A. ***This is a Doctoral Thesis Project***

Characterization of spatiotemporal patterns:
This thesis will combine both experimental and theoretical techniques in the generation of spatiotemporal patterns and their characterizations. Students who would like to tackle this project should be prepared to learn programming in C++ or equivalent. Most of the work will be done on our Silicon Graphics Fuel Workstation in Lab 357. It is reasonably fast and has superior graphics capabilities. On-going research (Edward Chikwana's project, for example) will generate several types of spatiotemporal patterns, and the student involved with this project should be able to reproduce such patterns and subsequently characterize them. An algorithmn for the generation of these patterns will be part of this thesis

Background: Space-time characterization of spatiotemporal patterns is not as well understood as temporal chaos. Spatiotemporally chaotic patterns exhibit very poor correlation in both space and time. They are, however, ubiquitous in reacting and diffusing chemical flows, convective transport of heat, and in charge transport in semiconductors[1]. We have always characterized spatiotemporal inhomogeneities using two-point correlation functions and dimension correlation lengths[2]. Unfortunately, averages of spatiotemporal chaos (SC) in experiments (ours included) and in simulations have demonstrated that the dynamics are strongly affected by boundaries[3]. We intend to utilize a recently discovered method for characterizing SC that can avoid the strong influences of boundaries: the *Karhunen-Loeve decomposition* (KLD)[4]. The KLD correlation length has been used to characterize extensive chaos locally in small subsystems of the larger dynamics based on the extensive growth of the KLD dimension. Since KLD correlation length is defined in a subsystem, it allows a dynamical measure of nonuniformities in space. The KLD is a classical statistical method which represents complex space-time data $U(t_i, \mathbf{x}_j)$ by a minimum number of space and time eigenmodes. This decomposition proceeds by organizing the discretized video-imaging data into a space-time matrix:

$$A_{ij} = U(t_i, \mathbf{x}_j) - <U(t_i, \mathbf{x}_j)>$$

where $<U(t_i, \mathbf{x}_j)>$ is the space-time average of the field $U(t_i, \mathbf{x}_j)$. The space-time matrix is of dimension T x X where T is the number of observation times t_i and X is the number of observation sites $\mathbf{x}_j$ within the subsystem. A singular value decomposition of this matrix provides an optimal 2-norm variance decomposition of the space-time matrix, **A**, such that the expansion of A_{ij} in terms the spatial eigenmodes and normalized mode amplitudes has a minimum squared error for a fixed number of expansion terms[4]. The weight of the expansion terms is given by their variance, which corresponds to the eigenvalues of the positive semidefinite covariance matrix $\mathbf{A}^T \mathbf{A}$. The KLD correlation length, ξ_{KLD} is a sensitive measure of the spatial dynamical inhomogeneities. It reveals substantial spatial nonuniformity of the dynamics at boundaries and can also detect slow spatial variations in system parameters. The length scale becomes an independent quantity which behaves similarly to the dimension correlation length but has a different parametric dependence than the two-point correlation length ξ_2 in coupled map lattices and convection data. The KLD correlation length has been successfully applied to the reaction-diffusion model as well as the Kuramoto-Shivashinsky equation[5]. All video imaging protocols now available can implement KLD.

References.
1.   Mikhailov, A. S.; Loskutov, A. Y. *Foundations of Synergetics Vol II*, 2nd edition, Springer, Berlin, 1996.
2.   O'Hern, C. S.; Egolf, D. A.; Greenside, H. S. 'Lyapunov spectral analysis of a nonequilibrium Ising-like transtion' *Phys. Rev. E.* **1996**, 53, 3373 - 3386.
3.   Eguiluz, V. M., Altrom, P.; Hernandez-Garcia, E.; Piro, O. 'Average patterns of spatiotemporal chaos' *Phys. Rev. E.* **1999**, 59, 2822 - 2825.
4.   Egolf, D. A.; Melnikov, I. V.; Bodenschartz, E. 'Importance of local pattern properties in spiral deffect chaos' *Phys. Rev. Lett.* **1998**, 80, 3228 - 3238.
5.   Meixner, M.; Zoldi, S. M.; Bose, S.; Scholl, E. 'Karhunen-Loeve local characterization of spatiotemporal chaos in a reaction-diffusion system' *Phys. Rev. E* **2000**, 61, 1382 - 1385.

(See the sketched figure below)
This project is difficult but a whole lot of fun!!! The student will be going into unchartered waters with respect to convective instabilities. The proposal will take advantage of an excitable chemical reaction to produce a dynamic interface. The student's research will be based on this interface: front speeds, chemical wavelengths, surface tension and other convective phenomena.

Hele-Shaw cell experiments: fingering and Rayleigh-Taylor Instabilities
Hydrodynamic deformations of interfaces between reactive fluids induced by chemical reactions at the wave front are commonplace in petroleum and pharmaceutical engineering[1]. Studies on these wave fronts have been very helpful in optimizing crude oil extractions in minimally depleted oil wells. The spatiotemporal and wave front dynamics that result from the interplay between hydrodynamics and chemical reactions can introduce a complex interplay between heat effects, viscosity, surface tension, and density variations. It is precisely the emergence of these numerous and complex effects that discouraged further studies into convective instabilities. In this thesis proposal, we feel a realistic model for such interfaces is well within reach, and that this model, no matter how simple, can be very useful in petroleum engineering and ocean layering dynamics. We have a very unique system that can be studied in vertical geometries: an exothermic autocatalytic chemical reaction[2]. Preliminary experiments in our laboratories have shown fingering in descending waves, double-diffusive convection, and Rayleigh-Taylor instabilities[3].
Double-diffusive convection: Double-diffusive convection (DDC) and the associated visually dramatic salt fingers are a very common natural phenomenon in the ocean and arise primarily as a result of the difference between thermal and saline diffusivities and the effective range of heat conduction[4-5]. The chlorite-thiourea reaction does exhibit DDC, but this phenomenon has not been studied further. The main prerequisite for DDC in our chemical system is a positive isothermal density difference for descending waves (i. e. product solution, on top, is heavier than the reactant solution, below). A negative isothermal density change should produce a planar front for descending waves, and pluming and fingering for ascending waves. In the chlorite-thiourea reaction, the isothermal density change, $\Delta\rho$ is $+2.8 \times 10^{-3}$ g cm^{-3} (ref. 6).
Rayleigh-Taylor instabilities: Rayleigh-Taylor instability (RTI) occurs at the interface of two fluids of different densities whenever the heavier fluid is decelerated by the lighter fluid[7]. This is especially so if density and pressure gradients are in opposite directions and vorticity, deposited at the interface through baroclinic torque, will cause the fluids to interpenetrate and mix. RTI presents a serious design challenge for inertial confinement fusion (ICF) capsules, where high density shells are decelerated by low density fuel[8]. This may lead to breakup of the shell prior to ignition. Isothermal, buoyantly unstable, autocatalytic chemical fronts are one such model system which can be used as a prototype to study the effects of coupling between chemical reactions and RTI-type of hydrodynamic instabilities[9]. If, as in our chemical systems, the result of a chemical front is to separate a denser solution over a lighter one; then the front can lose stability due to buoyancy effects which include cellular fingering deformations of the front. Such an instability has been observed for the iodate-arsenious acid reaction (IAA)[10]. Numerous experimental and theoretical studies have been done on this system in HS geometries[11]. The HS cell is basically two glass plates separated by a small gap width. Our reaction systems in this proposal are highly exothermic and so we expect dynamics that would differ greatly from the IAA system which has negligible heat effects.
Experimental setup: Our basic HS cell is 145 mm wide, and 165 mm deep with variable thicknesses that range from 1.5 mm to 3 mm. The cover for the HS cell also carries two electrodes, one on either side of it, for electrically triggering the wave. The basic geometry is shown in Figure 6. The whole HS cell is enclosed in a glove box thermostated at 25 $^{\circ}$C with minimum air drafts to reduce heat loss to the surroundings.   The wave will be observed in vertical cells and in cells slightly inclined off the vertical to examine the effect of gravity. Preliminary experiments have shown that there is an optimum temperature jump at the interface that can generate fingering, and it lies between 1.8 and 2.8 K. Higher temperature changes gave planar fronts with no fingering or DDC. The expansion coefficient of the product reaction renders it temporarily lighter than the reactants due to its elevated temperature over the reactants[12]. Any deformity at the wave front, however, as expected, will produce extensive viscous fingering instabilities with an indeterminate wavelength. During the interplay of thermal effects and density variations, there is a

specific temperature range where cellular patterns will emerge. This can allow us to experimentally determine the dispersion relation[13] as has been done for the IAA system. Generally, downward propagating waves will be buoyantly unstable.

Data Collection: The geometry of the cell ensures that most of the interesting data is based on a pseudo-two-dimensional set up. A CCD camera is placed alongside the HS cell broadwise against a neutral background. Data collection will include wave propagation velocities as functions of: gap width, initial reagent concentrations, solution viscosity (soluble starch), and tilt angle of the HS cell from the vertical. In particular, for a given set of initial conditions, how does the instability range respond with tilt angle? We expect the characteristic wavelength of the front to be strongly influenced by initial conditions, and that a slight curvature in the initial front profile will lead to larger Fourier amplitudes for the first few modes, resulting in smaller growth rates than expected. The spacing of the fingers (wavelength, λ), exclusive of the ends effects, can be plotted as a function of gap width of the HS cell. This is very important because these data will give us a range of gap width suitable for the evaluation of a dispersion relation. Very small gap widths do not produce fingers (strong boundary effects) and larger gap widths give fingers that overtake and interact with one another[14]. Linear analysis theory for convection-driven fingering gives a dimensionless control parameter, S, that controls the instability and is given by:[15]

$$S = \delta g d^3 / \nu D_c$$ where g is gravity acceleration, d is cell thickness, ν kinematic viscosity, and D_c the diffusion constant of the autocatalyst. The density change across the front is due to a combination of concentration changes and thermal expansion and is given in its non-dimensional form as: $\delta = (\rho_r/\rho_p) - 1$ where ρ_r and ρ_p are the densities of the reactants and the products respectively. Linear stability theory predicts, for an unbounded XZ plane, that fronts are unstable to convection rolls within a band of wavenumbers, q, with $0 \leq q \leq q_c(S)$ for $S > 0$. The critical wavenumber, $q_c \to 0$ as $S \to 0$. This linear theory will give us a starting point in our data collection. Does the strongly exothermic reaction front subscribe to this theory which was basically derived for fronts with minimal temperature effects? From our data we should be able to derive a plot for S vs the dimensionless wave vector of the instability.

To evaluate our dispersion relation, the wave front is tracked down the HS cell and subjected to a one-dimensional Fourier transform. An exponential function;

$$A(k, t) = A_0(k) \exp\{n(k)t\}$$ is fitted to the time evolution of the lowest modes, giving a growth rate n(k) for each of those modes. This can easily be achieved in the region of viscous fingering shielding in which no single finger will race too far ahead of the rest. Without any tip-splitting, the pattern evolution should undergo a continuous increase in main wavelength related to a shrinking band of unstable wavenumbers. The dispersion relation will be a plot of the wavenumber $(1/\lambda)$ vs growth rate n (s^{-1}).
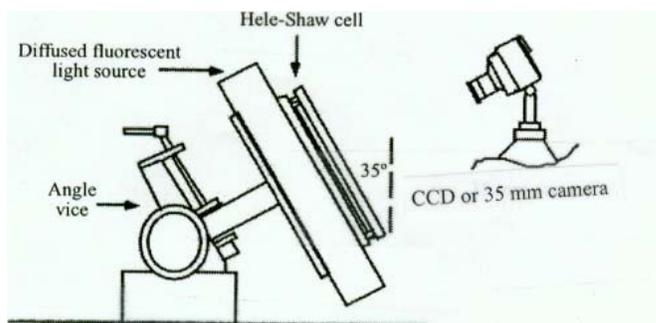

Figure 6. Hele-Shaw set up which can alter angle to the vertical. Recording device could be a still camera or a CCD camera.
(see *J. Fluid Mech*, 462, 161-183; Pringle and Glass)

Some specific experiments and useful techniques

(a) Control of stochastic triggering: Although the chemical systems being utilized can trigger lateral instabilities on their own; it has been found that induction times are extremely stochastic with, at times, the same initial concentrations triggering at very different times[16]. Triggering is controlled (among other parameters), by induction time and interfacial effects. Reactions with shorter induction times produce fast-moving waves, and produce spatiotemporal patterns of a shorter intrinsic length scale. Thus we intend to

trigger our reaction solutions exactly 60 s after mixing. 60 s is enough time to allow all physical ripples on the solution interface to disappear. *(b) Determination of temperature profile and spatial extent of reaction zone*. Ultimately, the temperature difference between the hot reacted region and the cold unreacted region is the most important parameter in driving the traveling wave as well as in developing spatiotemporal patterns. Our experiments need to determine the width over which the temperature difference, ΔT, subtends. The value of $\Delta T/\Delta x$ will determine the strength of thermocapillary forces which seem to be the most dominant in the horizontal plane. Our preliminary studies indicate that ΔT exists over a distance of not more than 3 mm. The front is thus very sharp and distinct. Thermocolor imaging should be useful here in determining width of the reaction zone. Acid-base indicators have been successfully employed to determine extent of reaction and hence the width of the reaction zones. The intensity of the indicator, especially methyl red, can be used to determine the extent of reaction if indicator change occurs around that pH range.

General References
1.   Huppert, H. E. 'The intrusion of fluid mechanics into geology' *J. Fluid Mech.* **1986**, 173, 557 - 594.
2.   Previous Hele-Shaw geometry research work has focused on the IAA system with negligible heat effects which could easily be dissipated away within the experimental apparatus.
3.   Martin, J.; Rakotomalala, N.; Salin, D.; Bockmann, M. 'Buoyancy-driven instability of an autocatalytic reaction front in a Hele-Shaw cell' *Phys. Rev. E* **2002**, 65, 0151605 (1 - 6).
4.   Schmitt, R. W. 'Why didn't Rayleigh discover salt fingers?' in *Double-Diffusive Convection*, American Geophysical Union, Geophysical Monograph 94, Brandt, A.; Fernando, H. J. S. eds. (1995).
5.   Schmitt, R. W. 'Double-diffusion in oceanography' *Ann. Rev. Fluid Mech.* **1994**, 26, 255 - 285.
6.   Chinake, C. R.; Simoyi, R. H. 'Fingering patterns and other interesting dynamics in the chemical wave generated by the chlorite-thiourea reaction' *J. Phys. Chem.* **1994**, 98, 4012 - 4019.
7.   Chandrasekhar, S. *Hydrodynamic and Hydromagnetic stability* Oxford University Press, (1961).
8.   Inogamov, N. A. 'Reduction of increment of Rayleigh-Taylor instability in specially designed multilayer inertial-confinement-fusion targets' *Phys. Rev. E.* **1998**, 57, 3352 - 3362.
9.   Carey, M. R.; Morris, S. W.; Kolodner, P. 'Convective fingering of an autocatalytic reaction front' *Phys. Rev. E* **1996**, 53, 6012 - 6015.
10.   Yang, J.; D'Onofrio, A.; Kalliadasis, S.; De Wit, A. 'Rayleigh-Taylor instability of reaction-diffusion acidity fronts' *J. Chem. Phys.* **2002**, 117, 9395 - 9408.
11.   Graf, F.; Meiburg, E.; Hartel, C. 'Density-driven instabilities of miscible fluids in a Hele-Shaw cell: linear stability analysis of the three-dimensional Stokes equations' *J. Fluid Mech.* **2002**, 451, 261 - 282.
12.   Chinake, C. R. Simoyi, R. H. 'Experimental studies of spatial patterns produced by diffusion-convection-reaction systems' *J. Chem. Soc. Faraday Trans.* **1997**, 93, 1345 - 1350.
13.   Carrilo, Ll.; Magdaleno, F. X.; Casademunt, J.; Ortin, J. 'Experiments in a rotating Hele-Shaw cell' *Phys. Rev. E* **1996**, 54, 6260 - 6267.
14.   Bockmann, M.; Muller, S. C. 'Growth rates of the buoyancy-driven instability of an autocatalytic reaction front in a narrow cell' *Phy, Rev. Lett.* **2000**, 85, 2506 - 2509.
15.   Wu, Y.; Vasquez, D. A.; Edwards, B. F.; Wilder, J. W. 'Transitions between convective patterns in chemical fronts' *Phys. Rev. E* **1995**, 52, 6175 - 6182.
16.   Khan, A. S. H.; Higginson, W. C. E. 'Kinetics of the reaction between chlorite and hexacyanoferrate(II) in aqueous solution; evidence for an interfacial redox reaction' *J. Chem. Soc. Dalton Trans. Inorganic Chemistry*, **1981**, 2537 - 2543.