DOE/ER/13897--10

DE90 002522

THE BEHAVIOR OF MATTER UNDER NONEQUILIBRIUM CONDITIONS: FUNDAMENTAL ASPECTS AND APPLICATIONS

Progress Report

April 15, 1989 - April 14, 1990

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October 1989

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER GRANT NUMBER DE-FG05-88ER13897

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The Behavior of Matter under Nonequilibrium Conditions:
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1. Introduction

As in the previous period, our work has been concerned with the study of the properties of nonequilibrium systems and especially with the mechanism of self-organization. As is well known, the study of self-organization began with the investigation of hydrodynamical or chemical instabilities studied from the point of view of macroscopic physics. The main outcome is that nonequilibrium generates spatial correlations of macroscopic range whose characteristic length is an intrinsic property and whose amplitude is determined by nonequilibrium constraints. A survey of the macroscopic approach to nonequilibrium states is given in the paper "Nonequilibrium States and Long Range Correlations in Chemical Dynamics," by G. Nicolis et al. (Appendix 1). However, over the last few years important progress has been made in the simulation of nonequilibrium situations using mainly molecular dynamics. It appears now that processes corresponding to self-organization as well as the appearance of long-range correlations can be obtained in this way starting from a program involving Newtonian dynamics (generally the laws of interaction correspond to hard spheres or hard disks). Examples of such types of studies leading to Bénard instabilities, to chemical clocks, or to spatial structure formation are given in Section 2 of this report. As a result, we may now view self-organization as a direct expression of an appropriate microscopic dynamics. This is the reason why we have devoted much work to the study of large Poincaré systems (LPS) involving continuous sets of resonances. These systems have been shown to lead, according to the constraints, either to equilibrium situations or to nonequilibrium states involving long range correlations. In Section 3, we discuss LPS in the frame of classical mechanics. Section 4 gives a brief account of our work in progress.

2. Microscopic Simulation of Nonequilibrium States

Let us review briefly a number of examples which have been studied over the last period.

A. Macroscopic Rate Equations in Exothermic Chemical Systems

A molecular dynamics computer experiment was set up to study the stationary properties of an exothermic gas phase chemical system. A discrepancy was observed between the results of the simulation and predictions from macroscopic chemical kinetics. The origin of this discrepancy was found to arise from the deformation of the Maxwell distribution by reactive collisions. Quantitative agreement with the corrected rate law has been established. Details are given in Appendix 2.

B. Simulation of Rayleigh-Bénard Convection

A detailed account is given in a paper by A. Puhl, M. Malek Mansour, and M. Mareschal (Appendix 3).

C. Microscopic Simulation of Chemical Oscillations and Pattern Formation

Chemical oscillations such as those occurring, for example, in the Brusselator have been studied by molecular dynamics by F. Baras, M. Malek Mansour and John Pearson. As a result, the occurrence of limit cycles and periodic oscillations have been established (see Appendix 4).

We want finally to mention recent, still unpublished work by Principal Investigator Ilya Prigogine and a colleague, Edouard Kestemont of Brussels. Here we start with a number of particles (hard disks) distributed according to a Maxwell distribution, as well as particles wet initially at the nodes of a regular two-dimensional lattice. It has been shown (see Appendix 5) that as time goes on, the first effect is that the Maxwell distribution is destroyed. In the second stage, the binary pair correlation between particles is progressively built up. Two important remarks: The tendency to disorder corresponding to the final Maxwell distribution is transformed, so to speak, into spatial order between the particles. This spatial order takes

longer and longer times for larger distances. We shall come back to the problem of the transformation of disorder into order in the next section of this report. Moreover, the building of equilibrium distributions in space involving large distances and large numbers of particles is occurring so slowly that we expect that no macroscopic system in our environment is likely to be in equilibrium. All that can be realized is a local equilibrium around each particle.

3. The Dynamical Basis of Self Organization in Classical Mechanics

In previous publications we have already emphasized the importance of LPS corresponding to continuous sets of resonances. These are the systems studied in kinetic theory (collisions) or in quantum theory (quantum jumps). The dynamics of such systems is described in the paper by Tomio Petrosky and Ilya Prigogine, "Poincaré's Theorem and Unitary Transformations for Classical and Quantum Systems " (Appendix 6) as well as in the paper "Subdynamics and Nonintegrable Systems," by T. Petrosky and H. Hasegawa (Appendix 7). We have since studied the flow of entropy as generated by resonances. A typical graph is given by Fig. 1.

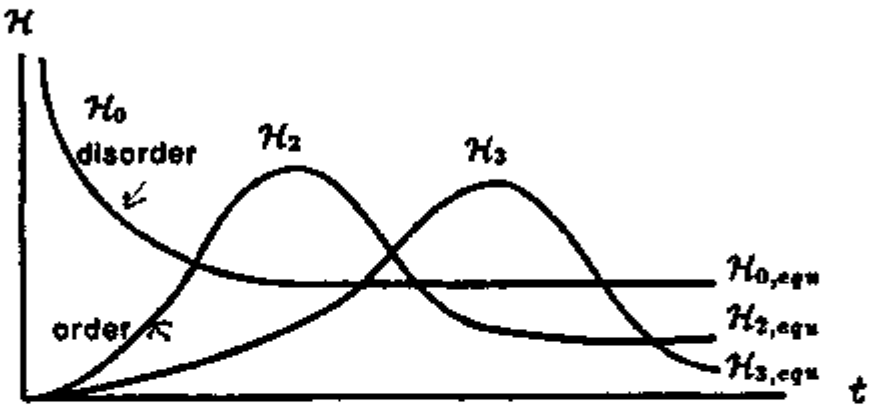

Figure 1

As can be seen, the initial information leads first to a decrease of $\mathcal{H}_0$ corresponding to a tendency towards the approach to a Maxwell–Boltzmann velocity distribution. However, simultaneously, we have an increase of $\mathcal{H}_2$ corresponding to a process involving an increasing order as $\mathcal{H}_2$ can be expressed in terms of pair correlations through the formula

$$\mathcal{H}_2 = \int dk \rho^2_{k,-k} = \int dr |g(r)|^2 \quad .$$

In an ideal system, ordering and disordering processes would cancel each other, and the dynamical information would be conserved. However, "high–order correlations" involving many particles are neither observable nor computable. As a result, the total available information is decreasing. This is the dynamical content of the second law of thermodynamics. It should be emphasized that, contrary to the view of classical physics, the loss of information or increase of entropy is not only related to disordering processes.

We have repeated similar experiments in quantum mechanics, and using especially the Friedrichs two–level situation. We have two possibilities, corresponding either to the excited state or to the bound state (see Fig. 2).

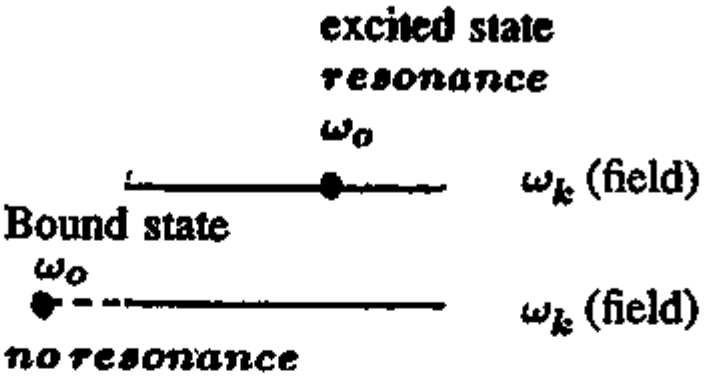

Figure 2

We can again study the evolution of the $\mathcal{H}$ function. For the bound case, we obtain Fig. 3, while for the excited state we obtain Fig. 4.

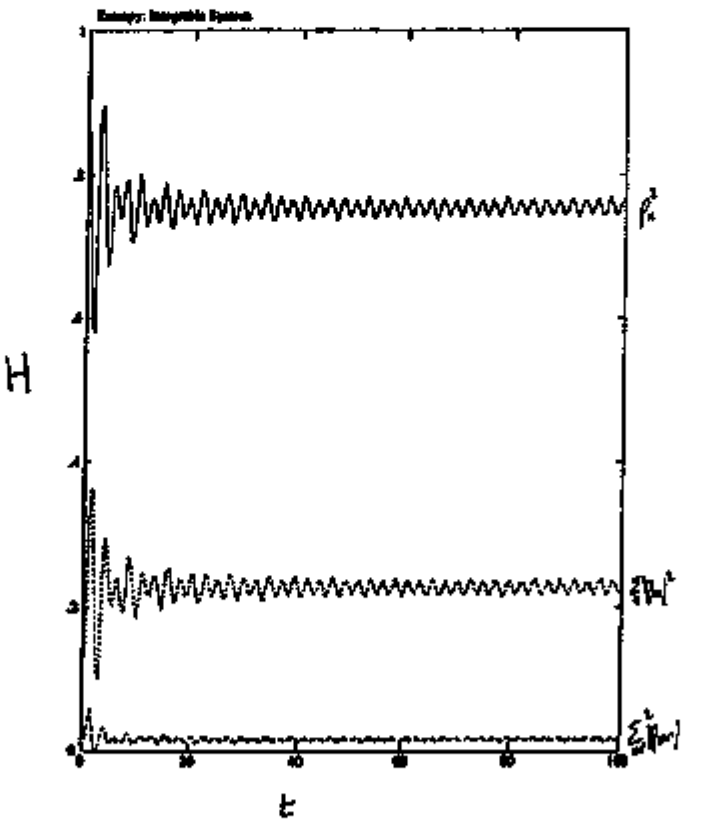

Figure 3

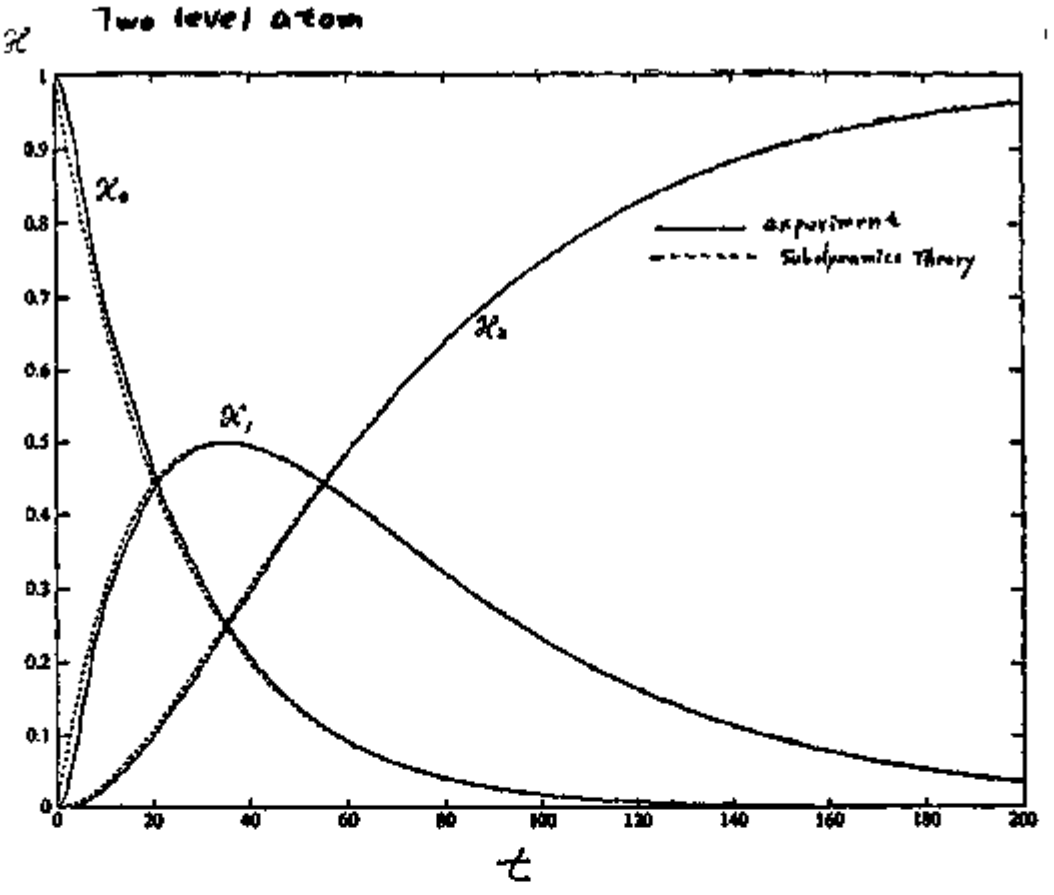

Figure 4

The difference is striking. For the excited case, which corresponds to LPS, we have a flow of correlations. As in the classical case, this leads ultimately to loss of control and loss of the concept of the wave function over a time on the order of the relaxation time. These results are being prepared for publication.

4. Numerical Simulations

The methods which we have developed open a number of perspectives from the point of view of numerical simulations. We hope to extend our results to cases which may involve phase transitions or a choice between various basins of attraction. Starting from disorder, what will be the type of spatial structure which will be chosen by the system? On the other hand, from the point of view of the LPS we extend them now to nonequilibrium situations which would permit us to model the type of systems which were studied previously on the phenomenological level. Looking back on Figure 4, it will be noticed that the contribution of $\mathcal{H}_2$ due to pair correlation goes through a maximum before reaching its equilibrium value. This maximum expresses precisely the existence of long-range correlations in nonequilibrium situations. We intend now to study the type of constraints — laser, external fields, and so on — which would stabilize the long-range coherence of the dynamical systems. In addition, our results will lead to a number of new predictions which we shall discuss in more detail in the next report.

A copy of our recent monograph, *Exploring Complexity*, by Ilya Prigogine and Grégoire Nicolis, has been sent separately to the Department of Energy Office of Basic Sciences.