

## Statistical Theory of Fragmentation

Sidney Redner

Center for Polymer Studies and Department of Physics  
Boston University, Boston, MA 02215, USA

*A general discussion of the kinetics of fragmentation processes is given. For a linear process, where fragmentation is driven by an external force, a scaling theory to describe the evolution of the cluster-size distribution is developed. General homogeneous systems, in which the break-up kernel is characterized by a homogeneity index  $\lambda$ , are treated. When  $\lambda > 0$ , corresponding to larger clusters more likely to break than small clusters, the scaled cluster size distribution,  $\phi(x)$ , decays with the scaled mass,  $x$ , as  $x^{-2} \exp(-ax^\lambda)$ , as  $x \rightarrow \infty$ . For small  $x$ ,  $\phi(x)$  approaches the log normal form,  $\exp(-a \ln^2 x)$ , if the breakup kernel has a small-size cutoff, while  $\phi(x)$  has a power law form in the absence of a cutoff. The conditions necessary for the existence of scaling are discussed. This reasoning also indicates that there is a "shattering" transition where mass is lost to a "dust" phase of zero-mass particles for  $\lambda < 0$ . For a collision induced, non-linear fragmentation process, the asymptotic behavior of "splitting" models, in which a two-particle collision results in one or both incident particles splitting in two, is analyzed. Scaling is found to hold for different ranges of homogeneity index for these models. Comparisons and contrasts are made between the kinetics of linear and collision-induced fragmentation.*

### 1. Introduction

A basic goal of this chapter is to provide a general theoretical account of the distribution of fragment sizes that results from fragmentation processes. Such processes are ubiquitous in nature, and they underlie phenomena such as polymer degradation, breakup of liquid droplets, crushing or grinding of rocks, and combustion.<sup>[1-8]</sup> These systems are often driven by a continuous external agent, such as repeated sledgehammer blows on a brittle piece of rock. This leads to a continuously evolving cluster size distribution in which the typical size decreases with time. As the typical size goes to zero, the lack of a characteristic size scale suggests that scaling and universality can be invoked to describe the nature of this distribution for sizes larger than the typical size.

I will discuss a purely kinetic, rate equation approach to describe the evolution of the cluster size distribution due to continuous fragmentation. This work has been

performed during the course of an enjoyable collaboration with Z. Cheng. equation approach has been extensively investigated in the mathematical and literature (see, *e.g.*, Refs. [9-12]), and there has been considerable progress a statistical mechanical viewpoint by the recent work of Ziff and coworkers. The basic viewpoint that I adopt is that scaling theory applied to the rate equation provides a simple, yet powerful way obtaining universal information about the nature of the solutions to the rate equations.<sup>[16,17]</sup> This methodology closely parallels recent developments made in understanding the kinetics of the inverse process of aggregation (see, *e.g.*, Refs. [18-21]). The rate equations are a mean-field description, in which it is assumed that each fragment experiences the average environment. In such an approach, the mass is the only relevant quantity that characterizes a fragment, *i.e.*, the cluster size distribution is taken to be spatially uniform. The microscopic details of the breakup processes are embodied by two kernels in the rate equations. One describes the *overall* rate at which a particle breaks, and a second which gives the *relative* masses of the products emerging from a breakup event.

Within the rate equation approach one may further classify fragmentation by whether the breakup is driven only by a homogeneous external agent, which is a purely *linear* process, or whether additional influences can also play a role in particle breakup. One such possibility is fragmentation induced by collisions between fragments, which might arise in an explosive-type process, or perhaps in the breakup of small eddies in a turbulent fluid flow.<sup>[22]</sup> As an idealization of such a situation, I will consider a *non-linear* fragmentation model, in which collisions between fragments are responsible for particle breakup, with fragmentation products continuously participating in repeated collisions and fragmentations.<sup>[23]</sup> While such a collision-induced model may be too idealized to be of direct practical relevance, the phenomenology of such processes is quite rich. Furthermore, there are parallels with the rate equations of the inverse process of aggregation, since both models are driven by the same type of bimolecular rate. Thus studies of collision-induced fragmentation may provide a useful first step in understanding non-linear effects in fragmentation kinetics.

## 2. Rate Equation Approach

Denote by  $c(x, t)$  the concentration of particles of mass  $x$  at time  $t$ . The time dependence of  $c(x, t)$  is accounted for by writing the system of rate equations that describes how  $c(x, t)$  evolves as a result of the break-up process. As mentioned previously, this approach represents an approximation of a mean-field character, as fluctuations in the spatial positions of the fragments and in their shape are ignored. While neglecting fluctuations may be quite drastic in some situations, such an approximation appears to be valid for comminution processes such as ball milling.<sup>[7]</sup> In such a system, there is thorough mixing of rock pieces by the turning of an enclosing circular drum, with fragmentation being caused by the falling of a steel ball on the rock. One should envision such a system when appealing to the rate equation approach.

Below, I outline some basic properties of the rate equations for both linear and non-linear fragmentation.

### 2.1 Linear fragmentation model

For a process in which break-up is driven by an external source, the evolution of

the cluster size distribution is described by the linear integro-differential equation<sup>[9-17]</sup>

$$\frac{\partial}{\partial t} c(x, t) = -a(x) c(x, t) + \int_x^\infty c(y, t) a(y) f(x|y) dy. \quad (1)$$

Here,  $a(x)$  is the *overall* rate at which  $x$  breaks, *i.e.*,  $a(x) dt$  is proportional to the probability that an  $x$ -mer breaks in a time interval  $dt$ , and  $f(x|y)$  is the *relative* breakup rate, *i.e.*, the conditional probability, or rate, at which  $x$  is produced from the breakup of  $y$ . The first term on the right hand side of Eq. (1) thus accounts for the "loss" of  $x$ -mers due to their breakup, while the second term accounts for the "gain" of  $x$ -mers due to the breakup of particles with mass  $y > x$ .

The cluster size distribution that results from Eq. (1) is determined by the details of the reaction kernels  $a(x)$  and  $f(x|y)$ . I shall restrict ourselves to *homogeneous* kernels, as this case encompasses most physically attainable and relevant situations. Homogeneity implies that  $a(x)$  has the power law form,  $a(x) = x^\lambda$ , thus defining the homogeneity index  $\lambda$ . Homogeneity also implies that  $f(x|y)$  depends only on the ratio  $x/y$ , *i.e.*,  $f(x, y)$  has the form  $y^{-1} b(x/y)$ . Mass conservation imposes the condition  $\int_0^1 x b(x) dx = 1$ , and we choose  $\int_0^1 b(x) dx$ , which is the average number of fragments produced in a breakup event, to be finite.

## 2.2 Collision-induced fragmentation model

For breakup driven by collisions between fragments, the interparticle interaction is now specified by the collision kernel  $K(x, y)$ , which gives the rate at which an  $x$ -mer and a  $y$ -mer meet, and the break-up kernel  $B(x|y, z)$ , which describes the rate at which  $x$ -mers are generated as result of the break-up of a  $y$ -mer in a collision between a  $y$ -mer and a  $z$ -mer. The rate equations for  $c(x, t)$  now are,<sup>[16,17]</sup>

$$\begin{aligned} \frac{\partial c(x, t)}{\partial t} = & -c(x, t) \int_0^\infty K(x, y) c(y, t) dy \\ & + \int_0^\infty dz \int_x^\infty K(y, z) B(x|y, z) c(y, t) c(z, t) dy \end{aligned} \quad (2)$$

The two terms on the right-hand side account for the loss and gain of  $x$ -mers by fragmentation, respectively. Loss of  $x$ -mers arises because of collisions of  $x$ -mers with any of the particles in the system, while gain of  $x$ -mers arises from collisions in which the mass of  $y$  is larger than  $x$ . In this non-linear model, the collision kernel is symmetric, *i.e.*,  $K(x, y) = K(y, x)$ , while mass conservation implies that  $y = \int_0^y x B(x|y, z) dy$ .

In analogy with both linear fragmentation and with aggregation, one generally considers only systems with homogeneous collision kernels, *i.e.*

$$K(ax, ay) = a^\lambda K(x, y). \quad (3)$$

For the break-up kernel, there is a considerable latitude of possibilities, as many dependences of  $B(x|y, z)$  and  $K(x, y)$  on their arguments lead to physically reasonable microscopic processes. I will concentrate on a general class of "splitting" models which retain the essential nonlinearity of collision-induced fragmentation, but are simple enough to be analyzed analytically. They are:

MODEL I: Both particles split exactly in two in a collision.

MODEL II: Only the larger particle splits in two.

MODEL III: Only the smaller particle splits in two.

Models II and III represent the two extreme and opposite situations in which the larger, or the smaller clusters are more susceptible to breakup, respectively.

### 3. Scaling

I will mainly focus on solutions to the rate equations that can be cast into a scaling form. Scaling solutions are emphasized for several reasons. First, the kernels for which scaling holds represent most physically relevant systems. Second, the scaling ansatz reduces a two variable problem to a single variable problem, thus providing a simpler description of the problem. Third, a scaling solution is universal in the sense that it is independent of the initial condition. Thus scaling provides a robust classification scheme for the solutions.

To analyze the rate equations, I use the familiar scaling ansatz for the cluster size distribution,<sup>[18-21]</sup>

$$c(x, t) = s(t)^{-2} \phi(x/s(t)), \quad (4)$$

where  $s(t)$  is a typical particle mass. According to this scaling ansatz, the distribution of fragment sizes is not a function of mass and time separately, but rather is a function only of the ratio of the mass to the typical mass,  $s(t)$ . The prefactor of  $s(t)^{-2}$  is required by mass conservation. This scaling form also implies that the moments of the cluster size distribution are all related. Define the  $\alpha^{\text{th}}$ -moment of the cluster-size distribution and the  $\alpha^{\text{th}}$ -moment of the scaling function, by

$$M_\alpha(t) = \int_0^\infty x^\alpha c(x, t) dx, \quad m_\alpha = \int_0^\infty x^\alpha \phi(x) dx. \quad (5)$$

These are just the Mellin transforms of  $c(x, t)$  of  $\phi(x)$ , respectively (except for a trivial shift of 1 in the definition of  $\alpha$ ). From this, the “bare” and “scaled” moments are related by

$$M_\alpha(t) = m_\alpha s(t)^{\alpha-1}, \quad (6)$$

and in particular,

$$s(t) = m_0/M_0(t). \quad (7)$$

This states that the typical size varies as the inverse of the cluster concentration. These moment relations follow solely from the ansatz (4); therefore they are common to both fragmentation *and* aggregation. Notice that in the scaling ansatz there are two free parameters, namely the amplitude of  $s(t)$  and the amplitude of  $\phi(x)$ . Without loss of generality, one may normalize both  $m_1$  and  $m_0$  to 1 in order to fix these two free parameters. Let us now exploit this scaling formulation to obtain asymptotic solutions to the rate equations.

## 4. Solutions to the Rate Equations for Linear Fragmentation

### 4.1 Moment relations

For the linear model, substituting Eq. (4) into (1), and defining  $\xi = x/s$ , yields the scaling equations

$$\omega[2\phi(\xi) + \xi \phi'(\xi)] = -\xi^\lambda \phi(\xi) + \int_\xi^\infty \phi(\eta) \eta^{\lambda-1} b\left(\frac{\xi}{\eta}\right) d\eta, \quad (8)$$

$$\dot{s} s^{-(1+\lambda)} = -\omega, \quad (9)$$

where  $\omega > 0$  is the separation constant, and the overdot denotes the time derivative. From Eq. (9), the typical fragment size has the time dependence,

$$s(t) \sim \begin{cases} t^{-1/\lambda}, & \text{for } \lambda > 0 \text{ and } t \rightarrow \infty, \\ e^{-\omega t}, & \text{for } \lambda = 0 \text{ and } t \rightarrow \infty, \\ (t_c - t)^{1/|\lambda|}, & \text{for } \lambda < 0 \text{ and } t < t_c. \end{cases} \quad (10)$$

To find the solution to Eq. (8), one converts it to a relation involving the moments of  $\phi(\xi)$  by multiplying both sides by  $\xi^\alpha$  and integrating over all  $\xi$ . An important point in this derivation is that the second term on the right-hand side of Eq. (8) leads to the integral

$$\int_0^\infty d\xi \int_\xi^\infty \xi^\alpha \eta^{\lambda-1} \phi(\eta) g(\xi/\eta) d\eta, \quad (11a)$$

and the order of integration can be interchanged to yield

$$\int_0^\eta d\xi \int_0^\infty \xi^\alpha \eta^{\lambda-1} \phi(\eta) g(\xi/\eta) d\eta. \quad (11b)$$

Now by introducing the moments of the reduced break-up kernel

$$L_\alpha = \int_0^1 x^\alpha b(x) dx, \quad (12)$$

and in terms of the moments,  $m_\alpha$ , of the scaling function, one obtains the linear recursion relation

$$m_{\alpha+\lambda} = \omega \frac{1-\alpha}{L_\alpha-1} m_\alpha. \quad (13)$$

Notice that the explicit dependence on the kernel is contained *only* in  $L_\alpha$ . This suggests that many of the results that follow from this recursion relation will be universal in nature.

To determine the asymptotic behavior of the cluster size distribution, I make extensive use of the following "correspondence" procedure to relate the moment function,  $m_\alpha$ , and its inverse Mellin transform,  $\phi(x)$ . First, Eq. (13) is used to compute the reduced moments for a discrete set of equidistant  $\alpha$  values. Next, "smoothness" is invoked, in which the form of the moments from the discrete set  $\{\alpha\}$  is extended to continuous values of  $\alpha$ . Finally, one computes the inverse Mellin transform to reconstruct the functional form of the scaling function. Although such a procedure is not mathematically precise, this correspondence is supported by available exact solutions, and it is reasonable to assume that it will be correct for physically realizable fragmentation processes.

#### 4.2 Cluster size distribution in the large $x$ limit

The large  $x$  behavior of  $\phi(x)$  corresponds to  $m_\alpha$  for large values of  $\alpha$ . To obtain this latter quantity, substitute  $\alpha = k\lambda$ , with  $k$  a positive integer, iterate Eq. (13), and use the fact  $m_0 = 1$ . This leads to

$$m_{k\lambda} = \omega^{k-1} \prod_{n=1}^{k-1} \frac{n\lambda - 1}{1 - L_{n\lambda}}. \quad (14)$$

For large  $k$ ,  $m_{k\lambda}$  is dominated the large- $n$  factors in the product. Concomitantly, the large  $n$  behavior of  $L_{n\lambda}$  depends only on the limiting form of  $b(x)$  at  $x$  near 1 (*i.e.*, in the limit of production of large fragments). Thus the form of  $m_{k\lambda}$  is universal in that specific details of a model appear only in the homogeneity index and in the limiting form of  $b(x)$  for  $x \rightarrow 1$ ; other aspects of the breakup kernel are irrelevant.

For illustration purposes, consider the general class of kernels which have the form for  $x$  near 1

$$b(x) = b(1) + O((1-x)^\mu) \quad (15)$$

where  $b(1) \geq 0$  and  $\mu > 0$  are constants. For this form of  $b(x)$ , one has

$$L_\alpha = b(1)/\alpha + O(\alpha^{-(\mu+1)}), \quad (16)$$

for large  $\alpha$ . Using this in Eq. (14) eventually leads to

$$m_{k\lambda} \propto (k-1)! (\omega\lambda)^{k-1} (k-1)^{(b(1)-1)/\lambda}. \quad (17a)$$

Employing Stirling's approximation now yields

$$m_\alpha \rightarrow c \left(\frac{\omega}{e}\right)^{\alpha/\lambda} \alpha^{(b(1)-1)/\lambda - 1/2} \alpha^{\alpha/\lambda}, \quad \text{for } \alpha \rightarrow \infty, \quad (17b)$$

where  $c$  is a constant and where  $k$  has been replaced by  $\alpha/\lambda$ . Although Eq. (17a) is valid only for a discrete set of equidistant values of  $\alpha$ , one expects that Eq. (17b) is generally true, since the moment function is a smooth function of  $\alpha$  in the large  $\alpha$  limit.

Owing to this universality of  $m_\alpha$ , it follows that the corresponding functional form of  $\phi(x)$  is also universal. One can now deduce the general form of  $\phi(x)$  by computing the inverse Mellin transform of  $m_\alpha$ . This gives

$$\phi(x) \sim x^{b(1)-2} \exp(-ax^\lambda) \quad (x \rightarrow \infty). \quad (18)$$

It can be verified directly that this form for  $\phi(x)$  for large  $x$  indeed yields the large- $\alpha$  form for the moments  $m_\alpha$  given in Eq. (17).

More generally, the above result for  $\phi(x)$  can be extended to general homogeneous kernels by noticing that the controlling factor,  $\alpha^{\alpha/\lambda}$  in Eq. (17b), is responsible for the quasi-exponential form,  $\exp(-ax^\lambda)$ , in  $\phi(x)$ . This controlling factor arises from the kernel-independent quantity,  $\prod_{n=1}^{k-1} [n\lambda - 1]$ . Consequently, the scaling function has the *universal* controlling factor  $\exp(-ax^\lambda)$  for large  $x$ , for kernels with homogeneity index  $\lambda$ .

#### 4.3 Cluster size distribution in the small $x$ limit

In the small- $x$  limit, there is a lesser degree of universality since the small mass tail is not influenced by particles of the typical size. One does find, however, that there are only two possible generic scaling forms for  $\phi(x)$  at small  $x$ , whose applicability depends on whether or not the moments  $L_{-\alpha}$  exist for all  $\alpha$ . To obtain  $\phi(x)$  in the small- $x$  limit, one requires the behavior of  $m_{-\alpha}$  as  $\alpha \rightarrow \infty$ . Accordingly, choose  $\alpha = 1 - k\lambda$  in Eq. (13) and iterate to arrive at the analog of Eq. (14), namely,

$$m_{1-k\lambda} = \omega^{-k} \frac{\prod_{n=1}^k [L_{1-n\lambda} - 1]}{\prod_{n=1}^k n\lambda}. \quad (19)$$

In analogy with the case of large positive  $\alpha$ , the dependence of  $m_{1-k\lambda}$  on  $k$  for large  $k$  is controlled by the limiting form of  $b(x)$  for  $x$  near 0.

To appreciate the consequences of this fact, let us first treat the general case of kernels that are cut off at small fragment sizes, *i.e.*, “flaking off” of infinitesimal size pieces in a breakup event is not allowed. For example, consider  $b(x) = 0$  for  $x < x_0$ , with  $0 < x_0 < 1$  and  $b(x) = b_1(x - x_0)^\mu$  for  $x \rightarrow x_0^+$ . That is, the smallest fragment that can be created from breaking a piece of size  $y$  is  $x_0 y$ . For this case,  $L_{1-\alpha} \sim c \cdot x_0^{-\alpha} / \alpha^{1+\mu}$ , for large  $\alpha$ , where  $c$  is a constant independent of  $\alpha$ . Substituting this leading behavior into Eq. (19), yields

$$m_{1-k\lambda} \sim \left(\frac{c}{\omega \lambda^{\mu+2}}\right)^k \cdot (k!)^{-\mu-2} \cdot x_0^{-\lambda(k+1)k/2}. \quad (20)$$

In terms of  $\alpha = 1 - k\lambda$ , the controlling factor of  $m_{-\alpha}$  has a universal form,

$$\exp[-\alpha^2(\ln x_0)/2\lambda], \quad (21)$$

as it is only in the lower order contributions in Eq. (20) that dependence on  $\mu$  appears. By taking the inverse Mellin transform, the controlling factor of  $\phi(x)$  has the classical log-normal form<sup>[24,25]</sup>

$$\phi(x) \sim \exp\left[-\frac{\lambda}{2 \ln x_0}(\ln^2 x)\right] \quad (x \rightarrow 0). \quad (22)$$

More generally, for an arbitrary kernel  $b(x)$  with a small-size cutoff, one can verify that the controlling factor in Eq. (21) arises from  $\prod_{n=1}^k [L_{1-n\lambda} - 1]$  in Eq. (19). Since for any  $b(x)$  with a cutoff, there always exists some  $0 < x_0 < 1$  such that  $L_{-\alpha} > x_0^{-\alpha}$ , this product leads to a factor which diverges at least as fast as  $\exp(c\alpha^2)$  as  $\alpha \rightarrow \infty$ . Thus one concludes that, in general,  $\phi(x)$  decays as  $\exp[-(\ln^2 x)/4c]$ , or slower, as  $x \rightarrow 0$ .

The log-normal form can be obtained from a simple multiplicative argument which appears to contain the essence of a repeated fragmentation process with a small size cutoff.<sup>[25,26]</sup> According to this process, the mass of a given fragment schematically evolves as

$$x_0 \rightarrow x_1 \rightarrow x_2 \rightarrow \cdots \rightarrow x_N, \quad (23)$$

where the successive reduction factor  $r_k = x_k/x_{k-1}$  is a random variable with a well-behaved distribution, for a kernel with a small-mass cutoff. Consequently, the central limit theorem states that  $\log x_N = \sum_{k=0}^N \log r_k$  will be normally distributed, so that  $x_N$  will be distributed log-normally.

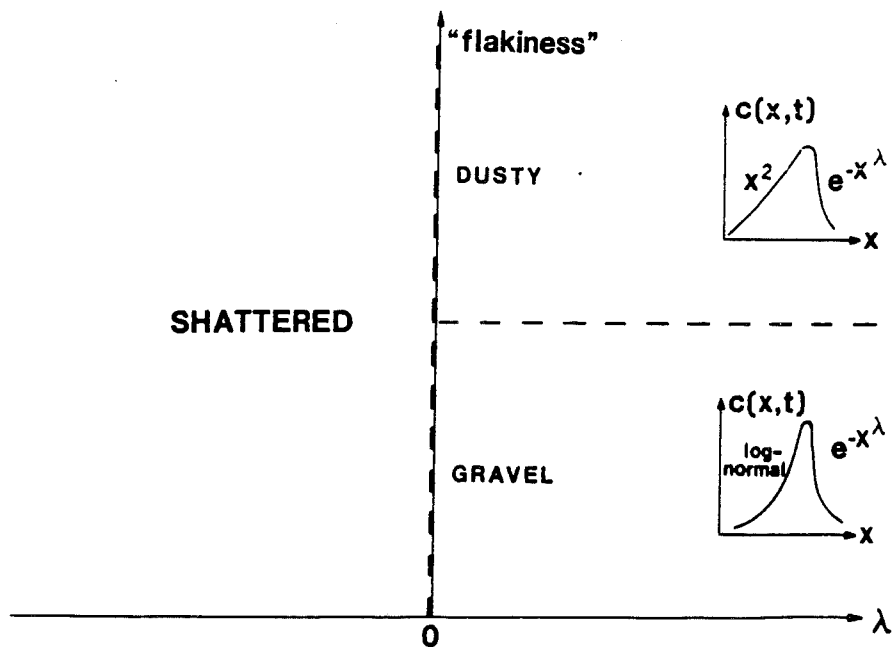
A second general universality class for the small- $x$  behavior of  $b(x)$  is the situations where “flaking off” of infinitesimal size pieces in a single fragmentation is allowed. This corresponds to a kernel with no cutoff at the small-size limit. For example, for the kernel  $b(x) \sim x^\nu$  for small  $x$ , it follows, by solving for  $m_\alpha$  in terms of  $m_{\alpha+\lambda}$  in Eq. (13), that  $m_\alpha$  diverges whenever  $L_\alpha$  diverges. This occurs for  $\alpha$  less than a critical value  $\alpha_c$ , which is less than 0, since  $m_0$  is finite. For  $\alpha$  close to  $\alpha_c$  one keeps only the leading term in Eq. (13) to give

$$m_\alpha = L_\alpha \frac{m_{\alpha_c+\lambda}}{\omega(1-\alpha_c)} \propto L_\alpha = \int x^\alpha b(x) dx. \quad (24)$$

This implies that  $\phi(x)$  coincides with  $b(x)$ , so that

$$\phi(x) \sim x^\nu \quad (x \rightarrow 0). \quad (25)$$

Eqs. (22) and (25) provide the asymptotic small  $x$  behavior of  $\phi(x)$  for an encompassingly wide class of breakup kernels. The range of possibilities for the system can be conveniently summarized by the "phase diagram" of Fig. 1.



**Figure 1** "Phase diagram" for linear fragmentation in the plane defined by the homogeneity index  $\lambda$  and a loosely-defined parameter, the "flakiness" of the relative breakup rate. Small flakiness corresponds to a vanishingly small probability of small flakes being produced in a single breakup event, *i.e.*, a small-size cutoff in  $b(x)$ , while large flakiness corresponds to the opposite limit of a power law tail in  $b(x)$ . In the phase plane there is a "shattered" phase for  $\lambda < 0$ , while for  $\lambda \geq 0$  there is a "gravel" phase for small flakiness and a "dusty" phase for large flakiness. The fragment size distributions corresponding to these latter two phases are also shown.

#### 4.4 Existence of scaling

Thus far, I have merely assumed that scaling holds for  $\lambda > 0$ . I now show that  $\lambda > 0$  is a necessary condition for scaling, and give a plausibility argument that  $\lambda > 0$  is also a sufficient condition for scaling. First notice that  $\lambda < 0$  implies no scaling. If scaling existed for  $\lambda < 0$ , then Eq. (10) predicts that  $s(t)$  vanishes in a finite time, and from Eq. (7),  $M_0(t)$  is singular. This contradicts the fact, from Eq. (1), that  $c(x, t)$  must decay exponentially in time, or slower, for any value of  $x$ . Hence scaling solutions do not exist when  $\lambda < 0$ .

To argue that  $\lambda > 0$  is a sufficient condition for scaling, first write the "bare" moment relation which is derived directly from the rate equation (1),

$$\dot{M}_\alpha = (L_\alpha - 1) M_{\alpha+\lambda}. \quad (26)$$



For  $\alpha = 1 - k\lambda$ , it is possible to solve for the moments iteratively. Starting with  $M_1(t) = 1$ , Eq. (26) gives  $M_{1-\lambda}(t) = (L_{1-\lambda} - 1)t + \text{const.}$ , where  $L_{1-\lambda} - 1$  is a positive constant. Continuing this process, one finds the asymptotic solution,

$$M_{1-k\lambda} \sim \frac{1}{k!} \prod_{j=1}^k (L_{1-j\lambda} - 1) t^k \quad (27)$$

for a discrete set of index values  $1 - k\lambda$ . This is the same time dependence as in Eq. (6) with  $\alpha = 1 - k\lambda$ . Invoking our smoothness postulate, wherein the form of  $M_\alpha$  for arbitrary  $\alpha$  interpolates smoothly between the moments defined on the discrete set, then Eq. (26) reproduces the temporal behavior of the moments from the scaling ansatz. It is important to note that for a diminishment process such as fragmentation, the *negative* moments of the cluster size distribution are the fundamental quantities that characterize the evolution of the cluster size distribution. They play the corresponding role of the positive moments of the cluster size distribution in growth phenomena such as aggregation.

#### 4.5 Shattering transition

An intriguing aspect of fragmentation processes is the possibility of a “shattering” transition, in which mass is “lost” to a phase of zero mass particles. This represents an inverse to the phenomenon of gelation, in which the mass of the “sol” phase is lost to the phase consisting of the infinite gel molecule. The potential existence of shattering depends on the mass dependence of the overall cluster breakup rate. If very small clusters break up sufficiently rapidly, then the entire fragmentation process is dominated by a cascade of very rapid breakup of smaller and smaller fragments. Mathematically, both gelation and shattering are signaled by the condition  $M_1 < 0$ . As discussed first by McGrady and Ziff<sup>[15]</sup> in the context of a particular fragmentation model, both shattering and breakdown of scaling were found to occur when  $\lambda < 0$ , *i.e.*, whenever the breakup rate favors the fragmentation of small clusters over large clusters. I now show generally that  $\lambda < 0$  is a necessary and sufficient condition for the existence of shattering.

To locate the shattering transition, consider Eq. (26) for  $\alpha = 1 + \epsilon$ , in the limit  $\epsilon \rightarrow 0$ ,

$$\dot{M}_1 = (L_{1+\epsilon} - 1) M_{\lambda+1+\epsilon}. \quad (28)$$

Since  $L_\alpha$  approaches 1 as  $\alpha \rightarrow 1$  (mass conservation),  $\dot{M}_1$  can be nonzero only if  $M_{\lambda+1+\epsilon}$  diverges as  $\epsilon \rightarrow 0$ . Without loss of generality, suppose that initially there is no particle with a mass larger than unity, so that will be no particle with a mass larger than unity at any later time. Thus,  $M_\alpha$  is non-decreasing as  $\alpha$  decreases, at any fixed time. This fact, together with  $M_1 < \infty$ , imply that  $M_\alpha$  can diverge only for  $\alpha < 1$ . Thus a necessary condition for shattering is  $\lambda < 0$ .

To show that  $\lambda < 0$  is also a sufficient condition for shattering, let us assume the converse and derive a contradiction. For  $\lambda < 0$ , Eq. (26) gives

$$\dot{M}_{1+|\lambda|} = (L_{1+|\lambda|} - 1) M_1. \quad (29)$$

Since it has been assumed that there is no shattering,  $M_1$  remains fixed, so that the right hand side is a negative constant. This implies that  $M_{1+|\lambda|}$  and hence  $c(x, t)$  would vanish at a finite time. On the other hand, from Eq. (1),  $c(x, t)$  decays exponentially

in time, or slower, for any value of  $x$ . This contradiction implies that a sufficient condition for shattering is  $\lambda > 0$ .

An important feature of shattering in linear fragmentation is that, from Eq. (29), mass loss starts right at  $t = 0$ . This is in contrast to the corresponding situation of the gelation transition in coagulation, where mass loss does not occur until a finite gel time has been reached.

## 5. Solutions to the Rate Equations for Collision-Induced Fragmentation

For collision-induced fragmentation, one anticipates that the cluster-size distribution will evolve into a scaling form in the long-time limit for a certain range of parameter values that characterize the reaction kernel. Thus using the scaling ansatz in Eq. (2), and assuming that the collision kernel has a homogeneity index  $\lambda$ , one arrives at the integro-differential equation for the scaling function

$$\begin{aligned} \omega[\xi\phi'(\xi) + 2\phi(\xi)] = & -\phi(\xi) \int_0^\infty K(\xi, \eta)\phi(\eta) d\eta \\ & + \int_0^\infty d\zeta \int_\xi^\infty K(\eta, \zeta)B(\xi|\eta, \zeta)\phi(\eta)\phi(\zeta) d\eta \end{aligned} \quad (30)$$

and for the time dependence one finds

$$\dot{s} s^{-\lambda} = \omega^{-1}, \quad (31)$$

with solution,

$$s(t) \sim \begin{cases} t^{\frac{1}{1-\lambda}}, & \text{for } \lambda > 1 \text{ and } t \rightarrow \infty, \\ e^{-\omega t}, & \text{for } \lambda = 1 \text{ and } t \rightarrow \infty, \\ (t_c - t)^{\frac{1}{\lambda-1}}, & \text{for } \lambda < 1 \text{ and } t < t_c. \end{cases} \quad (32)$$

From Eq. (32), a shattering transition now occurs at  $\lambda_s = 1$ . For  $\lambda < \lambda_s$ , the total number of clusters diverges in a finite time and mass is not conserved. Interestingly the critical value of  $\lambda$  is unity, corresponding to a situation where smaller particles are relatively less likely to collide. However, this inhibitory feature is compensated by the relatively rapid production of small clusters by two-body collisions. In linear fragmentation, there is no amplification coming from a collision process, so that shattering first appears only when the break-up of clusters of all sizes contribute equally to the fragmentation process, *i.e.*,  $\lambda_s = 0$ .

To understand the overall features of nonlinear fragmentation, let us now turn to the three splitting models discussed earlier. Because clusters split exactly in half, the mass  $x$  can be written in the discrete form  $x = 2^{-n}$  with integer  $n$ . This discretization greatly simplifies the analysis of the rate equations. The asymptotic solutions to the rate equations for the splitting models will be obtained in the regime where scaling holds. Numerically, this occurs when  $\lambda > \lambda_c$ , where  $\lambda_c$  is model dependent and less than one in general.

Before delving into mathematical details, it is worthwhile to summarize the basic results graphically. For the splitting models, the basic classifying feature is whether

reactions of small fragments with large fragments dominates over, or is dominated by, small-small reactions. (In any case, large-large reactions are irrelevant asymptotically.) In Models I and II, the larger of the two colliding fragments always splits. Therefore large-small reactions eventually dominate, as large clusters become effectively the most reactive as the fragment size distribution evolves. As I will show in the next section, this gives rise to a peaked fragment size distribution, as shown in the phase diagram for collision-induced fragmentation (Fig. 2(a)). On the other hand, in model III, small-small reactions eventually dominate. Consequently large clusters become "frozen out" of the fragmentation process at long times, leaving behind an appreciable "residue" of large clusters. These qualitative features of the fragment size distributions have strong parallels with the corresponding phase diagram of aggregation processes, as indicated in Fig. 2(b).

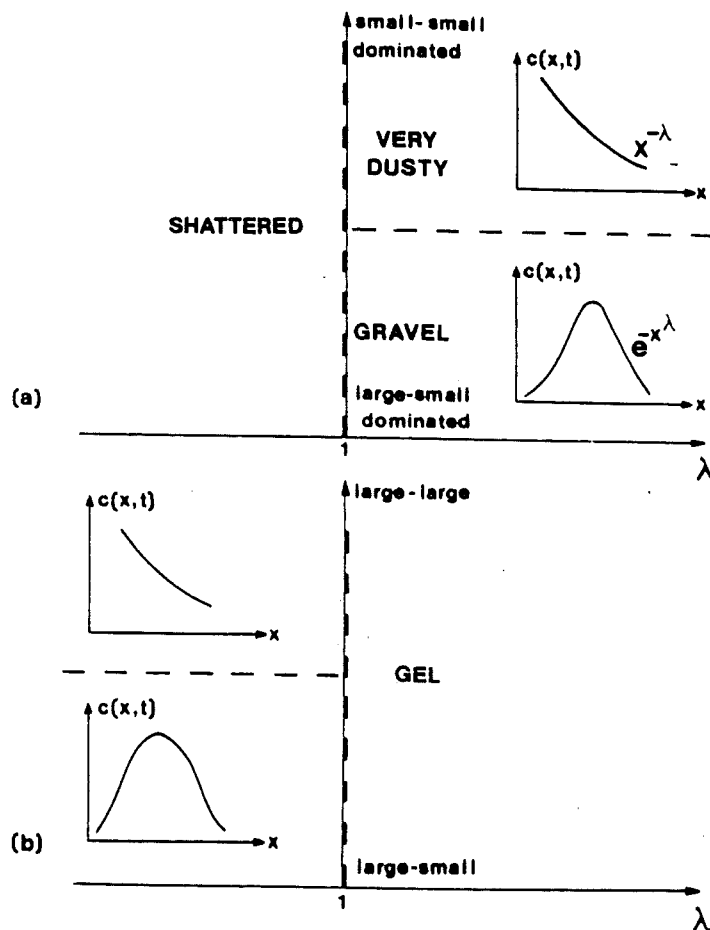


Figure 2 (a) Phase diagram for collision-induced fragmentation in the plane defined by  $\lambda$  and a second parameter which quantifies the relative importance of large-small versus small-small reactions. The shattered phase now occurs for  $\lambda < 1$ , while for  $\lambda \geq 1$ , there is a gravel phase when large-small reactions dominate, and a "very dusty" phase when small-small reactions dominate. For comparison, the phase diagram for a general aggregation processes is shown in (b). The mechanisms that lead to either a monotonic or non-monotonic cluster size distribution appear to be common to both aggregation and fragmentation.

Now I turn to a quantitative analysis of the behavior in the splitting models.

### 5.1 Model I: Both particles split upon collision

For concreteness, let us assume that the collision rate has the product form,  $K(x, y) = (xy)^{\lambda/2}$ . Then the rate equations for this model can be written in the form,

$$\frac{dc_n}{dt} = [-2^{-\lambda n/2} c_n + 2 \cdot 2^{-\lambda(n-1)/2} c_{n-1}] \left[ \sum_{j=0}^{\infty} 2^{-\lambda j/2} c_j \right]. \quad (33)$$

The first term accounts for the loss of  $2^{-n}$ -mers due to their collision with all other clusters in the system. Similarly, the second term accounts for the gain of  $2^{-n}$ -mers due to the collision of a  $2^{-(n-1)}$ -mer with other clusters. The additional factor of 2 arises because two  $2^{-n}$ -mers are produced from the breakup of a  $2^{-(n-1)}$ -mer.

Of some pedagogical interest is the case  $\lambda = 0$ , *i.e.*, the rate of fragmentation is mass independent. With the initial condition  $c_n(0) = M\delta_{n,0}$ , the exact solution, found by elementary methods, is

$$c_n(t) = \frac{1}{n!} \frac{t_c - t}{t_c^2} \left( 2 \ln \frac{t_c}{t_c - t} \right)^n, \quad (34)$$

where the shattering time  $t_c = 1/M$ . Mass is conserved for times  $t < t_c$ , but then shattering occurs in which the cluster concentrations of all finite sizes vanish.

For general  $\lambda$ , Model I can be recast as a linear fragmentation model by introducing a rescaled time  $t' = \int^t d\tau M_{\lambda/2}(\tau)$ . In this effective linear model, the parameters that characterize the breakup kernel are related to those of the corresponding non-linear model by  $\lambda' = \lambda/2$ ,  $b(x) = 2\delta(x - 1/2)$ . From our results for the linear model, one therefore concludes that the scaling is valid for  $\lambda > 0$ , but that a shattering transition of an intrinsically non-linear nature, as embodied, for example, by the solution given in Eq. (34), occurs for  $\lambda < 1$ .

In the scaling regime ( $\lambda > 0$ ), the mapping to the linear model, together with the results quoted in Eqs. (18) and (22) yields the asymptotic behaviors for the non-linear model,

$$\phi(x) \sim \begin{cases} \exp[-x^{\lambda/2}] / x^2, & (x \rightarrow \infty); \\ \exp[\frac{\lambda}{4 \ln 2} (\ln^2 x)], & (x \rightarrow 0), \end{cases} \quad (35a)$$

where  $x = 2^{-n}/s(t)$  and  $s(t)$  is determined by Eq. (32). From the scaling ansatz, this can be rewritten in term of  $c_n(t)$  as,

$$c_n(t) \sim \begin{cases} 2^{2n} \exp[-(2^{-n}/s(t))^{\lambda/2}], & (s(t) \ll 2^{-n}); \\ s(t)^{-2} \exp[\frac{\lambda}{4 \ln 2} (\ln^2 2^{-n}/s(t))], & (s(t) \gg 2^{-n}). \end{cases} \quad (35b)$$

In summary, the behavior of Model I closely resembles that of linear fragmentation with a small-size cutoff in the relative breakup rate.

### 5.2 Model II: Larger particle splits upon collision

For this model, let us take for the collision rate  $K(x, y) = x^\lambda$ , if  $x \geq y$ , and  $K(x, y) = y^\lambda$  otherwise. This represents the appropriate adaptation of the product

form for the collision rate in Model I for the case where only the larger cluster splits. The rate equations for this process are,

$$\begin{aligned}\frac{dc_n}{dt} &= -2^{-\lambda n} c_n \sum_{j=n}^{\infty} c_j + 2 \cdot 2^{-\lambda(n-1)} c_{n-1} \sum_{j=n-1}^{\infty} c_j, \\ &\equiv -\gamma^n c_n \sum_{j=n}^{\infty} c_j + 2\gamma^{n-1} c_{n-1} \sum_{j=n-1}^{\infty} c_j.\end{aligned}\quad (36)$$

In the long-time limit, one expects that  $c_n$  will decay to zero for any fixed  $n$ , while the total number of clusters increases indefinitely. Therefore the lower limits on both sums can be extended to 0, so that one arrives at rate equations very similar to Eq. (33) of Model I. Accordingly, let us introduce the rescaled time variable  $\tau = \int^t dt' M_0(t')$  which linearizes the rate equations (36) to the form

$$\frac{dc_n(\tau)}{d\tau} = -\gamma^n c_n(\tau) + 2\gamma^{n-1} c_{n-1}(\tau).\quad (37)$$

One can again appeal to the general results for linear fragmentation to infer that the behavior of Model II is qualitatively similar to that of Model I.

However, a more direct solution will be given, which also serves as a check of the scaling ansatz for Model II. Using elementary methods, the solution to Eq. (37) can be written as

$$c_n(\tau) = e^{-\gamma^n \tau} \left[ a_n - 2\gamma^{n-1} \int_{\tau}^{\infty} d\tau' e^{\gamma^n \tau'} c_{n-1}(\tau') \right],\quad (38a)$$

where

$$a_n = c_n(0) + 2\gamma^{n-1} \int_0^{\infty} d\tau' e^{\gamma^n \tau'} c_{n-1}(\tau')\quad (38b)$$

is positive. In this solution, one makes use of the boundary condition that all the cluster concentrations of finite mass are equal to zero at infinite time. Another reason for choosing the infinite limit for the integral is that the contribution of this integral becomes vanishingly small as  $\tau \rightarrow \infty$ , and this feature permits the asymptotic solution to be found. Since  $c_n(\tau)$  is non-negative for any  $n$ , Eq. (38a) provides the bound,

$$c_n(\tau) \leq a_n e^{-\gamma^n \tau}.\quad (39a)$$

Substituting this bound for  $c_{n-1}$  in Eq. (37) and performing the integral, one deduces that  $a_n e^{-\gamma^n \tau}$  also represents a lower bound for  $c_n(\tau)$ . Thus for  $\lambda > 0$  and large  $\tau$ ,

$$c_n(\tau) \sim a_n e^{-\gamma^n \tau}.\quad (39b)$$

The determination of the amplitude  $a_n$  cannot be performed by simply substituting Eq. (39b) into (35b), since Eq. (39b) is valid only for large  $\tau$ . However, one can proceed by Laplace transforming Eqs. (37) and (38b), thus reducing them to linear recursion relations. Defining the Laplace transform  $\tilde{c}_n(\sigma) = \int_0^{\infty} d\tau c_n(\tau) e^{-\sigma \tau}$ , Eq. (37) becomes

$$\tilde{c}_n(\sigma) = \frac{c_n(0) + 2\gamma^{n-1} \tilde{c}_{n-1}(\sigma)}{\sigma + \gamma^n},\quad (40a)$$

while the recursion relation for  $a_n$  takes the form,

$$a_n = c_n(0) + 2 \cdot \gamma^{n-1} \tilde{c}_{n-1}(-\gamma^n). \quad (40b)$$

Upon iterating Eq. (37a), the dominant contribution to  $\tilde{c}_{n-1}(-\gamma^n)$ , is proportional to  $(2/\gamma)^{n-1}$  as  $n \rightarrow \infty$ , for  $\lambda > 0$  and for a monomer-only initial condition. Consequently Eq. (40b) gives  $a_n \propto 2^n$ , and this then yields the asymptotic solution,

$$c_n(t) \sim 2^{2n} \exp[-2^{-\lambda n} \tau(t)], \quad (\tau \rightarrow \infty). \quad (41)$$

Up to an overall constant factor this asymptotic solution should be independent of the initial condition.

To express  $c_n$  explicitly as a function of the time, one first needs to determine the time dependence of  $\tau$ . By invoking scaling, one deduces that  $M_0(t) \sim 1/s(t)$ . Consequently,  $\tau = \int^t M_0(t') dt'$  can be identified with  $s(t)^{-\lambda}$ . As a result,  $c_n(t)$  can be expressed in the scaling form in the long-time limit,

$$c_n(t) \sim 2^{2n} \exp[-(2^{-n}/s(t))^\lambda]. \quad (42a)$$

In the scaling regime ( $\lambda > 0$ ), Eq. (42a) can be recast in the scaling form

$$\phi(x) \sim \exp[-x^\lambda] / x^2, \quad (x \rightarrow \infty), \quad (42b)$$

where  $x = 2^{-n}/s(t)$  and  $s(t)$  is determined by Eq. (32). Since Eq. (42b) is obtained independent of the scaling assumption, the validity of the scaling ansatz for  $\lambda > 0$  has thus been demonstrated.

### 5.3 Model III: Smaller particle splits upon collision

In close analogy with Model II, let us now take for the collision rate  $K(x, y) = x^\lambda$ , if  $x \leq y$ , and  $K(x, y) = y^\lambda$  otherwise. The rate equations for this process are,

$$\frac{dc_n(t)}{dt} = -\gamma^n c_n \sum_{j=0}^n c_j + 2\gamma^{n-1} c_{n-1} \sum_{j=0}^{n-1} c_j. \quad (43)$$

To obtain the asymptotic behavior, one first notes that the rate equation for  $c_0(t)$  may be easily solved to yield the long-time solution

$$c_0(t) \sim 1/t. \quad (44)$$

Let us now show that  $c_n$  has the same time dependence as  $c_0$  for all  $n$ . First, define the new variables,

$$R_n(\tau) = c_n(t)/c_0(t), \quad (45)$$

$$\tau = \int^t dt' c_0(t') \sim \ln t.$$

In terms of these rescaled variables, Eq. (43) becomes,

$$\frac{dR_n(\tau)}{d\tau} = -\gamma^n [R_n^2(\tau) - A_n(\tau)R_n(\tau) - B_n(\tau)] \quad n > 0 \quad (46)$$

where

$$\begin{aligned}
 A_n(\tau) &= \gamma^{-n} - \sum_{j=0}^{n-1} R_j(\tau) \\
 B_n(\tau) &= 2\gamma^{-1} R_{n-1}(\tau) \sum_{j=0}^{n-1} R_j(\tau).
 \end{aligned}
 \tag{47}$$

By noticing that  $A_n(\tau)$  and  $B_n(\tau)$  involve only the  $R_j(\tau)$ 's with  $j < n$ , it is not difficult to show inductively that the ratio  $R_n(\tau)$  converges to a positive constant  $r_n$ , for any  $n$ , in the long-time limit. Thus one concludes that

$$c_n(t) \sim r_n/t. \tag{48}$$

From a detailed analysis of the recursion relations that determine  $r_n$ , one ultimately finds the asymptotic solution

$$c_n(t) \sim \begin{cases} 2^{n\lambda}/t, & \lambda \geq 1, \\ 2^{n(1+\lambda)/2}/t, & 1 > \lambda \geq -1, \\ 2^{n(1+\lambda)}/t, & -1 > \lambda. \end{cases}
 \tag{49}$$

A salient feature of this solution is that the cluster size distribution at fixed time has a power-law dependence of the mass. This gives rise to the anomalously large residue of large clusters which persists at long times, as illustrated in Fig. 2. Notice also that only the first line can be expressed as a function of the scaling variable  $2^{-n}/s(t)$ . Thus scaling evidently breaks down for  $\lambda < 1$ .

## 6. Summary and Discussion

A general treatment of linear and collision-induced fragmentation processes has been given within the framework of the rate equations. This is an approach of a mean-field character, as fluctuations in the spatial positions of the clusters, as well the variability in cluster shape are ignored. In the rate equations for linear fragmentation, the microscopic details of the breakup events are accounted for by two kernels: an overall breakup rate which specifies the rate at which a fragment of a given mass breaks, and the relative breakup rate, which gives the size distribution of products from a single breakup event. Within the scaling regime, the homogeneity index  $\lambda$  of the overall breakup rate is the crucial parameter which characterizes the properties of the cluster size distribution. For linear fragmentation models, the asymptotic scaling solutions to the rate equations were obtained both in the large and small mass limits. The conditions for the existence of scaling solutions and also the basic features of the shattering transition were also discussed.

To gain some insight into the behavior that can occur when non-linear effects play a role in particle breakup, a class of collision-induced fragmentation models was considered. In order to treat models which exhibit the essential non-linear nature of collision-induced breakup, yet are simple enough to analyze in detail, three types of "splitting" models were introduced, in which a fragmenting cluster always breaks into two equal-sized pieces. In Model I, both colliding fragments split in two upon collision, while in Models II and III, only the larger or only the smaller of the two colliding fragment splits in two, respectively. For these models, scaling is valid for

different ranges of  $\lambda$ . Model III is rather unique in that large clusters are "frozen out" of the fragmentation process at long time. This leads to a monotonic fragment size distribution, with a power law tail at large masses, while the distribution in Models I and II is non-monotonic and decays quasi-exponentially for large mass. Moreover, in Model III the concentration of fragments of any finite size decays as a power law in time, and in Models I and II it decays exponentially.

While the rate equations approach provides a useful and comprehensive account of a wide range of fragmentation phenomena, there are many interesting questions of potential experimental relevance that are worth addressing. Most importantly, it is necessary to develop approximations which can take inhomogeneities of various types into account. While the assumption of perfect mixing is probably appropriate for ball milling types of comminution processes, it is clearly inadequate in many geophysical situations, for example, where fragments remain in fixed spatial positions throughout the breakup process. Attempts to account for this type of spatial inhomogeneity have been attempted, but primarily at a qualitative level. It is also clear that the rate of fragmentation processes should generally depend on the cluster shape. Whether this shape dependence can be accounted for by averaging over all possible fragment shapes has yet to be understood. Finally, in many fragmentation processes there are various non-linear and non-local effects. When breakup is driven by high pressures, there can be a transfer of stress across many fragments. When fragments possess considerable kinetic energy, non-linear effects, induced by collisions may play a substantial role. The understanding of the kinetics in these types of systems should pose rich areas for new research.

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