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Fragmentation of particles with more than one degree of freedom

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A class of fragmentation models is introduced in which the particles have more than one degree of freedom. The class of models is discussed in general terms, and analytical results are presented for a particular case of particles with two degrees of freedom. The models are compared analytically and numerically with previously solved one-dimensional models. In addition, we present exact solutions to the "standard" fragmentation equation when the fragmentation rate $F(x,y)=xy(x+y)^{\alpha}$ for both $\alpha=+1$ and -1. The scaling form of these models is discussed.

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I. INTRODUCTION

Fragmentation is a common phenomenon that occurs in a diverse set of physical systems. These include polymer degradation [1–3], rock crushing and grinding (comminution) [4], droplet breakup [5], and fiber length reduction [6]. This wide variety of applications has stimulated many theoretical attempts to find the evolution in time of the particle size distribution as a function of the initial conditions and the fragmentation rates. These studies have led to solutions of particular problems using either a combinatorial or statistical approach, or by solving the kinetic equation directly. More recently this phenomenon has been addressed using scaling theory, and a dynamical phase transition (the "shattering transition") has been observed.

A number of authors have obtained exact solutions to the fragmentation equation; Ziff and McGrady [3,7–9] found solutions for the binary breaking model with a number of different fragmentation rules, and a general scaling theory was constructed which incorporated these models. In [10], a number of simplified models of degradation were solved, including a model in which each bond breaks in the center with one of two unequal fragmentation rates. The fragmentation rate of a particular bond was determined by its length. The dependence of the fragmentation rate on the length of the chain was considered in [1,2] and applied to the acid hydrolysis of dextran [1]. In particular, the cases of random scission, of a Gaussian probability of scission, and of scission at the center of the chain were considered [2]. A model in which each bond had a different probability of breaking was examined in [11]. This was motivated by a desire to understand the kinetics of cross linked structures, as was the work in [12]. Other workers [13] have generalized the standard mean field coagulation equation to include the effects of fragmentation and have obtained values for the critical exponents of the resulting steady state size distribution. These were compared with the exponents obtained from numerical simulations of this system in dimensions 1, 2, and 3; the upper critical dimension was found to be less than 1.

The general form of the multiple fragmentation equation is given (see, for instance, [9]) by

$$\frac{\partial c(x,t)}{\partial t}=-a(x)c(x,t)+\int_x^{\infty}a(y)b(x|y)c(y,t)dy \;, \qquad (1)$$

where $a(x)$ gives the rate of fragmentation of particles of size x, $b(x|y)$ is the average number of particles of size x produced when a particle of size y breaks up, and $c(x,t)$ is the concentration of particles of size x at time t. To conserve the total mass of the particles we have that

$$\int_0^y xb(x|y)dx=y \;, \qquad (2)$$

and the average number of particles produced by the fragmentation of a particle of size y is given by

$$\langle N(y)\rangle=\int_0^y b(x|y)dx \;. \qquad (3)$$

Restrictions are placed on the possible choices of $b(x|y)$ by Eqs. (2) and (3), given that physically we require $\langle N(y)\rangle \geq 2$.

Most analytical studies have concentrated on the special case of binary fragmentation where two particles are produced per fragmentation event. In this case Eqs. (1)–(3) can be written, in terms of a single function $F(x,y)$, as follows:

$$a(x)=\int_0^x F(x-y,y)dy \;, \qquad (4)$$

where to ensure there are two fragments per event,

$$b(x|y)=\frac{2F(x,y-x)}{a(y)} \;, \qquad (5)$$

and the fragmentation equation becomes

$$\frac{\partial c(x,t)}{\partial t}=-c(x,t)\int_0^x F(y,x-y)dy +2\int_x^{\infty}F(x,y-x)c(y,t)dy \;. \qquad (6)$$

$F(x,y)$ gives the rate at which particles of size $x+y$ break up into particles of size x and y. These equations

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have been solved (see [3,7–9]) for $F=1$, xy, and $(x+y)^\alpha$. A scaling theory was constructed (originally for models of aggregation [14]) by writing the particle size distribution in the limit $x\to 0$ and $t\to\infty$ as

$$c(x,t)\approx t^w x^\tau \Phi(xt^z) , \tag{7}$$

where $\Phi(\xi)\to 1$ as $\xi\to 0$ and $\Phi(\xi)\to 0$ as $\xi\to\infty$. The exponents τ, w, and z are related by

$$w=z(\tau+2) \tag{8}$$

due to mass conservation. The dynamical scaling exponents for some different kernels is given in Table I. Providing that the scaling function $\Phi(\xi)$ is well behaved as $\xi\to 0$, all initial conditions will yield these forms in the scaling regime.

For some choices of the fragmentation rate a shattering transition is observed. In particular, when the rate increases sufficiently fast with decreasing particle size, a cascading breakup occurs and a finite amount of mass is transferred to particles with zero mass [8,15,16]. This is analogous to the sol-gel transition in coagulating systems and is accompanied by a violation of dynamical scaling. The borderline of this phenomenon is signified by an exponential growth with time of the number of particles [3]. For kernels $F(x,y)=(x+y)^\alpha$, the borderline case is $\alpha=-1$; for $\alpha>-1$ dynamical scaling is obeyed; for $\alpha<-1$ a shattering transition is seen.

In this paper we generalize the fragmentation equation and the associated constraints to particles with more than one degree of freedom. In real fragmentation processes the particles have both size and shape. A particle may be chosen for fragmentation at a rate that is a function of its area or volume, but the way in which it is fragmented will be, in general, dependent on its precise dimensions. If two particles have the same area but one is long and thin and the other is almost square, they may be equally likely to fragment because they have the same area, but the long thin particle is much more likely to split down its long side, whereas the square particle is equally likely to split down either side. In previous studies all these properties were represented by a single parameter.

TABLE I. The dynamical scaling exponents for the kernels 1, xy, and $(x+y)^\alpha$.

Exponent \ $F(x,y)$	1	xy	$(x+y)^\alpha$ ($\alpha>-1$)
z	1	$\frac{1}{3}$	$1/(1+\alpha)$
τ	0	1	0

We also consider two problems of binary fragmentation in which the particles are characterized by a single parameter. In particular, we consider $F(x,y)=xy(x+y)^\alpha$ for both $\alpha+1$ and -1. This was motivated by a desire to see which universality class models of this type fell into, they could reasonably be assumed to be in the same class as xy or $(x+y)^\alpha$. We obtain, for the first time, exact solutions for the particle size distributions in these models and discuss both the dynamic scaling and the existence of a shattering transition for these systems.

II. PARTICLES WITH TWO OR MORE FREE PARAMETERS

Equations (1)–(3) can be generalized to the case of multidimensional particles by introducing $a(L_1,L_2,\ldots,L_d)$, the rate at which particles, characterized by d variables $L_1,L_2,\ldots,L_d$ are chosen for fragmentation. Keeping the same notation as in the Introduction, let $b(L_1,L_2,\ldots,L_d|L_1',L_2',\ldots,L_d')$ denote the average number of particles with $L_1,L_2,\ldots,L_d$ produced from a particle $L_1',L_2',\ldots,L_d'$. As before, the average number of particles produced is given by

$$\langle N(L_1,L_2,\ldots,L_d)\rangle=\int_0^{L_1}dL_1'\cdots\int_0^{L_d}dL_d' b(L_1',L_2',\ldots,L_d'|L_1,L_2,\ldots,L_d) , \tag{9}$$

and the conservation of mass requires that

$$\int_0^{L_1}dL_1'\cdots\int_0^{L_d}dL_d' L_1'L_2'\cdots L_d' b(L_1',L_2',\ldots,L_d'|L_1,L_2,\ldots,L_d)=L_1L_2\cdots L_d . \tag{10}$$

The fragmentation equation itself becomes

$$\begin{aligned}\frac{\partial f(L_1,L_2,\ldots,L_d,t)}{\partial t}=&-a(L_1,L_2,\ldots,L_d)f(L_1,L_2,\ldots,L_d,t)\\&+\int_{L_1}^{\infty}dL_1'\cdots\int_{L_d}^{\infty}dL_d' a(L_1',L_2',\ldots,L_d')b(L_1,L_2,\ldots,L_d|L_1',L_2',\ldots,L_d')\\&\times f(L_1',L_2',\ldots,L_d',t) .\end{aligned} \tag{11}$$

Equations (9)–(11) form a complete set of equations, which define the fragmentation process given rates a and b and an initial condition. The functions a and b must be chosen to make the equations physically meaningful and b must be chosen to satisfy (9) and (10), given, as before, the physical constraint that $\langle N\rangle\geq 2$.

If we consider breaking particles characterized by two parameters into two pieces, so that the rate of choosing a particle, $a(L_1,L_2),=L_1L_2$ and

$$b(L_1',L_2'|L_1,L_2)=\{L_1\delta(L_1-L_1') +L_2\delta(L_2-L_2')\}/a(L_1,L_2) , \quad (12)$$

then this gives a fragmentation equation of

$$\frac{\partial f(L_1,L_2,t)}{\partial t}=-L_1L_2f(L_1,L_2,t) +L_2\int_{L_1}^{\infty}dL_1'f(L_1',L_2,t) +L_1\int_{L_2}^{\infty}dL_2'f(L_1,L_2',t) . \quad (13)$$

This process chooses particles for fragmenting with a probability proportional to their "area" and creates two products by splitting them down one of their two sides. The side to be cut is chosen with a probability proportional to its length; the other side is unaffected. These particles may be viewed as rectangles, which undergo splitting down lines parallel to their sides.

We can obtain an equation for the moments $M_{nm}(t)$, defined by

$$M_{nm}(t)=\int_0^{\infty}dL_1\int_0^{\infty}dL_2L_1^nL_2^mf(L_1,L_2,t) , \quad (14)$$

by multiplying by $L_1^nL_2^m$ and integrating with respect to L_1 and L_2. This yields

$$\frac{\partial M_{nm}(t)}{\partial t}=\left[\frac{1}{(n+1)}+\frac{1}{(m+1)}-1\right]M_{n+1m+1}(t) . \quad (15)$$

Solving this set of equations analytically for the particle size distribution is difficult; instead we present some numerical simulations of this system in the next section (see Fig. 1).

We will now proceed to discuss another of the many possible models in detail to illustrate the difference between this approach and previous studies where one-dimensional particles have been considered. We consider the case of a two-dimensional particle with $a=1$ and $b(L_1',L_2'|L_1,L_2)=4/L_1L_2$. It is easy to verify that this choice of a and b is consistent with (9) and (10) and that it corresponds to breaking a particle into 4 with a fragmentation rate that is inversely proportional to the product of the two parameters associated with that particle. From now on we will refer to this product as the area of the particle. These fragmentation rules mean that every particle is equally likely to fragment irrespective of its area and is the analog of choosing $F(x,y)=1/(x+y)$ for a particle with one free parameter. The average area is

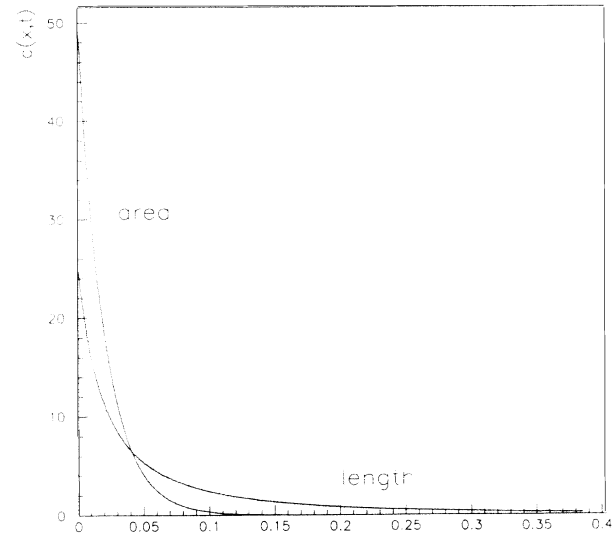

FIG. 1. Area and length probability distributions at the same moment in time for a system in which a particle is chosen for fragmentation with a rate proportional to its area, and then each side is equally likely to be split [see Eq. (13)].

conserved, whereas in the one free parameter system it is the average length that is the conserved quantity. The fragmentation equation (11) becomes

$$\frac{\partial f(L_1,L_2,t)}{\partial t}=-f(L_1,L_2,t) +4\int_{L_1}^{\infty}\frac{dL_1'}{L_1'}\int_{L_2}^{\infty}\frac{dL_2'}{L_2'}f(L_1',L_2',t) . \quad (16)$$

This equation can be solved by rewriting it in terms of the moments of the probability distribution $M_{nm}(t)$ [defined in (14)] to reveal

$$\frac{\partial M_{nm}(t)}{\partial t}=\left[\frac{4}{(n+1)(m+1)}-1\right]M_{nm}(t) , \quad (17)$$

which can be solved to give

$$M_{nm}(t)=l_1^nl_2^m\exp\left\{-t\left[1-\frac{4}{(n+1)(m+1)}\right]\right\} , \quad (18)$$

where the particle at $t=0$ is of size $l_1\times l_2$. Notice that the average area $M_{11}(t)$ is time independent. It is simple to rearrange this expression to give

$$M_{nm}(t)=l_1^nl_2^me^{-t}+l_1^nl_2^m\sum_{j=1}^{\infty}\frac{(-t)^j}{j!}\sum_{s=1}^{j}\binom{j}{s}\left[\frac{-4}{(n+1)(m+1)}\right]^s . \quad (19)$$

Reversing the order of the summations in the second term of (19), using

$$\frac{1}{(n+1)^s}=\frac{1}{(s-1)!}\frac{(-1)^{s-1}}{l_1^{n+1}}\int_0^{l_1}\left[\ln\left[\frac{l_1}{y_1}\right]\right]^{s-1}y_1^ndy_1 \quad (20)$$

and a similar expression for $(m+1)^{-S}$ involving l_2 and y_2 and then comparing the result with the definition of $M_{nm}(t)$ in (14), gives the probability distribution as

$$f(y_1,y_2,t)=e^{-t}\delta(y_1-l_1)\delta(y_2-l_2)+\frac{4te^{-t}}{l_1l_2}\sum_{r=0}^{\infty}\frac{(4t)^r}{(r!)^2(r+1)!}\left[\ln\left[\frac{l_1}{y_1}\right]\ln\left[\frac{l_2}{y_2}\right]\right]^r . \tag{21}$$

The time dependent probability distribution for the area, $c(A,t)$, can be obtained via

$$c(A,t)=\int_0^\infty dL_1\int_0^\infty dL_2\delta(A-L_1L_2)f(L_1L_2,t) \tag{22}$$

to give

$$c(A,t)=\delta(A-l_1l_2)e^{-t}+\frac{4te^{-t}}{l_1l_2}\sum_{r=0}^{\infty}\frac{(4t)^r}{(r+1)!(2r+1)!}\left[\ln\left[\frac{l_1l_2}{A}\right]\right]^{2r+1} . \tag{23}$$

This can be compared with the result for a one-dimensional particle where $F(x,y)$, the rate at which a particle of size $x+y$ is split into two particles of size x and y, is equal to $1/(x+y)$. The solution [7] for the size distribution is

$$f(x,t)=\delta(x-l)e^{-t}+\frac{2te^{-t}}{l}\sum_{r=0}^{\infty}\frac{(2t)^r}{r!(r+1)!}\left[\ln\left[\frac{l}{x}\right]\right]^r , \tag{24}$$

where l is the length of the particle at $t=0$. This result differs from that from the two-parameter model; the summation in the second term has a number of differences. If one were to expand both expressions for small time the difference would become apparent at second order, the order at which the logarithmic divergence appears. In the two-dimensional problem, as in one dimension, this forms the borderline case for the shattering transition. Kernels which diverge less quickly as the size of the particle gets smaller do not exhibit the transition.

III. NUMERICAL RESULTS

We have performed simulations of a number of different systems in which the particles are characterized by two parameters, and there were two products per fragmentation event. We present the results of some of these simulations here, in particular those with a fragmentation rate of 1 and hence where the probability of choosing a particular particle for fragmentation is proportional to its area. Once a particle is chosen for fragmentation, one side is split and the other side is left unchanged. In Fig. 1 there is a graph of the probability distribution of the area (product of the two sides) and the length of the two sides when each side had an equal (0.5) chance of being split. This is the problem described by Eqs. (12)–(15). The probability distributions for the two sides are identical and the area and side distributions are plotted at the same time. Initially, the system contained one particle with $l_1=l_2=1$. The side distribution can be obtained from $f(L_1,L_2,t)$ by integrating over L_1 or L_2. In Fig. 2 there is the side probability distribution for this system and that of two other systems; one when the longest side is always chosen for fragmentation and one when one side is chosen with probability 0.6. The equations for the latter two systems can be obtained by substituting $a(L_1,L_2)=L_1L_2$ and

$$b(L_1',L_2'|L_1,L_2)=2\{L_1\theta(L_2-L_1)\delta(L_1-L_1')+L_2\theta(L_1-L_2)\delta(L_2-L_2')\}/a(L_1,L_2) , \tag{25}$$

and

$$b(L_1',L_2'|L_1,L_2)=\{6L_1\delta(L_1-L_1') +4L_2\delta(L_2-L_2')\}/5a(L_1,L_2) , \tag{26}$$

respectively, into Eq. (11). [In Eq. (25), $\theta(L_1-L_2)$ is the Heaviside step function.] Obviously, these three systems have the same area probability distribution for all time and, as can be seen from the numerical simulations, different length probability distributions.

IV. '$1-d$' SOLUTIONS

In this section two solutions are presented to the one-parameter fragmentation model in which two products are obtained per fragmentation event. These are obtained

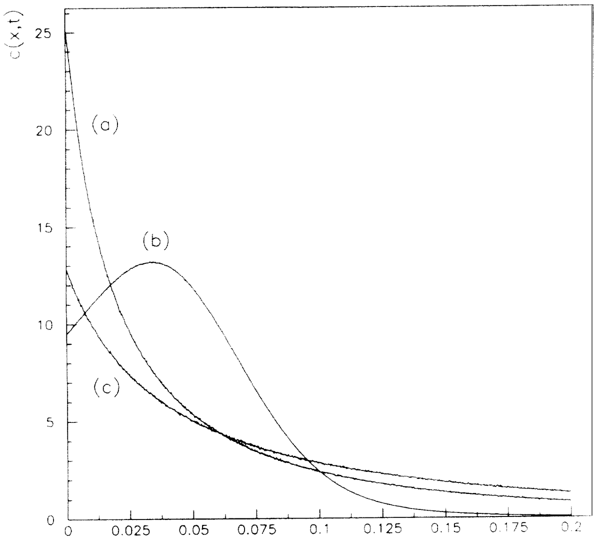

FIG. 2. Length probability distributions at equal times for systems in which the particle is chosen for fragmentation with a rate proportional to its area, and a particular side is chosen for splitting (a) with probability 0.5, (b) if it is the larger side, and (c) with probability 0.6.

for the case of the kernel $F(x,y)=xy(x+y)^{\alpha}$ for both $\alpha=+1$ and -1. When the kernel takes this form, the moment equation becomes

$$\frac{\partial M_n(t)}{\partial t}=\left[\frac{2}{(n+2)(n+3)}-\frac{1}{6}\right]M_{n+\alpha+3}(t) . \quad (27)$$

The explicit time dependent solution for the particle size distribution for this general problem would be of interest for various experimental systems, though the solution for $\alpha=0$ has been obtained elsewhere [3,7]. For $\alpha=-3$ the zeroth moment grows exponentially with time, which is the signature of the crossover to the singular, shattering behavior for $\alpha<-3$.

For a monodisperse initial condition, the nth moment is given by

$$M_n(t)=l^n\,{}_2F_2\left[\frac{n-1}{\alpha+3},\frac{n+6}{\alpha+3};\frac{n+2}{\alpha+3},\frac{n+3}{\alpha+3};\frac{-tl^{\alpha+3}}{6}\right], \quad (28)$$

where ${}_2F_2(a,b;c,d;x)$ is the generalized hypergeometric function.

While the explicit time dependent particle size distribution is difficult to obtain from Eq. (28) for general α, the solutions for $\alpha=+1$ and -1 are relatively simple; Charlesby's method [17] can be used for $\alpha=+1$ to obtain

$$c(y,t)=\delta(y-l)e^{-tl^4/6}+2tly\int_y^l e^{-tz^4/6}dz . \quad (29)$$

This solution yields exponents $z=\frac{1}{4}$ and $\tau=1$, which do not coincide with values obtained for any model solved previously. For $F(x,y)=xy/(x+y)$ we can use the same method to obtain

$$c(y,t)=\delta(y-l)e^{-tl^2/6}+\frac{2ty}{l}\int_y^l e^{-tx^2/6}dx + \frac{5}{6}t^2y^3l\left\{\int_y^l dw\left[\frac{1}{w^3}-\frac{w}{y^2l^2}\right]\int_w^l e^{-tz^2/6}dz\right\}, \quad (30)$$

which gives a scaling form of

$$c(y,t)=t^{3/2}y\Phi(\xi) \quad (31)$$

with $\xi=yt^{1/2}$ and

$$\Phi(\xi)=\frac{5l}{12}\int_{\xi}^{\infty}\left[1-\frac{\xi^2}{u^2}\right]\exp\left[\frac{-u^2}{6}\right]du . \quad (32)$$

This yields exponents $z=\frac{1}{2}$ and $\tau=1$, which do not fall into any of the universality classes identified previously. This solution is unusual in that the exact solution and the scaling form are significantly different from one another. Consequently, the explicit time dependence of the size distribution cannot be recovered from the scaling form, as has been done for some simpler models [9]. These two results, and that for $F(x,y)=xy$, suggest that for kernels $F(x,y)=xy(x+y)^{\alpha}$ the exponents are $\tau=1$ and $z=1/(3+\alpha)$.

V. CONCLUSIONS

We have introduced a class of fragmentation models in which the size and shape of the particles are characterized by more than one variable. A model where the particles are characterized by two parameters has been solved exactly and a number of different models have been examined numerically. We found that the introduction of more than one parameter to characterize the size and shape of a particle can have a significant effect on the kinetics of the fragmentation process.

A set of fragmentation processes in which the kernel is given by $F(x,y)=xy(x+y)^{\alpha}$ was introduced and solved explicitly for $\alpha=+1$ and -1. For $\alpha=-1$, the full solution was significantly different from the scaling solution. We conjectured that for kernels of this form the dynamical scaling exponents are given by $\tau=1$ and $z=1/(3+\alpha)$.

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