Reaction diffusion with initially separated reactants: Functional integral approach

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A method based on the Feynman-Kac formula is suggested to analyze the solutions of the $A+B\rightarrow C$ reaction-diffusion system with initially separated reactants. It enables us to reproduce and improve earlier results which were based on empirical approximations. We also roughly estimate an upper time limit for this approach to be valid. It is possible that this limit is the applicability limit for the mean-field approach. [S1063-651X(97)03907-X]

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Reaction-diffusion processes are of great interest for the scientific community. Numerous efforts have been made to understand their properties qualitatively as well as quantitatively. Basically, there are three approaches to deal with this problem. The microscopic one, which makes use of the field-theoretical machinery, has been implemented for some simple systems [1]. Other works analyze long-time behavior of the system by means of scaling arguments (e.g., [2]). A different approach which is based on the analysis of mean-field differential equations, known also as the reaction-diffusion equations (see, for instance, [3]), is supported experimentally [4]. However, one should be aware that the validity of them is limited, i.e., for long enough times they fail. Therefore, the determination (or estimation) of this crossover time is an important problem.

This paper suggests an approach to solve the mean-field reaction-diffusion equations with the aid of the Feynman-Kac formula [5]. Such a treatment enables one to obtain *analytically* the first-order correction to the *reaction production rate* which has been previously approximated from numerical calculations [6]. We also provide a rough time limit for the validity of our solution. This limit becomes the validity limit for the mean-field equation, provided that a certain mathematical difficulty could be overcome.

We consider a reaction-diffusion system with initially separated reactants along the x axis. Its mean-field description is given by the following set of differential equations for the mean local concentrations per unit length ρ_a,ρ_b:

$$\frac{\partial\rho_a}{\partial t}=D_a\nabla^2\rho_a-k\rho_a\rho_b,$$
$$\frac{\partial\rho_b}{\partial t}=D_b\nabla^2\rho_b-k\rho_b\rho_a, \tag{1}$$

where D_a,D_b are diffusion constants and k is the reaction rate constant. These equations are subject to the initial conditions

$$\rho_a(x,0)=a_0H(x),\quad \rho_b(x,0)=b_0[1-H(x)], \tag{2}$$

where a_0 and b_0 are the initial densities, and $H(x)$ is the Heaviside step function. It is convenient to describe reactive effects by using a dimensionless reaction parameter

$$\varepsilon=\frac{k}{\sqrt{a_0b_0D_aD_b}}. \tag{3}$$

We define dimensionless parameters $\alpha(x,t)=a_0^{-1}\rho_a(x,t)$, $\beta(x,t)=b_0^{-1}\rho_b(x,t)$, $\xi=x\sqrt{a_0b_0}$, and $\tau=ta_0b_0\sqrt{D_aD_b}$, the ratio of diffusion constants $D=\sqrt{D_a/D_b}$, and the ratio of initial concentrations $r=\sqrt{a_0/b_0}$. Then Eq. (1) takes the form

$$\frac{\partial\alpha}{\partial\tau}=D\frac{\partial^2\alpha}{\partial\xi^2}-\frac{\varepsilon}{r}\alpha\beta,$$
$$\frac{\partial\beta}{\partial\tau}=\frac{1}{D}\frac{\partial^2\beta}{\partial\xi^2}-\varepsilon r\beta\alpha. \tag{4}$$

Accordingly, Eq. (2) becomes

$$\alpha(\xi,0)=H(\xi),\quad \beta(\xi,0)=1-H(\xi). \tag{5}$$

The Feynman-Kac formula [5] enables one to rewrite the set of equations (4) using functional integrals

$$\alpha(\xi,\tau)=\int_{\mathbf{C}[0,\tau]}\exp\left\{-\frac{\varepsilon}{r}\int_0^\tau\beta(t,y(t)+\xi)\,dt\right\}\times\varphi(y(\tau)+\xi)\,\mu_{2D}(dy),$$
$$\beta(\xi,\tau)=\int_{\mathbf{C}[0,\tau]}\exp\left\{-\varepsilon r\int_0^\tau\alpha(t,y(t)+\xi)\,dt\right\}\times\psi(y(\tau)+\xi)\,\mu_{2/D}(dy), \tag{6}$$

where the functional Gaussian measures $\mu_{2D}(dy)$, and $\mu_{2/D}(dy)$ are defined by their first two moments $m(\tau)=0$ and $C_d(s,\tau)=d\ \min(s,\tau)$. Here d is equal to $2D$ and $2/D$ for the first and second equation correspondingly. The initial functions $\varphi(\xi)\equiv\alpha(\xi,0)=H(\xi)$ and $\psi(\xi)\equiv\beta(\xi,0)=1-H(\xi)=H(-\xi)$ were defined by Eq. (5).

Now expanding the integrand exponents in Eq. (6) in the power series one first obtains the zeroth order which is trivial

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$$\alpha_0(\xi,\tau)=\int_{\mathbf{C}[0,\tau]} H(y(\tau)+\xi)\ \mu_{2D}(dy)$$
$$=\frac{1}{2}\left[1+\mathrm{erf}\left(\frac{\xi}{\sqrt{4D\tau}}\right)\right],$$
$$\beta_0(\xi,\tau)=\int_{\mathbf{C}[0,\tau]} H(-y(\tau)-\xi)\ \mu_{2/D}(dy)$$
$$=\frac{1}{2}\left[1-\mathrm{erf}\left(\frac{\xi\sqrt{D}}{\sqrt{4\tau}}\right)\right]. \tag{7}$$

An important question to be addressed here is the validity limit of this approximation. Looking at Eq. (6) one infers that to assure the series convergence, a norm of the operator $L(f)\equiv\varepsilon r^{\pm 1}\int_0^\tau f(t)\ dt$ should be finite for every function f from the space of solutions of this system. Since very little is known about this functional space, in the subsequent analysis we accept a quite natural assumption that the above mentioned norm is bounded.

The first-order term is nontrivial and written as

$$\alpha_1(\xi,\tau)=-\frac{\varepsilon}{r}\int_{\mathbf{C}[0,\tau]}\left\{\int_0^\tau \beta_0(y(t)+\xi,t)\ dt\right\}$$
$$\times H(y(\tau)+\xi)\ \mu_{2D}(dy),$$
$$\beta_1(\xi,\tau)=-\varepsilon r\int_{\mathbf{C}[0,\tau]}\left\{\int_0^\tau \alpha_0(y(t)+\xi,t)\ dt\right\}$$
$$\times H(-y(\tau)-\xi)\ \mu_{2/D}(dy). \tag{8}$$

To get analytic expressions for further analysis we shall use the following approximations [7]:

$$\int_{\mathbf{C}[0,\tau]}\left\{\int_0^\tau F\left(\frac{y(t)}{\sqrt{t}}\right)\ dt\right\}H(y(\tau)+\xi)\ \mu_{2D}(dy)$$
$$\approx \tau I_1^{(1)}(F)$$
$$=\tau F(0)\alpha_0(\xi,\tau)+\tau\frac{F(1)-F(-1)}{3\sqrt{\pi}}\sqrt{D}\exp\left(-\frac{\xi^2}{4D\tau}\right),$$
$$\int_{\mathbf{C}[0,\tau]}\left\{\int_0^\tau F\left(\frac{y(t)}{\sqrt{t}}\right)\ dt\right\}H(-y(\tau)-\xi)\ \mu_{2/D}(dy)$$
$$\approx \tau I_2^{(1)}(F)$$
$$=\tau F(0)\beta_0(\xi,\tau)-\tau\frac{F(1)-F(-1)}{3\sqrt{\pi D}}\exp\left(-\frac{D\xi^2}{4\tau}\right).$$

It can be verified by straightforward calculation that this approximation is exact for the first-order polynomials. It is a particular case of *given accuracy formulas* which is widely used for practical calculation of functional integrals [7]. These formulas are an analog of the well-known Gauss integration formulas [8] for the usual finite-dimensional integrals. Thus these formulas are exact for functional polynomials of the first, second, and so on degree correspondingly. In this paper we use the formulas that are exact for the first and second degree polynomials only. Therefore, the main properties of the Gauss integration remain valid (with some reservations) in the functional integral case. Namely, being *exact* for some (two, three, and so on) starting terms of the Taylor decomposition, they usually supply a very good approximation for the *whole* series representing a smooth (nonoscillating) function. Therefore, the parameter of the Taylor expansion is formally a small parameter of the problem. Closer examination of the exact conditions of convergence can be found in [9].

Substituting F by β_0 and α_0 [see Eq. (8)] one gets

$$\alpha_1(\xi,\tau)=-\frac{\varepsilon\tau}{r}\alpha_1^{(1)}(\xi,\tau)$$
$$=-\frac{\varepsilon\tau}{r}\left\{\frac{1}{4}\left[1-\mathrm{erf}\left(\frac{\xi\sqrt{D}}{2\sqrt{\tau}}\right)\right]\left[1+\mathrm{erf}\left(\frac{\xi}{2\sqrt{D\tau}}\right)\right]\right.$$
$$+\frac{1}{6}\sqrt{D/\pi}\left[\mathrm{erf}\left(\frac{\sqrt{D}}{2}\left(\frac{\xi}{\sqrt{\tau}}-1\right)\right)\right.$$
$$\left.\left.-\mathrm{erf}\left(\frac{\sqrt{D}}{2}\left(\frac{\xi}{\sqrt{\tau}}+1\right)\right)\right]\exp\left(-\frac{\xi^2}{4D\tau}\right)\right\},$$

$$\beta_1(\xi,\tau)=-\varepsilon r\tau\beta_1^{(1)}(\xi,\tau)$$
$$=-\varepsilon r\tau\left\{\frac{1}{4}\left[1+\mathrm{erf}\left(\frac{\xi}{2\sqrt{D\tau}}\right)\right]\left[1-\mathrm{erf}\left(\frac{\xi\sqrt{D}}{2\sqrt{t}}\right)\right]\right.$$
$$+\frac{1}{6}\frac{1}{\sqrt{D\pi}}\left[\mathrm{erf}\left(\frac{1}{2\sqrt{D}}\left(\frac{\xi}{\sqrt{\tau}}-1\right)\right)\right.$$
$$\left.\left.-\mathrm{erf}\left(\frac{1}{2\sqrt{D}}\left(\frac{\xi}{\sqrt{\tau}}+1\right)\right)\right]\exp\left(-\frac{D\xi^2}{4\tau}\right)\right\}.$$

As we just mentioned the small parameter of our problem is a parameter of the corresponding Taylor expansion. Specifically, in our case it is $\xi\tau^{-1/2}$ and therefore our approximation is expected to be good if $\xi\tau^{-1/2}\ll 1$. However, we stress again that for our very smooth functional it gives a very good approximation in a whole range of $\xi\tau^{-1/2}$. In order to illustrate the whole-range accuracy of the approximation made we plot, in Fig. 1, $\alpha_1^{(1)}$, $\beta_1^{(1)}$ along with $\alpha_1^{(2)}$, $\beta_1^{(2)}$ obtained on the basis of the formulas exact for the second-order polynomials [7]

$$\int_{\mathbf{C}[0,\tau]}\left\{\int_0^\tau F\left(\frac{y(t)}{\sqrt{t}}\right)\ dt\right\}H(y(\tau)+\xi)\ d\mu_{2D}(y)$$
$$\approx \tau I_1^{(1)}(F)+\tau[F(\sqrt{2})-F(1)+F(-\sqrt{2})-F(-1)]$$
$$\times\left[D\alpha_0(\xi,\tau)-\frac{\xi\sqrt{D}}{4\sqrt{\pi\tau}}\exp\left(-\frac{\xi^2}{4D\tau}\right)\right],$$

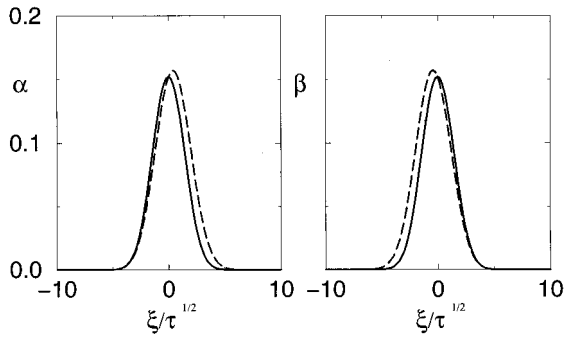

FIG. 1. Comparison plot for the first and second approximations. The left panel shows $\alpha_1^{(1)}$ and $\alpha_1^{(2)}$, while the right panel — $\beta_1^{(1)}$ and $\beta_1^{(2)}$. Solid lines are first approximation, dashed lines are second approximation.

$$\int_{\mathbf{C}[0,\tau]}\left\{\int_0^\tau F\left(\frac{y(t)}{\sqrt{t}}\right)\,dt\right\}H(-y(\tau)-\xi)\,d\mu_{2/D}(y)$$
$$\approx \tau I_2^{(1)}(F)+\tau[F(\sqrt{2})-F(1)+F(-\sqrt{2})-F(-1)]$$
$$\times\left[\frac{1}{D}\beta_0(\xi,\tau)+\frac{\xi}{4\sqrt{D\pi\tau}}\exp\left(-\frac{D\xi^2}{4\tau}\right)\right].$$

Figure 1 clearly demonstrates that the deviations do not exceed several percent worth for the whole range. As we said above this sequence of approximations is convergent and then we are dealing with the Cauchy sequence. Therefore, the pointwise difference between the next (third) approximation and the second one is necessary smaller than that between the second and the first ones shown in Fig. 1.

We next use these results to calculate the location of the center of the reaction front $\zeta(t)$. Following previous publications [2,3,6], this quantity is defined as the position at which the local production rate

$$R(x,t)=a_0b_0\sqrt{D_aD_b}\varepsilon\,\alpha(x,t)\beta(x,t) \tag{9}$$

has its maximum. Then, differentiating the product $[\alpha_0(\xi,\tau)+\alpha_1(\xi,\tau)][\beta_0(\xi,\tau)+\beta_1(\xi,\tau)]$ with respect to ξ, and resolving the resulting equation, one gets in a good approximation

$$\zeta(t)=\sqrt{\pi}\frac{\left(\frac{1}{\sqrt{D}}-\sqrt{D}\right)\tau^{-1/2}+\frac{\varepsilon M}{2}\tau^{1/2}}{2\tau^{-1}+\varepsilon N}, \tag{10}$$

where M and N are time-independent constants which are found to be

$$M=\left(\frac{\sqrt{D}}{r}-\frac{r}{\sqrt{D}}\right)-\frac{4}{3\pi}\left(\frac{D^{3/2}}{r}-\frac{r}{D^{3/2}}\right)-\left(\frac{1}{\sqrt{D}}-\sqrt{D}\right)$$
$$\times\left(\frac{1}{r}+r\right),$$

$$N=\left(\frac{1}{\sqrt{D}}-\sqrt{D}\right)\left(\frac{\sqrt{D}}{r}-\frac{r}{\sqrt{D}}\right)-\frac{2}{3}\left(\frac{1}{r}+r\right).$$

This result Eq. (10) is in excellent agreement with the Taitelbaum's *et al.* empirical approximation [6].

The most interesting property of the reaction front is the possibility of changing its direction of motion, which has been experimentally confirmed [6]. It is possible if $D>1,\ M>0$ or $D<1,\ M<0$. Using the identity

$$\frac{D^{3/2}}{r}-\frac{r}{D^{3/2}}=\left(\frac{\sqrt{D}}{r}-\frac{r}{\sqrt{D}}\right)\left(D+\frac{1}{D}-1\right)+\left(\frac{1}{r}+r\right)$$
$$\times\left(\sqrt{D}-\frac{1}{\sqrt{D}}\right)$$

one rewrites the expression for M in the form

$$M=\left(\sqrt{D}-\frac{1}{\sqrt{D}}\right)\left(\frac{1}{r}+r\right)\left(1-\frac{4}{3\pi}\right)+\left(\frac{\sqrt{D}}{r}-\frac{r}{\sqrt{D}}\right)$$
$$\times\left[1+\frac{4}{3\pi}-\frac{4}{3\pi}\left(D+\frac{1}{D}\right)\right].$$

From here one observes that the direction change occurs if $D>1,\ r<1$ or $D<1,\ r>1$ and $1+(4/3\pi)-(4/3\pi)(D+1/D)>0$. By recovering D we get $\frac{1}{8}(3\pi+4-\sqrt{(3\pi+12)(3\pi-4)})<D<\frac{1}{8}(3\pi+4+\sqrt{(3\pi+12)(3\pi-4)})$ or $0.33<D<3.03$. This inequality is a sufficient condition for the direction to change.

A sufficient condition for the direction *not* to change is $D>1,\ M<0$ or $D<1,\ M>0$. From the estimation

$$M\leqslant\left(\frac{\sqrt{D}}{r}-\frac{r}{\sqrt{D}}\right)P,\quad \text{for } D>1,\quad r<1,$$

$$M\geqslant\left(\frac{\sqrt{D}}{r}-\frac{r}{\sqrt{D}}\right)P,\quad \text{for } D>1,\quad r>1,$$

where $P=3-(4/3\pi)-(4/3\pi)(D+1/D)$, we infer that the sufficient condition $P<0$ is obeyed if $D<\frac{1}{8}(9\pi-4-\sqrt{(9\pi+4)(9\pi-12)})$ $(D<0.17)$ or $D>\frac{1}{8}(9\pi-4+\sqrt{(9\pi+4)(9\pi-12)})$ $(D>5.90)$.

The explicit expressions we obtained for α and β enable one to make some conclusions about their validity. Namely, in the vicinity of the point $\xi\tau^{-1/2}=0$ (where our approximation is *exact*) functions α and β take the form

$$\alpha\approx\frac{1}{2}-\frac{\tau\varepsilon}{4r}+\frac{\tau\varepsilon}{3r\sqrt{\pi}}\operatorname{erf}\left(\frac{\sqrt{D}}{2}\right)+o\left(\frac{\xi}{\sqrt{\tau}}\right),$$

$$\beta\approx\frac{1}{2}-\frac{\tau r\varepsilon}{4}+\frac{\tau r\varepsilon}{3\sqrt{\pi}}\operatorname{erf}\left(\frac{1}{2\sqrt{D}}\right)+o\left(\frac{\xi}{\sqrt{\tau}}\right).$$

Thus a sufficient conditions for the solutions of system (4) to be positive reads (for $D<1$)

$$\tau<\frac{6}{(3\sqrt{\pi}-4)}\frac{r}{\varepsilon},$$

or (for $D>1$)

$$\tau < \frac{6}{(3\sqrt{\pi}-4)} \frac{1}{r\varepsilon},$$

respectively, which means that after $t \sim k^{-1}$ our approach may not be valid.

There are two possible reasons for this failure. The first one is the two approximations we made in the course of calculations. However, as we demonstrated above, the approximation made to calculate the integrals in Eq. (8) is a very reliable one in the whole range. Moreover, it becomes exact at the point where the failure appears.

Another approximation has been done to deal with Eq. (6). Its validity depends on whether the norm of operator $L(f) \equiv \varepsilon r^{\pm 1} \int_0^\tau f(t)\, dt$ is finite or infinite on the functional space of solutions of system (6). While the assumption about the bounded norm sounds very likely we cannot prove it rigorously. Then, at the moment, we cannot eliminate this reason for certain.

However, if both the approximations are valid then the failure should be attributed to the limitation of the mean-field equations (4). In other words, $t \sim k^{-1}$ is, probably, the applicability limit for the mean-field approach.

In summary, we have developed a mathematical approach to deal with reaction-diffusion mean-field equations. It was checked against an analytical fitting reported before. We have also estimated the applicability limit for our solutions and discussed possible reasons for this limitation.

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