

Kinetics in coagulation-annihilation processes

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We investigate the combined role of coagulation and annihilation in processes involving particles of two kinds. When two clusters meet they either coagulate (if they contain particles of the same kind) or a pairwise annihilation of particles according to the $A+B\rightarrow 0$ scheme takes place, so that (at most) one cluster survives. We monitor the temporal evolution of the number of particles and of the number of clusters in the system. We present numerically determined scaling laws, which we justify through analytical considerations.

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INTRODUCTION

The basic bimolecular reaction $A+B\rightarrow 0$ was investigated extensively in the past decade, based on the discovery of its fluctuation-dominated kinetics [1,2]. The reaction shows a large number of (highly nontrivial) scaling features (with respect to the number of particles, to the front forms, and to the self-organization [3–17]) which are due to fluctuation effects.

Nonetheless, the standard system $A+B\rightarrow 0$ is oversimplified, in that no particle interactions (except for the reaction of particles of different kinds) are considered. Such interactions are of utmost importance in recombination of charge carriers in semiconductors and in charged particle-antiparticle annihilation processes [17–19]. In former works [20,21] we have investigated situations with interactions, and have displayed the ensuing nonlinear equations [similar to those of Kardar, Parisi, and Zhang (KPZ) [22]].

Here we consider short-range forces, which involve both particles of the same and of different kinds. We start with an equal number of A and B particles and follow the scheme introduced by Krapivsky [23,24]. If two clusters of particles of the same kind, containing n and m particles, respectively, meet each other, they coagulate and form a cluster with $n+m$ particles; if two clusters containing particles of a different kind meet, they form one new cluster containing $|n-m|$ particles of the kind that was in the majority. The reaction thus reads



and



where the product P depends on $p=n-m$ and is A_p for $p>0$, B_{-p} for $p<0$, and 0 for $p=0$.

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Attractive elastic forces in solids or van der Waals forces in liquids, which act on all particles involved [17,19], lead to Eqs. (1); for biological applications of this scheme, see Refs. [23,24]. Note that at long times the concentration of clusters gets small and the details of the short-range forces are irrelevant; the main role of the forces is to stabilize the clusters.

Note that a realistic study of clusters has to account for the dependence of the diffusion coefficient D and of the reaction radius r_0 on the mass of the cluster. Let m be the number of particles inside the cluster. Now D and r_0 depend both on m and also on the structure (i.e., compact, linear, or fractal) of the object, an important aspect in polymerization, in colloidal aggregation, and in the coalescence of droplets (see Refs. [25–27]). For example, one expects $D\sim m^{-p}$ and $r_0\sim m^q$ (e.g., for a spherical cluster in three dimensions (3D) one has, according to Stokes' law and Einstein's relation, $p=\frac{1}{3}$).

SIMULATIONS

We model the diffusion of the particles and of the clusters through nearest-neighbor random walks on lattices, taking a square and a simple cubic lattice in 2D and in 3D, respectively. In all cases the total number of sites is set to 10^6 , which corresponds to linear dimensions of 10^6 , 10^3 , and 10^2 in $d=1, 2$, and 3 , respectively. Periodic boundary conditions are used. With dimension $d=2$ and 3 the maximal simulation time T_{\max} is limited by finite-size effects; we take $T_{\max}=3\times 10^4$ in $d=2$ and $T_{\max}=10^4$ in $d=3$, respectively. The initial number of particles of each kind is 10^5 . For simplicity we take that each cluster occupies one lattice site, which implies $q=0$. When two clusters meet on the same site, they react according to Eqs. (1). During one time step of the algorithm, we check each cluster once on the average to see whether it moves. To account for the dependence of the diffusion coefficient on the cluster's mass, we take the probability for a cluster to make a step to be exactly m^{-p} . For p we use here $p=0, 1$, and 2 .

We monitor the concentration of particles, $n(t)$, and that of clusters, $N(t)$. The results of the simulations are shown in Figs. 1–3 on double-logarithmic scales. The

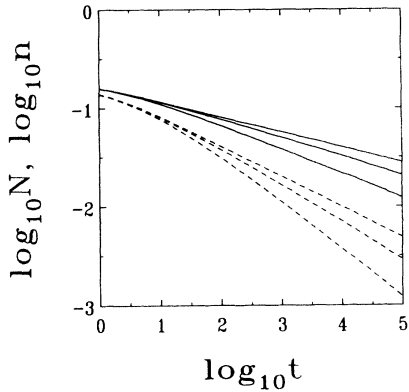


FIG. 1. The time dependence of the concentration of particles, $n(t)$ (solid lines) and that of clusters, $N(t)$ (dashed lines) in 1D. The curves correspond to $p=2, 1$, and 0 , from top to bottom. See the text for details.

data presented for $p=0$ in 2D and 3D are averaged over five realizations of the system; the rest of the data correspond to one realization each.

From the figures we readily infer that at longer times both $n(t)$ and $N(t)$ follow power laws. One has

$$n(t) \sim t^{-\alpha} \quad (2)$$

and

$$N(t) \sim t^{-\beta}. \quad (3)$$

In Table I we give the values of the exponents α and β obtained from a least-squares fit to the data in the time interval $100 < t < T_{\max}$. One observes the close similarity of the 2D and 3D data and the fact that $\beta=2\alpha$. Note that the numerical values of α and β for $p=0$ in $d=1$ are close to $\frac{1}{4}$ and $\frac{1}{2}$, respectively, as obtained in Ref. [24], while the values for $p=0$ in $d=2$ and 3 are close to the mean-field exponents $\frac{1}{2}$ and 1 .

SCALING APPROACH

Here we present some theoretical arguments to justify these findings and to express α and β analytically. This also sheds light on the critical dimension of the problem;

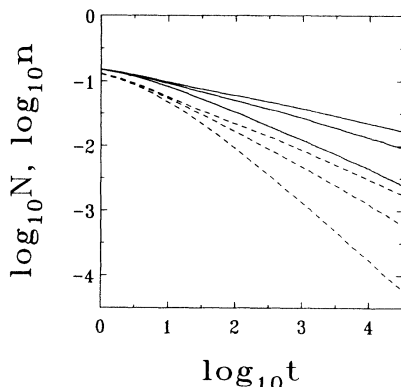


FIG. 2. Same as in Fig. 1, but for $d=2$.

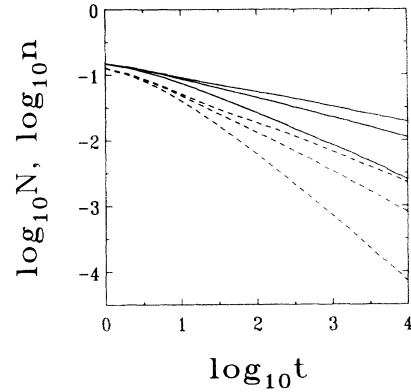


FIG. 3. Same as in Fig. 1, but for $d=3$.

as we proceed to show, this marginal dimension separates two different regimes, both of which are fluctuation dominated. In this respect our reaction scheme is significantly different from the one considered by Ovchinnikov and Zel'dovich [1], by Kang and Redner [3,4], and by Zumofen, Blumen, and Klafter [5].

First we consider the situation in $d \leq 2$, for which the random walks are compact, and start from the visited-volume picture of the reaction [5]. In the late stages of the reaction (when the monomer density gets to be low), the cluster coagulation proceeds mainly according to the simple $C+C \rightarrow C$ scheme: a full annihilation (disappearance) of two colliding clusters occurs only in the rather improbable situation that they consist of an equal number of particles of different kinds. Let us denote by $V(t)$ the mean volume (number of lattice sites) visited by the cluster during the time t . Clusters within the same volume explore essentially the same territory and hence react with each other. Assuming that at time t there is one cluster per mean visited volume $V(t)$, one has

$$N(t) = V^{-1}(t). \quad (4)$$

The visited volume is related to the diffusion length $L(t)$ through

$$V(t) = L^d(t), \quad (5)$$

while $L(t)$ depends on the number of particles in the cluster through the diffusion coefficient. The picture is that the cluster simply gathers all the particles that existed at the beginning within its visited volume; thus the mean number of particles inside the cluster is equal to the number of excess particles of one kind within the volume. According to Poisson statistics, the last quantity is proportional to the square root of the total initial number of particles within $V(t)$, i.e.,

$$m(t) \sim [n(0)V(t)]^{1/2}.$$

The mean concentration of particles is then

$$n(t) = m(t)N(t) \simeq n(0)^{1/2} V^{-1/2}(t). \quad (6)$$

From Eqs. (4) and (6) one concludes that $\alpha = \beta/2$ and that $m(t) \sim t^\alpha$. Now we consider the time dependence of the diffusion length,

TABLE I. Values of the exponents α and β obtained from a least-squares fit to the data in the time interval $100 < t < T_{\max}$.

		$d=1$		$d=2$		$d=3$	
		Num.	Scal.	Num.	Scal.	Num.	Scal.
$p=0$	α	0.24	$\frac{1}{4}$	0.45	$\frac{1}{2}$	0.50	$\frac{1}{2}$
	β	0.47	$\frac{1}{2}$	0.89	1	0.98	1
$p=1$	α	0.19	$\frac{1}{5}$	0.30	$\frac{1}{3}$	0.31	$\frac{1}{3}$
	β	0.38	$\frac{2}{5}$	0.60	$\frac{2}{3}$	0.61	$\frac{2}{3}$
$p=2$	α	0.15	$\frac{1}{6}$	0.23	$\frac{1}{4}$	0.23	$\frac{1}{4}$
	β	0.31	$\frac{1}{3}$	0.48	$\frac{1}{2}$	0.46	$\frac{1}{2}$

$$L(t) = \left[\int_0^t D(t) dt \right]^{1/2} \sim \left[\int_0^t m^{-p}(t) dt \right]^{1/2}, \quad (7)$$

and obtain for the exponent β using Eqs. (4), (6), and (7):

$$\beta = \frac{2d}{4+pd}. \quad (8)$$

The values of the exponents α and β obtained according to Eq. (8) are also listed in Table I. The numerical values for the exponents in 1D are in good agreement with our scaling estimate, Eq. (8). The larger deviations in 2d let us suspect the appearance of logarithmical corrections, which are not rendered well by simple scaling.

Note that in the case $p=0$, the exponent $\alpha = \beta/2 = d/4$ is the same as for the $A+B \rightarrow 0$ reaction without clusterization. This may lead to the (unwarranted) conclusion that in this case the coagulation is in line with the standard scaling approach of Refs. [3,4], which assumes that the slowest relaxation in the system (which determines the reaction's behavior) is the diffusional smoothing of the concentration fluctuations. As we proceed to show, turning to $d=3$, cluster coagulation is even slower, so that it is decisive for the decay pattern.

The small differences in the numerically determined exponents α and β for 2D and for 3D witness in favor of the hypothesis that $d=2$ is marginal, in fact, distinct from fluctuation-controlled kinetics, whose marginal dimension is $d=4$. For $p=0$ it can be also seen from the fact that in $d=2$ the values of exponents given by Eq. (8) coincide with their mean-field values obtained in Refs. [23,24]. Hence the transition is related here to the compactness of the random walks rather than to the smoothing out of the fluctuations.

Now we present scaling considerations for the case $2 < d < 4$ and take into account the fact that in $d > 2$ the random walks are not compact, so that Eq. (5) no longer holds. On the other hand, for cluster coagulation, Eqs. (4) and (6) are still valid. For $d > 2$ the concentration of clusters, which obeys $C+C \rightarrow C$, is well described by

$$\frac{dN(t)}{dt} = -kN^2(t), \quad (9)$$

where k is a reaction-rate coefficient [5,7,28]. For constant D and reaction radius r_0 one has $k \sim Dr_0^{d-2}$. If one lets D and r_0 depend on the cluster size, say, as $D \sim m^{-p}$ and $r_0 \sim m^q$, then D , r_0 , and k become time

dependent. Integrating Eq. (9) in this case gives, for not-too-short times,

$$N(t)^{-1} \simeq \int_0^t k(t) dt \sim \int_0^t D(t) [r_0(t)]^{d-2} dt \sim \int_0^t [m(t)]^{-p+(d-2)q} dt. \quad (10)$$

We now estimate $m(t)$. From Eqs. (4) and (10) it follows that

$$V(t) \sim \int_0^t [m(t)]^{-p+(d-2)q} dt. \quad (11)$$

On the other hand, $m(t)$ is proportional to the number of excess particles of one kind within the visited volume, i.e.,

$$m(t) \sim [n(0)V(t)]^{1/2}.$$

This, together with Eq. (11), determines $V(t)$ and then $N(t)$. Setting $N(t) \sim t^{-\beta}$, i.e., $V(t) \sim t^\beta$, one has $m(t) \sim t^{\beta/2}$, which with Eq. (11) leads to the relation

$$\beta = \frac{2}{2+p-q(d-2)}. \quad (12)$$

For the special case $r_0 = \text{const}$ (i.e., $q=0$) used in our simulations, it follows that

$$\beta = \frac{2}{2+p}. \quad (13)$$

In $d=2$, Eq. (13) coincides with Eq. (7), showing that $d=2$ is marginal, in agreement with our discussion above. Moreover, α follows from Eq. (6), $\alpha = \beta/2$. These values for α and β are also presented in Table I. Note that the marginal dimension $d=2$ separates two different fluctuation-controlled (nonclassical) regimes, as $m(t)$ and therefore $n(t)$ are governed by Poisson fluctuations.

CONCLUSIONS

Here we considered a basic model for the $A+B \rightarrow 0$ reaction under coagulation. The numerical simulations and a scaling analysis show that the decay laws are

governed by cluster coagulation, which is slower than the smoothing out of the fluctuations. We calculated the exponents of the decay laws as a function of the dependence of the diffusion on cluster size. The marginal dimension for the reaction is 2; it divides two different regimes, *both of which* are fluctuation dominated.

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- [1] A. A. Ovchinnikov and Ya. B. Zel'dovich, *Chem. Phys.* **28**, 215 (1978).
- [2] D. Toussaint and F. Wilczek, *J. Chem. Phys.* **78**, 2642 (1983).
- [3] K. Kang and S. Redner, *Phys. Rev. Lett.* **52**, 955 (1984).
- [4] K. Kang and S. Redner, *Phys. Rev. A* **32**, 435 (1985).
- [5] G. Zumofen, A. Blumen, and J. Klafter, *J. Chem. Phys.* **82**, 3198 (1985).
- [6] L. W. Anacker and R. Kopelman, *Phys. Rev. Lett.* **58**, 289 (1987).
- [7] R. Kopelman, *Science* **241**, 1620 (1988).
- [8] K. Lindenberg, B. J. West, and R. Kopelman, *Phys. Rev. Lett.* **60**, 1777 (1988).
- [9] H. Schnörer, V. Kuzovkov, and A. Blumen, *Phys. Rev. Lett.* **63**, 805 (1989).
- [10] B. J. West, R. Kopelman, and K. Lindenberg, *J. Stat. Phys.* **54**, 1429 (1989).
- [11] E. Clément, L. Sander, and R. Kopelman, *Phys. Rev. A* **39**, 6455 (1989).
- [12] L. A. Harmon, L. Li, W. Anacker, and R. Kopelman, *Chem. Phys. Lett.* **163**, 463 (1989).
- [13] I. M. Sokolov, H. Schnörer, and A. Blumen, *Phys. Rev. A* **44**, 2388 (1991).
- [14] G. Zumofen, J. Klafter, and A. Blumen, *J. Stat. Phys.* **65**, 1015 (1991); *Phys. Rev. A* **44**, 8390 (1991).
- [15] F. Leyvraz and S. Redner, *Phys. Rev. Lett.* **66**, 2168; *Phys. Rev. A* **46**, 3132 (1992).
- [16] M. Araujo, H. Larralde, S. Havlin, and H. E. Stanley, *Phys. Rev. Lett.* **71**, 3592 (1993).
- [17] V. Kuzovkov and E. Kotomin, *Rep. Progr. Phys.* **51**, 1479 (1988).
- [18] V. Kuzovkov and E. Kotomin, *J. Chem. Phys.* **98**, 9107 (1993).
- [19] V. Kuzovkov and E. Kotomin, *J. Stat. Phys.* **72**, 127 (1993).
- [20] I. M. Sokolov and A. Blumen, *Europhys. Lett.* **21**, 855 (1993).
- [21] I. M. Sokolov, P. Argyakis, and A. Blumen, *J. Phys. Chem.* **98**, 7256 (1994).
- [22] M. Kardar, G. Parisi, and Y.-C. Zhang, *Phys. Rev. Lett.* **56**, 889 (1986).
- [23] P. L. Krapivsky, *Physica A* **198**, 135 (1993); **198**, 157 (1993).
- [24] P. L. Krapivsky, *Physica A* **198**, 150 (1993).
- [25] G. Oshanin, M. Moreau, and S. Burlatsky, *Adv. Coll. Interface Sci.* (to be published).
- [26] P. Meakin, *Physica A* **165**, 1 (1990).
- [27] R. Jullien, *New J. Chem.* **14**, 239 (1990).
- [28] A. A. Ovchinnikov, S. F. Timashev, and A. A. Belyy, *Kinetics of Diffusion Controlled Chemical Processes* (Nova Science, New York, 1989).