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Nonequilibrium Phase Transitions and Chemical Instabilities

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The effect of inhomogeneous fluctuations on instabilities in various nonlinear chemical models is studied in terms of concepts developed in the theory of equilibrium phase transitions.

KEY WORDS: Dissipative structure; nonequilibrium phase transition; chemical instability; reaction–diffusion equation; symmetry breaking.

1. INTRODUCTION

The similarity between equilibrium phase transitions and instabilities in systems driven far from equilibrium has been pointed out by various authors.[1,2] Great progress has been achieved recently in the study of equilibrium phase transitions. For instance, the theory of the renormalization group has furnished techniques to assess the effect of the inhomogeneous fluctuations.[3] Also, the concept of spontaneous symmetry breaking has proved a useful tool in the derivation of general relations for the correlation functions independently of any approximation.[4] It is the main purpose of this paper to review the possibility and the opportunity of applying these concepts to the understanding of order and structures in nonequilibrium systems mainly in chemical models. The paper is organized as follows. In Section 2, the model is presented. Section 3 is devoted to the study of nonequilibrium critical phenomena in multiple-steady-state systems. In Section 4 the emergence of spatial periodic patterns is discussed, whereas Section 5 summarizes the role of the fluctuations near the Hopf bifurcation leading to chemical oscillations.

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2. THE REACTION–DIFFUSION EQUATIONS

We consider open systems in which a set of chemical reactions is taking place. For the sake of brevity we suppose isothermal and mechanical equilibrium. The phenomenological rate equations for the local concentrations of the intermediate species $\{X_i\}$ then take the form

$$\partial_t X_i = f_i(\{X_j\}, \lambda) + D_i \nabla^2 X_i \tag{2.1}$$

$\{D_i\}$ are the diffusion coefficients, $\{f_i\}$ the rates of change of $\{X_i\}$ due to chemical reactions, and λ stands for a set of parameters describing the external constraints. We assume natural boundary conditions (infinite systems or periodic conditions).

Starting from the homogeneous steady state $\{X_i^0\}$ corresponding to the law of mass action at equilibrium, these systems are able to display a large variety of instabilities when one increases the external constraint (λ) beyond the linear regime around thermal equilibrium. In the deterministic description the bifurcation theory may be applied to study the vicinity of these transition points. However, many authors have stressed the need to include the local fluctuations in the description of systems in which a coherent behavior takes place on the macroscopic level.[1,2] In chemical systems, the fluctuations have been mainly analyzed using the master equation approach. In this birth and death description, the fluctuations are modeled as Markov processes in the appropriate phase space.[1] In the inhomogeneous case, this theory leads to multivariate master equations whose complex structure is now the object of interesting studies.[5] We have adopted a more phenomenological approach in which the influence of the fluctuations is taken into account in a plausible but more or less ad hoc manner. Following the Landau–Lifshitz theory of fluctuating hydrodynamics we add a Langevin term $\xi_i(r,t)$ to the right-hand side of Eq. (2.1). Because these noise terms describe processes on a shorter range in space and time than the coarse-grained scale of our description, we assume[6]

$$\langle \xi_i(r,t)\xi_j(r',t')\rangle = 2\left[\Gamma_{ij}^c(r) + \nabla^2\Gamma_{ij}^d(r)\right]\delta(r-r')\,\delta(t-t') \tag{2.2}$$

If we further assume that the system remains in a state of local equilibrium throughout the entire transition region, the coefficients Γ^c and Γ^d may be determined by a local fluctuation-dissipation theorem.[7] Indeed, the nonequilibrium phase transitions involve macroscopic disturbances which do not modify the fluctuations on a microscopic scale where the short-scale equilibrating processes remain efficient in maintaining local equilibrium.

We first investigate the stability of the homogeneous steady state $\{X_i^0\}$

with respect to infinitesimal perturbations. Linearizing Eq. (2.1), we get

$$x_q^i(t) = X_q^i(t) - X_i^0 = \frac{1}{L^{d/2}} \int dr\, e^{iqr} x(r)$$

$$\partial_t x_q^i(t) = L_{ij}(q^2, \lambda) x_q^j(t) \tag{2.3}$$

where

$$L_{ij}(q^2, \lambda) = (\partial f_i / \partial x_j)_0 - q^2 D_i$$

The stationary state is asymptotically stable if all the eigenvalues of the matrix L_{ij} have negative real parts. Among the various instabilities which may develop when λ is varied, we consider in this paper the following three possibilities:

1. L_{ij} has one eigenvalue $\omega_q(\lambda) = 0$ for $q = 0$ and $\lambda = \lambda_c$, corresponding to transitions between homogeneous steady states.

2. L_{ij} has one eigenvalue $\omega_q(\lambda) = 0$ for $|q| = q_c$ ($q_c \neq 0$) and $\lambda = \lambda_c$; this soft mode instability induces the formation of stationary periodic structures (Turing instability).

3. L_{ij} has two complex conjugate eigenvalues with zero real part when $\lambda = \lambda_c$, $q_c = 0$. This hard mode instability may lead to time-periodic solutions of the limit cycle type.

3. CRITICAL PHENOMENA IN MULTIPLE-STEADY-STATE SYSTEMS

As a prototype we consider the Schlögl model[8]

$$\begin{aligned} A + 2X &\underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X \\ B + X &\underset{k_4}{\overset{k_3}{\rightleftharpoons}} C \end{aligned} \tag{3.1}$$

Using standard notations,[5] the deterministic rate equation for the Fourier transform $x_q(t)$ of the local concentration may be written in the case of an ideal mixture:

$$\begin{aligned} \partial_{\bar{\tau}} x_q(\bar{\tau}) = &-\left[(3+\delta)a^2 + q^2\bar{D}\right]x_q + L^{-d/2} 3a \sum_k x_{q-k} x_k \\ &- L^{-d} \sum_k \sum_{k'} x_k x_{k'} x_{q-k-k'} + L^{d/2}(1+\delta')a^3 \end{aligned} \tag{3.2}$$

where

$$\bar{\tau} = k_2 t; \qquad \frac{k_1}{k_2} = 3; \qquad \frac{k_3 b}{k_2} = (3+\delta)a^2; \qquad \frac{k_4 c}{k_2} = (1+\delta')a^3$$

and $\bar{D} = D_X/k_2$, where D_X is the diffusion coefficient of the intermediate species X.

The nonequilibrium critical point is characterized by $\delta = 0$, $\delta' = 0$, $x_C = a$. The fluctuations $y_q = x_q/a - 1$ around this point obey the following equation:

$$\partial_\tau y_q = -(\delta + q^2 D) y_q + L^{d/2}(\delta' - \delta) - L^{-d} \sum_k \sum_{k'} y_k y_{k'} y_{q-k-k'} + \eta_q(\tau) \tag{3.3}$$

with $a^2\bar{\tau} = \tau$ and $D = \bar{D}/a^2$.

Because the diffusion-originated contribution to the noise in Eq. (2.1) is negligible in the long-wavelength limit, we assume

$$\langle \eta_q(\tau)\eta_{q'}(\tau')\rangle = 2\Gamma \delta_{q,-q'} \delta(\tau - \tau') \tag{3.4}$$

with $\Gamma \simeq 1/a = \text{const}$. The stationary solution of the Fokker–Planck equation corresponding to (3.3) takes the form

$$P_{st}(\{y_k\}) = \mathcal{N} \exp[-\mathcal{F}(\{y_k\})] \tag{3.5}$$

where $\mathcal{N}$ is a normalization constant and

$$\mathcal{F}(\{y_k\}) = \frac{1}{\Gamma} \sum_k \left[\left(\frac{\delta}{2} + \frac{Dk^2}{2} \right) |y_k|^2 + L^{d/2}(\delta - \delta') y_0 + \frac{1}{4} L^{-d} \sum_{k'} \sum_{k''} y_k y_{k'} y_{k''} y_{-k-k'-k''} \right] \tag{3.6}$$

Recently, Nicolis and Malek-Mansour[5] have analyzed the multivariate master equation for the same model using a singular perturbation approach. They have shown that near the critical point, the system may be described by a generalized potential identical to (3.6). The kinetic potential obtained by integrating the differential form $d_x P$ occurring in the Glansdorff–Prigogine[1] criterion reduces to the functional (3.6) sufficiently close to the instability $\delta, \delta' \to 0$.

The analogy of the potential (3.5) with the Ginzburg–Landau Hamiltonian is striking; the amplitude of the critical mode plays here the role of the order parameter, in agreement with the Landau–Hopf picture. As a result, the renormalization-group methods can be applied in order to evaluate the nonclassical exponents characterizing the critical point for $d < 4$.[3] We get, for instance, at the order $\epsilon = 4 - d$,

$$\langle y_q \rangle = (-\delta)^\beta \delta_{q,0} \quad \left[\beta = \tfrac{1}{2} - \tfrac{1}{6}\epsilon + O(\epsilon^2)\right] \quad \text{if} \quad \delta < 0, \delta = \delta' \tag{3.7}$$

$$\langle y_q \rangle = (\delta')^{1/\bar{\delta}} \delta_{q,0} \quad \left[\bar{\delta} = 3 + \epsilon + O(\epsilon^2)\right] \quad \text{for} \quad \delta = 0$$

Similarly, the correlation function $g_q = \langle y_q y_{-q} \rangle$ satisfies as $\delta \to 0$ ($\delta = \delta'$)

the scaling form

$$g(q) = (1/\delta^{\gamma})D(q^2/\delta^{2\nu}) \tag{3.8}$$

with $\gamma = 1 + \frac{1}{6}\epsilon + O(\epsilon^2)$ and $\nu = \frac{1}{2}\gamma + O(\epsilon^2)$.

A similar analysis can be applied to other multiple-steady-state systems, such as, for instance, photothermal instabilities or the Edelstein model, where an adiabatic elimination of the stable modes must be performed in order to derive the generalized potential.[9] In principle, one can transpose the concept of universality class to nonequilibrium critical phenomena: each static class of universality is determined by the space dimensionality and the number n of unstable modes at the critical point. However, all the chemical models studied up to now belong to the same class $n = 1$ isomorphic to the Ising model. The domain of validity of the mean-field theory can be estimated by the Ginzburg criterion.[3] In the notations of formula (3.6) it takes the form

$$\Gamma/(l_0^3\delta^{1/2}) < 1 \qquad (d = 3) \tag{3.9}$$

where $l_0 = D^{1/2} = (D_X\tau_{\text{chem}})^{1/2}$ and τ_{chem} is a characteristic chemical relaxation time.

Since we have supposed in the estimation of the noise that the microscopic fluctuations are not modified by the macroscopic constraints, Γ is of the same order of magnitude as in equilibrium phase transitions. On the contrary, the correlation length far from the critical point l_0 is much greater for nonequilibrium phase transitions because of its macroscopic nature. As a consequence, the width of the nonclassical critical region $\delta_{\text{GL}} \simeq 1/l_0^6$ is reduced with respect to the case of equilibrium phase transitions. Only for very fast chemical reactions and slow diffusion would the nonclassical behavior be experimentally attainable. Nevertheless, due to the large variability of the chemical rate constants, chemical instabilities remain the best candidate for the observation of nonclassical indices.

On the other hand, when diffusion becomes more efficient than the chemical reactions, l_0 is very great and finite-size effects rapidly become important. Indeed, when $\delta = \delta_0 = (l_0/L)^2$ (L is a characteristic length of the reactor), the main contribution in (3.6) comes from the spatially uniform fluctuations ($y_{q=0}$). The order parameter then behaves coherently over the whole system. Using the standard auxiliary field technique, the static correlation function may be calculated exactly. From (3.6) we get when $\delta = \delta'$

$$\langle y^2 \rangle = \frac{1}{2}\left(\frac{2\Gamma}{\Omega}\right)^{1/2} \frac{D_{-3/2}\left(\delta(\Omega/2\Gamma)^{1/2}\right)}{D_{-1/2}\left(\delta(\Omega/2\Gamma)^{1/2}\right)} \tag{3.10}$$

where $D_{-n/2}(n)$ is a parabolic cylinder function. Using the asymptotic

expansions of these functions below threshold $\delta(\Omega/2\Gamma)^{1/2} > 1$, we get $\langle y^2 \rangle \simeq \Gamma/\delta\Omega$, whereas far above ($\delta < 0$), $|\delta|(\Omega/2\Gamma)^{1/2} > 1$, we obtain $\langle y^2 \rangle \simeq |\delta|$. At the instability $\langle y^2 \rangle$ remains finite and it is given by

$$\langle y^2 \rangle = 2\left(\frac{\Gamma}{\Omega}\right)^{1/2} \frac{\Gamma(3/4)}{\Gamma(1/4)} \qquad (\delta = 0) \tag{3.11}$$

The $\frac{1}{2}$-power dependence in the volume has been derived previously for this model using a master equation approach.[10] Away from the critical point this zero-dimensional transition looks like mean field theory; however, it becomes rounded when $\delta \sim \delta_r = \Gamma/\Omega$. Similar results have been obtained in zero dimension for complex order parameters in the case of the laser threshold, small superconducting particles, and the Bénard instability.[11]

For most equilibrium phase transitions, one has $\delta_0 \ll \delta_{GL}$ and the size effects may be safely neglected, whereas for many nonequilibrium instabilities $\delta_{GL} \ll \delta_0$, which prevents the observation of the effects due to inhomogeneous fluctuations.

4. PHASE TRANSITIONS TO NONUNIFORM STEADY STATES

We now consider the "Brusselator" reaction scheme[1]:

$$A \xrightarrow{k_1} X$$

$$B + X \xrightarrow{k_2} Y + D$$

$$2X + Y \xrightarrow{k_3} 3X$$

$$X \xrightarrow{k_4} E$$

The system is driven by keeping A in excess, whereas D and E are instantly removed. The concentration of the injected B then plays the role of λ, the control parameter. If we use the standard scaled variables, the rate equations for the local concentrations are

$$\partial_t X_q(t) = A - (B + 1 - q^2 D_X) X_q(t) + L^{-d} \sum_k \sum_{k'} X_k X_{k'} Y_{q-k-k'} \tag{4.1}$$

$$\partial_t Y_q(t) = B X_q(t) - q^2 D_Y Y_q(t) - L^{-d} \sum_k \sum_{k'} X_k X_{k'} Y_{q-k-k'}$$

The inhomogeneous fluctuations around the uniform steady state $X_0 = A$, $Y_0 = B/A$ then satisfy

$$\begin{pmatrix} \partial_t x_q \\ \partial_t y_q \end{pmatrix} = K_q \begin{pmatrix} x_q \\ y_q \end{pmatrix} + N_q \begin{pmatrix} +1 \\ -1 \end{pmatrix} \tag{4.2}$$

where

$$K_q = \begin{pmatrix} B - 1 - q^2 D_X & A^2 \\ -B & -A^2 - q^2 D_Y \end{pmatrix} \tag{4.3}$$

and

$$N_q = L^{-d/2} \sum_k x_k \left(\frac{B}{A} x_{q-k} + 2A y_{q-k} \right) + L^{-d} \sum_k \sum_{k'} x_k x_{k'} y_{q-k-k'} \tag{4.4}$$

When

$$\left(\frac{D_X}{D_Y} \right)^{1/2} \equiv \eta < \frac{1}{A} \left[(1 + A^2)^{1/2} - 1 \right]$$

simple linear stability analysis predicts that a soft transition appears as the first instability.

Indeed, for

$$B = B_c = (1 + A\eta)^2, \qquad |\mathbf{q}| = q_c = \left(A^2 / D_X D_Y \right)^{1/4} \tag{4.5}$$

the slow mode

$$S_q = \left(\frac{1 + A\eta}{A\eta} x_q + y_q \right) \frac{\eta^2}{\eta^2 - 1} \tag{4.6}$$

with frequency

$$\omega_q^S = \frac{B_c D_Y q_c^2}{A_c} \left[\frac{B - B_c}{B_c} + \frac{2D_X}{B_c} (|\mathbf{q}| - q_c)^2 \right] \tag{4.7}$$

becomes unstable.

In this Gaussian description, the transition behavior is characteristically second order.

On the other hand, the rapidly decaying modes

$$R_q = \left[\frac{\eta}{A} (1 + A\eta) x_q + y_q \right] \frac{1}{1 - \eta^2} \tag{4.8}$$

with frequency

$$\omega_q^R = (A/\eta)(1 + A\eta)(\eta^2 - 1) \tag{4.9}$$

which couple to the slow mode through the nonlinear terms are taken care of by a procedure of adiabatic elimination,[2] valid in the vicinity of the instability ($\omega_S \ll \omega_R$); to lowest order

$$R_q \propto - \frac{L^{-d/2}}{\omega_q^R} \sum_k S_k S_{q-k} \tag{4.10}$$

yielding the following time-dependent Ginzburg–Landau[3] equation for the critical mode written in dimensionless variables:

$$\partial_\tau \sigma_q = -\frac{\delta \mathcal{F}}{\delta \sigma_{-q}} + \xi_q(\tau) \tag{4.11}$$

The characterization of the noise has been given in (2.2), and the Brazovskii[12] "free energy" $\mathcal{F}$ is

$$\begin{aligned}\mathcal{F} = {} & \frac{1}{2}\sum_k \left[r_0 + D(|\mathbf{k}| - q_c)^2\right]|\sigma_k|^2 \\ & + L^{-d/2}\frac{v}{3!}\sum_k \sum_{k'} \sigma_k \sigma_{k'} \sigma_{-k-k'} \\ & + L^{-d}\frac{u}{4!}\sum_k \sum_{k'} \sum_{k''} \sigma_k \sigma_{k'} \sigma_{k''} \sigma_{-k-k'-k''}\end{aligned} \tag{4.12}$$

with

$$\sigma_q = \left(\frac{q_c^2 B_c D_Y}{\Gamma|\omega^R|}\right)^{1/2} S_q = \gamma S_q$$

$$D = 4D_X/B_c, \qquad r_0 = (B_c - B)/B_c, \qquad \tau = \gamma^2 \Gamma t$$

The detailed structure of the coupling functions $v = v(A, \eta, \Gamma)$ and $u = u(A, \eta, \Gamma)$ will not be needed here.[13]

The essential feature of the potential, which has occurred in a variety of situations, lies in its degeneracy. There exists an infinite number of equivalent order parameters each associated with the choice of a set of wave vectors of length q_c. Each set is characterized by the number of vectors and their relative orientation. We will show that the nonlinear terms provide a pattern selection mechanism already in the mean-field picture. We will then test the influence of the fluctuations on such structures.

The problem of the nucleation of these structures remains an open problem and will not be considered here.

4.1. Landau Theory

In the mean field approximation the most probable configurations (which minimize $\mathcal{F}$) are such that $D(|\mathbf{q}| - q_c)^2 = 0$. They are therefore characterized by an order parameter of the form

$$\begin{aligned}\bar{\sigma}_q &= \sum_{i=1}^{m} \bar{\sigma}_{q,q_i} \delta_{|q_i|,q_c} \\ &= \sum_{i=1}^{m} a_i(\delta_{q,q_i} + \delta_{q,-q_i})\delta_{|q_i|,q_c}\end{aligned} \tag{4.13}$$

or

$$\bar{\sigma}(r) = 2\sum_{i=1}^{m} a_i \cos\left[q_c(\mathbf{1}_{q_i} \cdot \mathbf{r}) \right]$$

where we have chosen m pairs of vectors q_i and $-q_i$ to form our pattern.

Then the functional (4.12) becomes in this approximation

$$\begin{aligned} V = {} & \frac{r_0}{2} L^{-d/2} \sum_k \sum_{k'} \bar{\sigma}_k \bar{\sigma}_{k'} \delta_{k+k',0} \\ & + \frac{v}{3!} L^{-d} \sum_k \sum_{k'} \sum_{k''} \bar{\sigma}_k \bar{\sigma}_{k'} \bar{\sigma}_{k''} \delta_{k+k'+k'',0} \\ & + \frac{u}{4!} L^{-3d/2} \sum_k \sum_{k'} \sum_{k''} \sum_{k'''} \bar{\sigma}_k \bar{\sigma}_{k'} \bar{\sigma}_{k''} \bar{\sigma}_{k'''} \delta_{k+k'+k''+k''',0} \end{aligned} \tag{4.14}$$

We first consider situations where the m pairs are "independent." By this we mean that

$$\delta_{k^\alpha + k^\beta + k^\gamma, 0} = 0$$

and

$$\delta_{k^\alpha + k^\beta + k^\gamma + k^\delta, 0} = \delta_{k^\alpha + k^\beta, 0} \delta_{k^\gamma + k^\delta, 0}$$

or permutations thereof. Then, putting (4.13) into (4.14) and collecting all terms, we get

$$V_m = r_0 \sum_{i=1}^{m} a_i^2 + \frac{u}{4} \sum_{i=1}^{m} a_i^4 + u \sum_{i=1}^{m} \sum_{j<i} a_i^2 a_j^2 \tag{4.15}$$

Then straightforwardly we obtain the equation of state

$$\frac{1}{2} \frac{\partial V_m}{\partial a_i} = h_i = r_0 a_i + \frac{u}{2} \sum_{i=1}^{m} a_i^3 + u \sum_{i=1}^{m} \sum_{j<i} a_i a_j^2 \tag{4.16}$$

(where the h_i are fictitious symmetry-breaking fields) and the elements of the inverse susceptibility matrix

$$\begin{aligned} \frac{1}{2} \frac{\partial V_m}{\partial a_i \partial a_i} &= r_{ii} = r_0 + u \sum_{j=1}^{m} a_j^2 \\ \frac{1}{2} \frac{\partial V_m}{\partial a_i \partial a_j} &= r_{ij} = u a_i a_j \end{aligned} \tag{4.17}$$

For all $h_i = 0$, the amplitudes are all equal to

$$a_i = a = \begin{cases} 0, & B < B_c \\ \left[-2r_0/(2m-1)u \right]^{1/2}, & B > B_c \end{cases} \tag{4.18}$$

which is again characteristic of a second-order transition, as indeed the

susceptibility diverges at $B = B_c$:

$$r_{ii} = -r_0/(2m-1) \tag{4.19}$$

The relative stability of the various phases may be calculated by comparison of the corresponding generalized thermodynamic potentials (4.14) (in this scale, the uniform phase with $a = 0$ has $V_0 = 0$):

$$V_m = -\left[m/(2m-1)\right] r_0^2/u < V_0$$

and

$$V_m > V_{m-1}$$

Therefore the stablest phase (with "independent vectors") corresponds to $m = 1$. In this case the concentration varies periodically in the direction conjugate to q_1 and

$$\bar{\sigma}_1(r) = \left[8(B - B_c)/B_c u\right]^{1/2} \cos(q_c x) \tag{4.20}$$

This situation presents great analogies with the roll pattern of the convective instability.

When $m = 4$, a new possibility arises, as the four pairs may, for instance, be along the diagonals of a cube, in which case we have noncoplanar wave vectors satisfying the quadrangular relation $\delta_{q_1+q_2+q_3+q_4,0}$ giving extra contributions to the potential:

$$V_{\text{fcc}} = V_4 + 2u a_1 a_2 a_3 a_4 \tag{4.21}$$

There is then a transition of second-order type to a structure where the concentration maxima have fcc periodicity. However, $V_{\text{fcc}} > V_1$.

On the other hand, when we have sets of vectors arranged to form equilateral triangles, we get contributions from the cubic terms. The simplest case occurs for $m = 3$, the triangle itself. Then

$$V_{\text{tr}} = V_3 + v a_1 a_2 a_3 \tag{4.22}$$

and the corresponding equation of state in zero fields is

$$a\left(r_0 + va + \tfrac{5}{2} u a^2\right) = 0 \tag{4.23}$$

leading to a first-order subcritical transition giving rise to rod-like structures with 2d hexagonal periodicity

$$\bar{\sigma}_{\text{tr}}(r) = 2a\left\{\cos(q_c x) + \cos\left[\tfrac{1}{2} q_c\left(x + \sqrt{3}\, y\right)\right] + \cos\left[\tfrac{1}{2} q_c\left(x - \sqrt{3}\, y\right)\right]\right\} \tag{4.24}$$

We expect on the basis of symmetry arguments due to Landau that there will be no critical point. The new phase appears for $r_0 = r_{\text{tr}} = v^2/10u$;

however, the stability exchange with the uniform phase takes place at $r_0 = r'_{tr} = 4v^2/45u$. The pattern is immediately reminiscent of the Bénard hexagonal cell structure. This analogy may be carried even further. Depending on the sign of v, the maxima of concentration define, respectively, a triangular ($v < 0$) or a honeycomb ($v > 0$) lattice corresponding in the convection problem respectively to l- and g-hexagons as defined by Busse.[14],[3]

For $m = 6$, the triangles can be chosen to form an octahedron. The equation state is then

$$a\left(r_0 + 2va + \tfrac{11}{2}ua^2\right) = 0 \tag{4.25}$$

We thus obtain, again subcritically, structures with 3d cubical symmetry,

$$\begin{aligned}\bar{\sigma}_{oct}(r) = 2a\Big[&\cos\left(\tfrac{1}{2}q_c\sqrt{2}\,x\right)\cos\left(\tfrac{1}{2}q_c\sqrt{2}\,y\right)\\ &+ \cos\left(\tfrac{1}{2}q_c\sqrt{2}\,x\right)\cos\left(\tfrac{1}{2}q_c\sqrt{2}\,z\right)\\ &+ \cos\left(\tfrac{1}{2}q_c\sqrt{2}\,y\right)\cos\left(\tfrac{1}{2}q_c\sqrt{2}\,z\right)\Big]\end{aligned} \tag{4.26}$$

The corresponding parameters are

$$r_{oct} = (2/11)v^2/u, \qquad r'_{oct} = (16/99)v^2/u$$

When $v < 0$ the pattern of the concentration maxima forms a bcc lattice, whereas $v > 0$ leads to filamental structures with cubic symmetry. These structures are the first to appear, a situation which presents analogies with the theory of the freezing transition.[15],[4]

Using mean field theory, we have predicted the occurrence of a great variety of patterns. The stability analysis shows that a selection among these emerges. It shows that when $v \neq 0$ various structures may appear through successive first-order transitions, from patterns having cubic symmetry to the formation of rolls (see Fig. 1). Many analogous analyses for various systems have been carried out, among which we mention, because of their close relation to this work, the Bénard problem[14,16] and morphogenesis.[2]

[3] In l-hexagons ($v < 0$), often realized in liquids, the fluid rises near the center of the cells. Conversely, in g-hexagons ($v > 0$) it rises along the boundaries of the cells, as happens typically in gases. The dominant cause for the existence of $v \neq 0$ in the convective instability is the temperature dependence of the viscosity.

[4] There, it has been observed experimentally that almost all metals on the left-hand side of the periodic table are known to be bcc near the melting line at low pressure.

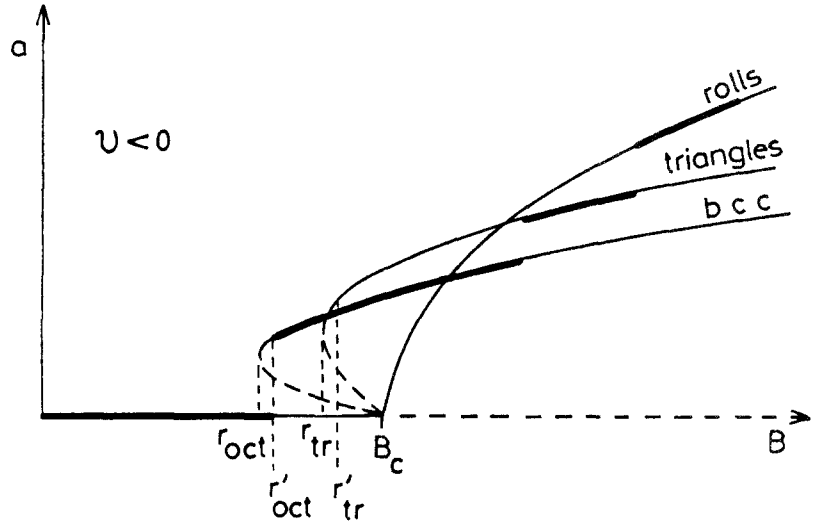

Fig. 1. Bifurcation diagram (schematic) in the mean field approximation. Heavy lines denote the stablest structures. $\tilde{r} = B_c(1 + r)$.

4.2. Effects of Fluctuations

As shown by Brazovskii,[12] the fluctuations deeply alter the mean field picture. We first analyze the situation in the light of general symmetry arguments. In the ordered phase the Ward–Takahashi identities that result from the breakdown of translational symmetry lead to the following relations between the elements of the inverse correlation matrix $r_{ij} = (g)_{ij}^{-1}$:

$$\sum_{j=1}^{m} (r_{ij} - r_{i-j})\alpha_{ij} = \frac{h}{a_i}, \qquad \forall i \in \{1, \ldots, m\} \tag{4.27}$$

where h is a fictitious symmetry-breaking field, the α_{ij} are factors which depend on the structure considered, and

$$g_{ij} = \langle \sigma_{q_i} \sigma_{q_j}^* \rangle - \langle \sigma_{q_i} \rangle \langle \sigma_{q_j} \rangle$$

In particular, for structures characterized by m independent pairs of wave vectors, the relations (4.27) reduce to

$$r_{ii} - r_{i-i} = h/a_i \tag{4.28}$$

$$r_{ik} - r_{i-k} = 0, \qquad \forall i, k \in \{1, \ldots, m\}$$

from which it is easily found that the corresponding correlation functions g_{ii} and g_{i-i} diverge as h^{-1} for small fields. This is a consequence of the high degree of degeneracy of the order parameter. As a result, long-range fluctuations may develop in all the ordered phases. The response of the

system to a long-wavelength deformation of the structure

$$\sigma'(\mathbf{r}) = \sigma(\mathbf{r} - \xi \cos k \cdot r) \tag{4.29}$$

may be computed ($|\xi|$ infinitesimal and $|\mathbf{k}|/q_c \ll 1$).

In zero field, the increment to the functional (4.12) is

$$\delta \mathcal{F}_k = \frac{i}{2} \sum_q (|\mathbf{q}| - q_c)^2 \frac{1}{2} (\mathbf{q} \cdot \xi) \left[\sigma_q (\sigma_{-q+k} + \sigma_{-q-k}) - (\sigma_{q+k} + \sigma_{q-k}) \sigma_{-q} \right] \tag{4.30}$$

The following Schwarz inequality has to be satisfied:

$$\langle \sigma_{q_i+k} \sigma_{-q_i-k} \rangle \langle \delta \mathcal{F}_k \, \delta \mathcal{F}_k^* \rangle \geqslant |\langle \sigma_{-q_i-k} \delta \mathcal{F}_k^* \rangle|^2 \tag{4.31}$$

and may be evaluated, since for any operator K, we have

$$\langle K \delta \mathcal{F}_k^* \rangle = \langle K \rangle_{\mathcal{F}} - \langle K \rangle_{\mathcal{F} + \delta \mathcal{F}_k} \tag{4.32}$$

Furthermore, using the consequences of the Ward–Takahashi identities that result from the breakdown of rotational symmetry, we get the following Bogoliubov inequalities[4]:

$$g_{q_i+k, q_i+k} \geqslant (\mathbf{q_i} \cdot \xi)^2 a_i^2 \left[2 \sum_{j=1}^{m} \left(K_{j,+}^2 + K_{j,-}^2 \right) (\mathbf{q_j} \cdot \xi)^2 a_j^2 \right]^{-1} \tag{4.33}$$

where

$$K_{j,\pm}^2 = (|\mathbf{q_j} \pm \mathbf{k}| - q_c)^2$$

These formulas imply the destruction of any long-range order by fluctuations for $d \leqslant 2$ infinite systems. For structures characterized by m independent pairs of wave vectors, the rotational symmetry argument leads to the more stringent inequalities

$$g_{q_i+k, q_i+k} \geqslant 1 / \left\{ 4 \left[4 (\mathbf{q_i} \cdot \mathbf{k})^2 + k^4 \right] \right\} \tag{4.34}$$

As a consequence, all of these structures are also destroyed by the fluctuations in infinite $d = 3$ systems (for $m = 1$, this result is analogous to the impossibility of one-dimensional crystals existing in three-dimensional systems as argued by Landau and Peierls), and only the structures characterized by wave vectors that satisfy definite angular relations (i.e., bcc, hexagonal prisms, fcc, etc.) remain. In contrast, the first-order transitions induced by the cubic terms ($v \neq 0$) are only slightly affected by fluctuations (as long as $v^2/u \ll |r|$), whereas the second-order transition to a fcc structure is transformed into a first-order transition as shown below.

The mean field picture is thus qualitatively modified. However, finite dimensions may stabilize some structures by inhibiting the long-range fluctuations. This happens, for instance, in three dimensions when

$r^{1/2}q_c^{-1}\ln q_c L \ll 1$ (L is the linear dimension of the system). In this regime, Brazovskii's approximation leads to the following equation for the inverse susceptibility associated with a pattern of m independent modes ($r_{ii} = r$; $\alpha \sim q_c^{d-1}$):

$$(2m-1)r + \alpha u D^{-1/2} r^{-1/2} + r_0 = 0 \tag{4.35}$$

The equation of state in the absence of an external field may then be written as ($\{\alpha_i\} = \sigma$)

$$r\sigma - \tfrac{1}{2}u\sigma^3 = 0 \tag{4.36}$$

Therefore the corresponding nonuniform state may arise with a finite amplitude $\sigma_m = (2r_m/u)^{1/2}$ when

$$-r_0 \geqslant r_m = 3(2m-1)^{1/3}(\alpha u/2D^{1/2})^{2/3} \tag{4.37}$$

This structure becomes more stable than the uniform state for $r_m < r'_m < \sqrt{2}\, r_m$, where r'_m defines the first-order transition temperature. The stability of the structure increases with decreasing m and the patterns with small m are the first to appear, contrary to the conclusions reached by Brazovskii.[12] However, for finite dimensions the system eventually develops fluctuations, the correlation length of which becomes larger than the size of the system itself. Indeed, when

$$r_0 \simeq D/L^2 \simeq 1/L^2 q_c^2 = r_L \tag{4.38}$$

the problem becomes zero-dimensional with all the consequences discussed in Section 3.

On the other hand, the fluctuations invalidate the Landau mean-field theory when

$$r_0 \simeq r_m \simeq (q_c^3 u)^{2/3} \tag{4.39}$$

For equilibrium phase transitions, it is well known that $r_L \ll r_m$. On the other hand, for most instabilities far from equilibrium $r_L > r_m$ and the transition takes place in the zero-dimensional regime. Because of their flexibility, chemical instabilities might, however, be an exception. We thus see that there appear two classes of dissipative structures. In the first, because they must be stabilized by the finite dimensions of the systems, the general theorems resulting from the breakdown of the translation and rotation symmetry are not applicable. On the contrary, in the second class the instability is analogous with equilibrium first-order transitions, such as crystallization.

5. HARD MODE TRANSITION TO CHEMICAL OSCILLATIONS

A hard mode transition to chemical oscillations occurs in the Brusselator at $B = B_c' = 1 + A^2$ and $q = 0$ when $\eta > (1/A)[(1 + A^2)^{1/2} - 1]$, since in this case $B_c' < B_c$. Around this instability point the linear stability analysis gives as characteristic eigenfrequencies

$$\omega_q = \tfrac{1}{2}\Big(B - B_c' - q^2(D_X + D_Y) \pm 2iA\Big\{1 + \tfrac{1}{2}\big[q^2(D_X - D_Y)\big] - (1/4A^2)\big[B - B_c' - q^2(D_X - D_Y)^2\big]\Big\}\Big) \tag{5.1}$$

The corresponding eigenvectors (at the lowest order in $B - B_c'$ and q^2) are

$$R_q = \frac{i - A}{2i}\left(\frac{A + i}{A}x_q + y_q\right); \qquad S_q = R_q^* \tag{5.2}$$

The associate nonlinear Langevin equations may easily be written in the rotating wave approximation (valid in the vicinity of the instability where $A \gg B - B_c'$) as

$$\partial_\tau W_k = -\big[r + ck^2\big]W_k - u\int^\Lambda dk' \int^\Lambda dk''\, W_{k-k'-k''}W_{k'}^* W_{k''} + \eta_k \tag{5.3}$$

with

$$W_k = R_k e^{iA\tau}, \qquad \langle \eta_k \eta_{k'}^* \rangle = 2\Gamma\delta(\tau - \tau')\delta(k - k')$$

$$r = r_1 + ir_2, \qquad c = 1 + ic_2, \qquad u = u_1 + iu_2$$

$$r_1 = \frac{B_c' - B}{B_c'}, \qquad r_2 = \frac{1}{2A}\frac{(B - B_c')^2}{B_c'}, \qquad c_2 = \frac{2A(D_X - D_Y)}{D_X + D_Y}$$

$$u_1 = \frac{(A^2 + 2)B_c'^{d-1}}{2A^2(D_X + D_Y)^d}, \qquad u_2 = \frac{(4 - 7A^2 + 4A^4)B_c'^{d-1}}{3A^3(D_X + D_Y)^d} \tag{5.4}$$

$$\tau = 2B_c't, \qquad k^2 = \frac{(D_X + D_Y)}{B_c'}$$

Here also the noise term has been taken constant. These equations admit no potential and the critical behavior is obtained through the direct application of the dynamical renormalization group on these kinetic equations. Let us not that when r, c, u are real the system is an $n = 2$, time-dependent Ginzburg–Landau model. The general case (r, c, u complex) has been extensively studied by Hentschel[17] and we review his results as applied to the specific case of the Brusselator. The mean field behavior of the system deduced from (5.3) is given by

$$\langle W_k(\tau) \rangle = W(\tau)\delta_{k,0} = |W(\tau)|e^{-i\omega\tau}\delta_{k,0} \tag{5.5}$$

with

$$|W(\tau)|^2 = \begin{cases} \dfrac{-r_1}{u_1 - (u_1 + r_1|W(0)|^{-2})\exp(2r_1\tau)}, & r_1 \neq 0 \\ \dfrac{|W(0)|^2}{1 + 2u_1|W(0)|^2\tau}, & r_1 = 0 \end{cases}$$

$$\omega = r_2 + u_2|W(\tau)|^2$$

$$\langle W_k^*(\tau)W_k(0)\rangle = \frac{2\Gamma}{r_1 + k^2}\exp\left\{-\left[r_1 + k^2 + i(r_2 + c_2k^2)\right]\tau\right\}$$

The system consequently exhibits at $r_1 = 0$ a second-order-like transition to chemical oscillations, since in the limit $\tau \to \infty$, Eq. (5.5) gives

$$|W(\tau)| \to \begin{cases} 0, & r_1 > 0 \\ (|r_1|/u_1)^{1/2}, & r_1 < 0 \end{cases}$$

$$\omega \to \begin{cases} r_2, & r_1 > 0 \\ r_2 + u_2|r_1|/u_1, & r_1 < 0 \end{cases}$$

The effect of the fluctuations on this instability may be computed with the use of the dynamical renormalization group. Let us recall that it is defined by the following change of scale:

$$k \to k' = sk$$
$$\Lambda \to \Lambda' = s\Lambda$$
$$W \to W' = s^a W$$

the frequency scaling $\omega \to \omega' = s^z\omega$, and the operation consisting in the elimination of the wave vectors in the domain $\Lambda/s < k < \Lambda$. This procedure may be performed on the diagrammatic expansion in u of any quantity and leads for $B \to B_c'$ to the following Wilson–Fisher recursion relations for Γ, u, r at the lowest order in $\epsilon = 4 - d$ [the scaling exponent of the order parameter a has been chosen as usual by requiring that $c_1 = 1$ remain unchanged, $a = (d-2)/2 + o(\epsilon^2)$]:

$$\Gamma_{l+1}^{-1} = s^{2-z}\Gamma_l^{-1}\left[1 + o(\epsilon^2)\right]$$

$$r_{l+1} = s^2\left[r_l + 8K_4u_l\left(1 - s^{-2} - 2r_l\ln s\right)\right], \qquad r_l \ll 1$$

$$u_{l+1} = s^\epsilon\left[u_l - 8K_4\left(\frac{u_l^2}{1 + ic_2} + 4u_lu_{1l}\right)\ln s\right]$$

The existence of a nonvanishing fixed point value for Γ requires $z = 2 + o(\epsilon^2)$. One consequently finds two fixed points: the Gaussian one, $r^* = u^*$

$= 0$ stable for $d > 4$; and the nontrivial one:

$$r_1^* = -\epsilon/5, \qquad u_1^* = \epsilon/5K_4$$
$$r_2^* = -c_2\epsilon/5, \qquad u_2^* = c_2\epsilon/5K_4$$

Here also the fact that r^* and u^* are of order ϵ justifies the expansion procedure used to derive the recursion relations. The critical behavior of the system in then given through the linearized recursion relations around the fixed point, leading to the following scaling fields:

For $d > 4$ we have

$$r_1 \to s^2 r_1, \qquad r_2 \to s^2 r_2$$
$$u_1 \to s^\epsilon u_1, \qquad u_2 \to s^\epsilon u_2$$

In this case the critical indices are classical, since

$$W_k(\tau; r_1, r_2, u_1, u_2) \to sW_{sk}(\tau s^{-2}; s^2 r_1, s^2 r_2, s^\epsilon u_1, s^\epsilon u_2), \qquad \epsilon < 0$$

Namely the correlation function $\langle W_k^*(\tau) W_k(0) \rangle$ behaves as

$$2\Gamma(k) \exp\left[-\Gamma\tau/\tau(k)\right]$$

where

$$\tau^{-1}(k) = k^2 + \xi_1^{-2} + i\left(c_2 k^2 + \xi_2^{-2}\right) = k^{-2} g(k\xi_1, k\xi_2)$$
$$\Gamma(k) = \Gamma/\left(k^2 + \xi_1^{-2}\right) = k^{-2} f(k\xi_1)$$

the two correlation lengths are defined as

$$\xi_1 = r_1^{-1/2}, \qquad \xi_2 = r_2^{-1/2}$$

and the corresponding critical indices are

$$\Gamma(0) \sim \mathrm{Re}\,\tau^{-1}(0) \sim r_1^{\gamma_1}, \qquad \mathrm{Im}\,\tau^{-1}(0) \sim r_2^{\gamma_2}$$
$$\xi_1 \sim r_1^{-\nu_1}, \qquad \xi_2 \sim r_2^{-\nu_2}$$

with $\gamma_1 = \gamma_2 = 1$ and $\nu_1 = \nu_2 = \frac{1}{2}$.

For $d < 4$ the scaling fields are

$$g_1 = r_1 + K_4 u_1, \qquad g_2 = (r_2 - c_2 r_1) + K_4(u_2 - c_2 u_1)$$
$$g_3 = u_2 - c_2 u_1, \qquad g_4 = u_1 - u^*$$

and

$$W_k(\tau; g_1, g_2, g_3, g_4)$$
$$= sW_{sk}(\tau s^{-2}; s^{2-2\epsilon/5} g_1; s^2 g_2, s^{-\epsilon/5} g_3, s^{-\epsilon} g_4), \qquad \epsilon > 0$$

We have in this case

$$\Gamma(k) = \Gamma/\left(k^2 + \xi_1^{-2}\right) = k^{-2} f(k\xi_1)$$
$$\tau^{-1}(k) = k^2 + \xi_1^{-2} + i\left[c_2\left(k^2 + \xi_1^{-2}\right) + \xi_2^{-2}\right] = k^{-2} g'(k\xi_1, k\xi_2)$$

and

$$\xi_1 = g_1^{-\nu_1}, \qquad \xi_2 = g_2^{-\nu_2}$$

with

$$\nu_1 = \frac{1}{2 - 2\epsilon/5}, \qquad \nu_1 = \frac{1}{2}$$

while $\gamma_1 = 2\nu_1$ and $\gamma_2 = 2\gamma_2$.

The conclusion of this analysis is that in the disordered phase the fluctuations modify the critical behavior for $d < 4$ in the following way:

1. The critical point is shifted, since it is now defined by $g_1 = r_1 + K_4 u_1 = 0$ or $\bar{B}_c = B_c'(1 + K_4 u_1)$, where $\bar{B}_c$ is the true critical value of B.

2. The scaling behavior of the correlation functions is given with nonclassical exponents associated to two correlation lengths.

Due to the similarities between this model and the Ginzburg–Landau model, the study of the ordered phase would be of particular interest, since one expects the existence of Goldstone modes in this regime. The effects of these modes may deeply affect the dynamics of the system and we hope to come back to this problem in the future.

6. CONCLUSIONS

We have illustrated the application of the methods of equilibrium phase transitions to nonlinear chemical models in the vicinity of instability points. We have shown that the system can in principle display departures from the mean field predictions even qualitatively. In most hydrodynamic instabilities and in the case of the laser threshold these deviations from the classical theory are hidden by finite-size effects, which determine the behavior near transitions. Due to the large variability of chemical rate constants, chemical systems remain good candidates for the observation of nonclassical behavior despite the great experimental difficulties. On the other hand, in certain driven condensed matter systems, the various recombination processes may be described in terms of a phenomenological reaction–diffusion equation similar to (2.1) and the conclusions of this paper might be of some relevance in such a context.

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