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Noise-induced phase transition of the dimer–monomer (DM) reaction model

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Abstract

Considering the gas-phase fluctuations in the Monte Carlo simulation, we construct a stochastic differential equation and the corresponding Fokker–Planck equation to describe the state evolution of the dimer–monomer (DM) surface reaction model. We find that the well-known first-order irreversible phase transition characteristic of the DM model may be viewed as a noise-induced transition. © 1998 Elsevier Science B.V.

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The subject of reaction kinetics and irreversible phase transitions (IPTs) in surface catalysis has gained increasing attention in recent years. The dimer–monomer (DM) model: $A + \frac{1}{2}B_2 \rightarrow AB$, which is also known as the ZGB model, has been extensively studied since the work of Ziff, Gulari and Barshad [1,2]. This model is based upon the Langmuir–Hinshelwood (LH) mechanism, i.e. both the reactants are adsorbed on the surface. It is assumed that the reaction occurs according to the following steps:

$$A_g + S \rightarrow A_a, \quad B_2 + 2S \rightarrow 2B_a, \quad A_a + B_a \rightarrow AB_g + 2S,$$
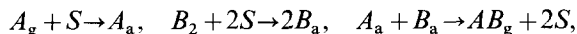
where subscript g and a refer to gaseous and adsorbed species, respectively, and S denotes an empty site. In a Monte Carlo simulation (MCS), the monomer A adsorbs at single empty sites with rate y_A, the dimer B_2 adsorbs at adjacent pairs of

empty sites with rate $y_B = 1 - y_A$, and the reaction between different species adsorbed at adjacent pairs of sites occurs instantaneously. The most distinctive feature of the DM model is the occurrence of a first-order A-poisoning IPT at high $y_A = y_2$ and a second-order B-poisoning IPT at low $y_A = y_1$. When evolving from an initial lattice half empty and half saturated by A, $y_2 = 0.525$; while for initially empty lattice, $y_2 = 0.5277$ [3,4]. For both cases, the second-order IPT exists at $y_1 = 0.3905$.

Some theoretical approaches have also been proposed to describe the DM model [5–17]. Exact rate equations for site concentrations and the probability of various larger configurations to which they couple, can be readily obtained after accounting for all adsorption or reaction events which create or destroy these configurations. However, near the first-order IPT, where the steady-state correlation length is finite, approxi-

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mate treatment of the spatial ordering usually produces reasonably accurate results. Such treatments include site approximation (SA) [5,7–11] which neglects all correlations, pair approximation (PA) [5–8,11,12] accounting for nearest-neighbour correlations, the Kirkwood or superposition approximation (KA)[7], the Mamada–Takano approximation (MTA) [13–15] and the complete stochastic ansatz [13–17] which considers long-range correlations. Better predictions of the second-order IPT-value y_1 are obtained if higher-order correlations are accounted for, which indicates that long-range correlations are very important near y_1. All these treatments, however, predict the same spinodal point, $y_s = 0.561$, for the DM model (the first-order IPT occurs here according to these treatments), showing that long-range correlations are not so important in the neighbourhood of the first-order IPT.

One notes, however, the MCS value of the first-order IPT $y_2 = 0.525$ is substantially below $y_s = 0.561$. According to the discussion in the last paragraph, this discrepancy is not due to the approximation of the correlations. One may argue that the effect of the initial condition should be accounted for, say, a half empty initial lattice is used to determine y_2 in MCS [1,2] while y_s is obtained from an initially empty lattice. When using an initially empty lattice in the MCS, one obtains $y_2 = 0.5277$ rather than 0.561. However, on the other hand, although for $x_{AA}^0 = x_{SS}^0 = 0.5$ (here x_{ij}^0 represents the initial coverage of ij-pairs), PA-MFT predicts $y_2 = 0.5241$ [5] which is in agreement with the MCS. Evans [7] argued that this may be an artifact of the MFT approximation and the results should be viewed with scepticism. Further works [6,12] using PA-MFT also indicated that it cannot be uniformly determined which initial condition to choose in the MFT approximation to maintain consistency with the MCS results. Evans has proposed the epidemic analysis and scaling approach [7] to study the critical behaviour near y_2. He argued that the DM model has somewhat "bistable" feature [10] between a low x_A reactive state and the A-poisoning state and when y_A goes across y_2, the stable reactive state predicted by MFT becomes "metastable" and, therefore, a first-order phase transition occurs, for example the

system jumps into the more stable A-poisoning state.

From the above discussions, one concludes that another factor rather than long-range correlation and initial condition should be responsible for the occurrence of the metastability and the discrepancy between y_2 and y_s. In fact, noise often plays an important role in non-equilibrium nonlinear systems. The fluctuations of the control parameters can lead to multiplicative noise which may result in noise-induced transitions [18,19]. For example, noise can induce bistability in the monomer–monomer model, while a MFT description of which deterministically predicts monostability [20]. Very recently, a study of the Brusselator model has shown that noise can induce new spatial and temporal structures [21]. Note that in the MCS of the DM model, the fluctuation of the adsorption rate of A or B_2 is unavoidable, which should be considered in the descriptions of the state-evolution of the system. This fluctuation may result in a loss of stability of the reactive state at another spinodal point $y_s' < 0.561$ and one expects that the first-order IPT obtained by MCS may be viewed as a noise-induced phase transition.

Since correlation is not so important close to y_2, we can begin with the SA-MFT deterministic equations of motion:

$$\frac{dx_A}{dt} = y_A x_S (1 - x_B)^4 - 2 y_B x_S^2 [1 - (1 - x_A)^3], \quad (1)$$

$$\frac{dx_B}{dt} = 2 y_B x_S^2 (1 - x_A)^3 - y_A x_S [1 - (1 - x_B)^4], \quad (2)$$

where x_i ($i = A$, B or S) stands for i-site concentration and $x_S = 1 - x_A - x_B$. Note that in the present paper, we will consider y_A as a stochastic variable and assume that it is modulated by an additive Gaussian white noise (see the text below).

To construct the Langevin equation and, accordingly, the Fokker–Planck equation, we will first reduce the two coupled nonlinear equations to the state evolution equation of x_A. Note that in the steady state, the sticking probability of A and B_2 are exactly equal:

$$y_A x_S = 2 y_B x_S^2. \quad (3)$$

Therefore, near the steady state, one expects that Eq. (3) also holds approximately, say

$$y_A x_S - 2y_B x_S^2 = \epsilon, \qquad (4)$$

where ϵ is a small quantity near zero. Hence one has

$$\bar{x}_S \simeq \frac{y_A}{2y_B} - \frac{\epsilon}{y_A}. \qquad (5)$$

Substituting Eq. (5) back into Eqs. (1) and (2), we obtain

$$\frac{dx_A}{dt} = y_A \bar{x}_S [(1 - x_B)^4 + (1 - x_A)^3 - 1] \qquad (6)$$
$$+ \epsilon[1 - (1 - x_A)^3],$$

$$\frac{dx_B}{dt} = y_A \bar{x}_S [(1 - x_B)^4 + (1 - x_A)^3 - 1] - \epsilon(1 - x_A)^3.$$

$$(7)$$

Note that near the A-poisoning IPT point, x_A and x_B are anti-correlated, i.e. dx_A/dt and dx_B/dt have contrasting signs. If y_A is very close to y_2, both MCS and PA-MFT show that before the system is poisoned by A or reaches the reactive steady-state, there exists a long relaxation time when x_S hardly varies [5,22]. Thus, one can reasonably assume that, near y_2 and near the steady state,

$$\frac{dx_A}{dt} + \frac{dx_B}{dt} \simeq 0. \qquad (8)$$

Finally, we obtain the deterministic equation of motion with respect to x_A:

$$\frac{dx_A}{dt} = y_A \bar{x}_S [(x_A + \bar{x}_S)^4$$
$$+ (1 - x_A)^3 - 1] + \epsilon(1 - x_A)^3, \qquad (9)$$

where $\bar{x}_S$ is given by Eq. (5). Note that this equation only holds close to y_2 and close to the steady-state. Based on Eq. (9), one can take into account fluctuations of y_A and then determine the influence of noise on the bifurcation character of the system.

We can now account for the fluctuation of the adsorption rate of A simply by replacing y_A by $y_A + \Gamma(t)$, where $\Gamma(t)$ is the Gaussian white noise

with:

$$\langle \Gamma(t) \rangle = 0, \quad \langle \Gamma(t)\Gamma(t') \rangle = 2D\delta(t - t'), \qquad (10)$$

where D denotes the noise intensity. Here, the use of a Gaussian white noise is a standard procedure, for in most situations the magnitudes of external fluctuations are distributed according to Gaussian distribution which can be understood as a consequence of the central limit theorem. One should note that this may result in certain problems due to the unlimited fluctuations associated with Gaussian white noise. However, one expects that this would not affect the conclusion of the present paper.

According to Eq. (9), the stochastic differential equation (Langevin equation) reads (we rewrite x_A by x):

$$\frac{dx}{dt} = f(x, \epsilon) + g(x, \epsilon)\Gamma(t), \qquad (11)$$

where

$$f(x, \epsilon) = -y_A \bar{x}_S [(x + \bar{x}_S)^4$$
$$+ (1 - x)^3 - 1)] + \epsilon(1 - x)^3,$$

$$g(x, \epsilon) = -\frac{y_A(2 - y_A)}{2(1 - y_A)^2} [(x + \bar{x}_S)^4 + (1 - x)^3 - 1]$$
$$+ 4y_A \bar{x}_S \left[\frac{1}{(1 - y_A)^2} - \frac{\epsilon}{y_A^2} \right] (x + \bar{x}_S)^3.$$

The corresponding Fokker–Planck equation reads

$$\frac{\partial \rho(x, t)}{\partial t} = -\frac{\partial}{\partial x} [f(x, \epsilon)\rho(x, t)]$$
$$+ D\frac{\partial}{\partial x} \left[g(x, \epsilon)\frac{\partial}{\partial x} g(x, \epsilon)\rho(x, t) \right], \qquad (12)$$

where $\rho(x, t)$ is the probability density. To obtain the steady state solution, one sets $\epsilon = 0$ and $\partial\rho(x, t)/\partial t = 0$. Here, we would like to explain the role of ϵ used in the present paper. In fact, we first take advantage of ϵ to reduce the two coupled

nonlinear equations to the evolution equation of x_A, Eq. (9), which is used to construct the Langevin equation and the corresponding Fokker–Planck equation. Finally, since we only consider the steady-state bifurcation character of the system, we reset ϵ to zero.

Hence the steady-state solution is given by

$$\rho^{st}(x, \epsilon = 0) =$$

$$N \exp \left\{ \int_0^x \frac{f(y, \epsilon = 0) - Dg(y, \epsilon = 0)g'(y, \epsilon = 0)}{Dg^2(y, \epsilon = 0)} \, dy \right\},$$

(13)

where N is a normalization constant and $g'(x, \epsilon)$ denotes the derivative of $g(x, \epsilon)$ with respect to its argument x. The extrema $\bar{x}$ of the steady-state density obey the following equation (notice the maxima of $\rho^{st}(x, \epsilon = 0)$ correspond to the steady-state coverage of A species):

$$f(\bar{x}, \epsilon = 0) - Dg(\bar{x}, \epsilon = 0)g'(\bar{x}, \epsilon = 0) = 0. \quad (14)$$

For small values of y_A there are two solutions for Eq. (14), $\bar{x}_<$ and $\bar{x}_> (\bar{x}_< \leq \bar{x}_>)$, in the interval [0, 1], which coalesce when $y_A = y_s$, where y_s denotes the spinodal point. The lower branch $(\bar{x}_<)$ is stable and the higher branch $(\bar{x}_>)$ unstable. Therefore, when y_A increases from 0, the system evolves into a low-$\bar{x}_A$ reactive steady-state until $y_A = y_s$, it jumps into the A-poisoning state such that a first-order transition occurs. If $D = 0$ and $\epsilon = 0$, one finds that in the reactive steady-state $\bar{x}$ satisfies

$$(\bar{x}_S + \bar{x})^4 + (1 - \bar{x}_A)^3 - 1 = 0, \quad (15)$$

such that a spinodal point exists at $y_s = 0.561$. This is in agreement with Ref. [5]. If $D \neq 0$ and $\epsilon = 0$, we find a left-shifting of the spinodal point. In Fig. 1, we show the solutions of Eq. (14) for different values of D. When $D \simeq 0.0022$, the spinodal point exists at $y_s \simeq 0.525$, which coincides with the MCS value of the first-order IPT.

In the present paper, we have considered the fluctuation of y_A in the DM model and constructed a stochastic differential equation and the corresponding Fokker–Planck equation for the state evolution of the system, especially in the vicinity of the first-order A-poisoning transition point. The
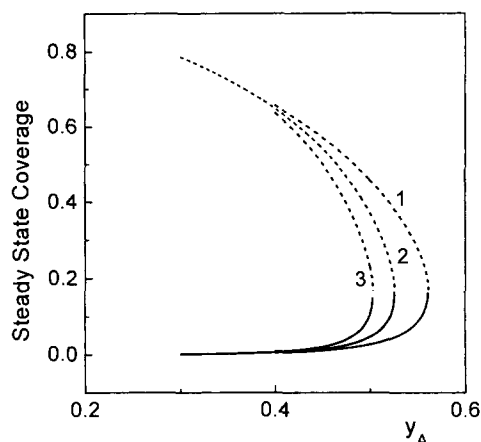

Fig. 1. The extrema of the steady-state density $\rho^{st}(x, \epsilon)$ for three different values of D and $\epsilon = 0$. The dash branches denote the maxima and the solid branches the minima. At the spinodal point the two branches coincide. (1) $D = 0$, $y_s = 0.561$; (2) $D = 0.0022$, $y_s = 0.5258$; (3) $D = 0.005$, $y_s = 0.5033$.

maxima of the probability density with respect to x_A gives the steady-state coverage of A species. We find the spinodal point y_s is left-shifted if the noise intensity D is increased. For a rather small noise intensity $D \simeq 0.0022$, y_s changes from 0.561, which is the spinodal point of the deterministic equations of motion, to 0.525, which is obtained by Monte Carlo simulation. From this point of view, we argue that the occurrence of the metastability, proposed by Evans, results from external noise in the gas-phase and, therefore, the first-order IPT in the DM model may be viewed as a noise-induced phase transition.

Acknowledgements

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