

Experimental determination of Ginzburg-Landau parameters for reaction-diffusion systems

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We describe an experimental method to determine the parameters of the complex Ginzburg-Landau (CGL) equation for chemical reaction-diffusion systems, solely using measurements on homogeneous systems together with diffusion constants. The necessary eigenvectors and growth rate of oscillations from an unstable focus are obtained experimentally. The method applies to systems of any number of reacting species and allows predictions of wave properties of real chemical systems. With more than two diffusing species the diffusion parameter may have a negative real part thus requiring corrections to the CGL equation.

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The complex Ginzburg-Landau equation has been extensively used for studying waves such as spirals [1,2] and turbulence [3–5] in the chemical and biological reaction diffusion systems [6,7] as well as in hydrodynamics [8]. It describes the slow variation in space and time of the amplitude of local oscillators. For systems with a supercritical Hopf bifurcation (in the corresponding homogeneous system), the equation can be systematically derived by expansion to lowest nontrivial order in a small parameter related to the distance (in parameter space) from the bifurcation [3].

The complex Ginzburg-Landau equation is thus universal for classes of phenomena in diverse fields, and results obtained in one field may be useful for understanding corresponding phenomena in other fields and may stimulate further research there. Chemical systems have a large number of parameters that are easily controlled experimentally. Consequently, it is possible to design chemical systems with particularly interesting combinations of parameters. Wave phenomena observed in chemical and biological systems under such conditions are of interest in their own right as well as for studies of analogous physical phenomena.

Most treatments of reaction diffusion systems have been limited to cases with one or two diffusive chemical species. The complex Ginzburg-Landau equation applies to more general chemical systems, typically having a state space of high dimensions which it effectively reduces to two. The relation to actual chemical systems, although known theoretically [3], has never been established experimentally. It is the purpose of this paper to show how this can be done: we show how the parameters of the complex Ginzburg-Landau equation for space-dependent systems can be determined from measurements on the corresponding homogeneous (well-stirred) system together with diffusion constants of the involved chemical species (the diffusion matrix). The parameters determined experimentally by the method apply to reactions in open or closed spatial reactors provided the complex Ginzburg-Landau equation is applicable to the system to a sufficiently good approximation.

Consider a homogeneous chemical reaction system with rate equation $dc/dt = f(c; \mu)$, with a stationary point $c_0(\mu)$ which is stable for $\mu < 0$ and becomes unsta-

ble by a supercritical Hopf bifurcation at $\mu = 0$. The Jacobi matrix $J(c; \mu)$ at the bifurcation point $J_0 = J(c_0; 0)$ has a pair of purely imaginary eigenvalues. The normalized eigenvectors are defined by $J_0 \cdot u_{\pm} = \pm i \omega_0 u_{\pm}$, $u^{\pm} \cdot J_0 = \pm i \omega_0 u^{\pm}$, $u^{\pm} \cdot u_{\pm} = 1$, and $u^{\pm} \cdot u_{\mp} = 0$.

If the system is unstirred, the concentration vector $c(x, t; \mu)$ is governed by a reaction-diffusion equation

$$\frac{\partial c}{\partial t} = f(c; \mu) + D \cdot \nabla^2 c,$$

in which D is the diffusion matrix. For $\mu \equiv \epsilon^2 > 0$ close to a Hopf bifurcation the motion in the plane of the c space defined by u_+ is best described in terms of a long range and slowly varying amplitude, $W(s, \tau)$, depending on scaled position and time variables $s = \epsilon x$ and $\tau = \epsilon^2 t$, defined to lowest orders in ϵ as

$$c(x, t; \mu) = c_0 + \{ \epsilon W(s, \tau) \exp(i \omega_0 t) u_+ + c.c. \},$$

in which $c.c.$ denotes the complex conjugate of the first term in brackets. The complex amplitude $W(s, \tau)$, which does not depend explicitly on μ , satisfies the complex Ginzburg-Landau equation [3]

$$\frac{\partial W}{\partial \tau} = \lambda_1 W - g |W|^2 W + d \nabla_s^2 W. \quad (1)$$

The parameters are defined in terms of D and an expansion of f in $u = c - c_0$ and μ ,

$$f(c; \mu) = J(c_0; \mu) \cdot u + M(c_0; \mu) : uu + O,$$

$$J(c_0; \mu) = J_0 + \mu J_1 + \dots; \quad M(c_0; \mu) = M_0 + \mu M_1 + \dots,$$

in which the term O is zero for bimolecular kinetics and can thus be ignored for real chemical systems. We have used a dyadic notation in which $M:uu$ is a vector for which the i th component is $M_{ijk} u_j u_k$ with summation over j and k understood. The parameter g is defined in terms of M_0 (see Ref. [3]) whereas $\lambda_1 = \sigma_1 + i \omega_1 = u^+ \cdot J_1 \cdot u_+$, and

$$d = d' + i d'' = u^+ \cdot D \cdot u_+. \quad (2)$$

If $d' > 0$ and $\sigma_1 > 0$, we may introduce reduced variables T , S , and A through [3] $\tau = T/\sigma_1$, $s = [d'/\sigma_1]^{1/2} S$,

and $W = [\sigma_1/|g'|]^{1/2} \exp(i\omega_1\tau)A$. The Ginzburg-Landau equation is then transformed to the simpler form

$$\frac{\partial A}{\partial T} = A - (1+i\alpha)|A|^2 A + (1+i\beta)\nabla_S^2 A \quad (3)$$

in terms of the two real parameters $\alpha = g''/g'$ and $\beta = d''/d'$.

The left eigenvector \mathbf{u}^+ of the Jacobi matrix at a supercritical Hopf bifurcation can be obtained directly from quenching experiments [9–11]. Sometimes the right eigenvector u_+ can be obtained from the experimental left eigenvectors by using the biorthogonality relations [12] between left and right eigenvectors. In general, it may be determined from models of the homogeneous reaction systems systematically fitted to the quenching data at the supercritical Hopf bifurcation using an efficient method in terms of “extreme currents” [13].

We shall briefly indicate how \mathbf{u}^+ is obtained: it is a vector in the dual space of the space of concentrations of the species that are involved in the oscillations. The s th component of \mathbf{u}^+ is essentially the reciprocal of a quantity we have called a quenching amplitude f_s which is obtained experimentally as follows [9–11].

The small limit-cycle oscillations that exist just beyond the bifurcation, can be stopped by addition of species s if the addition shifts the instantaneous state of the system to some point on the stable manifold of the saddle focus (the fixed point that became unstable at the Hopf bifurcation), see Fig. 2 of Ref. [11].

If the change of concentration of species s by the addition is q_s (before reactions have taken place) and the phase at which the successful quenching was made is ϕ_s , then f_s is by definition $f_s = -q_s \exp(i\phi_s)$. The s th component of \mathbf{u}^+ is thus

$$(\mathbf{u}^+)_s = -\exp(i\phi_s)/q_s. \quad (4)$$

Similarly, the s th component of the right eigenvector \mathbf{u}_+ can be expressed in terms of the amplitudes a_s and phases θ_s of the oscillations of species s as [11]

$$(\mathbf{u}_+)_s = a_s \exp(-i\theta_s)/2. \quad (5)$$

The diffusion parameter d and the ratio β are determined by Eq. (2). Consider, e.g., a three-dimensional system with species denoted by x , y , and z . For a diagonal matrix, $D = \text{diag}(D_x, D_y, D_z)$, we obtain from Eqs. (4) and (5)

$$d = v_x D_x + v_y D_y + v_z D_z, \quad (6)$$

in which (for $s = x, y$, or z)

$$v_s = v'_s + i v''_s \\ = (\mathbf{u}^+)_s (\mathbf{u}_+)_s = \frac{a_s}{2q_s} \exp[i(\phi_s - \theta_s)].$$

The generalization to arbitrary dimension is straightforward.

From quenching experiments with the Belousov-Zhabotinsky reaction [10] we find quenching concentrations q_s and phases ϕ_s (Ref. [10], Table I) and recon-

TABLE I. Experimental coefficients for the expression (6) giving the diffusion parameter d for the Belousov-Zhabotinsky reaction at a Hopf bifurcation [10].

s	v'_s	v''_s
HBrO ₂	0.45	-0.024
Br ⁻	-0.158	-0.90
Ce ⁴⁺	0.72	0.92

structed oscillation amplitudes a_s and phases θ_s (Ref. [10], Table II). From Eq. (7) we then obtain the coefficients v given in Table I. Here x , y , and z refer to HBrO₂, Br⁻, and Ce⁴⁺, respectively. If we use $D_y = 1.6 \times 10^{-5}$ cm²/s for diffusion in water from standard tables and estimate $D_x = 1 \times 10^{-5}$ cm²/s and $D_z = 0.6 \times 10^{-5}$ cm²/s we get $d = (0.6 - i0.9) \times 10^{-5}$ cm²/s. This gives the ratio $\beta = -1.4$.

It is interesting to note that the real part of d would become negative if D_y were sufficiently large, namely, if

$$D_y > 2.8D_x + 4.6D_z. \quad (8)$$

This inequality will hardly be satisfied for any realistic estimates of D_x and D_z , but negative values of d' cannot be excluded for other Hopf bifurcation points where the coefficients v_s will be different.

The important point is, however, that the diffusion constants and the eigenvectors are completely unrelated so negative d' exists and must be expected to occur commonly in chemical reaction diffusion systems. However, such systems are still to be discovered. When $d' < 0$ the solutions to the complex Ginzburg-Landau equation become unstable, and higher-order corrections must be included in order to model the system in a similar way.

The nonlinearity parameter g and the ratio α can be determined from the recorded time series of a quenching experiment [10,14]. For a homogeneous (well-stirred) system the kinetic equations correspond to a Ginzburg-Landau equation with $D=0$. By defining $W(\tau) = R(\tau) \exp[i\theta(\tau)]$ with R and θ real, we get [3]

$$\frac{dR}{d\tau} = \sigma_1 R - g'R^3, \quad \frac{d\theta}{d\tau} = \omega_1 - g''R^2,$$

or in terms of the time t and amplitude $a = \epsilon W$,

$$\frac{da}{dt} = \sigma a - g'a^3, \quad (9)$$

$$\omega(a; \mu) = \omega_0 + \frac{d\theta}{dt} = \omega_0 + \mu\omega_1 - g''a^2, \quad (10)$$

in which $\sigma = \mu\sigma_1$. The limit cycle is $a = a_s$ for which $da/dt = 0$,

$$a_s = (\sigma/g')^{1/2}. \quad (11)$$

The slope of the tangent to the envelope of the time series at the half-amplitude point, $a = a_s/2$, is [from Eq. (9)]

$$s_{1/2} = \left. \frac{da}{dt} \right|_{a=a_s/2} = \sigma a_s/2 - g'a_s^3/8,$$

see Fig. 1. Hence,

$$g' = \left(\frac{8}{3}\right) s_{1/2} / a_s^3. \quad (12)$$

From Eq. (10) we get

$$g'' = [\omega(0; \mu) - \omega(a_s; \mu)] / a_s^2 \equiv \Delta\omega / a_s^2, \quad (13)$$

so

$$\alpha = g'' / g' = (3/8) \Delta\omega a_s / s_{1/2}. \quad (14)$$

From Fig. 1(a) for the cerium-catalyzed Belousov-Zhabotinsky (BZ) system [10] we find $g' = 9 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$ and estimate $g'' \approx 3 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}$, so $\alpha \approx 0.3$. (The unit M denotes mol/dm³.) The results for g'' and α are rather uncertain. From Fig. 1(b) for the Briggs-Rauscher system [14] a more accurate determination of α is possible: we find $\alpha = 1.4$ for that system. The parameters d and β can also be obtained for the Briggs-Rauscher system via optimized models using the method of Ref. [13], but we have no results yet. The specific results quoted in this paper apply to the Hopf bifurcation points given in Refs. [10] and [14].

When experimental parameters are used to describe a closed reaction diffusion system the best initial conditions for the closed system are obtained by preparing the initial

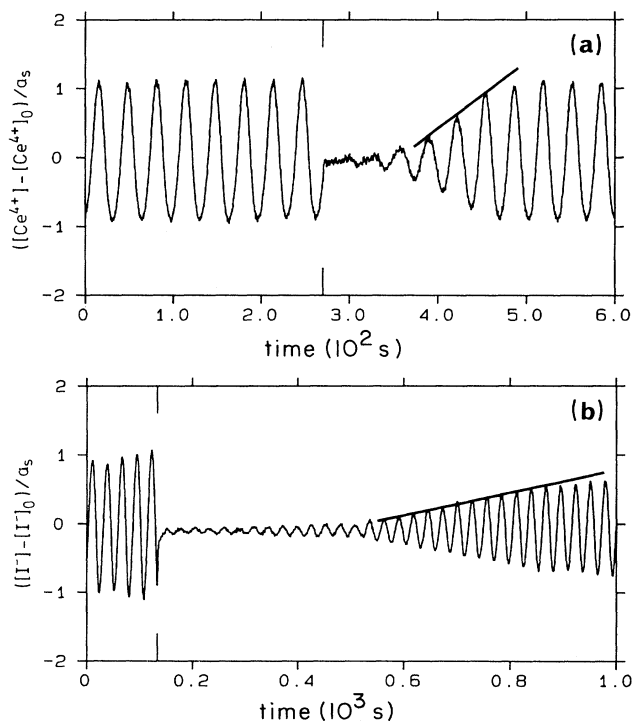


FIG. 1. The nonlinearity parameter $g = g' + ig''$ and the ratio $\alpha = g'' / g'$ for the Ginzburg-Landau equation are obtained from a recorded time series of a quenching experiment for (a) the Belousov-Zhabotinsky reaction [10] and (b) the Briggs-Rauscher reaction [14] using Eqs. (12)–(14). For each curve the tangent to the envelope at the half-amplitude point is shown. Its slope $s_{1/2}$ is used to determine g' whereas g'' is determined from the frequencies of the (infinitesimally) small oscillations and the limit-cycle oscillations. The results for α are $\alpha \approx 0.2$ (a) and $\alpha = 0.4$ (b).

state of the reaction mixture in a continuous-flow stirred tank reactor at the conditions used to determine the parameters. We believe the parameters apply to more general initial conditions, but a discussion of that question is outside the scope of this paper.

As an immediate application of experimentally determined Ginzburg-Landau parameters, we indicate how the asymptotic wave length λ of spiral waves can be obtained. From the analytic and numerical spiral wave solutions to the complex Ginzburg-Landau equation obtained by Hagan [1], we find the wavelength as $\lambda = (|d|/\sigma)^{1/2} 2\pi/k$ in which $|d|$ is the modulus of the complex diffusion parameter and k is a scaled asymptotic wave number defined by Hagan. (It should be noted that Hagan's scalings differ slightly from the ones used here.)

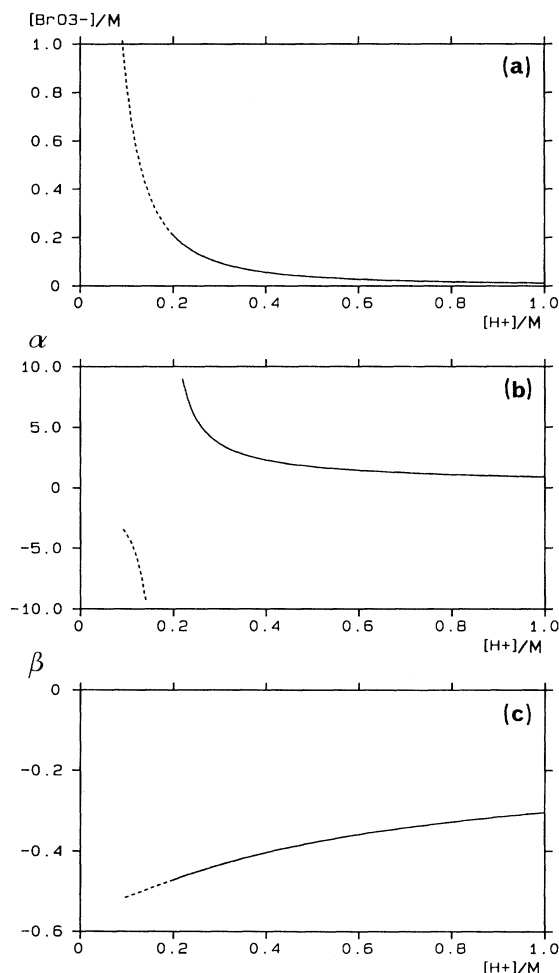


FIG. 2. Hopf bifurcation diagram and Ginzburg-Landau parameters α and β , calculated along the bifurcation curve for the standard Oregonator model [17] of the BZ reaction. The model is defined by reactions (A1)–(A5) in the Appendix to Ref. [11] with rate constants $k_1 = 1.6 \text{ M}^{-3} \text{ s}^{-1}$, $k_2 = 2.5 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$, $k_3 = 33 \text{ M}^{-2} \text{ s}^{-1}$, $k_4 = 3000 \text{ M}^{-1} \text{ s}^{-1}$, $k_5 = 0.33 \text{ s}^{-1}$, and $f = 0.30$, according to Field and Fösterling [18]. The bifurcation parameters are the concentrations of H^+ and BrO_3^- . The solid (dashed) parts of the curves represent supercritical (subcritical) bifurcations.

The dimensionless wave number k is obtained from Hagan's Fig. 5 with his parameter q replaced by Eq. (B6) of his Appendix B, using $q = -\alpha$ and his parameter z defined by $\tan(z) = \beta$. From our estimated α and β for the BZ system, we get $k = 0.3$. By using the complex diffusion parameter d together with $\sigma = 0.0156 \text{ s}^{-1}$ obtained from our Fig. 1(a) we predict the result $\lambda = 6 \text{ mm}$. Thus, at the distance from the Hopf bifurcation studied in the experiments [10], Ginzburg-Landau spirals should be observable in ordinary laboratory experiments.

The parameter g' is closely related to the Floquet exponent of the limit cycle. It is positive on the supercritical branch of the Hopf bifurcation curve and vanishes at a transition to subcriticality [15]. Since g'' is regular, α diverges as the transition point is approached. This means that if g'' is positive the Ginzburg-Landau equation may allow turbulent solutions [5] sufficiently close to the transition, where, however, a quintic correction term may be needed for some reaction diffusion systems [16].

The complex Ginzburg-Landau equation may also be useful in computational modeling of a real chemical system if its reaction mechanism is known or assumed. Such

mechanisms may involve dozens of active chemical species, and the study of waves and turbulence by numerical integration of the reaction-diffusion equations is beyond the capacity of existing computers. Near a supercritical Hopf bifurcation such systems may be treated by a Ginzburg-Landau equation with parameters that can be easily calculated from the kinetics [3].

As an illustrative example we show in Fig. 2 a Hopf bifurcation curve together with the parameters α and β along the curve, calculated from the Oregonator model [17] of the Belousov-Zhabotinsky reaction. The Oregonator has successfully been used to describe oscillations in the BZ system. The results in Fig. 2 indicate the considerable range of α and β accessible in chemical systems by choice of points of operation. However, the main result of this paper is the method of determining actual Ginzburg-Landau parameters from experiments on specific systems.

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