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ON DIFFERENT STOCHASTIC APPROACHES TO SYSTEMS WITH MULTISTATIONARY BEHAVIOUR*

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A system with one order parameter x obeying a polynomial kinetic law is discussed. Different approaches to the corresponding stochastic equation of motion are compared. Assuming that the system considered is an open chemical system we constructed an appropriate master equation and compared the resulting stationary probability distribution to those obtained by adding a stochastic source term to the macroscopic equation of motion (which yields a Langevin equation or an equivalent Fokker-Planck equation). In the so-called thermodynamical limit the two distributions have the form const $\times \exp(-V\Psi)$, where V is the volume of the system and Ψ an appropriate potential: a kinetic potential in the Langevin approach and a stochastic potential in the master equation approach. Both approaches are equivalent if the corresponding potentials have the same global minimum (minima).

1. *Introduction*

It turned out in the recent time that the concept of the order parameter, originally introduced by Landau to treat structural phase transitions, has proved very useful in the theory of phenomena arising in open, far-from-equilibrium systems, such as laser, hydrodynamical systems, chemical reaction systems etc. (see for review Haken [1, 2]).

The properties of the systems (in particular, their temporal behaviour) are described by one or several order parameters, i.e. very few degrees of freedom replace the great number of degrees of freedom of the subsystems.

The order parameter x (or a set of such parameters $x_1, \ldots, x_q$) represents the behaviour of the system on a macroscopic scale, and is thus a macroscopic variable. Often the equations for such order parameters acquire a rather simple structure with respect to their time dependence. Typical equations are

$$\frac{dx_j}{dt} = \dot{x}_j = f_j(x_1, \ldots, x_q), \tag{1}$$

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where f_j are, in general, nonlinear functions. In the following we discuss systems with one order parameter x only. The order parameter equation (or the macroscopic equation of motion, or the kinetic law) has the form

$$\dot{x} = f(x) = -\frac{dF}{dx}, \tag{2}$$

where $F(x)$ will be called a kinetic potential. States for which $f(x) = 0$ and $f'(x) < 0$, i.e. minima of the potential F are then steady (= stable and stationary) states. In the limit $t \to \infty$ the systems achieves one of its steady states (multistationary behavior). Here we say that the potential F governs the kinetics of the system.

Since the systems of interest are macrosystems consisting of a great number of microsystems (subsystems), e.g. chemical systems consist of a great number of reacting molecules, the fluctuations of the order parameters play an important role. Furthermore, the surroundings exerts fluctuations on the system. There are several ways to incorporate fluctuations in the deterministic order equations (1).

1. The Langevin method

We add a stochastic and/or external driving force $Q(t)$:

$$\dot{x} = f(x) + Q(t). \tag{3}$$

Therefrom one may deduce a Fokker-Planck equation:

$$\dot{p}(x) = -\left(\frac{\partial}{\partial x}\right)[K_1(x)p(x)] + \tfrac{1}{2}\left(\frac{\partial^2}{\partial x^2}\right)[K_2(x)p(x)], \tag{4}$$

where $p[x(t)]dx$ is the probability that the order parameter takes a value from the interval x, $x + dx$, at a time t. One usually takes

$$K_1(x) = f(x), \quad K_2(x) = C = \text{const}, \tag{5}$$

cf., for example, Haken [1].

2. The "master equation" approach

One assumes that the chosen set of macroscopic variables (order parameters) constitute a Markov process. As a consequence of this Markov assumption the probability density $p(x, t)$ obeys a Chapman-Kolmogorov or master equation

$$\dot{p}(x, t) = \int \{w(x|y)p(y, t) - w(y|x)p(x, t)\}\, dy. \tag{6}$$

A solution provides both the macroscopic equations for the rate of change of the quantity x, and the fluctuations around this macroscopic behaviour. From the master equation, via Kramers-Moyal expansion one gets again the Fokker-Planck equation:

$$\frac{\partial p}{\partial t} = -\frac{\partial}{\partial x} c_1(x)p + \tfrac{1}{2} \frac{\partial^2}{\partial x^2} c_2(x)p, \tag{7}$$

where $c_j(x)$ are "jump moments"

$$c_j(x) = \int (y-x)^j w(y|x)dy \tag{8}$$

see also van Kampen [3].

In the following we discuss the correspondence between the macroscopic evolution given by Eq. (2) and its both stochastic pictures (3) and (6) for systems where $f(x)$ is a polynomial. Those systems exhibit a multistationary behavior.

In Section 2 we establish the correspondence between the macroscopic evolution and a corresponding stochastic differential equation. The resulting stationary probability distribution for the variable x has the form const × exp $(-VF(x))$, where V is the volume and $F(x)$ is the kinetic potential.

In Section 3 we discuss the "master equation" approach. For the system considered, under special assumptions on the transition probabilities, a stationary probability solution may be easily found. In the thermodynamical limit it takes the form const × exp $(-V\Phi(x))$, where Φ is a "stochastic potential". Thus the comparison of both stochastic approaches may be reduced to a comparison of the potentials. In both cases the steady states for the macroscopic equation (2) correspond to local minima of the potentials. We also estimate a mean transition time between neighbouring steady states in the master equation approach.

2. *The Langevin approach*

Instead of the deterministic process (2) we consider a stochastic process $x(t)$ described by a stochastic differential equation

$$dx_\varepsilon(t) = f(x_\varepsilon(t))dt + \varepsilon\xi(t) \; (\varepsilon > 0), \tag{9}$$

where $\xi(t)$ is a "white noise", and $dx(t)$ denotes the so-called stochastic derivative of the process $x(t)$. It was proved (cf. [4]) that

$$\lim_{\varepsilon\to 0} \lim_{t\to\infty} P(|x_\varepsilon(t)-x_0| < d) = 1, \tag{10}$$

where $P(\;)$ denotes a probability, x_0 is one of points where the kinetic potential $F(x)$ attains its global minimum and $d > 0$ is an arbitrary constant. Following van Kampen [5] and Kubo et al. [6] we put $\varepsilon \sim V^{-1/2}$, where V is the volume of the system. Thus the transition $\varepsilon \to 0$ in (10) corresponds to the so-called thermodynamical limit.

The same conclusion can be expressed in terms of the stationary probability distribution of the process (9), which is of the form

$$p_\varepsilon(x) = c_\varepsilon \exp\left(-\frac{2}{\varepsilon^2}F(x)\right) = c_V \exp(-VF(x)). \tag{11}$$

In the thermodynamical limit the distribution becomes the δ-distribution peaked about the global minimum of F (a sum of δ-distributions if they are more than one states where F achieves its global minimum, cf. van Kampen [7]). The distribution (11) follows also from the Fokker-Planck equation (4) by setting $K_2 = 2/V$, cf. also Haken [1].

3. *The master equation approach*

Since the Langevin approach can be applied to a quite arbitrary process (2), the master equation approach requires a special shape of the kinetic function $f(x)$. We assume that

$$f(x) = a(x) - b(x), \tag{12}$$

where

$$a(x) = \alpha_1 x^{r-1} + \alpha_3 x^{r-3} + \ldots + \alpha_r,$$

$$b(x) = \alpha_0 x^r + \alpha_2 x^{r-2} + \ldots + \alpha_{r-1} x, \tag{13}$$

and

$$\alpha_i \geqslant 0, \quad i = 0, 1, \ldots, r, \alpha_0 > 0.$$

The kinetics (12) may be realized in an open chemical system. Then we identify x with a concentration of molecules called X, and the equation $\dot{x} = a(x) - b(x)$ describes a process where X is created by an autocatalytical reaction, i.e. its generation rate $a(x)$ is proportional to x (cf. (13)), and it decays by an autocatalytic reaction with the rate $b(x)$. In the master equation approach we investigate the number of molecules n as an integer-valued random variable, $n = 0, 1, \ldots, N$. The master equation (6) is assumed in the form

$$\dot{P}(n, t) = w(n, n-1)P(n-1, t) + w(n, n+1)P(n+1, t) - [w(n+1, n) + w(n-1, n)]P(n, t), \tag{14}$$

where $w(n, m)$ are transition probabilities per unit time (cf., for example, Haken [2], p. 279). The mean value of the quantity (n/V) corresponds then to the macroscopic concentration x. The transition probabilities are obtained from the phenomenological rate functions $a(x)$, $b(x)$ in the following way:

$$w(n+1, n) = V\left[\alpha_1 \frac{(n)_{r-1}}{V^{r-1}} + \ldots + \alpha_r\right],$$

$$w(n-1, n) = V\left[\alpha_0 \frac{(n)_r}{V^r} + \ldots + \alpha_{r-1} \frac{n}{V}\right],$$

$$w(N+1, N) = w(-1, 0) = 0, \tag{15}$$

where we denoted $(n)_k = n(n-1)\ldots(n-k+1)$, cf. also [2, 8–10]. One can easily show that for large N the transition probabilities are proportional to the phenomenological rate functions:

$$w(n+1, n) \cong Va\left(\frac{vn}{N}\right), \quad w(n-1, n) \cong Vb\left(\frac{vn}{N}\right), \tag{16}$$

where $v = N/V$. The number of states is finite ($n = 0, 1, \ldots, N$); if $\alpha_r > 0$ then the stationary probability distribution exists [11] and satisfies the equation

$$w(n, n-1)P(n-1) + w(n, n+1)P(n+1) - [w(n+1, n) + w(n-1, n)]P(n) = 0. \tag{17}$$

It follows immediately that

$$P(n) = P(0)\prod_{i=0}^{n-1}\frac{w(i+1,\, i)}{w(i,\, i+1)}, \tag{18}$$

where $P(0)$ is determined by the normalization condition.

In the thermodynamical limit ($N \to \infty$, $V \to \infty$, but $v = N/V < \infty$) the distribution (18) takes the form

$$P(n) = c_V \exp\left(-V\Phi(n/V)\right), \tag{19}$$

where $\Phi(n/V)$ is a "stochastic potential"

$$\Phi(x) = -\int_0^x (\ln a(s) - \ln b(s))ds. \tag{20}$$

The proof is indicated in Appendix. Thus, the stationary distribution in the master equation approach has an analogical form to that obtained by the Langevin approach. However, the two distributions are determined by two various potentials, the kinetic potential $F(x)$ and the stochastic potential $\Phi(x)$. Now, we compare the potentials. Let $Z \subset [0, v]$ be the set of roots $z_1 < z_2 < \ldots < z_q \leqslant v$ of the polynomial $f(x)$. Denote by S the set of stable roots, and by G and Γ the sets of points where F and Φ attain global minimum, respectively. We have the following relations:

1. $z_1 \in S$, $z_2 \notin S$, $z_3 \in S$, ... etc.
2. If $z_i \in Z$, then $\ln a(z_i) - \ln b(z_i) = 0$. For $z_i \in S \; \frac{d}{dx}(\ln a(z_i) - \ln b(z_i)) < 0$.
3. F and Φ attain local minima at each point from S.
4. $F(z_1) < 0$ and $\Phi(z_1) < 0$. (21)
5. If $Z = \varnothing$ (the empty set) then $G = \Gamma = \{v\}$.
6. $F(x) < 0$ and $\Phi(y) < 0$ whenever $x \in G$ and $y \in \Gamma$.

Define an integer-valued function $n(x)$, $0 \leqslant n(x) \leqslant N$, $x \in [0, v]$ such that

$$\frac{vn(x)}{N} \leqslant x \leqslant \frac{v(n(x)+1)}{N}, \tag{22}$$

i.e.

$$\langle n(x) \rangle = \frac{n(x)}{V} \leqslant x \leqslant \frac{n(x)+1}{V} = \langle n(x)+1 \rangle.$$

The following property of the probability distribution (19) can be proved:

$$\lim_{N\to\infty} P_N(\langle n(x)\rangle) = 0 \quad \text{for} \quad x \notin \Gamma, \quad x \in [0, v],$$

$$\lim_{N\to\infty} P_N(\langle n(y_i)\rangle) = p_i > 0 \quad \text{for} \quad y_i \in \Gamma = \{y_1, \ldots, y_k\}, \tag{23}$$

and

$$\sum_{i=1}^{k} p_i = 1.$$

(We denoted $P(n) = P_N(\langle n \rangle)$ to emphasize the dependence on N.) The proof follows from the definition of the potential Φ and from the relation (19). For an arbitrary but fixed $x \in [0, v]$, $x \notin \Gamma$, we have

$$P_N(\langle n(x) \rangle) \cong P_N(0) \exp\left(-\frac{N}{v} \Phi(\langle n(y_i) \rangle) + R_N(\langle n(y_i) \rangle) \right)$$

$$\times \exp\left\{ \frac{N}{v} [\Phi(\langle n(y_i) \rangle) - \Phi(\langle n(x) \rangle)] + c(\langle n(x) \rangle) - c(\langle n(y_i) \rangle) \right\} \tag{24}$$

for $y_i \in \Gamma$, see also Appendix, relations (A2) and (A5). Since

$$\Phi(y_i) = \Phi(y_j), \qquad \Phi'(y_i) = \Phi'(y_j), \tag{25}$$

then

$$\lim_{N \to \infty} \frac{N}{v} [\Phi(\langle n(y_i) \rangle - \Phi(\langle n(y_j) \rangle)] = 0, \tag{26}$$

and the following inequality holds

$$P_N(0) \exp\left\{ -\frac{N}{v} \Phi(\langle n(y_i) \rangle) + R_N(\langle n(y_i) \rangle) \right\}$$

$$\leqslant \{ \sum_{j=1}^{k} \exp [c(\langle n(y_j) \rangle) - c(\langle n(y_i) \rangle)] \}^{-1}. \tag{27}$$

Inserting this in (24) we obtain

$$P_N(\langle n(x) \rangle) \leqslant a_1 \exp\left(-\frac{Na}{v} \right), \tag{28}$$

which implies the first of the relations (23). According to the inequality (28) and to the normalization conditions for P_N's we obtain

$$\lim P_N(\langle n(y_i) \rangle) = a_2 > 0 \tag{29}$$

for an arbitrary $y_i \in \Gamma$. Because of the relation (26) and the following one

$$\frac{P_N(\langle n(y_i) \rangle)}{P_N(\langle n(y_j) \rangle)} = \exp\left\{ \frac{N}{v} [\Phi(\langle n(y_j) \rangle) - \Phi(\langle n(y_i) \rangle)] + c(\langle n(y_i) \rangle) - c(\langle n(y_j) \rangle) \right\}$$

the second of the relations (23) holds.

Using methods of the theory of Markov processes (cf., e.g., Ref. [12], Chap. IV) one can estimate the mean time of transition between states $y_i, y_{i+1} \in \Gamma$. Denoting the time by $t_{\mathrm{N}}(i, i+1)$ we have

$$t_N(i, i+1) \geqslant a_2 \exp\left\{\frac{Na_1}{v} - \ln N + \ln v + c(\langle n(y_i)\rangle) - c(\langle n(x)\rangle)\right\}, \tag{30}$$

where x is an arbitrary point from an open interval (y_i, y_{i+1}), a_2 is a certain constant, and the constant a_1 is defined by

$$\Phi(\langle n(x)\rangle) - \Phi(\langle n(y_i)\rangle) \geqslant a_1 > 0. \tag{31}$$

Thus we have

$$\lim_{N\to\infty} t_N(i, i+1) = \infty, \qquad \lim_{N\to\infty} t_N(i+1, i) = \infty. \tag{32}$$

Comparing relations (23) and (10) we obtain that the master equation approach and the Langevin approach predict the same final state if and only if $G = \Gamma$, i.e. the potentials F and Φ have the same global minima. A simple example shows that the minima may differ. Let z_1, z_2, z_3 be the roots of the polynomial

$$f(x) = a(x) - b(x) = \alpha_3 + \alpha_1 x^2 - \alpha_2 x - \alpha_0 x^3. \tag{33}$$

We have

$$\begin{aligned} \alpha_1 &= \alpha_0(z_1 + z_2 + z_3), \\ \alpha_2 &= \alpha_0(z_1 z_2 + z_1 z_3 + z_2 z_3), \\ \alpha_3 &= \alpha_0(z_1 z_2 z_3). \end{aligned} \tag{34}$$

Let us fix

$$\alpha_0 > 0, \qquad z_3 \in (0, v), \qquad u \in (0, 1), \tag{35}$$

and take

$$z_1 = u z_3, \qquad z_2 = y\,\frac{u+1}{2}\,z_3. \tag{36}$$

Inserting (36) into (34) and (33, one can prove that for a suitable chosen $y > 1$ we have

$$F(z_3) - F(z_1) > 0, \qquad \Phi(z_3) - \Phi(z_1) < 0, \tag{37}$$

i.e. $z_1 \in G$, $z_3 \notin G$ and $z_1 \notin \Gamma$, $z_3 \in \Gamma$. In this example the Langevin method would predict the state z_1 as the final state, and the master equation approach would indicate z_3 as the final state.

4. *Conclusions*

The stationary behaviour of macroscopic systems with one order parameter can be described in terms of certain potentials. In the macroscopic (deterministic) picture the system tends asymptotically (i.e. for $t \to \infty$) to one of minima of the kinetic potential F.

The same potential determines the shape of the stationary probability distribution in the stochastic Langevin approach. The probability attains its maximum at a global minimum of F. Another potential Φ (the stochastic potential) determines the stationary probability distribution in the master-equation approach. Here again the maxima of the probability coincide with global minima of the potential Φ. However, the latter may differ from the global minima of F. Then the two stochastic approaches predict different final states of the system.

We discussed various types of potentials for systems with one order parameter ("one internal degree of freedom" in terms of the catastrophe theory). According to the discussion of Wentcel and Frejdlin [4] it seems that the concept of the kinetic potential may be very useful also for systems with several order parameters, and, in particular, for non-gradient systems, e.g. for chemical systems exhibiting oscillatory, or limit cycle behaviour (Brusselator, Oregonator, etc.).

APPENDIX

We consider the probability distribution (18)

$$P(n) = P(0) \prod_{i=0}^{n-1} \frac{w(i+1, i)}{w(i, i+1)},$$

where $w(n, m)$ are defined by formulas (15). With respect to (16) and (23) the distribution can be written in the form

$$P(n) = P_N(\langle n\rangle) = P_N(0) \exp\{\sum_{i=1}^{n} [\ln a(\langle i-1\rangle) - \ln b(\langle i\rangle)]\}. \tag{A1}$$

Using the well-known Euler-McLaurin summation formula we obtain

$$\sum_{i=1}^{n} \{\ln a(\langle i-1\rangle) - \ln b(\langle i\rangle)\}$$

$$= \frac{N}{v}\left\{\int_{\langle 1\rangle}^{\langle n\rangle} (\ln a(x) - \ln b(x))dx\right\} + R_N(n), \tag{A2}$$

where

$$R_N(n) = G_N(n) + H_N^1(n) + H_N^2(n),$$

and

$$G_N(n) = \tfrac{3}{2}\ln \alpha_r - \tfrac{1}{2}[\ln a(\langle n\rangle) + \ln b(\langle n+1\rangle)] - \tfrac{1}{2}\ln b(\langle 1\rangle),$$

$$H_N^1(n) = \frac{N}{2v} \sum_{i=1}^{n} \int_0^{\langle 1\rangle} \left(z^2 - \frac{zv}{N}\right) \frac{B(\langle i+1\rangle - z)}{(\langle i+1\rangle - z)^2}\, dz,$$

$$H_N^2(n) = \frac{N}{2v}\sum_{i=1}^{n}\int\limits_{0}^{\langle 1\rangle}\left(z^2-\frac{zv}{N}\right)A(\langle i\rangle - z)dz,$$

$$A(y) = \frac{d^2}{dy^2}\ln a(y), \qquad B(y) = y^2\frac{d^2}{dy^2}\ln b(y). \tag{A3}$$

One can verify that

(1) $\lim\limits_{N\to\infty} H_N^1(n(x)) = c(x)$ uniformly for $x \in [0, v]$.

(2) $\lim\limits_{N\to\infty} H_N^2(n) = 0$.

(3) $\lim\limits_{N\to\infty} G_N(n)/N = 0$. (A4)

Thus, in the limit $N \to \infty$ the distribution $P(n) = P_N(\langle n\rangle)$ takes the form

$$P_N(\langle n\rangle) \cong P_N(0)\exp\left\{-\frac{N}{v}\Phi(\langle n\rangle)+c(x)+\ln N\right\} \cong c_N\exp\left\{-\frac{N}{v}\Phi(\langle n\rangle)\right\}, \tag{A5}$$

or

$$P(n) = c_V\exp\left\{-V\Phi\left(\frac{n}{V}\right)\right\},$$

where $\Phi(x)$ is the stochastic potential defined by (20).

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