Exact asymptotic solution of an aggregation model with a bell-shaped distribution

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Abstract

We present in a detailed manner the scaling theory of irreversible aggregation characterized by the set of reaction rates $K(k,l) = 1/k + 1/l$, as well as a minor generalisation thereof. In this case, it is possible to evaluate the scaling function exactly. By this we mean that it is expressed as the unique solution of an ordinary differential equation with given boundary conditions. This can be solved numerically to high accuracy, making a highly detailed analysis of the scaling behaviour possible. The results confirm the far more general results of earlier work concerning a general scaling theory for so-called reaction rates of Type III. On the other hand, the behaviour of large aggregates at fixed time, that is, not in the scaling limit, which had been up to now analysed in an approximation valid in the limit of small times, can be determined more precisely in this case, and is shown to display subtle differences from the small-time approximation.
I. INTRODUCTION

Irreversible aggregation is the process whereby aggregates grow by the scheme

\[ A_k + A_l \xrightarrow{K(k,l)} A_{k+l}, \]  

with no backward reaction. Here \( A_k \) denotes an aggregate consisting of \( k \) elemental aggregates (monomers) and \( K(k,l) \) denotes the dependence of the rate at which the aggregation occurs, as a function of the masses of the 2 aggregates.

Such processes occur in a broad variety of physical systems. Thus in aerosols and colloids these are quite common, as well as in many other contexts. The concentration \( c_j(t) \) of aggregates of mass \( j \) varies according to the following kinetic equation

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

The size dependence of the \( K(k,l) \) is determined by the detailed physics of the process under study. For aerosols which diffuse and coalesce irreversibly in three dimensions, for instance, a standard approximation for the rate is given by

\[ K(k,l) = [R(k) + R(l)] [D(k) + D(l)] \]  

where \( R(k) \) describes the typical radius of an aggregate of mass \( k \) and \( D(k) \) its diffusion constant. If the aggregates are spherical objects, we have \( R(k) \) proportional to \( k^{1/3} \) and similarly \( D(k) \) goes as \( k^{-1/3} \).

A general scaling theory for the solutions of \( (2) \) was developed by [1–3] following initial earlier work in [4], and reviewed in [5]. In it, it is assumed that there exist a function \( S(t) \) diverging as \( t \to \infty \), which corresponds to the typical size of the aggregate size distribution at time \( t \), and a function \( \Phi(x) \) such that

\[ c_j(t) \sim [S(t)]^{-2} \Phi \left( \frac{j}{S(t)} \right). \]  

The scaling theory makes two kinds of predictions. One is extremely general, and concerns the rate of growth of \( S(t) \). Let the reaction kernel \( K(k,l) \) be homogeneous of degree \( \lambda \), that is

\[ K(ak,al) = a^\lambda K(k,l) \]  

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at least asymptotically as $k,l \to \infty$. Then the typical size $S(t)$ grows as

$$S(t) \simeq t^{1/(1-\lambda)} \quad (t \to \infty).$$

(6)

A more detailed analysis concerns the small-$x$ behaviour of $\Phi(x)$, which leads to the distribution of cluster sizes for sizes much less, as well as much larger, than the typical size.

To this end, we need to define another exponent characterising the behaviour of $K(k,l)$ for very different values of $k$ and $l$: first let us define

$$K(k,l) = k^\lambda K \left( \frac{l}{k} \right).$$

(7)

The exponents $\mu$ and $\nu$ are then given by

$$K(x) \simeq x^\nu \quad (x \to \infty),$$

(8a)

and

$$K(x) \simeq x^\mu \quad (x \to 0).$$

(8b)

It follows immediately from the definition that

$$\mu + \nu = \lambda$$

(9)

For example, if we take the case of the rates $K(k,l)$ given by (3):

$$K(k,l) = \left( k^{1/3} + l^{1/3} \right) \left( k^{-1/3} + l^{-1/3} \right),$$

(10)

we find the values $\lambda = 0$, $\mu = -1/3$ and $\nu = 1/3$.

These exponents define to a large extent the nature of the scaling behaviour of the system. First, all our considerations pertain to the case $\lambda < 1$. When $\lambda > 1$, a divergence of the typical size followed by loss of mass to an infinite aggregate occurs at finite time. Rates for $\lambda < 1$ are divided in 3 broad types, according to the sign of $\mu$. Type I corresponds to $\mu > 0$, Type II to $\mu = 0$, and Type III to $\mu < 0$. The kernel \[3\] is thus of Type III.

The scaling function behaves for $x \ll 1$ differently for the 3 types. For type I we have

$$\Phi(x) \simeq x^{-\tau}, \quad \tau = 1 + \lambda$$

(11)

for $x \ll 1$. This means that there is a broad range of sizes over which the aggregates are power-law distributed. On the other hand, Type II kernels behave in a quite non-universal manner. In most known cases, $\Phi(x)$ also goes as a power $x^{-\tau}$, but for a value of $\tau$ which
depends on the detailed behaviour of \( K(k,l) \). Finally, Type III kernels have a scaling function \( \Phi(x) \) which goes faster than any power towards zero as \( x \to 0 \). Specifically

\[
\Phi(x) \simeq \text{const.} \cdot x^{-\lambda} \exp\left(-\text{const.} \cdot x^{-|\mu|}\right).
\] (12)

The aggregate sizes do not show a great variation and their distribution is sometimes described as being bell-shaped.

Another issue is the behaviour of \( \Phi(x) \) for \( x \gg 1 \). In that case, \( \Phi(x) \) always decays exponentially, but also has a correction exponent \( \theta \) defined by

\[
\Phi(x) \simeq \text{const.} \cdot x^{-\theta} \exp\left(-\text{const.} \cdot x\right).
\] (13)

For all kernels we have

\[
\theta = \lambda,
\] (14)

except in the case \( \nu = 1 \), for which a similar lack of universality exists as for the \( x \ll 1 \) behaviour when \( \mu = 0 \) [2].

There are several rate kernels for which (2) can be solved exactly. Interestingly, if we limit ourselves to the non-gelling case \( \lambda \leq 1 \), they are all of type II; the most prominent examples are

\[
K_1(k,l) = \alpha + \beta(k + l),
\] (15a)

\[
K_2(k,l) = 2 - q^k - q^l \quad (q < 1),
\] (15b)

\[
K_3(k,l) = \alpha \delta_{k,1} \delta_{l,1} + \beta (\delta_{k,1} + \delta_{l,1}) + \gamma,
\] (15c)

\[
K_4(k,l) = \alpha + \beta \left[(-1)^k + (-1)^l\right] + \gamma(-1)^{k+l}.
\] (15d)

where \( \alpha, \beta, \) and \( \gamma \) are arbitrary constants, positive or zero [6–9]. It would thus be of interest to obtain any kind of rigorous information on kernels of type I or III. In particular, it is of interest to obtain exact, or at least accurate, asymptotic results, for a kernel of type III, since these are the kind that arises in the most natural way in aerosol physics.

In the following we consider the case, also treated earlier in [10], given by

\[
K(k,l) = \frac{1}{k} + \frac{1}{l},
\] (16)

as well as the faintly more general version

\[
K(k,l) = \frac{1}{\alpha k + \beta} + \frac{1}{\alpha l + \beta},
\] (17)
for $\alpha \geq 0$ and $\beta > -\alpha$ arbitrary. Here, the main result we shall show is that the scaling behaviours of (16) and (17) are rigorously identical. This has $\lambda = \mu = -1$, so that we have

$$S(t) \simeq \sqrt{t}. \quad (18)$$

and presumably

$$\Phi(x) \simeq \text{const.} x^{-1} \cdot \exp (-\text{const.} \cdot x^{-1}) \quad (x \ll 1). \quad (19)$$

On the other hand, for $x \gg 1$, we obtain

$$\Phi(x) \simeq \text{const.} \cdot x \exp (-\text{const.} \cdot x). \quad (20)$$

In the following we shall show rigorously the above relations, and additionally evaluate explicitly the different constants involved. We further provide a technique to evaluate the scaling function to high accuracy. We shall also obtain subleading corrections to the behaviours stated above.

Beyond the scaling limit, some other issues can also be treated. In particular we discuss the large-time behaviour of clusters of fixed size, which cannot be found via scaling. Similarly, the limit of large sizes for clusters at a fixed given time can be treated to a high degree of accuracy. In earlier treatments [15, 16], this behaviour was obtained through an approximation valid only in the limit of small times. Here we solve exactly this small-time limit for the reaction rates (16) and show that it does not coincide rigorously with the finite-time large size behaviour: whereas the former is a purely exponential decay with a constant prefactor, the latter involves a correction to the prefactor inversely proportional to the squared size.

II. PROBLEM AND FUNDAMENTAL EQUATIONS

The Smoluchowski’s equations (2) read, for the case we are interested in

$$\dot{c}_j = \sum_{k=1}^{j-1} \frac{c_k c_{j-k}}{\alpha k + \beta} - \frac{c_j}{\alpha j + \beta} \sum_{k=1}^\infty c_k - c_j \sum_{k=1}^\infty \frac{c_k}{\alpha k + \beta} \quad (21)$$

Kernels of the form

$$K(k, l) = f(k) + f(l) \quad (22)$$
can be treated using a standard transformation, introduced by Lushnikov [11]. We introduce
the new dependent and independent variables
\[ N(t) = \sum_{k=1}^{\infty} c_k(t) \quad (23a) \]
\[ \phi_j = \frac{c_j}{N(t)} \quad (23b) \]
\[ ds = N(t)dt. \quad (23c) \]
In these, the equations (21) read
\[ \frac{d\phi_j}{ds} = \sum_{k=1}^{j-1} \frac{\phi_k \phi_{j-k}}{\alpha k + \beta} - \frac{\phi_j}{\alpha j + \beta} \quad (24) \]
This can be carried through for any kernel of the form (22) and eliminates the non-recursive
removal terms, which is always a considerable step towards the solution. Indeed, it is clear
that an exact expression for \( \phi_j(s) \) can always be obtained recursively, by solving a linear
equation with a (recursively known) inhomogeneity. The rapidly growing complexity of the
resulting expressions makes this approach impractical. As an example, the first 4 values
yield, for the special case \( \alpha = 1 \) and \( \beta = 0 \):
\[ \phi_1(s) = e^{-s} \quad (25a) \]
\[ \phi_2(s) = \frac{2e^{-2s}}{3} (e^{3s/2} - 1) \quad (25b) \]
\[ \phi_3(s) = \frac{e^{-3s}}{56} (-48e^{3s/2} + 27e^{8s/3} + 21) \quad (25c) \]
\[ \phi_4(s) = \frac{2e^{-4s}}{36855} (13000e^{3s/2} - 10935e^{8s/3} - 5460e^{3s} + 
6944e^{15s/4} - 3549) \quad (25d) \]
In the present case additional progress can be made: define the generating function
\[ G(z, s) := \sum_{j=1}^{\infty} \frac{\phi_j(s)}{\alpha j + \beta} e^{-jz}. \quad (26) \]
(24) then reads
\[ \alpha G_{zz}(z, s) - \beta G_z(z, s) = [\alpha G_z(z, s) - \beta G(z, s)] G(z, s) + G(z, s) \quad (27) \]
Frequently, being able to cast a problem as a PDE in the way we have done here leads
straightforwardly to the full solution. This is not the case here: the PDE (27) is surprisingly
complex—even for \( \alpha = 1 \) and \( \beta = 0 \)—and I have made no headway at all.
Let us then look at the scaling limit. Using the standard approach discussed for example in [5], the scaling theory predicts the existence of a function $S(t)$ which grows as $\sqrt{t}$ and of a function $\Phi(x)$ such that

$$\lim_{t \to \infty} \sum_{j=1}^{\infty} j c_j(t) f \left( \frac{j}{S(t)} \right) = \int_{0}^{\infty} x \Phi(x) f(x) dx$$

(28)

holds for all appropriate functions $f(x)$. Putting $f(x) = 1/x$—which is possibly a problem from a rigorous viewpoint, but we are now only making plausibility considerations—one immediately obtains that

$$N(t) = \text{const.} \cdot S(t)^{-1} = O(t^{-1/2}).$$

(29)

From this follows that we expect the following scaling form for $G(z,s)$:

$$G(z,s) = \frac{1}{s} \Psi(zs).$$

(30)

Putting this into (27) leads to

$$\alpha \rho \Psi'' = \alpha \Psi \Psi' + \Psi$$

(31)

The dependence on $\alpha$ is readily scaled away by redefining

$$\Psi_\alpha(\rho) = \Psi(\rho/\alpha)$$

(32)

and $\Psi(\rho)$ satisfies the equation

$$\rho \Psi'' = \Psi \Psi' + \Psi$$

(33)

independently of $\alpha$. Again I have not been able to find a solution of this apparently simple equation. In Appendix A I show a large number of detailed properties of (33). In particular, I show that there is a unique solution such that $\Psi(x)$ is positive, smooth at the origin and monotonically decreasing to zero. Solutions smooth at the origin are characterised by the initial conditions

$$\Psi(0) = 1, \quad \Psi'(0) = -1, \quad \Psi''(0) = \kappa,$$

where $\kappa$ is arbitrary. The unique monotonically decreasing positive solution is characterised by a uniquely defined value $\kappa_0$ numerically found to be between 1.45582 and 1.45583. All
other solutions of the type described by (34) diverge or become negative, where \( \kappa > \kappa_0 \) leads to divergence and \( \kappa < \kappa_0 \) to negative values. Since the latter behaviours cannot arise in the kind of function we are looking for, it is clear that the unique solution defined by \( \kappa = \kappa_0 \) is the only acceptable one.

The fact that the solution of (21) actually tends towards the scaling solution defined by (33) follows from the work of Norris [12], whereas the fact that the integro-differential equation which the scaling function can be shown to satisfy [3] actually has a solution under fairly general circumstances, was shown in [13]. The peculiar feature of our approach, however, resides in the very explicit nature of the equations to be solved, and the rather immediate, though somewhat tedious, character of the proof of existence, which is entirely constructive. It is performed in detail in Appendix A. We also show in Appendix B in detail that (33) also follows from the well-known integro-differential equation introduced in [3, 4].

III. SCALING RESULTS

Let us first establish a connection between \( G(z, s) \) and \( \Phi(x) \). Let us take \( S(t) \) to be equal to \( s \). We then have

\[
\sum_{j=1}^{\infty} j c_j(t) \exp \left( -\frac{j \rho}{s} \right) = N(s) \sum_{j=1}^{\infty} j \phi_j(t) \exp \left( -\frac{j \rho}{s} \right) = s^2 N(s) \partial_{\rho}^2 G \left( \frac{\rho}{s}, s \right).
\]

In the scaling limit, we have

\[
\lim_{s \to \infty} \sum_{j=1}^{\infty} j c_j(t) \exp \left( -\frac{j \rho}{s} \right) = \int_0^{\infty} dx \Phi(x) e^{-\rho x}.
\]

We thus have

\[
\lim_{s \to \infty} \left[ s^2 N(s) \partial_{\rho}^2 G \left( \frac{\rho}{s}, s \right) \right] = \int_0^{\infty} dx \Phi(x) e^{-\rho x}.
\]

Now we know that if \( sG(\rho/s, s) \) tends to a limit, that limit is the function \( \Psi(\rho) \) defined by (33) and described in greater detail in Appendix A. As we have stated before, it is uniquely determined by the differential equation (33) together with the conditions that it be regular at \( x = 0 \) and positive and finite for all positive values of \( x \). We thus obtain

\[
\lim_{s \to \infty} [sN(s)] \partial_{\rho}^2 \Psi(\rho) = \int_0^{\infty} dx \Phi(x) e^{-\rho x}.
\]
and hence
\[ s\Psi(\rho) = \lim_{s \to \infty} \left[ sN(s) \right] \int_0^\infty dx \frac{\Phi(x)}{x} e^{-\rho x}. \] (39)

We thus see that, up to a constant which we shall later show to be equal to \( \kappa_0 \), \( \Psi(\rho) \) is the Laplace transform of \( \Phi(x)/x \), where \( \Phi(x) \) is the ordinary scaling function for the concentrations \( c_j(t) \).

**A. Large-time behaviour of moments and connection between \( t \) and \( s \)**

Using the definition of \( \Phi(x) \) in (36) with \( \rho = 0 \), we obtain the identity
\[ \int_0^\infty x \Phi(x) dx = 1, \] (40)
from which we obtain from (38) that
\[ \lim_{s \to \infty} [sN(s)] = \frac{1}{\Psi''(0)} = \kappa_0^{-1}, \] (41)
thereby showing the claim made after (39). Since the derivatives of \( \Psi(\rho) \) at the origin can all be computed recursively in terms of \( \kappa_0 \), we have
\[ \mu_n(s) = \sum_{j=1}^\infty j^n c_j(t) \]
\[ = N(s)s^n \sum_{j=1}^\infty j^n \phi_j(s) \]
\[ = (-1)^{n+1} \partial_{\rho}^{n+1} \Psi(\rho) \bigg|_{\rho=0} \kappa_0^{-1} s^{n-1} \] (42)
so that we can compute the asymptotic behaviour of the moments \( \mu_n(s) \):
\[ \mu_n(s) = m_n^{(\infty)} s^{n-1}, \] (43a)
\[ m_n^{(\infty)} = \kappa_0^{-1} (-1)^{n+1} \partial_{\rho}^{n+1} \Psi(\rho) \bigg|_{\rho=0}. \] (43b)

We can further obtain the asymptotic connection between \( s \) and \( t \). Indeed, since asymptotically \( \kappa_0 s N(s) \) tends to 1, we have
\[ \lim_{s \to \infty} \frac{2t(s)}{\kappa_0 s^2} = 1. \] (44)

Moreover, along these lines, the fact that \( \Psi(0) = 1 \) tells us that
\[ \lim_{s \to \infty} \left( s^2 \sum_{j=1}^\infty \frac{c_j}{j} \right) = \kappa_0^{-1}. \] (45)
Finally, the result obtained in Lemma 3 of Appendix A yields a result for the asymptotic behaviour of yet another moment:

\[
\lim_{s \to \infty} s^3 \sum_{j=1}^{\infty} \frac{c_j}{j^2} = \int_{0}^{\infty} \frac{\Phi(x)}{x^2} dx
\]

\[
= \kappa_0^{-1} \int_{0}^{\infty} d\rho \int_{0}^{\infty} dx \frac{\Phi(x)}{x} e^{-\rho x}
\]

\[
= \kappa_0^{-1} \int_{0}^{\infty} d\rho \Psi(\rho)
\]

\[
= \frac{5}{2\kappa_0}
\] (46)

Thus the asymptotic behaviour of all moments with \( n \geq -2 \) is determined in elementary terms from the knowledge of \( \kappa_0 \).

Even though it is possible to obtain the \( m_n^{(\infty)} \) explicitly by a recursion, it is not possible to obtain an explicit expression for them. Determining their asymptotic behaviour as \( n \to \infty \) is therefore not trivial. Clearly, this depends on the nature of the singularity of \( \Psi(\rho) \) closest to the origin. From the results of Appendix A, Lemma 2, we see that the coefficients of the series development of \( \Psi(\rho) \) are real and of alternating sign, so that this singularity, which we denote by \(-\Lambda\), must lie on the negative real axis. Its value cannot be expressed in elementary terms from \( \kappa_0 \), but it can be computed numerically by integration of (33) up to values of \( \rho \) close to \(-\Lambda\). This is carried out in detail in Appendix C, together with other numerical evaluations. Its position is found to have the value \( \Lambda \simeq 1.576132 \ldots \)

The leading behaviour of the singularity at \(-\Lambda\) is readily found, by matching orders of divergence, to be a simple pole, with a residue \( 2\Lambda \). In other words

\[
\Psi(\rho) \simeq \frac{2\Lambda}{\rho + \Lambda}
\] (47)

for \( \rho \) near \(-\Lambda\), up to singular terms of higher order. Deciding whether or not such corrections exist is a bit more intricate, and is carried out in Appendix D. One finds that there is in fact a correction given by

\[
\Psi(\rho) = \left[ \frac{2\Lambda}{\rho + \Lambda} - 2 - \frac{2}{3} (\rho + \Lambda) \ln (\rho + \Lambda) \right] [1 + o(1)].
\] (48)

From this then follows that there exists a real number \( \Lambda > 0 \) such that

\[
m_n^{(\infty)} = \frac{2}{\kappa_0} (n + 1)! \Lambda^{-n} \left[ 1 - \frac{2}{3n(n + 1)} \right] [1 + o(1)] \quad (n \to \infty).
\] (49)
Here the correction in \( n^{-2} \) corresponds to the singularity found in (48).

In all the preceding considerations, the scaling limit has been used. It may be asked whether this is legitimate. The problem is that small clusters, even in the infinite time limit, are not necessarily described by the scaling limit, as discussed for instance in [8]. The results above thus strictly speaking do not apply to the moments as defined by (42), but rather to moments defined as

\[
\bar{\mu}_{n,\epsilon}(s) = \sum_{j \geq \epsilon s} j^n c_j(s). \tag{50}
\]

The basic result (43a) should thus read rather

\[
m_n(\infty) = \lim_{\epsilon \to 0} \lim_{s \to \infty} \left[ s^{-(n-1)} \frac{s}{\epsilon s} \bar{\mu}_{n,\epsilon}(s) \right]. \tag{51}
\]

It turns out, however, that these refinements are unnecessary, and that (43a) is correct as it stands. The proof is a bit intricate and is thus relegated to Appendix E.

\[\text{B. Behaviour of small clusters}\]

Another important issue is the behaviour of \( \Phi(x) \) close to the origin, that is, the behaviour of cluster of size much less than the typical size \( S(t) \propto s \propto \sqrt{t} \). This corresponds to the behaviour of \( \Psi(\rho) \) for \( \rho \to \infty \). As shown in Appendix A, Lemma 6, \( \Psi(\rho) \) decays as \( 2\Gamma \sqrt{\rho} K_1(2\sqrt{\rho}) \), where \( \Gamma \) is an undetermined positive constant and \( K_1 \) is a modified Bessel function [14]. Asymptotically, this means that

\[
\Psi(\rho) = \sqrt{\pi} \Gamma \rho^{1/4} \exp(-2\sqrt{\rho}) \left[ 1 + o(1) \right] \tag{52}
\]

Note again that the constant \( \Gamma \) does not have an explicit expression in terms of \( \kappa_0 \), but it can be obtained to high accuracy by numerical integration of (33), which leads to the value \( \Gamma \approx 1.70787 \). The details are discussed in Appendix C.

It is readily calculated that

\[
2\sqrt{\rho} K_1(2\sqrt{\rho}) = \int_0^{\infty} \frac{\exp(-1/x)}{x^2} e^{-\rho x} \, dx, \tag{53}
\]

which leads to

\[
\Phi(x) = \frac{\Gamma}{\kappa_0} \frac{\exp(-1/x)}{x} \left[ 1 + o(1) \right] \quad (x \to 0). \tag{54}
\]

This is in agreement with the results of [10] as well as with the general scaling results derived for instance in [5].
We may further ask about the next-to-leading asymptotic small-\(x\) behaviour of \(\Phi(x)\), or correspondingly, the next-to-leading asymptotic large-\(\rho\) behaviour of \(\Psi(\rho)\). This can be obtained as follows: define

\[
H(\rho) = 2\Gamma\sqrt{\rho} K_1(2\sqrt{\rho}), \tag{55}
\]

which is the exact asymptotic behaviour of \(\Psi(\rho)\) and consider

\[
\Psi_1(\rho) = \frac{\Psi(\rho)}{H(\rho)} . \tag{56}
\]

Clearly \(\Psi_1(\rho)\) approaches 1 as \(\rho \to \infty\). If we now rewrite (33) for \(\Psi_1(\rho)\), we find

\[
\rho\Psi''_1 + 2\rho \frac{H'}{H} \Psi'_1 = H\Psi_1\Psi'_1 + 2H'\Psi_1^2 . \tag{57}
\]

Replacing \(\Psi_1\) by its limiting value we obtain

\[
\rho\Psi''_1 + 2\rho \frac{H'}{H} \Psi'_1 = H\Psi'_1 + 2H' . \tag{58}
\]

This is a first order linear equation for \(\Psi'_1(\rho)\). We now perform the substitution

\[
\Psi'_1 = H^{-2}\chi \tag{59}
\]

which leads to

\[
\rho\chi'(\rho) = H(\rho)\chi(\rho) + H'(\rho)H(\rho)^2. \tag{60}
\]

Since \(H\) is rapidly decaying, we see that \(\chi\) tends to a limiting value, which is of the order of the integral of the inhomogeneity, that is, \(H(\rho)^3\) as \(\rho \to \infty\). We thus conclude that

\[
\Psi'_1(\rho) \approx H(\rho)^2\chi(\rho) \approx H(\rho) \quad (\rho \to \infty). \tag{61}
\]

From this follows that the order of magnitude of the correction to scaling is \(\rho H(\rho)^2\), in other words

\[
\Psi_1(\rho) = 1 + \text{const.} \cdot \rho^{3/2} \exp(-4\sqrt{\rho}) \tag{62}
\]

But the Laplace transform of \(x^{-9/2} \exp(-4/x)\) is given by

\[
\frac{\sqrt{\pi}}{1024} e^{-4\sqrt{\rho}} (64\rho^{3/2} + 96\rho + 60\sqrt{\rho} + 15) \tag{63}
\]

which has the same large-\(\rho\) asymptotic behaviour as \(\Psi_1(\rho)\), implying that \(\Phi(x)/x\) has the same subdominant small-\(x\) behaviour as \(x^{-9/2} \exp(-4/x)\). In other words, the correction goes to zero as \(x \to 0\) exponentially faster than the leading behaviour, and with a different correction exponent. Explicitly

\[
\Phi(x) = \frac{\Gamma}{\kappa_0} \frac{\exp(-1/x)}{x} [1 + o(1)] + \text{const.} \cdot \frac{\exp(-4/x)}{x^{7/2}} [1 + o(1)]. \tag{64}
\]
C. Behaviour of large clusters

We may also ask how $\Phi(x)$ behaves as $x \to \infty$, in other words, how does the concentration of large clusters behave. Since $\Psi(\rho)$ is well-defined and finite over a finite range of negative values of $\rho$, it follows from (39) that $\Phi(x)/x$ decays exponentially as $x \to \infty$. More information is obtained by referring to our results on the nearest singularity of $\Psi(\rho)$, which is at $\rho = -\Lambda$. As discussed earlier, see (48), this singularity is a simple pole with residue $2\Lambda$ and a correction term of the form $(\rho + \Lambda) \ln(\rho + \Lambda)$.

We therefore have, see Appendix D:

$$\kappa_0 \int_0^\infty \frac{\Phi(x)}{x} e^{-\rho x} dx = \left[ \frac{2\Lambda}{\rho + \Lambda} - 2 - \frac{2}{3} (\rho + \Lambda) \ln (\rho + \Lambda) \right] [1 + o(1)]$$

(65)

in the limit $\rho \to -\Lambda$ Since the Laplace transform $\chi(\rho)$ of

$$-\frac{2}{3} \exp \left( -\Lambda x \right) \frac{x^2 + b}{x^2}$$

(66)

has the same asymptotic behaviour for $\rho \to -\Lambda$ as the correction to $\Psi(\rho)$ for any positive value of $b$, we obtain the following asymptotic expression for $\Phi(x)$ as $x \to \infty$:

$$\Phi(x) = 2\kappa_0^{-1} \exp \left( -\Lambda x \right) \left( \Lambda x - \frac{2}{3x} \right) [1 + o(1)].$$

(67)

We have pointed out above the approximate value of $\Lambda$, which we compute in Appendix C.

IV. BEHAVIOUR AT LARGE TIMES FOR AGGREGATES OF FIXED SIZE

In the previous Section we have analysed the behaviour of aggregates having a size proportional to the typical size, namely of size $xS(t)$, for values of $x$ which are either $x \ll 1$ or $x \gg 1$. In the following, we shall look at aggregates of fixed size, in the limit $s \to \infty$.

Consider the system of equations (24). Inductively it is easily seen that each $\phi_j(s)$ is a finite linear combination of decaying exponentials. Indeed, let

$$\phi'_j(s) = F_j(s) - \phi_j(s)/j$$

(68)

and assume $F_j(s)$ to consist of a finite linear combination of decaying exponentials. It is then easy to show that $\phi_j(s)$ is a linear combination of these same exponentials and $\exp(-s/j)$ for instance using the Laplace transform approach.
FIG. 1. Value of $k\alpha_k$ for $2 \leq k \leq 15$ plotted as a function of $1/k$. One sees that the extrapolation to a limiting value seems reasonable. The line is a least-squares fit through the points with $k \geq 5$ and yields an asymptotic value of 1.71.

If we denote by $\sigma_{j,k}$ the decay rates and by $\Sigma_j$ the set of all the rates that correspond to $\phi_j(s)$, we have

$$\phi_j(s) = \sum_k \alpha_k \exp(-\sigma_{j,k}s).$$

(69)

Inductively we also show that

$$\Sigma_j = \bigcup_{k=1}^{j-1} (\Sigma_k + \Sigma_{j-k}) \cup \left\{ \frac{1}{j} \right\}$$

(70)

where the sum of two sets is defined as the set of all possible sums between elements of both sets.

From this follows that the slowest decay rate in $\Sigma_j$ is always $1/j$. The next lowest decay rate in $\Sigma_j$ arises from the sum of the 2 lowest rates of $\Sigma_{j/2}$. This means that the next lowest decay rate of $\Sigma_j$ is of the order $4/j$.

This implies that each $\phi_j(s)$ has exactly one exponential contribution of the form $\exp(-s/j)$. In other words, the large-time decay of $\phi_j(s)$ is exactly $\alpha_j \exp(-s/j)$ for a given value of $\alpha_j$. Hence the behaviour of $c_j(s)$ is given by

$$c_j(s) = \frac{\alpha_j}{s} e^{-s/j} \quad (s \to \infty)$$

(71)

This is qualitatively similar to the scaling result, which states that for $x \ll 1$

$$\Phi(x) = \frac{\Gamma}{\kappa_0} \frac{\exp(-1/x)}{x} [1 + o(1)]$$

(72)

and this would suggest that

$$\alpha_j \simeq j^{-1}.$$  

(73)
It is possible, of course, to evaluate the $\alpha_j$ recursively, but it is not possible to find for them an explicit expression. On the other hand, one can evaluate the $\alpha_j$ explicitly for $1 \leq j \leq 15$ and verify that, at least for these values, (73) appears to hold to a good approximation: we show the product $k\alpha_k$ in Figure 1 for $2 \leq k \leq 15$, as a function of $1/k$ and it appears reasonably to extrapolate to a well-defined value. The explicit values of $\alpha_j$ are also tabulated in Table II.

We thus find the large-time behaviour of fixed size aggregates to be consistent with the scaling behaviour of aggregates of size small with respect to the typical size. While such agreement is not in itself surprising, it should be pointed out that this is not a necessary feature of aggregating models: several counterexamples have been discussed, for instance, in [5]. Indeed, this coincidence goes even beyond the leading order: as noted above, the next to leading order for the large-time exponential decay consists of decay rates of the order of $4/j$, so that one has

$$\phi_j(s) = \alpha_j \exp(-s/j) + \alpha'_j \exp(-4s/j).$$

(74)

Here the $\alpha'_j$ are the prefactors corresponding to the decay rate $4/j$. Again this fits well with the behaviour of the scaling function, which displays both a decay of type $\exp(-1/x)$, with a correction of order of $\exp(-4/x)$. On the other hand, the order of the $\alpha'_j$ cannot be estimated, as there are too few expressions for $\phi_j(s)$ available.

V. BEHAVIOUR AT LARGE SIZES FOR FIXED TIMES

The behaviour at large sizes for fixed times has been assumed to be similar to the behaviour for large sizes at very small times. This can be understood qualitatively by imagining that, at time $t$, the system has acquired a typical size $S(t)$. We may now coarse grain the system in such a way that all aggregates within a (large) multiple of $S(t)$ are viewed as monomers. On that scale, all aggregates of large size are much larger than all aggregates that have been produced at that time, and we may therefore proceed similarly to the case in which monomers altogether dominate the cluster size distribution.

In the limit of small times, we may make the following Ansatz, which solves the system (2) in leading order of $t$, which is taken here to be the small parameter:

$$c_j(t) = \lambda_j t^{j-1} [1 + O(t)]$$

(75)
TABLE I. The values of $\alpha_j$ as defined in (73) for $2 \leq j \leq 15$, evaluated from exactly computed fractions.

| $j$ | $\alpha_j$ |
|-----|-------------|
| 2   | 0.666666666666667 |
| 3   | 0.482142857142857 |
| 4   | 0.376828110161443 |
| 5   | 0.309065279025988 |
| 6   | 0.261879521457270 |
| 7   | 0.227157280354022 |
| 8   | 0.200546422642681 |
| 9   | 0.179506571151271 |
| 10  | 0.162456450838603 |
| 11  | 0.148360805859407 |
| 12  | 0.136513680323195 |
| 13  | 0.126417243694629 |
| 14  | 0.117710416149960 |
| 15  | 0.110124961934082 |

Putting (75) into (2) leads to the recursion

$$(j - 1)\lambda_j = \frac{1}{2} \sum_{k=1}^{j-1} K(k, j - k)\lambda_k\lambda_{j-k}.$$  (76)

This simply reflects the fact that at short times, loss terms are dominated by the (recursive) production terms. For the case we consider, we are led to

$$(j - 1)\lambda_j = \sum_{k=1}^{j-1} \frac{\lambda_k\lambda_{j-k}}{k} \quad (j \geq 2)$$  (77)

where $\lambda_1 = 1$, since we assume that the initial distribution has concentration 1 of monomers.

This recursion can be solved by introducing the generating function

$$F(x) = \sum_{j=1}^{\infty} \frac{\lambda_j}{j} e^{-jx}.$$  (78)

This satisfies the following differential equation:

$$F''(x) + F'(x) = -F(x)F'(x).$$  (79)
where the initial condition \( \lambda_1 = 1 \) translates into the boundary condition:

\[
\lim_{x \to \infty} [e^x F(x)] = 1. \tag{80}
\]

The general solution of (79) which goes to zero as \( x \to \infty \) is given by

\[
F(x) = \frac{2ae^{-x}}{1 - ae^{-x}}, \tag{81}
\]

with \( a \) arbitrary. If we now use (80), we obtain

\[
a = \frac{1}{2}. \tag{82}
\]

From this readily follows

\[
\lambda_j = 2^{-(j-1)}j, \tag{83}
\]

which can also be checked directly by substitution into (77). Again this is in good agreement with the general predictions of [15, 16]. Indeed, in these references it is shown that the behaviour of the general recursion (76) is given by

\[
\lambda_j \simeq j^{-\theta} R^j, \tag{84}
\]

where \( R \) is a non-universal constant and \( \theta \) is an exponent given by the general formula

\[
\theta = \lambda, \tag{85}
\]

except when \( \nu = 1 \), which is a singular case. Since we have \( \lambda = \mu = -1 \), the result (83) is in full agreement with the predictions. Again, these results were also derived in [10].

For the general case we obtain

\[
(j - 1)\lambda_j = \frac{1}{2} \sum_{k=1}^{j-1} \frac{\lambda_k \lambda_{j-k}}{\alpha k + \beta}. \tag{86}
\]

But the corresponding differential equation for the generating function

\[
F(x) = \sum_{j=1}^{\infty} \frac{\lambda_j}{\alpha j + \beta} e^{-jx}. \tag{87}
\]

is given by

\[
\alpha F''(x) + (\alpha - \beta) F'(x) + [\alpha F'(x) - \beta F(x)] F(x) = 0 \tag{88}
\]

and cannot be solved explicitly. It is readily seen, however, that the behaviour for large \( j \) of the \( \lambda_j \), or equivalently, the behaviour of \( F(x) \) near its singularity nearest to the origin, on the negative real axis, is identical to that obtained for the \( \alpha = 1, \beta = 0 \) case.
Note that the behaviour at finite times is in agreement with the scaling prediction to leading order. To subleading order, however, we have seen in (67), that the singularity of $\Psi(\rho)$ is a pole modified by a correction of order $(\rho + \Lambda)\ln(\rho + \Lambda)$. This implies a correction of relative order $1/x^2$ to the leading behaviour $xe^{-x}$ of the scaling function for large $x$. This implies that there is a discrepancy between the small-time approximation, which leads to an exact exponential decay for the concentrations at large sizes, and the scaling function, which displays a correction $-2/(3x^2)$.

In Appendix [we present arguments suggesting that in fact there are also similar corrections to the simple pole singularity of $G(z, t)$ at fixed finite $t$, contrary to the small-time approximation. This means that both the large-size limit of the aggregate size distribution at fixed times and the scaling limit for large values of $x$ behave similarly. On the other hand, the simpler approximation involving a recursion relation valid for small times does not accurately capture these features. Earlier work [15, 16], not being able to describe subleading effects, had stated that the small-time approximation and the scaling behaviour coincided and had thus assumed that

VI. CONCLUSIONS

To summarise, we have derived an exact ordinary differential of second order for the Laplace transform of the scaling function of the solution for Smoluchowski’s equations (2) for the rate kernel

$$K(k, l) = \frac{1}{\alpha k + \beta} + \frac{1}{\alpha l + \beta}. \quad (89)$$

We show that this differential equation has a unique solution with the properties required of the Laplace transform of a scaling function. From this we obtain a large number of accurate asymptotic results involving the detailed behaviour of the scaling function both for $x \gg 1$ and $x \ll 1$. Similarly we obtain the amplitudes for the large time behaviour of all the integer moments

$$m_n(s) = \sum_{j=1}^{\infty} j^n c_j(s) \quad (90)$$

for $n \geq -2$, as well as the detailed asymptotic connection between $s$ and $t$. The detailed behaviour of the scaling function coincides quite well with the general predictions of the scaling theory, as described for instance in [5].
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Appendix A: Qualitative behaviour of the fundamental equation

In the following, we shall prove the following theorem

**Theorem 1** The solutions of the problem

\[ \rho \Psi'' = \Psi (\Psi' + 1) \]  (A1)

which are smooth and positive at \( \rho = 0 \) and satisfy \( \Psi''(0) \neq 0 \) fall into three mutually disjoint classes:

1. Those which cross the \( \rho \) axis at some value \( \rho_0 \) of \( \rho \). These then remain negative for all \( \rho > \rho_0 \). They go asymptotically as \(-\rho + \text{const.}\).

2. Those which reach a positive minimum at some positive value \( \rho_0 \) of \( \rho \). These grow for all \( \rho > \rho_0 \), until they eventually diverge to positive infinity at some finite positive value of \( \rho \).

3. A unique function with \( \Psi(0) = 1 \), \( \Psi'(0) = -1 \) and \( \Psi''(0) = \kappa_0 \) given by a unique positive value satisfying \( 1.45582 < \kappa_0 < 1.45583 \). This function goes to zero as \( \text{const.} \cdot 2\sqrt{\rho}K_1(2\sqrt{\rho}) \) as \( \rho \to \infty \) on the positive real axis.

The results follow from a tedious sequence of lemmas

**Lemma 1** Any solution of (A1) smooth at \( \rho = 0 \) and with \( \Psi(0) > 0 \) and \( \Psi''(0) \neq 0 \) satisfies \( \Psi(0) = -\Psi'(0) = 1 \)

Indeed, if \( \Psi'(0) \neq -1 \), then, since \( \Psi(0) \neq 0 \), \( \Psi''(\rho) \) diverges to \( \infty \) as \( \rho \to 0 \), so \( \Psi(\rho) \) cannot be smooth. One now rewrites (A1) as follows

\[ \rho(1 - \Psi) \Psi'' = \Psi (\Psi' + 1 - \rho \Psi'') . \]  (A2)

Since we have assumed the smoothness of \( \Psi(\rho) \) near \( \rho = 0 \), by Taylor’s theorem applied to \( \Psi'(\rho) \) for \( \rho \) near 0, the r.h.s. of (A2) is of order \( O(\rho^2) \) as \( \rho \to 0 \). Since \( \Psi''(0) \neq 0 \), it follows
that the l.h.s. can only be of the same order if \(1 - \Psi\) vanishes linearly in \(\rho\) as \(\rho \to 0\). We have thus shown the lemma. Note that the hypothesis \(\Psi''(0) \neq 0\) is indeed necessary, since \(\Psi = b - \rho\) is an exact solution of (A1) for all \(b\), and thus does not satisfy the Lemma’s conclusion.

In the following, we shall exclusively limit ourselves to solutions satisfying the hypotheses of Lemma 1. We shall denote them as regular solutions.

**Lemma 2** There is a family of regular solutions of (A1) indexed by the arbitrary real parameter \(\kappa = \Psi''(0)\). These solutions are analytic in an appropriately small neighbourhood of the origin.

Define \(z = \Psi - 1 + \rho\). (A1) then becomes

\[
\rho z'' - z' = zz' - \rho z'. \tag{A3}
\]

From Lemma 1, we know that \(z(0) = z'(0) = 0\). Now if we consider the leading order behaviour of both terms of (A3) if \(z = \kappa \rho^2 / 2\), we find that the equation is identically satisfied for all values of \(\kappa\). If we now substitute

\[
z(\rho) = \frac{\kappa \rho^2}{2} + \sum_{n=3}^{\infty} (-1)^n a_n \rho^n \tag{A4}
\]

formally in (A3), we obtain the following recurrence relations

\[
a_2 = \frac{\kappa}{2}, \tag{A5}
\]

\[
a_{m+1} = \frac{1}{m^2 - 1} \left( \sum_{k=2}^{m-1} ka_k a_{m-k+1} + ma_m \right) \quad (m \geq 2) \tag{A6}
\]

We now show that the series defined by (A4) has a finite radius of convergence. To this end, choose \(R\) such that \(a_2 \leq R^2\). Without loss of generality, we further require \(R > 1\). Let now \(K\) denote the largest number such that \(a_k \leq R^k\) for all \(k \leq K\). We know by definition that \(K \geq 2\). Let us assume it to be finite and lead this to a contradiction. We have

\[
a_{K+1} = \frac{1}{K^2 - 1} \left( \sum_{k=2}^{K-1} ka_k a_{K-k+1} + ka_K \right)
\]

\[
\leq \frac{R^{K+1}}{K^2 - 1} \left( \sum_{k=2}^{K-1} k + \frac{K}{R} \right)
\]

\[
\leq \frac{K - 1}{2(K + 1)} R^{K+1}
\]

\[
\leq \frac{R^{K+1}}{2}, \tag{A7}
\]
where the inequality on the third line follows from $R > 1$. The inequality is thus also satisfied for $K + 1$, in contradiction to the definition of $K$ as the largest number for which it holds. The solution of (A1) having a given value of $\kappa$ thus exists and is unique in an appropriate neighbourhood of $\rho = 0$. Its existence and uniqueness beyond these limits follow from the usual existence and uniqueness theorem for ODE’s, whose hypotheses clearly hold for $\rho > 0$. The Lemma is thus completely proved.

**Lemma 3** Let $\Psi(\rho)$ be any regular solution of (A1) with the property of being integrable over the positive real axis. Then one has

\[
\int_0^\infty \Psi(\rho) \, d\rho = \frac{5}{2},
\]

(A8)

Note that we say nothing here concerning either the existence or the uniqueness of such solutions. To prove (A8), we rewrite (A1) as

\[
\frac{d^2}{d\rho^2} [\rho \Psi(\rho)] = \frac{d}{d\rho} \left( \frac{\Psi(\rho)^2}{2} + 2\Psi(\rho) \right) + \Psi(\rho)
\]

(A9)

and integrate from 0 to infinity on both sides, from which the lemma immediately follows from the fact that $\Psi(0) = 1$ and $\Psi'(0) = -1$.

**Lemma 4** Let $\Psi(\rho)$ be a regular solution of (A1) and assume that there is an $\rho_0 > 0$ such that $\Psi'(\rho_0) = 0$ and $\Psi(\rho_0) > 0$. Then there is an $\rho_1 > \rho_0$ such that $\Psi(\rho)$ diverges monotonically to infinity as $\rho \to \rho_1$, and $\Psi(\rho)$ grows monotonically from $\rho_0$ to $\rho_1$.

From (A1) follows that $\Psi''(\rho_0) > 0$, so that there is an $\epsilon > 0$ such that $\Psi'(\rho) > 0$ for all $\rho_0 < \rho < \rho_0 + \epsilon$. Define $\rho_1$ as the first value of $\rho$ for which the existence theorem for (A1) fails (I do not yet claim that $\rho_1 < \infty$). Then $\Psi'(\rho) > 0$ for all $\rho_0 < \rho < \rho_1$, for otherwise there would be an $\rho_2$, $\rho_0 < \rho_2 < \rho_1$, such that $\Psi'(\rho_2) = 0$. But this implies that $\Psi'(\rho)$ somewhere decreased between $\rho_0$ and $\rho_2$, which contradicts the positivity of $\Psi''(\rho)$ for $\rho_0 < \rho < \rho_2$.

Now let us sketch a proof that $\rho_1 < \infty$ (this will not really be important for us later). Suppose the contrary. Since $\Psi'(\rho)$ always increases strictly, $\Psi(\rho)$ grows at least linearly in $\rho$ as $\rho \to \infty$. From this follows from (A1) that $\Psi''(\rho)$ is of order one as $\rho \to \infty$. Hence $\Psi'(\rho)$ goes as $\rho$ as $\rho \to \infty$. But we may then, for sufficiently large $\rho$, approximate (A1) by

\[
\rho \Psi'' = \Psi \Psi',
\]

(A10)

which can be solved exactly, and indeed has a singularity for finite values of $\rho$. 

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Lemma 5 Let $\Psi(\rho)$ be a regular solution of (A1) such that $\Psi(\rho_0) = 0$ for some $\rho_0 > 0$. Then $\Psi(\rho)$ is negative for all $\rho > \rho_0$. It asymptotically behaves as $b - \rho$ for some constant $b$.

Since for $\rho \leq \rho_0$, $\Psi(\rho) > \Psi(\rho_0) = 0$, we have $\Psi'(\rho_0) \leq 0$. Assume first that $\Psi'(\rho_0) = 0$. Then the initial conditions at $\rho_0$ would be identical to those of the exact solution of (A1) $\Psi(\rho) = 0$. This violates the uniqueness theorem for ODE’s valid at $\rho_0$. We thus have $\Psi'(\rho_0) < 0$, and the solution thus becomes negative in some interval $[\rho_0, \rho_0 + \epsilon]$. Further, since $\Psi'(0) = -1$ and $\Psi''(\rho) \geq 0$ for all $0 \leq \rho \leq \rho_0$, see (A1), it follows that $\Psi'(\rho_0) > -1$. Thus the solution for $\rho > \rho_0$ is initially negative with $\Psi''(\rho) < 0$. $\Psi'(\rho)$ thus decreases as $\rho$ increases, but it can never attain the value $-1$. Indeed, if it did so for some value of $\rho$, say $\rho_1$, then $\Psi(\rho)$ would have, at $\rho_1$, the same value and the same derivative as the exact solution of (A1), $\Psi(\rho) = -\rho + \rho_1 + \Psi(\rho_1)$; this is again in contradiction with the uniqueness theorem for ODE’s. The fact that $\Psi(\rho)$ goes asymptotically as $b - \rho$ is shown in much the same way as the appearance of a singularity at finite $\rho$ in Lemma 4: it is enough to analyze (A10) for $\Psi' > -1$.

Lemma 6 Let $\Psi(\rho)$ be a regular solution of (A1), with $\Psi(\rho) > 0$ for all $\rho > 0$ and tends to zero as $\rho \to \infty$. Then there is a constant $\Gamma$ such that

$$
\lim_{\rho \to \infty} \frac{\Psi(\rho)}{2\sqrt{\rho} K_1(2\sqrt{\rho})} = \Gamma \quad (A11)
$$

From Lemma 4 we see that such a solution may neither have a minimum, nor ever become zero. It thus decays monotonically to zero. Since it follows from (A1) that $\Psi''(\rho) > 0$ for all
\( \rho > 0, \Psi'(\rho) \) is monotonically increasing for all \( \rho > 0 \). It follows that \( \Psi'(\rho) \) also tends to zero as \( \rho \to \infty \). Under these conditions, it is clear that (A1) can, for \( \rho \gg 1 \), be approximated by the linear equation

\[
\rho \Psi'' = \Psi \tag{A12}
\]

which has the two exact solutions \( \sqrt{\rho} I_1(2\sqrt{\rho}) \) and \( \sqrt{\rho} K_1(2\sqrt{\rho}) \). The Lemma is proved, since the former diverges exponentially.

**Lemma 7** Let \( \Psi_1(\rho) \) and \( \Psi_2(\rho) \) be the two solutions such that \( \Psi_i''(0) = \kappa_i \) for \( i = 1, 2 \) and let \( \kappa_1 < \kappa_2 \). Then for all \( \rho > 0 \) such that no \( \Psi_i(\rho) \) has either diverged or become negative, \( \Psi_1(\rho) < \Psi_2(\rho) \).

From the Taylor series of \( \Psi_i(\rho) \), it immediately follows that \( \Psi_1(\rho) < \Psi_2(\rho) \) as well as \( \Psi_1'(\rho) < \Psi_2'(\rho) \) on a sufficiently small open interval \((0, \epsilon)\). Assume now that the Lemma’s conclusion fails. Then there is a smallest \( \rho_0 \) for which \( 0 < \Psi_1(\rho_0) = \Psi_2(\rho_0) < \infty \). Again, since the two solutions are not identical, it follows from the uniqueness theorem for ODE’s that \( \Psi_1'(\rho_0) \neq \Psi_2'(\rho_0) \) and thus that \( \Psi_1'(\rho_0) > \Psi_2'(\rho_0) \). There hence exists a smallest \( \rho_1 \) with \( 0 < \rho_1 < \rho_0 \), such that \( \Psi_1'(\rho_1) = \Psi_2'(\rho_1) \). Since \( \Psi_i''(\rho) > 0 \) for all \( 0 < \rho \leq \rho_1 \), \( \Psi_i'(\rho) \) is growing in this interval. Since \( \Psi_1'(\rho) < \Psi_2'(\rho) \) for \( 0 < \rho < \rho_1 \), we have \( \Psi_1''(\rho_1) > \Psi_2''(\rho_1) \). But this, together with the already established facts that \( \Psi_1(\rho_1) < \Psi_2(\rho_1) \) (since \( 0 < \rho_1 < \rho_0 \)) and that \( \Psi_1'(\rho_1) = \Psi_2'(\rho_1) \) (by definition of \( \rho_1 \)) lead to a contradiction with (A1). The Lemma is thus proved.

**Lemma 8** There exist solutions that go negative, as well as solutions that develop a positive minimum.

If we choose \( \kappa = 0 \), then the corresponding solution is \( \Psi(\rho) = 1 - \rho \). This becomes negative at \( \rho = 1 \). By continuous dependence on initial conditions, solutions with sufficiently small positive values of \( \kappa \) will go negative at some positive value of \( \rho \). It remains to show that, for \( \kappa \) sufficiently large, the solutions develop a minimum. From Lemma 2 follows that, for \( \kappa \) sufficiently large \( 2/\kappa \) is within the radius of convergence of the series of \( \Psi(\rho) \), since the latter is larger than \( (2/\kappa)^{1/2} \). One also readily shows by induction on (A6) that there exist constants \( \gamma_m \) independent of \( \kappa \) such that

\[
a_m \leq \gamma_m \kappa^{m-2} \quad (m \geq 3) \tag{A13}
\]
One may thus evaluate $\Psi'(2/\kappa)$ using the power series (A4) and obtain

$$\Psi'\left(\frac{2}{\kappa}\right) = 1 + O\left(\frac{1}{\kappa}\right),$$

which becomes positive for sufficiently large $\kappa$. The existence of a minimum then follows from $\Psi'(0) = -1$.

Note that this Lemma could also be obtained rigorously through careful numerical work. It would be enough to establish the Lemma’s conclusions, say, for $\kappa = 0.1$ and $\kappa = 2$ respectively.

**Lemma 9** There exists a unique solution satisfying the hypotheses of Lemma 6.

Using the theorem concerning the continuous dependence of the solutions of ODE’s on initial conditions, we see that the set $S_1$ of $\kappa$ such that the solution goes negative is open. So is the set $S_2$ of $\kappa$ such that a positive minimum arises. From Lemma 7 additionally follows that both these sets are of the form $(-\infty, \kappa_1)$ and $(\kappa_2, \infty)$, with $\kappa_1 \leq \kappa_2$. It follows from Lemma 8 that these are both finite numbers. I show that the solution corresponding to $\kappa_1$ remains positive everywhere and goes to 0 as $\rho \to \infty$. That it is positive follows from the definition and the fact that $S_1$ is open, so that $\kappa_1 \notin S_1$. Since $\kappa_1 \leq \kappa_2$, we also have $\kappa_1 \notin S_2$, so that the function must be monotonically decreasing. Indeed, all functions corresponding to values of $\kappa$ in the interval $[\kappa_1, \kappa_2]$ must have these properties. Thus all these functions must tend to a limit.

Let us now show that no solution of (A1) can remain positive, monotonically decreasing, and tend to a value different from 0. Let the asymptotic value of $\Psi(\rho)$ be $a$. From (A1) follows

$$\Psi(\rho) = 1 - \rho + \int_0^\rho dw_1 \int_0^{w_1} dw_2 \frac{\Psi(w_2) [\Psi'(w_2) + 1]}{w_2}.$$  

(A15)

Since $\Psi'(\rho)$ goes asymptotically to zero and $\Psi(\rho)$ goes to $a$, one immediately gets from (A15) that $\Psi(\rho)$ diverges as $\rho \ln \rho$ as $\rho \to \infty$, in contradiction to the assumption.

All solutions corresponding to $\kappa$ values inside $[\kappa_1, \kappa_2]$ are thus positive and go to zero. Now denote the solutions corresponding to the values $\kappa_1$ and $\kappa_2$ by $\Psi_1(\rho)$ and $\Psi_2(\rho)$ respectively. Since they go to zero, they both behave for $\rho \to \infty$ as $\sqrt{\rho} K_1(2\sqrt{\rho})$, see Lemma 6, and are thus integrable. Let us now assume that $\kappa_1 < \kappa_2$. By Lemma 7 it follows that $\Psi_1(\rho) < \Psi_2(\rho)$. Since both are integrable, both satisfy (A8), by Lemma 3. But two positive functions satisfying $\Psi_1(\rho) < \Psi_2(\rho)$ cannot have the same integral. It is thus necessary that $\kappa_1 = \kappa_2$.
and the solution that goes to zero is in fact unique by Lemma 2. The common value of \( \kappa_1 = \kappa_2 \) is what we have called \( \kappa_0 \). Its numerical value is easily estimated through straightforward numerical integration of (A1). We have found that \( \Psi(\rho) \) becomes negative for \( \kappa = 1.45582 \) whereas it has a positive minimum for \( \kappa = 1.45583 \). If needed, greater accuracy can be attained, but the approach is not trivial and is sketched in C. A plot of the function is provided in Figure 2.

Appendix B: Derivation of (33) from the integro-differential equation for the scaling function

As described in detail in [5], the scaling function \( \Phi(x) \) generally satisfies the following weak integral relation:

\[
\int_{0}^{\infty} x^2 \Phi(x) f'(x) dx = \int_{0}^{\infty} dx dy xK(x,y)\Phi(x)\Phi(y) \left[ f(x + y) - f(x) \right], \tag{B1}
\]

where \( f(x) \) is an arbitrary function. If we substitute it by the family of functions \( \delta(x-a) \), we obtain the well-known integro-differential equation described initially in [4] and in a much more general context in [3].

It turns out to be more convenient, however, to substitute \( f(x) \) by an arbitrary exponential \( \exp(-\rho x) \). This yields for the case at hand

\[
\rho \int_{0}^{\infty} x^2 \Phi(x)e^{-\rho x} dx = \int_{0}^{\infty} dx dy \left( 1 + \frac{x}{y} \right) \Phi(x)\Phi(y)e^{-\rho x} \left[ 1 - e^{-\rho y} \right]. \tag{B2}
\]

Let us now define

\[
\Psi(\rho) = \xi \int_{0}^{\infty} \frac{\Phi(x)}{x} e^{-\rho x} dx, \tag{B3}
\]

where \( \xi \) is a constant we later adjust. Then (B2) becomes

\[
-\xi \rho \Psi'''(\rho) = \Psi'(\rho)\Psi'(0) - [\Psi'(\rho)]^2 + \Psi''(\rho)\Psi(0) - \Psi''(\rho)\Psi(\rho). \tag{B4}
\]

This is integrated to

\[
-\xi \rho \Psi''(\rho) = \Psi(\rho)\Psi'(0) - \Psi(\rho)\Psi'(\rho) + \Psi'(\rho) \left[ \Psi(0) - \xi \right]. \tag{B5}
\]

The additive constant is seen to vanish by considering the large-\( \rho \) behaviour. Setting \( \rho = 0 \) leads to \( \xi = \Psi(0) \) and hence

\[
\rho \Psi(0)\Psi''(\rho) = \Psi(\rho) \left[ \Psi'(\rho) - \Psi'(0) \right]. \tag{B6}
\]
The values of $\Psi(0)$ and $\Psi'(0)$ can be set equal to one by appropriate scaling, thereby leading to \(33\). A minor point remains: \(B3\) does not yield the same proportionality constant as that found in \(39\). This depends on the fact that the form \(B1\) of the integro-differential equation for $\Phi(x)$ implicitly assumes a definition of the typical size $S(t)$ different by a constant factor from that used in the body of the text.

**Appendix C: The numerical determination of $\kappa_0$, $\Gamma$, and $\Lambda$**

Whereas the determination of $\kappa_0$ to the accuracy stated in Appendix \(A\) is reasonably straightforward, going any further requires some more detailed considerations. The difficulty is that for any value of $\kappa \neq \kappa_0$, the distance to the exact solution grows exponentially. In order to obtain a solution valid up to a given distance $L$, we thus need an initial condition that is accurate to an accuracy of $\exp(-\text{const.}/L)$.

On the other hand, solving the equation near $\rho = 0$ leads to loss of accuracy due to the vicinity of the origin. The way this can be solved is to compute many terms of the Taylor series of $\Psi(\rho)$, say 60, and to use these to compute $\Psi(\epsilon)$ for $\epsilon$ moderately small (I used $\epsilon = 0.01$ and 0.005) to an accuracy of, say, 60 decimals. One then integrates \(33\) to very high accuracy until one reaches a value of $\rho$ with $\Psi'(\rho) > 0$ or $\Psi(\rho) < 0$. We define an interval $[\kappa_-, \kappa_-]$, where for $\kappa_-$ $\Psi(\rho)$ becomes negative, whereas for $\kappa_+$ $\Psi'(\rho)$ becomes positive. The interval is then iteratively halved until sufficient precision is reached. In this way we determine

$$\kappa_0 = 1.455824941943054763\ldots$$

(C1)

where the decimals displayed are correct.

For the asymptotic ratio of $\Psi(\rho)$ and the asymptotic form $2\sqrt{\rho}K_1(2\sqrt{\rho})$, we plot this ratio minus an estimated value of $\Gamma$ given by 1.70787 and show this in Figure 3.

The nearest singularity of $\Psi(\rho)$ is a simple pole, as can be seen analytically. To obtain an accurate numerical estimate, the simplest option is to take the first 100 coefficients of the Taylor series

$$\Psi(\rho) = 1 - \rho + \sum_{k=2}^{\infty} a_k \rho^{k-1}$$

(C2)

where $a_2 = \kappa_0/2$, at least to good accuracy. We then use these to estimate the radius of convergence via the ratio test. Since the Taylor coefficients are alternating, the nearest
FIG. 3. Ratio $\Psi(\rho)/[2\sqrt{\rho}K_1(2\sqrt{\rho})] - \Gamma$, where $\Gamma = 1.70787$. The plateau corresponds to the region of $\Psi(\rho)$ which corresponds to high accuracy to the asymptotic region, and where the deviations at $x \gg 1$ which lead eventually to the divergence of $\Psi(\rho)$, do not yet dominate.

FIG. 4. Ratio $a_k/a_{k+1}$ shifted by 1.5761395 plotted as a function of $1/k$, for $20 \leq k \leq 100$.

singularity lies on the negative real axis. The result is shown in Figure 4 and appears to yield a result of about 1.576 13.

As a cross-check, a Padé analysis was performed. In particular, a series of diagonal Padé approximants $[M, M]$ with $20 \leq M \leq 45$ was generated on the Taylor series mentioned above. It is found that there is consistently a zero of the denominator closest to the origin, and that its value does not vary much from one approximant to the other: we plot this in Figure 5 and further show in Figure 6 the set of all zeroes of the denominator of the $[40, 40]$
FIG. 5. Zero of the denominator of the Padé approximant shifted by 1.576132, as a function of the latter’s order, for $20 \leq k \leq 45$.

FIG. 6. Zeroes of the denominator of the Padé approximant of order $[40, 40]$ having norm less than 3. The value of the nearest zero is unambiguous, and spurious zeroes do not appear. The zeroes accumulating near the closest zero are an indication of the existence of additional logarithmic singularities, as discussed in the text and shown in Appendix D.

As a final test, we use the Padé approximants evaluated above to compute the residue of the zero. The residue of a rational function $N(x)/D(x)$ at a zero $x_0$ of $D(x)$ is given by

$$\text{Res}_{x=x_0} \frac{N(x)}{D(x)} = \frac{N(x_0)}{D'(x_0)} \quad (C3)$$

which is readily evaluated and which, when divided by 2, yields 1.5761294 for the approximant of order $[40, 40]$. Since we had argued that the residue is $2\Lambda$, this is quite satisfactory agreement.
Appendix D: The singularity of $\Psi(\rho)$

As has been shown in the body of this work, the function $\Psi(\rho)$ has a singularity which is dominated by a simple pole at some point $-\Lambda$ on the negative real axis. Here we proceed to show that there exists a correction to the singularity, and that the full behaviour of $\Psi(\rho)$ is given by

$$\Psi(\rho) = \left[ \frac{2\Lambda}{\rho + \Lambda} - 2 - \frac{2}{3} (\rho + \Lambda) \ln(\rho + \Lambda) \right] \left[ 1 + o(1) \right] \quad (D1)$$

This is shown as follows: define $y = \rho + \Lambda$. Equation (33) becomes

$$(-\Lambda + y)\Psi''(y) - \Psi(y)\Psi'(y) - \Psi(y) = 0. \quad (D2)$$

We now consider the singularity near $y = 0$. Matching leading singularities, we find that the leading behaviour is $2\Lambda/y$. To eliminate a subleading singularity of $4\Lambda/y^2$, we additionally need to correct this expression to $2\Lambda/y - 2$. Let us now define $v(y)$ by

$$v(y) = y^{-1} \left( \Psi(y) - \frac{2\Lambda}{y} + 2 \right) \quad (D3)$$

It satisfies the following equation

$$(\Lambda - y) \left[ y^2 v''(y) + 4yv'(y) + 2 \right] + yv(y) \left[ y^2 v'(y) + y - 2 + yv(y) \right] = 0. \quad (D4)$$

Clearly $v(y)$ cannot be bounded at $y = 0$, since otherwise, by taking the limit of the l.h.s. of (D4) for $y \to 0$, we obtain the contradictory relation $2\Lambda = 0$. Assuming a power law $y^p$ with $p > 0$, we see that

$$p(p + 3) = 0, \quad (D5)$$

so that only $p = -3$ is acceptable, which dominates the leading singularity and is thus unacceptable. This leads to assume a logarithmic divergence. Putting the ansatz $v(y) = \alpha \ln y$ leads to $\alpha = -2/3$ by eliminating the leading singularity. A similar analysis to the above shows that the difference between $v(y)$ and $(-2/3) \ln y$ remains finite at $y = 0$, from which (D1) follows.

Appendix E: Scaling behaviour holds for the moments

In the following, we show that for all $n \in \mathbb{Z}$, the quantities $\mu_n(t)$ and $\tilde{\mu}_{n,\epsilon}(t)$, see (42) and (50), behave identically in the limit of $\epsilon \to 0$. This involves showing that the sum

$$\Delta_{n,\epsilon}(t) = \sum_{j < \epsilon s} j^n c_j(s) \quad (E1)$$
is negligible as compared to $\tilde{\mu}_{n,\epsilon}(s)$, which is of order $s^{n-1}$.

The proof proceeds along somewhat different lines for $n \leq 0$ and $n \geq 2$. For $n = 1$ the result is self-evident. We start with the latter case.

We note the fact that, since $\mu_1 = 1$, we always have the inequality

$$c_j(s) \leq \frac{1}{j}$$

for all $s$. It follows that

$$\Delta_{n,\epsilon}(t) \leq \max_{1 \leq j \leq \epsilon s} j^{n-1} \leq (\epsilon s)^{n-1},$$

which is indeed negligible with respect to $s^{n-1}$.

For the case $n \leq 0$, we first consider the case $n \leq -1$. We thus have

$$\Delta_{n,\epsilon}(s) = \sum_{j=1}^{M} j^n c_j(s) + \sum_{j=M+1}^{\infty} j^n c_j(s)$$

$$\leq \sum_{j=1}^{M} j^n \alpha_j \exp(-s/j) + \sum_{j=M+1}^{\infty} j^{n-1}$$

$$\leq K_M \exp(-s/M) + CM^n$$

where the $\alpha_j$ are defined as in (74) and $C$ is a fixed constant of order one. We now take for $M$ a fixed, large number such that $CM^n \leq \epsilon$. As $s \to \infty$, the first term in the upper bound goes to zero. We thus see that, apart from a quantity that goes to zero as $s \to \infty$, $\Delta_{n,\epsilon}(s)$ is of order $\epsilon$ and the result is shown.

For $n = 0$ the result follows from the fact that

$$\dot{\mu}_0 = -\mu_0 \mu_{-1}.$$  

Since the theorem holds for all other moments, it follows for $\mu_0$.

**Appendix F: Singularity structure of $G(z,s)$ at finite times**

Here we show that at any given fixed time, the nearest singularity of the generating function $G(z,s)$—lying, as usual, on the negative real axis—is a pole with a logarithmic correction of the same type as that observed as in the scaling function $\Psi(\rho)$. We denote this closest singularity by $-z_c(s)$

At small times the leading behaviour of the $\phi_j(s)$ is

$$\phi_j(s) = \lambda_j s^{j-1} \left[1 + O(s)\right],$$

30
where the $\lambda_j$ are given by $[83]$. This suggests introducing the following scaling form

$$G(z, s) = \frac{1}{s} H(z - \ln s, s). \quad (F2)$$

If we introduce the new variable $x = z - \ln s$, the differential equation for $H(x, s)$ becomes

$$H_{xx} - H_x - HH_x = s (H_x - H). \quad (F3)$$

This equation has the following amusing property: if we set the Ansatz

$$H(x, s) = \sum_{m=0}^{\infty} s^m f_m(x), \quad (F4)$$

the $f_m(x)$ can be determined recursively as the solution of an ODE, which is nonlinear, but explicitly solvable, for $m = 0$, and linear inhomogeneous for $m \geq 1$.

The equation for $f_0(x)$ is

$$f_0'' - f_0' + f_0 f_0' = 0. \quad (F5)$$

The solution is given by

$$f_0(x) = -1 - C_1 \cot \left( C_1 (x - x_0) \right), \quad (F6)$$

where $C_1$ and $x_0$ are integration constants. Without loss of generality we may put the singularity at the origin by setting $x_0 = 0$ and replace the cotangent by a simple pole, setting

$$f_0(x) = -1 - \frac{2}{x} \quad (F7)$$

Now $f_1$ solves the equation

$$f_1''(x) + \left( \frac{2}{x} + 1 \right) f_1'(x) - \frac{2f_1(x)}{x^2} + \frac{2}{x} + 1 = 0. \quad (F8)$$

This has the solution

$$f_1(x) = \frac{1}{x^2} \left\{ 4e^{-x} \text{Ei}(x) - \left[ P_3(x) + 2 \left( (x^2 - 2x + 2) \ln x \right) \right] + C_2 \right\} \quad (F9)$$

$$P_3(x) = x^3 - (C_1 + 3) x^2 + 2 (C_1 + 2) x - 2C_1 \quad (F10)$$

Developing around $x = 0$ to third order yields

$$f_1(x) = \frac{2C_1 + C_2 + 4\gamma}{x^2} - \frac{2C_1 + C_2 + 4\gamma}{x} + C_1 + \frac{C_2}{2} + 2\gamma + \frac{x}{18} (-3C_2 - 12 \ln x - 12\gamma + 4) + \frac{x^2}{72} (3C_2 + 12 \ln x + 12\gamma - 25) + \frac{x^3}{1800} (-15C_2 - 60 \ln x - 60\gamma + 137) \quad (F11)$$
up to terms of order 4. Here again \( C_1 \) and \( C_2 \) are integration constants and \( \gamma \) is Euler’s constant. We cannot have an \( x^{-2} \) singularity, so we set \( C_1 = -2\gamma - C_2/2 \). This gives

\[
f_1(x) = x^3 \left( -\frac{C_2}{120} - \frac{\ln x}{30} - \frac{\gamma}{30} + \frac{137}{1800} \right) + \\
x^2 \left( \frac{C_2}{24} + \frac{\ln x}{6} + \frac{\gamma}{6} - \frac{25}{72} \right) + \\
x \left( -\frac{C_2}{6} - \frac{2\ln x}{3} - \frac{2\gamma}{3} + \frac{2}{9} \right).
\]

We thus find that the first order correction in \( s \) has an \( x \ln x \) correction to the leading \(-2/x\) behaviour, exactly similarly to the behaviour of the scaling function \( \Psi(\rho) \) near its closest singularity \(-\Lambda\).

We thus have as an approximate expression for \( G(z, s) \) for \( s \) small: close to the singularity \( z_c(s) \). We thus have approximately:

\[
G(z, s) = -\frac{2}{z + z_c(s)} - 1 - \frac{2s}{3} [z + z_c(s)] \ln [z + z_c(s)]
\]

(F13)

and this correction, too, amounts to a correction of \(-2/(3n^2)\) to the prefactor of the pure exponential decay. This prefactor, on the other hand, depends on constants, the value of which cannot be determined. Note the considerable similarity to the results obtained for the scaling function. This suggests that the scaling limit is attained rather smoothly in the limit of large sizes.

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