The Behavior of Matter under Nonequilibrium Conditions:

Fundamental Aspects and Applications

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PROGRESS REPORT
"The Behavior of Matter under Nonequilibrium Conditions:
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Our report contains a brief summary of what has been achieved over the period of the contract. We have studied the behavior of matter under nonequilibrium conditions on three levels: (1) on the microscopic level in the frame of classical mechanics or of quantum theory; (2) on the stochastic level, which includes fluctuations; and (3) on the phenomenological, macroscopic level described by nonlinear equations. We first report on the level (1), then report on the levels (2) and (3).

Microscopic description

The results obtained in this portion of the project are due to I. Prigogine, T. Petrosky, H. Hasegawa, S. Tasaki, D.J. Driebe and W. Saphir. In short, we have shown that Poincaré's celebrated classification of dynamical systems into integrable and nonintegrable systems has wide ranging consequences for the very formulation of dynamics.

The dynamics of nonintegrable systems appears to follow new laws, presenting quite specific features. Poincaré's theorem prevents the existence of solutions of the eigenvalue problem associated with the Hamiltonian (or to the Liouville operator) which are analytic in the coupling constant. These analytic solutions diverge as a result of resonances. It is our conviction that in the future, the nonintegrability theorem of Poincaré will be considered as a turning point somewhat similar to the discovery that classical mechanics leads to divergences when applied to black-body radiation.

Let us recall that the work of Kolmogorov, Arnold and Moser (the so-called KAM theory) has shown that for sufficiently small values of the coupling constant (as well as other conditions which can be found in every textbook dealing with the "new" mechanics), the majority of trajectories remain periodic. In this sense the KAM theory shows that in some situations Poincaré's divergences are "harmless". However, this is not so for Large Poincaré systems (LPS) which are characterized by a continuous spectrum and continuous sets of resonances.

The general philosophy behind our approach is formulated in Appendix 1, Time, Dynamics and Chaos – Integrating Poincaré's Nonintegrable systems. In Appendix 2, we describe in detail the relation between Poincaré's theorem and the eigenvalue problem.

An important tool for the solution of the eigenvalue problems in LPS, subdynamics, is described in Appendix 3. To make the reader more familiar with subdynamics, two applications have been included in Appendices 4 and 5.

Appendices 6 and 7 deal with the main content of our new approach, which cures Poincaré's divergences through the introduction of a suitable time ordering of dynamical states. In simple cases, such as the Friedrichs model, this reordering may be performed in the Hilbert space (see Appendix 6). We have to express the fact that the unstable state occurs *before* the emission of photons. However, in general we need the introduction of a "second" internal time to order the dynamical states. The basic idea of our work is that this second time corresponds to the flow of correlations as it occurs, for example, in many-body systems leading to correlations involving an ever increasing number of particles (or degrees of freedom). That means, however, that this time ordering can only be performed in the density matrix space (on the level of Gibbs ensembles). A basic result is that in this way we eliminate all Poincaré's divergences and obtain a new formulation of dynamics on the level of the statistical ensembles, which includes broken time symmetry and irreversibility. Specifically, in the case of quantum theory, we show that the concept of wave functions is not applicable to LPS (and therefore to systems involving interacting fields).

It is well known today that irreversibility plays an essential role in the description of fundamental aspects of nature. Still, the microscopic description, both in classical and quantum mechanics, is in terms of time-reversible laws (see Appendix 1). This may be called the time paradox, and has been at the center of

the work of our group for many years. A turning point in our research was the realization that Poincaré's classification of integrable and nonintegrable systems may play a major role in this context. Poincaré's theorem is of obvious relevance for the theory of irreversible processes, as Poincaré's integrability prevents, so to speak, dissipativity. However, the close relation between Poincaré's theorem, kinetic theory and field theory is a recent result. Indeed, as shown in Appendix 2, there exists a close relation between Poincaré's theorem and the so-called collision operator of kinetic theory. We may therefore expect that once we would be able to integrate LPS, we would automatically obtain a formulation of dynamics including irreversibility. A first step towards the integration of LPS was the development of the "subdynamics" theory, which shows that we can split the dynamical evolution of LPS into independent evolutions, corresponding to subspaces, characterized by a set of complete orthonormal but nonhermitian projection operators. Again, while the idea of subdynamics had been developed by our group already in 1968, the relation with Poincaré's theorem was only understood recently. The theory of subdynamics is summarized in Appendix 3.

Appendix 4 deals with the evolution of a dilute gas towards equilibrium, including both the appearance of disorder (in the velocity) and order (in the spatial correlations), time going on. For dilute gases, it has been customary since Boltzmann to associate the approach to equilibrium to an increase of disorder. However, for finite densities, we have also to include the appearance of order as expressed in terms of spatial correlations. Therefore, the approach to equilibrium in classical fluids presents both aspects: production of disorder in the velocity distribution, and production of order in the spatial distribution of molecules. This interplay of order and disorder can be elegantly described by subdynamics.

In Appendix 5 we consider a situation usually studied by mapping theory on the level of trajectories. Here we use subdynamics to describe the evolution of a statistical ensemble, in which particles are deflected by a periodic potential regularly distributed in a one-dimensional system. With a suitable choice of parameters, we can follow in detail the appearance of chaos, through positive Lyapunov exponents, and the transformation of motion (described by classical trajectories) into diffusive motion (described by Fokker–Planck type equations). We show that for short times there is a near compensation of diffusion and anti-diffusion terms. Time going on, the anti-diffusion terms are damped, and we obtain an auto-catalytic mechanism, bringing the system to a time evolution described by diffusive motion.

We come now to the main part of this report: the derivation of a new formulation of dynamics for LPS. Let us emphasize the difference between the approach which we use now and what has been done by our group before. In our previous work it was tacitly assumed that the Liouivillian, being hermitian, has only real eigenvalues. To include dissipation we therefore introduced a non-unitary, non-factorizable transition A leading from ρ to a new "physical" ρ'

$$\rho' = A\rho.$$

This physical ρ' would then satisfy a modified Liouiville equation which would include dissipation and the second law of thermodynamics. Unfortunately there exists a whole class of transformations A and it appeared impossible until now to introduce supplementary conditions which would fix A uniquely.

Our present approach is based on the observation that the time ordering as mentioned above leads to an extension of the Liouiville space allowing the appearance of complex eigen-distributions without any need to perform first a transformation. We consider successively two situations. The first corresponds to the case in which we may introduce the time ordering in the Hilbert space. As mentioned, this is possible for the so-called Friedrichs model. The natural time ordering expresses that the emission of radiation occurs after the preparation of the unstable state. This leads to a generalization of quantum mechanics in which the usual Hamiltonian eigenvalue problem is replaced by a complex eigenvalue problem which can be solved exactly. The usual Hilbert space is in this way extended to include generalized eigenstates involving complex distributions. In this way we may integrate a class of Poincaré's nonintegrable systems. In the case of the Friedrichs model we may compare our solution to the original Friedrichs' solution which is not analytic in the coupling constant (the unstable particle is dissolved in the continuum whatever the value of the coupling constant). It is remarkable that the Hamiltonian in the extended Hilbert space remains hermitian and the

time evolution remains unitary in spite of the decay of the unstable particle.

In our method the quantum mechanical state is expressed as a superposition of basis states with a broken time symmetry. This leads to a temporal description for the evolution of the quantum state which is quite appealing. The particle decays, time going on, and produces a field corresponding to outgoing waves. This decay is irreversible in the sense that we can introduce an operator corresponding to a Lyapounov function whose average value taken over an arbitrary state decreases monotonically and takes its minimum value when the unstable particle has decayed. In this way, spontaneous decay becomes indeed an irreversible event. We have here a very simple example of a dynamical description which incorporates irreversibility. Also, it should be emphasized that our complex spectral representation can be obtained by a perturbation calculation. This is of great importance as beyond the Friedrichs model the usual methods fail to produce an explicit spectral representation.

However, as mentioned, it is only in very simple situations such as the Friedrichs model that our "time ordering" can be performed in the frame of the Hilbert space. The general case involves time ordering in the Liouville space of density matrices. The quantum state has then to be described by a density matrix whose time evolution can be expressed in terms of a complete basis formed by density matrices with a broken time symmetry. Here the time ordering is based on the idea of a flow of correlations which was already previously widely used in the formulation of nonequilibrium statistical mechanics, starting with the monograph by the main investigator (Nonequilibrium Statistical Mechanics, Wiley–Interscience, New York, 1962).

In LPS, correlations involving an ever increasing number of particles (or degrees of freedom) build up, time going on. Our time ordering means that creation of higher order correlations is "future-oriented" while the transition to lower-order correlations is "past-oriented". This distinction is reflected by different analytic continuations for the propagators associated with the various processes. The basic result of our theory is that we can now derive a complete set of eigen-distributions of L_H which are non-factorizable in contrast to what happens for integrable systems. The main example studied in Appendix 7 refers to scattering. This is a simple example where we can follow the main features of our approach, such as the asymptotic disappearance of the wave function. We also predict deviations from usual quantum mechanics starting with the three-body scattering problem.

We expect that nature makes use of the alternative dynamics applicable to LPS. This belief is based on the various general arguments:

1) Most dynamical systems in nature are indeed LPS.
2) Our method eliminates all Poincaré's divergences.
3) In addition, it goes further by giving a constructive method for the spectral representation of the Liouville operator for situations such as interacting fields, where no constructive method was available.
4) It takes into account resonances between the "bras" and "kets" of usual quantum mechanics.
5) It includes time symmetry breaking and the second law of thermodynamics, and therefore solves the "time paradox".
6) It agrees with previous work on statistical mechanics (starting with the Van Hove l^2t limit and including the non-Markovian master equation).
7) It shows that LPS are "mixing", and includes the approach to equilibrium (which remains a mystery as long as a point is mapped to a point in classical mechanics, and a wave function is transformed into a wave function in quantum mechanics).
8) It limits the concept of wave function, and avoids therefore the well known conceptual difficulties of quantum mechanics, namely the collapse of the wave function and the measurement problem, (as it provides a dynamical definition of the measurement apparatus, which according to our approach has to be a LPS).
9) We have tested extensively the predictions of our approach for classical systems (radiation damping, mapping problems, etc.) as well as in simple cases for quantum mechanical systems (Friedrichs model). In every case, the numerical agreement has been excellent. We are preparing the publications which

will give the results of our numerical validations.

Macroscopic level with stochastic description

The results obtained in this portion of the project are due to J.E. Pearson M. Malek Mansour, and F.Baras. The primary result is the successful simulation of complex macroscopic chemical phenomena at the microscopic level. In particular, we have focused on self-organization processes: i.e. on transitions from states constant in space and time to states periodic in space or time.

The simplest example of self-organizational phenomena in chemical systems are simple periodic oscillations in the concentrations of the reacting species. Such limit-cycle oscillations typically have a macroscopic period on the scale of minutes or hours. A macroscopic time scale implies many collisions per macroscopic time unit with a correspondingly high computational cost. We thus have limited studies to dilute gas phase reactions in order to avail ourselves of the method pioneered by G.A. Bird. Bird's method is up to 1000 times faster than traditional molecular dynamics simulations and is valid for a dilute Boltzmann gas. It is thus restricted to binary collisions.

It was necessary to construct a new model chemical oscillator in order to meet the constraints imposed by the dilute Boltzmann gas hypothesis. Existing model oscillators involved either/or trimolecular collisions, several separated time scales, or complex reaction schemes containing many reacting species. We developed the following simple three component reaction in order to develop the simulation techniques.

$$U + V \rightarrow W + V$$
$$V + V \rightarrow W$$
$$V \rightarrow \text{products}$$
$$+ \text{ Feed terms}$$
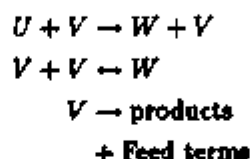
A deterministic analysis of this model has been carried out. The model contains a variety of bifurcation theoretic phenomena including saddle-node bifurcations, Hopf bifurcations, Takens-Bogdanov bifurcations, limit-cycles, mushrooms, and isolated branches of solutions. To our knowledge this is the first model chemical oscillator with neither separation of time scales nor trimolecular collisions.

The microscopic simulations of the above reaction scheme under the assumption of perfect mixing gave good agreement with the macroscopic rate equations. These results have been published (see Appendix 8 an 9). When the perfect mixing assumption is dropped the reaction is capable of spontaneously forming spatial concentration patterns. We have successfully simulated such steady state patterns. (Laboratory observations of such patterns have recently been reported by groups in Bordeaux and in Texas.) We are at present continuing work on these simulations. Spatially-distributed systems generally have several attractors. This is simply a consequence of spatial symmetries and of the fact that several different spatial modes lose stability nearly simultaneously. In MD simulations large fluctuations tend to kick the system from one attractor to another. We are currently involved in a search of parameter space to locate regions where the consequences of the fluctuations are minimal.

The most interesting direction to go with such simulations will be the simulation of chemically reacting hydrodynamic flows. Simulation techniques for such systems are presently in their infancy. The reaction of the flow with the boundaries results in a moving boundary value problem. To model such a system from the macroscopic point of view is beyond the capabilities of present computational techniques. On the other hand, to model such a system from the microscopic view point, one need allow for the additional complication of particle-boundary interactions, but such considerations are conceptually simple. One can add or take away boundary sites as particles collide with the boundary depending on whether the local concentration is near or far from the solubility limit. With the advent of massively parallel computers, such simulations are feasible. They are of obvious geophysical interest and would presumably be useful in the recovery of fossil fuels.

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We anticipate no unobligated balances to exist in the accounts at
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Ilya Prigogine, P.I. and
Tomio Petrosky, Co-P.I.

date: 12/19/90

List of Publications

1. I. Prigogine, "Time, Dynamics and Chaos", Presentation at Nobel Conference XXVI, Gustavus Adolphus College, Saint Peter, Minnesota, October 2 and 3, 1990.
2. T. Petrosky and I. Prigogine, "Poincaré's Theorem and Unitary Transformations for Classical and Quantum Systems", *Physica* 147 A (439) 1988.
3. T. Petrosky and H. Hasegawa, "Subdynamics and Nonintegrable Systems", *Physica A* 160 (351) 1989.
4. D. J. Driebe and T. Petrosky, "Order and Disorder in the Approach to Equilibrium of a Classical Gas", submitted to *Physica A*.
5. H. Hasegawa and W. Saphir, " Subdynamics and Classical Chaotic Systems" (preprint).
6. T. Petrosky, I. Prigogine and S. Tasaki, "Quantum Theory of Non-Integrable Systems", to appear in *Physica A* (1990).
7. T. Petrosky and I. Prigogine, "Alternative Formulation of Classical and Quantum Dynamics for Non-Integrable Systems", submitted to *Physica A*.
8. F. Baras, J.E. Pearson, M. Malek Mansour, "Microscopic Simulation of Chemical Oscillations in Homogeneous Systems," *J. Chem. Phys.* 93(8), October 1990.
9. A. Arneodo, J. Elezgaray, J. Pearson, and T. Russo, "Instabilities of Front Patterns in Reaction-Diffusion Systems," submitted to *Physica D*.

papers removed and cycled separately—