# STOCHASTIC REACTION KINETICS = "NONEQUILIBRIUM THERMODYNAMICS" OF THE STATE SPACE?

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Relations between the deterministic and stochastic models of a complex chemical reaction are presented. Indications are given about the possible development of a quasi-thermodynamic theory of reaction kinetics by the aid of stochastic processes.


Приводятся зависимости между детерминистической и стохастической моделями сложных химических реакций. Были сделаны выводы относительно возможного развития квази-термодинамической теории реакционной кинетики на основе стохастических процессов.


## 1. INTRODUCTION

In a previous paper we constructed Kolmogorov equations for the stochastic model with a continuous time parameter and discrete state space (CDS model) of a complex chemical reaction /6/. The description given by these equations is

equivalent to that given by the Kramers-Moyal-Stratanovich equation /3, 5, 7/ which holds (under certain assumptions) for Markov processes with continuous time parameter:

$$\partial_t g(x,t) = \sum_{n=1}^{\infty} \frac{1}{n!} \left( -\frac{\partial}{\partial x} \right)^n D_n(x) \, g(x,t), \qquad (1)$$

where $g(\underline{x},t)$ is the absolute probability density function of the process $\xi(t)$, and

$$D_n(x) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} E\left( \left( \xi(t+\Delta t) - \xi(t) \right)^n \mid \xi(t) = x \right) \qquad (2)$$

is the velocity of the n-th conditional moment, an n-th order tensor.[*] As the velocities of the conditional moments exist and are finite in the CDS modell of a complex chemical reaction, eq. (1) holds for this case as well.


## 2. STOCHASTIC AND DETERMINISTIC MODELS

### 2.1 Velocity of the conditional expectation = deterministic reaction rate

THEOREM 1: The velocity of the conditional expectation of the usual CDS model of a complex chemical reaction coincides with the reaction rate of the usual deterministic model with continuous time parameter and continuous state space (CCD model):

$$D_1(x) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} E\left( \xi(t+\Delta t) - \xi(t) \mid \xi(t) = x \right. = f(\underline{x}) \qquad (3)$$

(Partially, this motivates why $f(x)$ is referred to as generalized reaction rate.) The theorem has been demonstrated in Ref. /8/.

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[*] Here $(\eta)^n$ is a direct product of n factors, thus it is an n-th order tensor

## 2.2 Consistency in mean

In special cases it can be shown - by the aid of probability generating func-
tions - that the system of differential equations for the first moments coincides
with deterministic kinetic equations in so far as the second and higher moments
are omitted. Especially in the case of complex chemical reactions consisting of
unicomponent reactions, the CDS model is consistent in mean with the CCD
model. (The equations for the first moments do not contain the higher moments.)

## 2.3 Deterministic reaction rate = "drift" velocity

Upon omitting the higher than first order velocities of conditional moments
in eq. (1) the following so called "drift"-equation is obtained:

$$\partial_t g(x,t) + \sum_{i=1}^{m} \frac{\partial}{\partial x_i} ( D_1(x) \, g(x,t)) = 0, \tag{4}$$

with the following conditions:

$$g(x,t) \geq 0, \quad \int g(x,t) \, dx = 1, \quad g(x,0) = \delta_D \tag{5}$$

where $\delta_D$ is a $\delta$-distribution. If we consider eq. (4) as a partial differential
equation for distributions, we can prove the following.

THEOREM 2: The unique solution of (4) satisfying conditions (5) is the $\delta_{x(t)}$
distribution, where $x(t)$ is the solution of the initial value problem

$$\dot{x}(t) = f(x) \; ; \qquad x(0) = D \tag{6}$$

Theorem 2 can be proved by solving eq. (4) treated as a differential equation
for functions and taking into consideration the conditions. The foundations of the

procedure are described in Ref. /2, 9/. The fact that $D_1(x)$ is an analytical function (it is a polynomial) is essentially utilized, however, its actual form is indifferent, so the theorem applies not only to chemical reactions.

The meaning of Theorem 2 is that

— the motion derived from the deterministic model (the solution of initial value problem (6) may be considered as a special stochastic process subordinated to eq. (1) not containing velocities of higher than first order moments (Lax /4/):

— by assuming that the velocities of the higher order conditional moments are zero in the case of a motion described by a stochastic process, the solution of kinetic equation (6), i.e. a deterministic motion, is obtained.

## 3. QUASI-THERMODYNAMIC MOTION IN THE STATE SPACE

In the validity range of "pure reaction kinetics", i.e. where physical transport processes are disregarded, the state of the system is characterized by the probability density function $g(x, t)$. We have seen that the Kramers-Moyal-Stratanovich equation describes the temporal evolution of the system. This equation is formally analogous to the source-free continuity equation of nonlinear transport theory (cf. /1/). The motion in the state space of the chemical components is the resultant of "convective" and "conductive" motions in the state space. The deterministic motion coincides with the motion derived from the solution of the drift equation. This motion can be considered as "convective" in the state space. The velocity of "conductive" motion corresponds to velocities of the higher conditional moments.

The motion can be visualized in such a way that the shape of the density (cloud) characterizing the state of the system is not deformed by the "convective" (=deterministic) motion, the cloud is only shifted by it. The effect of fluctuations is the spreading of the cloud. Though convective motion in the real three-dimen-

sional space is not a dissipative process, i.e. it does not change the entropy of the system, the "convective" motion of the chemical reaction is a dissipative motion. Namely, the state space of the chemical components is anisotropic.

Our present aim was nothing more than to shed some light on the features of the thermodynamics of state space (a notion introduced by Fényes, see e.g. Ref. /1/) for the special case of chemical reactions.

<div align="center">*</div>

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