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Chemical freezing of phase separation in immiscible binary mixtures

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We discuss the thermodynamic and kinetic conditions under which chemical reactions may prevent the coarsening terminating spinodal decomposition and freeze the unmixing of binary mixtures at some early, pattern forming, stage of evolution. Under very general conditions, we establish that (i) this pattern freezing phenomenon can only occur in nonequilibrium systems the level of dissipation of which exceeds a finite, nonzero threshold value; (ii) at least two independent chemical processes must take place; (iii) chemistry must be destabilizing, which requires that at least one of these processes must be autocatalytic; (iv) pattern formation is possible even outside of the spinodal region, i.e., without involving a phase separation phenomenon, in unsymmetrical mixtures where the potential energies between pairs of identical particles are sufficiently different. This latter condition replaces for nonideal chemically reacting binary mixtures the *unequal diffusion coefficients condition* which governs the appearance of Turing patterns in the classical reaction-diffusion theory. [S1063-651X(97)13708-4]

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I. INTRODUCTION

The phase ordering dynamics of a binary mixture, such as a binary alloy, quenched from a high-temperature, homogeneous state to a point below the spinodal line is well known [1]. In this domain, the mixture is unstable with respect to long wavelength, small amplitude concentration fluctuations and, at first, decomposes into two coexisting phases exhibiting an interconnected, labyrinthine morphology. Subsequently, on a long time scale, this pattern slowly coarsens and finally transforms into two homogeneous macroscopic phases separated by a minimal interfacial boundary region. This coarsening, also called Ostwald ripening, is due to the fact that in the spinodal domain, all nonzero Fourier modes with a wave number k smaller than some upper cutoff value k_u are unstable, while the zero mode $k=0$ is only marginally stable. Under those conditions, the dynamics selects a spatial organization which originates from the amplification of large wavelength modes, i.e., it corresponds to vanishingly small wave numbers ($k \rightarrow 0$). Indeed, though the growth of these large scale modes is extremely slow because it requires the diffusion of matter over large distances, in the end, it governs the spatial organization because it minimizes free energy.

Over the last twenty years, several theoretical studies have investigated the idea that coupling spinodal decomposition with chemical reactions may, in the absence of hydrodynamic effects, freeze this coarsening process and stabilize a stationary inhomogeneous state characterized by an intrinsic wavelength; i.e., a wavelength determined by molecular and kinetic parameters rather than by externally imposed boundary conditions and/or geometrical constraints [2–6,8].

In general, the starting point of these theoretical studies is a nonlinear diffusion equation, deriving from a square-gradient free energy functional [9], in which source terms are added to model the chemical reactions occurring in the mixture. So far, the choice of these chemical terms has relied either on intuitive considerations [2,4–6,8], or on a master equation derivation which exploits the kinetic similarities of some chemical reactions with spin-exchange processes [3]. This basically mean field type of approach was pioneered by Huberman [2], who predicted that the influence of chemistry on spinodal decomposition may not only narrow the band of unstable modes, but more importantly, introduce a lower cutoff k_{ℓ}, below which all modes, and in particular, the mode $k=0$, are stable. Considering a two step autocatalytic reaction, this author further showed, within the framework of this autocatalytic model, that chemistry restricts the size of inhomogeneities which arise during spinodal decomposition under conditions where the system is out of equilibrium with respect to both chemical equilibrium and phase composition.

The theoretical results reported in more recent works support this prediction that chemistry may suppress the coarsening which normally terminates the isothermal phase separation of immiscible, incompressible fluids. More than that even in these studies, this suppression is obtained thanks to chemical processes which are considerably simpler than the one considered by Huberman, hence, suggesting that the phenomenon in question *is ubiquitous in nature* [5], and that the class of chemical reactions, which qualify as candidates for a possible experimental demonstration, is extremely broad. A major simplification in this respect, is the fact that in none of the models studied recently, is the chemistry involved autocatalytic: typically, the reactions considered are simple isomerization processes, such as $A \rightleftharpoons B$, [3,4,8], association-dissociation reactions, such as $A+B \rightleftharpoons C$ [5], or standard adsorption-desorption surface reactions [6].

This apparently extremely general effect of chemistry on spinodal decomposition is, however, obtained through a procedure which we find thermodynamically unsatisfactory [10], because it consists in adopting chemical rate laws which, contrary to those adopted for diffusion, do not take into account the nonideality of the systems considered. More precisely, it amounts to assuming that, somehow, far from thermodynamic equilibrium, the relationship binding chemical affinities to activity coefficients [11,12] may be neglected and that, as a result, it then becomes possible to model chemical and diffusional processes as being independent from each other [13].

The conditions for which this *far from equilibrium independency assumption* (FFEIA) applies are unclear. Our objective here is, therefore, to investigate the behavior of mixtures undergoing phase separation in the presence of chemical reactions along a different line of approach which (i) does not rely on the FFEIA, (ii) allows us to encompass equilibrium, as well as far from equilibrium situations, and (iii) is based on thermodynamic considerations which are model independent.

We shall study the case of chemically reactive binary mixtures which is also the case investigated in previous works. We shall limit ourselves to situations which involve no hydrodynamic effects. From a chemical point of view, this means that we restrict ourselves to reaction schemes which *a priori* rule out the occurrence of pressure or density variations of chemical origin. No other assumption will be made concerning the kinetics of the chemical processes considered.

It is characteristic of chemical reactions and diffusion that the thermodynamic forces governing these processes are related, being function, in the first case, of the chemical potentials and, in the second case, of the chemical potentials spatial derivatives. The thermodynamic fluxes conjugate to these forces, i.e., the chemical reaction rates and diffusion rates, are thus also function of the chemical potentials; this relationship is, furthermore, well known if one admits the validity of the usual phenomenological laws relating thermodynamic forces and fluxes. Under those conditions, choosing the chemical potentials determines the coupling between diffusional and chemical processes. In particular, it determines the equilibrium state towards which reaction-diffusion systems evolve in the absence of external constraints. As embodied in the classical Duhem-Jouget theorem [11], it results therefrom that in equilibrium systems, diffusional stability automatically insures the stability of chemical equilibrium. In order to determine what happens to this classical stability relationship under nonequilibrium conditions, question which underlies the present study, it is essential in modeling chemical and diffusional fluxes to respect this property that both kinds of fluxes are given functions of the same chemical potentials, which themselves are thermodynamic quantities subjected to well-defined, general requirements.

We undertake the investigation of the behavior of binary mixtures undergoing simultaneously spinodal decomposition and chemical reactions by addressing this problem in detail in Sec. II. Taking as usual in mean field approaches, the square-gradient free energy as starting point, we discuss the form that chemical potentials must have within this framework to be thermodynamically consistent. Subsequently, we express in terms of these chemical potentials the generalized reaction-diffusion equation governing the spatiotemporal behavior of the system. We analyze the linear stability properties of the uniform steady state solutions of this equation in Sec. III. We derive from this analysis in Secs. IV A and IV B, the thermodynamic and kinetic conditions under which chemical reactions may introduce a lower cutoff k_l which (i) excludes the zeroth mode from the band of unstable modes, (ii) permits to avoid the phenomenon of coarse graining, and (iii) allows instead for the freezing of spinodal decomposition at an intermediary stage. This analysis allows us to predict also that the difference in potential energies between pairs of identical particles plays an essential role in the stability properties of the systems considered here. Notably, the value of this parameter determines whether or not there can already exist a finite band of unstable modes outside of the spinodal domain; in other words, whether or not a symmetry breaking instability may be observed which leads to pattern formation without involving the unmixing phase transition. The results are illustrated on an example in Sec. IV C.

II. MODELING OF CHEMICALLY REACTIVE BINARY MIXTURES

A. Free energy and chemical potentials

We consider a binary mixture subjected to isothermal, isobaric conditions which below (above) some critical temperature T_c, exhibits a miscibility gap. As usual, we suppose that the coarse grained concentrations of the components 1 and 2 forming this mixture, respectively, $c_1(\mathbf{r})$ and $c_2(\mathbf{r})$ (expressed in mass per unit volume), can be defined at each space point $\mathbf{r}$. In functional form, the Gibbs free energy of this system can be written as

$$G=\int d\mathbf{r}g(\mathbf{r}), \tag{1}$$

where $g(\mathbf{r})$ is a free energy density, $d\mathbf{r}$ denotes a volume element, and integration extends over the entire system. Working in the spirit of the treatments currently adopted to study the problem at hand, we assume that composition gradients are small compared to the reciprocal of intermolecular distances and we expand $g(\mathbf{r})$ about its value g^b for a bulk phase of uniform composition. Assuming further that no external field or other source of spatial anisotropy is present, we only retain in this expansion the terms compatible with the tensoral invariance of $g(\mathbf{r})$ with respect to symmetry operations of rotation [9]. To the leading order, this yields

$$g(\mathbf{r})=g^b(c_1,c_2)+\frac{1}{2}\sum_{i,j=1}^{2}\kappa_{ij}(c_1,c_2)\nabla c_i\cdot\nabla c_j. \tag{2}$$

The scalar term g^b takes into account the nonideal, energetic and/or entropic destabilizing effects responsible for the spinodal decomposition of uniform bulk phases. The κ_{ij}'s describe the interactions between i-j pairs of particles and are the elements of a symmetric matrix when the medium is isotropic. Contrary to g^b, these gradient terms should always be stabilizing: in the spinodal domain, their effect should insure the minimization of interfacial boundary regions and the existence of an upper cutoff k_u, on the band of unstable Fourier modes.

As explained in the introduction, it is important in order to study the coupling of chemical reactions and spinodal decomposition, to take into account that these two processes are controlled by thermodynamic forces which are linked to the components chemical potentials μ_1 and μ_2. The remaining part of this section serves the purpose of setting up the reaction-diffusion equation obeyed by the system dynamics in agreement with this requirement and in as general form form as possible.

Let us first explicate that in Eq. (2), $g(\mathbf{r})$ is a first order homogeneous function of the concentrations c_i. For any number α, one has

$$g^b(\alpha c_1,\alpha c_2)=\alpha g^b(c_1,c_2), \tag{3a}$$

$$\kappa_{ij}(\alpha c_1,\alpha c_2)=\alpha^{-1}\kappa_{ij}(c_1,c_2). \tag{3b}$$

Choosing α to be equal to the density $\rho=c_1+c_2$, we reexpress the functional dependence of g^b and of the κ_{ij} in terms only of the coarse grained massic fraction $x\equiv x_1(\mathbf{r})=c_1/\rho$, so that the free energy density (2) thus rewrites as $[x_2(\mathbf{r})=1-x]$

$$g(\mathbf{r})=\rho g^b(x)+\frac{1}{2}\sum_{i,j=1}^{2}\frac{\kappa_{ij}(x)}{\rho}\nabla c_i\cdot\nabla c_j. \tag{4}$$

Assuming that the density $\rho=c_1+c_2$ is constant throughout the system, immediately transforms this expression into the familiar Cahn-Hilliard form

$$g(\mathbf{r})=\rho\left[g^b(x)+\frac{\kappa(x)}{2}(\nabla x)^2\right], \tag{5}$$

where $\kappa(x)=\kappa_{11}(x)+\kappa_{22}(x)-2\kappa_{12}(x)$ measures that contribution to nonideality which arises from the existence of an unbalance between the mean attractive forces between like molecules and the attractive force between unlike molecules. This parameter must be positive so that *per se* the occurrence of inhomogeneities results in an increased free energy. Surface tension effects then insure that concentration gradients cannot grow *ad infinitum* and that the spinodal instability is bounded by an upper cutoff; as a consequence, inhomogeneities corresponding to large wave numbers (small wavelengths) are always damped.

Given that $\rho=c_1+c_2$ is constant, it could seem, at first sight, that introducing this factor in Eq. (4) complicates notations unnecessarily. This is the case when spinodal decomposition takes place in the absence of chemical reactions: to write down the diffusion equation describing the system evolution, it is then sufficient to know the chemical potential difference

$$\Delta\mu\equiv\mu_1-\mu_2=\frac{\delta G(x,1-x)}{\delta x},$$

so that the factor $\rho=c_1+c_2$ may be forgotten. Here however, we need to keep track of the complete dependence of G with respect to c_1 and c_2. Indeed, later on, to incorporate chemical reactions and write down the reaction-diffusion equation giving the system evolution, we shall need to know the chemical potentials of each component separately. In deriving the latter from the classical defining relations

$$\mu_1=\frac{\delta G(c_1,c_2)}{\delta c_1}, \tag{6}$$

$$\mu_2=\frac{\delta G(c_1,c_2)}{\delta c_2}, \tag{7}$$

it is essential to remember that c_1 and c_2 must be treated as independent quantities. Replacing expression (4) for g in Eq. (1) and using Eqs. (6) and (7), we obtain that

$$\mu_1=\mu_1^b(x)-\tfrac{1}{2}[\kappa(x)+\Delta(x)]\nabla^2 x$$
$$-\tfrac{1}{2}\,\partial_x[x\ \ \kappa(x)+\Delta(x)](\nabla x)^2, \tag{8}$$

$$\mu_2=\mu_2^b(x)+\tfrac{1}{2}[\kappa(x)-\Delta(x)]\nabla^2 x$$
$$+\tfrac{1}{2}\,\partial_x[(1-x)\ \ \kappa(x)-\Delta(x)](\nabla x)^2, \tag{9}$$

where μ_1^b and μ_2^b are the bulk chemical potentials of the components, and $\Delta(x)\equiv\kappa_{11}(x)-\kappa_{22}(x)$ measures deviations from ideality which arise when the attractive forces pulling together identical molecules are different; clearly, this contribution to nonideality is distinct from the one described by $\kappa(x)$. Depending upon whether $\Delta(x)$ is equal to zero or not, we shall call the mixture symmetrical or unsymmetrical. The deviations of $\Delta(x)$ from zero may be due to a difference in the range over which the interactions between pairs of identical particles operate as well as to a difference in the intensities of the attractive forces. In this sense, the notion of symmetry used here is more general than the one associated with symmetrical mixtures classically [14]. In deriving Eqs. (8) and (9) we have used the classical relation

$$x\ \frac{\partial\mu_1^b(x)}{\partial x}+(1-x)\frac{\partial\mu_2^b(x)}{\partial x}=0, \tag{10}$$

which the bulk chemical potentials $\mu_1^b(x)$, and $\mu_2^b(x)$ must satisfy in view of the extensivity properties of G. Equation (10) is of particular interest for the following because it allows us to specify the bulk chemical potentials μ_1^b and μ_2^b in terms of a single unknown function $Z(x)$. One has

$$\mu_1^b(x)=\mu_1^0+\int_1^x dx'(1-x')\ \ Z(x'), \tag{11}$$

$$\mu_2^b(x)=\mu_2^0-\int_0^x dx'x'Z(x'), \tag{12}$$

where the chemical potentials μ_1^0 and μ_2^0 of components 1 and 2 in pure form are functions of temperature and pressure only. The integrations extend from the situation in which the components are pure to the one in which they form a uniform mixture the composition of which is given by $c_1=\rho x, c_2=\rho(1-x)$. In terms of the chemical potentials (8),(9), the free energy density writes as $g(\mathbf{r})=c_1\mu_1+c_2\mu_2$. Integrating the Laplacian terms of this expression over a volume of mixture enclosed by a surface on which boundary terms vanish [9], we recover the Cahn-Hilliard form (5) where g_b is given by

$$g^b(x)=\rho[x\mu_1^b(x)+(1-x)\mu_2^b(x)]. \tag{13}$$

Noteworthy, while the chemical potentials (8),(9) depend on the self-interactions difference $\Delta(x)$, the usual Cahn-Hilliard free energy (5) does not. As a result, classically $\Delta(x)$ plays no role in the spinodal decomposition problem of purely diffusive binary mixtures. We shall see below that this situation changes in the presence of chemistry. Chemical rates are, in general, more complicated functions of chemical potentials than diffusion and as a rule they depend upon $\Delta(x)$ explicitly. The latter quantity becomes then an essential parameter for the stability properties of the mixture.

B. Examples: Perfect and regular solutions

With the derivation of expressions (5) and (8) and (9) the relations existing between the square-gradient free energy density of a binary mixture and the chemical potentials of its components have been stated in general form. This formalism involves essentially three unknown functions, $Z(x)$, $\kappa(x)$ and $\Delta(x)$, which have to be determined on the basis of the properties particular to the system considered.

The first two functions govern the behavior of purely diffusive systems. For the sake of concreteness, before we pursue our general treatment, let us specify these functions for two classical types of mixtures: perfect and regular solutions. Our purpose here is purely illustrative. The results established in the next sections will not be restricted to the choice of a particular mathematical form for $Z(x)$ and $\kappa(x)$.

For simplicity and without loss of generality, we set $\rho=1$ in the following. We first consider the case of two components forming a perfect solutions in a uniform bulk phase. This corresponds to the choice

$$\kappa(x)=0,$$

$$Z(x)=\frac{RT}{x(1-x)}.$$

Replacing these expressions and Eqs. (11)–(13) in Eq. (5), it immediately follows that $g\equiv g(\mathbf{r})$ is constant in space and represents the free energy density of a perfect solution,

$$g=g^0+RT[x\ \ln(x)+(1-x)\ln(1-x)]. \tag{14}$$

$g^0=\mu_1^0x+\mu_2^0(1-x)$ is the free energy density before mixing; the second term is the entropy of mixing which is of ideal form.

As a second example, we consider a symmetrical nonuniform regular solution with a constant, stabilizing surface tension term. This amounts to putting

$$\kappa(x)=\kappa>0 \quad (\kappa=\text{const}),$$

$$Z(x)=\frac{RT}{x(1-x)}-2\Omega,$$

and yields

$$g(\mathbf{r})=g^0+RT[x\ln(x)+(1-x)\ln(1-x)]+\Omega x(1-x)+\frac{\kappa}{2}(\nabla x)^2, \tag{15}$$

where Ω measures the bulk nonideality; when $\Omega>0$, this system exhibits a critical point for $x=x_c=1/2$ and $T=T_c=\Omega/2R$ [11,14].

C. Diffusive flux and spinodal instability

The rate of diffusion is proportional to the divergence of the flux $\mathbf{J}_x$ of particles 1 with respect to particles 2. The thermodynamic force $\mathbf{F}$, driving this process is the gradient of the chemical potential difference between molecules 1 and 2 ($\mathbf{F}=-\nabla[\mu_1-\mu_2]$). To relate $\mathbf{J}_x$ and $\mathbf{F}$, we adopt the usual phenomenological law

$$\mathbf{J}_x=-L(x)\nabla(\mu_1-\mu_2), \tag{16}$$

where $L(x)$ is a function of composition (Onsager's coefficient), the positivity of which is required in order that entropy production be positive. In the absence of chemistry, the diffusion equation for x thus reads

$$\partial_t x=\nabla[L(x)\nabla(\mu_1-\mu_2)]. \tag{17}$$

The stability of a homogeneous state $x=x_0$ is easily determined by considering the evolution of a small perturbation $\delta x(\mathbf{r},t)=x(\mathbf{r},t)-x_0$, that moves the system away from this state

$$\partial_t\delta x(\mathbf{r},t)=L_0\nabla^2[\delta\mu_1(\mathbf{r},t)-\delta\mu_2(\mathbf{r},t)]. \tag{18}$$

Here, L_0 stands for $L(x_0)$. We also introduce the simplified notations $\kappa_0=\kappa(x_0)$, $Z_0=Z(x_0)$ and $\Delta_0=\Delta(x_0)$. The expressions for $\delta\mu_1$ and $\delta\mu_2$ are calculated from relations (8) and (9) after substituting in them expressions (11) and (12) for the bulk chemical potentials. This yields

$$\delta\mu_1(\mathbf{r},t)=\left[(1-x_0)Z_0-\frac{\kappa_0+\Delta_0}{2}\nabla^2\right]\delta x(\mathbf{r},t), \tag{19}$$

$$\delta\mu_2(\mathbf{r},t)=\left[-x_0Z_0+\frac{\kappa_0-\Delta_0}{2}\nabla^2\right]\delta x(\mathbf{r},t). \tag{20}$$

Equation (18) may now be written in Fourier space as

$$\partial_t\delta x(k,t)=L_0k^2[\mu_1'(x_0,k)-\mu_2'(x_0,k)]\delta x(k,t), \tag{21}$$

where, μ_1' and μ_2' are obtained from Eqs. (19) and (20):

$$\mu_1'(x_0,k)=(1-x_0)Z_0+\tfrac{1}{2}[\kappa_0+\Delta_0]k^2, \tag{22}$$

$$\mu_2'(x_0,k)=-x_0Z_0-\tfrac{1}{2}[\kappa_0-\Delta_0]k^2. \tag{23}$$

Replacing Eqs. (22) and (23) in Eq. (21), yields that the linear growth coefficient of mode k is given by

$$\Gamma(k)=-L_0k^2[Z_0+\kappa_0k^2]. \tag{24}$$

Since κ_0 must be positive, the sign of $Z_0=\partial^2g(x)/\partial x^2$ at $x=x_0$ determines the nature of the free energy extremum; the homogeneous states is stable for positive Z_0. If Z_0 is negative, the homogeneous state x_0 is unstable with respect to perturbations the wave numbers k of which lie in the range

$$0<k<\sqrt{-Z_0/\kappa_0}\equiv k_u. \tag{25}$$

In that case, the system leaves the homogeneous state and tends to develop two domains of different concentration separated by an interface. The condition $Z_0=0$ thus defines the so-called spinodal domain. The growth factor of the fastest growing mode during the early evolution of spinodal decomposition, i.e.,

$$k_f=\sqrt{-Z_0/2\kappa_0}, \tag{26}$$

is then given simply by

$$\Gamma(k_f)=L_0\frac{Z_0^2}{4\kappa_0}. \tag{27}$$

D. Coupling of diffusion and chemical reactions

Suppose now that in addition to diffusion, the composition of the binary mixture may also vary due to chemical reactions and/or relaxation phenomena (excitation processes, conformational changes, photochemical processes, etc.). Suppose further that there are R linearly independent processes of this sort, and that the mixture is an open system in contact with external reservoirs of constant composition which may maintain it out of thermodynamic equilibrium.

The molecular mechanisms underlying these processes need not be detailed. It suffices for our general purpose to know that they amount to transformations which interconvert the mixture components into each other. Phenomenologically, these processes can be represented in chemical reaction form as

$$a_{1r}X_1+a_{2r}X_2+\sum_i a_{ir}B_i\rightleftharpoons b_{1r}X_1+b_{2r}X_2+\sum_i b_{ir}B_i, \tag{28}$$

where the index $r=1,\ldots,R$ labels the chemical transformations, the B_i's represent the composition variables describing the state of the external reservoirs and the coefficients a_{jr},b_{jr}, $(j=1,2,i)$ represent the molecularities of components 1, 2 and B_i, respectively, in the forward and backward direction of chemical reaction r.

As the external reservoirs composition and the mixture density are constant, the mass balance equation giving the spatiotemporal evolution of the system reads

$$\rho\partial_t x=\sum_{r=1}^{R}\nu_{1r}M_1w_r+\nabla\cdot[L(x)\nabla(\mu_1-\mu_2)], \tag{29}$$

where w_r is the rate of reaction r. (We are primarily interested in the influence of chemical reactions on unmixing under isobaric conditions; we want to avoid the additional complications which pressure and density variations, leading to the need of introducing hydrodynamic equation into the description, would entail.) Since mass is conserved in chemical reactions, the stoichiometric coefficients, $\nu_{kr}=b_{kr}-a_{kr}$, and molecular masses, M_k of components 1 and 2 $(k=1,2)$ are linked by the relation

$$\sum_{k=1}^{2}\nu_{kr}M_k=0 \quad (\forall r). \tag{30}$$

It is therefore convenient for the following to define $\nu_r\equiv\nu_{1r}M_1=-\nu_{2r}M_2$, and putting $\rho=1$, to rewrite Eq. (29) more simply as

$$\partial_t x=\sum_{r=1}^{R}\nu_r w_r+\nabla\cdot[L(x)\nabla(\mu_1-\mu_2)]. \tag{31}$$

Two qualitatively different kinds of transformations are encompassed by Eq. (28) according to whether or not the reservoirs in contact with the mixture are involved. In the latter case, one has $a_{ir}=b_{ir}=0$ $(\forall i)$ so that only the components 1 and 2 of the mixture participate in the reaction. In the former case, at least some of the a_{ir} and b_{ir} coefficients are different from zero and the reaction is a reservoir ''driven'' reaction or exchange process. In driven reactions some of the B_i's may act as catalysts, e.g., when $a_{ir}=b_{ir}$.

To each reaction rate w_r is associated a thermodynamic force, or chemical affinity $\mathcal{A}_r$. With the notations

$$\overrightarrow{\mu}_r=a_{1r}M_1\mu_1+a_{2r}M_2\mu_2+\overrightarrow{\mu}_{Br}, \tag{32}$$

$$\overleftarrow{\mu}_r=b_{1r}M_1\mu_1+b_{2r}M_2\mu_2+\overleftarrow{\mu}_{Br}, \tag{33}$$

where $\overrightarrow{\mu}_{rB}=\Sigma a_{ir}M_{B_i}\mu_{B_i}$ and $\overleftarrow{\mu}_{rB}=\Sigma b_{ri}M_{B_i}\mu_{B_i}$, the affinity $\mathcal{A}_r$ can be expressed in terms of chemical potentials as

$$\mathcal{A}_r=\overrightarrow{\mu}_r-\overleftarrow{\mu}_r, \tag{34}$$

while the reaction rates $w_r=\overrightarrow{v}_r(\overrightarrow{\mu}_r)-\overleftarrow{v}_r(\overleftarrow{\mu}_r)$ are the difference of two terms corresponding, respectively, to the direct rate of reaction $\overrightarrow{v}_r$, which depends upon $\overrightarrow{\mu}_r$, and to the reverse rate of reaction $\overleftarrow{v}_r$ which depends upon $\overleftarrow{\mu}_r$.

By definition, thermodynamic equilibrium is the state for which the affinity and rate of each chemical reaction simultaneously vanish

$$\mathcal{A}_r=0, \quad w_r=0. \tag{35}$$

We conclude therefrom that, when $\overleftarrow{\mu}_r=\overrightarrow{\mu}_r\equiv\widetilde{\mu}_r$, the equality $\overrightarrow{v}_r(\widetilde{\mu}_r)=\overleftarrow{v}_r(\widetilde{\mu}_r)$ must hold. Since, this equality has to be obeyed independently from the value of $\widetilde{\mu}_r$, the functions $\overrightarrow{v}_r(\cdot)$ and $\overleftarrow{v}_r(\cdot)$ must be identical so that we may set $\overrightarrow{v}_r(\cdot)=\overleftarrow{v}_r(\cdot)=v_r(\cdot)$. The most general expression for the rate of a chemical reaction is thus

$$w_r=v_r(\overrightarrow{\mu}_r)-v_r(\overleftarrow{\mu}_r). \tag{36}$$

It is well-known that thermodynamics does not determine chemical reaction rates; it only imposes that at equilibrium the relations (35) hold. The fact that the functions $\overrightarrow{v}_r$ and $\overleftarrow{v}_r$ have to be equal, is not in contradiction with this statement. Indeed, the reaction rate itself w_r is not prescribed since it still contains the unknown function v_r. Our analysis does not require that a particular form for this function v_r be postulated. In addition, by the thermodynamic postulate that the entropy production of linearly independent chemical processes must be positive, w_r and $\mathcal{A}_r$ must always have the same sign. This implies that v_r must be a monotonically increasing (nonlinear) function.

When the affinity is small, Eq. (36) reduces to the linear relation $w_r=\gamma\mathcal{A}_r$, where γ is a positive constant. For the general nonlinear regime, it is usual to write the reaction rate as

$$w_r = v_r(\vec{\mu}_r)(1 - \exp[-\mathcal{A}_r/RT]), \tag{37}$$

which is compatible with (36) if $v_r(\mu) \propto \exp(\mu/RT)$.

At this stage, it is important to stress that a wide variety of reaction-diffusion systems can be described by Eq. (31). Nevertheless, in Sec. III, we shall see that the stability properties of their uniform stationary states can be classified quite simply into four general categories once the chemical potentials are known and the thermodynamic requirements mentioned above concerning the rates w_r are taken into account.

III. LINEAR STABILITY OF HOMOGENEOUS STATIONARY STATES

A. Linear growth coefficients $\tilde{\Gamma}(k)$

Contrary to what happens with purely diffusive systems (cf. Sec. II C), in the case of chemically reacting mixtures, the homogeneous stationary state concentrations x_0 can no longer be chosen at will. For a given temperature and pressure, their value is fixed by the chemical reactions and the state of the external reservoirs with which the system exchanges matter and energy, i.e., by the solutions x_0 of the conservation relation

$$\sum_{r=1}^{R} \nu_r[v_r(\vec{\mu}_r(x_0)) - v_r(\overleftarrow{\mu}_r(x_0))] = 0. \tag{38}$$

Using the same notations as in Sec. II C, the linear stability of these states with respect to a small perturbation $\delta x(\mathbf{r},t)$ is given by

$$\partial_t \delta x(\mathbf{r},t) = \left[\sum_{r=1}^{R} \nu_r(\delta v_r(\vec{\mu}_r) - \delta v_r(\vec{\mu}_r)) + L_0 \nabla^2(\delta\mu_1 - \delta\mu_2) \right]. \tag{39}$$

The quantities $\delta v_r(\vec{\mu}_r)$ and $\delta v_r(\vec{\mu}_r)$ given by

$$\delta v_r(\vec{\mu}_r) = \left. \frac{dv_r}{d\vec{\mu}_r} \right|_{\vec{\mu}_r(x) = \vec{\mu}_r(x_0)} \delta\vec{\mu}_r(\mathbf{r},t) = \vec{v}\,'_r \delta\vec{\mu}_r(\mathbf{r},t), \tag{40}$$

$$\delta v_r(\overleftarrow{\mu}_r) = \left. \frac{dv_r}{d\overleftarrow{\mu}_r} \right|_{\overleftarrow{\mu}_r(x) = \overleftarrow{\mu}_r(x_0)} \delta\overleftarrow{\mu}_r(\mathbf{r},t) = \overleftarrow{v}\,'_r \delta\overleftarrow{\mu}_r(\mathbf{r},t), \tag{41}$$

define $\vec{v}\,'_r$ and $\overleftarrow{v}\,'_r$. Introducing the dimensionless parameters

$$z_0 = \left(\frac{L_0}{\kappa_0 \vec{v}\,'_1} \right)^{1/2} Z_0, \quad \rho_r = \frac{\overleftarrow{v}\,'_r}{\vec{v}\,'_r},$$

$$\tau_r = \left(\frac{\kappa_0}{L_0 \vec{v}\,'_1} \right)^{1/2} \vec{v}\,'_r, \quad \delta = \frac{\Delta_0}{\kappa_0}, \tag{42}$$

and proceeding as in Sec. II C, the linear growth coefficient $\tilde{\Gamma}(k)$ corresponding to the rescaled time and space variables

$$\tilde{t} = \vec{v}\,'_1 t, \quad \tilde{\mathbf{r}} = \left[\frac{L_0 \kappa_0}{\vec{v}\,'_1} \right]^{-1/4} \mathbf{r}, \tag{43}$$

can be written in compact form as

$$\tilde{\Gamma}(k) = -k^4 + [M_0(\delta) - z_0]k^2 + N_0 z_0. \tag{44}$$

The explicit expressions for $M_0(\delta)$ and N_0 are

$$M_0(\delta) = C_1(x_0)\delta + C_2(x_0), \tag{45}$$

$$N_0 = C_1(x_0)(1 - 2x_0) + C_2(x_0), \tag{46}$$

with

$$C_1(x_0) = \sum_{r=1}^{R} \frac{\nu_r \tau_r}{2}[a_{1r}M_1 + a_{2r}M_2 + (b_{1r}M_1 + b_{2r}M_2)\rho_r], \tag{47}$$

$$C_2(x_0) = \sum_{r=1}^{R} \frac{\nu_r \tau_r}{2}[a_{1r}M_1 - a_{2r}M_2 - (b_{1r}M_1 - b_{2r}M_2)\rho_r]. \tag{48}$$

The ρ_r''s and τ_r''s are positive functions whatever the value of $x_0 \in [0,1]$. Furthermore, it should be kept in mind that the value of x_0, as given by Eq. (38), does not depend on the coefficients κ_{ij} multiplying the gradient terms of g, and thus does not depend on δ. This is noteworthy because δ largely controls the system stability. Indeed, one may already observe that in the expression for $\tilde{\Gamma}(k)$ [cf. Eq. (44)], δ only appears in the term of order k^2; by varying δ, the sign and magnitude of this term, and hence the stability of x_0, can be modified at will.

B. Classification of instabilities

For nonreactive systems, it has been shown in Sec. II C that the change of sign of Z_0, or equivalently here of z_0, defines the boundary of the spinodal domain: $Z_0 < 0$ is the condition under which Eq. (24) admits a finite band of unstable modes which includes the mode $k = 0$. Here, in order to classify the wider class of behaviors which become possible in the presence of chemistry, we remark the following.

(i) Since the linear stability of the homogeneous stationary state solutions of Eq. (38) with respect to the mode $k = 0$ is given by

$$\tilde{\Gamma}(0) = N_0 z_0, \tag{49}$$

and hence, only depends on the sign of the functions N_0 and z_0, the stability diagrams reporting the behavior of $\tilde{\Gamma}(k)$ can be divided into the four basic cases described in Sec. III B 1–4.

(ii) In the large wave numbers domain ($k \to \infty$), the eigenvalues $\tilde{\Gamma}(k)$ are always negative: surface tension, which prevents too sharp interfaces to develop, and diffusion, which is all the more important that the wavelength of spatial heterogeneities is small, cooperate to damp short wavelength fluctuations efficiently. As a consequence, if at $k=0$, $d\tilde{\Gamma}(0)/dk^2 = M_0(\delta) - z_0$ is positive, $\tilde{\Gamma}(k)$ must pass through a maximum for

$$k = \tilde{k}_f = \left(\frac{M_0(\delta) - z_0}{2} \right)^{1/2}. \tag{50}$$

(iii) Replacing this expression of $\tilde{k}_f$ in Eq. (44), one finds that there exists a finite band of unstable modes, from which the mode $k=0$ is excluded, if the inequalities

$$\tilde{\Gamma}(0) = N_0 \; z_0 < 0, \tag{51}$$

and

$$\begin{aligned} \tilde{\Gamma}(\tilde{k}_f) &= \left[\frac{M_0(\delta) - z_0}{2} \right]^2 + N_0 z_0 > 0 \\ &= \tfrac{1}{4} C_1(x_0)^2 \delta_0^2 + \frac{C_1(x_0)}{2} [C_2(x_0) - z_0] \delta_0 \\ &\quad + \tfrac{1}{4} [C_2(x_0) - z_0]^2 + N_0 z_0 > 0 \end{aligned} \tag{52}$$

are fulfilled.

(iv) In strongly unsymmetrical mixtures, i.e., in the limit $|\delta| \to \infty$, inequality (52) is always satisfied. Looking for the transition point where $\tilde{\Gamma}(\tilde{k}_f)$ passes from the negative to the positive values, so that the finite band of unstable modes appears, we consider Eq. (52) as an equation in δ and solve for its roots. This yields the values

$$\delta_{\pm} = \frac{1}{C_1(x_0)} [-C_2(x_0) + z_0 \pm 2\sqrt{-N_0 z_0}], \tag{53}$$

which replaced in Eq. (50) permit to calculate the wave number k_c corresponding to this point of marginal stability. One has

$$k_c = (-z_0 N_0)^{1/4}. \tag{54}$$

In brief, the main outcome of the above analysis, is that if the mode $k=0$ is stable [cf. inequality (51)], and if the self-interaction difference parameter δ does not belong to the interval (δ_-, δ_+),

$$\delta \ni (\delta_-, \delta_+), \tag{55}$$

then the uniform stationary state x_0 is unstable with respect to a finite band of wave numbers,

$$0 < k_- \leqslant k \leqslant k_+, \tag{56}$$

the boundaries of which can be written in terms of the values of $\tilde{k}_f$ and k_c, given by Eqs. (50) and (54), as [it is easy to verify that when Eq. (55) holds, the value of $\tilde{k}_f$ is always larger than that of k_c]

$$k_{\pm} = \tilde{k}_f \sqrt{1 \pm \sqrt{1 - (k_c/\tilde{k}_f)^4}}. \tag{57}$$

Let us now analyze more in detail the four cases which may be encountered depending on the sign of z_0 and N_0.

1. Turing kind of instability

If $z_0 > 0$ and $N_0 < 0$, the uniform stationary state x_0 lies above the spinodal line and $\Gamma(0) < 0$. The components of the mixture are thus miscible. Nevertheless, pattern formation could take place if the value of δ fulfills condition (55). No phase separation being involved, the symmetry breaking instability appearing in that case is reminiscent of the *Turing instability* well known in classical reaction-diffusion theory. The originality of the instability mechanism found here, however, is that it does not require the diffusion coefficients of two reactants, the so-called ''activator'' and ''inhibitor,'' to be unequal. Instead, it is the difference of self-interactions between identical particles which controls the formation of patterns with an intrinsic wavelength. If condition (55) is not satisfied, i.e., if $\delta(x_0) \in (\delta_-, \delta_+)$, $\tilde{\Gamma}(k) < 0$ for all values of k and the stationary state x_0 is stable.

2. Spinodal instability

If $z_0 < 0$ and $N_0 < 0$, the stationary state x_0 lies below the spinodal line. There exists a band of unstable modes which includes the uniform perturbation mode $k=0$. We conclude that spinodal decomposition should proceed in this case essentially as in the absence of chemistry. The fastest growing mode is either Eq. (50) or the mode $k=0$, depending upon whether $M_0(\delta) - z_0 > 0$ or not. When the system is strongly unsymmetrical, the early growth of $\tilde{k}_f$ is faster than that of the fastest mode of the purely diffusive case. Indeed, under the transformation (42) and (43) expressions (26) and (27) become in dimensionless form $k_f = \sqrt{-z(x_0)/2}$ and $\Gamma(k_f) = z(x_0)^2/4$. By comparing with Eqs. (50) and (52), it is clear that for $|\delta(x_0)| \to \infty$, the inequality $\tilde{\Gamma}(\tilde{k}_f) - \Gamma(k_f) > 0$ holds.

3. Chemical instability

If $z_0 > 0$ and $N_0 > 0$, the stationary state x_0 lies above the spinodal line. Nevertheless, there exists a band of unstable modes which includes the uniform perturbation mode $k=0$. This instability originates from nonlinearities associated with the reaction scheme considered rather than from the nonideality of molecular interactions in the mixture. It should in general involve a multistationary state phenomenon and is in this respect distinct from spinodal decomposition or from the Turing kind of instability described in case 1. As in the preceding case, depending upon whether $M_0(\delta) - z_0 > 0$ or not, the fastest growing mode is either Eq. (50) or the mode $k=0$; again also in strongly asymmetric mixtures, $\tilde{k}_f$ grows more rapidly than the fastest mode of the purely diffusive system.

4. Ostwald ripening freezing instability

If $z_0 < 0$ and $N_0 > 0$, the stationary state x_0 lies below the spinodal line, but if $\delta(x_0) \in (\delta_-, \delta_+)$, one has $\tilde{\Gamma}(k) < 0$ for all values of k: the chemical reactions completely inhibit the phase separation. If on the contrary, $\delta(x_0) \ni (\delta_-, \delta_+)$, there exists a finite band of unstable modes,

$$0 < k_{\ell} \equiv k_- < k < k_+ \equiv \tilde{k}_u, \tag{58}$$

which excludes the mode $k=0$. This is the interesting case where patterns with an intrinsic wave length may appear while at the same time the mixture is immiscible. As explained in the introduction, such a behavior amounts in the terminology introduced by [6,7] to a freezing of the Ostwald ripening stage of phase separation. We shall, therefore, refer to it as the *Ostwald ripening freezing instability* (ORFI). The following properties are noteworthy: (i) It is clear from their definitions that the purely diffusive upper cutoff, $k_u=\sqrt{z_0}$ [cf. Eq. (25) rewritten using Eq. (43)], and the lower and upper boundaries of the unstable modes band, respectively, k_- and k_+ [cf. Eqs. (50), (54), and (57)], depend on different parameters and hence, can be varied independently from each other. For example, only $k_\pm$ depends on δ and on the concentrations B_i maintained constant in the external reservoirs. It is thus to be expected that by changing these concentrations, one may vary the position of the unstable band $(k_\ell,\tilde{k}_u)$ with respect to that of the purely diffusive system. In fact, these two bands could even become disconnected, so that $k_u<k_\ell<\tilde{k}_u$, if the inequality

$$-C_1(x_0)[\delta+x_0]z_0>0 \tag{59}$$

holds, in which case, chemistry hampers the damping by diffusion of large k modes.

We shall not, in the present work, attempt to determine and to classify the great variety of patterns which appears once the homogeneous stationary state x_0 becomes unstable. This requires a nonlinear analysis which we plan to report elsewhere [16]. The objective of our discussion in Sec. IV is to precise more explicitly the thermodynamic and kinetic properties which condition the appearance of patterns and of the ORFI just defined. The results of this discussion are illustrated by simulating numerically the behavior of an example in Sec. IV C.

IV. THERMODYNAMIC AND KINETIC CONDITIONS ON THE CHEMICAL FREEZING OF PHASE SEPARATION

A. Dissipation threshold

Let us first consider what kind of instability may occur if the homogeneous state is an equilibrium state $(x_0=x_e)$. At equilibrium, all the affinities vanish $[\vec{\mu}(x_e)=\overleftarrow{\mu}(x_e)]$ and consequently $\vec{v}_r'=\overleftarrow{v}_r'\equiv v_r'$, or equivalently, $\rho_r(x_e)=1$. In that case, the parameters M_0,N_0 reduce to

$$M_e=N_e=-\sum_{r=1}^{R}\nu_r^2\tau_r, \tag{60}$$

so that the eigenvalue equation simply reads

$$\tilde{\Gamma}_e(k)=-[k^2-N_e][k^2+z_e]. \tag{61}$$

We have mentioned in Sec. II D that the v_r are monotonically growing functions; their derivatives are thus always positive and so are the τ_r. Equation (60) shows that the parameters M_e and N_e are always negative at equilibrium *independently of the functions τ_r in the reaction rates* and *independently of the functions κ_e and z_e appearing in the free energy*. As Eq. (61) shows and in agreement with Duhem-Jouget theorem, the stability properties of homogeneous equilibrium state are thus entirely determined by the sign of z_e which controls diffusional stability.

The spinodal instability can then be observed at equilibrium in the domain corresponding to the spinodal region of nonreactive systems $[z(x_e)<0]$. On the contrary, the ORFI can never be observed under equilibrium conditions since N_e is always negative in that case.

Furthermore, since $N(x_e)$ is strictly negative at equilibrium, the ORFI can only appear if the external baths drive and maintain the system at a finite distance from its chemical equilibrium state. To see this, let us suppose that x_0 belongs to the thermodynamic branch of steady states [15] and lies close to the equilibrium state: $x_0=x_e+\delta x_0$, with $|\delta x_0|/x_e\ll 1$. The first terms in the expansion of N_0 are

$$N_0=N_e+\frac{dN}{dx_0}\delta x_0+\cdots, \tag{62}$$

and the minimal distance from equilibrium at which the condition $N_0>0$ may be realized, is

$$\delta x_0>\left|\frac{N_e}{\frac{dN}{dx_0}}\right|. \tag{63}$$

The amplitude of the distance from equilibrium δx_0 has thus a lower bound below which the ORFI cannot be observed. It is equivalent to conclude that the ORFI is a dissipative instability, or that the patterns are *dissipative structures* [15].

B. Properties of reaction schemes

In order that the ORFI be possible, the chemical scheme must include at least two reactions $(R\geqslant 2)$. Indeed, if $R=1$, the stationary condition for homogeneous states is equivalent to the equilibrium condition and we have shown in the preceding section that the ORFI cannot be observed at equilibrium. Furthermore, the scheme must include at least one autocatalytic reaction, i.e., a reaction in which the stoichiometric coefficients of at least one component of the mixture (X_1 or X_2) are nonzero for both the direct and the reverse transformations ($a_{r1}\neq 0$, $b_{r1}\neq 0$ or $a_{r2}\neq 0$, $b_{r2}\neq 0$). Indeed, if all the reactions in the scheme are nonautocatalytic, they can be rewritten as

$$\nu_r X+\sum_i a_{ri}B_i\rightleftharpoons \nu_r Y+\sum_i b_{ri}B_i, \tag{64}$$

where ν_r stands now for a_{r1} and b_{r2}. In that case, the parameter $N(x_0)$ reduces to

$$N(x_0)=-\frac{1}{2}\sum_{r=1}^{R}\nu_r^2\tau_r(x_0)[1-x_0+\rho(x_0)(1+x_0)], \tag{65}$$

which is negative and the ORFI is impossible. Hence, it is interesting to note that simple reaction schemes cannot give rise to the ORFI. In particular, binary systems undergoing simple reactions like $B_1+X \rightleftharpoons Y+B_2$ will not induce pattern formation, even under far from thermodynamic equilibrium conditions.

C. Example

To illustrate by an example the ORFI described in Sec. III, we consider the following two step autocatalytic reaction scheme:

$$B_1+2X_1+X_2 \rightleftharpoons 3X_1+B_2, \tag{66a}$$

$$B_1+X_1+X_2 \rightleftharpoons 2X_2+B_2. \tag{66b}$$

B_1 and B_2 are initial and final products the concentrations of which are kept constant by external reservoirs. The mixture free energy is defined by choosing for $z(x)$ the regular solution form

$$z(x)=\frac{RT}{x(1-x)}-2\Omega. \tag{67}$$

In the reservoir, for simplicity, we suppose that the mixture of B_1, B_2 is ideal and define accordingly their chemical potentials as

$$\mu_{B_1}=\Psi+RT\ \ln(x_{B_1}), \tag{68}$$

$$\mu_{B_2}=\Psi+RT\ \ln(1-x_{B_1}). \tag{69}$$

Adopting for the reaction rates the exponential form (37), the kinetic equation for x reads

$$\begin{aligned}\partial_t x=\tau_1&\left[\exp\left(\frac{\mu_{B_1}+2\mu_1+\mu_2}{RT}\right)-\exp\left(\frac{3\mu_1+\mu_{B_2}}{RT}\right)\right]\\&-\tau_2\left[\exp\left(\frac{\mu_{B_1}+\mu_1+\mu_2}{RT}\right)-\exp\left(\frac{2\mu_2+\mu_{B_2}}{RT}\right)\right]\\&+L\nabla^2(\mu_1-\mu_2),\end{aligned} \tag{70}$$

where

$$\mu_1=\mu_1^0+RT\ \ln(x)+\Omega(1-x)^2-\frac{\kappa+\Delta}{2}\nabla^2 x-\frac{\kappa}{2}(\nabla x)^2, \tag{71}$$

$$\mu_2=\mu_2^0+RT\ \ln(1-x)+\Omega x^2+\frac{\kappa-\Delta}{2}\nabla^2 x-\frac{\kappa}{2}(\nabla x)^2. \tag{72}$$

We have seen that the affinity $\mathcal{A}_T/RT=2\ \ln(x_{B_1}/x_{B_2})$ of the overall reaction

$$2B_1 \rightleftharpoons 2B_2 \tag{73}$$

cannot be taken equal to zero, which implies that x_{B_1} cannot be equal to 1/2. Here, we set $x_{B_1}=0.87$ and, for simplicity, we take the parameters depending on the intermolecular interactions as being constant: $\kappa(x)\equiv\kappa=1.0$, $\Delta(x)\equiv\Delta=-0.3$, and $\Omega=2.2$. Letting further the chemical relaxation times τ_1, τ_2 as well as the Onsager coefficient L and RT be equal to one, and choosing for to the reference chemical potentials the values $\mu_1^0=0.122, \mu_2^0=0.183, \Psi=-0.288$ one finds that Eq. (70) admits three homogeneous stationary solutions x_0, namely: $x_0^a=1/2, x_0^b=0.024\,279$ and $x_0=x_0^c=0.269\,59$. The stationary state $x=x_0^b$ is stable for all k's, while $x=x_0^c$ is unstable for a range of k values which includes the mode $k=0$. The stationary state $x=x_0^a$, which lies in the spinodal region, on the contrary, is unstable with respect to the finite band of wave number $k_-\approx 0.3453<k<k_+\approx 0.5295$ from which the mode $k=0$ is excluded. Taking this state as average initial condition and integrating Eq. (70) numerically, one finds (see Fig. 1) that instead the Ostwald ripening process which would be observed in the absence of chemistry, a stable pattern with hexagonal symmetry finally establishes itself in the course of time.

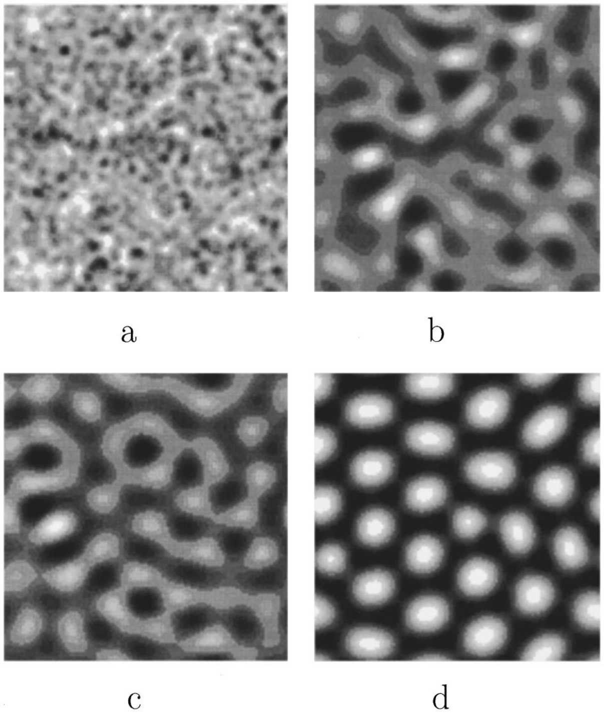

FIG. 1. Snapshots of the density profile, for example, (70) for (a) $t=0$, (b) $t=200$, (c) $t=450$, and (d) $t=30\,000$. The domain size is 90×90 and the simulation is made with 128×128 points. The values of the parameters are given in the text.

A complete discussion of the various nonlinear behaviors which may arise in models such as (66a) and (66b) will be presented elsewhere.

V. CONCLUSION

To investigate the idea that chemical reactions may freeze the unmixing of immiscible mixtures at an early stage of spinodal decomposition, we have developed an approach which is based on general thermodynamic arguments, encompasses equilibrium as well as nonequilibrium situations and does not rely on the FFEIA.

Within the framework of this approach, we have established that the linear stability properties of chemically reacting binary mixtures can be classified into four categories, one of which (case 4, Sec. III) corresponds to the soft mode stabilization effect leading to phase separation freezing. To encounter this case, it is indispensable that the system considered be dissipative, that it undergoes a chemical process comprising at least two independent reaction steps and that at least one of these steps be autocatalytic. It is a remarkable fact that those properties are exactly those of the model studied by Huberman in his twenty year old pioneering paper [2].

From a kinetic point of view, our results do not support the recent claims that the chemical freezing of phase separation is an ubiquitous phenomenon [5] susceptible to be observed with very simple chemistry. The monomolecular systems, involving a single reaction step of the form $A \rightleftharpoons B$, which have been introduced recently to study the ORFI must be considered as ''toy'' models. They have, however, the advantage of simplicity and of furnishing an appropriate description of a certain experimentally realizable situation [7]. As such, they could be viewed as a convenient ansatz for approximating the more complex chemical interactions and reaction schemes which need to be considered in reality. It is also worth mentioning that the recent molecular dynamic studies which have been devoted to the ORFI [17], and which constitute another approach for this problem do not show any chemical freezing of the spinodal decomposition with the reaction $A \rightleftharpoons B$. This result, which suggests that hydrodynamics may affect the coupling between reactions and phase separation, is a point which deserves further investigation.

Finally, our results draw attention to the enlarged variety of symmetry breaking instabilities which may be encountered in nonideal systems, even in domains of parameter space where the occurrence of phase transitions can be excluded. This feature which we have reported earlier in the case of anisotropic ternary mixtures [18] is further illustrated by the chemically reacting binary systems considered here, notably by their behavior in response to variations of the self-interaction parameter δ.

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[1] For reviews, see e.g., J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8; K. Binder, in *Phase Transformations of Materials* (Material Science and Technology 5), edited by P. Haasen (VCH, Weinheim, 1991).

[2] B. A. Huberman, J. Chem. Phys. **65**, 2013 (1976); see also, D. J. Scalapino and B. A. Huberman, Phys. Rev. Lett. **39**, 1365 (1977); E. Coutsias and B. A. Huberman, Phys. Rev. B **24**, 2592 (1981).

[3] S. Puri and H. L. Frisch, J. Phys. A **27**, 6027 (1994).

[4] S. C. Glotzer, D. Stauffer, and N. Jan, Phys. Rev. Lett. **72**, 4109 (1994).

[5] S. C. Glotzer, E. A. Di Marzio, and M. Muthukumar, Phys. Rev. Lett. **74**, 2034 (1995).

[6] J. Verdasca, P. Borckmans, and G. Dewel, Phys. Rev. E **52**, 4616 (1995).

[7] Q. Tran-Cong, T. Nagaki, O. Yano, and T. Soen, Macromolecules **24**, 1505 (1991). For recent experimental results, see A. Imagawa and Q. Tran-Cong, *ibid.* **28**, 8388 (1995); Q. Tran-Cong and A Harada, *ibid.* **76**, 1162 (1996), and the references cited therein.

[8] J. J. Christensen, K. Elder, and H. C. Fogedby, Phys. Rev. E **54**, 2212 (1996).

[9] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958).

[10] R. Lefever, D. Carati, and N. Hassani, Phys. Rev. Lett. **75**, 1674 (1995).

[11] I. Prigogine and R. Defay, *Chemical Thermodynamics* (Longmans, Green, New York, 1962).

[12] M. Gitterman, J. Stat. Phys. **58**, 707 (1990).

[13] S. C. Glotzer, D. Stauffer, and N. Jan, Phys. Rev. Lett. **75**, 1675 (1995).

[14] G. N. Lewis and M. Randall, *Thermodynamics* (Longmans, Green, New York, 1961); E. A. Guggenheim, *Thermodynamics* (North-Holland, Amsterdam, 1967).

[15] P. Glansdorff and I. Prigogine, *Thermodynamics of Structure, Stability and Fluctuations* (Wiley-Interscience, New York, 1971); G. Nicolis and I. Prigogine, *Selforganization in Nonequilibrium Systems* (Wiley-Interscience, New York, 1977).

[16] D. Carati and R. Lefever (in preparation).

[17] S. Toxvaerd, Phys. Rev. E **53**, 1 (1996).

[18] R. Lefever and D. Carati, Physica A **213**, 90 (1995).