# Chapter 4

# 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.

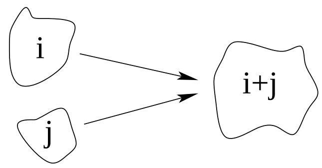


Figure 4.1: Clusters of mass $i$ and mass $j$ merge irreversibly into a cluster of mass $i+j$.

### The Master Equations

The starting point for treating aggregation is the infinite set of master equations that describes how the cluster mass distribution changes with time. These master equations are

$$\frac{dc_k(t)}{dt} = \frac{1}{2} \sum_{\substack{i,j \\ i+j=k}} K_{ij}\, c_i(t)\, c_j(t) - c_k(t) \sum_{i=1}^{\infty} K_{ik}\, c_i(t). \tag{4.1}$$

The first term on the right-hand side of (4.1) describes the gain in the concentration of clusters of mass $k = i+j$ due to the coalescence of clusters of mass $i$ and mass $j$. The second term accounts for the loss of clusters of mass $k$ due to their reaction with other clusters. In the approximation of well-mixed reactants, the rate at which an $i$-mer and $j$-mer meet is $K_{ij}c_ic_j$, and the prefactor $\frac{1}{2}$ in the gain term ensures the correct accounting of reactions between same-mass clusters.[1]

In equations (4.1), 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 $k$

[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 limit. Thus the prefactor $\frac{1}{2}$ properly accounts for the the relative fraction of same-mass pairs. The loss term for same-mass pairs in (4.1) 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.

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 (4.1) admit an important integral of motion — the mass density

$$M(t) = \sum_{k\geq 1} k\, c_k(t) \tag{4.2}$$

is conserved. To verify this conservation law we write

$$\frac{dM}{dt} = \sum_k k\,\frac{dc_k}{dt} = \sum_k \sum_{i+j=k} \frac{1}{2} K_{ij}\,(i+j)\,c_i\,c_j - \sum_k \sum_i K_{ik}\,k\,c_i\,c_k = 0. \tag{4.3}$$

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.

## 4.1 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 the first paper about aggregation (Smoluchowski, 1917). A crude physical justification of the model is based on the form of the reaction kernel for Brownian aggregation. From Sec. 2.5, the reaction rate for spherical aggregates that undergo Brownian motion is [see Eq. (2.51)]

$$\begin{aligned} K_{ij} &\sim (D_i + D_j)(R_i + R_j) \propto (i^{-1/3} + j^{-1/3})(i^{1/3} + j^{1/3}) \\ &= 2 + \left(\tfrac{i}{j}\right)^{1/3} + \left(\tfrac{j}{i}\right)^{1/3}. \end{aligned} \tag{4.4}$$

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

$$\frac{dc_k}{dt} = \sum_{i+j=k} c_i c_j - 2c_k \sum_{i=1}^{\infty} c_i \equiv \sum_{i+j=k} c_i c_j - 2c_k\, N \tag{4.5}$$

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

$$\begin{aligned}
\dot{c}_1 &= -2c_1\, N \\
\dot{c}_2 &= c_1^2 - 2c_2\, N \\
\dot{c}_3 &= 2c_1\, c_2 - 2c_3\, N \\
\dot{c}_4 &= 2c_1\, c_3 + c_2^2 - 2c_4\, N \\
\dot{c}_5 &= 2c_1\, c_4 + 2c_2\, c_3 - 2c_5\, N \\
\dot{c}_6 &= 2c_1\, c_5 + 2c_2\, c_4 + c_3^2 - 2c_6\, N\,,
\end{aligned} \tag{4.6}$$

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 simplest initial condition to avoid cluttered formulae. In the context of aggregation, the monomer-only initial condition

$$c_k(0) = \delta_{k,0} \tag{4.7}$$

is the most natural and simplest choice. If not stated otherwise, we shall always assume such an initial condition in the following. Before solving the initial-value problem (4.5)–(4.7), let us look at the moments of the mass distribution, where much information can be gleaned with relative 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. (4.5) we deduce

$$\begin{aligned}
\frac{dM_n}{dt} &= \sum_{k=1}^{\infty} k^n\, \dot{c}_k = \sum_{k=1}^{\infty} k^n \Big[\sum_{i+j=k} c_i c_j - 2c_k \sum_{i=1}^{\infty} c_i\Big] \\
&= \sum_{i,j}^{\infty} (i+j)^n\, c_i\, c_j - 2M_n\, M_0,
\end{aligned} \tag{4.8}$$

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

$$\begin{aligned}
\dot{M}_0 &= \sum_{i,j} c_i\, c_j - 2M_0^2 = -M_0^2 \\
\dot{M}_1 &= \sum_{i,j} (i+j)\, c_i\, c_j - 2M_1 M_0 = 0 \\
\dot{M}_2 &= \sum_{i,j} (i^2+2ij+j^2)\, c_i\, c_j - 2M_2 M_0 = 2M_1^2 \\
\dot{M}_3 &= \sum_{i,j} (i^3+3i^2j+3ij^2+j^3)\, c_i\, c_j - 2M_3 M_0 = 6M_1 M_2 \\
\dot{M}_4 &= \sum_{i,j} (i^4+4i^3j+6i^2j^2+4ij^3+j^4)\, c_i\, c_j - 2M_4 M_0 = 8M_1 M_3 + 6M_2^2
\end{aligned} \tag{4.9}$$

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

$$N(t) = \frac{1}{1+t}\,. \tag{4.10}$$

Solving equations (4.9) 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 (4.5) are recursive and therefore they can be solved one by one. For the monomer-only initial condition, we substitute $N(t)$ from (4.10) into the first of (4.6) 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

$$c_k(t) = \frac{t^{k-1}}{(1+t)^{k+1}}\,. \tag{4.11}$$

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

**Elimination of loss terms**

One useful trick that often simplifies master equations is based on eliminating loss terms. For example consider the concentration ratio $\phi_k \equiv c_k/c_1$, whose master equation is readily shown to be

$$\frac{d\phi_k}{dt} = c_1 \sum_{i+j=k} \phi_k \phi_j\,. \tag{4.12}$$

Thus the loss term has indeed disappeared. We now define the rescaled time

$$\tau = \int_0^t dt'\, c_1(t') \tag{4.13}$$

so that the master equation reduces to $\phi_k' = \sum_{i+j=k} \phi_i\, \phi_j$, where the prime denotes differentiation with respect to $\tau$. Solving for the first few $\phi_k$, it is immediately clear that the solution is $\phi_k = \tau^{k-1}$. To relate $\tau$ and the time $t$, we substitute the already-established monomer density $c_1 = (1+t)^{-2}$ into (4.13) and find $\tau = t/(1+t)$. Finally, substituting into $c_k = \phi_k\, c_1$, we re-derive (4.11).

The elegant closed-form solution (4.11) 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. 4.2). 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. The resulting equations have the same form as Eqs. (4.12), from which 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 $c_k \sim t^{-2}$.

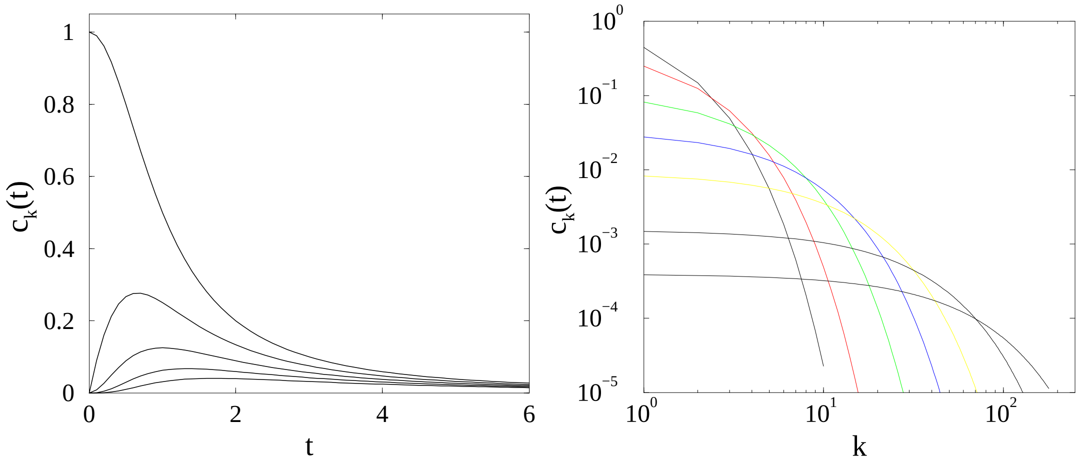


Figure 4.2: Left: Cluster concentrations $c_k(t)$ versus time for constant kernel aggregation for $k = 1, 2, 3, 4, 5$ (top to bottom). The concentrations approach a common limit as $t \to \infty$, as predicted by the scaling form in Eq. (4.11). Right: $c_k(t)$ versus $k$ on a double logarithmic scale for $t = 1, 2, 5, 10, 20, 50$, and 100 (upper left to lower right).

### Exponential ansatz

Solutions to the master equations often have an exponential form — equation (4.11) 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

$$c_k(t) = A(t)\, a(t)^{k-1}, \tag{4.14}$$

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 (4.14) into the master equations (4.5), and dividing both sides of the equation by $c_k$, we find

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

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

$$\dot{A} = -\frac{2A^2}{1-a}; \qquad \dot{a} = A. \tag{4.15}$$

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 (4.15). Substituting $A = (1-a)^2$ back into (4.15) we immediately find

$$A = \frac{1}{(1+t)^2}; \qquad a = \frac{t}{1+t}, \tag{4.16}$$

thus reproducing the solution for $c_k(t)$ in Eq. (4.11).

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.

**Example 1**. *Exponentially decaying initial data.* Let $c_k(0) = (1-q)^2 q^{k-1}$ where $0 < q < 1$; the monomer-only initial condition is recovered for $q \to 0$. We use the exponential ansatz (4.14) with $A = (1-a)^2$ and now we must solve $\dot{a} = (1-a)^2$ subject to $a(0) = q$. We find

$$a(t) = 1 - \frac{1-q}{1+(1-q)t}\,, \qquad A(t) = \left[\frac{1-q}{1+(1-q)t}\right]^2$$

The parameter $q$ does not affect the qualitative asymptotic behavior. For instance, for fixed mass, the densities approach the common limit $t^{-2}$ as $t \to \infty$. When both mass and time diverge in such a way that the ratio $k/t$ remains finite, the mass distribution attains a scaling form $c_k \simeq t^{-2}\exp(-k/t)$.

### 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

$$\mathcal{C}(z,t) \equiv \sum_{k=1}^{\infty} c_k(t) z^k, \tag{4.17}$$

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 (4.6), multiply by $z^k$, and sum over all $k$. This gives

$$\frac{d\mathcal{C}}{dt} = \sum_k \sum_{i+j=k} c_i z^i \, c_j z^j - 2\sum_k c_k z^k \, \sum_i c_i = \mathcal{C}^2 - 2\,\mathcal{C}N \tag{4.18}$$

Here 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. This reduction to a product is the crucial 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

$$\mathcal{C} = \frac{1}{1+t}\,\frac{z}{1-(z-1)t}\,. \tag{4.19}$$

Expanding (4.19) 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. (4.11).

For an *arbitrary* initial condition the generating function is

$$\mathcal{C}(z,t) = (1+t)^{-2}\,\frac{\mathcal{C}_0(z)}{1-\frac{t}{1+t}\mathcal{C}_0(z)}\,, \tag{4.20}$$

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 (4.20) 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.

**Example 2**. *Initial data with finite support.* The monomer-only initial condition is the simplest example of initial data with finite support. The next simplest possibility is an initial state that consists of a mixture of monomers and dimers, that is $c_1(0), c_2(0) > 0$, with $c_1(0) + c_2(0) = 1$, while $c_j(0) = 0$ for $j \geq 3$. Then $\mathcal{C}_0(z) = c_1(0)z + c_2(0)z^2$ so that (4.20) gives

$$\mathcal{C}(z,t) = (1+t)^{-2}\,\frac{c_1(0)z + c_2(0)z^2}{1-\frac{t}{1+t}\left[c_1(0)z + c_2(0)z^2\right]}$$

To expand of this generating function in powers of $z$, we rewrite the quadratic polynomial in the denominator as $(1-z/z_1)(1-z/z_2)$, where $z_{1,2}(t)$ are the roots of the polynomial. Then we present $[(1-z/z_1)(1-z/z_2)]^{-1}$ as a combination of $(1-z/z_1)^{-1}$ and $(1-z/z_2)^{-1}$, and expand each of these factors as a geometric series. Explicit results can be similarly obtained if aggregation begins with a mixture of monomers, dimers, trimers, and 4−mers, while $c_j(0)=0$ for $j\geq 5$. The denominator of the generating function is now a polynomial of degree 4 whose roots can be explicitly computed. Then writing $[(1-z/z_1)(1-z/z_2)(1-z/z_3)(1-z/z_4)]^{-1}$ as a combination of $(1-z/z_i)^{-1}$, explicit formulae could be obtained. Since a generic polynomial of degree 5 and higher cannot be factored, there do not exist explicit results for the mass distribution if the initial condition contains clusters of mass $\geq 5$.

Despite the lack of explicit results for arbitrary initial mass distributions with finite support, the generating function solution (4.20) allows us to deduce the important *asymptotic* behaviors. Consider an initial mass distribution that vanishes for masses larger than $m$, that is, $c_j(0)=0$ for $j\geq m+1$. While we cannot compute the roots of the polynomial

$$1-\frac{t}{1+t}\left[c_1(0)z+c_2(0)z^2+\ldots+c_m(0)z^m\right]=0$$

for $m\geq 5$, we only need the the smallest root $z_1$ because it contribution, $(z_1)^{-k}$, dominates those of all other roots for large $k$. Because this smallest root is close to 1 in the long-time limit, we write $z_1=1+\epsilon$ and note that

$$\mathcal{C}_0(z)=c_1(0)z_1+c_2(0)z_1^2+\ldots+c_m(0)z_1^m=1+M(0)\epsilon+O(\epsilon^2),$$

where $c_1(0)+c_2(0)+\ldots+c_m(0)=1$ is the initial cluster density and $c_1(0)+2c_2(0)+\ldots+mc_m(0)=M(0)$ is the initial mass density. Using this result for $\mathcal{C}_0(z)$ in Eq. (4.20), the generating function becomes

$$\mathcal{C}(z,t)\approx\frac{1}{1+t}\,\frac{1+M(0)\epsilon}{1-tM(0)\epsilon}\simeq\frac{1}{t^2M(0)z_1}\,\frac{1}{1-z/z_1},$$

where the smallest root of the generating function $z_1=1+1/[M(0)t]$. Now expanding in a power series in $z$, we obtain the scaling form for the mass distribution

$$c_k\simeq\frac{1}{M(0)\,t^2}\;e^{-k/[M(0)t]}\,. \tag{4.21}$$

**Example 3**. *Algebraically decaying initial data.* If the initial mass distribution is unbounded and decays slowly, pathological behavior may occur. One such example is

$$c_k(0)\to\frac{C}{k^\alpha}\qquad\text{when}\quad k\gg 1. \tag{4.22}$$

The exponent $\alpha$ should be larger than one, since the zeroth moment of the mass distribution must converge — otherwise the master equations (4.5) are ill-defined. Apart from this restriction, the decay exponent $\alpha$ is arbitrary. In particular, if $\alpha\leq 2$, the first moment diverges, $M(0)=\infty$, and the asymptotic (4.21) no longer holds.

Let $1<\alpha<2$ (the marginal $\alpha=2$ case is more tedious due to the presence of logarithms). The generating function $\mathcal{C}_0(z)$ encoding the initial data has the following asymptotic behavior in the $z\uparrow 1$ limit:

$$\mathcal{C}_0(z)=1+C\Gamma(1-\alpha)\,(1-z)^{\alpha-1}+\ldots \tag{4.23}$$

To establish this we first note that $\mathcal{C}_0(z=1)=N(0)=1$. Next we differentiate the generating function $\mathcal{C}_0(z)$, use (4.22), and take the $z\uparrow 1$ limit to yield

$$\frac{d\mathcal{C}_0}{dz}=\sum_{k\geq 1}kc_k(0)z^{k-1}\simeq C\int_0^\infty dk\,k^{1-\alpha}\,e^{k\ln z}\simeq C\int_0^\infty dk\,k^{1-\alpha}\,e^{-k(1-z)}=C\Gamma(2-\alpha)(1-z)^{\alpha-2} \tag{4.24}$$

Integrating this we indeed obtain (4.23). Using (4.23), taking the limits $t\to\infty$ and $z\uparrow 1$, and keeping only leading terms we transform (4.20) into

$$\mathcal{C}(z,t)=\frac{t^{-1}}{1+Dt(1-z)^{\alpha-1}}\,,\qquad D=-C\Gamma(1-\alpha)$$

This expression is compatible with the scaling form

$$c_k\simeq t^{-1}(Dt)^{-1/(\alpha-1)}\,f_\alpha(w)\,,\quad w=k/(Dt)^{1/(\alpha-1)} \tag{4.25}$$

of the mass distribution. Indeed, a calculation analogous to that of (4.24) gives

$$\mathcal{C}(z,t) = \sum_{k\geq 1} c_k(t) z^k \simeq t^{-1} \int_0^\infty dw\, f_\alpha(w)\, e^{-ws} = \frac{t^{-1}}{1+s^{\alpha-1}}$$

where $s = (Dt)^{1/(\alpha-1)}(1-z)$. Therefore the scaling function $f_\alpha(w)$ is the inverse Laplace transform of $(1+s^{\alpha-1})^{-1}$. The small and large $s$ asymptotics of the Laplace transform imply corresponding large and small $w$ behaviors of the scaling function

$$f_\alpha(w) \simeq \begin{cases} \frac{1}{\Gamma(\alpha-1)}\, w^{-(2-\alpha)} & w \to 0 \\ -\frac{1}{\Gamma(1-\alpha)}\, w^{-\alpha} & w \to \infty \end{cases} \tag{4.26}$$

For instance, let $\alpha = 3/2$. In this situation, the scaling function has an explicit expression

$$f_{3/2}(w) = \frac{1}{\sqrt{\pi w}} - e^w \mathrm{erfc}\left(\sqrt{w}\right)$$

in terms of the error function.

In the marginal case $\alpha = 2$, the analysis is essentially the same, e.g. (4.23) becomes

$$\mathcal{C}_0(z) = 1 + C\,(1-z)\ln(1-z) + \ldots$$

The scaling solution is a pure exponential

$$c_k(t) = t^{-2}(C\ln t)^{-1}\, \exp\left[-\frac{k}{Ct\ln t}\right]$$

and only the appearance of logarithms in the scaling variable and in the prefactor shows distinguishes from the standard scaling behavior valid for all $\alpha > 2$.

Overall, for $\alpha \geq 2$ the scaling function is universal and pure exponential, while for each $1 < \alpha < 2$ there is a specific scaling function $f_\alpha(w)$ that is the inverse Laplace transform of $(1+s^{\alpha-1})^{-1}$. These scaling functions are still universal in that they are independent on details of the initial data (small mass behavior, the amplitude $C$, *etc.*), the only relevant feature is the magnitude of the decay exponent $\alpha$.

## Product Kernel, $K_{ij} = ij$

When the rate of aggregation is a sufficiently increasing function of masses of the reacting clusters, gelation can occur. This is the phenomenon in which a finite fraction of the total mass of the system condenses into an infinite-mass cluster in a finite time — such as the setting of Jello. The product kernel represents and 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 naturally arises for monomers that consist of $f$-functional reactive endgroups (Fig. 4.3). 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. Thus

$$K_{ij} = [(f-2)i+2][(f-2)j+2] = (f-2)^2 ij + 2(f-2)(i+j) + 4. \tag{4.27}$$

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.

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

$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i+j=k} ij\; c_i c_j - kc_k \sum_i i\, c_i = \frac{1}{2}\sum_{i+j=k} ij\; c_i c_j - kc_k. \tag{4.28}$$

There is already a subtlety in merely writing the master equations. 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, $\sum kc_k$, includes all finite clusters *and* the gel, so that $\sum kc_k = 1$. However, when we compute the rate equation for the first moment by summing the master equations, the resulting sum, $\sum k\dot{c}_k$, is not necessarily conserved because the term associated with the infinite-mass cluster is not included in this sum. We will return to this point shortly.

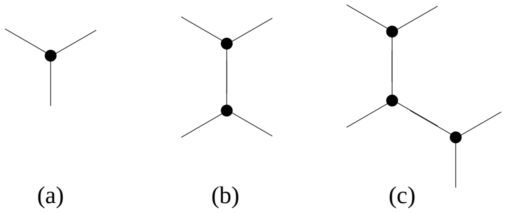


Figure 4.3: Small $k$-mers of 3-functional units. (a) Monomer. (b) Dimer. (c) Trimer.

**Moments**

If we were unaware of the existence of a singularity, the quickest way to detect that something odd may occur is from the behavior of the moments. Summing equations (4.28) we get

$$\frac{dN}{dt} = \frac{1}{2}\sum_{i,j} ic_i\, jc_j - \sum_k kc_k = \frac{1}{2} - 1 = -\frac{1}{2} \tag{4.29}$$

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 (4.29) 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

$$\frac{dM_2}{dt} = \sum_k k^2\, \dot{c}_k = \frac{1}{2}\sum_i\sum_j \left[(i+j)^2(ic_i)(jc_j) - k^3 c_k\right] \tag{4.30}$$

$$= \frac{1}{2}\sum_i\sum_j \left[(i^3c_i)(jc_j) + (ic_i)(j^3c_j) + 2(i^2c_i)(j^2c_j) - k^2 c_k\right] \tag{4.31}$$

$$= M_2^2. \tag{4.32}$$

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 (4.30) 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:

$$\frac{dM_3}{dt} = \frac{1}{2}\sum_{i,j}(i+j)^3 ic_i\, jc_j - \sum_k k^4 c_k\,, = 3M_3M_2 \tag{4.33}$$

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

$$\frac{dM_4}{dt} = \frac{1}{2}\sum_{i,j}(i+j)^4 ic_i\, jc_j - \sum_k k^5 c_k = 4M_4M_2 + 3M_3^2\,, \tag{4.34}$$

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. (4.28), 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

$$\begin{aligned}
\frac{\partial \mathcal{E}}{\partial t} &= \frac{1}{2}\sum_{i,j}(i+j)ij\, c_i\, c_j\, e^{yk} - \sum_k k^2 c_k\, e^{yk} \\
&= \frac{1}{2}\sum_i i^2 c_i\, e^{yi}\sum_j jc_j\, e^{yj} + \frac{1}{2}\sum_i c_i\, e^{yi}\sum_j j^2 c_j\, e^{yj} - \sum_k k^2 c_k\, e^{yk} \\
&= (\mathcal{E}-1)\frac{\partial \mathcal{E}}{\partial y}. \qquad (4.35)
\end{aligned}$$

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 (4.35) 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. (4.35) 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 out the common factor in the denominator to obtain the implicit, but linear equation for the generating function

$$\frac{\partial(\mathcal{E}, y)}{\partial(\mathcal{E}, t)} = \frac{\partial y}{\partial t}\Big|_{\mathcal{E}} = 1 - \mathcal{E}. \qquad (4.36)$$

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 $\mathcal{E}(t=0) = \sum kc_k\, e^{yk}|_{t=0} = e^y$, or $y(t=0) = f(\mathcal{E}) = \ln \mathcal{E}$. Hence we arrive at the implicit solution

$$\mathcal{E}\, e^{-\mathcal{E}t} = e^{y-t}. \qquad (4.37)$$

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. (4.40) 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 $k^{\text{th}}$ term in the series expansion of $\mathcal{E}$ divided by $k$, we obtain the remarkably simple result

$$c_k(t) = \frac{k^{k-2}}{k!}\, t^{k-1}\, e^{-kt}\,. \qquad (4.38)$$

[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:

$$A_n = \frac{1}{2\pi i}\oint \frac{y}{x^{n+1}}\,dx = \frac{1}{2\pi i}\oint \frac{y}{x^{n+1}}\,\frac{dx}{dy}\,dy = \frac{1}{2\pi i}\oint \frac{y}{f(y)^{n+1}}\,f'(y)\,dy. \tag{4.39}$$

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. (4.39) 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

$$y = \sum_{n\geq 1}\frac{n^{n-1}}{n!}\,x^n. \tag{4.40}$$

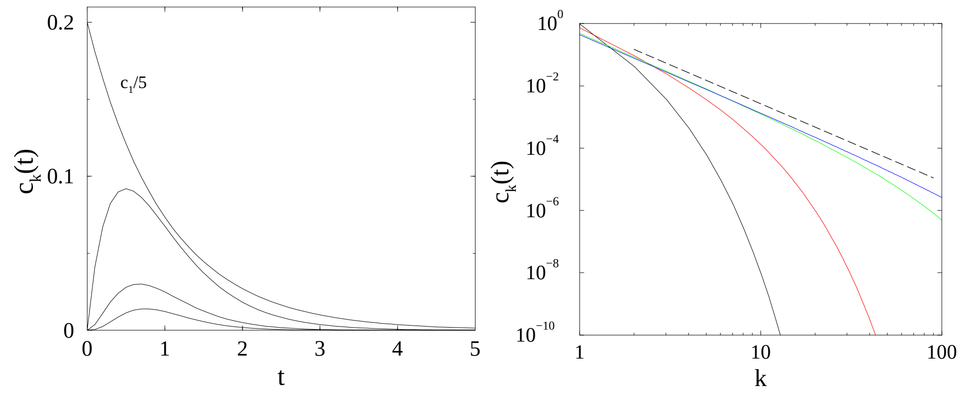


Figure 4.4: Left: Cluster concentrations $c_k(t)$ versus time for the product kernel for $k = 1, 2, 3, 4$ (top to bottom, with $c_1$ divided by 5). Right: $c_k(t)$ versus $k$ for $t = 0.1, 0.4, 0.8$, and 0.9 on a double logarithmic scale (upper left to lower right). The dashed line has slope $-5/2$.

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

$$c_k(t) \simeq \frac{k^{k-2}}{\sqrt{2\pi k}}\left(\frac{e}{k}\right)^k t^{k-1}\,e^{-kt} \underset{t=1-\epsilon}{\longrightarrow} \frac{e^{-k\epsilon^2/2}}{\sqrt{2\pi}\,k^{5/2}}, \tag{4.41}$$

where we have approximated $e^{-k(t-\ln t-1)}$ by $e^{-k(1-t)^2/2}$ for $t \to 1$. 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, (4.41) gives the scaling form for the mass distribution

$$c_k(t) \simeq s^{-5/2}\Phi(k/s) \qquad \text{with} \quad \Phi(z) = \frac{1}{\sqrt{2\pi}}\,\frac{e^{-z/2}}{z^{5/2}}, \tag{4.42}$$

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 (4.37) for the generating function and then use $g \equiv 1 - M_1$ to give

$$g = 1 - e^{-gt}\,. \tag{4.43}$$

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. (4.43) is not analytically soluble, the limiting behaviors of Eq. (4.43) can be obtained perturbatively. Just past the gelation time, we write $t = 1 + \delta$ and expand (4.43) for small $\delta$, while for $t \to \infty$, we write $g = 1 - \epsilon$ and expand for small $\epsilon$. These give

$$g = \begin{cases} 0 & \text{for} \quad t < 1 \\ 2(t-1) - 8(t-1)^2/3 + \ldots & \text{for} \quad t \downarrow 1 \\ 1 - e^{-t} - te^{-2t} + \ldots & \text{for} \quad t \to \infty. \end{cases} \tag{4.44}$$

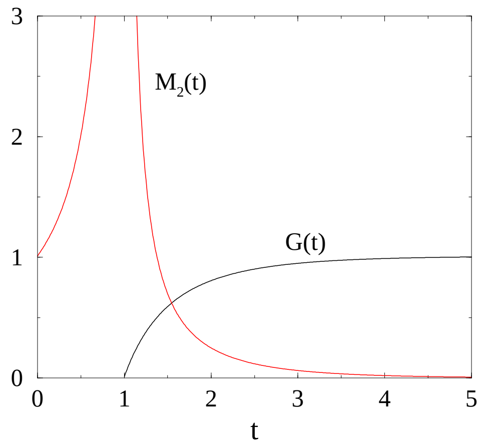


Figure 4.5: Time dependence of the mass of gel phase and the mean mass of the finite clusters.

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

$$\begin{aligned} \frac{dM_0}{dt} &= \frac{1}{2}\sum_{i,j} ic_i\,jc_j - \sum_k kc_k \\ &= \frac{1}{2}\,(1-g)^2 - (1-g) = \frac{g^2-1}{2}. \end{aligned} \tag{4.45}$$

[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 (4.29) is correct only in the pre-gel regime. Using the results of (4.44) for $g$, we obtain

$$M_0 = \begin{cases} 1 - t/2 & \text{for} \quad t \le 1; \\ 1 - t/2 + 2(t-1)^3/3 + \dots & \text{for} \quad t \downarrow 1; \\ e^{-t} + (t/2)\, e^{-2t} + \dots & \text{for} \quad t \to \infty. \end{cases} \tag{4.46}$$

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. (4.37), differentiate with respect to $y$, and set $y = 0$ to give

$$M_2(t) = \left[ \frac{1}{\mathcal{E}(y\!=\!0, t)} - t \right]^{-1}, \tag{4.47}$$

with $\mathcal{E}(y = 0, t) = 1$ in the sol phase and $\mathcal{E}(y = 0, t) = 1 - g = e^{-gt}$ [see Eq. (4.43)] in the gel phase. Therefore,

$$M_2(t) = \begin{cases} (1-t)^{-1} & \text{for} \quad t < 1; \\ (e^{gt} - t)^{-1} & \text{for} \quad t > 1. \end{cases} \tag{4.48}$$

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. 4.5).

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

For the sum kernel, the master equations now are

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} (i+j)\, c_i c_j - c_k \sum_i (i+k)\, c_i \,. \tag{4.49}$$

Let's start by studying the moments of the mass distribution. The rate equations for the first few moments are:

$$\begin{aligned} \dot{M}_0 &= -M_1 M_0 \\ \dot{M}_2 &= 2M_1 M_2 \\ \dot{M}_3 &= 3M_1 M_3 + 3M_2^2 \\ \dot{M}_4 &= 4M_1 M_4 + 10 M_2 M_3 \end{aligned} \tag{4.50}$$

and generally the $n^{\text{th}}$ moment obeys

$$\dot{M}_n = n M_1 M_n + \frac{1}{2} \sum_{a=2}^{n-1} \binom{n+1}{a} M_a M_{n+1-a}$$

for $n \geq 2$. Solving the moment equations for the monomer-only initial condition ($M_n(t) = 1$ for all $n \geq 0$) we obtain

$$\begin{aligned} M_0(t) &= e^{-t} \\ M_2(t) &= e^{2t} \\ M_3(t) &= 3\,e^{4t} - 2\,e^{3t} \\ M_4(t) &= 15\,e^{6t} - 20\,e^{5t} + 6\,e^{4t}\,. \end{aligned} \tag{4.51}$$

Generally for $n \geq 2$ the moment $M_n$ involves the combination of exponentials $e^{(2n-2)t}, e^{(2n-3)t}, \ldots, e^{nt}$. All moments remain finite at all times implying that there is no gelation.

One subtle feature of sum kernel aggregation is that the definition of the typical aggregate mass $s(t)$ has an apparent ambiguity. Two natural definitions for the typical mass are:

$$s(t) = \frac{\sum_{k\geq 1} k c_k(t)}{\sum_{k\geq 1} c_k(t)} = \frac{M_1(t)}{M_0(t)}\,, \quad \text{and} \quad s(t) = \frac{\sum_{k\geq 1} k^2 c_k(t)}{\sum_{k\geq 1} k c_k(t)} = \frac{M_2(t)}{M_1(t)}\,.$$

However, if scaling holds, the ratio $M_{n+1}/M_n$, or even a more complicated expression $(M_{n+m}/M_n)^{1/m}$, should be equally acceptable definitions of the typical mass; for example, for constant-kernel aggregation any of the above definitions for the typical mass grow linearly with time. However, for sum-kernel aggregation we have $M_1/M_0 = e^t, (M_2/M_0)^{1/2} = e^{3t/2}, (M_3/M_0)^{1/3} \sim e^{5t/3}$, *etc.* This unconventional behavior is an outcome of a small-mass singularity in the mass distribution. However, for a scaling combination of moments that does not involve $M_0$, we would find a typical mass that grows as $s \sim e^{2t}$.

The master equations for the sum kernel can be solved in a number of ways. One approach is to change variables to eliminate the loss terms. This transformation is easier to see if instead of the densities $c_k$ we consider the ratios $\psi_k \equiv c_k/N$. These ratios satisfy

$$\psi_k' = \sum_{i+j=k} i\,\psi_i\psi_j - k\,\psi_k, \tag{4.52}$$

where the prime denotes differentiation with respect to the rescaled time $\tau = \int_0^t dt'\,N(t') = 1 - e^{-t}$. Now we use $\Psi_k \equiv I\,\psi_k$ instead of $\psi_k$, with $I$ being the integrating factor $I = \exp[\int_0^\tau d\tau'\,f_k(\tau')]$. Equations (4.52) now become

$$\Psi_k' = \sum_{i+j=k} i\,\Psi_i\,\Psi_j\,. \tag{4.53}$$

These equations are recurrent and can be solved one by one. For the monomer-only initial condition, $\Psi_k(0) = \delta_{k,1}$, we find $\Psi_1 = 1, \Psi_2 = \tau, \Psi_3 = \frac{3}{2}\tau^2$, *etc.* These results suggest the exponential ansatz $\Psi_k = a_k\,\tau^{k-1}$. Substituting this ansatz into (4.53), the amplitudes satisfy an algebraic recursion formula

$$(k-1)a_k = \sum_{i+j=k} i\,a_i\,a_j\,, \qquad a_1 = 1. \tag{4.54}$$

To solve this recursion, we introduce an exponential generating function $\mathcal{A}(z) = \sum_k a_k e^{kz}$ that recasts (4.54) into $d\mathcal{A}/dz = \mathcal{A}/(1-\mathcal{A})$, with solution $\mathcal{A}\,e^{-\mathcal{A}} = e^z$. This is almost the same form as the implicit solution for the generating function in the product kernel, Eq. (4.37), and it follows, after applying the Lagrange inversion formula (4.40), that the solution is $a_k = k^{k-1}/k!$. Finally, we unfold the above transformations to obtain $c_k(t)$:

$$c_k(t) = \frac{k^{k-1}}{k!}\,(1-e^{-t})^{k-1}\,e^{-t}\,e^{-k(1-e^{-t})}\,. \tag{4.55}$$

When both $k$ and $t$ are large, we use Stirling's approximation and expand the logarithm to simplify the above formula to

$$c_k(t) \simeq \frac{e^{-t}}{\sqrt{2\pi k^3}}\,e^{k[\ln(1-e^{-t})+e^{-t}]} \to \frac{e^{-t}}{\sqrt{2\pi k^3}}\,e^{-ke^{-2t}/2}\,. \tag{4.56}$$

This expression shows that the typical mass $s \sim e^{2t}$. The anomalous behavior of the zeroth moment is a consequence of the algebraic $k^{-3/2}$ prefactor, which causes a divergence in $\sum_k c_k$ at small masses — hence

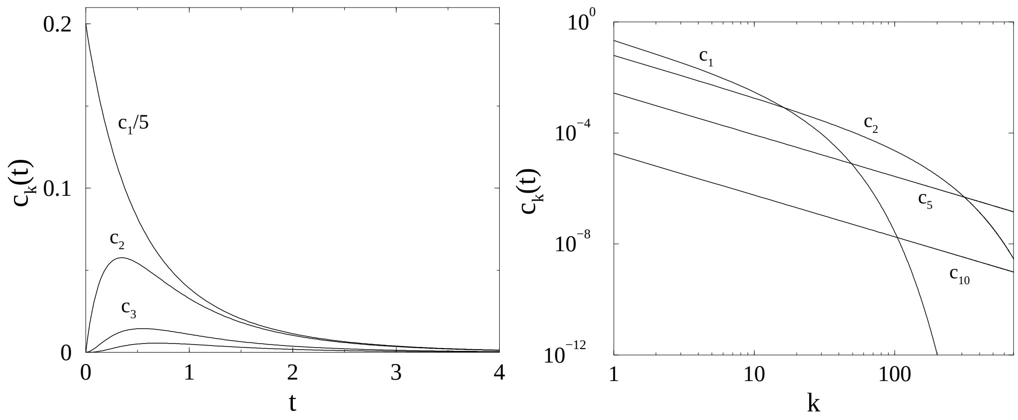


Figure 4.6: Left: Cluster concentrations $c_k(t)$ versus time for the sum kernel for $k = 1, 2, 3, 4$ (with $c_1$ divided by 5). Right: $c_k(t)$ versus $k$ for $t = 1, 2, 5$, and 10 on a double logarithmic scale. For small $k$ The straight lines have slope $-3/2$.

the zeroth moment does not probe the typical mass. For the higher moments we can use (4.56) and replace the sum by an integral to give the asymptotic behavior

$$M_n(t) \simeq \int_0^\infty dk\, k^n\, \frac{e^{-t}}{\sqrt{2\pi k^3}}\, e^{-ke^{-2t}/2} = \frac{2^{n-1}\Gamma\left(n-\frac{1}{2}\right)}{\sqrt{\pi}}\, e^{2(n-1)t} \qquad n > 0\,, \tag{4.57}$$

from which the typical size measures $(M_{n+m}/M_n)^{1/m}$ all scale as $e^{2t}$ for any $m, n > 0$.

A quicker route to the solution for the sum kernel relies on an unexpected connection with the product kernel system. We start by writing the master equation (4.49) as

$$\dot{c}_k + c_k + k\, c_k\, N = \sum_{i+j=k} i\, c_i\, c_j\,, \tag{4.58}$$

where we use the fact that $\sum i\, c_i = 1$. Introducing the integrating factor $I = \exp[\int_0^t dt'\,(1 + k\, N(t')]$, with $N = e^{-t}$, the quantity $\psi_k = I\, c_k$ obeys

$$\begin{aligned}
\dot{\psi}_k &= \sum_{i+j=k} i\, c_i\, c_j\; e^{[t+k(1-e^{-t})]} \\
&= e^{-t} \sum_{i+j=k} i\; c_i\, e^{[t+i(1-e^{-t})]}\; c_j\; e^{[t+j(1-e^{-t})]} \\
&= e^{-t} \sum_{i+j=k} i\, \psi_i\, \psi_j.
\end{aligned} \tag{4.59}$$

Next we define again $d\tau = e^{-t}\, dt$ to obtain $\psi' = \sum_{i+j=k} i\, \psi_i \psi_j$. Finally, by introducing the generating function $\mathcal{A}(z) = \sum \phi_k\, e^{zk}$, we recast the recursion formula for $\phi_k$ into $\frac{\partial \mathcal{A}}{\partial \tau} = \mathcal{A}\frac{\partial \mathcal{A}}{\partial z}$. This is the same equation of motion (4.35) for the generating function $\mathcal{E} - 1$ in the product kernel, except with the time-like variable $\tau$ instead of $t$. We therefore obtain a similar solution for the cluster concentrations as in the product kernel, but as a function of $\tau$ rather than $t$.

## Other Simple Kernels

The general polymerization kernel written in Eq. (4.27)

$$K_{ij} = A + B(i + j) + Cij\,, \tag{4.60}$$

which is a linear combination of the constant, sum, and product kernels, is also soluble. Its solvability cannot be deduced by 'superposition' because the master equations are nonlinear. However, because the constant, sum, and product kernels are separately solvable by the generating function technique, and also accounting for the fact that the sum and product kernels are intimately related, it is not too surprising that the general polymerization kernel is tractable. For $C > 0$, the product term dominates and the system undergoes gelation; if $C = 0$, the sum term dominates when $B > 0$, and the typical mass grows exponentially with time. The model (4.60) is valuable because it represents most of exactly soluble aggregation models.[4]

A more challenging problem is to study kernels with more rapid aggregation, such as

$$K_{ij} = (i+j)^2 \quad \text{or} \quad K_{ij} = (ij)^2 \ . \tag{4.61}$$

Formally, these kernels are amenable to generating function techniques, but the resulting partial differential equations for the generating function are intractable because they are non-linear and higher than first order [compare with (4.36) for the product kernel]. Physically, we anticipate that the model $K_{ij} = (i+j)^2$ undergoes gelation, since it is at least as 'reactive' than the product kernel. However, even the simple moment method does help in extracting basic information. To see the cause of the trouble, consider explicit rate equations for the first few moments:

$$\begin{aligned}
\dot{M}_2 &= 2M_1M_3 + 2M_2^2\\
\dot{M}_3 &= 3M_1M_4 + 9M_2M_3\\
\dot{M}_4 &= 4M_1M_5 + 14M_2M_4 + 10M_3^2\\
\dot{M}_5 &= 5M_1M_6 + 20M_2M_5 + 35M_3M_4
\end{aligned} \tag{4.62}$$

Equations (4.62) are *hierarchical* — the equation for each $\dot{M}_n$ contains a *higher* moment $M_{n+1}$. In our previous examples, the moment equations were recurrent, and hence solvable one by one.

Hierarchical equations are generally unsolvable, and all attempts to find exact or asymptotic solutions of equations (4.62) have failed. The reason for this failure is not mathematical, but conceptual for this specific case of $K_{ij} = (i+j)^2$, because a gel appears *instantaneously* — $t_g = 0^+$ ! This spectacular behavior occurs not only for the kernel $K_{ij} = (i+j)^2$, but for a wide class of models with asymptotically homogeneous kernels of the form

$$K_{1,j} = K_{j,1} \sim j^\nu \quad \text{when} \quad j \to \infty \tag{4.63}$$

with $\nu$ strictly greater than 1. The applicability of such models to real aggregation processes is questionable[5] because the number of active sites on a cluster should not increase faster than its size. This implies that the ratio $K(1,j)/j$ is bounded as $j \to \infty$, leading to the upper bound $\nu \leq 1$.

## 4.2 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 $\int u\, f(u)\, du = 1$.

[4]The remaining exactly solved models include the exponential kernel $K_{ij} = 2 - q^i - q^j$ with $0 < q < 1$, that interpolates between the constant kernel, $K_{ij} = 2$ when $q = 0$, and the sum kernel, $K_{ij} \simeq (1-q)(i+j)$ when $q \to 1-0$. The other exactly solved model is the parity-dependent kernel where $K_{ij}$ takes 3 distinct values depending on whether $i, j$ are both even, both odd, or one index is even and the other is odd.

[5]Nevertheless, kernels with $\nu > 1$ have been proposed in various contexts, *e.g.*, for gravitationally attracting particles.

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 simpler single-variable systems that can be analyzed individually. Further, a scaling solution is independent of the initial conditions[6] 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 $\lambda$, 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 $\nu$, 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 (4.4), the reaction rate for spherical aggregates that undergo Brownian motion. For this kernel, $(\lambda, \nu) = (0, 1/3)$.

The role of the indices $\lambda$ and $\nu$ 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 simplest soluble case of $K_{ij} = 1$. However the asymptotic behavior of this class is sensitive to details of the reaction rates.

[6] Apart from a trivial dependence on a few basic features, like the total mass; see *e.g.*, Eq. (4.21). Exceptions to the rule that initial conditions do not affect the scaling function arise if the initial data have slowly decaying tails; see example 3 in Sec. 4.1. Such initial data are considered pathological.

- **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

$$\dot{c}(x,t) = \frac{1}{2}\int_0^x dy\, K(y, x-y)\, c(y,t)\, c(x-y,t) - \int_0^\infty dy\, K(x,y)\, c(x,t)\, c(y,t) \tag{4.64}$$

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 (4.64), 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

$$\mathcal{K}(u) = \frac{1}{2}\int_0^u dv\, K(v, u-v)\, f(v)\, f(u-v) - \int_0^\infty dv\, K(u,v)\, f(u)\, f(v)\,, \tag{4.65}$$

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

$$\frac{\dot{s}(t)}{s(t)^\lambda} = -\frac{\mathcal{K}(u)}{2f(u) + uf'(u)} \equiv \Lambda. \tag{4.66}$$

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 $\Lambda$. (Actually, there is a time dependence hidden in $\epsilon$ on the right-hand side 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:

$$s(t) \sim \begin{cases} t^{1/(1-\lambda)} \equiv t^z & \lambda < 1; \\ e^{\Lambda t} & \lambda = 1; \\ (t_g - t)^{-1} & 1 < \lambda \le 2. \end{cases} \tag{4.67}$$

For non-gelling systems the time dependence of the typical mass is primarily determined by the homogeneity index $\lambda$; other features of the reaction rate such as the second homogeneity index $\nu$ 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 $\lambda$.

The time dependence (4.67) 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 $\Delta t$ 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 (4.67).

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 (4.66),

$$2f(u) + uf'(u) + \Lambda^{-1}\mathcal{K}(u) = 0 \tag{4.68}$$

with $\mathcal{K}(u)$ given by (4.65). The non-linear integro-differential equation (4.68) is complicated, and the full understanding of the behavior of the scaling function $f(u)$ is still lacking. It is certainly impossible to solve (4.68) 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 exhibits a fairly simple behavior, namely it is exponential

$f(u) \propto e^{-au}$; the detailed behavior of the kernel affects only the prefactors. The behavior of the scaling function when the scaled mass is small is much 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

$$c_k \sim \frac{1}{s^2}\left(\frac{k}{s}\right)^{-\tau} \sim k^{-\tau}\, t^{-(2-\tau)z} \tag{4.69}$$

The exponent $\tau$ 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

$$\dot{c}_1 = -c_1 \sum_{j\geq 1} K_{1j}\, c_j \tag{4.70}$$

Since $K_{1j} \sim j^{\nu}$ and $c_j \sim j^{-\tau}$, the sum on the right-hand side of (4.70) 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. (4.69), 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.

## 4.3 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 the simplest situation of 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 simplest case of an initially empty system, $c_k(0) = 0$.

### Constant kernel

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

$$\dot{c}_k = \sum_{i+j=k} c_i c_j - 2c_k N + \delta_{k,1}\,. \tag{4.71}$$

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

$$N(t) = \tanh t. \tag{4.72}$$

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 much 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 (4.71) into the differential equation [compare with Eq. (4.18)]

$$\dot{\mathcal{C}}(z,t) = \mathcal{C}(z,t)^2 - 2\mathcal{C}(z,t)N(t) + z\,. \tag{4.73}$$

As in Eq. (4.18), 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

$$\mathcal{C}(z,t) = N(t) - \sqrt{1-z}\,\tanh\left(t\sqrt{1-z}\right) \longrightarrow 1 - \sqrt{1-z} \qquad t \to \infty. \tag{4.74}$$

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

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

that follows from the basic gamma function identity $a\Gamma(a) = \Gamma(a+1)$. Finally, using $\Gamma(\frac{1}{2}) = \sqrt{\pi}$, we obtain[7]

$$c_k = \frac{1}{\sqrt{4\pi}}\,\frac{\Gamma(k-\frac{1}{2})}{\Gamma(k+1)}\,. \tag{4.75}$$

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

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

to obtain the tail of the steady-state mass distribution

$$c_k \simeq \frac{1}{\sqrt{4\pi}}\,\frac{1}{k^{3/2}} \qquad\qquad k \gg 1\,. \tag{4.76}$$

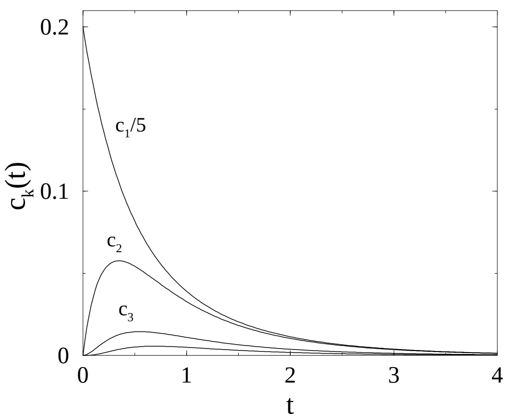


Figure 4.7: Left: Cluster mass distribution for constant-kernel aggregation with a steady monomer input. **figure not done yet.**

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 (4.76). However, we can give a simple 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 (4.76), 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

$$t = \sum_{k=1}^{\infty} kc_k(t) \approx \sum_{k=1}^{k_*} kc_k \sim \sum_{k=1}^{k_*} k^{-1/2} \sim k_*^{1/2}\,, \tag{4.77}$$

leading to $k_* \sim t^2$. Thus the bulk of the population follows the steady-state power-law distribution (4.75) whose leading edge is cut off at $k_* \sim t^2$ (Fig. 4.7).

This qualitative picture can be sharpened by an exact analysis. To extract the densities from the generating function (4.74) we substitute the series representation

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

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

into (4.74) and expand in powers of $z$ to yield

$$c_k(t) = \frac{1}{t^3}\sum_{n=-\infty}^{\infty}\left(n+\frac{1}{2}\right)^2\pi^2\left[1+\left(n+\frac{1}{2}\right)^2\frac{\pi^2}{t^2}\right]^{-k-1} . \tag{4.78}$$

In the long-time limit, we replace the sum on the right-hand side of (4.78) 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 (4.75). On the other hand, when $k$ and $t \to \infty$ such that $\kappa = k/t^2$ remains finite, (4.78) simplifies to

$$c_k(t) = \frac{1}{t^3}\sum_{n=-\infty}^{\infty}\left(n+\frac{1}{2}\right)^2\pi^2\exp\left[-\left(n+\frac{1}{2}\right)^2\pi^2\,\kappa\right] . \tag{4.79}$$

When the mass $k \gg k_*$, we may keep only the first term in (4.79) to give the leading asymptotic behavior of the mass density

$$c_k(t) = \frac{\pi^2}{4\,t^3}\,e^{-\pi^2\kappa/4} , \tag{4.80}$$

so that large-mass clusters are exceedingly rare as shown in Fig. 4.7.

## Generalized sum kernel

In epitaxial surface growth, a constant flux of atoms impinges on a clean surface. In a suitable temperature range, these incident atoms adsorb irreversibly and then diffuse freely on the surface. Mobile adatoms can then merge to form dimers, trimers, *etc.*, and islands of all sizes can diffuse on the surface and continue to aggregate. The growth of islands is therefore driven by the combined effects of irreversible aggregation, island diffusion, and steady monomer input.

The mechanism underlying island diffusion is that adatoms on the edge of an island can hop to neighboring sites on the periphery (Fig. 4.8). Consider a large island of linear size $R$. In a time interval $\Delta t \sim R^2$, an adatom on the edge typically explores the entire island boundary,[8] and hence in a time interval $\Delta t$, each periphery adatom moves by a distance $R$ from its original position. This diffusion of periphery adatoms leads to an effective center-of-mass displacement of the island $\delta x \sim R/R^2 \sim R^{-1}$. If each periphery adatom diffuses independently, the total center-of-mass displacement $\Delta x$ will be the sum of $R$ independent identically distributed random variables. Consequently $\Delta x \sim \sqrt{R(\delta x)^2} \sim R^{-1/2}$. Thus the effective diffusion coefficient of an island of linear dimension $R$ scales as $D_R \sim (\Delta x)^2/\Delta t \sim R^{-3}$. Since the mass of an island of linear size $R$ scales $k \sim R^2$, we conclude that the effective diffusion coefficient of an island of mass $k$ scales as

$$D_k \sim k^{-3/2} . \tag{4.81}$$

The *generalized sum kernel* now arises by using the Smoluchowski formula $K_{ij} \propto (D_i + D_j)(R_i + R_j)^{d-2}$ in the diffusion-controlled limit [see Eq. (2.50)] for the aggregation rate of an $i$-mer and $j$-mer on the surface. Here $R_j$ is the radius of a $j$-mer and $D_j$ is its diffusion coefficient. For a two-dimensional surface[9], the kernel reduces to $K_{ij} \sim D_i + D_j$. For the purposes of this discussion, we write $D_j \propto j^\nu$, where $\nu$ is the mobility exponent that equals 3/2 for periphery diffusion, but could be different for other surface relaxation mechanisms.

Let's now determine the steady-state solution to the master equations for the generalized sum kernel with steady monomer input. The master equations are

$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i+j=k}(i^\nu + j^\nu)\,c_i c_j - c_k\sum_{j\geq 1}(i^\nu + k^\nu)c_j + \delta_{k,1} . \tag{4.82}$$

[8]We tacitly assume that periphery diffusion smooths the boundary so that the perimeter of the island scales as $R$.

[9]The term $(R_i + R_j)^{d-2}$ in the Smoluchowski formula should be replaced by the slowly varying factor $1/\ln(R_i + R_j)$ that we ignore in this presentation.

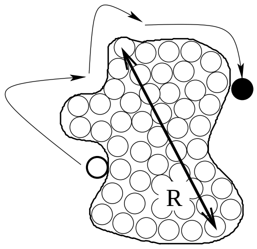


Figure 4.8: Left: Schematic illustration of effective island diffusion by the motion of an adatom at the periphery of an island.

We now introduce the two generating functions

$$\mathcal{A}(z) = \sum_{k\geq 1} k^\nu c_k\, z^k\,, \quad \mathcal{C}(z) = \sum_{k\geq 1} c_k\, z^k\,, \tag{4.83}$$

as well as $A = \mathcal{A}(z=1) = \sum_{k\geq 1} k^\nu c_k$, to reduce the master equation (4.82) to

$$\mathcal{A}(z)\mathcal{C}(z) - \mathcal{A}(z)N - \mathcal{C}(z)A + z = 0\,. \tag{4.84}$$

Since the mass distribution decays algebraically when $\nu = 0$, it is natural that this decay holds when $\nu \neq 0$; thus we assume that $c_k \to C\,k^{-\tau}$ when $k \gg 1$. To determine the decay exponent $\tau$ and the amplitude $C$ we determine the singular behavior of the generating functions from this hypothesized mass distribution. From appendix???, the behavior $c_k \to C\,k^{-\tau}$ when $k \gg 1$ is equivalent to the algebraic behavior of the generating functions $\mathcal{C}(z)$ and $\mathcal{A}(z)$ in the $z \uparrow 1$ limit:

$$\begin{aligned}\mathcal{A}(z) &= A + C\Gamma(1-\tau+\nu)\,(1-z)^{\tau-\nu-1} + \ldots\\ \mathcal{C}(z) &= N + C\Gamma(1-\tau)\,(1-z)^{\tau-1} + \ldots\end{aligned} \tag{4.85}$$

Substituting these expansions for $\mathcal{A}$ and $\mathcal{C}$ and into (4.84) and matching the constant terms as $z \to 1$ yields $AN = 1$. Matching then the first correction terms in $(1-z)$ and using the reflection formula for the gamma function, $\Gamma(z)\Gamma(1-z) = \pi \mathrm{cosec}\, \pi z$, we obtain the decay exponent $\tau$ and the amplitude $C$

$$\tau = \frac{3+\nu}{2}\,, \qquad C = \sqrt{\frac{1-\nu^2}{4\pi}\,\cos\left(\frac{\pi\nu}{2}\right)}\,. \tag{4.86}$$

We many now estimate the crossover time by the same reasoning that led to (4.77):

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

to give the characteristic mass

$$k_* \sim t^{2/(1-\nu)}\,. \tag{4.87}$$

Our analysis has relied on the assumption that the system reaches a stationary state. Specifically, we have tacitly assumed that both the sums $N = \sum c_k$ and $A = \sum k^\nu c_k$ converge, which means that the decay exponent should simultaneously satisfy $\tau > 1$ and $\tau > 1+\nu$. These inequalities in conjunction with $\tau = (3+\nu)/2$ impose the bounds on the mobility exponent

$$-1 < \nu < 1\,, \tag{4.88}$$

for the steady state to exist. When $\nu \to -\infty$, aggregates of any size are relatively immobile. In the extreme case of $\nu = -\infty$, *any* aggregate is immobile and this limit leads to the phenomenologically rich island growth model.

## 4.4 Island Growth Model

In the previous section, the mobility of an island was a rapidly decreasing function of its size. The *island growth* model represents the extreme limit in which islands of mass 2 or greater are immobile. As a result, islands grow only by the *addition* of mobile adatoms to their boundaries; there is no longer any aggregation *per se*. The island growth model has dramatically different behavior than that in the generalized sum kernel because a steady state no longer occurs. This model also nicely illustrates the power and the limitations of a scaling analysis for the mass distribution.

The elemental steps of island growth 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 deposition rate. When only monomers are mobile, the reaction kernel is $K_{ij} \sim D_i + D_j \sim D(\delta_{i,1} + \delta_{j,1})$. This leads to the master equations

$$\begin{aligned} \frac{dc_1}{dt} &= -c_1^2 - c_1 \sum_{k=1}^{\infty} c_k + F \\ \frac{dc_k}{dt} &= c_1(c_{k-1} - c_k) \quad k \geq 2. \end{aligned} \tag{4.89}$$

Here we absorb the diffusivity $D$ into the time variable and the parameter $F$ becomes the ratio of the deposition rate (measured in number of adatoms per site per unit time) to the diffusivity $D$. In experimental applications the (dimensionless) parameter $F$ is usually small and can be varied over a wide range. The master equations (4.89) involve several important assumptions that should be highlighted at the outset:

- Dilute islands. This limit corresponds to the submonolayer regime defined by $Ft \ll 1$ where islands are widely separated so that there is no possibility of proximal merging.
- Point-like (single-site) islands. This assumption is not as drastic as might appear at first sight because in two dimensions the reaction rate depends only logarithmically on the island radius.
- Mean-field master equations. This assumption is difficult to justify. Immobile islands can be viewed as "traps" and for the simplest example of randomly-distribution traps (see Chapter 9), fluctuation effects arise in all spatial dimensions. Hence the applicability of a mean-field description for two dimensions is questionable. Moreover, the input generates traps dynamically and its role on the applicability of the master equations is unknown.
- Freely diffusing adatoms and stable, immobile islands. This assumption is certainly questionable — small islands may be unstable, and even stable islands may undergo an effective diffusion.

To solve the master equations (4.89) it is most useful to first sum them to obtain the rate equation for the total density $N$:

$$\frac{dN}{dt} = F - c_1 N. \tag{4.90}$$

It is also helpful to partition the system into monomers and immobile islands — those of mass 2 or greater. Let $I$ be the density of these immobile islands, $I = \sum_{k \geq 2} c_k$. Then monomers and islands satisfy the coupled equations

$$\begin{aligned} \frac{dc_1}{dt} &= -2c_1^2 - c_1 I + F \\ \frac{dI}{dt} &= c_1^2. \end{aligned} \tag{4.91}$$

One useful consequence of this partitioning is that it is obvious that the island density monotonically increases with time, and that $c_1 \to 0$ as $t \to \infty$. To verify that this latter assertion is true suppose the opposite; namely, $c_1 \to$ const. as $t \to \infty$. Then $I$ would grow linearly with time, and the leading behavior of the monomer equation would be $\dot{c}_1 \approx -c_1 I$, which gives the contradiction that $c_1$ vanishes as $t \to \infty$. Thus we conclude that $c_1 \to 0$ for $t \to \infty$. Using this result, the leading terms in the master equation for $c_1$ are $F - c_1 I = 0$, which gives $c_1 \simeq F/I$. Substituting this result into the second of (4.91) then gives

$$I(t) = (3t)^{1/3} F^{2/3}\,, \qquad c_1(t) \simeq \frac{F^{1/3}}{(3t)^{1/3}}. \tag{4.92}$$

These growth laws cannot hold indefinitely because the end of the submonolayer regime, in which there is less than adatom per adsorption site on average, is eventually reached. This regime obviously ends before $t_{\rm max} \sim F^{-1}$. Thus the maximal island density at the end of the submonolayer regime is

$$I_{\rm max} \sim F^{1/3}. \tag{4.93}$$

The theory that we now present applies only for $t < t_{\rm max}$.

To solve for the island densities we introduce the auxiliary time variable $\tau = \int_0^t c_1(t')\,dt'$ to recast the master equations (4.89) for immobile islands ($k \geq 2$) to those of the Poisson process

$$\frac{dc_k}{d\tau} = c_{k-1} - c_k\,. \tag{4.94}$$

To understand the asymptotic behavior, we treat $k$ as continuous and approximate the difference by derivative to obtain the linear wave equation

$$\left(\frac{\partial}{\partial \tau} + \frac{\partial}{\partial k}\right) c_k(\tau) = 0. \tag{4.95}$$

The general solution is $c_k(\tau) = f(\tau - k)$, where $f$ is an arbitrary function that is determined by matching the solution to $c_1$, which plays a role of a boundary condition. Since $c_1(\tau) = f(\tau - 1)$, the solution simply is $c_{k+1}(\tau) = c_1(\tau - k)$. Using the definition of $\tau$ and Eq. (4.92) for $c_1$, we have

$$\tau \simeq \frac{1}{2}\, F^{1/3} (3t)^{2/3}\,, \qquad c_1(\tau) \simeq F^{1/2} (2\tau)^{-1/2}\,, \tag{4.96}$$

which then gives

$$c_k(\tau) \simeq \frac{F^{1/2}}{\sqrt{2(\tau - k)}}\,. \tag{4.97}$$

The salient feature of this result is that the island distribution does not reach a steady state but rather is characterized by wave propagation.

While this wave solution works well over an intermediate range of island sizes $k$, it cannot apply at the extremes of $k$. For small $k$, the replacement of $c_k - c_{k-1}$ by $\frac{\partial c}{\partial k}$ is unjustified. More seriously, (4.97) must be erroneous when $k \geq \tau$. However, we can solve (4.94) exactly by introducing the Laplace transform $\widehat{c}_k(s) = \int_0^\infty c_k(\tau)\, e^{-s\tau}\, d\tau$ to recast this equation into $s\widehat{c}_k(s) = \widehat{c}_{k-1}(s) - \widehat{c}_k(s)$, from which we obtain

$$\widehat{c}_{k+1}(s) = (s+1)^{-1}\, \widehat{c}_k(s) = \ldots = (s+1)^{-k}\, \widehat{c}_1(s).$$

Because $\widehat{c}_{k+1}(s)$ is expressed as a product, its inverse Laplace transform is just the convolution of the inverse transforms of the two factors in the product:

$$c_{k+2}(\tau) = \frac{1}{k!} \int_0^\tau c_1(\tau - u)\, u^k\, e^{-u}\, du, \tag{4.98}$$

where $u^k\, e^{-u}/k!$ is the inverse Laplace transform of $(s+1)^{-k}$. We now use the Laplace method to show that this exact solution approaches the approximate wave equation solution (4.97) when $k, \tau \to \infty$, with $k/\tau < 1$. For large $k$, we expand the sharply-peaked factor $u^k e^{-u} = e^{k \ln u - u}$ about its maximum at $u^* = k$ and extend the integration to an infinite range to give

$$c_{k+2}(\tau) \simeq \frac{e^{k \ln k - k}}{k!} \int_{-\infty}^{\infty} c_1(\tau - k - \epsilon)\, e^{-\epsilon^2/2k}\, d\epsilon\,, \tag{4.99}$$

where $\epsilon = u - k$. Compute this Gaussian integral and using Stirling's approximation for the factorial $k! \simeq \sqrt{2\pi k}\,(k/e)^k$ then gives $c_{k+2}(\tau) \simeq c_1(\tau - k)$.

The exact solution (4.98) also allows us to resolve the apparent singularity of the approximate solution (4.97) near $k = \tau$. Laplace's method still applies and it tells us that the change of behavior occurs in an inner layer of width $\sqrt{\tau}$ around $k \approx \tau$. This suggests to introduce the 'layer' variable

$$k \to \infty, \quad \tau \to \infty, \quad y \equiv \frac{k-\tau}{\sqrt{2\tau}} = \text{finite} \tag{4.100}$$

We write $u = k - w\sqrt{2\tau}$ and proceed in the same way as in calculation (4.99):

$$\begin{aligned} c_{k+2}(\tau) &\approx \frac{e^{k\ln k - k}}{k!}\sqrt{2\tau}\int_{\xi}^{\infty} c_1[\sqrt{2\tau}\,(w-y)]\, e^{-w^2}\, dw \\ &\approx \frac{1}{\sqrt{2\pi\tau}}\sqrt{2\tau}\,\frac{F^{1/2}}{(2\tau)^{1/4}}\int_y^{\infty}\frac{e^{-w^2}}{\sqrt{2(w-y)}}\, dw \end{aligned}$$

In the second step we additionally used the asymptotic (4.96) of the monomer density. Therefore within the inner layer (4.100) the density has a scaling form

$$c_k(\tau) = \frac{F^{1/2}}{(4\pi\tau)^{1/4}}\, G(y) \tag{4.101}$$

with scaling function

$$G(y) = \int_y^{\infty}\frac{dw}{\sqrt{w-y}}\, e^{-w^2} \tag{4.102}$$

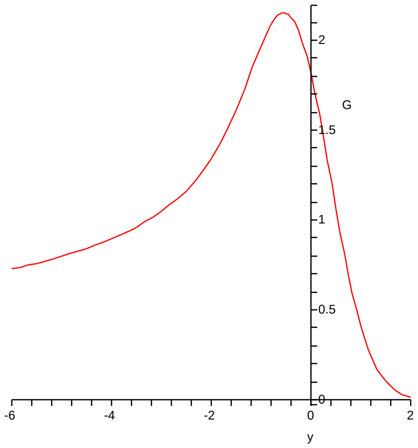


Figure 4.9: The scaled island size distribution $G(y)$ near the peak.

The singularity in the approximate solution is totally resolved — the maximal density does not diverge, it actually decays as $\tau^{-1/4} \propto t^{-1/6}$ although of course it greatly exceeds the density in the bulk of the mass distribution that decays as $t^{-1/3}$.

The island distribution near the peak (see Fig. 4.9) has the maximal density at $k - \tau \approx -0.541\sqrt{2\tau}$. When $y \to -\infty$, the right-hand side of Eq. (4.102) simplifies to

$$\int_y^{\infty}\frac{e^{-w^2}}{\sqrt{w-y}}\, dw \to \frac{1}{\sqrt{-y}}\int_{-\infty}^{\infty} e^{-w^2}\, dw = \sqrt{\frac{\pi}{-y}}$$

Using this in conjunction with (4.100), (4.101) we recover (4.97). Similarly when $y \to \infty$, the integral on the right-hand side of Eq. (4.102) is estimated by writing $w = y + x/(2y)$ to give

$$\int_{\xi}^{\infty}\frac{e^{-w^2}}{\sqrt{w-y}}\, dw = \frac{e^{-y^2}}{\sqrt{2y}}\int_{-\infty}^{\infty} e^{-x-x^2/(4y^2)}\,\frac{dx}{\sqrt{x}} = \sqrt{\frac{\pi}{2y}}\, e^{-y^2}$$

up to terms of the relative order $O(y^{-2})$ and smaller.

## 4.5 Finite Systems

Thus far, we've treated aggregation in the thermodynamic limit. However, real systems are finite. We now examine properties of aggregation that arise from finiteness. For example, aggregation eventually ends because all the mass condenses into a single cluster. What is the average condensation time? What is the distribution of the condensation time? How many clusters are present at time $t$ and what is the distribution of the number of clusters? These types of questions become central in finite systems.

Finite-size aggregating systems are much harder to analyze than the corresponding infinite systems. This fact may seem puzzling at first sight because a system with just 2 or 3 clusters is certainly simpler than its infinite analog. However, the description of a system with, say, 77 clusters is quite challenging. The source of the difficulty stems from the fact that the full description of a finite aggregating system is encoded in the string of non-negative integers $(N_1, N_2, \ldots, N_N)$, where each $N_k(t)$ is the number of clusters of mass $k$ at time $t$. These cluster densities must always satisfy the constraint $\sum_{k=1}^{N} kN_k = N$. In this section, we use $N$ for the total initial number of monomers; we reserve the notation $N(t)$ for the cluster density in a infinite system.[10] For a finite system the quantities $N_k(t)$ are *random* so that we need to deal with the probability distribution for each $N_k(t)$. Moreover, the $N_k$'s are coupled and one must study the probability distribution $P(N_1, N_2, \ldots, N_N; t)$. While it is straightforward to write equations that govern this probability distribution that happen to linear, an exact analysis of these multivariate equations is cumbersome even for the simplest reaction kernels.

For infinite systems, the quantities $N_k(t)$ are asymptotically *deterministic*. This determinism represents a huge simplification for the dynamics. There exist fluctuations, of course, but their relative magnitude vanishes in the $N \to \infty$ limit. Quantitatively, the anticipated behavior of $N_k(t)$ is

$$N_k(t) = Nc_k(t) + N^{1/2}\xi_k(t)\,,$$

with the densities $c_k(t)$ satisfying the deterministic master equations for the infinite-system limit. This decomposition of the densities into a deterministic part and much smaller fluctuating component is a natural approach for dealing with finite-size effects in non-equilibrium systems. In the following sections, however, we discuss examples where finiteness is an all-encompassing feature.

### Constant kernel aggregation

The finite-size constant-kernel aggregating system is the only example that is readily soluble because one can ignore the masses of the clusters to address questions about the condensation time and other general features. The simplest quantity is the total number of clusters. The cluster number is a stochastic variable that changes from $m$ to $m-1$ at a rate $r_m = m(m-1)/N$. here, the transition rate $r_m$ must be proportional to the total number of distinct pairs, $\binom{m}{2}$, and we can determine the normalization by demanding that for $m = N = 2$ the rate should equal 1. Since the average time for the event $m \to m-1$ is $\Delta t_m = r_m^{-1}$, the time $T_k$ until $k$ clusters remain therefore is

$$\begin{aligned}
\langle t_k\rangle = \sum_{m=N}^{k+1} \Delta t_m &= N\left[\frac{1}{N(N-1)} + \frac{1}{(N-1)(N-2)} + \cdots + \frac{1}{k\cdot(k+1)}\right] \\
&= N\left[\left(\frac{1}{N-1} - \frac{1}{N}\right) + \left(\frac{1}{N-2} - \frac{1}{N-1}\right) + \cdots + \left(\frac{1}{k+1} - \frac{1}{k}\right)\right] \\
&= \frac{N}{k} - 1. \qquad (4.103)
\end{aligned}$$

Thus the average completion time until a single cluster remains is $T \equiv \langle t_1\rangle = N - 1$.

[10] As usual, we assume the monomer-only initial condition: $N_k(0) = N\delta_{k,1}$ so that the population therefore condenses into a single cluster of mass $N$ at the end of the reaction.

At the next level of detail, we study the probability $P_m(t)$ that the system contains $m$ clusters at time $t$. This probability evolves as

$$\frac{dP_m}{dt} = r_{m+1}P_{m+1} - r_m P_m, \tag{4.104}$$

subject to the initial condition $P_m(0) = \delta_{m,N}$. We impose the boundary conditions $P_{N+1} \equiv 0$, so that this equation applies for all $1 \le m \le N$. To solve (4.104), we Laplace transform it to give

$$(s + r_m)P_m(s) = \delta_{m,N} + r_{m+1}P_{m+1}(s). \tag{4.105}$$

For $m = N$ we get $P_N(s) = (r_N + s)^{-1}$, from which we then solve the rest of Eqs. (4.105) recursively. The last and most important quantity is $P_1(s)$, the Laplace transform of the probability that the system consists of a single cluster. This probability is given by

$$P_1(s) = \prod_{m=2}^{N} \frac{r_m}{s + r_m} = \prod_{m=2}^{N} \left[1 + \frac{sN}{m(m-1)}\right]^{-1}. \tag{4.106}$$

In the large-$N$ limit, we may set to upper limit to infinity and use the identity

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

to express the solution in the compact form

$$P_1(s) \simeq \pi N s \ \sec\left(\frac{\pi}{2}\sqrt{1-4sN}\right). \tag{4.107}$$

The moments of the condensation time $\langle t_1^n \rangle$ may now be read off from the power-series expansion of the Laplace transform, $P_1(s) = \sum_{n\ge 0} \frac{(-s)^n}{n!}\langle t_1^n\rangle$. The leading behavior of these moments is $\langle t^n \rangle \simeq C_n N^n$, with the first three coefficients $C_1 = 1$, $C_2 = \frac{\pi^2}{3} - 2$, and $C_3 = 12 - \pi^2$. Because the Laplace transformed distribution (4.107) obeys scaling in the large-$N$ limit, *i.e.*, $P_1(s) = \phi(z)$ with $z = sN$, the distribution of condensation times is a function of the scaled time $tN^{-1}$,

$$P_1(t) = N^{-1}\Phi\left(tN^{-1}\right). \tag{4.108}$$

The limiting behavior of the scaling function $\Phi(x)$ can be obtained by inverting the Laplace transform and gives the asymptotic behavior

$$\Phi(x) \simeq \begin{cases} 6\, e^{-x} & x \to 0; \\ \frac{1}{4}\left(\frac{\pi}{x}\right)^{7/2} e^{-\pi^2/4x} & x \to \infty. \end{cases} \tag{4.109}$$

The standard $1/N$-expansion technique shows that the number distribution becomes Gaussian (see highlight)

$$P_m(t) \to \frac{1}{\sqrt{2\pi\Delta^2}} \exp\left[-\frac{(m - \langle m \rangle)^2}{2\Delta^2}\right], \tag{4.110}$$

in the thermodynamic limit, $N \to \infty$. The average number of clusters, $\langle m \rangle = Nc$ with $c = (1+t)^{-1}$, merely reproduces the infinite system size result. Fluctuations in the number of clusters, characterized by the variance $(\Delta m)^2 = N\sigma^2$ with $\sigma^2 = \frac{1}{3}[(1+t)^{-1} - (1+t)^{-4}]$, become negligible compared with the mean, $\Delta m/\langle m \rangle \sim N^{-1/2}$. Moreover, the number of clusters is a *self-averaging* quantity as $m$ approaches the deterministic value $\langle m \rangle$ in the thermodynamic limit.

**$1/N$-expansions**

This canonical method for solving the master equation is demonstrated for (4.104). Since $m$ is large, the continuum limit is taken (to leading order, $m^2 - m \cong m^2$):

$$\frac{d}{dt}P(m) = N^{-1}\left(\frac{\partial}{\partial m} + \frac{1}{2}\frac{\partial^2}{\partial m^2}\right)\left(m^2 P\right). \tag{4.111}$$

Anticipating that averages and variances grow linearly with $N$, a transformation of variables from the extensive ($N$-dependent) variable $m$ to the intensive ($N$-independent) variable $\alpha$ is made

$$m = Nc + N^{1/2}\alpha. \tag{4.112}$$

We now seek the distribution $F(\alpha)$ for the initial condition $F_0(\alpha) = \delta(\alpha)$.
The original master equation (4.111) is transformed using $\partial/\partial m = N^{-1/2}\partial/\partial\alpha$ and $d/dt = \partial/\partial t - N^{1/2}(dc/dt)\partial/\partial\alpha$ as follows

$$\frac{\partial}{\partial t}F - N^{1/2}(dc/dt)\frac{\partial}{\partial\alpha}F = N^{-1}\left(N^{-1/2}\frac{\partial}{\partial\alpha} + \frac{1}{2}N^{-1}\frac{\partial^2}{\partial\alpha^2}\right)[(Nc + N^{1/2}\alpha)^2 F]. \tag{4.113}$$

The leading $\mathcal{O}(N^{1/2})$ order terms vanish because the concentration satisfies $dc/dt = -c^2$, while the next leading $\mathcal{O}(N^0)$ order terms vanish when the distribution $F(\alpha)$ satisfies the Fokker-Planck equation

$$\frac{\partial}{\partial t}F(\alpha) = 2c\frac{\partial}{\partial\alpha}\left[\alpha F(\alpha)\right] + \frac{1}{2}c^2\frac{\partial^2}{\partial\alpha^2}F(\alpha). \tag{4.114}$$

The solution to such a second order equation with linear coefficients in the first derivative term is always Gaussian (see van Kampen's book). Thus, it is characterized by the moments $\langle\alpha\rangle$ and $\sigma^2 \equiv \langle\alpha^2\rangle$.
Multiplying the Fokker-Planck equation by $\alpha$ and integrating by parts once yields $\frac{d}{dt}\langle\alpha\rangle = 0$. Since the average vanishes initially, $\langle\alpha(t)\rangle = 0$. Multiplying (4.114) by $\alpha^2$ and integrating by parts twice, yields $\frac{d}{dt}\sigma^2 = -4c\,\sigma^2 + c^2$. Using $c = (1+t)^{-1}$ and the initial condition $\sigma^2(0) = 0$, fluctuations in the variable $\alpha$ are characterized by the variance $\sigma^2 = \frac{1}{3}[(1+t)^{-1} - (1+t)^{-4}]$. The variable $\alpha$ is Gaussian-distributed

$$F(\alpha) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left[-\frac{\alpha^2}{2\sigma^2}\right]. \tag{4.115}$$

The essence of the transformation (4.112) is that it separates the stochastic part $N^{1/2}\alpha$ from the deterministic part $Nc$.

## Product kernel aggregation

For an infinite system, a gel forms at time $t_g = 1$ that contains a finite fraction of the mass of the entire system. In contrast, for a finite system, the corresponding feature is the appearance of a "giant" cluster that is distinct from the rest of the mass distribution. What is the size of this giant cluster? When does it first appear? We can answer these questions in a simple way by exploiting results about the infinite system in conjunction with basic ideas from extreme-value statistics.

For a finite but large system, the expected number of clusters of mass $k$ for $t \lesssim 1$ is, from the leading behavior of Eq. (4.41),

$$N_k \simeq N c_k(t) \simeq \frac{N}{\sqrt{2\pi}\,k^{5/2}}\,e^{-k(1-t)^2}.$$

There will then be a large number of monomers, dimer, trimers, *etc.*, but for sufficiently large $k$ there will be few or even no clusters of this size. From basic extreme statistics considerations (see matters of technique), the size of the largest cluster $k_{\max}$ is determined by the criterion that there should be one cluster of the population whose size lies in the range $(k_{\max}, \infty)$. That is,

$$\sum_{k\geq k_{\max}} N_k \simeq \int_{k_{\max}}^{N} dk\,\frac{N}{\sqrt{2\pi}\,k^{5/2}}\,e^{-k(1-t)^2/2} = 1. \tag{4.116}$$

Prior to the gelation time, we may estimate this integral by noting that the exponential factor is dominant, so that all other factors in (4.116) can be evaluated at the lower limit. At the gelation time, one can evaluate the integral without any approximation. Beyond the gelation time, it is much simpler to use the fact that there exists a gel whose fraction $g$ is determined by Eq. (4.43). Assembling the results of these small calculations, the mass of the largest cluster is asymptotically given by

$$k_{\max} \sim \begin{cases} (\ln N)/(1-t)^2 & t<1 \\ N^{2/3} & t=1 \\ Ng & t>1. \end{cases} \tag{4.117}$$

For an infinite system, the gelation transition is sharp. On the other hand, a phase transition cannot occur in a finite system. Instead, a drastic change occurs within a narrow time range known as the *scaling window*; *finite-size scaling* refers to the study of critical behavior in this region. The width of the scaling window can be estimated by equating the expressions for $k_{\mathrm{rmax}}$ in (4.117) below and at $t=1$ to give[11] $(1-t)^{-2} \sim N^{2/3}$. Consequently, the width of the scaling window is proportional to $N^{-1/3}$.

We can also estimate the condensation time from the exact expressions for the $k$-mer densities for the infinite system given in Eq. (4.38). These exact results tell us that most finite clusters are monomers in the long-time limit:

$$c_1 = e^{-t} \quad \gg \quad c_2 = \frac{1}{2}\, t\, e^{-2t} \quad \gg \quad c_3 = \frac{1}{6}\, t^2\, e^{-3t} \quad etc.$$

The condition that a single monomer remains in the system, $Nc_1 = 1$, provides the criterion that determines the condensation time to be

$$t_1 \simeq \ln N\,. \tag{4.118}$$

Condensation occurs much more quickly in product-kernel aggregation than constant-kernel aggregation because of the overwhelmingly large reactivity of the largest clusters. In contrast to constant-kernel aggregation, where the condensation time distribution (that is, it remains a random quantity in the $N\to\infty$ limit), for the product kernel aggregation the condensation time becomes deterministic in the $N\to\infty$ limit.

## Instantaneous gelation

As mentioned in passing earlier in this chapter, there is exists the somewhat pathological, but nevertheless quite surprising, feature of instantaneous gelation for reaction kernels that obey the scaling $K(1,j) = K(j,1) \sim j^\nu$ with $\nu > 1$. That is, the gel appears at a time $t = 0^+$! The finite system provides a deeper understanding of this peculiar phenomenon.

For concreteness, we consider generalized product kernels of the form $K(i,j) = (ij)^\lambda$ with $\lambda > 1$. Then the master equations (4.1) for the infinite system become

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} (ij)^\lambda\, c_i\, c_j - k^\lambda\, c_k \sum_i l^\lambda c_i. \tag{4.119}$$

We assume that $N$ is very large, so the master equations (with $c_k = N_k/N$, where $N_k$ is the *average* number of clusters of mass $k$) should provide a good approximation. At short times, we may neglect the loss terms and we immediately find the densities grow with time as $c_k \simeq A_k t^{k-1}$ as in the case of the constant reaction kernel. The coefficients satisfy the recursion relations

$$(k-1)A_k = \frac{1}{2} \sum_{i+j=k} (ij)^\lambda\, A_i\, A_j \tag{4.120}$$

for $k \geq 2$ and with $A_1 = 1$. For large $k$, the dominant contribution to the sum is $(k-1)^\lambda A_{k-1}$. Keeping only this leading term, the recursion simplifies to $(k-1)A_k = (k-1)^\lambda A_{k-1}$, so that $A_k \sim [(k-1)!]^{\lambda-1}$. Then the average number of clusters of mass $k$ is

$$N_k = Nc_k \sim N[(k-1)!]^{\lambda-1}\, t^{k-1}. \tag{4.121}$$

[11] The same result is obtained by equating the estimates (4.117) at and above $t=1$, and using $g \sim t-1$.

The first dimer appears when the condition $N_2 = 1$ holds, which gives the dimer appearance time $t_2 \sim N^{-1}$. Generally, the time of the first appearance of a cluster of size $k+1$ is given by $N_{k+1} = 1$, which gives the condition

$$t_{k+1} \sim (k!)^{-(\lambda-1)/k} N^{-1/k}. \tag{4.122}$$

Physically, the time for the first appearance of a $k$-mer should increase monotonically with $k$. However, (4.122) is monotonic only for sufficiently small $k$. This is a manifestation of the break-down of the master equations. Statistical fluctuations in the number of clusters of a given size are overwhelming, and average quantities such as $\langle N_k \rangle$ do not faithfully characterize the behavior (instead, the detailed probability distribution is needed). We anticipate that the largest cluster at this time, the giant cluster, absorbs the entire system mass.

The gelation time $t_g$ can be estimated from the condition $t_{k_g} = t_{k_g+1}$. Using the Stirling formula, the size of the giant cluster grows logarithmically with the system size,

$$k_g \sim \ln N. \tag{4.123}$$

The giant cluster nucleates at a size that is much smaller compare with the product kernel case. Moreover, the gelation time $T_g \equiv t_{k_g}$ is $T_g \sim [\ln N]^{-(\lambda-1)}$. Once nucleated, the giant cluster grows according to $\frac{dk}{dt} = N^{-1}(N-k)k^\lambda \sim k^\lambda$, and the time for this growth process is found by integration,

$$T_N - T_g \sim \int_{k_g}^{N} \frac{dt}{dk} \sim \int_{k_g}^{N} dk\, k^{-\lambda} \sim k_g^{1-\lambda} - N^{1-\lambda} \sim k_g^{1-\lambda}. \tag{4.124}$$

Therefore, the condensation time is of the same order as the gelation time, $T_N \sim T_g$, so it vanishes logarithmically with system size,

$$T_N \sim [\ln N]^{-(\lambda-1)}. \tag{4.125}$$

This extremely slow decay indicates that in practice, it may be difficult to distinguish instant gelation from ordinary gelation.

# Problems

## Section 4.1

1. Use the generating function technique to solve for the $n^{\text{th}}$ term in the Fibonacci sequence, $F_n$. This sequence is defined by the recursion $F_n = F_{n-1} + F_{n-2}$, with the boundary conditions $F_1 = F_2 = 1$.

2. Investigate the initial condition $c_k(0) = 2^{-k}$ in constant-kernel aggregation. Solve for the cluster concentrations.

3. Determine the 3[rd] and 4[th] moments of the cluster mass distribution for product kernel aggregation with the monomer-only initial condition. Show that

$$M_3(t) = \begin{cases} (1-t)^{-3} & \text{for} \quad t<1; \\ e^{2gt}(e^{gt}-t)^{-3} & \text{for} \quad t>1; \end{cases}$$

and

$$M_4(t) = \begin{cases} (1+2t)(1-t)^{-5} & \text{for} \quad t<1; \\ (e^{4gt}+2te^{3gt})(e^{gt}-t)^{-5} & \text{for} \quad t>1. \end{cases}$$

More generally, show that near the gel point the moments $M_n$ diverge according to

$$M_n \simeq \frac{2^{n-2}\,\Gamma(n-3/2)}{\Gamma(1/2)}\,|1-t|^{-(2n-3)} \tag{4.126}$$

which follows from Eq. (4.42).

4. Consider the addition process that can be represented as $A_1 + A_k \to A_{k+1}$, where the rate of each reaction is the same, except for the reaction between monomers, $A_1 + A_1 \to A_2$ which proceeds at a twice larger rate. (Why?) This process represents the growth of immobile islands on a surface due to the irreversible attachment of mobile monomers (Section 4.4). Let the process begins with monomer-only initial condition.

   (a) Introduce an auxiliary time that allows to linearize the master equations.

   (b) Determine the island size distribution at infinite time.

   (c) Show that the approach to the final state is exponential.

5. Consider the same addition process as in the previous problem but assume that the reaction is $K_{ij} = i\delta_{j,1} + j\delta_{i,1}$. Show that

$$c_k(t) = \left[(1-e^{-t})^{k-1} - k^{-1}(1-e^{-t})^k\right](2-e^{-t})^{-k}$$

## Section 4.2

6. Use the scaling approach to determine the mass distribution for constant-kernel aggregation; that is, solve Eq. (4.66) for the scaling function.

## Section 4.3

In all problems for this section, the system is initially empty, the input is a time-independent source of monomers that has started at $t = 0$, the strength of the input is set to unity so that mass density is $M = t$.

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

   (a) Show that the monomer density is given by

$$c_1 = \frac{1}{2}\left[\frac{t}{\cosh^2 t} + \tanh t\right].$$

   (b) Solve recursively Eqs. (4.71) and derive a formal solution

$$c_k(t) = \frac{1}{\cosh^2 t}\int_0^t dt'\, \cosh^2 t' \sum_{i+j=k} c_i(t')c_j(t').$$

8. Consider the sum kernel aggregation with input.

   (a) Verify that the total density is given by

$$N(t) = \int_0^t dt'\, e^{(t'^2-t^2)/2}$$

   Show that $N(t)$ exhibits a non-monotonous behavior — it grows, reaches a maximum, and then decays to zero, $N \simeq t^{-1}$ when $t \gg 1$.

   (b) Show that the density of monomers also initially increases, then decreases, and asymptotically decays as $c_1 \simeq t^{-1}$.

   (c) Show that the density of dimers decays as $c_2 \simeq t^{-3}$.

   (d) Verify that generally $c_k \simeq A_k\, t^{-(2k-1)}$ in the long time limit.

   (e) Find a recursion for the amplitudes $A_k$ and show that these amplitudes form a sequence **A088716** from *The On-Line Encyclopedia of Integer Sequences.*

9. Investigate the product kernel aggregation with input.
   (a) Show that in the pre-gel regime, the second moment is $M_2 = \tan t$. Use this solution to argue that gelation occurs at $t_g = \pi/2$.
   (b) Show that $N = t - t^3/6$ in the pre-gel regime.
   (c) Show that $M_3 = \tan t + \frac{2}{3}\tan^3 t$ in the pre-gel regime.
   (d) Show that the density of monomers is
   $$c_1(t) = \int_0^t dt'\, e^{(t'^2 - t^2)/2}$$
   throughout the evolution.

## Section 4.4

10. Verify that the scaling function (4.102) can be expressed via the modified Bessel function
$$G(y) = \sqrt{\frac{y}{2}}\, e^{-y^2/2}\, K_{1/4}(y^2/2)$$

11. Consider the model (4.129) with unstable dimers.
    (a) Show that the exact solution (4.127) has a scaling form
    $$c_k(\tau) = \frac{F^{2/3}\lambda^{1/3}}{(18\tau)^{1/3}}\, G(y)$$
    in the scaling region (4.100) with scaling function
    $$G(y) = \frac{1}{\sqrt{\pi}} \int_y^\infty \frac{dw}{(w-y)^{2/3}}\, e^{-w^2}$$
    (b) Plot $G(y)$.
    (c) Verify that the density $c_k$ is maximal at $k - \tau \approx -0.333\sqrt{2\tau}$, and its value decays as $\tau^{-1/3} \propto t^{-1/4}$.

12. Assume that islands of mass $\geq n$ are stable, while lighter islands are unstable.
    (a) Show that $c_1 \propto t^{-1/(n+1)}$.
    (b) Show that $c_n \propto t^{-(n-1)/(n+1)}$.
    (c) Show that $I_{\max} \propto F^{(n-1)/(n+1)}$.

13. Investigate the effect of island instability in the island growth model Consider the simplest situation where dimers are unstable, namely each dimer can break into two mobile adatoms with rate $\lambda$, while all larger islands are stable. Proceed in the same way as for the case where dimers are stable and show that asymptotically $I = F^{3/4}(4t/\lambda)^{1/4}$, while $c_1 = F^{1/4}(4t/\lambda)^{-1/4}$ and $c_2 = F^{1/2}(4t\lambda)^{-1/2}$. Also show that the exact solution for the densities of stable islands ($k \geq 3$) is
$$c_{k+3}(\tau) = \frac{1}{k!} \int_0^\tau du\, c_2(\tau - u) u^k e^{-u}\ . \tag{4.127}$$
Finally show that the maximal island density which is reached at the end of the submonolayer regime now follows the scaling law
$$I_{\max} \propto F^{1/2}\ . \tag{4.128}$$

Solution: The rate equations for monomers and dimers are

$$\begin{aligned}\frac{dc_1}{dt} &= F - c_1(c_1+N) + 2\lambda c_2\\ \frac{dc_k}{dt} &= c_1(c_1-c_2) - \lambda c_2\end{aligned} \tag{4.129}$$

while the densities of stable islands continue to evolve according to Eqs. (4.89). The total density of stable islands obeys

$$\frac{dI}{dt} = c_1 c_2\,, \qquad I \equiv \sum_{k\geq 3} c_k = N - c_1 - c_2\,. \tag{4.130}$$

The leading behavior of these equations gives that $I(t)$ grows while $c_1, c_2$ decay, so from (4.129) we deduce the asymptotic relations $c_1 = F/I$ and $\lambda c_2 = c_1^2$. Substituting these results into (4.130) gives a differential equation for $I(t)$ whose solution is

$$I = F^{3/4}(4t/\lambda)^{1/4}\,, \tag{4.131}$$

while the asymptotic densities of adatoms and dimers are

$$c_1 = F^{1/4}(4t/\lambda)^{-1/4}\,, \quad c_2 = F^{1/2}(4t\lambda)^{-1/2}\,. \tag{4.132}$$

Following the analysis method given in Sec. 4.4, the approximate wave equation solution is now $c_{k+2}(\tau) = c_2(\tau-k)$, where

$$\tau = \frac{4}{3}\left(\frac{\lambda F}{4}\right)^{1/4} t^{3/4}\,, \quad c_2(\tau) = F^{2/3}\lambda^{1/3}(3\tau)^{-2/3}\,,$$

while the exact solution for all stable island densities ($k \geq 3$) is

$$c_{k+3}(\tau) = \frac{1}{k!}\int_0^\tau du\, c_2(\tau-u)u^k e^{-u} \tag{4.133}$$

Note that in addition to different time dependence, the maximal island density which is reached at the end of the submonolayer regime now follows a different scaling law

$$I_{\max} \propto F^{1/2} \tag{4.134}$$

## Section 4.5

14. Determine the mass of the largest cluster in a finite system in constant-kernel aggregation.