Asymptotic Behavior of Densities in Diffusion-Dominated Annihilation Reactions

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We obtain rigorous bounds on the long-time behavior of the densities $\rho_A(t)$ and $\rho_B(t)$ of species A and B, which diffuse and annihilate upon meeting, i.e., $A+B\rightarrow$ inert. For equal initial densities $\rho_A(0)=\rho_B(0)$, the density goes to zero asymptotically as $t^{-d/4}$ for dimensions $d\leq 4$ and as t^{-1} for $d\geq 4$. When $\rho_A(0)<\rho_B(0)$, $\rho_A(t)\sim\exp(-\lambda_1\sqrt{t})$, $\rho_A(t)\sim\exp(-\lambda_2 t/\ln t)$ for $d=1,2$, respectively, and $\rho_A(t)\sim\exp(-\lambda_d t)$ for $d\geq 3$.

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There has been much interest in recent years following the seminal papers by Ovchinikov and Zeldovich[1] and by Toussaint and Wilczek,[2] in the time evolution of the density of chemically reacting species whose long-time behavior is dominated by diffusive fluctuations.[3] A typical example is the case of two species, A and B, which diffuse independently and react, "when they meet," to form an inert species: $A+B\rightarrow$ inert. The question of interest is the asymptotic behavior of the densities $\rho_A(t)$ and $\rho_B(t)$ given some initial uniform densities $\rho_A(0)$ and $\rho_B(0)$. If we neglect the diffusive fluctuations, i.e., assume that the reactants are stirred rapidly, then the law of mass action applies,

$$\frac{d\rho_A(t)}{dt}=\frac{d\rho_B(t)}{dt}=-k\rho_A(t)\rho_B(t)\,. \tag{1}$$

The solution of (1) gives an exponential decay of the concentration of the minority component, say A, for $\rho_A(0)<\rho_B(0)$, and a power-law decay $\rho_A(t)=\rho_B(t)\sim c/t$ for equal initial concentrations. We shall refer to the above behavior, which is independent of the space dimension d in which the reaction takes place, as mean-field behavior. It is intuitively clear that when there is no stirring and the atoms have to find each other by diffusion, the decay of the densities may be slower since there will be a tendency for longer persistence of particles in spatial regions created by fluctuations in which either the A or B species dominates.

Other systems of interest are the one-species models of particles which coalesce, i.e., $A+A\rightarrow A$, or combine to form something inert, i.e., $A+A\rightarrow$ inert. In mean-field theory, the density $\rho(t)$ in both cases satisfies the equation $d\rho(t)/dt=-k\rho(t)^2$, which leads to the behavior $\rho(t)\sim c/t$. The question again is what happens when particles have to diffuse in order to meet.

As already mentioned, there is much literature on this topic. Unfortunately, the answers given in that literature do not always agree. This is particularly so in the binary (two-species) case, with $\rho_A(0)<\rho_B(0)$. It therefore seems useful to obtain and present some mathematically exact results. This is what we do here. We also note briefly some old results which are often rediscovered or gotten plain wrong in the physics literature.

There are various microscopic versions of the above systems. The particles can move continuously or be restricted to lattice sites, the reaction can take place with varying probabilities depending on the distance between the particles, etc. All these variations should be (and in some cases can be proven to be) irrelevant for the long-time behavior of the concentrations.

The models we shall consider here will consist of particles on the d-dimensional cubic lattice Z^d. At $t=0$, the state of the system is described by the following translation-invariant product measure: At each site the numbers of particles of each species have Poisson distributions with means $\rho_A(0)$ and $\rho_B(0)$ for the binary model (case I), and $\rho(0)$ for the one-component model (case II). The results do not change if we consider an initial product measure where at $t=0$ each site is occupied by at most one particle with probabilities $\rho_A(0)$ and $\rho_B(0)$ corresponding to types A and B, respectively.

The time evolution of the systems proceeds via a combination of diffusion and reaction dynamics. For $t>0$, each particle performs an independent random walk in continuous time with unit jump rate. The reaction dynamics in case I is specified by the rule that when an A and B meet, i.e., they are at the same site at $t>0$, they combine and annihilate. Thus for $t>0$, each site will contain only A's or B's or be empty. For case II we shall consider the model with coalescence—for $t>0$ all (A) particles at a site become one without any subsequent change in their jump rates. These results hold without change for the corresponding one-component annihilating case. Finally, we shall also consider case I′ in which the B particles are fixed. That is, B particles neither move nor are annihilated upon being met by A particles. (The A particles disappear, however.) In case I′, the B particles are thus traps for the A particles.

In the next section we present our new results on the asymptotic behavior of the densities $\rho_A(t)$ and $\rho_B(t)$ for case I and some old results of Bramson and Griffeath[4] for case II and of Donsker and Varadhan[5] for case I'.

We begin with case I which has two subcases $\rho_A(0)=\rho_B(0)$ and $\rho_A(0)<\rho_B(0)$. The next two theorems give upper and lower bounds on the expected densities $\rho_A(t)$ and $\rho_B(t)$ for these cases.

Theorem 1.—Suppose $\rho_A(0)=\rho_B(0)$. There exist positive constants c_d and C_d such that

$$c_d/t^{d/4}\le\rho_A(t)=\rho_B(t)\le C_d/t^{d/4},\quad d\le 4, \tag{2}$$

$$c_d/t\le\rho_A(t)=\rho_B(t)\le C_d/t,\quad d\ge 4. \tag{3}$$

Theorem 2.—Suppose $\rho_A(0)<\rho_B(0)$. Let $\gamma=\rho_B-\rho_A$ (which is independent of t). There exist constants c_d, C_d, λ_d, and Λ_d such that

$$\rho_A(t)\le C_1\exp[-\Lambda_d\gamma g_d(t)], \tag{4}$$

where

$$g_d(t)=\begin{cases}\sqrt{t}, & d=1,\\ t/\ln t, & d=2,\\ t, & d\ge 3.\end{cases} \tag{5}$$

Note that Eqs. (2)–(5) describe the (suitably defined) asymptotic density of $\rho_A(t)$. Of course, $\rho_B(t)\to\gamma$ as $t\to\infty$. The case $\rho_A(0)<\rho_B(0)$ can be contrasted with case I' where the B's are fixed. In that case the Donsker-Varadhan theorem[5] shows that the density of A particles, denoted by $\bar\rho_A(t)$, satisfies

$$\bar\rho_A(t)\sim\exp(-\lambda_d t^{d/d+2}), \tag{6}$$

for all d ($\sim$ here means that upon replacing λ_d by $\lambda_d\pm\epsilon$, one obtains upper and lower bounds). The reason for the difference will be discussed below.

For case II there is only one type of particle; these particles coalesce with one another. We quote the results of Bramson and Griffeath[4] for the density $\rho(t)$ starting from all sites occupied:

$$\rho(t)\approx[m_d g_d(t)]^{-1}. \tag{7}$$

Here $m_1=\sqrt{\pi}$, $m_2=\pi$, and m_d for $d\ge 3$ is the probability that two random walkers, starting at adjacent sites in Z^d, will eventually meet; $\rho(t)\approx f(t)$ here means that $\rho(t)/f(t)\to 1$ as $t\to\infty$. The constants in (7) are sharp and are really independent of the initial density. The result for the annihilating case $A+A\to$ inert is obtained from (7) by our dividing the right-hand side by two, i.e., the asymptotic densities in this case are just one-half of those in the coalescing case.

Here we attempt to give a flavor of the arguments entering the proofs of some of the bounds in theorems 1 and 2. Complete proofs will be published elsewhere.[6]

We begin with the lower bound in Eq. (2). The idea here is to compare (couple) the actual process involving diffusion and annihilation with another process in which the particles only diffuse independently, i.e., the reaction is turned off. Let $\xi(t)$ and $\eta(t)$ denote the configurations of the particles on the lattice at time t for these processes. Define now $\mathcal{D}_R(t;\xi)$ and $\mathcal{D}_R(t:\eta)$ to be (No. of A particles) − (No. of B particles) for the processes ξ and η present at time t in a cube of side R (denoted by D_R) centered at the origin. It is then not difficult to show that starting from the same initial Poisson distribution for both processes (which is, in fact, a stationary measure for the independent diffusion process η)

$$\langle|\mathcal{D}_R(t;\xi)-\mathcal{D}_R(0;\xi)|\rangle\le\langle|\mathcal{D}_R(t;\eta)-\mathcal{D}_R(0;\eta)|\rangle\le c_d R^{(d-1)/2}t^{1/4}. \tag{8}$$

The first inequality in (8) is proven for any initial configuration $\xi(0)=\eta(0)$ by construction of a sequence of processes intermediate between ξ and η where the rule $A+B\to$ inert (which is the same as having the pair A,B glued together after they meet) is successively changed to A and B going their independent ways after meeting at more and more sites. At each step, this comparison increases the fluctuations of (No. of A) − (No. of B) in the cube D_R. The second inequality follows from the observations that (1) any change in $\mathcal{D}_R(t;\eta)$ comes from particles crossing the surface of D_R, which has area $2dR^{d-1}$, (2) these particles will generally start within a distance of order $\sqrt{t}$ from the surface, and therefore that (3) for the independent processes η, the expected absolute value of net crossing of A's minus that of B's by time t has in the equal density case a bound proportional to the square root of $2dR^{d-1}\sqrt{t}$. We now observe that

$$\langle|\mathcal{D}_R(t:\xi)|\rangle\ge\langle|\mathcal{D}_R(0;\xi)|\rangle-\langle|\mathcal{D}_R(t:\xi)-\mathcal{D}_R(0;\xi)|\rangle\ge C_d'[\rho_A(0)]^{1/2}R^{d/2}-C_d R^{(d-1)/2}t^{1/4}. \tag{9}$$

The bound on $\langle|\mathcal{D}_R(0;\xi)|\rangle$ comes from the assumption that the initial distribution is independent at each site. Now choose R at time t to be $R_t=a\sqrt{t}$. For a large enough, we have the right-hand side of (9) bounded below by $bR_t^{d/2}$ for some $b>0$. By symmetry, the expected density of A particles, $\rho_A(t)$, is bounded below by $\frac{1}{2}R_t^{-d}\langle|\mathcal{D}_{R_t}(t:\xi)|\rangle$. If we plug in the bound for $\mathcal{D}_{R_t}(t;\xi)$ and substitute for R_t, the proof of the inequality on the right-hand side of (2) is complete.

The lower bound in (3) ought to be fairly obvious on an intuitive level because of mean-field reasoning or any of a number of other comparisons (for instance, by anticipated negative correlations between unlike particles at neighboring sites or by comparison with the model $A+A\to$ inert). We have been able to show this bound, but only by less direct reasoning. The reader is invited to come up with his or her own simple (but rigorous) argument!

The upper bounds for (2) and (3) can be derived to-

gether. A substantial amount of work is required here. One creates a mechanism that enables one to show that no matter what the configuration of particle types is at a given time, there is enough mixing occurring so that at future times the particles have been redistributed and their densities have decreased correspondingly. This reasoning involves ordinary-differential-equation–like comparisons; it has already been applied in a simpler format to case II.[4]

We now discuss theorem 2, where $\gamma=\rho_B(0)-\rho_A(0)>0$. In Ref. 1, and in some papers in Ref. 3, the asymptotic behavior for the model was equated with that of case I′ as in (6). To see why one should instead expect faster decay than for case I′, consider the following rough estimates in $d=1$.

In the Donsker-Varadhan case, an A particle starting at 0 will not meet any of the stationary B particles by time t if both (1) the A particle does not leave the interval $[-L,L]$ by time t and (2) there are no B particles in $[-L,L]$, for some $L>0$. The probability of (2) is clearly bounded below by $\exp(-a\gamma L)$ for some $a>0$. Similarly, the probability that the A particle does not leave this interval during the time $[0,t]$ with $t=L^3$ is also bounded below by $\exp(-bL)$, $b>0$. (This can be seen by our dividing t into L pieces, each of duration $\tau=L^2$. The probability of both not leaving the interval $[-L,L]$ during the time period τ and ending up inside $[-\frac{1}{2}L,\frac{1}{2}L]$ is some constant $p>0$. The desired probability is therefore at least p^L.) Multiplying the two bounds, we see that the probability of this A particle not being trapped by time t is at least $\exp(-\lambda_1 t^{1/3})$, with $\lambda_1=a+b$.

The situation is entirely different when the B particles also move as in case I. First, note that the typical distance a B particles moves in time t is $\sqrt{t}$. Also, it is easy to show (with standard large-deviation estimates) that the probability that there are initially at least $\gamma\sqrt{t}$ more B particles than A particles on the interval $[-\sqrt{t},\sqrt{t}]$ is at least $1-\exp(-\Lambda\gamma\sqrt{t})$, $\Lambda>0$. The probability that none of these "surplus" B particles ever hits the A particle starting at 0 will consequently be at most $\exp(-\Lambda'\gamma\sqrt{t})$, $\Lambda'>0$, except on a set of probability $\exp(-\Lambda\gamma\sqrt{t})$. Addition of these two probabilities gives the bound $\exp(-\Lambda_1\gamma\sqrt{t})$, $\Lambda_1=\min(\Lambda,\Lambda')$, which corresponds to the upper bound in (4). This of course differs from the lower bound for case I′ that we just derived.

One can also argue heuristically to obtain (5) and (6) in theorem 2. The lower bounds are easy to motivate in all cases, even if we neglect the disappearance of B particles which meet A particles. Up to bounded multiples, the term $g_d(t)$, in (5) and (7), is the number of sites typically visited by an unbiased random walker in d dimensions. Since each site is occupied by a B particle with probability at most $1-\exp[-\rho_B(0)]$, the probability of an A particle not meeting any B particle up to time t is at least of order $\exp[-\rho_B(0)g_d(t)]$. This gives the heuristics for the lower bounds in theorem 2.

One must work harder for the upper bounds, although these bounds are again based on $g_d(t)$. The basic idea is the following. The density B particles which "survive forever" will be γ. These particles will, after nearly all the A particles have disappeared, move about independently and therefore be fairly evenly distributed with density γ. Now consider one of the few surviving A particles after some time. The average number of B particles which will attempt to occupy its site grows at least as a multiple of $g_d(t)$ as t increases. The near independence of the B particles then implies that the survival probability of the A particles decreases exponentially in $g_d(t)$.

We note here the obvious, namely, that there are all sorts of related models and variations of $A+B\rightarrow$ inert about which one can ask questions. For instance, what is the asymptotic behavior of $\rho_A(t)$ for $A+B\rightarrow$ inert with $\rho_A(0)=\rho_B(0)$ as in theorem 1 but with B particles stationary? One can introduce the model with n types $A_1,\ldots,A_n$ which satisfy $A_i+A_j\rightarrow$ inert for $i\neq j$; the model reduces to case I for $n=2$. Avraham and Redner[7] have derived an interesting formula for $\rho_{A_i}(t)$ under $\rho_{A_1}(0)=\cdots=\rho_{A_n}(0)$. One can also ask more detailed questions concerning the local structure of processes. For instance, for $A+B\rightarrow$ inert one apparently has more clustering in low dimensions than in high dimensions with A particles or with B particles dominating local areas. This type of question becomes particularly interesting when particles are introduced into the system (e.g., at a steady rate) to compensate for the depletion which is continually occurring, say, in the model $A+B\rightarrow$ inert. It seems[2,3,8] that $d=2$ is a critical dimension in the sense that for $d<2$ (including the Sierpinski gasket in $d=2$) local clustering becomes more and more pronounced as $t\rightarrow\infty$, whereas for $d>2$ it does not.

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