**FUNDAMENTAL STUDIES OF FLUID MECHANICS:
STABILITY IN POROUS MEDIA**

DE-FG03-87ER13673

FINAL REPORT

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Introduction

This is the final report for our grant "Fundamental Studies of Fluid Mechanics: Stability in Porous Media", DE-FG03-87ER13673. This grant to Stanford University expired on 09/14/2003 and was transferred to UCSB and given a new grant number, DE-FG03-01ER15134 when the PI moved from Stanford to UCSB in 2001. Thus, the work on this grant continued in an uninterrupted fashion from its beginning until it was completed in December, 2004. Accordingly, this final report is in most respects identical to the final report for the UCSB grant, DE-FG03-01ER15134.

Our work has been concerned with theoretical, computational and experimental studies of a variety of flow and transport problems that are of generic interest and applicability in energy-related and energy-intensive processes. These include the following.

(i) Problems associated with oil recovery: the global economy continues to be dependent on the stable and predictable supply of oil and fossil fuels. This will remain the case for the near term, as current estimates are that world production of oil will peak between 2025 and 2100, depending on assumptions regarding growth. Most of these resources reside in porous rocks and other naturally occurring media. Studies of flow-induced instabilities are relevant to the areas of secondary and enhanced oil recovery.

(ii) Small scale and Stokes flows: flows in microgeometries and involving interfaces and surfactants are of interest in a myriad of energy-related contexts. These include: pore-level modeling of the fundamental processes by which oil held in porous materials is mobilized and produced; heating and cooling energy cycles involving significant expenditure of energy in conditioning of human environments, heat pipes, and compact heat exchangers; and energy efficiency in large scale separation processes such as distillation and absorption - processes that underlie the chemical process industries.

(iii) Coating flows: these are of interest in information technologies, including the manufacture of integrated circuits and data storage and retrieval devices. It is estimated that 50-70% of the starting raw materials and intermediate devices in information technology processes must be discarded as a result of imperfections and failure to meet specifications. These in turn are often the result of the inability to control fluid-mechanical processes and flow instabilities.

Our work over the grant period is primarily fundamental in nature. We are interested in establishing general principles and behaviors that relate to a variety of processes in a variety of contexts. Our work has focused and will continue to focus on fluid mechanical phenomena that are of interest in energy-related technologies, with an emphasis on interfacial flows.

This progress report covers the period, April 2001– April 2005 in detail. Work accomplished earlier than that has already been reported as part of the continuation requests. Only the main achievements are summarized. More detail is contained in the various journal articles published during the last grant period, which have been conveyed to the DOE grant monitor under separate cover.

Students Supervised

We have worked with a number of graduate students, postdoctoral fellows, and collaborators.

PhD Students

Dr. Ali Mazouchi - Dr. Mazouchi completed his PhD in Mechanical Engineering at Stanford University in Fall, 2002. He is currently working at Tavanza Inc., Santa Clara CA.

Dr. Thomas Ward - Dr Ward completed his PhD in Mechanical Engineering at UCSB in Fall, 2003 and is currently a postdoctoral fellow at Harvard University.

Ms. Carolyn Gramlich - Ms. Gramlich is a fourth year PhD student in Mechanical Engineering at UCSB. She passed her qualifying examination in Fall, 2004 and will complete her degree by Fall, 2005.

Postdoctoral Fellows

Dr. Volodia Ajaev - Dr. Ajaev received his PhD in Applied Mathematics from Northwestern Univ. He joined the group in Fall, 2000 and left in Spring, 2001 to take up an academic position in the Math Department at SMU, Dallas.

Dr. Juan Fernandez - Dr. Fernandez received his PhD in Physics at ESPCI, Paris. He joined the group in 2001 and left UCSB in Summer, 2003 to take up an academic position in Sevilla, Spain.

Dr. Rouslan Krechetnikov - Dr. Krechetnikov received his PhD in Mechanical Engineering at Univ. of Notre Dame. He joined the group approximately two years ago and will leave in August, 2004 to take up a postdoc in Math at Caltech.

Collaborator

Prof. Serafim Kalliadasis, Chemical Engineering Department, University of Leeds, Leeds, UK. Prof. Kalliadasis co-authored two papers with the PI, the work for which was completed during reciprocal visits between them.

Published Papers Acknowledging DOE support (2000-present)

Papers in print

1. "Thermocapillary Migration of Long Bubbles in Cylindrical Capillary Tubes", with Ali Mazouchi, *Physics of Fluids*, 12, 542 (2000).
2. "Steady Free-Surface Thin Film Flows over Topography", with S. Kalliadasis & C. Bierlarz, *Physics of Fluids*, 12, 1889 (2000).
3. "Thermocapillary Migration of Long Bubbles in Polygonal Tubes. Part I: Theory", with A. Mazouchi, *Phys. Fluids* 13, 1594 (2001).
4. "Steady Vapor Bubbles in Rectangular Microchannels", with V. Ajaev, *J. Colloid Interface Sci.* 240, 259 (2001).
5. "Free Surface Stokes Flow over Topography", with Ali Mazouchi, *Phys. Fluids* 13, 2751 (2001).
6. "Stability of Free-Surface Thin Film Flows over Topography", with S. Kalliadasis, *J. Fluid Mech.* 448, 387 (2001).
7. "Three-dimensional Steady Vapor Bubbles in Rectangular Microchannels", with V. Ajaev, *J. Colloid Interface Sci.* 144, 180 (2001).
8. "Electrohydrodynamically Driven Chaotic Mixing in a Translating Drop", with Thomas Ward, *Phys. Fluids*, 13, 3521 (2001).

9. "Birefringent Strands in Polymer Flow in a Co-Rotating Two-Roll Mill", with I. Lee, N. Kapur, P.H. Gaskell, & M. D. Savage, *J. Non-Newtonian Fluid Mechanics*, 104, 33 (2002).
10. "Optimal Leveling of Flow over Topography by Marangoni Stresses", with C. Gramlich, S. Kalliadasis, & C. Messer, *Phys. Fluids* 14, 1841 (2002).
11. "Dynamic Response of Geometrically Constrained Vapor Bubbles", with V. Ajaev & S.J.S. Morris, *J. Colloid Interface Sci.* 254, 346 (2002).
12. "Thermocapillary Migration of Long Bubbles in Polygonal Tubes. Part II: Experiments", with E. Lajeunesse, *Phys. Fluids* 15, 308 (2003).
13. "Viscous Fingering with Chemical Reaction: Effect of in-situ Production of Surfactants", with J. Fernandez, *J. Fluid Mech.* 480, 267 (2003).
14. "Electrohydrodynamically driven chaotic mixing in a translating drop. Part II. Experiments", with T. Ward, *Phys. Fluids* 15, 2987 (2003).
15. "On a new surfactant-driven fingering phenomenon in a Hele-Shaw cell", with R. Krechetnikov, *J. Fluid Mech.* 509, 103 (2004).
16. "Time-Dependent Free Surface Stokes Flows with a Moving Contact Line, I. Flow over Plane Surfaces", with Ali Mazouchi & C. M. Gramlich, *Phys. Fluids* 16, 1647 (2004).
17. "Time-Dependent Free Surface Stokes Flows with a Moving Contact Line, II. Flow over Wedges and Trenches", with C. M. Gramlich & Ali Mazouchi, *Phys. Fluids* 16, 1660 (2004).
18. "Chemical reaction-driven tip-streaming phenomena in a pendant drop", with Juan Fernandez, *Phys. Fluids* 16, 2548 (2004).
19. "On physical mechanisms in chemical reaction-driven tip-streaming", with R. Krechetnikov, *Phys. Fluids* 16, 2556 (2004).

Papers in press

20. "Experimental study of a surfactant-driven fingering phenomenon in a Hele-Shaw cell", with Juan Fernandez and Rouslan Krechetnikov, to appear in *J. Fluid Mech.* (2005).

Papers submitted

21. "Chaotic streamlines in a translating drop with a uniform electric field", with Thomas Ward, submitted to *J. Fluid Mech.* (2003): favorably reviewed and under revision.
22. "Domain size and surfactant effects in the Landau-Levich problem", with Rouslan Krechetnikov, submitted to *J. Fluid Mech.* (2004).
23. "Experimental study of dip-coating over rough surfaces and with surfactant solutions", with Rouslan Krechetnikov, submitted to *Phys. Fluids* (2004)

Invited Talks, Seminars, and Presentations

Major Invited Talks and Plenary Lectures - G. M. Homsy

"Interfacial Flows in Microgeometries and Microgravity", Invited Talk, Gordon Conference, Gravitational Effects in Physico-Chemical Systems, Colby-Sawyer College, NH: July, 2001

"Some Recent Problems in Interfacial Flows", Invited Keynote Talk, AIChE meeting, Reno, NV: November, 2001.

"Some Stokes Flow Problems in Coating: Beyond Lubrication Theory", 4th European Coating Symposium, Brussels

"Some Interfacial Flow Problems", Talks given in conjunction with G. M. Homsy being the Midwest Mechanics Speaker for 2001-2002 at Mechanical/Aerospace Engineering, IIT, Chicago; Aerospace Engineering, Notre Dame; Mechanical Engineering, Univ. Michigan; and Mechanics and Aerospace Engineering, Univ. Minnesota

"Novel Marangoni Flows", invited talk at "Microfluidics in the 21st Century", IPAM, UCLA: November 2002.

"Novel Marangoni Flows", invited distinguished speaker, 10th Enzo Levi Seminar, UNAM, Mexico City: March 2003.

"Stokes flow over topography: how contact lines get in and out of etch pits", European Coating Flow Symposium, Fribourg Switzerland, September 2003.

Other Presentations

The Principal Investigator and his students have given many other presentations of DOE-sponsored work over the last grant period. These include departmental seminars by the PI at Caltech, UCLA, UCSD, Yale, ESPCI (Paris), Univ. Florida, Stanford, MIT, Univ. Minnesota, Princeton, University of Chicago, and over 20 contributed papers at annual meetings of the AIChE and the Division of Fluid Dynamics of the APS. These will not be listed separately in the interests of brevity.

Research Summaries

Here we give summaries of the results obtained over the last grant period. Citations in square brackets refer to the list of papers given above. Our work on viscoelastic flow [9] is not described here. Full details of all the work are given in the papers themselves.

Viscous fingering in the presence of surfactants and chemical reactions

Viscous fingering is a well-known phenomenon, involving the unstable propagation of a less viscous fluid into a more viscous fluid in either porous media or in Hele-Shaw cells. This phenomenon is well-studied in the case of Newtonian, non-reactive fluid pairs.

Our work in [13] studied viscous fingering in Hele-Shaw cells in the presence of chemical reactions that produce surfactants *in-situ*. The fingering patterns were *significantly different* than without reaction, and were characterized through the dependence of the fractal dimension as a function of the dimensionless reaction rate constant. The patterns are significantly more compact and the displacement efficiency increased over the non-reactive case.

Our work in [15, 20] involved a different type of fingering in the presence of surfactants. It was found that driving a meniscus into a bath of surfactants in the case when the walls of the Hele-Shaw cell were pre-coated with a surfactant led to a new instability. This instability was characterized by "fingers" in the spanwise direction, which, in contrast to the more conventional case, did not propagate into the fluid, but rather equilibrated at finite amplitude. A linear theory was developed [15] that exposed the basic mechanism, and experiments [21] were done with a well-characterized surfactant that verified the main premises of the theory and provided preliminary insight into the nonlinear dynamics.

Chemically-driven oscillatory tip-streaming in drops

During the process of measurement of interfacial tension in the presence of chemical reactions that produce surfactant, we discovered an intriguing phenomenon that we reported in [18]. Strong Marangoni stresses due to a variation in the degree of completion of the reaction leads to a strong extensional flow near the tip of a drop held in a small hypodermic needle. The simultaneous lowering of the surface tension and the extensional flow lead to capillary numbers in excess of those required to initiate tip-streaming of small droplets from the tip of the mother drop. Somewhat remarkably and unexpectedly, this tip streaming then repeats in a quasi-periodic fashion for several minutes (until the reactants are exhausted). Several of the more obvious aspects of the problem, including the sustaining of oscillations by Marangoni stresses, the repulsive interactions between drops, and the existence of a cone-like solution to the Stokes equations, are discussed quantitatively in [19].

Coating flows

Coating flows pertain to the subject of the flow and adhesion of liquids to solid substrates. All coating processes involve contact lines – the common line between solid, liquid and a third fluid – and coating theory and practice seeks to predict and control the thickness of the liquid coating that is applied. A significant body of knowledge exists for the coating of Newtonian liquids over mathematically smooth substrates. Our work has focused on the effect of topography, since it is rare if at all that coating processes are concerned with smooth substrates.

The effect of topography was investigated in [2, 5] which dealt with predictions of the coating flow profiles over regular etch pits. The primary effect was the introduction of *significant* non-uniformities in the thickness of the coating layer. Both lubrication theory [2] and the full Stokes flow [5] were considered, with some surprising connections between the two. In spite of the formal breakdown of lubrication theory for sharp profiles such as steps, it was found that the theory is surprisingly accurate in these cases, especially at low capillary number.

Work in [6] considered the stability of such non-uniform coatings: they are predicted to be linearly stable against small disturbances, but topography may act to significantly amplify the effect of upstream perturbations. Work in [10] showed that surface tension gradients can be used effectively to level what would otherwise be a non-uniform coating.

In two companion papers, [16,17], we considered the extremely difficult problem of simulation of the motion of contact lines over smooth substrates and how contact lines interact with topographies. This led to an understanding of how contact lines get in and out of etch pits and surface features, to the identification of three mechanisms by which coating can be unsuccessful, and to a regime map showing the range of coatable etch features as a function of the speed of coating, aspect ratios, and contact angles (wettability).

Finally, we have considered the classical problem of dip-coating for the important case of coating from bounded pools of liquid [22]: we find interesting and unanticipated changes in flow topology for bounded pools, which has important implications for the coating of surfactant solutions. Experiments conducted in our laboratory for coating over rough substrates and with surfactant solutions [24] have shown effects that defy conventional wisdom and which are unexplained by any of the current theories.

Electrohydrodynamically induced chaotic mixing in drops

Mixing of fluids can be very slow in low Reynolds number flows. In addition, the transport of heat or mass can be similarly slow if the flow structure contains significant regions of closed streamline patterns, regardless of the Peclet number. The reason is that the net

transport rate is limited by transport across streamlines which, in a steady flow, is diffusion limited. Chaotic advection has been generally recognized as an attractive way to mix fluids that would otherwise would be very difficult to mix (because of the high fluid viscosity, low velocity, or small scale size of the flow.)

We have explored the possibility of using electrical stresses in dielectric liquids to promote chaotic flows and mixing internal to drops. A pair of companion papers [8, 14] deals with the use of axisymmetric electrohydrodynamic flows (EHD) to mix fluid in a translating drop. The theory put forward in [8] suggests that it should be possible to mix the entire volume of a drop in a rapid fashion by appropriate choices of amplitude and frequency of a modulated electric field. The experiments in [14] validate the theory in all its important aspects. This approach was then extended in [21] to study steady three-dimensional chaotic streamlines that can be produced by inclining the electric field with respect to the settling direction. Remarkably, theory predicts that it is possible in principle to use a small $O(\epsilon)$ misalignment to produce a mixed region of $O(1)$. This is accomplished by certain discrete events in which Lagrangian fluid particles cross what would otherwise be a separatrix of the motion. Three dimensional particle tracking in experiments [21] have identified these events and verified their importance in the mixing process.

Bubbles in microchannels and microgeometries

Bubbles in microchannels are important in a wide variety of MEMS applications, including switches, actuators, valves and pumps. Our work has focused on both experimental and theoretical studies of flow and heat transfer problems related to bubbles in microchannels.

As series of papers [1, 3, 12] dealt with the issue of the manipulation of the speed and position of a long bubble in a cylinder of either circular or rectangular cross-section. We asked the question "can surface tension gradients be used to migrate a long bubble, and if so, how fast would it go?" We were able to answer this question theoretically [1,3] – migration is extremely slow in a circular cylinder, and a bubble moves fastest in a rectangular cylinder of a certain aspect ratio. The theory was based on all parameters associated with the dimension of the microchannel (Reynolds number, Peclet number and Bond number) being small. Experiments in [12] verified the zero gravity (small Bond number or small microchannel) theory and showed how a simple correction can be applied to estimate the increase in speed due to a vertical asymmetrical placement of the bubble within the cross-section.

Another series of papers [4, 7, 11] dealt theoretically with the problem of vaporization of liquid within a microchannel. The problem was formulated in [4, 7] as a free boundary with a global constraint, i.e. given the thermal conditions, find the shape and size of a vapor bubble such that evaporation near the hotter parts of the boundary balances condensation elsewhere. We solved this problem using matched asymptotic expansions, where both the evaporation and condensation rates were developed as local solutions using thin film or lubrication theory type approximations. This in turn required some modeling of the contact line region, which we did using the concept of disjoining pressure. The model was then extended in [11] to include dynamic effects. Experimental verification of many of the predictions is now underway in our group, funded by a recent NSF grant.