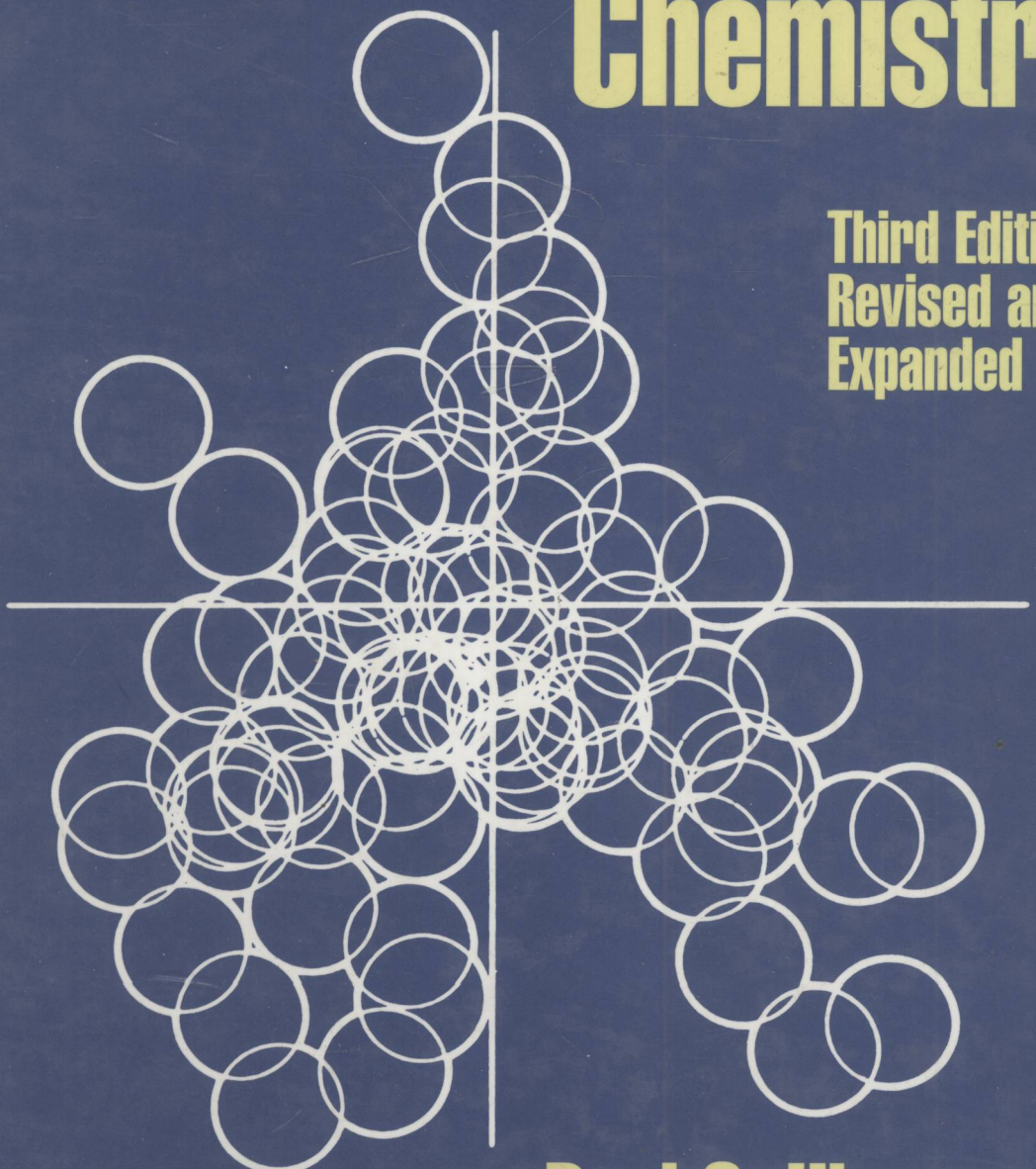
# Principles of Colloid and Surface Chemistry

Third Edition, Revised and Expanded



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## Third Edition, Revised and Expanded

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# Principles of Colloid and Surface Chemistry

# Preface to the Third Edition

The face of colloid and surface chemistry has changed dramatically in the 10 years since the last edition of this book appeared in print. Advances in instrumentation now make it possible for us to "see"—and, indeed, to *manipulate*—individual atoms on a surface. Molecular engineering of polymers, surfactants, and particles is now within reach for fabricating novel advanced materials and for preparing capsules (liposomes) for drug delivery and gene therapy. Direct measurements of colloidal and surface forces are now commonplace, and colloidal dispersions are now used as models for studying equilibrium and non-equilibrium thermodynamics and flow behavior of *atomic* (as well as *geological*) systems—phenomena that are otherwise not easily accessible to the experimentalist. Colloid and surface chemistry is a truly interdisciplinary subject today, and its content and significance have no bounds.

This richness has its rewards, as has been documented in a number of advanced monographs and a few graduate-level books in recent years. However, it has its drawbacks as well, as those who use colloids and surface chemistry are drawn from increasingly diverse backgrounds. Introductory textbooks that are suitable for such a diverse group of students and professionals remain almost as rare today as they were a decade ago. This need for an introductory book accessible to everyone, regardless of background, even from the perspectives of the traditional applications of colloid and surface chemistry, cannot be overemphasized. For example, in the chemical industries alone, almost two-thirds of the operations or products involve powders and suspensions. A report from Du Pont researchers [Ennis, B., Green, J., and Davies, R., *Chemical Engineering Progress*, **90**(4), 32–43 (1994)] notes that of the roughly 3000 products manufactured by Du Pont, about 60% are marketed as powders, dispersions, or suspensions and that the processing of another 20% involves particles or suspensions. Industries employ engineers and scientists of all types, and the rather tight curriculum requirements in most areas of science and engineering seldom allow even a minimal preparation of university graduates for working with materials in particulate form.

Factors such as the above have shaped our approach to the present edition. The philosophy behind the first two editions was that most of the material in the book should be a natural extension of an introductory physical chemistry course at the undergraduate level and should be accessible to anyone (students as well as practicing engineers and scientists) with such a background. This remains the rule in the present edition as well. In our opinion, this orientation is essential for giving a firm foundation in colloids and surfaces to the diverse audience, which typically includes individuals from almost all branches of engineering and the sciences.

Keeping these factors in mind, we have updated many topics and have introduced new features that draw attention to exciting developments that go beyond the scope of the present volume. Among the major revisions and additions made are the following:

1. A major portion of Chapter 1 has been rewritten. In addition to providing a broad overview of the basic issues of importance in colloids and to introducing much of

what is presented in the rest of the book, Chapter 1 now includes modern developments in instrumentation such as scanning probe microscopy and spectroscopy, and atomic and surface force measurements; a brief introduction to "model" colloids and their uses; and an introduction to fractal dimensions of aggregates and surfaces.

2. A number of vignettes are sprinkled throughout Chapter 1 to provide motivation for and to illustrate the concepts introduced in the chapter and in the rest of the book. These vignettes also serve as vehicles for conveying the excitement of the subject and as introductions to advanced concepts that are beyond the scope of the book. They cover a rather broad array of disciplines ranging from environmental remediation and separation technologies to biological and medical sciences and polymer composites, and they thus reveal the breadth of the present as well as the potential applications. In addition to the vignettes in Chapter 1, each of the other 12 chapters contains a vignette highlighting the material covered in the chapter and establishing the connections to other chapters or advanced developments.
3. Chapter 4 now goes beyond an introduction to Newtonian viscosity and flow of Newtonian dispersions. In addition to a basic introduction to viscosity and the Navier-Stokes equation, the chapter now includes the Krieger-Dougherty relation for concentrated dispersions, elements of non-Newtonian rheological behavior of dispersions, electroviscous effects, and a summary of the definitions and physical significance of dimensionless groups essential for estimating and quantifying rheological properties of dispersions.
4. Chapter 5, on scattering techniques, has been updated to include measurement of fractal dimensions of aggregates, intraparticle and interparticle structure, dynamic light scattering and relation between light scattering and complementary measurements based on scattering of X-ray and neutrons.
5. Chapter 7 now includes an introduction to structural transitions in Langmuir layers and examples of applications of Langmuir and Langmuir–Blodgett films.
6. Chapter 8 has been revised to include a discussion of the critical packing parameter of surfactants and its relation to the structure of resulting surfactant aggregates. This simple geometric basis for the formation of micelles, bilayers, and other structures is intuitively easier to understand for a beginning student.
7. Chapters 9 and 10 of the second edition (dealing with physical adsorption at gas/solid interfaces and microscopy, spectroscopy and diffractometry of metal surfaces, respectively) have been pared down and consolidated into one chapter (new Chapter 9, on adsorption on gas/solid interfaces). The outdated materials or materials extraneous to the main thrust of the book from the old Chapter 10 have been eliminated and only the discussion of low-energy electron diffraction (LEED) has been retained.
8. Chapters 11–13 of the second edition, which discussed van der Waals forces (old Chapter 11), electrical double layers (old Chapter 12), electrokinetic phenomena (old Chapter 13), and colloid stability (old Chapters 11 and 12), have been restructured and new materials on colloid stability and polymer/colloid interactions have been added. For example:
   - In the new version, Chapter 10 focuses exclusively on van der Waals forces and their implications for macroscopic phenomena and properties (e.g., structure of materials and surface tension). It also includes new tables and examples and some additional methods for estimating Hamaker constants from macroscopic properties or concepts such as surface tension, the parameters of the van der Waals equation of state, and the corresponding state principle.
   - Chapters 11 and 12 in the present edition focus exclusively on the theories of electrical double layers and forces due to double-layer interactions (Chapter 11) and electrokinetic phenomena (Chapter 12). Chapter 11 includes expressions for interacting spherical double layers, and both chapters provide additional examples of applications of the concepts covered.

- The new Chapter 13 collects the material on colloid stability previously distributed between old Chapters 11 and 12 and integrates it with new material on stability ratio and slow and fast coagulation, polymer-induced forces, and polymer-induced stabilization and destabilization.

This rearrangement makes the presentation of colloidal forces, colloid stability, and electrokinetic phenomena more logical and pedagogically more appealing.

Numerous cross-references link the materials in the various chapters; however, many of the chapters are self-contained and can stand alone, thus offering the instructor the flexibility to mix and match the topics needed in a particular course. Moreover, we have also introduced a number of other features to make the present edition more useful and convenient as a textbook *and* for self-study. For example:

1. A collection of Review Questions has been added at the end of each chapter. These should be useful not only for class assignments but also as a self-assessment tool for students.
2. The references at the end of each chapter have been grouped into two sets, one containing annotated general references (usually other textbooks, monographs or review articles) and the second with special references of narrower scope. The level of each annotated reference (undergraduate, graduate, or advanced) has also been included in the annotations, as an additional aid to students and instructors.
3. All illustrations have been redrawn, and a number of new illustrations, tables, and examples have been added. (Appendix D presents a list of all the worked-out examples and the corresponding page numbers.)
4. The presentation in each chapter has been divided into a number of sections and subsections so that the headings of the sections and subsections can serve as guideposts for students.

As it is often said, when it comes to textbooks, one never "finishes" writing a book—one just "abandons" it! There is a lot we would like to do further with this book, but these changes must wait for the next edition. We would be pleased indeed to hear comments, suggestions, and recommendations for potential revisions and additions from anyone who uses this book, so that everyone can benefit from the collective wisdom of the community at large.

*Paul C. Hiemenz*
*Raj Rajagopalan*

# Acknowledgments

A number of colleagues have been kind enough to send us comments or recent research papers, reviews, or related materials for the third edition. The information we received has shaped our thinking and has influenced the contents and the organization of the present edition, and we would like to recognize the assistance and interest of these individuals here. In particular, we would like to thank Prof. Nicholas Abbott (UC, Davis), Prof. John Anderson (Carnegie Mellon), Dr. Rafat R. Ansari (NASA Lewis, Cleveland, OH), Prof. John C. Berg (Univ. of Washington), Prof. Daniel Blankschtein (MIT), Dr. Krishnan Chari (Kodak, Rochester, NY), Dr. Reg Davies (Du Pont, Wilmington, DE), Prof. Menachem Elimelech (UCLA), Prof. H. Scott Fogler (Michigan), Prof. George Hirasaki (Rice), Dr. Norio Ise (Rengo Corp., Fukui, Japan), Prof. Jacob N. Israelachvili (UC, Santa Barbara), Prof. Charles Knobler (UCLA), Prof. Josip Kratohvil (Clarkson), Prof. J. Adin Mann (Case Western), Prof. Jacob Masliyah (Alberta), Prof. Egon Matijevic (Clarkson), Dr. S. Mehta (ARCO, Plano, TX), Prof. Clarence Miller (Rice), Dr. Ian Morrison (Xerox, Rochester, NY), Prof. Brij M. Moudgil (Florida), Dr. Cherry A. Murray (AT&T, Murray Hill, NJ), Prof. R. Nagarajan (Penn State), Prof. Robert Ofoli (Michigan State), Prof. Kyriakos Papadopoulos (Tulane), Prof. Dennis C. Prieve (Carnegie Mellon), Prof. Clay Radke (UC, Berkeley), Dr. Mihail C. Roco (NSF), Prof. Robert Rowell (Univ. of Massachusetts), Prof. William B. Russel (Princeton), Prof. Robert Schechter (UT, Austin), Prof. Ken Schmitz (Univ. of Missouri, Kansas City), Prof. Dinesh Shah (Florida), Prof. P. Somasundaran (Columbia), Prof. Frank M. Tiller (Houston), Prof. Theo van de Ven (McGill), Prof. Carol Van Oss (SUNY, Buffalo), Prof. Darsh T. Wasan (IIT, Chicago), and Prof. Mark Wiesner (Rice).

Some of RR's colleagues at the University of Houston, especially Profs. Kishore K. Mohanty, Richard Pollard, Jay D. Schieber, Cindy L. Stokes, Frank M. Tiller, and Richard C. Willson, read and offered comments on some of the vignettes used in the book. Their interest and assistance have contributed significantly to the clarity of the final versions that appear in the book.

RR would also like to thank his students and coworkers, who played a major role throughout the preparation of the present edition. Mr. Roger Seow did much of the laborious task of scanning the second edition into the computer and fixing all the errors generated by the usually less-than-perfect optical character recognition programs. His remarkable attention to details and organizational skills made the initial stages of the preparation of the text appear almost effortless. Mr. Nikhil Joshi stepped in subsequently to attend to the endless printing and reprinting of the figures, tables, and text for the final stage. We are greatly indebted to both. Dr. Jean François Guérin, Dr. Yongmei Wang, Ms. Carlisa Harris, Ms. Sheryl L. Horton, Mr. Randy Diermeier, Mr. Jorge Jimenez, Mr. Dang Nhan, Mr. K. Srinivasa Rao, Mr. Antonio Rodriguez, and Mr. Sameer Talsania have been extremely patient despite the fact that their research projects frequently took second place to the preparation of the book.

The Media Center at the University of Houston deserves special recognition for its excellent work in preparing the initial versions of the drawings of most of the illustrations.

Finally, we would like to thank the folks at Marcel Dekker, Inc.—particularly Ted Allen and Eric F. Stannard, Production Editors, and Sandy Beberman, Assistant Vice President—for their infinite patience and, of course, for their characteristically friendly and courteous assistance.

# Preface to the Second Edition

In the preface to the first edition, I stated that this is "primarily a textbook, written with student backgrounds, needs, and objectives in mind." This continues to be true of the second edition, and many of the revisions I have made are attempts to make the book even more useful than its predecessor to student readers. In addition, colloid and surface science continue to flourish. In preparing the second edition I have also attempted to "open up" the coverage to include some of the newer topics from an ever-broadening field.

A number of differences between the first and second editions can be cited which are readily traceable to either one or both of the foregoing considerations.

Two new chapters have been added which explore—via micelles and related structures and metal surfaces under ultra-high vacuum—both "wet" and "dry" facets of colloids and surfaces. Although neither of these areas is new, both are experiencing an upsurge of activity as new instrumentation is developed and new applications are found.

A number of chapters have been overhauled so thoroughly that they bear only minor resemblance to their counterparts in the first edition. The thermodynamics of polymer solutions is introduced in connection with osmometry and the drainage and spatial extension of polymer coils is discussed in connection with viscosity. The treatment of contact angle is expanded so that it is presented on a more equal footing with surface tension in the presentation of liquid surfaces. Steric stabilization as a protective mechanism against flocculation is discussed along with the classical DLVO theory.

Solved problems have been scattered throughout the text. I am convinced that students must work problems to gain mastery of the topics we discuss. Including examples helps bridge the gap between the textbook presentation of theory and student labors over the analysis and mechanics of problem solving.

SI units have been used fairly consistently throughout the book. Since the problems at the ends of the chapters are based on data from the literature and since cgs units were commonly used in the older literature, the problems contain a wider assortment of units. A table of conversions between cgs and SI units is contained in Appendix B.

I am very much aware of the many important topics that the book fails to cover or, worse yet, even mention. However, lines must be drawn somewhere both to keep the book manageable in size and cost and to have it useful as the basis for a course. As it is, I have added a good deal of new material without deleting anywhere near as much of the old. I have tried to select for inclusion topics of fundamental importance which could be developed with some internal coherence and with some continuity from a (prerequisite) physical chemistry course.

A number of users of the first edition communicated with me, pointing out errors and offering suggestions for improvement. I appreciate the feedback of these correspondents, and hope that the revisions I have made at least partially reflect their input.

I want to express my thanks to Carol Truett for expertly drawing the new illustrations and giving a "new look" to the old ones. I also appreciate the assistance of Lisa Scott in the preparation of the manuscript. Thanks, also, to Reuben Martinez for helping me with the proofreading and indexing. Lastly, let me again invite users to call errors and/or obscurities to my attention, and to thank them in advance for doing so.

*Paul C. Hiemenz*

# Preface to the First Edition

Colloid and surface chemistry occupy a paradoxical position among the topics of physical chemistry. These are areas which have traditionally been considered part of physical chemistry and are currently enjoying more widespread application than ever due to their relevance to environmental and biological problems. At the same time, however, colloid and surface chemistry have virtually disappeared from physical chemistry courses. These topics are largely absent from the contemporary general chemistry course as well. It is possible, therefore, that a student could complete a degree in chemistry without even being able to identify what colloid and surface chemistry are about.

The primary objective of this book is to bridge the gap between today's typical physical chemistry course and the literature of colloid and surface chemistry. The reader is assumed to have completed a course in physical chemistry, but no prior knowledge of the topics under consideration is assumed. The book is, therefore, introductory as far as the topic subjects are concerned, although familiarity with numerous other aspects of physical chemistry is required background.

Since physical chemistry is the point of departure for this presentation, the undergraduate chemistry major is the model reader toward whom the book is addressed. This in no way implies that these are the only students who will study the material contained herein. Students majoring in engineering, biology, physics, materials science, and so on, at both the undergraduate and graduate levels will find aspects of this subject highly useful. The interdisciplinary nature of colloid and surface chemistry is another aspect of these subjects that contributes to their relevance in today's curricula.

This is primarily a textbook, written with student backgrounds, needs, and objectives in mind. There are several ways in which this fact manifests itself in the organization of this book. First, no attempt has been made to review the literature or to describe research frontiers in colloid and surface chemistry. A large literature exists which does these things admirably. Our purpose is to provide the beginner with enough background to make intelligible the journals and monographs which present these topics. References have been limited to monographs, textbooks, and reviews which are especially comprehensive and/or accessible. Second, where derivations are presented, this is done in sufficient detail so that the reader should find them self-explanatory. In areas in which undergraduate chemistry majors have minimal backgrounds or have chronic difficulties—for example, fluid mechanics, classical electromagnetic theory, and electrostatics—the presentations begin at the level of general physics, which may be the student's only prior contact with these topics. Third, an effort has been made to facilitate calculations by paying special attention to dimensional considerations. The cgs-esu system of units has been used throughout, even though this is gradually being phased out of most books. The reason for keeping these units is the stated objective of relating the student's experiences to the existing literature of colloid and surface chemistry. At present, the cgs-esu system is still the common denominator between the two. A fairly detailed list of conversions between cgs and SI units is included in Appendix C. Finally, a few problems are included in

each chapter. These provide an opportunity to apply the concepts of the chapter and indicate the kinds of applications these ideas find.

Not all who use the book will have the time or interest to cover it entirely. In the author's course, about two-thirds of the material is discussed in a one-quarter course. With the same level of coverage, the entire book could be completed in a semester. To cover the amount of material involved, very little time is devoted to derivations except to answer questions. Lecture time is devoted instead to outlining highlights of the material and presenting supplementary examples.

The underlying unity which connects the various topics discussed here is seen most clearly when the book is studied in its entirety and in the order presented. Time limitations and special interests often interfere with this ideal. Those who choose to rearrange the sequence of topics should note the subthemes that unify certain blocks of chapters. Chapters 1 through 5 are primarily concerned with particle characterization, especially with respect to molecular weight; Chapters 6 through 8, with surface tension/free energy and adsorption; and Chapters 9 through 11, with flocculation and the electrical double layer. Subjects of special interest to students of the biological sciences are given in Chapters 2 to 5, 7, and 11.

Colloid chemistry and surface chemistry each span virtually the entire field of chemistry. The former may be visualized as a chemistry whose "atoms" are considerably larger than actual atoms; the latter, as a two-dimensional chemistry. The point is that each encompasses all the usual subdivisions of chemistry: reaction chemistry, analytical chemistry, physical chemistry, and so on. The various subdivisions of physical chemistry are also represented: thermodynamics, structure elucidation, rate processes, and so on. As a consequence, these traditional categories could be used as the basis for organization in a book of this sort. For example, "The Thermodynamics of Surfaces" would be a logical chapter heading according to such a plan of organization. In this book, however, no such chapter exists (although not only chapters but entire volumes on this topic exist elsewhere). The reason goes back to the premise stated earlier: These days most undergraduates know more about thermodynamics than about surfaces, and this is probably true regardless of their thermodynamic literacy/illiteracy! Accordingly, this book discusses surfaces: flat and curved, rigid and mobile, pure substances and solutions, condensed phases and gases. Thermodynamic arguments are presented—along with arguments derived from other sources—in developing an overview of surface chemistry (with the emphasis on "surface"). A more systematic, formal presentation of surface thermodynamics (with the emphasis on "thermodynamics") would be a likely sequel to the study of this book for those who desire still more insight into that aspect of two-dimensional chemistry. Similarly, other topics could be organized differently as well. Only time will tell whether the plan followed in this book succeeds in convincing students that chemistry they have learned in other courses is also applicable to the "in between" dimensions of colloids and the two dimensions of surface chemistry.

The notion that molecules at a surface are in a two-dimensional state of matter is reminiscent of E. A. Abbott's science fiction classic, *Flatland.** Perusal of this book for quotations suitable for Chapters 6, 7, and 8 revealed other parallels also: the color revolt and light scattering, "Attend to Your Configuration" and the shape of polymer molecules, and so on. Eventually, the objective of beginning each chapter with a quote from *Flatland* replaced the requirement that the passage cited have some actual connection with the contents of the chapter. As it ends up, the quotes are merely for fun: Perhaps those who are not captivated by colloids and surfaces will at least enjoy this glimpse of *Flatland.*

Finally, it is a pleasure to acknowledge those whose contributions helped bring this book into existence. I am grateful to Maurits and Marcel Dekker for the confidence they showed and the encouragement they gave throughout the entire project. I wish to thank Phyllis Bartosh, Felecia Granderson, Jennifer Woodruff, and, especially, Mickie McConnell and Lynda Parzick for making my sloppy manuscript presentable. My appreciation also goes to Bob Marvos, George Phillips, and, especially, Dottie Holmquist for their work on the figures,

*E. A. Abbott, *Flatland* (6th ed.), Dover, New York, 1952. Used with permission.

which are such an important part of any textbook. I also wish to thank Michael Goett for helping with proofreading and indexing. Finally, due to the diligence of the class on whom this material was tested in manuscript form, the book has 395 fewer errors than when it started. For the errors that remain, and I hope they are few in number and minor in magnitude, I am responsible. Reports from readers of errors and/or obscurities will be very much appreciated.

*Paul C. Hiemenz*

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