"Shattering" Transition in Fragmentation

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For particles undergoing fragmentation with a rate $a(y) \sim y^{\beta+1}$, where y is the particle size, a cascading process occurs when $\beta < 1$ in which smaller particles break up at increasingly rapid rates, resulting in mass being lost to a phase of "zero"-size particles. The cascading of the breakup rate, or "shattering," produces a fractal dust, similar to a Cantor dust, with dimension $0 < D_f < 1$, and is analogous to, but opposite from, the process of gelation found in aggregating systems.

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Particle fragmentation occurs in many important physical processes, including polymer degradation,[1-4] grinding or crushing,[5-7] and droplet breakup.[8,9] Because of its wide applicability there has been considerable interest in predicting theoretically the evolution of the particle-size distribution during fragmentation. Explicit distributions have been found through statistical and combinatorial arguments[10-12], as well as through a kinetic-equation approach.[13-15] In most of this work solutions have been found for only the case where the breakup rate is independent of the size of the object and all fragments are produced with equal probability.

In many physical situations, however, the breakup rate is not independent of particle size or other properties.[2,3] Here we report new solutions to the fragmentation equation for classes of breakup rates which depend on particle size. We find that when the breakup rate increases sufficiently fast as the size of the particles decreases, a cascading of the breakup occurs such that mass is lost to zero-size particles. This cascading process is analogous to the gelation transition which occurs in coagulating systems. We call this cascade "shattering" to reflect the rapid production of very small particles. We also find that the number of particles that are formed during a breakup event does not influence the shattering transition. These results suggest that in general (not just for the class of models we considered) the rate of comminution of small particles, rather than the number of fragments produced or their size distribution, determines whether shattering occurs.

The evolution of the particle-size distribution for a continuous system undergoing fragmentation is described by[6,16,17]:

$$\partial c(x,t)/\partial t = -a(x)c(x,t) + \int_x^\infty a(y)b(x\,|\,y)c(y,t)\,dy. \tag{1}$$

Here $c(x,t)$ is the concentration of particles of size (or length) x. The first term on the right-hand side represents the loss of particles of size x because of their breaking up into smaller particles, where $a(x)$ is the rate at which particles of size x break. The second term represents the increase of particles size x because of the breakup of larger ones, where $b(x\,|\,y)$ is the distribution of products from a particle of size y breaking.

Since $b(x\,|\,y)$ is the rate of production of particles of size x from those of size y it must be normalized so that mass is conserved: $\int_0^y xb(x\,|\,y)dx = y$. The expected number of particles is given by $\bar{N}(y) = \int_0^y b(x\,|\,y)dx$. For the case of binary breakup $b(x\,|\,y)$ is symmetric, $b(x\,|\,y) = b(y-x\,|\,y)$, and $\bar{N} = 2$. For $\bar{N} > 2$, $b(x\,|\,y)$ is not symmetric but satisfies the following condition which expresses the requirement that the breakup process is a single event with no rearrangement of the mass allowed:

$$\int_0^z xb(x\,|\,y)dx \geq \int_{y-z}^y (y-x)b(x\,|\,y)dx, \tag{2}$$

where $z < y/2$. This inequality states that when a break occurs such that a particle $x \geq y/2$ is formed, the mass contained within the smaller fragments $(y-x)$ must contribute to particles whose size is less than or equal to the total mass of the fragments smaller than $(y-x)$. A sufficient condition for (2) to be satisfied is that $b(x\,|\,y)$ is a monotonically decreasing function of x. If the system is limited to binary breakup, then the equality holds in (2) since one small particle $(< y/2)$ will be formed for each larger one $(> y/2)$.

We consider the case where $a(y) = y^{\beta+1}$, and where the distribution of product fragments has the form $b(x\,|\,y) = f(y)x^\nu$. The normalization condition implies $f(y) = (\nu+2)/y^{\nu+1}, \nu > -2$. This $b(x\,|\,y)$ satisfies (2) for $\nu \leq 0$ and is symmetric for $\nu = 0$ (which is the binary-breakup case). For $\nu < 0$, the expected number of particles produced per breakup event is > 2. For $-1 < \nu < 0$ it follows that $\bar{N} = (\nu+2)/(\nu+1)$, independent of y. If $-2 < \nu \leq -1$ an infinite number of particles is expected from each fragmentation event as $\bar{N} = \infty$, yet mass conservation is still satisfied.

Substitution of the above expressions for $a(x)$ and $b(x|y)$ into (1) gives

$$\partial c(x,t)/\partial t = -x^{\beta+1}c(x,t) + (\nu+2)\int_x^\infty y^{\beta-\nu}x^\nu c(y,t)dy. \tag{3}$$

By application of the transformations $z = x^{(\nu+2)/2}$, $g(z,t) = c(x,t)/x^\nu$, (3) is reduced to the equation for binary fragmentation:

$$\partial g(z,t)/\partial t = -z^{\alpha+1}g(z,t) + 2\int_z^\infty w^\alpha g(w,t)dw, \tag{4}$$

with $\alpha = (2\beta-\nu)/(\nu+2)$. Equation (4) has been studied extensively in the past (although mainly for $\alpha = 0$).[10-12,18] If $g(z,t,\alpha)$ is the solution of (4) then the solution of (3) will be given by

$$c(x,t,\beta,\nu) = x^\nu g(x^{(\nu+2)/2}, t, (2\beta-\nu)/(\nu+2))$$

with the initial conditions transforming similarly. For a monodisperse initial condition, $c(x,0) = \delta(x-l)$, the solutions transform as

$$c(x,t,\beta,\nu,l) = (\nu+2)/2l^{-\nu/2}x^\nu g(x^{(\nu+2)/2}, t, (2\beta-\nu)/(\nu+2), l^{(\nu+2)/2}),$$

where $g(z,t,\alpha,L)$ is the solution to (4) for $g(z,0) = \delta(x-L)$. Thus this class of rate kernels for multiple fragmentation may be transformed into a binary fragmentation model.

For a monodisperse, initial condition (3) may be solved by substitution of the series expansion:

$$c(x,t) = \exp(-tl^{\beta+1})\left[\delta(x-l) + \sum_{k=1}^\infty B_k \frac{t^k}{k!}\right]. \tag{5}$$

Equating like powers of t, and solving recursively for $B_k(x)$, we find

$$\begin{aligned} c(x,t) &= \exp(-tl^{\beta+1})\left[\delta(x-l) + (\nu+2)l^{\beta-\nu}x^t\sum_1^\infty \frac{t^k(l^{\beta+1}-x^{\beta+1})^{k-1}[1+(\nu+2)/(\beta+1)]^{k-1}}{(k-1)!k!}\right] \\ &= \exp(-tl^{\beta+1})\left[\delta(x-l) + (\nu+2)tl^{\beta-\nu}x^\nu \mathcal{M}((\beta+\nu+3)/(\beta+1), 2, (l^{\beta+1}-x^{\beta+1})t)\right], \end{aligned} \tag{6}$$

where $\mathcal{M}(a,b,z)$ is Kummer's confluent hypergeometric function and $(a)_k = a(a+1)(a+2)\cdots(a+k-1)$.[19] The details of this derivation (for the binary-breakup case) are given elsewhere.[20] By using Kummer's transformation on $\mathcal{M}$,[19] we can rewrite (6) as

$$c(x,t) = \exp(-tl^{\beta+1})\delta(x-l) + (\nu+2)tl^{\beta-\nu}x^\nu \exp(-tx^{\beta+1})\mathcal{M}((\beta-\nu-1)/(\beta+1), 2, (x^{\beta+1}-l^{\beta+1})t). \tag{7}$$

The moments of the distribution are given by

$$\begin{aligned} M_n &= l^n \exp(-tl^{\beta+1})\mathcal{M}((\nu+2)/(\beta+1), (n+\nu+1)/(\beta+1), tl^{\beta+1}) \\ &= l^n \mathcal{M}((n-1)/(\beta+1), (n+\nu+1)/(\beta+1), -tl^{\beta+1}), \end{aligned} \tag{8}$$

where $M_n = \int_0^\infty x^n c(x,t)dx$.

For the Kummer's function $\mathcal{M}(a,b,z)$, $a = 0, -1, -2, -3, \ldots$ the series expansion for the function terminates after $-a$ terms and (6) becomes an associated Laguerre polynomial, $L_n^{(1)}$. If we set

$$(\nu+2)/(\beta+1) \equiv m = -1, -2, -3, \ldots,$$

then (6) gives

$$c(x,t) = \exp(-tl^{\beta+1})[\delta(x-l) - (\beta+1)tl^{\beta-\nu}x^\nu L^{(1)}_{-m-1}(t(l^{\beta+1}-x^{\beta+1}))]. \tag{9}$$

Likewise, terminating solutions for (7) can be found if $m = 1,2,3,\ldots$. Thus we have a range of terminating closed form solutions in this model, with possible values of β between 1 and -3 and $-2 < \nu \leq 0$.

Here we are concerned mainly with solutions where $\beta < -1$ since this is where the phase transition occurs. First consider the case $\beta = -1$. Taking $\beta \to -1$, (6), (7), or (9) gives

$$c(x,t) = e^{-t}\left[\delta(x-l) + \left(\frac{t(\nu+2)}{\ln(l/x)}\right)^{1/2} l^{-\nu-1}x^\nu I_1(2[t(\nu+2)\ln(l/x)]^{1/2})\right], \tag{10}$$

where I_1 is the first-order modified Bessel function and $M_n = l^n \exp[(l-n)/(1+n+\nu)t]$. This exponential increase in the total number, M_0, is indicative that $\beta=-1$ is at a transition to singular behavior. The onset of this exponential growth is independent of ν.

For $\beta<-1$ and for all allowed values of ν, M_1 is time dependent. This time dependence of M_1 reflects the loss of mass to infinitesimally small particles. We refer to these smallest particles as the zero-limit dust. An explicit example is given by the case $m=-2$ or $\beta=-\nu/2-2$, for which (9) or (6) gives

$$c(x,t)=\exp(-tl^{-\nu/2-1})\{\delta(x-l)+(\nu+2)l^{-3\nu/2-1}x^{\nu}[t-\tfrac{1}{2}t^2(l^{-\nu/2-1}-x^{-\nu/2-1})]\}, \tag{11}$$

with

$$M_n=l^n\exp(-tl^{-\nu/2-1})\left[1+\frac{(\nu+2)tl^{-\nu/2-1}}{n+\nu+1}+\frac{(\nu+2)^2t^2l^{-\nu-2}}{(n+\nu+1)(2n+\nu)}\right]. \tag{12}$$

For $n=1$ the mass,

$$M_1=l\exp(-tl^{-\nu/2-1})(1+tl^{-\nu/2-1}+\tfrac{1}{2}t^2l^{-\nu-2}) \tag{13}$$

is a monotonically decreasing function of time.

Some discrete binary models corresponding to $\beta<-1$ can also be solved explicitly,[20] and serve to illustrate the nature of shattering. As an example we consider the case of a binary breakup model with $a_k=2/(k-1)$ and the distribution of products given by $b_{i|k}=1/(k+1)$. This model corresponds to $\beta=-2$ and $\nu=0$ in the continuous system. The concentrations c_k for a monodisperse initial condition, $c_k(0)=\delta_{kn}$, are[20]

$$\begin{aligned}
&c_n=e^{\tau/(n+1)},\\
&c_k=(n/k)[(n-k+1)e^{-\tau/(n+1)}-2(n-k)e^{-\tau/n}+(n-k-l)e^{-\tau/(n-1)}],\\
&c_1=n-\tfrac{1}{2}n[n(n-1)e^{-\tau/(n+1)}-2(n-1)(n-2)e^{-\tau/n}+(n-2)(n-3)e^{-\tau/(n-1)}],
\end{aligned} \tag{14}$$

where τ is the time for the discrete breakup system. This may be verified by direct substitution into the discrete version of the fragmentation equation. To find the continuum limit we let the size of the monomers be ε and take $\varepsilon\to 0$, with $n=l/\varepsilon$, $k=x/\varepsilon$, $\tau=\varepsilon t$, $\tau=\varepsilon t$, $c_k(\tau)=\varepsilon c(x,t)$. Then (14) becomes Eq. (11) with $\nu=0$. The monomers become a point of measure zero and disappear from the distribution, while the rest of the distribution becomes the finite phase with mass <1. The apparent loss of mass during shattering is a result of the continuum limit, and in a system with a lower-size cutoff the mass of the dust phase belongs to particles of size ε. The amount of mass in the monomers is precisely the missing mass $l-M_1$, where M_1 is given by (13).

If the particles are interpreted as linear rods (lines) undergoing a cutting process where no rearrangement of the products is allowed, then the space distribution of the dust will be a fractal, reminiscent of a Cantor dust.[21] This is illustrated in Fig. 1, which shows simulations of discrete cutting on a line for various values of $\beta\le 0$. The fractal dimension, D_f, of the dust spaced on the line can be found from the relation $\mathcal{N}(x>X)\sim X^{-D_f}$ as $X\to 0$ where $\mathcal{N}(x>X)$ is the number of uncut fragments of size x greater than X. In the limit $x\to 0$, (6) gives $c(x,t)\sim x^{-(\beta+3)}$ or

$$\mathcal{N}(x>X)\sim X^{-(\beta+2)}, \tag{15}$$

which implies that $D_f=\beta+2$ for $-2<\beta<-1$ and all ν. This distribution is similar to the classic Cantor set and may be interpreted as a "randomly" constructed dust. Here the "tremas" or "whey" correspond to the uncut segments with the dust of "curds" as the zero-limit dust. For $\beta=-1$ we find $D_f=1$ and the distribution is not yet a fractal, while for $\beta=-2$ the power-law behavior does not hold, since $\mathcal{N}$ is logarithmic. When $\beta<-2$, then $D_f<0$ and the distribution cannot be described as a fractal. We also note that, as with the transition to shattering behavior, ν has no effect on the fractal properties of the zero-limit dust.

This transition between finite-size particles and the zero-limit dust is remarkably similar to the gelation transition found in polymerization reactions, although gelation is essentially the opposite process.[22,23] In gelling systems an infinite-size cluster will form in a finite amount of time when the homogeneity λ of the aggregation rate kernel, $K(x,y)$, is greater than 1. Gelation is signaled by the larger moments becoming infinite in a finite amount of time. In shattering, mass is time dependent and smaller moments are undefined or infinite. Gelation and shattering are both *kinetic* phase transitions. In gelation the infinite gel cluster is one phase and the remaining particles are the sol, while in shattering systems the dust is the condensed phase and the remaining distribution is the other "finite" phase. Solutions for fragmenting systems show interesting scaling behavior for the limit $x\to 0$, $t\to\infty$ analogous to the $x\to\infty$, $t\to\infty$ scaling behavior for coagulating systems.[24,25] The fragmenting systems also have interesting dynamic scaling behavior, which we have discussed elsewhere.[20] We note that the steady-state scaling behavior of sys-

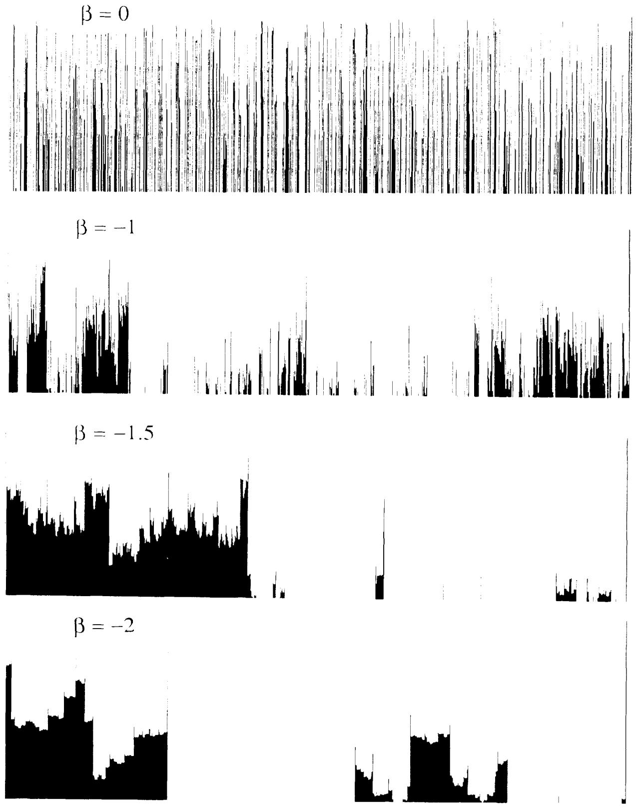

FIG. 1. Results of a continuous time, discrete space cutting process applied to a line for $\beta = 0, -1, -1.5, -2$, plotted as a function of time. The line is composed of 1024 segments with cuts shown in black and uncut regions shown as wide. As cutting proceeds, time increases in the vertical, downward direction. At a given time, the state of the system is found by drawing a horizontal line through the figure; solid black regions of two or more adjacent cuts represent clusters of monomers. Within each segment of n uncut bonds an individual bond is cut with a rate equal to $n^{-\beta}$. In the continuum limit ($\varepsilon \to 0$) the monomers become the "zero-limit dust" while the uncut segments (which are on all length scales) produce a fractal, power-law distribution of gaps between dust regions, when $\beta < -1$. The case $\beta = -2$ corresponds to the analytical solution (11) in the text, with $\nu = 0$.

tems undergoing coalescence and breakup has recently been considered by Family, Meakin, and Deutch.[26]

For this model of multiple fragmentation, the distribution of particles produced upon breakup, $b(x|y)$, has no effect on whether M_1 is time dependent or constant, and only β determines the transition to shattering. Based upon this result, we conjecture that shattering will occur whenever $\lim_{x\to 0} xa(x) = \infty$.

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Note added.—After acceptance of this paper, we have become aware that some mathematical aspects of our model of fragmentation were previously discussed in a somewhat different context by Filippov.[27]

[1]W. R. Johnson and C. C. Price, J. Polym. Sci. **45**, 217 (1960).

[2]A. M. Basedow, K. H. Ebert, and H. J. Ederer, Macromolecules **11**, 774 (1978).

[3]P. A. Glynn, B. M. Van Der Hoff, and P. M. Reilly, J. Macromol. Sci., Part A **6**, 1653 (1972).

[4]T. A. Bak and K. Bak, Acta Chem. Scand. **13**, 1997 (1959).

[5]J. J. Gilvarry, J. Appl. Phys. **32**, 391 (1961).

[6]A. R. Kerstein, private communication.

[7]L. Austin, K. Shoji, V. Bhatia, K. Savage, and R. Klimpel, Ind. Eng. Chem. Processes Des. Dev. **15**, 187 (1976).

[8]R. L. Curl, AIChE J. **9**, 175 (1963).

[9]M. Konno, K. Arai, and S. Saito, J. Chem. Eng. Jpn. **10**, 474 (1977).

[10]W. Kuhn, Ber. Dtsch. Chem. Ges. **63**, 1503 (1930).

[11]H. Mark and R. Simha, Trans. Faraday Soc. **35**, 611 (1940).

[12]E. W. Montroll and R. Simha, J. Chem. Phys. **8**, 721 (1940).

[13]P. J. Blatz and A. V. Tobolsky, J. Phys. Chem. **49**, 77 (1945).

[14]H. H. Jellinek and G. J. White, J. Polym. Sci. **6**, 745 (1951).

[15]A. Charlesby, Proc. Roy. Soc. London, Ser. A **224**, 120 (1954).

[16]Z. A. Melzak, Michigan Math J. **4**, 193 (1957), and Trans. Amer. Math. Soc. **85**, 547 (1957).

[17]J. M. Ball, J. Carr and O. Penrose, Commun. Math. Phys. **104**, 657 (1986).

[18]R. M. Ziff and E. D. McGrady, J. Phys. A **18**, 3027 (1985).

[19]*Handbook of Mathematical Functions,* edited by M. Abramowitz and I. Stegun (Dover, New York, 1964).

[20]R. M. Ziff and E. D. McGrady, Macromolecules **19**, 2513 (1986).

[21]B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1977).

[22]W. H. Stockmayer, J. Chem. Phys. **11**, 45 (1943).

[23]R. M. Ziff, J. Stat. Phys. **23**, 241 (1980).

[24]P. G. van Dongen and M. H. Ernst, Phys. Rev. Lett. **54**, 1396 (1985).

[25]T. Vicsek and F. Family, Phys. Rev. Lett. **52**, 1669 (1984).

[26]F. Family, P. Meakin, and J. M. Deutch, Phys. Rev. Lett. **57**, 727 (1986).

[27]A. F. Filippov, Theory Probab. Its Appl. (Engl. Transl.) **4**, 275 (1961).