

A PATH-INTEGRAL THEORY OF LASER-CONTROLLED REACTIONS WITH POSSIBLE APPLICATION TO PHOTOLITHOGRAPHY

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Equations of diffusion are solved for two components undergoing an isomerization reaction (a chemical reaction of the first order). The problem is analysed in regard to prospects for a local control of the chemical reaction by a laser beam. The final results are presented as functionals with a kernel calculable by the standard Feynman-Kac integration.

1. INTRODUCTION

As it is well known, intense fields of laser beams can foster chemical reactions which otherwise would be either absent or ineffective. These reactions may run in a very local way since the laser beams, or fractions of them transmitted through windows in diaphragms (masks), can be — when considered in terms of the geometric optics — as narrow as, say, ten times the optical wavelength. This is, of course, crucial for photolithographic techniques used in the contemporary microelectronics. Whilst the “industrial photolithography” has enabled production of integrated circuits with elements measuring about 3—5 micrometers [1], there are still possibilities to use the optical lithography for manufacturing circuits with elements as small as one micrometer or slightly less.

When studying laser-generated reactions (in a photoresist or another medium) confined to narrow regions, we must pay attention to two issues which were usually ignored in the classical theories of chemical reactions: i) non-uniformity of reaction rates (due to radial energy-density gradients in the laser beams) and ii) presence of high concentration gradients leading to non-negligible diffusion processes. Then, in general, the kinetic equations for the concentrations of the components entering the reactions may be non-linear since: i) the reactions may be of higher order than the first, and ii) the diffusion coefficients may depend on the concentrations.

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On the other hand, even when we refuse such complications and allow only for the first-order reactions, and for constancy of the diffusion coefficients, we are still faced with non-trivial kinetic equations, because there are many various potentialities for spatial and temporal modulations of the reaction rate coefficients.

Therefore, in the present paper we focus our attention on the following linear system of the diffusion-reaction equations:

$$\begin{aligned} \frac{\partial C_1}{\partial t} &= D_1 \nabla^2 C_1 - W_{12} C_1 + W_{21} C_2, \\ \frac{\partial C_2}{\partial t} &= D_2 \nabla^2 C_2 + W_{12} C_1 - W_{21} C_2. \end{aligned} \quad (1)$$

Here D_1 , D_2 and $W_{12}(\mathbf{r}, t)$, $W_{21}(\mathbf{r}, t)$, respectively, are two positive constants (diffusion coefficients) and two non-negative functions (reaction rate coefficients). Our aim is to show that the fundamental solution (i.e. Green's function) to equations (1) (for $t > 0$) can be expressed by means of the Feynman—Kac path integral [2, 3]. Recall that the Feynman—Kac integral

$$G(\mathbf{r}, t; \mathbf{r}_0) = \int_{\mathcal{r}_0^0}^{\mathcal{r}^t} \mathcal{D} \mathbf{r}(t) \exp \left\{ - \int_0^t d\tau \left[\frac{\mathbf{r}^2(\tau)}{4D} + V(\mathbf{r}(\tau), \tau) \right] \right\} \quad (2)$$

is the solution of the equation

$$\frac{\partial G}{\partial t} = D \nabla^2 G - V(\mathbf{r}, t) G, \quad t > 0, \quad (3)$$

satisfying the initial condition

$$G(\mathbf{r}, 0; \mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0). \quad (4)$$

Clearly, if we introduce the two-component function

$$\mathbf{C}(\mathbf{r}, t) = \begin{pmatrix} C_1(\mathbf{r}, t) \\ C_2(\mathbf{r}, t) \end{pmatrix} \quad (5)$$

we may define the 2×2 matrix Green's function

$$\mathbf{G}(\mathbf{r}, t; \mathbf{r}_0) = \begin{pmatrix} G_{11}(\mathbf{r}, t; \mathbf{r}_0) & G_{12}(\mathbf{r}, t; \mathbf{r}_0) \\ G_{21}(\mathbf{r}, t; \mathbf{r}_0) & G_{22}(\mathbf{r}, t; \mathbf{r}_0) \end{pmatrix} \quad (6)$$

so that

$$\mathbf{C}(\mathbf{r}, t) = \int d^3 r_0 \mathbf{G}(\mathbf{r}, t; \mathbf{r}_0) \mathbf{C}(\mathbf{r}_0, 0). \quad (7)$$

Then, interpreting D and V as 2×2 matrices,

$$D \rightarrow \mathbf{D} = \begin{pmatrix} D_1 & 0 \\ 0 & D_2 \end{pmatrix}, \quad V \rightarrow \mathbf{V} = \begin{pmatrix} W_{12} & -W_{21} \\ -W_{12} & W_{21} \end{pmatrix}, \quad (8)$$

we may say that equation (3) for $G \rightarrow \mathbf{G}$ is equivalent to equations (1). Thus, what we will present here is a two-component generalization of the Feynman—Kac problem.

If $D_1 \neq D_2$, the generalization is fairly difficult. It is rather surprising but it is not at all easy, for $D_1 \neq D_2$, to obtain exact solutions to equations (1) even in the simplest case when W_{12} , W_{21} are constants! Therefore, first we take $D_1 = D_2$. With this stipulation, we can derive—as shown in Section II—a path integral solution to equations (1) for the quite general functions W_{12} , W_{21} .

The rate coefficients W_{12} , W_{21} can be varied by laser beams. For instance, if a laser beam is permanently directed along an axis, say the z -axis, we may define W_{12} , W_{21} as axially symmetric functions simulating the energy-density profile of the beam. Then, taking the initial concentrations $C_1(\mathbf{r}, 0)$, $C_2(\mathbf{r}, 0)$ as z -independent, we treat equations (1) as two-dimensional (Section III).

In Section IV, reserved for the concluding remarks, we suggest how to make a short step forward by taking $D_1 \neq D_2$ but assuming that

$$|D_1 - D_2| \ll \frac{1}{2} (D_1 + D_2). \quad (9)$$

Under this condition, we can show that a perturbation theory with respect to the small parameter $|D_1 - D_2|$ is feasible.

II. FORMAL SOLUTION WITH $D_1 = D_2 = D$

Let j equal 1 or 2 (fixed column index); we are to solve the equations

$$\frac{\partial G_{ij}}{\partial t} = D \nabla^2 G_{ij} - W_{12} G_{ij} + W_{21} G_{ji}, \quad (10)$$

$$\frac{\partial G_{2i}}{\partial t} = D \nabla^2 G_{2i} + W_{12} G_{ij} - W_{21} G_{ji},$$

with respect to the initial conditions

$$G_{ij}(\mathbf{r}, 0; \mathbf{r}_0) = \delta_{ij} \delta(\mathbf{r} - \mathbf{r}_0). \quad (11)$$

We define the functions

$$G_j = G_{ij} + G_{ji}, \quad (12)$$

$$g_j = G_{ij} - G_{ji}, \quad (13)$$

so that

$$G_{ij} = \frac{1}{2}(G_j + g_j), \quad (14)$$

$$G_{ji} = \frac{1}{2}(G_j - g_j), \quad (15)$$

Then equations (10) are transformed as follows:

$$\frac{\partial G_j}{\partial t} - D \nabla^2 G_j = 0, \quad (16)$$

$$\frac{\partial g_j}{\partial t} - D \nabla^2 g_j + (W_{21} + W_{12})g_j = (W_{21} - W_{12})G_j. \quad (17)$$

Independent of the index j , the initial condition for G_j is

$$G_j(\mathbf{r}, 0; \mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0). \quad (18)$$

Equation (16) gives the solution

$$G_j(\mathbf{r}, t; \mathbf{r}_0) = \frac{1}{(4\pi Dt)^{3/2}} \exp \left[-\frac{(\mathbf{r} - \mathbf{r}_0)^2}{4Dt} \right] \quad (19)$$

for $t > 0$. For the functions g_j , we have the initial conditions

$$g_j(\mathbf{r}, 0; \mathbf{r}_0) = (-1)^{j+1} \delta(\mathbf{r} - \mathbf{r}_0) \quad (20)$$

For fixed j , we define Green's function $\gamma_j(\mathbf{r}, t; \mathbf{r}_0)$ satisfying the equation

$$\frac{\partial \gamma_j}{\partial t} - D \nabla^2 \gamma_j + (W_{21} + W_{12})\gamma_j = 0, \quad t > 0, \quad (21)$$

and the initial condition

$$\gamma_j(\mathbf{r}, 0; \mathbf{r}_0) = \delta(\mathbf{r} - \mathbf{r}_0). \quad (22)$$

Then we obtain the formula

$$g_j(\mathbf{r}, t; \mathbf{r}_0) = (-1)^{j+1} \{\gamma_j(\mathbf{r}, t; \mathbf{r}_0)\} + \quad (23)$$

$$+ \int_0^t dt' \int d^3r' \gamma_j(\mathbf{r}, t-t'; \mathbf{r}') [W_{21}(\mathbf{r}', t') - W_{12}(\mathbf{r}', t')] G_j(\mathbf{r}', t'; \mathbf{r}_0).$$

Thus, the problem has been reduced to solving equation (21) with respect to condition (22). The direct comparison with relations (2), (3) and (4) yields the result

$$\begin{aligned} \gamma_j(\mathbf{r}, t; \mathbf{r}_0) = & \int_{t_0=0}^{t_1=t} \mathcal{D} \mathbf{r}(\tau) \exp \left\{ -\int_0^t d\tau \left[\frac{r^2(\tau)}{4D} + (W_{21}(\mathbf{r}(\tau), \tau) + \right. \right. \\ & \left. \left. + W_{12}(\mathbf{r}(\tau), \tau)) \right] \right\}. \end{aligned} \quad (24)$$

If this functional integral (the Feynman—Kac) integral) can be calculated explicitly, the problem may be viewed as solved. Formulae (14), (15) give us the components $G_{ij}(\mathbf{r}, t; \mathbf{r}_0)$ of Green's function \mathbf{G} , and then, for any initial distributions $C_1(\mathbf{r}, 0)$, $C_2(\mathbf{r}, 0)$, we can, employing formula (7), calculate instantaneous concentration profiles $C_1(\mathbf{r}, t)$, $C_2(\mathbf{r}, t)$ for $t > 0$.

III. DIFFUSION OF TWO-LEVEL MOLECULES IN A LASER BEAM

In this Section, we will exemplify the general analysis shown in Section II and solve a problem interesting to experimentalists. We consider an ensemble of molecules (or defects, "clusters", etc., in a crystalline or another medium) at some temperature T ; before the time instant $t_0 = 0$, the ensemble is in thermodynamic equilibrium. Let the molecules have two energies: E_1 and E_2 , $E_1 < E_2$. With a certain probability, each molecule, being in the state X_1 with the energy E_1 , may pass (undergoing some stereochemical change) into the state X_2 with the energy E_2 . For simplicity, we assume that the energies E_1 , E_2 correspond to non-degenerated quantum-mechanical states. The corresponding transition probabilities (per unit time) are $W_{12} \equiv W(X_1 \rightarrow X_2)$, $W_{21} \equiv W(X_2 \rightarrow X_1)$. Thus, we may interpret the reaction



as an isomerization process. If the geometric form of the molecules is roughly the same in both states X_1 and X_2 , we may also assume that their diffusion coefficients are practically equal. Respectively, we may use equations (1) with $D_1 = D$, $D_2 = D$ for C_1 , C_2 . For $t < 0$, C_1 and C_2 are constants; we denote them C_{1e} , C_{2e} . We define also the total equilibrium concentration of the molecules:

$$C_e = C_{1e} + C_{2e}. \quad (26)$$

According to the Boltzmann principle, we have the relations:

$$C_{ie} = C_e \frac{e^{-\beta E_i}}{e^{-\beta E_1} + e^{-\beta E_2}}; \quad i = 1, 2; \quad \beta = \frac{1}{k_B T}. \quad (27)$$

Let us now assume that a laser beam of frequency $\omega = (E_2 - E_1)/\hbar$ is switched on at $t_0 = 0$ along the z -axis. The radial energy-density profile of the beam is

given by a function $\varphi(x, y) = \varphi(\sqrt{(x^2 + y^2)})$. For example, it is possible to use — as in quantum electronics [4] — a Gaussian profile:

$$\varrho_a(r) = \varrho_a(x, y) \sim \varphi(x, y) = A \exp\left(-\frac{x^2 + y^2}{2L^2}\right) \quad (28)$$

where $A > 0$ is a dimensionless maximum amplitude.

If $E_2 - E_1 \gg k_B T$, then $C_{1e} \gg C_{2e}$; the molecules in the state X_2 have a mean "spontaneous lifetime" $\tau_s > 0$. With this concept, we may write the transition rate coefficients in the form

$$W_{12} = \frac{1}{\tau_s} [f_0 + \varphi(x, y)], \quad (29)$$

$$W_{21} = \frac{1}{\tau_s} [f_0 + 1 + \varphi(x, y)],$$

where

$$f_0 = \frac{1}{e^{k(E_2 - E_1)} - 1} = \text{const.} \quad (30)$$

The solutions C_1, C_2 do not depend on z ; therefore, we write the diffusion-reaction equations as follows:

$$\frac{\partial C_1}{\partial t} = D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) C_1 - \frac{f_0 + \varphi}{\tau_s} (C_1 - C_2) + \frac{C_2}{\tau_s}, \quad (31)$$

$$\frac{\partial C_2}{\partial t} = D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) C_2 + \frac{f_0 + \varphi}{\tau_s} (C_1 - C_2) - \frac{C_2}{\tau_s}.$$

For the functions

$$C = C_1 + C_2, \quad c = C_1 - C_2, \quad (32)$$

equations (31) pass into the following ones:

$$\frac{\partial C}{\partial t} - D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) C = 0, \quad (33)$$

$$\frac{\partial c}{\partial t} - D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) c + \frac{2f_0 + 1 + 2\varphi}{\tau_s} c = \frac{C}{\tau_s}. \quad (34)$$

Equation (33) gives the trivial solution

$$C(x, y, t) = C_s = \text{const.} \quad (35)$$

We define

$$c_e = C_{1e} - C_{2e} \quad (36)$$

and

$$b(x, y, t) = c(x, y, t) - c_e. \quad (37)$$

Noting that

$$C_e = (2f_0 + 1) c_e, \quad (38)$$

$$\frac{\partial b}{\partial t} - D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) b + \frac{2f_0 + 1 + 2\varphi}{\tau_s} b = -\frac{2c_e}{\tau_s} \varphi(x, y). \quad (38)$$

Defining its Green's function $K(x, y, t; x_0, y_0)$ by the equation

$$\frac{\partial K}{\partial t} - D \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) K + \frac{2}{\tau_s} \varphi(x, y) K = 0, \quad t > 0, \quad (39)$$

$$K(x, y, 0; x_0, y_0) = \delta(x - x_0) \delta(y - y_0), \quad (40)$$

we may write b in the form

$$b(x, y, t) = -\frac{2c_e}{\tau_s} \int_0^t dt \exp\left[-\frac{2f_0 + 1}{\tau_s}(t - t')\right] \iint dx' dy' K(x, y, t - t'; x', y') \cdot \varphi(x', y'). \quad (41)$$

For any function $\varphi(x, y)$, the Green function (i.e. the kernel of functional (41)) can be expressed as the Feynman—Kac integral:

$$K(x, y, t; x_0, y_0) = \int_{x_0, y_0, 0}^{x, y, t} \mathcal{D}x(\tau) \mathcal{D}y(\tau) \exp\left\{-\int_0^t d\tau \left[\frac{\dot{x}^2(\tau) + \dot{y}^2(\tau)}{4D} + \varphi(x(\tau), y(\tau)) \right]\right\}. \quad (42)$$

This can be calculated numerically by adopting a Monte-Carlo method. Upon another occasion, computer programs for numerical calculations of the Feynman—Kac integrals were implemented by Kolibiar [5, 6].

IV. CONCLUDING REMARKS

Our aim here was to present a theory in its general formulation. Input constants of this theory may vary by many orders of magnitude and their estimation is a problem significant in its own right; for us, D_1, D_2 and τ_s are phenomenological parameters.

For our analysis of the diffusion-reaction problem given by equations (1), it was indeed labour-saving to have equalized the diffusion constants D_1, D_2 . Now, let us assume that $D_1 \neq D_2$ but $|D_1 - D_2|$ is small enough in comparison with

$$D = \frac{1}{2}(D_1 + D_2). \quad (43)$$

We use the denotation

$$\delta = D_1 - D_2; \quad (44)$$

this parameter may be either positive or negative. We write

$$C_1 = C_1^{(0)} + Q_1, \quad C_2 = C_2^{(0)} + Q_2, \quad (45)$$

where $C_1^{(0)}, C_2^{(0)}$ are "non-perturbed" solutions satisfying the equations

$$\begin{aligned} \frac{\partial C_1^{(0)}}{\partial t} &= D \nabla^2 C_1^{(0)} - W_{12} C_1^{(0)} + W_{21} C_2^{(0)}, \\ \frac{\partial C_2^{(0)}}{\partial t} &= D \nabla^2 C_2^{(0)} + W_{12} C_1^{(0)} - W_{21} C_2^{(0)}. \end{aligned} \quad (46)$$

After inserting expressions (45) into equations (1), we obtain — with respect to equations (46) — the following nonhomogeneous equations for the functions Q_1, Q_2 :

$$\begin{aligned} \frac{\partial Q_1}{\partial t} - D \nabla^2 Q_1 + W_{12} Q_1 - W_{21} Q_2 &= \frac{\delta}{2} \nabla^2 (C_1^{(0)} + Q_1), \\ \frac{\partial Q_2}{\partial t} - D \nabla^2 Q_2 - W_{12} Q_1 + W_{21} Q_2 &= -\frac{\delta}{2} \nabla^2 (C_2^{(0)} + Q_2). \end{aligned} \quad (47)$$

Generally, we write the series

$$Q_i = \sum_{n=1}^{\infty} \delta^n \cdot q_i^{(n)} \quad (48)$$

where the functions $q_i^{(n)}$ are δ -independent. To calculate the first-order (in δ) functions $q_i^{(1)}$ ($i = 1, 2$), we omit Q_1, Q_2 on the right-hand side of equations (47); to calculate $q_i^{(2)}$, we substitute $Q_i \rightarrow \delta \cdot q_i^{(1)}$ on the r.h. side, and so on. At each step of this iteration procedure, we can employ the common Feynman—Kac integral in the same way as in Section II.

Similarly, we are able to apply the iteration calculation in case of the laser-accelerated reaction analysed in Section III.

There is still another point that should be emphasized. The success in reducing our two-component diffusion-reaction problem to the Feynman—Kac inte-

gral has derived from the symmetry of the reaction matrix \mathbf{V} (cf. definition (8)). On the other hand, it is easy to imagine a situation when the components X_1, X_2 , while taking part in reaction (25), may be subject to some trapping as well. Actually, in the original Kac treatment of equation (3), the function $V(r, t)$ was interpreted as a trapping coefficient ($V \geq 0$). Now, we may introduce two trapping coefficients V_1, V_2 selectively ($V_1 \neq V_2$) for X_1, X_2 and define a generalized reaction matrix

$$\mathbf{V} = \begin{pmatrix} W_{12} + V_1 & -W_{21} \\ -W_{12} & W_{21} + V_2 \end{pmatrix}. \quad (49)$$

Then the process of thought, as put forward in the present paper, is no more practicable. Fortunately, however, we can overcome this difficulty by another path-integral theory. As this new theory does formally look more complicated, our purport was first to write a preparatory text — the present paper — in anticipation of the more advanced one [7] where the matrix \mathbf{V} is taken with general trapping coefficients V_1, V_2 .

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ТЕОРИЯ ИНТЕГРАЛОВ ПО ТРАЕКТОРИЯМ ДЛЯ РЕАКЦИЙ, УПРАВЛЯЕМЫХ ПРИ ПОМОЩИ ЛАЗЕРНОГО ПУЧКА, И ЕЕ ВОЗМОЖНОЕ ПРИМЕНЕНИЕ В ФОТОЛИТОГРАФИИ

В работе найдено решение уравнений диффузии для двух компонент, подвергшихся реакции изомеризации (химическая реакция первого порядка). Приведен анализ решения с точки зрения переплетения локального управления химической реакцией при помощи лазерного пучка. Конечные результаты представлены в виде функционалов с ядром, которое можно вычислить при помощи стандартных интегралов по траекториям Фейнмана—Кача.