Scaling and crossover properties of a new solvable model of aggregation kinetics

1999 J. Phys. A: Math. Gen. 32 7719

(http://iopscience.iop.org/0305-4470/32/44/310)

J. Phys. A: Math. Gen. **32** (1999) 7719–7744. Printed in the UK PII: S0305-4470(99)05321-4

Scaling and crossover properties of a new solvable model of aggregation kinetics

F Leyvraz†
Centro Internacional de Ciencias, Cuernavaca, Morelos, Mexico

Received 21 June 1999

Abstract. In a previous paper, a new reaction kernel for the Smoluchowski equations of aggregation was solved exactly. This kernel, $K(j,k) = 2 - q^j - q^k$, for $0 < q < 1$ a real positive quantity, interpolates between two well understood exactly solved cases, namely that of $K(j,k) = 2$ and that of $K(j,k) = j+k$. This new model, however, shows a number of unexpected features, not found in either of the two limiting cases. It is shown that this model has a remarkable behaviour with respect to the commonly accepted scaling theory. On the one hand, it satisfies a rigorous form of the scaling hypothesis, but, on the other hand, it clearly violates some relations which are ordinarily assumed to follow from it. These issues are discussed, as well as the nature of the singular limit in which q is very close to one, for which our kernel becomes close to the sum kernel mentioned above. In particular, the form of the crossover between two kernels with different degrees of homogeneity can be discussed here in an exact way.

1. Introduction

In this paper I study a model for the kinetics of irreversible aggregation solved in a previous paper [1]. In this process, aggregates A_j, which are characterized by their mass j, react by sticking to one another to form a larger aggregate:

$$A_j + A_k \xrightarrow[K(j,k)]{} A_{j+k}. \tag{1.1}$$

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 [2]:

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

The prefactor $\frac{1}{2}$ is conventional, to account for double counting. Here, and always below, a superimposed dot denotes differentiation with respect to time t. These should, in general, be solved for arbitrary non-negative initial conditions $c_j(0)$. However, it is generally found

† Permanent address: Centro de Ciencias Físicas, University of Mexico, Av. Universidad s/n, Col. Chamilpa, Cuernavaca, Morelos, Mexico.

that the qualitative behaviour for arbitrary rapidly decaying solutions is similar to that of the 'monodisperse' initial condition

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

Since the technical details for general initial conditions are quite complex, I shall in general limit myself to the initial conditions (1.3).

The Smoluchowski equations (1.3) are an infinite set of coupled nonlinear ordinary differential equations (ODEs). Few cases, corresponding to specific kernels $K(k,l)$ have been solved exactly; there is, however, a well developed, albeit non-rigorous, scaling theory that deals with a fairly general class of models (see below). In a previous paper [1], the exact solution for a new reaction kernel, namely

$$K(k,l) = 2 - q^k - q^l = 2 - \mathrm{e}^{-bk} - \mathrm{e}^{-bl} \tag{1.4a}$$

was developed, where q is a real number, $0 < q < 1$, and

$$q = \mathrm{e}^{-b} \tag{1.4b}$$

where q and b will be used interchangeably in the following. In this paper, I shall pursue two goals. First, I wish to show how the well understood scaling theory applies to this model, for large times and large aggregate sizes. Secondly, I show how, when b is close to zero, a large range of times develops, for which the dynamics of (1.2) is described by that of the linear sum kernel $K(k,l) = b(k+l)$.

This paper is organized as follows. In section 2, some of the well known facts about the Smoluchowski equations (1.2) for general kernels are reviewed. In particular, the scaling theory is described, which generally gives a satisfactory qualitative description of the behaviour of the solution of (1.2) for large times and large aggregate sizes. I discuss in particular detail the applicability of scaling theory for aggregates of fixed size at large times, since it is shown later that our model shows unexpected behaviour in this respect. In section 3, the solution found in [1] is displayed for the sake of easier reference. In section 4, it is shown that a rigorous statement of the scaling hypothesis holds in our model. In section 5, I discuss how this can be reconciled with apparently anomalous behaviour for the $c_j(t)$ at fixed j and large t. In section 6 the crossover behaviour in the limiting case in which b tends to zero is studied. In section 7 I present conclusions and open problems.

2. Scaling

In this section I give a brief overview of standard scaling theory. This sets out to describe the large-time behaviour of the functions $c_j(t)$, in particular for large values of j. First, let us make some obvious qualitative remarks:

- 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 (1.2) proceeds, while the concentration $c_j(t)$ of each specific species of mass j decreases eventually towards zero,

$$\lim_{t\to\infty} [c_j(t)] = 0. \tag{2.1}$$

- The total mass of the aggregates is conserved,

$$\sum_{j=1}^{\infty} j c_j(t) = \sum_{j=1}^{\infty} j c_j(0) = 1 \tag{2.2}$$

where the last equality can always be attained by an appropriate rescaling of the $c_j(t)$ together with a corresponding time rescaling.

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 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 and which is not accounted for in the sum (2.2) [3, 4]. This phenomenon is known as *gelation*. I 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:

$$c_j(t) \approx j^{-2}\Phi[j/s(t)] \tag{2.3}$$

where the function $\Phi(x)$ is a 'scaling function' which vanishes quickly (indeed exponentially [5]) as $x \to \infty$. This is known as the *scaling ansatz* for Smoluchowski's equations and it was studied in detail in [5, 6] among others. The prefactor j^{-2} is motivated by the property (2.2) of mass conservation, as we shall see below. Note that I do not specify in (2.3) how the approximate equality is to be interpreted. I shall return to this issue later.

The initial observation, borne out by experimental work, simulations and exact results, is the existence of a certain number of exponents [7] describing the behaviour of the concentrations $c_j(t)$ for large times. Let us first define them. For arbitrary ρ the moments $M_\rho(t)$ behave as follows:

$$M_\rho(t) \equiv \sum_{j=1}^{\infty} j^\rho c_j(t) = A_\rho t^{\delta_\rho}[1 + \mathrm{o}(1)] \qquad (t \to \infty). \tag{2.4}$$

Note that mass conservation fixes δ_1 to be zero. Furthermore, for j fixed,

$$c_j(t) = B_j t^{-w_j}[1 + \mathrm{o}(1)] \qquad (t \to \infty) \tag{2.5}$$

whereas for j large at large fixed times

$$c_j = C(t)j^{-\tau}[1 + \mathrm{o}(1)]. \tag{2.6}$$

This last statement holds over the range of those values of j which are large compared to one but small compared to the size $s(t)$ of the typical aggregate at time t, $1 \ll j \ll s(t)$. If t is large enough, this range of j can be made arbitrarily large, since $s(t)$ diverges as $t \to \infty$, so that the exponent τ is indeed usually well defined, though we will see instances in the following, in which many different behaviours can be observed in the range $1 \ll j \ll s(t)$. In these cases, the definition (2.6) becomes ambiguous or inappropriate. Indeed, one might say that the existence of a well defined exponent τ is yet another of these regularities which have been consistently observed experimentally, numerically and in exactly solved models.

Between these exponents, there exist the following relations, generally called 'scaling laws' because they can be justified, to some extent, on the basis of the scaling ansatz (2.3), as will appear more clearly below. First, for all j,

$$w_j = w \tag{2.7a}$$

$$w = (2 - \tau)\,\delta_2 \tag{2.7b}$$

where w denotes the common value of all exponents w_j. Furthermore,

$$\delta_\rho = (\rho - 1)\,\delta_2 \qquad \text{if} \quad \rho \geqslant \tau - 1 \tag{2.8a}$$

$$\delta_\rho = -w. \qquad \text{if} \quad \rho \leqslant \tau - 1. \tag{2.8b}$$

Note that relation (2.8*a*) is consistent with mass conservation (that is, $\delta_1 = 0$), whereas (2.8*b*) is incompatible with it, unless $w = 0$, which cannot hold in any model in which the typical size grows without limit, so that each individual concentration tends to zero as $t \to \infty$, see (2.5) and (2.7*a*). Thus one concludes that

$$\tau \leqslant 2 \tag{2.9}$$

so that for $\rho = 1$, equation (2.8*a*) holds, rather than (2.8*b*).

The above relations hold in many cases, both empirical (namely related to experiments) and numerical (based on the numerical solution of specific models), as well as in some solved models [5, 6], though counterexamples are also known [8]. Thus, for the constant kernel,

$$K(k, l) = 2 \tag{2.10}$$

one finds for the monodisperse initial condition (1.3)

$$c_j(t) = \frac{1}{(t+1)^2}\left(\frac{t}{t+1}\right)^{j-1} = j^{-2}\Phi[j/(t+1)][1 + \mathrm{O}(j/t^2)] \tag{2.11}$$

for $t \to \infty$, where

$$\Phi(x) = x^2 \mathrm{e}^{-x}. \tag{2.12}$$

For arbitrary initial conditions with all moments finite, it is not possible to make such a sharp statement, and one has instead (see appendix A),

$$c_j(t) = j^{-2}(j/t)^2 \exp(-j/t)[1 + \mathrm{O}(j/t^2) + \rho_j] \tag{2.13a}$$

when t becomes large, where

$$\rho_j = \mathrm{O}(a^j) \qquad (a < 1) \tag{2.13b}$$

for $j \to \infty$ under an additional technical assumption stated precisely in appendix A to prevent such initial conditions as $c_j(0) = \delta_{j,2}/2$, which lead to $c_{2j+1}(t) = 0$ for all t and all j, in contradiction to (2.13*a*) and (2.13*b*). From these results or otherwise, it is easy to obtain

$$M_\rho(t) = \Gamma(\rho + 1)t^{\rho-1}[1 + \mathrm{o}(1)] \qquad (\rho > -1). \tag{2.14}$$

From this follows

$$\delta_\rho = \rho - 1 \qquad (\rho > -1). \tag{2.15}$$

From (2.12) and (2.13) one then obtains

$$\tau = 0. \tag{2.16}$$

On the other hand, from (2.13) again, one finds

$$w_j = w = 2 \tag{2.17}$$

for all j. In this example, one therefore sees that all scaling laws are satisfied and the approximate equality (2.3) is satisfied in the strict form (2.13).

The scaling theory of aggregation, which is used to justify the above findings, starts from the following rigorous observations: consider a kernel $K(\sigma, \sigma')$ of homogeneity degree λ, that is, such that

$$K(a\sigma, a\sigma') = a^{\lambda} K(\sigma, \sigma') \tag{2.18}$$

for arbitrary real positive values of $a > 0$. Further consider the continuous equations

$$\begin{aligned}\dot{c}(\sigma, t) = \tfrac{1}{2} \int_0^\infty \mathrm{d}\sigma' \int_0^\infty \mathrm{d}\sigma'' \, K(\sigma', \sigma'') \, c(\sigma', t) \, c(\sigma'', t) \\ \times [\delta(\sigma' + \sigma'' - \sigma) - \delta(\sigma' - \sigma) - \delta(\sigma'' - \sigma)]\end{aligned} \tag{2.19}$$

which reduce to (1.2) if the initial condition is given by

$$c(\sigma, 0) = \sum_{k=1}^{\infty} c_k(0) \, \delta(\sigma - k). \tag{2.20}$$

One now observes that (2.19) is invariant under the action of the following one-parameter group of transformations:

$$(S_\gamma c)(\sigma, t) = \gamma^2 c(\sigma/\gamma, t/\gamma^{1-\lambda}) \tag{2.21}$$

with $\gamma > 0$ a positive real number. Note that this action conserves the total mass

$$\int_0^\infty \sigma c(\sigma, t) \, \mathrm{d}\sigma \tag{2.22}$$

as well, if the latter is finite. One now looks for solutions that are invariant under the action of S_γ. It is clear that such are given by

$$c(\sigma, t) = \sigma^{-2} \Phi\big[\sigma/[(1-\lambda)t]^{1/(1-\lambda)}\big] \tag{2.23}$$

where $\Phi(x)$ is an arbitrary function and the time scale has been set in such a way as to simplify the integral equation below, see (2.24). Putting this ansatz into (2.19), one obtains after some non-trivial manipulations [5]

$$\Phi(x) = \int_0^x \frac{\mathrm{d}y}{y} \int_{x-y}^\infty \frac{\mathrm{d}z}{z^2} K(y, z) \, \Phi(y) \, \Phi(z). \tag{2.24}$$

If this equation has solutions, then it is seen [5] that these lead to a scaling solution of (2.19). I am not aware of any rigorous results on the existence and uniqueness theory of this equation, but a considerable body of work exists, which examines the behaviour of $\Phi(x)$ under the hypothesis that it exists [5, 9].

To arrive at precise statements, one requires the knowledge of another exponent, namely μ, which is defined by

$$\lim_{\sigma \to 0} \frac{K(1, \sigma)}{\sigma^\mu} = C > 0. \tag{2.25}$$

In this case, it has been shown that, for $0 < \mu$ and $\lambda < 1$ the function $\Phi(x)$ behaves as

$$\Phi(x) = C x^{-2+\tau'} [1 + \mathrm{o}(1)] \qquad (x \to 0) \tag{2.26}$$

where

$$\tau' = 1 + \lambda. \tag{2.27}$$

For $\mu = 0$ no general results are available, whereas for $\mu < 0$ the function $\Phi(x)$ approaches zero faster than any power as $x \to 0$.

So far, the theory described could presumably be made rigorous. However, the description of one single solution of (2.19) is not of much use. The power of scaling theory arises from a number of other assumptions, the status of which is far more difficult to assess.

First, it is assumed that any rapidly decaying initial condition of the system (2.19), say with all moments finite, will, for large times, evolve into a scaling solution, at least for large values of σ. It is unclear how to prove this, or even under what assumptions it is true. Equally, it is not obvious in which form convergence should take place. For simple systems, such as the constant kernel, we have seen that (see (2.13)) the difference between the scaling form and the exact solution can be bounded quite explicitly, in a way that allows control of this difference, even when j is fixed instead of being large. For more general systems, however, no such estimates are known.

Furthermore, scaling theory states that the scaling function only depends on such coarse features as λ and μ, when these are taken to refer only to some asymptotic behaviour of the kernel $K(\sigma, \sigma')$ for large values of σ and σ'. For scaling theory to be of any practical use such statements are very important, since no realistic kernel is exactly homogeneous. However, such claims have received no confirmation from exact solutions and at best little from numerical work. In this respect, our kernel lends itself to analysis and I shall show in section 4 that the following sharp form of convergence towards a scaling form can be proved: one defines $t_j(x)$, from an assumed given positive, increasing function of t, $s(t)$, which we shall call the 'typical size' of the aggregates, through the implicit equation

$$j/s[t_j(x)] = x. \tag{2.28}$$

The meaning of the time $t_j(x)$ is the following: let x be an arbitrary number (of the order of one). Then, at some time t, j will be equal to $xs(t)$, that is, the size j under consideration will be precisely a fraction x of the typical size. The time $t_j(x)$ is therefore precisely this time as a function of j and x. From this it follows that (2.3) can be rewritten as

$$\lim_{j\to\infty} \left\{ j^2 c_j[t_j(x)] \right\} = \Phi(x). \tag{2.29}$$

This is exactly the result I shall prove in the next section concerning the kernel (1.4). It will be seen that for this kernel one can choose

$$s(t) = t \tag{2.30}$$

and the scaling function $\Phi(x)$ on the right-hand side of (2.30) turns out to be exactly the same as for the constant kernel, thus partially vindicating the usual claims of universality.

We now proceed to discuss the way in which the scaling assumption can be used to explain, at least partially, the results stated at the beginning of this section. Define, again following current usage, the exponent z as follows:

$$s(t) = Dt^z[1 + \mathrm{o}(1)] \qquad (t \to \infty). \tag{2.31}$$

From the above remarks, it follows that

$$z = \frac{1}{1 - \lambda}. \tag{2.32}$$

Note first that if the convergence to the scaling solution is so strong that $c_j(t)$ for finite values of j is well described by $j^{-2}\Phi[j/s(t)]$, then it follows that

$$\tau = \tau'. \tag{2.33}$$

Under this hypothesis, let us now evaluate $M_\rho(t)$ as follows (again via (2.3):

$$M_\rho(t) \approx \sum_{j=1}^{\infty} j^{\rho-2}\Phi[j/s(t)]$$
$$= s(t)^{\rho-2}\sum_{j=1}^{\infty}\left(\frac{j}{s(t)}\right)^{\rho-2}\Phi[j/s(t)] \approx s(t)^{\rho-1}\int_0^{\infty} x^{\rho-2}\Phi(x)\,\mathrm{d}x \qquad (2.34)$$

provided the final integral is convergent at $x = 0$, convergence at infinity being guaranteed by the fact [4, 9] that $\Phi(x)$ is exponentially decaying as $x \to \infty$. This corresponds, using (2.33), to the inequality

$$\rho > \tau - 1 \qquad (2.35)$$

consistently with (2.8*a*). Moreover, (2.34), via (2.31) and (2.4), entails

$$\delta_\rho = (\rho - 1)z \qquad (2.36)$$

and hence in particular

$$\delta_2 = z \qquad (2.37)$$

so that z and δ_2 can be identified.

Clearly, the above derivations lack rigour. However, confidence in their validity is widespread, being upheld by the observation that both the amplitude and the exponents in the leading large-time behaviour of the moments are given correctly by (2.34) in both exactly solved models with constant and linear sum kernels.

It is, however, easy to exhibit a simple counterexample to the above treatment. Let us consider the following expression for the concentrations:

$$c_j(t) = t^{-2}\left(\frac{t}{t+1}\right)^j + \frac{2^{-j}}{t}. \qquad (2.38)$$

This distribution does not correspond to any known specific model, though it is inspired from an exact solution (see [8]). It satisfies the scaling ansatz (2.3) with

$$s(t) = t \qquad \Phi(x) = x^2\mathrm{e}^{-x} \qquad (2.39)$$

as is rigorously established using (2.29). On the other hand, it is clear from (2.6), (2.31) and (2.5) that in this case

$$\tau' = 0 \qquad z = 1 \qquad (2.40)$$

but

$$w = 1. \qquad (2.41)$$

Hence (2.7*b*) is inconsistent with (2.40) and (2.41). Moreover, it is easily seen that (2.38) via (2.4) yields

$$\delta_\rho = -1 \qquad (-1 < \rho < 0) \qquad (2.42)$$

in violation of the 'scaling law' (2.7*b*). Again, at fixed j and for large times, the range $1 \ll j \ll t$ has a subrange $1 \ll j \ll \ln t$, in which $c_j(t)$ decays exponentially in j, in contradistinction to the constant behaviour predicted from the fact that $\tau' = 0$. Thus we have an instance in which the definition of τ given in (2.6) is inappropriate.

To understand what is going wrong, we look in more detail at this example. The problem occurs on substituting the first terms in the sum in (2.34) by the scaling expression. It is generally not allowed to substitute, say, $c_1(t)$ by $\Phi[1/s(t)]$. The error committed when this is done cannot be controlled, as the above example shows. It is not, of course, necessary that the neglected term fall off exponentially in j, but it is remarkable that even such a rapidly vanishing term (as $j \to \infty$) is sufficient to cause the scaling laws to fail.

It is thus seen that the scaling ansatz may motivate or suggest the scaling laws, but cannot prove them. A separate issue is whether the scaling assumption holds at all for large times and large j. In the artificial model shown above it clearly does. In our model, I shall show in section 4 that scaling in the sense of (2.29) with (2.28) does hold, whereas we shall see in section 5 that the 'scaling laws' do not.

In conclusion, therefore, let us emphasize that, contrary to a widespread belief, the so-called 'scaling laws' do not follow from the scaling ansatz, at least not when scaling is interpreted in its usual sense, see above, and the exponents are also defined as above. This is an important issue, since data analysis both in experimental and numerical work generally proceeds along the lines sketched at the beginning of this section.

3. Summary of the solution

In this section I display the solution, described in [1], of the evolution equations (1.2) with the initial conditions (1.3). This section is merely for ease of reference: no derivations of the formulae presented are included and for these the interested reader is referred to [1]. The following well known transformation [3] is performed. Define

$$\phi_j(\theta) = \frac{c_j(t)}{\sum_{k=1}^{\infty} c_k(t)} = \frac{c_j(t)}{M_0(t)} \tag{3.1a}$$

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

$$\mathrm{d}\theta = \mathrm{d}t \sum_{k=1}^{\infty} c_k(t) = \mathrm{d}t\, M_0(t). \tag{3.1b}$$

This change of variable can be explicitly inverted, as shown in [1], but we shall not need this in the following.

One then finds the following recursion, which in principle yields exact expressions for $\phi_j(\theta)$,

$$\phi_j(\theta) = \exp[-(1-q^j)\theta] \sum_{k=1}^{j-1} \left[(1-q^k) \int_0^{\theta} \mathrm{d}\theta'\, \phi_k(\theta')\, \phi_{j-k}(\theta')\, \mathrm{e}^{(1-q^j)\theta'} \right]. \tag{3.2}$$

However, these expressions quickly become unwieldy and do not yield an understanding of the solution.

One now defines the following generating function:

$$H(\zeta, \theta) = \sum_{j=1}^{\infty} \phi_j(\theta)\, \mathrm{e}^{bj\zeta} - 1. \tag{3.3}$$

The solution, as given in [1], consists of an explicit expression for $H(\zeta, \theta)$. Before we go any further, however, note that (3.3) entails for j a non-zero positive integer the formula

$$\phi_j(\theta) = \frac{b^{-j}}{j!} \left(\mathrm{e}^{-b\zeta} \frac{\partial}{\partial \zeta} \right)^j H(\zeta, \theta) \bigg|_{\zeta=-\infty} \tag{3.4a}$$

thus allowing the evaluation of all $c_j(t)$ once $H(\zeta, \theta)$ is known.

To present the solution, we need the definition of the q-exponential†,

$$e_q(x) = \prod_{l=0}^{\infty}(1 - q^l x)^{-1} \tag{3.5a}$$

$$e_q(x) = \sum_{r=0}^{\infty} \frac{x^r}{(q;q)_r} \tag{3.5b}$$

where $(a;q)_n$ is the q-factorial

$$(a;q)_n = \prod_{l=0}^{n-1}(1 - aq^l). \tag{3.6}$$

The equivalence of the two expressions for $e_q(x)$, (3.5*a*) and (3.5*b*), is a well known identity [10]. It is then found that [1]

$$H(\zeta,\theta) = -\frac{\partial}{\partial\theta} \ln \sum_{r=0}^{\infty} \frac{q^{-r\zeta}\exp(\theta q^r)}{(q;q)_r} \tag{3.7a}$$

$$H(\zeta,\theta) = -\frac{\partial}{\partial\theta} \ln\left\{\sum_{r=0}^{\infty} \frac{q^{-r\zeta}}{(q;q)_r}[\exp(\theta q^r) - 1] + e_q(q^{-\zeta})\right\} \tag{3.7b}$$

$$H(\zeta,\theta) = -\frac{\partial}{\partial\theta} \ln[1 + S(\zeta,\theta)] \tag{3.7c}$$

$$S(\zeta,\theta) = \frac{1}{e_q(q^{-\zeta})} \sum_{r=0}^{\infty} \frac{q^{-r\zeta}}{(q;q)_r}[\exp(\theta q^r) - 1]. \tag{3.7d}$$

Let us now, for notational convenience, introduce the quantity $T(q)$:

$$T(q) = -\frac{1}{b}\frac{\partial}{\partial\zeta} e_q(q^{-\zeta})\bigg|_{\zeta=0} = 1/e_q(q). \tag{3.8}$$

Note that this definition entails that $T(0) = 1$ and $1 < T(q) < \infty$ for $0 < q < 1$. To obtain a full solution, the connection between θ and the time t is required. This is given by (see [1])

$$t = T(q)\sum_{r=0}^{\infty} \frac{\exp(\theta q^r) - 1}{(q;q)_r} = T(q)\left[\exp\theta - 1 + \sum_{r=1}^{\infty} \frac{\exp(\theta q^r) - 1}{(q;q)_r}\right] \tag{3.9}$$

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

For the zeroth moment $M_0(t)$, one obtains exactly

$$M_0(t) = \sum_{k=1}^{\infty} c_k(t) = \left[T(q)\sum_{r=0}^{\infty} \frac{q^r \exp(\theta q^r)}{(q;q)_r}\right]^{-1}. \tag{3.10}$$

This formula, together with (3.9), provides an exact, if implicit, expression for $M_0(t)$. For large θ, (3.9) yields $t = T(q)\,\mathrm{e}^{\theta}[1 + \mathrm{o}(1)]$. Note that these results imply that θ goes to infinity when t does. Thus the above manipulations are indeed consistent. Hence, at large times (3.10) yields

$$M_0(t) = \sum_{k=1}^{\infty} c_k(t) = t^{-1}[1 + \mathrm{o}(1)]. \tag{3.11}$$

† see, for example, the chapter on the q-binomial theorem in [10].

Concerning the large-time behaviour of $c_j(t)$ at fixed j, it is shown in [1] that at large times,

$$c_j(t) = \frac{[t/T(q)]^{-(2-q^j)}}{T(q)(q;q)_{j-1}}[1 + \mathrm{o}(1)]. \tag{3.12}$$

As pointed out before, the moments can be computed explicitly from a knowledge of $H(\zeta,\theta)$. In particular, the expression for $M_2(t)$ is found to be, in mixed but useful notation, see (3.9),

$$M_2(t) = 2t + Q(q) + \frac{2\sum_{r=1}^{\infty} r q^r \mathrm{e}^{\theta q^r}/(q;q)_r}{\sum_{r=0}^{\infty} q^r \mathrm{e}^{\theta q^r}/(q;q)_r} \tag{3.13a}$$

$$Q(q) = 1 - 2\sum_{l=1}^{\infty} \frac{q^l}{1-q^l}. \tag{3.13b}$$

One therefore finds for large times, via (3.11),

$$M_2(t) = [2t + Q(q)][1 + \mathrm{O}(t^{-2+q})] = 2t + Q(q) + \mathrm{O}(t^{-1+q}). \tag{3.14}$$

It is further shown in [1] that a similar behaviour holds for all n at large times, namely,

$$M_n(t) = n!\,t^{n-1}\left[1 + \tfrac{1}{2}(n-1)Q(q)t^{-1} + \mathrm{O}(t^{-2+q})\right]. \tag{3.15}$$

Note finally that an expression similar to (3.13) can also be derived for the inverse of the zeroth moment, namely

$$M_0(t)^{-1} = t + 1 - T(q)\sum_{r=1}^{\infty} \frac{\exp(\theta q^r) - 1}{(q;q)_{r-1}}. \tag{3.16}$$

4. The solution in the scaling limit

To compute the scaling limit means to see how the functions $c_j(t)$ behave in the limit (2.29). Various results already obtained (such as the fact that the second moment behaves asymptotically as t, see (3.14), as well as the generalization to arbitrary moments, see (3.15)) suggest that the typical size $s(t)$ grow as t. We therefore define according to (2.28)

$$t_j(x) = j/x. \tag{4.1}$$

The scaling limit (2.29) then translates, using (3.1*a*) and (3.11) into the following statement for $\phi_j(t)$ (note that I deviate here from my convention of showing $\phi_j(\theta)$ as a function of θ. This is because the quotient j/t is important and does not translate into a simple expression in terms of θ)

$$\lim_{j\to\infty}\left[j\phi_j(j/x)\right] = \lim_{j\to\infty}\left[jc_j(j/x)/M_0(j/x)\right] = \Phi(x)/x \tag{4.2}$$

where the large-time expression for $M_0(t)$ given by (3.11) has been used. In the following, I will show that this formula holds, with the function $\Phi(x)$ appropriate to the constant kernel case, see (2.13).

To show this I use the following expression for $\phi_j(\theta)$.

$$\phi_j(\theta) = \frac{b}{2\pi\mathrm{i}}\int_{-\pi\mathrm{i}/b}^{\pi\mathrm{i}/b} H(\zeta,\theta)\,\mathrm{e}^{-bj\zeta}\,\mathrm{d}\zeta \tag{4.3}$$

as entailed by (3.3). This is Cauchy's integral formula applied to an exponential series, or it can be viewed as a Fourier integral, since $H(\zeta,\theta)$ is periodic in ζ with period $2\pi\mathrm{i}/b$. I shall use the following strategy. First, I show that the integrand has only one singularity in ζ near the imaginary axis on the strip $|\mathrm{Re}\,\zeta| < \pi/b$. This will allow one to move the contour to the right. One then picks up the contribution from the singularity, which yields the desired result, and shows that the shifted integral goes to zero in the limit (4.2).

I shall often use the general identity

$$\frac{1}{e_q(q^\zeta)}\sum_{r=0}\frac{q^{r\zeta}f(q^r)}{(q;q)_r}=\sum_{m=0}^{\infty}\frac{f^{(m)}(0)}{m!}(q^\zeta;q)_m \tag{4.4}$$

valid for an arbitrary function $f(z)$ analytic inside a circle with centre $z=0$ and radius larger than one. This is shown in appendix B. From it one obtains, in particular, the following expression for $S(\zeta,\theta)$:

$$S(\zeta,\theta)=\sum_{m=1}^{\infty}\frac{\theta^m}{m!}(q^{-\zeta};q)_m. \tag{4.5}$$

This shows that $S(\zeta,\theta)$ is analytic throughout the whole ζ-plane, since the sum in (4.5) is convergent for all ζ. To identify the singularities in ζ of $H(\zeta,\theta)$ one therefore need only consider the location of the zeros of

$$R(\zeta,\theta)=1+S(\zeta,\theta) \tag{4.6}$$

under the hypothesis that θ is large, since this asymptotic behaviour is the one of interest.

In appendix C, I show that $R(\zeta,\theta)$ has only one set of zeros, $\zeta_s(t)+\mathrm{i}k\pi/b$ for all integer values of k, which approaches the imaginary axis as $t\to\infty$. Since the integral in (4.3) only involves the strip $|\mathrm{Im}\,\zeta| < \pi/b$, only the (real) value $\zeta_s(t)$ is relevant. In appendix C, I show that this zero satisfies the inequality

$$|\zeta_s(t)-(bt)^{-1}|=\mathrm{O}(t^{-2}\ln t). \tag{4.7}$$

Furthermore, as stated above, $\zeta_s(t)$ is the *only* zero with this property, that is, there exists a (time-independent) constant K such that there are no zeros beyond the ones just mentioned in the strip $0\leqslant \mathrm{Re}\,\zeta < K$. This allows one to move the path of integration in the exact expression (4.3) of $\phi_j(\theta)$ to the right by K. One therefore has, from (4.3)

$$\begin{aligned}\phi_j(\theta)&=-b\operatorname*{Res}_{\zeta=\zeta_s(t)}H(\zeta,\theta)\,\mathrm{e}^{-bj\zeta}+\frac{b}{2\pi\mathrm{i}}\int_{K-\pi\mathrm{i}/b}^{K+\pi\mathrm{i}/b}H(\zeta,\theta)\,\mathrm{e}^{-bj\zeta}\,\mathrm{d}\zeta\\&=-b\operatorname*{Res}_{\zeta=\zeta_s(t)}H(\zeta,\theta)\,\mathrm{e}^{-bj\zeta}+\mathrm{O}[\exp(-bKj)]\end{aligned} \tag{4.8}$$

for j large. We shall see below that the residue gives the correct result in the scaling limit, so we would like to show that the remaining integral term disappears in this limit. From (4.8) it follows that the integral decays exponentially in *j at fixed time*. One therefore needs to estimate the growth of $H(\zeta,\theta)$ uniformly on the interval of integration in (4.8) as a function of t, in order to show that the integral term indeed goes to zero when $j\to\infty$ and $j=xt$.

To this end, note first that, for large t, using (3.7*d*)

$$S(\zeta,\theta)=\frac{1}{e_q(q^{-\zeta})}\mathrm{e}^{\theta}+\mathrm{O}[\mathrm{e}^{(1-q)\theta}]. \tag{4.9}$$

From this it follows that for t sufficiently large, the value of $S(\zeta,\theta)$ is uniformly bounded away from -1 in the strip $0 \leqslant \mathrm{Re}\,\zeta < K$, so that the denominator $1+S(\zeta,\theta)$ in the expression (3.7c) for $H(\zeta,\theta)$ is of the order of one. Since one has, from (3.7c):

$$H(\zeta,\theta) = \frac{\partial S(\zeta,\theta)/\partial\theta}{1+S(\zeta,\theta)} \tag{4.10}$$

it only remains to estimate the numerator from above. One has

$$\begin{aligned} \left|\frac{\partial S(\zeta,\theta)}{\partial\theta}\right| &\leqslant \frac{1}{|e_q(q^{-\zeta})|}\sum_{r=0}^{\infty}\frac{|q^{-r(\zeta-1)}|}{(q;q)_r}\,\mathrm{e}^{\theta q^r} \\ &\leqslant K_1(\zeta)\mathrm{e}^{\theta} \end{aligned} \tag{4.11}$$

where the constant $K_1(\zeta)$ is independent of θ. From this it follows that the numerator of (4.10) grows at most linearly in t, whereas an exponential decay in j is implied by (4.8). From this it follows that in the scaling limit the integral can indeed be neglected.

It now remains to show that the contribution due to the singularity $\zeta_s(t)$ yields the expected scaling behaviour

$$-b\operatorname*{Res}_{\zeta=\zeta_s(t)} H(\zeta,\theta)\,\mathrm{e}^{-bj\zeta} = -b\,\mathrm{e}^{-bj\zeta_s(t)}\left.\frac{\partial S(\zeta,\theta)/\partial\theta}{\partial S(\zeta,\theta)/\partial\zeta}\right|_{\zeta=\zeta_s(t)}. \tag{4.12}$$

Using (3.8) one finds

$$\frac{\partial S(\zeta,\theta)}{\partial\zeta} = bT(q)\,\mathrm{e}^{\theta} + \mathrm{O}(\zeta) + \mathrm{O}[\zeta^2\exp(q\theta)]. \tag{4.13}$$

Since one evaluates (4.13) at $\zeta_s(t)$ for large t, the two last terms on the right are negligible. Similarly,

$$\frac{\partial S(\zeta,\theta)}{\partial\theta} = -bT(q)\zeta\,\mathrm{e}^{\theta} + \mathrm{O}(\zeta\,\mathrm{e}^{q\theta}) \tag{4.14}$$

so that one finally obtains

$$-b\operatorname*{Res}_{\zeta=\zeta_s(t)} H(\zeta,\theta)\,\mathrm{e}^{-bj\zeta} = b\zeta_s(t)\exp[-bj\zeta_s(t)][1+\mathrm{o}(1)] = \frac{1}{t}\mathrm{e}^{-j/t}[1+\mathrm{o}(1)] \tag{4.15}$$

in the limit of large times. From these considerations, together with the estimates (4.11) and (4.9) on the remainder term, one finds that our model scales in the same way as the constant kernel case.

5. Validity of the scaling laws

As was pointed out already in section 2, the existence of the scaling limit is *not* equivalent to the various scaling laws which are usually assumed to follow from it. As was discussed in detail in section 2, the scaling limit concerns the simultaneous limit of large aggregate sizes and large times, when the ratio $j/s(t)$ is kept fixed, where $s(t)$ denotes some suitable measure of typical size. On the other hand, many exponents which are commonly used in the analysis of numerical and experimental data refer, at least in part, to the behaviour of $c_j(t)$ at *fixed* j for large times, or at fixed $j \ll s(t)$ as t becomes large. Here I contrast the two behaviours in the case of our model defined in (1.4), since it shows the issues involved quite nicely.

In the previous section, I have shown that the scaling limit exists, that is, that

$$\lim_{j\to\infty} j^2 c_j(j/x) = x^2\mathrm{e}^{-x}. \tag{5.1}$$

From this it follows, in the notation of section 2, that

$$\tau' = 0. \tag{5.2}$$

However, at fixed j for large t, one finds from (3.12)

$$w_j = 2 - q^j. \tag{5.3}$$

Thus, the very first law concerning the w exponent is violated, since the different w_j are distinct. On the other hand, as follows from (5.1), the exponent z is equal to unity. Thus, we are led to suppose, according to (2.7) and (2.37), that

$$\tau = 0. \tag{5.4}$$

However, again, we see that a different result follows from the exact result (3.12). Indeed, for large t,

$$c_j(t) = \frac{T(q)}{t^2} \frac{\exp[q^j \ln(t/T(q)]}{(q;q)_{j-1}} \tag{5.5}$$

where the j-independent prefactor has been separated from the j-dependent part. Note now that over the range

$$1 \ll j \ll b^{-1} \ln \ln[t/T(q)] \tag{5.6}$$

$c_j(t)$ depend strongly on j, decaying faster than any power, in stark contradiction to the prediction $\tau = 0$. In fact, one sees here precisely an instance in which there exist two infinitely broad ranges of j inside the range $1 \ll j \ll s(t) = t$, for which the behaviour of $c_j(t)$ as a function of j is quite different.

Similarly, the exponents δ_ρ for the moments will not, in general be correctly given by the scaling law (2.8). Indeed, from (2.36) one obtains for our kernel (1.4*a*),

$$\begin{aligned} \delta_\rho &= \rho - 1 \qquad (\rho \geqslant -1) \\ \delta_\rho &= -2 \qquad\quad (\rho \leqslant -1). \end{aligned} \tag{5.7}$$

However, manifestly

$$M_\rho(t) \geqslant c_1(t) = \mathrm{O}(t^{-2+q}) \tag{5.8}$$

implying that for all ρ,

$$\delta_\rho \geqslant -2 + q \tag{5.9}$$

so that (5.7) cannot hold if $-1 < \rho < -1+q$. Summarizing, we find that the small aggregates definitely do not behave as suggested by the scaling limit. That is, the limit $j \to \infty, t \to \infty$ at a fixed value of $x = j/s(t)$ cannot be interchanged with the limit $x \to 0$. A similar phenomenon occurs [8] in the context of a model, in which the reaction rate $K(k,l)$ is allowed to depend on the parity of k and l. However, this case could reasonably be considered as somewhat artificial. On the other hand, the model described here is a reasonable one: it merely describes the effect of having small aggregates being slightly less reactive than others. Under these circumstances, current opinion concerning the large-time behaviour of small aggregates and its relation to true scaling exponents should presumably be reviewed.

6. The $b \to 0$ limit

In this section, I analyse the dependence of the various quantities of interest on the parameter q in the singular limit $q \to 1$. To this end it is clearly undesirable to have any 'hidden' q dependence. For this reason one redefines the generating function, see (3.3),

$$\tilde{H}(\zeta, \theta) = H(b\zeta, \theta) = H(\zeta / \ln q^{-1}, \theta) = \sum_{j=1}^{\infty} \phi_j(\theta)\, \mathrm{e}^{j\zeta} - 1. \tag{6.1}$$

With this definition, the distance of the singularities in ζ of $\tilde{H}(\zeta, \theta)$ from the imaginary axis provide information on the behaviour of $\phi_j(\theta)$ as a function of j, with no q-dependent prefactors.

Let us first quote a few results on the linear sum kernel,

$$K(k, l) = b(k + l) \tag{6.2}$$

which will be helpful in understanding the behaviour of our model. If one performs the various substitutions sketched in section 3 on the linear sum kernel (see [1] for greater details), one obtains the following: for the relation between t and θ, using the elementary relation for the moments in the kernel (6.2),

$$\dot{\mu}_0(t) = -b\mu_0(t)\mu_1(t) = -b\mu_0(t) \tag{6.3}$$

where one defines

$$\mu_n(t) = \sum_{j=1}^{\infty} j^n c_j^{(0)}(t) \tag{6.4}$$

and $c_j^{(0)}(t)$ is the solution of (1.2) with the initial condition (1.3) for the kernel (6.2). From (6.3) and (3.1b) it follows that

$$b\theta = 1 - \mathrm{e}^{-bt} \tag{6.5a}$$

yielding

$$\mathrm{d}t = \frac{\mathrm{d}\theta}{1 - b\theta}. \tag{6.5b}$$

Note that in this case, in contrast to the case of our kernel (1.4), θ saturates to $1/b$ as $t \to \infty$. Thus, the scaling limit should be viewed as the limit $b\theta \to 1$. For the linear sum kernel, there is no physically meaningful solution beyond $b\theta$ equal to unity, though the functions $\phi_j^{(0)}(\theta)$ do possess an analytic continuation valid for all θ. A well known result shows that they are given by [11]

$$\phi_j^{(0)}(\theta) = a_j (b\theta)^{j-1} \mathrm{e}^{-bj\theta} \tag{6.6}$$

where the a_j are the following combinatorial coefficients [11]:

$$a_j = \frac{j^{j-2}}{(j-1)!} = \frac{\mathrm{e}^j}{\sqrt{2\pi}} j^{-3/2}[1 + \mathrm{O}(j^{-1})]. \tag{6.7}$$

In our model, as we shall see, matters are a bit more subtle, since $\theta \to \infty$ as $t \to \infty$, no matter what the value of q. Nevertheless, the time interval such that

$$|1 - b\theta| \ll 1 \tag{6.8}$$

is significant, since it is the region over which intermediate scaling behaviour is expected. Indeed, from (6.5*b*), one sees that if our model were exactly the sum kernel, the range defined by (6.8) would simply cover all large times.

Let us then analyse the behaviour of the exact relation (3.9) connecting t and θ for θ large with respect to one but not with respect to $(1-q)^{-1}$, see (3.9). In this time range the approximate relation $t = T(q)\,\mathrm{e}^{\theta}$ given in section 3 cannot be used. Let us now set

$$\epsilon = 1 - (1-q)\theta. \tag{6.9}$$

Note that small positive ϵ correspond to the limit of large but intermediate times, for which our model, see (1.4), is expected to behave similarly to the linear sum model characterized by (6.2). In appendix D it is shown that

$$\frac{\mathrm{d}t}{\mathrm{d}\theta} = M_0(t)^{-1} = \frac{1}{1-(1-q)\theta}\left\{1 + \mathrm{O}\left[(b/\epsilon^2)\ln^3(\epsilon^2/b)\right]\right\}. \tag{6.10}$$

Therefore, it is seen that $\mathrm{d}t/\mathrm{d}\theta$ and hence the zeroth moment are close to the expression for the linear sum kernel as long as $\epsilon^2 \gg b$. As is further shown in appendix D, one has the following approximate expression for $t(\theta)$:

$$t(\theta) = \frac{1}{1-q}\ln[1-(1-q)\theta]^{-1}\left[1 + \mathrm{O}(b\epsilon^{-2+\Delta})\right] \tag{6.11a}$$

for arbitrary $\Delta > 0$. Thus it is seen that the relation between t and θ is again close to the one that exists for the linear sum case, as long as $\epsilon^2 \gg b$ or equivalently

$$t \ll \frac{\ln b^{-1}}{2b} \qquad b\mathrm{e}^{-2bt} \ll 1 \tag{6.11b}$$

which can clearly only be satisfied if $b \ll 1$. Note that this result might have been expected on intuitive grounds: indeed, for the sum kernel $b(k+l)$, the typical size $s(t)$ goes as e^{2bt}, as is seen, for example, from the behaviour of $\mu_2(t)$, see (6.4). Thus, for times at which (6.11) is violated, the typical size in the sum kernel is larger than b^{-1}, so that the correspondence between the sum kernel (6.2) and ours is lost. On the other hand, the scaling behaviour described in section 4 is recovered as soon as

$$(1-q)\theta \gg 1 \tag{6.12}$$

since this is the necessary condition to neglect the summands with $r \geqslant 1$ in (3.9). Equivalently, this gives the requirement that $t \gg \exp(1/b)$. There is clearly a very large range of intermediate times $\ln b^{-1}/(2b) \ll t \ll \exp(1/b)$. For these, however, I do not know whether a simple description is possible at all. Further work is needed to analyse this transition range.

So far, I have only discussed the relation between t and θ in our model in the time range (6.11) and in the linear sum kernel case. Now I discuss the relation between the $\phi_j(\theta)$ in our model and the corresponding functions for the linear sum kernel. The first and most obvious remark refers to the recursive nature of equations (3.2). From (3.2) it follows that for any fixed j

$$\phi_j(\theta) = \phi_j^{(0)}(\theta)\left[1 + \mathrm{O}(b^2\theta)\right]. \tag{6.13}$$

This is a peculiar result: the true linear sum kernel has no physical solution beyond $b\theta = 1$. On the other hand, the closeness between the solution of our kernel and the analytical continuation of the solution for the linear sum kernel persists well beyond this limit, as long as we restrict our attention to *fixed* j only. It should be pointed out that the constant implied by the error term $O(b^2\theta)$ is non-uniform in j, that is, for large values of j, the prefactor in this error term may well become large.

On the other hand, it is immediately clear that (6.13) cannot hold for all j as soon as $b\theta$ is larger than unity, since in that case all $\phi_j(\theta)$ would be monotonically decreasing, in contradiction to the normalization condition $\sum_{j=1}^{\infty}\phi_j = 1$ implied by the definition of ϕ_j (3.1*a*). Thus, as soon as $b\theta$ passes unity, $\phi_j(\theta)$ must deviate from $\phi_j^{(0)}(b\theta)$ significantly for sufficiently large j, though for any fixed value of j, the two functions remain close up to $b\theta$ of the order of $1/b$. Note further that this result has only minor implications for the functions $c_j(t)$, since these are connected to the $\phi_j(\theta)$ by the change of variables (3.1*a*) which destroys the connection implied by (6.13), since it involves $M_0(t)$, which in turn involves arbitrary values of j.

A remark concerning the opposite extreme is also easy to derive: namely, for any value of t, no matter how small, there are values of j so large that the qualitative behaviour of the linear sum kernel (6.2) differs from that predicted for ours. This can be seen as follows. For $j \to \infty$ at fixed time, the asymptotic behaviour of the linear sum kernel is such that there is an $a(t) > 1$ so that, for all times t

$$\lim_{j\to\infty} j^{3/2} c_j(t)\, a(t)^j \tag{6.14}$$

exists and is a finite positive number. On the other hand, in our kernel, it is apparent from (3.7*c*) and (3.7*d*) that the generating function is the quotient of two entire functions. Thus the singularities in the complex plane can only be poles. Using (4.5), one convinces oneself that, for small θ, $1 + S(\zeta, \theta)$ can only have a simple zero, whereas for large times this follows from the analysis in section 4. Whether multiple zeros are possible at all is doubtful. From this follows, using standard Tauberian theorems [12], that there is an $a(t) > 1$ so that

$$\lim_{j\to\infty} c_j(t)\, a(t)^j \tag{6.15}$$

exists and is a finite positive number. Thus the behaviour at large j of the two systems is quite different. (This was to be expected on the grounds of qualitative arguments, which show that this behaviour depends only on the asymptotic degree of homogeneity of the kernel [13].)

I now wish to estimate the range of times over which all $\phi_j(\theta)$ which contribute significantly to the total mass remain close to $\phi_j^{(0)}(\theta)$ for a given value of b as well as the time range over which the various moments of our system behave similarly to those of the linear sum kernel. It is shown in appendix E that

$$|M_n(\theta) - \mu_n(\theta)| = O[b^2\epsilon^{-2(n-1)}]. \tag{6.16}$$

One finds, from the exact solution of the linear sum kernel, that

$$\mu_n(\theta) = O[\epsilon^{-(2n-3)}]. \tag{6.17}$$

Thus, as long as $b^2 \ll \epsilon$, one sees from (6.16) and (6.17) that the difference between the two moments is much less than the moments themselves. Thus our kernel is again well approximated for all moments of fixed order n as long as $b^2 \ll \epsilon$, which is the same condition stated in (6.11*a*) and (6.11*b*). Again, the above estimates are not uniform in n, so that even for small times, it is presumably possible to find moments in which the two kernels deviate significantly. The order n of these moments would, however, go to infinity as $b \to 0$. This is linked with the fact, already discussed above, that the concentrations corresponding to very large aggregates are always different for the two kernels.

If the typical size is defined by $M_2(t)$, one sees from (3.14) and the above considerations that the typical size reached when ϵ is of the order of $b^{-1/2}$ is of the order of b^{-1} both in our systems and in the linear sum kernel. Thus one sees that the analogy of behaviour between the linear sum kernel model and our model is lost once the typical size goes beyond b^{-1}. This was, of course, to be expected, since the approximate equality

$$K(j,k) = b(j+k)[1 + \mathrm{O}(bj, bk)] \tag{6.18}$$

fails when j or k becomes of the order of b^{-1}.

7. Conclusions

To sum up, I have analysed the explicit solution of the Smoluchowski equations for the kinetics of aggregation found in an earlier paper [1], with respect to its scaling properties. This solution was for the case in which the reaction rates are given by

$$K(j,k) = 2 - q^j - q^k. \tag{7.1}$$

This kernel has the remarkable property of interpolating, in the limit when $q \to 1$, between two well studied kernels, namely the constant kernel and the linear sum kernel. Further, it can be viewed as a correction to the constant kernel, thus allowing one to test whether the predictions of scaling theory concerning the universality of behaviour for large times and large values of j are indeed satisfied.

The results are complicated and in a sense mixed. Thus, for example, the large-time behaviour at fixed j is very different indeed, since one has

$$c_j(t) = \frac{[t/T(q)]^{-(2-q^j)}}{T(q)(q;q)_{j-1}}[1 + \mathrm{o}(1)] \tag{7.2}$$

in contradistinction to the constant kernel, for which at long times all $c_j(t)$ decay as t^{-2}, that is, with the same exponents, and furthermore with the same prefactor. Here all the exponents depend on j and the amplitude as well. However, as was shown in section 4, a rigorous scaling result does hold for our system also, and it is identical to the corresponding one for the constant kernel, namely

$$\lim_{j\to\infty} j^2 c_j(j/x) = x^2 \mathrm{e}^{-x}. \tag{7.3}$$

However, for the constant kernel the results of (7.3) can actually be extended down to the case where j is fixed and $t \to \infty$. As (7.2) shows, this is not the case for our model.

Finally, I studied the limiting behaviour of the functions $c_j(t)$ in the limit $q \to 1$, for which the kernel shows a transient behaviour similar to that of the linear sum kernel. Such transients are of physical interest, since they occur, for example, when an aggregation process passes from being dominated by molecular diffusion to being driven by sedimentation. Again the picture is quite complex: for fixed values of j, the similarity between the solutions of our kernel and those of the linear kernel extend *beyond* the times for which the solutions of the linear sum kernel are physically meaningful! This must, of course, be taken to mean that our solutions coincide with the analytic continuation of the linear sum kernel solution, even when the latter has ceased to represent a solution of the equations. This is presumably to be interpreted as a phenomenon akin to that of gelation: there, in some cases (Flory model of gelation [14]), the analytical continuation of the solution remains meaningful even at times for which it fails to keep constant mass. In the case of gelation, this is due to the presence of an infinite cluster which takes up the remaining mass. In the case of our model, the analytical continuation of the solution of the linear sum kernel also fails to preserve mass, but the remaining mass is simply taken up by clusters, the mass of which increases to infinity as $q \to 1$. These actually make up most of the mass, so no contradiction is involved.

On the other hand, if one wishes to know when the low-order moments are the same for both model, one finds that this is exactly the case as long as the typical size is less than $(1-q)^{-1}$ in either of the two systems. However, it should be emphasized that this similarity only holds for those $c_j(t)$ which contribute significantly to the mass. If one goes at fixed t to arbitrarily high values of j, and thus far beyond the typical size at time t, one will always find great differences between the two models, no matter how small t is.

Acknowledgments

It is a pleasure to thank the Centro Internacional de Ciencias (CIC), and in particular Professor T H Seligman, for the pleasant hospitality and fruitful working atmosphere that was instrumental in originating and carrying out this research. I acknowledge with gratitude the contribution of Professor Francesco Calogero, without which this paper would not have been possible. I also wish to thank Professor Natig Atakishiyev for several useful discussions and his friendly advice. Finally, the financial support of DGAPA project IN112998 is also gratefully acknowledged.

Appendix A

Here I show how the solutions of (1.2) in the constant kernel case approach the scaling limit for arbitrary initial conditions $c_j(0)$, as long as the $c_j(0)$ decay exponentially in j and the greatest common denominator of those values of j for which $c_j(t) \neq 0$ is one. For definiteness' sake I will further assume that the total mass is equal to unity, that is

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

To solve (1.2) in the case

$$K(k,l) = 2$$

for arbitrary initial conditions $c_j(0)$, one introduces

$$G(\zeta, t) = \sum_{j=1}^{\infty} c_j(0)(\zeta^j - 1). \tag{A.2}$$

In [15] it is shown that

$$G(\zeta, t) = \frac{g(\zeta)}{1 - tg(\zeta)} \tag{A.3}$$

where

$$g(\zeta) = \sum_{j=1}^{\infty} c_j(0)(\zeta^j - 1). \tag{A.4}$$

From the assumptions made on $c_j(0)$, it follows that $g(\zeta)$ is an analytic function on a disc of radius R with $R > 1$ and that on any circumference of radius $\rho < R$ it takes a strict maximum at ρ. It therefore follows that $g(\zeta)$ has a zero at $\zeta = 1$, and further, that there exists an $R_1 > 1$ such that any zeros of $g(\zeta)$ have an absolute value greater than R_1. From Rouché's theorem it follows that the zeros of $1-tg(\zeta)$ all lie at a distance of the order of $1/t$ from the corresponding zero of $g(\zeta)$. From this it follows that there is an $R_2 > 1$ such that there is only one zero of $1-tg(\zeta)$ inside the circle of radius R_2. From (A.1) and Cauchy's theorem one obtains

$$c_j(t) = \frac{1}{2\pi\mathrm{i}}\int_{|\zeta|=R_2}\frac{g(\zeta)}{\zeta^{j+1}[1-tg(\zeta)]}\,\mathrm{d}\zeta - \operatorname*{Res}_{\zeta=\zeta_0(t)}\frac{g(\zeta)}{[1-tg(\zeta)]\zeta^{j+1}} \tag{A.5}$$

where $\zeta_0(t)$ is the zero of $1-tg(\zeta)$ closest to $\zeta = 1$. This can be evaluated as follows:

$$1/t = g[\zeta_0(t)] = g'(1)[\zeta_0(t)-1] + \mathrm{O}(t^{-2}) \tag{A.6}$$

from which follows, since

$$g'(1) = \sum_{j=1}^{\infty} jc_j(0) = 1 \tag{A.7}$$

that

$$\zeta_0(t) = 1 + t^{-1} + \mathrm{O}(t^{-2}). \tag{A.8}$$

One now needs to evaluate the residue in (A.5) as well as to estimate the integral. The residue is given by

$$\begin{aligned} -\operatorname*{Res}_{\zeta=\zeta_0(t)}\frac{g(\zeta)}{[1-tg(\zeta)]\zeta^{j+1}} &= \frac{g[\zeta_0(t)]}{tg'[\zeta_0(t)]\zeta_0(t)^{j+1}} \\ &= t^{-2}\big[1+t^{-1}+\mathrm{O}(t^{-2})\big]^{-(j+1)} \\ &= t^{-2}\mathrm{e}^{-j/t}\big[1+\mathrm{O}(j/t^2)\big] \end{aligned} \tag{A.9}$$

for large t. As for the integral, it can be estimated as follows:

$$\begin{aligned} \left|\frac{1}{2\pi\mathrm{i}}\int_{|\zeta|=R_2}\frac{g(\zeta)}{1-tg(\zeta)}\frac{\mathrm{d}\zeta}{\zeta^{j+1}}\right| &\leqslant \frac{1}{2\pi}\int_{\zeta=R_2}\left|\frac{g(\zeta)}{1-tg(\zeta)} - \frac{g(0)}{1-tg(0)}\right|\frac{\mathrm{d}\zeta}{R_2^{-(j+1)}} \\ &= \mathrm{O}(t^{-2}R_2^{-j-1}]. \end{aligned} \tag{A.10}$$

From (A.10) and (A.9) the result readily follows.

Appendix B

Here we prove the identity (4.4). If $f(z)$ is holomorphic inside a circle with convergence radius larger than unity, one has for $0 < q < 1$,

$$f(q^r) = \sum_{m=0}^{\infty}\frac{f^{(m)}(0)}{m!}q^{rm} \qquad (r \geqslant 0). \tag{B.1}$$

Since the convergence in (B.1) is absolute, we can insert this expression in the left-hand side of (4.4) and interchange the order of summation obtaining thereby

$$\begin{aligned} \frac{1}{e_q(q^\zeta)}\sum_{r=0}\frac{q^{r\zeta}f(q^r)}{(q;q)_r} &= \frac{1}{e_q(q^\zeta)}\sum_{m=0}^{\infty}\frac{f^{(m)}(0)}{m!}\sum_{r=0}^{\infty}\frac{q^{r(m+\zeta)}}{(q;q)_r} \\ &= \frac{1}{e_q(q^\zeta)}\sum_{m=0}^{\infty}\frac{f^{(m)}(0)}{m!}e_q(q^{m+\zeta}) \\ &= \sum_{m=0}^{\infty}\frac{f^{(m)}(0)}{m!}(q^\zeta;q)_m \end{aligned} \tag{B.2}$$

which is just the formula we set out to prove. Note that in the second line we used the definition of the q-exponential as a sum, see (3.5*b*), and in the third line its definition as a product, see (3.5*a*).

Appendix C

In the following, I will prove the various statements made in section 4 concerning the distribution of zeros of the function $R(\zeta, \theta)$ defined by (4.6). For large θ, one compares $R(\zeta, \theta)$ with

$$R_0(\zeta, \theta) = 1 + (1 - q^{-\zeta})t. \tag{C.1}$$

Here and in the following, I shall mix the use of t and θ freely, it being always understood that the two are related through equations (3.9). Define $\zeta_0(t)$ as the zero of $R_0(\zeta, \theta)$ nearest to the origin. Clearly,

$$\zeta_0(t) = \frac{1}{b} \ln[(1 - 1/t)^{-1}]. \tag{C.2}$$

Next let us introduce the following notation:

$$G(\zeta, \theta) = \frac{S(\zeta, \theta)}{1 - q^{-\zeta}} \tag{C.3}$$

from which, via (3.9) I obtain

$$t = G(0, \theta). \tag{C.4}$$

Hence

$$\left|R(\zeta, \theta) - R_0(\zeta, \theta)\right| = \left|1 - q^{-\zeta}\right|\left|G(\zeta, \theta) - G(0, \theta)\right|. \tag{C.5}$$

Using Cauchy's inequality, one now finds, taking Z to be any real number greater than $|\zeta|$ but less than unity,

$$|\zeta| < Z < 1 \tag{C.6}$$

that there holds the inequality

$$\left|G(\zeta, \theta) - G(0, \theta)\right| \leqslant \frac{\zeta}{Z - \zeta} \max_{|\zeta'|=Z} \left|G(\zeta', \theta)\right|. \tag{C.7}$$

I now estimate $G(\zeta, \theta)$ from above for $|\zeta| = Z$ at large times,

$$|G(\zeta, \theta)| \leqslant K_0(Z, q) \sum_{r=0}^{\infty} \frac{q^{-rZ}}{(q;q)_r} (\mathrm{e}^{\theta q^r} - 1) \tag{C.8}$$

where

$$K_0(Z, q) = \max_{\zeta'=Z} \left|e_q(q^{-\zeta'})\right|^{-1}. \tag{C.9}$$

If one now introduces a number M such that

$$q \leqslant \theta q^M \leqslant 1 \tag{C.10}$$

and uses the inequality

$$|\mathrm{e}^x - 1| \leqslant Kx \qquad (0 \leqslant x \leqslant 1) \tag{C.11}$$

where

$$K = e - 1 \tag{C.12}$$

one obtains from (C.8)

$$
\begin{aligned}
|G(\zeta,\theta)| &\leqslant K K_0(Z,q) \sum_{r=0}^{M-1} \frac{q^{-rZ}}{(q;q)_r}(\mathrm{e}^{\theta q^r}-1) + \frac{K K_0(Z,q)}{(q;q)_\infty} \sum_{r=M}^{\infty} q^{r(1-Z)}\theta \\
&\leqslant K_1 q^{-MZ}\mathrm{e}^{\theta} + K_2\theta
\end{aligned}
\tag{C.13}
$$

since $Z < 1$. Here K_1 and K_2 are abbreviations for constants in which some prefactors have been absorbed for simplicity of notation. From (C.10) one now obtains for large t

$$
|G(\zeta,\theta)| = \mathrm{O}(t \ln t) \tag{C.14}
$$

uniformly in ζ as long as $|\zeta| < Z$. Using (C.5), (C.7) and (C.14) one finally obtains

$$
\left|R(\zeta,\theta) - R_0(\zeta,\theta)\right| < K_3(t)\frac{|\zeta(1-q^{-\zeta})|}{|Z-\zeta|} = \mathrm{O}[K_3(t)\zeta^2] \tag{C.15}
$$

the last equality being valid for ζ appropriately small, and

$$
K_3(t) = \mathrm{O}(t \ln t) \tag{C.16}
$$

for t large. Now one defines the following (time-dependent) contour C_t around $\zeta_0(t)$, see (C.2):

$$
\left|q^{-\zeta} - q^{-\zeta_0(t)}\right| = \frac{K_4(t)}{t}\frac{|\zeta(1-q^{-\zeta})|}{|Z-\zeta|}. \tag{C.17}
$$

If I now choose

$$
K_4(t) = C K_3(t) \tag{C.18}
$$

with $C > 1$ a positive real number larger than unity, it follows that

$$
\begin{aligned}
|R_0(\zeta,\theta)| &= \left|1 + (1-q^{-\zeta})t\right| \\
&= t\left|q^{-\zeta_0(t)} - q^{-\zeta}\right| \\
&= K_4(t)\zeta^2.
\end{aligned}
\tag{C.19}
$$

From this it follows that

$$
|R(\zeta,\theta) - R_0(\zeta,\theta)| < |R_0(\zeta,\theta)| \tag{C.20}
$$

on C_t, so that by the argument principle (Rouché's theorem), $R(\zeta,\theta)$ has the same number of zeros as $R_0(\zeta,\theta)$ within C_t, namely exactly one. This fact allows one to locate accurately the zero of $R(\zeta,\theta)$ and hence the singularity in $H(\zeta,\theta)$ at large times. Indeed, from (C.2) there follows

$$
\zeta_0(t) = \frac{1}{bt}\left[1 + \mathrm{O}(t^{-1})\right]. \tag{C.21}
$$

From (C.17) there follows that, if one denotes by $\zeta_s(t)$ the zero of $R(\zeta,\theta)$, then for large times

$$
\left|\zeta_s(t) - \zeta_0(t)\right| \leqslant \frac{K_4(t)}{t}\frac{|\zeta_s(t)(1-q^{-\zeta_s(t)})|}{|Z-\zeta_s(t)|} = \mathrm{O}(t^{-2}\ln t). \tag{C.22}
$$

Thus it follows that

$$
\zeta_s(t) = \frac{1}{bt}\left[1 + \mathrm{O}(t^{-1}\ln t)\right]. \tag{C.23}
$$

It would, obviously, be interesting to know whether the logarithmic correction could be dispensed with. The problem, however, seems to be difficult.

Now note that the above inequalities do not require ζ to be arbitrary small. In fact, if $K_4(t)$ is taken to grow linearly as t, one finds that there is a neighbourhood of the imaginary axis, of width of the order of one, such that no zeros of $R(\zeta, \theta)$ are found within it, save those of the form $\zeta_s(t) + 2\pi \mathrm{i}k/b$ for arbitrary integer values of k. Thus we have shown all the required properties of the zeros of $R(\zeta, \theta)$ and the consequences stated in section 4 concerning the scaling behaviour of the solution follow.

Appendix D

In this appendix I show how an approximate connection between t and θ can be derived for $b \ll 1$ and moderate times t. To this end I use an expression for $\mathrm{d}t/\mathrm{d}\theta$, which can be derived from (3.9) using the identity (4.4),

$$\frac{\mathrm{d}t}{\mathrm{d}\theta} = \sum_{m=0}^{\infty} \frac{\theta^m}{m!}(q;q)_m. \tag{D.1}$$

If one now assumes that $(1-q)\theta$ is less than unity, then the following inequalities can be used

$$lq^l \leqslant \frac{1-q^l}{1-q} \leqslant l \tag{D.2}$$

which lead to

$$(1-q)^m q^{m(m+1)/2} m! \leqslant (q;q)_m \leqslant (1-q)^m m!. \tag{D.3}$$

Substituting in (D.1), this gives

$$\sum_{m=0}^{\infty} [(1-q)\theta]^m q^{m(m+1)/2} \leqslant \frac{\mathrm{d}t}{\mathrm{d}\theta} \leqslant \sum_{m=0}^{\infty} [(1-q)\theta]^m = \frac{1}{1-(1-q)\theta}. \tag{D.4}$$

From these inequalities, it follows that for $(1-q)\theta$ less than unity, $\mathrm{d}t/\mathrm{d}\theta$ can be well approximated by the right-hand side of (D.4). More precisely

$$\begin{aligned} \left| \frac{\mathrm{d}t}{\mathrm{d}\theta} - \frac{1}{1-(1-q)\theta} \right| &\leqslant \sum_{m=0}^{\infty} [(1-q)\theta]^m \left[1 - q^{m(m+1)/2}\right] \\ &\leqslant \sum_{m=0}^{M-1} [1 - q^{m(m+1)/2}] + \sum_{m=M}^{\infty} [(1-q)\theta]^m \\ &\leqslant M\left[1 - q^{M(M-1)/2}\right] + \frac{[(1-q)\theta]^M}{1-(1-q)\theta} \end{aligned} \tag{D.5}$$

where M can be chosen arbitrarily.

To obtain the sharpest possible result from (D.4), let us choose, defining ϵ as in (6.9):

$$M = \frac{\ln(\epsilon^2 b^{-1})}{\epsilon}. \tag{D.6}$$

One then obtains

$$\frac{\mathrm{d}t}{\mathrm{d}\theta} = \frac{1}{1-(1-q)\theta}\{1 + \mathrm{O}[(b/\epsilon^2)\ln^3(\epsilon^2/b)]\} \tag{D.7}$$

as stated in the text. Inequality (D.5) can also be integrated term by term to yield

$$t(\theta) = \frac{1}{1-q}\ln\left[1-(1-q)\theta\right]^{-1}\left[1 + \mathrm{O}(b\epsilon^{-2+\Delta})\right]. \tag{D.8}$$

Thus all the results stated in the text are shown.

Appendix E

In this appendix, I wish to estimate the difference between the two kernels for those values of j which contribute significantly to the mass. Specifically, I wish to estimate the difference between $M_n(t)$ and $\mu_n(t)$. To this end, one estimates the difference between the two generating functions for small positive values of ζ, yet for values of ζ which are not very close to the singularity. This singles out those values of j which contribute most to all moments (since moments correspond to derivatives of the generating functions at the origin) and hence provides the solution to our problem.

This is done as follows. Rewriting the basic equation for $H(\zeta,\theta)$ derived in [1] (equation (2.18)) in terms of $\tilde{H}(\zeta,\theta)$ one finds

$$\frac{\partial\tilde{H}}{\partial\theta}(\zeta,\theta) = \tilde{H}(\zeta,\theta)\big[\tilde{H}(\zeta,\theta) - \tilde{H}(\zeta-b,\theta)\big] \tag{E.1}$$

as long as ζ is less than the nearest singularity, which is on the real axis, since all the coefficients of the Taylor series of $\tilde{H}(\zeta,\theta)$ are positive. Under these circumstances, one can rewrite the difference as follows:

$$\tilde{H}(\zeta,\theta) - \tilde{H}(\zeta-b,\theta) = b\frac{\partial\tilde{H}}{\partial\zeta}(\zeta,\theta) - \frac{b^2}{2\pi\mathrm{i}}\int_C \frac{\tilde{H}(w)}{(w-\zeta)^2(w-\zeta+b)}\,\mathrm{d}w \tag{E.2}$$

where C is a contour enclosing both b and the origin. For the linear sum kernel, standard manipulations using the same variable transformations as used in the beginning of section 2 lead to

$$\frac{\partial\tilde{H}_0}{\partial\theta}(\zeta,\theta) = b\tilde{H}_0(\zeta,\theta)\frac{\partial\tilde{H}_0}{\partial\zeta}(\zeta,\theta) \tag{E.3}$$

where

$$\tilde{H}_0(\zeta,\theta) = \sum_{j=1}^{\infty}\phi_j^{(0)}(\theta)\,\mathrm{e}^{j\zeta}. \tag{E.4}$$

One then needs to estimate the difference between $\tilde{H}_0(\zeta,\theta)$ and $\tilde{H}(\zeta,\theta)$. Equation (E.3) can be solved using the method of characteristics, to yield the following implicit solution: using an initial condition corresponding to (1.3),

$$\tilde{H}_0(\zeta,0) = \mathrm{e}^{\zeta} - 1 \tag{E.5}$$

one obtains

$$\tilde{H}_0[\zeta - (\mathrm{e}^{\zeta}-1)b\theta,\theta] = \mathrm{e}^{\zeta} - 1. \tag{E.6}$$

Now define

$$\chi(\zeta,\theta) = \zeta - b\theta(\mathrm{e}^{\zeta}-1). \tag{E.7}$$

This function reaches a maximum value at

$$\zeta_c(\theta) = -\ln b\theta = \epsilon + \mathrm{O}(\epsilon^2) \tag{E.8}$$

which is greater than zero as long as $b\theta < 1$, which contains the range of interest. One has

$$\chi_c(\theta) \equiv \chi[\zeta_c(\theta),\theta] = -\ln(b\theta\,\mathrm{e}^{1-b\theta}) = \epsilon^2/2 + \mathrm{O}(\epsilon^3). \tag{E.9}$$

Thus the function $\chi(\zeta, \theta)$ can be inverted as long as $\chi < \chi_c(\theta)$ or equivalently $\zeta < \zeta_c(\theta)$. The inverse, which is denoted by $\zeta(\chi, \theta)$, is then chosen to be the branch such that

$$\zeta(0, \theta) = 0. \tag{E.10}$$

From (E.6) and the above definitions it follows that

$$\tilde{H}_0[\chi(\zeta, \theta), \theta] = \mathrm{e}^{\zeta} - 1 \tag{E.11}$$

or equivalently,

$$\tilde{H}_0(\chi, \theta) = \exp[\zeta(\chi, \theta)] - 1. \tag{E.12}$$

One then considers the function

$$E(\zeta, \theta) = \tilde{H}[\zeta - (\mathrm{e}^{\zeta} - 1)b\theta, \theta] - (\mathrm{e}^{\zeta} - 1) \tag{E.13}$$

as a measure of the deviation between the approximate and the true functions. Substituting in (E.1) one finds the following equation for $E(\zeta, \theta)$:

$$\begin{aligned} \frac{\partial E}{\partial \theta}(\zeta, \theta) &= bE(\zeta, \theta)\frac{\partial \tilde{H}}{\partial \zeta}[\chi(\zeta, \theta), \theta] + \tilde{H}[\chi(\zeta, \theta), \theta] \\ &\quad \times \left\{ \tilde{H}[\chi(\zeta, \theta), \theta] - \tilde{H}[\chi(\zeta, \theta) - b, \theta] - b\frac{\partial \tilde{H}}{\partial \zeta}[\chi(\zeta, \theta), \theta] \right\}. \end{aligned} \tag{E.14}$$

As long as the series for $\tilde{H}(\zeta, \theta)$ converges, the last term in brackets is always negative, since $\tilde{H}(\zeta, \theta)$ is a series with positive coefficients. From this it follows that

$$E(\zeta, \theta) \leqslant 0 \tag{E.15}$$

as long as the series for $\tilde{H}(\zeta, \theta)$ remains convergent and ζ is real and positive. Hence, for $\zeta < \zeta_c(\theta)$ real positive, one has

$$\tilde{H}(\chi, \theta) \leqslant \tilde{H}_0(\chi, \theta) = \exp[\zeta(\chi, \theta), \theta] - 1 = \mathrm{O}(\epsilon). \tag{E.16}$$

Therefore, $\tilde{H}(\chi, \theta)$ has no singularities for $\chi < \chi_c(\theta)$, so that (E.16) is valid in this range. In the following, I shall limit myself to a range of ζ uniformly bounded away from $\zeta_c(\theta)$, such as

$$0 < \zeta \leqslant \zeta_1(\theta) = \zeta_c(\theta)/2. \tag{E.17}$$

From inequality (E.16), various estimates on the derivatives and the differences of $\tilde{H}(\zeta, \theta)$ can be derived using Cauchy's integral formula. Indeed,

$$\begin{aligned} \left| \frac{\partial \tilde{H}(\zeta, \theta)}{\partial \zeta} \right| &\leqslant \frac{1}{2\pi} \int_C \frac{|\tilde{H}(\chi, \theta)|}{|\chi - \chi(\zeta, \theta)|^2} \\ &\leqslant |\exp\{\zeta[\chi_1(\theta), \theta]\} - 1| \mathrm{O}[\chi_1(\theta)^{-1}] = \mathrm{O}(\epsilon^{-1}) \end{aligned} \tag{E.18}$$

where

$$\chi_1(\theta) = \chi[\zeta_1(\theta), \theta] = \mathrm{O}(\epsilon^2) \tag{E.19}$$

and C is a contour chosen to lie entirely to the left of $\chi_1(\theta)$ but surrounding $\chi(\zeta, \theta)$. This is possible as long as $b\theta < 1$, which will always be assumed hereinafter.

Similarly, one obtains for the difference

$$\left| \tilde{H}(\chi, \theta) - \tilde{H}(\chi - b, \theta) - b\frac{\partial \tilde{H}(\chi, \theta)}{\partial \chi} \right| \leqslant \frac{b^2}{2\pi} \int_C \frac{|\tilde{H}(w, \theta)|}{|w - \chi|^2 |w - \chi + b|} \tag{E.20}$$

where C is a contour as in (E.18). One then estimates the right-hand side of (E.20) from above by

$$\frac{b^2\chi_1(\theta)H[\chi_1(\theta),\theta]}{(2\pi)\min_{w\in C}|w-\chi|^3} = \mathrm{O}(b^2\epsilon^{-3}). \tag{E.21}$$

Thus one obtains, from (E.14)

$$\frac{\partial E(\zeta,\theta)}{\partial\theta} = bE(\zeta,\theta)\frac{\partial\tilde{H}}{\partial\zeta}[\chi(\zeta,\theta)] + \mathrm{O}(b^2\epsilon^{-2}) \tag{E.22}$$

and hence

$$|E(\zeta,\theta)| = \mathrm{O}(b^2\epsilon^{-2}) \tag{E.23}$$

uniformly for all $\zeta < \zeta(\chi_1(\theta),\theta)$.

From this, one obtains the following estimate on the difference between the exact moments of our model and the corresponding moments of the linear sum model. Let

$$\begin{aligned}\mu_n(\theta) &= \sum_{j=1}^{\infty} j^n\phi_j^{(0)}(\theta)\\ &= \frac{n!}{2\pi}\int_C \frac{\tilde{H}_0(\chi,\theta)}{\chi^{n+1}}\,\mathrm{d}\chi\\ &= \frac{n!}{2\pi}\int_C \frac{\exp[\zeta(\chi,\theta)]-1}{\chi^{n+1}}\,\mathrm{d}\chi\end{aligned} \tag{E.24}$$

where C is a contour entirely to the left of $\chi_1(\theta)$ but surrounding the origin.

From this one obtains

$$|M_n(\theta)-\mu_n(\theta)| \leqslant \frac{n!}{2\pi}\int_C \frac{|E[\zeta(\chi,\theta),\theta]|}{|\chi|^{n+1}}\,\mathrm{d}\chi \tag{E.25}$$

where again the contour C is to the left of $\chi_1(\theta)$ and surrounds the origin. From the above estimates one concludes that

$$|M_n(\theta)-\mu_n(\theta)| = \mathrm{O}[b^2\epsilon^{-2(n-1)}] \tag{E.26}$$

as stated in the text.

References

[1] Calogero F and Leyvraz F 1999 *J. Phys. A: Math. Gen.* **32** 7697
[2] Smoluchowski M v 1916 *Z. Phys.* **17** 557
Chandrasekhar S 1943 *Rev. Mod. Phys.* **15** 1
[3] Hendriks E, Ernst M H and Ziff R M 1983 *J. Stat. Phys.* **31** 519
[4] Leyvraz F and Tschudi H R 1982 *J. Phys. A: Math. Gen.* **15** 1951
[5] van Dongen P G J and Ernst M H 1985 *Phys. Rev. Lett.* **54** 1396
van Dongen P G J and Ernst M H 1988 *J. Stat. Phys.* **50** 295
[6] Friedlander S K and Wang C S 1966 *Coll. J. Interface Sci.* **22** 126
Lushnikov A A 1973 *Coll. J. Interface Sci.* **45** 549
Kolb M 1984 *Phys. Rev. Lett.* **53** 1653
[7] Vicsek T and Family F 1984 *Phys. Rev. Lett.* **52** 1669
[8] Leyvraz F and Redner S 1986 *Phys. Rev. Lett.* **57** 163
Leyvraz F and Redner S 1987 *Phys. Rev.* A **36** 4033
[9] van Dongen P G J 1987 *Physica* A **145** 15
[10] Gasper G and Rahman M 1990 *Basic Hypergeometric Series (Encyclopedia of Mathematics and its Applications vol 35)* ed G-C Rota (Cambridge: Cambridge University Press)

[11] van Dongen P G J and Ernst M H 1983 *J. Phys. A: Math. Gen.* **16** L327
Spouge J L 1983 *J. Phys. A: Math. Gen.* **16** 767
[12] Whittaker E T and Watson G N 1944 *A Course in Modern Analysis* (Cambridge: Cambridge University Press)
[13] Ernst M H, Hendriks E and Leyvraz F 1984 *J. Phys. A: Math. Gen.* **17** 2137
[14] Ziff R M 1980 *J. Stat. Phys.* **23** 241
[15] Leyvraz F and Tschudi H R 1980 *J. Phys. A: Math. Gen.* **13** 1867