I. Introduction and Executive Summary

Energy technologies of all kinds are restricted by the limited availability of useful quantities of high quality samples of appropriate materials. Also, many promising materials show sample-to-sample variations in physical properties resulting from inhomogeneities on length scales in the range 2nm - 20 μm which originated during liquid-state stages of sample preparation. In addition, the energy consumption in the fabrication of materials for all applications is process dependent. All these considerations indicate that improvements in our ability to process materials are of great importance to the DOE mission.

All the work of this project, past and present, addresses basic science questions which are related to the processing of materials. This project is aimed at understanding the growth of interfaces and the evolution of patterns on interfaces, both macroscopic and microscopic. Three series of laboratory experiments are proposed for the next cycle of the grant:

1. a study of the changes in patterns available to the growth of a macroscopic interface when that interface is grown over one of a variety of "microscopic" lattices,

2. a study of reversible aggregation of colloidal particles in a mixed solvent, and of the interactions and relaxations of both solvent and suspended particles when thermodynamic conditions are changed for a liquid matrix with suspended particles or fibres, and

3. an investigation of the sedimentation of particles in a quasi-two-dimensionsal viscous fluid, with attention both to the dynamics of the flow and to the roughness of the resulting surface of settled particles.
As described below, each of the three series of experiments has more than one variant, each of which is designed to bring out a selected feature of the problem. All have been selected to be sufficiently simple that one can realistically hope to learn about the basic science of the problem, yet all hold the promise of teaching us something about important materials processing problems.

Pittsburgh is an ideal place to pursue this work. In addition to the PI's well-equipped laboratory (significantly enhanced three years ago when the University of Pittsburgh provided $75,000 in equipment as matching funds for this grant), two other well-known experimentalists (W.I. Goldburg and X.L. Wu) have adjacent laboratories in which they and their students and postdocs perform experiments on other but related kinds of soft condensed matter physics. The condensed matter theory groups of David Jasnow, Yadin Goldschmidt and their students and postdocs combine with our experimental community to form an unusually stimulating atmosphere for this kind of physical science. We also have regular interactions and shared seminars with the excellent statistical physics group at Carnegie-Mellon University.

Within the past two years, the PI has given invited talks on various aspects of pattern formation at four conferences (invited talks 13-16 in publication list), and an invited talk on our colloidal aggregation work has been scheduled for the Complex Fluids Symposium at the MRS Meeting in Boston in December, 1993. Seven Ph.D. students supervised by the PI have graduated during the past 10 years. Of these, three are in tenure stream positions doing research in this field (Nalini Easwar, just awarded tenure at Smith College; Steven
Rauseo, assistant professor at Wheaton College; and Ke-Qing Xia, assistant professor at the Chinese University in Hong Kong). One (Mark DiFrancesco, Bio-Control Inc.) is in an industrial position developing apparatus to use the multiple scattering of light from tissue for medical diagnosis. And the three most recent graduates are in postdoctoral research positions (Patrick Gallagher, Boston University; Beth May, Technical University of Copenhagen; and Hong Zhao, about to leave for Saclay). Two of the seven graduates (Easwar, May) are women, as is one of the four students currently associated with this project. The University of Pittsburgh fully supports one of the students on this project, and another current student is supported on an outside fellowship.

Section II is a review of work performed during the most recent cycle of the grant. As much as possible this has been organized to match the categories of experiments proposed in Section III. In this way, Section II provides the background material which motivates the proposed experiments.
II. Research Accomplishments During the Period 11/90-Present

In this section we outline the accomplishments of the past grant cycle, with special emphasis on results which are relevant to work proposed in the next section. Detailed descriptions of some of the work presented in this section can be found in the appended reprints, appendices A-E. In the first years of this project the objectives stated in the introduction were best pursued by studying the simplest available pattern formation problems (in particular, our work focused on the Saffman-Taylor instability and the development of viscous fingers in a Hele-Shaw cell) and by studying phase separation of a mixed solvent which was imprisoned inside a polymeric gel. Much progress has been made on understanding the viscous fingering Hele-Shaw problem. Even though there are still poorly understood aspects of the dynamics of the problem, enough progress has been made that our recent work has aimed to add controlled perturbations to the "simple" problem and measure the extra features brought into the pattern formation problem by the perturbations.

In a similar programmatic evolution, several features of the early experiments on phase separation inside a gel raised questions about the behavior and role of wetting/adsorption inside a composite material. Accordingly, in recent experiments we have been forced back to a more basic level of trying to watch individual parts of a composite system rearrange when thermodynamic variables are changed.

Motivated by the results of the earlier experiments, our work during the most recent grant cycle has involved: a) adding perturbations to simple pattern formation situations to observe the dynamics of the processes, look for regularities and try to understand how such
perturbations bring extra richness into the process of pattern evolution, and b) designing simple composite systems wherein we can observe rearrangement of the components under changed thermodynamic conditions.

II. A. Pattern Evolution in Perturbed Hele-Shaw Flows

In the basic Hele-Shaw flow, fluid trapped between parallel plates whose separation, b, is smaller than any other length scale in the problem has been shown to obey Darcy's law

$$\vec{v} = -M \vec{\nabla} p$$

with

$$M = b^2 / 12 \mu$$

where $\vec{v}$ is the velocity field for the flow, $p$ is the pressure, $M$ the mobility, and $\mu$ the shear viscosity of the fluid.

If the fluid is incompressible, $\vec{\nabla} \cdot \vec{v} = 0$, and the pressure field must obey the Laplace equation

$$\nabla^2 p = 0$$

The Saffman-Taylor instability arises and produces an unusually simple pattern formation problem when an interface between two fluids is driven through a Hele-Shaw cell with lower viscosity advancing against higher (or with low density fluid below higher). In this case the flow is governed by equation 3 with boundary conditions set to ensure that the normal components of velocity match across the interface

$$v_{1n} = v_{2n}$$
and that the pressure jump across the interface obeys the Laplace law

$$\Delta p = \sigma K(v)$$  \hspace{1cm} (5)

where $\sigma$ is the interfacial tension and $K$ is the local interfacial curvature. $K$ is shown as a function of $v$ because the thickness of the film left on the wall by the wetting fluid, and thus the curvature of the interface across the gap, are in general velocity dependent\(^9\)\(^{10}\)\(^{11}\)\(^{12}\). Ideally, one would like to be able to write down plausible corrections to all of equations 3, 4, and 5 for each perturbation added to the problem. The next subsection (II. A.1) presents such a case and the interesting results which proceeded from studying that case. Then Sections II. A. 2 and II. A. 3 present cases where intriguing experimental simplicity has been observed for physically interesting perturbations but where stronger approximations have to be made if full sets of dynamical equations with interfacial boundary conditions are to be developed.

II. A. 1. Gradient-in-Gap Flow (Hong Zhao and James V. Maher, in collaboration with Chuck Yeung and Jaume Casademunt of David Jasnow's theoretical group)

Adding complexity to the Saffman-Taylor problem has been shown to change the problem, sometimes dramatically, but in ways that show significant regularity\(^{13}\)\(^ {36}\). Appendix A is a reprint\(^{37}\) of a careful study of a small perturbation introduced by setting the plates of a Hele-Shaw cell slightly out of parallel. This introduces a small spatial dependence to the mobility, adding a term to the dynamical equation (Appendix A, equation 2) and also modifying the boundary conditions in a way that can be written down with reasonable
assumptions (Appendix A, equations 3 and 4). The resulting equations are very close to those of directional solidification in its quasi-static limit, with the relevant lengths arising from easily controllable spatial dimensions and wetting properties of the cell walls. (In Appendix A the analog of the thermal length has the opposite sign from that needed to bring the problem into close analogy to directional solidification, but the dynamical equation being investigated is the same as in quasi-static solidification; the intention here is to learn about growth dynamics in cases simple enough that theory and experiment can stay in close contact, not to pretend that the analogies with solidification are exact.) To summarize our results, we measured the breakup of the initially flat interface under a variety of flow rates and at five different values of the gap-gradient, and we also measured the shape and stability of the late-stage single finger pattern under the same range of flow conditions and gap gradients. All gap-gradients which we studied were so small that the linear stability analysis for the breakup of the flat interface predicted that the difference between growth rates for the perturbed case and those of the basic parallel-plate case would be unmeasurably small for all unstable wavenumbers. Nevertheless, we observed a small but clearly significant effect, with the observed dominant wavelength as a function of dimensionless control parameter decreasing systematically with the magnitude of the gap-gradient but not with the sign of the gradient. This can be seen in Figures 5 through 8 of Appendix A. At present we do not have a satisfactory explanation for the discrepancy between observation and theory; this is especially puzzling because the assumptions which entered the theoretical treatment were all quite plausible. The lack of dependence on the sign of the perturbation suggests a second order effect. Effects of the gap-gradient perturbation on the late stage single finger were
much more dramatic, as might be expected for this case where even a small perturbation can plausibly produce large effects after a long time and where the cumulative effect of a small gradient is in any case large after the interface has travelled a long distance in the cell. The single finger becomes much less stable than a single finger in the unperturbed cell (same glass plates, set in parallel, with the instability coming from inevitable macroscopic perturbations, as has been discussed elsewhere\textsuperscript{5,6,7,8}) if the gradient is positive (cell gap growing larger as the interface advances) and becomes much more stable when the gradient is negative. These changes in stability are accompanied by changes in shape with the less stable, growing-gap finger showing a flattened tip on which disturbances easily grow and the narrowing-gap finger showing a sharper tip on which disturbances are quickly swept away before having much of a chance to grow. For pictures of tip shapes, see Figures 1 and 2 of Appendix A, and for stability limits as a function of gap-gradient, see Figures 3 and 4 of the same appendix.

II. A. 2. Displacement of a Concentrated Polymer Solution in a Hele-Shaw Cell

\textbf{(Hong Zhao and James V. Maher)}

Appendix B is a reprint of a paper\textsuperscript{41} in which we discussed the range of pattern types which are achievable in a Hele-Shaw flow when the displaced fluid is a concentrated aqueous homopolymer solution and the invading fluid is water. Previous work\textsuperscript{42,43,44} had shown that in some circumstances the patterns formed in such a solution have a strong resemblance to objects formed by diffusion-limited-aggregation (DLA) calculations\textsuperscript{45}. This previous work had also led most people to expect that in all circumstances we would see highly branched
flow, with little or no growth in the "fjords" left behind by the advancing interface. As can be seen from Figure 2 of Appendix B, it is possible in some circumstances to have significant growth in the regions left behind the advancing fingers (almost none of the dense regions in the patterns shown in that figure result from early growth, prior to the onset of the instability; rather, they have resulted from growth in the fjords behind the fingers). Despite the wide array of pattern shapes which become possible once the displaced fluid is a concentrated polymer solution, it is nevertheless possible to collapse some of the observed length scales with an empirically determined parameter which combines all four of the experimental control parameters (the polymer concentration, the molecular weight of the polymer, the rate at which water is injected into the cell, and the gap in the Hele-Shaw cell). Adapted from a suggestion by DeGennes, this parameter attempts to form a ratio of the expected fluid mechanical shear rate (imposed by our forcing fluid from our syringe pump into the cell) to a characteristic relaxation rate of the polymer solution (the ratio of the plateau modulus to the low shear-rate viscosity). An attractive feature of using simple homopolymers rather than polymers of more complicated architecture in this experiment is that there are reasonably well established power laws relating the viscoelastic moduli of the polymer solution to the concentration and molecular weight of the polymer. It was indeed possible to use such power laws to form a characteristic number which collapsed our observed initial length scales and also the peak and mean modes of modal analyses of the patterns (see equation 1 and Figures 3 and 4 of Appendix B), and such a collapse had not, to our knowledge, been achieved before with any other array of complicated patterns. Unfortunately, the number which worked in collapsing the data only worked with the concentration dependence left out of the low-
shear-rate viscosity. Thus the number is empirically based and has no theoretical support, even though its discovery resulted from related theoretical reasoning. As will be discussed below in the proposal chapter (Section III.A.3), we hope that further work will allow us to understand this problem, by either providing some theoretical justification for the result or by showing that the correct power laws can be used if sufficiently monodisperse polymers are employed. The existence of power-law-dependent mechanical properties for homopolymer solutions makes them a very attractive testing ground for regularities in nonlinear dynamics.

II. A. 3. **Anisotropy Effects from Etched Plates (Kathleen McCloud and James V. Maher)**

Knowing that dramatic effects can be achieved by perturbing flows with wires\textsuperscript{15,16,28,30,31,33}, bubbles \textsuperscript{17,23,24}, disks\textsuperscript{18}, etched grooves\textsuperscript{16,19,22}, and etched arrays\textsuperscript{13,16,20,21,25,26,27} on one of the plates of a Hele-Shaw cell, we have recently measured the effect on steady state flow in a rectangular Hele-Shaw cell of introducing a small, controllable anisotropy in the form of an etched lattice of very regular, shallow grooves on one of the plates. We have made measurements with two different lattices, one of squares (0.400 ± 0.005mm center-to-center, 0.200 ± 0.005mm groove width and 0.090 ± 0.005mm depth) and one of rectangles (0.800 ± 0.005mm by 0.400 ± 0.005mm with 0.200 ± 0.005mm groove width and 0.090 ± 0.005mm depth).

These are finer etchings and somewhat closer tolerances than have been used in most previous etched plate experiments, and we have used them to study somewhat smaller values of the experimental anisotropy parameter \( a = \Delta b / b \) where \( \Delta b \) is the depth of the etched
grooves and b is the gap in the Hele-Shaw cell) than have been investigated in most other experiments. Our capillary lengths have varied between 2 mm and 9 mm so any one part of an advancing interface is affected by at least three and possibly by as many as twenty cells of the underlying lattice. In previous perturbation discussions it has frequently been assumed that individual wires, scratches or structured cells are comparable to or larger than the capillary length. Sarkar and Jasnow have argued that, if the length scale of the underlying lattice is enough smaller than any other length scale in the interfacial growth problem, the mobility tensor can be constructed from a coarse-grained averaging process, yielding identical eigenvalues and a basically unchanged dynamical equation (i.e., the Laplace eqn.) for lattices with square or hexagonal symmetry and non-identical eigenvalues and, in principal, a significantly changed dynamical equation for other symmetries. Our etchings are sufficiently fine that we may have reached the limit Sarkar and Jasnow discuss, in which case effects we see with our square-lattice cell should be attributable to the effects of the lattice on the interfacial boundary values while effects from the rectangular lattice could come from either the dynamical equation or the altered boundary values. We find significant effects on the width and stability of the steady state finger for both the square and rectangularly etched cells, with much larger effects in the case of rectangular etching. Figure 1 shows the width of the steady-state finger as a function of inverse capillary number for flows at a variety of values of the anisotropy parameter when the channel is oriented parallel to an axis of the squares. At this orientation the fingers widen as anisotropy increases. Figure 2 shows finger width vs inverse capillary number at a variety of values of the anisotropy parameter for each of three different orientations of the channel to the long axis of the rectangles. Here
Square Lattice

($\theta = 0^\circ$)

FIGURE 1
(θ = 0°)

\[
\begin{array}{c}
\lambda \\
0.80 & 0.75 & 0.70 & 0.65 & 0.60 & 0.55 & 0.50 \\
\end{array}
\]

\[
\begin{array}{c}
\frac{1}{B^*} \\
20 & 40 & 60 & 80 & 100 \\
\end{array}
\]

- a = 0.16
- a = 0.11
- a = 0.05
- a = 0.0 (smooth cell)

(θ = 10°)

\[
\begin{array}{c}
\lambda \\
0.80 & 0.75 & 0.70 & 0.65 & 0.60 & 0.55 & 0.50 \\
\end{array}
\]

\[
\begin{array}{c}
\frac{1}{B^*} \\
20 & 40 & 60 & 80 & 100 \\
\end{array}
\]

- a = 0.16
- a = 0.106
- a = 0.056
- a = 0.0 (smooth cell)

(θ = 45°)

\[
\begin{array}{c}
\lambda \\
0.80 & 0.75 & 0.70 & 0.65 & 0.60 & 0.55 & 0.50 \\
\end{array}
\]

\[
\begin{array}{c}
\frac{1}{B^*} \\
20 & 40 & 60 & 80 & 100 \\
\end{array}
\]

- a = 0.25
- a = 0.16
- a = 0.0 (smooth cell)

**FIGURE 2**
the fingers widen with increasing anisotropy at small angles (0° and 10°) and narrow at 45° (half way between the axes of the rectangular array, but not along the diagonal of the rectangles). We have not yet measured finger properties at any angles other than 0°, 10° and 45°. While it was previously said that fingers should narrow with anisotropy, we know of no calculation which actually took the underlying lattice and its orientation explicitly into account and predicted narrow fingers at all orientations. We expect there to be no serious inconsistency with theory here, but instead a potentially interesting surprise that the narrowing is at 45 degrees rather than along the easy axis of the array. It will be important to see how calculations will agree with the observed widths at different orientational angles.

We also find that the fingers become much less stable with increasing anisotropy when the channel is oriented parallel to the axis of the array and that they are roughly as stable as in the zero-anisotropy case when oriented at other angles (even at 10 degrees off the easy axis). This angle-dependent stability is shown in Figure 3 which compares the range of inverse capillary number at which instability appears as a function of anisotropy parameter for two different orientations of the channel. All capillary numbers have been corrected for wetting effects as in the work of Tabelling and Libchaber\textsuperscript{11,12} and Park and Homsy\textsuperscript{9,10}. The work just described is only a beginning of the many quantitative tests which can be done of the available theoretical work on interface growth with this apparatus. Further discussion is thus deferred to the proposal section (III.A. 1).

II. B. Reversible Aggregation of Colloidal Particles (Patrick D. Gallagher, M. Levant Kurnaz and James V. Maher)
FIGURE 3

STABILITY

\[ \frac{1}{B} \]

\[ \theta = 0^\circ \]
\[ \theta = 45^\circ \]
\[ \theta = 10^\circ \]

anisotropy a
In our earlier work on phase separation of mixed fluids inside a gel\textsuperscript{52,53,54}, we observed frozen composition fluctuations for a mixed solvent imprisoned in a highly swollen polymeric gel as the temperature of the system was brought toward the range where the free liquid mixture would phase separate. Superimposed on the strong light scattering from the frozen fluctuations was a weak, temporally fluctuating signal which showed a nondiffusive autocorrelation function, presumably from slow hopping of the system from one metastable trap to another. While the observed phenomena showed many features which could be explained by treating the polymer strands inside the gel as imposing a random field on the mixed solvent\textsuperscript{55–60}, the phenomena were too robust and appeared under conditions which were contrived to put the system out of the random field regime (i.e., we saw "random field effects" under conditions in which we had almost certainly succeeded in making the correlation length of the solvent fluctuations much smaller than the correlation length of the gel strands). This suggested that more routine wetting/adsorption might underlie the observations, but little is known as yet about the wetting of strongly curved surfaces inside composite materials\textsuperscript{61–67}. While other groups have emphasized the wetting of interior surfaces in more rigid porous materials like vicor glass\textsuperscript{68,69} and silica gels\textsuperscript{70–72}, we have tried to study effects on exterior surfaces such as the surfaces of fibres and colloidally suspended spheres in samples most of whose volume is filled with a mixed solvent. Our recent work has been a study of very dilute, colloidally suspended, charge-stabilized polystyrene latex spheres in 2,6-lutidine + water (LW) mixtures of various compositions. Beysens et al.\textsuperscript{73–75} had shown that the same solvent mixture could produce reversible aggregation of silica particles in the solvent’s one phase region near the demixion temperature. We extended that
result by using particles whose surface charge densities could be more accurately specified and whose size distributions were more monodisperse. In addition we made a thorough study of the system behavior in the solvent's two phase region, a project which shed considerable light on several aspects of the problem.

Appendix C is a reprint of our recent paper on the system's two-phase behavior\textsuperscript{76}. Briefly, we found that the colloidal particles partitioned very strongly into one solvent phase when the system was brought to thermodynamic equilibrium near the critical point in the two-phase region. Which phase was preferred by the particles depended on the measured surface charge density of the particles (by this we mean the surface charge density measured by the manufacturer\textsuperscript{77} by titration. Even though this charge density obviously depends on the local pH of the solution, the titration measurement presumably tells us something important about the density of sulphonate groups on the surfaces of the polystyrene spheres, and we find that it serves as a good predictor of phase behavior for our system.) High charge-density particles prefer the water-rich phase and lower charge-density particles prefer the lutidine-rich phase. For any particles, there is a temperature in the two phase region such that, when the temperature is farther than this point from the critical temperature, the particles no longer partition exclusively into the preferred phase, but instead become willing to populate the interface (even though almost all particles still stay in the preferred phase and only a very small part of the population go into the unpreferred phase). This temperature is presumed to be related to the wetting temperature for these particles (this point is discussed in more detail in Appendix C), and the dependence of this temperature on the surface charge density of the particles is shown in Figure 6 of Appendix C. As is discussed in the appendix, our two-phase
results can be shown to be in good qualitative agreement with standard thermodynamic models for colloidal systems if the models are extended to include the singular temperature dependence of the particle-liquid wetting and liquid-liquid interactions near the critical point. We also observed crystalline ordering of the particles on the interface at temperatures where the population of particles on the liquid-liquid interface was high.

Appendix D is a reprint of our recent paper on the reversible aggregation of PLS in the one phase LW region near the LW coexistence curve. In this paper we show that the side of the coexistence curve on which the aggregation takes place depends on the surface charge-density of the spheres. Knowing from the two phase work which phase particles of a given surface-charge-density prefer, we find that the aggregation always occurs on the side of the critical composition which is rich in the unpreferred solvent (see Figure 1 in Appendix D). In addition we find that the aggregation curve does not join the coexistence curve near the temperature at which the particles in a two phase sample begin to populate the interface (if one interprets this temperature as a wetting temperature, then the aggregation curve stays in the one-phase region far beyond the wetting temperature). Dynamic light scattering measurements discussed in Appendix D show no indication of the formation of a layer coating the particle surfaces, but the discussion shows that it is hard to interpret the significance of the dynamic measurements for such a layer. However, the dynamic light scattering does show (see Figure 2 of Appendix D) that the aggregate sizes grow as the cube root of the time. This result, that the volume of the aggregates increases linearly with time is consistent with Smoluchowski kinetics in the diffusion limited regime but indicates that the aggregates are relaxing to dense objects as they add particles. A similar
result has been reported by Broide and Beysens\textsuperscript{80}. The current status of this work is that there is a rather large region in the one-phase, near-critical zone of a solvent mixture in which our charge-stabilized colloidal particles will reversibly aggregate. While the attractive forces which must be present to produce such aggregation are presumably related to the composition gradients of the solvent near the particle surfaces, it is not easy to specify the nature of the attraction (see discussion in Appendix D), other than to say that the binding presumably arises from a secondary minimum in the effective potential since falling into the van der Waals minimum would produce irreversible aggregation\textsuperscript{81}. Two promising avenues for future work are discussed below in the proposal chapter (see section III.B.1).

II. C. Sedimentation of Monodisperse Silica Particles in Oil (M. Levant Kurnaz, Kathleen McCloud, Hong Zhao and James V. Maher)

We have recently begun a study of the growth of surfaces at the bottom of a quasi-two-dimensional container (40cm by 40cm by 0.1cm) of heavy paraffin oil when a large number (\textasciitilde ten thousand) of 0.06cm -diameter silica particles fall through the oil from the top of the container. While the hydrodynamics of such a sedimentation project is nontrivial\textsuperscript{82-97} (and our plans to study some aspects of the dynamical problem will be discussed below in the proposal chapter, Section III.C.1), our first approach has simply been to treat the developing surface at the container bottom as an interesting growing rough surface\textsuperscript{98-140}. Since the hydrodynamic interactions which produce correlations among the particles can in principle be long range, this is a system which would fall into the KPZ class\textsuperscript{113} only if screening and averaging of interactions were to result in effective short range forces with added Gaussian
noise. As is well known, many existing interface growth experiments\textsuperscript{129-136,139} show significant differences from the KPZ roughness exponents. While there may be good theoretical reasons for such discrepancies (especially in terms of correlations in noise)\textsuperscript{115,119,124,137,138}, it is of interest to study distinct cases such as sedimentation where the basic growth law for the interface might be expected to be different in a way which careful work may be able to elucidate. In addition, sedimentation is of practical importance for materials processing and possibly for filtering\textsuperscript{83-85}.

In our preliminary work we have taken two approaches to this interfacial growth problem. In the first, we ignored the dynamics of interface development and measured the rough surfaces only after all particles had settled. Figure 4 shows several patterns formed by taking the cell with particles in whatever configuration resulted from the previous sedimentation run, inverting the cell and then measuring the pattern after all particles had settled. By digitizing the patterns and measuring difference patterns, we find that correlations die out within one settling run unless the initial configuration was carefully prepared to be very atypical. For example, if we shift the cell to create a triangle of particles in one corner and then invert the cell with a side parallel to the floor, it takes three inversions to fully forget the initial triangle, but after the triangle has been forgotten, run-to-run fluctuations show correlations as weak as those seen between runs separated by as many as several dozen inversions of the cell. In this way we have measured about 50 independent surfaces, digitized their patterns and analyzed their roughness by determining their rms height fluctuations, \( W \), as a function of the length, \( L \), of the averaging interval. This gives a power law \( W \sim L^{\alpha_s} \) with \( \alpha_s = 0.7 \pm 0.1 \) over the range \( 0.1 \text{cm} < L < 2 \text{cm} \) and another exponent \( \alpha_r = 0.9 \pm 0.1 \).
for 2cm<L. The roughness at large length scales arises from "sand dunes" which undulate at their peaks and sometimes show sharper cusplike structures in their troughs. In our second approach, we have measured a time series of patterns as particles settle onto the bottom of the apparatus. Figure 5 shows \( W(L,t) \) for three values of the time in this time series. The roughness exponent for short length scales can be seen to be roughly constant in time, while the exponent for large length scales starts out small and grows to the large value characteristic of the end of a run. This is shown in Figure 6 where the exponents are shown as a function of time for that one time series. (The late-stage \( \alpha \) measured in this first time series is smaller than our average value by one standard deviation.) We have since measured another time series and are in the process of analyzing it; we do not know whether the temporal fluctuations will prove to be larger than the fluctuations at the end of runs, but if they are not, then the growth exponent for this process, \( \beta \), is approximately 0.5. Interestingly, this gives a sum \( \beta + \alpha/\beta = 2.1 \), consistent with the value of 2 that would be expected for a system with Galilean invariance\(^{100,139,140}\). We do not yet have a value of \( \beta \) for growth at large length scales. There is never any observable rearrangement of the interface as a particle settles down, nor is there observable motion of the particle after it attaches itself to the interface. On the other hand, overhangs are never observed and the hydrodynamics of the last stages of a particle's approach to the interface may be quite subtle.

Several extensions of this project are planned, so further discussion is to be found below in the proposal section III.C.

II. D. Capillary-Wave Relaxation for a Meniscus between Miscible Liquids (S.
Now consider the time series:

\[ t = 13.72 \, \text{s} \]

\[ t = 18.22 \, \text{s} \]

\[ t = 61.00 \, \text{s} \]

**FIGURE 5**
\( \alpha_s \) stays constant around 0.7

\( \alpha_1 \) rises to its final value with time!

**FIGURE 6**
Appendix E is a reprint of a recent paper in which we used surface light scattering to study the relaxation of capillary waves at an interface between two miscible liquids. We used a mixture of liquids (isobutyric acid + water, IBW) with a convenient critical point so we could form a good equilibrium interface, measure its capillary wave relaxation to calibrate our surface light scattering and then quench the system into its one-phase region, measuring the light scattering as a function of time after the system reached temperature (but obviously not composition) equilibrium. Diffusion is a sufficiently slow process that it takes many hours for the interface to dissolve away and many hundreds of hours for the unstirred system to reach composition equilibrium. In the mean time, the interface exhibits some integrity against rapid change, an effective surface tension. While the need for an effective interfacial tension has been known for some time to investigators of patterns developing at interfaces between miscible liquids, there were few previous attempts to measure the effective interfacial tension and none of these measured the capillary wave spectrum. As can be seen in Appendix E, we have measured the capillary wave relaxation rates at several wavenumbers in the range $50 \text{cm}^{-1} < q < 350 \text{cm}^{-1}$, and we have found that the effective interfacial tension indeed dies off very slowly with time after the temperature change. A purely diffusive model which ignores gravity-stabilization effects in the dissolution of the interface can only fit the data by using a diffusion constant which is several orders of magnitude smaller than the value at two-phase equilibrium. (This does not mean that gravity has been left out of the basic analysis of the data; the wavenumber range of the experiment spans the region in which gravity switches from having a noticeable effect on the capillary wave dispersion relation (low
wavenumbers) to having no noticeable effect (high wavenumbers). The dispersion-relation analysis of the light scattering autocorrelation functions as a function of wavenumber always included gravity in extracting the interfacial tensions shown in Figure 3 of Appendix E, but the simple diffusive model used to produce the curve shown in that figure had no gravitational effects included.) Simulations by Rogers and Jasnow\textsuperscript{149} mentioned in Appendix E used a magnetic analog system and found a dramatic slowing down of the dissolution of the interface when an external field, possibly like gravity, was turned on.
END

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