European Science Foundation

Program "Stochastic Dynamics: fundamentals and applications" (STOCHDYN)

FINAL REPORT CONCERNING THE WORKSHOP

"STOCHASTIC EFFECTS IN LIESEGANG PATTERN FORMATION"

1. Summary of the Programme

This very successful meeting gathered together about a dozen of the worldwide most active scientists working in this field, as well as a few younger Ph.D. students. During this four-day meeting, 13 talks were given and 3 round-tables were conducted. Moreover, the location of the workshop (the Villa Laret) was particularly suitable to nucleate a large number of informal and very fruitful discussions between the participants.

2. Programme scientific objectives

This workshop aimed at addressing the influence of stochasticity on the dynamics of nonequilibrium Liesegang pattern formation, both from a theoretical and an experimental point of view. Its potential relevance in engineering patterns in mesoscopic and microscopic devices has been analyzed. The workshop combined the efforts of both theoreticians and applied scientists in presenting the latest developments in the field, and in establishing the relevant directions for further conjoint studies.

3. Assessment of results achieved

In a first talk, Prof. Z. Rácz gave a historical overview of the research on Liesegang patterns.

The developments in the field were reviewed with the aim of establishing a common ground and language for further discussions. Rácz started with the characterization of the experimentally observed patterns and emphasized those aspects where noise plays an important role (spirals, inverse patterns, band splitting). Regarding the theories, Rácz concentrated on Model B version (describing the phase separation of the reaction product in the wake of the reaction front), which was shown to reproduce all the generic laws (time-, spacing-, width-, and Matalon-Packter law) that are associated with Liesegang phenomena. It was also emphasized that stochastic features must be added even to this theory in order to account for such phenomena as e.g. the band-splitting which may be an important mechanism for producing microscopic patterns.

In the second talk, Dr. I. Lagzi showed that simple diffusion processes coupled with non-linear dynamics (arising from chemical reactions) may produce various patterns. Liesegang phenomenon was probably one of the first spatiotemporal patterns ever studied. Recently, the trends in the investigation of the precipitation pattern formation were either to revisit and punctuate the existing empirical regularities, or the observation and description of the pattern formation in more complex situations (e.g., the redissolution of the precipitation zones due to complex formation, resulting in moving patterns; or a systemstic analysis of the influence of various initial and boundary conditions on pattern formation). A novel result was reported concerning a hysteresis phenomenon in a reaction-precipitation system which qualitatively differs from activator-inhibitor or cubic autocatalytic systems, where Turing patterns have been previously reported.

Then Prof M. Droz and N. Chevalier discussed the problem of the role of the noise in reaction-diffusion systems and particularly in the formation of Liesegang patterns. First it was shown that noise or fluctuations can play a crucial role in homogeneous or inhomogeneous sytems, especially in low-dimensional configurations. Theoretical and numerical evidences were given to determine the upper critical dimension above which the chemical fluctuations become relevant. In a second part, a microscopic investigation of the spinodal decomposition scenario for the formation of Liesegang patterns was discussed. Numerical simulations of a microscopic model with competition between Glauber and Kawasaki-like dynamics were described, and the consequences of the presence of the noise were analyzed in details. The problem was also approached at the level of a generalized Langevin equation, and the difficulties and advantages of this approach were discussed.

Dr. T. Antal discussed the formation of agates and inverse Liesegang patterns in the framework of driven Cahn-Hilliard equation. This situation describes a situation where the reagents necessary to the formation of the bands are already present in the gel, and additionally something (e.g., heat or a certain chemical) diffuses out of the system. The resulting band structure may present an inverse spacing law, which makes this model a simple candidate to describe the emergence of the experimentally observed inverse banding phenomenon.

The important problem concerning the role of an external electric field as a control parameter of the formation of Liesegang patterns was approched by two speakers.

Evolution of Liesegang patterns in an electric field was studied experimentally in the $AgNO_3/K_2Cr_2O_7$/gelatine system by Dr. I. Lagzi and collaborators.

An extended form of the width law, which takes into account the effect of a constant electric field, was proposed. Using perturbed concentrations in a supersaturation model, it was predicted that the stochastic precipitate pattern distribution depends on the electric field strength.

The same problem was discussed from a more "first-principle" theoretical point of view by Dr. I. Bena. The dynamics was described by a Cahn-Hilliard equation with a moving source term representing the reaction zone, while the electric field enters through its effects on the properties of the reaction zone. It was shown that the electric field changes both: (i) the motion of the front. Besides the diffusion component, the front may acquire a drift component in the case of a "reverse" electric field, i.e., that is unfavorable to the reaction.(ii) the amount of reaction product left behind the front. In the case of a "direct" field – i.e., that favors the reaction by driving the reagents towards the reaction zone – the concentration of the reaction product grows linearly behind the front; while in the case of a reverse field the concentration profile is decreasing. The main conclusion was that the number of precipitation bands becomes finite in a finite electric field.

These studies open serious perspectives of using the electric field as a flexible control parameter in Liesegang pattern formation. Moreover, the way is opened for theoretical studies on the role of the electric field in smoothening out the effect of thermal noise that has been reported in some recent experiments.

Prof. M. Tsapatis discussed the problem of the formation of Turing and Liesegang patterns.

The fabrication of periodic structures and regular patterns is desirable for the development of functional materials and devices with applications ranging from electro-optics and photonics, to microreactors and biosensors. Many of the current techniques for materials patterning rely on topdown processing by removing material from predetermined locations (e.g., lithography, ablating, etching). Due to high development and production costs, as well as physicochemical constraints, such approaches cannot meet the increasing demand for patterned materials with features of reduced size, controlled chemical composition and multi-dimensional periodicity over extended regions. Therefore, alternative, bottom-up, strategies including self-assembly, microcontact printing, surface and block co-polymer directed assembly, masked chemical vapor deposition and micro-molding are intensively pursued. It is possible to use the phenomena of Turing patterns and Liesegang rings (where, by the interplay of reaction and diffusion, regular chemical patterns are produced) in order to fabricate micrometer-size patterns in porous media. Two developments were presented and discussed: Titania Liesegang rings by chemical vapor deposition, and the proposal to create periodic deposits by self-assembly driven through a Turing pattern precursor.

Conditions for the spontaneous self-organization in deposition processes were discussed

Then Prof. D. Vlachos presented a model for the spontaneous formation of patterned deposits in porous media, reminiscent of Liesegang rings (LR) formation in gels. Simulations showed that under certain conditions the frontal deposition of continuous solid film changed to quasi-periodic pattern formation of bands. Bifurcation analysis of a simpler, skeleton model explained LR formation as an instability of a uniformly propagating plane reaction front to a time-periodic solution. A theoretical stability criterion, developed in the case of strong concentration gradients, suggested that key parameters in pattern formation are the critical concentration for nucleation and the speed of the autocatalytic growth reaction. While these deterministic simulations provided insights into the onset of bands, they cannot address the effect of noise. Two multiscale simulation tools were presented for including stochasticity effects on nucleation.

Dr. P. Hantz presented experimental results on the formation of macroscopic and microscopic precipitation patterns in the $NaOH + CuCl2$, $NaOH+AgNO3$ and $CuCl2+K3[Fe(CN)6]$ reaction-diffusion systems in polivinylalcohol and agarose hydrogel media. The primary, macroscopic patterns patterns in thin gel sheets consisted of precipitate trapezoids with a growing edge, that finally evolved to precipitate triangles. In gel columns, formation of helicoids, target and cardioid-like patterns, as well as emergence of irregular Liesegang banding had been observed. The secondary, microscopic patterns were built up of regular precipitate sheets, that can have a very small wavelength, up to a couple of micrometers. Formation of the secondary patterns, and their most important properties have been modeled as a phase separation described by the Cahn-Hilliard equation with a Gaussian source term.

Prof. B.A. Grzybowski discussed the problem of using spontaneous chemical processes to perform complex tasks in micro and nano fabrication. He described several experimental techniques, as for example playing with the gel thickness, to produce self-organized nano-structures. Applications to Fresnel lenses and creation of substrates for cells orientation were presented. The problem of the limit of smallness of these patterns was also approached.

Dr. I. Daruka examined the dynamics of alloy growth by vapor deposition and bulk diffusion, and predicted a new type of self-organized growth. When material was deposited at a composition unstable against spinodal decomposition, he found three distinct regimes depending on growth rate. Intermediate growth rates lead to spontaneous formation of a superlattice with layers parallel to the surface. Slow growth leads to more complex three-dimensional decomposition. For fast growth, the alloy composition remained uniform near the surface, with a composition wave propagating up from the interface.

4. **European "added-value' and visibility of the Programme**

The large majority of the participants to this workshop were coming from European Community countries. In particular, this workshop allowed to enlarge the scientific collaboration between the Hungarian and Swiss scientists working in this field. Exchange with USA scientists was also very important for promoting EC science.

5. **Programme finance and management**

Besides the financial support of ESF, the organization of this meeting was possible thanks to the support of the University of Geneva. Indeed, it was possible for us to organize this workshop in the Villa Laret, which offers an exceptional environment for such a workshop, at prices a lot cheaper than regular hotel facilities. Moreover the cost of the renting of the Villa (rooms and seminar places) adding to 5440.- CHF, was payed by the University of Geneva.

6. **Publicity**

A WEB site, containing all the talks given during the workshop, as well as additional relevant material, has been created and is opened to anyone interested. See: http://theory.physics.unige.ch/SilsMaria/

7. **Future perspectives**

As a result of this workshop, several collaborations on various new aspects of the problem have already started. This should lead to several publications in journals of international audience.

8. **Appendices:**

LIST OF PARTICIPANTS

- **Dr. Tibor Antal**, Physics Department, Boston University, 590 Commonwealth Avenue, Boston MA 02215, USA.
  ANTAL@bu.edu
- **Dr. Ioana Bena**, Theoretical Physics Department, University of Geneva, 24, Quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland
  Ioana.Bena@physics.unige.ch
- **Dr. Eric Bertin**, Theoretical Physics Department, University of Geneva, 24, Quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland
  Eric.Bertin@physics.unige.ch
- **Nicolas Chevalier**, Ecole Polytechnique Fédérale de Lausanne, Faculté des Sciences de Base, 1015 Lausanne, Switzerland
  nicolas.chevalier@epfl.ch
- **Dr. István Daruka**, Eotvos University, Department of Biological Physics, H-1117 Budapest Pazmany Peter stny. 1/A, Hungary
  idaruka@angel.elte.hu
- **Prof. Michel Droz**, Theoretical Physics Department, University of Geneva, 24, Quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland
  Michel.Droz@physics.unige.ch
- **Prof. Bartosz A. Grzybowski** , Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Rd., Evanston, Illinois 60208, USA
  grzybor@northwestern.edu
- **Dr. Peter Hantz**, Babes-Bolyai University of Kolozsvár, Department of Theoretical Physics, Strada Mihail Kogalniceanu Nr. 1/B, Ro-3400 Cluj, Romania.
  hantz@general.elte.hu
- **Dr. István Lagzi**, Department of Physical Chemistry, Eötvös University, P.O. Box 32, H-1518 Budapest, Hungary
  lagzi@vuk.chem.elte.hu
- **Kirsten Martens**, Theoretical Physics Department, University of Geneva, 24, Quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland
  Kirsten.Martens@physics.unige.ch

- **Péter Pápai**, Institute for Theoretical Physics, Eötvös University, Pázmány sétány 1/a, 1117 Budapest, Hungary
  popep@freemail.hu
- **Prof. Zoltán Rácz**, Hungarian Academy of Sciences and Institute for Theoretical Physics, Eötvös University, Pázmány sétány 1/a, 1117 Budapest, Hungary
  racz@general.elte.hu
- **Prof. Michael Tsapatsis**, Chemical Engineering and Materials Science, University of Minnesota, 151 Amundsen Hall, Minneapolis 55455 0132, USA
  tsapatsi@cems.umn.edu
- **Prof. Dionisios G. Vlachos**, Department of Chemical Engineering and Center for Catalytic Science and Technology, University of Delaware, Newark, Delaware 19716-3110, USA
  vlachos@che.udel.edu

PROGRAM OF THE WORKSHOP

Sunday, 15-th of January 2006

- Arrival and registration at Sils-Maria, Chesa Laret (Switzerland).
- **19:00 H:** Welcome address and dinner.

Monday, 16-th of January 2006

- **09:00 - 10:00 H: Zoltán Rácz**, *Historical overview*
- **10:00 - 11:00 H: István Lagzi**, *Experimental advances in Liesegang patterns generation and control*
- **11:00 - 11:30 H: Coffee break**
- **11:30 - 12:30 H: Michel Droz**, *On the relevance of stochasticity on Liesegang pattern formation*
- **17:00 - 18:30 H: Round-table discussion**, *On different theoretical approaches in studying Liesegang patterns*

Tuesday, 17-th of January 2006

- **09:00 - 9:30 H: Tibor Antal**, *Possible formation of agates by spinodal decomposition*
- **09:30 - 10:00 H: István Lagzi**, *Formation of Liesegang patterns in the presence of an electric field: experimental aspects*

- **10:00 - 11:00 H: Ioana Bena**, *Formation of Liesegang patterns in the presence of an electric field: theoretical aspects and the influence of noise*
- **11:00 - 11:30 H: Coffee break**
- **11:30 - 12:30 H: Michael Tsapatsis**, *Turing versus Liesegang: two different noisy scenarios*
- **16:30 - 17:15 H: Dionisios Vlachos**, *Insights into stochasticity of Liesegang ring formation from nonlinear analysis and multiscale Monte Carlo simulation*
- **17:15 - 17:45 H: Nicolas Chevalier**, *Generalized Langevin description for noisy Liesegang patterns*
- **17:45 - 19:00 H: Round-table discussion**, *Stochasticity: what influence, what level of description ?*

Wednesday, 18-th of January 2006

- **09:00 - 09:45 H: Peter Hantz**, *Pattern formation in a new class of precipitation reaction*
- **09:45 - 10:45 H: Bartosz A. Grzybowski**, *Liesegang ring at micro and nanoscales*
- **10:45 - 11:15 H: Coffee break**
- **11:15 - 12:15 H: Istvan Daruka**, *Self-Assembled Superlattice by Spinodal Decomposition during Growth*
- **17:15 - 18:00 H: Round-table discussion**, *Practical applications of Liesegang patterns: what perspectives ?*
- **18:00 - 18:30 H: Closing remarks and directions for further development**

Thursday, 19-th of January 2006

- Departure