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COLLOIDAL DISPERSIONS

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To Priscilla, Joy, and Jane

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W. B. Russel, D. A. Saville and W. R. Schowalter
Frontmatter
More information

CONTENTS

PREFACE

Colloid science has its roots in nineteenth- and early twentieth-century discoveries concerning the behavior of minute particles. Its early development was stimulated by controversies regarding the very existence of molecules. Scientific interest, along with technological and biological applications, fostered several definitive monographs and textbooks in the 1930s and 1940s. However, interest in the field declined within many academic circles after the Second World War, especially in the United States, despite continued and widespread industrial applications. The resurgence of interest that began in the early 1960s arose from mutually reinforcing events. New technological problems appeared in, for example, the manufacture of synthetic dispersions for coatings, enhanced oil recovery, the development of new fuels, environmental pollution, ceramics fabrication, corrosion phenomena, biotechnology, and separations processes. In addition, monodisperse suspensions of colloidal particles of diverse sorts became readily available and advances in our understanding of fluid mechanics on the colloidal scale burgeoned almost simultaneously. Further stimuli were provided by the appreciation by colloid scientists of advances in the theory of interparticle forces coupled with the development of several new experimental techniques. Forces and particle properties have long been difficult to measure accurately on the colloidal scale and numerical values were often the result of a long uncertain chain of inference. The new techniques made possible direct, accurate measurements of size, shape, and concentration, as well as the attractive and repulsive forces between surfaces separated by a few nanometers. The advancements made over the last thirty years convinced us of the need for a broad synthesis, integrating recent discoveries with those of earlier times so as to treat dynamic as well as equilibrium properties of dispersions.

This book addresses the physical side of colloid science; the subjects range from the individual forces acting between submicron particles suspended in a liquid through the equilibrium and dynamic properties of the dispersion. The relevant forces include Brownian motion, electrostatic repulsion, attraction due to dispersion forces, attraction and repulsion caused by soluble polymers, and viscous forces arising from relative motion between the particles and the liquid. The balance between Brownian motion and the interparticle forces decides issues concerning stability and phase behavior in quiescent systems. Imposition of external fields alters the structure to produce complex effects, i.e., electrokinetic phenomena (electric field), sedimentation (gravitational field), diffusion (concentration/chemical potential gradient), and non-Newtonian rheology (shear field).

Our aim is to impart a quantitative understanding grounded in basic theory and coupled to experiments on well-characterized model systems. This provides the broad grasp of fundamentals which lends insight and helps develop the intuitive sense needed to isolate essential features of scientific and technological problems and to design critical experiments. The book is suitable both as a text for an advanced graduate course in chemical engineering, physical chemistry, physics, or applied mathematics, and as a reference for those doing industrial or academic research. Most of the material is accessible to those with a basic knowledge of mechanics and mathematics. Although exposure to fluid mechanics, statistical mechanics, and electricity and magnetism is assumed, the subjects in the book are introduced in a self-contained manner. Likewise, some facility with differential equations and vectors and tensors is required. Those interested in probing further can deepen their understanding by referring to the original works cited herein.

The book developed from complementary research interests among the authors, fostered initially by general grants from the Dreyfus and Xerox Foundations. This led to an advanced graduate course, first taught at Princeton in 1978 and now offered in alternate years. The writing began in earnest during WBR's tenure as the Olaf A. Hougen Professor in the Department of Chemical Engineering at the University of Wisconsin in 1984.

We are indebted to our students for their contributions, some of which appear explicitly in the text, as well as the interactions which advanced our understanding of the subject. In addition, we acknowledge the critical reading and constructive comments on portions of the text by Chip Zukoski and Alice Gast. Finally, we thank Elizabeth B. Bixby for her ability to deal with what appeared to be an endless sequence of revisions; her threats of divine retribution helped make the process convergent.

W.B.R., D.A.S., W.R.S.
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Frontmatter
More information

UNITS AND PHYSICAL CONSTANTS

The International Metric System ('SI', from the French, *Système Internationale d' Units*) used here employs the following base units:

Quantity	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Temperature	kelvin	K
Amount	mole	mol
Electric current	ampere	A

The units derived from this set are:

Quantity	Unit	Symbol	Definition
Force	newton	N	$1\ \mathrm{kg\,m\,s^{-2}}$
Pressure	pascal	Pa	$1\ \mathrm{kg\,m^{-1}\,s^{-2}}$
Energy	joule	J	$1\ \mathrm{kg\,m^{2}\,s^{-2}}$
Electric charge	coulomb	C	$1\ \mathrm{s\,A}$
Electric potential	volt	V	$1\ \mathrm{kg\,m^{2}\,s^{-3}\,A^{-1}}$
Frequency	hertz	Hz	$2\pi\ \mathrm{rad\,s^{-1}}$
Capacitance	farad	F	$1\ \mathrm{kg^{-1}\,m^{-2}\,s^{4}\,A^{2}}$

Of course the units of the derived quantities can be expressed in terms of one another, e.g.,

$$1\,\mathrm{F} = 1\,\mathrm{C/V}.$$

The fundamental laws involve a number of physical constants. Those used here are:

Constant	Symbol	Numerical value
Avogadro's constant	N_A	6.02552×10^{23} molecules/mole
Boltzmann's constant	k	1.38054×10^{-23} J/K
Magnitude of charge on an electron	e	1.60210×10^{-19} C
Permittivity of the vacuum	ε_0	8.854×10^{-12} C^2/N m^2
Planck's constant	$2\pi\hbar$	6.6256×10^{-34} J s
Speed of light	c	2.9979×10^8 m/s

Miscellaneous conversion factors

Standard acceleration due to gravity, g	9.8066 m/s^2
Atmospheric pressure	$1.013\,25 \times 10^5$ Pa
kT/e at 298.16 K	25.69×10^{-3} V
1 molar solution, M	1 mol/(dm)^3
1 liter	$1.000\,0028 \times 10^{-3}$ m^3

Prefixes

Meters, kilograms, seconds and the like are not always convenient scales but various multiples are. The commonly used scale factors are listed below:

kilo,k	hecto,h	deca,da	deci,d	centi,c	milli,m	micro,μ	nano,n
10^3	10^2	10	10^{-1}	10^{-2}	10^{-3}	10^{-6}	10^{-9}

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Frontmatter
More information

MATHEMATICAL SYMBOLS

The mathematical symbols denoting constants and variables of one sort or another are defined in the text at their point of introduction. Symbols used in equations are defined as follows:

Symbol	Meaning
$\equiv$	is identical to
$=$	is equal to
$\sim$	is asymptotically equal to (in some limit)
$\approx$	is approximately equal to
$\leq$	is less than or equal to
$\ll$	is much less than
$\rightarrow$	tends to
$f=O(\varepsilon)$	limit $f/\varepsilon<\infty$ as $\varepsilon\rightarrow 0$
$f=o(\varepsilon)$	limit $f/\varepsilon=0$ as $\varepsilon\rightarrow 0$

