

## Small roughness fluctuations in the layer between two phases

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(Received 20 December 1979)

A recently studied autocatalytic chemical reaction model for a nonequilibrium first-order phase transition is applied to fluctuations in surface density at the phase boundary. The model is exactly soluble for the dynamics of small fluctuations. The analysis also carries through for fluctuations from solitary solutions.

### I. INTRODUCTION

A reaction model for a chemical instability was constructed especially because it combines simplicity with the capacity to show the phenomenon of a nonequilibrium phase transition of first order.<sup>1</sup> The inclusion of diffusion of a distinguishable "autocatalytic" component turns this model into a system which shows a close analogy to the liquid-gas system. The nonequilibrium steady states with steadily running reaction are very similar to the equilibrium states of the liquid-gas system. The density of the gaseous phase corresponds to a lower concentration  $n_1$  and that of the liquid phase, to a higher concentration  $n_2$  of the autocatalytic chemical component in the reaction model. The temperature and the pressure in the equilibrium-state diagram of the liquid-gas system correspond to the steady-state concentrations of two other chemical components held constant by adequate feeding of the reactor. The two "phases" separate into different domains in space with minimal interface. Thus the domains become spherical like droplets or bubbles. The coexistence value of the concentration which in the analogy to the liquid-gas system corresponds to vapor pressure depends like vapor pressure on the curvature of the interface. In case of a plane interface it is determined by a Maxwellian construction.

The model is in many respects simpler than the models for the liquid-gas system, in particular with respect to the dynamics of the nonstationary states. Thus it was analyzed in different respects by different authors.<sup>2-17</sup> In the so-called deterministic description, which will be used in this paper, dynamics is given in the form of a differential equation in space and time for the concentration of the autocatalytic component. Other descriptions are the stochastic theories in which the concentration or the particle number of this component is dealt with as a random quantity. This is done by a master equation description or

by the introduction of fluctuating Langevin forces.

The simplicity of the model allows rigorous mathematical analysis of many questions that cannot be answered directly for the liquid-gas system. Thus the model can help to find features which are, up to slight variations, common with the latter system and with other systems showing an equilibrium or nonequilibrium phase transition. We use the model in that spirit in this paper to discuss the dynamical behavior of small fluctuations in the interface layer between the two coexisting phases. We also show that the results can be extended to slowly moving solitary states. These are nonstationary states which describe a moving interface due to a feeding. The conditions for such states differ from the conditions for the steady coexistence state of the two phases. These solitary states correspond to a vaporization or to a condensation process.

### II. DYNAMICAL EQUATIONS

The chemical reaction system is given by the reaction equations



between molecules of species  $A, B, C, X$ . The concentrations of  $A, B, C$  are held constant in space and time by adequate feeding. The concentration  $n$  of the "autocatalytic" species  $X$  is variable. The species  $X$  can diffuse in space owing to Fick's law. By adequate choice of units for time, length, and concentrations the dynamical equation takes the form

$$\dot{n} = \varphi(n) + \nabla^2 n \quad (2.3)$$

with the kinetic rate function

$$\varphi(n) = -n^3 + 3\alpha n^2 - \beta n + \gamma, \quad (2.4)$$

where  $\alpha, \beta, \gamma$  are the concentrations of  $A, B$ , and  $C$ , respectively. The choice of units which leads to the factor 3 will prove to be convenient.

The dynamics given by Eqs. (2.3) and (2.4) are more general than the special reaction system given by (2.1) and (2.2) and can be considered as the proper basis of the model. We are interested in particular in the case where the control parameter  $\beta$ , which in the analogy to the liquid-gas system corresponds to the temperature, is below the critical value

$$\beta_c = 3\alpha^2, \quad (2.5)$$

because then

$$\varphi(n) = -(n - n_1)(n - n_2)(n - n_3) \quad (2.6)$$

has three real roots

$$n_1 \leq n_3 \leq n_2. \quad (2.7)$$

In the homogeneous reactor without diffusion  $n_1$ ,  $n_2$  represent two stable steady states, and  $n_3$  an unstable steady state. Steady states are the time-dependent solution of the dynamical equation (2.3). If diffusion is included, the two phases  $n_1, n_2$  can coexist in different domains in space. We are interested in particular in a plane interface between the phases. Such a state is steady only if  $\gamma$  has the special coexistence value which is obtained by the Maxwellian construction; that is,  $\gamma$  must have the value for which  $\varphi(n)$  satisfies

$$\int_{n_1}^{n_2} dn \varphi(n) = 0. \quad (2.8)$$

Then

$$n_1 = n_3 - \nu_0, \quad (2.9)$$

$$n_2 = n_3 + \nu_0. \quad (2.10)$$

This yields

$$n_3 = \alpha, \quad (2.11)$$

$$\nu_0^2 = \beta_c - \beta. \quad (2.12)$$

With

$$\nu = n - \alpha \quad (2.13)$$

we can write

$$\varphi = -\nu(\nu^2 - \nu_0^2). \quad (2.14)$$

The detailed contour of the interphase layer is described by the dependence of  $\nu$  on the Cartesian coordinate  $x_3$ , normal to the layer. In the steady state of coexisting phases

$$\nu = \nu_0 \tanh \sigma x_3 \equiv \nu^* = \nu_0 \zeta. \quad (2.15)$$

The dynamical equation (2.3) with vanishing  $\dot{n}$  shows that

$$2\sigma^2 = \nu_0^2. \quad (2.16)$$

We replace  $x_3$  by the new variable  $\zeta$  introduced by Eq. (2.15) for which

$$\frac{\partial}{\partial x_3} = \sigma(1 - \zeta^2) \frac{\partial}{\partial \zeta}. \quad (2.17)$$

For the description of fluctuations in the interphase layer we introduce  $\psi$  by

$$\nu - \nu^* = \nu_0 \psi \quad (2.18)$$

and transform the dynamical equation (2.3) into the form

$$\sigma^{-2} \dot{\psi} = [(1 - \zeta^2) \mathfrak{D}_2^2 + \sigma^{-2} \Delta] \psi - 6\zeta \psi^2 - 2\psi^3 \quad (2.19)$$

with the operators

$$\Delta = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}, \quad (2.20)$$

$$\mathfrak{D}_1^m = \frac{\partial}{\partial \zeta} \left( (1 - \zeta^2) \frac{\partial}{\partial \zeta} \right) + [l(l+1) - (1 - \zeta^2)^{-1} m^2]. \quad (2.21)$$

The latter is the linear operator of the differential equation for the Legendre functions  $P_l^m(\zeta)$

$$\mathfrak{D}_1^m P_l^m(\zeta) = 0. \quad (2.22)$$

### III. REGRESSION OF SMALL FLUCTUATIONS

For small fluctuations the terms in Eq. (2.19) which are nonlinear in  $\psi$  can be neglected. This leads to

$$\sigma^{-2} \dot{\psi} = (1 - \zeta^2) \mathfrak{D}_2^2 \psi + \sigma^{-2} \Delta \psi. \quad (3.1)$$

There is no complete set of solutions separable in  $\zeta, x_1, x_2, t$ . However, a separation in  $\zeta$  and the new variables

$$\xi_i = \sigma(1 - \zeta^2)^{1/2} x_i \quad (i = 1, 2), \quad (3.2)$$

$$\tau = \sigma^2(1 - \zeta^2)t \quad (3.3)$$

is successful. Expressed in these variables the dynamical equation assumes the form

$$\frac{\partial}{\partial \tau} \psi = \left( \mathfrak{D}_2^2 + \frac{\partial^2}{\partial \xi_1^2} + \frac{\partial^2}{\partial \xi_2^2} \right) \psi. \quad (3.4)$$

Let  $\chi(\xi_1, \xi_2)$  be the solutions of the eigenvalue problem for the differential equation

$$\left( \frac{\partial^2}{\partial \xi_1^2} + \frac{\partial^2}{\partial \xi_2^2} + \tilde{k}^2 \right) \chi = 0 \quad (3.5)$$

with suitable boundary conditions leading to eigenvalues  $\tilde{k}$ . As the introduction of  $\xi_i$  by Eq. (3.2) is connected with the distinction of a zero point of  $x_i$  in the interface, we can immediately write

$$\chi = J_\mu(\tilde{k}\rho) e^{i\mu\phi} \quad (3.6)$$

with

$$\xi_1 + i\xi_2 = \rho e^{i\phi} \quad (3.7)$$

in terms of the Bessel functions  $J_\mu$  of integer order  $\mu$ , provided that no finite boundaries are

present. The variable  $\rho$  is related to the cylindrical coordinate

$$r = (x_1^2 + x_2^2)^{1/2} \quad (3.8)$$

by

$$\rho = \sigma(1 - \zeta^2)^{1/2} r. \quad (3.9)$$

The separation ansatz

$$\psi = u(\zeta) \chi(\rho, \Phi) e^{-\tilde{\lambda} r} \quad (3.10)$$

leads to the differential equation for  $u$ :

$$\mathfrak{D}_1^2 u(\zeta) = 0, \quad (3.11)$$

where

$$l(l+1) = 6 + \tilde{\lambda} - \tilde{k}^2. \quad (3.12)$$

We require that the fluctuations are restricted to the interphase layer. Therefore  $u$  has to vanish for infinite  $x_3$  corresponding to  $\zeta^2$  going to 1. This is possible only for

$$u(\zeta) = CP_l^2(\zeta) \quad (3.13)$$

with integer  $l \geq 2$ . These solutions form an orthogonal system of functions which is complete in the space of functions in the interval between +1 and -1 and vanishing in these limiting points proportional to  $1 - \zeta^2$ . Any fluctuation which vanishes not slower than these functions as  $\zeta^2$  approaches 1 is a linear combination of the modes given by Eq. (3.10). These modes are explicitly written with use of Eq. (3.6)

$$\psi = CP_l^2(\zeta) J_\mu(kr) e^{i\mu\Phi} e^{-\lambda t}, \quad (3.14)$$

where

$$k = \sigma(1 - \zeta^2)^{1/2} \tilde{k}, \quad (3.15)$$

$$\lambda = \sigma^2(1 - \zeta^2) \tilde{\lambda}. \quad (3.16)$$

Thus for a given  $k$  we obtain

$$\lambda = k^2 + \sigma^2(1 - \zeta^2)[l(l+1) - 6]. \quad (3.17)$$

Of particular interest is the case that the eigenvalues  $k$  are restricted by cylindrical boundary conditions, for instance, if  $\psi$  has to vanish for a certain radius  $r=R$ . Then  $kR$  are the zeros of  $J_\mu(x)$ . The coefficient

$$\sigma = \left[ \frac{1}{2}(\beta_c - \beta) \right]^{1/2} \quad (3.18)$$

vanishes as the system approaches its critical point. This corresponds to a critical slowing down of the fluctuations. Equation (3.17) is a dispersion equation connecting  $\lambda$  with  $k$ . The mode  $l=2$  for vanishing small  $k$  is time independent. It describes an infinitesimal shift of the interface

$$\tanh\sigma(x_3 + \delta x_3) = \tanh\sigma x_3 + \frac{1}{3} P_2^2(\zeta) \delta x_3 + \dots \quad (3.19)$$

That such a shift does not regress is a conse-

quence of the invariance of the dynamical equation (2.3) against a shift in space.

#### IV. EXTENSION TO THE SOLITARY SOLUTIONS

If  $\gamma$  is different from the coexistence value which is determined by the Maxwellian construction, no steady plane interface between the two phases can exist. Yet nonstationary states are possible in which the plane interface moves with a constant velocity. These states are of the general type of solitary solutions; solutions are so-called which do not change in an adequate moving system of reference.

If the Maxwellian construction is not satisfied,

$$\frac{1}{2}(n_1 + n_2) = \bar{n} \quad (4.1)$$

is different from  $n_3$ . We write

$$\nu = n - \bar{n}, \quad (4.2)$$

$$\nu_0 = \frac{1}{2}(n_2 - n_1), \quad (4.3)$$

$$n_3 = \bar{n} + \nu_0 a. \quad (4.4)$$

Then we obtain

$$\psi = -(\nu - \nu_0 a)(\nu^2 - \nu_0^2). \quad (4.5)$$

As ansatz for a solitary solution we choose

$$\tilde{\nu} = \nu_0 \zeta(x_3, t) \quad (4.6)$$

with

$$\zeta(x_3, t) = \tanh\sigma(x_3 - ct), \quad (4.7)$$

where  $c$  is the constant velocity of the interface into the  $x_3$  direction. This function  $\tilde{\nu}$  satisfies the equation

$$\begin{aligned} \dot{\tilde{\nu}} - \varphi(\tilde{\nu}) - \frac{\partial^2}{\partial x_3^2} \tilde{\nu} = \nu_0(1 - \zeta^2) \\ \times [-c\sigma - \nu_0^2(\zeta - a) + 2\sigma^2\zeta]. \end{aligned} \quad (4.8)$$

The right-hand side vanishes and thus  $\tilde{\nu}$  indeed becomes a solution of the dynamical equation if Eq. (2.15) holds and if

$$c = 2\sigma a. \quad (4.9)$$

Thus the solitary solution is

$$\tilde{\nu} = \sigma 2^{1/2} \tanh\sigma(x_3 - 2\sigma a t). \quad (4.10)$$

Now we write small fluctuations from such a solution as

$$\nu - \tilde{\nu} = \nu_0 \psi. \quad (4.11)$$

After linearization in  $\psi$ , the dynamical equation takes the form

$$\dot{\psi} = \nu_0^2(1 - 3\zeta^2 + 2a\zeta)\psi + \nabla^2\psi. \quad (4.12)$$

If we generally go over from  $x_3$  to the variable  $\zeta$ , we obtain

$$\sigma^{-2}\dot{\psi} = (1 - \zeta^2)\mathcal{D}_2^2\psi + \sigma^{-2}\Delta\psi + 4a\zeta\psi \quad (4.13)$$

which differs from Eq. (3.1) by the addition of the last term.

We again introduce new variables  $\xi, \tau$  by Eqs. (3.2) and (3.3) where, to be sure,  $\zeta$  now is given by Eq. (4.7). The separation ansatz of Eq. (3.10) leads to

$$[\mathcal{D}_1^2 + 4a\zeta(1 - \zeta^2)^{-1}]u(\zeta) = 0, \quad (4.14)$$

instead of Eq. (3.11), where again Eq. (3.12) holds.

If the velocity of the solitary solution and with it  $a$  is small enough, the new term with  $a$  in Eq. (4.14) can be dealt with as a small perturbation. The unperturbed solution is

$$u_0(\zeta) = CP_1^2(\zeta). \quad (4.15)$$

Let

$$u = u_0 + u_1 \quad (4.16)$$

be the perturbed solution. Then we obtain for the first approximation a perturbation  $\delta\bar{\lambda}$  of  $\bar{\lambda}$  by the relation

$$\delta\bar{\lambda} \int_{-1}^{+1} d\zeta u_0^2 = -4a \int_{-1}^{+1} d\zeta \zeta(1 - \zeta^2)^{-1} u_0^2. \quad (4.17)$$

Owing to the antisymmetry of the integrand at the right-hand side,  $\delta\bar{\lambda}$  vanishes in the first order of the perturbation. Hence, in the reference frame moving with the layer, the fluctuations in the solitary solutions for the interface layer are the same as those of the stationary layer if the velocity of the solitary solution is slow enough. Strictly speaking, changes in the behavior of the fluctuations can occur only in second or higher order of  $a$ .

#### V. SOME CONCLUDING REMARKS

The simple cubic model represented by (2.3) and (2.4) is not only useful because it leads to exactly

soluble equations. We wish to point out that the model also has the characteristic that it becomes an exact model in the vicinity of the critical region, for all but pathological cases. This is because the cubic is the first nonvanishing term in the expansion of the isotherms in the vicinity of the critical point, just as the quadratic is the first nonvanishing term in the expansion of a potential in the vicinity of a minimum.

Lastly, we wish to point out that the exact soluble model presented here should be looked upon as a first step toward more realistic analyses of one kind of surface roughening. By introducing additional inhomogeneous terms into Eqs. (2.3), (2.4), and (2.19), one can represent forces and constraints that are at the command of the experimentalist. One can envision, for example, introducing boundaries or fields that vary spatially, such as variable-diameter pipes with axes along the  $x_3$  direction. In the neighborhood of the critical region, where the correlation length is large, such variations can be expected to have significant influence on the behavior of the two-phase system.

The stability of fluctuations of finite size is a problem for which this model seems appropriate, and we have begun to consider it.

#### ACKNOWLEDGMENTS

The authors would like to acknowledge the hospitality of the Aspen Center for Physics, where this work was started, during a workshop supported by the National Science Foundation. R. S. B. would also like to express his thanks to Chemistry Laboratory III, The University of Copenhagen, where his part of the research was completed. We want to thank Dr. D. B. Abraham and Dr. O. J. Heilmann for reading the manuscript.

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