$ behaves as t^{-2} at large times. On the other hand, the moments behave in leading order at large times exactly like the moments of the constant kernel, though differences appear at higher orders.

1. Introduction

In this paper we introduce and study a new solvable model for the kinetics of irreversible aggregation. In this process aggregates A_j, which are characterized by their mass j, react by sticking to one another to form a larger aggregate:

$$A_j + A_k \underset{K(j,k)}{\longrightarrow} A_{j+k}. \tag{1.1}$$

The non-negative quantities $K(j,k) = K(k,j)$ are the mass-dependent rates at which the aggregates stick to each other. Using the law of mass-action, namely the assumption that the collision rate between two aggregates of masses j and k is given by $K(j,k)c_j c_k$, where $c_j(t)$ is the concentration of aggregate A_j at time t, one obtains the following set of equations for $c_j(t)$, which are known as the Smoluchowski equations [1]:

$$\dot{c}_j = \frac{1}{2}\sum_{k,l=1}^{\infty} K(k,l)c_k c_l\big[\delta_{k+l,j} - \delta_{k,j} - \delta_{l,j}\big]. \tag{1.2}$$

The prefactor $\frac{1}{2}$ is conventional, to account for double counting. Here, and always below, a superimposed dot denotes differentiation with respect to the time t.

The Smoluchowski equations (1.2) are an infinite set of coupled nonlinear ordinary differential equations (ODEs). A few cases, corresponding to specific kernels $K(k,l)$, have been solved exactly; there is, however, a well developed, albeit non-rigorous, phenomenological 'scaling theory' that deals with a fairly general class of models [2]. The purpose and scope of this paper is to exhibit a new case which can be solved and to analyse

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its behaviour; as discussed by one of us (FL) in a separate paper [3], this also contributes to a better understanding of the validity and the limits of 'scaling theory'.

Let us briefly review some well known qualitative features of the time evolution of aggregation kinetics as described by the Smoluchowski ODEs (1.2), complemented by the 'monodisperse' initial condition

$$c_j(0) = \delta_{j,1}. \tag{1.3}$$

(An arbitrary constant in the right-hand side of this equation can be eliminated by rescaling both the concentrations and the time appropriately.) Most of the qualitative considerations given below also hold for more general initial conditions than (1.3), though the extension of the quantitative analysis is usually non-trivial. The qualitative behaviour is expected to be unaffected as long as all moments (see (1.9) below) of the initial concentrations are finite. Hence we focus hereafter mainly on the monodisperse initial condition (1.3).

The Smoluchowski equations (1.2) have no equilibrium (time-independent) solutions. This follows physically from the absence of a backward reaction in (1.1) and (1.2). Thus the range of concentrations which contribute significantly to the total mass increases as reaction (1.1) proceeds, while the concentration $c_j(t)$ of each specific species of mass j decreases eventually towards zero,

$$\lim_{t\to\infty}[c_j(t)] = 0. \tag{1.4}$$

The total mass of the aggregates is conserved,

$$\sum_{j=1}^{\infty} j c_j(t) = \sum_{j=1}^{\infty} j c_j(0) = 1 \tag{1.5}$$

where the last equality can always be attained by a suitable rescaling of the concentrations $c_j(t)$ and time, and will hereafter always be assumed. The validity of this conservation law is proven by summing (1.2) over j from 1 to infinity and noticing that, since all the terms inside the square brackets cancel out, the right-hand side vanishes. It should be pointed out that this conclusion is invalidated by convergence problems if $c_j(t)$ decays too slowly in j. In this case there occurs a systematic *decrease* in the total mass of the aggregates. This decrease is physically interpreted as the formation of an infinite aggregate containing a finite portion of the mass, which is not accounted for in the sum (1.5) [4, 5]. This phenomenon is known as *gelation*. We shall not, however, be dealing with it here.

Since, at larger times, the range of masses which contribute significantly to the total mass increases, it is appropriate to study the regime in which j and t are both large, and j maintains a given proportion x with respect to a so-called 'typical size' $s(t)$ which goes to infinity as $t \to \infty$. It is then natural to make the following ansatz:

$$c_j(t) \approx j^{-2}\Phi[j/s(t)] \tag{1.6}$$

where the function $\Phi(x)$ is a 'scaling function' which vanishes quickly as $x \to \infty$. This is known as the *scaling ansatz* for Smoluchowski's equations and it has been extensively investigated (see, for instance, [2, 3, 6]). The prefactor j^{-2} is motivated by the property (1.5) of mass conservation [2].

So far, the only exactly solved models were related more or less directly with the following general form of the reaction rates [7]:

$$K(j,k) = a + b\,(j+k) + cjk \tag{1.7}$$

where a, b and c are non-negative constants (of course, a common factor can be eliminated from these three constants by rescaling the time in (1.2)). If $c > 0$, then gelation occurs at a finite time. Otherwise, the scaling theory applies, as reported in [2], and the following results hold. If

$$K(j,k) = 2 \tag{1.8a}$$

the Smoluchowski equations (1.2) with (1.3) admit the following solution [1, 7]:

$$c_j(t) = \frac{t^{j-1}}{(t+1)^{j+1}}. \tag{1.8b}$$

It is then easily seen that the scaling ansatz (1.6) applies asymptotically ($t \to \infty$, $j \to \infty$ and $x = j/t$ finite) with

$$s(t) = t + 1 = t\big[1 + \mathrm{O}(t^{-1})\big] \qquad \Phi(x) = x^2 \mathrm{e}^{-x}. \tag{1.8c}$$

For the moments $M_n(t)$ of the $c_j(t)$, generally defined by the standard formula

$$M_n(t) \equiv \sum_{j=1}^{\infty} j^n c_j(t) \tag{1.9}$$

equation (1.8*b*) entails

$$M_0(t) = \frac{1}{1+t} \tag{1.10a}$$

$$M_2(t) = 2t + 1 \tag{1.10b}$$

$$M_n(t) = \sum_{m=0}^{n} \mathcal{S}_n^{(m)} m!\, t^{m-1} \qquad (n \geqslant 1) \tag{1.10c}$$

where n is an integer and $\mathcal{S}_n^{(m)}$ are the Stirling numbers of the second kind [8] defined as follows:

$$j^n = \sum_{m=0}^{n} \mathcal{S}_n^{(m)} \frac{j!}{(j-m)!}. \tag{1.10d}$$

Equation (1.10*c*) follows from (1.8*b*) and the definition of the Stirling numbers of the second kind (1.10*d*), together with the following elementary identity:

$$\sum_{j=1}^{\infty} \frac{j!}{(j-n)!} x^j = x^n \frac{\mathrm{d}^n}{\mathrm{d}x^n} \frac{1}{1-x} = x^n \frac{\mathrm{d}^n}{\mathrm{d}x^n} \left(\frac{x}{1-x}\right) = \left(\frac{n!x^n}{(1-x)^{n+1}}\right) \qquad (n \geqslant 1) \tag{1.11}$$

for integer n. Hence at large times ($t \to \infty$)

$$M_0(t) = t^{-1}\big[1 - t^{-1} + \mathrm{O}(t^{-2})\big] = t^{-1} - t^{-2} + \mathrm{O}(t^{-3}) \tag{1.12a}$$

$$M_2(t) = 2t\big[1 + (2t)^{-1}\big] = 2t + 1 \tag{1.12b}$$

$$M_n(t) = n!\, t^{n-1}\big[1 + \tfrac{1}{2}(n-1)\, t^{-1} + \mathrm{O}(t^{-2})\big]. \tag{1.12c}$$

If instead

$$K(j,k) = b(j+k) \tag{1.13a}$$

the solution is also known [7]:

$$c_j(t) = a_j (1 - \mathrm{e}^{-bt})^{j-1} \mathrm{e}^{j\mathrm{e}^{-bt}} \mathrm{e}^{-bt} \tag{1.13b}$$

where the constants a_j are the following combinatorial coefficients [7]:

$$a_j = \frac{j^{j-2}\mathrm{e}^{-j}}{(j-1)!} = \frac{j^{-3/2}}{\sqrt{2\pi}}[1 + \mathrm{O}(j^{-1})] \qquad (1.13c)$$

where the second equality follows from Stirling's formula. Hence the scaling ansatz (1.6) still holds, with

$$s(t) = \mathrm{e}^{2bt} \qquad \Phi(x) = \sqrt{\frac{x}{2\pi}}\mathrm{e}^{-x/2} \qquad (1.13d)$$

as can be checked from (1.13*b*) and (1.13*c*). The first and second moments can also be evaluated in closed form [7]:

$$M_0(t) = \mathrm{e}^{-bt} \qquad (1.14a)$$

$$M_2(t) = \mathrm{e}^{2bt}. \qquad (1.14b)$$

The exact expressions for the higher moments $M_n(t)$ become unwieldy for large n, but at large times they are given by

$$M_n(t) = (2n-3)!!\,\mathrm{e}^{2(n-1)bt}\left[1 + \mathrm{O}(\mathrm{e}^{-bt})\right] \qquad (n \geqslant 2) \qquad (1.15)$$

for integer n, as shown in appendix A. Note that, in contradistinction to the constant kernel case, the second and the zeroth moment are not inversely proportional to each other at large times (see (1.12*a*), (1.12*b*) and (1.14*a*), (1.14*b*)). On the other hand, in this case the zeroth moment and the monomer concentration $c_1(t)$, see (1.13*b*), (1.13*c*) and (1.14*a*), go asymptotically to zero at large times in the same way,

$$\frac{c_1(t)}{M_0(t)} \equiv \frac{c_1(t)}{\sum_{j=1}^{\infty} c_j(t)} = \exp[-1 + \exp(-bt)] = \mathrm{e}^{-1}[1 + \mathrm{O}(\mathrm{e}^{-bt})]. \qquad (1.16)$$

In the following we focus on the new solvable model characterized by the kernel

$$K(j,k) = 2 - \mathrm{e}^{-bj} - \mathrm{e}^{-bk} = 2 - q^j - q^k \qquad (1.17a)$$

where b is a positive constant, $b > 0$, and

$$q = \mathrm{e}^{-b} \qquad (1.17b)$$

is a positive constant which is less than unity, $0 < q < 1$. Hereafter we will use the constants q or b at our convenience. Clearly, if $b \gg 1$, the kernel (1.17*a*), (1.17*b*) differs little from the constant kernel (1.8*a*) for all (positive integer) values of the indices j and k, yet we find below some remarkable differences in the behaviour of the corresponding concentrations $c_j(t)$ and moments $M_n(t)$. If instead $b \ll 1$, then the kernel (1.17*a*) for values of j and k much less than $1/b$,

$$j \ll 1/b \qquad k \ll 1/b \qquad (1.18a)$$

takes the form

$$K(j,k) = b\,(j+k)[1 + \mathrm{O}(bj, bk)]. \qquad (1.18b)$$

Hence it approximates the linear sum kernel (1.13*a*) rather than the constant kernel (1.8*a*). Of course, for large values of the indices,

$$j \gg 1/b \qquad k \gg 1/b \qquad (1.19)$$

the kernel (1.17*a*), (1.17*b*) again approximates the constant kernel (1.8*a*). Hence the study of our model, see (1.17*a*) and (1.17*b*), in the case $b \ll 1$, sheds some light, using exact results, on the crossover between two different types of kernels [3]. Indeed, as is shown in the scaling theory [4], the asymptotic degree of homogeneity in j and k of the kernel $K(j,k)$ is the most relevant factor in characterizing its scaling behaviour. The solution of our model in the case of $b \ll 1$ will allow one to investigate the behaviour of an aggregating system with a kernel $K(j,k)$, see (1.17*a*) and (1.17*b*), which, over a broad range of lower mass values, is homogeneous of degree one, see (1.18*b*), but is asymptotically ($j \to \infty$) homogeneous of degree zero, see (1.17*a*) and (1.17*b*) [3]. Clearly, such crossovers exist in nature, because aggregates may undergo *qualitative* changes in their behaviour as their size increases.

In section 2 we provide the solution of the system (1.2) with the initial condition (1.3), to the extent of obtaining a closed expression for the generating function of the concentrations. We also give expressions for the concentrations $c_1(t)$ and $c_2(t)$ of monomers and dimers as well as for the moments $M_0(t)$ and $M_2(t)$, see (1.9); of course

$$M_1(t) \equiv \sum_{j=1}^{\infty} j c_j(t) = 1 \tag{1.20}$$

see (1.5) and (1.3). We also identify the asymptotic behaviours at large time of all concentrations $c_j(t)$ and moments $M_n(t)$; a comparison of these behaviours with that of the constant kernel case is also made. Some aspects of these findings are surprising because they do not reproduce current expectations based on scaling theory; this is discussed in some detail by one of us (FL) in a separate paper [3]. In section 3 we summarize our results and offer some indications on future developments.

2. The solution

In this section we show how to solve the evolution equations (1.2) with the initial conditions (1.3) and the kernel (1.17*a*) and (1.17*b*). We focus on the generating function of the concentrations and obtain a rather explicit form for it. We then extract various results from it as outlined above and compare them with analogous results for the constant kernel case (to which our case indeed reduces for $q = 0$, see (1.17*a*), (1.17*b*) and (1.8*a*)).

The kernel (1.17*a*) and (1.17*b*) is of the form

$$K(j,k) = f(j) + f(k) \tag{2.1a}$$

with

$$f(j) = 1 - \mathrm{e}^{-bj} = 1 - q^j. \tag{2.1b}$$

For all kernels of type (2.1*a*) there exists a transformation [4] which yields a substantial simplification of the problem. Define

$$\phi_j(\theta) = \frac{c_j(t)}{\sum_{k=1}^{\infty} c_k(t)} = \frac{c_j(t)}{M_0(t)} \tag{2.2a}$$

together with the change of time variable from t to θ according to the definition

$$\mathrm{d}\theta = \mathrm{d}t \sum_{k=1}^{\infty} c_k(t) = \mathrm{d}t\, M_0(t). \tag{2.2b}$$

Note that this is a somewhat implicit change of independent variable. However, once the quantities $\phi_j(\theta)$ are known, the change can be inverted by summing (2.2*a*) multiplied by j over j from one to infinity and using (1.5). There obtains

$$\sum_{j=1}^{\infty} j\phi_j(\theta) = \left(\sum_{j=1}^{\infty} c_j(t)\right)^{-1} \tag{2.3}$$

which, via (2.2*a*), yields

$$c_j(t) = \frac{\phi_j(\theta)}{\sum_{k=1}^{\infty} k\phi_k(\theta)} \tag{2.4}$$

as well as, via (2.2*b*),

$$\mathrm{d}t = \mathrm{d}\theta \sum_{k=1}^{\infty} k\phi_k(\theta). \tag{2.5}$$

These formulae, (2.5) and (2.4), allow one to recover the original concentrations $c_j(t)$ as well as $t = t(\theta)$ from the quantities $\phi_j(\theta)$.

It is easily seen, using (2.2*a*), that the Smoluchowski equations (1.2) take the following simpler form:

$$\frac{\mathrm{d}\phi_j}{\mathrm{d}\theta} = \sum_{k=1}^{j-1} f(k)\,\phi_k\phi_{j-k} - f(j)\,\phi_j \tag{2.6}$$

with the initial condition

$$\phi_j(0) = \delta_{j,1} \tag{2.7}$$

which corresponds to the monodisperse initial condition (1.3). Hereafter $\theta = 0$ for $t = 0$. In (2.6) and elsewhere, a sum vanishes if the upper limit is less than the lower limit. From (2.6) and (2.7), one finds

$$\phi_j(\theta) = \phi_j(0)\,\mathrm{e}^{-f(j)\theta} + \mathrm{e}^{-f(j)\theta} \sum_{k=1}^{j-1} f(k) \int_0^{\theta} \mathrm{d}\theta'\,\phi_k(\theta')\,\phi_{j-k}(\theta')\,\mathrm{e}^{f(j)\theta'}. \tag{2.8}$$

This allows one to solve (2.6) with (2.7) recursively, but the expressions rapidly become unwieldy. Note that (2.2*a*) implies the identity (normalization formula)

$$\sum_{j=0}^{\infty} \phi_j(\theta) = 1. \tag{2.9}$$

We now define the generating function

$$\tilde{F}(\zeta, \theta) = \sum_{j=1}^{\infty} \phi_j(\theta)\,\mathrm{e}^{j\zeta} \tag{2.10}$$

as well as a (pseudodifferential) operator T_f which acts on power series in e^{ζ} in the following manner:

$$T_f\left[\sum_{j=1}^{\infty} a_j \mathrm{e}^{j\zeta}\right] = \sum_{j=1}^{\infty} f(j)\,a_j \mathrm{e}^{j\zeta}. \tag{2.11}$$

Note that T_f is a well defined operator for a large class of functions $f(j)$. In particular, however, if $f(j)$ is a polynomial in j,

$$f(j) = \sum_{n=0}^{N} f_n j^n \tag{2.12}$$

then T_f is a linear differential operator with constant coefficients acting on the variable ζ,

$$T_f = \sum_{n=0}^{N} f_n \left(\frac{\partial}{\partial \zeta}\right)^n. \tag{2.13}$$

Equations (2.6) for $\phi_j(\theta)$ then yield, via (2.10), the following (pseudodifferential) equation for $\tilde{F}(\zeta,\theta)$:

$$\frac{\partial \tilde{F}}{\partial \theta}(\zeta,\theta) = [\tilde{F}(\zeta,\theta) - 1](T_f \tilde{F})(\zeta,\theta). \tag{2.14}$$

It is thus seen that any model characterized by a kernel of the sum form (2.1*a*) leads to this equation. The models considered so far have involved ordinary differential operators T_f, so that (2.14) generally became a (nonlinear) partial differential equation. Our model involves instead a difference operator.

Indeed, let us now specialize to our case, see (2.1*b*). It is then notationally convenient to redefine the generating function by writing

$$F(\zeta,\theta) = \sum_{j=1}^{\infty} \phi_j(\theta)\, \mathrm{e}^{bj\zeta} \tag{2.15}$$

instead of (2.10). Then (see (2.11) and (2.1*b*))

$$(T_f F)(\zeta,\theta) = F(\zeta,\theta) - F(\zeta - 1,\theta). \tag{2.16}$$

Hence, if we now define

$$H(\zeta,\theta) = F(\zeta,\theta) - 1 \tag{2.17}$$

we obtain from (2.14) and (2.16) the following nonlinear differential-difference equation for $H(\zeta,\theta)$:

$$\frac{\partial H}{\partial \theta}(\zeta,\theta) = H(\zeta,\theta)[H(\zeta,\theta) - H(\zeta-1,\theta)]. \tag{2.18}$$

Before proceeding to solve this equation, let us note that (2.15) and (2.17) entail the formula

$$\phi_j(\theta) = \frac{b^{-j}}{j!}\left(\mathrm{e}^{-b\zeta}\frac{\partial}{\partial \zeta}\right)^j H(\zeta,\theta)\bigg|_{\zeta=-\infty} \qquad (j \geqslant 1) \tag{2.19a}$$

or equivalently

$$\phi_j(\theta) = \frac{1}{j!}\left(\frac{\partial}{\partial \eta}\right)^j H(b^{-1}\ln\eta,\theta)\bigg|_{\eta=0}. \tag{2.19b}$$

Let us now show how the evolution equation (2.18) is solved. A major simplification occurs by writing $H(\zeta,\theta)$ in the following quotient form:

$$H(\zeta,\theta) = \frac{h(\zeta-1,\theta)}{h(\zeta,\theta)}. \tag{2.20}$$

Then (2.18) is satisfied if $h(\zeta,\theta)$ satisfies the following *linear* equation:

$$\frac{\partial h}{\partial \theta}(\zeta,\theta) = -h(\zeta-1,\theta). \tag{2.21}$$

Let us note that $h(\zeta,\theta)$ is not uniquely determined by $H(\zeta,\theta)$. The latter, of course, is unique, once the initial conditions are specified, as it is defined via (2.15) and (2.17) in terms of the system of ODEs (2.6) for which existence and uniqueness theorems exist.

To solve (2.21) we define the following Fourier generating function $\Lambda(\zeta,\theta,\rho)$:

$$\Lambda(\zeta,\theta,\rho) = \sum_{k=-\infty}^{\infty} h(\zeta-k,\theta)\,\mathrm{e}^{\mathrm{i}\rho k}. \tag{2.22}$$

It is then easily seen, via (2.21), that $\Lambda(\zeta, \theta, \rho)$ satisfies the linear ODE in θ

$$\frac{\partial \Lambda}{\partial \theta}(\zeta, \theta, \rho) = -\mathrm{e}^{-\mathrm{i}\rho}\Lambda(\zeta, \theta, \rho) \tag{2.23a}$$

entailing

$$\Lambda(\zeta, \theta, \rho) = \Lambda(\zeta, 0, \rho)\exp(-\theta \mathrm{e}^{-\mathrm{i}\rho}). \tag{2.23b}$$

From this last expression and (2.22) it is easy to obtain the following expression for $h(\zeta, \theta)$:

$$h(\zeta, \theta) = \sum_{m=0}^{\infty} \frac{(-\theta)^m}{m!} h(\zeta - m, 0). \tag{2.24}$$

There remains to evaluate the initial data $h(\zeta, 0)$, and for this we must now specify the initial conditions. We refrained from doing so until now to keep our treatment general. Now we specify that the system is initially monodisperse, see (1.3) and (2.7). Hence, via (2.15) and (2.17),

$$H(\zeta, 0) = \mathrm{e}^{b\zeta} - 1. \tag{2.25a}$$

This yields, via (2.20) at $\theta = 0$, the following recurrence relation for $h(\zeta, 0)$:

$$h(\zeta, 0) = (\mathrm{e}^{b\zeta} - 1)^{-1} h(\zeta - 1, 0) \tag{2.25b}$$

which can be solved to yield, up to an irrelevant (see (2.20)) multiplicative constant,

$$h(\zeta, 0) = \mathrm{e}^{\mathrm{i}\pi\zeta} \prod_{l=0}^{\infty} \left[1 - \mathrm{e}^{b(\zeta - l)}\right]^{-1}. \tag{2.25c}$$

Inserting this formula in (2.24) one finally obtains

$$h(\zeta, \theta) = \sum_{m=0}^{\infty} \frac{(-\theta)^m}{m!} \mathrm{e}^{\mathrm{i}\pi(\zeta - m)} \prod_{l=m}^{\infty} \left[1 - \mathrm{e}^{b(\zeta - l)}\right]^{-1} = \mathrm{e}^{\mathrm{i}\pi\zeta} \sum_{m=0}^{\infty} \frac{\theta^m}{m!} \prod_{l=m}^{\infty} \left[1 - \mathrm{e}^{b(\zeta - l)}\right]^{-1}. \tag{2.26}$$

Clearly, we have glossed over some details, such as the convergence of the trigonometric sum in (2.22). However, the final result (2.26) is obviously well defined (except at some specific poles) and it can be verified straightforwardly that it satisfies both the evolution equation (2.21) and the initial condition (2.25*c*).

Combining the definition (2.20) of $H(\zeta, \theta)$ in terms of $h(\zeta, \theta)$ with equation (2.21) satisfied by $h(\zeta, \theta)$ one obtains

$$H(\zeta, \theta) = -\frac{\partial}{\partial \theta} \ln[h(\zeta, \theta)]. \tag{2.27}$$

Clearly, in this equation, one can multiply $h(\zeta, \theta)$ by any function which does not depend on θ without affecting the final result. After some such manipulations, one finally obtains

$$H(\zeta, \theta) = -\frac{\partial}{\partial \theta} \ln\left[\sum_{m=0}^{\infty} \frac{\theta^m}{m!} \prod_{l=0}^{\infty} (1 - q^l q^{m-\zeta})^{-1}\right] \tag{2.28a}$$

$$= -\frac{\partial}{\partial \theta} \ln\left[\sum_{m=0}^{\infty} \frac{\theta^m}{m!} \prod_{l=0}^{\infty} \frac{1 - q^{l-\zeta}}{1 - q^{l+m-\zeta}}\right] \tag{2.28b}$$

where, of course, we used the definition of q (1.17*b*). Let us re-emphasize that the right-hand side of (2.28*b*) is a well defined expression (both the infinite product and the sum clearly converge since $0 < q < 1$) and that it satisfies the evolution equations (2.18) and the initial condition (2.25*a*). Note that (2.28*b*) entails

$$H(0, \theta) = 0 \tag{2.29}$$

which clearly corresponds, via (2.17) and (2.15), to the normalization formula (2.9).

We now massage the expression (2.28) a bit more, to make its analysis more tractable. To this end we recall the definition of the q-exponential†,

$$e_q(x) = \prod_{l=0}^{\infty}(1 - q^l x)^{-1} \tag{2.30a}$$

as well as that of the q-factorial $(x; q)_n$, defined as follows for non-negative integer values of n:

$$(x; q)_n = \prod_{l=0}^{n-1}(1 - xq^l) \qquad (n \geqslant 1) \tag{2.30b}$$

$$(x, q)_0 = 1. \tag{2.30c}$$

The names q-exponential and q-factorial can be understood if one looks at the limit $q \to 1$: in this case one finds the limiting values

$$\lim_{q\to 1}[(1 - q)^{-n}(q; q)_n] = n! \tag{2.30d}$$

$$\lim_{q\to 1} e_q[(1 - q)x] = \exp(x). \tag{2.30e}$$

From the definition of $e_q(x)$ in (2.30*a*) it follows that $e_q(x)$ also satisfies the following recursion relation:

$$\frac{1}{x}\left[e_q(x) - e_q(qx)\right] = e_q(x) \tag{2.30f}$$

which is a discrete analogue of the differential equation for the exponential function. From this relation or otherwise, one derives the well known identity [9]

$$e_q(x) = \sum_{r=0}^{\infty} \frac{x^r}{(q; q)_r}. \tag{2.31}$$

By using it (with $x = q^{m-\zeta}$) we can rewrite (2.28*a*) as follows:

$$H(\zeta, \theta) = -\frac{\partial}{\partial\theta} \ln\left\{\sum_{r=0}^{\infty} \frac{q^{-r\zeta} \exp(\theta q^r)}{(q; q)_r}\right\} \tag{2.32a}$$

$$H(\zeta, \theta) = -\frac{\partial}{\partial\theta} \ln\left\{\sum_{r=0}^{\infty} \frac{q^{-r\zeta}}{(q; q)_r}\left[\exp(\theta q^r) - 1\right] + e_q(q^{-\zeta})\right\} \tag{2.32b}$$

$$H(\zeta, \theta) = -\frac{\partial}{\partial\theta} \ln[1 + S(\zeta, \theta)] \tag{2.32c}$$

where $S(\zeta, \theta)$ is defined as

$$S(\zeta, \theta) = \frac{1}{e_q(q^{-\zeta})} \sum_{r=0}^{\infty} \frac{q^{-r\zeta}}{(q; q)_r}\left[\exp(\theta q^r) - 1\right]. \tag{2.33}$$

Note that in (2.32*b*) we have added and subtracted in the argument of the logarithm the q-exponential function $e_q(q^{-\zeta})$, see (2.31).

† See, for example, the chapter on the q-binomial theorem, in particular equation (1.3.15) in [9].

The form (2.32*c*) is convenient because the function $[e_q(q^{-\zeta})]^{-1}$, see (2.30*f*), is entire in ζ and it has a simple zero at $\zeta = 0$,

$$\left[e_q(q^{-\zeta})\right]^{-1} = (1 - q^{-\zeta})\left[e_q(q^{1-\zeta})\right]^{-1} \tag{2.34a}$$

see (2.30*a*), so that, in the neighbourhood of $\zeta = 0$,

$$\left[e_q(q^{-\zeta})\right]^{-1} = -T(q)b\zeta\left\{1 + Q(q)b\zeta/2 + \mathrm{O}[(b\zeta)^2]\right\} \tag{2.34b}$$

$$T(q) = 1/e_q(q) = \prod_{l=0}^{\infty}(1 - q^{l+1}) = \left[\sum_{r=0}^{\infty}\frac{q^r}{(q;q)_r}\right]^{-1} \tag{2.34c}$$

$$Q(q) = 1 - 2\sum_{l=1}^{\infty}\frac{q^l}{1 - q^l} \tag{2.34d}$$

where we have introduced the quantities $T(q)$ and $Q(q)$ for notational convenience. Note that this definition entails

$$T(0) = 1 \qquad Q(0) = 1 \tag{2.34e}$$

$$1 < T(q) < \infty \qquad -\infty < Q(q) < 1 \qquad (0 < q < 1). \tag{2.34f}$$

It is therefore easy to evaluate $H(\zeta, \theta)$, as well as its ζ-derivatives, at $\zeta = 0$. In particular, in addition to (2.29), we obtain

$$\left.\frac{\partial H(\zeta,\theta)}{\partial\zeta}\right|_{\zeta=0} = bT(q)\frac{\partial}{\partial\theta}\sum_{r=0}^{\infty}\frac{\exp(\theta q^r) - 1}{(q;q)_r} = bT(q)\sum_{r=0}^{\infty}\frac{q^r\exp(\theta q^r)}{(q;q)_r}. \tag{2.35}$$

This formula is convenient to connect the 'new time' θ with the 'real time' t. Indeed, (2.5), (2.17) and (2.15) entail

$$b\,\mathrm{d}t = \mathrm{d}\theta\left.\frac{\partial H(\zeta,\theta)}{\partial\zeta}\right|_{\zeta=0} \tag{2.36}$$

hence we obtain

$$t = T(q)\sum_{r=0}^{\infty}\frac{\exp(\theta q^r) - 1}{(q;q)_r} = T(q)\left[\exp(\theta) - 1 + \sum_{r=1}^{\infty}\frac{\exp(\theta q^r) - 1}{(q;q)_r}\right] \tag{2.37}$$

where the integration constant has been chosen so that $\theta = 0$ for $t = 0$.

Now we can also obtain the behaviour of $M_0(t)$ in real time. Indeed, equation (2.2*b*) entails

$$M_0(t) = \sum_{k=1}^{\infty}c_k(t) = (\mathrm{d}t/\mathrm{d}\theta)^{-1} \tag{2.38a}$$

hence, from (2.37),

$$M_0(t) \equiv \sum_{k=1}^{\infty}c_k(t) = \left[T(q)\sum_{r=0}^{\infty}\frac{q^r\exp(\theta q^r)}{(q;q)_r}\right]^{-1}. \tag{2.38b}$$

This formula, together with (2.37), provides an exact, if implicit, expression for $M_0(t)$.

For large θ, equation (2.37) yields

$$t = T(q)\,\mathrm{e}^{\theta}\left\{1 + \frac{\mathrm{e}^{-(1-q)\theta}}{1-q} + \mathrm{O}\left[\mathrm{e}^{-(1-q^2)\theta}\right]\right\} \tag{2.39a}$$

which is easily inverted to yield

$$\mathrm{e}^{\theta} = \frac{t}{T(q)}\left\{1 - \frac{[t/T(q)]^{-(1-q)}}{1-q} + \mathrm{O}\left[\left(\frac{t}{T(q)}\right)^{-(1-q^2)}\right]\right\}. \tag{2.39b}$$

Note that these results imply that θ goes to infinity when t does. Thus the above manipulations are indeed consistent.

Hence, at large times,

$$M_0(t) \equiv \sum_{k=1}^{\infty} c_k(t) = \frac{\mathrm{e}^{-\theta}}{T(q)}\left\{1 - \frac{q\mathrm{e}^{-(1-q)\theta}}{1-q} + \mathrm{O}\big[\mathrm{e}^{-(1-q^2)\theta}\big]\right\} \tag{2.40a}$$

and using (2.39*b*) this also yields

$$M_0(t) \equiv \sum_{k=1}^{\infty} c_k(t) = t^{-1}\left\{1 + \left[\frac{t}{T(q)}\right]^{-(1-q)} + \mathrm{O}\left[\left(\frac{t}{T(q)}\right)^{-(1-q^2)}\right]\right\}. \tag{2.40b}$$

It is of interest to compare this last formula with the corresponding one for the constant kernel (1.8*a*), see (1.12*a*). The first remark is that, while the dominant term at large t in (1.12*a*) and (2.40*b*) coincide, the first correction terms differ not only in their time dependence (the exponent of t) but even in their sign (see (2.34*e*)). This is somewhat surprising, since, at least for $b \gg 1$, namely for q close to zero, our model resembles the constant kernel case (see the discussion after (1.17)). Indeed, for $q = 0$ (as opposed to q nearly zero) equation (2.37) yields $t = \exp(\theta) - 1$, see (2.34*d*). Hence for $q = 0$, equation (2.38*a*) yields exactly (1.10*a*). We see therefore that the first correction terms in (1.12*a*) and (2.40*b*) have opposite signs, no matter how small q is, as long as it does not vanish; but the results coincide for $q = 0$. This paradox is resolved when one notes that the higher-order correction terms in (2.40*b*), which were left uncomputed, become, in the limit $q \to 0$, of the same order as the leading correction. Let us moreover point out that the corrections appearing in (2.40*b*) are of a different nature from that appearing in (1.12*a*). The latter is a so-called *analytic correction* [10] which can be removed by a simple shift of the time variable. The corrections in (2.40*b*) cannot be so removed.

To sum up, in our model the behaviour at large time of the zeroth moment $M_0(t)$ displays significant differences from that of its counterpart in the constant kernel case. The leading behaviours are in fact identical, see (1.12*a*) and (2.40*b*), but there exist non-leading terms in (2.40*b*) with exponents which depend on the parameter q of the model.

Let us now compute the monomer concentration $c_1(t)$. From (2.6) with $j = 1$ and (2.1*b*) we obtain

$$\frac{\mathrm{d}\phi_1}{\mathrm{d}\theta} = -(1-q)\,\phi_1. \tag{2.41}$$

Hence, using the monodisperse initial condition (2.7),

$$\phi_1(\theta) = \exp[-(1-q)\theta]. \tag{2.42}$$

(This formula is also obtained, of course, from (2.8).) Hence, from the definition (2.2*a*) of the quantities $\phi_j(\theta)$ and from (2.38*b*),

$$c_1(t) = \frac{1}{T(q)}\left\{\sum_{r=0}^{\infty} \frac{q^r \exp\big[(1-q+q^r)\theta\big]}{(q;q)_r}\right\}^{-1}. \tag{2.43}$$

This, in conjunction with (2.37), provides an exact, albeit implicit, expression for $c_1(t)$. In the limit of large times this yields

$$c_1(t) = \frac{\mathrm{e}^{-(2-q)\theta}}{T(q)}\left\{1 - \frac{q\mathrm{e}^{-(1-q)\theta}}{1-q} + \mathrm{O}\big[\mathrm{e}^{-(1-q^2)\theta}\big]\right\} \tag{2.44a}$$

hence, via (2.39*b*)

$$c_1(t) = [T(q)]^{1-q} t^{-(2-q)} \left\{ 1 + 2\left[\frac{t}{T(q)}\right]^{-(1-q)} + \mathrm{O}\left[\left(\frac{t}{T(q)}\right)^{-(1-q^2)}\right] \right\}. \tag{2.44b}$$

The comparison with the constant kernel case, which (see (1.8*b*) with $j = 1$) yields

$$c_1(t) = t^{-2}\left[1 - t^{-1} + \mathrm{O}(t^{-2})\right] \tag{2.45}$$

is remarkable. Both the exponent, $-2 + q$, and the amplitude $[T(q)]^{1-q}$, of the leading term in (2.44*b*) go over, as $q \to 0$ (see (2.34*d*)), to the corresponding values, -2 and 1, in (2.45). However, again we find a difference in sign in the first correction terms, see (2.45), (2.44*b*) and (2.34*e*). The resolution of this paradox is the same as in the previous case: as $q \to 0$, the higher-order corrections which were not computed, see (2.44*b*), become of the same order as the leading-order correction. On the other hand, the difference in the leading behaviour for $q > 0$ is more remarkable. The relevance of this finding to scaling theory is discussed in [3].

As we have seen, the corrections to the total number density $M_0(t)$ are *anomalous*. In fact, the *absolute* size of the leading correction term in (2.40*b*) decays proportionally to t^{-2+q}, that is, exactly in the same way as the monomer, see (2.44*b*). What is more, the amplitude of this correction term is the same, so that

$$M_0(t) - 1/t - c_1(t) = \mathrm{O}\left[\left(\frac{t}{T(q)}\right)^{-(2-q^2)}\right]. \tag{2.46}$$

Thus we see that the *leading correction* to the total number density $M_0(t)$, which we called *anomalous* because it differs from the corresponding correction in the constant kernel case, is in fact entirely due to the contribution of $c_1(t)$ to $M_0(t)$.

Let us now look at the behaviour of $c_2(t)$. A computation entirely similar to that performed for $\phi_1(\theta)$ yields, via (2.8),

$$\phi_2(\theta) = \exp[-(1-q^2)\theta]\frac{1 - \exp[-(1-q)^2\theta]}{1-q}. \tag{2.47}$$

Using (2.2*a*) and (2.38*a*) one finds

$$c_2(t) = \frac{1 - \exp[-(1-q)^2\theta]}{(1-q)T(q)} \left\{ \sum_{r=0}^{\infty} \frac{q^r \exp[(q^r - q^2 + 1)\theta]}{(q;q)_r} \right\}^{-1} \tag{2.48}$$

and for large t this yields, via (2.39*b*),

$$c_2(t) = (1-q)^{-1}[T(q)]^{1-q^2} t^{-2-q^2} \left\{ 1 - \left[\frac{t}{T(q)}\right]^{-(1-q)^2} + (q+2)\left[\frac{t}{T(q)}\right]^{-(1-q)} \right.$$
$$\left. -3\left[\frac{t}{T(q)}\right]^{-(1-q)(2-q)} + \mathrm{O}[t^{-(1-q^2)}] \right\} \tag{2.49}$$

where the last computed term in the right-hand side is only meaningful if $\frac{1}{2} < q < 1$. Note the proliferation of correction terms with different orders of magnitude. This phenomenon becomes more pronounced as j increases; moreover, as we shall see below, the large-time limit for fixed j is only attained for a range of times the lower limit of which grows rapidly with j.

Concerning the large-time behaviour of $c_j(t)$ at fixed j, we show below that at large times

$$c_j(t) = [(q;q)_{j-1}]^{-1}[T(q)]^{1-q^j} t^{-(2-q^j)}[1 + \mathrm{o}(1)]. \tag{2.50}$$

Let us prove immediately that the order of magnitude behaviour given by this formula is correct, relegating the evaluation of the amplitude in (2.50) to appendix B. For the leading term of (2.50) to provide a good approximation to $c_j(t)$, however, it is necessary that this term be much larger than the leading correction term. As follows from (2.53) below, or the computation in appendix B, this correction always decays more slowly than t^{-2}. For (2.50) to describe the true behaviour of $c_j(t)$, it is therefore necessary that

$$t^{-(2-q^j)} \gg t^{-2} \tag{2.51a}$$

implying

$$\ln t \gg q^{-j}. \tag{2.51b}$$

Note that, since all measures of characteristic size, such as $M_{n+1}(t)/M_n(t)$ for $n \geqslant 1$, grow linearly in t (see (2.61) below), at time t only those aggregates whose size j is of order $\ln \ln t$ or less have attained their asymptotic behaviour: a first indication of possible differences between asymptotic behaviour in time at fixed size j and at vanishing ratio j/t. This is discussed in more detail in [3].

We prove the result (2.50) by induction. We assume that for all $k < j$,

$$\phi_k(\theta) = \alpha_k \exp[-\theta(1-q^k)][1+\mathrm{o}(1)]. \tag{2.52}$$

Here the α_k denote unspecified constants. However, from (2.8) and (2.1*b*) one obtains

$$\phi_j(\theta) = \exp[-(1-q^j)\theta] \sum_{k=1}^{j-1} \left[(1-q^k) \int_0^{\theta} \mathrm{d}\theta' \phi_k(\theta')\, \phi_{j-k}(\theta')\, \mathrm{e}^{(1-q^j)\theta'} \right]. \tag{2.53}$$

From (2.52) there follows that the integral converges as $\theta \to \infty$, so that

$$\phi_j(\theta) = \alpha_j \exp[-\theta(1-q^j)][1+\mathrm{o}(1)] \tag{2.54}$$

consistently with (2.52). Via (2.2*a*), (2.40*a*) and (2.39*b*) this confirms (2.50). Q.E.D

Let us finally study the moments $M_n(t)$ of the concentrations, see (1.9). They can be evaluated by means of the expression

$$M_n(t) = b^{-n} \left(\sum_{j=1}^{\infty} c_j(t) \right) \frac{\partial^n H(\zeta,\theta)}{\partial \zeta^n} \bigg|_{\zeta=0} \tag{2.55}$$

entailed by (1.9), (2.2*a*), (2.15) and (2.17). The expression for $M_2(t)$ is thereby found to be (from (2.32*c*) with (2.33) via (2.34))

$$M_2(t) = 2T(q) \sum_{r=0}^{\infty} \frac{\mathrm{e}^{\theta q^r} - 1}{(q;q)_r} + \frac{2\sum_{r=0}^{\infty} r q^r \mathrm{e}^{\theta q^r}/(q;q)_r}{\sum_{r=0}^{\infty} q^r \mathrm{e}^{\theta q^r}/(q;q)_r} + Q(q) \tag{2.56}$$

with $Q(q)$ defined by (2.34*d*), which will be used below whenever convenient. Note that this quantity diverges as $q \to 1$. From (2.55) there obtains, in mixed but useful notation, see (2.37),

$$M_2(t) = 2t + Q(q) + \frac{2\sum_{r=1}^{\infty} r q^r \mathrm{e}^{\theta q^r}/(q;q)_r}{\sum_{r=0}^{\infty} q^r \mathrm{e}^{\theta q^r}/(q;q)_r}. \tag{2.57}$$

One therefore finds for large times,

$$M_2(t) = 2t + Q(q) + \frac{2q}{1-q} \exp[\theta(q-1)] + \mathrm{O}\big\{\exp[\theta(q^2-1)]\big\} \tag{2.58a}$$

and hence, via (2.39*b*)

$$M_2(t) = 2t + Q(q) + \frac{2q}{1-q}[t/T(q)]^{q-1}] + \mathrm{O}\{[t/T(q)](q^2-1)\}. \qquad (2.58b)$$

Note the remarkable structure of this expression: it differs from $M_2(t)$ for the constant kernel case, see (1.10*b*), in the next-to-leading order by an additive constant, which diverges as $q \to 1$. This fact is related to the existence of a transient behaviour over a large range of times in which $M_2(t)$ grows exponentially in t, see (1.14). This is discussed in detail in [3].

Note, moreover, that no correction of order t^{-1+q} appears in (2.58) relative to the leading term. We show in appendix C that this is indeed true for all n and that

$$M_n(t) - M_n^{(0)}(t) = -[1 - Q(q)][(n-1)/2]n!\,t^{n-2} + \mathrm{O}(t^{n-3+q}) \qquad (n \geqslant 2) \qquad (2.59)$$

where $M_n^{(0)}(t)$ is the nth moment for the constant kernel case as given in (1.12*c*). From (2.59) and (1.12*c*) one then obtains

$$M_n(t) = n!\,t^{n-1}\left[1 + \frac{n-1}{2}Q(q)\,t^{-1} + \mathrm{O}(t^{-2+q})\right] \qquad (n \geqslant 2). \qquad (2.60)$$

Note finally that an expression similar to (2.57) can also be derived for the inverse of the zeroth moment, namely

$$[M_0(t)]^{-1} = t + 1 - T(q)\sum_{r=1}^{\infty}\frac{\exp(\theta q^r) - 1}{(q;q)_{r-1}}. \qquad (2.61)$$

This is obtained from (2.37) and (2.38) using the relation

$$(q;q)_r = (q;q)_{r-1}(1 - q^r) \qquad (2.62)$$

implied by (2.30*b*) and (2.30*c*)

3. Summary and outlook

In this paper we have introduced and solved the new model of aggregation kinetics characterized by the Smoluchowski evolution equations (1.2) with the kernel (1.17*a*) and (1.17*b*), focusing mainly on the solution identified by the 'monodisperse' initial condition (1.3). We have, in particular, obtained explicit formulae for the long-time behaviour of the concentrations $c_j(t)$ and of the moments $M_n(t)$ (see (1.9)): (2.50) with (2.34*c*) gives the leading term as $t \to \infty$ of $c_j(t)$, (2.40*b*) with (2.34*c*) gives the leading term, as well as the first correction, of $M_0(t)$ as $t \to \infty$ and likewise (2.60) with (2.34*c*) for $M_n(t)$ with $n \geqslant 2$ (for $n = 1$ the result is trivial, see (1.5)). Exact, if not quite explicit, formulae are also given for the concentrations $c_j(t)$ and the moments $M_n(t)$ for all time, especially for low values of the 'mass' index j and of the 'moment' index n: see (2.43) and (2.48) with (2.37) and (2.34*c*) for $c_1(t)$ and $c_2(t)$; as well as (2.38*b*) and (2.57) with (2.47) and (2.34*c*) for $M_0(t)$ and $M_2(t)$. We also compared these findings with the corresponding results for the prototypical Smoluchowski model characterized by a constant kernel [1] (to which our model reduces for $q = 0$); this is further discussed in a separate paper by one of us (FL) [3], where the limiting case of our model with $q \to 1$ is elaborated upon and used to illustrate the 'crossover' phenomenon manifested by our model with q very close to unity, in which case the kernel (1.17) is well approximated by the linear kernel $K(j,k) = b\,(j+k)$ for a large range of (low) values of the 'mass' indices j and k but approximates the constant kernel $K(j,k) = 2$ when the indices j and k become very large. This 'crossover' phenomenon is of interest for applications, since kernels featuring such a behaviour correspond to situations characterized by an aggregation phenomenology whose nature changes as the size of the clusters increases. Such situations are beyond the range of conventional scaling theory, so that an exact result in this respect is of interest [3].

A remarkable feature of our findings is the difference displayed by the behaviour at large times of the moments $M_n(t)$ in our model, relative to their counterparts in the constant kernel model; a difference which shows up, however, only in the next-to-leading terms (see (2.40*b*) and (1.12*a*), as well as (2.60) and (1.12*c*)). Analogous results had been obtained in a variant of the constant kernel case, featuring a kernel whose only dependence on the mass indices is via their parity [11]. We plan to treat this model in a subsequent paper [12], because we have obtained some results for it that go beyond those known hitherto [11].

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Appendix A

Here we prove (1.14) and (1.15). Using (1.2) one finds for $M_n(t)$, see (1.9),

$$\dot{M}_n(t) = \tfrac{1}{2} \sum_{k,l=1}^{\infty} \left[(k+l)^n - k^n - l^n\right] K(k,l) c_k c_l. \tag{A.1}$$

For the linear kernel $K(k,l) = b\,(k+l)$, this becomes, for non-negative integer values of n (to which we restrict ourselves throughout this appendix)

$$\dot{M}_0 = -bM_0M_1 = -bM_0 \tag{A.1a}$$

$$\dot{M}_n(t) = b \sum_{m=1}^{n-1} \binom{n}{m} M_{m+1} M_{n-m} \qquad (n \geqslant 2) \tag{A.1b}$$

with the initial conditions (see (1.3) and (1.9))

$$M_n(0) = 1. \tag{A.2}$$

In (A.2) we also used mass conservation, see (1.20); clearly (A.2) together with (A.4) yields (1.14*a*).

We then note that (A.1*b*) with (1.20) yields

$$\dot{M}_2 = 2bM_2 \tag{A.3}$$

and this, together with (A.3), gives (1.14*b*).

To prove (1.15) we make the ansatz

$$M_n(t) = \alpha_n \mathrm{e}^{2(n-1)bt}[1 + \mathrm{O}(\mathrm{e}^{-bt})] \qquad (n \geqslant 2). \tag{A.4}$$

As shown by (1.14*b*), this is correct for $n = 2$ (indeed, trivially, for $n = 1$ as well, see (1.20)). We now show by induction on n that it is true for all values of $n > 2$. Assume (A.4) to be true for all values of the moment index up to $n - 1$. Then (A.1*b*) yields via (1.20)

$$\dot{M}_n = bnM_n + b\mathrm{e}^{2b(n-1)t}[1 + \mathrm{O}(\mathrm{e}^{-bt})] \sum_{m=1}^{n-2} \binom{n}{m} \alpha_{m+1}\alpha_{n-m} \qquad (n \geqslant 3). \tag{A.5}$$

Define

$$\mu_n(t) = M_n(t)\,\mathrm{e}^{-bnt} \qquad (n \geqslant 3). \tag{A.6}$$

Equation (A.5) then becomes

$$\dot{\mu}_n = b\mathrm{e}^{b(n-2)\,t}[1 + \mathrm{O}(\mathrm{e}^{-bt})]\sum_{m=1}^{n-2}\binom{n}{m}\alpha_{m+1}\alpha_{n-m} \qquad (n \geqslant 3). \tag{A.7}$$

Hence

$$\mu_n(t) = \alpha_n \mathrm{e}^{b(n-2)\,t}[1 + \mathrm{O}(\mathrm{e}^{-bt})] \qquad (n \geqslant 3) \tag{A.8}$$

for large times t, where

$$(n-2)\alpha_n = \sum_{m=1}^{n-2}\binom{n}{m}\alpha_{m+1}\alpha_{n-m} \qquad (n \geqslant 3). \tag{A.9}$$

Of course, in the right-hand-side of (A.9), $\alpha_2 = 1$, see (A.4) and (1.14*b*). To complete the proof we need to show that

$$\alpha_n = (2n-3)!! \qquad (n \geqslant 2). \tag{A.10}$$

To this end, we introduce the generating function

$$F(x) = \sum_{n=2}^{\infty}\frac{\alpha_n}{n!}x^n. \tag{A.11}$$

Via (A.9), one then obtains for $F(x)$

$$x\frac{\mathrm{d}F}{\mathrm{d}x} - 2F = F\frac{\mathrm{d}F}{\mathrm{d}x} \tag{A.12}$$

with $F(0) = F'(0) = 0$, see (A.12). It is then easily verified that

$$F(x) = 1 - x - \sqrt{1-2x} \tag{A.13}$$

from which (A.10), hence (1.15), follow.

Appendix B

In this appendix we prove (2.50). Via (2.39), (2.2*a*) and (2.40), it is equivalent to

$$\phi_r(\theta) = \frac{\mathrm{e}^{-(1-q^r)\theta}}{(q;q)_{r-1}}[1 + \mathrm{o}(1)]. \tag{B.1}$$

To prove this formula, we use (2.32*a*) and obtain

$$H(\zeta,\theta) = -\frac{\sum_{r=0}^{\infty}[q^r/(q;q)_r]\mathrm{e}^{(q^r-1)\theta}\mathrm{e}^{br\zeta}}{1 + \sum_{r=1}^{\infty}[\mathrm{e}^{(q^r-1)\theta}/(q;q)_r]\mathrm{e}^{br\zeta}}. \tag{B.2}$$

The right-hand side of (B.2) can be expanded to yield

$$H(\zeta,\theta) = -\sum_{r_0=0}^{\infty}\frac{q^{r_0}}{(q;q)_{r_0}}\mathrm{e}^{(q^{r_0}-1)\theta}\mathrm{e}^{br_0\zeta}\sum_{N=0}^{\infty}(-1)^N\left[\sum_{s=1}^{\infty}\frac{1}{(q;q)_s}\mathrm{e}^{(q^s-1)\theta}\mathrm{e}^{bs\zeta}\right]^N. \tag{B.3}$$

In this expression, we collect all terms contributing to the factor multiplying $\mathrm{e}^{br\zeta}$, with r a non-negative integer, and single out those which dominate in the limit $\theta \to \infty$. Via (2.17) and

(2.15), this yields the large-time behaviour of $\phi_r(\theta)$. Up to a sign, all these terms are of the form

$$\frac{q^{r_0}}{(q;q)_{r_0}} \exp[(q^{r_0}-1)\theta] \prod_{k=1}^{N} \frac{\exp[(q^{s_k}-1)\theta]}{(q;q)_{s_k}} \tag{B.4}$$

where $r_0 \geqslant 0$ and $s_k \geqslant 1$, as implied by the limits of the r_0 and s summations in (B.3). Since the terms must combine to contribute to the coefficient of $e^{br\zeta}$ we must have

$$r_0 + \sum_{k=1}^{N} s_k = r. \tag{B.5}$$

From (B.4) one sees that the sum associated to the set of indices r_0 and s_k, with $1 \leqslant k \leqslant N$, has the following behaviour as a function of θ:

$$C(r_0, s_1, \ldots, s_N) \exp\left\{\left[q^{r_0} + \sum_{k=1}^{N} q^{s_k} - (N+1)\right]\theta\right\} \tag{B.6}$$

where $C(r_0, s_1, \ldots, s_N)$ is independent of θ.

For $0 < q < 1$

$$q^r + q^s \leqslant 1 + q^{r+s} \tag{B.7a}$$

since

$$(1-q^r)(1-q^s) \geqslant 0. \tag{B.7b}$$

If we now apply (B.7a) iteratively, we obtain (see (B.5))

$$q^{r_0} + \sum_{k=1}^{N} q^{s_k} \leqslant N + q^{r_0 + \sum_{k=0}^{N} s_k} = N + q^r. \tag{B.8}$$

From this follows, see (B.6), that, in the $\theta \to \infty$ limit, no term grows more than

$$\exp[(q^r - 1)\theta]. \tag{B.9}$$

It now remains to determine the cases in which the growth is precisely proportional to (B.9). There are only two possibilities:

(a) $r_0 = r$: in this case all s_k must be zero (see (B.5)). This implies that N is equal to zero and gives the contribution

$$-\frac{q^r}{(q;q)_r} \exp[(q^r-1)\theta]. \tag{B.10}$$

(b) $s_1 = r$. In this case N must be unity and r_0 vanishes. This yields the contribution

$$\frac{1}{(q;q)_r} \exp[(q^r-1)\theta]. \tag{B.11}$$

Summing both contributions, (B.10) and (B.11), and using (2.63), we obtain

$$\phi_r(\theta) = \frac{\exp[(q^r-1)\theta]}{(q;q)_{r-1}} \tag{B.12}$$

and this concludes our proof, see (B.1).

Appendix C

In this appendix we prove (2.59), namely

$$M_n(t) - M_n^{(0)}(t) = -n!\frac{n-1}{2}[1 - Q(q)]t^{n-2} + \mathrm{O}(t^{n-3+q}) \qquad (n \geqslant 2) \tag{C.1}$$

where n is an integer and $Q(q)$ is defined by (2.34*c*). $M_n(t)$, respectively, $M_n^{(0)}(t)$ are the nth moments, see (1.9), in our model, respectively, in the constant kernel case (see (1.10) and (1.12)).

We first establish the following fact. Consider the sum

$$N_{m,p}(\theta) = \sum_{j=1}^{\infty} j^m \phi_j(\theta)\,\mathrm{e}^{-bpj} \tag{C.2}$$

where m is a non-negative integer, $p > 0$ is a positive number and the quantities $\phi_j(\theta)$ are defined by (2.2) for our model. Then we claim that, as $t \to \infty$,

$$N_{m,p}(\theta) = \mathrm{O}[t^{-(1-q)}]. \tag{C.3}$$

(Note that here we use a mixed notation, see (2.39)). To show this, we first note that our treatment, see (2.15) and (2.17), implies that

$$N_{m,p}(\theta) = b^{-m}\frac{\partial^m}{\partial\zeta^m}[H(\zeta,\theta)+1]\bigg|_{\zeta=-p}. \tag{C.4}$$

However, it follows from the expression (2.33) of $S(\zeta,\theta)$ and from (2.32*c*) that $H(\zeta,\theta)$ has no singularities to the left of $\mathrm{Re}\,\zeta = 0$. We can therefore write

$$N_{m,p}(\theta) = \frac{m!\,b^{-m}}{2\pi\mathrm{i}}\int_{C_p}\frac{H(\zeta,\theta)+1}{(\zeta+p)^{m+1}} \tag{C.5}$$

where C_p is a contour enclosing $-p$ and keeping always to the left of $\mathrm{Re}\,\zeta = 0$. Let us choose it to be a circle of radius $p/2$, for definiteness' sake. It then follows from (C.5) that the positive quantity $N_{m,p}(\theta)$, see (C.2), satisfies the inequality:

$$N_{m,p}(\theta) \leqslant \frac{2^{m+1}b^{-m}m!}{p^m}\max_{C_p}|H(\zeta,\theta)+1|. \tag{C.6}$$

Let us now use the expression (2.32*a*) of $H(\zeta,\theta)$:

$$H(\zeta,\theta)+1 = \frac{\sum_{r=0}^{\infty}\mathrm{e}^{\theta q^r}q^{-r\zeta}(1-q^r)/(q;q)_r}{\sum_{r=0}^{\infty}\mathrm{e}^{\theta q^r}q^{-r\zeta}/(q;q)_r}. \tag{C.7}$$

Via (C.7) and (C.6) we then obtain as $\theta \to \infty$

$$N_{m,p}(\theta) \leqslant \frac{2^{m+1}b^{-m}m!}{p^m}\max_{C_p}\left[\mathrm{e}^{-(1-q)\theta}q^{-\zeta}\right]. \tag{C.8}$$

From (C.8) and (2.39) one therefore sees that

$$N_{m,p}(\theta) = \mathrm{O}[t^{-(1-q)}]. \tag{C.9}$$

The preliminary result (C.3) is therefore proven.

Using the Smoluchowski equations (1.2) and the definition (1.9), we write (again see (A.1)) the evolution equations for the moments $M_n(t)$:

$$\dot{M}_n = \tfrac{1}{2}\sum_{k,l=1}^{\infty} K(k,l)c_k c_l\big[(k+l)^n - k^n - l^n\big] \tag{C.10a}$$

$$\dot{M}_n = \tfrac{1}{2}\sum_{m=1}^{n-1}\binom{n}{m}\sum_{k,l=1}^{\infty} k^m l^{n-m} K(k,l)c_k c_l. \tag{C.10b}$$

Let us now define

$$\tilde{M}_n(t) = \sum_{j=1}^{\infty} j^n c_j(t)\,\mathrm{e}^{-bj} \tag{C.11a}$$

entailing, via (C.2) and (2.2*a*),

$$\tilde{M}_n(t) = M_0(t)\,N_{n,1}(t). \tag{C.11b}$$

To estimate the order of magnitude of $\tilde{M}_n(t)$, we use (C.3) and (2.40*b*), getting thereby

$$\tilde{M}_n(t) = \mathrm{O}(t^{-2+q}). \tag{C.12}$$

Thus the order of magnitude of $\tilde{M}_n(t)$ is independent of n. This is not surprising, since it only depends on small values of j, thanks to the exponential cut-off function (last term in the right-hand-side of (C.11*a*)).

From (C.10*b*) and the definition (1.17*a*) of our kernel one obtains

$$\dot{M}_n = \sum_{m=1}^{n-1}\binom{n}{m}(M_m - \tilde{M}_m)M_{n-m}. \tag{C.13}$$

We already know that

$$M_1(t) = 1 = \mathrm{O}(1) \tag{C.14}$$

for large t, see (1.5). Let us assume

$$M_k(t) = \mathrm{O}(t^{k-1}) \tag{C.15}$$

for $1 \leqslant k < n$. It then readily follows (from (C.13), (C.15) and (C.12)) that

$$M_n(t) = \mathrm{O}(t^{n-1}). \tag{C.16}$$

a result which is therefore proven by induction, for all non-negative integer values of n.

In the case of the constant kernel it is easily seen that the moments (see (1.10*c*))

$$M_n^{(0)}(t) = \sum_{m=0}^{n}\mathcal{S}_n^{(m)} m!\,t^{m-1} \qquad (n \geqslant 1) \tag{C.17}$$

satisfy the set of ODEs

$$\dot{M}_n^{(0)} = \sum_{m=1}^{n-1}\binom{n}{m}M_m^{(0)}M_{n-m}^{(0)} \qquad (n \geqslant 1) \tag{C.18}$$

which are the analogous equations to (C.10*b*) for the case of the constant kernel.

We now define

$$\mu_n(t) = M_n(t) - M_n^{(0)}(t) \qquad (n \geqslant 1). \tag{C.19}$$

Note that (1.20), which holds for all models, entails

$$\mu_1(t) = 0. \tag{C.20}$$

Using (C.19), (C.13) and (C.18) we find

$$\dot{\mu}_n = \sum_{m=1}^{n-1} \binom{n}{m} \left[-M_m \tilde{M}_{n-m} + 2\mu_m M_{n-m} - \mu_m \mu_{n-m} \right] \tag{C.21a}$$

with the initial condition (see (C.19), and recall that (A.3) holds for all models with monodisperse initial conditions, see (1.9) and (1.3)),

$$\mu_n(0) = 0. \tag{C.21b}$$

Let us now determine the order of magnitude of $\mu_n(t)$ for large t. From (C.19), (2.58) and (1.10b) follows that

$$\mu_2(t) = Q(q) - 1 + \mathrm{O}\left(t^{-1+q}\right). \tag{C.22}$$

We now make the ansatz

$$\mu_m(t) = d_m t^{m-2} + \mathrm{O}(t^{m-3+q}) \qquad (m \geqslant 2) \tag{C.23}$$

and show it to be correct by induction using (C.21a). For $m = 2$ this statement is already proven by (C.22), with

$$d_2 = Q(q) - 1 \tag{C.24}$$

and it also holds for $n = 1$ with

$$d_1 = 0 \tag{C.25}$$

see (C.20). We therefore assume that (C.23) holds for $1 \leqslant m < n$ and show that it then holds for $m = n$. Using (C.19) as well as the asymptotic behaviour of $M_n^{(0)}(t)$ given by (1.12) one finds in the right-hand side of (C.21a)

$$\begin{aligned} \dot{\mu}_n(t) = \sum_{m=1}^{n-1} \binom{n}{m} & \left\{ -m!\, t^{m-1} \tilde{M}_{n-m}(t) + 2\left[d_m t^{m-2} + \mathrm{O}(t^{m-3+q}) \right] \right. \\ & \left. \times (n-m)!\, t^{n-m-1} + \mathrm{O}(t^{n-4}) \right\} \qquad (n \geqslant 3). \end{aligned} \tag{C.26}$$

From this and the order of magnitude estimates of $\tilde{M}_n(t)$, see (C.12), it follows that

$$\dot{\mu}_n(t) = 2n!\, t^{n-3} \sum_{m=2}^{n-1} \frac{d_m}{m!} + \mathrm{O}(t^{n-4+q}) \qquad (n \geqslant 3). \tag{C.27}$$

Hence by integration (see (C.21b)),

$$(n-2)\mu_n(t) = 2n!\, t^{n-2} \sum_{m=2}^{n-1} \frac{d_m}{m!} + \mathrm{O}(t^{n-3+q}) \qquad (n \geqslant 3). \tag{C.28}$$

Equation (C.23) is thereby proven. Moreover, one obtains (from (C.23) and (C.28))

$$(n-2)d_n = 2n! \sum_{m=2}^{n-1} \frac{d_m}{m!} \qquad (n \geqslant 3) \tag{C.29}$$

entailing, as can be easily verified,

$$d_n = \frac{n!}{2}(n-1)d_2 \qquad (n \geqslant 3). \tag{C.30}$$

Via (C.24), (C.19) and (C.23), this yields (C.1). Q.E.D.

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