A Course on Fluid Interfaces

INTERFACIAL PHENOMENA

JOHN BERG
University of Washington
Seattle, Washington 98105

A WIDE VARIETY of topics involving fluid interfaces have, in the minds of chemical engineers, begun to coalesce into a single area of study which might be called "interfacial phenomena". This is occurring primarily for two reasons: first, the increasing recognition of the importance of interfacial effects in chemical engineering practice, and second, the increasing neglect of interfacial topics in conventional course sequences in chemistry and physics. These it seems are reasons not unlike those which gave birth to a unified study of the transport phenomena in chemical engineering.

The diversity of problems in the realm of interfacial phenomena is staggering. Space would not permit an attempt at a complete listing, but a small sample might include: wetting, spreading, foaming, colloid stability, sedimentation, interfacial turbulence, cellular convection, micelle formation, solubilization, detergent action, nucleation, flow through porous media, lung mechanics, structure of cell membranes, reactions in monolayers, evaporation suppression, adhesion, lubrication, mechanics of bubbles and drops, fluid phase catalysis, meniscus stability, adsorption kinetics and equilibria, surface rheology, active transport, and electrical double layers.

One feature which most interface problems have in common with each other is that, in addition to being problems in interfacial phenomena, they are also problems in one or more presently recognized fields of study, such as hydrodynamics, thermodynamics, statistical mechanics, physiology, electro-chemistry, etc. The resultant "crazy-quilt" nature of the subject of interfacial phenomena is evident in such books as Davies and Rideal (4), Adamson, (2), and Osipow, (9). With the partial exception of Davies and Rideal, a feature which most "comprehensive" books on the subject have in common is that they are written from the chemists' point of view. They often neglect topics of vital interest to the chemical engineer, particularly those involving the fluid mechanics of interfaces and the consequent effects on heat and mass transfer. This material must be gathered from the relatively recent chemical engineering literature.

John Berg was educated at Carnegie Tech (B.S.) and University of California, Berkeley (Ph.D. '64). His research interests are in interfacial phenomena, in particular, the investigation of thermodynamic and transport properties of multicomponent interfaces, surface tension driven flows, and the surface chemistry of the lung. He is presently an associate professor at the University of Washington.

The problem facing one who would construct a course on interfacial phenomena for chemical engineers is to formulate the essential skeleton of fundamentals common to all fluid interface studies and to flesh-out this skeleton with sufficient examples to illustrate the principles. The pitfall to avoid is the presentation of a parade of examples with insufficient attention to the common ground between them.

SUMMARY OF PRESENT COURSE

A GRADUATE LEVEL course in Interfacial Phenomena is offered by the author at the University of Washington in alternate years and has thus far been given in the Spring quarters of 1968 and 1970. The course requires one quarter each of graduate level thermodynamics and fluid mechanics as prerequisites. Many of the problems of interfacial phenomena provide excellent opportunities to combine these generally non-intersecting disciplines. Although the specific content of the course differed significantly in its first and second offerings, and will change yet again in its subsequent offerings, a skeletal outline is presented in Table I. The course content is necessarily flexible to permit incorporation of the most recent research results obtained both in our

TABLE I
TOPICAL OUTLINE OF COURSE IN INTERFACIAL PHENOMENA

I. Surface Tension and Capillary Statics (2, ch. 1; 5, ch. 1)
   A. The concept of surface tension; the "membrane model"
   B. The equation of Young and Laplace
   C. Meniscus configurations and contact angles. (3, ch. 5)
   D. Measurement of static surface tension (1, ch 9)
   E. Measurement of dynamic surface tension
   F. Stability of static meniscii (10)
   G. The effect of curvature on the thermodynamic properties of bulk phases. (5, chs. 15-16)
II. The Thermodynamics of Capillary Systems (5, chs. 1-7)
   A. Definition of simple capillary systems
   B. The Gibbs dividing surface
   C. Relative adsorption and its direct measurement
   D. First Law calculations for capillary systems; surface tension of pure components (5, ch. 11)
   E. Fundamental equations for capillary systems
   F. The Gibbs adsorption equation
III. Thermodynamic Properties of Some Important Capillary Systems
   A. Surface tension of simple solutions; the monolayer model (5, chs. 12-13)
   B. Solutions of non-colloidal electrolytes
   C. Solutions of surface active agents (1, ch. 3; 9, chs. 8-9)
   D. Monolayers of insoluble surfactants (1, ch. 2; 6; 7)
   E. A general phase rule for capillary systems (5, ch. 6)
IV. Capillary Dynamics (8, chs. 7-8)
   A. Boundary conditions at fluid interfaces
   B. The Newtonian fluid interface
   C. Surface transport properties (4, chs. 4-5)
   D. Case study of circulating drops and bubbles
   E. Case study of cellular convection and interfacial turbulence

group and elsewhere. No textbook is followed, but copious use of references is made. A few of the principle ones are inserted by number into the outline below and listed in Table II.

I. Capillary Statics

THE FIRST MAJOR area examined is "capillary statistics", i.e. the determination of static equilibrium configurations of fluid interfaces and the forces they exert on solids in contact with them. Following a preliminary discussion of the molecular nature of transition regions between bulk phases, the 'membrane model" of the mobile interface is presented. The position of the "membrane" (the "surface of tension") and the value of the surface tension, σ, are chosen to make the model mechanically equivalent to the complex layer which is actually the interface. The model leads to the Young-Laplace equation: $\Delta p = 2\sigma\kappa_m$, where Δp is the pressure difference across the interface and κ_m its mean curvature. Following a discussion of the geometry of surfaces in space, the derivation is presented from both the force-balance and variational points of view. The force-balance derivation, in which the surface curvature is written as $1/r_1 + 1/r_2$, the sum of the two plane curvatures, has a simple physical appeal and lends itself well to the consideration of simpler special cases such as surfaces or axial or bilateral symmetry. The variational derivation can readily be extended (by examining the *second* variation of the systems' total potential energy) to a consideration of problems of meniscus stability.

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The most important application of capillary statics is to the measurement of equilibrium surface tension. This is accomplished through the measurement of the position or shape of the fluid interface or of the force it exerts on a solid object imbedded in it. The capillary rise, maximum

TABLE II.
SOME TEXTUAL REFERENCES ON INTERFACIAL PHENOMENA

1. Adam, N. K., "The Physics and Chemistry of Surfaces," Dover (1968) (1941 edition).
2. Adamson, A. W., "Physical Chemistry of Surfaces," Interscience (1967).
3. Bickerman, J. J., "Surface Chemistry for Industrial Application," Academic Press (1947).
4. Davies, J. T. and E. K. Rideal, "Interfacial Phenomena," Academic Press (1961).
5. Defay, R., I. Prigogine, A. Bellemaus and D. H. Everett, "Surface Tension and Adsorption," Longmans (1966).
6. Gaines, G. L., "Insoluble Monolayers at Liquid-Gas Interfaces," Interscience (1966).
7. Harkins, W. D., "The Physical Chemistry of Surface Films," Reinhold (1952).
8. Levich, V. G., "Physicochemical Hydrodynamics," Prentice-Hall (1962).
9. Osipow, L. I., "Surface Chemistry," Reinhold (1962).
10. Satterlee, H. M. and W. C. Reynolds, "The Dynamics of the Free Liquid Surface," NSF Tech. Rep. LG-2 (1964).

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bubble pressure, drop weight and Wilhelmy slide methods are examined in some detail, and computer solutions of the Young-Laplace equation are used where applicable. Although not strictly studies in capillary statics, two methods for measurement of "dynamic" (i.e., time-dependent) surface tension are also described at this point: the oscillating elliptical jet and the contracting circular jet.

The unit is concluded with a discussion of the effect of curvature on the thermodynamic properties of bulk phases, in particular the altered vapor pressure of liquids in small capillaries or as fine droplets and the altered solubility of finely divided solids or finely dispersed liquids. The Young-Laplace equation gives the relationship between the pressure difference and curvature while the usual Poynting factor gives the effect of pressure change on the fugacity of the liquid or solid in question.

II. Thermodynamic Framework

THE SECOND PART of the course deals with the classical thermodynamics of capillary systems per se. A "simple capillary system" is defined as a pair of simple bulk phases together with the interface between them. Such a system is subject to p-V work associated with both the bulk phase parts and σ-A work associated with the interface. A state postulate is formulated for such systems in "partial equilibrium", as defined by Defay, et al (5). The system is taken to be in internal thermal and mechanical equilibrium (as defined by the Young-Laplace equation) but not necessarily in equilibrium with respect to chemical reactions or adsorption of components from the bulk phases to the interface. In order to define the amounts of adsorption of the various components, as well as other extensive properties to be associated with the interface itself, a model of the capillary system must be employed, such as that of the Gibbs dividing surface. The interface is replaced with a geometrical surface and the bulk phase portions of the system are assumed homogeneous up to this surface. Requiring thermodynamic equivalence between the actual system and the model defines quantities to be associated with the dividing surface as "surface excesses". The formal thermodynamics of capillary systems is developed using the Gibbs model, but the Guggenheim model (in which the interface is treated as a region of finite thickness, across which properties vary) and the monolayer model (in which the interface is treated as a single monolayer of molecules whose composition differs from that of both bulk phases) are also used in subsequent applications. The formulation based upon the Gibbs model is of course rigorous, but the surface excesses it defines are highly sensitive to the dividing surface location, which for plane surfaces is indeterminate. Therefore, *relative* adsorptions, whose values are invariant with respect to dividing surface location, are used. The cornerstone of the thermodynamics of capillary systems is the Gibbs adsorption equation, which provides a rigorous equilibrium relationship between relative adsorptions, surface tension, and bulk phase chemical potentials.

III. Thermodynamic Properties

USING THE FORMAL thermodynamics developed above, the surface properties of a number of types of systems are investigated. The study of solutions of non-surfactant, non-electrolyte solutes is based primarily on the monolayer model. Equating chemical potentials of all components between the surface monolayer and the bulk phase leads to the set of Butler equations:

$$\sigma = \sigma_i + \frac{RT}{a_i} \ln \frac{\gamma_i^\sigma X_i^\sigma}{\gamma_i \; X_i}$$

where σ is thesurface tension of the solution, σ_i that of pure component i, a_i the molar area of i in the surface, and $V_i^\sigma X_i^\sigma$ and $\gamma\, X$ the activities of component i in the surface and substrate, respectively. Ideal, regular, athermal, and associated solution models are used in both the bulk solution and surface monolayer to predict surface tension and surface composition of the solutions. Solutions of inorganic electrolytes are treated next, with emphasis on the modifications that must be made in the Gibbs equation for treatment of electrolyte systems. Solutions of surfactants are treated in detail, with special attention given to the phenomena of micellization and solubilization. Insoluble monolayers are treated

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next, with emphasis on the two-dimensional phase behavior they exhibit. In the context of the discussion of insoluble monolayers, wetting and spreading phenomena are discussed in some detail, and a general phase rule for capillary systems is developed.

IV. Capillary Dynamics

THE UNIT ON "capillary dynamics" concerns surface tension driven (or surface tension influenced) fluid flow. Interfacial effects enter the problem via the boundary conditions, producing discontinuities in both the normal and tangential stress balances at the fluid interface. The normal stress discontinuity is proportional to the surface curvature, as given by the Young-Laplace equation: $2\sigma(T,X)\,\kappa_m$, while the tangential stress discontinuity is equal to the lateral variation of the surface tension: $\mathrm{grad}_s\sigma(T,x)$, where grad_s refers to the surface gradient. Both force components may be appreciable in magnitude, and their evaluation requires knowledge of the surface tension dependence upon temperature and composition, i.e. thermodynamic information of the type studied in the foregoing work. When variations of surface tension are caused by variation in temperature and/or composition, the flow equations must be solved together with the thermal energy equation and/or diffusion equations.

When highly surface active solutes are present, $\mathrm{grad}_s\sigma$ is proportional to the surface gradient of the surfactant adsorption, i.e. $(\partial\sigma/\sigma\Gamma)\ \mathrm{grad}_s\Gamma$. The surfactant distribution is given in turn by a surface material balance:

$$\frac{\partial\Gamma}{\partial t} + \mathrm{div}_s(\Gamma v_s - D_s\mathrm{grad}_s\Gamma) + j_n' + j_n'' = 0$$

where v_s is the surface velocity, D_s the surface diffusivity, and j_n' and j_n'' fluxes of surfactant from the adjoining bulk phases. The rate of interchange of material between interface and bulk may be governed by adsorption-desorption kinetics, molecular diffusion, or convective diffusion.

Finally, concentrated surfactant monolayers have been shown to possess intrinsic rheological properties, in particular surface viscosity. Terms involving the intrinsic surface rheological properties are incorporated into the tangential force boundary condition for such systems. Attention is focused on current studies, such as those in progress in our laboratory, of thermodynamic and transport properties of monolayers in multicomponent systems and their application to flow problems.

A case study is made of the circulation within drops and bubbles moving through viscous media and the effects of temperature and composition variations upon such flows. A second case study of hydrodynamic analysis is made of "interfacial turbulence", and its effect on mass transfer.

LECTURE AND LABORATORY DEMONSTRATIONS

MUCH OF THE MATERIAL covered in this course lends itself to interesting and illuminating lecture or laboratory demonstration. C. V. Boys' monograph: "Soap Bubbles and the Forces which Mould Them" describes many possibilities. Suspending soap films on wire frames of various shapes to illustrate Plateau's problem (Determine the surface of minimum area passing through a given closed curve or set of curves in space) is a convincing illustration of a special case of the Young-Laplace equation. Advantage was taken of on-going research projects among the author's graduate students to provide laboratory demonstrations of the capillary rise and contracting circular jet methods for measuring static and dynamic surface tensions, respectively, as well as the Langmuir film balance technique for studying insoluble monolayers. Schlieren optics were used to display surface tension driven flows during mass transfer, and the excellent film by L. Trefethen "Surface Tension in Fluid Mechanics," Educ. Services, Inc. (1964) was used to illustrate numerous capillary phenomena.

CONCLUSION

The interest in this course shown by the graduate students in Chemical Engineering at Washington has been truly gratifying. Almost all of them either take or audit the class, and many express interest in taking topical courses which are extensions of material covered in this course. What is perhaps most gratifying of all is the wealth of constructive criticism and helpful suggestions these students provide.