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New universality class for gelation in a system with particle breakup

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We introduce a model of coagulation with single-particle breakoff, described by the kernels $K_{ij}=ij$ and $F_{ij}=\alpha((j+1)\delta_{i1}+(i+1)\delta_{j1})$. For α above a critical value α_c, the system either gels or reaches a steady-state size distribution, depending upon initial conditions. Below α_c, gelation always occurs. At $\alpha=\alpha_c$, the scaling exponent τ, which describes the large-size behavior of the steady-state size distribution, is $\frac{7}{2}$ rather than the usual value $\frac{5}{2}$, indicating that this process belongs to a new universality class of gelation.

Irreversibly coagulating systems have long been at the center of experimental and theoretical study of colloidal phenomena, aerosol dynamics, and polymerization. More recently, the more general problem of coagulation with fragmentation has begun to receive attention. The introduction of breakup into a system makes the attainment of steady-state size distributions possible and recent work has concentrated on describing reversible systems as they approach these steady states.[1-5] Aizenman and Bak[2] have studied the approach to equilibrium of the Blatz-Tobolsky[6] model, which describes reversible kinetics of linear polymerization, while van Dongen and Ernst[3] studied the reversible kinetics for branched polymers. Family, Meakin, and Deutch[4] have introduced a scaling exponent to relate the breakup strength to the steady-state size distribution and have performed computer simulations to verify this result. Very recently, Sorensen, Zhang, and Taylor[5] have developed a general stability criterion for reaching steady-state size distributions for reversible coagulation, assuming homogeneous coagulation and fragmentation rate kernels.

In this Rapid Communication we introduce a coagulation-fragmentation model which does not fall into previously studied classes: it does not satisfy detailed balance, and does not have a homogeneous fragmentation kernel. Yet this system can reach a steady state, depending upon the relative strength of fragmentation to coagulation and, in some cases, also upon the initial conditions. At a critical value of this relative strength, we find a scaling exponent τ whose value $\frac{7}{2}$ indicates a new universality class of gelation.

We consider a system where the fragmentation involves the breakoff of only a single particle at a time. This process is described by a coagulation matrix K_{ij}, which gives the rate of combination of i-mers and j-mers, and fragmentation function f_k, which gives the rate of breakoff of single particles from k-mers ($f_1=0$):

$$c_i+c_j \xrightarrow{K_{ij}} c_{i+j}\,, \quad c_1+c_{k-1} \xleftarrow{f_k} c_k\,, \tag{1}$$

where c_k is the concentration of k-mers ($k>0$). The fragmentation process considered here is a special case of the general binary fragmentation,[7] described by a breakup matrix F_{ij}, which gives the intrinsic rate that $(i+j)$-mers break into an i-mer and j-mer. In our model, F_{ij} has nonzero terms in only the first row and column (i.e., $F_{ij}=f_{i+1}\delta_{j1}+f_{j+1}\delta_{i1}$). The kinetics of this process are described by the equation

$$\frac{dc_k}{dt}=\frac{1}{2}\sum_{i+j=k}K_{ij}c_ic_j-c_k\sum_{j=1}^{\infty}K_{kj}c_j+f_{k+1}c_{k+1}-f_kc_k+\delta_{k1}\sum_{j=1}^{\infty}f_jc_j\,, \tag{2}$$

which is a generalization of Smoluchowski's coagulation equation. The last term in Eq. (2) reflects the special treatment that monomers must be given, since they are formed from the breakup of any cluster. One can easily verify that the mass $M_1\equiv\sum kc_k$ is conserved by Eq. (2).

This coagulation-fragmentation process is of interest in situations where particles are broken off one at a time, such as by mechanical grinding, or where particles are held by many bonds and the only breakoff possible is a single particle. Equation (2) has also been written to represent an aerosol undergoing simultaneous coagulation and evaporation.[8] It also serves as an interesting example of a coagulation-fragmentation process in which detailed balance at the steady state is not possible. That is, if $\bar{c}_k$ is the steady-state value of the concentrations, then detailed balance requires $K_{ij}\bar{c}_i\bar{c}_j=F_{ij}\bar{c}_{i+j}$. Detailed balance is clearly not possible here because of the zero elements in F_{ij}.

Here we consider specifically the model with $K_{ij}=ij$ and $f_k=\alpha k$ ($k>1$). This coagulation kernel corresponds to the reaction limited growth of cross-linked or branched polymers, and is known to lead to a gelation transition (growth of infinite particles) in a finite period of time, when there is no fragmentation. The breakup function f_k corresponds to a monomer loss rate proportional to the particle size. The parameter α gives the relative strength of this fragmentation process over the coagulation process. Equation (2) then becomes

$$\frac{dc_k}{dt}=\frac{1}{2}\sum_{i+j=k}ijc_ic_j-kc_k+\alpha[(k+1)c_{k+1}-kc_k+\delta_{k1}]\,, \tag{3}$$

where we have assumed that the concentrations have been scaled such that the conserved mass $M_1\equiv\sum kc_k=1$ (before gelation, if it occurs).

The equations for the moments $M_n \equiv \sum k^n c_k$ are found by multiplying Eq. (3) by k^n and summing over all k. We find

$$\frac{dM_0}{dt} = -\tfrac{1}{2} + \alpha(1-c_1)\,, \tag{4a}$$

$$\frac{dM_2}{dt} = M_2^2 - 2M_2\alpha + 2\alpha\,, \tag{4b}$$

$$\frac{dM_3}{dt} = 3M_3(M_2-\alpha) + 3\alpha M_2\,, \tag{4c}$$

$$\frac{dM_n}{dt} = nM_n(M_2-\alpha) + \tfrac{1}{2}\sum_{l=2}^{n-2}\binom{n}{l} M_{l+1}M_{n-l+1} + \alpha\left[M_1 + \sum_{l=2}^{n}\binom{n}{l}(-1)^l M_{n-l+1}\right] \quad (n>3)\,. \tag{4d}$$

Note M_0 cannot be determined by solving Eq. (4a) since it depends upon c_1, which in turn depends upon all other c_k, which cannot be determined. However, M_2 is soluble and M_3 and higher moments can, in principle, be found. From these the long-time behavior of the size distribution can be deduced, and it is not necessary to have a solution for M_0.

Three regimes of the breakup strength α lead to a different long-time behavior in this system. These regimes may be deduced from the steady-state solution $\overline{M}_2$, which follows from Eq. (4b):

$$\overline{M}_2 = \alpha - \sqrt{\alpha^2 - 2\alpha}\,. \tag{5}$$

Only the negative root is applicable since $\overline{M}_2 \to 1$ as $\alpha \to \infty$. Equation (5) requires that $\alpha^2 - 2\alpha \geq 0$, leading to the following necessary condition for steady-state behavior to result:

$$\alpha \geq 2 \equiv \alpha_c\,. \tag{6}$$

It follows that α_c is a critical value, above which steady-state solutions are possible and below which no steady-state solution exists and (as will be shown) gelation occurs. The borderline case $\alpha = \alpha_c$ will be shown to lead to a new universality class of gelation.

$0 < \alpha < \alpha_c$. In this case Eq. (4b) becomes

$$\frac{dx}{dt} = -x^2 - \mu^2\,, \tag{7}$$

where $\mu \equiv \sqrt{2\alpha - \alpha^2} > 0$ and $x \equiv \alpha - M_2$. A solution for x is immediate:

$$x = \frac{x(0) - \mu\tan(\mu t)}{1 + [x(0)/\mu]\tan(\mu t)}\,. \tag{8}$$

Equation (8) implies gelation since x always diverges at a finite time t_g given by $t_g = -1/\mu\arctan[\mu/x(0)]$. When $x(0) < 0$, $0 < t_g < \pi/2\mu$, and when $x(0) > 0$, $\pi/2\mu < t_g < \pi/\mu$. Furthermore, it may be shown that the moments in general diverge as

$$M_n \sim \frac{B_n}{(t_g - t)^{2n-3}} \quad (n \geq 2)\,, \tag{9}$$

where the constants B_n are recursively determined. Assuming the scaling form $c_k \sim k^{-\tau'}\phi(|t_g - t|k^\sigma)$ for $t \to t_g$, which implies $M_n \sim (t_g - t)^{(n-\tau'+1)/\sigma}$, we find the usual result for the ij coagulation kernel,[9,10] $\tau' = \frac{5}{2}$ and $\sigma = \frac{1}{2}$.

$\alpha = \alpha_c$. For this case Eq. (4b) becomes $dx/dt = -x^2$, which has the solution

$$x = \frac{x(0)}{1 + x(0)t}\,, \tag{10}$$

whose behavior depends upon the initial condition $x(0)$. If $x(0) < 0$ then x diverges (gelation) at $t_g = -x(0)^{-1}$ and we have the scaling behavior $c_k \sim k^{-5/2}$ at $t = t_g$. If $x(0) \geq 0$, we find that $x \to 0$ as $t \to \infty$, indicating a steady-state solution.

$\alpha > \alpha_c$. Equation (4b) becomes

$$\frac{dx}{dt} = \beta^2 - x^2\,, \tag{11}$$

where $\beta \equiv \sqrt{\alpha^2 - 2\alpha} > 0$. Solution for x is given by

$$x = \frac{\beta\tanh(\beta t) + x(0)}{1 + [x(0)/\beta]\tanh(\beta t)}\,. \tag{12}$$

As for the case $\alpha = \alpha_c$, the long-time behavior of Eq. (12) depends upon the initial condition $x(0)$. If $x(0) < -\beta$ gelation occurs at $t_g = (1/\beta)\operatorname{arctanh}[\beta/x(0)]$ and the asymptotic size distribution $c_k \sim k^{-5/2}$, $k \to \infty$, $t = t_g$ results. If, however, $x(0) > -\beta$, then $x \to \beta$ as $t \to \infty$. Figure 1 shows a phase portrait of $x(t)$ for this regime of values for α.

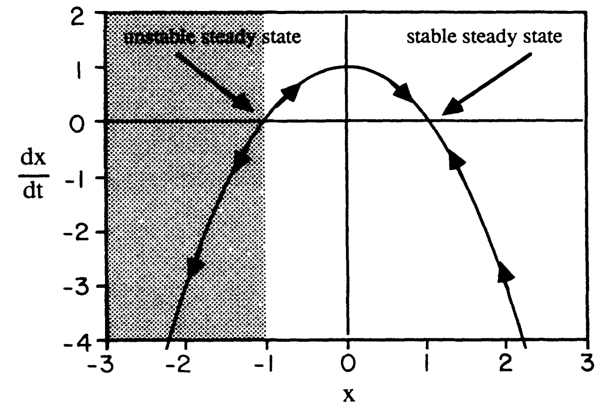

FIG. 1. Phase portrait of x for the case $\alpha > \alpha_c$ where we have taken $\beta = 1$. The shaded area shows all values of x that will lead to gelation. For all other values of x the system will reach the stable steady state $x = \beta = 1$.

When steady-state solutions are possible [i.e., $M_2(0) \leq \alpha + \sqrt{\alpha^2 - 2\alpha}$ and $\alpha \geq \alpha_c$], the higher moments $\overline{M}_n$ follow from Eqs. (4):

$$\overline{M}_n = \frac{1}{n(\alpha - \overline{M}_2)}\left\{\tfrac{1}{2}\sum_{l=2}^{n-2}\binom{n}{l}\overline{M}_{l+1}\overline{M}_{n-l+1} + \alpha\left[\overline{M}_1 + \sum_{l=2}^{n}\binom{n}{l}(-1)^l\overline{M}_{n-l+1}\right]\right\} \quad (n \geq 3)\,. \tag{13}$$

It may be seen from the above that all $\overline{M}_n$ for $n>2$ diverge as $a \to a_c^+$ with the asymptotic behavior

$$\overline{M}_n \sim A_n \epsilon^{-(n-5/2)} \quad (\epsilon \to 0), \tag{14}$$

where $\epsilon \equiv a - a_c$ and the A_n satisfy a recursive relation. If we assume a two-parameter scaling form for the steady-state concentrations $\bar{c}_k \sim k^{-\tau} f(\epsilon k^{\omega})$ for $k \to \infty$, $\epsilon \to 0$, $\epsilon k^{\omega} = \text{const}$, then the moments will diverge as

$$\overline{M}_n \sim \epsilon^{-(n-\tau+1)/\omega} \quad (\epsilon \to 0) \tag{15}$$

valid for $n > \tau - 1$. Comparing Eq. (14) with Eq. (15), we find $\omega = 1$ and $\tau = \frac{7}{2}$.

In most previously studied gelling models[9,10] with $K_{ij} \sim ij$, τ', which describes the asymptotic size behavior at $t = t_g$, is given by $\frac{5}{2}$. The value $\tau = \frac{7}{2}$ found here (which applies for $t = \infty$ and $a = a_c$) indicates that this process belongs to a new universality class of gelation. Note that τ cannot be $\frac{5}{2}$ and must be >3 because M_2 is finite. The other exception is the model of Hendriks and Ziff,[11] in which feed and withdrawal terms are added to the coagulation equation with a resulting τ differing from $\frac{5}{2}$.

We are interested in the scaling behavior for large times and for $\epsilon \to 0$ ($a \to a_c^+$). It is convenient to use β, which goes to zero as $2^{3/4}\epsilon^{1/2}$ as $\epsilon \to 0$. Then, in the scaling limit $t \to \infty$, $\beta \to 0$ such that $\beta t = \text{const}$, we find, from Eq. (12),

$$x \sim \frac{\beta}{\tanh(\beta t)} \tag{16}$$

independent of $x(0)$. The scaling laws for small ϵ at $t = \infty$ and large t at $\epsilon = 0$ follow from Eq. (16) and are given by

$$a - M_2 = x \sim \begin{cases} 2^{3/4}\epsilon^{1/2} & (\epsilon \to 0,\ t = \infty), \\ 1/t & (t \to \infty,\ \epsilon = 0). \end{cases} \tag{17}$$

The above scaling behavior may also be derived directly from the exact solution, Eq. (12).

The scaling function for M_3 can be deduced by rewriting Eq. (4c) as

$$\frac{dy}{dt} = -3xy + \gamma^2, \tag{18}$$

where $y \equiv M_3 + a$ and $\gamma \equiv 3a^2$. Substituting Eq. (16) into Eq. (18) and solving for y gives

$$y \sim \frac{\gamma}{3\beta} \frac{[\cosh(\beta t) - 1]^2 [\cosh(\beta t) + 2]}{\sinh^3(\beta t)}. \tag{19}$$

The scaling behavior follows directly from Eq. (19) and is given by

$$M_3 \sim y \sim \begin{cases} \gamma_c/(3 \times 2^{3/4}\epsilon^{1/2}) & (\epsilon \to 0,\ t = \infty), \\ \gamma_c t/4 & (t \to \infty,\ \epsilon = 0), \end{cases} \tag{20}$$

where $\gamma_c \equiv 3a_c^2$. We note that the exact solution of y can also be found from Eqs. (12) and (18), and it leads to Eqs. (19) and (20) in the scaling limit.

For conditions in which steady-state size distributions are possible, the explicit solution for the size concentrations, $\bar{c}_k$, may be found from the generating function $g \equiv \sum k z^k c_k$. Multiplying Eq. (3) by z^k, summing over all k, and taking the derivative equal to 0, we find

$$\tfrac{1}{2} g^2 + (-1 - a + a/z) g + (\tfrac{1}{2} - a + za) = 0, \tag{21}$$

which gives

$$g = 1 - (a/z)(1-z)(1 - \sqrt{1 - 2z/a}). \tag{22}$$

Expanding Eq. (22) for a series in powers of z implies

$$\bar{c}_k = \frac{(2k)![(a-2)k + (a+1)]}{k \times k!(k+1)!(2a)^k(2k-1)}. \tag{23}$$

Using the Stirling approximation for large k gives

$$\bar{c}_k \sim \frac{1}{k^{7/2}} \left(\frac{2}{a}\right)^k \frac{(a-2)k + (a+1)}{2\sqrt{\pi}}. \tag{24}$$

When $a = 2$, Eq. (24) becomes $c_k \sim (3/2\sqrt{\pi}) k^{-7/2}$, which gives the power-law dependence on k derived earlier from the scaling of the moments. The scaling function for $\bar{c}_k$ as $\epsilon \to 0$ and $k \to \infty$ such that $\epsilon k = \text{const}$ follows from Eq. (24):

$$\bar{c}_k \sim k^{-7/2} f(\epsilon k), \quad f(x) \equiv \frac{3}{2\sqrt{\pi}} \left(1 + \frac{x}{3}\right) e^{-x/2}. \tag{25}$$

In conclusion, we find that the long-time behavior of this system is dependent upon the value of the breakup constant a. In the regime $0 < a < a_c$, the system always gels and the size distribution has the asymptotic behavior $c_k \sim k^{-5/2}$ at $t = t_c$. For the regime $a > a_c$, the system reaches one of two states: (i) If $M_2(0) > a + \sqrt{a^2 - 2a}$ gelation occurs and the asymptotic behavior of the size distribution at the gel point is described by the usual exponent $\tau' = \frac{5}{2}$; (ii) if $M_2(0) \le a + \sqrt{a^2 - 2a}$, a steady-state size distribution is reached in which detailed balance cannot be satisfied. When $a = a_c$ the behavior also depends upon the initial conditions. When $M_2(0) > a$, gelation occurs at $t_g = 1/[M_2(0) - a]$ and the asymptotic behavior of the size distribution is again described by the exponent $\tau' = \frac{5}{2}$. When $M_2(0) \le a$, the system undergoes a new kind of gelation in which the third and higher moments are infinite and $c_k \sim k^{-7/2}$.

The scaling results for M_2, M_3, and c_k are consistent with a three-parameter scaling relation for the c_k:

$$c_k \equiv k^{-\tau} F(k/t^z, \epsilon k^{\omega}), \quad a > a_c, \quad M_2(0) \le a + \sqrt{a^2 - 2a}, \tag{26}$$

with $\tau = \frac{7}{2}$, $z = 2$, $\omega = 1$, and where $F(0,y) = f(y)$, $F(x,0) = g(x)$, and $F(x,y) \to 0$ for either $x \gg 1$ or $y \gg 1$. However, we have only verified this scaling form for the limiting cases $t \to \infty$ and $\epsilon \to 0$.

We have also studied the system described by Eq. (2) with $f_k = ak$ and the more general coagulation kernel $K_{ij} = Aij + B(i+j) + C$, where $A > 0$, $B, C \ge 0$. The long-time behavior of this system is the same as for the ij kernel presented in this paper, except that the critical value below which gelation always occurs and above which steady state is possible is given by $a_c = A + B + \sqrt{A^2 + A(2B+C)}$.

We have also deduced the long-time behavior of the system described by the kernels $K_{ij}=ij$ and $f_k=a(k-1)$. In this case M_0 may be found exactly, and is given by

$$M_0=(1-1/2a)+[M_0(0)-1+1/2a]e^{-at}.$$

However, M_2 is coupled to M_0 and cannot be solved for general initial conditions other than $M_0(0)=\overline{M}_0$. Still, it may be shown that both M_2 and M_3 satisfy the scaling relations given by Eqs. (16) and (19) except that $\beta=\sqrt{a^2-2a-1}$ and $a_c=1+\sqrt{2}$.

Finally, we note that the dependence of the long-time behavior of this system upon a breakup constant contrasts with the recent results of Sorensen, Zhang, and Taylor.[5] They have shown that the stability of solutions of a coagulation-fragmentation system obeying the homogeneity relationships $K_{ai,aj}=a^{\lambda}K_{ij}$ and $F_{ai,aj}=a^{\delta}F_{ij}$ depends only upon the homogeneity exponents λ and δ, and not upon a constant coefficient. In contrast, for our system, in which F_{ij} does not obey the homogeneity relation and therefore is not in the class of models considered in Ref. 5, we have shown that the stability of the system depends upon the constant coefficient a.

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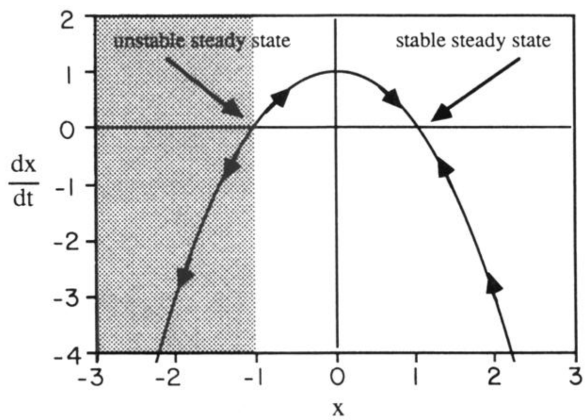

FIG. 1. Phase portrait of x for the case $\alpha > \alpha_c$ where we have taken $\beta = 1$. The shaded area shows all values of x that will lead to gelation. For all other values of x the system will reach the stable steady state $x = \beta = 1$.