Phase Transition in Chemical Turbulence through Global Feedback

— *Relevance to Catalytic CO Oxidation on Pt Surfaces* —

Yoji KAWAMURA[1] and Yoshiki KURAMOTO[2]

[1]*Department of Physics, Kyoto University, Kyoto 606-8502, Japan*
[2]*Department of Mathematics, Hokkaido University, Sapporo 060-0810, Japan*

(Received July 4, 2005)

A new form of phase transition in chemical turbulence, which is characterized by the emergence of small-amplitude collective oscillations out of the strongly turbulent background, was previously shown to exist in the complex Ginzburg-Landau equation with global feedback. We show in this report that a realistic dynamical-system model for the catalytic CO oxidation on the Pt surfaces also exhibits a similar transition under experimentally accessible parameter values.

Chemical turbulence involving large spatial degrees of freedom generally occurs in oscillatory reaction-diffusion systems under suitable conditions.[1)] In recent years, considerable attention has been attracted to the problem of controlling chemical turbulence. As a remarkable fact, it was found that turbulence in oscillatory reaction-diffusion systems with large spatial extension can completely be suppressed through global feedback.[2)–6)] This was found in recent experiments on catalytic CO oxidation on the Pt surfaces,[4),6)] and the same fact was reconfirmed with a corresponding theoretical model.[4),5)] Results from some theoretical and numerical works on an even simpler model, i.e., the complex Ginzburg-Landau equation with global feedback also support the above finding.[2),3)]

In a previous analysis of the complex Ginzburg-Landau equation with global feedback,[7)] we showed that, preceding the complete suppression of chemical turbulence, a different type of transition, which is characterized by the emergence of small-amplitude collective oscillations out of a strong turbulent background, occurs at much weaker feedback intensity. In the absence of the feedback, the oscillation amplitude of a suitably defined mean field quickly relaxes to the zero value, which is due to its coupling with the turbulent fluctuations. We interpreted the transition, which becomes possible once a global feedback has been introduced, as a consequence of a complete cancellation of this effective damping of the mean field with the effect of its growth caused by the global feedback. Furthermore, the transition is found to be well described, although phenomenologically, with a noisy Stuart-Landau-type equation governing the mean field. In the present article, we extend our previous analysis to the realistic dynamical-system model mentioned above, and show how a similar transition can occur under experimentally accessible parameter conditions.

The realistic model to be considered (called model A below for the sake of brevity) is given by[4),5)]

$$\partial_t u = k_1[p_{\rm co} + \mu_m p_\mu(\bar{u} - u_{\rm st})]s_{\rm co}(1-u^3) - k_2 u - k_3 uv + D\nabla^2 u, \tag{1}$$

$$\partial_t v = k_4 p_{\rm o_2}[s_{1\times1}w + s_{1\times2}(1-w)](1-u-v)^2 - k_3 uv, \tag{2}$$

$$\partial_t w = k_5 \left(\frac{1}{1 + \exp\left(\frac{u_0 - u}{\delta u}\right)} - w \right), \tag{3}$$

where u, v, and w denote the CO coverage, the O coverage, and the local fraction of the Pt surface, respectively. $\mu_m (\geqslant 0)$, $\bar{u}$, and $u_{\rm st}$ represent the feedback intensity, the spatial average of u, and the u-value in the steady-state solution, respectively. In the present paper, all parameters except for the feedback parameters are assumed to take the same values as in Refs. 4) and 5), satisfying the condition that the corresponding reaction-diffusion system stays in a turbulent regime in the absence of feedback (i.e. $\mu_m = 0$). For the sake of simplicity, we also assume that there is no time-delay in the feedback and that the sign of the feedback intensity is positive. Although these choices differ from those in Refs. 4) and 5), they should not be unrealistic experimentally. In what follows, we first argue that our choice of the feedback parameters gives a good correspondence between the two models, i.e., model A and the complex Ginzburg-Landau-type model we analyzed previously. Then, we show how the transition considered here is possible in model A under this modified condition.

We now try to reduce model A to the complex Ginzburg-Landau equation near the Hopf bifurcation. Redefining u, v, and w by the quantities measured from their steady-state values obtained in the absence of feedback ($\mu_m = 0$), we may write Eqs. (1)–(3) as

$$\partial_t u = \mathcal{F}_u + D_{uu} \nabla^2 u + \mu_m M_{uu} \bar{u}, \tag{4}$$

$$\partial_t v = \mathcal{F}_v, \tag{5}$$

$$\partial_t w = \mathcal{F}_w. \tag{6}$$

The element D_{uu} of the diffusion matrix $\hat{D}$ and the element M_{uu} of the coupling matrix $\hat{M}$ associated with the global feedback are respectively given by

$$D_{uu} = D, \tag{7}$$

and

$$M_{uu} = k_1 p_\mu s_{\rm co} \left(1 - u_{\rm st}^3\right). \tag{8}$$

The above are the only non-vanishing elements of $\hat{D}$ and $\hat{M}$. The real vector field $\boldsymbol{\mathcal{F}} \equiv (\mathcal{F}_u, \mathcal{F}_v, \mathcal{F}_w)$ represents a local limit-cycle oscillator whose steady-state is set at $(0, 0, 0)$ as mentioned. Nonlinear effects of the feedback term have been neglected because we are concerned with the situation where the characteristic amplitude of the mean field $\bar{u}$ remains relatively small.

By applying the center-manifold reduction to the above system, on the assumptions that the local oscillators are near the Hopf bifurcation point and that the effect of global feedback is small enough to be treated perturbatively, we obtain the following complex Ginzburg-Landau equation supplemented with a global feedback term

$$\partial_t W = p\lambda W - g\left|W\right|^2 W + d\nabla^2 W + \mu_m m \bar{W}. \tag{9}$$

Here the real number p gives the bifurcation parameter, and $\bar{W}$ represents the spatial average of the complex amplitude W. The parameters λ, g, d, and m are generally complex. In particular, d and m are given by the formulae[1)]

$$d = \boldsymbol{U}^{\dagger}\hat{D}\boldsymbol{U}, \tag{10}$$

$$m = \boldsymbol{U}^{\dagger}\hat{M}\boldsymbol{U}, \tag{11}$$

where $\boldsymbol{U}^{\dagger}$ and $\boldsymbol{U}$ are, respectively, the left and right eigenvectors of the purely imaginary eigenvalues of the Jacobian matrix associated with each local system $\boldsymbol{\mathcal{F}}$ at criticality about the steady state. Note that positivity of $\mathrm{Re}\, d$ is generally guaranteed by virtue of the condition that the uniform steady-state must be stable below the bifurcation point. This means that, via the relation $m = dM_{uu}/D_{uu}$, $\mathrm{Re}\, m$ is also positive. The last condition is important for suppressing turbulence with the global feedback.[2),3)] In fact, under the conditions described above, a complete suppression of turbulence is possible in model A.

Let us now show some numerical evidence for the transition considered here in model A, namely the appearance of small-amplitude collective oscillations preceding the complete suppression of turbulence as we increase the feedback intensity. We should note that the spatial dimension is irrelevant because the nature of the transition is the mean field type.[7)] Therefore, we confined our study to one-dimensional systems. The system length L must be sufficiently large in order that the threshold of the transition may sharply be defined. In our numerical simulation, the oscillatory continuum was replaced with a long array of oscillators with sufficiently small and fixed separation Δx between neighboring oscillators and zero-flux boundary conditions were imposed. Let the total number of the oscillators be N. As a suitable order parameter characterizing the transition, we take the amplitude of the mean field $\bar{u}$, which is denoted with Amp $\bar{u}$. We expect that the onset of the collective oscillation obeys the law of the classical second order phase transition or the supercritical Hopf bifurcation which occurs at $\mu_m = \mu_{mc}$. Thus, for small $\varepsilon_m \equiv \mu_m - \mu_{mc}$ and infinite N, Amp $\bar{u}$ should obey the square-root law Amp $\bar{u} \sim \sqrt{\epsilon_m}$. As we argued previously,[7)] for large but finite N, this square-root law may be generalized to a finite-size scaling form

$$\langle \mathrm{Amp}\ \bar{u} \rangle\, N^{1/4} = F\left(\varepsilon_m\, N^{1/2}\right), \tag{12}$$

where $\langle \cdot \rangle$ represents a long-time average, and F is a function (called the scaling function) depending on ε_m and N only through $\varepsilon_m N^{1/2}$. Figure 1 summarizes our numerical results for various ε_m and N, displayed in the form of $\langle \mathrm{Amp}\ \bar{u} \rangle\, N^{1/4}$ vs $\varepsilon_m N^{1/2}$ for different values of N. As we see, these data form almost an identical curve, which we take as evidence for the existence of a phase transition.

In conclusion, we found in the present report that the realistic model for the catalytic CO oxidation on the Pt surfaces admits a critical condition for the appearance of small-amplitude collective oscillations out of a strongly turbulent background. Since the parameter conditions assumed there would be experimentally realizable, a verification of this type of transition in real systems is strongly hoped.

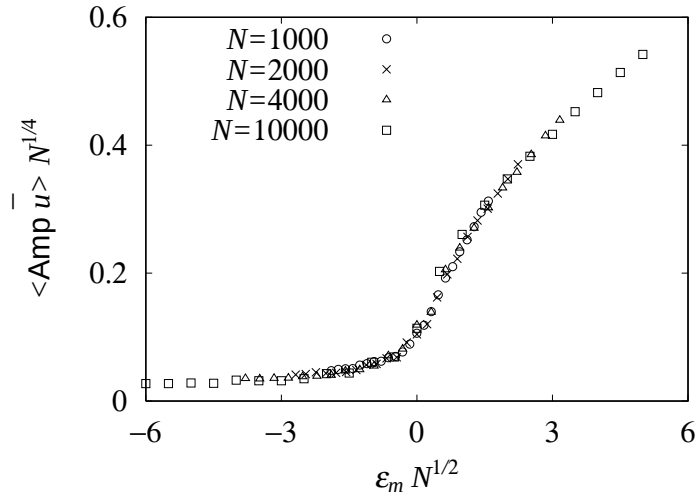

Fig. 1. Numerically obtained order parameter curves for different system sizes for the CO oxidation model (model A) where the spatial dimension is one and zero-flux boundary conditions are assumed. The data shown are those rescaled by using the finite-size scaling law given by Eq. (12). Parameter values are $k_1 = 3.14 \times 10^5$ s^{-1}mbar^{-1}, $k_2 = 10.21$ s^{-1}, $k_3 = 283.8$ s^{-1}, $k_4 = 5.860 \times 10^5$ s^{-1}mbar^{-1}, $k_5 = 1.610$ s^{-1}, $s_{\rm CO} = 1.0$, $s_{1\times1} = 0.6$, $s_{1\times2} = 0.4$, $u_0 = 0.35$, $\delta u = 0.05$, $D = 40$ μm^{2}s^{-1}, $p_{\rm CO} = 4.81 \times 10^{-5}$ mbar, $p_{\rm O_2} = 13.0 \times 10^{-5}$ mbar, $p_\mu = 1.0 \times 10^{-5}$ mbar, $u_{\rm st} = 0.3358$, which give $\mu_{mc} \simeq 0.225$. In this numerical simulation, an explicit Euler integration scheme with a constant time step $\Delta t = 0.001$ s and a fixed grid size $\Delta x = 4.0$ μm are employed.

References

1) Y. Kuramoto, *Chemical Oscillations, Waves, and Turbulence* (Springer, 1984; Dover, 2003).
2) D. Battogtokh and A. S. Mikhailov, Physica D **90** (1996), 84.
3) D. Battogtokh, A. Preusser and A. S. Mikhailov, Physica D **106** (1997), 327.
4) M. Kim et al., Science **292** (2001), 1357.
5) M. Bertram and A. S. Mikhailov, Phys. Rev. E **67** (2003), 036207.
6) M. Bertram et al., Phys. Rev. E **67** (2003), 036208.
7) Y. Kawamura and Y. Kuramoto, Phys. Rev. E **69** (2004), 016202.