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Stochastic Analysis of a Chemical Reaction with Spatial and Temporal Structures

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A stochastic analysis of the spatial and temporal structures in the Prigogine–Lefever–Nicolis model (the Brusselator) is presented. The analysis is carried out through a Langevin equation derived from a multivariate master equation using the Poisson representation method, which is used to calculate the spatial correlation functions and the fluctuation spectra in the Gaussian approximation. The case of an infinite three-dimensional system is considered in detail. The calculations for the spatial correlation functions and the fluctuation spectra for a finite system subject to different kinds of boundary conditions are also given.

KEY WORDS: Brusselator; chemical reactions; chemical oscillations; correlations; fluctuations; instabilities; Langevin equations; master equations; Poisson representation; reaction–diffusion systems.

1. INTRODUCTION

Recently Chaturvedi *et al.*[1] and Gardiner and Chaturvedi[2] have developed a new technique for solving multivariate chemical master equations introduced by Kitahara,[3] Gardiner *et al.*,[4] and van Kampen.[5] The technique is based on an expansion of the probability distribution in Poisson distributions. This enables the chemical master equations to be transformed into exact Fokker–Planck equations, from which one can derive equivalent Langevin equations, which may then be solved perturbatively to obtain a complete asymptotic expansion for the various moments in the inverse powers of the system size. This method has been discussed at length in Ref. 2, where its applications to various linear and nonlinear systems were given.

The purpose of this paper is to consider in detail its application to a well-studied example, the Brusselator.[6–8] This model has been analyzed from various points of view by a number of authors. Glansdorff and Prigogine have

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carried out the stability analysis of the deterministic equation in Ref. 6 and found that with the combination of diffusion and nonlinear chemical kinetics, as a certain chemical parameter is varied, the steady state, which is initially homogeneous, may give rise to a dissipative structure which is spatially organized (the soft mode instability) or to temporal oscillations (the hard mode instability). A detailed analysis of the solutions of the deterministic equations for a finite one-dimensional system subject to various boundary conditions was given by Auchmuty and Nicolis[(9)] using Hopf bifurcation theory. Post-instability solutions of the deterministic equations for a one-dimensional system with periodic boundary conditions have also been investigated by Kuramoto and Tsuzuki[(10)] using their reductive perturbation approach. A stochastic treatment of this model without diffusion has been given by Tomita *et al.*[(11)] using a Fokker–Planck equation derived on the basis of van Kampen's system size expansion method.[(12)] They also used numerical methods to investigate the behavior of the variances beyond the hard mode instability. Portnow and Kitahara[(13)] calculated the variances for this model without diffusion using a Langevin equation derived from a path integral method. Effects of diffusion on the fluctuations have been analyzed by Nicolis *et al.*[(14)] using a nonlinear master equation.[(15)] Lemarchand and Nicolis[(16)] calculated the correlation functions for a finite one-dimensional system subject to two kinds of boundary conditions using cumulant expansion methods. Combining van Kampen's system size expansion method with the reductive perturbation method, Mashiyama *et al.*[(17)] and Kuramoto and Tsuzuki[(18)] have calculated the correlation functions in the neighborhood of the critical points. Similar results have been obtained by Wunderlin and Haken[(19)] in their work on scaling theory for nonequilibrium systems. Some interesting features of the fluctuation spectrum for this model have been investigated by Mazo[(20)] and Deutch *et al.*[(21)]

In none of the above is there a complete calculation of the correlation structure and the fluctuation spectra for a three-dimensional system, and this is the principal content of our paper. Our methods are based on a perturbative solution of the Poisson representation Langevin equations and are not reliable very close to a critical point. Other boundary conditions are easily treated and we illustrate this in Section 6.

A brief outline of the paper is as follows. In Section 2 we derive the Langevin equations for the Brusselator using the Poisson representation method. Section 3 contains a discussion of the stability of the homogeneous steady state. In Section 4 we calculate the spatial correlation functions for a three-dimensional infinite system and discuss their behavior as the instability point is approached. In Section 5 we calculate the two-time correlation functions and the fluctuation spectra and briefly discuss some of its salient features. In Section 6 we formulate the Langevin equations for finite systems subject to various boundary conditions and indicate how the correlation functions and the fluctuation spectra may be calculated. As noted above, the only work on this problem is that due to Lemarchand and Nicolis, whose results are straightforwardly obtained by our techniques. This section is a separate development, which uses the methods developed in the first five sections but is really logically independent of them. The reader not interested in this aspect of the problem may omit reading this section. Section 7 contains a few concluding remarks. In the appendices we give some results that follow from a linear Langevin equation, which are included for completeness.

2. FORMULATION OF THE LANGEVIN EQUATION FOR THE BRUSSELATOR

The reaction mechanism for the Brusselator is[6]

$$\begin{gathered} \mathrm{A} \xrightarrow{k_1} \mathrm{X}, \qquad \mathrm{B} + \mathrm{X} \xrightarrow{k_2} \mathrm{Y} + \mathrm{D}, \\ 2\mathrm{X} + \mathrm{Y} \xrightarrow{k_3} 3\mathrm{X}, \qquad \mathrm{X} \xrightarrow{k_4} \mathrm{E} \end{gathered} \tag{1}$$

A master equation which describes the reaction (1) as occurring locally within cells (volume ΔV) of the system, labeled by indices $i, j, \ldots$, with diffusion viewed as a transfer of molecules from cell i to cell j with a probability per molecule per unit time of d_{ij}^X and d_{ij}^Y, can be written[3-5]

$$\begin{aligned} dP(\mathbf{X}, \mathbf{Y}, t)/dt = \sum_{i,j} & [d_{ij}^X(X_i + 1)P(X_i + 1, X_j - 1, \hat{\mathbf{X}}, \mathbf{Y}, t) - d_{ij}^X X_j(P(\mathbf{X}, \mathbf{Y}, t) \\ & + d_{ij}^Y(Y_i + 1)P(\mathbf{X}, Y_i + 1, Y_j - 1, \hat{\mathbf{Y}}, t) - d_{ij}^Y Y_j P(\mathbf{X}, \mathbf{Y}, t)] \\ & + \sum_i \{[k_1 A P(X_i - 1, \hat{\mathbf{X}}, \mathbf{Y}, t) \\ & + k_3 B(X_i + 1)P(X_i + 1, \hat{\mathbf{X}}, Y_i - 1, \hat{\mathbf{Y}}, t) \\ & + k_3(X_i - 1)(X_i - 2)(Y_i + 1)P(X_i - 1, \hat{\mathbf{X}}, Y_i + 1, \hat{\mathbf{Y}}, t) \\ & + k_4(X_i + 1)P(X_i + 1, \hat{\mathbf{X}}, \mathbf{Y}, t)] \\ & - [k_1 A + k_2 B X_i + k_3 X_i(X_i - 1) Y_i + k_4 X_i]P(\mathbf{X}, \mathbf{Y}, t)\} \end{aligned} \tag{2}$$

Here the d_{ij} can be chosen (as in Ref. 4) to vanish unless i and j represent adjacent cells, but we shall not always require this in this paper. In general, the important results are insensitive to the exact form of the d_{ij}, as long as they decrease rapidly as the distance between cells i and j increases.

The macroscopic chemical kinetics of this system are

$$\begin{aligned} \partial\rho_X(\mathbf{r}, t)/\partial t &= D_X \nabla^2\rho_X(\mathbf{r}, t) + \kappa_1 - \kappa_2\rho_X(\mathbf{r}, t) + \kappa_3\rho_X{}^2(\mathbf{r}, t)\rho_Y(\mathbf{r}, t) - \kappa_4\rho_X(\mathbf{r}, t) \\ \partial\rho_Y(r, t)/\partial t &= D_Y \nabla^2\rho_Y(\mathbf{r}, t) + \kappa_2\rho_X(\mathbf{r}, t) - \kappa_3\rho_X{}^2(\mathbf{r}, t)\rho_Y(\mathbf{r}, t) \end{aligned} \tag{2a}$$

where ρ_X and ρ_Y are the concentrations of X and Y and we have taken account of the cell size dependence of k_1, k_2, k_3, k_4, A, and B by writing

$$\kappa_1 \, \Delta V = k_1 A, \qquad \kappa_2 = k_2 B, \qquad \kappa_3(\Delta V)^{-2} = k_3, \qquad \kappa_4 = k_4$$

The diffusion coefficient D_X is given by

$$D_X = \sum_i |\mathbf{r}_i - \mathbf{r}_j|^2 d_{ij}^X \tag{2b}$$

with a similar equation for D_Y.

Following Refs. 1 and 2, we expand $P(\mathbf{X}, \mathbf{Y}, t)$ in Poisson distributions:

$$P(\mathbf{X}, \mathbf{Y}, t) = \int \left[\prod_i d\alpha_X(i) \, d\alpha_Y(i) \frac{[\alpha_X(i)]^{X_i}}{X_i!} \frac{[\alpha_Y(i)]^{Y_i}}{Y_i!} e^{-\alpha_X(i)} e^{-\alpha_Y(i)} \right] f(\boldsymbol{\alpha}_X, \boldsymbol{\alpha}_Y, t) \tag{3}$$

and substitute (3) in (2) to obtain a Fokker–Planck equation for the quasiprobability distribution

$$\begin{aligned}
\frac{\partial f(\boldsymbol{\alpha}_X, \boldsymbol{\alpha}_Y, t)}{\partial t} & \\
= -\sum_i \frac{\partial}{\partial \alpha_X(i)} & \Bigg\{ \Bigg[\sum_j D_{ij}^X \alpha_X(j) + \kappa_1 \, \Delta V - \kappa_2 \alpha_X(i) \\
& + \kappa_3 (\Delta V)^{-2} \alpha_X^2(i) \alpha_Y(i) - \kappa_4 \alpha_X(i) \Bigg] f(\boldsymbol{\alpha}_X, \boldsymbol{\alpha}_Y, t) \Bigg\} \\
& - \sum_i \frac{\partial}{\partial \alpha_Y(i)} \Bigg\{ \Bigg[\sum_j D_{ij}^Y \alpha_Y(j) + \kappa_2 \alpha_X(i) \\
& - \kappa_3 (\Delta V)^{-2} \alpha_X^2(i) \alpha_Y(i) \Bigg] f(\boldsymbol{\alpha}_X, \boldsymbol{\alpha}_Y, t) \Bigg\} \\
& + \sum_i \left(\frac{\partial^2}{\partial \alpha_X^2(i)} - \frac{\partial^2}{\partial \alpha_X(i) \, \partial \alpha_Y(i)} \right) [2\kappa_3 (\Delta V)^{-2} \alpha_X^2(i) \alpha_Y(i)] f(\boldsymbol{\alpha}_X, \boldsymbol{\alpha}_Y, t) \\
& - \sum_i \left(\frac{\partial^3}{\partial \alpha_X^3(i)} - \frac{\partial^3}{\partial \alpha_X^2(i) \, \partial \alpha_Y(i)} \right) [2\kappa_3 (\Delta V)^{-2} \alpha_X^2(i) \alpha_Y(i)] f(\boldsymbol{\alpha}_X, \boldsymbol{\alpha}_Y, t)
\end{aligned} \tag{4}$$

where

$$D_{ij} = d_{ij} - \left(\sum_k d_{ik} \right) \delta_{ij} \tag{5}$$

This Fokker–Planck equation is an exact consequence of the master equation, though the quasiprobability need not have all the attributes of a probability, as shown in Ref. 2.[2] However, it is shown in Ref. 2 that exactly

[2] For example, f can in general be positive, negative, or even a function of a complex variable, and its variances can be negative, though those of P are always positive.

equivalent Langevin equations can always be derived, though this involves, in this case, the incorporation of a new form of Langevin source, which we have called third-order noise, to account for the third-order derivatives occurring in (4). Fortunately, these do not contribute to the leading terms in the expansion of the mean and correlation functions in inverse powers of ΔV (which is assumed to be large) and will therefore be omitted. The resulting Fokker–Planck equation is then exactly equivalent to the Langevin equation,

$$\frac{d}{dt}\begin{pmatrix}\eta_X(i,t)\\ \eta_Y(i,t)\end{pmatrix} = \begin{pmatrix}\sum_j D_{ij}^X\eta_X(j,t) + \kappa_1 - \kappa_2\eta_X(i,t) + \kappa_3\eta_X{}^2(i,t)\eta_Y(i,t) - \kappa_4\eta_X(i,t)\\ \sum_j D_{ij}^Y\eta_Y(j,t) + \kappa_2\eta_X(i,t) - \kappa_3\eta_X{}^2(i,t)\eta_Y(i,t)\end{pmatrix}$$

$$+ \epsilon[4\kappa_3\eta_X{}^2(i,t)\eta_Y(i,t)]^{1/2}\begin{pmatrix}1 & -1/2\\ -1/2 & 0\end{pmatrix}^{1/2}\begin{pmatrix}\xi_X(i,t)\\ \xi_Y(i,t)\end{pmatrix} \tag{6}$$

where

$$\begin{gathered}\eta_\mu(i,t) = (\Delta V)^{-1}\alpha_\mu(i,t), \qquad \mu = X, Y\\ \epsilon = (\Delta V)^{-1/2}\\ \langle\xi_\mu(i,t)\rangle = 0, \qquad \langle\xi_\mu(i,t)\xi_\nu(j,t')\rangle = \delta_{\mu\nu}\,\delta_{ij}\,\delta(t-t')\end{gathered} \tag{7}$$

The mean and the correlation function in X_i, Y_i variables are related to those in η_μ through the following relations:

$$\langle\rho_\mu(i,t)\rangle \equiv \langle\mu_i(t)\rangle/\Delta V = \langle\eta_\mu(i,t)\rangle \tag{8a}$$

$$\begin{aligned}\langle\rho_\mu(i,t),\rho_\nu(j,t)\rangle &\equiv \left\langle\frac{\mu_i(t)}{\Delta V},\frac{\nu_j(t)}{\Delta V}\right\rangle\\ &= \langle\eta_\mu(i,t)\rangle\,\delta_{\mu\nu}\frac{\delta_{ij}}{\Delta V} + \langle\eta_\mu(i,t),\eta_\nu(j,t)\rangle\end{aligned} \tag{8b}$$

A perturbative solution of (6) is achieved by expanding $\eta_\mu(i,t)$ in powers of ΔV,

$$\eta_\mu(i,t) = \eta_{\mu,0}(i,t) + \epsilon\eta_{\mu,1}(i,t) + \cdots \tag{9}$$

In the present work we shall limit ourselves to calculating the correlation functions in the Gaussian approximation, which amounts to retaining only the first two terms in the expansion (9).[2]

Substituting this expansion in (6), we get

$$\frac{d}{dt}\begin{pmatrix}\eta_{X,0}(i,t)\\ \eta_{Y,0}(i,t)\end{pmatrix} = \begin{pmatrix}\sum_j D^X_{ij}\eta_{X,0}(j,t) + \kappa_1 - \kappa_2\eta_{X,0}(i,t)\eta_{Y,0}(i,t) \\ \quad + \eta^2_{X,0}(i,t)\eta_{Y,0}(i,t) - \eta_{X,0}(i,t) \\ \sum_j D^X_{ij}\eta_{Y,0}(j,t) + \kappa_2\eta_{X,0}(i,t) - \eta^2_{X,0}(i,t)\eta_{Y,0}(i,t)\end{pmatrix} \tag{10}$$

and

$$\begin{aligned}\frac{d}{dt}\begin{pmatrix}\eta_{X,1}(i,t)\\ \eta_{Y,1}(i,t)\end{pmatrix} &= \begin{pmatrix}\sum_j D^X_{ij}\eta_{X,1}(j,t)\\ \sum_j D^Y_{ij}\eta_{Y,1}(j,t)\end{pmatrix} \\ &\quad + \begin{pmatrix}2\eta_{X,0}(i,t)\eta_{Y,0}(i,t) - \kappa_2 - 1 & \eta^2_{X,0}(i,t)\\ -2\eta_{X,0}(i,t)\eta_{Y,0}(i,t) + \kappa_2 & -\eta^2_{X,0}(i,t)\end{pmatrix}\begin{pmatrix}\eta_{X,1}(i,t)\\ \eta_{Y,1}(i,t)\end{pmatrix} \\ &\quad + 2[\eta^2_{X,0}(i,t)\eta_{Y,0}(i,t)]^{1/2}\begin{pmatrix}1 & -1/2\\ -1/2 & 0\end{pmatrix}^{1/2}\begin{pmatrix}\xi_X(i,t)\\ \xi_Y(i,t)\end{pmatrix}\end{aligned} \tag{11}$$

where for simplicity we have put $\kappa_3 = \kappa_4 = 1$.

The relations (8a) and (8b) become

$$\langle\rho_\mu(i,t)\rangle = \langle\eta_{\mu,0}(i,t)\rangle + O(\epsilon^2) \tag{12}$$

$$\begin{aligned}\langle\rho_\mu(i,t), \rho_\nu(j,t)\rangle &= \langle\eta_{\mu,0}(i,t)\rangle\,\delta_{\mu\nu}\,\delta_{ij}/\Delta V \\ &\quad + (1/\Delta V)\langle\eta_{\mu,1}(i,t)\eta_{\nu,1}(j,t)\rangle + O(\epsilon^4)\end{aligned} \tag{13}$$

For the sake of brevity we shall introduce the following matrix notation:

$$S(i,j,t) = M(i,t)(\delta_{ij}/\Delta V) + (1/\Delta V)G(i,j,t) \tag{14}$$

where

$$S(i,j,t) \equiv \langle\rho(i,t), \rho^T(j,t)\rangle \tag{15}$$

$$M_{\mu\nu}(i,t) \equiv \langle\eta_{\mu,0}(i,t)\rangle\,\delta_{\mu\nu} \tag{16}$$

$$G(i,j,t) \equiv \langle\eta_1(i,t)\eta_1{}^T(j,t)\rangle \tag{17}$$

Now the homogeneous steady-state solution of the deterministic equation (10) is

$$\eta_{X,0}(i,t) = \kappa_1, \qquad \eta_{Y,0}(i,t) = \kappa_2/\kappa_1 \tag{18}$$

Substituting (18) in (11), we get

$$\frac{d}{dt}\begin{pmatrix}\eta_{X,1}(i,t)\\ \eta_{Y,1}(i,t)\end{pmatrix} = \begin{pmatrix}\sum_j D^X_{ij}\eta_{X,1}(j,t)\\ \sum_j D^Y_{ij}\eta_{Y,1}(j,t)\end{pmatrix} + \begin{pmatrix}\kappa_2 - 1 & \kappa_1{}^2\\ -\kappa_2 & -\kappa_1{}^2\end{pmatrix}\begin{pmatrix}\eta_{X,1}(j,t)\\ \eta_{Y,1}(j,t)\end{pmatrix}$$
$$+ 2(\kappa_2\kappa_1)^{1/2}\begin{pmatrix}1 & -1/2\\ -1/2 & 0\end{pmatrix}^{1/2}\begin{pmatrix}\xi_X(i,t)\\ \xi_Y(i,t)\end{pmatrix} \tag{19}$$

In the present work the matrix d_{ij}, thus far unspecified, will be assumed to have the following standard form:

$$d_{ij} = \begin{cases} d & \text{if } i, j \text{ are nearest neighbors}\\ 0 & \text{otherwise}\end{cases} \tag{20}$$

Other choices for d_{ij} are possible, which would give different short-wavelength behavior, but the more interesting long-wavelength behavior would be the same as that given by the choice in (20).[2]

Presently, we shall solve (19) for an infinite, continuous system. A discussion of the solutions of (19) for a finite system with various boundary conditions is given in Section 4.

In the continuum notation (19) and (14) become

$$(d/dt)\boldsymbol{\eta}_1(\mathbf{r},t) = -A\boldsymbol{\eta}_1(\mathbf{r},t) + B\boldsymbol{\xi}(\mathbf{r},t) \tag{21}$$

$$S(\mathbf{r},\mathbf{r}',t) = M(\mathbf{r},t)\,\delta(\mathbf{r}-\mathbf{r}') + G(\mathbf{r},\mathbf{r}',t) \tag{22}$$

where $\mathbf{r}$ is a continuous label and

$$A = \begin{pmatrix}-D_X\nabla^2 - \kappa_2 + 1 & \kappa_1{}^2\\ \kappa_2 & -D_Y\nabla^2 + \kappa_1{}^2\end{pmatrix} \tag{23}$$

$$B = 2(\kappa_2\kappa_1)^{1/2}\begin{pmatrix}1 & -1/2\\ -1/2 & 0\end{pmatrix}^{1/2} \tag{24}$$

and $D = dl^2$, l being the cell length. (For a discussion of certain difficulties involved in going over to a continuum notation and their clarification, the reader is referred to Ref. 2, Section 9.)

3. STABILITY OF THE HOMOGENEOUS STEADY STATE

The Fourier transform of Eq. (19) is

$$(d/dt)\tilde{\boldsymbol{\eta}}_1(\mathbf{q},t) = -\tilde{A}(q^2)\tilde{\boldsymbol{\eta}}_1(\mathbf{q},t) + B\tilde{\boldsymbol{\xi}}(\mathbf{q},t) \tag{25}$$

It is clear from (25) that the homogeneous steady state will be stable provided that the eigenvalues of $\tilde{A}(q^2)$ have positive real parts. These eigenvalues are given by

$$\begin{aligned}\lambda_1, \lambda_2 = \tfrac{1}{2}[(D_X + D_Y)q^2 + 1 + \kappa_1{}^2 - \kappa_2 \\ \pm \{[(D_X + D_Y)q^2 + \kappa_1{}^2 + 1 - \kappa_2]^2 \\ - 4[(D_Xq^2 - \kappa_2 + 1)(D_Yq^2 + \kappa_1{}^2) + \kappa_1{}^2\kappa_2]\}^{1/2}]\end{aligned} \tag{26}$$

$$= \tfrac{1}{2}\{(D_X + D_Y)q^2 + 1 + \kappa_1{}^2 - \kappa_2 \pm [(\delta - \kappa_2 + \kappa_1{}^2)^2 - 4\delta\kappa_1{}^2]^{1/2}\} \tag{27}$$

where $\delta = 1 + (D_X - D_Y)q^2$. The homogeneous steady state becomes unstable when the real parts of λ_1 and λ_2 become negative. The marginal situation corresponds to the case when one or both of the real parts of λ_1, λ_2 go to zero and occurs if (a) λ_1, λ_2 real and positive and $\lambda_2 \to 0^+$ (the soft mode instability); (b) λ_1, λ_2 complex and $\mathrm{Re}(\lambda_1, \lambda_2) \to 0^+$ (the hard mode instability). It follows from (27) that:

$$(\delta - \kappa_2 + \kappa_1{}^2)^2 - 4\delta\kappa_1{}^2 > 0 \tag{28}$$

For $\delta < 0$, λ_1 and λ_2 are always real. For $\delta > 0$, λ_1 and λ_2 are real if either

$$\kappa_2 > (\sqrt{\delta} + \kappa_1)^2 \qquad \text{or} \qquad \kappa_1 < (\sqrt{\delta} - \kappa_1)^2 \tag{29}$$

λ_1 and λ_2 are real and positive if, in addition to (29), we have

$$(D_X + D_Y)q^2 - \kappa_2 + 1 + \kappa_1{}^2 > 0$$

i.e.,

$$\kappa_2 < 1 + \kappa_1{}^2 + (D_X + D_Y)q^2 \tag{30}$$

and

$$(D_Xq^2 - \kappa_2 + 1)(D_Yq^2 + \kappa_1{}^2) + \kappa_1{}^2\kappa_2 > 0$$

i.e.,

$$\kappa_2 < 1 + D_Xq^2 + (\kappa_1{}^2/D_Yq^2) + (D_X\kappa_1{}^2/D_Y) \tag{31}$$

$\lambda_2 \to 0^+$ along the real axis with λ_1 real and positive if (29) and (30) are satisfied and

$$\kappa_2 \to \kappa_{2S}(q^2) \equiv 1 + D_Xq^2 + (\kappa_1{}^2/D_Yq^2) + (D_X\kappa_1{}^2/D_Y) \tag{32}$$

from below. With κ_1, D_X, and D_Y fixed, the minimum of $\kappa_{2s}(q^2)$ occurs at

$$|q| = \kappa_1/(D_XD_Y)^{1/2} \tag{33}$$

and its minimum value is

$$\kappa_{2S} = [1 + \kappa_1(D_X/D_Y)^{1/2}]^2 \tag{34}$$

Equation (34) gives the threshold for the soft mode instability. As κ_2 is increased beyond κ_{2S}, the system exhibits spatial oscillations characterized by a wave vector given by (33).

(ii) λ_1 and λ_2 are complex if $(\delta - \kappa_2 + \kappa_1{}^2)^2 - 4\delta\kappa_1{}^2 < 0$, i.e.,

$$(\sqrt{\delta} - \kappa_1)^2 < \kappa_2 < (\sqrt{\delta} + \kappa_1)^2, \qquad \delta > 0 \tag{35}$$

and have positive real parts if

$$(D_X + D_Y)q^2 + 1 + \kappa_1{}^2 - \kappa_2 > 0$$

i.e.,

$$\kappa_2 < 1 + \kappa_1{}^2 + (D_X + D_Y)q^2 \tag{36}$$

λ_1 and λ_2 become purely imaginary as

$$\kappa_2 \to \kappa_{2H}(q^2) \equiv 1 + \kappa_1{}^2 + (D_X + D_Y)q^2 \tag{37}$$

from below. The minimum of $\kappa_{2H}(q^2)$ occurs at

$$q = 0 \tag{38}$$

and hence the threshold for the hard mode instability is

$$\kappa_{2H} = 1 + \kappa_1{}^2 \tag{39}$$

As κ_2 is increased beyond κ_{2H}, the system exhibits temporal oscillations.

Which of the two instabilities occurs first depends on the relative magnitude of D_X and D_Y. Thus the soft mode instability occurs first if

$$\kappa_{2S} < \kappa_{2H}$$

i.e.,

$$\left(\frac{D_X}{D_Y}\right)^{1/2} < \left(1 + \frac{1}{\kappa_1{}^2}\right)^{1/2} - \frac{1}{\kappa_1} \tag{40}$$

and vice versa.

4. SPATIAL CORRELATION FUNCTIONS BELOW THE INSTABILITY THRESHOLDS

(a) From a two-dimensional Langevin equation of the type (25) in the steady state one can derive the following expression for $\tilde{G}(\mathbf{q}, \mathbf{q}')$ in terms of $\tilde{A}$ and B:

$$\tilde{G}(\mathbf{q}, \mathbf{q}') \equiv \delta(\mathbf{q} + \mathbf{q}')\tilde{G}(\mathbf{q})$$

$$\tilde{G}(q) = \frac{(\operatorname{Det} \tilde{A})B^2 + [\tilde{A} - (\operatorname{Tr} \tilde{A})I]B^2[\tilde{A} - (\operatorname{Tr} \tilde{A})I]^T}{2(\operatorname{Det} \tilde{A})(\operatorname{Tr} \tilde{A})} \tag{41}$$

This relation is derived in Appendix A.

Substituting for $\tilde{A}(q^2)$ and B^2 in (41) and using (22), we obtain the following expression for the Fourier transform of the spatial correlation function:

$$\tilde{S}(\mathbf{q}, \mathbf{q}') = \delta(\mathbf{q} + \mathbf{q}')\tilde{S}(q)$$

$$\tilde{S}(\mathbf{q}) = M + \tilde{G}(\mathbf{q}) = M + \frac{H(q^2)}{[(q^2 + \beta_1{}^2)(q^2 + \beta_2{}^2)(q^2 + \beta_3{}^2)]} \tag{42}$$

where

$$M = \begin{pmatrix} \kappa_1 & 0 \\ 0 & \kappa_2/\kappa_1 \end{pmatrix}$$

$$H(q^2) = \frac{2\kappa_1\kappa_2}{D_X D_Y(D_X + D_Y)} \tag{43}$$

$$\times \begin{pmatrix} \begin{array}{l} (D_Y q^2 + \kappa_1{}^2) \\ \quad \times [(D_X + D_Y)q^2 - \kappa_2 + 1] + \kappa_1{}^2\kappa_2 \end{array} & -(D_Y q^2 + \kappa_1{}^2)(D_X q^2 + 1) \\ -(D_Y q^2 + \kappa_1{}^2)(D_X q^2 + 1) & (D_X q^2 + 1) \end{pmatrix}$$

$$\beta_1{}^2 = \frac{1 - \kappa_2 + \kappa_1{}^2}{D_X + D_Y}$$

$$\beta_2{}^2, \beta_3{}^2 = \frac{1}{2}\left(\frac{D_X\kappa_1{}^2 + D_Y(1 - \kappa_2)}{D_X D_Y}\right. \tag{44}$$

$$\left. \pm i\left\{\frac{4\kappa_1{}^2\kappa_2}{D_X D_Y} - \left[\frac{D_X\kappa_1{}^2 + D_Y(1 - \kappa_2)}{D_X D_Y}\right]^2\right\}^{1/2}\right)$$

Splitting the second term on the rhs of (42) into partial fractions and performing the Fourier inversion, we get the following expression for the spatial correlation function in three space dimensions:

$$S(|\mathbf{r} - \mathbf{r}'|) = M\,\delta(\mathbf{r} - \mathbf{r}') + \frac{a_1 \exp(-\beta_1|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}$$

$$+ \frac{a_2 \exp(-\gamma_1|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \cos(\gamma_2|\mathbf{r} - \mathbf{r}'|)$$

$$+ \frac{a_3 \exp(-\gamma_1|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \sin(\gamma_2|\mathbf{r} - \mathbf{r}'|) \tag{45}$$

where

$$\beta_1 = \left(\frac{1 - \kappa_2 + \kappa_1{}^2}{D_X + D_Y}\right)^{1/2} \tag{46}$$

$$\begin{aligned}\beta_2, \beta_3 &= \frac{1}{2\sqrt{D_X}}\left[\left\{\left[1 + \kappa_1\left(\frac{D_X}{D_Y}\right)^{1/2}\right]^2 - \kappa_2\right\}^{1/2}\right.\\ &\qquad \left. \pm\, i\left\{\kappa_2 - \left[1 - \left(\frac{D_X}{D_Y}\right)^{1/2}\kappa_1\right]^2\right\}^{1/2}\right] \qquad (47)\\ &\equiv \gamma_1 \pm i\gamma_2\end{aligned}$$

$$a_1 = \frac{H(-\beta_1{}^2)}{|(\beta_2{}^2 - \beta_1{}^2)|^2} \tag{48a}$$

$$a_2 = \frac{1}{\operatorname{Im}(\beta_2{}^2)} \operatorname{Re} \frac{H(-\beta_2{}^2)}{\beta_2{}^2 - \beta_1{}^2} \tag{48b}$$

$$a_3 = \frac{1}{\operatorname{Im}(\beta_2{}^2)} \operatorname{Im} \frac{H(-\beta_2{}^2)}{\beta_2{}^2 - \beta_1{}^2} \tag{48c}$$

The expression for the spatial correlation function is characterized by two correlation lengths,

$$l_{c,1} = \frac{1}{\beta_1} = \left(\frac{D_X + D_Y}{1 - \kappa_2 + \kappa_1{}^2}\right)^{1/2} \tag{49}$$

$$l_{c,2} = \frac{1}{\gamma_1} = \left[1 + \kappa_1\left(\frac{D_X}{D_Y}\right)^{1/2}\right]^2 - \kappa_2 \tag{50}$$

and a wave vector

$$\gamma_2 = \{\kappa_2 - [1 - \kappa_1(D_X/D_Y)^{1/2}]^2\}^{1/2} \tag{51}$$

(b) We treat the behavior of $S(|\mathbf{r} - \mathbf{r}'|)$ near the instability thresholds as follows.

(i) As $\kappa_2 \to \kappa_{2S}$

$$l_{c,2} \to \infty \tag{52}$$

and γ_2 approaches the critical wave vector

$$q_c = \kappa_1/(D_X D_Y)^{1/2} \tag{53}$$

and the spatial correlation function contains, apart from an exponentially decreasing term, a purely oscillatory term modulated by a $1/|\mathbf{r} - \mathbf{r}'|$ term.

Actually, in this limit, the coefficients of the oscillatory terms become infinite, which perhaps reflects the nonvalidity of the Gaussian approximation near the critical point.

(ii) As $\kappa_2 \to \kappa_{2H}$

$$l_{c,1} \to \infty \tag{54}$$

and (45) gives

$$S(|\mathbf{r} - \mathbf{r}'|) = a_1' \frac{1}{|\mathbf{r} - \mathbf{r}'|} + a_2' \frac{\exp(-\gamma_1'|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|)} \cos(\gamma_2'|\mathbf{r} - \mathbf{r}'|)$$

$$+ a_3' \frac{\exp(-\gamma_1'|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \sin(\gamma_2'|\mathbf{r} - \mathbf{r}'|) \tag{55}$$

where a_1', a_2', etc., are the values of a_1, a_2, etc., as $\kappa_2 \to \kappa_{2H}$. Thus as $\kappa_2 \to \kappa_{2H}$, the spatial correlation function is characterized by a long-range $1/|\mathbf{r} - \mathbf{r}'|$ term.

5. TWO-TIME CORRELATION FUNCTIONS AND THE FLUCTUATION SPECTRUM

In the Gaussian approximation as defined earlier the two-time correlation functions in the steady state are given by

$$T(\mathbf{q}, \mathbf{q}', t) \equiv \langle \rho(\mathbf{q}, t), \rho^T(\mathbf{q}', t') \rangle = \{\exp[-\tilde{A}(q^2)|t|]\}\tilde{S}(\mathbf{q}, \mathbf{q}') \tag{56}$$

Defining

$$\tilde{T}(\mathbf{q}, \mathbf{q}', t) = \delta(\mathbf{q} + \mathbf{q}')T(\mathbf{q}, t) \tag{57}$$

we get

$$\tilde{T}(\mathbf{q}, t) = \{\exp[-\tilde{A}(q^2)t]\}\tilde{S}(\mathbf{q}) \tag{58}$$

The exponential factor on the rhs of (56) represents the response of the mean concentration to a small change in the initial conditions. For nonequilibrium situations this result has been derived by Kitahara[3] using path integral methods and also by Gardiner and Chaturvedi[2] using the Poisson representation method.

From an experimental point of view, a quantity of interest is the fluctuation spectrum defined by

$$F(\mathbf{q}, \omega) = (1/2\pi) \int_{-\infty}^{\infty} dt\, e^{-i\omega t}\tilde{T}(\mathbf{q}, t) \tag{59}$$

A qualitative discussion of the fluctuation spectrum for the Brusselator has been given by Deutch *et al.*,[21] who also explore the possible use of light scattering for its measurement. A general but comprehensive discussion of the use of light scattering experiments for a study of concentration fluctuations in chemically reacting systems may also be found in Ref. 22. In such experiments, one typically measures the intensity of the scattered light, which is directly related to a linear combination of the matrix elements of $F(\mathbf{q}, \omega)$. In the following we give a complete calculation of the fluctuation spectra.

Using (56) and the Langevin equation (25), we derive in Appendix B the following expression for the fluctuation spectrum in terms of the matrices $\tilde{A}$, B^2, and M:

$$F(\mathbf{q}, \omega) = (1/2\pi)(i\omega I + \tilde{A})^{-1}[B^2 + M\tilde{A}^T + \tilde{A}M](-i\omega I + \tilde{A}^T)^{-1} \quad (60)$$

Substituting for $\tilde{A}$, B^2, and M in (60), we get

$$\begin{aligned} F(\mathbf{q}, \omega) &= P(\omega, \mathbf{q}) \\ &\quad \times (\{\omega^2 - [(D_X q^2 - \kappa_2 + 1)(D_Y q^2 + \kappa_1{}^2) + \kappa_1{}^2\kappa_2]\}^2 \\ &\quad + \omega^2[(D_X + D_Y)q^2 + 1 + \kappa_1{}^2 - \kappa_2]^2)^{-1} \end{aligned} \quad (61)$$

where the matrix elements of $P(\omega, \mathbf{q})$ are

$$\begin{aligned} P_{XX}(\omega, \mathbf{q}) &= (\kappa_1/\pi)\{(D_X q^2 + \kappa_2 + 1)\omega^2 \\ &\quad + (D_Y q^2 + \kappa_1{}^2)[(D_Y q^2 + \kappa_1{}^2)(D_X q^2 + \kappa_2 + 1) - \kappa_1{}^2\kappa_2]\} \end{aligned} \quad (62a)$$

$$\begin{aligned} P_{XY}(\omega, \mathbf{q}) &= P^*_{YX}(\omega, \mathbf{q}) \\ &= -(\kappa_1\kappa_2/\pi)\{\omega^2 + [(D_X q^2 + \kappa_2 + 1)(D_Y q^2 + \kappa_1{}^2) - \kappa_1{}^2\kappa_2] \\ &\quad + 2i\omega(D_X q^2 + 1)\} \end{aligned} \quad (62b)$$

$$\begin{aligned} P_{YY}(\omega, \mathbf{q}) &= (\kappa_2/\pi\kappa_1)[(D_Y q^2 + \kappa_1{}^2)\omega^2 + (D_Y q^2 + \kappa_1{}^2)(D_X q^2 - \kappa_2 + 1)^2 \\ &\quad + 2\kappa_1{}^2\kappa_2(D_X q^2 + 1)] \end{aligned} \quad (62c)$$

The fluctuation spectrum has poles in the ω plane at

$$\omega = \pm i\Gamma \pm \omega_0 \quad (63)$$

where

$$\Gamma = \tfrac{1}{2}[(D_X + D_Y)q^2 + 1 + \kappa_1{}^2 - \kappa_2] \quad (64)$$

$$\begin{aligned} \omega_0 &= \tfrac{1}{2}\{4[(D_X q^2 - \kappa_2 + 1)(D_Y q^2 + \kappa_1{}^2) + \kappa_1{}^2\kappa_2] \\ &\quad - [(D_X + D_Y)q^2 + 1 + \kappa_1{}^2 - \kappa_2]^2\}^{1/2} \\ &= \tfrac{1}{2}[4\delta\kappa_1{}^2 - (\delta - \kappa_2 + \kappa_1{}^2)^2]^{1/2} \end{aligned} \quad (65)$$

(i) It follows from the discussion in Section 3, Eq. (28), that below the soft mode instability threshold ω_0 is imaginary, in which case the fluctuation spectrum is of the following form:

$$F(\omega, \mathbf{q}) = \frac{1}{\pi\kappa_1} \frac{P(\omega, \mathbf{q})}{[\omega^2 + (\Gamma - |\omega_0|)^2][\omega^2 + (\Gamma + |\omega_0|)^2]} \quad (66)$$

and therefore has a peak at $\omega = 0$.

As the soft mode instability threshold is approached, $|\omega_0| \to \Gamma$ and (64) becomes

$$F(\mathbf{q}, \omega) = \frac{1}{\pi\kappa_1} \frac{P(\omega, \mathbf{q})}{(\omega^2 + 4\Gamma^2)\omega^2} \quad (67)$$

which exhibits an infinitely sharp peak at $\omega = 0$.

(ii) Below the hard mode instability, it follows from Section 3, Eq. (35), that ω_0 is real and in this case the fluctuation spectrum has the following form:

$$F(\mathbf{q}, \omega) = \frac{P(\omega, \mathbf{q})}{[(\omega - \omega_0)^2 + \Gamma^2][(\omega + \omega_0)^2 + \Gamma^2]} \tag{68}$$

Leaving aside the ω dependence of $P(\omega, q)$, the fluctuation spectrum in this case consists of two peaks situated at $\omega = \pm\omega_0$ with a half-width equal to Γ.

As the hard mode threshold is approached, Γ decreases monotonically, i.e., the peaks become sharper. If κ_2 is initially less than $\delta + \kappa_1{}^2$, ω_0 increases, and as κ_2 becomes greater than $\delta + \kappa_1{}^2$, ω_0 begins to decrease and at the threshold it becomes equal to κ_1. Thus at the threshold the peak separation becomes

$$2\omega_{0c} = 2\kappa_1$$

and the width of the peaks becomes

$$\Gamma_c = \tfrac{1}{2}(D_X + D_Y)q^2$$

and arises purely due to diffusive effects.

The ω dependence of $P(\omega, \mathbf{q})$ gives rise to a slight skewness of the two peaks, but the qualitative features of the fluctuation spectrum remain basically the same.

6. LANGEVIN EQUATIONS WITH BOUNDARY CONDITIONS

In this section we consider the application of the Langevin equations derived from Poisson representation methods to finite discrete and continuous one-dimensional systems and show how to calculate the spatial and correlation functions and fluctuation spectra when various boundary conditions are imposed on the system. The only previous work on this problem is that due to Lemarchand and Nicolis,[16] who use the cumulant expansion method to calculate spatial correlation functions in a finite one-dimensional system subject to two types of boundary conditions: (a) fixed-concentration boundary conditions and (b) zero-flux boundary conditions. We shall confine ourselves to these two types of boundary conditions and rederive the results of Lemarchand and Nicolis[16] rather simply. From the following discussion it will also become clear how one may carry out similar calculations for other types of boundary conditions, for example, periodic boundary conditions. The generalization to three-dimensional finite systems is also straightforward.

6.1. Fixed-Mean-Concentration Boundary Conditions

Here we consider a finite one-dimensional system consisting of $n + 2$ cells labeled 0, 1,..., n, $n + 1$. We assume that the probability distributions in the boundary cells 0 and $n + 1$ are Poisson distributions with means equal to the mean steady-state concentration. This boundary condition in terms of $\eta_\mu(i, t)$ variables implies that $\eta_\mu(0, t)$ and $\eta_\mu(n + 1, t)$ are nonfluctuating variables equal to the steady-state concentration. (It should be noted that if the probability distribution in the boundary cells is assumed to factorize from that for the system cells, then as a consequence of the linear coupling between the two through diffusion only the mean number in the boundary cells appears as a parameter in the reduced master equation for the system cells and consequently the results are insensitive to the precise nature of the probability distribution in the boundary cells.) Thus in this case we get the same results as those of Lemarchand and Nicolis,[16] who consider fixed-concentration boundary conditions, i.e., $P(X) = \delta_{X,X_0}$ in the boundary cells.

From the above discussion it follows that the appropriate linearized Langevin equation in this case is

$$\frac{d}{dt}\begin{pmatrix}\eta_{X,1}(i, t)\\ \eta_{Y,1}(i, t)\end{pmatrix} = \begin{pmatrix}\sum_j D^X_{ij}\eta_{X,1}(j, t)\\ \sum_j D^Y_{ij}\eta_{Y,1}(j, t)\end{pmatrix} + \begin{pmatrix}\kappa_2 - 1 & \kappa_1{}^2\\ -\kappa_2 & -\kappa_1{}^2\end{pmatrix}\begin{pmatrix}\eta_{X,1}(i, t)\\ \eta_{Y,1}(i, t)\end{pmatrix}$$

$$+ \epsilon(4\kappa_1\kappa_2)^{1/2}\begin{pmatrix}1 & -1/2\\ -1/2 & 0\end{pmatrix}^{1/2}\begin{pmatrix}\xi_X(i, t)\\ \xi_Y(i, t)\end{pmatrix}, \quad i = 1,..., n \tag{69}$$

subject to the boundary conditions

$$\eta_{\mu,1}(0, t) = \eta_{\mu,1}(n + 1, t) = 0 \tag{70}$$

In the continuum limit (69) and (70) become

$$\frac{d}{dt}\begin{pmatrix}\eta_{X,1}(r, t)\\ \eta_{Y,1}(r, t)\end{pmatrix} = \begin{pmatrix}d_X l^2\nabla^2 + \kappa_2 - 1 & \kappa_1{}^2\\ -\kappa_2 & d_Y l^2\nabla^2 - \kappa_1{}^2\end{pmatrix}\begin{pmatrix}\eta_{X,1}(r, t)\\ \eta_{Y,1}(r, t)\end{pmatrix}$$

$$+ 2(\kappa_2\kappa_1)^{1/2}\begin{pmatrix}1 & -1/2\\ -1/2 & 0\end{pmatrix}^{1/2}\begin{pmatrix}\xi_X(r, t)\\ \xi_Y(r, t)\end{pmatrix} \tag{71}$$

and

$$\eta_\mu(0, t) = \eta_\mu(L, t) = 0 \tag{72}$$

where l is the cell length and L is the length of the system.

6.2. Zero-Flux Boundary Conditions

Here we consider the situation in which there is no diffusion between the system cells and the boundary cells. This can be taken into account by modifying the diffusion matrix D_{ij} to

$$D_{ij} - d\delta_{i,1}(\delta_{j,0} - \delta_{j,1}) - d\delta_{i,n}(\delta_{j,n+1} - \delta_{j,n})$$

where the extra terms cancel the terms present in D_{ij} that allow for diffusion between the cell 1 (n) and 0 ($n + 1$). The corresponding Langevin equation then becomes

$$\frac{d}{dt}\begin{pmatrix}\eta_{X,1}(i,t)\\ \eta_{Y,1}(i,t)\end{pmatrix} = \begin{pmatrix}\sum_j D_{ij}^X\eta_{X,1}(j,t) - d^X\delta_{i,1}(\eta_{X,1}(0,t) - \eta_{X,1}(1,t)) \\ \quad - d^X\delta_{i,n}(\eta_{X,1}(n+1,t) - \eta_{X,1}(n,t)) \\ \sum_j D_{ij}^Y\eta_{Y,1}(j,t) - d^Y\delta_{i,1}(\eta_{Y,1}(0,t) - \eta_{Y,1}(1,t)) \\ \quad - d^Y\delta_{i,n}(\eta_{Y,1}(n+1,t) - \eta_{Y,1}(n,t))\end{pmatrix}$$
$$+ \begin{pmatrix}\kappa_2 - 1 & \kappa_1^2\\ -\kappa_2 & -\kappa_1^2\end{pmatrix}\begin{pmatrix}\eta_{X,1}(i,t)\\ \eta_{Y,1}(i,t)\end{pmatrix}$$
$$+ (4\kappa_1\kappa_2)^{1/2}\begin{pmatrix}1 & -1/2\\ -1/2 & 0\end{pmatrix}^{1/2}\begin{pmatrix}\xi_X(i,t)\\ \xi_Y(i,t)\end{pmatrix}, \qquad i = 1,\dots,n \tag{73}$$

which may equivalently be written as Eq. (69) subject to the boundary conditions

$$\eta_{\mu,1}(0,t) - \eta_{\mu,1}(1,t) = 0, \qquad \eta_{\mu,1}(n,t) - \eta_{\mu,1}(n+1,t) = 0 \tag{74}$$

In the continuum limit the appropriate Langevin equation is (71) subject to the boundary conditions

$$\left.\frac{\partial\eta_{\mu,1}(r,t)}{\partial r}\right|_{r=0} = \left.\frac{\partial\eta_{\mu,1}(r,t)}{\partial r}\right|_{r=L} = 0 \tag{75}$$

In both cases the equations for $\eta_{\mu,1}(i, t)$ are identical but because of the boundary conditions, different Fourier expansions are required to diagonalize the diffusion terms. The appropriate Fourier expansions are given below.

(a) $$\eta_{\mu,1}(i,t) = \sum_{q=1}^{n}\tilde{\eta}_{\mu,1}(q,t)\sin[iq\pi/(n+1)] \tag{76}$$

In the continuum limit

$$\eta_{\mu,1}(r,t) = \sum_{q=1}^{\infty}\tilde{\eta}_{\mu,1}(q,t)\sin(qr\pi/L) \tag{77}$$

and

$$\text{(b)}\qquad \eta_{\mu,1}(i,t) = \sum_{q=1}^{n} \tilde{\eta}_{\mu,1}(q,t)\cos[(q-1)(2i-1)\pi/2n] \tag{78}$$

In the continuum limit

$$\eta_{\mu,1}(r,t) = \sum_{q=0}^{\infty} \tilde{\eta}_{\mu,1}(q,t)\cos(q\pi r/L) \tag{79}$$

Substituting these and similar expansions for ξ_μ in the corresponding Langevin equations, we get

$$(d/dt)\tilde{\boldsymbol{\eta}}_1(q,t) = -\tilde{A}'(q^2)\tilde{\boldsymbol{\eta}}_1(q,t) + B\tilde{\boldsymbol{\xi}}(q,t) \tag{80}$$

with

$$\langle\tilde{\xi}_\mu(q,t)\rangle = 0, \qquad \langle\tilde{\xi}_\mu(q,t)\tilde{\xi}_\nu(q',t')\rangle = h(q,q')\,\delta(t-t') \tag{81}$$

where

$$\tilde{A}'(q^2) = \begin{pmatrix} d_X g(q) + 1 - \kappa_2 & -\kappa_1{}^2 \\ \kappa_2 & d_Y g(q) + \kappa_1{}^2 \end{pmatrix} \tag{82}$$

and

$$\text{(a)}\qquad g(q) = 2\left(1 - \cos\frac{q\pi}{n+1}\right), \qquad h(q,q') = \frac{2}{n+1}\,\delta_{q,q'}$$

In the continuum limit

$$g(q) = l^2q^2\pi^2/L^2, \qquad h(q,q') = (2/L)\,\delta_{q,q'}$$

and

$$\text{(b)}\qquad g(q) = 2\left(1 - \cos\frac{(q-1)\pi}{n}\right), \qquad h(q,q') = \frac{2}{n}\,\delta_{q,q'}\left(1 - \frac{\delta_{q,1}}{2}\right)$$

In the continuum limit

$$g(q) = l^2q^2\pi^2/L^2, \qquad h(q,q') = (2/L)\,\delta_{q,q'}(1 - \tfrac{1}{2}\delta_{q,0})$$

The Fourier transform of the steady-state spatial correlation functions and the fluctuation spectrum can be calculated using (80), (42), and (58).

Although the above discussion applies to a one-dimensional system, its generalization to more than one dimension is straightforward.

Having thus calculated $\tilde{G}(q,q')$, one may derive expressions for $G(i,j)$ by appropriate Fourier inversions and for the one dimensional case one obtains results identical to those given by Lemarchand and Nicolis.[16] The Fourier inversions are possible analytically only for a one-dimensional continuous system and we find with Lemarchand and Nicolis[16] that near the soft mode instability threshold, $G(i,j)$ can be decomposed into a short-range part consisting of decaying exponentials and a long-range, linearly damped oscillatory part of the following form:

$$b_1\gamma_2(L - r)\cos[\gamma_2(L - r)]\sin(\gamma_2 r') + b_2\gamma_2 r'\sin[\gamma_2(L - r)]\cos(\gamma_2 r') + b_3 \tag{83}$$

where γ_2 has been defined previously.

In the limit of $L \to \infty$, (83) is divergent. Direct calculation of $G(r, r')$ for an infinite one-dimensional system shows that as the soft mode instability threshold is approached, $G(r, r')$ actually becomes infinite. However, it should be remembered that these results are derived in the Gaussian approximation, whose validity at the critical point is questionable.

7. CONCLUSIONS

We have calculated in the Gaussian approximation the spatial correlation functions and the fluctuation spectra of the Brusselator for a three-dimensional infinite system below the instability thresholds. We have shown that as the soft mode instability threshold is approached from below the spatial correlation functions exhibit an oscillatory behavior modulated by a $1/|r - r'|$ term. At the critical point, however, the spatial correlations become infinite. The fluctuation spectrum in this limit exhibits an infinitely sharp peak at $\omega = 0$. In the case of the hard mode instability the spatial correlation functions at the instability point exhibit a long-range $1/|r - r'|$ behavior. The fluctuation spectrum in this case exhibits two peaks below the instability thresholds and as the instability threshold is approached the peaks move toward each other, at the same time becoming sharper until at the critical point the separation becomes twice the critical frequency and the widths of the peaks are determined solely by the diffusive effects.

We have also shown how the spatial correlation functions and the fluctuation spectra may be calculated for a finite one-dimensional system subject to boundary conditions and have obtained results in agreement with those of Lemarchand and Nicolis.[16] In this case, as the soft mode instability threshold is approached, we find, with Lemarchand and Nicolis, that the spatial correlation functions have a long-range, linearly damped part with coefficients proportional to the size of the system, becoming divergent in the limit of an infinite system.

All the above results rely on the Gaussian approximation and are obtained straightforwardly by our methods as compared to other techniques to the same degree of approximation.

If it is desired, the corrections to the Gaussian approximation can be calculated systematically from our Langevin equations, although this would require incorporation of the noise sources corresponding to the third-order derivatives in the Fokker–Planck equation, the necessary techniques for which were explained in Ref. 2. At the critical point this perturbation method with the inverse of the cell size as the expansion parameter breaks down. It should be noted that most of the work done to date on calculation of the correlation functions near the critical points uses the distance from the critical point as an expansion parameter but relies on a Fokker–Planck equation which already assumes the Gaussian approximation. Given the non-validity of the Gaussian approximation near the critical points, this procedure seems rather questionable. Our Langevin equations, however, provide an exact starting point for doing calculations near the critical points without having to rely on the Gaussian approximation. Work along these lines is proceeding.

APPENDIX A

The solution of the linear Langevin equation (25) is

$$\tilde{\eta}_1(\mathbf{q}, t) = \int_0^t \{\exp[-\tilde{A}(t - t')]\} B\tilde{\xi}(\mathbf{q}, t) \tag{A1}$$

which gives

$$\tilde{G}(\mathbf{q}, \mathbf{q}', t) \equiv \langle \tilde{\eta}_1(\mathbf{q}, t)\tilde{\eta}_1{}^T(\mathbf{q}, t)\rangle = \delta(\mathbf{q} + \mathbf{q}') \int_0^t \exp(-\tilde{A}t')\, B^2 \exp(-\tilde{A}^T t') \tag{A2}$$

and hence

$$\tilde{G}(\mathbf{q}, t) = \int_0^t \exp(-\tilde{A}t')\, B^2 \exp(-\tilde{A}^T t') \tag{A3}$$

In the steady state, taking the limit $t \to \infty$ in (A3), we get

$$\tilde{G}(\mathbf{q}) = \int_0^\infty \exp(-\tilde{A}t')\, B^2 \exp(-\tilde{A}^T t') \tag{A4}$$

It follows from (A4) that

$$\tilde{A}\tilde{G} + \tilde{G}\tilde{A}^T = \int_0^\infty \frac{d}{dt} [\exp(-\tilde{A}t')\, B^2 \exp(-\tilde{A}^T t')]\, dt' = B^2 \tag{A5}$$

Now since every matrix obeys its characteristic equation, which in the two-dimensional case is

$$\tilde{A}^2 - (\mathrm{Tr}\, \tilde{A})\tilde{A} + (\mathrm{Det}\, \tilde{A}) = 0 \tag{A6}$$

it follows that $\exp(-\tilde{A}t)$ is a polynomial in $\tilde{A}$ of degree 1. Thus, taking into account Eq. (A4) for $\tilde{G}$, $\tilde{G}$ must have the following form:

$$\tilde{G} = \alpha B^2 + \beta(\tilde{A}B^2 + B^2\tilde{A}^T) + \gamma\tilde{A}B^2\tilde{A}^T \tag{A7}$$

Substituting (A6) in (A4) and using (A5), we find that (A5) is satisfied provided that

$$\begin{gathered} \alpha + (\operatorname{Tr} \tilde{A})\beta - (\operatorname{Det} \tilde{A})\gamma = 0 \\ 2(\operatorname{Det} \tilde{A})\beta + 1 = 0, \qquad \beta + (\operatorname{Tr} \tilde{A})\gamma = 0 \end{gathered} \tag{A8}$$

Solving (A8) for α, β, and γ and substituting in (A6), we get

$$\tilde{G} = \frac{(\operatorname{Det} \tilde{A})B^2 + [\tilde{A} - (\operatorname{Tr} \tilde{A})I]B^2[\tilde{A} - (\operatorname{Tr} \tilde{A})I]^T}{2(\operatorname{Tr} \tilde{A})(\operatorname{Det} \tilde{A})} \tag{A9}$$

APPENDIX B

From the definition of the fluctuation spectrum of Eq. (59) it follows that

$$F(\mathbf{q}, \omega) = (1/2\pi) \int_0^\infty e^{-i\omega t} T(\mathbf{q}, t)\, dt + \int_{-\infty}^0 e^{-i\omega t} T(\mathbf{q}, t) \tag{B1}$$

Changing $t \to -t$ in the second term on the rhs of (B1) and using the following property of the steady-state two-time correlation function

$$T(\mathbf{q}, -t) = T^T(\mathbf{q}, t) \tag{B2}$$

we get

$$F(\mathbf{q}, \omega) = (1/2\pi) \int_0^\infty e^{-i\omega t} T(\mathbf{q}, t) + \int_0^\infty e^{i\omega t} T^T(\mathbf{q}, t) \tag{B3}$$

Substituting for $T(\mathbf{q}, t)$ from (56), we get

$$F(\mathbf{q}, \omega) = (1/2\pi)(i\omega I + \tilde{A})^{-1}\tilde{S}(\mathbf{q}) + \tilde{S}(\mathbf{q})(-i\omega I + \tilde{A}^T)^{-1} \tag{B4}$$

which gives

$$(i\omega I + \tilde{A})F(\mathbf{q}, \omega)(-i\omega I + \tilde{A}^T) = (1/2\pi)[A\tilde{S} + \tilde{S}\tilde{A}^T] \tag{B5}$$

using the relation

$$\tilde{S} = M + \tilde{G} \tag{B6}$$

and (A5), we get

$$F(\mathbf{q}, \omega) = (1/2\pi)(i\omega I + \tilde{A})^{-1}[M\tilde{A}^T + \tilde{A}M + B^2](-i\omega I + \tilde{A}^T)^{-1} \tag{B7}$$

A corresponding result has been derived by Lax[23] for the Langevin equations arising from classical noise.

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