

Nucleation in Systems with Multiple Stationary States

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We consider a reaction diffusion system, far from equilibrium, which has multiple stationary states (phases) for given ranges of external constraints. If two stable phases are put in contact, then in general one phase annihilates the other and in that process there occurs a single front propagation (soliton). We investigate the macroscopic dynamics of the front structure and velocity for two model systems analytically and numerically, and for general reaction-diffusion systems by a suitable perturbation method. The vanishing of the soliton velocity establishes the analogue of the Maxwell construction used in equilibrium thermodynamics. The problem of nucleation of one phase imbedded in another is studied by a stochastic theory. We show that if the reaction dynamics is derived from a generalized potential function then the macroscopic steady states are extrema of the probability distribution. We use this result to obtain an expression for the critical radius of a nucleating phase and confirm the prediction of the stochastic theory by numerical solution of the deterministic macroscopic kinetics for a model system.

1. INTRODUCTION

Chemical reaction mechanisms with macroscopic rate laws of sufficient non-linearity in systems maintained far from equilibrium may have multiple stationary stable states¹⁻⁶ for given external constraints. We refer to each such state as a phase and transitions between phases are possible. The analogy of the theory of phase transitions and critical phenomena to transitions between stable states and critical (marginal stability) points has been discussed in some detail, both at the macroscopic and statistical mechanical level of analysis.⁷⁻⁹ In this paper we investigate the nucleation of one phase within another phase, as well as the conditions of coexistence of two phases (the analogue of the Maxwell construction). These problems have been considered by: Kobatake⁷ who showed for a particular case the similarity of the behaviour of the generalized entropy production³ in transitions between stable branches of steady states, and the Gibbs free energy in equilibrium phase transitions; by Schlögl,⁸ who took into account reaction and diffusion and treated coexistence of phases and the analogue of the Maxwell construction for one variable systems with the help of a mechanical analogy; and by Nicolis, Malek-Mansour, van Nypelseer and Kitahara,¹⁰ who analyzed the onset of instability as a nucleation process, derived a non-linear master equation for that purpose, and applied that result to some examples.

We approach these problems from two different points of view. First, in section 2 we investigate the macroscopic dynamics of two stable stationary states of semi-infinite extent, at given external constraints, placed in contact with each other. Except for one value of the constraints, one phase annihilates the other and in that process there occurs a single-front propagating wave, a soliton. We investigate the behaviour of the concentration profile and velocity of such a wave for two model systems analytically and numerically and show that the values of the external constraints for zero soliton velocity establish the Maxwell construction.

Further we study these quantities for general reaction-diffusion systems by a suitable perturbation method and find that the soliton velocity vanishes linearly in the deviation of the external constraint from its value at the Maxwell construction.

Next, in section 3, we discuss some aspects of a stochastic theory of instability phenomena on the basis of a Fokker-Planck equation assumed for a reaction-diffusion system. That equation can be solved for the steady state probability distribution for which the reaction dynamics is obtainable from a generalized potential function. In that case we show that the macroscopic steady states are extrema of the probability distribution, maxima for stable steady states. We apply this theory to analyze the behaviour of a system consisting initially of a nucleus of one phase embedded in an infinite bulk of the other phase; we do so in a manner similar to the conventional treatment of nucleation in first order phase transitions.^{11, 12} We thus obtain an expression for the critical radius for such a nucleus above which the nucleus grows, and below which it disappears in time. This prediction agrees with numerical solutions of the deterministic diffusion-reaction equation for a simple model system.

2. MACROSCOPIC DYNAMICAL THEORY

We consider a diffusion-reaction system for which the macroscopic deterministic equation of motion is

$$\frac{\partial \psi}{\partial t}(\mathbf{r}, t) = \mathbf{D} \nabla^2 \psi + F[\psi, \lambda]. \quad (2.1)$$

The symbols denote: ψ , a column vector of concentrations and possibly other state variables such as temperature; \mathbf{r} , spatial coordinates; t , time; \mathbf{D} , a matrix of diffusion coefficients; F , the variations due to chemical reaction; and λ , the set of external constraints (boundary concentrations of species, light intensity in an illuminated system,⁵ etc.). We assume that: 1. the diffusion matrix is constant and symmetric and the diffusion process is stable in that in the absence of reaction eqn (2.1) with $F = 0$) the steady state solution is stable; 2. F is analytic in ψ and λ . We consider systems for which there exist two stable stationary states (and one unstable stationary state) in a given range of λ . Thus if, in a one-dimensional system (coordinate x) we prepare two systems under identical external constraints, one system in one stable state (one phase) and the other system in the other stable state (the other phase), then the boundary at $x = 0$ between the two systems will move in one direction or another depending on λ . There occurs a single front propagation,¹³ a soliton, in which one phase annihilates the other. We shall find the condition for coexistence of two such systems (phases) to be zero soliton velocity, or a standing front at a given λ . We therefore seek wave solutions of (2.1) which are most readily studied in a reference frame moving with the front. We define the phase

$$\phi = x - vt, \quad (2.2)$$

where the soliton velocity v is a function of λ . With (2.2) the partial differential eqn (2.1) is converted into an ordinary differential equation

$$\mathbf{D} \frac{d^2 \psi}{d\phi^2} + v \frac{d\psi}{d\phi} + F[\psi, \lambda] = 0, \quad (2.3)$$

which is a nonlinear eigenvalue equation for v at a given λ . Coexistence occurs when $v = 0$ at $\lambda = \lambda_M$. The value of λ_M is obtained from eqn (2.4) which may be interpreted as an eigenvalue equation for λ_M ,

$$\mathbf{D} \frac{d^2 \psi_0}{d\phi^2} + F[\psi_0, \lambda_M] = 0. \quad (2.4)$$

We first consider a soluble model system and then present an analysis for more general $\{\mathbf{D}, \mathbf{F}\}$ systems.

The model system consists of a single species with third-order kinetics which obey the equation

$$\frac{\partial \psi}{\partial t} = D \frac{\partial^2 \psi}{\partial x^2} - q(\psi - a)(\psi - b)(\psi - c). \tag{2.5}$$

Homogeneous steady states occur at $\psi^* = a, b, c$, where these parameters are arbitrary functions of λ . We take $b \geq c \geq a, q > 0$, and thus only states a and b are stable to small homogeneous perturbations. If we define a new variable u such that

$$u \equiv \frac{\psi - a}{b - a},$$

then we obtain

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} - q(b - a)^2 u(u - 1) \left(u + \frac{(c - a)}{(b - c)} \right). \tag{2.6}$$

This is identical in form to a model considered by Montroll.¹² In terms of our notation his solutions for soliton fronts are

$$\psi(\phi) = a + (b - a)(1 + \exp(\pm \beta \phi))^{-1} \tag{2.7}$$

where

$$\beta = \left(\frac{q}{2D} \right)^{\frac{1}{2}} (b - a). \tag{2.8}$$

The front velocity is given by

$$v = (\frac{1}{2}qD)^{\frac{1}{2}}(a + b - 2c). \tag{2.9}$$

Coexistence occurs at $v = 0$, i.e.,

$$c = \frac{1}{2}(a + b) \text{ at } \lambda = \lambda_M, \tag{2.10}$$

which is obvious from the symmetry of the trilinear kinetics for which the two stable states a and b are located symmetrically about the unstable state c .

It is interesting to take a particular case and analyze it further. Let

$$F = -q\psi(\psi^2 - 2\psi + 1/\lambda). \tag{2.11}$$

Then $v = (\frac{1}{2}qD)^{\frac{1}{2}}[3(1 - 1/\lambda)^{\frac{1}{2}} - 1]$ and $\beta = (q/2D)^{\frac{1}{2}}[1 + (1 - 1/\lambda)^{\frac{1}{2}}]$, from (2.8, 9). The uniform steady states and the soliton velocity are shown in fig. 1(a) and (b). Coexistence is found at $\lambda_M = 9/8$. With this we obtain the structure of the coexistence region to be

$$\psi_{\text{coex.}}(x) = \frac{1}{3}(1 + \exp(\pm \beta_M x))^{-1}, \tag{2.12}$$

where $\beta_M = \frac{1}{3}(8q/D)^{\frac{1}{2}}$; the structure is shown in fig. 2.

We note from fig. 1(b) that the velocity passes through the origin at λ_M with a finite but non-zero slope $|(dv/d\lambda)_{\lambda_M}| \neq \infty$. This general property provides a useful aid in determining λ_M experimentally.

Next we consider the general system (2.1) by analyzing the solutions of the front eqn (2.3) in the vicinity of λ_M . To do so we introduce a parameter A to be defined at a later stage in the development, which measures the deviation of the system from coexistence conditions. In general, A is a function of λ ,

$$\lambda = \sum_{n=0}^{\infty} \lambda_n A^n, \tag{2.13}$$

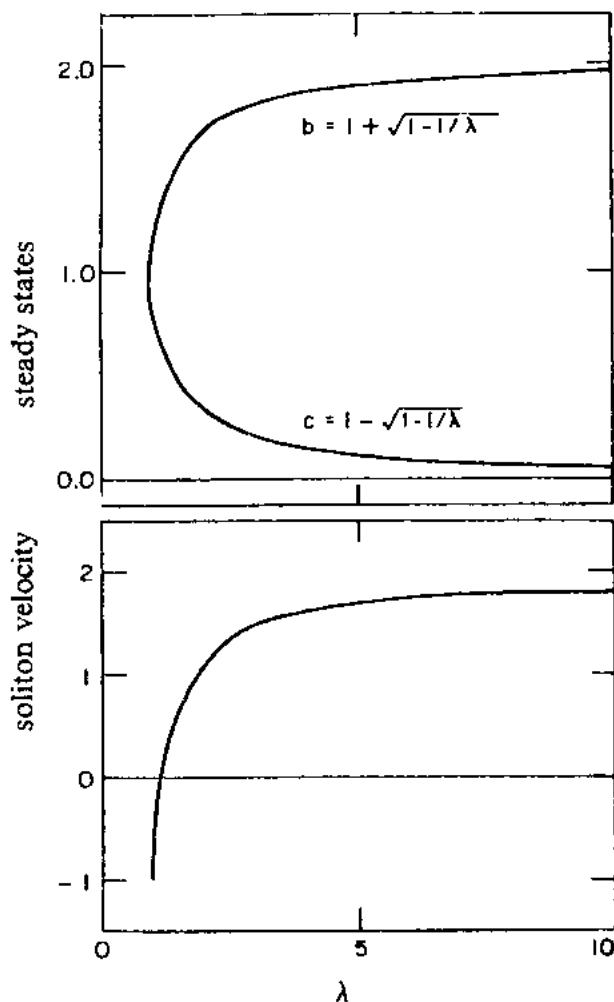


FIG. 1.—Steady states and soliton velocity versus the parameter λ for the model system eqn (2.11).

and we expect that A approaches zero proportional to the factor $(\lambda - \lambda_M)$ raised to some positive power. Furthermore ψ and v depend on A ,

$$\psi = \sum_{n=0}^{\infty} \psi_n(\phi) A^n \quad (2.14)$$

$$v = \sum_{n=0}^{\infty} v_n A^n. \quad (2.15)$$

Such expansions have been employed elsewhere for the study of chemical waves.¹⁵ On substitution of the expansions (2.13-15) into (2.3) we recover to zero'th order in A ,

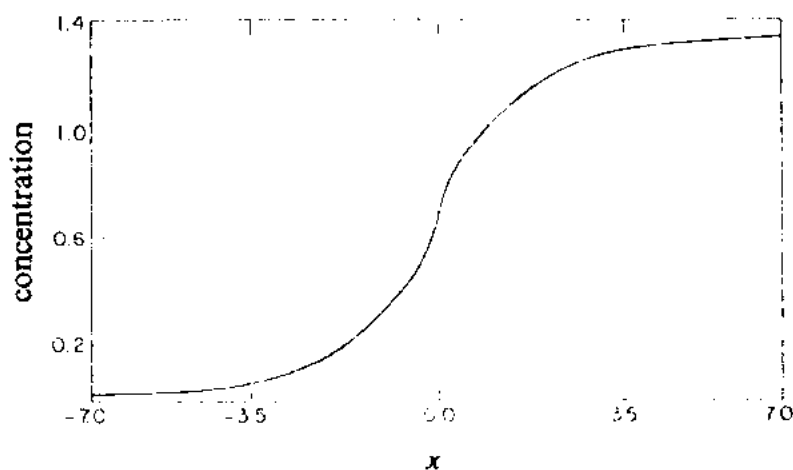


FIG. 2.—Structure of the coexistence region versus distance, eqn (2.12), for the model system eqn (2.11).

eqn (2.4), with the boundary conditions of the system being one stable stationary state at $x = -\infty$, and the other stationary stable state at $x = +\infty$. We also have by definition in this order $v_0 = v(\lambda_M) = 0$.

To first order in the parameter A we find

$$-\mathcal{L}\psi_1 = v_1 \frac{d\psi_0}{d\phi} + \left(\frac{\partial F}{\partial \lambda}\right)_0 \lambda_1 \quad (2.16)$$

with the operator \mathcal{L} defined by

$$\mathcal{L} \equiv D \frac{d^2}{d^2\phi^2} + \Omega \quad (2.17a)$$

$$\Omega \equiv (\partial F / \partial \psi)_0 \quad (2.17b)$$

and the subscript 0 following differentiation implies evaluation in lowest order. We note that differentiation of (2.4) with respect to ϕ yields

$$\mathcal{L} \frac{d\psi_0}{d\phi} = 0. \quad (2.18)$$

We assume that $d\psi/d\phi$ is the only eigenfunction of \mathcal{L} with zero eigenvalue. $\mathcal{L}^{-1}(d\psi/d\phi)$ does not exist and hence the solution of (2.8) for ψ_1 cannot be found for arbitrary (v_1, λ_1) . The problem is overcome by a proper choice of these coefficients. We then define a vector Θ such that

$$\mathcal{L}^+\Theta = 0, \quad (2.19)$$

where \mathcal{L}^+ is the adjoint operator of \mathcal{L} . If we define an inner product

$$(A|B) = \sum_i \int_{-\infty}^{\infty} d\phi A_i^* B_i, \quad (2.20)$$

where the sum on i runs over all species, then from (2.17, 20) \mathcal{L}^+ is given by

$$\mathcal{L}^+ = D^+ \frac{d^2}{d\phi^2} + \Omega^+. \quad (2.21)$$

(By assumption we have $D^+ = D$, Onsager's relations).

We can be assured of the solubility of the first order eqn (2.16) if we can choose v_1 and λ_1 such that the r.h.s. of (2.16) is orthogonal to the zero eigenvalue function $d\psi_0/d\phi$. Thus we obtain by use of the adjoint eigenfunction to $d\psi_0/d\phi$, that is Θ , see (2.19), that

$$v_1(\Theta|(d\psi_0/d\phi)) + \lambda_1(\Theta|(\partial F/\partial \lambda)_0) = 0. \quad (2.22)$$

The coefficient of v_1 may be chosen to be unity by proper normalization of Θ . Hence if the coefficient of λ_1 is finite, then this relation can be satisfied for finite v_1, λ_1 . Finally $(\partial F/\partial \lambda)_0$ approaches constant values as $|\phi| \rightarrow \infty$. A necessary condition for solubility is $\int_{-\infty}^{\infty} d\phi |\Theta(\phi)| < \infty$ in order to find $\lambda_1, v_1 \neq 0$. For systems where $\Omega^+ = \Omega$, \mathcal{L} is self adjoint and therefore $\Theta = d\psi_0/d\phi$. Since $d\psi_0/d\phi$ is localized to the region of the soliton front, it satisfies the necessary condition of solubility. However we have not investigated this condition for systems with $\Omega^+ \neq \Omega$.

It is sufficient to all orders to choose $\lambda_{n \geq 2} = 0$; thus with the convenient choice $\lambda_1 = 1$ we have

$$A \equiv \lambda - \lambda_M. \quad (2.23)$$

To first order the perturbation solution is

$$\psi(\phi)_{\lambda \rightarrow \lambda_M} \approx \psi_M(\phi) - \mathcal{L}^{-1} \left\{ \left(\frac{dv}{d\lambda} \right)_M \frac{d\psi_0}{d\phi} + \left(\frac{\partial F}{\partial \lambda} \right)_M \right\} (\lambda - \lambda_M) + \dots \quad (2.24)$$

$$v_{\lambda \rightarrow \lambda_M} \approx - \left[\frac{\Theta |(\partial F / \partial \lambda)_M|}{\Theta |(d\psi_0 / d\phi)|} \right] (\lambda - \lambda_M) + \dots \quad (2.25)$$

For the one variable system (2.5-12) we have verified these relations using the equation $\Theta = d\psi_0/d\phi$.

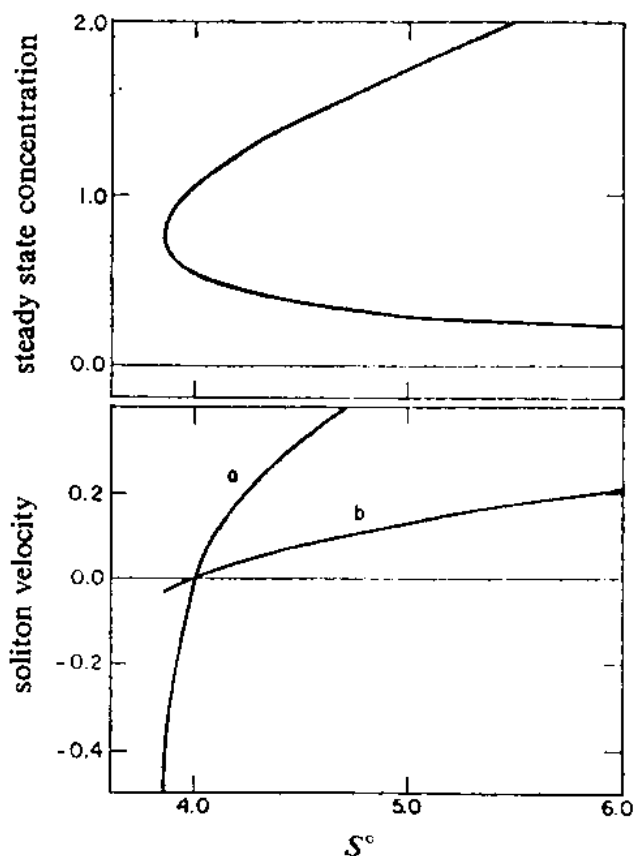


FIG. 3.—Steady state concentration and soliton velocity versus S^0 for the model system described in Appendix A. For curve (a) the diffusion coefficients D_S , D_P are both 1 and for curve (b) $D_S = 1$ and $D_P = 0.05$.

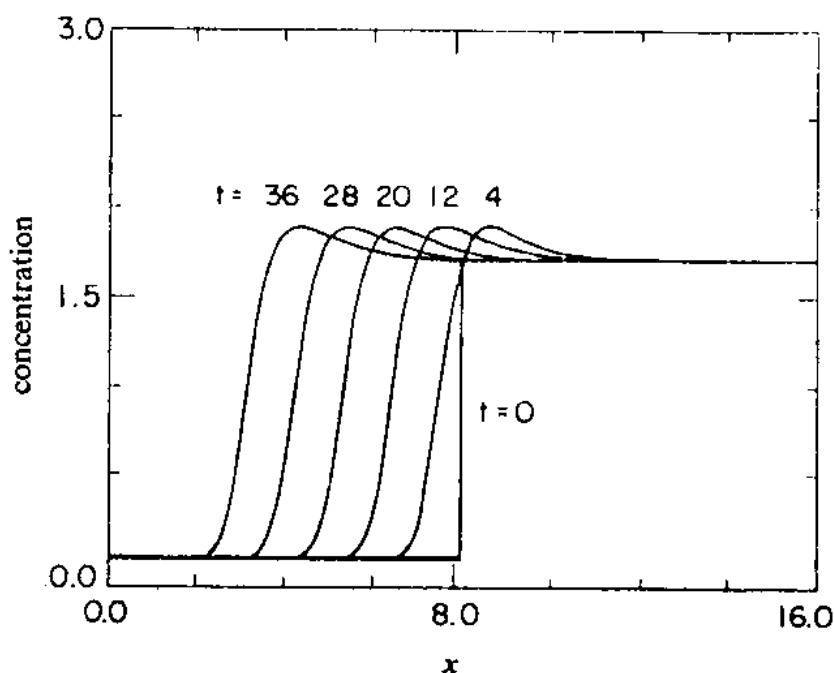


FIG. 4.—Soliton structure against distance at different times for the model system, Appendix A. The diffusion coefficients are $D_S = 1$, $D_P = 0.05$. The external concentration $S^0 = 5$.

Finally we note that the structure and velocity of the soliton depends in general not only on the reaction term F but also on the diffusion matrix D . If D is equal and diagonal then it may always be eliminated from the equation for the soliton front by a suitable scaling of the length, $\phi \rightarrow (\sqrt{D})\phi'$. However for more complex diffusion matrices this simple scaling no longer holds. In Appendix A we consider a two species system with rate mechanism



where S° , P° are maintained constant, and the activity of the enzyme E depends on P .

In fig. 3 we show the steady state concentration P^* as a function of S° and the results of the numerical integration of the partial differential equations yielding the variation of the soliton velocity against the concentration of S° for various choices of diffusion coefficients of S and P . For this system the value of S° at coexistence (λ_M of the general theory) does not appear to depend on the choice of diffusion coefficients to within the accuracy of the numerical computations; the results of the stochastic theory, section 3, indicate no dependence on that choice for systems for which the kinetics is derivable from a generalized potential function.

In fig. 4 we show the soliton structure for the same system (Appendix A) for the choice of diffusion coefficients $D_S = 1$, $D_P = 0.05$, and $S^\circ = 5$.

3. STOCHASTIC THEORY

Our treatment is based on a model in which to the set of reaction diffusion rate equations we add a stochastic source term to account for fluctuations in the system. The set of concentrations at each spatial point becomes then our set of stochastic variables. It is convenient to make this set discrete by dividing the system into cells of homogeneous composition. We thus consider the system of volume V to be partitioned into N cells each of volume $\bar{v} = V/N$. The macroscopic reaction kinetics is again given by

$$\left(\frac{d\psi}{dt} \right)_{rx} = F[\psi], \quad (3.1)$$

with a similar equation for ψ_n in the n th cell. The rate of change of numbers of particles of any species, $\chi_n = \bar{v}\psi_n$, due to diffusion is

$$\left(\frac{d\chi_n}{dt} \right)_{diff.} = \bar{v}^{1-(2/d)} \mathbf{D} \sum_i (\psi_{n+i} - \psi_n) \quad (3.2)$$

where the sum extends over the $2d$ nearest neighbour cells (d is the dimensionality of the system). The factor of $\bar{v}^{1-2/d}$ comes from multiplying by the surface area $\bar{v}^{1-1/d}$ of the cell and dividing by the characteristic length ($\bar{v}^{1/d}$) of a cell such that $(\psi_{n+i} - \psi_n)/\bar{v}^{1/d}$ is an approximation to the concentration gradient. Now we write a Langevin equation for this system as

$$\frac{d\chi_n}{dt} = \bar{v}F[\psi_n] + \bar{v}^{1-2/d} \mathbf{D} \sum_i (\psi_{n+i} - \psi_n) + (2K\bar{v})^\dagger \quad (3.3a)$$

or

$$\frac{d\psi_n}{dt} = F[\psi_n] + \bar{v}^{-2/d} \mathbf{D} \sum_i (\psi_{n+i} - \psi_n) + \left(\frac{2K}{\bar{v}} \right)^\dagger \quad (3.3b)$$

For simplicity we take the stochastic term to be Gaussian and thus to satisfy the usual relations $\langle f_n(t) \rangle = 0$ and $\langle f_{\alpha n}(t') f_{\beta m}(t) \rangle = \delta_{\alpha\beta} \delta_{nm} \delta(t-t')$ (α, β denote different chemical

components). Eqn (3.3b) is equivalent to the following Fokker-Planck equation for the probability density of finding the concentration distribution ψ_n , $P[\Psi]$, in the system

$$\frac{\partial P[\Psi]}{\partial t} = -\sum_n \sum_\alpha \left\{ \frac{\partial}{\partial \psi_{\alpha n}} (M_{\alpha n}[\Psi]P) - \frac{K}{\bar{v}} \frac{\partial^2 P}{\partial \psi_{\alpha n}^2} \right\} \quad (3.4)$$

where $M_n[\Psi]$ (with components $M_{\alpha n}[\Psi]$) is given by

$$M_n[\Psi] = F[\psi_n] + \bar{v}^{-2/d} \mathbf{D} \sum_{i=1}^{2d} [\psi_{n+i} - \psi_n]. \quad (3.5)$$

and where Ψ denotes the "supervector" ψ_n ($n = 1 \dots N$) ($= \psi_{\alpha n}$ ($n = 1 \dots N$, α goes over the different chemical species)). In (3.4) K was taken for simplicity as a scalar matrix, $K = KI$, where I is the unit matrix. The integration of this many-variable Fokker-Planck equation for steady state conditions, $(\partial P/\partial t) = 0$, is possible provided the reaction kinetics are such that the curl of M is zero,¹⁶

$$\frac{\partial M_{\alpha n}}{\partial \psi_\beta} = \frac{\partial M_{\beta n}}{\partial \psi_\alpha} \quad (3.6)$$

This condition should be modified if \mathbf{D} is not a symmetric matrix or if K is not a scalar matrix. If (3.6) holds then we obtain

$$P[\Psi] = C \exp(-U[\Psi]) \quad (3.7)$$

where C is a normalization constant. For simplicity we assume now that we have a one-component system, for which (3.6) always holds. The results for a more general case with a symmetric diffusion matrix are given in Appendix C. We write $U[\psi]$ as

$$U[\psi] = -\frac{1}{K} \left[\bar{v} \sum_n \left\{ G[\psi_n] - (\bar{v}^{-2/d}) \frac{D}{2} \sum_{i=1}^d (\psi_n - \psi_{n+i})^2 \right\} \right], \quad (3.8)$$

which in the continuum limit

$$\left(\bar{v} \sum_n \rightarrow \int d^d r, (\psi_n - \psi_{n+i})/\bar{v}^{1/d} \rightarrow \frac{\partial \psi(\mathbf{r})}{\partial r_i} \right)$$

becomes

$$U[\psi(\mathbf{r})] = -\frac{1}{K} \int d\mathbf{r} \left\{ G[\psi(\mathbf{r})] - \frac{D}{2} [\nabla \psi(\mathbf{r})]^2 \right\}. \quad (3.9)$$

The function $G[\psi(\mathbf{r})]$ is defined by

$$G[\psi(\mathbf{r})] = \int_0^\psi dy F[y] \quad (3.10)$$

which in case of many chemical species should be understood as a line integral in ψ space. Condition (3.6) ensures that this line integral is well defined and does not depend on the integration path. It is interesting to note that (3.9) has the same form as the free energy in the Landau-Ginzburg theory¹¹ (there $G(\psi)$ is usually taken as a quartic form). Also critical phenomena have been discussed with Hamiltonians of that form.¹⁷

Having arrived at an expression for the steady state probability distribution $P[\psi]$ we show next that extrema in that distribution are given by the steady states of the deterministic equation. Differentiation of (3.7) yields

$$\delta P = -P \frac{\delta U}{\delta \psi} \delta \psi \quad (3.11)$$

or

$$\delta P = -\frac{P}{K} \int dr \{F[\psi] \delta\psi - D\nabla\psi \cdot \nabla\delta\psi\} \quad (3.12)$$

which on partial integration becomes

$$\delta P = -\frac{P}{K} \int dr \{F[\psi] + D\nabla^2\psi\} \delta\psi. \quad (3.13)$$

For P to be an extremum for the arbitrary variation $\delta\psi$ we must have the integrand vanish; that is the macroscopic condition for steady states. It can be further shown that stable steady states correspond to maxima of the probability distributions (see Appendix B). The system may be in a single stable stationary state (although there exist other such states at the same external constraints) and in that case the system is homogeneous, i.e., $F[\psi] = 0$. However, two (or more) stable stationary states may coexist and the distribution of concentrations is the solution of $D\nabla^2\psi + F[\psi] = 0$ for given boundary conditions. Note that this is exactly the equation for the zero velocity soliton structure (eqn (2.3) with $v = 0$).

The stochastic theory for the probability distribution of a system in a steady state may be applied to the problem of nucleation. Consider a spherical nucleus of radius R of one stable stationary state, labelled phase B, immersed in an infinite bulk of another stable stationary state, labelled phase A, both under the same external constraints. Thus we have $F[\psi_A] = F[\psi_B] = 0$ for the individual, homogeneous phase. For phase B immersed in A, however, we may inquire about the expected stability of the spherical nucleus, that is the nucleus is expected to evolve in the direction of increasing the probability of the overall structure (nucleus + bulk). The logarithm of the ratio of the probability distribution for B phase immersed in A phase, P_{BA} , to that of pure A phase, P_A is

$$K \ln \frac{P_{BA}}{P_A} = -\left\{ \frac{2\pi^{d/2}}{d\Gamma(d/2)} R^d [G(B) - G(A)] - \frac{2\pi^{d/2} R^{d-1} D}{\Gamma(d/2)l} (\psi_B - \psi_A)^2 \right\} \quad (3.14)$$

where l is the width of the interface region, and where we have approximated the gradient by $(\psi_B - \psi_A)/l$. In eqn (3.14) we have used the following expression for the surface area S and the volume V of a d -dimensional sphere (Γ is the Γ -function)

$$S = \frac{2\pi^{d/2}}{\Gamma(d/2)} R^{d-1}$$

$$V = \frac{2\pi^{d/2}}{d\Gamma(d/2)} R^d.$$

The derivative (with respect to R) of the r.h.s. of (3.14), set equal to zero, gives the radius of the sphere of phase B for which the l.h.s. of (3.14) is a minimum, that is (for a given l)

$$R_c = \frac{D(\psi_B - \psi_A)^2(d-1)}{l(G[\psi_B] - G[\psi_A])}. \quad (3.15)$$

If $G[\psi_B] > G[\psi_A]$, then there exists a distribution (characterized by R_c) of maximum "free energy" (minimum probability) such that for $R > R_c$ the nucleus will grow (as this is the direction of increasing the probability) and for $R < R_c$ it will disappear in time. If $G[\psi_B] < G[\psi_A]$ then no positive R_c exists. Finally, if $G[\psi_B] = G[\psi_A]$ then $R_c = \infty$, and phases A and B coexist with a planar (zero curvature) surface of contact. This condition is clearly the analogue of the Maxwell construction in equilibrium

phase transitions. Furthermore, we expect that this condition is equivalent to the one of zero soliton velocity and have confirmed the expectation for the example given by (2.5).

In a many component curl-free system with a symmetric non-scalar diffusion matrix, the result (see eqn (C.1), Appendix C) shows that the Maxwell construction is again given by the condition $G[\psi_B] = G[\psi_A]$.

We stress that the arguments presented here are based on probabilistic considerations, especially on the postulate that a system will evolve in the direction of increasing the probability. The result (3.15) is similar in many respects to that for the radius of critical nucleus in equilibrium first order phase transitions.^{11, 12} The contribution of the diffusion process to the "free energy" U , eqn (3.9), takes here the place of the surface tension in the equilibrium nucleation treatment. The appearance of the parameter l in eqn (3.15) takes into account the non-zero thickness of the interphase layer. It should be remembered that l is not an independent parameter but is determined by the external parameters. Also, the simplifying assumption of linear variation of the concentration ψ across the interphase layer limits the applicability of the result (3.15).

We compare the results of the stochastic theory to the solution of the deterministic dynamical equations. To this end we numerically integrated the one variable partial differential equation

$$\frac{\partial \psi}{\partial t} = D \nabla^2 \psi - \psi^3 + b\psi + c \quad (3.16)$$

in which the cubic polynomial $F(\psi) = -\psi^3 + b\psi + c$ plays the role of a chemical source term. For $b > 0$ and $|c| < (2b/3)(\sqrt{b/3})$ this equation has two stable and one

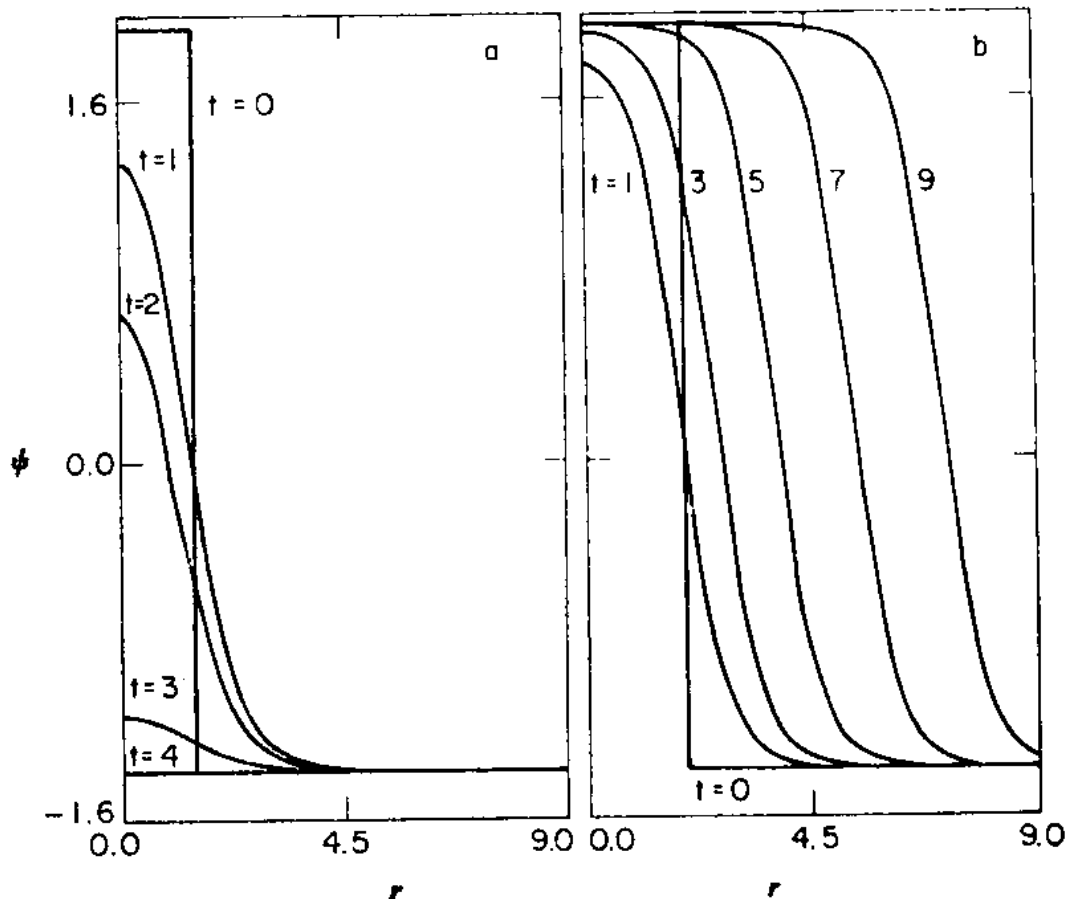


FIG. 5.—Evolution of a nucleus as a function of radial coordinate for various times, as obtained from numerical solution of eqn (3.16) with $b = 3$, $c = 1.5$ and $D = 1$. Figures at left and right are for initial radius smaller and larger than R_c respectively.

unstable homogeneous steady states. Denoting the two stable homogeneous steady states by ψ_A (phase A) and ψ_B (phase B) we put our initial condition to be a sphere of radius R centred around the origin and consisting of phase B, imbedded in a spherical region of phase A which in the computation process has to be taken finite but with radius R_1 much larger than R . Since the initial condition is spherically symmetric and the coefficients of (3.16) are constants, it is sufficient to consider the radial coordinate only. The boundary conditions are taken as $\partial\psi/\partial r = 0$ at $r = 0$ and at the larger bounding sphere.

Fig. 5 shows the time and space dependent solution to eqn (3.16) in three dimensions for the choice of coefficients $D = 1, b = 3, c = 1.5$ and for two different choices of the initial radius R : $R < R_c$ and $R > R_c$. The nucleus shrinks and disappears for $R < R_c$ and grows in time for $R > R_c$. It is interesting to note that the growth process (for $R > R_c$) accelerates for small R but the velocity approaches a constant for larger radii as the front becomes more planar. We calculate the velocity of a planar front (from eqn (2.9) using the steady state solutions $\psi_a = -1.38, \psi_b = 1.94$ (stable) and $\psi_c = -0.558$ (unstable)) to be 1.2, while from fig. 5*b*, the velocity for the largest radius obtained is 1.0.

TABLE 1.—CRITICAL RADIUS FOR NUCLEATION FOR THE SYSTEM GIVEN BY EQN (3.16)

c	R_c from numerical computations		R_c calculated from eqn (3.15) with $l = 2$	
	2 dimensions	3 dimensions	2 dimensions	3 dimensions
0.50	$2.6 < R_c < 3.2$		3.4	
0.75		$3.5 < R_c < 5.5$		4.6
1.00	$1.5 < R_c < 1.75$	$2.7 < R_c < 3.7$	1.7	3.4
1.25		$2.1 < R_c < 2.3$		2.6
1.50	$0.85 < R_c < 1.0$	$1.65 < R_c < 1.95$	1.05	2.1
1.75	$0.8 < R_c < 1.0$	$1.35 < R_c < 1.5$	0.9	1.75
1.875		$1.2 < R_c < 1.4$		1.6
2.0	$R_c < 0.5$	$R_c < 0.8$	0.7	1.35

In table 1 we present the results of numerical computation of R_c , as well as results based on eqn (3.15), for $b = 3$ and for different values of c in two and three dimensions. The calculations based on eqn (3.15) were done with $l = 2$ which is an estimate based on the numerical results such as given by fig. 5*b*. The agreement between the values of R_c as obtained from (3.15) and from numerical integration of (3.16) is fairly good for all the values of the parameter c that were tried, excluding the bifurcation value $c = 2$. (Our failure to provide a more accurate numerical answer for R_c near the bifurcation point is caused by the slow time evolution of the system near that point, which makes the numerical integration very expensive.) This agreement is remarkable as the two ways of obtaining R_c are different; one is based on solutions of the time-dependent deterministic equation, and the other on the steady state probability distribution.

To conclude this section we should note that even though the dynamics of nucleus growth as given by eqn (3.16) or fig. 5 give important information on the rate of nucleation of one phase within another, the rate of this process depends also on the rate of formation of nuclei by spontaneous fluctuations which is not discussed in the present work.

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APPENDIX A

For the reaction mechanism (2.26) the reaction-diffusion equations are

$$\frac{\partial S}{\partial t} = D \frac{\partial^2 S}{\partial x^2} + (S^\circ - S) - \mathcal{E}(P)S \quad (\text{A.1})$$

$$\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} + (P^\circ - P) + \mathcal{E}(P)S \quad (\text{A.2})$$

with all rate coefficients taken to be unity. The assumed form for the dependence of \mathcal{E} on P is

$$\mathcal{E}(P) = \frac{P^2}{1 + P + P^2} \quad (\text{A.3})$$

for which chemical examples are available.¹⁸ The steady state solutions of (A.1, 2) are

$$P^* = 0; \frac{1}{4}(S^\circ - 1) \pm \frac{1}{4}[(S^\circ - 1)^2 - 8]^{\frac{1}{2}}, \quad (\text{A.4})$$

which are shown in fig. 3a.

APPENDIX B

Here we show for the probability distribution given by eqn (3.7) and (3.9), that stationary points which correspond to stable macroscopic steady states are local maxima of the distribution, or minima of the potential $U[\psi]$ given by (see eqn (C.1))

$$U[\psi] = -1/K \int dr \{G[\psi(r)] - \frac{1}{2} \mathbf{D} : (\nabla \psi(r))^2\}. \quad (\text{B.1})$$

Let the steady state variable $\psi^*(r)$ satisfy the equation

$$F[\psi^*(r)] + \mathbf{D} \nabla^2 \psi^*(r) = 0, \quad (\text{B.2})$$

and let $\psi(r) = \psi^*(r) + \delta\psi(r)$. We assume that $\psi^*(r)$ corresponds to a stable steady state of the system. The first order (in $\delta\psi$) term of U then vanishes and the second order term is given by

$$\delta^2 U = -\frac{1}{2} \int dr \delta\psi \{ \mathbf{\Omega} + \mathbf{D} \nabla^2 \} \delta\psi \quad (\text{B.3})$$

where $\mathbf{\Omega} = (\partial F / \partial \psi)_{\psi^*}$. We have used the identity

$$\int dr \nabla W \cdot \nabla V = - \int dr W \nabla^2 V + \int W n \cdot \nabla V d\sigma \quad (\text{B.4})$$

and the fact that $\psi^*(r)$ and $\psi(r)$ must satisfy the same boundary conditions and therefore $(\delta\psi)_\Sigma = 0$. In eqn (B.4), Σ is the boundary of the system, $d\sigma$ is an element of this boundary and n is a unit vector perpendicular to the boundary. Since we assume that $\psi^*(r)$ is a stable steady state, the operator $\mathbf{\Omega} + \mathbf{D} \nabla^2$ must be negative definite and therefore $\delta^2 U$ in eqn (B.3) is positive. This establishes the fact that $U[\psi]$ is a minimum (and $F[\psi]$ is a maximum) for $\psi = \psi^*$.

APPENDIX C

Here we write the modified relations of section 3 for a many variable system and for a general symmetric diffusion matrix. The potential $U[\Psi]$ (eqn (3.9)) is given by

$$U[\Psi(r)] = -1/K \int dr \{G[\Psi(r)] - \frac{1}{2} \mathbf{D} : (\nabla \Psi(r))^2\} \quad (\text{C.1})$$

where

$$\mathbf{D}: (\nabla\psi(r))^2 \equiv \sum_{ij} D_{ij} \sum_k \frac{\partial\psi_i}{\partial r_k} \frac{\partial\psi_j}{\partial r_k}. \quad (\text{C.2})$$

The expression for the critical radius R_c is now replaced by

$$R_c = \frac{(\psi_B - \psi_A) \cdot \mathbf{D} \cdot (\psi_B - \psi_A)(d-1)}{l(G(\psi_B) - G(\psi_A))}. \quad (\text{C.3})$$

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