论文题目：表面反应体系中若干重要非线性问题的理论研究

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摘要

表面，在物理、化学和生物乃至生命科学的研究中都是一类非常重要的体系；表面上发生的动力学过程，许多都是在远离平衡条件下进行的非平衡非线性过程，它们往往表现出丰富的非平衡定态行为。如果我们把这些非平衡定态称为“非线性态”，则研究这些非线性态的性质、非线性态之间相互跃迁的规律，以及对非线性态实施有效控制的途径，对提示表面过程的本质，开发新的表面技术和探索生命过程的奥秘有着重要意义。本论文着重研究了非均相表面催化反应体系中的四类重要的非线性问题。

1．非平衡动力学相变

非平衡相变描述的是非线性体系在远离平衡的条件下，随着控制参量的变化，体系非平衡定态的数目和性质发生突变的现象。与平衡相变不同的是，对非平衡相变往往缺乏势函数的描述，因此往往也缺乏统一的理论。近年来，表面催化反应模型中的非平衡动力学相变问题越来越受到重视。我们以一氧化碳的表面催化反应为原型，用对近似平均场理论方法研究了双分子-单分子表面反应模型中出现的一级和二级动力学相变，理论结果和蒙特卡罗模拟很好地一致。以此基础上，我们进一步推广了对近似方法，将它应用到更复杂的表面反应模型：DD 模型中，我们发现，在二级相变点附近，表面近邻相关作用很重要，必须用对近似以上的理论方法来描述；但在一级相变点附近，相关作用是可以忽略的，这时用点近似平均场方法就能很好的预言（这方面的工作分别发表在 Surface Science, Physical Review E 和 J.Phys.A 上）。

2．非线性时空动力学行为及其控制

表面催化反应是一类典型的非均相催化反应，它们通常是在远离平衡条件下进行，因此常常表现出非常丰富的时空自组织行为：从化学多稳态，化学振荡到化学混沌；从脉冲波，孤波，螺旋波到湍流。研究对这些时空自组织行为进行有效的控制的途径，在理论研究和应用上都是一个非常重要的课题：这种控制既可以通过外加的反馈控制来实现，也可以通过改变介质的几何结构来实现。分形，作为描述复杂对象的一种几何语言，近年来受到了广泛关注。同混沌，孤子一道，分形已成为非线性科学的一个重要分支。由于化学中的许多研究对象，尤其是多孔催化剂的表面，往往需要用分形来描述，因此研究分形对其上的时空动力学行为的影响，一方面可以促进分形科学本身的发展，另一方面也可以措此探索介质的几何结构对动力学行为的控制。我们研究了分形结构上受限扩散对 CO 表面催化氧化体系非线性动力学行为的影响，并初步考察了一类确定性分形体系上时空有序结构的形成及其特征。我们发现，分形结构的存在，可以诱导产生振荡行为，也可以改变体系非平衡相变的定性特征；分形结构的多层次的缺陷分布，可以抑制体系的可激发性，也可以诱导产生新的时空动力学行为。

3．噪声诱导相变

非线性体系中，随机力（或噪声）往往起着人们直觉相反的作用：一定的条件下，无序的噪声可以转化为有序。噪声不仅可以使体系从一个非平衡定态跃迁到另一个非平衡定态，还能使体系演化到新的确定性系统所没有的时空有序结构上，这种新的“非线性态”完全是由噪声诱导产生的，因此称噪声诱导相变。在 Dimer-Monomer 模型的动力学相变研究中，一直有个悬而未决的问题：虽然对近似理论方法很成功，但理论预言的一级相变点的位置同模拟总有相当的差别。考虑到模拟过程中噪声的影响，我们提出了创新的观点：该一级相变实际上是噪声诱导的相变，从而成功地解释了两者的差别（这方面的论文投到 Surface Science Letter 后，很快被接收）。我们还进一步研究了噪声对描述可激发介质中斑图（Pattern）形成的反应扩散方程的影响。我们发现，当体系的控制参量受到噪声的扰动时，一种形式的斑图（如单螺旋）可以向另一种斑图（如双螺旋）转变，同时也可以出现新的噪声诱导的斑图（这方面的论文将发表在 Physical Review Letters）。

4．随机共振

非线性体系中，噪声可以和体系的信息传递起协作效应。在噪声的帮助下，弱的输入信号能够被相当地放大，且在噪声的强度取合适的值时，输出信号的信噪比会达到极大值，这就是随机共振现象。和噪声诱导相变类似，随机共振也体现了噪声在形式“序”方面所起的积极作用。人们有可能利用随机共振现象来实现被噪声污染的弱信号的检测、放大及非线性过滤。随机共振的概念自从被提出以解释古冰川气候的周期变化以来，已在科学研究的各个领域取得了广泛的应用，化学体系中随机共振现象的研究也正方兴未艾。我们着重研究了一氧化碳催化氧化体系和一氧化氮催化还原体系的随机共振现象，一方面深入了解了该体系的动力学特征，另一方面对实验可以有指导意义（这方面的论文已被 J.Chem.Phys.接收）。

Abstract

Surface systems are of great importance in chemistry, physics and biology studies. The processes occurring on surface are often far from equilibrium and nonlinear, and exhibit abundant nonequilibrium stationary states. The study of nonlinear dynamics and self-organization in heterogeneous surface catalysis reaction systems have gained growing attention in recent years. In this dissertation, we have studied four types of important nonlinear behavior in these systems:

1.Nonequilibrium Kinetic Phase Transition

Nonequilibrium phase transition occurs when the control parameter(s) vary, in which the number and character of the stationary states change. One often lacks a general theory to study nonequilibrium phase transition, because a nonequilibrium potential function is not available. The study of reaction kinetics and irreversible phase transition(IPT) on catalyst surface have gained growing attention. Inspired by the carbon monoxide oxidation reaction on Pt surface, we have studied the two IPTs, one of first order and the other of second order, characteristic of the Dimer-Monomer reaction model, by mean field theory(MFT) within pair approximation(PA). We find that PA-MFT can well reproduce the simulation results. Based on this work, we further

applied PA-MFT to more complex reaction models, such as the theoretical predictions with the simulation results, we get the correlation are important near the second-order IPT, but all levels of correlation can be neglected in the vicinity of the first-order IPT.

2.Nonlinear Spatiotemporal dynamics and its Control

A great variety of spatiotemporal pattern formation phenomena, such as chemical bistability, chemical oscillation, chemical chaos, spiral waves, solitary waves, chemical turbulence, etc., have been observed in surface catalysis reactions, including the carbon monoxide oxidation reaction. It's a important issue to study how to control these self-organization behaviors, Besides the feedback control methods, one might also try to realize the control by altering the geometry structure of the surface. As well known, fractal has been an effective term to describe complex objects, including the irregular question arises: what will happen to the spatiotemporal dynamics if the catalyst surface must be described by fractal? We have studied the influence of limited diffusion on fractal surface on the local dynamics of the CO oxidation system. "structure induced " oscillation and wave excitation are found, which implies that the spatiotemporal behavior on r\fractal system can have much new characters.

3.Noise-Induced Phase Transition

The role of stochastic force (noise) may be quite counter intuitive in nonlinear systems. Under specific conditions, noise can transits to order. Noise can not only lead to loss of stability of stationary states, but also can induce new stationary states which do not belong to the deterministic system. In the study of the DM model, one has a yet unresolved problem : though PA-MFT works well to reproduce the phase diagram, the theoretically predicted value of the first order IPT is substantially larger than the simulation result. This discrepancy is not due to correlation effects, because correlation can be neglected near the first order IPT. Considering the fluctuation of the mole fraction of the monomer in the gas phase, we assert that the first order IPT in the simulation may be viewed as a noise-induced transition .We have also studied the noise-induced pattern transition behavior in excitable media. A noise-induced bistability between single spiral wave(SSW) and double spiral wave(DSW) is observed. Furthermore, the DSW can be clockwise or anti-clockwise, which suggests the possibility of noise-induced chirality breaking.

4. Stochastic Resonance

The external signal, noise and nonlinear system can be coherent. With the variation of noise strength, the signal-to noise(SNR) ratio of the output signal can reach a maximum-that is the famous stochastic resonance phenomenon. Stochastic resonance also show the constructive role of noise on the observed saptiotemporal dynamics. One may use stochastic resonance to realize the detection , amplification and nonlinear filtering of small signals. Stochastic resonance is now of wide interest to scientists in all field of science, and the study of stochastic resonance in chemical systems are now developing . We have focused on the stochastic resonance behavior in the CO oxidation and NO+CO reduction reaction. We found that stochastic resonance behavior is quite widespread in chemical reaction systems.