Asymptotics of the Trapping Reaction

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20 April 2006

COWORKERS

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"*Tout le malheur des hommes vient d'une seule chose, qui est de ne savoir pas demeurer en repos, dans une chambre.*"

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"All the misfortune of man comes from the fact that he does not stay peacefully in his room."

INTRODUCTION

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Rate equation approach (trapping reaction):

$$\frac{d\rho_A}{dt} = -\lambda \rho_A \rho_B$$

$$\Rightarrow Q(t) \equiv \frac{\rho_A(t)}{\rho_A(0)} = \exp(-\lambda \rho_B t)$$

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Our primary goals are

1. To determine exactly the coefficients λ_d for $d \le 2$.
2. To determine the *leading corrections* to the asymptotic forms.
3. To investigate the *spatial fluctuations* of surviving A-particles.

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$$Q(t) \leq Q_U(t) = Q_{TAP}(t) = exp\left(-\frac{4}{\sqrt{\pi}}\,\rho_B(D_B t)^{1/2}\right)$$

where $Q_{TAP}(t)$ is the result for the "Target Annihilation Problem", corresponding to $D_A = 0$ (static A-particle with mobile traps).

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For general dimensions $d \leq 2$ the results have the Bramson-Lebowitz forms

$$Q_U(t) = \begin{cases} \exp(-\lambda_d t^{d/2}), & d < 2 \\ \exp(-\lambda_2 t/\ln t), & d = 2 \end{cases}$$

with

$$\lambda_d = \begin{cases} \frac{2}{\pi d}\sin\left(\frac{\pi d}{2}\right)(4\pi D_B)^{d/2}\rho_B, & d < 2 \\ 4\pi D_B \rho_B, & d = 2 \end{cases}$$

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Averaging over the initial position x, uniformly in the interval$(-L, L)$, gives

$$\bar{q} = 1 - \frac{1}{2L}\int_{-L}^{L} dx \ \mathrm{erfc}\left(\frac{|x|}{\sqrt{4D_B t}}\right) = 1 - \frac{1}{L}\,\frac{4}{\sqrt{\pi}}\,\sqrt{D_B t}$$

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The probability that *none* of N traps has reached the target is

$$Q_{TAP}(t) = \left(1 - \frac{1}{L}\frac{4}{\sqrt{\pi}}\sqrt{D_B t}\right)^N \Rightarrow \exp\left(-\frac{4}{\sqrt{\pi}}\rho_B\sqrt{D_B t}\right)$$

(in the limit $N \to \infty$, $L \to \infty$ with $\rho_B = N/L$ fixed).

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Create a fictitious box with edges at $x = \pm\ell/2$, and consider the subset of trajectories in which

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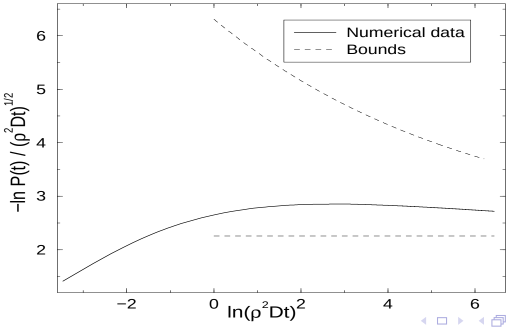
These trajectories are a subset of all trajectories for which the A-particle survives till time t, so

$$
\begin{aligned}
Q(t) \geq Q_L(t) &\sim \max_{\ell} \exp(-\rho_B \ell - \pi^2 D_A t/\ell^2)\, Q_{TAP}(t) \\
&\sim \exp[-\mathrm{const.}(\rho_B^2 D_A t)^{1/3}]\, Q_{TAP}(t)
\end{aligned}
$$

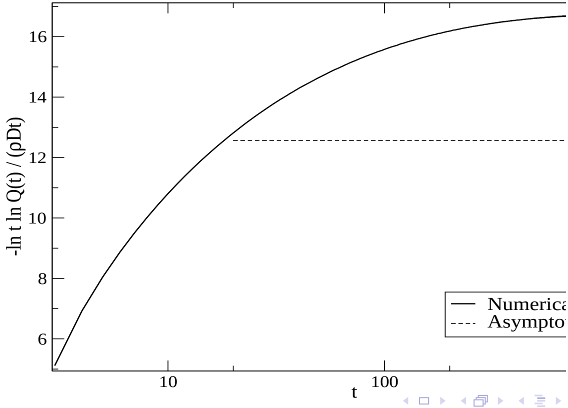
The prefactor is *subdominant* for $t \to \infty$:

$$
Q_L(t) \sim \exp\left(-\frac{4}{\sqrt{\pi}}\rho_B (D_B t)^{1/2} - \mathrm{const.}(\rho_B^2 D_A t)^{1/3}\right)
$$

Compare with data from Mehra and Grassberger (2002):



In two dimensions (Mehra and Grassberger (2002)):



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Consider the A and B particles to be *non-interacting* and consider events in which different B-particles hit the A-particle *for the first time*. These events are described by a *Poisson distribution* – the probability that the A-particle, *with a given trajectory* $z(t)$, has been hit by n different B-particles up to time t is

$$p_n = \frac{\mu^n}{n!} \exp(-\mu)$$

where $\mu = \mu[z(\tau)]$, $0 \leq \tau \leq t$, is a *functional* of the A-particle trajectory $z(t)$.

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The probability of *no hits up to time t* is

$$Q(t) = \langle p_0(t) \rangle_z = \langle \exp(-\mu[z]) \rangle_z$$

where the average $\langle \ldots \rangle_z$ is taken over all A-particle trajectories weighted with the usual Wiener measure.

To determine $\mu[z]$ we calculate, in two ways, the probability density for a B-particle to reach $z(t)$ at time t (in a *noninteracting* system):

$$\rho_B = \int_0^t dt' \, \dot{\mu}(t') \, G_B \left(z(t), t | z(t'), t' \right)$$

where

$$G_B \left(z(t), t | z(t'), t' \right) = \frac{1}{[4\pi D_B (t - t')]^{1/2}} \exp \left(-\frac{[z(t) - z(t')]^2}{4 D_B (t - t')} \right)$$

is the B-particle diffusion propagator. For the target problem ($z(t) = 0$ for all t) this gives

$$\mu(t) = \mu_0(t) = \frac{4}{\sqrt{\pi}} \rho_B (D_B t)^{1/2}$$

as before.

PROOF OF THE PASCAL PRINCIPLE (AB, Majumdar, Blythe (2003); Moreau et al. (2003))

In general we can write $\mu[z] = \mu_0 + \mu_1[z]$. Then $\mu_1[z]$ satisfies the equation:

$$\mu_1[z] = \frac{1}{\pi} \int_0^t \frac{dt_1}{\sqrt{t - t_1}} \int_0^{t_1} \frac{dt_2}{\sqrt{t_1 - t_2}} \, \dot{\mu}(t_2) \, K(t_1, t_2)$$

where

$$K(t_1, t_2) = 1 - \exp\left(\frac{-[z(t_1) - z(t_2)]^2}{4D_B(t_1 - t_2)} \right)$$

The obvious inequalities $K(t_1, t_2) \geq 0$ and $\dot{\mu}[z] \geq 0$ prove that

$$\mu_1[z] \geq 0 \Rightarrow \mu[z] \geq \mu_0$$

i.e. the "Pascal principle" is proved.

PRE-ASYMPTOTIC CORRECTIONS (Anton, AB (2004))

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We attempt a perturbative treatment valid for $D_A \ll D_B$. Expand $\mu_1[z]$ to $O(z^2)$:

$$\mu_1[z] = \frac{\rho_B}{2\pi^{3/2} D_B^{1/2}} \int_0^t \frac{dt_1}{(t-t_1)^{1/2}} \int_0^{t_1} \frac{dt_2}{t_2^{1/2}(t_1-t_2)^{3/2}} [z(t_1)-z(t_2)]^2$$

Then

$$Q(t) = \exp[-\mu_0(t)] \langle \exp(-\mu_1[z]) \rangle_z$$

where the average is evaluated using the Wiener measure

$$P[z] \propto \exp\left(-\frac{1}{4D_A}\int_0^t \dot{z}^2(\tau)\, d\tau\right)$$

This is merely (!) the ratio of two Gaussian integrals, but is still nontrivial. We can simplify by restricting the path integrals to paths that begin and *end* at the origin: $z(0) = 0 = z(t)$, and make the Fourier decomposition

$$z(\tau) = \frac{2}{\pi}\sqrt{D_A t} \sum_{n=1}^{\infty} \frac{a_n}{n} \sin\left(\frac{n\pi\tau}{t}\right)$$

This gives

$$\langle \exp(-\mu_1[z]) \rangle_z = \int \prod_{n=1}^{\infty} \left(\frac{da_n}{\sqrt{2\pi}} \right) \exp\left(-\frac{1}{2} \sum_n a_n^2 - \frac{1}{2} g \sum_{m,n} A_{mn} a_n a_m \right)$$

where

$$\begin{aligned} g &= (4/\pi^{7/2}) \rho_B \, D_A \sqrt{t/D_B} \\ A_{mn} &= \frac{1}{mn} \int_0^1 \frac{dx}{\sqrt{1-x}} \int_0^x \frac{dy}{\sqrt{y}(x-y)^{3/2}} \phi_m(x,y) \phi_n(x,y) \\ \phi_m(x,y) &= [\sin(m\pi x) - \sin(m\pi y)] \end{aligned}$$

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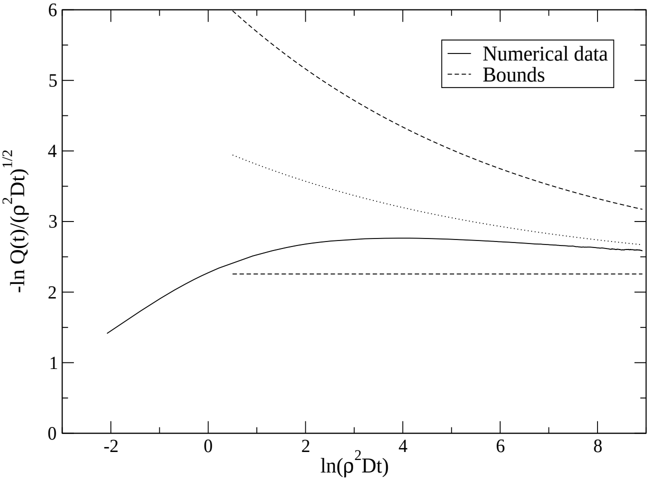
The convexity inequality, $\langle \exp x \rangle \geq \exp\langle x \rangle$, gives

$$\langle \exp(-\mu_1[z]) \rangle_z \geq \exp\left[-\frac{1}{2} \sum_{n=1}^{\infty} \ln(1 + gA_{nn}) \right]$$

Using $A_{nn} \to \sqrt{2}\pi^2 n^{-3/2}$ for $n \to \infty$ gives finally the improved lower bound, valid for $D_A \ll D_B$,

$$Q(t) \geq \exp\left[-\frac{4}{\sqrt{\pi}} \rho_B \sqrt{D_B t} - \frac{1}{\sqrt{3}} \left(32 \rho_B^2 \frac{D_A^2}{D_B} t \right)^{1/3} \right]$$



Numerical data
Bounds
-ln Q(t)/(ρ^2Dt)^1/2
ln(ρ^2Dt)
0
1
2
3
4
5
6
-2
0
2
4
6
8

SPATIAL FLUCTUATIONS OF SURVIVING TRAJECTORIES

(AB, Majumdar, Blythe (2003); Anton, AB (2005))

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Using once more the quadratic action functional gives the probability to find $z(t) = x$ as

$$p(x,t) = \mathcal{N} \exp(-S[z_{cl}]; x, t)$$

where z_{cl} is the classical path that minimises the action functional

$$S[z] = \frac{1}{4D_A} \int_0^t \dot{z}^2(\tau)\, d\tau + \mu[z]$$

under the boundary conditions $z(0) = 0$, $z(t) = x$.

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The calculation is lengthy and leads to the surprising result that $p(x,t)$ is Gaussian with variance

$$\langle x^2 \rangle = \mathrm{const.}\, \frac{\sqrt{D_B t}}{\rho_B},$$

independent of D_A (!), for large t.

To see how this is possible, consider the simpler problem of B-particles to the right of a fixed target located at $x = 0$. The probability distribution for the location of the left-most particle at time t, *given that none of the particles has reached the target*, is easily calculated:

$$p(x,t) = \frac{x}{\sigma^2(t)} \exp\left(-\frac{x^2}{2\sigma^2(t)}\right)$$

where

$$\sigma(t) = \left(\frac{\pi D_B t}{\rho_B^2}\right)^{1/4}$$

Now suppose there are B-particles to left and right. The typical gap size between the rightmost of the particles starting on the left and the leftmost of the particles starting on the right, *given no interactions between the two groups*, is of order $(D_B t/\rho_B^2)^{1/4}$. An intervening A-particle can explore this space with negligible probability cost provided $D_A \ll D_B$.

SUMMARY

1. Exact asymptotic forms have been obtained for the A-particle survival probability in the trapping reaction $A + B \to B$, for $d \leq 2$.
2. Leading corrections to asymptopia have been obtained in $d = 1$ (extensions to all $d \leq 2$ are straightforward in principle, but have not yet been done).
3. Surviving A-particles have subdiffusive fluctuations, $\langle x^2 \rangle \sim (D_B t)^{1/2}/\rho_B$ for small D_A, this result requiring $t \to \infty$ *before* $D_A \to 0$. Extensions to all $d \leq 2$ are again possible in principle.