

## Some Comments on Nonequilibrium Phase Transitions in Chemical Systems

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Two new approaches for investigating critical fluctuations near an instability point of unstable chemical models are proposed. The master equation approach is used. For a homogeneous system without the effect of diffusion, three single-component chemical systems exhibiting critical behavior are considered. The cumulant functions are expanded in a small parameter—the inverse size of the system—and singular perturbation solutions of the master equation are developed. Exponents describing the divergence of the second-order variance are found to be classical. For a system including diffusion effects, spatial correlations for a quasi-one-dimensional case are investigated by considering scale transformation behavior within the multivariate master equation formalism.

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**KEY WORDS:** Chemical reactions; fluctuations; instabilities; master equation; renormalization group; singular perturbations.

### 1. INTRODUCTION

The existence of instabilities leading to large-scale order in nonlinear systems driven away from thermodynamic equilibrium is well-established.<sup>(1,2)</sup> A particularly fascinating aspect of these phenomena is their relation to phase transitions. This question has recently attracted considerable interest, both for fluid dynamical<sup>(1)</sup> and for chemical instabilities.<sup>(3-6)</sup> Among the most important results of these investigations, one may quote the development of long-range spatial correlations of the fluctuations as the system approaches the instability point from below, and a concomitant enhancement of local

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values of the variances. An analysis<sup>(4)</sup> involving approximations equivalent to mean-field theory reveals that the correlation length diverges as  $(\lambda - \lambda_c)^{-1/2}$  and variances of fluctuations of the variables diverge as  $(\lambda - \lambda_c)^{-1}$ ;  $\lambda - \lambda_c$  is the distance from the instability point in terms of a bifurcation parameter  $\lambda$ . The critical exponents are analogous to the "classical" critical exponents in equilibrium phase transitions. Such classical exponent results have been obtained from several different starting points based on stochastic equations for chemical instabilities; e.g. the Langevin method,<sup>(3)</sup> the master equation approach,<sup>(4,5)</sup> and the fluctuation-dissipation hypothesis,<sup>(7)</sup> which are not necessarily equivalent.

Most theories of fluctuations are based on an approximate truncation of stochastic hierarchy equations. It is fair to say that, to date, there exists no systematic method of analysis of fluctuations in nonequilibrium systems in the "critical region" close to the instability point, where existing truncation techniques are certainly not justified. The purpose of the present work is to point out a few possibilities in this field, for the particular problem of chemical instabilities. The basic questions that will retain our attention involve the possible breakdown of the "mean-field" theoretical description and the development of new methods enabling study of the stochastic equations beyond the hitherto used truncation to second-order cumulants.

In Section 2, we discuss a general formulation of the "mean-field" theory in the master equation description of fluctuations for a *homogeneous* system (well-stirred system); attention is focused on the variance of a fluctuating variable near the critical point. Several simple models are used for illustrations. Deviations from "mean-field" theory are analyzed in Section 3 by using a singular perturbation approach to treat the terms neglected in the "mean-field" method. It is shown that the divergence of the variances and the values of critical exponents will remain "classical" when higher order nonlinear fluctuations are considered. The master equations used in Sections 2 and 3 include chemical fluctuations only; the role of diffusion is neglected there. In Section 4, we discuss spatial correlations by including diffusion; the resulting multivariate master equation is analyzed by considering its behavior under scale transformations. The idea is to show that the classical exponent can be obtained by considering first a truncated equation for pair correlations. It is then shown that such a renormalization group technique can be extended to a simple one-dimensional reacting model. An approximate renormalization group is found for such a model which gives a classical exponent. The status of a Langevin description of spatial fluctuations is briefly discussed.

In the final section, we discuss the applicability of these new developments, and some aspects of the models under consideration.

From the few model examples which we have examined by these tech-

niques, it seems that, for long-wavelength fluctuations, the qualitative conclusions of "mean-field" type theories are preserved and no anomalous critical behavior is obtained. Recently, Nicolis and Turner<sup>(8)</sup> have solved the spatially homogeneous fluctuation problem for Schlögl's model exactly; they also found that "classical" exponents describe the divergence of the second-order variance near the instability point.

## 2. MASTER EQUATION DESCRIPTION: "MEAN-FIELD" THEORETICAL LEVEL

In recent work by the Brussels group,<sup>(4,6)</sup> the New Zealand group,<sup>(5)</sup> and Haken<sup>(9)</sup> a description of fluctuations in chemical systems based on a multivariate master equation has been developed. The system is divided into spatial cells of length  $R$ , labeled  $1, 2, \dots, n$ , whose size can be chosen to be of the order of the mean free path, and can under no condition approach molecular dimensions or exceed the correlation length. Let  $\{x_i\}$  be the occupation numbers of cells  $i$ , and  $P(\{x_i\}, t)$  be the probability distribution of  $\{x_i\}$  at time  $t$ . Define a generating function  $F(\{s_i\}, t)$  as

$$F(\{s_i\}, t) = \sum_{x_i=0}^{\infty} \prod_i s_i^{x_i} P(\{x_i\}, t) \quad (1)$$

The birth-and-death master equation takes the form

$$\frac{\partial F}{\partial t} = \left( \frac{\delta F}{\delta t} \right)_{\text{chem}} + \sum_i d(s_{i+1} + s_{i-1} - 2s_i) \frac{\partial F}{\partial s_i} \quad (2)$$

The term  $(\delta F/\delta t)_{\text{chem}}$  describes the effect of chemical kinetics, and the second term describes the random exchange of species X between neighboring cells due to diffusion. We have

$$d = D/R^2 \quad (3)$$

with  $D$  the Fickian diffusion constant.

Suppose X participates in a number of reactions whose order ranges from 0 to  $k$ . Then the macroscopic rate of evolution of X would be of the form

$$dn_x/dt = a_k n_x^k + \dots + a_1 n_x + a_0 \quad (4)$$

where  $n_x$  is the concentration of X;  $a_k < 0$ , or else the time evolution diverges [see (24) for an example].

If (4) follows mass-action kinetics, the highest order term can only be the result of



On the other hand, from dimensional arguments and the local equilibrium

assumption, it follows that at least some of the lower order rate mechanisms should involve buffered chemicals A, whose number of particles is maintained *fixed* and *large* within each cell  $i$ . This suggests that one could seek solution of Eq. (2) in the form

$$F = \exp[A\phi(\{s_i\}, t)] \quad (6)$$

The equation for the cumulant generating function  $\phi$  has a complex structure. Note, however, that each  $r$ -order derivative of  $F$  in (2) with respect to  $s$ —corresponding to a term  $n_x^r$  in (4)—gives rise, in the  $\phi$  representation, to a sum of terms of the form

$$A \frac{\partial^r \phi}{\partial s_\alpha^r}, \quad A^2 \left( \frac{\partial^{r-1} \phi}{\partial s_\alpha^{r-1}} \right) \left( \frac{\partial \phi}{\partial s_\alpha} \right), \dots, \quad A^r \left( \frac{\partial \phi}{\partial s_\alpha} \right)^r \quad (7)$$

Dividing Eq. (2) by the highest power of  $A$ , one can initiate a perturbative-type solution in which all but the highest order term in  $A$  are neglected, to first approximation. We now show that in the presence of instability the zeroth-order term gives rise to a “mean-field” type theory. To avoid cumbersome equations, we will discuss the case of a homogeneous system first, and delay the problem of spatial fluctuation to Section 4. Consider a homogeneous chemical system; Eq. (2) without diffusion can be written in terms of the cumulant function  $\phi$  as

$$\partial \phi / \partial \tau = \sum_{r=0}^k A_r(s) (\partial \phi / \partial s)^r \quad (8)$$

with  $\tau = tA^{k-1}$ . Here higher order terms in the small quantity  $1/A$  have been neglected.

At the steady state, Eq. (8) can be solved to yield  $\phi$  subject to the normalization condition

$$\phi(s = 1) = 0 \quad (9)$$

However, it is just as good to evaluate the variance of the fluctuation, which is related to  $(\partial^2 \phi / \partial s^2)_{s=1}$ . Differentiating Eq. (8) with respect to  $s$ , one finds

$$\frac{\partial^2 \phi}{\partial s^2} \sum_{r=1}^k r A_r(s) \left( \frac{\partial \phi}{\partial s} \right)^{r-1} = - \sum_{r=0}^k \frac{dA_r(s)}{ds} \left( \frac{\partial \phi}{\partial s} \right)^r \quad (10)$$

We now take the limit  $s \rightarrow 1$ , from (4) and (8); it follows that

$$A_r(1) = a_r/n_A^k, \quad (\partial \phi / \partial s)_{s=1} = n_x/n_A \quad (11)$$

On the other hand, the sum on the left of (10) is just the coefficient appearing in the linearized stability equation for (4). In the presence of an instability this coefficient vanishes at the “critical point.” We conclude from (10) that

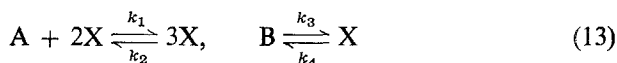
$$\langle \delta x^2 \rangle - \langle x \rangle = (\partial^2 \phi / \partial s^2)_{s=1} \rightarrow \infty \quad (12)$$

since the right-hand side of (10) is, in general, different from zero. Thus, by limiting the equation for  $\phi$  to the highest order term in  $A$ , one always predicts a sharp transition at the macroscopic instability point. Following the work reported in Refs. 4 and 5, one can convince oneself that this conclusion remains valid in the presence of diffusion.

We now evaluate the corresponding critical exponents. Rather than remaining general, we find it instructive to illustrate the analysis directly on three simple models.

### 2.1. Model A. A Trimolecular Model

On the nonlinear chemical rate models exhibiting nontrivial critical behavior, the simplest type is the model considered by Schlögl,<sup>(10)</sup>



The macroscopic rate equation is

$$dn_x/dt = -k_1 n_x^3 + k_2 n_A n_x^2 - k_3 n_x + k_4 n_B \quad (14)$$

and it may admit up to three positive steady-state solutions.

For simplicity, let  $k_1 = 1$ ,  $k_2 = 3$ . At the critical point where  $k_4^c n_B = n_A^3$  and  $k_3^c = 3n_A^2$ , the three solutions coalesce to

$$n_x^c = n_A \quad (15)$$

The behavior in the vicinity of this point is described by two parameters  $\delta$  and  $\delta'$  defined by

$$k_3 = (3 + \delta)n_A^2 \quad (16)$$

$$k_4 = (1 + \delta')n_A^3/n_B \quad (17)$$

which play the same role that temperature and pressure deviation from the critical point play in equilibrium phase transitions. The elementary catastrophe one is dealing with in crossing the critical point is known as *the cusp*.<sup>(11)</sup>

The equation for the generating function is (neglecting the effect of diffusion)

$$s^2 \left( \frac{d^3 F}{ds^3} - 3A \frac{d^2 F}{ds^2} \right) + (3 + \delta)A^2 \frac{dF}{ds} - (1 + \delta')A^3 F = 0 \quad (18)$$

or, in the cumulant function representation,

$$s^2 \left( \frac{1}{A^3} \frac{d^3 \phi}{ds^3} + \frac{3}{A} \frac{d\phi}{ds} \frac{d^2 \phi}{ds^2} - \frac{3}{A} \frac{d^2 \phi}{ds^2} \right) + s^2 \left[ \left( \frac{d\phi}{ds} \right)^3 - 3 \left( \frac{d\phi}{ds} \right)^2 \right] + (3 + \delta) \frac{d\phi}{ds} - (1 + \delta') = 0 \quad (19)$$

Neglecting terms containing  $1/A$  and  $1/A^2$ , we find an equation that allows explicit evaluation of  $\phi$  subject to the normalization condition  $\phi(s=1) = 0$ . At  $s=1$  this equation becomes identical to the macroscopic rate equation at the steady state. Hence  $(d\phi/ds)_{s=1}$  is equal to  $n_x/n_A$ , i.e., at the critical point

$$(d\phi/ds)_{s=1}^c = 1 \quad (20)$$

Let us now compute the variance by differentiating the  $A$ -independent part of (19). Setting  $s=1$ , we recognize in the left-hand side the coefficient appearing in the linearized stability equation for  $n_x$ . This coefficient, which is the analog of "isothermal compressibility" along the "isochore"  $\delta' = 0$ , vanishes as the *first* power of  $\delta$  as we approach the critical point. Hence

$$\left. \frac{d^2\phi}{ds^2} \right|_{s=1} = \frac{1}{A} [\langle x^2 \rangle - \langle x \rangle^2 - \langle x \rangle] = \frac{4}{\delta} \quad (21)$$

or

$$(\langle x^2 \rangle - \langle x \rangle^2)/A \propto 4/\delta \quad (22)$$

as  $\delta \rightarrow 0$ , since  $\langle x \rangle/A$  is always finite. The critical exponent defined in terms of the parameter  $\delta^{-1}$  is  $+1$ . The limit  $\delta \rightarrow 0$  from below is discussed in Ref. 8.

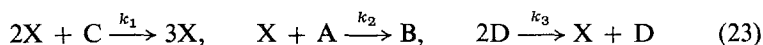
We have considered macroscopic fluctuations to lowest order in the expansion parameter  $1/A$ ; if macroscopic fluctuations and microscopic fluctuations are well separated, it is reasonable to expect the above analysis to hold. A similar analysis based on a  $1/V$  expansion, where  $V$  is the volume (an extensive quantity) of the system, has been carried out by Kubo *et al.*<sup>(12)</sup> and Van Kampen<sup>(13)</sup>; their attention was focused on the distribution function instead of the generating function.

Near a critical point, neglect of higher order terms in the  $1/A$  expansion is not justified since the terms dropped become large also. Consideration of these higher terms will be presented in Section 3. For the model of this section, these terms involve up to triple derivatives of the function  $\phi$ . Nicolis and Turner<sup>(8)</sup> have found an exact evaluation of the variance in the asymptotic limit.

In order to make the mathematics simpler, we wish to consider some simplified models which involve quadratic rate laws only. These models are somewhat pathological, as explained in Section 5, but their consideration will be justified when we discuss them separately.

## 2.2. Model B. Bimolecular Model with Two Steady States

Consider the following sequence of reactions:



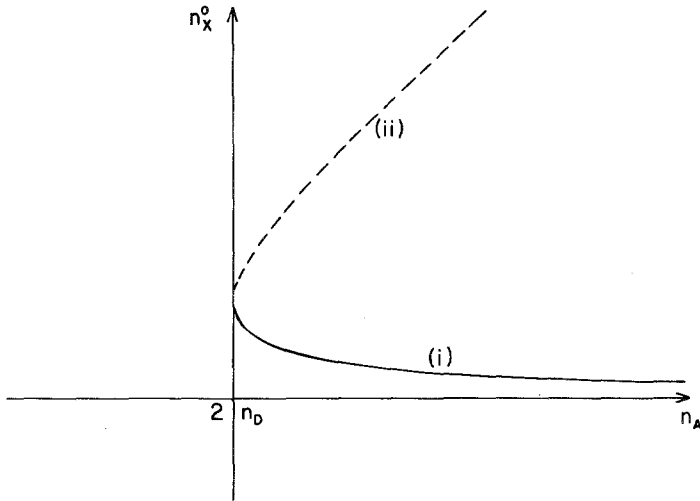


Fig. 1. Stability diagram for model B, Section 2.2. (i) Asymptotically stable branch; (ii) asymptotically unstable branch.

By setting  $k_1 C = 1$ ,  $k_2 = k_3 = 1$ , the macroscopic rate equation yields

$$dn_x/dt = n_x^2 - n_A n_x + n_D^2 \quad (24)$$

and the steady-state solutions are

$$n_x^0 = [n_A \pm (n_A^2 - 4n_D^2)^{1/2}]/2 \quad (25)$$

They are depicted in Fig. 1, where solid and dashed lines denote, respectively, asymptotically stable and unstable branches. Both branches disappear for  $n_A < 2n_D$ . Thus, the "critical point"  $n_A = 2n_D$  is not an instability point that leads to bifurcation phenomenon. Rather, it corresponds to the simplest of elementary catastrophes<sup>(11)</sup> known as *the fold*.

Strictly speaking, Eq. (23) is not a stable mechanism and model B is not a realistic chemical model; however, (24) can be viewed as a limiting case of model A where the cubic rate constant is very small, so that the upper stable branch is very far from the two branches considered here. This is typical in explosive reaction mechanisms. We wish now to investigate the fluctuations along branch (i) in Fig. 1 as the critical point is approached in this model.

The master equation in terms of the generating function in the steady state is

$$(s^3 + s^2) \frac{d^2 F}{ds^2} + A(1 - s) \frac{dF}{ds} + D^2(s - 1)F = 0 \quad (26)$$

In terms of the cumulant function representation, this becomes

$$\frac{1}{A} s^2 \frac{d^2 \phi}{ds^2} + s^2 \left( \frac{d\phi}{ds} \right)^2 - \frac{d\phi}{ds} + \lambda^2 = 0 \quad (27)$$

with  $\lambda^2 = D^2/A^2 = n_D^2/n_A^2$ . Note that the "critical" value of  $\lambda$  is  $\lambda_c = 1/2$ . Neglecting, as before, terms containing  $1/A$ , we find

$$s^2(d\phi/ds)^2 - (d\phi/ds) + \lambda = 0 \quad (28)$$

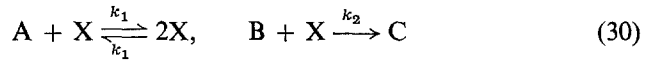
Again, we have

$$\left(\frac{d^2\phi}{ds^2}\right)_{s=1} = \frac{2(d\phi/ds)_{s=1}^2}{1 - 2(d\phi/ds)_{s=1}} \quad (29)$$

This diverges as  $n_A \rightarrow 2n_D$ . The divergence goes as  $(\lambda - \frac{1}{2})^{-1/2}$ . The exponent 1/2 should not necessarily be surprising here, as no obvious "order parameter" seems to exist in this model. Thus, we do not know what the "classical" exponent should be.

### 2.3. Model C. Bimolecular Model with One Trivial State

Consider another quadratic rate model,<sup>(5)</sup>



The macroscopic equation of evolution (letting  $k_{-1} = k_1 = k_2 = 1$ )

$$dn_x/dt = (n_A - n_B - n_x)n_x \quad (31)$$

gives two steady-state solutions

$$n_x^{(1)} = 0, \quad n_x^{(2)} = n_A - n_B \quad (32)$$

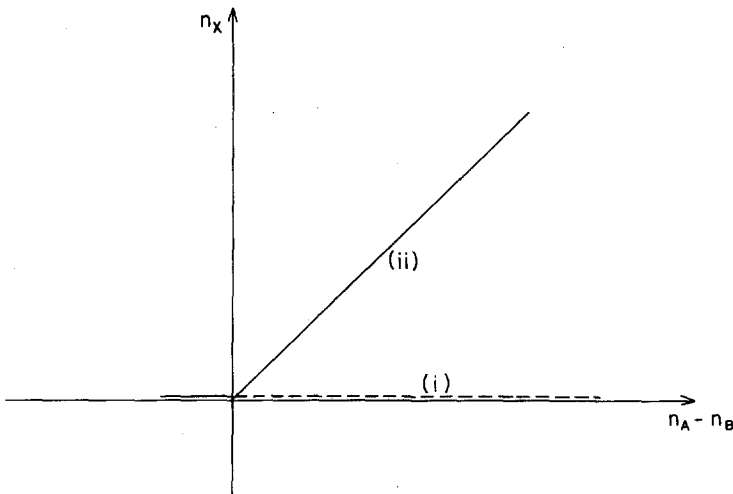


Fig. 2. Stability diagram for model C, Section 2.3. (i) Trivial branch; (ii) branch considered in the text.



At  $n_A = n_B$  the system undergoes a "second-order" transition depicted in Fig. 2.

In the cumulant function representation, the master equation gives

$$sA^2\left(\frac{d\phi}{ds}\right)^2 + sA\frac{d^2\phi}{ds^2} + (B - As)A\frac{d\phi}{ds} = 0 \quad (33)$$

Dividing through by  $A^2$  and neglecting terms containing  $1/A$ , we find

$$s\left(\frac{d\phi}{ds}\right)^2 + \left(\frac{B}{A} - s\right)\frac{d\phi}{ds} = 0 \quad (34)$$

To evaluate the variance, we differentiate once more,

$$\left(2s\frac{d\phi}{ds} + \frac{B}{A} - s\right)\frac{d^2\phi}{ds^2} = -\left(\frac{d\phi}{ds}\right)^2 + \frac{d\phi}{ds} \quad (35)$$

with

$$(d\phi/ds)_{s=1} = (n_A - n_B)/n_A \quad (36)$$

The variance of the fluctuation can be evaluated as

$$\frac{\langle \delta x^2 \rangle - \langle x \rangle^2}{A} = \left(\frac{d^2\phi}{ds^2}\right)_{s=1} = \frac{n_B}{n_A} \quad (37)$$

This is finite at the instability point, contrary to (12), even though  $\langle x \rangle = A(d\phi/ds)_{s=1} \rightarrow 0$ . But

$$\lim_{A \rightarrow B} \left(\frac{\langle \delta x^2 \rangle}{\langle x \rangle^2}\right)^{1/2} = \frac{n_B}{n_A} \frac{1}{n_A - n_B} \rightarrow \infty \quad (38)$$

That is, the relative fluctuations does diverge, like  $(n_A - n_B)^{-1}$ .

### 3. CORRECTIONS TO THE "MEAN-FIELD" THEORY VIEWED AS A PROBLEM OF SINGULAR PERTURBATION

We want now to assess the validity of neglecting higher order terms in  $1/A$  in the limit  $A \rightarrow \infty$  (macroscopic limit). As we have seen in the preceding section, these terms multiply higher derivatives of the function  $\phi$ . Thus, we have a *singular perturbation* problem,<sup>(14)</sup> whose zeroth approximation to the *outer solution* is provided by such equations as (21), (28), and (34).

One of the principal features of a singular perturbation is the occurrence of a *boundary layer*. In order to examine the possible formation of such layers in the problem under consideration, we must specify the boundary conditions for the function  $F$  or  $\phi$ . Although  $s$  varies in the interval  $(-1, 1)$ , we choose

to work in the interval  $(0, 1)$ . One boundary condition is due to the normalization condition for the distribution function

$$F(s = 1) = 1 \quad \text{or} \quad \phi(s = 1) = 0 \quad (39)$$

This condition can *always* be satisfied by the outer solution in the previous section.

In setting up the boundary condition at  $s = 0$ , we observe that, from the definition (1), it follows that

$$F(s = 0) = P(0), \quad \frac{dF}{ds}(s = 0) = P(1) \quad (40)$$

Now the values of  $P(0)$  and  $P(1)$  are between 0 and 1 and, more typically, vanishingly small as  $A \rightarrow \infty$ . Hence

$$0 \leq F(0) \leq 1, \quad 0 \leq \frac{dF}{ds}(0) \leq 1 \quad (41)$$

or in terms of the cumulant function  $\phi$  we have

$$\phi(0) < 0, \quad \frac{d\phi}{ds}(0) = \frac{1}{A} \frac{P(1)}{P(0)} \quad (42)$$

Usually, the ratio  $P(1)/P(0)$  can be computed explicitly from the kinetic scheme. For instance for the model B considered in Section 2, we have

$$dP(0)/dt = AP(1) - D^2P(0) \quad (43)$$

and

$$P(1)/P(0) = D^2/A \quad (44)$$

Now, since the outer (mean-field theoretical) approximate solution is derived from an equation of first order in  $s$ , it will in general *not* obey conditions (41) or (42). Thus, we expect the formation of a boundary layer near  $s = 0$  and the outer solution becomes unsatisfactory there. On the other hand, *no boundary layer is expected to arise in the vicinity of  $s = 1$ .*<sup>3</sup> All physical quantities pertaining to the behavior of fluctuations are computed from  $\phi$  and its derivatives at  $s = 1$ . Hence, we expect the outer solution to make sense even within the framework of singular perturbation, at least under certain conditions.

We now proceed to derive these conditions. Setting  $\epsilon = 1/A$ , one may always transform the equation for  $\phi$  into a system of first-order equations of the form

$$\epsilon \, du/ds = f(s, u, \epsilon) \quad (45)$$

where both  $u$  and  $f$  are  $r$ -dimensional vectors if  $r$  is the highest order derivative appearing in the equation for  $\phi(s)$ .

<sup>3</sup> On inspecting Eqs. (17) and (26) for  $F$  we may also remark that  $s = 0$  is an irregular singular point, whereas  $s = 1$  is a regular (nonsingular) point.

The outer solution  $w_o$  is given by

$$f(s, w_o, 0) = 0 \quad (46)$$

Setting

$$u(s) = v(s) + w_o(s) \quad (47)$$

we transform Eq. (45) to

$$\epsilon dv/ds = g(s, v, \epsilon) \quad (48)$$

with

$$g(s, 0, 0) = 0 \quad (49)$$

Hence, Eq. (48) can be written in the form

$$\epsilon dv/ds = \epsilon a(s) + A_0(s)v + h(s, v, \epsilon) \quad (50)$$

where the function  $h$  contains at least quadratic powers of  $v$  and  $\epsilon$ .

Now we make the following assumption.

**Assumption.**  $A_0$  can be diagonalized and has nonzero eigenvalues for  $|s| \leq s_0$ .

Note that at  $s = 1$ ,  $A_0$  becomes identical to the coefficient appearing in the linear stability analysis of the macroscopic rate equations. Hence if we remain below the instability point,  $\det[A_0(1)]$  will never vanish.

Under this assumption one can prove that<sup>(14,15)</sup> Eq. (50) admits solution of the form

$$v = \sum_{i=1}^n \epsilon^i v_i(s) \quad (51)$$

where the  $v_i(s)$  are holomorphic. Moreover, as  $\epsilon \rightarrow 0$ , (51) is the uniform asymptotic expansion of some function holomorphic in  $s$  and  $\epsilon$  for  $s \leq s_0$ ,  $0 < \epsilon \leq \epsilon_0$ , and the asymptotic expression can be differentiated termwise.

In conclusion, we have shown that if we remain off the critical point (although still in its neighborhood), the outer solution computed in Section 2 is a sound approximation to the behavior near  $s = 1$ . In particular the law of divergence of the variance and the values of the critical exponents will remain unaffected. The analysis of the inner solution, as well as the direct asymptotic evaluation of the steady-state solution in the case of Schlögl's model by Nicolis and Turner,<sup>(8)</sup> confirm these conclusions. Again, these arguments are not likely to be influenced by diffusion, which only intervenes in the outer expansion, provided the limit  $A \rightarrow \infty$  can be taken within each spatial cell. This limit, however, may well be unrealistic.

We wish to illustrate the above arguments by explicitly considering the bimolecular model B of Section 2. We start from (27), setting

$$d\phi/ds = u(s) \quad (52)$$

Then,

$$\epsilon \frac{du}{ds} + u^2 - \frac{1}{s^2}u + \frac{\lambda^2}{s^2} = 0 \quad (53)$$

The outer solution is given by

$$w_o = (1/2s^2)[1 - (1 - 4\lambda^2s^2)^{1/2}] \quad (54)$$

where the negative sign has been chosen to keep  $w_o$  finite at  $s = 0$  [see Eq. (42)].

With Eqs. (47) and (48), we have

$$\epsilon \frac{dv}{ds} + \left(2w_o - \frac{1}{s^2}\right)v + v^2 + \epsilon \frac{dw_o}{ds} = 0 \quad (55)$$

The coefficient of  $v$  is

$$A_o(s) = -(1/s^2)(1 - 4\lambda^2s^2)^{1/2} \quad (56)$$

Since  $s \leq 1$ ,  $A_o(s)$  remains different from zero as long as  $2\lambda < 1$ . Looking back at Section 2.2, we see that this inequality implies that we are not in the immediate vicinity of the "critical" point. This ensures the applicability of the Wasow theorem,<sup>(15)</sup> and at the same time, the validity of the outer expansion.

Now, with the expansion of (51), one can easily work out the first-order correction to the outer solution; substituting Eq. (51) into Eq. (55) and collecting powers of  $\epsilon$ , one has

$$\left(2w_o - \frac{1}{s^2}\right)v_1 + \frac{dw_o}{ds} = 0 \quad \text{or} \quad v_1 = \frac{s^2 dw_o/ds}{1 - 2s^2w_o} \quad (57)$$

To first order we have

$$d\phi/ds \approx (1/2s^2)[1 - (1 - 4\lambda^2s^2)^{1/2}] + v_1\epsilon \quad (58)$$

Then

$$\frac{d^2\phi}{ds^2} = \frac{dw_o}{ds} + \epsilon \frac{dv_1}{ds} = \frac{(1 - 4\lambda^2s^2)^{1/2} - 1}{s^3} + \frac{8\lambda^2s}{4s^2(1 - 4\lambda^2s^2)^{1/2}} + \epsilon \frac{dv_1}{ds} \quad (59)$$

As  $\lambda \rightarrow \frac{1}{2}$ , both  $dw_o/ds$  and  $dv_1/ds$  terms diverge as  $s = 1$ . But the important point is that  $\epsilon dv_1/ds$  in (59) is much smaller than  $dw_o/ds$  for the region  $\lambda = 1/2 + \eta$ , where  $\eta$ , although small, is large compared to  $\epsilon = 1/A$ . That is, we wish to consider a critical region  $\lambda = 1/2 + \eta$  where  $\eta$  is still large compared to microscopic deviations of order  $1/\text{Avogadro's number}$ . Then

$$\left(\frac{d^2\phi}{ds^2}\right)_{s=1} \xrightarrow{\eta \rightarrow 0} \frac{1}{\eta^{1/2}} \quad (60)$$

In other words, the outer ("mean-field" theoretical) solution dominates the divergent behavior near the critical point as long as we are not in the immediate critical region, where the  $\lambda$  parameter cannot be well defined anyway since microscopic fluctuations of  $A$  become important there. The behavior of fluctuations *at* the critical point was recently investigated by Van Kampen<sup>(13)</sup> and Nicolis and Turner.<sup>(8)</sup>

#### 4. SPATIAL CORRELATIONS

In the previous sections, we have investigated fluctuations of extensive quantities in a homogeneous chemical system near an instability point. The effect of diffusion was neglected. In this section, we will consider the coupling between diffusion and nonlinear kinetics; its effect is known to lead to long-range correlations<sup>(3,4)</sup> analogous to the well-known Ornstein-Zernike theory of correlation in equilibrium phase transitions.<sup>(16)</sup> In common with previous work,<sup>(3-5)</sup> a linearization procedure, similar to the mean-field-theoretical method discussed in Section 2, can be used. The correlation length  $\xi$  is found to vary as  $(\lambda - \lambda_c)^{-1/2}$  with classical exponent  $\nu = 1/2$ . This is not surprising in view of the parallel result,  $\langle \delta x^2 \rangle \sim (\lambda - \lambda_c)^{-1}$ , in a homogeneous system. Our starting point is the full stochastic equation (2).

For technical reasons, we limit ourselves to the investigation of slowly varying spatial fluctuations in the "hydrodynamic" range. We expect these to be the important ones when the rate of diffusion is much faster than that of the chemical reactions present. Although this approximation is equivalent to hitherto used truncation procedures, our principal goal is to show that it is possible to set up an analysis of spatial fluctuations which follows closely the modern theories of critical phenomena set forth by Kadanoff<sup>(17)</sup> and Wilson.<sup>(18)</sup>

The basic idea is to consider scale transformations of the basic master equation (2) for a multicell system in the manner of the Kadanoff construction.<sup>(17)</sup> If long-range correlations do exist, they can be found by looking at the way in which the bifurcation parameter (or instability parameter) is transformed in scaling. The concept of fixed point in such a transform will be related to the underlying instability point. In working with the cell block approach, our approach will be similar to the renormalization group theory of the Ising model used by Nauenberg.<sup>(19)</sup>

For the sake of simplicity, we will consider the simplest multivariate nonlinear reaction-diffusion model. Let us look at the chemical model C of Section 2.3 in a quasi-one-dimensional system. (Consider the reaction in a very long and narrow cylinder, for example.) Divide the system into small cell blocks of length  $R$ ;  $R$  should be of the order of the mean free path between X-X reactive collisions. We will allow a birth-and-death stochastic

description in each cell for chemical reactions and random exchange of X between nearest neighbor cells only. In terms of the multivariate generating function  $F(s_1, s_2, \dots)$  the master equation will be

$$\frac{\partial F}{\partial t} = \sum_i \left\{ [As_i^2 + B + d(s_{i+1} + s_{i-1} - 2s_i) - (A + B)s_i] \frac{\partial F}{\partial s_i} + \bar{\epsilon}(s_i - s_i^2) \frac{\partial^2 F}{\partial s_i^2} \right\} \quad (61)$$

with  $d = D/R^2$ ;  $D$  is the Fickian diffusion constant for the species X. The last term in (61) is due to the nonlinear step of the mechanism  $2X \rightarrow X + A$ . In (61),  $\bar{\epsilon}$  is its rate constant. We do not now take  $\bar{\epsilon} = 1$  as before.

In terms of

$$a = A/d, \quad b = B/d, \quad \epsilon = \bar{\epsilon}/d, \quad \tau = td$$

the master equation can be written as

$$\sum_i \left\{ [as_i^2 + b + (s_{i+1} + s_{i-1} - 2s_i) - (a + b)s_i] \frac{dF}{ds_i} + \epsilon(s_i - s_i^2) \frac{d^2 F}{ds_i^2} \right\} = 0 \quad (62)$$

in a steady-state system.

The pair correlation  $\langle x_i, x_j \rangle$  will be determined by the second derivative  $(\partial^2 F / \partial s_i \partial s_j)_{s_i=1, s_j=1}$ . From Eq. (62) this quantity will be related to  $\langle x_i x_j x_k \rangle$ , and an infinite hierarchy of equations relating each moment to the next higher order one can be written down, in general.

In order to simplify notation, let us fix one of the  $x_i$ , say  $x_0$ , to be a constant nonfluctuating value  $N$ . Then the correlation  $\langle x_0 x_i \rangle = \langle x_i \rangle N$ . From Eq. (62) one has

$$\epsilon \langle x_i^2 - x_i \rangle + (2 - l) \langle x_i \rangle = \langle x_{i+1} \rangle + \langle x_{i-1} \rangle, \quad l = a - b \quad (63)$$

If we neglect the nonlinear term ( $\epsilon$  term), all moments become decoupled; in particular we have

$$(2 - l) \langle x_i \rangle = \langle x_{i+1} \rangle - \langle x_{i-1} \rangle \quad (64)$$

The next step is to consider a superlattice by averaging over every other cell. Equation (64) can be written as

$$[(2 - l)^2 - 2] \langle x_i \rangle = \langle x_{i+2} \rangle + \langle x_{i-2} \rangle \quad (65)$$

Consider the  $i - 2$ ,  $i$ , and  $i + 2$  cells as neighboring cells with length  $2R$ . If one writes Eq. (65) as

$$(2 - l') \langle x'_i \rangle = \langle x'_{i+1} \rangle + \langle x'_{i-1} \rangle \quad (66)$$

it has the same form [Eq. (64)] as before. One has the parameter  $l$  transformed as

$$l' = 4l - l^2 \quad (67)$$

This transformation has two fixed points at  $l_1 = 0$  and  $l_2 = 3$ ; the slope of the transform is

$$\lambda_1 = \left. \frac{dl'}{dl} \right|_{l=0} = 4 > 1, \quad \lambda_2 = \left. \frac{dl'}{dl} \right|_{l=3} = -2 < 1 \quad (68)$$

Hence  $l = 0$  is a critical point ( $n_A - n_B = 0$ ).

The critical exponent  $\nu$  for correlation length  $\xi$  can be easily determined as

$$\nu = \ln 2 / \ln \lambda = 1/2 \quad (69)$$

a classical result!

Hence, by looking at the scale transform behavior of the parameter  $l$ , one can investigate critical behavior without actually solving the multivariate stochastic equation.

Now we want to see whether such a model can be applied to the nonlinear problem in a less trivial way. Consider the complete equation (63), which can be written as

$$(2 - l)\epsilon \langle x_i^2 - x_i \rangle + [(2 - l)^2 - 2] \langle x_i \rangle \\ = \langle x_{i+2} \rangle + \langle x_{i-2} \rangle - \epsilon [\langle x_{i+1}^2 - x_{i+1} \rangle + \langle x_{i-1}^2 - x_{i-1} \rangle] \quad (70)$$

The idea is again to try to write this equation in the form of

$$\epsilon' \langle x_i'^2 - x_i' \rangle + (2 - l') \langle x_i' \rangle \approx \langle x_{i+1}' \rangle + \langle x_{i-1}' \rangle \quad (71)$$

in the same form as the original equation except for an enlarged scale. In general, one would have

$$\epsilon' = f(\epsilon, l), \quad l' = g(\epsilon, l) \quad (72)$$

and similar procedures to find fixed points and critical exponents can be used. Here we want to illustrate this method on a special situation.

Consider the situation where the diffusion rate in and out of each cell is much larger than the quadratic rate of X, e.g.,

$$d \gg \bar{\epsilon} \quad (73)$$

Then  $\epsilon = \bar{\epsilon}/d$  can be considered as a small parameter. In this case, higher order correlations are dominated by diffusion and the linear rate law; one has

$$2(2 - l) \langle x_i x_{i+n} \rangle = \langle x_i x_{i+n-1} \rangle + \langle x_i x_{i+n+1} \rangle + \langle x_{i+n} x_{i+1} \rangle + \langle x_{i+n} x_{i-1} \rangle + O(\epsilon) \quad (74)$$

and

$$\langle x_i^2 - x_i \rangle = \frac{1}{2-l} \langle x_{i+1}x_i + x_{i-1}x_i \rangle + \frac{a}{2-l} \langle x_i \rangle + O(\epsilon) \quad (75)$$

Substitute (74) and (75) into Eq. (70); after some manipulation of equations, one has

$$\begin{aligned} & \left[ P - \frac{2 + O(\epsilon)}{PQ^2} \right] \epsilon \langle x_i^2 - x_i \rangle + \left[ S + \frac{(2-l')^2}{PQ} + O(\epsilon) \right] \langle x_i \rangle \\ &= \left[ 1 + \frac{S}{PQ} + O(\epsilon) \right] (\langle x_{i+2} \rangle - \langle x_{i-2} \rangle) + \frac{\epsilon}{PQ^2} (\langle x_{i+4}^2 - x_{i+4} \rangle \\ & \quad + \langle x_{i-4}^2 - x_{i-4} \rangle) \end{aligned} \quad (76)$$

with

$$P = 2 - l + \left[ 1 + \frac{2-l'}{(2-l)^2} \right] / [1 - 1/2(2-l)^2] \quad (77a)$$

$$Q = 2(2-l)^2 - 1 \quad (77b)$$

$$S = (2-l)^2 - 2 \quad (77c)$$

Now this equation is not quite the form we would like, due to the extra next-nearest-neighbor terms. The importance of these extra terms may depend on the dimensionality of the problem in hand. A ‘‘critical dimensionality’’ argument for neglecting these higher neighbor terms would be highly desirable here. In this paper, we will simply adopt the usual assumption made in the Kadanoff construction for the Ising model; we neglect all higher neighbor terms after each iteration. We will have an approximate renormalization group for the scaling transform, that is,

$$\epsilon' = [P - 2/PQ^2 + O(\epsilon)] / [1 + S/PQ + O(\epsilon)] \quad (78)$$

and

$$2 - l' = \frac{PQS + (2-l')^2}{PQ + S} + O(\epsilon) \quad (79)$$

One can immediately see that  $\epsilon = 0$  satisfies the fixed-point condition. For  $l$ , Eq. (79) is a complicated nonlinear transformation. Nonetheless, one can show by direct substitution that  $l = 0$  again satisfies the fixed-point condition. To assess the behavior near the fixed point  $l = 0$ , we compute

$$(dl'/dl)_{l=0} = 4 \quad (80)$$

Therefore the correlation length behaves as

$$\xi \propto (l - l_c)^{-1/2} = l^{-1/2} = (n_A - n_B)^{-1/2} \quad (81)$$



We have thus recovered the classical result again in a nontrivial way. This result is a direct consequence of the decoupling scheme of Eqs. (74) and (75), which, in turn, is motivated by the approximation (73) that diffusion dominates higher correlations. Similar conclusions have been reached by Gardiner *et al.*<sup>(5)</sup> in a Gaussian-like approximation for triplet correlations by more traditional methods. We wish to argue here that the condition  $d \gg \bar{\epsilon}$  is realizable in some actual situations. Consider a dilute gas of X; the diffusion constant is  $D \sim \lambda \bar{c}$ , where  $\lambda$  is the mean free path and  $\bar{c}$  is the mean molecular speed. Then  $d = D/\lambda^2 = \bar{c}/\lambda = 1/\text{mean time between collisions}$ , where the quadratic constant  $\bar{\epsilon}$  should be

$$\frac{\text{probability of effective reaction}}{\text{mean time between collisions}} = \frac{p}{\tau}$$

In case of high activation energy for the reaction,  $p \ll 1$ . Then one would indeed have  $d \gg \bar{\epsilon}$ .

The cell-block scaling method presented in this section has only been applied to the simple one-dimensional reaction-diffusion model; we have shown that the classical exponent can be obtained in a very easy way. As in similar problems for the Ising model,<sup>(20)</sup> extensions to higher dimensions become very complicated. Nonetheless, the problem is well-posed. More work is needed for more realistic models in three dimensions.

Another method using the renormalization group approach can be based on the so-called Langevin equation approach.<sup>(3)</sup> We will just make a few comments on this approach here. For a one-component reaction-diffusion system, the following Langevin equation was proposed by Nitzan *et al.*<sup>(3)</sup>:

$$\frac{\partial X}{\partial t} = -\frac{\partial \Phi(X, \lambda)}{\partial X} + D \nabla^2 X + f(\mathbf{r}, t) \quad (82)$$

On the right-hand side of this equation the first term represents the chemical rate and the second term is the normal diffusion. For the random term  $f(\mathbf{r}, t)$  one has

$$\langle f(\mathbf{r}, t) f(\mathbf{r}', t') \rangle = 2Q \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (83)$$

Under this condition, (82) can be solved by considering the probability distribution  $P(x, t)$  as a solution of a Fokker-Planck equation.<sup>(21)</sup> The steady-state solution is

$$P(X) \sim \exp\left\{-\int d\mathbf{r} [\Phi(X(\mathbf{r})) + \frac{1}{2}D(\nabla X)^2]\right\} \quad (84)$$

This is very much like a Landau-Ginzburg model for equilibrium phase transitions. Hence the renormalization group technique developed by Wilson can be applied to this problem in a straightforward way (the critical dimensionality in the case of cubic nonlinearities would then be expected to be 4).

In a one-dimensional case, this has been done by Scalapino *et al.*,<sup>(22)</sup> who show that no sharp transition occurs. This is in contrast to the result obtained in this section by the master equation approach. Recently Grossman<sup>(23)</sup> and Gardiner<sup>(24)</sup> have argued that the random force (83) is not consistent with the basic equations of conservation for a flow system. Alternative expressions for the random force have been proposed by Grossman,<sup>(23)</sup> Gardiner,<sup>(24)</sup> and Keizer.<sup>(7)</sup> These have not yet been applied to the problem of critical spatial correlations.

## 5. DISCUSSION

In conclusion, we have presented some techniques for treating nonlinear fluctuations for reaction–diffusion systems described by master equations. We have shown that a singular perturbation method can be formulated based on a  $1/A$  expansion of the cumulant function. Such an expansion is similar to the  $1/V$  expansion applied to the distribution function by Kubo *et al.*<sup>(12)</sup> and Van Kampen.<sup>(13)</sup> One would expect a time-dependent theory could also be developed for dynamic fluctuations. At present, our attention has only focused on the macroscopic fluctuations of steady states.

For spatial correlations, we explore the renormalization group approach based on cell scaling. The method has led to an interesting result near the critical point. It is not clear at present how to extend this technique to more complicated systems and higher dimensions. However, the basic idea of scaling transformation should apply, providing long-range correlations are developed. This has been shown in Section 4 with a highly simplified model.

We have been using very simple models in discussing these techniques. In fact two of the models are so simple that there are some trivialities associated with them; a few words should be said about them here.

For model C, the exact steady-state solution is known; it is

$$F(s) = 1 \quad (85a)$$

or

$$P(x) = \delta_{x,0} \quad (85b)$$

and this is not the approximate solution we considered for the nontrivial branch ( $n_x = n_A - n_B$ ). So how can an equation like (37) make sense? There are several ways out of this. Keizer<sup>(25)</sup> has suggested that the asymptotic limit of the master equation (in system size) is the important quantity, and that this limit must be taken *before* the  $t \rightarrow \infty$  limit. The  $t \rightarrow \infty$  limit corresponds to the approach to the steady state. From recent work of Kubo *et al.*<sup>(10)</sup> the time for approaching the steady state is  $\propto e^N$ , where  $N$  is proportional to the size of the system. In this limit, the extinction of  $X$  does not arise for an extended period of time. So although our approximate solution is not on

the same branch as the exact solution (85b), it will take a very long time to approach (85b). The system will practically stay forever on this nontrivial branch. Alternatively, one can note that by changing just one single transition probability, that for  $x = 0 \rightarrow x = 1$ , we will generate a model with a probability not concentrated on  $x = 0$ . The state  $x = 0$  is no longer an absorbing state. Of course, this amounts to changing the model. We believe the change is not unreasonable.

In fact, for a master equation of the form

$$\frac{\partial P}{\partial t} = t^+(x-1)P(x-1, t) + t^-(x+1)P(x+1, t) - [t^+(x) + t^-(x)]P(x, t) \quad (86)$$

the steady-state solution is given by

$$P_{ss}(x) = P_{ss}(0) \prod_{j=1}^x \frac{t^+(j-1)}{t^-(j)} \quad (87)$$

as may be readily verified by substitution.  $t^+(0) = 0$  for the mechanism given by (30). But if we set  $t^+(0) = \beta \neq 0$ , then

$$P_{ss}(x) = P_{ss}(0)\beta(B-1)! \frac{A^{x-1}}{x(B-x+1)!} \quad (88)$$

This distribution has a maximum at  $x = A - B$ , which is what one would expect from the macroscopic rate law. As long as  $A - B$  is not near zero, the distribution is rather narrow. We believe that it is this distribution that we are studying by our approximate methods.

Model B, Eq. (23), is also somewhat pathological if interpreted literally. In this case, the cause of the peculiarity of the generating function equation lies, not in extinction, but in explosion, because there is nothing in the mechanism (23) to counteract the autocatalytic growth. So the steady state cannot be truly steady under fluctuations. Of course, one would expect, again physically, that the reverse reaction of the first step in (23), neglected there, should become important if  $X$  becomes significantly large. In this case the model can be considered as a limiting case of model A where the upper branch is very far from the two steady-state branches considered. In a very large system, the time necessary for such very large-scale fluctuation can be very long.

For model B, Eq. (87) takes the form

$$P_{ss}(x) = P_{ss}(0) \prod_{j=1}^x \frac{(j-1)(j-2) + D^2}{Aj} \quad (89)$$

which grows like  $x!/A^x$  for  $x \rightarrow \infty$ . This is not normalizable. But note that  $P(x)$  has a sharp maximum at a value of  $x$  given by the macroscopic equation

(25). We believe that our approximate methods describe the behavior of a system in which the eventual large- $x$  divergence is suppressed by some mechanism, but which is described by (89) near the maximum.

So model B can be considered again valid in an *asymptotic* sense in Sections 2 and 3.

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