

# A Course on

## COLLOIDAL PHENOMENA

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**T**HE UNUSUAL AND USEFUL properties of colloidal suspensions originate with the forces acting upon and among the individual particles. Roughly speaking, the colloidal domain encompasses all particles large relative to the fluid molecules but sufficiently small to be responsive to thermal motion. At the lower end of this length scale Brownian effects dominate and, as with low molecular weight fluids, equilibrium among the interparticle forces prevails. Nonidealities caused by interparticle forces are generally thermodynamic rather than mechanical. In the 0.1-10  $\mu\text{m}$  range, however, diffusion becomes slow enough for external influences to upset this equilibrium with significant macroscopic consequences—electrokinetic phenomena, electrically driven separations, shear induced flocculation, and non-Newtonian rheology.

Scientific study in this field began in the 19th century with Robert Brown's observations of thermal motion and Thomas Graham's studies of diffusion, but practical applications appeared many centuries earlier. For example, the ancient Egyptians apparently produced inks by stabilizing aqueous dispersions of carbon black with natural substances such as gum arabic, egg albumin, and casein.

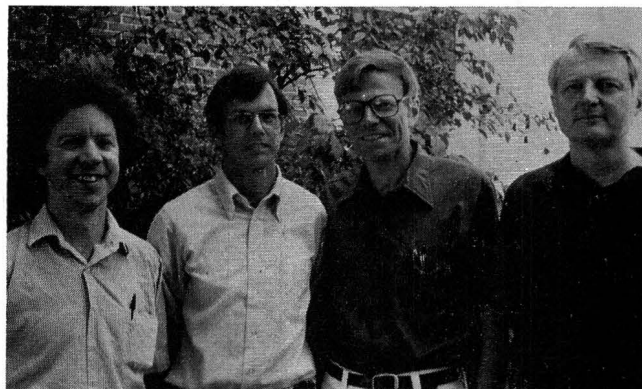
Today both the science and the engineering pertaining to colloids are well advanced. Monodisperse gold sols, polystyrene latices, silica, and hydrous metal oxides can be purchased or readily synthesized. These well-characterized model systems have served to significantly improve our

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... we developed a graduate course in Colloidal Phenomena to address the physical and dynamical side of colloid science ...

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After obtaining his undergraduate degree at Cal Tech and graduate degrees at Northwestern (M.S.) and Stanford (Ph.D.) **Dave Ollis** (on left) came to Princeton in 1969 where, in addition to research in catalysis, his recent work has included studies of particulates in the context of biochemical engineering problems. He is currently Professor of Chemical Engineering.

**Bill Russel's** (2nd from left) interests in the behavior of polyelectrolytes and other particulates in suspension began during a stint as NATO Postdoctoral Fellow at Cambridge shortly after he completed his PhD at Stanford in 1978. His B.S. and M.S. are from Rice University. His research in the behavior of small particles includes the behavior of gas phase suspensions and he is currently engaged in a study of coal hydrolysis with Dudley Saville. Russel is currently Associate Professor of Chemical Engineering.

Since coming to Princeton in 1957, **Bill Schowalter's** (3rd from left) research has centered on fluid mechanics, with an emphasis on the behavior of polymer melts and solutions and particulate suspensions. His undergraduate degree is from Wisconsin and his M.S. and Ph.D. are from Illinois. He is Professor of Chemical Engineering and Chairman of the Department.

**Dudley Saville** (right) came to Princeton in 1968 after stints in industrial research at Chevron Research and the Shell Development Company. His undergraduate degree is from the University of Nebraska and his PhD from Michigan. His current research includes studies of electrokinetic phenomena in suspensions and electrically stimulated aerosol filtration. He is Professor of Chemical Engineering.

quantitative understanding of phenomena and to provide standards for testing processes. Many other synthetic and natural colloids play central roles in the chemical process industries. These range from primary products such as pigments, cements, and carbon blacks to necessary components in the food processing, pharmaceutical, photographic, and pulp and paper industries. Most are associated with active research and development efforts.

Prompted by a confluence of research interests

among a number of faculty within the chemical engineering department we developed a graduate course in Colloidal Phenomena to address the physical and dynamical side of colloid science: colloidal stability, electrokinetic phenomena, separations techniques, and rheology. Excluded are characterization techniques such as light scattering and osmotic equilibrium as well as purely surface or interfacial phenomena. Nonetheless, the course provides a broad introduction for students entering a number of research areas. Our efforts have been supported in part by grants

from the Camille and Henry Dreyfus Foundation through their Innovation in Education in Chemistry Program and from the Xerox Corporation.

#### TECHNICAL CONTENT

THE LECTURES AND READINGS emphasize the fundamental physical chemistry and mechanics of colloidal suspensions beginning with the forces and fields operative at the particle scale and progressing through to separations processes and macroscopic properties (Table I). At each step quantitative theories and corresponding experi-

**TABLE I**  
**Course Outline**

#### INTRODUCTION

#### FORCES ACTIVE AT THE COLLOIDAL SCALE (W. B. Russel)

- Brownian motion
  - statistical description with probability densities
  - derivation of diffusivity from Langevin equation
  - role of hydrodynamic mobilities
  - formulation of conservation equations
- Dispersion forces
  - intermolecular forces
  - Hamaker theory for particles
  - application of Lifshitz theory
  - experimental verification
- Electrostatic forces
  - origin of surface charge
  - structure of equilibrium double layer
  - interparticle repulsion
  - experimental studies

#### COLLOIDAL STABILITY (W. B. Russel)

- Electrostatic stabilization
  - criterion for kinetic stability
  - kinetics of rapid flocculation
  - slow Brownian flocculation
  - shear-induced flocculation
- Steric stabilization
  - origin of repulsive force
  - experimental studies
  - simple theory for adsorbed layers

#### ELECTROKINETIC PHENOMENA (D. A. Saville)

- General description of phenomena
  - streaming current and potential
  - electro-osmosis and electrophoresis
  - electroviscous effects
- Processes within capillaries
  - non-equilibrium double layers
  - limiting solutions
  - experimental results
- Motion of suspended particles
  - perturbation expansions and solution techniques
  - effect of particle shape

- electrophoresis of polyelectrolytes
- primary electroviscous effect

#### SEPARATIONS PROCESSES (D. F. Ollis)

- Filtration
  - forces responsible for collection
  - trajectory analyses
  - macroscopic balances and filter design
- Field-Flow Fractionation
  - types of transverse fields
  - pulse velocity and dispersion
  - design considerations
- Flotation
  - isotherms and interfacial aspects
  - application of particle collection theories
  - experimental results
- Ultrafiltration
  - role of osmotic pressure
  - concentration polarization
- Continuous flow electrophoresis
  - principles and general analysis
  - hydrodynamic instabilities
  - application to separation of cells

#### SUSPENSION RHEOLOGY (W. R. Schowalter)

- Examples of non-Newtonian behavior of disperse systems
- General framework for analysis
  - description of microstructure
  - calculation of bulk stresses
  - dimensional analysis
- Dilute suspensions
  - rigid spheres
  - drops and elastic spheres
  - rigid ellipsoids and rotary Brownian motion
- Pair interactions: effect of colloidal forces
  - neutrally stable suspensions
  - effect of steric stabilization
  - electroviscous effects
  - flocculated suspensions
- Highly concentrated suspensions
  - lubrication analyses of hydrodynamics
  - dilatancy in plastisols
  - mechanics of ordered lattices

**Qualitative agreement with most data is unquestionable, but controversy persists because of a few significant qualitative and quantitative inconsistencies. Experiments with steric stabilization . . . indicate polymer-solvent interactions to dominate, but several schools of thought exist on the exact nature of the repulsive force.**

ments on well-characterized model systems are discussed, and areas in need of further theoretical or experimental study are highlighted.

The lectures begin with the forces acting on small particles suspended in liquids. For Brownian motion the classical treatments of Smoluchowski, Einstein, and Langevin suffice with a few extensions. Study of the viscous forces on small particles, i.e. fluid mechanics at low Reynolds numbers, began with Stokes and has experienced a resurgence of late because of interest in colloidal problems. The origins of those results relevant to the course are described briefly. The Hamaker treatment of the dispersion forces remains most useful but eventually may be supplanted by a simplified application of the rigorous Lifshitz theory; so both deserve examination. For electrostatic forces we use numerous limiting forms deduced from the nonlinear Poisson-Boltzmann equation. Despite their maturity each of these remains an active area of research; so notable recent developments, such as the direct measurement of electrostatic and dispersion forces, are reviewed as well.

Since the dispersion forces between suspended particles become strongly attractive at short range, flocculation can be avoided only by the intervention of longer range repulsive forces. Our treatment begins with the classical treatise of Verwey and Overbeek which synthesized several decades of work into a comprehensive theory for electrostatic stabilization. Qualitative agreement with most data is unquestionable, but controversy persists because of a few significant qualitative and quantitative inconsistencies. Experiments with steric stabilization, i.e. repulsion between layers of adsorbed polymer, indicate polymer-solvent interactions to dominate, but several schools of thought exist on the exact nature of the repulsive force. Although time does not permit a thorough exploration of such lingering questions, the nature of the controversy is outlined for the curious to pursue further.

When aqueous suspensions of charged particles, proteins, or synthetic macromolecules are subjected to an external electric field or are forced to flow, interesting electrokinetic phe-

nomena appear. In some cases the motion engendered by the field provides a means of characterization, e.g. the determination of charge by electrophoresis; in others the induced field retards the flow, as with electroviscous effects and the sedimentation potential. Analyses of these together with the analogous phenomena in charged capillaries are developed in detail from Stokes' and Maxwell's equations governing the mechanics and electrostatics, respectively. The topic is a rich one mathematically, because of innumerable perturbation expansions leading to analytical results, and phenomenologically, because of the coupling between the mechanical and electrical forces which deform the equilibrium double layer.

Following these fundamentals our focus shifts to larger scales, beginning with several separations processes which capitalize on either the colloidal forces or electrokinetic phenomena. The first topic, filtration, is an interesting application since small particles flowing near a large collector can be captured by any one of several forces. Analyses of the particle trajectories resulting from the balance among these forces yield collection efficiencies, which are then integrated into macroscopic balances to provide a systematic means for designing packed beds and fiber filters.

Two relatively new approaches to preparative separations employ an electric field transverse to a laminar channel flow. In field flow fractionation, a long flow path with a narrow channel permits selective redistribution of particles over the cross-section; pulses of species with different electrophoretic mobilities then travel with different axial velocities. Continuous flow electrophoresis, on the other hand, obtains spatial separation due to migration across a wider channel over a shorter flow path. In both processes dispersion and hydrodynamic instabilities can limit the separation and scale up. Here the lectures examine quantitative macroscopic analyses capable of handling these complications and thereby predicting process performance.

Many applications require both an understanding of and control over the mechanical properties of colloidal suspensions. During processing the viscosity and non-Newtonian charac-



**TABLE II**  
**Reading List**

- A. W. Adamson Physical Chemistry of Surfaces, 3rd. ed., Wiley, 1976.  
 J. T. Davies and E. K. Rideal Interfacial Phenomena, Academic Press, 1961.  
 A. Einstein Theory of Brownian Motion, Dover, 1956.  
 P. C. Hiemenz Principles of Colloid and Surface Chemistry, Dekker, 1977.  
 H. R. Kruyt (ed.) Colloid Science (2 vols.), Elsevier, 1952.  
 V. G. Levich Physicochemical Hydrodynamics, Prentice Hall, 1962.  
 J. Mahanty and B. W. Ninham Dispersion Forces, Academic Press, 1976.  
 E. Matijevic (ed.) Advances in Surface and Colloid Science, Vol. 7, Wiley, 1974.  
 W. R. Schowalter Mechanics of non-Newtonian Fluids, Pergamon, 1978.  
 D. J. Shaw Electrophoresis, Academic Press, 1969.  
 D. J. Shaw Introduction to Colloid and Surface Science, 2nd ed., Butterworths, 1970.  
 H. Sonntag and K. Strenge Coagulation and Stability of Disperse Systems, Halsted, 1972.  
 M. J. Spaarnay The Electrical Double Layer, Pergamon, 1972.  
 E. J. W. Verwey and J. Th. G. Overbeek Theory of the Stability of Lyophobic Colloids, Elsevier, 1948.

teristics may affect mixing, determine pumping costs, or provide a simple means for monitoring product quality. In addition, products such as paints, cosmetics, and foodstuffs fail without the desired rheological characteristics. While comprehensive theories remain beyond our grasp, we can systemically relate particular colloidal forces to types of non-Newtonian behavior. For example, rodlike particles generate viscosities which are thinning in shear flows but thickening in extension even at infinite dilution because of competition between orientation by flow and disorientation by rotary Brownian motion. Suspended spheres, however, must interact to cause non-Newtonian behavior. At moderate concentrations a range of phenomena may result, depending on the dominant interparticle force. In all situations the orientations and spatial distributions of the particles, which represent a balance among hydrodynamic and colloidal forces, determine the observed macroscopic stress. Rigorous analyses of several idealized systems are reviewed to provide some insight into the complex behavior of practical suspensions.

#### TEACHING THE COURSE

**M**ATERIAL PRESENTED BY THE individual faculty as listed in the course outline corresponds roughly to their research interests. Periodic aca-

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demically leaves and other teaching commitments normally cause us to omit one of the last two topics. The remainder fit gracefully into thirty-six lectures over twelve weeks.

Students electing the course to date have been chemical engineering PhD candidates. This means that they have encountered a graduate applied mathematics course, a few weeks of low Reynolds number fluid mechanics, and some statistical mechanics and quantum mechanics. Some have related thesis topics, while others may be scouting for areas of future research.

The lectures are supplemented with recommended readings in several basic texts and a number of monographs listed in Table II. Review articles and original papers also are cited as appropriate. In the future students will receive an organized set of notes made possible by the support from the Dreyfus Foundation. Finally, at the end of the term a series of informal seminars by industrial researchers, concerned with paint pigments, pulp and paper operations, or other colloidal problems, expose the class to the practical side of the subject.

Scattered homework problems provide intimate exposure to theoretical developments and data analysis, but the major requirement is a term paper. The topics offered attempt to identify a problem to which a student can make an original contribution, rather than serve solely as the focus for a literature review. Of course, this generates spectacular misses as well as some elegant work suitable for publication. Either way we stir some imaginations and enjoy the day of oral reports on the topics. □

#### ERRATA

**A Modified Carnot Cycle,**  
**Y. K. Rao, University of Washington**  
 Vol. 13, No. 3, Pages 147, 148

The Text should read as follows:

Pg. 147: Col. 1, line 4 from the bottom:  
 two reversible adiabatics (I and III) ...

Pg. 148: Col. 1, line 9:  
 dynamic states 3 and 3'.  $\Delta S_{III'} = R \ln (v_3'/v_3)$

Pg. 148: Col. 1, line 16:  
 Entropy change,  $\Delta S_{IV} = R \ln v_1/v_4'$ ;

Pg. 148: Col. 1, line 19:  
 $W = \sum W_i = Q_2 + Q_1' = RT_2 \ln(v_3/v_2) + RT_1 \ln(v_1/v_4')$

Pg. 148: Col. 1, line 21:  
 $\Delta S_{cycle} = R \ln (v_3/v_2) + R \ln (v_1/v_4') + R \ln (v_3'/v_3)$

Pg. 148: Col. 1, line 34:  
 ... The latter ...

Pg. 148: Col. 2, line 9 (Eq. 10):  
 ... =  $-Q_2/T_2 = R \ln (v_3/v_2)$

Pg. 148: Col. 2, line 10 (Eq. 11):  
 ... =  $-Q_1'/T_1 = -R \ln (v_1/v_4')$