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PROGRESS REPORT

THE BEHAVIOR OF MATTER UNDER NONEQUILIBRIUM CONDITIONS: FUNDAMENTAL ASPECTS AND APPLICATIONS IN ENERGY-ORIENTED PROBLEMS

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II. Summary of research made under contract No. DE-AS05-81ER10947 during the period 1984-1987.

Introduction

Let us enumerate a few areas where progress has been realized. (For a review of these questions, see references [1] and [2].)

1 State selection dynamics

During a symmetry-breaking transition, a system becomes extremely sensitive to small symmetry nonconserving interactions[3,4]. This sensitivity increases if the system is made to evolve through the transition point slowly Our theoretical predictions were verified both numerically and through electronic simulations[5] It has been pointed out that through such processes, parity nonconservation in weak-neutral-current interactions between the electron and the nucleons can become influential in the determination of the chirality of molecules The implications of this theory for the origin of the chirality of biomolecules have been pointed out

2 Polymerization under nonequilibrium conditions

Nonequilibrium conditions could lead to new sequence distributions of polymers[6] To understand these aspects more concretely, we studied the polymerization of mandelic acid This acid exists in two forms, R and S Its polymerization is a condensation with removal of water

$$S - R - R + S \rightleftharpoons S - R - R - S + H_2O \tag{1}$$

In parallel, there is a reaction interchanging polymer sequence. Specifically,

$$S - R - R - S + R - R - R \rightarrow S - R - R - R - R + R - S \qquad (2)$$

Nonequilibrium conditions can be created by starting with monomers and removing H_2O, so that the reverse reaction in (1) does not occur. It is then found that the polymer sequence is quite different from its equilibrium distribution, given essentially by the Flory formula

$$p(n) = (1 - \alpha)\alpha^{n-1} \quad , \qquad (3)$$

α being the extent of polymerization. This opens interesting perspectives in the enhancement of selectivity, which is one of the major problems of synthetic chemistry.

3. Inhomogeneous fluctuations in hydrodynamics and in completely mixed reactors

Fluids under thermal or mechanical constraints have quite different statistical properties compared to equilibrium. We recently employed a stochastic particle simulation based on the Boltzmann equation to study hydrodynamic fluctuations in a dilute gas under a temperature gradient. Various static correlation functions have been measured, and good agreement with the theoretical predictions of long range spatial correlations based on stochastic methods[7] has been obtained.

We proposed that computer experiments should be well described by the Landau-Lifshitz hydrodynamic fluctuation theory[8], so long as the assumption of local equilibrium was not violated. Excellent agreement with the particle simulation data validated this conjecture[9,10]. The results were also extended to fluids under stress[11].

Inhomogeneous fluctuations seem also to play an important role in the functioning of chemical reactors[12]. In most laboratory conditions, as well as on the industrial scale, chemical reactors are subjected to a vigorous stirring whose purpose is to mix the various constituents ensuring in this way a smooth, predictable release of chemicals in the course of time. However, mixing is never complete. As a result, the reaction dynamics is subjected to inhomogeneous perturbations, or, in other words, to a coupling with the hydrodynamic modes. We have recently analyzed this coupling[13-16] and found that it may induce a variety of bifurcation phenomena. These are expected to affect the yield and various other characteristics of the reactor.

4. Homoclinic bifurcations and mixed-mode oscillations. Applications in combustion

Multimodal oscillations, involving a sharp flash of activity followed by a train of a variable number of small amplitude oscillations have been observed in the Belousov-Zhabotinskii reaction and in hydrocarbon combustion. We have shown that bifurcations arising from the presence (for some parameter values) of a homoclinic orbit tangent to an unstable limit cycle provide a unified explanation of this phenomenon[17] Homoclinic tangencies to more complex manifolds, including Smale's horseshoe have also been studied[18]. An important feature, which actually simplifies considerably the analysis, is the presence of widely different time scales. This allows one to reduce the multi-dimensional dynamics to a one-dimensional map and apply efficiently the techniques of symbolic dynamics

In order to obtain a closer correspondence with combustion, a skeleton model has been proposed for the coupling between chemical and thermal effects[19] It consists of the following steps

Initiation $Y \xrightarrow{k_1} X$ (4.1)

High temp chain branching $X+Y \xrightarrow{k_2} fX$ (4.2)

Chain branching $X \xrightarrow{k_3} 2X$ (4.3)

High temp termination $X \xrightarrow{k_4} S_1$ (4.4)

Low temp termination $X \xrightarrow{k_5} S_2$ (4.5)

Here, Y represents the concentration of fuel and oxygen assumed to be equal, X denotes the autocatalytic chain carrier, and f is a suitable stoichiometric coefficient greater than unity. The main originality of the model is the introduction of a high temperature chain branching with activation energy satisfying $E_2 > E_1 > E_4 > E_3 > E_5$. This step describes the release of a great amount of heat following rapid consumption of fuel and oxygen, and is at the heart of ignition.

For a single set of plausible values of thermokinetic parameters and under conditions prevailing in CSTR, the model of (4.1) – (4.5) displays steady states, bistability, cool flame oscillations, oscillatory ignition, and complex ignition-cool flame oscillations when the reactant pressure P and the vessel temperature T_0 are varied as control parameters. The predicted P–T_0 state diagram compares fairly well with the experimental findings for the acetaldehyde/oxygen system. In addition, there is preliminary evidence of complex periodic states in a narrow range of parameter values. Specifically, two distinct sequences of states, in which m small amplitude oscillations, with m even or odd respectively, are superimposed on one period of the basic oscillation, are observed. We believe therefore that we have identified a "canonical" model which will eventually lead to a better understanding of the chemistry of combustion

5. Intrinsic randomness and spontaneous symmetry breaking in explosive systems

The phenomenon of transient bimodality discovered earlier by our group has been shown to give rise to a wide dispersion of ignition times, whose probability becomes strongly asymmetric and acquires a long tail[20] in the limit of high activation energies. More recently, we extended the stochastic study of explosive systems to account for spatially inhomogeneous fluctuations[21,22] We have shown that fluctuations give rise to unexpected symmetry-breaking phenomena. starting from a homogeneous distribution of temperature or concentration, the system develops appreciable spatial inhomogeneities during a time interval close to the ignition time As a result, there is a considerable dispersion of the position and occurrence time of the first "hot spot" initiated in the system

This spatial differentiation can be further characterized by following the time development of the spatial correlation function Again, starting from a uniform state (vanishing correlation function) the system builds during the ignition stage long range coherence, reflected by a nonuniform, monotonously decaying profile of the correlation function.

The effect of the system's size, of the boundary condition and of the geometry remain to be investigated Moreover, the role of the dimension of the hot spot initiated by a fluctuation in its subsequent evolution should be assessed.

6 Microscopic meaning of irreversibility

The important effect of nonequilibrium as witnessed by the various examples given in the preceding sections shows that a revision of the role of time on the microscopic level is necessary (See reference [1].) The implications of irreversibility in classical dynamics has become much clearer over the last few years. The microscopic meaning of irreversibility has also become much clearer. We may refer here to the beautiful paper by J. Lighthill[23], which emphasizes forcefully the role of the "temporal horizon" in dynamics, as related to the existence of Lyapunov exponents The distance between two neighboring trajectories increases then exponentially with time, as shown in the formula

$$\delta x_t = \delta x_0 \, e^{\lambda t} \quad , \tag{5}$$

where δx_0 is the initial distance and λ the positive Lyapunov exponent The existence of a positive Lyapunov exponent invalidates immediately the traditional arguments against irreversibility, associated with Poincaré's recurrence theorem Indeed, Poincaré's recurrence time is in general much larger than the Lyapunov time, and for sufficiently unstable systems the very concept of a trajectory is lost long before we can introduce the concept of recurrence Moreover, the idea of increase of randomness time going on (and, associated to it, of irreversibility) can now be explored for systems with only a few degrees of freedom

This contrasts with the situation which prevailed at Boltzmann's time, where irreversibility was associated solely with many-body systems, for which an exact solution of the equation of dynamics is out of the question

We cannot report here the advances which were achieved in the formal description of classical chaotic systems It suffices here to say that such systems present an intrinsic stochasticity and an intrinsic irreversibility, as they may be mapped through an invertible but non-unitary transformation into Markov chains[1,24].

But one of the problems of greatest interest today is the role of irreversibility in quantum theory. The situation of this theory is really unique On one side, it has rightly been called "the most successful of all physical theories". On the other side, controversies continue about its physical meaning and its range of applicability. It is important to notice that these controversies deal not only with epistemological aspects of quantum theory[25], but also with basic problems related to the meaning of the unstable particles, and more generally to quantum states with finite lifetimes[26].

This problem has been investigated in three recent papers [27,28,29]. The introduction of irreversibility into quantum mechanics leads to the fascinating possibility of a new formulation of quantum theory which leads to a number of predictions, some of which have been stated in our published papers Discussions with colleagues working in quantum optics and laser physics indicate that some of these effects may be amenable to experimental verification in the not too distant future We come back to these questions in the second part of this proposal