Cluster-Size Evolution in a Coagulation-Fragmentation System

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We derive a differential equation for the time evolution of the cluster mean size in a system of particles in which both coagulation and fragmentation are occurring. Both stable and unstable solutions exist. For the stable case the equilibrium mean size, number density, and characteristic relaxation time scale with the magnitude of the coagulation and fragmentation kernels and the total primary particle concentration, with exponents related to the homogeneities of the two kernels. For large displacements from equilibrium the size varies with a power law in time, whereas for small displacements the system relaxes exponentially.

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Irreversible coagulation processes have consumed a considerable amount of recent interest.[1,2] These studies have shown that the mean size and number density have time evolutions which depend on the homogeneity characteristics of the coagulation kernel. The less-studied case of coagulation with fragmentation is also of great importance due to its greater generality and the possibility of describing reversible systems both near and far from equilibrium.[3–7] The first work on a coagulation-fragmentation system appears to be that of Blatz and Tobolsky,[3] who studied a polymerization-depolymerization reaction for the special case of constant-rate coefficients (homogeneity equal to zero for each kernel). They found that the system approached a mean degree of polymerization at long time which depended on the ratio of the coagulation to fragmentation kernel magnitudes. Recently, Family, Meakin, and Deutch[7] studied the situation which arises when fragmentation was included with coagulation in the Smoluchowski equation. They also found that an equilibrium aggregate size was achieved at long times, and calculated a scaling exponent which described how this equilibrium size depended on the magnitude of the fragmentation kernel.

In the Letter we study the time evolution of the mean cluster size for the general case of coagulation with fragmentation. To do this we derive a simple differential equation which describes the time evolution of the particle mean size under the assumption that the size distribution has the scaling form. We find several new results: (1) The stability of the differential equation depends on the homogeneity of the coagulation and fragmentation kernels; thus the mean size does not always approach an equilibrium aggregate value. (2) When the differential equation is stable, the asymptotic mean size depends on the product of the monomer number density and the coagulation kernel divided by the fragmentation kernel with a scaling exponent. This is a more general result than the earlier work of Blatz and Tobolsky and Family, Meakin, and Deutch. Our result is a direct consequence of the evolution equation and does not rely upon assumptions used by Family, Meakin, and Deutch regarding the mean-size scaling properties. (3) The scaling exponent for equilibrium is related to the exponents that govern temporal growth and fragmentation. (4) A characteristic relaxation time for the approach to equilibrium is found which is also a function of monomer density, and coagulation and fragmentation kernel magnitude. (5) Small fluctuations from the equilibrium mean size relax exponentially. Finally, we show that our calculations agree well with the simulation of Family, Meakin, and Deutch.

We start with the Smoluchowski equation generalized to include fragmentation:

$$\frac{dn_k}{dt}=\frac{1}{2}\sum_{i+j=k}[K(i,j)n_in_j-F(i,j)n_{i+j}]-\sum_{j=1}^{\infty}[K(k,j)n_kn_j-F(k,j)n_{k+j}]. \tag{1}$$

In Eq. (1) $n_k(t)$ is the concentration of clusters with k monomers per cluster. We represent the coagulation kernel as $K(i,j)=k_c\Psi(i,j)$ and the fragmentation kernel as $F(i,j)=k_f\Phi(i,j)$ where $\Psi(1,1)=\Phi(1,1)=1$ and k_c and k_f are coagulation and breakup constants, respectively. Obviously, $n_k=n_k(k_c,k_f,t)$.

The mean size of the clusters, s, may be defined as

$$s(t)=M_2/M_1=\sum_{k=1}^{\infty}k^2n_k\left[\sum_{k=1}^{\infty}kn_k\right]^{-1}. \tag{2}$$

Here M_1 and M_2 are the first and second moments of the distribution, n_k. The time derivative of s is

$$\dot{S}=\dot{M}_2/M_1. \tag{3}$$

M_1 is the total number of single particles in the system and so it is constant.

To find the time derivative of the ith moment of the distribution, it is well known that one may multiply the Smoluchowski equation, Eq. (1), by k^i and sum over all k. If we assume that one may convert the sums to integrals with zero lower limits when k ranges over a large range, then one finds for the ith moment time derivative

$$\dot{M}_i = \frac{1}{2}\int_0^\infty du \int_0^\infty dv [K(u,v)n(u)n(v) - F(u,v)n(u+v)][(u+v)^i - u^i - v^i]. \tag{4}$$

Here u and v are the masses of the clusters, proportional to the numbers of monomers in the clusters. For the second moment, $i=2$,

$$\dot{M}_2 = \int_0^\infty du \int_0^\infty dv\, vu [K(u,v)n(u)n(v) - F(u,v)n(u+v)]. \tag{5}$$

We now use the scaling form of the size distribution,[8]

$$n(v,t) = M_1 s(t)^{-2}\phi(x), \tag{6}$$

where $x = v/s(t)$. Substitution into Eq. (5) yields

$$\dot{M}_2 = M_1^2 s^\lambda \int_0^\infty dx \int_0^\infty dy\, xy\, K(x,y)\phi(x)\phi(y) - M_1 s^{\alpha+2}\int_0^\infty dx \int_0^\infty dy\, xy\, F(x,y)\phi(x+y), \tag{7}$$

where use has been made of the homogeneity of the coagulation kernel, $K(au,av) = a^\lambda K(u,v)$, and fragmentation kernel, $F(au,av) = a^\alpha F(u,v)$. Use of Eq. (3) leads to our final expression for the time derivative of the mean size,

$$\dot{s} = M_1 a k_c s^\lambda - b k_f s^{\alpha+2}, \tag{8}$$

where

$$a = \int_0^\infty dx \int_0^\infty dy\, xy \Psi(x,y)\phi(x)\phi(y) \tag{9}$$

and

$$b = \int_0^\infty dx \int_0^\infty dy\, xy \Phi(x,y)\phi(x+y). \tag{10}$$

The constants a and b are both positive and the integrals are assumed to exist. Equation (8) is important in that it describes the temporal evolution of the mean cluster size.

We next examine the scaling behavior of Eq. (8), by rewriting it in terms of the reduced variables

$$s^* = s/s_0, \tag{11a}$$

$$t^* = t/t_0. \tag{11b}$$

The scaled equation should not be dependent on the details of the system; that is, we require

$$ds^*/dt^* = s^{*\lambda} - s^{*\alpha+2}. \tag{12}$$

Substitution of Eqs. (11) into Eq. (8) to achieve Eq. (12) yields

$$s_0 = (M_1 a k_c / b k_f)^y \tag{13}$$

and

$$t_0 = \frac{s_0^{1-\lambda}}{M_1 a k_c} = (M_1 a k_c)^{-(\alpha+1)y}(b k_f)^{(\lambda-1)y}, \tag{14}$$

where

$$y = (\alpha+2-\lambda)^{-1}. \tag{15}$$

When $s = s_0$, the right-hand side of Eq. (12) is zero, and so s does not change. Thus s_0 is the equilibrium value of s at long time, and t_0 is a characteristic time scale for the approach to equilibrium. Equation (13) is a generalization of the mean-size scaling results of both Blatz and Tobolsky[3] and Family, Meakin, and Deutch.[7] The results are logical in that as the coagulation term increases, s_0 increases, and conversely as the fragmentation term increases, s_0 decreases, both scaled by the exponent $y = (\alpha+2-\lambda)^{-1}$. This is the same exponent found by Family, Meakin, and Deutch, who used a scaling argument on their assumption that $s_0 \sim k_f^{-y}$ and the invariance of Eq. (1) under a scaling transformation to obtain y. The derivation above eliminates this assumption. For constant kernels $\alpha = \lambda = 0$, hence $y = \frac{1}{2}$ which is the exponent found by Blatz and Tobolsky. Also of interest is that for constant coagulation-fragmentation an increase in the total primary particle-number density will shift s_0 to larger values for a given system. This is logical because coagulation depends on the density of other particles whereas fragmentation does not.

Family, Meakin, and Deutch performed a numerical simulation of a coagulation-fragmentation system with a constant coagulation kernel, hence $\lambda = 0$, and a sum fragmentation kernel with $\alpha = -\frac{1}{2}$. We numerically solved Eq. (12) with these homogeneities and compare the calculated mean size versus time to the simulation. The comparison, shown in Fig. 1, is very good.

The stability of Eq. (8), or equivalently Eq. (12), can be determined by rewriting as

$$ds^*/dt^* = s^{*\lambda}(1 - s^{*\alpha+2-\lambda}). \tag{16}$$

Inspection of Eq. (16) shows that for $\alpha+2-\lambda > 0$, ds^*/dt^* is positive for $s^* < 1$ and negative for $s^* > 1$, which in either case forces $s^* \to 1$. This is the stable case. For $\alpha+2-\lambda < 0$, the opposite behavior is found and $s^* \to \infty$ or $s^* \to 0$ depending on whether $s^* > 1$ or

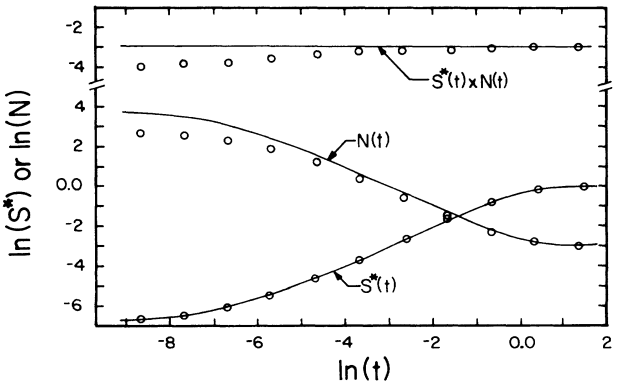

FIG. 1. Relative mean size, s^*, number density, N, and their product vs time for a coagulation-fragmentation system with $\lambda=0$ and $\alpha=-\frac{1}{2}$. The curve for s^* was derived by use of Eq. (12) and normalized to the same equilibrium size as found in the simulations of Family, Meakin, and Deutch (Ref. 7) which are represented by the circles.

$s^*<1$, respectively. This is the unstable case. Finally, it is easy to show with Eq. (8) that when $\alpha+2-\lambda=0$, the growth goes as t^z where $z=(1-\lambda)^{-1}$. Thus in summary the growth characteristics are

stable: $y^{-1}=\alpha+2-\lambda>0$,

unstable: $y^{-1}=\alpha+2-\lambda\leq 0$.

In the stable regime the time evolution far from equilibrium can be represented as power laws for both $s^*\ll 1$ and $s^*\gg 1$. For $s^*\ll 1$ Eq. (12) leads to $ds^*/dt^*\simeq s^{*\lambda}$, and thus $s^*\sim t^z$ where $z=(1-\lambda)^{-1}$ $(\lambda<1)$. For $s^*\gg 1$ fragmentation dominates and Eq. (12) leads to $ds^*/dt^*\simeq -s^{*\alpha+2}$, and thus $s^*\sim(c-t/z')^{z'}$ where c is a constant dependent upon the initial size and $z'=-(\alpha+1)^{-1}$. From this we find that the equilibrium exponent y is related to the dynamic exponents z and z' which govern the rate of nonequilibrium growth and fragmentation by

$$1/y=1/z-1/z'. \tag{17}$$

As the mean cluster size evolves, so does the total number of clusters N where

$$N=\sum_{k=1}^{\infty} n_k. \tag{18}$$

From the scaling form of $n_k(t)$ [Eq. (6)] one finds

$$N=M_1 s(t)^{-1}\int_0^{\infty}\phi(x)dx. \tag{19}$$

Combination with Eq. (13) leads to the equilibrium value of N behaving as

$$N_0\sim(k_f/k_c)^y M_1^{1-y}. \tag{20}$$

This behavior is rather interesting in that for $y<1$, N_0 increases with the monomer density, whereas for $y>1$, it decreases with the monomer number density. This behavior is a balance between coagulative forces that increase with monomer density and hence decrease N_0, and the simple dependence which would tend to increase N_0 if there were more monomers in the system. These tendencies balance when $y=1$ $(\alpha+1=\lambda)$ where N_0 does not depend on M_1.

Equation (19) implies that the product $s(t)N(t)$ should be a constant if a scaling size distribution has been achieved. The assumption of a scaling distribution was necessary to derive our evolution equation [Eq. (12)]. In Fig. 1 we plot sN versus time determined from the simulation of Family, Meakin, and Deutch. The product approaches a constant value implying a scaling distribution at long times when the mean size is >20 monomeric units, although it is constant to within a factor of 3 for the complete time range. Hence the scaling distribution assumption necessary for Eq. (12) is reasonably well satisfied in a practical sense. Also shown in Fig. 1 is $N(t)$ determined from the inverse of $s(t)$ and normalized to the experimental N_0.

We now consider in what manner a small fluctuation in s away from the equilibrium s_0 relaxes back to s_0 for the stable situation. Let δ be a small fluctuation given by

$$\delta=(s-s_0)/s_0=s^*-1. \tag{21}$$

Substitution into Eq. (12) and binomial expansion to first order yields

$$d\delta/dt^*=-y^{-1}\delta, \tag{22}$$

with solution

$$\delta=\delta_0 e^{-t/yt_0}. \tag{23}$$

Equation (23) shows that small fluctuations from the equilibrium size in a coagulation-fragmentation system relax back to equilibrium exponentially with characteristic time yt_0. Thus this dynamical system is analogous to more common thermodynamic systems in equilibrium. The time t_0 depends, of course, on the dynamical coefficients of coagulation and fragmentation through Eq. (14) which are microscopic properties, as opposed to dependence on macroscopic transport and thermodynamic coefficients in the usual thermodynamic picture. Whether this analogy can be applied for new insights to the microscopic-macroscopic connection, we do not yet know. In any event, it would be interesting to see if an equilibrated colloid would display these fluctuations.

In conclusion, we have found that the mean cluster size can evolve in time to an equilibrium size dependent on the ratio of strengths of the coagulation and fragmentation kernels and the primary particle concentration. Furthermore, the characteristic time of the approach to equilibrium is also dependent on these variables. Exponents in these relationships are determined by the homogeneities of the kernels. Both stable and nonstable

solutions exist as determined by the homogeneities. Small deviations from equilibrium in the stable situations relax exponentially. Further work should involve testing these predictions on real colloidal or aerocolloidal systems, and the intriguing possibility of describing thermodynamic relaxation in macroscopic systems in terms of coagulation and fragmentation of density or concentration fluctuations.

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