Spatial Correlations near Turing Instabilities: Criteria for Wavenumber Selection

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We analyze the probability distribution and spatial correlations around a stationary state of a general reaction−diffusion system. The stochastic description is based on a multivariate master equation. We use a WKB expansion of the probability density and determine the leading term, the stochastic potential, to second order in deviations from a homogeneous stationary state. For a system below, but near, a Turing instability, the spatial correlations become long range and display a macroscopic structure that will emerge after the bifurcation. We derive explicit expressions for both the probability density and the correlation function. For systems close to the instability, the correlation function is approximately an exponentially damped cosine function. We derive explicit expression for the correlation length and the amplitude of the correlation function; they are inversely proportional to the square root of the largest eigenvalue of the deterministic system. Our approach differs from earlier work in that systems with many chemical species are treated, asymptotic approximations are derived, correlations are given a geometrical picture in terms of eigenvectors of the Jacobian of an associated Hamiltonian system, and higher order terms in the stochastic potential are possible to obtain analytically (which we do not pursue). Results of the theoretical analysis are applied to the Sel'kov model. Exact and approximate solutions at lowest order agree well.

I. Introduction

A phenomenon of great interest, from both an historical and scientific standpoint, is the generation of stationary spatial patterns in nonlinear chemical systems through the interplay of reaction and diffusion. First proposed by Turing,[1] these structures are produced by a mechanism that is independent of the details of the kinetic system and geometric parameters. Instead, more general considerations allow the spontaneous development of patterns from spatially uniform stationary states.[2] Since their introduction, they have been used to explain various biological patterns: subcellular metabolic function, cellular differentiation, and morphogenesis.[3] These patterns arise as a system evolves from a homogeneous stable state through a marginally stable state. In the pretransitional regime, fluctuations play an important role by exploring nearby states. We study the probability density and correlations in systems close to, but before, Turing instabilities and show that as the instability point is approached correlations become very large in amplitude and develop a macroscopic spatial structure with the same wavelength as that of the pattern which develops beyond the instability. This enhancement of structured fluctuations provides a method for using fluctuations as predictors of Turing instabilities and macroscopic patterns in pre-Turing bifurcation systems.

Turing instabilities may arise in systems where there is some autocatalysis (positive feedback). Two variable systems generally have an identifiable activator and inhibitor (of the autocatalytic reaction) and may be classified as either activation−inhibition or activation−depletion, depending upon the signs of the linear evolution matrix. Diffusion tends to reestablish a homogeneous state. For the instability to arise, the diffusion coefficient of the inhibitor has to exceed that of the activator by an amount that depends upon the kinetics, though for most realistic models the difference must be at least an order of magnitude. This requirement has, until recently, prohibited experimental realization. To eliminate hydrodynamic currents, continuous flow unstirred reactors have been developed where reaction takes place in a thin layer of gel; in addition, the mobility of the activator is lowered by interaction with a low-mobility compound.[4−7] Experimental wavelengths are in the range $10^{-3}-1$ cm. Recent calculations suggest that Turing structures may also exist on a mesoscopic scale, $0.1-1$ μm.[8]

Theoretical studies of patterns and instabilities in spatially extended systems have treated both purely deterministic and stochastic systems. Work on deterministic systems has shown how nonlinear interactions between linearly unstable eigenmodes produce various patterns beyond the bifurcation.[2,9,10] Even low (spatial) dimension systems exhibit complex bifurcation diagrams. For example, in two dimensions, the Turing bifurcation may show the following sequence: a stable hexagonal structure appears subcritically; the primary bifurcation to a striped structure appears supercritically, but is unstable at first; the stripes become stable for higher parameter values and coexist with the hexagonal structure over an interval of parameter values[9] Stochastic treatments generally approach the problem on a mesoscopic level using a multivariate master equation. A result of the complexity of this equation, most studies have concentrated on nonpattern-forming bifurcations, specifically homogeneous cusp and Hopf bifurcations. Cusp bifurcations show "nonclassical" behavior of correlations in low spatial dimensional systems ($d < 4$).[11,12] In the case of a Hopf bifurcation, macroscopic oscillations may be destroyed by fluctuations in low dimensional ($d < 3$) systems.[13,14]

Previous work on the subject of this paper, fluctuations in systems close to the Turing instability, has yielded an explicit formula for the correlation function for two-variable systems in one spatial dimension.[15] This work truncates the moment equations and results in classical exponents for the divergence of the correlation length and variances within cells. Our work extends and simplifies these results to arbitrary numbers of species and dimensions. We use a different formalism, the

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stochastic potential,[16−19] which allows a geometrical interpretation of the probability density in terms of an unstable manifold of an associated Hamiltonian system. These equations also permit easy numerical evaluation of the global probability density. In this paper, we concentrate on local aspects of the stochastic potential. We approximate the Hamiltonian to second order in deviations from a homogeneous stationary state. This leads to a second-order approximation for the stochastic potential, the Gaussian approximation, which may be determined from matrix eigenvalue problems. Higher-order terms may be found through normal form transformations;[20] we do not pursue these here.

In the following sections, we present equations and summarize results; details of calculations are relegated to the Appendix. In section II.A, we summarize the multivariate master equation treatment of reaction−diffusion systems and introduce the stochastic potential. We formulate a Hamiltonian system, the solution of which determines paths that most probable fluctuations follow. The integral of the associated Lagrangian along these trajectories gives the stochastic potential. In section II.B, we discuss the solutions to the Hamiltonian system linearized about a stationary state. This leads to the Gaussian approximation of the stochastic potential. The correlation function is treated in section II.C. In section III.A, we give an approximation for spatial correlations in systems close to Turing instabilities; in section III.B, we illustrate our exact and approximate equations by numerical examples on the Selkov model. Section IV contains some concluding remarks.

II. Reaction−Diffusion Master Equation

A. General Formulation and WKB Approximation. In the following, we give a brief outline of the master equation formulation for a general reaction−diffusion system.[15] We consider m chemically active species in a volume $V = L^d$ in d-dimensional space. The length L along each spatial axis is divided into n segments, by which cells of volume $\Delta V = V/n^d$ are constructed. The cells are labeled by a vector $\mathbf{q} = (q_1, ..., q_d)$, $q_i = 1, ..., n$, and periodic boundary conditions are imposed $q_{n+1} = q_1$. We take as variables the numbers of particles $\{X_{\mathbf{q}\alpha}\}$ within cells and assume that they define a Markov process. These random variables change as a result of chemical reactions, which are modeled as jump Markov processes, and diffusion, which is modeled as a random walk between adjacent cells.[21] This leads to a multivariate master equation for the probability distribution $P(\{X_{\mathbf{q}\alpha}\},t)$:

$$\begin{aligned}\frac{\partial P}{\partial t} = &\sum_{\rho}\sum_{\mathbf{q}}[W_\rho(X_{\mathbf{q}} - \nu_\rho \rightarrow \mathrm{X}_{\mathbf{q}})\, P(\{X_{\mathbf{q}\alpha} - \nu_{\rho\alpha}\}) \\ &- W_\rho\,(\mathrm{X}_{\mathbf{q}} \rightarrow \mathrm{X}_{\mathbf{q}} + \nu_\rho)P] \\ &+ \sum_{\alpha}\frac{\tilde{D}_\alpha}{2d}\sum_{\mathbf{q},\mathbf{a}}[(X_{\mathbf{q}\alpha} + 1)\, P\,(X_{\mathbf{q}\alpha} + 1, X_{(\mathbf{q}+\mathbf{a})\alpha} - 1) \\ &- X_{\mathbf{q}\alpha}P] \end{aligned} \tag{1}$$

where the transition probability per unit time for the ρth reaction, W_ρ, is

$$W_\rho(\mathbf{X}_{\mathbf{q}} \rightarrow \mathbf{X}_{\mathbf{q}} + \nu_\rho) = k_\rho \Delta V^{1-\sum_\alpha \bar{\nu}_{\rho\alpha}} \prod_\alpha \frac{(X_{\mathbf{q}\alpha})!}{(X_{\mathbf{q}\alpha} - \bar{\nu}_{\rho\alpha})!} \tag{2}$$

The stoichiometric coefficient of X_α in the ρth chemical reaction is $\nu_{\rho\alpha}$; the order of the ρth reaction with respect to X_α is $\bar{\nu}_{\rho\alpha}$; the kinetic coefficient of the ρth reaction is k_ρ. Nearest neighbors of cell $\mathbf{q}$ are denoted $\mathbf{a}$. The jump frequency $\tilde{D}_\alpha$ of species α is related to Fick's diffusion coefficient by

$$\frac{\tilde{D}_\alpha}{2d} l^2 \approx D_\alpha \tag{3}$$

where $l = L/n$ is the characteristic length of a cell $l^d = \Delta V$.

Several conditions must be met for eq 1 to describe correctly reaction−diffusion systems.[22] Besides the Markovian assumption, local equilibrium must prevail, which requires a large number of molecules per cell. Also, the size of a cell must be small enough (less than the correlation length) that homogeneity holds and yet not so small that microscopic aspects, such as deviations from the Maxwell−Boltzmann velocity distribution, need to be incorporated. Typically, cell dimensions should be of the order of the reactive mean free path the distance a particle travels before it undergoes a reactive collision.

We consider ΔV as a large parameter, since a large number of particles are contained within a cell, and write P to leading order as an asymptotic WKB form:[16−19]

$$P(\{x_{\mathbf{q}\alpha}\},t) = K(\{x_{\mathbf{q}\alpha}\},t)\exp(-\Delta V\, S\,(\{x_{\mathbf{q}\alpha}\},t)) \tag{4}$$

where $x_{\mathbf{q}\alpha} = X_{\mathbf{q}\alpha}/\Delta V$. In the following, we are concerned with S, the stochastic potential (also referred to as the nonequilibrium potential), and neglect the prefactor K. Substituting eq 4 in eq 1, we obtain to leading order a Hamilton−Jacobi type of equation for the stochastic potential

$$\begin{aligned}-\frac{\partial S}{\partial t} = &\sum_{\rho}\sum_{\mathbf{q}} w_\rho(\mathbf{x}_{\mathbf{q}})\left[\exp\left(\sum_\beta \frac{\partial S}{\partial x_{\mathbf{q}\beta}}\nu_{\rho\beta}\right) - 1\right] + \\ &\sum_\alpha \frac{\tilde{D}_\alpha}{2}\sum_{\mathbf{q},\mathbf{a}} x_{\mathbf{q}\alpha}\left[\exp\left(-\frac{\partial S}{\partial x_{\mathbf{q}\alpha}} + \frac{\partial S}{\partial x_{(\mathbf{q}+\mathbf{a})\alpha}}\right) - 1\right] \\ \equiv &\, H\left(\{x_{\mathbf{q}\alpha}\}, \left\{\frac{\partial S}{\partial x_{\mathbf{q}\alpha}}\right\}\right)\end{aligned} \tag{5}$$

where

$$w_\rho(\mathbf{x}_{\mathbf{q}}) = \frac{W_\rho(\mathbf{X}_{\mathbf{q}} \rightarrow \mathbf{X}_{\mathbf{q}} + \nu_\rho)}{\Delta V} \tag{6}$$

Equation 5 is the Hamilton−Jacobi equation for an associated classical mechanical system with Hamiltonian H. Hamilton's equations of motion for the system with this Hamiltonian are given in the Appendix (eqs 47 and 48). These equations determine trajectories in $2mn^d$-dimensional phase space, whose concentration and momenta are $x_{\mathbf{q}\alpha}$ and $p_{\mathbf{q}\alpha}$, respectively. The stochastic potential satisfies the differential equation

$$\frac{\mathrm{d}S}{\mathrm{d}t} = L(\{x_{\mathbf{q}\alpha}\},\{x_{\mathbf{q}\alpha}\}) \tag{7}$$

along any trajectory of eqs 47 and 48, where the Lagrangian corresponding to the Hamiltonian H is

$$L = \frac{\partial S}{\partial t} + \sum_{\mathbf{q},\alpha}\frac{\partial S}{\partial x_{\mathbf{q}\alpha}}\frac{\mathrm{d}x_{\mathbf{q}\alpha}}{\mathrm{d}t} = \sum_{\mathbf{q},\alpha} p_{\mathbf{q}\alpha}\frac{\mathrm{d}x_{\mathbf{q}\alpha}}{\mathrm{d}t} - H \tag{8}$$

Equation 7 may be integrated along with Hamilton's equations to give the value of the stochastic potential along any classical trajectory. This holds for both stationary and time-dependent densities.

We are concerned with stationary distributions, for which the associated classical trajectories lie on the unstable manifold of the stationary state ($x_{\mathbf{q}\alpha} = x_s$, $p_{\mathbf{q}\alpha} = 0$).[23] On this (Lagrangian) manifold, the energy is zero. The classical trajectories, when projected down onto concentration space, determine most probable fluctuational paths (the characteristics).[19] For small deviations from the stationary state, these trajectories may be approximated by solutions to Hamilton's equations linearized about the stationary state. The unstable eigenvectors of the Jacobian matrix then determine the stationary density through eq 7. Details of this solution are supplied in the Appendix. In the following, we concentrate on the structure of the solutions for the probability density and correlation function.

B. Gaussian Approximation of the Stochastic Potential near a Stationary State. In this and the following sections, we consider systems in one spatial dimension. The general *d*-dimensional problem is treated in the Appendix. We follow the notation and method as developed in our earlier papers.[24,25]

We write an arbitrary periodic deviation from the stationary state, $u_{r\alpha} = x_{\mathbf{q}\alpha} - c_\alpha$, as a discrete Fourier series

$$u_{q\alpha} = f_{q\alpha} = \sum_{k=1-n/2}^{n/2} a_{k\alpha} e^{2\pi i k q/n} \tag{9}$$

where

$$a_{k\alpha} = \frac{1}{n}\sum_{q=1}^{n} f_{q\alpha} \mathrm{e}^{-2\pi i k q/n} \tag{10}$$

is the discrete Fourier transform of $f_{q\alpha}$. For convenience, we take the number of cells n to be even. This allows the independent Fourier terms to be expressed as $k = -n/2 + 1, \ldots, n/2$. Using the results in the Appendix (for the matrices V and *W*), we may write the stochastic potential for the above deviation (under periodic boundary conditions) as

$$S = \frac{n}{2}\sum_{k=1-n/2}^{n/2}\sum_{\alpha,\beta} a_{k\alpha} (\Xi_k^{-1})_{\alpha\beta} a_{k\beta} \tag{11}$$

where

$$\Xi_k = E_k F_k^{-1} \tag{12}$$

The matrices E_k and F_k are $m \times m$-dimensional matrices, whose columns are comprised of eigenvectors in the unstable space of the matrix in eq 59 of the Appendix. The subscript k denotes the wavenumber used in the eigenvalue problem. As discussed in the next section, the matrix Ξ satisfies a fluctuation−dissipation relation, from which the solution may also be found.

On letting the number of cells tend to infinity, we obtain a similar formula for the potential, eq 11, but with E and F determined by eq 61. In this limit, the sum on k extends to infinity and the coefficients are obtained from the Fourier transform of a continuous vector-valued function $f(r)$ on $(-L/2, L/2)$, where $r = qL/n$ and $q = 1 - n/2 \ldots n/2$:

$$a_{k\alpha} = \frac{1}{L}\int_{-L/2}^{L/2} f_\alpha(r)\, \mathrm{e}^{-2\pi i k r/n}\, \mathrm{d}r$$

Using the previous result for infinitely many cells and taking the infinite system size limit $L \to \infty$, we obtain

$$S[f] = \pi\left(\frac{L}{n}\right)^{-1}\int_{-\infty}^{\infty} \mathbf{g}(\eta)\cdot\Xi^{-1}(\eta)\mathbf{g}(\eta)\, \mathrm{d}\eta \tag{13}$$

where η ($=2\pi k/L$) is a continuous variable, $\Xi^{-1}(\eta)$ is the matrix inverse of $\Xi(\eta)$, and $\mathbf{g}(\eta)$ is the Fourier transform of $\mathbf{f}(x)$:

$$\mathbf{g}(\eta) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{e}^{i\eta r}\mathbf{f}(r)\, \mathrm{d}r \tag{14}$$

Now we have $\Xi(\eta) = E(\eta)F^{-1}(\eta)$ and columns of the matrices E and F are comprised of eigenvectors in the unstable space of the matrix eq 59 with $\tilde{A}(\eta)$ and $\tilde{B}(\eta)$, eq 61, replacing $\tilde{A}_k$ and $\tilde{B}_k$. Using the property that Ξ is an even function of η (see eq 17), we may write the probability density as

$$P[\mathrm{f}] = \exp(-2\pi \int_0^\infty \mathbf{g}(\eta)\cdot\Xi^{-1}(\eta)\bar{\mathbf{g}}(\eta)\, \mathrm{d}\eta) \tag{15}$$

The local density is determined by the structure of $\Xi^{-1}(\eta)$ as a function of η. In section III.A, we show that for a system close to a Turing instability, Ξ exhibits a maximum for η close to the Turing wavenumber. This enhanced probability of a structured fluctuation may be measured by the correlation function, which we discuss next.

C. Correlation Function. The spatial correlation function $\langle u_{q\alpha}u_{q'\alpha'}\rangle$ is related to the matrix VW^{-1} of the quadratic approximation of the stochastic potential, eq 57, through $(n/L)(VW^{-1})^{-1}$. Using the factorization of V and W, eqs 62−64, we obtain the following expression for a finite (even) number of cells n and length L:

$$\langle u_{q\alpha}u_{q'\alpha'}\rangle = L^{-1}\sum_{k=1-n/2}^{n/2} (\Xi_k)_{\alpha\alpha'} \mathrm{e}^{2\pi i k(q-q')/n} \tag{16}$$

This result is valid for general reaction schemes that are not too close to points of instability. We see that the correlation function is essentially the discrete Fourier transform of the matrix Ξ_k. Hence, the correlation range and structure is determined by this matrix as a function of k.

Using eq 59, we find that for each k, Ξ_k satisfies a fluctuation−dissipation relation

$$\tilde{A}_k\Xi_k + \Xi_k(\tilde{A}_k)^T + \tilde{B}_k = 0 \tag{17}$$

For a large number of cells and $k \gg L$, the matrices $\tilde{A}_k$ and $\tilde{B}_k$ tend to $-\eta^2 D$ and $2\eta^2 DC$, respectively, where $\eta = 2\pi k/L$ and C is the diagonal matrix of stationary state concentrations [see eq 61]. From this relation, we have the property that Ξ_k tends to C for $k \to \infty$. The contribution of a constant matrix C to the sum in eq 16 diverges with n. We separate this part from the sum and write the correlations as

$$\begin{aligned}\langle u_{q\alpha}u_{q'\alpha'}\rangle = {} & L^{-1}[nC_{\alpha\alpha'}\delta_{qq'} + (\Xi_0)_{\alpha\alpha'}] \\ & + \frac{2}{L}\sum_{k=1}^{n/2-1} (\Xi_k - C)_{\alpha\alpha'} \cos\frac{2\pi k}{n}(q-q') \\ & + \frac{1}{L}(\Xi_k - C)_{\alpha\alpha'}\cos\pi(q-q')\end{aligned} \tag{18}$$

The first term of this expression derives from a Poissonian distribution and is due to fluctuations caused by diffusion. The rest of the expression involves long-range correlations and is due to the coupling of reaction and diffusion. The correlation length is determined by the dependence of the prefactor of the cosine term, $\Xi_k - C$, on η. In the next section, we approximate this (structure) function for systems close to a Turing instability.

In the limit of infinitely many cells, the term with a Kronecker delta becomes $c_\alpha\delta_{\alpha\alpha'}\delta(r - r')$, where $\delta()$ denotes the Dirac

delta function. Letting the system size increase, $L \rightarrow \infty$, we may write the sum over k as an integral over η ($=2\pi k/L$):

$$\langle u_\alpha(r)\ u_{a'}(r')\rangle = c_\alpha \delta_{\alpha\alpha'}\delta(r-r') + h_{\alpha\alpha'}(r-r') \quad (19)$$

where

$$h_{\alpha\alpha'}(r-r') = \frac{1}{\pi}\int_0^\infty (\Xi(\eta) - C)_{\alpha\alpha'} \cos \eta(r-r')\, d\eta \quad (20)$$

The matrix $\Xi(\eta)$ satisfies a fluctuation−dissipation relation: eq 17 with the matrices $\tilde{A}_k$ and $\tilde{B}_k$ and the Fourier variable k replaced by $\tilde{A}(\eta)$, $\tilde{B}(\eta)$, [eq 61] and η, respectively. We note from eq 17 and the definitions of the matrices $\tilde{A}(\eta)$ and $\tilde{B}(\eta)$ that the matrix $\Xi(\eta)$ is an even function of η. The Fourier transform of eq 19 is simply the matrix Ξ:

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle u_{r\alpha}\, u_{r'\alpha'}\rangle\, e^{i\eta(r-r')}\, d(r-r') = \frac{1}{2\pi}\Xi_{\alpha\alpha'}(\eta) \quad (21)$$

The structure function $\Xi_{\alpha\alpha'}(\eta)$ determines the correlation amplitude and length through a cosine transform, eq 20. In the next section, we study the dependence of these properties on the distance to the bifurcation. We show that the maximum of $\Xi(\eta)$, which is near the critical wavenumber, increases without bound as the bifurcation point is approached.

III. Approximations and Numerical Results near a Turing Instability

A. Spatial Correlations near a Turing Instability. As shown in section II.C, the matrix Ξ determines the structure of the correlation function. The solution to the fluctuation−dissipation relation for $\Xi(\eta)$, eqs 17 and 68, may be expressed in terms of a matrix $U(\eta)$ that diagonalizes the Jacobian of the deterministic system, $\tilde{A}(\eta)$, eqs 60 and 61, and the eigenvalues of $\tilde{A}(\eta)$, denoted $\lambda_i(\eta)$, $i = 1, ..., m$. Straightforward calculations give the general solution as

$$\Xi(\eta) = -U(\eta)\, H(\eta)\, U^T(\eta)$$

$$H_{ij}(\eta) = \{U^{-1}(\eta)\, \tilde{B}(\eta)[U^T(\eta)]^{-1}\}_{ij}/(\lambda_i(\eta) + \lambda_j(\eta)) \quad (22)$$

where

$$[\tilde{A}(\eta)\, U(\eta)]_{ij} \equiv [(A - \eta^2 D)U(\eta)]_{ij} = \lambda_i(\eta)\, U_{ij}(\eta) \quad (23)$$

The matrix A is the Jacobian matrix for the homogeneous (well-stirred) deterministic system.

For a system that is close to a Turing instability, one of the eigenvalues of $\tilde{A}(\eta)$ tends to zero as the bifurcation point is approached. In this case, the dominant contribution to $H(\eta)$ comes from the term that contains the reciprocal of the near-zero eigenvalue, which we denote λ_1. Keeping only this term in eq 22 yields the approximation

$$\Xi_{\alpha\alpha'}(\eta) \approx \frac{\zeta^*(\eta)\cdot\tilde{B}(\eta)\, \zeta^*(\eta)}{2\lambda_1(\eta)}\, \zeta_\alpha(\eta)\, \zeta_{\alpha'}(\eta) \quad (24)$$

where the right and left eigenvectors of $A(\eta)$ corresponding to the eigenvalue $\lambda_1(\eta)$ are denoted $\zeta(\eta)$ and $\zeta^*(\eta)$, respectively:

$$\tilde{A}(\eta)\, \zeta(\eta) = \lambda_1(\eta)\, \zeta(\eta) \quad (25)$$

$$(\tilde{A})^T\zeta^*(\eta) = \lambda_1(\eta)\, \zeta^*(\eta) \quad (26)$$

We normalize these eigenvectors such that $\zeta^* \cdot \zeta = 1$.

In order to proceed further with this approximation of Ξ, eq 24, we need to determine how the eigenvalue closest to zero, $\lambda_1(\eta)$, depends on η and on the distance to the bifurcation. As a function of η, this eigenvalue exhibits a maximum at a critical point, which depends upon the distance to the bifurcation. We denote this critical point as $\eta_c(\epsilon)$, where ϵ is a (small) expansion parameter that is zero at the bifurcation. In the vicinity of this point, the eigenvalue is a quadratic function of $\eta - \eta_c(\epsilon)$. We consider both the distance to the bifurcation and the distance to the critical point as small and take as expansion parameters ϵ and $\Delta\eta = \eta - \eta_c(\epsilon)$. We expand the critical point in ϵ, $\eta_c(\epsilon) = \eta_0 + \epsilon\eta_1 + O(\epsilon^2)$, and write the eigenvalue as

$$\lambda_1(\eta) = \alpha(\epsilon)[\eta - \eta_c(\epsilon)]^2 + \beta(\epsilon)$$
$$= (\alpha_0 + \epsilon\alpha_1)(\Delta\eta)^2 + \epsilon\beta_1 + O(\epsilon^2) \quad (27)$$

We also expand the eigenvector corresponding to λ_1 and the matrix $\tilde{A}$:

$$\zeta(\epsilon,\Delta\eta) = \sum_{i=0}\sum_{j=0}\epsilon^i(\Delta\eta)^j\zeta^{(i,j)} \quad (28)$$

$$\tilde{A}(\epsilon, \Delta\eta) = A(\epsilon) - \eta^2 D = \sum_{i=0}\epsilon^i A_i - \eta^2 D$$

$$= \sum_{i=0}\epsilon^i A_i - (\eta_0 + \Delta\eta + \epsilon\eta_1 + ...)^2\, D \quad (29)$$

Putting these expressions into the eigenvalue problem, eq 25, and collecting terms with equal powers of ϵ, we obtain an hierarchy of equations to be solved for the coefficients. Then, for each power of ϵ, we collect terms with equal powers of $\Delta\eta$. For ϵ^0, we obtain

$$(\Delta\eta)^0:\ (A_0 - \eta_0{}^2 D)\, \zeta^{(0,0)} = 0 \quad (30)$$

$$(\Delta\eta)^1:\ (A_0 - \eta_0{}^2 D)\, \zeta^{(0,1)} = 2\eta_0 D\zeta^{(0,0)} \quad (31)$$

$$(\Delta\eta)^2:\ (A_0 - \eta_0{}^2 D)\, \zeta^{(0,2)} = 2\eta_0 D\zeta^{(0,1)} + (D + \alpha_0)\, \zeta^{(0,0)} \quad (32)$$

The solution to eq 30 is the eigenvector corresponding to eigenvalue zero (at the bifurcation point, $\epsilon = 0$); we denote this solution as ζ_0. We will also need the left eigenvector of the matrix in eq 30, which we denote ζ_0^*.

We may normalize the eigenvectors so that $\zeta_0 \cdot \zeta_0^* = 1$. Then, the solvability condition[26] for eqs 31 and 32 may be stated as the orthogonality of the right-hand sides of these equations to ζ_0^*. For eq 31, this condition is

$$\zeta_0^*\cdot D\zeta_0 = 0 \quad (33)$$

As there are no adjustable parameters, this equation should always be true for any system undergoing a Turing bifurcation. From the previous normalization of the eigenvectors, we see that the diffusion coefficients must not all be the same value. In two-species systems, the coefficients of the activator and inhibitor typically differ by an order of magnitude. Verification of eq 33 may be obtained by differentiating the full eigenvalue equation (with η dependence) with respect to η (at $\epsilon = 0$) and

evaluating the resulting derivative at $\eta = \eta_0$. As the solvability condition is always fulfilled, eq 31 may be solved for $\zeta^{(0,1)}$. To make the solution unique, it is necessary to add a (any) normalization condition, e.g. $\zeta^{(0,1)}\cdot\zeta_0^* = 0$ or 1.

The solvability condition for eq 32 for $\zeta^{(0,2)}$ determines the parameter α_0:

$$\alpha_0 = -2\eta_0\zeta_0^*\cdot D\zeta^{(0,1)} \tag{34}$$

To determine the other coefficients of interest, α_1, β_1, and η_1, we expand the order ϵ^1 equation in powers of $\Delta\eta$. Straightforward calculations give the expressions

$$(\Delta\eta)^0\colon\ (A_0 - \eta_0{}^2D)\zeta^{(1,0)} = -(A_1 - 2\eta_0\eta_1 D - \beta_1)\zeta^{(0,0)} \tag{35}$$

$$(\Delta\eta)^1\colon\ (A_0 - \eta_0{}^2D)\zeta^{(1,1)} = 2\eta_0 D\zeta^{(1,0)} + 2\eta_1 D\zeta^{(0,0)} - (A_1 - 2\eta_0\eta_1 D - \beta_1)\zeta^{(0,1)} \tag{36}$$

$$(\Delta\eta)^2\colon\ (A_0 - \eta_0{}^2D)\zeta^{(1,2)} = 2\eta_0 D\zeta^{(1,1)} + (D + \alpha_0)\zeta^{(1,0)} + 2\eta_1 D\zeta^{(0,1)} + \alpha_1\alpha^{(0,0)} - (A_1 - 2\eta_0\eta_1 D - \beta_1)\zeta^{(0,2)} \tag{37}$$

The solvability conditions for these equations (for $\zeta^{(1,0)}$, $\zeta^{(1,1)}$, and $\zeta^{(1,2)}$) determine the coefficients and $\zeta^{(l,i)}$ in succession:

$$\beta_1 = \zeta_0^*\cdot A_1\zeta_0 \tag{38}$$

$$\eta_1 = -\zeta_0^*\cdot[2\eta_0 D\zeta^{(1,0)} - (A_1 - \beta_1)\zeta^{(0,1)}]/\alpha_0 \tag{39}$$

$$\alpha_1 = -\zeta_0^*\cdot[2\eta_0 D\zeta^{(1,1)} - (A_1 - 2\eta_0\eta_1 D - \beta_1)\zeta^{(0,2)} + (D + \alpha_0)\zeta^{(1,0)}] + \eta_1\alpha_0/\eta_0 \tag{40}$$

Each vector $\zeta^{(1,i)}$ is uniquely determined by imposing a normalization condition, e.g., $\zeta_0^*\cdot\zeta^{(1,i)} = 0$.

The adjoint eigenvector $\zeta^*(\epsilon, \Delta\eta)$, which is needed in the approximation of Ξ, eq 24, may also be approximated near a Turing instability using an expansion in both ϵ and $\Delta\eta$ (cf eq 28). Substituting this power series into the eigenvalue equation and collecting like power terms, we arrive at a hierarchy of equations for $\zeta^{*(i,j)}$, which are the above equations, but with A_0 replaced by A_0^T. The solvability conditions for these equations are the same as those above and hence are satisfied once $\zeta^{(i,j)}$ are determined.

We may approximate the correlation function, eq 19, for systems close to a Turing instability, using the above expansions. Retaining only the dominant terms, we obtain the following expression for $\Xi_{\alpha\alpha'}(\eta)$

$$\Xi_{\alpha\alpha'}(\eta) \approx -\frac{\Phi_{\alpha\alpha'}}{\lambda_1(\eta)} \tag{41}$$

where the constant $\Phi_{\alpha\alpha'}$ is

$$\Phi_{\alpha\alpha'} = \frac{\zeta_0^*\cdot\tilde{B}(\eta_0)\zeta_0^*}{2}(\zeta_0)_\alpha\,(\zeta_0)_{\alpha'} \tag{42}$$

[We note that this expression may also be used in eq 13 to approximate the stochastic potential near a Turing instability.] Using $\lambda_1(\eta) \approx \alpha_0(\Delta\eta)^2 + \epsilon\beta_1$, we have the values at which $\Xi_{\alpha\alpha'}$ has half its maximum value at $\eta = \eta_0 \pm (\epsilon\beta_1/\alpha_0)^{1/2}$, i.e., the half width of $\Xi_{\alpha\alpha'}$ is $(\epsilon\beta_1/\alpha_0)^{1/2}$. We recognize that Ξ has a resonant line shape as in classical radiation theory.[27] The integral in eq 20 for the non-Poissonian part of the correlation function is

$$h_{\alpha\alpha'}(r) \approx -\frac{\Phi_{\alpha\alpha'}}{\pi}\int_{-\infty}^{\infty}\frac{\cos(\eta_c + \Delta\eta)r}{\alpha_0(\Delta\eta)^2 + \epsilon\beta_1}\,\mathrm{d}(\Delta\eta) \approx \frac{\Phi_{\alpha\alpha'}}{(\alpha_0\epsilon\beta_1)^{1/2}}\exp[-(\epsilon\beta_1/\alpha_0)^{1/2}|r|]\cos\eta_0 r \tag{43}$$

In this approximation, the correlation function is an exponentially damped cosine. The wavelength at leading order is that of the eigenvector corresponding to the maximum eigenvalue of the deterministic equations. The amplitude of the correlation function is inversely proportional to the square root of the maximum eigenvalue of the deterministic equations. We also obtain the correlation length as inversely proportional to the width of $\Xi_{\alpha\alpha'}$ and to the square root of the maximum eigenvalue:

$$l_{\mathrm{corr}} = \left(\frac{\alpha_0}{\epsilon\beta_1}\right)^{1/2} = \left(\frac{1}{2}\frac{\lambda_1''(\eta_c)}{\lambda_1(\eta_c)}\right)^{1/2} \tag{44}$$

where primes denote derivatives with respect to η. As the bifurcation point is approached, the correlation length and the correlation function diverge with a classical square root behavior. (This classical exponent is due to the Gaussian approximation and is not valid for systems very close to the bifurcation point.)

We note that the wavelength and correlation length (decay rate) are described by purely deterministic quantities: the critical wavenumber η_0; largest eigenvalue $\epsilon\beta_1$ [i.e., maximum of $\lambda_1(\eta)$]; the second derivative of λ_1 [with respect to η], α_0. The only term containing explicit stochastic influences is $\Phi_{\alpha\alpha'}$ which determines the amplitude of the correlation function.

B. Numerical Results. To illustrate our theoretical results, we carry out calculations for a two-variable model, the Selkov model.[28] The mechanism consists of the following chemical reactions

$$\mathrm{C}_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{X}, \quad \mathrm{X} + 2\mathrm{Y} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 3\mathrm{Y}, \quad \mathrm{Y} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \mathrm{C}_2 \tag{45}$$

The concentrations of the species C_1 and C_2, denoted the C_1 and C_2 same, are kept constant, while the concentrations of the two intermediates, denoted x and y, are allowed to vary. We use the following set of parameter values: $k_2 = 1.16$; $k_3 = 0.0016$; $k_4 = 0.00022$; $k_5 = 2$; $k_5C_2 = 5.17$, and take k_1C_1 as an externally controllable parameter. Under these constraints, the deterministic equation yields three homogeneous stationary states for the values of k_1C_1 under consideration. A Turing instability occurs at $k_1C_1 = a_0 = 111.8975$ for the stationary state $(x_s, y_s) = (36.1498, 37.5669)$.

This stationary state is stable for parameter values greater than a_0 and is unstable for parameter values less than a_0. A Turing structure grows out of the unstable stationary state for decreasing values of the parameter. At the bifurcation point,

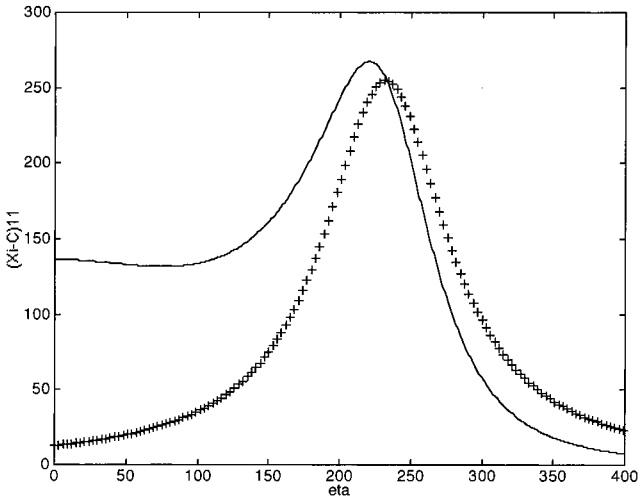

Figure 1. Dependence of $(\Xi - C)_{11}$, marked along the ordinate as (Xi-C)11, on the wavenumber η for a value of k_1C_1 well below the bifurcation value ($\epsilon = 2.102$). The solid line is the exact solution, eq 12, and the curve marked with + is the approximation, eq 41.

the critical wavenumber is $\eta = 231.57$. The matrices A and B are

$$A = \begin{pmatrix} -k_2 - k_3 y_s^2 & -2k_3 x_s y_s + 3k_4 y_s^2 \\ k_3 y_s^2 & 2k_3 x_s y_s - 3k_4 y_s^2 - k_5 \end{pmatrix} \qquad (46)$$

$$B = \begin{pmatrix} k_1C_1 + k_2 x_s + k_3 x_s y_s^2 + k_4 y_s^3 & -k_3 x_s y_s^2 - k_4 y_s^3 \\ -k_3 x_s y_s^2 - k_4 y_s^3 & k_3 x_s y_s^2 + k_4 y_s^3 + k_5 y_s + k_6 C_2 \end{pmatrix}$$

We take the distance parameter to be $\epsilon = k_1C_1 - a_0$ and compute the structure function $\Xi(\eta) - C$ and correlation function $h(r)$ for two values of k_1C_1, one relatively far from the bifurcation value, 114, and the other close to it, 112. We compare the approximations, eqs 41 and 43, with the exact results for both cases. The constants and vectors appearing in the approximations are $\zeta_0 = (0.3624, -0.9320)$, $\zeta_0^* = (-0.3066, -1.1922)$, $\zeta^{(0,1)} = (-2.124 \times 10^{-3}, 5.462 \times 10^{-4})$, $\Phi_{11} = 19.403$, $a_0 = -2.714 \times 10^{-5}$, $\beta_1 = -3.626 \times 10^{-2}$. (To compute the constant β_1, the first term of the expansion of A in the parameter ϵ is needed. Since A depends upon the stationary state solution (x_s, y_s), which is a zero of a cubic polynomial, we expand x_s and y_s in ϵ and determine the first-order corrections to the stationary state. These are used in the eq 46 to find A_1.)

In Figure 1, we plot a component of the structure function, $\Xi(\eta) - C$, for a parameter value near, but not in a perturbative sense, $\epsilon \approx 2$, the bifurcation value. The correlation function, $h(r)$, for the same parameter value is plotted in Figure 2. We compare each of these exact solutions with the approximations, eqs 41 and 43, which are indicated by + symbols. The approximation correctly predicts the location of the maximum of the structure function as well as its width. This is sufficient to give an approximate correlation function, Figure 2, that agrees quite well with the exact solution; the amplitude, period, and decay rate are all correctly described. Even for this relatively large distance from the Turing bifurcation, the correlation function exhibits a prominent oscillatory structure with a wavelength close to that of the Turing structure that occurs above the bifurcation.

In general, the critical wavenumber for the inverse of the deterministic eigenvalue $1/\lambda_1$, which determines the wavelength of the approximation, and that for the structure function do not

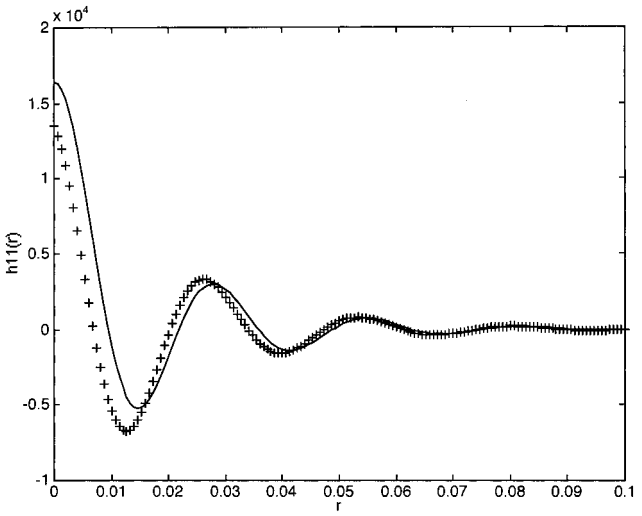

Figure 2. Dependence of the correlation function h_{11} on the distance r for the same parameter values as in Figure 1. The solid line denotes the exact solution, eq 20, and the + curve denotes the approximation, eq 43.

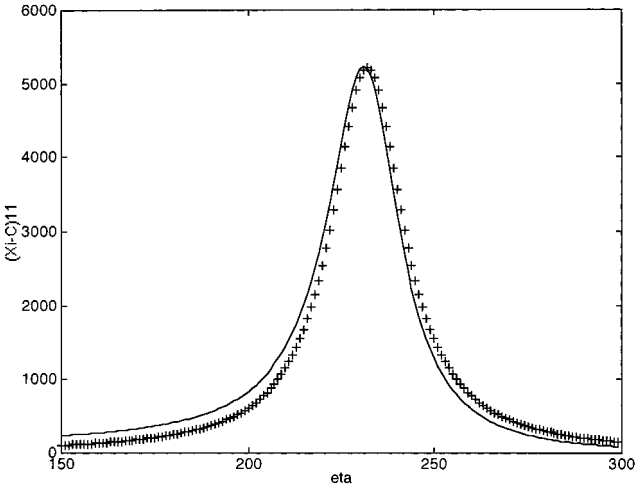

Figure 3. Dependence of $(\Xi - C)_{11}$, marked along the ordinate as (Xi-C)11, on the wavenumber η for a value of k_1C_1 close to the bifurcation value ($\epsilon = 0.1025$). The solid and + curves are exact and approximate solutions as described in Figure 1.

agree away from the bifurcation point. The difference between them is proportional to ϵ. This accounts for the slight offset of the two maxima in Figure 1. The effect of this discrepancy on the correlation function is minimized by a short correlation length for parameter values away from the bifurcation value.

Figures 3 and 4 show a component of the structure and correlation function for a parameter value close to the bifurcation value, $\epsilon \approx 0.1$. The correlation function exhibits a large correlation length, which spans several oscillations. As expected, the asymptotic approximations agree very well with the exact solutions.

IV. Conclusion

In this paper, we have derived explicit expressions for the stochastic potential and spatial correlation function (Gaussian approximation) for reaction−diffusion systems based on a master equation approach. These solutions are simple in structure, making them feasible to compute for systems with arbitrary numbers of species. For systems near Turing instabili-

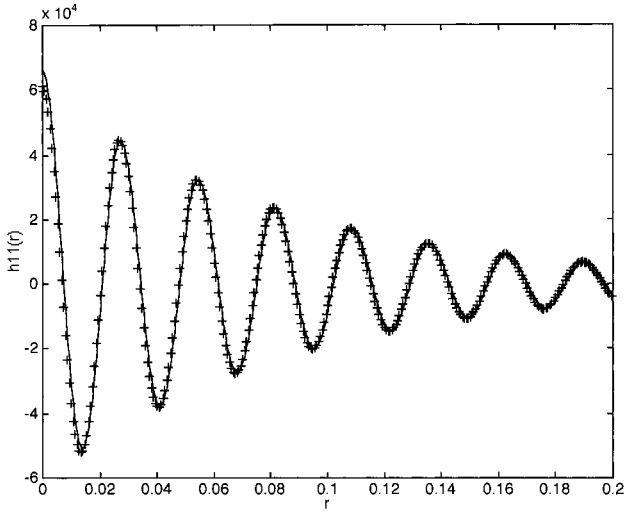

Figure 4. Dependence of the correlation function h_{11} on the distance r for the same parameter values as in Figure 3. The solid line denotes the exact solution, and the + curve denotes the approximation as described in Figure 2.

ties, we developed an approximate solution for the structure function h, from which equations for the potential and correlation function were obtained. The approximate solution for the correlation function is an exponentially damped sinusoidal function (cosine in one-dimensional systems). The amplitude is inversely proportional to the square root of the smallest eigenvalue (of the deterministic system), the correlation length is the reciprocal of the half width of the structure function, and the wavelength is near that of the Turing structure. Our theory shows that long-range structured correlations in systems below Turing bifurcations prefigure the spatially ordered macroscopic state that occurs above the bifurcation.

Our analysis also provides geometrical insight into fluctuations. The WKB approximation of the probability density of reaction−diffusion master equations reduces the leading order behavior to a problem of classical mechanics. The Hamiltonian of an associated system is expressed in terms of probabilities of elementary reaction rates and jumps between mesoscopic scale cells. In this approximation, the leading order term, eikonal, is given by the integral of the Lagrangian along a classical trajectory. Fluctuational trajectories are projections of classical trajectories onto concentration space. The stationary solution for the probability density of the master equation is described by solutions on the unstable manifold of the homogeneous stationary state of the deterministic equation. From this interpretation, most probable local fluctuations may be decomposed into unstable eigenvectors of the Jacobian matrix of Hamilton's equations.

Near the Turing bifurcation, higher order terms for the stochastic potential may be obtained through normal form transformations. These reduce the unstable manifold to that of the linear approximation to arbitrarily high order. However, in general, these transformations diverge as the bifurcation point is approached. To capture correct scaling and the potential at the bifurcation, the normal form for the Turing bifurcation point of the Hamiltonian system should to be studied.

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Appendix

A. General Solutions for the Stochastic Potential and Correlation Function. In this Appendix, we find approximate solutions to the multidimensional reaction−diffusion master equation. We follow the method and notation of our previous work on master equations.[24,25] From the Hamiltonian eq 5, Hamilton's equations of motion for $x_{\mathbf{q}\alpha}$ and $p_{\mathbf{q}\alpha} = \partial S/\partial x_{\mathbf{q}\alpha}$ are given by

$$\begin{aligned}\frac{dx_{\mathbf{q}\alpha}}{dt} &= \frac{\partial H}{\partial p_{\mathbf{q}\alpha}} \\ &= \sum_\rho w_\rho(\mathbf{x_q})\nu_{\rho\alpha}\exp\Big(\sum_\beta p_{\mathbf{q}\beta}\nu_{\rho\beta}\Big) \\ &\quad + \frac{\tilde{D}_\alpha}{2}\sum_{i=1}^{d}\{x_{\mathbf{q}\alpha}[-\exp(-p_{\mathbf{q}\alpha}+p_{(q_i-1)\alpha}) \\ &\quad - \exp(-p_{\mathbf{q}\alpha}+p_{(q_i+1)\alpha})] \\ &\quad + x_{(q_i-1)\alpha}\exp(-p_{(q_i-1)\alpha}+p_{\mathbf{q}\alpha}) \\ &\quad + x_{(q_i+1)\alpha}\exp(-p_{(q_i+1)\alpha}+p_{\mathbf{q}\alpha})\} \end{aligned} \tag{47}$$

$$\begin{aligned}\frac{dp_{\mathbf{q}\alpha}}{dt} &= -\frac{\partial H}{\partial x_{\mathbf{q}\alpha}} \\ &= -\sum_\rho \frac{\partial w_\rho(\mathbf{x_q})}{\partial x_{r\alpha}}[\exp(\sum_\beta p_{\mathbf{q}\beta}\nu_{\rho\beta}) - 1] \\ &\quad - \frac{\tilde{D}_\alpha}{2}\sum_{i=1}^{d}[-\exp(-p_{\mathbf{q}\alpha}+p_{(q_i-1)\alpha}) - 1 \\ &\quad + \exp(-p_{\mathbf{q}\alpha}+p_{(q_i+1)\alpha}) - 1] \end{aligned} \tag{48}$$

In these and the following expressions, we denote a change in the value of a coordinate from that of the vector $\mathbf{q}$ by a subscripted variable; all other coordinate values are equal to those of $\mathbf{q}$. The deterministic equation is obtained from eq 47 with $\mathbf{p} = 0$. The unstable manifold of the fixed point $(x_{\mathbf{q}\alpha}, p_{\mathbf{q}\alpha}) = (c_\alpha, 0)$ determines the time-invariant distribution through eqs 7 and 8.

For points close to the fixed point, the above equations may be approximated by linearizing about the stationary state:

$$\begin{aligned}\frac{du_{\mathbf{q}\alpha}}{dt} &= \sum_\beta A_{\alpha\beta}u_{\mathbf{q}\beta} + \sum_\beta B_{\alpha\beta}v_{\mathbf{q}\beta} \\ &\quad + \frac{\tilde{D}_\alpha}{2}\sum_i(-2u_{\mathbf{q}\alpha} + u_{(q_i-1)\alpha} + u_{(q_i-1)\alpha}) \\ &\quad + \tilde{D}_\alpha c_\alpha\sum_i(2v_{\mathbf{q}\alpha} - v_{(q_i-1)\alpha} - v_{(q_i+1)\alpha}) \end{aligned} \tag{49}$$

$$\frac{dv_{\mathbf{q}\alpha}}{dt} = -\sum_\beta A^T_{\alpha\beta}v_{\mathbf{q}\beta} - \frac{\tilde{D}_\alpha}{2}\sum_i(-2v_{\mathbf{q}\alpha} + v_{(q_i-1)\alpha} + v_{(q_i+1)\alpha}) \tag{50}$$

where $u_{\mathbf{q}\alpha} = x_{\mathbf{q}\alpha} - c_\alpha$ and $v_{\mathbf{q}\alpha} = p_{\mathbf{q}\alpha} - 0$ are small deviations, and

$$\begin{aligned}A_{\alpha\beta} &= \sum_\rho \frac{\partial w_\rho(\mathbf{c}_s)}{\partial x_\beta}\nu_{\rho\alpha} \\ B_{\alpha\beta} &= \sum_\rho w_\rho(\mathbf{c}_s)\nu_{\rho\alpha}\nu_{\rho\beta} \end{aligned} \tag{51}$$

The matrix A is the Jacobian for the well-stirred deterministic system, and B is the probability diffusion matrix of the Fokker–Planck approximation of the master equation for the homogeneous (well-stirred) system.

We note that in the limit of a continuous system, the above equations become

$$\frac{\partial}{\partial t}\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} A + D\nabla^2 & B - 2DC\nabla^2 \\ 0 & -A^{\mathrm{T}} - D\nabla^2 \end{pmatrix}\begin{pmatrix} u \\ v \end{pmatrix} \tag{52}$$

where $u = u(r, t)$ and $v = v(r, t)$ are m-dimensional vectors.

We may write the equations of motion for the deviations, eqs 49 and 50, more compactly in matrix form

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} M_1 & M_2 \\ 0 & -M_1^T \end{pmatrix}\begin{pmatrix} u \\ v \end{pmatrix} \tag{53}$$

where $u = u_{\mathbf{q}\alpha}$, and $v = v_{\mathbf{q}\alpha}$, are mn^d vectors. M_1 and M_1 are $mn^d \times mn^d$ matrices, which for periodic boundary conditions are

$$M_1 = \begin{pmatrix} A - \tilde{D} & \frac{1}{2}\tilde{D} & 0 \\ \frac{1}{2}\tilde{D} & A - \tilde{D} & \vdots \\ 0 & \vdots & \vdots \end{pmatrix},$$

$$M_2 = \begin{pmatrix} B + 2\tilde{D}C & -\tilde{D}C & 0 \\ -\tilde{D}C & B + 2\tilde{D}C & \vdots \\ 0 & \vdots & \vdots \end{pmatrix} \tag{54}$$

where we have written the part involving the matrix $\tilde{D}$ for only the first two spatial coordinates. Similar terms appear for each coordinate. We identify M_1 as the Jacobian matrix of the deterministic system and M_2 as the probability diffusion matrix.

The Hamiltonian for this system is $H^{(2)} = v \cdot M_1 u + {}^1/_2 v \cdot M_2 v$, where the superscript 2 denotes that only terms to second-order are kept. We approximate the stochastic potential near the stationary solution using the corresponding Lagrangian

$$\frac{\mathrm{d}S}{\mathrm{d}t} = v \cdot \dot{u} - H^{(2)}$$

$$= \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}(u \cdot v) \tag{55}$$

Assuming u, v starts from the stationary state (0, 0), we obtain $S(u) = ({}^1/_2) u \cdot v$, where u and v are solutions to eqs 52 or 53.

The unstable manifold of the stationary state determines the time-invariant density. In this linear approximation, we approximate the unstable manifold by eigenvectors in the unstable space of the matrix in eq 53. We denote the eigenvectors corresponding to eigenvalues λ_l, $l = 1, ..., mn^d$, with positive real parts as $(w^{(l)}, v^{(l)})$.

$$\begin{pmatrix} M_1 & M_2 \\ 0 & -M_1^T \end{pmatrix}\begin{pmatrix} w^{(l)} \\ v^{(l)} \end{pmatrix} = \lambda_l \begin{pmatrix} w^{(l)} \\ v^{(l)} \end{pmatrix} \tag{56}$$

A deviation from the stationary state can be expressed in terms of the eigenvectors $w^{(l)}$, and from eq 55 the stochastic potential can be determined. Let W and V denote matrices whose columns are the unstable eigenvectors $w^{(l)}$ and $v^{(l)}$, respectively. Then, a deviation can be written $u = Wy$, $v = Vy$, for some vector y. Then the stochastic potential is

$$S = \frac{1}{2}u \cdot v = \frac{1}{2}u \cdot VW^{-1}u \tag{57}$$

A simplification of the matrices V and W is possible by factoring eigenvector solutions into a spatial and a concentration or momentum part: $w^{(l)} = \rho_{\mathbf{q}}^{(l)} b_\alpha^{(l)}$, $v^{(l)} = \rho_{\mathbf{q}}^{(l)} d_\alpha^{(l)}$. We note that $\rho_q = \mathrm{e}^{2\pi i k q/n}$ satisfies the eigenvalue equation for one coordinate $\rho_{\mathrm{q}} - ({}^1/_2)\rho_{q-1} - ({}^1/_2)\rho_{q+1} = (1 - \cos 2\pi k/n)\,\rho_q$, which appears in eqs 49 and 50. For a d-dimensional system, we introduce a different notation and take the spatial function as

$$Q_{\mathbf{qk}} = \frac{1}{n^{d/2}}\mathrm{e}^{2\pi i \mathbf{k}\cdot\mathbf{q}/n} \tag{58}$$

where $\mathbf{k}$ and $\mathbf{q}$ are m-dimensional vectors, with $k_i = 1 - n/2$, ..., $n/2$ and $q_j = 1$, ..., n. We have normalized these functions so that $\sum_{\mathbf{q}} Q_{\mathbf{qk}} \bar{Q}_{\mathbf{qm}} = \delta_{\mathbf{km}}$. Substituting this form into eq 56 results in the following eigenvalue equation for matrices $E_{\mathbf{k}}$ and $F_{\mathbf{k}}$ whose columns are comprised of the solutions $b_\alpha^{(\mathbf{k})}$ and $d_\alpha^{(\mathbf{k})}$, respectively:

$$\begin{pmatrix} \tilde{A}_{\mathbf{k}} & \tilde{B}_{\mathbf{k}} \\ 0 & -(\tilde{A}_{\mathbf{k}})^T \end{pmatrix}\begin{pmatrix} E_{\mathbf{k}} \\ F_{\mathbf{k}} \end{pmatrix} = \begin{pmatrix} E_{\mathbf{k}}\Lambda_{\mathbf{k}} \\ F_{\mathbf{k}}\Lambda_{\mathbf{k}} \end{pmatrix} \tag{59}$$

where

$$\tilde{A}_{\mathbf{k}} = A - \mu_{\mathbf{k}}\tilde{D}, \quad \tilde{B}_{\mathbf{k}} = B + 2\mu_{\mathbf{k}}\tilde{D}C$$

$$\mu_{\mathbf{k}} = \sum_{i=1}^{d}\left(1 - \cos\frac{2\pi k_i}{n}\right) \tag{60}$$

The matrix $\Lambda_{\mathbf{k}}$ is diagonal and contains the eigenvalues of $-(\tilde{A}_{\mathbf{k}})^T$ (i.e., the eigenvalues of the deterministic system with reversed sign). Thus, the stochastic potential for the discrete cell problem is determined by the solutions to matrix eigenvalue equations.

In the limit of infinitely many cells (for finite or infinite L), we have the corresponding problem with the matrices $\tilde{A}_{\mathbf{k}}$ and $\tilde{B}_{\mathbf{k}}$ replaced by

$$\tilde{A}(\eta) = A - \eta^2 D, \tilde{B}(\eta) = B + 2\eta^2 DC$$

$$\eta^2 = \sum_{i=1}^{\mathrm{d}}\eta_i^2 \tag{61}$$

For finite L, the Fourier variable η_i takes on discrete values, $2\pi k_i/L$, $k_i = 0, 1, ...$, while for $L \to \infty$, the variable η_i is continuous. In both cases, the matrices $\tilde{A}$ and $\tilde{B}$ only depend upon the magnitude η and therefore, the eigenvalues and eigenvectors, eq 59, also only depend on the magnitude η.

We factor the matrices W (resp V) into a spatial matrix R and a concentration matrix E (resp momentum matrix F):

$$W = RE, \quad V = RF \tag{62}$$

where

$$R = (I_m Q_{\mathbf{qk}}) \tag{63}$$

and

$$E = \mathrm{diag}(E_{\mathbf{k}}), \quad F = \mathrm{diag}(F_{\mathbf{k}}) \tag{64}$$

In eq 63, I_m denotes the $m \times m$-dimensional unit matrix. The vector $\mathbf{q}$ labels the rows and $\mathbf{k}$ the columns, in which for each value of $\mathbf{q}$ and $\mathbf{k}$ there is an m-dimensional diagonal block consisting of element $Q_{\mathbf{qk}}$. From the orthonormality of $Q_{\mathbf{qk}}$, the matrix R is unitary, $R\bar{R}^T = 1$. From eq 57, the stochastic potential is ${}^1/_2 RFE^{-1}\bar{R}^T$.

Using the above factorization, we may express the stochastic potential in a simple form using the Fourier representation of a periodic function. We write a deviation from the stationary state as a Fourier series

$$u_{\mathbf{q}\alpha} = f_{\mathbf{q}\alpha} = \sum_{k_i=1-n/2}^{n/2} a_{\mathbf{k}\alpha} e^{2\pi i \mathbf{k}\cdot\mathbf{q}/n} \tag{65}$$

where

$$a_{\mathbf{k}\alpha} = \frac{1}{n^d}\sum_{q_i=1}^{n} f_{\mathbf{q}\alpha} e^{-2\pi i \mathbf{k}\cdot\mathbf{q}/n} \tag{66}$$

Then, using the above factorization of V and W, eqs 62−64, and the structure of R, we obtain the following expression for the potential [for finite length L and (even) number of cells n]:

$$S = \frac{n^d}{2}\sum_{k_1=1-n/2}^{n/2} \cdots \sum_{k_\alpha=1-n/2}^{n/2}\sum_{\alpha,\beta} a_{\mathbf{k}\alpha} (\Xi_{\mathbf{k}}^{-1})_{\alpha\beta} a_{\mathbf{k}\beta} \tag{67}$$

where $\Xi_{\mathbf{k}} = E_{\mathbf{k}}F_{\mathbf{k}}^{-1}$. The matrix $\Xi_{\mathbf{k}}$ satisfies a fluctuation−dissipation relation

$$\tilde{A}_{\mathbf{k}}\Xi_{\mathbf{k}} + \Xi_{\mathbf{k}}(\tilde{A}_{\mathbf{k}})^T + \tilde{B}_{\mathbf{k}} = 0 \tag{68}$$

which may be shown by solving each of the two $m \times m$ matrix equations in eq 59 for $\Lambda_{\mathbf{k}}$ and equating the resulting expressions. The formula for $n \to \infty$ and finite L is easily obtained from this equation and has the same form. In this case, the deviation is a function of a continuous variable $\mathbf{f}(\mathbf{r})$ and $a_{\mathbf{k}\beta}$ denotes the Fourier transform of $\mathbf{f}$. Also, the matrix $\Xi_{\mathbf{k}}$ is replaced by $\Xi(\eta) = E(\eta)F^{-1}(\eta)$, where $E(\eta)$ and $F(\eta)$ are solutions in the unstable space of the matrix eq 59 (with $\tilde{A}$ and $\tilde{B}$ defined in eq 61). Letting the system length increase, $L \to \infty$, we have

$$S = \frac{1}{2}\left(\frac{2\pi n}{L}\right)^d \int \sum_{\alpha,\beta} g_\alpha(\boldsymbol{\eta})\,(\Xi^{-1}(\eta))_{\alpha\beta} g_\beta(\boldsymbol{\eta})\,\mathrm{d}\boldsymbol{\eta} \tag{69}$$

where the integration is over the whole space R^d, $\eta_i = 2\pi k_i/L$, $r_i = Lq_i/n$ and g_α is the Fourier transform of f_α:

$$g_\alpha(\boldsymbol{\eta}) = \frac{1}{(2\pi)^d}\int e^{i\boldsymbol{\eta}\cdot\mathbf{r}} f_\alpha(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{70}$$

In making the transition from finite to infinite length, we have written the single sum over $\boldsymbol{\eta}$, in the discrete, finite L problem, as a double sum over $\boldsymbol{\eta}$ and $\boldsymbol{\eta}'$ and inserted a Kronecker delta $\delta_{\eta\eta'}$; in the large system size limit, this double sum can be converted to a double integral and the Kronecker delta becomes a Dirac delta function: $\delta_{\boldsymbol{\eta}\boldsymbol{\eta}'} \approx (2\pi/L)\delta(\boldsymbol{\eta} - \boldsymbol{\eta}')$. The above result for the stochastic potential gives the following expression for the approximate probability density in a large system:

$$P \approx \exp\left(-\frac{(2\pi)^d}{2}\int \mathbf{g}(\boldsymbol{\eta})\cdot\Xi^{-1}(\eta)\,\mathbf{g}(\boldsymbol{\eta})\,\mathrm{d}\boldsymbol{\eta}\right) \tag{71}$$

The spatial correlation function is related to the potential $(1/2)RFE^{-1}\bar{R}^T$ by $\langle u_{\mathbf{q}\alpha}u_{\mathbf{q}'\alpha'}\rangle = (\Delta V)^{-1}(REF^{-1}\bar{R}^T)_{\mathbf{q}\alpha,\mathbf{q}'\alpha'}$. Using the structure of E, F, and R, we obtain the correlation function for a finite length system composed of a finite number of cells:

$$\langle u_{\mathbf{q}\alpha}u_{\mathbf{q}'\alpha'}\rangle = L^{-d}\sum_{k_1=1-n/2}^{n/2} \cdots \sum_{k_d=1-n/2}^{n/2} (\Xi_{\mathbf{k}})_{\alpha\alpha'} e^{2\pi i \mathbf{k}\cdot(\mathbf{q}-\mathbf{q}')/n} \tag{72}$$

For increasing numbers of cells in a finite length system, the same relation holds for $\Xi(\eta)$, in which $\tilde{A}_{\mathbf{k}}$ and $\tilde{B}_{\mathbf{k}}$ are replaced by those for $\tilde{A}(\eta)$ and $\tilde{B}(\eta)$. For large η, the matrices $\tilde{A}(\eta)$ and $\tilde{B}(\eta)$ become $-\eta^2 D$ and $2\eta^2 DC$, respectively. The solution for $\Xi_{\mathbf{k}}$ in this limit is C. We separate this divergent part from the sum and write the correlation function as

$$\langle u_{\mathbf{q}\alpha}u_{\mathbf{q}'\alpha'}\rangle = (L/n)^{-d}\,C_{\alpha\alpha'}\delta_{\mathbf{q}\mathbf{q}'} + \frac{1}{L^d}\sum_{k_1=1-n/2}^{n/2} \cdots \sum_{k_d=1-n/2}^{n/2} (\Xi_{\mathbf{k}} - C)_{\alpha\alpha'} e^{2\pi i \mathbf{k}\cdot(\mathbf{q}-\mathbf{q}')/n} \tag{73}$$

Letting the number of cells and system length become large, $n \to \infty$, $L \to \infty$, we obtain the continuous version:

$$\langle u_\alpha(\mathbf{r})u_{\alpha'}(\mathbf{r}')\rangle = C_{\alpha\alpha'}(\mathbf{r}-\mathbf{r}') + h_{\alpha\alpha'}(\mathbf{r}-\mathbf{r}')$$

$$h_{\alpha\alpha'}(\mathbf{r}-\mathbf{r}') = \frac{1}{(2\pi)^d}\int (\Xi(\eta) - C)_{\alpha\alpha'}\, e^{i\boldsymbol{\eta}\cdot(\mathbf{r}-\mathbf{r}')}\,\mathrm{d}\boldsymbol{\eta} \tag{74}$$

The delta function term originates from a Poissonian distribution that is due to fluctuations caused by diffusion. The second term, h, the structure function, is due to coupling between reaction and diffusion, which causes long-range structure in spatial correlations. Using the property that the matrix $\Xi(\eta)$ is an even function of η, eq 68, we may limit integration to non-negative values of η_i, $i = 1, ..., d$:

$$h_{\alpha\alpha'}(\mathbf{r}-\mathbf{r}') = \frac{1}{\pi^d}\int_0^\infty \cdots \int_0^\infty (\Xi(\eta) - C)_{\alpha\alpha'} \times \cos\eta_1 (r_1 - r_1') \cdots \cos\eta_d (r_d - r_d')\,\mathrm{d}\eta_1 \cdots \mathrm{d}\eta_d \tag{75}$$

B. Approximations for Systems Close to Turing Bifurcations. The correlation function and stochastic potential for one-dimensional systems has been approximated in section III.A using the leading order expression for the structure function Ξ, eq 41. This expression for Ξ may also be used in approximations for higher dimensional systems, since $\Xi(\eta)$ only depends on the magnitude η.

We concentrate on three-dimensional systems, because of their physical importance. First, the multiple integral in eq 74 can be reduced to a single integral by converting to spherical coordinates. Integrating over the angles yields

$$h_{\alpha\alpha'}(r) = \frac{1}{2\pi^2}\int_0^\infty (\Xi(\eta) - C)_{\alpha\alpha'}\,\frac{\eta \sin \eta r}{r}\,\mathrm{d}\eta \tag{76}$$

where we denote the magnitude $r = |\mathbf{r} - \mathbf{r}'|$, and $\boldsymbol{\eta}\cdot(\mathbf{r}-\mathbf{r}') = \eta r\cos\theta$. Then using the approximation for $\Xi(\eta)$, eq 41, we obtain the explicit solution

$$h_{\alpha\alpha'}(r) \approx \frac{\eta_0\Phi_{\alpha\alpha'}}{2\pi}\,\frac{1}{(\alpha_0\epsilon\beta_1)^{1/2}}\,\frac{\sin\eta_0 r}{r}\exp\left(-\left(\frac{\epsilon\beta_1}{\alpha_0}\right)^{1/2} r\right) \tag{77}$$

where α_0, and $\epsilon\beta_1$, and $\Phi_{\alpha\alpha'}$ are determined by eqs 34, 38, and 42 of section III.A. We find that the amplitude and correlation length are the same as for a one-dimensional system. In particular, the amplitude diverges as the inverse of the square root of the largest eigenvalue (of the deterministic system) and the correlation length diverges as the inverse of the half width of the structure function.

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