Chapter 3

AGGREGATION

Aggregation is a fundamental non-equilibrium process in which reactive clusters join together irreversibly when they meet (Fig. 3.1) so that the typical mass of a collection of aggregates grows monotonically with time. Developing an understanding aggregation is important both because of its ubiquitous applications—such as the gelation of jello, the curdling of milk, the coagulation of blood, and the formation of stars by gravitational accretion—and because aggregation is an ideal setting to illustrate theoretical analysis tools. We schematically write aggregation as

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

That is, a cluster of mass $i + j$ is created at an intrinsic rate K_{ij} by the aggregation of a cluster of mass i and a cluster of mass j. The fundamental observables of the system are $c_k(t)$, the concentration of clusters of mass k at time t.

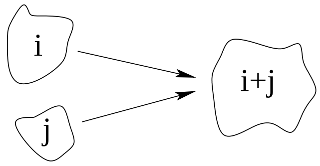

Figure 3.1: Schematic representation of aggregation. A cluster of mass i and mass j react to create a cluster of mass $i + j$.

The primary goal of this chapter is to elucidate the basic features of the mass distribution $c_k(t)$ and to understand which features of the reaction rate K_{ij} influence this distribution. In pursuit of this goal, we will write the master equations that describe the evolution of the cluster mass distribution in an infinite system and discuss some of its elementary properties. Next, we work out exact solutions for specific examples to illustrate both the wide range of phenomenology and the many useful techniques for analyzing master equations. We will then discuss the reaction rate in general terms and show how to calculate this rate. This discussion will naturally lead to the notion of *dynamical scaling*, which provides a simple way to obtain a general understanding of aggregation. Finally, we will discuss several important extensions of aggregation that exhibit rich kinetic properties.

The Master Equations

The traditional starting point for treating aggregation is the infinite set of equations that describe how the cluster mass distribution changes with time. For a general reaction rate K_{ij}, the master equations are:

$$\dot{c}_k(t) = \frac{1}{2} \sum_{\substack{i,j \\ i+j=k}} K_{ij}\, c_i(t)\, c_j(t) - c_k(t) \sum_{i=1}^{\infty} K_{ik}\, c_i(t). \tag{3.1}$$

Here the overdot denotes the time derivative. For conciseness, we will typically not write arguments of basic variables henceforth. The first term describes the gain in the concentration of clusters of mass $k = i + j$ due to the coalescence of a cluster of mass i with a cluster of mass j. This gain process occurs at the rate $K_{ij}c_ic_j$; the product c_ic_j gives the rate at which i-mers and j-mers meet, and the factor K_{ij}—the reaction kernel—is the rate at which k-mers are formed when i-mers and j-mers do meet. The second (loss) term accounts for the loss of clusters of mass k due to their reaction with clusters of arbitrary mass i. The prefactor of $\frac{1}{2}$ in the gain and loss terms ensure the correct counting of their relative contributions. To truly appreciate that the counting is correct, write out the first few master equations explicitly.

An important feature of the master equations is that the total mass (generally) is conserved. That is,

$$\sum_k k\,\dot{c}_k = \sum_k \sum_{i+j=k} \frac{1}{2} K_{ij}\,(i+j)\,c_i\,c_j - \sum_i \sum_k K_{ik}\,k\,c_i\,c_k = 0. \tag{3.2}$$

In the first term, the sum over k causes the sums over i and j to become independent and unrestricted. Thus the gain and loss terms become identical and the total mass is manifestly conserved.

While the master equation approach is the starting point in almost all studies of aggregation, its underlying assumptions and approximations should be noted at the outset, including:

- Bimolecular reactions. This assumes a dilute system so that higher-body interactions are negligible.
- Spatial homogeneity. The cluster densities are independent of spatial position. This is the mean-field assumption of a well-mixed system.
- Shape independence. The aggregate mass is the only dynamical variable; the role of cluster shape on evolution is not considered. Example: the coalescence of liquid droplets that always remain spherical.
- Thermodynamic limit. The system is assumed to be sufficiently large that discreteness effects can be ignored and cluster concentrations are continuous functions.

In spite of these limitations, the master equations capture many of the essential kinetic mechanisms of aggregation as we now discuss.

3.1 Exact Solutions

Although the master equations may appear formidable, they are exactly soluble for a number of prototypical special cases for which many incisive techniques have been developed. We discuss several of these approaches and apply them first to the case of the constant reaction kernel. Because of its simplicity, the constant kernel reaction is an ideal playground with which to build our understanding. We then turn to the more realistic (and more interesting) cases of the product and sum kernels, $K_{ij} = ij$ and $K_{ij} = i + j$, respectively. It is worth mentioning that the bilinear kernel, $K_{ij} = A + B(i + j) + Cij$, is also exactly soluble.

Constant Reaction Rates

It turns out to be convenient to choose $K = 2$. In this case the master equations are:

$$\dot{c}_k = \sum_{i+j=k} c_ic_j - 2c_k \sum_{i=1}^{\infty} c_i \equiv \sum_{i+j=k} c_ic_j - 2c_k\,N \tag{3.3}$$

where $N(t) = \sum_i c_i$, the zeroth moment of the mass distribution, is the concentration of clusters of any mass. The first few of these equations are explicitly:

$$\begin{aligned}
\dot{c}_1 &= -2c_1\, N \\
\dot{c}_2 &= c_1^2 - 2c_2\, N \\
\dot{c}_3 &= 2c_1\, c_2 - 2c_3\, N \\
\dot{c}_4 &= c_1\, c_3 + c_2^2 - 2c_4\, N \\
\dot{c}_5 &= c_1\, c_4 + c_2\, c_3 - 2c_5\, N \\
\dot{c}_6 &= c_1\, c_5 + c_2\, c_4 + c_3^2 - 2c_6\, N \\
&\vdots
\end{aligned} \tag{3.4}$$

Let's solve these equations subject to the monomer-only initial condition, $c_k(t = 0) = \delta_{k,0}$. Naively, these equations can be solved one by one because $N(t)$ can be determined separately and then the master equations have a recursive structure. Thus as the necessary preliminary, we determine $N(t)$. Summing Eq. (3.3) over all k, we find $\dot{N} = -N^2$, whose solution is

$$N(t) = \frac{N(0)}{1 + N(0)t} \to \frac{1}{t} \quad \text{as} \qquad t \to \infty. \tag{3.5}$$

Notice that the concentration does not depend on the initial concentration as $t \to \infty$. Substituting $N(t)$ into the first of (3.4) and integrating gives $c_1(t) = \frac{1}{(1+t)^2}$. Having found c_1, the master equation for c_2 becomes

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

This again can be integrated by elementary methods and the result is $c_2(t) = \frac{t}{(1+t)^3}$. In principle, this approach can be continued straightforwardly to yield $c_k(t)$ for all k.

Before leaving this pedestrian method, it is worth mentioning that much useful information can often be obtained from the much simpler equations for the moments of the mass distribution, $M_n(t) \equiv \sum_k k^n c_k(t)$. From the master equations (3.3) we already obtained the zeroth moment $M_0 = N$, and so we turn to higher moments. The moment equations are

$$\begin{aligned}
\dot{M}_n = \sum_{k=1}^{\infty} k^n\, \dot{c}_k &= \sum_{k=1}^{\infty} k^n \Big[\sum_{i+j=k} c_i c_j - 2c_k \sum_{i=1}^{\infty} c_i \Big] \\
&= \sum_{i,j}^{\infty} (i+j)^n\, c_i\, c_j - 2M_n\, M_0,
\end{aligned} \tag{3.6}$$

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

$$\begin{aligned}
\dot{M}_0 &= \sum_{i,j} c_i\, c_j - M_0^2 = -2M_0^2 \\
\dot{M}_1 &= \sum_{i,j} (i+j)\, c_i\, c_j - 2M_1 M_0 = 0 \\
\dot{M}_2 &= \sum_{i,j} (i^2 + 2ij + j^2)\, c_i\, c_j - 2M_2 M_0 = 2M_1^2 \\
&\vdots
\end{aligned} \tag{3.7}$$

Solving these equations one by one, we obtain $M_2 = 2t$, $M_3 = 3t^2$, $M_4 = 12t^3$, *etc.*; in general $M_k \propto t^{k-1}$. Because $M_1 =$ const. by mass conservation, the natural measure of the typical cluster mass is $M_2 = 2t$

We now turn to more holistic and elegant approaches for dealing with the master equations. One method is to consider an appropriately scaled concentration ratio rather than the concentration itself. Thus rewriting the master equation as

$$\dot{c}_k + 2c_k\,N = \sum_{i+j=k} c_i\,c_j,$$

introducing the integrating factor $I \equiv \exp\left[2\int^t N(t')\,dt'\right]$, the variable $\phi_k = c_k\,I$, and the rescaled time variable $dx = dt/I(t)$, we recast the master equation as

$$\phi_k' = \sum_{i+j=k} \phi_i\,\phi_j, \tag{3.8}$$

where the prime denotes differentiation with respect to x. This equation contains only gain terms, a feature that makes it easier to develop intuition about the form of the solution.

Solving for the first few ϕ_k it becomes immediately clear that the solution is $\phi_k = x^{k-1}$. Since c_1 and N may be determined separately, from which we obtain $\phi_1 = 1$, we can then unfold the transformations from (I, x) to (N, t). The rescaled time variable is

$$x = \int_0^t \frac{dt}{(1+t)^2} = \frac{t}{1+t},$$

and the integrating factor $I(t) = \exp(2\int_0^t N(t')\,dt') = (1+t)^2$, from which we obtain the exact solution

$$c_k(t) = \frac{t^{k-1}}{(1+t)^{k+1}} \longrightarrow \frac{1}{t^2}\,e^{-k/t}, \qquad t\to\infty. \tag{3.9}$$

Several points deserve emphasis: first, for fixed k, each $c_k(t)$ approaches a common limit that decays as t^{-2} as $t \to \infty$ (Fig. 3.2). Thus the mass distribution becomes flat for $k < s(t) \sim t$, as seen on the right side of the figure. The area under the mass distribution is therefore $t^{-2} \times t = t^{-1}$, which reproduces the time dependence of the total concentration of clusters. Finally, the limiting behaviors of c_k for short and long times can be determined by elementary considerations. The early-time behavior can be inferred by ignoring the loss terms in the master equations. The resulting equations have the same form as Eqs. (3.8), from which we immediately deduce that $c_k(t) \sim t^{k-1}$ for $t \ll 1$. Conversely for $t \to \infty$, there is no production of k-mers for fixed k. We may therefore ignore the gain terms in the master equation to give $\dot{c}_k \sim -2c_k N$, whose solution is $c_k \sim t^{-2}$.

As an alternative, consider the concentration ratio c_k/c_1 rather than the concentration itself. Since c_1 can be found separately, then the master equation for c_k/c_1 has the simpler form

$$\dot{\left(\frac{c_k}{c_1}\right)} = c_1 \sum_{i+j=k} \frac{c_i}{c_1}\,\frac{c_j}{c_1}. \tag{3.10}$$

It is now expedient to define the rescaled time variable $cx = c_1\,dt$ so that the master equation becomes $\psi_k' = \sum_{i+j=k} \psi_i\,\psi_j$, with $\psi_1 = 1$ by definition. We've seen that the solution is $\psi_k = x^{k-1}$. From $c_1 = (1+t)^{-2}$, we deduce that $x = (1+t)^{-1}$ and substituting into $c_k = \psi_k\,c_1$, we recover (3.9).

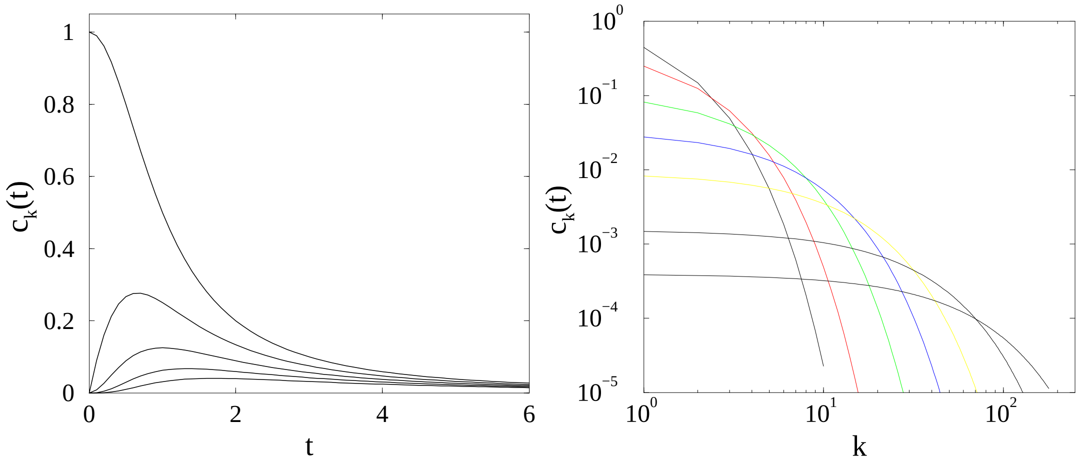

Figure 3.2: Left: Cluster concentrations $c_k(t)$ versus time for constant kernel aggregation for $k = 1, 2, 3, 4, 5$ (top to bottom). The concentrations approach a common limit as $t \to \infty$, as predicted by the scaling form in Eq. (3.9). Right: $c_k(t)$ versus k on a double logarithmic scale for $t = 1, 2, 5, 10, 20, 50$, and 100 (upper left to lower right).

Almost exponential solutions

The solutions to the master equations often have an "almost exponential" form (Eq. (3.9) 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 almost exponential ansatz is

$$c_k(t) = a(t)\, A(t)^{k-1}, \tag{3.11}$$

with the initial conditions $a(0) = 1$ and $A(0) = 0$. If one did not have the foresight to choose the correct power $k - 1$ for A, it quickly becomes evident in applying the method that the power should be $k - 1$. Thus there is less guesswork to this ansatz than might appear at first sight. Substituting this ansatz into the master equations, we find

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

Equating separately the terms with the coefficient $k - 1$ and those with coefficient independent of k gives

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

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 relatively clear from the degree of misalignment how to choose the correct power of A. Multiplying $\dot{a}$ by $1 - A$ and $\dot{A}$ by a, these two equations admit the conservation law

$$\dot{a}\,(1-A) = -2\dot{A}\, a,$$

from which we obtain $a = (1 - A)^2$. Substituting this back into the equations of motion for a and A, we immediately find

$$a = \frac{1}{(1+t)^2}; \qquad A = \frac{t}{1+t}, \tag{3.12}$$

thus reproducing the solution for $c_k(t)$ in Eq. (3.9).

A powerful general approach for solving the master equations is the generating function method. This technique is well-suited for aggregation because the master equations have a discrete convolution form.

The generating function transforms convolutions into products and the resulting equation is easily soluble. Defining the generating function

$$g(z,t) = \sum_{k=1}^{\infty} c_k(t) z^k, \tag{3.13}$$

we now take each of the equations for c_k in (3.4) multiply by z^k and sum over all k. This gives

$$\dot{g} = \sum_k \sum_{i+j=k} c_i z^i \, c_j z^j - 2 \sum_k c_k z^k \, \sum_i c_i = g^2 - 2\, g\, g(z{=}1). \tag{3.14}$$

To avoid cumbersome notation, we generally avoid writing the arguments of the generating function unless it is truly necessary, as above. We use the fact that the sum over k renders the two sums over i and j independent so that the first term reduces to a product. We can simplify (3.14) further by writing the equation for $g(z{=}1) = N(t)$, namely $\dot{g}(1) = -g(1)^2$. We then find that the generating function $h \equiv g - g(1)$ satisfies $\dot{h} = h^2$. This equation should be supplemented with an initial condition which, for the monomer-only initial condition, is $h(z, t = 0) = z - 1$. The solution is

$$h = \frac{z-1}{1-(z-1)t}. \tag{3.15}$$

This result can be recast into the series form

$$h = -\frac{1}{1+t} + \sum_{k=1}^{\infty} z^k \frac{t^{k-1}}{(1+t)^{k+1}}, \tag{3.16}$$

from which we may directly read off the mass distribution and thereby recover Eq. (3.9).

One issue that we have not yet addressed is the role of the initial condition. For rapidly decaying initial mass distributions, the initial condition is immaterial for the long-time behavior. As a simple but concrete example, consider the initial condition $c_k(0) = 2^{-k}$. Then at $t = 0$, we have $g(z, 0) = \frac{z/2}{1-z/2}$ and $h(z, 0) = \frac{z-1}{1-z/2}$. Thus the solution for the generating function is now

$$h = \frac{z-1}{1-z/2-(z-1)t}, \tag{3.17}$$

and expanding in a power series in z, we find

$$c_k(t) = \frac{1}{2}\frac{1}{(1+t)^2}\left(\frac{t+1/2}{1+t}\right)^{k-1} \sim \frac{1}{2t^2}\, e^{-k/2t} \qquad t \to \infty. \tag{3.18}$$

In the long-time limit, we reproduce the scaling form, albeit with the total mass of the system now equal to 2. More generally, if the initial mass distribution decays as a power law in k, $c_k(0) \sim k^{-\alpha}$, with $\alpha > 2$ to ensure that the total mass is finite, but $\alpha > 3$ so that higher moments diverge, then $c_k(t)$ approaches the scaling form $t^{-2}e^{-k/t}$, but with corrections that vanish only for fixed k/t and $t \to \infty$.

Product Kernel, $K_{ij} = ij$

The product kernel has the striking feature that gelation occurs at a time $t_c = 1$. Gelation means that a finite fraction of the total mass condenses into an infinite-mass cluster—just like the setting of Jello. Thus beyond the gelation time, the system divides into two phases: the gel phase that consists of the infinite cluster, and the remaining sol phase of finite clusters whose mass decreases with time. To appreciate why mass conservation fails, it is useful to reconsider the mass conservation statement given by Eq. (3.2). If there is a cluster of infinite mass, then there is a contribution of the loss term in this equation because of the existence of this infinite cluster that is not balanced by the gain terms. Thus the mass of all finite clusters necessarily decreases with time whenever an infinite cluster exists.

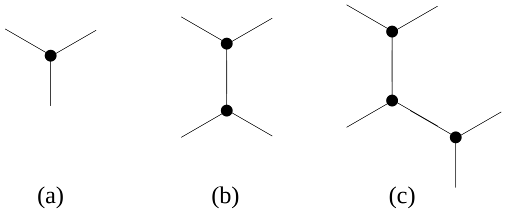

Figure 3.3: Small k-mers of 3-functional units. (a) Monomer. (b) Dimer. (c) Trimer.

The product kernel arises naturally for monomers that consist of f-functional reactive endgroups (Fig. 3.3). When two monomers react, the resulting dimer has $2f-2$ reactive endgroups, a trimer has $3f-4$ endgroups, and a general 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. Thus

$$K_{ij} = [(f-2)i+2][(f-2)j+2] = (f-2)^2 ij + 2(f-2)(i+j) + 4. \tag{3.19}$$

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. We focus here on the case of the pure product kernel.

For $K_{ij}=ij$, the master equations are

$$\dot{c}_k = \frac{1}{2}\sum_{i+j=k} ij\; c_i c_j - kc_k \sum_i i\, c_i \tag{3.20}$$

To solve these equations, the generating function approach is both convenient and powerful. For the present example, it turns out to be more useful to define $g(y,t)=\sum_k c_k(t)\, e^{yk}$ rather than $g=\sum_k c_k\, z^k$. Thus multiplying the equation for each $\dot{c}_k$ by e^{yk} and summing, we obtain

$$\dot{g} = \frac{1}{2}\sum ic_i\, e^{yi}\; jc_j\, e^{yj} - M\sum kc_k\, e^{yk} = \frac{1}{2}\left(\frac{\partial g}{\partial y}\right)^2 - \frac{\partial g}{\partial y}. \tag{3.21}$$

In the second equality, we assume mass conservation so that $M=1$, which is valid only before the gelation time $t_c=1$. Beyond t_c, one must reconsider the master equations with a time-dependent total mass to determine the mass distribution.

Differentiating Eq. (3.21) with respect to y, we find that the generating function $h=\frac{\partial g}{\partial y}$ satisfies $\frac{\partial h}{\partial t} = (h-1)\frac{\partial h}{\partial y}$. With $H=h-1$, we obtain

$$\frac{\partial H}{\partial t} = H\frac{\partial H}{\partial y}. \tag{3.22}$$

This is a first-order wave equation for H in which the wave velocity equals the wave amplitude itself. This non-linearity leads to wave breaking, a singularity that underlies the gelation transition. While the wave equation for $H=H(y,t)$ is non-linear, we can recast it as a linear equation by applying a Legendre transform so that the dependent variables become (H,t). We start with the inverse equation

$$\left(\frac{\partial t}{\partial H}\right)_y = \frac{1}{H}\left(\frac{\partial y}{\partial H}\right)_t, \tag{3.23}$$

and then use the connection between the partial derivatives of a function $y=y(H,t)$ at fixed y,

$$\left(\frac{\partial y}{\partial t}\right)_H \left(\frac{\partial t}{\partial H}\right)_y \left(\frac{\partial H}{\partial y}\right)_t = -1, \tag{3.24}$$

to obtain the linear implicit equation for the generating function

$$\left(\frac{\partial y}{\partial t}\right)_H = -H. \tag{3.25}$$

The solution is just $y = -Ht + f(H)$, where $f(H)$ is determined from the initial condition. For the monodisperse initial state $c_k(t=0) = \delta_{k1}$, $H(t=0) = \sum kc_k(e^{yk}-1)|_{t=0} = e^y - 1$, or $y = \ln(1+H)$. Thus the solution for the generating function is $y = \ln(1+H) - Ht$. We now return to $h = H+1$ and, for convenience in later manipulations, replace e^y by z. This gives the implicit solution

$$h\, e^{-ht} = z\, e^{-t}. \tag{3.26}$$

The generating function itself is obtained by the Lagrange inversion formula (see highlight). Identifying $y = ht$ and $x = zte^{-t}$ in Eq. (3.30) immediately gives

$$ht = \sum \frac{k^{k-1}}{k!}\,(zt)^k\, e^{-kt}.$$

Since $h = \frac{\partial g}{\partial y} = \sum k\, c_k\, e^{yk} = \sum k\, c_k\, z^k$, the density c_k equals the k^{th} term in the series for h as a function of z divided by k. This leads to the remarkably simple mass distribution

$$c_k(t) = \frac{k^{k-2}}{k!}\, t^{k-1}\, e^{-kt}. \tag{3.27}$$

Let's investigate the asymptotic behavior of this distribution. Using Stirling's approximation, we find

$$c_k(t) \sim \frac{k^{k-2}}{\sqrt{2\pi k}} \left(\frac{e}{k}\right)^k t^{k-1}\, e^{-kt} \longrightarrow \frac{1}{\sqrt{2\pi}}\,\frac{1}{k^{5/2}} \qquad t = 1.$$

For $t < 1$, c_k decreases exponentially with k. At $t = t_c = 1$, however, the mass distribution has a power-law tail that signals a singularity where an infinite-mass cluster first appears. The mass distribution also obeys scaling near the gelation point as $\exp[-k(t - \ln t - 1)] \to \exp[-k(1-t)^2/2]$, as $t \to 1$. Thus the mass distribution can be written as $c_k(t) \simeq s^{-5/2}\Phi(u)$, with characteristic mass $s = (1-t)^{-2}$, scaled mass $u = k/s$, and scaling function

$$\Phi(z) = (2\pi)^{-1/2} z^{-5/2} e^{-z/2}. \tag{3.28}$$

Lagrange inversion

The Lagrange inversion formula comes very handy in *generatingfunctionology*. It states that the solution of the equation

$$y\, e^{-y} = x \tag{3.29}$$

is the power series

$$y = \sum_{n=1}^{\infty} \frac{n^{n-1}}{n!}\, x^n. \tag{3.30}$$

To show this, we write $y = \sum_{n=1}^{\infty} A_n x^n$. Formally, the coefficients A_n are obtained by contour integration around a small circle centered at the origin

$$\begin{aligned} A_n &= \frac{1}{2\pi i}\oint \frac{y}{x^{n+1}}\, dx = \frac{1}{2\pi i}\oint \frac{y}{x^{n+1}}\,\frac{dx}{dy}\, dy, \\ &= \frac{1}{2\pi i}\oint \frac{(1-y)}{y^n}\, e^{ny}\, dy \\ &= \frac{1}{2\pi i}\oint \sum_{k=0}^{\infty} \frac{n^k}{k!}\left(y^{k-n} - y^{k+1-n}\right) dy \\ &= \frac{n^{n-1}}{(n-1)!} - \frac{n^{n-2}}{(n-2)!} = \frac{n^{n-1}}{n!}. \end{aligned}$$

First, we transform from the integration variable x to y and then we use the fact that since y and x are proportional to each other near the origin, the contour of the second integral is also a small circle about the origin. In the second line, we make the substitutions $\frac{dx}{dy} = (1-y)\, e^{-y}$ and $x = ye^{-y}$. Last, we find the residue by expanding the exponential in a power series and then merely reading off the coefficient of $\frac{1}{y}$ in the integral.

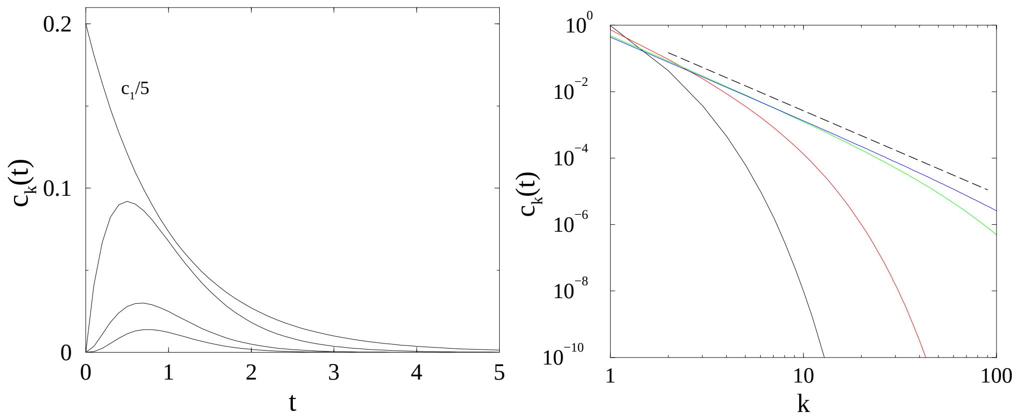

Figure 3.4: Left: Cluster concentrations $c_k(t)$ versus time for the product kernel for $k = 1, 2, 3, 4$ (top to bottom, with c_1 divided by 5). Right: $c_k(t)$ versus k for $t = 0.1, 0.4, 0.8$, and 0.9 on a double logarithmic scale (again upper left to lower right). The dashed line has slope $-5/2$.

Finally, let us determine the masses of the sol and gel phases near the gelation transition. Since the mass of the sol phase is $M = \sum kc_k = h(z = 1)$, we take the implicit equation for the generating function, $ht\, e^{-ht} = zt\, e^{-t}$, and substitute $z = 1$ to give

$$M\, e^{-Mt} = e^{-t}, \tag{3.31}$$

whose solution can be appreciated graphically. The left-hand side, $G(M) \equiv M\, e^{-Mt}$, has a single maximum at $M^* = 1/t$. At this point $G(M^*) = (t\, e)^{-1}$, which is always greater than e^{-t}. Therefore for $t < 1$, there is only a single solution in the physical region $M \leq 1$. However, for $t > 1$ there are two solutions—one at $M = 1$ and a second, physical solution that corresponds to $M < 1$ (Fig. 3.5). To obtain the time dependence of the mass in the sol phase (Fig. 3.5), we write $t = 1 + \delta$ and $M = 1 - \epsilon$ near the gel point, substitute these into Eq. (3.31), and expand for $\delta, \epsilon \to 0$ to find $\epsilon \sim 2\delta$. Conversely, for $t \gg 1$, M becomes vanishingly small and the equality $M\, e^{-Mt} = e^{-t}$ can self-consistently be replaced by $M \approx e^{-t}$.

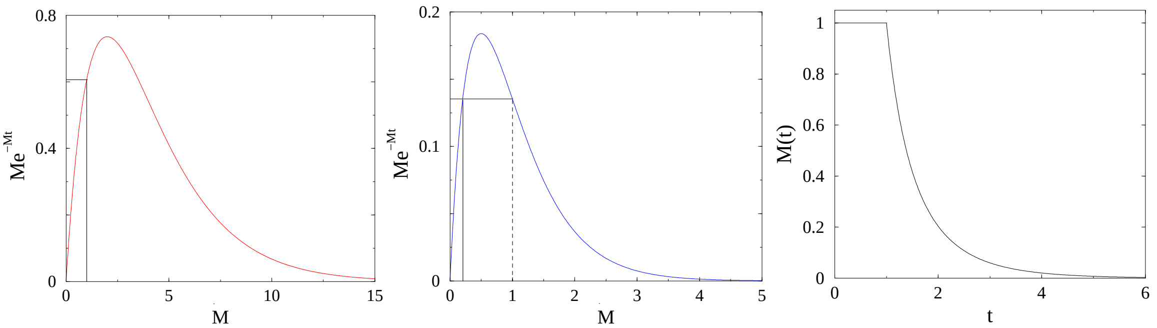

Figure 3.5: Two left panels: graphical solution to Eq. (3.31). Left: plot for $t = 1/2$. For $t < 1$, the maximum of $M\, e^{-Mt}$ has a single maximum at $M = 2$ and there is a single physical solution at $M = 1$. Center: plot for $t = 2$. For $t > 1$, the solution at $M = 1$ is unphysical (dashed) and the physical solution is at smaller value of $M < 1/2$. Right: the exact time dependence of the total mass of finite clusters (the sol phase).

It is worth mentioning that the moments again provide an easy route to a general understanding. From the master equation $\dot{c}_k = \frac{1}{2}\sum ij\, c_i c_j - kc_k\, M_1$, the zeroth moment, $N = \sum c_k$ obeys $\dot{N} = -\frac{1}{2}M_1^2$, or $\dot{N} = -1/2$ prior to the gelation transition. Hence $N(t) = N(0) - t/2$. Thus the number of clusters is reduced to 1/2 at the gelation transition for the monomer-only initial condition. Beyond the gel point, the master equation now gives $N \sim \frac{1}{4}e^{-2t}$ in the long time limit. We may determine the time dependence of the higher moments in a similarly. Prior to the gel point, the equation for the first moment $M_1 = \sum kc_k$ is

$$\dot{M}_1 = \frac{1}{2}\sum(i+j)\, ij\, c_i\, c_j - \sum k^2 c_k = M_2(M_1 - 1).$$

Since $M_1 = 1$ for all $t < t_c$, we merely recover the mass conservation statement. However, beyond the gel point, M_1 decreases exponentially with time as borne out by the moment equation.

The higher moments reveal the gelation transition. The rate equation for M_2 is

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

Before the gel point, this gives $M_2(t) = (1-t)^{-1}$ for the monomer-only initial condition. Thus the typical mass diverges at a critical time $t_c = 1$. Continuing in this vein, we find $\dot{M}_3 = 3M_3M_2$ with solution $M_3(t) = (1-t)^{-3}$. To summarize, we identify $t_c = 1$ as the gelation time, at which moments higher moments of the cluster mass distribution diverge.

Sum Kernel, $K_{ij} = i + j$

There are several instructive ways to deal with master equations for the sum kernel. One approach is based on the observation that works for any additive kernel, $K_{ij} = f_i + f_j$, for which the master equations are

$$\dot{c}_k = \frac{1}{2}\sum_{i+j=k}(f_i + f_j)\, c_i c_j - c_k \sum_i (f_i + f_k)\, c_i\,. \tag{3.32}$$

As in the constant kernel system, the cluster concentration satisfies $\dot{N} = -N\sum_i f_i c_i$. Then the master equation for the ratio $\psi_k = c_k/N$ becomes

$$\psi_k' = \sum_{i+j=k} f_i\, \psi_i \psi_j - f_k\, \psi_k, \tag{3.33}$$

where the prime denotes differentiation with respect to the rescaled time variable x, with $dx \equiv N\, dt$. Introducing the integrating factor $I = \exp(\int f_k\, dx)$ and $\Psi_k = I\, \psi_k$, the master equations for the sum kernel, $f(i) = i$, become

$$\Psi_k' = \sum_{i+j=k} i\, \Psi_i\, \Psi_j, \tag{3.34}$$

with the initial condition $\Psi_i(x=0) = \delta_{i,1}$. This system of equations may be reduced to an algebraic recursion formula by the almost-exponential ansatz $\Psi_k = a_k\, x^{k-1}$ to give

$$(k-1)a_k = \sum_{i+j=k} i\, a_i\, a_j, \tag{3.35}$$

supplemented with the initial condition $a_1 = 1$. By introducing the generating function $A(z) = \sum_k a_k e^{kz}$, we recast the above recursion into the differential equation $\partial A/\partial z = A/(1-A)$, with solution $A\, e^{-A} = e^z$. This is almost the same form as the implicit solution for the generating function in the product kernel, Eq. (3.26), and it is follows, after applying the Lagrange inversion formula (3.30), that the solution is $a_k = k^{k-1}/k!$.

Finally, we unfold all these transformations to obtain $c_k(t)$. We use the fact that the $\dot{N} = -N$, with solution $N(t) = e^{-t}$. Thus $x = \int_0^t e^{-t}\, dt = (1 - e^{-t})$. Then expressing all functions of x in terms of t, we find after some straightforward substitutions

$$c_k(t) = \frac{k^{k-1}}{k!}\, (1 - e^{-t})^{k-1}\, e^{-t}\, e^{-k(1-e^{-t})}. \tag{3.36}$$

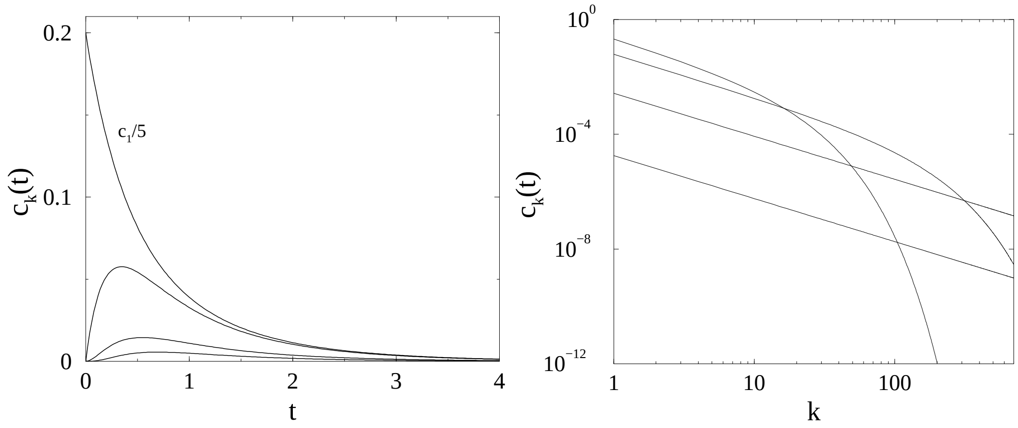

Figure 3.6: Left side: Cluster concentrations $c_k(t)$ versus time for the sum kernel for $k = 1, 2, 3, 4$ (top to bottom, with c_1 divided by 5). Right side: $c_k(t)$ versus k for $t = 1, 2, 5$, and 10 on a double logarithmic scale (again upper left to lower right). The straight lines have slope $-3/2$.

A quicker route to the solution for the sum kernel that relies on an unexpected connection with the product kernel system. We start by writing the master equation (3.32) as

$$\dot{c}_k + c_k + k\, c_k\, N = \sum_{i+j=k} i\, c_i\, c_j. \tag{3.37}$$

where we have used the fact that $\sum i\, c_i = 1$. Introducing the integrating factor $I = \exp(\int(1 + k\, N)$, with $N = e^{-t}$, the quantity $\psi_k = I\, c_k$ obeys

$$\begin{aligned}
\dot{\psi}_k &= \sum_{i+j=k} i\, c_i\, c_j\; e^{[t+k(1-e^{-t})]} \\
&= e^{-t} \sum_{i+j=k} i\; \{c_i\, e^{[t+i(1-e^{-t})]}\} c_j\; e^{[t+j(1-e^{-t})]} \\
&= e^{-t} \sum_{i+j=k} i\, \psi_i\, \psi_j.
\end{aligned} \tag{3.38}$$

Next we define $dx = e^{-t}\, dt$ to obtain $\psi' = \sum_{i+j=k} i\, \psi_i \psi_j$. Finally, by introducing the generating function $A(z) = \sum \phi_k\, e^{zk}$, we recast the recursion formula for ϕ_k into $\frac{\partial A}{\partial x} = A \frac{\partial A}{\partial z}$. This is the same equation of motion as in the product kernel, except with the time-like variable x instead of t. Thus we get the same solution for the concentrations as in the product kernel, but as a function of x rather than t. Thus the sum kernel system also undergoes gelation at a rescaled time $x = 1$, corresponding to physical time $t = \infty$.

3.2 Scaling

A major feature of aggregation kinetics is that only two features of the reaction rate matrix K_{ij} determine the asymptotic properties of the mass distribution. The first is the homogeneity index λ, defined by

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

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

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

For example, the product kernel is characterized by $(\lambda, \nu) = (2, 1)$, the constant kernel by $(\lambda, \nu) = (0, 0)$, and the "Brownian" kernel (for spherical droplets that move by Brownian motion) by $(\lambda, \nu) = (0, -1)$.

The role of these two indices may be best appreciated by considering the following pictorial form 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 fundamentally different universality classes. The general behavior associated with each of these classes are as follows:

- **Type I:** $LL \gg LS, SS$, corresponding to $\lambda > \nu$. Because of the high reactivity of large clusters they are few in number, while small clusters tend to remain. This leads to a monotonically decaying cluster mass distribution as a function of mass. The product kernel is an example of this type of system.
- **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 mass distribution with a well-defined peak.
- **Type II:** all three reactions are of the same order. This marginal class contains the simplest soluble case of $K_{ij} = 1$. However the long-time behavior of this class of systems is sensitively dependent on details of the reaction rates.

The distinction between these three universality classes is most naturally appreciated within a scaling description. As mentioned in Chapter 1, the basic idea of scaling is that the cluster mass distribution is not a function of mass and time separately, but rather, depends on these variables through a natural scaling combination, namely, the ratio of the mass to a well-defined typical mass. This simple observation allows us to separate the dependences on time and on the scaled mass and analyze simpler equations for each of these quantities. The power of the scaling approach is that it provides general results for the asymptotics of the cluster mass distribution in terms of generic features of the reaction kernel.

In the scaling approach, it is convenient to treat the mass as continuous; thus $c_k(t) \to c(x,t)$, with x a continuous variable. For this case, the master equations for aggregation become

$$\dot{c}(x,t) = \frac{1}{2}\int_a^x dy\, K(y, x-y)\, c(y,t)\, c(x-y,t) - \int_a^\infty dy\, K(x,y)\, c(x,t)\, c(y,t). \tag{3.39}$$

Here a is the minimum in the initial mass distribution. The scaling ansatz for the cluster mass distribution is

$$c(x,t) = \frac{1}{s(t)^2}\, f\Big(\frac{x}{s(t)}\Big);$$

that is, the distribution depends only on the scaled mass ratio, and the leading prefactor $s(t)^{-2}$ enforces mass conservation in a closed system, $\langle x\rangle = \int x\, c(x,t)\, dx = 1$. What is the right definition for the typical mass? From the scaling ansatz, the $n^{\rm th}$ moment of the mass distribution is

$$\langle x^n\rangle \equiv \int x^n\, \frac{1}{s^2}\, f(x/s)\, ds \propto s^{n-1}.$$

Thus $\langle x^n\rangle/\langle x^{n-1}\rangle$ for any n all have units of s and specific examples, such as $\frac{1}{\langle x^0\rangle} = \frac{1}{N}$ or $\langle x^2\rangle$ are reasonable measures of the typical mass as long as the cluster mass distribution itself is not too singular. When scaling holds, we can thus choose a definition for the typical mass that best suits the situation at hand.

There are several important reasons to emphasize scaling solutions. First, scaling generally provides the simplest route to the asymptotic solution of the master equations, especially in complicated situations, where exact solutions require considerable technical expertise. This simplification rests on the fact that the scaling ansatz reduces a two-variable problem to two separate single variable problems. This reduction is an important motivation for using the scaling approach for dynamic phenomena in general. Second, a scaling solution is universal in that it is independent of initial conditions. Thus scaling provides a robust classification of the solutions to the master equations for a wide wide class of aggregating systems.

Now let's use scaling to determine basic features of the cluster mass distribution. As discussed above, only the two characteristic indices of the reaction rate matrix—λ and μ—are needed to obtain asymptotic properties of the mass distribution. We first assume that the reaction rate is a homogeneous function of index λ, $K(ax, ay) = a^\lambda K(x, y)$. Substituting the scaling form $c(x,t) = s^{-2} f(x/s)$ into the master equation (3.39), 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

$$s^{\lambda-3}\left[\frac{1}{2}\int_\epsilon^u dv\, K(v, u-v)\, f(v)\, f(u-v) - \int_\epsilon^\infty dv\, K(u,v)\, f(u)\, f(v)\right],$$

with $v = y/s$ and $\epsilon = a/s$ Equating these two sides sides and re-arranging, the dependences on time and on the scaled mass u can be separated as

$$\frac{\dot{s}}{s^\lambda} = -\frac{\left[\frac{1}{2}\int_\epsilon^u dv\, K(v,u-v)\, f(v)f(u-v) - \int_\epsilon^\infty dv\, K(u,v)\, f(u)f(v)\right]}{2f(u) + uf'(u)} = \Lambda. \tag{3.40}$$

Since the left-hand side is a function of time only while the right-hand side is a function of u only, they are both equal to a constant, which is defined as the separation constant Λ.

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

$$s(t) \sim \begin{cases} t^{1/(1-\lambda)} & 0 \le \lambda < 1; \\ e^{\Lambda t} & \lambda = 1; \\ (t_c - t)^{-1} & 1 < \lambda \le 2. \end{cases} \tag{3.41}$$

Thus the time dependence depends *only* on the homogeneity index λ and not on any other feature of the reaction rates. It is worth mentioning that the pathology of *instant gelation* occurs for $\lambda > 2$, in which an infinite gel molecule appears for any positive time, no matter how small.

The behavior of the scaling mass distribution is more subtle and depends on the value of the index μ.

To be written: How to get information about the cluster size distribution from the scaling approach. Scaling relations between exponents.

3.3 Aggregation with Input

An important extension of irreversible aggregation is to augment it with steady monomer input. Let's first consider this process for a constant reaction kernel. With steady input, the aggregation process is described by the master equation

$$\dot{c}_k = \frac{K}{2}\sum_{i+j=k} c_i c_j - K c_k \sum c_i + F\delta_{k,1} \to \sum_{i+j=k} c_i c_j - 2c_k N + \delta_{k,1}. \tag{3.42}$$

The second equality represents a convenient dimensionless form of the master equation in which the concentrations are rescaled by $\sqrt{K/2F}$ and the time by $\sqrt{KF/2}$.

To solve this system, we first solve for the total density. By summing the master equations (3.42) over all k, we obtain $\dot{N} = -N^2 + 1$. For an initially empty system, the solution is

$$N(t) = \tanh t. \tag{3.43}$$

Thus the total concentration of clusters initially grows linearly with time but eventually saturates to the value 1. Once again, we can, in principle, successively solve for the k-mer concentrations one by one. However, the generating function approach is much more elegant. Thus we multiply each of the master equations by z^k and sum over all k to find that the generating function, $g(z,t) = \sum_{k=1}^{\infty} c_k(t) z^k$, satisfies (compare with Eq. (3.14))

$$\dot{g}(z,t) = g(z,t)^2 - 2g(z,t)N(t) + z. \tag{3.44}$$

As in our analysis of Eq. (3.14), it is convenient to define the generating function $h = g - g(z=1) = g - N$, that then satisfies the closed equation $\dot{h} = h^2 + (z-1)$. Solving for h, we then find the generating function $g(z,t)$ is

$$g(z,t) = N(t) - \sqrt{1-z}\, \tanh\left(t\sqrt{1-z}\right). \tag{3.45}$$

While the generating function has a simple form, we really want the cluster concentrations as a function of mass and time. We now give a simple but non-rigorous discussion, based on the method outlined in Appendix A.1, of how to extract this information from the generating function. We use the fact that probing the limit of large mass in the distribution necessarily corresponds to $z \to 1$ from below. Thus we let $z = 1-\epsilon$ and consider the limit $\epsilon \to 0$. We also use the fact that $g(z=1,t) \sim \int^{\infty} c(k,t)\, dt$ converges. Thus we may write the generating function as

$$\begin{aligned} g(z,t) = \sum_{k=1}^{\infty} c_k(t)\, e^{k\ln(1-\epsilon)} &\sim \int_1^{\infty} c(k,t) e^{-k\epsilon}\, dk \\ &= \int_1^{\infty} c(k,t)\left[1 - (1-e^{-k\epsilon})\right]\, dk \\ &\sim N(t) - \int_{1/\epsilon}^{\infty} c(k,t)\, dk. \end{aligned} \tag{3.46}$$

Here we have implicitly assumed that $c_k(t \to \infty)$ has the power-law dependence $c_k \sim k^{-\tau}$ for small k such that $\int^{\infty} c_k\, dk$ converges. Consequently, the exponential approach to 1 in the factor $1 - e^{-k\epsilon}$ can be replaced by a sharp cutoff from 0 to 1 at $k^* = 1/\epsilon$. Thus at long times, Eq. (3.46) shows that $g - N(t)$ will have the power-law tail $g(z, t \to \infty) \sim (1-z)^{\tau-1}$. Matching with the exact generating function in Eq. (3.45), we conclude that $c_k \sim k^{-3/2}$.

We can also extract the time-dependent behavior of the mass distribution by using the fact that $(1-z)$ corresponds to the inverse of a characteristic mass scale. For large times, the function $\tanh(t\sqrt{1-z})$ remains close to 1 until $k *^{\sim} (1-z)^{-1} \gg t^2$, after which the power-law tail is strongly cut off. Thus we expect the power-law mass distribution $k^{-3/2}$ for $1 \ll k \ll k^* \sim t^2$. This picture then gives for the total mass in the system,

$$M(t) = \sum_{k=1}^{\infty} k\, c_k(t) \sim \int_1^{k^*} k^{-1/2}\, dk \sim (k^*)^{1/2} \sim t.$$

The total mass equals the total elapsed time t, as it must for steady monomer input.

The generating function (3.45) can be inverted easily in the long-time limit, where the hyperbolic tangent function can be replaced by 1. Expanding the factor $\sqrt{1-z}$ in a power series in z and expressing the resulting factorials in the binomial coefficient in terms of the gamma function gives

$$c_k(\infty) = \frac{1}{2\sqrt{\pi}}\, \frac{\Gamma(k-\frac{1}{2})}{\Gamma(k+1)}\,. \tag{3.47}$$

Then from the large-k asymptotic form for the ratio of gamma functions we conclude that $c_k(\infty) \propto k^{-3/2}$.

Graph of the mass distribution is needed.

Another important example of aggregation with a steady source occurs in epitaxial surface growth phenomena. The typical experimental setting is a constant flux of atoms that impinges on a clean metal surface. In a suitable temperature range, the atoms adsorb irreversibly and diffuse freely on the surface. When two adatoms meet they merge to form a dimer. If islands of all sizes are mobile, the aggregation process continues *ad infinitum*, leading to a non-trivial size distribution for the adsorbate islands. Generally, the mobility of an island is a rapidly decreasing function of its size. A very beautiful model arises by making the drastic approximation that all islands of size 2 or greater are immobile. In this case, an island grows only by the *addition* of adatoms to its boundary. This statement is appropriate only during the early stages of this deposition and growth process so that there is no possibility for different islands to merge because of geometrical overlap.

The basic processes in this deposition and subsequent growth of immobile islands are

$$0 \xrightarrow{F} A_1 \qquad A_1 + A_1 \to A_2 \qquad A_1 + A_k \to A_{k+1},$$

where F is the input rate of monomers. Corresponding to these elemental steps, the master equations are:

$$\begin{aligned} \dot{c}_1 &= -c_1^2 - c_1 \sum_{k=1}^{\infty} c_k + F \\ \dot{c}_k &= c_1(c_{k-1} - c_k) \quad k \geq 2. \end{aligned} \tag{3.48}$$

We can understand the basic physics of this process quite simply by focusing only on the behavior of the monomers and of the immobile clusters—those whose mass is 2 or greater. We define I as the density of the immobile islands, $I = \sum_{k\geq 2} c_k$. Then the monomers and the islands satisfy the coupled but closed rate equations

$$\begin{aligned} \dot{c}_1 &= -2c_1^2 - c_1 I + F \\ \dot{I} &= c_1^2. \end{aligned} \tag{3.49}$$

A useful feature of this decomposition into monomers and immobile islands is that it is obvious that the island density monotonically increases with time. With a little trial and error, it is easy to verify that the only consistent possibility for c_1 is that it asymptotically decays in time. Thus assuming that c_1 decreases with time, the last two terms in the first line of (3.49) are dominant and we obtain $c_1 \sim 1/I$. Substituting this result into the second line of (3.49), we immediately obtain

$$I(t) \sim (3t)^{1/3} \qquad c_1(t) = \frac{1}{(3t)^{1/3}}. \tag{3.50}$$

Now we can solve for all the island densities by defining the rescaled time variable $dT = c_1 dt$ to convert the second line of (3.48) to

$$\frac{dc_k}{dT} = c_{k-1} - c_k. \tag{3.51}$$

Starting with the known result for c_1, we can straightforwardly solve Eq. (3.51) one by one. The resulting expressions are unwieldy, but the asymptotic behavior this can be obtained easily by going to the continuum limit in k. In this case, Eq. (3.51) becomes the wave equation

$$\frac{\partial c_k}{dT} + \frac{\partial c_k}{dk} = 0, \tag{3.52}$$

with solution $c_k(T) = f(T - k)$, where f is an arbitrary function that is fixed by matching the propagating wave to the initial condition. As a preliminary, we solve for T to give $T = \int dt/[(3t)^{1/3}] = (3t)^{2/3}/2$. Inverting this expression for t, Eq. (3.50) gives $C_1(T) = (2T)^{-1/2}$. Matching this result to $c_k(T) = f(T-k)$, we obtain, for $T \gg 1$, $c_1(T) = f(T-1) \approx f(T) = (2T)^{-1/2}$. Thus the final expression for c_k is:

$$c_k(T) = \frac{1}{[2(T-k)]^{1/2}}. \tag{3.53}$$

From this expression, it is easy to verify that the total number of islands is proportional to $t^{1/3}$, while the total mass in the system is proportional to t.

3.4 Exchange

Suppose that in an interaction event mass is exchanged rather than merged, as represented by the scattering event

$$A_i + A_j \xrightarrow{K_{ij;kl}} A_k + A_l.$$

Thus when two clusters of mass i and j interact, the outcome is two clusters of mass k and l, with $k+l = i+j$. Conventional aggregation corresponding to the special case $l = 0$. A natural setting for this reaction is the wealth distribution in a toy model of an economy in which interacting individuals repeatedly exchange capital. This exchange process gives a rich variety of mass (wealth) distributions as a function of the exchange rate and its dependence on the reactant masses. Here we investigate the generic exchange rule of "random" exchange: one mass unit is exchanged in an interaction, with the direction of the exchange independent of reactant masses.

For random exchange, the master equation for the concentration of clusters of mass k is

$$\dot{c}_k = N\left(c_{k+1} + c_{k-1} - 2c_k\right), \tag{3.54}$$

with $N(t) = \sum_{k=1}^{\infty} c_k$ the density of clusters. The first two terms account for the gain in c_k due to the exchanges $(j, k\pm 1) \to (j \mp 1, k)$, while the last term accounts for the loss in c_k by $(j,k) \to (j \pm 1, k \mp 1)$. Equations (3.54) apply for all $k \geq 1$ if we impose the absorbing boundary condition $c_0 = 0$. This means that if a cluster reaches zero mass, it is removed from the system. This absorbing boundary condition can be automatically satisfied by using the monomer-only initial condition that is augmented by an image contribution; that is, $c_k(0) = \delta_{k,1} - \delta_{k,-1}$.

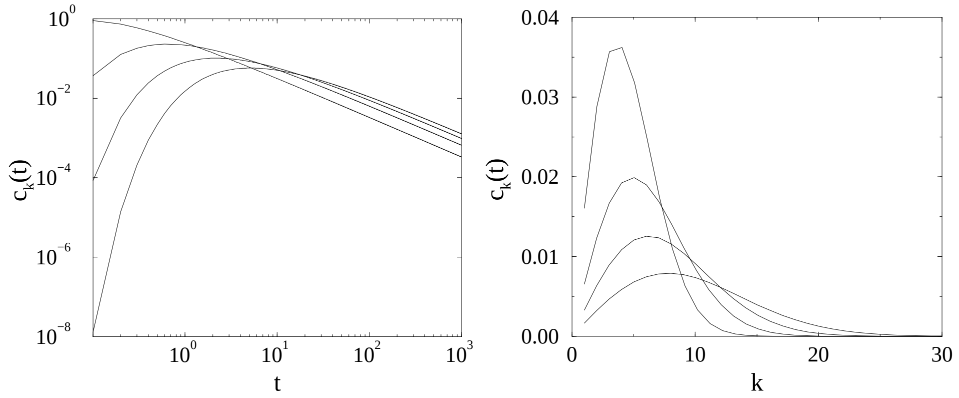

Figure 3.7: Left side: Cluster concentrations $c_k(t)$ versus time for the random exchange process for $k = 1, 2, 3, 4$ (top to bottom). Right side: $c_k(t)$ versus k for $t = 20, 50, 100$, and 200 (top to bottom).

Defining the rescaled time, $T = \int_0^t dt' N(t')$, we reduce Eq. (3.54) to the discrete diffusion equation

$$\frac{dc_k(T)}{dT} = c_{k+1}(T) + c_{k-1}(T) - 2c_k(T). \tag{3.55}$$

A standard way to solve this equation is to introduce the Fourier transform $c_\alpha(T) = \sum c_k(T)\cos k\alpha$ to transform the master equation into the ordinary differential equation $\dot{c}_\alpha = (e^\alpha + e^{-\alpha} - 2)c_\alpha$, with solution $c_\alpha(T) = c_\alpha(0)e^{2(\cos\alpha - 1)T}$. To invert this Fourier transform, we use the generating function representation for $I_k(z)$, the modified Bessel function of the first kind of order k,

$$e^{z\cos\alpha} = \sum_{k=-\infty}^{\infty} e^{i\alpha k} I_k(z).$$

After some simple steps, we find

$$c_k(T) = e^{-2T}\left[I_{k-1}(2T) - I_{k+1}(2T)\right] \sim \frac{k}{\sqrt{4\pi T^3}}\exp\left(-\frac{k^2}{4T}\right) \qquad T \to \infty. \tag{3.56}$$

Notice that the latter form coincides with the first-passage probability of one-dimensional diffusion on the infinite half line. The total density $N(T)$ is

$$N(T) = e^{-2T}\left[I_0(2T) + I_1(2T)\right] \sim (\pi T)^{-1/2} \qquad T \to \infty, \tag{3.57}$$

which is just the survival probability of diffusion on the infinite half line. To express this solution in terms of the physical time t, we write $t(T) = \int_0^T dT'/N(T')$ and obtain, in the long time limit,

$$N(t) \simeq \left(\frac{2}{3\pi t}\right)^{1/3}, \tag{3.58}$$
$$c_k(t) \simeq \frac{k}{3t}\,\exp\left[-\left(\frac{\pi}{144}\right)^{1/3}\frac{k^2}{t^{2/3}}\right].$$

This latter expression can be recast into the scaling form $c_k(t) \propto (N^2 x)\, e^{-x^2}$, with $x \propto kN$, where the prefactor again ensures that the total mass is conserved.

3.5 Finite Systems

Thus far our treatment of aggregation has been for infinite systems; however, real systems are always finite. We now focus on properties of aggregation that specifically stem from finiteness. For a finite system, aggregation eventually ends because all the mass has condensed into a single cluster. How many clusters are present at time t and what is the distribution of the number of clusters? What is the condensation time, where a single cluster remains, and its distribution? These types of first-passage questions become central in a finite system. We will focus on the number of clusters and the condensation time for constant-kernel aggregation where explicit and complete results can be obtained.

For constant-kernel aggregation let's first determine the number of clusters, m, and its distribution as a function of time. For simplicity, we consider the case of a constant reaction kernel. For a finite system, the cluster number is a stochastic variable in which the change $m \to m-1$ occurs with rate $r_m = m(m-1)/N$. Here, the transition rate r_m is proportional to the total number of distinct pairs, $\binom{m}{2}$ and the normalization is fixed by demanding that for $m = N = 2$ the rate should equal 1. Consequently, the average time for the event $m \to m-1$ is $dt_m = r_m^{-1}$ and the time T_k until k clusters remain is

$$\begin{aligned} T_k = \sum_{m=N}^{k+1} dt_m &= N\left[\frac{1}{N(N-1)} + \frac{1}{(N-1)(N-2)} + \cdots + \frac{1}{k\cdot(k+1)}\right] \\ &= N\left[\left(\frac{1}{N-1}-\frac{1}{N}\right) + \left(\frac{1}{N-2}-\frac{1}{N-1}\right) + \cdots + \left(\frac{1}{k+1}-\frac{1}{k}\right)\right] \\ &= \frac{N}{k} - 1. \end{aligned} \tag{3.59}$$

Thus the average condensation time until a single cluster remains is $T_1 = N - 1$.

At a more fundamental level, we study the probability $P_m(t)$ that the system contains m clusters at time t. This probability satisfies the master equation

$$\frac{d}{dt}P_m = r_{m+1}P_{m+1} - r_m P_m, \tag{3.60}$$

with the initial condition $P_m(0) = \delta_{m,N}$, and the boundary conditions $r_{N+1} = r_1 = 0$. This equation expresses the fact that the gain process $m+1 \to m$ occurs with rate r_{m+1} while the loss process $m \to m-1$ occurs with rate r_m. The boundary conditions simply reflect that the maximum and minimum possible number of clusters are N and 1, respectively. To solve the master equation (3.60), it is convenient to rewrite it in terms of the Laplace transform to give

$$(s + r_m)P_m(s) = \delta_{m,N} + r_{m+1}P_{m+1}(s). \tag{3.61}$$

Let's focus on the distribution of condensation times $P(t) \equiv P_1(t)$. Starting with $P_N(s) = (r_N + s)^{-1}$ for (3.61), we can solve the rest of these equations recursively to give

$$P(s) = \prod_{m=2}^{N} \frac{r_m}{s + r_m} = \prod_{m=2}^{N}\left[1 + \frac{sN}{m(m-1)}\right]^{-1}. \tag{3.62}$$

We are interested in the large N limit, where the product can be well-approximated by setting the upper limit to infinity. Then using the identity

$$\prod_{m=2}^{\infty}\left[1+\frac{x}{m(m-1)}\right]^{-1}=\pi x\,\sec\left(\frac{\pi}{2}\sqrt{1-4x}\right),$$

we may write the solution in the compact form

$$P(s)=\pi Ns\;\sec\left(\frac{\pi}{2}\sqrt{1-4sN}\right). \tag{3.63}$$

Expanding the Laplace transform as a power series, $P(s)=\sum_{n=0}^{\infty}\frac{(-s)^n}{n!}\langle t^n\rangle$, then gives the moments $\langle t^n\rangle$. The leading behavior is $\langle t^n\rangle\simeq C_nN^n$, with the first three coefficients $C_1=1$, $C_2=\pi^2/3-2$, and $C_3=12-\pi^2$. Because the distribution (3.63) obeys scaling in the large-N limit in which $P(s,N)=\phi(z)$ with $z=sN$, the distribution of condensation times becomes a function of the scaled time t/N,

$$P(t)=N^{-1}\Phi\left(tN^{-1}\right). \tag{3.64}$$

The limiting behavior of the scaling function $\Phi(x)$ can be obtained by inverting the Laplace transform. The Laplace transform (3.63) has an infinite set of simple poles located at $z_k=-k(k+1)$, with $k=0,1,2,\ldots$. The pole closest to the origin has the form $P(z)\cong 6(z+2)^{-1}$, which corresponds to an exponentially decaying distribution at large times $x\gg 1$, $\Phi(x)\simeq 6\exp(-2x)$. Conversely, the short-time behavior is obtained by Laplace inverting the large-z limit of Eq. (3.63), $P(z)\simeq 2\pi z\exp(-\pi\sqrt{z})$. This inversion can be done by the steepest-descent method. In summary, we obtain

$$\Phi(x)\simeq\begin{cases}6\,\exp(-x) & x\to 0;\\ \frac{1}{4}(\pi/x)^{7/2}\exp(-\pi^2/4x) & x\to\infty.\end{cases} \tag{3.65}$$

The completion time distribution is sharply cut off in both the short- and long-time limits. This same extreme tails also characterize the survival probability of a random walk in a finite interval.

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Problems

1. Use the scaling approach to determine the mass distribution for constant-kernel aggregation; that is solve Eq. (3.40) for the scaling function.

2. Solve for the mass distribution under greedy exchange as represented by $(j,k) \to (j+1, k-1)$ for $j \geq k$. Starting with the master equations

$$\dot{c}_k = c_{k-1} \sum_{j=1}^{k-1} c_j + c_{k+1} \sum_{j=k+1}^{\infty} c_j - c_k N - c_k^2, \tag{3.66}$$

show that the total density of clusters obeys $\frac{dN}{dt} = -c_1 N$. To solve the master equations, consider the continuum limit and show that they reduce to

$$\begin{aligned} \frac{\partial c(k,t)}{\partial t} &= -c_k(c_k + c_{k+1}) + N(c_{k-1} - c_k) + (c_{k+1} - c_{k-1}) \sum_{j=k}^{\infty} c_j, \\ &\simeq 2 \frac{\partial c}{\partial k} \left[\int_k^{\infty} dj\, c(j) \right] - N \frac{\partial c}{\partial k}. \end{aligned} \tag{3.67}$$

Next use the scaling ansatz $c_k(t) \simeq N^2 \mathcal{C}(kN)$, to reduce the master equations to

$$\begin{aligned} \frac{dN}{dt} &= -\mathcal{C}(0) N^3, \\ \mathcal{C}(0)[2\mathcal{C} + x\mathcal{C}'] &= 2\mathcal{C}^2 + \mathcal{C}' \left[1 - 2 \int_x^{\infty} dy \mathcal{C}(y) \right]. \end{aligned} \tag{3.68}$$

Solve this equation (hint: consider the equation for $\mathcal{B}(x) = \int_0^x dy\, \mathcal{C}(y)$) to show that the scaled distribution $\mathcal{C}(x) = \mathcal{B}'(x)$ coincides with the zero-temperature Fermi distribution,

$$\mathcal{C}(x) = \begin{cases} \mathcal{C}(0), & x < x_{\rm f}; \\ 0, & x \geq x_{\rm f}. \end{cases} \tag{3.69}$$

3. Use a direct calculation to find the first few k-mer densities for constant kernel aggregation with steady input.

4. Obtain the size of the largest cluster in a finite system in constant-kernel aggregation.