

PATTERN FORMATION IN CONVECTIVE-DIFFUSIVE TRANSPORT WITH REACTION

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It has long been recognized in the chemical engineering profession and in the physical and chemical sciences that material and energy transport play a central role in both the processing of materials and in chemical reactor performance. Much of the theoretical and numerical modeling efforts for transport and reaction, however, has traditionally been restricted to linearized models (*e.g.*, linear rates of reactions, linear irreversible thermodynamics for transport and dissipation, and neglecting convection as a source of nonlinearity).

It is now clear that approaches solely based on linear theories fail to describe many interesting properties of these systems; namely, spatial and temporal organization, the formation of patterns, and the existence of time-dependent, aperiodic states. In fact, the field of nonlinear dynamics (which encompasses a variety of distinct disciplines) has emerged as a

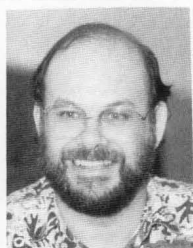
coherent subfield of science in the last decade. In the field of chemical engineering, pioneering efforts in the study of strongly nonlinear reaction-diffusion systems have been pursued by Amundson, Aris, and collaborators.^[1,2]

In general, when a system that is initially placed in a state of thermodynamic equilibrium is forced (and sometimes maintained) away from that state, its evolution can lead to a rich variety of phenomena, quite distinct from systems that are in, or close to, equilibrium. In some cases the system goes through a number of instabilities that lead to chaotic behavior. In others the evolution is through a succession of spatiotemporal patterns that may lead to complicated, albeit stationary, structures.

From a fundamental point of view, the common feature of all these systems is the essential role played by the nonlinearities in the relevant equations of the models. In most cases, the nonlinearities cannot be studied as perturbations around some well-characterized state, but rather they lead to qualitatively different behavior.

Our research focuses on several complementary aspects of problems that encompass convective-diffusive transport (with and without chemical reactions) in a variety of applications of current interest in chemical engineering. Four main areas of research will be reviewed here: 1) chemical and catalytic reacting systems, 2) biological and biochemical interacting systems, 3) convective instabilities in fluids and liquid crystals, and 4) crystal growth from the melt. They share a common methodology based on nonlinear dynamics, but since a general formulation (let alone a general solution) to all of the problems is out of the question at the present time, each research area focuses on the most relevant mechanisms and nonlinearities for the case at hand.

For example, the study of chemical and catalytic reacting systems is conducted in one spatial dimension and with considerably simplified convection. In the study of convective instabilities, only convective and diffusive transport is considered. In the latter case the system is also kept not too far above the



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threshold for the primary convective instability so that the emerging patterns are relatively simple (away from a turbulent state). The study of crystal growth from the melt allows for moving boundaries of arbitrary shape separating the various phases, but neglects convection.

The main goals of the research in all cases are characterization of all possible stationary states of the system (uniform and, more importantly, states which are non-uniform in space), determination of the stability of these stationary states when the parameters that can be controlled experimentally are changed (e.g., the composition of the reactants and the temperature of the reactor), and the calculation of the transient evolution between these stationary states.

HIERARCHICAL APPROACH FOR INTERACTIONS IN CHEMICAL, BIOCHEMICAL, AND BIOLOGICAL SYSTEMS

The overall objective of this part of our research is to investigate the chemical, biological, and biochemical structures and functions that arise from the reaction, diffusion, and convection of molecular species. The emphasis is on applying operator-theoretic techniques and inverse integral formulations to analyze the dynamics of transport and reaction problems with multicomponents and in multidimensional domains of hierarchical structure (shown, for example, schematically in Figure 1). Furthermore, the analysis is aided by group-theoretic methods^[3] and simulations performed in conventional and parallel supercomputers. A very wide range of naturally occurring or synthetically constructed chemical, biological, and biochemical phenomena can be studied within the framework of reaction and convective-diffusive transport.

Direct interactions result from the diffusive or convective coupling through adjoining boundaries between macromolecules, catalyst particles, organelles, and cells. Indirect interactions refer to interactions mediated by intervening fluid regions. Within the framework of the direct and indirect interactions, we seek to analyze the dynamic behavior of heterogeneous populations of macromolecules, catalyst particles, organelles, cells, and multicellular organisms from a hierarchical point of view.

In this hierarchical approach, a domain (e.g., a population of cells or organelles) is considered in terms of sub-domains (e.g., organelles or macromolecules) and the mathematical description accounts for the transport and reaction processes that occur inside these domains, as well as for those occurring

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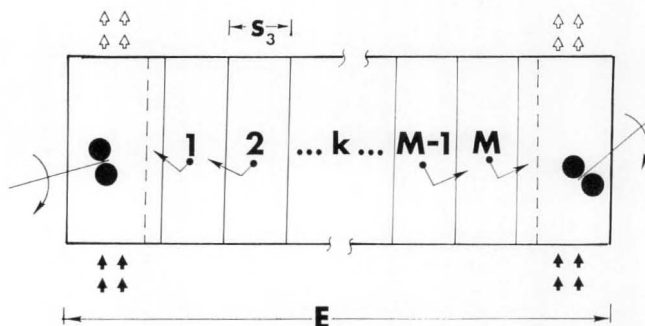


Figure 1. A single domain (which could itself be a subdomain of a larger domain), showing M subdivisions or layers such as the ones discussed in the text, and that corresponds to the model given in Eq. (1).

between the domains throughout the environmental media. This hierarchical description features an assemblage (or superstructure) based on units of "smaller" dimensions which may, in turn, display different degrees (or levels) of description.

This approach (although not entirely new) has not previously been fully exploited to describe the dynamics of biological and biochemical systems. Past efforts have focussed almost completely on extending the Rashevsky-Turing^[4,5] ideas to a variety of situations, but have failed to account for the indirect interactions which have been shown to be as important as the Rashevsky-Turing interactions in generating a rich variety of behaviors in catalytic reactors.^[6] Our research aims at elucidating the roles of both types of interactions.

The operator-theoretic technique allows a full characterization of the dynamic behavior of systems without the complete numerical solution to the governing differential models. This also allows for a coupling of different levels of information in a given system and thus leads to the analysis of the composite system in terms of the simpler systems. Furthermore, the inverse integral formulation allows for a very efficient numerical strategy to solve the complete nonlinear differential model using information provided by the operator formulation.

Chemical and Catalytic Reacting Systems

The field of pattern formation in catalytic reactors has been reviewed recently in the framework of di-

rect and indirect interactions.^[7] The analysis addresses a wide variety of aspects, including the introduction of a hierarchy of reactor models, mathematical techniques, previous work done in the field, and important problems to be investigated in future research efforts.

Direct Interactions • Recently, Locke and Arce^[8,13] have considered one-dimensional diffusion, reaction, and convection in a system of M-layers where the diffusion coefficients, the phase distribution coefficients, reaction rate constants, and convective transport coefficients were allowed to vary from one layer to the next. Coupling between the layers was modeled through equilibrium and flux boundary conditions, where the flux condition included both convection and diffusion. For one-dimensional transport which may include electrophoretic transport in rectangular coordinates, the general molar species continuity equation for the m^{th} layer is

$$\frac{\partial c_m}{\partial t} = -u_m \left(\frac{V}{L} \right)_m \frac{\partial c_m}{\partial x} + D_m \frac{\partial^2 c_m}{\partial x^2} + k_m f_m(c_m) \quad (1)$$

where

c = cross sectional area average molar species concentration

(V/L) = applied voltage per unit length

u = electrophoretic mobility

k = reaction rate constant

D = diffusion coefficient

f = function that contains the concentration and spatial variations of the reaction rate.

In the above model formulation, each layer is assumed to be a different phase, and therefore flux and equilibrium boundary conditions are required at the $M - 1$ interfaces. A general approach would require the addition of a material balance over well-mixed external regions in analogy with the approach of Ramkrishna and Amundson^[9-11] and Parulekar and Ramkrishna.^[12] This would give

$$V_0 \frac{dc_0}{dt} = c_{0f}F_0 - c_0F_0 + a \left[D_1 \left(\frac{\partial c_1}{\partial x} \right)_{x=0^+} - u_1 \left(\frac{V}{L} \right)_1 c_1(x=0^+) \right] \quad (2)$$

$$V_L \frac{dc_L}{dt} = c_{Lf}F_L - c_LF_L - a \left[D_M \left(\frac{\partial c_M}{\partial x} \right)_{x=L^-} - u_M \left(\frac{V}{L} \right)_M c_M(x=L^-) \right] \quad (3)$$

where

V = volume

c = molar concentration

F = volumetric flow into the mixed cells

a = cross sectional area of the membrane surfaces

The subscripts 0 and L represent the two well-mixed external regions, and f represents the feed streams into the two external regions (shown schematically in Figure 1).

The interactions between the different layers in this model can be considered to be direct interactions since the layers are physically and geometrically coupled at their (phase) boundaries. This is in contrast to coupling through indirect interactions that rely on an intermediate phase, such as a bulk fluid, to mediate the interactions between the two systems not physically adjacent. The model described here may be viewed as a prototype to investigate the behavior of cells immersed in a fluid environment. The system will feature an assemblage of domains as shown in Figure 1. The solution to the above models is being undertaken by using operator-theoretic methods.^[8-13] Current work is concerned with performing linear stability analysis for the case of reacting systems coupled with hydrodynamic and electrophoretic transport and diffusion.

Indirect Interactions • In a series of recent studies, Arce and Ramkrishna^[6,7,14] and Ramkrishna and Arce^[15-17] considered transport and reaction problems in catalytic reactors. This research has shown that indirect interactions are as important as the direct interactions in producing a wide variety of very interesting steady state and dynamic behaviors in catalytic reacting systems. Moreover, assemblies of catalyst particles showing only interactions mediated by the fluid medium are able to display a broader class of collaborative phenomena (*i.e.*, behaviors caused by the mutual interactions among the particles) than those found in assemblies showing only direct interactions. Assemblages of catalyst particles with only indirect interactions^[6,7] have uniform steady states that can show collaborative multiplicity and collaborative reversal of instability before breaking the symmetry. This allows the particle to preserve, partially, the stability inside the reactor. Pattern formation is displayed when the assembly of catalyst particles breaks the symmetry of the uniform steady state (see Figure 2).

Collaborative multiplicity and collaborative reversal of stability can also be observed in patterns; however, it is impossible for the assembly to show collaborative reversal of stability. The mathematical analysis that is used to study this multitude of phenomena is based on a theory that exploits the complete understanding of the isolated particle (or cell) in an operator-theoretic framework. Furthermore, the analysis has been pursued further by using sin-

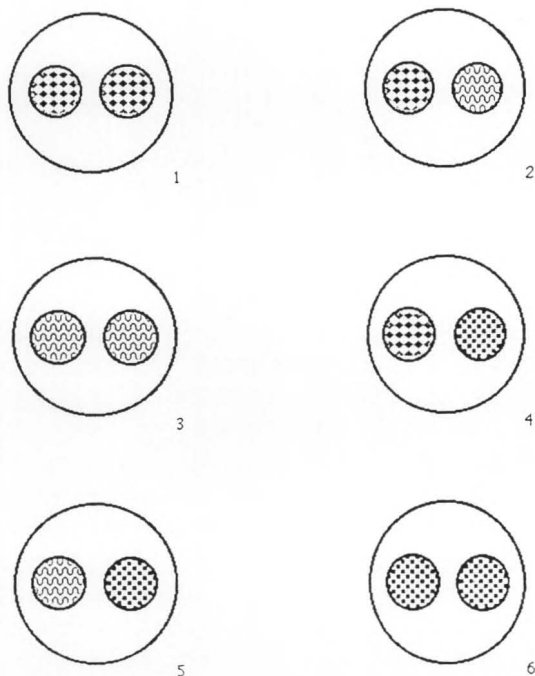


Figure 2. Pattern formation in a well-mixed system showing two individual interacting catalytic particles or cells. Configurations 2, 4, and 5 clearly show the cells in two different steady states. Different steady states inside each cell are schematically depicted with different patterns.

gularity theory and group-operator methods.^[18] In addition, the investigation has been extended to catalytic packed-bed reactors^[16] where indirect interactions among particles (with internal diffusion) are accounted for in an axial diffusive convective fluid.

This investigation is very relevant for describing the behavior of assemblies (or superstructures) of cells in terms of smaller domains (or units). These computations, which include the determination of regions of different behaviors in the parameter space and the identification of all the steady states, can be efficiently performed using an inverse integral formulation.^[19] This inverse integral formulation uses a non-linear integral operator of the Hammerstein-Volterra type with a kernel given by the Green function of the differential problem. The Green function can be computed in terms of the eigenvalues and eigenvectors of the differential linear (transport) operator without the reaction terms. This approach greatly simplifies the computations of steady states for different kinds of non-linear sources. Furthermore, the integral formulation is very suitable for implementation by parallel computer architectures and, therefore, the process of obtaining steady states from complex assemblages composed of several units (cells) can be greatly accelerated.

Biological and Biochemical Interacting Systems

Rapid advances in molecular and cellular biology over the last ten to twenty years have inspired research efforts in the development of molecular and metabolic engineering. In order to advance our abilities to create artificial systems through molecular and metabolic engineering, it is necessary to have a full understanding of the fundamental dynamics of living systems. Dynamical aspects of living systems include subcellular enzymatic reactions for cell growth and reproduction, enzymatic and genetic-level control processes, supracellular morphological development, cell cycles, and evolutionary processes. In addition to developing an understanding of how each separate level of process works, it is necessary to integrate different levels of structure into an overall framework that describes the interactions between these different levels.

The interplay of convective-diffusive transport with reaction yields a wide variety of steady-state and dynamic behavior in biochemical and biological systems. This includes oscillations, wave propagation, multiplicity of uniform stationary states, and (temporal and spatial) pattern formation. Oscillations occur in enzyme reactions, protein synthesis, cell cycles, muscle contraction, and many other cellular and physiological processes.^[20] Oscillations in the glycolytic pathway have been extensively studied both experimentally and theoretically. Most of the efforts in the literature have been devoted primarily to temporal variations and to the determination of stability conditions for non-linear chemical reactions with several components.^[20,21] Generally, in isothermal systems, it is necessary for the chemical reactions to exhibit non-linear kinetics in order for temporal patterns to occur. Higgins^[22] considered the general types of autocatalytic chemical reactions with positive or negative feedback that give rise to oscillatory variations of species concentrations. Some very current applications of temporal pattern formation involves modeling cell cycles via the recently determined key metabolic component cyclin.^[23]

Temporal variation alone, however, since it neglects all geometrical and spatial structure, cannot describe systems where spatial structure is important. Reaction/diffusion problems have been used to consider problems in biological morphological development, biochemical reactions, and population ecology since the ideas introduced by Rashevsky^[4,24] and Turing.^[5] Turing considered reaction and diffusion in a two-component and one-dimensional system.

Scriven and coworkers^[25,26] have developed a general analysis of multicomponent reaction and diffu-

sion in a single region coupled to other regions through indirect transfer expressions.

A large number of phenomena have subsequently been investigated from the perspective^[20,27] of reaction and diffusion within a single phase. What remains to be considered is a comprehensive approach to include systems of multicomponents in multiphase domains and a hierarchy of both direct and indirect interactions. The main goal of our research is the development of such a comprehensive approach.

Biological and biochemical systems can be broken down into a number of functional and structural units (*e.g.*, macromolecules, organelles, cells, tissues, populations, and communities). These units can in turn interact through direct or indirect means in analogy to the chemical reactor and separation models given above. Martin, *et al.*,^[28] have formulated a one-dimensional multiple layer diffusion and convection model for the transport of auxin, a plant hormone, up the stem of a plant. Their model is simpler than the one considered above by Locke and Arce^[8,13] and they have solved it using the cumbersome method of Laplace transform. This methodology gives no indication of the role of the different parameters on the dynamics of the process.

From a more general perspective, Almirantis and Papageorgiou^[29] have considered reaction boundary coupling between multiple layers in a one-dimensional system as a model of intercellular communication. They developed a stability analysis to determine the conditions for pattern formation. Operator theoretic methods can give a much clearer view of the stability criteria through an analysis of the spectrum of the operators. Currently, several geometrical configurations of cell systems are being investigated to determine their steady-state structure, linear stability, and pattern formation characteristics.

CONVECTIVE INSTABILITIES IN FLUIDS AND LIQUID CRYSTALS

The Rayleigh-Bénard instability in simple fluids is a classical fluid instability that has been well characterized both theoretically and experimentally, at least when the Rayleigh number is not too far from the critical Rayleigh number and the aspect ratio of the experimental cell is not too large.^[30,31] Under these conditions, when the system is brought above threshold, a convective instability occurs and the familiar pattern of convective rolls appears.

Although this is a simplified situation, it is very important in our understanding of nonlinear phenomena because the equations describing the sys-

tem are well known and the fluid parameters that appear in them can be measured with sufficient accuracy. Furthermore, experiments can be conducted under well controlled conditions. It therefore provides a good testing ground for many of the ideas of pattern formation in nonlinear systems and an opportunity for detailed and precise comparisons between the predictions given by well defined models and the experiments.

Unfortunately, for most commonly studied fluids the parameters of the fluid are such that systems comprising only a few convective rolls can be studied under normal laboratory conditions. The emerging structures are therefore greatly influenced by the geometry and size of the experimental cell. More recently, however, experiments have been conducted on gases^[32] or on the electro-hydrodynamic instability in nematic liquid crystals.^[33] The scale of the convective rolls in these cases is much smaller than the size of the cell and the issues discussed above are beginning to be studied in greater detail.

We have concentrated on the analysis of the stochastic Swift-Hohenberg equation.^[34] This equation describes the evolution of a scalar field, function of position \vec{r} and time t , that can be written in dimensionless form as

$$\frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[\varepsilon - (\nabla^2 + 1)^2 \right] \psi - \psi^3 + \xi(\vec{r}, t) \quad (4)$$

The quantity ε acts as control parameter. From $\varepsilon < 0$ the solution $y = 0$ is linearly stable, whereas at $\varepsilon = 0$ it becomes unstable to periodic solutions. The stochastic function, $\xi(\vec{r}, t)$, is normally assumed to be gaussian distributed and delta-correlated. This equation has been shown to be equivalent in the long-wavelength, long-time limit the Boussinesq approximation to the hydrodynamic equations that described convection in a simple fluid close to the convective instability. In that case, the stochastic contribution is related to the underlying thermal fluctuations in the fluid. More generally, this equation can be considered as a generic model that describes the formation of spatially periodic structures.

Three main issues are investigated. First, the question of pattern selection, namely which, out of the infinitely many linearly stable stationary states, is dynamically selected from typical initial conditions. Second, convective patterns are effectively one- or two-dimensional. Fluctuations might be expected to destroy the long-range order implicit in the convective pattern. The third issue is the transient dynamics of roll formation. Eq. (4) has been solved numerically on the Connection Machine 2 at SCRI. The

aspect ratio of the systems studied ranges in the hundreds (*i.e.*, several hundred convective rolls), much larger than systems that are experimentally feasible in simple fluids. As discussed above, recent experiments in nematic liquid crystals are beginning to be able to measure thermal fluctuations and to study ratios comparable to the sizes that we have used in our solutions. We expect that our predictions will be tested in these latter systems.

Figure 3 shows an example of our results^[35] with the various structures of the stationary solutions. The configurations shown are typical examples of stationary solutions obtained numerically (only a portion of the system size studied is shown for clarity). At zero amplitude of the fluctuations, $F' = 0$ (states labeled smectic), configurations of rolls possess both positional and orientational long-range order. At low values of F' (states labeled nematic) orientational correlations are long-ranged but the system is positionally disordered. Above the solid line in the figure, the pattern is completely disordered. The location of the solid line in the figure has been found numerically for one value of ϵ . A theoretical analysis that we have developed predicts that it is given by $F' \propto \epsilon$, which is what is plotted in the figure.

Work is now in progress to explore more complex situations with convection in non-Boussinesq sys-

tems, the decay of a long-wavelength instability of periodic patterns known as the Eckhaus instability, extensions to non-gradient systems, etc. The combination of experimental work and detailed numerical solutions to model systems is providing a number of very interesting results on the pattern forming properties of systems that are far from thermodynamic equilibrium.

CRYSTAL GROWTH FROM THE MELT

Crystal growth is but one example in the study of the evolution of the shape of the interfaces that separate domains of various phases during a phase transformation. Although this is one of the most studied examples, the same phenomenology also occurs in all phase transformations in which diffusive transport plays a dominant role in controlling the transformation rate (*i.e.*, diffusion of heat or of some chemical species). Examples are numerous, including the growth of semiconductor crystals from the melt, metal alloy casting, and the growth of protein crystals.

In the more general formulation, one is confronted with a nonlinear free boundary problem for which analytic solutions are rare.^[36] Even in the simpler case in which convective motion in the fluid phase is neglected, limited progress has been achieved in determining stable propagating solutions of the front that separates the different phases. A great deal is known about the existence of steady states and about their stability in systems that undergo some type or morphological instability to a finger-like or cellular structure.^[37] These studies have focused on models of directional or dendritic solidification of single component or multicomponent systems and models of viscous fingering in fluids. Intricate asymptotic analyses have yielded the stationary solutions of various models and, in some cases, the stability condition of such solutions to infinitesimal perturbations.

The approach that we have taken involves recasting the partial differential equations that describe mass diffusion in the phases and the appropriate boundary conditions on the moving interface, by an integrodifferential equation involving the coordinates of the interface alone, or "interface equation."^[38,39] This is accomplished by the introduction of the Green function for the diffusion operator in the various phases. The interface equation is then solved as an initial value problem for a given initial position of the interface. Studies to date have focused on the analysis of the evolution of the interface shape following the instability of a planar front. Recent studies by us and others^[39,40] are focusing on the tran-

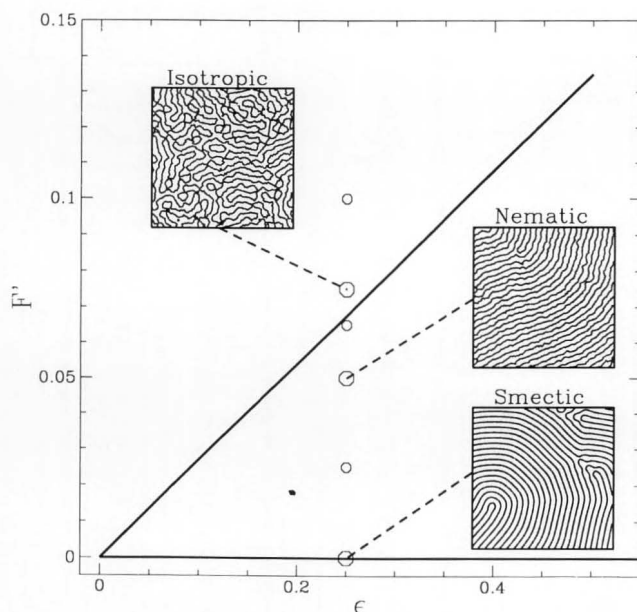


Figure 3. Portions of typical configurations obtained as stationary solutions of Eq. (4). The configurations labeled isotropic, nematic, and smectic correspond to intensities of the fluctuations $F' = 0.075, 0.05$, and 0 , respectively. In all these plots the lines drawn are the lines of $\psi(\vec{r}) = 0$.

sient dynamics of formation of periodic cellular structures (an example of such evolution is shown in Figure 4). Numerical studies reveal the existence of conventional stationary states in addition to traveling wave states or even chaotic structures. This rich behavior can be observed within a surprisingly narrow range of material and control parameters.

CONCLUSION

We have summarized a variety of problems concerning instabilities and the formation of patterns in convective-diffusive systems, with or without chemical reactions, that are being addressed in the chemical engineering department at FAMU/FSU. We focus our attention on novel mathematical approaches that combine analytical techniques and numerical work performed on conventional and parallel supercomputers. The analytic techniques center around operator-theoretic, group-theoretic, and Green function methods to study a variety of nonlinear processes in chemical and catalytic reacting systems, and pattern-forming instabilities in fluids and crystal growth. These methods allow the implementation of powerful numerical algorithms on vector and massively parallel supercomputers, such as those presently available at Florida State University.

ACKNOWLEDGMENT

Part of this work has been conducted in collaboration with other colleagues and former academic advisors. It is a pleasure to acknowledge K. Elder, D. Jasnow, M. Grant, H. Irazoqui, and D. Ramkrishna for very fruitful collaborations. One of us (PA) wants to thank Professor R.G. Carbonell for very interesting discussions and observations. PA and BL ac-

knowledge support from NASA-TRDA-204 and the FAMU/FSU College of Engineering. JV is supported by the Microgravity Science and Applications Division of the NASA under contract No. NAG3-1284 and by the Supercomputer Computations Research Institute, which is partially funded by the U.S. Department of Energy Contract No. DE-FC05-85ER25000.

REFERENCES

1. Aris, R., *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts*, Vols. 1,2, Oxford University Press (1975)
2. Morbidelli, M., A. Varma, and R. Aris, "Reactor Steady State Multiplicity and Stability," in *Chemical Reactor and Reactor Engineering*, J. Carberry and A. Varma, Eds., M. Dekker, New York (1987)
3. Hill, J.M., *Solution of Differential Equations by Means of One Parameter Group*, Pitman, Boston, MA (1982)
4. Rachevsky, N., "An Approach to the Mathematical Biophysics of Biological Self-Regulation and of the Cell Polarity," *Bull. Math. Bioph.*, **2**, 15 (1940)
5. Turing, A.M., "The Chemical Basis of Morphogenesis," *Proc. Roy. Soc. B.*, **237**, 5 (1952)
6. Arce, P., and D. Ramkrishna, "Pattern Formation in Catalytic Reactors: The Role of Fluid Mixing," *AIChE J.*, **37**, 71 (1991)
7. Arce, P., and D. Ramkrishna, "Pattern Formation in Catalytic Reactors, Latin American Applied Research," (in press)
8. Locke, B.R., and P. Arce, "Applications of Self-Adjoint Operators to Electrophoretic Transport, Enzyme Reactions, and Microwave Heating Problems in Composite Media: I. General Formulation," *Chem. Eng. Sci.*, (in press)
9. Ramkrishna, D., and N.R. Amundson, *Linear Operator Methods in Chemical Engineering*, Prentice-Hall, Englewood Cliffs, NJ (1985)
10. Ramkrishna, D., and N.R. Amundson, "Stirred Pots, Tubular Reactors, and Self-Adjoint Operators," *Chem. Eng. Sci.*, **29**, 1353 (1974)
11. Ramkrishna, D., and N.R. Amundson, "Transport in Composite Materials: Reduction to a Self-Adjoint Formalism," *Chem. Eng. Sci.*, **29**, 1457 (1974)
12. Parulekar, S.J., and D. Ramkrishna, "Analysis of Axially Dispersed Systems with General Boundary Conditions: III. Solution for Unmixed and Well-Mixed Appended Sections," *Chem. Eng. Sci.*, **39**, 1599 (1984)
13. Locke, B.R., and P. Arce, "Applications of Self-Adjoint Operators to Electrophoretic Transport, Enzyme Reactions, and Microwave Heating Problems in Composite Media: II. Electrophoretic Transport in Layered Membranes," submitted to *Chem. Eng. Sci.* April (1992)
14. Arce, P., and D. Ramkrishna, "Self-Adjoint Operators of Transport in Interacting Solid-Fluid Systems," *Chem. Eng. Sci.*, **41**, 1539 (1986)
15. Ramkrishna, D., and P. Arce, "Can Pseudo-Homogeneous Reactor Models be Valid?" *Chem. Eng. Sci.*, **44**, 1949 (1989)
16. Ramkrishna, D., and P. Arce, "Some Further Observations on Heterogeneous Catalytic Reactor Models: Pattern Formation in Catalytic Reactors," *Chem. Eng. Sci.*, **46**, 3123 (1991)
17. Ramkrishna, D., and P. Arce, "Self-Adjoint Operators of Transport in Interacting Solid-Fluid Systems II," *Chem. Eng. Sci.*, **43**, 933 (1988)
18. Arce, P.E., "Fluid Mediated Interactions Among Particles in

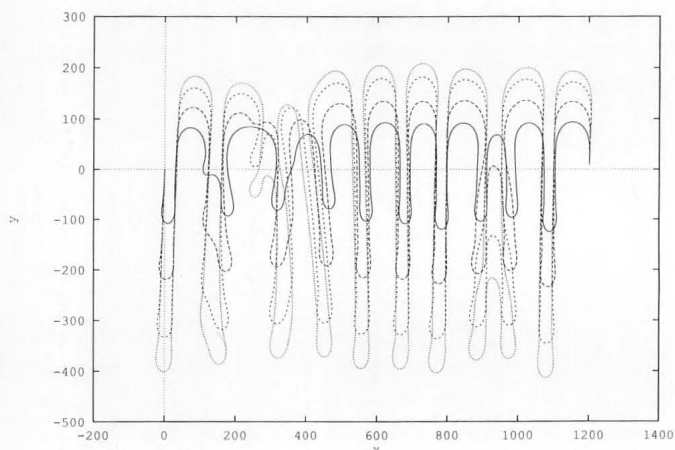


Figure 4. Example of the temporal evolution of an interfacial pattern separating the solid and fluid phases during directional solidification. The lines shown are different times following the instability of a planar front.

- a Catalytic Reactor," PhD Thesis, Purdue University (1990)
19. Arce, P., B.R. Locke, and B. Trigatti, "Transport and Reaction in Laminar Regime: A Boundary and Integral-Spectral Equation Approach," preprint (1992)
 20. Peacocke, A.R., *An Introduction to the Physical Chemistry of Biological Organization*, Oxford (1989)
 21. Nicolis, G., and I. Prigogine, *Self-Organization in Nonequilibrium Systems From Dissipative Structures to Order Through Fluctuations*, John Wiley and Sons, New York (1977)
 22. Higgins, J., *I. & E.C.*, **59**, 19 (1967)
 23. Norel, R., and Z. Agur, "A Model for the Adjustment of the Mitotic Clock by Cyclin and MPF Levels, *Science*, **251**, 1076 (1991)
 24. Rachevsky, N., *Mathematical Biophysics*, University of Chicago Press, Chicago, IL (1948)
 25. Gmitro, J.L., and L.E. Scriven, "A Physicochemical Basis for Pattern and Rhythm," in *Intracellular Transport*, K.B. Warren, ed., Academic Press (1966)
 26. Othmer, H.G., and L.E. Scriven, "Interactions of Reaction and Diffusion in Open Systems," *I. & E. C. Fund.*, **8**, 302 (1969)
 27. Britton, N.F., *Reaction-Diffusion Equations and Their Applications to Biology*, Academic Press, London (1986)
 28. Martin, M.H., M.H.M. Goldsmith, and T.H. Goldsmith, "On Polar Auxin Transport in Plant Cells," *J. Math. Biol.*, **28**,

- 197 (1990)
29. Almirantis, Y., and S. Papageorgiou, "Cross-Diffusion Effects on Chemical and Biological Pattern Formation," *J. Theoret. Biol.*, **151**, 289 (1991)
30. Newell, A.C., in *Lectures in the Science of Complexity*, edited by D.L. Stein, Addison-Wesley, Redwood, p. 107 (1989)
31. Ahlers, G., in *Lectures in the Science of Complexity*, edited by D.L. Stein, Addison-Wesley, Redwood, p. 175 (1989)
32. Bodenschatz, E., J.R. de Bruyn, G. Ahlers, and D.S. Cannell, *Phys. Rev. Lett.*, **67**, 3078 (1991)
33. Rehberg, I., S. Rasenat, M. de la Torre, W. Schöpf, F. Hörner, G. Ahlers, and H.R. Brand, *Phys. Rev. Lett.*, **67**, 596 (1991)
34. Swift, J., and P.C. Hohenberg, *Phys. Rev. A.*, **15**, 319 (1977)
35. Elder, K.R., J. Viñals, and M. Grant, *Phys. Rev. Lett.*, **68**, 3024 (1992)
36. Pelce, P., *Dynamics of Curved Fronts*, Academic Press, New York (1988)
37. Mullins, W.W., and R.F. Sekerka, *J. Appl. Phys.*, **34**, 323 (1963)
38. Caroli, B., C. Caroli, and B. Roulet, *J. Physique*, **48**, 1423 (1987)
39. Viñals, J., and D. Jasnow, in *Computer Simulations in Condensed Matter Physics IV*, edited by D.P. Landau, et al., Springer-Verlag, New York (1992)
40. Bennett, M.J., K. Tsiveriotis, and R.A. Brown, *Phys. Rev. B.*, **45**, 9562 (1992) □

NEURAL NETWORKS

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obtain the correct ordering for both the manipulated and the controlled variables, the engineer requires a great deal of process understanding.

An alternative methodology under study in the IPS Lab is very ambitious in that it seeks to pose the multivariable control design with objective prioritization as a multilevel optimization problem with binary variables. Binary variables can be visualized as on-off keys that switch controller and economic objectives and constraints on or off as appropriate to achieve the desired prioritization.

FUTURE DIRECTIONS

As our research in neural networks, optimization, and process control matures, the focus in the IPS Lab is shifting to demonstration of the methods in collaboration with local industry. One project has begun which seeks to use neural network-based methods for controlling the quality of parts produced from an injection molding process. A second project is employing similar methods for controlling the incineration of hazardous wastes. A third effort is exploring the use of neural networks for optimizing the efficiency of combustion of pulverized coal.

Such real-world implementations are important in process control research. When developments are restricted to simulated processes, the complete process character can be specified by the same researcher

who is responsible for the control system developments. Real plants, on the other hand, have a process character that is specified by nature, thereby truly testing the effectiveness of new developments.

Perhaps the most important aspect, however, is that real-world demonstrations permit developments to be tested by the ultimate user of the technology—the industrial practitioner. It is only when the technology is in the practitioner's hands that laboratory developments receive the critical evaluations which help guide subsequent improvements and refinements, and define new avenues for fruitful research.

REFERENCES

1. Achenie, L.E., and L.T. Biegler, "A Superstructure Based Approach to Chemical Reactor Network Synthesis," *Comp. Chem. Eng.*, **14**, 23 (1990)
2. Cooper, D.J., L. Megan, and R.F. Hinde, Jr., "Comparing Two Neural Networks for Pattern Based Adaptive Process Control," *AIChE J.*, **38**, 41 (1992)
3. Vegeais, J.A., D.B. Garrison, and L.E.K. Achenie, "Parallel NCUBE Implementation of a Layered, Feed-Forward Neural Network," AIChE meeting, Los Angeles, CA; Nov. (1991)
4. Cooper, D.J., L. Megan, and R.F. Hinde, Jr., "Disturbance Pattern Classification and Neuro-Adaptive Control," *IEEE Cont. Sys.*, **12**, 42 (1992)
5. Hinde, R.F., Jr., and D.J. Cooper, "Adaptive Process Control Using Pattern-Based Performance Feedback," *J. of Proc. Cont.*, **1**, 228 (1991)
6. Cooper, D.J., and A.M. Lalonde, "Process Behavior Diagnostics and Adaptive Process Control," *Computers and Chem. Eng.*, **14**, 541 (1990)
7. Prett, D.M., C.E. Garcia, and B.L. Ramaker, *The Second Shell Process Control Workshop*, Butterworths (1990) □