Self-Stirred vs. Well-Stirred Reaction Kinetics

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For low-dimensional reactions (on surfaces or in pores) and solid-state reactions the stirring mechanism is usually limited to self-stirring, i.e., self-diffusion. Simulations of A + A → A₂↑ reactions show classical behavior for *well-stirred* reactions but drastic nonclassical behavior for *self-stirred* reactions in low-dimensional systems: (1) one-dimensional system, (2) square lattice, (3) two-dimensional percolating cluster, (4) three-dimensional percolating cluster. In contrast, a three-dimensional isotropic system (cubic lattice) shows a near-classical behavior even for self-stirred reactions. Different universalities in kinetic behavior are shown for the well-stirred and for the self-stirred reactions.

Introduction

While most homogeneous reactions are easy to stir, and usually are well-stirred, this is not the case for most heterogeneous reactions. The combination of solid surfaces and low-dimensional topologies characterizes most heterogeneous reactions. It is difficult to stir such reactions. Thus the distinction between well-stirred and self-stirred reactions is of both theoretical and practical interest. In addition, most solid-state "physical" reactions, e.g., electron–hole recombination or exciton–exciton annihilation, are self-stirred, diffusion-limited reactions. Also, many biological reactions and biophysical reactions, such as fluorescence quenching, are mostly in the self-stirred regime. Here we give characteristic examples for two extreme cases of "diffusion-limited" reactions, the constantly and totally stirred reaction and the totally unstirred reaction.

The traditional formalism for homogeneous reactions[1,2] expresses the rate constant K in terms of the cylindrical volume V swept out by the reacting molecules (cross section a times mean distance l) per unit time:

$$K = dV/dt \qquad dV = a\,dl \tag{1}$$

$$K = a\,dl/dt \tag{1a}$$

For diffusion-limited reaction kinetics the equivalent Smoluchowski approach[2,3] replaces the mean velocity dl/dt by the diffusion constant (D), for long times

$$K = a'D \qquad t \to \infty \qquad (a' = \text{const}) \tag{2}$$

In a microscopic model where the Brownian motion is described in terms of molecular random walk,[4–6] dV/dt is naturally substituted by the volume which the walker sweeps out in unit time

$$K = b\,dn/dt \tag{3}$$

where b is the "volume" of the walker and dn/dt is the number of such volumes swept out in unit time. For instance, on a cubic lattice, with unit cell volume b, the walker sweeps out dn unit cells per unit time dt. The question arises: How does one count dn? Is it (I) the total number of unit cells swept out by the walker or is it (II) the *distinct* number of such cells swept out, on the average? We show here that, while for a well-stirred system (convection-stirred) the first approach (I) is correct, for a system that is only "self-stirred" by molecular diffusion, the second approach (II) applies. In a three-dimensional, isotropic system (like a cube) the difference between I and II is less than a factor of 2 (1.5164 for long times).[4] However, for lower dimensional systems the difference becomes dramatic (many orders of magnitude) and, moreover, K becomes a function of time (even at $t \to \infty$) in case II. Thus the problem is of much interest to heterogeneous reactions (e.g., surface reactions), where convection stirring (on the surface or inside the pores) is not a likely process.

We give here simulations of the rate constant for the reaction

$$A + A \to 0 \tag{4}$$

where the reaction product is either a photon (exciton annihilation reaction) or a species that leaves the active surface (as A₂↑). The simulations are performed for cubic lattices, square lattices, two- and three-dimensional critical percolation clusters, and a one-dimensional lattice.

Description of the Model

Two component lattices are generated by using the CMLT[7] for the cluster counting in two- and three-dimensional cases, while the one-dimensional case is simply a line of one component sites. The one-dimensional lattice was made of 10 000 sites. The two-dimensional lattice was 200 × 200 while the three-dimensional was 40 × 40 × 40. Particles are placed at random at $t = 0$ on the largest cluster only with an initial density $\rho_0 = 0.02$. For the percolating clusters we use occupational probabilities $p = 0.60$ (two-dimensional) and $p = 0.32$ (three-dimensional). Notice that ρ_0 is taken to be the number of particles divided by the total available number of sites, which at $p = 1$ is the lattice size, while at the percolation threshold it is much smaller. All particles move at random, simultaneously, at each time step, and a check is made at the end of each such step to find if any two particles occupy the same site. If they do they are both removed from the system; otherwise, their motion continues. Thus the only criterion for particle–particle annihilation is the occupation of one site by two particles at the end of each step. Notice that if three particles occupy one site, only two are removed; also, if two particles cross each other during their motion they both survive, since they never occupy the same site simultaneously.

In the diffusion-limited case a certain initial ρ_0 is generated and the particle density is monitored as a function of time. In the well-stirred case after each time step all remaining particles rerandomize their positions. This is done by simply removing all particles and repositioning them randomly on the lattice without any knowledge of their previous positions. Similarly, the particle density is monitored again as a function of time. The reported results are averages of 50–100 runs.

Results

The classical rate equation for the reaction A + A → 0 is obviously

$$-d\rho/dt = K\rho^2 \tag{5}$$

and the integrated rate equation is

$$\rho^{-1} - \rho_0^{-1} = Kt \tag{6}$$

where ρ is the reactant density at time t and ρ_0 that at $t = 0$. Using

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Figure 1. Rate coefficients K for one-dimensional lattice: (1) (squares) well-stirred reaction rate coefficient K^{WS}; (2) (octagons) self-stirred reaction rate coefficient (multiplied by 10) $K^{DL} \times 10$; (3) (triangles) reduced rate coefficient for self-stirred reaction, K_r^{DL}. N is the number of time ticks.
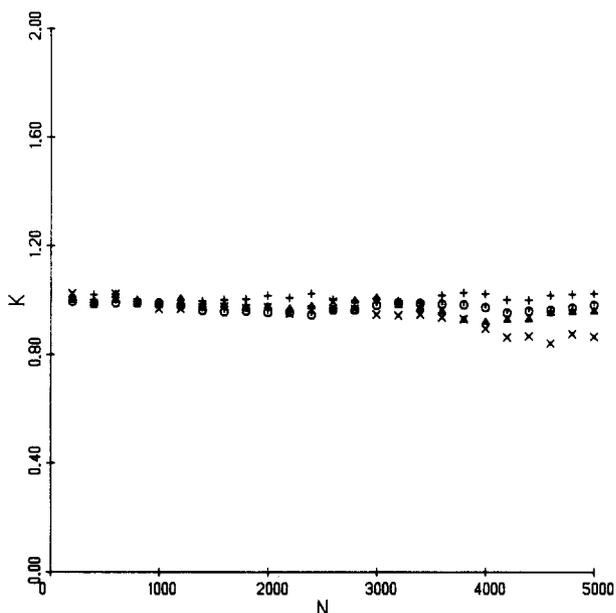
Figure 2. Rate coefficient K^{WS} for well-stirred reactions: (1) (plusses) on cubic lattice; (2) (octagons) on square lattice; (3) (triangles) on two-dimensional percolation cluster (guest occupation probability 0.60); (4) ($\times$ signs) on 3-dimensional percolating lattice (guest occupation probability 0.32).

the number of steps N in lieu of the time t, we get as our operational definition of the rate constant

$$K = N^{-1}(\rho^{-1} - \rho_0^{-1}) \qquad (7)$$

On the other hand, for diffusion-limited reactions with no external mixing, we have shown before[5,6] that the above classical expression should be replaced by a *reduced* rate constant

$$K_r = S^{-1}(\rho^{-1} - \rho_0^{-1}) \qquad (8)$$

where the "reduced time" S is really the average number of *distinct* sites visited by the random walker A (in N steps). From eq 7 we get K^{WS} for *well-stirred* reactions and K^{DL} for *diffusion-limited* reactions. Similarly K_r^{DL} stands for the *reduced* rate constant derived for *diffusion-limited* reactions (eq 8), etc.

The best illustration of the nature of our results can be seen from the simple case of the *one-dimensional lattice*. Figure 1 shows the *instantaneous* values of K^{WS}, K^{DL}, and K_r^{DL} as a function of time (N). As expected classically, for the well-stirred reaction K^{WS} is *constant in time*. Moreover, its value is practically *unity*
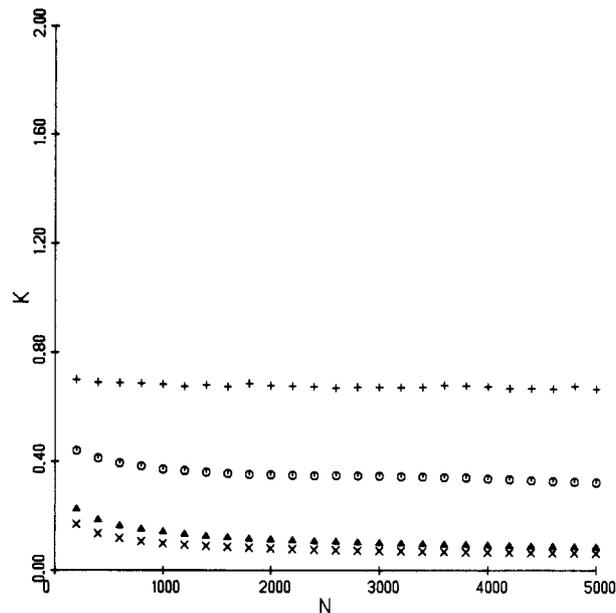
Figure 3. Rate coefficient K^{DL} for self-stirred (diffusion-limited) reactions. Lattices and designations as in Figure 2.
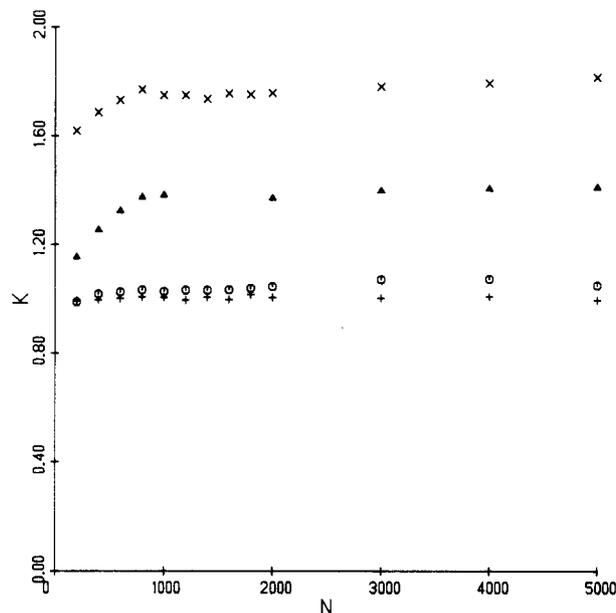
Figure 4. Reduced rate coefficient K_r^{DL} for self-stirred (diffusion-limited) reactions. Lattice and designations as in Figure 2.

(the density ρ is defined as particles per site, see below). In stark contrast, for the diffusion-limited reaction (self-stirred only) K^{DL} *decreases monotonically with time*. Moreover, its values are *much smaller than unity* (note change in scale). However, now the reduced rate constant K_r^{DL} is *constant in time* (for longer times). Moreover, its asymptotic value again is of the order of unity. For the self-stirred reactions it may thus be prudent to replace the classical K with a reduced K_r. However, the inescapable fact is that (for the self-stirred reaction) the classically defined K is *not* constant in time but rather a monotonically decreasing function of time.

A similar story is seen for the other simulated low-dimensional systems (while the three-dimensional cubic lattice is a special case). Figure 2 shows the behavior of *well-stirred* reactions for a cubic lattice, a square lattice, and percolating clusters in both two and three dimensions. We note that we consider both percolating systems to be *effectively low-dimensional*, judging by their effective dynamic dimension ("spectral dimension"[5,8]), which is only

(8) de Gennes, P. G. *C. R. Acad. Sci., Ser. 2* **1983**, *296*, 881.
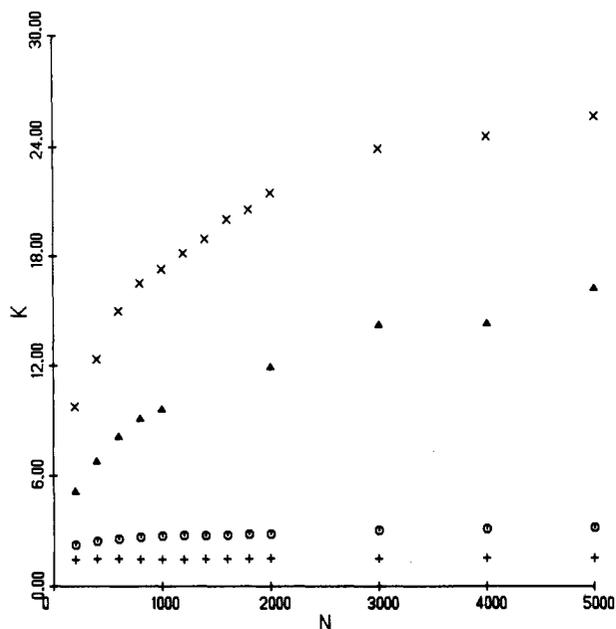
Figure 5. Reduced rate coefficient K_r^{WS} for well-stirred reactions. Lattices and designations as in Figure 2.

1.33. Like for the one-dimensional lattice, we see again the *time constancy* of K^{WS} for all systems. Furthermore, we again see it assume a value close to unity. Figure 3 shows diffusion-limited (self-stirred) reaction simulations for the same systems as Figure 2. For the three low-dimensional systems we see, as in Figure 1, that K^{DL} *decreases monotonically in time*. Only for the cubic lattice is K^{DL} constant in time. Moreover, for all shown topologies, K^{DL} is significantly *below unity* (as in the one-dimensional case). Again, for *diffusion-limited* (self-stirred) reactions we show the *reduced* rate constant K_r (see Figure 4). As for the one-dimensional case, we see K_r^{DL} approach (asymptotically) *constancy in time*. Its value is again of the order of unity. Finally, in Figure 5, we see a reduced rate constant K_r^{WS} plotted vs. time. *No constancy in time* is approached (except for the cubic lattice). Moreover, its values *increase with time* (except for the cubic lattice case). Thus the definition of K_r^{WS} is not very fruitful. It has the appearance of an *explosive* reaction, but this is misleading, as the traditional K^{WS} is simply *constant in time*.

Discussion and Summary

Diffusion-limited reactions are usually fast and have no significant activation energy. Often it is stated that a diffusion-limited reaction is one where "the kinetics are not reaction limited"; i.e., the rate limiting factor is the mere bringing together of the reactants. In this sense both our "well-stirred" and "self-stirred" models describe diffusion-limited reactions. However, most specific literature models for diffusion-limited reactions[2,3,9] do not include convective stirring but only self-stirring. On the other hand, both the "classical" theories of chemical kinetics[1] and the diffusion-limited ones[2,3] are effectively "mean field" theories where a random distribution of reactants is assumed or implied (neglecting some of the many-body correlations). The randomization approach obviously fits the well-stirred case. The self-stirred case (diffusion but not convection) has been addressed recently more explicitly.[9] Our results give a direct comparison of both cases and bear out previous intuitive or implicit notions.

Our simulations establish two separate "universalities" for the two modes of reaction. Our specific algorithm for the well-stirred case results in a rate *constant K* of about unity for all topologies. For the self-stirred case we corroborate a very different kind of universality, i.e., a K that is constant in *reduced time* but *not* in *real time*. The obvious exception is the isotropic, three-dimensional (cubic) lattice where the two universalities merge, i.e., reduced time and real time are proportional and, moreover, of the same order.

The combination of diffusion and reaction (no convection) generates a *nonrandom* spatial distribution, and this leads[9] to the time dependence of K. An analysis and comparison of the pair-correlation functions, for the two cases, will be given separately. While the nonrandomness of the distribution for these A + A reactions is significant, the deviations from randomness are not as drastic as for the A + B reaction.[10,11] The results of a more complete study over a range of percolation lattices and the related cross-over behaviors (from fractal to classical) will follow.

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Formation and Characterization of Microcrystalline Semiconductor Particles on Bilayer Lipid Membranes

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Microcrystalline cadmium, indium, copper, and zinc sulfides were generated in situ on the surfaces of bilayer lipid membranes (BLMs) prepared from bovine-brain phosphatidylserine (PS), glyceryl monooleate (GMO), and a synthetic, polymerizable surfactant [n-$C_{15}H_{31}CO_2(CH_2)_2$]$_2N^+(CH_3)CH_2C_6H_4CH$=CH_2, Cl^- (STYRS). Semiconductor-containing BLMs remained stable for days. Semiconductor formation on the BLM surface was monitored by optical microscopy, voltage-dependent capacitance measurements, and absorption and intracavity-laser-absorption spectroscopy. Band gap excitation of GMO–BLM-incorporated CdS resulted in the development of photovoltage. Irradiation of CdS incorporated into BLMs formed from STYRS (using a 350-nm cutoff filter) led to absorption losses due to the styrene moiety in the surfactant. Apparently, CdS sensitized the photopolymerization of STYRS BLMs.

Introduction

The importance of organizing small, uniform colloidal semiconductors in systems which favor efficient light harvesting and vectorial charge separation has been recognized.[1,2] Semiconductor

particles have been incorporated into reversed micelles,[3,4] polymer films,[5–9] surfactant vesicles,[10,11] clays,[14,15] Vycor glass,[16] and

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