ASYMPTOTIC BEHAVIOR OF DENSITIES IN DIFFUSION DOMINATED TWO-PARTICLE REACTIONS

Maury BRAMSON[a,1] and Joel L. LEBOWITZ[b,2]

[a]*Department of Mathematics, University of Wisconsin, Madison, WI 53706, USA*
[b]*Department of Mathematics and Physics, Rutgers University, New Brunswick, NJ 08903, USA*

We analyze the limiting behavior of the densities $\rho_A(t)$ and $\rho_B(t)$ for the diffusion controlled chemical reaction A + B → inert. We prove that for equal initial densities $\rho_A(0) = \rho_B(0)$ there is a change in behavior from $d \le 4$, where $\rho_A(t) = \rho_B(t) \sim C/t^{d/4}$, to $d \ge 4$, where $\rho_A(t) = \rho_B(t) \sim C/t$ as $t \to \infty$. For unequal initial densities $\rho_A(0) < \rho_B(0)$, $\rho_A(t) \sim e^{-C\sqrt{t}}$ in $d = 1$, $\rho_A(t) \sim e^{-Ct/\log t}$ in $d = 2$, and $\rho_A(t) \sim e^{-Ct}$ in $d \ge 3$. The term C depends on the initial densities and changes with d.

1. Introduction

Consider a system of particles of two types on $\mathbb{Z}^d$, A and B, which execute simple random walks in continuous time. That is, the motion of different particles is independent and a particle at site x will jump to a given one of its $2d$ nearest neighbors at rate $1/2d$. Particles are assumed not to interact with their own type – multiple A particles or multiple B particles can occupy a given site. However, when a particle meets a particle of the opposite type, both disappear. (When a particle simultaneously meets more than one particle of the opposite type, it will only cause one of these particles to disappear.)

To study the time evolution of this system one needs to specify an initial measure for the process. Various possibilities suggest themselves. We consider for concreteness the case in which one independently throws down A and B particles according to the homogeneous Poisson random measures with densities r_A and r_B; if there are initially both A and B particles at x, they immediately cancel each other out as much as possible. Our results (analyzing the system as $t \to \infty$) hold equally well for any other initial measures which are "sufficiently ergodic". We denote by ξ_t the random state of the system at time t and by $\xi_t(x) \in \mathbb{Z}$ the type and number of particles at $x \in \mathbb{Z}^d$; B's are counted as positive charges and A's as negative ones.

This process can serve as a model for the irreversible chemical reaction $A + B \rightarrow$ inert, were both particle types A and B are mobile. A and B can also represent matter and antimatter. (One can generalize the model to where the mobilities or jump rates are different for the two species, as long as they are both strictly positive.) There has been much interest in this model over the last several years following papers by Ovchinikov and Zeldovich [1], and Toussaint and Wilczek [2]; see Bramson and Lebowitz [3, 4], and refs. [5–8] for a more complete set of references. The main concern has been with the behavior of the densities in a spatially homogeneous system, i.e., with the expected number of A and B particles per site, $\rho_A(t)$ and $\rho_B(t)$, as $t \rightarrow \infty$. (The density of course does not depend on the site x.) The two basic cases are when (a) $0 < \rho_A(0) = \rho_B(0)$ (equal densities) and (b) $0 < \rho_A(0) < \rho_B(0)$ (unequal densities). Note that (a) corresponds to $0 < r_A = r_B$ and (b) to $0 < r_A < r_B$. Since $\rho_B(t) - \rho_A(t)$ must clearly remain constant for all t, one has $\rho_A(t) = \rho_B(t)$ in (a), and $\lim_{t \rightarrow \infty} \rho_B(t) = \rho_B(0) - \rho_A(0) > 0$ in (b).

In the work in ref. [4] summarized here, we provide for the first time a complete answer to the question: at what rate does $\rho_A(t) \rightarrow 0$? This includes the correct dependence of the time asymptotics on the initial density for different dimensions. We start with some heuristics.

2. Equal densities

For $\rho_A(0) = \rho_B(0)$, one can reason that $\rho_A(t)$ should decrease like $1/t^{d/4}$ for $d \leq 4$ and like $1/t$ for $d \geq 4$. The standard logic is that if one "neglects" the diffusive fluctuations in the number of the two types of particles present in a local region, as can be achieved physically by vigorous stirring, one can treat the positions of particles for the two types as being independent. The rate at which A particles meet B particles is then proportional to the density of each type present. This gives the "law of mass action" or mean field behavior

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

for appropriate $k > 0$. Since $\rho_A(t) = \rho_B(t)$, we have for the solution of (1)

$$\rho_A(t) \approx 1/kt, \quad \text{for large } t. \tag{2}$$

We use the following convention regarding "$\approx$" and "$\sim$": by $a(t) \approx b(t)$ we mean that $a(t)/b(t) \rightarrow 1$ as $t \rightarrow \infty$, whereas by $a(t) \sim b(t)$ we only mean that these functions are "close" – $a(t)/b(t)$ is of magnitude 1, or when appropriate, $\log a(t)/\log b(t)$ is of magnitude 1.

One can, on the other hand, also reason as follows. Let D_R denote the cube of side R which is centered at the origin. Also, let

$$\mathscr{D}_R(t) = (\#B \text{ particles}) - (\#A \text{ particles}) \qquad \text{at time } t \text{ in } D_R . \tag{3}$$

We denote by η_t the stochastic process which behaves the same as ξ_t, except that particles merely execute random walks without interacting (annihilating) when meeting other particles. It seems reasonable to guess that

$$E[|\mathscr{D}_R(t; \xi) - \mathscr{D}_R(0; \xi)|] \sim E[|\mathscr{D}_R(t; \eta) - \mathscr{D}_R(0; \eta)|] \tag{4}$$

for large R. It is not difficult to show for $r_A = r_B$ that

$$E[|\mathscr{D}_R(t; \eta) - \mathscr{D}_R(0; \eta)|] \leqslant C_{1,d}\sqrt{r_A}R^{(d-1)/2}t^{1/4} \tag{5}$$

for appropriate $C_{1,d}$. Hence if one believes (4), then

$$E[|\mathscr{D}_R(t; \xi) - \mathscr{D}_R(0; \xi)|] \leqslant C_{1,d}\sqrt{r_A}R^{(d-1)/2}t^{1/4} . \tag{6}$$

But for $r_A = r_B$,

$$E[|\mathscr{D}_R(0; \xi)|] \geqslant C_{2,d}\sqrt{r_A}R^{d/2} \tag{7}$$

for appropriate constants $C_{2,d}$. That is, there is a local fluctuation in the numbers of the A and B particles. By (6) and (7),

$$E[|\mathscr{D}_R(t; \xi)|] \geqslant C_{2,d}\sqrt{r_A}R^{d/2} - C_{1,d}\sqrt{r_A}R^{(d-1)/2}t^{1/4} . \tag{8}$$

Now choose R at time t to be $R_t = a\sqrt{t}$. For a large enough, (8) is at least $b\sqrt{r_A}R_t^{d/2}$ for some $b > 0$. By symmetry,

$$\rho_A(t) \geqslant \tfrac{1}{2}R_t^{-d}E[|\mathscr{D}_{R_t}(t; \xi)|] .$$

Plugging in the bound for $\mathscr{D}_{R_t}(t; \xi)$ and substituting for R_t, we obtain

$$\rho_A(t) \geqslant c\sqrt{r_A}/t^{d/4} , \tag{9}$$

with $c = b/2a^{d/2}$.

One needs to reconcile (9) with (2). The standard heuristics are that the term (9) measuring local fluctuations dominates in $d < 4$, whereas the mean field limit in (2) is accurate for $d \geqslant 4$. The densities $\rho_A(t)$ and $\rho_B(t)$ should

therefore decay asymptotically like $t^{-d/4}$ for $d \leq 4$ and t^{-1} for $d \geq 4$. Our first result verifies this behavior.

Theorem 1. Assume that the initial measure is Poisson with $r_A = r_B > 0$. There exist positive constants c_d and C_d such that

$$c_d \sqrt{r_A} / t^{d/4} \leq \rho_A(t) = \rho_B(t) \leq C_d \sqrt{r_A} / t^{d/4} , \qquad d < 4 ,$$

$$c_4 (\sqrt{r_A} \vee 1)/t \leq \rho_A(t) = \rho_B(t) \leq C_4 (\sqrt{r_A} \vee 1)/t , \qquad d = 4 , \qquad (10)$$

$$c_d/t \leq \rho_A(t) = \rho_b(t) \leq C_d/t , \qquad d > 4 ,$$

for large enough t. ($(\alpha \vee \beta)$ denotes the least upper bound of α and β.)

Presumably, $t^{d/4} \rho_A(t)$ in $d \leq 4$ and $t\rho_A(t)$ in $d \geq 4$ have limits as $t \to \infty$, although our techniques do not show this.

The asymptotic densities given here share certain similarities in common with those for two related simpler models. As done here, one can define a process consisting of particles on $\mathbb{Z}^d$ which execute independent simple random walks except when two particles attempt to occupy the same site. We now assume, however, that there is only one type of particle (say A), and that when two particles attempt to occupy the same site either (a) they coalesce into one particle and afterward behave as just one particle, or (b) they annihilate one another. The first model can be interpreted as the chemical reaction A + A → A, and is called coalescing random walk, while the second model corresponds to A + A → inert, and is called annihilating random walk. For each of these models at most one particle is permitted per site. It is most natural to consider the state where all sites are occupied as the initial state although the same limiting behavior holds for a much larger class of states.

The coalescing random walk is attractive. This says, basically, that adding more particles to the system initially will not diminish the number of particles later on. It is also the dual of the voter model. (Liggett [9] is the most complete general reference on interacting particle systems. Griffeath [10] and Durrett [11] are also useful references and emphasize the role of duality.) For these reasons, it is possible to analyze the density $\rho(t)$ and show that $\rho(t) \approx [\gamma_d g_d(t)]^{-1}$ where

$$g_d(t) = \begin{cases} \sqrt{t} , & d = 1 , \\ t/\log t , & d = 2 , \\ t , & d \geq 3 , \end{cases} \qquad (11)$$

and γ_d are appropriate constants. In particular, $\gamma_1 = \sqrt{\pi}$, $\gamma_2 = \pi$. The case $d = 1$

is easy and is an application of the above duality and the local central limit theorem. For $d \geq 2$, see Bramson and Griffeath [12]. The annihilating random walk can, it turns out (Arratia [13]), be compared directly to the coalescing random walk. Let $\tilde{\rho}(t)$ denote its density. Since $\tilde{\rho}(t)/\rho(t) \to 1/2$ as $t \to \infty$, one has $\tilde{\rho}(t) \approx \frac{1}{2}\rho(t)$. Note that for coalescing and annihilating random walk, $d = 2$ is where the crossover in asymptotic behavior of $\rho(t)$, $\tilde{\rho}(t)$ occurs, rather than at $d = 4$ for $A + B \to$ inert. This is connected in the first case with the recurrence of random walk in $d \leq 2$ and its transience in $d > 2$.

3. Unequal densities

For $\rho_A(0) < \rho_B(0)$, the asymptotic behavior of $\rho_A(t)$ should be quite different. Since $\lim_{t \to \infty} \rho_B(t) = \rho_B(0) - \rho_A(0) = r_B - r_A \equiv b > 0$, there is always at least density b of type B particles in the population. The density $\rho_A(t)$ must therefore decrease much more rapidly than if $\rho_A(0) = \rho_B(0)$. From (1), one would obtain

$$\frac{\mathrm{d}\rho_A(t)}{\mathrm{d}t} = -k[b + \mathcal{O}(1)]\,\rho_A(t)\,. \tag{12}$$

Consequently, one might expect that

$$\rho_A(t) = \rho_A(0)\,\mathrm{e}^{-k[b+\mathcal{O}(1)]t}\,. \tag{13}$$

On the other hand, as in the case $\rho_A(0) = \rho_B(0)$, local fluctuations could conceivable alter the relative proportions of type A and type B particles locally, and cause a different rate of decay. Presumably, as before, this change would be associated with lower dimensions. There are various different conclusions in the physics literature. In ref. [4], we show the following:

Theorem 2. Assume that $0 < r_A < r_B$ with the initial measures given before. There exist positive constants Λ_d and λ_d such that

$$\exp[-\Lambda_d \phi_d\, g_d(t)] \leq \rho_A(t) \leq \exp[-\lambda_d \phi_d\, g_d(t)] \tag{14}$$

for large enough t, where g_d is defined in (11) and

$$\phi_d = \begin{cases} (r_B - r_A)^2/r_B\,, & d = 1\,, \\ r_B - r_A\,, & d \geq 2\,. \end{cases} \tag{15}$$

The mean field limit is thus valid for $d \geq 3$, but not in $d = 1, 2$. The

dependence on initial densities is different in $d = 1$ from that in $d > 1$, which corresponds to (13). The reason is the presence of greater fluctuations in $d = 1$.

The methodology employed for theorems 1 and 2 involves in both cases different estimates for upper and lower bounds. Lower bounds for $r_A = r_B$ in $d \leqslant 4$ are obtained via the reasoning outlined in (4)–(9) and is quite simple. The mean-field lower bounds in (10) turn out (unexpectedly) to be much trickier: they 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 $A + A \rightarrow$ 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 $r_A = r_B$ can be derived together. 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 in ref. [12]. The derivation of the lower bound for $r_A < r_B$ is relatively easy if one neglects the dependence on r_A, r_B, but requires more work as formulated in (14) and (15). The derivation of the upper bound is more difficult and requires different techniques for $d > 1$ and for $d = 1$.

The case $r_A < r_B$ can be contrasted with the case where the B particles are fixed. In that case a result from Donsker–Varadhan [15] shows that the density of A particles, denoted by $\bar{\rho}_A(t)$, satisfies

$$\bar{\rho}_A(t) \sim \exp(-\bar{\lambda}_d t^{d/d+2}) \, ,$$

for all d (~ here means that upon replacing $\bar{\lambda}_d$ by $\bar{\lambda}_d \pm \epsilon$, one obtains upper and lower bounds).

We conclude by noting 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 $r_A = r_B$ 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 our case for $n = 2$. Avraham and Redner [5] have derived an interesting formula for $\rho_{A_i}(t)$ under $\rho_{A_i}(0) = \cdots = \rho_{A_n}(0)$. One can also ask more detailed questions concerning the local structure of processes. One can show that for $A + B \rightarrow$ inert, there is more clustering in low dimensions than a high dimensions with A particles or with B particles dominating local areas [16]. 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 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 at $t \rightarrow \infty$, whereas for $d > 2$ it does not. (See for example Lindenberg, West and Kopelman [5].)

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