"Phase Segregation Due to Simultaneous Migration and Coalescence"
NAG3-1389

Progress Report for January 1994 to November 1994

Principal Investigator: Dr. Robert H. Davis, Professor
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Second-Year Progress Report and Third-Year Planned Activities

Objectives

The primary objective of the research is to perform ground-based analysis and experiments on the interaction and coalescence of drops (or bubbles) leading to macroscopic phase separation. Migration of the drops occurs as a result of the individual and collective action of gravity and thermocapillary effects. Larger drops migrate faster than smaller ones, leading to the possibility of collisions and coalescence. Coalescence increases the rate of macroscopic phase separation, since the result is larger drops with higher migration rates. It is hoped that the understanding gained will lead to the design of microgravity experiments to further elucidate the mechanisms governing coalescence and phase separation.

Research Tasks

The processes described above are modeled using population dynamics balances which allow for spatial nonuniformities in finite systems. The interactions of pairs of drops or bubbles in dilute dispersions are accounted for using recent results obtained for collision efficiencies in gravity-induced, thermocapillary-induced, and combined motion of different-sized drops or bubbles (Zhang and Davis, 1991, 1992; Zhang *et al.*, 1993).

A significant effort is also devoted to the development and performance of ground-based experiments which may later be adapted for reduced-gravity flight opportunities. Optical techniques are used to follow the rate of accumulation of the dispersed phase in a separate layer due to simultaneous migration and coalescence of a variety of transparent immiscible systems. Microvideo and image analysis techniques are also used to follow the trajectories and coalescence of several interacting drops or bubbles of different sizes. These experiments are being performed under isothermal conditions, with motion and phase separation occurring due to gravity. It is hoped that a temperature gradient will be introduced later, so that thermocapillary as well as gravitational motion can be studied. In all cases, the results are compared with predictions of the theory.

Significance

The research provides a fundamental understanding of how drop or bubble migration due to gravitational and nongravitational mechanisms interacts cooperatively with coalescence to promote macroscopic phase separation in an immiscible dispersion. The experiments and theory provide a basis for studying and controlling the rate of phase separation in space science applications, such as processing liquid-phase miscibility gap metals, degassing molten materials, gassing cell cultures, and separating aqueous biphasic systems.

Progress To-date

The population dynamics equations for homogeneous dispersions having no spatial variation or phase separation have been solved for droplet growth due to the separate effects of Brownian, gravitational and thermocapillary motion and coalescence (Wang and Davis, 1993) and due to the combined effects of thermocapillary and gravitational motion and coalescence (Zhang *et al.*, 1993). Details are reported in the manuscripts and in the final technical report on NASA Grant NAG3-993. Included among the key results are the discoveries of *thermocapillary repulsion*, in which a highly conducting small drop will move faster than a nearby larger drop, thereby preventing coalescence, and of a *collision-forbidden region*, which occurs for antiparallel alignment of the temperature gradient and gravity vector due to the different dependencies of gravitational and thermocapillary relative motion on the separation distance of two drops or bubbles.

A theoretical analysis has been performed (Wang and Davis, 1994) for nonhomogeneous dispersions undergoing simultaneous phase separation and drop motion and coalescence due to gravity. A schematic of the process analyzed is shown in Figure 1. Numerical results are shown in Figures 2-4. Note that the average drop size and rate of phase separation initially increase due to coalescence, and then decrease due to the larger drops moving out of the suspension. The volume fraction of the dispersed phase continuously decreases as the drops rise or settle out of the dispersion. A key dimensionless parameter, N_τ, representing the ratio of sedimentation and coalescence time scales, governs the process.

Experiments to observe drop coalescence and phase segregation due to gravity have been performed with 1,2-propanediol drops in dibutyl sebacate and with an aqueous biphase mixture of 1% dextran (MW = 500,000) and 6.5% polyethylene glycol (MW = 8,000) by weight. In both cases, the drops are heavier than the continuous phase, in contrast to the results illustrated in Figs. 1 and 3. Results (Figs. 5 and 6) for the phase separation rate versus time are in good agreement with the theory and have been used to infer values for the composite Hamaker constant which represents the strength of the attractive van der Waals forces. Typical results for the position of the phase interface versus time are shown in Figure 5. Note that the S-shaped curve is indicative of coalescence--the initial phase-separation rate is slow, then it increases due to coalescence, and then it decreases as the larger drops move out of the dispersion.

Planned Research

The following tasks are planned for the third year:

1. **Modeling of Combined Gravitational and Brownian Coalescence**

   Population dynamics modeling of coalescence due to simultaneous gravitational and Brownian motion of drops or bubbles will be completed using the collision efficiencies recently predicted by Zinchenko and Davis (1994). These collision efficiencies show considerable synergism of the two mechanisms over a wide range of Péclet numbers.

2. **Experiments on Gravity-driven Coalescence and Phase Separation**

   Additional microvideo experiments will be used to observe and quantify drop coalescence and phase separation due to gravity under isothermal conditions for several liquid-liquid systems. Key predictions of theory which will be tested by the experiments include that drop coalescence increases with increasing drop concentration and container length, and that drop coalescence decreases with increasing drop viscosity. One or two manuscripts on the results will be written.

3. **Modeling of Thermocapillary-driven Coalescence and Phase Separation**

   The first portion of this task will be similar to our completed work for gravity motion, except that thermocapillary motion and collision efficiencies will replace those for gravity in a one-dimensional system. A key difference, however, is the implications of *thermocapillary repulsion* for which little or no coalescence and phase separation is expected at high drop thermal conductivities. A second portion involves other geometries, such as a container which is heated or cooled on all sides, rather than just at the top and bottom, so that drop migration toward the periphery or center occurs.

Publications

Davis, R. H., Wang, H., and Hawker, D., "Phase Segregation Due to Simultaneous Migration and Coalescence," *NASA Conf. Pub. No. 3276: 2nd Microgravity Fluids Conf.*, pp. 101-106 (1994).

Wang, H., *Modeling and Experimental Studies of Drop Coalescence and Phase Separation*, Ph.D. Thesis, Univ. Colorado (1994).

Wang, H. and Davis, R. H., "Droplet Growth Due to Brownian, Gravitational, or Thermocapillary Motion and Coalescence in Dilute Dispersions," *J. Colloid Interf. Science* **159**, 108-118 (1993).

Wang, H. and Davis, R. H., "Simultaneous Sedimentation and Coalescence of a Dilute Dispersion of Small Drops," *J. Fluid Mech.* (under review).

Zhang, X., Wang, H., and Davis, R. H., "Collective Effects of Temperature Gradients and Gravity on Droplet Coalescence," *Phys. Fluids A* **5**, 1602-1613 (1993).

Zhang, X. and Davis, R. H., "The Collision Rate of Small Drops Undergoing Thermocapillary Migration," *J. Colloid Interf. Sci.* **152**, 548-561 (1992).

Zhang, X. and Davis, R. H., "The Rate of Collisions of Small Drops Due to Brownian or Gravitational Motion," *J. Fluid Mech.* **230**, 479-504 (1991).

Zinchenko, A. Z. and Davis, R. H., "Gravity-induced Coalescence of Drops at Arbitrary Péclet Numbers," *J. Fluid Mech.* (in press).

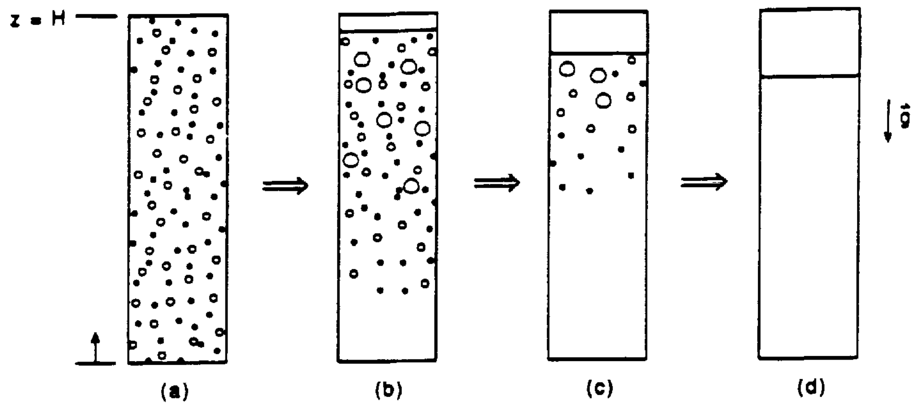

Fig. 1–Schematic of the time evolution of the phase separation process due to the simultaneous migration and coalescence of rising drops or bubbles.

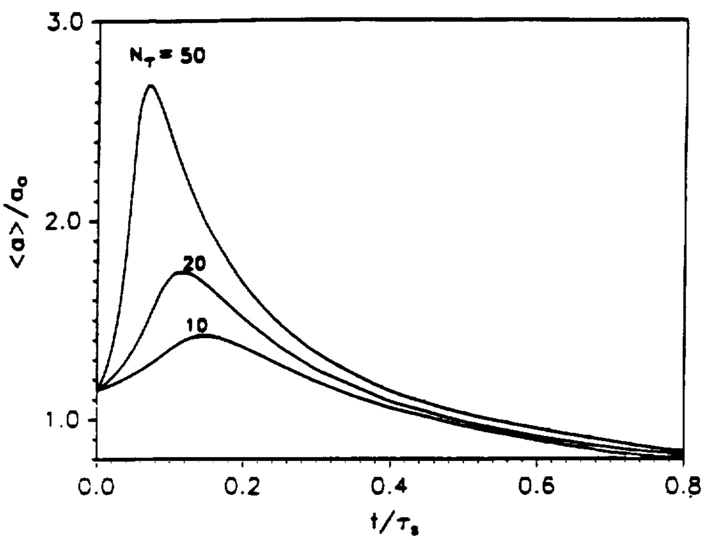

Fig. 2–Predicted time evolution of the average drop radius at $z/H = 0.5$ for a dispersion having $\hat{\mu}$=0.1 and $\hat{\sigma}$=0.2.

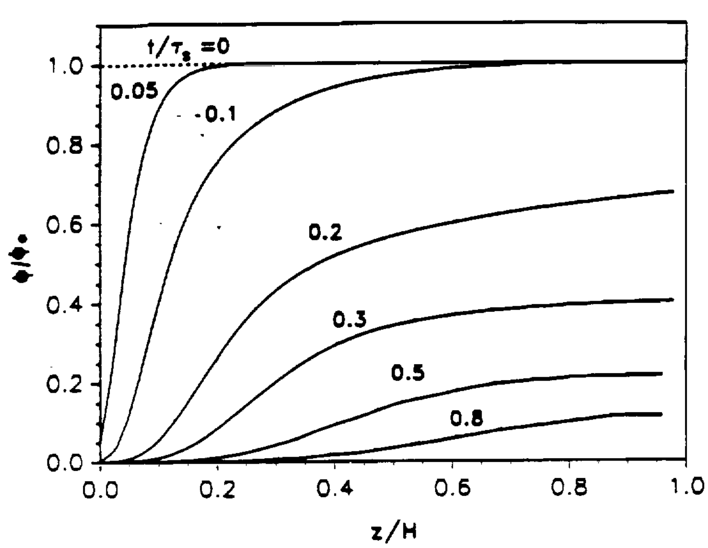

Fig. 3–Predicted variation of volume fraction with position at different times for a dispersion having $\hat{\mu} = 0.1$, $\hat{\sigma} = 0.2$, and $N_\tau = 20$.

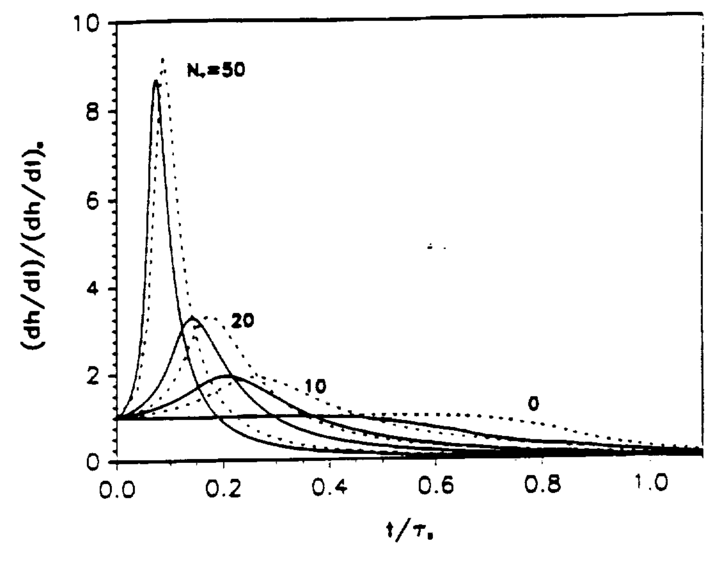

Fig. 4–Predicted rate of phase separation versus time for a dispersion having $\hat{\mu} = 0.1$, $\hat{\sigma} = 0.2$ (solid lines), $\hat{\sigma} = 0.1$ (dashed lines), $\phi_o = 0.05$ and different N_r in a container of finite depth.

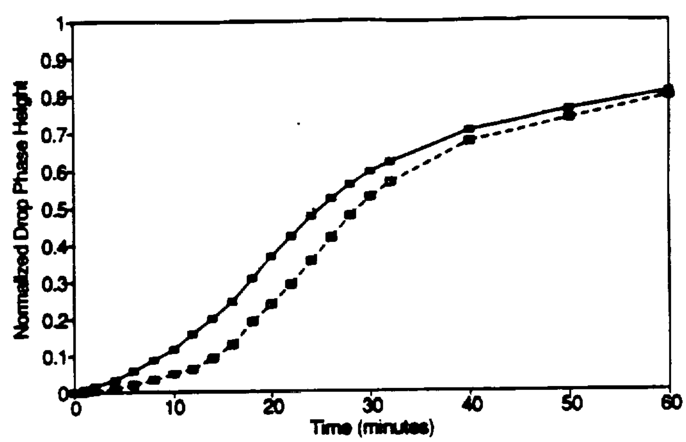

Fig. 5–Measured height of segregated minority phase (normalized by final height) versus time for 1,2-propanediol drops at $\phi_o = 0.034$ in dibutyl sebacate with H=10 cm (open squares) and H = 14.5 cm (closed squares).

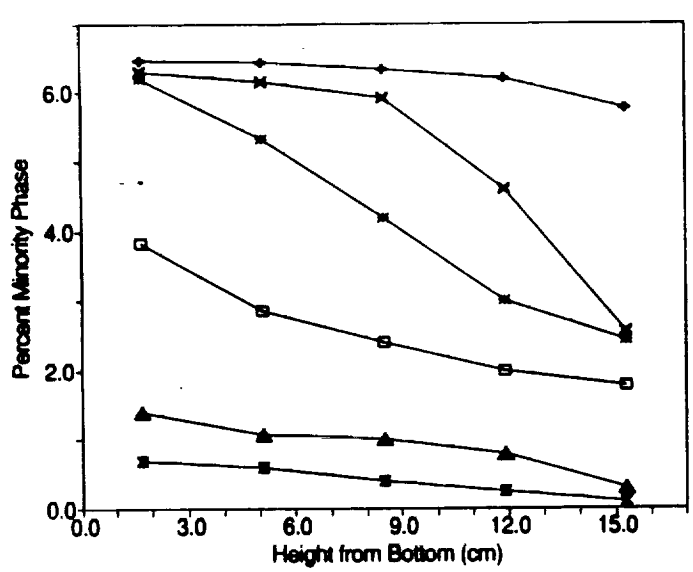

Fig. 6–Volume percentage of dispersed phase versus distance from the bottom of the curvette for dextran-rich drops at $\phi_o = 0.065$ in PEG-rich continuous phase with H = 17 cm at t = 15, 30, 45, 60, 120, and 240 min (top to bottom).