

The Onset of Instabilities in Nonequilibrium Systems

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The nonlinear master equation previously proposed by Malek-Mansour and Nicolis is applied to the analysis of unstable transitions leading to temporally or spatially organized patterns. The *correlation length* of the destabilizing fluctuations is determined, and a number of striking analogies with equilibrium phase transitions are pointed out.

KEY WORDS: Master equation; chemical kinetics; critical phenomena; nonequilibrium instabilities.

1. INTRODUCTION

In a previous series of papers, Prigogine and two of the present authors^(1,2) have developed a *local* theory of fluctuations in nonlinear systems far from thermodynamic equilibrium. A simplified version of this theory has led to a *nonlinear master* equation for the reduced probability distribution concerning a small subvolume ΔV within a macroscopic system. This equation reads

$$\frac{dP(X, \Delta V, t)}{dt} = R_{\text{ch}}(\Delta V) + \mathcal{D}\langle X \rangle [P(X-1, \Delta V, t) - P(X, \Delta V, t)] \\ + \mathcal{D}[(X+1)P(X+1, \Delta V, t) - XP(X, \Delta V, t)] \quad (1)$$

where X denotes a set of variables describing the composition of a chemically reacting mixture; hereafter X will be the numbers of particles of the chemical

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constituents; R_{ch} denotes the contribution of chemical reactions within ΔV to the evolution of $P(X, \Delta V, t)$; \mathcal{D} is a diffusion rate of exchange of particles across the surface surrounding ΔV ; the properties of this coefficient are analyzed in detail in Ref. 2; and $\langle X \rangle$ is the stochastic mean of X given by

$$\langle X \rangle = \sum_{X=0}^{\infty} XP(X, \Delta V, t) \quad (2)$$

The purpose of the present paper is to apply the nonlinear master equation to the analysis of fluctuations leading to instabilities. The existence of such instabilities in nonlinear systems involving chemical reactions and diffusion is now firmly established. Beyond instability these systems may evolve to states showing spatial or temporal order, which have been called *dissipative structures*. Our object here is to understand the *spontaneous onset* of these transitions through fluctuations by solving approximately the master equation (1). As we shall see, at the critical point of the unstable transition \mathcal{D} will be related to the chemical parameters of the system contained in the terms $R_{\text{ch}}(\Delta V)$. Now, as shown in Ref. 2 in an ideal mixture, \mathcal{D} is also related to the *range l* of the fluctuation through

$$\mathcal{D} = f(T)/l \simeq D/l, \quad (3)$$

where D is Fick's diffusion coefficient, l is the mean free path, and $f(T)$ is a function of the temperature. Thus, according to Eq. (3), the range of a fluctuation capable of destabilizing the reference state will depend on the rate of its growth as described by the chemical reactions, and vice versa. In the subsequent three sections we shall carry out these calculations in detail on simple chemical models involving, successively: marginally stable systems, systems giving rise to limit cycles, and systems giving rise to spatial dissipative structures.

Throughout the paper, a number of striking analogies with equilibrium phase transitions will be pointed out. Such analogies had to be expected from the very form of Eqs. (1)–(3), which take into account the coupling between spatial fluctuations through a *self-consistent field* type of approximation. This self-consistent field character of Eq. (1) is seen most clearly from its derivation reported in Ref. 2, where the direct correlations between the subvolume ΔV and the surroundings have been neglected in a first approximation.

In spite of the fact that spatial correlations are not taken into account explicitly in the present description, it will be natural to regard the range parameter l as a *coherence length*, that is, as the spatial dimension over which the fluctuations preserve a coherent character. This is related to the fact that, as we shall see in the sequel, the short-time behavior of fluctuations can be treated satisfactorily by means a *cumulant expansion* truncated to the second-

order moments. Because of this the characteristic parameters appearing in the equations for the second-order cumulants—which describe the effect of fluctuations—are *identical* to those appearing in the first moment equations. To a good approximation the latter are, in turn, related to the phenomenological equations of evolution. Thus, it can be claimed that a self-consistent master equation contains all pertinent parameters which are likely to influence the behavior of the system in the vicinity of the transition point.

2. MARGINALLY STABLE SYSTEMS

In this section we solve the master equation (1) for the Volterra–Lotka model:



All forward reaction rates are inversely proportional to a large number N_0 proportional to the size of the system.

It is well known^(1,3) that system (4) admits a nontrivial steady state solution:

$$X_0 \simeq \langle X \rangle = B, \quad Y_0 \simeq \langle Y \rangle = A \quad (5)$$

which is *marginally stable* and is surrounded by an infinity of closed trajectories in the $(\langle X \rangle, \langle Y \rangle)$ plane representing periodic behavior. This property makes this system (without diffusion) *structurally unstable* to all perturbations modifying even slightly the form of the evolution equations.

The master equation describing the fluctuations and including the effect of diffusion takes the form

$$\begin{aligned} \frac{dP(X, Y, t)}{dt} &= \frac{1}{N_0} [A(X-1)P(X-1, Y, t) - AXP(X, Y, t)] \\ &+ \frac{1}{N_0} [(X+1)(Y-1)P(X+1, Y-1, t) - XY P(X, Y, t)] \\ &+ \frac{1}{N_0} [B(Y+1)P(X, Y+1, t) - BY P(X, Y, t)] \\ &+ \mathcal{D}_X \langle X \rangle [P(X-1, Y, t) - P(X, Y, t)] \\ &+ \mathcal{D}_X (X+1)P(X+1, Y, t) - \mathcal{D}_X X P(X, Y, t) \\ &+ \mathcal{D}_Y \langle Y \rangle [P(X, Y-1, t) - P(X, Y, t)] \\ &+ \mathcal{D}_Y (Y+1)P(X, Y+1, t) - \mathcal{D}_Y Y P(X, Y, t) \end{aligned} \quad (6)$$

To solve this equation we transform to the generating function representation^(1,4)

$$F(s_1, s_2, t) = \sum_{X=0}^{\infty} \sum_{Y=0}^{\infty} s_1^X s_2^Y P(X, Y, t) \quad (7)$$

Moreover, we introduce the cumulant generating function by the relation⁽⁵⁾

$$F(s_1, s_2, t) = \exp[N_0 \psi(s_1, s_2, t)] \quad (8)$$

We scale the various parameters by N_0

$$A = \alpha N_0, \quad B = \beta N_0, \quad X = x N_0, \quad Y = y N_0 \quad (9)$$

and switch to new variables given by

$$\xi = s_1 - 1, \quad \eta = s_2 - 1 \quad (10)$$

Equation (6) becomes

$$\begin{aligned} \frac{\partial \psi}{\partial t} = & [\alpha \xi (\xi + 1) - \mathcal{D}_{x\xi}] \frac{\partial \psi}{\partial \xi} + [-\eta \beta - \mathcal{D}_{y\eta}] \frac{\partial \psi}{\partial \eta} \\ & + (\eta + 1)(\eta - \xi) \left(\frac{\partial \psi}{\partial \xi} \frac{\partial \psi}{\partial \eta} + \frac{1}{N_0} \frac{\partial^2 \psi}{\partial \xi \partial \eta} \right) + \mathcal{D}_{x\xi} \frac{\langle X \rangle}{N_0} + \mathcal{D}_{y\eta} \frac{\langle Y \rangle}{N_0} \end{aligned} \quad (11)$$

For N_0 large³ the second derivative term of ψ can be neglected in Eq. (11). Note that this imposes certain restrictions on the size of the volume ΔV , which, however, are fulfilled once the mixture is not extremely dilute. The truncated Eq. (11) admits solutions of the form

$$\psi = a_1 \xi + a_2 \eta + \frac{1}{2} b_{11} \xi^2 + b_{12} \xi \eta + \frac{1}{2} b_{22} \eta^2 + \dots \quad (12)$$

The coefficients b_{ij} describe the deviation of the fluctuations from the Poisson regime. Indeed, from Eqs. (11), (8), and (7), we find

$$\begin{aligned} N_0 a_1 &= \langle X \rangle, & N_0 a_2 &= \langle Y \rangle \\ N_0 b_{11} &= \langle \delta X^2 \rangle - \langle X \rangle, & N_0 b_{22} &= \langle \delta Y^2 \rangle - \langle Y \rangle, \\ N_0 b_{12} &= \langle \delta X \delta Y \rangle \end{aligned} \quad (13)$$

Substituting now (12) into (11), we obtain a set of five coupled nonlinear equations for the coefficients a_1, a_2, b_{ij} . A quasilinearization of these equations is possible by substituting a_1, a_2 by the deterministic averages given by (5). This restricts us automatically to fluctuations around the steady state and to a time scale sufficiently short for the fluctuations to modify the macroscopic

³ Recently, Kubo *et al.*⁽⁶⁾ developed systematically the mathematical properties of the master equations in the limit $N_0 \rightarrow \infty$.

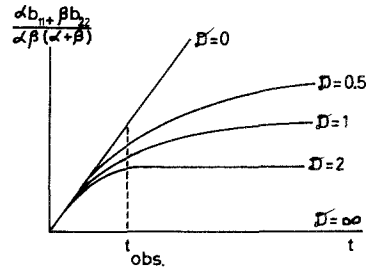


Fig. 1. Time dependence of $\alpha b_{11} + \beta b_{22}$ for various values of the parameter \mathcal{D} .

behavior. Since we are interested primarily in the *onset* of fluctuations, this procedure is legitimate. We obtain (setting also $\mathcal{D}_x = \mathcal{D}_y = \mathcal{D}$)

$$\begin{aligned} db_{11}/dt &= 2(\alpha\beta - \beta b_{12} - \mathcal{D}b_{11}) \\ db_{22}/dt &= 2(\alpha\beta + 2\alpha b_{12} - \mathcal{D}b_{22}) \\ db_{12}/dt &= -\alpha\beta + \alpha b_{11} - \beta b_{22} - 2\mathcal{D}b_{12} \end{aligned} \tag{14}$$

A first integral of (14) can easily be deduced. From the first two equations we have

$$(d/dt)(\alpha b_{11} + \beta b_{22}) = 2\alpha\beta(\alpha + \beta) - 2\mathcal{D}(\alpha b_{11} + \beta b_{22}) \tag{15}$$

Integrating with the initial condition

$$b_{11} = b_{22} = 0 \tag{16}$$

we obtain

$$\alpha b_{11} + \beta b_{22} = (1/\mathcal{D})\alpha\beta(\alpha + \beta)(1 - e^{-2\mathcal{D}t}) \tag{17}$$

A similar behavior is found for b_{12} .

Figure 1 represents this solution for various values of \mathcal{D} . For $\mathcal{D} = 0$ we find that fluctuations increase in time and remove the system from the Poisson regime. This is in agreement with previous calculations by Prigogine and Nicolis.⁽⁵⁾ On the other hand, the least finite value of \mathcal{D} appears to stabilize the system to a steady state for the fluctuations after a time which is longer, the smaller the \mathcal{D} . For $\mathcal{D} \rightarrow \infty$ the Poisson distribution is recovered, as expected from the general ideas advanced in our previous paper (Ref. 2). Comparing now with Eq. (3) relating \mathcal{D} to the size of the subsystem inside the volume ΔV , we arrive at the conclusion that there exists no finite critical coherence length of unstable fluctuations.⁴ This is a consequence of the structural

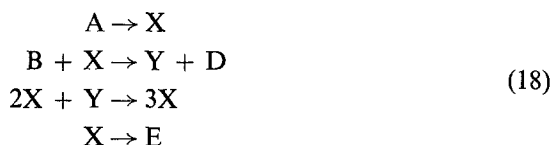
⁴ In fact, if the time scale of observation is sufficiently short (see Fig. 1), a similar phenomenon to nucleation would appear as the stabilized fluctuations will correspond only to a \mathcal{D} larger than some critical value, e.g., $\mathcal{D} \approx 2$ according to Fig. 1. It should be pointed out, however, that for such time scales the description adopted in this paper may well break down.

instability of the model at the marginal state as well as of the fact that in our analysis the phenomenon of *extinction* of the populations has not been taken into account. It is most likely that in a more accurate treatment, the condition that extinction should *not* occur will introduce a critical value of \mathcal{D} or, equivalently, of the coherence length of the fluctuations that could lead to extinction. This point has been verified in an exactly soluble model analyzed in Ref. 2.

In the next section we consider a model which, beyond the state of marginal stability, exhibits an instability leading to sustained oscillations of the limit cycle type.

3. THE ONSET OF A LIMIT CYCLE

We consider the autocatalytic chain⁽⁷⁾



The forward rate constants of the second and third steps are, respectively, of the order N_0^{-1} and N_0^{-2} , where N_0 is the size parameter introduced in the previous section.

The equations of mass balance for this scheme have been studied extensively both for spatially uniform systems^(7,8) and for inhomogeneous systems.^(7,9) The following properties have been established in the case of systems which are maintained macroscopically homogeneous:

- a. The system admits a single steady-state solution:

$$X_0 \simeq \langle X \rangle = A, \quad Y_0 \simeq \langle Y \rangle = (B/A)N_0 \quad (19)$$

- b. The steady state is

$$\begin{aligned} \text{a stable node for} & \quad 0 < \beta < (\alpha - 1)^2 \\ \text{a stable focus for} & \quad (\alpha - 1)^2 < \beta < \alpha^2 + 1 \\ \text{an unstable focus for} & \quad \alpha^2 + 1 < \beta < (\alpha + 1)^2 \\ \text{an unstable node for} & \quad \beta > (\alpha + 1)^2 \end{aligned}$$

where

$$\alpha = A/N_0, \quad \beta = B/N_0 \quad (20)$$

We may now write a master equation for system (18) including the effect of diffusion. We solve this equation by the method of cumulants described in the previous section and proceed to a quasilinearization of the first five

moment equations by substituting the mean values by the deterministic expression (19). It turns out that the results differ markedly when the diffusion rates \mathcal{D}_X and \mathcal{D}_Y for X and Y are equal or different. Both cases turn out to correspond to a distinct behavior of the *deterministic* equations of evolution, provided \mathcal{D}_i are replaced by the Fickian diffusion coefficients D_i . This analogy is a result of the asymptotic limit $N_0 \rightarrow \infty$, which permitted us to treat the small volume ΔV as a “macroscopic” system and to truncate the hierarchy of moment equations to the second-order cumulants. When $D_X = D_Y$ the macroscopic equations, subject to appropriate boundary conditions, lead to an oscillatory instability and subsequently to a uniform limit cycle regime for the entire system. In the case of $D_X \neq D_Y$ a symmetry-breaking instability becomes possible,^(7,9) leading to a space-dependent steady-state solution. In this section we shall investigate the onset of a limit cycle through fluctuations, postponing until Section 4 the analysis of spatial dissipative structures.

For $D_X = D_Y = D$, which in the stochastic formalism is translated by the equality $\mathcal{D}_X = \mathcal{D}_Y = \mathcal{D}$, the equation for the quantities b_{ij} introduced in the previous section reads

$$\begin{aligned} \frac{d}{dt} \begin{pmatrix} b_{11} \\ b_{12} \\ b_{22} \end{pmatrix} &= \begin{pmatrix} 2(\beta - 1) - 2\mathcal{D} & 2\alpha^2 & 0 \\ -\beta & \beta - \alpha^2 - 1 - 2\mathcal{D} & \alpha^2 \\ 0 & -2\beta & -2\alpha^2 - 2\mathcal{D} \end{pmatrix} \\ &\times \begin{pmatrix} b_{11} \\ b_{12} \\ b_{22} \end{pmatrix} + \begin{pmatrix} 4\alpha\beta \\ -\alpha\beta \\ 0 \end{pmatrix} \end{aligned} \tag{21}$$

It should be pointed out that a number of results in this paper rely on the truncation of the moment equations and the subsequent identification of the stochastic and deterministic means in the equations for the cumulants. The reason why this procedure is legitimate is that we deal with “smooth” transitions, where the dissipative structure emerges with a macroscopically infinitesimal amplitude slightly above the critical point. In contrast, in situations involving multiple steady states separated by a finite distance, the truncated moment equations become inadequate and one has to deal with the complete master equation.⁽¹⁰⁾

Let us now come back to Eq. (21). The eigenvalues of the matrix of the coefficients in these equations are

$$\begin{aligned} \omega_1 &= \beta - \alpha^2 - 1 - 2\mathcal{D} \\ \omega_{\pm} &= \beta - \alpha^2 - 1 - 2\mathcal{D} \pm [(\beta - \alpha^2 - 1)^2 - 4\alpha^2]^{1/2} \end{aligned} \tag{22}$$

Thus, system (21) will admit a stable steady-state solution under the following conditions:

(a) For any \mathcal{D} , if $0 < \beta < \alpha^2 + 1$ (23)

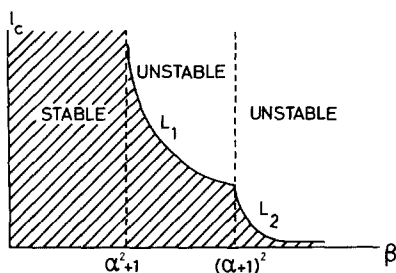


Fig. 2. Coherence length of a fluctuation at the critical point versus the chemical parameter β . Here $L_1 = f(T)[2/(\beta - \alpha^2 - 1)]$ and $L_2 = f(T)2\{[\beta - \alpha^2 - 1 + [(\beta - \alpha^2 - 1)^2 - 4\alpha^2]^{1/2}]\}$.

$$(b) \text{ For } \mathcal{D} > \frac{1}{2}(\beta - \alpha^2 - 1), \text{ if } \alpha^2 + 1 < \beta < (\alpha + 1)^2 \quad (24)$$

$$(c) \text{ For } \mathcal{D} > \frac{1}{2}\{\beta - \alpha^2 - 1 + [(\beta - \alpha^2 - 1)^2 - 4\alpha^2]^{1/2}\} \text{ if } \beta > (\alpha + 1)^2 \quad (25)$$

In these regions a local fluctuation will not increase. Thus, the reference state (19) will remain asymptotically stable.

We may now combine relation (23) to (25) with Eq. (3) relating \mathcal{D} to the coherence length l of the fluctuation. We define a critical length l_c by the relation

$$l_c = f(T)/\mathcal{D}_c \quad (26)$$

where \mathcal{D}_c is given by (24) and (25) when the equality sign is satisfied. Figure 2 represents the relation between l_c and the chemical parameter β .

It is instructive to phrase relation (26) in the language of equilibrium critical phenomena. To this end we consider the neighborhood of the first instability of the steady state—the analog of the critical point—defined by the value

$$\beta_c = \alpha^2 + 1 \quad (27)$$

Relation (26) becomes

$$l_c/2f(T) = 1/(\beta - \beta_c)^1 \quad (28)$$

Under the same conditions the *order parameter*, that is, the radius ρ of the limit cycle, varies as⁽⁹⁾

$$\begin{aligned} \rho &\propto (\beta - \beta_c)^{1/2} & \text{for } \beta > \beta_c \\ \rho &= 0 & \text{for } \beta \leq \beta_c \end{aligned} \quad (29)$$

Thus, the analogs of the critical exponents⁵ β^* and ν of equilibrium theory become

$$\beta^* = \frac{1}{2} \quad \nu = 1 \quad (30)$$

It is interesting to observe that in spite of the self-consistent field character of the master equation (1), there emerges a “nonclassical” exponent, namely

⁵ We introduce here the symbol β^* in order to avoid confusion with the chemical parameter β used throughout this paper.

$\nu = 1$, which in any theory of critical phenomena of the Landau type⁽¹¹⁾ is always equal to $\beta^* = \frac{1}{2}$. A close inspection of Eq. (3) reveals that⁽²⁾ this nonclassical behavior stems from the appearance of the relaxation length l_r in the equation relating \mathcal{D} and l , rather than of the coherence length l alone. This is in turn related to the *nonequilibrium* character of the phenomenon under consideration, which introduces into the theory the effect of long-wavelength excitations like sound waves whose velocity is related to the mean free path l_r . It is instructive to point out the similarity between this picture and the ideas underlying Wilson's extension of the Landau theory of equilibrium phase transitions⁽¹²⁾: The very essence of Wilson's approach is to introduce into the "classical theories" the influence of fluctuations with "intermediate" wavelengths, which are shown to modify deeply the behavior of the long-range correlations in the neighborhood of the critical point. The analogy with Wilson's theory will become more obvious when the correlation terms neglected in the derivation of Eq. (1) will be incorporated into the theory.

Note that a direct solution of the master equation (1) or a truncation of the moment equations to a higher level than that of the second-order cumulants might produce further deviations of the critical indices β^* and ν from the "classical" values, most probably in the form of nonsimple fractional or even irrational numbers. Moreover, the correspondence with the deterministic results will be less direct in this case.

Bearing these points in mind, one may now interpret Fig. 2 as follows.

Suppose that an internal fluctuation (the same reasoning holds for an external disturbance as well) appears at the vicinity of a point inside ΔV . If the range of this disturbance, i.e., the length over which it preserves a coherent character, is in the dashed region of Fig. 2, then the decay process of the local fluctuation (roughly measured by \mathcal{D}_c^{-1}) will take over and the disturbance will die out. For $\beta < \alpha^2 + 1$ even if an infinite coherence length is imposed the disturbance will decay, but for $\beta > \alpha^2 + 1$ disturbances whose range exceeds l_c will be amplified and spread throughout the system. The latter will remain stable with respect to fluctuations whose $l < l_c$. For $\beta > (\alpha + 1)^2$ the range of decaying fluctuations will decrease rapidly and finally, for in the unstable region ($\beta \gg \alpha^2 + 1$) the system will be unstable with respect to infinitesimal fluctuations.

The similarity with the ideas underlying *nucleation theory* is tempting and will be developed further in Section 5.

It is instructive to estimate l_c numerically. According to the mean free path theory of transport phenomena, we have

$$f(T) \simeq D/l_r \simeq \bar{c} \quad (31)$$

where \bar{c} is the mean thermal velocity (essentially the velocity of sound).

Thus, the value of l_c depends on two competing factors: the tendency to smear out a local inhomogeneity by thermal motion, as expressed by \bar{c} ; and the tendency to amplify this inhomogeneity, as expressed by the excess chemical rate $\beta - \alpha^2 - 1$. In a gas, $\bar{c} \simeq 10^3$ m/sec. Thus, for β, α, \dots , of the order of unity, l_c is a macroscopic length. In different terms, it is extremely difficult to form spontaneously in this type of system an unstable fluctuation, since one needs a macroscopic coherence length. On the other hand, if the reactions are very fast, with rate constants of the order of 10^6 sec^{-1} , then l_c becomes of the order of 10^{-3} cm or less. Another way to favor the formation of destabilizing fluctuations is to move far in the unstable region. Thus, for α and β of the order of $10(\alpha^2 + 1)$, l_c is reduced by a factor of ten. Finally, if the reaction occurs in a medium that does not propagate sound-like disturbances very efficiently, nucleation will again be enhanced with respect to what happens in a gaseous phase.

We close this section with a short remark concerning the composition fluctuations themselves within the volume ΔV . From Eq. (21) it becomes obvious that the latter diverge in the neighborhood of the reference state as (noting also that $\mathcal{D}_c \rightarrow 0$ at the critical point $\beta_c = \alpha^2 + 1$)

$$\overline{\Delta X^2} \propto \frac{1}{\omega_1} = \frac{1}{(\beta - \beta_c)^1} = \frac{1}{(\beta - \beta_c)^{2\beta^*}} \quad (32)$$

Again, this relation is analogous to the ones prevailing in equilibrium phase transitions.⁽¹³⁾ Analogies between chemical instabilities and phase transitions have also been pointed out by Nitzan *et al.*,⁽¹⁴⁾ Kuramoto and Tsuzuki,⁽¹⁵⁾ and McNeil and Walls.⁽¹⁶⁾

4. THE ONSET OF A SPATIAL DISSIPATIVE STRUCTURE

We consider now the more general case where X and Y in model (18) are characterized by two different coefficients \mathcal{D}_X and \mathcal{D}_Y . Previous analyses^(7,9) based on the solution of the macroscopic mass balance equations in the presence of diffusion have revealed the emergence of regular spatial patterns of chemical concentrations in a previously uniform medium. Here we want to understand the spontaneous *onset* of these patterns through fluctuations.

Following the same procedure as in Sections 2 and 3 and truncating the hierarchy of moment equations to the level of second-order cumulants, we obtain a differential system for the mean quadratic fluctuations which has the same form as in Eq. (21), except that the matrix of the coefficients is now given by

$$\begin{pmatrix} 2(\beta - 1) - 2\mathcal{D}_X & 2\alpha^2 & 0 \\ -\beta & \beta - \alpha^2 - 1 - \mathcal{D}_X - \mathcal{D}_Y & \alpha^2 \\ 0 & -2\beta & -2\alpha^2 - 2\mathcal{D}_Y \end{pmatrix} \quad (33)$$

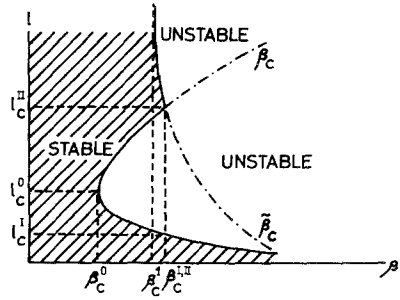


Fig. 3. Coherence length of a fluctuation at the critical point versus the chemical parameter β in the case of different diffusion coefficients. $\alpha = 2$, $\mathcal{D}_X/\mathcal{D}_Y = \frac{1}{5}$.

The eigenvalues of this matrix are

$$\begin{aligned} \omega_1 &= \beta - \alpha^2 - 1 - (\mathcal{D}_X + \mathcal{D}_Y) \\ \omega_{\pm} &= \beta - \alpha^2 - 1 - (\mathcal{D}_X + \mathcal{D}_Y) \pm \sqrt{\Delta} \end{aligned} \quad (34)$$

with

$$\Delta = [\beta - \alpha^2 - 1 - (\mathcal{D}_X + \mathcal{D}_Y)]^2 - 4(\mathcal{D}_X\mathcal{D}_Y - \beta\mathcal{D}_Y + \mathcal{D}_Y + \alpha^2\mathcal{D}_X + \alpha^2) \quad (35)$$

The second moment equation will admit a nonoscillatory instability of the steady-state solution under the following conditions:

$$\beta > \beta_c = 1 + \alpha^2 \frac{\mathcal{D}_X}{\mathcal{D}_Y} + \mathcal{D}_X + \frac{\alpha^2}{\mathcal{D}_Y} \quad (36)$$

$$\beta < \tilde{\beta}_c = 1 + \alpha^2 + \mathcal{D}_X + \mathcal{D}_Y \quad (37)$$

Introducing the coherence length l through the relations

$$\mathcal{D}_X \simeq D_X/l_l^X, \quad \mathcal{D}_Y \simeq D_Y/l_l^Y \quad (38)$$

we finally obtain

$$\beta_c = 1 + \alpha^2 \frac{D_X l_l^Y}{D_Y l_l^X} + \frac{D_X}{l_l^X} + \frac{\alpha^2 l_l^Y}{D_Y} \quad (39a)$$

$$\tilde{\beta}_c = 1 + \alpha^2 \frac{D_X}{l_l^X} + \frac{D_Y}{l_l^Y} \quad (39b)$$

Figure 3 represents the critical curves $l_c = l_c(\beta)$ corresponding to relations (39a) and (39b) in the $[l, \beta]$ plane for $\alpha = 2$ and $D_X/l_l^X = \frac{1}{5}(D_Y/l_l^Y)$.

The important new point is that in the region $\beta_c^0 < \beta < \beta_c^1$ (see Fig. 3) the instability of the reference state involves fluctuations of *finite* coherence length.⁶ In this same region, the imposition of large-scale fluctuations ($l \rightarrow \infty$)

⁶ See Graham⁽¹⁷⁾ for a similar remark in the context of the Bénard problem.

stabilizes the steady state. Beyond $\beta = \beta_c^1$, however, the behavior becomes similar to that outlined in the previous section. In contrast, the “order parameter” behaves in exactly the same way as in the limit cycle case. Indeed, the amplitude of the emerging dissipative structure beyond β_c^0 varies as⁽⁹⁾

$$\|x\| \propto (\beta - \beta_c^0)^{1/2} \quad (40)$$

At first sight, the occurrence of a finite coherence length and of a continuous order parameter seems paradoxical and difficult to fit in the frame of the more familiar equilibrium critical phenomena. A closer inspection, however, reveals the existence of a second characteristic coherence length⁷ which diverges as one moves to the critical point β_c^0 from the *pretransition region*. In this way the problem under consideration resembles closely the crystallization problem. In the latter, within the ordered phase there exists a finite correlation length (the lattice parameter), whereas in the disordered phase there appear long-range correlations up to the solidification point.

To see the appearance of the second coherence length in our problem, we consider the marginal stability equation (39a) in the equivalent form

$$\frac{1}{l^2} \theta_x + \left(1 + \alpha^2 \frac{\theta_x}{\theta_y} - \beta\right) \frac{1}{l} + \frac{\alpha^2}{\theta_y} = 0 \quad (41)$$

where

$$\theta_x = D_x/l_r^x, \quad \theta_y = D_y/l_r^y \quad (42)$$

We expect that the quantity $1/l$ will scale the spatial coordinate r_{12} appearing in the *correlation function* $g(\Delta V_1, \Delta V_2)$ between two spatial regions (see also the comments made at the end of the introduction):

$$g(\Delta V_1, \Delta V_2) \equiv g(r_{12}/l) \quad (43)$$

If $1/l$ is real, the function g will describe a self-maintained correlation of macroscopic range between spatial regions. In contrast, a complex value of $1/l$ will imply spatial damping in the form of evanescent waves emanating from ΔV . The point is that Eq. (41) gives rise to complex-valued l 's in the “disordered” region $\beta < \beta_c^0$. One finds

$$\frac{1}{l} = \frac{1}{l_1} \pm i \frac{1}{l_2} \quad (44)$$

⁷ The existence of a diverging correlation length in the Bénard problem was first pointed out by Zaitsev and Shliomis.⁽¹⁸⁾

where

$$\frac{1}{l_1} = -\frac{1}{2\theta_x} \left(1 + \alpha^2 \frac{\theta_x}{\theta_y} - \beta \right) \tag{45a}$$

$$\frac{1}{l_2} = \frac{1}{\theta_x} |\beta - \beta_c^0|^{1/2} (\beta - \beta_-)^{1/2} \tag{45b}$$

and

$$\beta_c^0 = \left[1 + \alpha \left(\frac{\theta_x}{\theta_y} \right)^{1/2} \right]^2, \quad \beta_- = \left[1 - \alpha \left(\frac{\theta_x}{\theta_y} \right)^{1/2} \right]^2 \tag{46}$$

If β is slightly subcritical, then

$$\beta_- < \beta < \beta_c^0 \tag{47}$$

and l_2 will indeed be a real quantity. As the critical point β_c^0 is approached, the length l_2 diverges as [see also Eq. (42)]

$$l_2 = \frac{D_x/l_r^x}{(\beta - \beta_-)^{1/2}} |\beta - \beta_c^0|^{-1/2} \tag{48}$$

i.e., according to a “classical exponent”

$$\nu = -\beta^* = -\frac{1}{2} \tag{49}$$

where β^* is the exponent appearing in the order parameter equation (40). Thus, the waves emanating from a region ΔV are no longer evanescent but give rise, instead, to a sustained regime characterized by the correlation length l_1 . A simple calculation shows that l_1 is identical to l_c^0 (see Fig. 3) at the critical point.

5. CONCLUDING REMARKS

In this paper we analyzed the transition to instability in a class of non-equilibrium systems, by means of a master equation containing explicitly the effect of the spatial range of fluctuations through a *mean field* type of approximation. This enabled us to compute the coherence length of the fluctuations in the region of marginal stability and to study its behavior in the vicinity of the “critical point” where the first instability occurs. We have pointed out some striking analogies with equilibrium critical phenomena and drawn attention on the relation between our approach and the ideas underlying the Landau–Wilson theory of phase transitions.

One of the most unexpected results is the emergence of an intrinsic coherence length of fluctuations in *spatially uniform* systems, even when the

latter undergo an instability preserving spatial homogeneity (Section 3). The appearance of such a coherence length seems more natural when the precursor of a *spatial* dissipative structure emerges through fluctuations (Section 4). Indeed, in the latter case there exists a characteristic length already in the macroscopic equations of evolution, namely the wavelength of the pattern emerging beyond the instability. In either case, the independence of the coherence length of both the microscopic properties at the atomic level as well as of the dimensions of the container is strongly reminiscent of the ideas underlying the *scaling hypothesis* in equilibrium critical phenomena. In essence, we have shown that the critical behavior of such time-dependent quantities as the fluctuations of composition $\overline{\Delta X^2}$ or the correlations $\overline{\Delta X \Delta Y}$ obeys “universal” laws involving an intrinsic coherence length.

As regards the critical behavior of the spatial correlation function, we may note that, in spite of the qualitative arguments advanced in the introduction as well as in connection with Eqs. (43)–(48), the study of this quantity is beyond the range of validity of the master equation (1). An explicit analysis of a multivariate master equation leading to the critical behavior of spatial correlations has been carried out recently by Lemarchand and Nocolis.⁽¹⁹⁾

In spite of the appealing analogies between nonequilibrium instabilities and equilibrium critical phenomena, one should be fully aware of the following important point. When an equilibrium phase becomes unstable, thermodynamics implies that the second differential of an appropriate potential vanishes:

$$(\delta^2\phi)_c = 0 \quad (50)$$

This, together with Einstein’s fluctuation law

$$P \propto \exp(\delta^2\phi/2k) \quad (51)$$

implies that the probability of large-scale fluctuations tending to destabilize the reference phase becomes of the order of unity. Now, to our knowledge, this result *cannot* be extended straightforwardly to nonequilibrium instabilities, for several reasons. First, according to Sections 3 and 4, the destabilizing fluctuations in this case should have a range exceeding some critical value. To estimate the probability of occurrence of such fluctuations, one has to solve the master equation [see Eqs. (1)–(3)] supplemented with an a priori estimation of the parameter l in terms of the characteristics of the medium. So far this has not been achieved. Nevertheless, it appears reasonable to expect that the system will still be dominated by short-range fluctuations. This would imply that the destabilizing fluctuations would be rather rare events. This resembles closely the phenomenon of nucleation in *first-order* transitions (see, e.g., Ref. 20). The analogy can in fact be pushed further.

Suppose a Gaussian assumption of the probability distribution of the macrovariables $\{N_j\}$ is made slightly below the critical point:

$$P \propto \exp \sum_{ijj'} a_{jj'}(l) \delta N_j(l) \delta N_{j'}(l) \quad (52)$$

where we have factorized the dependence of P on the coherence length l associated with the various « normal modes ». We know from Sections 3 and 4 that as $l \rightarrow l_c$ the fluctuations, once produced spontaneously through (52), will tend to destabilize the system. The probability of such fluctuations would be appreciable provided the matrix

$$\lim_{l \rightarrow l_c} a_{jj'}(l) \quad (53)$$

had a zero eigenvalue. Otherwise, the quantity

$$\sum_{i \leq l_c} a_{ijj'}(l) \langle \delta N_j(l) \delta N_{j'}(l) \rangle \quad (54)$$

would provide the *entropy of activation* that it would be necessary to overcome in order to enter into the unstable region. So far, no evidence for a zero eigenvalue of (53) exists for typical examples of chemical dissipative structures. In this respect, we may note that the important discovery of a *kinetic potential* in the Bénard problem⁽¹⁷⁾ arises from the fact that this problem can be reduced to a self-adjoint equation for a single variable. Moreover, the calculations reported in Ref. 16 follow the Langevin method of random forces, which are taken to be delta-correlated in space and time, an assumption which did not have to be invoked in the present work.

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