Coagulation with a Steady Point Monomer Source

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We investigate the phenomenon of coagulation with constant feed-in of monomers at a *single* point. For spatial dimension $d > 4$, the steady-state cluster concentration, $c(r)$, obeys Laplace's equation, while for $d < 4$, 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 $z = 4 - d$, $\tau = (d-6)/(d-4)$ for $d > 2$, and $z = 2$, $\tau = 1 + d/2$ for $d < 2$. For the linear chain, we outline an exact solution for which $c_k(r) \sim k^{-3/2}\phi(\mu)$, with $\phi(\mu) \sim \mu^{5/2}$ for $\mu = k/r^2 \to 0$, $c(r) \sim r^{-1}$, and the number of clusters increases with time t as $\ln t$. The effects of cluster drift and the presence of a sink are also considered.

With a steady feed-in of monomers, a coagulating system can reach a steady state.[1−6] This process typifies a wide variety of physical situations, ranging from the mass distribution of stars,[2] to cluster distributions in chemical reactors.[3] Theoretical approaches to elucidate these phenomena include mean-field theories, suitably modified to account for the input,[1−6] field theoretic treatments of annihilation reactions,[7] and analytic solutions in one dimension.[8] These treatments all assume that the source is spatially *homogeneous*. For such an input the steady-state concentration of clusters of mass k has the form $c_k \sim k^{-\beta}$, and in mean-field theory $\beta = \frac{3}{2}$ for reaction kernels with homogeneity index equal to zero.[1] This value of β appears to be a ubiquitous feature of steady-state coagulation in the mean-field limit.

In this Letter, we investigate steady-state coagulation in the presence of a spatially *localized* monomer input. We envision that this describes 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 therefore a relevant parameter in describing the cluster size distribution in this process. Concomitantly, our study also describes how the steady state of pure diffusion from a point source, i.e., the solution to Laplace's equation, is modified when clusters can coalesce.

Our study is based on an idealized lattice model of coagulation in which a new monomer is introduced at a *single* point (the origin) with probability s at each time step, and all the previously introduced clusters in the system undergo one random walk hop (Fig. 1). If two clusters happen to occupy the same lattice site, they are combined into a single point cluster whose mass is the sum of the masses of the two incident clusters.[9] We impose a constant coagulation rate by taking the merging of clusters to be independent of their masses. If the number of clusters is considered without regard to their masses, then this reduces to the two-body reaction $A + A \to A$ with a point source.

First consider our model within the framework of a continuum reaction-diffusion equation. Within this approximation, the concentration of clusters at a distance r from the source at time t, $c(r,t)$, obeys

$$\frac{\partial c(r,t)}{\partial t} = \frac{D}{r^{d-1}}\frac{\partial}{\partial r}\left[r^{d-1}\frac{\partial c(r,t)}{\partial r}\right]$$

$$+ s\delta(\mathbf{r}) - k\begin{cases} c^2(r,t), & d > 2; \\ -c^2(r,t)/\ln c(r,t), & d = 2; \\ c^{1+2/d}(r,t), & d < 2. \end{cases} \quad (1)$$

Here d is the spatial dimension, and the terms on the right-hand side account for diffusion, the localized source of "strength" s (which is "turned on" at $t = 0$), and the reaction, respectively. The form of the reaction term can be justified heuristically by noting that the reaction rate for a cluster at position r is proportional to $c(r,t)/\tau$, where τ is the time between successive collisions. A collision can be expected when the particle
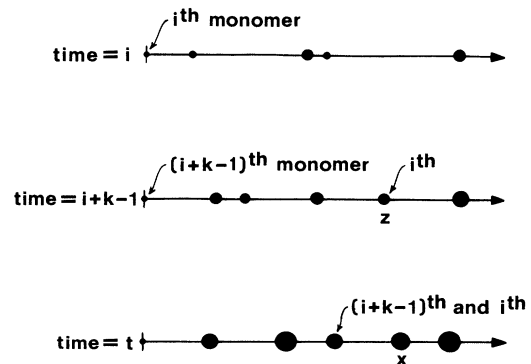

FIG. 1. Coagulation with a point monomer source on the linear chain. Illustrated is the event $A_{i,i+k-1}(x,t)$ in which (i) a monomer is injected at the origin at the ith time step, (ii) the monomer is at z at time step $i + k - 1$, when the $(i+k-1)$th monomer is injected, and (iii) these two monomers then coalesce and arrive at position x at time t.

visits $1/c(r,t)$ distinct sites. Using well-known results[10] for the number of distinct sites visited by a random walk in time t, $S(t)$, the collision time τ follows from the condition $S(\tau) \sim 1/c(r,\tau)$, leading to the reaction term in Eq. (1).

We now determine the condition for which the reaction term in Eq. (1) is relevant. For no reaction, the system obeys Laplace's equation and $c(r,t \to \infty)$ decays as $r^{-(d-2)}$ for $d > 2$, while for $d \le 2$ there is no steady state. In the limit of no reaction, the concentration about the point monomer source is isomorphic to the electrostatic potential of a point charge. For sufficiently large d, diffusing particles do not "see" each other far from the source, so that the Laplacian solution should continue to hold at large r, i.e., $c(r,t \to \infty) \sim r^{-(d-2)}$. Substituting this into Eq. (1) and asymptotically balancing the various terms shows that this solution is consistent only for $d > 4$. Thus $d = 4$ is a critical dimension, above which the reaction can be neglected, except for a trivial rescaling of the source strength, i.e., the source "charge."

For $d < 4$ the reaction term stabilizes a steady state even for $d < 2$. The power-law behavior for $d > 4$ and the $d = 1$ solution to Eq. (1), $c(r) \sim 1/(r + r_0)$ with r_0 a constant, suggest a power-law solution for $1 < d < 4$. Substituting a power law and matching the leading behaviors in Eq. (1) gives

$$c(r,t \to \infty) \sim \begin{cases} r^{-d}, & 1 \le d < 2; \\ r^{-2}\ln r, & d = 2; \\ r^{-2}, & 2 < d < 4. \end{cases} \tag{2}$$

(The case of $d = 2$ has to be treated separately because of the logarithmic factor in the reaction term.) This solution corresponds to a strongly localized concentration profile about the source with a radial flux of clusters that vanishes as $r \to \infty$.

After the source is turned on, the leading edge of the concentration profile will advance diffusively, i.e., as $\sqrt{t}$. The region ahead of this front is essentially empty, while the concentration approaches its steady-state value behind the front. Consequently, the total number of clusters in the system, $N(t)$, can be estimated by $N(t) \sim \int_0^{\sqrt{t}} r^{d-1} c(r) dr$. This gives

$$N(t) \sim \begin{cases} \ln t, & 1 \le d < 2; \\ (\ln t)^2, & d = 2; \\ t^{(d-2)/2}, & 2 < d < 4; \\ t, & d > 4. \end{cases} \tag{3}$$

The linear growth for $d > 4$ is a consequence of the Laplacian solution, $c(r) \sim r^{-(d-2)}$. However, for $d < 4$, the reaction is sufficiently strong to cause the total number of particles to grow more slowly than linearly in time. This corresponds to zero flux of clusters at large

distances, or equivalently, a source charge which has been renormalized to zero.

For coagulation in the presence of a steady point source, the reaction-diffusion equations that describe $c_k(r)$, the steady-state concentration of clusters of mass k at position r, are

$$\frac{D}{r^{d-1}} \frac{d}{dr}\left[r^{d-1}\frac{d}{dr}c_k(r)\right] + \frac{K}{2}\sum_{i+j=k} c_i(r)c_j(r)$$
$$- Kc_k(r)c(r) + s\delta(\mathbf{r})\delta_{k,1} = 0, \tag{4}$$

with $c(r) = \sum_k c_k(r)$. (Because of mass conservation, the mass density obeys Laplace's equation.) We expect that Eq. (4) describes the system for $d > 2$. For $d < 2$, however, we anticipate that the order of the reaction term should be modified, following Eq. (1). However, Eq. (4) *does* describe the asymptotic kinetics correctly in less than two dimensions, in the limit of a vanishingly small reaction rate.

By comparing with the classical rate equations for irreversible coagulation, we see that r^2 in Eq. (4) plays the dimensional role of a time. Consequently, one expects that the scaling *Ansatz*[5]

$$c_k(r) \sim k^{-\tau}\phi(kr^{-z}) \tag{5}$$

will describe the steady-state behavior. Here $k^*(r) \sim r^z$ is the typical size of particles at position r in the steady state. Substituting this scaling form into Eq. (4), balancing the asymptotically dominant terms, and also exploiting mass flux conservation yields the exponent values

$$z = 4 - d, \quad \tau = (d-6)/(d-4). \tag{6}$$

As discussed above, these exponents hold generally for $2 < d < 4$, and for $d \le 2$ in the limit of a vanishingly small reaction rate. For $d < 2$, a scaling analysis of Eq. (4), with the order of the reaction term modified similar to Eq. (1), leads to the exponent values $z = 2$ and $\tau = 1 + d/2$.

As a useful consistency check, we also solve Eq. (4) in one dimension by introducing the generating function $G(u,r) = \sum_{k=1}^{\infty} c_k(r)(u^k - 1)$ into the equation to yield (for $D = K = s = 1$)

$$G'' + \tfrac{1}{2}G^2 + (u-1)\delta(r) = 0, \tag{7}$$

with solution,

$$G(u,r) = -\frac{12}{r^2}\left[1 - \frac{2}{r}\left[\frac{6}{1-u}\right]^{1/3}\right]^{-2}, \quad r > 0. \tag{8}$$

This generating function can be written as $r^{-2} \times \Phi(r(1-u)^{1/3})$, whose inversion yields the scaling form $c_k(r) \sim r^{-5}\phi(kr^{-3})$, with the following limiting behavior,

$$c_k(r) \sim \begin{cases} k^{-5/3}, & k \gg r^3; \\ k^{-2/3}r^{-3}, & k \ll r^3. \end{cases} \tag{9}$$

This coincides with the scaling solution given in Eqs. (5) and (6).

For a unit reaction rate, i.e., clusters reacting whenever they meet, the impenetrability of the clusters permits an exact solution by mapping the interacting-random-walk system to a single random walk in two dimensions with boundary conditions imposed by the manifestations of the reaction.[11] The solution found by this approach obeys scaling, but with non-mean-field exponents. We now outline the ideas underlying this solution. We first treat an infinite system with isotropic diffusional cluster motion, and then generalize to a system in which the clusters undergo drift, and to a finite system with an absorbing sink.

To calculate the steady-state cluster concentration at position r, $c(r)$, and the total number of clusters, $N(t)$, we label the particle which is injected at the ith time step after the source is turned on as the ith monomer. Without loss of generality, the clusters are restricted to the half line $r > 0$. When a coalescence occurs, the newly formed cluster is defined to retain the larger of the two labels of the incident clusters, i.e., a cluster is "killed" only upon collision with its left-hand-side neighbor. Let $P_i(r,t)$ be the survival probability of the ith cluster at position r and time t, and let $P_i(t) = \sum_r P_i(r,t)$. Then $c(r) = \lim_{t\to\infty} \sum_{i=1}^{t} P_i(r,t)$, while $N(t)$ is the sum of the survival probabilities of all monomers injected before time t, and thus equals $\sum_{i=1}^{t} P_i(t)$.

Denoting the coordinate of the ith clusters as x_1 and that of its left neighbor as x_2, then $P_i(r,t)$ maps onto the survival probability of a random walk in two dimensions, with absorbing boundary conditions on the line $x_1 = x_2$ and *reflecting* boundary conditions on the line $x_2 = 0$ (Fig. 2). (The latter condition arises because the left neighbor must always be to the right of the origin.) This problem, in turn, coincides with the survival probability of a random walk in a planar quadrant with absorbing
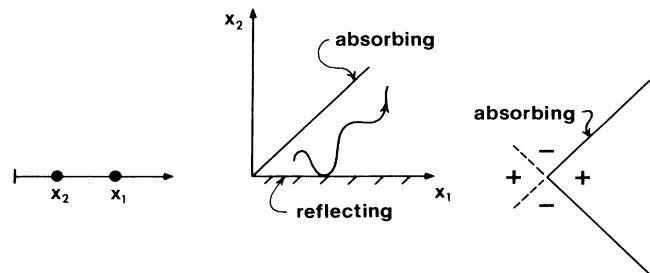

FIG. 2. Mapping of the collision process in one dimension to a bounded random walk in two dimensions. For the random walk in a quadrant with absorbing boundaries, the survival probability within the quadrant can be determined by introducing the images shown.

boundary conditions on the two bounding axes. By exploiting the image method (Fig. 2), we find

$$c(r) \sim 1/r, \quad N(t) \sim \ln t. \tag{10}$$

To compute the steady-state concentration profile of clusters of mass k, $c_k(r)$, we generalize Spouge's formalism,[11] which was developed for irreversible coagulation on the linear chain, to allow for a steady monomer input. For this task, the following notations are helpful. Define $P(A)$ to be the probability that the event A occurs. Let $A_{i,j}(r,t)$ be the "elemental" two-particle collision event that the ith and jth monomer are on the same site r at time t. Further, define the ith k-mer to be a cluster of mass k which contains the ith and the $(i+k-1)$th monomers. Then

$$c_k(r) = \lim_{t\to\infty} P(\text{a } k\text{-mer on } r \text{ at time } t)$$

$$= \lim_{t\to\infty} \sum_{i=1}^{t} P(i\text{th } k\text{-mer on } r \text{ at time } t).$$

From probability theory[11]

$$P(i\text{th } k\text{-mer on } r \text{ at time } t) = P(A_{i,i+k-1}(r,t)) - P(A_{i-1,i+k-1}(r,t)) - P(A_{i,i+k}(r,t)) + P(A_{i-1,i+k}(r,t)), \tag{11}$$

thus expressing $c_k(r)$ in terms of the $P(A_{i,j}(r,t))$, and the latter quantity can be calculated by mapping to an equivalent property of a two-dimensional random walk.

As an example, for the event $A_{i,i+k-1}(r,t)$ to occur, the ith monomer must first diffuse a (arbitrary) distance z from the source when the $(i+k-1)$th monomer is injected. These two monomers must later collide, with the reaction product diffusing to x at time t (Fig. 1). The probability of this event can therefore be formally written as

$$P(A_{i,i+k-1}(r,t)) = 2 \sum_{z=0}^{\infty} a(r,t-(i+k-1);z) \gamma_{k-1}(z), \tag{12}$$

where $\gamma_k(z) \sim (1/\sqrt{k}) e^{-z^2/k}$ is the Gaussian probability distribution for the ith monomer to start at the origin

and reach z in k time steps, and $a(r,t;z)$ is the collision probability that a particle initially at z coalesces with a particle initially at the origin, with the reaction product being at r at time t. In analogy with Spouge,[11] this collision probability can be written as

$$a(r,t;z) = [\gamma_t(r-z) + \gamma_t(r+z)] \sum_{w=r}^{\infty} \gamma_t(w)$$

$$+ \gamma_t(r) \left[\sum_{w=-z}^{r-z} + \sum_{w=z}^{r+z} \right] \gamma_t(w), \tag{13}$$

where the two additional terms involving $+z$ (compared to Spouge's result) arise from the restriction of the system to $r > 0$.

From Eqs. (11)-(13) and with considerable algebra,

we find the basic result

$$c_k(r) \sim k^{-3/2} \phi(\mu) , \qquad (14a)$$

where $\mu = k/r^2$, and where the scaling function is

$$\phi(\mu) = \int_0^\infty \frac{dz}{z^2} \{ \tan^{-1}(1+z) + \tan^{-1}(1-z) - \pi/2 \}$$
$$\times (z^4/\mu^2 - z^2/\mu - 1/4) e^{-z^2/\mu} . \qquad (14b)$$

The typical cluster size $k^*(r)$ scales as r^2, which follows from the recurrence of one-dimensional random walks. A particle that reaches r will have coalesced with essentially all the r^2 monomers subsequently injected into the system. From Eq. (14b) the asymptotic behavior of $\phi(\mu)$ is

$$\phi(\mu) \sim \begin{cases} 1/2 - 3/\mu, & \mu \to \infty ; \\ \mu^{5/2}, & \mu \to 0, \end{cases} \qquad (15)$$

giving rise to the limiting behavior of $c_k(r)$

$$c_k(r) \sim \begin{cases} k^{-3/2}, & r \ll k^{1/2} ; \\ k/r^5, & r \gg k^{1/2} . \end{cases} \qquad (16)$$

We can generalize the above results to the case where there is a superimposed outward radial cluster drift, in addition to diffusion. In the reaction-diffusion equation, this entails adding a convection term to Eq. (1). In the absence of reaction, the steady-state concentration now decays as r^{1-d}, and substituting this concentration profile in the reaction-convection-diffusion equation shows that the reaction is irrelevant for $d > d_c = 2$. Below two dimensions, if one assumes a power-law form for the concentration profile, self-consistency is obtained if $c(r) \sim r^{-d/2}$. Following a similar line of reasoning for the coagulation process with an imposed drift, one finds the exponents in the scaling Ansatz for $c_k(r)$ to be $-z = \tau - 1 = d/2 - 1$.

In one dimension, the arguments that led to Eq. (10) now yield

$$N(t) \sim t^{1/2}, \quad t \gg 1/v ;$$
$$c(r) \sim r^{-1/2}, \quad r \gg 1/v , \qquad (17)$$

where v is the drift velocity. In comparing Eq. (17) with (10), there is more empty space for newly injected monomers when drift occurs. This retards the reaction process and leads to $c(r)$ decaying more slowly and $N(t)$ increasing faster than in the case of no drift.

For an absorbing sink at $r = L$, the interesting quantity is the output flux, $C_k(L)$, i.e., the rate at which k-mers reach the sink. For this case, the new calculational feature is that the collision function $a(r,t;z)$ requires the solution of an infinite image problem, arising from the boundedness of the interval. For purely diffusing particles we find that $C_k(L)$ scales as $k^{-2}\Phi(\zeta)$, where $\zeta = k/L^2$, and where $\Phi(\zeta)$ has the asymptotic behavior

$$\Phi(\zeta) \sim \begin{cases} \zeta^{5/2} \exp[-\pi^2\zeta/16], & \zeta \sim \infty ; \\ \zeta^3, & \zeta \to 0 . \end{cases} \qquad (18)$$

In the limit of large μ, $C_k(r)$ in the finite system coincides with the flux at r in an infinite system. This follows because coagulation predominantly occurs near the origin, and a distant sink will have very little influence. However, to form a k-mer for large ζ ($k \gg L^2$), a particle must survive of the order of k time steps in order to collect k monomers before hitting the sink. The survival probability of a random walk in an interval of length L for k time steps, $\exp[-\text{const} \times k/L^2]$, therefore yields the large ζ controlling factor of $\Phi(\zeta)$ in Eq. (18). We also obtain the number of particles in the interval, $N(L)$, by noting that for large L, the behavior of $c(r)$ is not strongly affected by the sink, i.e., $c(r) \sim r^{-1}$ for $L - r \gg 1$. Since the primary contribution to $N(L)$ comes from the region near the source, we can write $N(L) \approx \int^L dr\, r^{-1} \sim \ln L$.

In summary, we have presented new results for steady-state coagulation in the presence of a point source of monomers. From the diffusion-reaction equation, we deduce three regimes of behavior: (i) $d > 4$, the pure diffusion regime; (ii) $2 < d < 4$, the diffusion-reaction regime; and (iii) $1 \le d < 2$, the strong-reaction regime. For cases (ii) and (iii) the scaling Ansatz $c_k(r) \sim k^{-\tau} \times \phi(kr^{-z})$ accounts for the behavior of the steady-state concentration profile of clusters of mass k. In one dimension we outlined an exact solution to the problem which is consistent with the scaling Ansatz. We also studied the effects of cluster drift and the effects of a sink. The k dependence of $c_k(r)$ is generally very different from a homogeneous-source system. Many of our results are confirmed by numerical simulations.

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