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A Note on the Bimodal Stationary Distributions in Hard Chemical Instabilities

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Over the past years there has been considerable activity in the application of birth and death stochastic equations to the analysis of nonlinear chemical reaction schemes (see Refs. 1–4 for reviews). Of particular interest are systems that exhibit multiple stationary states, as transitions between these states are analogous to first-order phase transitions.[3–5]

It has been claimed that the stationary distributions of such master equations are bimodal,[1–5] and that this bimodality is the stochastic analog of the deterministic hysteresis effect. It is the aim of this note to argue that the stationary distribution of the master equation is effectively unimodal when the thermodynamic limit is properly taken. Thus the hysteresis effect is shown to be of a kinetic origin, and not a property of the stationary character of the stochastic system.[6] The effective unimodality can be established for a general kinetic equation of the form

$$dx/dt = K(\alpha - x)(\beta - x)(\gamma - x) \tag{1}$$

Such an equation gives rise to three stationary states, two of which are generally stable and one of which is unstable.

The master equation corresponding to Eq. (1) can be written in the general birth and death form[7]

$$(1/K)\dot{P}_x(t) = L_{x-1,x}P_{x-1}(t) + L_{x+1,x}P_{x+1}(t) - L_{x,x}P_x(t) \tag{2}$$

where

$$\begin{aligned} L_{x-1,x} &= a_1 + b_1(x-1) + c_1(x-1)^2 + d_1(x-1)^3 \\ L_{x+1,x} &= a_2 + b_2(x+1) + c_2(x+1)^2 + d_2(x+1)^3 \\ L_{x,x} &= (a_1 + a_2) + (b_1 + b_2)x + (c_1 + c_2)x^2 + (d_1 + d_2)x^3 \end{aligned} \tag{2a}$$

Here, $P_x(t)$ is the distribution of the number of molecules x at time t.

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The order of magnitude of the parameters appearing in Eqs. (1) and (2) is dictated by the structure of the equations.[7] Denoting the size of the system (i.e., the number of particles) by N, we see from (1) that α, β, and γ are of $O(N)$ and therefore K is $O(1/N^2)$. As (2) must be consistent with (1) in the mean, a_1 and a_2 are $O(N^3)$, b_1 and b_2 are $O(N^2)$, c_1 and c_2 are $O(N)$, and d_1 and d_2 are $O(1)$.

We may now define the quantity[7]

$$G_x = L_{x,x+1}/L_{x+1,x} \tag{3}$$

It is well known[6] that the stationary distribution P_x^{st} of the master equation (2) is given by

$$P_x^{\mathrm{st}} = \theta_x / \textstyle\sum_{y=0}^{N} \theta_y \tag{4}$$

where

$$\theta_x = G_0 G_1 \cdots G_{x-1} \tag{5}$$

Thus if the stationary probability is bimodal with two peaks at $x = \alpha$ and $x = \gamma$, we can write the ratio of the probabilities of finding the system in these two points as

$$R = P_\alpha^{\mathrm{st}}/P_\gamma^{\mathrm{st}} = G_\alpha G_{\alpha+1} \cdots G_{\gamma-1} \tag{6}$$

(we assume $\alpha < \gamma$). Obviously

$$\ln R = \sum_{x=\alpha}^{\gamma-1} \ln G_x \tag{7}$$

Because of the ordering discussed above, if the size of the system is large, we can change variables in (7) and pass to the quasicontinuous variable $z = x/N$. Multiplying and dividing by N, we have

$$\ln R = N \sum \frac{1}{N} G(z) \tag{8}$$

and when passing to integration we finally get

$$\ln R \sim N \int_{\bar{\alpha}}^{\bar{\gamma}} G(z)\, dz \tag{9}$$

where $\bar{\alpha} = \alpha/N$ and $\bar{\gamma} = \gamma/N$. The ordering discussed above guarantees that $\bar{\alpha}$ and $\bar{\gamma}$ and consequently the integral in (9) are of $O(1)$. Therefore

$$R \sim \exp\{N \cdot O(1)\}$$

and when $N \to \infty$ the ratio is zero or infinite, depending on the sign of $\int G(z)\, dz$.

Thus we have shown that the stationary distribution is effectively unimodal, except at the point of coexistence of the two stationary states where $\int G(z)\,dz = 0$.

The result obtained here does not contradict the existence of hysteresis effects. As argued previously, hysteresis arises due to the separation of time scales that are involved in the evolution of the system. The time required for attaining stationarity [i.e., establishing the distribution (4)] τ_s is usually much longer than the relaxation time within each stable branch τ_R.[5-7] Thus, changing an external parameter on a time scale that is fast compared to τ_s but slow compared to τ_R will result in a hysteresis effect.

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