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

Progress Report

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PROGRESS REPORT

I. Brussels Group

Microscopic simulations and stochastic aspects
of hydrodynamic and chemical instabilities

The results obtained in this part of the project are due to G. Nicolis, M. Malek Mansour, F. Baras, M. Mareschal and J.-P. Boon from the University of Brussels, together with Professor F. Moss of the University of Missouri. The general objective has been to arrive at an understanding of the microscopic mechanisms involved in a hydrodynamic or chemical instability. To this end, molecular dynamics and Boltzmann–Monte Carlo simulations of the thermal explosion instability, the Rayleigh–Bénard instability, and of a chemical instability involving a second-order autocatalysis have been carried out. A detailed comparison with the phenomenological approach based on hydrodynamics and chemical kinetics has given some valuable information on the role of the fluctuations, the onset of long-range order and the range of validity of local equilibrium description and linear transport theory. To study further the stochastic versus the deterministic behavior, we have built, thanks to the collaboration of Professor Moss, an analog simulation laboratory allowing an easy realization of nonlinear dynamical systems driven by noise simulating the effect of thermodynamic fluctuations. What follows is a more detailed account of some quite recent results.

A. *Boltzmann–Monte Carlo simulation of combustion*

The typical time evolution occurring in thermal explosions is characterized by a long induction period followed by a short ignition stage, before the system reaches a plateau value corresponding to its unique attractor. The stochastic analysis elaborated in previous work by our group revealed the high sensitivity of such systems to stochastic perturbations or external origin or coming from internal fluctuations. For instance, we discovered a considerable dispersion of ignition times and the phenomenon of transient bimodality. Our main goal this year has been to confirm these rather unexpected results by molecular dynamics simulations.

In molecular simulations of combustion phenomena, the first problem to be solved is the microscopic modelling of an exothermic chemical reaction. In fact, the particles are not only characterized by their positions and velocities, but also by their internal energy. The simplest way is to assign a "color" to each particle, reflecting its internal state. In this way, a typical exothermic chemical reaction can be modelled by a process of color change coupled with release of some amount of energy whenever the relative kinetic energy of colliding particles is higher than a fixed threshold (activation energy). This prescription can easily be incorporated in a "classical" molecular simulation such as the Boltzmann–Monte Carlo simulation.

The Boltzmann–Monte Carlo simulation developed some years ago by Bird (also called "direct simulation

1

of Boltzmann equation") was designed mainly for simulations of dilute gas dynamics. This method was already used with success in different kinds of problems such as the study of shock waves or the statistical properties of systems submitted to very large nonequilibrium constraints. This year, we performed the extension of this simulation to gaseous reactive media.

We simulated a chemical reactor closed with respect to mass flow, in thermal contact with a reservoir maintained at a fixed temperature. The phenomenological description of such a reactor is quite well known. Typically, the equation describing this system is the heat conduction equation coupled with a chemical source term (in the limit of no consumption of reactant). The deterministic analysis reveals the existence of two kinds of behaviors: a subcritical behavior corresponding to the evolution toward a state close to the reservoir temperature and a supercritical one associated with explosion.

In our simulation, we considered 2000 (or 4000) hard spheres in a system of 10 (20) mean free paths in one direction (y) and periodic in two others, in contact with thermal walls at the y-boundaries. We gave the following prescription for the chemical reaction:

$$
\begin{array}{lll}
X + X & \rightarrow & X + X & K_{rel} < E_a \\
XC + X & \rightarrow & X + X + heat\ (q) & K_{rel} \geq E_a
\end{array}
$$
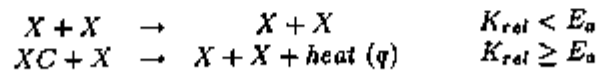
where K_{rel} is the relative kinetic energy along the line joining the centers of colliding particles and E_a is the activation energy. (Note that we have omitted the process of coloring in order to conform with the deterministic description which ignores the consumption of reactants in the first approximation.)

In the absence of heat release ($q = 0$), we recover the well-known Arrhenius law for different values of activation energy. When we incorporate the heat release, we observe the two kinds of behaviors predicted by the deterministic analysis dependence of the value of q:

q	3	4	4.64
behavior	subcritical	subcritical	supercritical (explosion)

Other parameters expressed in system units : length = 10 MFP (1 MFP = 30 molecular diameters), number density x (molecular diameter)^3 = 0.00755, E_a = 3.5, temperature of the walls = 1, k_B = .5, number of particles = 2000 .

2

The observed results are thus in qualitative agreement with the phenomenological description since we recover the critical differentiation between the two types of behavior at some critical threshold. The quantitative agreement is, however, not complete (the "experimental") critical value of some characteristic parameter is lower than the phenomenological one). We believe that the difference might come from the perturbation of the local Maxwell–Boltzmann distribution due to the exothermic reactions.

Within the framework of the simulation we have also analyzed the dynamics of the ignition process in the supercritical region ($q = 4.64$) and very close to the critical value. We have considered several (about one thousand) systems which are equivalent from a macroscopic point of view (same temperature, density,...). From the observed time trajectories, we have constructed the histogram of ignition times. Figure 1 shows the very broad distribution obtained. This result is very close to the one obtained from the stochastic description of a quite similar system: as the characteristic parameter approaches its critical value, the distribution of ignition times becomes very broad, and the maximum is substantially different from the deterministic ignition time, which belongs to the tail of the distribution.

These studies will be extended to systems developing flame fronts in order to sort out the molecular mechanisms leading to this phenomenon, which is at the heart of combustion.

B. *Analog simulations of complex dynamical systems*

An extremely large class of natural dynamical phenomena ranging from biology to astrophysics defy explicit analytical solution. Often those of such systems that are investigated experimentally exhibit such complexity that even numerical computation of the corresponding differential equation cannot provide a satisfactory interpretation. This is particularly true for systems with chaotic behavior. On the other hand, model systems with few degrees of freedom (e.g. three dynamical variables), despite their apparent mathematical simplicity, can show a high degree of complexity similar to the type of behavior observed in experimental systems and in natural phenomena. Mathematical theory of differential equations (the theory of dynamical systems) allows for prediction and — at least qualitative — characterization of scenarios describing evolution toward chaos. Digital computation appears as an indispensible technique to identify irregular solutions. As a complementary approach, analog simulation offers a fast, convenient, and powerful tool for the study of complex behavior, in particular for rapidly scanning and identifying regions of interest within larger areas. In addition, analog techniques deal with sets of differential equations by treating them as experimental systems, as regards in particular the noise intrinsic to such systems. The investigation of the effect of tunable colored noise is also easily performed.

During the present phase of the research, a laboratory for analog simulation of complex nonlinear dynamical systems has been set up in Brussels, thanks to the collaboration between our group and Professor F. Moss. A two-fold goal was reached: (i) the development of the basic instrumentation for the construction of electronic circuit models; (ii) the development of both hardware and software necessary to digitalize the analog signals and to perform the required statistical analysis on these signals. These realizations have

3

been completed and the set-up is now operational. Two model systems have been developed: a set of two coupled Brusselators, and an original model which can be described as a "Duffing-Van der Pol oscillator with memory". Conclusive tests on these models indicate that the laboratory set-up is presently in working condition. Research on these and related model systems is in progress.

C. *Chemical instabilities and reaction-diffusion dynamics in disordered media*

This work, which has been carried out by G. Nicolis and V. Altares, is the first attempt to study instabilities, bifurcations and self-organization when the dynamics takes place in a complex medium, characterized by some degree of disorder. Real-world materials belong, obviously, to this category. In addition, recent attempts to detect stationary spatial structures in chemical systems reported by the Austin, Bordeaux and Virginia groups are based on new types of chemical reactors in which porous or dispersed materials play a prominent role.

To model the complexity of the medium a small random contribution to the diffusion coefficients of the reacting species has been added. The properties of the stochastic diffusion operator in the absence of reactions have been analyzed under the assumption of a Gaussian stationary process whose correlation function behaves smoothly at the origin. It has been shown that in an infinite system there is anomalous (superdiffusive) behavior of the mean square displacement $< r^2 >$, arising from the correlations. On the other hand, in a finite system subjected to fixed boundary conditions it turns out that the disorder tends to reduce the value of the stationary diffusion flux.

When chemical reactions are incorporated, it is found that spatial disorder gives rise to three kinds of new contributions: a kinetics-dependent renormalization of the diffusion coefficients; an effective coupling between diffusion fluxes that would remain uncoupled in a homogeneous medium; and additional terms in the reaction-diffusion equations depending on higher powers of the gradient. It is expected that these effects might give rise to a *fluctuation-induced symmetry-breaking*. Specifically, it has been known for some time that chemical dynamics involving coupled species with nearly identical diffusion coefficients cannot generate spatial symmetry-breaking leading to steady state structures as a first bifurcation from the uniform state. But in a nonuniform medium, owing to the kinetics-dependent renormalization and coupling effects induced by the disorder, the effective diffusion coefficients might become sufficiently different; as a result, the conditions of spatial symmetry breaking might become satisfied. This possibility will be explored systematically in future work. We believe that similar studies would be useful in other contexts as well. Some obvious examples are pattern formation in geology and hydrodynamic instabilities.

4

II. Austin Group
Microscopic Meaning of Irreversibility

The research carried out by Principal Investigator I. Prigogine, Researchers T. Petrosky, H. Hasegawa and Z.Y. Chen and students D. Driebe, W. Saphir and J.Y. Lee of the U.T.-Austin group, together with Researcher P. Almirantis of the Brussels group, since the beginning of the project in April 1988 has concentrated on the microscopic meaning of irreversibility in matter-field interactions. We have developed a new approach to describing the temporal evolution of unstable microscopic systems incorporating dissipative processes. This new approach permits us to use perturbation analysis to describe so-called non-Markovian effects, such as phenomena related to Zeno's paradox (a short-time deviation of exponential decay), long tails, etc. With this new approach, we can draw a detailed picture of the structure of unstable particles, which appears to be a result of self-organization between the matter and the field. Several predictions of our theory have been verified by computer simulations. What follows is a more detailed account of some recent results.

A. *Theoretical results*

In the past, an essential role in the elucidation of irreversible processes was played by Poincaré's celebrated theorem on integrability, which constitutes a basis for the classification of dynamical systems [1,2]. Poincaré showed that resonances prevent integrability. This has led over the last decades to basic new developments such as those associated with KAM-theory. Therefore, an important problem is the extension of Poincaré's theorem to large systems, classical or quantum.

We have shown that in the case of large systems [3], Poincaré's theorem prevents the solution of the basic quantum mechanical problem, corresponding to the diagonalization of the Hamiltonian H by unitary transformation analytic in the coupling constant λ. Therefore, Heisenberg's eigenvalue problem, so basic for quantum mechanics, cannot be solved by analytic transformations for systems satisfying Poincaré's theorem. In all previous work on quantum theory, the analyticity condition was given up in such situations; but this leads to a quite unphysical description, as the properties of the system described by the Hamiltonian change discontinuously when the interaction is switched on. This is in contradiction with the requirement of structural stability which every physically acceptable description must satisfy.

We have shown that by giving up the condition of hermeticity [3,4,5,6] (that is, by including the irreversibility induced by unstable dynamics), we obtain a description which is analytic in λ. States which would be stable in the absence of interactions become unstable and decay with lifetimes which are long when λ is small. For λ sufficiently small, the temporal evolution of a system with Hamiltonian, H, differs (over any finite time interval) as little as we want from the free evolution characterized by the unperturbed Hamiltonian H_o. In brief, we obtain a "kinetic description", which reduces to the usual kinetic description in the limit of small λ, and leads to the formal solution of the initial value problem for the Liouville equation. Such a formal solution was already known previously [7], but was non-Markovian. Now all non-Markovian

5

effects can be calculated explicitly. These non-Markovian effects correspond to a kind of nonlinear causality. Information included in the initial conditions is transmitted to various degrees of freedom of the system and reacts back on the degrees of freedom which were excited at the initial time.

We have in this way obtained a new form of classical or quantum theory applicable to large nonintegrable systems. As mentioned, this is of special interest for quantum mechanics, as our method leads to the first classification of quantum dynamical systems. An essential feature is that the temporal evolution is not factorizable in the usual Hilbert space. As a result, the evolution is described in terms of the change of the probability density, and no longer in terms of probability amplitudes. It is quite natural that considerations based on a classification of dynamical systems limit the range of validity of the Schrödinger equation, exactly as they do in the case of classical dynamics for the validity of the concept of a trajectory.

We have started the application of our new method to the problem of matter–field interaction in classical electrodynamics. This was the starting problem of Planck's program [8], and led to the discovery of black-body radiation and the establishment of Planck's constant. However, Planck failed in his attempt to give a derivation of the black-body radiation from the emission process.

In work which is now in progress, we have provided the missing mechanism. We show that the initial condition, corresponding to an unstable state or to a charged harmonic oscillator together with a field vacuum, excites the degrees of freedom of the field, which then reacts back on the charge. This back reaction explains the deviations from exponential behavior. For short time, which we call the Zeno time, the charged harmonic oscillator transmits information about its frequency to the field. This corresponds to a self–organization process of the unstable particle on a microscopic scale. After the Zeno time the charged harmonic oscillator starts to radiate. We have studied this behavior using computer simulations [9,10].

B. *Numerical results*

Our theory predicts that whatever the initial conditions of the particle and the field, the behavior predicted by classical electrodynamics is reached after some time, which corresponds precisely to the building up of the right environment. To see this, we have performed numerical simulations of the simplified model of a classical charged oscillator interacting with a set of field oscillators. The results are shown in Figs. 1 and 2. There we show the time–dependence of the damping rate of the energy of the radiating harmonic oscillator.

In Fig. 2, one starts with an initial condition corresponding to the charged oscillator in motion and the field oscillators at rest or, equivalently, at the state of zero energy (this is the classical vacuum). One next solves on the computer the full (reversible) equations of motion, without making the phenomenological assumption of the existence of a damping constant. The result in Fig. 2 shows then that there is a short delay before the charged oscillator starts to radiate, which cannot be properly accounted for by the phenomenological equations available in the literature. To understand the origin of this delay let us recall that the radiation process involves a resonance between the material oscillator and the field oscillators. At the start though, there is no field oscillator available. As a first step the material oscillator has therefore

6

to produce the field oscillators; or, in other words, to create the right environment in order to be able to radiate. For this initial condition after a short time of the order of a/c, where a is the radius of the oscillator, the oscillator starts to radiate. (For the hydrogen atom this time scale is on the order of 10^{-18} sec.)

We may start different experiments with nonzero initial damping, but we obtain eventually the same damping (see Fig. 3). This self-organization process of the right environment persists over long times. Progressively, the particle creates a kind of bath in which it is then moving somewhat like a brownian particle. The long-time, non-exponential behavior originates in the interaction between the particle and this bath. The resulting brownian motion leads to a kind of *Zitterbewegung* which implies the added stochasticity for which Planck had looked unsuccessfully.

In this way, we begin to have a physical picture of the mechanism of production of photons by unstable particles. Curiously, there appears at the origin of radiation a kind of autocatalytic process. As we have mentioned, if we consider a harmonic oscillator with a well-defined frequency ω_o, radiation starts only after a time necessary to induce the vacuum normal modes corresponding to resonance with the oscillator.

This description of the interaction between matter and field is quite different from the traditional one: there are obviously no self-organization processes included in the Schrödinger equation. As is well known from classical and quantum electrodynamics, self-interactions are supposed to give rise to a renormalization. Here the concept of renormalization is no longer sufficient, as we have to consider dissipative processes, leading to well-defined dynamical behavior, largely independent of the initial conditions.

For us, these developments appear especially fascinating, as in our previous work we were involved in the description of nonequilibrium, "dissipative" structures in macroscopic physics. We see now that these structures have their parallel in the microscopic description.

The program which we intend to pursue over the next years is quite extensive. We have already performed some computer simulations in order to verify our predictions; we intend to continue these simulations. We have also to discuss the possibility of experiments which would show notably the role of the kind of boundary layer produced by excited states. We have also to discuss the predictions of our theory concerning the usual renormalization effects of quantum electrodynamics such as the Lamb shift.

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Fig. 1: Distribution of ignition times. Histogram of $X_1 : te$.

Fig. 2: The damping rate of the energy of the charged harmonic oscillator as a function of time. At $t = 0$ the energy for the field oscillators is zero (i.e., the unperturbed vacuum). The theoretical value of the relaxation time is evaluated at the resonance frequency and is given by $\tau = 1/\gamma_{th}$. After a short time of the order of a/c, where a is the radius of the oscillator, the oscillator starts to radiate. (For the hydrogen atom this time scale is on the order of 10^{-18} sec.)

Fig. 3: The damping rate of the energy of the charged harmonic oscillator as a function of time with several initial conditions. Whatever the initial condition, the behavior predicted by classical electrodynamics is reached after some time.
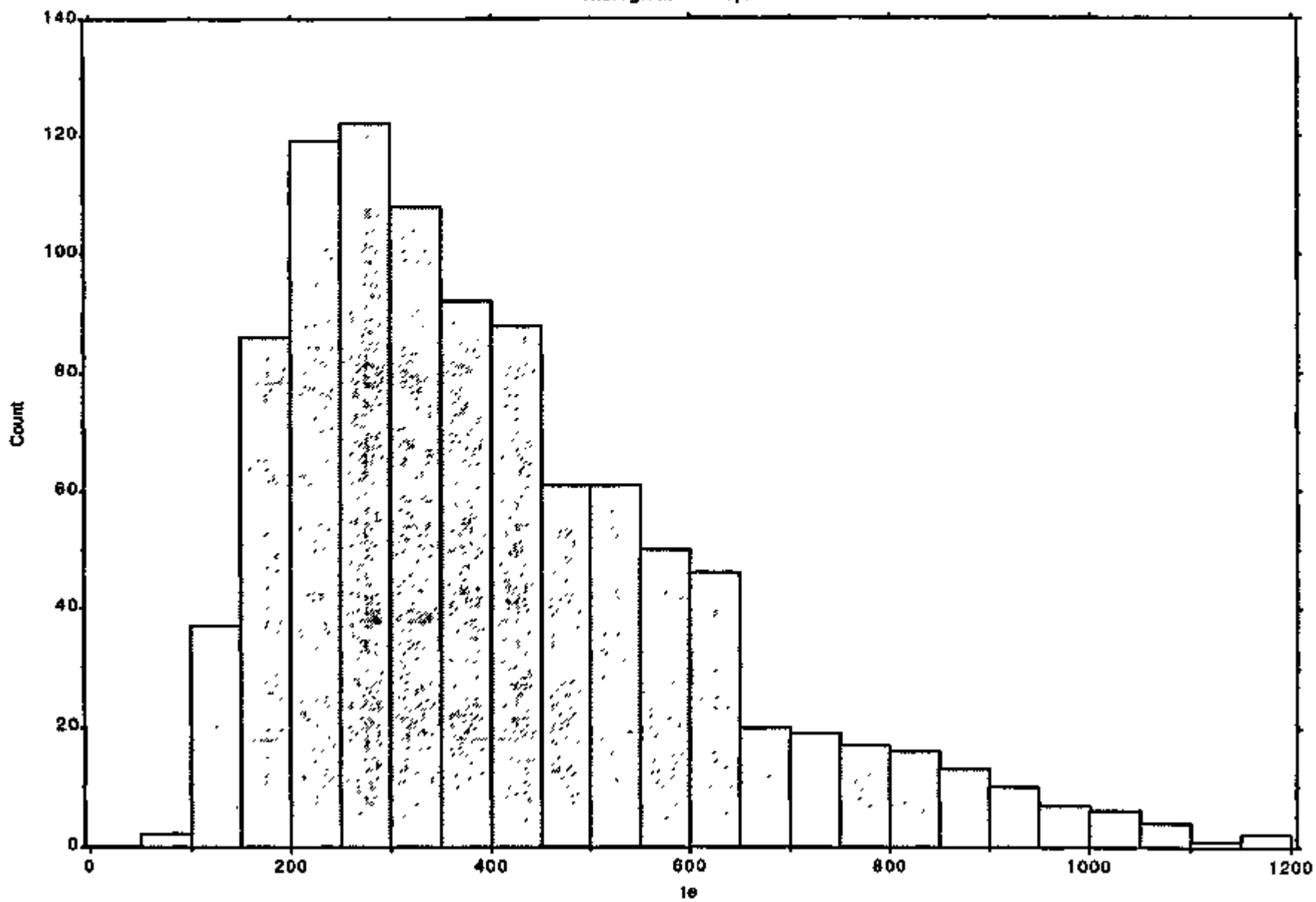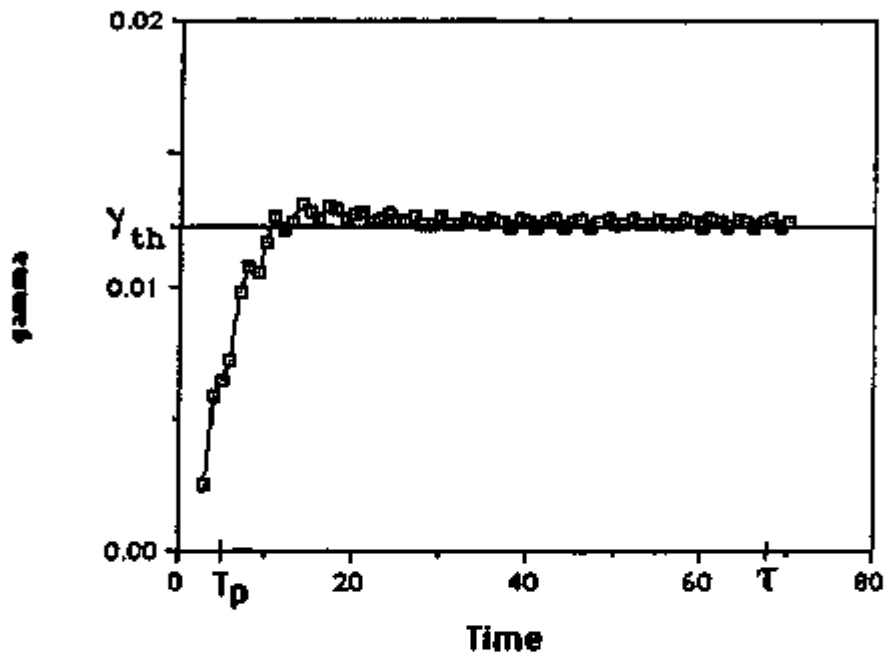
1000 réalisations

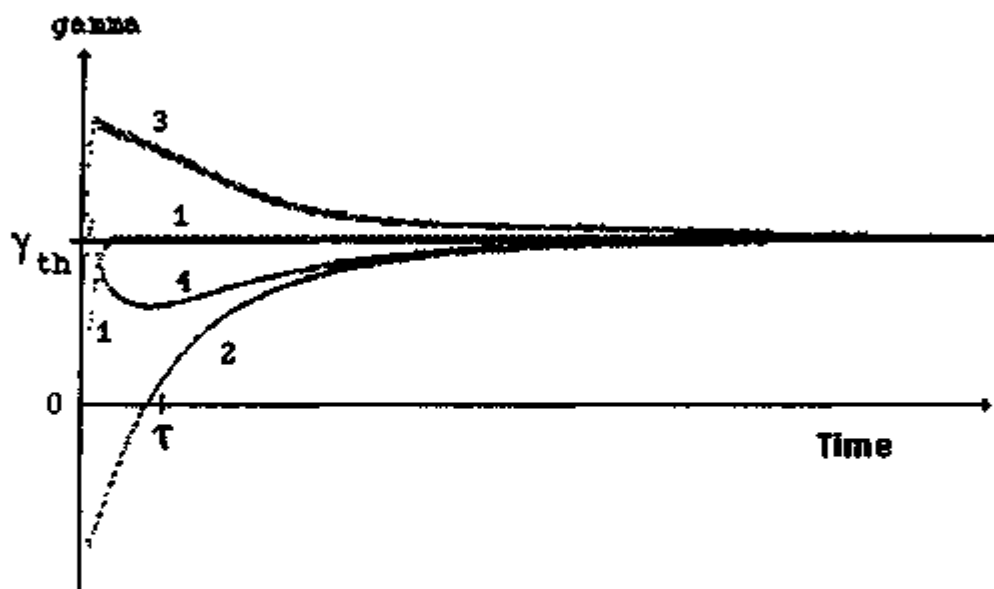Histogram of X_1: te

Figure 1

γ_{th} : Theoretical value of the damping coeff.

$\mathcal{T}$: Theoretical value of the relaxation time

T_p: Period of the harmonic oscillator

Figure 2

T : Theoretical value of the relaxation time

1. Unperturbed vacuum
2. Self accelerating
3. Over damping
4. Under damping

Figure 3

Listing of Publications

1. T. Petrosky and I. Prigogine, "Poincaré's Theorem and Unitary Transformations for Classical and Quantum Systems," *Physica* 147A (1988) 439–460.

2. I. Prigogine and T. Petrosky, "An Alternative to Quantum Theory," *Physica* 147 A (1988) 461–486.

3. I. Prigogine, "A New Microscopic Level of Irreversibility?," (to appear).

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8. G. Nicolis and V. Altares, "Physics of Nonequilibrium Systems," in Synergetics and Dynamic Instabilities (Soc. Italiana di Fisica, Bologna, 1988) 298–328.