Available online at www.sciencedirect.com
SCIENCE DIRECT®
PERGAMON
International Journal of Multiphase Flow 29 (2003) 1101–1116
International Journal of Multiphase Flow
www.elsevier.com/locate/ijmulflow

Appendix 4: Report of study group on microphysics ☆

Jean-Marc Delhaye [a,*], John B. McLaughlin [b]

[a] *Department of Mechanical Engineering, Clemson University, Clemson, SC 29634-0921, USA*
[b] *Department of Chemical Engineering, Clarkson University, Potsdam, NY 13699-5705, USA*

Abstract

This Report outlines scientific issues that involve microscopic phenomena in multiphase flows. A common theme is the need to understand the coupling between molecular scale phenomena and macroscopic phenomena. Phenomena to be discussed include boiling nucleation, contact line motion, flow regimes in microchannels, breakup and coalescence of fluid particles and jets, atomization and sprays, and the effects of surface-active molecules and drag-reducing polymers.

1. Introduction

The coupling between molecular and macroscopic phenomena is an important feature of many multiphase flows. For example, it is well known that relatively small concentrations of surfactants can promote the breakup of bubbles or drops in turbulent flows. However, there is also experimental evidence that some surfactants have the opposite effect. These phenomena are important since, for example, they affect the size distribution of bubbles in chemical reactors such as fermenters. There is no quantitative model that can predict whether a given surfactant will increase or decrease the average bubble diameter and the effect of the concentration of the surfactant on the bubble.

The difficulty in developing such models is due to: (1) the complexity of the macroscopic flows; (2) the lack of reliable molecular scale models that can describe the behavior of complex molecules; and (3) the incomplete understanding of interfacial chemistry and physics that is relevant

---

☆ Members of the Study Group on Microphysics in the Workshop on Scientific Issues in Multiphase Flow (May 7–9, 2002, Champaign-Urbana, IL) are Jean-Marc Delhaye (chair), John McLaughlin (co-chair), Vijay Dhir, Truc-Nam Dinh, Mostafa Ghiaasiaan, Gad Hetsroni, Juan Lasheras, Ellen Longmire, Rolf Reitz, Peter C. Wayner.

[*] Corresponding author.

E-mail addresses: delhaye@clemson.edu (J.-M. Delhaye), jmclau@clarkson.edu (J.B. McLaughlin).

0301-9322/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0301-9322(03)00082-X

for multiphase flows. The macroscopic flows are typically turbulent and involve extremely complex, time-dependent interfacial shapes. This behavior may be even more complicated in microchannels in which the flow regimes may be qualitatively different than in larger channels. Even if one considers only the macroscopic length scales, large Reynolds number flows can easily span 3 or 4 orders of magnitude in eddy sizes.

In many situations, the motion of contact lines is important. For example, let us consider the motion of a drop on a smooth surface in the absence of phase change. One can describe the motion of the liquid inside most of the drop with the Navier–Stokes equation. However, there is a breakdown of continuum theory near the contact line. In this region, conventional theory would predict a singularity. Several researchers have argued that the no-slip boundary condition at the liquid–solid interface should be relaxed near the point of contact and replaced with a given slip boundary condition. This introduces an additional parameter, involving the ratio of a molecular length scale to the drop radius, into the mathematical description of the problem. However, recent experiments involving rapid condensation of steam onto surfaces with wettability gradients (Daniel et al., 2001) indicate that the motion of a drop can be dramatically different from its motion in the absence of condensation. To understand this phenomenon as well as others to be discussed later, significant improvements in the understanding of the effects of condensation and evaporation on the motion of contact lines are needed. A related issue is the phenomenon of contact line pinning by chemical impurities or roughness on solid surfaces.

Heterogeneous nucleate boiling on solid surfaces is another area in which a better understanding of surface chemistry and physics is needed. Conventional theories focus on the effects of small cavities on the nucleation of bubbles. However, when one considers nucleate boiling on extremely smooth surfaces, other effects may be important. Specifically, if one considers the boiling of water or other highly polar liquids on smooth surfaces, there is some evidence that small hydrophobic "islands" on the surface play an important role in nucleating bubbles. There are a number of intriguing observations of the effects of various treatments that require a better understanding before one can reliably predict the performance of smooth heater surfaces.

The expression "microphysics" may also be understood to include phenomena that, while strictly macroscopic, involve phenomena that are qualitatively different from those that are observed in traditional engineering systems. In the field of multiphase flows, microchannels provide an important illustration of this notion. In a microchannel, phenomena such as interfacial tension and wettability play a far more important role than in conventional channel flows. Associated with this are flow regimes such as "froth flow" that have no counterpart in larger channels. There are important issues, such as the influence of sharp corners and the effects of wettability of surfaces, that must be understood before one can take full advantage of microchannels in numerous heat transfer and other applications.

One tool that may be useful in addressing some of the above issues is the molecular dynamics (MD) simulation. MD simulations have improved with the advances in computational power since the early 1960's. Early models considered two-dimensional hard disks. Later improvements incorporated attractive forces and three-dimensionality. Recent advances have included sophisticated models of polar molecules, including water (da Rocha et al., 2001). Such techniques are very promising for future work in several areas of multiphase flow science.

Several experimental tools have strong potential. These include particle image velocimetry (PIV), infrared thermometry, X-ray radiography, ultraviolet fluorescence, atomic force microscopy, scanning electron microscopy, X-ray diffraction spectroscopy, and others that are discussed in the papers that are referenced in this Report.

In what follows, a set of critical scientific issues in this area of research will be elaborated.

2. Critical scientific issues

2.1. Boiling nucleation

The nucleation of bubbles may occur either homogeneously or heterogeneously. In homogeneous nucleation, the bubbles appear spontaneously, without pre-existing interfaces, in the bulk of the liquid or on the wall. One would expect this to occur at the location of the spinodal curve, which is the locus of the minima of isotherms on the pressure-specific volume thermodynamic diagram. In most cases, the homogeneous nucleation temperature is approximately 0.9 T_c, where T_c is the critical temperature.

In practice, heterogeneous nucleation is more important than homogeneous nucleation because the superheats associated with heterogeneous nucleation are much smaller than those for homogeneous nucleation. Heterogeneous nucleation is generally associated with small cavities that contain trapped air or other non-condensable gases or vapor and they have sizes that are much larger than the critical radius for nucleation (Dhir, in press). Fig. 1 shows the nucleation of bubbles on an artificial cavity on the surface of a silicon wafer. The cavity has a square cross section with a side equal to 10 μm, and it is 100 μm deep. The cylinders in the picture are thermocouples; they are 1.58 mm in diameter.

The volume of gas trapped in a cavity depends on the magnitude of surface tension, the contact angle, the shape of the cavity, and the experimental conditions such as system pressure, liquid temperature, temperature of the heated surface, and dissolved gas content in the liquid. The wall temperature at which nucleate boiling occurs depends strongly on the availability of cavities with trapped air (unflooded cavities). Thus, as unflooded cavities become fewer and their size decreases, one might expect the heterogeneous nucleation temperature to approach the

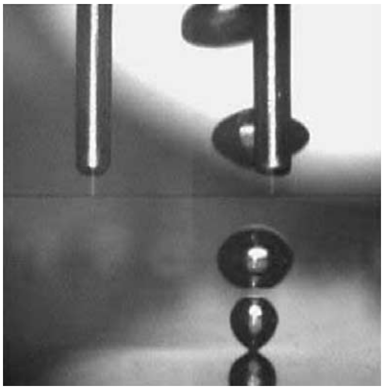

Fig. 1. Nucleation of vapor bubbles on an artificial cavity. (Courtesy of V. Dhir.)

homogeneous nucleation temperature. To predict the number of active sites on a heated surface, one must know the number and size of cavities with trapped gas. By minimizing the Helmholtz free energy of a system involving the liquid–gas interface in the cavity, one can develop a criterion (Wang and Dhir, 1993a,b) that a cavity will trap gas if the contact angle, ϕ, is greater than the minimum cavity angle, $\psi_{\min}$. For simple shapes, such as spherical or conical cavities, it is feasible to use this criterion. However, for a commercial surface, it would be necessary to have a knowledge of the size and shape of all cavities present on the surface in order to apply the above criterion.

It has been suggested (Mizukami, 1975; Nishio, 1985; Wang and Dhir, 1993a,b) that the instability of the gas/vapor nuclei in a cavity determines the incipience superheat. The vapor nucleus is stable if the curvature of the interface increases with an increase in vapor volume. Otherwise, the vapor bubble nucleus is unstable. Using this criterion, one may obtain an expression for the incipience superheat. The applicability of this criterion to copper surfaces of different wettabilities has been demonstrated (Wang and Dhir, 1993a,b) using water as the test liquid. The wettability was varied by oxidizing the surface.

The most difficult task is to predict the density of active nucleation sites. The active nucleation sites not only determine the phase structure adjacent to the heated surface, but also determine the mechanisms that contribute to the total heat transfer from the wall. The wall heat flux split between the liquid and vapor phases is also strongly influenced by the activity that takes place at a nucleation site. The following issues require further investigation:

- The physics of the process of entrapment in cavities of various sizes and shapes with advancing and receding interfaces, including the role of surface wettability.
- The effect of dissolved gases in the liquid on nucleation at the wall.
- The effect of absence of dissolved gases on the scavenging of trapped gas in the cavities.
- The behavior of the trapped gas–liquid interface during heating and up to the evolution of the embryo into a bubble.
- The activation/deactivation of nucleation sites due to temperature fluctuations in the solid and due to advancing and receding liquid–vapor interfaces over the cavities.
- The effect of various system variables such as pressure, liquid temperature, and flow velocity and properties of the solid on the above processes.

Another set of issues pertain to boiling nucleation on smooth surfaces. On such surfaces, the pre-existing nuclei (PEN) theory is not helpful. Experiments on nanoscopically smooth surfaces have been reported (Theofanous et al., 2002). On such surfaces, molecular scale surface inhomogeneities may be expected to play an important role in heterogeneous nucleation. Specifically, the BETA experiment (Dinh and Theofanous, in press) shows that nucleation of bubbles on titanium film heaters occurs at superheats equal to 5–7 K. The surfaces are 150 nm thick and have rms surface roughnesses equal to 4 nm. These observations are not consistent with the PEN theory and indicate the need to account for molecular scale phenomena. Further evidence for this idea is supplied by aging experiments in which the density of nucleation sites dramatically increases and one also observes an increase in the density of oxide islands on the surface. These experiments and others (Dinh and Theofanous, in press) provide motivation for another set of issues that require investigation:

- Based on the fact that heterogeneous nucleation occurs even on nanoscopically smooth surfaces, there is a need for new mechanistic approaches for treatment of heterogeneous nucleation in boiling on heater surfaces.
- Characterization of a heater surface nanomorphology and chemistry is necessary for a basic understanding of heterogeneous nucleation sites.
- Control of the experimental conditions and use of advanced instrumentation, such as infrared thermometry, X-ray radiography, and ultraviolet fluorescence, that enable accurate identification of nucleation events at high spatial and temporal resolution are needed.
- It is important to understand the dynamics of thin films (disjoining pressure, contact line motion) on a complex, non-uniform microscopic substrate. Such a substrate may be composed of either a Frenkel island (a small hydrophobic patch) or a Kuni nucleus (a site where vapor begins to form a drop).
- In order to develop an understanding of boiling in microchannels, it is critical to develop a basic understanding of nucleate boiling under geometrical constraints.
- It is of practical importance to determine whether nucleation in pool boiling is a self-limited response of a self-organized system to the externally imposed heat flux.
- How does hydrophobicity affect nucleation on nanoscopically smooth, cavity-free surfaces, and how can one use such knowledge to pattern a heater surface to control the coolability limit in boiling?
- How does exposure to air affect nucleation on nanoscopically smooth, cavity-free heater surfaces?

2.2. Contact lines

The importance of contact line motion in boiling nucleation has been mentioned in the previous subsection. The intermolecular interactions in the three phase contact line region are also important in many other situations such as adsorption, spreading, evaporation, condensation, wetting, and stability. Even if one considers spreading or sliding of drops on surfaces under isothermal conditions, there are issues that are not well understood at the present time. For example (Chen et al., 1997), measurements of contact angles at length scales of order 10^{-2} mm have been made by PIV, video microscopy, and digital image analysis. The results of these studies underscore the difficulty of characterizing or even defining the contact angle. Theoretical ideas about the static and dynamic contact angle and the role of intermolecular forces have been proposed (de Gennes, 1985). However, at present, there are no direct experimental investigations of contact angles at the molecular scales.

A related issue is the phenomenon of contact line pinning. It has been speculated that pinning occurs when a moving contact line encounters a geometrical irregularity or a hydrophobic patch (de Gennes, 1985). However, there are no direct experimental tests of these ideas or quantitative models that can predict when pinning will occur.

Condensation and evaporation introduce additional issues that are poorly understood at present. For example, a recent study (Daniel et al., 2001) considered the condensation of steam droplets onto a chemically treated silicon surface. The chemical treatment consisted of exposing the surface to silane vapor from a drop suspended a short distance above the surface. The silane molecules adsorbed onto the silicon and caused it to become hydrophobic. As a result, a contact angle gradient was created that caused small water drops to migrate toward more hydrophilic regions. Normally, the migration speeds of small drops is O(1 mm/s). However, when steam condensed on the surface, the migration speeds were O(1 m/s). This dramatic increase in speed was, apparently, related to the condensation process; when the steam supply was shut off, the migration speeds of the drops on the surface quickly dropped to their normal values.

Although a few speculations have been made about the above phenomenon, there is no existing theory that can explain it. This points to the need to develop a deeper understanding of contact line motion that incorporates the effects of condensation and evaporation. Such understanding would find immediate application to heterogeneous nucleate boiling. A number of issues must be considered in developing theories for equilibrium and non-equilibrium situations (Wayner, in press). A detailed discussion may be found in several published papers (Potash and Wayner, 1972; Reyes and Wayner, 1996; Wayner, 1991, 1994, 1999; Zheng et al., in press). In general, improved modeling and experimental evaluation of the coupling of temperature and cohesion/adhesion on the transport processes in the contact line are needed. Insufficient emphasis has been placed on interfacial effects (both stress and temperature with polar and apolar systems) in very small systems and how they affect the macroscopically viewed transport processes. Innovative use of interfacial chemistry can lead to improved processes and devices.

In sum, the following issues should be pursued:

- A fundamental understanding of the significance the contact angle for both static and dynamic situations is needed.
- A quantitative theory of contact pinning that incorporates both surface chemistry and roughness should be developed.
- The relative importance (and coupling) or viscous stresses, slip, surface diffusion, molecular kinetics/dynamics, evaporation/condensation, excess free energy, contact angle, and film shape on contact line motion should be established.
- It is necessary to evaluate the adsorption isotherm for vapor/substrate systems of importance of phase change situations (e.g., boiling and rewetting of a hot surface) and connect these results with macroscopic phase change studies.
- For partially wetting systems, dropwise condensation should be studied and related to the apparent contact angle with heat flux, contact line motion, and the free energy of the thin film region.
- The importance/effect of surface chemistry relative to roughness on phase change processes should be established.
- It would be of great practical value to determine whether it is feasible to develop desirable and robust surfaces with surface chemistry.

2.3. Microchannels

Networks of microchannels with hydraulic diameters in the 100 μm to 1 mm range have the capability for sustaining very large transport process rates in small volumes and are expected to play an important role in future energy systems such as fuel cells. Two distinguishing features of microchannel flows in energy systems of interest are: (1) the importance of capillary effects relative to gravitational effects; and (2) the importance of fluid inertia (Ghiaasiaan, in press). One may characterize these effects by introducing the Eötvös (*Eo*), phase Weber (We_{LS}, and We_{GS}), and phase Reynolds numbers (Re_{LS} and Re_{GS}) for the channel, with the latter two parameters defined based on gas and liquid-phase superficial velocities. Detailed discussions of two-phase flow in microchannels may be found in a recent paper (Ghiaasiaan and Abdel-Khalek, in press).

The parameter *Eo* compares the importance of gravity and surface tension. For the flows of interest, $Eo < 1$, implying small buoyancy effect. However, as a consequence of the large flow velocities, the Reynolds and Weber numbers are both much larger than unity. Typical orders of magnitude are $Re > 1$ and $We \sim 10^2$. The significance of the large Weber number is that, unlike flow in porous media, inertia is important, and the liquid–gas interface can have complex topologies. The hydraulic diameter in these microchannels is typically smaller than the Laplace length scale, itself representing the order of magnitude of the interfacial wavelength associated with Taylor instability. The Taylor instability-driven interfacial phenomena, while crucial to many two-phase flow and change-of-phase processes in large channels, may thus be irrelevant to microchannels. Furthermore, velocity and temperature gradients in microchannels are much larger than those observed in large channels, leading to relative time and length scales, and relative magnitudes of interfacial forces that are different than large channels. Another difference between microchannel flows and macroscopic flows lies in the relative importance of contact line motion in the former systems. This effect, while present in macroscopic flows, is likely to be much more important in microchannels, in particular when heterogeneous nucleation and boiling phenomena are concerned.

Past experimental studies are limited in scope and detail. With respect to adiabatic two-phase flow, these studies indicate that all major and common two-phase flow regimes occur in microchannels. However, their details, and conditions leading to various regime transitions, are different than for large channels, and macroscale models and correlations often do poorly when compared to microchannel data. As an example, Fig. 2 shows plug-slug flow in a 1 mm tube.

Furthermore, forced flow boiling processes appear to be significantly different than in large channels, primarily due to the potentially different heterogeneous bubble nucleation and boiling processes in microchannels (Ghiaasiaan, in press).

The critical issues pertaining to microchannels may be organized into two categories: issues for adiabatic flows and issues for flow boiling. For adiabatic flows, the issues are as follows:

Fig. 2. Plug-slug flow in a 1 mm diameter tube flow. (Reprinted with permission from *Int. J. Multiphase Flow.*)

- Experimental data covering a reasonable range of channel sizes (below 1 mm, in particular); and fluid pairs other than air/water-like pairs, are needed. The effects of liquid/gas density and viscosity ratios, surface tension, and surface wettability, in particular need to be examined.
- Channel geometries that contain multiple sharp corners are likely to be used extensively in practical applications. Data relevant to these flow passages are scarce and inadequate, however. Wettability of sharp corners may be particularly important.
- Flow regime identification has primarily been based on visual and photographic methods, and that has lead to much confusion. Objective methods for flow regime identification, to complement visual and photographic methods, or replace them when the test channel is not transparent, are needed.
- Flow regime details need to be investigated. This is particularly important for froth and annular flow patterns where disagreement between data and macro scale models is greatest. Details of annular flow are also important for understanding dryout in microchannels.

For flow boiling, the issues are as follows:

- Heterogeneous nucleation and boiling phenomena in microchannels subject to forced flow, and the behavior of micro bubbles after they are released, are unknown. Trends in the available forced flow boiling data suggest that these processes may have significant differences with what is known about macroscale boiling. Resolution of these issues is essential for understanding the apparent anomalies in the microchannel boiling curves, and other aspects of microchannel behavior.
- The details of the annular flow regime, and the phenomenology of processes that contribute to dryout need to be systematically investigated. Once again, trends in the available microchannel dryout data suggest a drastically different phenomenology than what is known about dryout in macroscale.

2.4. Breakup and coalescence

Breakup and coalescence of fluid objects play a crucial role in a broad spectrum of multiphase flow processes. Important examples include (Hanratty, in press; Longmire, in press; Reitz, in press):

- evolution of the bubble size distribution in stirred tanks and bubble columns,
- drop size distribution in liquid emulsions,
- breakup of liquid jets and the formation of sprays,
- atomization of liquid layers in two-phase flows.

The stumbling blocks to major breakthroughs in the above issues include microphysics issues as well as issues covered by the other Workshop Thrust Groups. Therefore, while this section will focus on issues that are primarily microscopic in nature, some overlap with the Reports for the other Thrust Groups is inevitable.

Perhaps the most relevant issues pertaining to breakup and coalescence of fluid objects are the microscopic conditions at the points of breakup and coalescence. Breakup of drops and bubbles involves intermolecular forces acting at micro or nanoscales. For example, if one considers a highly deformed bubble in a liquid, breakup may occur if a sufficiently thin liquid neck forms between two portions of the bubble. When the neck is sufficiently thin, intermolecular forces between the liquid molecules cause the neck to pinch off and two child bubbles result. In this respect, bubble breakup is similar to the coalescence of liquid drops in a gas. In the case of liquid breakup, intermolecular forces acting at micro and nanoscales must be overcome to separate neighboring layers of molecules. While the importance of molecular scale phenomena is clear, there are no predictive criteria or models that can be used to obtain quantitative results.

The above issues are directly relevant to computer simulations of breakup and coalescence. Some computer simulations perform computational "surgery" to implement breakup or coalescence. Front tracking methods, which are relevant over a broad spectrum of flow Reynolds numbers (Nobari et al., 1996; Nobari and Tryggvason, 1996), and boundary element methods, which are relevant for small Reynolds numbers, fall into this category. Other methods, such as VOF, level set methods, the phase field and second gradient methods, and the lattice Boltzmann method (LBM) allow breakup and coalescence to occur automatically. Fig. 3 shows a lattice Boltzmann simulation of bubble breakup in homogeneous turbulence (Qian et al., submitted).

With any of the above simulation methods, the critical issue is accuracy. The VOF and Level-Set methods handle coalescence and breakup "automatically" when the resolution of a thin film (or a thread) becomes less than a grid space or so. In this respect, they are probably similar to the LBM. This results in a rupture that depends strongly on the resolution, and it is therefore possible that low resolution results are qualitatively (not just quantitatively) different from those obtained with finer resolution. In the front tracking method one can explicitly specify a rupture criterion that does not directly relate to the resolution. These issues are discussed in more detail in a recent publication (Tryggvason et al., 2001). Clearly, it is extremely important that experimental and theoretical criteria for breakup and coalescence should be established.

Another issue that is directly related to the above topic is the role of surface-active molecules on the above processes. It is well known that surfactants, even when present in relatively small concentrations, can strongly affect the coalescence or breakup of fluid objects. However, no predictive models are available. For example, consider the breakup and coalescence of bubbles in turbulent flows. This process has been studied (Walter and Blanch, 1986) by measuring the size distribution of bubbles in a turbulent pipe flow. It was found that the effects of surfactants on the maximum stable bubble size were complex. One might expect that, by decreasing the surface tension, the maximum stable bubble size would decrease. However, in some cases, Walter and Blanch found the opposite effect. They were able to establish a rough criterion based on molecular

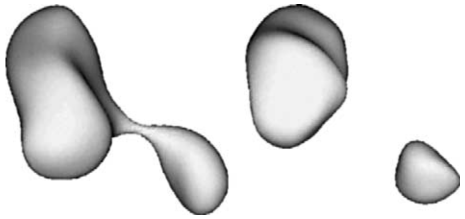

Fig. 3. A lattice Boltzmann simulation of bubble breakup in homogeneous turbulence.

weight. Surfactants of sufficiently small molecular weight always reduced the maximum stable bubble size, but surfactants with larger molecular weights increased the maximum stable bubble size when they were present in sufficiently small concentrations. It is not clear that one can generalize Walter and Blanch's findings to other surfactants. It is also not clear what causes the increase in the maximum stable bubble size in some cases. The increase may be related to the Marangoni stresses found in simulations of bubble deformation in axisymmetric strain flows (Stone and Leal, 1990). However, it must be pointed out that the simulations were restricted to Stokes flow, while the experiments involved bubble Reynolds numbers of $O(10^3)$. Also, the surfactant molecules were assumed to be insoluble in the liquid so that sorption kinetics were not considered in the simulations.

One can identify the following critical scientific issues pertaining to breakup and coalescence and related issues:

- Experiments and theoretical analyses are needed to establish rigorous criteria for the coalescence and breakup of fluid objects at the microscopic level. Without such criteria, current numerical simulation methods can, at best, be tested by indirect means.
- Experiments and molecular level simulations are needed to understand the role of surface-active molecules on breakup and coalescence.
- In coalescence, the macroscopic instabilities and events leading to rupture in real flows are not well characterized. For example, the individual effects of inertia, shearing, interfacial tension, and three-dimensional flow perturbations on the coalescence process are not well understood, especially in geometries where many "droplets" interact, such as dense sprays.
- It is important to develop theoretical frameworks that will enable one to couple macroscopic and microscopic behaviors into a physically meaningful and accurate model.
- For engine applications, the correlations used in collision and coalescence models need to be tested against fundamental experiments at high pressures since they come from sprays in entirely different regimes (rain drops and cloud physics).
- The relationship between drop breakup and drop shattering, and turbulence production and dissipation in sprays needs to be established.
- More experimental data is needed in order to improve wall impingement models. In particular, data on the secondary breakup of impinged drops is needed under high wall temperature ($T_w > 400$ K), gas temperature ($T_G > 700$ K) and density ($\rho > 20$ kg/m^3) conditions. More accurate models for the thickness of the wall film also need to be developed. Improved models should be able to model the spreading of a liquid film, and should account for the effect of wall wetting and liquid splashing.

2.5. Effects of surfactants on interfacial flows

In the previous section, it was pointed out that surfactants have a significant effect on breakup and coalescence phenomena. It is also well known that they strongly affect the rise velocity of bubbles and drops (McLaughlin, in press). For example, concentrations as low as 10^{-5} mol/m^3 of common surfactants can reduce the rise velocity of a 1 mm bubble by more than 50% (Zhang et al., 2001). This effect has been attributed to the formation of an immobilized surfactant cap on the bubble surface (Levich, 1962; McLaughlin, in press). Such changes not only affect bubble holdups in chemical reactors, but also dramatically reduce mass transfer rates (Lochiel and Calderbank, 1964). The observation of a significant enhancement of heat transfer in the pool boiling of surfactant solutions is also noteworthy (Hetsroni et al., 2001; Hetsroni and Mosyak, 1999). Clearly, these behaviors call into question the usefulness of simulations or models that do not consider the influence of surface-active materials on the behavior of systems with air–water interfaces.

Although it is well known that low concentrations of surfactants can have dramatic effects on simple two-phase flows, relatively little is known about their effects on complex two-phase flows. For example, there are numerous experimental results for the effects of surfactants on freely rising bubbles or on the damping of capillary waves, but relatively little is known about the effectiveness of surfactants in turbulent two-phase flows. A better understanding of the conformation, sorption kinetics, and effects of surfactants on interfaces would impact a large range of energy-related technologies including bioreactors, flotation and microflotation, enhanced oil recovery, sedimentation and filtration, and cleaning processes. The effects of surfactants on surface waves may also play a role in the sequestration of atmospheric carbon dioxide in the oceans because of their effect on capillary waves.

Many investigators (Chang and Franses, 1995) have modeled the sorption kinetics of surfactants onto interfaces with a two parameter model suggested by Langmuir. The parameters are the adsorption rate constant, β (m^3/mol-s), and the desorption rate constant, α (s^{-1}). The ratio of these constants may be determined by equilibrium measurements of the surface tension as a function of the concentration of surfactant. The actual values of the parameters are determined by dynamic surface tension measurements. It is known that the parameters depend on the surfactant concentration in the liquid, C (mol/m^3), as well as the surfactant concentration on the interface, Γ (mol/m^2). To model the effects of the adsorbed surfactant on the surface tension, γ, an equation of state is needed. For very small values of Γ, an ideal gas equation of state (e.g., Stone and Leal, 1990) is used. At larger concentrations, an equation of state (Frumkin, 1925) that involves a parameter, Γ_{m}, that represents the maximum possible surface concentration.

There are several issues that must be addressed in order to use the above modeling to describe moderate or high Reynolds number two-phase flows. First, the sorption rate constants are available only for a relatively small number of surfactants. Secondly, the sorption rate constants are known only in relatively small concentration ranges. These concentration ranges are dictated by the fact that, to obtain values of the sorption rate constants, one must perform experiments for conditions in which adsorption on the gas–liquid interface is the rate limiting step. In the past, such experiments were typically carried out at small Reynolds numbers and at fairly large concentrations of surfactant so that the liquid near the gas–liquid interface did not become depleted (which would make boundary layer mass transfer the rate limiting step). However, in many situations of interest, the Reynolds numbers are large and the concentrations of surfactant are much smaller than the concentrations for which experimental results for the sorption rate constants are available.

Recently, a possible solution to this problem has been suggested (Liao and McLaughlin, 2000; Wang, 2001). The idea is to measure the time-dependent rise velocity of a bubble in low concentration surfactant solutions and to compare the results with simulations that account for surfactant transport in the liquid and on the interface as well as sorption rate kinetics (Liao and McLaughlin, 2000). Measurements of bubble rise velocity for single bubbles in very dilute aqueous solutions of the non-ionic surfactant Triton X-100 show that the bubble achieves a maximum velocity that is close to the terminal velocity in pure water (Duineveld, 1995) before slowing down to its terminal velocity. Eventually, the rate of surfactant adsorption on the bubble surface becomes mass transfer limited (Zhang et al., 2001). However, at earlier times, sorption rate constants have a strong effect on the motion of the bubble. For example, during this initial period, bubbles in SDS solutions slow down an order of magnitude more gradually than in Triton X-100 solutions at the same molar concentration (Wang, 2001). Thus, by focusing on the first few seconds of the bubble's motion, one can observe differences attributable to the sorption kinetics. Preliminary results are available. For example, values for the sorption rate constants have been obtained for Triton X-100; previously, only lower bounds (at a much larger surfactant concentration) were available. It appears feasible to obtain results for other surfactants using the same approach.

A further complication is the effect of unsteadiness in the liquid phase. In the experiments discussed above, the only unsteadiness was that caused by the acceleration of the bubble. However, in situations of practical interest, the surrounding flow is likely to be turbulent as a result of stirring or processes involving other bubbles. This presents an additional challenge for modeling.

In sum, there are a number of scientific issues involving surfactants that should be addressed in order to make substantial progress in the understanding and modeling of two-phase flows:

- There is a need to obtain results for sorption kinetics rate parameters for surfactants for a wide range of concentrations.
- The usefulness of existing models of sorption kinetics in unsteady, high Reynolds number flows should be evaluated.
- The effects of surfactants on coalescence and breakup of bubbles or drops in turbulent two-phase flows involving bubbles or drops are only crudely understood. Careful experiments that can identify the various regimes of behavior are needed. For example, experiments with pairs of bubbles in motionless liquids suggest that, for "small" concentrations of surfactants, coalescence is inhibited by the adsorbed surfactants.
- The behavior of adsorbed surfactant molecules on the surfaces of bubbles in turbulent flows is not known. The surfactant cap model works well for bubbles or drops translating through motionless fluids, but it is not clear that such a model is useful for bubbles in turbulent flow. Do adsorbed surfactant molecules inhibit mass transfer in such situations?

2.6. Drag-reducing polymers

It is now established that the large-scale behavior of multiphase flows is dependent of small scale phenomena (Hanratty, in press). As our understanding of the microphysics improves, we have the opportunity to carry out basic studies in which methods for changing the behavior of multiphase flows are explored. One example is the use of structured tubes in heat transfer applications. However, most striking are recent experiments in which drag-reducing polymers were added to a gas–liquid flow.

These polymers were injected into a gas–liquid annular flow in a horizontal pipe. With mixture concentrations as low as 15 ppm, the violent annular flow could be changed into a stratified pattern with a relatively smooth interface and no entrainment. The explanation for this behavior is that the polymers destroy the disturbance waves. These waves are the loci at which atomization occurs; they also play an important role in causing the liquid to move up the walls of a horizontal pipe against the pull of gravity. More recent studies in Hanratty's laboratory have explored the influence of drag-reducing polymers on a highly agitated stratified flow for which the waves were so large that the interfacial drag was almost 20 times what would be observed for an interface without waves. The interfacial drag was greatly reduced, the liquid holdup was increased and, for increasing liquid flow rate, the transition to slug flow was delayed.

Experiments, such as these, show in a spectacular way that the macroscopic behavior of multiphase systems depends on small scale phenomena. They provide a test for our physical understanding and suggest new technological approaches.

A considerable literature exists on the influence of polymer additives on single phase flows. The number of investigations of their effect on gas–liquid flows is small (Rosehart et al., 1972; Otten and Fayed, 1971; Kang et al., 1997; Sylvester and Brill, 1976; Al-Sarkhi and Hanratty, 2001a,b). Decreases in the pressure drops are noted, but the most interesting aspect of these studies is the finding that flow patterns and wave patterns can be dramatically changed. A recent paper (Manfield et al., 1999) reviews the subject.

Polymers are found to destroy the turbulence in slugs. One of the consequences of this is that larger liquid flows are needed to initiate slugging. Slugs pick up liquid at their front and shed liquid at the back. If the shedding rate is greater than the pickup at the front, the slug becomes unstable. The increase in the critical liquid rate to generate slugs can be interpreted by an increase in the shedding rate in a reference frame moving with the velocity of the fluid in the slug, u_s. The back of a slug is pictured as the nose of a large bubble. The velocity of this bubble relative to the velocity of the fluid in the slug, V_B/u_s, determines the shedding rate. A number of investigators have suggested that V_B/u_s equals the ratio of the centerline velocity of the fluid in the slug to the average velocity (Woods and Hanratty, 1996). This gives $V_B/u_s \cong 1.2$ for a turbulent flow, in agreement with measurements of V_B. If the flow in the slug is laminar one could infer that $V_B/u_s \cong 1.5$. The change in V_B/u_s agrees with observations of an increase in the critical liquid height needed to generate slugs when polymers are added.

Another effect of polymers is the damping of waves. This gives rise to the destruction of disturbance waves. This, in turn, causes a change from an annular to a stratified flow, because atomization of the liquid layer ceases and because the ability of the liquid to climb up the wall is diminished. Polymers have also been observed to decrease the interfacial drag at the interface by changing wave properties. This, in turn, contributes to an increase in the liquid holdup.

The role of polymers in damping waves is not understood. One possibility is that elongated polymers at the interface introduce tensile stresses close to the interface and, therefore, have the same affect as increasing surface tension.

3. Conclusion

The issues summarized in this Report are significant scientific challenges. A common theme is the need to bridge the gap between the nanoscale, which can be studied with MD simulations, and the micrometer scale, which in many cases, sets the limit on currently available experimental techniques, such as PIV, that can elucidate macroscopic fluid motion and phase distributions. The following recommendations emerged from the Workshop:

- An approach that requires equal contributions of experimentation, simulation, and modeling is needed to fill the gap (modeling) between nanoscale (simulation) and microscale (experimentation).
- The microphysics area is perhaps the most challenging area of the four focus groups because the tools for bridging the gap from nanoscale to microscale are the least developed.
- Collaborative research involving academia, the DOE laboratories, and industry should be strongly encouraged because of the complexity and scope of problem.
- Sharing of computer simulation programs and experimental databases should be encouraged.

References

Al-Sarkhi, A., Hanratty, T.J., 2001a. Effect of drag reducing polymers on annular gas–liquid flow in a horizontal pipe. Int. J. Multiphase Flow 27, 1151–1162.

Al-Sarkhi, A., Hanratty, T.J., 2001b. Effect of pipe diameter on the performance of drag-reducing polymers in annular gas–liquid flows. Trans. Inst. Chem. Eng. 79, 402–408.

Chang, C.-H., Franses, E.I., 1995. Adsorption dynamics of surfactants at the air/water interface: a critical review of mathematical models, data, and mechanisms. Colloid. Interface. A: Physicochem. Eng. Aspect 100, 1–45.

Chen, Q., Ramé, E., Garoff, S., 1997. The velocity field near moving contact lines. J. Fluid Mech. 337, 49–66.

Daniel, S., Chaudhury, M.K., Chen, J.C., 2001. Fast drop movements resulting from the phase change on a gradient surface. Science 291, 633–636.

da Rocha, R.P., Johnson, K.P., Westacott, R.E., Rossky, P.J., 2001. Molecular structure of the water-supercritical CO_2 interface. J. Phys. Chem. B 105, 12092–12104.

de Gennes, P.G., 1985. Wetting: statics and dynamics. Rev. Modern Phys. 57, 827–863.

Dinh, T.N., Theofanous, T.G., in press. Nucleation phenomena in boiling: puzzles, issues, and avenues. Proceedings of the Workshop on Scientific Issues in Multiphase Flow, University of Illinois at Urbana-Champaign, May 7–9, Multiphase Science and Technology.

Dhir, V.K., in press. Nucleation site density. Proceedings of the Workshop on Scientific Issues in Multiphase Flow, University of Illinois at Urbana-Champaign, May 7–9, Multiphase Science and Technology.

Duineveld, P.C., 1995. The rise velocity and shape of bubbles in pure water at high Reynolds numbers. J. Fluid Mech. 292, 325–332.

Frumkin, A., 1925. Surface tension curves of the higher fatty acids and the equation of condition of the surface layer. Phys. Chem. 116, 466–484.

Ghiaasiaan, S.M., in press. Gas–liquid two-phase flow and boiling in microchannels. Proceedings of the Workshop on Scientific Issues in Multiphase Flow, University of Illinois at Urbana-Champaign, May 7–9, Multiphase Science and Technology.

Ghiaasiaan, S.M., Abdel-Khalek, S.I., in press. Two-phase flow in microchannels. Advances in Heat Transfer 34, 145–254, Multiphase Science and Technology.

Hanratty, T.J., in press. Contributions to the thrust group on the microphysics of multiphase flows. Proceedings of the Workshop on Scientific Issues in Multiphase Flow, University of Illinois at Urbana-Champaign, May 7–9, Multiphase Science and Technology.

Hetsroni, G., Mosyak, A., 1999. Thermal pattern and boiling enhancement of water containing cationic surfactants. In: Lerner, M., Mewes, D. (Eds.), Applied Optical Measurements. Springer-Verlag, Berlin.

Hetsroni, G., Zakin, J.L., Lin, Z., Mosyak, A., Poncallo, E.A., Rosenblit, R., 2001. The effect of surfactants on bubble growth, wall thermal patterns and heat transfer in pool boiling. Int. J. Heat Mass Transfer 44, 485–497.

Kang, C., Vancko, R.M., Green, A., Kern, H., Jepson, W., 1997. Effect of drag-reducing agents in multiphase pipelines. J. Energy Resour. Technol. 120, 15–19.

Levich, V.G., 1962. Physicochemical Hydrodynamics. Engelwood Cliffs, Prentice-Hall.

Liao, Y., McLaughlin, J.B., 2000. Bubble motion in aqueous surfactant solutions. J. Colloid Interface Sci. 224, 297–310.

Lochiel, A.C., Calderbank, P.H., 1964. Mass transfer in the continuous phase around axisymmetric bodies of revolution. Chem. Eng. Sci. 19, 471–484.

Longmire, E., in press. The importance of micro and macro scales in breakup and coalescence. Proceedings of the Workshop on Scientific Issues in Multiphase Flow, University of Illinois at Urbana-Champaign, May 7–9, Multiphase Science and Technology.

Manfield, P.D., Lawrence, C.J., Hewitt, G.F., 1999. Drag reduction with additives in multiphase flow: a literature survey. Multiphase Sci. Technol. 11, 197–221.

McLaughlin, J.B., in press. Numerical simulation of bubble motion in water. J. Colloid and Interface Science 184, 614–625, Multiphase Science and Technology.

McLaughlin, J.B., in press. The hydrodynamics of two-phase flows with surfactants. Proceedings of the Workshop on Scientific Issues in Multiphase Flow, University of Illinois at Urbana-Champaign, May 7–9, Multiphase Science and Technology.

Mizukami, K., 1975. Entrapment of vapor in re-entrant cavities. Lett. Heat Mass Transfer 2, 279–284.

Nishio, S., 1985. Stability of pre-existing vapor nucleus in uniform temperature field. Trans. Jpn. Soc. Mech. Engr., Ser. B 54–503, 1802–1807.

Nobari, M.R., Jan, Y.-J., Tryggvason, G., 1996. Head-on collision of drops—a numerical investigation. Phys. Fluids 8, 29–42.

Nobari, M.R.H., Tryggvason, G., 1996. Numerical simulations of three-dimensional drop collisions. AIAA J. 34, 750–755.

Otten, L., Fayed, A.S., 1971. Pressure drop and drag-reduction in two-phase non-Newtonian slug flow. Can. J. Chem. Eng. 54, 111–114.

Potash Jr., M., Wayner Jr., P.C., 1972. Evaporation from a two-dimensional extended meniscus. Int. J. Heat Mass Transfer 15, 1851–1863.

Qian, D., Sankaranarayanan, K., Sundaresan, S., Kontomaris, K., McLaughlin, J.B., 2002. Lattice Boltzmann simulations of deformable bubbles in homogeneous turbulence. Chem. Eng. Sci. (submitted).

Reitz, R., in press. Atomization and droplet breakup, collision/coalescence and wall impingement. Proceedings of the Workshop on Scientific Issues in Multiphase Flow, University of Illinois at Urbana-Champaign, May 7–9, Multiphase Science and Technology.

Reyes, R., Wayner Jr., P.C., 1996. A Kelvin–Clapeyron adsorption model for spreading on a heated plate. ASME J. Heat Transfer 118, 822–830.

Rosehart, R.G., Scott, D., Rhodes, E., 1972. Gas–liquid slug flow with drag-reducing polymer solutions. AIChE J. 18, 744–750.

Stone, H.A., Leal, L.G., 1990. The effects of surfactants on drop deformation and breakup. J. Fluid Mech. 220, 161–186.

Sylvester, N.D., Brill, J.P., 1976. Drag-reduction in two-phase annular mist flow of air and water. AIChE J. 22, 615–617.

Theofanous, T.G., Tu, J.P., Dinh, A.T., Dinh, T.N., 2002. The boiling crisis phenomenon. Part I: nucleation and nucleate boiling heat transfer. Exp. Thermal Fluid Sci. 26, 775–792.

Tryggvason, G., Bunner, B., Esmaeeli, A., Juric, D., Al-Rawahi, N., Tauber, W., Han, J., Nas, S., Jan, Y.-J., 2001. A front tracking method for the computations of multiphase flow. J. Comput. Phys. 169, 708–759.

Walter, J.F., Blanch, H.W., 1986. Bubble break-up in gas–liquid bioreactors: Break-up in turbulent flows. Chem. Eng. J. 32, B7–B17.

Wang, J., 2001. Experimental study of bubble motion and dissolution in dilute surfactant solutions. M.S. thesis, Clarkson University, Potsdam NY.

Wang, C.H., Dhir, V.K., 1993a. Effect of surface wettability on active nucleation site density during pool boiling of saturated water. J. Heat Transfer 115, 659–669.

Wang, C.H., Dhir, V.K., 1993b. On the gas entrapment and nucleation site density during pool boiling of saturated water. J. Heat Transfer 115, 670–679.

Wayner Jr., P.C., 1991. The effect of interfacial mass transport on flow in thin liquid films. Colloid. Surface. 52, 71–84.

Wayner Jr., P.C., 1994. Thermal and mechanical effects in the spreading of a liquid film due to a change in the apparent finite contact angle. ASME J. Heat Transfer 116, 938–945.

Wayner Jr., P.C., 1999. Intermolecular forces in phase-change heat transfer: 1998 Kern award review. AIChE J. 45, 2055–2068.

Wayner, P.C., Jr., in press. The physics of the contact line region of non-isothermal systems. Proceedings of the Workshop on Scientific Issues in Multiphase Flow, University of Illinois at Urbana-Champaign, May 7–9, Multiphase Science and Technology.

Woods, B.D., Hanratty, T.J., 1996. Relation of slug stability to shedding rate. Int. J. Multiphase Flow 22, 809–828.

Zhang, Y., McLaughlin, J.B., Finch, J.A., 2001. Bubble velocity profile and model of surfactant mass transfer to bubble surface. Chem. Eng. Sci. 56, 6605–6616.

Zheng, L., Wang, Y.-X., Plawsky, J.L., Wayner, P.C., Jr., in press. Langmuir.