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An Example of a Phase Transition in an Open Pseudobimolecular System

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A phase transition at microscopic level is exhibited for an open bimolecular chemical system. We also give another interpretation of an apparent incompatibility between the microscopic and the macroscopic analysis shown by J. Keizer.

KEY WORDS: Phase transition for an open bimolecular system; birth and death processes; hypergeometric function; saddle point method; critical fluctuation; microscopic and macroscopic analysis.

1. INTRODUCTION

We consider a chemical system with three reactants X, Y, C and the following nonlinear chemical reactions:

$$2X \underset{1}{\overset{1}{\rightleftarrows}} X + Y \underset{k''}{\overset{k}{\rightleftarrows}} 2Y + C \tag{1}$$

Here 1, 1, k, k'' are the constants of the reactions. Here, X, Y have varying concentrations and the concentration of C is held fixed; we shall write $k'' = k'C^{-1}$, where C denotes the concentration of C. The reactions $2X \rightleftarrows X + Y$ have been studied by M. Kac in Ref. 3; the result obtained is that the fluctuations are Gaussian and, after having performed the thermodynamic limit, the fluctuation of X is an Ornstein–Uhlenbeck process. Moreover, for nonisolated systems, this type of reaction has been studied by Malek–Mansour and Nicolis,[8] Keizer,[4] and analogous systems of bimolecular reaction have been studied by Schlögl[13] (bifurcation theory), Nicolis Prigogine,[9], Gortz and Walls,[2] Keizer,[5] Oppenheim *et al.*,[11] and Procaccia and Ross[12] (see also the recent review of McQuarrie and

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Keizer[6]). In particular the works Refs. 4 and 8 posed the question of the compatibility between macroscopic equation and microscopic analysis (given by the birth and death process). We shall exhibit here the same kind of phenomena but we shall propose another interpretation.

We begin by sketching our main results.

a. Consider the reactions (1) with $k'=0$, so that $C+2Y \to X+Y$ is absent, from the macroscopic point of view; it will be shown in Section 2 that $k=1$ is a bifurcation value; for $k \geqslant 1$, the stable equilibrium is $X=0$, and for $k<1$ we have a nonzero stable equilibrium.

b. Now we study the birth and death process in the stationary case; we suppose that we have N particles X and Y; denote by X and Y the number of particles X and Y, so that $X+Y=N$.

If we take $k'=0$ in (1), we see that $\langle X \rangle_{k'=0,N}=0$ for any N, so that the result predicted by this microscopic analysis seems to be in contradiction with the result of macroscopic analysis. This phenomenon was exhibited with other reactions for open systems in Refs. 4 and 8, for example,

c. Suppose now that we take $k'>0$ and let us compute $\langle X \rangle_{k',N}$, then take the thermodynamic limit ($N \to +\infty$) and only after that, take the limit $k' \to 0$. Then we recover the result predicted by the macroscopic analysis. This explanation is different from that of Keizer[4]; in this work, Keizer considers two reactions $A+X \to 2X$, $2X \to E$ (without converse reaction) and he obtains a contradiction between macroscopic analysis and birth and death process; in this case, using Kurtz's work, the limit must be taken in the following order: First perform for each finite time the thermodynamic limit, then take the limit for $t \to +\infty$. Here our explanation is different; we work only at $t=+\infty$ (in the stationary case), but the two limits are then the first thermodynamic limit and then the limit in $k' \to 0$. This means that we can use the stationary distribution for the birth and death process only if we take into account converse reactions (even with extremely small but nonzero constant); this conclusion seems to be quite natural from the point of view of chemistry.

d. Moreover, we can study the fluctuation when $k' \to 0$ (after having performed the thermodynamic limit): we define

$$R(k) = \lim_{k' \to 0} \lim_{N \to +\infty} \frac{\langle X^2 \rangle_{k',k,N} - (\langle X \rangle_{k',k,N})^2}{N}$$

Then we prove that for $k \to 1^-$, we have

$$R(k) \sim \frac{1}{2(1-k)^2} - \frac{2}{1-k} + O(1)$$

This means that fluctuation tends to infinity for $k \to 1^-$ and that we have a phase transition at the microscopic level.

We are now preparing another work in which we prove that the preceding phenomena are quite general; in fact, we extend our interpretation for trimolecular reaction with spatial diffusion. It seems that one has a first-order phase transition and that we have other interpretations of the results of Refs. 2, 5, and 12.

2. THE MACROSCOPIC ANALYSIS FOR $k' = 0$

Let x be the concentration of X; the macroscopic equation is

$$\frac{dx}{dt} = x^2(-2 + k + k') + x(1 - k - 2k') + k' \tag{2}$$

For $k' = 0$, the stationary solutions are $x = 0$, $(k-1)/(k-2)$. The linearization of (2) near $x = 0$ gives

$$\frac{dx}{dt} = x(1 - k)$$

so that $x = 0$ is unstable for $k < 1$ and stable for $k > 1$, $(k-1)/(k-2)$ is stable for $k < 1$ and unstable for $k > 1$. One gets the following bifurcation scheme shown in Fig. 1.

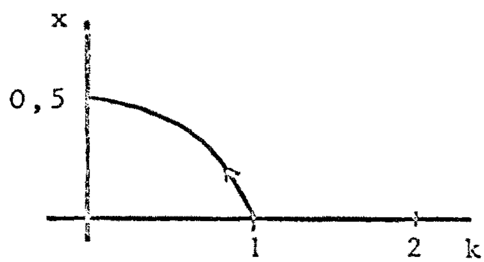

Fig. 1.

3. ANALYSIS OF THE BIRTH AND DEATH PROCESS

Let $X(t)$ be the birth and death process at time t when there are N particles in the system. The equations of definition are[7,8]

$$\begin{aligned}
\text{Prob}[X(t+dt) = X(t) + 1] &= \frac{dt}{N}\left[X(N-X) + k'(N-X)^2\right] \\
\text{Prob}[X(t+dt) = X(t) - 1] &= \frac{dt}{N}\left[kX(N-X) + X(X-1)\right] \\
\text{Prob}[X(t+dt) = X(t)] &= 1 - \frac{dt}{N}\left[X(N-X)(1+k)\right. \\
&\qquad \left. + X(X-1) + k'(N-X)^2\right]
\end{aligned} \tag{3}$$

The evolution equation of $P(X,t) = \mathrm{Prob}[X(t) = X]$ is then

$$\frac{dP(X,t)}{dt} = P(X+1,t)\frac{1}{N}\left[k(X+1)(N-X-1) + X(X+1)\right]$$
$$+P(X-1,t)\frac{1}{N}\left[(X-1)(N-X+1) + k'(N-X+1)^2\right]$$
$$-P(X,t)\frac{1}{N}\left[X(N-X)(1+k) + X(X-1) - \frac{k'}{N}(N-X)^2\right]$$

We shall denote $\langle\ \rangle_N$ the average with respect to this probability (suppressing N except if there is no risk of confusion); we obtain for $k' = 0$

$$\frac{d\langle X\rangle}{dt} = \frac{1}{N}\langle -kX(N-X) + X - 2X^2 + NX\rangle \tag{4}$$

If we write $\lim_{N\to+\infty}\langle X/N\rangle = x$ and if we suppose, as it is generally done, that $\langle (X/N)^2\rangle \simeq \langle X/N\rangle^2$ if $N\to+\infty$, we verify that (4) is then the macroscopic equation (2) for $k' = 0$ and this process is formally compatible with the macroscopic analysis.

Define as usual the generating function

$$f(s,t) = \sum_{X=0}^{N} s^X P(X,t)$$

A well-known computation gives[9]

$$N\frac{\partial f}{\partial t} = (1-s)\left\{\frac{\partial^2 f}{\partial s^2}\left[s(s+1-k) - k's^2\right]\right.$$
$$\left. + \frac{\partial f}{\partial s}\left[(1-N)(s-k) - k's(1-2N)\right] - k'N^2 f\right\} \tag{5}$$

For $k' = 0$, the stationary equation of (5) is

$$s(s+1-k)f'' - (N-1)(s-k)f' = 0$$

so that the only physical solution (which has to be a polynomial of degree $\leqslant N$ with non-negative coefficients) is $f(s) = 1$, so $P(0) = 1$, $P(X) = 0$, $0 < X < N$ and $\langle X\rangle_N = 0$ and $\langle X\rangle = \lim_{N\to+\infty}\langle X\rangle_N/N = 0$, which is in contradiction with the result of the macroscopic equation for $k < 1$.

This phenomenon has also been observed by Malek–Mansour and Nicolis[8] and commented upon by Keizer[4] for another bimolecular reaction in an open system.

4. ANALYSIS OF THE MEAN OF X FOR $k' \to 0$

We now take $k' \neq 0$ and we put in (5) $\sigma = -s[(1-k')/(1-k)]$. We get

$$\sigma(1-\sigma)\frac{df}{d\sigma^2} + \left[\frac{k}{1-k}(N-1) - \frac{\sigma}{1-k'} \times (-N+1-k'+2k'N)\right]\frac{df}{d\sigma} + \frac{k'N^2}{1-k'}f = 0$$

We write $\alpha = -N$, $\beta = k'N/(1-k')$, $\gamma = k/(1-k)(N-1)$, and we get for k and $k' < 1$ a hypergeometric function:

$$f_N(s) = F\left(-N, \frac{Nk'}{1-k'}, \frac{k(N-1)}{1-k}; -s\frac{1-k'}{1-k}\right)$$

(See, for example, Ref. 10.)

The case $k' = 1$, $k \neq 1$ gives a confluent hypergeometric function

$$f_N(s) = F\left(-N, \frac{k(N-1)}{1-k}; -\frac{sN}{1-k}\right)$$

We will take $k > k'$ (because we make k' tend to 0) and N so large that

$$\frac{k(N-1)}{1-k} > \frac{Nk'}{1-k'}$$

We get an integral representation of f_N by[10]

$$f_N(s) = \frac{\Gamma(k(N-1)/(1-k))}{\Gamma(Nk'/(1-k'))\Gamma(k(N-1)/(1-k) - k'N/(1-k'))} \times \int_0^1 \exp[N\varphi(t)]b^I(t)\,dt$$

where $b^I(t) = t^{-1}(1-t)^{-k/(1-k)-1}$,

$$\varphi(t) = \frac{k'}{1-k'}\log t + \left(\frac{k}{1-k} - \frac{k'}{1-k'}\right)\log(1-t) + \log\left(1 + st\frac{1-k'}{1-k}\right)$$

We can study the asymptotic of this integral by the saddle point method. The critical point of φ in $[0,1]$ is

$$t_0 = \frac{1 + \left[1 + (1-k')/(1-k)^2\right]^{1/2}}{2(1-k')/(1-k)^2}$$

then

$$I_N = \int_0^1 \exp[N\varphi(t)] b^I(t)\,dt \sim \exp[N\varphi(t_0)] b^I(t_0) \left[-\frac{\pi}{2N\varphi''(t_0)} \right]^{1/2}$$

We compute now $\langle X \rangle_N = (\partial \tilde{f}_N/\partial s)|_{s=1}$, where $\tilde{f}_N$ is the normalized solution $\tilde{f}_N(1) = 1$. We have

$$\frac{d}{ds} F\left(-N, \frac{Nk'}{1-k'}, \frac{k(N-1)}{1-k}, -\frac{s(1-k')}{1-k}\right)\Bigg|_{s=1}$$

$$= -\frac{1-k'}{1-k}\frac{d}{d\sigma} F\left(-N, \frac{Nk'}{1-k'}, \frac{k(N-1)}{1-k}, -\frac{1-k'}{1-k}\right)$$

$$= \frac{1-k'}{1-k}\frac{N^2k'(1-k)}{(1-k')k(N-1)} F$$

$$\times \left(-N+1, \frac{Nk'}{1-k'}+1, \frac{k(N-1)}{1-k}+1, -\frac{1-k'}{1-k}\right)$$

$$= \frac{N^2k'}{k(N-1)} \frac{\Gamma(k(N-1)/(1-k)+1)}{\Gamma\left(\frac{Nk'}{1-k'}+1\right)\Gamma\left(\frac{k(N-1)}{1-k}-\frac{Nk'}{1-k'}\right)}$$

$$\times \int_0^1 \exp[N\varphi(t)] b^\partial(t)\,dt$$

$$b^\partial(t) = (1-t)^{-k/(1-k)-1}\left(1+\frac{1-k'}{1-k}t\right)^{-1}$$

We deduce, using $\Gamma(x+1) = x\Gamma(x)$, that

$$\frac{\langle X \rangle_N}{N} \sim \frac{1-k'}{1-k}\frac{b^\partial(t_0)}{b^I(t_0)} = \left(\frac{1-k'}{1-k}t_0\right) = \left(1+\frac{1-k'}{1-k}t_0\right)^{-1}$$

But

$$\frac{1-k'}{1-k}t_0 = \frac{(1-k)+\left[(1-k)^2+4k'\right]^{1/2}}{2} \to 1-k \qquad \text{if} \qquad k' \to 0$$

$$\lim_{k'\to 0}\lim_{N\to+\infty}\frac{\langle X \rangle_N}{N} = \frac{1-k}{2-k}$$

So $\lim_{k'\to 0}\lim_{N\to+\infty}\langle X \rangle_N/N = (1-k)/(2-k)$, which is the result predicted by the macroscopic equation for $k' = 0$.

The conclusion for this model is that *we cannot suppress the converse reaction in the birth and death process before performing the thermodynamic* *limit. If we perform the thermodynamic limit and then suppress the converse reaction we obtain agreement with the macroscopic analysis.*

5. FLUCTUATION OF X NEAR $k = 1$: PHASE TRANSITION

We have

$$\langle X^2\rangle_N - \langle X\rangle_N^2 = \left.\frac{\partial^2 \tilde{f}_N}{\partial s^2}\right|_{s=1} + \left.\frac{\partial \tilde{f}_N}{\partial s}\right|_{s=1} - \left(\left.\frac{\partial \tilde{f}_N}{\partial s}\right|_{s=1}\right)^2$$

We will show that

$$\underline{\lim_{k'=0}\ \lim_{N\to+\infty} \frac{\langle X^2\rangle_N - \langle X\rangle_N^2}{N} \sim R(k)}$$

with

$$\underline{R(k) \sim \frac{1}{2}\,\frac{1}{(1-k)^2} - \frac{2}{1-k} + 0(1) \qquad \text{if} \qquad k \to 1^-}$$

The computation is quite unpleasant because we must apply the asymptotic expansion to a high order. We write

$$f_N(s)|_{s=1} = \frac{\Gamma(k(N-1)/(1-k))}{\Gamma\left(\frac{Nk'}{(1-k')}\right)\Gamma\left(\frac{k(N-1)}{(1-k)} - \frac{k'N}{(1-k')}\right)} \times \int_0^1 \exp[N\varphi(t)]\,b^I(t)\,dt$$

$$\left.\frac{df_N}{ds}\right|_{s=1} = \frac{N^2k'}{k(N-1)}\,\frac{\Gamma(k(N-1)/(1-k)+1)}{\Gamma\left(\frac{Nk'}{(1-k')}+1\right)\Gamma\left(\frac{k(N-1)}{(1-k)} - \frac{k'N}{(1-k')}\right)} \times \int_0^1 \exp[N\varphi(1)]\,b^\partial(t)\,dt$$

$$\left.\frac{d^2f_N}{ds^2}\right|_{s=1} = \frac{N^2k'[(N-1)k'+1]}{k[(N-2)k+1]}\,\frac{\Gamma(k(N-1)/(1-k)+2)}{\Gamma\left(\frac{Nk'}{(1-k')}+2\right)\Gamma\left(\frac{k(N-1)}{(1-k)} - \frac{Nk'}{(1-k')}\right)} \times \int_0^1 \exp[N\varphi(t)]\,b^K(t)\,dt$$

where

$$b^J(t) = t\left(1 + \frac{1-k'}{1-k}t\right)^{-1} b^I(t), \qquad b^K(t) = t^2 \times \left(1 + \frac{1-k'}{1-k}t\right)^{-2} b^I(t)$$

and $b^I(t)$ was defined before. In the three cases, the point t_0 where the phase is stationary, is the point t_0 that we have found earlier. Moreover, $\tilde{f}_n(s) = f_N(s)/f_N(1)$.

We denote by I_N, J_N, K_N the integrals appearing in f_N, f'_N, f''_N; we have

$$\tilde{f}'_N = \frac{1}{f_N} f'_N = \frac{N(1-k')}{1-k} \frac{J_N}{I_N}; \qquad \tilde{f}''_N = \frac{N(N-1)(1-k')^2}{(1-k)^2} \frac{K_N}{I_N}$$

Let us recall the full asymptotic expansion of the saddle point method for the integral

$$I_N = \int_0^1 g(t) \exp[N\varphi(t)]\, dt$$

(cf. Ref. 1) writing

$$-\varphi'(t) \sim \sum_{n \geqslant 0} a_n (t-t_0)^{n+1} \qquad \text{for} \qquad t \to t_0$$

$$g(t) \sim \sum_{n \geqslant 0} b_n (t-t_0)^n$$

$$-\frac{g(t)}{\varphi'(t)} \sim \sum_{n \geqslant 0} c_n (t-t_0)^{n-1}$$

$$u = \varphi(t) - \varphi(t_0) \sim \sum_{n \geqslant 0} \frac{a_n}{n+2} (t-t_0)^{n+2}$$

We can obtain $t - t_0$ from the last relation as an expansion in powers of $u^{1/2}$ and putting this expansion in $-g(t)/\varphi'(t)$, we get

$$-\frac{g(t)}{\varphi'(t)} \sim \sum \gamma_n u^{(n-1)/2}$$

If N tends to $+\infty$, the asymptotic expansion is

$$I_N \sim \exp[N\varphi(t_0)] \sum_{n \geqslant 0} \gamma_n \Gamma \frac{(n+1)}{2} N^{-(n+1)/2}$$

We have here

$$\gamma_0 = \frac{b_0}{(2a_0)^{1/2}}, \qquad \gamma_1 = \frac{1}{a_0}\left(b_1 - \frac{4}{3}\frac{a_1}{a_0} b_0\right),$$

$$\gamma_2 = \frac{\sqrt{2}}{a_0^{3/2}} \left[b_2 - \frac{5}{3}\frac{a_1}{a_0} b_1 + \frac{b_0}{a_0}\left(\frac{3}{2}\frac{a_1^2}{a_0} - \frac{7}{4} a_2\right)\right]$$

We shall denote by $b_k^I, b_k^J, b_k^K, \gamma_k^I, \ldots$ the numbers b_k, γ_k for the corresponding integrals I, J, K.

The number a_k depends only on the phase φ which is the same for the three integrals. We have

$$\frac{f_N'(1)}{f_N(1)} = \frac{1-k'}{1-k} N \frac{J_N}{I_N} = \frac{1-k'}{1-k} N \times \left[\frac{\gamma_0^J + (1/2)\gamma_1^J N^{-1/2} + (3/4)\gamma_2^J N^{-1} + \cdots}{\gamma_0^I + (1/2)\gamma_1^I N^{-1/2} + (3/4)\gamma_2^I N^{-1} + \cdots} \right]$$

so

$$\frac{f_N'(1)}{f_N(1)} = \frac{1-k'}{1-k} \frac{\gamma_0^J}{\gamma_0^I} (N + \alpha^J N^{1/2} + \beta^J + \cdots)$$

$$\alpha^J = \frac{1}{2}\left(\frac{\gamma_1^J}{\gamma_0^J} - \frac{\gamma_1^I}{\gamma_0^I} \right)$$

$$\beta^J = \frac{3}{4}\frac{\gamma_2^J}{\gamma_0^J} - \frac{1}{4}\frac{\gamma_1^J}{\gamma_0^J}\frac{\gamma_1^I}{\gamma_0^I} - \left[\frac{3}{4}\frac{\gamma_2^I}{\gamma_0^I} + \frac{1}{4}\left(\frac{\gamma_1^I}{\gamma_0^I}\right)^2 \right]$$

and also

$$\frac{f_N''(1)}{f_N(1)} = \frac{(1-k')^2}{(1-k)^2} N(N-1)\frac{K_N}{J_N}$$

$$= \left(\frac{1-k'}{1-k}\right)^2 (N-1)\frac{\gamma_0^K}{\gamma_0^I}(N + \alpha^K N^{1/2} + \beta^K + \cdots)$$

with the same notations for α^K, β^K except that we change J in K everywhere.

a. We study the term N^2 in $\langle X^2 \rangle_N - \langle X \rangle_N^2$; this term is

$$\left(\frac{1-k'}{1-k}\right)^2 \left[\frac{\gamma_0^K}{\gamma_0^I} - \left(\frac{\gamma_0^J}{\gamma_0^I}\right)^2 \right]$$

which is proportional to $b_0^K/b_0^I - (b_0^J/b_0^I)^2$, which is 0 because of the definition of $b_0^{I,J,K} = b^{I,J,K}(t_0)$.

b. We study the term in $N^{3/2}$; it is

$$\left(\frac{1-k'}{1-k}\right)^2 - \left[\frac{1}{2}\frac{\gamma_0^K}{\gamma_0^I}\left(\frac{\gamma_1^K}{\gamma_0^K} - \frac{\gamma_1^I}{\gamma_0^I} \right) - \left(\frac{b_0^J}{b_0^I}\right)^2 \frac{\sqrt{2}}{\sqrt{a_0}} \left(\frac{b_1^J}{b_0^J} - \frac{b_1^I}{b_0^I} \right) \right]$$

We must compare

$$b_1^K - \frac{b_0^K}{b_0^I} b_1^I \qquad \text{and} \qquad \frac{2b_0^J}{b_0^I}\left(b_1^J - \frac{b_0^J b_1^I}{b_0^I} \right)$$

The common value of these two terms is $2t_0[1 + (1 - k')/(1 - k)t_0]^{-3}b(t_0)$ so the terms in $N^{3/2}$ disappear.

c. Then, as we know, we see that the first term which remains is of order N. We look at these terms in N, in $f_N''(1)/f_N(1)$, in $f_N'(1)/f_N(1)$, and in $-[f_N'(1)/f_N(1)]^2$:

In $f_N''(1)/f_N(1)$,

$$\frac{(1-k')^2}{1-k}\left(\frac{\gamma_0^K}{\gamma_0^I}\beta^K - \frac{\gamma_0^K}{\gamma_0^I}\right) \equiv (\alpha - \beta)\left(\frac{1-k'}{1-k}\right)^2$$

In $f_N'(1)/f_N(1)$,

$$\frac{1-k'}{1-k}\,\frac{\gamma_0^J}{\gamma_0^I} \equiv \frac{1-k'}{1-k}\,\delta$$

In $[f_N'(1)/f_N(1)]^2$,

$$-\left(\frac{1-k'}{1-k}\right)^2\left(\frac{\gamma_0^J}{\gamma_0^I}\right)^2\left[2\beta^J + (\alpha^J)^2\right] \equiv -\left(\frac{1-k'}{1-k}\right)^2(\eta + \epsilon)$$

From now on, we can take $k' = 0$ and study the asymptotics if $k \to 1^-$. For $k' = 0$, $t_0 = (1-k)^2$.

The simpler terms are

$$\beta = \frac{\gamma_0^K}{\gamma_0^I} = \frac{b_0^K}{\gamma_0^I} = t_0^2\left(1 + \frac{t_0}{1-k}\right)^{-2} = O\big((1-k)^4\big)$$

$$\delta = \frac{\gamma_0^J}{\gamma_0^I} = \frac{b_0^J}{\gamma_0^I} = t_0\left(1 + \frac{t_0}{1-k}\right)^{-1} = O\big((1-k)^2\big)$$

They tend to 0 if $k \to 1$ after they have been multiplied by their respective factors $(1-k)^{-2}$ and $(1-k)^{-1}$.

We compute α, ϵ, η:

$$\alpha = \frac{1}{4}\left[\frac{3b_2^K}{b_0^I} - \frac{11}{3}\frac{a_1}{a_0}\frac{b_1^K}{b_0^I} + \frac{11}{3}\frac{a_1}{a_0}\frac{b_0^K}{b_0^I}\frac{b_1^I}{b_0^I} - \frac{3b_0^K b_2^I}{b_0^I b_0^I} - \frac{b_1^I b_1^K}{b_0^I b_0^I} + \frac{b_0^K(b_1^I)^2}{(b_0^I)^3}\right]$$

$$\epsilon = \frac{1}{2a_0}\left(\frac{b_1^J}{b_0^I} - \frac{b_0^J b_1^I}{b_0^I b_0^I}\right)^2$$

$$\eta = \frac{1}{2}\frac{b_0^J}{b_0^I}\left[\frac{3b_2^J}{b_0^I} - \frac{11}{3}\frac{a_1}{a_0}\frac{b_1^J}{b_0^I} + \frac{11}{3}\frac{a_1}{a_0}\frac{b_0^J b_1^J}{b_0^I b_0^I} - \frac{3b_0^J b_2^I}{b_0^I b_0^I} - \frac{b_1^I b_1^J}{b_0^I b_0^I} + \frac{b_0^J(b_1^I)^2}{(b_0^I)^3}\right]$$

We use expansions up to order 2 in powers of $1 - k$:

$$\frac{b_1^I}{b_0^I} \sim -\frac{1}{(I-k)^2} - \frac{1}{(1-k)} - (1-k) + o\big((1-k)^2\big)$$

$$\frac{b_2^I}{b_0^I} \sim \frac{1}{2}\left[\frac{2}{(1-k)^4} + \frac{2}{(1-k)^3} + \frac{1}{(1-k)^2} + \frac{3}{1-k} + 4(1-k) + 3(1-k)^2 + o\big((1-k)^2\big)\right]$$

$$a_0 = \varphi''(t_0) = -\frac{1}{(1-k)^2} + \frac{1}{1-k} - 3 + 2(1-k) - 5(1-k)^2 + o\big((1-k)^2\big)$$

$$a_1 = \frac{\varphi^{(3)}(t_0)}{2} = \frac{1}{(1-k)^3} - \frac{3}{(1-k)^2} + \frac{5}{1-k} - 10 + 12(1-k) - 21(1-k)^2 + \cdots$$

$$\frac{b_1^J}{b_0^I} = -2(1-k) + 3(1-k)^2, \qquad \frac{b_1^K}{b_0^I} \sim (1-k)^2 + \cdots$$

$$\frac{b_2^J}{b_0^I} \sim \frac{1}{2}\left[5 - 10(1-k) + 22(1-k)^2\right]$$

$$\frac{b_2^K}{b_0^I} \sim \frac{1}{2}\left[-6(1-k) + 39(1-k)^2\right]$$

from which we obtain the result.

6. REMARKS.

1. The function $f_N(1)$ plays the same role that the partition function of statistical mechanics plays. The physical quantities are obtained by studying the singularities when $N \to \infty$ of the derivatives of $\log f_N(s)$ at $s = 1$.

2. The phenomenon that we have shown in this work seems to be quite general: every bifurcation value of the parameter at the macroscopic level will correspond to a phase transition at the microscopic level the nature of which depends on the bifurcation. Moreover, when one suppresses some converse reaction before taking the thermodynamic limit, we can obtain a result in contradiction with the macroscopic analysis. We can announce

that we have obtained similar results for some kinds of trimolecular reaction of Schlögl type[13] (this analysis is harder than the preceding one and will appear soon). Moreover, we have also now some partial result in the case of diffusion reaction.

3. We also want to point out the work of Keizer,[6] where he shows that the fluctuations of a reactant fixed in average can stabilize an unstable state. Here, our reactant C is completely fixed. We hope to discuss this point in our model.

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REFERENCES

1. A. Erdelyi, *Asymptotic Expansions* (Dover, New York, 1956).
2. R. Görtz and D. Walls, *Z. Phys. B* **25**:423 (1976).
3. M. Kac, Fluctuations near and far from equilibrium, in *Statistical Mechanics and Statistical Methods in Theory and Application*, U. Landman, ed. (1977).
4. J. Keizer, *J. Chem. Phys.* **67**:1473 (1977).
5. J. Keizer, *Proc. Natl. Acad. Sci. USA* **75**:3023 (1978).
6. J. Keizer, *J. Stat. Phys.* **15**:477 (1976).
7. R. McQuarrie and J. Keizer, Fluctuations in chemically reacting systems, in *Theoretical Chemistry: Advances and Perspectives*, Vol. 6A (1981).
8. M. Malek–Mansour and G. Nicolis, *J. Stat. Phys.* **13**:197 (1975).
9. G. Nicolis and I. Prigogine, *Self-Organization in Non-Equilibrium System* (Wiley-Interscience, New York, 1977).
10. A. Nikiforov and V. Ouvarov, *Elements de la théorie des fonctions spéciales*, Mir, ed. (1974).
11. L. Oppenheim, K. Shuler, and G. Weiss, *Physica (Utrecht)* **88A**:191 (1977).
12. I. Procaccia and J. Ross, *J. Chem. Phys.* **67**:5565 (1977).
13. F. Schlögl, *Z. Phys.* **18**:321 (1972).