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Fluctuation effects in Smoluchowski reaction kinetics

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We introduce a new and extremely simple model for coagulation in which the reaction kernel K_{ij} in the Smoluchowski equation corresponding to the model can be adjusted exactly. For the special case of a constant K_{ij}, we deduce that for spatial dimension $d > d_c = 2$, the exact solution of the Smoluchowski equation is valid (mean-field theory). For $d < d_c$, fluctuations give rise to dimension-dependent kinetic exponents and a novel nonmonotonic cluster size distribution.

Coagluation is an important kinetic phenomenon that underlies a wide variety of applied science problems.[1,2] The classical approach for studying irreversible coagulation was first developed by Smoluchowski,[3,4] who wrote the following equation to describe the time evolution for the concentration of clusters of mass k, $c_k(t)$, under the assumption of binary collisions

$$\frac{dc_k(t)}{dt} = \frac{1}{2}\sum_{i+j=k} K_{ij}c_i(t)c_j(t) - c_k(t)\sum_{j>0} K_{jk}c_j(t) \quad . \tag{1}$$

In Eq. (1), the interaction kernel K_{ij} depends on the details of the collision process between i-mers and j-mers; this kernel embodies the dependence on i and j of the meeting probability of an i-mer and a j-mer. These include effects such as the mass dependence of the collision cross section and/or the diffusion constant.

The first term in (1) describes the increase in $c_k(t)$ owing to the coalescence of an i-mer and a j-mer with $i+j=k$, and the second term describes the decrease of $c_k(t)$ owing to the coalescence of a k-mer with other clusters. For specific forms of K_{ij}, a number of exact solutions and a variety of interesting asymptotic behaviors have been elucidated.[5-7]

It is important to emphasize that spatial fluctuations in $c_k(t)$ are not accounted for in Eq. (1). Thus, solutions of the Smoluchowski equation should be regarded merely as mean-field limits of the true kinetic behavior and these will be valid only above an upper critical dimension. Very recently, insights into the nature of coagulation kinetics in lower dimensions have been gained through numerical simulations,[8-10] and interesting features emerge which are not evident from an analysis of the Smoluchowski equation. Unfortunately, a connection with the mean-field predictions based on the solutions to the Smoluchowski equation cannot be readily made for two reasons. First, owing to the geometrical complexity of the constructed aggregates,[8,9] the functional form of the K_{ij} cannot be determined analytically, and second, the upper critical dimension of the simulated systems is not known.

In this Rapid Communication, we introduce a new and very simple model for coagulation in which the functional form of K_{ij} in the Smoluchowski coagulation equation corresponding to our model can be adjusted exactly. This is accomplished by retaining only the kinetic aspects of the cluster aggregation simulations mentioned above, and discarding the geometric aspects which are superfluous for kinetic considerations. Our model permits a direct comparison between numerical simulations and solutions of the Smoluchowski equation to be made. Moreover, owing to the simplicity of our model, simulations which are orders of magnitude more extensive than previous studies can be easily performed. From these simulations and by appealing to analogies with two-body decay reactions, we shall elucidate the role of spatial fluctuations on the kinetics of coagulation. Our primary result is that there exists an upper critical dimension $d_c = 2$, above which the solutions to the Smoluchowski equation provide an accurate description of coagulation. However, for $d < d_c$, fluctuations in the spatial distribution of clusters gives rise to non-mean-field kinetics characterized by dimension-dependent exponents and a nonmonotonic cluster size distribution.

In our model, clusters are defined to be *single* lattice sites. When two clusters of masses i and j meet, they coalesce into a single point cluster of mass $i+j$. Thus the technical complications of moving extended clusters, and the difficulty of deducing the form of K_{ij} for coalescence of extended clusters are both eliminated. It is now possible to achieve exactly many interesting functional forms for K_{ij} by assigning various mass dependences to both the interaction radius and diffusion constant of a given cluster. Here we shall treat only the simplest case of a constant $K_{ij}(t\ \forall\ i,j)$, and the generalization to other functional forms of K_{ij} will be treated in future publications.

A constant K_{ij} is achieved by assigning the same diffusion constant to each cluster, independent of mass, and by defining a collision between two clusters to occur only when the clusters are on the same lattice site. By these definitions, K_{ij} is manifestly a constant. This provides an idealized model for coagulation of Brownian particles,[3,4] where the effects of the growing collision cross section and decreasing diffusion constant as the cluster mass increases, are taken to approximately balance.

For a constant K_{ij}, the solution to Eq. (1) is given by

$$c_k(t) \sim t^{k-1}/(1+t)^{k+1} \underset{t\to\infty}{\longrightarrow} t^{-2}e^{-k/t} \quad , \tag{2a}$$

$$\sum_k c_k(t) \sim (1+t)^{-1} \quad . \tag{2b}$$

From the asymptotic form of $c_k(t)$ for large but fixed t, notice that the cluster size distribution decays monotonically; there is essentially no decay for small k, and then there is an exponential decay for k greater than a typical cluster size k^*, which grows linearly with time.

To study the effects of fluctuations in the constant kernel

coagulation process,

$$A_i + A_j \xrightarrow{K} A_k \ ,$$

we note that the reaction can be regarded more simply as the coalescence reaction, $A + A \rightarrow A$, if one ignores the masses of each cluster. We expect[11] that the latter reaction should be in the same universality class as $A + A \rightarrow 0$, for which it is known[12–16] that for spatial dimension $d < 2$, the density of A's, $\rho_A(t)$, decays as $t^{-d/2}$, while for $d > 2$, the rate equation (or mean-field) decay of t^{-1} is valid, and when $d = d_c = 2$, the decay is $(t/\ln t)^{-1}$ (Ref. 15). Owing to the analogies between the various reactions, the number of clusters in constant kernel coagulation, $\sum_k c_k(t)$, will be the same as $\rho_A(t)$ in the coalescence reaction.

To gain an initial insight into the kinetics of coagulation for $d < 2$, we introduce a time-dependent reaction kernel or rate constant into the Smoluchowski equation. Such a device has previously proved useful in understanding the non-mean-field decays in two-body reactions.[16] If one regards coagulation as the reaction $A + A \rightarrow A$, the associated rate equation, $\dot{\rho}_A(t) = -k\rho_A(t)^2$ can be modified to give the correct kinetics for $d < 2$, by choosing k proportional to $t^{d/2-1}$. This time dependence phenomenologically describes the decrease in the meeting probability of two A particles owing to the development of large-scale spatial inhomogeneities. For coagulation in $d < 2$, we are therefore led to choose $K_{ij} \sim \text{const} \times t^{d/2-1}$ to account empirically for fluctuation effects in the Smoluchowski equation. With this form of K_{ij} substituted in Eq. (1), one immediately finds solutions of the form given in Eq. (2), except that t is replaced by $t^{d/2}$ wherever it appears. Therefore, this approach predicts that the qualitative features of coagulation for $d > 2$ are reproduced in $d < 2$, but that quantitative modifications

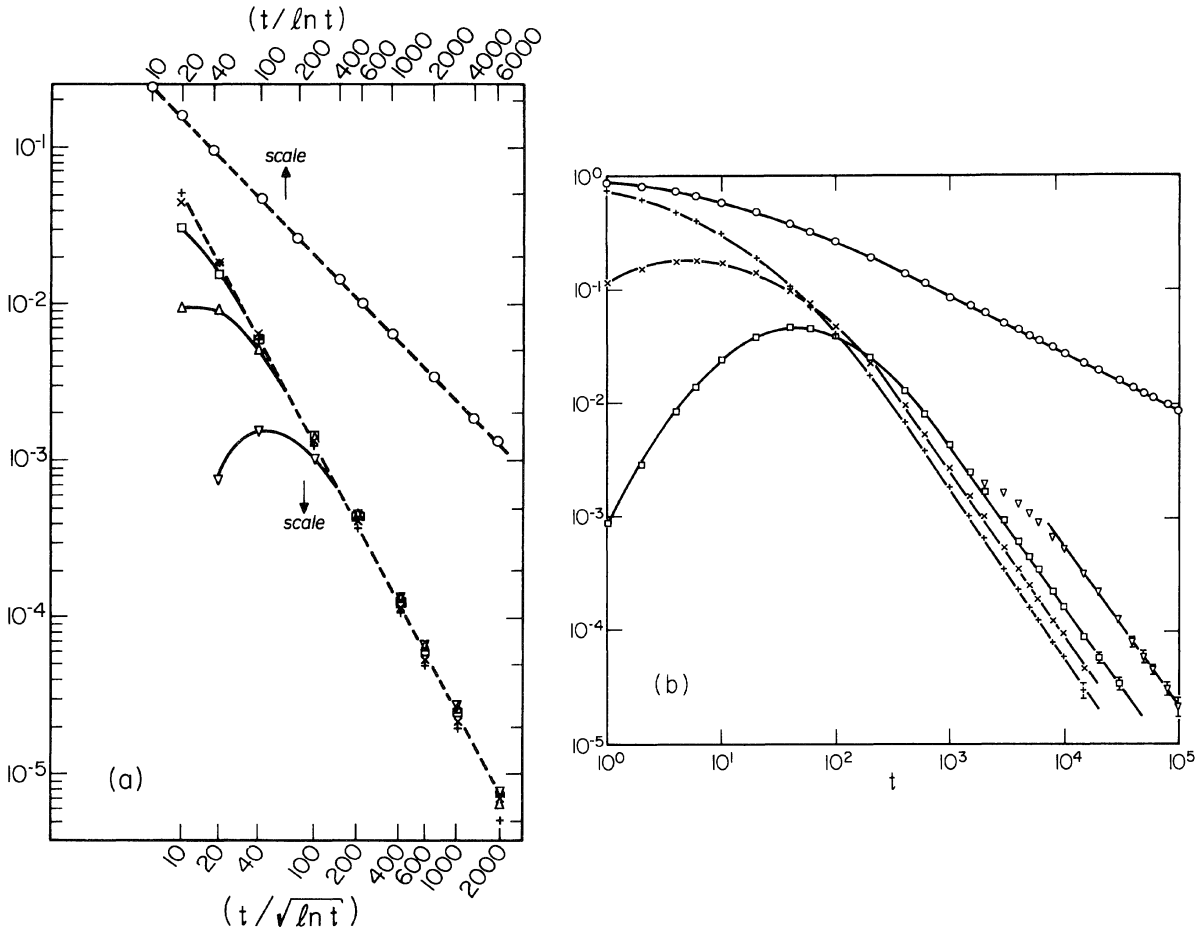

FIG. 1. (a) Typical simulation results for constant kernel coagulation on the square lattice based on 100 configurations with an initial state of 4×10^5 particles placed randomly on a $10^3 \times 10^3$ lattice. The decays of representative cluster densities (normalized by the initial density) are plotted on a double logarithmic scale. Note the different horizontal axes for $\sum_k c_k(t)$ and for the various $c_k(t)$ to illustrate the logarithmic corrections. The curves serve as guides to the eye, the dashed lines have slopes of -1 and -2, and for convenience, the values of t are labeled. (b) Typical simulation results on a linear chain of 10^6 sites based on 30 configurations with an initial state of 2×10^5 particles. Asymptotically, $\sum_k c_k(t)$ follows a straight line of slope $-1/2$, while the $c_k(t)$ follow straight lines of slope $-3/2$. The symbols refer to the following quantities: (○) $\sum_k c_k(t)$, (+) $c_1(t)$, (×) $c_2(t)$, (□) $c_4(t)$, (Δ) $c_8(t)$, and (▽) $c_{20}(t)$.

of kinetic exponents occur.

To test these predictions, we have performed numerical simulations for both the square lattice and the linear chain. Owing to the point nature of the clusters, percolation effects are irrelevant, and one may even choose an initial density equal to unity, which leads to more rapid convergence to asymptotic behavior. On the other hand, it appears that our model is in the same universality class as growing cluster-cluster aggregation in one dimension only, in the dilute limit. As long as the average intercluster distance is much larger than the typical cluster length, the influence of the growing cluster boundaries on the kinetics should be immaterial.

For the square lattice, we clearly observe that the total number of clusters, $\sum_k c_k(t)$ varies as $(t/\ln t)^{-1}$ [Fig. 1(a)]. Interestingly, one observes in Fig. 2(a) a weak nonmonotonicity is the cluster size distribution, in contradiction with Eq. (2a). Furthermore, each $c_k(t)$ appears to decay at the same rate for all k, and the data are well fit by the expression $(t/\sqrt{\ln t})^{-2}$. However, for the linear chain, the simulations disagree strongly with the predictions based on solving an "effective" Smoluchowski equation with a time-dependent reaction kernel [Fig. 1(b)]. We do observe that $\sum_k c_k \sim t^{-1/2}$, as predicted from the effective Smoluchowski equation, but $c_k(t)$ decays as $t^{-3/2}$, and the cluster size distribution is strikingly *nonmonotonic* in k [Fig. 2(b)].[17] This nonmonotonicity, and the decay of $c_k(t)$ faster than the effective Smoluchowski equation prediction, are closely connected. In order to understand this, it is helpful to write $c_k(t)$ in the following scaling form:[18]

$$c_k(t) \sim t^{-w} k^{\tau} f(k/t^z) \ , \tag{3}$$

where the power k^{τ} is included to describe the observed vanishing of $c_k(t)$ as $k \to 0$. As dictated by our simulation results, the scaling function $f(x) \to 1$ for $x << 1$, and $f(x)$ decays rapidly for $x >> 1$. In terms of this scaling form we have

$$\sum_k c_k(t) \sim t^{-w+(\tau+1)z} \ , \tag{4a}$$

$$\sum_k k c_k(t) \sim t^{-w+(\tau+2)z} \ . \tag{4b}$$

As already discussed, the first quantity varies as $t^{-1/2}$, while the second quantity is the total cluster mass, and is therefore a constant. Thus, we obtain $z = 1/2$ and $w = 1 + \tau/2$, and conclude that the nonmonotonicity of the cluster size distribution leads to a decay of $c_k(t)$ which may be faster than t^{-1}.

This line of reasoning does not predict the value of w, but we can give an argument that $w = 3/2$ for the linear chain, by making a connection between our model and Fisher's "vicious" random walk model.[19] The argument makes use of an assumption that the asymptotic decay of each $c_k(t)$ is independent of k; thus it will suffice to consider only the decay of the monomers. Focusing attention on a particular monomer, it will "decay" (i.e., coalesce) by reacting with either of its two nearest neighbors. These neighbors may grow in mass as a function of time, but this is immaterial for understanding the decay of the central monomer. It suffices, therefore, to consider only the three-body problem of a monomer and its nearest neighbors. For the monomer to survive, the two neighbors cannot meet, and the monomer cannot meet with either neighbor. The avoidance probability for any pair of particles varies as $t^{-1/2}$, and while each pair avoidance is not strictly independent, Fisher showed that the central particle will survive with probability $(t^{-1/2})^3 = t^{-3/2}$.

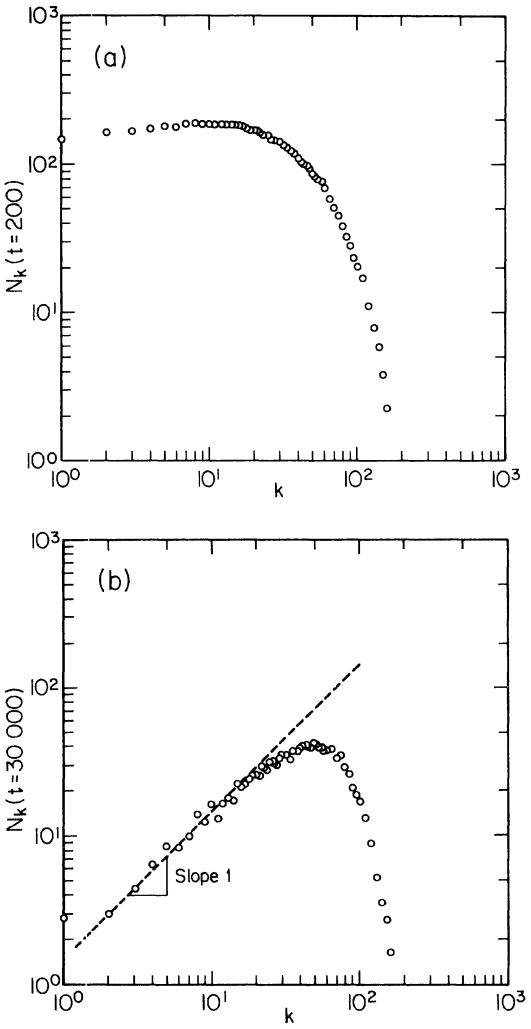

FIG. 2. (a) Cluster size distribution for the square lattice after 200 time steps and (b) the distribution for the linear chain after 30 000 time steps. Plotted are the number of clusters, $N_k(t)$, based on the same data shown in Fig. 1. In (b), the dashed line has slope +1.

This analogy now explains the decay observed in the simulations of coagulation on the linear chain. In addition, by scaling and the sum rules, Eqs. (4a) and (4b), we expect that the cluster size distribution will grow linearly with k for small k as observed in Fig. 2(b). The nonmonotonic cluster size distribution disagrees with the predictions of an effective Smoluchowski equation with a time-dependent but mass-independent K_{ij}. In order to derive the fluctuation-induced nonmonotonicity by an Smoluchowski-type equation, it appears that K_{ij} must acquire a mass dependence as well as a time dependence.

In conclusion, we have introduced an extremely simple, albeit idealized model for coagulation in which clusters remain point particles throughout the process. Through this model, we can make a direct connection with the Smoluchowski coagulation equation, and determine its range of validity. For the special case of a constant reaction kernel in the Smoluchowski equation, we find that it is valid above an upper critical dimension $d_c = 2$. For $d = 2$, simulations indicate that logarithmic corrections of the form

$$\sum_k c_k(t) \sim (t/\ln t)^{-1}$$

and

$$c_k(t) \sim (t/\sqrt{\ln t})^{-2}$$

should occur. For $d < 2$, fluctuations in the spatial distribution of the clusters renders a Smoluchowski equation description, which neglects these fluctuations, invalid. Our numerical simulations for the linear chain show that $\sum_k c_k(t) \sim t^{-1/2}$, while $c_k(t) \sim t^{-3/2}$. For the range $1 < d < 2$, normally achieved by a fractal set, dynamic phenomena are governed by the fracton dimension d_s.[20] For a fractal with $d_s < 2$, it is known that $\sum_k c_k(t)$ decays as $t^{-d_s/2}$ (Refs. 15 and 16). Furthermore, we note that the ratio $c_k(t)/\sum_k c_k(t)$ appears to be dimension independent, decaying as t^{-1}. This observation, together with the sum rules, Eqs. (4a) and (4b), suggest that $w = 1 + d_s/2$ and $\tau = 2/d_s - 1$; for example, on a percolation cluster at threshold, where d_s is believed to equal 4/3, we expect $w = 5/3$ and $\tau = 1/2$.

The simplicity of our model opens the possibility of many interesting generalizations. It will be worthwhile to study fluctuation effects in systems with reaction kernels of the form $K_{ij} \sim (i^\omega + j^\omega)$ and $(ij)^\omega$. The latter form leads to gelation in a finite time,[5,6] but fluctuations could strongly modify this behavior. Another interesting situation is reversible coagulation, where breakup processes can occur. Finally, it should be fruitful to study situations for which the solutions to the corresponding Smoluchowski equation is not known, so that the various universality classes of coagulation kinetics can be mapped out.

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