Four Lectures on Non-Equilibrium Statistical Physics

Sidney Redner, Boston University

June 16, 2009

Contents

1 AGGREGATION **2**
1.1 Exact Solutions 3
1.2 Scaling 12
1.3 Constant-Kernel Aggregation with Input 15

2 ADSORPTION **17**
2.1 Random Sequential Adsorption in One Dimension 17
2.2 Adsorption in Higher Dimensions 21
2.3 Extensions and Applications 24

3 FIRST-PASSAGE PROPERTIES **29**
3.1 Transience and Recurrence 29
3.2 Exit Probabilities and Exit Times 31
3.3 Reaction-Rate Theory 36

4 COMPLEX NETWORKS **39**
4.1 Erdös-Rényi Random Graph 39
4.2 Random Recursive Tree (RRT) 42
4.3 Preferential Attachment Networks 46

Chapter 1

AGGREGATION

In aggregation, reactive clusters join irreversibly whenever two of them meet. Aggregation is ubiquitous in nature: it underlies milk curdling, blood coagulation, and star formation by gravitational accretion. Aggregation also provides a beautiful example of many paradigmatic features of non-equilibrium phenomena, such as scaling, phase transitions, and non-trivial steady states. Schematically, we write aggregation as

$$A_i + A_j \xrightarrow{K_{ij}} A_{i+j},$$

in which a cluster of mass $i+j$ is created at an intrinsic rate K_{ij} by the aggregation of two clusters of mass i and mass j. The goal of this chapter is to determine the concentration of clusters of mass k at time t, $c_k(t)$, and to understand which features of the underlying reaction rate, or kernel, K_{ij} influence this distribution.

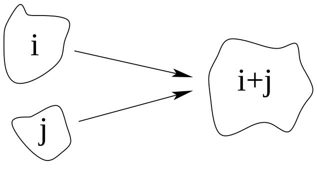

Figure 1.1: Clusters of mass i and mass j merge irreversibly into a cluster of mass $i+j$.

The Master Equations

The starting point for treating aggregation is an infinite set of master equations that describe how the cluster mass distribution evolves. In the approximation of well-mixed reactants, in which the rate at which an i-mer and j-mer meet is c_ic_j, the master equations may be written generally as

$$\frac{dc_k(t)}{dt} = \frac{1}{2}\sum_{i,j} K_{ij}\, c_i(t)c_j(t)\, \left[\,\delta_{i+j,k} - \delta_{i,k} - \delta_{j,k}\,\right]. \qquad (1.1a)$$

The delta functions account, in a foolproof manner, for the ways in which a k-mer can be created or removed. A k-mer is created by the coalescence of clusters of masses i and j with $i+j=k$, while a k-mer is removed when either i or j equals k and this cluster reacts with any other cluster. The leading factor of $\frac{1}{2}$ is for later convenience. Upon implementing the delta function constraints, the master equations become

$$\frac{dc_k(t)}{dt} = \frac{1}{2}\sum_{j=1}^{k-1} K_{j,k-j}\, c_j(t)\, c_{k-j}(t) - c_k(t)\sum_{i=1}^{\infty} K_{ik}\, c_i(t). \qquad (1.1b)$$

Notice that the prefactor $\frac{1}{2}$ in the gain term ensures the correct accounting of reactions between same-mass clusters.[1]

---

[1] It is helpful to consider a finite system to understand this factor. Denote by N_k the total number of clusters of mass k. For $i \neq j$ there are N_iN_j pairs of type ij, while the number of same-mass pairs is $\frac{1}{2}N_k(N_k-1) \to \frac{1}{2}N_k^2$ in the thermodynamic

In equations (1.1), and generally throughout chapter we tacitly assume that the mass k runs over the integers — this merely implies that we measure mass in terms of a minimal mass, and a cluster of mass k contains k primal, minimal-mass clusters. Primal clusters are called *monomers* while clusters of mass k are termed $k-$mers. With this convention regarding the mass, the reaction rates form an infinite symmetric matrix $K_{ij} = K_{ji}$. The master equations (1.1) admit an important integral of motion — the mass density

$$M(t) = \sum_{k\geq 1} k\, c_k(t) \tag{1.2}$$

is conserved. To verify this conservation law we write

$$\frac{dM}{dt} = \sum_k k\,\frac{dc_k}{dt} = \sum_k \sum_{i+j=k} \frac{1}{2} K_{ij}\,(i+j)\,c_i\,c_j - \sum_k \sum_i K_{ik}\,k\,c_i\,c_k = 0. \tag{1.3}$$

The outer sum over k causes the sums over i and j in the gain term to become independent and unrestricted. The gain and loss terms then cancel and therefore the mass density is manifestly conserved.

The master equations are the starting point in almost all studies of aggregation, and it is instructive to highlight the assumptions underlying this approach, including:

- The system is well mixed, and the reaction proceeds with a rate proportional to the product of reactant densities. This is the *mean-field* assumption.
- Bimolecular reactions. The system is sufficiently dilute so that higher-body interactions are negligible.
- Shape independence. The aggregate mass is the only dynamical variable; cluster shape play no role in the evolution. One such example is the aggregation of spherical liquid droplets.
- Thermodynamic limit. The system is sufficiently large that cluster concentrations are continuous functions; discreteness effects are ignored.

1.1 Exact Solutions

The master equations are a formidable infinite set of coupled non-linear differential equations that are soluble only for a few neat kernels. Many clever solution techniques have been developed for these kernels and we present several such approaches. We start with the constant reaction kernel because it represents an ideal playground to illustrate a variety of approaches. We then turn to more challenging cases of the product and sum kernels, $K_{ij} = ij$ and $K_{ij} = i + j$, respectively. These three examples represent most of the exactly solved models of aggregation.

Constant Reaction Rates

The constant kernel aggregation was proposed and solved in a seminal paper about aggregation by Smoluchowski in 1917. A crude physical justification of the model is based on the form of the reaction kernel for Brownian aggregation. The rate at which particles of diffusivity D hit a sphere of radius R is proportional to DR^{d-2}, where d is the spatial dimension. The generalization to a collection of diffusing spherical aggregates, each of radius R_i and diffusivity D_i, is then $K_{ij} = (D_i + D_j)(R_i + R_j)$. Since the radius scales as the cube root of the mass and the diffusivity is proportional to the inverse radius, the reaction rate becomes

$$\begin{aligned} K_{ij} &\simeq (i^{-1/3} + j^{-1/3})(i^{1/3} + j^{1/3}) \\ &= 2 + \left(\tfrac{i}{j}\right)^{1/3} + \left(\tfrac{j}{i}\right)^{1/3}. \end{aligned} \tag{1.4}$$

This Brownian kernel — as yet unsolved — shares one important feature with the constant kernel — both are invariant under the transformation $(i, j) \longrightarrow (ai, aj)$, that is, $K_{ai,aj} = K_{i,j}$. This suggests that

---

limit. Thus the prefactor $\frac{1}{2}$ properly accounts for the relative fraction of same-mass pairs. The loss term for same-mass pairs in (1.1) is $K_{kk}c_kc_k$ rather than $\frac{1}{2}K_{kk}c_kc_k$ since *two* clusters of mass k disappear in such a collision.

the constant kernel is a reasonable but uncontrolled approximation for the physically-important Brownian kernel.

For the constant kernel, we choose $K_{ij} = 2$ for convenience, and then the master equations are

$$\frac{dc_k}{dt} = \sum_{i+j=k} c_i c_j - 2c_k \sum_{i=1}^{\infty} c_i \equiv \sum_{i+j=k} c_i c_j - 2c_k\, N \tag{1.5}$$

where $N(t) = \sum_{k\geq 1} c_k(t)$ is the concentration of clusters of any mass. The first few of these equations are

$$\begin{aligned}
\dot{c}_1 &= -2c_1\, N \\
\dot{c}_2 &= c_1^2 - 2c_2\, N \\
\dot{c}_3 &= 2c_1\, c_2 - 2c_3\, N \\
\dot{c}_4 &= 2c_1\, c_3 + c_2^2 - 2c_4\, N \\
\dot{c}_5 &= 2c_1\, c_4 + 2c_2\, c_3 - 2c_5\, N \\
\dot{c}_6 &= 2c_1\, c_5 + 2c_2\, c_4 + c_3^2 - 2c_6\, N\,,
\end{aligned} \tag{1.6}$$

where the overdot denotes the time derivative.

One major lesson that emerges from studies of aggregation and other irreversible processes is that the asymptotic behavior (which is the most interesting characteristic of the system) depends on the initial condition in a trivial way, *e.g.*, in terms of the entire mass, while the detailed behavior of the initial data is irrelevant. Therefore it is convenient to choose the natural monomer-only initial condition

$$c_k(0) = \delta_{k,0}\,. \tag{1.7}$$

If not stated otherwise, we shall always assume such an initial condition in the following. Before solving the initial-value problem (1.5)–(1.7), let us look at the moments of the mass distribution, where considerable information can be gleaned with relatively little effort.

Moments

For master equations with neat kernels, the moments $M_n(t) \equiv \sum_{k\geq 1} k^n c_k(t)$ usually satisfy simple rate equations that may be solvable even if the master equations are unsolvable. Moments also immediately give us some basic information about the mass distribution, *e.g.*, the ratio $M_1/M_0 \equiv M/N$ gives an estimate for the average cluster mass.

In the case of the constant reaction rates, the moment equations are particularly simple. Using Eqs. (1.5) we deduce

$$\begin{aligned}
\frac{dM_n}{dt} &= \sum_{k=1}^{\infty} k^n\, \dot{c}_k = \sum_{k=1}^{\infty} k^n \Big[\sum_{i+j=k} c_i c_j - 2c_k \sum_{i=1}^{\infty} c_i \Big] \\
&= \sum_{i,j}^{\infty} (i+j)^n\, c_i\, c_j - 2M_n\, M_0,
\end{aligned} \tag{1.8}$$

where the sums over i and j are unrestricted in the second line. The explicit equations for the first few moments are

$$\begin{aligned}
\dot{M}_0 &= \sum_{i,j} c_i\, c_j - 2M_0^2 = -M_0^2 \\
\dot{M}_1 &= \sum_{i,j} (i+j)\, c_i\, c_j - 2M_1 M_0 = 0 \\
\dot{M}_2 &= \sum_{i,j} (i^2 + 2ij + j^2)\, c_i\, c_j - 2M_2 M_0 = 2M_1^2 \\
\dot{M}_3 &= \sum_{i,j} (i^3 + 3i^2 j + 3ij^2 + j^3)\, c_i\, c_j - 2M_3 M_0 = 6M_1 M_2 \\
\dot{M}_4 &= \sum_{i,j} (i^4 + 4i^3 j + 6i^2 j^2 + 4ij^3 + j^4)\, c_i\, c_j - 2M_4 M_0 = 8M_1 M_3 + 6M_2^2
\end{aligned} \tag{1.9}$$

For the monomer-only initial condition, $M_n(0) = 1$ for all $n \geq 0$. The solution for the zeroth moment $M_0 = N$ is

$$N(t) = \frac{1}{1+t}\,. \tag{1.10}$$

Solving equations (1.9) for the higher moments one by one we obtain $M_1 = 1$, $M_2 = 1+2t$, $M_3 = 1+6t+6t^2$, $M_4 = 1 + 14t + 36t^2 + 24t^3$, *etc.* In general, $M_n \simeq n!\, t^{n-1}$ as $t \to \infty$.

Pedestrian approach

The master equations (1.5) are recursive and therefore they can be solved one by one. For the monomer-only initial condition, we substitute $N(t)$ from (1.10) into the first of (1.6) and integrate to give $c_1(t) = (1+t)^{-2}$. Having found c_1, the master equation for c_2 becomes

$$\dot{c}_2 = (1+t)^{-4} - 2(1+t)^{-1}\, c_2$$

Solving this equation subject to $c_2(0) = 0$ gives $c_2(t) = t/(1+t)^3$. The next density satisfies

$$\dot{c}_3 = 2t(1+t)^{-5} - 2(1+t)^{-1}\, c_3\,, \qquad c_3(0) = 0$$

whose solution is $c_3(t) = t^2/(1+t)^4$. Continuing this recursive approach we find $c_4(t) = t^3/(1+t)^5$, then $c_5(t) = t^4/(1+t)^6$, *etc.* This pattern suggests the general solution

$$c_k(t) = \frac{t^{k-1}}{(1+t)^{k+1}}\,. \tag{1.11}$$

A direct argument using induction proves that this guess is correct.

The elegant closed-form solution (1.11) has many interesting asymptotic properties, including

1. For $t \to \infty$, $c_k \to t^{-2}\, e^{-k/t}$. Thus for fixed k, each $c_k(t)$ approaches a common limit that decays as t^{-2} as $t \to \infty$ (Fig. 1.2). For $k < t$, the mass distribution is nearly flat, as shown on the right side of the figure.
2. The area under the mass distribution is therefore proportional to $t^{-2} \times t = t^{-1}$, which reproduces the correct time dependence of the total concentration of clusters.
3. The short- and long-time limits of c_k can be easily determined without solving the full master equations. For the short-time behavior we ignore the loss terms in the master equations. From the resulting master equations, we obtain $c_k(t) \sim t^{k-1}$ for $t \ll 1$. Conversely for $t \to \infty$, there is no production of k-mers for fixed k. We therefore ignore the gain terms in the master equation to give $\dot{c}_k \sim -2c_k N$, whose solution is $c_k \sim t^{-2}$.

Exponential ansatz

Solutions to the master equations often have an exponential form — equation (1.11) is one such example. By making use of this assumption at the outset, we can simplify the rate equations considerably. For the case of the constant kernel, the appropriate exponential ansatz is

$$c_k(t) = A(t)\, a(t)^{k-1}, \tag{1.12}$$

with the initial conditions $A(0) = 1$ and $a(0) = 0$. Choosing the power $k-1$ for a makes the ansatz compatible with the monomer-only initial condition. Substituting the ansatz (1.12) into the master equations (1.5), and dividing both sides of the equation by c_k, we find

$$\frac{\dot{A}}{A} + (k-1)\frac{\dot{a}}{a} = (k-1)\frac{A}{a} - \frac{2A}{1-a}.$$

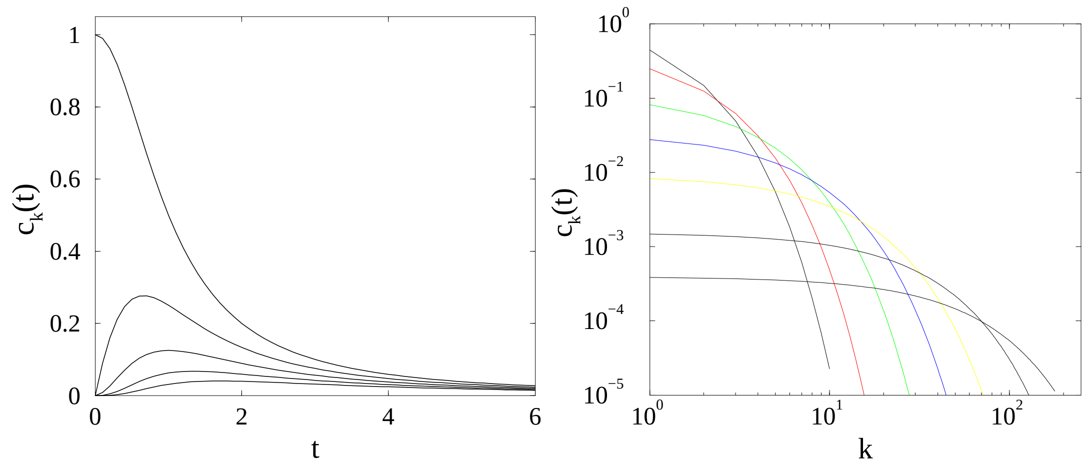

Figure 1.2: Left: Cluster concentrations $c_k(t)$ versus time for constant kernel aggregation for $k = 1, 2, 3, 4, 5$ (top to bottom). The concentrations approach a common limit as $t \to \infty$, as predicted by the scaling form in Eq. (1.11). Right: $c_k(t)$ versus k on a double logarithmic scale for $t = 1, 2, 5, 10, 20, 50$, and 100 (upper left to lower right).

Thus the exponential ansatz leads to k-dependent and k-independent components that we can equate separately to give

$$\dot{A} = -\frac{2A^2}{1-a}; \qquad \dot{a} = A. \tag{1.13}$$

If we had chosen a different power of a in the initial ansatz, there would not be the natural alignment of terms given above, but it would also be clear from the degree of misalignment how to choose the correct power of a. Since $\sum_{k\geq 1} kc_k = A\sum_{k\geq 1} ka^{k-1} = A(1-a)^{-2}$, mass conservation implies $A = (1-a)^2$; the same conservation law also follows from equations (1.13). Substituting $A = (1-a)^2$ back into (1.13) we immediately find

$$A = \frac{1}{(1+t)^2}; \qquad a = \frac{t}{1+t}, \tag{1.14}$$

thus reproducing the solution for $c_k(t)$ in Eq. (1.11).

The exponential ansatz has an advantage over the two previous approaches in that it involves less guesswork and it requires dealing with two (instead of infinitely many) differential equations. In addition, this ansatz works for all exponentially decaying initial conditions.

Generating function method

A powerful approach for solving the master equations is the generating function method. This technique is ideally-suited for aggregation because the master equations have a discrete convolution form that transform into an easily-soluble product by the generating function. The generating function is defined as

$$\mathcal{C}(z,t) \equiv \sum_{k=1}^{\infty} c_k(t) z^k, \tag{1.15}$$

and it encodes the entire mass distribution within a single function. To apply the generating function method to constant-kernel aggregation, we take each of the equations for c_k in (1.6), multiply by z^k, and sum over all k. This gives

$$\frac{d\mathcal{C}}{dt} = \sum_k \sum_{i+j=k} c_i z^i\, c_j z^j - 2\sum_k c_k z^k \, \sum_i c_i = \mathcal{C}^2 - 2\,\mathcal{C}N \tag{1.16}$$

Here the sum over k renders the two sums over i and j independent, so that the first term reduces to a product. This reduction to a product is the essential simplification of the generating function. Since the rate equation for N is $\dot{N} = -N^2$, the function $\mathcal{C}_- \equiv \mathcal{C} - N$ satisfies $\dot{\mathcal{C}}_- = \mathcal{C}_-^2$. This equation should be supplemented with an initial condition which is $\mathcal{C}_-(z, t = 0) = z - 1$, for the monomer-only initial condition. The solution is $\mathcal{C}_- = (z - 1)/[1 - (z - 1)t]$, from which we obtain

$$\mathcal{C} = \frac{1}{1+t}\,\frac{z}{1-(z-1)t}\ . \tag{1.17}$$

Expanding (1.17) as a power series in z gives

$$\mathcal{C}(z,t) = \sum_{k=1}^{\infty} z^k \frac{t^{k-1}}{(1+t)^{k+1}}\ .$$

From this form, we directly read off the mass distribution and thereby recover Eq. (1.11).

For an *arbitrary* initial condition the generating function is

$$\mathcal{C}(z,t) = (1+t)^{-2}\,\frac{\mathcal{C}_0(z)}{1-\frac{t}{1+t}\mathcal{C}_0(z)}\ , \tag{1.18}$$

where $\mathcal{C}_0(z) = \mathcal{C}(z, t = 0)$ and we also assume that $N(t = 0) = \mathcal{C}_0(z = 1) = 1$. Expanding the generating function (1.18) as a power series in z to obtain the densities $c_k(t)$ for all k is straightforward in principle but may be computationally tedious.

Product Kernel, $K_{ij} = ij$

When the aggregation rate is a sufficiently increasing function of the masses of the reacting clusters, gelation can occur in a finite time, in which a non-zero fraction of the total mass condenses into a single cluster (think of the setting of Jello). The product kernel represents an exactly soluble example of this spectacular feature. Beyond the gelation time, the system divides into two phases: the *gel*, or the infinite cluster, and the remaining *sol* of finite clusters whose total mass decreases with time.

The product kernel arises for monomers that consist of f-functional reactive endgroups (Fig. 1.3). When two monomers merge, the resulting dimer has $2f - 2$ reactive endgroups, a trimer has $3f - 4$ endgroups, and a k-mer has $kf - 2(k - 1) = (f - 2)k + 2$ endgroups. If all endgroups are equally reactive, the reaction rate between two clusters equals the product of the number of endgroups:

$$K_{ij} = [(f-2)i+2][(f-2)j+2] = (f-2)^2 ij + 2(f-2)(i+j) + 4. \tag{1.19}$$

The case $f = 2$ corresponds to linear polymers, for which K_{ij} is constant, while the product kernel arises for $f \to \infty$. For finite $f > 2$, the kernel is a linear combination of the constant, product, and sum kernels.

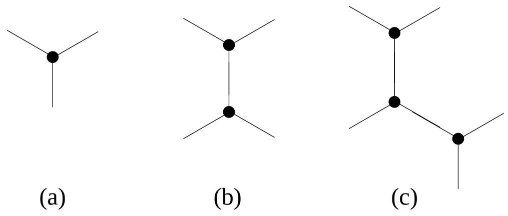

Figure 1.3: Small k-mers of 3-functional units. (a) Monomer. (b) Dimer. (c) Trimer.

Let us now focus on the pure product kernel, $K_{ij} = ij$, for which the master equations are

$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i+j=k} ij\ c_i c_j - k c_k \sum_i i\, c_i = \frac{1}{2}\sum_{i+j=k} ij\ c_i c_j - k c_k. \tag{1.20}$$

Notice that in the loss term, a k-mer disappears if it reacts with a cluster of *any* size, include an infinite-mass gel, if it exists. Thus the sum in the loss term, $\sum ic_i$, includes all finite clusters *and* the gel, so that $\sum ic_i = 1$. However, when we compute the rate equation for the first moment by summing the master equations, the left-hand side, $\sum k\dot{c}_k$, is not necessarily conserved because the term associated with the infinite-mass cluster is not part of this sum. We will discuss the subtlety of more detail below. Finally, product kernel aggregation is equivalent to the Erdös-Rényi random graph that will be discussed in section 4.1. Thus the solution to product kernel aggregation also provides many fundamental properties of the Erdös-Rényi random graph for free.

Moments

If we were unaware of the existence of a singularity, the quickest way to detect that something may be amiss is from the behavior of the moments. Summing equations (1.20) we get

$$\frac{dN}{dt} = \frac{1}{2}\sum_{i,j} ic_i\, jc_j - \sum_k kc_k = \frac{1}{2} - 1 = -\frac{1}{2} \tag{1.21}$$

The solution $N(t) = 1 - \frac{t}{2}$ vanishes at $t = 2$ and becomes negative when $t > 2$. This pathology is the sign that a gel appears at some t_g (that is less than 2), after which $\sum kc_k = 1$ is no longer valid. Thus equation (1.21) must be modified when $t > t_g$; we will see that the right modification ensures that the cluster density remains positive.

The above argument predict only the upper bound $t_g < 2$, but the behavior of higher moments suggests that the gelation time $t_g = 1$. Consider the second moment M_2, which evolves as

$$\frac{dM_2}{dt} = \sum_k k^2\, \dot{c}_k = \frac{1}{2}\sum_i\sum_j \left[(i+j)^2(ic_i)(jc_j) - k^3 c_k\right] \tag{1.22}$$

$$= \frac{1}{2}\sum_i\sum_j \left[(i^3 c_i)(jc_j) + (ic_i)(j^3 c_j) + 2(i^2 c_i)(j^2 c_j) - k^2 c_k\right] \tag{1.23}$$

$$= M_2^2. \tag{1.24}$$

Solving this equation subject to $M_2(0) = 1$ we obtain $M_2(t) = (1-t)^{-1}$. (For a general initial condition, the solution of (1.22) is singular when $t = 1/M_2(0)$.) The singularity is the sign of gelation, and suggests that gelation occurs at $t_g = 1$. However, is it possible that the third moment diverges earlier, so that gelation must have occurred earlier? The answer is *no*. Indeed, writing the rate equation for the third moment:

$$\frac{dM_3}{dt} = \frac{1}{2}\sum_{i,j}(i+j)^3 ic_i\, jc_j - \sum_k k^4 c_k \;= 3M_3M_2 \tag{1.25}$$

and solving subject to $M_3(0) = 1$ we obtain $M_3(t) = (1-t)^{-3}$. Similarly,

$$\frac{dM_4}{dt} = \frac{1}{2}\sum_{i,j}(i+j)^4 ic_i\, jc_j - \sum_k k^5 c_k = 4M_4M_2 + 3M_3^2\,, \tag{1.26}$$

whose solution is $M_4(t) = (1+2t)(1-t)^{-5}$. Using induction one may verify that all moments diverge at $t_g = 1$. However, the moment method does not allow one to probe the moments (and the mass distribution) beyond the gel point. For this more complete analysis we need the generating function technique.

Generating function approach

To solve Eqs. (1.20), it is convenient to use the *exponential* generating function $\mathcal{E}(y,t) \equiv \sum_k k\, c_k(t)\, e^{yk}$. This generating function encodes the sequence kc_k instead of the sequence c_k and makes the ensuing analysis slightly simpler. To determine the governing equation for $\mathcal{E}$ we multiply the master equation for each $\dot{c}_k$ by

$k\, e^{yk}$ and sum over k to obtain

$$\begin{aligned}\frac{\partial \mathcal{E}}{\partial t} &= \frac{1}{2}\sum_{i,j}(i+j)ij\, c_i\, c_j\, e^{yk} - \sum_k k^2 c_k\, e^{yk} \\ &= \frac{1}{2}\sum_i i^2 c_i\, e^{yi}\sum_j j c_j\, e^{yj} + \frac{1}{2}\sum_i c_i\, e^{yi}\sum_j j^2 c_j\, e^{yj} - \sum_k k^2 c_k\, e^{yk} \\ &= (\mathcal{E}-1)\frac{\partial \mathcal{E}}{\partial y}. \end{aligned} \tag{1.27}$$

This is the Burgers equation — the simplest non-linear hyperbolic equation. The salient feature of the Burgers equation is that it describes the development of shock waves. The appearance of a gel in product-kernel aggregation is closely related to this appearance of a shock wave.

Equations such as (1.27) can be transformed into a linear equation by the hodograph transformation[2] that interchanges the role of the dependent and independent variables. We first write partial derivatives in terms of the Jacobian:

$$\frac{\partial \mathcal{E}}{\partial t} = \frac{\partial(\mathcal{E},y)}{\partial(t,y)}.$$

Then Eq. (1.27) for the generating function can be re-written as:

$$\frac{\partial \mathcal{E}}{\partial t} = \frac{\partial(\mathcal{E},y)}{\partial(t,y)} = (\mathcal{E}-1)\frac{\partial \mathcal{E}}{\partial y} = (\mathcal{E}-1)\frac{\partial(\mathcal{E},t)}{\partial(y,t)}.$$

Now we cancel the common factor in the denominator to obtain the implicit, but linear equation for the generating function

$$\frac{\partial(\mathcal{E},y)}{\partial(\mathcal{E},t)} = \left.\frac{\partial y}{\partial t}\right|_{\mathcal{E}} = 1-\mathcal{E}. \tag{1.28}$$

The solution is simply $y = (1-\mathcal{E})t + f(\mathcal{E})$, where $f(\mathcal{E})$ is determined from the initial condition. For the monomer-only initial condition, the initial generating function is $\mathcal{E}(t=0) = \sum k c_k\, e^{yk}|_{t=0} = e^y$, or $y(t=0) = f(\mathcal{E}) = \ln \mathcal{E}$. Hence we arrive at the implicit solution

$$\mathcal{E}\, e^{-\mathcal{E}t} = e^{y-t}. \tag{1.29}$$

The generating function itself is obtained by the Lagrange inversion formula (see highlight below). Identifying $y = \mathcal{E}t$ and $x = te^{y-t}$ in Eq. (1.32) immediately gives

$$\mathcal{E}t = \sum_{k\geq 1}\frac{k^{k-1}}{k!}\, t^k\, e^{-kt}\, e^{yk}\,.$$

Since the density c_k equals the k^{th} term in the series expansion of $\mathcal{E}$ divided by k, we obtain the remarkable result

$$c_k(t) = \frac{k^{k-2}}{k!}\, t^{k-1}\, e^{-kt}\,. \tag{1.30}$$

---

[2] An alternative is to write $y = y(h,t)$, compute $dy = y_h dh + y_t dt$ and then relate the derivatives when $dy = 0$.

Lagrange inversion

Given a function $x = f(y)$, with $x \sim y$ for small y, what is the power-series representation of the inverse function $y(x) = \sum_{n\geq 1} A_n x^n$? The coefficients A_n are given by the Lagrange inversion formula. Formally, the coefficients A_n may be obtained by a contour integration around a small circle centered at the origin:

$$A_n = \frac{1}{2\pi i}\oint \frac{y}{x^{n+1}}\,dx = \frac{1}{2\pi i}\oint \frac{y}{x^{n+1}}\,\frac{dx}{dy}\,dy = \frac{1}{2\pi i}\oint \frac{y}{f(y)^{n+1}}\,f'(y)\,dy. \tag{1.31}$$

The crucial step is to transform from integrating over x to integrating over y. The transformed contour is also a small circle about the origin since y and x are proportional to each other near the origin.

Let's apply this inversion formula to $f(y) = y\,e^{-y} = x$. From Eq. (1.31) and using $\frac{dx}{dy} = (1-y)\,e^{-y}$, we have

$$A_n = \frac{1}{2\pi i}\oint \frac{y}{(y\,e^{-y})^{n+1}}\,(1-y)\,e^{-y}\,dy = \frac{1}{2\pi i}\oint \frac{1-y}{y^n}\,e^{ny}\,dy$$

To find the residue we simply expand the exponential in a power series and then read off the coefficient of $\frac{1}{y}$ in the integral. Thus

$$A_n = \frac{1}{2\pi i}\oint \sum_{k=0}^{\infty}\frac{n^k}{k!}\left(y^{k-n} - y^{k+1-n}\right)dy = \frac{n^{n-1}}{(n-1)!} - \frac{n^{n-2}}{(n-2)!} = \frac{n^{n-1}}{n!},$$

so that the series representation of the inverse function $y(x)$ is

$$y = \sum_{n\geq 1}\frac{n^{n-1}}{n!}\,x^n. \tag{1.32}$$

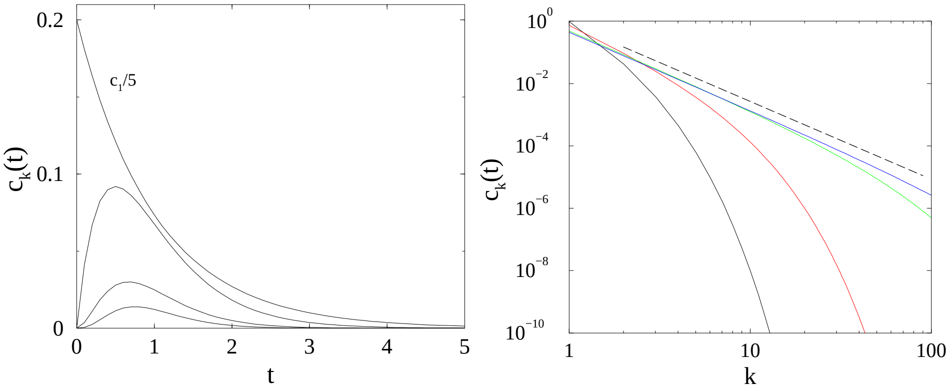

Figure 1.4: Left: Cluster concentrations $c_k(t)$ versus time for the product kernel for $k = 1, 2, 3, 4$ (top to bottom, with c_1 divided by 5). Right: $c_k(t)$ versus k for $t = 0.1, 0.4, 0.8$, and 0.9 on a double logarithmic scale (upper left to lower right). The dashed line has slope $-5/2$.

For the asymptotic behavior of this distribution, Stirling's approximation gives

$$c_k(t) \simeq \frac{k^{k-2}}{\sqrt{2\pi k}}\left(\frac{e}{k}\right)^k t^{k-1}\,e^{-kt} \;\underset{t\uparrow 1}{\longrightarrow}\; \frac{e^{-k(1-t)^2/2}}{\sqrt{2\pi}\,k^{5/2}}, \tag{1.33}$$

where we have approximated $e^{-k(t-\ln t-1)}$ by $e^{-k(1-t)^2/2}$ for $t \to 1$ from below. For $t \neq 1$, the mass distribution c_k decreases exponentially with k. At the gelation time $t = t_g = 1$, however, the mass distribution has a power-law tail that is a precursor of the singularity where an infinite-mass cluster first appears. Beyond t_g, the cluster population naturally divides into the sol and the gel phases. Near the gelation time, (1.33) gives the scaling form for the mass distribution

$$c_k(t) \simeq s^{-5/2}\Phi(k/s) \qquad \text{with} \quad \Phi(z) = \frac{1}{\sqrt{2\pi}}\,\frac{e^{-z/2}}{z^{5/2}}, \tag{1.34}$$

in which the characteristic mass is $s = (1-t)^{-2}$.

The behavior of the moments $M_n = \sum_{k\geq 1} k^n c_k$ of the mass distribution cleanly illustrates what is happening near the gelation transition. The most dramatic behavior occurs for the first moment $M_1 = \sum kc_k$ — ostensibly the total mass — which is conserved only for $t \leq t_g$. Beyond t_g, the sum in M_1 accounts for the mass of *finite* clusters only, while the contribution of an infinite-mass cluster is excluded. Thus $g \equiv 1 - M_1$ gives the fraction of the total mass that belongs to the infinite cluster or the gel. To find g, we substitute $y = 0$ in the implicit equation (1.29) for the generating function and then use $g \equiv 1 - M_1$ to give

$$g = 1 - e^{-gt}\,. \tag{1.35}$$

This equation always admits a trivial solution $g = 0$. For $t > 1$, however, there is an additional non-trivial solution in which the gel has a non-zero mass. While Eq. (1.35) is not analytically soluble, the limiting behaviors of Eq. (1.35) can be obtained perturbatively. Just past the gelation time, we write $t = 1 + \delta$ and expand (1.35) for small δ, while for $t \to \infty$, we write $g = 1 - \epsilon$ and expand for small ϵ. These give

$$g = \begin{cases} 0 & \text{for} \quad t < 1 \\ 2(t-1) - 8(t-1)^2/3 + \ldots & \text{for} \quad t \downarrow 1 \\ 1 - e^{-t} - te^{-2t} + \ldots & \text{for} \quad t \to \infty. \end{cases} \tag{1.36}$$

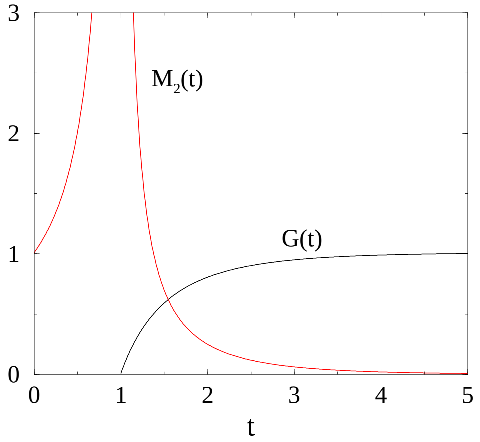

Figure 1.5: Time dependence of the mass of gel phase and the mean mass of the finite clusters.

Similarly we may obtain rate equations for all moments that are valid in the post-gel regime. For example, the zeroth moment, or the density of finite clusters, [3] $M_0 \equiv N = \sum c_k$, obeys

$$\begin{aligned} \frac{dM_0}{dt} &= \frac{1}{2}\sum_{i,j} ic_i\, jc_j - \sum_k kc_k \\ &= \frac{1}{2}\,(1-g)^2 - (1-g) = \frac{g^2-1}{2}. \end{aligned} \tag{1.37}$$

---

[3] For the zeroth moment, the distinction between the density of all clusters and finite clusters is immaterial since there is only a single infinite cluster.

This equation confirms our expectation that (1.21) is correct only in the pre-gel regime. Using the results of (1.36) for g, we obtain

$$M_0 = \begin{cases} 1 - t/2 & \text{for} \quad t \le 1; \\ 1 - t/2 + 2(t-1)^3/3 + \ldots & \text{for} \quad t \downarrow 1; \\ e^{-t} + (t/2)\, e^{-2t} + \ldots & \text{for} \quad t \to \infty. \end{cases} \tag{1.38}$$

Similarly, the rate equation for M_2 is

$$\begin{aligned} \dot{M}_2 &= \frac{1}{2}\sum_{i,j}(i+j)^2\, i\, j\, c_i\, c_j - \sum_{i,k} k^3\, c_k = \sum_{i,j}(i^3\, c_i\, j c_j + i^2\, c_i\, j^2\, c_j) - \sum_{i,k} k^3\, c_k \\ &= M_2^2 - M_3 g \end{aligned}$$

Before the gel point we recover the already known solution $M_2(t) = (1-t)^{-1}$. For $t > t_g$ the equation for M_2 involves g and M_3 which are not known explicitly. Therefore there is no explicit expression for M_2 and indeed for higher moments, in the post-gel regime.

Interestingly, the higher moments can be expressed in terms of g. First, we note that the moments for the population of finite clusters are just the derivatives of the generating function $\mathcal{E}$:

$$M_n = \left.\frac{\partial^{n-1}\mathcal{E}}{\partial y^{n-1}}\right|_{y=0}.$$

Let us consider the second moment. We take the logarithm of Eq. (1.29), differentiate with respect to y, and set $y = 0$ to give

$$M_2(t) = \left[\frac{1}{\mathcal{E}(y\!=\!0,t)} - t\right]^{-1}, \tag{1.39}$$

with $\mathcal{E}(y = 0, t) = 1$ in the sol phase and $\mathcal{E}(y = 0, t) = 1 - g = e^{-gt}$ [see Eq. (1.35)] in the gel phase. Therefore,

$$M_2(t) = \begin{cases} (1-t)^{-1} & \text{for} \quad t < 1; \\ (e^{gt} - t)^{-1} & \text{for} \quad t > 1. \end{cases} \tag{1.40}$$

For $t \to t_g$ from below, the second moment grows rapidly with time, while for large t, $M_2 \to 0$ as finite clusters are progressively engulfed by the gel (Fig. 1.5).

1.2 Scaling

Scaling exploits the observation that the typical cluster mass changes systematically with time so that a change in time scale corresponds to a change in mass scale. This equivalence is embodied by the *scaling ansatz*, which may be written as

$$c(x,t) = \frac{1}{s^2}\, f\left(\frac{x}{s}\right).$$

Here $s = s(t)$ is the typical cluster mass, x/s is the scaled mass, and $f(x/s)$ is the scaling function. Thus the fundamental system variables are not the mass and time, but rather, the scaled mass x/s and the time. The prefactor s^{-2} in front of the scaling function enforces mass conservation: $\int x\, c(x,t)\, dx = 1$ reduces to the manifestly time-independent relation $\int u\, f(u)\, du = 1$.

There are several reasons why scaling plays a central role in numerous non-equilibrium phenomena. The chief reason, of course, is that it tremendously simplifies and condenses the description — a function of one variable is infinitely simpler than a function of two variables. On a more technical level, scaling provides the simplest route to the asymptotic solution of the master equations, especially for problems where exact solutions are difficult or impossible to obtain. This simplification arises because the scaling ansatz separates a two-variable master equation into two single-variable systems that can be analyzed individually. Further, a scaling solution is independent of the initial conditions and thus is automatically constructed to focus on the interesting asymptotic behavior. Finally, scaling gives universal information aspects of the asymptotic mass distribution in terms of generic features of the reaction kernel and it provides a robust classification of the solutions to the master equations for many non-equilibrium processes; we will see this approach in action in many of the later chapters.

Before we can apply scaling, we need to settle on the "right" definition for the typical mass. From the scaling ansatz, the $n^{\rm th}$ moment of the mass distribution is

$$M_n = \int x^n \, \frac{1}{s^2}\, f(x/s)\, dx \sim s^{n-1}.$$

Hence for any value of n, the ratio M_{n+1}/M_n is proportional to s. Consequently, either $1/M_0$ or M_2 (where we set $M_1 = 1$) are good measures of the typical mass, as long as the cluster mass distribution itself is not too singular. When scaling holds, we can define the typical mass to best suit the situation.

We also need basic information about the matrix of reaction rates K_{ij} to determine the consequences of scaling. It turns out that only two features of this matrix determine the asymptotic properties of the mass distribution. The first is the homogeneity index λ, defined by

$$K_{ai,aj} \sim a^\lambda K_{ij},$$

that gives the overall mass dependence of the reaction rate. The second is the index ν, defined by

$$K_{1,j} = K_{j,1} \sim j^\nu,$$

that characterizes the relative importance of reactions between clusters of similar masses and disparate masses. For example, the constant kernel is characterized by $(\lambda,\nu) = (0,0)$ and the product kernel by $(\lambda,\nu) = (2,1)$. An important example is the "Brownian" kernel (1.4), the reaction rate for spherical aggregates that undergo Brownian motion. For this kernel, $(\lambda,\nu) = (0,1/3)$.

The role of the indices λ and ν may be best appreciated by considering the following pictorial representation of the reaction matrix

$$K_{ij} = \begin{pmatrix} SS & \cdots & SL & \cdots \\ \vdots & \ddots & \cdots & \cdots \\ LS & \vdots & LL & \ddots \\ \vdots & \vdots & \ddots & \ddots \end{pmatrix}$$

The meta-entries SS, $SL (= LS)$, and LL denote the reaction rates of small clusters with other small clusters, large-small interactions, and large-large interactions, respectively. The exactly-soluble examples discussed above are archetypes of three distinct universality classes with the following general behavior:

- **Type I:** $LL \gg LS, SS$, corresponding to $\lambda > \nu$. Because of the high reactivity of large clusters they quickly disappear, while small clusters tend to persist. The result is a cluster mass distribution that decays monotonically with mass. The product kernel typifies this type of system.
- **Type II:** all three reactions are of the same order. This marginal class contains the constant kernel $K_{ij} = 1$. However the asymptotic behavior of this class is sensitive to details of the reaction rates.
- **Type III:** $LS \gg LL, SS$, or $\lambda < \nu$. As the reaction develops, small clusters are quickly removed from the system because of the dominance of large-small interactions. Thus the system has a dearth of small clusters, leading to a peaked mass distribution.

Let's now apply scaling to determine basic features of the cluster mass distribution. In the continuum limit, the master equations for aggregation are

$$\dot c(x,t) = \frac{1}{2}\int_0^x dy\, K(y,x-y)\, c(y,t)\, c(x-y,t) - \int_0^\infty dy\, K(x,y)\, c(x,t)\, c(y,t) \tag{1.41}$$

Using homogeneity, $K(ax, ay) = a^\lambda K(x, y)$, and substituting the scaling form $c(x, t) = s^{-2} f(x/s)$ into the master equation (1.41), the left-hand side becomes

$$\dot{c}(x,t) = -\frac{\dot{s}}{s^3}\left[2f(u) + uf'(u)\right],$$

where $u = x/s$, while the right hand side is $s^{\lambda-3}\mathcal{K}(u)$, where

$$\mathcal{K}(u) = \frac{1}{2}\int_0^u dv\, K(v, u-v)\, f(v)\, f(u-v) - \int_0^\infty dv\, K(u,v)\, f(u)\, f(v)\,, \tag{1.42}$$

with $v = y/s$. Equating and re-arranging, the dependences on time and on the scaled mass u separate as

$$\frac{\dot{s}(t)}{s(t)^\lambda} = -\frac{\mathcal{K}(u)}{2f(u) + uf'(u)} \equiv \Lambda. \tag{1.43}$$

The left-hand side is a function of time only while the right-hand side is a function of u only, so that they are both separately equal to a constant — the separation constant Λ. (Actually, there is a hidden time dependence in Eq. (1.42) that disappears as long as the integrals converge at their lower limits.) This variable separation is a primary simplifying feature of the scaling ansatz.

The time dependence of the typical mass is determined from $\dot{s} = \Lambda s^\lambda$ and gives three different behaviors:

$$s(t) \sim \begin{cases} t^{1/(1-\lambda)} \equiv t^z & \lambda < 1; \\ e^{\Lambda t} & \lambda = 1; \\ (t_g - t)^{-1} & 1 < \lambda \le 2. \end{cases} \tag{1.44}$$

For non-gelling systems the time dependence of the typical mass is primarily determined by the homogeneity index λ; other features of the reaction rate such as the second homogeneity index ν affect only details. For instance, in the growth law $s(t) \simeq At^{1/(1-\lambda)}$, the amplitude A depends on details of the reaction kernel while the growth exponent $1/(1-\lambda)$ depends only on λ.

The time dependence (1.44) can also be obtained from the following heuristic argument. Assuming scaling with a typical cluster mass s at time t, the corresponding cluster density is of the order of $1/s$. Consider a time increment Δt during which all clusters react, so that the typical mass increases by $\Delta s \approx s$. This time increment is the inverse of an overall reaction rate. In turn, this rate is proportional to the reaction kernel $K(s, s) \sim s^\lambda$ and the concentration $1/s$. Hence $\frac{\Delta s}{\Delta t} \sim s \times (s^\lambda/s)$ which then reproduces (1.44).

We see that non-gelling systems correspond to $\lambda \le 1$, while for gelling systems $1 < \lambda \le 2$. We should keep in mind, of course, that the master equations are ill-posed if $\nu > 1$, as instantaneous gelation occurs in this case; our consideration of (homogeneous) aggregation kernels tacitly assumes that $\nu \le 1$.

The dependence of the scaling function f on the scaled mass u is governed by the u-dependent part of (1.43),

$$2f(u) + uf'(u) + \Lambda^{-1}\mathcal{K}(u) = 0 \tag{1.45}$$

with $\mathcal{K}(u)$ given by (1.42). The non-linear integro-differential equation (1.45) is complicated, and the full understanding of the behavior of the scaling function $f(u)$ is still lacking. It is certainly impossible to solve (1.45) for an arbitrary kernel, so 'understanding' refers to qualitative features: asymptotic behaviors, justifying the classification to type I, II, and III kernels, etc. For instance, it has been shown that when the scaled mass is large, $u \gg 1$, the scaling function has an exponential dependence $f(u) \sim e^{-au}$; the detailed behavior of the kernel affects only the prefactors. The behavior of the scaling function when the scaled mass is small is less robust. Many empirical results indicate that $f(u) \sim u^{-\tau}$ for $u \ll 1$. As a corollary, the time dependence of the density of small-mass clusters is given by

$$c_k \sim \frac{1}{s^2}\left(\frac{k}{s}\right)^{-\tau} \sim k^{-\tau}\, t^{-(2-\tau)z} \tag{1.46}$$

The exponent τ apparently depends on the detailed properties of the reaction kernel. A heuristic approach is to *assume* that the behavior of monomers represents the $u \to 0$ limit. The master equation for the monomer density is

$$\dot{c}_1 = -c_1 \sum_{j\ge 1} K_{1j}\, c_j \tag{1.47}$$

Since $K_{1j} \sim j^{\nu}$ and $c_j \sim j^{-\tau}$, the sum on the right-hand side of (1.47) converges if $\nu - \tau + 1 < 0$, and in this case the first first term provides a good estimate for the sum. Therefore $\dot{c}_1 \approx -K_{11}\, c_1^2$, leading to $c_1 \sim 1/t$. Matching this time dependence with that given in Eq. (1.46), we deduce the exponent relation $\tau = 1 + \lambda$. This power-law tail applies for $\nu - \tau + 1 = \nu - \lambda < 0$, that is, for Type I kernels.

1.3 Constant-Kernel Aggregation with Input

Many physical realizations of aggregation do not occur in a closed system, but instead a steady input helps drive the reaction. Examples of aggregation with input are diverse, and range from chemical processing in continuously-stirred tank reactor, to the distribution of star masses in the galaxy. In all cases, the interplay between input and aggregation leads to many new phenomena. Here we consider a constant input that begins at $t = 0$ and we limit ourselves to the situation of monomer input. Because the asymptotic behavior is again independent of initial conditions, we also consider only the case of an initially empty system, $c_k(0) = 0$.

The evolution of the mass distribution is now described by the master equation

$$\dot{c}_k = \sum_{i+j=k} c_i c_j - 2c_k N + \delta_{k,1}\,. \tag{1.48}$$

The total density satisfies $\dot{N} = -N^2 + 1$ whose solution is, for an initially empty system,

$$N(t) = \tanh t. \tag{1.49}$$

Hence the total density initially grows linearly with time but eventually saturates to 1.

The individual densities can be in principle found by solving the master equations one by one. However, again the generating function approach is a more potent tool. We introduce the generating function $\mathcal{C}(z,t) = \sum_{k\geq 1} c_k(t) z^k$ to recast the master equations (1.48) into the differential equation [compare with Eq. (1.16)]

$$\dot{\mathcal{C}}(z,t) = \mathcal{C}(z,t)^2 - 2\mathcal{C}(z,t)N(t) + z\,. \tag{1.50}$$

As in Eq. (1.16), it is convenient to define $\mathcal{C}_- = \mathcal{C} - N$ that then satisfies the closed equation $\dot{\mathcal{C}}_- = \mathcal{C}_-^2 + (z-1)$. Solving for $\mathcal{C}_-$, we obtain

$$\mathcal{C}(z,t) = N(t) - \sqrt{1-z}\,\tanh\left(t\,\sqrt{1-z}\right) \longrightarrow 1 - \sqrt{1-z} \qquad t \to \infty. \tag{1.51}$$

The generating function at infinite time can be inverted by expanding $\sqrt{1-z}$ in a power series in z

$$\begin{aligned}\sqrt{1-z} &= 1 + \tfrac{1}{2}(-z) + \tfrac{1}{2}\left(-\tfrac{1}{2}\right)\frac{(-z)^2}{2!} + \tfrac{1}{2}\left(-\tfrac{1}{2}\right)\left(-\tfrac{3}{2}\right)\frac{(-z)^3}{3!} + \tfrac{1}{2}\left(-\tfrac{1}{2}\right)\left(-\tfrac{3}{2}\right)\left(-\tfrac{5}{2}\right)\frac{(-z)^4}{4!} + \ldots \\ &= 1 - \frac{\Gamma(k-\frac{1}{2})}{2\Gamma(\frac{1}{2})}\frac{z^k}{\Gamma(k+1)}\,,\end{aligned}$$

In deriving of this expression we use the identity

$$a(a+1)\ldots(a+k-1) = \frac{\Gamma(a+k)}{\Gamma(a)}\,,$$

that follows from the basic gamma function identity $a\Gamma(a) = \Gamma(a+1)$. Finally, using $\Gamma(\frac{1}{2}) = \sqrt{\pi}$, we obtain[4]

$$c_k = \frac{1}{\sqrt{4\pi}}\,\frac{\Gamma(k-\frac{1}{2})}{\Gamma(k+1)}\,. \tag{1.52}$$

For the asymptotic behavior, we use the handy asymptotic relation for $k \gg 1$,

$$\frac{\Gamma(k+a)}{\Gamma(k+b)} \simeq k^{a-b}\,,$$

---

[4] In this section we write c_k instead of $c_k(\infty)$; whenever we treat a non-steady mass distribution, we write $c_k(t)$.

to obtain the tail of the steady-state mass distribution

$$c_k \simeq \frac{1}{\sqrt{4\pi}}\,\frac{1}{k^{3/2}} \qquad\qquad k \gg 1\,. \tag{1.53}$$

The steady-state mass distribution is heavy-tailed, as it must to produce a divergent mass density. At finite time, however, mass conservation requires that $\sum kc_k(t) = t$, so that the tail of the mass distribution must deviate from (1.53). However, we can give a qualitative argument that determines the time-dependent behavior: for sufficiently small masses $k \ll k_*$ the mass distribution $c_k(t)$ is very close to stationary form (1.53), while for $k \gg k_*$ the mass distribution is essentially zero. We determine the crossover mass k_* by requiring that the total mass in the system equals the elapsed time. Thus

$$t = \sum_{k=1}^{\infty} kc_k(t) \approx \sum_{k=1}^{k_*} kc_k \sim \sum_{k=1}^{k_*} k^{-1/2} \sim k_*^{1/2}\,, \tag{1.54}$$

leading to $k_* \sim t^2$. Thus the bulk of the population follows the steady-state power-law distribution (1.52) whose leading edge is cut off at $k_* \sim t^2$.

This qualitative picture can be sharpened by an exact analysis. To extract the densities from the generating function (1.51) we substitute the series representation

$$\pi\,\tanh(\pi x) = \sum_{n=-\infty}^{\infty} \frac{x}{x^2 + \left(n+\frac{1}{2}\right)^2}$$

into (1.51) and expand in powers of z to yield

$$c_k(t) = \frac{1}{t^3}\sum_{n=-\infty}^{\infty}\left(n+\frac{1}{2}\right)^2 \pi^2 \left[1+\left(n+\frac{1}{2}\right)^2\frac{\pi^2}{t^2}\right]^{-k-1}\,. \tag{1.55}$$

In the long-time limit, we replace the sum on the right-hand side of (1.55) by the integral over the variable $x = \left(\frac{1}{2}+n\right)\frac{\pi}{t}$. When $k \ll t^2$, we obtain

$$c_k \simeq \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{x^2\,dx}{(1+x^2)^{k+1}}\ ,$$

and computing the integral recovers (1.52). On the other hand, when k and $t \to \infty$ such that $\kappa = k/t^2$ remains finite, (1.55) simplifies to

$$c_k(t) = \frac{1}{t^3}\sum_{n=-\infty}^{\infty}\left(n+\frac{1}{2}\right)^2 \pi^2 \exp\left[-\left(n+\frac{1}{2}\right)^2 \pi^2\,\kappa\right]\,. \tag{1.56}$$

When the mass $k \gg k_*$, we may keep only the first term in (1.56) to give the leading asymptotic behavior of the mass density

$$c_k(t) = \frac{\pi^2}{4\,t^3}\; e^{-\pi^2\kappa/4}\ , \tag{1.57}$$

so that large-mass clusters are exceedingly rare.