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Fluctuations near nonequilibrium phase transitions to nonuniform states

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The influence of local fluctuations on a symmetry-breaking chemical instability is considered in terms of concepts developed in the theory of equilibrium phase transitions. It is shown that for infinite systems some predictions of the mean-field theory are qualitatively incorrect. Indeed, the fluctuations destroy any structure in one- and two-dimensional systems and some of them in three dimensions. The stabilizing effect of the finite dimensions on these structures is also discussed, and it is shown that in this case the fluctuations induce a weak first-order transition near the critical point of the mean-field theory.

I. INTRODUCTION

The similarity between equilibrium phase transitions and certain far-from-equilibrium instabilities has stimulated a great number of works mainly at the level of mean-field theory.[1,2] Recently there has been some progress in the extension of the analysis beyond the classical theory.[3,5] In this context we study the effects of local fluctuations on a symmetry-breaking transition in an open system. Namely, we consider the trimolecular model ("brusselator") in the vicinity of the instability leading to the onset of stable periodic structures ("dissipative structures").[1]

At equilibrium, the breaking of a continuous symmetry generates long-ranged fluctuations which deeply influence the static and the dynamic properties of these systems.[6] For instance, these fluctuations destroy in one and two dimensions the long-range order at any finite temperature. Therefore, it seems very attractive to consider the possibility of the occurrence of similar effects in nonequlibrium phase transitions. On the other hand, in the discussion of certain equilibrium transitions to nonuniform states Brazovskii has introduced a model whose important feature is the large degeneracy of the ordered states.[7] We show that the brusselator is equivalent near the instability to a time-dependent Ginzburg-Landau model analogous to Brazovskii's original model. Indeed it includes also an infinite number of order parameters each corresponding to a finite wave vector of length q_c. Moreover our generalized potential contains a cubic term in the order parameters leading to first-order transitions to periodic structures except at the point where this cubic term vanishes. At this point the mean-field theory predicts a second-order transition (isolated critical point). It is the main goal of this paper to assess the influence of spatial correlations on these structures in various dimensions essentially in the vicinity of this critical point.

The paper is organized as follows: in Sec. II, the model is presented and the linear analysis is developed. Section III is devoted to the study of the mean-field description. In Sec. IV, the effects of the inhomogeneous fluctuations is discussed in the weak-coupling limit. Section V contains a short conclusion.

II. MODEL

As a prototype of reaction scheme giving rise to dissipative structures, we consider the following trimolecular model[1] ("brusselator"):

$$A \xrightarrow{k_1} X, \quad B+X \xrightarrow{k_2} Y+D, \quad 2X+Y \xrightarrow{k_3} 3X, \quad X \xrightarrow{k_4} E.$$

For the sake of simplicity, we introduce the usual scaled variables.[1] We then consider an infinite system with natural boundary conditions. When the spatial nonuniformities are taken into account, the local scaled variables X and Y satisfy the following reaction-diffusion system:

$$\begin{aligned} \frac{\partial X}{\partial t} &= A-(B+1)X+X^2Y+D_x\nabla^2 X\,, \\ \frac{\partial Y}{\partial t} &= BX-X^2Y+D_y\nabla^2 Y\,, \end{aligned} \tag{2.1}$$

where D_x and D_y are the diffusion coefficients. As is well known, these equations admit only one homogeneous steady-state solution $X_S=A$, $Y_S=B/A$. The linear-stability analysis around this solution leads to the following dispersion relation for the characteristic frequencies $\omega_{\vec q}$:

$$\omega_{\vec q}^2+[A^2+1-B+(D_x+D_y)q^2]\omega_{\vec q} -[(B-1-q^2D_x)(A^2+q^2D_y)-A^2B]=0\,. \tag{2.2}$$

On increasing the value of B with A kept fixed, two kinds of instability may occur.

(a) $B_c=(1+A\eta)^2$, where $\eta=(D_x/D_y)^{1/2}$. At $B=B_c$, the homogeneous steady state ceases to be stable against the spatially inhomogeneous perturbations characterized by the wave number q_c such that $q_c^2 =A(D_xD_y)^{-1/2}$. Both the real and imaginary parts

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of ω vanish at the point (B_c, q_c). The new phase is a spatially nonuniform and frozen pattern.

(b) $B_c' = 1 + A^2$. At $B = B_c'$, the homogeneous steady state ceases to be stable against the spatially uniform but oscillatory perturbation. Only the real part of ω for $\vec{q} = 0$ vanishes at this point. The new phase is represented by a limit cycle in the X-Y plane. In this paper, we will consider values of the parameters such that

$$\eta < (1/A)[(1+A^2)^{1/2} - 1],$$

which leads to $B_c < B_c'$ and one has the first type of instability. The characteristic frequencies are then

$$\omega_{\vec{q}}^F = A_c = -(A/\eta)(1 + A\eta)(1 - \eta^2), \tag{2.3}$$

$$\omega_{\vec{q}}^S = (1/A_c)[(B_c - B)q_c^2 D_y + (q^2 - q_c^2)^2 D_x D_y]. \tag{2.4}$$

The slow mode $S_{\vec{q}}$, which corresponds to the right eigenvector associated to the eigenfrequency $\omega_{\vec{q}}^S$ which goes to zero for $B \to B_c$, $|\vec{q}| \to q_c$ is given by the following linear combination:

$$S_{\vec{q}} = \left(\frac{1 + A\eta}{A\eta} x_{\vec{q}} + y_{\vec{q}}\right) \frac{\eta^2}{\eta^2 - 1}, \tag{2.5}$$

where $x_{\vec{q}}$ and $y_{\vec{q}}$ are the Fourier transforms of the inhomogeneous fluctuations of X and Y around the steady state.

Gaussian approximation: Neglecting the nonlinear contributions, the correlation function of the S mode is readily obtained:

$$C_{SS}(\vec{q}, \omega) = \langle S_{\vec{q}}(\omega) S_{-\vec{q}}(-\omega)\rangle = \frac{|A_c|^2}{\omega^2 + [(B_c - B)q_c^2 D_y + (q^2 - q_c^2)^2 D_x D_y]}. \tag{2.6}$$

This result exhibits "critical slowing down" and the diverging "static susceptibility" characteristic of second-order phase transitions. The critical exponents are then those of the conventional theory. Indeed the correlation function is that which would be obtained from a time-dependent Ginzburg-Landau equation

$$\frac{\partial S_{\vec{q}}}{\partial t} = -\Gamma \frac{\delta F}{\delta S_{-\vec{q}}} + \eta_{\vec{q}}(t) \tag{2.7}$$

with a Gaussian "free energy"

$$F = \frac{1}{2|A_c|\Gamma} \int \frac{d^d q}{(2\pi)^d} [(B - B_c)q_c^2 D_y + (\vec{q}^2 - q_c^2)^2 D_x D_y]|S_{\vec{q}}|^2 \tag{2.8}$$

and assuming a Gaussian white noise

$$\langle \eta_{\vec{q}}(t)\rangle = 0, \quad \langle \eta_{\vec{q}}(t)\eta_{\vec{q}'}(t')\rangle = \Gamma\delta(\vec{q} + \vec{q}')\delta(t - t'). \tag{2.9}$$

At this level the description is equivalent to that carried out by Zaitsev and Shliomis[8] for the convective instability and that of Lemarchand and Nicolis[9] for the one-dimensional case of the present model.

Nonlinear terms: For B close to B_c, the linear theory predicts long-range fluctuations. One must therefore take into account the effects of nonlinear contributions which tend to couple such fluctuations. These terms also couple the slow and fast modes. However this coupling is weak because it is related to the trimolecular step in the reaction scheme and the corresponding chemical kinetic constant is small because the probability of a triple collision is indeed very small. One may therefore eliminate the fast mode adiabatically up to the second order in the nonlinearity. This then leads to the following new time-dependent Ginzburg-Landau equation[10] for the critical mode written in dimensionless variables

$$\frac{\partial \sigma_{\vec{q}}}{\partial \tau} = -\frac{\delta \mathfrak{F}}{\delta \sigma_{-\vec{q}}} + \zeta_{\vec{q}}(\tau), \tag{2.10}$$

with

$$\langle \zeta_{\vec{q}}(\tau)\rangle = 0, \quad \langle \zeta_{\vec{q}}(\tau)\zeta_{\vec{q}'}(\tau')\rangle = \delta(\vec{q} + \vec{q}')\delta(\tau - \tau') \tag{2.11}$$

because the characteristics of the noise are not fundamentally modified by the adiabatic elimination due to the separation of the time scales involved. The new "free energy" in Eq. (2.10) is given by[5]

$$\mathfrak{F} = \frac{1}{2}\int \frac{d^d q}{(2\pi)^d}[r_0 + \bar{D}(|\vec{q}| - q_c)^2]|\sigma_{\vec{q}}|^2 + \frac{v}{3!}\int \frac{d^d q}{(2\pi)^d}\int \frac{d^d q'}{(2\pi)^d}\sigma_{\vec{q}}\sigma_{\vec{q}'}\sigma_{-\vec{q}-\vec{q}'} + \frac{u}{4!}\int \frac{d^d q}{(2\pi)^d}\int \frac{d^d q'}{(2\pi)^d}\int \frac{d^d q''}{(2\pi)^d}\sigma_{\vec{q}}\sigma_{\vec{q}'}\sigma_{\vec{q}''}\sigma_{-\vec{q}-\vec{q}'-\vec{q}''}, \tag{2.12}$$

where

$$\sigma_{\vec{q}} = \left(\frac{q_c^2 B_c D_y}{\Gamma |A_c|}\right)^{1/2} S_{\vec{q}} = \gamma S_{\vec{q}},$$

$$\tau = \gamma^2 \Gamma t, \quad \bar{D} = 4D_x/B_c,$$

$$r_0 = (B_c - B)/B_c, \quad \zeta = \frac{1}{\gamma\Gamma}\eta,$$

$$v = \frac{3!\,\Gamma^{1/2}(1 - A\eta)}{A(1 - \eta^2)(1 + A\eta)^{7/2}},$$

$$u = \frac{4!\,\Gamma[A^2(1 - A\eta)(1 - \eta^4) + 2(A - \eta)^2]}{A^2(1 + A\eta)^6(1 - \eta^2)^2}.$$

To obtain (2.12), we have neglected the wave-vector dependence of the interaction functions v and u. On the other hand, one can show that u is positive for $A\eta < 2.73\ldots$ and negative for $A\eta > 3$. In the intermediate region the sign of u depends on the value of A. We here always consider $u > 0$. Were it negative, we would have to carry out the adiabatic elimination to higher order and this could possibly lead to the appearance of polycritical behavior.

The two essential features of the model are that it may possess an infinite number of equivalent order parameters each associated with a finite nonzero wavevector (of length q_c) and also that it contains cubic terms. Free energies containing the first of these two characteristics have been used to discuss phase transitions in weakly anisotropic antiferromagnets,[7] liquid crystals,[7] and the convective instability.[4] In contrast to other dissipative structures the characteristic wavelength q_c appearing in our reaction-diffusion model depends only on the intrinsic parameters of the systems.

III. MEAN-FIELD THEORY

We now derive the equation of state for the nonuniform phases in the mean-field approximation. In such a phase, the average

$$\sum_{i=1}^{m} \langle \sigma_{\vec{q}_i} \rangle = \sum_{i=1}^{m} a_i [\delta(\vec{q} + \vec{q}_i) + \delta(\vec{q} - \vec{q}_i)] \tag{3.1}$$

is nonzero for m vectors $\vec{q}_i$ such that $|\vec{q}_i| = q_c$. The fictitious symmetry-breaking fields conjugate to the $\langle \sigma_{q_i} \rangle$ are determined from the thermodynamic relations

$$h_{\vec{q}_i} = \delta\Phi / \delta\langle \sigma_{-\vec{q}_i} \rangle , \tag{3.2}$$

where the generalized thermodynamic potential Φ is the mean value of the Ginzburg-Landau functional

$$\Phi = \langle \mathfrak{F} \rangle , \tag{3.3}$$

which has been written in terms of the nonvanishing averages $\langle \sigma_{\vec{q}_i} \rangle$.

In the case $v = 0$, that we first consider, we readily obtain from (3.2) and (2.12) for m independent pairs of vectors:

$$h_{\vec{q}_i} = r_0 a_i + u a_i \sum_{j=1}^{m} a_j^2 - \tfrac{1}{2} u a_i^3 . \tag{3.4}$$

From the static correlation matrix

$$g_{\vec{q}\vec{q}'} = \langle \sigma_{\vec{q}} \sigma_{-\vec{q}'} \rangle - \langle \sigma_{\vec{q}} \rangle \langle \sigma_{-\vec{q}'} \rangle \equiv (r^{-1})_{\vec{q}\vec{q}'} \tag{3.5}$$

we get for the elements of the inverse susceptibility matrix

$$r_{\vec{q}_i \vec{q}_j} = r_0 + m u a_i^2 \quad (i = j) , \tag{3.6}$$

$$r_{\vec{q}_i \vec{q}_j} = u a_i a_j \quad (i \neq j) . \tag{3.7}$$

Hence, for all $h_{\vec{q}_i} = 0$, we find that all the amplitudes are equal to

$$a_i = a = \left(\frac{-2r_0}{2m - 1} \right)^{1/2} u^{-1/2} , \tag{3.8}$$

while

$$r_{\vec{q}_i \vec{q}_i} = \frac{-r_0}{2m - 1} . \tag{3.9}$$

This behavior is again characteristic of a second-order transition as it leads to a diverging static susceptibility.

When only one wave vector is excited the concentration varies periodically in one direction; this situation corresponds to the roll pattern for the convective instability and the helical structures in certain magnetic systems. One should also consider structures arising from noncoplanar wave vectors satisfying the quadrangular relation ($\vec{q}_i + \vec{q}_j + \vec{q}_k + \vec{q}_l = 0$ such that $|\vec{q}_\alpha| = q_c$) the simplest of which gives rise to fcc periodicity in real space.

On the other hand, if $v \neq 0$, the cubic terms induce structures whose wave vectors have to satisfy the relation ($\vec{q}_i + \vec{q}_j + \vec{q}_k = 0$ such that $|\vec{q}_\alpha| = q_c$). The simplest possibility is that of an equilateral triangle leading in three-dimensional real space to rodlike structures with two-dimensional hexagonal periodicity. We then obtain in zero fields,

$$r_0 a + v a^2 + \tfrac{5}{2} u a^3 = 0 \tag{3.10}$$

displaying a subcritical behavior as expected from the Landau theory.[10] We also expect on the basis of symmetry arguments that there will be no critical point. The corresponding transition "temperature" is $r_{\text{hex}} = v^2/10u$. In the convective instability phenomena this corresponds to the appearance of hexagonal patterns. The cubic terms may also generate three-dimensional structures, the simplest of which is an octahedron in q space corresponding to a bcc periodicity in real space. In this case

$$r_0 a + 2 v a^2 + \tfrac{11}{2} u a^3 = 0 , \tag{3.11}$$

also giving rise to a subcritical behavior with the following transition temperature:

$$r_{oct} = \tfrac{2}{11} v^2 / u .$$

This structure is the first to appear, a situation which presents analogies with the theory of the freezing transition where 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.[11]

All these situations are sketched qualitatively in Fig. 1. The relative stability of the various

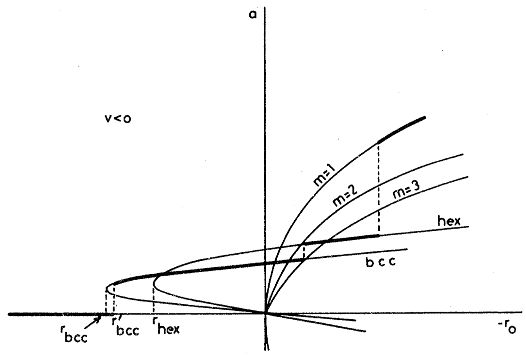

FIG. 1. (Schematic): bifurcation diagram in the mean-field approximation. Full lines denote the stablest structure.

phases may be obtained by comparison of the corresponding generalized thermodynamic potentials. The stablest phases are represented by plain lines in Fig. 1.

We conclude this section by stressing that a great variety of structures may appear originating through a second or first-order phase transition. These mean-field results may also be obtained, perhaps in a more systematic way, using group representation and bifurcation theory.[12]

Let us now analyze to what extent the fluctuations change this overall picture.

IV. INHOMOGENEOUS FLUCTUATIONS

In the presence of fluctuations, the inverse susceptibility now becomes

$$r = g^{-1}(|\vec{q}| = q_c) = r_0 - \Sigma(|\vec{q}| = q_c) \tag{4.1}$$

where the "self-energy" $\Sigma(\vec{q})$ may be expanded in powers of the interactions. We also consider the case $v = 0$ for which the mean-field theory predicts the existence of a second-order transitions. In the uniform phase ($r_0 > 0$) the Hartree approximation leads to

$$r_H = r_0 + \frac{u}{(2\pi)^d} \int \frac{d^dk}{r_H + \overline{D}(|\vec{k}| - q_c)^2} \tag{4.2}$$

or

$$r_H = r_0 + \alpha u \overline{D}^{-1/2} r_H^{-1/2}, \tag{4.3}$$

where $\alpha = \pi q_c^{d-1} S_d/(2\pi)^d$, S_d being the surface area of the unit sphere in d dimensions. It may be shown[7] that the higher-order terms may be neglected in (4.2) as long as $\alpha u |r_0|^{-3/2} \simeq 1$. In this region, $r \simeq r_H$ therefore never reaches zero and the fluctuations thus have a drastic effect on the second-order mean-field transition as the static susceptibility shows no divergence in this regime. It is important to remark that this conclusion is independent of the dimensionality; indeed the phase space associated with the critical fluctuations is described in the reciprocal space by a spherical shell which is in the lowest-order effectively one dimensional. The system has thus no critical dimensionality in the sense of the renormalization-group approach.[13] As a matter of fact if one unthinkingly applies the recipes of the renormalization group to this system, one does not find any fixed point in the neighborhood of the Gaussian fixed point which becomes unstable with respect to the interaction. Such an absence of a stable fixed point has been interpreted as an indication of either the existence of a first-order transition[14] of the suppression of the transition.

To analyze what becomes of the mean-field structures, we first make use of the general symmetry arguments which are at hand.

A. Symmetry

Owing to the breakdown of the translational symmetry at the instability we may derive general relations between the various elements of the correlation matrix. Their generating functional is defined as

$$e^{-\mathcal{G}} = \int \mathfrak{D}\sigma \exp\left[-\left(\mathfrak{F} - \sum_i h_{\vec{q}_i}\sigma_{-\vec{q}_i}\right)\right]. \tag{4.4}$$

The Brazovskii-Ginzburg-Landau functional $\mathfrak{F}$ is translation invariant and the fictitious symmetry-breaking fields have periodicity q_c^{-1}. Except for the source term, the integral is invariant under the infinitesimal transformation

$$\sigma'_{\vec{q}} = \sigma_{\vec{q}} + i\,\vec{q}\cdot\vec{\xi}\sigma_{\vec{q}}. \tag{4.5}$$

The variation of the source under this transformation leads to

$$\mathcal{G}(\{h_{\vec{q}_i}\}) = \mathcal{G}(\{h_{\vec{q}_i} - i\vec{q}_i\cdot\vec{\xi}h_{\vec{q}_i}\}) \tag{4.6}$$

or in differential form

$$\sum_i \frac{\partial \mathcal{G}}{\partial h_{\vec{q}_i}} \vec{\xi}\cdot\vec{q}_i h_{\vec{q}_i} = 0. \tag{4.7}$$

Considering a structure defined by a set of m *independent* pairs of vectors $\{\vec{q}_\alpha, -\vec{q}_\alpha\}$, we differentiate with respect to the corresponding fields and we get, setting all other fields equal to zero [$h_{\vec{q}_k}$ (where $\vec{q}_k \notin \{\vec{q}_\alpha, \vec{q}_{-\alpha}\}$)],

$$\vec{\xi}\cdot\sum_\alpha \frac{\partial^2\mathcal{G}}{\partial h_{\vec{q}_\alpha}\partial h_{\vec{q}_\beta}} \vec{q}_\alpha h_{\vec{q}_\alpha} - \vec{\xi}\cdot\frac{\partial \mathcal{G}}{\partial h_{\vec{q}_\beta}} \vec{q}_\beta = 0. \tag{4.8}$$

Because of the arbitrariness of the choice of ξ and of $\{\vec{q}_\alpha, -\vec{q}_\alpha\}$, one gets the following relations:

$$g_{\vec{q}_\alpha\vec{q}_\alpha} - g_{\vec{q}_\alpha -\vec{q}_\alpha} = \frac{a_\alpha}{h_{\vec{q}_\alpha}}, \quad \forall\alpha, \tag{4.9}$$

$$g_{\vec{q}_\alpha \vec{q}_\beta} - g_{\vec{q}_\alpha -\vec{q}_\beta} = 0\,, \quad \forall \alpha \neq \beta \tag{4.10}$$

when the $h_{\vec{q}_\alpha}$ are equal, all the $\vec{q}_\alpha$ are equivalent and one has ($h_{\vec{q}_\alpha} = h$, $\bar{g}_{\vec{q}_\alpha \vec{q}_\alpha} = g_D$, $g_{\vec{q}_\alpha -\vec{q}_\alpha} = g_{ND}$)

$$g_D - g_{ND} = a_\alpha / h\,, \tag{4.11}$$

$$g_{\vec{q}_\alpha \vec{q}_\beta} = g_{\vec{q}_\alpha -\vec{q}_\beta} = \bar{g}\,. \tag{4.12}$$

The structure of the inverse correlation matrix is now very simple and we easily obtain

$$r_D - r_{ND} = (g_D - g_{ND})^{-1} = h/a_\alpha\,. \tag{4.13}$$

In the weak-field limit, $r_D - r_{ND}$ goes to zero as h, while according to this conclusion and (4.12) the elements of the correlation matrix behave as

$$g_D \propto 1/h\,, \quad g_{ND} \propto 1/h\,, \tag{4.14}$$

while $\bar{g}$ and $g_D + g_{ND}$ are independent of h for *all* $B > B_c$. Let us note that relation (4.11) bears some analogy with the Hugenholtz-Pines theorem[15] in the theory of superfluidity.

When relations exist between the structural wave vectors this result may be extended. We merely quote the analogous resulting relations.

$m = 3$ (equilateral triangles):

$$(g_D - g_{ND}) - (\bar{g} - \bar{\bar{g}}) = \frac{a_\alpha}{h} = \frac{1}{(r_D - r_{ND}) - (\bar{r} - \bar{\bar{r}})}\,, \tag{4.15}$$

where $\bar{g} = g_{\vec{q}_\alpha \vec{q}_\beta}$ if $\vec{q}_\alpha$ and $\vec{q}_\beta$ are linked by a triangular relation whereas $\bar{\bar{g}} = g_{\vec{q}_\alpha \vec{q}_\beta}$ when no such relation exist.

$m = 4$ (rhombohedrons):

$$(g_D - g_{ND}) + (g' - g'') = \frac{a_\alpha}{h} = \frac{1}{(r_D - r_{ND}) + (r' - r'')}\,, \tag{4.16}$$

where $g' = g_{\vec{q}_\alpha \vec{q}_\beta}$ if $\vec{q}_\alpha$ and $\vec{q}_\beta$ are linked by a quadrangular relation whereas $g'' = g_{\vec{q}_\alpha \vec{q}_\beta}$ when no such relation exist and similarly for r' and r''.

$m = 6$ (octahedrons):

$$(g_D - g_{ND}) - 2(\bar{g} - \bar{\bar{g}}) = \frac{a_\alpha}{h} = \frac{1}{(r_D - r_{ND}) - (r' - r'') - 2(\bar{r} - \bar{\bar{r}})} \tag{4.17}$$

with similar notations as $m = 3$ and where $r' = r_{\vec{q}_\alpha \vec{q}_\beta}$ and $r'' = r_{\vec{q}_\alpha - \vec{q}_\beta}$ if $\vec{q}_\alpha$ and $\pm\vec{q}_\beta$ are not linked by a triangular nor a quadrangular relation. In these cases not only g_D and g_{ND}, but also $\bar{g}$ and $\bar{\bar{g}}$ behave as $1/h$ for weak symmetry-breaking fields.

Such divergencies are a consequence of the high order of degeneracy of the order parameter. As a result long-ranged fluctuations may develop in *all* the ordered phase. Indeed, by studying the response of the system to a long wavelength deformation of the structure

$$[\sigma'(\vec{r}) = \sigma(\vec{r} - \vec{\xi} \cos \vec{k} \cdot \vec{r})\,;\ \vec{\xi} \text{ and } |\vec{k}|/q_c \ll 1]\,,$$

we derive Bogolubov inequalities[16] in zero fields. The variation of the potential due to this infinitesimal deformation and which corresponds to the transformation

$$\sigma'_{\vec{q}} = \sigma_{\vec{q}} + \tfrac{1}{2} i \vec{q} \cdot \vec{\xi} (\sigma_{\vec{q}+\vec{k}} + \sigma_{\vec{q}-\vec{k}}) \tag{4.18}$$

is

$$\delta\mathfrak{F} = U_{\vec{k}}(\vec{\xi}) = \sum_{j=1}^{m} \frac{i \vec{q}_j \cdot \vec{\xi}}{2} \{ h_{\vec{q}_j} [\sigma_{-\vec{q}_j + \vec{k}} + \sigma_{-\vec{q}_j - \vec{k}}] - h_{-\vec{q}_j} [\sigma_{\vec{q}_j + \vec{k}} + \sigma_{-\vec{q}_j - \vec{k}}] \} + \frac{1}{2} \sum_{\vec{q}} (|\vec{q}| - q_c)^2 \frac{i \vec{q} \cdot \vec{\xi}}{2} \{ \sigma_{\vec{q}} [\sigma_{-\vec{q}+\vec{k}} + \sigma_{-\vec{q}-\vec{k}}] - [\sigma_{\vec{q}+\vec{k}} + \sigma_{\vec{q}-\vec{k}}] \sigma_{-\vec{q}} \}\,. \tag{4.19}$$

Moreover the following inequality has to be satisfied:

$$\langle \sigma_{\vec{q}_i + \vec{k}} \sigma_{-\vec{q}_i - \vec{k}} \rangle \langle U_{\vec{k}}(\vec{\xi}) U^*_{\vec{k}}(\vec{\xi}) \rangle \geq |\langle \sigma_{-\vec{q}_i - \vec{k}} U_{\vec{k}}(\vec{\xi}) \rangle|^2\,. \tag{4.20}$$

Owing to the fact that for any operator κ,

$$\langle \kappa U_{\vec{k}}(\vec{\xi}) \rangle = \langle \kappa \rangle_{\mathfrak{F}} - \langle \kappa \rangle_{\mathfrak{F} + \delta\mathfrak{F}}\,, \tag{4.21}$$

we obtain in zero fields

$$g_{\vec{q}_i + \vec{k}, \vec{q}_i + \vec{k}} \geq Q_{\vec{q}_i + \vec{k}}\,,$$

where

$$\kappa^2_{j,\pm} = (|\vec{q}_j \pm \vec{k}| - \vec{q}_c)^2\,,$$

$$Q_{\vec{q}_i + \vec{k}} = \frac{\frac{1}{2} (\vec{q}_i \cdot \vec{\xi})^2 a_i^2}{\sum_{j=1}^{m} (\kappa^2_{j,+} + \kappa^2_{j,-}) (\vec{q}_j \cdot \vec{\xi})^2 a_j^2 + \sum_{\vec{q}} [(|\vec{q} - \mathbf{k}| - q_c)^2 - (|\vec{q}| - q_c)^2] (\vec{q} \cdot \vec{\xi})^2 g_{\vec{q}, \vec{q}}}\,. \tag{4.22}$$

Then one finds easily that

$$|g_D(\vec{k}) - g_{ND}(\vec{k})| \geq 2Q_{\vec{q}_j+\vec{k}} \tag{4.23}$$

or for structures defined by m independent pairs of wave vectors

$$|r_D(\vec{k}) - r_{ND}(\vec{k})| \leq (2Q_{\vec{q}_j+\vec{k}})^{-1} . \tag{4.24}$$

These Bogolubov inequalities imply the destruction of any long-range order by the fluctuations for $\alpha \leq 2$ infinite systems.

In three-dimensional systems however the problem needs further discussion. Let us consider what happens if one rotates *one* vector of a structure (characterized by independent wave vectors), say $\vec{q}_i \rightarrow \tilde{\vec{q}}_i$. As a consequence of the rotational invariance, one has

$$g_{\tilde{\vec{q}}_i\tilde{\vec{q}}_i} = g_{\vec{q}_i\vec{q}_i} = a_i/h , \tag{4.25}$$

where $|\tilde{\vec{q}}_i| = |\vec{q}_i| = q_c$. But for an infinitesimal rotation

$$\tilde{\vec{q}}_i = \vec{q}_i + \vec{k}_\perp$$

where $\vec{q}_i \cdot \vec{k}_\perp = 0$. Therefore the combination of translational and rotational symmetry leads to the following stronger inequalities:

$$g_{\vec{q}_i+\vec{k},\vec{q}_i+\vec{k}} \geq \frac{1}{2(\kappa_{i,+}^2 + \kappa_{i,-}^2)} , \tag{4.26}$$

$$|r_D - r_{ND}| < 2(\kappa_{i,+}^2 + \kappa_{i,-}^2) . \tag{4.27}$$

As a consequence all these structures are destroyed by the fluctuations in infinite systems. For $m = 1$, this result is analogous to the impossibility for one-dimensional crystals to exist in three-dimensional systems as argued by Landau and Peierls.[10] For $m = 1$, our result is in contrast with Brazovskii's conclusion about the fluctuation-induced first-order transitions to such structures. His assumption to neglect the nondiagonal elements of the correlation matrix is inconsistent with the fact that the correlation length diverges in zero field for *all* m as proved in relation (4.27).

On the other hand, for structures constructed from wave vectors satisfying definite angular relations (as the triangular relation associated with the cubic term of the Ginzburg-Landau functional or nonplanar quadrangular relations because of the quartic term) the result depends effectively on the relative orientation of the wave vectors and is only invariant for the rotation of the q pattern as a whole. Therefore the following inequality holds:

$$g_{\vec{q}_i+\vec{k},\vec{q}_i+\vec{k}} \geq \frac{\frac{1}{2}(\vec{q}_i\cdot\vec{\xi})^2 a_i^2}{\sum_{j=1}^m (\kappa_{j,+}^2 + \kappa_{j,-}^2)(\vec{q}_j\cdot\vec{\xi})^2 a_j^2} . \tag{4.28}$$

As a consequence these structures are the only ones which may appear in infinite three-dimensional systems. They appear only through first-order transitions and the first to appear (with increasing B) corresponds to octahedrons in q space, i.e., a bcc lattice in real space.

B. Finite dimensions

We now discuss the stabilizing effect of boundaries on structures which are destroyed by fluctuations in infinite systems.

We first consider the situation when

$$(\sqrt{r}/q_c L) \ln q_c L \ll 1 .$$

The nondiagonal terms may then be dropped from the equations of state which are in Hartree approximation ($v = 0$ and m independent pairs of vectors):

$$h_{\vec{q}_i} = r_0 a_i + u a_i \sum_{j:1}^{m} a_j^2 - \tfrac{1}{2} u a_i^3 + \tfrac{1}{2} u a_i \int \frac{d^dk}{(2\pi)^d} g_{k,k} , \tag{4.29}$$

$$r_{\vec{q}_i\vec{q}_i} = r_0 + u \sum_{j:1}^{m} a_j^2 + \frac{u}{2} \int \frac{d^dk}{(2\pi)^d} g_{\vec{k},\vec{k}} , \tag{4.30}$$

$$r_{\vec{q}_i\vec{q}_j} = \tfrac{1}{2} u a_i a_j [2 - \delta(\vec{q}_i + \vec{q}_j)] . \tag{4.31}$$

If all $h_i = h$, these equations may be written for structures with m independent pairs of wave vectors

$$h = ra - \tfrac{1}{2} u a^3 , \tag{4.32}$$

with

$$(2m-1)r + \tilde{\alpha} u/\sqrt{r} + r_0 = 0 , \tag{4.33}$$

where $\tilde{\alpha} = \alpha \bar{D}^{-1/2}$. Therefore, nonuniform (metastable) states appear when

$$-r_0 \geq r_m = 3(2m-1)^{1/3}(\tilde{\alpha}u/2)^{2/3} ,$$

with a *finite* amplitude $a_m = (2r_m/u)^{1/2}$. Here one can discuss also the relative stability of the various structures by calculating the difference between the corresponding generalized thermodynamic potentials. If we compare the uniform and nonuniform phases, we obtain

$$\Delta\Phi_m = \Phi_m - \tilde{\Phi} = -(1/2u)[(2m-1)r^2 + \tilde{r}^2] + \tilde{\alpha}(r^{1/2} - \tilde{r}^{1/2}) , \tag{4.34}$$

where the tilde refers to the uniform phase. It is easy to show that the nonuniform structures become stabler than the uniform phase for r'_m ($r_m < r'_m < 2^{1/2} r_m$) where $\Delta\Phi_m$ changes sign. This then defines the first-order transition temperature. In their coexisting region, the smaller the value of m, the stabler the structure, therefore the structures with small m are the first to appear in contrast to Brazovskii's conclusion.[7]

Let us stress the fact that the fluctuations change the nature of the transition qualitatively: the mean-field second-order transition is transformed in this case into a weak first-order transition and the transition temperature is also shifted by the fluctuations.

We also want to point out that the preceding analysis is already applicable to study the effects of the fluctuations on the structures characterized by definite angular relations between the wave vectors in infinite systems. For fcc structures ($v=0$) the fluctuations also induce a weak first-order transition. If on the other hand $v\neq 0$ (hex, bcc) (but small $v^2/u \ll |r|$) the fluctuations have only a weak effect on the supercritical first-order transition.[7]

It is however important to note that in the case of finite-dimensional problems the system may develop fluctuations whose correlation length become larger than the size of the system itself. Then the problem becomes zero dimensional with all the consequences discussed by Graham in the case of hydrodynamical instabilities or in the case of the laser.[17] This arises when

$$r_0^{(0_d)} \sim \frac{D_x}{L^2 B_c} = \frac{A\eta}{(1+A\eta)^2}\frac{1}{L^2 q_c^2}, \tag{4.35}$$

where L is the size of the chemical reactor. This quantity depends on the nature of the reactive medium through the diffusion coefficient d_x ($d_x = k_4 D_x$) and the kinetic constant k_4 which corresponds to the elimination of X ($X\rightarrow E$), this process being a fast one. In liquid phases plausible values are

$d_x \sim 10^{-6}\,\mathrm{cm^2\,sec^{-1}}$, $B_c \sim 1$, $L \sim 10$ cm, $k_4 \gtrsim 10^{-4}\,\mathrm{sec^{-1}}$

leading to $r_0^{(0_d)} \simeq 10^{-4}$. This limit may however be reduced or enlarged by several orders of magnitude because of the wide range of variation of chemical parameters.

To discuss the experimental relevance ($d=3$) of the effects of the fluctuations on the mean-field theory one has to evaluate r_m which is the analog of a Ginzburg criterion for this system. The mean-field theory is then valid for values of r_0 such that

$$r_0^{3/2} \gg \frac{q_c^2 B_c^{1/2} u}{D_x^{1/2}} \sim \frac{\Gamma k_4^{3/2}}{d_x^{3/2}} \sim r_0^{3/2(\mathrm{MF})}. \tag{4.36}$$

To evaluate Γ, we use the local fluctuation dissipation theorem[18] as we argue that the system remains in a state of local equilibrium throughout the transition region. Then

$$\Gamma \sim (k_3/k_4)(X_S/N_0\Delta^3), \tag{4.37}$$

where $X_S = (k_1/k_4)\tilde{A}$ is the stationary concentration of X, Δ is the mean free path in the reactive medium and N_0 is Avogadro's number. Consequently

$$\Gamma \sim (\tilde{A}/N_0\Delta^3)(k_1 k_3/k_4^2) \tag{4.38}$$

and the validity of the mean-field theory may be assumed for

$$r_0 \gg r_0^{(\mathrm{MF})} \simeq \left(\frac{\tilde{A}}{N_0\Delta^3}\right)^{2/3}\left(\frac{k_1 k_3}{k_4^2}\right)^{2/3}\frac{k_4}{d_x}. \tag{4.39}$$

As one must have $k_1/k_4 \ll 1$, a plausible order of magnitude for this quantity is 10^{-2} in liquids ($k_1k_3/k_4^2 > 1$ (cgs), $\tilde{A}\sim 10^{-3}M\ \mathrm{cm^{-3}}$). On the other hand, to observe the effects of fluctuations one must also have $r_0^{(\mathrm{MF})} > r_0^{(0_d)}$. This condition may be written in general as

$$\frac{r_0^{(\mathrm{MF})}}{r_0^{(0_d)}} \sim \left(\frac{\tilde{A}}{N_0\Delta^3}\right)^{2/3}\frac{(k_1k_3k_4)^{2/3}}{d_x^2}L^2 > 1. \tag{4.40}$$

Therefore, it follows that the role of the fluctuations may be of experimental importance for reactions taking place in media with low diffusion coefficients and high reaction rates.[19] Let us also remark that the size of the noise is further reduced by the effective one-dimensional character of the problem [$\Gamma^{2/3}$ and not Γ^2 for $d=3$ in (4.36)].

So the behavior of the system would be zero dimensional or mean field in gases, but in liquids or electrolytes the effects of the inhomogeneous fluctuations on the symmetry-breaking transition could in principle be observable if the coupling of chemical and hydrodynamical modes do not affect the overall picture given here.

V. CONCLUSION

We have shown that the trimolecular model near the Turing instability may be discussed in terms of the concepts developed in the theory of equilibrium transitions to nonuniform states.

It furnishes a further example where the predictions of the mean-field treatment are *qualitatively* incorrect. Indeed the long-range fluctuations which develop in all the ordered phases destroy the structures which appear in the mean-field description of infinite one- and two-dimensional systems. They are also responsible for the nonexistence in three dimensions of infinite structures characterized by m independent wave vectors. On the other hand the structures specified by a set of related wave vectors (bcc, hexagonal prisms,...) may exist in infinite systems. Therefore there appear two classes of dissipative structures. In the first class, because they must be stabilized by the finite dimensions of the systems, the general theorems resulting from the breakdown of the translation symmetry are not applicable.

Whereas in the second class the instability is analogous with equilibrium first-order transition such as crystallization.

The chemical rate constants offer a much wider range of variation than the transport coefficients in usual liquids. As a result, for sufficiently fast reactions, the chemical instabilities might lead to the possibility of observing the effect of fluctuations in contrast with other nonequilibrium transitions such as convective instability which for physically realizable parameters take place in the zero-dimension regime.

Finally, we feel that our discussion could be transposed to Turing instabilities in other nonlinear chemical models.

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