

6. Aggregation and fragmentation kinetics

6.1. Cluster-size distributions and master equations

6.1.1. Cluster-size distributions and elementary processes

Aggregation and fragmentation are processes in which particles or clusters change their masses by merging or breaking apart. They occur in colloidal suspensions, polymer systems, aerosols, and astrophysical environments, where the growth and destruction of aggregates determine the evolving distribution of particle sizes.

In aggregation, two clusters merge to form a larger one,



where A_i denotes a cluster containing i elementary units, or *monomers*. We measure mass in monomer units, so that i and j are positive integers. The coefficient K_{ij} is the *aggregation kernel*, which determines the rate at which clusters of masses i and j merge.

In fragmentation, a cluster breaks into smaller fragments,



where F_{ij} characterises the breakup process. Fragmentation may be caused by external forces, thermal processes, or collisions with other particles.

Both processes conserve mass in each elementary event. However, aggregation reduces the number of clusters by one, while binary fragmentation increases it by one.

Our objective is to determine how the cluster-mass distribution evolves with time.

For discrete cluster masses, we introduce $c_k(t)$, the average number of clusters of mass k per unit volume at time t .

The complete set of concentrations,

$$\{c_1(t), c_2(t), c_3(t), \dots\},$$

specifies the cluster-mass distribution. Its evolution depends on the initial concentrations $c_k(0)$ and the rates of aggregation or fragmentation.

The kinetic description developed below assumes that the system is spatially homogeneous, so that the concentrations depend only on time. We also assume that the clusters are characterised by their masses alone; their shapes, orientations, and internal structures are not treated as independent dynamical variables.

6.1.2. Master equations for aggregation and fragmentation

Aggregation. Consider first the evolution of clusters of a specified mass k .

Their concentration changes through two processes: the formation of k -mers by aggregation of smaller clusters and the disappearance of existing k -mers when they merge with other clusters.

For a well-mixed system, the aggregation rate between clusters of different masses i and j , per unit volume, is $K_{ij}c_i c_j$.

The kernel is symmetric, $K_{ij} = K_{ji}$, since exchanging the two reacting clusters does not change the process.

The production rate of clusters of mass k is therefore

$$\left. \frac{dc_k}{dt} \right|_{\text{gain}} = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j.$$

The constraint $i + j = k$ ensures that the masses of the reacting clusters add up to k . The factor $1/2$ prevents double counting of the pairs (i, j) and (j, i) .

For example, the production rate of tetramers is

$$\left. \frac{dc_k}{dt} \right|_{\text{gain}} = K_{13} c_1 c_3 + \frac{1}{2} K_{22} c_2^2.$$

The first contribution arises from monomer–trimer aggregation, while the second represents aggregation of two dimers.

A cluster of mass k disappears when it merges with a cluster of any mass j . Summing over all collision partners gives

$$\left. \frac{dc_k}{dt} \right|_{\text{loss}} = -c_k \sum_{j \geq 1} K_{kj} c_j.$$

There is no factor $1/2$ in this term. When two clusters of equal mass k merge, the event rate contains a factor $1/2$, but each event removes two k -mers.

Combining the gain and loss contributions, we obtain the **Smoluchowski aggregation equations**,

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{j \geq 1} K_{kj} c_j. \quad (6.3)$$

These equations form an infinite system of coupled nonlinear differential equations. Their nonlinearity arises from the fact that aggregation requires the encounter of two clusters, so the reaction rates are proportional to products of concentrations.

The factorisation $c_i c_j$ is a mean-field approximation. It neglects correlations between the locations of reacting clusters and is appropriate when spatial mixing is sufficiently effective. We also assume that binary collisions dominate, while simultaneous encounters involving three or more clusters can be neglected.

Fragmentation. In fragmentation, the basic process is the reverse change in cluster masses: a parent cluster breaks into two smaller fragments.

It is often convenient to treat fragment masses as continuous variables, since a particle or object may break into pieces of essentially arbitrary relative masses.

We therefore introduce $c(x, t)$, defined such that $c(x, t) dx$ is the concentration of fragments with masses between x and $x + dx$.

Let $F(u, v) = F(v, u)$ denote the breakup-rate density for a parent of mass $u + v$ to produce fragments of masses u and v . The total breakup rate of a fragment of mass x is

$$R(x) = \int_0^x F(u, x - u) du. \quad (6.4)$$

A fragment of mass x disappears when it breaks, giving the loss term $-R(x)c(x, t)$.

Fragments of mass x are also produced by the breakup of larger fragments of mass $y > x$. Since either daughter fragment may have mass x , the corresponding gain term contains a factor of two.

The fragmentation master equation is therefore

$$\frac{\partial c(x, t)}{\partial t} = -R(x)c(x, t) + 2 \int_x^\infty c(y, t) F(x, y - x) dy. \quad (6.5)$$

An important distinction from aggregation is that Eq. (6.5) is **linear in the fragment concentration**. Each breakup event occurs independently of the presence of other fragments, as in fragmentation driven by an external mechanism.

If fragmentation is instead caused by collisions between particles, the breakup rates depend on the concentrations of the collision partners, and the resulting kinetic equations become nonlinear. We shall consider this case in Section 6.3.

6.1.3. Moments and conservation laws

Solving the master equations determines the complete cluster-mass distribution. However, important information about its evolution can often be obtained without finding every concentration.

For discrete cluster masses, we introduce the *moments of the mass distribution*,

$$M_n(t) = \sum_{k \geq 1} k^n c_k(t), \quad n = 0, 1, 2, \dots \quad (6.6)$$

The first three moments have direct physical interpretations:

$$\begin{aligned} M_0 &= \sum_{k \geq 1} c_k && \text{— cluster number density} \\ M_1 &= \sum_{k \geq 1} k c_k && \text{— mass density} \\ M_2 &= \sum_{k \geq 1} k^2 c_k && \text{— sensitive to large clusters} \end{aligned}$$

Higher moments place progressively greater weight on large clusters. In the solvable models below, concentrations are normalised to the initial monomer number density, so $M_1 = \rho = 1$ denotes the **normalised mass density**, not the mass of an individual cluster.

Moment equations for aggregation. Differentiating Eq. (6.6) and substituting the Smoluchowski equations gives

$$\frac{dM_n}{dt} = \frac{1}{2} \sum_{k \geq 1} k^n \sum_{i+j=k} K_{ij} c_i c_j - \sum_{k, j \geq 1} k^n K_{kj} c_k c_j.$$

In the gain term, the condition $i + j = k$ allows us to replace k^n by $(i + j)^n$ and perform the sum over k .

In the loss term, the symmetry of the kernel allows us to replace i^n by the equivalent symmetric expression $(i^n + j^n)/2$.

Consequently,

$$\frac{dM_n}{dt} = \frac{1}{2} \sum_{i, j \geq 1} K_{ij} c_i c_j [(i + j)^n - i^n - j^n]. \quad (6.7)$$

The term in square brackets is the change in the n -th moment produced by a single aggregation event: two clusters with masses i and j disappear and are replaced by one cluster of mass $i + j$.

For the first three moments, Eq. (6.7) gives

$$\begin{aligned} \frac{dM_0}{dt} &= -\frac{1}{2} \sum_{i, j} K_{ij} c_i c_j \leq 0, \\ \frac{dM_1}{dt} &= 0, \\ \frac{dM_2}{dt} &= \sum_{i, j} i j K_{ij} c_i c_j \geq 0. \end{aligned} \quad (6.8)$$

These relations express three fundamental properties of aggregation: the number of clusters decreases, the total mass is conserved, and the second moment increases as mass is transferred to larger clusters.

Two useful measures of cluster mass follow from the moments:

The total mass density divided by the cluster number density gives the **mean cluster mass**, expressed in monomer units:

$$s_N = \frac{M_1}{M_0}. \quad (6.9)$$

The **mass-weighted characteristic cluster mass**, which gives additional weight to large clusters, is

$$s_M = \frac{M_2}{M_1}. \quad (6.10)$$

The two measures need not coincide; s_M can diverge even when s_N stays finite.

Equation (6.8) assumes that the relevant sums converge and that all the mass is accounted for by the finite-cluster distribution. Section 6.2.2 distinguishes this distribution from the gel after gelation.

Conservation laws for fragmentation. For the continuous fragment-mass distribution, the total number and mass concentrations are

$$N(t) = \int_0^\infty c(x, t) dx, \quad M_1(t) = \int_0^\infty x c(x, t) dx. \quad (6.11)$$

Integrating Eq. (6.5) over all fragment masses and exchanging the order of integration in the gain term, we obtain

$$\frac{dN}{dt} = - \int_0^\infty R(x) c(x, t) dx + 2 \int_0^\infty c(y, t) \left[\int_0^y F(x, y-x) dx \right] dy.$$

The integral in square brackets is $R(y)$, by definition. Thus,

$$\frac{dN}{dt} = \int_0^\infty R(x) c(x, t) dx \geq 0. \quad (6.12)$$

Each binary fragmentation event increases the number of fragments by one.

To verify mass conservation, multiply Eq. (6.5) by x and integrate. The symmetry $F(x, y-x) = F(y-x, x)$ implies

$$2 \int_0^y x F(x, y-x) dx = y R(y).$$

The mass gained through daughter fragments therefore exactly balances the mass lost through breakup of their parent clusters, giving

$$\frac{dM_1}{dt} = 0. \quad (6.13)$$

Binary fragmentation conserves the total mass density while increasing fragment number density. Hence its mean fragment mass M_1/N decreases.

In the following sections, we shall examine these processes through exactly solvable models. We begin with the constant and product aggregation kernels, which illustrate the difference between continuous cluster growth and finite-time gelation.

6.2. Aggregation processes

We now consider two exactly solvable aggregation models. The first describes the gradual growth of clusters, while the second exhibits *gelation*: the formation of a macroscopic aggregate in finite time. Both follow from the Smoluchowski equations (6.3), but differ in their aggregation kernels.

6.2.1. Constant aggregation kernel

The simplest model assumes that the aggregation rate is independent of the masses of the reacting clusters:

$$K_{ij} = 2. \quad (6.14)$$

A physical motivation comes from diffusion-controlled coagulation. Let R_i be the radius and D_i the translational diffusion coefficient of a spherical cluster containing i monomers. For diffusion-limited sticking, the kernel is proportional to $(D_i + D_j)(R_i + R_j)$. Compact clusters have $R_i \propto i^{1/3}$, and the Stokes–Einstein relation gives $D_i \propto R_i^{-1}$. Therefore,

$$K_{ij} \propto (D_i + D_j)(R_i + R_j) \propto 2 + \left(\frac{i}{j}\right)^{1/3} + \left(\frac{j}{i}\right)^{1/3}.$$

For similar cluster masses, the dependence in the preceding expression is modest; for strongly unequal masses it is not. We adopt $K_{ij} = 2$ as a deliberately simplified approximation and use time units in which the kernel has this value. Initially, all clusters are monomers:

$$c_k(0) = \delta_{k1}.$$

The Smoluchowski equations become

$$\frac{dc_k}{dt} = \sum_{i+j=k} c_i c_j - 2Nc_k, \quad (6.15)$$

where $N(t) = \sum_k c_k(t)$ is the total cluster concentration.

Using the moment equations (6.8), we immediately obtain

$$\frac{dN}{dt} = -N^2, \quad \frac{dM_1}{dt} = 0, \quad \frac{dM_2}{dt} = 2M_1^2.$$

For the chosen initial conditions, integration gives

$$N(t) = \frac{1}{1+t}, \quad M_1(t) = 1, \quad M_2(t) = 1 + 2t. \quad (6.16)$$

The number density decreases while the normalised mass density remains $M_1 = 1$. Both $s_N = M_1/M_0$ and $s_M = M_2/M_1$ increase; their values are measured in monomer units.

To determine the complete mass distribution, notice that the kinetic equations can be solved recursively. For example,

$$\frac{dc_1}{dt} = -2Nc_1$$

gives $c_1 = (1+t)^{-2}$. The dimer concentration then follows from

$$\frac{dc_2}{dt} = c_1^2 - 2Nc_2,$$

yielding $c_2 = t/(1+t)^3$. The procedure can be continued, but a generating function provides a systematic solution for all k .

Introduce

$$C(z, t) = \sum_{k=1}^{\infty} c_k(t) z^k, \quad (6.17)$$

where z is an auxiliary variable. Multiplying Eq. (6.15) by z^k and summing over k , the convolution in the gain term becomes

$$\sum_{k \geq 1} z^k \sum_{i+j=k} c_i c_j = \sum_{i,j \geq 1} c_i c_j z^{i+j} = (\sum_i c_i z^i)(\sum_j c_j z^j) = C^2$$

Hence,

$$\frac{\partial C}{\partial t} = C^2 - 2NC. \quad (6.18)$$

Since $dN/dt = -N^2$, introducing $F = C - N$ reduces this equation to

$$\frac{\partial F}{\partial t} = F^2.$$

The initial condition $c_k(0) = \delta_{k1}$ gives $C(z, 0) = z$, and therefore $F(z, 0) = z - 1$. Integrating at fixed z ,

$$F(z, t) = \frac{z - 1}{1 - t(z - 1)}.$$

Returning to $C = F + N$, we obtain

$$C(z, t) = \frac{z}{(1+t)(1+t-tz)}. \quad (6.19)$$

Expanding the denominator as a geometric series,

$$\begin{aligned} C(z, t) &= \frac{z}{(1+t)^2} \sum_{m=0}^{\infty} \left(\frac{tz}{1+t} \right)^m \\ C(z, t) &= \sum_{k=1}^{\infty} \frac{t^{k-1}}{(1+t)^{k+1}} z^k. \end{aligned}$$

Comparing with the definition (6.17), we arrive at the exact cluster-mass distribution,

$$c_k(t) = \frac{t^{k-1}}{(1+t)^{k+1}}. \quad (6.20)$$

Physical interpretation. The exact solution describes how mass is progressively transferred from small to larger clusters.

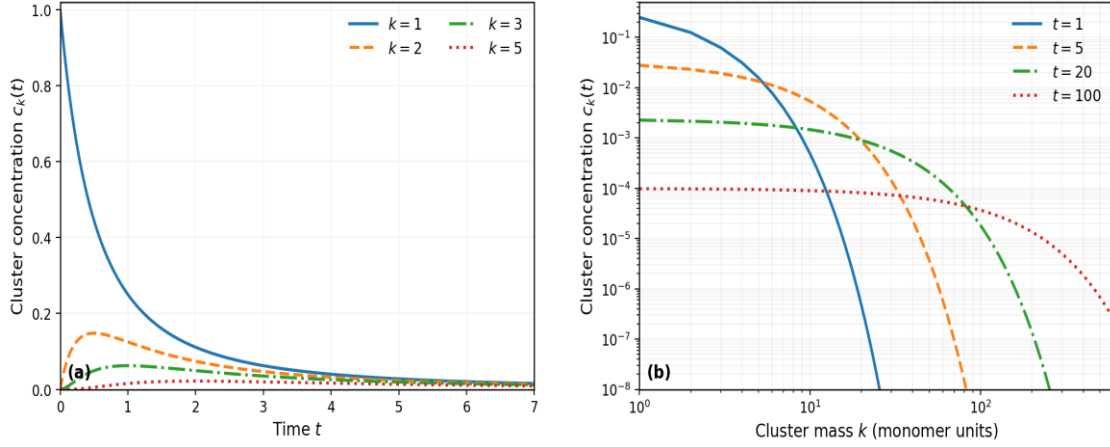


Figure 6.1. Constant-kernel aggregation. (a) Time evolution of concentrations for $k = 1, 2, 3, 5$. (b) Cluster-mass distributions at $t = 1, 5, 20, 100$. All curves independently calculated from the exact solution (6.20).

Figure 6.1(a) shows that the monomer concentration decreases monotonically, whereas concentrations of larger clusters first increase and then decrease as these clusters merge into still larger ones. Differentiating Eq. (6.20), we find that a population of k -mers reaches its maximum at

$$t_k^{\max} = \frac{k-1}{2}, \quad k \geq 2. \quad (6.21)$$

Thus, successively larger clusters reach their maximum concentrations at progressively later times.

Figure 6.1(b) shows the evolution of the complete distribution. At any finite time,

$$\frac{c_{k+1}(t)}{c_k(t)} = \frac{t}{1+t} < 1,$$

Thus, the concentration decreases monotonically with cluster mass at any finite time. As time increases, the ratio approaches unity and the distribution broadens. For $t \gg 1$, Eq. (6.22) gives $c_k(t) \simeq t^{-2}$ when $k \ll t$. Hence the distribution has an approximately constant region for cluster masses much smaller than t , as visible in Fig. 6.1(b).

The curves at different times cross because, over the time interval shown, some larger-cluster populations increase while smaller-cluster populations decrease. Each fixed cluster population with $k \geq 2$ eventually decreases after reaching its maximum in Eq. (6.21). The total mass density remains conserved.

For $t \gg 1$, with k/t fixed, Eq. (6.20) approaches

$$c_k(t) \simeq t^{-2} e^{-k/t}. \quad (6.22)$$

At late times, clusters containing k of order t monomers become important. Both cluster-size measures grow without a finite-time divergence in this model.

6.2.2. Product aggregation kernel and gelation

A qualitatively different behaviour arises when larger clusters aggregate more rapidly. Consider the *product kernel*,

$$K_{ij} = ij. \quad (6.23)$$

The product kernel describes a different mechanism from diffusion-controlled coagulation. Suppose a cluster containing i monomers has a number of accessible reactive sites proportional to i . If every site on one cluster can react with every site on another at the same rate, the number of

possible reactive pairs is proportional to ij . This motivates $K_{ij} \propto ij$ in an idealised, well-mixed reaction-site model, rather than from the geometrical collision cross-section of compact particles.

We again consider monomer-only initial conditions with $M_1(0) = 1$.

Before gelation, the Smoluchowski equations become

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} i j c_i c_j - k c_k, \quad (6.24)$$

where we have used $\sum_j j c_j = 1$.

From Eq. (6.8), the second moment satisfies

$$\frac{dM_2}{dt} = \sum_{i,j} i^2 j^2 c_i c_j = M_2^2.$$

With $M_2(0) = 1$,

$$M_2(t) = \frac{1}{1-t}. \quad (6.25)$$

Unlike the constant kernel, the second moment diverges at the finite time

$$t_g = 1. \quad (6.26)$$

The divergence of M_2 is a warning that the distribution is developing a strong large-cluster tail. The exact distribution below establishes what happens at this time.

The second moment is especially sensitive to large clusters: a cluster containing k monomers contributes a factor proportional to k^2 , even though its mass is proportional only to k . A growing population of very large clusters can therefore make M_2 diverge while the mass density stays finite.

In this model, the critical time is the onset of **gelation**. The gel denotes the macroscopic cluster; clusters of finite mass constitute the **sol**. The onset and subsequent gel mass are determined below.

To establish that gelation actually occurs, we need to examine the cluster-mass distribution.

Exact cluster-mass distribution. For the product kernel, it is convenient to use the mass-weighted generating function

$$E(y, t) = \sum_{k \geq 1} k c_k(t) e^{ky}. \quad (6.27)$$

Multiplying Eq. (6.24) by ke^{ky} and summing over k , we find

$$\frac{\partial E}{\partial t} = E \frac{\partial E}{\partial y} - \frac{\partial E}{\partial y}.$$

Hence,

$$\frac{\partial E}{\partial t} = (E - 1) \frac{\partial E}{\partial y}. \quad (6.28)$$

This nonlinear first-order partial differential equation can be solved by the method of characteristics.

Writing

$$\frac{\partial E}{\partial t} + (1 - E) \frac{\partial E}{\partial y} = 0,$$

we see that E is constant along curves satisfying

$$\frac{dy}{dt} = 1 - E.$$

For the monomer-only initial condition, $E(y, 0) = e^y$. A characteristic starting at y_0 therefore carries the value $E = e^{y_0}$, so that

$$y = y_0 + (1 - E)t = \ln E + (1 - E)t.$$

Rearranging gives the implicit solution

$$E e^{-Et} = e^{y-t}. \quad (6.29)$$

To recover the concentrations, write this relation as

$$E = e^{y-t} e^{tE}.$$

The Lagrange inversion formula gives the coefficients of the resulting power series:

$$E(y, t) = \sum_{k \geq 1} \frac{k^{k-1}}{k!} t^{k-1} e^{-kt} e^{ky}.$$

Comparing with Eq. (6.27), we obtain

$$c_k(t) = \frac{k^{k-2}}{k!} t^{k-1} e^{-kt}. \quad (6.30)$$

Equation (6.30) describes the finite clusters before gelation. Its extension to $t > 1$ assumes **sol-gel aggregation**: finite clusters can attach to the gel, so their loss rate still includes the total mass density $M_1^{\text{sol}} + g = 1$. This is a specific post-gel continuation of the model, not a consequence of the pre-gel equations alone.

Critical distribution at gelation. At $t = t_g = 1$,

$$c_k(1) = \frac{k^{k-2}}{k!} e^{-k}.$$

Using Stirling's approximation for large k ,

$$k! \simeq \sqrt{2\pi k} \left(\frac{k}{e}\right)^k,$$

we obtain

$$c_k(t_g) \simeq \frac{1}{\sqrt{2\pi}} k^{-5/2}. \quad (6.31)$$

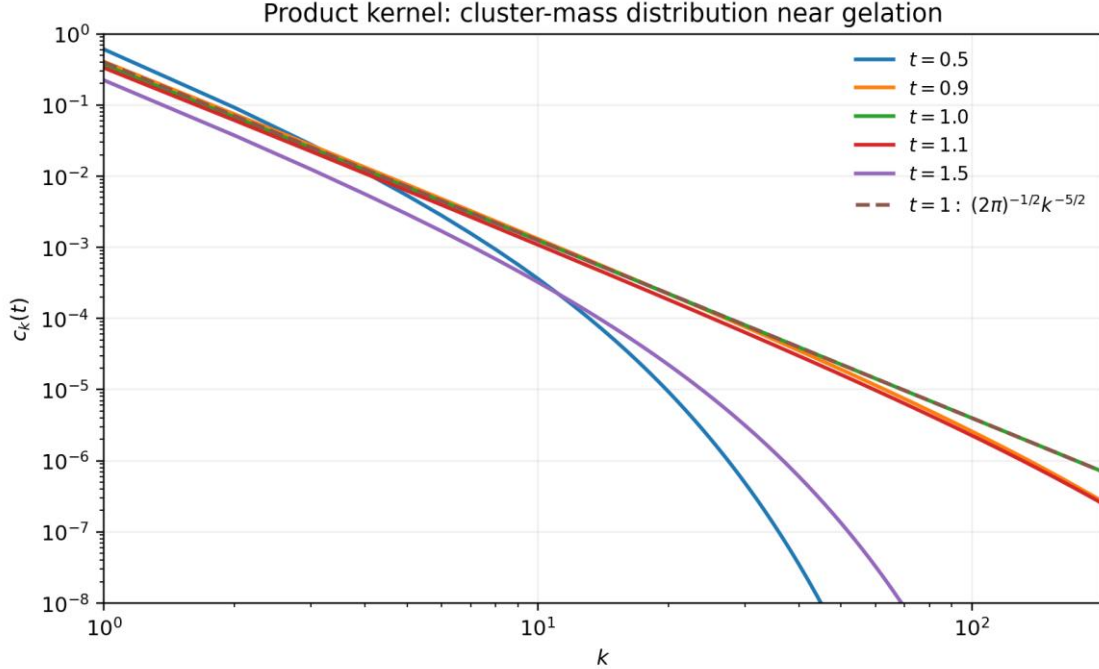


Figure 6.2. Product-kernel cluster-mass distributions before, at and after gelation, independently calculated from Eq. (6.30). The reference line shows the critical $k^{-5/2}$ decay.

At $t = 1$, the exponential cutoff of the large- k tail disappears and the distribution approaches the power law in Eq. (6.31). The plot is calculated directly from Eq. (6.30).

The exponent $5/2$ has an important consequence. The contributions of large clusters to the first and second moments behave as

$$M_1 \sim \sum_k k^{-3/2}, \quad M_2 \sim \sum_k k^{-1/2}.$$

The first sum converges, while the second diverges. Thus, at the gelation point, the total mass remains finite but the mass-weighted characteristic cluster mass M_2/M_1 diverges.

The divergence of M_2 does not mean that every cluster becomes large. The total mass in finite clusters remains finite at the threshold; the divergence comes from the long tail of the distribution.

Formation and growth of the gel. Let $g(t)$ denote the fraction of the total mass contained in the gel. The mass remaining in finite clusters is

$$M_1^{\text{sol}} = 1 - g.$$

Since $E(0, t) = M_1^{\text{sol}}$, setting $y = 0$ in Eq. (6.29) gives

$$(1 - g)e^{-t(1-g)} = e^{-t},$$

or

$$g = 1 - e^{-tg}. \quad (6.32)$$

For $t \leq 1$, the physical solution is $g = 0$. For $t > 1$, Eq. (6.32) also has a nonzero root; under the sol-gel continuation specified above, this root gives the gel mass fraction. Near the threshold,

$$g(t) \simeq 2(t - 1), \quad t \downarrow 1. \quad (6.33)$$

The gel mass fraction begins continuously at $t_g = 1$ and increases for $t > 1$ in this model.

After gelation, the second moment of the finite-cluster distribution is obtained by differentiating Eq. (6.29):

$$M_2^{\text{sol}}(t) = \left. \frac{\partial E}{\partial y} \right|_{y=0}.$$

This gives

$$M_2^{\text{sol}}(t) = \begin{cases} \frac{1}{1-t}, & t < 1, \\ \frac{1}{e^{tg(t)} - t}, & t > 1. \end{cases} \quad (6.34)$$

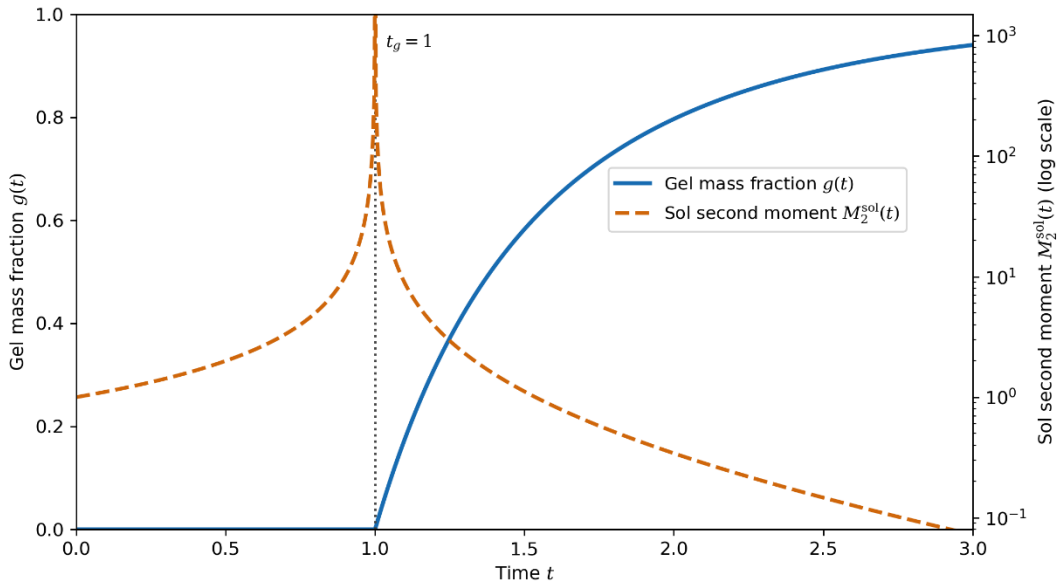


Figure 6.3. Gel mass fraction $g(t)$ (solid line, left axis) and second moment of the sol $M_2^{\text{sol}}(t)$ (dashed line, logarithmic right axis), calculated from Eqs. (6.32) and (6.34). The dotted line marks the gelation time $t_g = 1$.

Figure 6.3 shows that the second moment diverges as the system approaches gelation. Once the gel has formed, the second moment of the remaining finite clusters decreases because these clusters are progressively absorbed into the gel.

The total mass remains conserved, but it is now divided between the sol and gel:

$$M_1^{\text{sol}}(t) + g(t) = 1. \quad (6.35)$$

The constant and product kernels therefore illustrate two different outcomes of irreversible aggregation. When aggregation rates are independent of mass, cluster growth proceeds without a finite-time singularity. When the aggregation rate increases as the product of the reacting masses, the preferential growth of larger clusters leads to the formation of a macroscopic aggregate in finite time.

In the next section, we consider the complementary process of fragmentation, in which clusters break into smaller pieces. In particular, we shall see that sufficiently rapid fragmentation can produce a singularity of the opposite kind: the accumulation of mass in fragments of vanishing size.

6.3. Fragmentation processes

In aggregation, two clusters merge into one, reducing the total number of clusters. In fragmentation, a cluster breaks into smaller pieces, increasing their number while preserving the total mass.

Fragmentation may occur independently in each cluster, for example through the breaking of chemical bonds in polymers, or it may result from collisions between clusters. We consider one representative model of each process.

6.3.1. Binary fragmentation: Random scission

Consider a linear polymer in which each bond has the same probability of breaking per unit time. The number of bonds is approximately proportional to the polymer length, so its total breakup rate is proportional to its mass x .

Choosing units such that $R(x) = x$, we can derive the fragmentation equation from the general expression (6.5).

Consider a parent fragment of mass y , which breaks into two fragments of masses x and $y - x$.

The total breakup rate of the parent is $R(y)$. Since all positions along the polymer are equally likely to break, the cut position X , measured from one end, is uniformly distributed over the interval $0 < X < y$. Its probability density is therefore constant,

$$p(X | y) = \frac{1}{y}, \quad 0 < X < y,$$

where the factor $1/y$ follows from the normalisation condition

$$\int_0^y p(X | y) dX = 1.$$

Consequently, the probability that a cut occurs between x and $x + dx$ is

$$P(x < X < x + dx | y) = \int_x^{x+dx} \frac{dX}{y} = \frac{dx}{y}.$$

A fragment of mass x can be produced on either side of the cut. Thus, the expected number of daughter fragments with masses in $(x, x + dx)$, produced by one breakup event, is

$$\frac{2 dx}{y}.$$

Multiplying by the total breakup rate $R(y)$ and dividing by dx , the production-rate density of daughter fragments of mass x from one parent of mass y is

$$2 \frac{R(y)}{y}.$$

Equivalently, the fragmentation kernel appearing in Eq. (6.5) is

$$F(x, y - x) = \frac{R(y)}{y}.$$

Its normalisation is consistent with the total breakup rate:

$$\int_0^y F(x, y - x) dx = R(y).$$

The concentration of parent fragments with masses in $(y, y + dy)$ is $c(y, t) dy$. Summing the contributions of all parents with $y > x$, we obtain

$$\left. \frac{\partial c(x, t)}{\partial t} \right|_{\text{gain}} = 2 \int_x^\infty \frac{R(y)}{y} c(y, t) dy.$$

For random scission, $R(y) = y$, so $R(y)/y = 1$. The gain term therefore reduces to

$$\left. \frac{\partial c(x, t)}{\partial t} \right|_{\text{gain}} = 2 \int_x^\infty c(y, t) dy.$$

The loss term is $-R(x)c(x, t) = -xc(x, t)$. Combining both contributions, we obtain

$$\frac{\partial c(x, t)}{\partial t} = -xc(x, t) + 2 \int_x^\infty c(y, t) dy. \quad (6.36)$$

The first term describes the disappearance of fragments of mass x , while the second accounts for their creation from larger fragments. The cancellation between the total breakup rate $R(y) = y$ and the factor $1/y$, which follows from the uniform distribution of cut positions, explains the absence of an explicit mass-dependent rate in the gain term.

The evolution of the total fragment concentration,

$$N(t) = \int_0^\infty c(x, t) dx,$$

follows by integrating Eq. (6.36) over x :

$$\begin{aligned} \frac{dN}{dt} &= - \int_0^\infty x c(x, t) dx + 2 \int_0^\infty dx \int_x^\infty c(y, t) dy \\ \frac{dN}{dt} &= -M_1 + 2 \int_0^\infty y c(y, t) dy = M_1. \end{aligned}$$

The total mass M_1 is conserved. For $M_1 = 1$, integration gives

$$N(t) = N(0) + t. \quad (6.37)$$

Consequently, the number-average fragment mass decreases as

$$\langle x \rangle = \frac{M_1}{N(t)} = \frac{1}{N(0) + t}.$$

To determine the complete fragment-size distribution, consider an initial segment of unit length,

$$c(x, 0) = \delta(x - 1).$$

Suppose that cuts occur independently and uniformly along the segment, at unit rate per unit length. After time t , the number of cuts in an interval of length x is Poisson distributed with mean xt . The probability that this interval contains no cuts is therefore e^{-xt} .

There are three possible contributions to the fragment-size distribution.

An original segment that has undergone no cuts contributes $e^{-t} \delta(x - 1)$.

A fragment of length x adjacent to either endpoint is produced when a cut occurs at distance x from that endpoint and no cuts occur between them. Its contribution to the expected number of fragments in $(x, x + dx)$ is $te^{-xt} dx$ for each endpoint, giving $2te^{-xt} dx$.

Finally, a fragment in the interior must be bounded by two cuts separated by distance x , with no additional cuts between them. The left boundary can lie anywhere within a distance $1 - x$ from the left endpoint. Its contribution is therefore $t^2(1 - x)e^{-xt} dx$.

Combining these contributions, the distribution is the sum of the surviving initial segment and the continuous density of shorter fragments:

$$c(x, t) = e^{-t}\delta(x - 1) + c_{\text{cont}}(x, t) \quad (6.38)$$

The continuous contribution is given explicitly by

$$c_{\text{cont}}(x, t) = \begin{cases} e^{-xt}[2t + t^2(1 - x)], & 0 < x < 1, \\ 0, & \text{otherwise.} \end{cases}$$

The distribution has the required properties:

$$\int_0^\infty c(x, t) dx = 1 + t, \quad \int_0^\infty x c(x, t) dx = 1.$$

The first relation gives the increasing number of fragments, while the second confirms conservation of their total length.

At long times, the characteristic fragment length becomes of order t^{-1} . For $t \gg 1$ and xt finite, the term proportional to t^2 dominates Eq. (6.38), giving

$$c(x, t) \simeq t^2 e^{-xt}. \quad (6.39)$$

Thus, the distribution becomes increasingly concentrated at small fragment masses, while its total integral grows proportionally to time.

6.3.2. Collision-induced fragmentation and shattering

In random scission, a fragment breaks independently of the other fragments. In **collision-induced fragmentation**, breakup instead requires a collision between two fragments. One possible event is

$$A_x + A_{y+z} \rightarrow A_x + A_y + A_z, \quad (6.40)$$

The collision leaves one partner unchanged and splits the other into two fragments. Each such event conserves mass and increases the number of fragments by one.

We study an explicitly defined idealisation: (i) the collision kernel is constant, with value 2 in our time units; (ii) either collision partner has probability 1/2 of being the one that breaks; (iii) the selected fragment splits into two equal-mass pieces. These rules are chosen for solvability, not because real collisions always behave this way.

Fragment number density. Initially, all fragments have unit mass. After n equal splittings, their mass is $m_n = 2^{-n}$. Let $c_n(t)$ denote the number density of these fragments. The total fragment number density is therefore $N(t) = M_0(t) = \sum_{n=0}^\infty c_n(t)$.

For a symmetric constant collision kernel $K = 2$, the collision-event rate per unit volume is $1/2 KN^2 = N^2$. Every collision produces one additional fragment, so

$$\frac{dN}{dt} = N^2. \quad (6.41)$$

For the initial condition $N(0) = 1$, integration yields

$$N(t) = \frac{1}{1-t}. \quad (6.42)$$

For $0 \leq t < 1$, the number density increases and tends to diverge as t approaches $t_c = 1$ from below. Because mass density is conserved, $M_1 = 1$, the **mean fragment mass** is

$$\langle m \rangle = \frac{M_1}{N} = 1 - t,$$

Thus the number density increases without bound while the mean fragment mass decreases to zero as $t \rightarrow 1^-$. The behaviour of the full mass distribution still has to be established; the two moments alone do not describe it.

Fragment-mass distribution. We now examine how the number densities of the individual classes evolve.

In this constant-kernel model, a fragment participates in collisions at rate $2N$. Because it is chosen to break with probability $1/2$, its breakup rate is N . A fragment in class $n - 1$ creates two fragments in class n when it breaks. The gain and loss rates are therefore

$$\frac{dc_n}{dt} = N(t)[2c_{n-1} - c_n], \quad (6.43)$$

Here $c_{-1} = 0$. Summing Eq. (6.43) over n reproduces Eq. (6.41). Multiplication by 2^{-n} before summation gives

$$\frac{d}{dt} \sum_{n \geq 0} 2^{-n} c_n = 0,$$

confirming that every splitting preserves the total mass.

Introduce a rescaled time equal to the integrated breakup rate of an individual fragment,

$$\tau = \int_0^t N(t') dt' = -\ln(1 - t). \quad (6.44)$$

Since $d\tau/dt = N(t)$, Eq. (6.43) becomes

$$\frac{dc_n}{d\tau} = 2c_{n-1} - c_n.$$

For the initial condition $c_n(0) = \delta_{n0}$, the equation for $n = 0$ gives $c_0 = e^{-\tau}$. The remaining equations follow recursively by multiplying them by e^τ and integrating:

$$\frac{d}{d\tau} (e^\tau c_n) = 2e^\tau c_{n-1}.$$

This yields $c_n(\tau) = e^{-\tau} (2\tau)^n / n!$, or, in physical time,

$$c_n(t) = (1 - t) \frac{[-2\ln(1-t)]^n}{n!}. \quad (6.45)$$

How the singular behaviour is approached. A number density does not directly show where the conserved mass resides. The mass contained in class n , divided by the total mass density $M_1 = 1$, is the mass fraction

$$p_n(t) = 2^{-n} c_n(t) = e^{-\tau} \frac{\tau^n}{n!}. \quad (6.46)$$

This distribution is normalised, $\sum_{n=0}^{\infty} p_n = 1$, and is Poisson in the **splitting index** n , with mean and variance both equal to τ .

As $t \rightarrow 1^-$, the quantity $\tau = -\ln(1 - t)$ increases without bound. The mass fraction p_n is largest for n near τ , and appreciable mass lies in classes with $n = \tau + O(\sqrt{\tau})$. Because class n has mass 2^{-n} , the part of the distribution carrying most of the mass moves towards progressively smaller fragments.

The mass of the class at the peak of p_n differs by at most a factor of two from the scale

$$2^{-\tau} = (1 - t)^{\ln 2}.$$

This identifies how the mass-carrying part of the distribution shifts. It is **not** another definition of the mean fragment mass $M_1/N = 1 - t$.

To verify the redistribution directly, hold a cutoff index n_0 fixed as time varies. The mass fraction in the classes $0 \leq n \leq n_0$ is

$$P_{\leq n_0}(\tau) = e^{-\tau} \sum_{n=0}^{n_0} \frac{\tau^n}{n!}.$$

Because the cutoff is fixed, this fraction tends to zero as τ grows. The mass is being transferred to classes with $n > n_0$, corresponding to ever smaller fragments as t approaches t_c from below.

The finite-time divergence of fragment number density, accompanied by a progressive decrease of fragment masses while the total mass density remains conserved, characterises shattering in this idealised model. At every $t < 1$, all fragments retain nonzero masses.

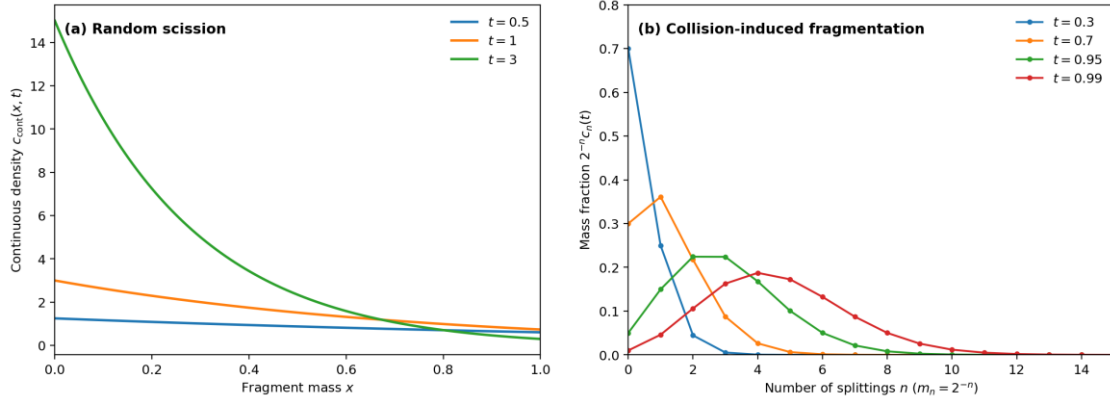


Figure 6.4. (a) Random-scission fragment-size distributions from Eq. (6.38), without the unbroken-segment delta peak. (b) Mass fractions of collision-induced fragments from Eq. (6.46); the mass shifts towards smaller fragments as t approaches 1.

The finite-time divergence depends crucially on the mass-independent collision kernel. Actual collision rates change as fragments become smaller, because their cross-sections and velocities change. Therefore the calculated critical time and divergence law belong to this idealised model and cannot be transferred to a physical material without specifying its collision mechanism.

The contrast with Section 6.2 is in the direction of mass transfer: aggregation shifts mass towards larger clusters, whereas the present collision-driven fragmentation model shifts it towards smaller fragments.

Source: P. L. Krapivsky, S. Redner and E. Ben-Naim, *A Kinetic View of Statistical Physics*, selected Sections of Chapters 5–6.