Numerical Study of Center of Reaction Front for Reaction-Diffusion System $nA + mB \longrightarrow C$ with Arbitrary Diffusivities

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Abstract We study the movement of the center of reaction front in the reaction-diffusion system $nA + mB \longrightarrow C$ for arbitrary diffusivities ($D_a \neq D_b$). We present numerical evidence that $x_f(t) \propto \sqrt{t}$ for all $t \in (0, \infty)$. Numerical experiments are carried out for $(n,m) = (1,1), (1,2), (2,1)$ and $(2,2)$ and for various $\frac{D_a}{D_b}$. Finite difference method is used. Empahsis is not on asymptotic behaviour or scaling, rather on verifying the stated claim for all t.

Key words: Reaction-Diffusion Equations, Reaction Front

1 Introduction

In case of a reaction $nA + mB \longrightarrow C$ in which the two reactants are initially separated, the formation of a reaction front is a well studied phenomenon. Galfi and Racz [1] assume that for the case when $(n,m) = (1,1)$, the width of reaction zone is negligible to the width of depletion zone in large time limit. Magnin [2] has expanded on this assumption for the general case (n,m). 1D and effectively 1D reaction-diffusion systems for the given chemical reaction with rate k are believed to be accurately described by following equations [2, 3, 5]:

$$\frac{\partial A(X,T)}{\partial T} = D_a \frac{\partial^2 A(X,T)}{\partial X^2} - knA^n(X,T)B^m(X,T) \tag{1}$$

$$\frac{\partial B(X,T)}{\partial T} = D_b \frac{\partial^2 B(X,T)}{\partial X^2} - kmA^n(X,T)B^m(X,T) \tag{2}$$

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$$\frac{\partial C(X,T)}{\partial T} = kA^n(X,T)B^m(X,T) \tag{3}$$

At $T = 0$, the reactants are separated at $X = 0$ with constant densities i.e. $A = a_0, B = 0$ for $X < 0$ and $A = 0, B = b_0$ for $X > 0$. To render the system dimensionless, characteristic length, time and concentration are introduced as [1, 2] $l = \sqrt{D_a/(ka_0)}, t = 1/(ka_0)$ and a_0. With these substitutions, equations (1), (2) and (3) become:

$$\frac{\partial a(x,t)}{\partial t} = \frac{\partial^2 a(x,t)}{\partial x^2} - na^n(x,t)b^m(x,t) \tag{4}$$

$$\frac{\partial b(x,t)}{\partial t} = \frac{D_b}{D_a}\frac{\partial^2 b(x,t)}{\partial x^2} - ma^n(x,t)b^m(x,t) \tag{5}$$

$$\frac{\partial c(x,t)}{\partial t} = a^n(x,t)b^m(x,t) \tag{6}$$

This problem, as described by J. Magnin [2], is an initial value problem over the domain $\Omega = \{(x,t)|(x,t) \in \mathbb{R} \times [0,\infty)\}$. Initial conditions are given by

$$a(x,0) = \theta(-x);\ \ b(x,0) = \frac{b_0}{a_0}\theta(x);\ \ c(x,0) = 0 \tag{7}$$

Here $\theta(x)$ is the Heaviside Step function and a_0 and b_0 are the initial concentrations of species A and B respectively. It is clear from the dimensionless equations that $\frac{D_b}{D_a}, n, m$ and $q = \frac{b_0}{a_0}$ are free parameters which completely describe the reaction-diffusion system. Many authors [1, 2, 3, 4, 9, 16] on the subject make a key assumption that $D_a = D_b$ for the sake of keeping mathematics within reach. Others [7, 11] describe the asymptotic behaviour of the system with arbitrary diffusivities as $t \longrightarrow \infty$. The center of reaction front x_f has been variably defined as the point where $a/n = b/m$ (Magnin, [2]) or as the point of maximal reaction rate (Koza et al. [11]) (which need not necessarily be the same points). We adopt the first definition. With this particular definition, it has been proved [2, 3] that for the dimensionless system in which $D_a = D_b$,

$$x_f(t) = 2\sqrt{t}\ erf^{-1}\left(\frac{a_0/n - b_0/m}{a_0/n + b_0/m}\right) = 2\sqrt{t}\ erf^{-1}\left(\frac{1-\frac{n}{m}q}{1+\frac{n}{m}q}\right) \tag{8}$$

To the best of our knowledge, no such analytical result yet exists in the case of $D_a \neq D_b$. Nonetheless, it seems possible that $x_f(t) \propto \sqrt{t}$ for all possible values of (D_a, D_b) and (n,m). The reason for this proposal is that the term $x/\sqrt{t}$ is the signature of diffusion process in general. Our aim in the present work is to provide compelling numerical evidence to support the claim that $x_f(t) = \eta\left(\frac{D_b}{D_a}, n, m, q\right)\sqrt{t}$ holds true for all values of $\frac{D_b}{D_a}, n, m$ and q as t runs through its domain $(0,\infty)$. $\eta\left(\frac{D_b}{D_a}, n, m, q\right)$ can be thought of as a constant of proportionality which depends on the parameters of the problem. We use finite difference method to solve the equa-

tions. To establish the accuracy of our method, we compare our numerical results with the analytical results in case of equal diffusivities ($D_a = D_b$). We also discuss the effect of grid refinement. Once the accuracy of our method has been established, we present the numerical results for the case of unequal diffusivities ($D_a \neq D_b$).

2 Numerical Method

We use Crank-Nicolson method to solve Eqn. (4) and (5). Discretization is given as follows:

$$\frac{a_j^{(k+1)} - a_j^{(k)}}{\Delta t} = \frac{1}{2}\left(\frac{a_{j-1}^{(k+1)} - 2a_j^{(k+1)} + a_{j+1}^{(k+1)}}{\Delta x^2} + \frac{a_{j-1}^{(k)} - 2a_j^{(k)} + a_{j+1}^{(k)}}{\Delta x^2}\right) - n(a_j^{(k)})^n (b_j^{(k)})^m \quad (9)$$

$$\frac{b_j^{(k+1)} - b_j^{(k)}}{\Delta t} = \frac{1}{2}\frac{D_b}{D_a}\left(\frac{b_{j-1}^{(k+1)} - 2b_j^{(k+1)} + b_{j+1}^{(k+1)}}{\Delta x^2} + \frac{b_{j-1}^{(k)} - 2b_j^{(k)} + b_{j+1}^{(k)}}{\Delta x^2}\right) - m(a_j^{(k)})^n (b_j^{(k)})^m \quad (10)$$

Here the subscript j represents spatial index and the superscript (k) represents time step. Since Eqn. (6) is decoupled from Eqn. (4) and (5), consistency and stability of it's numerical solution will have no effect on the other two. Hence we neglect the equation. Notice that the original problem is an Initial Value Problem. So ideally j runs through all non-negative integers. However, due to the finite memory constraints of any computing platform, we restrict the computational domain to $[-1,1]$ and let j run through 0,1,...,M where $2/\Delta x = M$. Since the left and right boundaries are reasonably far from the initial reaction zone, it is also reasonable to approximate the boundary conditions as follows:

$$\left.\frac{\partial a(x,t)}{\partial x}\right|_{x=-1} = \left.\frac{\partial a(x,t)}{\partial x}\right|_{x=1} = \left.\frac{\partial b(x,t)}{\partial x}\right|_{x=-1} = \left.\frac{\partial b(x,t)}{\partial x}\right|_{x=1} = 0 \quad (11)$$

We implement these boundary conditions numerically as follows:

$$a_0^{(k+1)} = a_1^{(k+1)}; \quad a_M^{(k+1)} = a_{M-1}^{(k+1)}; \quad b_0^{(k+1)} = b_1^{(k+1)}; \quad b_M^{(k+1)} = b_{M-1}^{(k+1)} \quad (12)$$

We note that the numerical boundary conditions can lead to only first order consistency at the boundary while Crank-Nicolson is expected to produce second order accuracy elsewhere in the computational domain. We overcome this problem by terminating the program run as soon as any of $|a_0^{(k)} - a_1^{(k)}|, |a_M^{(k)} - a_{M-1}^{(k)}|, |b_0^{(k)} -$

$b_1^{(k)}|, |b_M^{(k)} - b_{M-1}^{(k)}|$ is greater than $O(\Delta x^2)$. To detect the position of the center of reaction zone $x_f(t)$, we use linear interpolation between the grid points $x_0, x_1, ..., x_M$ at every time step. In particular,at every time step k, we find out the index $i \in \{0,1,2,...,M\}$ such that $(a_i^{(k)} - \frac{n}{m} b_i^{(k)})(a_{i+1}^{(k)} - \frac{n}{m} b_{i+1}^{(k)}) \leq 0$. Then we find out the location $x_f(t)$ by solving the two linear equations $\frac{y-a_i^{(k)}}{x-x_i} = \frac{a_{i+1}^{(k)} - a_i^{(k)}}{x_{i+1}-x_i}$ and $\frac{y-\frac{n}{m}b_i^{(k)}}{x-x_i} = \frac{n}{m}\frac{b_{i+1}^{(k)} - b_i^{(k)}}{x_{i+1}-x_i}$.

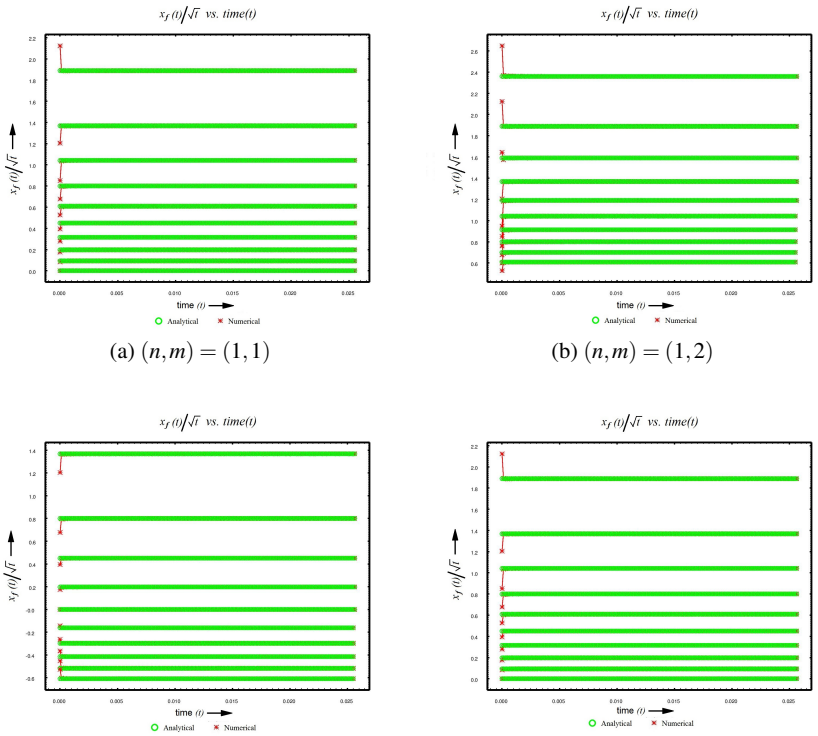
3 Results

3.1 Numerical Results for $\frac{D_b}{D_a} = 1$

In this case, $x_f(t)$ is given by $x_f(t) = 2\sqrt{t}\ erf^{-1}\left(\frac{1-\frac{n}{m}q}{1+\frac{n}{m}q}\right)$ In this section we compare the numerical results with analytical results and show that the numerical method described above indeed gives accurate results. All numerical tests have been carried out with the *FronTier* software library released and maintained by Stony Brook University, NY. The spike and a small oscillatory behaviour near $t = 0$ in Fig.1, can be explained by the fact that grid points are finite in number. Hence the Heaviside Step Function cannot be realized perfectly on any computational grid. This is illustrated in Fig.2. This fact is further verified by changing the grid-size. Fig.3 shows the effects of grid-size on the convergence of $x_f(t)/\sqrt{t}$. It can be seen that as the grid is refined, $x_f(t)/\sqrt{t}$ attains it's theoretical value at earlier time.

3.2 Numerical Results for $\frac{D_b}{D_a} \neq 1$

Previous section presents enough evidence to show that the numerical method described indeed gives results that match with theoretical results. This section presents numerical results for $D_b/D_a \neq 1$. No closed form analytical expression is available in this case. Hence, we provide numerical verification that $x_f(t)$ is proportional to $\sqrt{t}$. Due to the constraints of space, only a few results are presented here. However, tests were done for all of $D_b/D_a = 0.1, 0.2, ..., 1.0$, $q = 0.1, 0.2, ..., 1.0$ and $(n,m) = (1,1), (1,2), (2,1), (2,1)$. In each case, $x_f(t)/\sqrt{t}$ was a constant depending on parameters $D_b/D_a, n, m$ and q. As mentioned previously, q changes from 0.1 to 1.0 in steps of 0.1 as one moves from the topmost branch of each graph to the lowest branch.



(a) $(n,m) = (1,1)$ (b) $(n,m) = (1,2)$

(c) $(n,m) = (2,1)$ (d) $(n,m) = (2,2)$

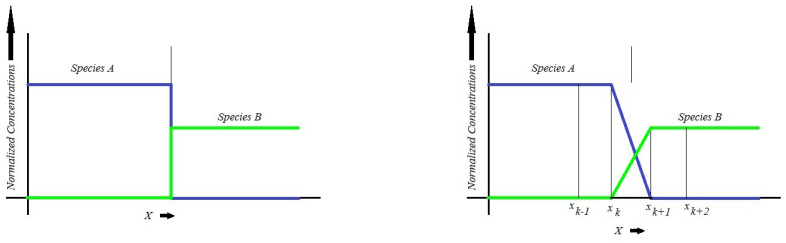
Fig. 1: $x_f(t)/sqrt(t)$ for $D_b/D_a = 1$ and different (n,m). In all figures, the topmost to lowermost branch corresponds to $q = 0.1, 0.2, ..., 1.0$ respectively.

4 Summary and Conclusion

We have presented enough numerical evidence to support the claim that $x_f(t)$ is proportional to $\sqrt{t}$ for every $D_b/D_a, n, m$ and q. Although the results are presented only for $n = 1,2$ and $m = 1,2$, and only for a few values of the stated parameters, we mention in passing that similar results were obtained for $D_b/D_a = 0.1, 0.2, ...1.0$ and for $q = 0.1, 0.2, ...1.0$. In our opinion, the results are consistent enough to support the claim.

References

1. Properties of the reaction front in an $A + B \longrightarrow C$ type reaction-diffusion process, *Physical Review A 1988, Volume 38, Number 6: 3151-3154,* L. Galfi and Z. Racz



(a) Ideal Profile (b) Numerical Implementation

Fig. 2: Implementation of Heaviside Step Function on a finite compuational grid

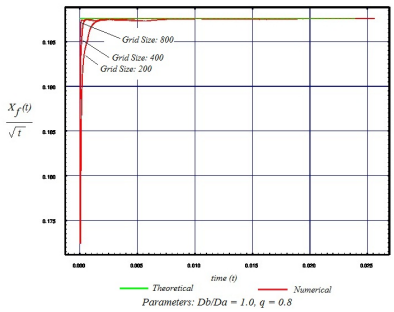
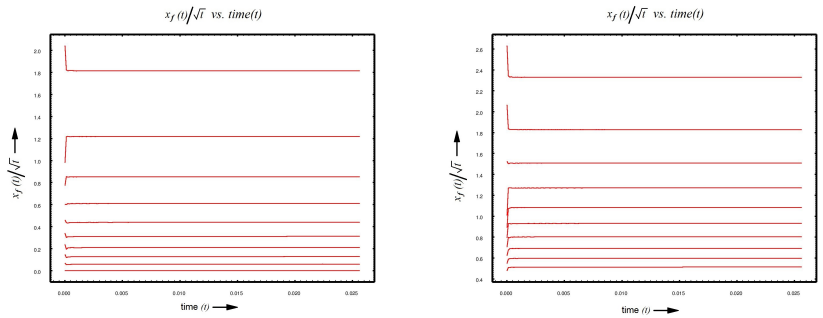


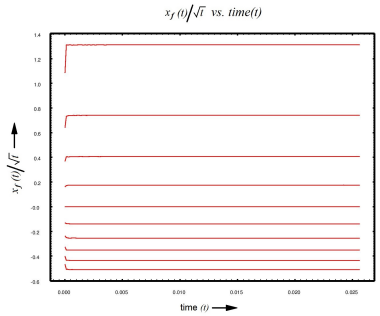
Fig. 3: $x_f(t)/\sqrt{t}$ vs t for varying grid size.

2. Properties of the asymptotic $nA + mB \longrightarrow C$ reaction-diffusion fronts, *Eur. Phys J. B 17 (2000): 673-678,* J. Magnin
3. Dynamic multiscaling of the recation-diffusion front for $mA + nB \longrightarrow C$, *Physical Review E, October 1995, Volume 52, Number 4,* S. Cornell, Z. Koza and M. Droz
4. Reaction front for $A + B \longrightarrow C$ diffusion-reaction systems with initially separated reactants, *Physical Review A, July 1992, Volume 46, Number 2,* H. Larralde, M. Araujo, S. Havlin and H. Stanley
5. Steady-State Reaction-Diffusion Front Scaling for $mA + nB \longrightarrow C$, *Physical Review Letters, June 1993, Volume 70, Number 24,* S. Cornell and M. Droz
6. Asymptotic behaviour of initially separated $A + B_{(static)} \longrightarrow C$ reaction-diffusion systems, *Physica A 240 (1997) 622-634,* Z. Koza
7. Reaction-Diffusion fronts in systems with concentration-dependent diffusivities, *Physical Review E 74, 036103 (2006),* P. Polanowski and Z. Koza
8. Reaction fronts in reversible $A + B \rightleftharpoons C$ reaction-diffusion systems, *Physica A 330 (2003) 160-166,* Z. Koza
9. Reversible and irreversible reaction fronts in two competing reaction system, *Nuclear Instruments and Methods in Physica Research B 186 (2002) 161-165,* M. Sinder, H. Taitelbaum, J. Pelleg
10. Asymptotic expansion for reversible $A + B \longleftrightarrow C$ reaction-diffusion process, *Physical Review E 66, 011103 (2002),* Z. Koza

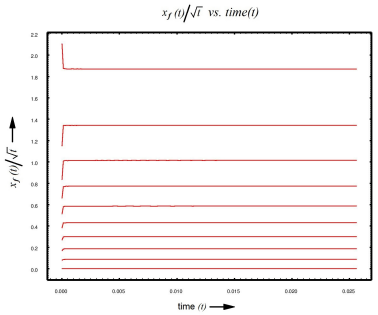


(a) $D_b/D_a = 0.2$, $(n,m) = (1,1)$

(b) $D_b/D_a = 0.4$, $(n,m) = (1,2)$



(c) $D_b/D_a = 0.6$, $(n,m) = (2,1)$



(d) $D_b/D_a = 0.8$, $(n,m) = (2,2)$

Fig. 4: $x_f(t)/\sqrt{t}$ vs. t for various D_b/D_a and (n,m)

11. The Long-time Behavior of Initially Separated $A+B \longrightarrow C$ Reaction-Diffusion Systems with Arbitrary Diffusion Constants, *J. Stat. Phys. 85, 179-191(1996),* Z. Koza
12. Some Properties of the $A+B \longrightarrow C$ Reaction-Diffusion System with Initially Separated Components, *Journal of Statistical Physics, Vol. 65, Nos. 5/6, 1991,* H. Taitelbaum, S. Havlin, J. Kiefer, B. Trus, and G. Weiss
13. Numerical analysis of reversible $A+B \longleftrightarrow C$ reaction-diffusion systems, *Eur. Phys. J. B 32, 507-511(2003),* Z. Koza
14. Simulation study of reaction fronts, *Physical Review A, December 1990, Volume 42, Number 12,* Z. Jiang and C. Ebner
15. Refined simulations of the reaction front for diffusion-limited two-species annihilation in one dimension, *Physical Review E, May 1995, Volume 51, Number 5,* S. Cornell
16. Role of fluctuations for inhomogeneous reaction-diffusion phenomena, *Physical Review A, Volume 44, Number 8, Oct. 1991,* S. Cornell, M. Droz, B. Chopard