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Rigorous Results in the Scaling Theory of Irreversible Aggregation Kinetics

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Abstract

The kinetic equations describing irreversible aggregation and the scaling approach developed to describe them in the limit of large times and large sizes are tersely reviewed. Next, a system is considered in which aggregates can only react with aggregates of their own size. The existence of a scaling solution of the kinetic equations can then be shown rigorously in the case in which the total mass of the system is conserved. A large number of detailed properties of the solution, previously predicted by qualitative arguments, can be shown rigorously as well in this system. In the case in which gelation occurs, some sketchy rigorous results are shown, and numerical evidence for the existence of a scaling solution is presented. These are the first explicit examples of typical scaling behaviour for systems exhibiting gelation.

1 Introduction

In many systems one finds that irreversible aggregation of "clusters" $A(m)$ of mass m occurs and plays an important role. Particular instances are aerosol physics, where suspended particles coagulate due to van der Waals forces, polymer chemistry and astrophysics (where the clusters may be quite varied, going from galaxies to planetary systems). In all these systems one is among other things interested in the cluster size distribution as a function of time. To obtain it one then relies on kinetic equations, derived from the following assumptions: let the reaction

$$A(m) + A(m') \underset{K(m,m')}{\longrightarrow} A(m+m') \tag{1.1}$$

occur at a *rate* $K(m, m')$, that is, let any two clusters of size m and m' react on a time scale given by $K(m, m')^{-1}$. If one further assumes that no spatial correlations build up, in other words, that we may use a mean-field model in which the probability of encounter of two clusters of masses m_1 and m_2 is proportional to the product of the concentrations of such clusters, one obtains the following kinetic equations for the concentrations $c(m,t)$ of clusters of mass m:

$$\dot{c}(m,t) = \frac{1}{2}\int_0^\infty dm_1\, dm_2 K(m_1,m_2)\, c(m_1,t)c(m_2,t)\times \\ \times\left[\delta(m-m_1-m_2)-\delta(m-m_1)-\delta(m-m_2)\right]. \tag{1.2}$$

These are an infinite set of coupled nonlinear ODE's, which represent a challenging problem. Few exact solutions are known, which are reviewed in [17].

From the form of the reaction scheme (1.1) as well as from the equations (1.2) it is clear that at the formal level the total mass M

$$M = \int_0^\infty m\, c(m,t) dm \tag{1.3}$$

is conserved. It is well known, however, that this is not generally true. If $K(m_1,m_2)$ grows fast enough with the mass, a finite amount of mass can escape to infinity in finite time. This phenomenon is known as gelation and is found explicitly for the reaction rates $K(m_1,m_2) = m_1 m_2$ [14, 18, 19, 26].

Existence and uniqueness results are known for (1.2). Let me state two which are representative: White [25] has shown that under the hypothesis

$$K(m_1,m_2) \le C(m_1+m_2) \tag{1.4}$$

and if the initial condition $c(m,0)$ has finite moments of arbitrary order, then the kinetic equations (1.2) have a unique solution for all positive times and this solution preserves mass. A complementary result obtained in [14] states the following: under the hypothesis

$$K(m_1,m_2) \le r(m_1)r(m_2) \\ r(m) = o(m), \tag{1.5}$$

the kinetic equations (1.2) have at least one (positive) solution for all positive times, which need not conserve mass. This was significantly extended in [11, 12], where it was shown that if

$$K(m_1,m_2) = r(m_1)r(m_2) + \alpha(m_1,m_2) \tag{1.6}$$

$$\alpha(m_1,m_2) = \alpha(m_2,m_1) \le A r(m_1)r(m_2) \tag{1.7}$$

for some positive constant A, then a global positive solution exists for all times. In this case all requirements of growth on $r(m)$ could be dropped, but the rate must now be dominated by a contribution of the product type. There also exists a rigorous result by Jeon [8], showing that no substantial improvement on White's theorem is possible: more precisely, for kernels satisfying (1.5) and additionally

$$K(m_1,m_2) \ge \epsilon (m_1 m_2)^\alpha \qquad (\alpha > 1/2) \tag{1.8}$$

for some $\epsilon > 0$, it is shown that gelation always occurs.

The rest of this paper is organized as follows: in Sections 2 and 3 I tersely review the definitions and predictions of scaling theory for non-gelling and gelling systems respectively. In Sectiond 4 and 5 I obtain specific results concerning the so-called diagonal kernel in the scaling limit. In Ssection 4 I treat the non-gelling case, for which both the existence and many qualitative properties of the solution can be rigorously established. These results are summarized in Theorem 1. In section 5 I discuss both the gelling case for which I am not able to show existence rigorously and the marginal case in which the homogeneity degree is one which, although non-gelling by White's theorem, lies outside the domain of application of Theorem 1. Existence and qualitative properties of the solution are summarized in Theorem 2. I present some conclusions in Section 6.

2 Scaling theory: The non-gelling case

Beyond the above results on existence of solutions, there has always been a great interest in knowing the qualitative behaviour of the solutions either in the large-time limit or, for gelling systems, for times immediately before the singularity. This has been attempted by the so-called scaling description of the Smoluchowski equations, to which we now turn. Here we consider the non-gelling case. Scaling theory is then concerned with the large-size behaviour of the cluster size distribution $c(m,t)$. It therefore deals exclusively with a limit in which time and size go jointly to infinity in a manner to be described shortly.

To proceed, I first need to classify the rates $K(m_1, m_2)$ according to the way in which they behave for large values of the arguments. One first assumes that they are at the very least asymptotically homogeneous, that is, there exists a λ such that

$$\overline{K}(x,y) = \lim_{s\to\infty}\left[s^{-\lambda}K(sx,sy)\right]. \tag{2.1}$$

It turns out that only the homogeneous limit $\overline{K}(x,y)$ is relevant in the scaling limit. One then needs to classify homogeneous kernels $\overline{K}(x,y)$ further according to the way they behave when x and y are very different. One may write $\overline{K}(x,y)$ in the form $x^\lambda k(y/x)$ and, since $\overline{K}(x,y)$ is symmetric, one has $k(1/\xi) = \xi^{-\lambda}k(\xi)$. The reaction kernel $\overline{K}(x,y)$ is therefore uniquely specified by the function $k(\xi)$ on the unit interval, which may further be chosen arbitrarily. For simplicity, let us now assume that $k(\xi)/\xi^\mu \to 1$ as $\xi \to 0$, which defines the exponent μ. It then follows that $k(\xi)/\xi^\nu \to 1$ as $\xi \to \infty$, where $\nu = \lambda - \mu$. The exponent ν should satisfy $\nu < 1$ for the classical existence theorems to hold, for which (1.4) is required. As stated above, there exist more general theorems [11, 12], extending to some cases for which $\nu > 1$, however I shall not consider these here.

We now turn to the description of the scaling theory for non-gelling systems: it was originally developed by Friedlander [6, 7] and later extended by Ernst and van Dongen [22]. The underlying idea is the following: if $K(m_1, m_2)$ is exactly homogeneous of order λ, then (1.2) may have self-similar solutions of the form

$$c(m,t) = Wt^{-2z}\Phi(mt^{-z}), \tag{2.2}$$

where W is an unimportant normalization and the exponent z is given by $z = 1/(1-\lambda)$. It is a straightforward computation to verify that this is the case if and only if the function $\Phi(x)$ satisfies the integral equation:

$$a^2\Phi(a) = \int_0^a dx\, x\Phi(x)\int_{a-x}^\infty dy\, \overline{K}(x,y)\Phi(y) \tag{2.3}$$

and the conditions

$$\int_0^\infty x\Phi(x)dx = 1$$
$$\Phi(x) \geq 0. \tag{2.4}$$

The problem of showing the existence of self-similar solutions is therefore reduced to the corresponding problem for (2.3). This, however, turns out to be quite difficult. Existence has recently been shown for three different specific (and rather typical) forms of the rate kernel $\overline{K}(x,y)$ in [5], namely:

$$\overline{K}_1(x,y) = (x^\alpha + y^\alpha)(x^{-\beta} + y^{-\beta}) \qquad (\alpha \in [0,1), \beta \in [0,\infty)) \tag{2.5a}$$
$$\overline{K}_2(x,y) = (x^\alpha + y^\alpha)^\beta \qquad (\alpha, \beta \in [0,\infty)) \tag{2.5b}$$
$$\overline{K}_3(x,y) = x^\alpha y^\beta + x^\beta y^\alpha \qquad (\alpha, \beta \in (0,1)). \tag{2.5c}$$

For these cases Fournier and Laurençot [5] have shown existence (though not uniqueness) of a positive solution to (2.3) decaying faster than every power for large argument and satisfying integrability conditions near the origin corresponding, for $\overline{K}_1$ and $\overline{K}_3$, to the results previously conjectured in the literature and described below. The kernel $\overline{K}_2$ is in a sense, as we shall see shortly, marginal and results in this case are far more fragmentary. In very closely related work Escobedo *et al.* [4] show existence of scaling solutions for a kernel of the same type as $\overline{K}_3$, but in the parameter range $-1 \leq \alpha \leq 0 \leq \beta \leq 1$ and $0 \leq \lambda < 1$.

Let me describe what is supposed to hold for the behaviour of the solution $\Phi(x)$ of (2.3) with the boundary condition (2.4). For the behaviour near the origin it has been convincingly argued by power counting arguments (see for example [22]) that the behaviour is different according to the sign of the exponent μ: if $\mu > 0$, then $\Phi(x)$ behaves as $x^{-(1+\lambda)}$, whereas if $\mu < 0$ it behaves as a stretched exponential:

$$\Phi(x) = \begin{cases} const. \cdot x^{-(1+\lambda)} & (\mu > 0) \\ const. \cdot \exp\left(-const. \cdot x^{-|\mu|}\right) & (\mu < 0), \end{cases} \tag{2.6}$$

where in the second case a power-law behaviour presumably exists as a prefactor. Finally, if $\mu = 0$, the behaviour near the origin is non-universal. This case is considerably more complex than the other two, and I shall not consider it any further. As an example, we may note that out of the kernels in (2.5a,2.5b,2.5c), $\overline{K}_1$ has $\mu = -\beta < 0$, $\overline{K}_2$ has $\mu = 0$ and $\overline{K}_3$ has $\mu = \max(\alpha,\beta) > 0$. We therefore see that the three cases are represented in the results of [5]. As noted there, it could be proved that, for $\overline{K}_1$, $\Phi(x)$ decays at the origin faster than any power, whereas for $\overline{K}_3$ it could be shown that

$$\int_0^\infty x^\rho \Phi(x)dx < \infty \tag{2.7}$$

for all $\rho > \lambda = \alpha + \beta$, which is a precise form of the statement made in (2.6) and therefore presumably optimal.

The behaviour for large values of x has been found by similar arguments in [23]. The result is that $\Phi(x)$ decays exponentially with a power-law correction, that is

$$\Phi(x) = const. \cdot x^{-\theta} \exp(-const. \cdot x), \tag{2.8}$$

where this defines the exponent θ. One then finds $\theta = \lambda$ for $\nu < 1$, whereas if $\nu = 1$ the behaviour is non-universal and θ cannot be evaluated in general.

3 Scaling theory: The gelling case

Let us now pass to the treatment of both the gelling case and that in which the degree of homogeneity $\lambda = 1$. In the former, it is generally assumed, on the basis of numerical work and exactly solved models, that most of the mass is contained in aggregates of non-singular size. In formulae

$$\lim_{M\to\infty}\lim_{t\to t_g}\int_0^M mc(m,t)dm = 1. \tag{3.1}$$

Since the distribution $mc(m,t)dm$ is concentrated on small clusters and does not, therefore, display the singular behaviour taking place at t_g, we should look at higher powers, in particular at the distribution $m^2c(m,t)dm$. Let us assume [17] that, after rescaling m by an appropriate factor, this distribution converges weakly to a distribution $x^2\Phi(x)dx$, that is,

$$\lim_{t\to\infty}\left[M_2(t)^{-1}\int_0^\infty dm\, m^2c(m,t)f\left(m(t_g-t)^{1/\sigma}\right)\right] = \int_0^\infty dx\, x^2\Phi(x)f(x)$$
$$M_2(t) = \int_0^\infty m^2c(m,t)dm. \tag{3.2}$$

Here the rate at which the typical size diverges is given traditionally by the exponent $-1/\sigma$. In order for these equations to be closed, however, we need further knowledge concerning the behaviour of $M_2(t)$ near t_g. This can be obtained by the following argument. It is clear that for gelation to occur the second moment must diverge at t_g. The concentrations $c(m,t_g)$ have therefore some kind of power-law behaviour which we may denote by $m^{-\tau}$. If we now take $M_2(t)$ to be approximated by

$$\int_0^{(t_g-t)^{-1/\sigma}} m^2c(m,t)dm = (t_g-t)^{-(3-\tau)/\sigma} \tag{3.3}$$

and if we additionally assume that the exponent τ characterizing particles of fixed size m as $t\to t_g$ coincides with a power-law singularity at the origin of the scaling regime, in other words, if we assume that particles of size very small with respect to the typical size have the same power-law singularity as particles of fixed size when that size goes to infinity, then we are led to the additional boundary condition

$$\Phi(x) = const.\cdot x^{-\tau} \qquad (x\to 0). \tag{3.4}$$

These assumptions from now on lead in a rather straightforward way to the following extension of (2.3) for gelling systems:

$$\int dx\left[(3-\tau)f(x)+xf'(x)\right]x^2\Phi(x) = \int dx\,dy\,\overline{K}(x,y)x\Phi(x)\Phi(y)\times$$
$$\times\left[(x+y)f(x+y)-xf(x)\right] \tag{3.5}$$

for all continuously differentiable functions $f(x)$. The problem is therefore reduced to a kind of non-linear eigenvalue problem: one must find a value of τ such that there exists a solution $\Phi(x)$ of (3.5) satisfying the boundary condition (3.4) and decaying sufficiently fast at infinity. We shall show in an explicit example, namely the so-called diagonal kernel $\overline{K}(x,y)$ given by $x^{\lambda+1}\delta(x-y)$, how the problem may be solved at least in practice and give strong numerical arguments for the existence and uniqueness of a solution.

For the exponent σ characterizing the divergence of the typical size, one obtains [17]

$$\sigma = 1 + \lambda - \tau, \tag{3.6}$$

in stark contrast with the non-gelling case, in which the corresponding exponent z could be expressed directly in terms of the known value λ. Here, on the other hand, (3.6) only yields a relation between two equally unknown quantities. There does exist [17] an interesting relation between σ and the correction to scaling exponent Δ of $\Phi(x)$ defined by

$$\Phi(x) = const. \cdot x^{-\tau}\left[1 + O(x^{\Delta})\right]. \tag{3.7}$$

It is then conjectured that (see [17] for details) that

$$\Delta = \sigma = 1 + \lambda - \tau. \tag{3.8}$$

In this paper we shall show rigorously for the case of the diagonal kernel that, if a solution to the non-linear eigenvalue problem described above actually exists, then the above relation holds.

4 The diagonal kernel: The non-gelling case

In the following we study in greater detail the so-called diagonal kernel given by $\overline{K}(x,y) = x^{\lambda+1}\delta(x-y)$ Physically, this means that only aggregates of the same size react with each other. This might at first be viewed with suspicion: for example, if one starts with initial conditions of the type $c(m,0) = \delta(m-m_0)$ then a very singular solution arises, in which only sizes of the form $2^k m_0$ occur. However, we may start from less singular initial conditions and should also remember that in the scaling limit any kernel which only allows reactions between nearby sizes would be described asymptotically by this kernel.

It follows from White's theorem [25] that $\lambda \le 1$ is non-gelling, whereas a specific study of this particular model [15, 1] shows that the system undergoes gelation for $\lambda > 1$[1]. In this section we only consider $\lambda < 1$, as the case $\lambda = 1$ turns out to be highly singular and best treated by methods akin to those used for the gelling case. One can then be quite explicit about the properties of the solution of (2.3):

Theorem 1. *Let the reaction kernel $\overline{K}(x,y)$ be given by $x^{\lambda+1}\delta(x-y)$ where $\lambda < 1$ and let Δ be the unique positive solution of the transcendental equation*

$$\frac{1+\Delta}{2} = \frac{1 - 2^{(\lambda-1)(\Delta+1)}}{1 - 2^{\lambda-1}}. \tag{4.1}$$

Then there is an $\epsilon > 0$ and a solution $\Phi(x)$ of (2.3) such that

$$\Phi(x) = x^{-(1+\lambda)}\left[\frac{1-\lambda}{1-2^{\lambda-1}} - cx^{\Delta} + O\left(x^{\Delta+\epsilon}\right)\right]. \tag{4.2}$$

[1]Note that this does not follow directly from Jeon's more general result in [8].

Here c is an arbitrary positive constant, which can be varied so as to set the normalization (2.4). Furthermore, if $\Phi(x)$ is of the form (4.2), then it is uniquely determined by c. Finally, $x^{1+\lambda}\Phi(x)$ is monotonically decreasing on $[0,\infty)$ as well as bounded by an exponential function $C\exp(-ax)$ for some positive constants C and a. It is also C^∞ on $[0,\infty)$ in the variable x^Δ.

Remark. Note that the Theorem makes no claim concerning uniqueness of $\Phi(x)$ if $\Phi(x)$ does not have the form (4.2). In particular, solutions having divergent second moments, as found in the case of the additive kernel by Menon and Pego [21] are not excluded for this kernel. It would certainly be of great interest to know whether such solutions exist. Finally, $x^{1+\lambda}\Phi(x)$ can be shown to be analytic in x^Δ in a neighbourhood of the origin. I believe, but cannot prove, that this is actually true for the entire positive real axis.

Proof. Let us first write (2.3) out explicitly in the case of the diagonal kernel. One finds

$$x^2\Phi(x) = \int_{x/2}^{x} dy\, y^{\lambda+2}\Phi(y)^2, \tag{4.3}$$

which can easily be rewritten as a “non-local” differential equation:

$$\frac{d}{dx}\left[x^2\Phi(x)\right] = x^{\lambda+2}\Phi(x)^2 - \frac{1}{2}\left(\frac{x}{2}\right)^{\lambda+2}\Phi\left(\frac{x}{2}\right)^2. \tag{4.4}$$

We now perform the following change of variables

$$\begin{aligned} \psi &= x^{1+\lambda}\Phi \\ y &= \frac{x^{1-\lambda}}{1-\lambda}, \end{aligned} \tag{4.5}$$

which casts (4.4) in the form

$$(1-\lambda)\frac{d}{dy}\left[y\psi(y)\right] = \psi(y)^2 - 2^{\lambda-1}\psi(2^{\lambda-1}y)^2. \tag{4.6}$$

It is clear that the only way in which such a function can tend to a constant value ψ_0 at the origin arises if

$$\psi_0 = \frac{1-\lambda}{1-2^{\lambda-1}}. \tag{4.7}$$

We therefore begin by searching for solutions of the type

$$\psi(y) = \psi_0 + \phi(y). \tag{4.8}$$

$\phi(y)$ then satisfies the equation

$$(1-\lambda)\left[y\phi(y)\right]' = 2\psi_0\left[\phi(y) - 2^{\lambda-1}\phi(2^{\lambda-1}y)\right] + \phi(y)^2 - 2^{\lambda-1}\phi(2^{\lambda-1}y)^2, \tag{4.9}$$

which always has the trivial solution $\phi(y) = 0$ corresponding to the solution of (4.3) given by $\Phi(x) = \psi_0 x^{-(1+\lambda)}$. The existence of such a formal solution, which cannot satisfy the normalization condition (2.4) is a well-known fact for all kernels of type I. We should therefore look for ways of violating uniqueness for the solution of (4.9), which can clearly only happen near the origin.

If we wish to construct a solution starting at ψ_0 and having the form (4.8), then $\phi(y)$ must initially be small. This suggests looking at the linearization of (4.9), which can be solved by an appropriate power law y^Δ. One then obtains the transcendental equation

$$\frac{1+\Delta}{2} = \frac{1-2^{(\lambda-1)(\Delta+1)}}{1-2^{\lambda-1}} = F(\Delta). \tag{4.10}$$

Here the second equality *defines* $F(\Delta)$. The solution is found to exist and to be unique: indeed, one finds $F(0) = 1 > 1/2$, but $F(\Delta)$ becomes less than $(1+\Delta)/2$ as $\Delta \to \pm\infty$, so (4.10) must have both a positive and a negative root. But since $F(\Delta)$ is concave, there are no more than two roots, so that the positive solution is unique as stated. Further, since $F(\Delta) > 1$ for all $\Delta > 0$, it follows from (4.10) that $\Delta > 1$.

It now remains to show that a solution $\phi(y)$ of the type described above indeed exists in a sufficiently small neighbourhood of the origin. To this end we introduce

$$\phi(y) = y^\Delta \left[-c + h(y)\right], \tag{4.11}$$

where c is an arbitrary constant, which we shall later take to be positive, but its sign is of no importance for the *local* result I am now proving. Using the transcendental equation (4.10) satisfied by Δ, we may now recast the equation (4.3) as follows

$$h(y) = \frac{1}{(1-\lambda)y^{1+\Delta}} \int_{2^{\lambda-1}y}^{y} dw\, w^\Delta \left\{2\psi_0 h(w) + w^\Delta \left[-c + h(w)\right]^2\right\}. \tag{4.12}$$

To show that this fixed point problem has a unique solution, it is sufficient to find a closed subset of a Banach space which is left invariant by the operator

$$T[h](y) = \frac{1}{(1-\lambda)y^{1+\Delta}} \int_{2^{\lambda-1}y}^{y} dw\, w^\Delta \left\{2\psi_0 h(w) + w^\Delta \left[-c + h(w)\right]^2\right\} \tag{4.13}$$

and in which T is a contraction. Define $C_{\infty,\epsilon}(y)$ to be the space of continuous functions vanishing at the origin and so that there exists a C such that

$$\zeta^{-\epsilon} g(\zeta) \le C \qquad (0 \le \zeta \le y). \tag{4.14}$$

If one then defines

$$\|h\|_{\infty,\epsilon} = \sup_{0\le w\le y} \left|w^{-\epsilon} h(w)\right|, \tag{4.15}$$

it is easy to see that the operator T maps $C_{\infty,\epsilon}(y)$ on itself as long as $\epsilon \le \Delta$. It is further straightforward to show that

$$\|T[h]\|_{\infty,\epsilon} \le C(\epsilon)\, \|h\|_{\infty,\epsilon} + a(y)\, \|h\|^2_{\infty,\epsilon} + b(y), \tag{4.16}$$

where $C(\epsilon) < 1$ whereas $a(y)$ and $b(y)$ go to zero as $y \to 0$. From this follows that T leaves a ball of appropriately small radius R invariant if ϵ is fixed and y is small enough.

To show that T is in fact a contraction on such a ball for y sufficiently small, one computes the norm of

$$T[h_1] - T[h_2] = \frac{1}{(1-\lambda)y^{1+\Delta}} \int_{2^{\lambda-1}y}^{y} dw\, w^{\Delta}\big\{2\psi_0\,[h_1(w) - h_2(w)] + \\ + w^{\Delta}\,[h_1(w) - h_2(w)]\,[h_1(w) + h_2(w) - 2c]\,\big\}. \tag{4.17}$$

For the first term one shows

$$\frac{1}{(1-\lambda)y^{1+\Delta+\epsilon}} \int_{2^{\lambda-1}y}^{y} dw\, w^{\Delta} 2\psi_0\,[h_1(w) - h_2(w)] \le \frac{2\psi_0}{1-\lambda} \int_{2^{\lambda-1}}^{1} dw\, w^{\Delta+\epsilon} \cdot \|h_1 - h_2\|_{\infty,\epsilon}\,. \tag{4.18}$$

It then readily follows from the equation (4.10) defining Δ that the numerical constant before $\|h\|_{\infty,\epsilon}$ is strictly less than one if $\epsilon > 0$. For the second term, on the other hand, one finds, as is easily checked, that it is bounded by

$$C(y)(\|h_1\|_{\infty,\epsilon} + \|h_2\|_{\infty,\epsilon})\,\|h_1 - h_2\|_{\infty,\epsilon} \tag{4.19}$$

where $C(y)$ goes to zero as y does. Since we have restricted ourseleves to a ball of given radius R, the prefactor $\|h_1\|_{\infty,\epsilon} + \|h_2\|_{\infty,\epsilon}$ is bounded by $2R$, so that the entire mapping T is indeed a contraction for y small enough.

To show global existence and decay to zero, we must first choose $c > 0$. From this immediately follows that there is a neighbourhood of zero in which the solution $\psi(y)$ is monotonically decreasing. One now shows using (4.6) that this property never disappears for any positive value of y. Indeed, if $\psi(y)$ were to increase for some value of y, it would have had to pass through a minimum at some value of y. Let y_0 be the first non-zero value of y for which $\psi'(y) = 0$. One then finds

$$\begin{aligned} 0 &= \psi(y_0)^2 - (1-\lambda)\psi(y_0) - 2^{\lambda-1}\psi(2^{\lambda-1}y_0)^2 \\ &< (1-2^{\lambda-1})\psi(y_0)^2 - (1-\lambda)\psi(y_0) \\ &< \psi(y_0)\Big[(1-2^{\lambda-1})\psi_0 - (1-\lambda)\Big] = 0, \end{aligned} \tag{4.20}$$

which is absurd. Here the first inequality follows from the monotonicity of $\psi(y)$ before y_0, and so does the second, since ψ_0 is the initial value of $\psi(y)$. Both are strict since $\psi'(y) \neq 0$ for $y < y_0$.

Once the local solution near the origin has been found, however, the equation (4.6) can be considered as an ODE and the standard existence and uniqueness results apply: indeed, the function $\psi(2^{\lambda-1}y)$ is *already known* at y. In other words, if $\psi_n(y)$ is defined to be $\psi(y)$ restricted to the interval I_n given by $[2^{(1-\lambda)(n-1)}, 2^{(1-\lambda)n}]$, then equation (4.6) can be viewed as an ODE connecting ψ_n' and ψ_{n-1}. This then allows a recursive application of the usual existence and uniqueness results, since there is, by the local result just proved, a unique solution for n sufficiently negative. Furthermore, the integral form of the equation for $\psi(y)$, which is given by

$$(1-\lambda)y\psi(y) = \int_{2^{\lambda-1}y}^{y} dw\, \psi(w)^2 \tag{4.21}$$

guarantees the positivity of $\psi(y)$ wherever it exists. With these remarks, standard theorems on ordinary differential equations yield global existence of $\psi(y)$ on the positive real axis.

Proving that $\psi(y)$ decays to zero exponentially fast as $y \to \infty$ is now straightforward: indeed, from (4.21) and the monotonicity properties of $\psi(y)$ follows immediately

$$\psi(y) \leq \frac{1 - 2^{\lambda-1}}{1-\lambda} \psi(2^{\lambda-1}y)^2 = \psi_0^{-1} \psi(2^{\lambda-1}y)^2, \tag{4.22}$$

from which one obtains exponential decay in the following way: since $\psi(y) < \psi_0$ for $y > 0$, by applying this identity repeatedly one eventually shows that there is an interval I_{n_0} such that $\psi(y) \leq M < 1$ on it. Now, if $x \in I_n$, it follows that the inequality (4.22) can be applied iteratively $n - n_0$ times to yield

$$\psi(y) \leq \psi_0^{-(n-n_0)} \psi(2^{(n-n_0)(\lambda-1)}y)^{2^{n-n_0}} \leq \psi_0^{-(n-n_0)} M^{2^{n-n_0}}, \tag{4.23}$$

from which exponential decay in y follows, since $y \in I_n$ means that $(1-\lambda)(n-1)\ln 2 \leq \ln y \leq (1-\lambda)n \ln 2$. Note that the prefactor increasing exponentially in n corresponds only to a power law in y and is therefore a subdominant correction.

I mention here an easier way of proving a local existence result, but which may be difficult to extend to an equally strong uniqueness result: one can make the Ansatz

$$\psi(y) = \psi_0 + \sum_{n=1}^{\infty} c_n y^{n\Delta} \tag{4.24}$$

and plug this in (4.6) keeping at first Δ a free parameter. A recursion for the c_n is easily derived, which is, however, in general inconsistent for c_1. The consistency condition is, of course, the transcendental equation (4.10) for Δ. c_1 can then be chosen arbitrarily, thereby determining the c_n uniquely. Convergence is also readily verified by inspection of the recurrence. This result shows as an added bonus that $\psi(y)$ is analytic in y^Δ around the origin.

From the result shown we have therefore proved that for each negative value of c_1 there exists a solution of the original equation (4.3) of the form

$$\Phi(x) = x^{-(1+\lambda)} \left[\psi_0 + \sum_{n=1} c_n x^{n\Delta} \right] \tag{4.25}$$

for small values of x and that this function exists on the entire positive real axis as a positive function which decays exponentially to zero. It therefore satisfies the scaling equation and all the boundary conditions imposed upon it, since it is easy to see that the normalization to one of the first moment of $\Phi(x)$ can be obtained through an appropriate choice of c_1, as the first moment is finite for functions of the type described by (4.25). ■

5 The diagonal kernel: The gelling case

Let us now consider the same diagonal kernel $x^{\lambda+1}\delta(x-y)$ but now for the case $\lambda \geq 1$. We first consider $\lambda > 1$ and then say a few words concerning the case for which $\lambda = 1$, which does not display gelation but for which the ordinary scaling ansatz described in the previous section is nevertheless inapplicable.

The relevant equation (3.5) reduces for the diagonal case to

$$\frac{d}{dx}\left[x^3\Phi(x)\right]-(3-\tau)x^2\Phi(x)=x^{\lambda+3}\Phi(x)^2-2^{-(\lambda+3)}x^{\lambda+3}\Phi(x/2)^2, \tag{5.1}$$

where $\Phi(x)$ should satisfy the boundary condition at zero

$$\Phi(x)=const.\cdot x^{-\tau}\qquad (x\to 0) \tag{5.2}$$

as well as a condition of rapid decay as $x\to\infty$. One now introduces new variables

$$\psi = x^{\tau}\Phi(x)$$
$$\zeta = \frac{x^{1+\lambda-\tau}}{1+\lambda-\tau}. \tag{5.3}$$

Note that in our new variables the condition (5.2) translates into the requirement that ψ be regular at the origin. We have also made the implicit assumption that $1+\lambda-\tau>0$: this is quite unproblematic, since through the relation (3.6) determining σ it follows that this must always hold if we wish to describe a gelling system.

The relation (5.1) now transforms to

$$\frac{d\psi}{d\zeta}=\psi(\zeta)^2-2^{2\tau-\lambda-3}\psi\big(2^{\tau-\lambda-1}\zeta\big)^2. \tag{5.4}$$

Local existence is here easy to show: one makes an ansatz in power series

$$\psi(\zeta)=\sum_{k=0}^{\infty}a_k\zeta^k. \tag{5.5}$$

It is then straightforward to determine a recursion for the a_k and to prove that it converges in a finite interval. No inconsistencies arise in this recursion, so we may simply set $a_0=1$. It follows that

$$a_1=1-2^{2\tau-\lambda-3}. \tag{5.6}$$

Let us then always limit ourselves to the case $\tau>(\lambda+3)/2$, so as to have an initially monotonically decaying function. Note here that this shows the claim made in the text, that the correction to scaling exponent of $\Phi(x)$ is $1+\lambda-\tau$: indeed, we have shown that around $\zeta=0$, $\psi(\zeta)$ is analytic, which together with the definition of ζ in (5.3) shows the result. In fact, the result obtained is stronger: it states that $\Phi(x)$ is of the form

$$\Phi(x)=x^{-\tau}f\left(x^{1+\lambda-\tau}\right), \tag{5.7}$$

where $f(\zeta)$ is a function analytic around zero.

Since $\tau>(\lambda+3)/2$ one can show that this leads, as in the preceding section, to global existence unless the solution becomes negative. It is a crucial difference with the previous case that this can actually happen for given values of τ, as we shall see shortly.

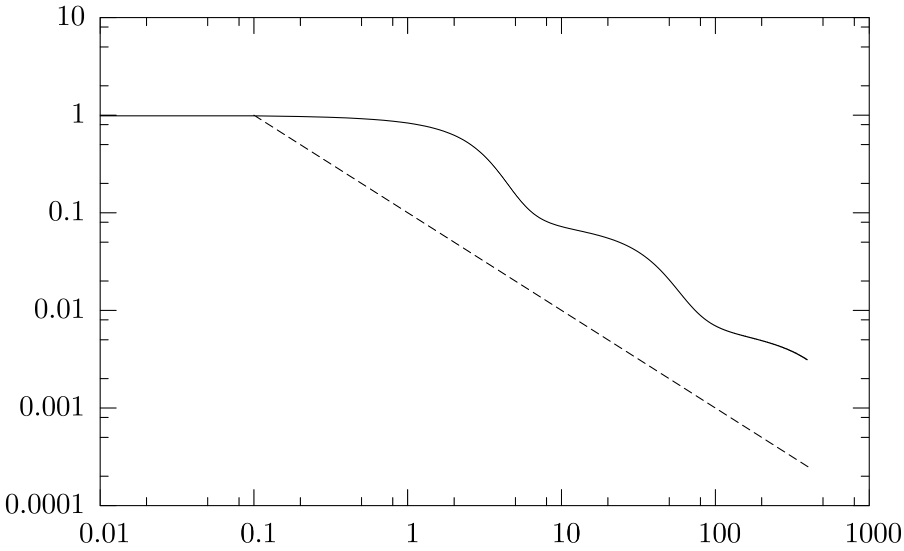

Figure 1. A solution of (5.4) corresponding to $\lambda = 2$ and $\tau = 2.6$ plotted as a function of ζ: the dotted curve corresponds to $1/\zeta$ behaviour. Note the overall parallelism as well as the logarithmic oscillations of the function. The occurrence of such oscillations is intriguing, as they have been tentatively reported by Lee [13] for the scaling function in non-gelling systems of type I. The curve shown here, on the other hand, is an inadmissible solution for a gelling system.

One proceeds as before: let ζ_0 be the first value of ζ for which $\psi'(\zeta) = 0$. Since $\psi(\zeta)$ is monotonically decreasing for $\zeta < \zeta_0$, one finds using (5.4) that $\psi'(\zeta_0) < 0$, which is clearly absurd.

Performing a detailed qualitative analysis of (5.4) is much more difficult than the corresponding task in the non-gelling case. I shall therefore appeal to numerical evidence, which seems to me quite compelling. Let us disregard considerations of uniqueness and look for a solution in the region $\tau > (\lambda+3)/2$, for which I know that the solution is always decreasing. $\psi(\zeta)$ therefore either crosses to negative values at some value of ζ, in which case it is surely not a physically relevant solution, or else it exists as a positive function for all positive values of ζ. In this latter case it is also easy to check that it must go to zero, as it cannot saturate to a constant non-zero value unless $\tau = (\lambda+3)/2$. If τ is barely larger than $(\lambda + 3)/2$, it is relatively easy to see that $\psi(\zeta)$ must cross to negative values and numerical work amply confirms this expectation. This is found by comparing (5.4) with

$$\frac{df}{d\zeta} = f(\zeta)^2 - (1+\epsilon)f(0)^2, \tag{5.8}$$

which is close, as for such values of τ $\psi(\zeta)$ is nearly constant. It then suffices to show that, for small values of ϵ, the solution of (5.8) crosses the negative axis for values of ζ at which the value $\psi(2^{\tau-\lambda-1}\zeta)$ is still close to its original value. Another asymptotic behaviour which is consistent with (5.4) is a ζ^{-1} decay. Such a decay can in fact be shown to occur in the case $\tau = \lambda + 1$, since (5.4) can then be solved exactly and is found to have this

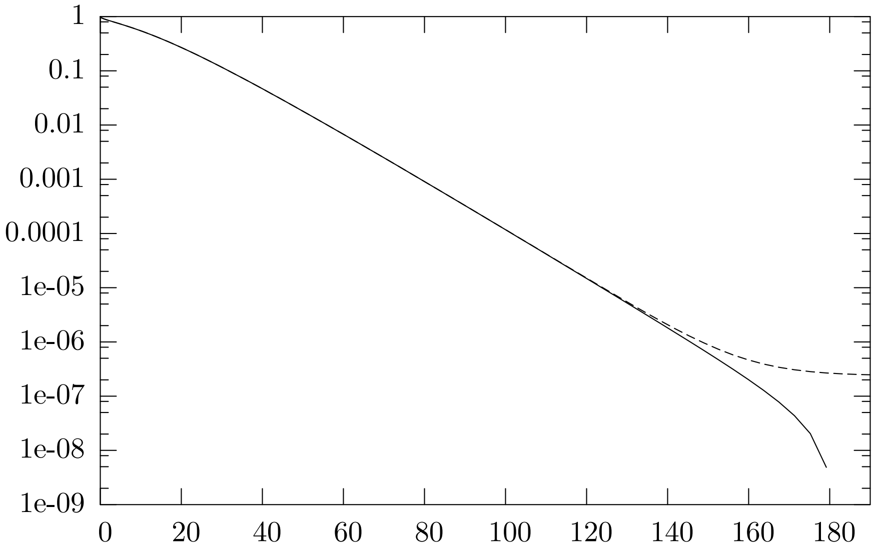

Figure 2. Two solutions of (5.4) for $\lambda = 2$ corresponding to two nearby values of τ plotted as a function of x, that is $\zeta^{1/(1+\lambda-\tau)}$): for the lower curve $\tau = 2.5542887$ whereas for the upper one $\tau = 2.5542888$. Note how one crosses over to negative values, whereas the other seems to saturate. Note also the rapid decay common to both curves, which suggests the existence of an exponentially decaying solution of (5.4) for some critical τ.

behaviour. Again, as shown in Fig. 1 for the case $\lambda = 2$ and $\tau = 2.6$, such a decay is indeed observed for values of τ somewhat larger than those for which a crossing to negative values was observed. What we want, however, is neither: negative values are unphysical and the ζ^{-1} is too slow to be acceptable. One needs a function having a rapid decay for large ζ. We may therefore ask whether between the two regimes there is a (conceivably unique) value of τ for which this occurs. In fact, we anticipate exponential decay in x and hence a corresponding streched exponential decay in ζ. Fig. 2 gives a striking confirmation of this suggestion: it plots for $\lambda = 2$ two quite nearby values of τ. For the lesser, we see a crossing to negative values, for the higher, a saturation apparently to a constant (but theory states this to be impossible, so it is presumably a ζ^{-1} behaviour), but both exhibit over a very large range exactly the expected exponential decay: for clarity I have plotted $\psi(\zeta)$ as a function of x on a semilogarithmic scale, for which the expected result is a straight line.

Let us end by some remarks concerning the limiting case $\lambda = 1$. If we refer to the results of the previous section for the non-gelling case, we find that they do not apply, as all equations become highly singular and the proofs all fail. The reason for this is to be found in the fact that if Theorem 1 were valid, $\Phi(x)$ would have an x^{-2} singularity at the origin, thereby precluding the use of the scaling hypothesis (2.3). Indeed, for (2.3) to hold, the normalization condition (2.4) is necessary, and this is contradicted by the existence of such a singularity. We therefore treat the subject as if it were a gelling case and study the second moment as in (3.2). This leads [17] to a typical size $s(t)$ of the form

$$s(t) = const. \cdot \exp(K\sqrt{t}) \tag{5.9}$$

and a function $\Phi(x)$ satisfying

$$\frac{d}{dx}\left[x^3\Phi(x)\right] - x^2\Phi(x) = x^4\Phi(x)^2 - (x/2)^4\Phi(x/2)^2, \tag{5.10}$$

which is merely (5.1) in the special case in which $\lambda = 1$ and $\tau = 2$.

We now state our results for this case:

Theorem 2. *For each $a_1 < 0$ (5.10) has a unique solution of the form*

$$\Phi(x) = x^{-2}\left[1 + \sum_{k=1}^{\infty} a_k x^k\right]. \tag{5.11}$$

$x^2\Phi(x)$ is monotonically decreasing on the positive real axis and bounded by an exponential function $C\exp(-ax)$ for some positive constants C and a. It is also C_∞ in $[0,\infty)$.

Remark. Note that there are other solutions to (5.10) which are not of the form (5.11). In particular, the same proof as below shows that there are solutions of the form

$$\Phi(x) = x^{-2}\left[\psi_0 + \sum_{k=1}^{\infty} a_k x^{k\Delta}\right] \tag{5.12}$$

for all $\psi_0 > 0$ where Δ is the unique positive solution of

$$\frac{\Delta}{2(1 - 2^{-\Delta})} = \psi_0. \tag{5.13}$$

It is readily seen, however, that these solutions bring no new scaling solutions, since the exponent Δ can be absorbed in the constant K of (5.9). I also am not sure whether solutions with power-law tails having a form different from (5.12) could exist.

Proof. The change of independent variable in (5.3) now becomes singular, so we merely change to

$$\psi = x^2\Phi(x). \tag{5.14}$$

Note that we still have the boundary condition $\psi(x)$ regular at the origin, corresponding to (5.2) for $\tau = 2$. This then yields

$$x\frac{d\psi}{dx} = \psi(x)^2 - \psi(x/2)^2. \tag{5.15}$$

One finds a solution as follows: the ansatz

$$\psi(x) = 1 + \sum_{k=1}^{\infty} a_k x^k \tag{5.16}$$

leads, as is readily verified, to a recurrence for the a_k which is consistent throughout and for which a_1 can be chosen arbitrarily, after which all a_k are uniquely determined. Convergence of the series (5.16) in a finite interval around zero is also easily checked. Again choose a_1 to be negative. It follows immediately that $\psi(x)$ is monotonically decreasing in a neighbourhood of the origin and hence, by an argument entirely similar to that presented in Section 4, wherever it exists on the positive real axis. The equation can also be rewritten in integral form as

$$\psi(x) = \int_{x/2}^{x} \frac{dy}{y} \psi(y)^2, \tag{5.17}$$

which shows that $\psi(x)$ is always positive on the positive real axis. This leads, using the same approaches as previously, to a global existence result for the solution of (5.10). From (5.17) one also immediately derives the inequality

$$\psi(x) \leq \ln 2 \, \psi(x/2)^2 \tag{5.18}$$

from which, as in the previous section, exponential decay of $\psi(x)$ is readily deduced. ■

6 Conclusions and outlook

Summarizing, we have shown that the equations describing the scaling function for the Smoluchowski equations describing irreversible aggregation have a unique solution within a given family of physically reasonable solutions when the reaction rates are of such a nature as only to allow reactions between aggregates of identical sizes. Since this kernel is dominated by diagonal reactions, it belongs to the so-called type I kernels. For these the very existence of a solution to the scaling equation (2.3) has sometimes been doubted, both on theoretical and numerical grounds: theoretically, because of the existence of a non-normalizable solution of the type $x^{-(1+\lambda)}$, which indicates that the constraint of fast decay at infinity must play an essential role in determining the solution. Numerical work on some kernels of type I also led to doubts concerning scaling [10], though these were later contradicted by [13], who showed that the previous finding may have been due to non-monotonic behaviour of the scaling function for the rates under consideration. For the diagonal case under study, I have not only rigorously shown existence in the non-gelling case, but also monotonicity. For the gelling case, on the other hand, it was suggested by numerical evidence that whenever $\tau > (\lambda + 3)/2$, there are only two possible behaviours in general, namely becoming negative or decaying algebraically to zero from above. Just at the border between these two unphysical behaviours, numerical evidence again strongly suggests that a positive and exponentially decaying solution exists. This then allows a determination of the exponent τ. As stated already in [17], it is not to be expected that the "standard" value $\tau = (\lambda + 3)/2$ broadly quoted in the literature should be generally valid. In fact, it follows from the considerations made in this paper that no solutions of this type can exist for the diagonal kernel. For the limiting case $\lambda = 1$, we have shown rigorously the existence of a solution of the scaling equation (3.5) derived from an assumed weak convergence of the (appropriately rescaled) measure $m^2 c(m,t)dm$ to a limiting distribution $x^2\Phi(x)dx$. These are related to the modified scaling ansatz introduced by van Dongen [24]. No such explicit solutions have, to my knowledge, been derived before.

Finally, it must be remembered that none of all this has any relevance unless it is somehow shown that the solutions of the time-dependent problem corresponding to the original Smoluchowski equations (1.2) can be shown to approach the scaling limit. It is possible that the recursive structure underlying the diagonal kernel might make this result somewhat easier to show. It remains, however, a formidable task, left to future research.

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