Kinetics of depolymerization

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An approach to finding exact solutions to the binary fragmentation equation is presented. This approach is used to solve a general class of exact solutions with a fragmentation rate $F(x,y)=(x+y)^{\alpha}\delta(x-y)$. This fragmentation rate describes a type of depolymerization in which the polymer chains always split in the middle at different rates that depend on the length of the polymer chain and the homogeneity index α. For $\alpha>0$, corresponding to the case where larger sized fragments are more likely to split into two equally sized pieces, the asymptotic form of the scaled cluster size distribution $\Phi(\xi)$ decays as $\xi^{-2}\exp(-\xi^{\alpha}/2\omega\alpha)$ as $\xi\to\infty$ and $\exp[-\alpha(\ln\xi)^2/2\ln 2]$ as $\xi\to 0$, where ξ is the scaled mass. For $\alpha<0$, we get a "shattering" transition. In this case, the scaled cluster size distribution has an asymptotic form that depends on the initial conditions. Finally, our approach is compared and contrasted with other approaches currently used to find exact solutions to the binary fragmentation equation.

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I. INTRODUCTION

Polymers degrade (depolymerize) in a variety of ways such as shear action [1,2], chemical attack [3], and exposure to nuclear, ultraviolet and ultrasonic radiation [4,5]. Theoretical predictions of the evolution with time of the size distributions of the polymers during such processes is of great interest and importance. There are two approaches in use. The first approach relies upon statistical and combinatorial arguments [6–8]. The second approach has been through the analysis of a kinetic equation modeling the depolymerization [9–11].

We favor the kinetic equation approach. Here, the fragmentation (depolymerization) process can be described by the evolution in time of the size distribution $c(x,t)$, where x is the size of the fragments (polymer chains) and t is the time, through a kinetic equation. This theoretical approach is mean field since fluctuations are ignored. Fragments are assumed to be distributed homogeneously at all times throughout the system, i.e., there is perfect mixing and the shape of the fragments is ignored. Thus, the size of the fragments is the only dynamical variable that characterizes a fragment in the kinetic equation approach. Much effort has been expended in finding exact solutions to the kinetic equation, in order to study specific practical problems and to provide a general understanding of the behavior of physical systems in which fragmentation occurs [3,12–19]. Additional solutions would be useful for both theoretical and practical applications.

Of considerable importance are scaling solutions. These are solutions in the long-time, small-size limit where the distribution evolves to a simpler form. This form is universal in the sense that it does not depend on the initial conditions. Most experimental systems evolve to the point where this behavior is reached. A scaling theory based on a linear kinetic equation has been derived for quite a large class of models [16,20–22].

The time evolution of the fragmentation process depends on the behavior of the probability of breakup for the fragments. For breakup rates increasing sufficiently quickly with decreasing size or mass, a cascading breakup occurs in which a finite part of the total mass is transferred to fragments of zero or infinitesimal mass. This so-called "shattering" [15,23] or "disintegration" [24] phenomenon is accompanied by violation of the usual dynamical scaling [20] as well as mass conservation.

We present an exact solution to a class of models via a different approach. This class of exact solutions has a fragmentation rate $F(x,y)=(x+y)^{\alpha}\delta(x-y)$, and represents a situation in which fragments always split into two equally sized pieces, although at different rates determined by α. This choice is motivated by experimental studies on systems undergoing depolymerization through shearing [25], stretching [26], and irradiation [4]. These studies found that bonds in the center of the polymer chains break preferentially to those at the ends. The basic features of scaling solutions, including the singular case where the inverse moments of the cluster size distribution fail to converge, are discussed. Scaling solutions to the rate equations for positive homogeneity index α are given. The asymptotic form of the fragment size distribution at large size is almost completely determined by the value of α. In the small-size limit, we determine the general conditions on the relative breakup rate, which is of the classical log-normal form for the small mass tail of the distribution. This is characteristic of a random multiplicative process [27]. Properties of the solution for long times and negative α are also discussed. The typical size is now determined by the initial size distribution rather than evolving dynamically. Criterion for the existence of a "shattering" transition are also discussed.

Finally, the approach developed in this paper is compared and contrasted with other approaches currently used to obtain exact solutions. Prospects for further research are suggested. In the appendix the approach developed in this paper is used to derive some well-known results [14].

II. MODEL AND SOLUTIONS

The general form of the binary fragmentation equation can be written as

$$\frac{\partial}{\partial t}c(x,t)=-c(x,t)\int_0^x dy\,F(x-y,y)+2\int_x^\infty dy\,c(y,t)F(y-x,x)\;, \tag{1}$$

where $F(x,y)=F(y,x)$ is the rate at which particles of size $(x+y)$ breakup into particles of size x and y.

In this paper we look at

$$F(x,y)=(x+y)^\alpha\delta(x-y)\;. \tag{2}$$

Then (1) becomes

$$(\partial/\partial t)c(x,t)=-\tfrac{1}{2}x^\alpha c(x,t)+2^{\alpha+1}x^\alpha c(2x,t)\;. \tag{3}$$

The initial conditions are

$$c(x,0)=f(x)\neq 0\;. \tag{4}$$

Although this problem is linear, it is not trivial to solve, even for monodisperse initial conditions (except when $\alpha=0$ [17]). We present a slightly different approach to solving such problems in which the initial conditions are nonzero.

Define the Laplace transform of $c(x,t)$ with respect to t by

$$\phi(x,s)=\int_0^\infty dt\,e^{-st}c(x,t)\;, \tag{5}$$

in which case $c(x,t)$ is given by the inverse Laplace transform

$$c(x,t)=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}ds\,e^{st}\phi(x,s)\;, \tag{6}$$

and $\mathrm{Re}(s)>\gamma$ to ensure convergence. Taking the Laplace transform of (3) with respect to t gives

$$\phi(x,s)=\frac{f(x)}{(s+\frac{1}{2}x^\alpha)}+\frac{2^{\alpha+1}x^\alpha\phi(2x,s)}{(s+\frac{1}{2}x^\alpha)}\;. \tag{7}$$

Iterating this expression yields

$$\phi(x,s)=\sum_{r=0}^\infty\{2^{r(r+1)\alpha/2+r}x^{r\alpha}f(2^rx)/(s+\tfrac{1}{2}x^\alpha)[s+\tfrac{1}{2}(2x)^\alpha][s+\tfrac{1}{2}(2^2x)^\alpha]\cdots[s+\tfrac{1}{2}(2^rx)^\alpha]\}\;. \tag{8}$$

Two cases must be distinguished at this point.

Case 1: $\alpha=0$. Performing a simple contour integration yields

$$c(x,t)=e^{-t/2}\sum_{r=0}^\infty\frac{(2t)^r}{r!}f(2^rx)\;. \tag{9}$$

For monodisperse initial conditions $f(x)=\delta(x-1)$ this becomes

$$c(x,t)=e^{-t/2}\sum_{r=0}^\infty\frac{t^r}{r!}\delta\left[x-\frac{l}{2^r}\right]\;, \tag{10}$$

which is the solution obtained by Bak and Bak [17].

Case 2: $\alpha\neq 0$. After performing the contour integrals we get

$$c(x,t)=e^{-\frac{1}{2}x^\alpha t}\left[f(x)+\sum_{r=1}^\infty 2^{r(r+1)\alpha/2+2r}f(2^rx)\times\sum_{k=0}^r\frac{e^{\frac{1}{2}x^\alpha(1-2^{k\alpha})t}}{\prod_{m\in I_k^r}(2^{m\alpha}-2^{k\alpha})}\right]\;, \tag{11}$$

where the set I_k^r is defined by

$$I_k^r=\{0,1,2,\ldots,k-1,k+1,\ldots,r\}\;. \tag{12}$$

For monodisperse initial conditions this becomes

$$c(x,t)=e^{-\frac{1}{2}l^\alpha t}\delta(x-l)+\sum_{r=1}^\infty 2^{r(r+1)\alpha/2+r}\delta\left[x-\frac{l}{2^r}\right]\times\sum_{k=0}^r\left[e^{-\frac{1}{2}(2^{k-r}l)^\alpha t}\Big/\prod_{m\in I_k^r}(2^{m\alpha}-2^{k\alpha})\right]\;. \tag{13}$$

We believe that the class of exact solutions for $\alpha\neq 0$ is new.

III. SCALING THEORY

The scaling ansatz for the cluster size distribution can be written as

$$c(x,t)\sim[s(t)]^{-2}\Phi[x/s(t)]\;, \tag{14}$$

for $t\to\infty$, where $s(t)$ is the size of a typical time-dependent cluster mass, and the exponent -2 is required by mass conservation. For splitting models, the transformation

$$c_n(t)=c(x,t)(dx/dn)dn \tag{15}$$

between the discrete and continuous forms of the cluster size distribution leads to a discrete version of the scaling ansatz [22]

$$c_n(t)\sim s(t)^{-1}\Phi(l/2^ns(t))\;, \tag{16}$$

where $x=1/2^n$ (and n is a positive integer). Substituting (15) into (3) gives

$$-\frac{1}{s(t)^{\alpha+1}}\frac{ds(t)}{dt}=\omega=\frac{[-\frac{1}{2}\Phi(\xi)+2^{\alpha+1}\Phi(2\xi)]\xi^\alpha}{\left[\xi\frac{d\Phi(\xi)}{d\xi}+2\Phi(\xi)\right]}\;, \tag{17}$$

where the separation constant ω is positive since $s(t)$ must be decreasing with time in a fragmenting system and $\xi=x/s(t)$. Then

$$s(t)\sim\begin{cases}t^{1/\alpha}, & \alpha>0,\quad t\to\infty\\ e^{-\omega t}, & \alpha=0,\quad t\to\infty\\ (t_c-t)^{1/|\alpha|}, & \alpha<0,\quad t<t_c.\end{cases} \tag{18}$$

These expressions are valid if scaling holds. Filipov [24] has shown that $\alpha>0$ is a necessary and sufficient condition for the validity of scaling. For $\alpha<0$ a singularity in $s(t)$ is encountered within a finite time t_c, and shattering is anticipated.

We have

$$\omega\left[\xi\frac{d\Phi(\xi)}{d\xi}+2\Phi(\xi)\right]=[-\tfrac{1}{2}\Phi(\xi)+2^{\alpha+1}\Phi(2\xi)]\xi^{\alpha}\ , \tag{19}$$

and in the scaling region $\alpha>0$. The case $\alpha=0$, for which scaling is not valid, will not be considered here.

Multiplying (19) by ξ^{β} and integrating from 0 to ∞ with the assumption that $\Phi(\xi)$ vanishes at these values yields, for $\beta\neq1$,

$$m_{\beta+\alpha}=\frac{\omega(1-\beta)}{\left[\dfrac{1}{2^{\beta}}-\dfrac{1}{2}\right]}m_{\beta}\ , \tag{20}$$

where the scaling moments m_β are defined by

$$m_{\beta}=\int_0^{\infty}d\xi\,\xi^{\beta}\Phi(\xi)\ , \tag{21}$$

which is precisely the Mellin transform of $\Phi(\xi)$ (except for a trivial shift of 1 in the definition of β). Similar calculations to those performed in [22] yield

$$\Phi(\xi)\sim\begin{cases}\xi^{-2}e^{-(\xi^{\alpha}/2\omega\alpha)}, & \xi\to\infty\\ e^{-(\alpha/2\ln2)(\ln\xi)^2}, & \xi\to0.\end{cases} \tag{22}$$

Then,

$$c_n(t)\sim\begin{cases}(l/2^n)^{-2}t^{-1/\alpha}e^{-(l^{\alpha}t/2^{n\alpha+1}\omega\alpha)}, & s(t)\ll l/2^n\\ t^{1/\alpha}e^{-(\alpha/2\ln2)[\ln(lt^{1/\alpha}/2^n)]^2}, & s(t)\gg l/2^n.\end{cases} \tag{23}$$

These results are of a similar form to those of Cheng and Redner [22], and are consistent with the solutions presented above.

IV. SHATTERING TRANSITION

Formally, the mass of the system is defined by

$$M(t)=\int_0^{\infty}dx\,xc(x,t)\ , \tag{24}$$

so that

$$\begin{aligned}\frac{dM(t)}{dt}&=\int_0^{\infty}dx\,x\frac{\partial c(x,t)}{\partial t}\\ &=\int_0^{\infty}dx\,x[-\tfrac{1}{2}x^{\alpha}c(x,t)+2^{\alpha+1}x^{\alpha}c(2x,t)]=0\ ,\end{aligned} \tag{25}$$

indicating that the mass is conserved. However, when the fragmentation rate increases sufficiently fast as the size of the fragments decreases to zero, a cascading of the fragmentation occurs such that mass is lost to zero-size fragments. This cascading process, which has been named "shattering" [15,23] or "disintegration" [24], is somewhat similar to gelation in coagulating systems, where mass is lost to an infinite gel molecule [28,29]. Gelation and shattering are signalled by the condition $dM(t)/dt<0$. When shattering is suspected a more subtle analysis than that used to derive (25) is required. Consider a cutoff mass $M_\varepsilon(t)$ defined by

$$M_{\varepsilon}(t)=\int_{\varepsilon}^{\infty}dx\,xc(x,t) \tag{26}$$

with

$$M_{\varepsilon}(t)\to M(t)\quad\text{as }\varepsilon\to0^{+}\ . \tag{27}$$

The cutoff mass loss is given by

$$dM_{\varepsilon}(t)/dt=-\tfrac{1}{2}\int_{\varepsilon}^{2\varepsilon}dx\,x^{\alpha+1}c(x,t)\ . \tag{28}$$

It was anticipated that shattering occurs for negative values of α, when scaling breaks down. When $\alpha<0$, we propose the ansatz

$$c(x,t)\sim e^{-\frac{1}{2}l^{-|\alpha|}t}\Phi(x/l),\quad x\to0,t\to\infty\ . \tag{29}$$

Substituting (29) into (3) yields

$$\Phi(x/l)=(x/l)^{|\alpha|-2}\ . \tag{30}$$

Hence,

$$c(x,t)\sim(x/l)^{|\alpha|-2}e^{-\frac{1}{2}l^{-|\alpha|}t} \tag{31}$$

as $x\to0$, and $t\to\infty$ with $\alpha<0$.

Substituting (31) into (28) gives

$$dM_{\varepsilon}(t)/dt\sim-(\ln2/2l^{|\alpha|-2})e^{-\frac{1}{2}l^{-|\alpha|}t}<0\ . \tag{32}$$

Thus shattering does occur for $\alpha<0$. It can be shown that shattering does not occur for $\alpha\geq0$.

V. DISCUSSION

Using a kinetic equation approach we have derived solutions of a fragmenting system for a model where the fragmentation is a function of the size of the piece breaking up, and the pieces always split into two equally sized pieces. These models have various applications. For example, the case $F(x,y)=(x+y)^{\alpha}\delta(x-y)$, with $\alpha>0$, describes a process where the rate of breakup increases with size. This type of fragmentation has been observed and studied when polymers degrade under tension (stretching) [26], or in the presence of a destructive force field such as ultrasound [4].

A scaling theory has been derived. The results are similar to those of Cheng and Redner [22], and appear to be consistent with the exact solutions presented in this paper. The shattering transition has been located and discussed. Again, the results agree with those already known for shattering [15,20,22–24].

The approach used to find solutions presented in this paper may be applied to other linear (fragmentation) problems in which $c(x,0)=f(x)\neq0$. The usual approach to such problems is to find a solution for monodisperse initial conditions $f(x)=\delta(x-1)$, then generalize to a solution for any initial conditions as follows:

$$c(x,t)=\int_0^{\infty}dl\,f(l)c_l(x,t)\ , \tag{33}$$

where $c_l(x,t)$ is the solution for monodisperse initial conditions. Another approach is that due to Charlesby [30]. Here, exact solutions are found by iterating the moment equations to find explicit expressions for the moments. The moments are then written in a form that resembles their definition and the form of the size distribution $c(x,t)$ is deduced by comparing the two expressions for the moments. This approach is very effective, albeit indirect. In our approach, which is much more direct, we solve the problem for any initial conditions, and avoid the issue of finding a solution for monodisperse initial conditions. The only difficulty one might encounter when applying our approach arises when one has to perform contour integrals to invert the Laplace transform $\varphi(x,s)$ to recover $c(x,t)$.

As a prospect for further research, it would be interesting to see what results one would obtain with the approach described above if one looked at problems with sources and sinks. With this approach it may be possible to investigate problems with time-dependent fragmentation rates.

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APPENDIX

We derive the results presented in [14] to illustrate how our approach works on a more general problem. Consider (1) for $F(x,y)=(x+y)^{\alpha}$. Then (1) becomes

$$\frac{\partial}{\partial t}c(x,t)=-x^{\alpha+1}c(x,t)+2\int_x^{\infty}dy\, y^{\alpha}c(y,t)\ , \tag{A1}$$

subject to the following initial conditions:

$$c(x,0)=f(x)\neq 0\ . \tag{A2}$$

Taking the Laplace transform of (1) with respect to t gives

$$\phi(x,s)=\frac{f(x)}{(s+x^{\alpha+1})}+\frac{2}{(s+x^{\alpha+1})}\int_x^{\infty}dx_1 x_1^{\alpha+1}\phi(x_1,s)\ . \tag{A3}$$

Iterating this expression, and swapping the order of the integrations as we go along, yields for $\alpha\neq -1$,

$$\phi(x,s)=\frac{f(x)}{(s+x^{\alpha+1})}+\frac{2}{(s+x^{\alpha+1})}\int_x^{\infty}dx_1 x_1^{\alpha}\frac{f(x_1)}{(s+x_1^{\alpha+1})}\sum_{r=0}^{\infty}\frac{1}{r!}\left[\frac{2}{(\alpha+1)}\ln\left[\frac{s+x_1^{\alpha+1}}{s+x^{\alpha+1}}\right]\right]^r\ . \tag{A4}$$

Or,

$$\phi(x,s)=\frac{f(x)}{(s+x^{\alpha+1})}+\frac{2}{(s+x^{\alpha+1})^{1+2/(\alpha+1)}}\int_x^{\infty}dx_1 f(x_1)x_1^{\alpha}(s+x_1^{\alpha+1})^{-1+2/(\alpha+1)}\ . \tag{A5}$$

For $\alpha=1,\ 0,\ -\frac{1}{3},-\frac{1}{2},-\frac{3}{5},\ldots,$ we can invert this by contour integration to obtain the following solution in closed form:

$$c(x,t)=e^{-x^{\alpha+1}t}f(x)+(\alpha+1)e^{-x^{\alpha+1}t}t\int_x^{\infty}dx_1 f(x_1)x_1^{\alpha}L^{(1)}_{-1+2/(\alpha+1)}(t(x^{\alpha+1}-x_1^{\alpha+1}))\ , \tag{A6}$$

where the associated Laguerre polynomial $L^{(1)}_{m-1}(x)$ is defined by

$$L^{(1)}_{m-1}(x)=\sum_{r=1}^{m}\frac{m!}{(m-r)!r!}\frac{(-x)^{r-1}}{(r-1)!}\ . \tag{A7}$$

To obtain a solution for $\alpha=-1$, one can apply the approach described above, or take the limit $\alpha\to -1$ in (A6) as in [14].

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