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There were three primary goals of this project. First, we elucidated fundamental aspects of the kinetics of diffusion-controlled reactions. While the rate equations provide a useful starting point for treating reaction kinetics, this approach neglects the effects of fluctuations, and these can play a dominant role in governing the kinetics in the diffusion-controlled limit. Thus it is crucial to determine exactly when and in what manner fluctuations manifest themselves. A second broad goal of this project was to map out the kinetics (over)				
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of general classes of aggregating and fragmenting systems. Intriguing non-universal behavior was found for aggregation processes in which there is more than one type of monomeric species. Novel steady-state properties were found in an aggregating system with localized input and output. A scaling theory was also developed to understand the kinetics of fragmentation processes. Our very general approach allowed us to classify essentially all previous results into simple universality classes. Finally, the dynamics of random multiplicative processes were studied, and the role of correlations in determining statistical properties was elucidated.

KINETICS OF DIFFUSION-CONTROLLED REACTIONS

FINAL REPORT

Sidney Redner

AUGUST 22, 1989

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1. Foreword

There were three primary goals of this project. First, we elucidated fundamental aspects of the kinetics of diffusion-controlled reactions. While the rate equations provide a useful starting point for treating reaction kinetics, this approach neglects the effects of fluctuations, and these can play a dominant role in governing the kinetics in the diffusion-controlled limit. Thus it is crucial to determine exactly when and in what manner fluctuations manifest themselves. A second broad goal of this project was to map out the kinetics of general classes of aggregating and fragmenting systems. Intriguing non-universal behavior was found for aggregation processes in which there is more than one type of monomeric species. Novel steady-state properties were found in an aggregating system with localized input and output. A scaling theory was also developed to understand the kinetics of fragmentation processes. Our very general approach allowed us to classify essentially all previous results into simple universality classes. Finally, the dynamics of random multiplicative processes were studied, and the role of correlations in determining statistical properties was elucidated.

These topics are treated in more detail in the following report. In Sec. 2, we discuss the role of fluctuations and conservation laws in diffusion-controlled reactions. In Sec. 3, the kinetics of various aggregation processes are discussed. In Sec. 4, general results for the kinetics of fragmentation are outlined. Finally, in Sec. 5, some novel properties of random and correlated multiplicative processes are treated.

2. Diffusion-Controlled Reactions: Fluctuations and Conservation Laws

The kinetics of chemical reactions have been extensively studied, both in the mean-field,¹⁻³ and in the diffusion-controlled limits.^{4,5} Generally, the behavior in the diffusion-controlled limit is considerably different than that of the mean-field limit, for systems of spatial dimension d less than the upper critical dimension d_c .⁶⁻⁹ This difference stems from the recurrent nature of diffusive motion in low-dimensional systems. Recurrence means that the reaction probability for nearby particles is unity, leading to large fluctuations in local concentrations of reactants. In contrast, for the mean-field, or rate equation description, the two-particle reaction probability is distance independent. Typical examples which illustrate this fundamental difference are 1-species annihilation,^{7,9,12} $A + A \rightarrow \text{inert}$, and 2-species annihilation,^{7,8} $A + B \rightarrow \text{inert}$. In the former case, the density decays as $t^{-d/2}$ for $d < d_c = 2$, while in the latter case the density decays as $t^{-d/4}$ for $d < d_c = 4$ when the initial densities of A and B are equal. Above the upper critical dimension, however, fluctuations become irrelevant and the density decays as $1/t$.

We studied a number of reactions whose behavior is considerably richer than the two aforementioned processes.¹⁰ In our n -species model, n distinct species react only with different species. In the limit $n = 2$, the reaction reduces to $A + B \rightarrow \text{inert}$, while for $n \rightarrow \infty$, the constraint of reacting only with different species becomes negligible, and the reaction becomes equivalent to $A + A \rightarrow \text{inert}$. For the interesting intermediate case of finite n , we determined the kinetics on the basis of conservation laws. For $n = 2$, the density difference is conserved both locally and globally, while for $n > 2$, the n -species reaction obeys a conservation law which is valid only *globally*. The ramifications of global vs. local conservation laws, together with the discrete nature of the system leads to the density decaying as $t^{-\alpha(n)}$, with $\alpha(n) = \frac{d}{2}(1 - \frac{1}{2(n-1)})$ for $d < d_c = \frac{4(n-1)}{2n-3}$. This unusual

result appears to agree with numerical simulations.¹⁰ Our approach was also applied to more realistic reaction processes; this work is still in progress.

3. Aggregation and Growth Kinetics

(a) 2-Species Aggregation

Aggregation is the irreversible bonding process $A_i + A_j \xrightarrow{K(i,j)} A_{i+j}$, where A_i denotes a cluster of mass i , and $K(i,j)$ is the rate at which an i -mer and a j -mer react to form a cluster of mass $i+j$. Much of the current understanding of aggregation kinetics is based on the analysis of rate equations.¹¹⁻¹⁵ These equations represent a mean-field approximation, as fluctuations in the cluster densities and shapes are ignored. Within this approximation, three broad classes of behavior may be delineated, which depend on general features of the dependence of the matrix of reaction rates on i and j .¹⁶ In "type-I" systems, the reaction of large clusters with other large clusters dominates over reactions between small clusters, while in "type-III" systems, large-small reactions predominate. The latter occurs in the aggregation of Brownian particles in solution,¹⁴ and is characterized by a sharply-peaked cluster-mass distribution. In "type-II" systems, all reactions are equivalent in a scaling sense.

We introduced simple, two-species aggregation models which exhibit unusual kinetic behaviors that lie outside this accepted general framework.¹⁷ These models are based on the observation of apparent parity-dependent reaction rates for the aggregation of carbon clusters.¹⁸ For our model, the exponents characterizing the kinetics are non-universal and depend on the values of the reaction rates. Furthermore, a conventional scaling description of the cluster-mass distribution is no longer valid. These novel features occur for models which ostensibly are in the universality class of constant-kernel coagulation.

We first considered a two-component system with constituent bifunctional monomers A and B , in which bonding occurs only between unlike species. This leads to aggregates which have the structure of an alternating linear copolymer. If we ascribe a "charge" $+1$ to the A 's and a charge -1 to the B 's, then a very simple and appealing physical picture of the aggregation process was developed. According to the restriction of A - B bonding and bifunctionality, the charge is restricted to 0 or to ± 1 , and three types of reactions can occur: (a) a positive and a negative cluster can join to form a neutral cluster, (b) two neutral clusters can join to form a larger neutral, and (c) a neutral and a charged cluster can join to form a heavier cluster with charge being conserved.

The charge conserving reaction (a) is isomorphic to $A + B \rightarrow \text{inert}$, while reaction (b) is a single-species fusion reaction, $A + A \rightarrow A$. These two processes have an upper critical dimension, $d_c = 4$,^{9,10} and $d_c = 2$,¹¹ respectively. The interplay between the charged and neutral clusters due to reaction (c), with the individual kinetic behaviors of these two species being very different, is the mechanism underlying many unusual kinetic properties.

In order to account for the consequences of this parity-dependence analytically, we calculated the solutions to the rate equations for a system with explicit parity-dependent reaction rates.¹⁸ The exponents describing the temporal behavior of the system were found to be non-universal functions of the microscopic reaction rates. Furthermore, in two special cases, we derived a full solution for the cluster-mass distribution and showed that conventional scaling fails. The origin of these intriguing results stems from two competing influences on the time dependence of neutral clusters: on one hand, reactions between

charged clusters act as an external source of neutral clusters, while processes involving one or two neutral clusters cause one neutral cluster to disappear. This again points to the interplay between neutral and charged clusters and the mechanism which leads to new phenomena. These novel effects may be expected to play role in the aggregation of charged objects, such as finely ground powders.

(b) Droplet Growth Kinetics

In the classical rate equation description of aerosol growth, i.e., spherical droplets which move by Brownian motion in three dimensions, the reaction kernel has the form $K(i, j) \propto 2 + (i/j)^{1/3} + (j/i)^{1/3}$. From the solution to the resulting system of rate equations,¹⁴ one obtains a non-monotonic cluster mass distribution, a total density decaying as t^{-1} , and the monomer density decaying as $\exp(-at^{1/3})$. In order to test the applicability of the rate equations for this case, we undertook large-scale simulations of this process. In addition to affording an unambiguous measurement of the reaction rates, this numerical approach allowed us to observe the kinetics of aerosol growth directly. Our results indicate that a three-dimensional system is not adequately described by a system of rate equations, as the rate of monomer decay is considerably slower than that predicted by the rate equations.¹⁹

In addition, the rate equation approach is based on the restriction to reactions occurring only by binary collisions. However, the kinetics was found to depend strongly on the initial density, suggesting that higher-order interactions are relevant. This feature is in strong contrast to the rate equation predictions. Moreover, for droplets of any degree of ramification, the volume density of the aggregates increases with time, causing higher-order interactions to become increasingly-important. This appears to be the source of the unusual density-dependent effects.

Our work on aerosol growth naturally led to the problem of droplet growth and coalescence on a tilted substrate, with ensuing "avalanches", whenever the droplet mass exceeds a given threshold value.²⁰ In addition to modelling raindrops on a windowpane, this model exemplifies transport in an open system in which there is a continuous input of matter, and in which there is an inertial transport "barrier". It has been suggested that such open systems naturally evolve to a self-organized critical state, with power law decay of dynamical correlation functions. The primary difference between the "sandpile" models used to model this self-organized criticality,²¹ and our model is that the former is entirely dissipative, while ours is governed by inertial effects. This contrast gives rise to fundamentally different physical behaviors in the two models.

In our model, there is a continuous deposition of mass on a "tilted" substrate, with avalanches occurring whenever the mass at a given site reaches a pre-assigned threshold value h_c . The avalanche is defined to sweep away all mass which is downhill from the avalanche event; there is no mechanism for stopping the avalanche once it starts. For a one-dimensional slope of length L , we found that the average avalanche size and the average time between avalanches in the steady-state scale as L^{1-1/h_c} , while the steady-state mass at a distance x from the top of the slope scales as x^{-1/h_c} . The distribution of times between successive avalanches is sharply peaked about its average value, so that there is a rapid decay of inter-avalanche correlations. Moreover, the dynamical behavior in the two limits of small and large h_c are quite different. In the former case, the downhill portion of the slope has time to fill up after an avalanche so that the position of successive avalanches is

only weakly correlated. However in the large h_c limit, the location of successive avalanches move progressively uphill until a "renewal" avalanche occurs which sweeps the slope clean. The dynamics associated with this unusual process were determined.

(c) Coagulation with Localized Sources and Sinks

The steady state of an aggregating system with a continuous input of monomers typifies a wide variety of physical situations,^{22,23} ranging from the mass distribution of stars,²⁴ to cluster distributions in chemical reactors.²⁵ The primary theoretical approach to elucidate these phenomena is the rate equations, suitably modified to account for the spatially homogeneous input.²²⁻²⁸ For such an input, the steady-state concentration of clusters of mass k has the form $c_k \sim k^{-\beta}$, with a universal exponent value $\beta = 3/2$ for reaction kernels with homogeneity index equal to zero.^{22,23}

We investigated steady-state coagulation in the presence of spatially *localized* monomer input.²⁹ One possible application is a smoke plume, where there is a steady input of small clusters at the lower end of the plume, with coagulation occurring as the smoke clusters rise. The distance from the source is a relevant parameter in describing the cluster size distribution in this process. We developed an idealized model in which monomer is introduced continuously at a *single* point (the origin), and all the previously-introduced clusters in the system undergo diffusion, and aggregation whenever two clusters meet.

This system exhibits a spatially-inhomogeneous steady state. For spatial dimension $d > 4$, the reaction is irrelevant in a scaling sense, and the dynamics is determined only by the steady point source. The steady-state cluster concentration, $c(r)$, therefore obeys Laplace's equation. For $d < 4$, the reaction becomes relevant, leading to a new type of reactive steady-state. The steady-state concentration of clusters of mass k a distance r from the source scales as $c_k(r) \sim k^{-\tau} \phi(kr^{-z})$, with $z = 4 - d$, $\tau = \frac{d-6}{d-4}$ for $d > 2$, and $z = 2$, $\tau = 1 + \frac{d}{2}$ for $d < 2$.

For the linear chain, we also calculated an exact solution for the problem which gives $c_k(r) \sim k^{-3/2} \phi(\mu)$, with $\phi(\mu) \sim \mu^{5/2}$ for $\mu = k/r^2 \rightarrow 0$, and $c(r) \sim r^{-1}$. For a source which is turned on at $t = 0$, the total number of clusters increases with time t as $\ln t$. This anomalously slow growth originates from the recurrent nature of diffusion. Because random walks always return to the source, an overwhelming number of input monomers aggregate relatively quickly with previously-introduced clusters. This gives rise to a strong "screening" of the source by the steady-state concentration profile. Corresponding results were also given for point-source coagulation in the presence of cluster drift and in the presence of a sink.

4. Kinetics of Fragmentation

A basic goal of our work was to provide a general theoretical description of the evolution of the fragment size distribution that results from irreversible, continuous fragmentation processes. Our treatment is based on applying scaling to obtain asymptotic information about the solutions to the rate equations for a general classes of models.³⁰ An important feature of fragmentation is that the typical cluster size decreases with time due to particle breakup. The vanishing of the typical size is analogous to the vanishing of the inverse correlation length for a system near a second order phase transition. Thus at long times, one can invoke scaling ideas and universality to describe the nature of the cluster size distribution.

We found that only a few details of the breakup process are relevant in determining basic features of the fragment size distribution at long times. Our approach parallels analogous developments in the investigation of the solutions to the rate equations for the inverse process of aggregation.^{16,31-33} For linear fragmentation, we considered homogeneous systems in which a cluster of mass x breaks up at a rate which varies as x^λ , and in which the rate of production of a fragment of mass x , from the breakup of a cluster of mass y , depends only on the ratio x/y . The corresponding rate equations are,^{30,34-36}

$$\frac{\partial c(x,t)}{\partial t} = -a(x)c(x,t) + \int_x^\infty c(y,t)a(y)f(x|y)dy. \quad (1)$$

Here $c(x,t)$ is the concentration of clusters of mass x at time t , $a(x) = x^\lambda$ is the *overall* rate at which x breaks, while $f(x|y) = y^{-1}b(x/y)$ is the *relative* breakup rate, i.e., the conditional probability at which x is produced from the breakup of y . The term $-a(x)c(x,t)$ accounts for the loss of x -mers due to their breakup, while the second term accounts for the gain of x -mers by the breakup of particles with mass $y > x$.

According to scaling, $c(x,t)$ is not a function of x and t separately, but rather is a function only of the ratio of the mass to a dynamically evolving typical cluster mass $s(t)$. That is,

$$c(x,t) = s^{-2} \phi(x/s(t)), \quad (2)$$

where the exponent -2 is required by mass conservation. With this ansatz, we found the following universal asymptotic behaviors for $\phi(x)$. In the large-mass limit, $\phi(x) \sim x^{b(1)-2} \exp(-ax^\lambda)$, where the constant a equals $1/(\lambda\omega)$. In the small-mass limit, there is a lesser degree of universality, since the small mass tail is not directly influenced by particles of the typical size. However, there are only two generic forms for $\phi(x)$, whose applicability depends on whether or not there is a cutoff in the smallest size fragment produced in a single breakup event. In the case where a cutoff exists, the controlling factor of $\phi(x)$ is the classical log-normal form $\phi(x) \sim \exp[-b(\ln x)^2]$ as $x \rightarrow 0$. In the opposite case where infinitesimally small flakes can be produced in a single breakup event, $\phi(x) \sim x^\nu$ as $x \rightarrow 0$.

We also showed that $\lambda > 0$ is the necessary and sufficient condition for the applicability of conventional scaling. For $\lambda < 0$, we developed a new scaling approach for which the typical mass is determined by the initial conditions.³⁰ In addition, systems characterized by $\lambda < 0$ undergo a shattering transition in which mass is lost to a "dust" phase of zero mass particles.^{35,36} The intriguing features of this shattering transition were elucidated.

Finally, we considered the role that non-linear effects might have on fragmentation. One potential example is fragmentation induced by collisions between fragments, as might arise in an explosive process, or in the breakup of small fluid eddies.³⁷ As an idealization, we treated *collision-induced* fragmentation, in which fragmentation products continuously participate in repeated collisions and fragmentations.³⁰ We introduced a particular class of "splitting" models for which a fragmenting cluster always breaks into two equal-sized pieces. In model I, both colliding fragments split in two upon collision, while in models II and III, only the larger, or only the smaller of the two colliding fragment splits in two, respectively. These models are essentially non-linear and very rich phenomenologically, yet still simple enough to solve.

Scaling was found to be valid for different ranges of λ . Model III is unique in that large clusters are "frozen out" of the fragmentation process at long time. This leads to

a monotonic fragment size distribution, with a power law tail at large masses, while the distributions in models I and II are non-monotonic and decay quasi-exponentially for large mass. In model III the concentration of fragments of any finite size decays as a power law in time, while in models I and II the concentrations decay exponentially. Some of these features strongly contrast with the behavior of linear fragmentation, and may therefore be useful as a diagnostic test for the mechanism underlying a particular fragmentation process.

5. Random Multiplicative Processes

(a) Probability distribution for random products

The statistical properties of the product of N random variables was elucidated.³⁸ We showed that the distribution of the product and the functional dependence of the moments are crucially sensitive to extreme events. There is no analog of a central limit theorem, as in the case of random additive processes, for which typical events are sufficient to determine the statistical properties of the sum of a large number of random variables. As a concrete example, we considered the statistical properties of an N -fold product in which the number z_1 appears with probability p and the number z_2 appears with probability $q = 1 - p$. For this process, the average value of the product, $\langle P \rangle$ equals $(pz_1 + qz_2)^N$, which is much larger than the most probable value, $P_{mp} = (z_1^p z_2^q)^N$, as $N \rightarrow \infty$.

In the limit of large N , a time-honored approximation for determining the distribution of products is based on noting that the logarithm of the product, $\ln P$, is the sum of N random variables, so that $\ln P$ obeys a Gaussian distribution. This leads to the classic *log-normal* form for the distribution of the product.³⁹ By this construction, however, information about the tail of the distribution has been lost, and these details are needed to calculate the higher moments. We have shown explicitly that the k^{th} moment of the product is determined by a distinct portion of the probability distribution. Thus the statistical properties of the moments cannot be captured within a single functional form for the probability distribution. We have determined the correct continuum limit to be a log-normal function, but one whose precise form depends on the order of the moment being considered.^{38,40} This emphasizes that there does not exist a unique scale which accounts for all the moments of the product.

We have also discussed how these features would appear in numerical simulations of random multiplicative processes. Numerically observed "averages" are determined by the extreme events that appear in a finite number of realizations of a random product, and we have derived the condition which specifies the nature of these extreme events. In an ensemble of R realizations of the N -fold product, the largest product value is characterized by a maximal number n_+ of appearances of the factor z_1 in the product. This maximal value is given³⁸ by the fundamental condition $n_+ \simeq Np + \sqrt{2Npq \cdot \ln R}$. Thus n_+ is greater than the typical value of $n = Np$ by an amount that is of the order of $\sqrt{N}$ when the scale of the simulation is small, i.e., typical random walk fluctuations, and n_+ approaches the maximum possible value of N only when the simulation is large enough to sample a finite fraction of all events, i.e., when $R \gtrsim R^* \sim O(2^N)$. When R reaches R^* , $\sqrt{N \cdot \ln R}$ becomes of the order of N , and the most extreme events in the entire sample space are now accessible. It is only when this finally happens that a simulation can provide accurate numerical estimates. The logarithmic dependence of the magnitude of the extreme event on the size of the ensemble provides the basis for an idealized, but quantitative account

of the crossover to asymptotic behavior. Thus numerical estimates from realistic-scale simulations of a random multiplicative process have no relation to true average values.

(b) Random walk in a random multiplicative environment

A natural outgrowth of the previous work on random multiplicative processes is the problem of a random walk moving in an environment containing traps and sources.⁴¹ This is a random multiplicative process, but one in which there are correlations induced by the diffusive motion of the random walker. Each time a random walk A visits a defect B (a trap or source), the reaction $A + B \rightarrow (1 + \epsilon)A + B$ takes place. That is, the defect is unaltered, while the random walker is "multiplied" by a factor $1 + \epsilon$. For $\epsilon > 0$, the ϵ new walkers are spawned when a walker meets the source, while if $-1 \leq \epsilon < 0$, the defect is a trap, and the incident walker is partially absorbed for $\epsilon > -1$, or totally absorbed, when $\epsilon = -1$. This model provides an idealized description for the number for neutrons in a radioactive material where radioactive nuclei acts as sources, and moderator acts as traps. We discussed the conditions that give rise to growth or decay of the average number of particles and elucidate the role of correlations in determining the asymptotic behavior of this type of multiplicative process.

For a single source-trap "dipole", we found an exact solution for the kinetics. There may be either a trap-dominated algebraic decay, or a source-dominated exponential growth of the number of walkers, depending on the distance L between the two defects. Interestingly, a very weak source ultimately dominates over an arbitrarily strong trap if L is large enough. The dipole was also useful for elucidating the role of correlations, induced by the successive visits of the walker to the same defect, in the multiplicative process governing the number of walkers. This shows that there is an equivalence between a random walker in the presence of a dipole of span L consisting of a source of strength σ and a trap of strength τ , and a random multiplication of the equiprobable factors σ^L and τ^L .

The role of rare events in determining the dynamics of a random walker was also seen from our treatment of a periodic source-trap distribution. For a period- L chain consisting of a source followed by $L - 1$ traps, the most probable number of random walks varies as $\sigma\tau^{(L-1)}$. Thus for $\sigma \sim 1/\tau^L$ one would expect no change in the density of the diffusing particles. However, we found that the condition for a stationary *average* number of walkers is $\sigma \sim 1/\tau$ as $L \rightarrow \infty$. This shows that the very rare walks which visit the source L times as frequently as any of the traps, dominate the average. Likewise, for a single source in a homogeneous background of traps, walks which stay confined near the source dominate the average, so that the effect of a single source may win over that of many traps. This leads to anomalous growth kinetics for the number of particles. In most practical situations, however, the sample of random walks available is much smaller than the complete ensemble of possible walks, and one observes most probable values rather than true averages. The dichotomy between these two behaviors has been emphasized.

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